Electronic Supplementary Information (ESI)

A microporous metal-organic framework with FeS_2 topology based on [$Zn_6(\mu_6$-O)] cluster for reversible sensing of small molecules

Jiehu Cui, Zhenzhong Lu, Yizhi Li, Zijian Guo, Hegen Zheng *

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, National Laboratory of Microstructures, Nanjing niversity, Nanjing 210093, P.R. China. E-mail: zhenghg@nju.edu.cn. Fax: 86-25-83314502.

Contents **Page**

Experimental Details

The luminescent spectra were recorded on WGY-10 spectrometer. IR absorption spectra of the complexes were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H, and N analyses were carried out with a Perkin–Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu–Kα radiation (λ = 1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA. Solid-state UV–vis diffuse reflectance spectra was obtained at room temperature using a Shimadzu UV-3600 double monochromator spectrophotometer, and $BaSO_4$ was used as a 100% reflectance standard for all materials. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The emission decay lifetimes were measured on Edinburgh instruments FLS920 fluorescence spectrometer. The as-synthesized samples were characterized by thermogravimetric

analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min^{-1} under N_2 atmosphere.

The vapor fluorescence quenching experiments by THF, methanol and ethanol were monitored following a similar method.[1,2]

Synthesis

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (33.4 mg, 0.1 mmol), TCOPM (37.6 mg, 0.1 mmol) was dissolved in 8 mL solution of DMF/H_2O (3:1, v/v) containing 1,4-bis(5-tetrazolyl) benzene. The final mixture was placed in a Parr Teflon-lined stainless steel vessel (10 mL) under autogenous pressure and heated at 85 °C for 3 d, then cooled down to the room temperature at 1 ^{0}C/min. A large quantity of pinky crystals $[Zn_{12}(\mu_6\text{-}O)_2(TCOPM)_4] \cdot 3H_2O \cdot 8NO_3 \cdot 8DMF$ (**1**⊃DMF) were obtained, which were washed with mother liquid, and dried under ambient conditions (Yield: 49% based on Zn). Anal. Calcd for $C_{111}H_{114}N_{16}O_{61}Zn_{12}$: C, 38.83, H, 3.34, N, 6.52; found: C, 39.07, H, 3.15, N, 6.41. IR (KBr, cm^{-1}): 3414(w), 3115(w), 2960(s), 1655(s), 1589(s), 1533(s), 1396(s), 1255(m), 1183(s), 1100(w), 839(w), 779(w), 665(m), 524(s). **1**⊃DMF was dipped in toluene, **1**⊃toluene was isolated. The activated **1**⊃DMF was obtained by heating **1**⊃DMF at 220 °C overnight under vacuum.

Gas adsorption of 1⊃DMF

Gas adsorption measurements were

performed using an ASAP 2020 M gas adsorption analyzer. UHP-grade gases were used in measurements. The hydrogen sorption isotherms were collected in the pressure range from 10^{-4} to 850 mmHg at 77 K in a liquid nitrogen bath. The gas sorption experiments of CO_2 and CH_4 at 273 K was carried out in an ice-water bath. The activated **1**⊃DM can be achieved by outgassing the sample at 220 °C overnight under vacuum. 70.5 mg activated ample was used for all gas adsorption measurements.

Synthesis of Na_3(TCOPM):

H_3TCOPM (2 mmol) was added to H_2O (8 ml) to form an aqueous solution, which

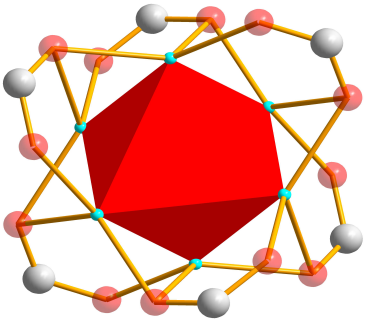
was then neutralized by NaOH (3 ml, 2M). The resultiong solution was heated, and Na_3(TCOPM) was separated out as a solid precipitate.

Reference: 1. T. Naddo, Y. Che, W. Zhang, K. Balakrishnan, X. Yang, M. Yen, J. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 6978. 2. Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* 1998, **120**, 11864-11873.

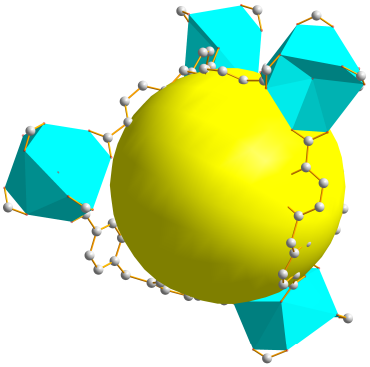
Table 1. Crystallographic data and structure refinement details for **1**⊃DMF and **1**⊃toluene.

compound	**1**⊃DMF	**1**⊃toluene
empirical formula	$C_{88}H_{58}N_8O_{53}Zn_{12}$	$C_{88}H_{58}N_8O_{53}Zn_{12}$
formula weight	2860.35	2859.99
crystal system	cubic	cubic
space group	$Ia\bar{3}$	$Ia\bar{3}$
a (Å)	22.5150(9)	22.5597(12)
b (Å)	22.5150(9)	22.5597(12)
c (Å)	22.5150(9)	22.5597(12)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Z	4	4
V (Å^3)	11413.4(14)	11481.5(11)
D_{calcd}(g cm^{-3})	1.665	1.655
μ(Mo Ka)(mm^{-1})	2.567	2.552
F(000)	5704.0	5704.0
R(int)	0.0844	0.0362
observed data [$I > 2\sigma(I)$]	1873	1620
R1,wR2 ($I > 2\sigma(I)$)	0.0398/0.1123	0.0351/0.0869
S	1.036	1.062

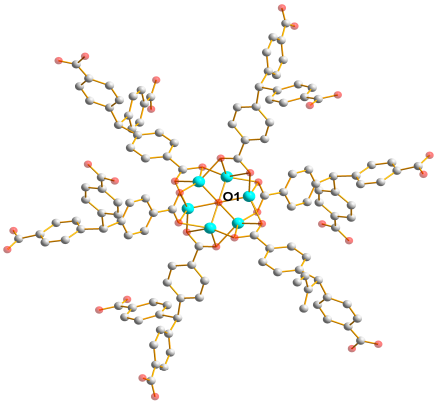
(a)



(b)



(c)



(d)

(e)

Figure S1. (a) The photo of as-made **1**⊃DMF**.** (b) - (e) are coordination environment of the Zn(II) ion in **1**⊃DMF. The hydrogen atoms are omitted for clarity.

