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Light Responsive Adsorbents for Carbon Capture

by

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Abstract

The discovery of novel light responsive adsorbents for carbon capture and release is reported here for the first time. These materials were found to exhibit dynamic or static photoswitchable properties in the broadband or visible light range during CO₂ adsorption measurements. Prior to the publication of my work, no dynamic photoswitchable adsorbent or full utilisation of visible light to trigger carbon capture and release was known. Thus the pioneering work presented in this thesis provides a significant breakthrough for the carbon capture technologies that could potentially allow the process to be operated at a significantly lower cost and energy than conventional methods.

Commonly, the separation of CO₂ from a stream of gases involves the chemisorption of CO₂ by amines, the release from which is triggered by pressure and temperature. Although it is an effective process, amine degradation and regeneration are the main problems in post-combustion capture technologies. The regeneration of amines requires a large energy input which can result in ~30 % reduction in power plant capacity. Such limitations prompted research on different sorbent materials that display reversible adsorption using low cost triggers. While temperature, pressure, pH and microwave stimuli responsive materials have potential applications in gas adsorption technologies, light, particularly in the visible light range is the least disruptive stimulus for triggering carbon capture and release efficiently and it is highly abundant in nature, in the form of sunlight. New classes of porous materials: Metal-organic Frameworks (MOFs) and porous aromatic frameworks (PAFs) were explored as potential CO₂ sorbent materials due to their excellent performance in CO₂ capture and tunable properties.

To achieve highly efficient utilisation of sunlight in carbon capture processes, porous materials with light responsive properties were developed according to the energy levels in the solar spectrum. The solar spectrum consists of 7 % ultraviolet, 47 % visible and 46 % infrared light. The concept of using non-filtered light as a practical approach was ideal. However, the use of filtered light to eliminate UV light and obtain visible light irradiation was also attractive as it constitutes the major fraction of solar radiation intensity. Furthermore, it is more environmentally friendly and greater exposure due to deeper light penetration could be achieved. Thus porous adsorbents that could respond to light in the broadband range or specifically in the visible light range were developed.

In the course of the research project, four novel light responsive materials were successfully developed; two of which respond in the broadband light range and the other respond in the visible light range. The first dynamically photoswitchable MOF (**Zn(AzDC)(4,4'-BPE)_{0.5}**) for reversible carbon capture and release was reported. The MOF contained azobenzene and stilbene derivative linker molecules, in which photoirradiation resulted in the fast-bending motion of these molecules. Thus, up to 42 % and 64 % static and dynamic photoresponse were achieved respectively. This was the highest dynamic photoresponse obtained at the time of publication. The development of more broadband light responsive adsorbents was conducted further in the research. The work led to the discovery of photoresponsive PAF containing diarylethene (**DArE**) guest molecules (**DArE@PAF-1**). The dynamic carbon capture and release was triggered by the interaction between photoactive **DArE** molecules with the PAF. At high guest loading concentration, photoresponse can reach up to 24 %.

As earlier work showed great promise for light triggered carbon capture applications, improvements were focused on using more penetrating light trigger, such as visible light. As a result, an adsorbent that could respond exclusively to visible light was developed. Furthermore, unique adsorption behaviour was obtained for a reversible carbon capture and release process. The introduction of visible light guest molecules (methyl red, **MR**) into the host (**Mg-MOF-74**) displayed a pressure-gate system, in which light could be used to tune the gate-opening pressure. Photoirradiation of the sample resulted in the photoswitching of the guest molecules, whereby lesser contact with the host allowed more adsorption sites to be accessible. Thus upon irradiation, a significant increase in CO₂ uptake adsorption of up to 84 % was obtained. This is the highest photoresponse ever reported to date under static condition using visible light trigger. Further development led to the discovery of a water stable adsorbent that is visible light responsive. Again, methyl red (**MR**) was used as the visible light responsive molecule. The incorporation of the guest molecule into water stable **MIL-53(Al)** resulted in a similar photoresponse trend, in which prolonged irradiation resulted in the increase in CO₂ uptake adsorption of up to 9 % at lower guest loading (15 wt %) and 46 % at higher guest loading (50 wt %).

The light responsive nature and recyclability of these adsorbents represents a new strategy for lowering the cost and energy for sorbent regeneration, a main problem associated with conventional carbon capture technologies.

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I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma in any university or equivalent institution, and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one original paper published in a peer reviewed journal and three unpublished publications. The core theme of the thesis is light responsive adsorbents for carbon capture. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the Department of Chemical Engineering under the supervision of Assoc Prof Bradley Ladewig and Dr Matthew Hill.

[The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of Chapters 4, 5, 6 and 7, my contribution to the work involved the following:

Thesis chapter	Publication title	Publication status	Nature and extent of candidate's contribution
4	Dynamic Photoswitching In Metal Organic Frameworks as Route to Low Cost Carbon Capture	Published	100 % - Experiment and analysis work, writing
5	Dynamic Photoswitching in DArE@PAF-1 for Carbon Capture and Release	Unpublished	100 % - Experiment and analysis work, writing
6	Visible Light Responsive MOF-74@MR with Pressure Gated Gas Adsorption Properties	Unpublished	100 % - Experiment and analysis work, writing

7	Tunable Visible Light Responsive MIL-53(Al)@MR for Carbon Capture	Unpublished	100 % - Experiment and analysis work, writing
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I have / have not (circle that which applies) renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

Signed: 

Date: 31/10/2014

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Abbreviations

atm	Atmosphere
AzDC	Azobenzene Dicarboxylate
BET	Brunauer-Emmett-Teller
BPE	1,2-bis(4-pyridyl)ethylene
DArE	Diarylethene
DCM	Dichloromethane
DMF	Dimethylformamide
DFT	Density Functional Theorem
DSB	Distyrylbenzene
D-R	Dubinin-Radushkevich
EtOH	Ethanol
Equiv.	Equivalent
FT-IR	Fourier Transform Infrared Spectroscopy
KBr	Potassium Bromide
LLCT	Ligand-to-Ligand
MeOH	Methanol
MIL	Matériaux de l'Institut Lavoisier
MLCT	Metal-to-Ligand
MOF	Metal-organic Framework
MOP	Metal-organic Polyhedra
MR	Methyl Red
NMR	Nuclear Magnetic Resonance
PAF	Porous Aromatic Framework
UV-VIS	Ultraviolet Visible
TGA	Thermogravimetric Analysis
ppm	Parts per million
PXRD	Powder X-Ray Diffraction

Symbols

Å	Ångström
b	Path length of the sample
brs	Broad singlet
c	Velocity of light or concentration
d	Doublet
E	Energy or molar absorbtivity
h	Planck's constant
I	Intensity of the radiation
I ₀	Initial radiation intensity
λ	Wavelength
wt %	Weight percent

Communication of Results

Publications

1. Lyndon, R., Konstas, K., Ladewig, B. P., Southon, P. D., Kepert, C. J., and M. R. Hill, *Dynamic photo-switching in metal-organic frameworks as a route to low-energy carbon dioxide capture and release*. Angewandte Chemie, 2013. **52**(13): p. 3695-3698.
2. Lyndon, R., Ladewig, B. P., and M. R. Hill, *Squeezing out CO₂. Post-combustion capture: metal-organic framework releases stored carbon dioxide in sunlight*. Carbon Management, 2014. **5**(1): p. 9-11.

Patent

1. WO Application 2014015383 A1, Bradley Ladewig, Richelle Lyndon, Matthew Hill, "Gas Separation Process", published Jan 30, 2014, assigned to Commonwealth Scientific And Industrial Research Organisation and Monash University.

Chapter 1

INTRODUCTION

1.1 Background

When sunlight passes through the Earth's atmosphere, some of the energy is reflected back to space, while a portion is absorbed by greenhouse gases [1]. These greenhouse gases, including water vapour, carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (NO_2), are able to absorb solar radiation and release heat into the atmosphere [1]. The increase in greenhouse gases in the atmosphere results in increased global temperatures, due to the greenhouse effect. The removal of these gases from the atmosphere is difficult due to their inertness, so they pose a risk of long-lasting global warming and climate change [1, 2].

CO_2 is one of the primary greenhouse gases that cause global warming [1, 2]. For many years, the concentration of CO_2 in the environment has varied between 180 and 280 ppm [2]. CO_2 is naturally present in the atmosphere and is constantly being exchanged in the atmosphere, as animals, plants and microorganisms are recycling it [1]. Unfortunately, the level of CO_2 emitted increased due to human activities, including industrial and agricultural practices, since the industrial revolution. For the past few years, the average annual increase was 2.07 ppm, which is more than double the rate in the 1960s [2]. The current level of CO_2 in the atmosphere stands at around 400 ppm, surpassing the suggested safe upper level of atmospheric CO_2 of 350 ppm [3]. It has been reported that the increased atmospheric CO_2 concentrations correlates to changes in temperature, precipitation, sea levels and ocean pH [2]. In July 2014, the average global temperature has reached the fourth highest on record for the month, at 0.64 °C above the 20th century average of 15.8 °C [4, 5]. The mitigation of global CO_2 emission stands as one of the greatest worldwide challenges of our time.

The main sources of CO_2 emissions are electricity generation using fossil fuels and transportation [6]. Transportation includes vehicles such as cars, trucks, trains, ships and aeroplanes, which emit CO_2 as the petroleum-based fuel is combusted to provide

propulsion. The most effective way to reduce these emissions is by reducing fossil fuel consumption [2]. Reduction in energy intensity through efficient utilisation has been demonstrated as one of the lowest-cost means of reducing CO₂ emissions. Renewable energy sources such as solar, biofuels and wind energy have been shown to be viable low CO₂ intensity replacements for fossil fuel power stations [2]. However, some of these technologies are still at the development stage and/or they only provide electricity intermittently (for example when the wind is blowing for wind turbines). In the absence of high-efficiency low-cost electricity storage, fossil fuel combustion will continue to be used as a key global energy source, and so there is an urgent need for new solutions to reduce the CO₂ emissions.

Currently, carbon capture and storage is seen as a potential near term approach to reducing global CO₂ emissions [2]. The strategies involve an efficient separation of CO₂ from gaseous mixture or water vapor, in which temperature and pressure changes are used to drive the separation process. However, the process involved is expensive and energy-intensive due to the large energy required for the regeneration of sorbent materials using temperature and pressure triggers [2]. Therefore, there is a critical need for improved separation strategies that will provide efficient, cost-effective technologies for carbon capture and release.

With this motivation, many researchers are seeking new materials and triggers for low cost carbon capture and release [2]. Sorbent materials must be very carefully selected to achieve a commercially viable carbon capture and release process. An ideal sorbent material must be capable of capturing a large amount of CO₂. However, CO₂ gas molecules must bind strongly to the sorbent material so that it is effectively and preferably completely separated from the gas mixture, whilst still being weak enough for the bound gas molecule to be released with minimal energy input. To overcome the limitations in the conventional carbon capture technologies, many novel adsorbents using new triggers have been developed to try and meet these often-conflicting requirements.

1.2 General Research Aim

The idea of using newly emerged adsorbent materials to capture and release CO₂, using naturally occurring triggers is highly attractive. A significant reduction in the energy cost component of the carbon capture process could potentially be achieved through this approach. Thus for this research, novel stimuli responsive materials have been investigated and developed using various synthetic approaches and characterisation methods, mainly focusing on the effect on gas adsorption properties in response to a specific stimulus.

A critical literature review has been conducted, identifying research gaps, and key research aims are specified in the next chapter.

1.3 Thesis Outline

The motivation of reducing CO₂ emissions using Metal-organic Frameworks (MOFs) and porous aromatic frameworks (PAFs) as new adsorbent materials and light as a novel trigger for a potential low cost carbon capture and release process was the main focus of this project. The results reported in this thesis are novel and represent pioneering work in the field of stimuli responsive carbon capture materials, particularly light responsive materials, and could help further accelerate the development of “next generation” light responsive materials. Improvements and developments on light responsive adsorbents were made over the course of the research. As a result, the experimental chapters will fall under two main categories: Chapter 4-5 are based on broadband light responsive materials and Chapter 6-7 are based on visible light responsive materials. The thesis is divided into eight chapters, which are summarised below.

Chapter 1 - Introduction

This chapter includes a brief historical review on climate change and carbon emissions, highlighting the need for developing novel strategies for carbon capture technologies. This section also includes the thesis outline.

Chapter 2 - Literature Review

An in-depth literature review on carbon capture technologies is presented, from current technologies and their challenges to emerging potential technologies using novel sorbents and triggers. To address the main issue of the energy intensive sorbent regeneration step in

carbon capture technologies, this chapter focusses on the use of light as a potential trigger for carbon capture and release from novel porous materials like Metal-organic Frameworks (MOFs) and Porous-Aromatic frameworks (PAFs). This chapter also identifies the research gap, where key research aims will be presented.

Chapter 3 - General Methods

General methods for synthesising and characterising photoresponsive adsorbent materials and their starting materials are presented in this chapter, along with the basic theory behind each characterisation technique.

Chapter 4 - Dynamic Photoswitching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release

This chapter is based on a published journal article in *Angewandte Chemie*, which has received media attention, and a patent application is pending. The work investigates a novel approach for incorporating light responsive groups into porous materials and presents its novel dynamic photoswitching behaviour upon broadband light irradiation. In this study, the photoresponse property of fully incorporated light responsive linker molecules in the MOF framework (**Zn(AzDC)(4,4'-BPE)_{0.5}**) was exploited to obtain a dynamic carbon capture and release process. This was achieved through the fast bending motions of the light responsive linker molecules. Control and mechanistic studies were conducted using various characterisation methods. This paper was the first published report of such dynamic photoswitching behaviour.

Chapter 5 - Photodynamic Switchable DArE@PAF-1 for Carbon Capture and Release

In this chapter, the dynamic photoswitching of **PAF-1** containing light responsive diarylethene (**DArE**) guest molecules upon broadband light irradiation was presented. The effect of different guest loading concentration on the photoresponse during CO₂ adsorption was investigated. A trade-off between photoresponse and adsorption capacity was observed. The dynamic and reversible photoswitching behaviour during CO₂ adsorption was triggered by the interaction between the guest molecules and the host. The possible mechanism was postulated based on various control and characterisation studies.

Chapter 6 - Visible Light Tunable Pressure-Gate System of Mg-MOF-74@MR for Carbon Capture and Release

This chapter discusses the significance of eliminating UV light from the broadband wavelength range and highlights the successful development of a novel visible light responsive adsorbent. This study focuses on the use of methyl red (**MR**) molecules as guest molecules in **Mg-MOF-74** to create an adsorbent that fully utilised a visible light trigger for carbon capture. A pressure-gate phenomenon was obtained upon guest loading. Photoirradiation of the material resulted in the opening of the gate and an increase in CO₂ uptake. Thus visible light allows the tuning of the gate-opening pressure to achieve a reversible carbon capture and release process. To this date, this behaviour has not been reported in the literature. Control and mechanistic studies showed that the mechanism involved the *trans*-to-*cis* photoisomerisation of **MR**. The photoirradiated CO₂ adsorbent displayed the highest photoresponse ever reported to date under static conditions.

Chapter 7 - Tunable Visible Light Responsive MIL-53(Al)@MR for Carbon Capture and Release

This chapter highlights the importance of using water stable adsorbents for carbon capture in industrial settings. Visible light responsive methyl red (**MR**) was again used as guest molecules. However, a water stable **MIL-53(Al)** was chosen as the host in this study. Similar photoresponse behaviour to previous results was observed, where the photoirradiated sample displayed higher CO₂ uptake capacity from the non-irradiated sample. The effect of different guest loading concentration on the photoresponse during CO₂ adsorption was also investigated and a trade-off between photoresponse and adsorption capacity was observed. Characterisation studies, once again, showed that *trans*-to-*cis* photoisomerisation of **MR** was responsible for the photoresponse obtained during CO₂ adsorption.

Chapter 8 - Conclusions and Recommendations

This section highlights and concludes the summary of the major findings reported over the course of the research. Based on the conclusion, future work is recommended for developing the ideal light responsive adsorbents for low cost carbon capture.

1.4 Graphical Abstract of Thesis

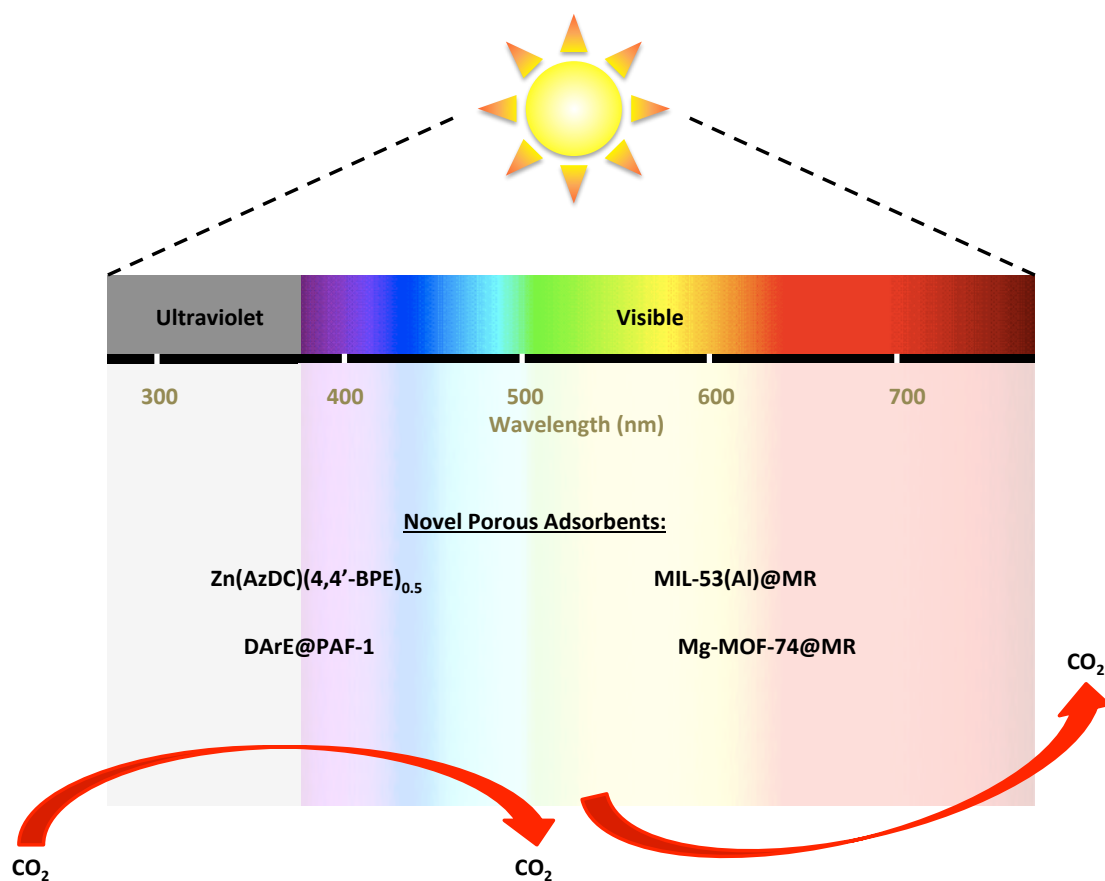


Figure 1. 1. Schematic representation of the novel light responsive adsorbents developed for carbon capture. Two broadband light responsive adsorbents ($\text{Zn(AzDC)(4,4'-BPE)}_{0.5}$ and DArE@PAF-1) and two visible light responsive adsorbents (Mg-MOF-74@MR and MIL-53(Al)@MR) were successfully prepared, showing reversible CO_2 capture and release. Spontaneous CO_2 release and enhanced CO_2 uptake were obtained upon photoirradiation respectively.

1.5 References

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Chapter 2

LITERATURE REVIEW

2.1 Current Carbon Capture Technologies

Fossil fuels are the world's main primary source of energy due to their relatively low cost and abundance (especially for coal) [1, 2]. The combustion of these fuels resulted in the release of heat, water vapour and carbon dioxide (CO_2), a greenhouse gas. As demands for energy have increased, the annual global emissions of CO_2 have increased by approximately 80 % between 1970 and 2004 [3]. Furthermore, the atmospheric CO_2 concentration reached ~ 400 ppm in 2013 and is projected to exceed 500 ppm by 2050 according to a business-as-usual scenario, with associated global warming of 4-5 °C and catastrophic impacts [4, 5]. Thus, there is a pressing need to develop strategies to reduce CO_2 emissions, especially those resulting from combustion of fossil fuels [2].

Alternate energy sources have been sought to reduce carbon emissions, such as, solar, wind, geothermal and hydropower [6, 7]. However, these technologies still need improvements to make them commercially desirable and viable [5, 7]. Conversion of CO_2 to useful chemical products is also considered a potential CO_2 reduction route [2, 6, 8]. For example, conversion of CO_2 into cyclic carbonates would be useful as solvents, chemical reagents and in biomedical applications [9-13]. However, the chemical conversion process is generally inefficient and a difficult synthetic problem as the CO_2 molecule is energetically very stable [8].

Meanwhile, large-scale carbon capture and sequestration (CCS) may play a key role in mitigating global climate change [2, 3]. The three main processes proposed are post-combustion capture, pre-combustion capture and oxy-combustion (Figure 2.1) [1, 3, 14].

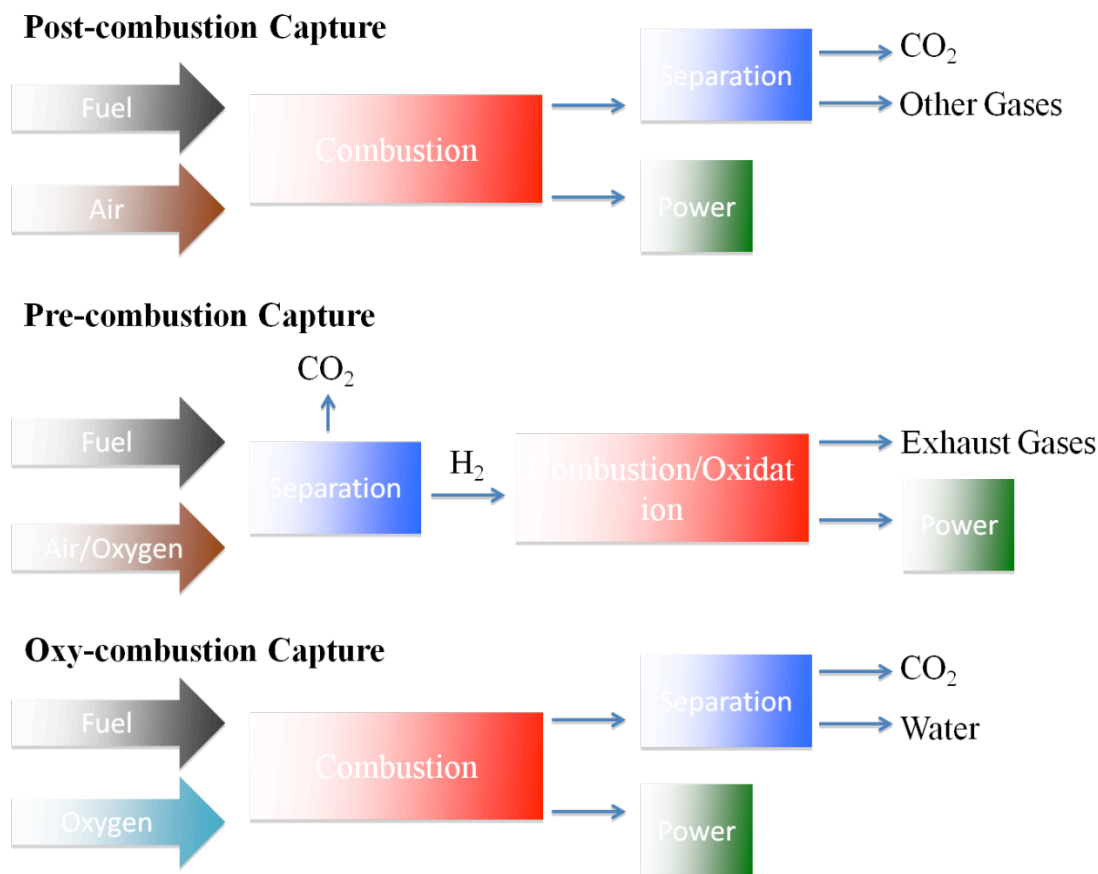


Figure 2. 1. Schematic representations of current conventional methods for carbon capture.

2.1.1 Post-combustion Capture

Post-combustion capture technologies are the most common and widely used process in many industries, in which the separation of CO₂ from the flue gas occurs after combustion [15]. The main aspect of this process that is still under development is to increase the concentration of CO₂ before sequestration, at a low energy cost [16]. The most well-established process involves the use of ~25-30 wt % aqueous amine solution, typically primary alkanolamine MEA, to absorb the flue gas containing CO₂ in an absorber column at 40 °C [2, 3]. At such a low temperature, the CO₂ reacts with the amine through a zwitterionic mechanism to form carbamates (Figure 2.2) [2, 3]. This CO₂-rich solvent is then pumped to a stripping column where it is heated at 100-140 °C and around atmospheric pressure to regenerate the solvent and release the CO₂ [2, 3]. The hot regenerated amine solution then flows through a heat exchanger, where the solvent is cooled and the CO₂ rich solvent going to the stripper column is pre-heated, before returning to the absorber column. High temperature is required to regenerate the solvent due to the high heat of formation associated with the carbamate production upon

absorption. The high-energy intensity process contributes to a parasitic energy loss of up to 30 % of the power plant capacity [3].

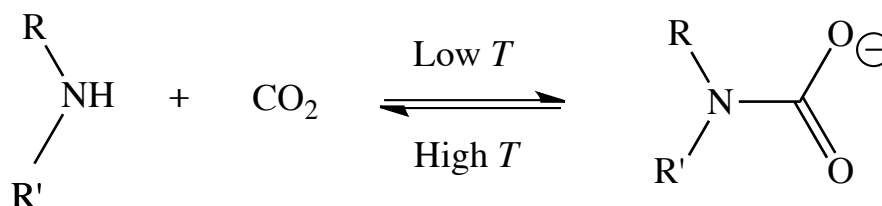


Figure 2. 2. Formation of a carbamate ion through a chemical reaction between CO₂ and an amine.

Post-combustion capture is a technologically mature process and could potentially be retrofitted into existing power plants. However, the process has other limitations. A high amount of energy is required to drive the separation process, contributing to a significant fraction of the energy cost. In addition, it suffers from solvent degradation and volatility problems [16, 17]. The volatility of water and amines could result in the loss of absorbent over time [5, 18]. Furthermore, amines are corrosive in nature and also decompose over time as the presence of residual oxygen in the flue stream causes oxidative degradation, forming nitrosamines [17, 19]. Contaminants such as sulfur oxides and nitrogen oxides also interfere with the absorption of CO₂ [17, 20].

In order to improve the technology, other materials with lower heat of absorption and regeneration energy have been sought to lower the energy costs. The use of other amine based materials with lower regeneration energy and less susceptible to degradation such as secondary amines (e.g. diethanolamine), tertiary amines (e.g. N-methyldiethanolamine), and sterically hindered amines (e.g. 2-amino-2-methyl-1-propanol) have been considered by lowering the carbamate stability and increasing the reaction rate with CO₂ [3, 5, 16, 17, 19, 21]. Inorganic solvents like aqueous ammonium carbonate have also been considered as an alternative due to their strong absorbing nature [22, 23]. However, the regeneration step is also energy intensive as the CO₂-rich solvent has to be heated to about 80 °C [3].

2.1.2 Pre-combustion Capture

Pre-combustion capture is another alternative to post-combustion technology, where the CO₂ separation process occurs before the combustion process. Firstly, the fossil fuel is converted into synthesis gas (syngas), containing CO, CO₂ and H₂ [24, 25]. CO₂ is then separated in a similar method as in the post-combustion process but it occurs at high partial pressures and at high temperatures of between 250 °C and 450 °C [3].

The use of elevated pressure and higher CO_2 concentration in the process lowers the energy capture penalty by about 50 % compared to that of post-combustion capture [26]. Although it has the advantage of lower energy requirement, the temperature and efficiency required for H_2 -rich gas turbine fuel is high and problematic [14]. Moreover, since the technology is new, retrofitting into existing plants is more difficult and currently it can only be applied to new power plants [27].

2.1.3 Oxy-combustion

Oxy-combustion is similar to the post-combustion processes. The fuel is combusted in pure oxygen instead of air to produce a highly concentrated CO_2 level and water vapour, which can be easily separated through condensation [24, 25]. The process is highly efficient and is more promising for new installations compared with post-combustion capture technology. However, like pre-combustion capture, the technology is still new and retrofitting of existing plant is not economical [14, 27]. There is also the requirement to produce pure (or highly enriched) O_2 from air, which is itself energy-intensive and represents a substantial parasitic energy loss.

With an increasing demand in global energy use, these current adsorption technologies still require substantial improvements in order to achieve an efficient process while consuming the least possible energy. Therefore, there is an urgent need to find a better approach, such that research on different carbon capture materials and the use of novel external stimuli have been proposed.

Amongst these conventional technologies, post-combustion capture would be the most practical to implement for current power plants and has the most potential for high efficiency energy conversion [15, 28, 29]. However, the high-energy requirement associated with sorbent regeneration has impeded the CO_2 capture efficiency. As a result, significant research into potential post combustion capture processes has been conducted as alternatives to the current amine absorption method [14].

2.2 External Triggers for Carbon Capture Technologies

2.2.1 Pressure and Temperature

Current methods utilise temperature or pressure swing absorption, in which the separation takes advantage of the solubility of gas at different temperature or pressure [3, 16]. These methods have been widely used in current carbon capture technologies such as post-combustion, pre-combustion and oxy-combustion [3, 5]. CO_2 has greater solubility in an amine solution at lower temperature and higher pressure, and poorer solubility at higher temperature and lower pressure [3, 5]. Solid sorbents currently used for carbon capture, such as zeolites and activated carbon, also utilise pressure swing adsorption where CO_2 affinity increases at higher pressure [3, 5].

Unfortunately, conventional carbon capture technologies can consume up to 40 % of the power output of a plant [3]. An economically viable process would require a reduction in the energy penalty much closer to the thermodynamic minimum of ~ 4 % [15]. Alongside the development of conventional carbon capture technologies, novel smart separation methods, like those can be found in nature, have gained a lot of interest in gas separation applications [5]. In theory, these materials may require less energy and could also be exploited to obtain tunability of the gas adsorption behaviour.

2.2.2 pH

pH-driven CO_2 capture and release utilises the shift between gaseous CO_2 and bicarbonate ion (HCO_3^-) in a solution that continuously shifts the pH between basic and acidic [30]. This method allows CO_2 recovery at atmospheric pressure without using heat and pressure. However, one of the limitations is that the presence of other species in flue gas such as sodium oxides and nitrous oxides could interfere with the pH and result in no significant change in the $\text{HCO}_3^-/\text{CO}_2$ equilibrium ratio.

Recent findings showed that CO_2 can be captured at a higher pH ($\text{pH} = 8$) and released at a lower pH ($\text{pH} = 6$), in which gaseous CO_2 is regenerated [31]. The pH-shift is generated by running a current through two chambers that have a narrow pH difference. In addition, an enzyme can be added to speed up the reaction kinetics [31]. However, the performance of the catalyst declined with continuous operation and more robust catalysts are required.

Another study reported that indirect pH swing using ammonium salts and antigorite source could facilitate carbon capture and storage [30, 32-34]. The process involves reacting CO_2 with rocks rich in magnesium and a mixture of ammonium salts (NH_4HCO_3 and $(\text{NH}_4)_2\text{CO}_3$) through pH swing to generate mineral carbonates. Although the process was proven feasible, developments are still required to reduce the large energy consumption of the process [32].

2.2.3 Microwave

Microwave heating has been proposed for post-combustion capture process to either capture or release CO_2 [35, 36]. This is because it is one of the most energy efficient systems for application of heat due to its high heating rate and short processing time where the irradiation can be delivered directly to the material through molecular interaction with the electromagnetic field [37]. It can take only a few minutes to reach a high temperature instead of hours in conventional heating systems [35]. The concept of using microwave-heating systems for CO_2 capture is still quite new and few studies have been reported.

Naturally occurring carbonates, called dolomite, in a packed bed and calcined form, have been considered for a microwave heating system to capture CO_2 at a low cost [36]. The process involved heating the calcined material to the carbonation temperature, where the calcium component converts to calcium carbonate and blocked the pores, and the magnesium component did not react and remained porous to allow CO_2 access [36]. After three cycles of calcination-carbonation using microwave heating, the packed bed was found to be highly regenerable and allowed a sustainable performance for carbon capture [36].

The CO_2 desorption rates of activated carbon packed beds using microwave heating and conventional heating at 70 °C and 130 °C have been compared recently [35]. The results showed that the overall desorption rate of CO_2 from the activated carbon is four times faster than that of conventional heating [35].

To this date, there has been no other report on CO_2 capture using microwave heating. Although this approach is promising, further research is still required to improve the system.

2.2.4 Light

Light, particularly natural sunlight, is an attractive trigger for low-energy CO₂ release. An ideal stimulus for triggering CO₂ capture and release requires a low or even zero energy cost, which makes light the best candidate for this application [38]. The amount of solar energy absorbed by Earth's atmosphere and surface annually is more than 3800 zettajoules [39]. As it is abundant in nature, it can be delivered instantaneously (albeit only during daylight periods) and the process is non-invasive [40]. The wavelengths can also be tuned using filters of specific spectral range. Broadband light delivers a wide range of light of different wavelengths ranging from 250-700 nm [41]. One advantage is that it offers a simpler light source with no filter requirements. However, broadband light also contains light in the UV range, which is biologically harmful and can potentially induce photodegradation of light responsive adsorbents [42-44]. Moreover, visible light accounts for 47 % of the rays that reach Earth's surface instead of a low fraction of 7 % for UV, and the sunlight radiates strongly in this region (Figure 2.3) [45, 46]. Thus, visible light (400-700 nm) is a highly attractive environmentally friendly source to induce a photoresponse [41]. Another option is to use infrared light where the spectral range lies between 700-900 nm [41]. The increase in wavelength offers deeper penetration into materials, thereby allowing greater light exposure for achieving stronger photoresponse [41]. The penetration depth can be quantified using a few equations. The rate of adsorption of light is proportional to the intensity of light of a specific wavelength and the penetration depth of light is generally expressed as a function of a wavelength. Upon penetration, light interacts with the atoms and electrons inside the material. Depending on the density of the material and wavelength used, light can travel very far into the material or lose its energy relatively quickly. The equation related to the energy of radiation during absorption is defined by Equation 2.1, where E is the energy of radiation, h is Planck's constant, c is the velocity of light and λ is the wavelength [41].

$$E = hc/\lambda \quad (2.1)$$

The absorption generally follows the Beer-Lambert law (Equation 2.2), where I is the intensity of the radiation at depth z , I_0 is the initial intensity at the surface, a is the absorption coefficient defined by the material and z is the penetration depth [41].

$$I = I_0 10^{-az} \quad (2.2)$$

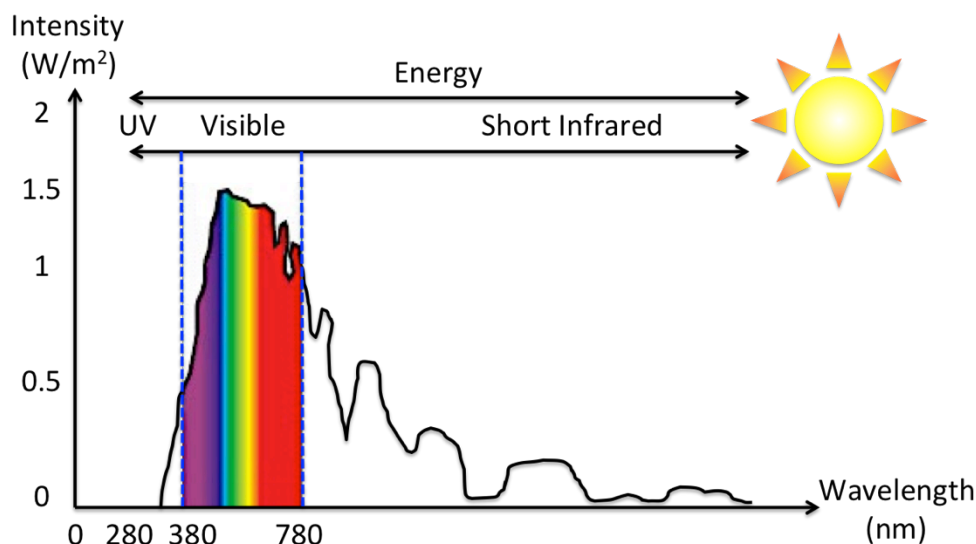


Figure 2. 3. Solar irradiation spectrum. Adapted from [47].

If a material can be made light responsive and displays a strong photoresponse, the cost of CO₂ capture and release may be drastically reduced. With the energy source being infinitely available, there could potentially be no or very little parasitic energy loss from the power station. Research on CO₂ capture using light has recently gained more attention due to its promising results [48, 49]. Light responsive Metal-organic Frameworks (MOFs) have recently been shown to capture and release CO₂ efficiently [48, 49]. Although there have been some studies reported, there has been very little research so far on light responsive materials for gas separation [48, 49]. As part of the research focus, light driven materials will be investigated and discussed in more details in the next section.

2.3 Light Responsive Materials

2.3.1 Adsorbents

New materials for carbon capture have been considered promising for post-combustion technologies [3, 5]. Most of them are focused on reducing the energy required for the regeneration step [3]. The use of solid adsorbents could offer significant advantages over chemical and physical absorbents in terms of energy efficiency [3]. This is because CO₂ adsorption involves either physisorption through van der Waals force, or chemisorption through covalent bonding between the gas molecules and the solid surface [3, 28]. The primary mechanism of CO₂ uptake in current solid adsorbents is through physisorption,

resulting from the interactions between the gas and the adsorbents [5]. Chemisorption only takes place if the adsorbent features reactive functional groups available for covalent bonding [50].

Porous solid adsorbents have increasingly gained more attention in gas separation applications because of their great potential to afford much lower cost and energy consumption [3, 28]. These materials can be purely inorganic, organic or in organic-inorganic hybrid form [3]. Their pore sizes range between 0.2 and 2 nm [5]. Solid sorbents currently used for carbon capture include zeolites, activated carbons, calcium oxides and alkaline and alkaline-earth hydrotalcites, in which they are in packed or fluidised bed and operate under pressure swing adsorption [3, 5, 51]. However, their performances are limited by their low gas uptake and selectivity, and the energy required for the regeneration of the adsorbent [5].

More recently, Metal-organic Frameworks (MOFs) [52-54] and Porous-aromatic Frameworks (PAFs) [55-57] have emerged and attracted much attention due to their inherently unique properties (Section 2.3.1.1-2.3.1.2). Furthermore, these adsorbents are found to respond to external stimuli, such as light, temperature, pressure and pH, which could lead to different properties [48, 58].

2.3.1.1 Metal Organic Frameworks

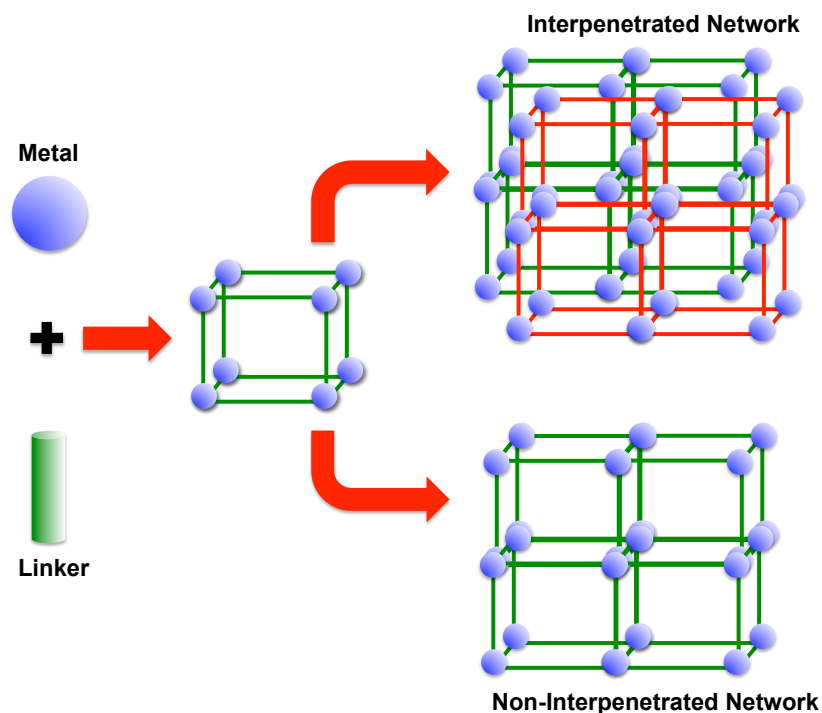


Figure 2. 4. Schematic representation of MOF synthetic routes whereby interpenetrated or non-interpenetrated network could form. Interpenetration occurs by the formation of two equivalent networks at the same time. Adapted from [59, 60].

Metal-organic Frameworks (MOFs) are microporous materials where the metal and ligand components that make up the three-dimensional network can be manipulated during synthesis or post-synthetically to obtain structural flexibility, high surface area and high porosity (Figure 2.4) [53, 61-65]. The properties of these materials depend on the metal ion geometry and the binding mode of the bridging ligand. The bridging organic ligands can range from ditopic to tritopic linkers with different properties, such as size, length, functionality, symmetry and flexibility [66]. The use of mixed linkers can also generate a more complex network topology, such as framework interpenetration [66]. Synthesis of these materials requires organic ligands and metal salts in a specific condition such as the solvent, the temperature of the environment and concentration of reactants [61]. Typically, solvothermal synthesis is used for MOF synthesis, but other methods such as microwave and hydrothermal reactions have been used [61]. The high tunability in their physical and chemical properties makes MOFs highly attractive for applications in catalysis [53, 61], gas separations [51, 61, 67], biomedical [61, 68-70], optical sensing [61, 71, 72] and fuel cell [53, 73-75] applications.

MOFs can be classified into three classes. First generation MOFs have microporous structures, which are sustained only by guest molecules and undergo irreversible framework collapse upon removal of guest molecules [59, 60]. Second generation MOFs are more robust and stable, in which permanent porosity can be achieved after removal of guest molecules and subsequent adsorption and desorption cycles of other guest molecules [59, 60]. MOFs are generally rigid in nature but can obtain flexibility and dynamicity upon exposure to certain stimuli. These materials are referred to as the third generation MOFs [59, 60]. Their ability to undergo reversible change in properties whilst retaining the overall framework structure makes them unique and highly attractive for various applications [60].

Many MOFs have been studied for their applications in gas separations. These microporous materials are not only chemically and thermally stable, but they also exhibit high porosity and surface area, which gives them very high capacity storage for gases such as H_2 [76-79], CH_4 [78, 80-83] and CO_2 [14, 78, 84, 85]. For example, NU-109 and NU-110, have a Brunauer-Emmet-Teller (BET) surface area of $7000\text{ m}^2/\text{g}$, the highest surface area reported to date [86]. The openness of the pores within the structures provides a great advantage for fast uptake of gases and removal of bound gases, thereby reducing the energy for adsorbent regeneration. Furthermore, they can display high gas selectivity [87-89]. MOF properties can be tuned using different metal centers and organic linkers, which can be further altered through post-synthetic modification [61, 90]. Such desirable properties make them extremely ideal for gas separation applications [14, 91].

Different structures allows gas to interact differently with MOFs and as a result, unique gas adsorption isotherms can be observed [92]. For example, two-step sorption isotherms can be obtained in MOFs with co-existing cages and channels [14]. Ultraporosity can further enhance the sorption steps into a sigmoidal isotherm [14]. Hysteretic sorption isotherm on the other hand, may be obtained as a result of narrow pore channels in the MOF framework [14]. A more complex isotherm involving a combination of the two isotherms can be observed from MOFs exhibiting flexible framework structure. Flexible MOFs can also display a sorption isotherm with a “gate-opening” feature where an increase in adsorption and reaches saturation can be achieved upon exposure to certain stimuli such as, guest molecules or pressure [14, 93, 94].

While these adsorbents show great promises for applications in gas separation, there has been very little research so far on light stimuli responsive MOFs for CO_2 capture [48, 49]. Various studies have shown that photoresponse properties could be introduced in MOFs

through using photoresponsive pendant groups [95-98], light responsive guest molecules [99-101] and photoresponsive linker molecules [38, 102, 103].

2.3.1.2 Porous Aromatic Frameworks

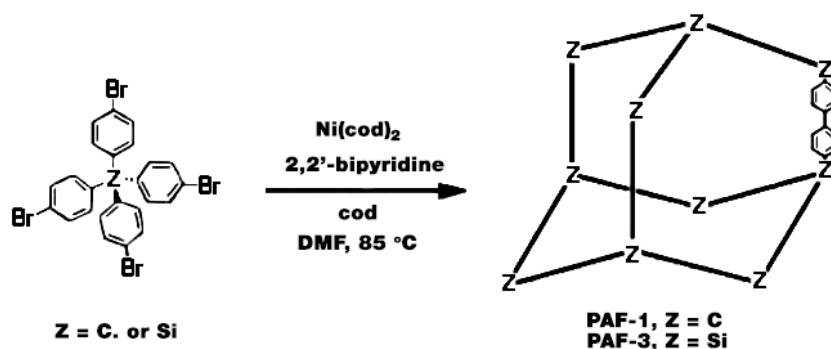


Figure 2. 5. General synthetic procedure for PAF preparation. Reprinted with permission from [104].
Copyright 2014 Royal Society of Chemistry.

Porous aromatic frameworks (PAFs) are similar to MOFs except that they are composed of microporous organic polymers [55]. They feature diamondoid networks due to their tetrahedral atomic or small molecular nodes and simple biphenyl units as struts (Figure 2.5-2.6) [55, 104]. Unlike most MOFs, PAFs have high physicochemical stability [55, 63]. The covalent bonding nature and cross-linked rigid phenyl framework in PAFs offer high thermal, chemical and hydrothermal stability [55, 63]. The combination of both high surface area and physicochemical stability makes PAFs an excellent candidate for gas separation applications, particularly CO₂ capture [105-110]. They are also considered in other applications such as catalysis [109, 111], optoelectronics [109] and biomedical technologies [112]. PAFs can exhibit BET surface areas as large as 5640 m²/g, high gas adsorption capacities and gas selectivity [57]. PAF-1, PAF-3 and PAF-4 have been reported to exhibit very high selectivity towards greenhouses gases, CO₂ and CH₄, against H₂, N₂, O₂ and Ar at 273 K and 1 bar [57]. Methods such as metalation, interpenetration, and optimisation of pore size and pore infiltration with reactive species has been used to improve the interaction between guest molecules and the host framework [106, 108]. The typical synthetic route involved the cross-coupling reactions of halogen-functionalised monomers [55]. Such a synthetic process still requires improvement to allow a more convenient and low cost method on a large scale [55].

To this date, literature on stimuli responsive or flexible PAFs for CO₂ capture has not been reported. However, it has been shown in the literature that photoresponse properties

of PAFs could be introduced by using photoresponsive pendant groups and photoresponsive linker molecules [58, 113].

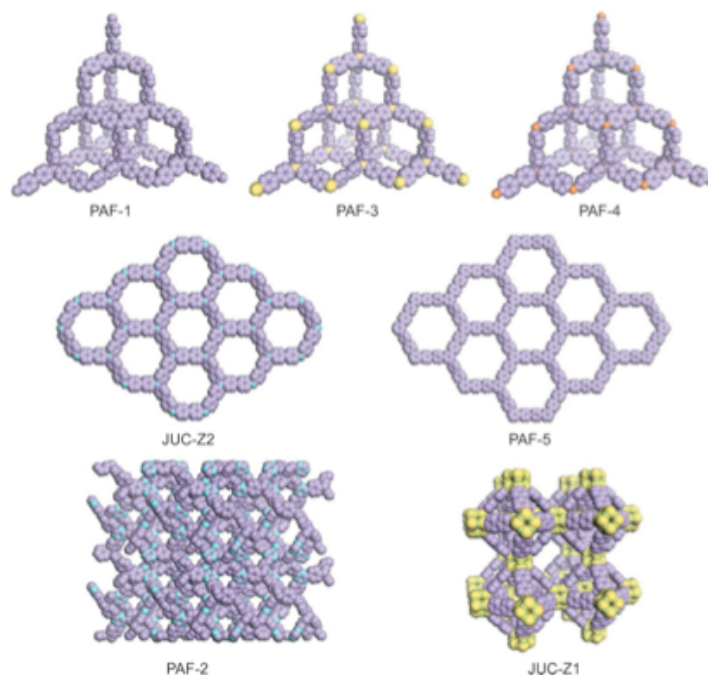


Figure 2. 6. Different structures of PAFs. Reprinted with permission from [55]. Copyright 2014 Royal Society of Chemistry.

2.3.2 Photochromes

Photochromes are able to irreversibly convert from one form to another upon light irradiation, in which some physical properties of the compounds, such as absorption spectra, fluorescence emission, conjugation, geometrical structures may be tuned [114]. Photoirradiation can be achieved by means of ultraviolet (UV), visible or infrared (IR) light. Well-known photochromic materials, whose colour and other properties can be triggered with light irradiation, have been used in applications in switches [115-117], memory devices [116, 118] and as dyes [119].

Under the branch of photochromic materials [114, 120], there are several functional groups, such as, azobenzene [121], diarylethene [117, 122], stilbenes [123], spiropyrans [124], viologens [125] and fulgides [126] (Figure 2.7). Their photochromic processes include photoisomerisation, photocyclisation and photoinduced electron transfer. However, each of these photoswitches has its advantages and disadvantages. For example, spiropyrans can exist in two isomers, in which they display vastly different properties [124].

However, it only shows photochromism when it is in solution [127]. On the other hand, fulgides can exhibit photochromism in solid form, but some of them are known for their low resistance to degradation [124, 126]. Viologens can change colour reversibly upon reduction and oxidation [125]. However, they can suffer from short repetition life as they display unstable coloration [128]. When incorporated into a host material such as a polymer, the transformations of these light responsive compounds can change the properties of the host such as their absorption or emission behaviour, the dipole moment and the polarisability of the molecule, making them highly desirable for triggering carbon capture and release [124]. For this project, the light responsive properties of azobenzene, stilbene and diarylethene derivatives are exploited for gas separation applications.

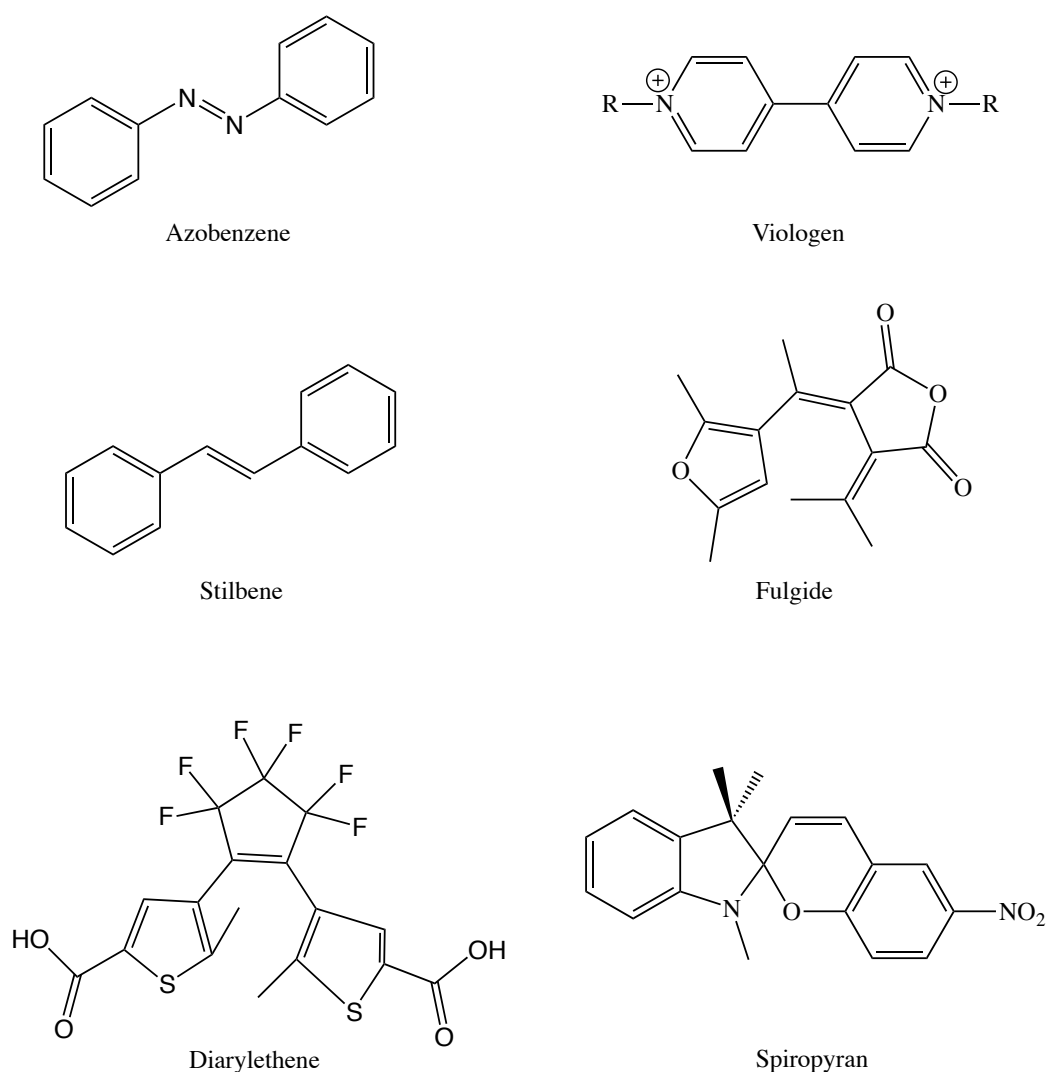


Figure 2. 7. Examples of different photochromic molecules.

2.3.2.1 Azobenzene

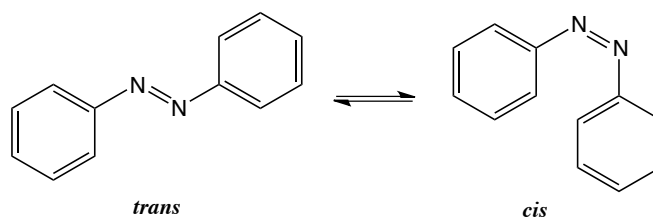


Figure 2. 8. Photoisomerisation of azobenzene.

Azobenzene is a well-known photochrome comprised of two phenyl rings linked by a nitrogen-nitrogen double bond (N=N) [129, 130]. It absorbs strongly in the blue region, resulting in an orange, red or yellow colour [121]. Modifications of the structure can result in a different colour, making them the largest dye group in commercial usage [131]. Another interesting property is its ability to undergo photoisomerisation using specific wavelengths of light, in which *cis* or *trans* isomers can exist, with the *trans* state being the stable form [121, 130]. The photochromism and structural formula of the parent azobenzene molecule is shown in Figure 2.8. Typically, the irradiation of the *trans* isomer with UV light yields the *cis* isomer, resulting in a decrease in the molecular length of the azobenzene molecules [121, 132]. Visible light irradiation is generally used to drive *cis* to *trans* isomerisation. However, since the *cis* form is less stable, the *cis* isomer can thermally relax back to the *trans* form [121].

Based on their thermal relaxation of the *cis*-to-*trans* photoisomerisation and the wavelength of adsorption required to trigger *trans*-to-*cis* isomerisation, azobenzene molecules can be classified in three classes: classic azobenzene, pseudo-stilbenes and amino-stilbenes [133]. In a classical azobenzene, the *trans* isomer absorbs in the UV range and the formed *cis* isomers can remain stable for days in the dark. On the other hand, a pseudo-stilbene displays a very fast thermal reversion and a far red-shifted absorption. Amino-azobenzene will have an intermediate lifetime and the *trans* absorption band is slightly red-shifted [133]. The *cis*-*trans* isomerisation of azobenzene occurs through the inversion or rotation of the N=N bond, and is accompanied by a large change in molecular conformation. Photoinduced isomerisations of azobenzene and its derivatives have found broad applications in molecular switches, optical data storage and biological systems [129, 134].

Azobenzene molecules have several advantages as photoswitches compared to other photochromic molecules [132]. They are chemically stable and easily synthesised, with some being commercially available [132]. The maximum yield of the *cis*-isomers through photoirradiation is typically around 70-80 %, although complete photoisomerisation to the *cis*-isomer is possible as azobenzene are free from side reactions unlike stilbenes molecules [132]. Azobenzene can be isomerised on a timescale from hours down to sub-nanoseconds for 10^5 - 10^6 cycles before fatigue [135, 136]. Prolonged irradiation displays negligible decomposition due to its remarkable photostability. The large variation in properties in different types of azobenzene offers a versatility advantage over other photochromic molecules as chemical functionalisation or substitution will have a large effect on the photophysical synthetic route [133]. Functionalisation of the azobenzene compound with various functional groups, particularly those that can donate electron density, such as thiol [137], amide [138-140], methoxy [138], dialkylamine [141] or ethylenic bridge [142] can shift the wavelengths of activation towards visible light region and improve stability of the *cis* isomers.

2.3.2.2 Stilbene

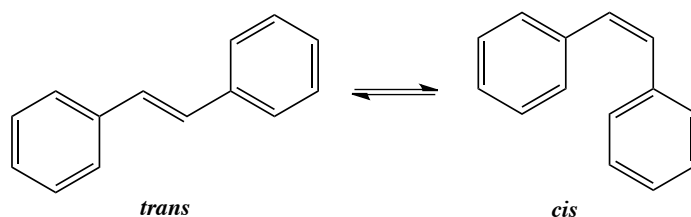


Figure 2. 9. Photoisomerisation of stilbene.

Similar to azobenzene, stilbenes consist of two phenyl rings but they are linked by a carbon to carbon double bond (C=C) [143]. They are widely used as photochromic molecules in dyes, scintillators and optical brighteners due to their intense absorption and fluorescence properties [143]. Stilbene and its derivatives also undergo reversible but competitive *trans-cis* isomerisation about double bonds under light irradiation, with the sterically hindered *cis* form being less stable (Figure 2.9) [143]. UV light promotes the *trans*-to-*cis* conversion, while the reversed path can be triggered by heat or UV light [123, 144]. The photoisomerisation of stilbenes competes with its photocyclisation pathway, in which the two aromatic carbons in the molecule couple and generate phenanthrenes as the by-product [144]. Photocyclisation can be prevented by functionalising the stilbene molecule

with amino or nitro substituents [144]. It is also known that stilbene molecules can undergo [2 + 2] photocycloaddition [102]. Unlike azobenzenes, one of the advantages of stilbenes is that the *cis*-form of stilbene is thermally stable and the photoisomerisation back to the *trans*-form does not occur thermally but requires light irradiation [132]. Furthermore, stilbene molecules are generally thermally and chemically stable [143]. However, there are disadvantages associated with stilbenes. Not only does the side-reaction product, phenanthrenes, shorten the life-cycle of the chromophore [133], but stilbenes also display low solubilities and photoisomerisation difficulties in rigid matrices [145]. The *trans*-to-*cis* isomerisation of stilbene utilises UV light irradiation [132]. However, the *cis*-to-*trans* isomerisation process requires UV light of an even shorter wavelength, which makes them not environmentally friendly [132]. These unfavourable aspects limits the use of stilbene as a photoswitch [132].

2.3.2.3 Diarylethene

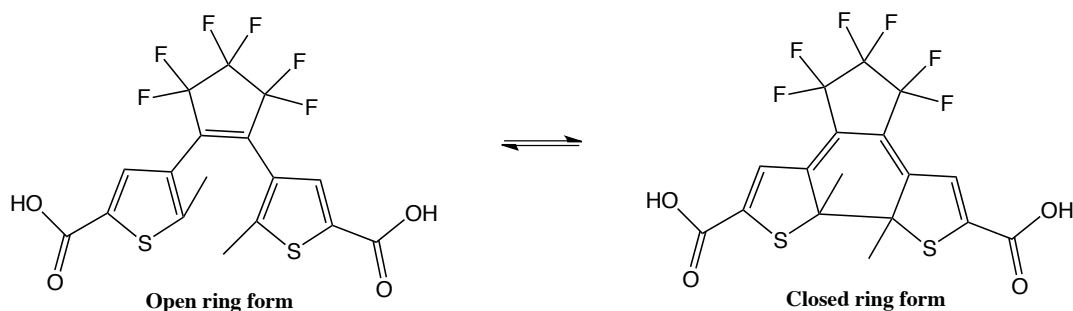


Figure 2. 10. Photocyclisation of diarylethene.

Diarylethenes are derivatives of stilbenes. The phenyl rings of stilbenes are replaced with five-membered heterocyclic rings like thiophene or furan rings [117, 122]. They have been used for potential application in molecular sensors [122, 146], optical data storage [122, 146] and photoswitches [38, 122, 146, 147]. Traditional photochromic molecules, such as azobenzenes, stilbenes and spiropyrans, are thermally unstable and often revert back to the most stable isomers in the dark [148]. Diarylethenes, however, are attractive due to their high thermal stability and photostability, with more than 10^4 photoinduced switching cycles and a lifetime of more than a thousand years at 30 °C [38, 124, 148]. The typical photoresponse mechanism involves the photocyclisation of the open ring state to the closed ring state, in which a six membered ring is obtained in the structure (Figure 2.10) [122, 149]. Visible and UV light irradiation promote the ring opening and the ring closing steps respectively [122, 149]. Unlike azobenzene and stilbene, the photocyclisation results

in a relatively small change in molecular conformation [124]. Although they are not ideal for the design of mechanically switchable systems, diarylethene displays high thermal stability and superb resistance to photodegradation as photocyclisation can be repeated many times [38, 132].

2.4 Incorporation of Flexible Light Responsive Group into Adsorbents

The introduction of a light response property in adsorbents is highly attractive for controlling CO₂ capture and release. However, there are very few studies reported in this area, leaving a gap in the research field and substantial work is necessary. A few strategies have been explored recently, including the use of a light responsive pendant group, guest molecules and linkers in adsorbents (Figure 2.11).

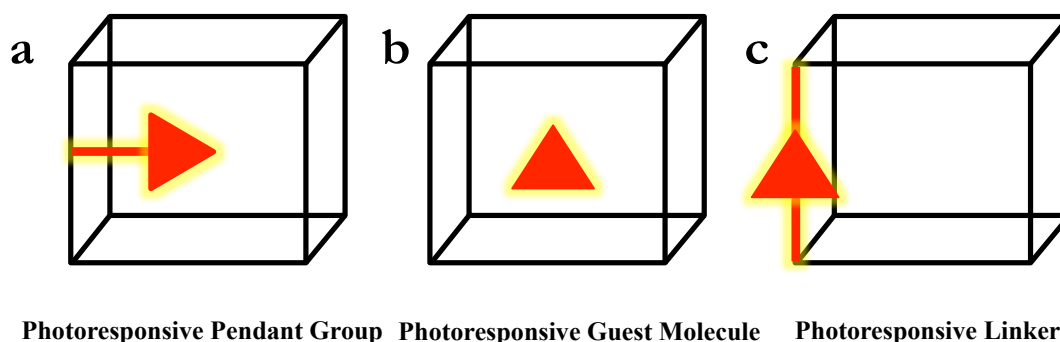


Figure 2. 11. Methods for the incorporation of a light responsive group (red) in porous adsorbents.

Three different methods have been reported to this date. The light responsive groups can be incorporated as pendant groups (a), guest molecules (b) or linker molecules (c).

2.4.1 Pendant Light Responsive Groups

One method for introducing light response in porous adsorbents is through incorporating a ligand containing a photoresponsive group that is covalently attached to the inner pore wall of MOF as a side chain. With the responsive group partially incorporated within the framework, greater flexibility of the ligand inside the MOF can be achieved upon light activation. In 2011, Modrow *et al.* reported the first porous MOF with photoswitchable azo molecules, CAU-5 [95]. The MOF displayed a total CO₂ uptake capacity of 50 cm³/g STP at 100 kPa at 298 K[95]. Although *trans-cis* photoswitching was detected in the UV-VIS result, photoswitching during gas adsorption was not reported.

In 2011, Zhou *et al.* reported that reversible light responsive gas adsorption effect could be achieved through the use of MOF with light responsive azobenzene pendant group, PCN-123 (Figure 2.12) [97]. Upon UV-irradiation, *trans*-to-*cis* isomerisation of the azobenzene pendant occurred, resulting in the release of adsorbed CO₂ from the MOF [97]. The *trans* azobenzene groups partially transformed into the *cis* state within 1 hour and after 5 hours, an overall decrease of 54 % of the originally adsorbed CO₂ was observed [97]. The adsorbent can be fully regenerated by standing at ambient conditions for a prolonged period of time or by heating the MOF at 60 °C for a day [97]. The slow photoisomerisation obtained upon UV irradiation is due to the rigidity of the MOF framework. Although the functionalisation of the pores with light responsive pendant groups can be used as a strategy to introduce photoswitchable property in adsorbents, photoswitching applications are still limited by steric restriction issues.

In a rigid framework, structural motions are hindered and photoresponse of light responsive compounds are difficult to achieve. In a more recent study, Yaghi *et al.* reported that such steric limitations can be overcome through the use of MOFs with the metal and organic components linearly stacked with each other, producing non-interpenetrated pores [98]. The improved photoswitching was due to the light responsive group being evenly spaced within the framework. However, its application in carbon capture was not reported [98].

Metal-organic Polyhedra (MOP), a self-assembled cage [150], functionalised with azobenzene pendant units on the surface has been reported to exhibit capture and release properties [96]. Although gas adsorption results were not reported, the mechanism for the capture and release of dyes, as guest molecules, is governed by the photoisomerisation of the azobenzene group [96]. UV light irradiation promoted the formation of a bigger pore cavity as intercage interactions due to the π - π interaction of neighbouring *trans* azobenzene between the MOPs were enhanced [96]. The trapped guest molecules in the big pore cavity were released when irradiated with visible light as intercage interaction weakened when the *trans*-to-*cis* isomerisation of azobenzene occurred [96].

The use of pendant groups is a promising method to overcome steric issues. The static pendant groups allow the switching of photoresponsive groups to occur in adsorbents without changing the overall framework. With the motivation of discovering more light

responsive adsorbents, more strategies to incorporate light responsive properties in adsorbents are being discovered.

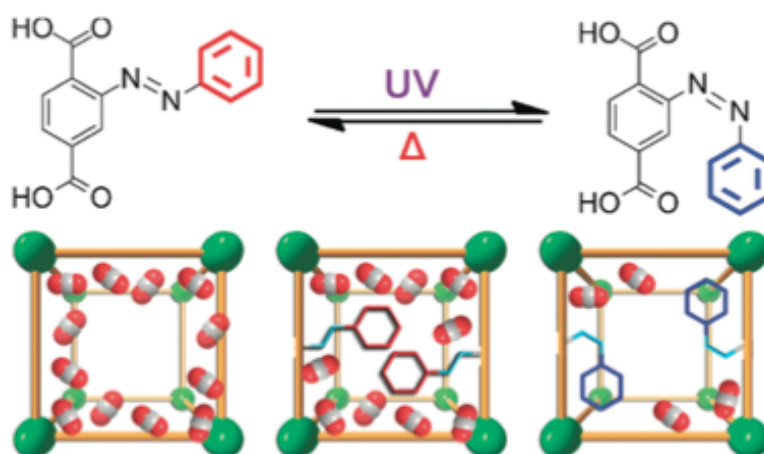


Figure 2. 12. *Trans-cis* isomerisation of an azobenzene pendant in PCN-123 framework. Reprinted with permission from [97]. Copyright 2014 American Chemical Society.

2.4.2 Guest Molecules Incorporation

It has been reported in several articles that dynamic structural transformations of flexible MOFs can be achieved through the adsorption and desorption of guest molecules [60, 151-157]. This method typically alters the pore geometry of MOFs while maintaining the overall framework structure. Recently, the inclusion of photochromic guest molecules has been shown to be a good strategy for obtaining new materials with optical properties [99-101].

The use of light on a MOF containing guest molecules was first reported in 2012 by Kitagawa *et al.* [99]. Azobenzene was used as the guest molecule in a flexible host (Figure 2.13). The photoisomerisation property was exploited to photoinduce reversible structural changes in the framework. The expansion of the framework after UV irradiation reportedly allowed more N_2 to diffuse into the pores, resulting in the switching of gas adsorption property [99].

Incorporation of azobenzene in other MOFs (i.e. MOF-5, MIL-68(Ga), MIL-68(In), MIL-53(Al)) has been attempted recently [101]. The results showed that the *trans-cis* isomerisations in some of these MOFs have been improved compared to that of pure solid azobenzene. However, when in a more structurally hindered environment, no photoisomerisation was observed [101].

In another report, a composite between a flexible MOF and distyrylbenzene (**DSB**), a dye molecule that display fluorescence property, has shown selective CO₂ adsorption over other atmospheric gases [100]. Adsorption of **DSB** molecules resulted in a structural transformation of the host [100]. The co-adsorption of CO₂ resulted in a large change in pore structure, in which the guest-to-host structural transmission led to the changed fluorescence property. Thus MOF containing **DSB** could act as a gas sensor [100].

