



A fast responsive photochromic SCC-MOF for photoswitching and information encryption

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ABSTRACT Constructing novel photoswitch silver-chalcogenolate cluster-based metal-organic frameworks (SCC-MOFs) presents a considerable challenge owing to their instability and limited stimulation-responsive properties. Herein, a novel photochromic SCC-MOF (Ag₁₂-BMPTC) was designed and synthesized using a diarylethene ligand and an SCC. Ag₁₂-BMPTC exhibits superior reversible photo-responsive characteristics under light irradiation (365 and 500 nm). This photoswitching behavior enables its potential applications in information encryption and chirality switches, making it as the first example of such capabilities in photochromic SCC-MOFs. This study not only expands the range of SCC-MOFs but also proposes a new strategy for designing and synthesizing novel photochromic materials.

Keywords: silver nanoclusters, metal-organic frameworks, photochromism, diarylethene, information encryption

INTRODUCTION

Silver nanoclusters have attracted extensive attention owing to their unique optical and luminescence properties [1–5]. However, their inherent instability has hindered extensive research on their potential applications. The stability and photophysical properties of metal clusters strongly depend on their metal cores, peripheral ligands, and chemical environment [6–8]. Therefore, enhancing the stability of metallic clusters and improving their optical properties can be effectively achieved by regulating peripheral ligands, utilizing mixed ligands, or using the ligand exchange method [9,10]. In this context, silver-chalcogenolate cluster-based metal-organic frameworks (SCC-MOFs) that are extended into networks using organic linkers have been developed to overcome the instability of silver clusters and expand their applications [11–15]. Recently, SCC-MOFs have emerged as a burgeoning class of porous materials and have attracted considerable research interest for applications in sensing, catalysis, photoswitching, and chirality [11–16]. In 2017, Zang's group [14] reported that substituting solvent molecules on the surface of the silver cluster through ligand engineering facilitates the formation of a stabilized SCC-MOF with improved emission properties. Importantly, the open

channel of SCC-MOF provides a stimuli response platform for O₂ and volatile organic compounds (VOCs), which enables applications in multi-color fluorescence switches; the switching mechanism was determined using single-crystal X-ray diffraction (SCXRD) analysis of the crystal structure. Subsequently, in 2019, Zang's group [15] reported a dual-node three-dimensional (3D) SCC-MOF based on an aggregation-induced emission ligand, exhibiting a unique ratiometric luminescence switch due to the absorption/desorption of guest molecules. The switching rate can be adjusted using different guest molecules. However, to date, reports on photoresponsive SCC-MOFs remain limited.

Under light exposure, photochromic molecules undergo a reversible shift, revealing distinct variances in the physical and chemical attributes of their isomers. These molecules have widespread applications as photoswitching function motifs in smart materials [17–26]. Dithienylethene derivatives can be converted into open or closed forms upon exposure to visible or ultraviolet (UV) light. They exhibit excellent rapid response, thermal stability, and fatigue resistance, making them one of the most promising photoswitching materials [27–29]. Researchers have achieved excellent reversible photoresponsive behaviors by incorporating dithienylethene derivatives in MOF systems [24–26]. To the best of our knowledge, SCC-MOFs modified with dithienylethene ligand as photoswitch materials and for potential information encryption applications have not been reported to date. Hence, the rational design and preparation of such photoswitch materials remain challenging.

In this study, a novel SCC-MOF (Ag₁₂-BMPTC) was obtained by employing a photochromic diarylethene ligand 1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene (BMPTC) and an SCC Ag₁₂[(S^tBu)₆(CF₃COO)₆(CH₃CN)₆] (Ag₁₂) using the ligand-exchange method. Ag₁₂-BMPTC exhibits reversible and ultrafast 365/500 nm-induced photochromic and photoresponsive properties and information encryption with noticeable color change. Thus, it has potential as a reversible photochromic smart/chiral material. More importantly, upon 365-nm light irradiation, the photoresponse time of Ag₁₂-BMPTC is only 0.1 s, and the photochromic mechanism can be ascribed to the photoisomerization and the spatial separation as well as the rigid framework of BMPTC. This study enriches SCC-MOF varieties and provides a new strategy for designing

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and synthesizing novel photochromic materials.

