

Potential photo-switching sorbents for CO<sub>2</sub> capture – A review

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## Abstract

Porous materials with photochromic units are currently under investigation as light allows for environmentally friendly and highly energy-efficient control. In the application of photoswitching materials to CO<sub>2</sub> capture, researchers have tried to endow metal-organic frameworks (MOFs) and porous organic polymers (POPs) with photoresponsive units. This review highlights photochromic units and methods used for different types of photoresponsive adsorbents of CO<sub>2</sub>, as well as some examples of adsorbents with photoswitches. These materials are also promising candidates for direct air capture of CO<sub>2</sub>. In particular, the process cost of regenerating an adsorbent may be reduced by using sorbents with light-induced regeneration. The key purpose of this review is to motivate more research into photo-switching sorbents that can be cycled many times to capture and release CO<sub>2</sub> by simply switching the light on and off.

**Keywords** CO<sub>2</sub> capture, sorbents regeneration, Photoresponsivity, Photoswitch, Direct air capture, Photochromic compounds

## Highlights

- As light is environmentally friendly, easily available, and non-invasive, using light to regenerate the adsorbents is regarded as one promising approach to improve sorbents.
- Photochromic units including azobenzenes, diarylethenes and spiropyrans have to be used to embed into the sorbents from photoswitching sorbents.
- Both metal-organic frameworks (MOFs) and porous organic polymers (POPs) have been designed with photoswitch to control the adsorption or release of CO<sub>2</sub>.
- Photoswitching sorbents are also promising candidates for direct air capture of CO<sub>2</sub>.

**Word Count: 7093**

## List of abbreviations including units and nomenclature

MOFs

Metal-organic frameworks

MOPs/POPs

Microporous/porous organic polymers

DAC

Direct air capture of CO<sub>2</sub>

AZBs

Azobenzenes

DARes

Diarylethenes

BET

Brunauer-Emmett-Teller

## 1. Introduction

As a major greenhouse gas, CO<sub>2</sub> emissions have already led to multiple, significant climate change events, including more frequent heatwaves, and both land and ocean temperature increases [1, 2]. As far as temperature is concerned, it has increased by approximately 1.0 °C since pre-industrial times, with the expectation of a 1.5 °C increase between 2030 and 2052 [3]. Currently, human activity is adding 25.7 Gt of CO<sub>2</sub> per year to the atmosphere [4]. CO<sub>2</sub> release mainly due to the release from either largely concentrated sources (e.g. fossil fuel power plants/chemical plant/cement factories) or point sources (e.g. transporting tools like cars, trucks, aeroplanes, heating and cooling systems in offices and at home) [5]. Therefore, it is globally acknowledged that CO<sub>2</sub> emissions must be reduced, and efforts should be concentrated on minimising both types mentioned above.

Adsorption from intermolecular forces between CO<sub>2</sub> and the surfaces of certain solid adsorbents is becoming increasingly attractive due to potentially lower energy consumption, good stability, non-volatility, and the possibility of obtaining high-purity CO<sub>2</sub> with high recovery [6, 7]. According to IUPAC recommendations, solid adsorbents can be classified as microporous materials (the pore size is smaller than 2 nm in diameter), mesoporous materials (pore size is in the range of 2–50 nm), and macroporous materials (the pore size is larger than 50 nm) [8]. Micro- and mesoporous materials, including metal-organic frameworks (MOFs) [9, 10], and amorphous microporous/porous organic polymers (MOPs/POPs) [11, 12], have been extensively researched as CO<sub>2</sub> adsorbents because they show relatively high CO<sub>2</sub> adsorption capacity as well as structural and chemical tunability. MOFs are 3D microporous crystalline solids consisting of organic bridging ligands and metal-based nodes with uniform pore sizes (diameters are around 3~20 Å) [13, 14]. Since they contain organic bridging ligands, MOFs can be designed with flexible and diverse chemical structures and functions. MOFs are applied for gas storage and separation because of their large surface areas, tunable pore sizes, structural variability, and controllable porous properties [15, 16]. POPs including polymers of covalent organic frameworks (COFs) [17], hyper-crosslinked polymers (HCP) [18], polymers of intrinsic microporosity (PIMs) [19], conjugated microporous polymers (CMPs) [20], and porous aromatic frameworks (PAFs) [21, 22] have potential in gas storage because of their relatively high porosity, stability, and adjustability.

Direct air capture of CO<sub>2</sub> (DAC), is the technology to direct extract CO<sub>2</sub> from the ambient, which is gaining increasing popularity [23, 24]. Firstly, it is a “carbon-negative” technology. Secondly, it can reduce CO<sub>2</sub> from both largely concentrated sources and point sources, without being limited to a specific location [25]. Thirdly, the sorbents used in DAC processes may be chosen to withstand contamination by typical pollutants in flue gas (SO<sub>x</sub>, NO<sub>x</sub>, mercury, etc.). It is reported that DAC could reach 1 GtCO<sub>2</sub>/a in 2050, which is predicted to be far from the potential market about 15 GtCO<sub>2</sub>/a in 2050 [24, 26]. However, in terms of real industrial applications, energy consumption and cost are currently significantly prohibiting factors. A DAC system is reported to require an annual cost of \$62 billion in 2050 [24, 27]. DAC is still in its infancy because of a lack of feasible sorbents for capturing CO<sub>2</sub> from ambient under atmospheric conditions, where very low concentrations (~400 ppm), relatively low pressure and temperature, and selectivity of CO<sub>2</sub>/N<sub>2</sub> present significant challenges.

NaOH solution has been largely used for the DAC process due to its low cost and the

1 feasibility of the technology, but it has many drawbacks such as a very large binding energy,  
2 the corrosiveness of strong NaOH solutions, and the vast energy consumption of the  
3 regeneration process [28]. Aqueous solutions of  $K_2CO_3$  have also been researched for the  
4 DAC process, however, the main drawback is that sorbent regeneration requires high  
5 temperatures (100–200°C), where  $KHCO_3$  is decomposed to  $K_2CO_3$  [29, 30]. The cost of using  
6 aqueous solutions to capture  $CO_2$  is reported to be 94–232 \$/t currently [31], and required  
7 thermal energy about 5.25 ~ 8.1 GJ/t $CO_2$  [32].  
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10 In contrast, solid adsorbents can reduce costs, ranging instead from 29 to 91 \$/t because of  
11 their lower heat of regeneration (45–70 kJ mol<sup>-1</sup>) [33, 34]. Solid sorbents have been  
12 identified as likely to show high selectivity for  $CO_2$ , high capacities of  $CO_2$  capture, fewer  
13 regeneration energies, and good stability [35]. MOFs are promising adsorbents for DAC  
14 because inorganic clusters and organic linkers provide MOFs with fabrication flexibility [32].  
15 Shekhah *et al.* demonstrated novel MOFs (SIFSIX-3-Cu) as DAC adsorbents, which could  
16 adsorb 54.6 mg g<sup>-1</sup>  $CO_2$  at 400 ppm, 298 K [36]. Amrit Kumar *et al.* evaluated Mg MOF  
17 74/Mg-dobdc in the DAC process, with 165 cm<sup>3</sup> g<sup>-1</sup> at 1 atm and 293 K [37].  
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21 Photoresponsive sorbents are attractive, as they are low-cost, have feasible regeneration,  
22 and good selectivity for  $CO_2$  over other gases even at atmospheric  $CO_2$  concentrations [38-  
23 40]. Sunlight is available almost everywhere and constitutes a renewable energy source,  
24 thus the cost of regenerating materials can be lower [41]. Moreover, photoresponsive  
25 sorbents embedded with photochromic units can absorb sunlight, along with a reversible  
26 change between “open” and “closed” conformations, so that photoresponsive sorbents can  
27 be regenerated feasibly [39, 42]. Photoresponsive functional groups like azobenzenes have  
28 been proven to increase gas selectivity for the MOFs/POPs sorbents of  $CO_2$  [40].  
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32 However, until now, a very limited number of reviews have focused on photoresponsive  
33 sorbents used for  $CO_2$  capture. Haiqing Li and Matthew R. Hill published a review article  
34 about three types of MOFs with the triggered release of stored gas, comprising  
35 light-responsive MOFs, magnetic MOFs, and dual stimuli-responsive MOFs [43]. Based on  
36 their work on light-responsive MOFs as  $CO_2$  adsorbents [44-47], they concluded that having  
37 guest light-responsive as the backbone of organic ligands is more conducive to  $CO_2$  capture  
38 and release than their incorporation as pendants and chemically grafting light-responsive  
39 motifs onto the organic ligands of the MOFs. They also highlighted that currently  
40 azobenzene and diarylethene are the predominant light-responsive groups. S. Castellanos *et al.*  
41 has also published a review about MOFs functionalized with azobenzene or  
42 dithienylethene derivatives to impart photoswitching behavior, where different strategies of  
43 photoswitchable MOFs are discussed [42]. In addition, we are unaware of a review of  
44 photoresponsive POPs as  $CO_2$  sorbents.  
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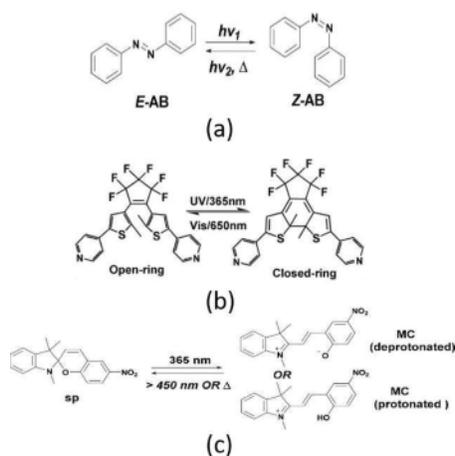
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49 In this review, potential photoswitching porous materials, including MOFs and POPs, are  
50 covered. The preparation strategies and commonly used photochromic units for these  
51 materials will be detailed, as well as the representative applications as photoswitching  $CO_2$   
52 sorbents. Further discussion about the possibility of photoswitching sorbents being applied  
53 in DAC will be illustrated. Most interestingly,  $CO_2$  sorbents can be produced with light “gates”  
54 or “switches” for low-energy regeneration of  $CO_2$ . Therefore, through the introduction of the  
55 appropriate photochromic unit, photoswitching materials are interesting candidate  
56 materials for DAC. Overall, the aim of this review of current research is to motivate more  
57 attention towards potential photoswitching sorbents of  $CO_2$ , as well as the research of  
58 photoswitching sorbents specifically for DAC.  
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## 2. Common photochromic units used in photoswitching materials

Photochromic molecules are the basis of the photoswitching materials, as they can undergo reversible isomerization under light with a specific wavelength. Photoisomerization is used to describe the structural change of photochromic molecular. Along with their structural changes, the photo-induced isomerization contributes to a modification of the chemical and physical properties such as the color change of the photochromic compounds, the refractive index, dielectric constant, and oxidation/reduction potential [48].