With very limited reports of photoinduced changes in adsorption property, the unique host-guest structural transmissions could potentially offer an efficient approach for developing stimuli responsive adsorbents that are advantageous for CO₂ capture.

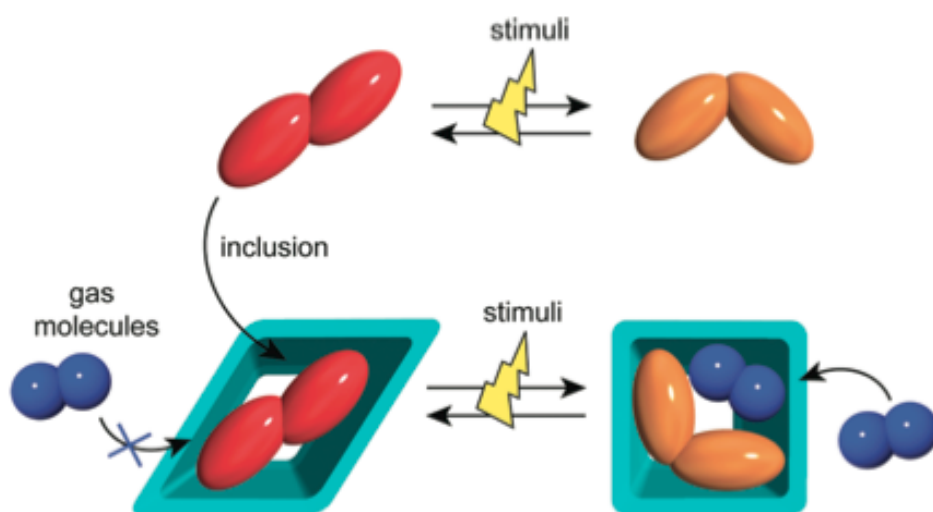


Figure 2. 13. *Trans-cis* isomerisation of photoactive guest molecules triggering structural change of the host framework. Reprinted with permission from [99]. Copyright 2014 American Chemical Society.

2.4.3 Use of Photoresponsive Linker Molecules

Despite reports of adsorbents containing light responsive groups in their backbones being widely available, there are no reports on their ability to undergo photoinduced structural change. As discussed above, this is because the linker containing photoresponsive groups are being held tightly in the framework. Therefore photoinduced structural motion of these linkers within the rigid framework is limited, preventing a large structural conformation to occur. The work contained in Chapter 4 was conducted and published prior to most of these reports in the literature.

In a previously reported article, linkers that can undergo chemical change by using a light trigger have been exploited to achieve photoswitchable gas adsorption properties. In this study, a MOF that possessed an azide moiety, which are known to generate triplet nitrines upon UV light irradiation, was used [158, 159]. Since these photoactive groups were exposed on the pore surface, the MOF, CID-N₃, exhibited low porosity [158]. The adsorption ability was enhanced after light activation due to the photochemical trapping of physisorbed gas molecules in the framework [158]. However, as chemical modifications occurred on the pore surface, no large structural movement was observed upon light irradiation.

In another report, MOFs containing 1,2-bis(4-pyridyl)ethylene (**BPE**), a stilbene derivative molecule, as one of the linkers in the framework, can undergo a structural change upon UV light irradiation [102]. With the neighboring **BPE** linkers being relatively close to each other within the framework, photodimerisations were able to take place during light irradiation, creating wider pore channels. As a result, different CO₂ adsorption isotherms were obtained, whereby a hysteresis step was observed in the non-irradiated MOF [102].

Recently, further improvements have been made towards adsorbents containing photoswitchable linkers. The development of diarylethene based MOF (**DMOF**) was reported to be responsive towards UV light during CO₂ adsorption and visible light during CO₂ adsorption or desorption (Figure 2.14) [38]. The photoresponse due to a local framework movement of diarylethene in the MOF backbone resulted in desorption capacities of 75 % and 76 % under static and dynamic conditions respectively [38]. Most reported light responsive adsorption experiments were carried out under static conditions where light irradiation of the sample took place prior to gas adsorption measurements [97, 99, 102]. However, due to the photoresponse mechanism involved for this MOF, real-time dynamic control of gas could be achieved. The first reported MOF containing diarylethene was found to exhibit reversible photoresponse towards light irradiation. However, their gas adsorption properties were not reported [103].

Recently, a PAF containing an azo group in the linker was found to exhibit high temperature CO₂ selectivity over N₂ [113]. The azo group in the linkers were able to repel N₂ due to a large entropy loss upon their adsorptions, making them ideal candidates for carbon capture applications [113].

With the use of the three main strategies for introducing optical properties in materials, more light responsive adsorbents for CO₂ capture is continually being developed and discovered. However, very little work has been done on this area. This leaves a gap in the research field and more research is necessary to motivate new renewable strategies for low cost and energy carbon capture processes.

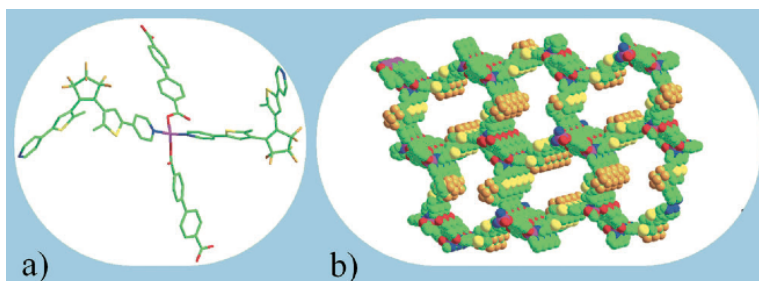


Figure 2. 14. Coordination of diarylethene to the Zn metal in DMOF (a). The view along the *b* axis of the 3D dia net (b) and the fivefold interpenetrating dia net. Colour code: C green, N blue, O red, Zn purple, S yellow, F orange. Reprinted with permission from [38]. Copyright 2014 John Wiley and Sons.

2.5 Research Gaps

Current technologies in carbon capture are highly energy intensive, particularly during the regeneration of sorbents, reducing the overall efficiency of the process. Furthermore, the sorbent materials are exposed to high temperatures over long periods of times, eventually resulting in their degradation.

To overcome the challenge of lowering the energy cost while increasing the energy efficiency of the process, new sorbent materials with specifically designed structures and desirable properties are needed. They need to be able to selectively bind CO₂ from a gas mixture and release it in a controlled fashion under external stimuli. In order to design and develop a desirable sorbent for carbon capture technologies, the mechanisms involved during gas adsorption and desorption must be fully understood. Currently the lack of understanding hinders the discovery and optimisation of ideal sorbents for future improved carbon capture technologies.

2.6 Research Aim

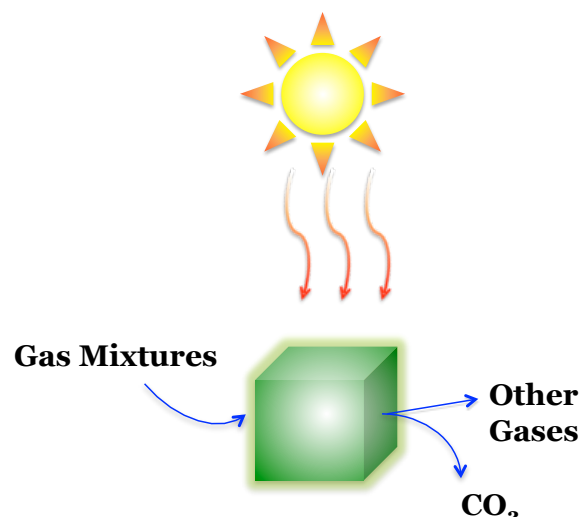


Figure 2. 15. Schematic representation of light activated adsorbent in a carbon capture and release system.

The main aim of this project is to develop and optimise recyclable light responsive adsorbents to address the problem of the high regeneration energy required by adsorbents for post-combustion capture (Figure 2.15). Thus, this could potentially lead to a lower cost and a more energy efficient renewable CO₂ capture and release process.

Two photoswitching conditions will be examined for gas adsorption experiments:

- Dynamic photoswitching
- Static photoswitching

With all of the current literatures conducted the light triggered gas adsorption under static conditions prior to the publication of Chapter 4, dynamic photoswitching condition will also be explored, as a strategy for a more controlled capture and release mechanism. Static condition involves the irradiation or relaxation of adsorbent sample prior to gas adsorption measurement, whereas dynamic photoswitching condition involves light switching taking place during the measurement.

In addition, two photoresponse properties that will be focused on this thesis:

- Adsorbents with broad spectral response range, such that of natural sunlight
- Adsorbents with spectral response in the visible region

The use of broadband light offers the advantage of using unfiltered light to trigger photoresponse for the carbon capture and release process. The use of visible light however, would further improve the use of light as a trigger in terms of providing deeper penetration and greater exposure into the adsorbents, potentially resulting in greater photoresponse, whilst being environmentally friendly.

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Chapter 3

GENERAL METHODS

3.1 Materials

The specific materials utilised for each study will be mentioned in the methods section in each experimental chapter. All starting materials were used without further purification. Solvents for MOF syntheses were obtained from a Solvent Dispensing System (SDS).

3.2 Synthetic Methods

3.2.1 MOF Synthesis

The MOFs in this work were synthesised *via* a hydrothermal or solvothermal route. A metal salt and organic ligand was dissolved or dispersed in water or organic solvent in a Schott bottle. For the hydrothermal method, the reaction mixture was then transferred to a Teflon lined stainless steel autoclave (Figure 3.1a), sealed and heated in an oven for 3 days. For the solvothermal method, the reaction mixture was transferred and distributed into 5 or 10 mL glass vials and sealed with Teflon caps, which were then heated in a MRC dry bath incubator (Thermoline Scientific) (Figure 3.1b). The product was then filtered, washed and solvent exchanged (Section 3.2.2). The activation of air-sensitive MOFs was conducted in a nitrogen filled glove box or using a Schlenk technique (Section 3.2.2 and 3.2.3).

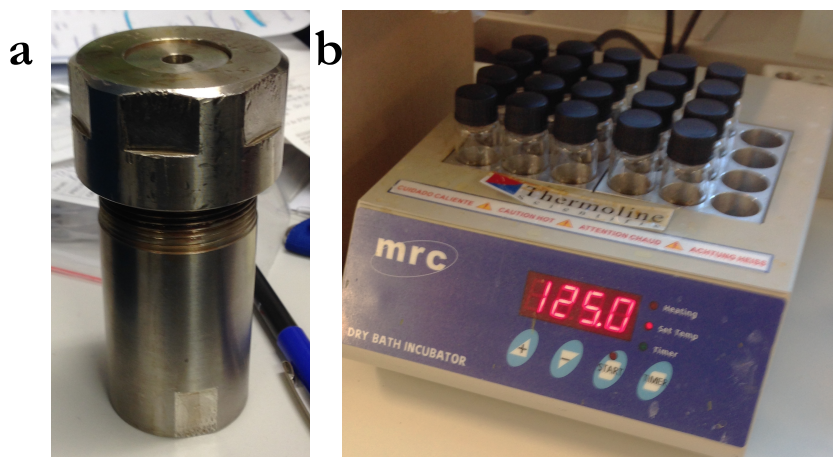


Figure 3. 1. The autoclave (a) and incubator (b) used in this study.

3.2.2 Solvent Exchange

In the MOF activation step, the occluded solvent obtained during synthetic preparation needed to be removed. However, due to the strong interaction between the solvent molecules within the framework, pore collapse or blockage could occur when using a conventional solvent removal method such as heating under vacuum or gas flow [1]. To overcome that issue, a mild evacuation condition is required and solvent exchange was performed. The process involved the exchange between the occluded solvent molecules with a lower boiling point solvent [1].

The solvents used were obtained from the Solvent Dispensing System (SDS) to ensure that the solvent was moisture free. The system consisted of a high vacuum pump and an argon supply. It operates by flowing the solvent through the drying columns under vacuum, while being simultaneously pushed with a positive pressure of argon out of the solvent kegs. The dried and degassed solvent is then dispensed under argon atmosphere into a flask.

To isolate air-sensitive MOF materials from atmospheric and solvent water, solvent exchange was performed in a nitrogen filled glove bag. The glove bag was connected to a purified nitrogen gas source and when sealed and clamped, the materials and tools in the glove bag were blanketed by nitrogen.

During solvent activation, the solid sample was soaked in the SDS solvent for several days in a pre-dried Schott bottle. The solvent was decanted and refilled with fresh SDS solvent after a few hours or in the following day. Several cycles of washing proceeded for several

days prior to activation under vacuum and heat, to ensure the complete exchange of solvent and to obtain a high surface area.

3.2.3 Schlenk Technique

The handling and activation of MOF samples is important as the exposure to ambient air and moisture can negatively influence the surface area of some MOFs [1]. To prevent sample degradation, the air-sensitive Schlenk technique was used to isolate and handle the materials from the atmosphere in a controlled environment. A Schlenk line consists of a dual manifold system, where two parallel gas tubes, one for inert gas and the other for the vacuum, were connected to several taps for multiple experiments to be performed simultaneously (Figure 3.2). The inert gas was fed through the cylinders of compressed purified gas to the manifold. Typically, nitrogen or argon gas cylinders (99.999 % ultra high purity) are used to provide the inert gas supply. However, since argon is more expensive than nitrogen, nitrogen was used for these experiments. Nitrogen gas exits the manifold through an oil bubbler, as a means of pressure release and visible monitoring of the gas flow. The oil bubbler was vented out near the fumehood exhaust. The vacuum manifold had one end fused-closed and the other end connected to the vacuum pump, separated by a cold trap. A cold trap prevents volatile or corrosive solvent vapors from entering the pump. The cold trap was immersed in a Dewar cooled with liquid nitrogen, to allow vapors and gases from the Schlenk line to condense. Two-way taps were used to prevent both the gas and vacuum lines from opening at the same time and to feed the inert gas directly into the vacuum pump.

Safety considerations are important when using a Schlenk line as an explosion could occur if the gas supply is opened when the vacuum system is not closed or if the vessel is heated on a vacuum line without a source of pressure release, such as a bubbler. In addition, if a stream of air enters the cold trap immersed in liquid nitrogen, liquid oxygen may condense in the trap. Liquid oxygen is extremely dangerous as it reacts violently with most organic substances. When such reactions occur in a confined space, an explosion could result. Implosion could also occur if a glass manifold with unseen cracks is used under vacuum.

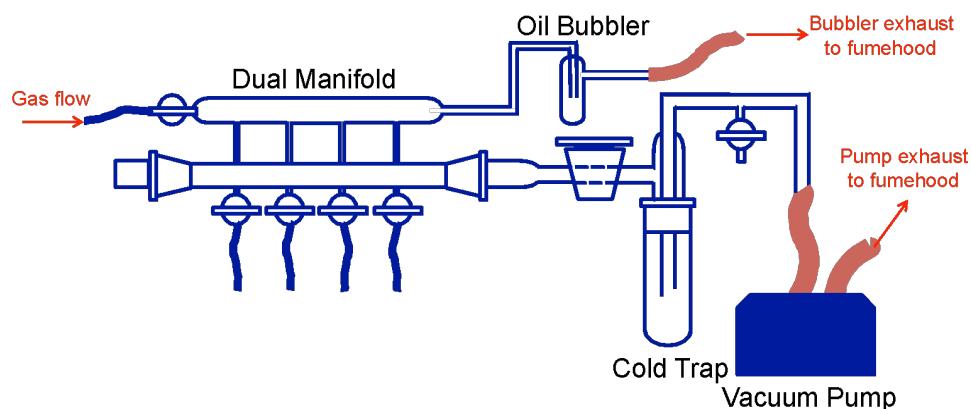


Figure 3. 2. Schematic representation of a Schlenk line set-up.

3.3 Characterisation Techniques

3.3.1 Gas Adsorption Measurements

Gas molecules can interact with sorbent materials through chemisorption or physisorption. In chemisorption, gas molecules chemically bond with the surface of the sorbent. On the other hand, the physical adsorption of gas involves the interaction of gas molecules on the surface of a porous solid through attraction or repulsion forces, such as dipole-dipole, hydrogen bonding or π - π interactions. The process is reversible, where the adsorbent material is in equilibrium with the adsorbed gas molecules at different relative pressures P/P_0 , resulting in different gas adsorption isotherms (Figure 3.3).

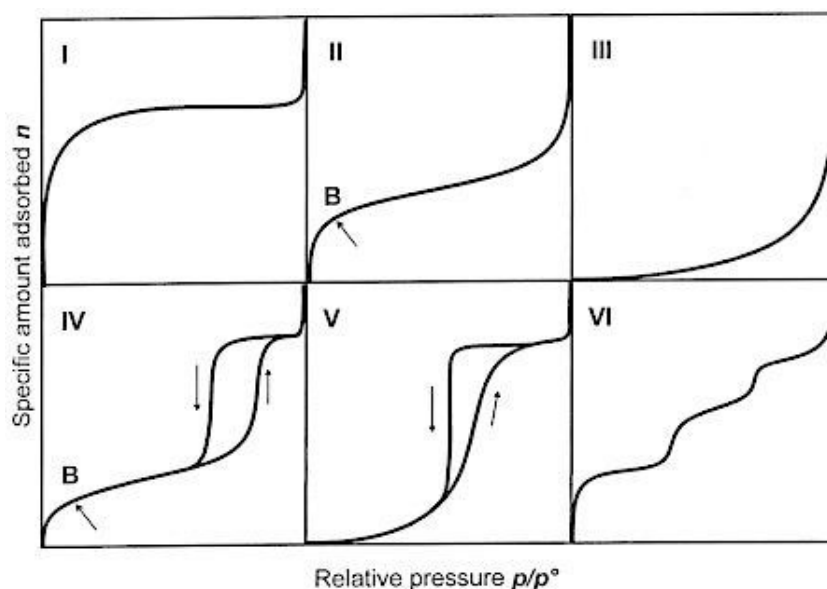


Figure 3. 3. The IUPAC classification of sorption isotherms [2].

Type I isotherm indicates a chemisorption or physisorption isotherm in microporous materials, where saturation is reached after filling of the micropores, indicated by the plateau. The steep increase at low pressure is due to micropore filling within the pores of the material. Type II and III isotherms describe the sorption behaviour of nonporous and macroporous materials with high and low energies of adsorption, respectively. Type IV and V isotherms display hysteresis loops, which apply to mesoporous materials with high and low energies of adsorption, respectively. Finally, type VI is a multistep isotherm that indicates that multiple pore sizes and multiple energies of adsorption exist.

The Brunauer-Emmett-Teller (BET) model is widely used to evaluate the adsorption isotherms of porous materials, where multiple layer adsorptions are proposed and the number of adsorbed layers is infinite at the saturation pressure. From type II – IV isotherms, the specific surface area of the adsorbents can be determined using the BET equation. The surface area of a sample can be calculated from the total volume of adsorbate adsorbed at equilibration pressure and the monolayer adsorption amount on 1 cm² of surface and entire surface. The measurement typically uses nitrogen (N₂) as the adsorbate and the temperature is carried out at the temperature of liquid N₂ (77 K). This is shown in Equation 3.1, where CSA is the analysis gas molecular cross-sectional area (nm²), S is the slope (g/cm³ STP) and Y_{INT} is the Y-intercept (g/cm³ STP). Microporous materials such as MOFs, commonly display type I isotherms [3]. Theoretically, the BET method cannot be applied for such microporous materials, such as MOFs, because the diameter of the pores is too small to allow multilayer formation [3]. However, it has been suggested that adsorption in MOFs occurs through a pore-filling mechanism instead of layer formation [3]. Pressure range chosen is typically within 0.05 < P/P₀ < 0.3 [3]. However Type I isotherm can also be defined by Rouquerol criteria, where the value of the BET constant resulting from the linear fit should be positive and have a value of at least 10 [4]. Furthermore, the monolayer capacity calculated from the linear fit must be located within the linear region chosen for the area of calculation [4].

$$SA_{BET} = \frac{CSA \times (6.023 \times 10^{22})}{(22414 \text{ cm}^3 \text{ STP}) \times (10^{18} \text{ nm}^2/\text{m}^2) \times (S + Y_{INT})} \quad (3.1)$$

Gas adsorption isotherms of samples were recorded at low pressure (0-1.2 bar) by a volumetric method using Micromeritics ASAP 2420 or Tristar II 3020 instruments (Figure 3.4). The main components of these instruments are analysis ports, sample tubes with isothermal jackets, P₀ tubes with isothermal jackets, which provide continuous P₀ readings

during analyses and long-life Dewars. ASAP 2420 has additional features such as the degassing ports and the independently controlled heating mantles to allow easy access for sample activation. These instruments operate by allowing multiple sample tubes to be injected with a chosen gas at a specific temperature within a specific pressure range. The pressures are measured and the volumes adsorbed as a result of pressure change are calculated. Longer analysis times could be obtained without refilling the Dewar, allowing analysis that involves longer times to equilibrium at each data point to be performed while unattended.

Prior to measurement, the sample was solvent exchanged, followed by sample activation under vacuum and heat. The sample was activated at a certain temperature under dynamic vacuum at 10^{-6} Torr for a certain period of time to remove any solvent molecules. Approximately 100 mg of dried activated sample was weighed in a pre-dried and weighed ASAP tube. Multiple replicate weights of the activated sample were taken and an average weight was calculated for both the empty tube and the added sample. Quartz ASAP tubes were used for experiments involving UV light and glass ASAP tubes were used for visible light switching experiments. An accurate weight of the degassed sample was calculated prior to analysis. Gas adsorption measurements were performed using ultra-high purity (99.999 %) CO₂, CH₄, H₂ and N₂ gas. The Brunauer-Emmett-Teller (BET) method was used to calculate the surface area of porous adsorbents in the low pressure range ($0.05 < P/P_o < 0.3$) [3].

Porous solids generally exhibit a wide distribution of sizes, contributing to the total adsorption isotherm in proportion to the fraction of the representative total area of the sample [5]. Therefore pore size distribution of the materials was determined by Density Functional Theory (DFT), a well known and versatile approach for calculating pore structures [6]. The DFT calculation was based on the adsorption of nitrogen at 77 K. Some of the CO₂ adsorption isotherms in the presence and absence of light at 273 K were fitted with the Dubinin-Radushkevich (D-R) equation in the range of relative pressure of $0.05 < P/P_o < 0.3$ to detect the change in pore size [7]. This was because the photoswitching experiment could not be conducted at 77 K as the condensation occurs on the tip of the optical fiber, preventing light from being delivered into the materials.

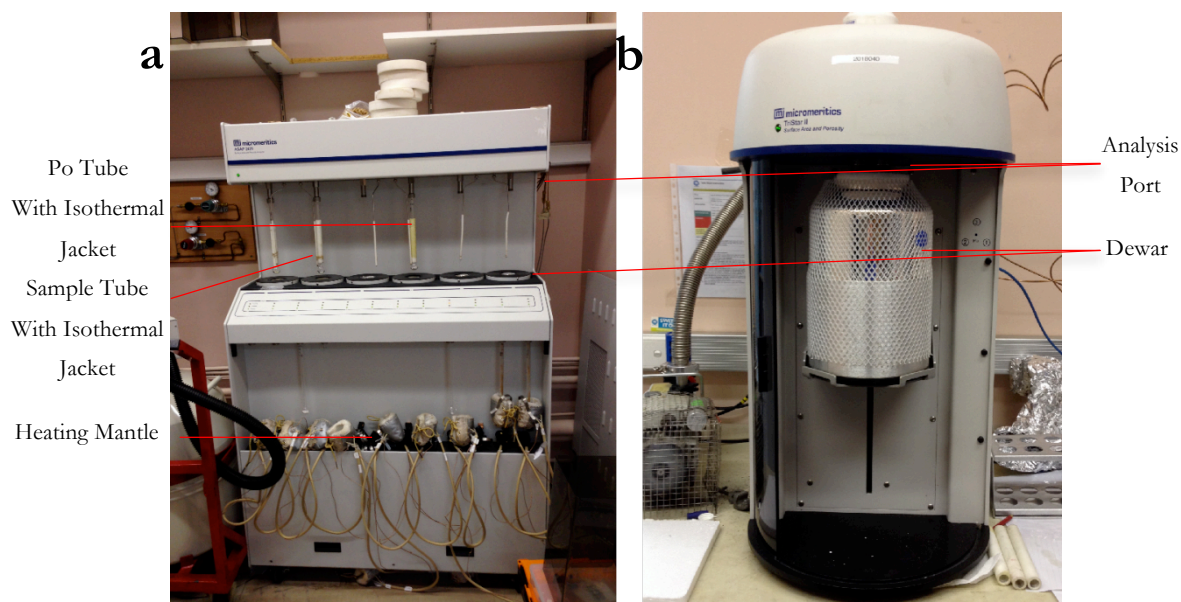


Figure 3. 4. Photos of the ASAP 2420 (a) and Tristar II 3020 (b) instruments.

3.3.2 General Light Responsive Gas Adsorption Experimental Set-up

Pre-weighed and dried custom made aluminium foiled quartz or glass ASAP tube was used for light switching experiments. A custom made light cell was used to contain the BET tube and light guide to allow maximum light exposure and coverage on the sample when the light was switched on (Figure 3.8). A Cole Palmer Model BT 15 heated circulating bath was used to maintain the temperature at 303 K or 273 K throughout the experiment. A temperature probe was wedged inside the light cell between the ASAP tube and light guide to monitor the temperature. Acticure® 4000 containing a high pressure 100 Watt mercury vapour short arc lamp was used as a UV-VIS light source to trigger the sample's light response during analysis. The light was fixed at the highest intensity output with no filter (200-500 nm) ($24,600 \text{ mW/cm}^2$), 365 nm filter ($5,600 \text{ mW/cm}^2$) or 400-500 nm filter ($8,100 \text{ mW/cm}^2$). The general set-up (Figure 3.5), and the actual experimental set-up on Tristar II 3020 (Figure 3.6) and ASAP 2420 (Figure 3.7) are shown in the figures below.

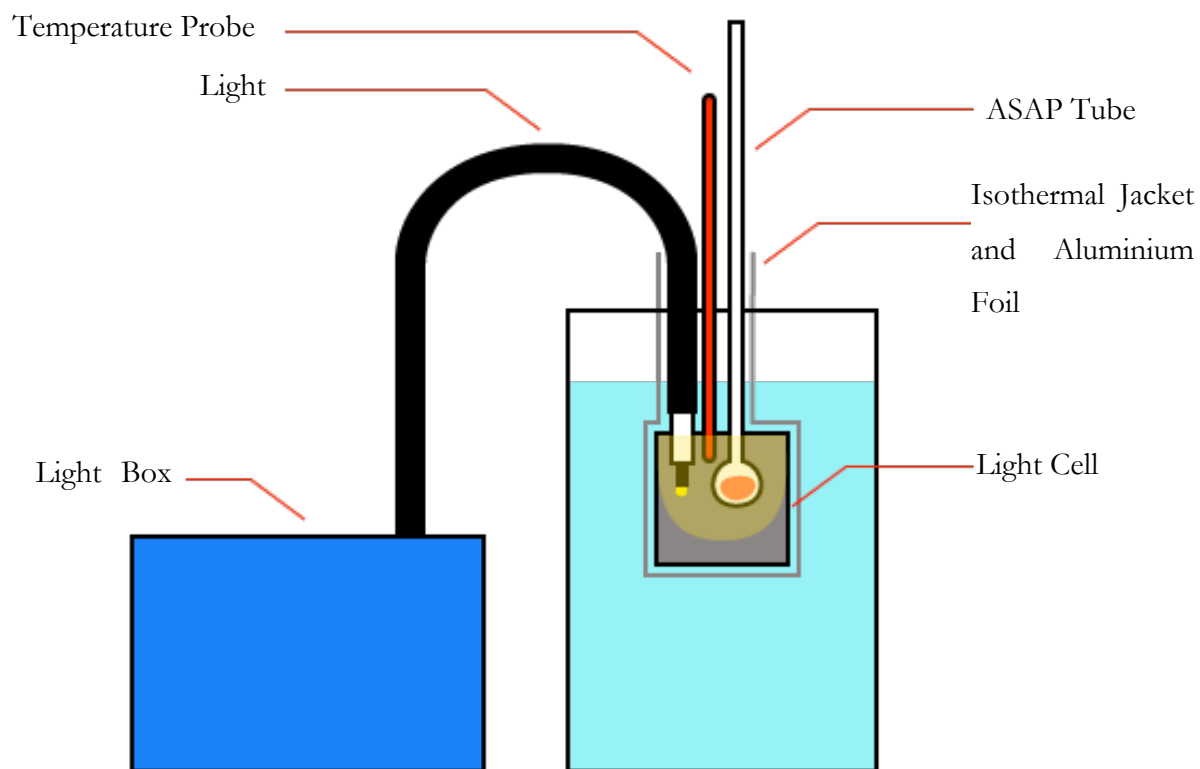


Figure 3. 5. Schematic representation of the general experimental set-up.

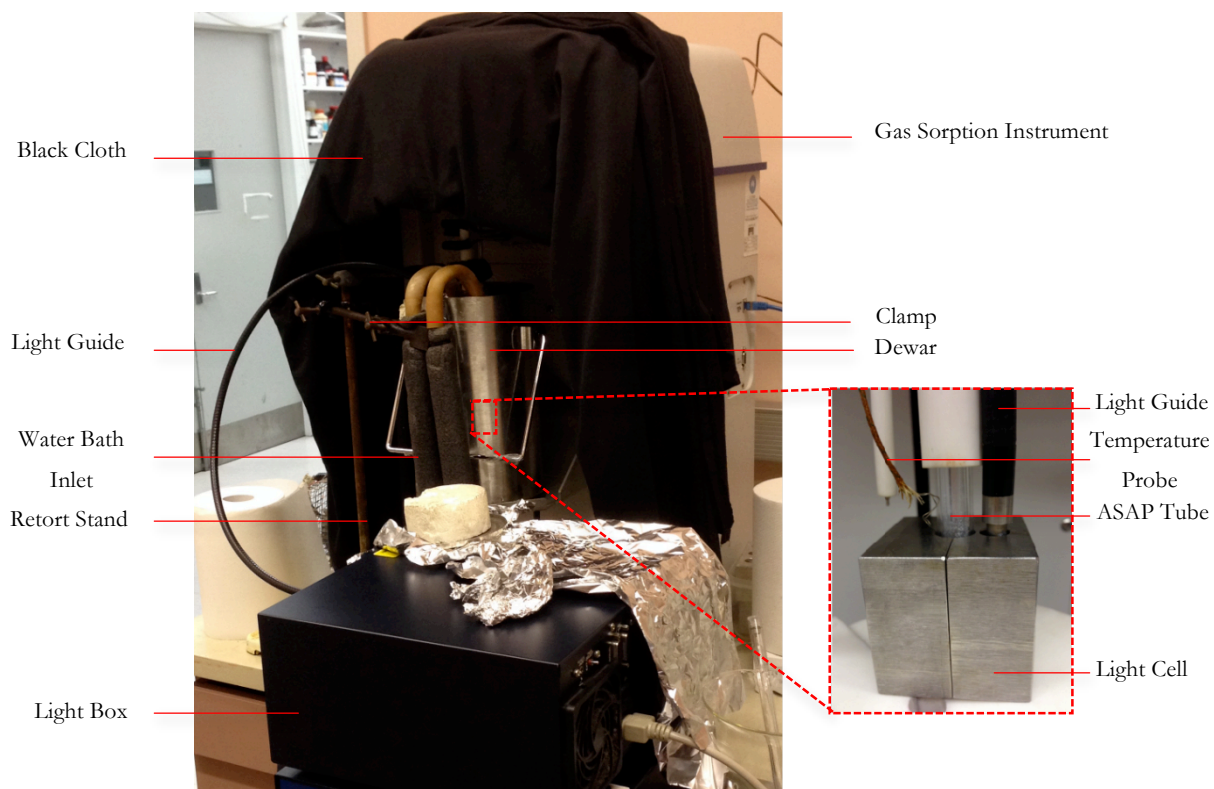


Figure 3. 6. Photos of the general set-up for conducting photoresponsive study on the Tristar II 3020 instrument. The inset shows a close-up look of the set-up inside the dewar.

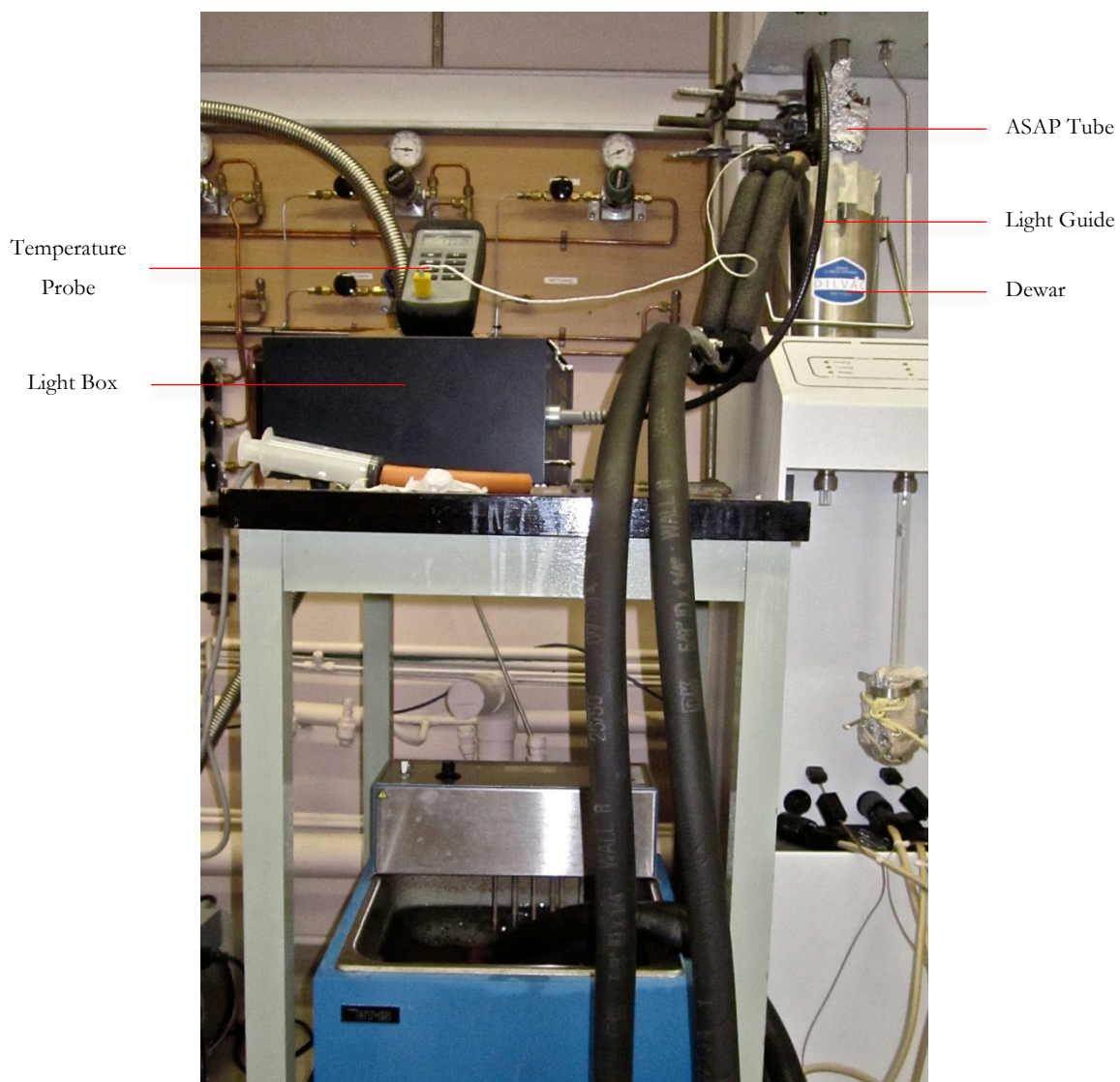


Figure 3. 7. A photo of the general set-up for conducting photoresponsive study on the ASAP 2420 instrument. A close-up photo of the set-up inside the dewar is shown in the inset of Figure 3.6.

Light Cell

The light cell is composed of two matching halves (Figure 3.8). One half has a machined socket for a light guide and the other half has no light socket. The hemispherical cavity in each half has a smooth machined surface finish and can fit the round bottom end of an ASAP tube when clasped together. The two components are secured with four screws.

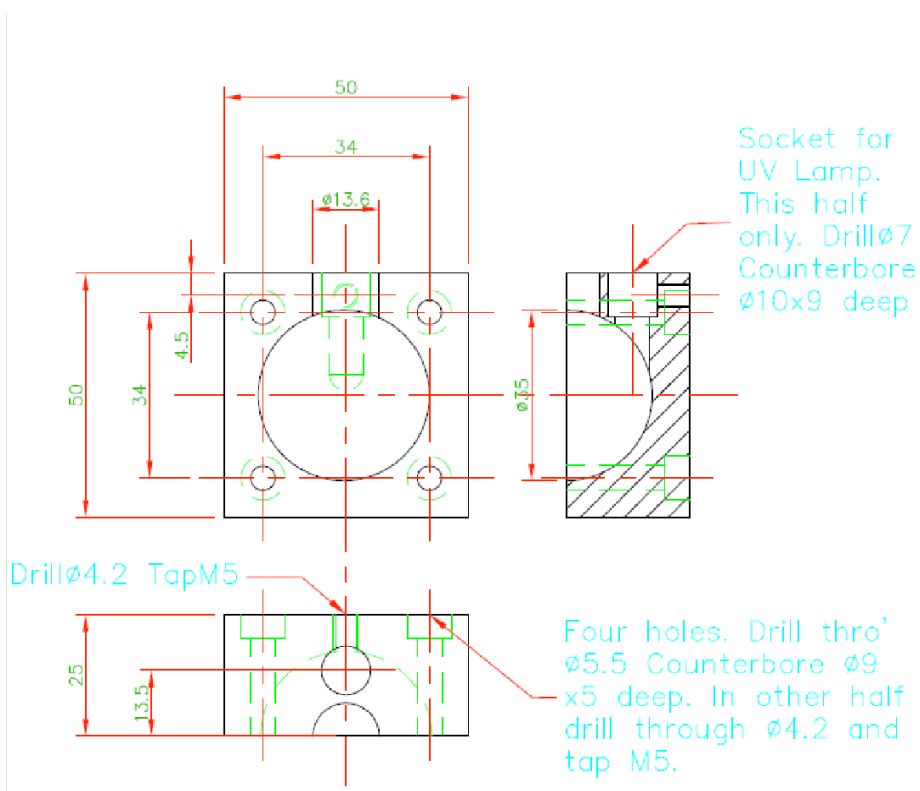


Figure 3. 8. Cross section of a light cell showing a light guide socket and a smooth-surfaced cavity to allow maximum light coverage on sample. The light cell is made of stainless steel.

Spectral Output

The spectral outputs for light with different wavelength using specific filters are shown below (Figure 3.9-3.11).

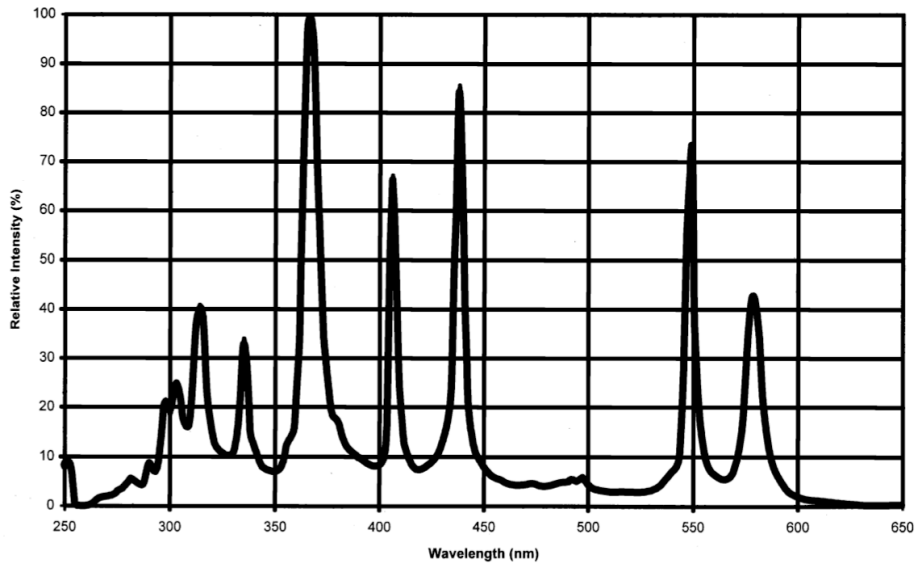


Figure 3. 9. Spectral output of light with no filter.

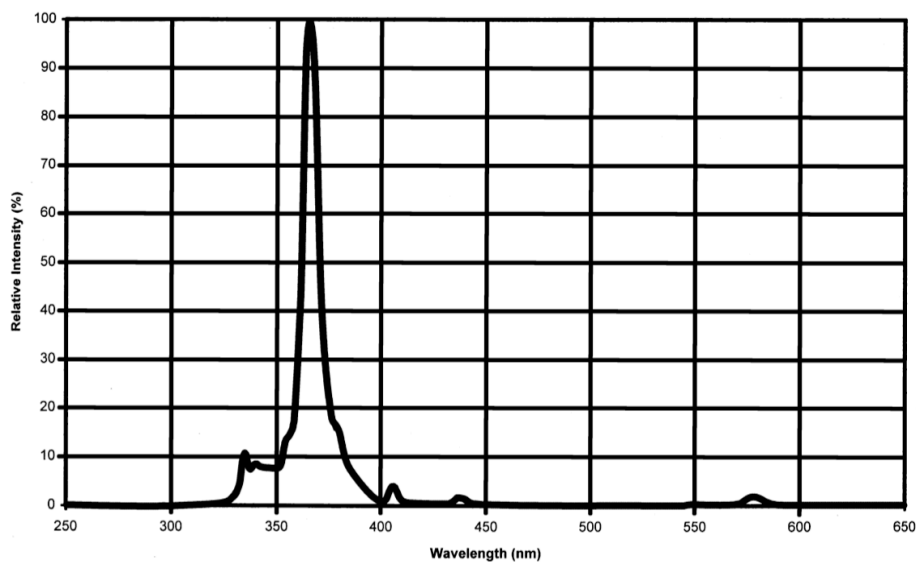


Figure 3. 10. Spectral output of light using the 365 nm filter.

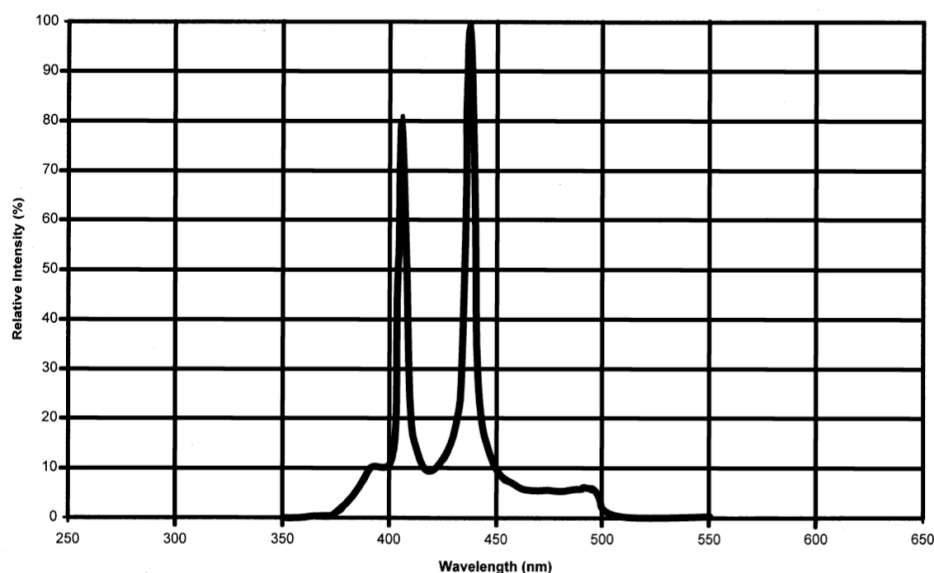


Figure 3. 11. Spectral output of light using the 400-500 nm filter.

3.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR is useful for determining and confirming the structure of an organic material of interest. Nuclei have positive charges and some behave as though they were spinning, generating a magnetic moment and a magnetic field [8]. In this work, H^1 NMR was used, where the spectra give information about the number of hydrogens in a molecule and how they are connected together. This technique utilises the absorption of molecules in the low-energy radio frequency range of an electromagnetic spectrum to generate excitation of nuclear spin states (Figure 3.12). The electrons surrounding the proton nuclei will behave differently in different compounds, depending on the chemical structure of the molecule and the magnetic field applied [8]. When protons in a molecule are surrounded by high or low electron densities, shielding or de-shielding from the applied magnetic field will occur respectively, resulting in differences in frequencies of absorption or chemical shifts [8].

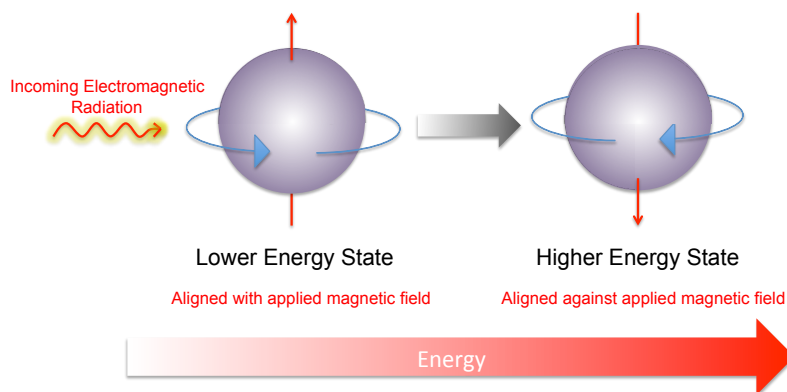


Figure 3. 12. Basic principle of NMR spectroscopy.

The preparation of NMR samples required samples to be dissolved in a deuterated solvent to avoid solvent protons from interfering the spectra. In a typical procedure, the sample was placed in a small glass tube and dropped into a magnet and the spectra were characterised by chemical shifts and by spin-spin coupling between protons. The integration of each peak allowed the relative number of protons in the molecule to be determined.

NMR spectra were recorded on Bruker BioSpin Av400X Spectrometers at 400 MHz in deuterated solvent as indicated. The signal-to-noise ratio increases with the square root of the number of scans. Therefore, 16 scans with 2 seconds acquisition time were collected for each measurement to ensure an adequate signal-to-noise ratio and spectral resolution was obtained. Deuterated solvents were used as a reference for determining proton chemical shifts of sample materials, in dilute solutions.

3.3.4 Ultraviolet Visible Spectroscopy (UV-VIS)

UV-Vis spectroscopy uses light in the visible and ultraviolet region to promote electronic transitions of sample materials from the ground state to the excited state [8]. The absorption of the sample will depend on the energy gap between the ground and excited state, where the materials with lower energy gap absorb in the longer wavelength region [8]. As light cannot penetrate solid samples due to their high opacity, absorption spectra were obtained through the reflection of light on the surface of the sample (Figure 3.13). The intensity of diffusely reflected light depended on multiple reflection, refraction, and scattering from the rough surface of the sample [8]. The spectrophotometer was calibrated against air and background correction was then carried out prior to measurement.

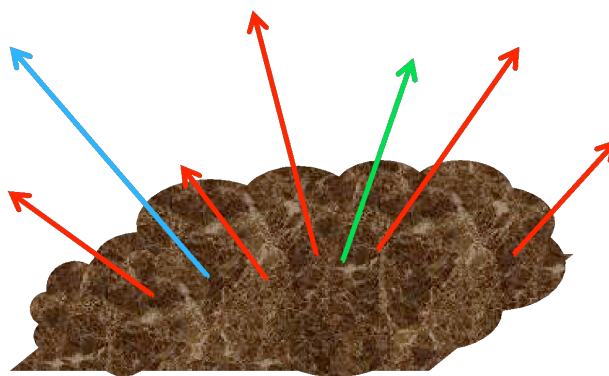


Figure 3. 13. Principle of diffuse reflection.

UV-Vis spectra were obtained using FlexStation® 3 Benchtop Multi-Mode Microplate Reader or Cary 60. The solid samples used were activated accordingly prior to measurements. For the FlexStation® 3 Benchtop Multi-Mode Microplate Reader, excitation and emission wavelengths of the sample in solid state were read in a Corning black flat clear bottom microplate in fluorescence reading mode at room temperature. Agilent Cary 60 UV-Vis spectrophotometer was used to measure the solid sample in KBr form. For photoresponse analyses, the sample was irradiated with light for a certain period of time and the spectra were recorded immediately after irradiation.

3.3.5 Fourier-Transform Infrared Spectroscopy (FT-IR)

FT-IR spectroscopy is useful for providing information on the chemical bonding of materials. The interaction of infrared light ($200\text{--}4000\text{ cm}^{-1}$) with the molecule through the excitation of vibrational modes to higher energy levels generated different absorption spectra (Figure 3.14) [8]. In FT-IR, the vibration of atomic bonds in the molecule was measured. An IR active molecule must display a dipole moment during vibration or have a permanent dipole moment. Different molecules absorb at different frequencies, depending on their structure. Absorption occurred when the frequency of the IR is the same as the vibrational frequency of a bond. Stronger bonds and light atoms typically vibrate at higher frequencies (cm^{-1}). The fingerprint region generally lies below 1500 cm^{-1} , where bending motions of different atomic bonds tend to overlap. The general experimental set-up consists of a radiation source, interferometer and detector. Sample spectra are obtained from the ratio of the sample in beam of light to a background spectra obtained without the sample. The spectra were recorded and processed through a Fourier transformation.

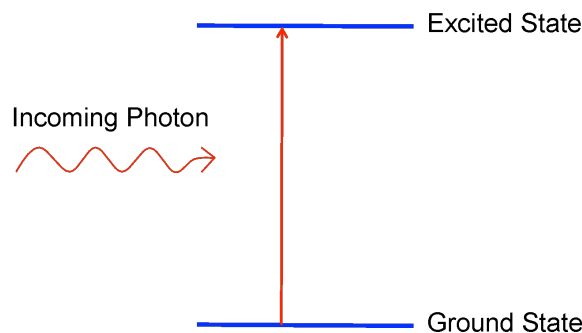


Figure 3. 14. Schematic diagram on the principle of FT-IR spectroscopy. The absorption of photon promotes the molecule to the excited state.

In some experiments, attenuated total reflection (ATR) was also used in conjunction with IR spectroscopy to allow samples to be analysed directly in their natural state with minimal or no sample preparation. In the ATR set-up used for these experiments, infrared radiation entered from the bottom of the ATR base, into a diamond crystal, with a relatively high refractive index (Figure 3.15) [9]. Consequently, a total internal reflection occurred, creating an evanescent wave that extends beyond the surface of the crystal into the sample in contact with the crystal, in which the detector then collected the reflected radiation [9].

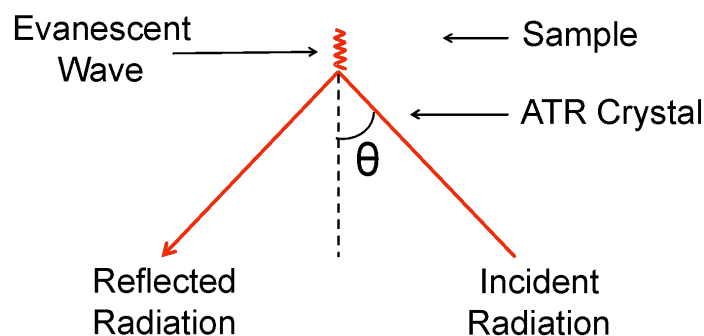


Figure 3. 15. Schematic diagram of a single reflection ATR.

Infrared spectra were obtained on Agilent Cary 630 in KBr form, where powdered samples were diluted in solid KBr and finely ground to obtain a homogenous mixture, with air as the background reference, or on Thermoscientific Nicolet 6700 in powder form. Time-resolved photoresponse experiments were conducted by irradiating the solid sample for a certain period of time and the spectra were recorded immediately after or during irradiation. The solid samples used were activated accordingly prior to measurements.

3.3.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a useful method for investigating changes in physical and chemical properties of sample materials [10]. The mass changes, due to thermal degradation, oxidation, reduction or evaporation of volatile components, are measured as a function of temperature [10]. For the purpose of this thesis, the recorded results were used to determine the material composition, moisture or solvent content, thermal stability and degradation mechanisms.

The general instrumental set-up consists of a high precision thermobalance, for allowing accurate sample weight measurement, within a programmable furnace. In these experiments, analyses were performed by gradually raising the temperature of a sample at a constant rate.

TGA data was obtained on a TGA Pyris 1, Mettler Toledo TGA/SDTA 851 or Mettler Toledo TGA/DSC1 instrument with the temperature ramped from room temperature to 700 °C at a heating rate of 5 °C/min under N₂ gas flow (20 mL/min). The experiment was performed under inert atmosphere (nitrogen) to minimize possible thermal oxidative degradation in air. Platinum and ceramic pans were used as they are reusable and can withstand high temperature of up to 700 and 1200 °C respectively. Furthermore, platinum pans have the advantage of being inert and easy to clean. The pans were thoroughly cleaned between experiments. Ethanol was used to clean a platinum solvent and ceramic pan was heated up to 1100 °C in a furnace for 2 hours. A platinum pan was used on TGA Pyris 1 and a 70 µL alumina pan was used on Mettler instruments to contain approximately 4 mg of the sample, which had been activated accordingly.

3.3.7 Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction is useful for determining crystal structures of a single crystal or powder sample through the diffraction of photons, neutrons and electrons. When an electron is exposed to an alternating electromagnetic field, such as a X-ray, they will oscillate with the same frequency as the field. Crystals are regular arrays of atom and X-rays are wavelike forms of electromagnetic radiation carried by photons. The collision of a photon with another atom will result in the absorption of the photon's energy and generate X-ray scattering. In a regular environment, the scattering will be produced as a regular array of spherical waves. Although most of the scattering will have destructive

interference, where the combining waves are out of phase and resulting in no energy leaving the sample, they add constructively in a few directions. As a result, X-ray beams will be diffracted from the sample at various directions, which can be determined by Bragg's law (Figure 3.16). Bragg's law uses the angle between the incident X-ray beam and the sample surface (θ) and the wavelength of the beam (λ) to determine the spacing between the diffracting planes (d) in the crystal lattice.

The diffraction patterns, which included different peak positions and shapes, were used to confirm and analyse the structural features of materials. Broad or sharp peaks would be obtained if the samples were amorphous or crystalline respectively. This is because in an amorphous sample, the atoms would be arranged in a random way, where as in crystalline samples, the atoms would be arranged in a regular manner.

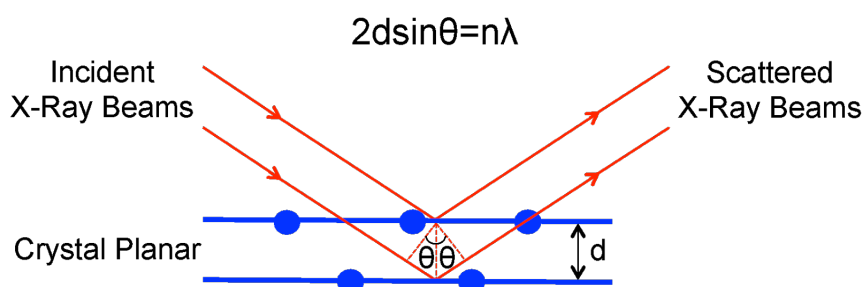


Figure 3. 16. Bragg's Law.

In a single crystal diffraction pattern, the periodic arrangement of atoms resulted in one family of peaks in the diffraction pattern. When solids are not single crystals, all possible diffraction peaks could be observed as they are composed of large numbers of small crystals. These solids are termed as polycrystalline materials. In this case, the diffraction peak is generated from X-rays scattering from an equal number of crystallites. Only a small fraction of crystallites in the sample actually contribute to the generated powder diffraction pattern as most crystallites are not properly oriented to diffract. Powder diffraction data were collected on the powder diffraction beamline at the Australian Synchrotron. Synchrotron X-ray radiation with an incident wavelength of $1.00 \text{ \AA}$ was used to collect data over the range of $2 < 2\theta < 20$ from samples sealed in 0.3 mm diameter quartz capillaries. PXRD data were also collected on the Bruker D8 Diffractometer (Cu $K\alpha$ radiation, 40 kV , 40 mA). The powder data were recorded in the range of $3.5 < 2\theta < 40$ with 0.020° 2θ step size and 0.4 or 1 seconds/step scan speed. For photoresponse experiments, activated light responsive samples were mounted on zero background plates (Figure 3.17). The powder

samples were left to relax in the dark under vacuum overnight prior measurements in air. The general set-up is shown in Figure 3.17, where the light source was positioned over the sample in a way that shadowing of the sample did not occur. A black cloth was used to cover the X-ray instrument when collecting samples in the dark.

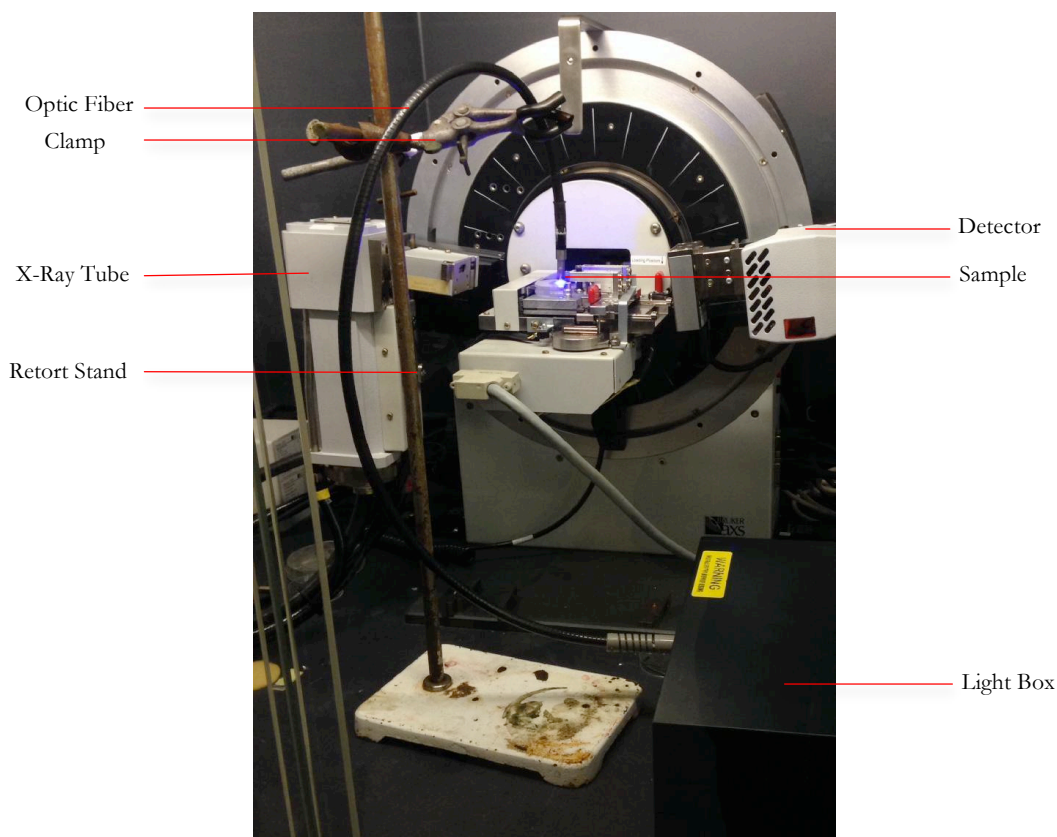


Figure 3. 17. A photo of a general set-up for conducting photoresponsive study on the Bruker D8 Diffractometer instrument.

3.4 References

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Declaration for Thesis Chapter 4

Declaration by candidate

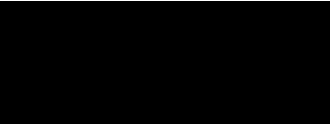
In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

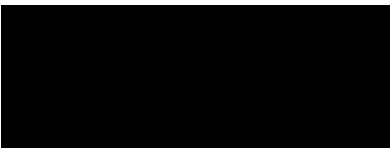
Nature of contribution	Extent of contribution (%)
Experiment and analysis work, writing	100

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
[name 1]	-	-
[name 2]	-	-
[name 3]	-	-

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		Date 31/10/2014
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Main Supervisor's Signature		Date 31/10/2014
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Chapter 4

DYNAMIC PHOTOSWITCHING IN METAL ORGANIC FRAMEWORKS AS ROUTE TO LOW ENERGY CARBON CAPTURE

^aThe work reported in this chapter was published in *Angewandte Chemie* in 2013.

Lyndon, R., Konstas, K., Ladewig, B. P., Southon, P. D., Kepert, C. J., and M. R. Hill, *Dynamic photo-switching in metal-organic frameworks as a route to low-energy carbon dioxide capture and release*. *Angewandte Chemie*, 2013. **52**(13): p. 3695-3698.

4.1 Introduction

Light responsive adsorbents have the potential for overcoming limitations and challenges of conventional carbon capture technologies, particularly post-combustion capture technology, as previously discussed in Chapter 2. Current adsorbent technologies that rely on pressure, temperature, or vacuum swings consume as much as 40 % of the production capacity of a power plant, most of which is associated with the liberation of CO₂ from the capture medium [1-3]. Ultimately this penalty, or parasitic energy load, must be brought closer to the thermodynamic minimum of about 4 % to avoid prohibitive cost increases [4, 5]. Given that the triggers for release of adsorbed carbon dioxide, such as vacuum and heating, are so energy intensive [1, 6-8], requiring energy from the power plant, there is strong motivation to develop new release triggers that do not require extra energy from the plant, using renewable energy sources such as the sun. In conjunction with this, adsorbents with maximum gas sorption efficiency can further reduce the costs compared to the conventional energy-intensive CO₂ gas separation process.

Light, and in particular concentrated sunlight, is an extremely attractive stimulus for triggering CO₂ release. If used with an adsorbent material that strongly absorbs sunlight

concomitant with the desorption of large amounts of CO₂, it may be possible to drastically reduce the energy costs. Perhaps the most attractive adsorbent candidates are Metal-organic Frameworks (MOFs), because of their large adsorption capacities [9-13], and the potential for incorporation of light responsive organic groups within the pore structure [11, 14]. MOFs are an important class of 3D crystalline porous materials comprised of metal centers and organic ligands, joined periodically to establish a crystalline porous array [12]. The large internal surface areas can be used to adsorb unprecedented quantities of gases [13, 15, 16], with particular interest in hydrogen [13, 17-24], methane [13, 21, 24-28], and carbon dioxide emergent [1, 3, 13, 18, 24, 29-31].

Methods for the incorporation of light responsive groups within MOFs include the use of pendant groups pointing into the pores [32], and filling of pores with light responsive guest molecules [33]. The responsive groups within these materials may then alter their conformation when exposed to filtered light which results in a change in adsorption capacity, as reported thus far for static conditions [32, 33]. In static condition, photoirradiation is conducted prior to each adsorption cycle measurement [32, 33]. Thus, the responsive groups within these MOFs can be statically set to one position or another. For use in photoswing CO₂ capture, MOFs that can respond dynamically, or to the broadband radiation found in sunlight whilst loaded with adsorbed gas, are ideal. This will increase the speed of operation and lower the energy costs because photoswitching experiment could be performed in real-time during adsorption measurements (Figure 4.5 and Figure 4.13).

Azobenzene and its derivatives are well-known photochromic molecules that can undergo clean and efficient reversible photoisomerisation about the azo bond (N=N) to *cis* and *trans* states upon irradiation (coordinated *trans*: $\lambda_{\text{max}} \approx 370$ nm, *cis*: $\lambda_{\text{max}} \approx 460$ nm) [34, 35]. As discussed previously in the literature, their photostability and versatility towards chemical functionalisation or substitution make them highly attractive for many applications as molecular switches, optical data storage and in biological system [36, 37].

The change in shape due to photoisomerisation can significantly change the properties of the host materials [38-40]. It has been reported that when azobenzenes are bound to solid materials, photoisomerisation could still occur, given that an adequate free volume is available in the material [38, 41]. For example, when densely packed, *trans*-to-*cis* photoconversion of azobenzenes in self-assembled monolayers (SAMs) on flat gold

surfaces could not proceed and showed no photoactivity [40]. However, when the free volume required for conformational changes was obtained through the use of unsymmetrical azobenzene molecules and mixed components for SAMs, reversible photoisomerisation on solid surfaces was achieved [40]. Photoisomerisation in such constrained environments is reported to predominantly proceed *via* the inversion mechanism, instead of rotation, as shown in experimental [42-44] and theoretical results [45, 46]. This is because the free volume required to convert to the other isomer is smaller, allowing facile photoisomerisation of some azobenzene molecules to occur even in rigid matrices or constrained environment [47]. Most azobenzene based MOFs reported in literatures displayed no photoswitching effect [48-52]. This is because the azo moieties were being fully incorporated, instead of partially incorporated on the solid matrices. Thus the robust nature of MOF frameworks generated steric hindrance on the movement due to photoswitching [32, 53].

Conversion of azobenzene to the 4,4'-dicarboxylate (**AzDC**), the elongated structure form, delivers a ligand that can be incorporated into MOF architectures. Furthermore, the bidentate pillar ligand *trans*-1,2-bis(4-pyridyl)ethylene (**4,4'-BPE**) has also been reported to demonstrate *cis-trans* photoisomerisability when coordinated to a metal complex [54-58]. Combination of these two ligands within zinc-based MOFs generates the triply interpenetrated framework **Zn(AzDC)(4,4'-BPE)_{0.5}**, which exhibits an open topology amenable to high capacity and selective adsorption of hydrogen and carbon dioxide over other gas molecules such as N₂, CO and CH₄ (Figure 4.1) [59]. Most multiply interpenetrated MOFs rarely exhibit permanent porosity [19, 60]. However, the 3D interpenetrated structure of this MOF afforded 1D pore channels of about 3.4 x 3.4 Å along the *c* axis and 3.6 x 3.6 Å along the other axis, such that gas-sorption properties were obtained (Figure 4.1). The permanent porosity was partly due to the three independent nets within the framework, creating 1 D pore channels within the triply interpenetrated topology, which are enforced by van der Waals interaction [19, 60].

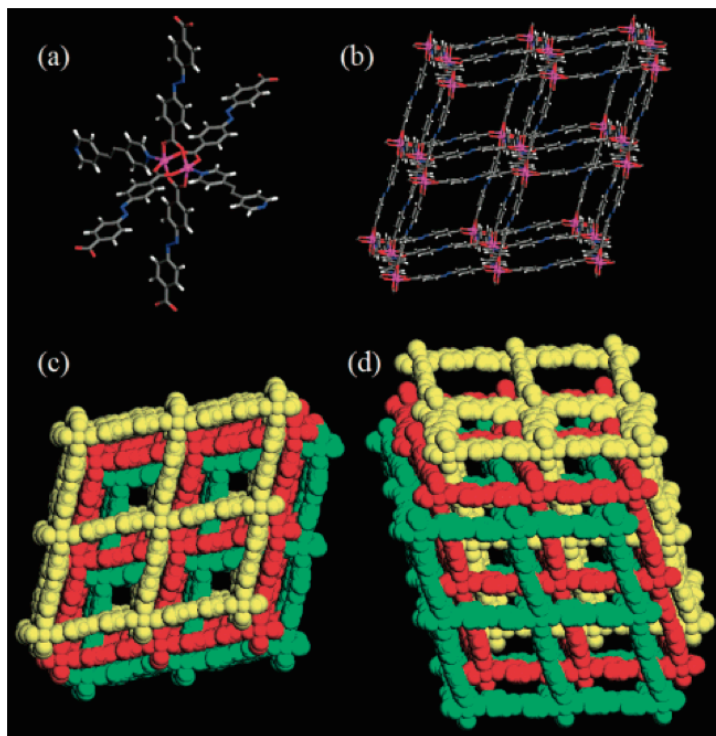


Figure 4. 1. X-ray crystal structure of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ showing a paddle wheel building unit and the coordination geometries (a), one of the three independent primitive cubic nets (b), a 1D channel of $3.4 \times 3.4 \text{ \AA}$ along the c axis (c), and a 1D channel of $3.6 \times 3.6 \text{ \AA}$ along the rectangular diagonal of the paddle wheel clusters (d). Colour code for a) and b): zinc, pink; carbon, gray; nitrogen, blue; oxygen, red; hydrogen, white. Reprinted with permission from [59]. Copyright 2014 American Chemical Society.

The triply interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ was prepared solvothermally using previously reported methods (Section 4.2.3) [59]. The framework is assembled from paddle wheel dinuclear Zn_2 units, bridging **AzDC** dianions and **4,4'-BPE** pillar ligands. The presence of two different light responsive linker molecules: **AzDC** and **4,4'-BPE**, could potentially allow their optical properties to be exploited to obtain potential dynamic photoswitching during CO_2 capture process. To the best of the author's knowledge, dynamic photoswitching could not be achieved for gas capture applications prior to the publication of this paper. In a recent publication, Luo *et al.* reported the photodynamic switching of a diarylethene based MOF developed by the group [61].

