Nonlinear optical and ferroelectric properties of a 3-D Cd(II) triazolate complex with a novel $(6^3)_2(6^{10}\cdot8^5)$ topology†

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A novel 3-D (3,6)-connected topological architecture, obtained by reacting $Cd(ClO_4)_2\cdot6H_2O$ with Htrtr (Htrtr = 3-(1,2,4-triazole-4-yl)-1*H*-1,2,4-triazole) under solvothermal conditions, presents a non-centrosymmetric polar packing arrangement, resulting in a strong second harmonic generation (SHG) response and ferroelectric property.

One of the most fascinating and significant targets of the crystal engineering is to design and synthesize materials with specific attributes such as profuse structural topologies,[1] chemical functions and physical properties.[2] Nonlinear second harmonic generation (SHG) and ferroelectric behavior are very useful and important physical properties in areas such as laser medicine, optical communication, signal processing, and the expanding field of integrated optics.[3] Absence of center of symmetry is the all-important and essential term for these materials. Despite the fact that a great deal of progress has been made in the syntheses of acentric structures,[4] there still remain challenges in the synthesis of non-centrosymmetric polar packing arrangements.

1,2,4-Triazole and its derivatives have been widely employed to design metal–organic coordination polymers (MOCPs) due to their importance in medicine, biology and industry. Although many studies have been carried out on 1,2,4-triazolate systems, their aims have been mainly on the structural development for novel topological architectures[5] and physical properties such as photoluminescence (PL), magnetism and spin-transition behavior,[6] but seldom on developing NLO[7] and ferroelectric properties. During our research on the assembly of MOCPs of triazole and its derivatives,[8] we selected the unsymmetrical bridging ligand Htrtr which is π-electron rich and Cd(II) cation as sources, and obtained a novel Cd(II) triazolate complex $[Cd(trtr)_2]_n$ (**1**) with non-centrosymmetric polar packing arrangement. Herein, we report the synthesis, structure, optical (NLO and PL) and ferroelectric properties, band structure, and the unprecedented (3,6)-connected topological network of **1**.

The solvothermal reaction‡ of $Cd(ClO_4)_2\cdot6H_2O$ or CdI_2 with Htrtr in H_2O–EtOH at 160 °C gave rise to the colourless crystals of **1**. Compound **1** is air stable and insoluble in common solvents. Powder X-ray diffraction study indicates that the products are phase-pure (Fig. S1, ESI†). Single-crystal X-ray diffraction analysis§ reveals that the title complex has a 3-D framework constructed from cadmium ions and μ_3-trtr ligands. The asymmetric unit of **1** contains one trtr ligand and half a cadmium ion (Fig. 1). The Cd1 atom, lying on a twofold axis, is coordinated by two N2, two N5 and two N6 atoms from six different trtr ligands to form a distorted octahedron, which can be considered as a six-connected node in the structure of **1**. The Cd–N bond distances in **1** range from 2.241(2) to 2.502(2) Å, comparable with those found in the literature.[7a,9] The trtr ligand adopts a μ_3-bridging mode with each N2, N5 or N6 atom ligating a Cd atom separately, affording a three-connecting node. As a result, the Cd centers are interconnected through μ_3-trtr ligands to generate a 3-D architecture. Unlike the known metal–Htrtr/trtr complexes,[9b,10] in which the Htrtr/trtr acts as a mono- or bidentate ligand to form 0-D or 1-D structures, the trtr ligand in **1** acts as a μ_3-bridge to link the metal atoms into a 3-D structure for the first time. The reaction condition may play a key role in the construction of the structure. In comparison with the known metal–Htrtr/trtr complexes synthesized by solution methods, the present compound was synthesized

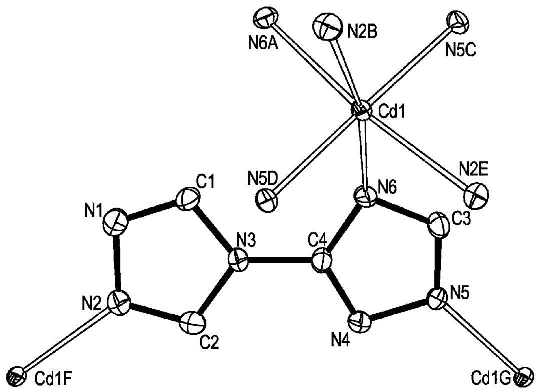

Fig. 1 ORTEP drawing of **1** with 50% thermal ellipsoids with hydrogen atoms being omitted for clarity. (Symmetry codes: A: $-x, 1-y, z$; B: $-1/4-x, 1/4+y, 3/4+z$; C: $1/4-x, 1/4+y, 1/4+z$; D: $-1/4+x, 3/4-y, 1/4+z$; E: $1/4+x, 3/4-y, 3/4+z$; F: $-1/4+x, 3/4-y, -3/4+z$; G: $1/4+x, 3/4-y, -1/4+z$).

