Tunable NLO Behavior

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Cation-Dependent Nonlinear Optical Behavior in an Octupolar 3D Anionic Metal–Organic Open Framework**

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Multipolar second-order nonlinear optical (NLO) materials have attracted much attention since the discovery, in the early 1990s, that donor–acceptor-substituted molecules with threefold rotational symmetry (octupolar chromophores) show an improved transparency/optical nonlinearity trade-off with respect to traditional dipolar chromophores as a result of the presence of four significant components of molecular hyperpolarizability.[1] Accordingly, an increasing number of 2D and 3D nondipolar molecular structures have recently been reported as a consequence of the revival and development of the harmonic light scattering technique.[2,3] Nevertheless, the noncentrosymmetric assembly of octupolar building blocks into an acentric bulk material, which is an essential requirement for second-order optical nonlinearity, remains a significant challenge.[3–5]

Coordination-driven self-assembly provides a unique opportunity to prepare ordered arrays of molecules and clusters and has led to significant progress in the construction of metal–organic frameworks (MOFs) with novel topologies and potentially exploitable functions.[6] One of the most interesting aspects concerning the properties of MOFs is their dependence on the included guest species, which provides new opportunities for fine-tuning these properties by varying the guests.[6f] The rational assembly of acentric MOFs with dipolar NLO chromophoric units based on unsymmetrical bridging ligands and metal centers with well-defined coordination geometries was explored some years ago,[7] although there is only one report of an octupolar-type solid with a 2D coordination network that displays a very strong second harmonic generation (SHG) response.[4]

Herein, we report the synthesis, structural characterization, and second-order NLO activity of the octupolar 3D complex $[(H_2NMe_2)_2Cd_3(C_2O_4)_4]\cdot MeOH\cdot 2\,H_2O$ (**1**), which has a 3D T_d-symmetric open framework that contains 3^55^3 and 3^45^4 cages. This open framework shows high ion-exchange capacities with the cations NH_4^+, Na^+, and K^+, and exhibits a very high and unprecedented guest-cation-dependent NLO activity.[8] This finding is of significant interest because cations have long been believed to make a negligible contribution to the second-order susceptibility of NLO crystals such as β-BaB_2O_4 and LiB_3O_5.[8,9]

The solvothermal reaction of $CdCO_3$ with $H_2C_2O_4$ (3:4 molar ratio) in a mixture of dimethylformamide (DMF) and methanol resulted in the formation of colorless, cubelike crystals of **1** in moderate yield. The formulation of **1** was supported by elemental analysis and thermogravimetric analysis (TGA), and its phase purity was supported by the powder X-ray diffraction (XRD) pattern of the bulk sample, which is consistent with the calculated pattern (see Figure S4 in the Supporting Information). It should be noted that performing the reaction in the presence of $HNMe_2$ (or H_2NMe_2Cl), NH_4Cl (or $NH_3\cdot H_2O$), NaCl, or KCl under otherwise identical conditions did not lead to the formation of a compound isotopic to **1**.

Compound **1** crystallizes in the cubic acentric space group $I\bar{4}3d$ and possesses a 3D porous coordination network.[10] The basic building block in **1** is a hexameric $[Cd_6(C_2O_4)_8]^{4-}$ ionic cluster with a bowl-shaped geometry in which six Cd atoms are linked by six oxalate anions to form two sets of equilateral triangles whose center lies on a threefold axis, as shown in Figure 1. Of the two types of Cd ions, one (Cd1) is coordinated by eight oxygen atoms from four oxalate anions to form a distorted dodecahedron and the other (Cd2) is coordinated by six oxygen atoms from four oxalate anions to form a distorted octahedron.

The hexameric base containing the two triangular $[Cd_3(C_2O_4)_4]^{2-}$ motifs possesses a threefold rotational symmetry and thus constitutes the octupolar NLO chromophoric unit in **1**. The face-to-face connection of a pair of inner and outer equilateral triangles gives rise to a $Cd_9(C_2O_4)_9$ trigonal prism with a 3^55^3 topology (Figure 2a and Figure S1 in the Supporting Information). Adjacent prisms running along the C_3 axis are related by an S_4 axis and are ideally positioned to generate a $Cd_{10}(C_2O_4)_8$ truncated tetrahedron with a 3^45^4 topology (Figure 2c and Figure S2 in the Supporting Information). This means that each 3^55^3 cage shares its pentagonal and triangular faces with three 3^45^4 cages and five 3^55^3 cages, respectively, while each 3^45^4 cage shares its pentagonal and triangular faces with eight 3^55^3 cages (see Figures S1 and S2 in the Supporting Information). To the best of our knowledge, this is the first example of a coordination cage with a 3^45^4 or 3^55^3 topology.[11] Both cages are highly porous and the pentagonal aperture on each face has effective dimensions