Herein we report the discovery of strong, low-energy photoresponse in $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ and find that the behaviour is dynamic and localised, irrespective of the use of broadband or filtered light sources. Previous researchers have not detected *cis-trans* changes where azo groups are part of the MOF wall and not as pendant groups in the pores [53, 62]. In the present work it is reported that bending about the azo group can be

observed to occur on a local scale in a dynamic fashion, perfect for on-line adsorbent regeneration. The effect was directly observed in the UV-Vis emission profiles and time-resolved infrared spectra, and indirectly through gas adsorption experiments with careful controls in place, and pore analysis calculations. We found agreement with the literature in that the effects could not be observed over larger length scales; synchrotron X-ray diffraction did not reveal a structural change [63, 64]. This unusual property was exploited to trigger the uptake and release of carbon dioxide in real time, during adsorption experiments. Exposure to UV light resulted in an instantaneous release of up to 64 % of the adsorbed CO₂ using broadband radiation, similar to concentrated solar sources. Furthermore, the response was found to be fully reversible. The dynamic, yet localised structural movements have been directly characterised spectroscopically, and isolated with several careful control experiments.

4.2 Methods

4.2.1 General

All reagents were used as purchased without further purification. 4-Nitrobenzoic acid and *trans*-1,2-bis(4-pyridyl)ethylene were purchased from Aldrich, zinc nitrate hexahydrate was from Chem Supply, dimethylformamide (DMF) and sodium hydroxide were from Merck, and Glucose was from Ajax Chemical.

4.2.2 Synthesis of Azobenzene Dicarboxylic Acid (AzDC)

AzDC was prepared according to a procedure previously reported by Liu *et al.* [65]. 4-Nitrobenzoic acid (15 g, 0.09 mol) was dissolved into an aqueous sodium hydroxide solution (51 g, 1.3 mol, in 225 mL water) by heating the solution. A hot aqueous glucose solution (101 g, 0.56 mol, in 150 mL water) was slowly added into the above solution at 50 °C, in which the initially formed yellow precipitate immediately turned into a brown solution upon further addition of glucose. The mixture was allowed to react overnight at room temperature to form a dark solution. Methanol was added to the aged solution until a bright brown precipitate formed. The filtered precipitate was dissolved in water, followed by acidification with acetic acid (20 mL), whereupon a light pink precipitate was obtained. The product was filtered, washed with excess water and dried overnight to yield the final product (4.92 g, 17 mmol, 38.5 %). ¹H NMR (DMSO, 400 MHz): δ (ppm) 8.04-8.06 (d,

4H), δ 8.18-8.20 (d, 4H), δ 13.0 (brs, 1H). ^{13}C NMR (DMSO, 500 MHz): 122.86, 130.72, 133.50, 154.17, 166.67.

4.2.3 Synthesis of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$

The MOF was solvothermally synthesised according to the procedure described by Zhou *et al.* [59]. A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, **AzDC** and **4,4'-BPE** was suspended in DMF (100 mL) and heated at 100 °C for 24 h. The resulting red block-shaped crystals formed were filtered and washed with DMF and hexane, and dried in air.

4.2.4 Characterisation Methods

Please refer to Chapter 3 for general characterisation procedures (Section 3.1-3.2).

The MOF used in this work was of high quality and comparable to those reported in the literature. The measured BET surface area of the activated MOF was 126 m^2/g (literature: 100 m^2/g) [59]. Other characterisation results, including the thermal analysis (Figure 4.3) and PXRD data (Figure 4.10), are in good agreement with the reported data in literature [59].

4.2.5 Broadband Light Irradiation Experiment

No filter was used and the light intensity was fixed at 24.6 W/cm^2 in the wavelength range (200-500 nm). Please refer to Chapter 3 for light responsive gas adsorption experimental set-up (Section 3.3.2).

4.3 Results and Discussions

The crystal structure shows that the framework is 3D triply interpenetrated in a primitive cubic structure with pore windows in the range of 3.4-3.6 Å (Figure 4.2) [59]. Optical switching property of $\text{Zn}(\text{AzDC})(4,4\text{-BPE})_{0.5}$ may be possible due to the presence of light responsive groups: **AzDC** and **4,4'-BPE**, within the framework.

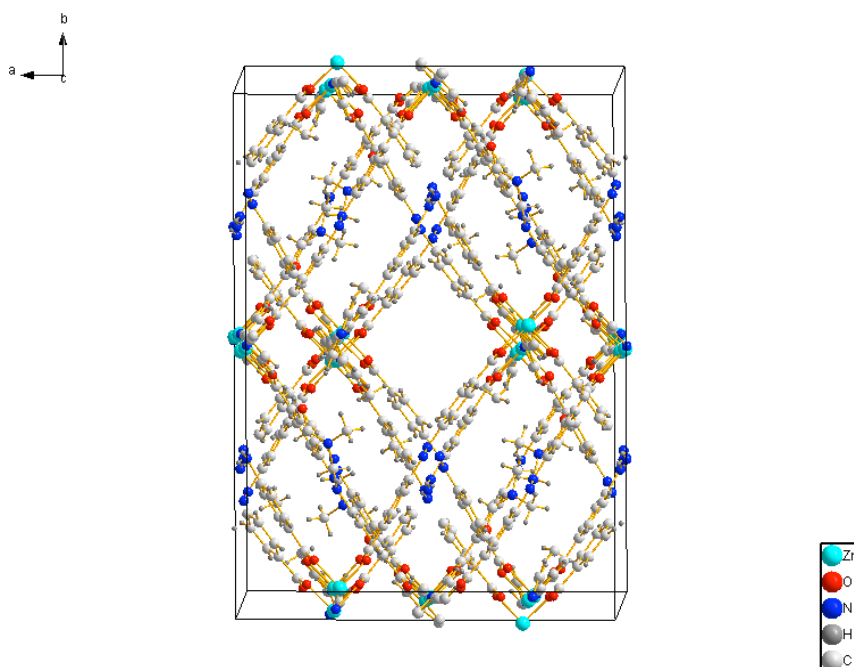


Figure 4. 2. Crystal structure of $\text{Zn}(\text{AzDC})(4,4\text{-BPE})_{0.5}$ [59].

Characterisation of the non-irradiated MOF was first obtained to ensure that the material obtained is comparable to the literature. From the TGA result, it is evident that after solvent exchange with dry methanol showing that the MOF is thermally stable up to 400 °C which is in accordance with the literature value (Figure 4.3) [59]. Upon the decomposition of the framework, approximately 55 % of the initial weight was lost. Different gas adsorption isotherms were also obtained to compare with those reported in literature (Figure 4.4) [59]. However, because of the interpenetrated nature of the sample resulted in restricted pore channels, adsorption capacity was dependent upon the equilibration times used. The hydrogen adsorption capacity in particular could have been optimised through extensive variations of the equilibration time, however this was not a focus of the work.

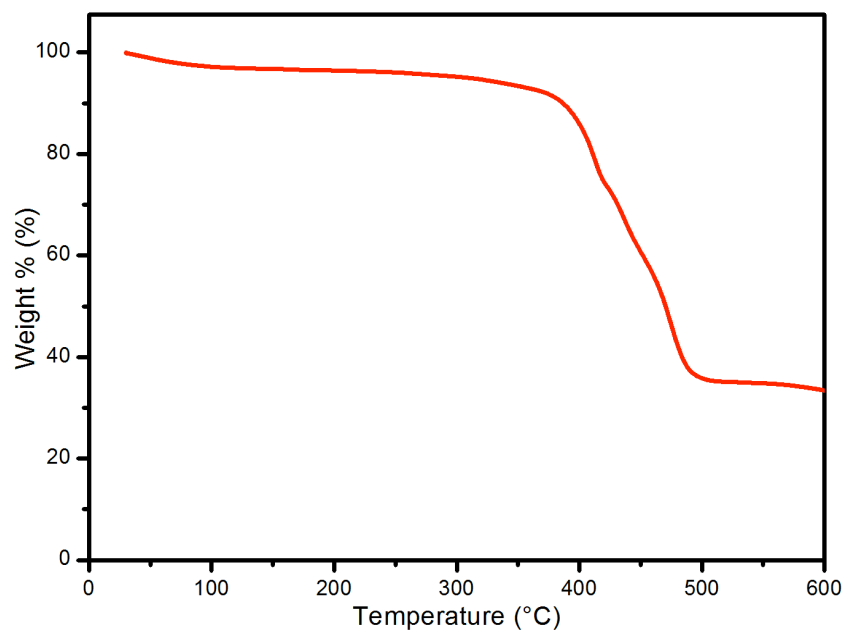


Figure 4. 3. TGA profile of methanol exchanged $\text{Zn(AzDC)(4,4-BPE)}_{0.5}$.

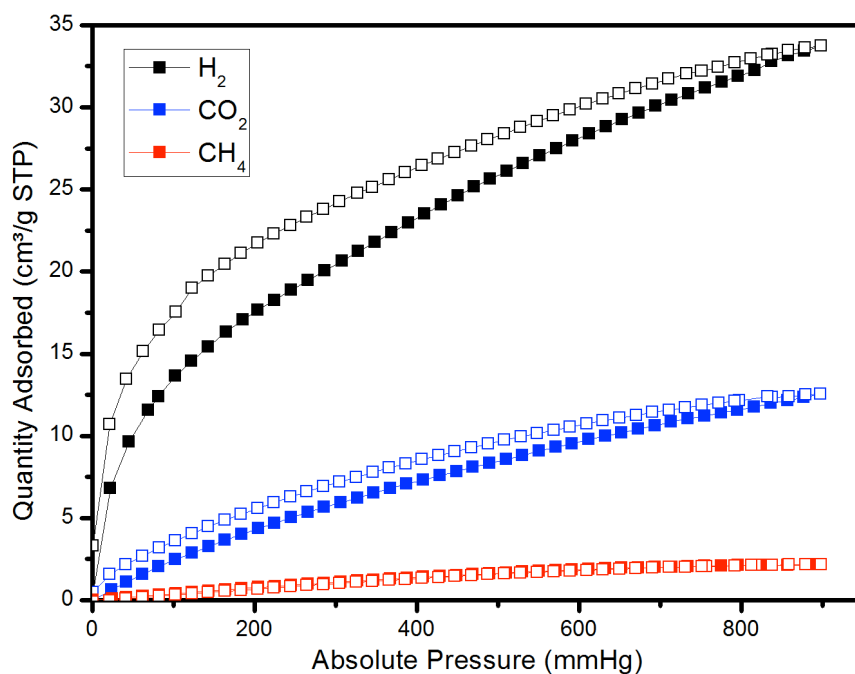


Figure 4. 4. Gas adsorption isotherms of $\text{Zn(AzDC)(4,4'-BPE)}_{0.5}$ at 77 K (hydrogen, black) and 298 K (carbon dioxide, blue; and methane, red). Solid and open shapes correspond to adsorption and desorption respectively.

4.3.1 Photoswitching mechanism

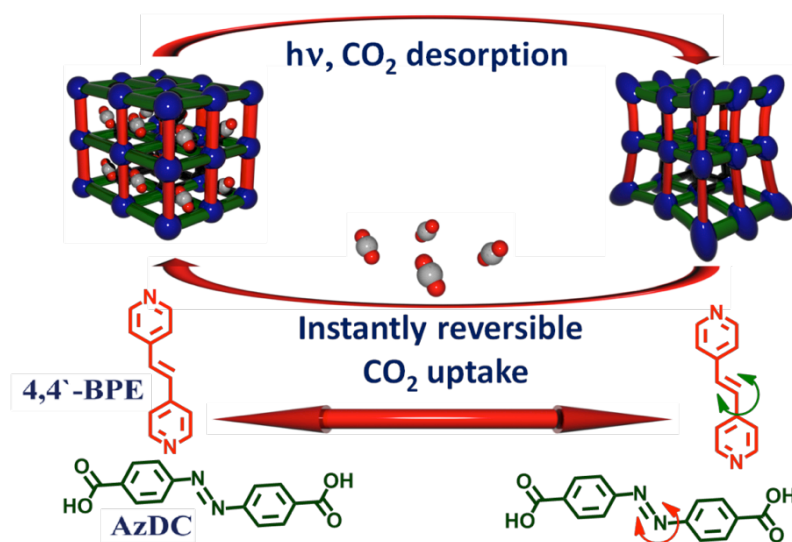


Figure 4. 5. Dynamic photoswitching in the light responsive MOF $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ leads to instantly reversible CO_2 uptake.

To examine the optical properties of the **AzDC** and **4,4'-BPE** light responsive linkers, PXRD, UV-Vis and FT-IR data were collected. *Trans*- and *cis*-**AzDC** $n\text{-p}^*$ (S1 state) and $p\text{-p}^*$ (S2 state) transitions can be detected at 455 and 380 nm in the excitation spectra, respectively (Figure 4.6). The coordination of **4,4'-BPE** to Zn results in a photoactive species under light irradiation [55]. The *trans* isomer of the **4,4'-BPE** ligand exhibits overlapping excitation bands of metal-to-ligand (MLCT) and ligand-to-ligand (LLCT) charge-transfers in the 310–375 nm region (Figure 4.7) [55]. Excitation in this region generates *trans*–*cis* isomerisation as shown in the excitation spectra where the MLCT band maximum shift to 285 nm [57]. Both *cis*-**AzDC** and **4,4'-BPE** can return to their *trans* state.

Photoresponsive studies in solid state revealed a photoactive framework. The excitation band at 380 nm and 455 nm observed in the UV-Vis spectrum is due to the *trans* and *cis* **AzDC** in the MOF respectively (Figure 4.6) [66]. The peak at 330 nm and 430 nm is characteristic of the *trans* and *cis* free **AzDC** ligand respectively [66]. The purpose of these experiments was to determine the likely absorption maxima for obtaining the strongest localised bending possible within the framework. On the other hand, the excitation wavelengths of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ at the 300 nm region and 285 nm correspond to the *trans*-**4,4'-BPE** and *cis*-**4,4'-BPE** peaks respectively. Free **4,4'-BPE** was found to have no photoactivity in the solid state.

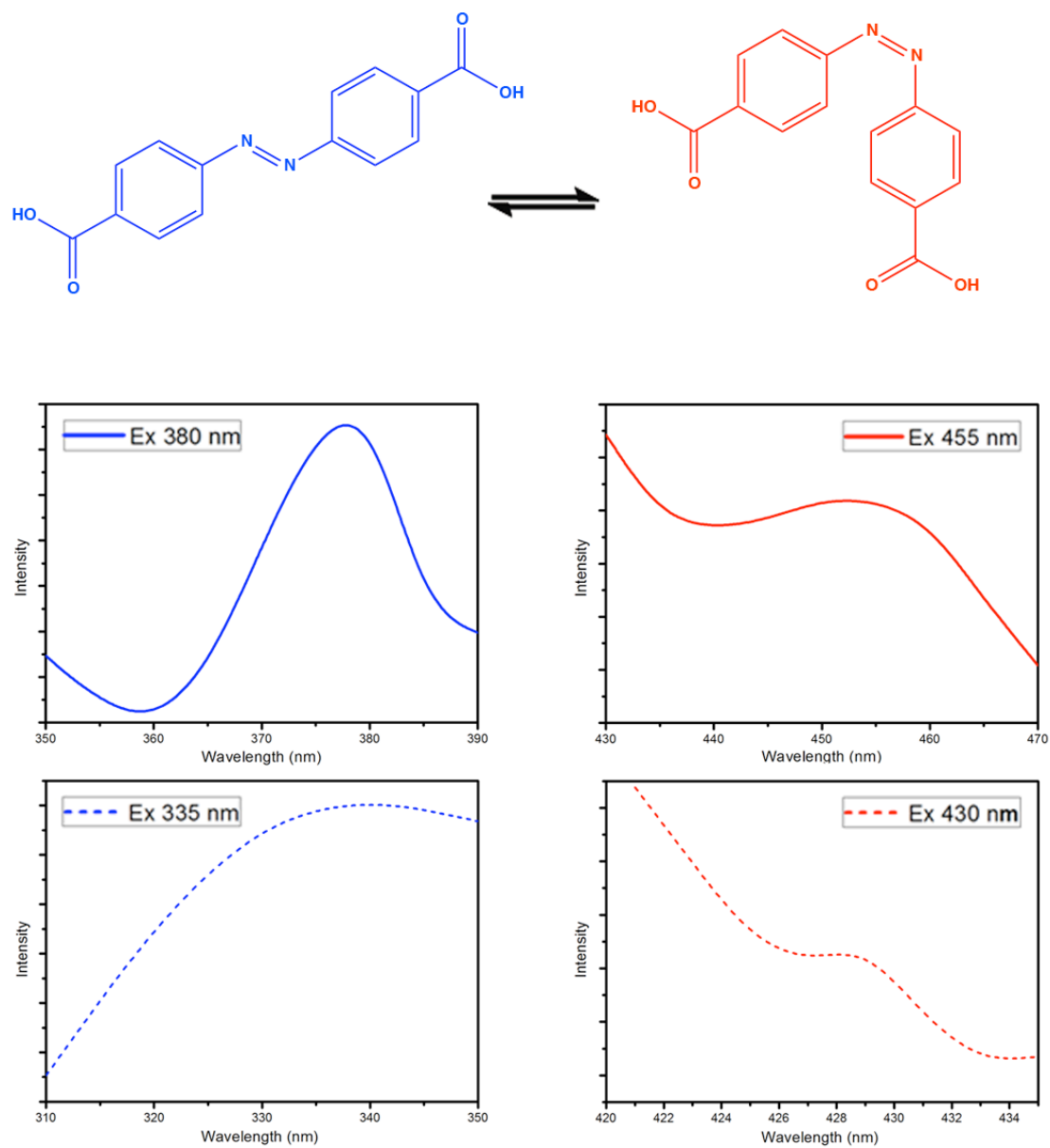


Figure 4. 6. Excitation spectra of AzDC ligand in the MOF (solid line) and free AzDC ligand (dashed line) with an emission wavelength of 370 nm (red) and 460 nm (blue).

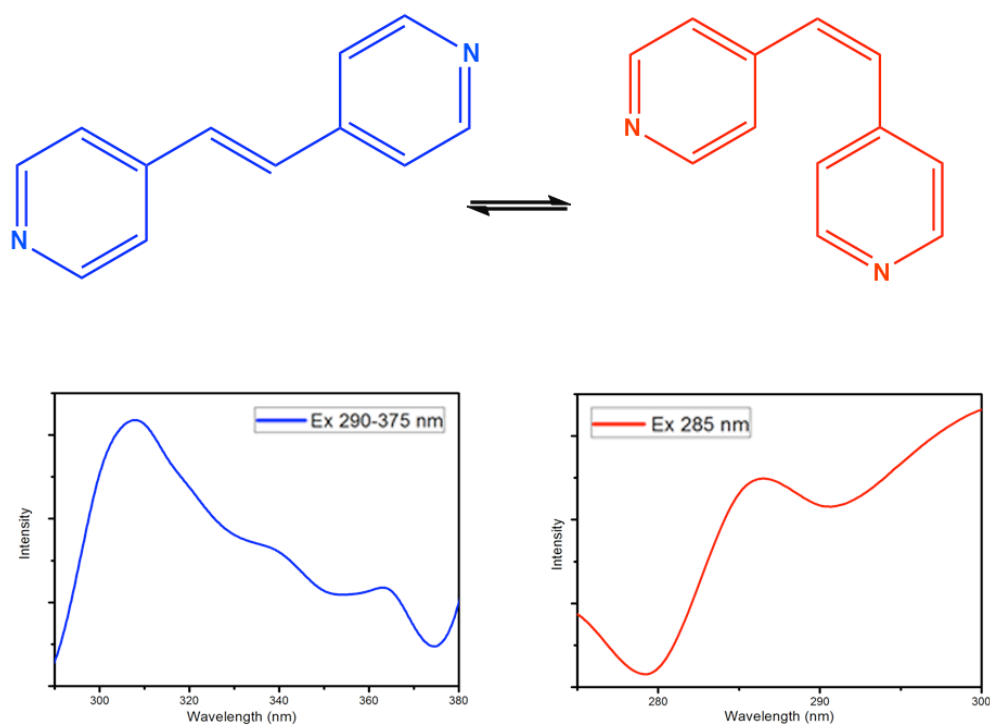


Figure 4. 7. Excitation spectra of 4,4'-BPE of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ with an emission wavelength of 250 (blue) nm and 370 nm (red).

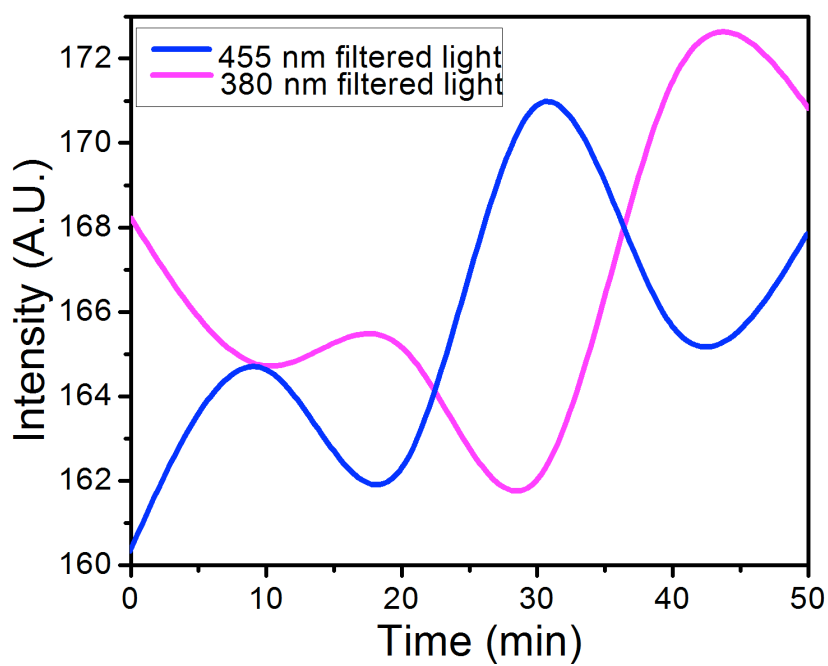


Figure 4. 8. UV-Vis spectra of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$. The material was continually irradiated with 455 nm (blue) and 380 nm (magenta) filtered light.

A further response study was conducted to gain a better understanding of the mechanism. The framework was continuously exposed to either 365 or 460 nm light and the intensity of the absorption peak was monitored. Continual irradiation led to oscillations between native and excited states witnessed with UV-Vis absorption. Absorption related to *trans*-**AzDC** and *cis*-**AzDC** moieties was found to be complementary and also periodically changing, regardless of whether the excitation wavelength promoted formation of either *cis* or *trans* structures (Figure 4.8). Under continuous irradiation from either 370 nm (promote *cis*-**AzDC**) or 460 nm light (promote *trans*-**AzDC**), small fractions of the structure were found to periodically oscillate between both isomeric conformations in a complementary fashion given the additive nature of *cis* and *trans* peaks across the two separate experiments (Figure 4.8). Similar additive effects were less clear from **4,4'-BPE** excitation profiles where there was considerable overlap, although this ligand also clearly underwent transitions whilst coordinated within the framework (Figure 4.9). Most likely, this continual reversion to native states even under irradiation that promotes an isomeric transformation stems from the structural stresses induced within the interpenetrated framework, due to the components also being critical to the topology, and not pendant to it. Furthermore, rapid changes predominantly through bending motions must occur throughout the framework to maintain the original triply interpenetrated framework and accommodate the constraints [67]. The changes could not be observed on a periodic scale however, with synchrotron X-ray diffraction experiments revealing no changes (Figure 4.10).

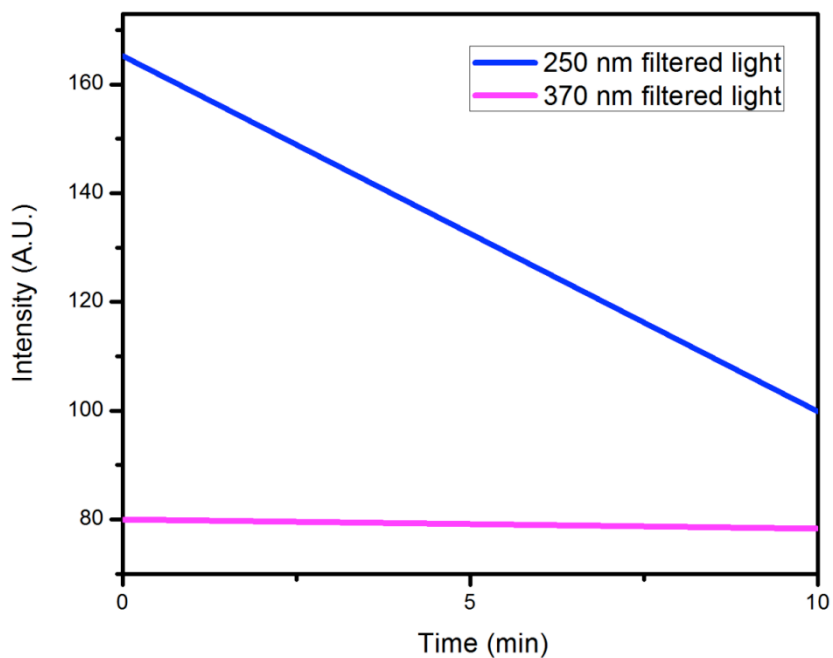


Figure 4. 9. Maximum intensity of *trans*- and *cis*- 4,4'-BPE peak at 310 nm (blue) and 285 nm (red) respectively. $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ was continually irradiated for 10 minutes with 370 nm (red) and 250 nm (blue) light at room temperature.

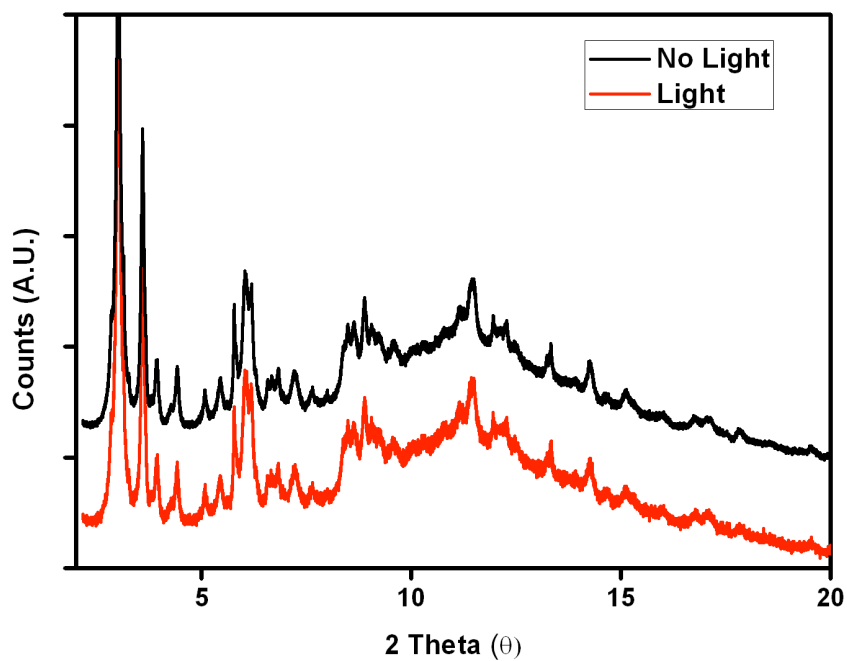


Figure 4. 10. Synchrotron PXRD of non-irradiated (black) and irradiated (red) $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$.

To characterise the presence of framework transformations due to light, PXRD experiments were conducted. However, structural transitions during photoresponse were local and dynamic, as synchrotron PXRD experiments did not reveal any periodic changes (Figure 4.10). Thus, FT-IR and UV-Vis analyses were conducted to further confirm that local dynamicity was occurring within the framework (Figure 4.6-4.12).

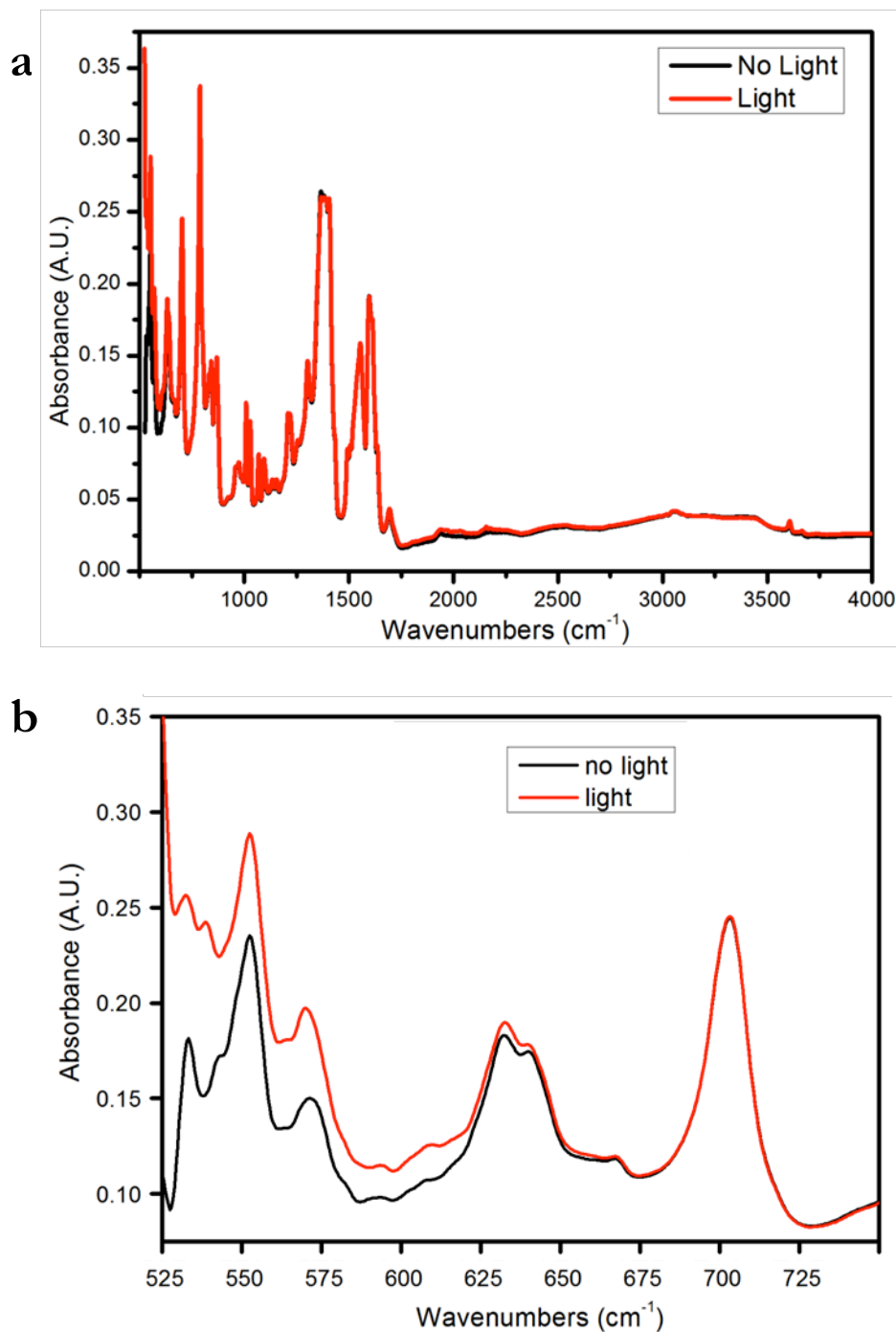


Figure 4. 11. The full FT-IR spectrum (a) of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ and a close up region in the FT-IR spectrum (b).

To directly observe the structural oscillations, time-resolved FT-IR spectroscopy under UV irradiation was performed (Figure 4.11-4.12). In the FT-IR spectra of the MOF, significant changes in peak intensity for the region of 540–700 cm^{-1} were observed under irradiation, whereas the remaining spectrum was unchanged (Figure 4.11). The peak intensity increase at 550 cm^{-1} can be attributed to C-C-C and C-C-N bending modes with **AzDC** [68], indicating low-energy structural variations about the azo group, which occurred due to the suppression of *cis*–*trans* isomerisation [69].

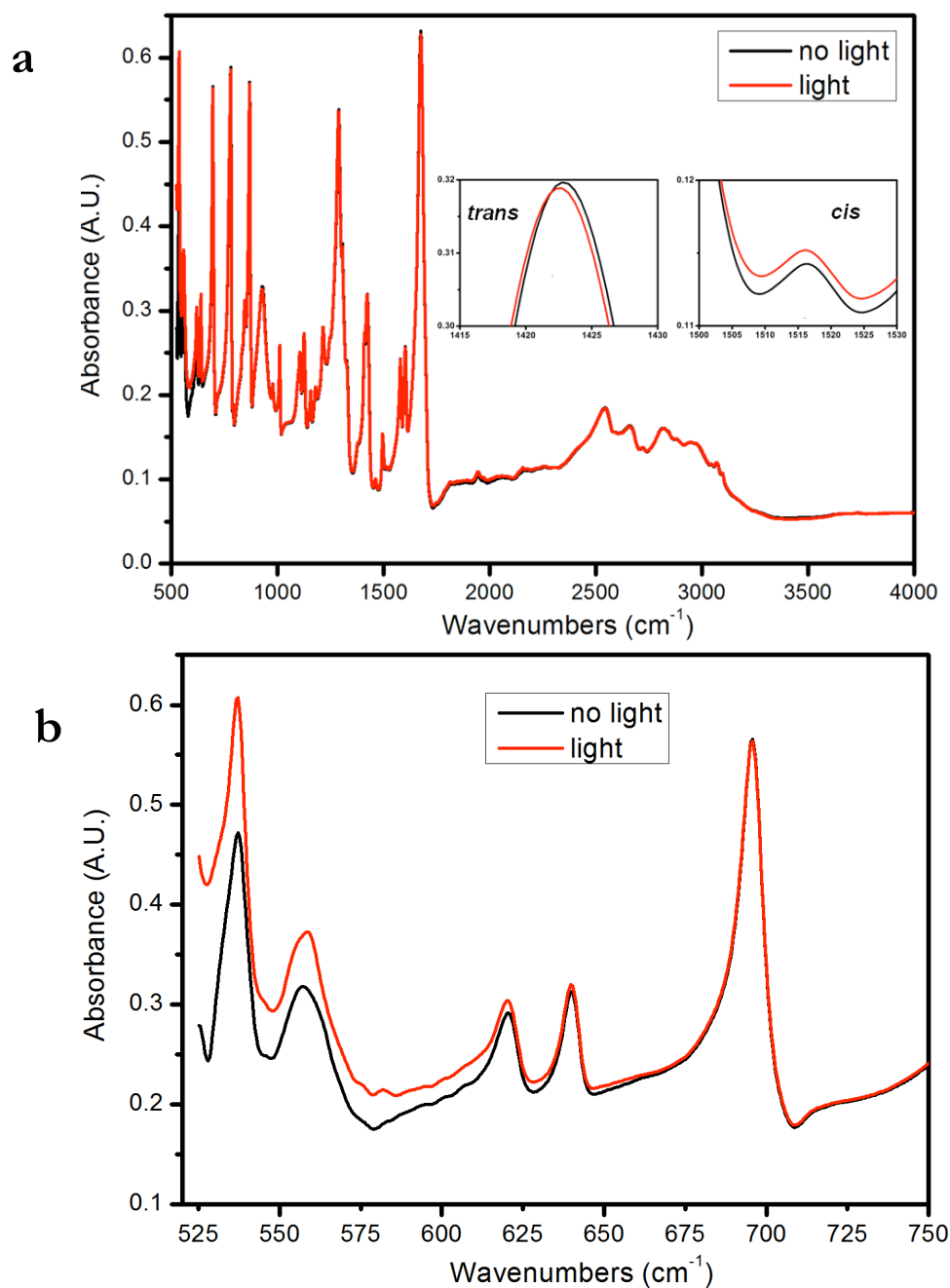


Figure 4. 12. The full FT-IR spectrum (a) of free AzDC ligand and a close up region in the FT-IR spectrum (b).

Similar experiments on the free ligand **AzDC** confirmed this effect (Figure 4.12). C-C-C- and C-C-N low energy FT-IR bending modes in **AzDC** were found to be excited by UV in both the ligand and the framework (Figure 4.11 and 4.12). An increase in intensity at 537 cm^{-1} indicated the activation of bending modes about the C-C-N bonds within the ligand. Furthermore, very minor peak increases in the free ligand at 1516 cm^{-1} were observed, assigned to higher energy *cis*-N=N stretching modes forming as the native trans material was excited [70]. These modes were not seen to change within the framework, highlighting the restricted **AzDC** in this structure, which could not undertake these transitions. This also explains why no changes were seen in the X-ray diffraction pattern (Figure 4.10). This result was also replicated with similar UV-Vis experiments, where only a small fraction of *cis* isomers were detected (Figure 4.8).

4.3.2 Dynamic Photoresponse in CO₂ adsorption

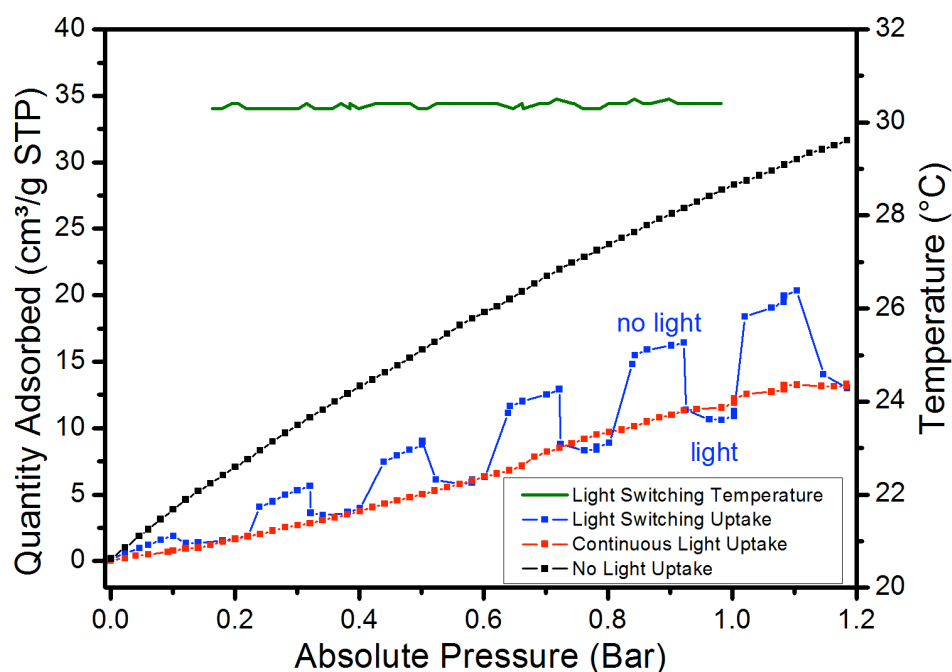


Figure 4. 13. CO₂ adsorption isotherms of Zn(AzDC)(4,4'-BPE)_{0.5} at 303 K in the presence of light (red), absence of light (black) and unfiltered light switching environment (blue).

Photoresponse was observed upon light irradiation of Zn(AzDC)(4,4'-BPE)_{0.5}, whereby adsorption and desorption of adsorbed CO₂, occurred in the absence and presence of light, respectively (Figure 4.13). Zn(AzDC)(4,4'-BPE)_{0.5} exhibits unprecedented dynamic switching under CO₂ adsorption, with a 42 % desorption capacity under static irradiation conditions (red and black curves), and as much as 64 % during dynamic measurements

(blue curve) (Figure 4.13). As shown in the FT-IR result, the C-C-N bending modes of **AzDC** and **4,4'-BPE** linker molecules are likely to be responsible for the spontaneous release of adsorbed CO₂ upon irradiation, in which the pore surface was activated and the surface energy was increased (Figure 4.11). Light irradiation increased the MOF surface energy, in which intermolecular interactions between CO₂ molecules and the surface weakened, and thus triggered instantaneous CO₂ release. Photodynamicity triggered by the free **AzDC** and **4,4'-BPE** molecules was not possible because of the small pores of the MOF (3.4 x 3.4 Å) (Figure 4.2) [59]. Dynamic irradiation isotherms follow values obtained under continuous irradiation conditions, however the reversal in uptake was not entirely complete under the dynamic measurement conditions employed. Collection of N₂ isotherms at 77 K have been attempted to probe the surface areas of the non-irradiated and irradiated MOF. However, the condensation at the light guide surface resulted in an inability to deliver light to the surface. CO₂ adsorption in the presence of light did not follow the D-R model and thus the surface area could not be obtained (Figure 4.14). This is due to gas adsorption at the surface being disturbed by the presence of UV light [71].

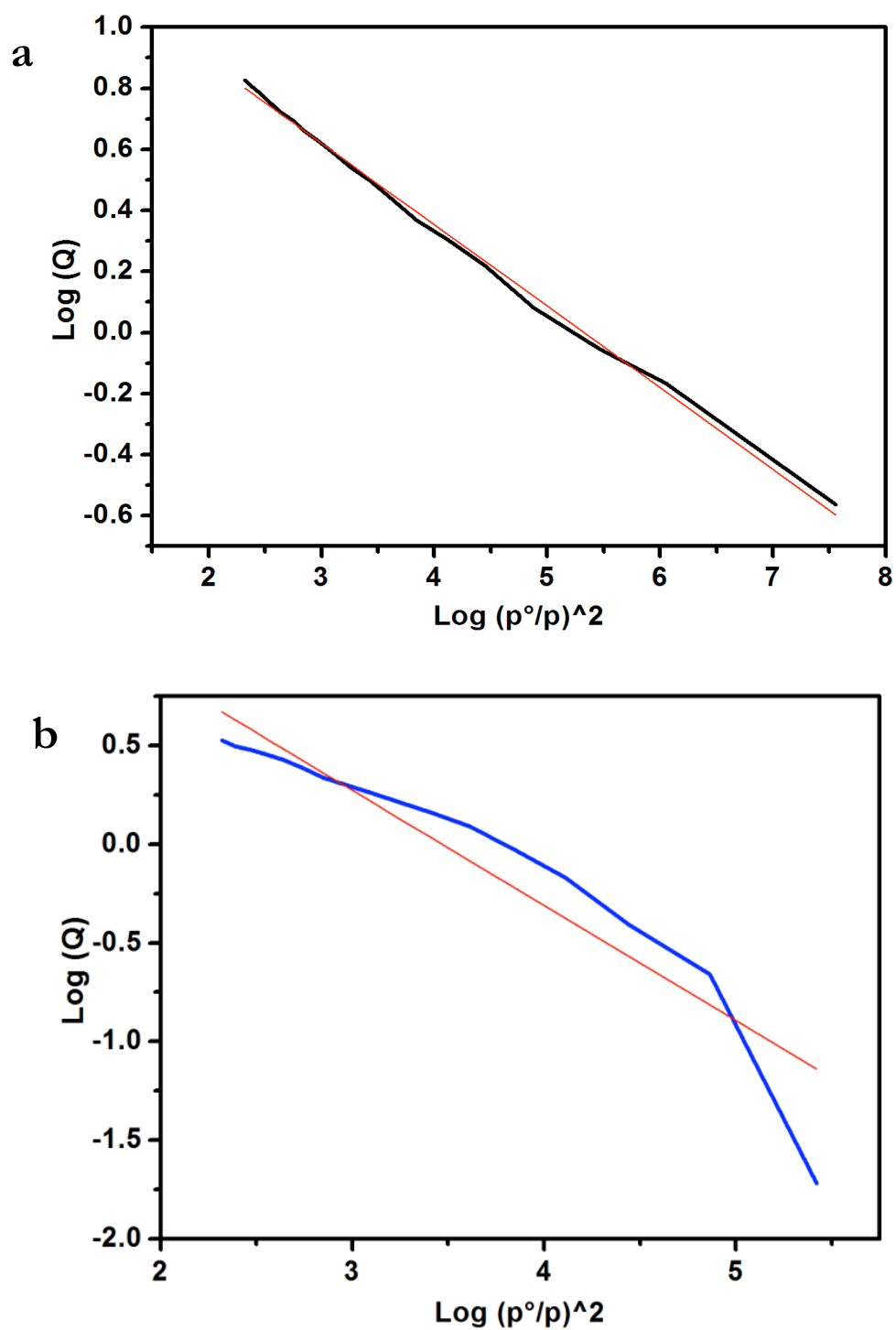


Figure 4. 14. CO₂ adsorption isotherm in the presence (blue) and absence (black) of light at 273 K was fitted with the Dubinin-Radushkevich (D-R) equation (red) to detect the change in pore size.

4.3.3 Influence of Filtered Light in CO₂ Adsorption

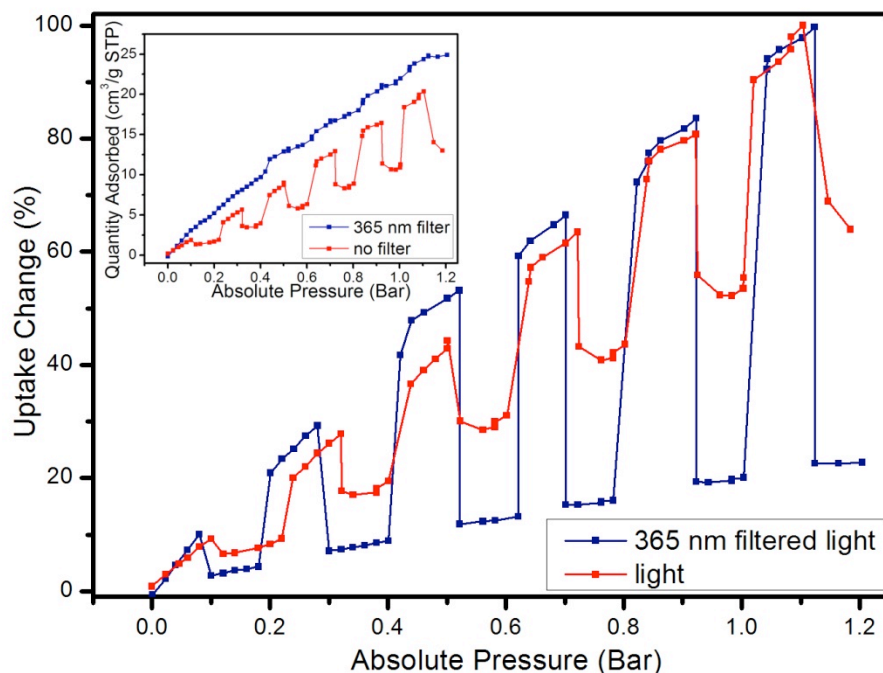


Figure 4. 15. Performance of photoswitching according to light wavelength, normalised for flux. 365 nm filtered light is optimal for *cis-trans* photoisomerisation of both AzDC and 4,4'-BPE ligands.

Inset: original data without normalisation.

Accounting for variations in raw uptake amounts, and changing flux gives Figure 4.15. The absolute CO₂ uptake is increased and the amount released upon light exposure lessened when a filtered light source, which has a lower flux, is used. Here it is shown that the efficiency of CO₂ release is greatly enhanced by the use of 365 nm filtered light (Figure 4.15). As shown in the UV-Vis result, filtering the light to 365 nm promoted photoisomerisation in both the **AzDC** and **4,4'-BPE** ligands, which was responsible for the photoresponse observed during gas adsorption experiments (Figure 4.15). In both cases the adsorption amounts in the absence of light irradiation are similar, yet CO₂ desorption is found to be more efficient with use of filtered 365 nm radiation. This effect is most pronounced at high partial pressures, yet it is notable that at partial pressures similar to those encountered in post-combustion capture gas streams (*ca.* 0.15 bar) that unfiltered light gives a very comparable response. The results imply that in cases where the light intensity is not a limiting factor, that filtration to 365 nm is preferable, but in other instances, unfiltered, concentrated sunlight will also perform almost as well, especially in post-combustion capture streams. Illuminations up to 20 W/cm² (200 solar equivalents) can be achieved using concentrated sunlight [72, 73].

A series of careful control experiments were undertaken to ensure that this phenomenon was not an experimental or material artefact, but due solely to the dynamic photoresponse observed. Careful localised temperature monitoring showed that the temperature varied by less than 0.2 °C, indicating that minor localised heating did occur, however it was not a significant factor in the uptake variation (Figure 4.16). Furthermore, experiments with control materials including SAPO-34 zeolite, and also a framework without known photoactive groups, Cu-BTC (Basolite C300), showed almost no CO₂ uptake variations upon UV irradiation (0.2 and 2 % vs. 64 % for **Zn(AzDC)(4,4'-BPE)_{0.5}**) (Figure 4.16). In comparison to the 64 % response in **Zn(AzDC)(4,4-BPE)_{0.5}**, the response is very low. An isobar has been measured, where temperature was changed with constant pressure, and these show that the temperature needs to rise by 25 K for the same uptake variation to be observed (Figure 4.17). A degree of the release may be due to general sample heating, although this is likely to be small given the negligible change in control samples.

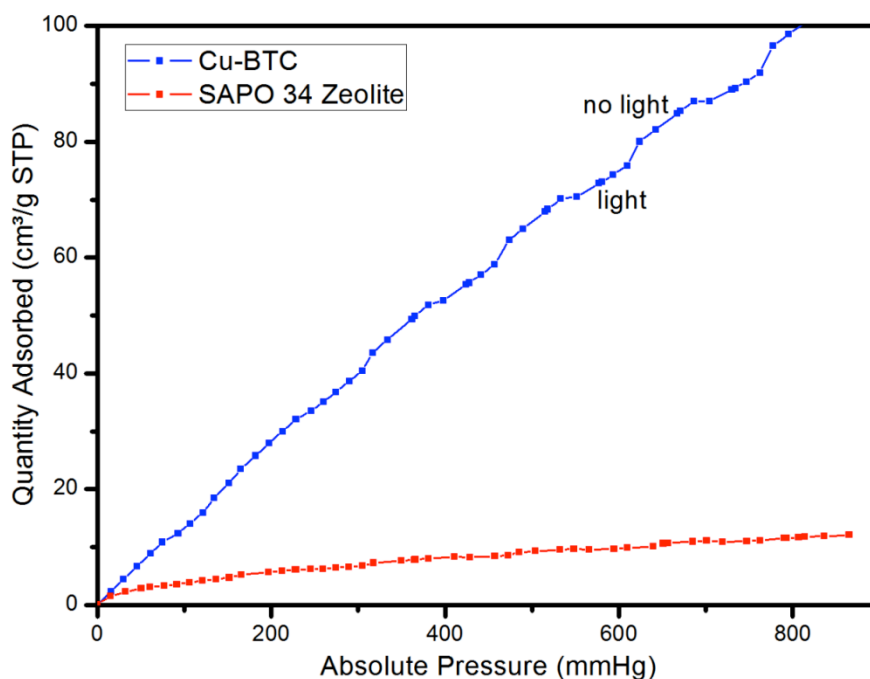


Figure 4. 16. Control experiments using non-photoactive materials to verify the effect of light on **Zn(AzDC)(4,4-BPE)_{0.5}**. CO₂ adsorption isotherms of Cu-BTC (blue) and SAPO-34 zeolite (red) at 303 K.

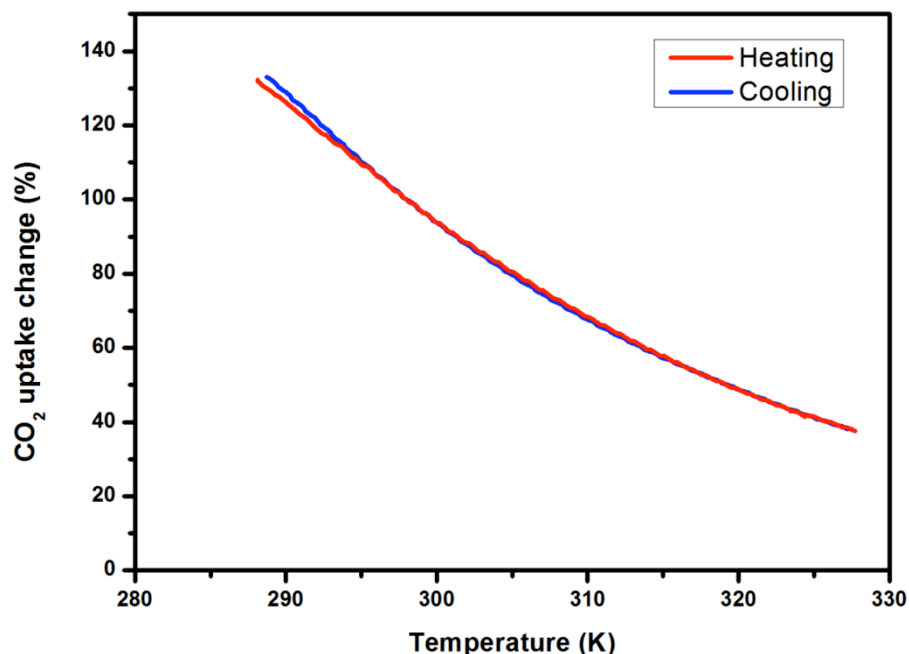


Figure 4. 17. An adsorption isobar of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ showing the dependence of the CO_2 uptake on sample temperature at 1 bar CO_2 . The temperature was ramped at 0.1 K/min from 288 to 328 K, then back to 288 K.

4.4 Conclusions

These remarkable results stem from the fact that the photoinduced structural changes in $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ are dynamic as witnessed both directly with UV-Vis and FT-IR experiments, and indirectly driving photoresponsive gas adsorption. The foregoing results demonstrate that the interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ can undergo dynamic light induced structural flexibility, which results in large variations in CO_2 uptakes. For the first time an experimental protocol was established to exploit this remarkable property for low-energy CO_2 capture and release. The variation in CO_2 capture performance was found to be exceptionally strong, as much as 64 % under dynamic measurements and 42 % under static conditions. Characterisation of the framework showed that the light induced structural flexibility is due to both the **AzDC** and **4,4'-BPE** ligands, occurring reversibly and on a local scale, even under irradiation that would promote formation on just one conformer. Detailed characterisation showed that the transitions occurred only on a short range scale, and in a dynamic fashion, accounting for a lack of detection on longer length scales, in line with previous studies. This approach represents a potential route to renewable energy CO_2 capture and release, and was found to remain effective under broadband irradiation. This means that unfiltered sunlight may

be used instead of the energy intensive temperature and pressure swings to release trapped gases. Further developments in this area include other mechanistic investigations, in further increasing the already strong response, developing similar responses in the visible region, and taking advantage of the performance within industrially relevant mixed gas streams.

4.5 References

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Declaration for Thesis Chapter 5

Declaration by candidate

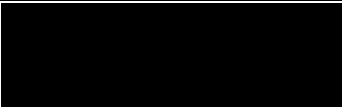
In the case of Chapter 5, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Experiment and analysis work, writing	100

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
[name 1]	-	-
[name 2]	-	-
[name 3]	-	-

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		Date 31/10/2014
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Main Supervisor's Signature		Date 31/10/2014
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Chapter 5

DYNAMIC PHOTOSWITCHING OF DARE@PAF-1 FOR CARBON CAPTURE AND RELEASE

5.1 Introduction

Photodynamic switching was proven to be promising for low cost carbon capture and release, as reported for the first time in Chapter 4. It overcomes the challenges encountered in conventional carbon capture technologies, where energy intensive vacuum, pressure or temperature swings were used to trigger the CO₂ release in order to regenerate the absorbents for the next cycle. As previously discussed, light is an attractive stimulus for triggering the capture and release of CO₂, owing to their abundant availability in nature and capability for instantaneous delivery into materials. Previous reports have shown that light responsive properties can be introduced to porous materials through the use of light responsive pendant groups or guest molecules [1, 2]. However, recently localised bending of photoresponsive linkers within the framework can also display photoresponse property, as demonstrated in Chapter 4 [3]. Photoresponse of up to 42 % and 64 % was achieved under static and dynamic photoswitching respectively [3]. Through this discovery, the dynamic photoswitching property was exploited for dynamic CO₂ capture and release [3]. As such, further development for a more improved dynamic light responsive system for novel carbon capture technologies was conducted.

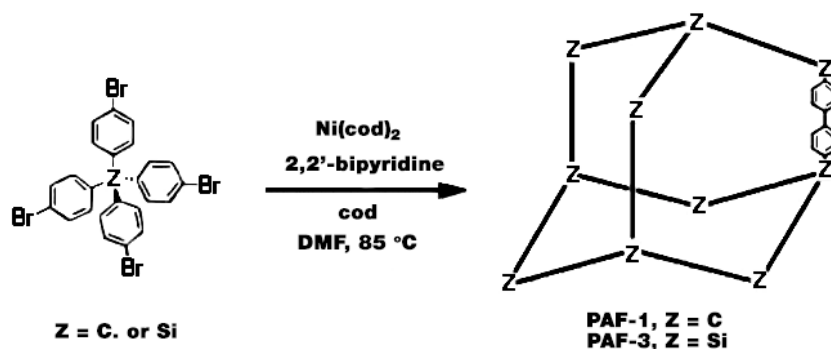


Figure 5.1. General synthetic procedure for PAF preparation. Reprinted with permission from [4].

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With the motivation to further develop the novel strategy, further research was conducted using different potential adsorbents and light responsive groups. Porous materials remain one of the most intensively studied classes of adsorbents for gas storage and separation applications, whereby gas can be adsorbed in the pores of the material [5-7]. Porous aromatic framework (PAFs), particularly **PAF-1**, is one of the most promising recent developments in the field of carbon capture materials [4]. They feature diamondoid networks where the tetrahedral atomic or small-molecular centers are connected by simple biphenyl units [4]. PAF materials are typically synthesised by the nickel catalysed Yamamoto-Ullmann cross-coupling of tetrakis(4-bromophenyl)methane monomers (Figure 5.1) [8-11]. PAF possesses those inherent properties displayed in MOFs such as; high surface area, high porosity, high gas uptake capability and tunable properties [8-11]. **PAF-1**, being one of the most porous versions of the PAF materials, can display BET surface areas of up to 5600 m²/g [11]. However, unlike most MOF materials, PAFs have the additional advantage of exhibiting high thermal and hydrothermal stability [8, 9, 12]. Recent literature reports showed that optical properties could be introduced in PAFs through the use of photoresponsive pendant groups and photoresponsive linker molecules [13, 14]. However, to this date, dynamic photoresponsive PAF materials for CO₂ adsorption have not yet been reported. Thus further research was conducted in order to achieve dynamic photoswitching of PAFs containing light responsive groups for carbon capture.

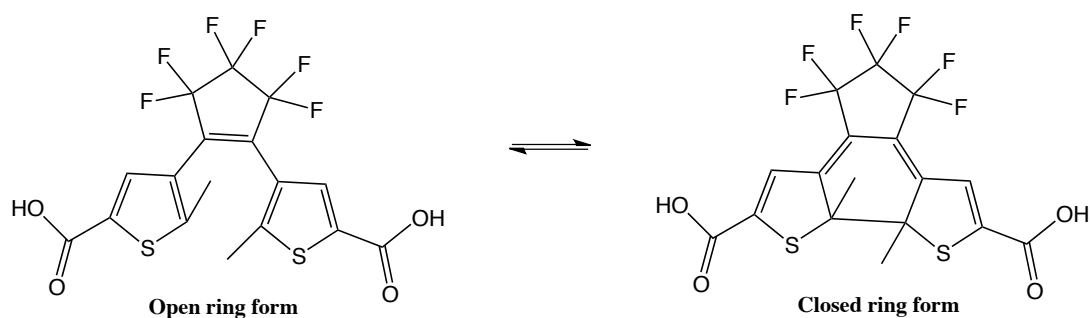


Figure 5. 2. Photocyclisation of diarylethene with carboxylic acid groups.

Amongst different photochromic molecules, diarylethenes (**DArE**) are well known photochromic π -conjugated organic molecules. They contain two aromatic groups that are double bonded together. **DArE** derivatives, particularly dithienylperfluorocyclopentene-based **DArE**, is an attractive guest molecule for photoswitching applications due to their high sensitivity, fatigue resistance towards repeated switching cycles and thermal stability [15-24]. As discussed in Chapter 2, the photoswitching mechanism involves the cyclisation of the open-ring and closed-ring isomers, following irradiation with UV and visible light, respectively [16, 25, 26]. Therefore, this would make them desirable for dynamic photoswitching carbon capture applications. The open ring isomer displays free rotation at the ethene and aryl groups, in which the two conformations, parallel and antiparallel forms exist and can exchange between each other, even at room temperature [27, 28]. However, photocyclisation can only proceed through the antiparallel conformation [29-31]. Upon ring-closing process, the colour generally changes from colourless to different colouration depending on the substituents [16]. The absorption band of the closed isomers in the visible region is due to the strongly conjugated system of the whole molecule, in which it can be further red-shifted by extending the conjugation length using various substituents such as long polyene chain, aryl groups and substituents attached in the 5-position of the thiophene rings [23, 32-37]. Chemically gated photochromism can be introduced through the preparation of **DArE** derivatives with interlocking arms, such as those with carboxylic acid groups or mercaptoalkyl groups at the external positions of the heterocyclic rings [29, 38]. This would effectively lock the molecule in the non-photoactive parallel form. Upon disruption of the hydrogen bonds or disulfide linkages, the molecules can isomerise back to the antiparallel form, regaining its photoactivity. Thus, gated photochromism could modulate the binding affinity of host-guest systems.

It has been shown that photoresponse can be achieved through the incorporation of diarylethene inside adsorbents [39-41]. For the purpose of this thesis, dithienylperfluorocyclopentene based **DArE** bearing carboxyl groups was chosen as guest molecules for **PAF-1**. The presence of long π -conjugation length and interlocking arms could potentially offer multiple non-covalent interactions in the host-guest complex, thereby potentially affecting the photoswitching capabilities upon gas adsorption. In this work, **PAF-1** containing photoresponsive **DArE** guest molecules with dynamic CO₂ capture and release property upon broadband light irradiation is being reported for the first time. In the previous work, photoresponsive linkers integrated within the Metal-organic Framework were used to trigger CO₂ release, in which 64 % desorption capacity was obtained under dynamic conditions [3]. Another recent article reported 76 % desorption capacity observed under dynamic conditions [42]. The use of **DArE** guest molecules can display desorption capacities of up to 26 % at high loading concentrations. The observed photodynamicity was due to host-guest competition between **DArE** and CO₂ inside the sterically hindered pores of the PAF. Furthermore, the presence of carboxyl groups in **DArE**, along with the aromatic nature of the host and guest molecules, allowed multi non-covalent interactions (e.g., hydrogen bonding, aromatic interaction) upon light irradiation [43-46]. The improved light responsive adsorbent system could potentially further reduce the adsorbent regeneration energy and hence low energy carbon capture could be achieved.

5.2 Methods

5.2.1 General

All reagents were used as purchased without further purification. All Schlenk equipment and glassware were dried (120 °C) for a minimum of 2 h.

5.2.2 Synthesis of PAF-1

PAF-1 was prepared and provided by Dr Kristina Konstas. **PAF-1** was synthesised according to the literature procedure to give an off white powder [8].

5.2.3 Synthesis of Diarylethene (DArE)

DArE was synthesised and provide by Daniel Keddie according to the following procedures:

5.2.3.1 Synthesis of Ethyl 5-methyl-2-thiophene-carboxylate (1)

5-methyl 2-carboxythiophene (12.4 g, 87.2 mmol) was dissolved in a solution of EtOH (480 mL) and conc. H₂SO₄ (15 mL). The reaction was heated under reflux for 20 h, after which the volume was reduced by half under reduced pressure, the reaction mixture quenched with saturated aqueous NaHCO₃. The resulting mixture was extracted with Et₂O (3 × 150 mL), washed with brine, dried (Na₂SO₄) and the solvent removed under reduced pressure to give ethyl 5-methyl-2-thiophene-carboxylate **1** as a colourless liquid (14.7 g, 86.2 mol, 99 %); ¹H NMR (400 MHz, CDCl₃) δ 1.32 (t, *J* = 7.1 Hz, 3H CH₂CH₃), 2.48 (s, 3H, CH₃), 4.29 (t, *J* = 7.1 Hz, 2H CH₂CH₃), 6.72 (d, *J* = 3.6 Hz, 1H, thienyl 4-*H*), 7.57 (d, *J* = 3.6 Hz, 1H, thienyl 3-*H*); ¹³C NMR (50 MHz, CDCl₃) δ 14.3 (ethyl CH₃), 15.7 (methyl CH₃), 60.8 (ethyl CH₂), 126.2 (thienyl C-4), 131.4 (thienyl C-2), 133.6 (thienyl C-3), 147.7 (thienyl C-5), 162.8 (C=O); LR-EI-MS *m/z* 170 (M⁺, 35 %), 142 (21), 125 (100). These data agree with that previously reported.[47]

5.2.3.2 Synthesis of 5-(Ethoxycarbonyl)-2-methyl-3-thienylboronic acid pinacol ester (2)

The synthesis was adapted from the previously reported literature procedure by Kawamorita *et al.* [48] and was achieved as follows: A Schlenk flask was charged with bis(pinacolato)diboron (21.9 g, 86.2 mmol, 1 equiv.), [Ir(OMe)(COD)]₂ (69 mg, 0.10 mmol, 0.11 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (52 mg, 0.20 mmol, 0.23 mol%) and the flask was subjected to three cycles of evacuation and backfilling with nitrogen. Subsequently a solution of ethyl 5-methyl-2-thiophene-carboxylate (14.7 g, 86.2 mmol, 1 equiv.) dissolved in dry heptane (110 mL) over 3Å mol sieves was degassed by three freeze/pump/thaw cycles and quantitatively transferred to the reaction vessel *via* cannula. The reaction was heated at 80 °C for 20h. Solvent was passed through a short plug of silica eluting with heptane then 10 % EtOAc/heptane to ensure complete elution of the product. The crude sample was subsequently purified by kugel-rohr distillation, isolated as the highest boiling point fraction, after distillation of the bis(pinacolato)diboron starting material, to give ethyl 5-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxylate **2** as a pale yellow solid (20.81 g, 70.3 mmol, 82%); ¹H NMR (400 MHz, CDCl₃) δ 1.30 (s, 12H, pinacolato CH₃), 1.32 (t, *J* = 7.1 Hz, 3H, CH₂CH₃), 2.67 (s, 6H, CH₃), 4.28 (d, *J* = 7.1 Hz, 2H, CH₂CH₃), 7.89 (s, 1H, thienyl 3-*H*); ¹³C NMR (50 MHz, CD₃OD) δ (9

of 10 signals were observed; no signal was observed for C directly bonded to B) 14.3 (CH_2CH_3), 16.3 (CH_3), 24.8 (pinacolato CH_3), 60.8 (CH_2CH_3), 83.5 (pinacolato C^*), 130.7 (thienyl C-2), 140.0 (thienyl C-3), 159.6 (thienyl C-5), 162.3 (thienyl C-5), ($\text{C}=\text{O}$); LR-EI-MS m/z 296 (M^+ , 98 %), 281 (40), 251 (60), 239 (100). HR-EI-MS m/z = found 296.1254 M^+ (calculated 296.1248 for $\text{C}_{14}\text{H}_{21}\text{BO}_4\text{S}$).

5.2.3.3 Synthesis of 1,2-Bis(5'-ethoxycarbonyl-2'-methyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (3)

The synthesis was adapted from the previously reported literature procedure by Hiroto *et al.* [49] and was achieved as follows: A Schlenk flask was charged with ethyl 5-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxylate (8.88 g, 30 mmol, 3 equiv.), PCy_3 (68 mg, 0.24 mmol, 2.4 mol%), CsF (13.7g, 90 mmol, 9 equiv.), $\text{Pd}_2(\text{dba})_3$ (56 mg,) and the flask was subjected to three cycles of evacuation and backfilling with nitrogen. Subsequently deoxygenated toluene/water (10:1, 33 mL in total) and 1,2-dichloro-3,3,4,4,5,5-hexafluoropentene (1.50 mL, 10 mmol) was added and the mixture heated at 110°C for 16 h. After which the reaction mixture was filtered through a plug of silica eluting with EtOAc and solvent removed under reduced pressure. The crude product was purified by column chromatography (SiO_2 , 5% EtOAc, *n*-heptane) yielding a viscous yellow oil that solidified upon standing. Recrystallisation from MeOH gave 1,2-bis(5'-ethoxycarbonyl-2'-methyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene **3** as a white powder (3.70 g, 7.22 mmol, 72 %); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (t, $J = 7.1$ Hz, 6H CH_2CH_3), 1.92 (s, 6H, CH_3), 4.33 (d, $J = 7.1$ Hz, 4H CH_2CH_3), 7.72 (s, 2H thienyl 4-*H*); ^{13}C NMR (50 MHz, CDCl_3) δ (8 of 11 signals were observed; no signals were observed for C's in cyclopentene ring due to coupling to F) 14.4 (CH_2CH_3), 15.1 (CH_3), 61.7 (CH_2CH_3), 125.5 (thienyl C-4), 132.5 (thienyl C-2), 132.9 (thienyl C-5), 148.6 (thienyl C-3), 161.4 ($\text{C}=\text{O}$); LR-EI-MS m/z 512 (M^+ , 63 %), 466 (100), 451 (60), 423 (75). HR-EI-MS m/z = found 512.0541 M^+ (calculated 512.0545 for $\text{C}_{21}\text{H}_{18}\text{F}_6\text{O}_4\text{S}_2$).

