Supporting Information for

Luminescent Microporous Metal-Metallosalen Frameworks with the Primitive Cubic Net

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1. Materials and General Procedures.

All of the chemicals are commercial available, and used without further purification. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out in an nitrogen atmosphere with a heating rate of 10 ^{o}C/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. ^{1}H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 100.63 MHz. Electrospray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometerusing dichloromethane-methanol as mobile phase. The N_2 adsorption isotherms was measured at 77 K by using a Micromeritics ASAP 2010 M+C system. Before the adsorption measurement, the sample was outgassed at 373 K in the port of the adsorption analyzer for 2 h. All the surface areas were calculated based on multi-point BET plots. High pressure adsorption measurement were carried out on a BELSORP-HP apparatus. The adsorption/desorption of H_2, CO_2 and CH_4 was measured using a volumeric adsorption system. Before the adsorption measurement, the sample was activated at 373 K in under vacuum (< 10^{-3} torr) for 24h.

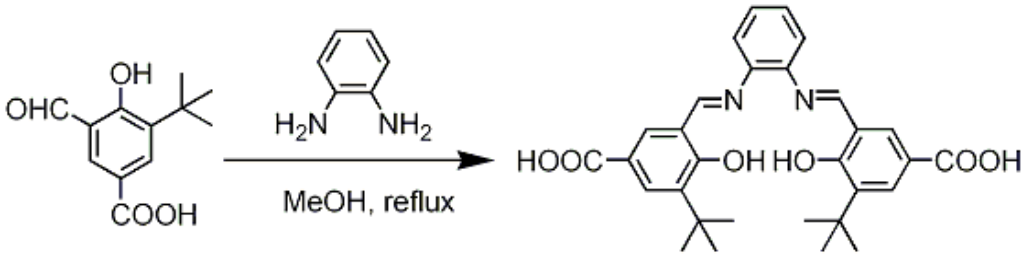
X-ray Crystallography. Single-crystal XRD data for compounds **1** and **2** were collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with Mo-Kα/ Cu-Kα radiation (λ = 1.54178 Å) at 123 K, respectively. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). Their structure were solved using direct method, and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). In the two complexes, the guest molecules and H-atoms were refined isotropically, while all other atoms were refined anisotropically. The single-crystal diffraction showed that the products **1** and **2** have the formula $[Zn_4O(Zn\mathbf{L})_3\ (DMSO)_5]\cdot 3DMSO\cdot 5H_2O$ and $[Zn_2O(Zn\mathbf{L})_2(bpy)\ (DMA)(H_2O)]\cdot 4DMA\cdot 4H_2O$, respectively. Crystal data and details of the data collection are given in **Table S1**, while the selected bond distances and angles are presented in **Table S2 and S3**.

Preparation of thin layers for photoluminescence study[1]

Quartz slides of dimension 1cm x 2 cm were first rinsed with de-ionized water and ethanol and then dried in the oven. Double sided tape was then applied to the upper half of the slide. For making the thin layers of the sample, the tape was peeled off from the slide after 5 minutes, so that the glue from the tape is stuck in the glass slide. The ground powder of the as-made sample was then sprinkled evenly onto the glued surface of the slide. The extra samples were removed by gentle tapping and putting the face of the slide down. By this process a very thin continuous layer of sample was formed on the glass surface. This glass was then used for the PL study of the sample. New slides with a thin layer were used for each of the quenching experiment. The original fluorescence spectra of each layer were collected before placing the particular glass slides onto each of the analytes.

The fluorescence response of the thin layers to the vapors of nitro-containing aromatics was ascertained by inserting the prepared thin layers into quartz cuvette at RT containing the analytes and cotton gauze, which prevents the direct contact of the thin layers with the analyte and helps to maintain a constant saturated vapor pressure. Thin layers were placed in the quartz cuvette and fluorescence spectra were measured after exposing the thin layers for a specific interval time.

2. Synthesis of H_4**L**



A solution of *o*-phenylenediamine (0.54 g, 5 mmol) in MeOH (50 ml) was added dropwise to 3-tert-butyl-5-formyl-4-hydroxybenzoic acid (2.22 g, 10 mmol) in MeOH (50 ml) at 60 °C. The reaction mixture was stirred at 60 °C for 2 h and the solvent was evaporated under vacuum. The orange powder of H_4**L** was washed with MeOH, and dried under reduced pressure (2.48 g, 96%).

3. Synthesis of compound **1** and **2**.

3.1 Synthesis of **1**

A mixture of $Zn(OAc)_2 \cdot 4H_2O$ (20.3 mg, 0.08 mmol), H_4**L** (20.6 mg, 0.04 mmol), DMSO (2 mL), and H_2O (0.5 mL) in a capped vial was heated at 80 °C for one day. yellow block-like crystals of **1** were filtered, washed with DMSO, MeOH and acetone, and dried at room temperature. The products can be best formulated as $[Zn_4O(Zn\mathbf{L})_3(DMSO)_5] \cdot 3DMSO \cdot 5H_2O$ on the basis of microanalysis, IR, TGA and the

single-crystal diffraction analysis. Yield: 19.8 mg (73.9%). Anal (%). Calcd for Calcd for $C_{106}H_{160}N_6O_{32}S_8Zn_7$: C 46.39, H 5.88, N 3.06, S 9.35. Found: C 46.25, H 5.84, N 3.03, S 9.40.

3.2 Synthesis of **2**

A mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (29.6 mg, 0.08 mmol), H_4**L** (20.6 mg, 0.04 mmol), 4, 4'-bipyridine (bpy) (7.68 mg, 0.04 mmol), DMA (2 mL), and H_2O (0.5 mL) Et_3N (one drop) in a capped vial was heated at 80 °C for 8 h. yellow strip-like crystals of **2** were filtered, washed with DMA and CH_2Cl_2, and dried at room temperature. The products can be best formulated as $[Zn_2O(Zn\mathbf{L})_2(bpy)\ (DMA)(H_2O)] \cdot 4DMA \cdot 4H_2O$ on the basis of microanalysis, IR, TGA and the single-crystal diffraction analysis. Yield: 33.1 mg (85%). Anal (%). Calcd for Calcd for $C_{90}H_{128}N_{11}O_{21}Zn_4$: C 55.11, H 6.58, N 7.85. Found: C 55.20, H 6.53, N 7.82.

