Supporting Information

Solvent-Induced SC-SC Transformation within the Zn^{II}-Triazole System: A Promising MnO_4^- Selective Luminescent Probe

Lin Cheng,[a,§] Ying Wang,*[,a,c,§] Dan-Dan Yang,[a] Ying-Xin Zhang,[a] Yi-Xuan Gao,[a] and Gregory S. Day,*[,b]

[a]Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key Laboratory of Inorganic-Organic Hybrid Functional Materials Chemistry, Ministry of Education, College of Chemistry, Tianjin Normal University, Tianjin 300387, China

*E-mail: wangying790601@163.com. ORCID: 0000-0002-8126-3325

[b]Department of Chemistry, Texas A&M Energy Institute, Texas A&M University, College Station, Texas, United States.

*E-mail: grsday@tamu.edu

[c]Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China.

§ L. Cheng and Y. Wang are co-first authors.

Experimental Section

General remarks. All the reagents were commercially available and used without further purification. The elemental analysis of carbon, nitrogen, and hydrogen was performed on a PerkinElmer 240 elemental analyzer. The photoluminescence spectra were recorded by an MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source.

X-ray Crystal Structure Determination. Diffraction data for the compounds **TTPA, TTPA'**, **1**, **2**, **3**, **4** and **4a** were performed on a SuperNova, Atlas diffractometer equipped with mirror-monochromated Cu$K\alpha$ radiation (λ = 1.5418 Å) at room temperature and Bruker APEX-II CCD with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS[1] was applied for all data. All the structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using SHELXL-2014[2]. All nonhydrogen atoms were refined anisotropically and H-atoms were also included at calculated positions and refined as riders. In compound **3**, water hydrogen atoms could not be entirely found in the Fourier difference map. Compound **4a** crystallized with $CHBr_3$, CH_3CH_2OH and H_2O solvent molecules, unfortunately they were not possible to obtain sensible chemical model. Squeeze[3] procedure was applied to remove the contribution of the disordered solvent to the structure factors in **3**, **4** and **4a**.

Synthesis of Tris(4-(1H-1,2,4-triazol-1-yl)phenyl)amine (TTPA)

A mixture of tris(4-bromophenyl)amine (20.0 mmol, 9.64 g), CuI (1 mmol, 0.19 g), 1,2,4-triazole (200.0 mmol, 13.80 g), 18-crown-6 (2.0 mmol, 0.53 g), and K_2CO_3 (200.0 mmol, 27.6 g) was suspended in 100 mL of DMF. The mixture was placed in a 250-mL two-necked round-bottom flask under N_2, was refluxed at 160 ^oC for 2 days, and then cooled to room temperature. Solvent was removed by distillation under vacuum, and the reaction mixture was added to 200 mL H_2O. The deposit was filtered and washed with water and dried under vacuum, producing a light blue powder. The crude product was separated by column chromatography ($CH_3COOCH_3CH_2$/CH_3OH

= 10:1) to a afford white crystalline powder (yield: 78%, 7.22 g, based on tris(4-bromophenyl)amine). After a second re-crystallization from H_2O or CH_3OH/H_2O (1:1 by volume), the products were obtained as light yellow rod-like (**TTPA**) or snowflake-like crystals (**TTPA'**). Elemental analysis calcd (%) for $C_{24}H_{20}N_{10}O$ (**TTPA**): C, 62.06; H, 4.34; N, 30.16. Found: C, 62.21; H, 4.26; N 30.18. Elemental analysis calcd (%) for $C_{24}H_{18}N_{10}$ (**TTPA'**): C, 64.56; H, 4.06; N, 31.37. Found: C, 64.51; H, 4.16, N, 31.18.

Synthesis of $[Mn(TTPA)(DMF)Cl_2]\cdot 0.5DMF\}_n$ (1)

A mixture of TTPA (0.0447 g, 0.1 mmol) and $MnCl_2\cdot 4H_2O$ (0.0198 g, 0.1 mmol) was dissolved in CH_3OH (1 mL), $CHCl_3$ (2 mL), DMF (1mL), and H_2O (6 mL). The mixture was place in a Teflon vessel (25 mL) under autogenous pressure and heated at 90 ^oC for 3 days and then cooled to room temperature for 12 h. Brown rod-shaped crystals of **1** were obtained, dried in air and collected in 30% yield (based on TTPA). Elemental analysis calcd. for $C_{28.5}H_{28.5}Cl_2MnN_{11.5}O_{1.5}$ (%): C, 50.19; H, 4.21; N, 23.62. Found: C, 50.08; H, 4.02; N, 23.54.

Synthesis of $[Cu(TTPA)Cl_2]\cdot CHCl_3\cdot 0.7H_2O\}_n$ (2)

A mixture of TTPA (0.0447 g, 0.1 mmol) and $CuCl_2\cdot 2H_2O$ (0.0170 g, 0.1 mmol) was dissolved in CH_3OH (1 mL), $CHCl_3$ (2 mL), and H_2O (6 mL). The mixture was place in a Teflon vessel (25 mL) under autogenous pressure and heated at 100 ^oC for 3 days and then cooled to room temperature for 12 h. Blue rod-shaped crystals of **2** were obtained, dried in air and collected in 40% yield (based on TTPA). Elemental analysis calcd. for $C_{25}H_{20.4}Cl_5CuN_{10}O_{0.7}$ (%): C, 42.11; H, 2.88; N, 19.65. Found: C, 41.95; H, 3.09; N, 19.70.

Synthesis of $\{[Fe(TTPA)(H_2O)Cl]Cl\cdot 8.75H_2O\}_n$ (3)

A mixture of TTPA (0.0447 g, 0.1 mmol) and $FeCl_2\cdot 4H_2O$ (0.0199 g, 0.1 mmol) was dissolved in H_2O (8 mL). The mixture was place in a Teflon vessel (25 mL) under autogenous pressure and heated at 100 ^oC for 3 days and then cooled to room temperature for 12 h. Yellow rod-shaped crystals of **3** were obtained, dried in air and collected in 40% yield (based on TTPA). Elemental analysis calcd. for $C_{48}H_{55.5}Cl_2FeN_{20}O_{9.75}$ (%): C, 48.23; H, 4.67; N, 23.44. Found: C, 48.78; H, 3.19; N,

23.87. The squeeze details show that the contributions of 727 electrons were removed from the unit cell, corresponding with some 90 electrons from the formula. Combined with CNH element analysis, we added 6.75 water molecules to the formula.

Synthesis of $[Zn(TTPA)(NO_3)_2]_n$ (4)

A mixture of TTPA (0.0447 g, 0.1 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.1 mmol) was dissolved in H_2O (6 mL). The mixture was place in a Teflon vessel (25 mL) under autogenous pressure and heated at 100 ^oC for 3 days and then cooled to room temperature for 12 h. Colorless rod-shaped crystals of **4** were obtained, dried in air and collected in 40% yield (based on TTPA). Anal. Calcd for $C_{24}H_{18}N_{12}O_6Zn$: C, 45.33; H, 2.85; N, 26.43. Found: C, 45.41; H, 2.79; N 25.75. The squeeze details show that the contribution of 344 electrons was removed form the unit cell. However, according to the CHN element analysis, we did not find solvent H_2O molecules. This is in consistent with the fact that the crystal products tend to undergo desolvation in air and thus the freshly prepared single crystal need to be mounted for XRD measurement by tube sealing technique.

Synthesis of $\{[Zn(TTPA)(NO_3)_2] \cdot 2CHBr_3\}_n$ (4a)

4 (1 mmol) was immersed into a CH_3OH (1 mL), $CHBr_3$ (2 mL), and H_2O (6 mL) solution for 6 h. Complex **4** maintained crystallinity throughout. There was no apparent change in the shape and color of the crystals. Colorless single crystals suitable for X-ray diffraction were obtained. Elemental analysis calcd. for $C_{26}H_{20}Br_6N_{12}O_6Zn$ (%): C, 27.36; H, 1.77; N, 14.72. Found: C, 27.28; H, 1.72; N, 14.27. According to the squeeze details, the contributions of 233 electrons were removed from the unit cell, which corresponds to one $CHBr_3$ molecule per formula with 112 electrons. So we added one $CHBr_3$ molecule per formula in accordance with CHN element analysis result.

