Eight Cd(II) coordination polymers with persistent room temperature phosphorescence: intriguing dual emission and time-resolved afterglow modulating

Yajie Li,[a] Tianyu Gai,[a] Yuejin Lin,[a] Wenjing Zhang,[a] Kai Li,[a] Yan Liu,[a] Yanquan Duan,[a] Baojun Li,[a] Jie Ding,*[a] Jinpeng Li*[a]

[a]College of Chemistry, Zhengzhou University, Zhengzhou 450001, Henan, P. R. China

Experimental section

General information and materials. 5-(1H-1,2,4-triazol-1-yl)nicotinic acid (**Htynca**) and other ancillary ligands were purchased from Jinan Henghua technology company. All commercially available chemicals materials are reagent grade quality and used without further purification. The FT-IR spectra were measured with KBr pellets and recorded on a BRUKER TENSOR 27 spectrophotometer in the range of 400-4000 cm^{-1} region. The luminescent spectra were recorded using a HITACHI F-4600 fluorescence spectrophotometer at room temperature. The excitation slit was 2.5 nm, the scan rate was 240 nm/min. Elemental analysis (C, H, and N) was carried out on a FLASH EA 1112 elemental analyzer.

How to make the logo icon. First, we use the toner printer (Printer model: HP LaserJet Professional M1136 MFP) to print the logo on a smooth piece of paper, utilize the tape to stick the logo down, then grind the crystal into powder and sprinkle the powder on the tape, finally, we get the logo "Zhengzhou University".

Computational details. All the DFT calculations were performed by using the Gaussian 09 suit of program.[1] The frontier molecular orbitals (FMOs) of all concerned complexes were predicted by single-point energy calculations to the X-ray crystal structures, with the B3LYP functional[2] and the mixed basis sets (LanL2DZ[3-5] for Cd(II), and 6-31g(d, p)[6,7] for the rest) adopted.

Synthesis of $[Cd(tynca)_2(H_2O)_4]\cdot 2H_2O$ 1: $Cd(OAc)_2\cdot 2H_2O$ (8.0 mg, 0.03 mmol), **Htynca** (5.7 mg, 0.03 mmol), 2,2'-bipy (4.7 mg, 0.03 mmol), 1 mL H_2O and 2 mL

CH_3CN were sealed in a 25 mL Teflon-lined steel vessel, which was heated at 80°C for 3 days, and then cooled to room temperature at the speed of 10°C/h. Colorless transparent block crystals of **1** in good quality were obtained. Yield: 57% based on cadmium. Anal. Calc. for $C_{16}H_{22}CdN_8O_{10}$: C, 32.09; H, 3.70; N, 18.71. Found: C, 32.72; H, 2.78; N, 19.09. IR (cm^{-1}, KBr): 3430w, 3138s, 1619w, 1524s, 1482s, 1360m, 1224s, 1060s, 906s, 742m, 673m, 562w.

Synthesis of $\{[Cd(tynca)_2(bix)]\cdot H_2O\}_n$ 2: In a 25 mL Teflon-lined stainless-steel container, **Htynca** (5.7 mg, 0.03 mmol) was dissolved in 2 mL methanol, 1 mL aqueous solution of $Cd(Ac)_2\cdot 2H_2O$ (8.0 mg, 0.03 mmol) and bix (8.2 mg, 0.03 mmol) was added into the above solution. The vessel was heated at 100°C for 72 h and then cooled to room temperature at the speed of 10°C/h. Colorless transparent block crystals of **2** in good quality were obtained. For **2**: Yield: 53% based on cadmium. Anal. Calcd. for $C_{30}H_{26}CdN_{12}O_5$: C, 48.24; H, 3.51; N, 22.50. Found: C, 48.14; H, 3.43; N, 22.35. IR (cm^{-1}, KBr): 3418m, 3022s, 2205s, 1615w, 1568m, 1478s, 1425s, 1369m, 1295s, 1187m, 1027s, 825m, 771m, 669m, 584s.

Synthesis of $\{[Cd(tynca)_2]\cdot H_2O\}_n$ 3: A mixture of $Cd(Ac)_2\cdot 2H_2O$ (8.0 mg, 0.03 mmol) and **Htynca** (5.7 mg, 0.03 mmol) was added to a mixed solvent of CH_3OH (2 mL) and H_2O (1 mL), and then heated at 120°C for 72 h in a 25 mL Teflon-lined stainless-steel vessel. After the reaction system was cooled to room temperature by a rate of 10°C/h. Colorless transparent block crystals of **3** were obtained. Yield: 55%, based on cadmium. Anal. Calcd for $C_{16}H_{12}CdN_8O_5$: C, 37.78; H, 2.38; N, 22.03. Found: C, 37.89; H, 1.97; N, 22.11. IR/cm^{-1} (KBr): 3346w, 3137w, 1862s, 1618w, 1482m, 1438m, 1359w, 1145m, 985m, 860s, 789m, 655m.

Synthesis of $[Cd(tynca)_2(H_2O)_2]$ 4: A mixture of $Cd(Ac)_2\cdot 2H_2O$ (8.0 mg, 0.03 mmol), **Htynca** (5.7 mg, 0.03 mmol) and btx (8.2 mg, 0.03 mmol) [btx = 1,4-bis(1,2,4-triazole-4-ylmethyl)benzene] was added into 3 mL of CH_3OH/H_2O (2:1). The final mixture was placed in a Teflon-lined stainless steel vessel (25 mL) under autogenous pressure and heated at 80°C for 3 days, then cooled to room temperature at the speed of 10°C/h. Colorless transparent block crystals of **4** in good quality were

obtained. For **4**: Yield: 53% based on cadmium. Anal. Calcd. for $C_{16}H_{14}CdN_8O_6$: C, 36.48; H, 2.68; N, 21.27. Found: C, 36.43; H, 2.51; N, 21.84. IR (cm^{-1}, KBr): 3441m, 2924s, 1623m, 1517s, 1486s, 1387m, 1281s, 1142s, 993s, 873s, 1070s, 752m, 668m, 560m.

The structure of **4** has been reported previously.[8]

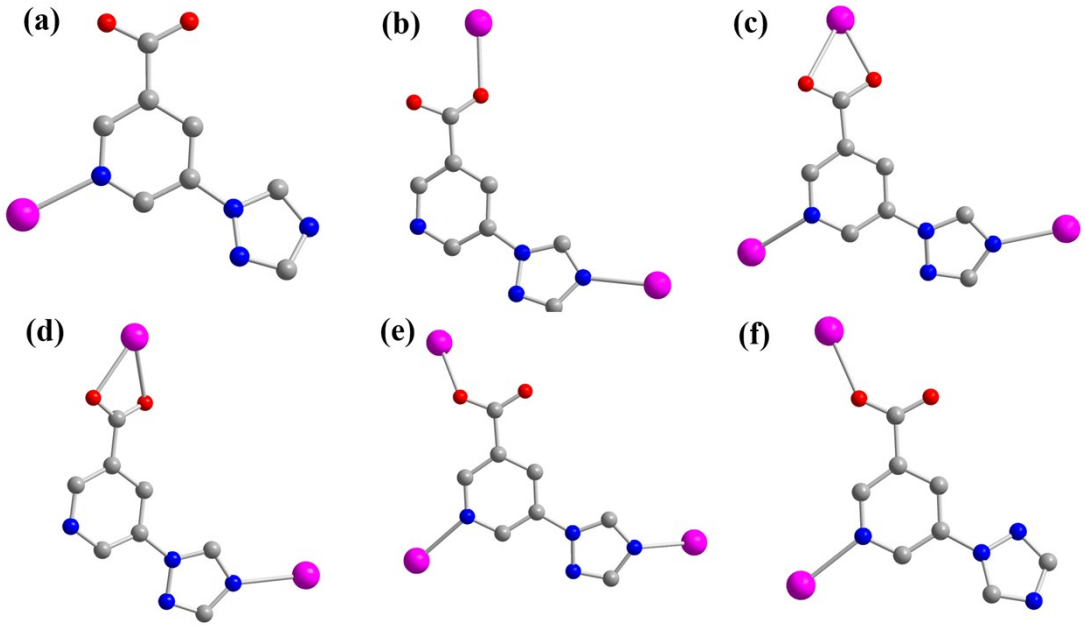
Synthesis of $[Cd(tynca)_2]_n$ 5: A mixture of $Cd(Ac)_2{\cdot}2H_2O$ (8.0 mg, 0.03 mmol), **Htynca** (5.7 mg, 0.03 mmol), pbbm (7.4 mg, 0.03 mmol) [pbbm = 1,1'-(1,3-propanediyl)bis-1H-benzimidazole)], 1 mL H_2O and 2 mL CH_3OH were placed in a 25 mL Teflon-lined steel vessel reactor, and then heated at 120°C for 3 days. After the mixture was cooled to room temperature at a rate of 10°C/h, colorless transparent block crystals of **5** were obtained. Yield: 60% based on cadmium. Anal. Calcd for $C_{16}H_{10}CdN_8O_4$: C, 39.16; H, 2.05; N, 22.84. Found: C, 39.13; H, 2.04; N, 22.82. IR/cm^{-1} (KBr): 3415m, 3192s, 2163s, 1622s, 1568m, 1483s, 1435s, 1369m, 1295s, 1187m, 1027s, 825m, 771m.

Synthesis of $\{[Cd(tynca)_2(bbbm)]\}_n$ 6: $Cd(Ac)_2{\cdot}2H_2O$ (8.0 mg, 0.03 mmol), **Htynca** (5.7 mg, 0.03 mmol) and bbbm (8.6 mg, 0.03 mmol) were added to a 3 mL mixed solvent of H_2O/CH_3OH (1:2) and the final mixture was heated at 80°C for 3 days. Colorless transparent block crystals in good quality were obtained. For **6**: Yield: 68% based on cadmium. Anal. Calcd. for $C_{34}H_{26}CdN_{12}O_4$: C, 52.42; H, 3.36; N, 21.57. Found: C, 52.12; H, 3.28; N, 21.36. IR/cm^{-1} (KBr): 3423m, 3100s, 1827w, 1510s, 1382s, 1281m, 985m, 861w, 744s, 670s, 564w.

Synthesis of $\{[Cd(tynca)_2(pbbbm)]\}_n$ 7: A mixture of $Cd(Ac)_2{\cdot}2H_2O$ (8.0 mg, 0.03 mmol), **Htynca** (5.7 mg, 0.03 mmol) and pbbbm (10.1 mg, 0.03 mmol) was added into a 3 mL mixed solvent of CH_3OH/H_2O (2:1). The final mixture was placed in a Teflon-lined stainless steel vessel (25 mL) under autogenous pressure, and heated at 100°C for 3 days. Then the mixture was cooled to room temperature at a cooling rate of 10°C/h, and filtered to obtain transparent bulk crystals. Yield: 73%, based on cadmium. Anal. Calcd for $C_{38}H_{28}CdN_{12}O_4$: C, 55.05; H, 3.40; N, 20.27. Found: C, 55.03; H, 3.22; N, 20.16. IR/cm^{-1} (KBr): 3423w, 3102s, 1760w, 1611s, 1588s, 1508w, 1380s, 1315m, 1174m, 982m, 792m, 548w.

Synthesis of $\{[Cd(tynca)(mbbbm)(Ac)]\cdot 3H_2O\}_n$ 8: Similarly to **2**, **8** was synthesized except using mbbbm (9.5 mg, 0.03 mmol) instead of bix and was placed in a Teflon vessel within the autoclave. Colorless transparent block crystals of **8** were obtained in 70% yield based on cadmium. Anal. Calcd. for $C_{32}H_{32}CdN_8O_7$: C, 51.04; H, 4.28; N, 14.88. Found: C, 50.19; H, 3.75; N, 13.79. IR (cm^{-1}, KBr): 3396w, 3136m, 1706s, 1603w, 1566w, 1460w, 1363w, 1262m, 1146m, 1088m, 878m, 755w, 671w.

Crystal Data Collection and Refinement. The data of **1**, **2**, **4**, **5**, **8** were collected on a Bruker APEX-II CCD diffractometer (Mo-*Kα* ray, λ=0.71073 Å) at temperature of 298 ± 1K, while the data of **3** were collected on a Rigaku Saturn 724 CCD diffractometer with graphite-monochromated (Mo-*Kα* ray, λ=0.71073 Å), and **6**, **7** were collected on a Bruker CCD area detector with graphite-monochromated (Mo-*Kα* ray, λ=0.71073 Å). All structures were solved with direct methods utilizing the SHELXS-97 crystallographic software package and refined with full-matrix least-squares technique with the SHELXL-2014 programs, respectively.[9,10] The processing parameters and crystallographic data for **1-8** were presented in Tables S1 and S2. Tables S3 and S4 show selected bond lengths (Å) and angles (deg) for **1-8**.



Scheme S1. Coordination modes of the **Htynca** in **1-8**.

Structural description of $[Cd(tynca)_2(H_2O)_4]\cdot 2H_2O$ (1).

