Electronic Supplementary Information

Five 1D to 3D Zn(II)/Mn(II)-CPs Based on Dicarboxyphenyl-terpyridine Ligand: Stepwise Adsorptivity and Magnetic Properties

Nan-Nan Bai, Lei Hou, Rui-Cheng Gao, Ji-Ye Liang, Fan Yang and Yao-Yu Wang*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, P.R. China. E-mail: wyaoyu@nwu.edu.cn

Contents

3.12 Photoluminescence properties of **1**, **2** and H_2dtp ligand.

Scheme S1 A series of carboxyphenyl-terpyridines.

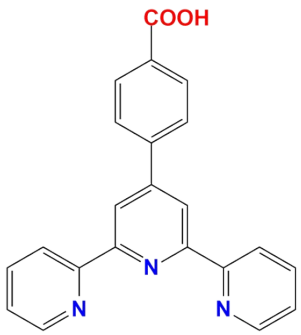
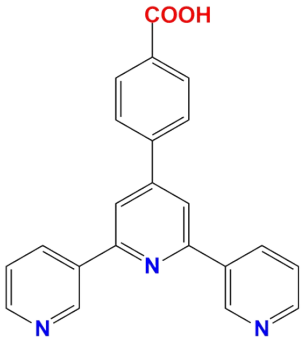
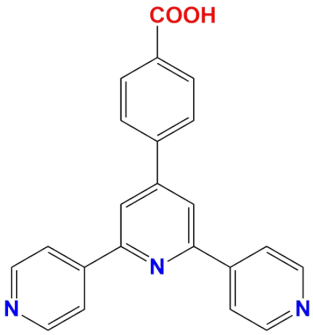
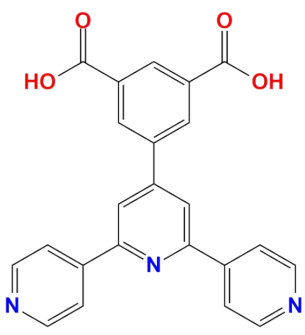
L1	L2	L3	L4
			

Table. S1 Crystal data and structure refinement for **1**-**5**.

Complexes	**1**	**2**	**3**
Empirical formula	$C_{23}H_{15}N_3O_5Zn$	$C_{23}H_{13}N_3O_4Zn$	$C_{46}H_{49}Mn_2N_6O_{19}$
Formula mass	478.75	460.73	1188.78
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*P2₁/n*	*Fdd2*	*P-1*
a [Å]	12.2314(17)	8.613(3)	11.367(4)
b [Å]	10.9907(16)	18.593(6)	11.691(4)
c [Å]	15.501(2)	38.594(12)	20.986(7)
α [º]	90	90	80.658(6)
β [º]	100.877(2)	90	74.738(5)
γ [º]	90	90	73.042(6)
V [Å^3]	2046.4(5)	6181(3)	2562.4(16)
Z	4	8	2
$D_{calcd.}$[mg·cm^{-3}]	1.554	0.990	1.424
μ [mm^{-1}]	1.242	0.818	0.582
F [000]	976.0	1872.0	1164
Reflections	12369/4894	7213/2600	12813 / 8872
R_{int}	0.0736	0.0360	0.0250
θ [º]	1.95-28.29	2.43-25.01	1.83-26.00
Goodness-of-fit on F^2	0.969	0.974	0.994
Final $R^{[a,b]}$ indices [$I>2\sigma(I)$]	R_1 = 0.0501 wR_2 = 0.1074	R_1 = 0.0336 wR_2 = 0.0761	R1 = 0.1160 wR2 = 0.3045

Complexes	**4**	**5**
Empirical formula	$C_{23}H_{14}ClMnN_3O_4$	$C_{23}H_{18}MnN_3O_{6.5}$
Formula mass	486.76	495.34
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*C2/c*
a [Å]	8.6165(14)	27.619(3)
b [Å]	10.7021(17)	12.3795(15)
c [Å]	10.9629(17)	13.8652(17)
α [º]	78.643(2)	90
β [º]	87.650(2)	118.922(2)

γ [º]	79.496(3)	90
V [Å^3]	974.5(3)	4149.4(8)
Z	2	8
$D_{calcd.}$[mg·cm^{-3}]	1.659	1.586
μ [mm^{-1}]	0.854	0.687
F [000]	494	2032
Reflections	6023 / 4448	10925 / 4036
R_{int}	0.0227	0.0484
θ [º]	1.895- 28.241	1.68-26.00
Goodness-of-fit on F^2	1.090	1.016
Final $R^{[a,b]}$ indices [$I>2\sigma(I)$]	R1 = 0.0603 wR2 = 0.1740	R_1 = 0.0417 wR_2 = 0.0989

[a]$R_1=\sum||F_o|-|F_c||/\sum|F_o|$, [b]$wR_2=[\sum w(F_o^2- F_c^2)^2/ \sum w(F_o^2)^2]^{1/2}$

Table. S2 Selected bond lengths (Å) and bong angles (º) for **1**-**5**.