4. Table S1. Crystal data and structure refinement for **1** and **2**..

Identification code	**1**	**2**
Empirical formula	$C_{100}\ H_{114}\ N_6\ O_{24}\ S_5\ Zn_7$	$C_{90}H_{128}N_{11}O_{21}Zn_4$
Formula weight	2401.86	1961.07
Temperature (K)	296(2) K	293(2)
Wavelength (Å)	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{(1)}/n$	$P2_{(1)}/n$
Unit cell dimensions	a = 22.286(2) Å b = 19.845(2) Å c = 34.290(4) Å α = 90° β =90.968(3)° γ = 90°	a = 23.0013(6) Å b = 14.0578(4) Å c = 31.2380(8) Å α = 90° β =90.881(2) ° γ = 90°
Volume ($Å^3$), Z	15163(3), 4	10099.5(5), 4
Density (calculated) (mg/m^3)	1.052	1.254
Absorption coefficient (mm^{-1})	1.208	1.647
F(000)	4952	3912
θ range for data collection (º)	1.37 to 27.62	3.45 to 50.34
Limiting indices	-28<=h<=28, -23<=k<=25, -43<=l<=44	-22<=h<=22, -14<=k<=13, -31<=l<=30

Reflections collected	163144	26804
Independent reflections	34348 [R(int) = 0.1591]	10141 [R(int) = 0.0420]
Completeness to theta	27.62 / 97.5 %	96.5 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	34348 / 22 / 1095	10141 / 39 / 880
Goodness-of-fit on F^2	1.028	0.986
Final R indices [I>2sigma(I)]	R1 = 0.0752, wR2 = 0.1597	R1 = 0.1055, wR2 = 0.2812
R indices (all data)	R1 = 0.1541, wR2 = 0.1755	R1 = 0.1146, wR2 = 0.2890
Largest diff. peak and hole ($e.Å^{-3}$)	1.051 and -1.012	1.237 and -0.833

5. Table S2. Selected Bond lengths [Å] and angles [°] for **1**

Zn(1)-O(4)	1.956(5)
Zn(1)-O(3)	1.987(4)
Zn(1)-O(19)	2.031(6)
Zn(1)-N(2)	2.066(5)
Zn(1)-N(1)	2.111(5)
Zn(2)-O(15)	1.965(4)
Zn(2)-O(16)	1.970(4)
Zn(2)-O(21)	1.988(6)
Zn(2)-N(3)	2.085(5)
Zn(2)-N(4)	2.087(4)
Zn(3)-O(11)#1	1.914(4)
Zn(3)-O(33)	1.924(3)
Zn(3)-O(18)#2	1.952(4)
Zn(3)-O(1)	1.980(4)
Zn(4)-O(33)	1.925(3)
Zn(4)-O(13)	1.939(4)
Zn(4)-O(7)	1.960(4)
Zn(4)-O(2)	2.007(4)
Zn(4)-Zn(6)	3.0818(9)
Zn(5)-O(33)	2.009(3)
Zn(5)-O(12)#1	2.066(4)
Zn(5)-O(23)	2.095(5)
Zn(5)-O(14)	2.114(4)

Zn(5)-O(6)#3	2.161(4)
Zn(5)-O(22)	2.186(5)
Zn(6)-O(33)	1.926(3)
Zn(6)-O(5)#3	1.941(4)
Zn(6)-O(8)	1.947(4)
Zn(6)-O(17)#2	1.988(4)
Zn(7)-O(9)	1.955(5)
Zn(7)-O(10)	1.960(5)
Zn(7)-O(20)	1.995(7)
Zn(7)-N(5)	2.100(5)
Zn(7)-N(6)	2.100(5)
O(5)-Zn(6)#4	1.941(4)
O(6)-Zn(5)#4	2.161(4)
O(11)-Zn(3)#5	1.914(4)
O(12)-Zn(5)#5	2.066(4)
O(17)-Zn(6)#6	1.988(4)
O(18)-Zn(3)#6	1.952(4)

O(4)-Zn(1)-O(3)	99.35(18)
O(4)-Zn(1)-O(19)	109.9(3)
O(3)-Zn(1)-O(19)	100.89(19)
O(4)-Zn(1)-N(2)	139.7(2)
O(3)-Zn(1)-N(2)	86.52(18)
O(19)-Zn(1)-N(2)	107.9(3)
O(4)-Zn(1)-N(1)	88.35(18)
O(3)-Zn(1)-N(1)	161.92(18)
O(19)-Zn(1)-N(1)	91.7(2)
N(2)-Zn(1)-N(1)	77.19(19)
O(15)-Zn(2)-O(16)	95.01(16)
O(15)-Zn(2)-O(21)	105.0(2)
O(16)-Zn(2)-O(21)	102.7(2)
O(15)-Zn(2)-N(3)	88.55(18)
O(16)-Zn(2)-N(3)	159.78(19)
O(21)-Zn(2)-N(3)	95.6(2)
O(15)-Zn(2)-N(4)	146.22(19)
O(16)-Zn(2)-N(4)	88.35(17)
O(21)-Zn(2)-N(4)	107.0(2)

