Chiral 3D/3D hetero-interpenetrating framework with six kinds of helices, 3D polyrotaxane and 2D network *via* one-pot reaction

Ming-Dao Zhang, Chang-Miao Di, Ling Qin, Qing-Xiang Yang, Yi-Zhi Li, Zi-Jian Guo, and He-Gen Zheng*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China

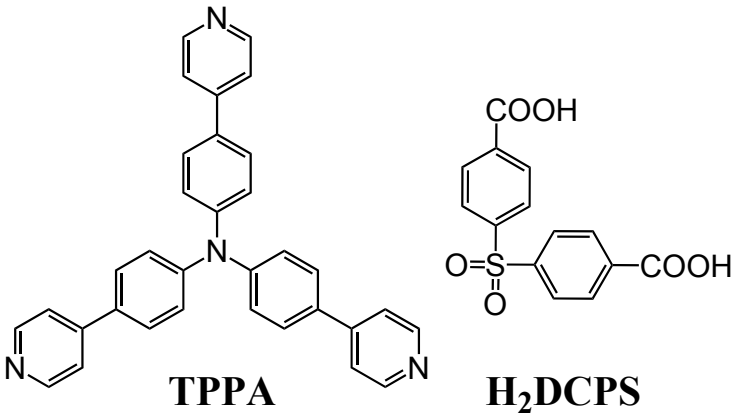
Materials and Measurements. Reagents and solvents employed were commercially available. TPPA was synthesized according to our previous report.[1] IR absorption spectra of the compounds were recorded in the range of 400-4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Mo-K_α radiation (λ = 0.71073 Å), in which the X-ray tube was operated at 40 kV and 40 mA. Luminescent spectra were recorded on a Perkin Elmer LS55 fluorescence spectrophotometer at room temperature.

Synthesis of TPPA. A mixture of tris(4-bromophenyl)amine (4.82 g, 10 mmol), $Pd(PPh_3)_4$ (0.580 g, 0.5 mmol), Pyridine-4-boronic acid (4.43 g, 36 mmol), 1 mM K_2CO_3 (40 mL, 40 mmol) and 1,4-dioxane (100 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. The reaction mixture was then heated to reflux for 24 h under N_2. After cooling to room temperature, the reaction mixture was extracted by $CHCl_3$ (3×150 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography with EtOAc as eluent to give the target compound TPPA as yellow solid (3.86 g, 81%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ, [ppm]: 7.22 (d, J = 3.5 Hz, 4H), 7.70 (d, J = 6.0 Hz, 4H), 7.83 (d, J = 3.5 Hz, 4H), 7.61 (d, J = 6.0 Hz, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ, [ppm]: 121.07, 124.70, 128.09, 132.83,

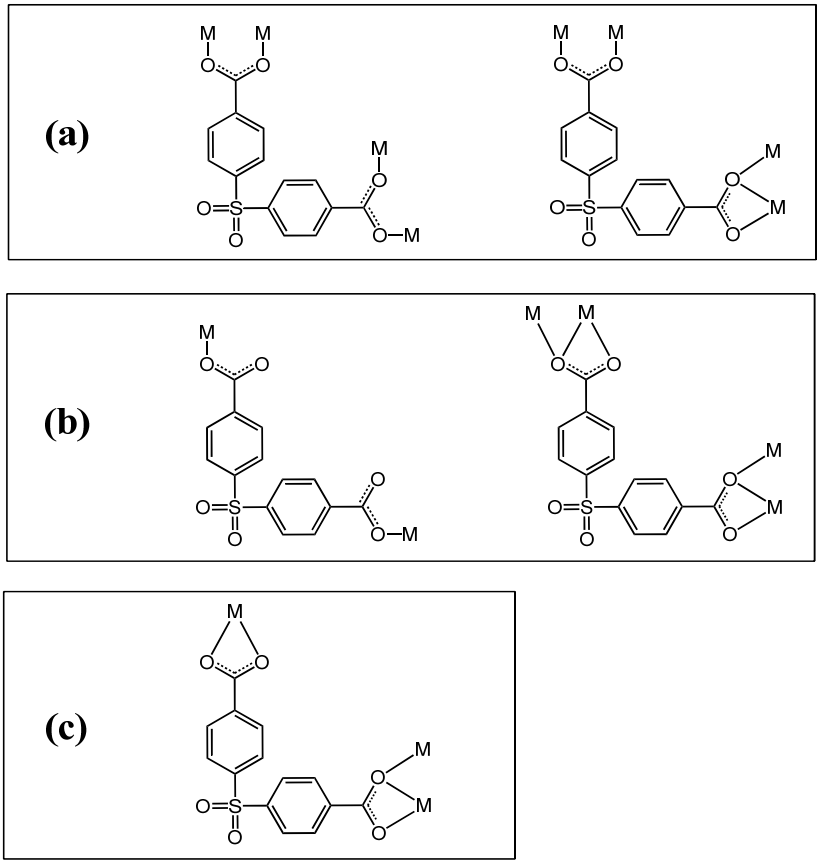
147.49, 147.86, 150.13. MS (ESI-MS): Calcd for $C_{33}H_{24}N_4$: 476.20; found, 477.58 {$[M+H]^+$}.

Synthesis of 1, 2, and 3. A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (30.1 mg, 0.1 mmol), TPPA (47.6 mg, 0.1 mmol) and 4,4'-dicarboxydiphenyl sulfone (45.9 mg, 0.15 mmol) was dissolved in 15 mL of DMF/MeCN/H_2O (1 / 1 / 2). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25 mL) under autogenous pressure and heated at 95 °C for 3d. Pale yellow crystals (**2**) and yellow crystals (**1** and **3**) were generated and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. The crystals were separated by hand picking and yield of the reaction were ca. 30% in **1**, 20% in **2**, 20% in **3** based on TPPA. The IR spectra of the corresponding complexes are shown in Fig. S10-S12.

X-ray Crystallography. X-ray crystallographic data of **1** and **3** were collected at room temperature by way of sealing the better single crystals in a quartz tube with mother liquor. X-ray crystallographic data of **2** were collected at room temperature using epoxy-coated crystals mounted on glass fiber. X-ray crystallographic data of these compounds were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Structure solutions were solved by direct methods and the non-hydrogen atoms were located from the trial structures and then refined anisotropically with *SHELXTL* using full-matrix least-squares procedures based on F^2 values.[2] Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The disordered C atoms and N atoms in **3** (N6, C44, C45, C46, C47 and C48) were refined using C or N atoms split over two sites with a total occupancy of 1. The distributions of peaks in the channels of **2** and **3** were chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining water molecule was removed by the SQUEEZE routine in PLATON.[3] The selected bond lengths and angles are given in Table S5-S7. A semiempirical absorption correction was applied using SADABS.[4] The topological analysis and some diagrams were produced using the TOPOS program.[5]



Scheme S1 Structures of TPPA and H_2DCPS



Scheme S2. Crystallographically established coordination modes of carboxylic groups in compounds **1** (b), **2** (a), and **3** (c).

