Controlled generation of acentric and homochiral coordination compounds from a versatile asymmetric ligand 4-(1*H*-1,2,4-triazol-3-yl)-4*H*-1,2,4-triazole†

Rui-Bo Zhang,[ab] Jian Zhang,[a] Zhao-Ji Li,[a] Ye-Yan Qin,[a] Jian-Kai Cheng[a] and Yuan-Gen Yao*[a]

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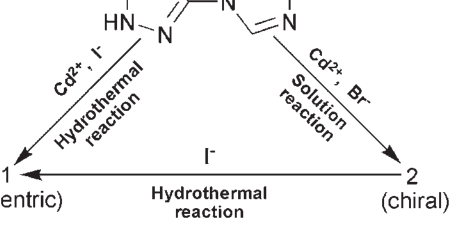
Luminescent acentric and homochiral coordination compounds, which possess new topological networks, multiple helical structures and NLO properties, have been generated through the control of a versatile asymmetric ligand as well as inorganic anions, and this suggests a new protocol for preparing acentric and chiral materials.

There is great current interest in the synthesis of acentric and chiral solids because of their potential applications in nonlinear optical (NLO) devices.[1] Particularly, since chirality plays a key role in biological systems and pharmacy,[2] an increasing amount of effort has been devoted to assemble chiral compounds. Some recent approaches have been successful in the synthesis of acentric and chiral complexes by using chiral or achiral ligands,[3] however, true rational control in constructing these materials still remains a distant prospect because of most complexes crystallizing in centric space groups. Therefore, employing a suitable asymmetric bridging ligand, especially for that possessing the atropisomeric conformation, may be a prerequisite to construct acentric and chiral coordination compounds.[4] Accordingly, our strategy for the generation of these materials is to employ an asymmetric ligand 4-(1*H*-1,2,4-triazol-3-yl)-4*H*-1,2,4-triazole (Hbtrz) as the bridging ligand. Our interest in Hbtrz is based on the fact that it is a hinge-like molecule. Two rigid triazole rings of Hbtrz are connected by a rotatable C–N bond, which endows it with subtle conformational adaptation and potential atropisomeric chirality. Those accompanying with its multiple coordinating nitrogen sites all facilitate the assembly of helical structures with inherent chirality.[5] Notably, these nitrogen sites may also serve as remote hydrogen-bonding donors or acceptors to form noncovalent helices. However, there isn't any study of the acentricity or chirality based on such a versatile asymmetric ligand so far.

In addition, it is known that inorganic anions can effectively induce the coordination mode of the organic ligand, and thus can control the structure of its complex.[6] By means of this inducement, assembling of structure-predictable acentric and chiral complexes can be controlled *via* deliberately selecting of appropriate inorganic anions. Nevertheless, systematical investigation of the anions-controlled generation of these materials is rarely known to our knowledge. Herein, we wish to report a controlled generation of acentric and chiral complexes by virtue of the versatility of Hbtrz as well as the inducement of inorganic anions (Scheme 1).

The hydrothermal reaction of Hbtrz with CdI_2 gave colorless prism crystals of $[Cd(btrz)_2]$ (**1**), which is three-dimensional (3D) and crystallizes in the polar and acentric space group *Fdd*2, with each Cd(II) center adopting a distorted octahedral site (Fig. 1a, Fig. S1, ESI†). Each deprotonated Hbtrz (btrz) in **1** adopts a quite asymmetric N1, N2, N6-bridging mode (μ_3), and the Cd–N bonds are significantly out of the triazole planes (with the Cd–N1-plane angle of 52.37°, Cd–N2-plane angle of −7.18°, and Cd–N6-plane angle of −12.22°). This asymmetric μ_3-bridging mode enables the 3D structure of **1**, and gives btrz the atropisomeric conformation with a dihedral angel of 10.78° between two triazole rings. Therefore, the asymmetric bridging mode and twisted conformation of btrz bring about the formation of helical chains. If we consider btrz as 3-connected nodes and Cd(II) as 6-connected nodes, four kinds of two-fold $(Cd\text{-}btrz)_n$ helices R1(*P*), R2(*P*), L1(*M*), and L2(*M*) can be well presented in this 3D network (Fig. 1b). Interestingly, incorporation of these helices can afford other two helices L3 (R1 + L1 + L2) and R3 (R1 + R2 + L2), and L3 is related to R3 by a *d* glide reflection (Fig. 1b, Fig. S2, ESI†), which leads to their opposite chirality. So **1** crystallizes in an acentric space group forming a *meso*-compound. From the study of **1**, we note that such an enrichment of helical structures is simultaneously embedded in a single complex, which is seldom encountered in metal–organic frameworks (MOFs) to our knowledge.