Referrence

1. G. M. Sheldrick, Program SADABS: Area-Detector Absorption Correction, **1996**, University of Göttingen, Germany.

2. G. M. Sheldrick, Acta Cryst. **2008**, *A64*, 112-122.

3. A. L. Spek, Acta Cryst. **2015**, *C71*, 9-18

Table S1 Crystallographic data and details of refinements for TTPA, TTPA', **1**-**4**, and **4a**.

	TTPA	**TTPA'**	**1**	**2**	**3**	**4**	**4a**
formula	$C_{24}H_{20}N_{10}O$	$C_{24}H_{18}N_{10}$	$C_{28.5}H_{28.5}Cl_2MnN_{11.5}O_{1.5}$	$C_{25}H_{20.4}Cl_5CuN_{10}O_{0.7}$	$C_{48}H_{55.5}Cl_2FeN_{20}O_{9.75}$	$C_{24}H_{18}N_{12}O_6Zn$	$C_{26}H_{20}Br_6N_{12}O_6Zn$
M (g mol^{-1})	464.50	446.48	681.97	712.90	1195.37	635.87	1141.37
crystal system	triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$	P-1	P-1
temperature	293(10)	173(2)	296(2) K	293(2) K	293 K	113(2) K	173.00(10) K
a (Å)	7.4910(4)	14.917(3)	18.5353(15)	17.897(2)	29.6595(7)	12.359(10)	10.9739(6)
b (Å)	11.4453(6)	20.459(4)	15.4936(15)	14.8153(15)	12.2726(5)	12.665(9)	12.7951(7)
c (Å)	13.0462(6)	15.642(3)	21.554(2)	21.628(2)	32.6526(9)	13.855(10)	13.6318(6)
α (º)	100.758(4)	90	90	90	90	75.70(3)	104.805(4)
β (º)	92.216(4)	116.312(3)	96.986(2)	98.305(11)	100.427(3)	72.44(2)	96.979(4)
γ (º)	93.539(4)	90	90	90	90	87.55(4)	91.525(5)
V (Å^3)	1095.35(9)	4278.9(14)	6143.9(10)	5674.6(11)	11689.2(6)	2002(3)	1833.50(17)
Z	2	8	8	8	8	2	2
F (000)	484.0	1856	2808	2888	4972	648	1096
ρ_{calc} (Mg m^{-3})	1.408	1.386	1.475	1.669	1.358	1.055	2.110
μ (mm^{-1})	0.768	0.090	0.650	1.281	0.420	0.657	9.129
data/restraints/params	4264/0/319	7533/0/613	5405/62/428	5003/12/388	10290/0/658	7041/36/388	6536/24/423
GOF on F^2	1.035	1.011	1.009	1.063	1.024	1.009	1.094
R_1[a] (I=2σ(I))	0.0378	0.0548	0.0542	0.0636	0.0719	0.0941	0.0682
ωR_2[b] (all data)	0.0979	0.1613	0.1436	0.1708	0.2122	0.2594	0.2018

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$. [b] $\omega R_2 = [\Sigma w(|F_o|^2-|F_c^2|^2/w|F_o^2|^2]^{1/2}$.

Table S2 Selected bond lengths [Å] and angles [º] for **TTPA**, **TTPA'**, **1**-**4**, and **4a**.

TTPA					
N(1)-N(2)	1.3699(15)	C(2)-C(3)	1.3846(17)	N(4)-N(5)	1.3652(14)
N(1)-C(4)	1.4262(15)	N(3)-C(7)	1.360(2)	C(5)-C(6)	1.3842(17)
C(1)-C(2)	1.3964(17)	C(3)-C(4)	1.3886(17)	C(9)-C(10)	1.3961(17)
N(1)-C(8)	1.3416(17)	N(3)-C(8)	1.3233(18)	N(4)-C(12)	1.4260(15)
C(1)-C(6)	1.4035(17)	C(4)-C(5)	1.3873(18)	C(9)-C(14)	1.3933(17)
N(2)-C(7)	1.3171(18)	N(4)-C(16)	1.3475(16)	N(10)-C(17)	1.4189(15)
C(21)-C(22)	1.3883(17)	C(20)-C(21)	1.3870(17)	C(19)-C(20)	1.3858(17)
C(18)-C(19)	1.3861(17)	C(17)-C(22)	1.4015(17)	C(17)-C(18)	1.3943(17)
C(13)-C(14)	1.3865(17)	C(12)-C(13)	1.3871(17)	C(11)-C(12)	1.3875(17)
C(10)-C(11)	1.3876(17)	N(10)-C(9)	1.4248(15)	N(10)-C(1)	1.4166(15)
N(9)-C(24)	1.3246(16)	N(9)-C(23)	1.3537(17)	N(8)-C(23)	1.3203(17)
N(7)-C(24)	1.3415(16)	N(7)-C(20)	1.4261(15)	N(7)-N(8)	1.3673(14)
N(6)-C(16)	1.3180(17)	N(6)-C(15)	1.3631(18)	N(5)-C(15)	1.3168(17)
N(9)-C(24)-N(7)	110.33(11)	N(2)-N(1)-C(4)	121.12(10)	C(5)-C(6)-C(1)	120.73(11)
C(8)-N(1)-N(2)	109.76(11)	N(2)-C(7)-N(3)	115.88(12)	C(8)-N(1)-C(4)	128.95(11)
N(3)-C(8)-N(1)	110.50(13)	C(7)-N(2)-N(1)	101.61(11)	C(10)-C(9)-N(10)	119.76(11)
C(8)-N(3)-C(7)	102.24(12)	C(14)-C(9)-N(10)	120.99(11)	N(5)-N(4)-C(12)	123.06(10)
C(14)-C(9)-C(10)	119.24(11)	C(16)-N(4)-N(5)	109.20(10)	C(11)-C(10)-C(9)	120.29(11)
C(16)-N(4)-C(12)	127.70(11)	C(12)-C(11)-C(10)	119.62(11)	C(15)-N(5)-N(4)	102.23(10)
C(11)-C(12)-N(4)	118.93(11)	C(16)-N(6)-C(15)	102.26(11)	C(13)-C(12)-N(4)	120.40(11)
N(8)-N(7)-C(20)	121.14(10)	C(13)-C(12)-C(11)	120.64(11)	C(24)-N(7)-N(8)	109.52(10)
C(14)-C(13)-C(12)	119.49(11)	C(24)-N(7)-C(20)	129.35(11)	C(13)-C(14)-C(9)	120.55(11)
C(23)-N(8)-N(7)	102.09(10)	N(5)-C(15)-N(6)	115.46(12)	C(24)-N(9)-C(23)	102.74(11)
N(6)-C(16)-N(4)	110.83(11)	C(1)-N(10)-C(9)	118.52(10)	C(18)-C(17)-N(10)	120.54(11)
C(1)-N(10)-C(17)	121.02(10)	C(18)-C(17)-C(22)	118.70(11)	C(17)-N(10)-C(9)	120.37(10)
C(22)-C(17)-N(10)	120.75(11)	C(2)-C(1)-N(10)	121.05(11)	C(19)-C(18)-C(17)	120.78(11)
C(2)-C(1)-C(6)	119.01(11)	C(20)-C(19)-C(18)	119.71(11)	C(6)-C(1)-N(10)	119.93(11)
C(19)-C(20)-N(7)	119.39(11)	C(3)-C(2)-C(1)	120.28(11)	C(19)-C(20)-C(21)	120.55(11)
C(2)-C(3)-C(4)	119.86(11)	C(21)-C(20)-N(7)	120.04(11)	C(3)-C(4)-N(1)	118.77(11)
C(5)-C(4)-N(1)	120.43(11)	C(21)-C(22)-C(17)	120.60(11)	C(5)-C(4)-C(3)	120.79(11)
C(20)-C(21)-C(22)	119.58(11)	N(8)-C(23)-N(9)	115.31(12)	C(6)-C(5)-C(4)	119.29(11)
TTPA'					
N(1)-C(17)	1.423(3)	N(1)-C(1)	1.428(3)	N(1)-C(9)	1.429(3)
N(2)-C(8)	1.335(4)	N(2)-N(3)	1.357(3)	N(2)-C(4)	1.434(3)
N(3)-C(7)	1.322(4)	N(4)-C(8)	1.319(4)	N(4)-C(7)	1.347(4)
N(5)-C(16)	1.349(3)	N(5)-N(6)	1.362(3)	N(5)-C(12)	1.428(3)
N(6)-C(15)	1.329(3)	N(7)-C(16)	1.325(3)	N(7)-C(15)	1.364(4)
N(8)-C(24)	1.340(4)	N(8)-N(9)	1.364(3)	N(8)-C(20)	1.427(3)
N(9)-C(23)	1.325(4)	N(10)-C(24)	1.325(4)	N(10)-C(23)	1.362(4)
N(11)-C(33)	1.423(3)	N(11)-C(25)	1.426(3)	N(11)-C(41)	1.428(3)
N(12)-C(32)	1.342(4)	N(12)-N(13)	1.362(3)	N(12)-C(28)	1.441(3)
N(13)-C(31)	1.326(3)	N(14)-C(32)	1.325(4)	N(14)-C(31)	1.362(4)
N(15)-C(40)	1.339(3)	N(15)-N(16)	1.374(3)	N(15)-C(36)	1.432(3)
N(16)-C(39)	1.324(3)	N(17)-C(40)	1.325(3)	N(17)-C(39)	1.358(4)
N(18)-C(48)	1.346(3)	N(18)-N(19)	1.374(3)	N(18)-C(44)	1.435(3)
N(19)-C(47)	1.321(4)	N(20)-C(48)	1.317(4)	N(20)-C(47)	1.366(4)
C(1)-C(6)	1.396(3)	C(1)-C(2)	1.400(3)	C(2)-C(3)	1.384(4)
C(3)-C(4)	1.387(4)	C(4)-C(5)	1.391(3)	C(5)-C(6)	1.375(4)
C(9)-C(10)	1.390(4)	C(9)-C(14)	1.394(4)	C(10)-C(11)	1.385(3)
C(9)-C(10)	1.390(4)	C(9)-C(14)	1.394(4)	C(10)-C(11)	1.385(3)
C(12)-C(13)	1.387(4)	C(13)-C(14)	1.384(3)	C(11)-C(12)	1.388(3)
C(17)-C(22)	1.396(4)	C(17)-C(18)	1.397(4)	C(18)-C(19)	1.383(4)
C(19)-C(20)	1.379(4)	C(20)-C(21)	1.391(4)	C(21)-C(22)	1.387(4)
C(25)-C(30)	1.395(3)	C(25)-C(26)	1.400(4)	C(26)-C(27)	1.382(3)

