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Diverse Structures of Metal – Organic Frameworks Based on Different Metal Ions: Luminescence and Gas Adsorption Properties

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Experimental Section

Materials and Methods: All chemicals and solvents except L ligand were of reagent-grade quality from commercial sources and were used without further purification. The L ligand was synthesized by the literature methods.[1] The IR absorption spectra of these complexes and L ligand were recorded in the range of 400-4000 cm^{-1} by means of a Nicolet (Impact 410) spectrometer with KBr pellets. Element analyses (C, H, N) were carried out on a Perkin-Elmer model 240C analyzer. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Mo Kα radiation (λ = 0.71073 nm), in which the X-ray tube was operated at 40 kV and 30 mA. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature (25 °C). The decay lifetimes were measured with an Edinburgh Instruments FLS920P fluorescence spectrometer in the solid state at room temperature (RT). Solid-state UV-vis diffuse reflectance spectra was obtained at room temperature using Shimadzu UV-3600 double monochromator spectrophotometer, and $BaSO_4$ was used as a 100% reflectance standard for all materials. Thermogravimetric analysis (TGA) was performed under a N_2 atmosphere with a heating rate of 10 K·min^{-1} by using a Perkin-Elmer thermogravimetric analyzer.

Crystal Structure Determination: Single crystal X-ray data of complexes **1**–**4** were collected at 293 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were referred to from the International Tables for X-ray Crystallography.[2] The structures were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically using full-matrix least-squares procedures based on F^2 values using SHELXTL (version 6.10) crystallographic software.[3] The H-atoms of lattice H_2O and DMF molecules in complex **3** were located in difference Fourier maps. The H-atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. Squeeze refinement was performed for complex **1**, **2** and **4** using PLATON [4] for their serious disorder, which shows one lattice DMF molecule in them. The contribution of the solvent atoms has been incorporated in both the empirical formula and formula weight of complexes **1** and **2**. Complex **4** was difficult to get good crystals for crystal structure determination though we tried many times. The crystal and refinement data are collected in Table 1. Selective bond distances and angles are given in Table S1 (Supporting Information). The topological analysis and some diagrams were produced using the TOPOS program.[5]

Synthesis of Complex 1: A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (14.55 mg, 0.05 mmol), L (18.9 mg, 0.05 mmol), and H_2OBA (21.0 mg, 0.1 mmol) was dissolved in 6.0 mL of DMF/H_2O (3.5/4.5). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 95 °C for 3 days and then cooled to room temperature. Claret-colored crystals of **1** were collected in 61% yield (based on L ligand). Elemental analysis calcd. for $C_{32}H_{28}N_2O_9Co$ (%): C, 59.68; H, 4.35; N, 4.35. Found: C, 59.77; H, 4.28; N, 4.42. IR (KBr, cm^{-1}): 3440m, 1678m, 1613vs, 1557m, 1489m, 1394vs, 1231vs, 1164m, 1060m, 1030m, 875m, 839m, 781m, 669m, 665w (Supporting Information Figure S6).

Synthesis of Complex 2: A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (14.85 mg, 0.05 mmol), L (18.9 mg, 0.05 mmol), and H_2OBA (21.0 mg, 0.1 mmol) was dissolved in 6.0 mL of DMF/H_2O (4.0/2.0). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 95°C for 3 days and then cooled to room temperature. The colourless block crystals were obtained. Yield of the reaction was ca. 51% based on L ligand. Elemental analysis calcd. for $C_{32}H_{28}N_2O_9Zn$ (%): C, 59.08; H, 4.31; N, 4.31. Found: C, 59.15; H, 4.24; N, 4.26. IR (KBr, cm^{-1}): 3442m, 1679m, 1616vs, 1574m, 1490m, 1395vs, 1229vs, 1164m, 1074m, 1031m, 874m, 840m, 781m, 699m, 655w (Supporting Information Figure S7).

Synthesis of Complex 3: A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (14.54 mg, 0.05 mmol), L (18.9 mg, 0.05 mmol), and H_2OBA (21.0 mg, 0.1 mmol) was dissolved in 6.0 mL of DMF/H_2O (4.5/1.5). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 95 °C for 3 days and then cooled to room temperature. Green crystals of **3** were collected in 65% yield (based on L ligand). Elemental analysis calcd. for $C_{35}H_{33}N_3O_9Ni$ (%): C, 60.14; H, 4.73; N, 6.01. Found: C, 60.08; H, 4.81; N, 6.04. IR (KBr, cm^{-1}): 3441m, 1671s, 1594vs, 1529s, 1488s, 1419vs, 1230vs, 1160m, 1029m, 876s, 845m, 782s, 697m, 659m (Supporting Information Figure S8).

Synthesis of Complex 4: A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (15.0 mg, 0.05 mmol), L (18.9 mg, 0.05 mmol), and H_2OBA (21.0 mg, 0.1 mmol) was dissolved in 6.0 mL of DMF/H_2O (5.0/1.0). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 95 °C for 3 days and then cooled to room temperature. The colourless block crystals of **4** were collected in 44% yield (based on L ligand). Elemental analysis calcd. for $C_{35}H_{33}N_3O_9Cd$ (%): C, 55.86; H, 4.39; N, 5.59. Found: C, 55.92; H, 4.42; N, 5.63. IR (KBr, cm^{-1}): 3442m, 1681m, 1599vs, 1555vs, 1486m, 1391vs, 1249vs, 1159m, 1078m, 879m, 837m, 783s, 688s, 660m (Supporting Information Figure S9).

Table S1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1-4**.

