

Dynamically responsive photonic metal–organic frameworks

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Abstract. Different from single and static photonic materials, dynamically responsive materials possess numerous advantages, such as being multifunctional, dynamically responsive, and able to provide multiple channels within spatially limited platforms, thus exhibiting great potential for application in the color-on-demand areas, including imaging, optical displays, anticounterfeiting, and encoding. Photonic functional metal–organic frameworks (MOFs), with highly designable framework structures and varieties of optical functional building units, possess broad research and application prospects in the field of photonics, which make it possible to design a promising platform with multifunctional and integrated photonic performance. In this review, beyond the preparation strategies of stimuli-responsive photonic MOFs, we also summarize the stimuli-responsive photonic MOFs regarding several most representative types of external stimuli (such as light, gas, pressure, and polarization). As shown, external stimulation endows the stimuli-responsive photonic MOFs with intriguing regulatable photonic properties: intensive and tunable emission, multiphoton-excitable luminescence, non-linear optical, circularly polarized luminescence, lasing, etc. Furthermore, their advanced representative applications, such as information encryption and anticounterfeiting display, biological imaging, chemosensing, and others, are also reviewed. The challenges are proposed and the prospects are addressed.

Keywords: stimuli-responsive; photonic properties; switchable materials; photochromic molecules; metal–organic frameworks.

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1 Introduction

Organisms in nature are able to change their appearance (such as color) or behavior in response to different environmental stimuli (including light, temperature, force, electricity, etc.).¹ For example, once the noctiluca is stimulated by the outside world, it will stimulate the body's instinct to emit light, which forms the fluorescent sea that we see. Therefore, these complicated stimuli-responsive natural systems provide inspiration for humanity and have given birth to biomimicry. Therefore, the stimuli-responsive behaviors of nature inspired scientists and engineers to create a wide range of smart materials by a mimicking strategy.² Therefore, stimuli-responsive smart materials are widely used in optoelectronic devices, lighting displays, biological applications, and others.^{1,3,4}

Since light stimuli have distinct advantages, such as convenience, speed, high spatiotemporal precision, being environmentally benign, and having a noninvasive manner, the light-responsive system has attracted more interest and been regarded to be a prominent candidate for the development of biotechnology and applications in controlled drug delivery and bioimaging.⁵ Among them, photoswitchable molecules (also named photochromic molecules) have been extensively studied as a type of classical stimuli-responsive materials. Photoswitchable molecules could switch between two discrete states upon different light irradiation, such as azobenzene (AZO),^{6,7} spiropyran (SP),^{8,9} diarylethene (DAE),^{5,10,11} dihydro-pyrenes,¹² stilbene,^{13,14} alkene-based motors,^{15,16} and so on.^{17,18} Specifically, trans–cis isomerization of AZO undergoes a light-induced photoisomerization process; colorless closed-ring isomer SP isomerizes to red-color open-ring isomer merocyanine (MC).¹⁷ DAE shows reversible photoswitch and significant differences in color from the colorless open-ring

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form to the strongly colored closed-ring form upon alternating UV light or visible light irradiation.¹¹ In summary, photochromic compounds are important owing to their reversability, controllability, excellent fatigue resistance and thermally irreversible properties, high photoisomerization quantum yields (QYs), and rapid response and can avoid generating waste compared to most chemical-responsive systems.^{9,17,19} That is to say, introducing photoswitchable molecules into combined materials can enhance the photophysical, electronic, mechanistic, or thermal properties of materials, which provide an excellent platform for the design of stimuli-responsive photonic materials.¹⁹

To date, a variety of stimuli-responsive, dynamic, and flexible metal–organic framework (MOF) materials have been documented in this review. As the name suggests, a special class of MOFs/porous coordination polymers (PCPs) are those that can reversibly change their framework structure when guest molecules (gas, solvent, and so on) are introduced or the external temperature stimuli change. This results in phenomena such as breathing (pore contraction) or gate opening (pore expansion), where pores open or contract upon adsorption, known as the breathing effect, gating effect, or shape-memory effect.^{20,21} Other groups also have reported many temperature-responsive flexible MOFs, such as MIL-53 series materials.²² More importantly, the fascinating characteristics of flexible MOFs have great potential applications in many fields, such as gas storage and separation, sensing, and guest capture and release.²³ Remarkably, the breathing effect and accompanying photophysical changes of flexible MOFs provide an excellent platform for the design of stimuli-responsive photonic MOFs.

The research on photonic functional materials involves the processes of absorption, generation, transmission, conversion, detection, storage, and display of photons, which is one of the important material foundations for exploring photonics phenomena and technologies. Because of their material properties, photonic functional materials, including inorganic and organic photonic materials, both have been widely studied. However, there are still areas that need urgent improvement. The preparation of inorganic materials usually requires high temperatures and relies on complex doping processes. Organic materials have poor photostability and are prone to concentration quenching in the solid state. Photonics performance regulation of materials refers to the control of certain internal/external factors to induce materials to produce dynamic and regularly changing photonics properties under light fields. Compared to a single static optical performance, dynamically adjustable optical and photonics performances are more suitable for the development of integrated, functional, and intelligent micro/nano-optoelectronic devices.²⁴ Researchers utilize a large number of materials to study controllable optical properties, explain changes, and expand regulatory methods to achieve the goal of “controlling” light through material media.^{25,26}

MOFs are an outstanding class of organic–inorganic porous materials and have gained immense attention from researchers over the last decades.^{27–29} The integration of high surface area, excellent crystallinity, tunable structure and porosity, diversity of morphology and modifiable chemical functionality endows them with great promise for gas storage and separation, chemical sensing, catalysis, pollutant treatment, drug delivery, and so on.^{19,28,30–43} Our group is committed to developing advanced photonic functional MOF materials. In the discussion of stimuli-responsive MOFs in this review, we continue the concept of

“multiphoton units” (MPUs) proposed in the previous literature (Fig. 1).²⁸ We consider MPUs of photonic functional MOFs, mainly comprising metal ions/clusters, organic ligands, and guests. In this review, we discuss stimuli-responsive MPUs (such as photoswitchable molecules and dyes) that could be incorporated into the framework of MOFs in three different ways: as a guest, as a ligands backbone, or as a ligands side group (Fig. 2).

Due to space limitations, the stimuli-responsive photonic MOFs involved in this review mainly include two types. The first type of particular interest of stimuli-responsive photonic MOFs can be found in a class of MOF materials whose structure and composition may change under external stimuli, including

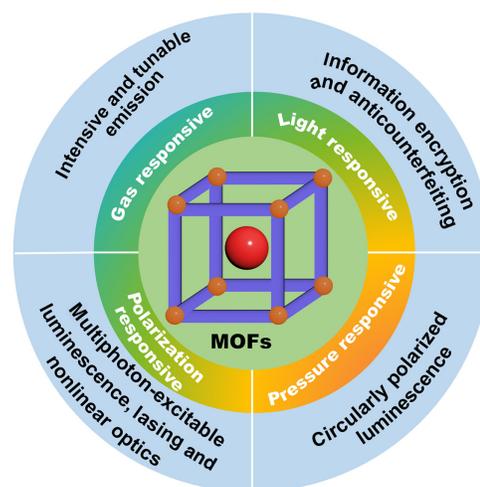


Fig. 1 Structure design, types of stimuli, mechanisms of property modulation, and applications of stimuli-responsive photonic MOFs in this review.

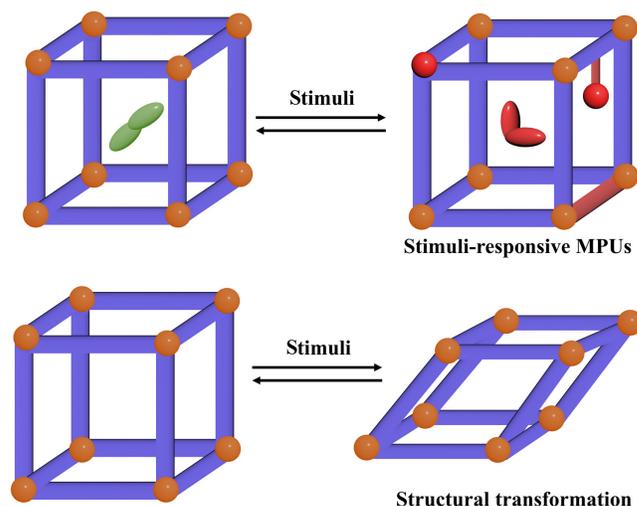


Fig. 2 Schematic representation and strategies for functionalization of stimuli-responsive photonic MOFs. Stimuli-responsive MPUs (e.g., photochromic molecules and dyes) as a guest, as a ligands backbone, or as a ligands side group. Structural transformation process of flexible MOFs under external stimuli.

(1) MOFs based on photoswitchable molecular-derived ligands and (2) flexible MOFs. Since photoswitchable molecules as a typical MPU could be integrated inside a MOF matrix, the pore size and pore environment of the photoswitchable MOFs will change under external stimuli, resulting in new functionalities.⁴⁴ The attractive stimuli-responsive photonic properties of flexible MOFs mainly originate from their flexibility and dynamic behavior. The second type of stimuli-responsive photonic MOFs is mostly focused on the MOF@guest materials, constructed by incorporating guest MPU (e.g., photoswitchable molecules and dyes) into the pores of the MOFs. Due to the synergistic effects, combination possibilities, controllable and ordered arrangements of guests and MOFs, MOFs are an optimal platform for controllable design and synthesis of the hybrid crystalline material with novel photonic function. In fact, a series of new photonic functionalities, including polarization-responsive nonlinear optics (NLO) or lasing behaviors have been successfully implemented in MOF@guest materials.^{45,46} Thanks to the response of photon building unit to external stimuli, the photonic properties of the photonic MOF materials can be regulated by controlling external stimuli.

In this review, stimuli-responsive photonic MOFs are summarized and classified in term of several representative external stimuli. Owing to space limitations, only some recent representative examples were selected to demonstrate the specific stimuli-responsive performance of each type of stimulus, which provides new insights and ideas for designing multifunctional stimuli-responsive photonic MOF materials. In the end, the future challenges of stimuli-responsive photonic MOFs are also briefly discussed.

2 Concept and Principles toward Stimuli-Responsive Photonic MOFs

2.1 Concept of Stimuli-Responsive Photonic Materials

Recently, stimuli-responsive photonic materials have gained immense attention, mainly owing to the rapid development of smart materials. The so-called stimuli-responsive photonic material refers to the material's specific perception and response to external stimuli (e.g., temperature, pressure, light, and pH) in the environment, specifically manifested in changes in optical or photonic properties.^{44,47} Up till now, various strategies have been developed to build stimuli-responsive photonic materials, including incorporating photoswitchable molecules, modifying side chains, and regulating topological structures.⁴⁸ However, there are still many difficulties and challenges in designing and constructing stimuli-responsive materials owing to the difficulty of completing switching behavior in confined environments as well as precisely regulating and controlling the molecular structure.

Nowadays, various approaches to construction of photoswitchable molecule-bound polymers have been developed.² In polymer systems, photoswitchable molecules as modification units can be bound to polymer networks through a noncovalent manner or be directly covalently connected to polymer molecular chains. Combining photochromic units with polymers provides a new strategy for developing functional materials.^{9,11,24,49} The polymer backbone has a much larger contribution to overall solubility than the photochromic groups. For example, Li et al. developed several examples about the construction of the photo-responsive luminescent polymeric hydrogels as well as their

applications in information encryption.^{50,51} However, photoswitchable polymer materials usually have complex synthesis routes (method of covalent immobilization), high requirements for reactants, and are not green enough, resulting in limited application scenarios.

Over the past few years, inorganic nanoparticles (NPs), such as gold NPs, lanthanide-doped upconversion NPs (UCNPs), and quantum dots (QDs), have been functionalized and combined for nondestructive optical memory and photoswitching applications.^{3,52–55} For example, Medintz and co-workers employed an immobilization approach to obtain SP-coated CdSe–ZnS core-shell QDs with ultimate control of Förster resonance energy transfer (FRET) efficiency and reversible dual-emitting luminescence.⁵⁶ Lee et al. reported a UCNP with orthogonal emissions when excited at 808 and 980 nm for controlled two-way photoswitching of SP.⁵⁷ Significantly, this article reported that UCNPs were dispersed in SP solution to achieve isomerization. However, the future development trend is to obtain solid-state photoswitchable luminescent materials that can produce rapid and significant color changes and excellent luminescence.

2.2 Benefits of Stimuli-Responsive Photonic MOFs

In this review, we point out that different stimuli-responsive MPUs allow precise control of the different photonic properties of MOFs. Stimuli-responsive photonic MOFs, against the photoswitch behavior as well as the interaction between photoresponsive units and stimulus sources, can serve as a model platform for research on the photophysics mechanism as well as developing next-generation multifunctional materials. Hence, the fabrication and application of stimuli-responsive photonic MOFs will be the research hotspots for a long time into the future. Next, we will summarize the advantages of stimuli-responsive photonic MOFs.

The immobilization of a stimuli-responsive guest (e.g., photochromic molecules and dyes) in MOFs can isolate the guests from each other, thus suppressing stimuli-responsive guest stack formation and protecting the fluorophores from the aggregation-caused quenching (ACQ) effect.⁹ As a result, emission QYs are increased. Due to the energy transfer (EnT) process between MOFs and the guest, the fluorescence of the guest can further be enhanced by constructing MOF@guest materials, which is particularly important for the development of switchable fluorescent materials.^{58,59} Due to the stability and designability of MOF structures, stimuli-responsive MPUs (e.g., photochromic molecules and dyes) could be introduced into the framework of MOFs in three different ways. When stimuli-responsive MPUs are introduced into the ligands of MOFs, the rigidity of MOFs greatly improves the stability of stimuli-responsive MPUs, which will promote the development of multifunctional photonics materials.