5.2.3.4 Synthesis of 1,2-Bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene (4)

1,2-Bis(5'-ethoxycarbonyl-2'-methyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (1.7 g, 3.3 mmol) was dissolved in THF (30mL) and added 60 mL of an aqueous solution of LiOH (1.3 g in 75 mL, 54.3 mmol) and stirred at 40°C for 4 h. After which the solution

was washed with Et₂O, combined organics back extracted with dilute NaOH (1 M), the combined aqueous fractions acidified with HCl (conc.) (dropwise to pH 1) and extracted with Et₂O, dried (Na₂SO₄) and the removed solvent under reduced pressure. Recrystallisation of the resulting residue from propan-2-ol gave 1,2-Bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene **4** as a pale greenish powder (1.1 g, 2.4 mmol, 73 %); ¹H NMR (400 MHz, CD₃OD) δ 1.96 (s, 6H, CH₃), 7.70 (s, 2H thienyl 4-*H*); ¹³C NMR (50 MHz, CD₃OD) δ (6 of 9 signals were observed; no signals were observed for C's in cyclopentene ring due to coupling to F) 13.6 (CH₃), 125.2 (thienyl C-4), 132.6 (thienyl C-2), 133.1 (thienyl C-5), 149.1 (thienyl C-3), 162.8 (C=O); LR-EI-MS *m/z* 456 (M⁺, 85 %), 438 (55), 423 (70), 395 (100). HR-EI-MS *m/z* = found 455.9912 M⁺ (calculated 455.9919 for C₁₇H₁₀F₆O₄S₂). These data agree with that previously reported [50, 51].

5.2.4 Preparation of DArE@PAF-1

Different concentrations of **DArE** were loaded in **PAF-1** (weight percentage diarylethene loading) in ~5 mL dry diethyl ether in Quartz ASAP tube. The solution was sonicated for 1 h to allow even loading distribution within the PAF. The solvent was then evaporated under N₂ atmosphere.

5.2.5 Characterisation Methods

Please refer to Chapter 3 for general characterisation procedures (Section 3.1-3.2).

The activated **PAF-1** used in this work has a BET surface area of 1967 m²/g (literature: up to 5600 m²/g). The surface area obtained is much lower to the reported data in literature [11, 52]. However, this was not the main focus of the research as the pore sizes were found to be large enough to contain the **DArE** guest molecules.

5.2.6 Broadband Light Irradiation Experiment

No filter was used and the light intensity was fixed at 24.6 W/cm² in the wavelength range (200-500 nm). Please refer to Chapter 3 for light responsive gas adsorption experimental set-up (Section 3.3.2).

5.3 Results and Discussions

In its natural state, **DArE** displays an open-ring structure, with a molecular diameter of 0.9-1.3 nm (molecular volume $300 \text{ \AA}^3$, average kinetic diameter: $10.7 \text{ \AA}$) (Figure 5.3). Thus **PAF-1** is a suitable host for the inclusions of **DArE**, as they exhibit pore dimensions larger than **DArE** molecules. The pore size distribution calculated from N_2 adsorption isotherm at 77 K indicated that **PAF-1** had a pore size range of 1.2-3 nm and pore volume of $0.9 \text{ \AA}^3$ (Figure 5.4a-b).

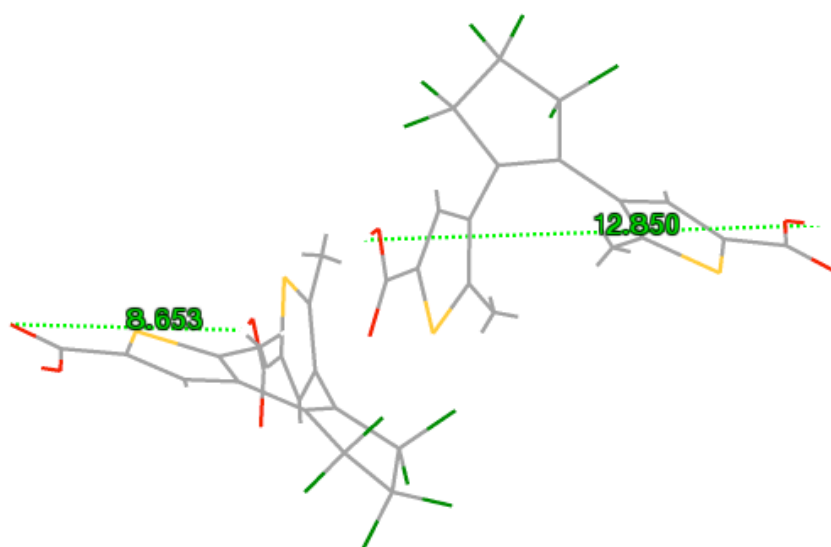


Figure 5.3. Crystal structure of open ring **DArE** [15]. The molecular diameter range from 0.9-1.3 nm.

The successful inclusion of **DArE** molecules in **PAF-1** was first suggested by the decrease in N_2 adsorption capacity (Figure 5.4a). Further analyses of the isotherm supported the result, indicated by the decrease in pore size distribution intensities, surface areas and total pore volume (Figure 5.4b-d) [16]. Varying concentrations of **DArE** from 1-50 wt % was loaded. The pore size distribution intensities, along with the surface area and total volume, gradually decreased with increasing loading concentrations of **DArE**. The result was expected as it indicated that the guest molecules progressively occupied more of the vacant sites within the **PAF-1** (Figure 5.4b).

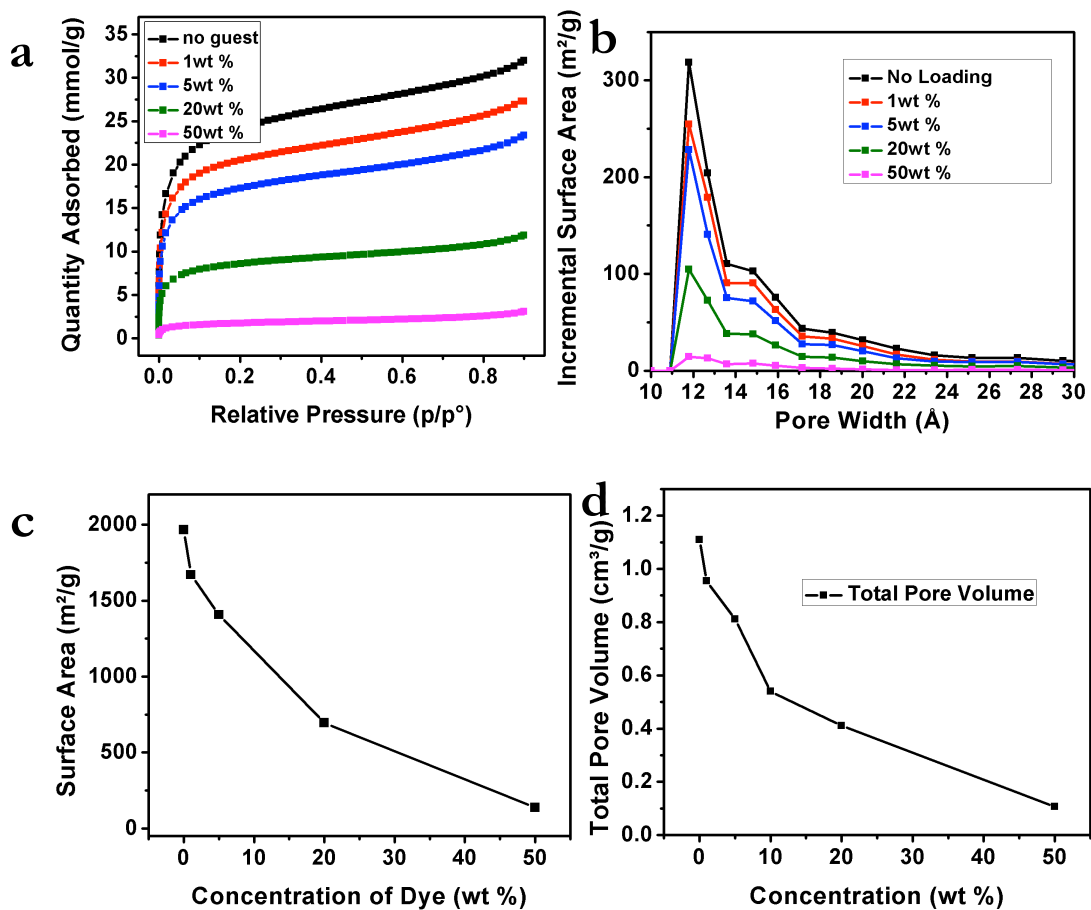


Figure 5.4. N₂ adsorption isotherm of PAF-1 (black) and DArE@PAF-1 (1 wt %, red; 5 wt %, blue; 20 wt %, green; 50 wt %, magenta) at 77 K (a) showing the effects of DArE loading concentrations on the pore size distributions (b), BET surface areas (c) and total pore volumes (d) of PAF-1.

5.3.1 Photoswitching Mechanism

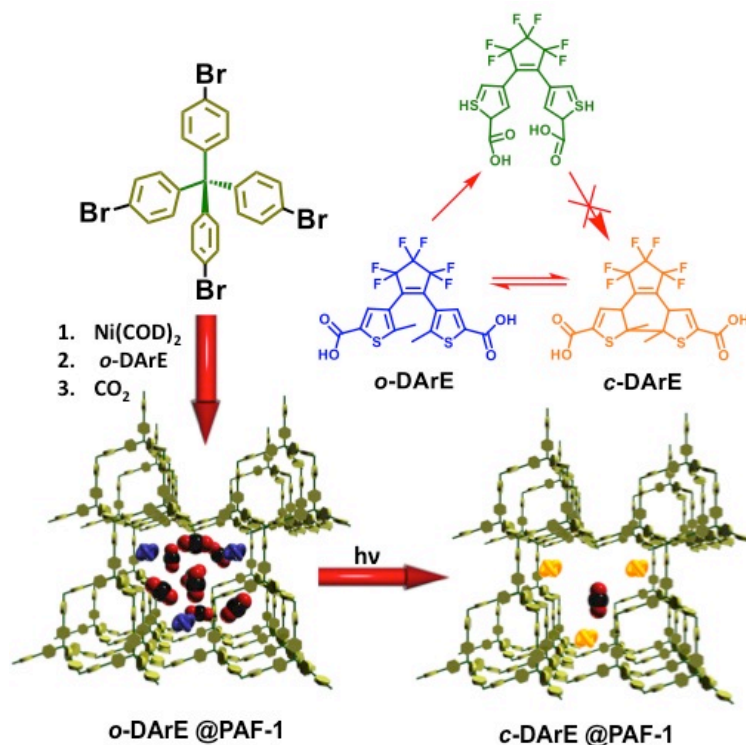


Figure 5.5. Dynamic photoswitching of light responsive DArE@PAF-1 led to instantly reversible CO_2 uptake.

A photoresponse study was conducted to assess the dynamic properties of **PAF-1** for potential dynamic gas adsorption. Solid-state UV-Vis and FT-IR were conducted to look at the photoswitching mechanism. Upon UV (340 nm) and visible (460 nm) excitation of the free **DArE** molecule, absorption peaks which correspond to the closed-ring (*c*-**DArE**) and open-ring **DArE** (*o*-**DArE**) at 450 and 580 nm, and 370 nm respectively were observed (Figure 5.6b) [15, 53]. These peaks were also observed in the sample prepared, confirming the presence of **DArE** with **PAF-1** (Figure 5.6c-d). To further analyse the photoresponse mechanism, the peak intensities at 460 and 370 nm exhibited by the free **DArE** and **DArE@PAF-1** during UV-Vis experiments were monitored by continually irradiating the materials with alternating UV and visible light. From the result, the peak intensities of *c*-**DArE@PAF-1** at 460 nm remained constant, whereas the peak intensities of *o*-**DArE@PAF-1** at 370 nm gradually decreased over several cycles (Figure 5.6f). Similar trends were observed in the free *o*-**DArE** molecule (Figure 5.6e). The slight decrease in peak intensities at 370 nm indicated that perhaps photocyclisation was inhibited.

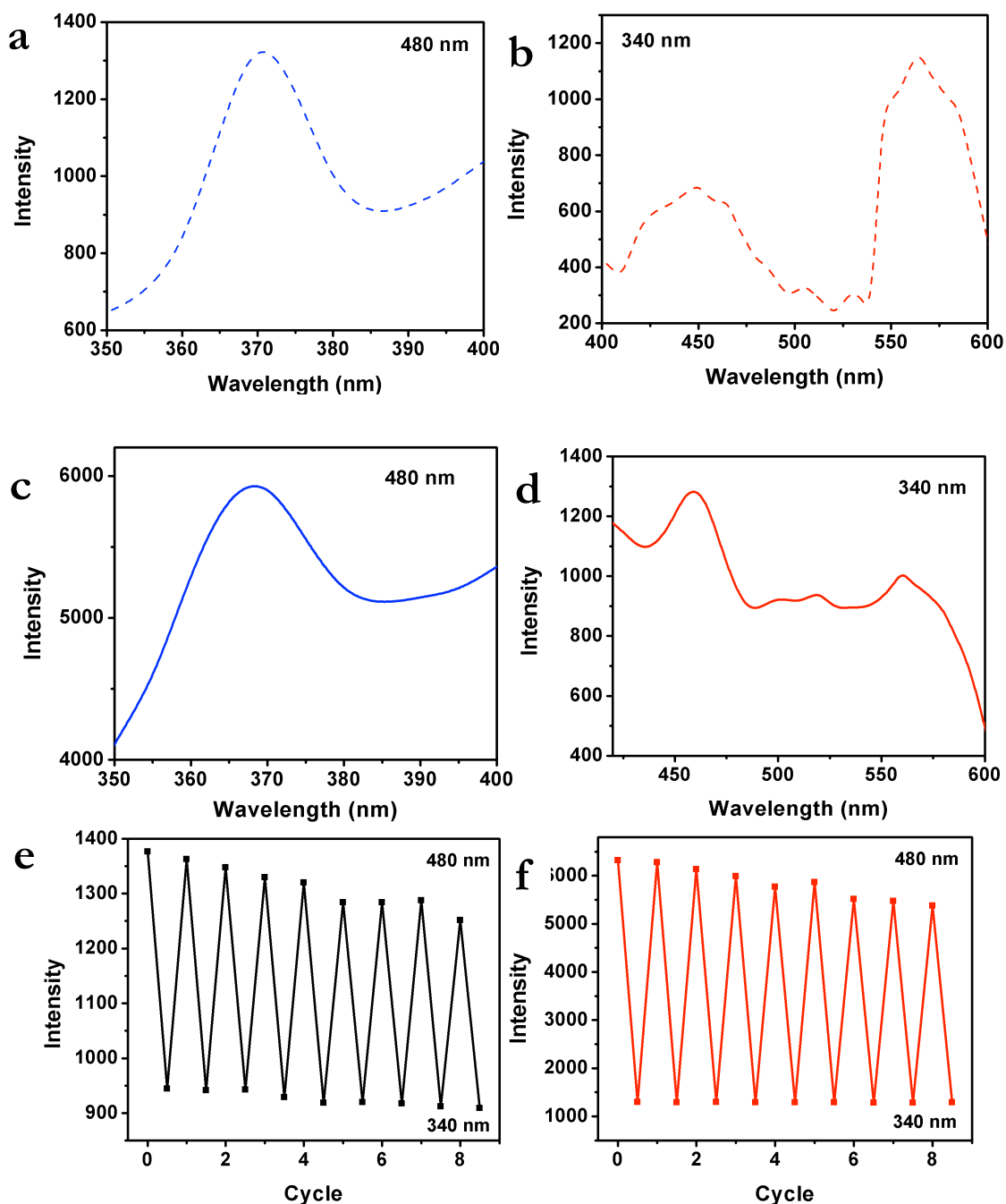


Figure 5.6. The peaks at 370 nm and 460 nm correspond to the open (blue) and closed (red) ring free DArE (dashed line) and DArE@PAF-1 (solid line) respectively. Changes in the intensities of solid-state UV Vis spectra of host free DArE (e) and DArE@PAF-1 (f) during alternate UV (340 nm)/ Vis (480 nm) light irradiation.

FT-IR results revealed the photoisomerisation behaviours of **DArE@PAF-1** in more detail. Upon light irradiation, the FT-IR spectrum of host-free **DArE** showed that the photogeneration of the closed ring isomer can be detected by the formation of 2 additional weak C-F absorption bands at 966 and 1013 cm^{-1} (Figure 5.8)[54]. However, these two signals were not observed in the FT-IR spectrum of **DArE@PAF-1** (Figure 5.7). This may

be due to the peaks associated with **DArE** photoresponse being too weak to be detected and had been masked by the PAF's peaks. Instead, the C=O (1688 cm^{-1}) and O-H (3000 cm^{-1}) peaks showed considerable broadening, suggesting that multiple intermolecular non-covalent interactions may be involved (Figure 5.7) [55].

Upon light irradiation, the formation of ***c*-DArE** exhibited a planar geometry which is less bulky compared to its twisted open structure [45, 56-58]. It has been shown that a typical **DArE** molecule expands upon ring-opening and shrinks upon ring-closing [16, 59]. Upon photocyclisation, the width of a typical **DArE** molecule could expand from 0.90 nm to 1.01 nm [59]. Thus aryl-perfluoraryl interactions became more favourable between the guest molecules and the host, and hence the peak broadening at 1688 cm^{-1} (Figure 5.7) [43, 44, 46, 60-62]. With the aromatic stacking occurring, the movements due to photocyclisation upon light irradiation would be suppressed. This was also confirmed in FT-IR spectra of irradiated **DArE@PAF-1** and free **DArE**, as shown by the reduction in peak intensities at 810, 985, 1035, 1140 and 1548 cm^{-1} regions (Figure 5.7-5.8) [54, 63]. These peaks correspond to the vibration modes of the thiophene and cyclopentene groups in **DArE** [54, 63]. The reduction in peak intensities was due to the loss of aromatic character of two thiophene rings in **DArE** upon ring closure [17, 18, 64]. Furthermore, this could also be contributed by the restricted movement of **DArE** guest molecules inside the pores of **PAF-1**. As a result, the ring bending vibration of the aryl and ethene groups around $500\text{-}600\text{ cm}^{-1}$ region was enhanced (Figure 5.7) [27, 65, 66].

In conjunction with the aromatic stacking, H-bonding was also detected at 3000 cm^{-1} (Figure 5.7) [44]. This was only observed in the FT-IR spectra of **DArE@PAF-1**, which suggested that intramolecular H-bonding between the carboxylic ends of the guest molecules may occur, a known phenomenon reported in the literature [27, 29, 30, 38]. The stable intramolecular H-bonds are unlikely to be broken without H-bond breaking agents [27, 29, 30, 38]. As **DArE** can exist in three conformers, the antiparallel ***o*-DArE** and ***c*-DArE** conformers may interconvert reversibly under broadband light irradiation, but some parallel ***o*-DArE** conformers may form in the process [29, 30, 67, 68]. The formation of the parallel conformer prevented photocyclisation back to its antiparallel form [29, 30, 67, 68]. This would explain the incomplete ring opening process observed in solid UV-Vis result (Figure 5.6). The presence of multiple interactions in light irradiated **DArE@PAF-1** may potentially trigger dynamic CO₂ adsorption. Competitive interaction between **DArE**

and CO₂ molecules with the host may be observed as adsorption would occur within a sterically demanding environment [43, 44, 46, 60-62].

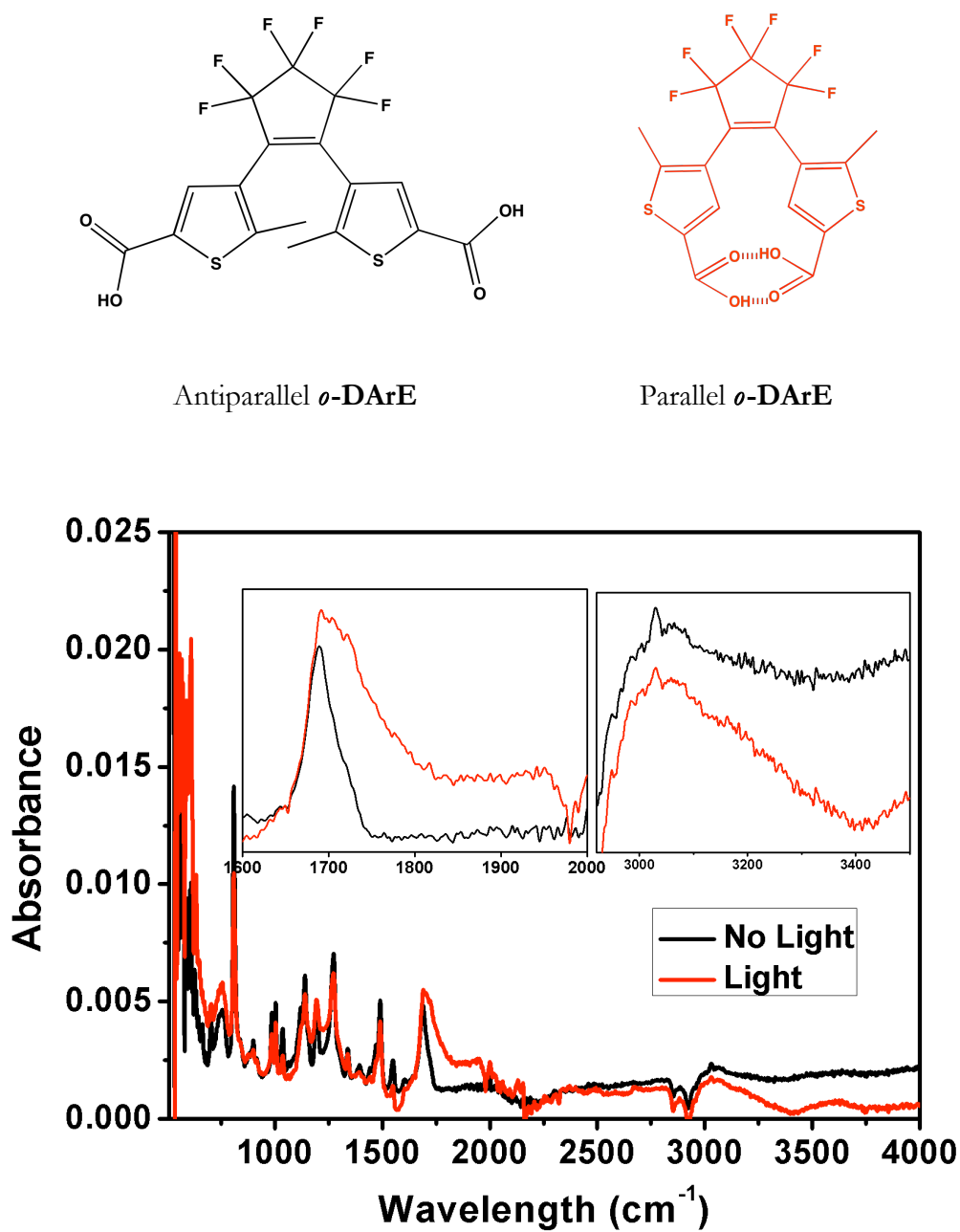


Figure 5.7. Full FT-IR spectrum of DArE@PAF-1 in the absence (black) and presence (red) light irradiation.

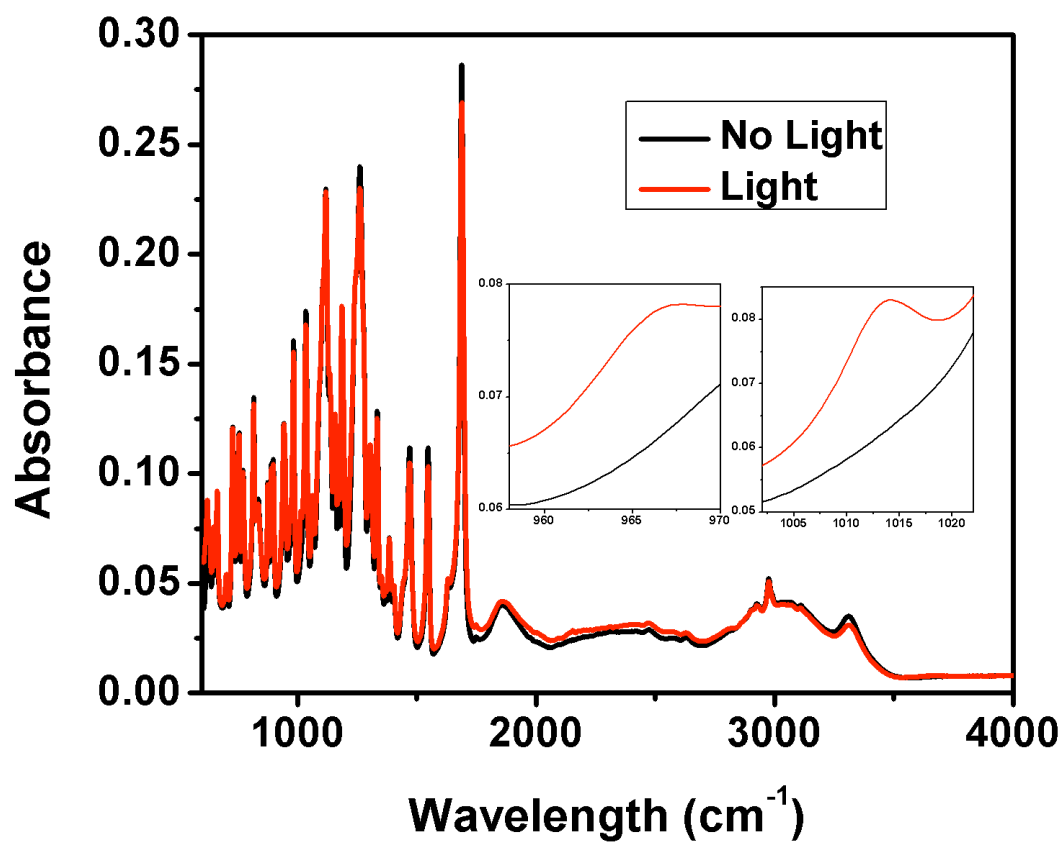
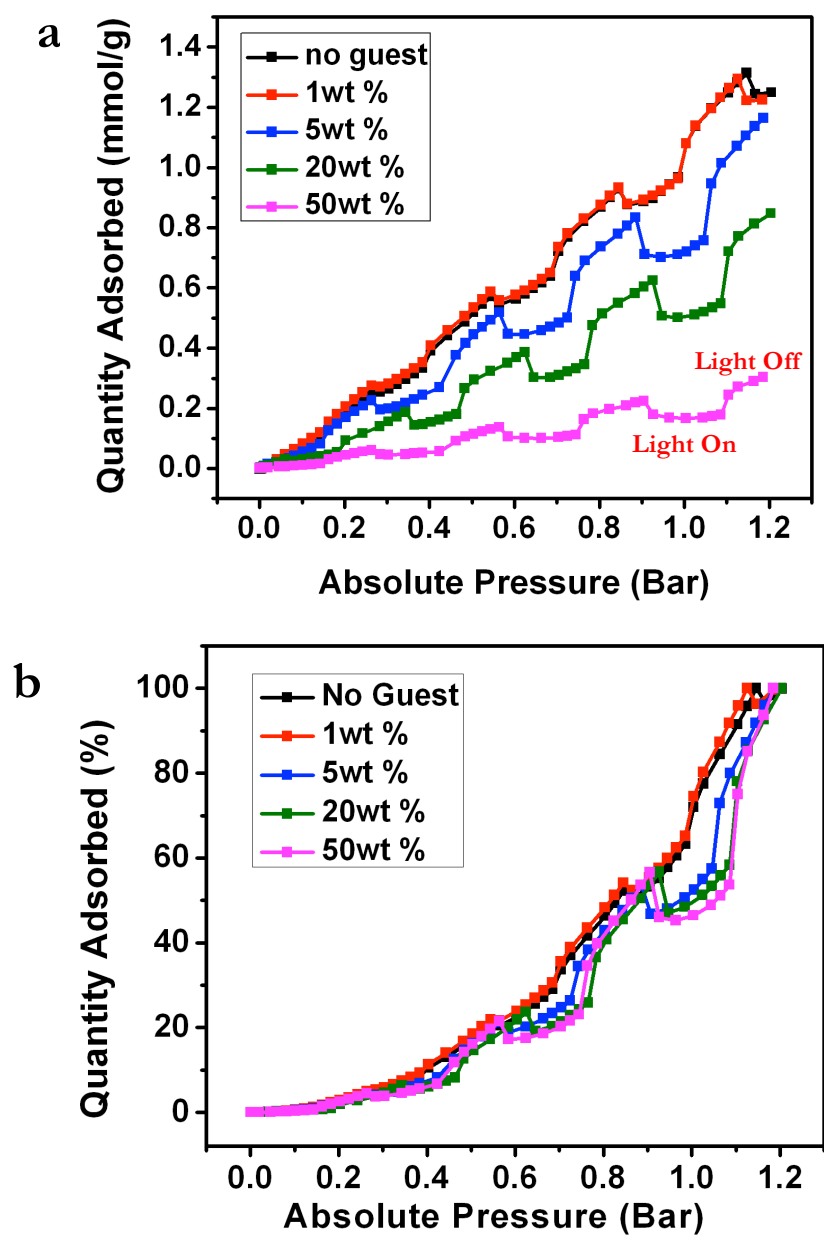


Figure 5.8. Full FT-IR spectrum of host-free DArE in the absence (black) and presence (red) light irradiation [54].

5.3.2 Photoresponse of DArE@PAF-1 with Varying Guest Loading Concentrations



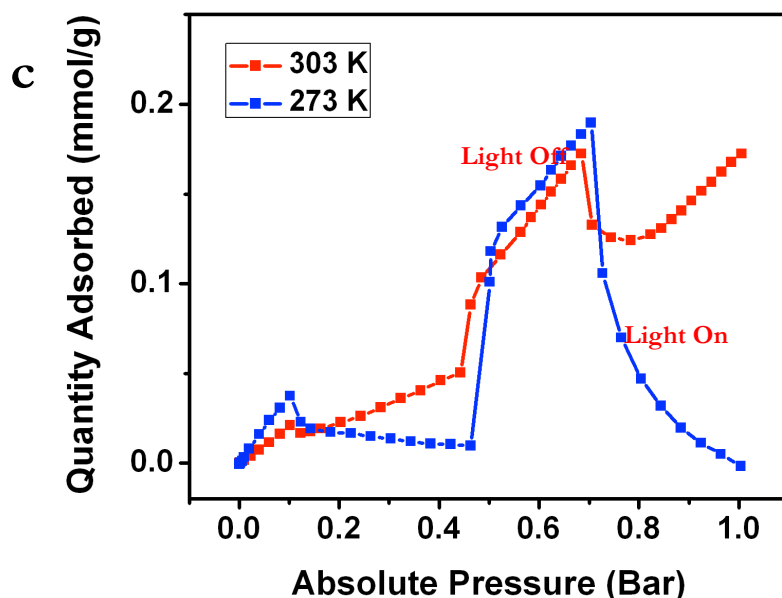


Figure 5.9. CO₂ adsorption isotherms of PAF-1 and DArE@PAF-1 at 303 K under photoswitching environment showed that CO₂ capture and release occurred reversibly in the absence and presence of light respectively (a). CO₂ sorption isotherms were normalised for clarity, showing that greater photoresponse was obtained with higher DArE loading concentrations (b). CO₂ sorption isotherms of 50 wt % DArE@PAF-1 at 303 K and 273 K were also compared to look at their adsorption behaviour.

To examine the potential of dynamic carbon capture and release in **DArE@PAF-1**, a photoswitching experiment was conducted during gas adsorption measurement (Figure 5.9). In this experiment, CO₂ capture and release occurred in the absence and presence of light respectively (Figure 5.9). The process was found to be reversible as adsorption and desorption was observed after each photoswitching cycle. The adsorption isotherm obtained under static irradiation matched those irradiated parts of the isotherm obtained under dynamic conditions (Figure 5.10). The observed photoresponse behaviour is similar to the reported work in Chapter 4 [3]. Such dynamicity was likely due to the increase in host-guest interactions upon the formation of the parallel *o*-**DArE** conformer [43, 44, 46, 60-62]. This would weaken the intermolecular interactions between CO₂ molecules and the adsorption sites, triggering instantaneous CO₂ release [3].

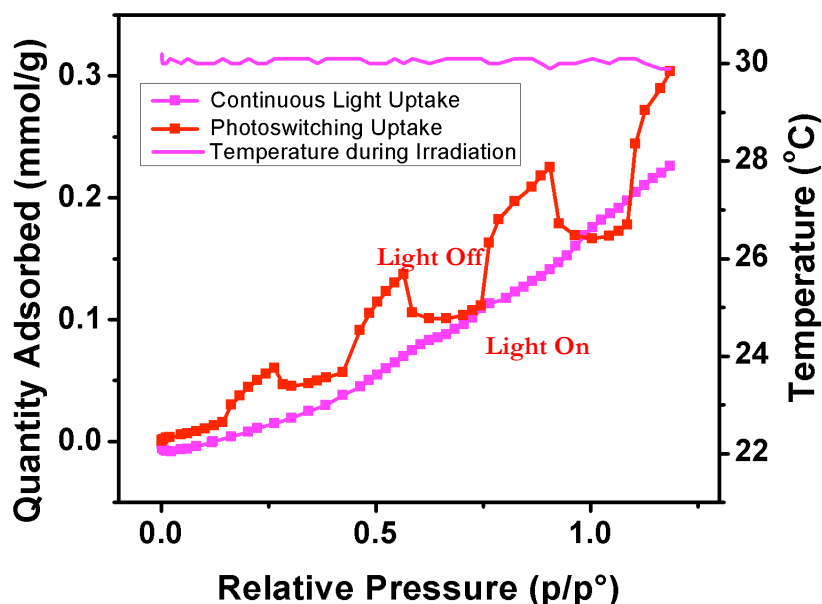


Figure 5.10. Dynamic vs static photoswitching of DArE@PAF-1 (50 wt %).

With varying concentrations of **DArE** loading, there was a trade-off between photoresponse and CO_2 uptake capacity. With the increase in **DArE** loading concentrations, a greater photoresponse was obtained (Figure 5.9a-b, 5.11a), which corresponded to the increase in photoactivity of **DArE** in **PAF-1**. To correlate photoactivity and CO_2 adsorption, CO_2 uptake capacity at 1 bar, which showed the largest photoresponse, was calculated and compared. When not irradiated, the CO_2 uptake capacity increased at higher loading concentration, but reduced when the loading concentration exceed 5 wt %, indicating an optimal loading concentration (Figure 11b). This suggested that perhaps competitive interactions between **DArE** and CO_2 with the host, preventing CO_2 from occupying the adsorption sites. Similar to Chapter 4, CO_2 adsorption in the presence of light did not follow the D-R model and change in pore sizes could not be determined (Figure 5.12). This is due to gas adsorption at the surface being disturbed by the presence of UV light [69]. Photoswitching experiment was also performed on unloaded **PAF-1** as a control study to ensure that the photodynamicity was mainly due to the presence of **DArE** molecules (Figure 5.9a). The low photoresponse exhibited by **PAF-1** was due to the aromatic nature of its framework.

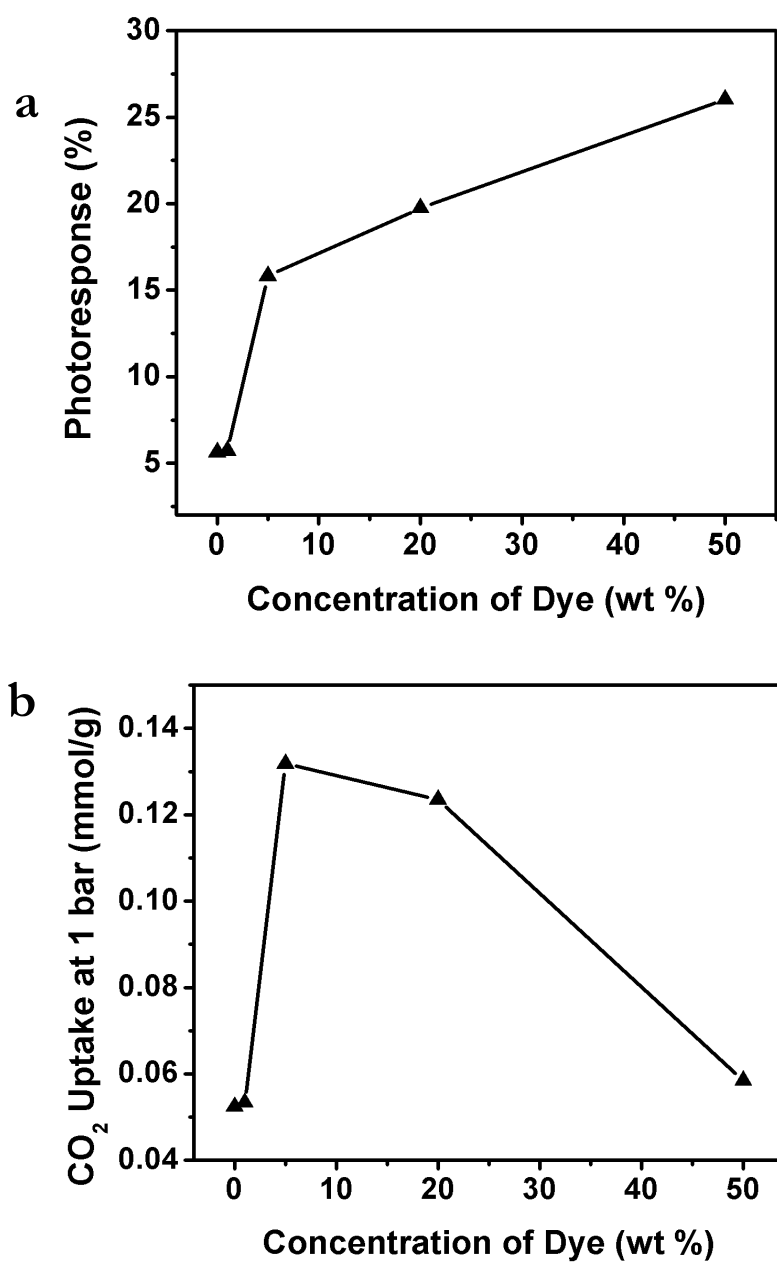


Figure 5.11. Trade-off between photoresponse (a) and CO₂ uptake capacity at 1 bar (b).

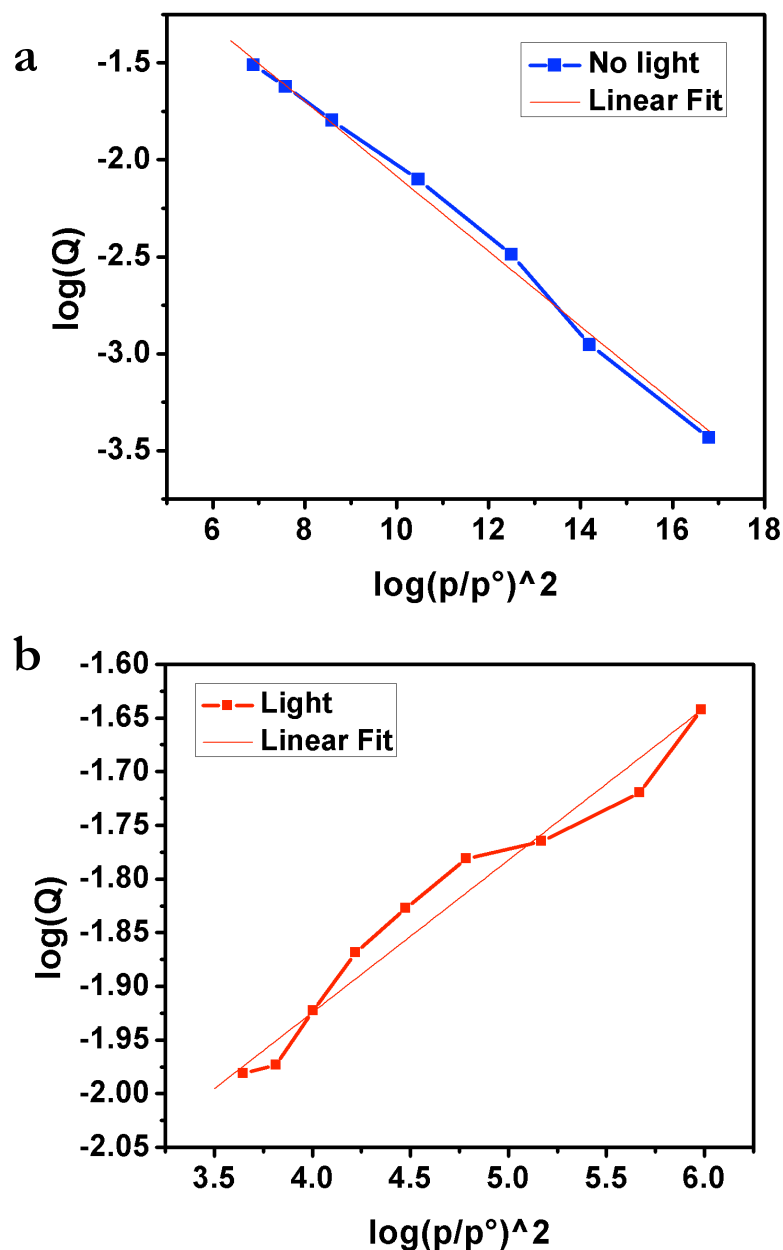


Figure 5. 12. CO₂ adsorption isotherm in the presence (red) and absence (blue) of light at 273 K was fitted with the Dubinin-Radushkevich (D-R) equation (red).

Adsorption kinetic studies showed that desorption capacities at 1 bar can increase by 65 % from 5 wt % to 50 wt % within 4 minutes of light irradiation (Figure 5.13a). Some CO₂ was re-adsorbed beyond this point, indicating that perhaps there was a small shift in the equilibrium, resulting in a slight preferential binding of CO₂ with the host. However, the equilibrium was shifted significantly towards DArE-PAF interactions at lower temperature, resulting in a complete CO₂ desorption within 9 minutes of irradiation (Figure 5.13b).

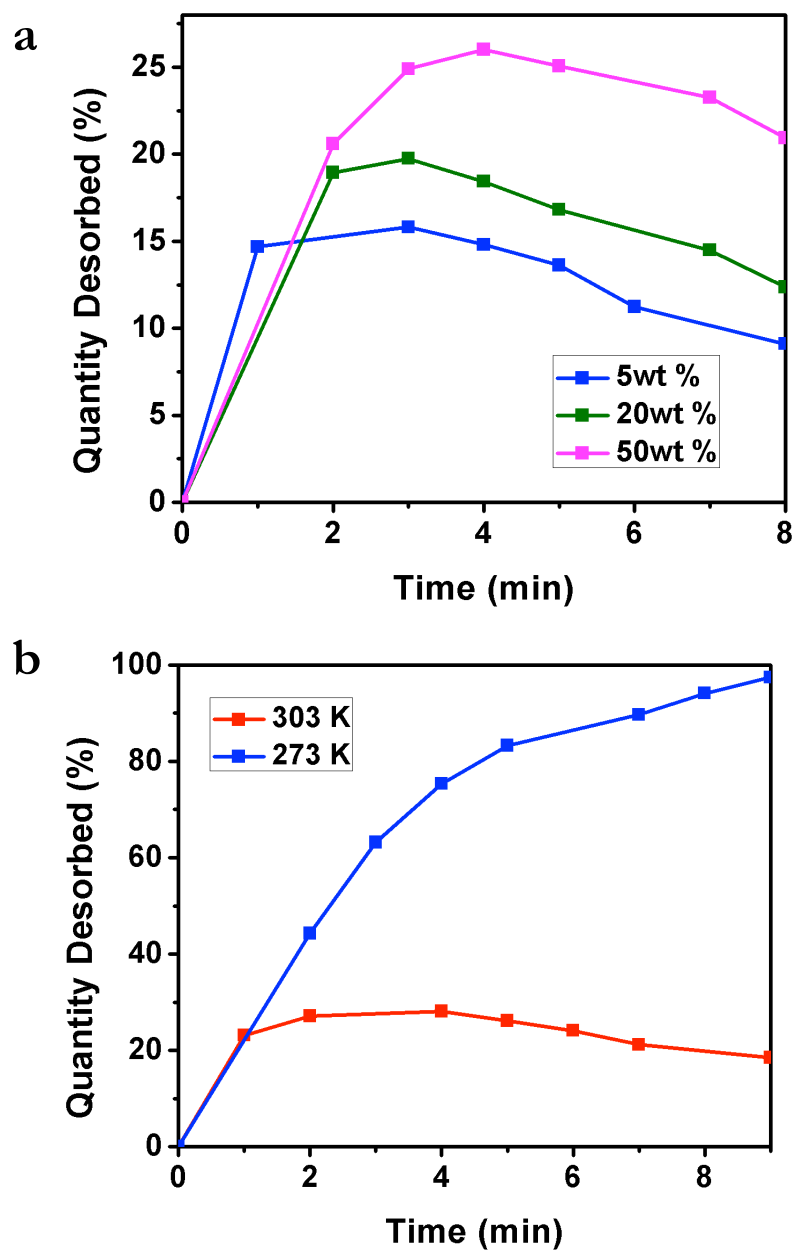


Figure 5.13. Kinetic studies of CO₂ adsorption at 303 K and 273 K at a pressure range of 0.6-1 bar, showing the effects of different guest loading concentrations (a) and temperature (b). 50 wt % DArE@PAF-1 was used for the latter experiment (b).

5.4 Conclusions

Photodynamic CO₂ capture and release from PAF containing photoactive guest molecules was demonstrated for the first time. Since the publication of the work reported in Chapter 4, only one MOF with **DArE** linker molecules was reported for the dynamic photoswitching property during gas adsorption. Similar to the results reported in Chapter 4, light could be switched on and off to trigger CO₂ desorption and adsorption respectively. In this work, the level of photoresponse could be modulated through using different **DArE** loading concentration. Results showed that stronger photoresponse, of up to 26 %, were obtained at higher concentrations (50 wt %), but beyond the optimum concentration of 5 wt %, the CO₂ uptake capacity gradually reduced. FT-IR and UV-Vis analyses suggested that guest-host interactions between **DArE** and **PAF-1**, particularly involving aromatic stackings and H-bonding, occurred upon photoirradiation. This indicated that photocyclisation of **DArE** was inhibited in a sterically hindered environment, promoting the formation of its parallel *o*-**DArE** conformer, which feature an intralocking or H-bonding arms. This mechanism is likely to be responsible for the dynamic carbon capture and release observed in the adsorption results. The PAF-**DArE** and CO₂-PAF interactions competed with each other, resulting in the spontaneous release of adsorbed CO₂ upon photoirradiation. Complete desorption of adsorbed CO₂ could be achieved at lower temperature as PAF-**DArE** interactions were dominant. This result provided significant evidence since Chapter 4, showing that broadband light irradiation could be used to effectively trigger carbon capture and release in real time. Thus, this further supported the concept of using unfiltered sunlight as a novel trigger for low cost carbon capture. To further advance the technology, improved light responsive adsorbents, particularly those that respond to only visible light, should be focused on.

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Declaration for Thesis Chapter 6

Declaration by candidate

In the case of Chapter 6, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Experiment and analysis work, writing	100

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
[name 1]	-	-
[name 2]	-	-
[name 3]	-	-

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's
Signature

		Date 31/10/2014
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Main
Supervisor's
Signature

		Date 31/10/2014
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Chapter 6

VISIBLE LIGHT RESPONSIVE MOF-74@MR WITH PRESSURE-GATED GAS ADSORPTION PROPERTIES

6.1 Introduction

The development of light responsive MOFs in order to control the capture and release of CO₂ has gained much attention recently [1-5]. In particular, those that exhibit a gate-opening phenomenon due to structural responses to specific adsorbate or variable pressures are highly attractive [6-9]. Previous results (Chapter 4 and 5) have demonstrated that the use of broadband light can trigger the photodynamic response of adsorbent materials during gas adsorption, offering the potential feasibility of using natural sunlight directly onto materials. However, UV light is needed, which is not environmentally friendly and can potentially degrade materials, sometimes into toxic by-products, overtime [10-12]. As discussed previously, different wavelengths of light penetrate into materials at different depths, depending on the optical density of the sample and intensity of light (Section 2.2.4) [13]. The relationship can be represented using the Beer-Lambert Law (Section 1.2.4) [13]. To improve the penetration level, longer wavelengths of light must be used to achieve greater photoresponse of light responsive materials. Natural sunlight radiates strongly in the visible range (400-700 nm) as it makes up for 47 % of the solar spectrum [14, 15]. UV light (200-400 nm) on the other hand, is strongly scattered and only comprises a tiny fraction (7 %) of the solar spectrum [14, 15] (Figure 2.3). Therefore utilising a large fraction of solar light could greatly enhance low-energy carbon capture and release.

Amongst various photochromic molecules, *o*-Methyl Red (**MR**), also known as Acid Red, is an attractive visible light responsive molecule. **MR** is an azobenzene derivative that has been widely used as an indicator dye or colouring agents. It has been extensively studied

for photochromism, inclusion complexes with cyclodextrin, structure [16] and pK_a determination [17]. Unlike most azobenzene derivative molecules that require UV light for photoisomerisation, **MR** molecules are able to undergo conformational changes from the natural *trans* state to the *cis* state upon visible light irradiation shorter than 590 nm (Figure 6.1) [16, 18, 19]. The relaxation of *cis*-**MR** back to the *trans* state can be achieved in the dark [18, 19]. This prompted the idea of using **MR** to introduce visible light properties in MOFs, in this particular case, **Mg-MOF-74**.

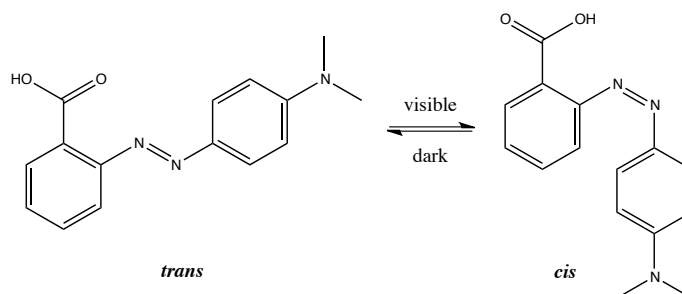
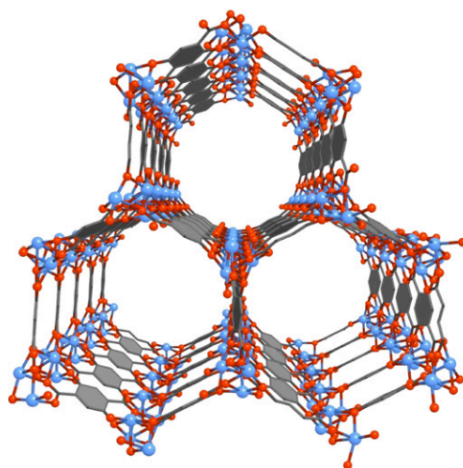


Figure 6. 1. Photoisomerisation of *o*-methyl red.

MOF-74 is highly attractive for gas separation applications as it exhibits high CO₂ adsorption capacity under atmospheric conditions and is considered as one of the more promising candidates for CO₂ capture (35.2 wt % CO₂ capacity at 1 atm at 298 K) [6, 20-23]. The MOF is composed of the 2,5-dihydroxyterephthalate ligand and unsaturated metal sites that forms 1D hexagonal pore structure, where the average pore diameter is ~ 11 Å [22]. The metal sites can be varied without changing the overall framework structure due to the metal oxidation state (M=Zn, Mg, Ni, Co, Mn, Ca and Sr) [22]. In the framework, each metal cluster at the vertices of the hexagons are connected by organic linkers and could coordinate with 6 atoms [24]. Due to the octahedral arrangement at the metal center, all of the ligand functional groups (carboxylate and alcohol) are deprotonated and all are coordinated to the metal atom: 5 oxygen atoms from the carboxyl and hydroxyl group of the organic ligand and 1 free site that was occupied by a solvent or water molecule prior to activation (Figure 6.2) [24]. Upon water removal from the pore channels, the metal coordination environment changes from octahedral to square pyramidal [25].



M-MOF-74
(M: Zn, Co, Ni, Mg)

Figure 6. 2. General Structure of M-MOF-74 where each metal centers are connected by 2,5-dihydroxyterephthalate ligands (blue and red circles represent the metal species and the oxygen atoms from the ligand respectively). Printed with permission from [26]. Copyright 2014 Elsevier.

The resulting five-coordinated metal centres in the activated form allow a high concentration of unsaturated metal cations to be exposed on the pore surface. It has been shown that these metal ions can act as Lewis acids and serve as the primary binding sites for gas molecules [27, 28]. A Lewis acid is an electron pair acceptor, which can readily react with a Lewis base, an electron pair donor. Unlike materials with flexible structures, where the removal of guest molecules result in structural collapse [29, 30], the structural rigidity of the MOF ensures that the open metal sites remain accessible for incoming guest molecules [31]. The featured Lewis acid sites can strongly polarize gas adsorbents, in which preferential adsorption to CO_2 over other gas molecules, such as N_2 or CH_4 could be obtained [31, 32]. The adsorbed CO_2 molecule reportedly forms a bent structure and binds through one of its oxygen atoms, while the rest of the molecules are free [27, 33]. This is because CO_2 can act as a stronger Lewis base due to its larger quadrupole moment and greater polarisability [32]. Upon increase in gas uptake, some CO_2 molecules are also adsorbed in the centre of the hexagonal channels [27]. These Lewis acids can also be further functionalised through post-synthetic modification. It has been shown that in a chemically robust MOF with well separated open metal sites, one amine of a diamine molecule can bind to a metal cation as a Lewis base, while the other amine can act as an adsorption site for gas molecules [34]. The general trend toward decrease in surface area in MOF-74 isostructural series is $\text{Mg} > \text{Co} > \text{Ni} > \text{Zn}$ through N_2 adsorption measurement at 77 K, which corresponds to the mass increase from the lighter alkali earth metal towards

the heavier transition metal [22]. However, research has shown that this is not simply due to the weight effect of the metal atom on adsorption sites [22]. The strength of the Lewis acid-base interactions depend on metal sites and the adsorbates respectively, exhibiting advantageous adsorption properties. For example, nickel based MOF-74 exhibit the highest methane adsorption capacity compared to their isostructural MOF-74 materials [28], whereas Fe and Mn based MOF-74 exhibits exceptionally strong preferential adsorption towards O_2 over N_2 [35]. For CO_2 adsorption, the general trend towards increase in capacity at 1 atm and 298 K in the MOF-74 isostructural series is Zn (24.4 wt %) < Ni (25.6 wt %) < Co (30.6 wt %) < Mg (35.2 wt %). The heat of adsorptions for Co-MOF-74, Ni-MOF-74 and **Mg-MOF-74** have initial heat adsorptions of 37, 41 and 47 kJ/mol respectively [22]. The general trend for the increase in CO_2 affinity can be correlated to the increase in the Lewis acidity of the metal centres. However, the exceptional CO_2 uptake of **Mg-MOF-74** could be attributed to the increase in the ionic character of the Mg-O bond (Figure 6.3) [22, 36]. In a CO_2 sequestration process, MgO is known to exhibit exothermic chemisorptions of CO_2 to form $MgCO_3$ [37]. However chemisorption does not occur in **Mg-MOF-74**, presumably because of the rigid nature of the framework preventing the chemical bond formation between Mg and O atoms [22]. The reported heat of adsorption value indicates a strong physisorption interaction but remains well below that of the energy obtained for chemisorptions, thus the reversibility of adsorption could be maintained [36].

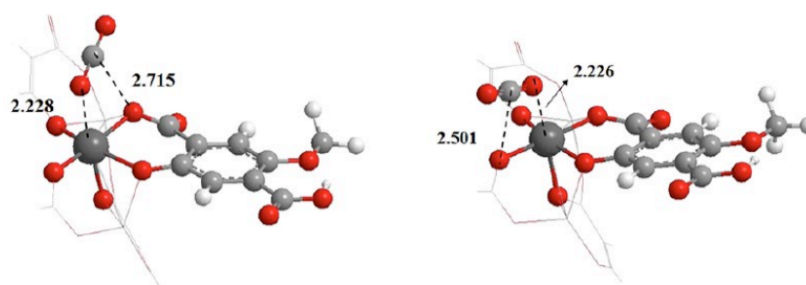


Figure 6. 3. Schematic representation of CO_2 coordinated in **Mg-MOF-74**. Reprinted with permission from [27]. Copyright 2014 American Chemical Society.

Therefore, amongst many MOF-74 materials, **Mg-MOF-74** is an attractive material for carbon capture due to its exceptionally high CO_2 uptake capacity (5.95 mmol/g, even at low pressure (<0.1 atm) at room temperature, and high heat of adsorption (47 kJ/mol) [36]. It has also been reported that when **Mg-MOF-74** is subjected to a gas stream containing similar content to that in industrial separations, it only adsorbs CO_2 and not CH_4 [22, 31]. Furthermore, the pores could retain a large amount of CO_2 , with a capacity

higher than any other achieved in MOFs, and is competitive with conventional materials, such as zeolites, with the highest capacities [31]. Facile CO₂ release could be obtained as a large amount of the captured CO₂ (80 %) can be liberated at room temperature, and complete removal can be achieved through heating the materials in mild conditions at 80 °C [31].

Light responsive MOF-74 bearing a photoswitchable azo group has been reported previously by Yaghi *et al.* However, their potential application in carbon capture was not reported [38]. To improve response in the visible light range, several studies have attempted the inclusion of amine moieties in porous adsorbents to extend their absorption to the visible region. However, their photoswitching and gas adsorption properties were not reported. To date, only one report has shown the use of visible light in adsorbents for carbon capture applications. A diarylethene based MOF has been shown to show photochromic response during gas adsorption [2]. However, this process only partially used visible light. Although visible light was used to further promote desorption during the gas desorption step, UV light was still used in order to promote adsorption during the gas adsorption step.

In order to fully utilise visible light, different visible light responsive adsorbents must be used. Thus, in this work, **MR** was used as the visible light responsive guest molecule and **Mg-MOF-74** as the host. Upon visible light irradiation, photoisomerisation of the partially incorporated **MR** guest molecules in the host resulted in a gate-opening behaviour, a previously unknown phenomenon. As a result, the total CO₂ uptake capacity was significantly increased by up to 84 %. To the best of the author's knowledge, this is the highest photoresponse ever reported through static irradiation, particularly with full utilisation of visible light for carbon capture.

6.2 Methods

6.2.1 General

All reagents were used as purchased without further purification. Magnesium nitrate hexahydrate and 2,5-dihydroxyterephthalic acid were purchased from Aldrich. Dichloromethane (DCM) and dimethylformamide (DMF) were from Merck.

6.2.2 Synthesis of Mg-MOF-74

Mg(NO₃)₂·6H₂O (1.96 g, 7.7 mmol), 2,5-dihydroxyterephthalic acid (0.47 g, 2.4 mmol) were dissolved in a solvent mixture of DMF (175 mL), EtOH (12.4 mL) and distilled water (12.6 mL) in a Teflon capped vial. The mixture was heated to 125 °C and the temperature was held for 20 h, followed by cooling the mixture to room temperature. The yellow powder was then solvent exchanged in DMF for 2 days, followed by MeOH twice a day for five days. The dried sample was then activated at 200 °C for 5 hours at a rate of 1 °C/min under vacuum overnight.

6.2.3 Synthesis of Mg-MOF-74@MR

Mg-MOF-74 (0.17 g) and methyl red (**MR**) (0.16 g) were mixed in DCM (5 mL) and the mixture was sonicated for 15 minutes and left overnight. The mixture was filtered and thoroughly washed with DCM to remove excess **MR**. **Mg-MOF-74@MR** was heated under vacuum at 150 °C overnight at a rate of 1 °C/min to ensure solvent removal. Due to the rigidity of the framework, the mixture was irradiated with visible light, to potentially allow for an easier incorporation of the guest molecules into the pore channels.

6.2.4 Characterisation Methods

Please refer to Chapter 3 for general characterisation procedures (Section 3.2-3.3).

The MOF used in this work was of high quality and comparable to those previously reported [24, 39, 40]. The measured BET surface area of the activated Mg-MOF-74 was 1418 m²/g (literature: 1640 m²/g) (Figure 6.16a) [24]. Other characterisation results, including the thermal analysis (Figure 6.6) [39], FT-IR (Figure 6.12) and PXRD data (Figure 6.5) [40], are in good agreement to the reported data in literature [24, 39, 40].

6.2.5 Visible Light Irradiation Experiment

A 400-500 nm filter was used to ensure irradiation of visible light with an intensity of 8,100 mW/cm². Please refer to Chapter 3 for light responsive gas adsorption experimental set-up (Section 3.3.2).

6.3 Results and Discussions

In its natural state, *trans*-**MR** displays a longitudinal axis of 13 Å and a width of 6 Å (molecular volume: 235 Å³, average kinetic diameter: 10.3 Å), whereas upon excitation with visible light, the *cis* form could become 8 % smaller (Figure 6.4) [18, 19]. The incorporation of azobenzene-like materials into porous adsorbents such as MOFs and cyclodextrin has been studied previously. Particularly, the inclusion of azobenzene-like molecules into channel-structured MOFs has been reported recently, where they could either be densely packed within the pore channels or caused pore deformation [4, 41]. **MR** could potentially be incorporated longitudinally within the 1D channels of the **MOF-74**. With the use of visible light, deeper light penetration would allow more guest molecules to respond within the framework. To ensure even distribution of **MR** in the MOF, the introduction of guest molecules was carried out through solvent diffusion technique (Section 6.2.3).

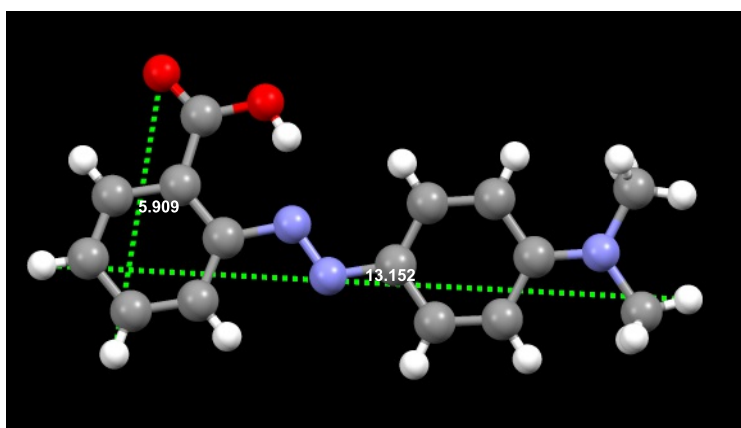


Figure 6. 4. *Trans*-methyl red showing long and short axis dimensions [42].

6.3.1 Influence of Methyl Red Guest Molecules on the Structural Conformation of MOF-74

PXRD data were collected to verify the presence of **MR** in **Mg-MOF-74@MR** and to look at the potential structural changes in the presence of **MR**. Upon incorporation, there was a general blue-shift in peak positions from those observed in the activated **Mg-MOF-74** itself, indicating there was a contraction within the MOF framework (Figure 6.5) [43]. Changes in the cell parameter were also observed, as suggested by the decrease and increase in peak intensities (Figure 6.5). This could be due to the partial incorporation of

MR. Lower crystallinity in **Mg-MOF-74@MR** could also indicate the presence of MOF-dye interaction, as shown by the general broadening of the peaks (Figure 6.5).

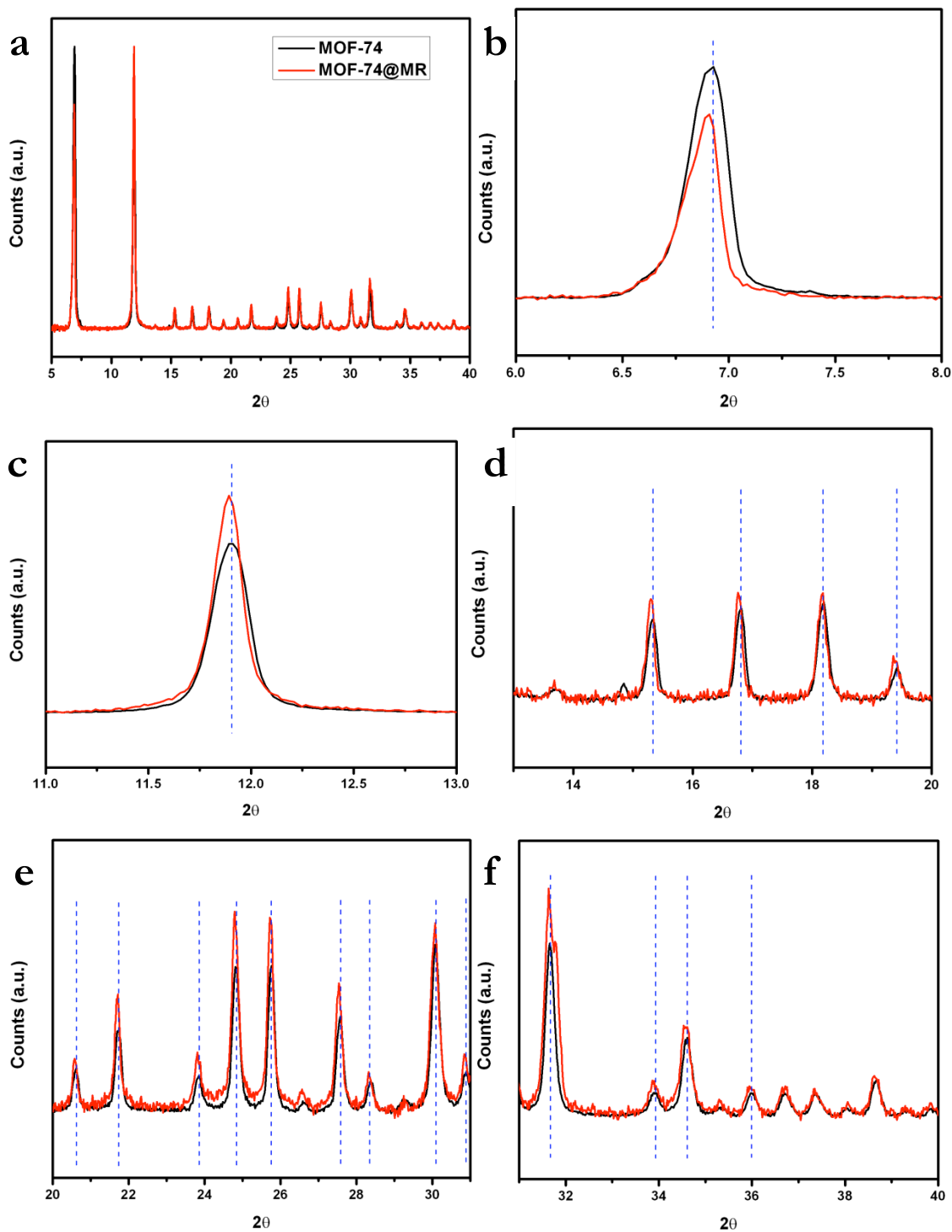


Figure 6. 5. Normalised PXRD data of Mg-MOF-74 and Mg-MOF-74@MR before irradiation. An overall spectra (a) and magnified regions of the spectra (b-f) were plotted to show general peak shifts and broadening upon MR loading.

The thermal behaviour of **Mg-MOF74@MR** showed that no free **MR** was present in the MOF as no weight loss step due to the degradation of **MR** at 180 °C was observed (Figure 6.6). This suggested that the **MR** molecules may be partially incorporated and have interacted with the organic ligands in the framework through aromatic interactions, further confirming the PXRD results (Figure 6.5). TGA curves of **Mg-MOF-74** and **Mg-MOF-74@MR** showed similar trend to each other. Weight loss due to moisture between 40-100 °C was seen in both TGA curves as they were exposed briefly in air prior to measurements [39]. The next main weight loss observed in both curves occurred from 300 °C onwards was attributed to the organic ligand decomposition (Figure 6.6) [39]. The thermal stability of the MOF is slightly reduced as the degradation step of **Mg-MOF74@MR** ended at a slightly lower temperature (660 °C) than that observed in the MOF itself (680 °C) (Figure 6.6). Furthermore, lower total percentage mass loss was obtained upon **MR** introduction (Figure 6.6). This could be due to the burning of more organic materials in the presence of **MR**, leaving more solid residues behind in the form of carbonaceous char.