Complex **1**			
Co(1)-O(3)#1	1.9752(14)	Co(1)-O(2)	1.9771(15)
Co(1)-N(2)	2.0521(15)	Co(1)-N(1)	2.0542(15)
O(3)-Co(1)#2	1.9752(14)	O(3)#1-Co(1)-N(2)	129.90(7)
O(3)#1-Co(1)-O(2)	106.04(7)	O(2)-Co(1)-N(2)	110.79(7)
O(3)#1-Co(1)-N(1)	107.17(6)	O(2)-Co(1)-N(1)	93.92(6)
N(2)-Co(1)-N(1)	102.99(6)		
Complex **2**			
Zn(1)-O(3)	1.9536(16)	Zn(1)-O(1)	1.9638(17)
Zn(1)-N(1)	2.0458(16)	Zn(1)-N(2)	2.0610(16)

O(3)-Zn(1)-O(1)	108.97(7)	O(3)-Zn(1)-N(1)	124.51(7)
O(1)-Zn(1)-N(1)	112.88(8)	N(1)-Zn(1)-N(2)	103.01(7)
O(3)-Zn(1)-N(2)	107.43(7)	O(1)-Zn(1)-N(2)	95.63(7)
Complex **3**			
Ni(1)-N(1)	2.031(2)	Ni(1)-O(2)	2.0457(19)
Ni(1)-N(2)	2.048(2)	Ni(1)-O(4)#1	2.072(2)
Ni(1)-O(1)	2.232(2)	Ni(1)-O(3)#1	2.107(2)
N(1)-Ni(1)-O(2)	96.99(9)	N(1)-Ni(1)-N(2)	96.12(9)
O(2)-Ni(1)-N(2)	96.93(8)	N(1)-Ni(1)-O(4)#1	99.19(8)
O(2)-Ni(1)-O(4)#1	157.24(9)	N(2)-Ni(1)-O(4)#1	97.15(9)
N(1)-Ni(1)-O(3)#1	161.57(8)	O(2)-Ni(1)-O(3)#1	98.43(8)
N(2)-Ni(1)-O(3)#1	91.98(9)	O(4)#1-Ni(1)-O(3)#1	63.29(7)
N(1)-Ni(1)-O(1)	89.86(8)	O(2)-Ni(1)-O(1)	61.94(7)
N(2)-Ni(1)-O(1)	158.66(8)	O(4)#1-Ni(1)-O(1)	102.10(8)
O(3)#1-Ni(1)-O(1)	88.53(8)		
Complex **4**			
Cd(1)-O(3)#1	2.224(4)	Cd(1)-O(4)#2	2.261(4)
Cd(1)-N(1)	2.364(4)	Cd(1)-N(2)	2.364(5)
Cd(1)-O(1)	2.360(5)	Cd(1)-O(2)	2.398(5)
O(3)#1-Cd(1)-O(4)#2	102.93(17)	O(3)#1-Cd(1)-N(1)	86.66(18)
O(4)#2-Cd(1)-N(1)	80.88(16)	O(3)#1-Cd(1)-N(2)	104.5(2)
O(4)#2-Cd(1)-N(2)	92.42(19)	N(1)-Cd(1)-N(2)	167.90(19)
O(3)#1-Cd(1)-O(1)	97.44(19)	O(4)#2-Cd(1)-O(1)	158.4(2)
N(1)-Cd(1)-O(1)	93.32(18)	N(2)-Cd(1)-O(1)	89.3(2)
O(3)#1-Cd(1)-O(2)	150.45(18)	O(4)#2-Cd(1)-O(2)	103.58(17)
N(2)-Cd(1)-O(2)	86.99(19)	N(1)-Cd(1)-O(2)	84.86(18)

O(1)#1-Cd(1)-O(1)	180.00(12)	O(1)-Cd(1)-O(2)	54.74(17)

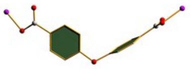
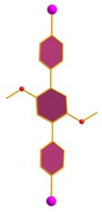
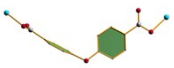
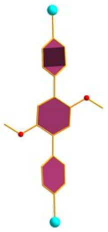
Symmetry codes: for **1**: #1 = *x* + 1/2, – *y* + 1/2, *z* + 1/2; #2 = *x* – 1/2, – *y* + 1/2, *z* – 1/2; for **3**: #1 = *x*, *y*, *z* + 1; for **4**: #1 = *x*, *y*, *z* + 1; #2 = – *x* + 2, – *y* + 1, – *z*.

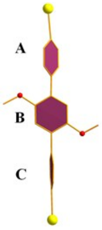
Table S2. Luminescence data for organic ligand and complexes in the solid state.

Compound	λ_{ex} [nm]	λ_{em} [nm] (lifetime [a], μs)
L ligand	335	428 [9.71 (50.88%), 1.30 (49.12%)]
Complex **2**	335	462 [10.47 (46.15 %), 1.27 (53.85%)]
Complex **4**	350	425 [9.17 (52.64%), 1.19 (47.36%)]

[a] The luminescent decay curves were fitted with a double-exponential decay function: Fit = $A+B_1\times\exp(-t/\tau_1)+B_2\times\exp(-t/\tau_2)$.

Table S3. The L and OBA^{2-} ligands conformations and the corresponding angles for **1–4**.

Complexes	Diagram of OBA^{2-}	$C\cdots O_{core}\cdots C$ (°)	Dihedral angle (°)	Diagram of L	Dihedral angle (°)
1-Co^{2+}		116.56(17)	83.57		39.37
2-Zn^{2+}		116.50(18)	82.18		37.43
3-Ni^{2+}		115.6(2)	88.13		65.05