Successful switching and communication of the majority of photoswitches under confinement require some degree of conformational freedom. For example, in the solid state, the crowded environment greatly limits the available freedom of switches; in the solution environment, the communication between an optical switch and these loosely restricted systems is weak. When assembling photochromic molecules into the cavity of a MOF or coordination cage, successful switching can be observed when there is an appropriate degree of freedom.¹² Benefiting from the unique bistable characteristics and excellent

fatigue resistance of molecular switches, rapid photoisomerization can be achieved in limited space environments of MOF \supset guests. By reasonably designing photochromic derivative ligands to reduce the spatial hindrance in MOFs, one must improve the photo-responsive performance of stimuli-responsive MOFs. Finally, stimuli-responsive MOFs can be further applied to the development of smart material, molecular machines, etc.

Due to the designability of MOF structures, introducing MPUs into the MOF framework can centralize multiple photonics centers in a multifunctional material, thereby endowing the material with new photonics functions. For example, introducing photochromic molecules into the MOF framework leads to effective intramolecular interactions between different MPUs due to the clear shape and size of the guest. On the other hand, this process enables MOFs to have light-responsive characteristics, which involve structural and photophysical changes. Such systems exhibit broad applications in light-controlled guest release, rewritable molecular inks, photodynamic therapy (PDT), and so on, which is the key to the development of multiresponsive materials and smart devices. In another case, through the inclusion of dyes into the pores of the MOFs, MOF \supset guest materials could demonstrate tunable NLO or lasing performance or even new photonic performance.

3 Stimuli-Responsive Photonic MOFs

3.1 Light-Responsive MOFs

3.1.1 Light-responsive MPUs as linker bone or side group

To begin with, stimuli-responsive MPUs, such as photoswitchable molecules, can serve as a class of molecular building blocks or organic ligands for constructing MOFs through coordination (Fig. 2). Typically, the light-responsive carboxylic acid linkers or pyridyl linkers are obtained by incorporation of photoswitchable molecules in the backbone of the linkers and then corresponding MOFs were formed through coordination.^{27,60} The DAE-based ligands are incorporated into the backbone of MOFs, while the photoisomerization of DAE is only accompanied by small structural changes and tiny decreases in the rigidity of the MOF.⁵⁹ As to the isomerization of trans–cis AZO and SP-MC, the photoisomerization processes are usually accompanied by large structural changes. For example, upon different external stimuli, this strategy could regulate the window size of MOF through photoisomerization process of trans–cis AZO, and the MOF could be further applied in switchable adsorption separation and contaminant removal.^{61–63}

There are also numerous photoswitchable side groups, such as AZO, DAE, and SP that can be incorporated into the ligands of MOFs (Fig. 2). For example, Wang et al. reported a photo-responsive AZO-functionalized mechanized UiO-68-azo for on-command cargo release.⁶⁴ Shustova et al. designed an SP derivative-based linker, 1',3',3'-trimethyl-6-nitro-4',7'-di(pyridin-4-yl) spiro[chromene-2,2'-indoline] (TNDS), which was incorporated into rigid MOF scaffolds by coordinating with Zn- or Zr-metal.⁶³

Given that (1) the isomerization process of photochromic molecules effectively triggers the structural transformation of MOFs, causing a sharp change in the adsorption properties of photoswitchable MOF materials, and (2) the reversible photoisomerization can bring about notable magnetic changes and an increase in the electronic conductance, photoswitchable ligand-based MOFs have shown great promise for gas storage

and separation,^{65–73} guest adsorption and diffusion,^{74–76} proton conductivity,^{77,78} drug-controlled release,⁶⁴ electronic devices,^{79,80} and so on⁸¹ in recent years. Apart from those applications, photo-switchable ligand-based MOFs also have contributed important progress to the field of photonics.

Next, we will review related works of light-responsive MOFs in EnT system design, light capture, singlet oxygen ($^1\text{O}_2$) generation, circularly polarized luminescence (CPL), and chemical detection in detail.

In 2013, Yaghi et al. demonstrated the synthesis of a photo-switchable AZO functionalized isorecticular MOF (azo-IRMOF-74-III) [$\text{Mg}_2(\text{C}_{26}\text{H}_{16}\text{O}_6\text{N}_2)$] for the controllable release of propidium dye upon an external light stimulus (such as laser on/off) (Fig. 3).⁸² Under light stimulation, the photoisomerization of photochromic molecules is accompanied by obvious changes in the ultraviolet (UV) absorption spectrum, which provides an excellent platform for the EnT process. For example, Shustova et al. fabricated a rigid scaffold of Zn-MOF using a photoswitchable DAE-based bis(5-pyridyl-2-methyl-3-thienyl)-cyclopentene (BPMTC) ligand and a tetrakis(4-carboxyphenyl)-porphyrin (H_4TCPP) ligand (Fig. 4).⁵⁹ In this case, a previously reported molecular D–A dyad approach was used in which BPMTC (A) was immobilized between H_4TCPP (D) layers. Under the irradiation of 365 and 590 nm light, BPMTC can switch between open form and closed form reversibly, leading

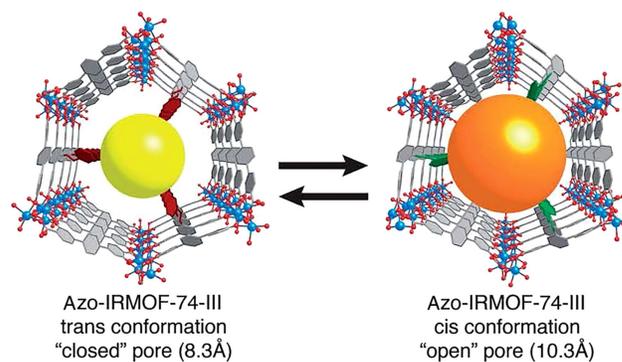


Fig. 3 Tuning of channel dimension in azo-IRMOF-74-III. Figures reproduced from Ref. 82.

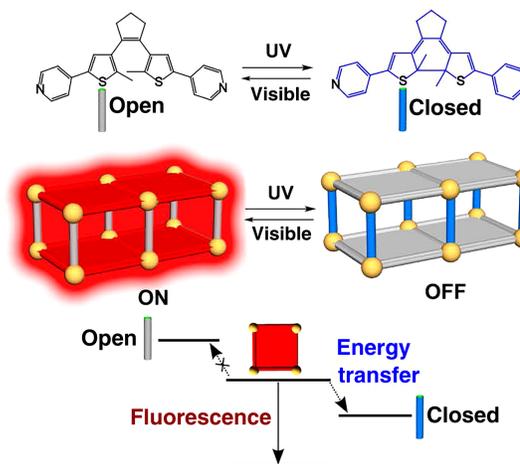


Fig. 4 EnT on demand: BPMTC photoisomerization-directed behavior of Zn-MOF. Figures reproduced from Ref. 59.

to changes in its absorption band (colorless to blue), and selectively quench the luminescence of H_4 TCPP, thus activating the MOF optical switch based on the EnT process. Time-resolved photoluminescence spectroscopy showed that the average emission lifetime of H_4 TCPP was decreased, which indicated a resonance EnT-based mechanism. In another case, they constructed a series of DAE and SP derivative-based linkers, such as TNDS, 1',1'',3',3'',3''',3''''-hexamethyl-6,6''-dinitro-4',4''-di(pyridin-4-yl)-7',7''-bispiro[chromene-2,2'-indoline] HDDB, and BPMTC linkers that were coordinated with Zn- or Zr-metal to obtain rigid MOF materials.⁶³ They also demonstrated the photochromic molecules that were immobilized in the scaffolds of MOFs, which can control the kinetics of the photoisomerization process. When exposed to acid vapor, the skeleton of MOF materials undergoes degradation leading to ligand release, which is accompanied by thermochromic shifts of over 100 nm and drastic emission changes (from purple to green). Following this route, in 2020, Feringa et al. built a visible-light-driven pillared-paddlewheel MOF with porphyrin (PdTCPP) as a light-harvesting unit and bispyridyl-derived molecular motor linker.¹⁶ In this MOF system, the photoswitch of the molecular motor was achieved upon irradiation with low-energy green light (530 nm), which indicated an efficient EnT from the porphyrin linker to the motor linker. Considering the unique long-wavelength-driven molecular motor, this MOF system is promising for future applications in photocatalysis, solar cells, and biosensing.

In consideration of the gigantic benefits of light control with high spatial and temporal resolution, catalytic performance can be regulated. The 1O_2 produced by catalytic oxidation process has applications in biological and medical systems (for example, PDT). One example of MOF EnT system containing mixed ligands was reported by Feringa and co-workers.⁵⁸ They demonstrated a noncovalent strategy to reversibly regulate on and off 1O_2 generation using a DAE photochromic switch and porphyrin photosensitizers. There, the effect is based on the efficient EnT from the porphyrin to the strongly colored closed-ring form of DAE upon irradiation at 420 nm, resulting in the 1O_2 generation conversion to the OFF state, while when the DAE unit is in the colorless open form, the 1O_2 generation state is ON. Zhou and co-workers also developed two classical pillar-layer structures, namely, PC-PCN (photochromic porous coordination network) and SO-PCN (singlet oxygen-generating PCN) with a 1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene (BPDTE) linker and a Zn-based tetrakis(4-carboxyphenyl)-porphyrin (TCPP) linker (Fig. 5).⁸³ Then they studied the reversible regulation over 1O_2 generation through competition between two EnT pathways upon UV (365 nm) or visible (>450 nm) light irradiation in SO-PCN. Furthermore, SO-PCN can efficiently catalyze the photooxidation of 1,5-dihydroxynaphthalene molecules. Subsequently, they continued to synthesize a DAE-based Zr-MOF for PDT.⁸⁴ By incorporating a porphyrin system (TCPP, dyad) and derivatization of DTE, 1,2-bis(5-(4-carboxyphenyl)-2-methylthien-3-yl)cyclopent-1-ene (BCDTE) to UiO-66, this Zr-MOF nanoplatfrom showed enhanced EnT-based PDT efficacy with excellent 1O_2 control.

Overcrowded olefin-based light-driven molecular motors enable large-scale repetitive unidirectional rotations. Although their behavior in solution has been well studied, relatively little research has been done on their behavior in the solid state. In view of this, Feringa and co-workers reported that a novel molecular motor unit embedded in a pillared-paddlewheel crystalline MOF could achieve unhindered, large-amplitude

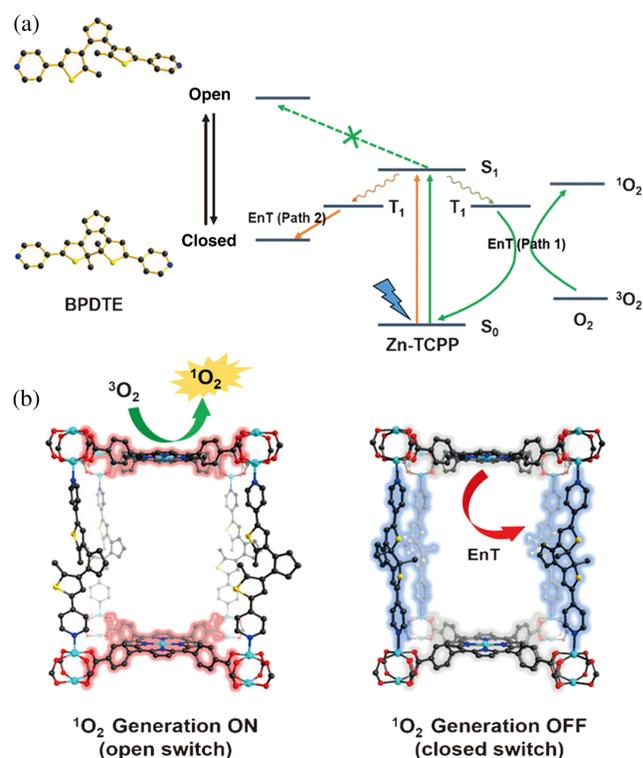


Fig. 5 (a) Proposed mechanism of EnT in SO-PCN. (b) Illustration of reversible switching in SO-PCN. Figures reproduced from Ref. 83.

unidirectional rotary motion under UV light irradiation and heating (Fig. 6).¹⁵ In particular, Raman spectroscopy allows the *in situ* monitoring of the isomerization process of the molecular motor in the crystalline moto-MOFs. Impressively, these linker-based “moto-MOFs” have promising potential for controlling dynamic function in crystalline materials.

Chirality is a central theme in nature and has important significance in biology, medicine, and other fields.⁸⁵ Among them, achieving dynamic control of chirality remains a huge challenge in the field of chemistry. In recent years, Heinke et al. developed several photoswitchable surface-mounted MOF (SURMOF)-based hybrid materials, which meet the developing trends of the controlled release of guest molecules and proton conduction.^{69,74,75,78} Interestingly, they also reported a chiral and enantioselective enrichment of crystalline nanoporous materials induced by CPL.⁸⁶ The scaffold of $Cu_2(F_2AzoBDC)_2$ (dabco) SURMOF material attached with a fluorinated AZOs side group (Fig. 7). The AZO side group undergoes a photoisomerization process between trans form and cis form upon green light and violet light irradiation, respectively. Depending on the CPL-handedness, CPL results in chiral photoresolution, causing an optically active material. This work opens new opportunities for photochromic molecular switches for information storage with CPL.

Photocycloaddition reaction is also one of the important strategies for constructing dynamic responsive luminescent materials. In particular, the photoisomerization process that occurs in MOF materials is based on stilbene derivative ligands.^{14,87,88} For instance, Lang et al. reported photoreactive olefinic species are integrated into a MOF, $[Zn(bdc)(3-F-spy)]$ (1, 3-F-spy = 4-(3-fluorostyryl)pyridine; H_2bdc = 1,4-benzenedicarboxylic acid).

