Metal–Organoboron Frameworks

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Chiral Octupolar Metal–Organoboron NLO Frameworks with (14,3) Topology**

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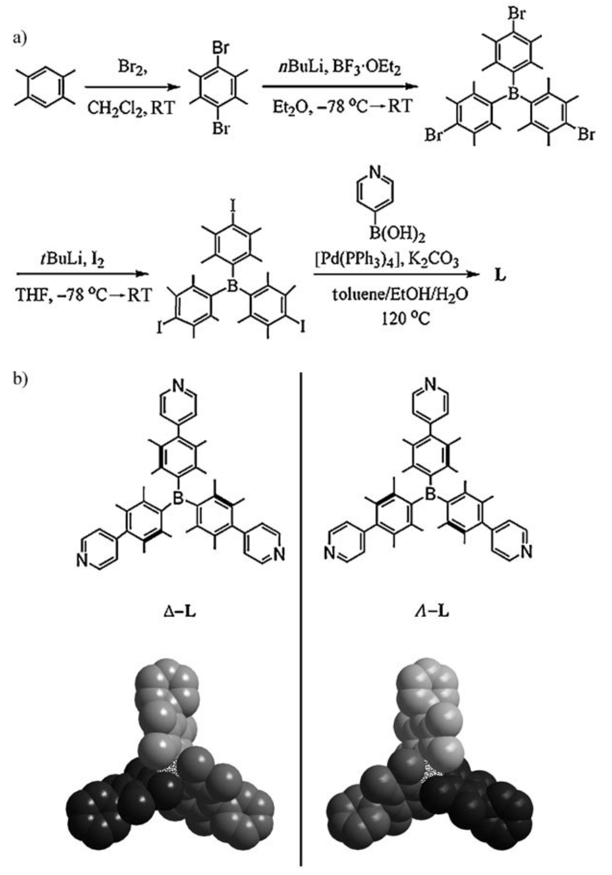
Multipolar second-order nonlinear optical (NLO) materials have become a topic of intense interest owing to the finding that donor–acceptor-substituted molecules with threefold rotational symmetry (octupolar chromophores) can have an improved transparency/optical nonlinearity tradeoff when compared with traditional dipolar chromophores.[1] While octupolar nonlinearity has been achieved at the molecular level,[2,3] its demonstration in multidimensional crystalline systems remains challenging.[3–5] Studies on the assembly of metal–organic frameworks (MOFs) from molecular building blocks, on the other hand, have uncovered methods to build extended structures with novel topologies and exploitable functions.[4–7] 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 NLO-active MOF materials, but the products normally do not adopt acentric trigonal structures or have weak NLO responses.[7]

We recently prepared serendipitously an organically templated 3D octupolar MOF exhibiting very strong and cation-dependent second harmonic generation (SHG) responses.[5c] We have now developed a strategy for the rational synthesis of 3D octupolar materials by carrying over both threefold symmetry and chirality of organic bridging ligands into MOFs through coordination assembly. To this end, we synthesized rigid trigonal tris(4-pyridylduryl)borane (**L**) featuring a three-coordinate boron chromophore.[8] The tridurylborane core adopts a propellerlike conformation to minimize repulsive interactions between its phenyl rings, and therefore it is helically chiral (Δ and Λ isomers) with D_3 octupolar symmetry as shown in Scheme 1. The vacant and low-lying $2p_\pi$ orbital on the boron center makes three-coordinate organoboron derivatives good electron acceptors that have versatile potential applications in organic light-emitting diodes and nonlinear optics.[8] Herein we present the assembly of chiral octupolar metal–organoboron frameworks with exceptional (14,3) topology[9] which display significant and, more interestingly, anion-tunable SHG responses.



Scheme 1. a) Synthesis of **L**. b) Two isomers of **L** and their space-filling depictions.