C(27)-C(28)	1.391(4)	C(28)-C(29)	1.385(4)	C(29)-C(30)	1.389(3)
C(33)-C(38)	1.395(3)	C(33)-C(34)	1.404(3)	C(34)-C(35)	1.382(3)
C(35)-C(36)	1.388(3)	C(36)-C(37)	1.390(3)	C(37)-C(38)	1.391(3)
C(17)-N(1)-C(1)	120.5(2)	C(17)-N(1)-C(9)	118.5(2)	C(1)-N(1)-C(9)	120.8(2)
C(8)-N(2)-N(3)	108.7(2)	C(8)-N(2)-C(4)	129.8(3)	N(3)-N(2)-C(4)	121.4(2)
C(7)-N(3)-N(2)	102.5(3)	C(8)-N(4)-C(7)	101.9(3)	C(16)-N(5)-N(6)	109.9(2)
C(16)-N(5)-C(12)	128.5(2)	N(6)-N(5)-C(12)	121.6(2)	C(15)-N(6)-N(5)	101.6(2)
C(16)-N(7)-C(15)	102.0(2)	C(24)-N(8)-N(9)	109.5(2)	C(24)-N(8)-C(20)	129.1(3)
N(9)-N(8)-C(20)	121.4(2)	C(23)-N(9)-N(8)	102.1(3)	C(24)-N(10)-C(23)	102.1(3)
C(33)-N(11)-C(25)	120.3(2)	C(33)-N(11)-C(41)	120.8(2)	C(25)-N(11)-C(41)	118.9(2)
C(32)-N(12)-N(13)	109.0(2)	C(32)-N(12)-C(28)	128.9(2)	N(13)-N(12)-C(28)	122.2(2)
C(31)-N(13)-N(12)	102.2(2)	C(32)-N(14)-C(31)	101.4(3)	C(40)-N(15)-N(16)	109.5(2)
C(40)-N(15)-C(36)	130.0(2)	N(16)-N(15)-C(36)	120.5(2)	C(39)-N(16)-N(15)	101.6(2)
C(40)-N(17)-C(39)	102.1(2)	C(48)-N(18)-N(19)	108.5(2)	C(48)-N(18)-C(44)	130.0(2)
N(19)-N(18)-C(44)	121.2(2)	C(47)-N(19)-N(18)	102.2(2)	C(48)-N(20)-C(47)	101.6(2)
C(6)-C(1)-C(2)	118.4(2)	C(6)-C(1)-N(1)	121.3(2)	C(2)-C(1)-N(1)	120.3(2)
C(3)-C(2)-C(1)	120.8(3)	C(2)-C(3)-C(4)	119.7(3)	C(3)-C(4)-C(5)	120.1(3)
C(3)-C(4)-N(2)	119.5(2)	C(5)-C(4)-N(2)	120.4(2)	C(6)-C(5)-C(4)	120.0(2)
C(5)-C(6)-C(1)	121.0(3)	N(3)-C(7)-N(4)	115.4(3)	N(4)-C(8)-N(2)	111.6(3)
C(10)-C(9)-C(14)	119.3(3)	C(10)-C(9)-N(1)	121.2(2)	C(14)-C(9)-N(1)	119.6(2)
C(11)-C(10)-C(9)	120.4(3)	C(10)-C(11)-C(12)	119.7(3)	C(13)-C(12)-C(11)	120.4(3)
C(13)-C(12)-N(5)	119.5(2)	C(11)-C(12)-N(5)	120.1(2)	C(14)-C(13)-C(12)	119.6(3)
C(13)-C(14)-C(9)	120.5(3)	N(7)-C(16)-N(5)	110.7(3)	C(22)-C(17)-C(18)	119.2(2)
C(22)-C(17)-N(1)	120.4(2)	C(18)-C(17)-N(1)	120.4(2)	C(19)-C(18)-C(17)	120.0(3)
C(20)-C(19)-C(18)	120.3(3)	C(19)-C(20)-C(21)	120.4(3)	C(19)-C(20)-N(8)	120.2(3)
C(21)-C(20)-N(8)	119.4(3)	C(22)-C(21)-C(20)	119.4(3)	C(21)-C(22)-C(17)	120.5(3)
N(9)-C(23)-N(10)	115.3(3)	N(10)-C(24)-N(8)	111.0(3)	C(30)-C(25)-C(26)	118.8(2)
C(30)-C(25)-N(11)	121.5(2)	C(26)-C(25)-N(11)	119.8(2)	C(27)-C(26)-C(25)	120.5(3)
C(26)-C(27)-C(28)	120.0(3)	C(29)-C(28)-C(27)	120.4(2)	C(29)-C(28)-N(12)	120.6(3)
C(27)-C(28)-N(12)	119.0(2)	C(28)-C(29)-C(30)	119.5(3)	C(29)-C(30)-C(25)	120.9(3)
N(13)-C(31)-N(14)	115.7(3)	N(14)-C(32)-N(12)	111.7(3)	C(38)-C(33)-C(34)	118.9(2)
C(38)-C(33)-C(34)	118.9(2)	C(38)-C(33)-N(11)	120.6(2)	C(34)-C(33)-N(11)	120.5(2)
C(35)-C(34)-C(33)	120.5(2)	C(34)-C(35)-C(36)	120.1(2)	C(35)-C(36)-C(37)	120.0(2)
C(35)-C(36)-N(15)	120.4(2)	C(37)-C(36)-N(15)	119.7(2)	C(36)-C(37)-C(38)	120.0(2)
C(37)-C(38)-C(33)	120.3(2)	N(16)-C(39)-N(17)	115.8(2)	N(17)-C(40)-N(15)	111.0(2)
C(42)-C(41)-C(46)	118.1(2)	C(42)-C(41)-N(11)	122.3(2)	C(46)-C(41)-N(11)	119.5(2)
C(43)-C(42)-C(41)	121.2(2)	C(42)-C(43)-C(44)	120.0(2)	C(45)-C(44)-C(43)	119.5(3)
C(45)-C(44)-N(18)	119.4(2)	C(43)-C(44)-N(18)	121.0(2)	C(46)-C(45)-C(44)	120.1(3)
C(45)-C(46)-C(41)	120.9(3)	N(19)-C(47)-N(20)	115.7(3)	N(20)-C(48)-N(18)	111.9(3)