N(3)-Zn(2)-N(4)	77.93(18)
O(11)#1-Zn(3)-O(33)	115.51(16)
O(11)#1-Zn(3)-O(18)#2	116.31(19)
O(33)-Zn(3)-O(18)#2	110.85(16)
O(11)#1-Zn(3)-O(1)	101.74(19)
O(33)-Zn(3)-O(1)	109.38(17)
O(18)#2-Zn(3)-O(1)	101.4(2)
O(11)#1-Zn(3)-Zn(4)	121.06(13)
O(33)-Zn(3)-Zn(4)	35.67(10)
O(18)#2-Zn(3)-Zn(4)	122.21(13)
O(1)-Zn(3)-Zn(4)	73.86(15)
O(33)-Zn(4)-O(13)	117.28(16)
O(33)-Zn(4)-O(7)	114.42(16)
O(13)-Zn(4)-O(7)	108.95(19)
O(33)-Zn(4)-O(2)	109.61(17)
O(13)-Zn(4)-O(2)	109.47(19)
O(7)-Zn(4)-O(2)	94.8(2)
O(33)-Zn(4)-Zn(6)	36.87(10)
O(13)-Zn(4)-Zn(6)	139.48(13)
O(7)-Zn(4)-Zn(6)	77.87(13)
O(2)-Zn(4)-Zn(6)	109.64(14)
O(33)-Zn(4)-Zn(3)	35.65(10)
O(13)-Zn(4)-Zn(3)	118.20(13)
O(7)-Zn(4)-Zn(3)	132.28(13)
O(2)-Zn(4)-Zn(3)	76.88(14)
Zn(6)-Zn(4)-Zn(3)	62.07(2)
O(33)-Zn(5)-O(12)#1	103.29(15)
O(33)-Zn(5)-O(23)	167.72(18)
O(12)#1-Zn(5)-O(23)	88.99(19)
O(33)-Zn(5)-O(14)	93.04(15)
O(12)#1-Zn(5)-O(14)	89.34(18)
O(23)-Zn(5)-O(14)	86.8(2)
O(33)-Zn(5)-O(6)#3	92.83(15)
O(12)#1-Zn(5)-O(6)#3	89.19(16)
O(23)-Zn(5)-O(6)#3	87.5(2)
O(14)-Zn(5)-O(6)#3	174.13(17)
O(33)-Zn(5)-O(22)	80.90(18)

O(12)#1-Zn(5)-O(22)	175.54(19)
O(23)-Zn(5)-O(22)	86.8(2)
O(14)-Zn(5)-O(22)	88.9(2)
O(6)#3-Zn(5)-O(22)	92.16(19)
O(33)-Zn(5)-Zn(6)	36.00(9)
O(12)#1-Zn(5)-Zn(6)	121.31(12)
O(23)-Zn(5)-Zn(6)	136.00(16)
O(14)-Zn(5)-Zn(6)	121.29(12)
O(6)#3-Zn(5)-Zn(6)	64.16(12)
O(22)-Zn(5)-Zn(6)	63.03(14)
O(33)-Zn(6)-O(5)#3	121.13(16)
O(33)-Zn(6)-O(8)	114.04(16)
O(5)#3-Zn(6)-O(8)	106.63(18)
O(33)-Zn(6)-O(17)#2	106.17(16)
O(5)#3-Zn(6)-O(17)#2	105.16(19)
O(8)-Zn(6)-O(17)#2	101.58(18)
O(33)-Zn(6)-Zn(4)	36.85(10)
O(5)#3-Zn(6)-Zn(4)	140.68(13)
O(8)-Zn(6)-Zn(4)	77.31(12)
O(17)#2-Zn(6)-Zn(4)	112.40(14)
O(33)-Zn(6)-Zn(5)	37.80(10)
O(5)#3-Zn(6)-Zn(5)	84.23(13)
O(8)-Zn(6)-Zn(5)	124.21(13)
O(17)#2-Zn(6)-Zn(5)	128.75(13)
Zn(4)-Zn(6)-Zn(5)	63.53(2)
O(9)-Zn(7)-O(10)	94.7(2)
O(9)-Zn(7)-O(20)	104.8(3)
O(10)-Zn(7)-O(20)	102.6(3)
O(9)-Zn(7)-N(5)	155.3(2)
O(10)-Zn(7)-N(5)	88.2(2)
O(20)-Zn(7)-N(5)	98.4(3)
O(9)-Zn(7)-N(6)	88.55(19)
O(10)-Zn(7)-N(6)	151.7(2)
O(20)-Zn(7)-N(6)	103.7(3)
N(5)-Zn(7)-N(6)	77.8(2)
Zn(3)-O(33)-Zn(4)	108.68(16)
Zn(3)-O(33)-Zn(6)	112.49(15)

Zn(4)-O(33)-Zn(6)	106.27(16)
Zn(3)-O(33)-Zn(5)	110.26(16)
Zn(4)-O(33)-Zn(5)	112.92(15)
Zn(6)-O(33)-Zn(5)	106.20(15)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+1/2,z+1/2 #2 x+1/2,-y+1/2,z-1/2
#3 x,y-1,z #4 x,y+1,z #5 x-1/2,-y+1/2,z-1/2
#6 x-1/2,-y+1/2,z+1/2

6. **Table S3**. Selected Bond lengths [Å] and angles [º] for **2**.

Zn(1)-O(6)#1	2.100(7)
Zn(1)-O(11)#2	2.103(7)
Zn(1)-N(6)#3	2.110(11)
Zn(1)-O(8)	2.113(7)
Zn(1)-O(13)	2.130(6)
Zn(1)-O(2)	2.188(7)
Zn(2)-O(1)	1.918(7)
Zn(2)-O(13)	1.931(6)
Zn(2)-O(7)	1.956(6)
Zn(2)-N(5)	2.033(4)
Zn(3)-O(3)	1.939(8)
Zn(3)-O(4)	1.951(8)
Zn(3)-O(14)	2.054(10)
Zn(3)-N(2)	2.059(8)
Zn(3)-N(1)	2.105(9)
Zn(4)-O(9)	1.962(7)
Zn(4)-O(10)	1.966(7)
Zn(4)-O(15)	2.039(11)
Zn(4)-N(4)	2.052(9)
Zn(4)-N(3)	2.087(8)
N(6)-Zn(1)#4	2.110(4)
O(6)-Zn(1)#5	2.100(7)
O(11)-Zn(1)#6	2.103(7)

