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 CO2 capture, researchers have tried to endow metal-organic frameworks (MOFs) and porous organic polymers (POPs) with photosensitive units. This review highlights photochromic units and methods used for different types of photosensitive adsorbents of CO2, as well as some examples of adsorbents with photoswitches. These materials are also promising candidates for direct air capture of CO2. 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 CO2 by simply switching the light on and off.

Keywords CO2 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 a 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 CO2.
- Photoswitching sorbents are also promising candidates for direct air capture of CO2.

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 CO2

AZBs
- Azobenzenes

DArEs
- Diarylethenes

BET
- Brunauer-Emmett-Teller
1. Introduction

As a major greenhouse gas, CO₂ 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 CO₂ per year to the atmosphere [4]. CO₂ 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 CO₂ emissions must be reduced, and efforts should be concentrated on minimising both types mentioned above.

Adsorption from intermolecular forces between CO₂ 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 CO₂ 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 CO₂ adsorbents because they show relatively high CO₂ 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 CO₂ (DAC), is the technology to direct extract CO₂ from the ambient, which is gaining increasing popularity [23, 24]. Firstly, it is a “carbon-negative” technology. Secondly, it can reduce CO₂ 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 (SOx, NOx, mercury, etc.). It is reported that DAC could reach 1 GtCO₂/a in 2050, which is predicted to be far from the potential market about 15 GtCO₂/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 CO₂ from ambient under atmospheric conditions, where very low concentrations (~400 ppm), relatively low pressure and temperature, and selectivity of CO₂/N₂ present significant challenges.

NaOH solution has been largely used for the DAC process due to its low cost and the
feasibility of the technology, but it has many drawbacks such as a very large binding energy, the corrosiveness of strong NaOH solutions, and the vast energy consumption of the regeneration process [28]. Aqueous solutions of K\textsubscript{2}CO\textsubscript{3} have also been researched for the DAC process, however, the main drawback is that sorbent regeneration requires high temperatures (100-200°C), where KHCO\textsubscript{3} is decomposed to K\textsubscript{2}CO\textsubscript{3} [29, 30]. The cost of using aqueous solutions to capture CO\textsubscript{2} is reported to be 94–232 $/t currently [31], and required thermal energy about 5.25 ~ 8.1 GJ/tCO\textsubscript{2} [32].

In contrast, solid adsorbents can reduce costs, ranging instead from 29 to 91 $/t because of their lower heat of regeneration (45–70 kJ mol\textsuperscript{-1}) [33, 34]. Solid sorbents have been identified as likely to show high selectivity for CO\textsubscript{2}, high capacities of CO\textsubscript{2} capture, fewer regeneration energies, and good stability [35]. MOFs are promising adsorbents for DAC because inorganic clusters and organic linkers provide MOFs with fabrication flexibility [32]. Shekhah et al. demonstrated novel MOFs (SIFSIX-3-Cu) as DAC adsorbents, which could adsorb 54.6 mg g\textsuperscript{-1} CO\textsubscript{2} at 400 ppm, 298 K [36]. Amrit Kumar et al. evaluated Mg MOF 74/Mg-dobdc in the DAC process, with 165 cm\textsuperscript{3} g\textsuperscript{-1} at 1 atm and 293 K [37].

Photoresponsive sorbents are attractive, as they are low-cost, have feasible regeneration, and good selectivity for CO\textsubscript{2} over other gases even at atmospheric CO\textsubscript{2} concentrations [38-40]. Sunlight is available almost everywhere and constitutes a renewable energy source, thus the cost of regenerating materials can be lower [41]. Moreover, photoresponsive sorbents embedded with photochromic units can absorb sunlight, along with a reversible change between “open” and “closed” conformations, so that photoresponsive sorbents can be regenerated feasibly [39, 42]. Photoresponsive functional groups like azobenzenes have been proven to increase gas selectivity for the MOFs/POPs sorbents of CO\textsubscript{2} [40].

However, until now, a very limited number of reviews have focused on photoresponsive sorbents used for CO\textsubscript{2} capture. Haiqing Li and Matthew R. Hill published a review article about three types of MOFs with the triggered release of stored gas, comprising light-responsive MOFs, magnetic MOFs, and dual stimuli-responsive MOFs [43]. Based on their work on light-responsive MOFs as CO\textsubscript{2} adsorbents [44-47], they concluded that having guest light-responsive as the backbone of organic ligands is more conducive to CO\textsubscript{2} capture and release than their incorporation as pendants and chemically grafting light-responsive motifs onto the organic ligands of the MOFs. They also highlighted that currently azobenzene and diarylethene are the predominant light-responsive groups. S. Castellanos et al. has also published a review about MOFs functionalized with azobenzene or dithienylethene derivatives to impart photoswitching behavior, where different strategies of photoswitchable MOFs are discussed [42]. In addition, we are unaware of a review of photoresponsive POPs as CO\textsubscript{2} sorbents.

In this review, potential photoswitching porous materials, including MOFs and POPs, are covered. The preparation strategies and commonly used photochromic units for these materials will be detailed, as well as the representative applications as photoswitching CO\textsubscript{2} sorbents. Further discussion about the possibility of photoswitching sorbents being applied in DAC will be illustrated. Most interestingly, CO\textsubscript{2} sorbents can be produced with light “gates” or “switches” for low-energy regeneration of CO\textsubscript{2}. Therefore, through the introduction of the appropriate photochromic unit, photoswitching materials are interesting candidate materials for DAC. Overall, the aim of this review of current research is to motivate more attention towards potential photoswitching sorbents of CO\textsubscript{2}, as well as the research of photoswitching sorbents specifically for DAC.
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 (−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](image)

**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-(arylazo)pyridines(PAP), has been used to prepare the light-triggered fluorescence modulation of Zn–porphyrins. In 2018, Dipanwita et al. embedded the MOF [Zn(1,4-bdc)(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 cannot adsorb N\(_2\) because of the pore blockage by the guest PAP in the trans form.

