# Four New Cd(II) Coordination Polymers with Mixed Multidentate N-Donors and Biphenyl-Based Polycarboxylate Ligands: Syntheses, Structures, and Photoluminescent Properties

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Ⓢ Supporting Information

ABSTRACT: Four new cadmium(II) coordination polymers (CPs), $\{[Cd(Hpptpd)(H_2bptta)]\cdot 8H_2O\}_n$ (**1**), $\{[Cd_2(Hpptpd)_2(bptta)(H_2O)_2]\cdot 4H_2O\}_n$ (**2**), $\{[Cd_2(pptpz)(bpta)(H_2O)]\cdot H_2O\}_n$ (**3**), and $\{[Cd(Hpptpz)(bpba)]\cdot 2H_2O\}_n$ (**4**) (Hpptpd = 2-(3-(4-(pyridin-4-yl)phenyl)-1H-1,2,4-triazol-5-yl)pyridine, Hpptpz = 2-(3-(4-(pyridin-4-yl)phenyl)-1H-1,2,4-triazol-5-yl)pyrazine, H_4bptta = 3,3',5,5'-biphenyltetracarboxylic acid, H_3bpta = 3,4',5-biphenyltricarboxylic acid, H_2bpba = 3,4'-biphenylbicarboxylic acid), were synthesized under hydrothermal conditions. The CPs were structurally characterized by single-crystal X-ray diffraction analyses and further characterized by infrared spectra (IR), elemental analyses, powder X-ray diffraction (PXRD), and thermogravimetric analyses (TGA). Complex **1** exhibits an unusual 2D + 2D → 2D parallel interpenetrated 6^3-**hcb** network. The adjacent 2D networks are interdigitated with each other to form the resulting three-dimensional (3D) supramolecular

architecture through the interbilayer $\pi\cdots\pi$ stacking between Hpptpd ligands and nonclassical C—H⋯O hydrogen bonds. Complex **2** is a one-dimensional (1D) molecular ladder along the *a* direction and further extended via hydrogen bonds into the 3D supramolecular framework. Complex **3** exhibits a novel complicated 3D (3,4,4,5)-connected framework with the Schläfli symbol of $(4\cdot 6^5)(4\cdot 6^7\cdot 8^2)(6^3)(6^4\cdot 8^2)$. Complex **4** manifests an intriguing layered structure with 5-connected cadmium atom as a unique node and can be simplified to an Archimedean $(3^3\cdot 4^4\cdot 5^3)$ **cem** topology with triangular and rectangular circuits. The topology of **4** could be alternately simplified to a 3,4-connected binodal layer with a V_2O_5-type network. The thermal stabilities and photoluminescence behaviors of them were also discussed.
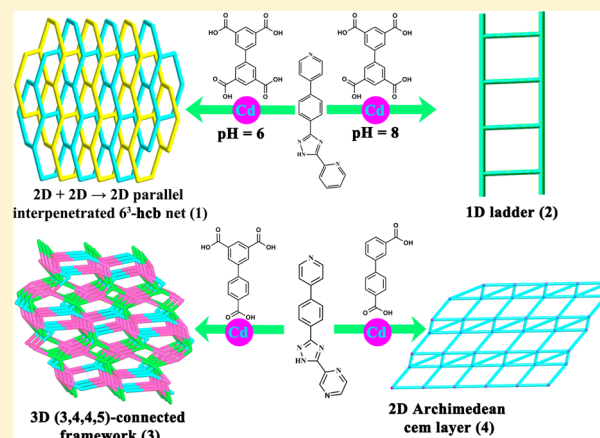
■ INTRODUCTION

In recent years, rational design and synthesis of coordination polymers (CPs), often referred to as metal−organic frameworks (MOFs), have been extensively studied not only for their fascinating crystal structures, variety of bonding topologies, but also for their potential applications in gas storage, catalysis, drug delivery, luminescence, NLO, magnet, and sensing.[1,2] To the best of our knowledge, the self-assembly of CPs depends on the structural character of the ligand,[3] coordination nature of the metal atom,[4] as well as other influence factors such as the temperature, pH value of the solution, and solvent system.[5,6] Among them, tactical synthesis or selection of the organic ligand and controlling reaction condition are key factors for achieving expected CPs.

The syntheses of new N-donor ligands are a long-standing fascination of chemists, and so far, many bi-, tri-, and multidentate N-donor ligands have been reported, but the study of multidentate N-donor ligands is still underdeveloped.[7] Unlike the common bipyridine or biimidazole ligands,[8] the multidentate N-donor ligands[9] such as 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazole are far from comprehensively unveiled

and especially attractive due to (i) they can act as not only bridging but also chelating ligands; (ii) the triazole can be neutral or anionic unit depending on whether the H atom on it is deprotonated; and (iii) it can adopt cis or trans transformations based on the rotation of the $C_{triazole}-C_{pyridine}$ bond. So this kind of ligand deserves to be further investigated in the field of crystal engineering.

Because the carboxyl group can assume many kinds of bridging or chelating modes to construct thrilling CPs, organic aromatic polycarboxylate ligands have been extensively employed in the preparation of CPs with novel structural motifs and interesting properties.[10] Among this kind of ligand, biphenyl-based tetra-, tri-, and bicarboxylates are especially interesting because the free rotation of two phenyl rings can afford different coordination conformations depending on the dihedral angle between them. As indicated by a CSD (Cambridge Structure Database) survey with the help of

ConQuest version 1.3,[11] only 9 H$_4$bptta-based, 10 H$_3$bpta-based, and 9 H$_2$bpba-based coordination complexes have been sporadically characterized and reported until now.[12] Furthermore, the combination of N-donor ligands with polycarboxylate is a good choice for the construction of novel topology and networks, which have been proved by us as well as many other groups.[13] However, it is accompanied by even more uncertain factors. Thus, the prediction of mixed-ligand architectures is a challenging scientific endeavor.[14]

Considering all of these above-mentioned, we consider that the simultaneous employment of N-donor ligands and biphenyl-based polycarboxylates (Scheme 1) will contribute