EXPERIMENTAL SECTION

Materials and reagents

All reagents and solvents, AgNO_3 , AgS^tBu , toluene, acetonitrile (CH_3CN), and ethanol (EtOH), are commercially available and can be used without further purification.

Synthesis of BMPTC

BMPTC was synthesized according to a literature method involving a photochromic ligand with coordination immobilization [27–29]. Briefly, the target product was obtained using a Suzuki coupling reaction of 1,2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene and 4-bromopyridine hydrochloride in the presence of *n*-BuLi, $\text{B}(\text{O}i\text{Bu})_3$, $\text{Pd}(\text{PPh}_3)_4$ and K_2CO_3 (Fig. 1a). The structure of BMPTC was confirmed using ^1H and ^{13}C nuclear magnetic resonance (NMR) (Figs S1 and S2).

^1H NMR (600 MHz, CDCl_3) δ 8.53 (dd, $J = 4.7, 1.4$ Hz, 1H), 7.34 (dd, $J = 4.7, 1.5$ Hz, 1H), 7.22 (s, 1H), 2.85 (t, $J = 7.5$ Hz, 1H), 2.15–2.08 (m, 1H), 2.02 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.24, 141.33, 137.31, 137.09, 136.68, 134.83, 126.30, 119.27, 38.47, 23.00, 14.64.

Synthesis of an Ag_{12} -BMPTC MOF

AgNO_3 (160 mg) and AgS^tBu (200 mg) were added to a mixed solution of CH_3CN (30 mL) and toluene (30 mL), respectively, fully dissolved and divided into 12 vials. After 4–5 days of volatilization, colorless bulk crystals appeared at the bottom. The crystals were filtered and added into a mixture of CH_3CN (2 mL) and toluene (2 mL) with BMPTC (8 mg). After 3–4 days of evaporation, dark hexagonal crystals appeared at the bottom (yield: 78.5% based on Ag). Elemental analysis: according to formula $\text{Ag}_{12}\text{C}_{186}\text{O}_{12}\text{N}_{12}\text{S}_{18}\text{F}_{18}\text{H}_{186}$, the calculated value (%): C 44.72; N 3.36; S 11.56; H 3.75. Experimental values (%): C 44.53; N 3.45; S 11.92; H 3.59.

