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# Microwave-assisted crystallization inclusion of spiropyran molecules in indium trimesate films with antidromic reversible photochromism<sup>†</sup>

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An indium trimesate metal–organic framework (JUC-120) which possesses a cubic zeolitic MTN topology, as a new analogue to MIL-100(Al, Fe or Cr) compounds, has been successfully synthesized. Its structure exhibits a mesoporous cage (26 Å) and high thermal stability. The assembly of nitrobenzospiropyran derivatives (BSP) into JUC-120 nanocrystals (BSP/JUC-120) is achieved by a microwave-assisted crystallization inclusion approach. The BSP/JUC-120 films have been prepared on quartz wafers by a spin-coating method. The successful encapsulation of BSP molecules into the mesopores of the JUC-120 structure has been verified by N<sub>2</sub> adsorption and TGA measurements. The photochromic properties of BSP/JUC-120 films are studied by the UV-Vis and fluorescence spectroscopies. More interestingly, metastable open merocyanine (OMC) species are directly generated from the closed spiropyran form (CSP) without photoirradiation and stabilized for a long period in the BSP/JUC-120 film. The open merocyanine isomer bleaches to the closed spiropyran form by ultraviolet or visible light, and the coloration is regained upon standing in the dark, exhibiting antidromic photochromism. Moreover, the BSP/JUC-120 film shows high reversibility and thermal stability of photochromism. This highly efficient MOF film is expected to be promising in the applications of optical devices.

### Introduction

Metal–organic frameworks (MOFs) are emerging as an extensive class of novel nanoporous crystalline materials, the structure of which is composed of metal ions or clusters joined by a variety of organic linkers through strong coordination bonds.<sup>1</sup> The versatile organic ligands and inorganic components enable molecular engineering of MOFs with topologically diverse and pleasing structures.<sup>2</sup> A library of possible structures with different properties of large pore size range (3.0–48.3 Å),<sup>3</sup> very high surface areas, and adjustable internal surface properties make MOFs of interest in gas storage,<sup>4</sup> catalysis,<sup>5</sup> magnetism,<sup>6</sup> and other potential applications.<sup>7</sup> Designing a target structure with specific properties and functionalities provides endless exploration in materials science. Besides the extraordinary degree of variability in MOF structures themselves, the tailored functionalization of MOFs offers new perspectives with expected properties and broadened applications. In addition to the modifications by selecting specific ligands or grafting functional groups *via* post synthesis,<sup>8</sup> the host–guest chemistry of MOFs allows an implementation of desirable properties by embedding guest molecules or clusters in the cavities. Recently, the utilization of MOFs for supporting metal nanoparticles has been attempted for heterogeneous catalysis<sup>9</sup> and hydrogen storage.<sup>10</sup> Therefore, the investigation of MOFs for host materials is attracting increasing attention although it is still in an early stage and thus remains a big challenge.

In addition to the aforementioned issues of internal properties, the external surface is another key factor for tailoring the properties of MOF materials for advanced applications. The possibility of controlling particle dimensions, creating more active sites and engineering crystal surfaces has been initiated for predetermined purposes. While great effort is continuing on the synthesis side, the parallel exploitation of MOF materials for industrial applications is currently under-developed. In particular, the processing of MOFs as thin films is a nascent domain and has attracted considerable interest for many applications,<sup>11</sup> such as membranes for separations,<sup>12</sup> and chemical sensors.<sup>13</sup> Furthermore, applying a thin film to a material allows us to make better tools, and leads to a smaller, flexible design and more efficient electronic or optical devices. Thus, many benefits are

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expected by the processing of MOF crystals into thin films with superior performances. Meanwhile, the supramolecular organization of guests into the uniform pores of MOF films provides a general methodology to gain control over molecular properties of guests and host–guest interactions. Further, MOFs supply additional stability and high dispersion of the incorporated active species due to their large range in pore sizes, well-defined pore systems, high adsorption ability and high thermal stability. From this point of view, MOF films are considered to be good candidates as the host materials.