4-Cd^{2+}		121.5(7)	53.95		A-B: 67.49 B-C: 79.51 A-C: 33.08

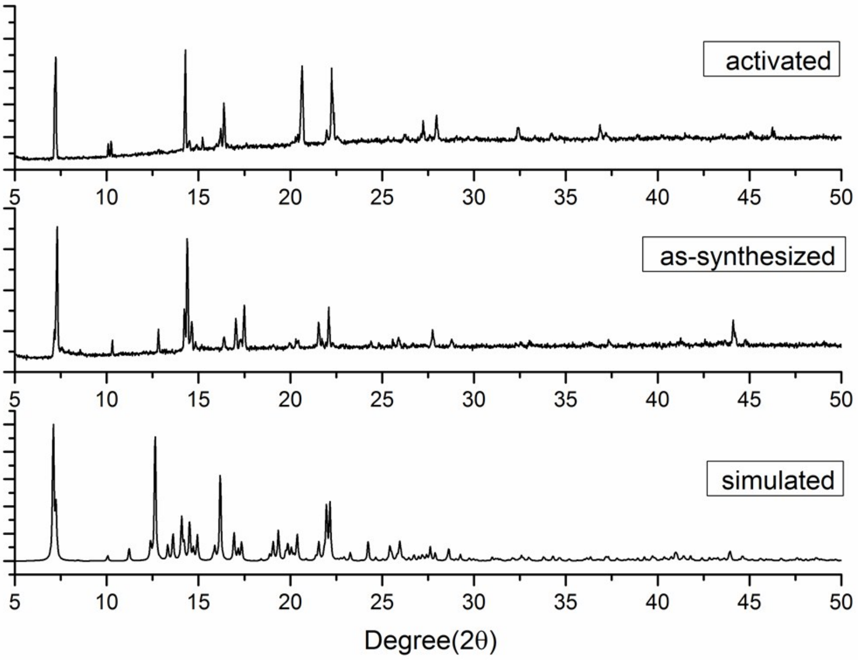


Figure S1. Powder X-ray diffraction patterns of complex **1**

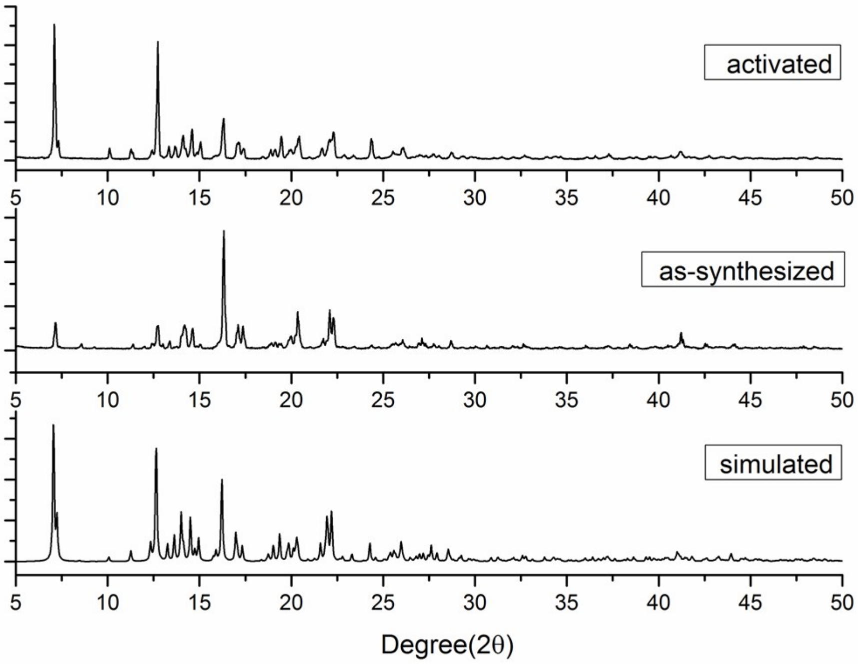


Figure S2. Powder X-ray diffraction patterns of complex **2**

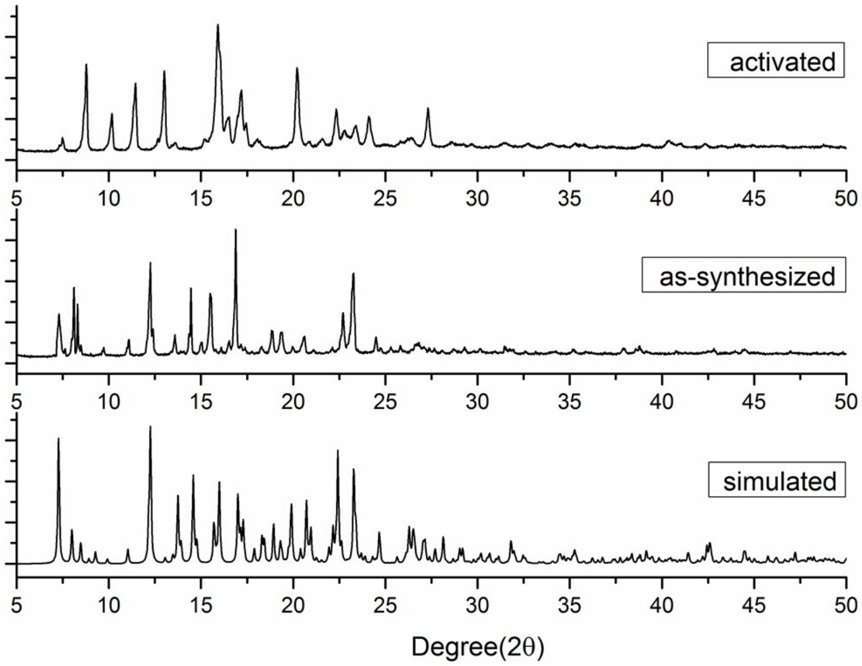


Figure S3. Powder X-ray diffraction patterns of complex **3**