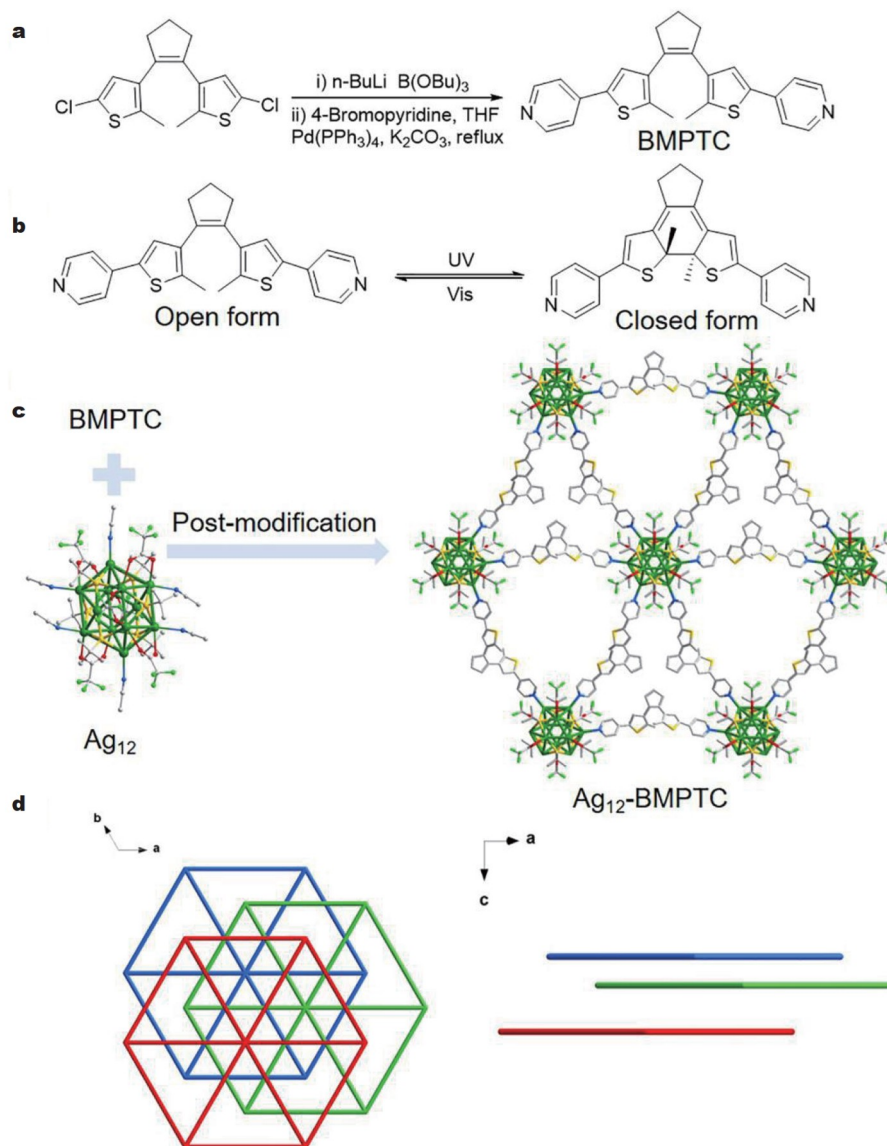


Figure 1 (a) Synthesis of the photochromic linker BMPTC. (b) Photoisomerization of BMPTC under UV and visible light. (c) Synthesis of Ag_{12} -BMPTC. (d) Topological structure of Ag_{12} -BMPTC.

Preparation of the photochromic patterns

A fine powder crystal of Ag_{12} -BMPTC was printed on filter paper by covering a stencil and using a high-speed camera (1000 fps) to capture the color change during continuous UV-lamp irradiation for 5 s. Alternatively, the crystal was removed after 60 s under UV-light irradiation, resulting in a distinct Chinese knot pattern printed in purple.

A composite of fine powder crystal Ag_{12} -BMPTC and vacuum grease was created using a wet-chemical process method. A school text, badge, and trees were printed using the Ag_{12} -BMPTC/vacuum grease mixture and vacuum grease as confusion labels. These patterns were irradiated under a 365-nm UV lamp for 1 min, and the color transitioned from white to dark purple. After 30 min irradiation with 500-nm light, the dark-purple patterns returned to their original color.

Characterization

SCXRD data were collected using a Bruker APEX-II CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 200 K. The structure was assessed with direct methods (SHELXS) and refined using full-matrix least squares in F^2 using the OLEX2, which utilizes the SHELXL-2015 module. The DIAMOND 3.2 software was used to visualize the crystal structure. The powder XRD (PXRD) patterns of the samples were obtained using a D/Max-3D diffractometer (Cu K α , $\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were obtained and analyzed using an ALPHA II spectrometer. Photochromic ligands change before and after UV irradiation. Thermal gravimetric analysis (TGA) was performed using a TANETZSCH STA 2500 thermal analyzer from room temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere (flow rate of 60 mL min^{-2}). A camera was used to capture the color transition. Solid-state UV-vis diffuse-reflectance spectra were recorded using a Hitachi UH4150 UV-vis spectrophotometer. The 365-nm UV lamp (8.3 mW cm^{-2}) and 500-nm lamp (3.5 mW cm^{-2}) were used.