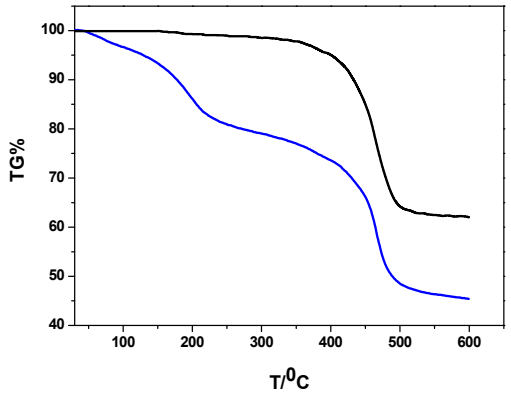


Figure S2. The curve of TGA of **1**⊃DMF (blue) and the activated **1**⊃DMF (black)**.**

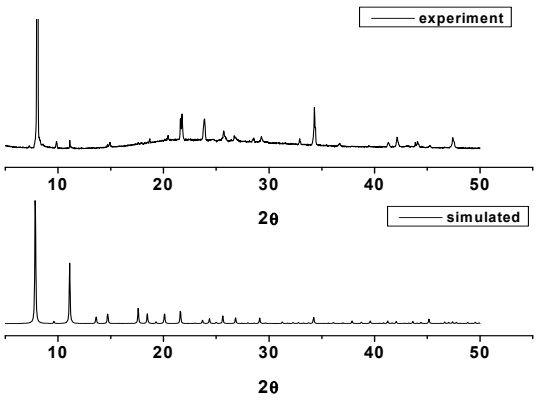


Figure S3. Powder x-ray diffraction patterns of stimulated and **1**⊃DMF.

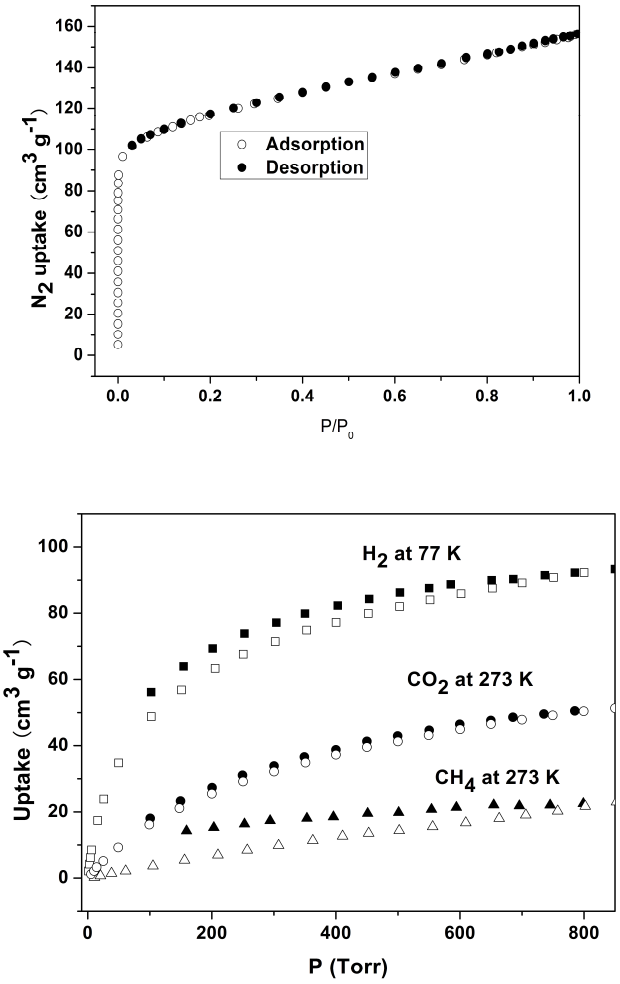


Figure S4. (a) N_2 gas adsorption and desorption isotherms of **1**⊃DMF. (b) H_2, CO_2 and CH_4 gas adsorption and desorption isotherms of **1**⊃DMF.

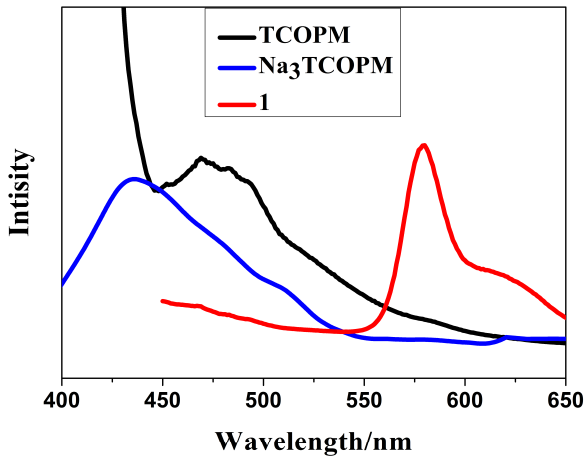


Figure S5. PL emission spectra measured of H3TCOPM (black), Na3TCOPM (blue) and 1⊃DMF (red) at room temperature.

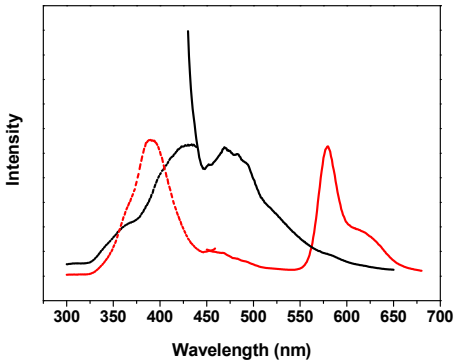


Figure S6. The solid PL excitation (dashed) and emission spectrum (solid) of H_3TCOPM (black) and **1**⊃DMF (red) at room temperature.

