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Controlled assembly of zero-, one- and two-dimensional metal-organic frameworks involving in situ ligand synthesis under different reaction pH

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ABSTRACT

Five cadmium(II) metal-organic frameworks, namely $[Cd(BIPA)(daf)(H_2O)_3] \cdot 2H_2O(1)$, $Cd_2(BDC)_2(pdon)_2-(H_2O)_2$ (2), Cd(BIPA)(pdon) (3), Cd(BIPA)(daf) (4) and $[Cd_2(BIPA)_2(pdon)_2] \cdot H_2O$ (5) $(H_2BIPA = 5-bromois ophthalic acid, H_2BDC = terephthalic acid, pdon = 1,10-phenanthroline-5,6-dione, daf = 4,5-diaza-fluoren-9-one), have been constructed from cadmium(II) salts with multi-carboxylate ligands and pdon ligands under different reaction pH. The framework structures of these polymeric complexes have been determined by the X-ray single crystal diffraction technique. The differences of the five metal-organic frameworks demonstrate that the reaction pH has an important effect on the structure of these complexes. The thermal analyses of these five complexes have been measured and discussed. Additionally, four complexes show strong fluorescence in the solid state at room temperature.$

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1. Introduction

The rational design and synthesis of metal-organic frameworks have been of increasing interest recently in materials science and chemical research since they may provide a new strategy for achieving solid functional materials with potential applications in the areas of catalysis, gas storage, magnetism and optics [1,2]. Consequently, a series of metal-organic frameworks with various structural motifs including honeycomb, brick wall, bilayer, ladder, herringbone, diamondoid and rectangular grid, have been deliberately designed and synthesized. Being an important subclass of metal-organic polymers, d¹⁰ metal complexes have been found to exhibit intriguing structures and photoluminescent properties [3]. A series of d¹⁰ metal-organic frameworks with bridging carboxvate ligands and phenanthroline-like terminal chelating ligands have been described recently [4]. So far, many efforts in this field have focused on the influence of ligand spacers of flexible bridging ligands on framework formation of their coordination polymers [5]. However, studies on the effects of the reaction pH on framework formation of complexes have rarely been reported [6].

Additionally, recent studies have revealed that crystal growth under hydrothermal conditions occasionally involves in situ ligand synthesis, which not only provides a powerful synthesis method for organic ligands that are difficult to synthesize but also represents a potential new direction for novel inorganic–organic hybrid network construction through crystal engineering [7,8]. Examples of in situ ligand syntheses under hydrothermal conditions include hydrolysis of –CN and –COOR groups [7], hydroxylation [8] and carbon–carbon bond formation by reductive coupling or oxidative coupling [9].

Taking into account the factors mentioned above, we have paid considerable interest to the reactions of various metal salts with multi-carboxylate ligands and the influence of the reaction pH on the structure of the resultant complexes, and we have found that the reaction pH is one of the key factors in the formation of the coordination architectures [10]. As an extension of our previous work, we are paying attention to 1,10-phenanthroline-5,6-dione (pdon) because of its peculiar reactivity (Scheme 1) in organic chemistry [11]. Two nucleophilic centers (nitrogen and oxygen lone pairs) are contained in the guinone-like pdon molecule, with all the non-hydrogen atoms being sp²-hybridized. The presence of two electronegative heteroatoms not only creates basic properties in the Lewis sense but also, because of conjugation, makes it possible to alter the electron density in different parts of the molecule. As a result, a dramatic change in reactivity can occur, which is not observed in the case of the corresponding aromatic homocyclic analogue, phenanthrenequinone. Herein we report on five new coordination polymers, namely $[Cd(BIPA)(daf)(H_2O)_3] \cdot 2H_2O$ (1), $Cd_2(BDC)_2(pdon)_2(H_2O)_2$ (2), Cd(BIPA)(pdon) (3), Cd(BIPA)(daf)(4) and $[Cd_2(BIPA)_2(pdon)_2] \cdot H_2O$ (5), obtained by the reaction of cadmium(II) salts with multi-carboxylate ligands and pdon ligands under different reaction pH, which involve in situ synthesis of 4,5diaza-fluoren-9-one (daf) from pdon.



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Scheme 1. Schematic representation of the possible transformation mechanism of pdon to daf.