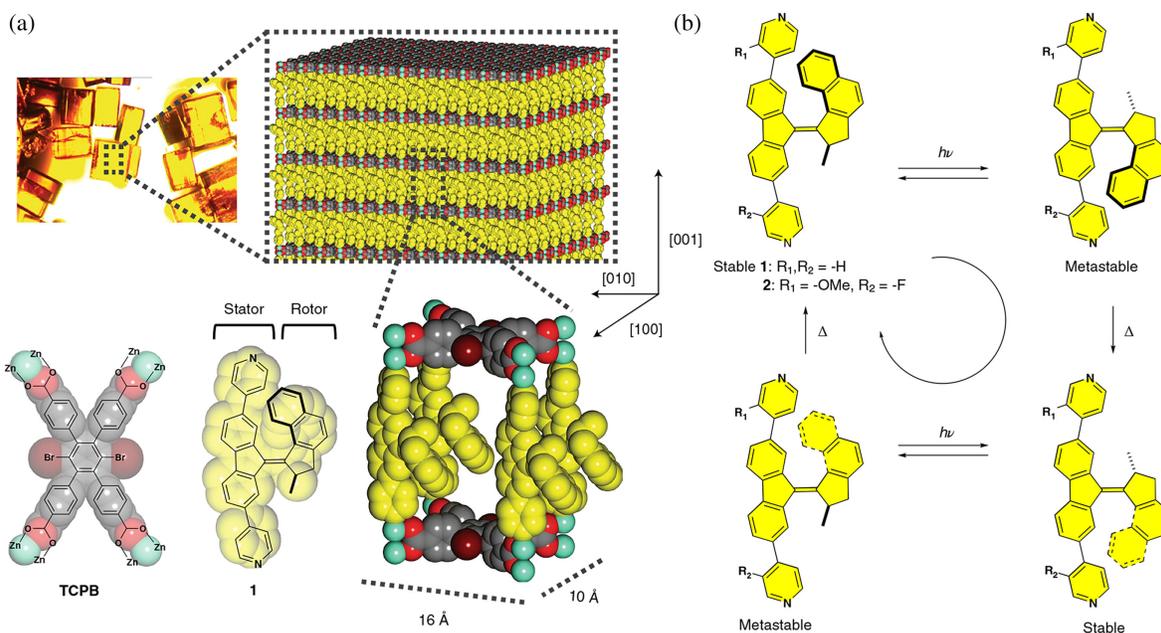


Fig. 6 (a) Schematic representation of structural moto-MOF1. (b) Photochemical and thermal isomerization of 1 incorporated in moto-MOF1. Figures reproduced from Ref. 15.

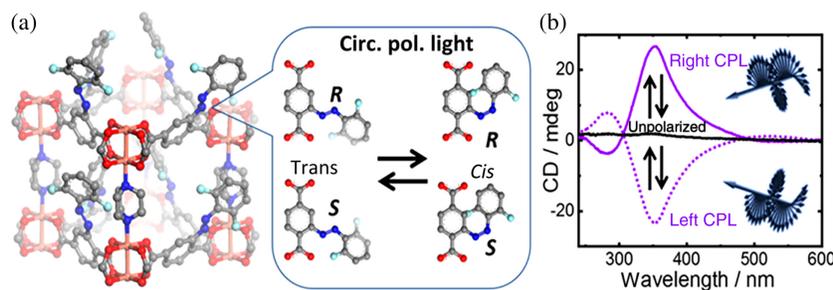


Fig. 7 (a) Schematic of the $\text{Cu}_2(\text{F}_2\text{AzoBDC})_2(\text{dabco})$ containing the fluorinated AZOs side groups. (b) CD spectra of the $\text{Cu}_2(\text{F}_2\text{AzoBDC})_2(\text{dabco})$ upon right- and left-CPL of 400 nm wavelength irradiation. Figures reproduced from Ref. 86.

This MOF 1 goes through [2+2] photodimerization reactions upon illumination by 365 nm UV light (Fig. 8).¹³ On this basis, other photopolymerization-driven polyvinyl alcohol composite film and stilbene-based $\text{Zn}_2(\text{sdc})_2$ (sdc = 4,4'-stilbenedicarboxylate) MOF film have also been reported by Lang and Gu and others.^{89–91}

As aforementioned, stimuli-responsive fluorescent MOFs have broad application prospects in security protection fields, such as information encryption and anticounterfeiting displays, mainly due to their ability to successfully prevent information or data from being stolen, mimicked, or forged.^{92,93} Among them, the biggest advantage of light-responsive MOFs is that their chemical and structural changes can be regulated through light stimulation, providing an alternative way for constructing MOFs with switchable optical absorption and fluorescence properties. Following this path, Qian et al. reported the first two-photon responsive MOF for three-dimensional (3D) two-photon patterning and fluorescence imaging (Fig. 9).⁹⁴ MOF “ZJU-56-0.20” was synthesized by a photoactive zwitterionic pyridinium linker 2,5-bis(isophthalic-5-yl)-1-methylpyridinium hydroxide ($\text{H}_4\text{L1-OH}$) and a 5,5'-(pyridine-2,5-diyl)-diisophthalic

acid ($\text{H}_4\text{L2}$) linker via a multivariate (MTV) strategy. Under UV light (365 nm), the fluorescence emission intensity of ZJU-56-0.20 gradually increases, accompanied by an obvious redshift of the emission band from 450 to 550 nm. Furthermore, they found that the same photochemical change could be induced with a 710 nm laser, but only created two-photon excited fluorescence (TPEF) without photochemical transformation using 900 nm laser as excitation wavelength. To take advantage of the TPEF, the 3D two-photon patterning was developed in which the pattern can be written and read reversibly with the altering 710 and 900 nm laser irradiation. It is worth noting that this work opens the door for two-photon responsive MOFs in 3D reconstruction and data storage.

In addition to the dynamic responsive luminescence of light-responsive ligands, dynamic responsive luminescence can also be achieved based on the changes of metal clusters. In another case, Milichko et al. demonstrated an all-optical MOF switch (HKUST-1, $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n$) [1,3,5-benzenetricarboxylic acid (BTC)].⁹⁵ There are reversible hydration and dehydration processes in the structure of HKUST-1, accompanied by color changes from cyan to navy. Owing to dehydration and the

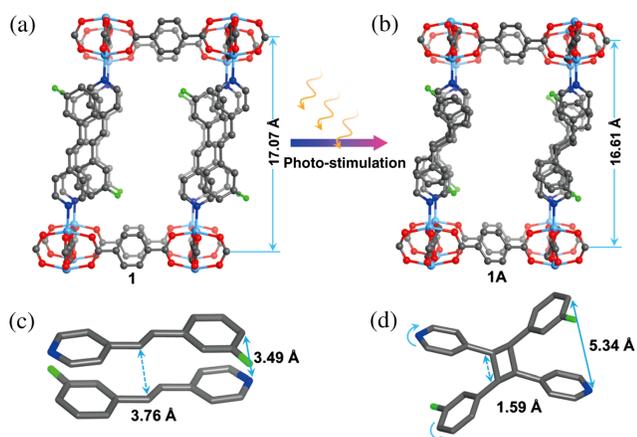


Fig. 8 Structural representation of photo-induced lattice contraction. (a) and (b) View along the *b* axis of 1 and 1A. (c) View of the head-to-tail molecular packing of photoreactive ligands in 1. (d) Structure of photodimerization ligand in 1A. Sky-blue arrows represent significant separations in 1 and 1A. Figures reproduced from Ref. 13.

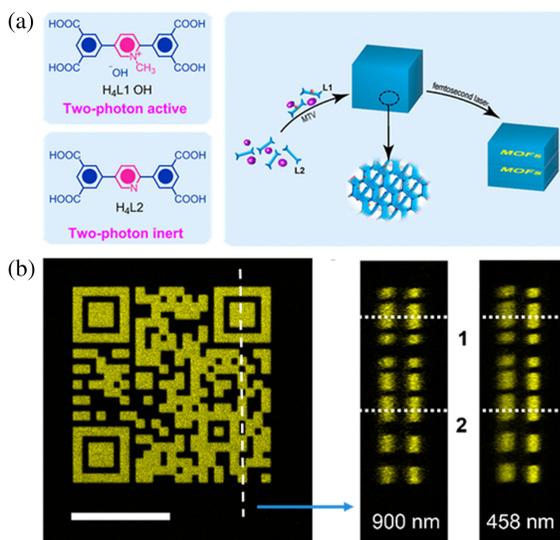


Fig. 9 (a) Schematic illustration of the zwitterionic and neutral tetracarboxylate linkers for the preparation of two-photon responsive MOFs and the femtosecond laser writing MOF single crystal. (b) Top view of TPEF image of a 2D code stack. Scale bar, 25 μm . Reconstructed lateral image along the indicated line in the left picture. Figures reproduced from Ref. 94.

concomitant shrinking of the structure-forming $[\text{Cu}_2\text{C}_4\text{O}_8]$ cages, a reversible blueshift of the absorption band was found upon ultrafast near-infrared (NIR) laser pulses radiated. In summary, the light-induced switching can reversibly turn off/on the visible light passing through the MOF single crystal, and the initial PL intensity can be controlled remotely via NIR laser pulses.

3.1.2 Light-responsive MPUs as guest

Since MOF has permanent porosity, uniform cavities, and tunable pore sizes, while the photoswitch process requires some

degree of freedom, the photoswitchable guests confined in the pores of MOFs can control their photophysical properties, which can be converted into photoswitch integration and meet the requirements of optical or photonic communications. On the other hand, the derivation and polymer of photochromic molecules are often complex and expensive. Comparatively speaking, several photoswitches and dyes are commercially available, so the preparation of light-responsive MOF@guest compounds does not have the aforementioned synthesis limitations, which can greatly overcome synthesis challenges.^{96,97}

Four factors need to be considered: (1) the photoisomerization of photoswitchable compounds can effectively impart structural transitions and switching of adsorption properties to a MOF host–guest composite; (2) taking SP as an example, the MC state has a positively charged indole group and a negatively charged phenolic group, which can be used as an important binding site for anions and cations; (3) the reversible photoisomerization of SP-MC could generate different mobile acidic protons in response to the light; and (4) the reversible photoisomerization can result in significant magnetic changes. Photoswitchable MOFs@guests have been extensively applied in gas storage and separation,^{6,61,98–100} sustainable water desalination,^{87,101,102} proton conductivity,¹⁰³ magnetic materials,¹⁰⁴ and photoelectronic devices^{105,106} in recent years.¹⁰⁷ However, research about photoswitchable host–guest MOFs in the field of optics and photonics is still in its infancy, so we only discuss several photoswitchable host–guest MOFs for optical anticounterfeiting and other applications to help readers understand the mechanism of this stimuli-responsive behavior.

Because obtaining photoswitchable host–guest MOFs systems is a challenging task, Zhu et al. encapsulated nitrobenzospiropyran (BSP) derivatives into pores of JUC-120 by a microwave-assisted crystallization inclusion route to obtain the BSP/JUC-120 films, which exhibit high reversibility and thermal stability of photochromism properties.¹⁰⁸ In another example, Benedict et al. confirmed that DTE is aligned within the pores of DMOF-1 through linear dichroism, and DMOF-1@DTE shows photochromic properties upon light irradiation.¹⁰⁹ In 2014, Klajn and co-workers described two families of porous aromatic framework (PAF) covalent incorporating the SP molecular switch. Upon desolvation of this material, the color of PhotoPAF-3.6% powder was observed to change from yellow to deep blue ($\lambda_{\text{max}} \approx 550 \text{ nm}$), suggesting the conformational freedom of SP-MC isomerization.¹¹⁰ In a recent paper, Ruschewitz et al. confirmed the successful incorporation of SP into the pores of different prototypical MOFs, including MOF-5, MIL-68(In), and MIL-68(Ga).¹¹¹ Surprisingly, strong photochromic behaviors were all observed in various pore environments.

As a special example, anthracene (ANT) is a special kind of photoswitchable compound that could undergo the process of photoisomerization and convert to nonfluorescent photodimer under UV irradiation. Interestingly, this photodimer can be decomposed by photochemical irradiation in the range of 250 to 290 nm or thermal decomposition at 250°C to 340°C. In 2019, Ameloot et al. first loaded ANT in the spherical cavity of a ZIF-8 framework to obtain an ANT@ZIF-8 photochromic system through a post-synthetic sublimation route [Figs. 10(a) and 10(b)].¹¹² The mechanism behind the photoswitching of ANT@ZIF-8 was systematically investigated. Upon UV light irradiation for 30 min, two yellow excimer ANT molecules from the pairs' photodimerization formed a nonluminescent photodimer; the other two ANT molecules displayed purple monomer

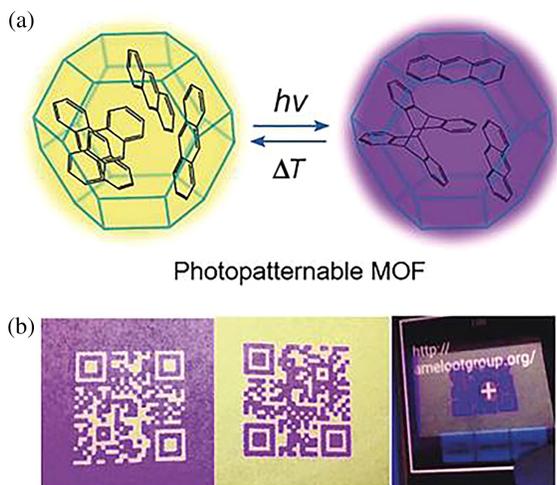


Fig. 10 (a) Proposed photodimerization reaction and restored process of ANT molecules upon UV light irradiation and thermal dissociation in the ZIF-8 cage. (b) Photopatterning on ANT@ZIF-8 based paper. Images of photopatterned QR codes under UV light (left). Decoding of QR codes with a smartphone (right). Figures reproduced from Ref. 112.

emission, which resulted in reversible yellow-to-purple photo-switching of the fluorescence emission. The reversible solid-state photoswitching and thermoswitching accessibility in ANT@ZIF-8 were further applied in photopatternable, erasable, and rewritable paper. In the subsequent work, Xu and co-workers reported Eu^{3+} @HPU-14@ZIF-8@ANT and Tb^{3+} @HPU-14@ZIF-8@ANT composites for the anticounterfeiting application by the same photodimerization reaction.¹¹³