Following the successful examples of zeolites for the incorporation of luminescent dye molecules or other organic compounds,14 an exploration of MOF films as host materials for photochromic molecules is underway. Photochromic materials can be defined as a class of compounds that change their color reversibly upon irradiation with light or by electromagnetic radiation.<sup>15</sup> Among numerous photochromic compounds,<sup>16</sup> spiropyran derivatives represent as a main family member of photochromic molecules.<sup>17</sup> The principle of photochromism for spiropyrans is based on the interconversion between the colourless "closed" spiropyran form (CSP) and a highly colored "open" merocyanine form (OMC), such as 1-(2-hydroxyethyl)-3.3-dimethylindolino-6'-nitrobenzopyrylospiran (BSP, Scheme 1). Upon UV irradiation of the stable colorless CSP form, the cleavage of the C-O bond takes place through a pericyclic reaction, followed by unfolding of the molecule to a colored planar OMC form which reverts back to the CSP form by spontaneously fading in the dark (direct photochromism).<sup>18</sup> Meanwhile, in less common cases, the photoinduced decolouration of the OMC form bleaches to the colorless CSP form, and regains colouration upon standing in the dark (reverse photochromism).19 Photochromism has been extensively studied, and photochromic materials have attracted much attention for a wide range of practical and advanced applications, including optical data storage,20 digital electronics,21 lasing effect22 and biocompatible materials.<sup>23</sup> However, most spiropyran molecules in the crystalline form generally do not undergo photochromic interconversion, which limits their applications. Additionally, the efficiency of these organic photochromic compounds is quite low due to photodegradation processes and fast relaxation of the energy-rich photoinduced state. Thus, the immobilization of photochromic molecules into rigid cavities of nanoporous materials has been attempted because of enhanced stability against thermal relaxation and improved photoswitching reversibility.24

The objective of the present study is to assemble the photochromic molecules in the nanoporous films and investigate the photochromic properties for advanced photonics or optics



**Scheme 1** Molecular structure and photoisomerization of 1-(2-hydroxyethyl)-3,3-dimethylindoline-6'-nitrobenzospiropyran (BSP).

applications. The feasibility of this concept has been exemplified by assembly of BSP compounds into the big mesopores of indium trimesate MOF via a microwave synthesis approach and then formed films by spin-coating method.<sup>25</sup> The structure of indium trimesate, designated as JUC-120, possesses the cubic zeolitic MTN topology based on indium cluster and trimesic acid (H<sub>3</sub>BTC) ligand, which is a new analogue to MIL-100(Al, Fe or Cr). Additionally, the titled spiropyran compound, BSP (Scheme 1), is successfully incorporated inside the supercages of JUC-120 crystals by crystallization, assisted by microwave heating, with the resultant product named BSP/JUC-120. The crystallization inclusion process involves the direct synthesis of host materials from the precursor, and the co-inclusion of dye molecules in the mixture solution can occur simultaneously during hydrothermal/solvothermal crystallization. Microwaveassisted crystallization inclusion<sup>25</sup> is employed in this study based on the following considerations. Microwave heating enables the preservation of the structure of the chromophore in the accommodated molecules which are sensitive towards hydrolysis and thermal heating during the conventional process. Also, microwave synthesis is an energy-saving process, involving a short reaction time. Moreover, when the size of the guest molecules exceeds the diameter of the cavity window of the host material, crystallization inclusion will show its superior advantages in comparison to the impregnation method. Furthermore, the photochromatic behaviors of the BSP/JUC-120 film are studied by UV-Vis and fluorescence spectroscopy. Upon photoirradiation of the BSP/JUC-120 film, the stabilization of the open merocyanine isomer bleaches to the closed spiropyran form, and the coloration is regained upon standing in the dark, exhibiting antidromic reversible photochromism.

#### Experimental

#### Materials

In $(NO_3)_3 \cdot xH_2O$  (aladdin reagent, Co., Ltd, Shanghai, China, 99%), trimesic acid (also called 1,3,5-benzenetricarboxylic acid, H<sub>3</sub>BTC, Sigma Aldrich, 99%), 1-(2-hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (TCI, >93.0%, BSP), anhydrous ethanol, methanol and *N*,*N*-dimethylformamide (DMF) as solvents were used as received.

