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Chirality- and Threefold-Symmetry-Directed Assembly of Homochiral Octupolar Metal−Organoboron Frameworks

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Homochiral octupolar metal−organoboron frameworks with the general formula $[M_2\mathbf{L}(OH)(MeOH)]\cdot 3H_2O$ [M = Co (**1**), Mn (**2**), Ni (**3**), Cu (**4**), Zn (**5**), Cd (**6**)] have been constructed from racemic C_3-symmetric tris(4-benzoic acid)tridurylborane and the divalent metal ions. Compounds **1**−**6** are isostructural and crystallize in the chiral cubic space group *F*432, and they adopt an eightfold-interpenetrating (10,3)-a network formed by linking bimetal building blocks with three bidentate carboxylate groups of bridging Λ-**L** ligands. Bulk crystals of each of the six compounds are not a racemic mixture, and their optical activity and enantiomeric nature were demonstrated by solid-state circular dichroism spectra. Consistent with their polar structures, the colorless compounds **5** and **6** exhibit powder second harmonic generation intensities 3−4 times higher than that of potassium dihydrogen phosphate, making them, to the best of our knowledge, the first two examples of NLO-active, homochiral octupolar metal−organic solids.

Introduction

There has been extensive research into developing multipolar second-order nonlinear optical (NLO) materials for high-performance electro-optic devices since the discovery that donor−acceptor-substituted molecules with threefold rotational symmetry (octupolar chromophores) can have an improved transparency/optical nonlinearity trade-off with respect to traditional dipolar chromophores.[1] While octupolar nonlinearity has subsequently been demonstrated at the molecular level with the revival and development of the harmonic light scattering technique, its demonstration in multidimensional crystalline systems remains a significant challenge.[2,3] Coordination-driven self-assembly, on the other hand, provides unique opportunities to prepare highly complex chemical systems from simple components and has led to significant progress in the construction of metal−organic frameworks (MOFs) with novel topologies and exploitable functions.[4−6] In principle, octupoles can be expressed in cubic, tetrahedral, and trigonal symmetries.[3] Trigonal molecules or bridging ligands are thus very useful building blocks for the construction of higher-dimensional octupolar supramolecular materials. However, the products normally do not adopt acentric trigonal structures or have weak NLO responses.[6]

Recently, we serendipitously prepared an organically templated three-dimensional (3D) octupolar MOF displaying a very strong and tunable second harmonic generation (SHG) response.[7] Subsequently, we explored the synthetic approach to octupolar polymeric materials by carrying over both threefold symmetry and chirality of organic bridging ligands into MOFs through self-assembly. Such a strategy has led to a series of chiral ocupolar NLO-active metal−organoboron frameworks through the use of rigid, trigonal, chiral tri(pyridyl)tridurylborane as a multidentate ligand.[8] The

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tridurylborane core features a three-coordinate boron chromophore and adopts a propeller-like conformation to minimize repulsive interactions between its phenyl rings, and therefore, it is a helically chiral substrate (Δ and Λ isomers) exhibiting D_3 octupolar symmetry. The vacant low-lying $2p_\pi$ orbital on the boron center makes three-coordinate organoboron derivatives good electron acceptors, leading to versatile potential applications in organic light-emitting diodes and nonlinear optics.[9] Therefore, triphenylborane-derived multiple ligands offer great potential for constructing chiral octupolar MOFs with interesting optoelectric properties and new functions. Herein we report the synthesis, structures, and NLO properties of six isostructral homochiral octupolar MOFs based on a new racemic tris(4-benzoic acid)tridurylborane ligand.

Experimental Section

General. All of the starting materials were obtained from commercial suppliers and used without further purification. Elemental analyses of C, H, and N were performed with an EA1110 CHNS-0 CE elemental analyzer. Inductively coupled plasma atomic emission spectroscopy (ICP−AES) was performed with a BAIRD ICP 2000 emission spectrometer. IR spectra (KBr pellet) were recorded in the 400−4000 cm^{-1} region on a Nicolet Magna 750 FT-IR spectrometer. UV−vis absorption spectra weres measured at room temperature with a PE Lambda 900 UV−vis spectrophotometer over the 400−2000 nm range. A $BaSO_4$ plate was used as a standard (100% reflectance) for the measurement of the optical diffuse reflectance spectrum. Solid-state circular dichroism (CD) spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). ^1H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at a resonance frequency of 400 MHz. Electrospray ionization mass spectrometry (ESI-MS) of the ligand was performed on an Agilent LC/MSD spectrometer. Thermogravimetric analysis (TGA) was carried out under an air atmosphere with a heating rate of 10 °C min^{-1} on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single-crystal reflection data.