The diffusion of 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
trans-to-cis isomerization occurred with azo content of 21% upon UV light (365 ± 10 nm), and cis-to-trans isomerization occurred with azo content of 1% upon either visible light (420–480 nm) or heating.

Interpenetration often occurs within MOFs, however, it should be avoided for the purpose of photoswitching to avoid the negative influence on CO₂ capture with photoswitches. In 2011, F. Modrow et al. reported interpenetrated azobenzene-derivatized MOFs, [Zn₂(NDC)₂(1)], by a solvothermal method using 3-azo-phenyl 4,4’ bipyridine(1), 2,6-naphthalene dicarboxylic acid, and Zn(NO₃)₂·6H₂O [52]. The azobenzene - derivatized linker was covalently incorporated into the MOFs with permanent porosity (surface area: 554 m² g⁻¹, micropore volume: 0.23 cm³ g⁻¹). In the switching experiments, it could be changed to the cis-isomer by exposure to UV light (λ = 365nm) for 1 h and the cis-isomer could be partially recovered with visible light (λ = 440nm) for 1 h or leaving at room temperature in the dark with a period of 24 h. The author mentioned the existence of interpenetration and the requirement of avoiding it.

In 2013, Brown et al. reported a non-interpenetrated photoswitching MOF, azo-IRMOF-74-III, synthesised using Mg(NO₃)₂·6H₂O and an azo-functionalized linker [53]. The isomerisation between trans- and cis- isomers of the azobenzenes was shown to influence the size and shape of the MOF pores. UV irradiation afforded the trans conformation, causing the size of the pore to increase from 8.3 Å to 10.3 Å. The Brunauer-Emmett-Teller (BET) surface of the sample showed notably higher, at 2410 m² g⁻¹.

2.2 Diarylethenes groups

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

In 2013, Katz et al. prepared MOFs incorporated with imidazolate-based dithienylethene switches, PSZ-1, based on ZIF-70 (synthesized by Zn (II), imidazole, and 2-nitroimidazole) via a solvent-assisted linker exchange method [55]. With the ring of dithienylethene open to close, PSZ-1 converted from yellow to violet crystals in UV light. When exposed to visible light, closed-PSZ-1 reverted to the open-PSZ-1. The BET surface area of PSZ-1 was 1250 m² g⁻¹.

2.3 Spiropyans groups

Apart from photochromic azobenzene, diarylethene, spiropyans (SP) also have been studied and loaded in MOFs for light-triggered ring open/closing reactions (Figure 1c). In the process of isomerisation with a corresponding colour change, heterocyclic ring cleaves at the C–O spiro bond with the production of merocyanine (MC), and it returns to the initial close-ring
form through heat treatment or irradiation by visible light (λ > 450 nm) or simple heating. Although the spiropyran-loaded MOFs have not been reported in the CO₂ switching field, further study is still worthwhile.

In 2015, Zn-MOF-74 crystal was introduced with spiroindolinobenzopyran (SPH) to obtain orange/yellow crystals SPH (SPH@MOF-74) [56]. Upon UV light irradiation (365 nm), SPH@MOF-74 converted to the dark yellow form. When the sample was heated at 80 °C, they converted to dark red form; whereas, after the cooling treatment at 0 °C for 50 h, the sample returned yellow.

3. The preparation method of photoswitching MOFs as CO₂ adsorbents

Photoswitching MOFs are perhaps one of the most promising stimuli-responsive functional materials due to their large adsorption capacities, and their flexibility in design that can be harnessed for the introduction of photochromic groups within their pore structure [39]. Light irradiation can increase the surface energy of MOFs, leading to the weakening of intermolecular interactions between CO₂ and the surface, thus triggering the release of CO₂. Generally, photochromic compounds are integrated within MOFs following one of the following four routes: (1) as a guest within MOFs inner cavities, (2) as surface pendant groups decorated the organic linkers of MOFs through a covalent bond, (3) as the backbone of the MOFs, or (4) by combining with chemical adsorption sites. As far as the CO₂ capture ability, the higher BET surface area can lead to better ability [57, 58]. However, in many cases, CO₂ capture capacity is decided by the combined effects from several factors including surface area and surface affinity towards CO₂ [59]. For the photoswitching MOFs as CO₂ sorbents, the influence of the photoswitching state relies on minor structural modifications and differences of the embedded groups [60].

3.1 As a guest within MOFs inner cavities

This first approach is challenging with respect to providing good performance in terms of pore size, effectiveness, and flexibility because pore space may be occupied by the guest molecules. In 2012, MOFs decorated with azobenzenes were demonstrated by Kitagawa et al., who accommodated trans-azobenzene inside the Zn₂(terephthalate)₂(triethylenediamine), at 120 °C for 12 h to form host-guest composites [61]. The tetragonal host structure completely transformed to orthorhombic networks upon UV light exposure while the trans azobenzene turned into cis-azobenzene (Figure 2).