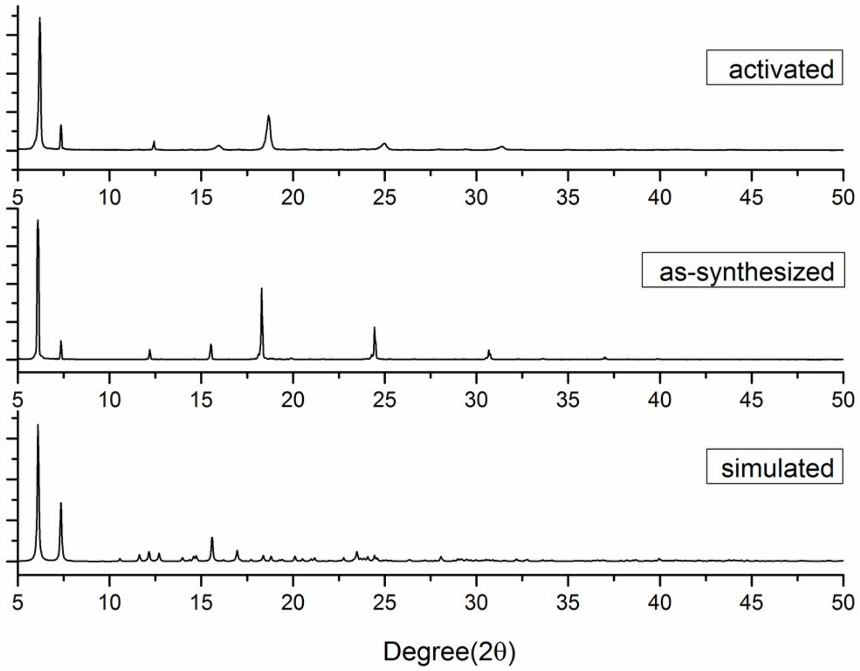


Figure S4. Powder X-ray diffraction patterns of complex **4**

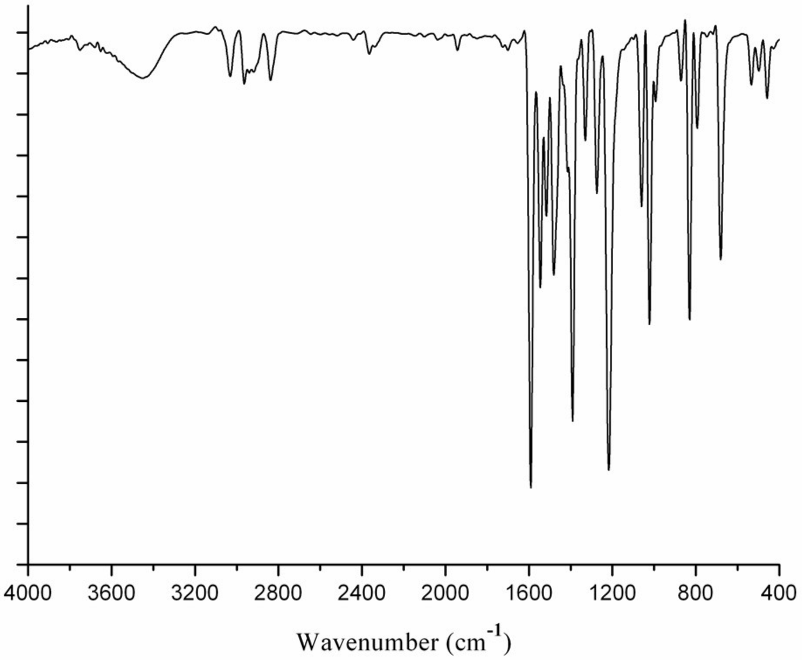


Figure S5. IR spectra of L ligand

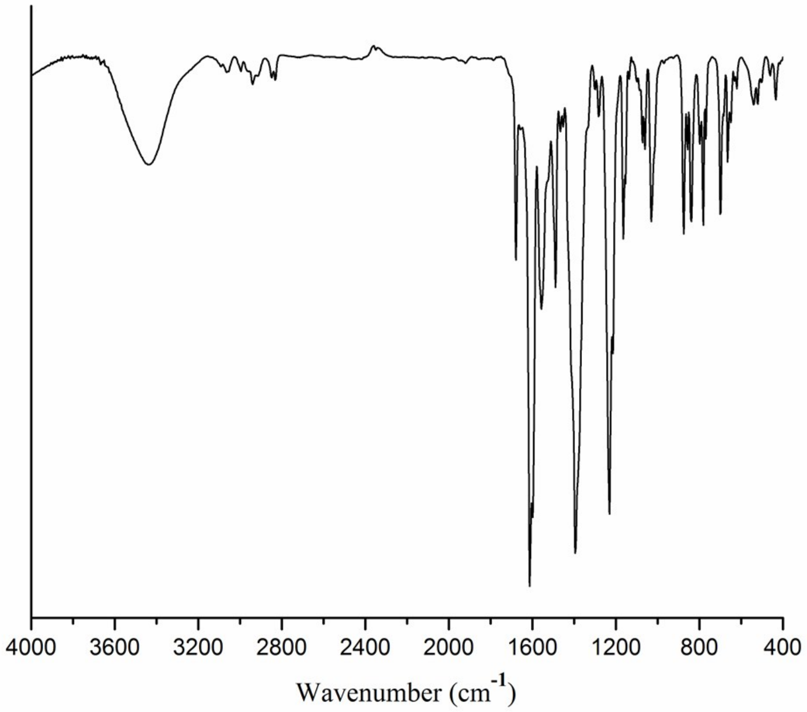


Figure S6. IR spectra of complex **1**

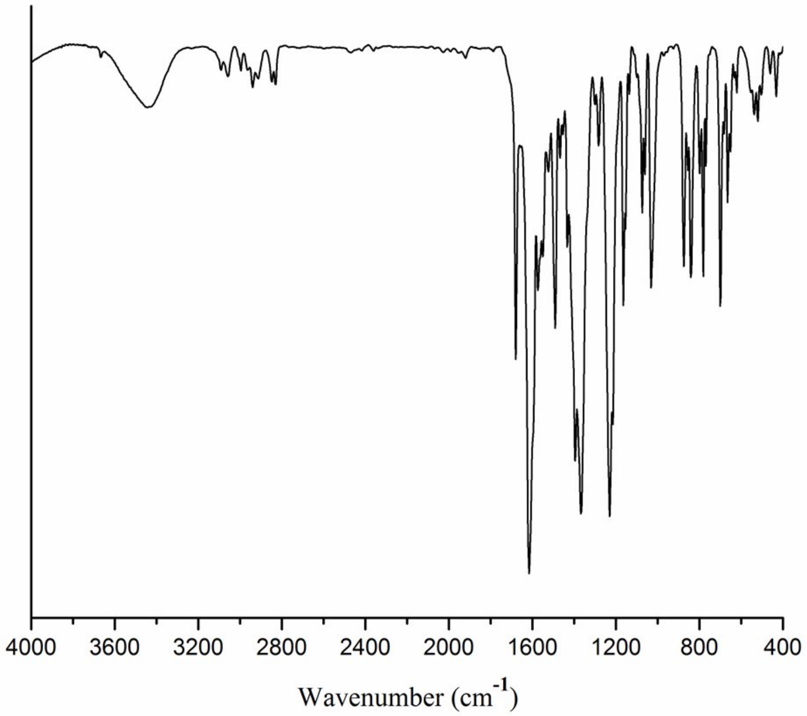


Figure S7. IR spectra of complex **2**

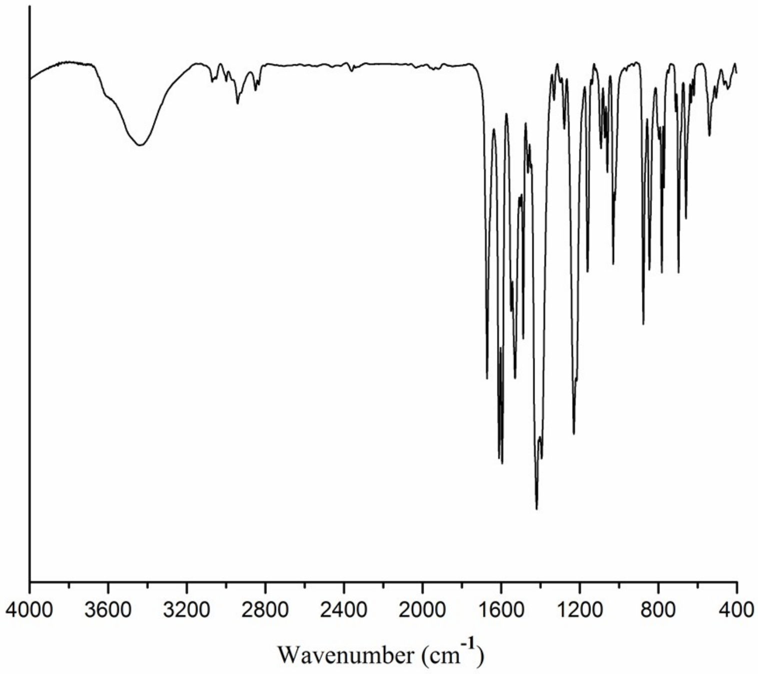