#### Preparation of BSP/JUC-120 suspension

The precursor solution of JUC-120 was prepared by mixing  $In(NO_3)_3 \cdot xH_2O$  (0.08 g, 0.215 mmol) and trimesic acid (0.068 g, 0.324 mmol) in a mixed solvent of H<sub>2</sub>O–DMF (1 : 1, 10 mL). Then, the solution above was transferred into a Teflon-lined microwave reactor (XT-9900 Intelligent Microwave Digestion System, Xintuo Analytical Instruments Co., LTD, Shanghai, China) and heated at 120 °C for 120 seconds at 1000 W with a constant pressure of 1 MPa. The suspension obtained was purified by centrifugation in three subsequent cycles (5000 rpm) using DMF and H<sub>2</sub>O, respectively, and dried at 80 °C. BSP/JUC-120 was also prepared by the same procedure as stated above, except that the organic photochromic compound BSP (0.057 mmol, 0.02 g) was introduced into the precursor solution under constant stirring for about 60 min in the dark. Further, the excess BSP on the external surface of JUC-120 was removed with

methanol in a Soxhlet extractor until no BSP molecules could be detected in the supernatant solution, and then the BSP/JUC-120 powders were re-dispersed in 10 mL methanol for further use.

#### Preparation of BSP/JUC-120 film

Prior to the preparation of MOF films, quartz wafers used as the substrates were pre-treated according to the reported literature.<sup>26</sup> Thin films of BSP/JUC-120 were prepared on quartz plates  $(1.5 \times 1.5 \text{ cm})$  by spin-coating the suspension of 5 g L<sup>-1</sup> with a speed of 5000 rpm for 30 s.<sup>27</sup>

#### Characterizations

The crystalline structure of JUC-120 crystals and BSP/JUC-120 films were determined by X-ray diffraction (XRD) measurements using a Riguku D/MAX2550 diffractometer with Cu-Ka radiation ( $\lambda = 1.5418$  Å) running at a voltage of 50 kV and a current of 200 mA. A solid-state <sup>13</sup>C CP/MAS NMR measurement was carried out on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. Raman spectra were recorded on a LabRam Aramis Raman microscope system (Horiba-JobinYvon) equipped with a multichannel air cooled charge-coupled device (CCD) detector. Spectra were excited using the 633 nm line of a HeNe narrow bandwidth laser (Melles Griot). FTIR spectra were collected on a Nicolet Impact 410 FTIR spectrometer at room temperature in the range of 400-4000  $\text{cm}^{-1}$ , with potassium bromide pellets. Dynamic light scattering (DLS) measurements of the suspension were performed with a Malvern Zetasizer-Nano instrument. The films were also characterized by field emission scanning electron microscopy (FE-SEM: JEOS JSM6700F). Nitrogen adsorptiondesorption measurements on the JUC-120 and BSP/JUC-120 powders were carried out using an Autosorb iQ2 adsorptometer, Quantachrome Instruments. Prior to the tests, the as-synthesized JUC-120 was refluxed in methanol for 24 h. Then, the JUC-120 and BSP/JUC-120 powders were degassed under vacuum overnight at 150 and 100 °C, respectively, in order to remove the methanol solvent trapped within the pores. The measurements were carried out at 77 K. Specific surface areas were determined using the Brunauer-Emmett-Teller (BET) equation over the range of relative pressures  $P/P_0$  between 0.01 and 0.3. The pore size distribution was calculated by applying the nonlocal density functional theory (NLDFT) method. TGA analysis was performed on the BSP/JUC-120 and JUC-120 samples in air (5 °C min<sup>-1</sup>) (Netzch Sta 449c thermal analyzer). For measuring BSP content in JUC-120 crystals using an analytical protocol, the typical procedure involves the digestion of BSP/JUC-120 powders (10 mg) in 25 mL EtOH containing 40 µL of HCl (37% aqueous solution) with sonication. Subsequently, the solution was transferred into a volumetric flask. The concentration of BSP was determined by UV spectroscopy using a standard plot, as shown in Fig. S1.<sup>†</sup>

#### Photochromism tests

Before the photochromism experiments, all samples were sealed to avoid any contamination, wrapped with tin foil, and stored at room temperature in the dark. External UV source (Hayashi LA-410, 25 mW cm<sup>-2</sup>, 320 nm <  $\lambda$  < 400 nm) and visible light source