![Figure 2](image)

**Figure 2.** Illustration of the conformational change triggered by light in the MOFs, Zn₂(terephthalate)₂(triethylenediamine), with azobenzene as the guest molecule (the red represents trans-AB while the orange represents cis-AB). Reprinted (adapted) with permission from 61. Copyright (2012) American Chemical Society.
The sample with trans-azobenzene could not adsorb N₂, but it could adsorb N₂ after UV irradiation with mostly cis-azobenzene. Then, by heating at 120 °C for 1 h, cis-azobenzene transformed reversibly back to trans-azobenzene, and N₂ adsorption decreased substantially.

In 2013, Walton et al. prepared photoresponsive DMOFs containing non-covalent DTEs (DMOF-1@DTE) by heating a mixture of DMOF-1 and DTE-o at 130 °C overnight [62]. Upon UV light irradiation (365 nm), the sample immediately turned from the colourless state to the dark red state. When it was exposed to visible light, the crystals reverted to their initial colourless state. The samples showed thermal stability when wrapped in foil and placed in the dark for one month. However, the authors did not present results for porosity or CO₂ capture tests. Moreover, this method has the significant shortcoming that pores may be occupied by the guest molecules and therefore space for the structural change induced by isomerisation is limited; thus, the sorption and photo-isomerisation of CO₂ sorbents may be weakened.

3.2 As surface pendant groups decorated the organic linkers by covalent bond

Currently, covalently bonding the photochromic unit to the organic linker as a surface pendant group has been much researched. In 2011, Park et al. synthesized CO₂ adsorbents, PCN-123 (PCN represents porous coordination networks) with each cubic cavity occupied by azobenzene groups (Figure 3) [63]. Under UV light and at 1 bar and 295K, CO₂ adsorption reduced from 41.21 mg g⁻¹ to 18.90 mg g⁻¹ for 5 h, which is significantly slower than the original trans-cis change of azobenzene groups. Additionally, the original state of the adsorbent recovered with almost unchanged CO₂ uptake capacity after 20 h in ambient conditions or gentle heating. Accordingly, the pore size distributions changed after UV irradiation and almost returned to the original state after heat treatment. The advantage of PCN-123 lies in the large capacities of CO₂ adsorption but the negligible ability of N₂ under facile reversion conditions, while its disadvantage is the slower isomerisation change of azobenzene groups due to its steric hindrance inside the pores.

![Figure 3](image.png)

Figure 3. (Top) The reverse isomerization of the PCN-123 upon UV irradiation/heat treatment. (Bottom) Illustration of CO₂ adsorption in MOF-5, trans PCN-123, and cis PCN-123. Reprinted (adapted) with permission from 63. Copyright (2012) American Chemical Society.

Some researchers report the success of photoswitches embedded in MOFs, but photoswitching CO₂ adsorption has been reported less. However, with the good capability of capturing CO₂ and demonstrating photoswitching, MOFs show the potential of being photoswitching adsorbents of CO₂. In 2012, Antje used Cr-MIL-101-NHz₂, p-phenylazobenzoylchloride (1) and 4-(phenylazo)phenylisocyanate (2) to obtain Cr-MIL-101_amide and Cr-MIL-101_urea [64]. Cr-MIL-101_amide and Cr-MIL-101_urea were
compared to confirm the influence of functional groups on the isomerisation of AZBs upon UV/Vis irradiation. In 2017, James et al. reported a 3D coordination framework, [Zn₄(tbazip)₃(bpe)₂(OH)₂]-bpe-{solvant} (where bpe = 1,2-di(4-pyridy)lethene), containing the photoactive ligand tbazip (tbazip = 5-((4-tert-butyl)phenylazo)isophthalic acid) [65]. The photoisomerization of trans-cis and cis-trans occurred successfully after exposure to UV light and the removal of light, respectively. The BET surface area of this MOF is 30 m² g⁻¹ and its CO₂ adsorption at 298 K reached up to 127.6 mg g⁻¹ at 1.1 bar.

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

3.3 As the backbone of the MOFs

The third way to design photoresponsive MOFs is to directly incorporate the photochromic units into the “backbone” of the ligands, which provide the space for the most dramatic photoisomerization.

In 2013, Hill et al. explored the design of a triply-interpenetrating porous framework, Zn(AzDC)(4,4'-BPE)₅, combining zinc-based MOFs with two photoresponsive ligands (4,4'-dicarboxylate (AzDC) and trans-1,2-bis(4-pyridyl)ethylene (4,4'-BPE)) [47]. With UV irradiation, the CO₂ adsorption decreased by 64% during dynamic measurements, performing better than that under static irradiation conditions (42%). Its high performance under dynamic conditions is an advantage of this material, along with its full reversibility.

In 2015, Luo et al. successfully introduced ABZs into Co₃(L)₂(AzDC)₃ (L=N₁, N₃-dipyridin-4-ylisophthalamade; H₂AzDC = 4,4'-diazene-1,2-diylbenzoate acid) to form ECUT-15 [66]. Under UV light at 298 K and 1 bar, the CO₂ adsorption capacities of ECUT-15 sharply decreased from 11.34 to 5.76 mg g⁻¹, representing a ~45% reduction. In the dynamic reversible adsorption/desorption test without/with UV light irradiation, the release of CO₂ increased up to 78% instantaneously. The change upon UV light exposure and instantaneous reversibility represents improve performance versus the results above.

