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Syntheses, Structures, and Photochemical Properties of Six New Metal–Organic Frameworks Based on Aromatic Dicarboxylate Acids and V-Shaped Imidazole Ligands

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ABSTRACT: Solvothermal reactions of 4,4'-bis(imidazol-1-yl)diphenyl ether (BIDPE) with deprotonated 1,4-benzenedicarboxylic acid (H₂bdc) in the presence of cadmium, zinc, cobalt, nickel, and manganese salts in H₂O or H₂O/DMF yielded six new complexes, namely, {[Co(BIDPE)(bdc)]₂·(H₂O)₂(DMF)}_n (1), {[Cd(BIDPE)(bdc)]₄·(H₂O)₄(DMF)₂}_n (2), {[Zn(BIDPE)(bdc)]₂· (H₂O)₂(DMF)}_n (3), [Cd₃(BIDPE)₂(bdc)₃]_n (4), and [Ni(BIDPE)(bdc)(H₂O)₂]_n (5), and [Mn(bdc)(BIDPE)(H₂O)]_n (6). These complexes were characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. Complexes 1 and 3 reveal a 2-fold interpenetrating three-dimensional (3D) framework constructed from BIDPE and H₂bdc with Co and Zn salts; complexes 2 and 4 have the same staring materials but possess different 3D frameworks and are prepared from BIDPE and H₂bdc under different reaction conditions. In complexes 5 and 6, BIDPE and H₂bdc link Ni and Mn centers, respectively, to generate 2D → 2D interlocked sheets. The thermal stabilities and photochemical properties of these new complexes have also been studied.

Introduction

Crystal engineering of coordination polymers has attracted great attention due to their novel architectures and potential applications in photochemical areas,¹ molecular magnetism,² heterogeneous catalysis,³ and molecular sorption.⁴ However, many factors, such as organic ligands,⁵ solvent systems,⁶ metal ions,⁷ and counterions,⁸ have been found to greatly influence the structures in the self-assembly process, and they may play a key role in predicting the construction of molecular architectures. Systematic studies of diversified conditions leading to different structures in the formation of coordination polymers are thus important and of intense interest.

Recently, a large number of mixed-ligand metal-organic frameworks (MOFs) have been reported,⁹ most of which contain N-containing ligands introduced into metal-polycarboxylate systems. The combination of different ligands may result in greater tunability of structural frameworks than that present with single ligands. Hence, a mixed-ligand is undoubtedly a good choice for the construction of new polymeric structures. Imidazole ligands have been used in the synthesis of unique MOFs which possess excellent coordination ability and allow free rotation of the imidazole ring to meet the requirement of coordination geometries of metal ions. Until now, a great number of ingenious MOFs have been synthesized designed based on imidazole ligands.¹⁰ Syntheses of new imidazole ligands are still a long-standing fascination of chemists, and we have designed and synthesized a new V-shape imidazole

ligand, 4,4'-bis(imidazol-1-yl) diphenyl ether (BIDPE), which may be regarded as a half-flexible ligand. To test the ability of this ligand to give new architectures and topologies, we have selected this new ligand, H₂bdc ligand (Scheme 1), and different bivalent metal salts, to prepare solvothermally six new coordination polymers with intriguing structures, namely, {[Co-(BIDPE)(bdc)]₂·(H₂O)₂(DMF)}_n (1), {[Cd(BIDPE)(bdc)]₄· (H₂O)₄(DMF)₂}_n (2), {[Zn(BIDPE)(bdc)]₂·(H₂O)₂(DMF)}_n (3), [Cd₃(BIDPE)₂(bdc)₃]_n (4), [Ni(BIDPE)(bdc)(H₂O)₂]_n (5), and [Mn(bdc)(BIDPE)(H₂O)]_n (6). All compounds were characterized by elemental analysis, IR spectra, and X-ray crystallography. The crystal structures, topological analyses, and thermal properties of these compounds are presented. In addition, the photochemical properties of these complexes are discussed in detail.