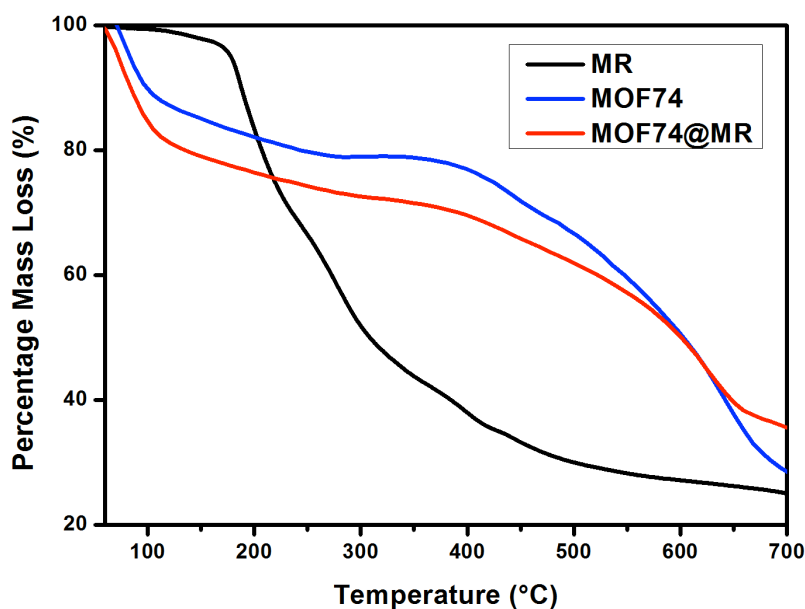


Figure 6. 6. TGA curves of Mg-MOF-74, MR and Mg-MOF-74@MR in N₂ (heating rate: 5 °C/min).

6.3.2 Photoswitching Mechanism

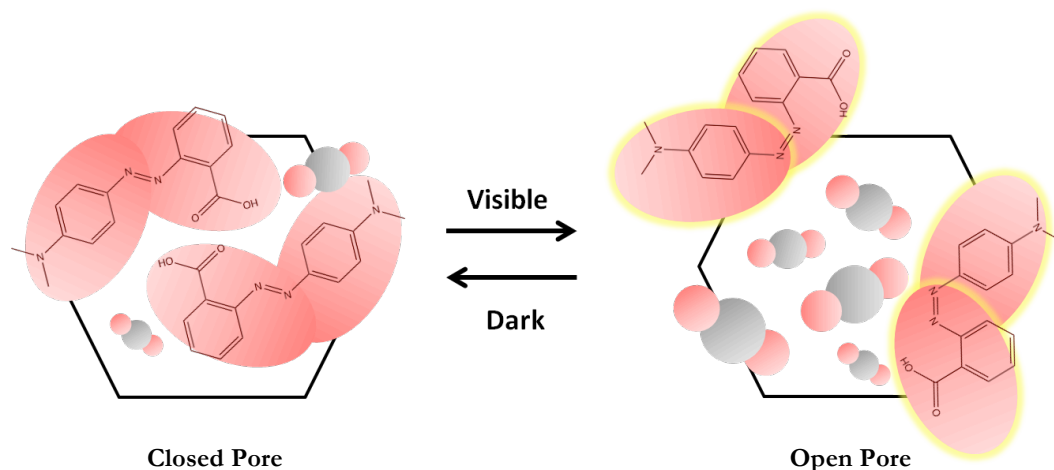


Figure 6. 7. Proposed mechanism for **Mg-MOF-74@MR** upon irradiation and relaxation.

Photoresponse studies were conducted in PXRD, UV-Vis and FT-IR experiments to determine the possible photoswitching mechanism. PXRD experiments of **Mg-MOF-74** showed that there were no long range structural changes detected upon photoirradiation, as expected, and in line with the results found in Chapter 4 (Figure 6.8a) [1]. No peak changes were detected either upon photoirradiation of **MR** itself, indicating that preferential orientation may have occurred in its amorphous form (Figure 6.8b) [44, 45]. However, there were subtle peak changes occurring in **Mg-MOF-74@MR** when irradiated with visible light. At an earlier stage of irradiation, increased in peak intensities at 6.9 and $11.9^\circ 2\theta$ and decreased in peak intensity at $26.6^\circ 2\theta$ were observed (Figure 6.9, Table 6.1). However, a slight gradual blue-shift in peak positions was observed upon prolonged irradiation (Figure 6.9, Table 6.1). The changes observed could be attributed to the **MR** photoswitching in the presence of the MOF (Figure 6.9), as this trend was not observed in the pure **MR** (Figure 6.8b). Further examination suggested that cell parameters at the a and c axes slightly reduced over time during irradiation period, thus leading to slight reduction in the cell volume (Figure 6.10). As peaks due to the host-free **MR** were not observed, the changes observed in **Mg-MOF@MR** could not be due to the **MR** itself (Figure 6.8b), confirming the previously discussed result that **MR** was perhaps partially incorporated in the MOF (Figure 6.5). The very small changes in cell parameters could be due to the rigidity of the **Mg-MOF-74** framework [31]. After leaving the post-irradiated **Mg-MOF@MR** in the dark for 5 hours, some peaks were found to have moved

back towards its initial position (Figure 6.9, Table 6.1). Therefore, indicating relaxation of the material due to *cis*-to-*trans* photoisomerisation of **MR** in the framework. As there was no significant changes in the overall peak positions or intensities, movement due to photoresponse could be predominantly localised. Localised dynamic movement has been previously reported in Chapter 4 [1].

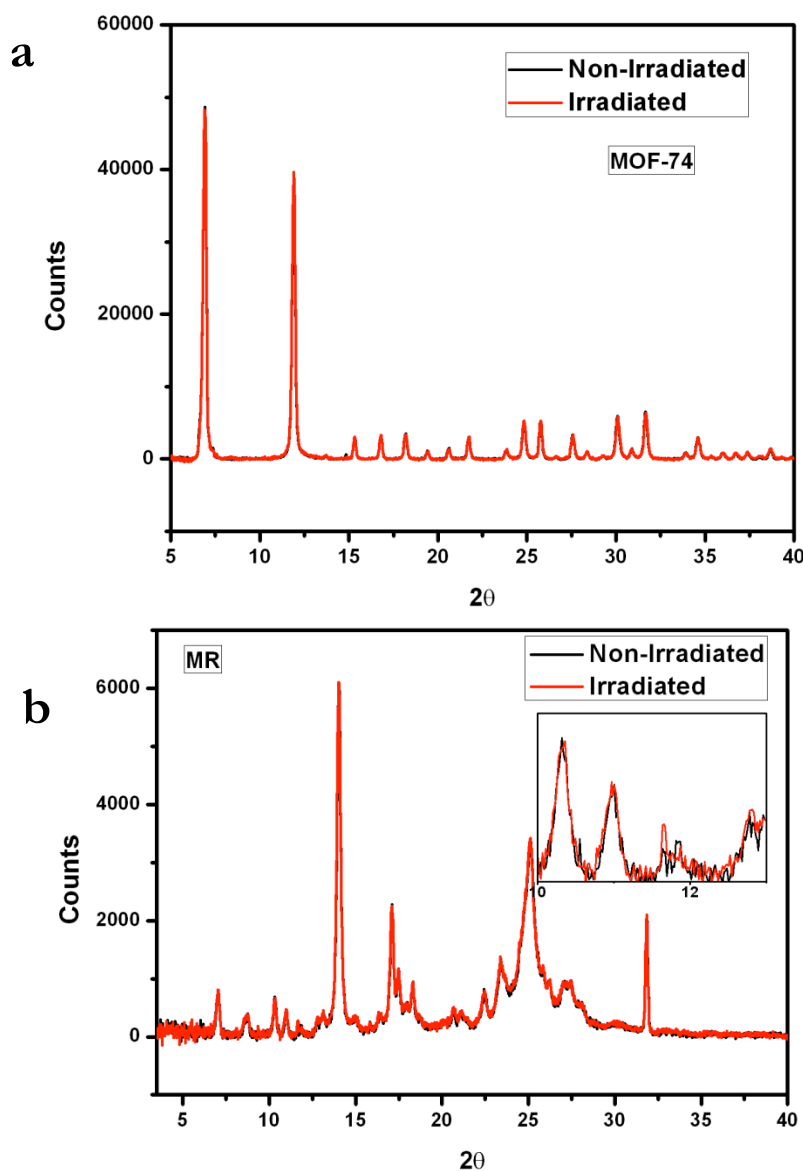


Figure 6. 8. PXRD patterns of non-irradiated and irradiated Mg-MOF-74 (a) and MR (b) in air with visible light (400-500 nm).

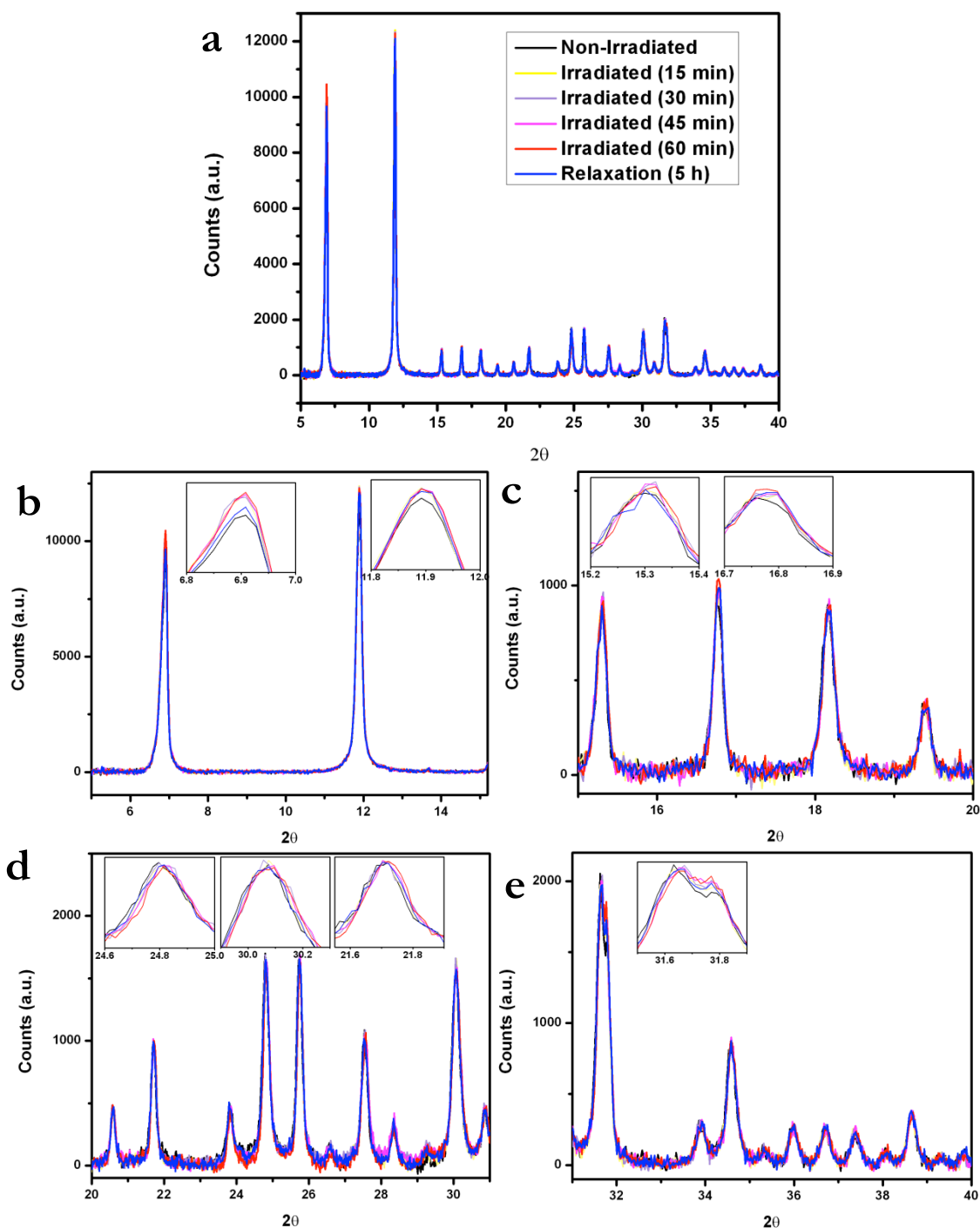
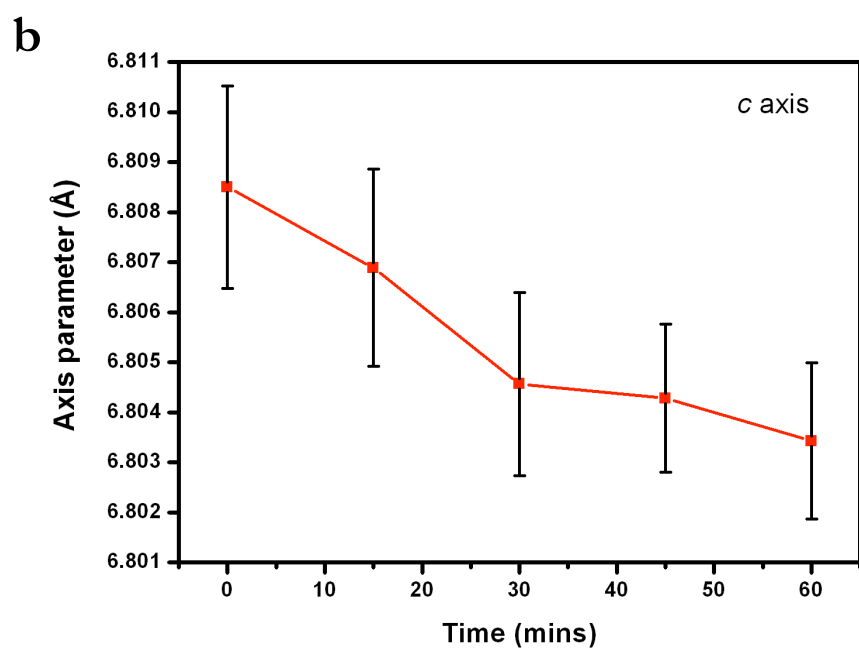
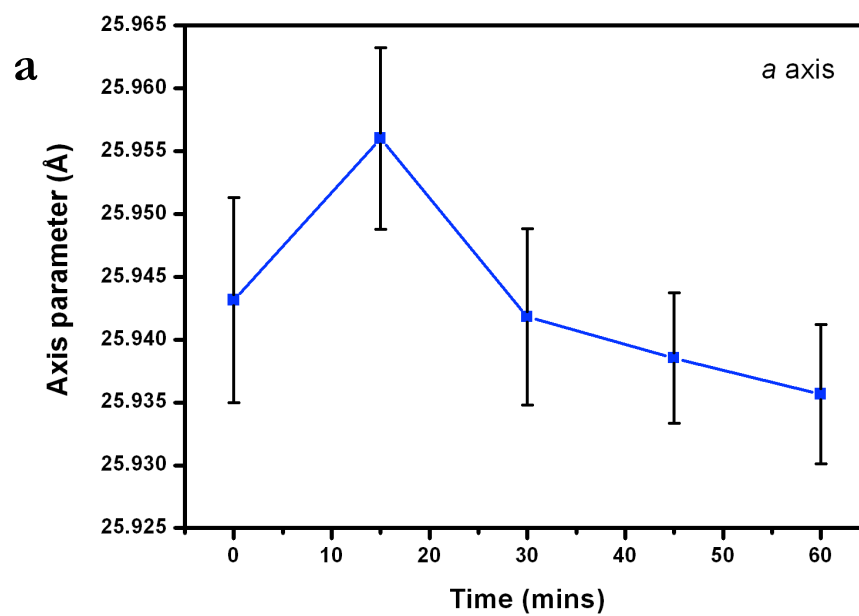


Figure 6. 9. PXRD data of non-irradiated (black), irradiated (yellow, purple, magenta and red) and post-irradiated (blue) Mg-MOF-74@MR. An overall spectra (a) and magnified regions of the spectra (b-e) were plotted to show the peak changes during and after visible light irradiation (400-500 nm). PXRD pattern of the post-irradiated sample was measured 5 hours after irradiation in the dark.

Table 6. 1 Observed peak changes in PXRD pattern of Mg-MOF-74@MR upon light irradiation, and its relaxation towards the initial peak locations and intensities post-irradiation. Y and N denote yes and no for observed relaxation.

Peak Changes	Peak Positions ($^{\circ}$ 2 θ)	Relaxation
Increased	6.9	Y
	11.9	N
	15.3	Y
	16.8	N
	20.6	Y
	31.6	Y
Decreased	26.6	Y
Red-shift	15.3	Y
	16.8	N
	18.2	Y
	20.6	Y
	21.7	Y
	24.8	Y
	25.8	Y
	27.5	Y
	30.1	Y
	30.9	Y
	31.6	Y



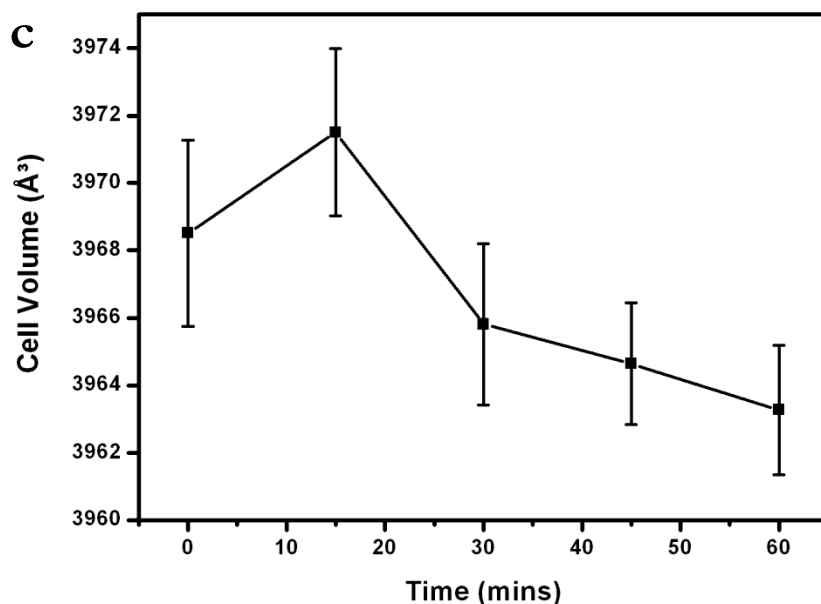
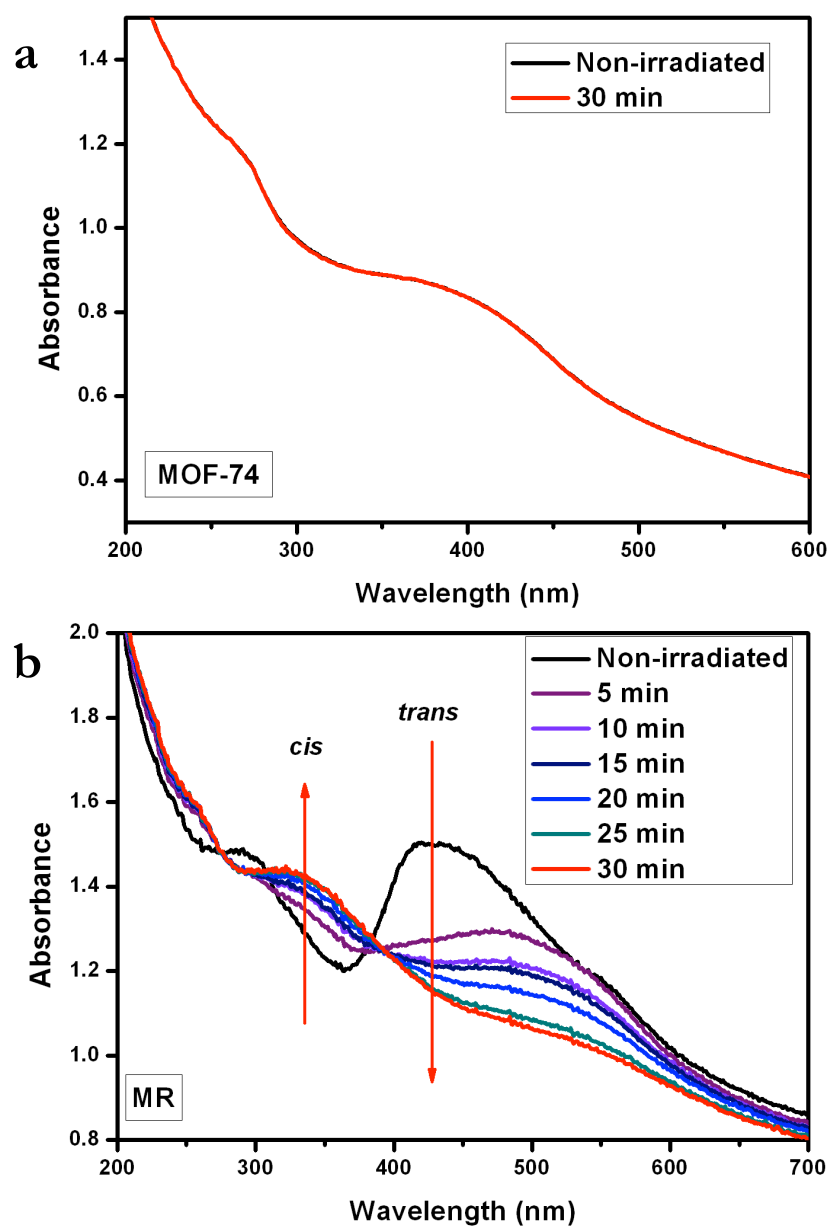


Figure 6. 10. Changes in cell parameters along the a axis (a), c axis (b) and cell volume (c) upon prolonged irradiation in Mg-MOF-74@MR.

In order to examine the optical properties of **Mg-MOF-74@MR**, several characterisation methods were conducted. UV-Vis and FT-IR spectra were collected in order to analyse the potential photoisomerisation of **MR** of **Mg-MOF-74@MR**. The UV-Vis spectrum of pure **MR** displayed characteristic absorption bands at 330 nm and 430 nm, which correspond to the *cis* and *trans* peaks (Figure 6.11b). When irradiated, a large fraction of the *trans* isomers appeared to have converted to the *cis* isomer within 30 minutes. This was indicated by the decrease in the *trans* absorption peak and increase in the *cis* absorption peak (Figure 6.11b).

The UV-Vis spectra of **Mg-MOF-74@MR** were collected to analyse the photoisomerisation trend. Upon irradiation of the sample, the slight increase in an absorption peak at 310 nm could be attributed to the *cis*-**MR** formation (Figure 6.11c). However, the typically more predominant decrease in an absorption peak due to *trans*-**MR** was not detected (Figure 6.11c). In **Mg-MOF-74@MR**, the absorption peak due to the MOF itself at ~400 nm may have masked the *trans*-**MR** peak (Figure 6.11a, c). MOF with terephthalate-based linkers are known to exhibit optical absorption in the UV-Vis region [46, 47]. Furthermore, the intensities of the *cis* and *trans*-**MR** absorption peaks would be much lower due to the lower **MR** concentration in the MOF compared to that of pure **MR**, resulting in the masking of the *trans*-**MR** peak. The *cis*-**MR**, and perhaps the *trans*-**MR**, absorption bands were blue-shifted by ~50 nm and ~90 nm (assuming the peak lied around the MOF absorption band) respectively (Figure 6.11c). The observed blue-shift

could indicate interactions between the guest molecules and the host, which confirmed the PXRD (Figure 6.5) and TGA results (Figure 6.6) [48].



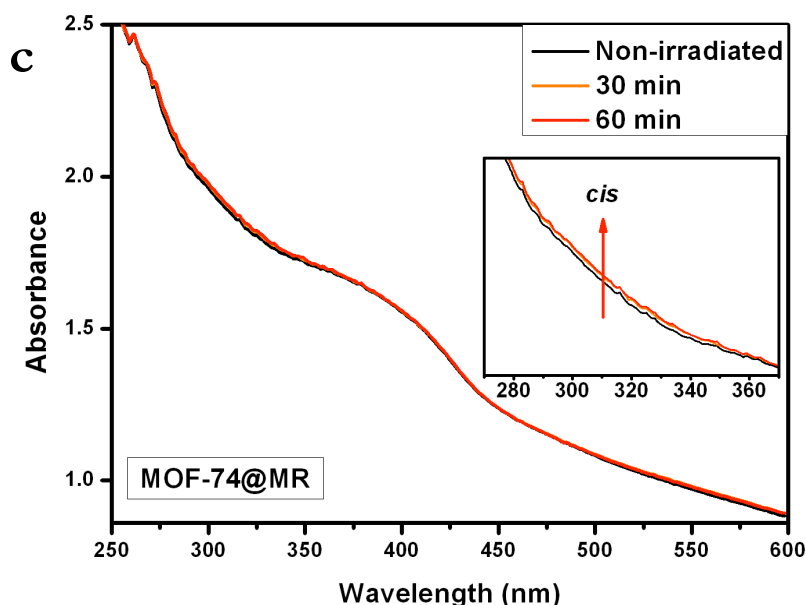
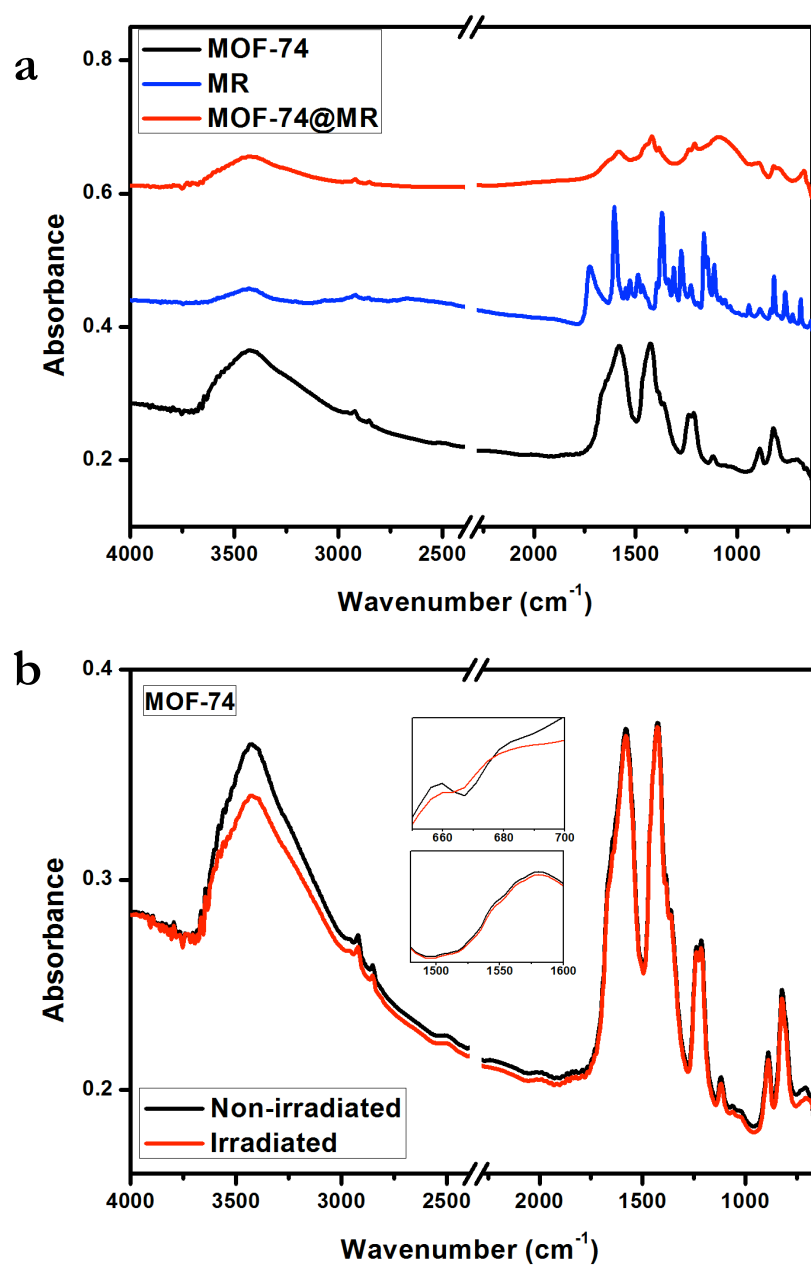


Figure 6. 11. UV-Vis spectra of non-irradiated and irradiated **Mg-MOF-74** (a), **MR** (b), **Mg-MOF-74@** (c) in air with visible light (400-500 nm).

FT-IR data were collected to further confirm the photoisomerisation of **MR** of **Mg-MOF-74@MR** (Figure 6.12, Table 6.2). Upon irradiation, the reduction of a broad peak at 3400 cm^{-1} and a peak at 700 cm^{-1} was observed in **Mg-MOF-74** itself (Figure 6.12b). This could be attributed to the hydroxyl band involved in the interaction with water molecules in air and the phenyl group of the ligand of **Mg-MOF-74**. The slight photoresponse observed was due to the presence of a conjugated system in the framework.

In the FT-IR of **MR**, characteristic vibration bands due to stretching of the azo group at 1560 cm^{-1} ($\nu_{\text{as}}(\text{N}=\text{N})$) and 1370 cm^{-1} ($\nu_{\text{s}}(\text{N}=\text{N})$), alkyl groups of aromatic and aliphatic groups in the $2800\text{--}4000\text{ cm}^{-1}$ range, phenyl groups at $\sim 700\text{--}800\text{ cm}^{-1}$ and 1600 cm^{-1} regions were observed (Figure 6.12c) [49, 50]. The formation of a new peak at 1520 cm^{-1} and reduction of peak intensities due to the azo group of *trans*-**MR** at 1560 cm^{-1} and 1370 cm^{-1} and phenyl group of *trans*-**MR** at 820 cm^{-1} were observed upon visible light irradiation (Figure 6.12c), indicating the formation of *cis*-**MR** [49, 50].

Most of the **MR** peaks could not be observed in **Mg-MOF-74@MR** as the signal may be too low to be detected or masked by the peaks from the host (Figure 6.12d). However, the formation of an additional peak at 1510 and 1540 cm^{-1} , and reduction of a phenyl group peak intensity at 680 cm^{-1} upon visible light irradiation could indicate the formation of the *cis* isomers (Figure 6.12d).



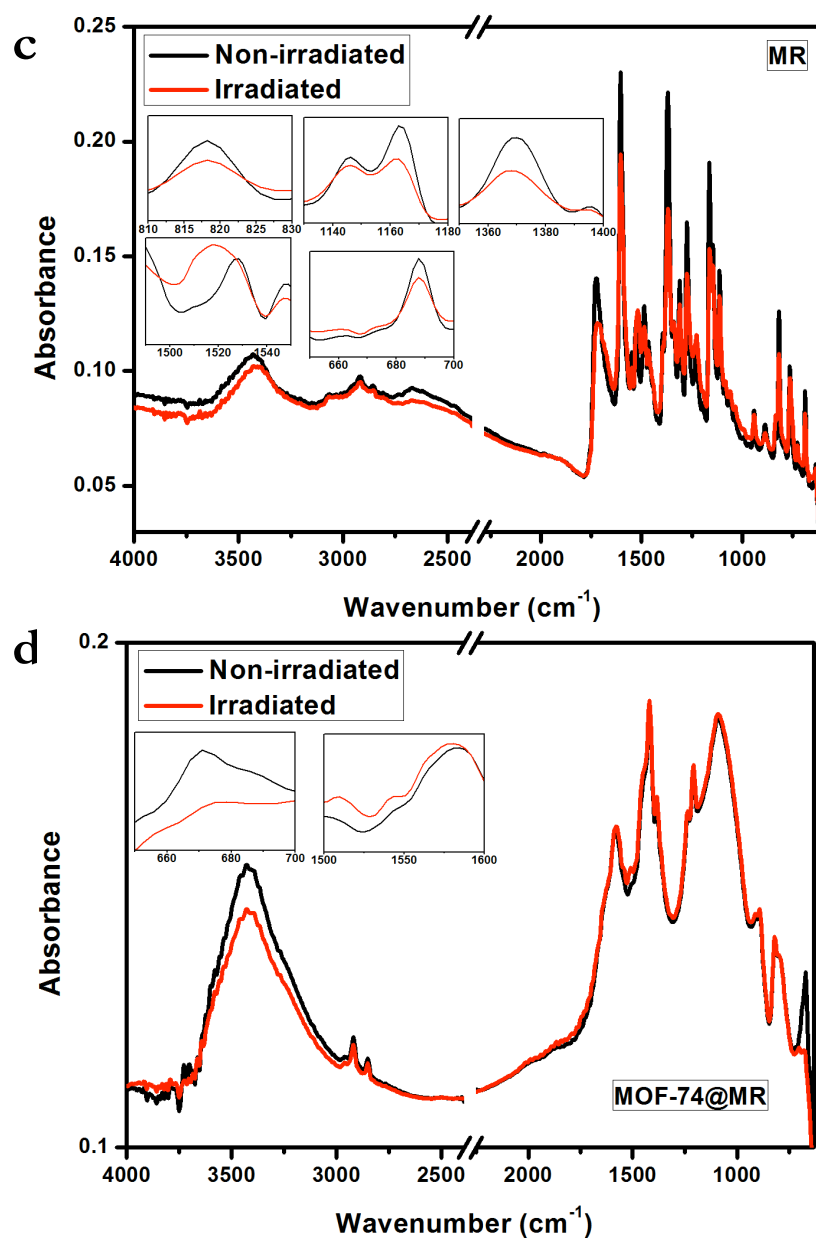


Figure 6. 12. FT-IR spectra of all the materials used in the study (a), and non-irradiated and irradiated Mg-MOF-74 (b), MR (c), Mg-MOF-74@MR (d) in air with visible light (400-500 nm).

Peak due to CO₂ in the atmosphere at ~2450 cm⁻¹ was omitted for clarity.

Table 6. 2. Observed peak changes in the FT-IR spectra of irradiated Mg-MOF-74, MR and Mg-MOF-74@MR.

Peak Changes	Peak locations (cm ⁻¹)		
	Mg-MOF-74	MR	Mg-MOF-74@MR
New Peak		1520	1510
			1540
Decreased	820	600-800	680
	890	820	3420
	1115	890	
	1210	950	
	1240	1110	
	1350	1145	
	1380	1165	
	1400	1275	
	1600	1275	
	3400	1310	
		1370	
		1395	
		1465	
		1485	
		1550	
		1600	
		1720	
		3400	
Increased		835	820
		1035	890
		1225	1090
			1210
			1240
			1380
			1420
			1450

6.3.3 Pressure Gated Effect on CO₂ adsorption in Visible Light Triggered Mg-MOF-74@MR

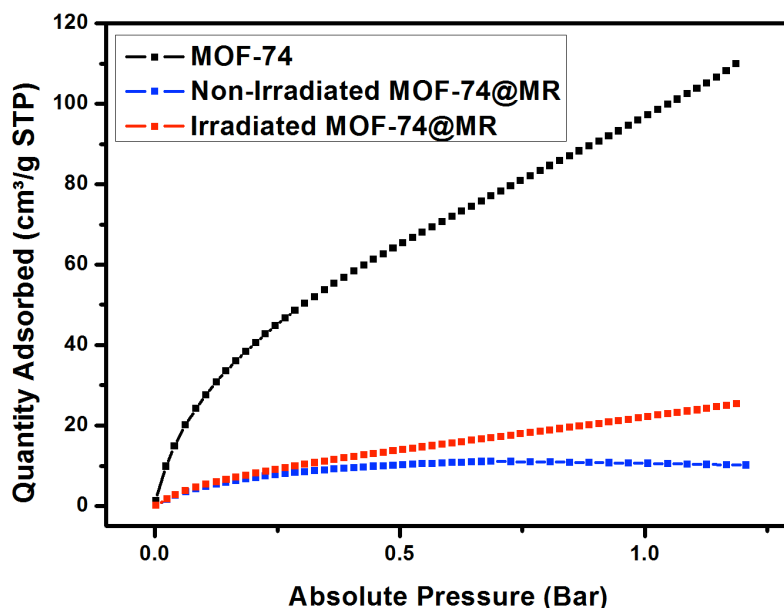


Figure 6. 13. CO₂ adsorption isotherms of non-irradiated Mg-MOF-74, and Mg-MOF-74@MR before and after irradiation at 303 K.

A light responsive pressure-gate system, previously an unknown behaviour, was observed in the CO₂ adsorption isotherms of **Mg-MOF-74@MR** at room temperature. Prolonged irradiation of the **Mg-MOF-74@MR** resulted in a gate opening absorption of CO₂, gradually increasing the CO₂ uptake capacity. Fully activated **Mg-MOF-74**, with a BET surface area of 1418 m²/g, pore volume of 4.7 Å³ and pore sizes of 5 and 10 Å was used in the experiment, which is comparable to the reported surface area and is close to average pore value (~11 Å) in literatures (Figure 6.16a) [22, 24, 40]. As expected, the introduction of **MR** resulted in the reduction in CO₂ uptake capacity with the maximum CO₂ uptake of 11 cm³/g STP for non-irradiated sample (Figure 6.13). To some extent, the presence of **MR** inhibited CO₂ from accessing the pores as saturation was reached at an absolute pressure of 0.7 bar [7, 51]. Various characterisation results indicated that photoswitching of **MR** could occur in the presence of the MOF. This indicated that the non-irradiated **MOF-74@MR** may contain the inactive **MR** state, limiting pore access for adsorption of gas molecules and reached saturation at 0.7 bar (Figure 6.13). Upon light irradiation, photoisomerisation of **MR** in the MOF to the active state may open up the pores as saturation point was no longer observed (Figure 6.13). Therefore this prompted the idea of investigating the potential effect of light irradiation in unblocking CO₂ adsorption sites.

Under dynamic photoswitching environment, significant carbon capture and release was not observed and saturation was reached at an even lower absolute pressure of 0.5 bar, indicating that perhaps, **MR** photoresponse in **Mg-MOF-74@MR** caused further pore blockage from closer contact of guest molecules to the framework. However, after a total irradiation of 30 minutes, pressure-gate opening was observed as no saturation point was observed and a 35 % increase in total CO₂ uptake was obtained (17 cm³/g STP) (Figure 14a). This could be due to the formation of the *cis*-**MR** guest molecules, as shown in the UV-Vis result whereby a large fraction of *cis* isomers was formed within 30 minutes of visible light irradiation (Figure 6.11b). The formation of more compact *cis*-**MR** guest molecules may have resulted in a lesser contact with the host and thus, pore opening occurred.

A similar experiment was conducted under static photoswitching condition on the next day to validate the pressure-gate effect in response to the visible light trigger. The result was in fact, reproducible, as the gate opening effect could be observed after 30 minutes of irradiation (Figure 14b). A 50 % increase in the total gas uptake capacity was obtained on a 30 minute irradiated **Mg-MOF-74@MR** (8 cm³/g STP). Subsequently, the total uptake was significantly enhanced when the sample was irradiated for 1 hour as 84 % increase in adsorption was obtained (25 cm³/g STP). To date, this is the highest photoresponse obtained under static conditions, especially with visible light irradiation [1, 2]. To determine the time required for maximum light triggered gas adsorption, longer irradiation of **Mg-MOF-74@MR** was conducted. However, no change in total CO₂ uptake was obtained after 2 hours, indicating that full photoresponse of **Mg-MOF-74@MR** can be achieved within 1 hour (Figure 14b).

Evidently, the increase in the overall gas uptake was much higher when photoswitching was performed under static conditions. This could be due to the movement of **MR** in **Mg-MOF-74@MR** during dynamic photoswitching preventing CO₂ from accessing the pores. Static photoswitching on the other hand, could overcome this issue as sample was irradiated before measurement, resulting in a higher total CO₂ uptake. It has also been shown previously that dynamic photoswitching exhibited lower gas uptake capacity compared to static photoswitching [1].

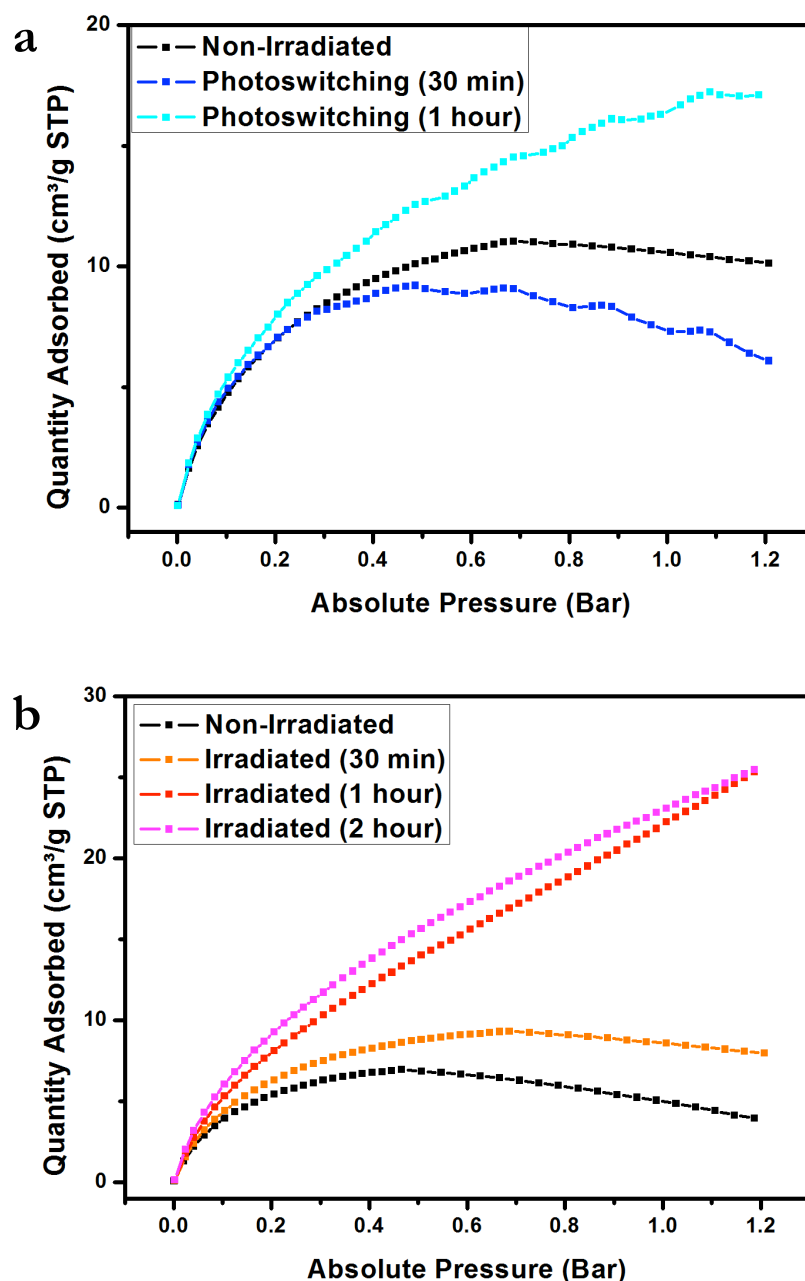


Figure 6.14. CO₂ adsorption isotherms of non-irradiated and irradiated Mg-MOF-74@MR under dynamic (a) and static (b) conditions at 303 K. Dynamic and static photoswitching experiments were carried out on day 1 and 2 respectively.

The process was found to be reversible as Mg-MOF-74@MR relaxed back to the initial state where gate-closing occurred overnight (Figure 6.15). However, a gradual decrease in overall performance of Mg-MOF-74@MR in the non-irradiated state can be observed with each overnight relaxation cycle. The relaxation of light irradiated sample in subsequent days exhibited a gas adsorption isotherm with an earlier saturation point as an absolute pressure of 0.5 bar was obtained in day 2 and 3 (Figure 6.15). Furthermore, the maximum CO₂ uptake capacities at saturation points after one cycle reduced by 36 %,

followed by further reduction of 19 % after two cycles (Figure 6.15). A previous report has shown that **Mg-MOF-74** displayed a loss in uptake capacity in consecutive cycles [31]. The relaxation of **MR** in **Mg-MOF-74@MR** could also gradually degrade the MOF. The gated system offers an advantageous process, like a dynamic photoswitching system, where controlled carbon capture could be obtained whilst providing potential CO₂ adsorption selectivity upon light trigger.

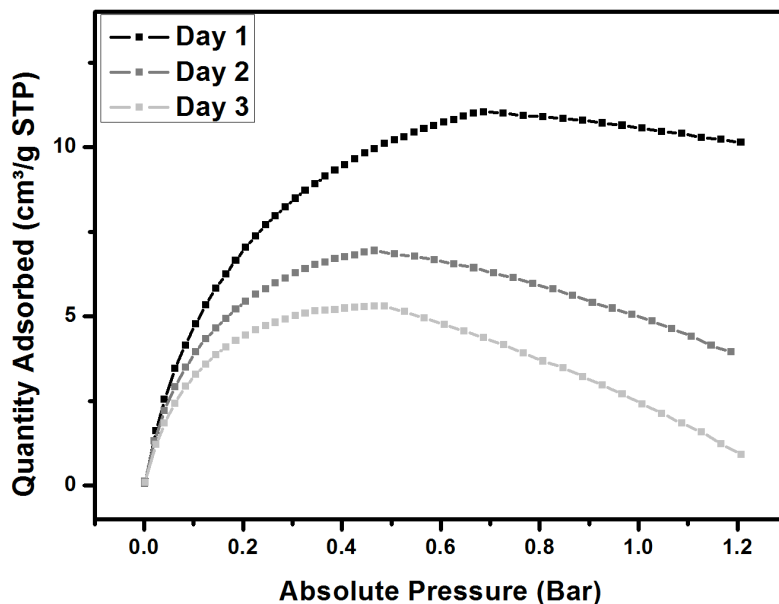


Figure 6. 15. CO₂ uptake performance of **Mg-MOF-74@MR** at 303 K after relaxation.

In the presence of **MR**, adsorption of N₂ at 77 K was dramatically reduced, with a slight increase in adsorption upon light irradiation (Figure 6.16). As previously reported in the CO₂ adsorption isotherm results obtained at 303 K (Figure 6.13), the presence of **MR** significantly reduced the gas uptake capacities, suggesting a decrease in the gas adsorption site. Often with small pores, pore blockage is obtained at lower temperature. To confirm this, pore size distributions of the non-irradiated and irradiated **Mg-MOF-74@MR** samples were analysed.

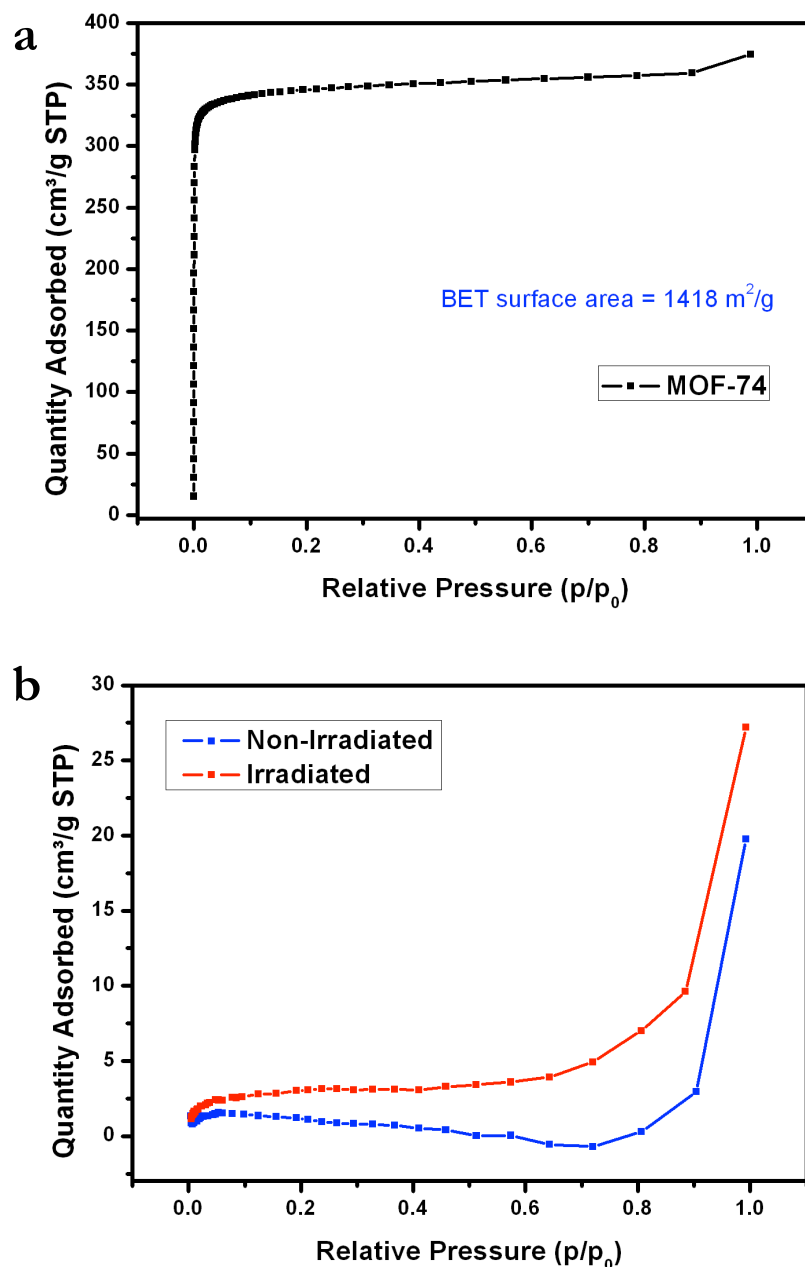


Figure 6. 16. N_2 adsorption isotherms of Mg-MOF-74 (a), and non-irradiated and irradiated Mg-MOF-74@MR at 77 K.

Pore size distributions using DFT analysis of N_2 adsorption isotherms showed that **Mg-MOF-74** without the guest molecules, two different pore sizes: 5 and 10 Å were obtained (Figure 6.17a). However in the presence of guest molecules **MR**, non-irradiated **Mg-MOF-74@MR** showed no porosity (Figure 6.17b). The result confirmed that pore size reduction was obtained. Although **Mg-MOF-74** is known to exhibit selective CO_2 uptake over N_2 at room temperature, complete blockage could not occur and some pores should still be detected as CO_2 uptake was observed prior to light irradiation [52]. N_2 isotherm of **MOF-74@MR** at 77 K showed an atypical shape of porous MOF (Figure 6.16b). At

lower temperature, pore blockage is often obtained. Since N_2 has a larger dynamic diameter than that of CO_2 , diffusion of the N_2 gas molecules into small pores would be more difficult, especially at lower temperature, resulting in pore blockage [53]. An increase in porosity was observed on post-irradiated samples where most pores were around 14 and 17 Å (Figure 6.17b). This might be due to the formation of the more compact *cis*-**MR** guest molecules, causing them to move away from MOF adsorption sites, without affecting the pore structure of the MOF. As a result, this created larger adsorption sites, which would be sufficient for some N_2 molecules to be adsorbed. Some mesopores were also detected from 50-100 Å, which may suggest the presence of interparticular voids (Figure 6.17b) [54, 55]. This could be attributed to the **MR** guest molecules being partially incorporated or coated on the surface of the MOFs, which may allow the guest molecules to interact with each other, forming larger cavities.

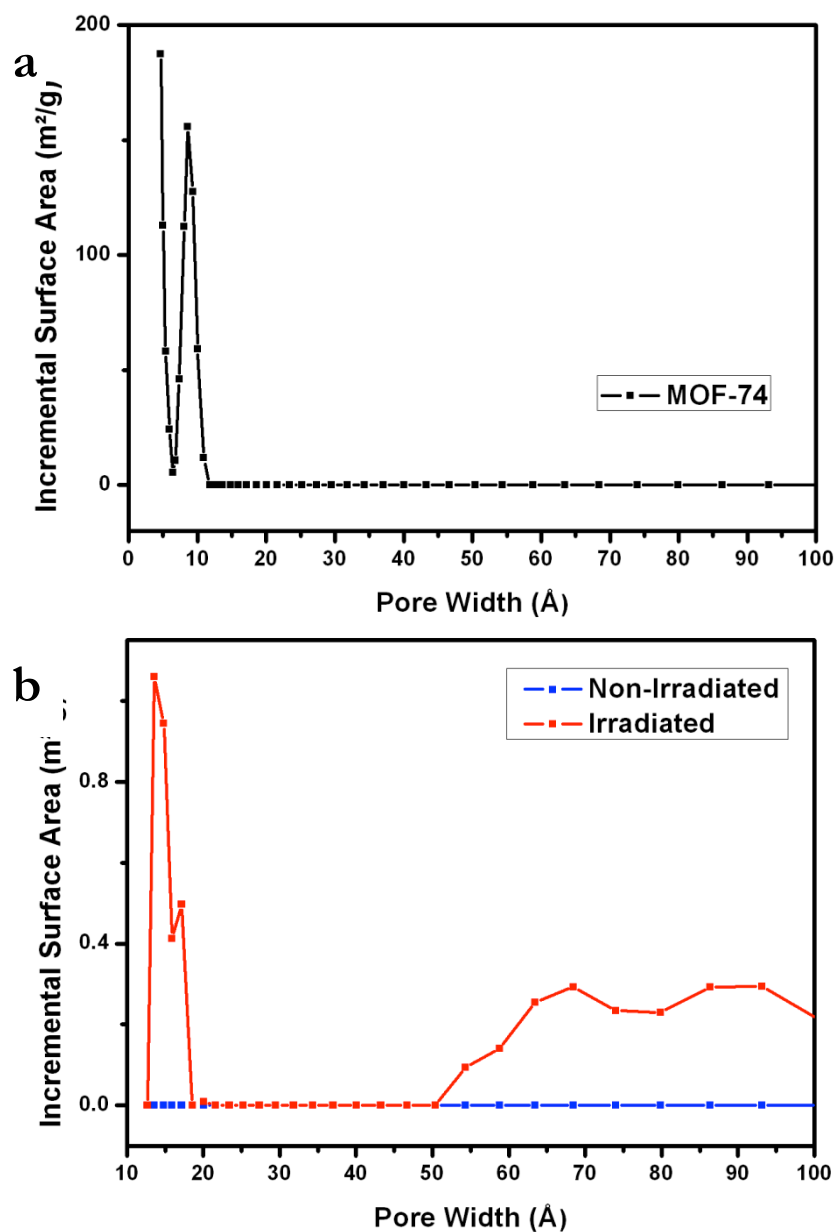


Figure 6. 17. Pore size distributions of Mg-MOF-74 (a), and non-irradiated and irradiated Mg-MOF-74@MR.

Control studies were performed to confirm the effect of **MR** in **Mg-MOF-74@MR** during gas adsorption. As shown in the previous chapter, both non-irradiated and irradiated **MR** showed no CO_2 uptake at 303 K (Figure 6.18b). Irradiation of **Mg-MOF-74** in the absence of **MR** showed very low photoresponse compared to those observed in **Mg-MOF-74@MR** as 12 % reduction in uptake capacity was obtained in the visible light range (Figure 6.18a). Therefore, the photoresponse of **Mg-MOF-74@MR** during gas adsorption was purely due to **MR**.

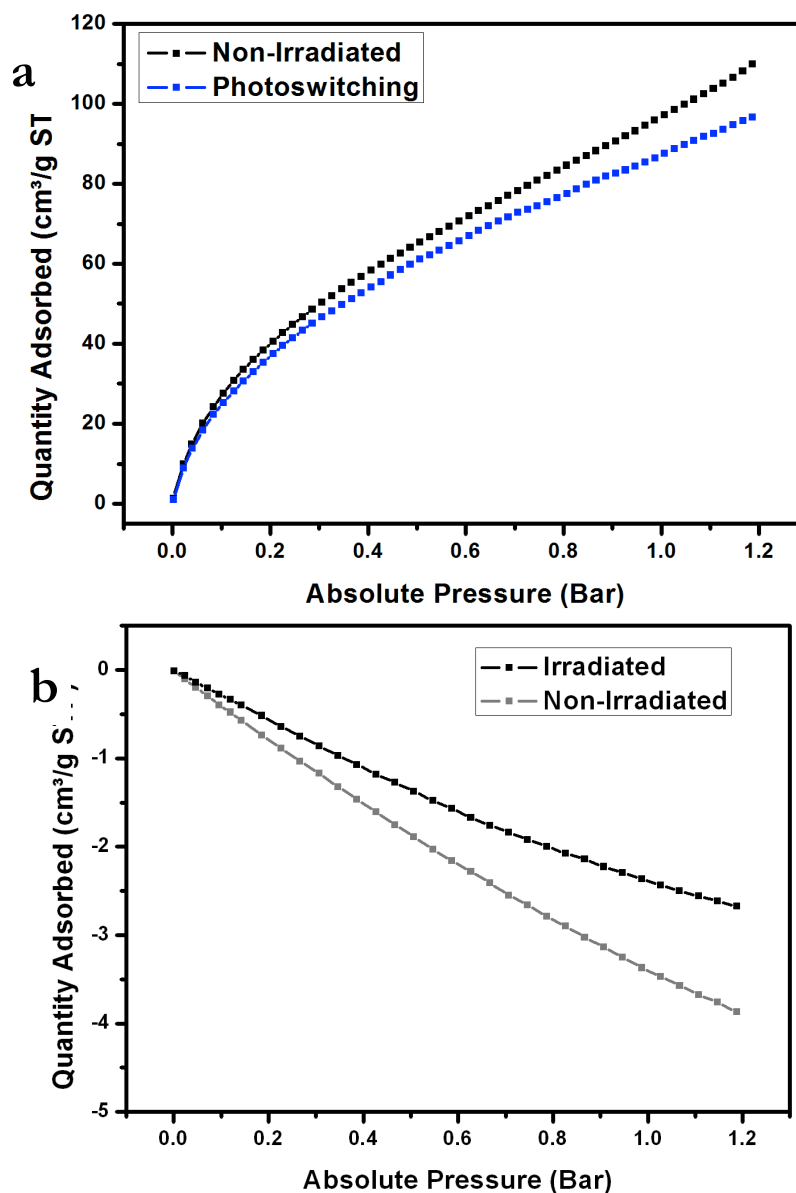


Figure 6. 18. CO₂ adsorption isotherm at 303 K of non-irradiated and irradiated Mg-MOF-74 and MR.

6.4 Conclusions

For the first time, a CO₂ adsorbent that can be exclusively controlled with a visible light trigger was successfully developed. In this work, a visible light responsive methyl red (MR) was used as the guest molecule and Mg-MOF-74 as the host. Unlike the previously reported studies in this thesis, UV light can be exclusively removed using visible light by filters, achieving a more environmentally friendly and efficient approach. To date, no

reversible carbon capture and release experiment has ever been conducted using exclusively visible light as the trigger.

The incorporation of **MR** into **Mg-MOF-74** introduced a pressure-gate opening behaviour upon CO₂ adsorption, a previously unknown phenomenon. The gate-opening pressure can be tuned through the use of visible light trigger, in which the total CO₂ uptake of **Mg-MOF-74@MR** can be significantly enhanced by up to 84 % upon prolonged irradiation (~1 hour). To the best of the author's knowledge, MOFs displaying visible light triggered gate-opening pressure for carbon capture has not yet been reported in the literature. Furthermore, this is the highest photoresponse obtained under static conditions, particularly with visible light irradiation, reported to date.

Control studies have been conducted to ensure that no false positive results were obtained. Very little or no photoresponse was observed in the CO₂ adsorption isotherm of the parent **Mg-MOF-74** by itself. The very low photoresponse could be due to the aromaticity nature of the framework. Photoresponse studies were conducted on the parent MOF materials in both UV-Vis and FT-IR experiments to ensure that the changes observed in **Mg-MOF-74@MR** upon photoirradiation was purely due to the presence of the **MR** in the host.

PXRD data showed slight structural expansion of the MOF framework upon **MR** incorporation. The photoswitching mechanism was confirmed by UV-Vis and FT-IR results, in which *trans*-to-*cis* photoisomerisation of **MR** occurred upon visible light irradiation. Thus the formation of the *cis*-**MR** resulted in a lesser contact with the host and adsorption sites became more accessible. The results also revealed the presence of host-guest interactions existed in the material. The presence of **MR** also increased pore blockage at lower temperature, as the larger gas molecules N₂ could not interact with the adsorption sites, as shown by the absence of N₂ adsorption and porosity calculated by N₂ isotherm at 77 K prior to irradiation. The lack of porosity calculated from the N₂ isotherm did not indicate complete blockage of the pores as CO₂ adsorption was still observed prior to irradiation. N₂ adsorption and porosity was increased slightly in the irradiated sample, confirming that the formation of the *cis*-**MR** and pore opening did occur after photoirradiation. This work showed that visible light could be used to potentially trigger carbon capture and release efficiently at a lower cost. Further work, such as using a water stable MOF as a host, needs to be carried out in order to develop a more efficient visible light responsive carbon capture materials.

6.5 References

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Declaration for Thesis Chapter 7

Declaration by candidate

In the case of Chapter 7, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Experiment and analysis work, writing	100

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
[name 1]	-	-
[name 2]	-	-
[name 3]	-	-

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		Date 31/10/2014
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Main Supervisor's Signature		Date 31/10/2014
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Chapter 7

TUNABLE VISIBLE LIGHT RESPONSIVE MIL-53(AL)@MR FOR CARBON CAPTURE

7.1 Introduction

Amongst different light stimuli, visible light is an attractive trigger. As discussed previously in Chapter 6, most light responsive materials are limited by their activation with UV light to convert between their photoactive forms [1-4]. Visible light can offer deeper penetration into the sample and greater sample exposure [5]. This penetration depth into the sample also depends on the optical density of the sample and the equation can be defined by the Beer-Lambert Law (Section 2.2.4) [5]. It could also eliminate the potential UV degradation of samples and create an environmentally friendly and safer approach [5]. With visible light being the most strongly irradiated and makes up 47 % of the natural sunlight, more research on using visible light triggers is needed to further advance the development of light responsive materials [6, 7] (Figure 2.3).

With the motivation of using visible light as potential trigger for a low cost carbon capture application, *o*-methyl red (**MR**) will be used as guest molecule again for this work. As discussed in Chapter 6, the azobenzene derivative molecules undergo *trans*-to-*cis* photoisomerisation upon visible light irradiation and *cis*-to-*trans* photoisomerisation in the dark (Figure 7.1) [8, 9]. Recent results, reported in Chapter 6, indicated that the incorporation of **MR** in **Mg-MOF-74** generated a pressure-gate effect, in which prolonged irradiation of the material resulted in a pressure-gate opening. The total CO₂ uptake of the irradiated **Mg-MOF@MR** was significantly increased by up to 84 %. To the author's knowledge, this was the highest photoresponse ever recorded under static photoirradiation, particularly with visible light irradiation. The promising result led to the motivation to further improve and develop another **MR** based visible light responsive adsorbent. Compared to the work reported in Chapter 6, the MOF used in this chapter is

water stable and has a flexible framework. Thus **MIL-53(Al)** would be a more desirable host for the photoswitching of **MR** guest molecules upon visible light irradiation.

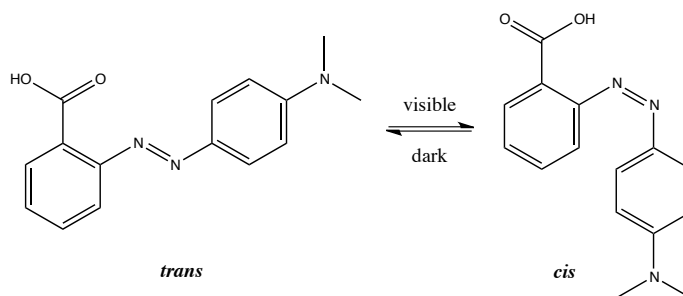


Figure 7. 1. Photoisomerisation of *o*-methyl red.

Specifically tailored MOFs that can exhibit light responsive properties have gained much interest recently in gas adsorption applications [1, 2, 10-12]. Structural stability for MOFs upon exposure to moisture is one of the many criteria required for gas storage and separations in industrial applications [13]. Unfortunately, the primary weakness for most MOFs are their instability in moist environments as shown in theoretical and experimental findings, hindering their applications in gas separation and storage [13]. For example, MOF-5, being a promising H₂ storage medium, suffers from having lower uptake performance after prolonged exposure in humid air [14, 15]. Theoretical simulation showed that MOF-5 is only water stable when exposed up to $\leq 4\%$ moisture [16]. This is because the interactions between Zn metal centers and O atoms coordinated in the framework is weak and is prone to reacting with water molecules, resulting in a structural collapse [16]. This was confirmed in experimental results, where the surface area of the MOFs significantly reduced and decomposed after exposure to humid air [17]. Another example is MOF-74, particularly **Mg-MOF-74**. As discussed in the previous chapter, MOF-74 serves as one of the most promising candidate for CO₂ separation applications. However the strength of the metal to ligand bond is weak. This results in lower water stability, reducing the CO₂ uptake performance upon exposure to air. As such, this significantly hinders their application and it is important to design new water stable MOFs.

Recently the motivation to improve their moisture stability led to the discovery of many water stable frameworks [18-22]. MOFs of the MIL series, which contain trivalent metal clusters, are well known for their water stability and show potential industrial applications, particularly in H₂ and CO₂ adsorptions [23, 24]. MIL-53 was initially reported with chromium [25] and aluminium [26]. The work was since extended to develop a range of MIL-53 materials containing Fe³⁺, Ga³⁺, In³⁺ and Sc³⁺ [27].

MIL frameworks, particularly **MIL-53(Al)**, are highly attractive due to its breathing effect and its stability and resistance to hydrolysis in neutral and acidic solution. They can be hydrothermally synthesised from low cost materials, aluminium metal clusters and terephthalate organic ligands. The infinite chains of *trans*-corner sharing octahedral metal species cross-linked by the ligands resulted in a porous network with 1D channels along the *a*-axis (Figure 7.2) [28].

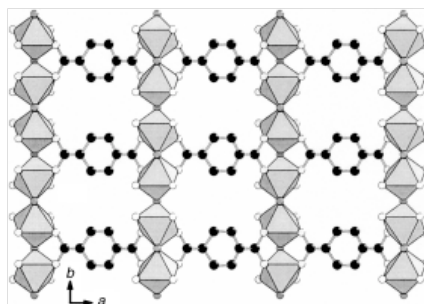


Figure 7. 2. Structure of the MIL-53(Al) framework is composed of infinite chains of corner-sharing $\text{AlO}_4(\text{OH})_2$ octahedra connected by the 1,4-benzenedicarboxylate ligands, in which the metal species are bridged by the hydroxyl groups (gray circles, square pyramids, represent the hydroxyl groups bridges and the metal clusters respectively). Reprinted with permission from [26].

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MIL-53(Al) displays reversible structural changes between different pore structures, open-pored and closed-pored, due to the framework interaction with guest molecules, or from specific pressure or temperature effects [29]. Upon structural oscillations, the unit cell volume increases up to 40 % [30]. In order to understand the flexible nature of the MOF, extensive research has been undertaken. Studies show that the activated MOF exposes the metal hydroxide chain, making the pore channels hydrophilic and prone to hydrogen bonding. Thus upon exposure to air, the hydroxyl groups of the inorganic chain can strongly H-bond with the adsorbed water molecules and it adopts a ‘closed’ structure [26]. Full structural reversibility could be achieved due to the absence of interaction, obtaining the ‘open’ structure (Figure 7.3). Another study indicated that the interaction between certain gas molecules and the framework at lower pressure upon gas adsorption could result in the shrinkage of the framework due to the narrowing of the pores [24]. However, pore opening could be achieved above a specific threshold pressure. The ‘open’ and ‘closed’ structure of the framework are often referred in literatures to as large pore (*-lp*) and narrow pore (*-np*) forms respectively, representing the accessible pore cavity in the frameworks [31]. The large structural changes between pore structures, in response to

various external triggers, are referred to as ‘breathing’ [31]. Mechanistic studies have been performed, both experimentally and theoretically, to provide useful insight on how the breathing effect works at a molecular level. The mechanism for the breathing of MIL-53 involves a twisting motion of the benzene groups of benzenedicarboxylate ligands, also known as π flipping, or distortion mode from the corner sharing octahedral metal clusters [31]. This could result in a layer-by-layer shear of the crystal, creating expansion and contraction of the unit cell volume [30]. The breathing effect of the MOFs can be tuned through synthetic functionalisation of the organic linkers, which could be attributed to the varying degree of interactions between guest molecules and the framework [31]. Such versatile structural flexibilities may allow greater structural transformations due to photoresponse.