Scheme 1. Structures of Multidentate N-Donor and Polycarboxylate Ligands Used in This Work
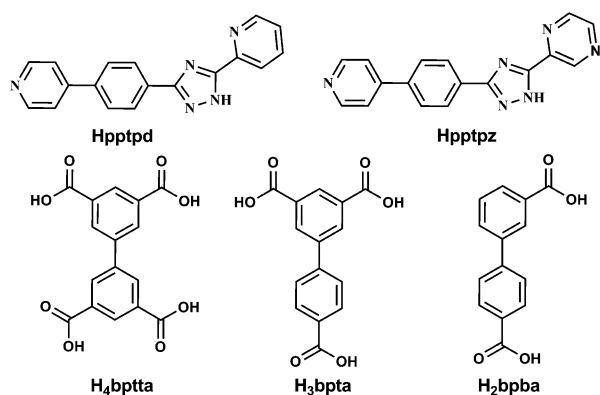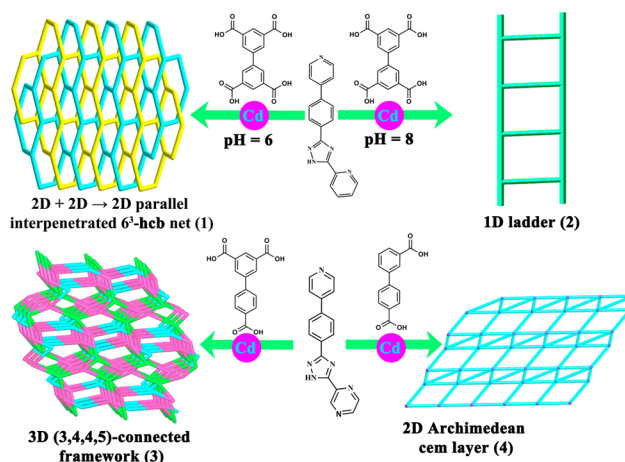

to the formation of various architectures and help chemists understand the process of self-assembly. Herein, we successfully apply this strategy and obtain four novel CPs, [{[Cd(Hpptpd)-(H$_2$bptta)]·8H$_2$O}$_n$ (**1**), {[Cd$_2$(Hpptpd)$_2$(bptta)-(H$_2$O)$_2$]·4H$_2$O}$_n$ (**2**), {[Cd$_2$(pptpz)(bpta)(H$_2$O)]·H$_2$O}$_n$ (**3**), and {[Cd(Hpptpz)(bpba)]·2H$_2$O}$_n$ (**4**) (Hpptpd = 2-(3-(4-(pyridin-4-yl)phenyl)-1H-1,2,4-triazol-5-yl)pyridine, Hpptpz = 2-(3-(4-(pyridin-4-yl)phenyl)-1H-1,2,4-triazol-5-yl)pyrazine, H$_4$bptta = 3,3′,5,5′-biphenyltetracarboxylic acid, H$_3$bpta = 3,4′,5-biphenyltricarboxylic acid, H$_2$bpba = 3,4′-biphenylbicarboxylic acid). Their structures range from the 2D + 2D → 2D parallel interpenetrated 6^3-**hcb** network, 1D ladder, 3D (3,4,4,5)-connected framework, to the 2D Archimedean **cem** layer (Scheme 2). Their syntheses, crystal structures, thermal stabilities, and photoluminescent properties are reported in this Article.

■ EXPERIMENTAL SECTION

Materials and General Methods. All chemicals and solvents used in the syntheses were of analytical grade and were used without further purification. The ligands Hpptpd and Hpptpz were synthesized by a similar method described in the literature.[15] C, N, and H analyses were performed on an EA1110 CHNS-0 CE 65 elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna750FT-IR spectrometer. Powder-XRD measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu Kα radiation. The fluorescent spectra were measured on an F-4500 fluorescence spectrophotometer (slit width, 5 nm; sensitivity, high). Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min.

Preparation of Complexes 1−4. {[Cd(Hpptpd)-(H$_2$bptta)]·8H$_2$O}$_n$ (**1**). A mixture of 3CdSO$_4$·8H$_2$O (51 mg, 0.067 mmol), Hpptpd (60 mg, 0.20 mmol), H$_4$bptta (50 mg, 0.15 mmol),

Scheme 2. Synthetic Procedures of Four CPs

2D + 2D → 2D parallel interpenetrated 6^3-**hcb** net (1)

1D ladder (2)

3D (3,4,4,5)-connected framework (3)

2D Archimedean **cem** layer (4)

NaOH (4.0 mg, 0.10 mmol), and 14 mL of H$_2$O was sealed in a 25 mL Teflon-lined stainless steel autoclave (pH ≈ 6) and heated at 170 °C for 3 days, and then slowly cooled to room temperature. Light yellow crystals of **1** were obtained in 82% yield based on Cd. Anal. Calcd for C$_{34}$H$_{37}$CdN$_5$O$_{16}$: C, 46.19; H, 4.22; N, 7.92. Found: C, 46.08; H, 4.05; N, 8.31. IR (KBr pellet, cm^{-1}): 3415 (vs), 1725 (vs), 1624 (vs), 1533 (vs), 1409 (s), 1367 (s), 1165 (m), 991 (m), 757 (s).

{[Cd$_2$(Hpptpd)$_2$(bptta)(H$_2$O)$_2$]·4H$_2$O}$_n$ (**2**). The synthesis of **2** was similar to that of **1**, but the NaOH (8 mg, 0.20 mmol) was used, and the pH value of the solution before reaction is ca. 8. Pale-yellow crystals of **2** were obtained in 54% yield based on Cd. Anal. Calcd for C$_{26}$H$_{22}$CdN$_5$O$_7$: C, 49.66; H, 3.52; N, 11.14. Found: C, 49.58; H, 3.25; N, 10.97. IR (KBr pellet, cm^{-1}): 3420 (vs), 1606 (vs), 1552 (vs), 1416 (s), 1367 (s), 1165 (m), 991 (m), 757 (s).

{[Cd$_2$(pptpz)(bpta)(H$_2$O)]·H$_2$O}$_n$ (**3**). A mixture of 3CdSO$_4$·8H$_2$O (51 mg, 0.067 mmol), Hpptpz (45 mg, 0.15 mmol), H$_3$bpta (43 mg, 0.15 mmol), NaOH (12 mg, 0.30 mmol), and 13 mL of H$_2$O was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 170 °C for 3 days, and then slowly cooled to room temperature. Yellow crystals of **3** were obtained in 73% yield. Anal. Calcd for C$_{32}$H$_{22}$Cd$_2$N$_6$O$_8$: C, 45.57; H, 2.63; N, 9.96. Found: C, 45.17; H, 2.73; N, 9.69. IR (KBr pellet, cm^{-1}): 3474 (vs), 1601 (vs), 1546 (vs), 1402 (vs), 1366 (vs), 770 (m), 731 (m).