Racemic **L** was synthesized in 70% yield by Suzuki coupling between 4-pyridylboronic acid and tris(iododuryl)-borane, which was obtained in four steps in good overall yield from readily available 1,2,4,5-tetramethylbenzene (Scheme 1). Ligand **L** was characterized by ^1H and ^{13}C NMR spectroscopy and ESI mass spectrometry. Single crystals of eight compounds with the general formula $[MX_2L]\cdot G$ [M = Cd, X = Cl, Br, I, NO_3, OAc, ClO_4 (**1a–1f**), $MX_2 = CuCl_2$ (**2**), $CoCl_2$ (**3**); G = $2H_2O$ for **1** and **2** and 3/2 $CH_3OH\cdot H_2O$ for **3**] were readily obtained in good yields by heating a mixture of $MX_2\cdot nH_2O$ and **L** in dimethylsulfoxide

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(DMSO), MeOH, and toluene at 80 °C for two days. The formulations were supported by the results of microanalysis, IR spectroscopy, and thermogravimetry (TGA).

A single-crystal X-ray diffraction study on **1b** revealed a neutral 3D open metal–organic network with (14,3) topology.[10] Compound **1b** crystallizes in the chiral trigonal space group *R*32, and the asymmetric unit contains two-thirds of a formula unit (Figure 1). Interestingly, **1b** has a 1:3 molar ratio of Δ and Λ conformations of **L**, both of which link three Cd centers through three pyridine groups. The Cd1 environment and Λ-**L** have crystallographic C_2 symmetry, and the Cd2 environment and Δ-**L** crystallographic D_3 symmetry, and all of them are inherently chiral. The coordination environment of the central B atom of each **L** is completely trigonal planar with the three duryl groups arranged in a propellerlike fashion. The dihedral angles between the boron and the duryl planes are 60.075° for Δ-**L** and 58.083 and 55.225° for Λ-**L**, and those between the duryl plane and the outer pyridyl plane are 59.351 for Δ-**L** and 75.715 and 81.818° for Λ-**L**. Both cadmium centers are coordinated in a trigonal-bipyramidal fashion by three pyridine groups from three Λ-**L** ligands (Cd2) or from two Λ-**L** and one Δ-**L** ligand (Cd1) in the equatorial plane and two Br^- anions on the axis. The $[CdBr_2(\Lambda\text{-}\mathbf{L})_3]$ motif has threefold rotational symmetry and thus constitutes the octupolar NLO chromophoric unit of **1b**.[3]

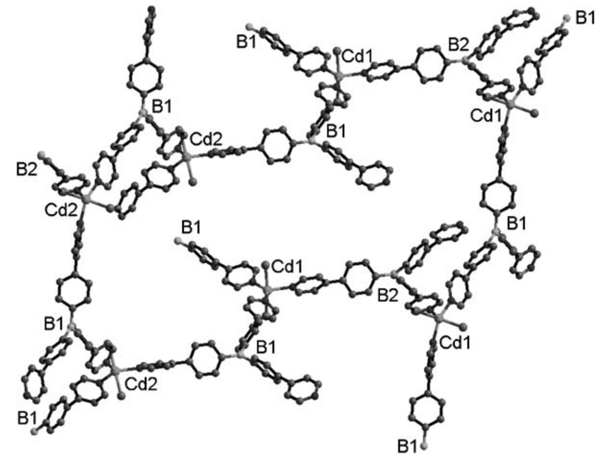

Figure 1. View showing the coordination environments of Cd centers and one 14-ring containing seven Cd and seven B centers in **1b**.

