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

U. G. Randika Lakmali[a,b] and Champika V. Hettiarachchi[*a,b]

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

$$hv_1, \Delta_1 \rightleftharpoons hv_2, \Delta_2 \tag{1}$$

Chromism is a reversible transformation of a compound between two chemical species having different absorption spectra and this change can be caused due to various external stimuli.[1] There are plenty of organic and inorganic systems showing photochromism or/and thermochromism, in which their colour change either by irradiation with electromagnetic radiation or upon by heating or cooling the system.[2] Among organic chromic compounds, spiropyrans are mainly well known as photochromic materials, in which upon irradiation with near UV light C_{spiro}-O bond in spiro (SP) form cleaves through a pericyclic reaction to give the ring open colored merocyanine (MC) form.[3-4] The MC form can be converted back to closed colourless SP form either by visible light irradiation or thermally at ambient temperature, as given in equation (1).[4,5] Most of the potential applications of them in the fabrication of nonlinear device components, optical memories and switches are mainly based on their photochromic behavior.[6,9] Unfortunately, at the ambient temperatures, these photochemical reactions are feasible predominantly in solutions and only very few compounds were reported 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 molecules.[11,13] Another drawback reported is, the low thermal stability of the coloured MC form.[8,14] However, even at ambient temperatures, MC form can be stabilized easily in polar solvents by forming hydrogen bonds between phenolate oxygen of MC and solvent molecules[15,16] or by complexing with metal ions.[6,17-20]
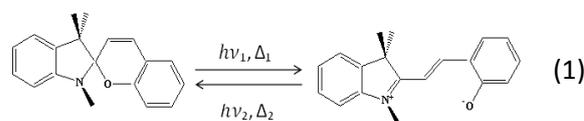
To overcome this MC-SP spontaneous thermal inter-conversion in the solid state, inclusion of photochromic spiropyrans into various solid matrices such as polymers,[21,22] β-cyclodextrin,[23,24] Zeolites[25,26] and sol-gels[27-29] etc. had been tried and accordingly, MC form was moderately stabilized 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 as potential materials for gas adsorption,[31] gas and liquid separation,[32,33] heterogeneous catalysis[34] 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 unsubstituted spirobenzopyran, dihydro-1'-3'-3'-trimethylspiro[2H-1-benzopyran-2,2'-(2H)-indoline] (SPH), which does not exhibit either photo or thermochromism in the 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 bensaldehyde in ethanol.[41] Pale yellow single crystals were grown from methanol and were characterized with ^{1}H-NMR and FT-IR spectroscopy(see ESI).

SPH was encapsulated into Zn-MOF-74 by refluxing a mixture 10.0 mg of SPH and 50.0 mg of MOF in 10.00 mL of chloroform for 4 hrs to obtain orange yellow, SPH enclosed Zn-MOF-74

(SPH@MOF-74) crystals without affecting the crystalline nature of MOF. The encapsulation capacity calculated revealed that 55% of SPH has been enclosed into the host material (details in ESI). Further, it was found that by changing the refluxing time, and the ratio between SPH and MOF, the amount of SPH molecules encapsulated can be controlled. In
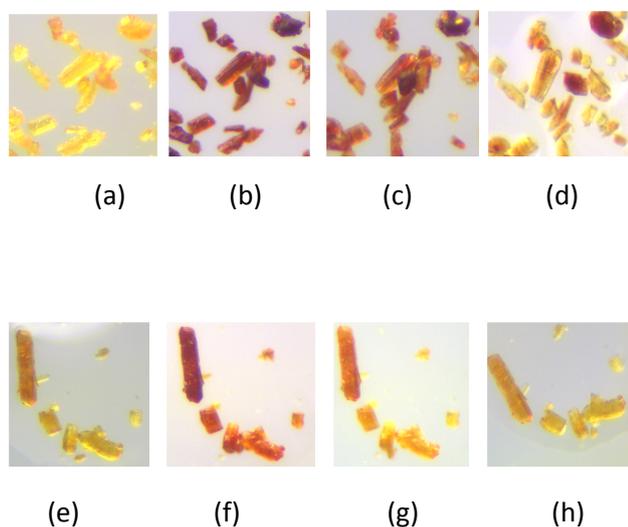

