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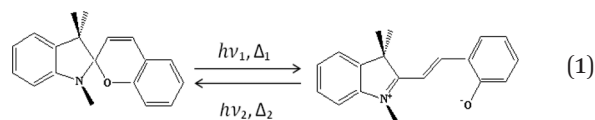
Pseudo crystalline state thermochromic and reverse-photochromic reactivity of spiroindolinobenzopyran upon encapsulation into Zn-MOF-74†

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After inclusion into the rigid channels of Zn MOF-74 crystals, molecules of spiroindolinobenzopyran (SPH) turned thermochromic by converting to its red merocyanine form on heating and reverse-photochromic by converting to its yellow spiro form under UV irradiation at 365 nm. However, SPH did not show any chromic reactivity in its pure solid form.

Chromism is a reversible transformation of a compound between two chemical species that have different absorption spectra and this change can be caused due to various external stimuli.¹ There are plenty of organic and inorganic systems that show photochromism and/or thermochromism, in which their colour change is caused either by irradiation with electromagnetic radiation or by heating or cooling the system.² Among the organic chromic compounds, spiropyranes are well known as photochromic materials, which upon irradiation with near UV light the C_{spiro}–O bond in the spiro (SP) form is cleaved through a pericyclic reaction to give the ring-open coloured merocyanine (MC) form.^{3,4} The MC form can be converted back to the closed colourless SP form either by visible light irradiation or thermally at an ambient temperature, as shown in eqn (1).^{4,5} Most of the potential applications for them in the fabrication of nonlinear device components, optical memories and switches are mainly based on their photochromic behavior.^{6–9} Unfortunately, at ambient temperatures, these photochemical reactions are feasible predominantly in solution and only very few compounds have been reported as having photo reactivity in the solid state too.^{10–12} Thus, most of their valuable commercial applications are still restricted in the solid state or in solid matrices mostly

due to tight packing in the solid state, which sterically hinders the reactivity of the molecules.^{11,13} Another drawback reported is the low thermal stability of the coloured MC form.^{8,14} However, even at ambient temperatures, the MC form can be stabilized easily in polar solvents by forming hydrogen bonds between the phenolate oxygen of MC and the solvent molecules^{15,16} or by complexing with metal ions.^{6,17–20}



To overcome this MC-SP spontaneous thermal inter-conversion in the solid state, inclusion of photochromic spiropyranes into various solid matrices such as polymers,^{21,22} β-cyclodextrin,^{23,24} Zeolites^{25,26} and sol-gels^{27–29} etc. has been tried and accordingly, the MC form was moderately stabilized in those matrices, though the photochromic properties were not much enhanced as anticipated.

Metal-organic frameworks (MOFs) are crystalline hybrid materials with ordered porous constructions.³⁰ These functionalized pores with interesting chemical and physical properties enable MOFs to be potential materials for gas adsorption,³¹ gas and liquid separation,^{32,33} heterogeneous catalysis³⁴ and drug delivery purposes.^{35,36} Furthermore, recently published data showed that MOFs are also ideal candidates to form inclusion complexes with organic and organometallic compounds.^{37–40}

In this paper, we describe how the photo and thermochromic properties of the unsubstituted spirobenzopyran, dihydro-1'-3'-3'-trimethylspiro[2H-1-benzopyran-2,2'-(2H)-indoline] (SPH), which does not exhibit either photo or thermochromism in its pure solid form, changed and enhanced drastically upon encapsulation into Zn-MOF-74 crystals. SPH was synthesized as reported before by the condensation reaction between 2-methylene-1,3,3-trimethylindoline and 2-hydroxy benzaldehyde in ethanol.⁴¹ Pale

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yellow single crystals were grown from methanol and were characterized with $^1\text{H-NMR}$ and FT-IR spectroscopy (see ESI†). As the host material, Zn-MOF-74 was selected among a large number of reported MOFs because of its rigid hexagonal shaped channel structure possessing a higher stability even at elevated temperatures.⁴² Yellow crystals of Zn-MOF-74 were synthesized using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2,5-dihydroxyterephthalic acid in DMF solvothermally according to the reported method⁴² and the structure was confirmed by comparing with the reported PXRD patterns and FT-IR spectra.