Complex **1**			
Zn(1)-O(1)#1	1.947(3)	O(1)#1-Zn(1)-O(3)	109.95(12)
Zn(1)-N(2)#2	2.077(3)	N(2)#2-Zn(1)-N(1)#2	75.47(12)
Zn(1)-N(1)#2	2.169(3)	N(2)#2-Zn(1)-N(3)#2	74.83(12)
Zn(1)-N(3)#2	2.217(3)	N(1)#2-Zn(1)-N(3)#2	149.37(12)
Zn(1)-O(3)	1.952(3)	O(3)-Zn(1)-N(2)#2	122.99(12)
O(1)#1-Zn(1)-N(2)#2	126.85(12)	O(3)-Zn(1)-N(1)#2	99.01(13)
O(1)#1-Zn(1)-N(1)#2	102.09(13)	O(3)-Zn(1)-N(3)#2	103.25(13)
O(1)#1-Zn(1)-N(3)#2	89.86(12)		
Symmetry transformations used to generate equivalent atoms: #1: -1/2+x, 1/2-y, -1/2 +z; #2: 1/2+x, 1/2-y, -1/2+z.			

Complex **2**			
Zn(1)-O(1)#3	1.972(3)	O(1)#4-Zn(1)-N(1)	98.63(19)
Zn(1)-O(1)#4	1.972(3)	O(1)#3-Zn(1)-N(1)	99.0(2)
Zn(1)-N(2)	2.060(5)	O(1)#3-Zn(1)-N(1)#2	98.63(19)
Zn(1)-N(1)	2.134(5)	O(1)#4-Zn(1)-N(1)#2	99.0(2)
Zn(1)-N(1)#2	2.134(5)	N(2)-Zn(1)-N(1)	75.32(12)
O(1)#3-Zn(1)-O(1)#4	105.39(18)	N(2)-Zn(1)-N(1)#2	75.32(12)
O(1)#3-Zn(1)-N2	127.31(9)	N(1)-Zn(1)-N(1)#2	150.6(2)
O(1)#4-Zn(1)-N2	127.31(9)		
Symmetry transformations used to generate equivalent atoms: #2: -3/2-x, -1/2-y, +z; #3: -1/4+x, -3/4-y, -1/4+z; #4: -5/4-x,1/4+y,-1/4+z.			

Complex **3**			
Mn(1)-O(11)	2.196(7)	N(4)-Mn(1)-N(6)	138.0(2)
Mn(1)-O(12)	2.235(7)	O(11)-Mn(1)-O(10)	85.0(3)
Mn(1)-N(5)	2.282(7)	O(12)-Mn(1)-O(10)	90.3(3)
Mn(1)-O(9)	2.290(6)	N(5)-Mn(1)-O(10)	152.4(2)
Mn(1)-N(4)	2.337(7)	O(9)-Mn(1)-O(10)	55.3(2)
Mn(1)-N(6)	2.343(7)	N(4)-Mn(1)-O(10)	82.8(2)

Mn(1)-O(10)	2.444(6)	N(6)-Mn(1)-O(10)	138.0(2)
Mn(2)-O(4)	2.198(6)	O(4)-Mn(2)-O(6)	86.4(3)
Mn(2)-O(6)	2.248(8)	O(4)-Mn(2)-N(2)	153.5(2)
Mn(2)-N(2)	2.254(7)	O(6)-Mn(2)-N(2)	92.5(3)
Mn(2)-N(3)	2.327(7)	O(4)-Mn(2)-N(3)	135.8(2)
Mn(2)-N(1)	2.334(7)	O(6)-Mn(2)-N(3)	96.4(3)
Mn(2)-O(5)	2.342(8)	N(2)-Mn(2)-N(3)	70.7(2)
Mn(2)-O(3)	2.525(7)	O(4)-Mn(2)-N(1)	83.6(2)
O(11)-Mn(1)-O(12)	171.8(3)	O(6)-Mn(2)-N(1)	84.0(3)
O(11)-Mn(1)-N(5)	99.4(3)	N(2)-Mn(2)-N(1)	69.9(2)
O(12)-Mn(1)-N(5)	87.9(3)	N(3)-Mn(2)-N(1)	140.6(2)
O(11)-Mn(1)-O(9)	87.3(3)	O(4)-Mn(2)-O(5)	89.4(3)
O(12)-Mn(1)-O(9)	84.5(3)	O(6)-Mn(2)-O(5)	175.9(3)
N(5)-Mn(1)-O(9)	151.4(2)	N(2)-Mn(2)-O(5)	91.2(3)
O(11)-Mn(1)-N(4)	94.4(3)	N(3)-Mn(2)-O(5)	86.5(3)
O(12)-Mn(1)-N(4)	91.7(3)	N(1)-Mn(2)-O(5)	95.7(3)
N(5)-Mn(1)-N(4)	69.8(2)	O(4)-Mn(2)-O(3)	54.9(2)
O(9)-Mn(1)-N(4)	137.8(2)	O(6)-Mn(2)-O(3)	84.8(3)
O(11)-Mn(1)-N(6)	82.6(3)	N(2)-Mn(2)-O(3)	151.5(2)
O(12)-Mn(1)-N(6)	96.5(3)	N(3)-Mn(2)-O(3)	81.4(2)
N(5)-Mn(1)-N(6)	69.5(2)	N(1)-Mn(2)-O(3)	137.5(2)
O(9)-Mn(1)-N(6)	84.1(2)	O(5)-Mn(2)-O(3)	92.7(3)