(a)   (b)   (c)   (d)

(e)   (f)   (g)   (h)

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

solutions, SPH ring opening MC formation reaction is photochromic triggered by UV irradiation and 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 hrs, they turned back to yellow as illustrated in Fig. 1a-1d. Especially, red crystals can be bleached to yellow under irradiation for 2 hrs at 365 nm due to fast reverse photochromism (Fig. 1e-1h). On the other hand, it took several weeks to months to decolorize red crystals back to yellow form at ambient conditions in a dark place. Here, 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, 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 too, there were peaks arising from crystal planes of the host (MOF) lattice only. There are, however, slight shifts found in the two most intense peaks at 2θ = 8.70° and 13.58° to

lower 2θ values. Additionally, there is a small new peak in the PXRD of SPH@MOF-74 at 2θ = 8.30°, which disappeared in the red crystals obtained after heating (Fig.2). Thus, all above 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
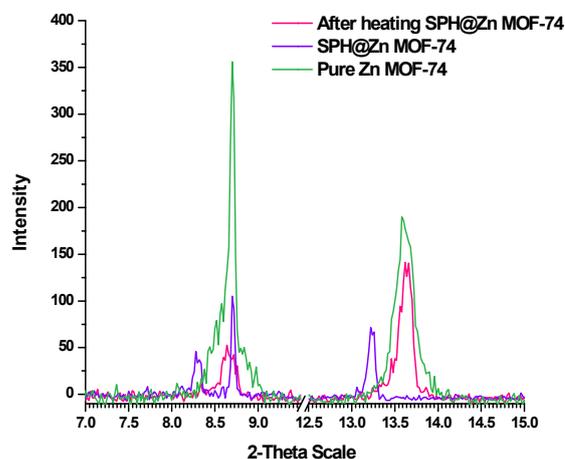

**Fig. 2** The X-ray powder diffraction patterns of pure Zn-MOF-74, SPH@MOF-74 before and after heating.

molecules have formed a crystalline phase in the host lattice and crystal structures of such materials are possible to determine using single crystal diffraction tecnique.[37,46] As the PXRD pattern of SPH@MOF-74 did not show such changes prominently, results indicate clearly that SPH molecules enclosed into the channels of the MOF-74 are not permanently attached to the cavity wall or not arranged within the host lattice possessing a 3D along range symmetric pattern. Further, to understand possible interactions between guest SPH molecules and the Zn-MOF-74 framework, FT-IR spectroscopy was used. Similar to PXRD data, 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 two spectra provided evidences 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.

Since SPH became predominantly thermochromic after inclusion imparting red colour to crystals on heating, to investigate this behaviour further, diffuse reflectance UV-Vis spectra were recorded for SPH@MOF-74 system after various treatments. With accords to the Figure 3a(red line), in the UV region of the *as-loaded* SPH@MOF-74, there are two bands maximising at 228 and 410 nm, resulting from 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 mins at 365 nm, (Figure 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 also enhanced with a blue shift appearing at 545 nm as a big hump nearby the 479 nm peak. This new photo-generated isomer should have a less
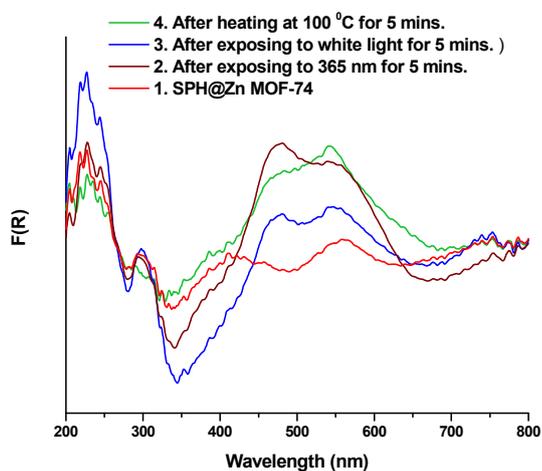
(a)
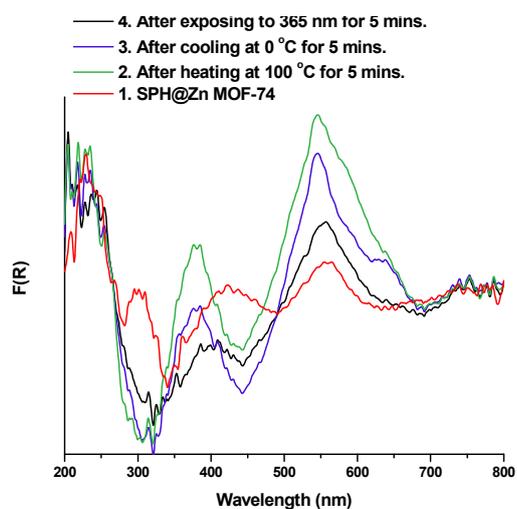
(b)