 $(\lambda > 420 \text{ nm})$  generated by xenon lamp (500 W) with UV-cut filter were used to irradiate the sample. UV-Vis spectra were recorded before and after irradiation with an external UV-light (Hayashi LA-410, 25 mW cm<sup>-2</sup>) for different time durations at room temperature using a Perkin-Elmer Lambda 900 spectrophotometer. Emission spectra were collected by fluorescence spectroscopy (Perkin-Elmer LS55 luminescence spectrometer) before and after exposure to external visible light (500 W xenon lamp with an interference filter,  $\lambda > 420$  nm) at different irradiation times. The time dependence of fluorescence intensity upon visible light irradiation was described by fitting the rate constant k (s<sup>-1</sup>) of the monoexponential function using the following eqn (1):

$$A_t = A_0 \exp(-kt) + A_{\rm th},\tag{1}$$

where  $A_t$  is the peak intensity at  $\lambda_{max}$  with test time and  $A_{th}$  reflects the thermal equilibrium between the closed and opened forms.<sup>24f</sup>

#### **Results and discussion**

#### General characterization of materials

The X-ray diffraction patterns collected from JUC-120 powder and the BSP/JUC-120 film deposited on the quartz wafer are shown in Fig. 1. The XRD pattern of JUC-120 (Fig. 1b) is similar to the simulated MIL-100(Cr)<sup>28a</sup> (Fig. 1a) by judging all apparent peak positions. Namely, as-synthesized JUC-120 is considered to possess MIL-100 structural type<sup>28</sup> based on the perfectly matching XRD data, and also supplemented as a new analogue to MIL-100(Al, Fe or Cr). Fig. 1c shows the XRD pattern of the BSP/JUC-120 film. No substantial differences are observed between the initial JUC-120 powder (Fig. 1b) and the BSP/JUC-120 film (Fig. 1c). As can be seen, the crystallinity is retained after BSP loading in the BSP/JUC-120 film.

To further elucidate the structure of the JUC-120 MOF material, NMR and Raman spectroscopy were employed to study the organic and inorganic components of JUC-120.The <sup>13</sup>C MAS NMR spectra of JUC-120 and the activated MIL-100(Al) are shown in Fig. 2, the spectra of which were recorded with a contact time of 5 ms. The spectrum of JUC-120 contains two main groups of peaks located at  $\delta = 134$  and 142 ppm, which are attributed to the C atoms of the phenyl ring, and the signal



**Fig. 1** XRD patterns of (a) simulated MIL-100(Cr), (b) as-synthesized JUC-120 powder and (c) the BSP/JUC-120 film.



Fig. 2  $^{13}$ C MAS NMR spectra of (a) the activated MIL-100(Al) and (b) JUC-120 samples.

coming from the carboxylic groups at  $\delta = 172$  ppm also appears.<sup>29</sup> Almost all the <sup>13</sup>C MAS NMR signals of JUC-120 are similar to its analogue, MIL-100(Al). The NMR result combined with supplementary IR spectra (Fig. S2†) sheds light on the structure similarity of JUC-120 and MIL-100(Al).

Additionally, Raman scattering measurements were carried out to give some information on the microenvironments of the inorganic components of the activated MIL-100(Al) (Fig. 3a) and JUC-120 (Fig. 3b) at room temperature. In the range of 100–600 cm<sup>-1</sup>, the four Raman peaks of the JUC-120 sample located at 137 and 177 cm<sup>-1</sup> are assigned to the In–In vibrations,<sup>30b</sup> and the other two peaks at 362 and 473 cm<sup>-1</sup> are associated with the stretching vibrations of In–O–In.<sup>30</sup> The slight shift between JUC-120 and MIL-100(Al) is interpreted as resulting from the different atom radii of indium and aluminum.