{[Cd(Hpptpz)(bpba)]·2H$_2$O}$_n$ (**4**). Synthesis of **4** was similar to that of **3**, but the H$_3$bpta was replaced by H$_2$bpba (35 mg, 0.20 mmol). Colorless crystals of **4** were obtained in 53% yield. Anal. Calcd for C$_{31}$H$_{24}$CdN$_6$O$_6$: C, 54.04; H, 3.51; N, 12.20. Found: C, 54.21; H, 3.73; N, 12.37. IR (KBr pellet, cm^{-1}): 3436 (vs), 1600 (vs), 1530 (vs), 1388 (vs), 1143 (m), 1013 (m), 974 (m), 816 (m), 756 (m).

X-ray Crystallography. Single crystals of complexes **1**−**4** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corp.) before being mounted on a glass fiber for data collection. Data for them were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each; each frame corresponds to a 0.5° scan in 5 s, followed by spot integration and least-squares refinement. For **1**−**4**, data were measured using ω scans of 0.5° per frame for 10 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.[16] Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[16] In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97[17] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[18] Atoms were located from iterative examination of difference F-maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as

Table 1. Crystal Data for 1−4

	compound			
	1	**2**	**3**	**4**
empirical formula	$C_{34}H_{37}CdN_5O_{16}$	$C_{26}H_{22}CdN_5O_7$	$C_{32}H_{22}Cd_2N_6O_8$	$C_{31}H_{24}CdN_6O_6$
formula weight	884.09	628.89	843.36	688.97
temperature/K	298(2)	298(2)	298(2)	298(2)
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	19.266(14)	9.814(3)	16.328(4)	10.4459(8)
b/Å	8.553(6)	10.860(3)	6.9755(17)	12.1007(10)
c/Å	27.325(19)	12.606(4)	27.246(6)	12.5575(10)
α/deg	90.00	105.473(3)	90.00	111.2940(10)
β/deg	108.189(16)	102.426(3)	101.760(4)	112.1980(10)
γ/deg	90.00	91.537(3)	90.00	99.4550(10)
volume/Å^3	4278(5)	1259.4(7)	3038.0(13)	1282.98(18)
Z	4	2	4	2
ρ_{calc}, mg/mm^3	1.149	1.611	1.844	1.690
μ/mm^{-1}	0.556	0.919	1.464	0.904
$F(000)$	1488.0	614.0	1664.0	656.0
2Θ range for data collection	4.76−50°	5.52−50°	2.54−50°	3.86−50°
reflections collected	20 992	8514	14 864	6064
independent reflections	7473 [R(int) = 0.058]	4332 [R(int) = 0.025]	5353 [R(int) = 0.056]	4362 [R(int) = 0.038]
data/restraints/parameters	7473/48/453	4332/0/343	5353/0/433	4362/0/379
GOF on F^2	0.970	1.018	1.020	1.144
final R indexes^a [$I \geq 2\sigma(I)$]	$R_1 = 0.049$, $wR_2 = 0.110$	$R_1 = 0.030$, $wR_2 = 0.063$	$R_1 = 0.038$, $wR_2 = 0.073$	$R_1 = 0.056$, $wR_2 = 0.175$
final R indexes [all data]	$R_1 = 0.069$, $wR_2 = 0.118$	$R_1 = 0.036$, $wR_2 = 0.065$	$R_1 = 0.059$, $wR_2 = 0.081$	$R_1 = 0.062$, $wR_2 = 0.185$
largest diff. peak/hole/e Å^{-3}	0.65/−0.79	0.32/−0.35	0.68/−0.47	1.22/−1.38

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

riding atoms with isotropic displacement parameters 1.2−1.5 times U_{eq} of the attached C atoms. There are some solvent-accessible void volumes in the crystals of **1**, **2**, and **4**, which are occupied by highly disordered water molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON[19] was used to remove these electron densities. All structures were examined using the Addsym subroutine of PLATON to ensure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table 1. Selected bond lengths and angles are collated in Table 2.

■ **RESULT AND DISCUSSION**

Synthesis and General Characterization. The synthesis for the target four complexes were performed in 25 mL Teflon-lined stainless steel vessels by utilizing the solvothermal method with the different stoichiometric ratio for the starting materials in the presence of NaOH. The one-pot mixture was heated to an appropriate temperature and held for 48−72 h, then cooled at a descent rate of 10 °C/h. Finally, the crystals suitable for the single-crystal X-ray diffraction analysis were obtained after cooling to room temperature. All of the complexes **1−4** are stable in the solid state upon exposure to air. They have poor solubility in common organic solvents and only are slightly soluble in a very high polarity solvents, such as DMF, DEF, and DMSO.

Powder X-ray diffraction (PXRD) has been used to check the phase purity of the bulk samples in the solid state. For complexes **1−4**, the measured PXRD patterns closely match the simulated patterns generated from the results of single-crystal diffraction data (Figure S1, Supporting Information), indicative of pure products. The IR spectra of complexes **1−4** also show characteristic absorption bands mainly attributed to the asymmetric (ν_{as}: ca. 1600 cm^{-1}) and symmetric (ν_s: ca. 1385 cm^{-1}) stretching vibrations of the carboxylic groups. No

band in the region 1690−1730 cm^{-1} indicates complete deprotonation of the carboxylic groups in **2−4**,[20] which is consistent with the result of the X-ray diffraction analysis.