1

Mn(1)-O(1)	2.242(3)	Mn(1)-N(4)	2.274(3)	Mn(1)-N(10)#2	2.289(3)
Mn(1)-N(7)#1	2.249(3)	Mn(1)-Cl(1)	2.4807(14)	Mn(1)-Cl(2)	2.5050(12)
O(1)-Mn(1)-N(7)	93.73(13)	O(1)-Mn(1)-N(4)	176.11(13)	N(7)#1-Mn(1)-N(4)	88.13(12)
O(1)-Mn(1)-N(10)#2	93.13(13)	N(7)#1-Mn(1)-N(10)#2	172.99(13)	N(4)-Mn(1)-N(10)#2	84.93(13)
O(1)-Mn(1)-Cl(1)	88.91(10)	N(7)#1-Mn(1)-Cl(1)	91.39(10)	N(4)-Mn(1)-Cl(1)	94.47(10)
N(10)#2-Mn(1)-Cl(1)	90.18(10)	O(1)-Mn(1)-Cl(2)	85.99(10)	N(7)#1-Mn(1)-Cl(2)	87.58(10)
N(4)-Mn(1)-Cl(2)	90.68(10)	N(10)#2-Mn(1)-Cl(2)	91.47(9)	Cl(1)-Mn(1)-Cl(2)	174.71(5)

2

Cl(1)-Cu(1)	2.376(2)	Cl(3)-Cu(1)	2.339(2)	Cu(1)-N(0AA)#1	1.980(5)
Cu(1)-N(1)	1.985(5)	Cu(1)-N(2)#2	2.205(6)	N(0AA)-Cu(1)#3	1.980(5）
N(0AA)#1-Cu(1)-N(1)	174.2(2)	N(0AA)#1-Cu(1)-N(2)#2	90.6(2)	N(1)-Cu(1)-N(2)#2	95.2(2)
N(0AA)#1-Cu(1)-Cl(3)	88.25(17)	N(1)-Cu(1)-Cl(3)	90.16(17)	N(2)#2-Cu(1)-Cl(3)	105.18(17)
N(0AA)#1-Cu(1)-Cl(1)	89.69(17)	N(1)-Cu(1)-Cl(1)	89.84(17)	N(2)#2-Cu(1)-Cl(1)	95.39(17)

3

Fe1-Cl1	2.332(3)	Fe1-N7	2.201(4)	Fe1-N91	2.220(4)
Fe1-O1	2.143(4)	Fe1-N191	2.187(4)	O1-Fe1-Cl1	176.74(12)
Fe1-N13	2.226(4)	O1-Fe1-N91	91.38(15）	O1-Fe1-N13	87.82(15)

O1-Fe1-N7	89.73(15)	O1-Fe1-N191	87.99(15)	N7-Fe1-Cl1	87.46(14)
N7-Fe1-N91	89.30(15)	N7-Fe1-N13	94.39(15)	N91-Fe1-Cl1	90.23(13)
N91-Fe1-N13	176.22(15)	N13-Fe1-Cl1	90.76(13)	N191-Fe1-Cl1	94.88(14)
N191-Fe1-N7	176.94(15)	N191-Fe1-N91	88.72(15)	N191-Fe1-N13	87.56(15)
4					
O(5)-Zn(1)	2.310(9)	O(1)-Zn(1)	2.007(6)	Zn(1)-N(6)#1	2.131(6)
O(4)-Zn(1)	2.264(5)	Zn(1)-N(10)#2	2.151(4)	O(1)-Zn(1)-N(1)	92.2(2)
Zn(1)-N(1)	2.116(5)	N(1)-Zn(1)-N(6)#1	93.3(2)	O(1)-Zn(1)-N(10)#2	86.9(2)
O(1)-Zn(1)-N(6)#1	109.3(3)	N(6)#1-Zn(1)-N(10)#2	92.2(2)	O(1)-Zn(1)-O(4)	162.6(3)
N(1)-Zn(1)-N(10)#2	174.4(2)	N(6)#1-Zn(1)-O(4)	87.7(2)	N(10)#2-Zn(1)-O(4)	88.44(18)
N(1)-Zn(1)-O(4)	90.76(18)	O(1)-Zn(1)-O(5)	113.8(4)	N(1)-Zn(1)-O(5)	85.3(2)
N(6)#1-Zn(1)-O(5)	136.9(3)	N(10)#2-Zn(1)-O(5)	90.0(2)	O(4)-Zn(1)-O(5)	49.4(3)
4a					
Zn01-O1	2.139(5)	Zn01-O5	2.166(5)	Zn01-O4	2.446(6)
Zn01-N10#1	2.115(5)	Zn01-N7#2	2.070(5)	Zn01-N3	2.074(5)
O1-Zn01-O5	176.85(17)	O1-Zn01-O4	121.81(18)	O5-Zn01-O4	55.90(18)
N10#1-Zn01-O1	88.4(2)	N10#1-Zn01-O5	94.1(2)	N10#1-Zn01-O4	149.6(2)
N7#2-Zn01-O1	91.3(2)	N7#2-Zn01-O5	86.3(2)	N7#2-Zn01-O4	84.2(2)
N7#2-Zn01-N10#1	100.4(2)	N7#2-Zn01-N3	163.3(2)	N3-Zn01-O1	87.4(2)
N3-Zn01-O5	94.3(2)	N3-Zn01-O4	82.4(2)	N3-Zn01-N10#1	96.2(2)

[a] Symmetry transformations used to generate equivalent atoms: For **1**: #1 $-x + 1, -y + 1, -z$; #2 $x, -y, z + 1/2$; #3 $x, -y, z - 1/2$. For **2**: #1 $-x + 2, y + 1, -z + 1/2$; #2 $-x + 2, -y + 1, -z + 1$; #3 $-x + 2, y - 1, -z + 1/2$. For **3**: #1 $-1/2 + x, 1/2 + y, +z$. For **4**: #1 $-x, -y + 1, -z + 1$; #2 $x - 1, y - 1, z + 1$; #3 $x + 1, y + 1, z - 1$. For **4a**: #1 $1 - x, -y, 2 - z$; #2 $1 + x, 1 + y, 1 + z$; #3 $-1 + x, -1 + y, -1 + z$.

Table S3 Hydrogen bonds and short contacts for TTPA [A and deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(13)-H(13)...N(9)#1	0.93	2.64	3.4571(17)	147
C(16)-H(16)...N(3)#2	0.93	2.49	3.3908(18)	163
C(24)-H(24)...O(1)#3	0.93	2.29	3.2128(17)	173
O(1)-H(1A)...N(5)#4	0.85	2.15	3.0021(16)	177
O(1)-H(1B)...N(9)	0.85	2.06	2.9078(16)	174

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x+2,-y,-z #3 -x+1,-y+2,-z+1 #4 -x,-y+1,-z+1

Table S4 Short contacts for TTPA' [A and deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8)...N(19)#1	0.95	2.56	3.497(4)	170
C(16)-H(16)...N(4)#2	0.95	2.60	3.222(4)	123
C(27)-H(27)...N(7)#3	0.95	2.61	3.165(4)	118
C(31)-H(31)...N(6)#4	0.95	2.50	3.413(4)	162
C(37)-H(37)...N(10)#5	0.95	2.64	3.572(4)	166
C(40)-H(40)...N(10)#5	0.95	2.45	3.303(4)	150
C(46)-H(46)...N(16)#3	0.95	2.64	3.267(4)	124
C(48)-H(48)...N(14)#6	0.95	2.59	3.479(4)	156

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+3/2 #2 -x+2,y+1/2,-z+3/2 #3 x,-y+1/2,z-1/2