Figure S8. IR spectra of complex **3**

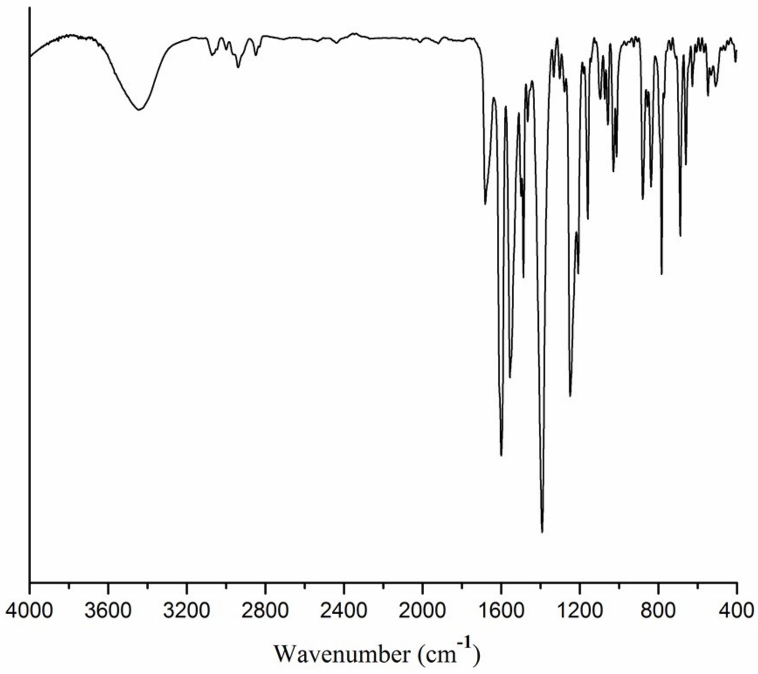


Figure S9. IR spectra of complex **4**

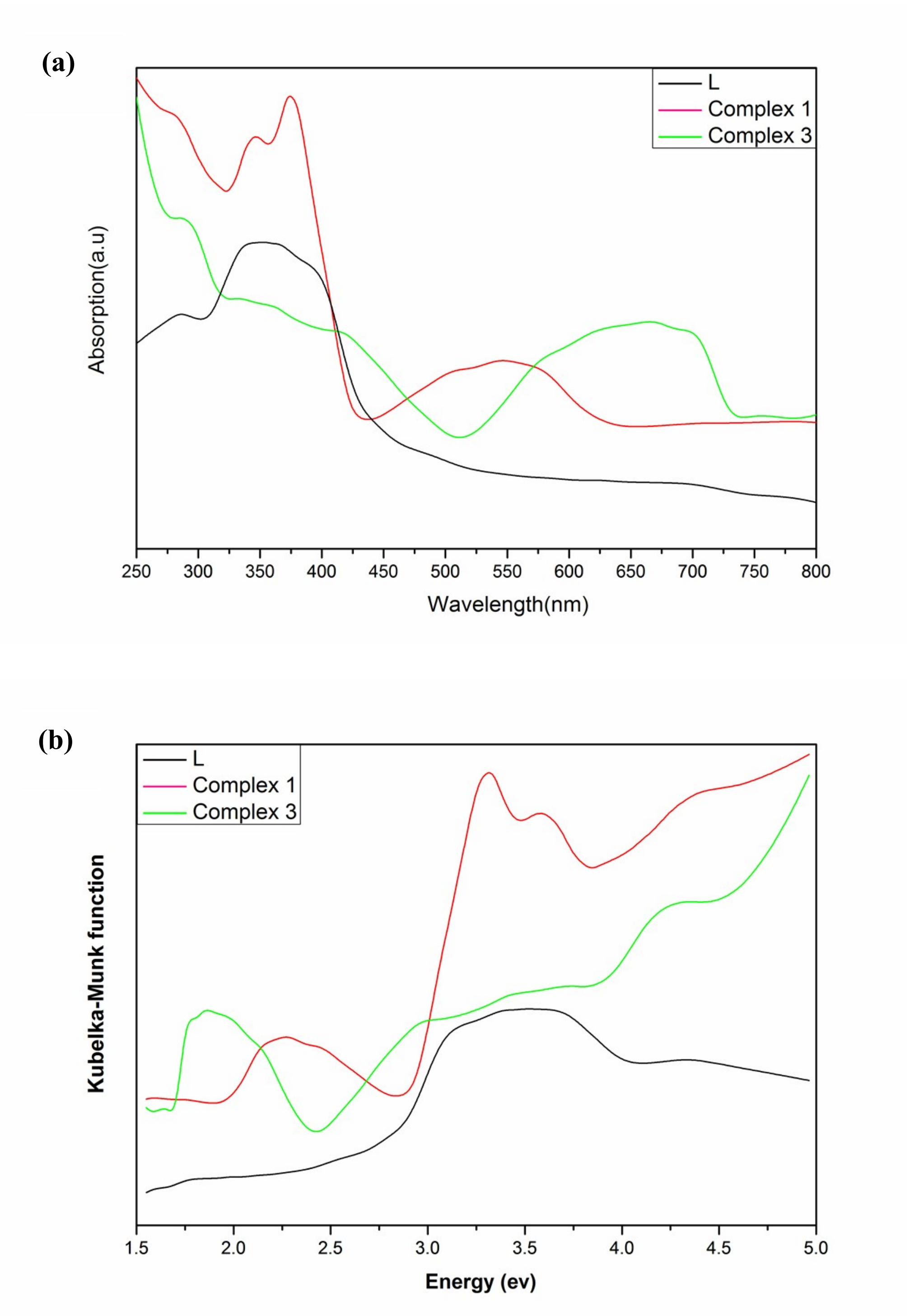


Figure S10. (a) UV-vis absorbance spectra and (b) Plot of Kubelka-Munk as a function of energy of **1**, **3** and corresponding ligand L at room temperature.

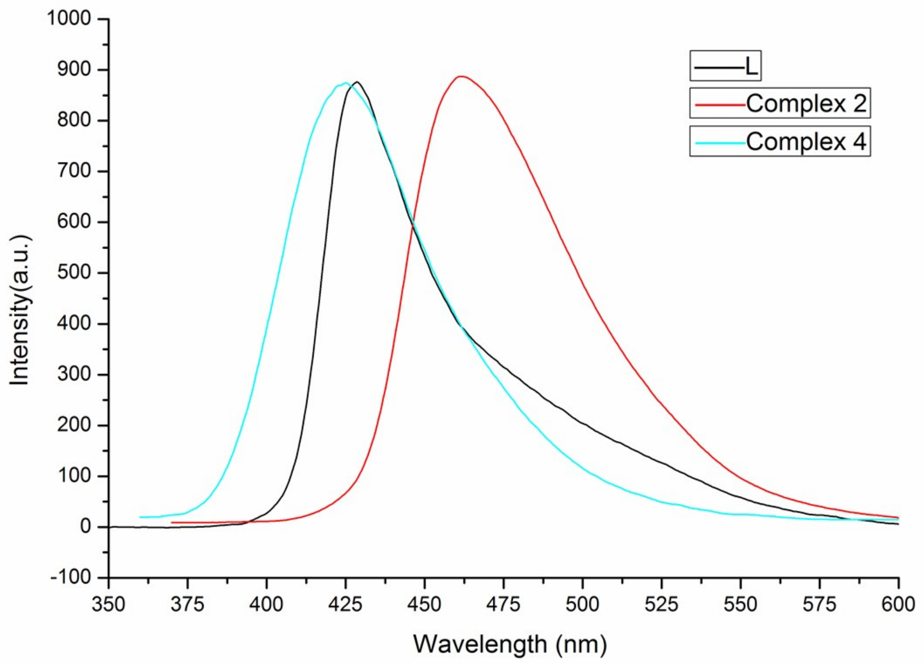