SPH was encapsulated into Zn-MOF-74 by refluxing a mixture of 10.0 mg of SPH and 50.0 mg of the MOF in 10.00 mL of chloroform for 4 h to obtain orange/yellow Zn-MOF-74 enclosed SPH (SPH@MOF-74) crystals without affecting the crystalline nature of the MOF. The encapsulation capacity calculation revealed that 55% of SPH has been enclosed in the host material (details in ESI†). Furthermore, it was found that by changing the refluxing time, and the ratio between SPH and the MOF, the amount of SPH molecules encapsulated can be controlled. In solution, the SPH ring opening MC formation reaction is photochromic and is triggered by UV irradiation and the ring closing SP formation bleaching reaction occurs either photochemically by visible light irradiation or thermally at ambient conditions.⁴³ Thus corresponding colour changes are visible only at very low temperatures.^{44,45} Surprisingly, when orange/yellow crystals of SPH@MOF-74 were irradiated with a 150 W UV lamp (365 nm), their colour changed to dark yellow. In contrast, upon heating at 80 °C, these orange/yellow crystals turned to dark red and by cooling at 0 °C for 50 h, they turned back to yellow as illustrated in Fig. 1a–d. Especially, red crystals can be bleached to yellow under irradiation for 2 h at 365 nm due to fast reverse photochromism (Fig. 1e–h). On the other hand, it took several weeks to months to decolourize red crystals back

to the yellow form at ambient conditions in a dark place. Here, the intensity of the red colour observed in crystals was highly dependent on the number of molecules encapsulated. As inspired colour changes were observed in crystals using a light microscope, powder X-ray diffraction (PXRD) patterns were collected for pure SPH, pure Zn-MOF-74 and SPH@MOF-74 before and after heating at 80 °C to confirm the successful inclusion of SPH (Fig. S1†). Interestingly, in the PXRD pattern of SPH@MOF-74, there were also peaks arising from the crystal planes of the host (MOF) lattice only. There are, however, slight shifts found in the two most intense peaks at $2\theta = 8.70^\circ$ and 13.58° to lower 2θ values. Additionally, there is a small new peak in the PXRD of SPH@MOF-74 at $2\theta = 8.30^\circ$, which disappeared in the red crystals obtained after heating (Fig. 2). Thus, all of the above results are indicative of a slight change in the unit cell parameters of the host after guest inclusion.^{37,45} Generally, in the PXRD patterns of crystalline host–guest materials, several new peaks arising from the new guest compound can also be observed, if guest molecules have formed a crystalline phase in the host lattice and crystal structures of such materials are possible to determine using the single crystal diffraction technique.^{37,46} As the PXRD pattern of SPH@MOF-74 did not show such changes prominently, the results indicate clearly that SPH molecules enclosed into the channels of the MOF-74 are not permanently attached to the cavity wall or are not arranged within the host lattice possessing a 3D long range symmetric pattern. Furthermore, to understand the possible interactions between guest SPH molecules and the Zn-MOF-74 framework, FT-IR spectroscopy was used. Similar to the PXRD data, the inclusion of SPH into MOF channels did not show significant changes in peak frequencies in the spectrum of the SPH@MOF-74 (Fig. S2–S4†). The similarity between the two spectra provided evidence for the absence of strong interactions between the guest and the host. Therefore, it is sure that SPH molecules have occupied positions randomly or are in motion within the channels of the Zn MOF-74 depending on the space available.

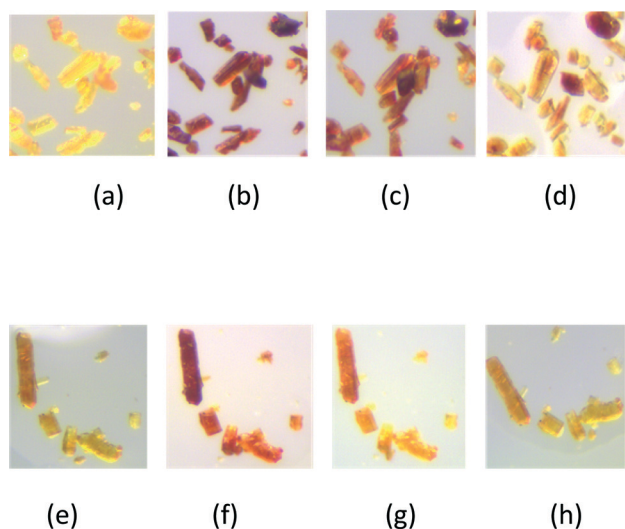


Fig. 1 Light microscope images of single crystals of SPH@MOF-74 (a) as-loaded, (b) heated at 80 °C, (c) cooled at 0 °C for 24 h, (d) cooled at 0 °C for 50 h; and SPH@MOF-74 (e) as-loaded, (f) heated at 80 °C, (g) UV irradiated for 1 h, (h) UV irradiated for 2 h.