#4 -x+1,-y,-z+1 #5 -x+1,-y+1,-z+1 #6 -x+1,y+1/2,-z+1/2

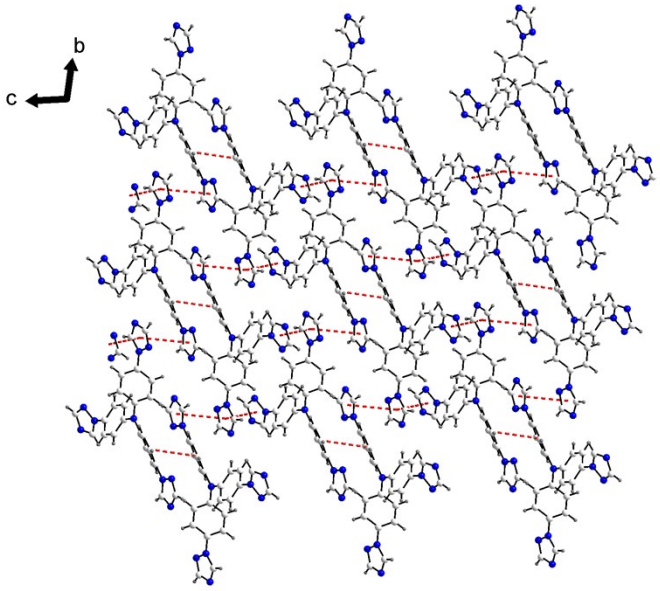

Fig. S1 π···π packing architecture of **TTPA** as viewed along the *a* axis. Blue, N; gray, C; red dashed line, π···π interaction. Analysis of the crystal packing of **TTPA** shows the existence of π···π interactions due to the distance between two neighbouring aromatic rings being measured at 3.24-3.41 Å. The free lattice water molecules also appears to engage in O-H···N hydrogen bonding with an angle of 146.5-173.5°. Such hydrogen bonding allows the **TTPA** ligands to generate a 3D supra-molecular framework.

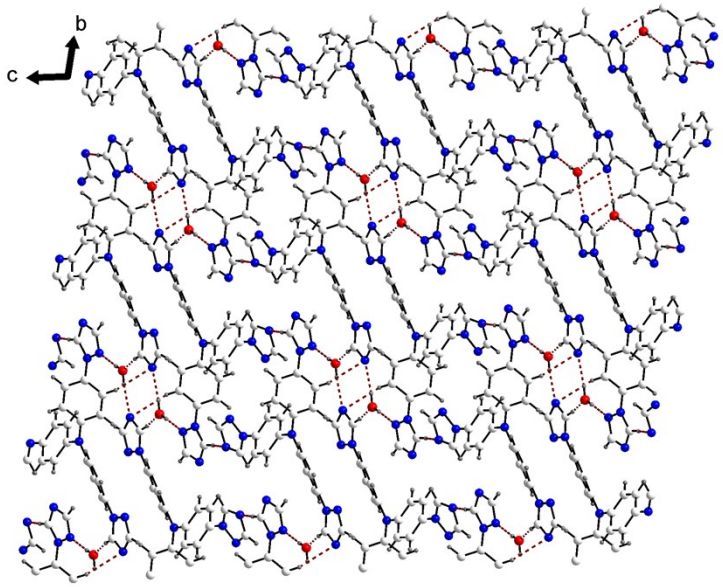

Fig. S2 3D supramolecular network of **TTPA**. Gray, C; red, O; red dashed line, hydrogen bond.

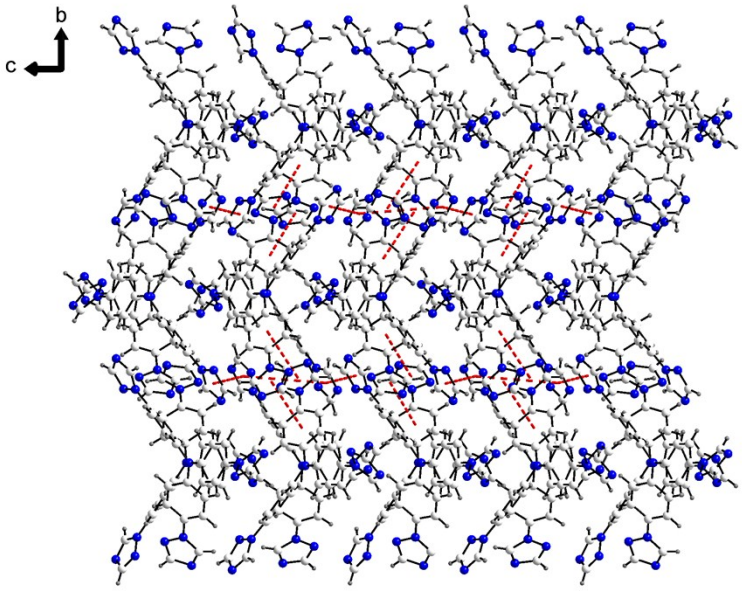

Fig. S3 π···π packing architecture of **TTPA'** as viewed along the *a* axis. Blue, N; gray, C; red dashed line, π···π interaction. The π···π distances between the aromatic rings of different molecules of **TTPA'** are 3.47-3.58 Å, which seem to be responsible for making **TTPA'** a 3D supra-molecular framework.

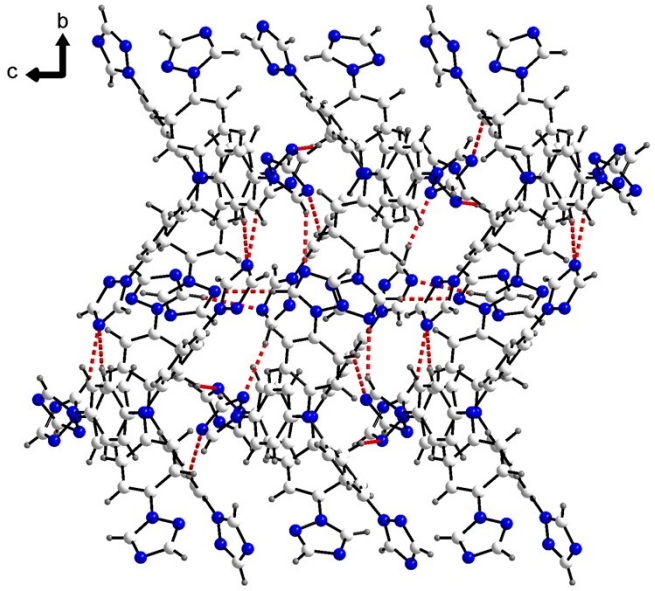

Fig. S4 3D supramolecular network of **TTPA'**. Gray, C; red, O; red dashed line, hydrogen bond.

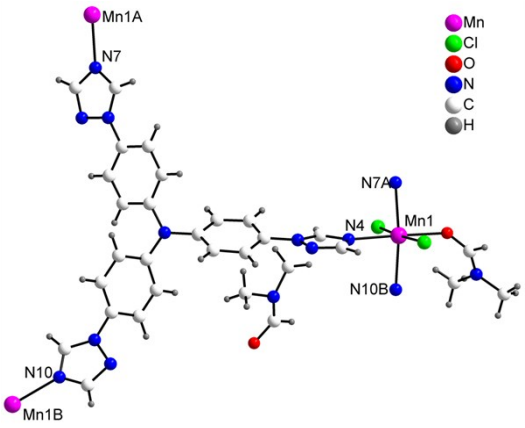

Fig. S5 View of the coordination environment of Mn^{2+} and the TTPA ligand in **1**. Purple, Mn; green, Cl; red, O; blue, N; gray, C; dark gray, H.

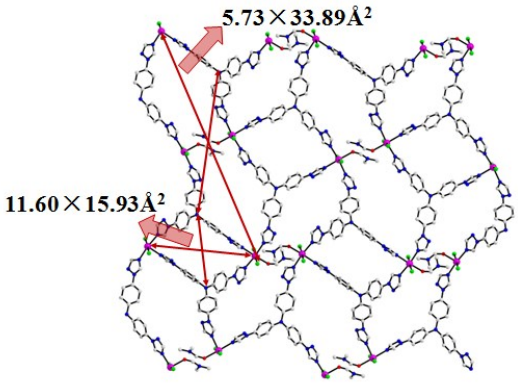

Fig. S6 Two types of windows in the 2D sheet of **1**. Purple, Mn; green, Cl; red, O; blue, N; gray, C.

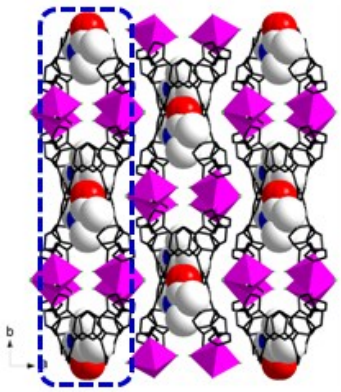

Fig. S7 The stacking of porous layers of **1** in an AA' sequence.

