

Supporting Information

A Dual Functional MOF as Luminescent Sensor for Quantitatively Detecting the Concentration of Nitrobenzene and Temperature

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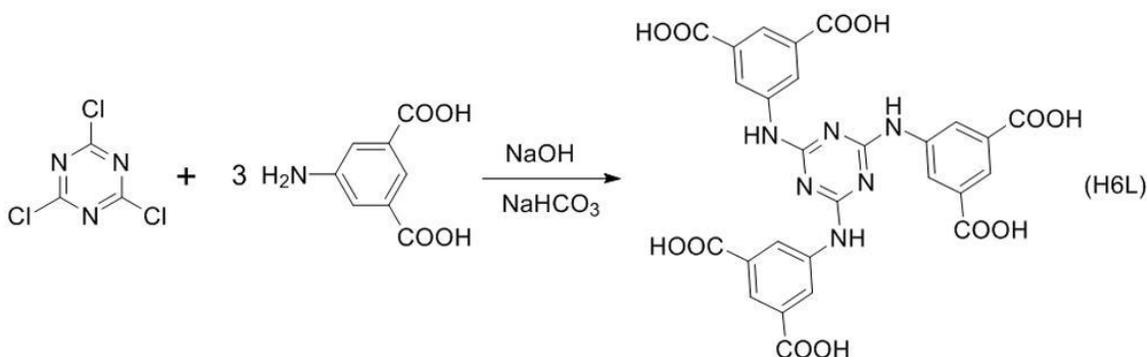
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1. Experimental Details

All reagents were purchased from Sigma-Aldrich or TCI and used as received unless otherwise indicated.

1.1 Synthesis of 2,4,6-tris(3,5-dicarboxyphenylamino)-1,3,5-triazine (H_6 TDPAT)

H_6 TDPAT was prepared according to the literature with minor modifications.^[1] 5-aminoisophthalic acid (15.2 g, 0.084 mol), NaOH (5.36 g, 0.134 mol), and NaHCO₃ (8.74 g, 0.104 mol) were added to 140 mL H₂O. The mixture was stirred at 0 °C for 30 min, followed by dropwise addition of cyanuric chloride (3.68 g, 0.02 mol) in 1,4-dioxane (70 mL). The mixture was then heated at 100 °C for 24h. The resulting solution was adjusted to pH = 2 with HCl solution. The solid was collected by filtration, rinsed several times with distilled water, and dried to give H_6 TDPAT (11.55 g, yield: 94%). ¹H NMR ([D₆]DMSO, 400 MHz): δ = 8.12 (3H), 8.47 (6H), 9.67 (3H), 13.0 (6H) ppm.



1.2 Synthesis of Zn-TDPAT

0.038g (0.061mmol) of H_6 TDPAT was dissolved in 4 mL of DMF, 2 mL of ethylene glycol, 0.5 mL of H₂O, and 0.079 g (0.266 mmol) of Zn(NO₃)₂·6H₂O. Upon adding 0.5 mL of HNO₃ (3.5 mol/L in DMF), the mixture was sealed in a small vial and heated at 80°C for 3 d. After cooling down to room temperature, colorless crystals were filtered and washed with DMF. The crystal has a formula of Zn₃(TDPAT)(H₂O)₃·3.125H₂O·4DMF, which was obtained from single crystal X-ray

diffraction analysis. Elemental analysis (% calc/found: C 38.65/39.04, H 4.31/4.55, N 11.56/11.89), and TGA (weight loss of 30 wt% before 200 °C). The PLATON SQUEEZE procedure was applied to recover 2815 electrons per unit cell in one void (total volume 16733 Å³); that is 176 electrons per formula unit. Lattice solvent water molecules (10 electrons/H₂O) and N,N-Dimethylformamide (40 electrons/DMF) were present, and the electrons recovered by SQUEEZE have been assigned as 1 water molecule and 4 DMF molecules per formula unit.

2. Characterization

2.1 Single Crystal X-ray Structure Determination

Data collection and structural analysis of crystal Zn-TDPAT was performed on a Rigaku RAXISRAPID. The data were processed with the PROCESS-AUTO processing program. All data were collected at -150 ± 2 °C. Direct methods were used to solve the structure using the SHELXL crystallographic software package.^[2] All non-hydrogen atoms were easily found from the difference Fourier map. All non-hydrogen atoms were refined anisotropically. PLATON/SQUEEZE^[3] was employed to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the generated data. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S1.