Complex **4**

Mn(1)-Cl(1)	2.3223(3)	N(1)-Mn(1)-N(3)	71.97(11)
Mn(1)-N(1)	2.201(3)	N(3)-Mn(1)-Cl(1)	101.54(9)
Mn(1)-N(3)	2.253(3)	O(1)#1-Mn(1)-N(1)	122.60(13)
Mn(1)-O(1)#1	2.061(3)	O(1)#1-Mn(1)-N(3)	106.47(12)
Mn(1)-N(2)	2.275(4)	N(1)-Mn(1)-N(2)	71.92(12)
O(1)#1-Mn(1)-Cl(1)	105.25(10	N(2)-Mn(1)-Cl(1)	98.99(10)
O(1)#1-Mn(1)-N(2)	96.56(12)	N(3)-Mn(1)-N(2)	143.61(12)
N(1)-Mn(1)-Cl(1)	131.80(10)		

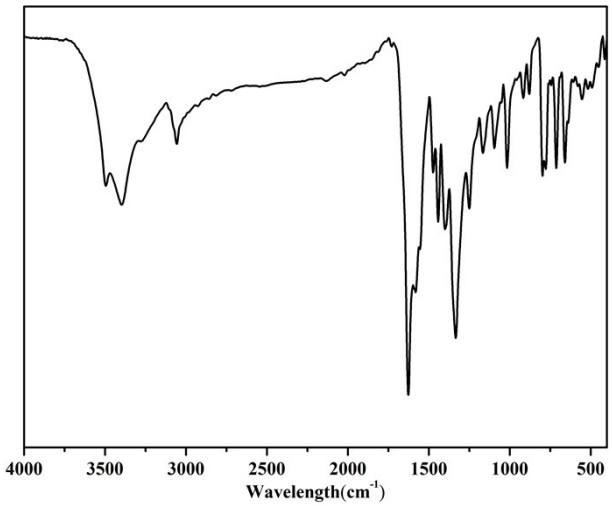
Symmetry transformations used to generate equivalent atoms: #1: x, y, z+1.

Complex **5**

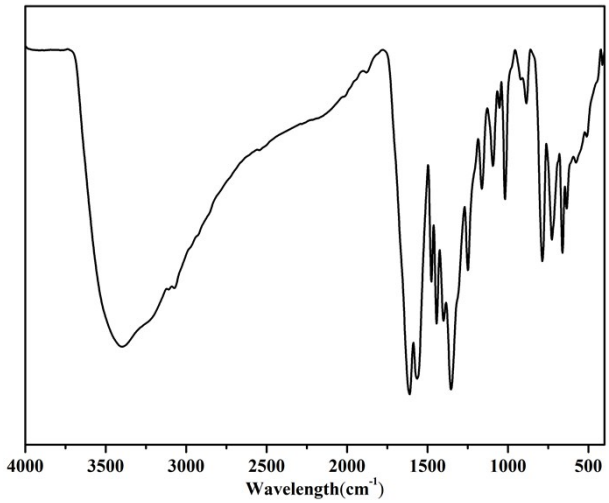
Mn(1)-N(1)	2.357(2)	O(1W)-Mn(1)-O(1)#1	87.88(7)
Mn(1)-N2	2.305(2)	O(1W)-Mn(1)-O(2)#1	89.39(7)
Mn(1)-N3	2.357(2)	O(2)#1-Mn(1)-N(1)	82.69(7)
Mn(1)-O(1)#1	2.4026(19)	O(2)#1- Mn(1)-N(2)	151.68(7)
Mn(1)-O(1W)	2.193(2)	O(2)#1-Mn(1)-N3	138.66(7)
Mn(1)-O(2)#1	2.2769(19)	O(2)#1-Mn(1)-O(1)#1	55.79(6)
Mn(1)-O(3)#2	2.1680(19)	O(3)#2-Mn(1)-N(1)	89.46(8)
N(1)-Mn1-O(1)#1	137.37(7)	O(3)#2-Mn(1)-N(2)	91.87(7)
N(2)-Mn(1)-N(1)	69.02(7)	O(3)#2-Mn(1)-N(3)	96.40(7)
N(2)-Mn(1)-N(3)	69.64(7)	O(3)#2-Mn(1)-O(1)#1	96.31(7)
N(2)-Mn(1)-O(1)#1	152.15(7)	O(3)#2-Mn(1)-O(1W)	170.76(7)