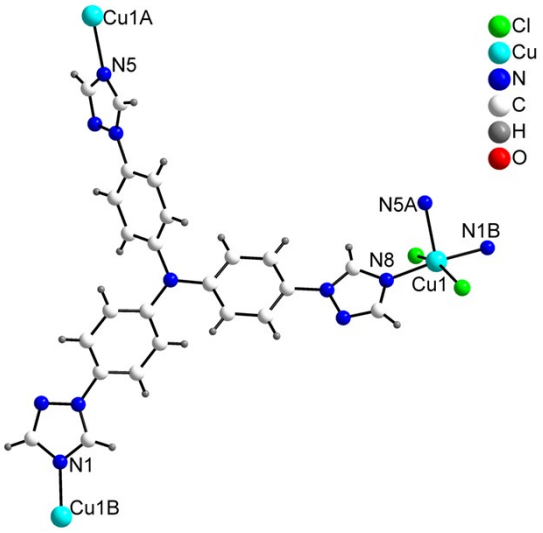

Fig. S8 View of the coordination environment of Cu^{2+} and the TTPA ligand in **2**.

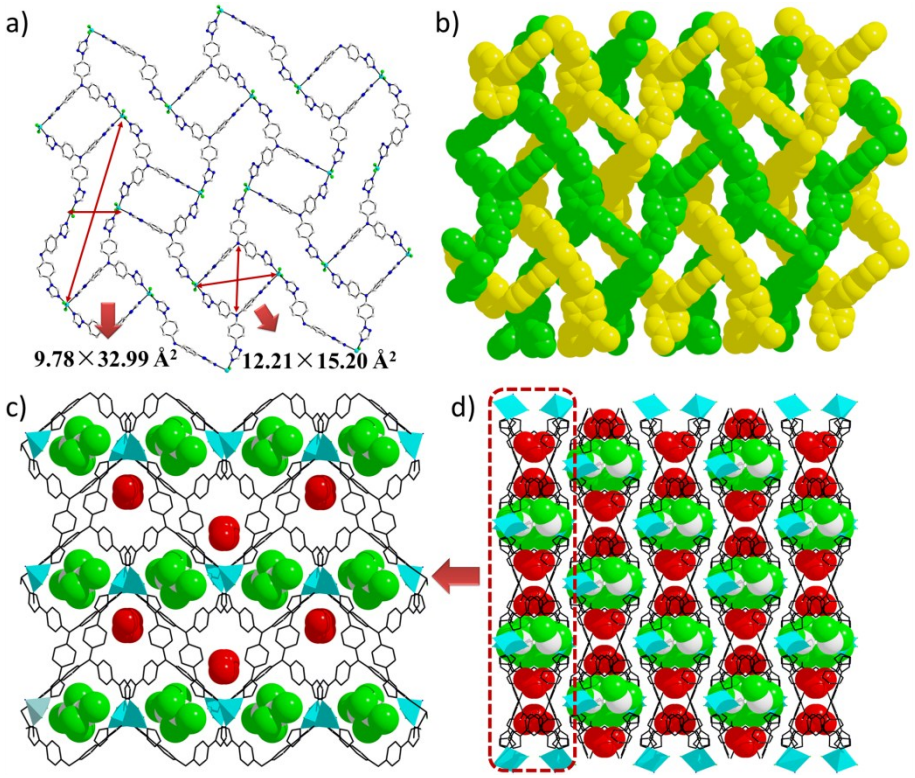

Fig. S9 (a) The 2D sheet of **2** with two types of windows (H atoms have been omitted for clarity). (b) Two-fold interpenetrated layer in **2** (green and yellow represent two interpenetrated sheets). (c) The free water and $CHCl_3$ molecules are located in the void of the porous layer. (d) The stacking of porous layers is in an -AA'- sequence.

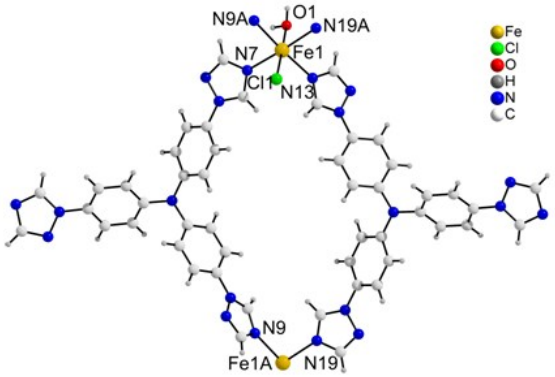

Fig. S10 View of the coordination environment of Fe^{2+} and the TTPA ligand in **3**.

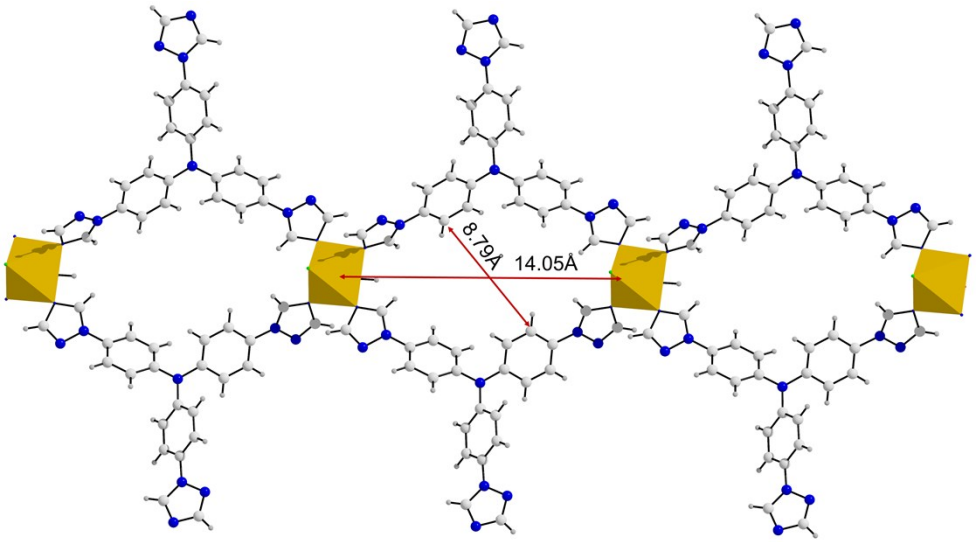

Fig. S11 Multi-fold interpenetrated layers in **3** (different colors represent different interpenetrated chains). Brown polyhedron, the coordination configuration of Fe^{II}; green, Cl; red, O; blue, N; gray, C; dark gray, H.

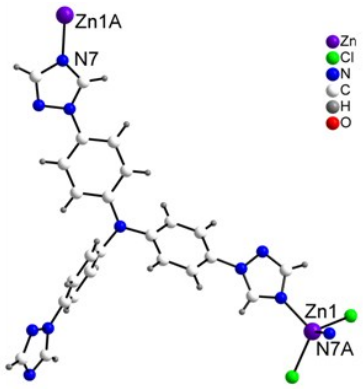

Fig. S12 View of the coordination environment of Zn^{2+} and the TTPA ligand in **4**.

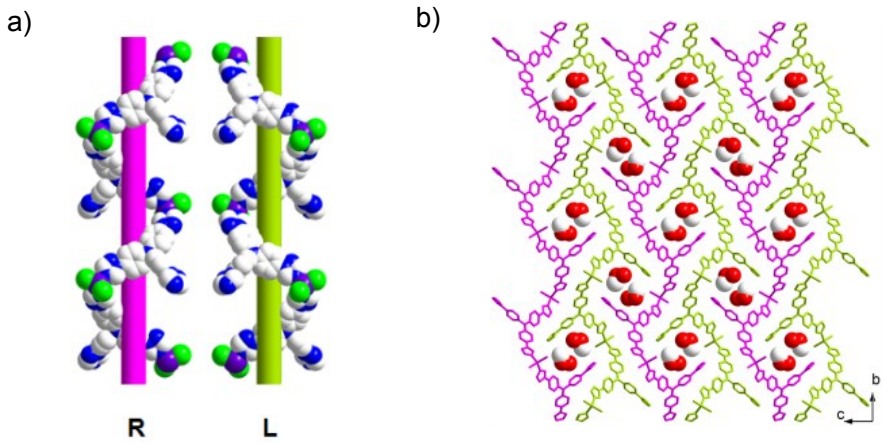

Fig. 13 (a) View of a pair of polyhedral chains of **4** (H atoms have been omitted for clarity); (b) Methanol and water molecules located in the voids of the framework of **4**. Purple and green chains represent different chiralities.