It is promising to incorporate photochromic molecules into MOF cavities for reversible optical data storage and information anticounterfeiting. In 2019, Li et al. loaded the open-form OF-DAE into the channel of the Eu-MOF ZJU-88 to obtain ZJU-88@OF-DAE material.¹¹⁴ DAE molecules undergo reversible open/closed ring structure transitions under alternating UV and visible light irradiation, corresponding to OF-DAE and CF-DAE, respectively. As to DAE@ZJU-88 composite, the red emission was gradually quenched via the FRET between CF-DAE and Eu^{3+} as OF-DAE transforms to CF-DAE upon 300 nm UV irradiation. Considering these unique advantages of this remote light-induced reversible on–off switching of the fluorescence emission, the DAE@ZJU-88 composite was developed as luminescent QR code. In addition, chiral porous crystalline materials have an ordered assembly structure, which is of great significance in the construction and performance improvement of CPL materials.⁸⁵ Recently, by designing “turn-on” DAE derivative (DAEC) and UCNPs-loaded chiral MOFs, Duan and co-workers realized multiple light responsive CPL solid-state switches, and the amplification of CPL was achieved through the EnT process.¹¹⁵ The light-responsive CPL-active L-MOF@DAEC was prepared by loading the DAEC into the chiral Ln-MOFs. Due to the reversible photoisomerization process of DAEC molecules, the downshifting (DS) CPL of L-MOF@DAEC reversibly switched from on to off under different light irradiation. Because of the effective EnT from the UCNPs to the ring-closed (DAECc) components, another L-UCMOF@DAEC composite with tunable UC-CPL was achieved upon NIR and visible light irradiation. In addition,

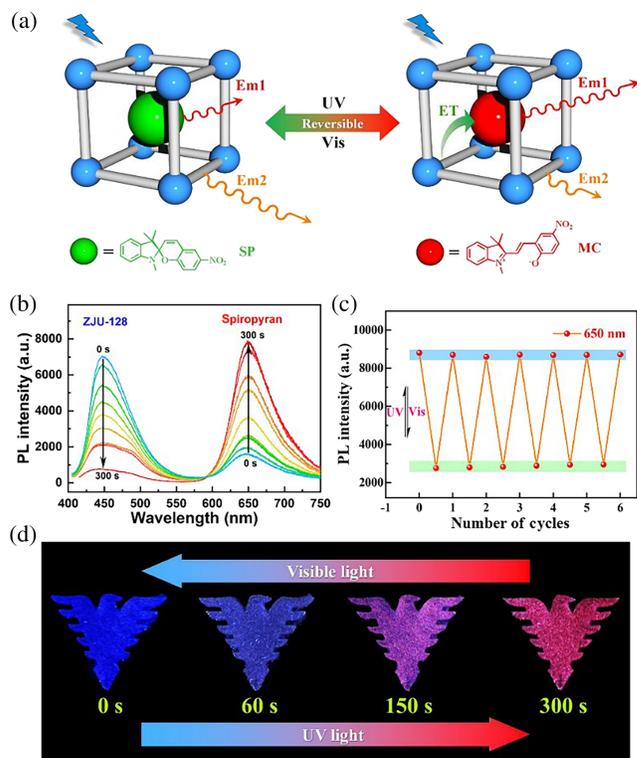


Fig. 11 (a) Schematic illustration of the photo-stimuli-responsive luminescence of the ZJU-128@SP. (b) Emission spectra of ZJU-128@SP excited at 395 nm under the UV (365 nm) irradiation with different times. (c) Reversible emission intensity changes at 650 nm upon alternating UV and visible light irradiation. (d) Photographs of ZJU-128@SP film under a 365 nm UV lamp irradiation with different times. Figures reproduced from Ref. 116.

compared to the DS-CPL of L-MOF@DAEC ($|glum| = 0.014$ to 0.020 at 546 nm), the UC-CPL of L-UCMOF@DAEC achieved an enhanced $|glum|$ of 0.078 at 546 nm.

Developing photo-stimuli-responsive luminescent materials that can be applied in security fields such as information encryption is currently an urgent challenge needing to be solved. Although various photoisomerizable molecules have been developed, they generally operated in solution because they were hampered in the solid state; the isomerization process requires some degree of conformational freedom. In addition, most of these materials exhibit the single “turn-on” or “turn-off” switching of fluorescence emission, which means that the stimuli-responsive luminescence is hard to be monitored when in the switch-off state, preventing the accurate quantitative readout of storage information. It is hoped that the designability of MOFs makes them become one of the solid-state light-responsive materials to address the above requirements [Fig. 11(a)]. It is precisely because the pore confinement of porous MOF crystals can suppress the nonradiative decay pathway of photochromic molecules, which avoids the ACQ effect caused by self-stacking; it effectively enhances the fluorescence behavior of photochromic molecules. Apart from that, the suitable distance between the MOF material (donor) and the photochromic molecules (acceptor) could effectively promote the EnT process as well as improve the fluorescence intensity and fluorescent QY of photochromic molecules. Furthermore, unlike the single and static fluorescent behavior of the conventional MOFs

system, the MOF \supset photochromic molecules composite is a dynamic dual-emissive platform that exhibits a time-dependent fluorescent color-tunable property and the dynamic tunable ratio of PL intensity, which is very important for dynamic information anticounterfeiting applications and high-security multiplexed encoding.

Hence, as proof of concept, Cui et al. reported a photo-stimuli-responsive dual-emitting ZJU-128 \supset SP composite, which was constructed by assembling SP molecule into ZJU-128, thus adopting a host–guest space-confined strategy.¹¹⁶ The UV-visible absorbance of SP-MC can be adjusted through the photoisomerization process of SP between ring-closed and ring-open forms. The significant FRET process between the blue-emitting ZJU-128 donor and the red-emitting SP acceptor can be adjusted dynamically by changing the stimulus source (UV/visible light) and stimulus time. Thereby, the fluorescence output and emission wavelength can be controlled dynamically [Figs. 11(b) and 11(c)]. Anticounterfeiting is a permanent issue owing to its abuse in banknotes, diplomas, product labels, and so on. Furthermore, due to the unusual dynamic properties of the color and fluorescence intensity of ZJU-128 \supset SP composites, a dual-emitting ZJU-128 \supset SP polydimethylsiloxane (PDMS) film has been constructed, which provides the method to reversibly regulate the output signal of advanced dynamic information anticounterfeiting compared with typical on–off switching information encryption materials [Fig. 11(d)]. On the other hand, the emissions intensity ratio between H₄TCPP ligand and SP (I_{447}/I_{650}) in dual-emitting ZJU-128 \supset SP provides a self-calibrated signal, which could eliminate the external interference and realization of the precise quantitative assessment. More interestingly, the dynamic dual-emitting feature and quantitative analysis of the intensity ratio of blue to red of ZJU-128 \supset SP architectures offer a promising strategy for multiplexed coding (for example, 3D/4D coding) and multilevel encryption. This work supplied an inspiration for the preparation of information encryption materials and advanced anticounterfeiting materials.

3.2 Gas-Responsive

The detection and monitoring of gases around the local environments, such as sulfur dioxide (SO₂), oxygen (O₂), hydrogen (H₂), hydrogen sulfide (H₂S), ammonia (NH₃), and volatile organic solvents (VOCs), are important due to the harmfulness and toxicity of some of them.¹¹⁷ Gas molecules will affect the electron migration during the MOF luminescence process, or produce specific recognition with groups on the ligand, resulting in “turn on” or “turn off” type fluorescence responses.

As mentioned earlier, the flexible MOFs can exhibit dynamic structural changes under external stimuli (such as gas), providing an excellent platform for constructing stimuli-responsive photonic materials. For instance, Kitagawa’s team introduced fluorescent reporter distyrylbenzene (DSB) into nanochannels of flexible PCP to realize a luminescence detection of gas molecules [Fig. 12(a)].¹¹⁸ The synthesized PCP-DSB material could selectively adsorb CO₂ over other atmospheric gases, such as N₂, O₂, and Ar. Intriguingly, under the pressure of CO₂ gas, the conformation of DSB molecules varied with the change of the pore shape and pore size of the host framework, which brings about the change of the fluorescence peak position and intensity. The PCP-DSB material exhibits various fluorescence responses to various gases that have similar physicochemical

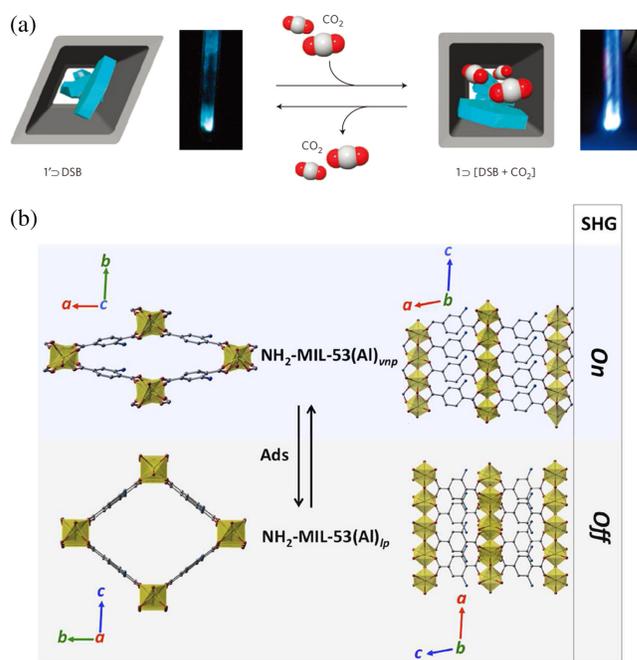


Fig. 12 (a) Schematic illustration of the sensing of CO₂ via monitoring of the configuration-related fluorescence emission of DSB in a flexible PCP framework. Figures reproduced from Ref. 118. (b) Schematic illustration of the breathing behavior of the NH₂-MIL-53(Al) as an NLO switch. Figures reproduced from Ref. 119.

properties, such as CO₂ and acetylene. NLO switches in the solid state are badly needed in the present, especially based on noncentrosymmetric framework materials. Gascon et al. also reported that the crystal structure of the flexible NH₂-MIL-53(Al) material changes after CO₂ absorption [from NH₂-MIL-53(Al)_{vp} to NH₂-MIL-53(Al)_{lp}], resulting in the disturbance of polar ordering for strong electronic groups-NH₂; then the NLO response switches from on to off [Fig. 12(b)]. The NLO response intensity of MOF is relatively obvious and can be used as a solid-state NLO switch.¹¹⁹ This work provides guidance for the preparation of ordered arrangement in MOF structures and the development of NLO switches induced by external stimuli (such as gas and light).

3.3 Pressure-Responsive

In this section, selected reports about the pressure-responsive behaviors of photonic MOFs will be discussed in detail. Piezofluorochromic or mechanofluorochromic materials have attracted attention for their practical applications, such as anticounterfeiting, mechanical sensing, data storage, and smart devices. The pressure-responsive photonic MOFs exhibit dynamically adjustable photophysical properties upon external pressure stimuli, such as grinding, shearing, scratching, stretching, cleaving, or compressing.^{1,49,120}

Owing to the unique luminescence merits of aggregation-induced emission (AIE) luminogens in the stacked state, plentiful AIEgens are pressure-responsive, which serve as an essential class of solid-state piezofluorochromic materials. In particular, AIE building blocks derived from AIEgens are an important means of AIE-MOFs construction strategy, which have interesting pressure-responsive properties.¹ In 2015, Zhou et al.

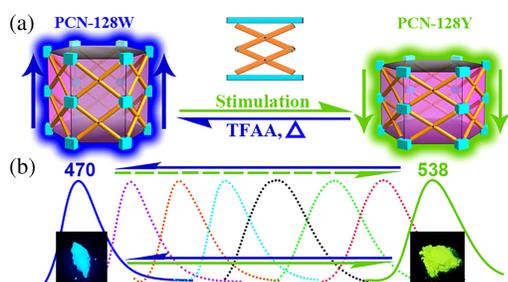


Fig. 13 (a) Schematic illustrating the reversible motion of the microscissor lift in PCN-128W and PCN-128Y. (b) Fluorescent spectra of PCN-128W and PCN-128Y at room temperature. Figures reproduced from Ref. 121.

introduced the first piezofluorochromic MOF, PCN-128, which is constructed by eight connected Zr_6 clusters and H_4 ETTC (4',4''',4''''',4''''''-(ethene-1,1,2,2-tetrayl)tetrakis-([1,1'-biphenyl]-4-carboxylic acid))) ligand (Fig. 13).¹²¹ When compressed, the white PCN-128W powder changed to a yellow PCN-128Y powder. The blue emitting (470 nm) PCN-128W converts to green emitting (538 nm) PCN-128Y under a UV 365 nm environment. Further, after treatment with trifluoroacetate (TFA), the compressed PCN-128Y can be recovered to PCN-128W. Further structural analysis indicates that the reversibility is mainly owed to the coordination of TFA groups, which restricted the movement of Zr_6 clusters, thereby preventing further deformation of the ETTC connector. In summary, studies on its transformation mechanism indicate that PCN-128W can be regarded as a pressure-responsive microscissor lift.

To further enrich pressure-responsive materials with tunable and controllable piezofluorochromic performance, another mixed-linker MOF, LIFM-66W was observed by Su and Pan et al.¹²² Later, a series of H_4 ETTC-based MOFs (LIFM-66, LIFM-114, LIFM-223, PCN-94, PCN-128) were prepared and then they compared the pressure-induced one/two/three-photon multiphoton excited fluorescence (MPEF) and fluorochromic performance [Fig. 14(a)].¹²³ Further analysis found that the MPEF of the MOFs is associated with the MOF's structural

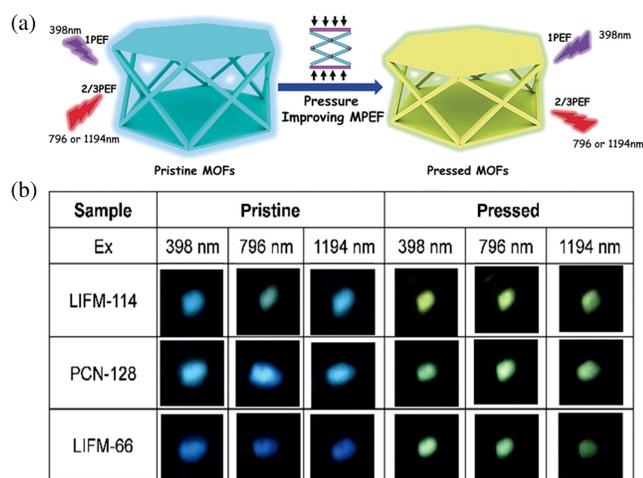


Fig. 14 (a) Structural characters and (b) selected photographic images in correlation with pressure-induced 1/2/3PEF of the AIE MOFs. Figures reproduced from Ref. 123.

characteristics, as well as the pressure-induced deformations process. In other words, the flexibility and deformability of the compressed MOFs greatly affect their emission intensity and color. Such AIE-MOFs featuring different pressure-dependent MPEF behavior within the same material could be a very attractive material. Su and co-workers reported a flexible two-fold interpenetrating LIFM-114 material with multiple external stimuli responses to solvents, heat, and pressure [Fig. 14(b)].¹²⁴ A reversible switch between the blue and green emission bands in LIFM-114 was achieved due to the obvious breathing contraction of the interpenetrated framework of LIFM-114 and related conformation change inside the ETTC linkers under different external stimuli.