### 2.1 Azobenzenes groups

Azobenzenes (AZBs) are perhaps the most widely used photochromic units, remaining particularly appealing today as they perform fast and efficient photo-isomerization [49]. AZBs constitute an azo group ( $\text{—N=N—}$ ) and appended aryl groups wherein E-to-Z (or *trans* to *cis*) isomerization occurs with  $\pi \rightarrow \pi^*$  electronic transitions when azobenzenes are exposed to UV light. Z-to-E isomerization occurs with  $n \rightarrow \pi^*$  electronic transitions upon absorption of visible light. The simplest and most basic AZB, azobenzene itself, comprises two phenyl rings and one N=N double bond (Figure 1 a). Azobenzene can transform from its *trans* isomer to its *cis* form under 365 nm UV light, and undergoes reverse isomerization when induced by 450 nm light or heating [38].



**Figure 1.** (a) Photoinduced isomerization of azobenzene. (b) Photoisomerization of DTEs. (c) Photoisomerization of Spiropyran.

In most cases, the azobenzene derivatives are selected by researchers. For example, one azo photochromic ligand, 2-(arylo)pyridines (PAP), has been used to prepare the light-triggered fluorescence modulation of Zn-porphyrins. In 2018, Dipanwita *et al.* embedded the MOF  $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})]_n$  (1), with PAP to introduce the isomerization within the pores of MOF by UV irradiation and reverse changed under thermal condition [50]. Notably, the MOF can not adsorb  $\text{N}_2$  because of the pore blockage by the guest PAP in the *trans* form.

The diffusion of  $\text{CO}_2$  within the porous crystalline nanochannel depends on the polar interaction with the azo-appended channel wall instead of a steric effect, which was reported by Huang *et al.* [51]. They proposed an azo-containing MOF (AzoMOF), where

1 *trans*-to-*cis* isomerization occurred with azo content of 21% upon UV light ( $365 \pm 10$  nm),  
2 and *cis*-to-*trans* isomerization occurred with azo content of 1% upon either visible light  
3 (420–480 nm) or heating.

4 Interpenetration often occurs within MOFs, however, it should be avoided for the purpose  
5 of photoswitching to avoid the negative influence on CO<sub>2</sub> capture with photoswitches. In  
6 2011, F. Modrow *et al.* reported interpenetrated azobenzene-derivatized MOFs,  
7 [Zn<sub>2</sub>(NDC)<sub>2</sub>(1)], by a solvothermal method using 3-azo-phenyl 4,4' bipyridine(1), 2,6-  
8 naphthalene dicarboxylic acid, and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O [52]. The azobenzene - derivatized linker  
9 was covalently incorporated into the MOFs with permanent porosity (surface area: 554 m<sup>2</sup> g<sup>-1</sup>,  
10 micropore volume: 0.23 cm<sup>3</sup> g<sup>-1</sup>). In the switching experiments, it could be changed to the  
11 *cis*-isomer by exposure to UV light ( $\lambda = 365$ nm) for 1 h and the *cis*-isomer could be partially  
12 recovered with visible light ( $\lambda = 440$ nm) for 1 h or leaving at room temperature in the dark  
13 with a period of 24 h. The author mentioned the existence of interpenetration and the  
14 requirement of avoiding it.

15 In 2013, Brown *et al.* reported a non-interpenetrated photoswitching MOF, azo-IRMOF-74-III,  
16 synthesised using Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and an azo-functionalized linker [53]. The isomerisation  
17 between *trans*- and *cis*- isomers of the azobenzenes was shown to influence the size and  
18 shape of the MOF pores. UV irradiation afforded the *trans* conformation, causing the size of  
19 the pore to increase from 8.3 Å to 10.3 Å. The Brunauer-Emmett–Teller (BET) surface of the  
20 sample showed notably higher, at 2410 m<sup>2</sup> g<sup>-1</sup>.

## 27 **2.2 Diarylethenes groups**

28 Compared to AZBs, diarylethenes (DArEs) have better thermal stability and higher fatigue  
29 resistance [54]. They constitute two aromatic groups linked by a C=C double which undergo  
30 reversible 6 $\pi$ -electrocyclic reactions when irradiated with light. The fundamental mechanism  
31 behind using DArEs involves cyclization and cyclo-reversion isomerization upon UV and  
32 visible light, respectively. These materials generally change from colourless to a variety of  
33 colours depending on their conjugation. To improve the stability of the photogenerated  
34 cyclic product, DArEs can be modified by replacing the C=C double bond or the aromatic  
35 units. For example, by ortho-substitution of the aromatic units, the resultant  
36 1,2-dithienylethene derivatives (DTEs) can change from the coloured form with UV light to  
37 the colourless form with visible light, which is reversible photocyclization reactions (Figure  
38 1b). MOFs containing diarylethenes are usually named as DMOFs. It is reported that the  
39 cyclization mechanisms of DTEs means less marked geometrical changes than for azo group-  
40 based ones.

41 In 2013, Katz *et al.* prepared MOFs incorporated with imidazolate-based dithienylethene  
42 switches, PSZ-1, based on ZIF-70 (synthesized by Zn (II), imidazole, and 2-nitroimidazole) *via*  
43 a solvent-assisted linker exchange method [55]. With the ring of dithienylethene open to  
44 close, PSZ-1 converted from yellow to violet crystals in UV light. When exposed to visible  
45 light, closed-PSZ-1 reverted to the open-PSZ-1. The BET surface area of PSZ-1 was 1250 m<sup>2</sup> g<sup>-1</sup>.

## 54 **2.3 Spiropyrans groups**

55 Apart from photochromic azobenzene, diarylethene, spiropyrans (SP) also have been studied  
56 and loaded in MOFs for light-triggered ring open/closing reactions (Figure 1c). In the process  
57 of isomerisation with a corresponding colour change, heterocyclic ring cleaves at the C–O  
58 spiro bond with the production of merocyanine (MC), and it returns to the initial close-ring  
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1 form through heat treatment or irradiation by visible light ( $\lambda > 450$  nm) or simple heating.  
2 Although the spiropyran-loaded MOFs have not been reported in the CO<sub>2</sub> switching field,  
3 further study is still worthwhile.

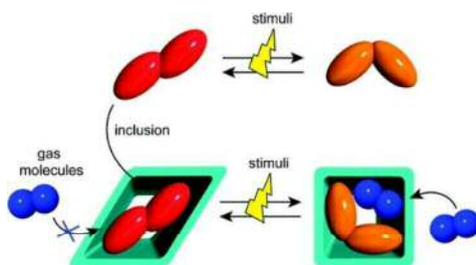
4 In 2015, Zn-MOF-74 crystal was introduced with spiroindolinobenzopyran (SPH) to obtain  
5 orange/yellow crystals SPH (SPH@MOF-74) [56]. Upon UV light irradiation (365 nm),  
6 SPH@MOF-74 converted to the dark yellow form. When the sample was heated at 80 °C,  
7 they converted to dark red form; whereas, after the cooling treatment at 0 °C for 50 h, the  
8 sample returned yellow.  
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### 10 11 12 13 14 **3. The preparation method of photoswitching MOFs as CO<sub>2</sub> adsorbents**

15 Photoswitching MOFs are perhaps one of the most promising stimuli-responsive functional  
16 materials due to their large adsorption capacities, and their flexibility in design that can be  
17 harnessed for the introduction of photochromic groups within their pore structure [39].  
18 Light irradiation can increase the surface energy of MOFs, leading to the weakening of  
19 intermolecular interactions between CO<sub>2</sub> and the surface, thus triggering the release of CO<sub>2</sub>.  
20 Generally, photochromic compounds are integrated within MOFs following one of the  
21 following four routes: (1) as a guest within MOFs inner cavities, (2) as surface pendant  
22 groups decorated the organic linkers of MOFs through a covalent bond, (3) as the backbone  
23 of the MOFs, or (4) by combining with chemical adsorption sites. As far as the CO<sub>2</sub> capture  
24 ability, the higher BET surface area can lead to better ability [57, 58]. However, in many  
25 cases, CO<sub>2</sub> capture capacity is decided by the combined effects from several factors including  
26 surface area and surface affinity towards CO<sub>2</sub> [59]. For the photoswitching MOFs as CO<sub>2</sub>  
27 sorbents, the influence of the photoswitching state relies on minor structural modifications  
28 and differences of the embedded groups [60].  
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#### 30 31 32 33 34 **3.1 As a guest within MOFs inner cavities**