Each Cd center in **1b** is thus linked by three ligands **L** and each ligand **L** is linked to three cadmium atoms to form a unique 3D framework (Figure 2). The network topology of **1b** can be described as an unprecedented binodal (14,3) net if the metal center is treated as one three-connected node, and the ligand **L** as another three-connected node. Although all metal centers and ligands have the same connection mode and topological symbol, their topological properties are distinct. The Cd1 and B1 nodes have the Schläfli symbol (14,3) and vertex long symbol of [14(4).14(8).14(8)], whereas the Cd2 and B2 nodes have corresponding symbols of (14,3) and [14(8).14(8).14(8)], respectively (see Figure S5 in the Supporting Information). This (14,3) network is self-penetrating, whereby the two smallest 14-rings pass through each other. The guest solvent molecules occupy the chiral channels running parallel to the helical axes (see Figure S6 in the Supporting Information).

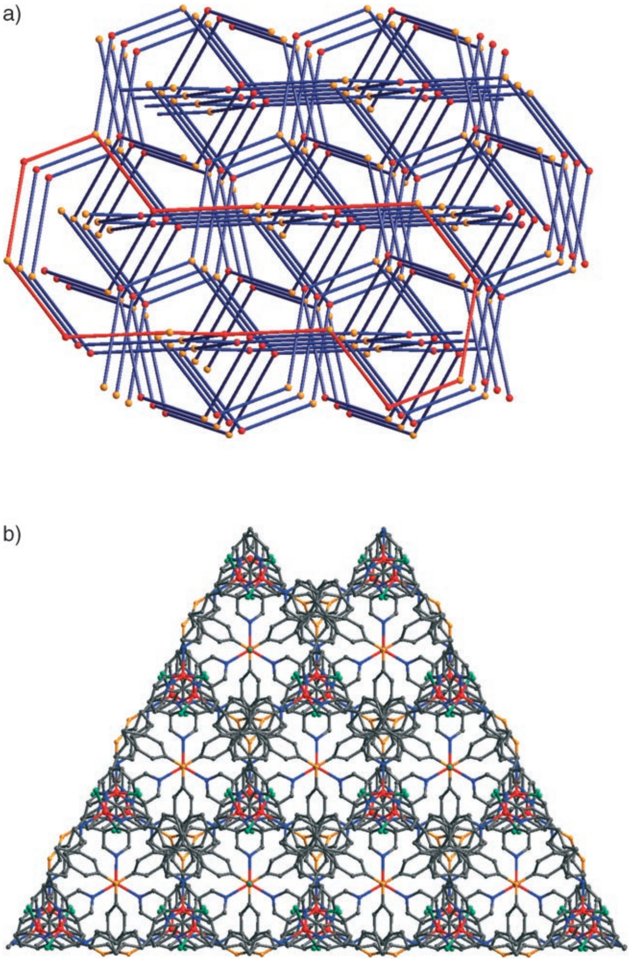

Figure 2. a) The (14,3) topology in **1b** (one 14-ring is highlighted with red lines). b) View of the 3D structure of **1b** along the threefold axis (guest molecules omitted for clarity; Cd red, B yellow, N blue, Br green, C gray).

Among numerous topological networks, the three-connected net is one of the most important and plausible target structures for designed synthesis.[9,11] The (12,3) net was suggested theoretically to be the largest (*n*,3) net by Wells[9] and was later demonstrated in an MOF by Robson et al.[11b] The present (14,3) net exceeds this limit and should provide an attractive network model for theoretical and synthetic studies on MOFs.

Although the synthesis of **1b** began from a racemic mixture of Δ- and Λ-**L**, spontaneous resolution occured on crystallization. Note that spontaneous resolution generally occurs completely and yields conglomerates of chiral crystals, each of which comprises only one enantiomer.[12] In the present case, partial but not complete spontaneous resolution of **L** was seen; each chiral crystal comprises a mixture of Δ- and Λ-**L** with 1:3 molar ratio. The enantiomeric excess of **L**, which propagates in all crystallographically equivalent directions, thus induces chirality, acentricity, and further octupolarity of the infinite network.