Based on the observations above, JUC-120, with a similar structure to MIL-100(Al), is constructed of indium(III) trimers linked by tricarboxylate groups that form supertetrahedra as building blocks, resulting in a cubic zeolitic MTN topology (Fig. 4). After the removal of the solvent molecules occluded in the pores, the cages with the free internal diameters of about 2.0 and 2.6 nm are accessible through small windows of 0.46 and 0.82 nm. Therefore, spiropyran derivative (BSP) molecules



**Fig. 3** Raman spectra of (a) the activated MIL-100(Al) and (b) JUC-120 samples.



**Fig. 4** Structure of JUC-120 (a) viewed along the [101] direction, and (b) MTN topology including two types of mesoporous cages.

 $(1.49 \times 0.85 \times 0.7 \text{ nm})$  would presumably be located in mesoporous cages of the MOF structure (JUC-120) by taking into account the molecular size and pore size.

The thermal stability of JUC-120 crystals was also followed by temperature-dependent XRD measurements. Fig. S3<sup>†</sup> shows the evolution of the XRD pattern for the as-synthesized sample after calcination in air at different temperatures. As seen in Fig. S3,<sup>†</sup> it can be found that JUC-120 retains the same structure below 370 °C, but its structure collapses at about 400 °C. This result shows that JUC-120 is a quite stable MOF material (stable up to 370 °C in air), which has a higher thermal stability than its counterparts of MIL-100(Cr, Fe) (275 °C in air).<sup>28a,b</sup> This high thermal stability provides a basis for the efficient evacuation of the solvent molecules in the pores.

The surface morphologies of JUC-120 and BSP/JUC-120 films were monitored by scanning electron microscopy (SEM). The SEM images of JUC-120 and BSP/JUC-120 films are shown in Fig. 5. As can be seen in Fig. 5a, JUC-120 nanoparticles around 750–850 nm in size with octahedral shape homogenously cover the quartz substrate. Meanwhile, the top view of the BSP/JUC-120 film is also shown in Fig. 5b. The crystals in the BSP/JUC-120 film exhibit a similar size and shape as JUC-120. The particle size of both samples in ethanol is determined by DLS measurements (Fig. 5c and d). The particle size distribution curves contain peaks around 794 and 657 nm for JUC-120 and BSP/JUC-120 respectively, and this result is consistent with the SEM



**Fig. 5** SEM images of (a) JUC-120 and (b) BSP/JUC-120 films deposited on quartz wafers. DLS data of (c) JUC-120 and (d) BSP/JUC-120 suspensions in ethanol.

analysis. The optical picture of BSP/JUC-120 suspension in ethanol is shown in Fig. S4.<sup>†</sup>

Thermogravimetric analysis (TGA) is a fundamental and effective method to determine the content of organic moieties in porous materials.<sup>31</sup> TGA curves of the activated JUC-120 and BSP/JUC-120 samples are presented in Fig. 6. Compared with the reference curve of the activated JUC-120 sample, there is a distinct weight loss for the BSP/JUC-120 sample between 235 and 330 °C, which can be attributed to the partial decomposition or combustion of the BSP species occupied in the pores. By analyzing the TGA data, it is calculated that there is approximately 8–9 wt% BSP loaded in the BSP/JUC-120 crystals, the amount of which is also verified by an analytical protocol with UV-Vis spectroscopy using a standard curve of BSP solutions (Fig. S1<sup>†</sup>).

The pore structure and related textural properties were followed by nitrogen sorption measurements. Nitrogen adsorptiondesorption isotherms for JUC-120 and BSP/JUC-120 are shown in Fig. 7, and the physical property list of these two samples is given in Table 1. For both samples, a steep increase in the adsorbed volume at low relative pressure is observed followed by a slight secondary uptake. There is much smaller uptake of nitrogen for the BSP/JUC-120 sample if taking its counterpart (JUC-120) as a comparison. Additionally, the surface area  $(S_{\text{BET}})$  and pore volume are reduced from 1456 to 267 m<sup>2</sup> g<sup>-1</sup>, and 0.636 to 0.123 cm<sup>3</sup> g<sup>-1</sup>, respectively, after BSP is loaded into the JUC-120 crystals (Table 1). These results are expected due to the large amount of BSP encapsulated in the pores. Estimation of the pore size distribution adopted by the nonlocal density functional theory (NLDFT) method shows three maxima at 14.3, 20.3 and 26 Å for JUC-120, attributed to small and large cages. It is noteworthy that the created large pores would serve as good hosts for the encapsulation of BSP molecules.