35 This first approach is challenging with respect to providing good performance in terms of  
36 pore size, effectiveness, and flexibility because pore space may be occupied by the guest  
37 molecules. In 2012, MOFs decorated with azobenzenes were demonstrated by Kitagawa *et*  
38 *al.*, who accommodated *trans*-azobenzene inside the  
39 Zn<sub>2</sub>(terephthalate)<sub>2</sub>(triethylenediamine), at 120 °C for 12 h to form host-guest composites  
40 [61]. The tetragonal host structure completely transformed to orthorhombic networks upon  
41 UV light exposure while the *trans* azobenzene turned into *cis*-azobenzene (Figure 2).  
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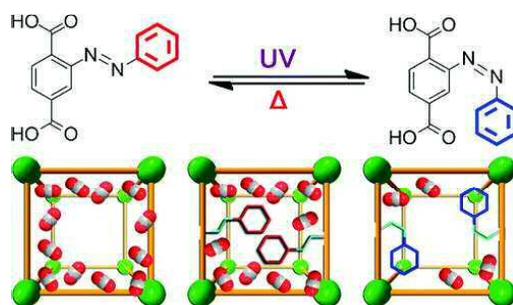
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55 **Figure 2.** Illustration of the conformational change triggered by light in the MOFs,  
56 Zn<sub>2</sub>(terephthalate)<sub>2</sub> (triethylenediamine), with azobenzene as the guest molecule (the  
57 red represents *trans*-AB while the orange represents *cis*-AB). Reprinted (adapted) with  
58 permission from 61. Copyright (2012) American Chemical Society.  
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1 The sample with *trans*-azobenzene could not adsorb N<sub>2</sub>, but it could adsorb N<sub>2</sub> after UV  
2 irradiation with mostly *cis*-azobenzene. Then, by heating at 120 °C for 1 h, *cis*-azobenzene  
3 transformed reversibly back to *trans*-azobenzene, and N<sub>2</sub> adsorption decreased substantially.

4 In 2013, Walton *et al.* prepared photoresponsive DMOFs containing non-covalent DTEs  
5 (DMOF-1@DTE) by heating a mixture of DMOF-1 and DTE-o at 130 °C overnight [62]. Upon  
6 UV light irradiation (365 nm), the sample immediately turned from the colourless state to  
7 the dark red state. When it was exposed to visible light, the crystals reverted to their initial  
8 colourless state. The samples showed thermal stability when wrapped in foil and placed in  
9 the dark for one month. However, the authors did not present results for porosity or CO<sub>2</sub>  
10 capture tests. Moreover, this method has the significant shortcoming that pores may be  
11 occupied by the guest molecules and therefore space for the structural change induced by  
12 isomerisation is limited; thus, the sorption and photo-isomerisation of CO<sub>2</sub> sorbents may be  
13 weakened.  
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### 17 3.2 As surface pendant groups decorated the organic linkers by covalent bond

18 Currently, covalently bonding the photochromic unit to the organic linker as a surface  
19 pendant group has been much researched. In 2011, Park *et al.* synthesized CO<sub>2</sub> adsorbents,  
20 PCN-123 (PCN represents porous coordination networks) with each cubic cavity occupied by  
21 azobenzene groups (Figure 3) [63]. Under UV light and at 1 bar and 295K, CO<sub>2</sub> adsorption  
22 reduced from 41.21 mg g<sup>-1</sup> to 18.90 mg g<sup>-1</sup> for 5 h, which is significantly slower than the  
23 original *trans-cis* change of azobenzene groups. Additionally, the original state of the  
24 adsorbent recovered with almost unchanged CO<sub>2</sub> uptake capacity after 20 h in ambient  
25 conditions or gentle heating. Accordingly, the pore size distributions changed after UV  
26 irradiation and almost returned to the original state after heat treatment. The advantage of  
27 PCN-123 lies in the large capacities of CO<sub>2</sub> adsorption but the negligible ability of N<sub>2</sub> under  
28 facile reversion conditions, while its disadvantage is the slower isomerisation change of  
29 azobenzene groups due to its steric hindrance inside the pores.  
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48 **Figure 3.** (Top) The reverse isomerization of the PCN-123 upon UV irradiation/heat  
49 treatment. (Bottom) Illustration of CO<sub>2</sub> adsorption in MOF-5, *trans* PCN-123, and *cis* PCN-  
50 123. Reprinted (adapted) with permission from 63. Copyright (2012) American Chemical  
51 Society.  
52

53 Some researchers report the success of photoswitches embedded in MOFs, but  
54 photoswitching CO<sub>2</sub> adsorption has been reported less. However, with the good capability of  
55 capturing CO<sub>2</sub> and demonstrating photoswitching, MOFs show the potential of being  
56 photoswitching adsorbents of CO<sub>2</sub>. In 2012, Antje used Cr-MIL-101-NH<sub>2</sub>, p-  
57 phenylazobenzoylchloride (1) and 4-(phenylazo)phenylisocyanate (2) to obtain Cr-MIL-  
58 101\_amide and Cr-MIL-101\_urea [64]. Cr-MIL-101\_amide and Cr-MIL-101\_urea were  
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1 compared to confirm the influence of functional groups on the isomerisation of AZBs upon  
2 UV/Vis irradiation. In 2017, James *et al.* reported a 3D coordination framework,  
3  $[Zn_4(tbazip)_3(bpe)_2(OH)_2] \cdot bpe \cdot \{solvent\}$  (where  $bpe = 1,2\text{-di}(4\text{-pyridyl})\text{ethene}$ ), containing the  
4 photoactive ligand  $tbazip$  ( $tbazip = 5\text{-}((4\text{-tert-butyl})\text{phenylazo})\text{isophthalic acid}$ ) [65]. The  
5 photoisomerization of *trans-cis* and *cis-trans* occurred successfully after exposure to UV  
6 light and the removal of light, respectively. The BET surface area of this MOF is  $30 \text{ m}^2 \text{ g}^{-1}$  and  
7 its  $\text{CO}_2$  adsorption at 298 K reached up to  $127.6 \text{ mg g}^{-1}$  at 1.1 bar.  
8

9 As far as these cases, the introduced surface pendant groups are bonded to the sorbents  
10 chemically, which adds to the stability of photoswitching sorbents. However, the pore size,  
11 effectiveness, and flexibility of the sorbent may be reduced because the pendant groups are  
12 still located within the pores.  
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### 15 3.3 As the backbone of the MOFs

16 The third way to design photoresponsive MOFs is to directly incorporate the photochromic  
17 units into the “backbone” of the ligands, which provide the space for the most dramatic  
18 photoisomerization.  
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20 In 2013, Hill *et al.* explored the design of a triply-interpenetrating porous framework,  
21  $Zn(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ , combining zinc-based MOFs with two photoresponsive ligands (4,4'-  
22 dicarboxylate (AzDC) and *trans*-1,2-bis(4-pyridyl) ethylene (4,4'-BPE)) [47]. With UV  
23 irradiation, the  $\text{CO}_2$  adsorption decreased by 64% during dynamic measurements,  
24 performing better than that under static irradiation conditions (42%). Its high performance  
25 under dynamic conditions is an advantage of this material, along with its full reversibility.  
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28 In 2015, Luo *et al.* successfully introduced ABZs into  $\text{Co}_3(\text{L})_2(\text{AzDC})_3$   
29 ( $\text{L} = \text{N}^1, \text{N}^3\text{-dipyridin-4-ylisophthalamide}$ ;  $\text{H}_2\text{AzDC} = 4,4'\text{-diazene-1,2-diyldibenzoate acid}$ ) to form  
30 ECUT-15 [66]. Under UV light at 298 K and 1 bar, the  $\text{CO}_2$  adsorption capacities of ECUT-15  
31 sharply decreased from 11.34 to  $5.76 \text{ mg g}^{-1}$ , representing a ~45% reduction. In the dynamic  
32 reversible adsorption/desorption test without/with UV light irradiation, the release of  $\text{CO}_2$   
33 increased up to 78% instantaneously. The change upon UV light exposure and instantaneous  
34 reversibility represents improve performance versus the results above.  
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37 In 2018, Bradley *et al.* synthesized Zn-azo-dabco MOF (Azo-DMOF-1) with both  
38 2-phenyldiazanyl terephthalic acid and 1,4-diazabicyclo[2.2.2]octane (DABCO) as the  
39 ligands [67]. The Azo-DMOF-1 exhibits a microporous structure with a BET surface area of  
40  $581 \text{ m}^2 \text{ g}^{-1}$ . The  $\text{CO}_2$  uptake of the original Azo-DMOF-1 was around 143.39 (273 K) and  $73.78$   
41  $\text{mg g}^{-1}$  (298 K). After UV irradiation, the  $\text{CO}_2$  adsorption decreased to 70.71 and  $52.19 \text{ mg g}^{-1}$   
42 at 273 and 298 K, respectively. In the dynamic photo-switching experiment, with the UV light  
43 switched on/off,  $\text{CO}_2$  adsorption reduced/returned to the original level.  
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46 Using organic ligands as the backbone of the MOF avoids the occupation of pore space, but  
47 in some cases, the isomerization of the organic ligands may be constrained. As shown in  
48 Table 1, the  $\text{CO}_2$  adsorption of MOFs is decreased after UV irradiation. However, there is one  
49 counter-example from Luo *et al.*, who reported DMOF,  $Zn(\text{L})(\text{bpdc})$ , consisting of  
50  $Zn(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ ,  $\text{H}_2\text{bpdc}$ , and diarylethene derivative (L) [68]. The sample turned blue upon  
51 exposure to 300 nm light for 1 min, while the blue colour disappeared with the exposure to  
52 visible light. Although this DMOF cannot adsorb  $\text{N}_2$ , it performed well in  $\text{CO}_2$ -adsorption tests.  
53 The  $\text{CO}_2$ -adsorption of DMOF increased after UV irradiation from  $9.00 \text{ mg g}^{-1}$  to  $39.48 \text{ mg g}^{-1}$   
54 at 298 K. This  $\text{CO}_2$  desorption capacity of this DMOF performs remarkably with visible light  
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(600 nm), with 75% or 76% change under static or dynamic irradiation, demonstrating promise for application in photoswitching adsorbents.