Table S1. Crystal data and structure refinement for Zn-TDPAT

Compound	Zn-TDPAT
Molecular formula	<u>C₂₇ H_{22.25} N₆ O_{17.13} Zn₃</u>
fw	<u>900.87</u>
crystal system	<u>tetragonal</u>
space group	<u>I4/m</u>
<i>a</i> , Å	<u>26.855(4)</u>
<i>b</i> , Å	<u>26.855(4)</u>
<i>c</i> , Å	<u>38.127(8)</u>

$V, \text{\AA}^3$	<u>27496(8) A³</u>
Z	<u>16</u>
$F(000)$	<u>7252</u>
$D_{\text{calcd}}(\text{g cm}^{-3})$	<u>0.87</u>
$T(\text{K})$	123(2)
Final R indices [$I > 2 \sigma(I)$]	<u>$R_1 = 0.0574$, $wR_2 = 0.1590$</u>
R indices (all data)	<u>$R_1 = 0.0865$, $wR_2 = 0.1700$</u>

2.2 PXRD Analysis

PXRD data were collected on a Rigaku D/max 2550 Powder X-ray Diffractometer.

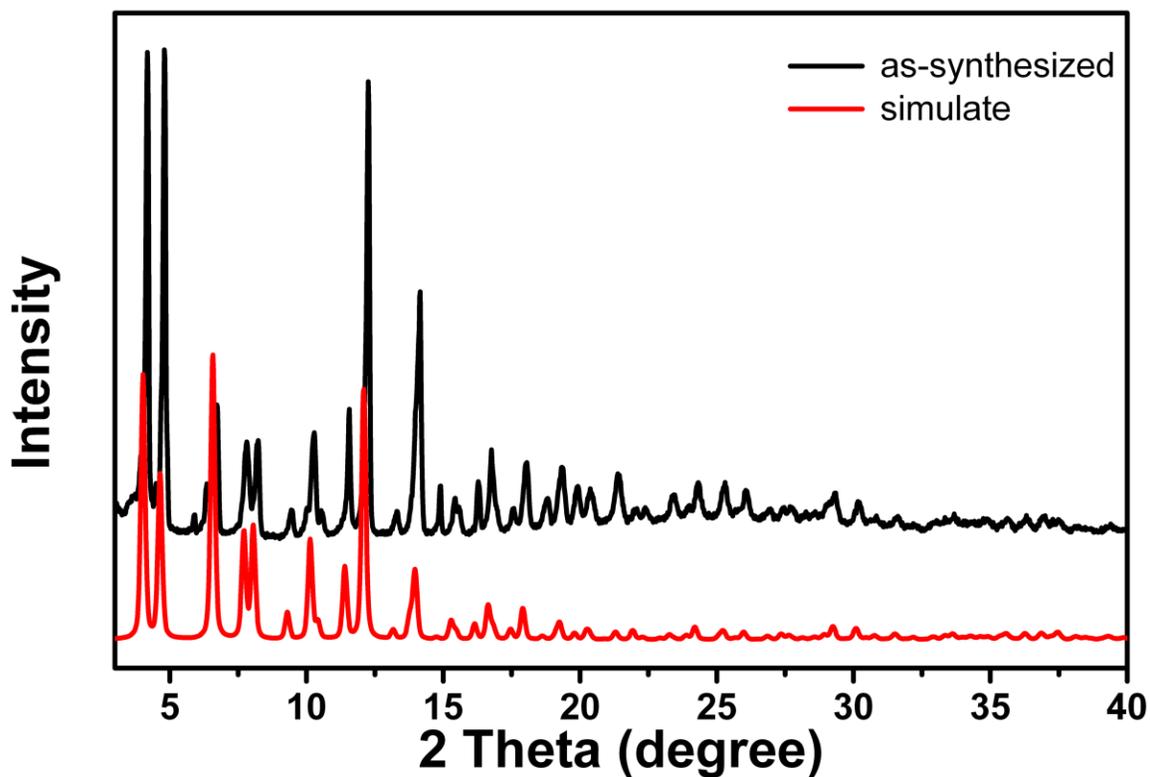


Fig. S1 PXRD of Zn-TDPAT

2.3 Thermogravimetric Analysis (TGA)

Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere with a

heating rate of 10 °C/min using TGA Q500 V20.10 Build 36.

