Organic solid-state photochromism using porous scaffolds

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Abstract

When exposed to light, organic photochromic molecules undergo a fast and reversible change in their electronic structure, resulting in a shift in color. Solid-state [composites? forms?] of these dphotochromes are more resistant to environmental factors and better suited for commercial settings than their solution forms. However, [solid-state matrices? the solid state?] frequently imposes geometric limitations on the photoisomerization of these compounds, reducing their photoswitching efficiency. This fundamental constraint considerably impedes the use of organic photochromes in real-world applications. A promising approach to preserving the photoswitching behavior of organic photochromes in the solid state is to incorporate the molecules within a robust porous scaffold featuring precisely designed pores, such as a metal-organic framework, covalent organic framework, or metal-organic cage. The physicochemical properties of these scaffolds—such as pore size and structure, hydrophobicity, and electronic character—determine the photoswitching efficiency of the integrated photochromes, and thus the photorepsonsive behavior of the material. There is, however, a dearth of understanding about which features of a porous matrix yield efficient solid photoswitchable materials, given a particular organic photochrome. In this Review, we address the outstanding challenges limiting solid-state photochromic materials based on organic photoswitches. We present design principles for identifying the optimal porous scaffolds for high-efficiency photochromic materials and conclude with the future opportunities of these materials.

Introduction

Photochromism—from the Greek words "phos" meaning light, and "chroma" meaning color[1]—is a phenomenon in which the color of a material is altered reversibly upon exposure to light. This phenomenon typically involves photo-induced electron or energy transfer, the breaking of chemical bonds, and the reorganization of molecular structure. The concept of photochromism dates back to the early 19th century, concurrent with the discovery of the first photochromic compounds[2,3]. Ever since their inception, photochromic materials have found extensive applications across various domains, ranging from optics and materials science to information storage and environmental remediation[4-8]. Although photochromism can manifest in both solution-phase and solid-state systems, the latter provides notable advantages for commercial settings[9,10]. Solid-state systems are more resilient to environmental variables such as temperature fluctuations, humidity, and exposure to solvents, and they possess excellent durability and mechanical properties, rendering them well-suited for enduring applications.

Organic photochromic molecules encounter challenges such as low photoefficiency, limited long-term durability, and a pronounced susceptibility to photo fatigue, in contrast to their inorganic counterparts in the solid state[11]. Consequently, despite their prevalence in academic research, organic photochromic materials have not been widely adopted in commercial and industrial sectors, even as photochromism as a field has steadily grown in industry[12]. Encapsulating organic photoswitches into the confined microenvironment of porous scaffolds has been considered a potential strategy to markedly improve their overall photochromic features and durability[13-16]. However, the geometric constraints imposed by the solid-state matrix often impede the molecules' photoisomerization process, limiting their potential as photochromic compounds[9,17,18]. Hence, a contemporary area of research aims to attainoptimal bulk photoresponsivity in durable nanoporous materials while preserving the molecular photoresponsivity features.

Advanced porous materials (APMs) encompass a diverse array of materials[19-21], including metal-organic frameworks (MOFs)[22-26], covalent-organic frameworks (COFs)[27-29], metal-organic cage or polyhedra (MOPs)[30-33], porous organic polymers (POPs)[34-36], MOF glasses[37,38], metal-organic gels (MOGs)[39,40], and various others[41-46]. The remarkable potential of such APMs lies in their ability to serve as host matrices, enabling the encapsulation of various organic photochromic molecules and maximizing their combined merits and performance[47-50]. These scaffolds possess interconnected networks of pores that facilitate the incorporation of photochromic molecules within their structures, preventing the molecules' agglomeration[51]. The distinctive attribute enables researchers to have greater control over the dispersion and alignment of photochromic species, resulting in improved photochromic functionality[13,52]. The permeable nature of these materials results in an enlarged surface area, offering more opportunities for interaction with incident light. Consequently, this translates into increased photoconversion efficiency, as the materials can effectively harness light energy and induce color changes. Moreover, certain porous scaffolds can be easily shaped into monolithic forms[39,53,54] or dissolved in common solvents[55], allowing for further processing into workable forms once unimaginable with conventional porous solids. Thus, porous scaffolds have emerged as a promising alternative in the development of high-performance and versatile solid-state photochromic systems for various practical applications in real-world settings.

Despite extensive research efforts that have been dedicated to investigating solid-state photochromism using various types of porous scaffolds (**Figure 1**), including zeolites, silica, and other related porous materials, there is still a lack of clear guidelines for identifying optimal porous host matrices that enable the production of efficient photoswitchable materials. In this Review, we summarize the [most common/promising?] organic photochromes and discuss the current challenges in applying these molecules to solid-state photochromism. We then introduce design guidelines to identify appropriate porous scaffolds (limited to APMs) with the most promising performance in organic-based photochromic solids. These insights are intended to foster the development of new solid-state photochromic systems endowed with enhanced functionality, thereby broadening their potential applications in real-world settings.

Photochromic molecules

Organic photoresponsive molecules are toggled between two photostationary states by manipulating light irradiation. The isomerization process entails a sequence of bond rotations and dissociationor formation events, which change the chemical structure and subsequently, the optical and electrical characteristics. The importance of organic photochromes stems from their intriguing color-switching capabilities[56], their synthetic accessibility, and the ease with which their physical responses can be engineered through slight structural modifications[57,58]. In addition, their structural versatility and tunability allows them to be compatible with various porous host materials (**Figure 2a**), enabling their smooth integration into multifunctional photochromic systems. This section introduces families of organic photoresponsive molecules that are easily integrated into porous scaffolds (**Figure 2b**).

Azo molecules

Azo compounds are distinguished by the existence of a central azo (-N=N-) group, which acts as the chromophore and enables isomerization between trans and cis configurations[59]. The trans isomers of azo-functionalized photoresponsive molecules are more thermodynamically stable compared to the cis isomers, mostly because of their highly planar structure and the increased distance between the aryl termini. A typical trans-azo compound demonstrates a π-π^* transition band when exposed to ultraviolet (UV) light, and an n-π^* absorption band when subjected to visible light. The trans-to-cis isomerization process leads to a notable decrease in the intensity of the π-π^* bands while producing a minor increase in the strength of the n-π^* bands[60]. Light irradiation causes electron transfer in both isomers, creating an unstable transient state that thermally relaxes to photostationary. As a result, there is constant competition between the forward and reverse isomerizations.

Spiropyran

Spiropyran molecules are characterized by a spirocyclic configuration that consists of two aromatic heterocycles bridged by a single sp^3-hybridized carbon atom[61]. When subjected to UV light, this spirocyclic configuration (known as the closed form) experiences a series of bond dissociations and molecular rearrangements that transform it into a zwitterionic merocyanine configuration (the open form)[62]. The closed form usually appears colorless or pale yellow, whereas the open form tends to have a colored appearance, which can range from purple to blue to green, depending on factors such as conjugation and solvent effects. This transformation induces a substantial alteration of molecular length from 12.2 Å to 14.0 Å, as well as an expansion of π-electron delocalization. Additionally, it converts the molecule from a hydrophobic state to a hydrophilic state [63]. Application of heat or visible light irradiation generally induces the reverse open-to-closed isomerization. These molecules are especially promising in fields such as optics, data storage, and sensing[63,64].

Diarylethene

Photochromic diarylethene derivatives consist of an ethene moiety that is surrounded by aromatic thiophene rings[65]. The typical isomerization of diarylethene from its open form to its closed form (six-membered ring), and vice versa, can be induced reversibly by exposure to UV or visible light, respectively. The open-to-closed photoisomerization expands the conjugated structure and thus substantially augments absorbance within the visible light range, triggering the molecule’s coloration[66]. Diarylethene molecules are typically colorless or very pale in an open form but vividly colored in their closed structures, such as blue, purple, or red. The primary features of diarylethene derivatives are impressive fatigue resistance and thermally irreversible properties, and they have prospective uses in molecular switches, information storage, and optoelectronic devices.

Donor-acceptor Stenhouse adducts (DASAs)

DASAs consist of three key components: electron-donating and electron-withdrawing groups, and a triene π-bridge between them. Depending on the chemical structure and substitution, the linear (highly conjugated) form of DASA can display strong colors ranging from yellow, orange, red, purple, or brown, in contrast to the colorlessness of the closed, cyclic form. The isomerization between linear and cyclic forms involves a total of fifteen intermediates[67]. DASA’s forward isomerization, from linear to cyclic, is induced by visible light—an advantageous characteristic compared to other photoswitches, [which usually need UV light for the forward process].[68] The reverse cyclic-to-linear isomerization occurs under heat. DASA possesses several other benefits, including exceptional fatigue resistance, elevated photoconversion efficiency, and remarkable thermal stability[69]. The prospective applications of these compounds in molecular switches, dynamic materials, and stimuli-responsive systems make them important to fields such as medication administration and sensing[70].

Naphthalenediimide

Naphthalene diimides are a class of electron-deficient compounds that can undergo a reversible one-electron reduction when exposed to an electron donor under irradiation, resulting in the formation of a stable radical anion[71]. These molecules contain an imide functional group, which serves as the key element governing their photochromic behavior[72]. This transformative event triggers a distinct and discernible alteration in color, allowing for visually noticeable changes. They have applications in smart coatings, optical filters, and color-changing materials across diverse industries[73,74].

Viologens

Viologen-based molecules feature a central bipyridinium core, which serves as the chromophore responsible for their photochromic behavior[75]. Upon exposure to light, viologens experience a reduction-oxidation (redox) process which triggers a characteristic color change. They have notable photoconversion efficiency, thermal stability, and adjustable redox characteristics, establishing them as crucial constituents in the advancement of photoresponsive materials, sensors, and electrochromic devices.

Fulgides

Fulgides encompass a central bismethylene-succinic anhydride moiety with an aromatic substituent. Fulgides convert from their open E-isomer to their C-form upon exposure to UV light[77], and the reverse occurs with visible light. In this context, the symbol E denotes the geometric arrangement of the double bond that connects the succinic anhydride and the aromatic ring, whereas the symbol C represents the closed configuration. Depending on molecular structure and environment, fulgides in their closed-ring, more-conjugated state can be yellow, red, orange, purple, or brown. Owing to breakage of conjugation in the molecule's π-system, the open-ring form is frequently colorless or pale. Fulgides possess distinctive characteristics, such as their ability to exhibit quick response times and demonstrate commendable fatigue resistance[78]. Fulgides exhibit potential in optoelectronic devices, as they possess photochromic features that can be utilized to manipulate and regulate light emission or electrical conductivity inside such devices[79,80].

Overcrowded alkenes

Overcrowded alkenes have a central core composed of multiple conjugated double bonds that are frequently organized in a polycyclic or cyclic structure. This arrangement causes a considerable level of strain within the molecule, resulting in exceptional photochromic characteristics[81]. Upon absorption of light, these molecules undergo reversible isomerization events, alternating between stable cis and trans configurations. This process involves the rotation of carbon-carbon double bonds, which is followed by alterations in molecular geometry and optical characteristics[82,83]. This reversible photoisomerization process allows for the manipulation of the molecule's electronic and steric properties, rendering overcrowded alkenes highly suitable for applications that demand light-induced responses[84].

Bottlenecks of organic solid-state photochromism

Although the benefits of solid-state organic photochromes make them more appropriate for commercial use than solution-phase photochromes, the practical implementation of the organic photochrome in the solid state still faces considerable obstacles (**Table 2**). These obstacles restrict the advancement of this field in commercial contexts. We now meticulously examine the prevalent challenges in organic solid-state photochromism that have not been systematically addressed in the current body of research.

Kinetics of photoisomerization

Compared to their solution state, organic photochromes in the solid state have reduced photochromic effectiveness, slow switching speeds, and limited color brightness. The photochromic efficiency may be influenced by the molecular structure of the photochromic molecules and the chemical environment of the solid matrix[85,86]. Furthermore, in the solid state, photochromic molecules easily aggregate with each other, which [decreases their molecular flexibility and ability to isomerize?] and lowers the switching rate of photochromismcompared to free molecules in solution[87,88]. Porous scaffolds provide a versatile platform for addressing the challenges associated with sluggish kinetics of photoisomerization. Through encapsulation, these scaffolds offer controlled environments, improved diffusion, and spatial confinement to prevent the aggregation of photochromic molecules and, consequently, to achieve solution-like photochromism in the solid-state.

