Metal-organic frameworks built from achiral 3-(5-(pyridin-4-yl)-4H-1,2,4-triazol-3-yl)benzoic acid: syntheses and structures of metal(II) complexes

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General Considerations

Solid-state photoluminescence spectra of all the compounds were measured at room temperature on an Edinburgh FLS920 fluorescence spectrometer equipped with an Edinburgh Xe900 xenon arc lamp as the exciting light source. TGA was performed on a NETZSCH STA 449C thermogravimetric analyzer in flowing N_2 with a heating rate of 10°C·min^{-1}.

Table S1 Selected bond lengths (Å) and angles (º) for complexes **1-4**

Complex 1			
Zn(1)-O(1)	1.935(2)	Zn(1)-N(1)#2	2.027(3)
O(1)#1-Zn(1)-O(1)	121.74(14)	O(1)#1-Zn(1)-N(1)#2	96.67(9)
O(1)-Zn(1)-N(1)#2	116.18(10)	N(1)#2-Zn(1)-N(1)#3	110.17(16)

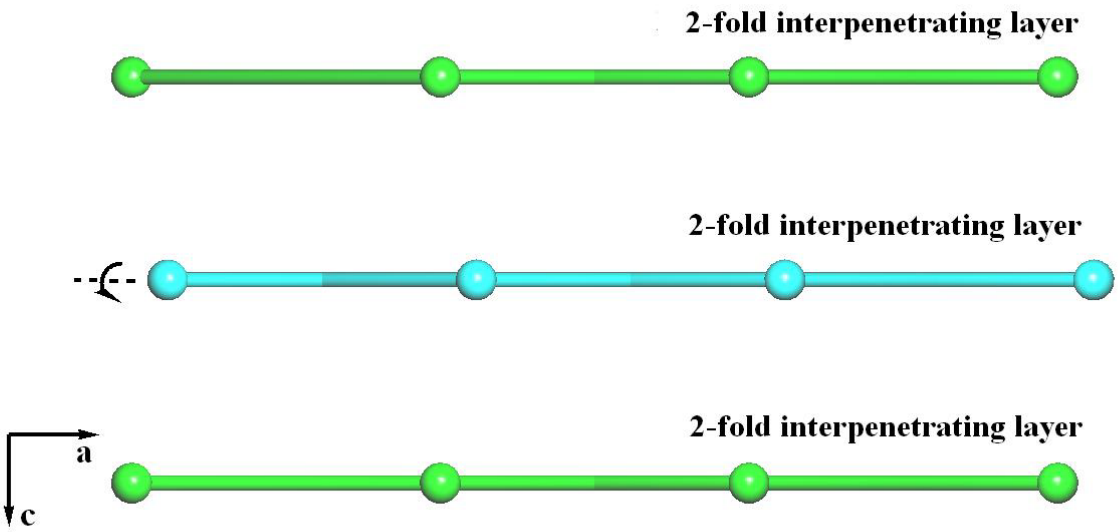
Complex 2			
Cd(1)-O(1)	2.287(2)	Cd(1)-O(3)	2.316(2)
Cd(1)-O(1)#4	2.287(2)	Cd(1)-N(1)#5	2.340(3)
O(1)#4-Cd(1)-O(3)	81.64(8)	O(1)-Cd(1)-O(3)	98.36(8)
O(1)#4-Cd(1)-O(1)	180.000(1)	O(3)-Cd(1)-N(1)#6	85.35(9)
O(3)-Cd(1)-N(1)#5	94.65(9)	N(1)#5-Cd(1)-N(1)#6	180.000(1)
Complex 3			
Co(1)-O(3)	2.049(16)	Co(1)-O(1)#1	2.262(18)
Co(1)-N(1)	2.099(2)	Co(1)-N(5)#2	2.144(19)
O(2)#7-Co(1)-O(1)#7	59.88(6)	O(3)-Co(1)-O(1)#7	155.86(7)
O(2)#7-Co(1)-N(1)	164.28(8)	O(5)-Co(1)-N(5)#8	175.77(8)
O(2)#7-Co(1)-N(5)#8	88.91(7)	N(1)-Co(1)-N(5)#8	91.13(8)
Complex 4			
Ni(2)-O(1)	2.034(2)	Ni(2)-O(3)	2.203(2)
Ni(2)-N(8)#9	2.057(2)	Ni(2)-N(4)#8	2.087(2)
O(4)-Ni(2)-O(3)	61.46(7)	O(1)-Ni(2)-O(3)	156.66(8)
O(5)-Ni(2)-N(4)#8	174.92(8)	O(4)-Ni(2)-N(4)#8	88.82(8)
N(8)#9-Ni(2)-O(3)	104.88(8)	N(8)#9-Ni(2)-N(4)#8	91.86(9)