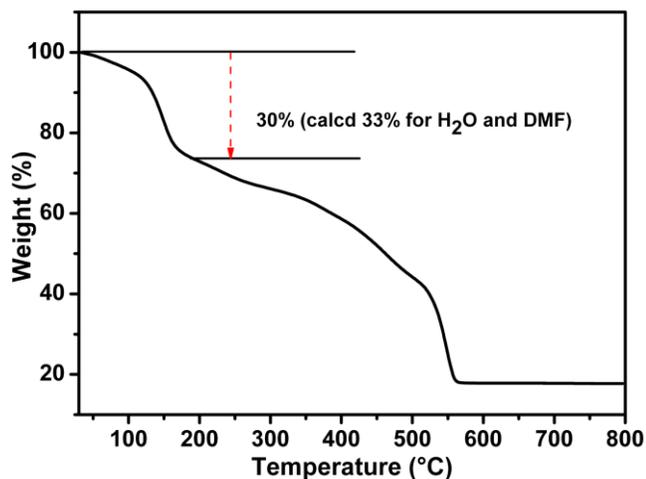


Fig. S2 TGA trace of Zn-TDPAT

2.4 General procedure for dye uptake measurements of Zn-TDPAT

Fresh crystals of **Zn-TDPAT** (4mg) were briefly dried on filter paper, and then soaked in a methanol solution of Brilliant Blue R-250 (BBR-250) or Crystal Violet (24 mM, 4 mL) overnight. The resulting dark blue or purple crystals were washed with water thoroughly until the washings became colorless. Water was used to wash the dye on the external surfaces of the crystals. The TGA data of the dye-loaded crystals are normalized to the same residue mass as that of the as-synthesized crystal. The additional weight loss at the ligand decomposition temperature of the dye-loaded MOFs is attributed to the decomposition of dye molecules in the MOF channels. For both BBR-250 and Crystal Violet, around 11 weight % dye is found to be included in the MOF channels/cavities.

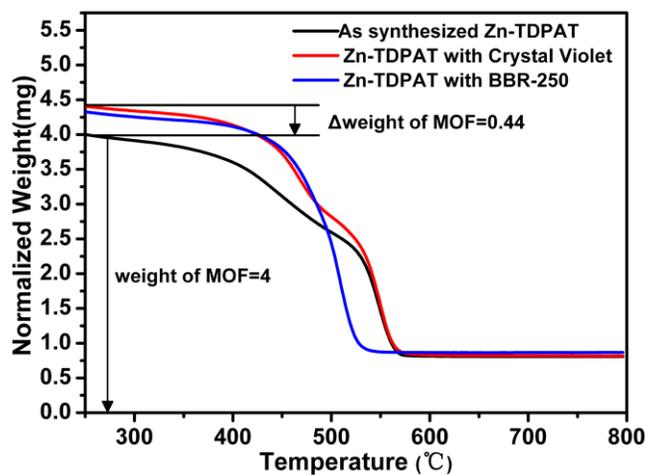


Fig. S3 TGA of dye-loaded crystals.

2.5 Solid-state luminescence spectra

The luminescence spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorometer. The quantum yield was recorded on Hamamatsu C9920-02 based on the PL method. The CIE coordinates is $x=0.159$ $y=0.110$.