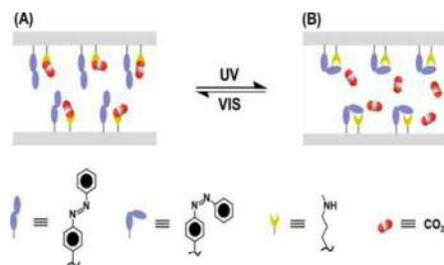
In terms of application, reusability, moisture resistance and chemical tolerance are very important. To overcome these challenges, Hill *et al.* reported a robust photoresponsive MOF, PCN 250, using 6 connected  $\text{Fe}_2\text{Co}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6$  metal clusters and tetratopic 3,3', 5,5'-azobenzene tetracarboxylic acid (ABTC) ligands [69]. The BET surface area of the sample was  $1486 \text{ m}^2\text{g}^{-1}$ , and its  $\text{CO}_2$  adsorption capacity was  $285.80$  (273 K) and  $136.05 \text{ mg g}^{-1}$  (298 K) at 1 bar, while the  $\text{CO}_2$  desorption can be altered by light intensity. In addition, after five cycles of  $\text{CO}_2$  adsorption/desorption at 120 mbar with the light switched off and separately with exposure to water, its stability was demonstrated in wet conditions ( $\text{CO}_2$  uptake and light-triggered  $\text{CO}_2$  desorption decreased by 7.3 % and 4.9 %, respectively).

### 3.4 Combining with chemical adsorption sites

The physical interaction between  $\text{CO}_2$  and the photochromic units can be enhanced by the introduction of photochromic units into adsorbents. One recent strategy has been used to prepare photoswitching adsorbents while also improving  $\text{CO}_2$  adsorption capacity through the introduction of active chemical sites and photochromic molecules at the same time. Therefore, the disadvantage of the weak interaction between  $\text{CO}_2$  molecules and adsorbents can be avoided.

In 2018, Sun's group demonstrated an interesting strategy in which both photoswitching AZBs and active amine were introduced into mesoporous silica simultaneously to afford photoswitching adsorbents, as shown in Figure 4 [70]. The BET surface area of  $\text{A}_2\text{P}_2\text{@MS}$  was  $797 \text{ m}^2\text{g}^{-1}$ . After UV irradiation, the  $\text{CO}_2$  adsorption capacity decreased because surface electrostatic potential increased, leading to the blockage of active sites. However, visible light irradiation led to *trans* azobenzene, thus active sites were again exposed and could capture  $\text{CO}_2$ . The  $\text{CO}_2$  adsorption amount of  $\text{A}_2\text{P}_2$  increased from  $72.4 \text{ mg g}^{-1}$  under UV light irradiation to  $112.3 \text{ mg g}^{-1}$  (35.6%) under visible light irradiation at 273K. As amines also contribute to good selectivity of  $\text{CO}_2/\text{CH}_4$ , this selection could also be tuned by the change of irradiation light. Subsequently, the researchers went on to report the preparation of photoresponsive MOF adsorbents through a similar strategy where specific chemical active sites (amines) were used together with azobenzene for  $\text{CO}_2$  capture [71]. The optimal sample showed  $85.25 \text{ mg g}^{-1}$  for  $\text{CO}_2$  adsorption capacity in the *cis* state, decreasing to  $53.63 \text{ mg g}^{-1}$  in *trans* state at 273K, corresponding to 45.6% of the adsorption capacity.

The drawback of the first and second approaches is the diminished pore size, limited



**Figure 4.** Control of  $\text{CO}_2$  adsorption behaviour through an interplay between amines sites and photoswitching molecules. Adapted with permission from [70]. Copyright (2018) American Chemical Society.

1 effectiveness, and lower flexibility of the sorbent because pore space is mostly occupied by  
2 the guest molecules. The third method may avoid these problems because no molecules  
3 occupy the pores, which brings full accessibility to the MOFs. But the disadvantage upon  
4 isomerization of geometrical changes in the backbone of the framework may constrain  
5 photoisomerization efficiency, where lies challenges. The fourth method represents a novel  
6 route to increasing CO<sub>2</sub> capture capacity at the same time as realizing a photoswitch, and  
7 thus the challenge lies in the design of the reaction between CO<sub>2</sub> molecules and the  
8 selection of functional groups in the porous materials. Photoswitching MOFs are promising  
9 sorbents for CO<sub>2</sub> because most MOFs show good adsorption capacity for CO<sub>2</sub>, and they  
10 possess controllable pore structure and adjustable pore surface properties. The main  
11 challenges are related to the selectivity to CO<sub>2</sub> adsorption. However, the bestowing of a  
12 photoswitching property to a porous material such that it can be controlled from an “on”  
13 state to an “off” state in a reversible pattern by light exposure will very likely reduce energy  
14 consumption in the overall process.  
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18 In addition, the amount of CO<sub>2</sub> captured after light irradiation is generally less than that  
19 before irradiation. It is noted that ECUT-15 shows very high performance, such that the  
20 changes under static and dynamic conditions were up to 45% and 78%, respectively. The  
21 capabilities of CO<sub>2</sub> adsorption and the pore size distribution may be affected by the hindered  
22 isomerization of AZBs inside MOF pores. Meanwhile, the reversible control for multiple  
23 cycles under UV or heating provide great potential for further research.  
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## 28 **4. Photoswitching POPs as CO<sub>2</sub> adsorbents**

29 Most reported POPs are designed with azo groups because they are sufficiently N<sub>2</sub>-phobic so  
30 that adsorption and selectivity of CO<sub>2</sub> can be enhanced. Generally, the photochromic unit  
31 can be attached to the polymeric backbone or the chain end [72]. The challenge of designing  
32 photoresponsive polymers lies in the relatively large free volume change associated with  
33 isomerization. However, few of them have made use of the potential of photoswitching  
34 adsorption and desorption of CO<sub>2</sub>.  
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### 39 **4.1 POPs embed with photoswitching units as CO<sub>2</sub> adsorbents**

40 At the beginning of POPs research using photochromic units, photo-switch is not focused. In  
41 2013, Coskun and Yavuz *et al.* synthesized azo-linked covalent organic polymers (azo-COPs)  
42 by catalyst-free direct coupling of aromatic nitro and amine moieties at 150 °C for 24 h [73].  
43 The BET surface areas of these azo-COPs were 635, 729, and 493 m<sup>2</sup> g<sup>-1</sup>, but their CO<sub>2</sub>/N<sub>2</sub>  
44 selectivity was unprecedentedly high (288.1 at 323 K).  
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48 In 2014, Zhang's group developed two types of Azo-POF (Azo-POF-1, Azo-POF-2) through a  
49 Zn-induced reductive homocoupling reaction on tetra(4-nitrophenyl) methane at 65 °C for  
50 36 hours [74]. The obtained CO<sub>2</sub> adsorption of Azo-POF-1 and Azo-POF-2 at 273/298 K and 1  
51 bar were 131/82.9 and 84.5/55.1 mg g<sup>-1</sup>, respectively. Azo-POF-2 exhibited a CO<sub>2</sub>/N<sub>2</sub>  
52 selectivity of 76/54 at 273/298 K.  
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55 In the same year, El-Kaderi *et al.* synthesized highly porous azo-containing organic polymers  
56 (ALPs) *via* oxidative coupling using tetra(4-aminophenyl) methane for 48 hours (at room  
57 temperature for 24 h, 60 °C for 12 h, and 80 °C for 12 h) [75]. All ALPs showed remarkable  
58 CO<sub>2</sub> adsorption capacities with the highest of 236 mg g<sup>-1</sup> at 273 K and 1 bar, and 143 mg g<sup>-1</sup>  
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1 at 298 K and 1 bar, as well as an outstanding BET surface area of about 1235 m<sup>2</sup>g<sup>-1</sup> (ALP-1).  
2 The researchers then attempted to synthesize new types of ALPs based on rigid star-shaped  
3 monomers with nitrogen-rich building units using the same method [76]. Star-like shapes are  
4 attractive designs because the relatively larger space and the better rigidity of the  
5 frameworks can inhibit a close-packed arrangement within crystals, thus contributing to the  
6 formation of porous molecular crystals where photoisomerization occurs. Among the series  
7 of polymers produced by this group, ALP-5 is outstanding among ALPs with relatively higher  
8 CO<sub>2</sub> adsorption capabilities of 196.24 mg g<sup>-1</sup> and 129.36 mg g<sup>-1</sup> at 1 bar and 273K/298K, and  
9 selectivity for CO<sub>2</sub>/N<sub>2</sub> of about 44 at 298 K.

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11  
12 In 2015, Lyu *et al.* used a similar method to prepare azo-linked porous polyporphyrins (azo-  
13 PPors) using meso-tetra(4-nitrophenyl) porphyrin and aromatic amines at 150 °C for 24 h  
14 [77]. The CO<sub>2</sub> adsorption capacity of the polymers reached up to 107.8 mg g<sup>-1</sup> at 1 bar, 273 K.

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17 Though such progress has been made, it is still desirable to propose a simpler and more  
18 efficient route to produce Azo-POPs with high adsorption capacity for CO<sub>2</sub> under milder  
19 conditions.