1 crystallizes in the triclinic system with space group *P*-1. As illustrated in Fig. S1a, the independent unit of **1** is composed of one Cd(II) cation, two **tynca**$^-$ ligands and four coordinated water molecules. Cd1 is six-coordinated mode and is bound by four oxygen atoms (O1, O1A, O2, O2A) from four coordinated water molecules and two nitrogen atoms (N3, N3A) from two **tynca**$^-$ ligands. The bond angles surrounding the Cd(II) ions vary from 87.01(11)º to 180º [O1-Cd1-O1A = 180º, O2-Cd1-O2A = 180º, N3-Cd1-N3A = 180º]. The bond length of Cd-N is 2.346(3) Å, and the Cd-O distances ranges from 2.281(3) to 2.296(3) Å. It is worth noting that the **tynca**$^-$ anion acting in mono-dentate coordination mode only takes part in coordination with metal ions through the nitrogen atoms, which is similar to the reported in $[Cd(L^1)(HL^1)](ClO_4)$ [2-((2-(dimethylamino)ethylimino)methyl)phenol (HL^1)] and $[Cd(HL^2)(L^2)](ClO_4)(H_2O)$ [methyl-2-pyridylmethylidenehy-drazinecarbodithioate (HL^2)].[11] The adjacent molecules are bridged by the inter-molecular C–H···O hydrogen bonds O2-H2B···O4 {H/O distances (bond angles): 2.19 Å [125.7º]}, C7–H7···O1 {H/O distances (bond angles): 1.99(3) Å [157.14(2)]} to form a 1D chains. The adjacent linear chains are further held together by means of the π···π interactions between two adjacent pyridine rings with a centroid-to-centroid separation of 3.95 Å,[12-15] resulting in a 2D structure (Fig. S1b).

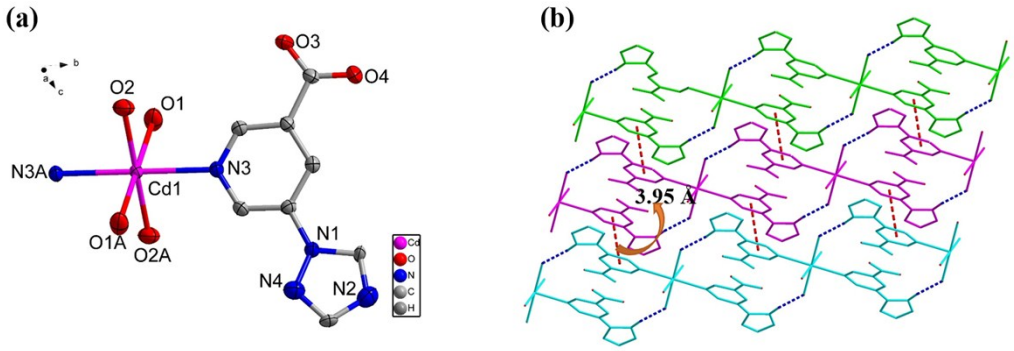


Fig. S1. (a) The surrounding coordination environment of **1** (symmetry codes for A: 1-x, -y, 1-z), all hydrogen atoms are omitted for clarity. (b) 2D supramolecular network constructed via C-H···O and the π···π stacking interaction.

Structural description of $\{[Cd(tynca)_2(bix)]\cdot H_2O\}_n$ (2).

X-ray diffraction analysis reveals that **2** is the monoclinic system with *C2/c* space group. As illustrated in Fig. S2a, each six-coordinated Cd(II) ion is in a distorted octahedral environment with two nitrogen atoms (N1B, N1C) and two oxygen (O1, O1A) atoms from four **tynca**$^-$ ligands, two nitrogen atoms (N4, N4A) from two bix ancillary ligands. The distance of Cd-O bonds is 2.3621(14) Å, while the Cd-N bond lengths are in the normal range [Cd1-N4 = 2.2857(16) Å, Cd1-N1 = 2.4531(15) Å]. The bond angles surrounding Cd(II) ions vary from 75.28(6)º to 180º [O1-Cd1-O1A = 180º, N1B-Cd1-N1C = 180º, N4-Cd1-N4A = 180º]. Bond lengths and bond angles around **2** are similar to those of Cd(II) polymers, such as $[Cd_2(L^1)_2(SCN)_2]_n$ [L^1 = 2-((2-(dimethylamino)ethylimino)methyl)phenol], $[CdL^2(SCN)_2]_n$ [L^2 = methyl-2-pyridylmethylidenehy-drazinecarbodithioate].[11] Two adjacent Cd(II) centers are linked by carboxyl oxygen, triazole nitrogen (**tynca**$^-$ ligands) and bix ligands forming 1D chain. The two adjacent chains are linked through intermolecular hydrogen bonds forming 2D structure, which was further extended to the 3D supramolecular structure through hydrogen bonds C1-H1···O1 {H/O distances (bond angles): 2.52(1) Å [122.0º]} (Fig. S2b).

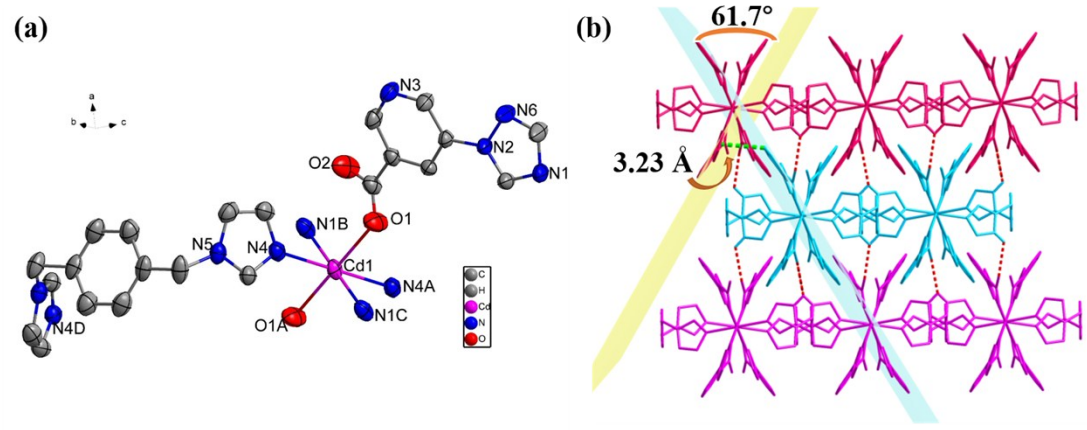


Fig. S2. (a) The surrounding coordination environment of **2** (symmetry codes for A: 1-x, -y, 1-z; B: x, -y, -0.5+z; C: 1-x, y, 1.5-z), all hydrogen atoms are omitted for clarity. (b) View of the 3D supermolecule structure constructed by hydrogen-bonding interactions in **2** along the *c* axis.

Structural description of $\{[Cd(tynca)_2]\cdot H_2O\}_n$ (3) and $[Cd(tynca)_2(H_2O)_2]$ (4).

Single crystal X-ray diffraction reveals that **3** crystallizes in a monoclinic crystal system with $P2_1/n$ space group, and exhibits a 2D structure (Fig. S3c). The independent unit consists of one Cd(II) ion, two **tynca**$^-$ ligands, and two lattice water molecules. As depicted in Fig. S3a, each seven-coordinated Cd(II) ion is in a single cap octahedron coordination environment with three nitrogen atoms (N1, N2B, N7C) from three **tynca**$^-$ ligands and four oxygen atoms (O3, O4, O5A, O6A) from two **tynca**$^-$ ligands, and two lattice water molecules in the asymmetric unit. The bond lengths of Cd-O (carboxylate) range from 2.317(3) to 2.619(3) Å [Cd1-O3 = 2.405(3) Å, Cd1-O4 = 2.378(3) Å, Cd1-O5A = 2.619(3) Å, Cd1-O6A = 2.317(3) Å], and the bond lengths of Cd-N are from 2.375 (3) to 2.448(4) Å [Cd1–N1 = 2.400 (3) Å, Cd1-N2B = 2.375 (3) Å, Cd1-N7C = 2.448(4) Å]. The bond lengths and the bond angles around Cd(II) (Table S3) are similar to other Cd(II) polymers, such as $[Cd_2(HL^5)Cl_4]_n$ and $\{[Cd_3(H_2L^5)_2Cl_8]\cdot 2H_2O\}_n$ {HL^5 = 2-{[2-(dimethylamino)ethylimino]methyl}-6-methoxyphenol}.[16] Each **tynca**$^-$ acts as a μ_3-bridge to link three Cd(II) ions through the pyridine nitrogen atoms, while each Cd(II) ion is surrounded by five **tynca**$^-$ ligands, which can be represented by a 5-connected node. Thus, the overall structure of **3** can be described as a (3,5)-connected net with a Schläfli symbol of $(3\cdot5^2)(3^2\cdot5^3\cdot6^4\cdot7)$ calculated by the TOPOS program (Fig. S3b).[17-19] Additionally, between pyridine and triazole ring of the **tynca**$^-$ ligand, the C–H···π interactions at 3.80 Å [dihedral angle: 85.2°]; H/π-plane separation: 2.87 Å] further stabilized the 3D structure (Fig. S3d).

Single-crystal X-ray diffraction reveals that **4** crystallizes in the monoclinic system with the $P2_1/n$ space group. It should be noted that the structure of **4** has been reported, and the description of its crystal structure is omitted.[8]

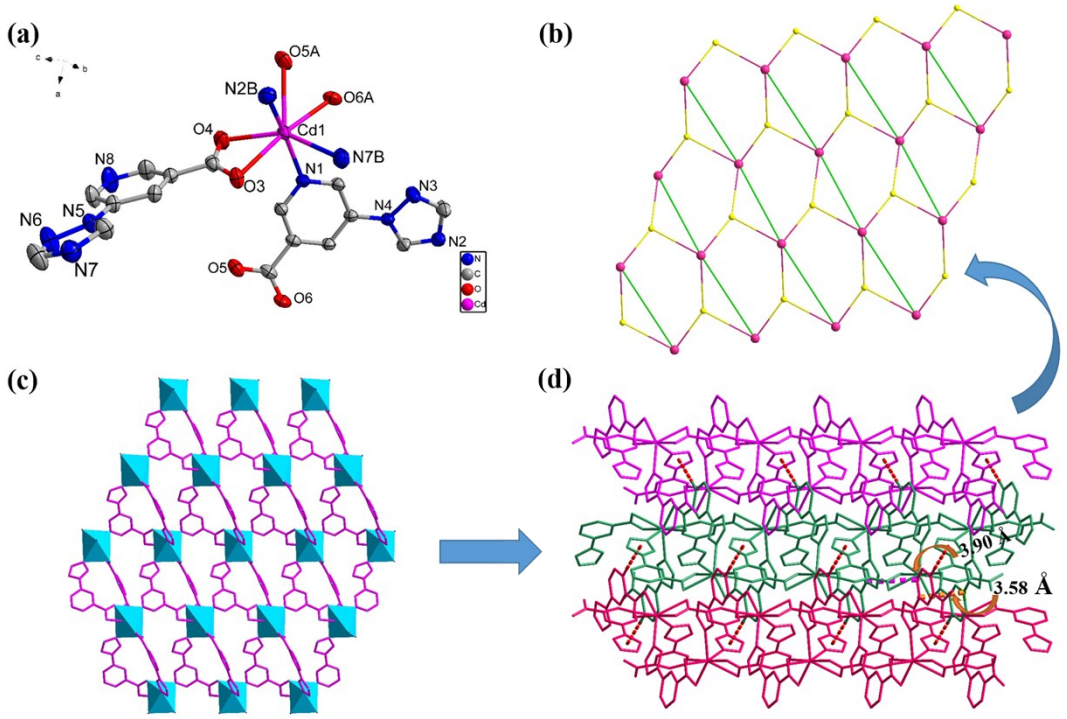


Fig. S3. (a) The surrounding coordination environment of **3** (symmetry codes for A: -1+x, y, z; B: -0.5+x, 1.5-y, -0.5+z), all hydrogen atoms are omitted for clarity. (b) 2D topology of **3**. (c) View of the 2D network along the *b*-axis. (d) 3D structure constructed via C-H···O interactions.