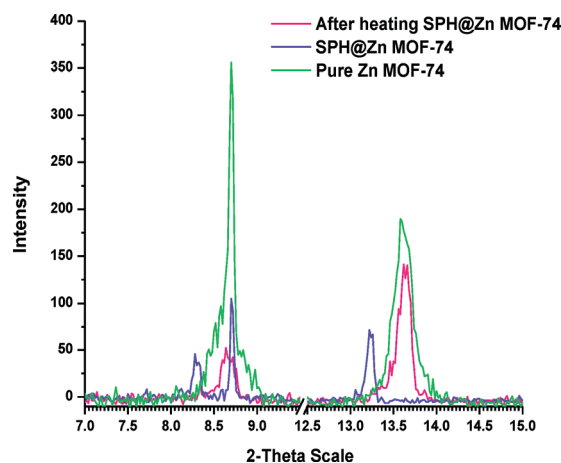


Fig. 2 The X-ray powder diffraction patterns of pure Zn-MOF-74, and SPH@MOF-74 before and after heating.

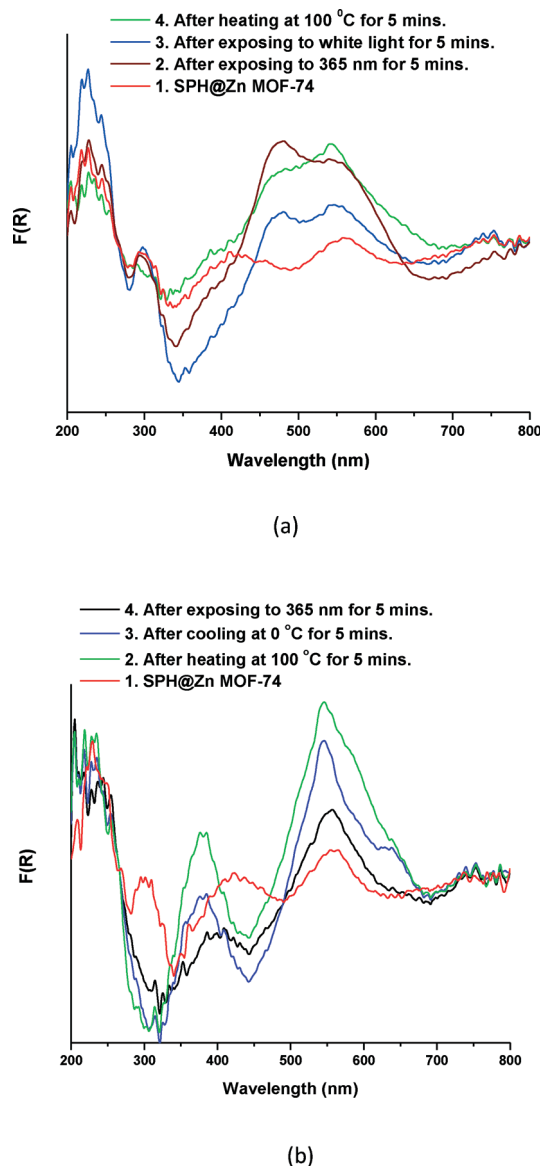


Fig. 3 UV-vis diffuse reflectance spectra [plotted as the Kubelka Munk function $F(R)$] of SPH@MOF-74. (a) UV irradiation followed by visible light irradiation and heating. (b) Heating followed by cooling and UV irradiation.

SPH became predominantly thermochromic after its inclusion, imparting a red colour to the crystals on heating, to investigate this behaviour further, diffuse reflectance UV-vis spectra were recorded for the SPH@MOF-74 system after various treatments. With accord to the red line in Fig. 3a, in the UV region of the *as-loaded* SPH@MOF-74, there are two bands maximising at 228 and 410 nm, resulting from the Zn-MOF-74 host lattice (Fig. S5†) and another band maximising at 296 nm arising from the indoline moiety of the closed SP form.³ The broad peak in the visible region with λ_{max} at 555 nm must be due to one of the XTX type (CTC/CTT/TTT) MC isomers (MC-1).^{3a,47} Interestingly, when the sample pellet was UV irradiated for 5 min at 365 nm, (Fig. 3a; brown line), a broad peak with strong intensity appeared at λ_{max} 479 nm

and the intensity of the broad peak initially found at 555 nm was also enhanced with a blue shift appearing at 545 nm and a big hump nearby the 479 nm peak. This new photo-generated isomer should have a less conjugated system than the MC-1 form observed in the *as-loaded* sample. Since the protonated MC form of SPH (MCH^+) was found at 410 and 428 nm in EtOH and hexane solutions respectively, when adding conc. HCl (Fig. S6 and details in ESI†), the peak at 479 nm cannot be attributed to the MCH^+ form. But, since the absorption wavelength of 479 nm is only about 70 nm greater than that of the MCH^+ form, this peak is most probably due to the hydrogen bonded zwitterionic form of the TTC isomer (MC-2), which is possible to make with hydrogen atoms available in the organic linkers of the MOF.^{25,40b}

