

## Electronic Supporting Information

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

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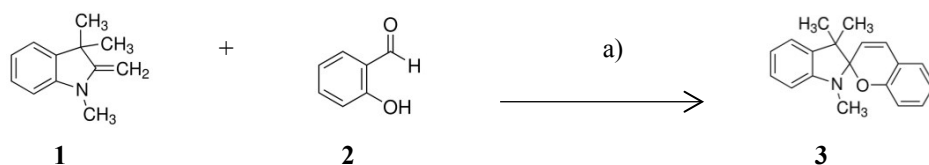
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**General :** Powder X-ray Diffraction patterns were collected on a SEIMENS D-5000 Diffractometer. The scattering intensity was measured over an angular range of  $3^\circ < 2\theta < 30^\circ$  with a step-size of  $(2\theta) = 0.02^\circ$ .  $^1\text{H}$  NMR spectrum of the SPH was recorded on a Varian 300 MHz Mercury VX powered spectrometer in  $\text{CDCl}_3$ . Diffuse reflectance UV-Vis spectra were recorded using a SHIMADZU UV-2450 UV-Vis spectrophotometer fitted with Praying Mantis accessory for 10% solid samples in  $\text{BaSO}_4$  after various treatments. Then the reflectance data were converted to absorbance data by the Kubellka Munk function. FT-Infrared spectroscopy studies were carried out on a SHIMADZU IR Prestige-21 spectrometer in the  $4000 - 400 \text{ cm}^{-1}$  region and taken as a 5% sample in KBr disk. The ultraviolet source of irradiation was a 150 W high-pressure mercury lamp obtained with a maximum at 365 nm. The colour changing temperature of encapsulated crystals was measured using IR thermometer Horiba IT-340. The crystal images were taken with a light microscope. The UV-Vis absorption data in solutions were collected using SHIMADZU Model UV-1800 UV-Vis spectrophotometer; MeOH and hexane were used as the respective polar and nonpolar solvents.

### Materials

1,3,3-Trimethyl-2-methyleneindoline (97%), Salicylaldehyde (98%), 2,5-Dihydrodyterephthalic acid (95%), N,N-Dimethylformamide,  $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$  were purchased from Sigma-Aldrich. All commercially obtained reagents were used as received. Absolute ethanol was analytical grade and distilled prior to use.

## Synthesis of 1',3',3'-trimethylspiro-[2H-1-benzopyran-2-2'-indoline] or SPH (**3**)



**Scheme S1.** Synthesis of **3**. Reagents and conditions: a) EtOH, reflux, 2 h.

Compound **3**(SPH) was synthesized according to the method described in literature with some modifications.<sup>1</sup> A solution of 1,3,3-Trimethyl-2-methyleneindoline (**1**) (1.77 mL, 10 mmol) in 10 mL ethanol was added drop wisely over 30 minutes of period into a solution of Salicylaldehyde (**2**) (1.07 mL, 10 mmol) in 10 mL of ethanol in 100 ml round bottom flask. Then the reaction mixture was refluxed over 2 hrs and cooled down to ambient temperature. The precipitate was filtered and washed with cold ethanol. The mother liquor and washings were collected and the solvent was evaporated with a rotary-evaporator to give a crude compound. The crude was washed several times with cold ethanol and recrystallized from ethanol to obtain light yellow rhomboidal shape crystals (1.6100 g, 58.08%). m.p. was 84-86 C.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): = 1.18 (s,3H,CH<sub>3</sub>), 1.33 (s, 3H, CH<sub>3</sub>), 2.75 (s,3H,NCH<sub>3</sub>), 6.52 (d,1H, J=9.75, CH ethylene), 6.70 (d,1H, J=9.75, CH ethylene), 6.82 (d,1H,J=4.5,aro), 6.85 ( d,1H,J=9.75,aro), 7.02 ( t,1H, J=6.00,aro), 7.06 ( d,1H, J=8.52, aro), 7.10 ( d,1H,J=3.75, aro), 7.15 (d,1H,J=3.00, aro), 7.17 ( d,1H,J=2.25,aro), 7.19 ( d,1H,J=1.50,aro).

FT-IR (cm<sup>-1</sup>): 890 C=CH, 955 O-C-N, 1025 C-C-N bend, 1089 C-O ester, 1100 C-O ester, 1164 C-O-C asymmetric stretching, 1250 C-O-C symmetric stretching, 1300 C-N (30), 1650 C=C.