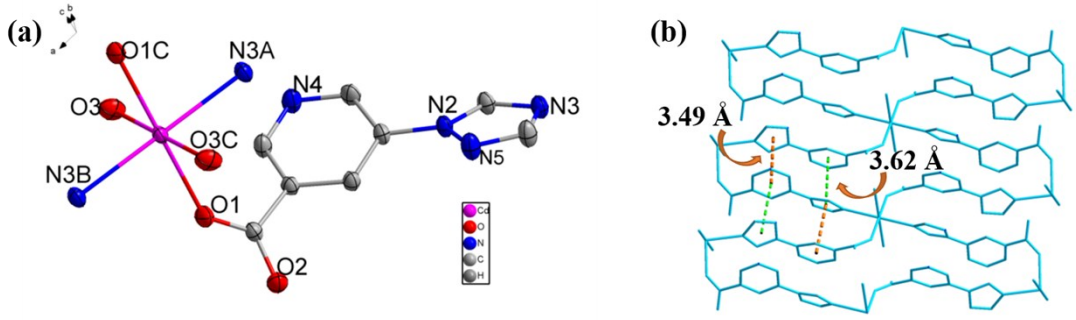


Fig. S4. (a) The surrounding coordination environment of **4** (symmetry codes for A: 1-x, 0.5+y, 0.5-z; B: 1+x, 1.5-y, 0.5+z; C: 2-x, 2-y, 1-z), all hydrogen atoms are omitted for clarity. (b) View of the 2D network along the *c*-axis

Structural description of $[Cd(tynca)_2]_n$ (5).

Single-crystal X-ray diffraction reveals that **5** crystallizes in the monoclinic system with $P2_1/c$ space group. As illustrated in Fig. S5a, each Cd(II) ion is in a six-

coordinated mode, in which Cd(II) is bonded to two triazole nitrogen atoms (N2B, N2C) from two **tynca**$^-$ ligands, two pyridine nitrogen atoms (N4D, N4E) from two different **tynca**$^-$ ligands and two carboxyl oxygen atoms (O1, O1A) from two different **tynca**$^-$ ligands. The observed bond distances in **5** are Cd-O = 2.256(2) Å, Cd-N2 = 2.422(2) Å, Cd-N4 = 2.386(2) Å, respectively, and the bond angles around Cd(II) vary from 84.73(5) to 180º [O1-Cd1-O1A = 180º, N2B-Cd1-N2C = 180º, N4D-Cd1-N4E = 180º]. These Cd-O and Cd-N bond lengths are close to those in other reported Cd(II) complexes, such as $[Cd_2(3,3'\text{-bpda})_2]_n$.[12-15] Two adjacent Cd(II) ions are linked through carboxylate group and pyridine nitrogen atoms from **tynca**$^-$ ligands to generate a 2D layer [Cd1···Cd1 = 7.496(48) Å] (Fig. S5b), and then the 2D layer are assembled into a 3D network structure via the connection of **tynca**$^-$ ligands. In order to better understand the framework of **5**, topology analysis was carried out. Each **tynca**$^-$ ligand connects three Cd(II) ions acting as a 3-connected node, while each Cd(II) ion is surrounded by six **tynca**$^-$ ligands, which can be represented by a 6-connected node. Hence, it can be considered as a (3,6)-connected *rtl* net with Schläfli symbol of $(4\cdot6^2)_2(4^2\cdot6^{10}\cdot8^3)$ topology (Fig. S5c).[17-19]

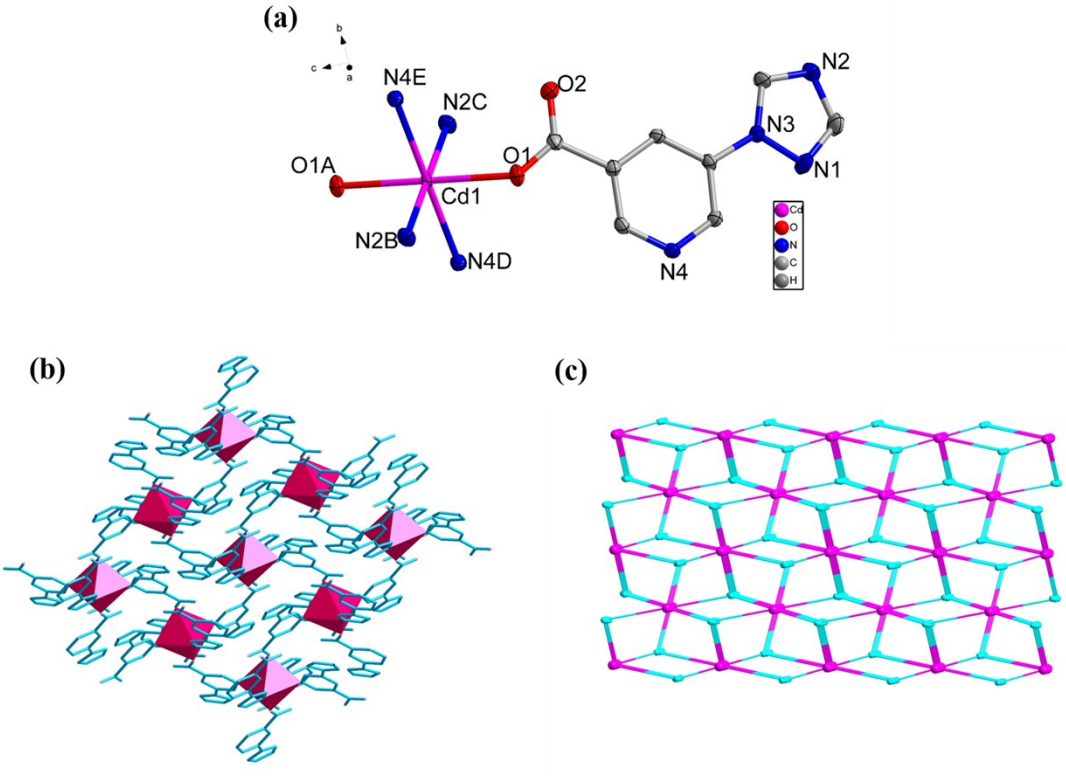


Fig. S5. (a) Coordination environment of the metal ion in **5** (symmetry codes for A: 2-x, 1-y, 2-z; B: 1+x, y, 1+z; C: 1-x, 1-y, 1-z; D: x, 0.5-y, 0.5+z; E: 2-x, 0.5+y, 1.5-z), all hydrogen atoms are omitted for clarity. (b) The 2D network. (c) Views of topology of **5** (The purple balls exhibit Cd(II) ions, the turquoise balls represented the **tynca**$^-$ ligands, respectively).

Structural description of {[Cd(tynca)$_2$(bbbm)]}$_n$ (6).

X-ray single crystal diffraction analysis shows that the **6** is a triclinic system with the space group *P-1*. As shown in Fig. S6a, the Cd(II) ion is six coordinated by two carboxyl oxygen atoms (O1, O1A) with monodentate coordination mode from two **tynca**$^-$ ligands, two pyridine nitrogen atoms (N1B, N1C) with monodentate mode from two **tynca**$^-$ ligands, two nitrogen atoms (N5, N5A) from two bbbm ancillary ligands. The above values are consistent with the reported data for the Cd(II) complex. Two adjacent Cd(II) ions are linked by **tynca**$^-$ ligands forming 2D framework along *b* direction (Fig. S6d). The adjacent 2D nets align to build up 3D supramolecular structure through hydrogen bonds: C8-H8···N4 [H8···N4 = 2.58 Å, C8-H8···N4 = 136.5°], C16-H16···N3 [H16···N3 = 2.63 Å, C16-H16···N3 = 129.0°] (Fig. S6c). To better understand the framework of **6**, topological analysis is carried out. According to the simplification principle, the structure of **6** exhibits a 2D topology network with six-connected Cd(II) ions, and two-connected **tynca**$^-$ and bbbm ligands which can be simplified into lines. Thus, the overall structure of **6** can be described as a 4-connected *flu* topology with the point symbol of $\{4^4 \cdot 6^2\}$ calculated by the TOPOS program (Fig. S6b).[17-19]

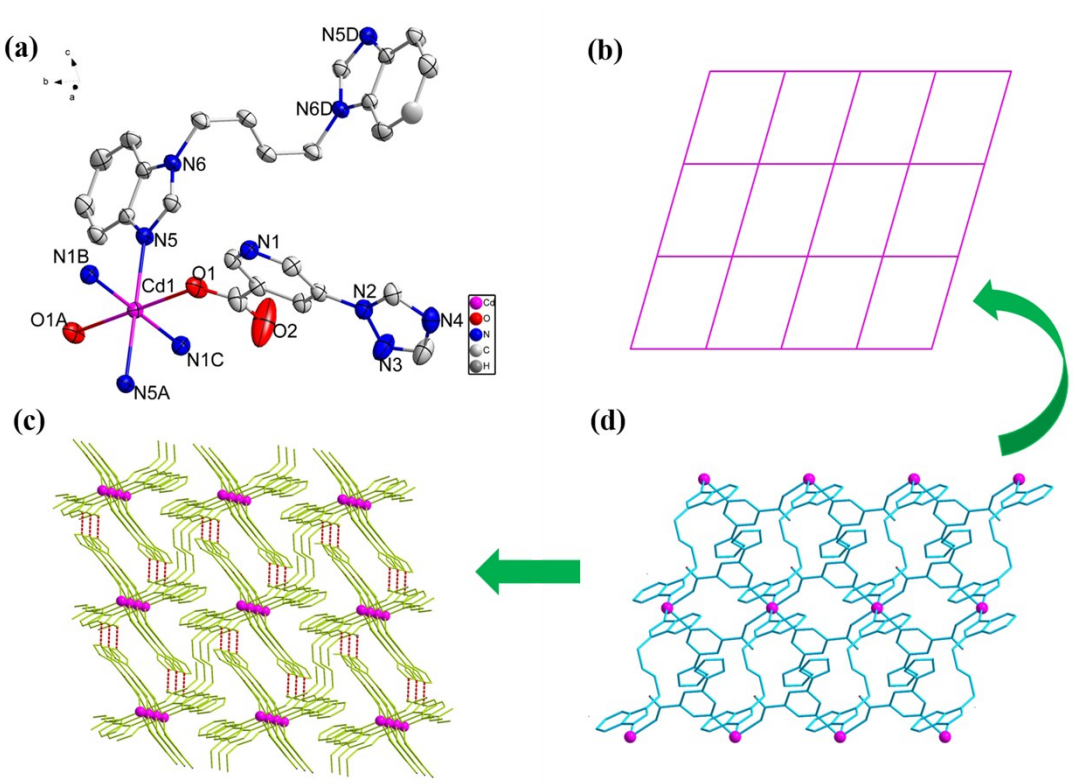


Fig. S6. (a) The unit structural of **6** (symmetry codes for A: 2-x, 1-y, 1-z; B: 1-x, 1-y, 1-z; C: 1+x, y, z), all hydrogen atoms are omitted for clarity. (b) 2D topology *sql* net with the Schläfli symbol of $\{4^4 \cdot 6^2\}$. (c) 3D structure constructed via C-H···N interactions. (d) View of 2D structure of **6**.

Structural description of $\{[Cd(tynca)_2(pbbbm)]\}_n$ (7).

X-ray single crystal diffraction data analysis shows that **7** belongs to the triclinic system with the space group *P-1,* which is a 2D structure. As shown in Fig. S7a, each six-coordinated Cd(II) ion is in a distorted octahedral environment with two pyridine nitrogen atoms (N3B, N3C) and two carboxyl oxygen atoms (O1, O1A) from four different **tynca**$^-$ ligands, and two imidazole nitrogen atoms (N1,N1A) from two different pbbbm ligands. The Cd-O bond length is 2.4043(13) Å, and the Cd-N bond lengths vary from 2.4537(15) Å to 2.2980(17) Å. These bond lengths are consistent with reported literatures. Along the *c* direction, the adjacent Cd(II) ions in **7** form a 1D chain by monodentate coordination of carboxyl oxygen atoms and pyridine nitrogen atoms of **tynca**$^-$ ligands, These chains are linked by pbbbm ligands to

produce a 2D structure (Fig. S7b). To better understand the framework of **7**, topological analysis is carried out, the cadmium atom can be considered as four-connected nodes, while the **tynca**$^-$ ligands and pbbbm ligands can be simplified into lines. It can be considered as a 4-connected *sql* net with Schläfli symbol of $\{4^4 \cdot 6^2\}$ topology (Fig. S7c).[17-19]

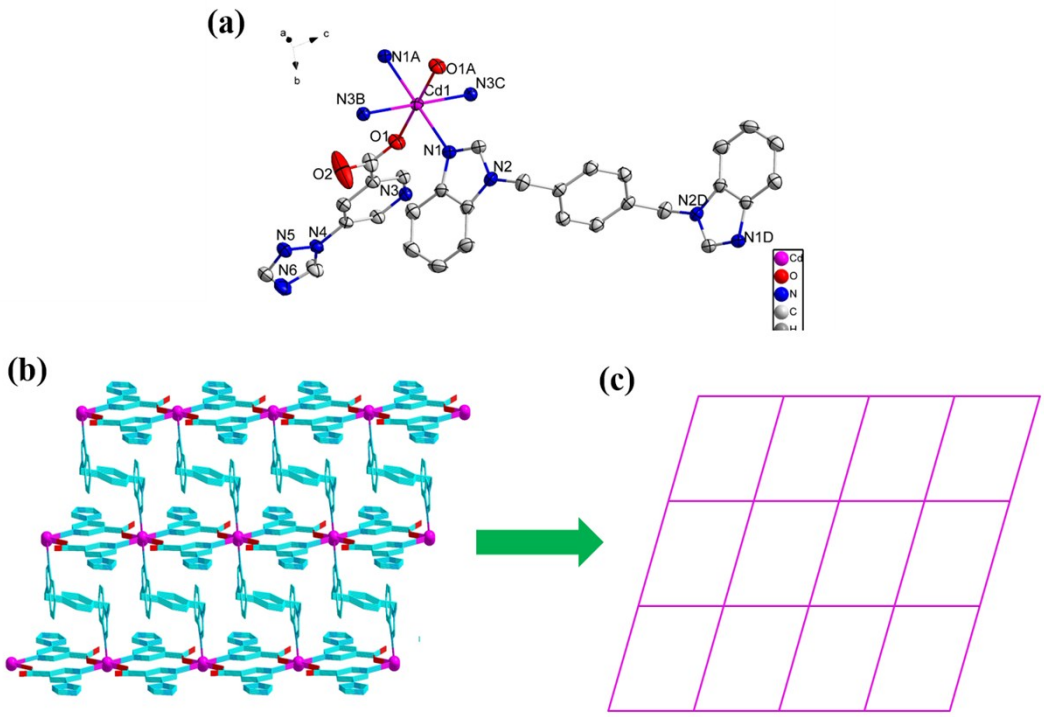


Fig. S7. (a) Coordination environment of the Cd(II) center in **7** (symmetry codes for A: 1-x, 1-y, 1-z; B: 1+x, y, z; C: -x, 1-y, 1-z), all hydrogen atoms are omitted for clarity. (b) View of 2D porous structure along the *c* axis in **7**. (c) View of the (4,4)-connected topology in the anionic framework of **7**.