Symmetry transformations used to generate equivalent atoms:

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

#6 -x+1/2,y-1/2,-z+3/2 #7 x,y,z+1 #8 x,y+1,z #9 x,y,z-1

(a)



(**b**)

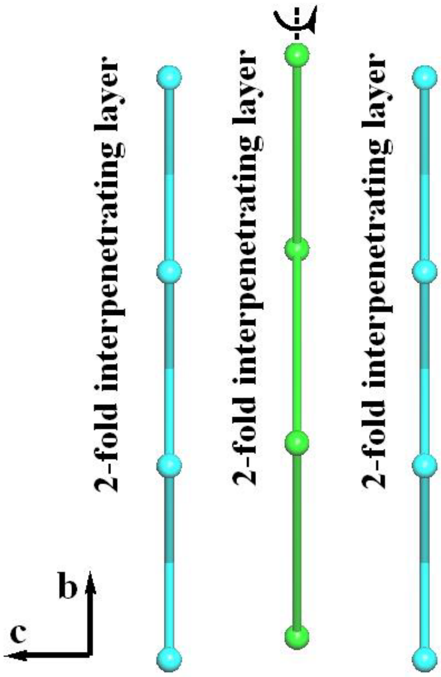


Fig.S1 Packing of the 2D layers (different layers denoted in different colors) in complex **1** generates two- fold axes (denoted as dotted line) along the *a* (**a**) and *b* directions, respectively (**b**).