### Synthesis of Zn MOF-74

Zn MOF-74 was prepared and activated according to the reported procedure.<sup>2</sup> Pure Zn MOF-74 was characterized using PXRD, FT-IR spectroscopy.

### Encapsulation of the SPH into Zn MOF-74 cavities

Encapsulation of the SPH was carried out by refluxing Zn MOF-74 (50 mg) and SPH (10 mg) in 10.00 mL of chloroform for 4 hours. After completion of the encapsulation,

suspension was filtered through a Büchner funnel with a sintered glass disc and the orange yellow residue of SPH@Zn-MOF-74 crystals were collected on the funnel and washed with 10 mL of chloroform. Powder X-ray diffraction data and FTIR data were collected to confirm the successive encapsulation. Diffuse reflectance UV-Vis spectra were recorded to study the photochromic and thermochromic behavior of SPH in Zn-MOF-74. Attenuated total reflectance spectra were obtained for pure and encapsulated samples to identify the host-guest interactions.

### **Investigation of the effects of acidity and basicity on the SPH in polar/non-polar solutions**

First 4 mM of SPH solutions in MeOH and Hexane were prepared. Then 1M HCl and 1M NaOH solutions were prepared. The effects of acids and bases in polar medium were studied by preparing following solution mixtures:

	4 mM SPH/ $\mu$ L	1M HCl solution/ $\mu$ L	Total amt of MeOH added /mL	Acid concentration/ $\mu$ M
Initial SPH solution in MeOH	10.00	-	5 mL+100 $\mu$ L	-
SPH in low acidic solution	10.00	10.00	5 mL+ 90 $\mu$ L	1.70
SPH in high acidic solution	10.00	50.00	5 mL+ 50 $\mu$ L	8.33

The effect of base in polar and non-polar media and the effect of acid in non-polar medium were studied by preparing solutions with similar concentrations as given above.

### **Calculation of encapsulation capacity of SPH**

50 mg of Zn MOF-74 was refluxed with 10 mg of SPH in chloroform media for 4 hrs. Then the encapsulated Zn MOF-74 crystals were separated from the mother liquor using a

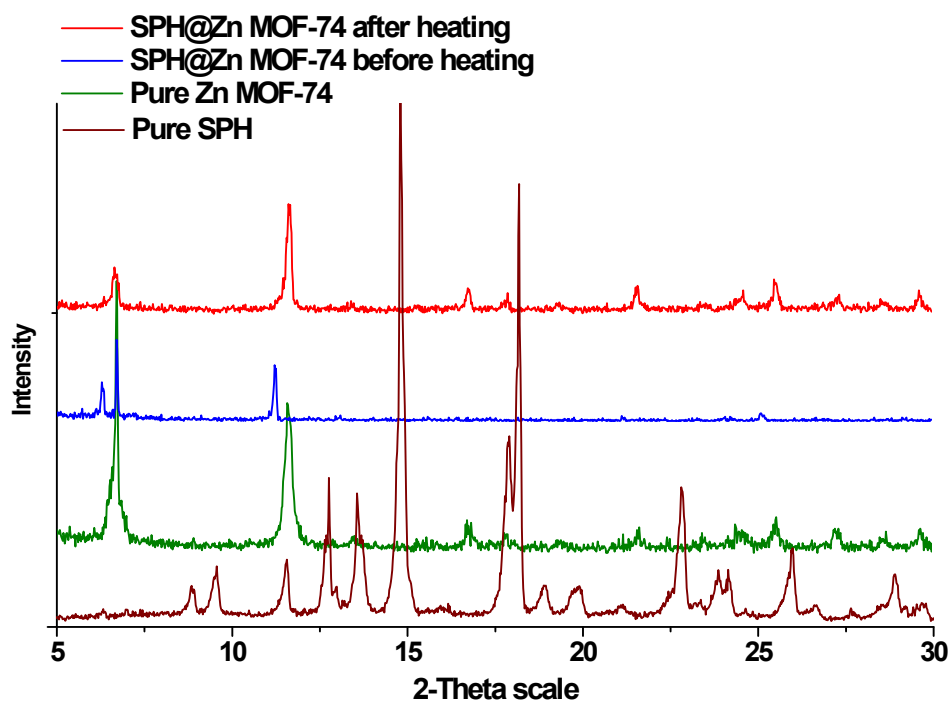
scintillated glass crucible. After that the encapsulated crystals were washed several times with chloroform to remove the encapsulated SPH and each washing was collected to a pre-weighed flask and evaporated the solvent and dried in an oven at 70 °C until obtained a constant weight. Finally, the % encapsulation capacity was calculated using the equation given below. The procedure was repeated for two trials and the average was taken as the % encapsulation capacity of the SPH.