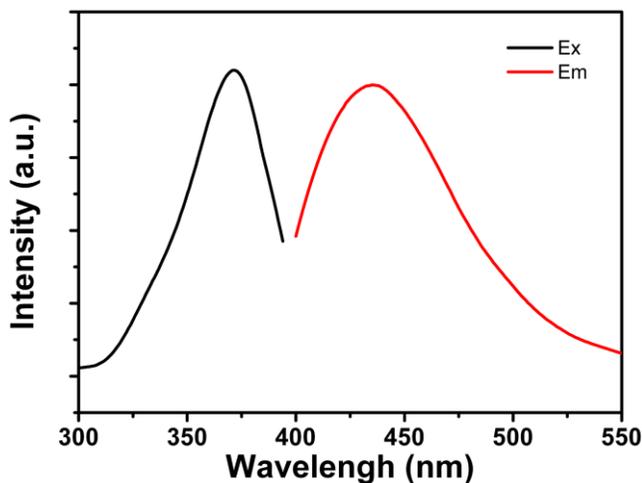


Fig. S4 The excitation and emission spectra for Zn-TDPAT

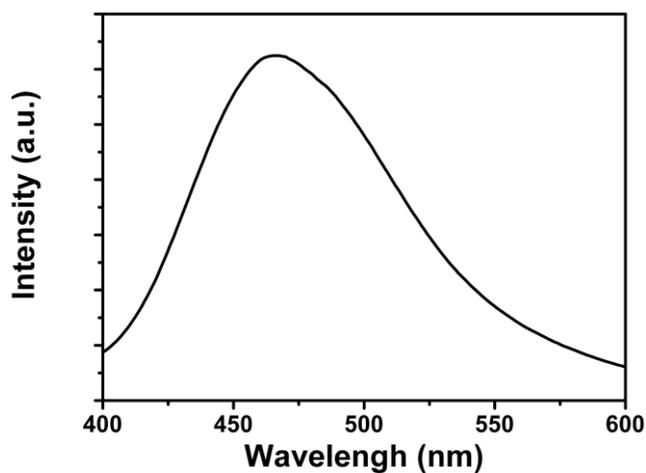


Fig. S5 The emission spectra for H₆TDPAT ($\lambda_{\text{ex}} = 370 \text{ nm}$).

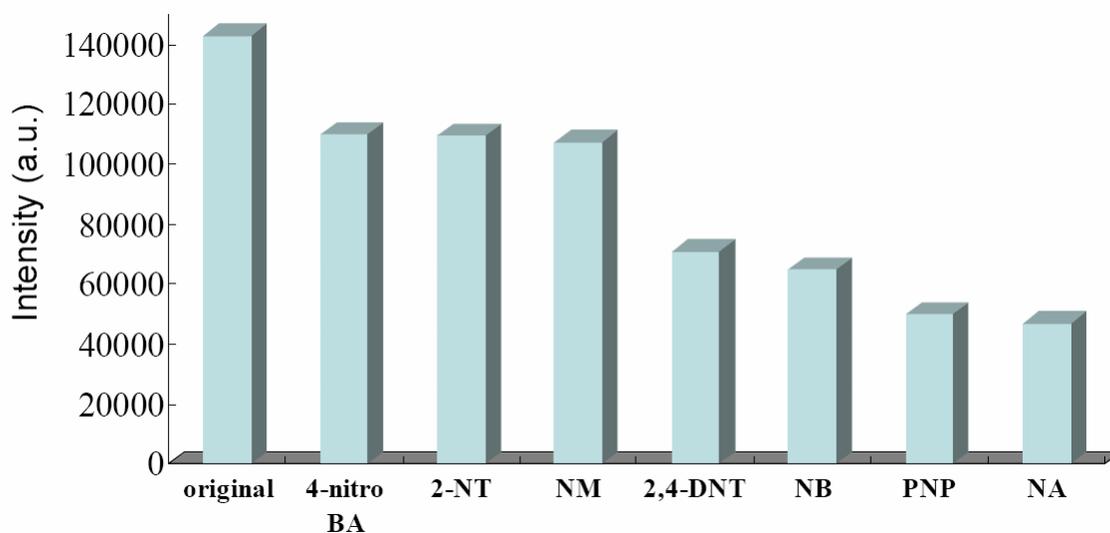


Fig. S6 Fluorescence intensity of Zn-TDPAT in different analytes at room temperature. Fresh crystals of Zn-TDPAT (5 mg) were then soaked in a methanol solution of different analytes (10 mM, 5 mL). 4-nitro BA (BA=benzyl alcohol), 2-NT (2-nitrotoluene), NM (nitromethane), PNP (p-nitro phenol), NA (nitroterephthalic acid)

2.6 IR Analysis

The infrared (IR) spectra were recorded within the 400- 4000 cm^{-1} region on a Nicolet Impact 410 FTIR 75 spectrometer using KBr pellets.