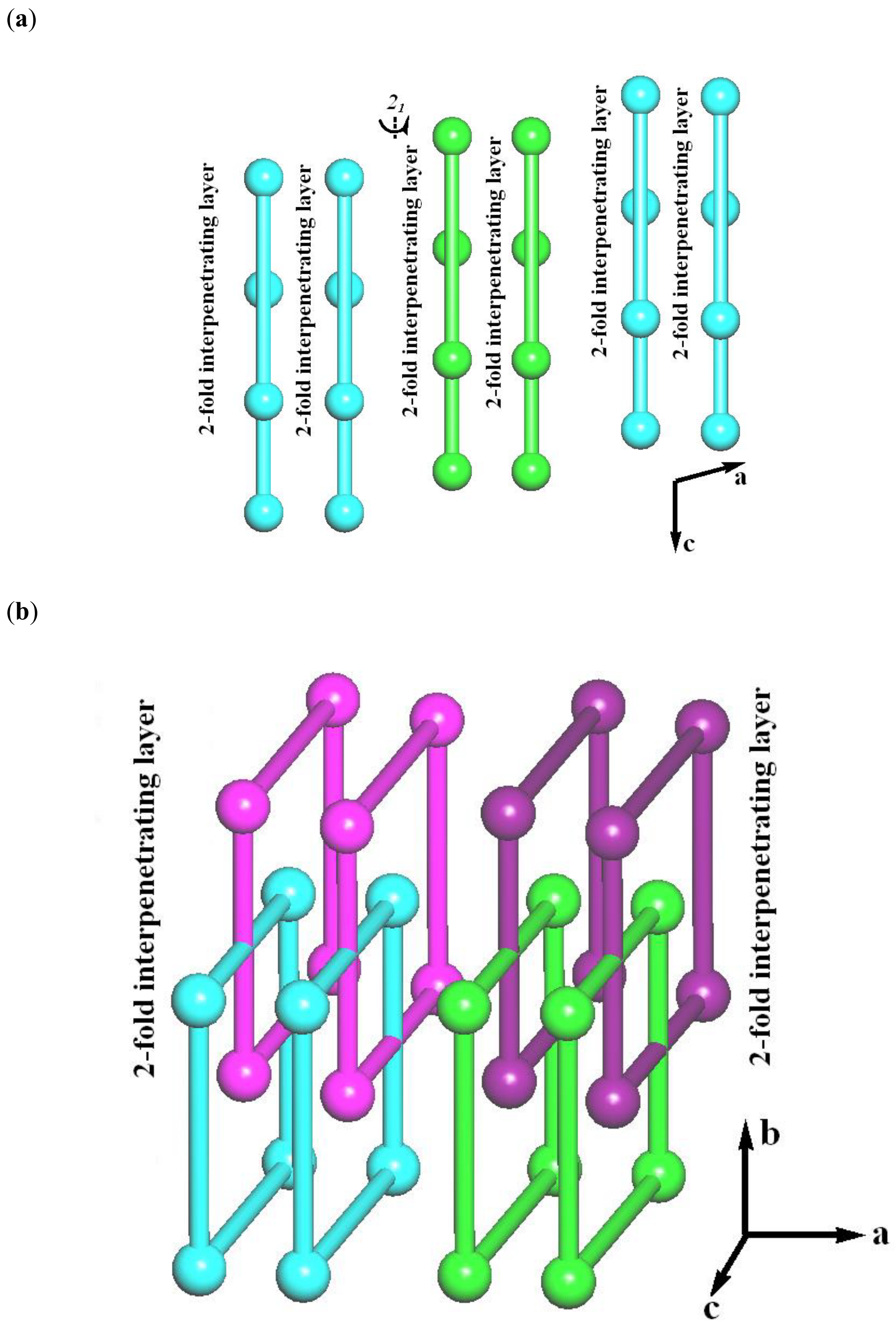


Fig.S2 Packing of the 2D layers in complex **3** generates 2_1 screw axis (denoted as dotted line) along the *c* direction (**a**) and inversion center between two neighboring interpenetrating 2D layers (**b**).