RESULTS AND DISCUSSION

Characterization of the photochromic linker and framework

Diarylethenes containing heterocyclic rings with low aromatic stabilization energy, such as pyridine rings, have delocalized π -electrons and readily undergo thermally irreversible photochromic reactions [30–32]. A photochromic linker with a diarylethene core was facilely synthesized (see Supplementary information, Figs S1 and S2). This specific linker was chosen owing to its excellent fatigue-resistant photochromic performance, thermal stability, and rapid response in the solid state (Fig. 1a, b). Moreover, the photochromic linker plays a pivotal role in the coordinative fixation within SCC-MOF scaffolds. Specifically, the pyridine nitrogen of the photochromic linker was coordinated with Ag_{12} clusters using a postmodification approach. Initially, room-temperature volatilization of CF_3COOAg and AgS^tBu in a mixed solution of CH_3CN -PhMe yielded colorless block-like crystals identified as $\text{Ag}_{12}(\text{S}^t\text{Bu})_6(\text{CF}_3\text{COO})_6(\text{CH}_3\text{CN})_6$, hereafter abbreviated as Ag_{12} cluster [13–15]. This structure represents a triclinic crystal system characterized by the $P1$ space group. The intrinsic structure of each Ag_{12} cluster encompasses an $\text{Ag}_{12}\text{S}_6^{6-}$ core characterized by six Ag(I) vertices. These vertices bear six CF_3COO^- and six CH_3CN molecules that can be substituted with a bridging N-linker to

produce an SCC-framework structure. Second, given the inherent versatility of assembling stimuli-responsive MOFs, the bidentate photochromic ligand BMPTC completely replaced the six CH_3CN molecules on the Ag_{12} cluster. This was achieved using a ligand-exchange strategy to afford a high-yield Ag_{12} -BMPTC framework with mauve block crystals (Fig. 1c). The transformation of cluster nodes produced quasi-isomers of Ag_{12} , a consequence of introducing the BMPTC linker (Fig. S3) [14]. SCXRD analysis revealed that Ag_{12} -BMPTC conforms to the trigonal crystal system, characterized by the $R3/m$ space group (Table S1). Each empty cuboctahedron Ag_{12} core was stabilized by Ag(I)–Ag(I) argentophilic and Ag(I)–S interactions. The Ag...Ag distances are 3.067 and 3.248 Å , and the Ag...S bond lengths ranged from 2.470 to 2.536 Å . These metrics present a more uniform profile than the bond length of Ag_{12} (Fig. S3). Moreover, six auxiliary CF_3COO^- ligands were bound to each Ag atom in the top and bottom triangular facets. One Ag_{12} cluster is linked to six other Ag_{12} clusters through Ag–N bonds by BMPTC linkers, giving rise to a highly ordered 2D network (Ag_{12} -BMPTC: CCDC 2290319). This network adopts an ABCABCABC... inclined parallel stacking pattern, in which the distance of separated BMPTC is 4.32 and 11.54 Å along the c axis (Fig. 1d). The PXRD analysis of the bulk crystal powders reveals identical features to the simulated pattern from SCXRD, confirming the excellent phase purity of the as-synthesized samples (Fig. S4). The TGA results suggest the robust stability of the Ag_{12} -BMPTC network, enduring temperatures up to approximately 130°C (Fig. S5).