Figure S11. Solid-state photoluminescent spectra of **2**, **4** and L ligand at room temperature.

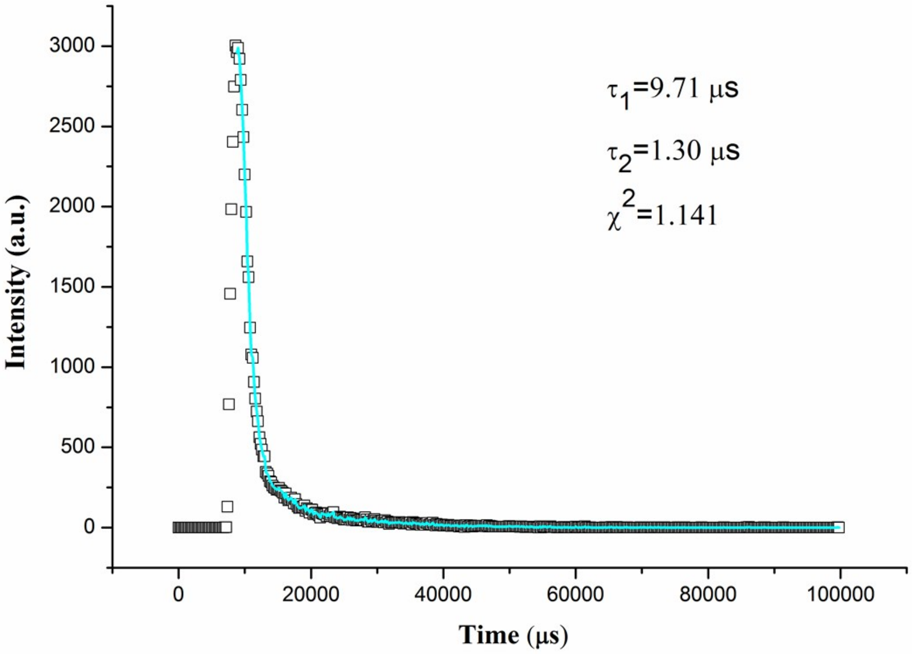


Figure S12. The fitted decay curve monitored at 428 nm for **L** ligand in the solid state at room temperature. The sample was excited at 335 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A+B_1\times\exp(-t/\tau_1)+B_2\times\exp(-t/\tau_2)$.