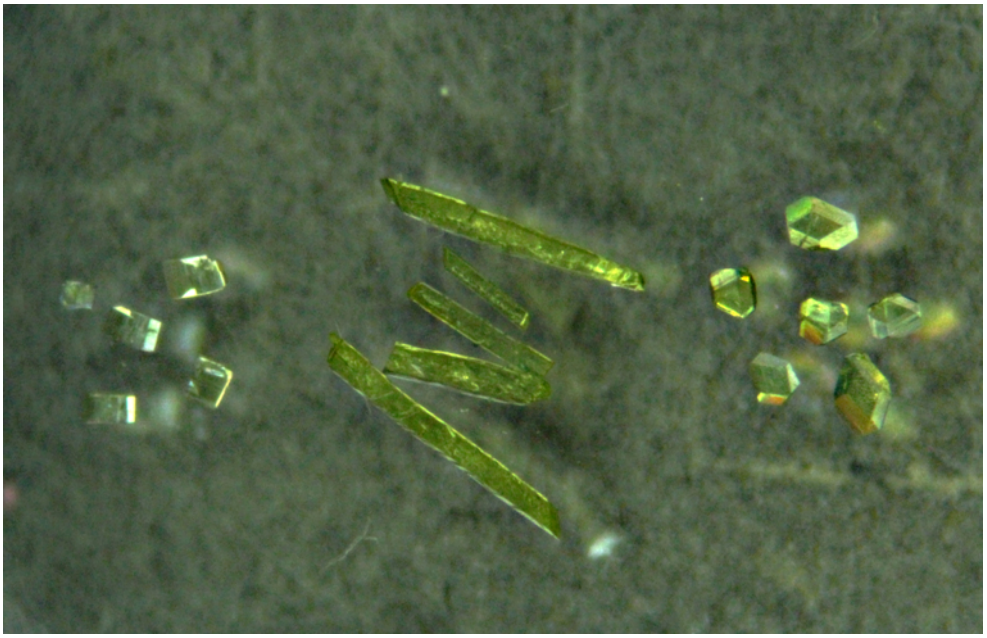


Fig. S1 The photograph of compound **1**-**3**: rodlike for **1** (middle), cuboid for **2** (left), rhomboidal for **3** (right).

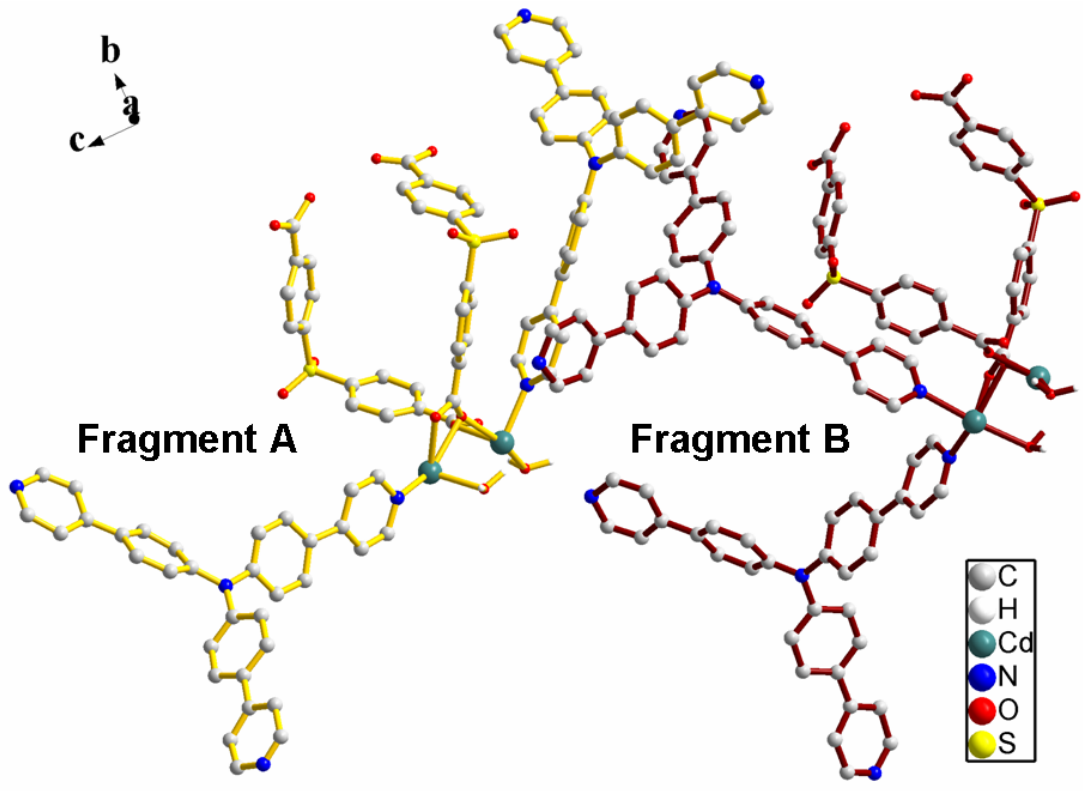


Fig. S2 The asymmetric unit including two distinct fragments (A and B) of **1**; the most hydrogen atoms and free solvent molecules are omitted.

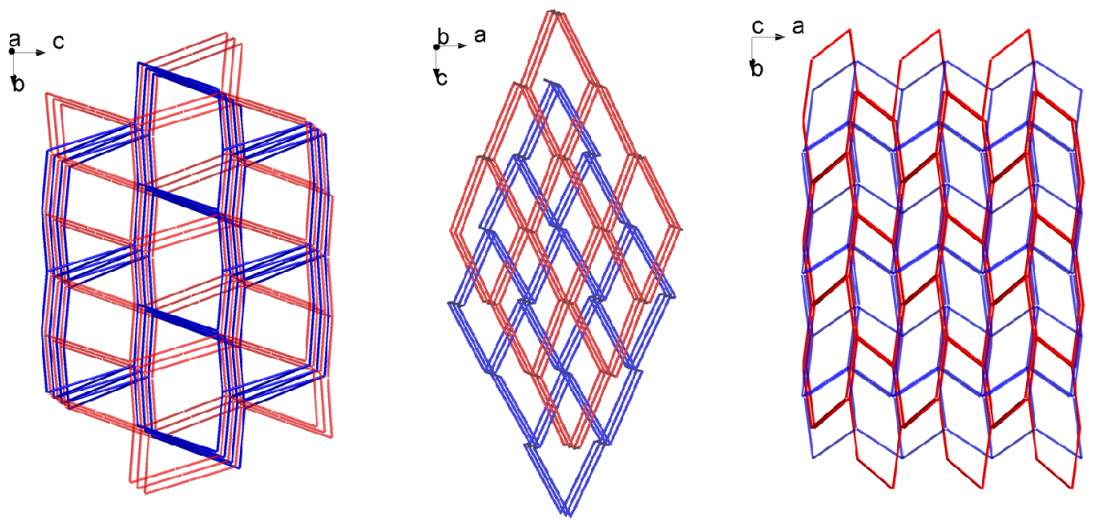


Fig. S3 Schematic view of the two-fold ***dia*** topology of structure **1** along *a*, *b*, or *c* axes. (Bidentate TPPA and $DCPS^{2-}$ in **1** are simplified as linkers)

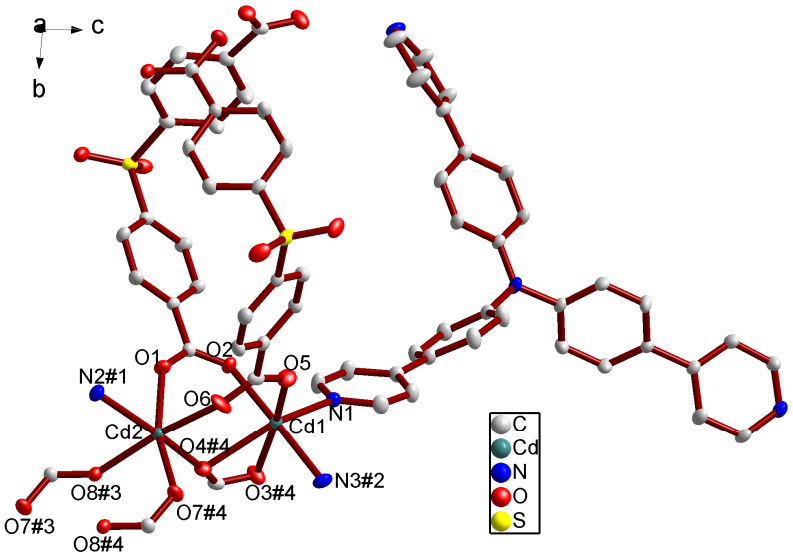


Fig. S4 Coordination environment of the Cd^{2+} ion in **2**. The hydrogen atoms are omitted for clarity(30% ellipsoid probability). Symmetry codes: #1 = 1 + x, y, -1 + z; #2 = 1 + x, 1 + y, z; #3 = 2 - x, 1 - y, -z; #4 = x, 1 + y, z.