Photophysical properties of the photochromic Ag_{12} -BMPTC framework

The photoswitching characteristics of diarylethene molecules are easily identified because of their facile structural transformation during photoisomerization. BMPTC exhibits two photoisomeric forms: open (colorless) and closed (colored). Upon irradiation of the open form with UV light (365 nm), a closed form between two heterocyclic thiophene groups was obtained. Notably, the BMPTC photoswitching is quite stable in both forms. This stability is mainly attributed to the “arm” of BMPTC, which exhibits relatively small changes in the same plane during isomerization and does not undergo drastic structural changes, especially in the solid state. Consequently, integrating into the SCC-MOF framework facilitates enhanced tunability and a multifaceted stimulus-responsive nature. As depicted in Fig. 2, we studied the photochromic behavior of an isolated single crystal compared with a single crystal in the Ag_{12} -BMPTC framework. Upon irradiation of the single crystal of the open form of Ag_{12} -BMPTC with UV light, dark-purple crystals were readily observed without magnification, suggesting the closure of the photochromic linker. After exposing these deep-purple crystals to visible light ($\lambda \geq 500 \text{ nm}$), the linker reverted to its open state. This is confirmed by the recovery of the mauve color, observed after approximately 30 min. The single-crystal structure of Ag_{12} -BMPTC was almost completely maintained upon alternating irradiation, thus demonstrating the excellent structural reversibility of the BMPTC linker within the framework. The PXRD and infrared spectroscopy revealed that the structural profiles of the open and closed forms remained almost unchanged, underscoring the maintained structural integrity of the framework (Figs S6 and S7). However, XRD analysis reveals that the dark-purple crystal structure displays a disordered form of the

BMPTC linker. This observation suggests that UV light may have limited penetration depth, thus only impacting the surface-level photochromic behavior of the crystal.

As with many diarylethene derivatives, the solid-state form of Ag_{12} -BMPTC MOF exhibits rapid photochromic properties at room temperature. Fig. 3a shows that the color shifts from milky white to deep purple within only 1.5 s under irradiation with a 365-nm UV lamp, which is noteworthy compared with other photochromic MOFs (Table S2). Remarkably, an ultrafast and distinct photochromic response was observed within an astonishingly short timeframe of 0.1 s, captured using a high-speed camera capable of recording 1000 frames per second. In addition, we measured the photochromic properties of Ag_{12} -BMPTC

MOFs using solid diffuse-reflectance spectroscopy (Fig. 3c). Before irradiation, the main absorption peak appeared at approximately 310 nm. In contrast, after 365-nm light irradiation, a new absorption peak appeared at approximately 588 nm. With prolonged illumination time, the absorption intensity at 588 nm gradually increased, while the intensity at 310 nm decreased, marked by the gradual deepening of the color of Ag_{12} -BMPTC.

Interestingly, the photochromic dark-purple sample of Ag_{12} -BMPTC (closed form) can be reverted to an initial milky white state by visible light above 500 nm or grinding (Fig. 3b, c). Compared with the BMPTC linker, Ag_{12} -BMPTC has a faster photoresponse time (Figs S8–S10). Furthermore, we investigated

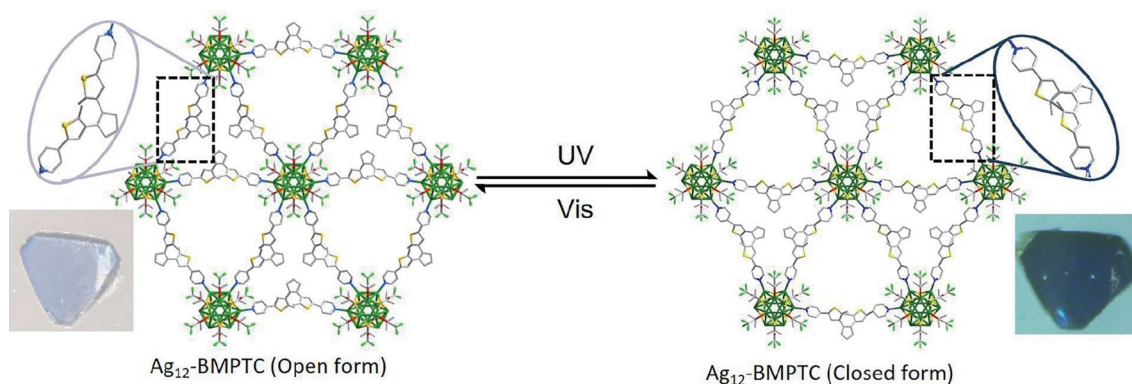


Figure 2 Illustration of the reversible photochromic behavior in the Ag_{12} -BMPTC framework. Lavender crystal (left) turns deep purple (right) upon 365-nm light irradiation and reverts back to lavender under 500-nm light irradiation.