In 2018, Bradley et al. synthesized Zn-azo-dabco MOF (Azo-DMOF-1) with both 2-phenyldiazenyl terephthalic acid and 1,4-diazabicyclo[2.2.2]octane (DABCO) as the ligands [67]. The Azo-DMOF-1 exhibits a microporous structure with a BET surface area of 581 m² g⁻¹. The CO₂ uptake of the original Azo-DMOF-1 was around 143.39 (273 K) and 73.78 mg g⁻¹ (298 K). After UV irradiation, the CO₂ adsorption decreased to 70.71 and 52.19 mg g⁻¹ at 273 and 298 K, respectively. In the dynamic photo-switching experiment, with the UV light switched on-off, CO₂ adsorption reduced/returned to the original level.

Using organic ligands as the backbone of the MOF avoids the occupation of pore space, but in some cases, the isomerization of the organic ligands may be constrained. As shown in Table 1, the CO₂ adsorption of MOFs is decreased after UV irradiation. However, there is one counter-example from Luo et al., who reported DMOF, Zn(L)(bpdc), consisting of Zn(NO₃)₂·6 H₂O, H₃bpdc, and diarylethene derivative (L) [68]. The sample turned blue upon exposure to 300 nm light for 1 min, while the blue colour disappeared with the exposure to visible light. Although this DMOF cannot adsorb N₂, it performed well in CO₂-adsorption tests. The CO₂ adsorption of DMOF increased after UV irradiation from 9.00 mg g⁻¹ to 39.48 mg g⁻¹ at 298 K. This CO₂ desorption capacity of this DMOF performs remarkably with visible light.
(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 Fe$_2$Co($\mu$-O)(CH$_3$COO)$_6$ metal clusters and tetrotropic 3,3’, 5,5’-azobenzene tetracarboxylic acid (ABTC) ligands [69]. The BET surface area of the sample was 1486 m$^2$g$^{-1}$, and its CO$_2$ adsorption capacity was 285.80 (273 K) and 136.05 mg g$^{-1}$ (298 K) at 1 bar, while the CO$_2$ desorption can be altered by light intensity. In addition, after five cycles of 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 (CO$_2$ uptake and light-triggered CO$_2$ desorption decreased by 7.3 % and 4.9 %, respectively).

3.4 Combining with chemical adsorption sites

The physical interaction between 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 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 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 A$_2$P$_2$@MS was 797 m$^2$g$^{-1}$. After UV irradiation, the 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 CO$_2$. The CO$_2$ adsorption amount of A$_2$P$_2$ increased from 72.4 mg g$^{-1}$ under UV light irradiation to 112.3 mg g$^{-1}$ (35.6%) under visible light irradiation at 273K. As amines also contribute to good selectivity of CO$_2$/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 CO$_2$ capture [71]. The optimal sample showed 85.25 mg g$^{-1}$ for CO$_2$ adsorption capacity in the cis state, decreasing to 53.63 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](image-url)
effectiveness, and lower flexibility of the sorbent because pore space is mostly occupied by
the guest molecules. The third method may avoid these problems because no molecules
occupy the pores, which brings full accessibility to the MOFs. But the disadvantage upon
isomerization of geometrical changes in the backbone of the framework may constrain
photoisomerization efficiency, where lies challenges. The fourth method represents a novel
route to increasing CO₂ capture capacity at the same time as realizing a photoswitch, and
thus the challenge lies in the design of the reaction between CO₂ molecules and the
selection of functional groups in the porous materials. Photoswitching MOFs are promising
sorbents for CO₂ because most MOFs show good adsorption capacity for CO₂, and they
possess controllable pore structure and adjustable pore surface properties. The main
challenges are related to the selectivity to CO₂ adsorption. However, the bestowing of a
photoswitching property to a porous material such that it can be controlled from an “on”
state to an “off” state in a reversible pattern by light exposure will very likely reduce energy
consumption in the overall process.

In addition, the amount of CO₂ captured after light irradiation is generally less than that
before irradiation. It is noted that ECUT-15 shows very high performance, such that the
changes under static and dynamic conditions were up to 45% and 78%, respectively. The
capabilities of CO₂ adsorption and the pore size distribution may be affected by the hindered
isomerization of AZBs inside MOF pores. Meanwhile, the reversible control for multiple
cycles under UV or heating provide great potential for further research.

4. Photoswitching POPs as CO₂ adsorbents

Most reported POPs are designed with azo groups because they are sufficiently N₂-phobic so
that adsorption and selectivity of CO₂ can be enhanced. Generally, the photochromic unit
can be attached to the polymeric backbone or the chain end [72]. The challenge of designing
photoresponsive polymers lies in the relatively large free volume change associated with
isomerization. However, few of them have made use of the potential of photoswitching
adsorption and desorption of CO₂.

4.1 POPs embed with photoswitching units as CO₂ adsorbents

At the beginning of POPs research using photochromic units, photo-switch is not focused. In
2013, Coskun and Yavuz et al. synthesized azo-linked covalent organic polymers (azo-COPs)
by catalyst-free direct coupling of aromatic nitro and amine moieties at 150 °C for 24 h [73].
The BET surface areas of these azo-COPs were 635, 729, and 493 m² g⁻¹, but their CO₂/N₂
selectivity was unprecedentedly high (288.1 at 323 K).

In 2014, Zhang’s group developed two types of Azo-POF (Azo-POF-1, Azo-POF-2) through a
Zn-induced reductive homocoupling reaction on tetra(4-nitrophenyl) methane at 65 °C for
36 hours [74]. The obtained CO₂ adsorption of Azo-POF-1 and Azo-POF-2 at 273/298 K and 1
bar were 131/82.9 and 84.5/55.1 mg g⁻¹, respectively. Azo-POF-2 exhibited a CO₂/N₂
selectivity of 76/54 at 273/298 K.