2. Experimental

2.1. Materials and methods

All commercially available chemicals and solvents were of reagent grade and were used as received without further purification. 1,10-Phenanthroline-5,6-dione (pdon) was synthesized following the published procedure [12]. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C Elemental Analyzer at the Analysis Center of Nanjing University. FT-IR spectra were recorded in the range 400–4000 cm⁻¹ on a Bruker Vector22 FT-IR spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a Xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width was 5.0 nm. All the measurements were carried out under the same experimental conditions. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N₂ with a heating rate of 20 °C min⁻¹.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $[Cd(BIPA)(daf)(H_2O)_3] \cdot 2H_2O(1)$

A mixture containing $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), pdon (21.0 mg, 0.1 mmol), H₂BIPA (16.6 mg, 0.1 mmol), NaOH (16.0 mg, 0.4 mmol), 5 ml H₂O and 5 ml CH₃OH (the pH value was 9) was heated at 160 °C for 3 days in a 25 ml Teflon lined stain-

Table 1				
Crystallographic	data	for	complexes	1 - 5

less steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, yellow platelet crystals were produced in a yield of 54%. *Anal.* Calc. for $C_{19}H_{19}N_2BrO_{10}Cd$: C, 36.36; H, 3.05; N, 4.46. Found: C, 36.33; H, 3.04; N, 4.44%. IR (KBr pellet, cm⁻¹): 3397 (br), 3057 (w), 1607 (s), 1582 (s), 1434 (m), 1376 (s), 1307 (m), 1183 (m), 1034 (w), 939 (w), 834 (m), 772 (m), 688 (m), 565 (m), 437 (m).

2.2.2. Synthesis of $Cd_2(BDC)_2(pdon)_2(H_2O)_2$ (2)

A mixture containing $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), pdon (21.0 mg, 0.1 mmol), H_2BDC (16.6 mg, 0.1 mmol), NaOH (8.0 mg, 0.2 mmol) and 10 ml H_2O (the pH value was 7) was heated at 160 °C for 3 days in a 25 ml Teflon lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, yellow platelet crystals were produced in a yield of 58%. *Anal.* Calc. for $C_{40}H_{24}N_4O_{14}Cd_2$: C, 47.59; H, 2.40; N, 5.55. Found: C, 47.61; H, 2.43; N, 5.57%. IR (KBr pellet, cm⁻¹): 3431 (br), 3053 (m), 2358 (w), 1663 (s), 1610 (s), 1576 (s), 1516 (m), 1496 (w), 1442 (m), 1404 (s), 1354 (s), 1311 (s), 1284 (s), 1226 (w), 918 (w), 866 (w), 846 (s), 818 (w), 771 (s), 725 (s), 715 (m), 696 (m), 641 (w), 610 (w), 564 (w), 438 (w).

2.2.3. Synthesis of Cd(BIPA)(pdon) (**3**)

An identical procedure to **2** was followed to prepare **3** except that H_2BDC was replaced by H_2BIPA , and the pH value was adjusted to 7 with NaOH, yield 64%. *Anal.* Calc. for $C_{20}H_9BrN_2O_6Cd$:

Compound	1	2	3	4	5
Empirical formula	C ₁₉ H ₁₉ N ₂ BrO ₁₀ Cd	C40H24N4O14Cd2	C ₂₀ H ₉ BrN ₂ O ₆ Cd	C ₁₉ H ₉ BrN ₂ O ₅ Cd	C40H20Br2N4O13Cd2
Formula weight	627.67	1009.43	565.60	537.59	1149.22
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbcn
a (Å)	6.9994(17)	10.7507(8)	13.9849(19)	14.131(3)	14.0658(14)
b (Å)	10.781(3)	14.5947(11)	7.8845(11)	8.0869(15)	9.5474(10)
c (Å)	15.018(4)	24.4109(18)	16.731(2)	16.515(3)	28.168(3)
α (°)	93.050(3)	90	90	90	90
β(°)	94.117(3)	98.4480(10)	100.079(2)	114.070(2)	90
γ (°)	101.272(3)	90	90	90	90
V (Å ³)	1105.9(5)	3788.6(5)	1816.4(4)	1723.2(5)	3782.7(7)
Ζ	2	4	4	4	4
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
$D_{\text{cacl}} (\text{g cm}^{-3})$	1.885	1.770	2.068	2.072	2.018
μ (mm ⁻¹)	2.853	1.200	3.446	3.623	3.313
F(000)	620	2000	1096	1040	2232
2θ _{max} (°)	25.05	25.00	25.05	25.05	25.04
Data collected	5238	18651	8630	8164	17591
Independent data	3760	6657	3208	3031	3306
R _{int}	0.0356	0.0828	0.0197	0.0255	0.1156
Data/restraints/parameters	3760/2/306	6657/4/541	3208/0/271	3031/0/253	3306/0/280
Goodness-of-fit	1.014	0.934	1.003	1.003	1.002
$R_1 \left[I > 2\sigma(I) \right]^{\rm a}$	0.0585	0.0541	0.0238	0.0245	0.0337
$wR_2 [I > 2\sigma(I)]^{b}$	0.1569	0.1215	0.0651	0.0656	0.0659

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$.