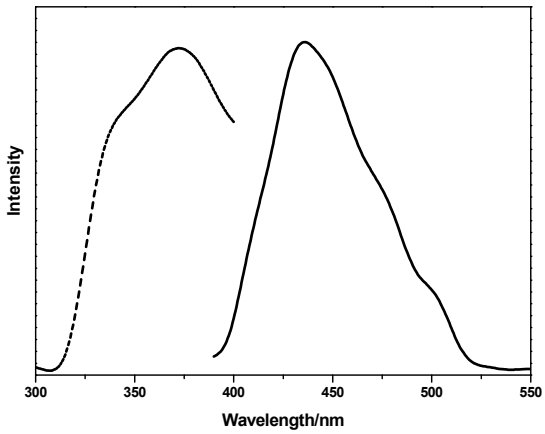


Figure S7. The solid PL excitation (dashed) and emission spectrum (solid) of Na_3TCOPM at room temperature.

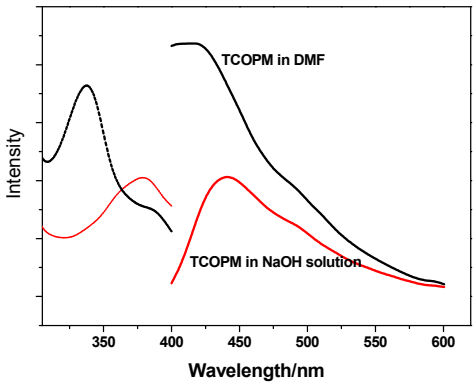


Figure S8. The PL excitation (dashed) and emission spectrum (solid) of H_3TCOPM in DMF or in

NaOH solution at room temperature.

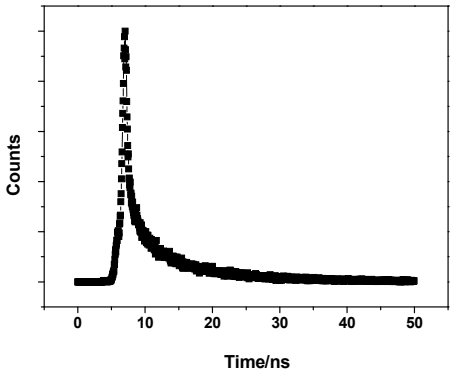


Figure S9. The emission decay lifetime of H_3TCOPM**.**

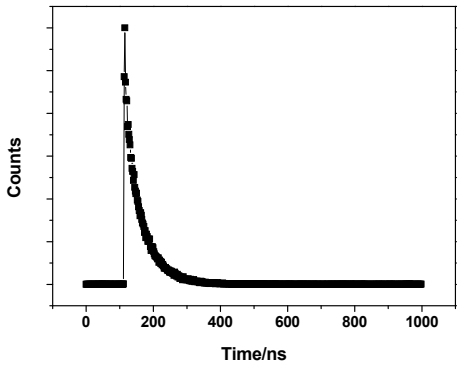


Figure S10. The emission decay lifetime of **1**⊃DMF**.**

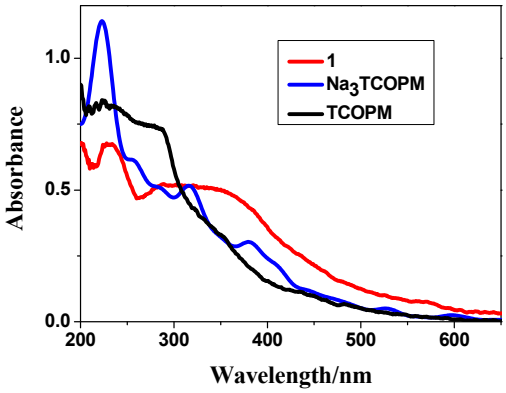


Figure S11. The solid UV spectra of H_3TCOPM (black), Na_3TCOPM (blue) and **1**⊃DMF (red).

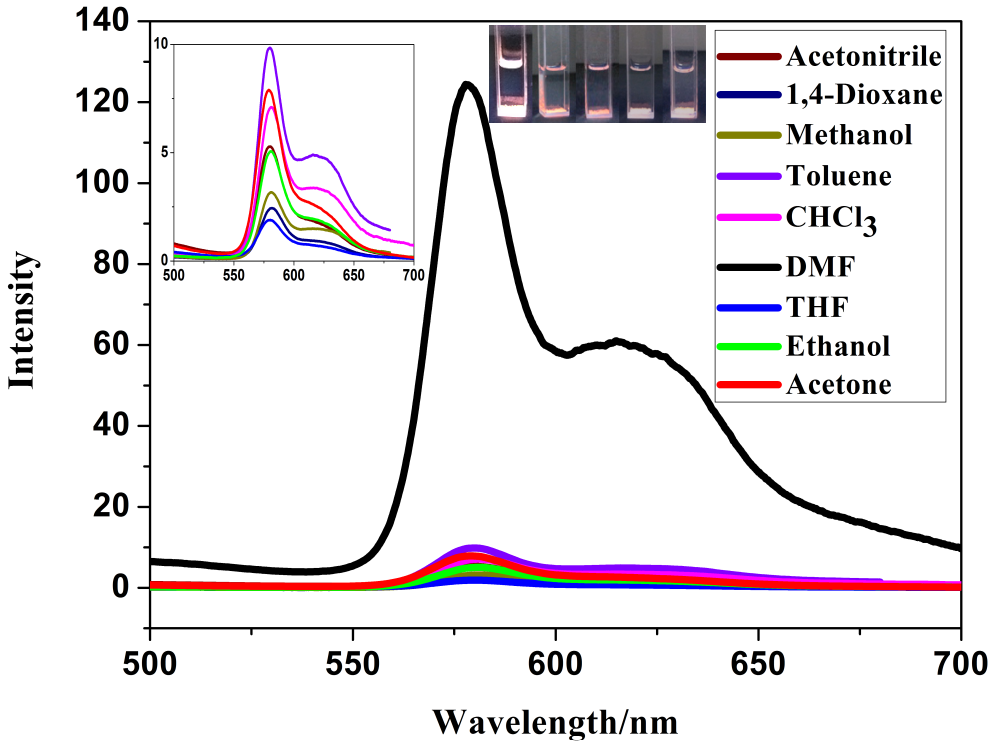


Figure S12. The PL spectra of **1** introduced to various pure solvent when excited at 390 nm and the photo of the PL: toluene, $CHCl_3$, methanol, THF from left to right under UV light at 365 nm. (The inset shows and the PL spectra of **1** in DMF, toluene, $CHCl_3$, methanol, THF solvents).