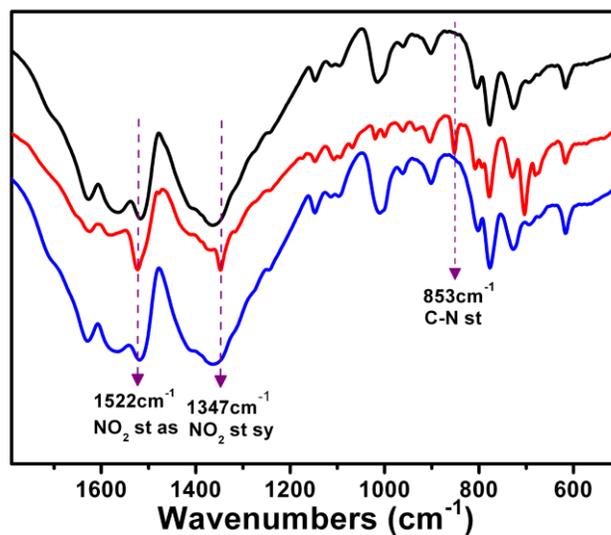


Fig. S7 Infrared spectra of as-made sample of Zn-TDPAT (black), Zn-TDPAT which is quenched by NB (red) and then washed with CH₃OH (blue).

2.7 XPS

The XPS data were collected on ESCALAB250.

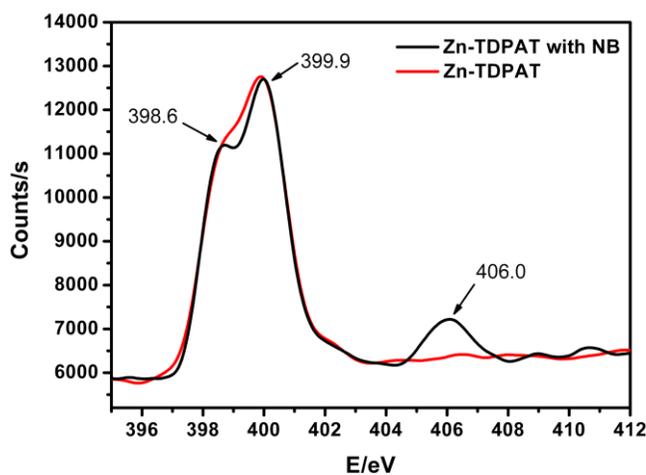


Fig. S8 XPS spectra of as-made sample of Zn-TDPAT (red), Zn-TDPAT which is quenched by NB (black). N-C (TDPAT⁶⁻) 399.9 eV, N=C (TDPAT⁶⁻) 398.6 eV, Ph-NO₂ 406.0 eV.

2.8 Reproducibility of Zn-TDPAT

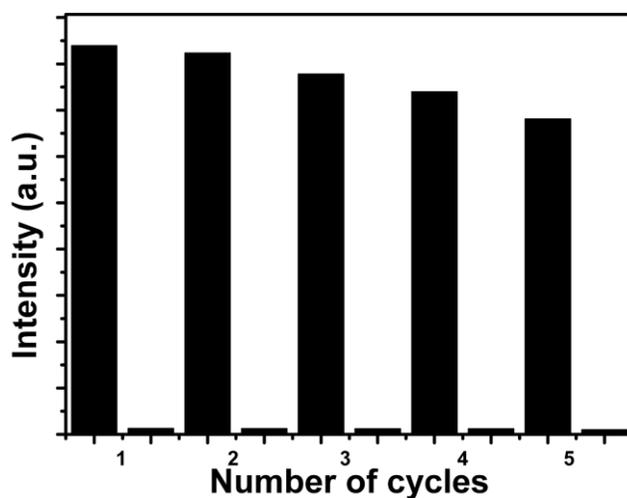


Fig. S9 Reproducibility of Zn-TDPAT dispersed in NB. The material was recovered by washing with DMF several times.

2.9 PXRD Analysis

PXRD data were collected on a Rigaku D/max 2550 Powder X-ray Diffractometer.