Structure Descriptions. *{[Cd(Hpptpd)(H$_2$bptta)]·8H$_2$O}$_n$ (1).* X-ray single-crystal diffraction analysis reveals that **1** is a 2D bilayer incorporating 1D double-strand helical chains. It crystallizes in the monoclinic crystal system with space group of $P2/c$. The asymmetric unit contains one Cd(II) ion, one Hpptpd ligand, one H$_2$bptta, and eight lattice water molecules. As shown in Figure 1a, the Cd1 is seven-coordinated by four O atoms from two H$_2$bptta ligands and three N atoms from two Hpptpd ligands, displaying a distorted pentagon-bipyramidal geometry. The Cd−O and Cd−N bond lengths are in the range of 2.264(3)−2.475(3) and 2.307(4)−2.350(4) Å, respectively, which are well-matched to those observed in similar complexes.[21] A pair of head-to-tail arranged Hpptpd ligands with a chelating + bridging mode bind two Cd(II) ions to form a centrosymmetric [Cd$_2$(Hpptpd)$_2$] subunit. The partially deprotonated H$_4$bptta shows a μ_2-η^1:η^0:η^1:η^0 coordination mode and acts as a Z-shaped linker extending the [Cd$_2$(Hpptpd)$_2$] subunits to a highly undulated layer. The single 2D layer could be simplified to a highly undulated 6^3-**hcb** network (Figure 1b) with the thickness of ca. 11 Å. The large metal−organic hexagons are sustained by two shorter Cd−(Hpptpd)$_2$−Cd links (Cd⋯Cd = 11.825(7) Å) and four larger Cd−H$_2$bptta−Cd bridges (Cd⋯Cd = 14.196(9) Å). Because of the large windows in this layer, two identical layers are penetrated with each other with a 2D + 2D → 2D parallel interpenetrated mode (Figure 1c).[22] According to Blatov's classification,[22a] the interpenetration can be classified as type Class **Ia**, Z_t = 2, which means two identical interpenetrated nets are generated by only translations and the translating vectors are [1, 0, 0]. This 2D bilayer contain rectangle-like channels

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1−4

Complex 1[a]							
Cd1−O6^i	2.264(3)	Cd1−O1	2.322(3)	Cd1−N5^{ii}	2.307(4)	Cd1−N1	2.350(4)
Cd1−N2	2.309(4)	Cd1−O2	2.475(3)				
O6^i−Cd1−N5^{ii}	92.17(12)	N2−Cd1−N1	72.01(11)	O6^i−Cd1−N2	132.91(10)	O1−Cd1−N1	90.04(12)
N5^{ii}−Cd1−N2	102.77(12)	O6^i−Cd1−O2	133.31(9)	O6^i−Cd1−O1	79.79(10)	N5^{ii}−Cd1−O2	86.97(12)
N5^{ii}−Cd1−O1	96.71(12)	N2−Cd1−O2	92.35(9)	N2−Cd1−O1	140.16(10)	O1−Cd1−O2	54.09(9)
O6^i−Cd1−N1	88.58(12)	N1−Cd1−O2	97.40(13)	N5^{ii}−Cd1−N1	173.24(12)		
Complex 2[b]							
Cd1−O3^i	2.264(2)	Cd1−N2	2.308(2)	Cd1−O1W	2.274(2)	Cd1−N1	2.421(2)
Cd1−O1	2.276(2)	Cd1−O2	2.559(2)				
O3^i−Cd1−O1W	91.33(8)	O1−Cd1−N1	165.63(7)	O3^i−Cd1−O1	109.01(7)	N2−Cd1−N1	71.02(8)
O1W−Cd1−O1	88.46(8)	O3^i−Cd1−O2	158.79(8)	O3^i−Cd1−N2	118.26(8)	O1W−Cd1−O2	77.42(8)
O1W−Cd1−N2	140.26(9)	O1−Cd1−O2	53.51(7)	O1−Cd1−N2	104.33(8)	N2−Cd1−O2	80.56(8)
O3^i−Cd1−N1	84.82(8)	N1−Cd1−O2	112.14(7)	O1W−Cd1−N1	87.28(8)		
Complex 3[c]							
Cd1−N3	2.209(4)	Cd2−O2	2.209(3)	Cd1−O4^i	2.244(3)	Cd2−N2	2.270(4)
Cd1−N6^{ii}	2.298(4)	Cd2−O1^{iv}	2.279(3)	Cd1−O1W	2.315(3)	Cd2−O6^v	2.295(3)
Cd1−N1	2.613(4)	Cd2−O5^v	2.339(4)	Cd1−O3^{iii}	2.641(4)		
N3−Cd1−O4^i	127.55(13)	O1W−Cd1−O3^{iii}	168.25(11)	N3−Cd1−N6^{ii}	135.94(14)	N1−Cd1−O3^{iii}	107.60(11)
O4^i−Cd1−N6^{ii}	87.91(13)	O2−Cd2−N2	127.48(13)	N3−Cd1−O1W	113.06(13)	O2−Cd2−O1^{iv}	101.20(12)
O4^i−Cd1−O1W	84.94(12)	N2−Cd2−O1^{iv}	87.48(12)	N6^{ii}−Cd1−O1W	92.95(13)	O2−Cd2−O6^v	100.94(13)
N3−Cd1−N1	68.04(12)	N2−Cd2−O6^v	129.98(13)	O4^i−Cd1−N1	157.34(13)	O1^{iv}−Cd2−O6^v	95.47(13)
N6^{ii}−Cd1−N1	88.25(13)	O2−Cd2−O5^v	115.27(13)	O1W−Cd1−N1	72.97(11)	N2−Cd2−O5^v	88.68(13)
N3−Cd1−O3^{iii}	77.31(12)	O1^{iv}−Cd2−O5^v	136.29(13)	O4^i−Cd1−O3^{iii}	92.99(11)	O6^v−Cd2−O5^v	55.97(13)
N6^{ii}−Cd1−O3^{iii}	75.39(12)						
Complex 4[d]							
Cd1−O2^i	2.183(4)	Cd1−N6^{iii}	2.285(5)	Cd1−O1	2.244(4)	Cd1−N3	2.335(5)
Cd1−O3^{ii}	2.245(4)	Cd1−N1	2.354(5)				
O2^i−Cd1−O3^{ii}	83.43(17)	N6^{iii}−Cd1−N3	93.88(17)	O1−Cd1−O3^{ii}	178.78(14)	O2^i−Cd1−N1	114.33(16)
O2^i−Cd1−O1	97.47(16)	O3^{ii}−Cd1−N3	82.55(17)	O2^i−Cd1−N6^{iii}	82.74(17)	O1−Cd1−N1	83.69(16)
O1−Cd1−N6^{iii}	84.60(17)	O3^{ii}−Cd1−N1	95.19(17)	O2^i−Cd1−N3	165.13(17)	N3−Cd1−N1	71.98(16)
O3^{ii}−Cd1−N6^{iii}	96.34(18)	N6^{iii}−Cd1−N1	160.41(19)	O1−Cd1−N3	96.61(16)		

[a]Symmetry codes: (i) x, −y + 1, z + 1/2; (ii) −x, −y, −z + 1. [b]Symmetry code: (i) x + 1, y, z. [c]Symmetry codes: (i) x + 1, y, z; (ii) x, −y + 1/2, z + 1/2; (iii) −x, y − 1/2, −z + 3/2; (iv) −x, y + 1/2, −z + 3/2; (v) x, −y + 3/2, z − 1/2. [d]Symmetry codes: (i) −x + 3, −y + 2, −z + 1; (ii) x + 1, y, z; (iii) −x + 2, −y + 1, −z + 1.