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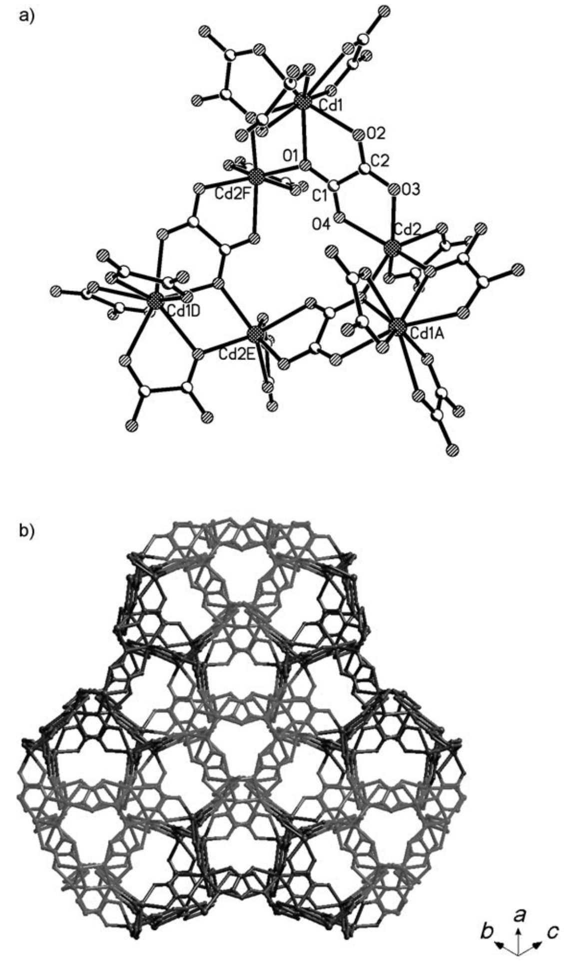

Figure 1. a) A view of the $[Cd_6(C_2O_4)_8]^{4-}$ octupolar building block in **1** and b) a view of the octupolar 3D anionic open framework of **1** (all guest molecules have been omitted for clarity).

of about 4.3 × 5.2 Å^2 (Figures 2b and 2d). Sharing of the pentagonal windows with neighboring cages gives rise to multidirectional zig-zag channels.

Overall, face-to-face intercage packing in **1** leads to an octupolar, 3D anionic supercage network with rare, crystallographically imposed T_d symmetry (Figure 1b). The trigonal prism in **1** has an open truncated-conic cavity with effective dimensions of about 2.8 × 4.3 × 5.2 Å^3. This cavity is occupied by disordered water and methanol molecules. Each truncated tetrahedron has an open spherical cavity with an effective diameter of about 5.9 Å, which is occupied by two disordered $H_2NMe_2^+$ ions (see Figure S3 in the Supporting Information). These ammonium cations are located around the pentagonal windows and form complicated hydrogen-bonding interactions with neutral guest molecules and the atoms in the walls of the anionic framework.

Calculations using the PLATON program[12] suggest that the effective volume available for inclusion is about 2205.8 Å^3, which is 34.7% of the crystal volume. TGA shows that **1** loses 8.4% of its total weight on heating to 140 °C, which corresponds to the loss of all the neutral guest molecules from the network (calcd: 8.0%) and starts to decompose at 290 °C (see Figure S8 in the Supporting