O(6)#1-Zn(1)-O(11)#2	99.4(3)

O(6)#1-Zn(1)-N(6)#3	90.8(11)
O(11)#2-Zn(1)-N(6)#3	86.0(12)
O(6)#1-Zn(1)-O(8)	87.7(3)
O(11)#2-Zn(1)-O(8)	172.0(3)
N(6)#3-Zn(1)-O(8)	90.1(12)
O(6)#1-Zn(1)-O(13)	92.0(3)
O(11)#2-Zn(1)-O(13)	88.6(3)
N(6)#3-Zn(1)-O(13)	174.3(11)
O(8)-Zn(1)-O(13)	95.0(2)
O(6)#1-Zn(1)-O(2)	174.6(3)
O(11)#2-Zn(1)-O(2)	86.0(3)
N(6)#3-Zn(1)-O(2)	90.0(12)
O(8)-Zn(1)-O(2)	87.0(3)
O(13)-Zn(1)-O(2)	87.6(3)
O(1)-Zn(2)-O(13)	112.8(3)
O(1)-Zn(2)-O(7)	117.2(3)
O(13)-Zn(2)-O(7)	105.3(3)
O(1)-Zn(2)-N(5)	104.1(3)
O(13)-Zn(2)-N(5)	111.6(3)
O(7)-Zn(2)-N(5)	105.8(3)
O(3)-Zn(3)-O(4)	92.3(3)
O(3)-Zn(3)-O(14)	103.4(4)
O(4)-Zn(3)-O(14)	103.0(4)
O(3)-Zn(3)-N(2)	152.7(4)
O(4)-Zn(3)-N(2)	89.4(3)
O(14)-Zn(3)-N(2)	102.7(4)
O(3)-Zn(3)-N(1)	87.9(3)
O(4)-Zn(3)-N(1)	153.2(4)
O(14)-Zn(3)-N(1)	103.0(4)
N(2)-Zn(3)-N(1)	78.7(3)
O(9)-Zn(4)-O(10)	93.3(3)
O(9)-Zn(4)-O(15)	105.2(4)
O(10)-Zn(4)-O(15)	99.0(4)
O(9)-Zn(4)-N(4)	146.4(4)
O(10)-Zn(4)-N(4)	89.2(3)
O(15)-Zn(4)-N(4)	107.5(4)
O(9)-Zn(4)-N(3)	88.1(3)

O(10)-Zn(4)-N(3)	159.7(4)
O(15)-Zn(4)-N(3)	100.2(4)
N(4)-Zn(4)-N(3)	78.7(3)

Symmetry transformations used to generate equivalent atoms:

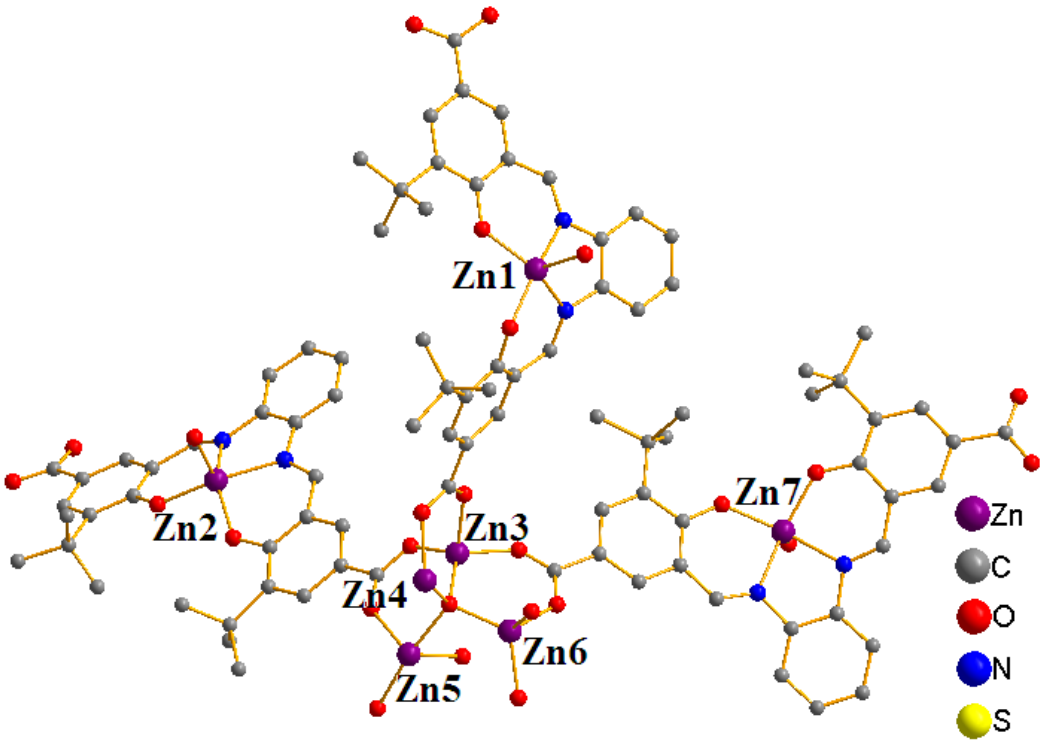
#1 x-1/2,-y+3/2,z+1/2 #2 x-1/2,-y+3/2,z-1/2