Synthesis of Tris((4-carboxyl)phenylduryl)borane (H_3L). A mixture of Tris(iododuryl)borane (4.73 g, 6 mmol), 4-(methoxycarbonyl)phenylboronic acid (6.48 g, 36 mmol), K_2CO_3 (8.28 g, 60 mmol), and $Pd(PPh_3)_4$ (0.69 g, 0.6 mmol) was weighed into a 500 mL Schlenk flask, to which toluene (160 mL) and 3:5 $EtOH/H_2O$ (80 mL) were added subsequently under a dry N_2 atmosphere. The mixture was heated to reflux with stirring and maintained at this temperature for 18 h. The reaction mixture was cooled to room temperature and diluted with CH_2Cl_2. The combined organic layers were washed several times with brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (20:1 hexane/EtOAc) to afford tris((4-methoxycarbonyl)phenylduryl)borane as a white solid. ^1H NMR ($CDCl_3$): δ 1.83 (s, 18H), 2.06 (s, 18H), 3.95 (s, 9H), 7.22 (d, J = 7.2 Hz, 6H), 8.09 (d, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 167.5, 149.3, 148.8, 142.4, 136.0, 131.0, 129.8, 128.4, 127.4, 52.3, 20.4, 18.1.

Tris((4-methoxycarbonyl)phenylduryl)borane obtained in the previous step was dissolved in 2:1 THF/MeOH (30 mL), and 5 M NaOH was added until the pH reached 10−11. After the solution was stirred at room temperature overnight, it was concentrated under reduced pressure and then acidified with dilute hydrochloric acid (2−3 M). The resulting mixture was stirred for a moment and then filtered, washed with water, and dried in vacuo to give H_3**L** (2.85 g, 62% in total) as a white solid. ^1H NMR (DMSO): δ 1.79 (s, 18H), 2.04 (s, 18H), 6.98 (d, J = 8 Hz, 6H), 7.91 (d, J = 8 Hz, 6H). ^{13}C NMR (DMSO): δ 167.9, 149.2, 147.8, 142.8, 135.9, 131.2, 130.2, 130.1, 129.7, 20.5, 18.4.

Table 1. Crystal Data and Structure Refinement for Complex **1**

empirical formula	$C_{52}H_{53}BCo_2O_8$
formula weight	934.61
temperature	293(2) K
wavelength	0.71073 Å
crystal system	cubic
space group	$F432$
unit cell dimensions	a = 35.740(3) Å
volume, Z	45651(6) $Å^3$, 32
density (calculated)	1.088 mg cm^{-3}
absorption coefficient	0.625 mm^{-1}
F(000)	15 616
crystal size	0.15 × 0.15 × 0.12 mm
θ range for data collection	2.96 to 23.99°
limiting indices	$-36 \leq h \leq 40, -40 \leq k \leq 37, -40 \leq l \leq 31$
reflections collected	49 899
independent reflections	2800 (R_{int} = 0.0663)
completeness to θ = 23.99	91.1%
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2800/3/194
goodness of fit on F^2	1.156
final R indices [$I > 2\sigma(I)$]	R1 = 0.1124, wR2 = 0.2567
R indices (all data)	R1 = 0.1441, wR2 = 0.2861
absolute structure parameter	−0.02(8)
largest diff. peak and hole	0.769 and −0.575 e $Å^{-3}$

Table 2. Selected Bond Lengths and Bond Angles for **1**

Bond Lengths (Å)			
Co(1)−O(2)	1.942(9)	Co(2)−O(1)	1.901(7)
Co(1)−O(3)	2.127(15)	Co(2)−O(4)	1.989(19)
Co(1)−Co(2)	2.375(5)	B(1)−C(11)	1.569(7)
Bond Angles (deg)[a]			
O(2a)−Co(1)−O(2)	118.52(16)	O(4)−Co(2)−Co(1)	180.0(8)
O(2)−Co(1)−O(3)	97.0(4)	C(11b)−B(1)−C(11)	119.999(5)
O(2)−Co(1)−Co(2)	83.0(4)	C(1)−O(1)−Co(2)	112.0(8)
O(3)−Co(1)−Co(2)	180.0(6)	C(1)−O(2)−Co(1)	120.6(11)
O(1a)−Co(2)−O(1)	119.89(5)	C(18)−O(3)−Co(1)	116.4(14)
O(1)−Co(2)−O(4)	88.0(4)	C(10)−C(11)−B(1)	120.8(7)
O(1)−Co(2)−Co(1)	92.0(4)	C(12)−C(11)−B(1)	121.8(7)

[a] Symmetry transformations used to generate equivalent atoms: (a) $-z, x, -y$; (b) $y - {}^1/_2, z + {}^1/_2, x$.