N(3)-Mn(1)-N(1)	138.40(7)	O(3)#2-Mn(1)-O(2)#1	86.21(7)
N(3)-Mn(1)-O(1)#1	82.99(7)	O(2)#1- Mn(1)-N(2)	151.68(7)
O(1W)-Mn(1)-N(1)	81.92(8)	O(2)#1-Mn(1)-N3	138.66(7)
O(1W)-Mn(1)-N2	88.15(8)	O(2)#1-Mn(1)-O(1)#1	55.79(6)
O(1W)-Mn(1)-N3	92.27(7)		

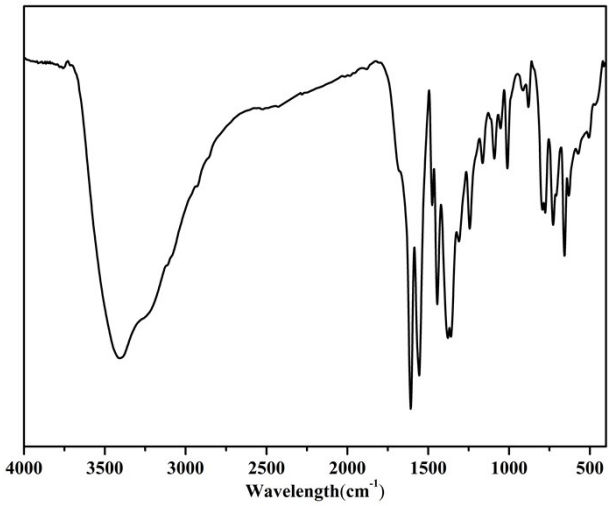
Symmetry transformations used to generate equivalent atoms: #1: 1/2+x, 1/2-y, 1/2 +z; #2: -x, 1-y, 1-z.



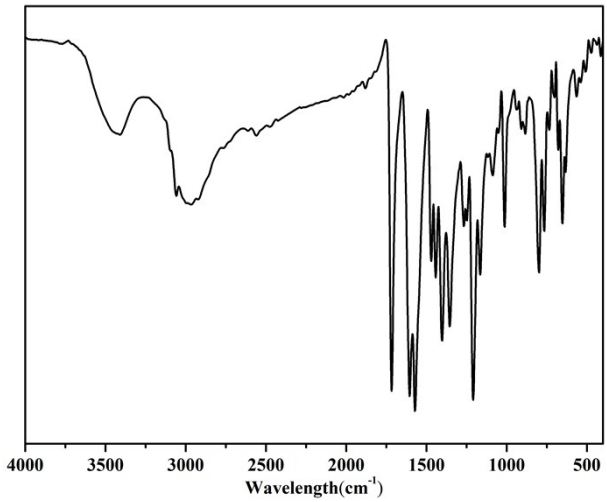
(a)



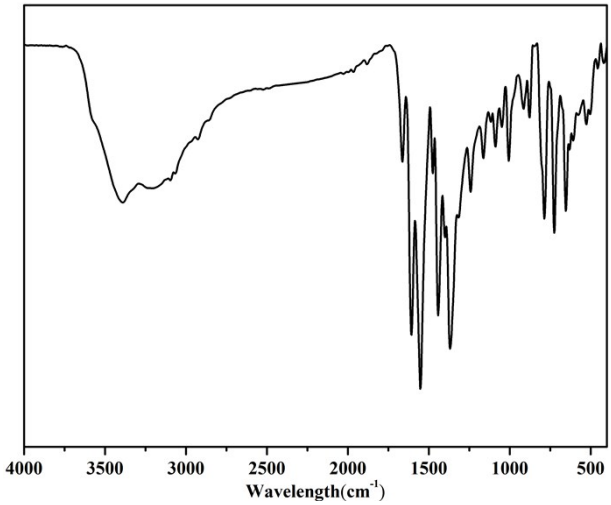
(b)



(c)



(d)



(e)

Fig. S1 The IR spectra for complexes **1(a)**, **2(b)**, **3(c)**, **4(d)** and **5(e)**.

