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Isomer separation, conformation control of flexible cyclohexanedicarboxylate ligand in cadmium complexes†

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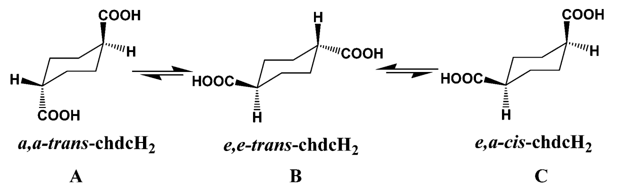
Two 2D cadmium coordination polymers have been prepared using flexible 1,4-cyclohexanedicarboxylic acid ($chdcH_2$) under hydrothermal condition, the conformations of $chdcH_2$ were separated completely in the synthetic reactions.

The rational design and construction of inorganic–organic hybrid materials by flexible multidentate ligands have received considerable attention[1–3] due to their novel structures as well as their special functional properties.[4–6] However the control of the conformation of flexible ligands in the synthetic reactions is still an exciting challenge to chemists. 1,4-Cyclohexanedicarboxylic acid ($chdcH_2$) possesses three preponderant conformations of two carboxylic groups and is usually attainable in a mixture of *cis* and *trans* conformations. As shown in Scheme 1, conformation A is the least stable and is able to change to its conformer B easily.[7] However, it is a little more difficult when C becomes B because the α-protons should be deprotonated to accelerate the equilibrium although B is thermodynamically more stable. Although selective coordination of chdc ligand in cobalt and nickel compounds has been reported,[4a,8] only single conformation (*cis* or *trans*) of the ligand was recognized in the synthetic reactions. By changing pH value, the ratio of *cis* and *trans* chdc ligand in a lanthanide compound can be successfully controlled under hydrothermal condition.[9] To date, there is no report on complete separation of *cis*/*trans* conformations of $chdcH_2$ in the reaction systems of the same metal ions. Our synthetic approach starts by focusing on finding the reactions where the *cis* and *trans* conformations of $chdcH_2$ can be separated completely under certain conditions. Unfortunately, when we employed lanthanide ions with high coordination number or transition metal ions with small atomic radii, the experiments failed. Hence, Cd^{II} ion was used in our experiment, we hope the large atomic radii and alterable coordination geometry of Cd^{II} ion is helpful for the separation of *cis* and *trans* conformations. In this communication, we wish to report the first example of coordination polymers constructed with cadmium ions in which the *cis*/*trans* conformations of 1,4-cyclohexanedicarboxylic acid were separated completely.

We first studied the hydrothermal reaction of $Cd(NO_3)_2{\cdot}4(H_2O)$, 1,4-cyclohexanedicarboxylic acid ($chdcH_2$, mixture of *cis* and *trans* in a ratio of 3 : 2) and 1,10-phenanthroline in the molar ratio of 1 : 2 : 1 at a pH value of 3.3 and a temperature of 130 °C. $[Cd_2(\textit{cis}\text{-chdc})_2(phen)_2]{\cdot}3.5H_2O$ (**1**) was collected as colorless prism crystals in a yield of 57.2%.‡ X-ray crystal structure analysis§ reveals the central Cd^{II} ion of **1** is coordinated by five oxygen atoms from three different carboxylate groups and two nitrogen atoms from phen. 1,4-cyclohexanedicarboxylic acid is deprotonated and only *e,a-cis*-$chdc^{2-}$ ligand (L_1) is present in the complex. L_1 links three Cd^{II} ions in chelate and chelate-bridged mode to form an infinite zigzag chain with a 2_1 helix along the *b* axis. The adjacent chains are connected together by the bridged oxygen atoms of the carboxylate groups into a layer in which right- and left-handed chains are alternating. The phen ligands take up the other two vertexes of the coordination polyhedron and keep the layer from growing to a 3D framework (Fig. 1). In the packing arrangement of **1**, the layers form a 3D framework *via* strong π–π packing interactions of 1,10-phen (the distances of the phen planes range from 3.4264 to 3.4887 Å) in slipped stacking mode according to the classification of Janiak.[10] The hydrogen bonding interactions between lattice water molecules and oxygen atoms of carboxylate groups also help to improve the stability of the final architecture.