Sunlight-induced isomerization

The majority of photoswitching occurs when exposed to UV light. However, owing to inherent limitations such as limited penetrability, photobleaching impact, and being harmful to humans, UV light is difficult to meet the demands of real-world applications[89]. Utilizing natural light as a means to control photoresponsivity is a desirable approach for practical uses of solid-state photoresponsive materials. Nevertheless, under natural light, the efficacy of isomerization is hindered by the intricate interplay between forward and backward processes of photoresponsive molecules, exemplified by azo compounds, spiropyran, diarylethenes, and anthracene. In this case, DASA stands out as a highly interesting contender because its isomerization process is controlled by visible light. A porous architecture offers a higher surface area [than a…], increasing interaction between the embedded photochromes and incident light, thus amplifying the photochromic response. The uniform distribution of photochromes within the material ensures consistent color changes when exposed to sunlight rather than patchy or uneven responses. In addition, the design of porous scaffolds can be tailored to optimize sunlight absorption, further improving the efficiency of sunlight-induced coloration.

Photo-fatigue resistance

Some solid photochromic materials have low photo fatigue resilience **[meaning?],** impacting their practical efficacy and reliability. An common factor is the accumulation of structural defects or damage within the molecular structure during photoisomerization[90], which can impede the photochromic reaction. The presence of photochemical side reactions is an additional factor contributing to reduced photosensitivity. Resistivity to photo-fatigue can be improved by various means, such as molecular design, materials engineering, and incorporation into porous scaffolds[91]. The porous scaffold acts as a protective barrier by shielding the embedded photochromes from environmental stresses and reducing deterioration, preserving their photochromic properties over time. Furthermore, the interaction between the photochromes and scaffold matrix promotes uniform distribution and chemical stability, further mitigating fatigue-inducing phenomena such as photobleaching and extending the operational lifespan of the embedded photochromes.

Durability

The insufficient long-term stability markedly hinders the implementation of photochromic materials in commercial settings. UV light exposure, moisture, and temperature fluctuations have a detrimental influence on the efficacy and longevity of photochromic materials. UV radiation, a prevalent constituent of sunshine, presents a substantial threat to the longevity of photochromic materials. Extended exposure to UV light has the potential to initiate photochemical reactions within photochromic molecules, resulting in modifications to their molecular composition[92]. Moisture, as an environmental factor, plays a pivotal role in the deterioration of host matrices, ultimately resulting in the material's degradation. With the presence of hydroxyl enrichment on the surface, numerous materials exhibiting porous structures demonstrate are hydrophilic and able to absorb water molecules from the surrounding atmosphere. [Although hydrophilicity is useful in certain cases?], it could pose a major issue for photoswitches that are sensitive to moisture. Fluctuations in temperature, too, influence the stability of photochromic materials, because they cause thermal stresses that deteriorate the molecular structures of organic photochromes. Incorporating the organic photochromes into porous scaffolds can enhance the photochromes' durability and longevity. The scaffold functions as a physical barrier, protecting the embedded photochromes from UV radiation, moisture/water vapor, and providing resistance to temperature flactuations.

Mechanical stiffness

The process of photoisomerization involves conformational changes and thus relies heavily on molecular flexibility[93,94]. However, the mobility and rotational behavior of photochromic molecules are constrained within polymer matrices characterized by a high degree of stiffness[95]. As a result, their ability to perform the necessary structural rearrangements and isomerization is limited[96]. Soft polymer matrices can alleviate mechanical constraints and improve the mobility of photochromic guests[97]. However, soft matrices have reduced mechanical robustness and are prone to deformation, resulting in diminished durability and resilience to environmental factors such as temperature fluctuations, humidity levels, and mechanical stress. Although practical applications favor rigid matrices, they can often restrict photochromic behavior. When the organic photochromes are confined within the cavity of the porous hosts, they are isolated from the surrounding environment. This confinement enables the photochromes to undergo photoisomerization even within mechanically rigid polymers, unlocking their full photoresponsive potential.

Sensitivity to thickness

Owing to the limited permeability of induced UV light, the greater depths of solid-state components might receive a very low intensity of light[9]. This is primarily caused by absorption and scattering phenomena. Hence, achieving photoresponsive materials with substantial thickness continues to pose a formidable challenge. The SURMOF concept is a solution to this issue. It is possible to fine-tune the thickness of SURMOF films to an extent that permits the excitation of virtually all photoactive moieties contained within the MOF[98]. In addition, SURMOF films may be more readily analyzed using UV-Vis spectroscopic techniques compared to their powdery counterparts, since light scattering is reduced. A viable alternative to SURMOFs are photoswitches that are triggered by visible and near-infrared (NIR) light, which have the benefit of increased depth penetration through materials in comparison to UV light[99].

Porous scaffold-based photochromism

Since azobenzene was incorporated into the nanopores of molecular sieves, like zeolite and silica, in 1997[100], the employment of porous solids as supports for solid-state photochromic materials has developed considerably. This section explores intrinsic (where the photochrome is part of the framework) and extrinsic (where the photochrome is a guest molecule inside the pore) strategies for creating highly efficient solid-state photochromic materials using different porous matrices (**Figure 3**). In addition to the illustrative examples discussed here (**Table 3**), there exists a substantial body of research that could not be included in detail (see Supplementary information, Supplementary Tables 1-9).

Intrinsic approach

In the intrinsic method, the photochromic molecule is incorporated [covalently?] into [precursor/building block/linker?] molecules before they are assembled into the porous solid, making them intrinsically part of the porous material. It is a highly effective strategy for producing solid-state photochromic materials with a substantially high conformation of the isomerization process. This approach disperses the photoswitches uniformly throughout the solid state, prevents leaching of the photoswitch, and reduces intermolecular aggregation, all of which enhance photochromic reactions. The incorporation of lengthy and soft alkyl chains into the photochromic molecules sometimes enhances the separation between the light-sensitive molecules, hence improving the overall isomerization process in the solid phase[101]. Photochromic components can be integrated into crystalline scaffolds as pendant side groups of the linker or as the linker backbone itself, contingent upon geometric constraints and synthetic capabilities.

Side group

The photo-switchable moiety can be incorporated as a pendant side group of the linker molecule (**Table 1**). As a component of the linker backbones, the lack of a guest or pendant group within the pores of porous scaffold allows for the complete utilization of the pore space, making it available for a multitude of functions[102,103]. This approach was introduced by functionalizing the [concave/inner side] of a [bent/V-shaped] linker molecule with an azobenzene side group, and then assembling these linkers with metal ions to form a coordination cage. The side groups all face the interior of the cage, and their photoisomerization causes a change in the cavity's hydrophobicity **[why is this?]** and thus affinity for a hydrophobic guest molecule. Thus, photoswitching the cage allows reversible uptake and release of the guest[104]. The synthesis of a twofold interpenetrated photoswitchable MOF, CAU-5 ($[Zn_2(NDC)_2(\mathbf{1})]$, **1**= 3-azo-phenyl-4,4′-bipyridine, 2,6-naphthalenedicarboxylic acid) was likewise achieved through this method[105]. This specific MOF showcases an exceptional capacity to undergo a reversible switch of the azo functionality within its porous scaffold. Similarly, optically sensitive MOPs were constructed with organic linkers that had been modified with azobenzene as a side group[106]. The MOPs demonstrated an impressive ability to capture and release guest molecules through a reversible isomerization process.

A photochromic porous aromatic framework was constructed from linkers containing pendant spiropyran groups, which jut into the framework pores[107]. Because metal cations bind to the charged merocyanine form but not the neutral spiropyran form, the framework demonstrated the ability to trap and release metal ions from solution, controlled by light. Additionally, these materials exhibited a unique form of chromism that is induced by the solvation and desolvation of the network. Porous solids that have been built from linkers based on overcrowded alkene were able to modulate porosity in response to light and heat[17]. The side group approach has additionally been effective at fabricating photochromic thin films[108]. Thin films with azobenzene side groups allow light to readily control properties like diffusion[109], permeability, membrane separation factors[110], and proton-conduction properties of guest molecules[111,112]. Nevertheless, there are instances where the progression of isomerization processes is impeded[113].

Backbone

Photoactive moieties can also be directly incorporated into the porous solid as the coordinative linker backbone (**Table 1).** This approach is anticipated to result in a substantially greater and more striking light-induced structural transformation than the side group approach, as the framework itself changes, not only its pendant groups. The concept of coordinatively immobilizing the photoswitch as part of the framework was first explored for diarylethene and spiropyran derivatives[16,117-121] and was subsequently expanded to encompass NDI, viologen, and other organic photoswitches[122-127].

Photoswitchable triply interpenetrated MOFs ($Zn(AzDC)(4,4'\text{-}BPE)_{0.5}$) were synthesized by coordinating two distinct photochromic linkers, trans-1,2-bis(4-pyridyl)-ethylene (4,4'-BPE) and 4,4'-dicarboxylate (AzDC), to Zn ions[114]. The pore diameters of the framework were considerably influenced by the inclusion of two photoresponsive groups, both of which underwent light-driven isomerization. This dramatic change in pore size with light enabled the immediate uptake and release of CO_2. Photochromic diarylethene compounds were coordinatively immobilized as pillars in a porphyrin-based MOF, making it light-driven and dynamically regulated[115]. The porphyrin-based linker functioned as the donor, facilitating the transmission of excitation energy to the diarylethene-based acceptor [bis(5-pyridyl-2-methyl-3-thienyl)-cyclopentane, BPMTC]. UV light irradiation of the resulting MOFs transformed BPMTC from its open-ring configuration to its closed-ring configuration. As a consequence, the luminescence of the MOF was subsequently extinguished. The restoration of the photoluminescence of the MOF can be accomplished through exposure to visible light. By employing the same kind of pyridine-terminated diarylethene, it is feasible to fabricate an interpenetrated Zn-MOF (Zn(L)-(bpdc)·solvents; L = diarylethene derivative; bpdc = biphenyl dicarboxylate), that exhibits reversible photochromism[116].

A two-dimensional MOF based on viologen linkers and Eu ions exhibits the ability to change color from yellow to blue/purple in a reversible manner when stimulated by both light and electricity[125]. This reversible phenomenon arises from the transfer of free electrons from the electron-rich carboxylate oxygen atom to the electron-deficient viologen group. In addition, a 3D noninterpenetrated pillar-layered photochromic MOF, denoted as $[Zn_2(HFIPBB)_2(DPNDI)]\cdot 8DMF$, was synthesized utilizing NDI-based linker N,N'-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (DPNDI)[128]. The photochromic material transformed its color from yellow to dark green when exposed to sunlight, and subsequently returned to its initial color when placed in a dark room for a number of days at room temperature.

The backbone approach can likewise be applied to other porous scaffolds such as COFs, POPs, and MOPs[129]. The use of spiropyran-based building units in a COF allows for the manipulation of its electrical characteristics in response to light[130]. This is achieved by ensuring that the COF induces a significant structural rearrangement of the SP molecule during its photoisomerization process. When exposed to UV irradiation, the spiropyran derivative isomerizes to generate the charge-separated merocyanine form within the COF, resulting in a notable enhancement of around 40% in conductivity. A self-assembling photochromic coordination cage utilizing a diarylethene photoswitch as a ligand, is capable of transitioning between a structurally flexible form and a rigid form upon exposure to UV or white light[131]. Introducing diarylethene-type moieties into the polymer backbone of a POP leads to a photoswitchable POP, which demonstrates the initial occurrences of heterogeneous photoswitchable photocatalysis[132]. A hydrogen-bonded crosslinked organic framework, HCOF-101, was created through the bonding of carboxylic acid dimers. This nanopore material underwent a 70% isomerization from trans-to-cis when exposed to 442 nm light irradiation, thanks to the infusion of hydrazone[133]. More recently, initial findings have been presented on solid-state photochromic materials derived from a MOF-glass structure. These materials incorporate two 1D diarylethene-based coordination polymers, ACP1 $[Ag_2(cis\text{-}dbe)(CF_3SO_3)_2]$ and $Ag_2(cis\text{-}dbe)(CF_3CO_2)_2]$[134]. In the glassy state, the cis-dbe (cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene) linker demonstrated the ability to undergo reversible photochromism[135,136].

Design of porous scaffolds

Unlike conventional material design outlines where porosity, pore type, surface hydrophobicity, and electronic features hold paramount importance, the intrinsic approach reshapes these priorities. Here, the covalently linked photochromic units within the framework render such factors relatively less pivotal, as these units become integral components of the porous scaffold. Porous hosts endowed with both coordination bonds, exemplified by MOFs, cages, metal-organic gels, and MOF-based glasses, are more suitable for the side group strategy compared to the backbone strategy. This is because having the photochromic unit as the backbone is associated with a large structural change to the material during photoisomerization, which substantially compromises the stability of a material held together by coordination bonds. In contrast, covalently bonded porous scaffolds like COFs, POP, and PAFs are typically more chemically stable, rendering them suitable for both strategies of the intrinsic approach. Moreover, the flexibility of the porous host plays a crucial role in accommodating the substantial structural changes that are inherent to the process of photoisomerization. Flexible frameworks, which can adapt and undergo conformational changes without compromising structural integrity, are therefore preferred over rigid counterparts.