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using the solvothermal technique, indicating the solvothermal condition has a tendency to force maximal coordination modes for bridging ligands.[11]

The detailed structure of **1** can be described in a stepwise manner. The trtr ligands link Cd atoms through the N2 and N5 atoms to form a right-handed helical chain extending along the *c* axis with the helical pitch being 7.319(2) Å (Fig. 2(a)). The helical chains arrange in parallel along the *a* direction by sharing Cd centers to form a sheet of (4,4) topology. Contrarily, its adjacent (4,4) sheets are made up of left-handed helical chains. The adjacent sheets are linked in parallel to each other in an –ABAB– fashion through interlamellar Cd1–N6 bonds to form the 3-D structure of **1** (Fig. 2(b)). A better insight into the 3-D network of **1** can be achieved by application of a topological approach. As mentioned above, the architecture of **1** can be reduced to a binodal structure with six-connected (Cd atoms) and three-connected (trtr ligands) nodes, adopting an unprecedented $(6^3)_2(6^{10}\cdot8^5)$ topology (the first symbol for trtr ligands, the second for Cd centers),[12] as shown in Fig. 2(d).

Up to now, fifteen examples have been reported with 3-D (3,6)-connected topology, including the familiar pyrite-like network (FeS_2 with S···S bonds ignored, $(6^3)_2(6^{12}\cdot8^3)$).[12,13] The 3-D structures of pyrite and **1** are all constructed by stacking (4,4) sheets in parallel, however, different from the sheet of **1** which is constructed by the same helical chains, the sheet in pyrite is constructed by alternate left- and right-handed helical chains (Fig. S2 and S3, ESI†).

Second-order nonlinear optical effects were examined to confirm the physical properties deriving from the assignment of **1** to crystal class *mm*2 (point group C_{2v}) with an acentric space group (*Fdd*2). A powdered sample of **1** is SHG active with a signal six times that of KH_2PO_4,[14] which is the strongest among the known triazolate systems.[7] The powder SHG response of **1** is attributed mainly to a good donor–accepter system (Fig. 2(c)) and the orderly arrangement of the organic moieties. Each helical chain in **1**, which is similar to a head-to-tail main-chain NLO polymer,[15] exhibits a dipole moment along the *c* axis owing to the counteracting of the moments of trtr ligands along the *a* and *b* directions (Fig. 2(a)). Due to the packing of the helical chains and sheets in parallel, the whole 3-D crystal structure also has a dipole moment along the *c* direction (Fig. 2(a) and Fig. S4, ESI†), which strengthens the hyperpolarizability of **1** to result in a good SHG response. The polar point group C_{2v} of **1**, one of the 10 polar point groups, implies compound **1** may have the potential to exhibit ferroelectric property. The measurement of electric hysteresis loop shows that compound **1** exhibits a ferroelectric behavior with a remnant polarization (P_r) of 3.94 nC cm^{-2}, coercive field (E_c) of 2.28 kV cm^{-1} and saturated polarization (P_s) of *ca.* 9.51 nC cm^{-2} (Fig. 3), similar to those found in the compound $[Eu(tta)_3{\cdot}L]$ (tta = 2-thenoyltrifluoroacetonate, L = (−)-4,5-pinene bipyridine/(+)-4,5-pinene bipyridine) and a homochiral trinuclear discrete Ni(II) complex reported by Xiong and You and co-workers.[4d,4e] To the best of our knowledge, compound **1** represents the first example with ferroelectric property among metal triazolate complexes. Thermogravimetric analysis shows that compound **1** is thermally stable up to *ca.* 390 °C (Fig. S5, ESI†). The high thermal stability, insolubility in common solvents, as well as the low absorptivity and wide transparency range (Fig. S6, ESI†) of **1** make it a fine candidate for NLO and ferroelectric materials.

The diffuse reflection spectrum of **1** reveals the presence of an optical gap of 4.44 eV (Fig. 4(a)), which is consistent with its color. The band structure of solid-state compound **1** shows an indirect bandgap of 4.05 eV (Fig. S7, ESI†), which is comparable with the experimental value. The bands can be assigned according to total and partial density of states (DOS) (Fig. 4(c)). It is shown that both the top of valance bands and the bottom of conduction bands are mainly contributed from N-2p and C-2p states, so the optical adsorption of **1** is ascribed to the charge transition from the occupied hybrid states of N-2p and C-2p to the empty hybrid states.