In the same year, EI-Kaderi et al. synthesized highly porous azo-containing organic polymers
(ALPs) via oxidative coupling using tetra(4-aminophenyl) methane for 48 hours (at room
temperature for 24 h, 60 °C for 12 h, and 80 °C for 12 h) [75]. All ALPs showed remarkable
CO₂ adsorption capacities with the highest of 236 mg g⁻¹ at 273 K and 1 bar, and 143 mg g⁻¹
at 298 K and 1 bar, as well as an outstanding BET surface area of about 1235 m²g⁻¹ (ALP-1). The researchers then attempted to synthesize new types of ALPs based on rigid star-shaped monomers with nitrogen-rich building units using the same method [76]. Star-like shapes are attractive designs because the relatively larger space and the better rigidity of the frameworks can inhibit a close-packed arrangement within crystals, thus contributing to the formation of porous molecular crystals where photoisomerization occurs. Among the series of polymers produced by this group, ALP-5 is outstanding among ALPs with relatively higher CO₂ adsorption capabilities of 196.24 mg g⁻¹ and 129.36 mg g⁻¹ at 1 bar and 273K/298K, and selectivity for CO₂/N₂ of about 44 at 298 K.

In 2015, Lyu et al. used a similar method to prepare azo-linked porous polyporphyrins (azo-PPors) using meso-tetra(4-nitrophenyl) porphyrin and aromatic amines at 150 °C for 24 h [77]. The CO₂ adsorption capacity of the polymers reached up to 107.8 mg g⁻¹ at 1 bar, 273 K.

Though such progress has been made, it is still desirable to propose a simpler and more efficient route to produce Azo-POPs with high adsorption capacity for CO₂ under milder conditions.

In 2015, Liu’s group used oxidative polymerization to produce Azo-MOPs with azo-type ligands: tetraakis(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) as the building blocks and t-BuOCl/NaI as the oxidant at room temperature (e.g., 25 °C, 1 h) [78]. The Azo-MOPs (pore diameters < 2 nm) were applied for CO₂ adsorption and conversion at room temperature, with high adsorption capacity and thermal stability. Azo-MOP-2 exhibited the best CO₂ adsorption among the four Azo-MOPs in their work, at 134.8 mg g⁻¹ (1 bar and 273 K).

In 2018, Huang et al. reported a quick route to prepare azo-linked POPs via a NaBH₄-mediated coupling reaction on four-folded nitro-containing monomers [79]. The BET surface areas of the Azo-POPs reached 1478 m²g⁻¹, scalable to the 5 g scale. According to their analysis results of the mechanism, the reaction type (coupling reaction) and the reducing agent (NaBH₄) are the main reasons for the large surface areas.

The studies above focus on the synthesis of POPs embedded with azo groups and used as CO₂ adsorbents; however, none of them report photoresponsivity, unlike the following studies. Taking advantage of the structural change resulting from photoisomerization, the porosity and CO₂ adsorption/desorption may be controlled.

4.2 Photoswitching POPs as CO₂ adsorbents

In 2014, Zhang’s group developed the photoswitching UCBZ polymer series with five types of diamine through Schiff-base chemistry at 150 °C [80]. Their pore size distributions and CO₂ adsorption capacity can be reversibly transformed upon UV irradiation. CO₂ adsorption of the UCBZ polymer increased by the conversion from trans-isomer to cis-isomer. Among the UCBZ series, UCBZ-1 was the highest in terms of CO₂ adsorption (76.61 mg g⁻¹ at 273 K and 1 atm), which climbed to 98.21 mg g⁻¹ upon nine-minute UV irradiation (29% increase). The reason given for the material’s photo-responsiveness was the negative effect of bearing a bulky substituent. In addition, these POPs were shown to have good stability and nearly full reversibility since similar adsorption properties were found after multiple cycles of alternating external stimuli.
In 2015, Baroncini et al. reported a series of star-like and rigid crystals, E4-1(a–c), based on Mills coupling at room temperature [81]. By using different nitrosobenzene moieties with H, Me, or t-Bu, their porosity increased with the size of the end groups. Exposure to UV light, the crystallinity and porosity of E4-1(a–c) disappeared, but the crystals were reproduced with porosity, upon visible light irradiation or heating. Reversible switching between “on” and “off” corresponding to porous and non-porous states was successful. The porous crystals of E4-1c were reported to have maximum CO₂ adsorption of 805.36 mg g⁻¹ and 628.57 mg g⁻¹ at 10 bar and 273 and 298 K, respectively. The selectivity of CO₂/N₂ was observed to be as high as 80 for the E4-1b compound.

In 2019, Li et al. also proposed a smart polymer membrane, Azo-COP-2, which showed exceptionally efficient CO₂ photoswitching in both static and dynamic conditions [82]. Azo-COP-2 was prepared without a metal catalyst on tetranitrophenyl methane at 150°C for 24 h. In both static and dynamic experiments with exposure to UV light, the CO₂ adsorption capacity of Azo-COP-2 significantly dropped from 93.28 mg g⁻¹ to 73.04 mg g⁻¹ at 273 K, and from 56.32 mg g⁻¹ to 46.2 mg g⁻¹ at 298 K.