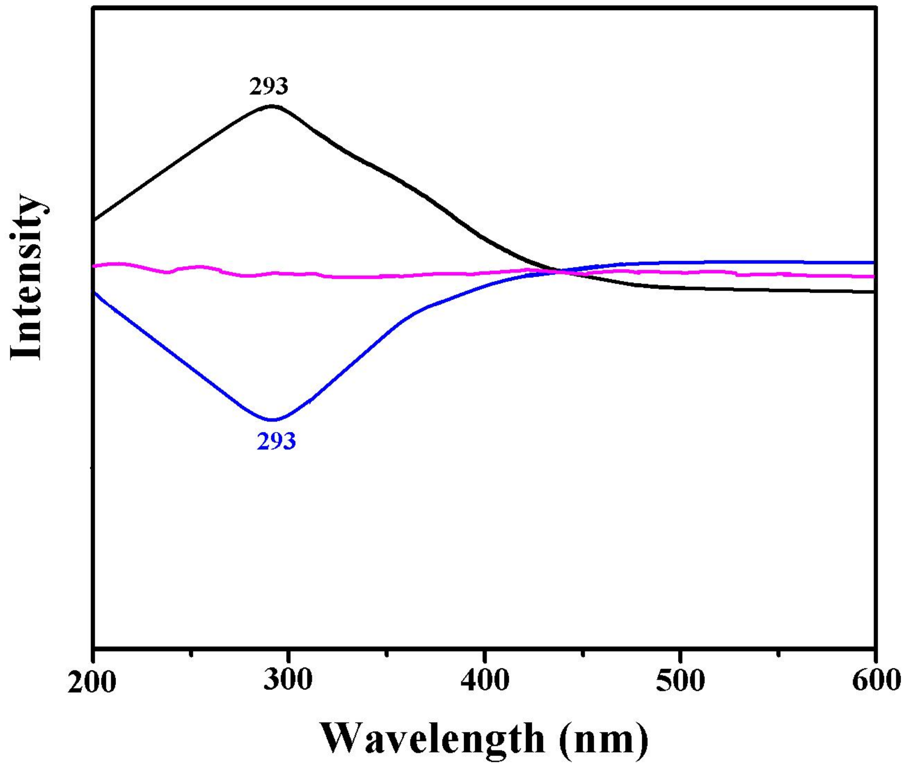
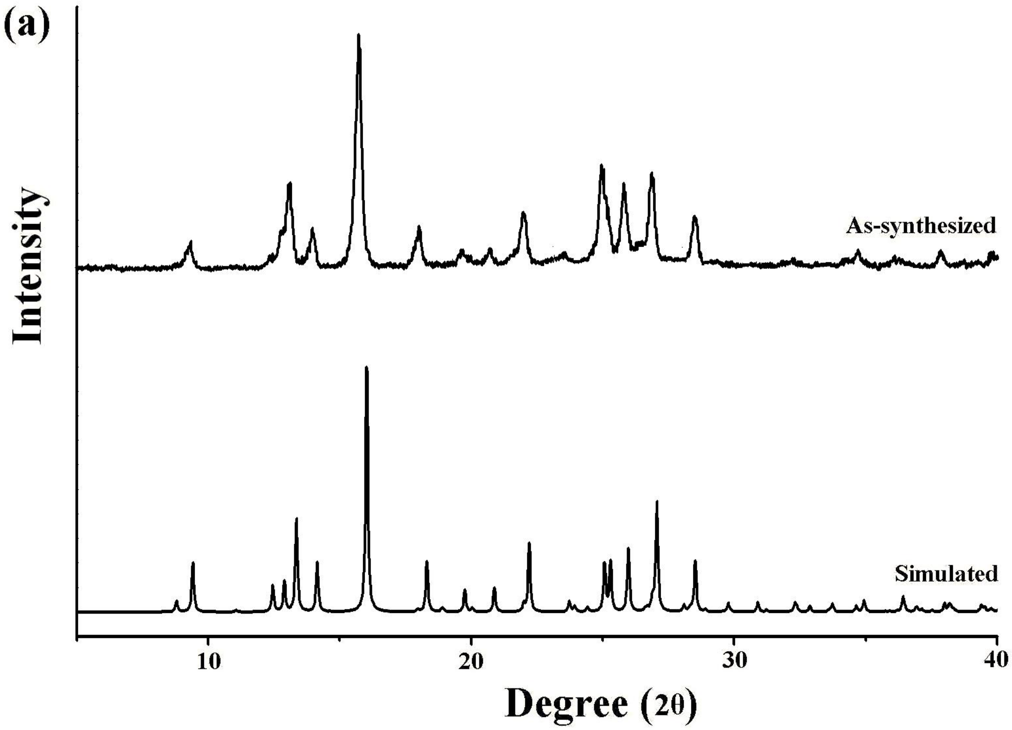