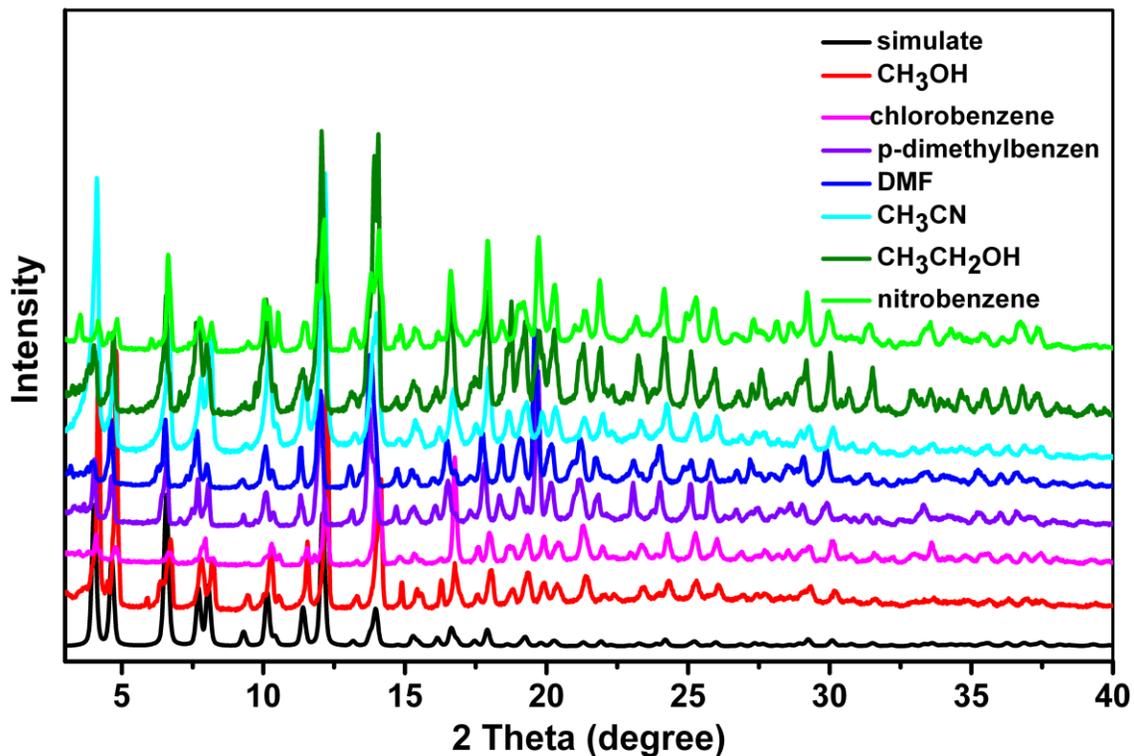


Fig. S10 Comparison of PXRD of Zn-TDPAT in different solvents

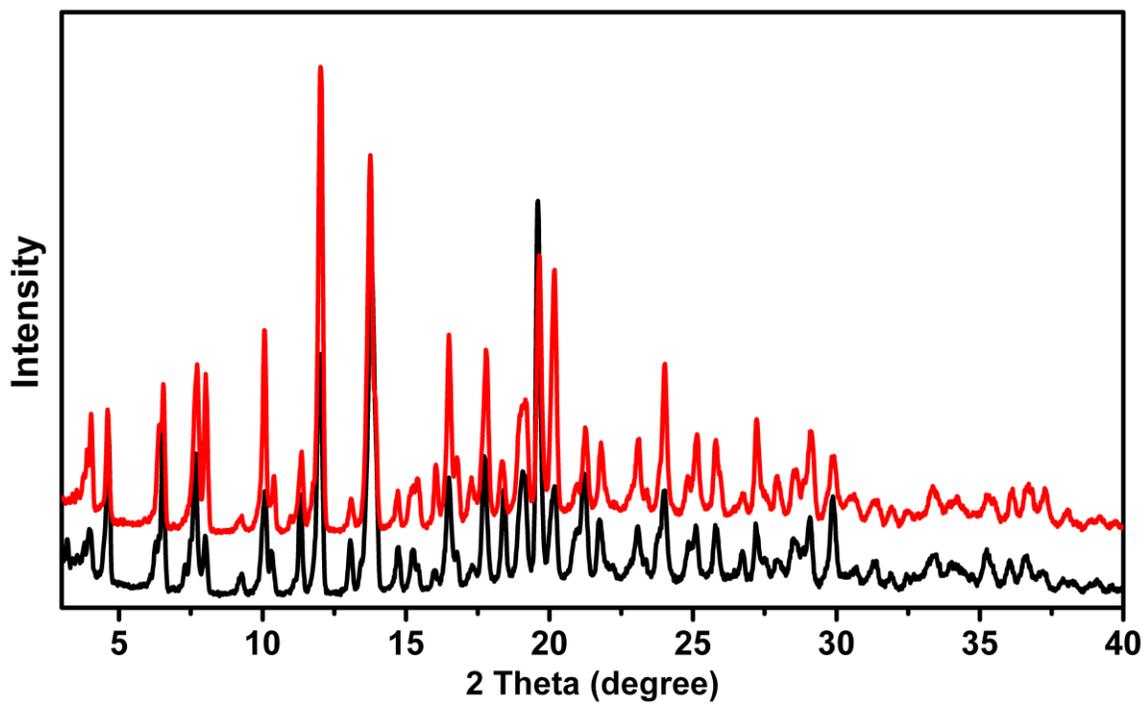


Fig. S11 Comparison of PXRd of the as-made sample of Zn-TDPAT(black) and Zn-TDPAT which is quenched by NB and then washed with DMF (red).