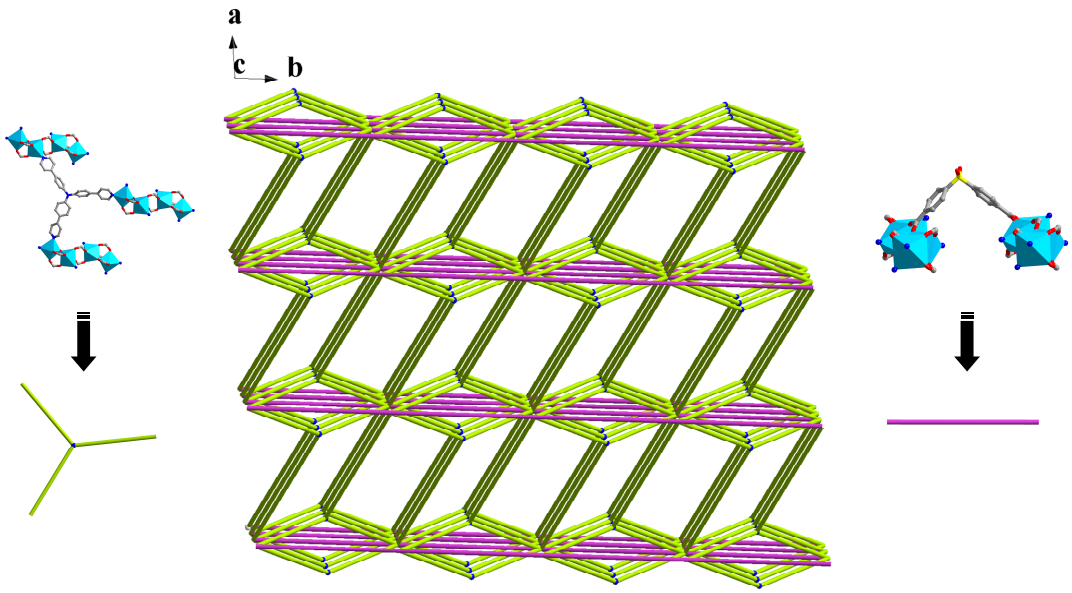


Fig. S5 Schematic view of the ***tfz-d*** topology of structure **2**.

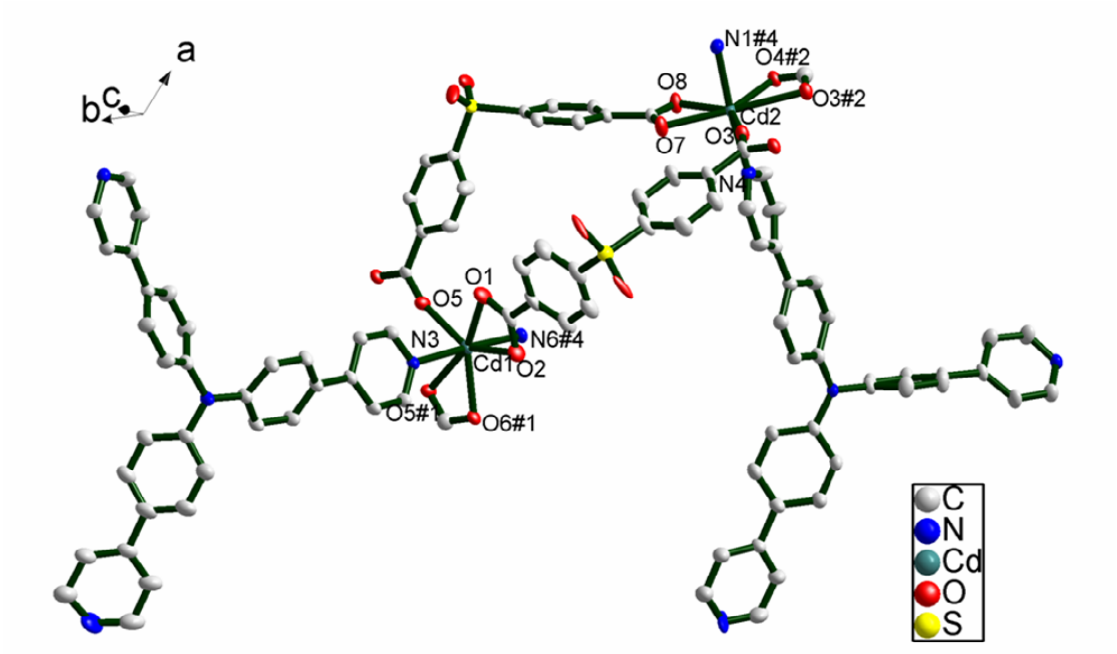


Fig. S6 Coordination environment of the Cd^{2+} ion in **3**. The hydrogen atoms are omitted for clarity(30% ellipsoid probability). Symmetry codes: #1 = 1 - x, 1 - y, 1 - z; #2 = 2 - x, -y, 1 - z; #3 = 1 - x, -y, -z; #4 = 2 - x, 1 - y, 2 - z.

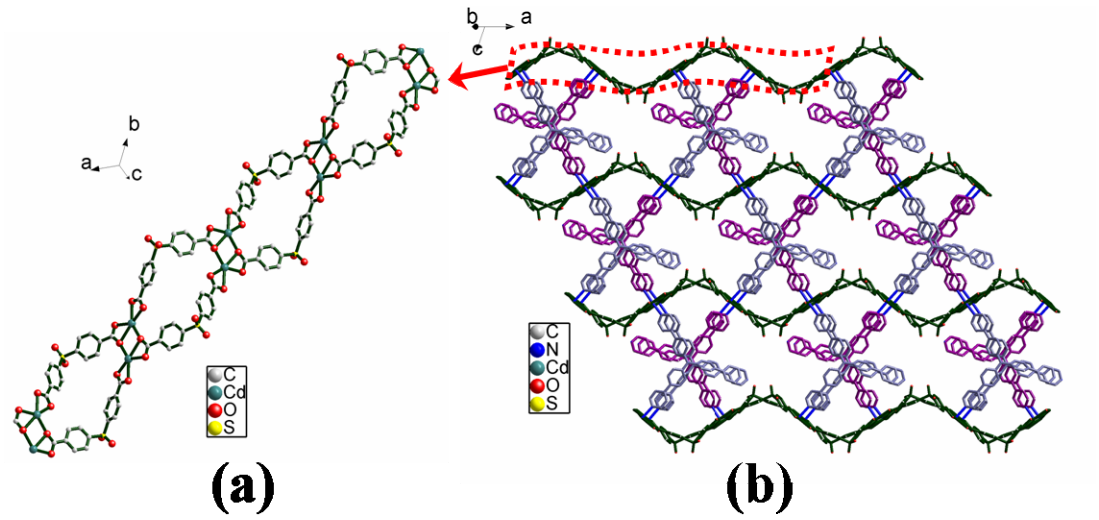


Fig. S7 (a) A view of 1D monolayer Cd-DCPS straps in **3**; (b) A perspective view of the 2D network in **3**.