Structural description of $\{[Cd(tynca)(mbbbm)(OAc)]\cdot 3H_2O\}_n$ (8).

The crystal data shows that **8** is the triclinic system with *P-1* space group. As illustrated in Fig. S8a, the asymmetric unit consisted of one **tynca**$^-$ ligand, one mbbbm ancillary ligand and one acetic acid along with three noncoordinated water molecules. Each Cd(II) ion is seven-coordinated by two nitrogen atoms (N3, N6A) from two mbbbm ligands, two oxygen atoms (O1, O6) from one acetic acid, two carboxylate

oxygen atoms (O2, O7) and one nitrogen atom (N1B) from two **tynca**$^-$ ligands. The bond lengths of Cd-O and Cd-N are 2.3352(16)-2.6113(15) Å and 2.3037(16)-2.3716(17) Å, respectively. The bond angles around Cd(II) vary from 52.36(5)° to 173.98(6)°, which are similar to those reported literatures.[20] In **8**, the ligand **tynca**$^-$ possesses one type of coordination mode: μ_2-*k*N: *k*O,O' and the ligand mbbbm utilized μ_2-*k*N: *k*N′ coordination mode. All carboxylate oxygen atoms adopt O/O chelate mode (O2/O7, O1/O6), and the Cd(II) ions are connected by mbbbm to give rise to a 1D double-chain structure, in which the Cd1-Cd1 distance is 9.0208(4) Å. The 1D chains are bridged by the inter-molecular C-H···O hydrogen bonds C12-H12···O2 {H/O distances (bond angles): 2.65(1) Å [153.3 º]} to form a 2D plane structure (Fig. S8b). The 2D layers are further extended into a 3D supramolecular structure by O3-H3A···N2 {H/O distances (bond angles): 2.08(3) Å [168.0º] hydrogen-bonding interactions between the pyridine nitrogen atoms and solvent water molecules.

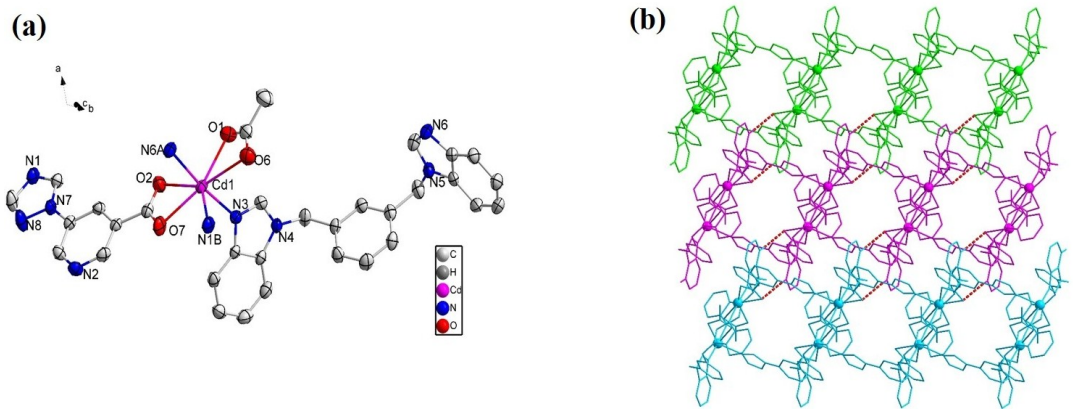


Fig. S8. (a) The coordination environment of **8** with hydrogen atoms and free water molecules omitted for clarity (symmetry codes for A: 2-x, 2-y, 1-z; B: x, 1+y, z). (b) View of the structure of **8** showing hydrogen bonding interaction (red dotted line).

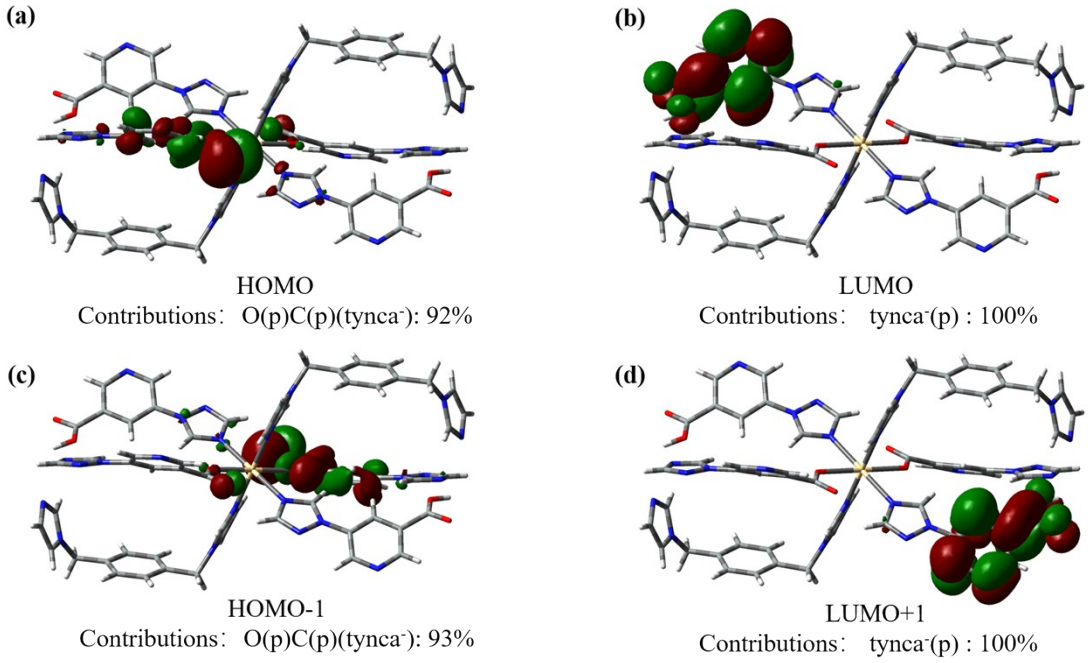


Fig. S9. Contour plots of the relevant (a) HOMO, (b) LUMO, (c) HOMO-1 and (d) LUMO+1 with the main atomic orbital contributions for **2**.

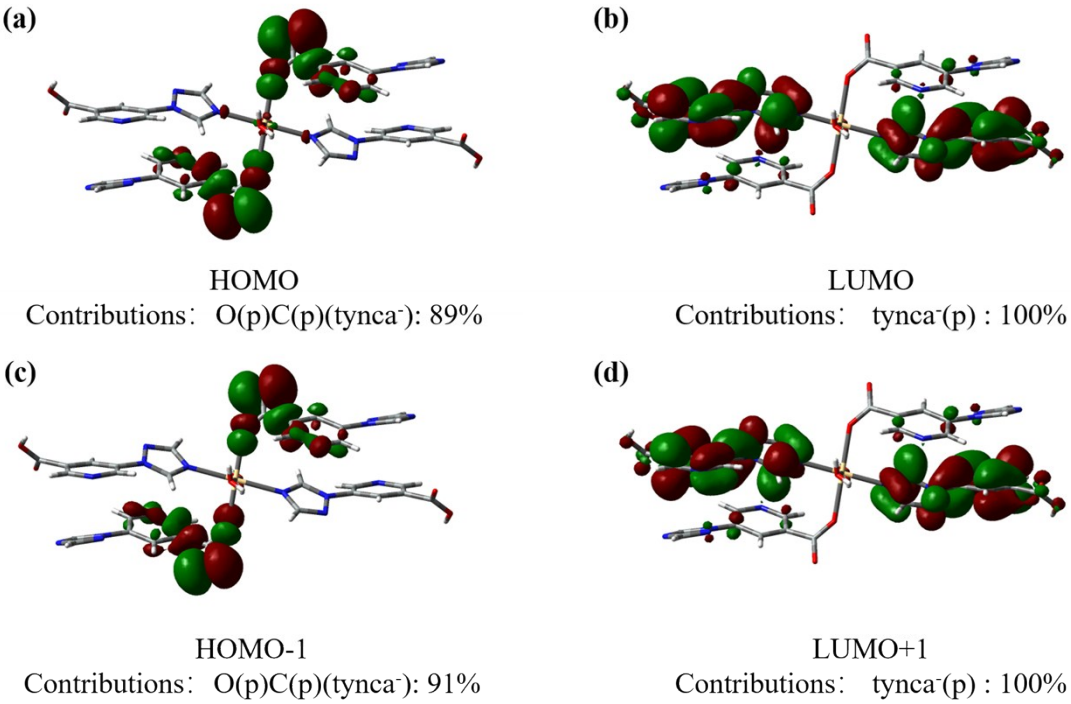


Fig. S10. Contour plots of the relevant (a) HOMO, (b) LUMO, (c) HOMO-1 and (d) LUMO+1 with the main atomic orbital contributions for **4**.

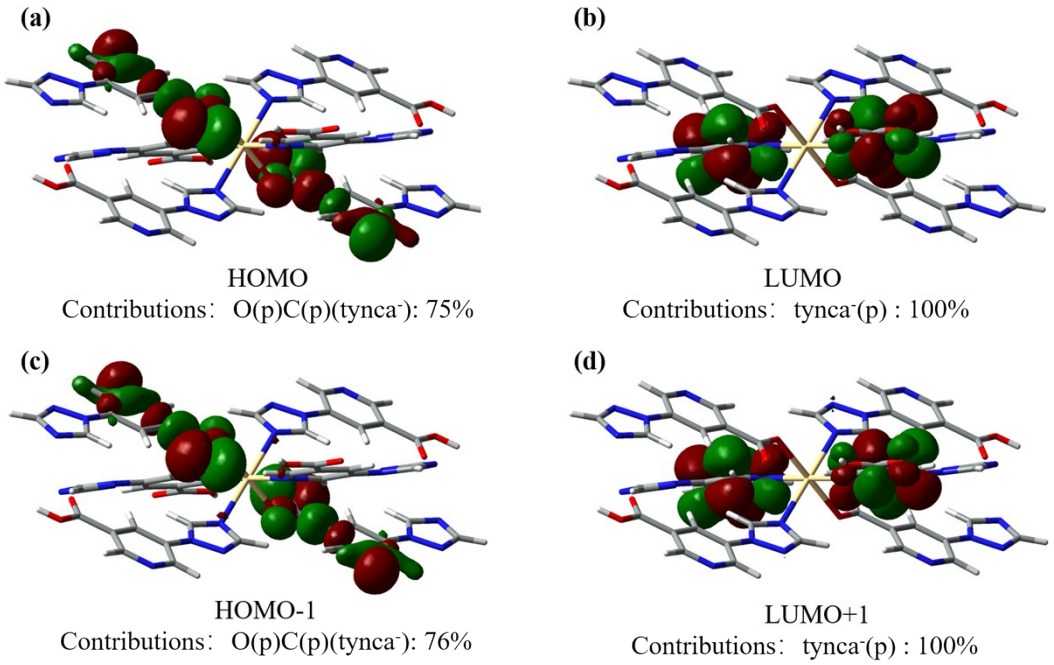


Fig. S11. Contour plots of the relevant (a) HOMO, (b) LUMO, (c) HOMO-1 and (d) LUMO+1 with the main atomic orbital contributions for **5**.