Aside from the AZBs used widely in these types of POPs, studies using DArE groups have also been carried out. In 2015, Hill et al. accommodated DArE within porous aromatic framework-1 (PAF-1) to form DArE@PAF-1, which displayed photo-switching of CO₂ capture and release at room temperature [44]. Desorption of CO₂ increased by 65% (at 1 bar) by four-minute light irradiation. By analysing the competitive interactions between DArE and CO₂ molecules with the host, the authors reached the conclusion that multiple interactions may trigger CO₂ spontaneously release.

In 2018, Luo et al. used triptycene (2,6,14 triiodotriptycene, P1) and diarylethene (2,6-diiodotriptycene, P2) via a Pd(0)-catalysed Suzuki coupling reaction (P1: at 80 °C for 48 h, P2: at 80 °C for 72 h) to gain linear and star-shaped porous polymers [83]. These two types of POPs displayed a reversible change in their specific surface areas and total pore volumes, owing to the photoisomerization of DArEs upon UV or visible light exposure. In detail, colour, surface area, and pore volume are converted in the solid form or THF solution under UV light (254 nm) for a few minutes. With the isomerization of DArE upon UV light irradiation, the total pore volumes of P1/P2 decreased from 0.131/0.130 cm³ g⁻¹ to 0.121/0.100 cm³ g⁻¹.

When the light source was changed to visible light, the total pore volumes of P1 and P2 increased to 0.126 and 0.127 cm³ g⁻¹, respectively.

In summary, POPs with photoswitching units have been synthesized through a range of methods as shown in Table 2. Among them, the reductive homocoupling reaction is used most frequently. In terms of the synthesis process, preparation of E4-1a/b/c is the most feasible as it is photoswitching, time-efficient, conducted in the atmosphere, and scalable to the 5 g. On the other hand, Azo-POP-1 shows the highest surface area among the POPs mentioned here (1478 m² g⁻¹), but the study lacked related test results for further application such as the CO₂ adsorption test before and after irradiation under both static and dynamic states. ALP-1 also performs well in BET surface area (1235 m² g⁻¹) and CO₂ adsorption (143 mg g⁻¹), while its synthesis depends on the use of transition-metal catalysts (e.g., CuBr/pyridine), which is a significant problem in the real application. Therefore, a catalyst-free method has been introduced, but the low surface area of Azo-COP-2 is a significant disadvantage. Some of the aforementioned POPs have been researched for their sorption capacity of CO₂ and the selectivity of CO₂/N₂. For example, as shown in Table 2, Azo-COP-2 shows excellent CO₂/N₂ selectivity (109.6 at 273K and 130.6 at 298K). In addition,
POPs with photoswitching units have been synthesized through reductive homocoupling reactions, oxidative coupling, catalyst-free direct coupling, oxidative polymerization, Mills coupling, and Suzuki coupling reaction. Among them, the reductive homocoupling reaction is expected to be time-efficient and lend itself to simple operating conditions, and potentially large-scale production. Most of the POPs with photoresponsive units are star-shaped because this shape can provide more space for the arrangement of the low-density molecular self-assembly within crystals.

In Table 2, two notable photo-switching POPs (UCBZ-1 and Azo-COP-2) are shown. The UCBZ polymers series are a special class of polymers because their adsorption capacity increases upon UV light irradiation, which is opposite to photo-switching MOFs. It is thought that the bulky substituents on the AZBs groups reduce the degree of responsiveness. On the other hand, COFs are more similar to MOFs in terms of structure as they are covalent, porous and crystalline containing organic units, ordered structure and nanopores [84]. Thus, COFs demonstrate a similar photoswitching phenomenon, in that CO\(_2\) adsorption reduced after UV irradiation. Besides, COFs are interesting because they are low in mass density, highly thermally stable, and permanently porous [85].