#3 x,y+1,z #4 x,y-1,z #5 x+1/2,-y+3/2,z-1/2

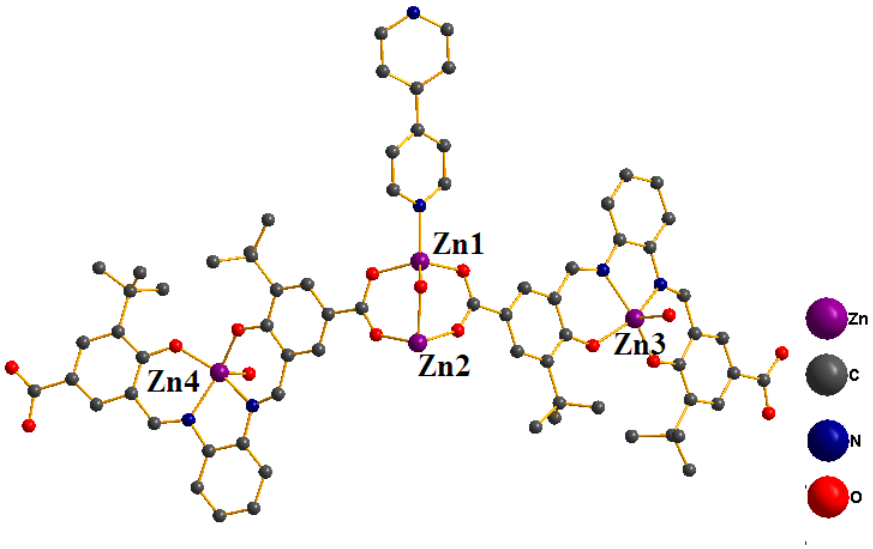
#6 x+1/2,-y+3/2,z+1/2

7. Additional X-ray crystallographic structures of **1** and **2**.

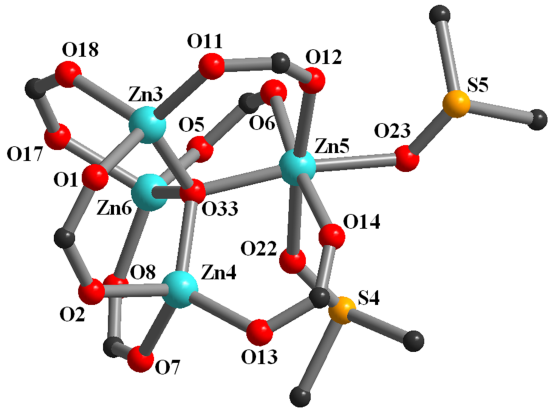
7.1. Figure S1. The asymmetric unit of **1**.



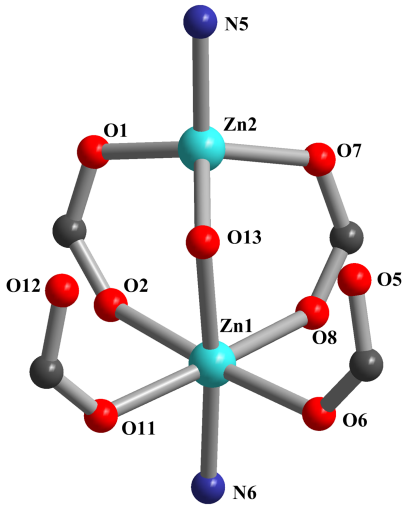
7.2 Figure S2. The asymmetric unit of **2**.



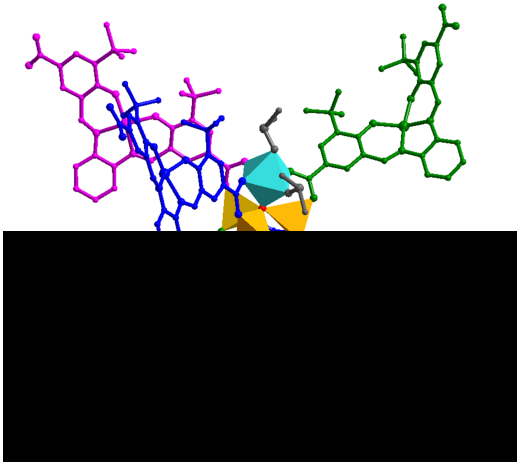
7.3. Figure S3. Coordination environment of Zn_4O cluster in **1**. Hydrogen atoms are omitted for clarity.



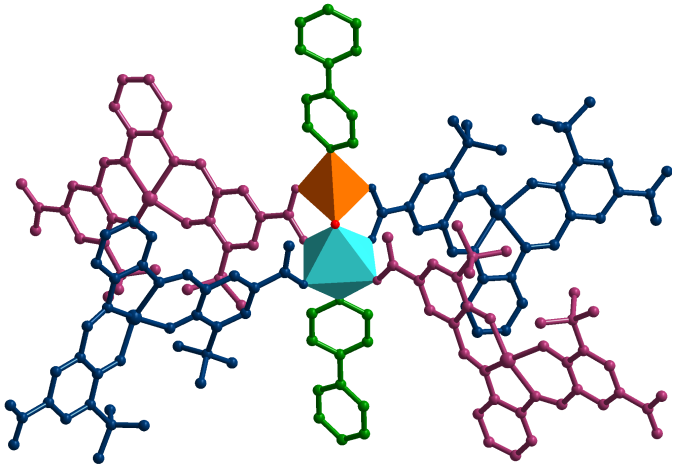
7.4. Figure S4. Coordination environment of $Zn_2O(CO_2)_4$ cluster in **2**. Hydrogen atoms are omitted for clarity.



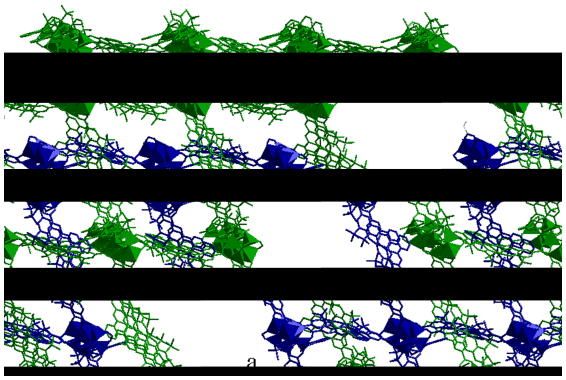
7.5. Figure S5. View of the link mode between Zn_4O cluster and metallosalen ligands.