Experimental Section

Materials and Measurements. The reagents and solvents employed were commercially available and used as received. IR absorption spectra of the complexes were recorded in the range of 400-4000 cm⁻ ona Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H, and N analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å), in which the X-ray tube was operated at 40 kV and 40 mA. NMR spectra were recorded on a Bruker NMR 500 DRX spectrometer. Solid-state UV-vis diffuse reflectance spectra were obtained at room temperature using a Shimadzu UV-3600 double monochromator spectrophotometer, and BaSO₄ was used as a 100% reflectance standard for all materials. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature.



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The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin-Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min⁻¹ under N₂ atmosphere.

Synthesis of 4,4'-Bis(imidazol-1-yl)diphenyl Ether (BIDPE). A mixture of Cu₂O (0.07 g, 0.5 mmol), 4,4'-dibromodiphenyl ether (3.24 g, 10 mmol), imidazole (2.72 g, 4.0 mmol), and K₂CO₃ (5.52 g, 4.0 mmol) in anhydrous DMF (30 mL) in a 100-mL two-necked round-bottom flask under N2 was stirred at 150 °C for 48 h. The reaction mixture was filtered, and then the filtrate was added into 200 mL of H₂O. The deposit was filtered and washed with water and dried in vacuum to afford the product in 80%. ¹H NMR: (CDCl₃, 500 Hz) δ 7.39 (d, J = 9.0 Hz, 4H), 7.21 (s, 2H), 7.26 (s, 2H), 7.38 (d, J = 9.0 Hz, 4H), 7.82 (s, 2H) ppm (Supporting Information, Figure S1). MS (EI): m/z = 303 (M⁺). Anal. Calcd for C₁₈H₁₄N₄O: C, 71.51; H, 4.67; N, 18.53. Found: C, 71.48; H, 4.55; N, 18.66. IR (KBr, cm⁻ ¹): 3122(w), 3108(w), 1510(s), 1304(m), 1234(s), 1170(m), 1108(m), 1061(s), 961(m), 910(m), 869(m), 829(s), 762(m), 657(s), 520(m). Melting point: 150-151 °C.

Synthesis of {[**Co**(**BIDPE**)(**bdc**)]₂·(**H**₂**O**)₂(**DMF**)}_{*n*}(1). A mixture of Co(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol), H₂bdc (16.6 mg, 0.1 mmol), and BIDPE (30.2 mg, 0.1 mmol) in 12 mL of DMF/H₂O (3:1, v/v) was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 90 °C for 3 days. Purple crystals were obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions to give 1 in 66% yield based on BIDPE. Anal. Calcd for C₅₄H₄₄O₁₃N₉Co₂: C, 56.65; H, 3.87; N, 11.01. Found: C, 56.62; H, 3.85; N, 11.04. IR (KBr, cm⁻¹): 3439(w), 3415(w), 2361(w), 1649(m), 1613(m), 1578(s), 1518(s), 1384(s), 1307(w), 1237(s), 1175(w), 1122(m), 1067(s), 1013(w), 964(w), 835(m), 751(s), 653 (m), 528(m).

Synthesis of { $[Cd(BIDPE)(bdc)]_4 \cdot (H_2O)_4(DMF)_2$ }_n (2). A mixture of Cd(NO₃)₂ · 4H₂O (30.1 mg, 0.1 mmol), H₂bdc (16.6 mg, 0.1 mmol), and BIDPE (30.2 mg, 0.1 mmol) was dissolved in 12 mL of DMF/H₂O (3:1, v/v). The final mixture was placed in a Parr Teflonlined stainless steel vessel (15 mL) under autogenous pressure and heated at 90 °C for 3 days. The large quantities of colorless-plank crystals of **2** were obtained in 76% yield based on BIDPE. Anal.

Scheme 1. Two N-Containing and Dicarboxylate Ligands



4,4'-bis(imidazol-1-yl) phenyl ether (BIDPE) 1,4-benzenedicarboxylate (H2bdc)

Calcd for $C_{110}H_{98}O_{28}N_{18}Cd_4$: C, 51.43; H, 3.81; N, 9.82. Found: C, 51.35; H, 3.85; N, 9.83. IR (KBr, cm⁻¹): 3456(w), 3115(w), 1554(s), 1518(s), 1383(s), 1240(s), 1123(m), 1067(s), 1015(w), 964(w), 930(w), 855(m), 824(s), 745(s), 653(m), 531(m).