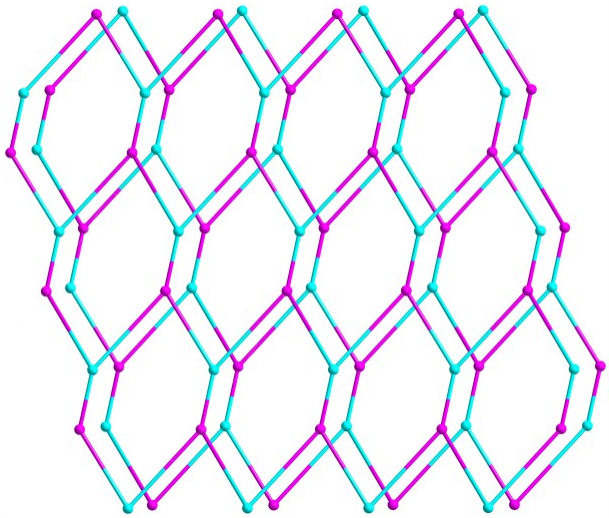


Fig. S2 Schematic representation of an uninodal, 3-connected network with the point symbol of $\{6^3\}$ of **1**.

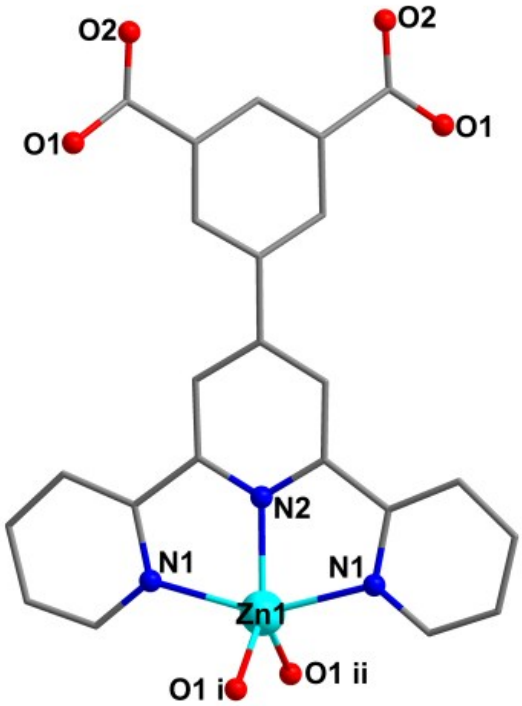


Fig. S3 The coordination environments of Zn(II) ions in **2** (Symmetry codes: i 3/4-x, -1/4+y, 1/4+z; ii 1/4+x, 1/4-y, 1/4+z).

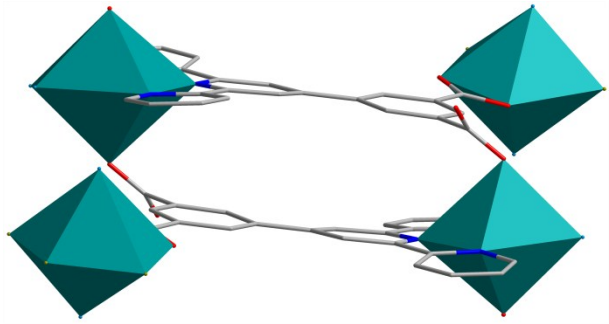


Fig. S4 The distorted quadrangle of complex **2**.

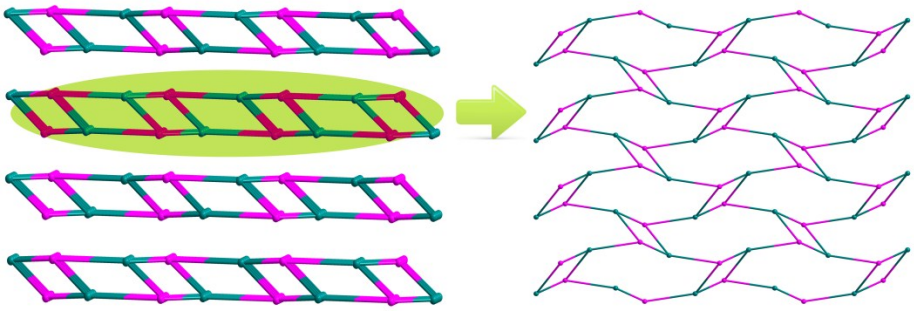
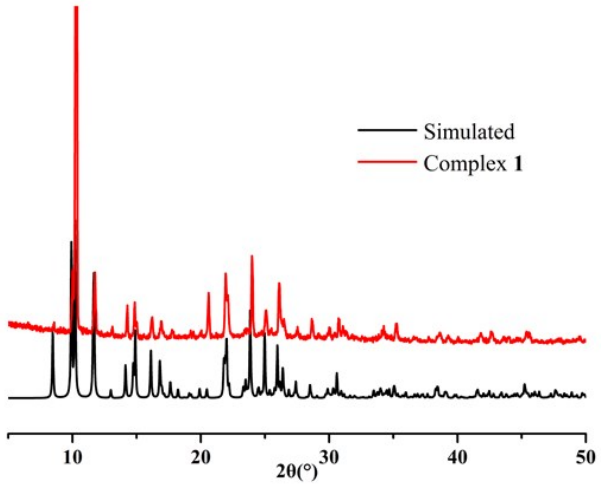
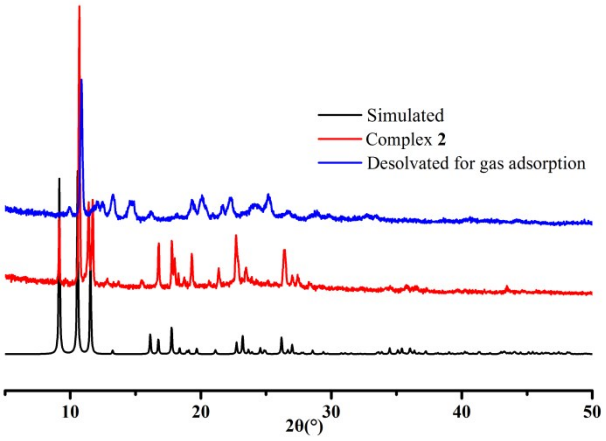