Apart from the previously reported work about pressure-responsive AIE-MOFs,¹²⁵ Zou et al. showed the green-emitting $Tb(BTC)(H_2O)_6$ with pressure-responsive performance (Fig. 15).¹²⁶ When the pressure below 2.5 GPa, $Tb(BTC)(H_2O)_6$ behaved obvious PL enhancement. It is worth noting that when the pressure is completely released and maintained for more than half a year, the QY of the $Tb(BTC)(H_2O)_6$ material increases significantly from 50.6% to 90.4%. Further research suggests that the mechanism of this pressure-responsive MOF can be attributed to the enhanced hydrogen bonds lock causing enhanced intersystem crossing to effectively drive ligand-to-metal energy transfer. In addition, the same group found that a non-emission MOF-2 and $Y(BTC)(H_2O)_6$ also exhibit pressure-responsive photoluminescence.^{127,128} Moggach et al. also reported pressure-induced photoluminescence of Hf-peb MOF due to the linker rotation.¹²⁹

3.4 Polarization-Responsive

The asymmetry between the direction of vibration and propagation is called the polarization phenomenon. The polarization of light can provide the possibility for the analysis and processing of scattered light signals. Polarized light has been extensively applied in optical modulation devices, radar remote sensing, high-resolution display, and other fields.^{45,130} However, microcavity laser materials with high polarization emission (>99%) have rarely been reported. Among them, high-order multiphoton pumped polarized microlasers have important application prospects in biophotonics, such as bioinformatics imaging and PDT.^{130–133}

The A- π -D push-pull type molecules (A = acceptor and D = donor) possess a strong intramolecular charge transfer effect, such as dyes. It is essential that the centrosymmetric multipolar geometry of A- π -D type molecules possesses donor groups and acceptor groups, resulting in an enhanced polarizability, which is a prerequisite for strong NLO/multiphoton absorption (MPA) response.^{131,134} On the basis of their previous work about bio-MOF-1 \supset DMASM (DMASM, 4-[*p*-(dimethylamino)styryl]-1-methylpyridine), size-matched inclusion of dyes periodically aligned in one-dimensional (1D) pores of MOFs, which will improve the pore confinement efficiency of MOFs. Therefore, Qian et al. reported an anionic MOF crystal $H_2[Zn_3O(CPQC)_3]$ (ZJU-68) with subnanoscale 1D channels, which was designed using zinc ion and a novel multidentate organic bridging ligand 7-(4-carboxylic acid phenyl)-3-carboxylic acid-quinoline (H_2 CPQC).¹³⁵ The *in situ* assembly method successfully controlled the chromophore ion DMASM with unidirectional transition dipole moment to assemble into channels of ZJU-68, thus resulting in the host-guest hybrid single crystal

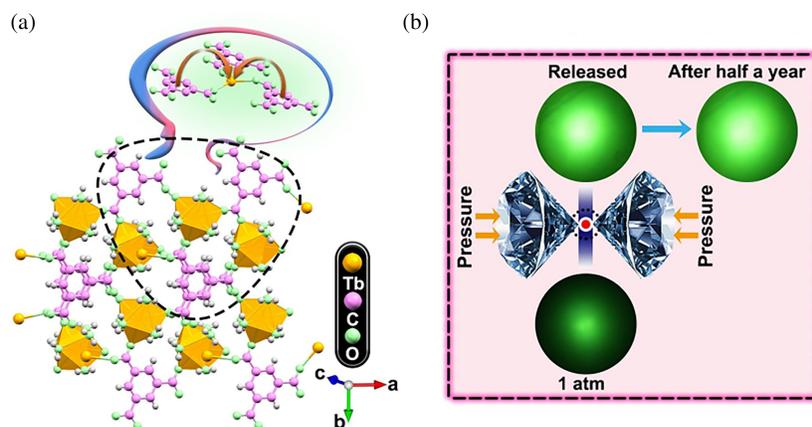


Fig. 15 (a) Structure of Tb(BTC)(H₂O)₆. (b) Optical images of Tb(BTC)(H₂O)₆ at 1 atm and upon complete release of the pressure. Figures reproduced from Ref. 126.

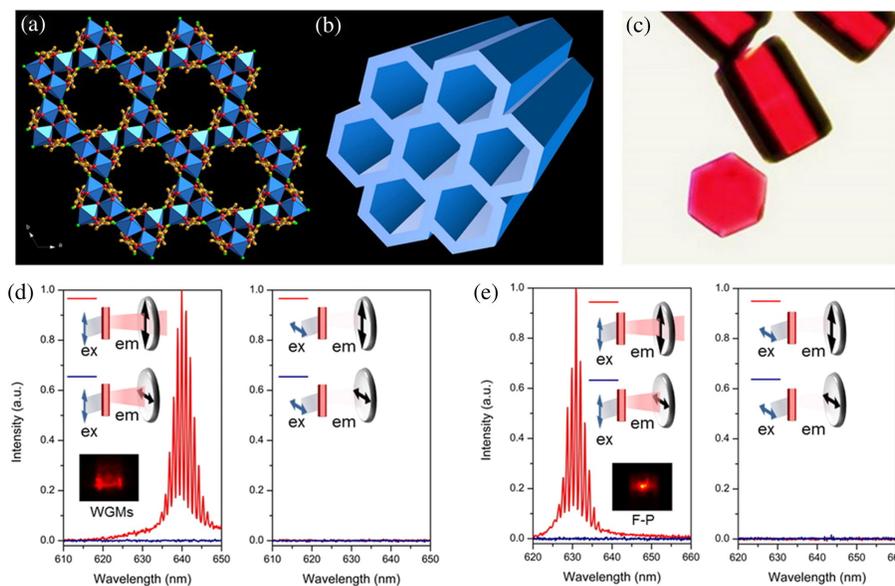


Fig. 16 (a), (b) Structure and (c) red color of ZJU-68@DMASM crystal viewed along the crystallographic *c* direction. Intensity-dependent emission spectra of 3PP (d) WGMs and (e) F-P from crystal with pump/emission-detected polarization combinations at two angles $\theta = 0$ deg and $\theta = 90$ deg, excited at 1380 nm. Figures reproduced from Ref. 135.

ZJU-68@DMASM (Fig. 16). Due to the highly oriented and periodic arrangement of DMASM in the 1D ordered channels of ZJU-68, the assembly concentration of DMASM could be further increased to enhance the QY from 0.45% of DMASM solution to 24.28% of ZJU-68@DMASM. Particularly, a low lasing threshold of the 3PP lasing has been successfully achieved upon excitation at 1380 nm. Both the 3PP WGMs optical-feedback mechanisms and especially F-P lasing in ZJU-68@DMASM microcrystals show a high degree of polarization (DOP, over 99.9%). These results provide a new approach and theoretical basis for the design and construction of novel multiphoton pumped polarized microcavity laser materials and devices.

MOF materials with NLO performance have broad application prospects in photoelectric conversion, optical switches, optical information processing, temperature sensors, biological

imaging, and detection of living tissues. A single NLO response is difficult to meet the development of multifunctional integrated materials or devices. The development of new materials with multiple NLO response integration, especially the design of materials with controllable NLO performance is a topic with some research urgency. However, there is still a lack of suitable material systems and construction strategies, making it difficult to integrate multiple NLO properties into the same micro/nano-material and achieve performance control. Switching between different strong signals [second-harmonic generation (SHG), two-photon fluorescence (TPF), and so on] in a single medium could avoid signal cross-contamination. Qian et al. selected 1-ethyl-4-[4-(*p*-dimethylaminophenyl)-1,3-butadienyl]pyridinium perchlorate (LDS-722) dye encapsulated into ZJU-68 by an *in situ* self-assembly strategy.¹³⁶ The polarization direction and transition dipole moment are highly arranged along the

ID channel of ZJU-68, resulting in the second- and third-order NLO effects. The polarization ratios of TPF and SHG are both as high as 99%. The above NLO performance is excitation wavelength-dependent. Consequently, the signal output of TPF/laser, SHG, and THG can be controlled by adjusting the excitation wavelength. Switching between two-photon-pumped (TPP) lasing and SHG signals is scientifically significant but difficult to achieve. Therefore, Qian et al. proposed the concept of NLO building units (NBUs); two types of D-A type NBUs were reasonably arranged in MOF single crystals to achieve polarization-regulated multiple NLO performances. Specifically, they introduced a dipolar donor (D)–acceptor (A) DSM dye to a 1D channel of MOF to prepare the ZJU-24-Eu \supset DSM host–guest material (Fig. 17).¹³⁷ ZJU-24-Eu was precisely fabricated using an octupolar electron D–A structural 4',4''',4''''-nitriлотris[1,10-biphenyl]-4-carboxylic acid (H₃NBB) ligand. By changing the polarization direction of NIR femtosecond lasers and the angle between the long axis of the crystal (θ_{Ex}), hybrid single crystals exhibit SHG signals that are excitation polarization-dependent, with maximum SHG signals at $\theta_{\text{Ex}} = 90$ deg. The spatial arrangement of two-photon dye DSM and the smooth surface of regular MOF crystals enable ZJU-24-Eu \supset DSM single crystals to behave with the strongest TPP laser when emitted at $\theta_{\text{Ex}} = 0$ deg. Therefore, the alternating occurrence of SHG and TPP lasers can be controlled by orthogonally changing the excitation polarization direction from the angle $\theta = 0$ deg to 90 deg, with a DOP of 81.2% and 96.1%, respectively.

Constructing heterostructures is an effective method for integrating and spatially separating multiple optically active media in a single structure with component gradients. The design and fabrication of controllable MOF heterostructures through epitaxial growth strategy enable them to obtain the multiwavelength and multicolor emission. Qian et al. used *in situ* assembly of cationic linear dye molecules DMASM, (E)-1-methyl-4-(2-(1-methyl-1H-pyrrol-2-yl)vinyl)pyridinium (MMPVP) and 4-((1E,3E)-4-(4-(dimethylamino) phenyl)buta-1,3-dienyl)-1-methylpyridinium (DPBDM) in the channels of ZJU-68 to obtain homoepitaxy ZJU-68 \supset DPBDM+DMASM+MMPVP microcrystals. Surprisingly, this hybrid MOF heterostructure achieved dynamically tunable multicolor single-mode highly polarized lasing.¹³⁸ Following this method, a composition-graded DABP@DASE@ZJU-68 heterostructure was fabricated through the same strategy with the inclusion of two

dye molecules E-4(4-dimethylaminostyryl)-1-ethylpyridinium (DASE) and 4-((1E,3E)-4-(4(dimethylamino) phenyl) buta-1,3-dien-1-yl)-1-methylpyridinium (DABP) into ZJU-68 channels.¹³⁹ On the basis of this excited position-dependent two-photon polarized lasing in NIR region, an extension work is carried out. Similarly, LDS-798@LDS-722@ZJU-67 heterostructure (LDS-798, 4-[4-[4-(dimethylamino)phenyl]-1,3-butadienyl]-1-ethyl quinolinium perchlorate) was constructed and used for three-level photonic encoding based on the switchable dual-wavelength NIR lasing.¹⁴⁰ It increases the complexity and security of photonic tags, making the MOF-based heterostructure promising for advanced anticounterfeiting and information encryption in the future.

In addition to a strategy to construct MOF heterostructures, Qian et al. also designed a novel sandwich-like MOF-based mixed-matrix membrane to realize NLO switching.¹⁴¹ A new anionic MOF material H₂[Mn₃O(C₁₇H₉NO₄)₃] (ZJU-67) with 1D channels was synthesized by manganese ion and H₂CPQC ligands. DASE@ZJU-67 and spirooxazine were utilized as laser emission unit and absorption unit, respectively, which were hierarchically encapsulated in PDMS (Fig. 18). Due to the strong space confinement and high-concentration gain media, DASE@ZJU-67 exhibits anisotropic two-photon lasing in the red band with E^{th} of 1.95 mJ/cm² and a high degree of linear polarization of $\sim 99.9\%$ ($\lambda_{\text{Ex}} = 1064$ nm). Owing to the rapid photochemical reaction of photochromic molecules, the molecular structure changes reversibly under light stimuli, which results in the sharp red absorption band variations, ultimately causing a decrease in emission or quenching of the upconversion laser.

Similar to the MOF \supset dye host–guest system developed by Qian's group, Boom et al. used a one-step solvothermal approach to construct oriented surface-bound MOFs (sMOFs), mainly through the control of morphology as well as the dimensions of the crystal;¹⁴² they then successfully encapsulated resorufin sodium salt into the 1D channels of the sMOFs (Fig. 19). Due to the aligned arrangement of dyes in the crystal, hybrid MOF crystals exhibit red-polarized emission with a high polarization degree. In their next work, the same group demonstrated the size-selective encapsulation of dyes in differently sized channels of MOFs.¹⁴³ The AdDB ligand-based MOF has two types of continuous channels, which is suitable for inclusion of sodium resorufin (SR) and sodium fluorescein (SF) dyes.