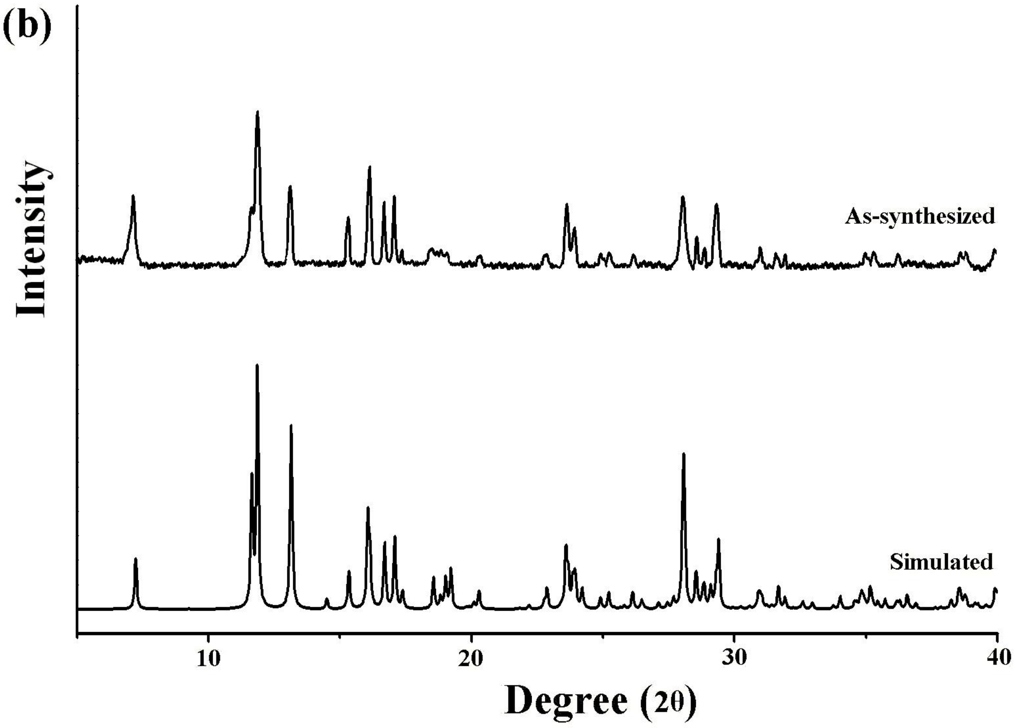
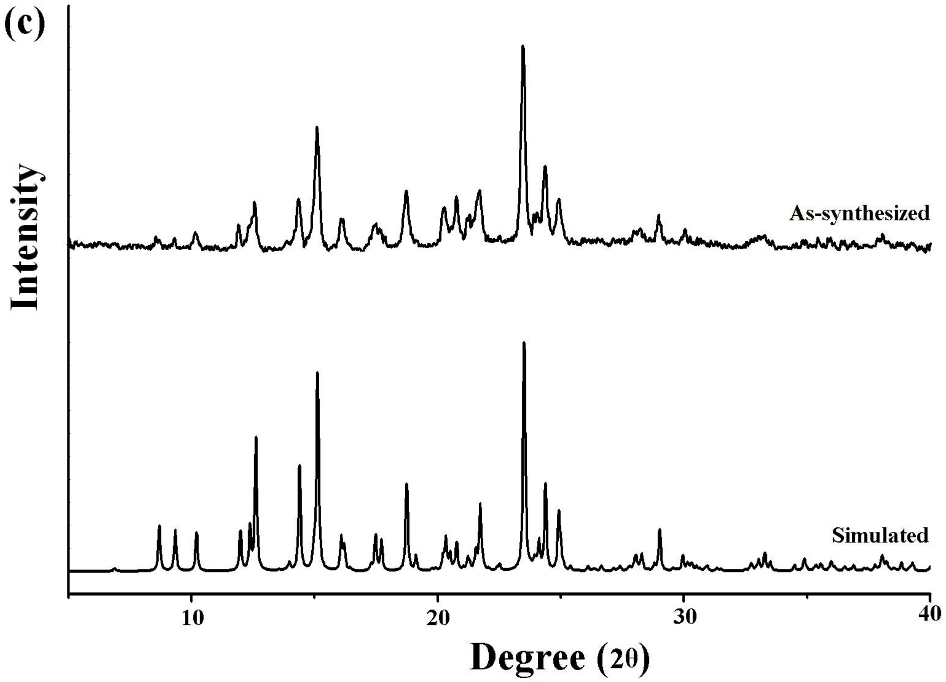