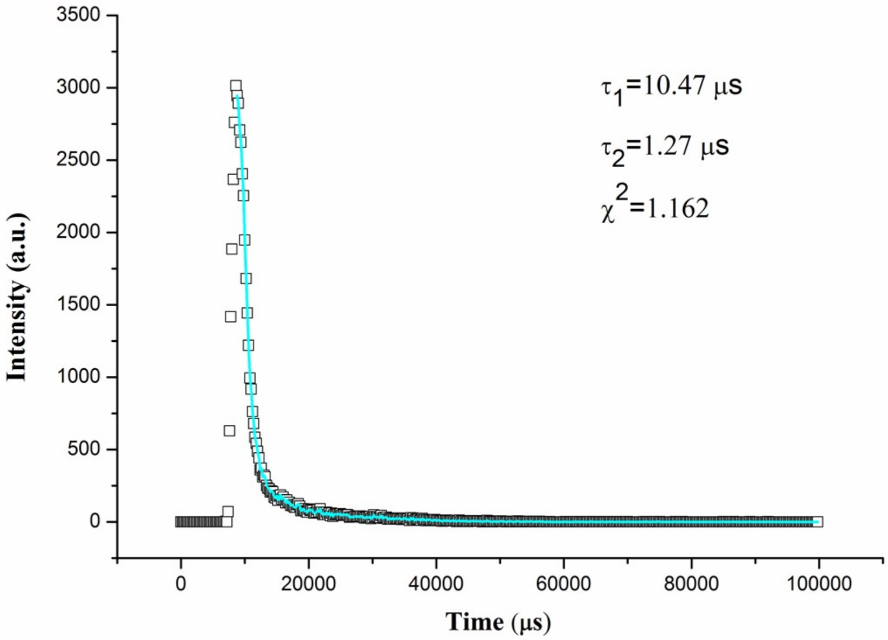


Figure S13. The fitted decay curve monitored at 420 nm for complex **2** in the solid state at room temperature. The sample was excited at 350 nm. Blank circles: experimental data; Solid line: fitted by Fit = A+B$_1$×exp(-t/τ$_1$)+B$_2$×exp(-t/τ$_2$).

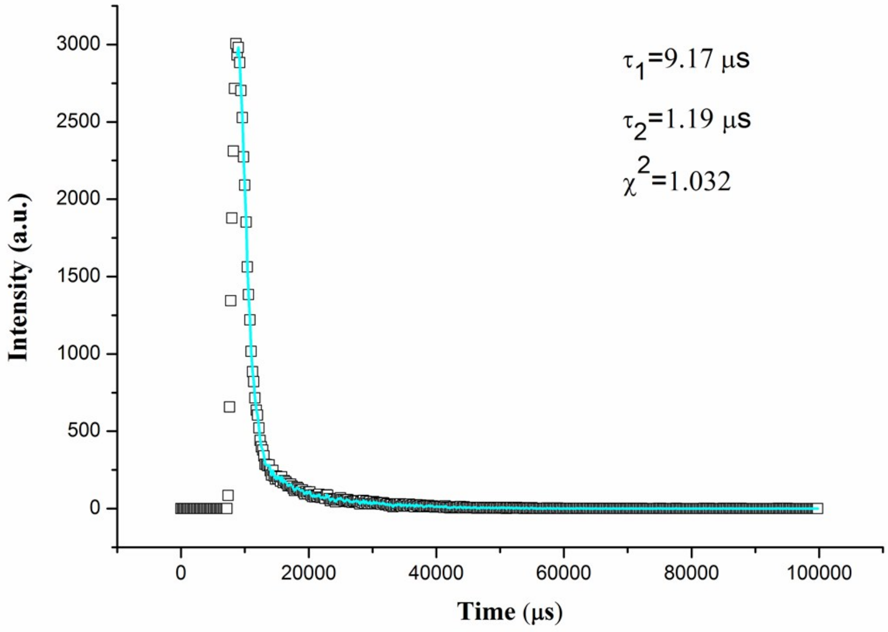


Figure 14. The fitted decay curve monitored at 461 nm for complex **4** in the solid state at room temperature. The sample was excited at 340 nm. Blank circles: experimental data; Solid line: fitted by Fit = A+B$_1$×exp(-t/τ$_1$)+B$_2$×exp(-t/τ$_2$).