#### Photochromic properties of BSP/JUC-120 film

Inspired by the successful encapsulation of BSP molecules inside the mesopores, this type of material is further employed to investigate the optical properties. Based on the aforementioned advantages of thin film construction, BSP/JUC-120 films were prepared on quartz substrates by a spin-coating method. Two optical images of the film are shown in Fig. 8a. One is the freshly



**Fig. 6** TGA curves of the activated JUC-120 (black) and BSP/JUC-120 samples (gray).



**Fig. 7** N<sub>2</sub> adsorption–desorption isotherms of JUC-120 and BSP/JUC-120 samples.

prepared sample before irradiation and the other one is after irradiation with an external UV source. The color change of the BSP/JUC-120 film from pink to colorless is induced by UV light  $(320 \text{ nm} < \lambda < 400 \text{ nm})$ . This means that photochromism is taking place during UV light irradiation. Conversely, the color of this film would revert back to pink in the dark, which sheds light on its reverse photochromism. In order to study in detail, UV-Vis spectroscopy is used to study the optical properties of the BSP/ JUC-120 film. UV-Vis spectra of the BSP/JUC-120 film during the irradiation by an external UV light are shown in Fig. 8b, and its corresponding absorbances versus irradiation time is depicted in Fig. S5.<sup>†</sup> Before photoirradiation, the film shows an absorption maximum at 556 nm together with one weaker absorption at 523 nm, originating from BSP molecules in an OMC form.<sup>24c,i</sup> These results indicate that the BSP molecules in the OMC form are stabilized in the assembled JUC-120 film, which is rarely observed. When exposed to the UV light, this absorption band at 556 nm suffers a continuous decrease with increasing irradiation time, indicating a conversion of OMC to CSP. It is well known that the OMC form of BSP molecules possesses a metastable configuration, which is found in the polar and hydrophilic microenvironments. Meanwhile, those BSP molecules in the stable CSP form are present in non-polar and hydrophobic systems. This antidromic photochromism behavior for BSP molecules incorporated in the JUC-120 structure can be explained by the relatively high polarity of JUC-120 nanocrystals due to the polar In-OH and In-H<sub>2</sub>O groups in the structure.<sup>27</sup> These polar (In-OH and In-H<sub>2</sub>O) groups allow the stabilization of the molecules with an open merocyanine structure, and thus decelerate the rate of thermal OMC-CSP isomerizations, which coincides with the observation of spiropyran molecules trapped in other porous solid matrices.<sup>24c-i</sup>

Table 1 Textural data of surface areas, pore size and pore volume measured by  $\mathrm{N}_2$  sorption

	$S_{\rm BET} ({ m m}^2 { m g}^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore diameter (Å)
JUC-120	1456	0.636	14–26
BSP/JUC-120	267	0.123	



**Fig. 8** (a) Photographic images of the BSP/JUC-120 film with and without external UV irradiation, (b) UV-Vis spectra of the BSP/JUC-120 film before (1) and after the UV irradiation at different times ((2): 2 min, (3): 5 min, (4): 10 min, (5): 20 min).

Control over the fading speed of photochromic materials is interesting for applications requiring a particularly fast or slow fading speed, such as in ophthalmic lenses, photochromic coatings and security printing ink. Recently, BSPs have been shown to exhibit fluorescence in the visible region for their excited/ energy-rich OMC form, not the CSP form. Therefore, the fluorescence properties of the BSP/JUC-120 film are monitored by supplementary fluorescence spectroscopy to study the kinetics of the decoloration of the excited species in the fading process. Thus, the decoloration process is exemplified by the consecutive irradiation of the BSP/JUC-120 film from an external and strong visible light source (500 W xenon lamp with an interference filter,  $\lambda > 420$  nm). Subsequently, the fluorescence spectra are recorded with an excitation wavelength of  $\lambda_{ex} = 500$  nm. Fig. 9a shows the evolving spectra with irradiation time. As shown in Fig. 9a, two distinguished peaks at 578 and 616 nm appear instantly before the excitation, which are assigned to the OMC species.<sup>24i</sup> The fading process is followed by variations of the peak intensities in



