A green luminescent 1-D helical tubular dipyrazol-bridged cadmium(II) complex: a coordination tube included in a supramolecular tube

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Fig. S1 Ball-stick view of the asymmetrical unit of 1.

In the asymmetrical unit of 1, there is 0.5 Cd²⁺ ion, 0.5 H₂Me₄bpz ligand and one H₂bidc⁻ anion, respectively.

Fig. S2 View of the construction of the coordination helical tubes of 1 running along c axis.
The combination of bitopic H$_2$Me$_4$bpz with metal ions leads to two types of coordination helical chains with opposite chirality as shown in Fig 2, S2, possessing a 2$_1$ screw axis parallel to $c$ with a pitch of 8.392(2) Å. The left- and right-handed helical chains are further weaved by H$_2$bidc$^-$ anions through chelating the adjacent two Cd$^{2+}$ ions parallel to $c$ axis to make the elliptical helical tubes with opposite chirality.

![Fig. S3 The helical tube of 1 viewed along c axis.](image)

The dimension of the coordination helical tube is about 3.77 Å × 8.70 Å. The one of the two methyl groups of H$_2$Me$_4$bpz point away from the Cd–H$_2$Me$_4$bpz helical chains and into the coordination helical tubes, then, the elliptical coordination tubes became the smaller approximate circular tubes.

![Fig. S4 The [Cd$_2$(H$_2$bidc)$_2$] units like butterflies settling on the two sides of the tube.](image)
The [Cd₂(H₂bidc)₂] units like butterflies settled on the two sides of these tubes (Fig 1, S6).

**Fig. S5** The construction of the supramolecular helical tube in the combination of quintuple-helical-chain with single-helical-chain in the structure of 1, (a) view of the supramolecular helical tube; (b) View of the supramolecular helical channels made of quintuple-helical-chain containing unclosed 48-membered ring along the [001] direction. Five helical chains of the quintuple-helical-chain are equivalent. [In the structure, four [Cd(H₂bidc)]ₙ units are linked by N–H···O hydrogen bonds through two repeated -Cd1-O2-C6-O1···H4A-N4-C10-C9-C8-C7-C6-O2-Cd1-O2-C6-C7-C8-C9-C10-N4-H4A···O1-C6-O2- linkages to give rise to helical channels containing quintuple-helical-chain with the pitch of 8.392(2) Å along the c-axis; (c) View of the supramolecular helical channels made of single-helical-chain containing unclosed 34-membered ring along the [001] direction. In the structure, the Cd atoms are linked by carboxyl groups of O1C6O2 and N–H···O hydrogen bonds through two repeated -Cd1-O2-C6-O1···H4A-N4-C10-C9-N3-Cd1-N3-C14-N4-H4A···O1-C6-O2- linkages to give rise to helical channels along the c-axis.**

In compound 1, H₂Me₄bpz and H₂bidc ligands both can act not only as a hydrogen-bond acceptor but also as a hydrogen bond-donor, so there are complex strong hydrogen bonds between them. Four [Cd(H₂bidc)]ₙ units are linked by N–H···O hydrogen bonds (N···O: 2.659 Å and 2.895 Å)
to form a nano-size elliptical supramolecular helical channels with the dimension of 17.04 Å×8.70 Å. The supramolecular helical channels, which are made of quintuple-helical chains, are further weaved by single-helical chains to make the tubular walls. As shown in Figure S7, the walls of the supramolecular helical tubular channels can be described as two parts: one part is the helical channels made of the quintuple-helical-chain containing five equivalent helical chains (Figure S7b), another is single-helical-chain (Figures S7c). The quintuple-helical-chain are further weaved by the single-helical-chain with the same helical orientation each other through sharing Cd vertices to form a unique helical tubular combination.

**Fig. S6** The construction of the tube-in-tube structure viewed along c axis: (a) The coordination helical tube through Cd-N, Cd-O coordination bonds; (b) The supramolecular helical tube built from four [Cd(H₂bide)]ₙ units linked by N–H···O hydrogen bonds; (c) View of the coordination helical tube in the supramolecular helical tube.

**Fig. S7** The construction of the tube-in-tube structure viewed along b axis: (a) The coordination helical tube running along c axis; (b) The tube-in-tube structure.
Four [Cd(H$_2$bidc)$_2$]$_n$ units are linked by N–H···O hydrogen bonds (N···O: 2.659 Å and 2.895 Å) to form a nano-size elliptical supramolecular helical channels with the dimension of 17.04 Å×8.70 Å, and the coordination helical tube with the same-handness is contained in it.

![Diagram](image1)

**Fig. S8** View of a 16-membered hydrogen bond ring in boat-like conformation comprised of four carboxylate groups by O–H···O hydrogen bonds.

The uncoordinated carboxylate groups point to the channels. Four carboxylate groups comprised a 16-membered ring in boat-like conformation by O–H···O hydrogen bonds (O···O: 2.595 Å).

![Diagram](image2)

**Fig. S9** The PXRD pattern of 1 and simulated respectively.

The good accordance of the experimental PXRD patterns with the simulated patterns indicates phase purity of 1.
The IR spectrum (Fig S9) of 1 exhibits the strong and sharp absorption peaks, of 1562 and 1488 cm\(^{-1}\) attributed to the \(\nu_{as}\) and \(\nu_s\) vibration of the carboxylate group, respectively, and peaks at 1702 cm\(^{-1}\) corresponding to the \(\nu(C=O)\) of carboxylic acid, indicating that the carboxyl groups of H\(_2\)bide ligands are not completely deprotonated. The broad bands at 3155-2500 cm\(^{-1}\) indicate the presence of O-H and N-H, and the existence of hydrogen bonding interaction. These facts are consistent with the X-ray diffraction results.

![Fig. S10 IR spectrum of 1](image)

![Fig. S11 UV-Visible absorption spectrum of 1.](image)
In the UV absorption spectra, the strong absorptions at 304 nm for compound 1. (Fig. S11), is ascribed to the π→π* transitions of ligands.

![Fig. S12](image1.png)

Fig. S12 View of three types of hydrogen bonds.

![Fig. S13](image2.png)

Fig. S13 Excitation spectrum of 1
The luminescence decay curves of 1 at room temperature are well fit into a triexponential function as $I = A + B_1 \times \exp(-t/\tau_1) + B_2 \times \exp(-t/\tau_2) + B_3 \times \exp(-t/\tau_3)$. The emission decay lifetimes are $\tau_1 = 0.10$ ns (10.48%), $\tau_2 = 7.82$ ns (48.85%) and $\tau_3 = 1.96$ ns (40.67%) ($\chi^2 = 1.379$) for 1.