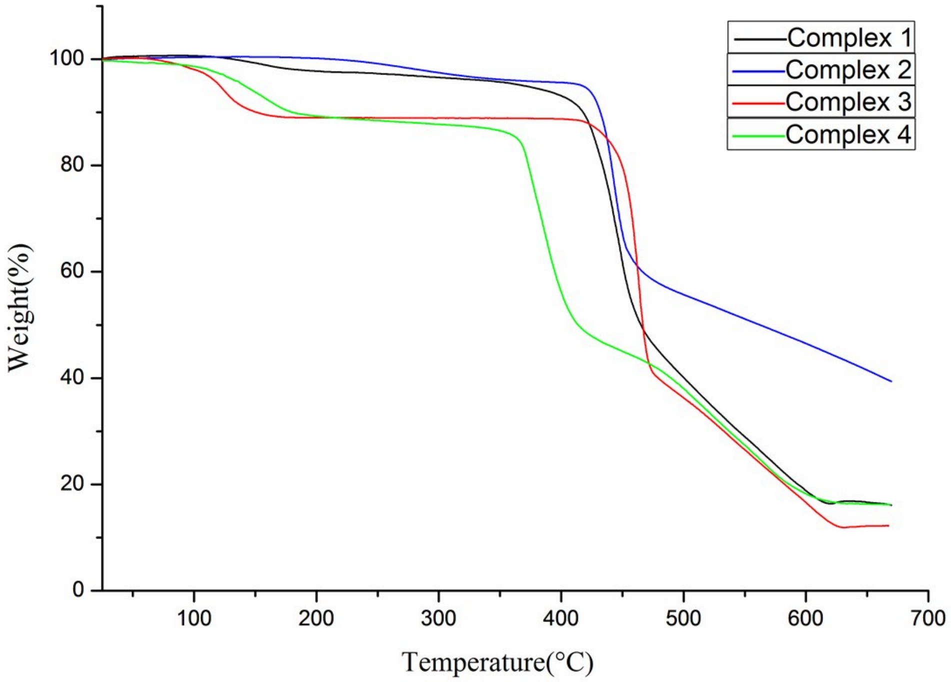


Figure S15. The TGA diagrams of complexes **1-4.**

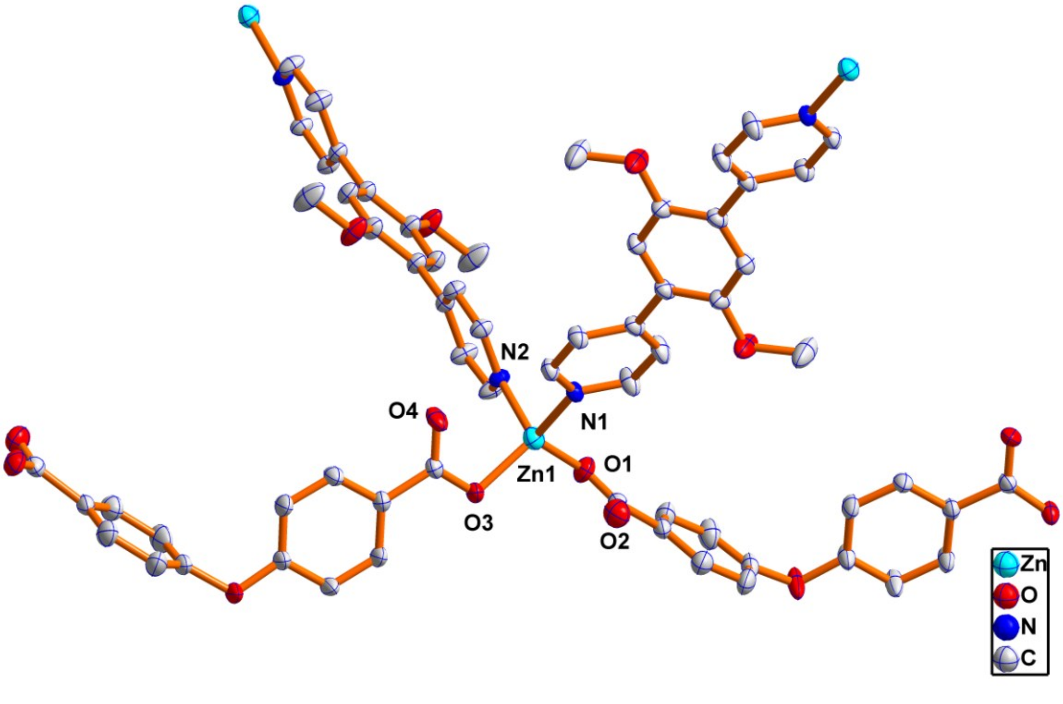


Figure S16. Coordination environment of the Zn(II) ion in **2**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability);

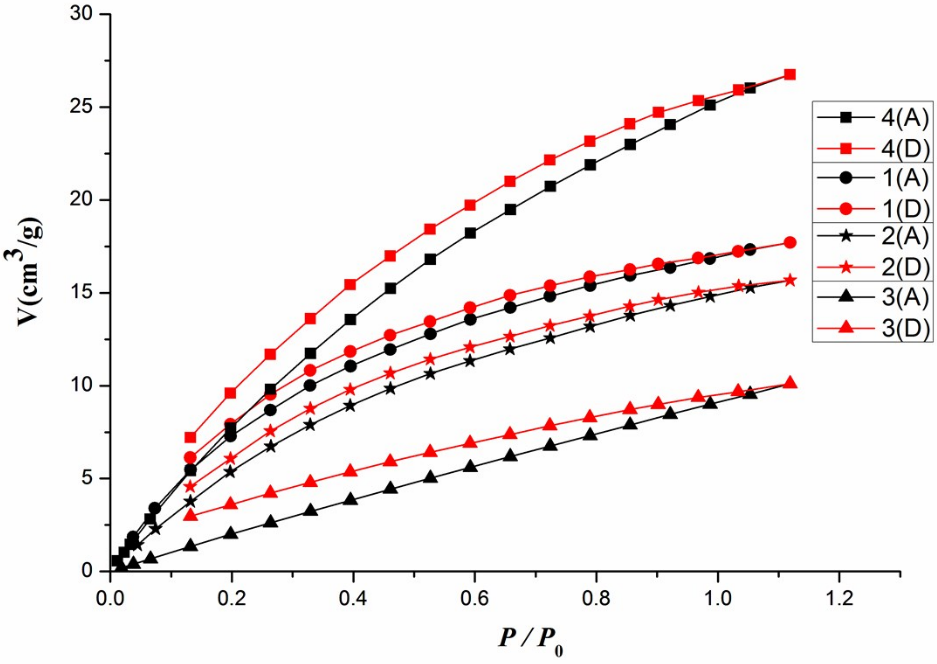


Figure S17. CO_2 sorption isotherms for **1** (circle), **2** (star), **3** (triangle) and **4** (square) at temperature 295 K. Black and red colour represent adsorption and desorption, respectively.

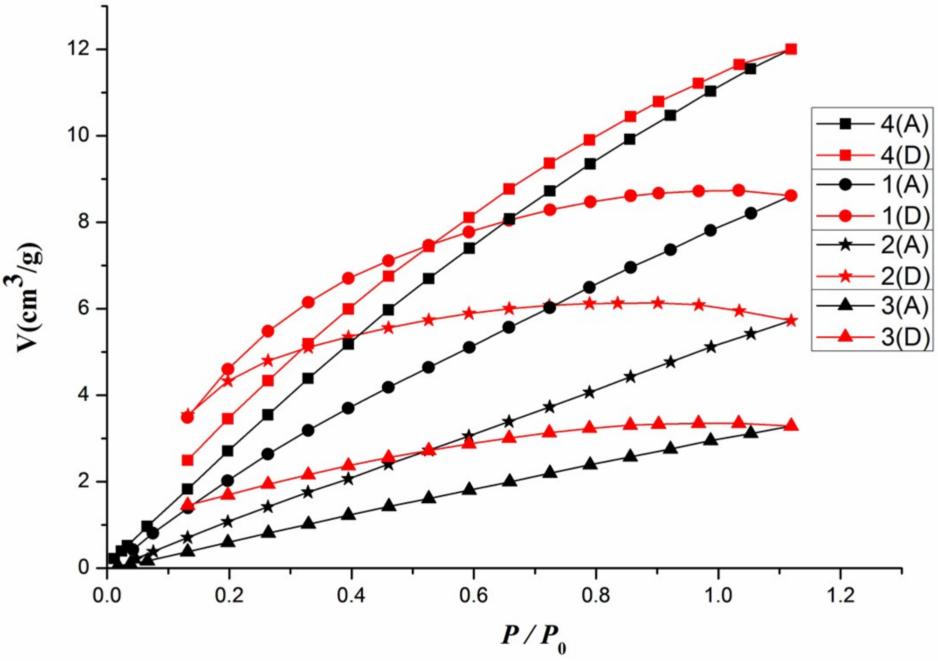


Figure S18. CH_4 sorption isotherms for **1** (circle), **2** (star), **3** (triangle) and **4** (square) at temperature 273 K. Black and red colour represent adsorption and desorption, respectively.

References

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