Fig.S3 The solid-state CD spectra of the odd single crystals (black, blue) and the bulk sample (pink) of complex **1.**


(a)
Intensity
As-synthesized
Simulated
10
20
30
40
Degree (2θ)


(b)
Intensity
As-synthesized
Simulated
10
20
30
40
Degree (2θ)



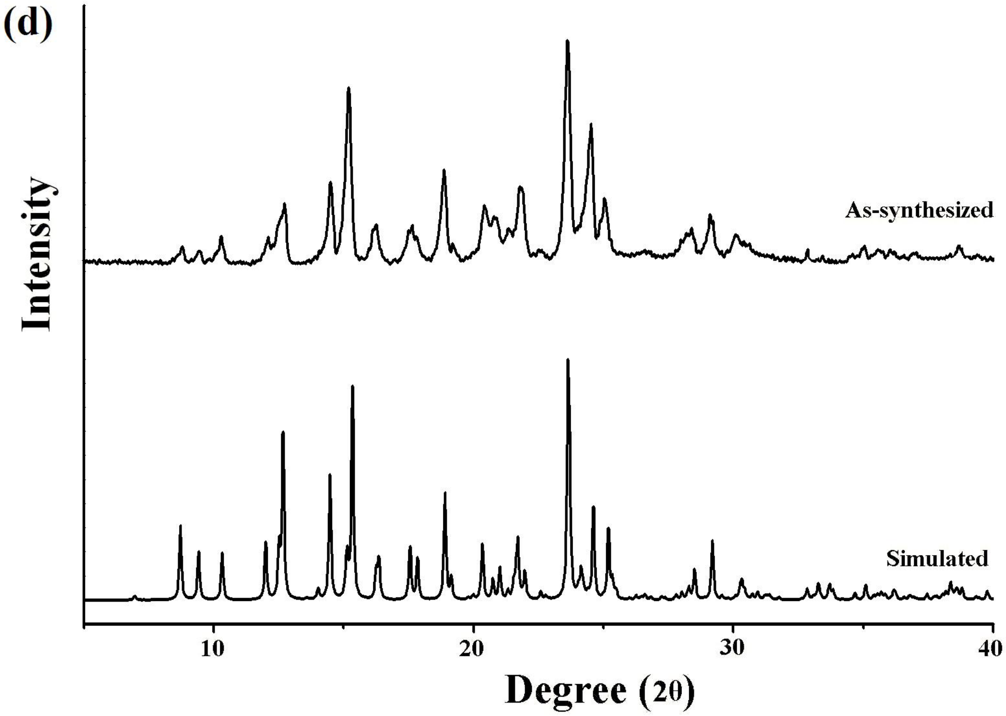


Fig.S4 The PXRD patterns of complexes **1** (**a**), **2** (**b**), **3** (**c**) and **4** (**d**).