Synthesis of Complexes 1−6. A mixture containing 0.005 mmol of $M(NO_3)_2 \cdot 6H_2O$ (M = Co, Ni, Cu, Zn, Cd) or $MnCl_2 \cdot 4H_2O$ and 0.005 mmol of H_3**L** was placed in a small vial containing dimethylacetamide (DMA) (3.0 mL) and MeOH (1.0 mL). The vial was sealed, heated at 100 °C for 2 days, and allowed to cool to room temperature. Crystals suitable for X-ray diffraction were collected by filtration, washed with diethyl ether, and dried in air. The products were formulated as [M_2**L**(OH)(MeOH)]·$3H_2O$ [M = Co (**1**), Mn (**2**), Ni (**3**), Cu (**4**), Zn (**5**), Cd (**6**)] on the basis of microanalysis, IR spectroscopy, and TGA. The metal contents were determined by ICP−AES.

[Co_2L(OH)(MeOH)]·$3H_2O$ (**1**). Purple crystals. Yield: 6.8 mg, 69%. IR (KBr, cm^{-1}): 3542(w), 2912(w), 1608(s), 1552(w), 1396(s), 1298(w), 1266(m), 1174(m), 1096(m), 1018(w), 996(m), 950(s), 872(w), 846(w), 786(s), 722(m), 694(w), 670(w), 640(w), 608(w). Anal. Calcd for $C_{52}H_{59}BCo_2O_{11}$: C, 63.17; H, 6.01; Co, 11.92. Found: C, 62.84; H, 6.00; Co, 11.87.

[Mn_2L(OH)(MeOH)]·$3H_2O$ (**2**). Light-yellow crystals. Yield: 5.1 mg, 51%. IR (KBr, cm^{-1}): 3380(m), 2910(w), 1582(w), 1392(s), 1262(m), 1174(m), 1138(w), 1094(m),

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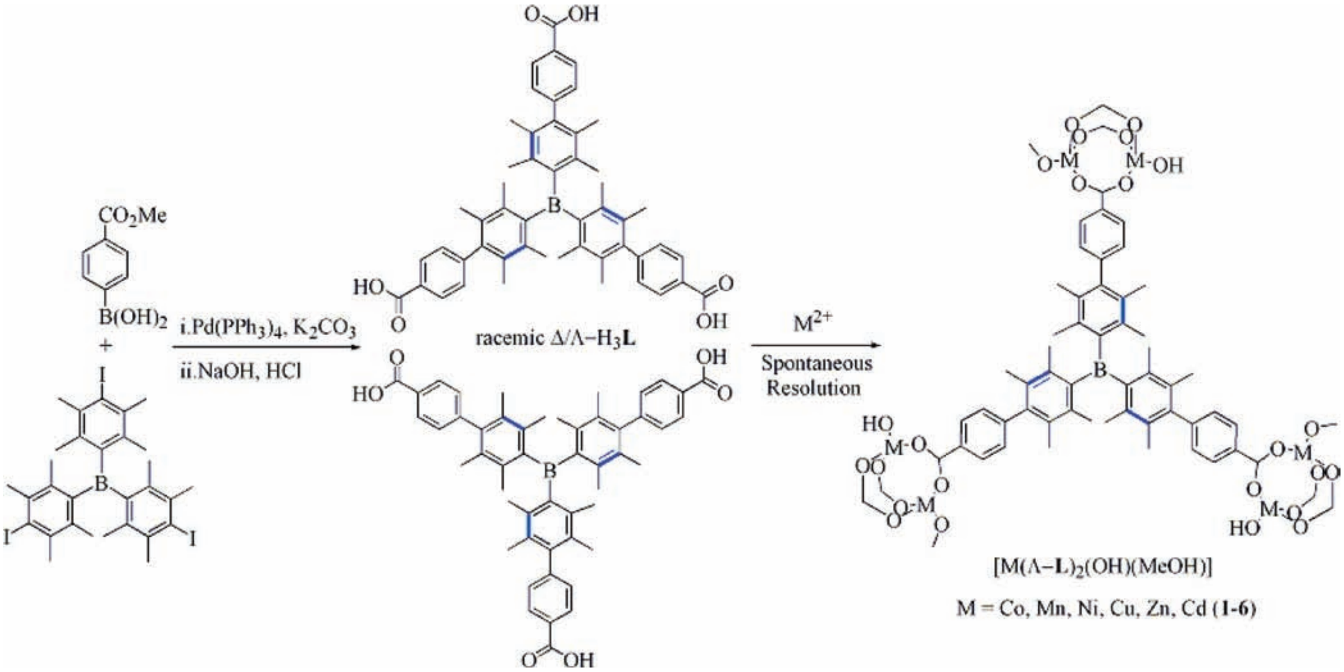
Scheme 1