Challenges

Although the intrinsic approach offers good molecular distribution of the guests throughout the porous solid and prevents the formation of second phases, this approach still faces a number of obstacles that need to be addressed in order to advance solid-state photochromism. The primary difficulty lies in the extensive synthetic endeavors required to produce linker molecules that feature the desired photoactive species as a side group or backbone. Photocrystallographic measurements of intrinsically photoswitchable frameworks and cage compounds are challenging owing to the inherent difficulty of producing a crystalline substance that remains structurally unchanged under photo-induced conditions. The kinetics of photoisomerization are also not as fast in framework-incorporated photoswitches as those of switches in solution. Furthermore, the risk of structural collapse that occurs during recurrent isomerization remains a challenge to be resolved in the absence of a fixed framework. For example, a photochromic UiO-type framework with azo-functionalized struts degraded upon exposure to white light[137]. Nevertheless, the degradation could be effectively managed by using a low light intensity, as it was observed that higher light intensity accelerated degradation. Likewise, an azo-based photochromic COF similarly loses its overall crystallinity as it undergoes photoisomerization[138]. The aforementioned issues can be avoided by employing the extrinsic approach to fabricate porous switchable solids.

Extrinsic approach

Introducing photoresponsive molecules extrinsically—as non-coordinative guests inside porous scaffolds—eliminates the need for complex synthetic modifications of the photochromes, while still offering the advantages of a crystalline matrix, such as spatial separation of the guests and resistance to photobleaching. These guest photoresponsive molecules exhibit solvent-like behavior owing to their exceedingly low concentrations within the pores (**Table 1**).

The photochromes can be confined within the pores primarily using either molecular diffusion or crystallization (**Table 1**). Using molecular diffusion, guests can be loaded in the solvent phase, or, if they have relatively low melting points (such as azo and spiropyran), through melting or gas phase methods. With solvent diffusion and crystallization methods, it is important to completely remove the entrapped solvent from the porous scaffold afterwards.

Although the concept of a MOF was proposed by 1995[139], it was not until 2010 that a photoswitch, stilbene, was successfully incorporated inside the nanopores of a MOF, $[\{(ZnI_2)_3(tris(4\text{-}pyridyl)triazine)_2\}.x(C_6H_5NO_2)]_n$[140]. In this work, the MOF facilitated the photoisomerization of stilbene exclusively in the solution phase by acting as a catalyst. Later, a notable advancement—photoisomerization in one direction in the solid phase—was demonstrated when azobenzene was encapsulated into a flexible porous coordination polymer ($[Zn_2(terephthalate)_2(triethylenediamine)]_n$) or MOF [141]. Light irradiation induced azobenzene's E→Z isomerization inside the MOF pore, transforming the flexible host material into a tetragonal and orthorhombic superposition. Since then, there has been extensive investigation into an extrinsic approach for the generation of solid-state photochromism[142-158].

The extrinsic approach was used to develop a photochromic cage by incorporating spiropyran into two flexible octahedral coordination cage molecules[159]. The encapsulated spiropyrans retained their ability to undergo photoswitching inside the cage. The resulting light-responsive cage demonstrated a phenomenon known as negative photochromism, where it transformed into a colorless state when exposed to blue light. In addition, encapsulating organic photochromes in a porous cage has been shown to enhance their kinetics and fatigue resistance, as in the case of photochromic dihydropyrene inside the octahedral coordination cage $Pd^{II}_6L_4$; L = 1,3,5-tris(1-imidazolyl)benzene[91,160-163].

Similarly, a solid-state photoresponsive PAF was prepared by the extrinsic approach. The diarylethene guest 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene was loaded into the PAF-1 framework, which then demonstrated the ability to capture and release CO_2 dynamically when exposed to a wide range of light[164]. The observed photodynamics resulted from the host-guest competition between the diarylethene and CO_2 within the sterically hindered, confined pores of the host.

Design of porous scaffolds

Despite numerous examples of photoswitchable solids synthesized using extrinsic strategies, clear guidelines for selecting appropriate porous scaffolds for specific photochromic guests are still lacking. This is primarily because the isomerization process of confined guest molecules is likely to be substantially influenced by the physicochemical environment within the scaffold nanopores[142].

The primary criterion of the extrinsic approach is that the pore size of the scaffold typically should be larger than the dimensions of the photochromic guest to be encapsulated. In addition to size, the shape [and/or structure?] of the pore also influences photochromic behavior (**Figure 3**). Cage-type pores, which are discrete three-dimensional cavities, are generally considered the optimal choice for solid-state photochromic applications. The cage structure acts as a physical barrier that confines the guests within its walls and prevents their diffusion or release. Meanwhile, channel-type pores, which interconnect through open pathways, allow the photochromic guests to move freely through the pore network. The diffusing guests often aggregate with each other, which reduces the photochromic behavior of the material.

We now describe appropriate porous scaffolds for the most widely explored photochromic guests: azo molecules, spiropyran, diarylethene-type molecules, DASAs, and fulgides. (Viologens, naphthalenediimides and overcrowded alkenes are typically used only in the intrinsic approach, as the linker backbones (see Supplementary information, Supplementary Table 8).)

The closed-to-open photoisomerization of spiropyran entails a consecutive series of events that includes the breaking of bonds, rearrangement of molecules, and alteration of electron configuration. As a result, it expands the π-electron delocalization and transitions from a less hydrophilic state to a more hydrophilic form. This forward photoisomerization can occur in a limited number of porous solids, but even in these solids, prolonged exposure to high irradiation time or intensity can lead to photobleaching of the photoswitch, which is not conducive to durability. Hence, the porous scaffold must be carefully chosen to enhance both the photoisomerization efficiency and the longevity of the materials. In a study last year using spiropyran guests, a few guidelines were proposed for selecting an optimal porous scaffold for photochromic materials that efficiently harness sunlight[165]. When spiropyran derivatives were enclosed within the ZIF-71 MOF ($Zn(dcIm)_2$; dcIm= 4,5-dichloroimidazolate), the resulting composites exhibited a much faster switching rate and greater resilience to fatigue compared to both the pristine photoswitch in solution and embedded in a nonporous polymer matrix. This study found that electron-deficient pore surfaces are not suitable for achieving sunlight-induced photochromism. The optimal pore size (greater or equal to the open-form size of the guest) and hydrophobicity (intermediate hydrophobicity) of porous scaffold matrices are likewise crucial to achieve SP-based efficient solid-state photochromic materials.

The process of isomerizing simple azobenzene from its trans (9 Å) to cis (5.5 Å) form results in a substantial change in dipole moment (0.52 to 3.08 Da) and requires an approximate free volume of 120-250 Å[170]. Hence, to demonstrate efficient photochromism within a scaffold, azo-containing guests must have enough pore volume to isomerize freely. One of the key approaches to improve the photoefficiency of this photoswitch is through the functionalization of the azo substituents as a side group of the linker backbones. The planarity and conjugated structure of trans-Azo promote intermolecular aggregation in the solid state, resulting in a decrease in the molecular energy of the trans-isomer. This, in turn, impedes the process of trans-to-cis isomerization. This issue can be remedied by the introduction of the functional groups onto the ortho-position of the phenyl ring, which lowers the planarity of the trans azo and therefore, reduces the intermolecular aggregation in solids[171]. A recent study has demonstrated that substituting the benzene ring with azoarenes (arylazo-3,5-dimethylisoxazoles derivatives) results in the enhanced stability of the cis isomer and effective photochromism in the solid-state[172]. It is worth noting that there is still a conspicuous absence of complete integration of all desirable structural features in a single material.

Open-to-closed photoisomerization of a diarylethene-type compound expands the conjugated structure, which leads to a notable enhancement in absorbance within the visible light spectrum. Consequently, porous scaffolds that have hydrophobic pores are expected to enable superior photoisomerization of their guests compared to solids with hydrophilic pores. [173]. There have been only a few reports of diarylethene derivatives incorporated into porous scaffold as guests. Therefore, future investigations are needed to systematically analyze the optimal physicochemical environment of a porous scaffold.

The isomerization properties of DASAs are greatly affected by the physicochemical attributes of the nanopores, including their geometric dimensions, configuration, and polarity. One study, in which

DASA molecules were incorporated into the pores of MIL-68(Al) and MIL-101(Cr), examined the correlation between the chemical environment of the MOF and the isomerization kinetics and efficiency[167]. MIL-68(Al) pores hindered linear-to-cyclic isomerization while promoting the cyclic-to-linear isomerization. Conversely, the isomerization behavior in MIL-101(Cr) follows a similar order of magnitudes to the solutions. Given the limited literature on DASA guests in porous scaffolds, further studies are necessary to establish a full set of guidelines for their hosts.

Fulgides have not yet been extensively studied as a guest in porous scaffolds. One study encapsulated the fulgide molecule Aberchrome 670 within two MOF hosts, MOF-5 and MIL-68(In), with different levels of polarity[168]. It was noted that the composites exhibited comparable photochromic performance overall, despite the hosts' different polarities. Another work found that Aberchrome 670 has a preference for porous scaffolds (UiO-68 in this case) with a pore size bigger than that of Aberchrome 670 itself, as well as a somewhat nonpolar environment[174]. However, there are many opportunities for conducting further investigation on fulgide-based porous photoswitches to unravel the influence of porous scaffolds.

Challenges

Scaffolds must also be designed to bolster the durability of the photoswitches. For example, guest leaching and intermolecular aggregation within the nanopores are substantial concerns with the extrinsic approach, but these challenges can be partially avoided by employing porous scaffolds with cage-based pores instead of channel-type pores. Eliminating trapped reactants and surplus solvent molecules that have become confined in the cavity of the porous scaffolds are also major challenges. Porous structures that are hydrophilic, such as porous coordination solids and carboxylate-based MOFs possessing a surface enriched with hydroxyl groups, can attract and absorb water molecules from the surrounding air[175-177]. However, this characteristic could be detrimental for moisture-sensitive photoswitches, potentially leading to unfavorable degradation. For example, the linear DASA coordinates in conjunction with water molecules and attains stability in a cyclic state, which remains unchanged in the absence of light. It is imperative to consider this effect during the initial phase of the scaffold design process[178].

Other porous scaffolds

In addition to the [modular/chemically designed?] porous scaffolds discussed above, organic photoswitches have likewise been embedded into more traditional porous solids, such as [mesoporous silica, zeolites / molecular sieves…?] to construct photoresponsive solid-state materials.

Mesoporous silica nanoparticles with azobenzene-functionalized pores demonstrated promise as light-driven dynamic nanoimpellers for delivering and releasing anticancer medications within living cells[185]. The incorporation of merocyanine spiropyran into the nanopores of mesoporous silica was successfully achieved using liquid assisted methods[186]. The SP present in the porous silica film demonstrated rapid photoisomerization when exposed to UV radiation, completing the process within 30 seconds. By comparison, under identical conditions, isomerization was undetectable in a single monolayer of spiropyran applied to a nonporous dense silica film.

Azo molecules loaded in zeolites were found to align parallel to the straight nanochannels, which can be attributed to the molecules' rod-like structure. Subsequent to this finding, extensive investigation has been dedicated to the application of zeolites as substrates for solid-state photoresponsive materials. Melamine sponge was also employed in solid-state photochromism through the attachment of spiropyran-containing polymers to its surface[187]. The sponge treated with spiropyran underwent closed-to-open isomerization within 30 minutes when exposed to 365 nm UV light. This reaction resulted in a noticeable color shift, transforming the sponge from a pale pink shade to a deep purple color. In another work, dip coating and thermocuring techniques were utilized to coat a layer of spiropyran-grafted PDMS onto a melamine sponge[188]. The isomerization from the closed to open state was achieved in 160 seconds when exposed to UV light, whereas reverting to the closed state in the absence of light required more than 70 minutes.

To manufacture a color-changing textile, thiol-ene click chemistry was used to securely attach a solid-state photochrome onto cotton fabrics[189]. Upon exposure to 365 nm UV light, the pale-yellow (closed form) cotton fabric transformed to purple (open form) within only 10 seconds. The purple cotton fabric was also found to exhibit a rapid rate of color fading when subjected to dark conditions for 5 minutes, to green light for less than 50 seconds, and to heating at 90 °C for 5 seconds.

A supramolecular host-guest complex that exhibits great flexibility yet maintains a reasonably stable chemical structure and can offer ample intrinsic mobility for photoresponsive molecules. A set of photoresponsive rotaxanes were synthesized through the use of spiropyran as one of the axle stoppers[190]. The solid-state closed-to-open isomerization of spiropyran occurs rapidly when the macrocyclic molecule is present on the axle. The incorporation of TPE into the macrocyclic molecule enabled reversible fluorescence switching in the solid powder state, which could be regulated by both UV and visible light irradiation.