Compared to photo-switching MOFs, less attention has been paid to photo-switching POPs. However, POPs are also a very potential candidate as CO\(_2\) sorbents attributing to their relatively good porosity, stability, and adjustability. Two major challenges should be considered with respect to photoresponsive POPs for capturing CO\(_2\). The first challenge is the balance of various performance indicators for porous materials under irradiation, including adsorbent ability, CO\(_2\)/N\(_2\) selectivity, thermal stability, water stability, and light stability. The second important point is that the functionalized materials need to be able to accommodate reversible isomerization of photoactive moieties, as most of these switches (including AZBs and stilbenes) undergo large conformational changes upon isomerization. Hence, conformational freedom is required, although typically difficult under confinement.
### Table 2. Comparison of POPs in synthesis, surface area, CO₂ uptake and corresponding CO₂/N₂ selectivity at 273/298 K and 1 bar.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Monomer</th>
<th>Reaction type</th>
<th>Reaction conditions</th>
<th>Surface area ( \text{m}^2 \text{g}^{-1} )</th>
<th>CO₂ uptake ( \text{mg g}^{-1} )</th>
<th>CO₂/N₂ selectivity(^a)</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Azo-COP-2</td>
<td>Aromatic nitro and amine moieties</td>
<td>catalyst-free direct coupling</td>
<td>KOH, DMF, 150 °C, 24 h</td>
<td>729</td>
<td>-</td>
<td>-(109.6)/-(130.6)</td>
<td>[73]</td>
</tr>
<tr>
<td>Azo-POF-1</td>
<td>Tetrakis(4-nitrophenyl)methane, 1,1,2,2-Tetrakis(4-nitrophenyl)methane</td>
<td>reductive homocoupling reaction</td>
<td>Zn, NaOH, 65 °C 36 h</td>
<td>712</td>
<td>131.0/82.9</td>
<td>69(52)/46(37)</td>
<td>[74]</td>
</tr>
<tr>
<td>ALP-1</td>
<td>Tetra(4-aminophenyl) methane</td>
<td>oxidative coupling</td>
<td>CuBr, THF/toluene, 25–80 °C, 48 h</td>
<td>1235</td>
<td>236.0/143.0</td>
<td>35(40)/27(28)</td>
<td>[75-76]</td>
</tr>
<tr>
<td>Azo-PPor-1</td>
<td>Meso-tetra(4-nitrophenyl) porphyrin and aromatic amines</td>
<td>direct couplings</td>
<td>KOH, DMF, 150 °C, 24 h</td>
<td>750</td>
<td>107.8/-</td>
<td>-</td>
<td>[77]</td>
</tr>
<tr>
<td>Azo-MOPs-2</td>
<td>Tetrakis(4-aminophenyl) methane(A-1), 2,6,14-triaminotriptycene(A-2), 2,6,14-triaminotriptycene(A-2), 1,3,5-tris(4-aminophenyl)benzene(A-3) and tris(4-aminophenyl)amine (A-4)</td>
<td>oxidative polymerization</td>
<td>tBuOCl/NaCl, Solvent, 25 °C, 1 h</td>
<td>706</td>
<td>134.8/-</td>
<td>-</td>
<td>[78]</td>
</tr>
<tr>
<td>Azo-POP-1</td>
<td>Tetra (4-nitrophenyl) methane (TPM-4NO₂), Tetra(4-nitrophenyl)adamantane (TPA-4NO₂), 1,1,2,2-tetrakis(4-nitrophenyl)ethene</td>
<td>reductive homocoupling polymerization</td>
<td>NaBH₄, DMF, 85 °C, 30 min</td>
<td>1478</td>
<td>-</td>
<td>-</td>
<td>[79]</td>
</tr>
<tr>
<td>UCBZ-1</td>
<td>Diamines, 1, 3, 5-triformylphloroglucinol, 1,4-dioxane (4 mL), mesitylene</td>
<td>Schiff-base chemistry</td>
<td>Acetic acid, 150 °C, &gt;2 h</td>
<td>980</td>
<td>76.6→98.2(^b)</td>
<td>-</td>
<td>[80]</td>
</tr>
<tr>
<td>E₄₁b</td>
<td>4-tetra(4-aminophenyl)methane, b: 4-nitrotoluene</td>
<td>Mills coupling</td>
<td>CH₃COOH, RT, overnight</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>[81]</td>
</tr>
<tr>
<td>Azo-COP-2</td>
<td>Tetrakisnitrophenyl methane, phenylenediamine</td>
<td>metal catalyst-free method</td>
<td>KOH, DMF, 150 °C, 24 h</td>
<td>554</td>
<td>93.3/56.3→7</td>
<td>3.0/46.2(^c)</td>
<td>[82]</td>
</tr>
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<td>P2</td>
<td>Diarylethene boric acid with 2, 6-diiodotriptycine and 2, 6, 14-triiodotriptycine</td>
<td>Suzuki coupling reaction</td>
<td>Pd(PPh₃)₄, THF, 80 °C, 48 h</td>
<td>41/36(^d)</td>
<td>-</td>
<td>-</td>
<td>[83]</td>
</tr>
</tbody>
</table>

\(^a\) Selectivity (mol mol\(^{-1}\)) was calculated by the initial slope method and the IAST method in brackets at 273/298K.

\(^b\) The adsorption was tested at 273K and 1 atm. before and after UV irradiation for 9 minutes, increased by 29%.

\(^c\) Under the static experiment, the CO₂ adsorption was test before and after UV irradiation.

\(^d\) 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 CO₂/H₂O or CO₂/N₂ at atmospheric concentrations.

Visible-light control on adsorption and desorption of CO₂ 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 CO₂ 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), CO₂ 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 CO₂ 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 CO₂ 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).

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 CO₂ uptake (51% at 273 K and 34% at 298 K) under UV light irradiation than that before UV light irradiation. During dynamic experiments of CO₂ adsorption, CO₂ 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 CO₂ 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 CO₂/N₂ selectivity, and facile photoisomerization reactions between

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Figure 5. Visible light-triggered MOF-74@MR and MIL-53(Al)@MR for CO₂ uptake. Reprinted (adapted) with permission from 45. Copyright (2015) American Chemical Society.
isomers. Thus, space, where photochromic units are to be incorporated into porous materials, should be considered in advance. Third, specifically for DAC applications, the porous materials selected need to be stable in the air to avoid material decomposition. Although many of the photoswitching porous materials have been shown to retain performance for consecutive cycles, it is important and necessary to test the repeatability and stability of the materials under ambient conditions. Fourth, the cost of synthesis must also be considered, which is a vital element when considering this type of application. Any expensive reagent in sorbent synthesis is undesirable, as it negatively impacts both the scalability and sustainability of the technology. Due to a relatively small market for photochromic units, many need to be synthesized in the lab, which inevitably increases costs. Using light to regenerate these materials is economical, but the cost of the incorporated photochromic unit should also be accounted for. Finally, a challenge also lies in the use of UV light, which may limit the application. Using UV light implies the use of thin layers of the sorbent material since the penetration depth of UV radiation is inherently low. This constraint, therefore significantly decreases the attainable volumetric performance and visible-light-sensitive materials may be preferable.