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.

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 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 hydrogens available in organic linkers of the MOF.[25,40(b)]

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

Further, since the conjugation of 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 closed SP form in the system. But, when this UV irradiated pellet was irradiated with white light again for 5 min, intensities of 479 and 545 nm peaks reduced markedly, while that of the 296 nm peak increased slightly indicating the conversion of MC isomers to SP isomers(Fig.3a; blue line). Fascinatingly, when the white light irradiated pellet was heated at 80°C for 5 mins(Fig. 3a; green line), 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 in the peak at 479 nm. The most importantly, the peak found at 296 nm, attributable to the SP form available in the system, disappeared completely after heating and a small hump appeared newly around 375 nm. These observations indicate the conversion of all molecules in the SP form to MC form.

In the next set of experiments illustrated in Fig. 3b, the pellet 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.[25(a),48-50] Besides, the peak corresponding to SP form at 296 nm disappeared completely showing the transformation of all SP form molecules to MC form. Although intensities of both peaks at 378 and 545 nm reduced noticeably upon cooling the heated sample pellet, 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 this spectrum (Figure 3b; black line). This signifies that the red MC-3 form is unable to convert to MC-2 form easily, though the intensity 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 in the dark, whereas yellow/orange crystals did not convert to red upon storing

under the same conditions. This reveals clearly that Zn-MOF-74 channels are mostly nonpolar and can stabilize the nonpolar SP form.

Conclusions

All above data clearly show that SPH moleules have diffused into the Zn-MOF-74 channels in closed, nonpolar SP form as well as in open, polar MC-1 form by producing orange crystals due to the coexistence of both forms without destroying the host crystal lattice. 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 channels of MOF-74 have provided enough space for SPH molecules to react freely within single crystals of host, as if SPH molecules were in solutions. 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 SPH molecules are randomly arranged inside the channels of the host lattice. Most importantly, SPH reactivity observed here is completely different from its reactivity in solutions, in which SPH gives red MC-3 form upon UV irradiation.[43] Yet, open coordinately unsaturated Zn metal sites available in Zn-MOF-74 and polar-nonpolar characters of 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 Zn meal centers and linker ligands on the thermochromic and photochromic activity of SPH and to study these propety changes quantitatively by encapsulating SPH into several other MOF-74 hosts with different metal centers.

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Notes and reference

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†Electronic supplementary information available (ESI): Experimental details including synthesis, encapsulation and encapsulation capacity calculation, powder XRD patterns, FTIR spectra, UV-Vis diffuse reflectance and absorbance data.

1 P. Bamfield, *Chromic Phenomena : Technological Applications of Colour Chemistry* Royal Society of Chemistry, Cambridge, 2010

2 (a) R. Pardo, M. Zayat and D. Levy, Chem. *Soc. Rev*., 2011, **40**, 672–687. (b) X. Cao, N. Wang, J. Y. Law, S. C. Joachim Loo, S. Magdassi, and Yi Long, *Langmuir*, 2014, **30**, 1710–1715. (c) W. (c) Sun, Y. Li, W. Shi, X. Zhao and P. Fang, *J. Mater. Chem*., 2011, **21**, 9263-9270. (d) P. Kiria , G. Hyettb , R. Binionsa, *Adv. Mat. Lett*., 2010, **1**, 86-105.