Future perspectives

The integration of organic photochromic molecules into porous scaffolds to form multifunctional photoresponsive materials has become a focal point in advancing nanoscience and nanotechnology. Unlike zeolite host materials, the surface characteristics of porous scaffolds markedly impact the photochromism properties, thanks to the tunable chemical environment within their pores. Integrating photochromic molecules with nanoelectronics enables optical manipulation at both the molecular and macroscopic levels, which contributes to the potential development of novel intelligent devices. These photoresponsive materials are being widely employed in reversible optical data storage, photoswitchable fluorescence and cell detection, smart windows and coatings, self-cleaning surfaces, ion sensors, sorption study, anticounterfeiting applications, targeted therapy, photolithography, artificial muscles, nanotechnology, and nanomedicine, to name just a few.

Nonetheless, solid-state photochromic materials based on organic photoswitches and porous scaffolds still require much further development before they are commercially viable. From an economic standpoint, non-covalently associating photochromic dyes in porous scaffolds (through the extrinsic approach) continues to be a cost-effective avenue of research by virtue of the photochromes' solution-like behavior[146]. Even so, the mobility of non-covalently bound guest molecules makes it difficult to precisely characterize and understand the interactions between the molecules and pore surfaces. Moreover, the correlation between the loading of guests and the process of isomerization in the extrinsic approach is an important and understudied factor. The host frameworks are strongly influenced by the minimal loading of the photoresponsive molecules and favor guest-guest interactions when the loading amount is quite large. Being able to determine the local structures inside the pores—and thus the precise loading and localization of the photochromic molecules within them—will aid in understanding the fundamental dynamics of the host-guest and guest-guest interactions.

Natural sunlight-induced photochromism in the solid state is indispensable for commercial and real-world use. Although numerous examples of sunlight-induced photochromism in solid materials have been achieved, any fundamental design strategy for reliably producing this effect in porous solids remains unclear. Similarly, long-wavelength-induced light is preferred for solid-state photoresponsive materials owing to its good penetrability[191]. There is limited research in this direction, but appropriate molecular design and chemical modification of the photoresponsive molecule can also provide photochromism that is generated by long-wavelength light.

Photoresponsive molecules with reverse photochromic behavior are an excellent alternative for facilitating efficient solid-state photochromism. This is because the process of discoloration, starting from the outer layer, does not significantly impede the penetration of light into the inner space, ensuring fast and efficient photoisomerization. Two or more photochromic guest inclusions within a porous scaffold are also desirable because multiple guests can interact with each other,offering distinct guest-guest interactions, such as charge transfer or electron hopping, that can lead to intriguing material features such as in the design of the photon-driven molecular pump. The induction of chirality and optical activity in photoresponsive materials through the use of circularly polarized light is an emerging research topic for its potential in chiral resolution and information storage[192,193].

Fabrication of thin films is an attractive goal for expanding the potential applications of solid photochromic materials, because porous scaffolds are traditionally grown as single crystals or polycrystalline powders. The particle size of porous scaffold powders commonly falls within the micrometer range, resulting in considerable scattering effects in the UV and visible regions of the electromagnetic spectrum. The aforementioned phenomena are avoided in monolithic forms or thin films, as well as in SURMOFs[194]. The enhancement of light penetration in SURMOFs is achieved by increasing the surface-to-volume ratio of the particles in the MOF. Although fabricating SURMOFs using layer-by-layer procedures is a relatively simple process, achieving distinct boundaries between different types of MOFs is challenging when working with MOFs in powder form[195]. The creation of organic/inorganic heterointerfaces is important in several applications, such as photon upconversion and charge separation in solar cells. The study of molecule-surface interactions is currently constrained by a lack of comprehensive research, resulting in a limited understanding of the fundamental mechanisms involved in such systems.

In summary, we expect future research to examine possibilities for photoswitch-in-porous-scaffold systems that extend beyond the manipulation of adsorption capacities, diffusion coefficients, or membrane separation factors. The potential for further investigation is found in the light-induced modulation of electronic properties and the conduction of protons demonstrated by these devices. In the context of contemporary applications, there is widespread recognition that the use of photochromic dyes, either within or as components of porous scaffolds, represents the most appropriate choice. drive future industrial advancement in the years to come.

Competing interests statement

The authors declare no competing interests.

Author contributions

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Display items

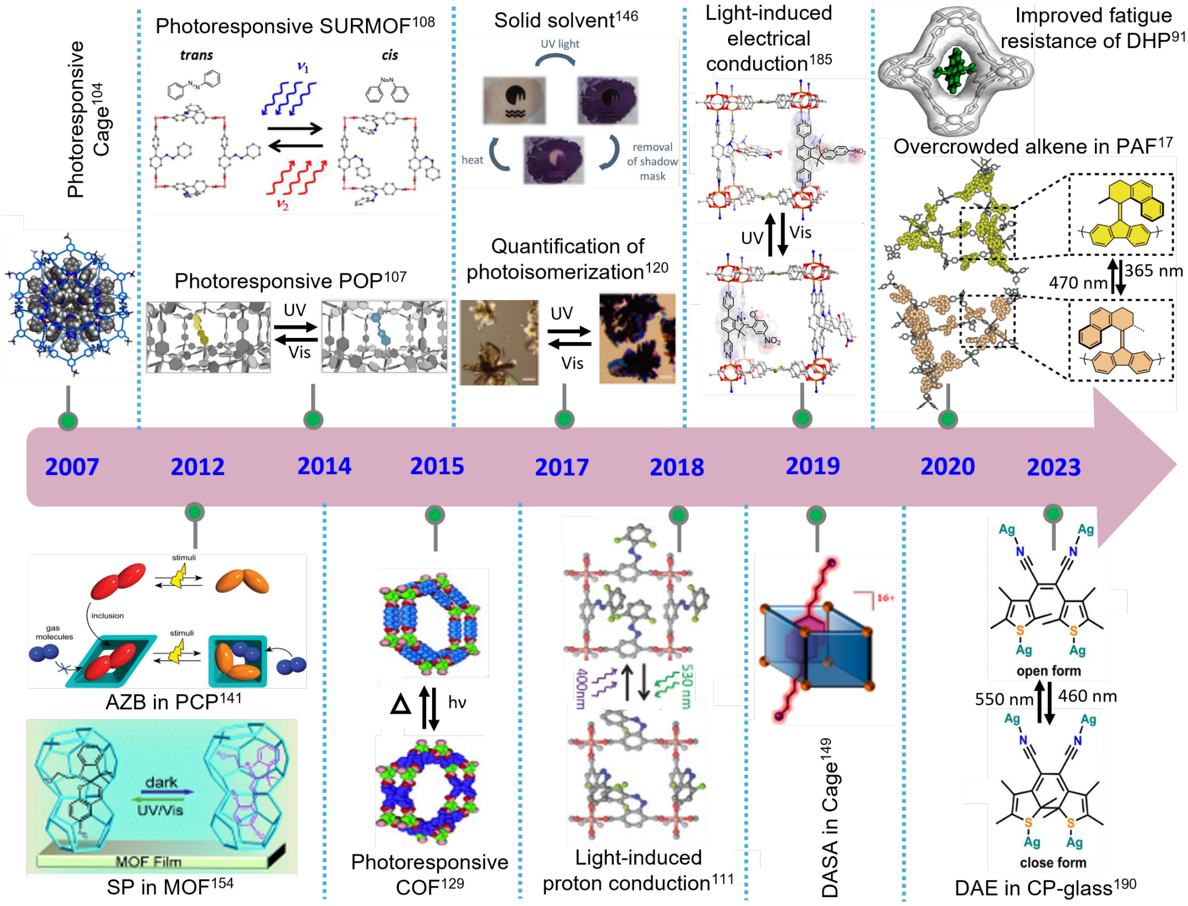
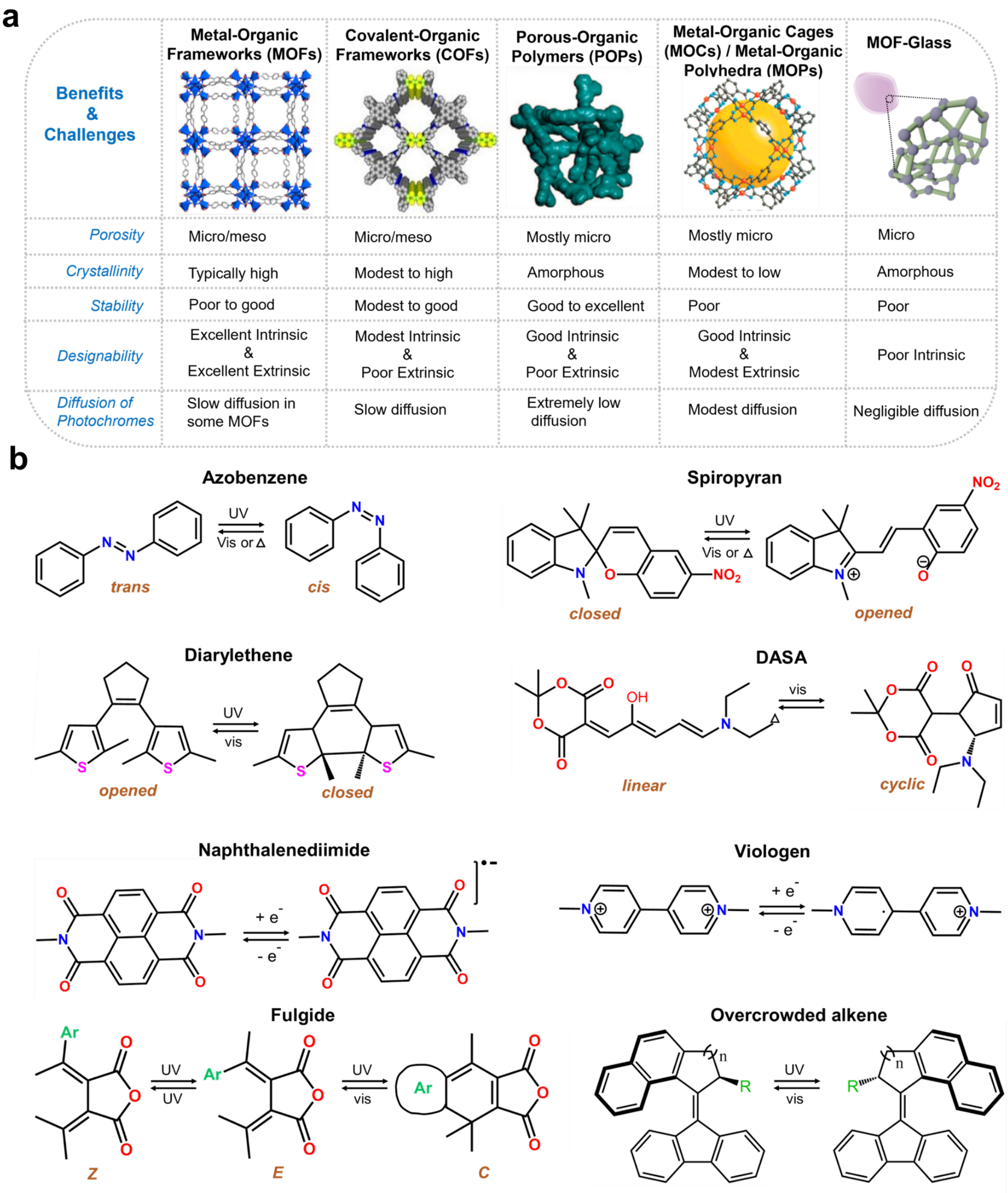


Figure 1. Key achievements in solid-state photochromism employing various porous scaffolds and organic photochromic molecules over the past decade. PCP, porous coordination polymer; AZB, azobenzene; DASA, donor-acceptor Stenhouse adducts; DAE, diarylethene; POP, porous organic polymer; SURMOF, surface-mounted MOF; PAF, porous aromatic framework; DHP, dihydropyrene. All the figures are adopted with the permission from the aforementioned (with figures) reference number.



Benefits & Challenges	Metal-Organic Frameworks (MOFs)	Covalent-Organic Frameworks (COFs)	Porous-Organic Polymers (POPs)	Metal-Organic Cages (MOCs) / Metal-Organic Polyhedra (MOPs)	MOF-Glass
Porosity	Micro/meso	Micro/meso	Mostly micro	Mostly micro	Micro
Crystallinity	Typically high	Modest to high	Amorphous	Modest to low	Amorphous
Stability	Poor to good	Modest to good	Good to excellent	Poor	Poor
Designability	Excellent Intrinsic & Excellent Extrinsic	Modest Intrinsic & Poor Extrinsic	Good Intrinsic & Poor Extrinsic	Good Intrinsic & Modest Extrinsic	Poor Intrinsic
Diffusion of Photochromes	Slow diffusion in some MOFs	Slow diffusion	Extremely low diffusion	Modest diffusion	Negligible diffusion

Figure 2. Choices of porous scaffolds and organic photoswitches. (a) Different porous scaffolds present benefits and challenges in the production of solid-state photochromic materials. (b) Organic photoswitchable molecules that have been included in porous scaffolds. UV, ultra-violet; vis, visible (light). The figure of MOFs is reproduced from REF[26], ACS; the COF is reproduced from REF[29], Wiley; the POP figure is reproduced from REF[36], ACS; the MOP figure is reproduced from REF[33], ACS.