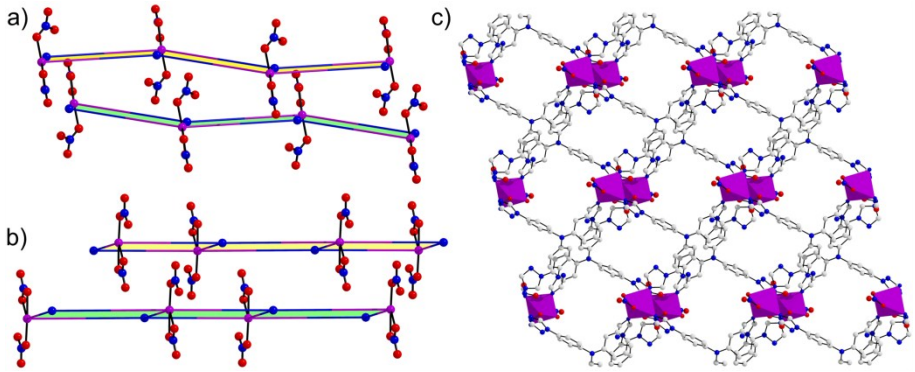

Fig. S14 (a) The configuration of the ladder-like chains in **4** (a) and **4a** (b). (c) The 3D framework stacked by the ladder-like chains along the *a* axis.

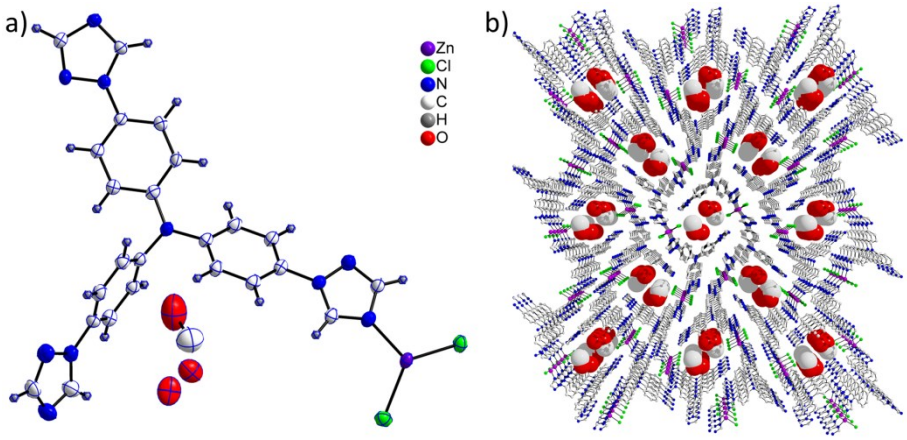

Fig. S15 (a) Ellipsoid view of the asymmetric unit of **4**. (b) The methanol and water molecules located in the voids of the framework.

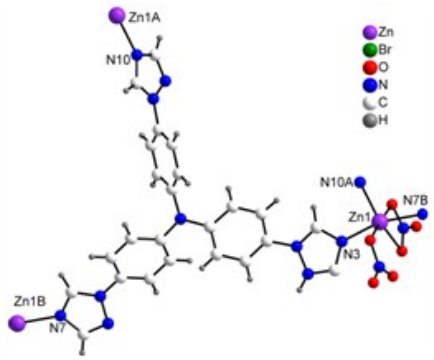

Fig. S16 View of the coordination environment of Zn^{2+} and the TTPA ligand in **4a**.

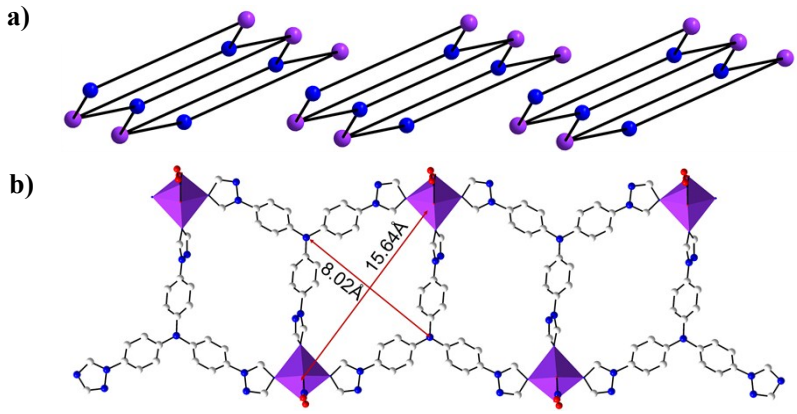

Fig. S17 (a) The 1D chain structure of **4a** along the *a* axis. (b) Simplified chain composed of Zn centers and TTPA ligands as three-connected nodes (purple: Zn, blue: TTPA ligands) arranging in an alternating manner to produce a thick layer.

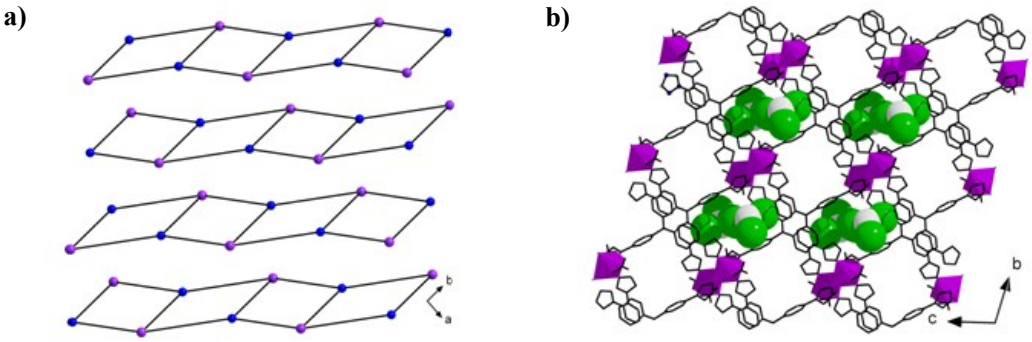

Fig. S18 (a) The packing view of the thick layers of **4a** along the *a* axis. (b) The $CHBr_3$ molecules are located in the voids of the stacking network.

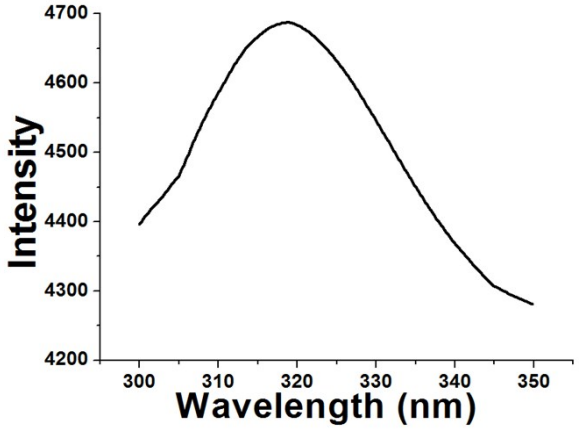

Fig. S19 Emission spectra of solutions of **TTPA** in DMF at room temperature (1×10^{-4} M).

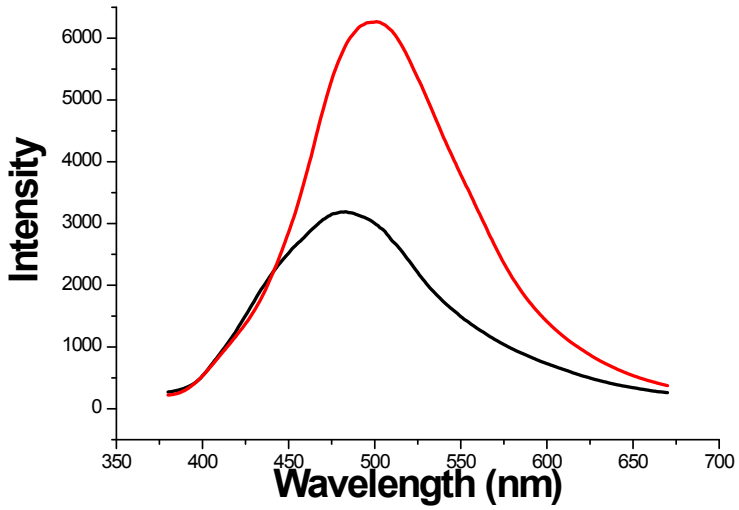

Fig. S20 Emission spectra of solutions of **4** and **4a** at room temperature (1×10^{-4} M). Black, **4**; red, **4a**.