^b $wR_2 = |\sum w(|F_0|^2 - |F_c|^2)| / \sum |w(F_0)^2|^{1/2}, w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]. P = (F_0^2 + 2F_c^2)/3.$

C, 42.47; H, 1.60; N, 4.95. Found: C, 42.51; H, 1.63; N, 4.98%. IR (KBr pellet, cm⁻¹): 3422 (br), 1609 (vs), 1566 (s), 1489 (w), 1478 (w), 1438 (m), 1397 (m), 1375 (s), 1282 (w), 1151 (w), 1125 (w), 932 (w), 771 (s), 738 (m), 696 (m), 524 (m), 435 (m).

2.2.4. Synthesis of Cd(BIPA)(daf) (4)

The preparation of **4** was similar to that described for **1** except that the pH of the solution of H_2BIPA was adjusted to 8 rather than 9, yield: 51%. *Anal.* Calc. for $C_{19}H_9BrN_2O_5Cd$: C, 42.45; H, 1.69; N, 5.21. Found: C, 42.48; H, 1.67; N, 5.19%. IR (KBr pellet, cm⁻¹): 3436 (br), 3051 (m), 2361 (w), 1657 (s), 1608 (s), 1576 (s), 1519 (m), 1485 (w), 1444 (m), 1403 (s), 1371 (s), 1321 (s), 1286 (s), 1233 (w), 1121 (w), 1109 (w), 1045 (w), 1033 (w), 935 (w), 921 (w), 867 (w), 839 (s), 821 (w), 773 (s), 722 (s), 691 (m), 646 (w), 608 (w), 562 (w).

2.2.5. Synthesis of $[Cd_2(BIPA)_2(pdon)_2] \cdot H_2O(5)$

A mixture containing $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), pdon (21.0 mg, 0.1 mmol), H₂BIPA (24.5 mg, 0.2 mmol), NaOH (6.0 mg, 0.15 mmol) and 10 ml H₂O (the pH value was 6) was heated at 180 °C for 3 days in a 25 ml Teflon lined stainless steel vessel under autogenous pressure. After the reaction mixture was

Table 2

Selected bond lengths (Å) and angles (°) for complex $\boldsymbol{1}$

Cd(1)-O(2W)	2.294(4)	Cd(1)-O(1)	2.467(4)
Cd(1)-O(1W)	2.345(4)	Cd(1)-N(1)	2.467(4)
Cd(1)–O(2)	2.350(4)	Cd(1)-N(2)	2.515(5)
Cd(1)-O(3W)	2.361(4)		
O(2W)-Cd(1)-O(1W)	175(1)	O(1W)-Cd(1)-N(1)	95(1)
O(2W) - Cd(1) - O(2)	93(1)	O(2)-Cd(1)-N(1)	155(1)
O(1W) - Cd(1) - O(2)	89(1)	O(3W)-Cd(1)-N(1)	74(1)
O(2W) - Cd(1) - O(3W)	98(1)	O(1)-Cd(1)-N(1)	149(1)
O(1W) - Cd(1) - O(3W)	85(1)	O(2W)-Cd(1)-N(2)	93(1)
O(2)-Cd(1)-O(3W)	81(1)	O(1W)-Cd(1)-N(2)	82(1)
O(2W)-Cd(1)-O(1)	89(1)	O(2)-Cd(1)-N(2)	132(1)
O(1W) - Cd(1) - O(1)	90(1)	O(3W)-Cd(1)-N(2)	142(1)
O(2)-Cd(1)-O(1)	54(1)	O(1)-Cd(1)-N(2)	79(1)
O(3W)-Cd(1)-O(1)	135(1)	N(1)-Cd(1)-N(2)	72(1)
O(2W) - Cd(1) - N(1)	82(1)		