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21 In 2015, Liu's group used oxidative polymerization to produce Azo-MOPs with azo-type  
22 ligands: tetrakis(4-aminophenyl)methane(A-1), 2,6,14-triaminotriptycene(A-2), 1,  
23 3,5-tris(4-aminophenyl)benzene(A-3) and tris(4-aminophenyl)amine (A-4) as the building  
24 blocks and t-BuOCl/NaI as the oxidant at room temperature (e.g., 25 °C, 1 h) [78]. The Azo-  
25 MOPs (pore diameters < 2 nm) were applied for CO<sub>2</sub> adsorption and conversion at room  
26 temperature, with high adsorption capacity and thermal stability. Azo-MOP-2 exhibited the  
27 best CO<sub>2</sub> adsorption among the four Azo-MOPs in their work, at 134.8 mg g<sup>-1</sup> (1 bar and 273  
28 K).

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31 In 2018, Huang *et al.* reported a quick route to prepare azo-linked POPs *via* a NaBH<sub>4</sub>-  
32 mediated coupling reaction on four-folded nitro-containing monomers [79]. The BET surface  
33 areas of the Azo-POPs reached 1478 m<sup>2</sup>g<sup>-1</sup>, scalable to the 5 g scale. According to their  
34 analysis results of the mechanism, the reaction type (coupling reaction) and the reducing  
35 agent (NaBH<sub>4</sub>) are the main reasons for the large surface areas.

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38 The studies above focus on the synthesis of POPs embedded with azo groups and used as  
39 CO<sub>2</sub> adsorbents; however, none of them report photoresponsivity, unlike the following  
40 studies. Taking advantage of the structural change resulting from photoisomerization, the  
41 porosity and CO<sub>2</sub> adsorption/desorption may be controlled.

#### 42 43 44 45 **4.2 Photoswitching POPs as CO<sub>2</sub> adsorbents**

46  
47 In 2014, Zhang's group developed the photoswitching UCBZ polymer series with five types of  
48 diamine through Schiff-base chemistry at 150 °C [80]. Their pore size distributions and CO<sub>2</sub>  
49 adsorption capacity can be reversibly transformed upon UV irradiation. CO<sub>2</sub> adsorption of  
50 the UCBZ polymer increased by the conversion from *trans*-isomer to *cis*-isomer. Among the  
51 UCBZ series, UCBZ-1 was the highest in terms of CO<sub>2</sub> adsorption (76.61 mg g<sup>-1</sup> at 273 K and 1  
52 atm), which climbed to 98.21 mg g<sup>-1</sup> upon nine-minute UV irradiation (29% increase). The  
53 reason given for the material's photo-responsiveness was the negative effect of bearing a  
54 bulky substituent. In addition, these POPs were shown to have good stability and nearly full  
55 reversibility since similar adsorption properties were found after multiple cycles of  
56 alternating external stimuli.

1 In 2015, Baroncini *et al.* reported a series of star-like and rigid crystals, E4-1(a–c), based on  
2 Mills coupling at room temperature [81]. By using different nitrosobenzene moieties with H,  
3 Me, or t-Bu, their porosity increased with the size of the end groups. Exposure to UV light,  
4 the crystallinity and porosity of E4-1(a–c) disappeared, but the crystals were reproduced  
5 with porosity, upon visible light irradiation or heating. Reversible switching between “on”  
6 and “off” corresponding to porous and non-porous states was successful. The porous  
7 crystals of E4-1c were reported to have maximum CO<sub>2</sub> adsorption of 805.36 mg g<sup>-1</sup> and  
8 628.57 mg g<sup>-1</sup> at 10 bar and 273 and 298 K, respectively. The selectivity of CO<sub>2</sub>/N<sub>2</sub> was  
9 observed to be as high as 80 for the E4-1b compound.

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12 In 2019, Li *et al.* also proposed a smart polymer membrane, Azo-COP-2, which showed  
13 exceptionally efficient CO<sub>2</sub> photoswitching in both static and dynamic conditions [82]. Azo-  
14 COP-2 was prepared without a metal catalyst on tetranitrophenyl methane at 150°C for 24 h.  
15 In both static and dynamic experiments with exposure to UV light, the CO<sub>2</sub> adsorption  
16 capacity of Azo-COP-2 significantly dropped from 93.28 mg g<sup>-1</sup> to 73.04 mg g<sup>-1</sup> at 273 K, and  
17 from 56.32 mg g<sup>-1</sup> to 46.2 mg g<sup>-1</sup> at 298 K.

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20 Aside from the AZBs used widely in these types of POPs, studies using DArE groups have also  
21 been carried out. In 2015, Hill *et al.* accommodated DArE within porous aromatic  
22 framework-1 (PAF-1) to form DArE@PAF-1, which displayed photo-switching of CO<sub>2</sub> capture  
23 and release at room temperature [44]. Desorption of CO<sub>2</sub> increased by 65% (at 1 bar) by  
24 four-minute light irradiation. By analysing the competitive interactions between DArE and  
25 CO<sub>2</sub> molecules with the host, the authors reached the conclusion that multiple interactions  
26 may trigger CO<sub>2</sub> spontaneously release.

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30 In 2018, Luo *et al.* used triptycene (2,6,14 triiodotriptycene, P1) and diarylethene  
31 (2,6-diiodotriptycene, P2) via a Pd(0)-catalysed Suzuki coupling reaction (P1: at 80 °C for 48 h,  
32 P2: at 80 °C for 72 h) to gain linear and star-shaped porous polymers [83]. These two types  
33 of POPs displayed a reversible change in their specific surface areas and total pore volumes,  
34 owing to the photoisomerization of DArEs upon UV or visible light exposure. In detail, colour,  
35 surface area, and pore volume are converted in the solid form or THF solution under UV light  
36 (254 nm) for a few minutes. With the isomerization of DArE upon UV light irradiation, the  
37 total pore volumes of P1/P2 decreased from 0.131/0.130 cm<sup>3</sup> g<sup>-1</sup> to 0.121/0.100 cm<sup>3</sup> g<sup>-1</sup>.  
38 When the light source was changed to visible light, the total pore volumes of P1 and P2  
39 increased to 0.126 and 0.127 cm<sup>3</sup> g<sup>-1</sup>, respectively.

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42  
43 In summary, POPs with photoswitching units have been synthesized through a range of  
44 methods as shown in Table 2. Among them, the reductive homocoupling reaction is used  
45 most frequently. In terms of the synthesis process, preparation of E4-1a/b/c is the most  
46 feasible as it is photoswitching, time-efficient, conducted in the atmosphere, and scalable to  
47 the 5 g. On the other hand, Azo-POP-1 shows the highest surface area among the POPs  
48 mentioned here (1478 m<sup>2</sup> g<sup>-1</sup>), but the study lacked related test results for further  
49 application such as the CO<sub>2</sub> adsorption test before and after irradiation under both static  
50 and dynamic states. ALP-1 also performs well in BET surface area (1235 m<sup>2</sup> g<sup>-1</sup>) and CO<sub>2</sub>  
51 adsorption (143 mg g<sup>-1</sup>), while its synthesis depends on the use of transition-metal catalysts  
52 (e.g., CuBr/pyridine), which is a significant problem in the real application. Therefore, a  
53 catalyst-free method has been introduced, but the low surface area of Azo-COP-2 is a  
54 significant disadvantage. Some of the aforementioned POPs have been researched for their  
55 sorption capacity of CO<sub>2</sub> and the selectivity of CO<sub>2</sub>/N<sub>2</sub>. For example, as shown in Table 2,  
56 Azo-COP-2 shows excellent CO<sub>2</sub>/N<sub>2</sub> selectivity (109.6 at 273K and 130.6 at 298K). In addition,  
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1 POPs with photoswitching units have been synthesized through reductive homocoupling  
2 reactions, oxidative coupling, catalyst-free direct coupling, oxidative polymerization, Mills  
3 coupling, and Suzuki coupling reaction. Among them, the reductive homocoupling reaction is  
4 expected to be time-efficient and lend itself to simple operating conditions, and potentially  
5 large-scale production. Most of the POPs with photoresponsive units are star-shaped  
6 because this shape can provide more space for the arrangement of the low-density  
7 molecular self-assembly within crystals.  
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10 In Table 2, two notable photo-switching POPs (UCBZ-1 and Azo-COP-2) are shown. The UCBZ  
11 polymers series are a special class of polymers because their adsorption capacity increases  
12 upon UV light irradiation, which is opposite to photo-switching MOFs. It is thought that the  
13 bulky substituents on the AZBs groups reduce the degree of responsiveness. On the other  
14 hand, COFs are more similar to MOFs in terms of structure as they are covalent, porous and  
15 crystalline containing organic units, ordered structure and nanopores [84]. Thus, COFs  
16 demonstrate a similar photoswitching phenomenon, in that CO<sub>2</sub> adsorption reduced after  
17 UV irradiation. Besides, COFs are interesting because they are low in mass density, highly  
18 thermally stable, and permanently porous [85].  
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21 Compared to photo-switching MOFs, less attention has been paid to photo-switching POPs.  
22 However, POPs are also a very potential candidate as CO<sub>2</sub> sorbents attributing to their  
23 relatively good porosity, stability, and adjustability. Two major challenges should be  
24 considered with respect to photoresponsive POPs for capturing CO<sub>2</sub>. The first challenge is  
25 the balance of various performance indicators for porous materials under irradiation,  
26 including adsorbent ability, CO<sub>2</sub>/N<sub>2</sub> selectivity, thermal stability, water stability, and light  
27 stability. The second important point is that the functionalized materials need to be able to  
28 accommodate reversible isomerization of photoactive moieties, as most of these switches  
29 (including AZBs and stilbenes) undergo large conformational changes upon isomerization.  
30 Hence, conformational freedom is required, although typically difficult under confinement.  
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**Table 2.** Comparison of POPs in synthesis, surface area, CO<sub>2</sub> uptake and corresponding CO<sub>2</sub>/N<sub>2</sub> selectivity at 273/298 K and 1 bar.