Synthesis of {[**Zn**(**BIDPE**)(**bdc**)]₂ · (**H**₂**O**)₂(**DMF**)}_{*n*} (3). Compound **3** was prepared in a process similar to that for compound **1**. Zn(NO₃)₂ · 6H₂O (29.7 mg, 0.1 mmol), H₂bdc (16.6 mg, 0.1 mmol), and BIDPE (30.2 mg, 0.1 mmol) were dissolved in 12 mL of DMF/H₂O (3:1, v/v). Colorless-plank crystals of **3** were obtained in 65% yield based on BIDPE. Anal. Calcd for C₅₄H₄₄O₁₃N₉Zn₂: C, 56.02; H, 3.83; N, 10.89. Found: C, 55.98; H, 3.87; N, 10.91. IR (KBr, cm⁻¹): 3416(w), 3139(w), 1593(s), 1519(s), 1396(m), 1351(s), 1239(s), 1172(w), 1122(s), 1066(s), 1013(w), 829(s), 750(s), 653(m), 529(m).

Synthesis of $[Cd_3(bdc)_3(BIDPE)_2]_n$ (4). Compounds 4 and 2 have the same stoichiometric ratios of staring materials, but the reaction conditions are different. The materials were dissolved in 10 mL of distilled water. The pH value of the solution was adjusted to 7.0 by addition of 1 M NaOH solution. The final mixture was sealed in a 15 mL Parr Teflon-lined stainless-steel vessel and heated at 140 °C for 3 days. After the reaction system was cooled to room temperature, colorless block crystals of 4 were obtained (yield: 53% based on BIDPE). Calcd for C₆₀H₄₀O₁₄N₈Cd₃: C, 50.25; H, 2.81; N, 7.81. Found: C, 50.21; H, 2.84; N 7.86. IR (KBr, cm⁻¹): 3358(m), 3133(m), 3072 (w), 1719(w), 1542(s), 1514(m), 1378(s), 1304(w), 1230(s), 1120(s), 1058(s), 1016(w), 933(w), 866(s), 751(s), 650(m).

Synthesis of [Ni(bdc)(BIDPE)(H₂O)₂]_{*n*} (5). Compound 5 was prepared by a process similar to that yielding compound 1 by using Ni(NO₃)₂·4H₂O (25.4 mg, 0.1 mmol), H₂bdc (16.6 mg, 0.1 mmol), and BIDPE (30.2 mg, 0.1 mmol) in 8 mL of DMF and H₂O (1:1, v/ v). Green crystals were obtained (yield: 56% based on BIDPE). Anal. Calcd for C₂₆H₂₂O₇N₄Ni: C, 55.65, H; 3.95; N, 9.98. Found: C, 55.62; H, 3.97; N, 10.04. IR (KBr, cm⁻¹): 3441(w), 3127(w), 1552(s), 1515(s), 1377(s), 1272(w), 1244(s), 1169(w), 1132(w), 1211(s), 1104(w), 1060(s), 1039(m), 971(w), 898(s), 880(s), 829(s), 783(s), 718(s), 666 (m), 570(m), 540 (s).

Synthesis of $[Mn(bdc)(BIDPE)(H_2O)]_n$ (6). Compound 6 was prepared in a manner similar to that used for compound 1 by using MnCl₂·4H₂O (19.7 mg, 0.1 mmol), H₂bdc (16.6 mg, 0.1 mmol), and BIDPE (30.2 mg, 0.1 mmol) in 10 mL of DMF and H₂O (1:4, v/v). Colorless crystals were obtained (yield: 56% based on BIDPE). Anal. Calcd for C₂₆H₂₀N₄O₆Mn: C, 57.89; H 3.74; N, 10.39. Found: C, 57.93; H, 3.81; N, 10.41. IR (KBr, cm⁻¹): 3421(w), 3133(w), 1669(s), 1568(w), 1518(s), 1380(m), 1304(m), 1240(s), 1173(m), 1119(m), 1060(s), 1011(w), 960(w), 927(w), 838(s), 731(s), 654(s), 527 (s).