1018(w), 950(s), 872(w), 786(m), 718(m), 692(w), 668(w), 640(w), 610(w). Anal. Calcd for $C_{52}H_{59}BMn_2O_{11}$: C, 63.68; H, 6.06; Mn, 11.60. Found: C, 63.33; H, 5.94; Mn, 11.53. Unit cell: a = 35.917(5) Å; α = 90°; V = 46336(12) Å^3.

[Ni$_2$L(OH)(MeOH)]·3H$_2$O (**3**). Light-green crystals. Yield: 5.34 mg, 54%. IR (KBr, cm^{-1}): 2916(w), 1658(m), 1504(m), 1416(s), 1372(w), 1264(m), 1174(w), 1096(s), 1018(w), 992(w), 948(s), 864(s), 788(s), 762(w), 722(m), 698(w), 640(w). Anal. Calcd for $C_{52}H_{59}BNi_2O_{11}$: C, 63.20; H, 6.02; Ni, 11.88. Found: C, 62.93; H, 5.97; Ni, 11.81. Unit cell: a = 35.535(12) Å; α = 90°; V = 44870(25) Å^3.

[Cu$_2$L(OH)(MeOH)]·3H$_2$O (**4**). Blue crystals. Yield: 7.1 mg, 71%. IR (KBr, cm^{-1}): 3394(s), 2914(w), 1608(s), 1398(s), 1264(w), 948(w), 872(w), 848(w), 784(m), 758(w), 722(m), 696(m), 638(w), 606(w). Anal. Calcd for $C_{52}H_{59}BCu_2O_{11}$: C, 62.59; H, 5.96; Cu, 12.74. Found: C, 62.21; H, 5.90; Cu, 12.55. Unit cell: a = 35.74(3) Å; α = 90°; V = 45651(60) Å^3.

[Zn$_2$L(OH)(MeOH)]·3H$_2$O (**5**). Colorless crystals. Yield: 6.2 mg, 62%. IR (KBr, cm^{-1}): 3456(m), 2912(w), 1614(s), 1538(m), 1424(m), 1396(s), 1302(m), 1264(s), 1216(s), 1170(m), 1066(m), 1028(m), 952(s), 864(s), 826(w), 804(s), 754(w), 704(w), 656(m), 614(m). Anal. Calcd for $C_{52}H_{59}BZn_2O_{11}$: C, 63.36; H, 5.94; Zn, 13.06. Found: C, 62.98; H, 5.87; Zn, 13.01. Unit cell: a = 35.650(7) Å; α = 90°; V = 45307(15) Å^3.

[Cd$_2$L(OH)(MeOH)]·3H$_2$O (**6**). Colorless crystals. Yield: 6.5 mg, 59%. IR (KBr, cm^{-1}): 3436(s), 2918(w), 1606(m), 1534(m), 1398(s), 1298(w), 1264(m), 1174(w), 1094(w), 1018(w), 950(m), 860(m), 786(w), 722(m), 696(w), 638(w). Anal. Calcd for $C_{52}H_{59}BCd_2O_{11}$: C, 57.00; H, 5.43; Cd, 20.52. Found: C, 56.62; H, 5.37; Cd, 20.24. Unit cell: a = 35.917(5) Å; α = 90°; V = 46336(12) Å^3.