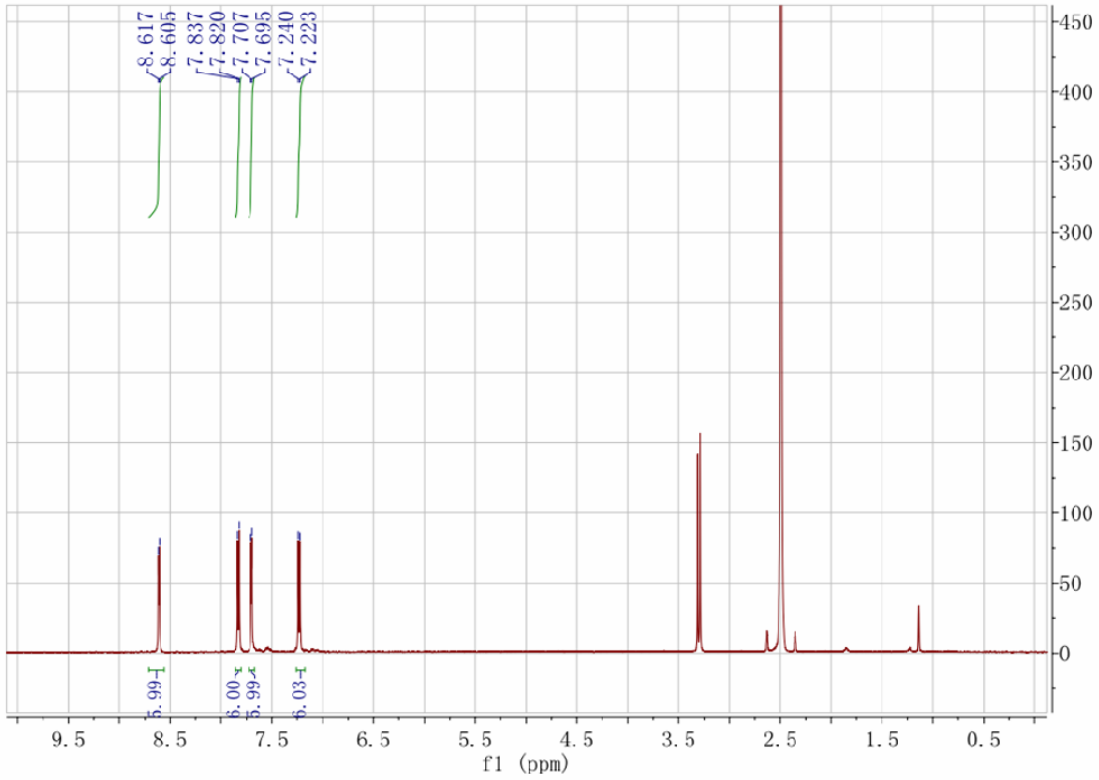


Fig. S8 The ^{1}H NMR spectra of TPPA

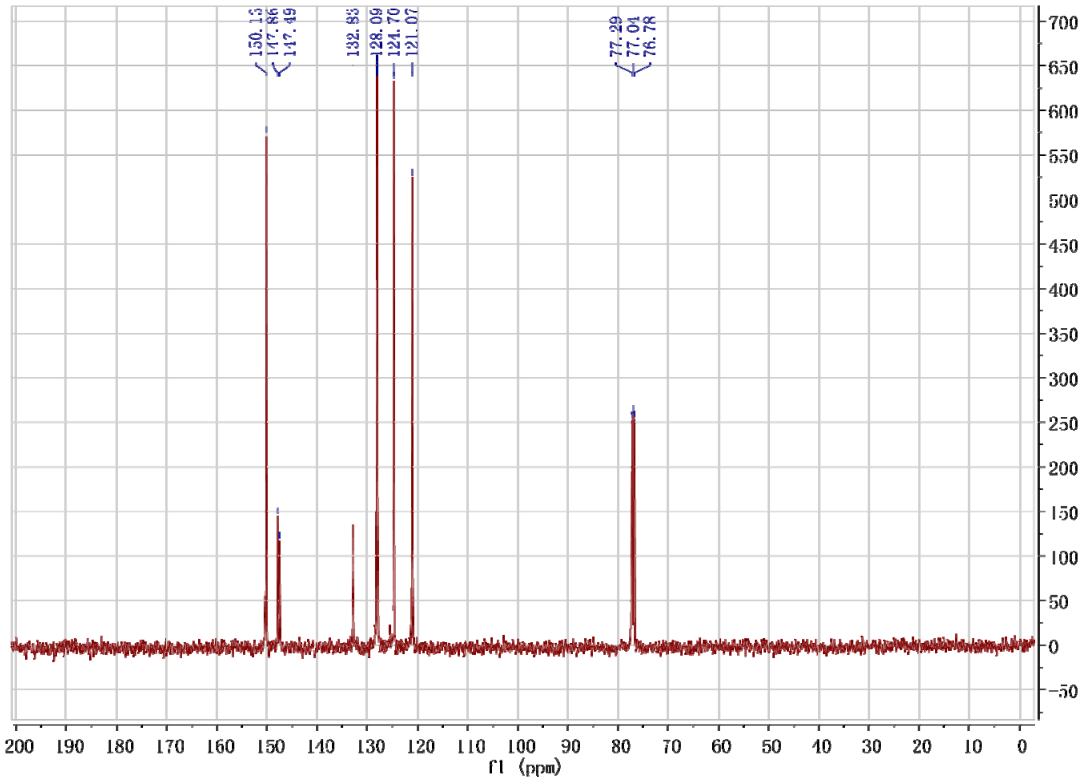


Fig. S9 The ^{13}C NMR spectra of TPPA

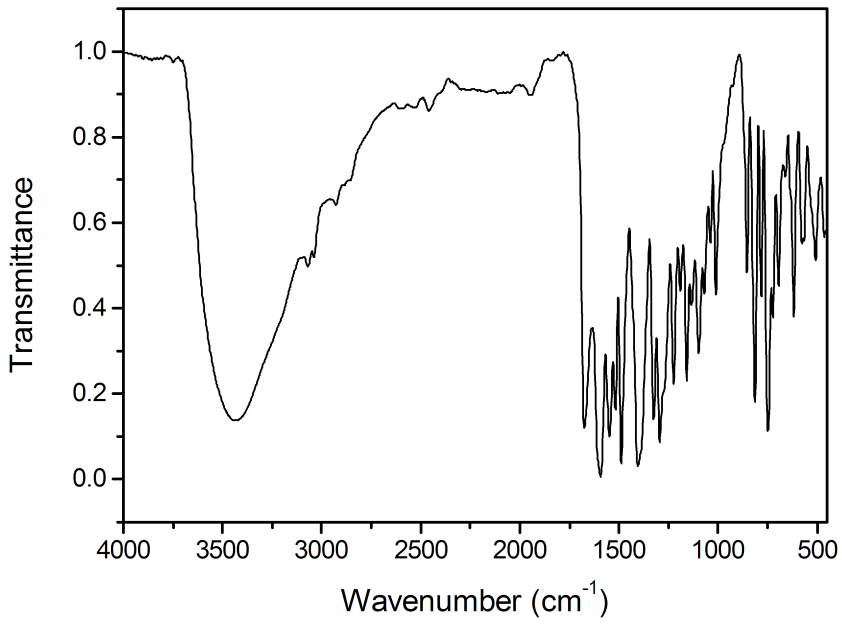


Fig. S10 IR spectrum of **1** at room temperature.

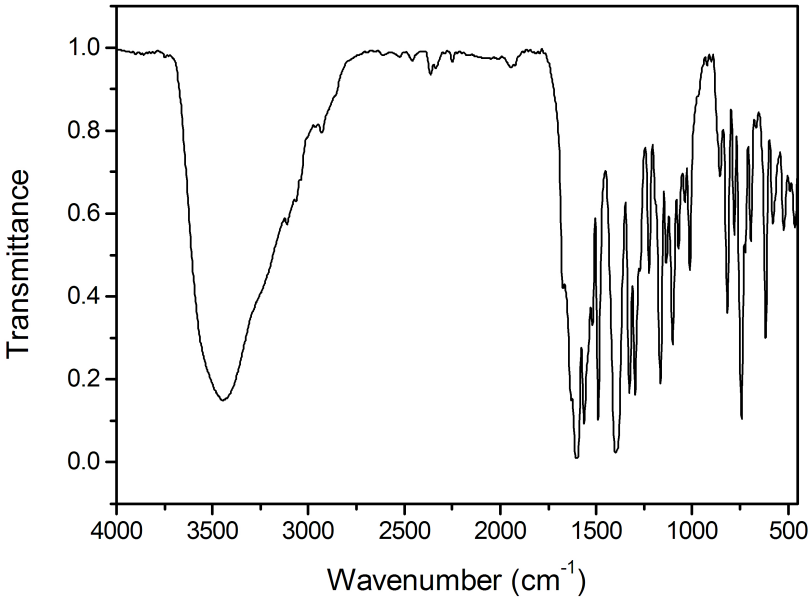


Fig. S11 IR spectrum of **2** at room temperature.