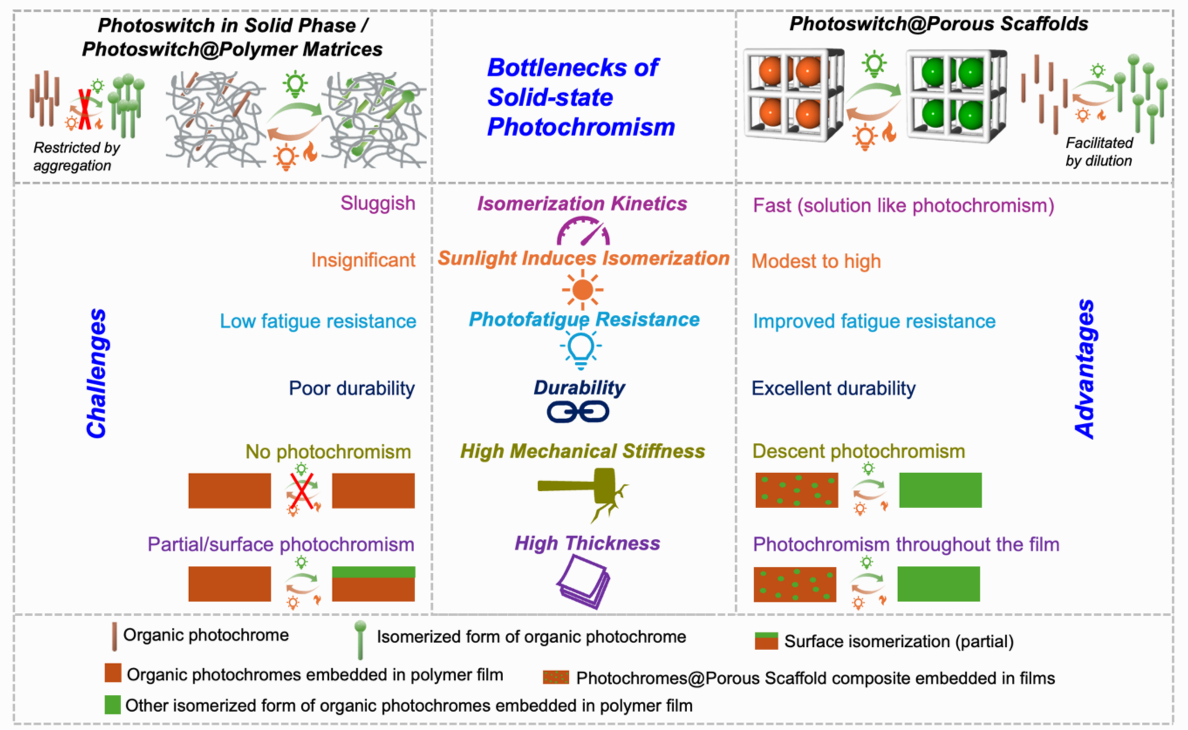


Figure 3. Design options for efficient photoswitchable solids utilizing porous scaffolds. The figures related to the backbone[121], side group[166], extrinsic[152], large and small pore[142], cage and channel type pore shape[167], intermediate and strongly hydrophobic[168], intermediate hydrophobic, and strong hydrophobic[168], electron-deficient[169], efficient photochromism[165] are adopted with permission from the relevant reference number.

Table 1. Approaches to producing solid-state photochromic materials using organic photoswitches incorporated into various porous scaffolds.

Design approach		**Benefits**	**Porous scaffolds**	**Organic photoswitches**
Intrinsic	Side group	Uniform distribution; Reduced aggregation; Minimized leaching	MOFs COFs POPs MOPs MOF-glasses	Spiropyrans Diarylethenes Azo molecules Naphthalenediimides Viologens Overcrowded alkenes
	Backbone			

Extrinsic	Loading via molecular diffusion	Loading via solvent phase	Avoids complex synthetic procedure; Solution-like photochromism; Enhanced durability	MOFs COFs POPs MOPs	Spiropyrans Diarylethenes Azobenzene DASAs Fulgides Viologens
		Loading via melting			
		Loading via gas phase infiltration			
	Loading via crystallization				

Table 2. Properties of photoswitches in a nonporous polymer matrix versus a porous scaffold.

Property	**Photoswitch in nonporous polymer matrix**	**Photoswitch in porous scaffold**
Isomerization kinetics	Sluggish	Fast (solution-like)
Sunlight-induced isomerization	Insignificant	Modest to high
Photofatigue resistance	Low	Improved over polymer matrix?
Durability	Poor	Excellent
Photochromism with high mechanical stiffness	None	[decent]
Photochromism with high thickness	Partial/surface photochromism	Photochromism throughout film

Table 3. Major achievements in solid-state photochromism utilizing porous scaffolds.

Material	***Porous Scaffolds***	***Organic photoswitch***	***Design Approach***	**Applications**	**Refs**
Azobenzene loaded AlPO4-5, ZSM-5, Silicate-1	Zeolite/Silica	Azobenzene	Extrinsic	Investigation of photochromic behavior	100
$[\text{Zn}_2(\text{terephthalate})_2(\text{triethylenediamine})]_n$	Flexible MOF	Azobenzene	Extrinsic	Light and heat-triggered gas adsorption	141

DTE@$Zn_2(BDC)_2(DABCO)$	MOF	DAE	Extrinsic	Investigation of photoisomerization	179
$Mg_2(C_{26}H_{16}O_6N_2)$ [Azo-IRMOF-74- III]	MOF	Functionalized azo	Intrinsic (side group)	Light-induced cargo release	180
$Cu_2(BPDC)_2(BiPy)$	SURMOF	Functionalized azo	Intrinsic (side group)	Light-driven uptake and release of guests	108
Functionalized MOP	MOP	Functionalized Azo	Intrinsic (side group)	Photo-induced guest capture and release	106
PhotoPAF-3.6	POP	Functionalized SP	Intrinsic (backbone)	Solvent-free acidochromism, light-controlled capture and release of metal ions	107
$Zn_2(DBTD)(BPMTC)$ [PC-PCN] and $Zn_2(ZnTCPP)(BPMTC)$ [SO-PCN]	MOF	Functionalized DAE	Intrinsic (backbone)	Heterogeneous catalysis	181
$Mg_4(BIPA\text{-}TC)_2(OH)(DMF)3$ [Mg-NDI]	MOF	Functionalized NDI	Intrinsic (backbone)	Inkless and erasable printing	122
SP-1@$Zn_4O(BDC)_3$ [MOF-5] SP-1@Ga(OH)(BDC).0.9DMF.xH_2O [MIL-68-(Ga)] SP-1@In(OH)(BDC).DMF.xH_2O [MIL-68-(In)] SP 1@Al(OH)(BDC) MIL-53-(Al)]	MOF {MOF-5, MIL-68(Ga), MIL-68(In), MIL-53(Al)}	NSP	Extrinsic	Investigation of photochromism	146
[$Zn_4(bdc)_4(Lo)_2$. 4DMF.H_2O]n	Soft porous crystal	Functionalized DAE	Intrinsic (backbone)	Investigation of quantitative photoisomerization	120
2D MONs	2D MOF	Functionalized 2,2-diphenylbenzopyran	Intrinsic (backbone)	Investigation of photochromism	96

NSP@Cage	Cage	Functionalized NSP	Extrinsic	Self-erasing image	159
Zn_2(DBTD)(TNDS)	MOF	Functionalized NSP	Intrinsic (backbone)	Light driven electronic behavior	121
ANT@Zn(MeIm)$_2$ (ZIF-8)	MOF {ZIF-8}	Anthracene	Extrinsic	Photopatterning	152
COF-O and COF-C	COF	Functionalized DAE	Intrinsic (backbone)	Conductivity-driven lightemitting diode (LED) switching	182
{[Eu(RL)(NO_3)$_2$(H_2O)](H_2O)}n	MOF	MOF	Functionalized viologen	Intrinsic (backbone)	125
PSF	PAF	Functionalized overcrowded alekene	Intrinsic (side group)	Light and heat-driven gas adsorption	17
CON	COF	Functionalized azo	Intrinsic (backbone)	Light-driven molecular sieving separations	183
Fulgide@ $Zn_4O(BDC)_3$ [MOF-5] Fulgide@ In(OH)(BDC).DMF.xH_2O [MIL-68(In)]	MOF {MOF-5, MIL-68-(In)}	Fulgide	Extrinsic	Investigation of photochromism	168
Photoswitchable host-guest complexes	Cage	PAH (polycyclic aromatic hydrocarbon)	Extrinsic	Photochromism of multiple guests	184
[Ag_2(cis-dbe) (CF_3SO_3)$_2$] AgCP1 and Ag_2(cis-dbe)(CF_3CO_2)$_2$] (AgCP2)	MOF-Glass	Functionalized DAE	Intrinsic (Backbone)	Selective gas sorption behaviors ofacetylene over CO_2	134
NSP@ Zn(dcIm)$_2$ [ZIF-71(20)]	MOF {ZIF-71}	Derivatives of SP	Extrinsic	Prototype smart windows, self-erasing rewritable devices, and anticounterfeiting	165

ZSM, Zeolite Socony Mobil-5; DTE, 1,2-bis(2,5-dimethyl-thien-3-yl)- perfluorocyclopentene; BDC, benzene-1,4-dicarboxylic acid; DABCO, 1,4-Diazabicyclo[2.2.2]octane; IRMOF, iso-reticular metal-organic framework; BPDC, biphenyl-4,4′-dicarboxylate; BiPy, 4,4′-bipyridine; DBTD, 3′,6′-dibromo-4′,5′-bis(4-carboxyphenyl)-1[1,1′:2′,1″-tetraphenyl]-4,4″-dicarboxylate ; PC-PCN, photochromic porous coordination network; SO-PCN, singlet oxygen-generating porous coordination network; PCN, porous coordination network; TCPP, tetrakis(4-carboxyphenyl)porphyrin; BPMTC, bis(5-pyridyl-2-methyl-3-thienyl)cyclopentane; H_4BIPA-TC, diisophthalic acid ; DMF, N,N-dimethylformamide; MON, metal-organic framework nanosheet; DBTD, 3′,6′-dibromo-4′,5′-bis(4-carboxyphenyl)-[1,1′,2′,1″-terphenyl]-4,4″-dicarboxylate; TNDC, 1′,3′,3′-trimethyl-6-nitro-4′,7′-di(pyridin-4-yl)spiro-[chromene-2,2′-indoline]; MeIm, 2-methylimidazolate ; ANT, anthracene ; PSF, porous switchable frameworks; CON, covalent organic nanosheet ; cis-dbe, cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene; dcIm, 4,5-dichloroimidazolate.

References

1 Badour, Y., Jubera, V., Andron, I., Frayret, C. & Gaudon, M. Photochromism in inorganic crystallised compounds. *Opt. Mater.: X* **12**, 100110, (2021).

2 Hirshberg, Y. Photochromie Dans La Serie De La Bianthrone. *C. R. Hebd. Seances Acad. Sci.* **231**, 903-904, (1950).

3 Bouas-Laurent, H. & Dürr, H. Organic photochromism. *Pure Appl. Chem.* **73**, 639-665, (2001).

4 Ru, Y. *et al.* Recent progress of photochromic materials towards photocontrollable devices. *Mater. Chem. Front.* **5**, 7737-7758, (2021).

5 Zhang, J., Zou, Q. & Tian, H. Photochromic materials: more than meets the eye. *Adv. Mater.* **25**, 378-399, (2013).

6 van Leeuwen, T., Lubbe, A. S., Štacko, P., Wezenberg, S. J. & Feringa, B. L. Dynamic control of function by light-driven molecular motors. *Nat. Rev. Chem.* **1**, 0096, (2017).

7 Leith, G. A. *et al.* Dynamically Controlled Electronic Behavior of Stimuli-Responsive Materials: Exploring Dimensionality and Connectivity. *Adv. Energy Mater.* **12**, 2100441, (2021).

8 Huang, Q. & Wu, C. Photoswitching metal organic frameworks development and applications on environmental related topics. *Mater. Today Sustain.* **18**, 100149, (2022).

9 Sun, F. & Wang, D. Toward real-world applications: promoting fast and efficient photoswitching in the solid state. *J. Mater. Chem. C* **10**, 13700-13716, (2022).

10 Wang, S., Fan, W., Liu, Z., Yu, A. & Jiang, X. Advances on tungsten oxide based photochromic materials: strategies to improve their photochromic properties. *J. Mater. Chem. C* **6**, 191-212, (2018).

11 Ohko, Y. *et al.* Multicolour photochromism of TiO2 films loaded with silver nanoparticles. *Nat. Mater.* **2**, 29-31, (2003).