X-ray Crystallography. Single crystals of 1-6 were prepared by the methods described in the synthetic procedures. X-ray crystallographic data of 1-6 were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements

Table 1. Crystallographic Data and Structure Refinement Details for Complexes 1-6

	1	2	3	4	5	6
formula	C54H44O13N9C02	C110H97O28N18Cd4	C54H44O13N9Zn2	C60H40O14N8Cd3	C ₂₆ H ₂₂ O ₇ N ₄ Ni	C ₂₆ H ₂₀ N ₄ O ₆ Mn
formula weight	1140.8	2569.66	1157.76	1434.20	561.17	539.40
crystal system	tetragonal	tetragonal	tetragonal	monoclinic	monoclinic	monoclinic
space group	$I4_1/acd$	$I4_1/acd$	I4 ₁ /acd	P21/n	P21/n	P21/c
a (Å)	18.4905(17)	18.903(3)	18.3863(17)	9.961(2)	6.3784(9)	12.1170(16)
$b(\mathbf{A})$	18.4905(17)	18.903(3)	18.3863(17)	17.750(4)	17.552(3)	18.247(2)
c (Å)	61.775(8)	62.293(9)	61.935(12)	15.444(4)	22.179(3)	21.183(3)
α (deg)	90.00	90.00	90.00	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00	92.662(5)	93.715(3)	97.541(3)
γ (deg)	90.00	90.00	90.00	90.00	90.00	90.00
$V(A^3)$	21121(4)	22258(6)	20937(5)	2727.8(11)	2477.9(6)	4643.1(11)
Z	16	8	16	2	4	8
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.435	1.533	1.469	1.746	1.504	1.543
$\mu(Mo K\alpha) (mm^{-1})$	0.702	0.838	0.991	1.237	0.838	0.621
F(000)	9360.0	10400	9520.0	1424	1160	2216
tot, uniq data	4614	4856	4611	4790	4841	8710
R(int)	0.0825	0.078	0.1171	0.0678	0.0641	0.0692
observed data $[I > 2\sigma(I)]$						
$[I > 2\sigma(I)]$	3209	3713	2118	3507	2884	5102
R1, wR2 $[I > 2\sigma(I)]$	0.0754, 0.1657	0.0627, 0.1853	0.0635, 0.1588	0.0477, 0.1346	0.0518, 0.0929	0.0566, 0.0979
S	1.082	1.120	1.009	1.084	0.855	0.952
min and max. resd dens $(e \cdot \text{\AA}^{-3}) (e \cdot \text{\AA}^{-3})$	-0.413, 0.646	-1.407, 1.761	-1.119, 0.665	-2.19, 2.23	-0.342, 0.383	-0.348, 0.411



Figure 1. (a) Coordination environment of the Co(II) ion in 1. The hydrogen atoms are omitted for clarity. Symmetry codes: (#1) 0.5 + x, 1 - y, *z*. (b) Views of the 1D wavelike chain with a helical channel of BIDPE ligands and Co ions. (c) Views of the 1D zigzag chain of bdc²⁻ and Co ions. (d) Views of 1D helical channels. (e) Perspective of 3D framework in 1 along the *a* axis. (f) Illustration of solvents position. (g) Schematic representation of a single 3D framework of compound 1. (h) 2-fold interpenetrating framework in 1.

were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures of **1–6** were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2 values.¹¹ The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The relevant crystallographic data are presented in Table 1, while the selected bond lengths and angles are given in Supporting Information Table S1.