Scheme 1 Controlled generation of **1** and **2**.

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[a] *The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. E-mail: yyg@fjirsm.ac.cn*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

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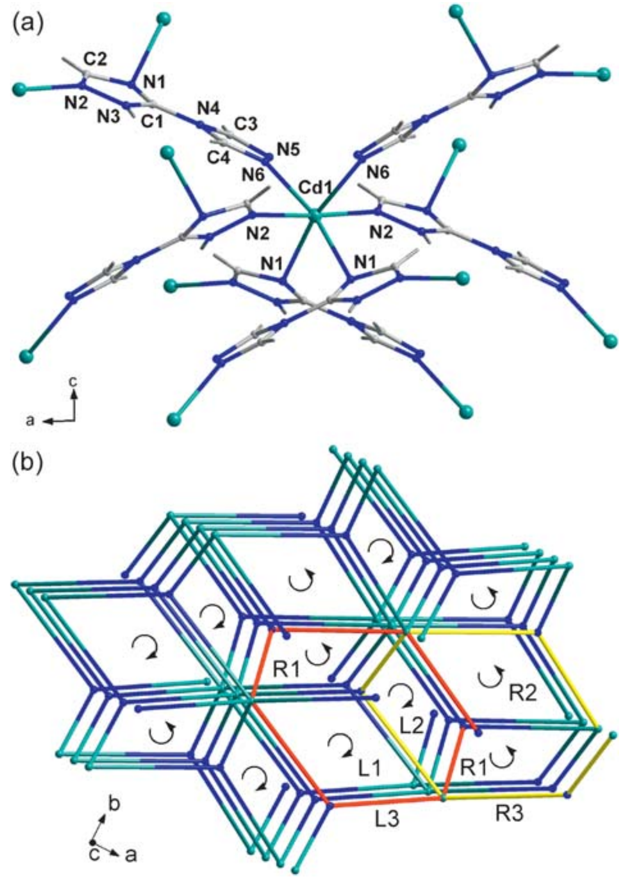

Fig. 1 (a) View of the distorted octahedral Cd(II) site and the asymmetric μ_3-bridging mode of btrz in **1**. (b) The new 3D topological net of **1**, showing (Cd-btrz)$_n$ helices L1–L3 and R1–R3. (L3 and R3 highlighted in red and yellow, respectively).

Furthermore, the 3,6-connected topological net of **1** is new (Fig. 1b), which can be presented with a Schläfli symbol $(6^3)_2(6^{10}\cdot8^5)$ and with a long vertex symbol $6\cdot6\cdot6\cdot6\cdot6\cdot6\cdot6\cdot6\cdot6_2\cdot6_2\cdot8_2\cdot8_2\cdot8_2\cdot8_4\cdot8_6\cdot8_8$, $6\cdot6_2\cdot6_3$. It is noteworthy that this net is built from a simple binary complex and is inherently acentric. These remarkable features are quite significant to prepare acentric solids with NLO properties in a straightforward and predictable way. The observed powder second harmonic generation (SHG) efficiency of **1** is 4.0 times that of potassium dihydrogen phosphate (KDP) (see ESI†).[7] The large SHG efficiency of **1** may be due to its dense chromophores, which are related with the tight-connected 3D structure and the cohesiveness of **1**.[8] All these topological and optical properties enable **1** to be an excellent candidate for NLO materials.

We note that μ_3-bridging btrz induces *meso*-helices in **1**, which obstructs to obtain the desired homochiral compound. It is known that 1,2,4-triazole often bridges two metal centers through N1 and N2 positions affording one-dimensional (1D) chains,[9] so we consider that this bridging mode accompanying with the conformational adaptation of Hbtrz is likely to produce 1D helical chains with homochirality. In this study, through the inducement of bridging Br$^-$ ions, the desired N1, N2-bridging mode was successfully accomplished, because the strong steric hindrance of the Br$^-$ ions can effectively block the μ_3-bridging mode of Hbtrz and thus induce the low dimensional (1D) structure.