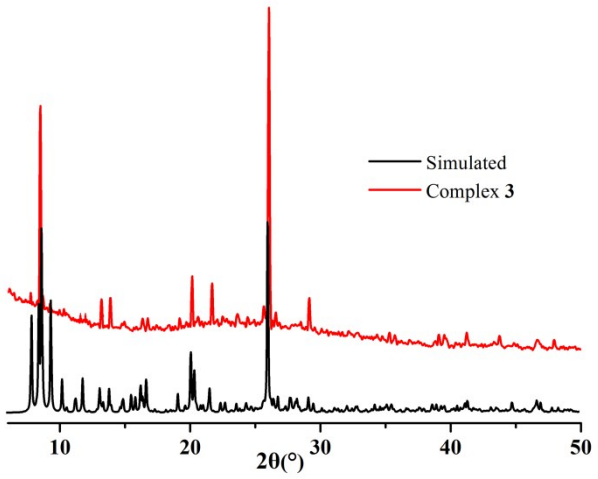
Fig. S5 Schematic representation of a uninodal, 3-connected network with the point symbol of $\{4\cdot8^2\}$ of **5**.



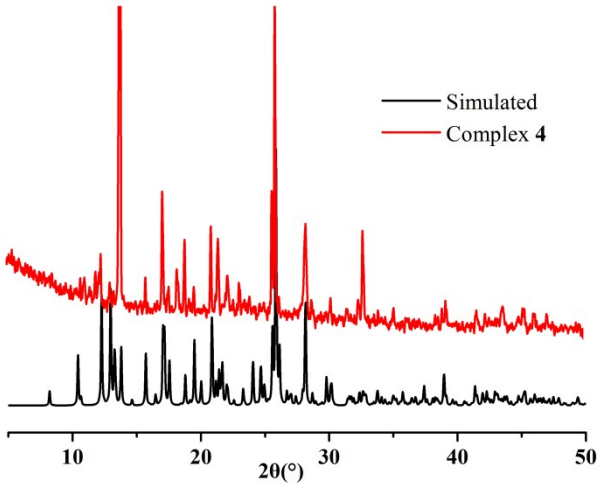
(a)



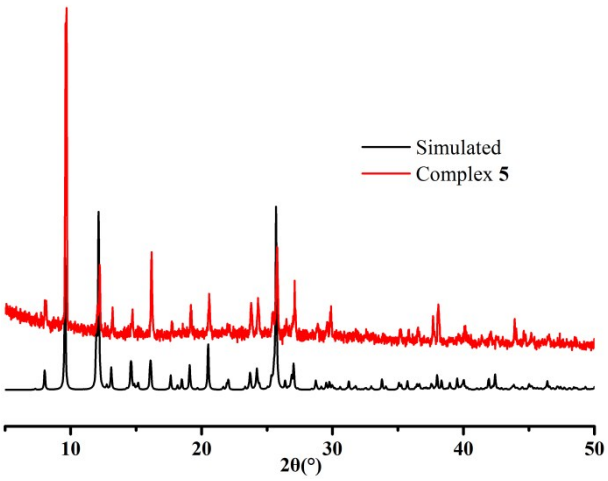
(b)



(c)



(d)



(e)

Fig. **S6** PXRD patterns of complexes **1(a)**, **2(b)**, **3(c)**, **4(d)** and **5(e)** simulated from the X-ray single-crystal structure, experimental samples and desolated samples.