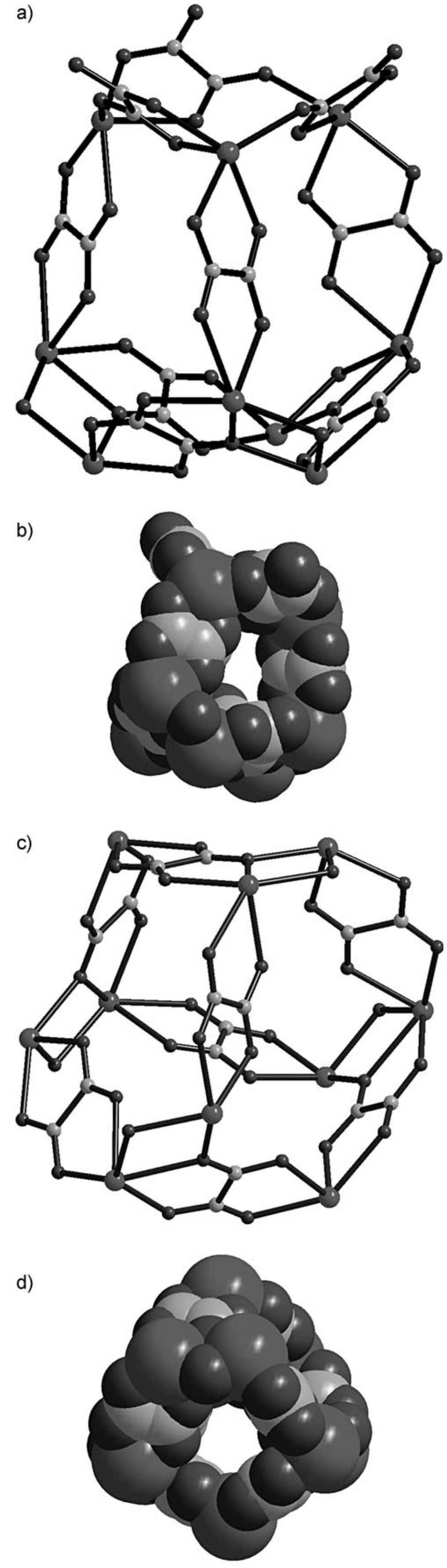

Figure 2. a) The polyhedral $3^5 5^3$ cage and b) its space-filling mode, and c) the polyhedral $3^4 5^4$ cage and d) its space-filling mode.

Information). A combination of TGA and powder XRD experiments indicates that the framework and crystallinity of **1** remain intact upon complete removal of all the included CH_3OH and water molecules (see Figure S5 in the Supporting Information).

The cation-exchange capacity of **1** was also examined. Complete replacement of $H_2NMe_2^+$ by NH_4^+, Na^+, or K^+ was accomplished by heating **1** in saturated solutions of NH_4Cl, NaCl, or KCl, respectively, in a capped screw vial or a teflon-lined stainless-steel vessel at 60 °C for five days, as confirmed by inductively coupled plasma analysis (ICP), elemental analysis, and/or solid-state ^{13}C NMR spectroscopy. According to powder XRD analysis, the exchanged materials have a lower crystallinity (see Scheme S1 and Figures S6, S7, and S9 in the Supporting Information). All attempts to substitute Cs^+ and alkaline-earth metal cations such as Mg^{2+} for $H_2NMe_2^+$ in **1** proved unsuccessful.

Preliminary Kurtz powder SHG measurements on **1** were performed to confirm its acentricity and to evaluate its potential as a second-order NLO material. Compound **1** has a powder SHG intensity of 150 versus α-quartz, which is about 15 times higher than that of technologically useful KH_2PO_4[13] and 1.5 times higher than that of previously reported 2D octupolar MOFs.[4] This means that **1** is the first NLO-active, 3D metal–organic solid based on octupolar building blocks, and, to the best of our knowledge, this is the strongest SHG intensity reported for an MOF to date.[7]

The NH_4^+-, Na^+-, and K^+-exchanged samples of **1** were studied to investigate the influence of the cation on the SHG response (Figure 3). These compounds show powder SHG intensities of 155, 90, and 110, respectively, versus α-quartz. To examine the effect of a low crystallinity on the SHG intensity of the host framework by cation exchange, the Na^+ ions in the exchanged sample (low crystallinity) were replaced again by $H_2NMe_2^+$ species (see Figure S7 in the Supporting Information). The re-exchanged product was also found to exhibit low crystallinity, but gave a powder SHG intensity of 147 versus α-quartz, which compares well with the value of **1**. The decrease in the crystallinity of the host framework therefore has no apparent effect on its SHG behavior and the change in the SHG intensity on cation exchange must be a cation-dependent phenomenon.

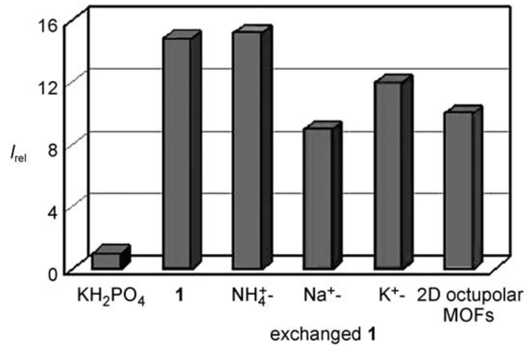

Figure 3. A comparison of the SHG intensities of KH_2PO_4, **1**, the NH_4^+-, Na^+-, and K^+-exchanged samples of **1**, and the known 2D octupolar MOFs[4] (the intensity value of KH_2PO_4 is set as 1).