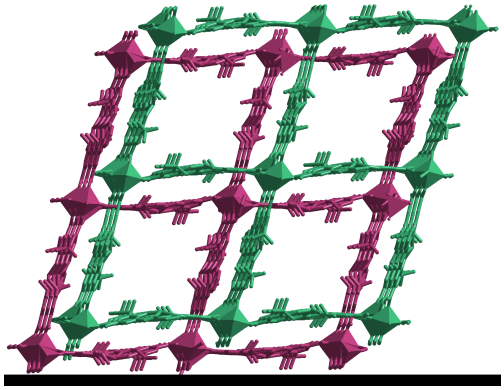
7.6. Figure S6. View of the link mode between $Zn_2O(CO_2)_4$ cluster and metallosalen ligands.



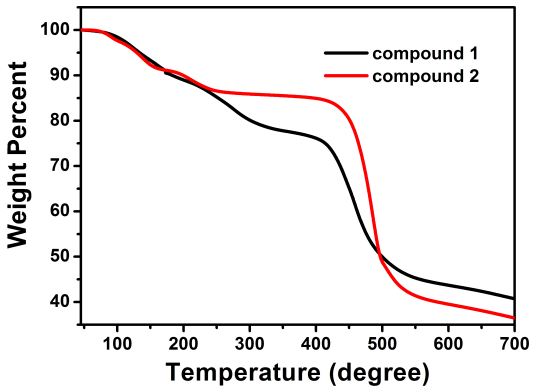
7.7. Figure S7. Two-fold interpenetrating 3D structure of **1** viewed down the ***b*** direction

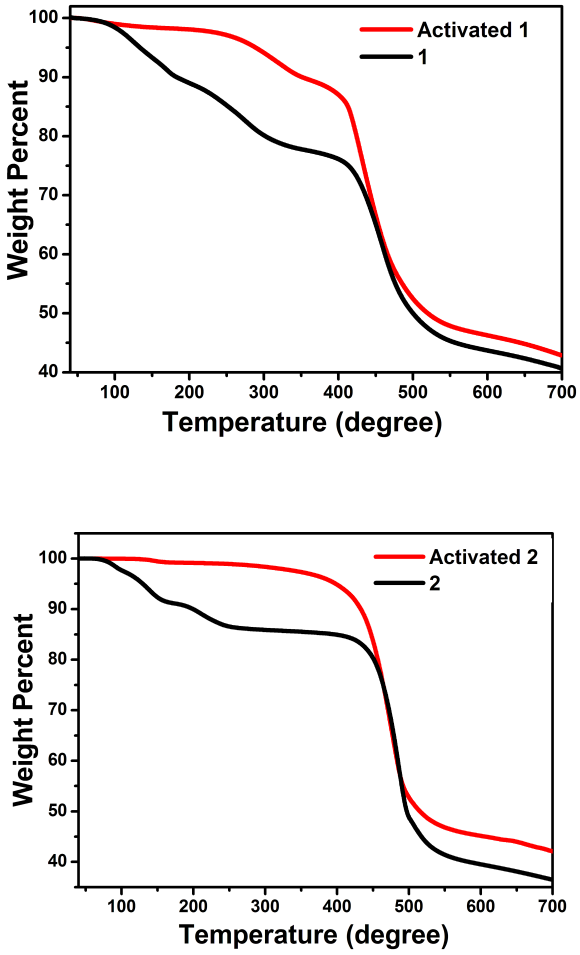


7.8. Figure S8. Two-fold interpenetrating 3D structure of **2** viewed down the ***b*** direction

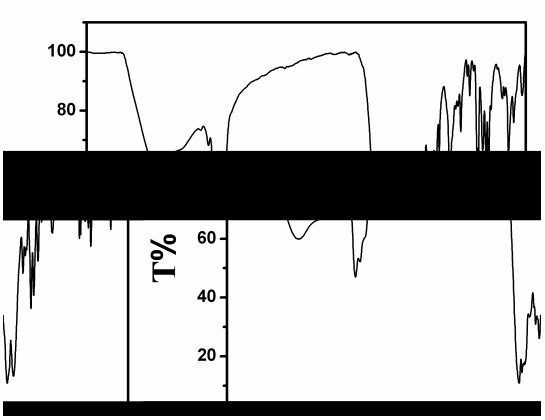


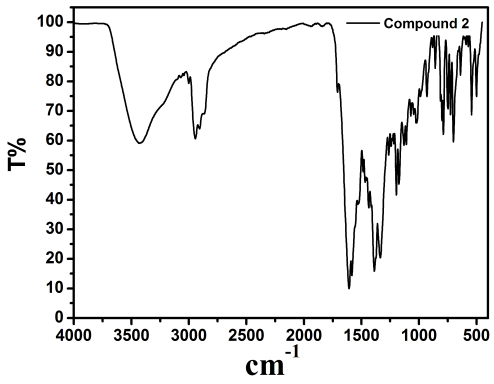
8.Figure S9. TGA curves of **1** , **2** and their activated samples.