6. Conclusion

Up to now, azobenzene, diarylethenes and their derivatives are the most attractive and promising. A variety of reports have focused on using them to introduce photochromic units into porous materials. Herein, this paper reviews different types of photoswitching porous materials and demonstrates four ways to embed photochromic units into MOFs including: as a guest within MOFs inner cavities, as surface pendant groups decorated the organic linkers of MOFs through a covalent bond, as the backbone of MOFs and by combining with chemical adsorption sites. With photo-switching control, captured CO$_2$ usually decreases after light irradiation. ECUT-15 shows the best performance that the CO$_2$ adsorption capacity sharply decreased by 45% and 78% under static and dynamic conditions, respectively. It is noted that the strategy of combining both physisorption and chemisorption is also a potential route, as it can contribute photo-switching and reversibility under visible light irradiation (the CO$_2$ adsorption amount increased by 55.1 under visible light irradiation).

POPs with a switch triggered by light are reported less than MOFs. However, POPs are known to present greater stability in a variety of conditions and possess greater diversity in synthetic routes. More importantly, some reports of POPs prepared with AZBs or DArEs have shown high surface area by BET (Azo-POP-1: 1478 m$^2$ g$^{-1}$), CO$_2$ adsorption (ALP-1: 143 mg g$^{-1}$) and CO$_2$/N$_2$ selectivity (Azo-COP-2: 110 at 273K and 131 at 298K). Therefore, there are great opportunities to be found in researching photoswitching POPs, albeit with associated challenges. Very recently, two cases have illustrated that POPs with photoswitches can be used to control CO$_2$ capture and release.

Most interestingly, if photo-switching porous materials are to be applied in DAC, CO$_2$ emissions can be captured and released utilizing the renewable energy source of light. Currently, several photo-switching porous materials, like JUC-62, have demonstrated high stability at ambient conditions, and unchanged photoswitching functionality after ambient storage. With respect to further applying photoswitching materials for DAC technologies, these materials must be tested under ambient conditions to confirm simultaneously unchanged photo-responsivity, high CO$_2$ capture capacity, high stability, and high selectivity
Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgment

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References


[74] Lu J, Zhang J. Facile synthesis of azo-linked porous organic frameworks via reductive


Figure 1

Chemical structures and reactions:

1. E-AB and Z-AB with transition states $h \nu_1$ and $h \nu_2 + \Delta$.

2. Open-ring and Closed-ring structures with transitions UV/365nm and Vis/650nm.

3. sp and MC (deprotonated) structures with transitions 365 nm or > 450 nm OR \( \Delta \).

4. MC (protonated) structure.
Figure 2
Table 1. Comparison of the change in CO$_2$ adsorption of photo-switching MOF upon light irradiation at about 298K, 1bar.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>CO$_2$ adsorption / mg g$^{-1}$, (STP)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before UV</td>
<td>After UV</td>
</tr>
<tr>
<td>PCN-123$^a$</td>
<td>41.21</td>
<td>18.90</td>
</tr>
<tr>
<td>Zinc-based MOFs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ECUT-15$^b$</td>
<td>11.34</td>
<td>5.76</td>
</tr>
<tr>
<td>Azo-DMOF-1</td>
<td>73.78</td>
<td>52.19</td>
</tr>
<tr>
<td>JUC-62</td>
<td>82.78</td>
<td>53.99</td>
</tr>
</tbody>
</table>

$^a$ 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>
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<tr>
<th>Materials</th>
<th>Monomer</th>
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<th>Reaction conditions</th>
<th>Surface area ($m^2 \cdot g^{-1}$)</th>
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<td>oxidative polymerization</td>
<td>tBuCl/NaCl, Solvent, 25 °C, 1 h</td>
<td>706</td>
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<tr>
<td>Azo-POP-1</td>
<td>Tetra(4-nitrophenyl)methane (TPM-4NO$_2$), Tetrakis(4-nitrophenyl)adamantane (TPA-4NO$_2$), 1,1,2,2-tetrakis(4-nitrophenyl)ethene</td>
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<td>980</td>
<td>76.6→98.2$^b$</td>
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<td>E$_{2,1b}$</td>
<td>4: tetra(4-aminophenyl)methane, b: 4-nitrosotoluene</td>
<td>Mills coupling</td>
<td>CH$_3$COOH, RT, overnight</td>
<td>-</td>
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<td>Azo-COP-2</td>
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<tr>
<td>P2</td>
<td>Diarylethene boric acid with 2, 6-diiodotripycene and 2, 6, 14-triiodotripycene</td>
<td>Suzuki coupling reaction</td>
<td>K$_2$CO$_3$, Pd(PPh$<em>3$</em>)$_4$, THF, 80 °C, 48 h</td>
<td>41/36$^d$</td>
<td>--</td>
<td></td>
<td>[83]</td>
</tr>
</tbody>
</table>

$^a$ Selectivity (mol mol$^{-1}$) was calculated by the initial slope method and the IAST method in brackets at 273/298K.

$^b$ The adsorption was tested at 273K and 1 atm. before and after UV irradiation for 9 minutes, the CO$_2$ uptake was increased by 29%.

$^c$ Under the static experiment, the CO$_2$ adsorption was test before and after UV irradiation.

$^d$ BET surface area of P2 before and after UV irradiation.
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- Full-length article (Word count)  
- Review article (Word count)  
- Retractions (Word count)  
- Corrigendum (Word count)  
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