Results and Discussion

Crystal Structure of $\{[Co(BIDPE)(bdc)]_2 \cdot (H_2O)_2(DMF)\}_n$ (1). X-ray analysis reveals that compounds 1, 2, and 3 are isostructural. These compounds are self-assembled from the BIDPE and bdc^{2-} anions with Co(II), Cd(II), or Zn(II) salts, which are further connected into a 3D network. Hence, only the crystal structure of compound 1 is described in detail here. Compound 1 crystallizes in the tetragonal space group $I4_1/acd$. The asymmetric unit of 1 contains an independent Co(II) cation, one bdc^{2-} anion, one BIDPE ligand, one free water, and half a disordered DMF molecule. As shown in Figure 1a, carboxylate groups of bdc^{2-} adopt two coordination modes: one carboxylate group adopts a monodentate coordinates to the same Co center by adopting a chelating coordinated by three carboxylic O atoms from two H₂bdc ligands and two nitrogen atoms from two BIDPE ligands to

Scheme 2. Crystallographically Established Coordination Modes of Carboxylic Groups in Compounds 1–6



form a distorted trigonal bipyramidal geometry. The Co–O lengths are in the range of 1.989(4)-2.387(4) Å, and the Cd–N lengths are 2.036(4)-2.0575(4) Å, which are all similar to those values found in other Co(II) complexes.

The neighboring Co(II) ions are linked by BIDPE ligands to form an infinitely wavelike 1D helical chain along the a axis (Figure 1b): the Co \cdots Co distance is 18.103 Å, and the N-Co-N angle is 101.18(18)°. Similarly, the neighboring Co(II) ions are connected by bdc^{2-} to form an infinitely 1D zigzag chain along the c axis (Figure 1c). The Co···Co distance is 10.879 Å, and the dihedral angle of two carboxylic acids is $84.147(2)^{\circ}$. An interesting feature in this complex is that left-handed and right-handed 1D helical channels exist alternately running along the *c* axis (-BIDPE-Co-BIDPE-Co-BIDPE-Co-), and the size is $8.395 \times 8.395 \text{ Å}^2$ (Figure 1d). The bdc²⁻ links these 1D helical chains to form a 3D framework composed of helical chains of opposite handness (Figure 1e). The framework contains three kinds of channels, A, B, and C; channel C is small and water molecules filled it in, while channel A is large and water and DMF molecules filled it in, and medium sized channel B is occupied by DMF, with all these slovents making the framework more stable (Figure 1f). A better insight into the nature of this intricate framework can be achieved by the application of a topological approach, reducing multidimensional structures to a simple node and connection nets. The Co(II) ions can be regarded as 4-connected nodes, and all crystallographical independent BIDPE ligands act as linkers. Therefore, the whole structure can thus be symbolized as a $\{8^6\}$ topology (Figure 1g). Structures containing 3D four-connected nets are reported, such as well-known diamond (6⁶), NbO ($6^4 \cdot 8^2 \cdot a$ and $6^4 \cdot 8^2 \cdot b$ net), and PtS ($4^2 \cdot 8^4$ net). While a four-connected {8⁶} net is not specifically identified by Wells,¹² related reports have existed.¹³ Because of the spacious nature of a single network, it allows another identical network to penetrate it, leading to a 2-fold interpenetrated structure (Figure 1h).

Compounds 1, 2, and 3 are isostructural, but the coordination environments of Cd(II) in 2 (Supporting Information, Figure S2) and Zn(II) in 3 (Supporting Information, Figure S3) were changed. Cd(II) ions are in an octahedral coordination environment of four carboxylic O atoms from two H₂bdc ligands and two nitrogen atoms from two BIDPE ligands, with the carboxylate groups of the bdc^{2–} ligand adopting chelating bidentate coordination modes (Scheme 2b), while Zn(II) ions are in a tetrahedral coordination environment of two carboxylic O atoms from two H₂bdc ligands and two nitrogen atoms from two BIDPE ligands. The carboxylate groups of the bdc^{2-} ligand adopt unidentate coordination modes (Scheme 2c). The bond angles and lengths are listed in Table S1.