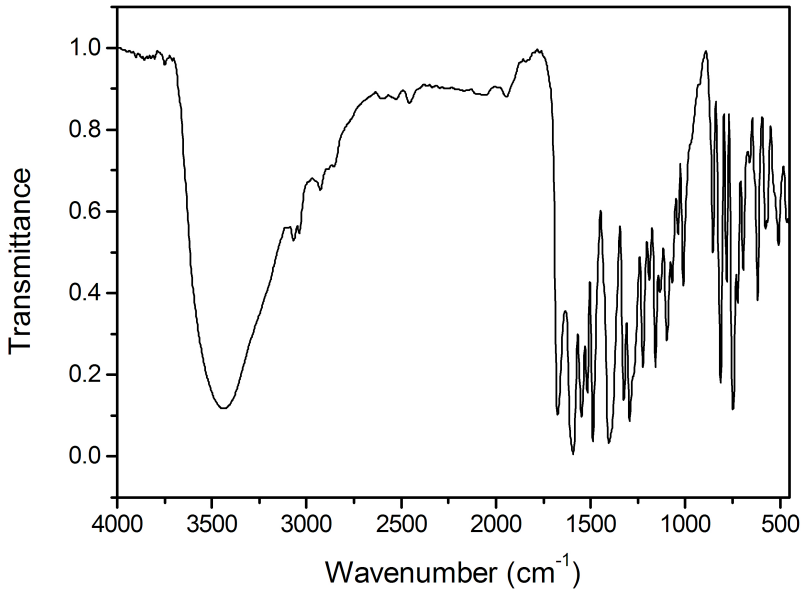


Fig. S12 IR spectrum of **3** at room temperature.