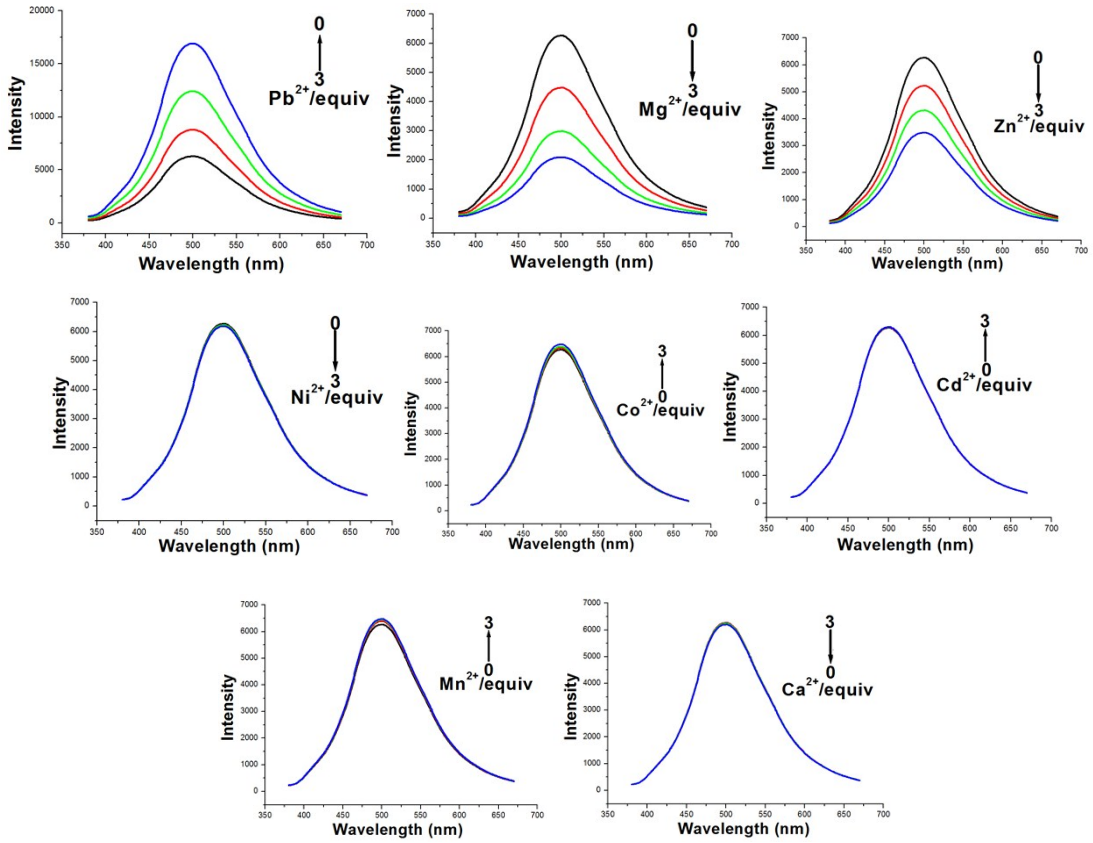

Fig. S21 Emission spectra of complex **4a** in DMF (10^{-3} M) at room temperature in the presence of 0-3 equiv of Pb^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}.

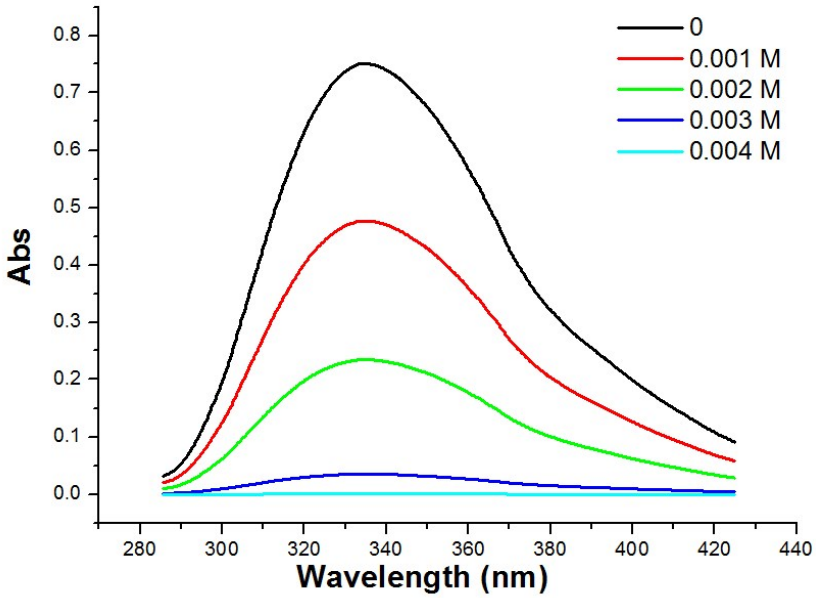

Fig. S22 Photoluminescent spectra of **4a** during different concentration of Pb^{2+}-inclusion process at room temperature.

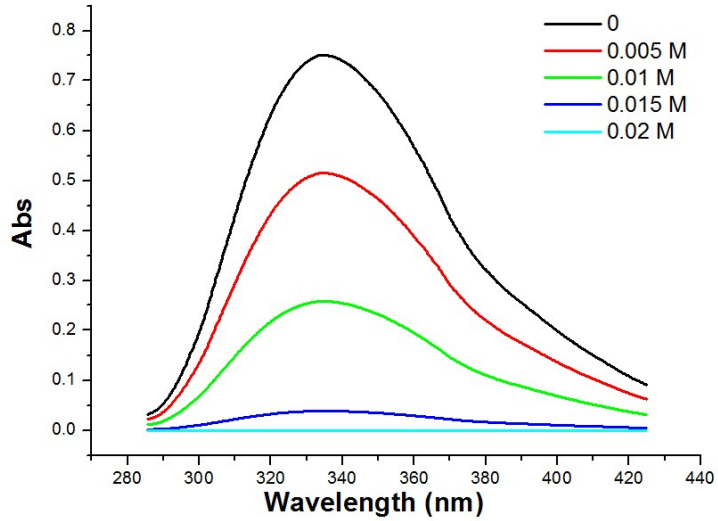

Fig. S23 Photoluminescent spectra of **4a** during different concentration of MnO_4^--inclusion process at room temperature.

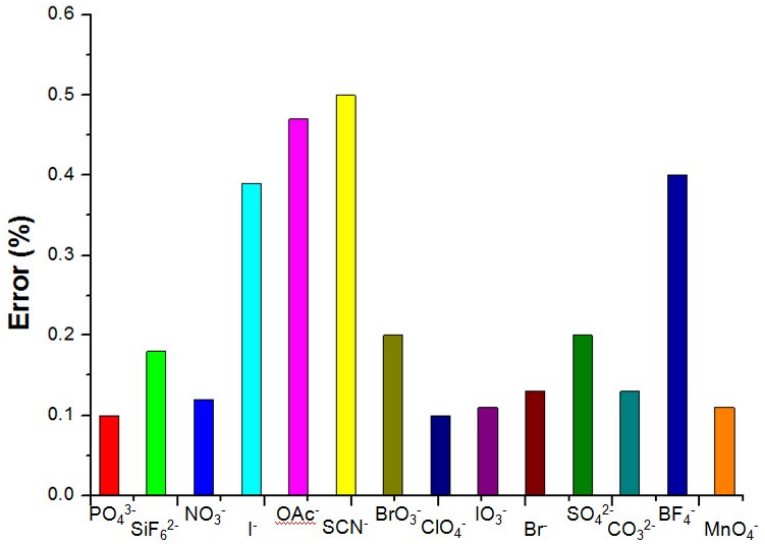

Fig. S24. Error bars of photoluminescent spectra of **4a** with various anions (10^{-2} M).