$$\% \text{ of SPH encapsulated} = \frac{\text{Amount de-encapsulated from the Zn MOF-74}}{\text{Total amount used for encapsulation}} \times 100\%$$

**Table.01. Calculated values for encapsulation capacity of SPH**

Trial	Amount de-encapsulated/ g	Encapsulation capacity
01	0.005	50%
02	0.006	60%
Average encapsulation capacity		55%

#### Powder X-ray diffraction patterns



**Fig S1.** PXRD patterns of pure SPH, pure Zn MOF-74 and SPH@Zn MOF-74 before heating and after heating.

## FT-IR spectra of pure compounds

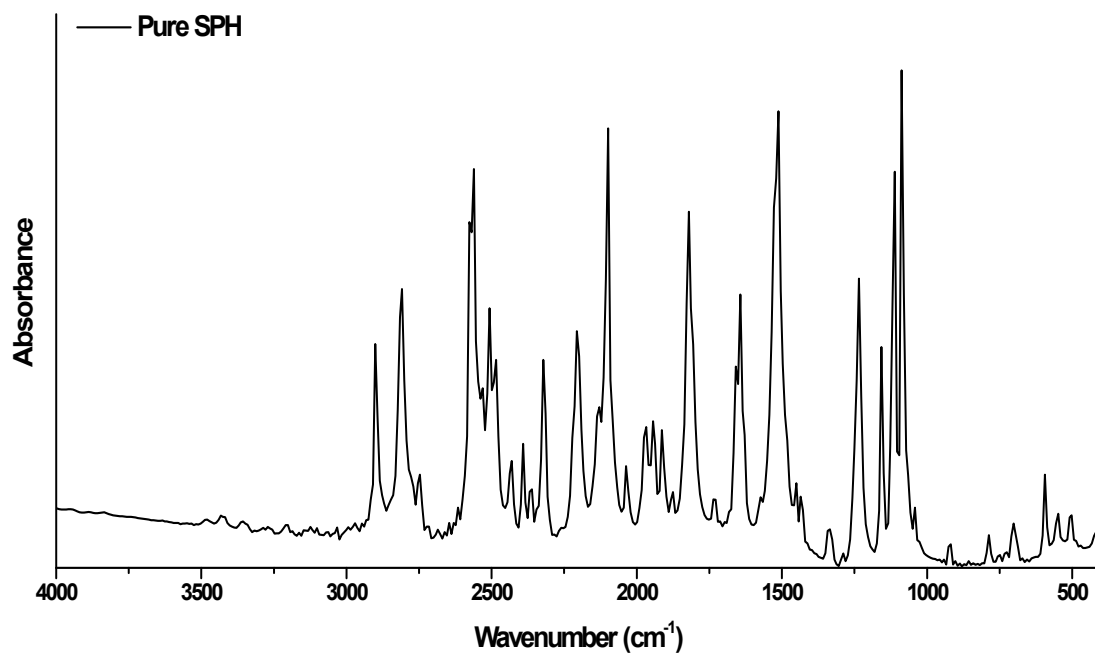


Fig. S2. FT-IR spectra of pure SPH.