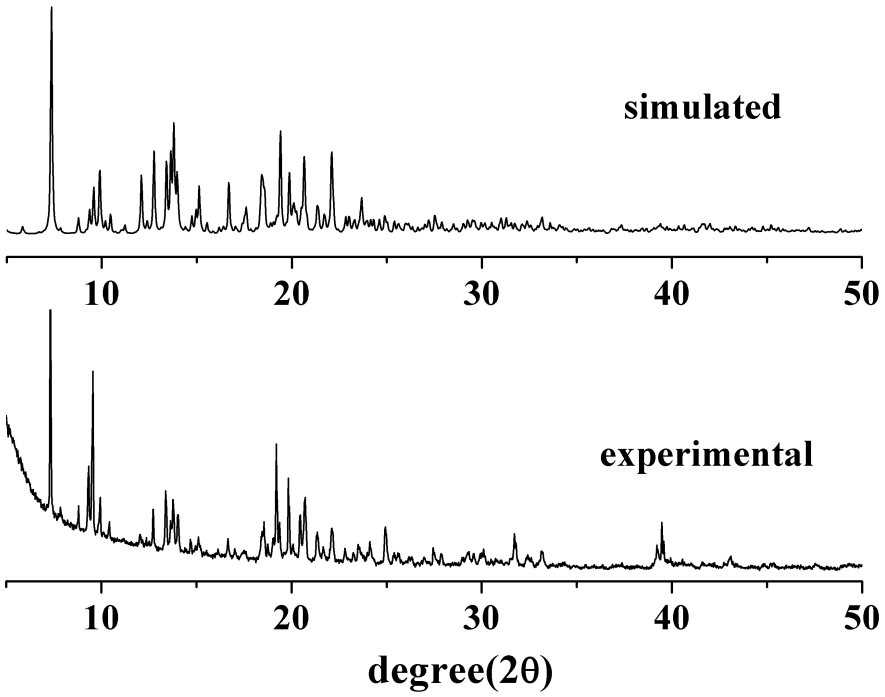


Fig. S13 Powder X-ray diffraction patterns of compound **1**

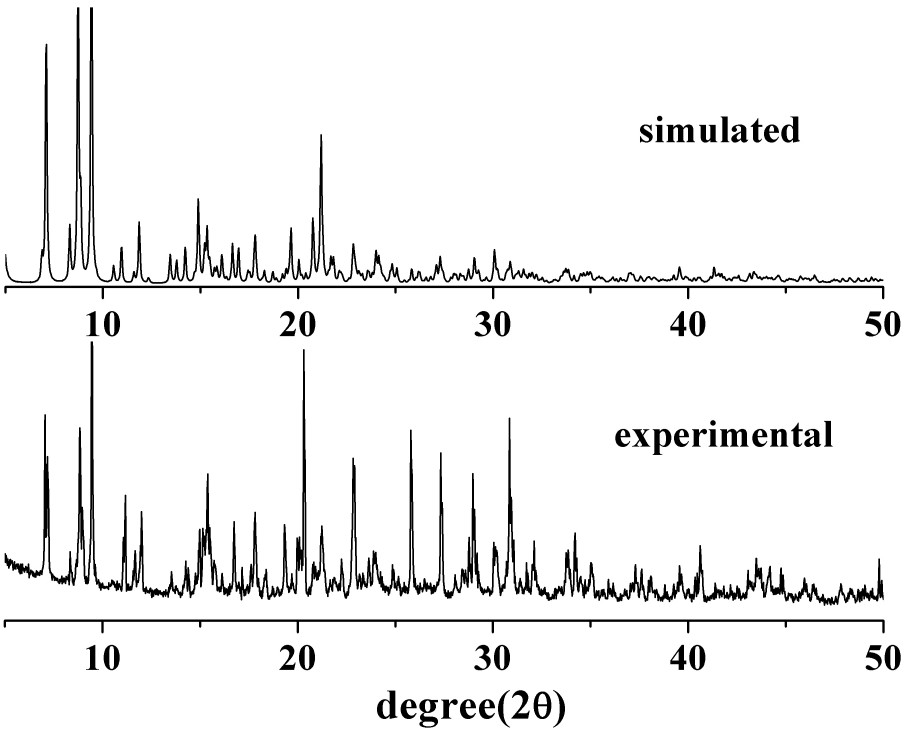


Fig. S14 Powder X-ray diffraction patterns of compound **2**

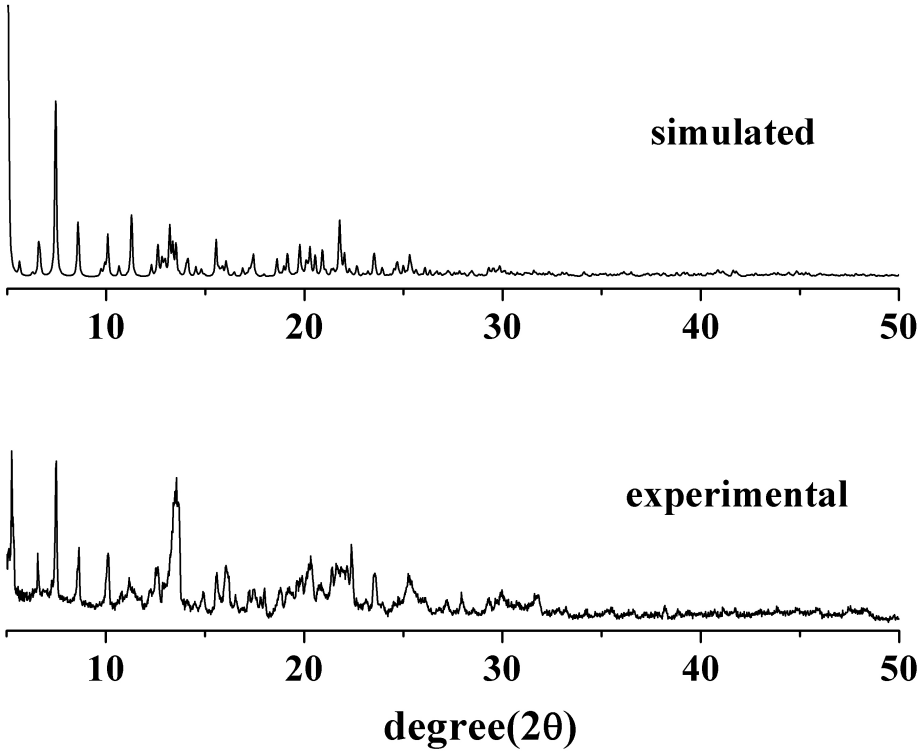


Fig. S15 Powder X-ray diffraction patterns of compound **3**

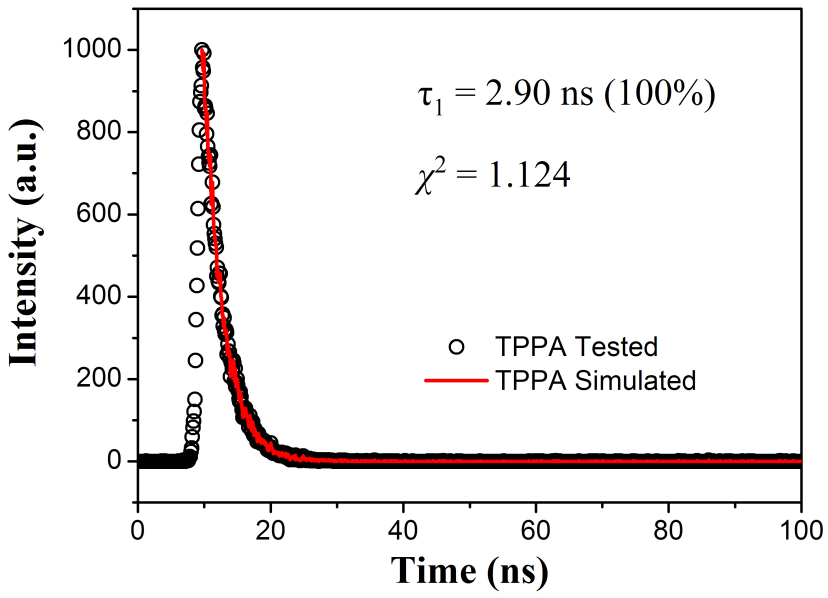


Fig. S16 The fitted decay curve monitored at 520 nm for free TPPA ligand in the solid state at room temperature. The sample was excited at 405 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A + B_1 \times \exp(-t / \tau_1) + B_2 \times \exp(-t / \tau_2)$.

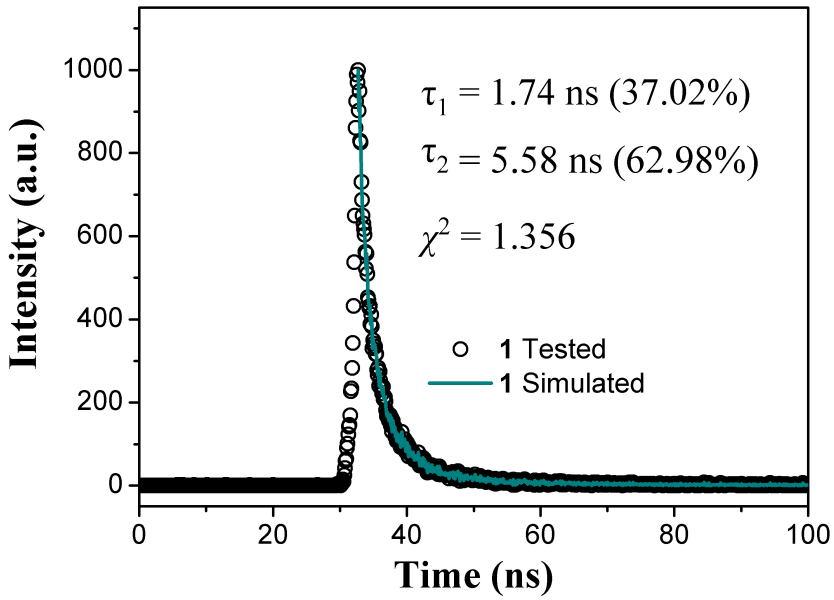


Fig. S17 The fitted decay curve monitored at 508 nm for compound **1** in the solid state at room temperature. The sample was excited at 405 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A + B_1 \times \exp(-t / \tau_1) + B_2 \times \exp(-t / \tau_2)$.

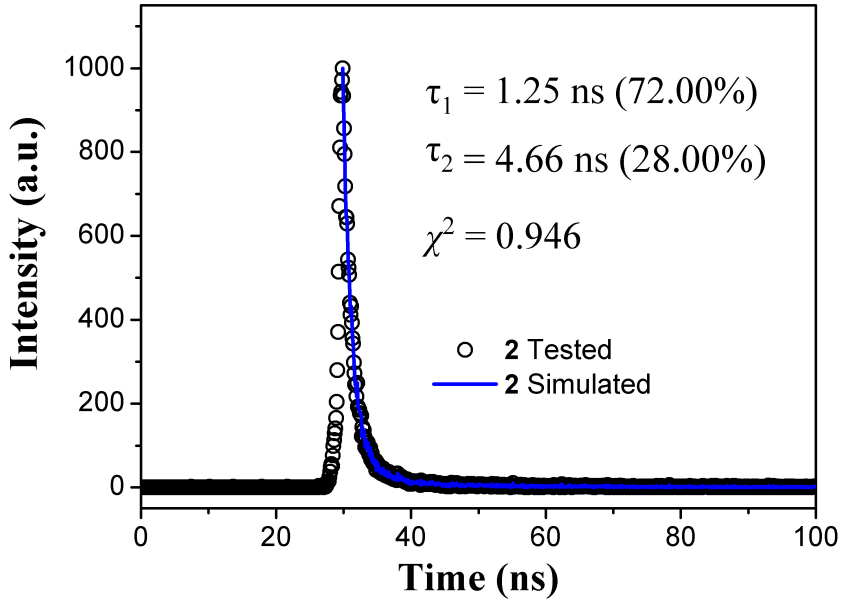


Fig. S18 The fitted decay curve monitored at 453 nm for compound **2** in the solid state at room temperature. The sample was excited at 405 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A + B_1 \times \exp(-t / \tau_1) + B_2 \times \exp(-t / \tau_2)$.

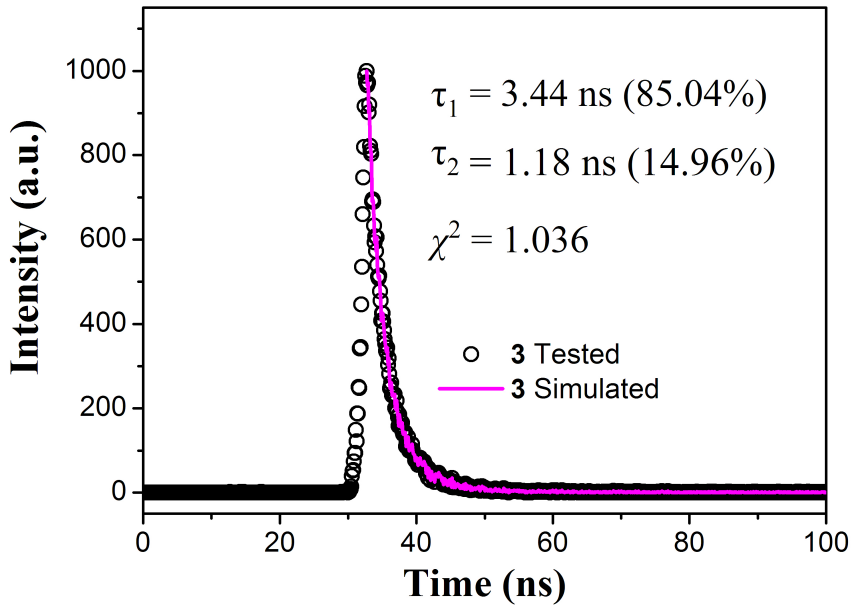


Fig. S19 The fitted decay curve monitored at 488 nm for compound **3** in the solid state at room temperature. The sample was excited at 405 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A + B_1 \times \exp(-t / \tau_1) + B_2 \times \exp(-t / \tau_2)$.