X-ray Crystallography. We collected about a dozen data sets for **1** on a SATURN70 CCD diffractometer or a Rigaku Mercury CCD/AFC diffractometer. The best data set was collected on a Rigaku SATURN70 CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 173 K and was used for structure solution and refinement. The empirical absorption correction was applied using the SADABS program.[10] The structure was solved using direct methods and refined by full-matrix least squares on F^2.[11]

The cobalt atoms were found to be seriously disordered around the threefold axis. However, we failed to model the disordered Co sites by using occupancies (e.g., 50:50, 60:40, 70:30, 80:20, and 90:10), which led to extremely high Co thermal parameters and/or unreasonable Co−O bond lengths. The CH_3 group of methanol was disordered around the threefold axis as well, but could not be modeled. To resolve these issues, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.[12] Unfortunately, the quality of the resulting structure was not obviously improved. All non-H atoms except for the disordered ones were refined anisotropically. Crystal data and details of the data collection are given in Table 1. Selected bond distances and angles are presented in Table 2.

Second Harmonic Generation Measurements. Kurtz powder SHG measurements were performed on ground samples. Particle sizes were graded using standard sieves; sizes from 90 to 120 μm were studied. The fundamental wavelength of 1064 nm from a Nd:YAG laser was used. The ground samples were phase-matchable materials, as confirmed by a powder XRD study (Figure S7 in the Supporting Information). The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. The powder second harmonic signals were compared to that of α-quartz to determine the relative SHG efficiencies of the samples. For comparison, sieved KH_2PO_4 (KDP) powder (90−120 μm) was also measured and used as an additional reference. For each sample, the average value from three measurements is reported.

Results and Discussion

As shown in Scheme 1, the new racemic ligand tris((4-carboxyl)phenylduryl)borane (H_3**L**) was synthesized in 62%

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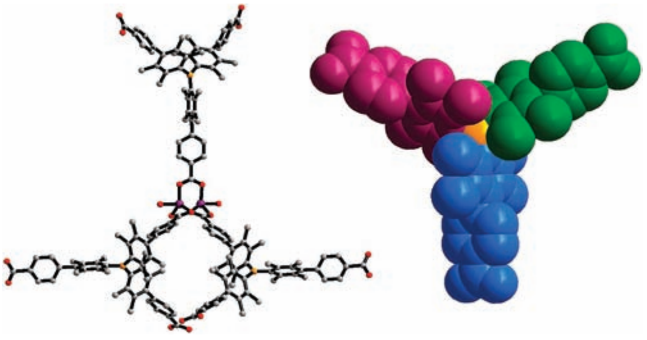

Figure 1. (left) [Co_2**L**(OH)(MeOH)] building block in **1**. The disordered CH_3 group of methanol has been omitted for clarity. Color code: Co, purple; B, yellow; O, red; C, gray. (right) Space-filling model of the **L** ligand.

overall yield by a Pd-catalyzed Suzuki coupling reaction between 4-(methoxycarbonyl)phenylboronic acid and tris(iododuryl)borane followed by hydrolysis with dilute HCl. The precursor tris(iododuryl)borane was obtained in four steps in good overall yield from the readily available tetramethylbenzene.[9] The H_3**L** ligand was characterized by ^1H and ^{13}C NMR and ESI-MS.

Single crystals of six compounds with the general formula [M_2**L**(OH)(MeOH)]·$3H_2O$ [M = Co (**1**), Mn (**2**), Ni (**3**), Cu (**4**), Zn (**5**), Cd (**6**)] were obtained in moderate yields by heating a mixture of $MX_2 \cdot nH_2O$ and **L** in DMA and MeOH at 100 °C for 2 days. The formulations of **1**−**6** were established by a combination of single-crystal X-ray structure analysis, elemental analyses, IR spectroscopy, and TGA.

A single-crystal X-ray diffraction study performed on **1** revealed a neutral 3D open metal−organic network with the (10,3)-a topology. **1** crystallizes in the chiral cubic space group *F*432, with one-third of a formula unit in the asymmetric unit. The basic building block for **1** is a dimeric [Co_2(**L**)(OH)(H_2O)] cluster, which lies on a crystallographic C_3 axis and is bridged by three bidentate carboxylate groups of three **L** ligands (Figure 1). Both Co centers adopt distorted tetrahedral geometries by coordinating to three carboxylate oxygen atoms and one methanol or one hydroxyl group, with Co−O bond lengths ranging from 1.901(7) to 1.942(9) Å. Each **L** ligand adopts the Λ conformation and links three pairs of dicobalt units through its three bidentate carboxylate groups. The central boron of the **L** ligand lies on a crystallographic threefold axis as well and is completely trigonal planar, with the three duryl groups arranged in a propeller-like fashion. The dihedral angle between the boron plane and the duryl plane is 50.5°, and that between the duryl plane and the outer phenyl plane is 87.2°. The dicobalt unit possesses a threefold rotational symmetry and thus constitutes the octupolar NLO chromophore unit of **1**. The network topology of **1** can be described as a binodal (10,3)-a net when the dicobalt motif is treated as one three-connected node and the trigonal **L** ligand as another three-connected node (Figure 2). A pair of such independent networks is interwoven to form 1D tubular channels with an opening of ~3 nm × 3 nm. The much larger intraframework spaces shown in Figure 2 are occupied by three pairs of other identical but independent networks, giving a total of eight interpenetrating networks. Consequently, **1** has minimal void space, which is occupied by water molecules.