The larger NLO activities of the protonated amine-templated samples relative to those of the alkali metal ion templated ones (Figure 3) can probably be related to the ability of organic amines to form multiple hydrogen bonds with the atoms in the walls of the anionic framework, which may modulate the charge transfer between $H_2NMe_2^+$ and the $[Cd_3(C_2O_4)_4]^{2-}$ chromophoric units in the crystalline state and generate electronic asymmetry.[14,15] Although guest-dependent properties of MOFs have recently drawn much attention, no guest effects on nonlinear optics have been reported to date.[6f] Our result therefore demonstrates for the first time that the selective enclosure of guest molecules or ions can be exploited to finely tune the polarity and optical properties of porous materials.[6]

Various controversies still exist, however, with regard to the role of cations such as alkali metal ions in NLO crystals such as β-BaB_2O_4 and LiB_3O_5.[8,9] According to the anionic group theory,[8] for example, the overall SHG coefficient of NLO crystals is the geometrical superposition of the microscopic second-order susceptibility of the anionic groups (or molecules for organic crystals), and has negligible contribution from the cations. Further studies to elucidate the origin of the guest-dependent NLO properties reported herein are currently underway. Compound **1** and its derivatives exhibit high thermal and solution stabilities and are totally transparent in the visible region, which makes them attractive candidates for future practical applications.

In conclusion, we have reported the self-assembly of an unprecedented organically templated 3D porous cadmium oxalate solid which features an octupolar T_d-symmetric supercage structure and has a very high SHG activity. In particular, we have demonstrated that the anionic framework has a high cation-exchange capacity and a clear cation-dependent SHG activity, which provides a means for the rational synthesis of acentric MOFs with multipolar NLO chromophoric building blocks. This class of materials will provide a new impetus to examining the potential applications of non-neutral porous solids as novel optical materials.

Experimental Section

Synthesis of **1**: A mixture of $CdCO_3$ (174 mg, 1.0 mmol), $H_2C_2O_4$ (120 mg, 1.33 mmol), DMF (8 mL), and MeOH (6 mL) was sealed in a 25-mL teflon-lined stainless-steel vessel and heated at 170 °C for 7 days. The mixture was then cooled to room temperature and the colorless cube-like crystals formed were collected, washed with distilled water and diethyl ether, and dried in air. Yield: 120 mg (42 % based on Cd). C,H,N elemental analysis calcd for $C_{13}H_{24}Cd_3N_2O_{19}$: C 18.38, H 2.85, N 3.30; found: C 18.02, H 2.97, N 3.24. IR (KBr): $\tilde{\nu}$ = 3150 (m), 1632 (s), 1426 (s), 1310 (m), 1210 (w), 1167 (w), 875 (w), 830 (s), 672 cm^{-1} (w). The product is air stable and insoluble in water and common organic solvents such as DMF and dimethyl sulfoxide. Based on the results of elemental analysis, IR spectroscopy, and TGA, **1** is best formulated as $[(H_2NMe_2)_2Cd_3(C_2O_4)_4]\cdot MeOH\cdot 2H_2O$. Single-crystal X-ray diffraction studies showed that **1** contains 2/3 MeOH and 4/3 H_2O guest molecules per formula unit.

A typical ion-exchange experiment: A freshly ground sample of polycrystalline **1** (0.012 mmol, 20 mg) was placed in a solution of NaCl (0.39 mmol, 23 mg) in water (4 mL) and methanol (2 mL). The mixture was then heated in a 10-mL capped vial or a 13-mL teflon-lined stainless-steel vessel at 60 °C for 5 days. The exchanged sample was then isolated by filtration and washed several times with water, acetone, and diethyl ether. Powder XRD diffraction experiments indicated that the anionic framework of **1** is retained but with low crystallinity upon exchange of the cation. Based on the results of ICP analysis and elemental analysis, the product can be formulated as $[Na_2Cd_3(C_2O_4)_4]\cdot 5H_2O$. The K^+- and NH_4^+-exchanged products can be formulated as $[K_2Cd_3(C_2O_4)_4]\cdot 4H_2O$ and $[(NH_4)_2Cd_3(C_2O_4)_4]\cdot 5H_2O$, respectively, in a similar manner, while the $H_2NMe_2^+$-re-exchanged product formed from the Na^+-exchanged material can be formulated as $[(H_2NMe_2)_2Cd_3(C_2O_4)_4]\cdot 3H_2O$ (see the Supporting Information).

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[10] Crystal data of **1**: cubic, $I\bar{4}3d$ (no. 220), $a = 18.518(2)$ Å, $V = 6350.0(12)$ Å^3, $Z = 12$, $T = 298$ K, $F(000) = 5096$, $\rho_{calcd} = 2.737\ g\,cm^{-3}$. $\mu(Mo_{K\alpha}) = 3.099\ mm^{-1}$ ($\lambda = 0.71073$ Å), 14204 measured reflections, 1175 independent reflections ($R_{int} = 0.0331$), 76 refined parameters, $R_1(F) = 0.0355$, $wR_2(F^2) = 0.0969$ for 1245 reflections with $I > 2\sigma(I)$, GOF = 1.145. CCDC-639538 contains 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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