Fig. 9 (a) The fluorescence emission spectra of the BSP/JUC-120 film over time upon the external visible light irradiation at room temperature; (b) the decay curve of the corresponding fluorescence intensity ( $\lambda_{\rm em} = 578$  nm) *versus* time.

the visible region at 578 and 616 nm upon the irradiation of the film (Fig. 9a). The photorelaxation from OMC (pink) to CSP (colorless) proceeds slowly, as observed from the decrease of the fluorescence intensity with irradiation time. Additionally, in order to measure the kinetics for photo-induced decoloration of the OMC species, the time-resolved emission is followed by the peak intensity at 578 nm in the fluorescence spectra for 143 min, vielding an exponential decoloration curve (Fig. 9b). The curve is fitted using curve-fitting software. As can be seen, the first-order exponential model fits accurately the kinetics of photobleaching of the BSP/JUC-120 film (eqn (1)). The fitting parameters for the spectroscopic data are displayed in Table 2. This slow decay rate in the kinetics measurement may be due to strong host-guest interactions between the BSP molecules and JUC-120 crystals. The BSP molecules are confined in the cages of JUC-120 crystals during crystallization assisted with microwave heating, avoiding the formation of In-BSP precipitates (Fig. S6<sup>†</sup>). The pore confinement would isolate the BSP molecules each other in the different cages, which is indicated by the presence of 0.84 molecules occupied in one pore (the calculation method is described in the ESI<sup>†</sup>). This confinement effect would also increase the steric hindrance of the ring-closing process from the OMC to CSP form, and hence leads to lengthen the weighted-average half-life of the excited species (bleaching by visible light) as observed in this study ( $k_{\rm vis} = 6.89 \times 10^{-4} \text{ s}^{-1}$ ,  $t_{1/2} = 1006$  s, Table 2). This half-life value gives an indication for strong lightfastness, far longer than that in DMF solution ( $k_{vis} = 1.64 \times 10^{-2} \text{ s}^{-1}$ ,  $t_{1/2} =$ 42 s) or a polymer (poly-*n*-butylmethacrylate) matrix ( $k_{vis} =$  $1.15 \times 10^{-2} \text{ s}^{-1}$ ,  $t_{1/2} = 60 \text{ s}$ .<sup>24</sup> Furthermore, compared with literature data on the half-lives of spiropyrans incorporated into ordered porous materials, BSP molecules in JUC-120 crystals exhibit longer half-lives  $(t_{1/2})$  than those of mesoporous materials (Si-MCM-41,  $t_{1/2} = 108-162$  s), but a bit shorter than some faujasite-type microporous materials (HY,  $t_{1/2} = 2.3 \times 10^3$  s) (Table S1<sup>†</sup>).<sup>24e</sup>

The resistant ability towards thermal relaxation is another important factor for the long-term stability of photochromic materials in order to realize the potential applications. The fluorescence spectra of the BSP/JUC-120 film in the dark were recorded at various times at room temperature (Fig. 10 inset). Negligible differences are observed between the spectra. This points to a good preservation of the BSP molecules in the OMC form. In more detail, the variations of fluorescence intensities ( $\lambda_{em} = 578$  nm) as a function of time are plotted in Fig. 10. No big loss in the intensity is observed even when placed in the dark after one week at room temperature. According to the calculation using eqn (1), the fluorescence decay constant for the thermal decoloration ( $k_{thermal}$ ) and half-life ( $t_{1/2}$ ) of the OMC form in the JUC-120 film are estimated to be  $3.78 \times 10^{-9}$  s<sup>-1</sup> and  $2.65 \times 10^{8}$ 

 
 Table 2
 Fitting parameters of the spectroscopic data for the photoinduced decoloration of the BSP/JUC-120 film

$A_0$	$k_{\mathrm{vis}}{}^{a}$ (s <sup>-1</sup> )	$A_{ m th}$	$R^2$
0.0989	$6.89  imes 10^{-4}$	0.063	0.995

<sup>*a*</sup> The kinetic constant calculated from the fluorescence intensity decay curve for photoinduced decoloration.