12 Corns, S. N., Partington, S. M. & Towns, A. D. Industrial organic photochromic dyes. *Color. Technol.* **125**, 249-261, (2009).

13 Leith, G. A. *et al.* Confinement-guided photophysics in MOFs, COFs, and cages. *Chem. Soc. Rev.* **50**, 4382-4410, (2021).

14 Wang, L. & Li, Q. Photochromism into nanosystems: towards lighting up the future nanoworld. *Chem. Soc. Rev.* **47**, 1044-1097, (2018).

15 Grommet, A. B., Feller, M. & Klajn, R. Chemical reactivity under nanoconfinement. *Nat. Nanotechnol.* **15**, 256-271, (2020).

16 Rice, A. M. *et al.* Photophysics Modulation in Photoswitchable Metal-Organic Frameworks. *Chem. Rev.* **120**, 8790-8813, (2020).

17 Castiglioni, F. *et al.* Modulation of porosity in a solid material enabled by bulk photoisomerization of an overcrowded alkene. *Nat. Chem.* **12**, 595-602, (2020).

18 Gui, B. *et al.* Immobilizing Organic-Based Molecular Switches into Metal-Organic Frameworks: A Promising Strategy for Switching in Solid State. *Macromol. Rapid Commun.* **39**, 1700388, (2018).

19 Zhao, D., Thallapally, P. K., Petit, C. & Gascon, J. Advanced Porous Materials: Design, Synthesis, and Applications in Sustainability. *ACS Sustainable Chem. Eng.* **7**, 7997-7998, (2019).

20 Cheng, Y. D. *et al.* Advanced Porous Materials in Mixed Matrix Membranes. *Adv. Mater.* **30**, 1802401, (2018).

21 Makal, T. A., Li, J. R., Lu, W. G. & Zhou, H. C. Methane storage in advanced porous materials. *Chem. Soc. Rev.* **41**, 7761-7779, (2012).

22 Horike, S., Shimomura, S. & Kitagawa, S. Soft porous crystals. *Nat Chem* **1**, 695-704, (2009).

23 Maurin, G., Serre, C., Cooper, A. & Ferey, G. The new age of MOFs and of their porous-related solids. *Chem. Soc. Rev.* **46**, 3104-3107, (2017).

24 Lustig, W. P. *et al.* Metal-organic frameworks: functional luminescent and photonic materials for sensing applications. *Chem. Soc. Rev.* **46**, 3242-3285, (2017).

25 Babal, A. S. *et al.* Parts-per-billion (ppb) selective iodine sensors leveraging metal-organic framework nanoenvironment. *Mater. Today* **58**, 91-99, (2022).

26 Wang, C. *et al.* Dye@bio-MOF-1 Composite as a Dual-Emitting Platform for Enhanced Detection of a Wide Range of Explosive Molecules. *ACS Appl. Mater. Interfaces* **9**, 20076-20085, (2017).

27 Lyle, S. J., Waller, P. J. & Yaghi, O. M. Covalent Organic Frameworks: Organic Chemistry Extended into Two and Three Dimensions. *Trends Chem.* **1**, 172-184, (2019).

28 Huang, N., Wang, P. & Jiang, D. L. Covalent organic frameworks: a materials platform for structural and functional designs. *Nat. Rev. Mater.* **1**, 16068, (2016).

29 Chen, X. Y. *et al.* Covalent Organic Frameworks: Chemical Approaches to Designer Structures and Built-In Functions. *Angew. Chem. Int. Ed.* **59**, 5050-5091, (2020).

30 Mollick, S., Fajal, S., Mukherjee, S. & Ghosh, S. K. Stabilizing Metal-Organic Polyhedra (MOP): Issues and Strategies. *Chem. Asian J.* **14**, 3096-3108, (2019).

31 Ahmad, N., Younus, H. A., Chughtai, A. H. & Verpoort, F. Metal-organic molecular cages: applications of biochemical implications. *Chem. Soc. Rev.* **44**, 9-25, (2015).

32 Hasell, T. & Cooper, A. I. Porous organic cages: soluble, modular and molecular pores. *Nat. Rev. Mater.* **1**, 16053, (2016).

33 Eddaoudi, M. *et al.* Porous metal-organic polyhedra: 25 Å cuboctahedron constructed from 12 Cu2(CO2) paddle-wheel building blocks. *J. Am. Chem. Soc.* **123**, 4368-4369, (2001).

34 Lee, J. S. M. & Cooper, A. I. Advances in Conjugated Microporous Polymers. *Chem. Rev.* **120**, 2171-2214, (2020).

35 Mohamed, M. G., EL-Mahdy, A. F. M., Kotp, M. G. & Kuo, S. W. Advances in porous organic polymers: syntheses, structures, and diverse applications. *Mater. Adv.* **3**, 707-733, (2022).

36 Jiang, J. X. *et al.* Synthetic control of the pore dimension and surface area in conjugated microporous polymer and copolymer networks. *J. Am. Chem. Soc.* **130**, 7710-7720, (2008).

37 Bennett, T. D. *et al.* Hybrid glasses from strong and fragile metal-organic framework liquids. *Nat. Commun.* **6**, 8079, (2015).

38 Hou, J. W. *et al.* Metal-organic framework crystal-glass composites. *Nat. Commun.* **10**, (2019).

39 Hou, J., Sapnik, A. F. & Bennett, T. D. Metal-organic framework gels and monoliths. *Chem. Sci.* **11**, 310-323, (2020).

40 Zhang, J. Y. & Su, C. Y. Metal-organic gels: From discrete metallogelators to coordination polymers. *Coord. Chem. Rev.* **257**, 1373-1408, (2013).

41 Bennett, T. D. & Horike, S. Liquid, glass and amorphous solid states of coordination polymers and metal–organic frameworks. *Nat. Rev. Mater.* **3**, 431-440, (2018).

42 Che, S. & Fang, L. Porous Ladder Polymer Networks. *Chem* **6**, 2558-2590, (2020).

43 Horike, S. & Kitagawa, S. The development of molecule-based porous material families and their future prospects. *Nat. Mater.* **21**, 983-985, (2022).

44 Slater, A. G. & Cooper, A. I. Function-led design of new porous materials. *Science* **348**, aaa8075, (2015).

45 Giri, N. *et al.* Liquids with permanent porosity. *Nature* **527**, 216-220, (2015).

46 Fulvio, P. F. & Dai, S. Porous Liquids: The Next Frontier. *Chem* **6**, 3263-3287, (2020).

47 Grommet, A. B., Lee, L. M. & Klajn, R. Molecular Photoswitching in Confined Spaces. *Acc. Chem. Res.* **53**, 2600-2610, (2020).

48 Kim, C. R., Uemura, T. & Kitagawa, S. Inorganic nanoparticles in porous coordination polymers. *Chem. Soc. Rev.* **45**, 3828-3845, (2016).

49 Rösler, C. & Fischer, R. A. Metal-organic frameworks as hosts for nanoparticles. *CrystEngComm* **17**, 199-217, (2015).

50 Mollick, S., Fajal, S., Saurabh, S., Mahato, D. & Ghosh, S. K. Nanotrap Grafted Anion Exchangeable Hybrid Materials for Efficient Removal of Toxic Oxoanions from Water. *ACS Cent. Sci.* **6**, 1534-1541, (2020).

51 Gutiérrez, M., Zhang, Y. & Tan, J. C. Confinement of Luminescent Guests in Metal-Organic Frameworks: Understanding Pathways from Synthesis and Multimodal Characterization to Potential Applications of LG@MOF Systems. *Chem. Rev.* **122**, 10438-10483, (2022).

52 Bigdeli, F., Lollar, C. T., Morsali, A. & Zhou, H. C. Switching in Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **59**, 4652-4669, (2020).

53 Martin-Illan, J. A. *et al.* Macroscopic Ultralight Aerogel Monoliths of Imine-based Covalent Organic Frameworks. *Angew. Chem. Int. Ed.* **60**, 13969-13977, (2021).

54 Horike, S., Nagarkar, S. S., Ogawa, T. & Kitagawa, S. A New Dimension for Coordination Polymers and Metal-Organic Frameworks: Towards Functional Glasses and Liquids. *Angew. Chem. Int. Ed.* **59**, 6652-6664, (2020).

55 Mollick, S. *et al.* Hydrophobic Shielding of Outer Surface: Enhancing the Chemical Stability of Metal-Organic Polyhedra. *Angew. Chem. Int. Ed.* **58**, 1041-1045, (2019).

56 Three-dimensional optical data storage using photpochromic materials. *Chem. Rev.* **100**, 1777-1788, (2000).

57 Browne, W. R. & Feringa, B. L. Making molecular machines work. *Nat. Nanotechnol.* **1**, 25-35, (2006).

58 Russew, M. M. & Hecht, S. Photoswitches: From Molecules to Materials. *Adv. Mater.* **22**, 3348-3360, (2010).

59 Mukhopadhyay, R. D., Praveen, V. K. & Ajayaghosh, A. Photoresponsive metal–organic materials: exploiting the azobenzene switch. *Mater. Horiz.* **1**, 572-576, (2014).

60 Bandara, H. M. & Burdette, S. C. Photoisomerization in different classes of azobenzene. *Chem. Soc. Rev.* **41**, 1809-1825, (2012).

61 Kortekaas, L. & Browne, W. R. The evolution of spiropyran: fundamentals and progress of an extraordinarily versatile photochrome. *Chem. Soc. Rev.* **48**, 3406-3424, (2019).

62 Klajn, R. Spiropyran-based dynamic materials. *Chem. Soc. Rev.* **43**, 148-184, (2014).

63 Keyvan Rad, J., Balzade, Z. & Mahdavian, A. R. Spiropyran-based advanced photoswitchable materials: A fascinating pathway to the future stimuli-responsive devices. *J. Photochem. Photobiol. C Photochem. Rev.* **51**, (2022).

64 Ali, A. A., Kharbash, R. & Kim, Y. Chemo- and biosensing applications of spiropyran and its derivatives - A review. *Anal. Chim. Acta* **1110**, 199-223, (2020).

65 Irie, M., Fukaminato, T., Matsuda, K. & Kobatake, S. Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. *Chem. Rev.* **114**, 12174-12277, (2014).

66 Matsuda, K. & Irie, M. Diarylethene as a photoswitching unit. *J. Photochem. Photobiol.* **5**, 169-182, (2004).

67 Zulfikri, H. *et al.* Taming the Complexity of Donor-Acceptor Stenhouse Adducts: Infrared Motion Pictures of the Complete Switching Pathway. *J. Am. Chem. Soc.* **141**, 7376-7384, (2019).

68 Helmy, S. *et al.* Photoswitching Using Visible Light: A New Class of Organic Photochromic Molecules. *J. Am. Chem. Soc.* **136**, 8169-8172, (2014).

69 Peterson, J. A., Neris, N. M. & de Alaniz, J. R. Tethered together: DASA design towards aqueous compatibility. *Chem. Sci.* **14**, 13025-13030, (2023).

70 Lerch, M. M., Szymanski, W. & Feringa, B. L. The (photo)chemistry of Stenhouse photoswitches: guiding principles and system design. *Chem. Soc. Rev.* **47**, 1910-1937, (2018).

71 Bhosale, S. V. *et al.* Naphthalene diimides: perspectives and promise. *Chem. Soc. Rev.* **50**, 9845-9998, (2021).

72 Bhosale, S. V., Jani, C. H. & Langford, S. J. Chemistry of naphthalene diimides. *Chem. Soc. Rev.* **37**, 331-342, (2008).

73 Al Kobaisi, M., Bhosale, S. V., Latham, K., Raynor, A. M. & Bhosale, S. V. Functional Naphthalene Diimides: Synthesis, Properties, and Applications. *Chem. Rev.* **116**, 11685-11796, (2016).

74 Chlebosz, D., Goldeman, W., Janus, K., Szuster, M. & Kiersnowski, A. Synthesis, Solution, and Solid State Properties of Homological Dialkylated Naphthalene Diimides-A Systematic Review of Molecules for Next-Generation Organic Electronics. *Molecules* **28**, 2940, (2023).

75 Kamogawa, H. & Ono, T. Redox Photochromism in Films of Viologens and Related-Compounds Bearing Long-Chain Alkyl-Groups. *Chem. Mater.* **3**, 1020-1023, (1991).

76 Yokoyama, Y. Fulgides for Memories and Switches. *Chem. Rev.* **100**, 1717-1740, (2000).

77 Francini, F., Ottavi, G., Sansoni, P. & Tiribilli, B. Characterisation of fulgides in a solid matrix as recording materials for optical components. *Opt. Commun.* **130**, 235-240, (1996).

78 Weerasekara, R. K., Uekusa, H. & Hettiarachchi, C. V. Multicolor Photochromism of Fulgide Mixed Crystals with Enhanced Fatigue Resistance. *Cryst. Growth Des.* **17**, 3040-3047, (2017).