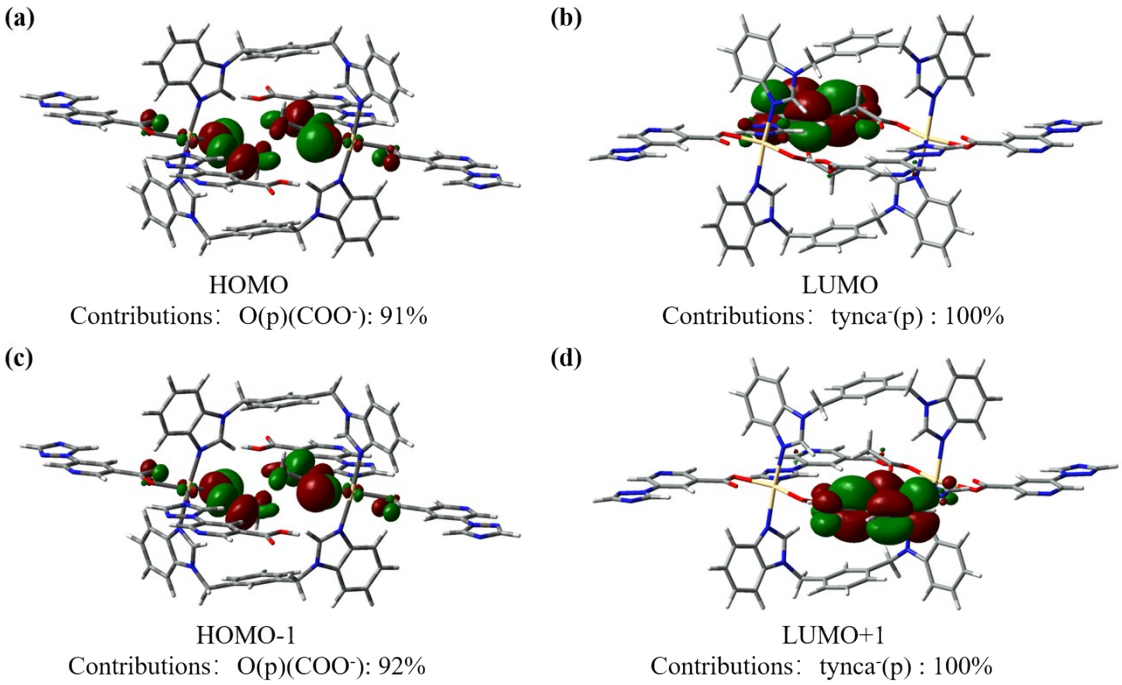


Fig. S12. Contour plots of the relevant (a) HOMO, (b) LUMO, (c) HOMO-1 and (d) LUMO+1 with the main atomic orbital contributions for **8**.

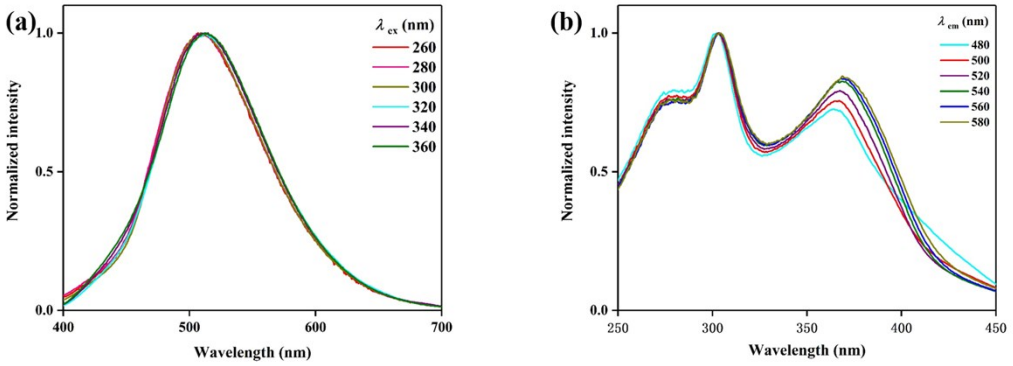


Fig. S13. (a) Phosphorescence emission and (b) excitation spectra of **1** in solid state at room temperature.

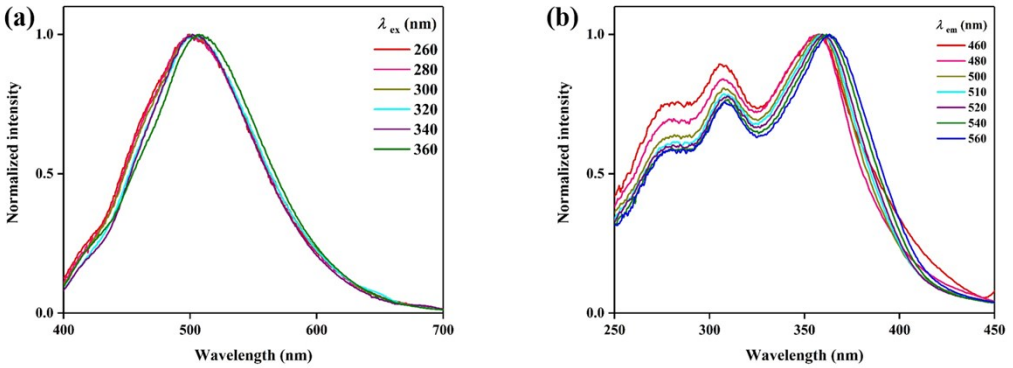


Fig. S14. (a) Phosphorescence emission and (b) excitation spectra of **2** in solid state at room temperature.

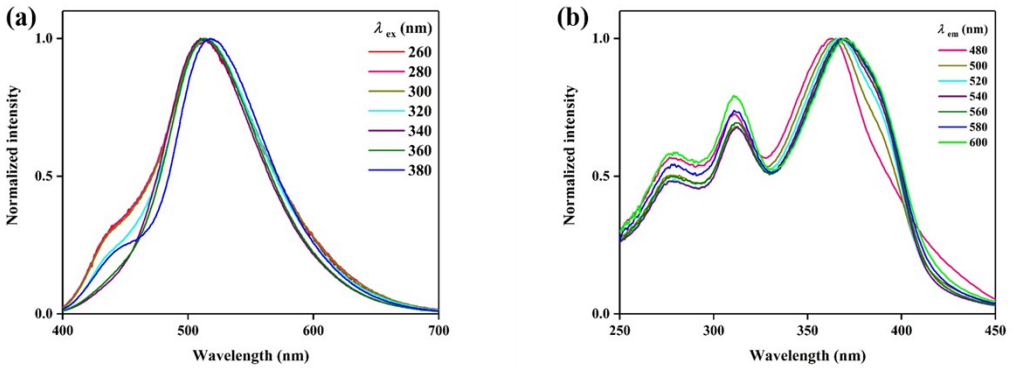


Fig. S15. (a) Phosphorescence emission and (b) excitation spectra of **3** in solid state at room temperature.

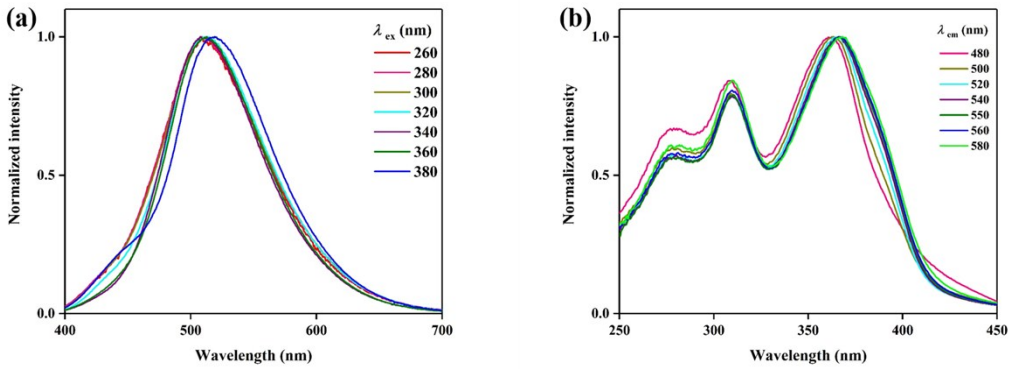


Fig. S16. (a) Phosphorescence emission and (b) excitation spectra of **4** in solid state at room temperature.

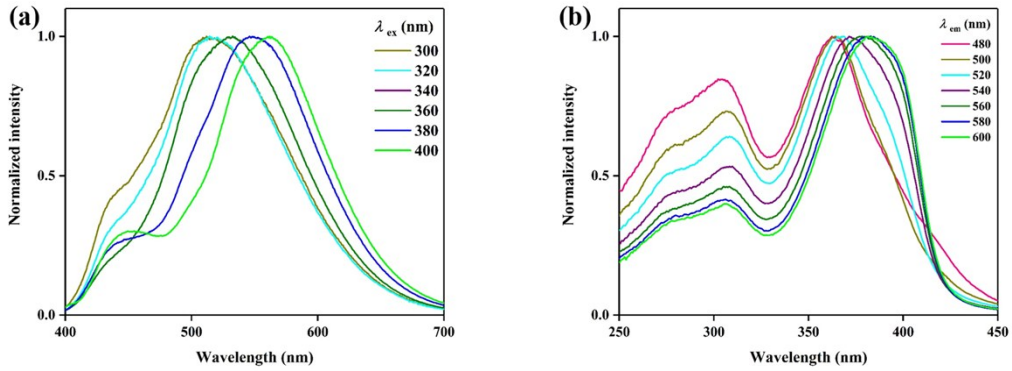


Fig. S17. (a) Phosphorescence emission and (b) excitation spectra of **5** in solid state at room temperature.

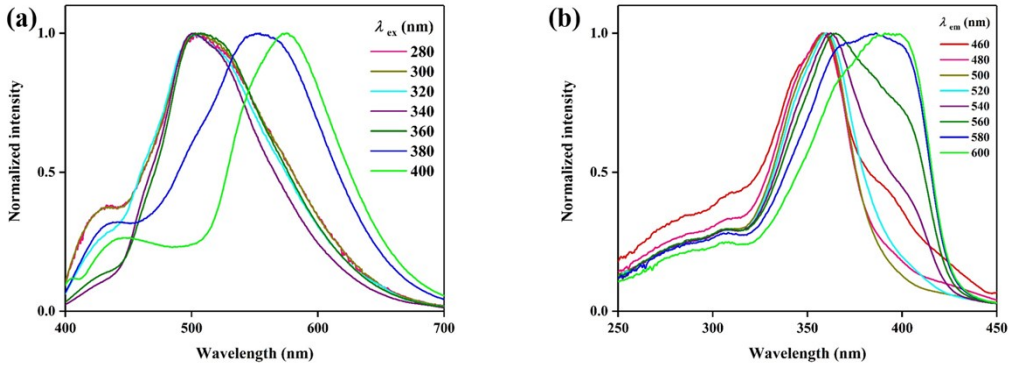


Fig. S18. (a) Phosphorescence emission and (b) excitation spectra of **6** in solid state at room temperature.

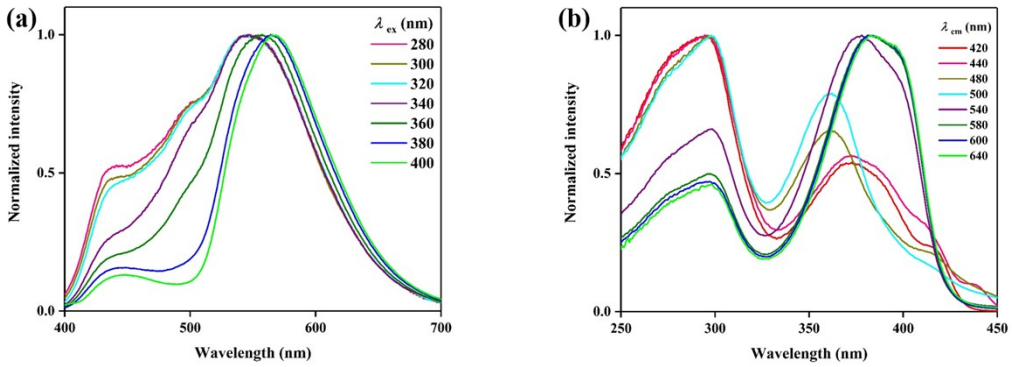


Fig. S19. (a) Phosphorescence emission and (b) excitation spectra of **7** in solid state at room temperature.