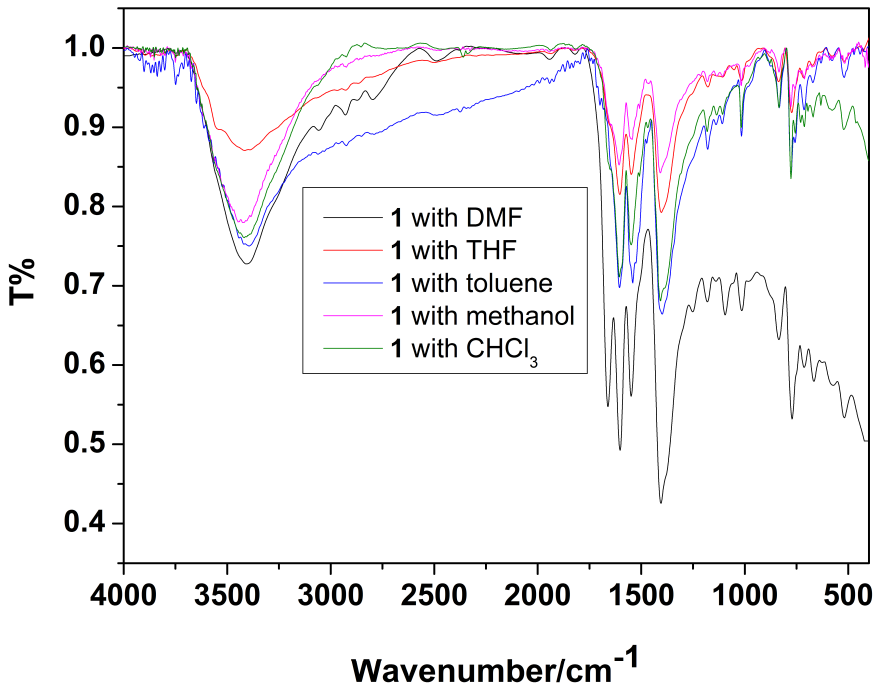
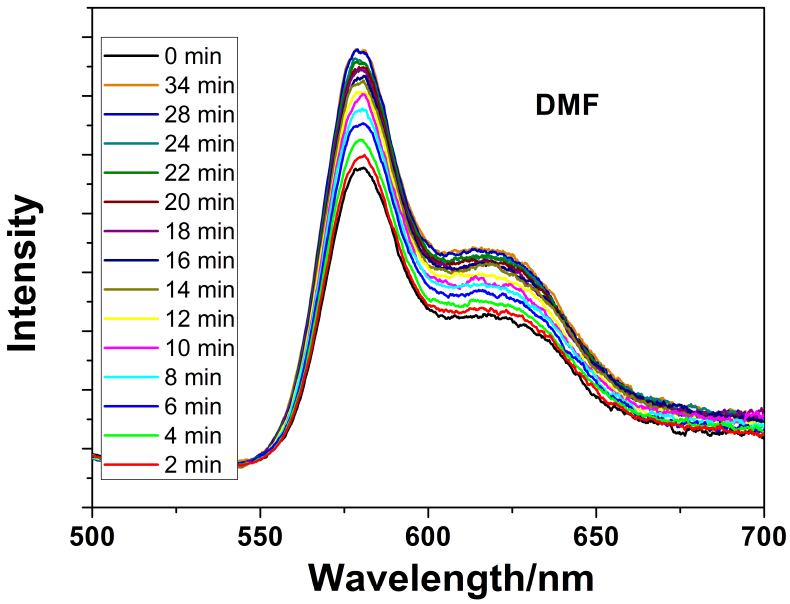
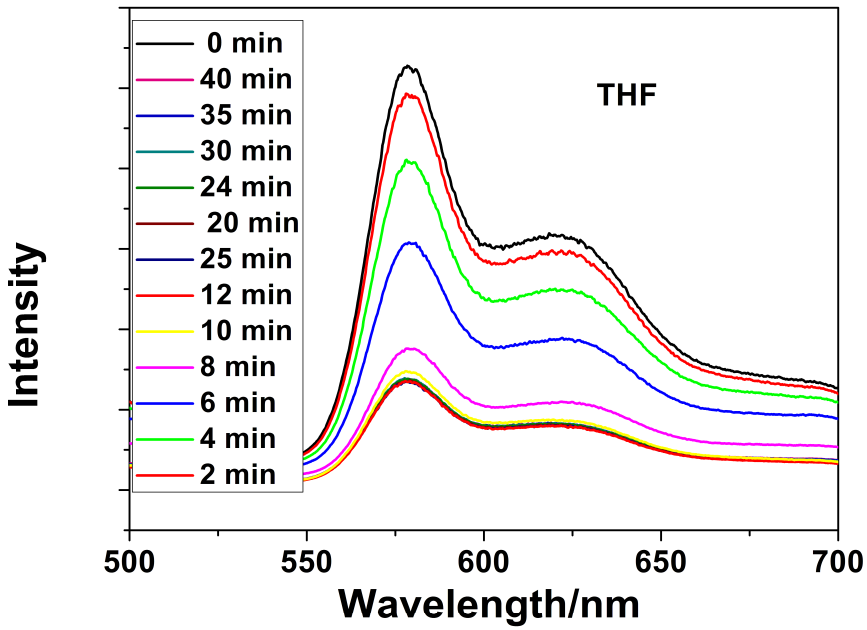
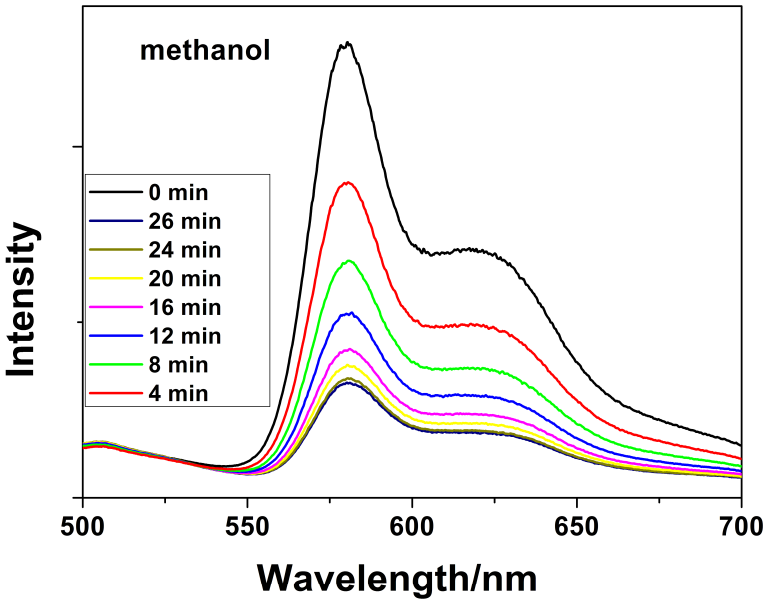