(Figure 1d), in which guest water molecules resided. The solvent-accessible void of **1** was calculated by PLATON analysis as 38.9% of the crystal volume (1662.7 out of the 4278.0 Å^3 unit cell volume). In addition, the adjacent bilayers are further interdigitated to generate a 3D framework (Figure 1e) reinforced by the interbilayer $\pi \cdots \pi$ stacking between Hpptpd ligands with the shortest centroid···centroid separation of 3.791(4) Å and nonclassical C−H···O hydrogen bond of 3.182(12) Å.

{[Cd$_2$(Hpptpd)$_2$(bptta)(H$_2$O)$_2$]·4H$_2$O}$_n$ (2). Structural analysis indicates that complex **2** is a 1D ladder and crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit of **2** is composed of one crystallographically independent Cd(II) ion, one Hpptpd ligand, half bptta lying about inversion centers, one coordinated water molecule, and two free water molecules. As shown in Figure 2a, the Cd1 is located in a severely distorted octahedral geomtry, completed by two N atoms belonging to the same Hpptpd ligand and four O atoms from two bptta and one aquo ligand. The average Cd−O and Cd−N distances are 2.343(2) and 2.365(2) Å. The bond angles around Cd1 range from 53.51(7) to 165.63(7)°. Differently, the Hpptpd only acts as chelating ligand using its adjacent triazole and pyridine units in **2**, and the bptta adpots μ_4-η^1:η^1:η^1:η^1 coordination mode to bind the Cd(II) centers, giving a 1D ladder motif (Figure 2b). The hydrogen bonds between Hpptpd and lattice water

molecule (N3−H3···O2W^{iv} = 2.796(3), O2W−H2WA···N5^{iii} = 2.781(3) Å), coordinated and uncoordinated water molecules (O1W−H1WA···O2W^{ii} = 2.809(3) Å), and bptta and lattice water molecule (O2W−H2WB···O2 = 2.696(3) Å) extend the 1D ladder to the resulting 3D supramolecular framework (Figure 2c) (symmetry codes: (ii) −x + 1, −y + 2, −z + 1; (iii) x, y, z − 1; (iv) −x + 1, −y + 1, −z + 1).

{[Cd$_2$(pptpz)(bpta)(H$_2$O)]·H$_2$O}$_n$ (3). X-ray single-crystal diffraction analysis reveals that **3** is a complicated 4-nodal (3,4,4,5)-connected 3D framework. It crystallizes in the monoclinic crystal system with space group of $P2_1/c$. The asymmetric unit consists of two Cd(II) ions, one pptpz, one bpta, one aquo ligand, and one uncoordinated water molecule. As depicted in Figure 3a, two Cd(II) centers are in slightly different coordination geometries. The Cd1 locates in a distorted CdN$_3$O$_3$ octahedral geometry, completed by three N atoms from two pptpz (Cd1−N3 = 2.209(4), Cd1−N6^{ii} = 2.298(4), Cd1−N1 = 2.613(4) Å), two carboxyl O atoms from two bpta, and one water molecule (Cd1−O4^i = 2.244(3), Cd1−O3^{iii} = 2.641(4), Cd1−O1W = 2.315(3) Å). The Cd2 is coordinated by one pptpz (Cd2−N2 = 2.270(4) Å) and three bpta ligands (Cd2−O2 = 2.209(3), Cd2−N2 = 2.270(4), Cd2−O1^{iv} = 2.279(3), Cd2−O6^v = 2.295(3), Cd2−O5^v = 2.339(4) Å), giving a distorted CdNO$_5$ octahedron. Both Cd− N and Cd−O bond lengths are in the normal ranges. The
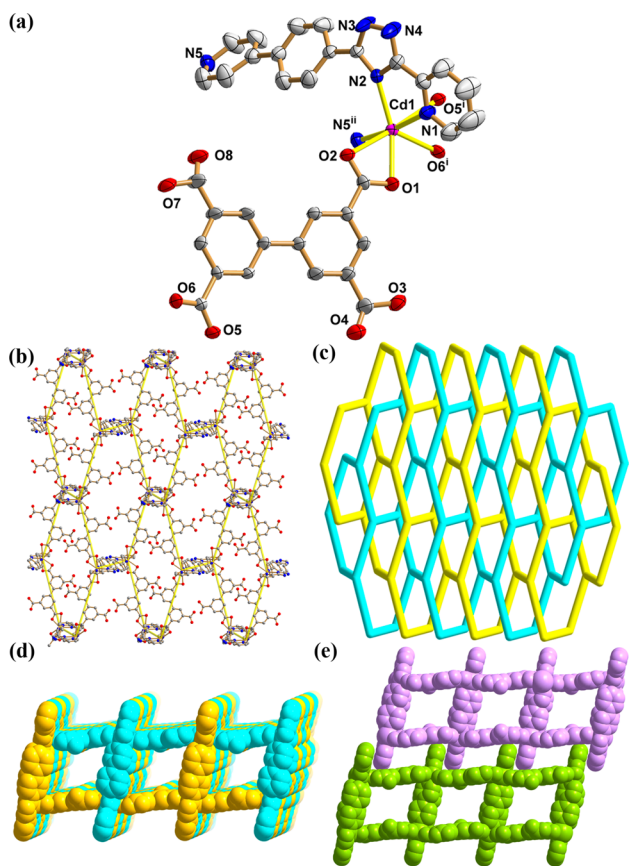
Figure 1. (a) The coordination environment of Cd(II) ion in **1** with the thermal ellipsoids at 50% probability level. (b) Presentation of 2D 6^3-**hcb** network (purple ball, Cd; red ball, O; blue ball, N; gray ball, C). (c) Simplified 2D + 2D → 2D parallel interpenetrated undulated 6^3-**hcb** networks. (d) Space-filling view of the interpenetrated 6^3-**hcb** networks. (e,f) The interdigitated 2D layers incorporating interbilayer $\pi\cdots\pi$ stacking (symmetry codes: (i) x, $-y + 1$, $z + 1/2$; (ii) $-x$, $-y$, $-z + 1$).