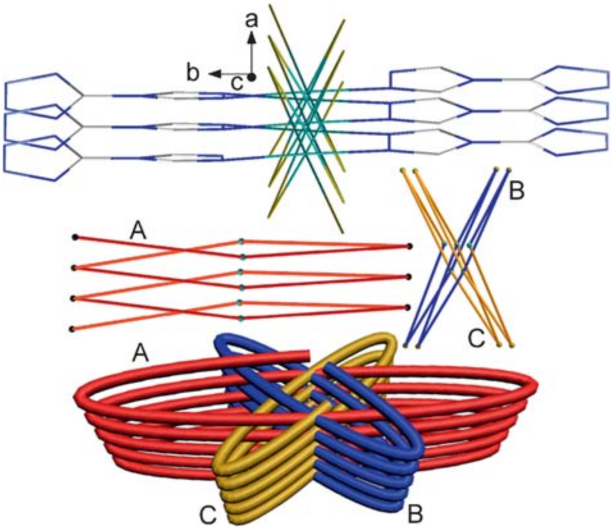

Fig. 2 The 1D structure of **2**, and schematic presentations of the single helix A, the double-stranded helices B and C and the coaxial triple-stranded helical structure.

Slow evaporation of either an originally mixed or hydrothermally treated solution of Hbtrz and $CdBr_2\cdot4H_2O$ could afford colorless prism crystals of $[Cd(Hbtrz)Br_2]\cdot(H_2O)$ (**2**), which crystallizes in a chiral space group $I2_12_12_1$ with the Flack parameter of $-0.014(17)$ indicating the homochirality of the randomly picked crystal. In this 1D structure, each metal atom is bonded to two transoid Hbtrz ligands and four Br atoms forming a distorted octahedral geometry (Fig. S3, ESI†). Similar to **1**, Cd–N bonds in **2** are also out of the triazole ring (Fig. S4, ESI†). As a result, Cd(II) centers in **2** are arranged on 2_1 screw axis, leading to multiple helices along the *c* axis, *i.e.* (Cd–Hbtrz)$_n$ (A) and (Cd–Br)$_n$ (B and C) helical chains (Fig. 2a). The single helix A, built from the metal centers and the Hbtrz ligands, is left-handed with a pitch of 7.14 Å. The double-stranded helices B and C consist of two intertwined Cd–Br chains, and both of them are right-handed, possessing the same pitches as that of A. Coaxial helices A, B and C twisting with each other afford another triple-stranded helical structure (Fig. 2a), which is seldom reported to our knowledge.

Notably, two triazole rings in **2** are quite twisted with a dihedral angel of 33.72°, and this twisting is crucial not only to induce the bent linkage of Cd(II) sites, but also to direct the free nitrogen sites of Hbtrz toward the O atoms of the guest H_2O molecules to form hydrogen-bonding interactions. These O–H···N hydrogen bonds (3.172 Å) linking the Hbtrz ligands afford another left-handed helical chain (D) along the *a* axis, which is perpendicular to Cd(II) involved triple-stranded helices (A, B and C) and bridges them with the same chirality into a homochiral 3D network (Fig. 3a and b). Because the helix A and D are respectively built from two different triazole rings of the same Hbtrz ligand, the atropisomeric chirality translation between these helices occurs, so does the spontaneous resolution when they conglomerate to a homochiral network. Hence, Hbtrz in **2** manifests a versatility to assemble