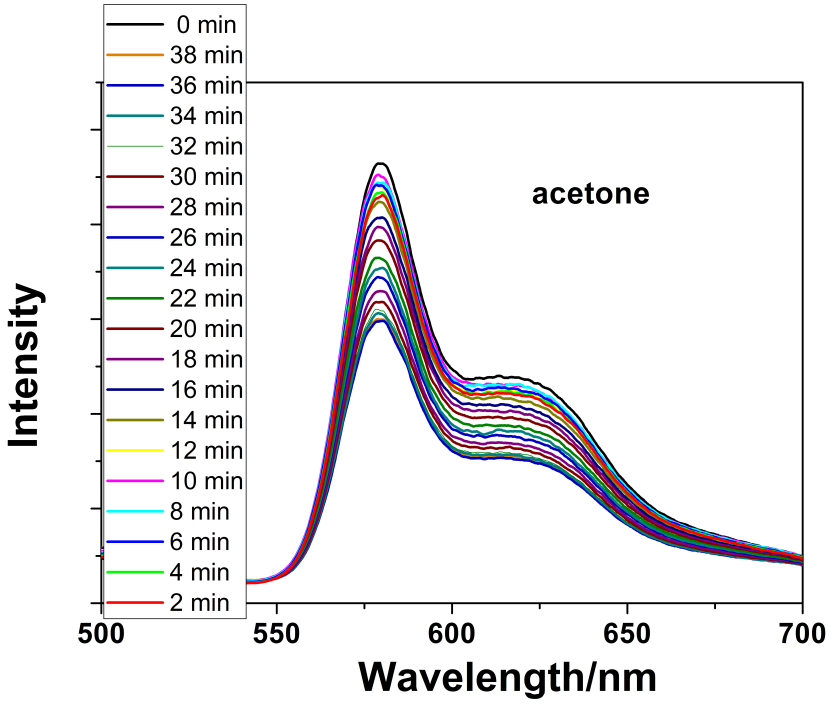
Figure S13. FT-IR spectroscopy of **1**⊃DMF (black), **1**⊃toluene (blue), **1**⊃methanol (pink), **1**⊃

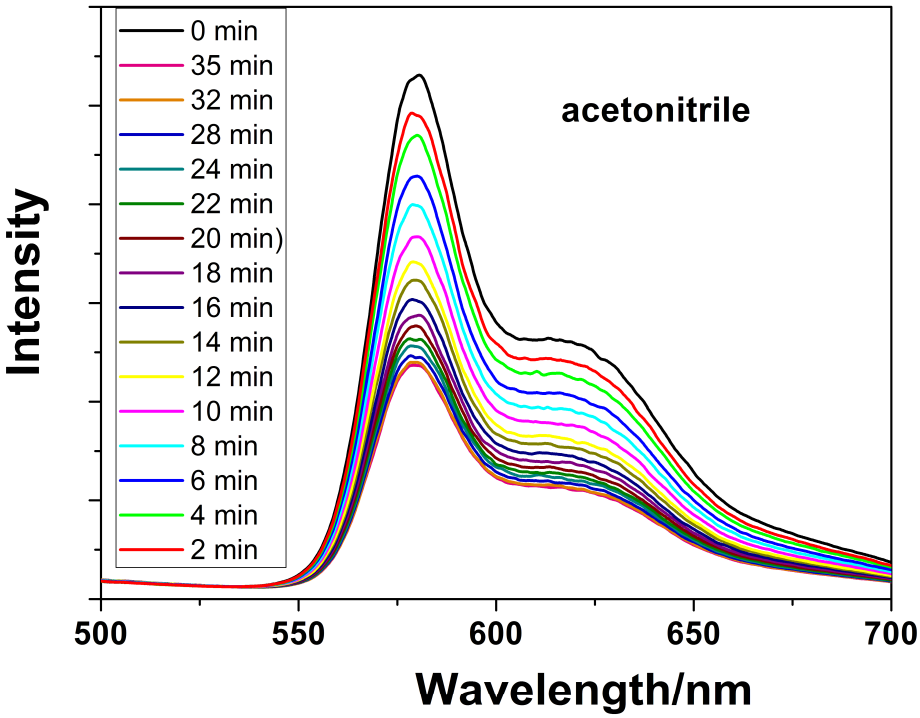
$CHCl_3$ (green) and **1**⊃THF (red). The disappearance of the strong peak at 1659 cm^{-1}(C=O stretching peak of DMF) indicates the exchanging of DMF.