3 (a) R. Klajn, *Chem. Soc. Rev*., 2014, **43**, 148. (b) V. I. Minkin, *Chem. Rev*., 2004, **104**, 2751. (c) N. P. Ernsting, B. Dick, and T. A. Engeland, *Pure Appl. Chem.*, 1990, **62**(8), 1483. (d) S. Swansburg, E. Buncel, and R. P. Lemieux, *J. Am. Chem. Soc*., 2000, **122**(28), 6594.

4 S. R. Keum, M. S. Hur, P. M. Kazmaie and E. Bunce, *Can. J. Chem*., 1991, **69**, 1940.

5 X. Xie, G. A. Crespo, G. Mistlberger & E. Bakker, *Nature Chem*., 2014, **6**, 202.

6 A. Plaquet and B. Champagne, *Molecules*, 2014, **19**, 10574.

7 G. Berkovic, V. Krongauz and V. Weiss, *Chem. Rev*., 2000, **100**(5), 1741.

8 Y. Hirshberg, *J. Am. Chem. Soc*., 1956, **78**(10), 2304.

9 B. Seefeldt, R. Kasper, M. Beining, J. Mattay, J. A. J. N. Kemnitzer, K. H. Drexhage, M. Heilemanna and M. Sauer, *Photochem. Photobiol. Sci*., 2010, **210**(9), 213.

10 S. Bénard and P. Yu, *Adv. Mater*., 2000, **12**, 48.

11 J. Harada, Y. Kawazoea and K. Ogawa, *Chem. Commun*., 2010, **46**, 2593.

12 B. S. Lukyanov, A. V. Metelitsa, N. A. Voloshin, Y. S. Alexeenko, M. B. Lukyanova, G. T. Vasilyuk, S. A. Maskevich and E. L. Mukhanov,Int. *J. of Photoeng*., 2005, **7**(1), 17.

13 S. Iyengar and M.C. Biewer, *Cryst. Growth Des*., 2005, **5** (6),2043.

14 E. Berman, R. E. Fox and F. D. Thomson, *J. Am. Chem. Soc*., 1959, **81**(21), 5605.

15 R. Rosario, D. Gust, M. Hayes, *J. Springer* and A. A. Garcia, *Langmuir*, 2003, **19**(21), 8801.

16 S. Ciampi, P. K. Eggers, N. L. Haworth, N. Darwish, P. Wagner, M. L. Coote, G. G. Wallacea and C. L. Raston, *Chem. Commun*., 2015, **51**, 4815.

17 J. D. Winkler, C. M. Bowen, and V. Michelet,*J. Am. Chem. Soc.*, 1998, **120**(13), 3237.

18 K. AlexanderandH. G. Chibisov, *Chem. Phys*., 1998, **237**(3), 425.

19 Tian, J. Ren and He, *Sensors*, 2007, **7**(12), 3166.

20 (a) M. Natali, L. Soldi and S. Giordani, *Tetrahedron*, 2010, **38**(18), 7612. (b) R. T. F. Jukes, B. Bozic , F. Hartl, P. Belser, and L. De Cola, *Inorg. Chem*., **2006**, **45** (20), pp 8326.

21 A.V. Lyubimov, N. L. Zaichenko and V. S. Marevtsev, *J. of Photochem. Photobio A: Chem*., 1990, **120**(1), 55.

22 Lin andJ. Shyong, *Eur. Polym*. J.,2003,**39**(8), 1693.

23 Biewer, S. Iyengar and C. Michael, *Cryst. Growth Des*., 2005, **5**(6), 2043.

24 L. F Wang, J-W Chen, J-W Chen, *Mater. Chem. Phys*., 2012, **136**(1), 151.

25 (a) I. Casades, M. Álvaro, H. García and M. N. Pillai, *Photochem. Photobiol. Sci*., 2002, **1**, 219. (b) I. Kahle and S. Spange, *J. Phys. Chem. C ,* 2010, **114**, 15448. (c) R. Q. Albuquerque , J. Kühni , P. Belser and L. De Cola, *ChemPhysChem*,2010,**11**, 575

26 C. Schomburg, M. Wark, Y. Rohlfing, G. Schulz-Ekloff and D. Wöhrle, *J. Mater. Chem*., 2001, **11**, 2014. (b) K. D. Dubois, C. Liu, G. Li, *Chemical Physics Letters,* 2014, **598**, 53.