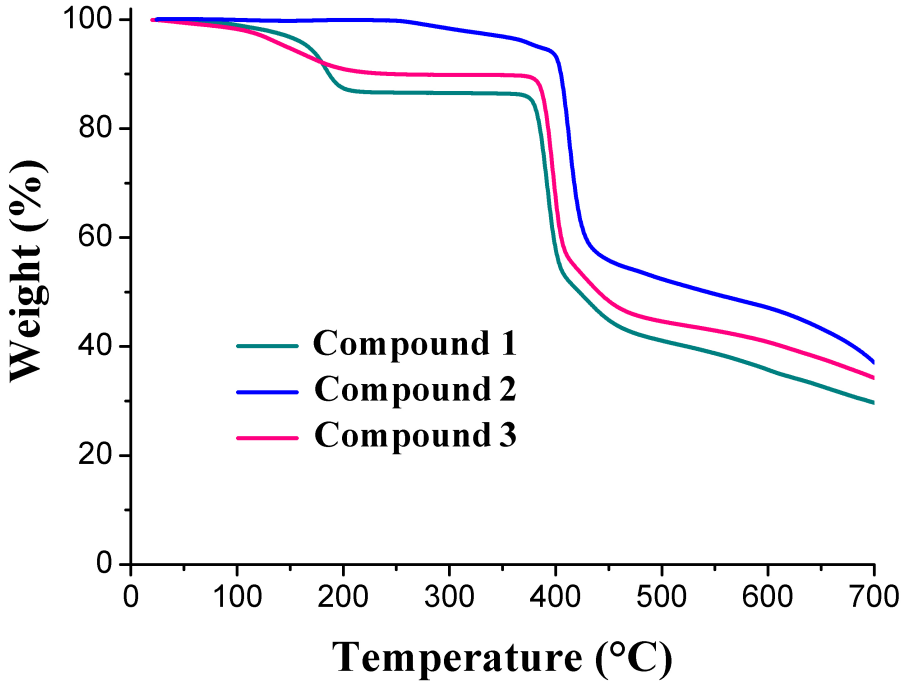


Fig. S20 TG plots of compounds **1-3**.

Table S1. Detailed parameters extracted from photoluminescent properties of **1-3** and free ligands

Compound	λ_{ex} /nm	λ_{em} /nm	Lifetime[b]/ns (Rel)[a]
H_2DCPS	354	387	
1	433	508	1.74 (37.02%), 5.58 (62.98%)
2	380	453	1.25 (72.00%), 4.66 (28.00%)
3	433	488	3.44 (85.04%), 1.18 (14.96%)
TPPA	420	520	2.90 (100%)

[a] The emission peak of free H_2DCPS ligand can not be excited at the wavelength of laser device (405 nm), so the lifetime of free H_2DCPS ligand is not listed here.

Table S2. Summary of products synthesized by ligands and solvents with different ratios.[a]

DMF/MeCN/H_2O / **n(TPPA)/n(H_2DCPS)**	**2/1/3**	**1/1/2**	**1/2/3**
2/1	**1**	**1**	**1**
3/2	**1**	**1**	**1**
1/1	**1**(trace)+**2**(trace)+**3**	**1**+**2**(trace)+**3**	**1**(trace)+**2**(trace)+**3**
2/3	**1**(trace)+**2**+**3**	**1**+**2**+**3**	**2**+**3**
1/2	**2**+**3**(trace)	**2**+**3**	**2**+**3**
1/3	**2**+**3**(trace)	**2**+**3**(trace)	**2**+**3**(trace)
1/4	**2**	**2**	**2**

[a] Sum of the concentrations of ligands: C(TPPA)+C(H_2DCPS) = 2 mM, 95 °C, 3 days.

Table S3. Summary of products synthesized under conditions of different temperatures, Cadmium salts, and solvents.[a]

DMF/MeCN/H_2O / Temp(°C)	1/0/1	1/0/2	2/1/3	1/1/2	1/2/3	0/1/1	CdX_2
80	**3**	**3**	**3**	**3**	**3**	No	$Cd(NO_3)_2$
90	**3**	**3**	**2**(trace)+**3**	**2**(trace)+**3**	**3**	No	$Cd(NO_3)_2$
95	**3**	**3**	**1**(trace)+**2**(trace)+**3**	**1**+**2**+**3**	**2**(trace)+**3**	No	$Cd(NO_3)_2$
100	**3**	**3**	**2**(trace)+**3**	**2**(trace)+**3**	**2**(trace)+**3**	No	$Cd(NO_3)_2$
110	**3**	**3**	**3**	**3**	**3**	No	$Cd(NO_3)_2$
120	No	No	No	**3**	**3**	No	$Cd(NO_3)_2$
130	No	No	No	No	No	No	$Cd(NO_3)_2$
140	No	No	No	No	No	No	$Cd(NO_3)_2$
95	No	No	No	**3**	**3**	No	$Cd(SO_4)_2$
95	No	No	No	No	No	No	$Cd(OAc)_2$
95	No	No	No	No	No	No	$CdCl_2$

[a] Ratio of amount of ligands: n(TPPA)/n(H_2DCPS) = 1/1, 3 days.

Table S4. Summary of the product isolated at different times.[a]

Time (h)	Products
6	**3**
12	**3**
18	**2**(trace)+**3**
24	**2**(trace)+**3**
30	**2**+**3**
36	**2**+**3**
42	**1**(trace)+**2**+**3**
48	**1**(trace)+**2**+**3**
54	**1**(trace)+**2**+**3**
60	**1**+**2**+**3**
66	**1**+**2**+**3**
72	**1**+**2**+**3**

[a] n(TPPA)/n(H_2DCPS) = 2/3, DMF/MeCN/H_2O = 1/1/2, 95 °C.

Table S5. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Cd1-O8#1	2.211(4)	Cd2-O3	2.345(4)	Cd3-O11	2.457(4)
Cd1-O1W	2.249(4)	Cd2-N6#2	2.365(5)	Cd4-O4W	2.283(4)
Cd1-O5	2.257(4)	Cd2-O4	2.479(4)	Cd4-O9#3	2.310(4)
Cd1-N3	2.310(5)	Cd2-O1	2.594(4)	Cd4-N12	2.328(5)
Cd1-O1#1	2.391(4)	Cd3-O15#1	2.222(4)	Cd4-N9	2.333(5)
Cd1-O4	2.476(4)	Cd3-O14	2.228(4)	Cd4-O12	2.350(4)
Cd2-O2W	2.299(4)	Cd3-O3W	2.230(4)	Cd4-O11	2.466(4)
Cd2-O2#1	2.308(4)	Cd3-N13#4	2.333(5)	Cd4-O10#3	2.555(4)
Cd2-N5	2.324(5)	Cd3-O10#3	2.451(4)		