Calculation of adsorption heat for CO_2 uptake using Viral 2 model

$$ln = \ln N + 1/T \sum_{i=0}^{m} aiN^{I} + \sum_{i=0}^{n} biN^{i}$$

$$Q_{st} = -R\sum_{i=0}^{m} aiN^{i}$$

The above equation was applied to fit the combined CO_2 isotherm data for desolvated **2** at 273K and 298K, where *P* is pressure, N is the adsorbed amount, T is the temperature, *ai* and *bi* are virial coefficients, and *m* and *n* are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant.

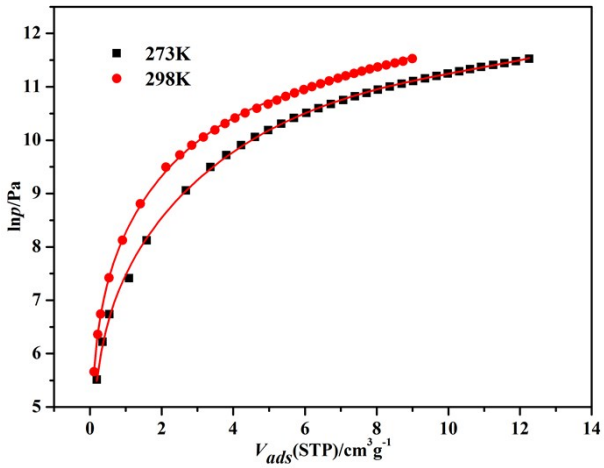


Fig. S7 Virial analysis of CO_2 adsorption data at 273 and 298K for **2**. Fitting results: a0 = -2369.49, a1 = -334.72, a2 = 146.28, a4 = 0.01023, Chi^2 = 0.00127, R^2 =0.99949.

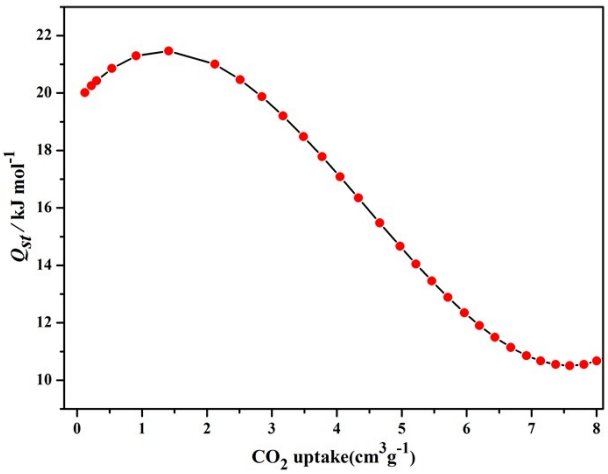


Fig. S8 Isosteric heat of CO_2 adsorption for **2** estimated by the virial equation from the adsorption isotherms at 273 and 298K.

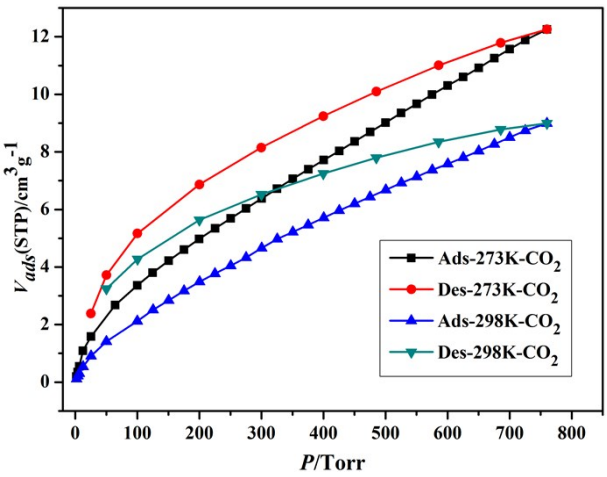


Fig. S9 CO_2 adsorption and desorption isotherm at 273K and 298K of **2**.

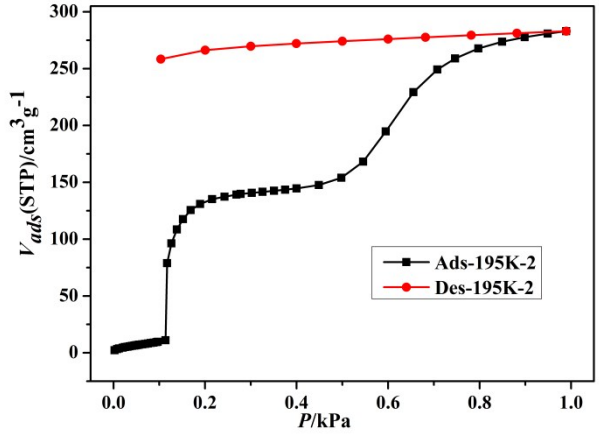


Fig. S10 Repeat cycle of CO_2 adsorption at 195 K on the same material of **2**.