27 I. Casades, S. Constantine, D. Cardin, H. García, A. Gilbert and F. Márquez, *Tetrahedron,* 2000, **56**(36), 6951.

28 S. Spagnoli, D. Block, E. Botzung-Appert, I. Colombier, P. L. Baldeck, A. Ibanez , and A. Corval ,*J. Phys. Chem. B*, 2005, **109**(18), 8587.

29 S. J. Lee, S. H. Jung, S-H. Lee, W. S. Han and J. H. Jung *J. Nanosci. Nanotechnol*., 2009, **9**, 1.

30 J. L.C. Rowsell, and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**(1-2), 3

31 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**(5554), 469.

32 J-R. Li, R. J. Kuppler and H-C. Zhou, *Chem. Soc. Rev*., 2009, **38**, 1477.

33 Yan, C-X. Yang and X. Ping, *Anal. Chem*., 2011, **83**(18), 7144.

34 J.Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. B. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev*., 2009, **38**, 1450.

35 P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J-S Chang, Y. K. Hwang, V. Marsaud, P-N. Bories and L. Cynober, *Nature Mater*., 2010, **9**, 172.

36 S. R. Miller,D. Heurtaux, T. Baati, P. Horcajada, J-M. Grenèche and C. Serre, *Chem. Commun*., 2010, **46**, 4526.

37 D. Hermann, H. Emerich, R. Lepski, D. Schaniel and U. Ruschewitz*, Inorg. Chem*., 2013, **5**(52), 2744.

38 H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2003, **27**, 523.

39 M. Meilikhov, K. Yusenko and R. A. Fischer, *J. Chem. Soc., Dalton Trans*., 2009, 600.

40 S. Hermes, F. Schröder, S. Amirjalayer, R. Schmid and R. A. Fischer, *J. Mater. Chem*., 2006, **16**, 2464. (b) F. Zhang, X. Zou, W. Feng, X. Zhao, X. Jing, F. Sun, H. Rena and G. Zhu, *J. Mater. Chem.,* 2012, **22**, 25019

41 C. F. Koelsch and W. R. Workman, *J. Am. Chem. Soc*., 1952, **74,** 6288.

42 T. G. Glover, G.W. Peterson, B. J. Schindler, D. Britt, and O. Yaghi, *Chem. Eng. Sci*., 2011, **66**(2), 163.

43 (a)T.Bercovici, E. Fischer,*J. Am. Chem. Soc*., 1964, **86**(24), 5687–5688, (b) E.Fischer, Y.J.Hirshberg, *J. Chem. Soc*., 1952, 4522, (c) Y. Hirshberg and E. Fischer, ,*J. Chem. Soc*.,1954, 297.

44 Y. Hirshberg and E. Fischer, *J. Chem. Soc*., 1954, 3129.

45 P. Canepa, K. Tan, D. Yingjie, L. Hongbing, Y. J. Chabalb and T. Thonhauser, *J. Mater. Chem*. A, 2015, **3**, 986.

46 S. Das and P. K. Bharadwaj, *Cryst. Growth Des*., 2007,**7**(6), 1192 (b) H. Kim, H. Chun, G. H. Kim, H. S Leeb and K. Kim, *Chem. Commun*., 2006, 2759. (c) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai and M. Fujita, *nature protocols,* 2014, **9**, 246. (d) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, *NATURE* 2013, **495**, 461

47 J. C. Wohl and D. Kuciauskas, *J. Phys. Chem*. B 2005, **109**, 22186

48 C. F. Koelsch, *J. Org. Chem*., 1951, **16**, 1362.

49 J. H. Day, *Chem.Rev*., 1962, 65.

50 X. Q. Song, J. W. Zhou, Y. T. Li and Y. W. Tang, *J. Photochem. Photobiol., A*, 1995, **92**, 99.