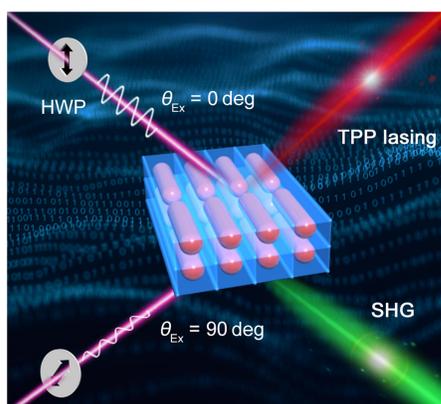


Fig. 17 Aligned dyes in a ZJU-24-Eu \supset DSM crystal for switchable polarized-excitation-responsive SHG and TPP lasing. Figures reproduced from Ref. 137.

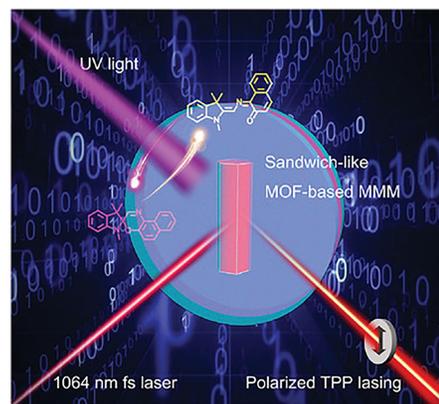


Fig. 18 Schematic diagram of sandwich-like MOF-based mixed-matrix membranes to realize NLO switching. Figures reproduced from Ref. 141.

Interestingly, the SR/SF@MOF crystals are dichroic under polarized light, and the yellow emission from SF (donor) at 541 nm is gradually decreased and accompanied by a red emission of around 608 nm of SR (acceptor) that increases. Further analysis indicates that a significant FRET process was achieved when the SR concentration was increased. The FRET mechanism has been verified by fluorescence lifetime and photobleaching of the acceptor SF.

Similarly, D-A type derived ligands can be used as building blocks and NLO/MPA photonic units of MOFs, such as triphenylamine-derived linkers, dye-derived linkers, and others, that have been reported.^{144–146} On the basis of the previous work, D-A type ligands-based MOFs that exhibit polarized NLO/MPA performance have also been developed. For instance, a seven-fold interpenetrated MOF (1) is transformed into an eight-fold interpenetrated MOF (2) by a single crystal-to-single-crystal approach.¹⁴⁷ The transformation of these two MOFs is accompanied by significant improvements of the SHG performance (ca. 125 times) and TPF performance (ca. 14 times). In 2019, Ji et al. obtained a rhodamine B (Rh B) dye-coordinated MOF with a high thermal and chemical stability. This dye-coordinated MOF microplate could achieve a low-threshold multiphoton-pumped microlaser without an external cavity (Fig. 20).¹⁴⁸ Particularly, the lasing thresholds are in the range from 0.34 to 0.12 $\mu\text{J cm}^{-2}$ upon various optical pumping conditions, mainly owing to the exciton–polariton lasing mechanism as well as the large MPA cross sections of the three dye-coordinated MOF microplates. Subsequently, they continued to demonstrate the stack of 2D nanosheets of rhodamine B molecular network for constructing a MOF with a large polariton–polariton scattering strength (g).¹⁴⁹ In 2022, Liu et al. employed a mixed ligand strategy to synthesize a series of

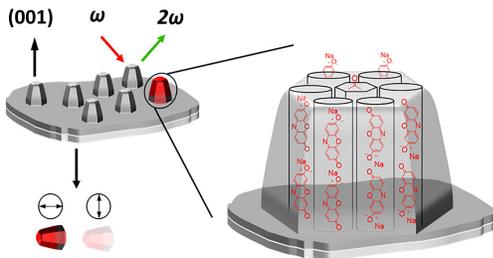


Fig. 19 Chiral and SHG-active MOFs formed in solution and on surfaces. Figures reproduced from Ref. 143.

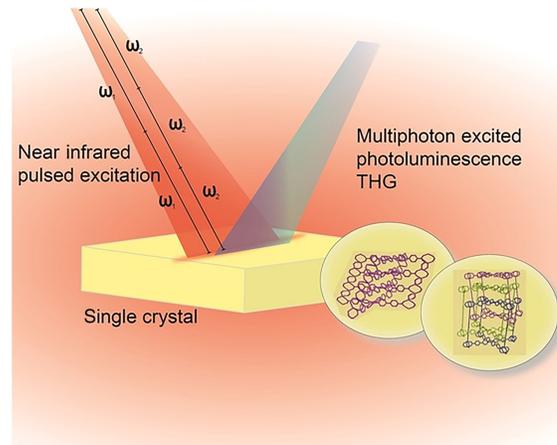
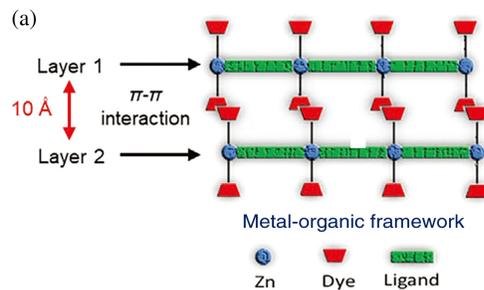


Fig. 21 Series of highly efficient MPA of zinc-AIEgen MOFs. Figures reproduced from Ref. 150.

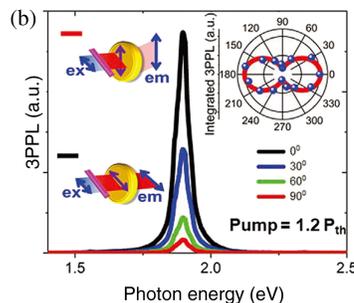


Fig. 20 (a) Layered structure of a MOF microplate with stable π – π interaction between adjacent layers. (b) Three-photon-pumped lasing spectra recorded at four different emission polarization angles (from 0 deg to 90 deg). Figures reproduced from Ref. 148.

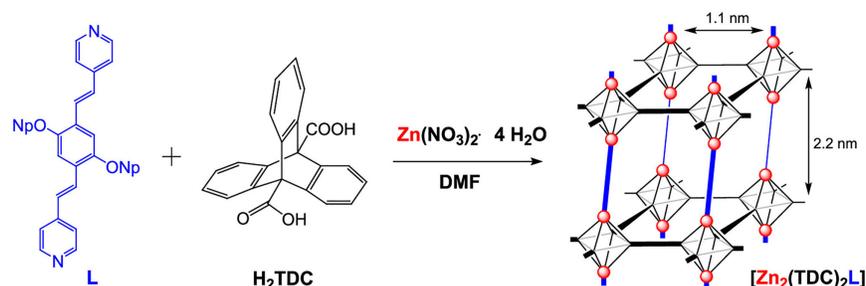


Fig. 22 Illustration of the structure of TDC-MOF-8. Figures reproduced from Ref. 151.

Table 1 Features and suggested or examined applications of select stimuli-responsive photonic MOFs.

MOF	Switchable component	Switching mechanism	Stimulus	Application(s)	References
Azo-IRMOF-74-III	AZO ligand	Cis/trans isomerization	Light	Dye (propidium iodide) release	82
Zn-MOF	BPMTc ligand	Ring opening/closing	Light	EnT system	59
SO-PCN	BPDTE ligand	Ring opening/closing	Light	¹ O ₂ generation and photocatalysis	83
UiO-66-TCPP-BCDTE	BCDTE ligand	Ring opening/closing	Light	¹ O ₂ generation	84
ZnTPP + (1)	DAE ligand	Ring opening/closing	Light	¹ O ₂ generation	58
PdTCPP MOF	Molecular motor ligand	Cis/trans isomerization	Light	EnT system	16
Moto-MOF1	Molecular motor ligand	Cis/trans isomerization	Light	Unidirectional rotary motion	15
Cu ₂ (F ₂ AzoBDC) ₂ (dabco)	F ₂ AzoBDC ligand	Cis/trans isomerization	Light	Circularly polarized light	86
[Zn(bdc)(3-F-spy)]	3-F-spy	Photocycloaddition reaction	Light	Photoactuators	13
Zn ₄ O(sdc) ₆	Stilbene ligand	Photocycloaddition reaction	Light	Photopatterning	90
ZJU-56-0.20	Zwitterionic pyridinium linker	Photoactive zwitterionic	Light	3D two-photon patterning	94
HKUST-1	(Cu ₂ C ₄ O ₈) cages	Dehydration and shrinking	Light	Light-induced switching	95
JUC-120	BSP guest	Ring opening/closing	Light	Photonic and optical devices	108
DMOF-1@DTE	DTE guest	Ring opening/closing	Light	Photochromic properties	109
SP@MOF-5	SP guest	Ring opening/closing	Light	Photochromic properties	111
ANT@ZIF-8	ANT guest	Photodimerization reaction	Light	Photopatterned QR codes	112
ZJU-88∩OF-DAE	DAE guest	Ring opening/closing	Light	Data storage	114
L-MOF∩DAEC	DAEC guest	Ring opening/closing	Light	Circularly polarized light	115
ZJU-128∩SP	SP guest	Ring opening/closing	Light	Information encryption	116
PCN-128W	H ₄ ETTC ligand	Microscissor lift	Pressure	Adjustable luminescence	121
LIFM-66W	H ₄ ETTC ligand	Conformation change	Pressure	Adjustable luminescence	122
LIFM-114	H ₄ ETTC ligand	Conformation change	Pressure	MPEF behavior	123
Tb(BTC)(H ₂ O) ₆	—	Enhanced hydrogen bonds lock	Pressure	Adjustable luminescence	126
Hf-peb	H ₂ peb ligand	Linker rotation	Pressure	Adjustable luminescence	129
PCP-DSB	Pore shape	Breathing effect	Gas	Adjustable luminescence	118

Table 1 (Continued).

MOF	Switchable component	Switching mechanism	Stimulus	Application(s)	References
NH ₂ -MIL-53(Al)	Groups-NH ₂	Order arrangement	Gas	SHG switch	119
ZJU-68-DMASM	DMASM dye	Order arrangement	Polarization	3PP lasing	135
ZJU-24-DMSM	DSM dye	Order arrangement	Polarization	SHG and lasing switching	137
DASE@ZJU-67	DASE dye	Order arrangement	Polarization	Lasing switching	141
SR/SF@MOF	SR and SF dye	Order arrangement	Polarization	EnT system	143
RhB-coordinated MOF	RhB dye	D-A type ligands	Polarization	Lasing	148
Zn-TCPE-L1	An2Py pillar ligands	D-A type ligands	Polarization	2PPL, 3PPL, and THG	150
TDC-MOF-8	Np-P4VB	Order arrangement	Polarization	Polarized emission	151

4 Conclusions and Perspectives

Many studies have shown the unique advantages and broad applications of stimuli-responsive photonic MOFs in the past few years. In this review, we mainly discussed the representative results of stimuli-responsive photonic MOFs upon different types of external stimuli, including light, force, gas, and polarization. We emphasized the basic work principles, to provide a better understanding of the stimuli-responsive process and then gave guidance for the design and fabrication of desirable stimuli-responsive photonic MOF materials.

So far, although some crucial progress has been achieved in dynamic responsive MOFs, the development of stimuli-responsive photonic MOFs is still in its infancy, far behind its gas storage and separation applications. Therefore, there is an urgent need to further develop smart dynamic responsive photonic MOFs and control their responsive behavior as needed, which will greatly improve and promote optoelectronic applications.

First, it is necessary to design and fabricate photoswitchable molecule-based ligands for the construction of stimuli-responsive photonic MOFs. Meanwhile, currently reported stimuli-responsive MPU-based ligands are mainly carboxyl- or pyridyl-based. Therefore, exploring chelating groups of MPUs-based ligands will enrich the coordination patterns and luminescent properties of stimuli-responsive MOFs. On the other hand, there are still numerous switchable moieties that have not been converted to ligands of MOFs.

Second, multivariate components and multifunction could be integrated into the dynamically responsive photonic MOF materials. The tunable and designable structure of stimuli-responsive MOFs as well as the synergistic effect between different MPUs could affect their photonic performance. Therefore, it is necessary to systematically consider the relationship between corresponding photonic properties and material preparation strategies, structural modulation as well as synergistic effects, which will promote the rapid development of photonic functional MOFs. For example, traditional photoswitchable moieties (such as DAE) have intrinsic shortcomings—weak emission and lower QY. Hence, by rational design of a FRET system between MOFs and a photoswitchable moiety-based guest, tunable structure and luminescence and even photonic function will be achieved, which could reveal the structure-activity relationship of stimuli-responsive behaviors and expand its application fields.

Third, applications of photoswitchable MOFs still need to be explored in the future. For example, much more attention should be paid to the development of stimuli-responsive MOF-based photonic biosensors for intracellular sensing, which will achieve meaningful advancements in biomedical diagnostics, therapeutics, and so on. In addition, developing alternative cost-effective and high-quality luminescent materials with good encryption capabilities for advanced information storage (such as 3D/4D coding) and security protection applications remains an urgent challenge.

Fourth, we reviewed the fluorescence properties and applications of photochromism MOFs, although the NLO properties, upconversion, and lasing in stimuli-responsive MOFs are rarely discussed. However, according to reports, AZO and SP dyes or derivatives can also exhibit NLO and lasing properties. Therefore, the introduction of photoswitchable molecules into MOF channels and the orderly arrangement of photoswitchable chromophores in MOFs are expected to achieve the NLO, upconversion luminescence, and laser performance in dynamically responsive MOFs. Note that this is also one of the important topics currently being studied by our group. It is undoubtedly one of the important development trends in the future to apply them to photonic biological imaging and PDT.

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References

1. J. Zhang et al., “Stimuli-responsive AIEgens,” *Adv. Mater.* **33**(32), 2008071 (2021).
2. Y. Wang et al., “Stimuli-induced reversible proton transfer for stimuli-responsive materials and devices,” *Acc. Chem. Res.* **54**(9), 2216–2226 (2021).
3. M. Grzelczak et al., “Stimuli-responsive self-assembly of nanoparticles,” *Chem. Soc. Rev.* **48**(5), 1342–1361 (2019).
4. P. Yang et al., “Stimuli-responsive polydopamine-based smart materials,” *Chem. Soc. Rev.* **50**(14), 8319–8343 (2021).
5. M. Li and W.-H. Zhu, “Sterically hindered diarylethenes with a benzobis (thiadiazole) bridge: enantiospecific transformation and reversible photosuperstructures,” *Acc. Chem. Res.* **55**(21), 3136–3149 (2022).