Table 3

Selected bond lengths (Å) and angles (°) for complex 2

Cd(1)-O(1)	2.163(6)	Cd(2)-O(2W)	2.243(6)
Cd(1)-O(1W)	2.221(6)	Cd(2)-O(8)#1	2.337(6)
Cd(1)-N(1)	2.328(7)	Cd(2)-N(3)	2.345(7)
Cd(1)-O(6)	2.327(6)	Cd(2)-N(4)	2.355(8)
Cd(1)-N(2)	2.397(6)	Cd(2)-O(7)#1	2.398(5)
Cd(1)-O(5)	2.398(5)	Cd(2)-C(40)#1	2.734(8)
Cd(2)–O(4)	2.204(5)		
O(1)-Cd(1)-O(1W)	91.2(2)	O(4)-Cd(2)-N(3)	155.1(3)
O(1)-Cd(1)-N(1)	87.6(2)	O(2W)-Cd(2)-N(3)	89.9(2)
O(1W)-Cd(1)-N(1)	114.8(2)	O(8)#1-Cd(2)-N(3)	95.8(2)
O(1)-Cd(1)-O(6)	96.3(2)	O(4)-Cd(2)-N(4)	90.8(2)
O(1W)-Cd(1)-O(6)	149.9(2)	O(2W)-Cd(2)-N(4)	124.0(2)
N(1)-Cd(1)-O(6)	94.7(2)	O(8)#1-Cd(2)-N(4)	90.1(2)
O(1)-Cd(1)-N(2)	158.1(2)	N(3)-Cd(2)-N(4)	69.7(3)
O(1W)-Cd(1)-N(2)	94.8(2)	O(4)-Cd(2)-O(7)#1	115.9(2)
N(1)-Cd(1)-N(2)	70.7(2)	O(2W)-Cd(2)-O(7)#1	91.3(2)
O(6)-Cd(1)-N(2)	89.1(2)	O(8)#1-Cd(2)-O(7)#1	54.5(2)
O(1)-Cd(1)-O(5)	110.1(2)	N(3)-Cd(2)-O(7)#1	89.0(2)
O(1W)-Cd(1)-O(5)	94.9(2)	N(4)-Cd(2)-O(7)#1	137.2(2)
N(1)-Cd(1)-O(5)	145.4(2)	O(4)-Cd(2)-C(40)#1	111.0(2)
O(6)-Cd(1)-O(5)	55(1)	O(2W)-Cd(2)-C(40)#1	118.8(2)
N(2)-Cd(1)-O(5)	90.4(2)	O(8)#1-Cd(2)-C(40)#1	26.9(2)
O(4)-Cd(2)-O(2W)	88.4(2)	N(3)-Cd(2)-C(40)#1	91.4(2)
O(4)-Cd(2)-O(8)#1	99.7(2)	N(4)-Cd(2)-C(40)#1	113.5(2)
O(2W)-Cd(2)-O(8)#1	145.0(2)		

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

slowly cooled down to room temperature, yellow pillar crystals were produced in a yield of 71%. *Anal.* Calc. for $C_{40}H_{20}Br_2N_4O_{13}Cd_2$: C, 41.80; H, 1.75; N, 4.86. Found: C, 41.82; H, 1.77; N, 4.83%. IR (KBr pellet, cm⁻¹): 3455 (br), 3056 (m), 2357 (w), 1667 (s), 1608 (s), 1574 (s), 1513 (m), 1495 (w), 1439 (m), 1405 (s), 1356 (s), 1314 (s), 1286 (s), 1227 (w), 1147 (w), 1123 (m), 1107 (w), 1043 (w), 1032 (w), 935 (w), 919 (w), 864 (w), 843 (s), 821 (w), 768 (s), 723 (s), 719 (m), 694 (m), 637 (w), 607 (w), 562 (w), 441 (w).

2.3. X-ray crystallography

The crystallographic data collections for complexes1-5 were carried out on a Bruker Smart Apex II CCD with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293(2) K using the ω -scan technique. The data were integrated using the same program, which also corrected the intensities for Lorentz and polarization effects [13]. An empirical absorption correction was applied using the sadabs program [14]. The structures were solved by direct methods using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [15,16]. The hydrogen atoms of water molecules were located from difference Fourier maps and the other hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package. The details of the crystal parameters, data collection and refinement for four complexes are summarized in Table 1. Selected bond lengths and angles with their estimated standard deviations for 1, 2, 4 and 5 are shown in Tables 2–5, respectively.