Materials	Monomer	Reaction type	Reaction conditions	Surface area (m <sup>2</sup> g <sup>-1</sup> )	CO <sub>2</sub> uptake (mg g <sup>-1</sup> )	CO <sub>2</sub> /N <sub>2</sub> selectivity <sup>a</sup>	Ref.
Azo-COP-2	Aromatic nitro and amine moieties	catalyst-free coupling	direct KOH, DMF, 150 °C, 24 h	729	-	-(109.6)/-(130.6)	[73]
Azo-POF-1	Tetrakis(4-nitrophenyl)methane, 1,1,2,2-Tetrakis(4-nitrophenyl)ethane	reductive reaction	Zn, NaOH, 65 °C 36 h	712	131.0/82.9	69(52)/46(37)	[74]
ALP-1	Tetra(4-aminophenyl) methane	oxidative coupling	CuBr, THF/toluene, 25–80 °C, 48 h	1235	236.0/143.0	35(40)/27(28)	[75–76]
Azo-PPor-1	Meso-tetra(4-nitrophenyl) porphyrin and aromatic amines	direct couplings	KOH, DMF, 150 °C, 24 h	750	107.8/-	-	[77]
Azo-MOPs-2 (N = 1–4)	Tetrakis(4-aminophenyl) methane(A-1), 2,6,14-triaminotriptycene(A-2), 1,3,5-tris(4-aminophenyl)benzene(A-3) and tris(4-aminophenyl)amine (A-4)	oxidative polymerization	<sup>t</sup> BuOCl/NaCl, Solvent, 25 °C, 1 h	706	134.8/-	-	[78]
Azo-POP-1 (N = 1–3)	Tetra (4-nitrophenyl)methane (TPM-4NO <sub>2</sub> ), Tetra(4-nitrophenyl)adamantane (TPA-4NO <sub>2</sub> ), 1,1,2,2-tetrakis(4-nitrophenyl)ethene	reductive homocoupling polymerization	NaBH <sub>4</sub> , DMF, 85 °C, 30 min	1478	-	-	[79]
UCBZ-1	Diamines, 1, 3, 5-triformylphloroglucinol, 1,4-dioxane (4 mL), mesitylene	Schiff-base chemistry	Acetic acid, 150 °C, >2 h	980	76.6→98.2 <sup>b</sup>	-	[80]
E <sub>4-1b</sub>	4: tetra(4-aminophenyl)methane, b: 4-nitrosotoluene	Mills coupling	CH <sub>3</sub> COOH, RT, overnight	-	-	80	[81]
Azo-COP-2	Tetrakisnitrophenyl methane, phenylenediamine	metal method	catalyst-free KOH, DMF, 150 °C, 24 h	554	93.3/56.3→7	-	[82]
P2	Diarylethene boric acid with 2, 6-diodotriptycene and 2, 6, 14-triiodotriptycene	Suzuki coupling reaction	K <sub>2</sub> CO <sub>3</sub> , Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF, 80 °C, 48 h	41/36 <sup>d</sup>	--	-	[83]

<sup>a</sup> Selectivity (mol mol<sup>-1</sup>) was calculated by the initial slope method and the IAST method in brackets at 273/298K.<sup>b</sup> The adsorption was tested at 273K and 1 atm. before and after UV irradiation for 9 minutes, increased by 29%.<sup>c</sup> Under the static experiment, the CO<sub>2</sub> adsorption was test before and after UV irradiation.<sup>d</sup> BET surface area of P2 before and after UV irradiation.

## 5. Application of Photo-switching materials applied in DAC

Most of the photoresponsive sorbents have not been used to confirm whether they are suitable for DAC. But some research results do imply the potential for photoswitching porous materials in DAC. Used as DAC sorbents, they should perform well in terms of physical/chemical stability, selectivity of CO<sub>2</sub>/H<sub>2</sub>O or CO<sub>2</sub>/N<sub>2</sub> at atmospheric concentrations.

Visible-light control on adsorption and desorption of CO<sub>2</sub> is more attractive as the application can be used more widely. Lyndon *et al.* demonstrated visible photoresponsive o-methyl red (MR) guest molecules on Mg-MOF-74 and MIL-53(Al) (Figure 5) [45]. Under static conditions in visible light, MOF-74@MR and MIL-53(Al)@MR adsorbed CO<sub>2</sub> and relaxed to the previous state after left in the dark. The total uptake of MOF-74@MR increased by 84% after it was statically irradiated for 1 h. For MIL-53(Al), CO<sub>2</sub> uptake increased by 46%, with 50 wt% guest loading upon visible light irradiation. The increase was said to be due to the pore opening effect derived from the movement of MR as it changed from *trans* to *cis* form by irradiation. Mg-MOF-74 is a promising adsorbent for DAC because of its good CO<sub>2</sub> adsorption capacity under atmospheric conditions, while the flexible MIL-53(Al) is also attractive due to its structural stability under the moisty condition [86]. The disadvantage of MOF-74@MR is the gradually diminishing performance in consecutive relaxation cycles, while MIL-53(Al) is lower in CO<sub>2</sub> uptake. However, both materials are promising since they are derived from cheap and widely available resources, follow easy preparation procedures and have low-cost operating conditions (visible light used, rather than UV).



**Figure 5.** Visible light-triggered MOF-74@MR and MIL-53(Al) @MR for CO<sub>2</sub> uptake. Reprinted (adapted) with permission from 45. Copyright (2015) American Chemical Society.

Cu-azobenzene tetracarboxylate MOF (JUC-62), reported by Prasetya and Ladewig, demonstrated highly efficient photoswitching, and was proven to be stable at ambient conditions [87]. Its dynamic photo-switching functionality remained unchanged, which also offers opportunities for its application in DAC. JUC-62 showed lower CO<sub>2</sub> uptake (51% at 273 K and 34% at 298 K) under UV light irradiation than that before UV light irradiation. During dynamic experiments of CO<sub>2</sub> adsorption, CO<sub>2</sub> adsorption decreased under the UV light but could return to the initial state without UV light.

To date, various types of photoswitching porous materials have been applied as CO<sub>2</sub> sorbents. The key to preparing materials that can be regenerated by light and applied in DAC are as follows. First, the introduced photochromic units should show high fatigue resistance for high repeatability. AZBs, DArEs, and their derivatives have been shown to behave well as incorporated moieties that introduce such photoswitching functionality. Second, the resultant photoswitching porous materials must show excellent properties such as high adsorption, excellent CO<sub>2</sub>/N<sub>2</sub> selectivity, and facile photoisomerization reactions between

1 isomers. Thus, space, where photochromic units are to be incorporated into porous  
2 materials, should be considered in advance. Third, specifically for DAC applications, the  
3 porous materials selected need to be stable in the air to avoid material decomposition.  
4 Although many of the photoswitching porous materials have been shown to retain  
5 performance for consecutive cycles, it is important and necessary to test the repeatability  
6 and stability of the materials under ambient conditions. Fourth, the cost of synthesis must  
7 also be considered, which is a vital element when considering this type of application. Any  
8 expensive reagent in sorbent synthesis is undesirable, as it negatively impacts both the  
9 scalability and sustainability of the technology. Due to a relatively small market for  
10 photochromic units, many need to be synthesized in the lab, which inevitably increases costs.  
11 Using light to regenerate these materials is economical, but the cost of the incorporated  
12 photochromic unit should also be accounted for. Finally, a challenge also lies in the use of  
13 UV light, which may limit the application. Using UV light implies the use of thin layers of the  
14 sorbent material since the penetration depth of UV radiation is inherently low. This  
15 constraint, therefore significantly decreases the attainable volumetric performance and  
16 visible-light-sensitive materials may be preferable.  
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## 22 **6. Conclusion**

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25 Up to now, azobenzene, diarylethenes and their derivatives are the most attractive and  
26 promising. A variety of reports have focused on using them to introduce photochromic units  
27 into porous materials. Herein, this paper reviews different types of photoswitching porous  
28 materials and demonstrates four ways to embed photochromic units into MOFs including: as  
29 a guest within MOFs inner cavities, as surface pendant groups decorated the organic linkers  
30 of MOFs through a covalent bond, as the backbone of MOFs and by combining with chemical  
31 adsorption sites. With photo-switching control, captured CO<sub>2</sub> usually decreases after light  
32 irradiation. ECUT-15 shows the best performance that the CO<sub>2</sub> adsorption capacity sharply  
33 decreased by 45% and 78% under static and dynamic conditions, respectively. It is noted  
34 that the strategy of combining both physisorption and chemisorption is also a potential  
35 route, as it can contribute photo-switching and reversibility under visible light irradiation  
36 (the CO<sub>2</sub> adsorption amount increased by 55.1 under visible light irradiation).  
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41 POPs with a switch triggered by light are reported less than MOFs. However, POPs are  
42 known to present greater stability in a variety of conditions and possess greater diversity in  
43 synthetic routes. More importantly, some reports of POPs prepared with AZBs or DArEs have  
44 shown high surface area by BET (Azo-POP-1: 1478 m<sup>2</sup> g<sup>-1</sup>), CO<sub>2</sub> adsorption (ALP-1: 143 mg g<sup>-1</sup>)  
45 and CO<sub>2</sub>/N<sub>2</sub> selectivity (Azo-COP-2: 110 at 273K and 131 at 298K). Therefore, there are great  
46 opportunities to be found in researching photoswitching POPs, albeit with associated  
47 challenges. Very recently, two cases have illustrated that POPs with photoswitches can be  
48 used to control CO<sub>2</sub> capture and release.  
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52 Most interestingly, if photo-switching porous materials are to be applied in DAC, CO<sub>2</sub>  
53 emissions can be captured and released utilizing the renewable energy source of light.  
54 Currently, several photo-switching porous materials, like JUC-62, have demonstrated high  
55 stability at ambient conditions, and unchanged photoswitching functionality after ambient  
56 storage. With respect to further applying photoswitching materials for DAC technologies,  
57 these materials must be tested under ambient conditions to confirm simultaneously  
58 unchanged photo-responsivity, high CO<sub>2</sub> capture capacity, high stability, and high selectivity  
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at ambient conditions.