6. K. Ohara et al., “The catalytic *Z* to *E* isomerization of stilbenes in a photosensitizing porous coordination network,” *Angew. Chem. Int. Ed.* **49**(32), 5507–5509 (2010).
7. W. Danowski et al., “Photoresponsive porous materials,” *Nanosci. Adv.* **3**(1), 24–40 (2021).
8. A. Abdollahi et al., “Photoluminescent and chromic nanomaterials for anticounterfeiting technologies: recent advances and future challenges,” *ACS Nano* **14**(11), 14417–14492 (2020).
9. R. Klajn, “Spiropyran-based dynamic materials,” *Chem. Soc. Rev.* **43**(1), 148–184 (2014).
10. M. Irie, “Diarylethenes for memories and switches,” *Chem. Rev.* **100**(5), 1685–1716 (2000).
11. H. B. Cheng et al., “Future-oriented advanced diarylethene photoswitches: from molecular design to spontaneous assembly systems,” *Adv. Mater.* **34**(16), 2108289 (2022).
12. A. B. Grommet et al., “Molecular photoswitching in confined spaces,” *Acc. Chem. Res.* **53**(11), 2600–2610 (2020).
13. Y. X. Shi et al., “Fabrication of photoactuators: macroscopic photomechanical responses of metal–organic frameworks to irradiation by UV light,” *Angew. Chem. Int. Ed.* **58**(28), 9453–9458 (2019).
14. T.-Y. Xu et al., “Engineering photomechanical molecular crystals to achieve extraordinary expansion based on solid-state [2 + 2] photocycloaddition,” *J. Am. Chem. Soc.* **144**(14), 6278–6290 (2022).
15. W. Danowski et al., “Unidirectional rotary motion in a metal–organic framework,” *Nat. Nanotechnol.* **14**(5), 488–494 (2019).
16. W. Danowski et al., “Visible-light-driven rotation of molecular motors in a dual-function metal–organic framework enabled by energy transfer,” *J. Am. Chem. Soc.* **142**(19), 9048–9056 (2020).
17. A. M. Rice et al., “Photophysics modulation in photoswitchable metal–organic frameworks,” *Chem. Rev.* **120**(16), 8790–8813 (2020).
18. Z. Zhang et al., “Stepping out of the blue: from visible to near-IR triggered photoswitches,” *Angew. Chem. Int. Ed.* **134**(31), e202205758 (2022).
19. E. A. Dolgoplova et al., “Photochemistry and photophysics of MOFs: steps towards MOF-based sensing enhancements,” *Chem. Soc. Rev.* **47**(13), 4710–4728 (2018).
20. Y. Sakata et al., “Shape-memory nanopores induced in coordination frameworks by crystal downsizing,” *Science* **339**(6116), 193–196 (2013).
21. Z. Chang et al., “Flexible metal–organic frameworks: recent advances and potential applications,” *Adv. Mater.* **27**(36), 5432–5441 (2015).
22. G. Férey and C. Serre, “Large breathing effects in three-dimensional porous hybrid matter: facts, analyses, rules and consequences,” *Chem. Soc. Rev.* **38**(5), 1380–1399 (2009).
23. K. Chen et al., “Gating effect for gas adsorption in microporous materials—mechanisms and applications,” *Chem. Soc. Rev.* **51**, 1139–1166 (2022).
24. F. Xu and B. L. Feringa, “Photoresponsive supramolecular polymers: from light-controlled small molecules to smart materials,” *Adv. Mater.* **35**(10), 2204413 (2023).
25. W. Bogaerts et al., “Programmable photonic circuits,” *Nature* **586**(7828), 207–216 (2020).
26. C. Fenzl et al., “Photonic crystals for chemical sensing and biosensing,” *Angew. Chem. Int. Ed.* **53**(13), 3318–3335 (2014).
27. R. Haldar et al., “Advanced photoresponsive materials using the metal–organic framework approach,” *Adv. Mater.* **32**(20), 1905227 (2020).
28. Y. Cui et al., “Photonic functional metal–organic frameworks,” *Chem. Soc. Rev.* **47**(15), 5740–5785 (2018).
29. H.-Q. Zheng et al., “Development on fluorescence sensing properties of lanthanide metal–organic frameworks,” *J. Chin. Ceram. Soc.* **50**(12), 3165–3184 (2022).
30. T. He et al., “Chemically stable metal–organic frameworks: rational construction and application expansion,” *Acc. Chem. Res.* **54**(15), 3083–3094 (2021).
31. H. Wang and J. Li, “Microporous metal–organic frameworks for adsorptive separation of C5–C6 alkane isomers,” *Acc. Chem. Res.* **52**(7), 1968–1978 (2019).
32. J.-D. Xiao and H.-L. Jiang, “Metal–organic frameworks for photocatalysis and photothermal catalysis,” *Acc. Chem. Res.* **52**(2), 356–366 (2019).
33. L. Feng et al., “Metal–organic frameworks based on group 3 and 4 metals,” *Adv. Mater.* **32**(44), 2004414 (2020).
34. C. Cong and H. Ma, “Photonic metal–organic frameworks,” *Adv. Opt. Mater.* **9**(19), 2100733 (2021).
35. W. Cao et al., “Energy transfer in metal–organic frameworks and its applications,” *Small Struct.* **5**(3), 2000019 (2020).
36. H.-Q. Zheng et al., “Precise design and deliberate tuning of turn-on fluorescence in tetraphenylpyrazine-based metal–organic frameworks,” *Research* **2022**, 9869510 (2022).
37. Z. Jiang et al., “Enhanced luminescence in multivariate metal–organic frameworks through an isolated-ligand strategy,” *J. Mater. Chem. C* **10**(29), 10473–10479 (2022).
38. H.-Q. Zheng et al., “Boosting the photoreduction activity of Cr(VI) in metal–organic frameworks by photosensitizer incorporation and framework ionization,” *J. Mater. Chem. A* **8**(33), 17219–17228 (2020).
39. D. Zhao et al., “Recent progress on porous MOFs for process-efficient hydrocarbon separation, luminescent sensing, and information encryption,” *Chem. Commun.* **58**(6), 747–770 (2022).
40. Y. Tang et al., “Luminescent metal–organic frameworks for white LEDs,” *Adv. Opt. Mater.* **9**(23), 2001817 (2020).
41. Y. Jiao et al., “Photoresponse within dye-incorporated metal–organic architectures,” *Coord. Chem. Rev.* **430**, 213648 (2021).
42. Z. Zhou et al., “Stimuli-responsive metal–organic framework nanoparticles for controlled drug delivery and medical applications,” *Chem. Soc. Rev.* **50**(7), 4541–4563 (2021).
43. R. Medishetty et al., “Nonlinear optical properties, upconversion and lasing in metal–organic frameworks,” *Chem. Soc. Rev.* **46**(16), 4976–5004 (2017).
44. J. Dong et al., “Stimuli-responsive metal–organic frameworks enabled by intrinsic molecular motion,” *Nat. Mater.* **21**, 1334–1340 (2022).
45. H. He et al., “MOF-based organic microlasers,” *Adv. Opt. Mater.* **7**(17), 1900077 (2019).
46. G. A. Leith et al., “Confinement-guided photophysics in MOFs, COFs, and cages,” *Chem. Soc. Rev.* **50**(7), 4382–4410 (2021).
47. A. J. McConnell et al., “Stimuli-responsive metal–ligand assemblies,” *Chem. Rev.* **115**(15), 7729–7793 (2015).
48. Q. Guan et al., “Stimuli responsive metal organic framework materials towards advanced smart application,” *Mater. Today* **64**, 138–164 (2023).
49. Q. Qi et al., “Force-induced near-infrared chromism of mechanophore-linked polymers,” *J. Am. Chem. Soc.* **143**(42), 17337–17343 (2021).
50. Z. Li et al., “Photoresponsive luminescent polymeric hydrogels for reversible information encryption and decryption,” *Adv. Sci.* **6**(21), 1901529 (2019).
51. Z. Li et al., “Photoresponsive supramolecular coordination polyelectrolyte as smart anticounterfeiting inks,” *Nat. Commun.* **12**(1), 1363 (2021).
52. K. Zheng et al., “Rewritable optical memory through high-registry orthogonal upconversion,” *Adv. Mater.* **30**(30), 1801726 (2018).
53. Z. Chu et al., “Supramolecular control of azobenzene switching on nanoparticles,” *J. Am. Chem. Soc.* **141**(5), 1949–1960 (2018).
54. M. Sawczyk and R. Klajn, “Out-of-equilibrium aggregates and coatings during seeded growth of metallic nanoparticles,” *J. Am. Chem. Soc.* **139**(49), 17973–17978 (2017).

55. J.-C. Boyer et al., “Two-way photoswitching using one type of near-infrared light, upconverting nanoparticles, and changing only the light intensity,” *J. Am. Chem. Soc.* **132**(44), 15766–15772 (2010).
56. L. Zhu et al., “Light-controlled molecular switches modulate nanocrystal fluorescence,” *J. Am. Chem. Soc.* **127**(25), 8968–8970 (2005).
57. J. Lai et al., “An upconversion nanoparticle with orthogonal emissions using dual NIR excitations for controlled two-way photoswitching,” *Angew. Chem. Int. Ed.* **53**(52), 14419–14423 (2014).
58. L. Hou et al., “Reversible photochemical control of singlet oxygen generation using diarylethene photochromic switches,” *J. Am. Chem. Soc.* **136**(3), 910–913 (2014).
59. D. E. Williams et al., “Energy transfer on demand: photoswitch-directed behavior of metal–porphyrin frameworks,” *J. Am. Chem. Soc.* **136**(34), 11886–11889 (2014).
60. L. Heinke and C. Wöll, “Surface-mounted metal–organic frameworks: crystalline and porous molecular assemblies for fundamental insights and advanced applications,” *Adv. Mater.* **31**(26), 1806324 (2019).
61. N. Yanai et al., “Guest-to-host transmission of structural changes for stimuli-responsive adsorption property,” *J. Am. Chem. Soc.* **134**(10), 4501–4504 (2012).
62. H. Sato et al., “Photochemically crushable and regenerative metal–organic framework,” *J. Am. Chem. Soc.* **142**(33), 14069–14073 (2020).
63. D. E. Williams et al., “Flipping the switch: fast photoisomerization in a confined environment,” *J. Am. Chem. Soc.* **140**(24), 7611–7622 (2018).
64. X. Meng et al., “Mechanized azobenzene-functionalized zirconium metal–organic framework for on-command cargo release,” *Sci. Adv.* **2**(8), e1600480 (2016).
65. J. Park et al., “Reversible alteration of CO₂ adsorption upon photochemical or thermal treatment in a metal–organic framework,” *J. Am. Chem. Soc.* **134**(1), 99–102 (2012).
66. Y. Zheng et al., “Flexible interlocked porous frameworks allow quantitative photoisomerization in a crystalline solid,” *Nat. Commun.* **8**, 100 (2017).
67. F. Bigdeli et al., “Switching in metal–organic frameworks,” *Angew. Chem. Int. Ed.* **59**(12), 4652–4669 (2020).
68. Y. X. Li et al., “Reversible light-controlled CO adsorption via tuning π -complexation of Cu⁺ sites in azobenzene-decorated metal–organic frameworks,” *Angew. Chem. Int. Ed.* **61**(46), e202212732 (2022).
69. Z. Wang et al., “Tunable molecular separation by nanoporous membranes,” *Nat. Commun.* **7**(1), 13872 (2016).
70. F. Luo et al., “Photoswitching CO₂ capture and release in a photochromic diarylethene metal–organic framework,” *Angew. Chem. Int. Ed.* **126**(35), 9452–9455 (2014).
71. C. B. Fan et al., “Significant enhancement of C₂H₂/C₂H₄ separation by a photochromic diarylethene unit: a temperature- and light-responsive separation switch,” *Angew. Chem. Int. Ed.* **56**(27), 7900–7906 (2017).
72. Y. Jiang et al., “Maximizing photoresponsive efficiency by isolating metal–organic polyhedra into confined nanoscaled spaces,” *J. Am. Chem. Soc.* **141**(20), 8221–8227 (2019).
73. Y. Jiang et al., “Process-oriented smart adsorbents: tailoring the properties dynamically as demanded by adsorption/desorption,” *Acc. Chem. Res.* **55**(1), 75–86 (2022).
74. Y. Jiang et al., “Nanoporous films with oriented arrays of molecular motors for photoswitching the guest adsorption and diffusion,” *Angew. Chem. Int. Ed.* **62**(3), e202214202 (2022).
75. L. Heinke et al., “Photoswitching in two-component surface-mounted metal–organic frameworks: optically triggered release from a molecular container,” *ACS Nano* **8**(2), 1463–1467 (2014).
76. B. J. Furlong and M. J. Katz, “Bistable dithienylethene-based metal–organic framework illustrating optically induced changes in chemical separations,” *J. Am. Chem. Soc.* **139**(38), 13280–13283 (2017).
77. A. B. Kanj et al., “Proton-conduction photomodulation in spiro-pyran-functionalized MOFs with large on–off ratio,” *Chem. Sci.* **11**(5), 1404–1410 (2020).
78. K. Müller et al., “Switching the proton conduction in nanoporous, crystalline materials by light,” *Adv. Mater.* **30**(8), 1706551 (2018).
79. E. A. Dolgoplova et al., “Connecting wires: photoinduced electronic structure modulation in metal–organic frameworks,” *J. Am. Chem. Soc.* **141**(13), 5350–5358 (2019).
80. C. R. Martin et al., “Heterometallic actinide-containing photoresponsive metal–organic frameworks: dynamic and static tuning of electronic properties,” *Angew. Chem. Int. Ed.* **133**(15), 8152–8160 (2021).
81. C. R. Martin et al., “Stimuli-modulated metal oxidation states in photochromic MOFs,” *J. Am. Chem. Soc.* **144**(10), 4457–4468 (2022).
82. J. W. Brown et al., “Photophysical pore control in an azobenzene-containing metal–organic framework,” *Chem. Sci.* **4**(7), 2858–2864 (2013).
83. J. Park et al., “Photochromic metal–organic frameworks: reversible control of singlet oxygen generation,” *Angew. Chem. Int. Ed.* **54**(2), 430–435 (2015).
84. J. Park et al., “Controlled generation of singlet oxygen in living cells with tunable ratios of the photochromic switch in metal–organic frameworks,” *Angew. Chem. Int. Ed.* **55**(25), 7188–7193 (2016).
85. T. Zhao et al., “New perspectives to trigger and modulate circularly polarized luminescence of complex and aggregated systems: energy transfer, photon upconversion, charge transfer, and organic radical,” *Acc. Chem. Res.* **53**(7), 1279–1292 (2020).
86. A. B. Kanj et al., “Chirality remote control in nanoporous materials by circularly polarized light,” *J. Am. Chem. Soc.* **143**(18), 7059–7068 (2021).
87. R. Ou et al., “Photoresponsive styrylpyrene-modified MOFs for gated loading and release of cargo molecules,” *Chem. Mater.* **32**(24), 10621–10627 (2020).
88. Q.-H. Guo et al., “Single-crystal polycationic polymers obtained by single-crystal-to-single-crystal photopolymerization,” *J. Am. Chem. Soc.* **142**(13), 6180–6187 (2020).
89. Z.-Y. Yang et al., “Photopolymerization-driven macroscopic mechanical motions of a composite film containing a vinyl coordination polymer,” *Angew. Chem. Int. Ed.* **62**(20), e202302429 (2023).
90. N. Li et al., “Erasable photopatterning of stilbene-based metal–organic framework films,” *Small Methods* **7**, e2201231 (2023).
91. M. Nakagawa et al., “Beyond the conventional limitation of photocycloaddition reaction in the roomy nanospace of a metal–organic framework,” *J. Am. Chem. Soc.* **145**(22), 12059–12065 (2023).
92. H. Zhou et al., “Responsive luminescent MOF materials for advanced anticounterfeiting,” *Chem. Eng. J.* **431**, 134170 (2021).
93. J. Liu et al., “Achieving multicolor long-lived luminescence in dye-encapsulated metal–organic frameworks and its application to anticounterfeiting stamps,” *ACS Appl. Mater. Interfaces* **10**(2), 1802–1809 (2018).
94. J. Yu et al., “Two-photon responsive metal organic framework,” *J. Am. Chem. Soc.* **137**(12), 4026–4029 (2015).
95. N. K. Kulachenkov et al., “Photochromic free MOF-based near-infrared optical switch,” *Angew. Chem. Int. Ed.* **59**(36), 15522–15526 (2020).
96. G. C. Thaggard et al., “Metal–photoswitch friendship: from photochromic complexes to functional materials,” *J. Am. Chem. Soc.* **144**(51), 23249–23263 (2022).
97. A. B. Grommet et al., “Chemical reactivity under nanoconfinement,” *Nat. Nanotechnol.* **15**(4), 256–271 (2020).