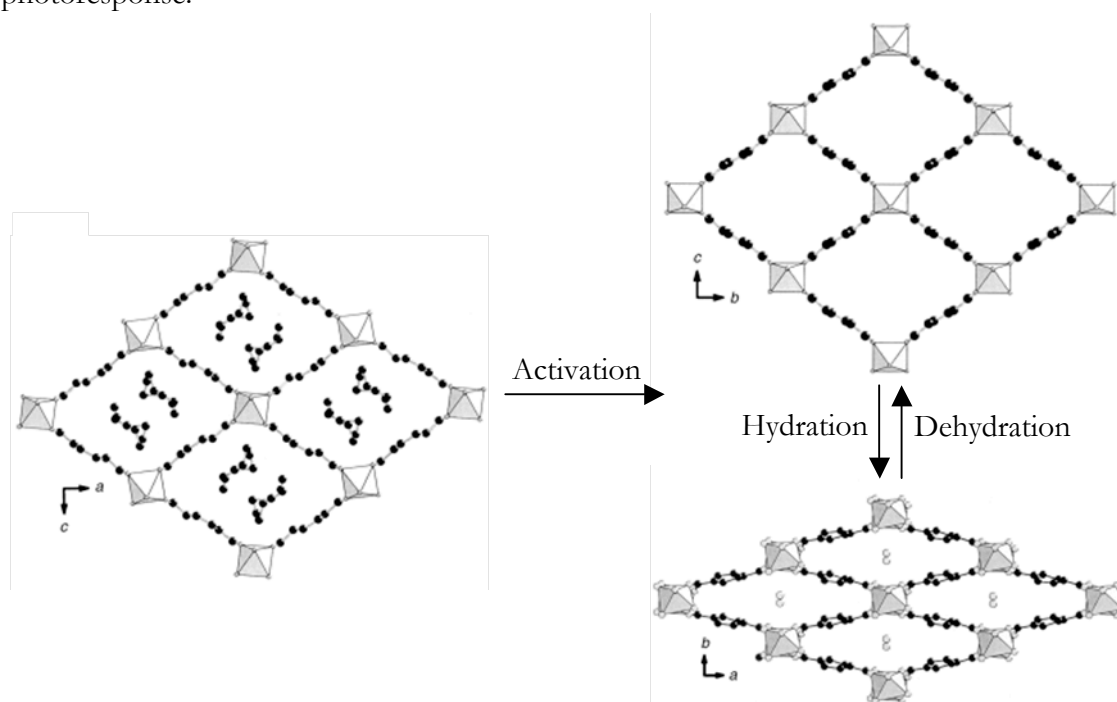


Figure 7. 3. Schematic representation of the breathing of MIL-53(Al) showing the channel system.

In this case the removal of free ligand molecules upon activation affords the open structure. The hydration-dehydration of the MOF results in a structural oscillation between the closed and open structure respectively. Reprinted with permission from [26]. Copyright 2014 John Wiley and Sons.

In this report, the introduction of **MR** in a water stable **MIL-53(Al)** also showed visible light response where the overall CO_2 uptake capacity of **MIL-53(Al)@MR** can be enhanced up to 46 % upon visible light irradiation at room temperature. This was due to the *trans*-to-*cis* photoisomerisation of the partially incorporated **MR** guest molecules in the host upon photoirradiation

7.2 Methods

7.2.1 General

All reagents were used as purchased without further purification. Aluminium oxide nonahydrate and terephthalic acid were purchased from Aldrich, and dichloromethane (DCM) was from Merck.

7.2.2 Synthesis of MIL-53(Al)

The synthetic procedure for **MIL-53(Al)** was modified according to the previously reported procedures [26, 32]. Aluminium oxide nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (1.34 g, 3.6 mmol), and terephthalic acid (0.30 g, 1.8 mmol) were mixed in 5 mL of distilled water in a Teflon autoclave. The mixture was heated to 200 °C and the temperature was held for 72 h, followed by cooling the mixture to room temperature. The off-white powder was filtered and washed thoroughly with distilled water. Purification methods (calcination and solvent activation) were carried out for the removal of unreacted and embedded terephthalic acid. Firstly, as-synthesised **MIL-53(Al)** samples were calcined at 330 °C for 3 days. This was then followed by sonicating the sample in DMF at 70 °C for 1 h. Finally, the sample was soaked in MeOH for 2 days. The sample was then filtered, washed with MeOH and dried to give a white powder. Further activation of **MIL-53(Al)** involved heating the sample at 200 °C at a rate of 1 °C/min under vacuum overnight.

7.2.3 Synthesis of MIL-53(Al)@MR

MIL-53(Al) (15 wt %: 0.51 g, 1.4 mmol, 50 wt %: 0.62 g, 1.6 mmol) and methyl red (**MR**) (15 wt %: 0.19 g, 0.7 mmol, 50 wt %: 0.62 g, 2.3 mmol) were mixed in DCM and the mixture was sonicated for about 15 minutes and left overnight. The mixture was filtered and thoroughly washed with DCM to remove excess **MR**. The orange coloured **MIL-53(Al)@MR** was heated under vacuum at 150 °C overnight at a rate of 1 °C/min to ensure solvent removal.

7.2.4 Characterisation Methods

Please refer to Chapter 3 for general characterisation procedures (Section 3.2-3.3).

The MOF used in this work was of high quality and comparable to those reported in the literature. The measured BET surface area of the activated **MIL-53(Al)** is 1213 m²/g

(literature: 1235 m²/g) (Figure 7.14a) [26]. Other characterisation results, including the thermal analysis (Figure 7.6) [26], FT-IR (Figure 7.11) [32] and PXRD data (Figure 7.5a) [26, 32], are in good agreement to the reported data in literature [26, 32].

7.2.5 Visible Light Irradiation Experiment

A 400-500 nm filter was used to ensure irradiation of visible light with an intensity of 8,100 mW/cm². Please refer to Chapter 3 for light responsive gas adsorption experimental set-up (Section 3.3.2).

7.3 Results and Discussions

As discussed previously, *trans*-**MR** is 13 Å long and 6 Å wide (molecular volume: 235 Å³, average kinetic diameter: 10.3 Å) (Figure 7.4) [33]. Upon *cis* isomerisation, the size of the molecule could become 8 % smaller [8, 9]. Depending on the pore structure of the host, guest molecules could either densely pack themselves within the pore channels, or cause pore deformation [2, 34]. The inclusion of azobenzene molecules into **MIL-53(Al)** pores has been reported recently [34]. The *trans*-azobenzene molecules of 1.2 nm length were found to be densely packed within the 1D channels of **MIL-53(Al)** [34]. However, in a sterically hindered environment, the photoisomerisation with UV light was not observed [34]. With the use of visible light, deeper light penetration could potentially trigger most of the **MR** of **MIL-53(Al)**@**MR** to display a photoresponse in a flexible environment. To ensure even distribution of **MR** in the MOF, the introduction of guest molecules was carried out through a solvent diffusion technique as described in Section 7.2.3.

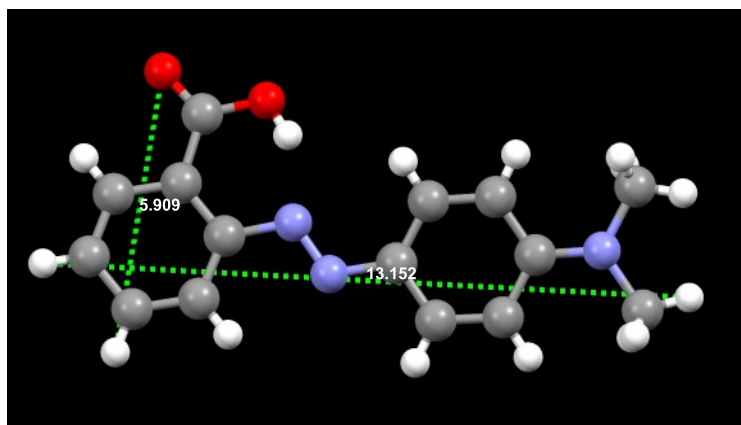


Figure 7. 4. *Trans*-methyl red showing long and short axis dimensions [33].

7.3.1 Influence of Methyl Red Guest Molecules on the Structural Conformation of MIL-53(Al)

PXRD data were collected to verify the presence of **MR** in **MIL-53(Al)@MR** and to look at the potential structural changes in the presence of **MR** and upon irradiation. The PXRD of the activated **MIL-53(Al)** showed that the open structure was obtained, which was the most suitable structural form for **MR** loading [26]. Several peak shifts can be observed when **MR** was present in the MOF. The observed red-shift and blue-shift of peaks indicated that structural deformations were not uni-directional, which could be attributed to the shrinkage and expansion of the MOF framework (Figure 7.5) [35]. This may confirm that **MR** guest molecules possibly have been partially incorporated within the pore channels of the MOF framework. Small peak shifts and peak intensity changes as a result of guest infiltration have been previously reported in literatures [34, 36]. The peak shifts were significantly more pronounced with higher guest loading, suggesting more shrinkage and expansion. There was also a general broadening of peaks in the diffraction data with the increase in **MR** loading (Figure 7.5). This might indicate the lowering in crystallinity as **MR** molecules were loaded in the MOFs, which could be evidence of a MOF-MR interaction.

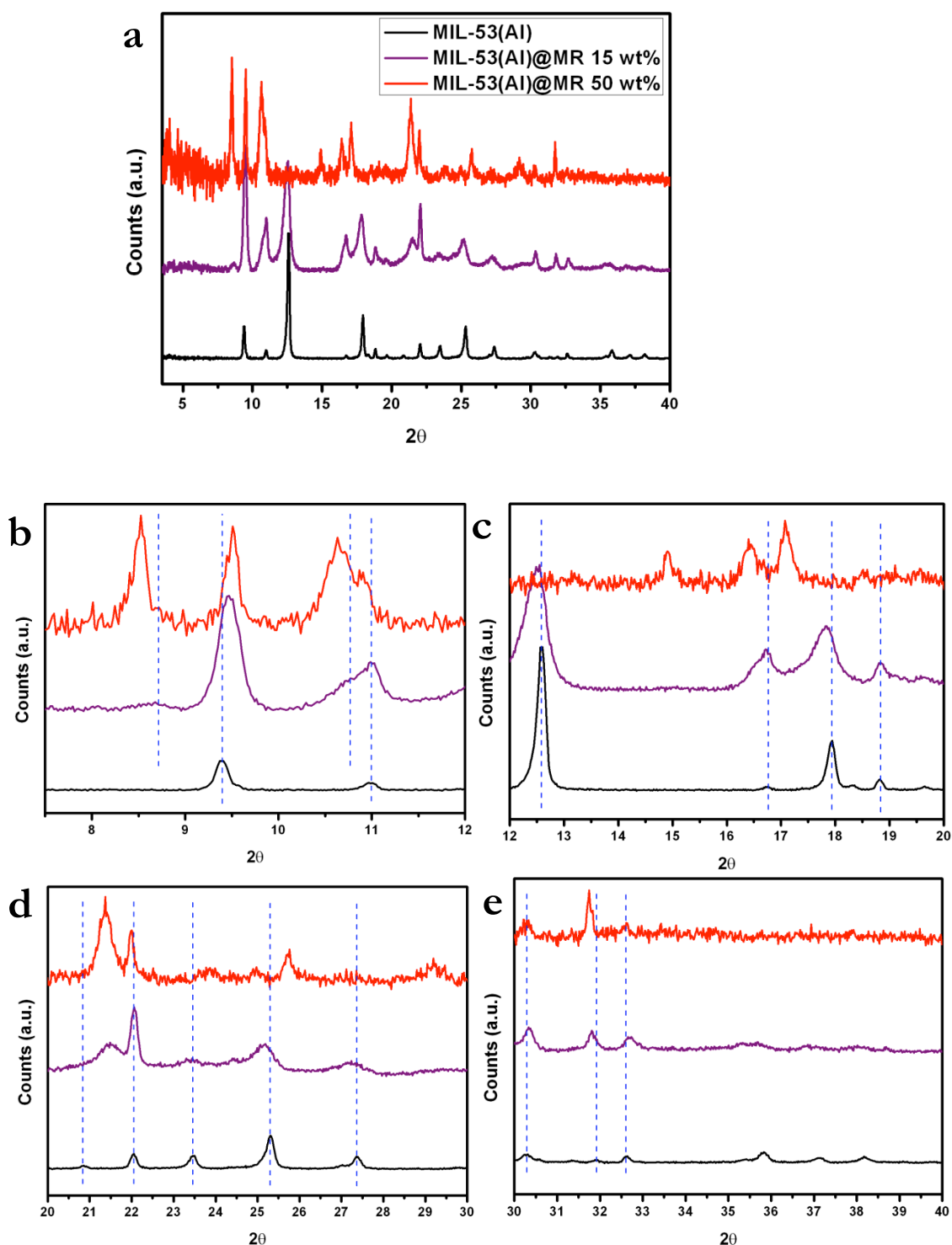


Figure 7. 5. Normalised PXRD data of MIL-53(Al) and MIL-53(Al)@MR 15 wt % and 50 wt % guest loading before irradiation. An overall spectra (a) and magnified regions of the spectra (b-e) were plotted to show general peak shifts and broadening with different MR loadings.

The thermal behaviour of **MIL-53(Al)@MR** further provides physical information on the presence of **MR** in **MIL-53(Al)**, as shown in Figure 7.6. Analyses on the parent materials were also conducted for comparison. Three events can be observed in **MIL-53(Al)** TGA

curve due to the loss of water, free terephthalic acid and formation of amorphous Al_2O_3 due to the loss of terephthalate linkers between 25-100 °C, 300-400 °C and 500-600 °C respectively (Figure 7.6). Although the measurement was carried out under N_2 , all of the open pored **MIL-53(Al)** samples have been exposed to air for a certain period of time and hydration of the samples was expected to occur. The presence of free terephthalic acid was negligible as only ~2 % weight loss was observed (Figure 7.6). Only one event was observed in **MR** TGA curve with the onset temperature for degradation of **MR** is at 180 °C (Figure 7.6).

The increase in **MR** loading decreased the dehydration process at 25-100 °C with 3 % and no mass loss obtained for 15 wt % and 50 wt % **MIL-53(Al)@MR** respectively. This could be due to the increase of pore blockage by **MR** molecules at higher guest loading, preventing water absorption. In the presence of **MR**, the thermal stability of free and bound ligands appeared to have reduced as degradation steps occurred earlier beginning at 300 °C and 500 °C respectively. No clear weight loss step which could be attributed to loss of **MR** from the MOF was evident. Perhaps, the **MR** molecules may have interacted with the free terephthalic acid and bound terephthalate linkers within the framework through aromatic interactions as no additional degradation step due to the **MR** itself were observed. Therefore, the increase in organic content may reduce their thermal stabilities [37, 38]. This further confirmed the PXRD results where the observed broadening of peaks could be due to host-guest interaction respectively (Figure 7.5). Lower total percentage mass loss was obtained with the increase in guest loading. This may be due to more solid residues being left behind in the form of carbonaceous char originating from the **MR** incorporation.

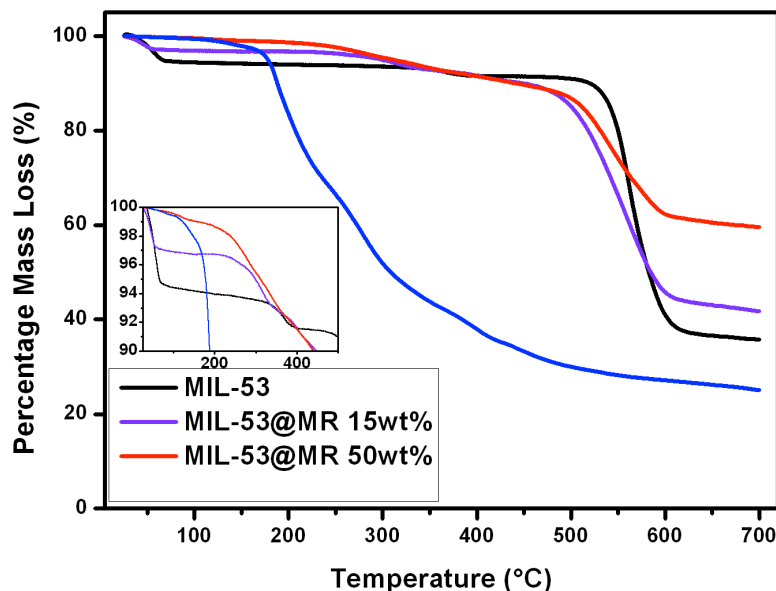


Figure 7. 6. TGA curves of MIL-53(Al), MR, MIL-53(Al)@MR (15 and 50 %wt) in N₂ (heating rate: 5 °C/min).

7.3.2 Photoswitching mechanisms

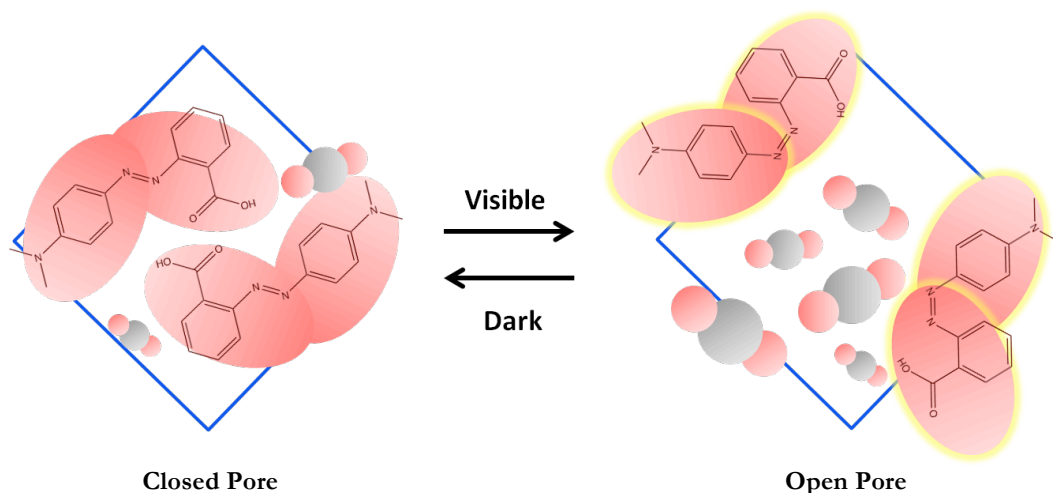
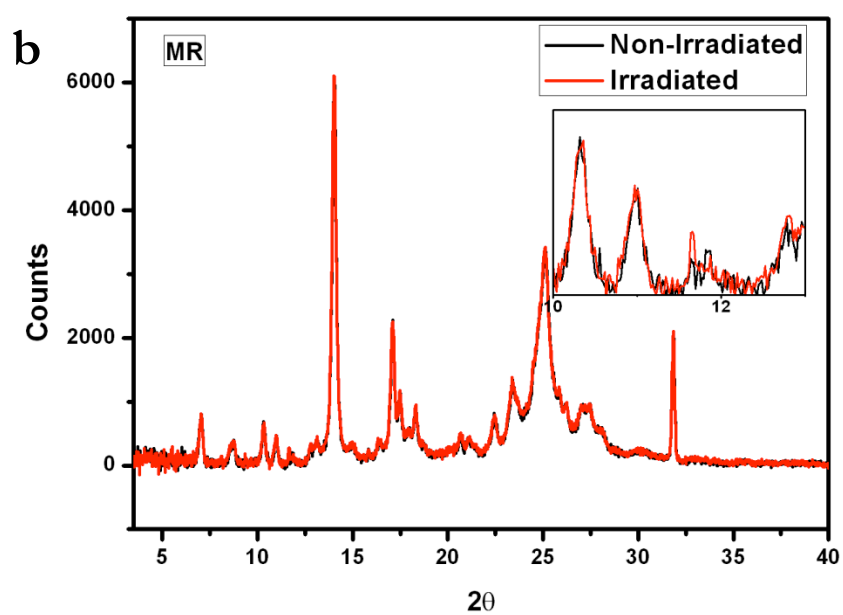
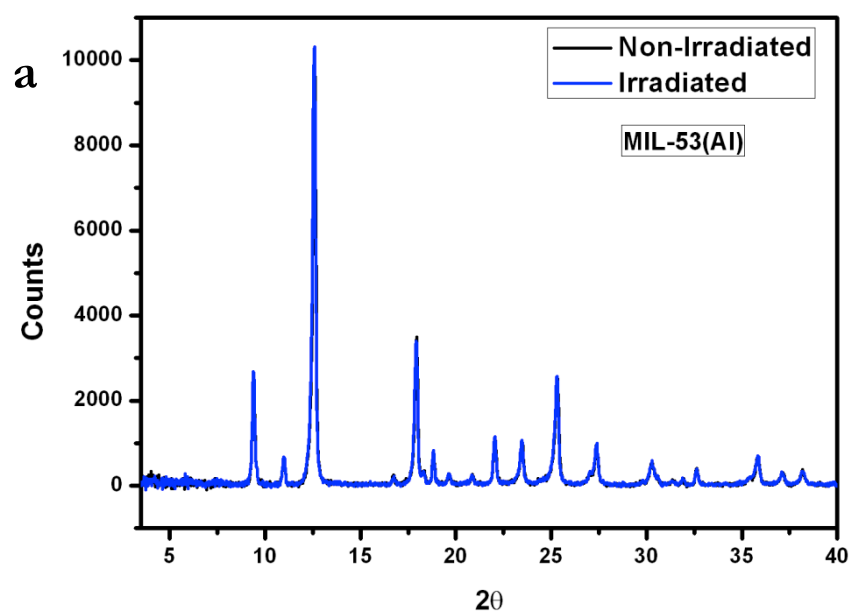


Figure 7. 7. Proposed mechanism for MIL-53(Al)@MR upon irradiation and relaxation.

Various characterisation techniques were used to understand the mechanism behind their light switching properties upon visible light irradiation. Photoresponse study was conducted during PXRD experiment. As **MIL-53(Al)** is known for its breathing behaviour, photoresponse study of the MOF itself was also conducted during PXRD experiment. The result showed no response upon visible light irradiation as expected (Figure 7.8a). However, PXRD of **MIL-53(Al)@MR** showed that there was no peak

shifts detected during light irradiation, suggesting that the movement due to photoresponse was perhaps localised (Figure 7.8c-d). This result is similar to that reported in Chapter 4 where an azobenzene based MOF displayed no change in the PXRD patterns as a function of irradiation [10]. The PXRD data of pure **MR** was also obtained to determine whether there was free **MR** present in the framework (Figure 7.8b). The result showed that no peaks due to the pure **MR** were present in the **MIL-53(Al)@MR** diffraction pattern. This indicated that the **MR** molecules present in the framework might have interacted with the host. The irradiation of the pure **MR** also showed no obvious peak changes due to photoresponse. This could indicate that preferential orientation may occur in its amorphous form, as reported in the literature for azo-based material [39, 40]. Thus UV-Vis (Figure 7.9) and FT-IR (Figure 7.11) were used to detect the photoresponse of **MIL-53(Al)@MR**.



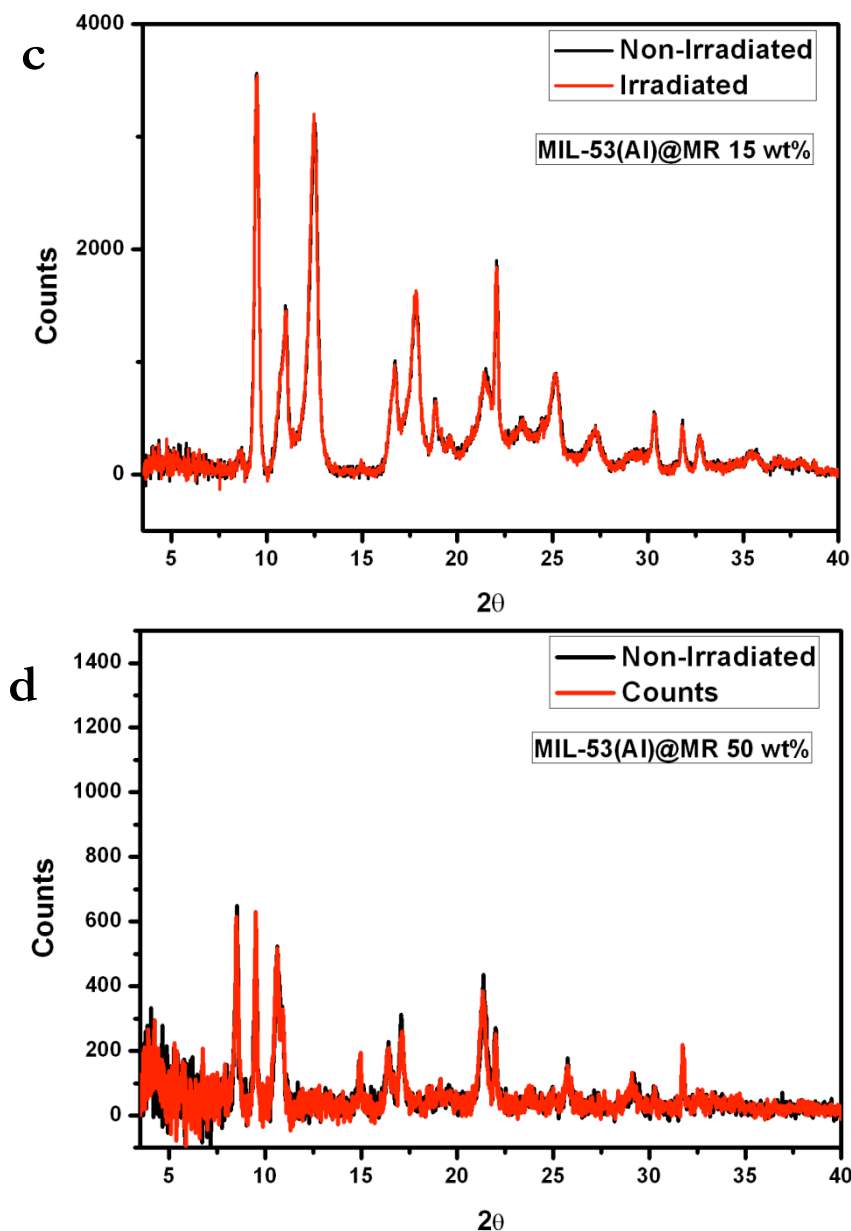
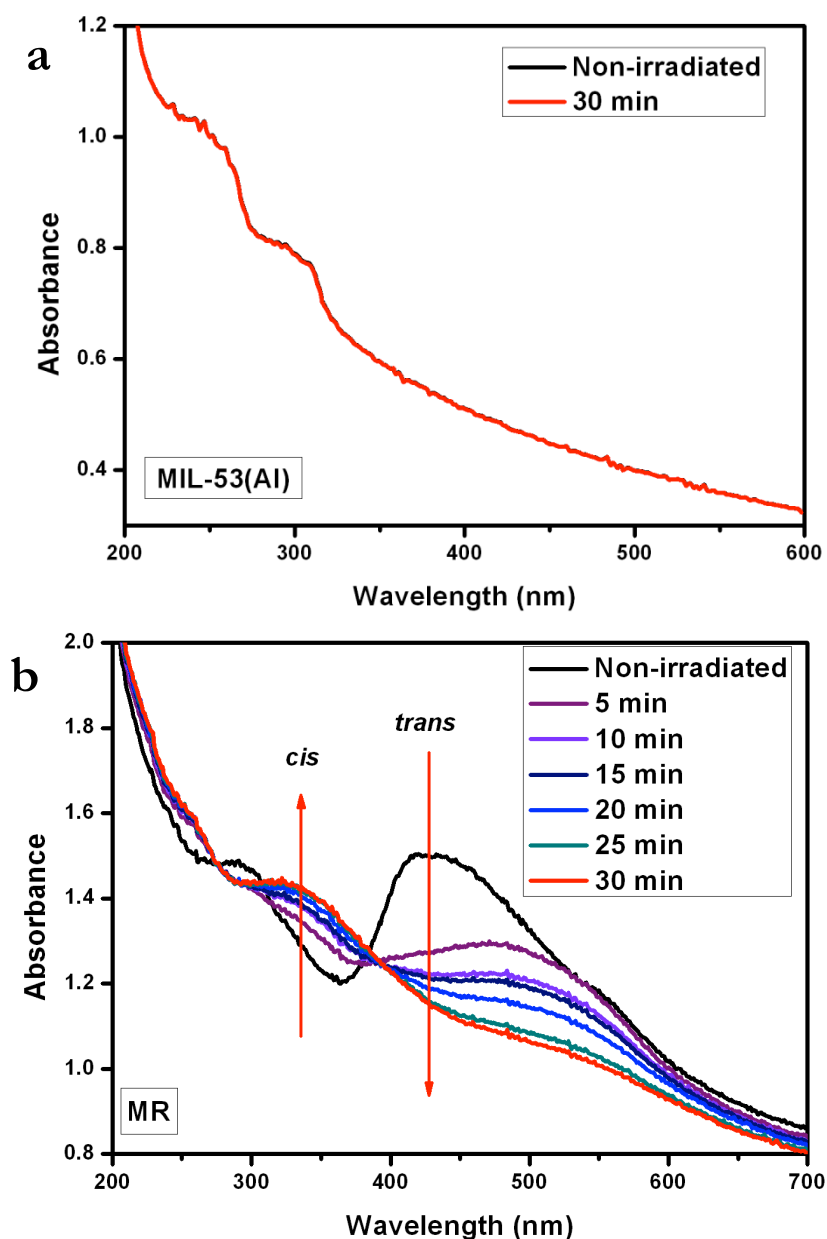


Figure 7. 8. PXRD patterns of non-irradiated and irradiated MIL-53(Al) (a), MR (b), MIL-53(Al)@MR 15 wt % (c) and 50 wt % (d) in air with visible light (400-500 nm).

Although photoswitching was not observed in PXRD data (Figure 7.8), UV-Vis (Figure 7.9) and FT-IR spectra (Figure 7.11) confirmed the photoisomerisation of **MR** of **MIL-53(Al)@MR**. In the UV-Vis spectra, **MIL-53(Al)** did not show any absorption in the visible range and was unresponsive towards visible light (Figure 7.9a). The irradiation of pure **MR** with visible light resulted in a decrease in the *trans*-**MR** absorption band at 430 nm and an increase in the *cis*-**MR** absorption band at 330 nm (Figure 7.9b). A large fraction of the *trans* isomers appeared to have converted to the *cis* isomer within 30 minutes of irradiation. The presence of absorption peaks due to **MR** were observed in

MIL-53(Al)@MR. However, their absorption peaks were red-shifted by ~ 60 nm for *trans* ($\lambda_{\text{max}} \approx 490$ nm) and ~ 30 nm for *cis* ($\lambda_{\text{max}} \approx 360$ nm) at a much lower intensity from that of the free **MR** (Figure 7.9b-c). The observed red-shift could be due to the increase in the electron density from the interaction of **MR** molecules with the host, lowering the photoisomerisation energy barrier [41-44]. This also further confirmed the PXRD (Figure 7.5) and TGA (Figure 7.6) results regarding the presence of host-guest interaction. The lower absorption intensities were expected due to the lower **MR** concentration in the MOF than that obtained in the pure **MR**. Perhaps, photoisomerisation of some **MR** guest molecules were hindered in a more constricted environment, as reported in previous literatures [1, 11, 45]. Similar to the UV-Vis spectra of **MR**, the *trans* and *cis* peaks continually decreased and increased respectively upon visible light irradiation.



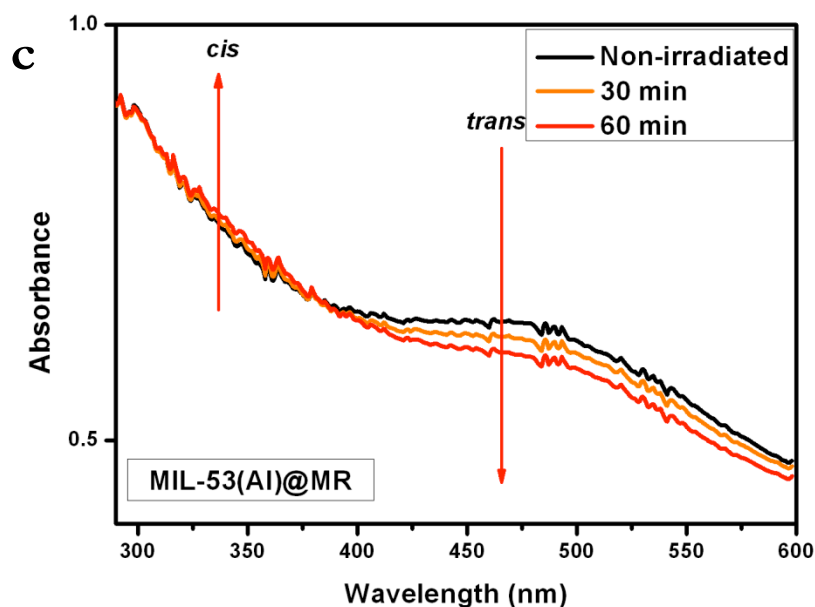


Figure 7. 9. UV-Vis spectra of non-irradiated and irradiated MIL-53(Al) (a), MR (b), MIL-53(Al)@MR 50 wt % (c) in air with visible light (400-500 nm).

FT-IR results also suggested that photoisomerisation of **MR** in **MIL-53(Al)@MR** may have occurred (Figure 7.11, Table 7.1). The IR spectra of irradiated **MIL-53(Al)** were collected in air. The result exhibited an increase in an OH band, that may be involved in the H-bond interactions with trapped water, at $3500\text{--}3600\text{ cm}^{-1}$ region, and a decrease in the aromatic stretching band at $\sim 1600\text{ cm}^{-1}$. The slight photoresponse observed could be due to the aromaticity of the ligands that made up the framework [46]. FT-IR also showed that very little terephthalic acid was present in fully activated **MIL-53(Al)** (Figure 7.10), which further confirmed the TGA (Figure 7.6) result of the activated **MIL-53(Al)**. This indicated that the photoresponse of **MR** occurred without the interference of free organic ligands.

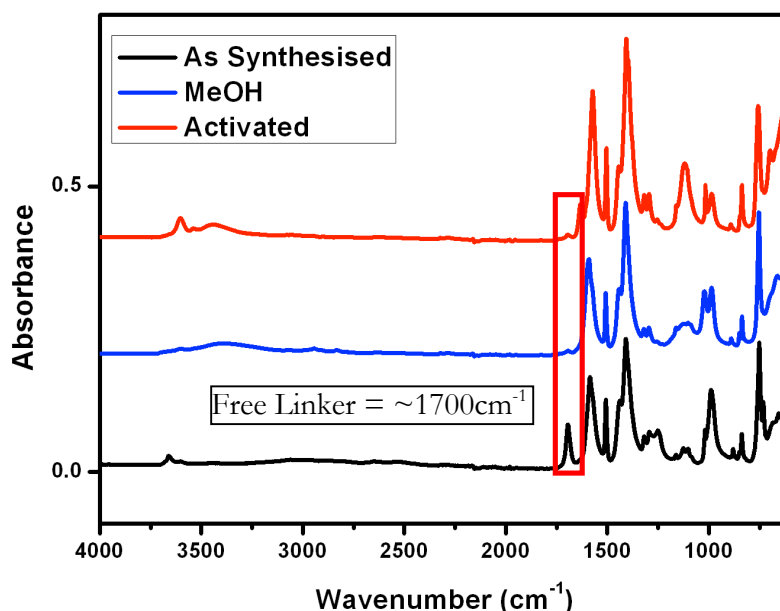
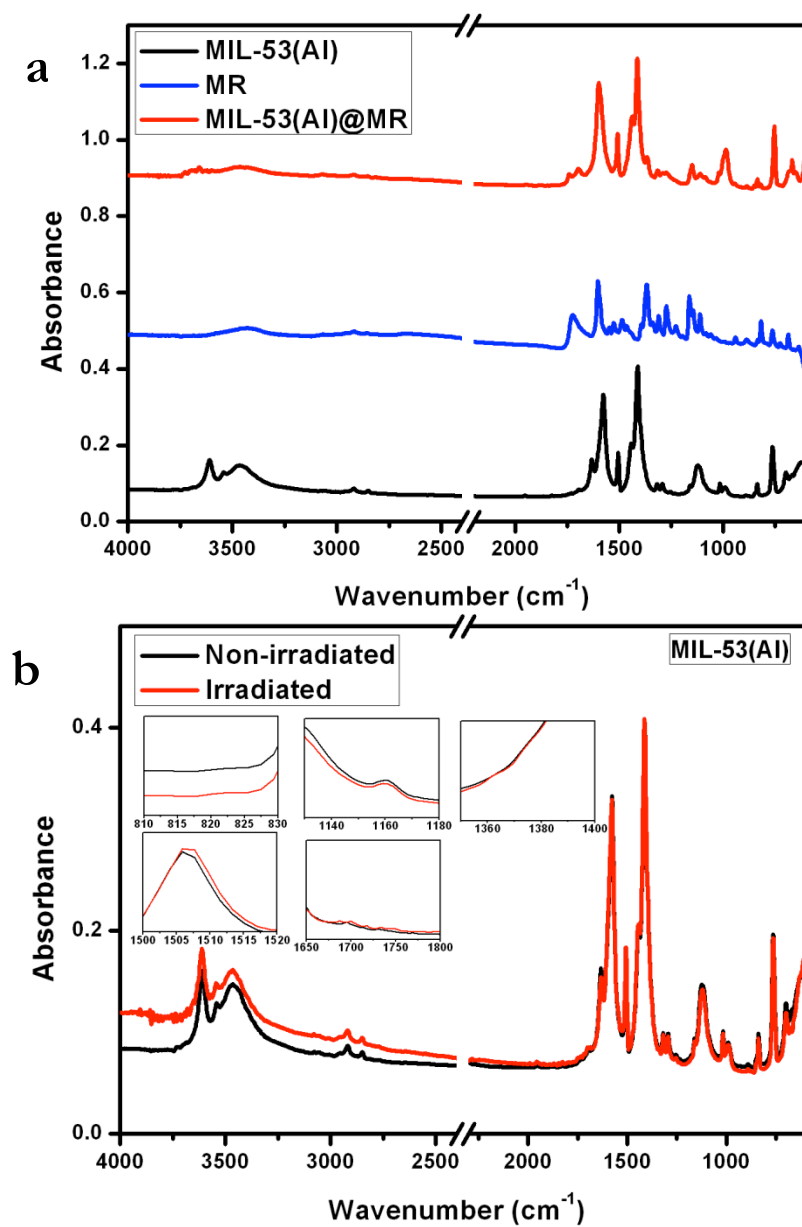


Figure 7. 10. FT-IR spectra of as-synthesised, Methanol exchanged and activated MIL-53(Al) to indicate the removal of free terephthalic acid as shown by the elimination of a peak at $\sim 1690\text{ cm}^{-1}$.

MR showed characteristic vibration bands due to stretching of the azo group in 1560 and 1370 cm^{-1} , alkyl groups of aromatic and aliphatic groups in the $2800\text{--}400\text{ cm}^{-1}$ range, carbonyl group at 1720 cm^{-1} , and phenyl groups at $\sim 700\text{--}800\text{ cm}^{-1}$ and 1600 cm^{-1} regions (Figure 7.11c, Table 7.1) [47, 48]. Upon visible light irradiation, a new peak at 1520 cm^{-1} was formed, and the peaks due to the azo group of *trans*-**MR** at 1560 cm^{-1} and 1370 cm^{-1} , carbonyl group at 1720 cm^{-1} , C-O group at 1150 cm^{-1} and phenyl group of *trans*-**MR** at 820 cm^{-1} were reduced, which could be ascribed to the formation of the *cis* isomer (Figure 7.11c, Table 7.1) [47, 48].

Most of the **MR** modes and peaks due to MOF-MR interaction could not be observed in **MIL-53(Al)@MR** as the signal may be too low or masked by the **MIL-53(Al)** peaks (Figure 7.11, Table 7.1). However, the increase in the peak intensity of the azo group of *trans*-**MR** at 1510 cm^{-1} , and reduction of peak intensities of the phenyl group, azo group and carbonyl group at 820 , 1370 and 1740 cm^{-1} respectively, could be attributed to the formation of the *cis*-**MR** (Figure 7.11d, Table 7.1).



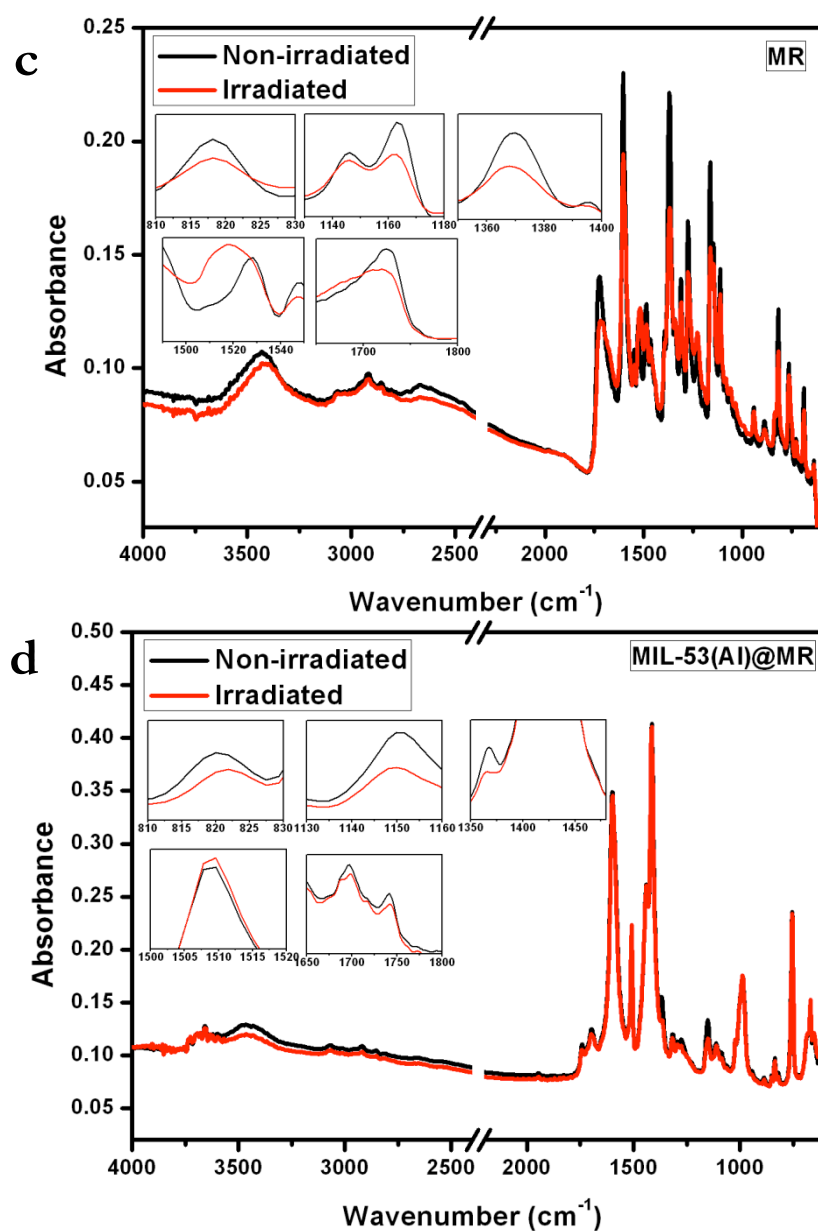


Figure 7. 11. FT-IR spectra of all the materials used in the study (a), and non-irradiated and irradiated MIL-53(Al) (b), MR (c), MIL-53(Al)@MR 50 wt % (d) in air with visible light (400-500 nm). Peak due to CO_2 in the atmosphere at $\sim 2450 \text{ cm}^{-1}$ was omitted for clarity.

Table 7. 1. Observed peak changes in the FT-IR spectra of irradiated MIL-53(Al), MR and MIL-53(Al)@MR 50 wt %.

Peak Changes	Peak locations (cm ⁻¹)		
	MIL-53(Al)	MR	MIL-53(Al)@MR
New Peak		1520	
Decreased	700	600-800	750
	760	820	820
	835	890	835
	850	950	850
	990	1110	885
	1015	1145	945
	1120	1165	1085
	1160	1275	1110
	1320	1275	1150
	1575	1310	1315
	1630	1370	1365
	3450	1395	1415
		1465	1440
		1485	1600
		1550	1700
		1600	1740
		1720	3450
		3400	
Increased	1415	835	650
	1445	1035	670
		1225	680
			1510

7.3.3 Enhanced CO₂ Uptake of MIL-53(Al)@MR Upon Visible Light Irradiation

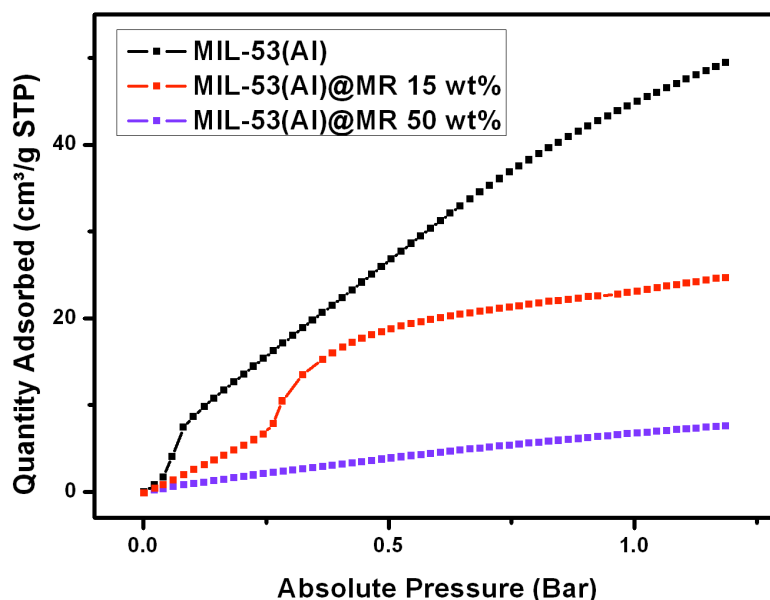
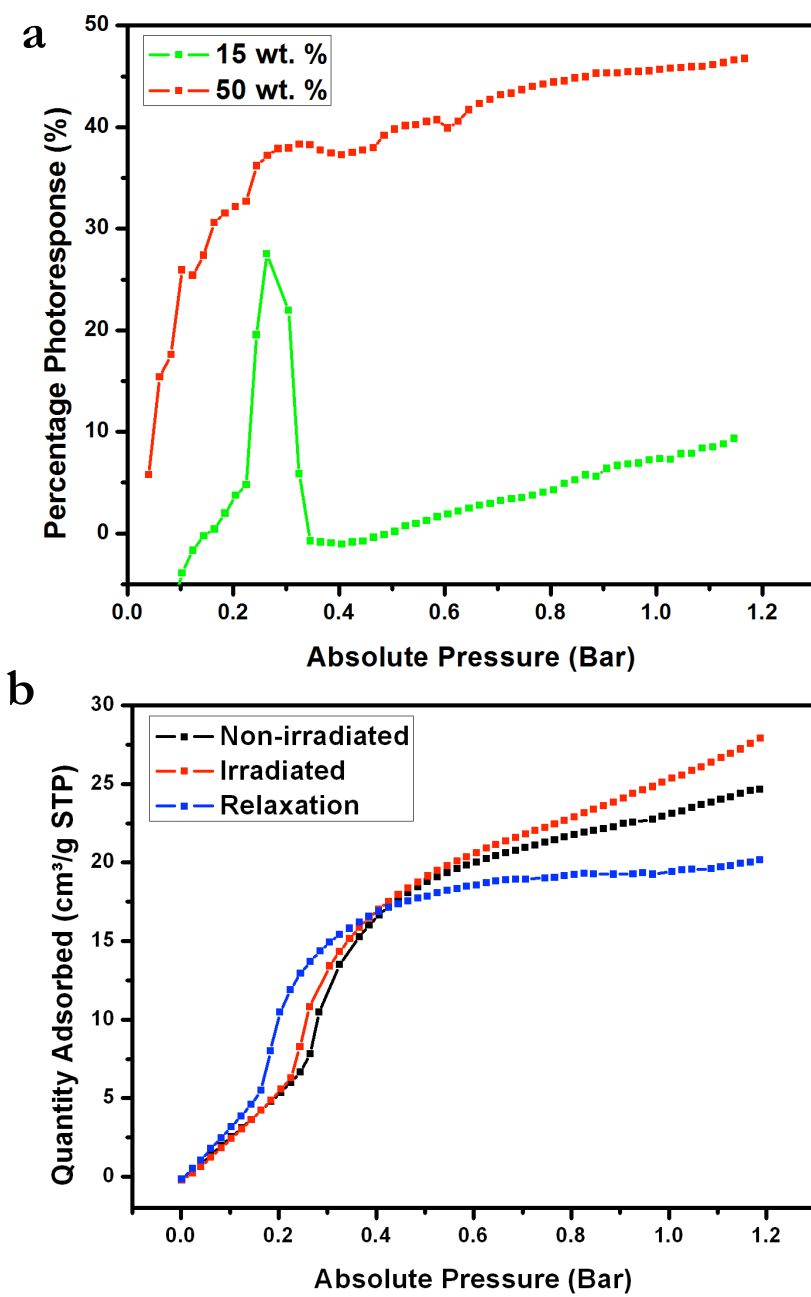


Figure 7. 12. CO₂ adsorption isotherms of MIL-53(Al), and MIL-53(Al)@MR with 15 wt % and 50 wt % before irradiation at 303 K.

To evaluate the visible light response of **MIL-53(Al)@MR** during adsorption, CO₂ adsorption isotherms were collected. The result showed that **MIL-53(Al)@MR** exhibited an interesting photoresponse on gas adsorption upon photoswitching at room temperature. Fully activated **MIL-53(Al)**, with a BET surface area of 1213 m²/g, pore volume of 8.6 Å³ and a pore size of 10 Å was used in the experiment, which is comparable to the reported surface area in literatures (Figure 7.14a) [26]. As expected, the inclusion of **MR** in **MIL-53(Al)** reduced the total CO₂ uptake capacity. A 49 % and 84 % reduction from that of pure **MIL-53(Al)** were observed in 15 and 50 wt % **MIL-53(Al)@MR** respectively (Figure 7.12).

Like the previously reported results in Chapter 6, dynamic photoswitching during gas adsorption could not be observed and slightly lower uptake was obtained. This suggested that the photoresponse of **MIL-53(Al)@MR** inhibited pore access for CO₂ through close contact of the host framework with the guest molecules.



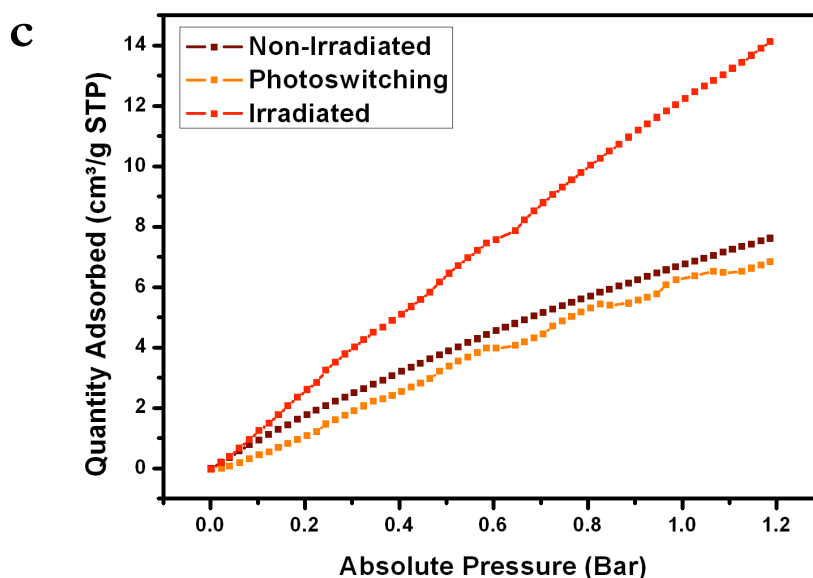


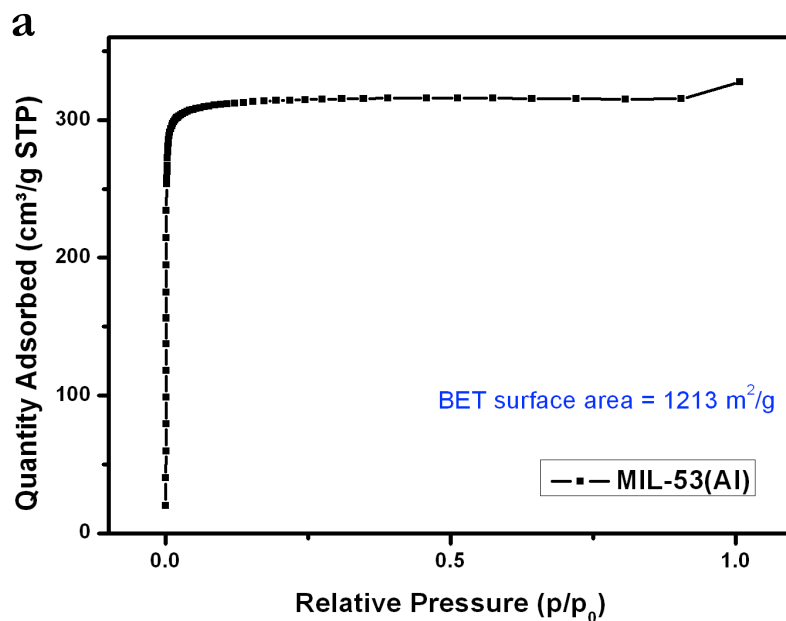
Figure 7.13. Percentage photoresponse obtained with different MR loading concentrations in MIL-53(Al) (a). Effect of visible light irradiation on CO₂ adsorption isotherms of MIL-53(Al)@MR with 15 wt % (b) and 50 wt % (c) guest loading under dynamic and static photoswitching conditions at 303 K.

Upon visible light irradiation, an increase in photoresponse was obtained. The increase in the total gas uptake was further enhanced at higher guest loading (Figure 7.13). At 15 wt % guest loading, the CO₂ uptake capacity of MIL-53(Al)@MR was increased by 9 % to an uptake of 28 cm³/g STP from 25 cm³/g STP (Figure 7.13a, b). However, a gating effect was observed, with a peak showing a sudden increase of CO₂ uptake by 28 % at 0.3 bar, followed by a decrease in photoresponse level (Figure 7.13c). This could be due to the flexible nature of the MOF framework upon guest accommodation [49]. This was not observed at higher MR loading where the pore environment would be more constricted. The CO₂ uptake effect was more pronounced at 50 wt % guest loading where uptake was significantly increased up to 46 % from 8 cm³/g STP to 14 cm³/g STP (Figure 7.13a, c). The observed photoresponse could be due to the formation of more compact *cis* conformers upon irradiation, resulting in a lesser contact with the MOF framework and opening of the pores, allowing more CO₂ molecules to access the adsorption sites upon irradiation, as shown in the characterisation results (Section 7.3.2). Evidently, there was a tradeoff between the guest loading concentration and strength of photoresponse. The increase in the amount of MR reduced the overall CO₂ uptake whilst obtaining stronger photoresponse. Although gas adsorption sites were inhibited by the increase of MR guest

molecules, more **MR** could respond to light and thus, greater photoresponse could be achieved.

Relaxation of **MIL-53(Al)@MR** back to the initial state could be achieved after leaving the sample under vacuum overnight in the dark, suggesting the formation of the *trans*-isomer [8, 9]. However, the gas adsorption performance of non-irradiated sample after relaxation reduced as lower uptake capacity was obtained, indicating that perhaps degradation have occurred.

The N₂ adsorption capacity of **MIL-53(Al)@MR** at 77 K was found to be significantly low compared to that of **MIL-53(Al)** (Figure 7.14). Similar to light triggered CO₂ adsorption, increase in uptake was observed when sample was light irradiated (Figure 7.14b). The presence of **MR** could be responsible for the dramatic reduction in N₂ adsorption capacity. As CO₂ uptake could be observed even when in the non-irradiated state, some degree of porosity should be detected (Figure 7.12-7.13). At lower temperature, pore blockage is often obtained. The reduction in porosity in presence of **MR** made N₂ molecules, that has a larger kinetic diameter than that of CO₂, more difficult to access the pores [50].



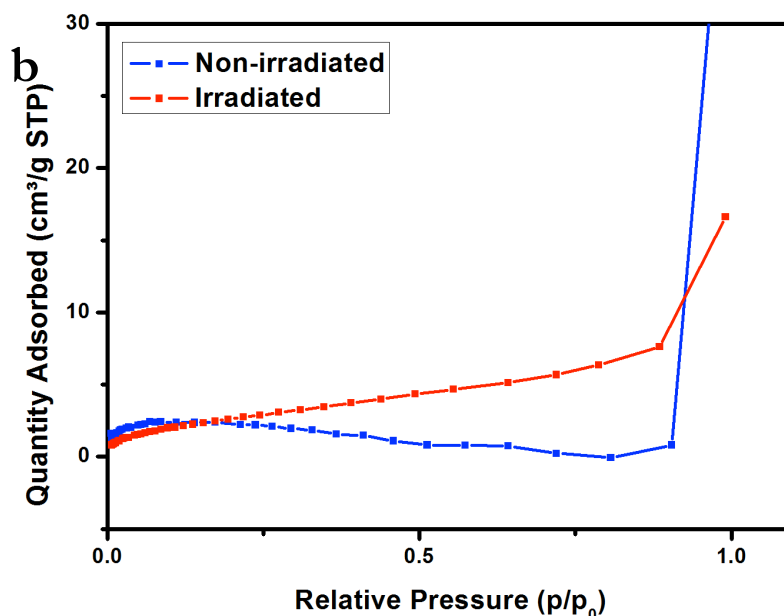


Figure 7. 14. N₂ adsorption isotherms of MIL-53(Al) (a), and non-irradiated and irradiated MIL-53(Al)@MR 50 wt % at 77 K.

MIL-53(Al) exhibited a narrow pore size distribution centered at 10 Å with a molecular volume of 8.6 Å (Figure 7.15a). A similar trend to that reported in Chapter 6 was observed, where the incorporation of guest molecules resulted in no N₂ adsorption (Figure 14b) and thus, no porosity was obtained (Figure 7.15b). Perhaps this was due to the **MR** molecules covering the adsorption sites and prevented N₂ adsorption prior irradiation. As **MR** in its natural state exists in the extended *trans* form and thus they would occupy the most space around the adsorption sites. This phenomenon was also observed in literatures involving photoisomerisation of azobenzene or its derivatives in MOFs [2, 11]. However, when irradiated, a broad pore size distribution was observed ranging from 16 to 50 Å (Figure 7.15b). The observed mesopores suggested that partial incorporation in the pores of the MOF or coating of the MOF surface may have occurred, allowing the less constricted part of the guest molecules to interact with each other, creating larger pore sites [3, 51]. Complete blockage of the pores did not occur as CO₂ adsorption could be observed prior to irradiation of the same **MIL-53(Al)@MR** sample (Figure 7.12-7.13).

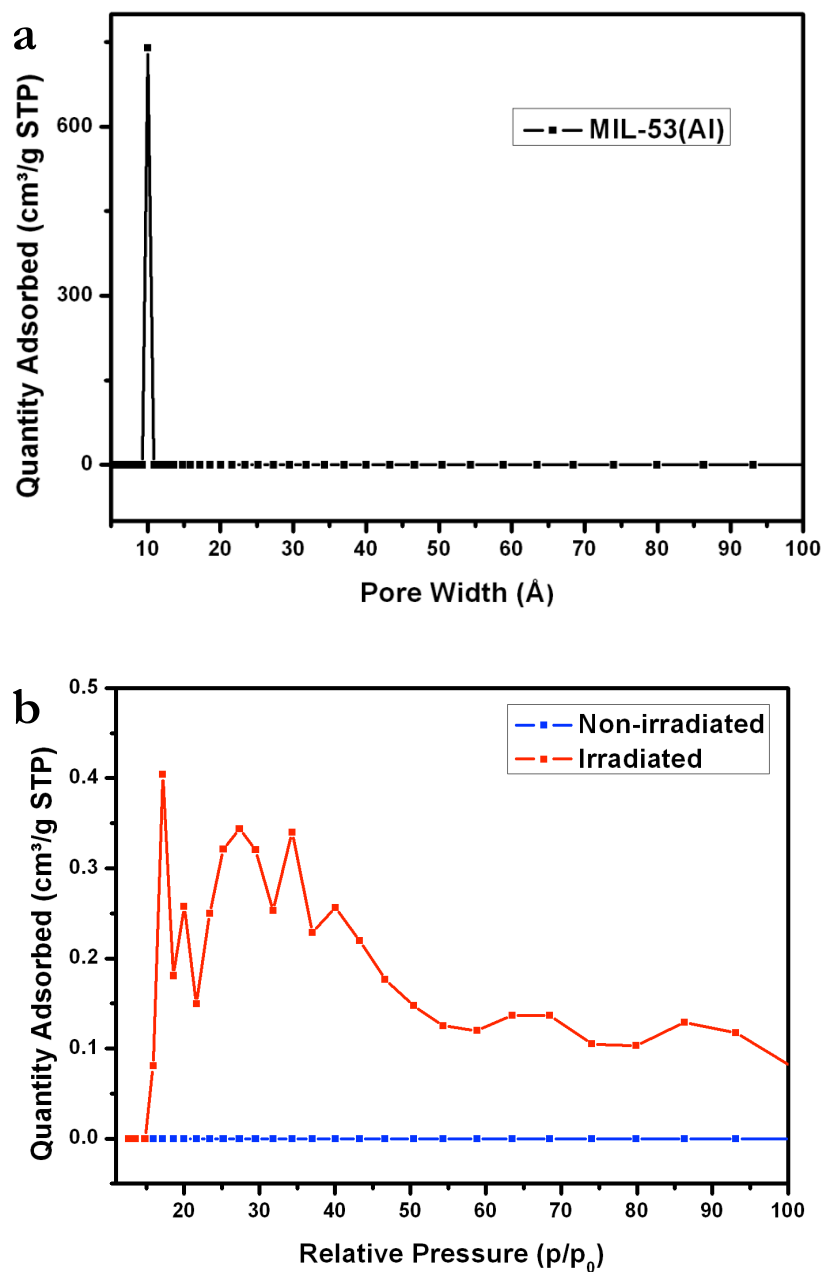


Figure 7.15. Pore size distributions of MIL-53(Al) (a), and non-irradiated and irradiated MIL-53(Al)@MR 50 wt %, which were calculated from N₂ adsorption isotherm at 77 K.

Control photoresponsive gas adsorption experiment was conducted on the starting materials: **MIL-53(Al)** and **MR** (Figure 7.16). Both non-irradiated and irradiated **MR** showed no CO₂ uptake at 303 K (Figure 7.16b). Furthermore, irradiation of **MIL-53(Al)** in the absence of **MR** showed a very low photoresponse ($\sim 0.6\%$) in the visible light range, which could be attributed to the aromatic nature of the MOF (Figure 7.16a). This indicated that the host-guest interaction in **MIL-53(Al)@MR** and the photoisomerisation of **MR** in the MOF upon visible light irradiation, contributed to the photoresponse obtained during gas adsorption.

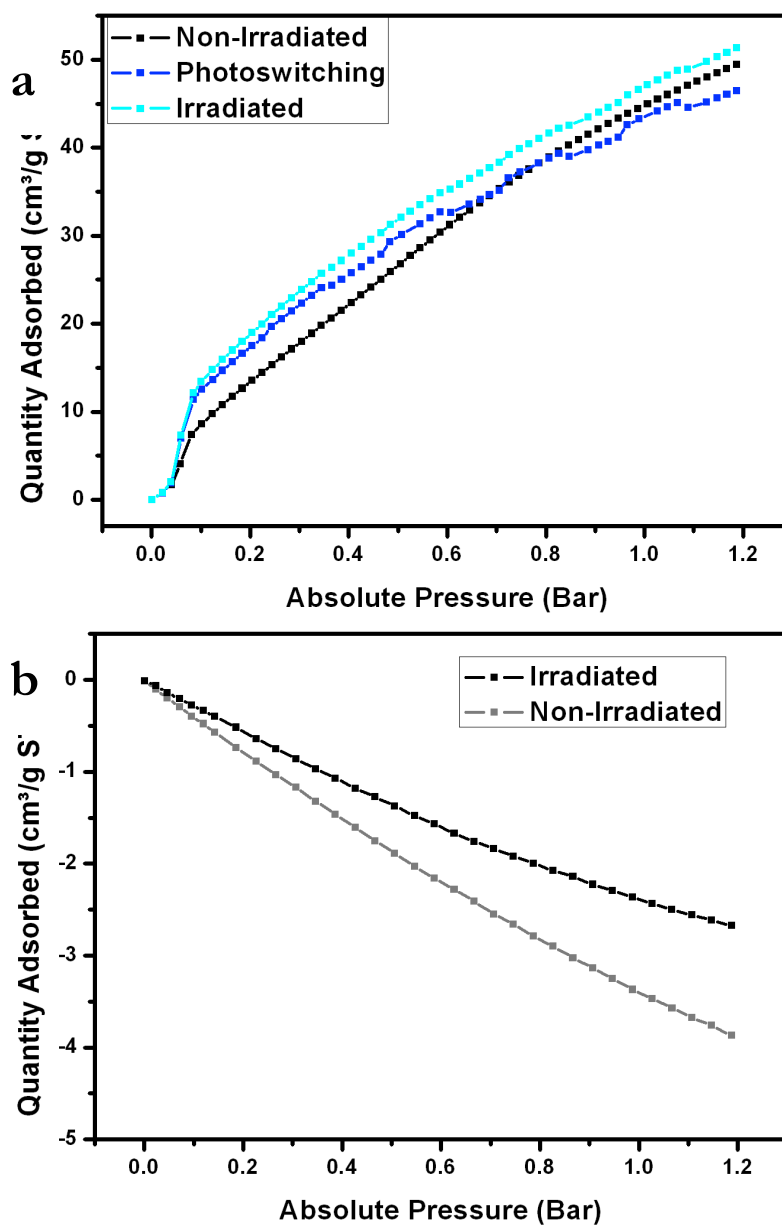


Figure 7. 16. CO₂ adsorption isotherms at 303 K of non-irradiated and irradiated MIL-53(Al) (a) and MR (b) at 303 K with visible light (400-500 nm).

7.4 Conclusions

In order to improve the previously developed work on **MR** based visible light responsive adsorbent (Chapter 6), a water stable and flexible MOF, **MIL-53(Al)**, was used as the host the **MR** guest molecules. For the first time, visible light photoresponse of a water stable **MIL-53(Al)** during gas adsorption was made possible through the use of **MR** as the light responsive guest molecules. The effect of CO₂ uptake capacity and the photoresponse of **MIL-53(Al)**@**MR** with different guest loading concentrations have been analysed through a gas adsorption study. Although the increase in **MR** loading resulted in a lower

CO₂ uptake capacity than that of **MIL-53(Al)** itself, greater photoresponse was obtained. The introduction of **MR** guest molecules significantly decreased the total CO₂ uptake capacity of the sample materials. However, photoresponse increased with the increase of guest loading concentrations. At 15 wt % guest loading, the CO₂ uptake capacity was increased by 9 %, followed by a further increase in uptake capacity up to 46 % at 50 wt % guest loading.

Several control studies were conducted to ensure no false positive results were obtained. The photoisomerisation of **MR** occurred without the interference from free terephthalic acid as the FT-IR and TGA results showed they were present at very low amount in the fully activated **MIL-53(Al)**. Furthermore, photoresponse was attributed to the combination of **MR** in **MIL-53(Al)**. This is because both non-irradiated and irradiated methyl red showed no CO₂ uptake at 303 K and the irradiation of **MIL-53(Al)** showed very low photoresponse (~0.6 %) in the visible light range. With **MIL-53(Al)** being known for its “breathable” structures, photoresponse PXRD data were also collected. The irradiation of the MOF did not result in any peak shifts or changes in peak intensities.

Further studies were undertaken to understand the mechanism involved upon visible light irradiation. Photoisomerisation of **MR** in **MIL-53(Al)** was confirmed through UV-Vis and FT-IR spectroscopies, where photoirradiation resulted in *trans*-to-*cis* photoconversion. The mechanism also involved a host to guest interaction as shown in the UV-Vis, PXRD and TGA results, in which absorption bands due to **MR** were red-shifted, peak broadening became more pronounced with higher guest loading and no clear weight loss step due to the decomposition of **MR** were observed respectively. PXRD result also indicated that no pure **MR** molecules were present in the MOF. Thus the photoresponse observed during gas adsorption measurements could be attributed to the formation of the *cis*-**MR** isomers, where its compact configuration may have reduced their contact with the host and host-guest interaction, allowing more CO₂ to access the adsorption sites. To this date, MOFs that display photoresponse exclusively in the visible range have not been reported in literatures. Thus this result further advanced the development of light responsive adsorbents and further supported the potential use of light responsive adsorbents in low cost carbon capture technologies.

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Chapter 8

CONCLUSIONS & FUTURE WORK

8.1 Conclusions

This thesis displays a pioneering work in the exploration of light responsive adsorbents for carbon capture and release. In this thesis, the discoveries of novel photoresponsive adsorbents (broadband and visible light responsive) for carbon capture and release are reported for the first time. Such key breakthroughs offer a new route for recycling CO₂ emissions using renewable energy and holds great promises for the future in reducing emissions from fossil fuels.

The primary focus of this research was to develop light responsive adsorbents for carbon capture applications, particularly focusing on lowering the energy and increasing the efficiency of the sorbent regeneration from that of conventional technologies. MOFs and PAFs were chosen as adsorbents of interest as they have an appealing aspect in terms of their structural diversities and gas adsorption capacities. Furthermore, to overcome the challenge of using high temperature and pressure to liberate CO₂ from the sorbent in conventional technologies, light was a highly attractive trigger. By adding photoresponsive properties to each adsorbent of interest, the potential of exploiting a renewable energy source such as natural sunlight, could potentially significantly reduce the overall cost and energy to reduce carbon emission. Sunlight consists of a wide spectral range and thus broadband and visible light triggers were investigated. This could offer the benefit of a practical non-filtered light delivery, or a more environmentally friendly and deeper light penetration into the sample respectively.