Single-crystal X-ray structure determinations revealed that **1c, 2**, and **3** are all isostructural to **1b**, while cell-parameter determinations and powder X-ray diffraction studies established that **1a**, **1d**–**1f** are also isostructural to **1b**. The phase purity of the bulk samples of **1**–**3** was established by comparison of their observed and simulated X-ray powder diffraction patterns (see Figure S7 and S8 in the Supporting Information). Calculations with the PLATON program[13] indicated that **1** has about 16% of total volume occupied by solvent molecules. Thermogravimetric analysis showed that guest molecules can be removed at 80 and 130 °C, and the frameworks are stable up to about 380 °C. Powder XRD experiments on **1b** and **1c** indicated that their frameworks and crystallinity remain intact on complete removal of guest molecules (see Figure S9 and S10 in the Supporting Information).

Kurtz powder SHG measurements were performed on **1** to confirm its acentricity and to evaluate its potential as a second-order NLO material.[14] Compound **1a** has a powder SHG intensity of 15 versus α-quartz, which is about 1.5 times higher than that of technologically useful potassium dihydrogenphosphate.[15] To investigate the influence of anions on the SHG response, **1b**–**1f** were studied. They showed powder SHG intensities of 24, 35, 11, 20, and 17, respectively, versus α-quartz (Figure 3). Clearly, the iodide exhibits the strongest, and the nitrate the weakest harmonic response. The harmonic responses of **1** are evidently realized by noncentric arrays of bridging organoboron skeletons through metal centers. The anion-dependent NLO activities of **1** probably can be related to different abilities of the anions to bind cations, which may modulate charge transfer between metal centers and organoboron ligands in coordination networks to generate adequate electronic asymmetry.[3a] Anion-responsive properties of assembled materials have recently drawn much attention but have not yet been well studied in MOFs.[16,17] Further studies to elucidate the origin of the anion-tunable NLO properties reported herein are underway.

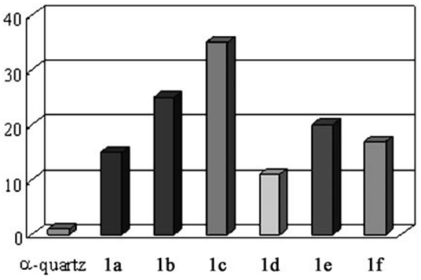

Figure 3. Comparison of the SHG intensities of α-quartz (set as unity) and **1a**–**1f**.

The SHG measurements on freshly evacuated samples of **1b** and **1c** revealed intensities of 26 and 35, respectively, versus α-quartz, both of which compare favorably with the values of the pristine materials. This indicates that NLO behaviors of the present frameworks are stable and are independent of guest removal and uptake. Moreover, **1a**–**1f** exhibit high thermal and solution stability and are totally transparent in the visible region, and this makes them attractive candidates for future practical applications.

In conclusion, we have developed a rational synthetic approach towards chiral octupolar NLO-active solids based on 3D coordination networks by using chiral and C_3-symmetric tris(pyridylduryl)borane as multidentate ligand. Current efforts are centered on optimizing the optical responses of this type of materials by end-functionalizing the arms of the octupolar units and making organoboron-based assemblies with unique and practically useful opto-electronic functions.

Experimental Section

Synthesis of **1**–**3**: A mixture of $MX_2{\cdot}n\,H_2O$ (0.005 mmol) and **L** (0.005 mmol) was placed in a small vial containing DMSO (1 mL), CH_3OH (2 mL), and toluene (0. 5 mL). The vial was sealed, heated at 80 °C for two 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. All products are stable in air and are insoluble in water and common organic solvents. Crystals of **1a**–**1f** are colorless, **2** is blue, and **3** is purple. Yield: **1a**, 3.0 mg, 70%; **1b**, 3.8 mg, 81%; **1c**, 3.8 mg, 72%; **1d**, 3.1 mg, 68%; **1e**, 3.5 mg, 71%; **1f**, 3.5 mg, 78%; **2**, 3.5 mg, 86%; **3**, 3.3 mg, 80%. Elemental analysis calcd (%) for $C_{45}H_{52}BBr_2CdN_3O$ (**1b**): C 56.90, H 5.52, N 4.42; found: C 56.11, H 5.48, N 4.39; IR (KBr): $\tilde{\nu} = 3432$ (m), 2986 (w), 1610 (s), 1558 (w), 1420(m), 1394(s), 1300(w), 1260(m), 1218(m), 1068(s), 954(m), 862(m), 820 (m), 802 (m), 652 (m), 614 cm^{-1}(w). IR and analytical data for **1a**, **1c**–**f**, **2**, and **3** can be found in supporting information.