Fig. 10 Time dependence of the fluorescence intensity ( $\lambda_{em} = 578$  nm) for the OMC-form of BSP/JUC-120 in the dark at room temperature. The inset shows the fluorescence emission spectra of the BSP/JUC-120 film for various times (0 h, 3 d, and 7 d).

s, respectively, which is comparable to the best results in previous reports (Table S1†).<sup>24g</sup> This observation shows that the BSP molecules entrapped in the cages of the JUC-120 crystals can hardly undergo rotational movements, thus suppressing CSP isomerization. The long retardation to the thermal-stable CSP form validates the pore confinement effect, which is consistent with the results of light-fading experiments. It can be concluded that the thermal stability of the open merocyanine form of the accommodated BSP molecules in the porous MOFs is improved significantly, which provides further proof that JUC-120 MOF is a good candidate as a host material. Based on the spectroscopy studies above, there are two decisive parameters in controlling the photochromic properties of the BSP/JUC-120 film, namely the polar groups (In–OH and In–H<sub>2</sub>O) in the structure and pore confinement.

The reversibility of photochromism is another required index in the design of photochromic materials for optical devices.<sup>24c</sup> The reversibility of the photochromic properties of the BSP/ JUC-120 film is evaluated by a coloration–decoloration process. Fig. 11a shows the evolution of the fluorescence intensities for one coloration–decoloration cycle. It can be seen that photoirradiation results in a decrease of BSP molecules in the OMC form irradiated by the visible light for 20 min, and thereafter, the portion of BSP molecules in their open form is increased in the



**Fig. 11** (a) Changes in fluorescence intensity of the BSP/JUC-120 film ( $\lambda_{em} = 578 \text{ nm}$ ,  $\lambda_{ex} = 500 \text{ nm}$ ) with irradiation of visible light for 20 min and in the dark for 120 min. (b) The emission intensities ( $\lambda_{em} = 578 \text{ nm}$ ) of the BSP/JUC-120 film after ten repetitions with reversibly switching the irradiation from the visible light to dark.

dark for 120 min, judging from the increasing intensities. The intensity changes of the film within one full cycle reveal a reversible configuration change of BSP molecules during the coloration and decoloration processes. The time-resolved fluo-rescence emission intensities upon the testing cycles by reversibly switching from visible light irradiation to dark is shown in Fig. 11b. No significant loss is observed in the intensities after ten consecutive applications of the film. It is suggested that this film possesses high reversibility, which provides a basis for the fabrication of photochromic devices.

#### Conclusions

A new hybrid MOF (JUC-120) material, with indium as the metal centers and trimesate as carboxylate ligands, has been synthesized. The XRD, NMR and Raman characterizations indicate that JUC-120 possesses a cubic zeolitic MTN topology as a new analogue to MIL-100(Al, Fe or Cr). The results of nitrogen sorption reveal that this MOF material possesses large pore size (26 Å) with high surface area ( $S_{\text{BET}} = 1456 \text{ m}^2 \text{ g}^{-1}$ ) and high thermal stability (up to 370 °C in air). Besides, the assembly of photochromic compounds into JUC-120 nanocrystals is exemplified by nitrobenzospiropyran derivative (BSP) using a microwave-assisted crystallization inclusion approach. About 8-9 wt% BSP compounds are encapsulated into the JUC-120 crystals during the direct synthesis process, which is determined by TGA analysis and an analytical measurement. Further, BSP loaded JUC-120 films (BSP/JUC-120) are prepared by spincoating of their suspension on quartz wafers. The photochromic properties of the as-prepared films are investigated by UV-Vis spectroscopy. It is found that metastable open merocyanine (OMC) species are entrapped in the BSP/JUC-120 film, which is attributed to the large pore size and unique host-guest interactions. Additionally, the photochromic properties of BSP molecules in the BSP/JUC-120 film were studied in detail by fluorescence spectroscopy. The long-term stability of the OMC configuration rather than the CSP form against light/photo and thermal relaxation is observed in the JUC-120 crystals due to the pore confinement effect. Furthermore, the BSP/JUC-120 film displays high reversibility of photochromism. The BSP/JUC-120 films are a novel type of host-guest material and are of potential interest for advanced applications in photonics or optical devices.

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