3. Results and discussion

3.1. Crystal structures of complexes 1-5

3.1.1. $[Cd(BIPA)(daf)(H_2O)_3] \cdot 2H_2O(1)$

X-ray single-crystal structural analysis revealed that complex **1** crystallizes in the triclinic space group $P\bar{1}$ and that the pdon ligand

Table 4	
Selected bond lengths (Å) and angles (°) for complex 4	

Cd(1)-O(1)	2.222(2)	Cd(1)-N(2)	2.378(3)
Cd(1)-O(3)#1	2.228(2)	Cd(1)-N(1)	2.477(3)
Cd(1)-O(2)#2	2.298(2)		
O(1)-Cd(1)-O(3)#1	89.71(9)	O(2)#2-Cd(1)-N(2)	107.41(8)
O(1)-Cd(1)-O(2)#2	101.12(8)	O(1)-Cd(1)-N(1)	108.39(8)
O(3)#1-Cd(1)-O(2)#2	84.55(8)	O(3)#1-Cd(1)-N(1)	161.06(9)
O(1)-Cd(1)-N(2)	151.48(9)	O(2)#2-Cd(1)-N(1)	86.46(8)
O(3)#1-Cd(1)-N(2)	92.88(9)	N(2)-Cd(1)-N(1)	73.99(9)

Symmetry transformations used to generate equivalent atoms: #1 - x + 1, y - 1/2, -z + 3/2; #2 - x + 1, -y + 1, -z + 1.

Table 5	
Selected bond lengths (Å) and angles (°) for complex 5	;

Cd(1)-O(4)#1	2.185(3)	Cd(1)-N(1)	2.322(3)
Cd(1)-O(3)#2	2.254(2)	Cd(1)-N(2)	2.352(2)
Cd(1)-O(2)	2.257(2)	Cd(1)-O(1)	2.561(2)
O(4)#1-Cd(1)-O(3)#2	96.7(1)	O(2)-Cd(1)-N(2)	176.30(9)
O(4)#1-Cd(1)-O(2)	83.94(9)	N(1)-Cd(1)-N(2)	70.64(9)
O(3)#2-Cd(1)-O(2)	92.90(9)	O(4)#1-Cd(1)-O(1)	137.21(9)
O(4)#1-Cd(1)-N(1)	114.3 (1)	O(3)#2-Cd(1)-O(1)	88.90(9)
O(3)#2-Cd(1)-N(1)	142.81(9)	O(2)-Cd(1)-O(1)	53.36(8)
O(2)-Cd(1)-N(1)	109.69(9)	N(1)-Cd(1)-O(1)	82.16(8)
O(4)#1-Cd(1)-N(2) O(3)#2-Cd(1)-N(2)	92.6(1) 88.70(9)	N(2)-Cd(1)-O(1)	

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

was transformed in situ into daf during the hydrothermal process. The asymmetric unit in **1** consists of one Cd(II) atom, one BIPA ligand, three coordinated water molecules and two lattice water molecules. Each Cd(II) atom is seven-coordinated with a distorted pentagonal bipyramidal geometry, being coordinated by two nitrogen atoms of one daf in a chelate mode, two oxygen atoms of one carboxylate group and three aqua ligands. Two nitrogen atoms (N1, N2) and three oxygen atoms (O1, O2, O3W) lie in the equatorial plane, while the other two other aqua ligands occupy the apical positions, as shown in Fig. 1a. The coordination bond lengths and angles around the Cd(II) centre are in the range 2.294(4)– 2.515(5) Å and 54.08(14)–175.65(13)°, respectively, as listed in Table 2.

The coordination modes of BIPA and BDC in this work are summarized in Scheme 2. As can be seen in Scheme 2a, one carboxylate group adopts a bidentate chelating mode and the other carboxylate group remains depronated and does not take part in the coordination. As a result complex **1** is a zero-dimensional complex and is further linked into a 1D chain structure through $\pi \cdots \pi$ interactions (Fig. 2b).

In the packing structure of **1**, as shown in Fig. 1c, the 1D chains are firstly linked into a 2D layer by $O-H\cdots O$ hydrogen bonds between the oxygen atoms of the coordinated water molecules (O2W and O3W) and the carboxylate group from adjacent chains, with $O\cdots O$ distances ranging from 2.744(6) to 2.874(6) Å (Table S1). Then the 2D layers are further connected through $O-H\cdots O$ hydrogen bonds between the oxygen atoms of the coordinated water molecules (O1W and O2W) and the oxygen atoms of the lattice water molecules (O4W and O5W) with $O\cdots O$ distances of 2.744(6) and 2.756(3) Å (Fig. 1c, Table S1).