Significantly, a variety of metal ions, such as Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, can be incorporated in this organoboron-based (10,3) architecture. The single-crystal X-ray diffraction data for compounds **2**−**6** were extremely weak, and only **3** and **6** could give preliminary frameworks, but single-crystal X-ray structure determination, cell parameter determination, and/or powder X-ray diffraction studies established that **2**−**6** are isostructural to **1**. The phase purity of bulk samples of **1**−**6** was established by comparison of their observed and simulated powder X-ray diffraction patterns, as shown in Figure 4. All of the products are stable in air and insoluble in water and common organic solvents. Calculations using the PLATON program indicate that **1** has 20.0% of its total volume occupied by solvent molecules.[12] TGA revealed that water guest molecules could be removed in the temperature range from 80 to 130 °C (Figure 5). Powder XRD experiments indicate that the framework and crystallinity of **1**, **5**, and **6** remain intact upon complete removal of guest molecules (Figure 6).

The electronic spectra of H_3**L** show two major $\pi \rightarrow \pi^*$ transitions at 240 and 357 nm. Upon the formation of compound **1**, the absorption at 357 nm remains unshifted, while the higher energy transition of the ligand has blue-shifted by about 32 nm. In addition, there are two new bands around 562 and 511 nm for **1**, which are probably due to d−d transitions of Co^{2+} in a tetrahedral geometry.[13] The solid-state circular dichroism (CD) spectrum measurements in KCl pellets confirmed the optical activity and enantiomeric nature of **1**. It exhibits a positive Cotton effect at 278 nm and a negative Cotton effect at 331 nm. The solid-state CD spectra of **2**−**6** (Figure 3) are similar to that of **1**, indicating that the **L** ligands adopt the Λ conformation as well and compounds **1**−**6** all have the same enantiomeric nature.

After the synthesis of **1**, thin-layer chromatography analysis showed that some unreacted H_3**L** ligand remained in the supernatant, but its CD spectrum was silent. Therefore, although the synthesis of **1** began from a racemic mixture of Δ- and Λ-H_3**L**, spontaneous resolution with simultaneous inversion of the absolute conformation around the boron of H_3L occurs upon crystallization. Spontaneous resolution, however, generally yields a conglomerate (racemic mixture of chiral crystals). The chiral (10,3)-a network is of great importance in the field of MOFs, and its chirality arises from the ⟨100⟩ fourfold and ⟨111⟩ threefold helices of the same handedness propagating in all crystallographically equivalent directions.[14,15] Such bulk materials, however, tend to be racemic even though the single crystals are chiral.[15] Nevertheless, in the present case, the **L** ligands adopt the same handedness of chirality bearing D_3 symmetry, thus inducing the enantiopurity and further octupolarity of the infinite network. The initial crystals generated may seed the handedness of the bulk product in