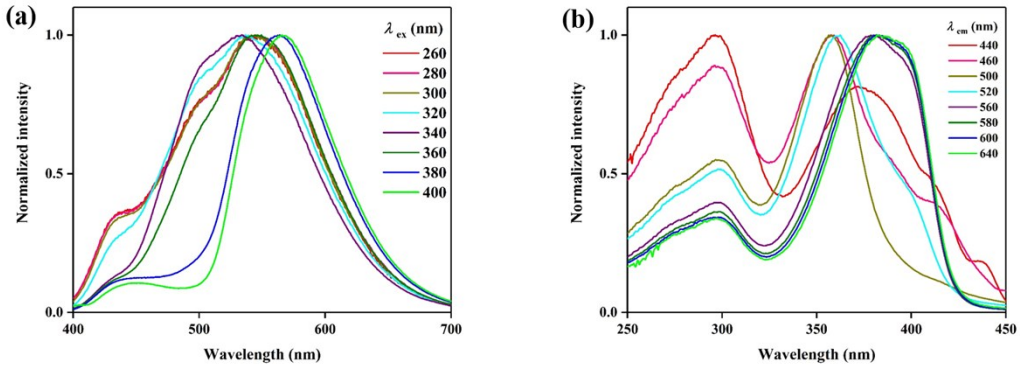


Fig. S20. (a) Phosphorescence emission and (b) excitation spectra of **8** in solid state at room temperature.

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

Polymers	**1**	**2**	**3**	**4**
Formula	$C_{16}H_{22}CdN_8O_{10}$	$C_{30}H_{26}CdN_{12}O_5$	$C_{16}H_{12}CdN_8O_5$	$C_{16}H_{14}CdN_8O_6$
Fw	598.81	747.03	508.74	526.75
Temp(K)	273(2)	273(2)	293(2)	273(2)
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073
Crystal syst	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	*C*2/*c*	$P2_1/n$	$P2_1/c$
a(Å)	6.7891(3)	15.3531(6)	7.8845(16)	11.8905(12)
b(Å)	9.2405(5)	9.3697(3)	13.283(3)	7.0905(7)
c(Å)	10.2651(5)	20.8123(7)	16.761(3)	11.8905(12)
α(deg)	63.9630(10)	90	90	90
β(deg)	85.828(2)	96.3600(10)	92.25(3)	117.29
γ(deg)	74.158(2)	90	90	90
V(Å^3)	555.82(5)	2975.51(18)	1754.0(6)	890.87(15)
Z	1	4	4	2
D_c(g·cm^{-3})	1.789	1.668	1.926	1.964
F(000)	302	1512	1008	524
θ range for data collection(deg)	3.124~27.552	3.791~27.521	2.875~ 24.998	3.431~27.532
Reflections collected/unique	13215/2562	37452/3416	11416/3086	16743/2042
Data/ restraints / params	2562/32/160	3416/0/231	3086/4/261	2042/0/154
Goodness-of-fit on F^2	1.164	0.855	1.064	0.950
Final R_1[a], wR_2[b]	0.0395, 0.1192	0.0232, 0.0567	0.0377, 0.0847	0.0174, 0. 0514

[a]$R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [b]w$R2 = [w(|F_o^2| - |F_c^2|)^2 / w|F_o^2|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, where a = 0.0775 and b = 0.82 for **1**, a = 0.0389 and b = 3.23 for **2**, a = 0.0338 and b = 5.74 for **3**, a = 0.0377 and b = 0.26 for **4**.

Table S2. Crystal data and structure refinement for **5-8.**

Polymers	**5**	**6**	**7**	**8**
Formula	$C_{16}H_{10}CdN_8O_4$	$C_{34}H_{26}CdN_{12}O_4$	$C_{38}H_{28}CdN_{12}O_4$	$C_{32}H_{32}CdN_8O_7$
Fw	490.72	779.07	829.12	753.05
Temp(K)	273(2) K	293(2)	298(2)	293(2)
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073
Crystal syst	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	*P-1*	*P-1*	*P*-1
a(Å)	7.388(6)	7.8141(4)	7.8187(4)	10.4677(3
b(Å)	10.819(10)	10.2469(4)	10.1384(6)	10.8554(4)
c(Å)	10.378(9)	10.6245(5)	11.6046(7)	15.6411(5)
α(deg)	90	74.524(2)	85.031(2)	105.3270(10)
β(deg)	104.621(18)	81.5110(10)	71.678(2)	104.9370(10)
γ(deg)	90	72.4110(10)	73.577(2)	100.2210(10)
V(Å^3)	802.7(12)	779.45(6)	837.62(8)	1597.63(9)
Z	2	1	1	2
D_c(g·cm^{-3})	2.030	1.660	1.644	1.565
F(000)	484	394	420	768
θ range for data collection(deg)	3.416~27.497	1.994~ 27.634	2.094~27.841	3.263~27.508
Reflections collected/unique	18099/1827	14712/3615	15530/3918	30705/7307
Data/ restraints / params	1827/1/133	3615/6/232	3918/6/250	7307/0/451
Goodness-of-fit on F^2	1.034	1.074	1.110	1.064
Final R_1[a], wR_2[b]	0.0179, 0.0400	0.0220, 0.0559	0.0260, 0.0749	0.0283, 0.0610

[a]$R_1 = \| \|F_o\| - \|F_c\| \| / \|F_o\|$. [b] w$R2 = [w(\|F_o^2\| - \|F_c^2\|)^2 / w\|F_o^2\|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, a = 0.0212 and b = 0.39 for **5**, a = 0.0284 and b = 0.38 for **6**, a = 0.0458 and b = 0.32 for **7**, a = 0.0304 and b = 0.43 for **8**.

Table S3. Selected bond lengths (Å) and angles (deg) for **1**-**4.**

1					
Cd(1)-O(1)#1	2.281(3)	Cd(1)-O(1)	2.281(3)	Cd(1)-O(2)#1	2.296(3)
Cd(1)-O(2)	2.296(3)	Cd(1)-N(3)#1	2.346(3)	Cd(1)-N(3)	2.346(3)
O(1)#1-Cd(1)-O(1)	180.0	O(1)#1-Cd(1)-O(2)#1	88.12(13)	O(1)-Cd(1)-O(2)#1	91.88(13)
O(1)#1-Cd(1)-O(2)	91.88(13)	O(1)-Cd(1)-O(2)	88.12(13)	O(2)#1-Cd(1)-O(2)	180.0
O(1)#1-Cd(1)-N(3)#1	87.01(11)	O(1)-Cd(1)-N(3)#1	92.99(11)	O(2)#1-Cd(1)-N(3)#1	89.65(11)
O(2)-Cd(1)-N(3)#1	90.35(11)	O(1)#1-Cd(1)-N(3)	92.99(11)	O(1)-Cd(1)-N(3)	87.01(11)
O(2)#1-Cd(1)-N(3)	90.35(11)	O(2)-Cd(1)-N(3)	89.65(11)	N(3)#1-Cd(1)-N(3)	180.0
2					
Cd(1)-N(4)	2.287(1)	O(1)#2-Cd(1)-N(1)#3	75.29(5)	N(4)-Cd(1)-O(1)#2	89.30(6)
Cd(1)-N(1)#3	2.453(1)	N(4)-Cd(1)-N(1)#3	87.06(6)	N(4)-Cd(1)-N(4)#2	180
N(1)-Cd(1)#4	2.453(1)	O(1)-Cd(1)-N(1)#4	75.29(5)	N(4)#2-Cd(1)-O(1)	89.30(6)
Cd(1)-O(1)	2.362(1)	N(4)#2-Cd(1)-O(1)#2	90.70(6)	O(1)-Cd(1)-O(1)#2	180
Cd(1)-N(1)#4	2.453(1)	N(4)#2-Cd(1)-N(1)#3	92.94(6)	O(1)-Cd(1)-N(1)#3	104.71(5)
Cd(1)-N(4)#2	2.288(2)	N(4)-Cd(1)-N(1)#4	92.94(6)	N(4)#2-Cd(1)-N(1)#4	87.06(6)
N(4)-Cd(1)-O(1)	90.70(6)	O(1)#2-Cd(1)-N(1)#4	104.71(5)	N(1)#3-Cd(1)-N(1)#4	180
3					
Cd(1)-O(6)#1	2.317(3)	Cd(1)-N(2)#2	2.375(3)	Cd(1)-O(4)	2.378(3)
Cd(1)-N(1)	2.400(3)	Cd(1)-O(3)	2.405(3)	Cd(1)-N(7)#3	2.448(4)
Cd(1)-O(5)#1	2.619(3)	N(2)#2-Cd(1)-N(1)	160.78(12)	O(6)#1-Cd(1)-N(7)#3	80.93(11)
O(5)-Cd(1)#6	2.619(3)	N(2)#2-Cd(1)-O(3)	79.70(11)	O(6)#1-Cd(1)-N(2)#2	105.27(1)
N(2)-Cd(1)#4	2.375(3)	N(2)#2-Cd(1)-O(4)	95.83(12)	O(6)#1-Cd(1)-N(1)	85.07(1)
O(6)-Cd(1)#6	2.317(3)	N(2)#2-Cd(1)-O(5)#1	75.17(1)	O(6)#1-Cd(1)-O(3)	172.39(1)
N(7)-Cd(1)#5	2.448(4)	O(6)#1-Cd(1)-O(4)	128.97(10)	N(1)-Cd(1)-O(3)	88.57(1)
O(4)-Cd(1)-O(3)	55.01(10)	N(2)#2-Cd(1)-N(7)#3	83.57(12)	O(4)-Cd(1)-N(7)#3	148.34(1)
N(1)-Cd(1)-N(7)#3	82.12(12)	O(3)-Cd(1)-N(7)#3	94.08(11)	O(6)#1-Cd(1)-O(5)#1	52.61(9)
O(4)-Cd(1)-N(1)	89.70(11)	O(4)-Cd(1)-O(5)#1	90.94(10)	N(1)-Cd(1)-O(5)#1	123.25(1)
O(3)-Cd(1)-O(5)#1	134.93(1)	N(7)#3-Cd(1)-O(5)#1	119.09(11)		
4					
Cd(1)-O(3) #1	2.2757(15)	O(3)#1-Cd(1)-O(3)	180.00(13)	O(3)#1-Cd(1)-N(3)#2	99.22(6)

Cd(1)-O(3)	2.2757(15)	O(3)#1-Cd(1)-O(1)#1	92.20(6)	O(3)-Cd(1)-N(3)#2	80.78(6)
Cd(1)-O(1) #1	2.2908(14)	O(3)-Cd(1)-O(1)#1	87.80(6)	O(1)#1-Cd(1)-N(3)#2	95.74(5)
Cd(1)-O(1)	2.2908(14)	O(3)#1-Cd(1)-O(1)	87.80(6)	O(1)-Cd(1)-N(3)#2	84.26(5)
Cd(1)-N(3)#2	2.3299(16)	O(3)-Cd(1)-O(1)	92.20(6)	O(3)#1-Cd(1)-N(3)#3	80.78(6)
Cd(1)-N(3)#3	2.3299(16)	O(1)#1-Cd(1)-O(1)	180.00(2)	O(1)#1-Cd(1)-N(3)#3	84.26(5)
O(3)-Cd(1)-N(3)#3	99.22(6)	O(1)-Cd(1)-N(3)#3	95.74(5)	N(3)#2-Cd(1)-N(3)#3	180.0

Symmetry transformations used to generate equivalent atoms:

For **1**: #1, -x+1,-y,-z+1.

For **2**: #1, -x+1,y,-z+1/2; #2, -x+1,-y,-z+1; #3, x,-y,z-1/2; #4, -x+1,y,-z+3/2.

For **3**: #1, x-1,y,z; #2, x-1/2,-y+3/2,z+1/2; #3, x-1/2,-y+3/2,z-1/2; #4, x+1/2,-y+3/2,z-1/2; #5, x+1/2,-y+3/2,z+1/2; #6 x+1,y,z.

For **4**: #1, -x+2,-y+2,-z+1; #2, x+1,-y+3/2,z+1/2; #3, -x+1,y+1/2,-z+1/2; #4, -x+1,y-1/2,-z+1/2.

Table S4. Selected bond lengths (Å) and angles (deg) for **5**-**8**.