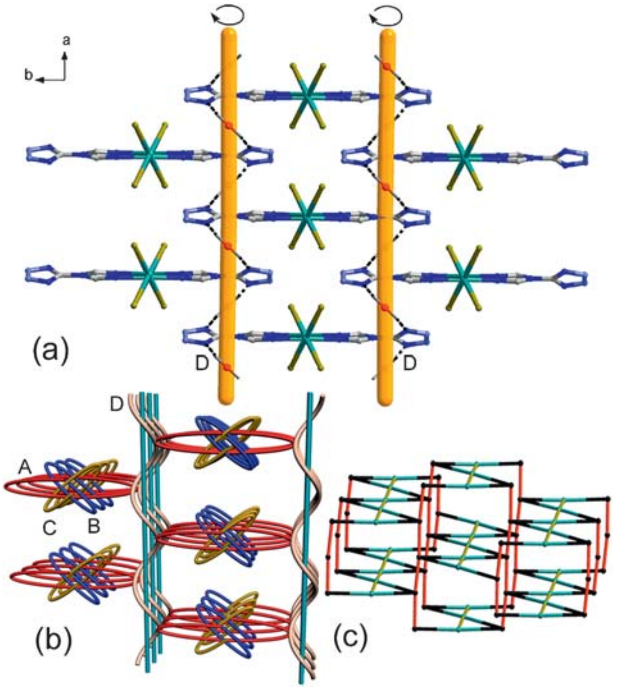

Fig. 3 (a) View of the 3D supramolecular network of **2** showing the hydrogen bond constructed helices (D). (b) Schematic presentation of the 3D network of **2**. (c) The new 4,4-connected topological net of **2**.

chiral helices both through covalent bonds and through hydrogen bonds. Moreover, if considering Cd(II) and Hbtrz as 4-connected nodes, bromide ligands and water molecules as linkers, the whole structure can be presented as a new 4,4-connected net with a Schläfli symbol $(3{\cdot}8^5)(3^2{\cdot}8^3{\cdot}9)$ and a long vertex symbol $(3{\cdot}8_2{\cdot}8_2{\cdot}8_2{\cdot}8_2{\cdot}8_2)$ $(3{\cdot}3{\cdot}8_2{\cdot}8_2{\cdot}8_2{\cdot}9_4)$ (Fig. 3c). The SHG efficiency of **2** is 1.5 times that of KDP, which also confirms its acentricity.

Recently, photoluminescent Cd(II) complexes have been intensively investigated for their potential applications as new luminescent materials.[10] The photoluminescent properties of **1** and **2** have been investigated in the solid state at room temperature. Compounds **1** and **2** all exhibit strong and broad fluorescent emission bands with maximum at 424 and 436 nm, upon excitation at 325 and 287 nm, respectively (Fig. S5, ESI†). Since the free Hbtrz ligand has a fluorescent emission at 452 nm ($\lambda_{\mathrm{ex}} = 370$ nm) in the solid state,[11] which is similar to the emissions of **1** and **2**, their photoluminescence behaviors may be assigned as the intraligand π–π^* transitions.[10] The fluorescence lifetime τ of **1** and **2**, all fitted biexponentially to two components, are on the nanosecond timescale (Fig. S6, ESI†). The thermal stabilities of **1** and **2** were analyzed by TG on-line coupled with QMS (quadrupole mass spectrometer) (Fig. S7 and S8, ESI†). Compound **1** manifests a high thermal stability with its TG curve unchanged up to 400 °C, which is related with its stable and dense covalent 3D framework. For **2**, the loss of lattice H_2O occurs below 200 °C (exptl, 4.27%; calcd, 4.23%), and no other decomposition is observed up to 300 °C (see ESI†).

For **2**, seven single crystals were randomly picked for X-ray diffraction, and the refined results indicate that they all have the same absolute structure (see ESI†). This reveals that, at the very least, the bulk samples of **2** consist predominantly of the same enantiomorph, and that they are probably chirally pure. Interestingly, when the hydrothermal reaction of KI and **2** was carried out, compound **1** could be obtained again (Scheme 1, and ESI†), which means that in this study, I^- ions play a key role in forming acentric compound **1** even though they are not incorporated into the final products. This suggests through the effective control of inorganic anions (Br^- and I^-) under appropriate conditions, acentric and chiral complexes can be rationally prepared and even have the possibility to transform.

In summary, an acentric and a homochiral coordination compound have been successfully generated under controlling of the versatile asymmetric ligand Hbtrz as well as inorganic anions. They all possess new topological networks and multiple helical structures, exhibiting second-order nonlinear optical and photoluminescence properties. The interesting spontaneous resolution of **2** and the anions-controlled transformation from **2** to **1** are observed as well. The result reported here offers a new protocol for reasonably preparing acentric and chiral solids with desired structures and physical properties.

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