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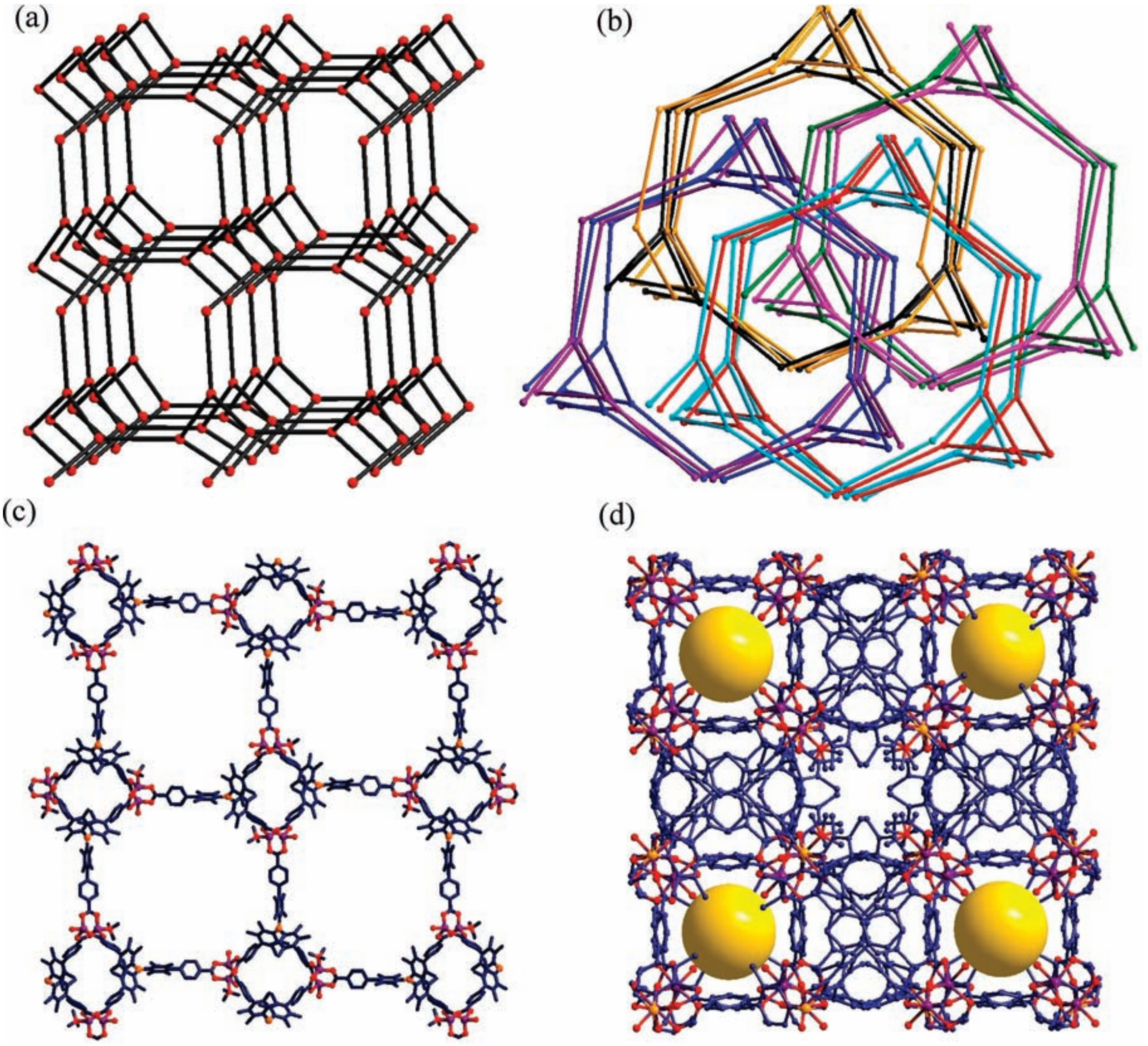

Figure 2. (a) Scheme showing the (10,3) topology of **1**. (b) Interpenetration of eight independent (10,3) nets in **1**. (c) View of one independent chiral network of **1** along the *a* axis (the CH_3 group of methanol is disordered around the threefold axis). (d) 3D structure of **1** along the *a* axis. The channel is highlighted by a yellow sphere, and the guest molecules have been omitted for clarity. Color code: Co, purple; B, yellow; O, red; C, blue.

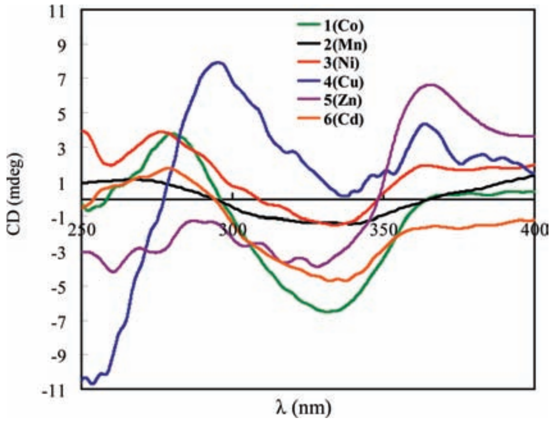

Figure 3. Solid-state CD spectra of **1**−**6**.

the crystal growth, and thus, the particular handedness of the bulk is formed.[16] Further study to elucidate the origin of the enantiomeric excess reported herein is currently underway.