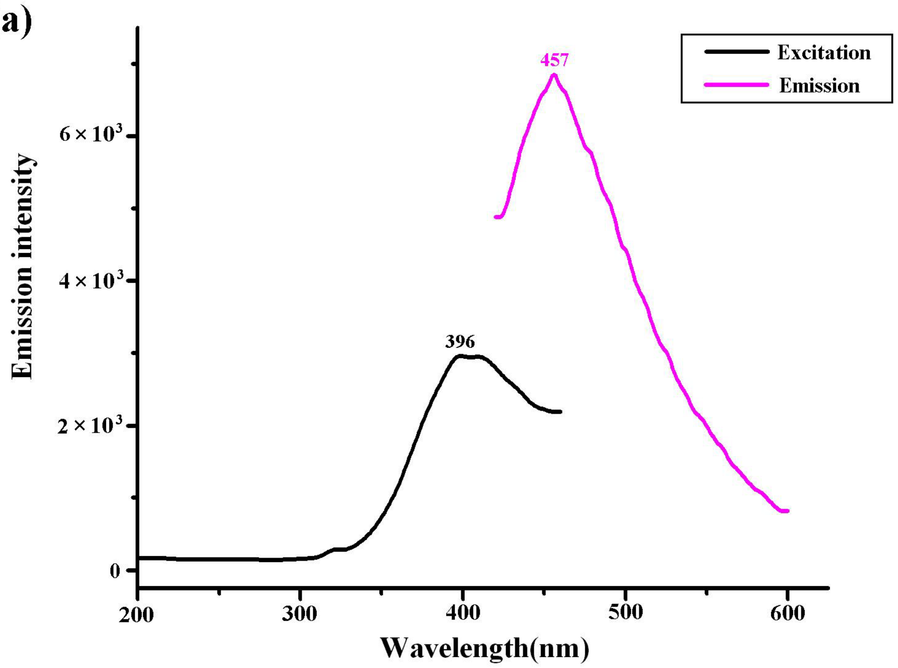
Photoluminescence Property The XRD powder patterns of complexes **1-4** are shown in **Fig.S4** in the supporting information. All the peaks of the four compounds can be indexed to their respective simulated XRD powder patterns, indicating each of the four compounds is pure phase. The photoluminescence properties of complexes **1-2** together with the free ligand **HL** were studied in the solid state at room temperature. The excitation and emission spectra of the complexes and the free organic ligand **HL** are depicted in **Fig. S5**.

As shown in **Fig. S5a**, **HL** in the solid state displays intense emission peaks at 457 nm when excitation at 396 nm. The emissions of the organic ligand may be ascribed to the $\pi^* \rightarrow n$ transitions.[1]

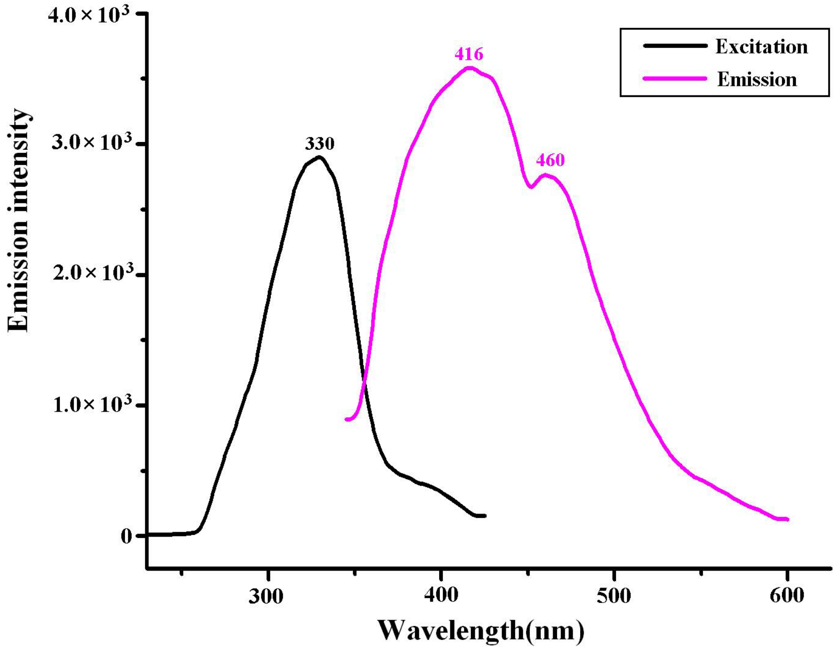
In order to avoid ligand-ligand interaction, the emission spectrum of **HL** in dilute DMF solution (5×10^{-5} mol $\cdot l^{-1}$) is also measured. **HL** shows emission peaks at 416 and 460 nm when excitation at 330 nm (**Fig. S5b**), which is similar to the emission of **HL** in the solid state but with the reduced emission intensity (**Fig. S5a-b**), indicating the solvent DMF has effect on the photoluminescence property of **HL**.