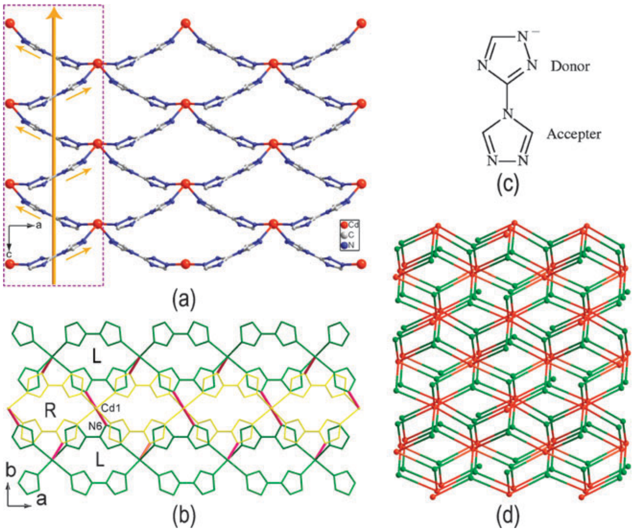

Fig. 2 (a) A (4,4) sheet made up of parallel right-helical chains (the yellow arrows represent dipoles of trtr ligands); (b) 3-D architecture of **1** based on sheets interlinked by Cd1–N6 bonds (red lines: Cd1–N6 bonds); (c) donor–accepter system of trtr; (d) a schematic view of the $(6^3)_2(6^{10}\cdot8^5)$ topology of 3-D network of **1**. Nodes: red, Cd atoms; green, trtr ligands.

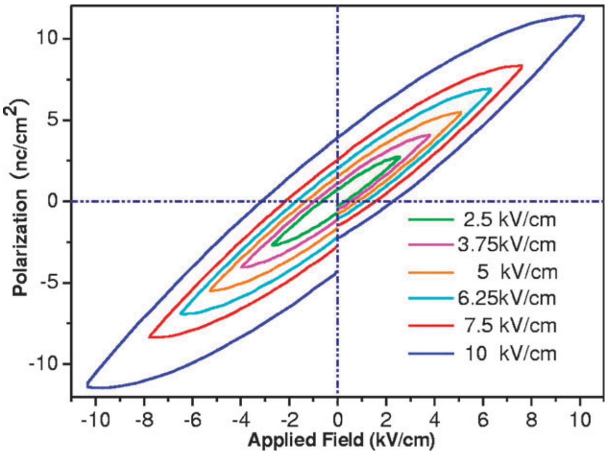

Fig. 3 Electric hysteresis loop of a pellet obtained from a powdered sample of **1**.

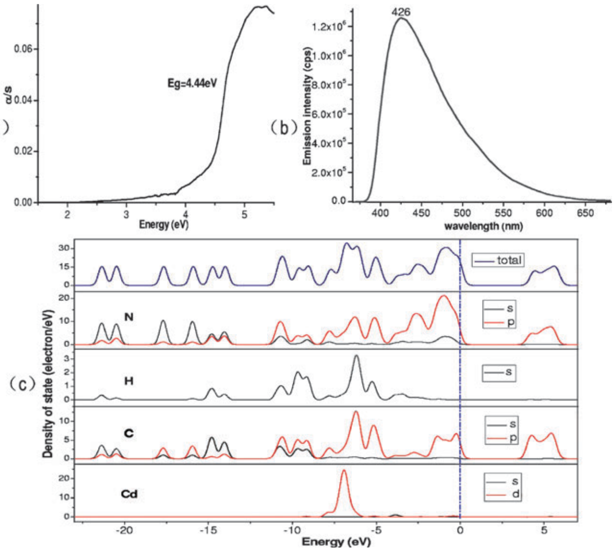

Fig. 4 (a) Diffuse reflection spectrum of **1**; (b) PL emission spectrum of **1** in the solid state; (c) the total and partial DOS of **1**.

The PL spectrum study at room temperature shows that compound **1** emits an intense blue light centered at 426 nm upon photo-excitation at 350 nm (Fig. 4(b)). The fluorescence spectrum of **1** can be assigned as an intraligand π–π* transition due to the similar emissions of pure Htrtr ligand (Fig. S8, ESI†) and **1**, as well as the above-mentioned calculation results.

In summary, we have prepared a 3-D Cd(II) triazole complex with an unprecedented $(6^3)_2(6^{10}\cdot8^5)$ network and the strongest SHG effect in the triazolate system. The ferroelectrical property is first investigated in the triazolate system, which opens a new avenue to ferroelectric materials through MOCPs. The present work shows that triazolate compounds have broad potential in the application for NLO and ferroelectric materials. We will extend this approach to the syntheses of other acentric MOCPs.

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Notes and references

‡ *Synthesis* of **1**: A mixture of Htrtr (108 mg, 0.8 mmol), $Cd(ClO_4)_2\cdot6H_2O$ (168 mg, 0.4 mmol) or CdI_2 (146 mg, 0.4 mmol), water (3 mL) and ethanol (6 mL) was loaded into a 25-mL Teflon-lined steel autoclave, and heated at 160 °C for 4 days, yielding colourless crystals of **1**. Yield: 60% (based on Htrtr ligand). Anal. (%): Calc.: C, 25.11; H, 1.58; N, 43.93. Found: C, 25.26; H, 1.54; N, 43.42.

§ *Crystal data* for **1**: $C_8H_6CdN_{12}$, M_r = 382.65, orthorhombic, *Fdd*2, a = 16.024(5), b = 18.856(6), c = 7.319(2) Å, V = 2211.4(11) Å^3, T = 293(2) K, Z = 8, D_c = 2.299 g cm^{-3}, μ = 1.994 mm^{-1}. Final R indices [$I > 2\sigma(I)$], $R1$ = 0.0138, $wR2$ = 0.0352. GoF on F^2 = 1.015.

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