Novel light responsive adsorbents that display unique adsorption behaviour were developed successfully in this research. In this research, light of different spectral regions (broadband or visible light) were exploited to probe the photoactivity of different adsorbents containing light responsive groups. These linker molecules were incorporated as linker molecules or guest molecules. The synthesised samples were characterised using

PXRD, NMR, FT-IR, UV-Vis, TGA and gas sorption, in which the starting adsorbent materials were verified through previous reports in literature. These characterisation techniques were also utilised to gain a better understanding on the mechanisms involved during photoirradiation. Photoresponse studies were conducted during gas sorption analyses under dynamic or static conditions to compare their sorption behaviours. The following are the main conclusions of the research presented in each experimental chapters (chapter 4-7):

1. Photoresponsive properties was discovered for the first time in **Zn(AzDC)(4,4'-BPE)_{0.5}** a MOF which contained fully incorporated azobenzene linker molecules in the framework, using broadband light as the trigger. Carbon capture and release was able to be performed under dynamic and static photoswitching condition, whereby absorption and desorption occurred upon switching off and switching on the light respectively. Dynamic photoswitchable gas sorption has not been reported in literature prior to the publication of this paper.

This phenomenon was unexpected as light responsive molecules were known to exhibit no photoactivity in a constricted environment, such as MOF frameworks. Only the partially or non-incorporated light responsive groups have ever been reported for their photoactivity in literature. This was because the motions associated with their photoswitching mechanisms were not hindered. It was later found that photoswitching occurred on a local dynamic scale, whereby photoisomerisation did not occur due to the steric hindered environment, but fast bending motion of these linkers were detected as shown in the PXRD and FT-IR results respectively. These fast-bending motions facilitated the reversible CO₂ capture and release process. Photoresponse of up to 42 % and 64 % was achieved under static and dynamic photoswitching respectively.

The result indicated that broadband light, which could represent the wide range of wavelengths emitted by sunlight, could be used for the first time to directly control and dynamically triggers the carbon capture and release. This represents a significant breakthrough and a foundation for developing more light responsive adsorbents for a low cost carbon capture and release process.

2. The discovery led to another development of a broadband light responsive adsorbent, **DArE@PAF-1**. The increase of diarylethene (**DArE**) concentrations in **PAF-1** gradually reduced the total CO₂ uptake capacities, as well as the surface areas. Similar to the work reported in the previous chapter, the capture and release of CO₂ can be triggered reversibly by switching the light off and on respectively. Stronger photoresponse, of up to 26 %, was obtained at higher concentrations (50 wt %). However beyond the optimum concentration of 5 wt %, the CO₂ uptake capacity gradually reduced. Photoresponse studies suggested that the interaction between **DArE** and **PAF-1** upon photoirradiation could trigger the dynamic carbon capture and release.
3. As successful development of broadband light responsive adsorbents has been achieved, more work was focused on development adsorbents that are responsive in the visible light region. This would further advance the development of photoresponsive carbon capture materials. This is because natural sunlight radiates strongly in the visible light region and visible light could offer deeper light penetration into materials whilst being environmentally friendly. Thus visible light would be more advantageous over light containing UV. To this date, no adsorbents exhibit full visible light response in carbon capture and release.

Visible light responsive adsorbent (**Mg-MOF-74@MR**) was reported for the first time. The presence of visible light responsive guest molecules, methyl red (**MR**), in the MOF decreased the CO₂ uptake capacity but a unique photoresponse was obtained. CO₂ capture was achieved through the use of visible light trigger. Pressure-gate phenomenon was observed upon **MR** loading, in which the opening of the gate was obtained through prolonged visible light irradiation, increasing the CO₂ uptake capacity by up to 84 %. To date, this is the highest photoresponse obtained through static photoirradiation, especially with visible light irradiation. Host-guest interaction between **MR** and **Mg-MOF-74** was detected in several characterisation studies. The photoisomerisation of the partially incorporated **MR** upon visible light irradiation suggested that the formation of the more compact *cis* conformation resulted in the reduction of host-guest contact, allowing for more CO₂ to be adsorbed. The study showed that visible light could be used to trigger the pressure-gate opening, allowing for reversible carbon capture and release to

occur. This could potentially provide an environmentally friendly and cost effective process in carbon capture applications.

4. To further improve the work on developing visible light responsive adsorbent, the challenge of water stability in industrial processes was addressed. A water stable adsorbent, **MIL-53(Al)**, was successfully used as a host for methyl red (**MR**) for the first time. In this work, the photoresponse level was investigated at different **MR** loadings. At lower **MR** loading (15 wt %), CO₂ uptake was increased by 9 %. This was further increased by up to 46 % at higher guest loading (50 wt %). The mechanism also involved the photoisomerisation of the partial incorporation of **MR**, in which host-guest interaction was reduced upon *cis* formation, allowing for more CO₂ to be adsorbed. The results showed that a light responsive water stable adsorbent could be potentially used industrially for carbon capture applications.

These major findings provide a new strategy for lowering the cost and energy of a carbon capture and release process. Further research should be conducted to advance the discovery of more light responsive materials for carbon capture technologies.

8.2 Future Directions

The developments in the emerging field of stimuli responsive materials for carbon capture and release could accelerate the discovery of newly designed materials and approach for lowering the cost and energy of a carbon capture process. The novel light responsive adsorbents reported in this work represent a significant step forward in improving carbon capture applications. However, further progress in their development should be carried out in order to understand the mechanisms responsible for changing the properties of the materials, particularly the gas adsorption properties. This includes the interaction between the light stimulus and the adsorbent materials, and the molecular interactions of the gas molecules at the adsorption sites in the presence and absence of light.

In this project, broadband light and visible light responsive adsorbents were developed, whereby the photoswitching of adsorbents during gas adsorption were conducted under dynamic and static condition. Adsorbents which can respond to light with longer range of wavelength, such as visible light was developed as an improvement for the previously reported results in the earlier thesis chapters. However, the loss in CO₂ uptake capacities in consecutive cycles limited the overall performance of the adsorbent. In gas separation applications, adsorbents would need to be stable under air, where water is present as a component in a gas mixture. This was overcome by using water stable adsorbents later in the project (e.g. **PAF-1** and **MIL-53(Al)**). However, most adsorbents, particularly MOFs, still suffer from this problem. Thus further mechanistic study is important in developing light responsive adsorbents that can display a large CO₂ uptake and release capacities with long term stability over multiple regeneration cycles.

An attempt to detect structural response upon photoirradiation in PXRD was undertaken. However, there was a possibility of preferred orientation of the material and therefore other characterisation techniques, including UV-Vis and FT-IR, were used. To eliminate this problem, PXRD data could be determined by measuring diffraction in three dimensions through rotating and tilting the sample with respect to the X-ray beam. This way the orientation distribution of the sample can be calculated, providing a more accurate diffraction data.

Another design problem that was not addressed in thesis is that most of these adsorbents cannot be synthesised in high yield. Large-scale synthesis is a very important aspect in the world of industrial applications. Although this was not the main focus of this research

project, it is important to realise that a method to for synthesising the adsorbents in large quantities at high efficiency is required to further afford a commercially and economically viable solution.

By gaining a full understanding of the system, the structure and properties of the adsorbents, obtained at high yield, could be specifically modulated and further improved to obtain an optimal performance in response to light during carbon capture. This could significantly lower the cost and energy of the process as adsorbents could be easily regenerated and reused.

Appendix

Publications and Press Releases Relevant to Thesis

In order of appearance:

- Published paper reported in Chapter 4 and the journal back cover (Angewandte Chemie)
- Invited peer reviewed paper (Carbon Management)
- Patent
- Selected Press Releases (URLs)

Dynamic Photo-Switching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release**

Richelle Lyndon,* Kristina Konstas, Bradley P. Ladewig, Peter D. Southon, Prof Cameron J. Kepert, and Matthew R. Hill*

For post-combustion carbon dioxide capture technology to realize widespread viability, the energy costs must be drastically reduced. Current adsorbent technologies that rely on pressure, temperature, or vacuum swings consume as much as 40% of the production capacity of a power plant, most of which is associated with the liberation of CO₂ from the capture medium.^[1] Ultimately this penalty, or parasitic energy load, must be brought closer to the thermodynamic minimum of about 4% to avoid prohibitive cost increases.^[2] Given that the triggers for release of adsorbed carbon dioxide, such as vacuum and heating, are so energy intensive,^[1a,3] requiring energy from the power plant, there is strong motivation to develop new release triggers that do not require extra energy from the plant, using renewable energy sources such as the sun. In conjunction with this, adsorbents with maximum gas sorption efficiency can further reduce the costs compared to the conventional energy-intensive CO₂ gas separation process.

Light, and in particular concentrated sunlight, is an extremely attractive stimulus for triggering CO₂ release. If used with an adsorbent material that strongly absorbs sunlight concomitant with the desorption of large amounts of CO₂, it may be possible to drastically reduce the energy costs.

Perhaps the most attractive adsorbent candidates are metal–organic frameworks (MOFs), because of their large adsorption capacities,^[4] and the potential for incorporation of light-responsive organic groups within the pore structure.^[4c,5] MOFs are an important class of 3D crystalline porous

materials comprised of metal centers and organic ligands, joined periodically to establish a crystalline porous array.^[4d] The large internal surface areas can be used to adsorb unprecedented quantities of gases,^[4c,6] with particular interest in hydrogen,^[4c,7] methane,^[4c,7c,h,8] and carbon dioxide emergent.^[1a,c,4c,7b,h,9]

Methods for the incorporation of light-responsive groups within MOFs include the use of pendant groups pointing into the pores,^[10] and filling of pores with light-responsive guest molecules.^[11] The responsive groups within these materials may then alter their conformation when exposed to filtered light which results in a change in adsorption capacity, as reported thus far for static conditions.^[10,11]

The responsive groups within these MOFs can be statically set to one position or another. For use in photo-switching carbon dioxide capture, MOFs that can respond dynamically, or to the broadband radiation found in sunlight whilst loaded with adsorbed gas, are ideal. This will increase the speed of operation and lower the energy costs (see Figure 1)



Figure 1. Dynamic photo-switching in the light-responsive MOF Zn-(AzDC)(4,4'-BPE)_{0.5} leads to instantly reversible CO₂ uptake.

Azobenzene and its derivatives are well-known photochromic molecules that can undergo clean and efficient reversible photoisomerization about the azo bond to *cis* and *trans* states upon irradiation (coordinated *trans*: $\lambda_{\text{max}} \approx 370$ nm, *cis*: $\lambda_{\text{max}} \approx 460$ nm).^[12] Conversion of azobenzene to the 4,4'-dicarboxylate (AzDC) delivers a ligand that can be incorporated into MOF architectures. Furthermore, the pillar ligand *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-BPE) has also been reported to demonstrate *cis*–*trans* photoisomerizability when coordinated to a metal complex.^[13] Combination of these two ligands within zinc-based MOFs generates the triply

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interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$, which exhibits an open topology amenable to high capacity and selective adsorption of hydrogen and carbon dioxide (see Figure SI-1).^[14]

The triply interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ was prepared solvothermally using previously reported methods (see Supporting Information).^[14] The framework is assembled from paddle wheel dinuclear Zn_2 units, bridging AzDC dianions and 4,4'-BPE pillar ligands. Photoresponsive studies in solid state revealed a photoactive framework. *Trans*- and *cis*-AzDC $n\text{-}\pi^*$ (S1 state) and $\pi\text{-}\pi^*$ (S2 state) transitions can be detected at 455 and 380 nm in the excitation spectra, respectively (Figure SI-5). The coordination of 4,4'-BPE to Zn results in a photoactive species under light irradiation.^[13b] The *trans* isomer of the 4,4'-BPE ligand exhibits overlapping excitation bands of metal-to-ligand (MLCT) and ligand-to-ligand (LLCT) charge-transfers in the 310–375 nm region (Figure SI-6 in the Supporting Information).^[13b] Excitation in this region generates *trans*–*cis* isomerization as shown in the excitation spectra where the MLCT band maximum shift to 285 nm.^[13d] Both *cis*-AzDC and 4,4'-BPE can return to their *trans* state.

Herein we report the discovery of strong, low-energy photoresponse in $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ and find that the behavior is dynamic and localized, irrespective of the use of broadband or filtered light sources. Previous researches have not detected *cis*–*trans* changes where azo groups are part of the MOF wall and not as pendant groups in the pores.^[15] In the present article it is reported that bending about the azo group can be observed to occur on a local scale in a dynamic fashion, perfect for on-line adsorbent regeneration. The effect was directly observed in the UV/Vis emission profiles and time-resolved infrared spectra, and indirectly through gas adsorption experiments with careful controls in place, and pore analysis calculations. We found agreement with the literature in that the effects could not be observed over larger length scales; synchrotron X-ray diffraction did not reveal a structural change.^[16] This unusual property was exploited to trigger the uptake and release of carbon dioxide in real time, during adsorption experiments. Exposure to UV light resulted in an instantaneous release of up to 64% of the adsorbed CO_2 using broadband radiation, similar to concentrated solar sources. Furthermore, the response was found to be fully reversible. The dynamic, yet localized structural movements have been directly characterized spectroscopically, and isolated with several careful control experiments.

As shown in Figure 2, $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ exhibits unprecedented dynamic switching under CO_2 adsorption, with a 42% desorption capacity under static irradiation conditions (red and black curves), and as much as 64% during dynamic measurements (blue curve). Light irradiation increased the MOF surface energy, in which intermolecular interactions between CO_2 molecules and the surface weakened, and thus triggered instantaneous CO_2 release. Dynamic irradiation isotherms follow values obtained under continuous irradiation conditions, however the reversal in uptake was not entirely complete under the dynamic measurement conditions employed. Such dynamicity could not be triggered by free AzDC and 4,4'-BPE molecules because of the small

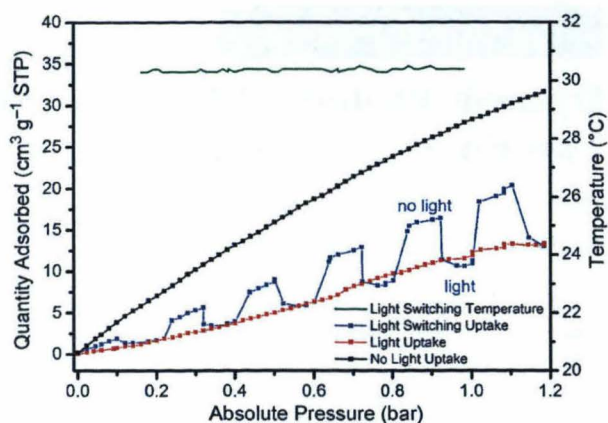


Figure 2. CO_2 adsorption isotherms of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ at 303 K in the presence of light (red), absence of light (black), and unfiltered light switching environment (blue). Temperature fluctuations were not observed during the light switching experiment (green). The light intensity was fixed at 24.6 W cm^{-2} in the wavelength range of 200–500 nm (STP = standard temperature and pressure).

pores of the MOF ($3.4 \times 3.4\text{ \AA}$).^[14] A series of careful control experiments were undertaken to ensure that this phenomenon was not an experimental or material artefact, but due solely to the dynamic photoresponse observed. Careful localized temperature monitoring showed that the temperature varied by less than 0.2°C , indicating that minor localized heating did occur, however it was not a significant factor in the uptake variation (Figure 2). Furthermore, experiments with control materials including SAPO-34 zeolite, and also a framework without known photoactive groups, Cu-BTC (Basolite C300), showed almost no CO_2 uptake variations upon UV irradiation (0.2 and 2% vs. 64% for $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$), see Figure SI-10. An isobar has been measured, where temperature was changed with constant pressure, and these show that the temperature needs to rise by 25 K for the same uptake variation to be observed (Figure SI-11). A degree of the release may be due to general sample heating, although this is likely to be small given the negligible change in control samples.

To directly observe the structural oscillations, time-resolved FTIR spectroscopy under UV irradiation was performed, (Figure 3a,b). Significant changes in peak intensity for the region of $540\text{--}700\text{ cm}^{-1}$ were observed under irradiation, whereas the remaining spectrum was unchanged. The peak intensity increase at 550 cm^{-1} can be attributed to C–C–C and C–C–N bending modes with AzDC,^[17] indicating low-energy structural variations about the azo group, which occurred due to the suppression of *cis*–*trans* isomerization.^[18] These bending modes are likely to be responsible for the spontaneous release of adsorbed CO_2 upon irradiation, in which the pore surface was activated and the surface energy was increased (Figure 3b). Similar experiments on the free ligand AzDC confirmed this effect (Figure 3a). An increase in intensity at 537 cm^{-1} indicated the activation of bending modes about the C–C–N bonds within the ligand. Furthermore, very minor peak increases in the free ligand at

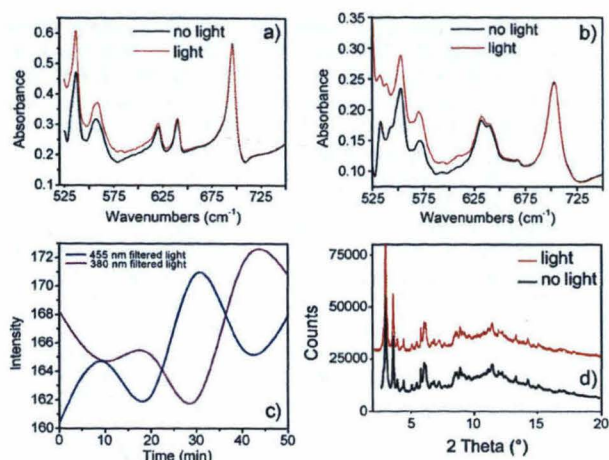


Figure 3. C–C and C–N low-energy FTIR bending modes in AzDC were found to be excited by UV light in both a) the ligand and b) the framework. c) Continual irradiation led to oscillations between native and excited states witnessed with UV/Vis absorption. d) It was confirmed that the transitions were local and dynamic, as synchrotron XRD experiments did not reveal any periodic changes.

1516 cm^{-1} were observed, assigned to higher energy *cis*-N=N stretching modes forming as the native *trans* material was excited.^[19] These modes were not seen to change within the framework, highlighting the restricted AzDC in this structure, which could not undertake these transitions. This also explains why no changes were seen in the X-ray diffractogram (Figure 3d). This result was also replicated with similar UV/Vis experiments, where only a small fraction of *cis* isomers were detected (Figure 3c). The framework was continuously exposed to either 365 or 460 nm light and the intensity of the absorption peak is monitored. Absorption related to *trans*-AzDC and *cis*-AzDC moieties was found to be complementary and also periodically changing, regardless of whether the excitation wavelength promoted formation of either *cis* or *trans* structures. Under continuous irradiation from either 370 nm (promote *cis*-AzDC) or 460 nm light (promote *trans*-AzDC), small fractions of the structure were found to periodically oscillate between both isomeric conformations in a complementary fashion given the additive nature of *cis* and *trans* peaks across the two separate experiments. Similar additive effects were less clear from 4,4'-BPE excitation profiles where there was considerable overlap, although this ligand also clearly underwent transitions whilst coordinated within the framework (Figure SI-7). Most likely, this continual reversion to native states even under irradiation that promotes an isomeric transformation stems from the structural stresses induced within the interpenetrated framework, due to the components also being critical to the topology, and not pendant to it. Furthermore, rapid changes predominantly through bending motions must occur throughout the framework to maintain the original triply interpenetrated framework and accommodate the constraints.^[20] The changes could not be observed on a periodic scale however, with synchrotron X-ray diffraction experiments revealing no changes (Figure 3d).

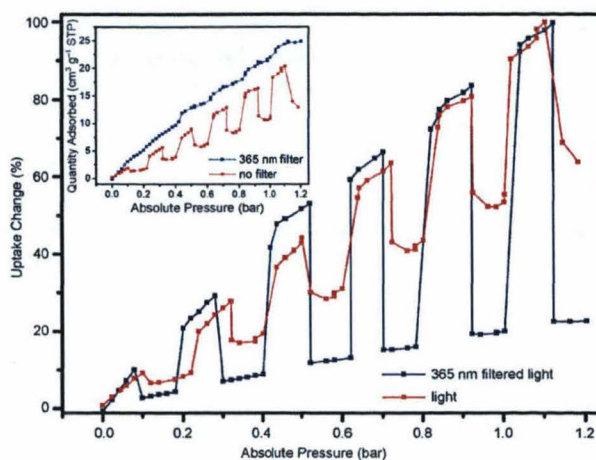


Figure 4. Performance of photo-switching according to light wavelength, normalized for flux. Filtered light of 365 nm is optimal for *cis*-*trans* photoisomerization of both AzDC and 4,4'-BPE ligands. Inset: original data without normalization.

Figure 4 (inset) shows that the absolute CO_2 uptake is increased and the amount released upon light exposure lessened when a filtered light source, which has a lower flux, is used. Filtering the light to 365 nm promotes photoisomerization in both the AzDC (Figure 3b) and 4,4'-BPE ligands (Figure SI-6). Accounting for variations in raw uptake amounts, and changing flux gives Figure 4. Here it is shown that the efficiency of CO_2 release is greatly enhanced by the use of 365 nm filtered light. In both cases the adsorption amounts in the absence of light irradiation are similar, yet CO_2 desorption is found to be more efficient with use of filtered 365 nm radiation. This effect is most pronounced at high partial pressures, yet it is notable that at partial pressures similar to those encountered in post-combustion capture gas streams (ca. 0.15 bar) that unfiltered light gives a very comparable response. The results imply that in cases where the light intensity is not a limiting factor, that filtration to 365 nm is preferable, but in other instances, unfiltered, concentrated sunlight will also perform almost as well, especially in post-combustion capture streams. Illuminations up to 20 W cm^{-2} (200 solar equivalents) can be achieved using concentrated sunlight.^[21] These remarkable results stem from the fact that the photoinduced structural changes in $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ are dynamic as witnessed both directly with UV/Vis and FTIR experiments, and indirectly driving photoresponsive gas adsorption.

The foregoing results demonstrate that the interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ can undergo dynamic light-induced structural flexibility, which results in large variations in CO_2 uptakes. For the first time an experimental protocol was established to exploit this remarkable property for low-energy CO_2 capture and release. The variation in CO_2 capture performance was found to be exceptionally strong, as much as 64% under dynamic measurements and 42% under static conditions. Characterization of the framework showed that the light-induced structural flexibility is due to both the AzDC and 4,4'-BPE

ligands, occurring reversibly and on a local scale, even under irradiation that would promote formation on just one conformer. Detailed characterization showed that the transitions occurred only on a short range scale, and in a dynamic fashion, accounting for a lack of detection on longer length scales, in line with previous studies.

This approach represents a potential route to renewable energy CO₂ capture and release, and was found to remain effective under broadband irradiation. This means that unfiltered sunlight may be used instead of the energy-intensive temperature and pressure swings to release trapped gases.

Further developments in this area include other mechanistic investigations, in further increasing the already strong response, developing similar responses in the visible region, and taking advantage of the performance within industrially relevant mixed gas streams.

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Supporting Information

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Dynamic Photo-Switching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release**

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Cameron J. Kepert, and Matthew R. Hill**

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Section 1: Experimental Procedures S1

S1.1 General

All reagents were used as purchased without further purification. 4-Nitrobenzoic acid and *trans*-1,2-bis(4-pyridyl)ethylene were purchased from Aldrich, zinc nitrate hexahydrate was from Chem Supply, dimethylformamide (DMF) and sodium hydroxide were from Merck, and Glucose was from Ajax Chemical.

S1.2 Synthesis of **AzDC** (1)

Ligand 1 was prepared according to procedure previously reported work by Liu *et al.*^[1] 4-Nitrobenzoic acid (15.0304 g, 0.09 mol) was dissolved into an aqueous sodium hydroxide solution (51.0039 g, 1.28 mol, in 225 ml water) by heating the solution. A hot aqueous glucose solution (101.0159 g, 0.56 mol, in 150 ml water) was slowly added into the above solution at 50 °C, in which the initially formed yellow precipitate immediately turned into a brown solution upon further addition of glucose. The mixture was allowed to react overnight at room temperature to form a dark solution. Methanol was added to the aged solution until a bright brown precipitate formed. The filtered precipitate was dissolved in water, followed by acidification with acetic acid (20 mL), whereupon a light pink precipitate was obtained. The product was filtered, washed with excess water and dried overnight to yield the final product (4.92 g, 17 mmol, 38.5 %). ¹H NMR (DMSO, 400 MHz): δ (ppm) 8.04-8.06 (d, 4H), δ 8.18-8.20 (d, 4H), δ 13.0 (brs, 1H). ¹³C NMR (DMSO, 500 MHz): 122.86, 130.72, 133.50, 154.17, 166.67.

S1.23 Synthesis of **Zn(AzDC)(4,4'-BPE)_{0.5}** (2)

Framework 2 was solvothermally synthesized according to the procedure described by Zhou *et al.*^[2] A mixture of Zn(NO₃)₂·6H₂O, **1** and **4,4'-BPE** was suspended in DMF (100 mL) and heated at 100 °C for 24 h. The resulting red block-shaped crystals formed were filtered and washed with DMF and hexane, and dried in air.

BET surface area: 126.4575 m²/g (literature: 100 m²/g).^[2]

Section 2: Gas Adsorption Measurement S2

S2.1 General Gas Adsorption Procedures

Gas adsorption isotherms of activated **2** were recorded at low pressure (0 - 1.2 bar) by a volumetric method using a Micromeritics ASAP 2040 instrument. Approximately 100 mg of dried methanol exchanged sample was weighed in a pre-dried and weighed Quartz BET tube. The sample was evacuated and activated at 150 °C under dynamic vacuum at 10^{-6} Torr for at least 24 h to remove any solvent molecules. An accurate weight of the degassed sample was measured prior to analysis. Gas adsorption measurements were performed using ultra-high purity H₂, CO₂ and CH₄ gas.

S2.2 Gas Adsorption Isotherms

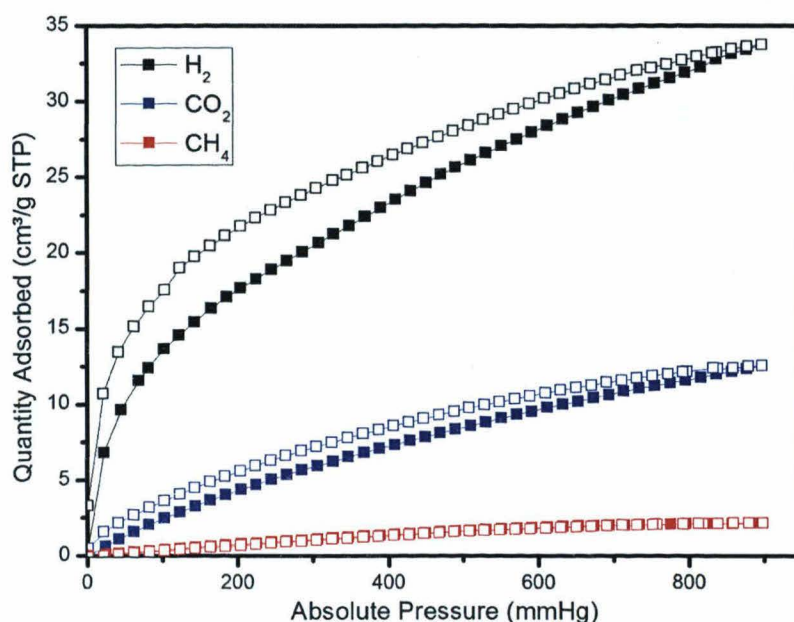


Figure SI-1: Gas adsorption isotherms of Zn(AzDC)(4,4'-BPE)_{0.5} at 77 K (hydrogen, black) and 298 K (carbon dioxide, blue; and methane, red). Solid and open shapes correspond to adsorption and desorption respectively.

S2.3 Dubinin Raduskevich Isotherm

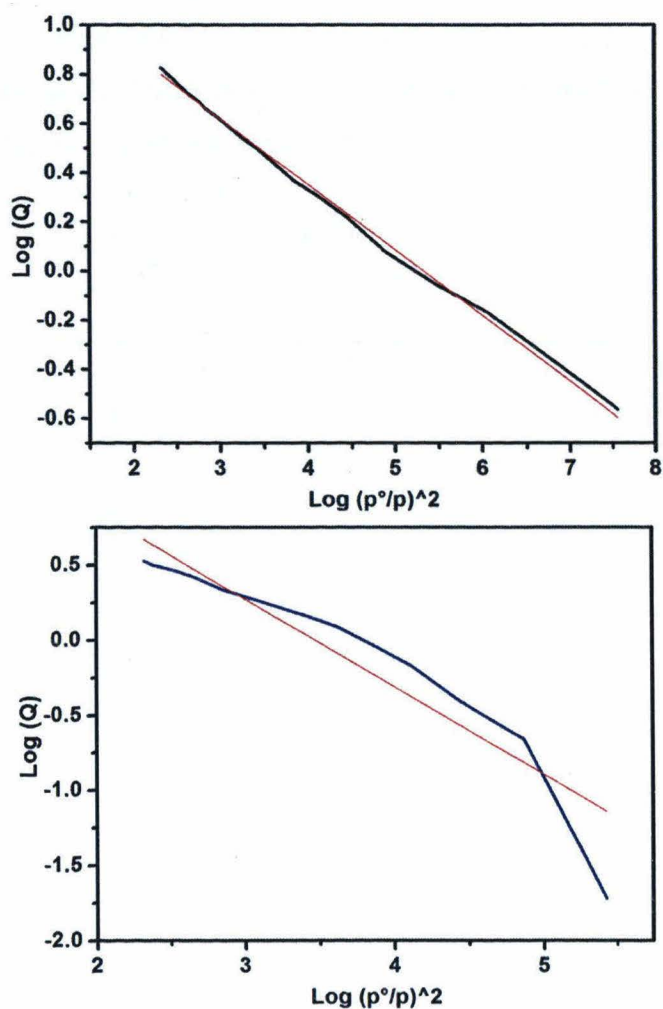


Figure SI-2: CO₂ adsorption isotherm in the presence (blue) and absence (black) of light at 273 K was fitted with the Dubinin-Radushkevich (D-R) equation (red) to detect the change in pore size.

CO₂ adsorption in the presence of light did not follow the D-R model. This is due to gas adsorption at the surface being disturbed by the presence of UV light.^[3]

Section 3: Thermogravimetric Analysis (TGA) S3

S3.1 General Thermogravimetric Analysis Procedures

TGA data was obtained on a TGA Pyris 1 instrument with a heating rate of 5 °C/min under N₂ gas flow (20 ml/min). A platinum pan was used to contain approximately 4 mg of the sample, which had been solvent exchanged with dry methanol and degassed at 150 °C.

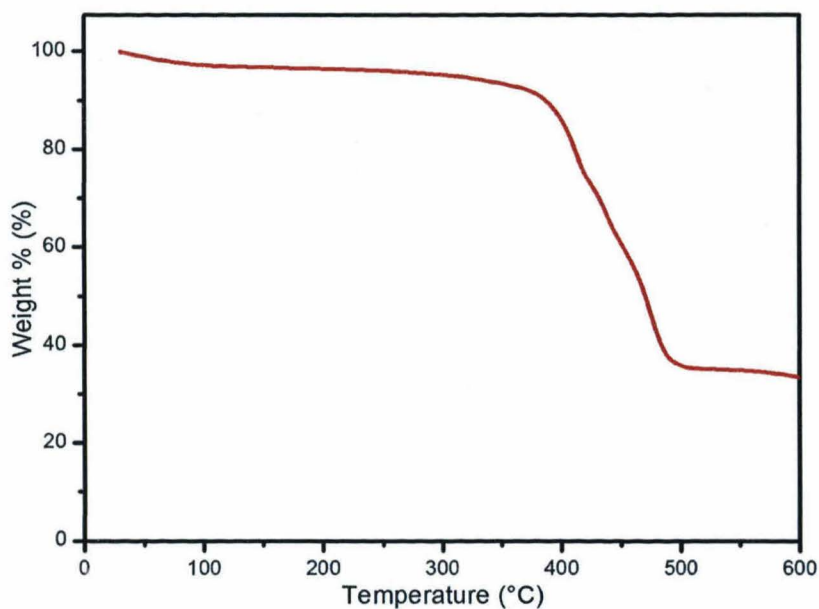


Figure SI-3: TGA profile of Zn(AzDC)(4,4-BPE)_{0.5} after solvent exchange with dry methanol showing that the MOF is thermally stable up to 400 °C which is in accordance with the literature value.^[2]

Section 4: X-Ray Diffraction S4

S4.1 X-Ray Crystal Structure

Crystal unit cell structure of **2** was constructed using Diamond v3.1.

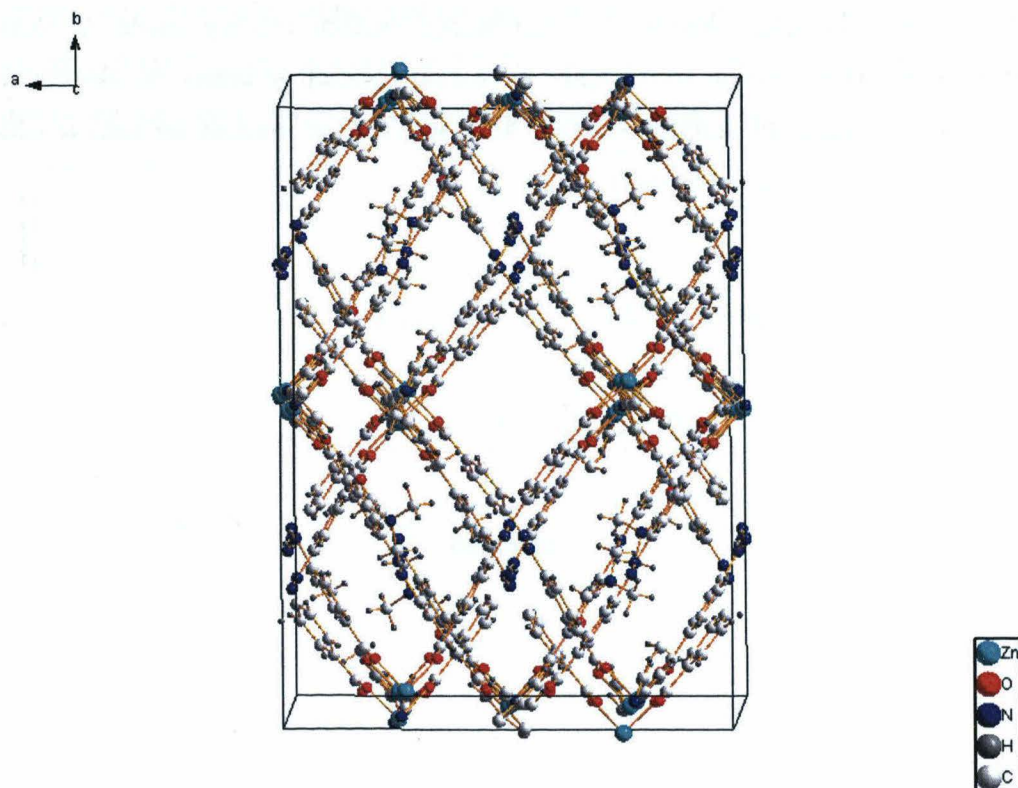


Figure SI-4: Crystal structure of $\text{Zn}(\text{AzDC})(4,4\text{-BPE})_{0.5}$.^[2]

The framework is 3D triply interpenetrated in a primitive cubic structure. This results in pore windows in the range of 3.4-3.6 Å.

Section 5: Photo-Response Characterisation S5

S5.1 General Photo-Response Characterization Procedure

All samples were used in solid state. Free ligand refers to unbound ligand in a solid state. Solid-state UV-VIS spectra were obtained using FlexStation® 3 Benchtop Multi-Mode Microplate Reader in fluorescence bottom reading mode at room temperature. The emission wavelengths were kept constant to detect the absorption (or excitation) peaks of samples. Acticure 4000 was used to irradiate the sample with unfiltered light in FTIR experiment.

S5.2 Excitation Spectra of AzDC

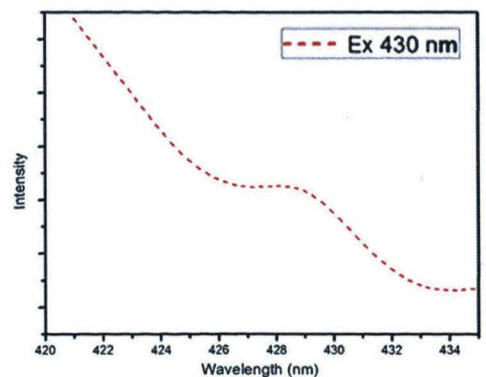
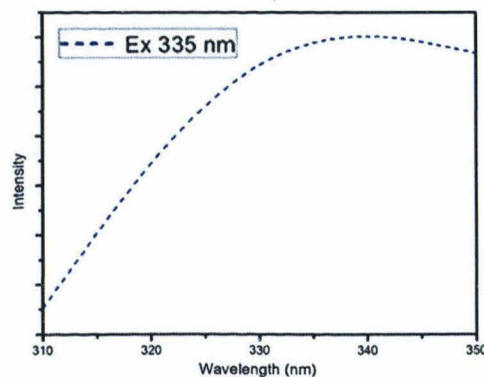
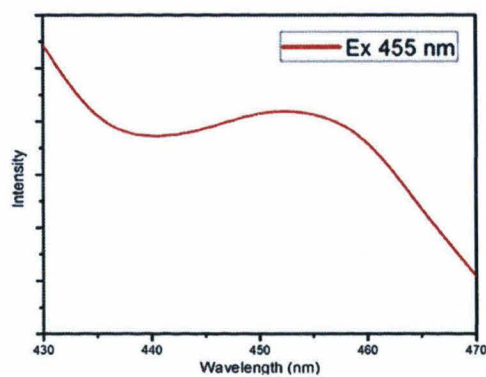
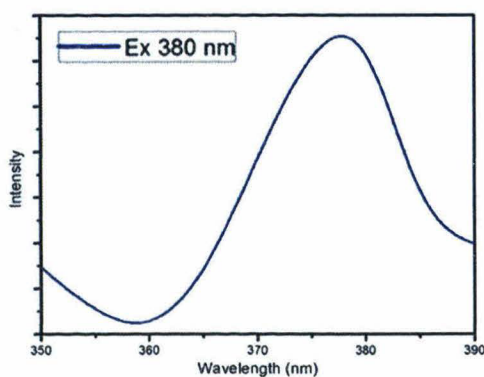
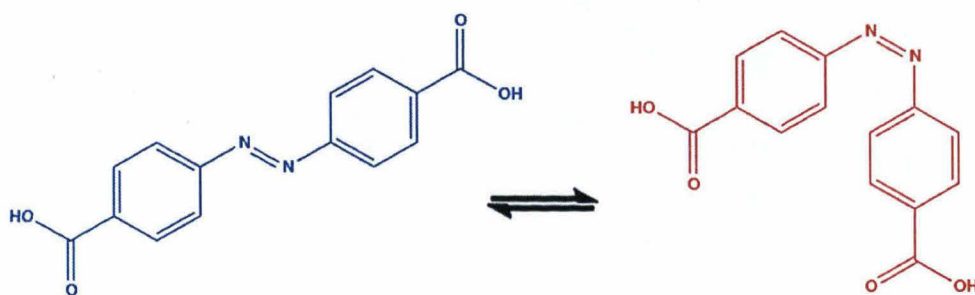


Figure SI-5: Excitation spectra of **AzDC** ligand in **2** (—) and free **AzDC** ligand (···) with an emission wavelength of 370 nm (red) and 460 nm (blue).

The excitation band at 380 nm and 455 nm is due to the *trans* and *cis* **AzDC** in **2** respectively. The peak around 330 nm and 430 nm is characteristic of the *trans* and *cis* free **AzDC** ligand respectively.^[4] The purpose of these experiments was to determine the likely absorption maxima for obtaining the strongest localised bending possible within the framework.

S5.3 Excitation Spectra of 4,4'-BPE

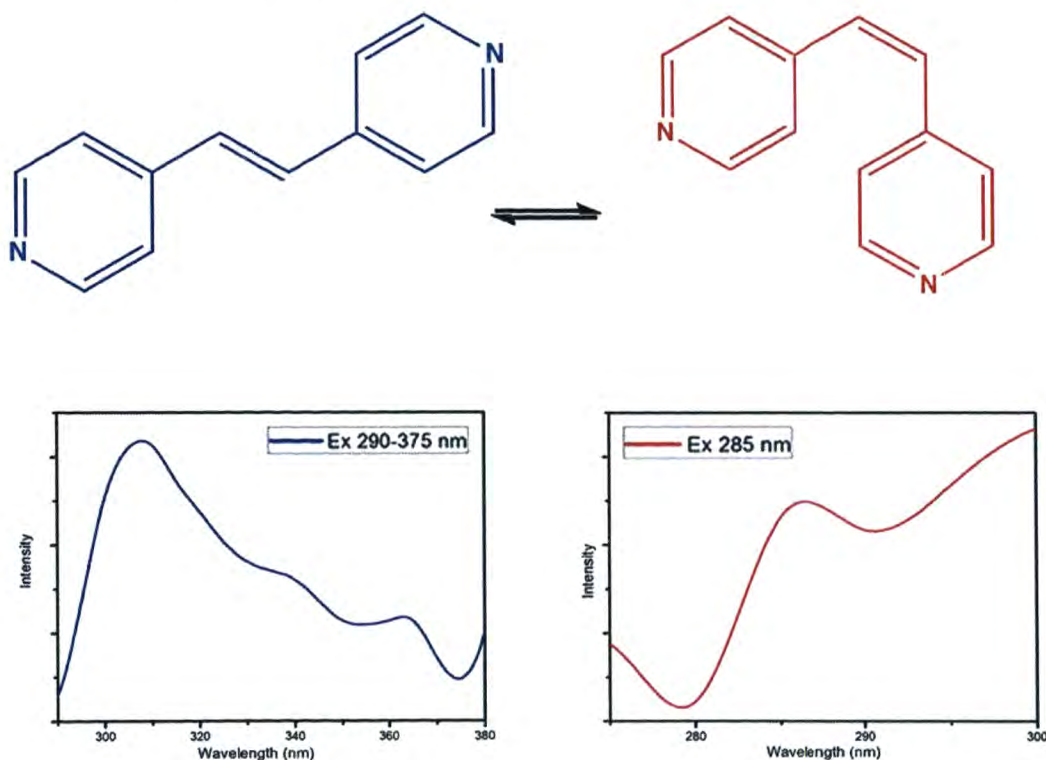


Figure SI-6: Excitation spectra of 4,4'-BPE of Zn(AzDC)(4,4'-BPE)_{0.5} with an emission wavelength of 250 (blue) nm and 370 nm (red).

The excitation wavelengths at the 300 nm region and 285 nm correspond to the *trans* and *cis* peaks respectively. Free BPE was found to have no photoactivity in the solid state.

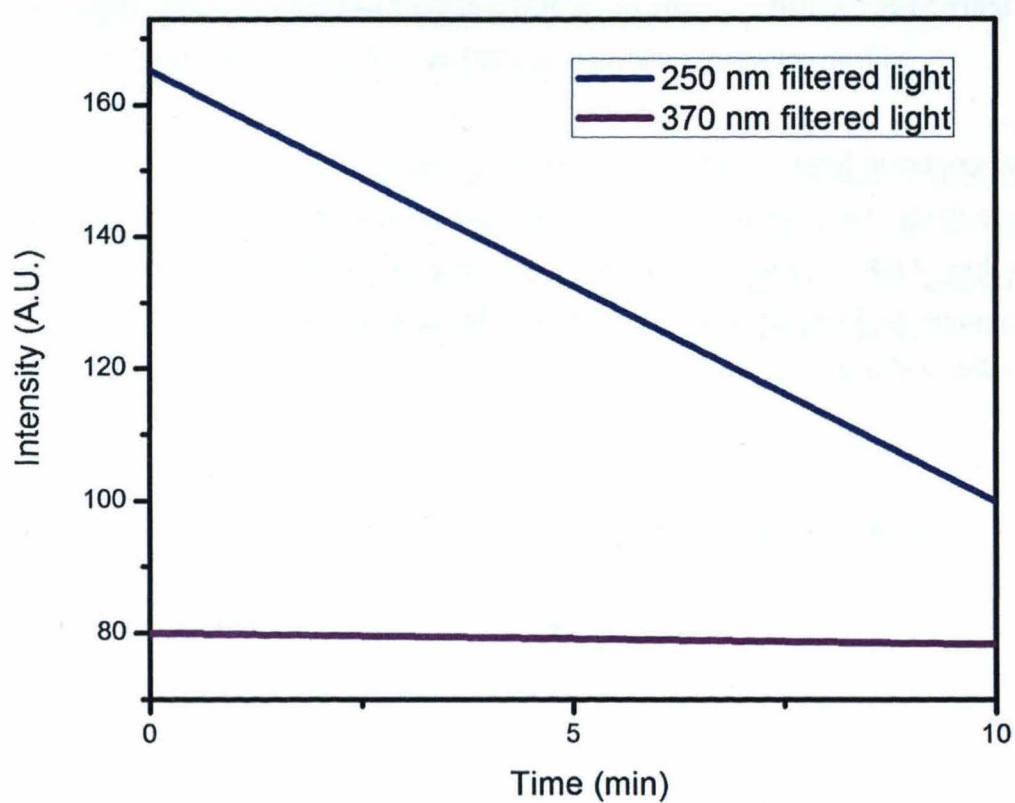


Figure SI-7: Maximum intensity of *trans*- and *cis*- **4,4'-BPE** peak at 310 nm (blue) and 285 nm (red) respectively. $\text{Zn}(\text{AzDC})(\text{4,4'-BPE})_{0.5}$ was continually irradiated for 10 minutes with 370 nm (red) and 250 nm (blue) light at room temperature.

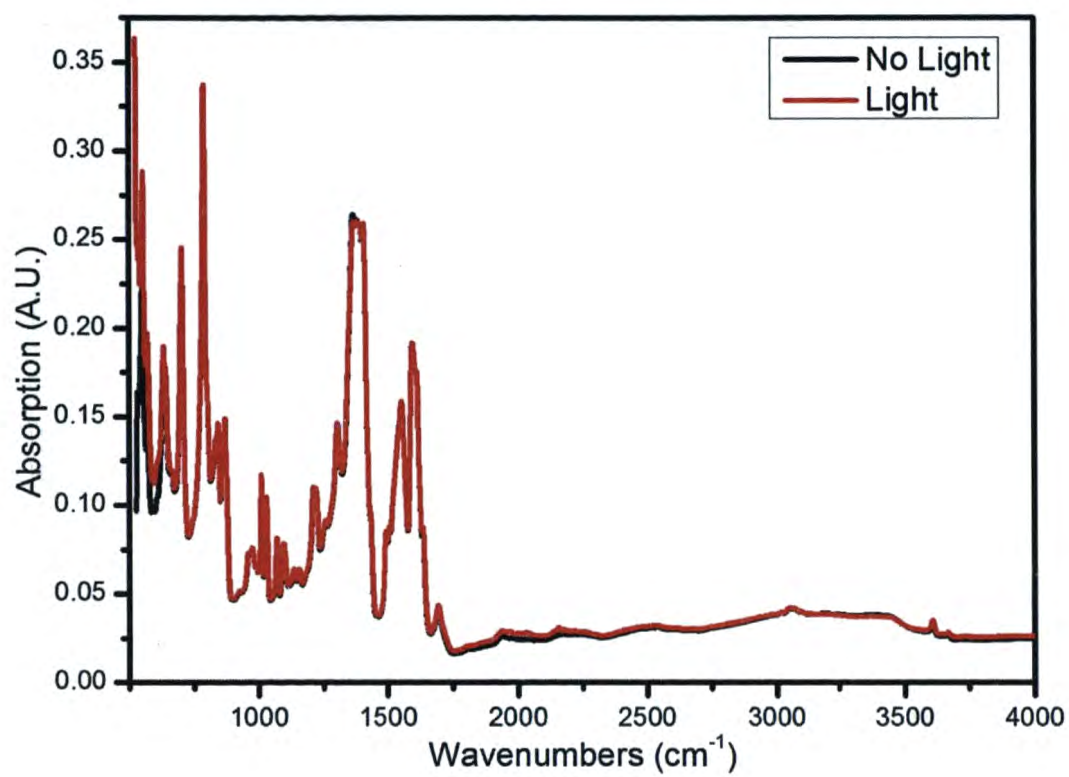


Figure SI-8: Full FTIR spectrum of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ showing that major band intensity changes are only seen in the highlighted range in the main manuscript.

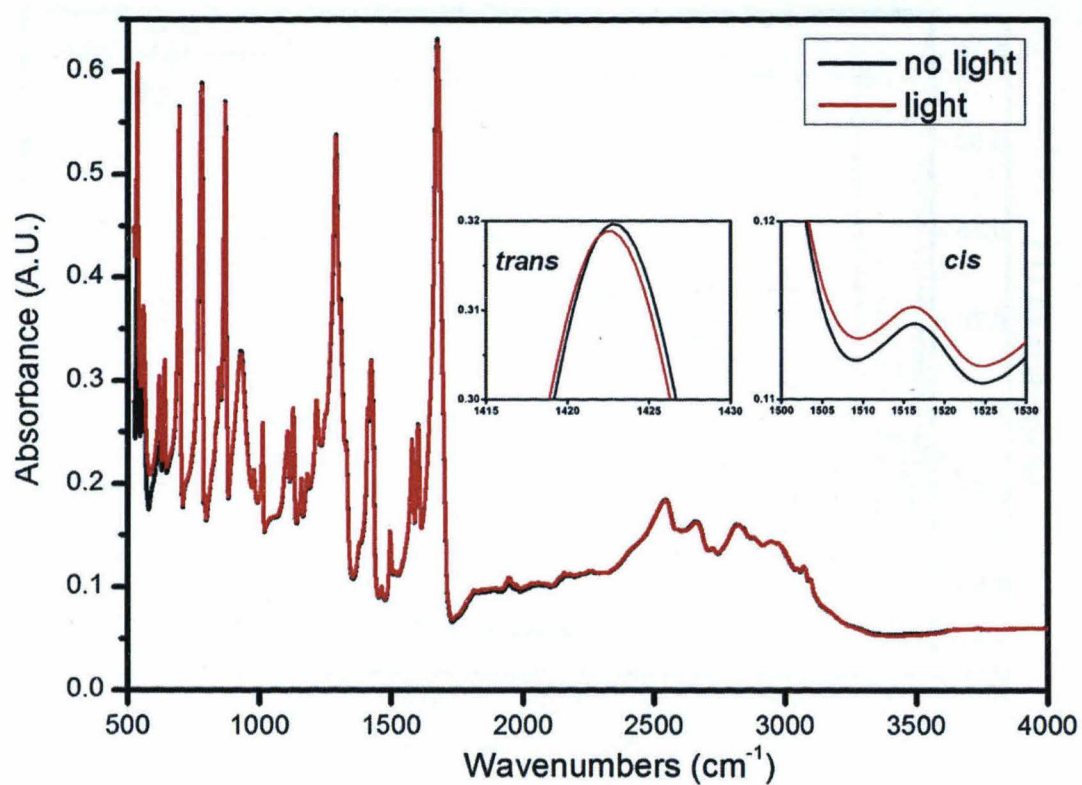


Figure SI-9: Full FTIR spectrum of free **AzDC** ligand showing that there was very minor increase and decrease in the *cis* and *trans* peak during light irradiation respectively (insets).

Section 6: Light-Responsive Control Experiments S6

S6.1 General Light-Responsive Control Procedure

Cu-BTC and SAPO-34 zeolite were chosen as non-photoactive porous materials for a control study. Approximately 100 mg of degassed sample was used in a Quartz BET tube. Cu-BTC was activated at 150 °C for 24 h and SAPO-34 zeolite was activated at 90 °C for 1 h, then at 350 °C for 5 h. The experiment was conducted by switching the unfiltered light on and off throughout the analysis. An adsorption isotherm and isobar were measured on an IGA-002 gravimetric instrument (Hidden-Isochema). A CO₂ adsorption isotherm up to 1 bar was measured at 298 K, and was consistent with the isotherms measured previously for this material without irradiation. To measure an adsorption isobar, the sample was loaded into the sample holder as a fine slurry in methanol, dried under vacuum, then evacuated at 150 °C for 8 hours. The pressure was set to 1 bar CO₂ and the temperature was ramped at 0.1 K/min from 288 to 328 K, then back to 288 K.

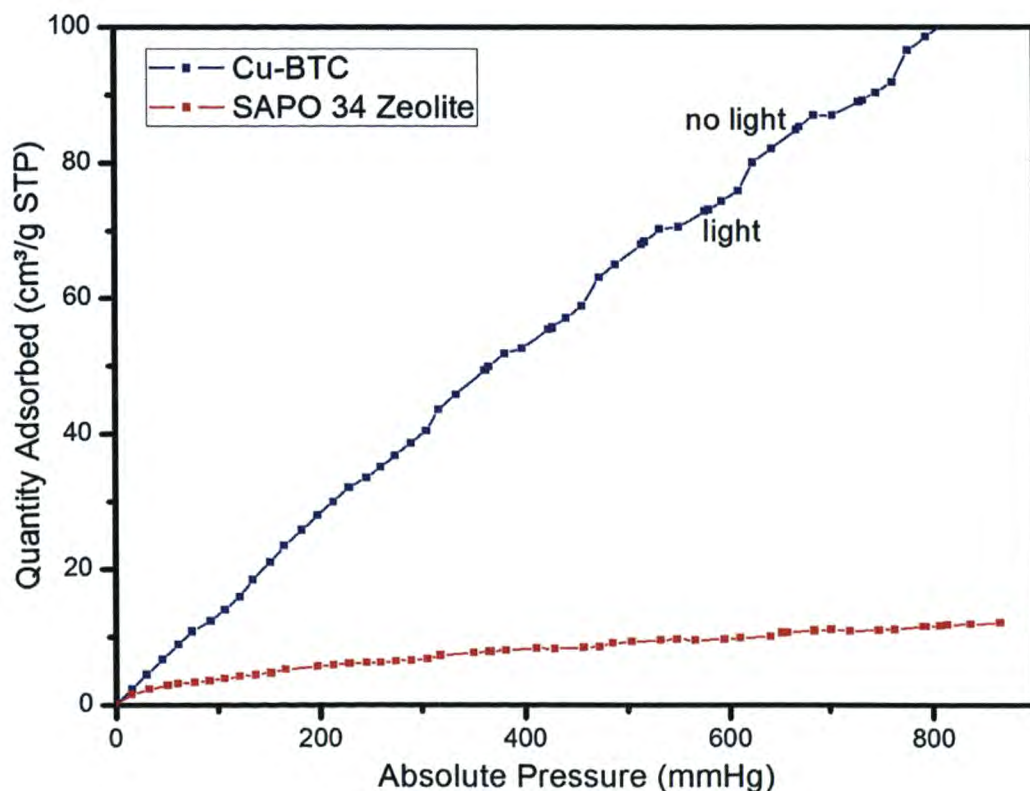


Figure SI-10: Control experiments using non-photoactive materials to verify the effect of light on Zn(AzDC)(4,4-BPE)_{0.5}. CO₂ adsorption isotherms of Cu-BTC (blue)

and SAPO-34 zeolite (red) at 303 K.

Cu-BTC and SAPO-34 zeolite show up to approximately 0.2 % and 2 % responsiveness respectively. In comparison to the 64 % response in $\text{Zn}(\text{AzDC})(4,4\text{-BPE})_{0.5}$, the response is very low.

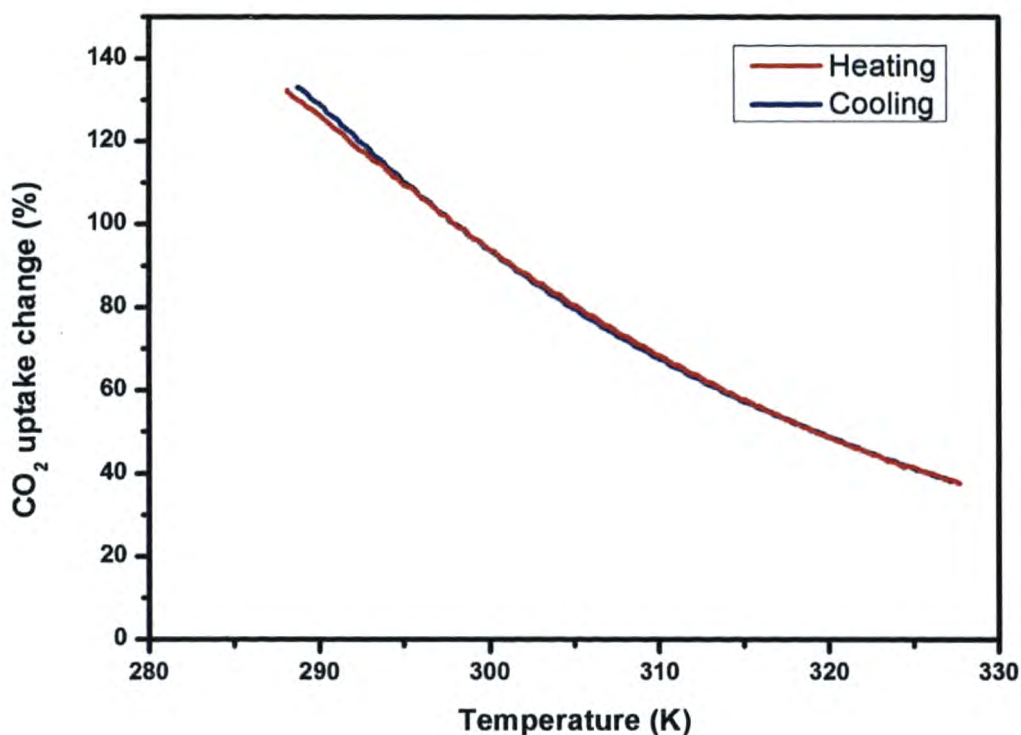


Figure SI-11: An adsorption isobar of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ showing the dependence of the CO_2 uptake on sample temperature at 1 bar CO_2 . The temperature was ramped at 0.1 K/min from 288 to 328 K, then back to 288 K.

Section 7: Light-Responsive Gas Adsorption Experimental Setup S7

S7.1 General Light-Responsive Gas Adsorption Experimental Setup

A pre-weighed and dried custom made aluminium foil coated quartz BET tube was used for the light experiment. A custom made BET light cell was used to contain the BET tube and light guide to allow maximum light exposure and coverage on the sample when the light was switched on. A Cole Palmer Model BT 15 heated circulating water bath was used to maintain the temperature at 303 K or 273 K throughout the experiment. Bath temperature was found to vary by less than 0.1 °C.

Digitech QM-1600 type-K thermocouple probe (sensitivity: $\sim 41 \mu\text{V}/^\circ\text{C}$, temperature range: $-200\text{ }^\circ\text{C}$ to $+1250\text{ }^\circ\text{C}$) was wedged inside the light cell between the quartz BET tube and light guide to monitor the temperature. Acticure® 4000 was used as a UV-VIS light source to trigger the sample’s light response during analysis. The light (high pressure 100 W mercury vapor short arc) was fixed at the highest intensity output with no filter (200 - 500 nm) ($24,600 \text{ mW}/\text{cm}^2$) and 365 nm filter ($5,600 \text{ mW}/\text{cm}^2$). Photoswitching occurs at approximately 10-minute interval to allow clear detection of CO_2 capture and release. Photo-response effect can be observed within 2 minutes.

S7.2 BET Light Cell

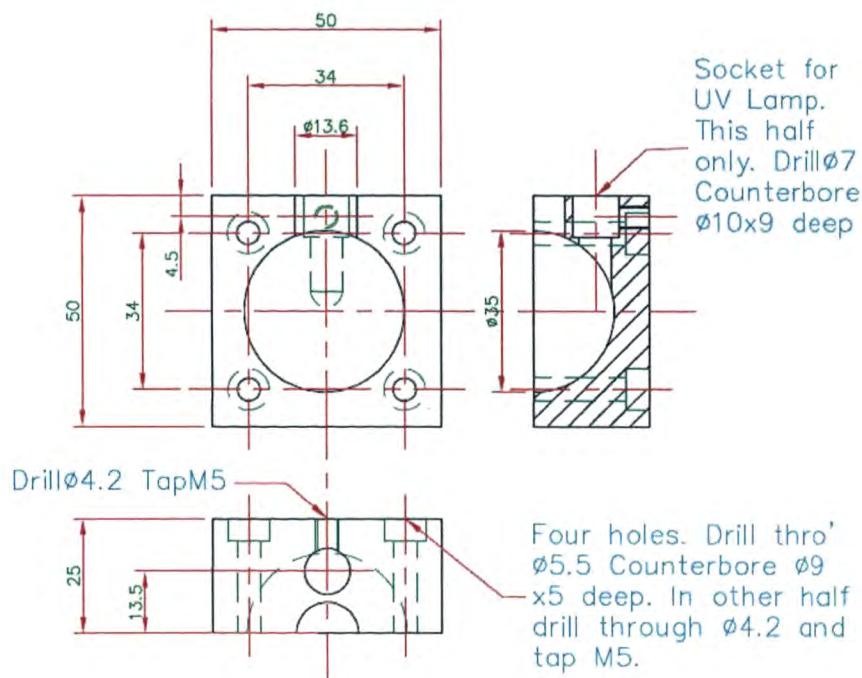


Figure SI-12: Cross section of a BET light cell showing a light guide socket and a smooth-surfaced cavity to allow maximum light coverage on the sample. The BET light cell is made of stainless steel.

S7.3 Light-Responsive Gas Adsorption Experimental Setup

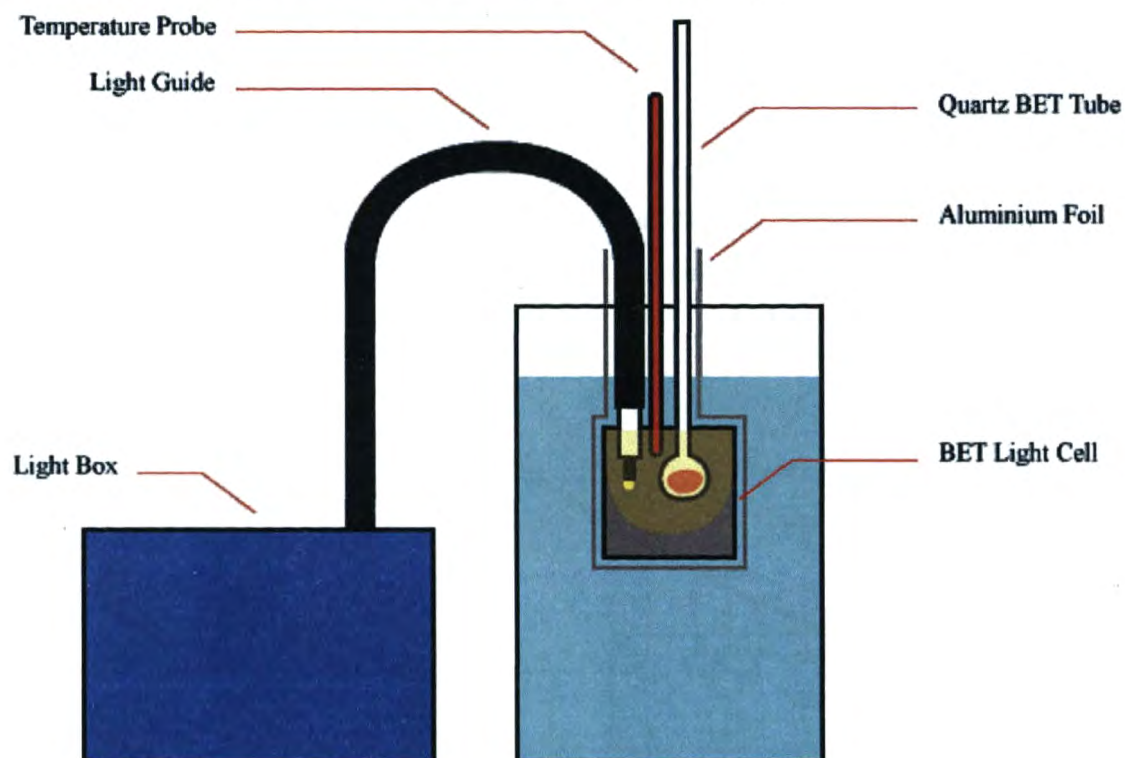


Figure SI-13: Schematic representation of the experimental setup.

S7.4 Spectral Output

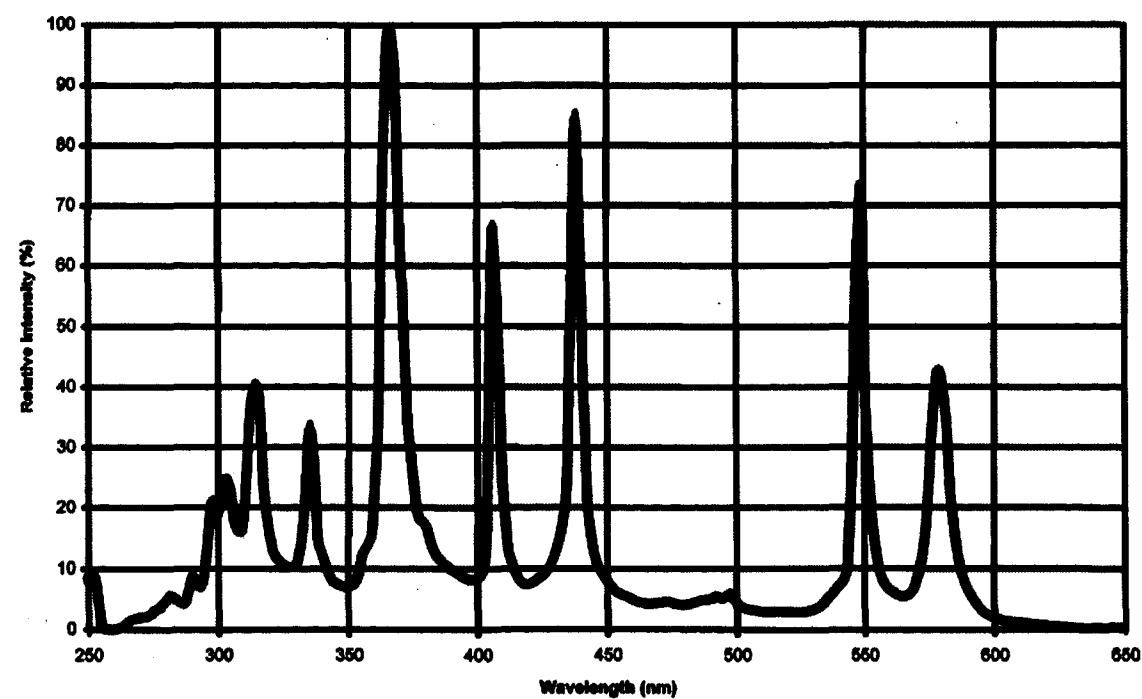


Figure SI-14: Spectral output of light using no filter.

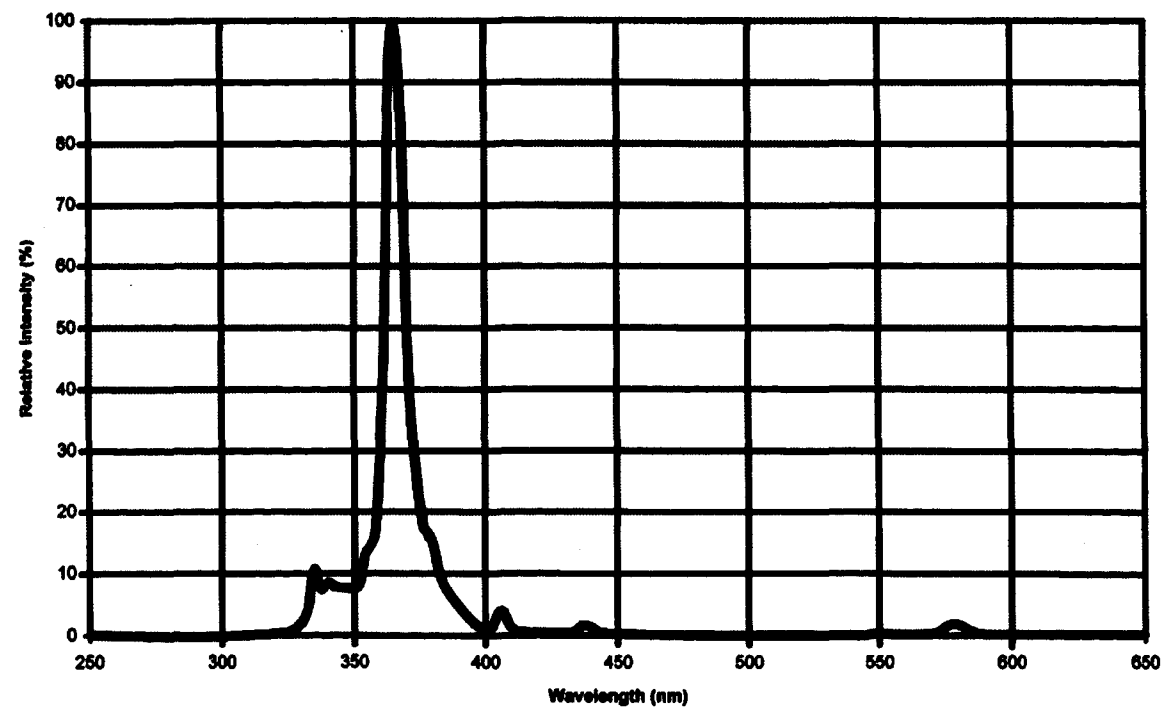


Figure SI-15: Spectral output of light using the 365 nm filter.