Complexes **1** and **2** in the solid state display emission bands at 414 (λ_{ex} = 350 nm) (**Fig.S5c**) and 454 nm (λ_{ex} = 397 nm) (**Fig.S5d**), respectively. Due to the $3d^{10}$ valence electron configuration of Zn(II) and Cd(II) ion, the emission band of the Zn(II) and Cd(II) complexes may be assigned to the LMCT as previously reported.[2]

(a)


Excitation
Emission
457
396
Emission intensity
6 × 10³
4 × 10³
2 × 10³
0
200
300
400
500
600
Wavelength(nm)

(b)


Excitation
Emission
416
460
330
Emission intensity
4.0 × 10³
3.0 × 10³
2.0 × 10³
1.0 × 10³
0
300
400
500
600
Wavelength(nm)

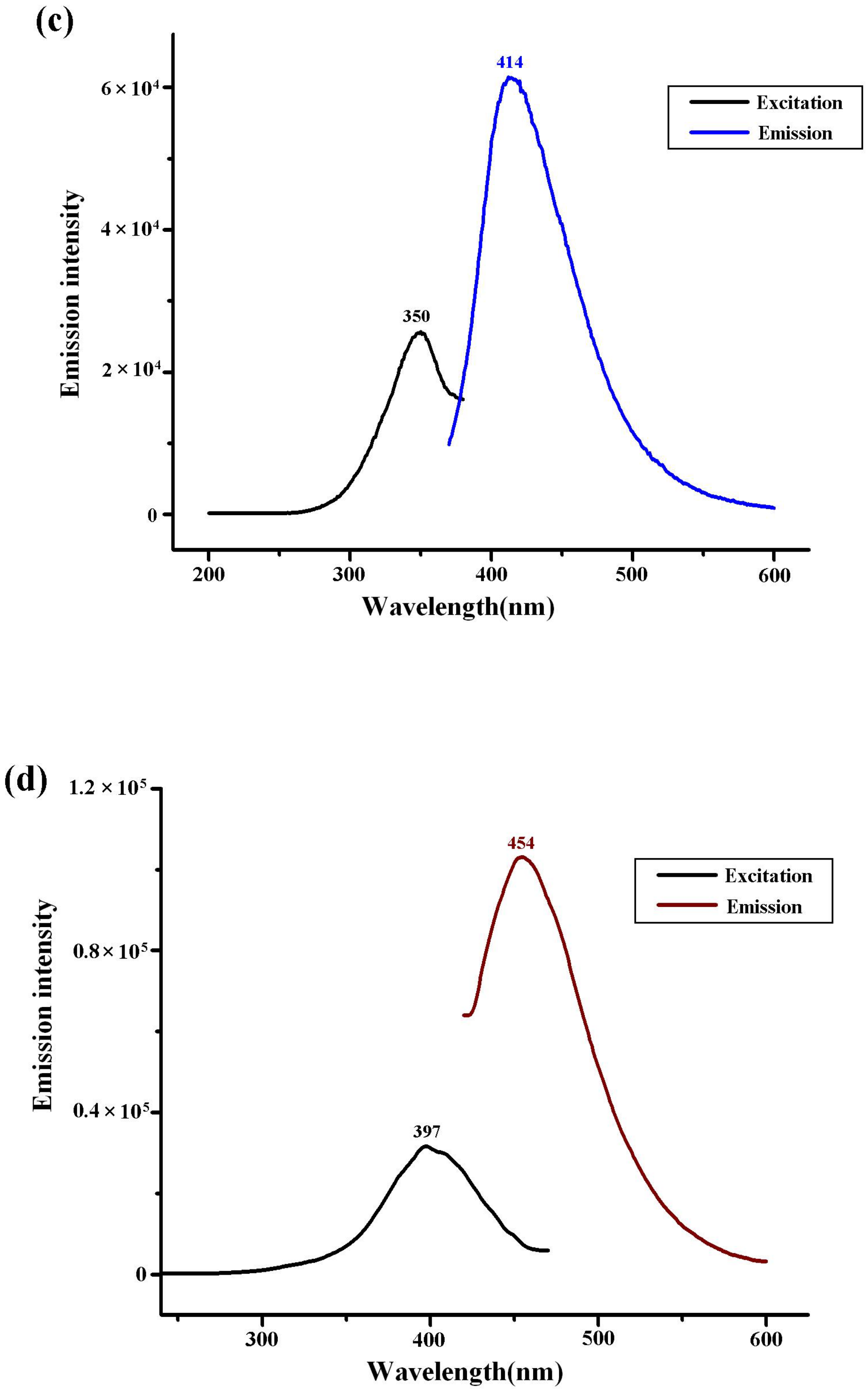


Fig. S5 Solid-state excitation and emission spectra at room temperature for the free organic ligand **HL** (**a**), complexes **1** (**c**) and **2** (**d**), and the excitation and emission spectra for the DMF solution of **HL** (**b**).

Thermal stability of complexes 1-4 In order to examine the thermal stability of the four complexes, thermogravimetric analyses (TGAs) were carried out. The samples were heated up to 750 °C in N_2. The TGA curve of complex **1** shows one step weight loss of 5.5 % between 30 and 100°C corresponding to the loss of lattice water molecules (calc. 5.7 wt%). Decomposition of the host framework began at 320 °C (**Fig. S6**).

Complex **2** releases its solvent water molecules between 30 and 150°C with a loss of 17.8 wt% (calc. 17.5 wt %). The complex loses its coordinated water molecules in the range of 320-350 °C (calcd.: 4.4 %; observed: 4.5 %). Decomposition of the organic component began at 350 °C (**Fig. S6**).

As for complexes **3** and **4**, they exhibits one step weight loss of 3.1 wt % (calc. 2.9 wt %) in the range of 30-110 °C, corresponding to the loss of uncoordinated water molecules (**Fig. S6**). The loss of coordinated water happens in the range of 320-350 °C (calcd.: 2.9 %; observed: 3.1 %). The decomposition of the organic component began at 400 °C.

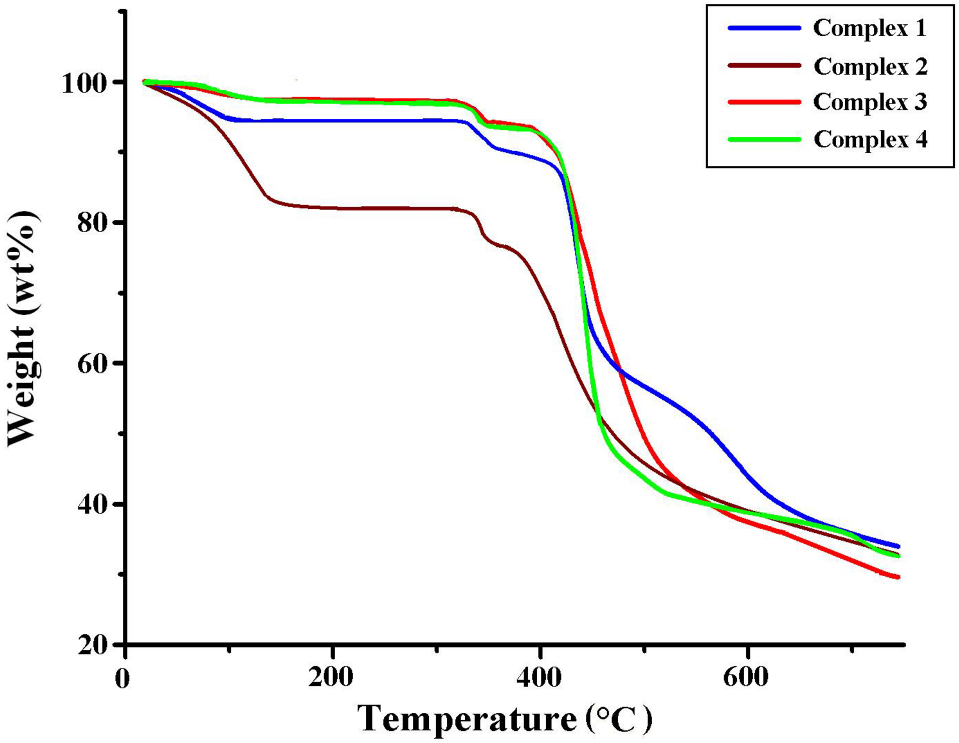


Fig.S6 Thermogravimetric curves of complexes **1-4**.

References

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