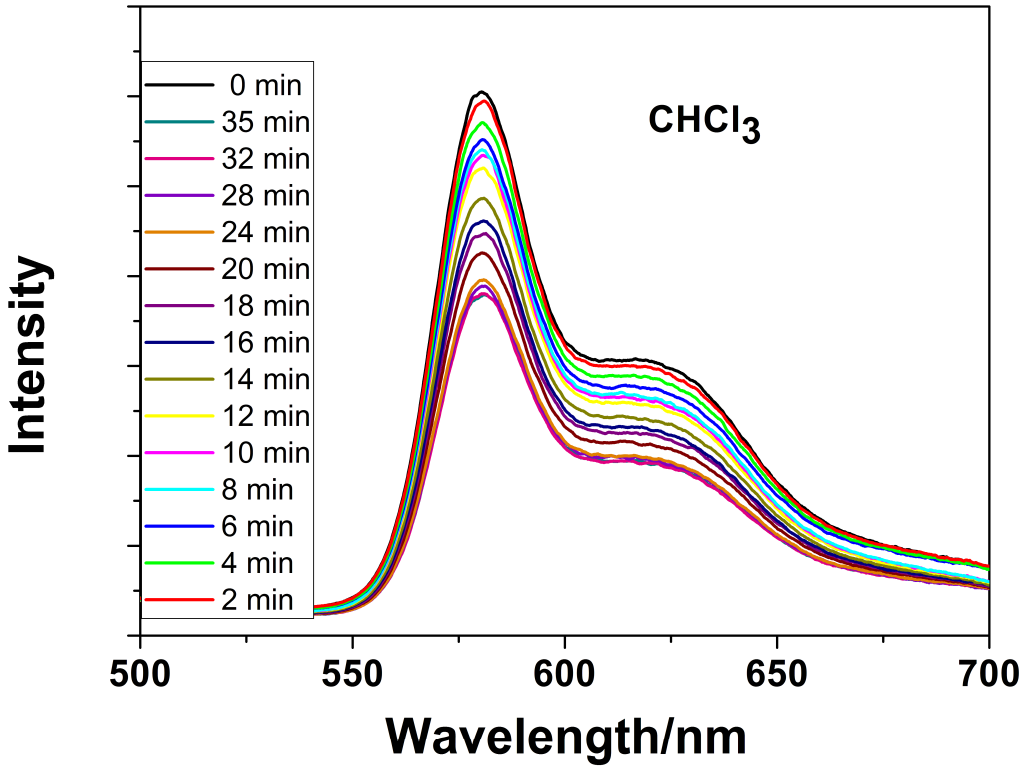





methanol
0 min
26 min
24 min
20 min
16 min
12 min
8 min
4 min
Intensity
500
550
600
650
700
Wavelength/nm


0 min
38 min
36 min
34 min
32 min
30 min
28 min
26 min
24 min
22 min
20 min
18 min
16 min
14 min
12 min
10 min
8 min
6 min
4 min
2 min
acetone
Intensity
500
550
600
650
700
Wavelength/nm


0 min
35 min
32 min
28 min
24 min
22 min
20 min)
18 min
16 min
14 min
12 min
10 min
8 min
6 min
4 min
2 min
acetonitrile
Intensity
500
550
600
650
700
Wavelength/nm


0 min
35 min
32 min
28 min
24 min
20 min
18 min
16 min
14 min
12 min
10 min
8 min
6 min
4 min
2 min
CHCl3
Intensity
500
550
600
650
700
Wavelength/nm