Although pdon was used as the original organic reagent in the preparation of **1**, the daf ligand was unexpectedly found in the final



Fig. 1. (a) Coordination environment of the Cd(II) atom in complex **1** with the ellipsoids drawn at the 30% probability level, hydrogen atoms and water molecules are omitted for clarity. (b) Side view of **1** showing the 1D chain structure through $\pi \cdots \pi$ interactions (the coordinated water molecules and lattice water molecules are omitted for clarity). (c) Projection of the structure of **1** along *a*-axis (dotted lines represent hydrogen-bonding).

products, which indicates an in situ transformation of pdon into daf during the course of the hydrothermal treatment. As shown in the literature [8] on ligand reactions under hydrothermal conditions in the presence of metal ions, the ligation of the metal ion will cause some decrease of electron density on the aromatic ring of the organic ligand, and hence promote nucleophilic attack by water molecules or hydroxy groups. In this case, it seems most probable that the hydroxy groups act effectively as nucleophiles, attacking the carbonyl carbon atoms of pdon. As a result, the hydration of the carbonyl groups of pdon furnishes an intermediate diol or even a double diol. When the sp² carbonyl carbon atoms become sp³hybridized, the carbon-carbon bond is then cleaved, probably because of the crowding, resulting in the formation of daf. The formation mechanism of daf in 1 shows some similarity to that of dimethyl 2,2'-bipyridine-3,3'-dicarboxylate in a previously reported pure organic reaction [11b]. Although the exact mechanism of ligand transformation has not vet been proved, slow hydrolysis of the carbonyl groups ensures that an excess of NaOH remains in solution, thereby promoting the formation of less soluble polymeric networks. Equally important, the in situ slow daf formation also ensures the growth of large single crystals that are suitable for X-ray structure determination.

3.1.2. Cd₂(BDC)₂(pdon)₂(H₂O)₂ (**2**)

Single-crystal X-ray diffraction analysis revealed that complex 2 is a 1D zigzag coordination polymer. The asymmetric unit of 2 contains two cadmium atoms, two BDC ligands, two pdon ligands and two coordinated water molecules. As illustrated in Fig. 2a, the two Cd atoms are both six-coordinated by three oxygen atoms from two different BDC ligands, two nitrogen atoms from one pdon molecule and one oxygen atom from a coordination water molecule to give a distorted octahedral geometry. The Cd-O bond lengths fall in the range 2.163(6)-2.398(5) Å and the Cd-N bond lengths fall in the range 2.328(7)-2.397(6) Å (Table 3), which are in good agreement with those found in other Cd-containing coordination frameworks [17]. The BDC^{2–} ligands acts as a bidentate bridging ligand, but the coordination modes of the carboxyl groups are different. one adopt a bis(bidentate) chelating mode, while the other adopts a bis(monodentate) mode (Scheme 2d and e). Each BDC ligand bridges two cadmium atoms to form a 1D zigzag infinite chain (Fig. 2b) with Cd···Cd distances of 11.551 and 11.191 Å. The 1D zigzag chains form a 2D undulating network due to hydrogenbonding interactions between the coordinated water molecule and the carboxylate group (Table S1). Adjacent 2D networks are ultimately extended into a 3D supramolecular structure through π - π stacking interactions with a centroid-to-centroid distance of 3.775(3) Å between pdon ligands (Fig. 2c).

3.1.3. Cd(BIPA)(pdon) (3) and Cd(BIPA)(daf) (4)

The results of X-ray crystallographic analysis revealed that complexes **3** and **4** crystallize in the same monoclinic $P2_1/c$ space group with similar cell parameters (Table 1), which indicate that they are isomorphous and isostructural. Thus, as a typical example, only the structure of **4** is described here in detail. The asymmetric unit of **4** consists of one Cd(II) atom, one BIPA ligand and one daf ligand. The Cd(II) atom is in a square-pyramidal coordinated geometry with three oxygen atoms and two nitrogen atoms. Two oxygen atoms (Cd1–O1 = 2.222(2) Å, Cd1–O2 = 2.298(2) Å) from two carboxylate groups of the BIPA ligands and two nitrogen atoms (Cd1–N1 = 2.477(3) Å, Cd1–N2 = 2.378(3) Å) from one def ligands are ligated to the Cd(II) ion in the quasi-plane, with another oxygen atom belonging to the third BIPA ligand (Cd1–O3 = 2.228(2) Å) being located in the axial position (Table 4), as displayed in Fig. 3a.