Scheme 1

As illustrated above, at high temperature and pH value, $chdcH_2$ may favor conformation B (Scheme 1). Thus, we raised the reaction temperature to 180 °C and pH value to 8.5, hoping to isolate the complex with only the *trans* conformation ligand. As expected, complex $[Cd_4(\textit{trans}\text{-chdhH})_2(\textit{trans}\text{-chdc})_3(phen)_4](\textit{trans}\text{-chdcH}_2){\cdot}6H_2O$ (**2**) with only *trans* ligand was obtained as colorless crystals in 42.6% yield.‡ X-ray crystal structure analysis§ shows the structure of **2** is much more complicated than that of **1**. Each Cd^{II} ion is coordinated by four oxygen atoms from carboxylate groups and two nitrogen atoms from phen in a distorted octahedral geometry. There exist four kinds of *trans*-chdc ligands (Fig. 2): protonated *e,e-trans*-$chdcH_2$ (L_2) acts as guest molecules, partly deprotonated *e,e-trans*-$chdcH^-$ ligands (L_3) links two Cd^{II} ions by its bridging carboxylate group, deprotonated *e,e-trans*-$chdc^{2-}$ ligand (L_4) links two Cd^{II} ions by its two chelating carboxylate groups, deprotonated *e,e-trans*-$chdc^{2-}$ ligand (L_5) links four Cd^{II} ions by its two bridging carboxylate groups. Every two Cd^{II} ions are linked together by L_4 to form a basal unit. Such units are connected by the bridging oxygen atoms of L_3 and the strong π–π packing interactions of 1,10-phen (the distance between phen planes in the same layer is 3.451Å and that between phen planes of the different layers is 3.4757 Å) in slipped stacking mode[10] into an infinite zigzag chain. The chains are further interlinked by L_5 to

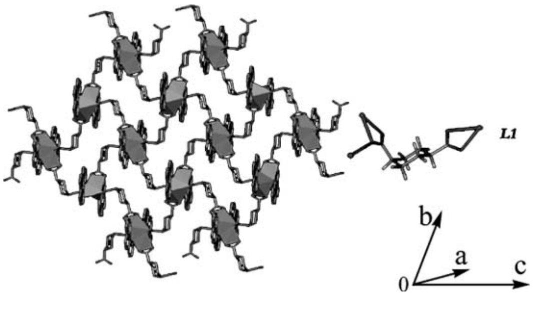


Fig. 1 The layer structure of $[Cd_2(\textit{cis}\text{-chdc})_2(phen)_2]{\cdot}3.5H_2O$ (**1**).

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† Electronic supplementary information (ESI) available: NMR spectra for $chdcH_2$ under different conditions, XRPD patterns and the π–π stacking information for the two complexes. See http://www.rsc.org/suppdata/cc/b4/b407405j/

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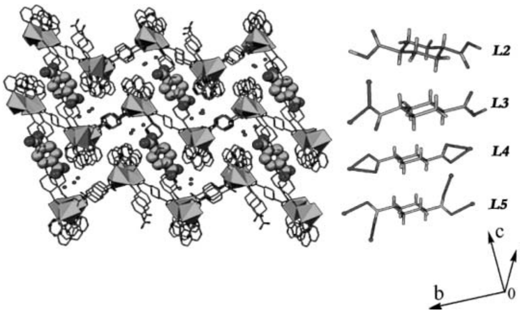

Fig. 2 The packing arrangement of [Cd$_4$(*trans*-chdhH)$_2$(*trans*-chdc)$_3$-(phen)$_4$](*trans*-chdcH$_2$)·6H$_2$O (**2**).

form an undulating layer with rhombic grid. The most interesting feature of **2** is that there exists a socket constructed by the phen ligands and the *trans*-chdcH$^-$ ligands (L_3) on the surface of the wavy layer. Every two sockets on the adjacent layers gear to each other to form a capsule in which the guest *e,e-trans*-1,4-cyclohexane dicarboxylic acid (L_2) is enveloped. Probably the *e,e-trans*-conformation of L_3 ligands makes the capsule possesses selectivity to recognize *e,e-trans*-chdcH$_2$ (L_2) rather than *e,a-cis*-chdcH$_2$ molecules. Meanwhile, the other parts of the tunnel between the layers are filled by the lattice water molecules and plentiful hydrogen bonding interactions are found between the lattice water molecules and the carboxylate groups, by which the layers are connected into a 3D framework.

The TGA curve of **1** reveals that the first weight loss from 89.56 to 112.27 °C (6.2%) may be attributed to the loss of all the lattice water molecules (6.4%). The second stage occurs at above 422.31 °C (68.7%), in agreement with the calculated value (67.6%), indicating the loss of all the organic ligands and the decomposition of the complex. For **2**, the first weight loss (11.9%) from 78.43 to 132.66 °C corresponds to the removal of the lattice water (Calc: 12.2%) and one chdcH$_2$ molecule per unit, and the weight loss of 66.1% (Calc: 65.5%) over 391.73 °C shows the decomposition of the coordination chdc and phen ligands.