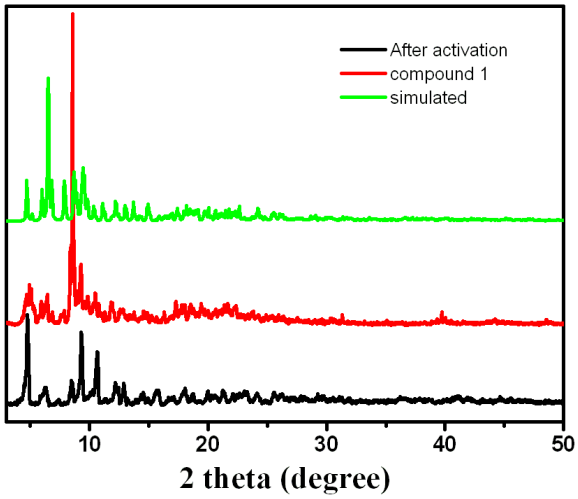


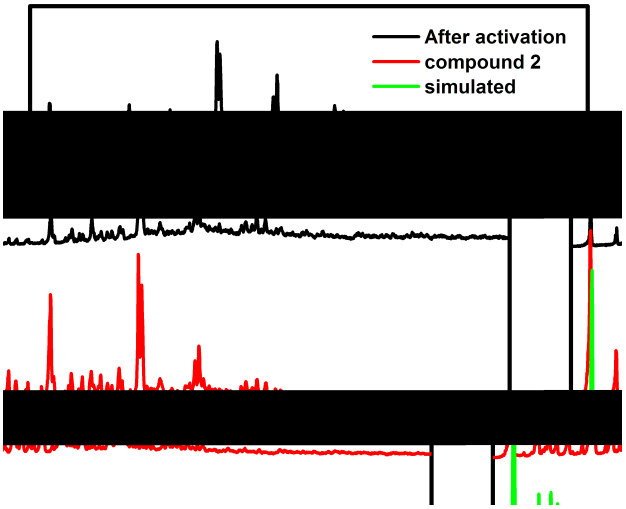
9. **Figure S10.** IR spectra of **1**(top) and **2**(down).



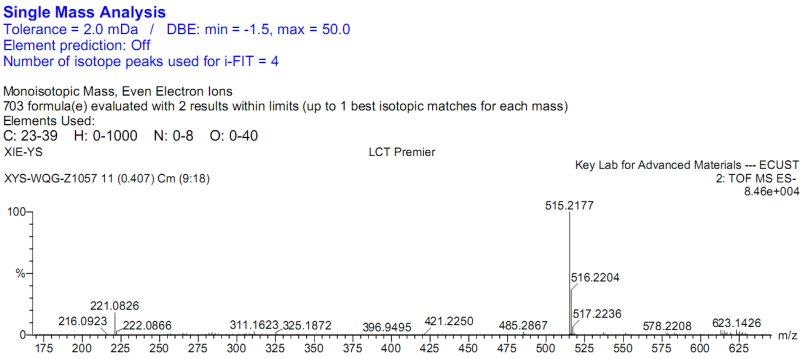


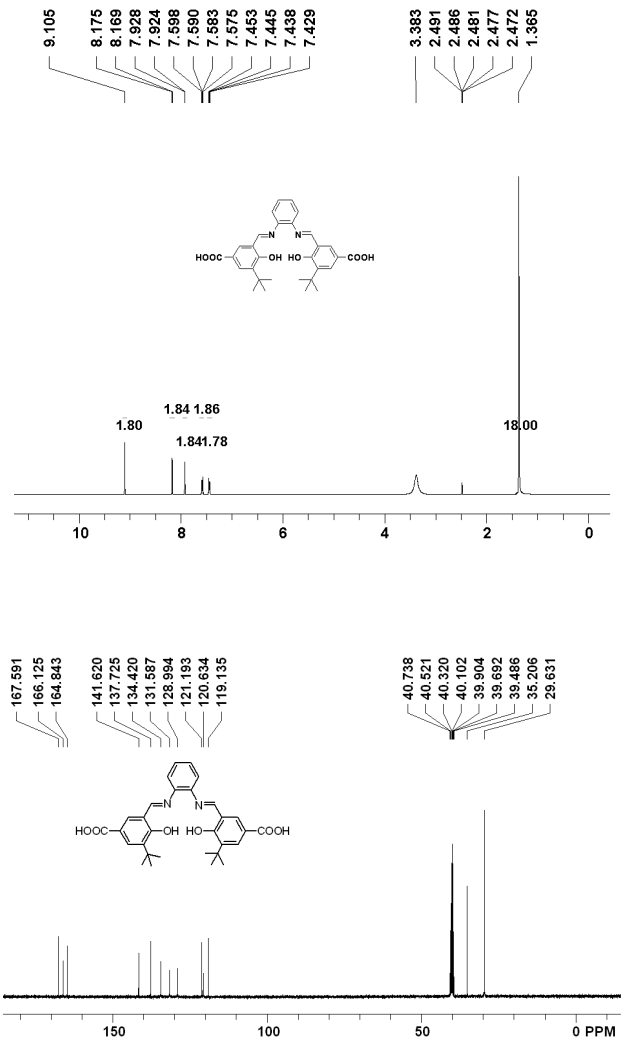
10. Figure S11. PXRD patterns of **1** and activated **1**.



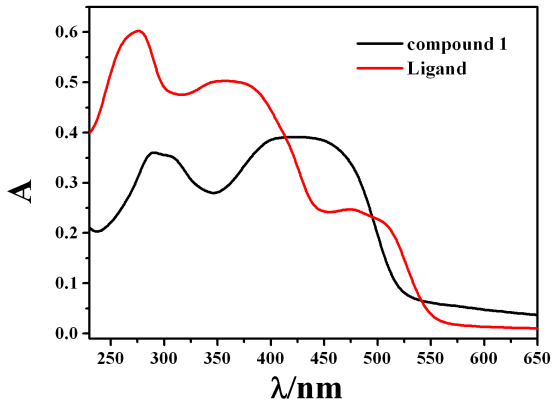


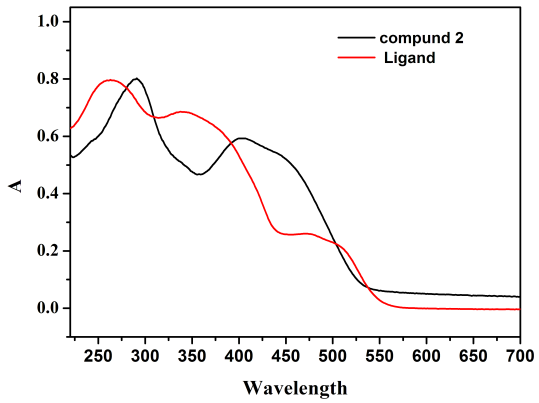
11. Figure S12. ESI-MS, ^{1}H and ^{13}C NMR spectra of H_4**L**