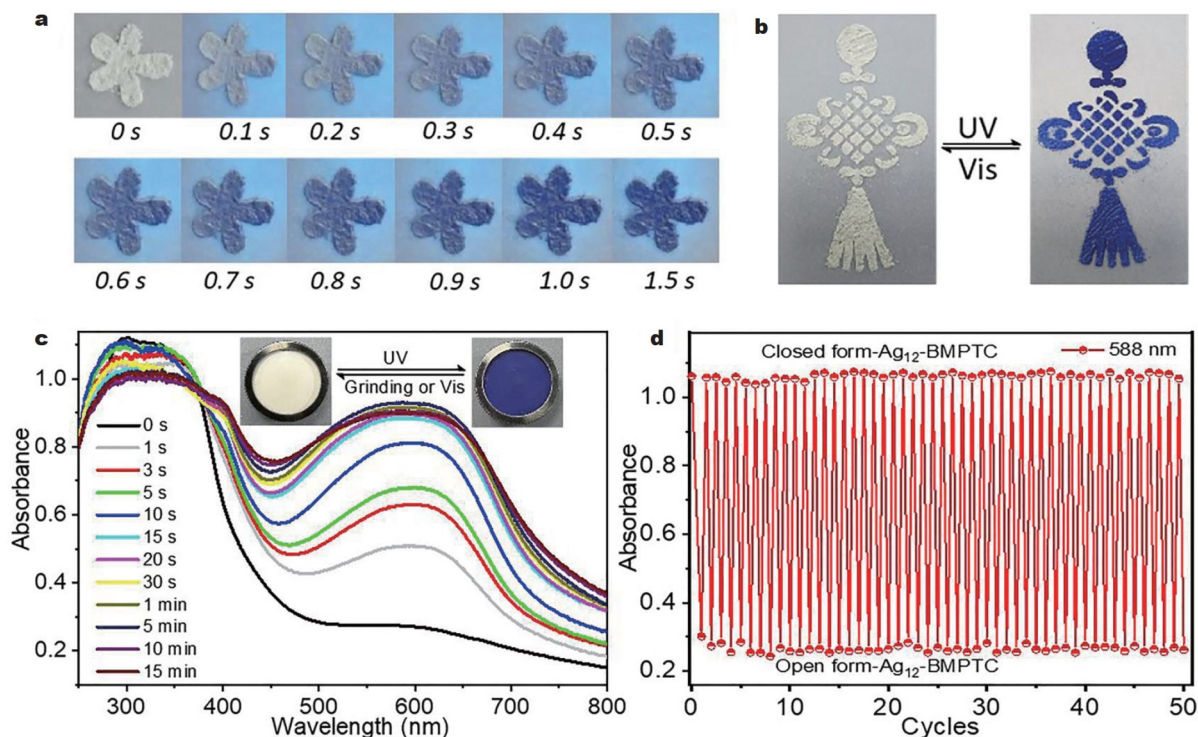


Figure 3 (a) Photographs illustrating the color change of Ag_{12} -BMPTC under continuous illumination with 365-nm UV light. (b) Photographs of the coated paper stenciled with “Chinese knot” using 365-nm UV light. (c) UV-vis diffuse-reflectance spectra of Ag_{12} -BMPTC under continuous 365-nm UV light. Inset: photographs of Ag_{12} -BMPTC before and after illumination. (d) Absorbance changes of Ag_{12} -BMPTC upon alternating 365-nm UV light and 500-nm visible light.

the fatigue resistance of Ag₁₂-BMPTC under alternating exposure to 365-nm light for 1 min and 500-nm light for 30 min. As illustrated in Fig. 3d, the photochromic properties of Ag₁₂-BMPTC remained favorable after 50 cycles upon alternating illumination, suggesting satisfactory photochromic stability. The PXRD patterns and FT-IR spectra of Ag₁₂-BMPTC exhibited no significant difference before and after irradiation (Figs S6 and S7), indicating that the illumination decolorates the sample surface but does not change the internal framework of the crystal.