79 Jiao, Y. *et al.* Fulgide Derivative-Based Solid-State Reversible Fluorescent Switches for Advanced Optical Memory. *CCS Chem.* **4**, 132-140, (2022).

80 Chen, Y., Wang, C. M., Fan, M. G., Yao, B. L. & Menke, N. Photochromic fulgide for holographic recording. *Opt. Mater.* **26**, 75-77, (2004).

81 Wang, H., Bisoyi, H. K., Zhang, X., Hassan, F. & Li, Q. Visible Light-Driven Molecular Switches and Motors: Recent Developments and Applications. *Chem. Eur. J.* **28**, e202103906, (2022).

82 Jiang, Y. Z., Danowski, W., Feringa, B. L. & Heinke, L. Nanoporous Films with Oriented Arrays of Molecular Motors for Photoswitching the Guest Adsorption and Diffusion. *Angew. Chem. Int. Ed.* **62**, e202214202, (2023).

83 Danowski, W. *et al.* Unidirectional rotary motion in a metal-organic framework. *Nat. Nanotechnol.* **14**, 488-+, (2019).

84 van Leeuwen, T., Lubbe, A. S., Stacko, P., Wezenberg, S. J. & Feringa, B. L. Dynamic control of function by light-driven molecular motors. *Nat. Rev. Chem.* **1**, 0096, (2017).

85 Weis, P., Wang, D. S. & Wu, S. Visible-Light-Responsive Azopolymers with Inhibited π-π Stacking Enable Fully Reversible Photopatterning. *Macromolecules* **49**, 6368-6373, (2016).

86 Torres-Pierna, H., Ruiz-Molina, D. & Roscini, C. Highly transparent photochromic films with a tunable and fast solution-like response. *Mater. Horiz.* **7**, 2749-2759, (2020).

87 Priimagi, A., Kaivola, M., Rodriguez, F. J. & Kauranen, M. Enhanced photoinduced birefringence in polymer-dye complexes: Hydrogen bonding makes a difference. *Appl. Phys. Lett.* **90**, 121103, (2007).

88 Anzai, J. I. & Osa, T. Photosensitive Artificial Membranes Based on Azobenzene and Spirobenzopyran Derivatives. *Tetrahedron* **50**, 4039-4070, (1994).

89 Tian, J. *et al.* Sunlight-induced photo-thermochromic smart window based spiropyran-functionalized copolymer for UV shielding and sunlight management. *Prog. Org. Coat.* **160**, 106531, (2021).

90 Chan, J. C. H., Lam, W. H. & Yam, V. W. W. A Highly Efficient Silole-Containing Dithienylethene with Excellent Thermal Stability and Fatigue Resistance: A Promising Candidate for Optical Memory Storage Materials. *J. Am. Chem. Soc.* **136**, 16994-16997, (2014).

91 Canton, M. *et al.* Improving Fatigue Resistance of Dihydropyrene by Encapsulation within a Coordination Cage. *J. Am. Chem. Soc.* **142**, 14557-14565, (2020).

92 Malatesta, V. *et al.* Oxidative-Degradation of Organic Photochromes. *Mol. Cryst. Liq. Cryst.* **246**, 303-310, (1994).

93 Ercole, F., Malic, N., Davis, T. P. & Evans, R. A. Optimizing the photochromic performance of naphthopyrans in a rigid host matrix using poly(dimethylsiloxane) conjugation. *J. Mater. Chem.* **19**, 5612-5623, (2009).

94 Williams, D. R. M. & Fredrickson, G. H. Cylindrical Micelles in Rigid-Flexible Diblock Copolymers. *Macromolecules* **25**, 3561-3568, (1992).

95 Ercole, F., Davis, T. P. & Evans, R. A. Photo-responsive systems and biomaterials: photochromic polymers, light-triggered self-assembly, surface modification, fluorescence modulation and beyond. *Polym. Chem.* **1**, 37-54, (2010).

96 Mukhopadhyay, A., Maka, V. K., Savitha, G. & Moorthy, J. N. Photochromic 2D Metal-Organic Framework Nanosheets (MONs): Design, Synthesis, and Functional MON-Ormosil Composite. *Chem* **4**, 1059-1079, (2018).

97 Lyubimov, A. V., Zaichenko, N. L. & Marevtsev, V. S. Photochromic network polymers. *J. Photochem. Photobiol. Chem.* **120**, 55-62, (1999).

98 Haldar, R., Heinke, L. & Woll, C. Advanced Photoresponsive Materials Using the Metal-Organic Framework Approach. *Adv. Mater.* **32**, e1905227, (2020).

99 Tokunaga, A. *et al.* Photochromic Reaction by Red Light via Triplet Fusion Upconversion. *J. Am. Chem. Soc.* **141**, 17744-17753, (2019).

100 Hoffmann, K., Marlow, F. & Caro, J. Photoinduced switching in nanocomposites of azobenzene and molecular sieves. *Adv. Mater.* **9**, 567-570, (1997).

101 Zhang, L., Deng, Y., Tang, Y., Xie, C. & Wu, Z. Solid-state spiropyrans exhibiting photochromic properties based on molecular flexibility. *Mater. Chem. Front.* **5**, 3119-3124, (2021).

102 Kanj, A. B., Muller, K. & Heinke, L. Stimuli-Responsive Metal-Organic Frameworks with Photoswitchable Azobenzene Side Groups. *Macromol. Rapid Commun.* **39**, 1700239, (2018).

103 Drake, H. F., Day, G. S., Xiao, Z., Zhou, H.-C. & Ryder, M. R. Light-induced switchable adsorption in azobenzene- and stilbene-based porous materials. *Trends Chem.* **4**, 32-47, (2022).

104 Murase, T., Sato, S. & Fujita, M. Switching the interior hydrophobicity of a self-assembled spherical complex through the photoisomerization of confined azobenzene chromophores. *Angew. Chem. Int. Ed.* **46**, 5133-5136, (2007).

105 Modrow, A., Zargarani, D., Herges, R. & Stock, N. The first porous MOF with photoswitchable linker molecules. *Dalton Trans.* **40**, 4217-4222, (2011).

106 Park, J., Sun, L. B., Chen, Y. P., Perry, Z. & Zhou, H. C. Azobenzene-functionalized metal-organic polyhedra for the optically responsive capture and release of guest molecules. *Angew. Chem. Int. Ed.* **53**, 5842-5846, (2014).

107 Kundu, P. K., Olsen, G. L., Kiss, V. & Klajn, R. Nanoporous frameworks exhibiting multiple stimuli responsiveness. *Nat. Commun.* **5**, 3588, (2014).

108 Heinke, L. *et al.* Photoswitching in two-component surface-mounted metal-organic frameworks: optically triggered release from a molecular container. *ACS Nano* **8**, 1463-1467, (2014).

109 Heinke, L. Diffusion and photoswitching in nanoporous thin films of metal-organic frameworks. *J. Phys. D: Appl. Phys.* **50**, 193004, (2017).

110 Wang, Z. *et al.* Tunable molecular separation by nanoporous membranes. *Nat. Commun.* **7**, 13872, (2016).

111 Muller, K. *et al.* Switching the Proton Conduction in Nanoporous, Crystalline Materials by Light. *Adv. Mater.* **30**, 1706551, (2018).

112 Chen, Y. K. *et al.* A visible light/heat responsive covalent organic framework for highly efficient and switchable proton conductivity. *Chem. Sci.* **13**, 5964-5972, (2022).

113 Wang, Z. B. *et al.* Photoswitching in nanoporous, crystalline solids: an experimental and theoretical study for azobenzene linkers incorporated in MOFs. *Phys. Chem. Chem. Phys.* **17**, 14582-14587, (2015).

114 Lyndon, R. *et al.* Dynamic photo-switching in metal-organic frameworks as a route to low-energy carbon dioxide capture and release. *Angew. Chem. Int. Ed.* **52**, 3695-3698, (2013).

115 Williams, D. E. *et al.* Energy transfer on demand: photoswitch-directed behavior of metal-porphyrin frameworks. *J. Am. Chem. Soc.* **136**, 11886-11889, (2014).

116 Luo, F. *et al.* Photoswitching CO(2) capture and release in a photochromic diarylethene metal-organic framework. *Angew. Chem. Int. Ed.* **53**, 9298-9301, (2014).

117 Thaggard, G. C. *et al.* Metal-Photoswitch Friendship: From Photochromic Complexes to Functional Materials. *J. Am. Chem. Soc.* **144**, 23249-23263, (2022).

118 Martin, C. R. *et al.* Stimuli-Modulated Metal Oxidation States in Photochromic MOFs. *J. Am. Chem. Soc.* **144**, 4457-4468, (2022).

119 Thaggard, G. C. *et al.* Confinement-Driven Photophysics in Hydrazone-Based Hierarchical Materials. *Angew. Chem. Int. Ed.* **62**, e2022117, (2023).

120 Zheng, Y. T. *et al.* Flexible interlocked porous frameworks allow quantitative photoisomerization in a crystalline solid. *Nat. Commun.* **8**, 100, (2017).

121 Dolgopolova, E. A. *et al.* Connecting Wires: Photoinduced Electronic Structure Modulation in Metal-Organic Frameworks. *J. Am. Chem. Soc.* **141**, 5350-5358, (2019).

122 Garai, B., Mallick, A. & Banerjee, R. Photochromic metal-organic frameworks for inkless and erasable printing. *Chem. Sci.* **7**, 2195-2200, (2016).

123 Li, W. B. *et al.* Photochromic Metal-Organic Framework for High-Resolution Inkless and Erasable Printing. *ACS Appl. Mater. Interfaces* **14**, 8458-8463, (2022).

124 Zhou, Y., Qin, L., Wu, M. K. & Han, L. A Bifunctional Anionic Metal-Organic Framework: Reversible Photochromism and Selective Adsorption of Methylene Blue. *Cryst. Growth Des.* **18**, 5738-5744, (2018).

125 Fu, T. *et al.* A viologen-based multifunctional Eu-MOF: photo/electro-modulated chromism and luminescence. *Chem. Commun.* **56**, 13093-13096, (2020).

126 Aulakh, D., Nicoletta, A. P., Varghese, J. R. & Wriedt, M. The structural diversity and properties of nine new viologen based zwitterionic metal-organic frameworks. *CrystEngComm* **18**, 2189-2202, (2016).

127 Zhao, G. Z., Liu, W. Y., Yuan, F. & Liu, J. J. Two host-guest 2D MOFs based on hexyl viologen cations: Photochromism. *Dyes Pigm.* **188**, 108800, (2021).

128 Han, L. *et al.* Syntheses, Crystal Structures, and Physical Properties of Two Noninterpenetrated Pillar-Layered Metal-Organic Frameworks Based on N,N'-Di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide Pillar. *Cryst. Growth Des.* **13**, 4260-4267, (2013).

129 Huang, N., Ding, X. S., Kim, J., Ihee, H. & Jiang, D. L. A Photoresponsive Smart Covalent Organic Framework. *Angew. Chem. Int. Ed.* **54**, 8704-8707, (2015).

130 Leith, G. A. *et al.* A Dual Threat: Redox-Activity and Electronic Structures of Well-Defined Donor-Acceptor Fulleretic Covalent-Organic Materials. *Angew. Chem. Int. Ed.* **59**, 6000-6006, (2020).

131 Han, M. *et al.* Light-triggered guest uptake and release by a photochromic coordination cage. *Angew. Chem. Int. Ed.* **52**, 1319-1323, (2013).

132 Sun, N. N., Wang, C. M., Wang, H. L., Gao, X. W. & Jiang, J. Z. Photonic Switching Porous Organic Polymers toward Reversible Control of Heterogeneous Photocatalysis. *ACS Appl. Mater. Interfaces* **12**, 56491-56498, (2020).

133 Liang, R. *et al.* A Heteromeric Carboxylic Acid Based Single-Crystalline Crosslinked Organic Framework. *Angew. Chem. Int. Ed.* **60**, 23176-23181, (2021).

134 Fan, Z. *et al.* Formation of Porosity toward Acetylene upon Vitrification of Non-porous Photochromic Coordination Polymer Crystals. *Chem. Mater.* **35**, 3859-3866, (2023).

135 Ma, N. & Horike, S. Metal-Organic Network-Forming Glasses. *Chem. Rev.* **122**, 4163-4203, (2022).

136 Das, C. & Henke, S. Smoke in the MOF liquid. *Nat. Mater.* **22**, 809-810, (2023).

137 Epley, C. C. *et al.* Cargo delivery on demand from photodegradable MOF nano-cages. *Dalton Trans.* **46**, 4917-4922, (2017).

138 Zhang, J. *et al.* A novel azobenzene covalent organic framework. *CrystEngComm* **16**, 6547-6551, (2014).

139 Yaghi, O. M., Li, G. M. & Li, H. L. Selective Binding and Removal of Guests in a Microporous Metal-Organic Framework. *Nature* **378**, 703-706, (1995).