Crystal Structure of $[Cd_3(BIDPE)_2(bdc)_3]_n$ (4). The crystal structure of 4 was solved in the space group P2(1)/n. The asymmetric unit of 4 contains two crystallographically independent cadmium ions (Cd1 and Cd2), of which Cd2 (1.0, 0.0, 0.5) is localized on a special position, one and a half bdc²⁻ anions, and one BIDPE ligand. As shown in Figure 2a, the carboxylate groups of bdc²⁻ adopt three different coordination modes, in which one bonding carboxylate group is chelating in a bidentate mode, one is bridging bidentate, and the other is in the chelating-bridging tridentate mode (Scheme 2d and e). The Cd(II) atoms are bridged by carboxylate ligands to form a linear trinuclear cluster unit $Cd(1)\cdots$ $Cd(2)\cdots Cd(1)$ with the $Cd(1)\cdots Cd(2)$ distance of 3.946(3) Å. The Cd(2) center is six-coordinated to form an octahedral geometry by four O (O2, O33, O2#1, O33#1) atoms from H₂bdc ligands in an equatorial position and two N(N3, N3#1) atoms from BIDPE in an axial position. The four O atoms are almost in a plane, the Cd–O lengths are in the range 2.326(5) - 2.348(4) Å, and the Cd-N length is 2.280(5) Å. Cd(1) is also six-coordinated and resides in a distorted octahedral coordination environment: five O atoms from three H₂bdc ligands and one N atom from the BIDPE ligand. The Cd–O lengths are in the range 2.256(5)–2.754(5) Å, and the Cd-N length is 2.281(6) Å, which are all similar to those found in other Cd(II) complexes.

Each trinuclear Cd cluster coordinates to six bdc^{2-} anions to form a 3D brick wall framework containing rectangle channels along the *a* axis with 44-remember rings (Figure 2b). The size is about 17.750 × 9.987 Å². The rectangle channels were filled by coordinated BIDPE ligands, which link trinuclear Cd clusters through N coordination to form a 3D network (Figure 2c). To reduce multidimensional structures to simple node and connection nets, the trinuclear Cd cluster can be regarded as 10-connected nodes, all crystallographically independent BIDPE, and the bdc^{2-} ligands linkers. Therefore, the whole structure can thus be symbolized as a $\{4^{41} \cdot 6^4\}$ topology (Figure 2d).

Crystal Structure of [Ni(bdc)(BIDPE)(H₂O)₂]_n (5). Compound 5 is self-assembled from the BIDPE ligand as V-shaped linker motifs and bdc²⁻ anions as linking rods that are further connected and interpenetrated to give a $2D \rightarrow 2D$ network. Single crystal X-ray analysis reveals compound 5 crystallized in the monoclinic crystal system, space group $P2_1/n$. The asymmetric unit of 5 contains one Ni(II) cation, one BIDPE ligand, one bdc²⁻ anion, and two coordinated water molecules. As shown in Figure 3a, the coordination environment around the Ni(II) cation can be described as a slightly distorted octahedron geometry of two unidentate carboxylic oxygen atoms (O2, O5#2) and two coordinated water O atoms (O3, O4) at the equatorial position with the other two coordinated N atoms (N1, N3#3) at the axial positions. The Ni-O distances are in the range 2.047(2)-2.122(2) A, and the Ni–N distances are 2.032(3)–2.039(3) A.

The neighboring Ni(II) ions are linked by the BIDPE ligands and bdc^{2-} anions to form an infinitely wavelike 2D sheet. In this sheet, the BIDPE ligands arranged in an opposite construction to form distorted tetragon grids about 9.375 × 7.517 Å² large (Figure 3b). Of particular interest, the most striking feature of complex **5** is that a pair of identical 2D single nets interlocked with each other (Figure 3c). As shown



Figure 2. (a) Coordination environment of the Cd(II) ion in 4. Hydrogen atoms are omitted for clarity. Symmetry codes: (#1) 2 - x, -y, 1 - z. (b) Views of the 3D brick wall framework by bdc^{2-} and Cd anions along the *a* axis. (c) Views of the 3D framework of 4 along the *a* axis. (d) Schematic representation of a single 3D framework of compound 4.

in Figure 3d, the channels of each network are threaded by one bdc-Ni-bdc rod of another network, and vice versa.