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[10] Crystal data for **1b**: Trigonal, $R32$, $a = 18.169(3)$, $c = 47.599(10)$ Å, $V = 13607(4)$ Å^3, $Z = 12$, $T = 293$ K, $F(000) = 5784$, $\rho_{\text{calcd}} = 1.391\ \text{g cm}^{-3}$. $\mu(\text{Mo}_{\text{K}\alpha}) = 2.281\ \text{mm}^{-1}$ ($\lambda = 0.71073$ Å), 35530 measured reflections, 5316 independent reflections ($R_{\text{int}} = 0.1018$), 321 refined parameters, $R_1 = 0.0542$, $wR_2 = 0.1458$ for 4483 reflections with $I > 2\sigma(I)$, Flack parameter $= 0.025(16)$, GOF $= 1.089$. Crystal data for **1c**: Trigonal, $R32$, $a = 18.343(3)$, $c = 48.214(10)$ Å, $V = 14049(4)$ Å^3, $Z = 12$, $T = 293$ K, $F(000) = 6216$, $\rho_{\text{calcd}} = 1.481\ \text{g cm}^{-3}$. $\mu(\text{Mo}_{\text{K}\alpha}) = 1.821\ \text{mm}^{-1}$ ($\lambda = 0.71073$ Å), 21869 measured reflections, 5504 independent reflections ($R_{\text{int}} = 0.0316$), 321 refined parameters, $R_1 = 0.0437$, $wR_2 = 0.1151$ for 4983 reflections with $I > 2\sigma(I)$, Flack parameter $= 0.00(3)$, GOF $= 1.022$. Crystal data for **2**: Trigonal, $R32$, $a = 17.830(3)$, $c = 47.730(10)$ Å, $V = 13140(4)$ Å^3, $Z = 12$, $T = 293$ K, $F(000) = 5124$, $\rho_{\text{calcd}} = 1.232\ \text{g cm}^{-3}$, $\mu(\text{Mo}_{\text{K}\alpha}) = 0.659\ \text{mm}^{-1}$ ($\lambda = 0.71073$ Å), 31213 measured reflections, 5152 independent reflections ($R_{\text{int}} = 0.047$), 325 refined parameters, $R_1 = 0.0576$, $wR_2 = 0.1582$ for 4627 reflections with $I > 2\sigma(I)$, Flack parameter $= 0.019(18)$, GOF $= 1.048$. Crystal data for **3**: Trigonal, $R32$, $a = 17.674(3)$, $c = 48.066(10)$ Å, $V = 13002(4)$ Å^3, $Z = 12$, $T = 293$ K, $F(000) = 5304$, $\rho_{\text{calcd}} = 1.284\ \text{g cm}^{-3}$. $\mu(\text{Mo}_{\text{K}\alpha}) = 0.561\ \text{mm}^{-1}$ ($\lambda = 0.71073$ Å), 34054 measured reflections, 5075 independent reflections ($R_{\text{int}} = 0.065$), 331 refined parameters, $R_1 = 0.0664$, $wR_2 = 0.1815$ for 4253 reflections with $I > 2\sigma(I)$, Flack parameter $= 0.00(3)$, GOF $= 1.079$. CCDC-676714, CCDC-676715, CCDC-676716, and CCDC-676717 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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