Figure 2. (a) The coordination environment of Cd(II) ions in **2** with the thermal ellipsoids at 50% probability level. (b) Space-filling view of the 1D ladder. (c) Ball-and-stick view of 3D supramolecular framework incorporating hydrogen bonds (purple ball, Cd; red ball, O; blue ball, N; gray ball, C) (symmetry codes: (i) $x + 1$, y, z; (v) $-x + 1$, $-y + 2$, $-z + 2$).

Hpptpz in **3** is deprotonated to become an anionic ligand and adopts a tridentate coordination mode. The bpta with a μ_5-η^1:η^1:η^1:η^1:η^1:η^2 coordination mode combines with tridentate pptpz to bind the Cd(II) centers, giving a complicated 3D framework, which is further consolidated by classical O/N–H···O and nonclassical C–H···O/N hydrogen bonds, abundant $\pi\cdots\pi$ stacking interactions between triazole and phenyl ring or pyridine and phenyl ring ranging from 3.488(3) to 3.492(3) Å, and significant anion(carboxyl group)···π interaction between O2 and electron-deficient pyrazine ring (Cg···O2^{iii} = 3.041(4) Å; Cg is centroid of N1/C1/C2/N2/C3/C4, Figure S2 in the Supporting Information). To clearly understand such a complicated architecture, the topological method is used to simplify the structure. Topologically, both Cd1 and Cd2 can be seen as a 4-connected node, while the pptpz and bpta act as 3- and 5-connected nodes, respectively, and then the overall 3D framework can be rationalized as a 4-nodal (3,4,4,5)-connected framework (Figure 3b) with the Schläfli symbol of $(4\cdot6^5)$-$(4\cdot6^7\cdot8^2)(6^3)(6^4\cdot8^2)$ (symmetry codes: (i) $x + 1$, y, z; (ii) x, $-y + 1/2$, $z + 1/2$; (iii) $-x$, $y - 1/2$, $-z + 3/2$; (iv) $-x$, $y + 1/2$, $-z + 3/2$; (v) x, $-y + 3/2$, $z - 1/2$).

{[Cd(Hpptpz)(bpba)]·2H$_2$O}$_n$ (**4**). Complex **4** exhibits a 5-connected 2D layered structure with a rare **cem** topology. It crystallizes in the triclinic crystal system with space group of $P\bar{1}$. There is one crystallographically independent Cd(II) ion, one
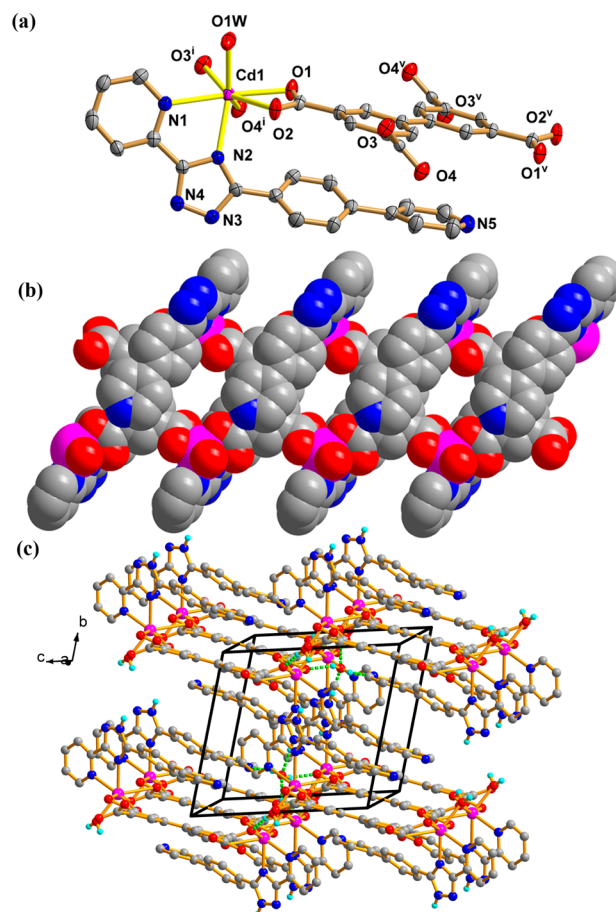
Hpptpz, and one bpba in the asymmetric unit of **4**. As depicted in Figure 4a, the Cd(II) center locates in a CdN$_3$O$_3$ octahedral coordination geometry, completed by three N atoms from two Hpptpz and three O atoms from three bpba liagnds. The Cd–N and Cd–O bond lengths are in the ranges of 2.285(5)–2.354(5) and 2.183(4)–2.245(4) Å. The bond angles around Cd1 range from 71.98(16)° to 178.78(14)°. Similar to **1**, a pair of head-to-tail arranged Hpptpz ligands with a chelating + bridging mode bind two inversion-related Cd(II) ions to form a centrosymmetric [Cd$_2$(Hpptpz)$_2$] subunit, which is extended to the resulting 3D framework by the bpba with a μ_3-η^1:η^1:η^1 coordination mode.