Crystal Structure of [Mn(bdc)(BIDPE)(H₂O)]_n (6). We have tried to use Mn(NO₃)₂, but the crystal was not very well ordered and cannot fix the structure; when Mn(NO₃)₂ was replaced by MnCl₂, better crystals were obtained. The crystal structure of **6** was solved in the space group $P2_1/c$. As depicted in Figure 4a, compound **6** consists of two parts with two types of coordination environments around the Mn(II) ions. The two Mn(II) ions all have distorted octahedron geometry with three carboxylic O atoms from bdc²⁻ anions and one coordinated water O atom at the equatorial plane and two N atoms from two BIDPE ligands at the axial position. The Mn–O distances are in the range 2.087(4)–

2.340(4) Å, and the Mn–N distances are 2.233(5)–2.253(4) Å. Similar to the case for compound **5**, the neighboring Mn(II) ions are linked by BIDPE ligands and bdc^{2–} anions to form two infinitely wavelike 2D sheets (Figure 4b), in which every two BIDPE ligands and bdc^{2–} anions link four Mn atoms to form distorted tetragon grids about 10.622 × 9.788 and 10.592 × 9.022 Å². The most striking feature of complex **6** is that these two different 2D sheets interlocked each other (Figure 4c). Further inspection shows that the coordinated water molecules and carboxylate groups from another sheet are actually contacting each other by strong H-bonding (O···O distances range from 2.616 to 2.790 Å). Obviously, these H-bonded interactions are also available for increasing the stability of the whole crystal structure of **6** (Figure 4d).



Figure 3. (a) Coordination environment of the Ni(II) ion in 5. The hydrogen atoms are omitted for clarity. Symmetry codes: (#1) 0.5 + x, 0.5 - y, 0.5 + z. (b) Views of 2D sheet. (c) Views of interlocked framework in 5. (d) Schematic representation of interlocked 2D framework of compound 5.

Configuration of BIDPE. To the best of our knowledge, flexible ligands freely rotate to meet the requirement of coordination geometries of metal ions in the assembly process. In this paper, the V-shaped BIDPE ligand also has some characteristics of flexible ligands. It can slightly change the angle to meet the requirement of coordination. The angles can be assessed by comparing the $N \cdots O_{core} \cdots N$ angle defined by the central oxygen atom and the coordinated nitrogen atoms of the imidazole groups. In order to illuminate the influence of the angles, six compounds are list in Table 2.

Photochemical Properties. Luminescent compounds are of great interest due to their various applications in chemical sensors and photochemistry. The luminescent properties of free ligands BIDPE, and H_2 bdc, with complexes 2, 3, and 4 have been investigated in the solid state at room temperature, as depicted in the Supporting Information (Figure S4). An intense emission of the free H2bdc and BIDPE ligands was observed with wavelength from 370 to 410 nm ($\lambda_{max} = 390$ and 395 nm), which could be attributed to the $\pi^* - \pi$ transitions. Complexes 2, 3, and 4 exhibit emission characteristics similar to those of the free H₂bdc and BIDPE ligands. The emission peaks at 420 nm ($\lambda_{ex} = 360$ nm) in **2**, 425 nm ($\lambda_{ex} =$ 354 nm) in 3, and 440 nm ($\lambda_{ex} = 350$ nm) in 4 show a small red shift compared with that of the H₂bdc and BIDPE ligands, which is probably due to enhanced conjugation in the ligands upon metal coordination. In addition, the UV-vis absorption spectra of compounds 1-6 were carried out in crystalline state at room temperature (BIDPE and H₂bdc in solid state) (Figure S5). BIDPE and H₂bdc show intense absorption peaks at 220–320 nm, which can be ascribed to $\pi - \pi^*$ transitions of the ligands. Energy bands of complex 1 from

480 to 580 nm and of complex **5** from 580 to 620 nm and from 350 to 390 nm are assigned as d-d transitions, while lower energy bands from 310 to 350 nm are assigned as metal-to-ligand charge-transfer (MLCT) transitions.¹⁴