## Conflicts of interest

There are no conflicts of interest to declare.

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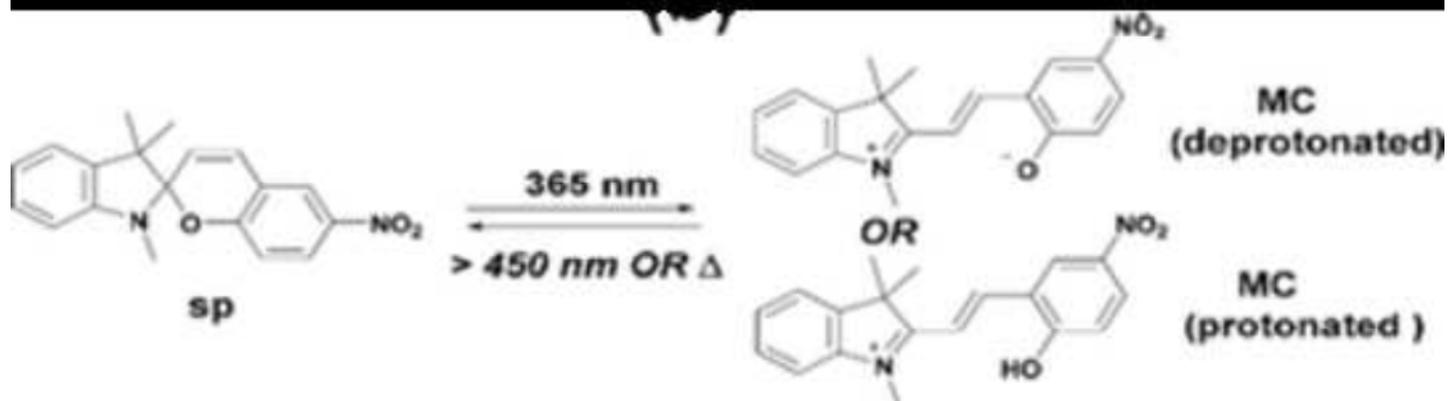
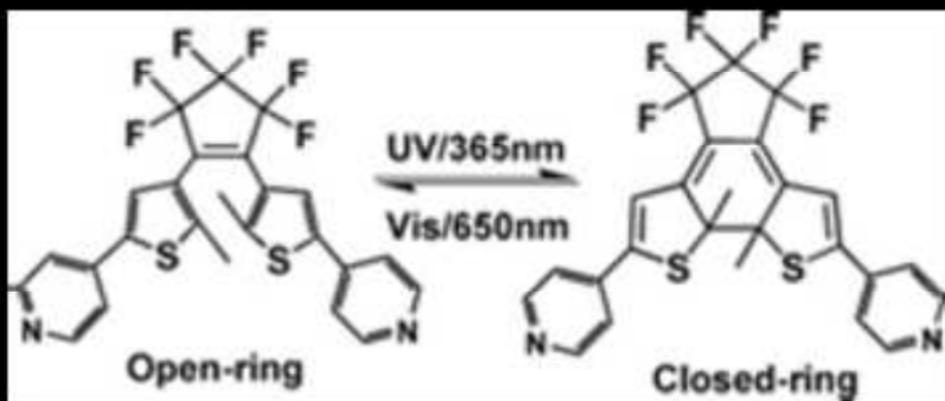
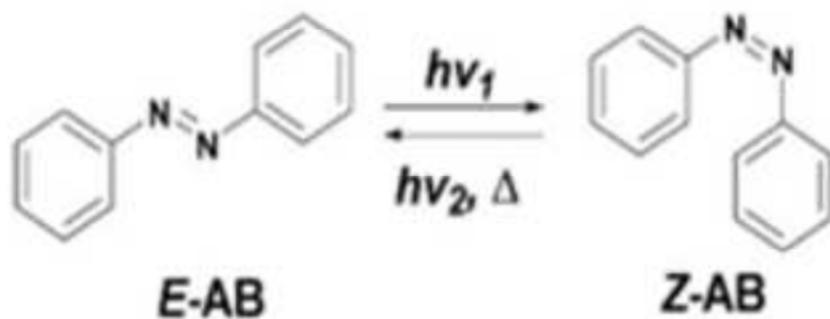
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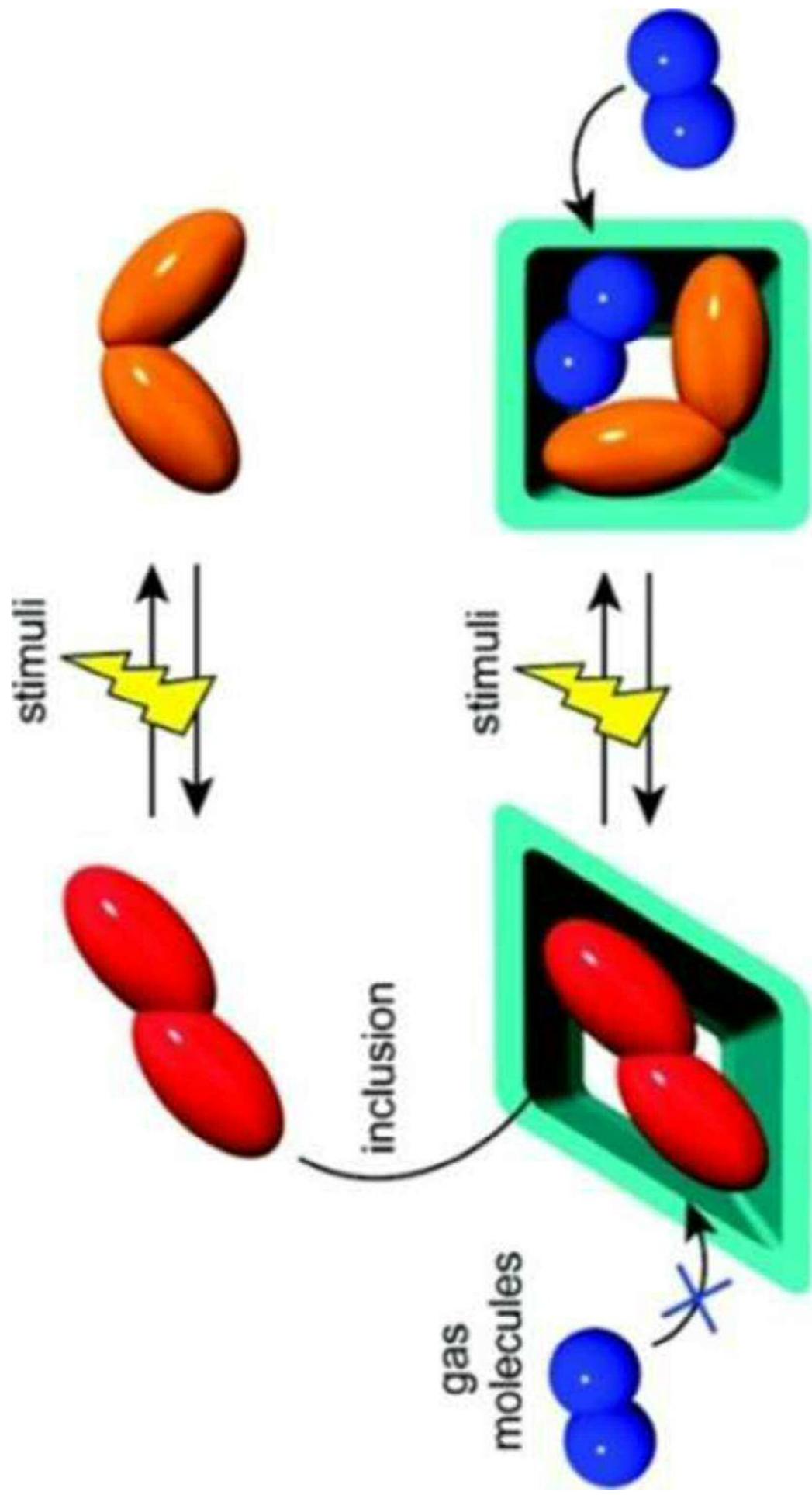
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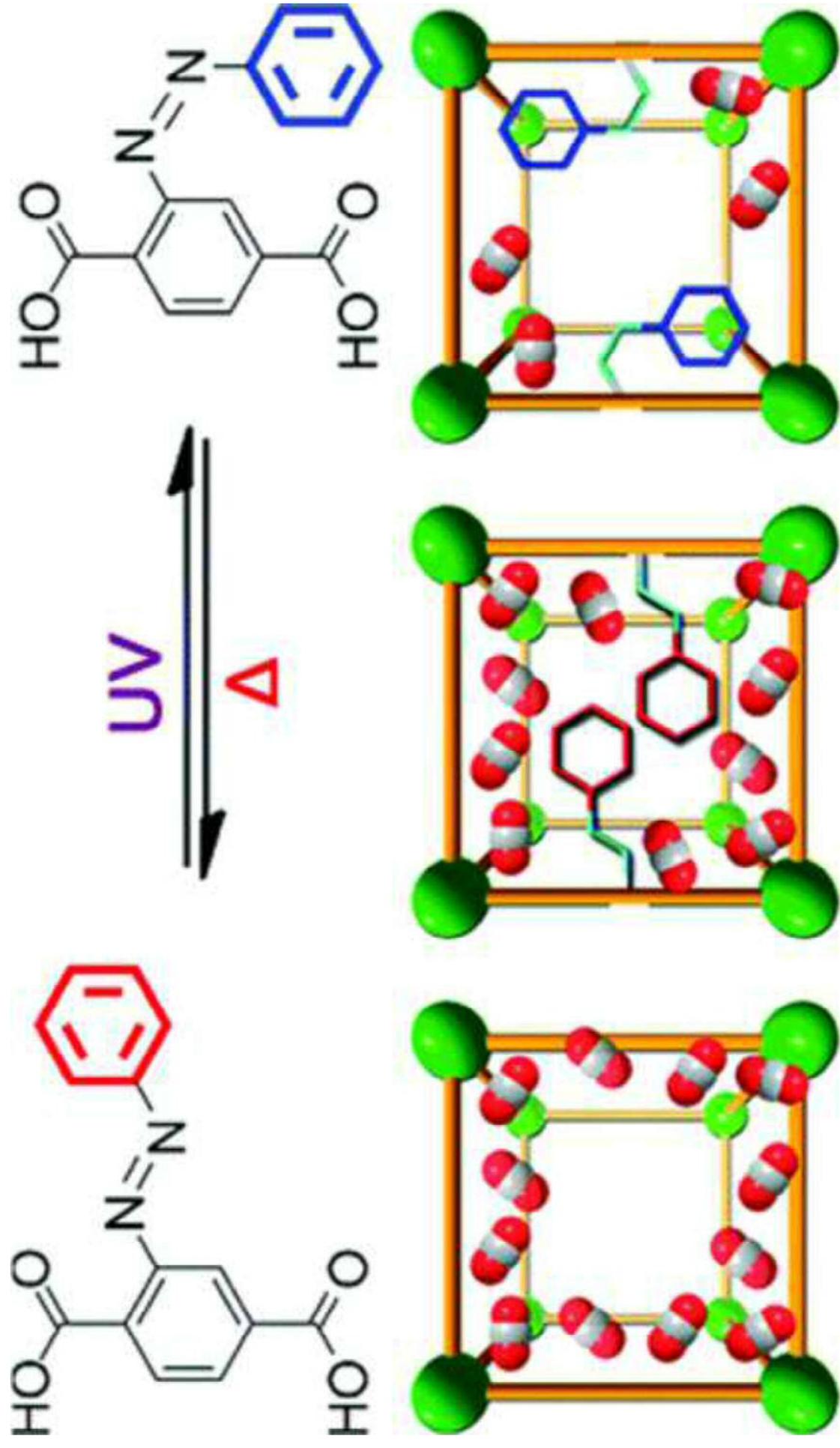
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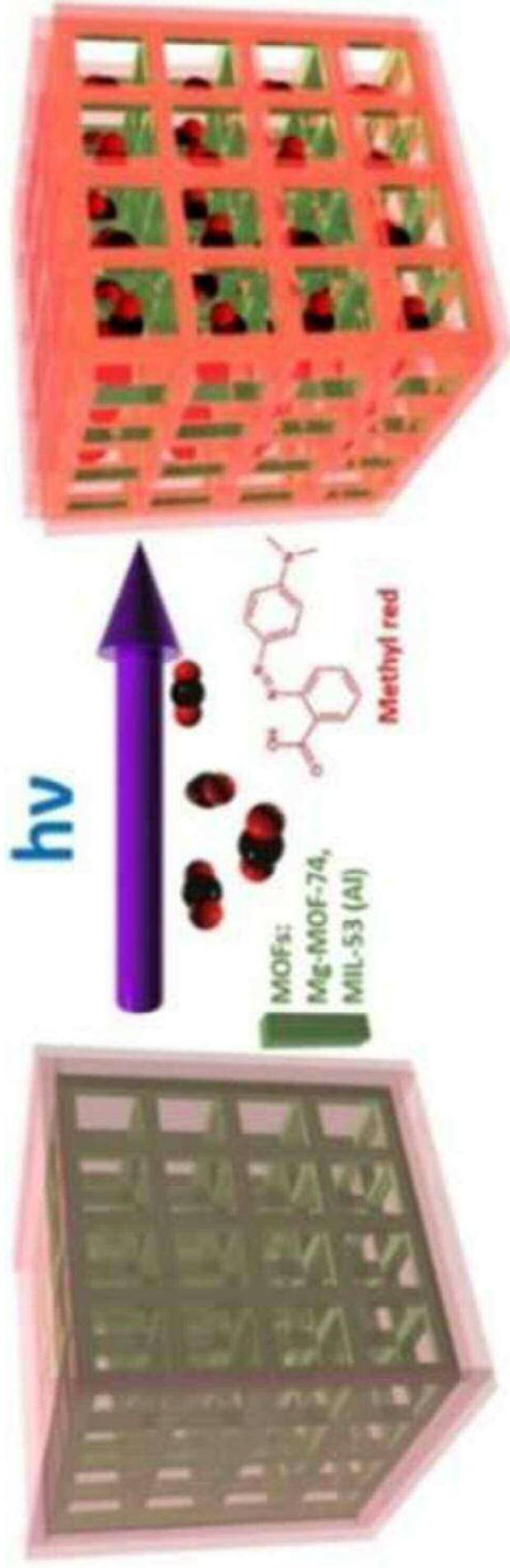
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**Table 1.** Comparison of the change in CO<sub>2</sub> adsorption of photo-switching MOF upon light irradiation at about 298K, 1bar.