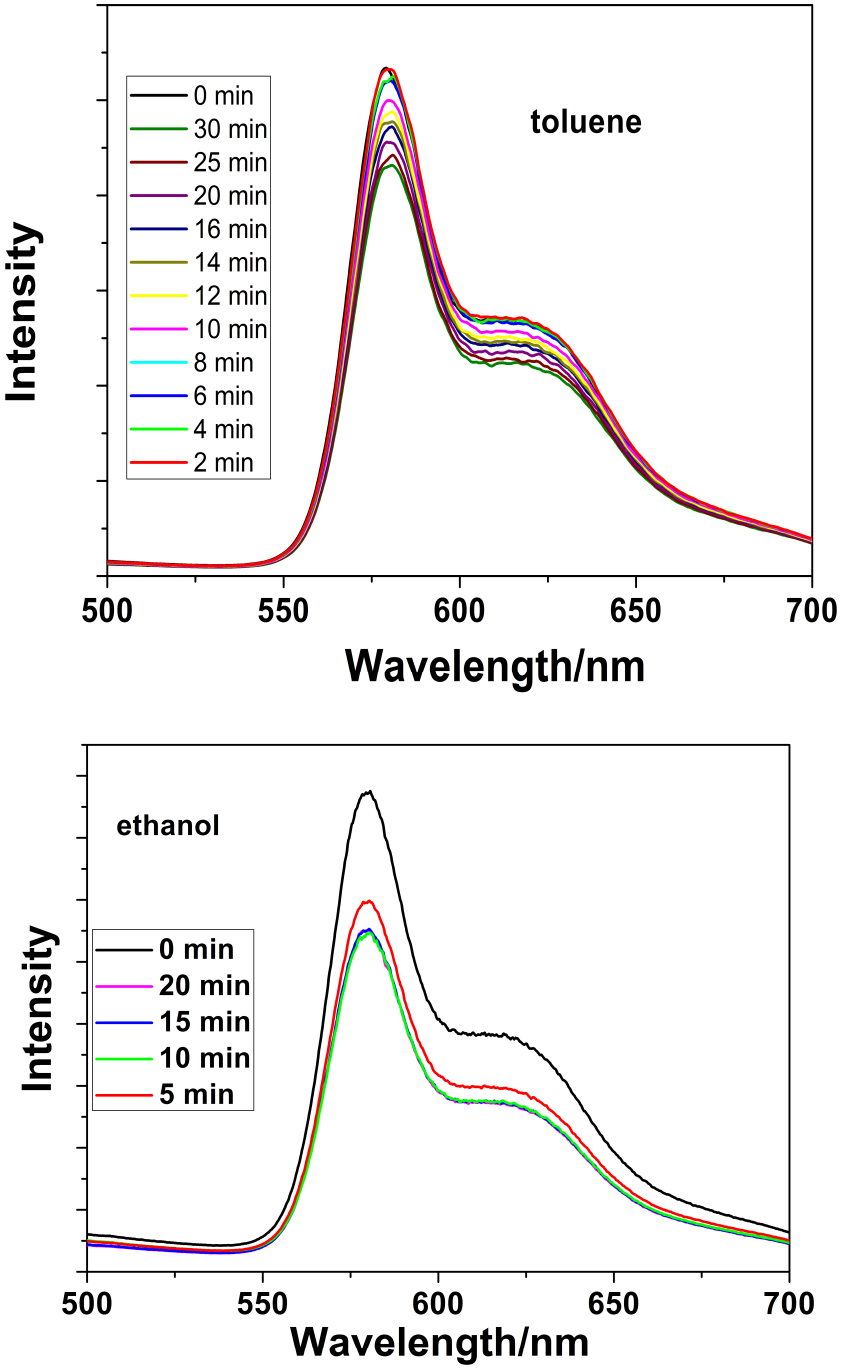


Figure S14. Emission spectra of **1**⊃DMF upon exposure to the vapor of DMF, toluene, acetone, $CHCl_3$, acetonitrile, ethanol, methanol, 1,4-dioxane and THF at various tine intervals.

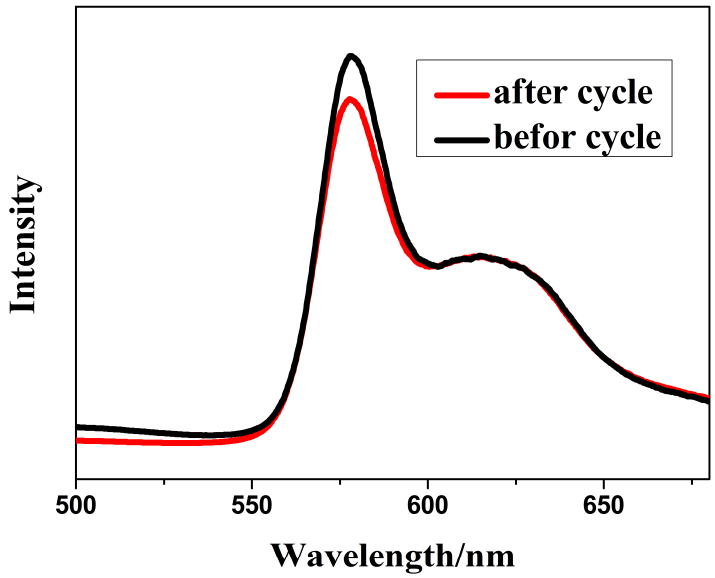


Figure S15. The PL spectra of **1**⊃DMF after four cycles at λ_{ex} = 390 nm.

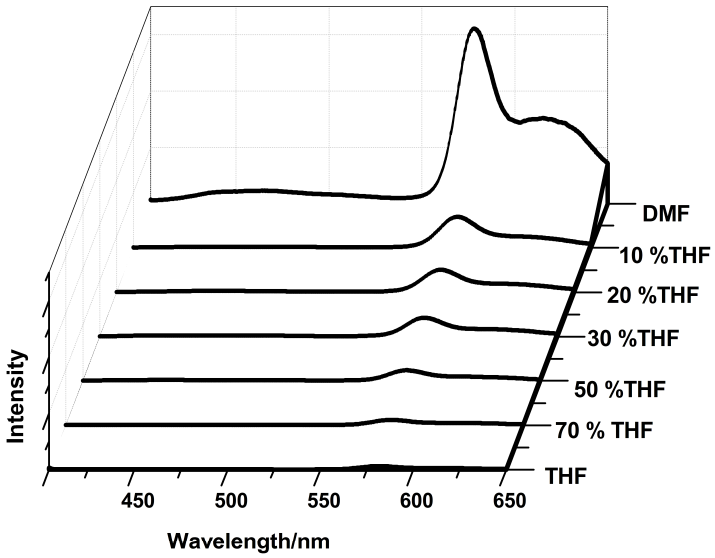


Figure S16. The PL spectra of 1 ⊃DMF in the presence of various volumes THF in DMF (excited at 390 nm)

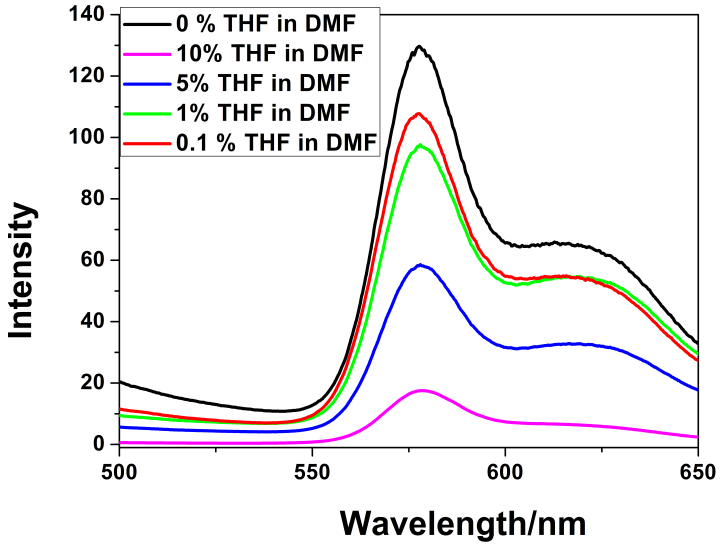


Figure S17. The PL spectra of **1**⊃DMF in the presence of various volumes (10%, 5%,1%, 0.1% and 0%) THF in DMF (excited at 390 nm).