5					
Cd(1)-O(1)#1	2.256(2)	Cd(1)-O(1)	2.256(2)	O(1)#1-Cd(1)-N(2)#5	87.70(6)
Cd(1)-N(4)#3	2.386(2)	O(1)-Cd(1)-N(4)#3	95.27(5)	N(4)#3-Cd(1)-N(2)#5	90.46(7)
N(2)-Cd(1)#6	2.422(2)	O(1)-Cd(1)-N(2)#4	87.70(6)	O(1)#1-Cd(1)-N(4)#2	95.27(5)
Cd(1)-N(2)#4	2.422(2)	O(1)-Cd(1)-N(4)#2	84.73(5)	O(1)#1-Cd(1)-N(4)#3	84.73(5)
N(4)-Cd(1)#7	2.386(2)	N(4)#2-Cd(1)-N(4)#3	180.0	O(1)#1-Cd(1)-N(2)#4	92.30(6)
Cd(1)-N(4)#2	2.386(2)	N(4)#2-Cd(1)-N(2)#4	90.46(7)	N(4)#3-Cd(1)-N(2)#4	89.54(7)
Cd(1)-N(2)#5	2.422(2)	O(1)-Cd(1)-N(2)#5	92.30(6)	N(4)#2-Cd(1)-N(2)#5	89.54(7)
O(1)#1-Cd(1)-O(1)	180	N(2)#4-Cd(1)-N(2)#5	180		

6					
Cd(1)-N(5)	2.324(1)	N(5)-Cd(1)-N(5)#1	180	O(1)#1-Cd(1)-N(1)#2	79.48(5)
Cd(1)-O(1)#1	2.372(1)	N(5)-Cd(1)-O(1)#1	93.75(5)	O(1)-Cd(1)-N(1)#3	79.48(5)
Cd(1)-N(1)#2	2.449(1)	N(5)-Cd(1)-O(1)	86.25(5)	N(5)#1-Cd(1)-O(1)	93.75(5)
Cd(1)-O(1)	2.372(1)	N(5)#1-Cd(1)-O(1)#1	86.25(5)	O(1)-Cd(1)-O(1)#1	180
Cd(1)-N(5)#1	2.324(1)	N(5)#1-Cd(1)-N(1)#2	90.54(5)	O(1)-Cd(1)-N(1)#2	100.52(5)
Cd(1)-N(1)#3	2.449(1)	N(5)-Cd(1)-N(1)#3	90.54(5)	N(5)#1-Cd(1)-N(1)#3	89.46(5)
N(5)-Cd(1)-N(1)#2	89.46(5)	O(1)#1-Cd(1)-N(1)#3	100.52(5)	N(1)#2-Cd(1)-N(1)#3	180

7					
Cd(1)-N(1)#1	2.2980(17)	O(1)#1-Cd(1)-N(3)#3	81.03(5)	N(1)#1-Cd(1)-N(3)#2	90.75(6)
Cd(1)-O(1)	2.4043(13)	N(1)#1-Cd(1)-O(1)	85.65(6)	O(1)-Cd(1)-N(3)#2	81.02(5)
Cd(1)-N(3)#2	2.454(2)	N(1)#1-Cd(1)-O(1)#1	94.35(6)	N(1)-Cd(1)-O(1)#1	85.65(6)
Cd(1)-O(1)#1	2.404(1)	N(1)-Cd(1)-O(1)	94.35(6)	O(1)#1-Cd(1)-O(1)	180
Cd(1)-N(3)#3	2.454(2)	N(1)-Cd(1)-N(3)#2	89.25(6)	O(1)#1-Cd(1)-N(3)#2	98.97(5)
Cd(1)-N(1)	2.298(2)	N(1)#1-Cd(1)-N(3)#3	89.25(6)	N(1)-Cd(1)-N(3)#3	90.75(6)
N(1)#1-Cd(1)-N(1)	180	O(1)-Cd(1)-N(3)#3	98.98(5)	N(3)#2-Cd(1)-N(3)#3	180

8					
Cd(1)-N(3)	2.304(1)	N(3)-Cd(1)-N(1)#2	94.94(6)	N(3)-Cd(1)-N(6)#1	173.98(6)

Cd(1)-N(6)#1	2.350(2)	N(6)#1-Cd(1)-N(1)#2	88.44(6)	N(3)-Cd(1)-O(1)	87.91(6)
Cd(1)-O(2)	2.611(2)	N(1)-Cd(1)#3	2.3716(17)	N(6)-Cd(1)#1	2.3501(16)
Cd(1)-O(7)	2.3463(16)	N(3)-Cd(1)-O(7)	94.49(6)	O(1)-Cd(1)-O(7)	149.50(6)
Cd(1)-O(1)	2.3352(16)	O(1)-Cd(1)-N(6)#1	86.10(6)	O(7)-Cd(1)-N(6)#1	91.01(6)
Cd(1)-N(1)#2	2.3715(17)	O(1)-Cd(1)-N(1)#2	130.30(6)	O(7)-Cd(1)-N(1)#2	79.85(6)
Cd(1)-O(6)	2.603(2)	N(3)-Cd(1)-O(6)	91.80(6)	O(1)-Cd(1)-O(6)	52.36(5)
O(7)-Cd(1)-O(6)	157.36(5)	N(6)#1-Cd(1)-O(6)	84.02(6)	N(1)#2-Cd(1)-O(6)	77.95(6)
N(3)-Cd(1)-O(2)	91.22(5)	O(1)-Cd(1)-O(2)	97.35(5)	O(7)-Cd(1)-O(2)	52.26(5)
N(6)#1-Cd(1)-O(2)	90.19(5)	N(1)#2-Cd(1)-O(2)	132.07(5)	O(6)-Cd(1)-O(2)	149.39(5)

Symmetry transformations used to generate equivalent atoms:

For **5**: #1, -x+2,-y+1,-z+2; #2, x,-y+1/2,z+1/2; #3, -x+2,y+1/2,-z+3/2; #4, x+1,y,z+1; #5, -x+1,-y+1,-z+1; #6 x-1,y,z-1; #7 -x+2,y-1/2,-z+3/2.

For **6**: #1, -x+2,-y+1,-z+1; #2, x+1,y,z; #3, -x+1,-y+1,-z+1; #4, x-1,y,z; #5, -x+2,-y,-z+2.

For **7**: #1, -x+1,-y+1,-z+1; #2, -x,-y+1,-z+1; #3, x+1,y,z; #4, x-1,y,z; #5, -x,-y+2,-z+2.

For **8**: #1, -x+2,-y+2,-z+1; #2, x,y+1,z; #3, x,y-1,z.

Table S5. Hydrogen bonds in **1**-**4**, **6**-**8**.

D-H···A	D-H	d(H···A)	d(D···A)	∠(DHA)
1				
O(1)-H(1B)···O(5)	0.95	1.73	2.662(4)	167.2
O(2)-H(2B)···O(4)#2	0.85	2.19	2.773(4)	125.7
O(1)-H(1A)···O(2)#1	1.01	2.60	3.289(4)	125.4
O(2)-H(2B)···O(4)#2	0.85	2.19	2.773(4)	125.7
O(5)-H(5B)···O(3)#3	0.86	1.85	2.695(4)	171.1
O(5)-H(5A)···O(4)#4	0.86	2.27	2.744(4)	114.4
C(6)-H(6)···O(5)#1	0.93	2.55	3.221(4)	129.5
C(7)-H(7)···O(1)#5	0.93	1.99	2.868(5)	156.7
C(8)-H(8)···O(2)#6	0.93	1.90	2.821(5)	169.5
2				
C(17)-H(17)···O(3A)#5	0.92(3)	2.62(3)	3.342(9)	136(2)
C(17)-H(17)···O(3)#5	0.92(3)	2.59(3)	3.142(4)	119(2)
O(2)-H(2)···N(3)#6	0.88(3)	2.21(3)	2.9995(18)	151(3)
C(16)-H(16)···O(3A)#7	0.93	2.18	2.964(7)	142.0
C(16)-H(16)···O(3)#7	0.93	2.29	2.904(4)	123.1
C(10)-H(10)···O(3)	0.93	2.46	3.224(6)	139.8
C(7)-H(7)···O(2)#8	0.93	2.45	3.368(2)	168.0
C(1)-H(1)···O(2)#8	0.93	2.66	3.432(2)	141.1
C(1)-H(1)···O(1)#4	0.93	2.52	2.997(2)	112.0
3				
O(7)-H(1WA)···N(3)#7	0.850(10)	2.33(4)	3.128(7)	157(8)
O(7)-H(1W)···O(5)	0.850(10)	1.94(3)	2.740(6)	157(6)
C(18)-H(18)···O(6)#2	0.93	2.35	2.964(5)	123.1
C(12)-H(12)···O(7)#8	0.93	2.42	3.326(6)	163.5
C(10)-H(10)···O(6)#1	0.93	2.64	3.243(5)	123.0
C(16)-H(16)···O(7)#8	0.93	2.31	3.229(6)	169.7

C(15)-H(15)···O(5)#3	0.93	2.57	3.108(5)	117.2
4				
C(7)-H(7)···O(2)#5	0.93	2.32	3.139(2)	146.1
6				
C(16)-H(16)···N(3)#6	0.93	2.63	3.291(3)	129.0
C(11)-H(11)···O(1)#1	0.93	2.51	3.295(2)	142.6
C(8)-H(8)···N(4)#7	0.93	2.58	3.315(2)	136.5
C(8)-H(8)···O(1)	0.93	2.55	3.147(2)	122.5
C(5)-H(5)···O(2)#4	0.93	2.07	2.970(2)	163.2
C(1)-H(1)···O(1)#3	0.93	2.54	3.088(2)	117.6
C(7)-H(7A)···O(2)#4	0.93	2.40	3.237(3)	149.9
7				
C(32)-H(32)···O(2)#4	0.93	2.35	3.228(3)	156.7
C(24)-H(24)···O(1)#2	0.93	2.36	3.044(2)	130.1
C(23)-H(23)···O(2)#4	0.93	2.03	2.958(3)	173.8
C(15)-H(15B) ···N(6)#6	0.97	2.55	3.501(3)	167.6
C(4)-H(4)···O(2)	0.93	2.66	3.588(4)	176.8
8				
O(4)-H(4B)···O(1)#4	0.88(4)	1.96(4)	2.781(3)	154(3)
O(5)-H(5B)···O(4)	0.81(4)	1.93(4)	2.744(3)	178(4)
O(5)-H(5A)···O(6)#5	0.74(4)	2.07(4)	2.782(3)	162(4)
O(3)-H(3B)···O(5)#3	0.80(4)	1.98(4)	2.756(3)	162(4)
O(3)-H(3A)···N(2)#6	0.86(3)	2.08(3)	2.930(3)	168(3)
C(30)-H(30)···O(2)#1	0.93	2.57	3.362(3)	143.8
C(24)-H(24)···O(3)#7	0.93	2.58	3.325(3)	137.9
C(24)-H(24)···O(6)#1	0.93	2.60	3.097(3)	114.2
C(12)-H(12)···O(2)#8	0.93	2.65	3.507(3)	153.3
C(9)-H(9)···O(1)	0.93	2.65	3.215(3)	120.0
C(3)-H(3)···O(5)#8	0.93	2.64	3.373(4)	136.7

C(1)-H(1)···O(7)#3	0.93	2.46	3.013(3)	118.1
C(15)-H(15)···O(7)	0.93	2.55	3.301(3)	138.5

Symmetry codes:

For **1**: #1, -x+1,-y,-z+1; #2, x,y-1,z; #3, -x+1,-y+1,-z; #4, x+1,y-1,z; #5, -x+1,-y+1,-z+1; #6, x,y,z+1.

For **2**: #1, -x+1,y,-z+1/2; #2, -x+1,-y,-z+1; #3, x,-y,z-1/2; #4, -x+1,y,-z+3/2; #5, -x+3/2,-y+1/2,-z+1; #6, x-1/2,y+1/2,z; #7, x,-y,z+1/2; #8, x,y-1,z.

For **3**: #1, x-1,y,z; #2, x-1/2,-y+3/2,z+1/2; #3, x-1/2,-y+3/2,z-1/2; #4, x+1/2,-y+3/2,z-1/2; #5, x+1/2,-y+3/2,z+1/2; #6, x+1,y,z; #7, -x+1,-y+1,-z+1; #8, -x+2,-y+1,-z+1.

For **4**: #1, -x+2,-y+2,-z+1; #2, x+1,-y+3/2,z+1/2; #3, -x+1,y+1/2,-z+1/2; #4,-x+1,y-1/2,-z+1/2; #5, -x+1,-y+1,-z.

For **6**: #1, -x+2,-y+1,-z+1; #2, x+1,y,z; #3, -x+1,-y+1,-z+1; #4, x-1,y,z; #5, -x+2,-y,-z+2; #6, x,y,z+1; #7, -x+1,-y,-z+1.

For **7**: #1, -x+1,-y+1,-z+1; #2, -x,-y+1,-z+1; #3, x+1,y,z; #4, -x+1,y,-z+3; #5, -x,-y+2,-z+2; #6, x+1,y,-z+1.

For **8**: #1, -x+2,-y+2,-z+1; #2, x,y+1,z; #3, x,y-1,z; #4, x-1,y,z; #5, -x+1,-y+2,-z+1; #6, x,y,z+1; #7, x+1,y+1,z; #8, -x+1,-y+1,-z+1.

Table S6. The exponential lifetime (τ_i), preexponential factor (A_i) and variance (χ^2) of **1-8** at room temperature.