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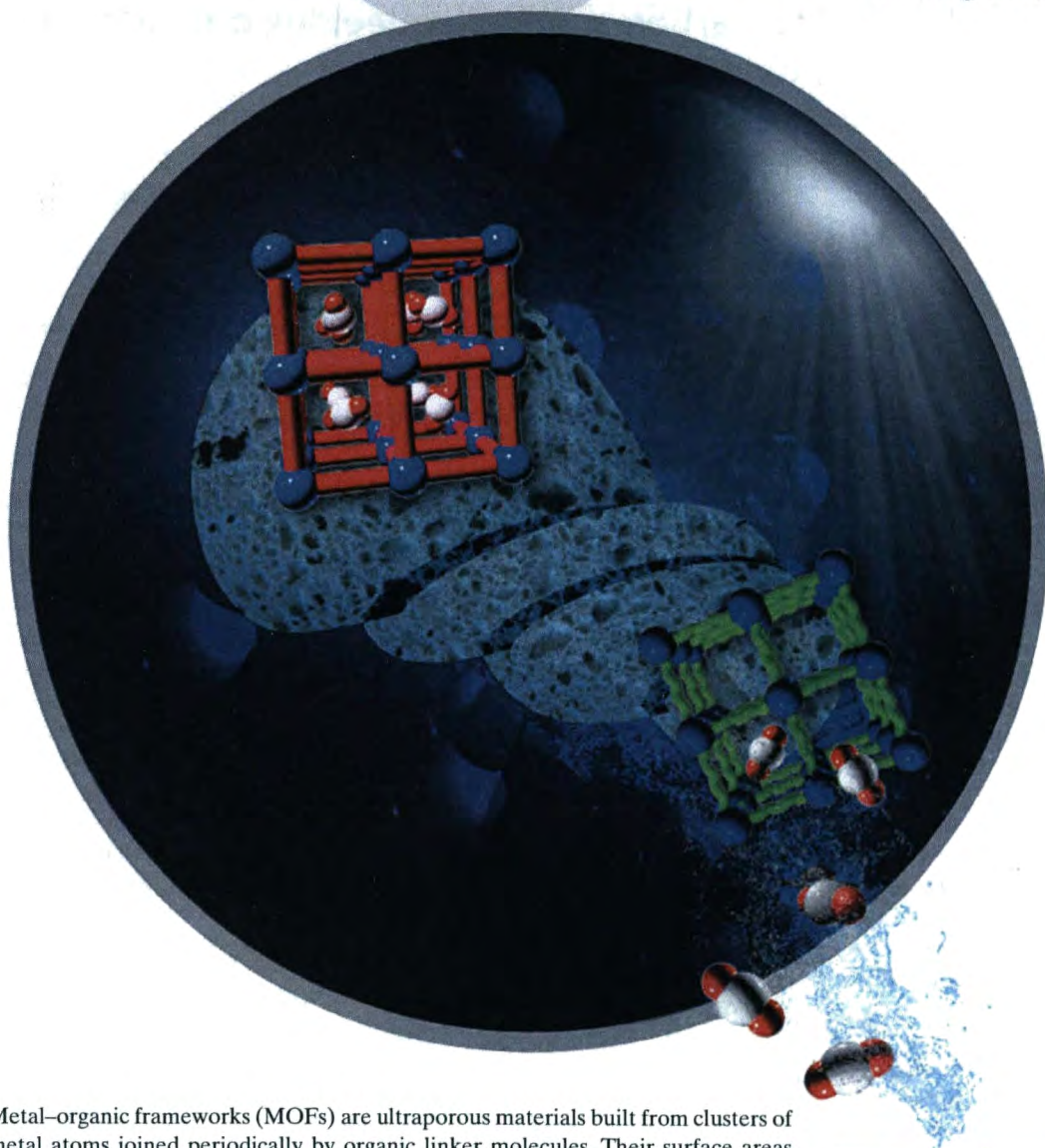
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Metal–organic frameworks (MOFs) are ultraporous materials built from clusters of metal atoms joined periodically by organic linker molecules. Their surface areas and tunable surface chemistry make them excellent candidates for the capture of carbon dioxide. In their Communication (DOI: 10.1002/anie.201208197), R. Lyndon, M. R. Hill et al. report a MOF that has been constructed with light-responsive linker molecules which are activated upon exposure to light and release the stored carbon dioxide.

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The carbon sponge: squeezing out captured carbon dioxide

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The carbon sponge: squeezing out captured carbon dioxide

Carbon Management (2014) 5(1), 9–11



“...it is clear that genuine breakthroughs in carbon-capture technologies ... will be required to enable power generation from fossil fuels in a carbon constrained future.”

Bradley P Ladewig^{*1}, Richelle Lyndon^{1,2} & Matthew R Hill^{**2}



Keywords: adsorption ■ carbon dioxide ■ light ■ metal organic framework ■ triggered release ■ UV

Carbon-capture technologies for the removal of carbon dioxide from industrial process streams have been intensively researched, both in academia and industry, for several decades. Governments worldwide have devoted enormous sums of research funding to advancing carbon capture technologies, especially to demonstrate them on pre-commercial and, eventually, the commercial scale. The impetus to make these investments are twofold.

First, governments can claim that they are directing resources to efforts that will reduce the carbon emission intensity of existing industries, especially power generation from fossil fuels such as coal. Superficially this is true, as without doubt the successful adoption of carbon capture-technologies in base load power generation from fossil fuels would reduce atmospheric carbon dioxide emissions. However, the fact that the power generation and allied industries are major employers is not lost on political minds, and so directing funding to potentially extending the extent or lifetime of those existing industries has pragmatic benefits too.

The second major reason to support the development of viable carbon capture technologies suitable for power

generation is to protect the other major industries that rely on reliable, low-cost base load electricity generation, such as manufacturing and electro-refining. This is particularly the case in Victoria, Australia, which contains vast brown coal (lignite) reserves that could easily provide another 500 years of low-cost power generation at current consumption rates. If a technological option was available, which allowed for the continued use of brown coal (a very low-cost fuel) to generate electricity with minimal carbon dioxide emissions, then fossil-fuel rich regions such as Victoria could enjoy an enormous competitive advantage in terms of electricity supply costs.

The current state-of-the-art in carbon-capture technologies reveals that no one technology has reached the technological maturity and, more importantly, the required cost per ton of carbon dioxide removed, to be commercially adopted [1,2]. Perhaps the most mature technology that can be used at significant scale is the use of liquid absorbents such as amine solutions, which can scrub carbon dioxide from a mixed gas stream and be regenerated using steam or heat, releasing the carbon dioxide in concentrated form in a separate stream, ready

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for compression, transport and usually some form of sequestration. This approach has been successfully used in the natural gas industry for removing carbon dioxide from largely methane streams, a process called 'sweetening'. However, for power generation units, the size of the capture plant using amine absorbents would be enormous, and the power to operate it could easily consume a significant fraction of the power output of the power station.

“ The current state-of-the-art in carbon-capture technologies reveals that no one technology has reached the technological maturity and, more importantly, the required cost per ton of carbon dioxide removed, to be commercially adopted. ”

Various membrane technologies have been proposed and validated at small to medium scales. This includes the use of polymeric membranes to remove carbon dioxide from combustion gas streams that have been cooled and cleaned to remove particulates and certain chemical species that are known to damage the membranes. This approach is also capital intensive, as the feed stream is usually available at pressure barely above ambient, which means that various configurations of vacuum pumps and membrane stages are required to obtain sufficient driving force for gas transport across the membrane. Very large membrane areas are inevitably required and, while membranes have the unique advantage that large areas can be packed into relatively compact modules with high area-to-volume ratios, the cost of the membranes becomes prohibitively high. Ceramics, metal oxides and other inorganic membranes in different configurations have also been proposed as carbon-capture technologies, however these usually require the reconfiguration of power-generation technology to use enriched oxygen as the feed gas (which has the benefit of producing a combustion product largely free of nitrogen). Alternatively, the fuel may be gasified to produce a syngas-type mixture, which is then passed through membranes to produce hydrogen and other gas streams suitable for combustion, sequestration or otherwise. While very high performance inorganic membranes have been demonstrated at small scales, the production of defect-free large scale inorganic membranes has proved extremely difficult and is a major limitation to this technology.

Gas adsorption onto solid adsorbents is another long-established technology that is being pursued as a carbon-capture possibility, but again there are significant challenges related to the size and cost of the equipment that would be required to treat the enormous flow rates resulting from power stations.

The inherent parasitic energy loads of many prospective carbon-capture technologies limits the maximum attainable efficiencies. While liquid amines and some membranes are likely to find first-generation adoption, widespread application will be best suited to those technology solutions with drastically lowered parasitic energy loads. Consequently, methods that readily utilize alternative energy sources as part of the process are attractive. With this in mind, we have developed materials that can utilize solar radiation to release captured carbon dioxide.

Metal-organic frameworks (MOFs) are a paradigm-shifting family of materials. Consisting of metal atoms or clusters joined periodically by organic linking species, MOFs are hybrid materials with an ultraporous array of uniform pores in which unprecedented surface areas are housed. These surfaces can be tuned to provide exceptional capacity and selectivity for carbon dioxide adsorption. We have previously shown that MOFs have exceptional gas storage and separation characteristics [3–8], and their use in advanced membrane topologies [9–13].

“ Termed the 'solar sponge', the structure was able to release approximately 64% of the adsorbed carbon dioxide within just a few seconds. ”

Our team utilized a zinc-based MOF constructed from azobenzene and bipyridyl ethane organic linkers, substances known to change shape, or strongly absorb UV light [14]. After adsorption of carbon dioxide, we found that localized bending modes induced within these responsive organic components could instantly induce the release of this adsorbed gas when the samples were exposed to concentrated light while loaded with carbon dioxide. Furthermore, we found that while this was most effective at 365 nm, the absorption maximum for the MOF, the effect was still significant when simple, broadband UV radiation was employed. This gives the best of both worlds in a future application. Termed the 'solar sponge', the structure was able to release approximately 64% of the adsorbed carbon dioxide within just a few seconds.

Our discovery of the use of photo-swing adsorption is a general result that could be applied to all candidate adsorbents 'squeezing' out adsorbed carbon dioxide with application of broad spectrum light.

There are many challenges to using this type of capture process at any significant scale and the authors are currently working through those with colleagues around the world, but regardless of whether this particular breakthrough leads to a commercial reality, it is clear that genuine breakthroughs in carbon-capture technologies, and not just incremental improvements on the existing

technologies, will be required to enable power generation from fossil fuels in a carbon constrained future.

Financial & competing interests disclosure

The authors acknowledge financial support from the Science and Industry Endowment Fund. The authors are co-applicants on a PCT Patent application entitled 'Gas Separation Process', based on the

process described in this Editorial. The authors have no other relevant affiliations or financial involvement with any organization or entity with a financial interest in or financial conflict with the subject matter or materials discussed in the manuscript apart from those disclosed.

No writing assistance was utilized in the production of this manuscript.

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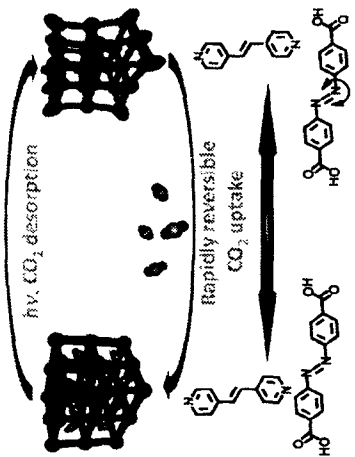


Figure 1

[Continued on next page]

(57) Abstract: A process for the separation of a gas from a gas stream using metal organic framework that is reversibly switchable between a first conformation that allows the first gas species to be captured in the metal organic framework, and a second conformation that allows the release of the captured first gas species, using light as the switching stimulus. The metal organic framework may comprise a metal and one or more ligands, in which the ligands contain an isomerizable group within the molecular chain that forms a link between adjacent metal atoms in the metal organic framework.

GAS SEPARATION PROCESSES

Field

The present application relates to gas separation processes, such as processes for the separation or removal of carbon dioxide from other gases in a gas stream. The present application therefore has particular application in the area of post-combustion carbon dioxide capture technology.

Background

In order for post-combustion carbon dioxide capture technology to realize widespread viability, the energy cost of this technology must be drastically reduced. Current adsorbent technologies that rely on pressure, temperature or vacuum swing adsorption consume as much as 40 % of the power plant's production capacity, most of which is associated with the liberation of the CO₂ from the capture medium. Ultimately this penalty, or parasitic energy load, must be brought closer to the thermodynamic minimum of about 4 % to avoid prohibitive cost increases. Given that the triggers for release of adsorbed carbon dioxide are so energy intensive and are based on energy from the power plant, there is strong motivation to develop new, low energy release triggers, utilising renewable energy sources. In conjunction with this, adsorbents with maximum performance can further reduce the cost compared to the conventional energy intensive CO₂ gas separation process.

A range of different types of materials have been considered for use in separation materials for the separation of selected gases, and notably CO₂ from a gas stream. Materials include porous organic polymers and metal-Organic Frameworks (MOFs), amongst others. MOFs are an important class of 3D crystalline porous materials comprised of metal centres and organic ligands, joined periodically to establish a crystalline porous array. The large internal surface areas can be used to adsorb large quantities of gases, such as hydrogen, methane and carbon dioxide.

Methods for the incorporation of light responsive groups within MOFs include use of pendant groups pointing into the pores, and filling of pores with light responsive guest molecules. The responsive groups within these materials may then change their conformation when exposed to filtered light which results in a change in adsorption capacity (in static conditions). Whilst these initial results are exciting, there are inherent limitations in the approaches reported to date. Firstly there is a requirement for specific wavelengths of light to trigger the conformational change. Second, the mode of regeneration in materials studied to date has involved mechanisms that take considerable time to achieve removal of the adsorbed species. Some mechanisms require the application of considerable energy in the form of heat.

An adsorbent that can respond to a broad light spectrum similar to solar radiation, and/or possess relatively fast photo-switching that directly releases CO₂ would offer enhanced, lower energy routes to light-triggered CO₂ release.

Summary

According to the present invention, there is provided a process for the separation of a first gas species from a gas stream using a gas separation material comprising a metal organic framework that is reversibly switchable between a first conformation that allows the first gas species to be captured in the metal organic framework, and a second conformation that allows the release of the captured first gas species on the use of light as the switching stimulus, the process comprising:

- contacting a gas stream containing the first gas species with the gas separation material comprising the metal organic framework in the first conformation to capture the first gas species,
- releasing the separated first gas species from the gas separation material by switching the conformation of the metal organic framework to the second conformation, and
- confining the metal organic framework to the first conformation to regenerate the gas separation material.

The process typically comprises a further step of reusing the regenerated gas separation material for the separation of the first gas species from the gas stream.

The term "light" is used broadly to refer to light from the visible and/or ultraviolet spectrum. The term encompasses either filtered light of a selected wavelength, or unfiltered light, or light having a broad wavelength range (broadband wavelength). According to one preferred embodiment, the light is light of broadband wavelength. According to another embodiment, the light is sunlight, such as concentrated sunlight.

Light, and in particular concentrated sunlight, is an extremely attractive stimulus for triggering CO₂ release. For the first time, it has been found that metal organic frameworks of a suitable type that (i) are capable of capturing or adsorbing gases such as CO₂, (ii) strongly absorb sunlight which provides a stimulus for reversibly and rapidly changing their conformation, and (iii) adsorb gas or release the adsorbed gas through this conformational change. This process can achieve the required gas uptake and release with low energy cost, as is required for commercially viable gas separation processes. The process allows for reduced reliance on coal as an energy source.

The "use" of light as the switching stimulus encompasses the application and removal of light. According to preferred embodiments, light is the only switching stimulus. Thus, the metal organic framework is one that is reversibly switchable between a first

conformation that allows the first gas to be captured in the metal organic framework and a second conformation that releases the captured first gas species on the use of light as the only switching stimulus. It has been found by the present applicants that light is the only switching stimulus for the MOFs of preferred embodiments, so that no additional energy input such as heat application is required.

According to some embodiments, the second conformation is achieved on application of light (e.g. through irradiation of the MOF with light). In this embodiment, the switching of the metal organic framework to the first conformation to regenerate the gas separation material is triggered by removal of light. Thus, in such embodiments, the process comprises the step of:

- releasing the separated first gas species from the gas separation material by applying light to switch the metal organic framework to the second conformation and release the captured first gas species.

According to some embodiments, the conformation that is achieved on application of light is a conformation that is under tension, and removal of the light results in spontaneous reversal to the structure of the other conformation. This is an important characteristic of preferred embodiments, as this allows for the rapid reversible change in conformation to be achieved on removal of the light stimulus. As an example, the second conformation may be one that is under tension, and removal of the light results in spontaneous reversal to the first conformation. The first conformation is not under tension. "Rapid" in this context refers to a time period of not more than 30 seconds.

Details of suitable metal organic frameworks that have the properties required for use in the present claimed process are set out in the detailed description below. In general terms, according to some embodiments, the metal organic framework is an interpenetrated metal organic framework. The metal organic framework may be one that is triply interpenetrated, although other degrees of interpenetration are possible.

According to another aspect, there is provided the use of a metal organic framework that is reversibly switchable between a first conformation and a second conformation on the use of light as the switching stimulus, as a gas separation material for the separation of a first gas species from a second gas species in a gas stream through adsorption of the first gas species from the gas stream when in the first conformation, and release of the first gas species through switching to the second conformation. The switching to the second conformation may be through the application of light.

According to a further aspect, there is provided a gas separation device comprising the gas separation material described herein. The gas separation device may be in any suitable form, such as in the form of a gas separation membrane, or a gas separation cartridge.

Brief Description of the Figures

Figure 1 is a schematic illustration showing dynamic photoswitching in the light responsive MOF of one embodiment, Zn(AzDC)(4,4'-BPE)_{0.5}, which leads to rapidly reversible CO₂ uptake.

Figure 2 is a graph of the CO₂ adsorption isotherms of Zn(AzDC)(4,4'-BPE)_{0.5} at 303 K in the presence of light (squares), absence of light (triangles) and unfiltered light switching environment (circles). Temperature fluctuations were not observed during the light switching experiment. The light intensity was fixed at 24.6 W cm⁻² in the wavelength range (200-500 nm).

Figure 3 is a series of graphs demonstrating C-C-C and C-C-N low energy FTIR bending modes in AzDC which were found to be excited by UV in both the ligand (see graph (a)) and the in the MOF Zn(AzDC)(4,4'-BPE)_{0.5} (see graph (b)). Graph 3(c), which is a graph of the intensity of oscillation of trans (solid line) and cis (dashed line) MOF upon prolonged exposure to 380 nm and 455 nm light, demonstrates that continual irradiation of the MOF led to oscillations between native and excited states witnessed with UV-Vis absorption. Free 4,4'-BPE in the solid state was found to be non-photoactive. Graph 3(d) shows the results of the synchrotron PXRD experiments, which confirm that the transitions were local and dynamic, since no periodic changes are revealed.

Figure 4 is a graph of the photoswitching performance according to light wavelength, adjusted for variation in flux. 365 nm filtered light is optimised for cis-trans photoisomerisation of both AzDC and BPE ligands, which are ligands of the MOF of one embodiment.

Figure 5 is a graph of the gas adsorption isotherms of Zn(AzDC)(4,4'-BPE)_{0.5} at 77 K (hydrogen, squares) and 298 K (carbon dioxide, triangles; and methane, circles).

Figure 6 shows the PXRD of unirradiated (dashed line; top line) and light irradiated (solid line – lower line) (AzDC)(4,4'-BPE)_{0.5}. No filter was used when the light source was switched on.

Figure 7 shows the crystal structure of Zn(AzDC)(4,4'-BPE)_{0.5}.

Figure 8 shows the excitation spectra of AzDC ligand in Zn(AzDC)(4,4'-BPE)_{0.5} (solid line) and free AzDC ligand (dashed line) with an emission wavelength of 370 nm (left side spectra) and 480 nm (right side spectra).

Figure 9 shows the excitation spectra of 4,4'-BPE of Zn(AzDC)(4,4'-BPE)_{0.5} with an emission wavelength of 250 nm (left side) and 370 nm (right side).

Figure 10 is a graph of gas adsorption isotherms for control experiments using non-photoactive materials to verify the effect of light on Zn(AzDC)(4,4'-BPE)_{0.5}. The CO₂

adsorption isotherm at 303 K of Basolite C300 is reflected by the line connecting the circle points, and of Silica Alumina is reflected by the line connecting the square points.
Figure 11 is a schematic illustration of the process for separating a first gas species from a gas stream using a gas separation material comprising a MOF according to one embodiment.

Figure 12 is a schematic illustration of a gas separation device in the form of a cartridge being used the process of one embodiment.

Figure 13 is a graph of the spectral output of light using the 365 nm filler.

Detailed Description

The present application is based on the development of a metal organic framework that was selected based on its potential to have properties making it suitable for use in gas separation materials. A number of surprising features were found to be embodied in the studied metal organic framework, which now guide the selection and development of additional metal organic frameworks having the properties required for use in gas separation materials which rely on light as the (or the only) switching mechanism.

The term "gas separation material" is used in a general sense to refer to a material that enables the required separation of gases. The gas separation material may be in the form of a gas separation membrane, or in the form of a gas separation adsorbent of any physical construction, such as a particulate adsorbent material or otherwise. The gas separation material may form part of a gas separation device, such as a gas separator, gas separation cartridge, or any other device, equipment or apparatus used in the treatment of a gas stream. The gas separation material may consist of the metal organic framework, or the metal organic framework may constitute one component of the gas separation membrane, or gas separation adsorbent.

Metal organic frameworks are a well known class of chemical compounds. Metal organic frameworks comprise metal atoms (or metal centres) and organic ligands that bridge between the metal atoms to establish a crystalline porous array.

One of the ligands that was selected for use in developing the studied metal organic framework is based on azobenzene. Azobenzene and its derivatives are photochromic molecules that can undergo clean and efficient reversible photoisomerisation about the azo bond to *cis*- and *trans*-state upon visible and UV light irradiation respectively (coordinated *trans*:- λ_{max} ~370 nm, *cis*:- λ_{max} ~460 nm). Conversion of azobenzene to the 4,4'-

dicarboxylate (AzDC) delivers a ligand that can be incorporated into MOF architectures.

A second ligand selected for the studied metal organic framework was the ligand *trans*-bis(4-pyridyl)ethylene (4,4'-BPE), which has *cis*-*trans* photo-isomerisability when coordinated to a metal complex (coordinated *trans* 4,4'-BPE: λ_{max} ~280-310 nm, coordinated *cis* 4,4'-BPE: λ_{max} ~280 nm). This second ligand is of a class referred to as a

"pillar ligand", which is capable of co-ordinating to two metal atoms, to create pillars between two planar metal-ligand arrays.

The combination of these two ligands within a zinc-based MOF generates the triply interpenetrated framework Zn(AzDC)(4,4'-BPE)_{0.5}, which exhibits an open topology amenable to high capacity and selective adsorption of hydrogen and carbon dioxide. This is shown schematically in Figure 1.

The strong photo-response in Zn(AzDC)(4,4'-BPE)_{0.5} that has been identified for the first time herein, is dynamic and localized in nature, irrespective of the use of broadband or filtered light sources. This unusual property has been able to be exploited to trigger the uptake and release of carbon dioxide in real-time, during adsorption experiments, which demonstrate that gas separation materials comprising such MOFs can be utilised in very cost-effective processes for gas separation. Exposure to UV light resulted in an instantaneous release of up to 69 % of the adsorbed CO₂ using broadband radiation, similar to concentrated solar sources. Furthermore, the response was found to be fully reversible. The dynamic, yet localized structural movements have been directly characterized with a suite of light and X-Ray based experiments, and isolated to being a factor solely of the UV radiation with several careful control experiments.

Based on the results achieved with Zn(AzDC)(4,4'-BPE)_{0.5}, the applicants have identified a range of variations that can be made on the MOF structure while still achieving the desired performance outcomes that will enable other MOFs to be used in the process of the present application.

Zn(AzDC)(4,4'-BPE)_{0.5} is an interpenetrated metal organic framework. Specifically, Zn(AzDC)(4,4'-BPE)_{0.5} is a triply interpenetrated metal organic framework, or in other words, has 3-fold interpenetration. This is a concept that is well understood in the art of the invention. Interpenetration refers to the intersection of independent nets or networks of the basic molecule (Zn(AzDC)(4,4'-BPE)_{0.5} in this case) each being of the same structure. In the case of 3-fold interpenetration, 3 independent nets or networks intersect each other.

According to preferred embodiments, other MOFs that can be used in the present application are interpenetrated metal organic frameworks. These may have 2-fold, 3-fold, 4-fold or greater degrees of interpenetration. According to one embodiment, the MOF has 3-fold interpenetration.

Other categories of MOFs of the prior art with cavities that may enable the capture and release of gas species rely on a bulky pendant group being tethered to the ligand via an isomerisable functional group (such as an azo group). In such pendant-group containing MOFs, the tethered group projects into a cavity created by the MOF, and out of the cavity when subjected to a stimulus (such as heat stimulus) to cause the bulky group to project into the cavity, and light to fold the bulky group out of the cavity). Examples of bulky pendant

groups include phenyl rings. The MOFs suited for use in the present application are preferably free of bulky pendant groups.

A further category of MOFs of the prior art with cavities that may enable the capture and release of gas species are guest-host MOFs. These MOFs rely on a 3D host framework which is rigid and does not change conformation on application of a stimulus, containing within the cavities an isomerisable guest molecule which is isomerisable on the application of a stimulus. The guest molecule has one conformation that allows a gas species to fit within the pore with the guest molecule, or another conformation that fills or obstructs the cavity so as to prevent the gas species from being retained within the pore. The MOFs suited for the present application are preferably free of an isomerisable guest molecule.

The MOFs of particular interest in the present application comprise a metal species, and one or more ligands. The metal species may be denoted M.

The metal species may be selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Mg, Ca, Sr, Ba, Zr, Ti and lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), and combinations thereof. According to some embodiments, the metal species is selected from the group consisting of Zn, Y, Mg, Ca, Sr, Ba, Zr, Ti and lanthanides and combinations thereof. In some embodiments the MOF comprises a single metal species. It will be understood that these metals are positively charged, and that the molecule will include a counterion or counterions for charge balancing.

The MOF preferably comprises at least one ligand containing an isomerisable group within the molecular chain that forms a link between adjacent metal atoms in the MOF. This accordingly excludes ligands containing a pendant group attached via an isomerisable group (such as an azo group). Examples of such ligands are azo benzene 4,4'-dicarboxylate (AzDC) and 4,4'-bipyridyl ethene (BPE). The concept of the requirement that there be "an isomerisable group within the molecular chain that forms a link between adjacent metal atoms in the MOF" is explained by reference to these examples. In these examples, the isomerisable azo ($-N=N-$) or ethene ($-CH=CH-$) group, respectively, form a part of the main chain through which adjacent metal atoms are attached through coordination of the ligand to the metal atoms.

The MOF is capable of a conformational change between a first conformation and a second conformation. The conformational change is a structural change in the molecule. Structural change refers to a change in the relative locations of atoms in the MOF. One example is a change from a *cis*-isomer to a *trans*-isomer, or vice versa. Other examples of structural changes are ring opening/ring closing rearrangements of atoms and other structural movements within ring systems, such as conversions between chair and boat ring system configurations. The component of the MOF that changes conformation is the ligand component of the MOF.

The ligand undergoing a conformational (i.e. structural) change, such as isomerisation, suitably involves a structural change or isomerisation within the length of the molecule.

In some embodiments, the MOF comprises a photochromic ligand. Photochromic materials are materials that change colour on exposure to light. Photochromic materials commonly provide a colour change effect by undergoing a structural or electronic change on exposure to light. Correspondingly, a photochromic ligand is a photochromic material that is in the form of a ligand. Ligand is a term well understood in chemistry and in this context refers to a molecule that co-ordinates to a metal atom by way of donating electrons to free orbitals of the metal atom. The ligands of particular interest are bidentate or polydentate. There may be one or more photochromic ligands in the MOF. Examples of photochromic ligands include azobenzenes, triarylmethanes, stilbenes, azastilbenes, nitrones, fulgides, spiropyrans, naphthopyrans, spiro-oxazines and quinines.

In some embodiments, the MOF comprises one or more ligands containing one or more of the following isomerisable groups:

- azo ($-N=N-$),
- ethene ($-C=C-$),
- aza ($-N=C-$),
- nitron ($-C=N^+(O^-)-$),
- polyene group capable of a ring closing/opening reaction, a specific example of which is a diaryl ethenes, a class which includes fulgides,
- two heterocyclic groups joined by a spiro-carbon atom, capable of ring opening and closing, of which spiropyrans and spirooxazines are examples, and
- a chiral carbon atom (which may be chiral in the free ligand, or only when coordinated to one or more metal atoms, of which triarylmethane is an example).

The above isomerisable groups are suitably within the molecular chain of the ligand. This language excludes isomerisable groups that are pendant to the main chain of the ligand. To establish whether a group is within the molecular chain of the ligand, one can trace through the atoms from one end (co-ordinating to the metal atom) to the other, and provided the isomerisable group (or part of the isomerisable group) must be passed through in at least one route between the ends, then the isomerisable group forms part of the molecular chain.

In some embodiments, the MOF comprises two ligands, each containing an isomerisable group within the molecular chain. The form of isomerisation may be a *cis-trans* isomerisation or any other isomerisation that results in a structural change (a conformational change) in the MOF, as described previously.

In some embodiments, the MOF comprises one or more ligands containing a photoisomerisable azo or ethene bond enabling reversible isomerisation between the cis- and trans- state. The azo or ethene bond is suitably within the ligand chain bridging between metal atoms. In other words, the azo or ethene group is not pendant to the main chain of the ligand.

In some embodiments, suitable ligands may be selected from the following structures:

- A. $L^1-X^a-Ar-N=N-Ar-X^b-L^2$
- B. $L^1-X^b-CH=CH-X^a-L^2$
- C. L^1-X^a -oligothiophene- X^b-L^2 .

In which each of L^1 , L^2 and L^3 is independently a co-ordination linking group capable of co-ordinating with the metal atom,

X^a is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl and $-N=N-$, provided that any $-N=N-$ group does not immediately adjoin any other $-N=N-$ group;

X^b is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl and $-CH=CH-$;

X^c is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl, $-N=N-$ and $-CH=CH-$, provided that any $-N=N-$ group does not immediately adjoin any other $-N=N-$ group; Ar is a substituted or unsubstituted aryl; and "oligothiophene" is a substituted or unsubstituted oligothiophene comprising from 2 to 8 thiophene units.

It is noted that in the above ligand definitions, the bond attachment through the aromatic rings or the thiophene units is through any suitable ring atom. It is also noted that the X^a at the end of each molecule may be of a different definition, although in some embodiments, both X^a 's are the same. This applies equally for X^b and X^c .

Where reference is made to substitution, suitable substituents may be selected from the group consisting of: $-H$, $-NH_2$, $-BR$, $-Cl$, $-NO_2$, $-CH_3$, $-OCH_2R_1$, and $-O-CH_2R_2$, wherein R_1 is an alkyl or alkene of from about 1-5 carbons, and R_2 is an aryl or substituted aryl. Substituents on the aryl group in the case of R_2 may be selected from the group consisting of $-H$, $-NH_2$, $-BR$, $-Cl$, $-NO_2$, $-CH_3$, and $-OCH_2R_1$. Alkyl refers to C1-C6 straight chain, branched or cyclic alkyl, including methyl, ethyl, propyl, tert-butyl and so forth. Alkene refers to C2-C6 straight chain or branched alkenes, including 1-propene, 1-butene, 1,3-butadiene, and so forth.

L^1 , L^2 and L^3 each represent a co-ordination linking group capable of co-ordinating with the metal atom. Such groups are sometimes referred to as "linkers" in the art. The range of groups containing this function include carboxylate groups and N-donor rings such as imidazole, pyrazole, pyridyl and triazole, carbamate, thiocarbamate and so forth. The

N-donor rings may be substituted or unsubstituted. The substituents may be selected from the group consisting of $-H$, $-NH_2$, $-BR$, $-Cl$, $-NO_2$, $-CH_3$, and $-OCH_2R_1$. In some embodiments, the N-donor ring is unsubstituted.

According to some embodiments, each of L^1 , L^2 and L^3 is independently selected from the group consisting of carboxylate and pyridyl rings. In some embodiments, L^1 is carboxylate. In some embodiments, L^2 is carboxylate. In some embodiments, L^3 is pyridyl.

X^a is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl and $-N=N-$.

According to some embodiments, X^a comprises an alternating series of substituted or unsubstituted aryl groups and $-N=N-$. According to some embodiments, X^a comprises one or a sequence of substituted or unsubstituted aryl groups. In some embodiments, X^a is a sequence of substituted or unsubstituted phenyl groups. In some embodiments, the number of aryl groups is between 2 and 5. In some embodiments, X^a is a sequence of between 2 and 5 phenyl groups. According to some embodiments, X^a is a substituted or unsubstituted aryl. In some embodiments, X^a is substituted or unsubstituted phenyl. In some

embodiments, X^a is phenyl. As noted above, X^a at each end of the molecule may be the same or different. When different, one X^a may be denoted $X^{a'}$, and X^a has the same definition as for X^a . According to some embodiments, each X^a is the same.

X^b is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aromatic rings and $-CH=CH-$. According to some embodiments, X^b is a direct bond. According to some embodiments, X^b is one or a sequence of substituted or unsubstituted aryl groups.

According to some embodiments, X^b comprises an alternating series of substituted or unsubstituted aryl groups and $-CH=CH-$. In some embodiments, X^b is a sequence of substituted or unsubstituted phenyl groups. In some embodiments, the number of aryl groups is between 2 and 5. In some embodiments, X^b is a sequence of between 2 and 5 phenyl groups. According to some embodiments, X^b is a substituted or unsubstituted aryl. In some embodiments, X^b is substituted or unsubstituted phenyl. In some embodiments, X^b is phenyl. As noted above, X^b at each end of the molecule may be the same or different.

When different, one X^b may be denoted $X^{b'}$, and X^b has the same definition as for X^b . According to some embodiments, each X^b is the same.

X^c is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl, $-N=N-$ and $-CH=CH-$. According to some embodiments, X^c is a direct bond. According to other embodiments, X^c is one or a sequence of substituted or unsubstituted aryl groups. According to some

embodiments, X^c comprises an alternating series of substituted or unsubstituted aryl groups and $-CH=CH-$. In some embodiments, X^c is a sequence of substituted or unsubstituted phenyl groups. In some embodiments, the number of aryl groups is between 2 and 5. In

some embodiments, X^c is a sequence of between 2 and 5 phenyl groups. According to some embodiments, X^c is a substituted or unsubstituted aryl. In some embodiments, X^c is substituted or unsubstituted phenyl. In some embodiments, X^c is phenyl. As noted above, X^c at each end of the molecule may be the same or different. When different, one X^c may be denoted X^{c1} and X^c has the same definition as for X^c . According to some embodiments, each X^c is the same.

The term "aryl" used either alone or in compound words such as "substituted aryl", denotes single, polynuclear, conjugated and fused residues of aromatic hydrocarbons or aromatic heterocyclic ring systems. Examples of aryl include phenyl, biphenyl, terphenyl, quaterphenyl, phenoxyphenyl, naphthyl, tetrahydronaphthyl, anthracenyl, dihydroanthracenyl, benzanthracenyl, dibenzanthracenyl, phenanthrenyl, fluorenyl, pyrenyl, indenyl, azulenyl, chrysenyl, pyridyl, 4-phenylpyridyl, 3-phenylpyridyl, thienyl, furyl, pyrrolyl, furanyl, imadazolyl, pyrrolydiny, pyridinyl, piperidinyl, indolyl, pyridazinyl, pyrazolyl, pyrazinyl, thiazolyl, pyrimidinyl, quinolinyl, isoquinolinyl, benzofuranyl, benzothienyl, purinyl,

quinazolinyl, phenazinyl, acridinyl, benzoxazolyl, benzothiazolyl and the like. According to some embodiments, the aryl is a carbocyclic aryl group. According to alternative embodiments, the aryl is heteroaryl and contains 1 to 4 heteroatoms independently selected from N, O and S. According to some embodiments, the aryl group contains a single ring (and therefore excludes fused ring systems). According to some embodiments, the aryl is phenyl or substituted phenyl. According to some embodiments, the aryl is an unsubstituted aryl, such as phenyl.

The oligothiophene may be a dithiophene. The bonding between the thiophene rings may be 4,4', or 2,5' or otherwise.

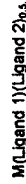
The MOF preferably comprises two different ligands.

In some embodiments, the MOF comprises a ligand of structure A and a ligand of structure B. In some embodiments, the MOF comprises a ligand of structure A and a ligand of structure C. In some embodiments, the MOF comprises a ligand of structure B and a ligand of structure C.

It will be understood that the relative number of ligands per metal atom may be

uneven.

Thus, in some embodiments, the MOF may be of the formula:



Ligand 1 refers to a ligand of a first type, and Ligand 2 to a ligand of a second type.

Ligand 1 may be of structure A, and Ligand 2 of structure B, as described previously. Thus, the MOF may be of the formula $M(A)(B)_{0.5}$. Other combinations of ligands A, B and C are possible.

The MOF may comprise paddlewheel dinuclear M_2 units, with bridging by Ligand 1, and pillars formed by Ligand 2. Ligand 1 may be a di-anionic ligand, such as a dicarboxylate ligand, and Ligand 2 may be a di-N-donor ring containing ligand, such as a dipyridyl ligand.

The MOF preferably is able to release at least 40%, preferably at least 45%, at least 50%, at least 55%, at least 60% or at least 65% of the adsorbed (separated) first gas species. The MOFs studied in the examples was capable of 69% release of the adsorbed gas species. Thus, the process of the present application may comprise:

- releasing at least 40% of the separated first gas species from the gas separation material by switching the conformation of the metal organic framework to the second conformation.

The amount may be even greater, as indicated by the preferred percentages of gas release indicated previously.

The first gas species may be carbon dioxide. The gas stream will comprise a second (and possibly further) gas species. The second gas species may be selected from the group consisting of N_2 , O_2 , H_2 , CO , CH_4 and so forth, including combinations thereof. According to other embodiments, the first gas species is one of N_2 , O_2 , H_2 , CO or CH_4 . The first gas species is selectively separated from the second gas species in the gas stream, such that at least 90%, or at least 95%, at least 99% or 100% of the adsorbed gas species is the first gas species.

The gas stream may be an exhaust gas stream, such as a power plant exhaust gas stream.

Studies on $Zn(AzDC)(4,4'-BPE)_{0.5}$

The synthesis of the triply interpenetrated framework $Zn(AzDC)(4,4'-BPE)_{0.5}$ and studies on its properties are set out in the Examples below. The framework is assembled from paddle wheel dinuclear Zn_2 units, bridging AzDC di-anions and 4,4'-BPE pillar ligands. Photoreversible studies in solid state revealed a photoactive framework. *Trans*- and *cis*-AzDC $n-\pi^*$ (S1 state) and $\pi-\pi^*$ (S2 state) transitions can be detected at 455 nm and 380 nm in the excitation spectra respectively (Figure 10). The coordination of 4,4'-BPE to Zn results in a photoactive species under light irradiation. The *trans* isomer of 4,4'-BPE ligand exhibits overlapping excitation bands of metal to ligand charge transfer and intra-ligand charge transfer in the 310-375 nm region. Excitation in this region generates *trans*-*cis* isomerisation. Both *cis*-AzDC and 4,4'-BPE can return to their *trans* state.

As shown in Figure 2, $Zn(AzDC)(4,4'-BPE)_{0.5}$ exhibits unprecedented dynamic switching under CO_2 adsorption, with a 240 % variation in capacity under static irradiation conditions, and as much as 69 % during dynamic measurements. Dynamic irradiation isotherms follow values obtained under continuous conditions, however the reversal in

uptake was not entirely complete under the dynamic measurement conditions employed. A series of careful control experiments were undertaken to ensure that this phenomenon was not an experimental or material artefact, but due solely to the dynamic photo-response observed. Careful localized temperature monitoring showed that the temperature varied by less than 0.2°C, ruling out localized heating as a significant effect. Furthermore, experiments with control materials including - SAPO 34 zeolite, and also a framework without photoactive groups, Cu-BTC, showed almost no CO₂ uptake variations (0.2-2 % vs 69 % for Zn(AzDC)(4,4'-BPE)(0.5), see Figure 12. To the best of our knowledge, this MOF exhibits the strongest light response reported to date. In the only comparable experiment, conducted under static conditions, a 30 % uptake fluctuation was observed.

Figure 3 shows that significant changes in peak intensity for the region 540-700 cm⁻¹ were observed under irradiation, whereas the remaining spectrum was unchanged. Peak intensity increase at 550 cm⁻¹ can be attributed to C-C-C and C-C-N bending modes with AzDC, indicating low energy structural variations about the azo group, which occurred due to the suppression of *cis-trans* isomerisation. These bending modes are likely to be responsible for the spontaneous release of adsorbed CO₂ upon irradiation, in which the pore surface was activated and the surface energy was increased (Figure 3b). Similar experiments on the free ligand AzDC confirmed this effect (Figure 3a). An increase in intensity at 537 cm⁻¹ indicated the activation of bending modes about the C-C-N bonds within the ligand. Furthermore, very minor peak increases in the free ligand at 1516 cm⁻¹ were observed, assigned to higher energy *cis-N=N* stretching modes forming as the native *trans* material was excited. These modes were not seen to change within the framework, highlighting the restricted nature of AzDC in this structure, which could not undertake these transitions. This also explains why no changes were seen in XRD (Figure 3d). This result was also replicated with similar UV-Vis experiments, where only a small fraction of *cis* isomers were detected (Figure 3c). The framework was continuously exposed to either 365 nm or 460 nm light and the intensity of the absorption peak is monitored. Absorption related to *trans*-AzDC and *cis*-AzDC moieties was found to be complementary and also periodically changing, regardless of whether the excitation wavelength promoted formation of either *cis* or *trans* structures. Under continuous irradiation from either 370 nm (promote *cis*-AzDC) or 460 nm light (promote *trans*-AzDC), small fractions of the structure were found to periodically oscillate between both isomeric conformations in a complementary fashion given the additive nature of *cis*- and *trans*- peaks across the two separate experiments. Similar additive effects were less clear from 4,4'-BPE excitation profiles where there was considerable overlap, although this ligand also clearly underwent transitions whilst coordinated within the framework. Most likely, this continual reversion to native states even under irradiation that promotes an isomeric transformation stems from the structural stresses induced within the interpenetrated framework, due

to the components also being critical to the topology, and not pendant to it. Furthermore, rapid changes predominantly through bending motions must occur throughout the framework in order to maintain the original triply interpenetrated framework and accommodate the constraints.

Figure 4 shows that absolute CO₂ uptake is increased and the amount released upon light exposure lessened when a filtered light source, which has a lower flux, is used. Filtering the light to 365 nm promotes photoisomerisation in both the AzDC and BPE ligands (Figures 10 and 11). Accounting for variations in raw uptake amounts, and changing flux gives Figure 4. Here it is shown that the efficiency of CO₂ release is greatly enhanced by the use of 365 nm filtered light. In both cases the adsorption amounts in the absence of light irradiation are similar, yet CO₂ desorption is found to be more efficient with use of filtered 365 nm radiation. This effect is most pronounced at high partial pressures, yet it is notable that at partial pressures similar to those encountered in post-combustion capture gas streams (ca. 115 mmHg) that unfiltered light gives a very comparable response. The results imply that in cases where light intensity is not a limiting factor, that filtration to 365 nm is preferable, but in other instances, unfiltered, concentrated sunlight will also perform almost as well, especially in post combustion capture streams. Illuminations up to 20 W/cm² (200 solar equivalents) can be achieved using concentrated sunlight. These remarkable results stem from the fact that the photo-induced structural changes in Zn(AzDC)(4,4'-BPE)_{0.5} are dynamic.

The foregoing results demonstrate that the interpenetrated framework Zn(AzDC)(4,4'-BPE)_{0.5} can undergo dynamic light-induced structural flexibility, which results in large variations in CO₂ uptakes. For the first time an experimental protocol was established to exploit this remarkable property for low energy CO₂ capture and release. The variation in CO₂ capture performance was found to be exceptionally strong, as much as 69 % under dynamic measurements, increasing to 240 % in static conditions. Characterisation of the framework showed that the structural flexibility is due to both the AzDC and BPE ligands, occurring reversibly and on a local scale, even under irradiation that would promote formation on just one conformer. This is akin to a twisted rope that spontaneously unwinds when sufficiently twisted.

This approach represents a route to renewable energy CO₂ capture and release, and was found to remain effective under broadband irradiation. This means that unfiltered sunlight may be used instead of the energy intensive temperature and pressure swings to release trapped gases.

The present invention will now be described in further detail with reference to the following non-limiting examples which demonstrate the principles underlying the present invention.

Examples

Section 1: Experimental Procedures S1

S1.1 Synthesis of AzDC (1) – "Ligand 1"

4-Nitrobenzoic acid (15.0304 g, 0.09 mol) was dissolved into an aqueous sodium hydroxide solution (51.0039, 1.28 mol, in 225ml water) by heating the solution. A hot aqueous glucose solution (101.0159g, 0.56mol, in 150ml water) was slowly added into the above solution at 50°C, in which the initially formed yellow precipitate immediately turned into a brown solution upon further addition of glucose. The mixture was allowed to react overnight at room temperature to form a dark solution. Methanol was added to the aged solution until a bright brown precipitate formed. The filtered precipitate was dissolved in water, followed by acidification with acetic acid (20 mL), whereupon a light pink precipitate was obtained. The product was filtered, washed with excess water and dried overnight to yield the final product (4.92 g, 17mmol, 38.5 %). ¹H NMR (DMSO, 400 MHz): δ (ppm) 8.04-8.06 (d, 4H), δ 8.18-8.20 (d, 4H), δ 13.0 (brs, 1H). ¹³C NMR (DMSO, 500 MHz): 122.86, 130.72, 133.50, 154.17, 168.67.

S1.2 Synthesis of Zn(AzDC)(4,4'-BPE)_{0.6}(2) – "Framework 2"

Framework 2 was solvothermally synthesized according to a general procedure described by Zhou *et al.* B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky, H.-C. Zhou, *Inorganic Chemistry* 2007, 46, 8480-8492. A mixture of Zn(NO₃)₂·6H₂O, 1 and 4,4'-BPE was suspended in DMF (100 mL) and heated at 100 °C for 24 h. The resulting red block-shaped crystals formed were filtered and washed with DMF and hexane, and dried in air. BET surface area: 126.4575 m²/g.

Section 2: Gas Adsorption Measurement S2

S2.1 General Gas Adsorption Procedures

Gas adsorption isotherms of activated Framework 2 were recorded at low pressure (0 - 1.2 bar) by a volumetric method using a Micromeritics ASAP 2040 instrument. Approximately 100 mg of dried methanol exchanged sample was weighed in a pre-dried and weighed Quartz BET tube. The sample was evacuated and activated at 150 °C under dynamic vacuum at 10⁻⁴ Torr for at least 24 h to remove any solvent molecules. An accurate weight of the degassed sample was calculated prior to analysis. Gas adsorption measurements were performed using ultra-high purity H₂, CO₂ and CH₄ gas. The gas adsorption isotherms are shown in Figure 5.

Section 3: X-Ray Powder Diffraction (PXRD) S4

S3.1 General PXRD Procedure

PXRD data was recorded using a Bruker D8 Advance X-ray Diffractometer with CuK α radiation (40kV, 40mA) monochromatised with a graphite sample monochromator was employed to determined the X-ray diffraction patterns. Each sample was scanned over the 2-theta range 5 to 65° with a step size of 0.02° and a count time of 4 seconds per step. The PXRD pattern broadens when the as synthesized 2 is solvent exchanged with dry methanol. This is a typical feature of the interpenetrated frameworks as the slight change in the structure resulted from the changes in guest content and composition.

S3.2 Photo-response PXRD Patterns

PXRD data was obtained using the powder diffraction beamline at the Australian Synchrotron with an incident wavelength of 1.00 Å. The sample was sealed in a 0.3 mm diameter quartz capillary and examined over the range of 2 < 2 θ < 82. Using ActiCore® 4000 as the UV-VIS light source, the sample was irradiated with light throughout the measurement. The results are shown in Figure 6.

S3.3 X-Ray Crystal Structure

Crystal unit cell structure of 2 was constructed using Diamond v3.1. This is shown in Figure 7.

Section 4: Photo-Response Characterisation S5

S4.1 General Photo-Response Characterization Procedure

Coming black flat clear bottom microplate using FlexStation® 3 Benchtop Multi-Mode Microplate Reader in fluorescence bottom reading mode at room temperature. The excitation spectra of AzDC is shown in Figure 8. The excitation band at 380 nm and 455 nm is due to the *trans* and *cis* AzDC in 2 respectively. The peak around 330 nm and 430 nm is characteristic of the *trans* and *cis* free AzDC ligand respectively. Figure 9 shows the excitation spectra of the ligand 4, 4'BPE. The excitation wavelengths at the 300 nm region and 285 nm correspond to the *trans* and *cis* peaks respectively. Free BPE was found to have no photoactivity in the solid state.

Section 5: Light-Responsive Control Experiments S6

S5.1 General Light-Responsive Control Procedure

Basolite C300 and Silica Alumina were chosen as non-photoactive porous materials for a control study. Approximately 1mg of degassed sample was used in Quartz BET tube. Basolite C300 was activated at 150 °C for 24 h and Silica Alumina was activated at 80 for

1 h, then at 350 °C for 5 h. The experiment was conducted by switching the unfiltered light on and off throughout the analysis. The gas adsorption isotherms are shown in Figure 10. Basolite C300 and Silica Alumina show up to approximately 0.2 % and 2 % responsiveness respectively. In comparison to the 69% response in Zn(A₂DC)(4-BPE)_{0.5}, the response is very low. This is due to the sudden change in condition when the light was switched on.

Section 6: Light-Responsive Gas Adsorption Experimental Setup S7

S6.1 General Light-Responsive Gas Adsorption Experimental Setup

Pre-weighed and dried custom made aluminium foiled quartz BET tube was used for light experiment. A custom made BET light cell was used to contain the BET tube and light guide to allow maximum light exposure and coverage on the sample when the light was switched on. A Cole Palmer Model BT 15 heated circulating bath was used to maintain the temperature at 303 K or 273 K throughout the experiment. A temperature probe was wedged inside the light cell between the quartz BET tube and light guide to monitor the temperature. Actiure® 4000 was used as a UV-VIS light source to trigger sample's light response during analysis. The light was fixed at the highest intensity output with no filter (200 - 500 nm) (24,600 mWcm⁻²) and 365 nm filter (5,600 mWcm⁻²). The spectral output for light filtered with a 365 nm filter is shown in Figure 13.

Section 7: Gas Separation Device Setup S7

The separation process is illustrated schematically in Figure 11. In the absence of the activating light (Figure 11a), a gas stream containing a first (target) gas species, comes into contact with the MOF adsorbent, while the MOF is in a first conformation that allows the target gas species to be captured. The non-adsorbed gas continues through the adsorbent, as illustrated. Then, as shown in Figure 11b, the separated gas species is released from the gas separation material by irradiating the MOF with light (hv) which results in switching of the conformation of the metal organic framework to the second conformation which forces the gas species out of the material. The MOF may be located within an arrangement that includes an adsorbed gas release passageway, which can be opened so as to channel the adsorbed (and released) gas species in a different direction to the non-adsorbed gas. The non-adsorbed gas species passageway can be closed during this operation. After removal of the adsorbed gas species, the MOF is regenerated and ready for use in the adsorption of more of the first gas species.

One specific arrangement for the gas separation device is illustrated in Figure 12.

In Figure 12, the gas separation device comprising MOF adsorbent is in the form of a cartridge that is positioned in a cartridge receiver within a gas stream. Feed gas passes through the cartridge in the absence of light, during which time the MOF is in a first conformation that allows the target gas species to be captured, and the non-adsorbed gas

flows through the cartridge (in the direction illustrated by the arrow headed to the top right hand corner). Then the separated gas species is released from the gas separation material by irradiating the MOF with light (hv) while a permeate gas is channelled through the cartridge, allowing the separated gas to be drawn out of the MOF in the cartridge and out of the MOF in the permeate gas stream. After removal of the adsorbed gas species, the MOF is regenerated and ready for use in the adsorption of more of the first gas species.

CLAIMS:

1. A process for the separation of a first gas species from a gas stream using a gas separation material comprising a metal organic framework that is reversibly switchable between a first conformation that allows the first gas species to be captured in the metal organic framework, and a second conformation that allows the release of the captured first gas species on the use of light as the switching stimulus, the process comprising:
 - contacting a gas stream containing the first gas species with the gas separation material comprising the metal organic framework in the first conformation to capture the first gas species,
 - releasing the separated first gas species from the gas separation material by switching the conformation of the metal organic framework to the second conformation, and
 - switching the metal organic framework to the first conformation to regenerate the gas separation material.

10 species,

- releasing the separated first gas species from the gas separation material by switching the conformation of the metal organic framework to the second conformation, and

- switching the metal organic framework to the first conformation to regenerate the gas separation material.

2. The process of claim 1, wherein the metal organic framework comprise a metal and one or more ligands.
3. The process of claim 2, wherein the metal organic framework comprises at least one ligand containing an isomerisable group within the molecular chain that forms a link between adjacent metal atoms in the metal organic framework.

4. The process of claim 2, wherein the metal organic framework comprises one or more ligands containing a photoisomerisable group enabling reversible isomerisation between the cis- and trans- state within the molecular chain bridging between metal atoms.

5. The process of any one of claims 2 to 4, wherein the metal organic framework comprises one or more ligands containing a photoisomerisable azo or ethene bond enabling reversible isomerisation between the cis- and trans- state within the molecular chain bridging between metal atoms.

6. The process of any one of claims 2 to 5, wherein the metal organic framework comprises two different ligands each comprising a photoisomerisable azo or ethene bond enabling reversible isomerisation between the cis- and trans- state within the molecular chain bridging between metal atoms.

7. The process of any one of claims 2 to 6, wherein the metal is selected from the group consisting of: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Mg, Ca, Sr, Ba, Zr, Hf, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and combinations thereof.

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8. The process of claim 7, wherein the metal species is selected from the group consisting of Zn, Y, Mg, Ca, Sr, Ba, Zr, and Ti.

9. The process of any one of claims 2 to 8, wherein the ligands are selected from the following structures:

- A. $L^a-X^a-Ar-N=N-Ar-X^b-L^a$
- B. $L^b-X^b-CH=CH-X^a-L^b$
- C. L^c-X^c -oligothiophene- X^c-L^c .

10 in which each of L^a , L^b and L^c is independently a co-ordination linking group capable of co-ordinating with the metal atom,

X^a is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl and $-N=N-$, provided that any $-N=N-$ group does not immediately adjoin any other $-N=N-$ group;

X^b is a direct bond, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl and $-CH=CH-$;

X^c is a direct bond, or a chain comprising one group, or a chain comprising one group, or a sequence of groups, selected from the group consisting of substituted or unsubstituted aryl, $-N=N-$ and $-CH=CH-$, provided that any $-N=N-$ group does not immediately adjoin any other $-N=N-$ group;

Ar is a substituted or unsubstituted aryl; and

oligothiophene is a substituted or unsubstituted oligothiophene comprising from 2 to 8 thiophene units.

10. The process of claim 9, wherein L^a , L^b and L^c are each independently selected from the group consisting of carboxylate and N-donor rings.

11. The process of claim 9, wherein L^a , L^b and L^c are each independently selected from the group consisting of carboxylate and pyrrolyl.

12. The process of any one of claims 9 to 11, wherein X^a is selected from the group consisting of aryl, substituted aryl, and a sequence of substituted or unsubstituted aryl groups.

13. The process of claim 12, wherein X^a is substituted or unsubstituted phenyl.

14. The process of claim 12, wherein X^a is phenyl.

15. The process of any one of claims 9 to 14, wherein X^b is a direct bond.

16. The process of any one of claims 9 to 15, wherein the metal organic framework comprises a ligand of structure A and a ligand of structure B.
17. The process of any one of claims 9 to 15, wherein the metal organic framework comprises a ligand of structure A and a ligand of structure C.
18. The process of any one of claims 9 to 15, wherein the metal organic framework comprises a ligand of structure B and a ligand of structure C.
19. The process of any one of claims 9 to 15, wherein the metal organic framework is of the formula $M(A)(B)_x$, in which M refers to a metal, and A and B are as defined in any one of claims 9 to 15.
20. The process of claim 19, wherein the metal organic framework is $M(AzDC)(4,4'-BPE)_x$.
21. The process of claim 20, wherein the metal organic framework is $Zn(AzDC)(4,4'-BPE)_x$.
22. The process of any one of the preceding claims, further comprising:
- reusing the regenerated gas separation material for the separation of the first gas species from the gas stream.
23. The process of any one of the preceding claims, wherein the light is light of broadband wavelength.
24. The process of any one of the preceding claims, wherein the light is sunlight.
25. The process of any one of the preceding claims, wherein light is the only switching stimulus.
26. The process of any one of the preceding claims, wherein the second conformation is achieved on application of light.
27. The process of any one of the preceding claims, wherein the conformation that is achieved on application of light is a conformation that is under tension, and removal of the light results in spontaneous reversal to the structure of the other conformation.

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28. The process of any one of the preceding claims, wherein the metal organic framework is an interpenetrated metal organic framework.
29. The process of any one of the preceding claims, wherein the MOF is able to release at least 40% of the adsorbed first gas species when switched to the second conformation.
30. The process of any one of the preceding claims, wherein the first gas species is carbon dioxide.
31. Use of a metal organic framework that is reversibly switchable between a first conformation and a second conformation on the use of light as the switching stimulus, as a gas separation material for the separation of a first gas species from a gas stream, through adsorption of the first gas species from the gas stream when in the first conformation, and release of the first gas species through switching to the second conformation.
32. The use of claim 30, wherein light is the only switching stimulus.
33. The use of claim 31 or claim 32, wherein the metal organic framework comprise a metal M and one or more ligands.
34. The use of any one of claims 31 to 33, wherein the metal organic framework comprises at least one ligand containing an isomerisable group within the molecular chain that forms a link between adjacent metal atoms in the metal organic framework.
35. A gas separation device comprising gas separation material, the gas separation material comprising a metal organic framework that is reversibly switchable between a first conformation and a second conformation on the use of light as the only switching stimulus, wherein the first conformation allows the adsorption of a first gas species, and the second conformation allows the release of the first gas species.
36. The gas separation device of claim 35, which is in the form of a gas separation membrane or a gas separation cartridge.
37. The gas separation device of claim 34 or claim 35, wherein the metal organic framework comprises at least one ligand containing an isomerisable group within the molecular chain that forms a link between adjacent metal atoms in the metal organic framework.

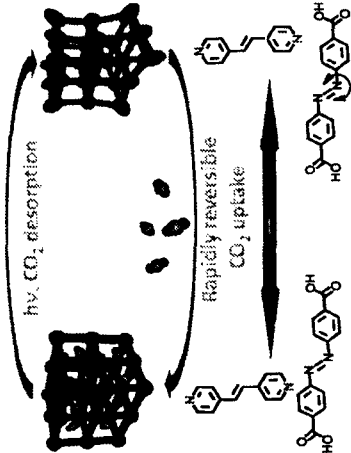


Figure 1

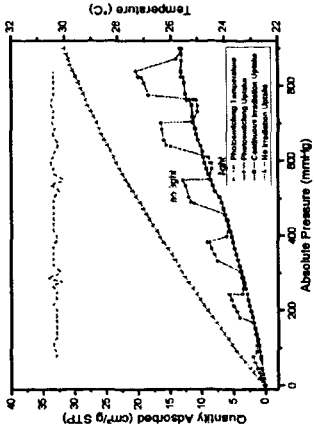


Figure 2

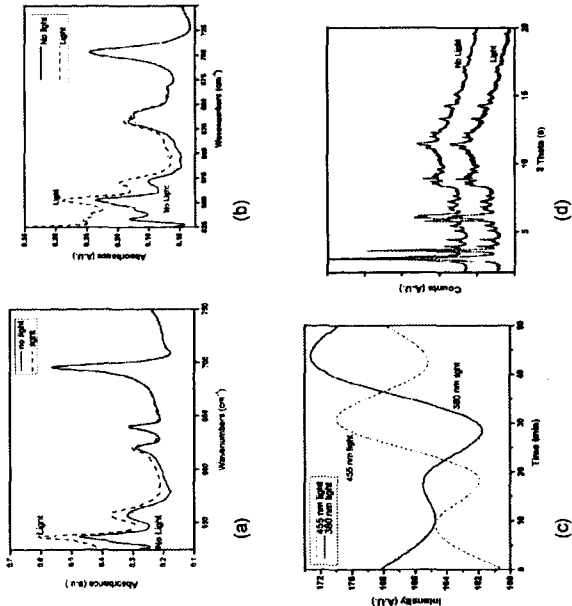


Figure 3

- 3/8 -

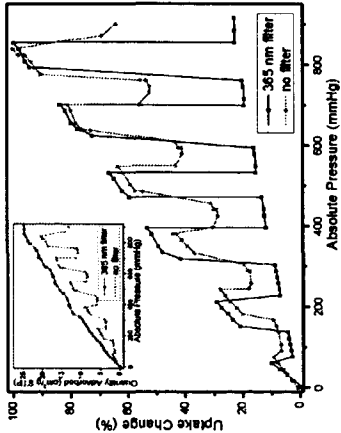


Figure 4

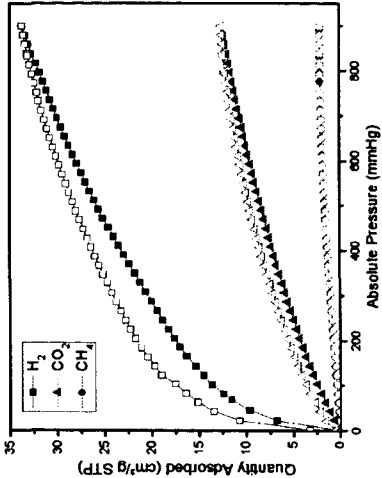


Figure 5

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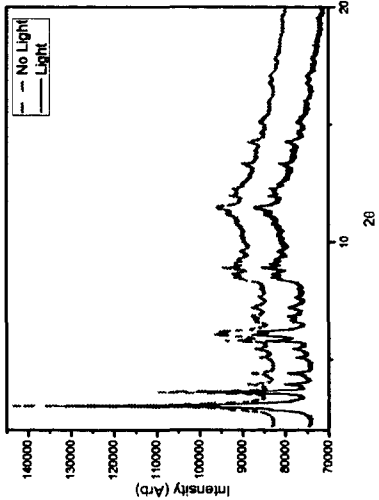


Figure 6

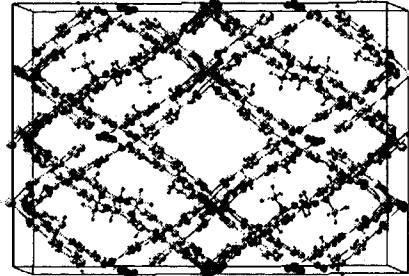


Figure 7



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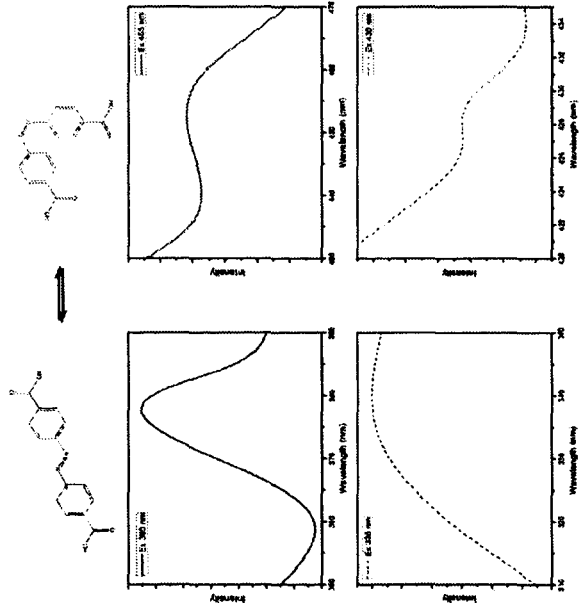


Figure 8

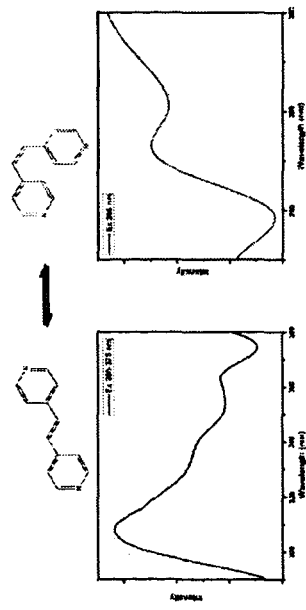


Figure 9

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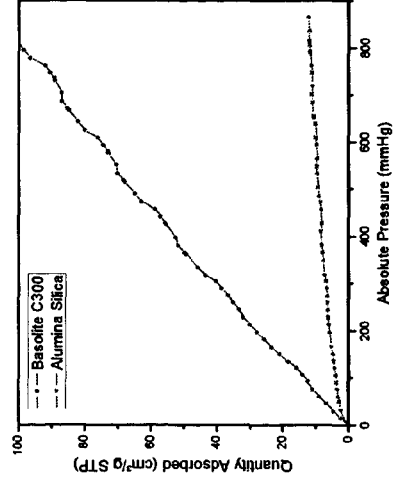


Figure 10

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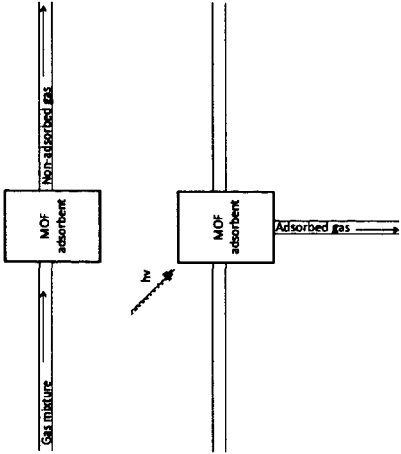


Figure 11a

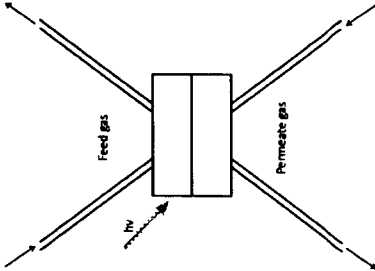


Figure 11b

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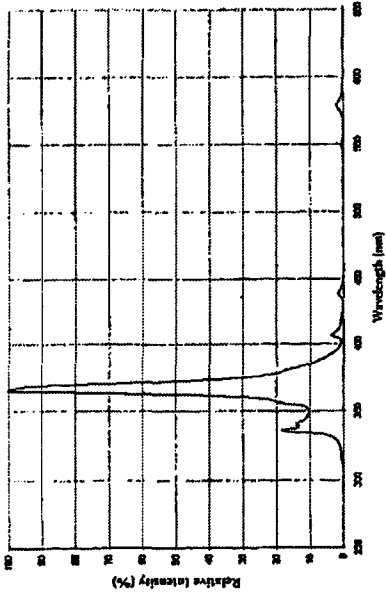


Figure 12

Press Releases:

Source	URL
Monash University	http://www.monash.edu.au/news/show/carbon-sponge-could-soak-up-coal-emissions
CSIRO	http://www.csiro.au/Portals/Media/CSIRO-solar-sponge-soaks-up-CO2-emissions.aspx
Australian Synchrotron	http://www.synchrotron.org.au/aussyncbeamlines/powder-diffraction/highlights-pd/solar-sponge-mofs
Chemical Engineering in Australia	http://www.engineersaustralia.org.au/sites/default/files/s_hado/Learned%20Groups/Colleges/Chemical%20College/feb13_cea_final.pdf
Tcetoday	https://www.tcetoday.com/~media/Documents/TCE/Articles/2013/861/861innovations.pdf
SpaceDaily	http://www.spacedaily.com/reports/Carbon_sponge_could_soak_up_coal_emissions_999.html
The Register (UK)	http://www.theregister.co.uk/2013/02/13/csiro_carbon_capture_sponges/
Wiley (USA)	http://au.wiley.com/WileyCDA/PressRelease/pressReleaseId-107640.html