Topologically, each Cd(II) atom has five nearest neighbors, so each Cd(II) can be simplified into 5-connected node, so the resulting structure can be reduced to a 5-connected **cem** Archimedean layered net with $(3^3\cdot4^4\cdot5^3)$ topology (Figure 4b) comprised of stacked triangles and rectangles. The vertex symbol for the five connected node is $[3\cdot3\cdot3\cdot4\cdot4.*.*.*.*.*]$. An alternative perspective of this layered coordination polymer topology can be obtained by treating the μ_3-bpba as 3-connected nodes, and the Cd(II) atom as 4-connected nodes joining to three bpba ligands and one other Cd(II) atom through Hpptpz. The resulting 3,4-connected binodal layer topology (Figure 4c) mimics a V$_2$O$_5$-type structure, with a Schläfli symbol of $\{4^2\cdot6^3\cdot8\}\{4^2\cdot6\}$. As compared to the
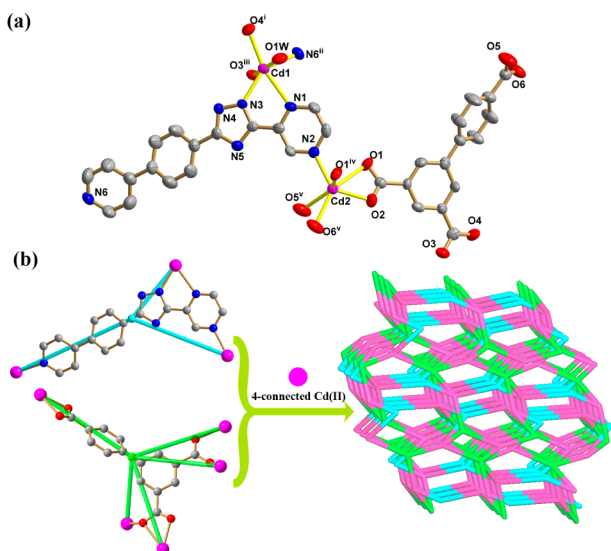
Figure 3. The coordination environment of Cd(II) ions in **3** with the thermal ellipsoids at 50% probability level. (b) Simplified 3D 4-nodal (3,4,4,5)-connected framework (purple ball, Cd; red ball, O; blue ball, N; gray ball, C) (symmetry codes: (i) $x + 1$, y, z; (ii) x, $-y + 1/2$, $z + 1/2$; (iii) $-x$, $y - 1/2$, $-z + 3/2$; (iv) $-x$, $y + 1/2$, $-z + 3/2$; (v) x, $-y + 3/2$, $z - 1/2$).
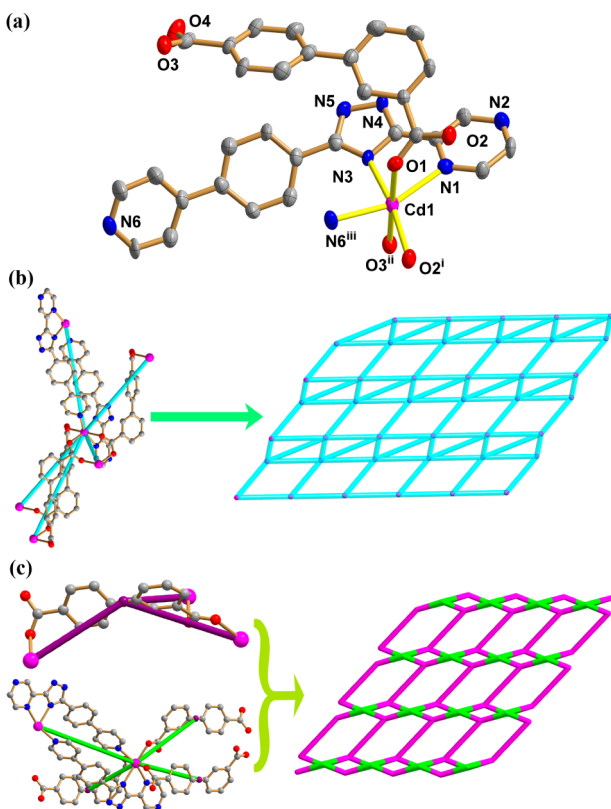

Figure 4. (a) The coordination environment of Cd(II) ion in **4** with the thermal ellipsoids at 50% probability level. (b) Network perspective of the 5-connected **cem** Archimedean layered net topology in **4**. (c) Alternate binodal topological perspective of **4**. The purple and green spheres represent the 3-connected bpba ligand and 4-connected Cd atom nodes, respectively (purple ball, Cd; red ball, O; blue ball, N; gray ball, C) (symmetry codes: (i) $-x + 3$, $-y + 2$, $-z + 1$; (ii) $x + 1$, y, z; (iii) $-x + 2$, $-y + 1$, $-z + 1$).

commonly encountered 5-connected uninodal net with common **bnn** (hexagonal boron nitride),[23] **sqp** (square planar pyramidal) topology,[24] CPs with **cem** topology were limitedly reported,[25] although some examples have been referenced to the Reticular Chemistry Structure Resource (RSCR) database.

Structural Discussion. Four new CPs with multidentate N-ligand and biphenyl-based tetra-, tri-, and bicarboxylates have been synthesized and described. All of these CPs, with the same metal center, were synthesized under similar conditions, but they exhibit distinct coordination structures. The number of coordination sites, coordination modes, and conformations of the organic ligand are decisive factors in shaping up the supramolecular architecture of the resultant CPs; that is to say, slight changes in one or more can have a significant influence on the final structures.

As shown in Scheme 3, both N- and O-donors show different coordination modes. The N-donors adopt different coordina-

Scheme 3. Schematic Representations of the Coordination Modes of Multidentate N-Ligand and Biphenyl-Based Tetra-, Tri-, and Bicarboxylates in 1−4
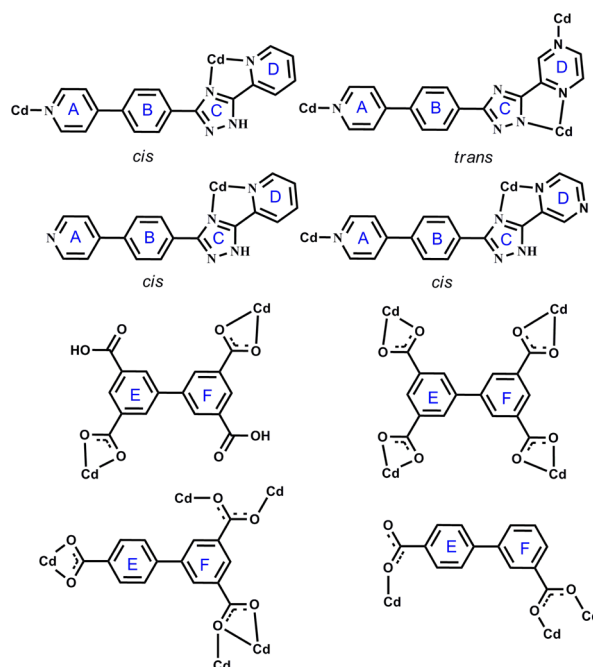

tion modes ranging from the bidentate-chelating + monodentate bridging, bidentate-chelating, to bidentate-chelating + bidentate-bridging modes, while O-donors exhibit μ_2-, μ_4-, μ_5-, and μ_3-modes in **1−4**, respectively. In **1−4**, multidentate N-ligand and biphenyl-based polycarboxylates have four and two aromatic rings, respectively, which could freely rotate along the C−C bonds to adjust themselves to match with the coordination preferences. Considering the conformations of these ligands, we defined six important geometric parameters, α, β, γ, δ, ε, θ, which represent the dihedral angles between aromatic rings A/B, B/C, C/D, A/C, B/D, and E/F, respectively (Scheme 2). The details about these angles were compiled in Table 3. Notably, in **3** and **4**, the Hpptpz ligands adopt completed opposite conformations, cis and trans, respectively. Recently, Tong et al. obtained a 2D Fe(II) CP based on 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazole (2,4-Hbpt), a shorter counterpart of Hpptpd. In that CP, they observed uncommon cis-to-trans isomerization of 2,4-Hbpt phenomenon