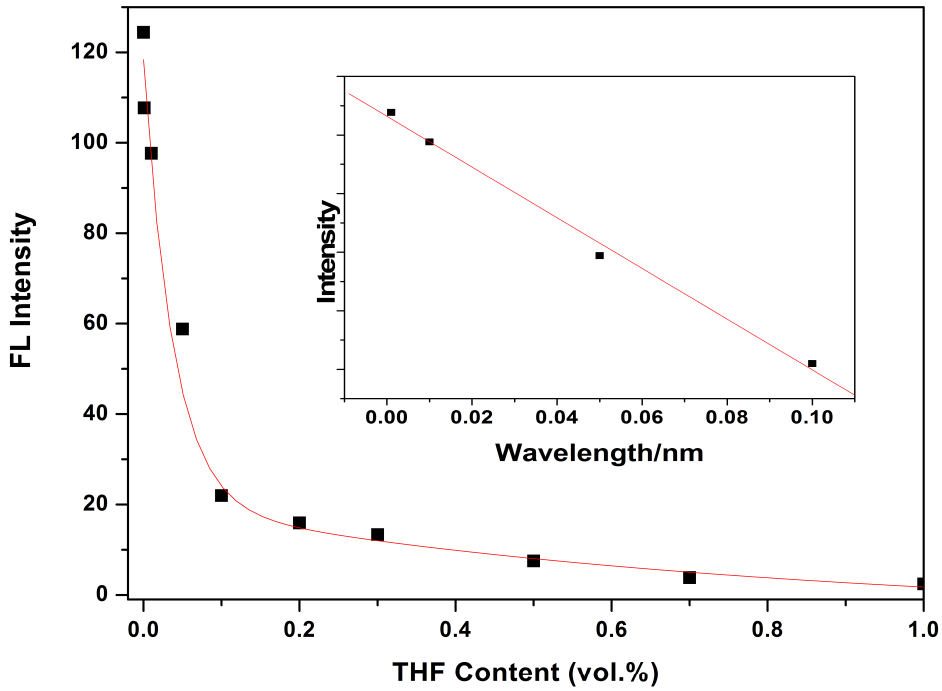


Figure S18. The PL intensity of **1**⊃DMF as a function of THF content in DMF. The inset shows the emission quenching linearity relationship (detection limit) of **1**⊃DMF between 0.1% and 1% (volume proportion).

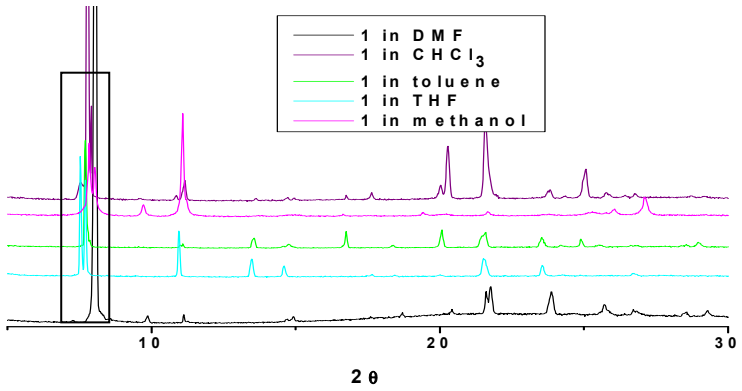


Figure S19. Powder x-ray diffraction patterns of **1**⊃DMF in different solvents.

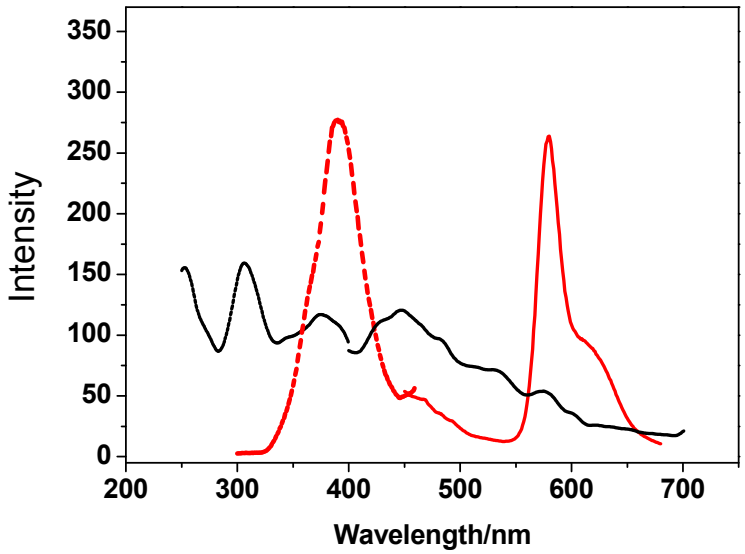


Figure S20. The PL excitation (dashed) and emission spectrum (solid) of **1**⊃DMF(red) the activated **1**⊃DMF(black).

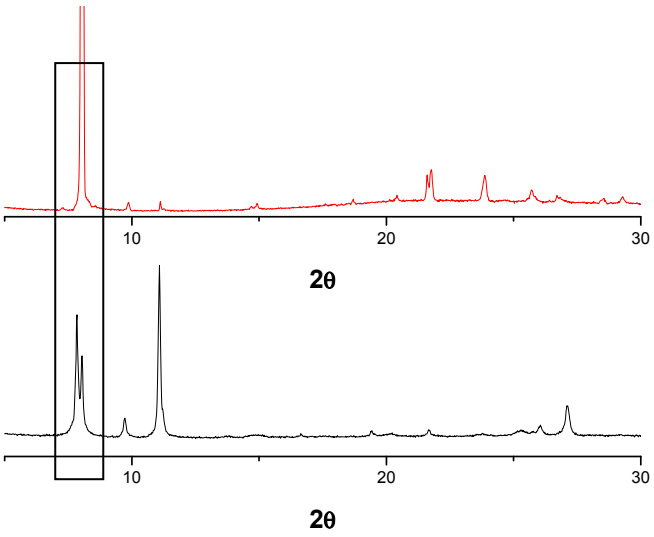


Figure S21. Powder x-ray diffraction patterns of **1**⊃DMF (red) and the activated **1**⊃DMF (black).