In conclusion, we have successfully separated *cis* and *trans* conformations of 1,4-cyclohexanedicarboxylic acid in the syntheses of Cd^{II} polymeric complexes in hydrothermal reactions through changing the reaction temperature and pH value. ^{1}H-NMR experiments show that the *cis*/*trans* ratio of chdcH$_2$ retains after simply heating the ligand in water or the reaction mixture without the formations of the two complexes, illustrating the separation of the confomations of chdcH$_2$ may be accomplished during the formations of the complexes. The work may provide useful strategy for the control of the conformation of flexible ligand in the field of crystal engineering. Further work is underway and will be reported in a full paper.

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Notes and references

‡ Preparation of [Cd$_2$(*cis*-chdc)$_2$(phen)$_2$]·3.5H$_2$O (**1**): 0.15 g (0.5 mmol) of Cd(NO$_3$)$_2$·4(H$_2$O), 0.17 g (1.0 mmol) of 1,4-cyclohexanedicarboxylic acid (chdcH$_2$, mixture of *cis* and *trans* in a ratio of 3 : 2) and 0.09 g (0.5 mmol) of 1,10-phenanthroline were dissolved in 20 mL of distilled water and the pH value was adjusted to 3.3 with dilute aqueous KOH solution. The solution was heated in a 25 mL Teflon-lined reaction vessel at 130 °C for 50 h and then cooled to room temperature during 12 h. Colorless prism crystals of **1** were collected with a yield of 57.2%. Calcd. for C$_{40}$H$_{43}$N$_4$O$_{11.5}$Cd$_2$ (%): C, 48.43; H, 4.37; N, 5.67; Found: C, 48.49; H, 4.32; N, 5.71. Preparation of [Cd$_4$(*trans*-chdhH)$_2$(*trans*-chdc)$_3$(phen)$_4$](*trans*-chdcH$_2$)·6H$_2$O (**2**): 0.15 g (0.5 mmol) of Cd(NO$_3$)$_2$·4(H$_2$O), 0.26 g (1.5 mmol) of 1,4-cyclohexanedicarboxylic acid (chdcH$_2$, mixture of *cis* and *trans* in a ratio of 3 : 2) and 0.09 g (0.5 mmol) of 1,10-phenanthroline were dissolved in 20 mL of distilled water. The pH value was adjusted to 8.5 with aqueous KOH solution. The solution was heated at 180 °C for 83 h and then cooled to room temperature during 12 h. Colorless crystals of **2** were collected with a yield of 42.6%. Calcd. for C$_{48}$H$_{54}$O$_{15}$N$_4$Cd$_2$ (%): C, 49.91; H, 4.72; N, 4.85; Found: C, 50.12; H, 4.77; N, 4.91. The purity of the two complexes is confirmed by XRPD experiments.

§ Crystallographic Data: (C$_{40}$H$_{43}$N$_4$O$_{11.5}$Cd$_2$), M = 988.62, triclinic, P–1, a = 11.6798(2), b = 13.0060(1), c = 14.1926(3), α = 90.8330(10)°, β = 113.6790(10)°, γ = 90.2230(10)°, V = 1974.13(6) Å^3, Z = 2, D_c = 1.663 Mg m^{-3}, Mo–Kα radiation (λ = 0.71073 Å), 10216 reflections collected, 6850 unique ($R_{(int)}$ = 0.0367), final R_1 = 0.0552, wR_2[**I**>2*Sigma(**I**)*] = 0.1077, Goof = 1.047 for **1**; and C$_{48}$H$_{54}$O$_{15}$N$_4$Cd$_2$, M = 1151.75, triclinic, P–1, a = 10.5609(2), b = 12.7878(2), c = 18.5575(2) Å, α = 80.6360(10)°, β = 85.7320(10)°, γ = 72.9910(10)°, V = 2363.69(6) Å^3, Z = 2, D_c = 1.618 Mg m^{-3}, Mo–Kα radiation (λ = 0.71073 Å), 12154 reflections collected, 8167 unique ($R_{(int)}$ = 0.0317), atom C48 is disordered over two orientations (C48 and C48′) of different probability (occupation factors for C48 and C48′ refined to: C48 = 76%, C48′ = 34%), final R_1 = 0.0591, wR_2[**I**>2*Sigma(**I**)*] = 0.1061, Goof = 1.158 for **2**. Both structures were solved by direct methods with SHELX-97 software package and all non-hydrogen atoms were treated anisotropically.§ CCDC reference numbers: 224331 and 224329.

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