Table 3. Dihedral Angles between Different Aromatic Rings in 1–4

|	1	2	3	4
α/deg	28.3(2)	25.41(17)	28.6(3)	21.9(4)
β/deg	38.4(2)	44.68(17)	11.5(3)	34.4(4)
γ/deg	4.4(3)	4.92(16)	2.2(2)	11.7(4)
δ/deg	66.2(2)	70.09(17)	22.1(3)	55.1(4)
ε/deg	42.3(3)	49.60(15)	12.7(2)	45.2(4)
θ/deg	5.4(3)	0	39.2(2)	34.8(4)

without loss of crystallinity, accompanying the totally different spin-crossover behaviors.[26] By comparison, we found that both N- and O-donors can modulate their conformations and coordination modes to fine-tune themselves to satisfy the coordination preference of metal centers and the lower energetic arrangement in the assembly process. In addition, structures of **1** and **2** are also controlled by pH values. The higher pH value (~8) could make H_4bptta completely deprotonated, and vice versa. So different coordination sites and modes create the structural discriminations between **1** and **2**. Affected by above-mentioned factors, CPs **1–4** show highly diverse structures ranging from the 2D + 2D → 2D parallel interpenetrated bilayer structure, 1D ladder, 3D (3,4,4,5)-connected framework, to 2D Archimedean **cem** layer.

Thermal Analysis. The TG analysis was performed in N_2 atmosphere on polycrystalline samples of CPs **1–4**, and the TG curves are shown in Figure 5. In four compounds, all CPs have
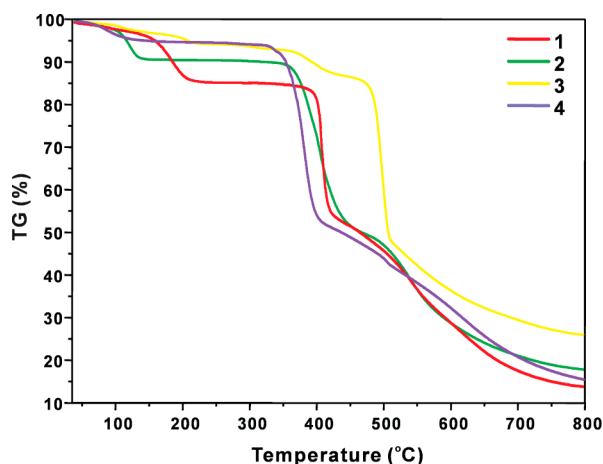
Figure 5. TGA curves for CPs **1–4**.

two identifiable weight loss steps. For **1**, the first weight loss in the temperature range of 50–210 °C is consistent with the removal of lattice water molecule (obsd 15.5%, calcd 16.3%). The anhydrous network does not decompose until 380 °C, and then the collapse of the network of **1** occurs. For **2**, the first weight loss from 60 to 140 °C is attributed to the loss of four lattice water molecules (obsd 10.4%, calcd 11.5%). Above 350 °C, it starts to lose its ligands a result of thermal decomposition. For **3**, the loss of coordinated and uncoordinated water molecules (obsd 5.1%, calcd 4.3%) is observed before 201 °C. The weight loss corresponding to the release of organic ligands is observed from 350 to 515 °C. For **4**, the weight loss of 4.9% from 40 to 115 °C is attributed to the loss of the free water molecules (calcd 5.2%). The weight loss corresponding to the release of organic ligands starts at 325 °C.

Photoluminescence Properties. The emission spectra of **1–4** were examined in the solid state at room temperature, shown in Figure 6. The free Hpptpd and Hpptpz ligand is
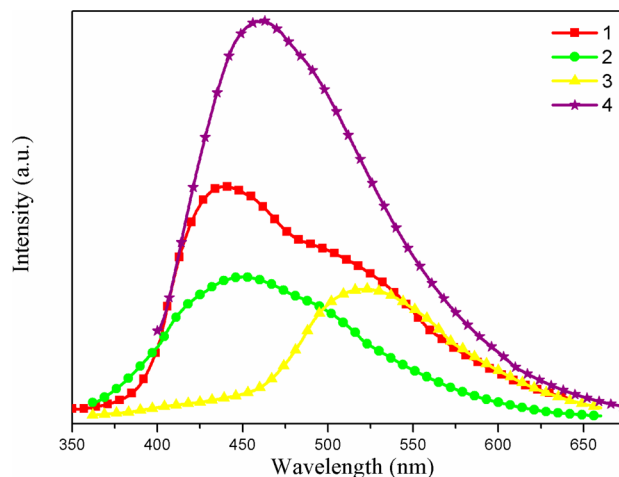
Figure 6. Photoluminescences of CPs **1–4**.

nearly emission silent in the range 350–550 nm under the excitation at 300 nm at room temperature. The emission spectra for **1–4** exhibit maximum emission peaks at 441, 450, 523, and 461 nm, respectively. Both emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature because the Cd(II) ion is difficult to oxidize or reduce due to its d^{10} configuration.[27] Thus, they may be assigned to intraligand ($\pi^* \rightarrow$ n or $\pi^* \rightarrow \pi$) emission.[28] The enhancement of luminescence in d^{10} complexes may be attributed to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.[29] The difference of the emission behaviors for **1–4** probably derives from the differences in the rigidity of solid-state crystal packing.

CONCLUSIONS

Four new CPs based on new designed multidentate N-donors and biphenyl-based polycarboxylates have been synthesized and characterized. These ligands show various coordination sites, modes, as well as conformations; therefore, highly diverse structures ranging from the 2D + 2D → 2D parallel interpenetrated 6^3-**hcb** network, 1D ladder, 3D (3,4,4,5)-connected framework, to the 2D Archimedean **cem** layer are formed. The results also justify that the alliance of new nitrogen-containing and polycarboxylate ligands is good for diversity of the possible structures and topologies. Work is also underway to determine the effects of other coligands on the composition and structure of the supramolecular assemblies.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, and powder X-ray diffraction (PXRD) patterns for **1–4**; CCDC 907922–907925. This material is available free of charge via the Internet at http://pubs.acs.org.

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