Sample name	CO <sub>2</sub> adsorption / mg g <sup>-1</sup> , (STP)			Ref.
	Before UV	After UV	Percent Change	
PCN-123 <sup>a</sup>	41.21	18.90	54%	63
Zinc-based MOFs	-	-	42%	47
ECUT-15 <sup>b</sup>	11.34	5.76	45%	66
Azo-DMOF-1	73.78	52.19	29%	67
JUC-62	82.78	53.99	34%	87

- a. Adsorption change is influenced by time. Here the data is obtained after a 1-hour irradiation at 295 K.
- b. The change under dynamic conditions was found to be up to 75%. 45% is observed under static conditions.

**Table 2.** Comparison of POPs in synthesis, surface area, CO<sub>2</sub> uptake and corresponding CO<sub>2</sub>/N<sub>2</sub> selectivity at 273/298 K and 1 bar.

Materials	Monomer	Reaction type	Reaction conditions	Surface area (m <sup>2</sup> g <sup>-1</sup> )	CO <sub>2</sub> uptake (mg g <sup>-1</sup> )	CO <sub>2</sub> /N <sub>2</sub> selectivity <sup>a</sup>	Ref.
Azo-COP-2	Aromatic nitro and amine moieties	catalyst-free coupling	direct KOH, DMF, 150 °C, 24 h	729	-	-(109.6)/-(130.6)	[73]
Azo-POF-1	Tetrakis(4-nitrophenyl)methane, 1,1,2,2-Tetrakis(4-nitrophenyl)ethane	reductive reaction	Zn, NaOH, 65 °C 36 h	712	131.0/82.9	69(52)/ 46(37)	[74]
ALP-1	Tetra(4-aminophenyl) methane	oxidative coupling	CuBr, THF/toluene, 25–80 °C, 48 h	1235	236.0/143.0	35(40)/ 27(28)	[75-76]
Azo-PPor-1	Meso-tetra(4-nitrophenyl) porphyrin and aromatic amines	direct couplings	KOH, DMF, 150 °C, 24 h	750	107.8/-	-	[77]
Azo-MOPs-2 (N = 1–4)	Tetrakis(4-aminophenyl) methane(A-1), 2,6,14-triaminotriptycene(A-2), 1,3,5-tris(4-aminophenyl)benzene(A-3) and tris(4-aminophenyl)amine (A-4)	oxidative polymerization	<sup>t</sup> BuOCl/NaCl, Solvent, 25 °C, 1 h	706	134.8/-	-	[78]
Azo-POP-1 (N = 1–3)	Tetra (4-nitrophenyl)methane (TPM-4NO <sub>2</sub> ), Tetra(4-nitrophenyl)adamantane (TPA-4NO <sub>2</sub> ), 1,1,2,2-tetrakis(4-nitrophenyl)ethene	reductive homocoupling polymerization	NaBH <sub>4</sub> , DMF, 85 °C, 30 min	1478	-	-	[79]
UCBZ-1	Diamines, 1, 3, 5-triformylphloroglucinol, 1,4-dioxane (4 mL), mesitylene	Schiff-base chemistry	Acetic acid, 150 °C, >2 h	980	76.6→98.2 <sup>b</sup>	-	[80]
E <sub>4-1b</sub>	4: tetra(4-aminophenyl)methane, b: 4-nitrosotoluene	Mills coupling	CH <sub>3</sub> COOH, RT, overnight	-	-	80	[81]
Azo-COP-2	Tetrakisnitrophenyl methane, phenylenediamine	metal method	catalyst-free KOH, DMF, 150 °C, 24 h	554	93.3/56.3→7	-	[82]
P2	Diarylethene boric acid with 2, 6-diodotriptycene and 2, 6, 14-triiodotriptycene	Suzuki coupling reaction	K <sub>2</sub> CO <sub>3</sub> , Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF, 80 °C, 48 h	41/36 <sup>d</sup>	--	-	[83]

<sup>a</sup> Selectivity (mol mol<sup>-1</sup>) was calculated by the initial slope method and the IAST method in brackets at 273/298K.

<sup>b</sup> The adsorption was tested at 273K and 1 atm. before and after UV irradiation for 9 minutes, the CO<sub>2</sub> uptake was increased by 29%.

<sup>c</sup> Under the static experiment, the CO<sub>2</sub> adsorption was test before and after UV irradiation.

<sup>d</sup> BET surface area of P2 before and after UV irradiation.



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