We further evaluated the practical application potential of Ag₁₂-BMPTC for information security, anticounterfeiting and encryption technologies. The evaluation was based on the reversible photochromic properties of Ag₁₂-BMPTC under alternating irradiation of 365 and 500 nm (Fig. 4a). First, we prepared Ag₁₂-BMPTC/vacuum grease composites using a wet-chemical process method. Subsequently, we printed a potential information security and anticounterfeiting pattern using the Ag₁₂-BMPTC/vacuum grease mixture as the ink. A school text, badge, and trees were printed using the Ag₁₂-BMPTC/vacuum grease mixture. In addition, we selected vacuum grease as a confusion label. Fig. 4b–d show faint patterns on the printed paper, approaching milky white when viewed in daylight. Under irradiation with the 365-nm UV lamp, dark-purple patterns appeared, clearly observable with the naked eye. In particular, the landscape painting with trees, wild goose, and deer patterns stood vividly on the printed paper. After 30 min irradiation with 500-nm light, the dark-purple patterns returned to their original color. Furthermore, leveraging the advantage of photochromic functionality, we devised an encryption system based on Ag₁₂-BMPTC. For the purpose, the Ag₁₂-BMPTC/vacuum grease mixture and vacuum grease were patterned into an 8888-shaped module. They demonstrated identical optical appearance in ambient light but presented the decrypted security codes “2023”

and “1956” under 365-nm light irradiation (Fig. 4e). Additionally, a sea landscape painting was presented by modulating Ag₁₂-BMPTC photochromic behavior, containing incomplete, false, and correct information (Fig. 4f). In conclusion, the Ag₁₂-BMPTC material is a promising candidate for information security and encryption technologies and has the potential to be deployed as a reversible processable pigment.

Owing to its reversible photochromic effect, Ag₁₂-BMPTC was combined with a chiral scaffold, demonstrating potential chiral switch properties. When achiral Ag₁₂-BMPTC was introduced into the previously reported chiral medium of chiral binaphthalene di-octadecamidemethoxy (*R*- or *S*-BDA) [33] a chiral composite was obtained as a chiral film (Fig. S11). This chiral film exhibited either left-handed or right-handed chiral signals of Ag₁₂-BMPTC, respectively. We speculate that the source of the chirality of Ag₁₂-BMPTC is mainly associated with the supramolecular chirality induction facilitated by *R*- or *S*-BDA. More importantly, the chiral composite has favorable chiral fatigue resistance, indicating its potential as a chiral switch. This study is the first example of SCC-MOFs introduced into chiral media to generate chirality switches.

CONCLUSIONS

A novel 2D SCC-MOF framework (Ag₁₂-BMPTC) was constructed using a ligand-exchange strategy at room temperature. Ag₁₂-BMPTC displays reversible photochromic behavior from milky white to dark purple upon exposure to daylight, UV-light irradiation, and grinding. Intriguingly, the photoresponse time is only 0.1 s under 365-nm irradiation. The photochromic mechanism can be ascribed to the photoisomerization of the BMPTC ligand. Furthermore, Ag₁₂-BMPTC exhibits excellent reversible photoswitching properties at alternating irradiation of 365 and 500 nm. These attributes hold promise for applications in information security and anticounterfeiting and chirality