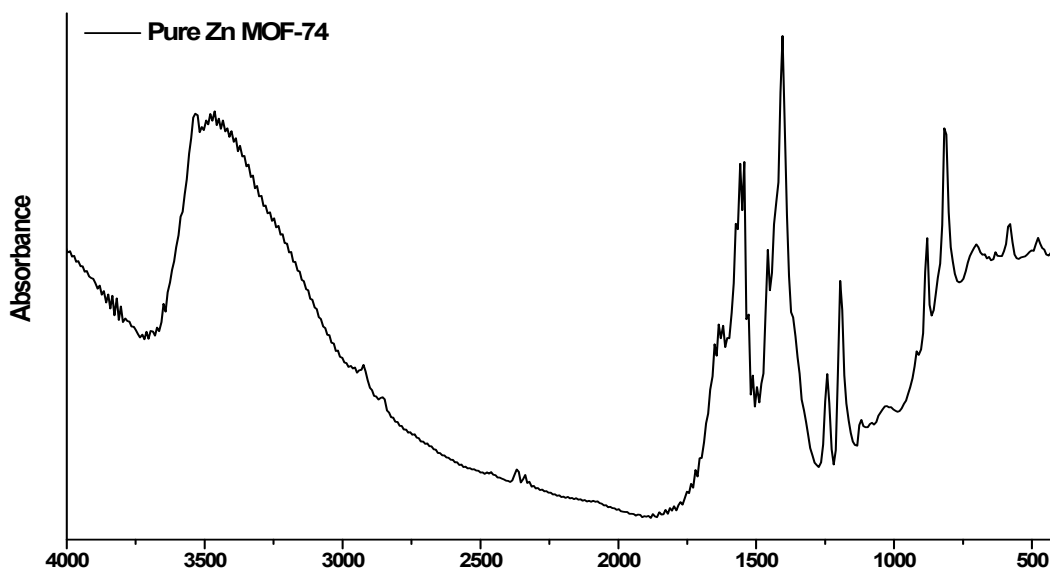


Fig S3. FT-IR spectra of pure Zn MOF-74 before encapsulation.

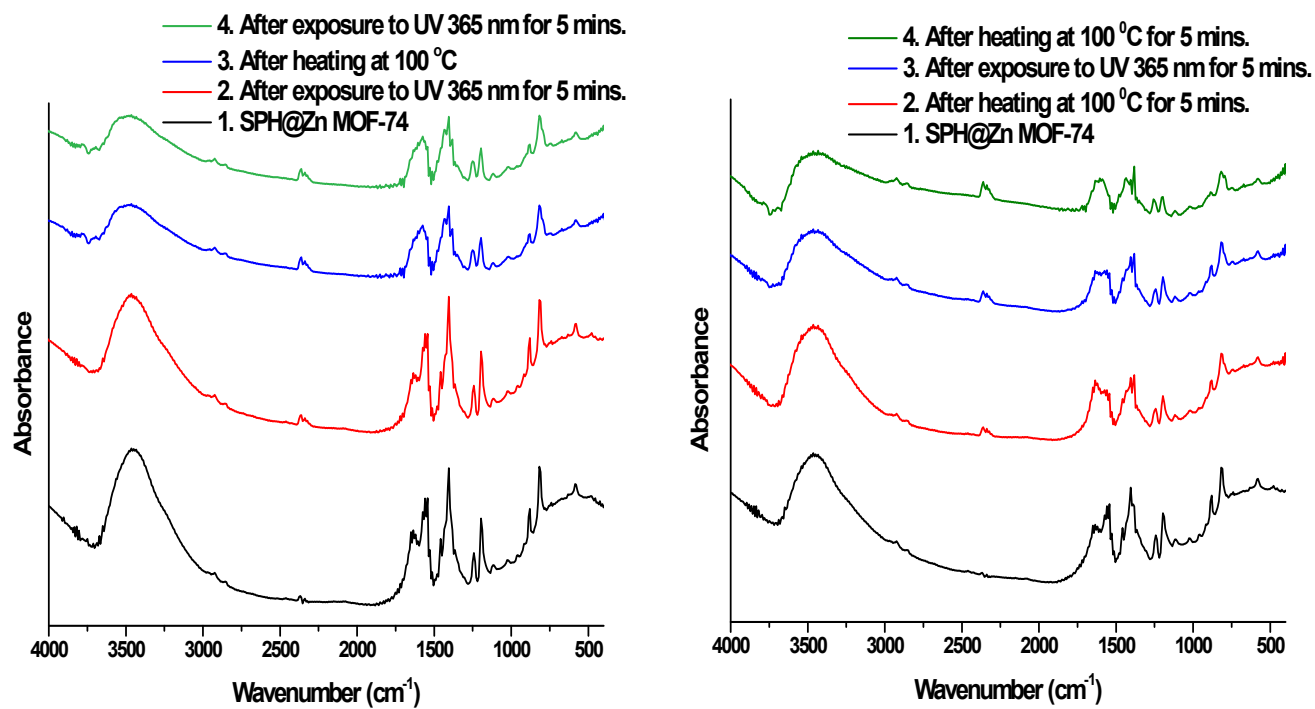


Fig. S4. FT-IR spectra of SPH@MOF-74 after UV irradiation (left) and after heating (right).