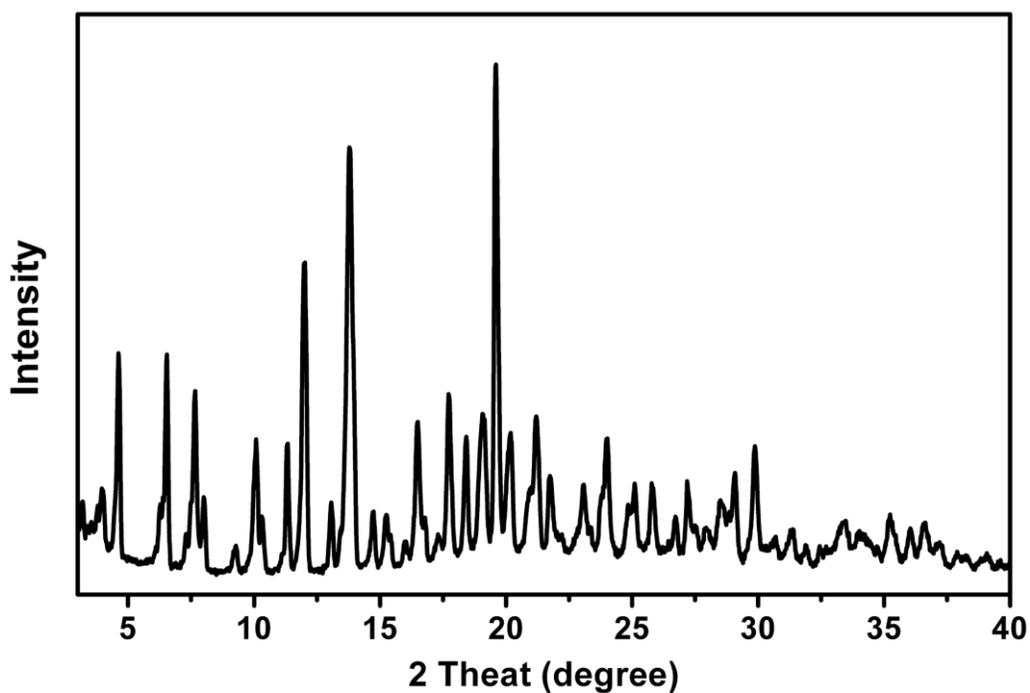


Fig. S12 PXRd of Zn-TDPAT after freezing at 77K.

References

- [1] X. Zhao, H. He, T. Hu, F. Dai, D. Sun, *Inorg. Chem.* **2009**, *48*, 8057.
- [2] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.
- [3] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.