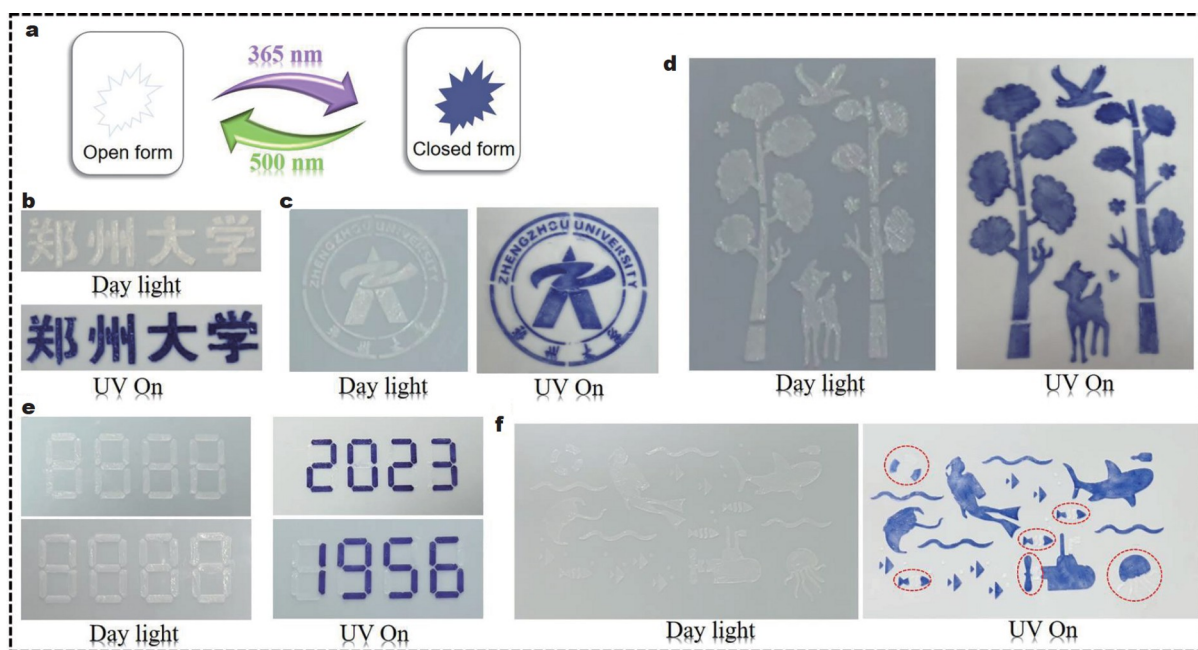


Figure 4 Application of Ag₁₂-BMPTC-coated film in a reversible reusable-display. (a) The model pattern of Ag₁₂-BMPTC was colored by 365-nm irradiation and restored by 500-nm irradiation. (b–d) Patterning application of Ag₁₂-BMPTC-coated film of the irradiation cycle. (e, f) Potential performance of the information security and anticounterfeiting patterns during the irradiation cycle.

switches. This study enriches the diversity and performance range of SCC-MOFs and provides a new strategy for designing and synthesizing novel photochromic materials.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.



Yu-Pan Song is a MD student under Dr Li's supervision at the Green Catalysis Center and College of Chemistry, Zhengzhou University. Her interest focuses on the preparation and optical properties of cluster-based framework materials.



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Bo Li received her PhD degree in chemistry from Zhengzhou University. Her research interests focus on the study of optical properties of cluster-based assembly materials.

一种快速响应的光致变色SCC-MOF用于光开关和信息加密

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摘要 由于银硫簇的不稳定性和有限的刺激响应特性, 构建新型的具有光开关性质的银-硫簇基金属有机框架 (SCC-MOF) 面临着重大挑战. 基于此, 本文设计并合成了一种新型光致变色的 SCC-MOF (Ag_{12} -BMPTC), 该材料利用二芳基乙烯配体和银硫簇前驱体通过溶剂缓慢挥发而得到. Ag_{12} -BMPTC 在 365 和 500 nm 光照射下表现出优异的可逆光响应特性. 此外, 这种光开关性质为其在信息加密和手性开关方面提供了潜在应用. 本研究不仅扩大了 SCC-MOF 的种类, 而且为设计和合成新型光致变色材料提供了新的思路和潜在应用.