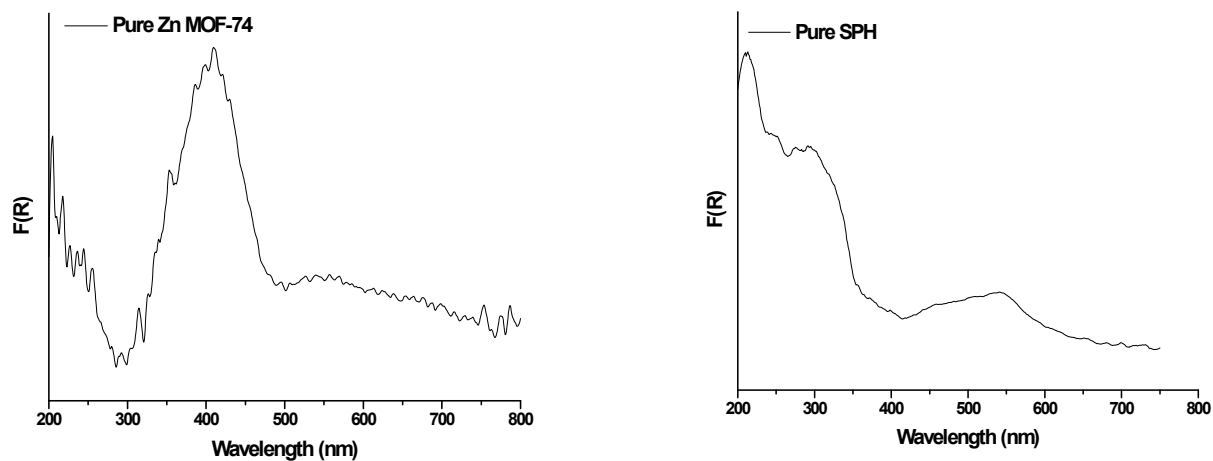
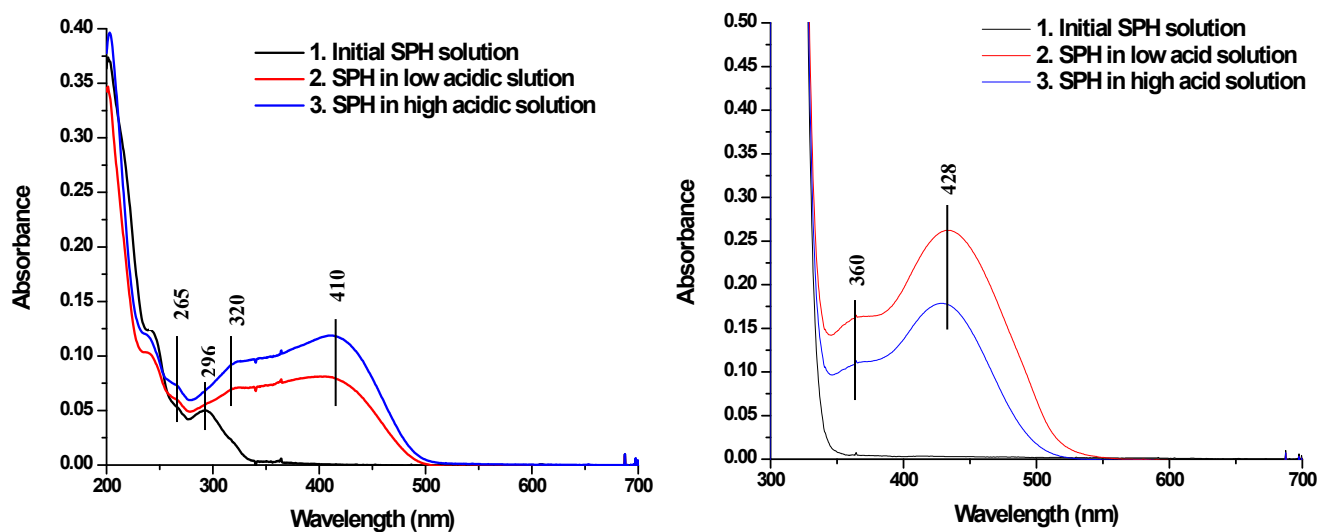


Fig. S5. Solid state UV-Vis spectra of pure Zn MOF-74 (left) and Pure SPH (right).



**Fig. S6.** UV-Vis spectra of 0.007  $\mu\text{M}$  SPH in MeOH, spectral changes after adding 1.70  $\mu\text{M}$  and 8.33  $\mu\text{M}$  HCl (left) and UV-Vis spectra of 0.007  $\mu\text{M}$  SPH in hexane, spectral changes after adding 1.70  $\mu\text{M}$  and 8.33  $\mu\text{M}$  HCl (right).

## References:

- (1) C.F. Koelsch, and W.R Workman, *J. Am. Chem. Soc.* **1952**, 74, 6288-6289.
- (2) T. G. Glover, G. W. Peterson, B. J. Schindler, D. Britt, and O. Yaghi, *Chemical Engineering Science*, **2011**, 66, 163-170.