98. T. Haneda et al., “Thermo-to-photo-switching of the chromic behavior of salicylideneanilines by inclusion in a porous coordination network,” *Angew. Chem. Int. Ed.* **46**(35), 6643–6645 (2007).
99. D. Mutruc et al., “Modulating guest uptake in core–shell MOFs with visible light,” *Angew. Chem. Int. Ed.* **58**(37), 12862–12867 (2019).
100. A. Knebel et al., “Azobenzene guest molecules as light-switchable CO₂ valves in an ultrathin UiO-67 membrane,” *Chem. Mater.* **29**(7), 3111–3117 (2017).
101. T. Qian et al., “Efficient gating of ion transport in three-dimensional metal–organic framework sub-nanochannels with confined light-responsive azobenzene molecules,” *Angew. Chem. Int. Ed.* **132**(31), 13151–13156 (2020).
102. R. Ou et al., “A sunlight-responsive metal–organic framework system for sustainable water desalination,” *Nat. Sustain.* **3**(12), 1052–1058 (2020).
103. H.-Q. Liang et al., “A light-responsive metal–organic framework hybrid membrane with high on/off photoswitchable proton conductivity,” *Angew. Chem. Int. Ed.* **59**(20), 7732–7737 (2020).
104. K. P. Xie et al., “Guest-driven light-induced spin change in an azobenzene loaded metal–organic framework,” *Angew. Chem. Int. Ed.* **60**(52), 27144–27150 (2021).
105. S. Garg et al., “Conductance photoswitching of metal–organic frameworks with embedded spiropyran,” *Angew. Chem. Int. Ed.* **58**(4), 1193–1197 (2019).
106. Y. Yang et al., “Electroactive covalent organic framework enabling photostimulus-responsive devices,” *J. Am. Chem. Soc.* **144**(35), 16093–16100 (2022).
107. G. C. Thaggard et al., “Traffic lights for catalysis: stimuli-responsive molecular and extended catalytic systems,” *Angew. Chem. Int. Ed.* **62**(29), e202302859 (2023).
108. F. Zhang et al., “Microwave-assisted crystallization inclusion of spiropyran molecules in indium trimesate films with antidromic reversible photochromism,” *J. Mater. Chem.* **22**(48), 25019–25026 (2012).
109. I. M. Walton et al., “Photo-responsive MOFs: light-induced switching of porous single crystals containing a photochromic diarylethene,” *Chem. Commun.* **49**(73), 8012–8014 (2013).
110. P. K. Kundu et al., “Nanoporous frameworks exhibiting multiple stimuli responsiveness,” *Nat. Commun.* **5**(1), 3588 (2014).
111. H. A. Schwartz et al., “Solution-like behavior of photoswitchable spiropyran embedded in metal–organic frameworks,” *Inorg. Chem.* **56**(21), 13100–13110 (2017).
112. M. Tu et al., “Reversible optical writing and data storage in an anthracene-loaded metal–organic framework,” *Angew. Chem. Int. Ed.* **58**(8), 2423–2427 (2019).
113. Y. Wang et al., “Application in anticounterfeiting for multistimuli smart luminescent materials based on MOF-on-MOF,” *Inorg. Chem.* **60**(19), 15001–15009 (2021).
114. Z. Li et al., “Loading photochromic molecules into a luminescent metal–organic framework for information anticounterfeiting,” *Angew. Chem. Int. Ed.* **58**(50), 18025–18031 (2019).
115. T. Zhao et al., “Multi-light-responsive upconversion-and-downshifting-based circularly polarized luminescent switches in chiral metal–organic frameworks,” *Adv. Mater.* **33**(33), 2101797 (2021).
116. H.-Q. Zheng et al., “Photo-stimuli-responsive dual-emitting luminescence of spiropyran-encapsulated metal–organic framework for dynamic information encryption,” *Adv. Mater.* **35**(26), 2300177 (2023).
117. H.-Y. Li et al., “Functional metal–organic frameworks as effective sensors of gases and volatile compounds,” *Chem. Soc. Rev.* **49**(17), 6364–6401 (2020).
118. N. Yanai et al., “Gas detection by structural variations of fluorescent guest molecules in a flexible porous coordination polymer,” *Nat. Mater.* **10**(10), 787–793 (2011).
119. P. Serra-Crespo et al., “NH₂-MIL-53(Al): a high-contrast reversible solid-state nonlinear optical switch,” *J. Am. Chem. Soc.* **134**(20), 8314–8317 (2012).
120. P. She et al., “Recent progress in external-stimulus-responsive 2D covalent organic frameworks,” *Adv. Mater.* **34**(22), 2101175 (2022).
121. Q. Zhang et al., “Piezofluorochromic metal–organic framework: a microscissor lift,” *J. Am. Chem. Soc.* **137**(32), 10064–10067 (2015).
122. C.-X. Chen et al., “Visualization of anisotropic and stepwise piezofluorochromism in an MOF single crystal,” *Chem* **4**(11), 2658–2669 (2018).
123. C.-X. Chen et al., “Pressure-induced multiphoton excited fluorochromic metal–organic frameworks for improving MPEF properties,” *Angew. Chem. Int. Ed.* **58**(40), 14379–14385 (2019).
124. C.-X. Chen et al., “All roads lead to Rome: tuning the luminescence of a breathing catenated Zr-MOF by programmable multiplexing pathways,” *Chem. Mater.* **31**(15), 5550–5557 (2019).
125. X. Guo et al., “Stimuli-responsive luminescent properties of tetraphenylethene-based strontium and cobalt metal–organic frameworks,” *Angew. Chem. Int. Ed.* **59**(44), 19716–19721 (2020).
126. Y. Wang et al., “Maximized green photoluminescence in Tb-based metal–organic framework via pressure-treated engineering,” *Angew. Chem. Int. Ed.* **61**(48), e202210836 (2022).
127. T. Zhang et al., “Brightening blue photoluminescence in non-emission MOF-2 by pressure treatment engineering,” *Adv. Mater.* **35**, 2211729 (2023).
128. Y. Wang et al., “Pressure engineering toward harvesting the bright deep-blue-light emission in Y-based metal–organic frameworks,” *Adv. Funct. Mater.* **33**, 2300109 (2023).
129. A. Sussardi et al., “Correlating pressure-induced emission modulation with linker rotation in a photoluminescent MOF,” *Angew. Chem. Int. Ed.* **132**(21), 8195–8199 (2020).
130. D. M. Jameson and J. A. Ross, “Fluorescence polarization/anisotropy in diagnostics and imaging,” *Chem. Rev.* **110**(5), 2685–2708 (2010).
131. G. S. He et al., “Multiphoton absorbing materials: molecular designs, characterizations, and applications,” *Chem. Rev.* **108**(4), 1245–1330 (2008).
132. E. E. Hoover and J. A. Squier, “Advances in multiphoton microscopy technology,” *Nat. Photonics* **7**(2), 93–101 (2013).
133. L. Guo and M. S. Wong, “Multiphoton excited fluorescent materials for frequency upconversion emission and fluorescent probes,” *Adv. Mater.* **26**(31), 5400–5428 (2014).
134. M. Pawlicki et al., “Two-photon absorption and the design of two-photon dyes,” *Angew. Chem. Int. Ed.* **48**(18), 3244–3266 (2009).
135. H. He et al., “Polarized three-photon-pumped laser in a single MOF microcrystal,” *Nat. Commun.* **7**, 11087 (2016).
136. H. Li et al., “Tunable nonlinear optical responses based on host-guest MOF hybrid materials,” *Sci. China. Mater.* **64**(3), 698–705 (2021).
137. L. Zhang et al., “Aligned chromophores in a host-guest MOF crystal for switchable polarized nonlinear optical response,” *J. Mater. Chem. C* **10**(40), 14915–14920 (2022).
138. H. He et al., “Controllable broadband multicolour single-mode polarized laser in a dye-assembled homoepitaxial MOF microcrystal,” *Light-Sci. Appl.* **9**(1), 138 (2020).
139. H. Li et al., “Switchable two-photon pumped polarized lasing performance in composition-graded MOFs based heterostructures,” *Adv. Opt. Mater.* **8**(23), 2001089 (2020).
140. L. Zhang et al., “Tunable NIR lasing in MOF for multi-level complex photonic barcodes,” *Adv. Opt. Mater.* **11**(6), 2202714 (2023).
141. H. Li et al., “Polarized laser switching with giant contrast in MOF-based mixed-matrix membrane,” *Adv. Sci.* **9**(17), 2200953 (2022).

142. Q. Wen et al., “Chiral and SHG-active metal–organic frameworks formed in solution and on surfaces: uniformity, morphology control, oriented growth, and postassembly functionalization,” *J. Am. Chem. Soc.* **142**(33), 14210–14221 (2020).
143. Q. Wen et al., “Energy transport in dichroic metallo-organic crystals: selective inclusion of spatially resolved arrays of donor and acceptor dyes in different nanochannels,” *Angew. Chem. Int. Ed.* **62**(4), e202214041 (2023).
144. H. S. Quah et al., “Multiphoton harvesting metal–organic frameworks,” *Nat. Commun.* **6**(1), 7954 (2015).
145. D. C. Mayer et al., “Controlling multiphoton absorption efficiency by chromophore packing in metal–organic frameworks,” *J. Am. Chem. Soc.* **141**(29), 11594–11602 (2019).
146. L. Zhang et al., “Structural variation and switchable nonlinear optical behavior of metal-organic frameworks,” *Small* **17**(6), 2006649 (2021).
147. Z. Chen et al., “Giant enhancement of second harmonic generation accompanied by the structural transformation of 7-fold to 8-fold interpenetrated metal–organic frameworks (MOFs),” *Angew. Chem. Int. Ed.* **59**(2), 833–838 (2020).
148. D. Kottlilil et al., “Multiphoton-pumped highly polarized polariton microlasers from single crystals of a dye-coordinated metal–organic framework,” *Adv. Funct. Mater.* **30**(32), 2003294 (2020).
149. D. Kottlilil et al., “Triple threshold transitions and strong polariton interaction in 2D layered metal–organic framework microplates,” *Adv. Mater.* **35**(13), 2209094 (2023).
150. N. Liu et al., “Highly efficient multiphoton absorption of zinc-AIEgen metal-organic frameworks,” *Angew. Chem. Int. Ed.* **61**(12), e202115205 (2022).
151. H. Wang et al., “Metal–organic framework with color-switching and strongly polarized emission,” *Chem. Mater.* **31**(15), 5816–5823 (2019).
152. X. Yang et al., “Lanthanide metal–organic framework microrods: colored optical waveguides and chiral polarized emission,” *Angew. Chem. Int. Ed.* **56**(27), 7853–7857 (2017).
153. K. Pei et al., “Polarized emission of lanthanide metal–organic framework (Ln-MOF) crystals for high-capacity photonic barcodes,” *Adv. Opt. Mater.* **10**(3), 2102143 (2022).

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