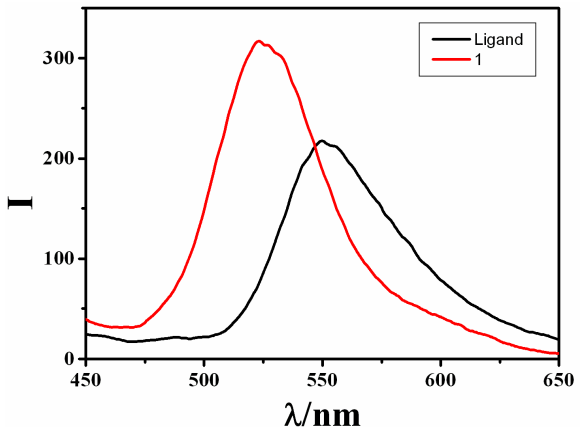


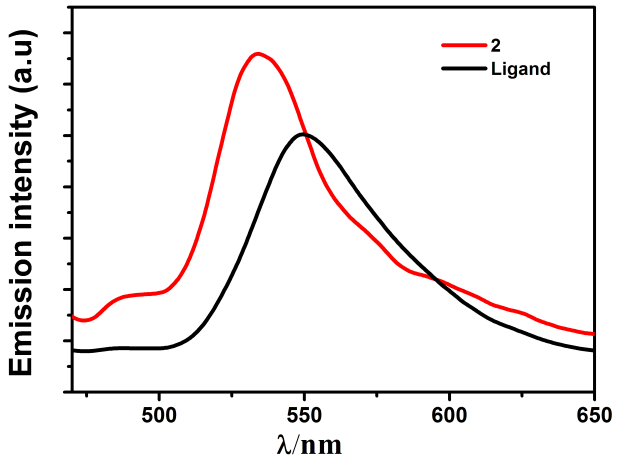
12. Figure S13. UV/Vis absorption spectra of **1, 2** and H_4**L** in the solid state.



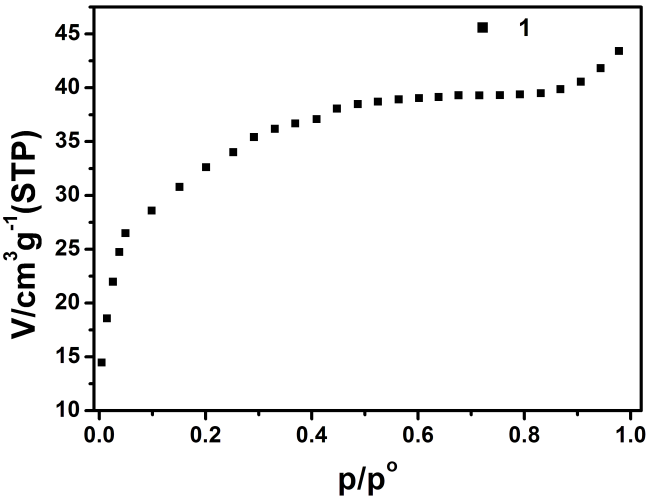


13. Figure S14. Photoinduced emission spectra of **1**, **2** and H_4**L** in the solid state at room temperature.

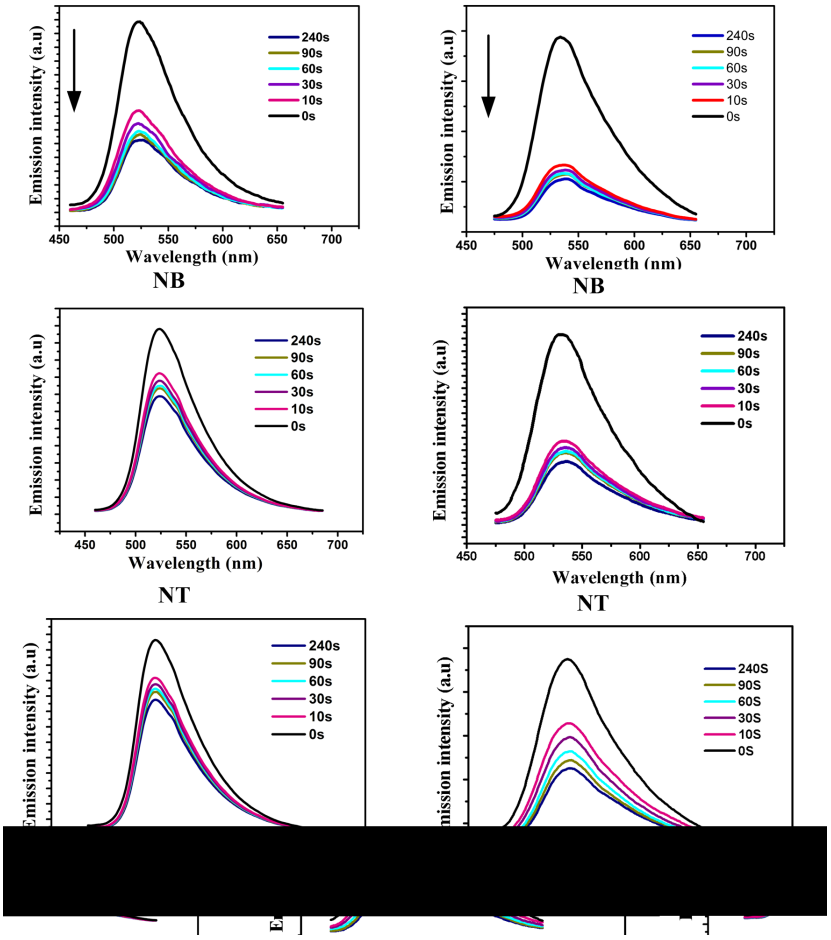




14. **Figure S15.** Nitrogen sorption isotherm (77 K) of activated **1**.



15. **Figure S16.** Time-dependent fluorescence spectra of **1** (left) and **2** (right) upon exposure to nitroaromatic vapor.



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1.(a) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am.Chem. Soc.*, 2011, **133**, 4153. (b) B. Xu, X. Wu, H. Li, H. Tong and L. Wang, *Macromolecules*, 2011, **1**, 3.