Thermal Analysis and XRD Results. To characterize the complexes more fully in terms of thermal stability, their thermal behaviors were studied by TGA (Supporting Information, Figure S6). For complex 1, a rapid weight loss of the lattice water molecules of 3.15% (calcd 3.25%) was observed from 30 to 110 °C. The second weight loss of 5.11% (calcd 5.07%) from 110 to 280 °C is attributed to the loss of DMF molecules. The structure decomposed at 390 °C. For complex 2, a rapid weight loss of 4.15% (calcd 4.20%) is observed from 25 to 135 °C, which is attributed to the loss of the lattice water, while the second weight loss of 5.59% (calcd 5.68%) from 140 to 290 °C is attributed to the loss of DMF molecules, and then the structure decomposed from 360 °C. The TGA curve of 3 shows a weight loss of 5.25% from 20 to 240 °C from the loss of lattice water and DMF molecules, and the framework collapsed at 390 °C. The anhydrous compound 4 begins to decompose at 353 °C. In the case of 5, a weight loss is observed from 20 to 165 °C, which is attributed to the release of the coordinated water with a weight loss of 6.41% (calcd 6.42%). The network collapsed at 330 °C. TGA of 6 shows a 3.33% (calcd 3.38%) weight loss between 100 and 245 °C due to loss of coordinated water molecules. The framework collapsed at 320 °C. To confirm whether the crystal structures are truly representative of the bulk materials, PXRD experiments were carried out for 1-6. The PXRD experimental and computer-simulated patterns of the corresponding complexes are shown in the Supporting



Figure 4. (a) Coordination environment of the Mn(II) ion in 6. Hydrogen atoms are omitted for clarity. (#1) x, 0.5 - y, -0.5 + z; (#2) 1 + x, 0.5 - y, 0.5 + z; (#3) x, 0.5 - y, 0.5 + z. (b) Views of interlocked framework in 6. (c) Schematic representation of 2-fold interlocked 2D framework of compound 6. (d) O-H···O interaction between two sheets.

Tahla 2	Different	Angles	of RID	PF I	igand
Table 2.	Different	Angles	01 DID	гег	лдани

compound	$N{\cdots}O_{core}{\cdots}N$	conditions	dimensions
1	138.819(8)°	DMF/H ₂ O (3/1), 90 °C	3D
2	137.088(7)°	DMF/H ₂ O (3/1), 90 °C	3D
3	133.982(9)°	DMF/H ₂ O (3/1), 90 °C	3D
4	115.952(9)°	H ₂ O, 140 °C	3D
5	118.836(5)°	DMF/H ₂ O (1/1), 90 °C	2D
6	114.077(5)°,	DMF/H ₂ O (1/4), 90 °C	2D
	116.128(6)		

Information (Figures S7–S12); they show that the bulk synthesized materials and the measured single crystals are the same. XRPD patterns of different temperatures can prove that their structures are retained, though the solvents are lost. When the temperatures continue rising, the peaks of XRPD will become weak, but the structure is still retained until the structure decomposes (Figures S13–S17).

Conclusion

In summary, six new complexes have been synthesized by the self-assembly of BIDPE, H_2 bdc ligands, and various metal ions under solvothermal conditions. The results show that the adjusting of the linker's shapes caused by different coordination modes is good for diversity of the produced structures. Compounds 1, 2, and 3 have similar 3D frameworks. Complex 4 possesses trinuclear Cd clusters (SBU), which are linked by bdc^{2–} and BIDPE to form a 3D framework. Complex 5 is an intercatenated 2D framework, while complex 6 is composed of two 2D sheets. In addition, the photochemical properties have been investigated. Subsequent works will be focused on the structures and properties of a series of coordination complexes constructed by BIDPE ligand with more auxiliary ligands and metal ions.

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Supporting Information Available: Crystallographic data in CIF format, selected bond lengths and angles, and patterns of photochemistry, TGA, and PXRD in PDF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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