Angle	(deg)	Angle	(deg)	Angle	(deg)
O8#1-Cd1-O1W	109.25(16)	O3-Cd2-N6#2	89.21(15)	O3W-Cd3-O11	162.24(15)
O8#1-Cd1-O5	162.51(15)	O2W-Cd2-O4	87.50(15)	N13#4-Cd3-O11	87.44(16)
O1W-Cd1-O5	85.09(15)	O2#1-Cd2-O4	128.34(14)	O10#3-Cd3-O11	79.31(14)
O8#1-Cd1-N3	96.38(17)	N5-Cd2-O4	144.72(15)	O4W-Cd4-O9#3	94.02(16)
O1W-Cd1-N3	100.60(18)	O3-Cd2-O4	53.79(14)	O4W-Cd4-N12	89.13(17)
O5-Cd1-N3	90.52(17)	N6#2-Cd2-O4	88.32(16)	O9#3-Cd4-N12	86.91(17)
O8#1-Cd1-O1#1	85.42(16)	O2W-Cd2-O1	79.71(15)	O4W-Cd4-N9	175.89(17)
O1W-Cd1-O1#1	90.88(15)	O2#1-Cd2-O1	53.04(14)	O9#3-Cd4-N9	88.96(18)
O5-Cd1-O1#1	84.38(16)	N5-Cd2-O1	136.91(15)	N12-Cd4-N9	93.87(19)
N3-Cd1-O1#1	167.01(18)	O3-Cd2-O1	129.75(14)	O4W-Cd4-O12	88.01(15)
O8#1-Cd1-O4	83.19(15)	N6#2-Cd2-O1	101.28(16)	O9#3-Cd4-O12	177.20(15)
O1W-Cd1-O4	164.83(15)	O4-Cd2-O1	77.30(13)	N12-Cd4-O12	91.19(16)
O5-Cd1-O4	81.25(16)	O15#1-Cd3-O14	161.11(16)	N9-Cd4-O12	89.12(17)
N3-Cd1-O4	86.16(17)	O15#1-Cd3-O3W	109.89(16)	O4W-Cd4-O11	89.05(15)
O1#1-Cd1-O4	81.27(14)	O14-Cd3-O3W	84.33(16)	O9#3-Cd4-O11	128.65(15)

O2W-Cd2-O2#1	95.81(15)	O15#1-Cd3-N13#4	99.63(16)	N12-Cd4-O11	144.43(16)
O2W-Cd2-N5	90.78(16)	O14-Cd3-N13#4	88.82(16)	N9-Cd4-O11	86.88(16)
O2#1-Cd2-N5	86.90(16)	O3W-Cd3-N13#4	102.64(16)	O12-Cd4-O11	53.24(14)
O2W-Cd2-O3	86.73(15)	O15#1-Cd3-O10#3	83.88(15)	O4W-Cd4-O10#3	77.99(14)
O2#1-Cd2-O3	176.68(15)	O14-Cd3-O10#3	84.03(15)	O9#3-Cd4-O10#3	53.75(14)
N5-Cd2-O3	90.93(16)	O3W-Cd3-O10#3	88.94(14)	N12-Cd4-O10#3	136.79(16)
O2W-Cd2-N6#2	175.38(15)	N13#4-Cd3-O10#3	165.75(15)	N9-Cd4-O10#3	101.60(16)
O2#1-Cd2-N6#2	88.33(16)	O15#1-Cd3-O11	82.28(15)	O12-Cd4-O10#3	128.70(14)
N5-Cd2-N6#2	91.50(18)	O14-Cd3-O11	81.25(16)	O11-Cd4-O10#3	77.16(13)

Symmetry codes: #1 = 1-*x*, -0.5+*y*, 1.5-*z*; #2 = -0.5+*x*, 0.5-*y*, 2-*z*; #3 = 1-*x*, -0.5+*y*, 0.5-*z*; #4 = 0.5-*x*, -*y*, -0.5+*z*.

Table S6. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**.

Bond	**Length (Å)**	**Bond**	**Length (Å)**	**Bond**	**Length (Å)**
Cd1-O5	2.222(2)	Cd2-O7#4	2.220(2)	Cd2-O4#4	2.403(2)
Cd1-O2	2.240(2)	Cd2-O1	2.264(2)	Cd2-N2#1	2.380(3)
Cd1-O3#1	2.368(2)	Cd2-O6	2.280(2)	Cd1-N1	2.334(3)
Cd1-O4#1	2.450(2)	Cd2-O8	2.286(2)	Cd1-N3#2	2.323(3)

Angle	**(deg)**	**Angle**	**(deg)**	**Angle**	**(deg)**
O5-Cd1-O2	88.76(10)	O5-Cd1-O4#4	117.90(9)	O6-Cd2-O8#3	170.68(9)
O5-Cd1-N3#2	89.70(10)	O2-Cd1-O4#4	82.80(8)	O7#4-Cd2-N2#1	103.62(10)
O2-Cd1-N3#2	177.45(10)	N3#2-Cd1-O4#4	96.13(10)	O1-Cd2-N2#1	84.11(9)
O5-Cd1-N1	107.15(10)	N1-Cd1-O4#4	133.66(9)	O6-Cd2-N2#1	97.62(11)
O2-Cd1-N1	88.09(9)	O3#4-Cd1-O4#4	53.96(8)	O8#3-Cd2-N2#1	83.11(9)
N3#2-Cd1-N1	94.31(10)	O7#4-Cd2-O1	163.29(9)	O7#4-Cd2-O4#4	91.33(10)
O5-Cd1-O3#4	171.33(10)	O7#4-Cd2-O6	79.03(9)	O1-Cd2-O4#4	84.71(8)
O2-Cd1-O3#4	92.80(10)	O1-Cd2-O6	85.32(9)	O6-Cd2-O4#4	96.84(10)
N3#2-Cd1-O3#4	88.42(11)	O7#4-Cd2-O8#3	91.75(8)	O8#3-Cd2-O4#4	84.65(8)
N1-Cd1-O3#4	81.44(9)	O1-Cd2-O8#3	103.99(8)	N2#1-Cd2-O4#4	160.91(9)

Symmetry codes: #1 = 1 + x, y, -1 + z; #2 = 1 + x, 1 + y, z; #3 = 2 - x, 1 - y, -z; #4 = x, 1 + y, z.

Table S7. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Cd1-N6#4	2.308(7)	Cd1-O1	2.421(4)	Cd2-O3	2.351(4)
Cd1-N3	2.330(4)	Cd1-O5#1	2.559(3)	Cd2-O7	2.352(4)
Cd1-O5	2.340(4)	Cd2-N4	2.310(4)	Cd2-O8	2.419(4)
Cd1-O6#1	2.351(4)	Cd2-N1#4	2.331(4)	Cd2-O3#2	2.588(3)
Cd1-O2	2.404(4)	Cd2-O4#2	2.339(3)		

Angle	(deg)	Angle	(deg)	Angle	(deg)
N6#4-Cd1-N3	177.3(3)	O2-Cd1-O1	53.88(15)	N1-Cd2-O7	87.97(15)
N6#4#4-Cd1-O5	94.9(3)	N6-Cd1-O5	93.9(2)	O4-Cd2-O7	142.85(14)
N3-Cd1-O5	87.18(14)	N3-Cd1-O5	84.94(13)	O3-Cd2-O7	86.71(13)
N6-Cd1-O6	90.0(2)	O5-Cd1-O5	74.25(13)	N4-Cd2-O8	91.95(15)
N3-Cd1-O6	87.34(13)	O6-Cd1-O5	52.79(12)	N1-Cd2-O8	91.71(16)
O5-Cd1-O6	127.03(12)	O2-Cd1-O5	141.25(14)	O4-Cd2-O8	88.81(13)
N6-Cd1-O2	86.8(3)	O1-Cd1-O5	161.98(15)	O3-Cd2-O8	141.13(12)
N3-Cd1-O2	92.58(15)	N4-Cd2-N1	175.71(14)	O7-Cd2-O8	54.46(14)
O5-Cd1-O2	144.37(14)	N4-Cd2-O4	90.07(15)	N4-Cd2-O3	91.25(14)
O6-Cd1-O2	88.49(14)	N1-Cd2-O4	87.77(14)	N1-Cd2-O3	84.49(13)
N6-Cd1-O1	97.3(2)	N4-Cd2-O3	90.24(15)	O4-Cd2-O3	52.61(13)
N3-Cd1-O1	84.43(15)	N1-Cd2-O3	88.31(15)	O3-Cd2-O3	77.39(13)
O5-Cd1-O1	90.73(14)	O4-Cd2-O3	130.00(13)	O7-Cd2-O3	162.57(14)
O6-Cd1-O1	140.87(14)	N4-Cd2-O7	95.98(16)	O8-Cd2-O3	141.29(13)

Symmetry codes: #1 = 1 - x, 1 - y, 1 - z; #2 = 2 - x, -y, 1 - z; #3 = 1 - x, -y, -z; #4 = 2 - x, 1 - y, 2 - z.

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