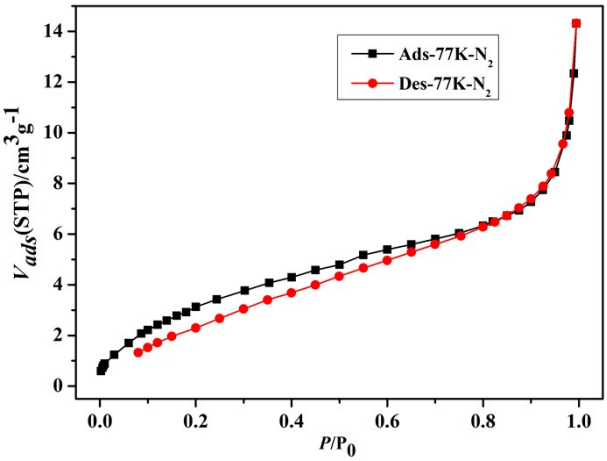


Fig. S11 N_2 adsorption and desorption isotherm at 77 K of **2**.

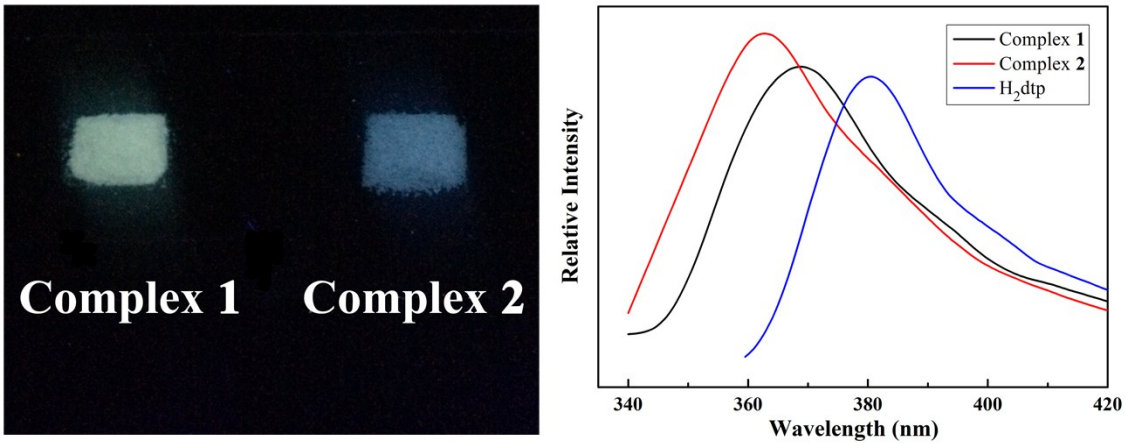


Fig. S12 Photoluminescent picture of **1**, **2** under UV light (right) and photoluminescence properties of **1**, **2** and H_2dtp ligand (left).

Photoluminescence properties

The CPs with d^{10} metal centres and conjugated ligands are of great interest due to their unique luminescent properties.[1] The solid-state fluorescent properties of **1** and **2** as well as free H_2dtp ligand were studied at room temperature with excitation at 320 nm (Fig. S12), all complexes exhibit a broad emission. H_2dtp shows emission with a maximum at 380 nm. Complexes **1** and **2** display emission with the maxima at 369 nm and 362 nm, respectively, which can be attributed to inter-ligand charge transfer of H_2dtp. The blue shifts from that of free ligand could be tentatively assigned to the coordination of dtp with metal centres.[2]

References

1. (a) Y. Yu, X. M. Zhang, J. P. Ma, Q. K. Liu, P. Wang and Y. B. Dong, *Chem. Commun.*, 2014, 50, 1444. (b) P. Lama and P. K. Bharadwaj, *Cryst. Growth Des.*, 2011, 11, 5434. (c) L. Sun, H. Z. Xing, J. Xu, Z. Q. Liang, J. H. Yu and R. R. Xu, *Dalton Trans*., 2013, 42, 5508. (d) A. Santra and P. K. Bharadwaj, *Cryst. Growth Des.,* 2014, 14, 1476. (e) B. Gole, A. K. Bar and P. S. Mukherjeez, *Chem. Commun.,* 2011, 47, 12137. (f) Y. L. Li, Y. Zhao, P. Wang, Y. S. Kang, Q. Liu, X. D. Zhang, and W. Yin Sun. *Inorg. Chem.* 2016, 55, 11821.
2. (a) Y. X. Ren, S. S. Xiao, X. J. Zheng, L. C. Li and L. P. Jin, *Dalton Trans*., 2012, **41**, 2639. (b) S. Parshamoni, H. S. Jena, S. Sandaand and S. Konar, *Inorg. Chem. Front*., 2014, **1**, 611. (c) C. P. Li, Q. Yu, J. Chen and M. Du, *Cryst. Growth Des*., 2010, **10**, 2650.