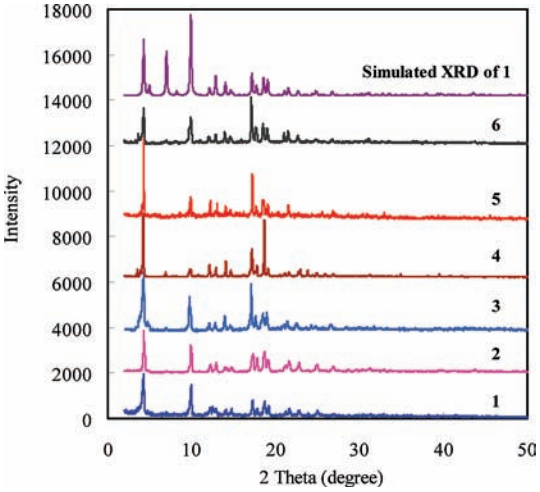

Figure 4. PXRD patterns of **1**−**6** and the simulated XRD pattern of **1**.

Kurtz powder SHG measurements on compounds **5** and **6** were performed to further confirm their acentricity as well as to evaluate their potential as second-order NLO materials.

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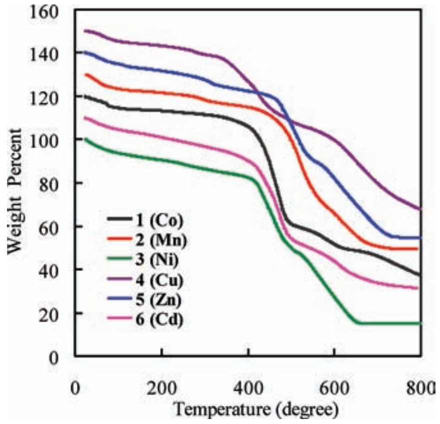

Figure 5. TGA curves for **1**−**6**.

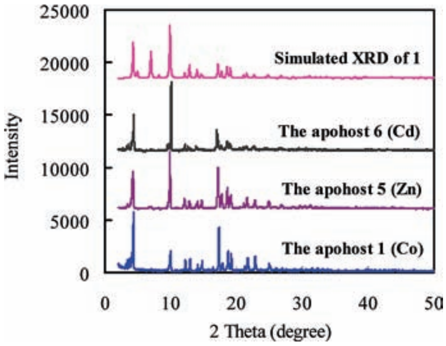

Figure 6. PXRD patterns of the apohosts **1**, **5**, and **6** and the simulated XRD pattern of **1**.

Compounds **5** and **6** exhibited powder SHG intensities of 31 and 44, respectively, versus α-quartz, which are about 3−4 times higher than those of technologically useful KDP.[17] SHG measurements were also performed on freshly evacuated samples of **5** and **6**, which exhibited SHG intensities of 30 and 45 versus α-quartz and compared favorably to the pristine materials. Therefore, the NLO behaviors of the framework structures of **5** and **6** are stable and are independent of external stimuli such as guest removal and uptake. The second harmonic responses of **5** and **6** are evidently realized by the acentric array of bridging organoboron skeletons through metal centers. Among second-order NLO materials, nonracemic chiral species are underdeveloped but especially significant because their harmonics depend on the direction of light polarization upon excitation by circularly polarized light.[18] **5** and **6** are the first two examples of NLO-active, homochiral octupolar metal−organic solids, and to our knowledge, **6** exhibits the strongest SHG intensity that has been reported for a homochiral MOF to date.[19] Moreover, **5** and **6** exhibit high thermal and solution stabilities and are totally transparent in the visible region (Figure S5 in the Supporting Information), making them attractive candidates for future practical applications.

Conclusions

We have developed a simple synthetic approach leading to homochiral octupolar NLO-active solids based on 3D coordination networks that uses racemic and C_3-symmetric tris(4-benzoic acid)tridurylborane as a multidentate ligand. The polar metal−organoboron frameworks adopt an eightfold interpenetrating (10,3)-a topology and exhibit powder second harmonic generation signals 3−4 times larger than that of KDP. Current efforts are focused on optimization of the optical responses of this type of material by end-functionalizing the arms of the octupolar units and the synthesis of other organoboron-based assemblies with unique and practically useful optic-electronic functions.

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Supporting Information Available: X-ray crystallographic file in CIF format for **1**, structural models, TGA curves, UV−vis spectra, ESI-MS data, and PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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