On the other hand, a 470 nm peak may also be possible to arise from an XCX-type (CCC/TCT/TCC/CCT) MC form, because conjugation in XCX forms should be lower than that of XTX forms.^{3,47}

Furthermore, since the conjugation of the 545 nm peak is only about 10 nm lower than that of the MC-1 form found in the *as-loaded* sample and the pellet became red, the 545 nm peak must be due to the most stable TTC zwitterionic form (MC-3).⁴⁷ However, in the same spectrum, the peak at 296 nm did not alter significantly by indicating the presence of some amount of the closed SP form in the system. But, when this UV irradiated pellet was irradiated with white light again for 5 min, the intensities of the 479 and 545 nm peaks reduced markedly, while that of the 296 nm peak increased slightly indicating the conversion of the MC isomers to SP isomers (Fig. 3a; blue line). Fascinatingly, when the white light irradiated pellet was heated at 80 °C for 5 min (Fig. 3a; green line), the intensities of the two peaks at 479 and 545 nm were enhanced again. This increment was much more significant in the peak at 545 nm than that of the peak at 479 nm. Most importantly, the peak found at 296 nm, attributable to the SP form available in the system, disappeared completely after heating and a new small hump appeared at around 375 nm. These observations indicate the conversion of all of the molecules in the SP form to the MC form.

In the next set of experiments, illustrated in Fig. 3b, the pellet that was prepared with *as-loaded* SPH@MOF-74 was heated first. As exhibited by the spectrum in green, a new peak appeared at 375 nm and the peak initially observed at 555 nm was blue shifted to 546 nm with a great enhancement. Though the thermochromic ring-opening reaction takes place *via* quinoidal formation, those two peaks can be attributed to the formation of the conjugated zwitterionic MC-3 form, because the quinoidal form is short lived.^{25a,48–50} Besides, the peak corresponding to the SP form at 296 nm disappeared completely showing the transformation of all SP form molecules to the MC form. Although the intensities of both peaks at 378 and 545 nm reduced noticeably upon cooling the heated sample pellet, the 296 nm peak did not change significantly, but a new peak appeared at 638 nm. This observation reflects that the reverse SP formation reaction (bleaching) occurs very slowly upon cooling through the

formation of a new XTX-MC form (blue line). When the cooled pellet was irradiated at 365 nm for 5 min, the prominent peak observed earlier at 479 nm for MC-2 (when the *as-loaded* sample was UV irradiated), did not appear in the spectrum (Fig. 3b; black line). This signifies that the red MC-3 form is unable to convert to the MC-2 form easily, though the intensities of the two existing peaks at 545 and 378 nm reduced drastically with a red shift to 554 and 385 nm respectively. Additionally, it was observed that red crystals became orange/yellow again upon keeping them in the dark, whereas orange/yellow crystals did not convert to red upon storing them under the same conditions. This reveals clearly that Zn-MOF-74 channels are mostly nonpolar and can stabilize the nonpolar SP form.

Conclusions

All of the above data clearly show that SPH molecules have diffused into the Zn-MOF-74 channels in the closed, nonpolar SP form as well as in the open, polar MC-1 form by producing orange crystals due to the coexistence of both forms without destroying the host crystal lattice. The molecules enclosed became both thermally and photochemically reactive forming different isomers depending on the reaction path way. One reason for this change must be that the channels of MOF-74 have provided enough space for the SPH molecules to react freely within the single crystals of the host, as if the SPH molecules were in solution. On the other hand, this phenomenon can be referred to as pseudo crystalline state reactivity too, as only the host molecules are in the single crystal form and the SPH molecules are randomly arranged inside the channels of the host lattice. Most importantly, the SPH reactivity observed here is completely different from its reactivity in solutions, in which SPH converts to the red MC-3 form upon UV irradiation.⁴³ Yet, the open coordinately unsaturated Zn metal sites available in Zn-MOF-74 and polar-nonpolar characteristics of the channels also must have a strong influence on this different behaviour exhibited by SPH. Thus, further investigations are now in progress to understand the role of the Zn metal centers and the linker ligands on the thermochromic and photochromic activities of SPH and to study these property changes quantitatively by encapsulating SPH into several other MOF-74 hosts with different metal centers.

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