140 Ohara, K., Inokuma, Y. & Fujita, M. The catalytic Z to E isomerization of stilbenes in a photosensitizing porous coordination network. *Angew. Chem. Int. Ed.* **49**, 5507-5509, (2010).

141 Yanai, N. *et al.* Guest-to-host transmission of structural changes for stimuli-responsive adsorption property. *J. Am. Chem. Soc.* **134**, 4501-4504, (2012).

142 Hermann, D., Emerich, H., Lepski, R., Schaniel, D. & Ruschewitz, U. Metal-organic frameworks as hosts for photochromic guest molecules. *Inorg. Chem.* **52**, 2744-2749, (2013).

143 Schwartz, H. A., Schaniel, D. & Ruschewitz, U. Tracking the light-induced isomerization processes and the photostability of spiropyrans embedded in the pores of crystalline nanoporous MOFs IR spectroscopy. *Photochem. Photobiol. Sci.* **19**, 1433-1441, (2020).

144 Schwartz, H. A. & Ruschewitz, U. *Photoactive Molecules within MOFs. Dyes and Photoactive Molecules in Microporous Systems*. pp 105-153 (Eds.; Vol. 183, 2020, pp 105-153).

145 Schwartz, H. A. *et al.* Novel Photoactive Spirooxazine Based Switch@MOF Composite Materials. *ChemPhotoChem* **4**, 195-206, (2020).

146 Schwartz, H. A., Olthof, S., Schaniel, D., Meerholz, K. & Ruschewitz, U. Solution-Like Behavior of Photoswitchable Spiropyrans Embedded in Metal-Organic Frameworks. *Inorg. Chem.* **56**, 13100-13110, (2017).

147 Hermann, D., Schwartz, H. A., Werker, M., Schaniel, D. & Ruschewitz, U. Metal-Organic Frameworks as Hosts for Fluorinated Azobenzenes: A Path towards Quantitative Photoswitching with Visible Light. *Chem. Eur. J.* **25**, 3606-3616, (2019).

148 Bhandari, P., Modak, R., Bhattacharyya, S., Zangrando, E. & Mukherjee, P. S. Self-Assembly of Octanuclear Pt/Pd Coordination Barrels and Uncommon Structural Isomerization of a Photochromic Guest in Molecular Space. *JACS Au* **1**, 2242-2248, (2021).

149 Saha, R. *et al.* Unusual Behavior of Donor-Acceptor Stenhouse Adducts in Confined Space of a Water-Soluble PdII8 Molecular Vessel. *J. Am. Chem. Soc.* **141**, 8638-8645, (2019).

150 Howlader, P., Mondal, B., Purba, P. C., Zangrando, E. & Mukherjee, P. S. Self-Assembled Pd(II) Barrels as Containers for Transient Merocyanine Form and Reverse Thermochromism of Spiropyran. *J. Am. Chem. Soc.* **140**, 7952-7960, (2018).

151 Saha, R. & Mukherjee, P. S. Chemistry of photoswitching molecules in the confined nanospace of aqueous molecular vessels. *Dalton Trans.* **49**, 1716-1720, (2020).

152 Tu, M. *et al.* Reversible Optical Writing and Data Storage in an Anthracene-Loaded Metal-Organic Framework. *Angew. Chem. Int. Ed.* **58**, 2423-2427, (2019).

153 Tu, M., Ramírez, M. L. D., Ibarra, I. A., Hofkens, J. & Ameloot, R. Fluorescence Photoswitching in a Series of Metal-Organic Frameworks Loaded with Different Anthracenes. *Eur. J. Inorg. Chem.* **2021**, 2986-2992, (2021).

154 Zhang, F. *et al.* Microwave-assisted crystallization inclusion of spiropyran molecules in indium trimesate films with antidromic reversible photochromism. *J. Mater. Chem.* **22**, 25019-25026, (2012).

155 Uemura, T., Washino, G., Yanai, N. & Kitagawa, S. Controlled Encapsulation of Photoresponsive Macromolecules in Porous Coordination Polymer. *Chem. Lett.* **42**, 222-223, (2013).

156 Garg, S. *et al.* Conductance Photoswitching of Metal-Organic Frameworks with Embedded Spiropyran. *Angew. Chem. Int. Ed.* **58**, 1193-1197, (2019).

157 Schwartz, H. A., Ruschewitz, U. & Heinke, L. Smart nanoporous metal-organic frameworks by embedding photochromic molecules - state of the art and future perspectives. *Photochem. Photobiol. Sci.* **17**, 864-873, (2018).

158 Walton, I. M. *et al.* Photo-responsive MOFs: light-induced switching of porous single crystals containing a photochromic diarylethene. *Chem. Commun.* **49**, 8012-8014, (2013).

159 Samanta, D. *et al.* Reversible chromism of spiropyran in the cavity of a flexible coordination cage. *Nat. Commun.* **9**, 641, (2018).

160 Samanta, D. *et al.* Reversible photoswitching of encapsulated azobenzenes in water. *Proc. Natl. Acad. Sci. U. S. A.* **115**, 9379-9384, (2018).

161 Wang, J. H. *et al.* Altering the Properties of Spiropyran Switches Using Coordination Cages with Different Symmetries. *J. Am. Chem. Soc.* **144**, 21244-21254, (2022).

162 Pesce, L., Perego, C., Grommet, A. B., Klajn, R. & Pavan, G. M. Molecular Factors Controlling the Isomerization of Azobenzenes in the Cavity of a Flexible Coordination Cage. *J. Am. Chem. Soc.* **142**, 9792-9802, (2020).

163 Gemen, J., Ahrens, J., Shimon, L. J. W. & Klajn, R. Modulating the Optical Properties of BODIPY Dyes by Noncovalent Dimerization within a Flexible Coordination Cage. *J. Am. Chem. Soc.* **142**, 17721-17729, (2020).

164 Lyndon, R. *et al.* Tunable Photodynamic Switching of DArE@PAF-1 for Carbon Capture. *Adv. Funct. Mater.* **25**, 4405-4411, (2015).

165 Mollick, S. *et al.* Resilient photoswitchable metal-organic frameworks for sunlight-induced on-demand photochromism in the solid state. *Chem. Eng. J.* **476**, 146727, (2023).

166 Park, J. *et al.* Reversible alteration of CO2 adsorption upon photochemical or thermal treatment in a metal-organic framework. *J. Am. Chem. Soc.* **134**, 99-102, (2012).

167 Sun, F. *et al.* Fast photochromism in solid: Microenvironment in metal-organic frameworks promotes the isomerization of donor-acceptor Stenhouse adducts. *Chem. Eng. J.* **427**, 132037, (2022).

168 Eichler, C. *et al.* Paving the Way to the First Functional Fulgide@MOF Hybrid Materials. *Chem. Mater.* **33**, 3757-3766, (2021).

169 Furlong, B. J. & Katz, M. J. Bistable Dithienylethene-Based Metal-Organic Framework Illustrating Optically Induced Changes in Chemical Separations. *J. Am. Chem. Soc.* **139**, 13280-13283, (2017).

170 Naito, T., Horie, K. & Mita, I. Photochemistry in Polymer Solids.11. The Effects of the Size of Reaction Groups and the Mode of Photoisomerization on Photochromic Reactions in Polycarbonate Film. *Macromolecules* **24**, 2907-2911, (1991).

171 Samanta, S. *et al.* Photoswitching Azo Compounds in Vivo with Red Light. *J. Am. Chem. Soc.* **135**, 9777-9784, (2013).

172 Kumar, P., Srivastava, A., Sah, C., Devi, S. & Venkataramani, S. Arylazo-3,5-dimethylisoxazoles: Azoheteroarene Photoswitches Exhibiting High-Isomer Stability, Solid-State Photochromism, and Reversible Light-Induced Phase Transition. *Chem. Eur. J.* **25**, 11924-11932, (2019).

173 Jiang, Y. Z. *et al.* Substrate-Bound Diarylethene-Based Anisotropic Metal-Organic Framework Films as Photoactuators with a Directed Response. *Angew. Chem. Int. Ed.* **62**, e202218052, (2023).

174 Li, C., Zhang, Z. J. & Heinke, L. Nanoporous Metal-Organic Framework Thin Films with Embedded Fulgide for Light-Modulated Guest Adsorption and Diffusion. *Langmuir* **38**, 13103-13108, (2022).

175 Abtab, S. M. T. *et al.* Reticular Chemistry in Action: A Hydrolytically Stable MOF Capturing Twice Its Weight in Adsorbed Water. *Chem* **4**, 94-105, (2018).

176 Hasell, T., Schmidtmann, M., Stone, C. A., Smith, M. W. & Cooper, A. I. Reversible water uptake by a stable imine-based porous organic cage. *Chem. Commun.* **48**, 4689-4691, (2012).

177 Sun, C., Sheng, D. F., Wang, B. & Feng, X. Covalent Organic Frameworks for Extracting Water from Air. *Angew. Chem. Int. Ed.* **62**, e202303378, (2023).

178 Wang, D. S. *et al.* Inducing molecular isomerization assisted by water. *Commun. Chem.* **2**, 118, (2019).

179 Walton, I. M. *et al.* Photo-responsive MOFs: light-induced switching of porous single crystals containing a photochromic diarylethene. *Chem. Commun.* **49**, 8012-8014, (2013).

180 Brown, J. W. *et al.* Photophysical pore control in an azobenzene-containing metal-organic framework. *Chem. Sci.* **4**, 2858-2864, (2013).

181 Park, J., Feng, D., Yuan, S. & Zhou, H. C. Photochromic metal-organic frameworks: reversible control of singlet oxygen generation. *Angew. Chem. Int. Ed.* **54**, 430-435, (2015).

182 Yu, F. *et al.* Photostimulus-Responsive Large-Area Two-Dimensional Covalent Organic Framework Films. *Angew. Chem. Int. Ed.* **58**, 16101-16104, (2019).

183 Liu, J. T. *et al.* Smart covalent organic networks (CONs) with "on-off-on" light-switchable pores for molecular separation. *Sci. Adv.* **6**, eabb3188, (2020).

184 Gemen, J. *et al.* Ternary host-guest complexes with rapid exchange kinetics and photoswitchable fluorescence. *Chem* **8**, 2362-2379, (2022).

185 Lu, J., Choi, E., Tamanoi, F. & Zink, J. I. Light-activated nanoimpeller-controlled drug release in cancer cells. *Small* **4**, 421-426, (2008).

186 Yamaguchi, T., Imwiset, K. J. & Ogawa, M. Efficient Negative Photochromism by the Photoinduced Migration of Photochromic Merocyanine/Spiropyran in the Solid State. *Langmuir* **37**, 3702-3708, (2021).

187 Zhu, H. G. *et al.* A Robust Absorbent Material Based on Light-Responsive Superhydrophobic Melamine Sponge for Oil Recovery. *Adv. Mater. Interfaces* **3**, 1500683, (2016).

188 Hong, P. *et al.* Fabricated of Superhydrophobic Silanized Melamine Sponge with Photochromic Properties for Efficiency Oil/Water Separation. *Adv. Polym. Technol.* **2019**, 1-8, (2019).

189 Fan, J. *et al.* High tri-stimulus response photochromic cotton fabrics based on spiropyran dye by thiol-ene click chemistry. *Cellulose* **27**, 493-510, (2020).

190 Nhien, P. Q. *et al.* Highly Efficient Forster Resonance Energy Transfer Modulations of Dual-AIEgens between a Tetraphenylethylene Donor and a Merocyanine Acceptor in Photo-Switchable [2]Rotaxanes and Reversible Photo-Patterning Applications. *ACS Appl. Mater. Interfaces* **12**, 47921-47938, (2020).

191 Zhang, Z. W. *et al.* Stepping Out of the Blue: From Visible to Near-IR Triggered Photoswitches. *Angew. Chem. Inter. Ed.* **134**, e202205758, (2022).

192 Kanj, A. B. *et al.* Chirality Remote Control in Nanoporous Materials by Circularly Polarized Light. *J. Am. Chem. Soc.* **143**, 7059-7068, (2021).

193 Koehler, T., Strauss, I., Mundstock, A., Caro, J. & Marlow, F. Reversible Photoalignment of Azobenzene in the SURMOF HKUST-1. *J. Phys. Chem. Lett.* **12**, 8903-8908, (2021).

194 Heinke, L. & Wöll, C. Surface-Mounted Metal-Organic Frameworks: Crystalline and Porous Molecular Assemblies for Fundamental Insights and Advanced Applications. *Adv. Mater.* **31**, 1806324, (2019).

195 Semrau, A. L. *et al.* Surface-Mounted Metal-Organic Frameworks: Past, Present, and Future Perspectives. *Langmuir* **37**, 6847-6863, (2021).