Compound	Fluorescence				Phosphorescence					
	λ_F (nm)	τ (ns)	A (%)	χ^2	λ_P (nm)	τ_1/ms (λ_P/nm)	A_1 (%)	τ_2/ms (λ_P/nm)	A_2 (%)	χ^2
Htynca	409	8.8	100	1.10	–	–	–	–	–	–
1	399	4.5	100	1.24	508	43	100	–	–	0.95
2	419	5.2	100	1.16	508	129	100	–	–	1.21
3	420	6.5	100	1.17	510	179	100	–	–	1.28
4	417	4.6	100	1.25	512	201	100	–	–	1.28
5	422	8.8	100	1.09	543	41(565)	25.60	144(513)	74.40	1.02
6	419	5.7	100	1.10	520	38(572)	20.74	183(509)	79.26	1.01
7	430	6.1	100	1.07	561	52(567)	49.52	194(~510)	50.48	1.27
8	423	4.8	100	1.22	555	62(568)	41.08	236(~510)	58.92	1.22

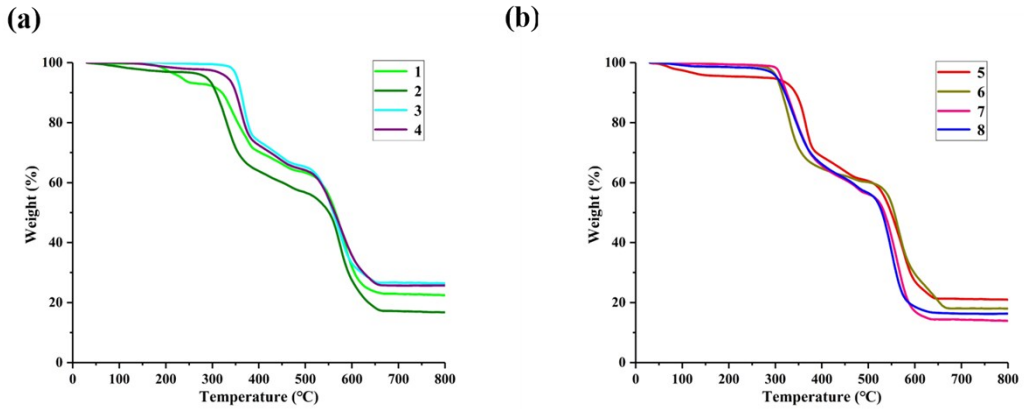


Fig. S21. (a) Thermogravimetric (TG) analysis curves of **1-4.** (b) Thermogravimetric (TG) analysis curves of **5-8.**

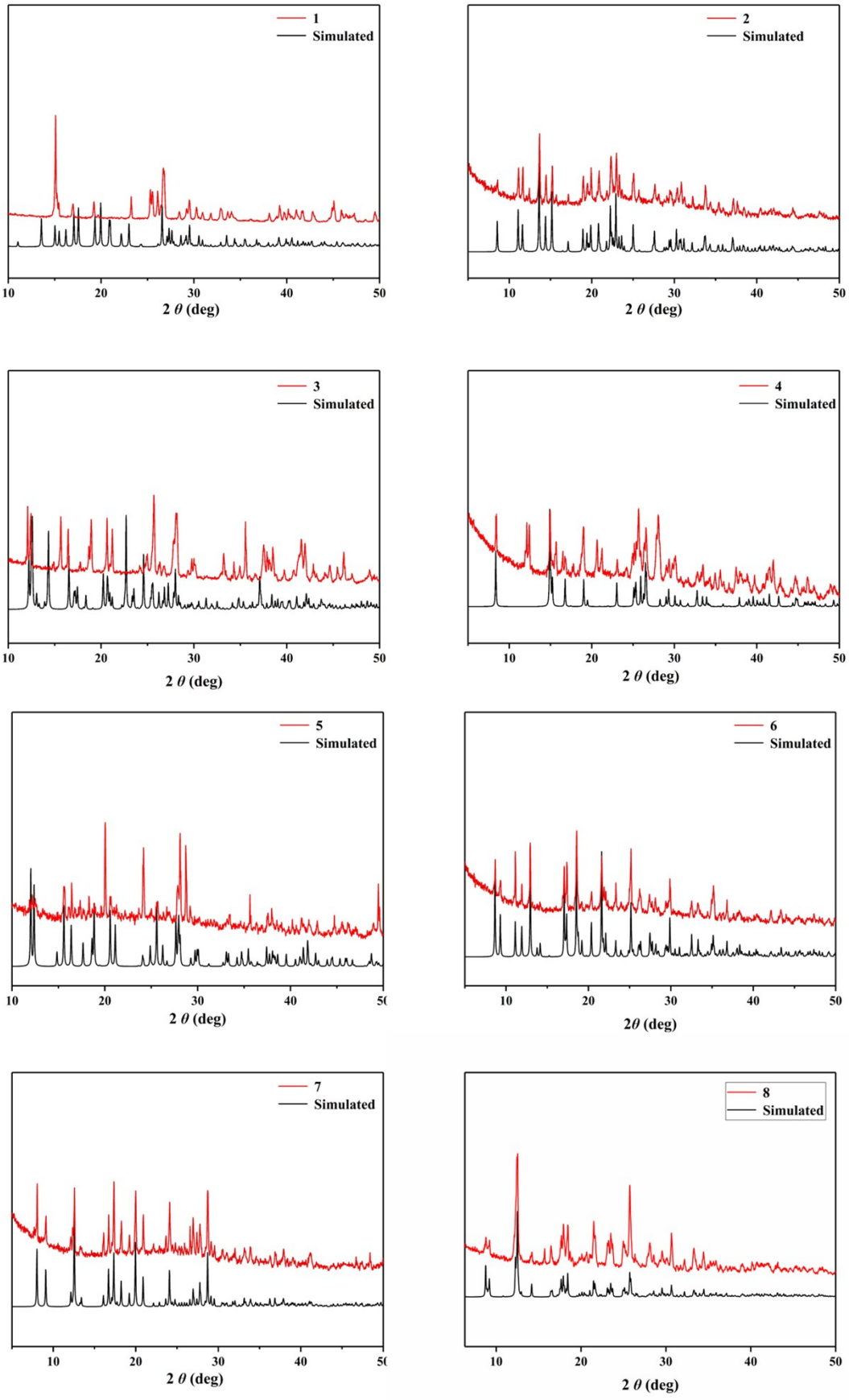
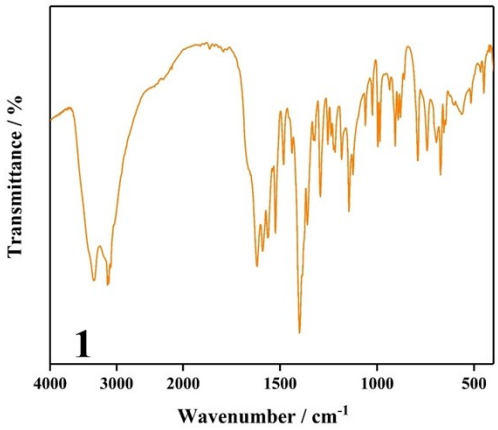
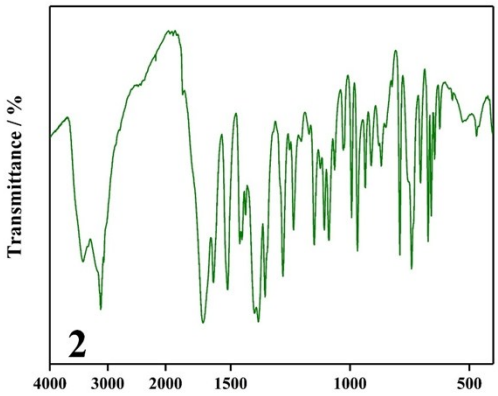


Fig. S22. Simulated and as synthesized PXRD patterns of **1-8**.


Transmittance / %
1
4000 3000 2000 1500 1000 500
Wavenumber / cm-1


Transmittance / %
2
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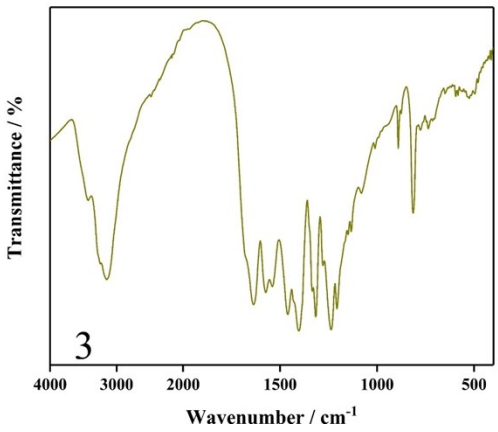
Transmittance / %
3
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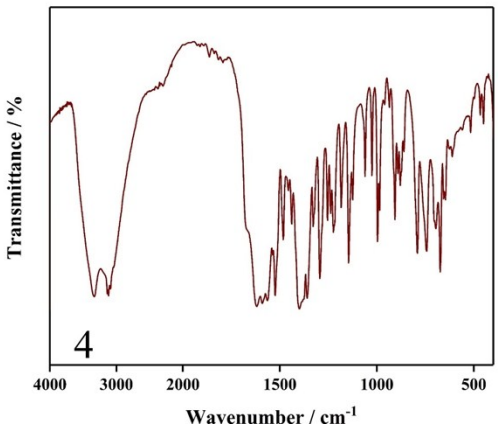
Wavenumber / cm-1


Transmittance / %
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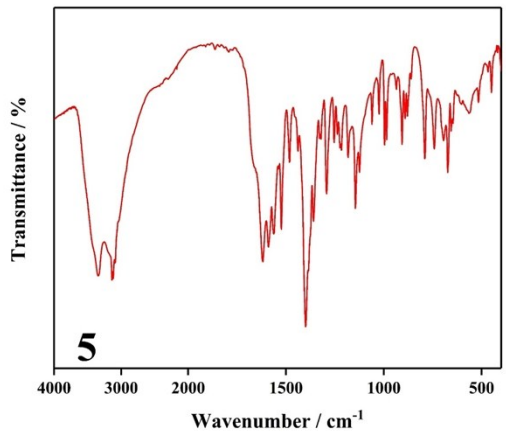
Wavenumber / cm-1


Transmittance / %
5
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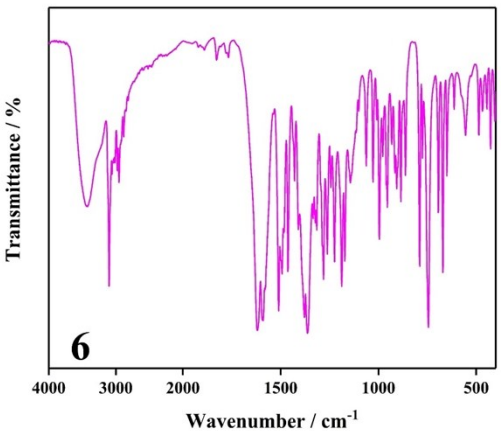
Wavenumber / cm-1


Transmittance / %
6
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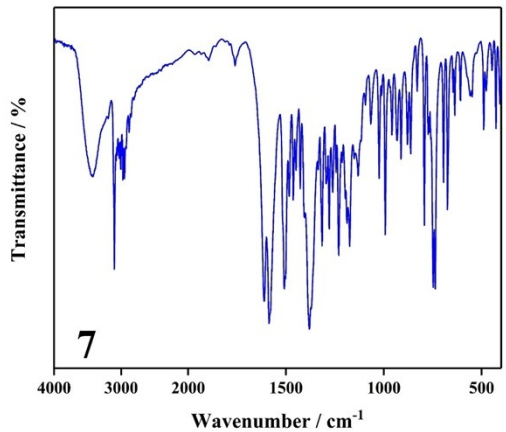
Wavenumber / cm-1


Transmittance / %
7
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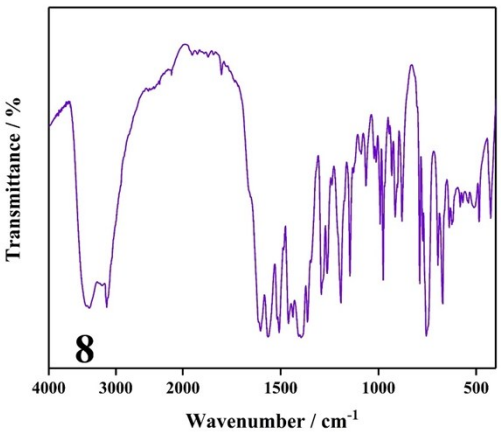
Wavenumber / cm-1


Transmittance / %
8
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Wavenumber / cm-1

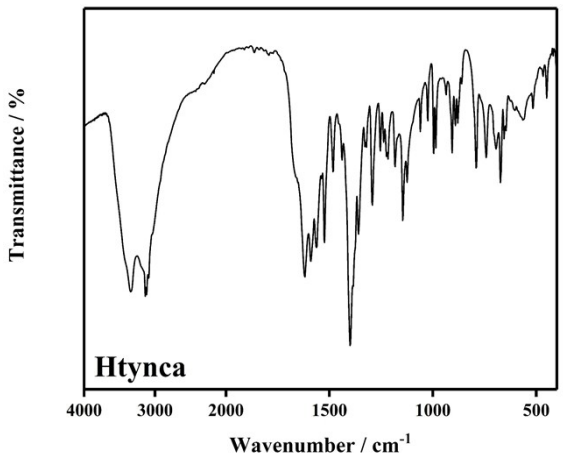

Fig. S23. The FT-IR spectra of ligand and **1-8.**

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