Different from that of complex **1**, each BIPA ligand acts as a triconnector linking three Cd(II) atoms in complex **4** (Scheme 2c), one of carboxylate groups is connected with one Cd(II) atom through a monodentate O atom, while the other bonds with two Cd(II) atoms, consequently resulting in the formation of a 2D layer (Fig. 3b). The 2D layer is developed in an undulated bilayer pattern parallel to the *bc*-plane. By treating the Cd(II) atom as a single node and connecting the nodes according to the connectivity defined by the geometrical centers of the benzene rings of the BIPA ligands, a distorted 2D (4.8^2) network (denoted the feb net) [18] sustained by 3-connected nodes is then yielded, as illustrated in Fig. 3c. The van de Waals interactions extend the 2D layer into a 3D supramolecular net.

3.1.4. $[Cd_2(BIPA)_2(pdon)_2] \cdot H_2O(5)$

In order to further investigate the pH influence on the formation and structure of the complex, the pH value of the ligand solution was carefully adjusted to 6.0, while the other experimental conditions remained the same as those used for the preparation of **3**. As a result, complex **5** was obtained with an entirely different structure. The asymmetric unit of complex **5** contains one Cd ion, one



Scheme 2. Coordination modes of the BIPA and BDC ligands in complexes 1-5.

а

С







Fig. 2. (a) Coordination environment of the Cd(II) atom in complex **2** with the ellipsoids drawn at the 30% probability level, hydrogen atoms are omitted for clarity. (b) Onedimensional zigzag chain structure of complex **2**. (c) Projection of the structure of **2** along *a*-axis (dotted lines represent hydrogen-bonding).

pdon ligand, one BIPA ligand and half of the lattice water molecule. As shown in Fig. 4a, the Cd atom shows a distorted-octahedral

geometry, being chelated by two N atoms from one pdon ligand. The remaining four coordination sites are occupied by four oxygen



Fig. 3. (a) Coordination environment of the Cd(II) atom in complex **4** with the ellipsoids drawn at the 30% probability level, hydrogen atoms are omitted for clarity. (b) 2D layer structure of complex **4** along the *a*-axis. (c) Projection of the structure of **4** showing the (4.8^2) net based on Cd atoms and BIPA ligands.

atoms from three BIPA ligands. The Cd–O bond lengths are in the range 2.185(3)–2.561(2) Å and the Cd–N bond lengths are 2.322(3) and 2.352(2) Å (Table 5). In complex **5**, the BIPA ligands adopt a coordination mode different from those in complexes **1**, **3** and **4**: it acts as a tri-connector to link three Cd atoms through one bis-monodentate carboxylic O atom from one carboxylate group and a bidentate carboxylic O atom from the other carboxyl-ate group, as depicted in Scheme 2b.

As shown in Fig. 4b, the bidentate carboxylic group links two Cd atoms in a syn-anti fashion to form a one-dimensional zigzag chain structure with a Cd...Cd separation of 5.135(3) Å, in which the distances are in the normal range compared with those reported (4.972-5.256 Å) in the literature [19]. The 1D Cd(CO₂) chains are further bridged into a two-dimensional undulating bilayer structure through the other carboxylate group. Interestingly, when viewed along the *b*-axis, the two-dimensional layer contains rectangular windows with dimensions of ca. $4.974 \times 5.535 \, \text{\AA}^2$ that are occupied by pdon ligands and the lattice water molecules. By treating the Cd(II) atom as a single node and connecting the nodes according to the connectivity defined by the geometrical centers of the benzene rings of the BIPA ligands, a distorted 2D (4.10^2) network (denote the KIb net) [20] sustained by three-connected nodes is then yielded, as illustrated in Fig. 4c. The van de Waals interactions extend the 2D layer into a 3D supramolecular framework.

3.2. Effect of synthetic conditions on the structures of the complexes

It has been reported that synthetic conditions, such as pH value, reaction temperature, solvent, etc., are the key factors in assembling MOFs. As to the synthesis of **1**, **3** and **4**, all the reaction conditions are the same except for the difference of the reaction pH. As a result, complex **1**, obtained at a relatively high pH value, is a OD structure with the Cd(II) center bonded by three water molecules,

and it is accompanied by an in situ reaction. While in **4**, obtained at a slightly lower pH than **1**, a more complicated 2D network was generated, also accompanied by an in situ reaction. However for **3**, obtained at a pH close to 7, its framework is similar to that of **4**, but the in situ reaction did not happen in the absence of alkali. Therefore, a rough conclusion could be made that the pdon ligand can be converted into the daf ligand in the presence of alkali, which is in agreement with the previous reports [21].

In addition, it might be ascribed to the fact that the carboxylate ligands were deprotonated before the in situ reaction by a comparison of **3** and **4**. From the points discussed above, it is suggested that the increase of reaction pH may result in a different connectivity of the carboxylate ligand, controlling the in situ reaction and further fabricating a more complicated structure.

3.3. Properties

3.3.1. Luminescent properties

Inorganic–organic hybrid coordination complexes, especially with d¹⁰ metal centers, have been investigated for fluorescence properties owing to their potential applications as luminescent materials, such as light-emitting diodes (LEDs) [22]. Therefore, in the present study, the photoluminescence properties of **2–5** as well as free H₂BIPA and the H₂BDC ligand were investigated in the solid state at room temperature. As shown in Fig. 5, there are two intense emission peaks at 413 and 435 nm ($\lambda_{ex} = 310$ nm) for **2**, 421 and 442 nm ($\lambda_{ex} = 330$ nm) for **3**, 422 and 450 nm ($\lambda_{ex} = 334$ nm) for **5**. For excitation wavelengths between 280 and 480 nm, there is no obvious emission observed for free H₂BIPA and H₂BDC under the same experimental conditions, while it is reported that free pdon shows fluorescence emission in the solid state. The emission bands for phen are at 371 and 395 nm ($\lambda_{ex} = 290$ nm) [23], and compared with the pdon ligand a clear



Fig. 4. (a) Coordination environment of the Cd(II) atom in complex **5** with the ellipsoids drawn at the 30% probability level, hydrogen atoms are omitted for clarity. (b) Bilayer structure of complex **5** along the *a*-axis. (c) Projection of the structure of **5** showing the (4×10^2) net based on Cd atoms and BIPA ligands.

red shift occurs in **2**, **3** and **5**, which might also be attributed to a ligand-to-metal charge transfer (LMCT) transition [24]. There is only a intense emission peak at 406 nm for **4**, which means a red shift of ca. 40 nm relative to that of the free daf (λ_{max} = 375 nm) [25]. We tentatively assign it to a LMCT transition [26].

3.3.2. Thermal properties

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stabilities of **1–5**. The results show that complexes **1–5** are very stable in air at ambient temperature, which make them potential candidates for practical applications. The samples were heated up in air at 1 atm pressure with a heating rate of 20 °C min⁻¹, as shown in Fig. 6. The TGA curve shows that**1** is stable up to 96 °C. A weight loss of 5.6% occurred in the temperature range 96–128 °C, presumably due to the removal of two lattice water molecules (calcd. 5.7%). A total weight loss of 8.4% occurred in the temperature range 136–200 °C, mainly corresponding to the removal of the one coordinated water molecule per formula unit (calcd. 8.6%). Another weight loss of 65.7% occurred in the temperature range 300–465 °C, corresponding to the removal of one BIPA ligand and one pdon ligand per formula unit (calcd. 66.2%), no weight losses were observed up to 800 °C, indicating the complete deposition of the complex with the formation of CdO as the final product. The TGA curve of **2** shows that the first weight loss of 3.4% between 110 and 160 °C corresponds to the loss of the two coordinated water molecule per formula unit (calcd. 3.56%), then



Fig. 5. The emission spectra of 2–5 in the solid state at room temperature.



Fig. 6. TG curve of complexes 1-5.

it was stable up to 290 °C. The framework collapsed in the temperature range 290–800 °C before the final formation of a metal oxide. The TGA curve shows that **3** and **4** are stable up to 300 °C. The framework collapsed in the temperature range 300–800 °C, suggesting that the organic ligands decompose slowly over a wide temperature range. The TGA curve of **5** shows that the first weight loss of 1.51% between 90 and 136 °C corresponds to the loss of the one lattice water molecules (calcd. 1.57%), and then it is stable up to 280 °C. The framework collapsed in the temperature range 280– 800 °C, before the final formation of a metal oxide.

4. Conclusion

In summary, we have synthesized five novel metal-organic frameworks based on multi-carboxylate ligands and a chelate ligand by hydrothermal reactions. The successful syntheses of the five complexes indicate that it is promising to build up unusual architectures via a different reaction pH, thus opening up a new field in the preparation of metal coordination polymers with potential luminescent properties.

5. Supplementary data

CCDC 675859, 666353, 675860, 675861 and 675862 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. These data

can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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