Helical Coordination Polymers

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Supramolecular Helix-to-Helix Induction: A 3D Anionic Framework Containing Double-Helical Strands Templated by Cationic Triple-Stranded Cluster Helicates**

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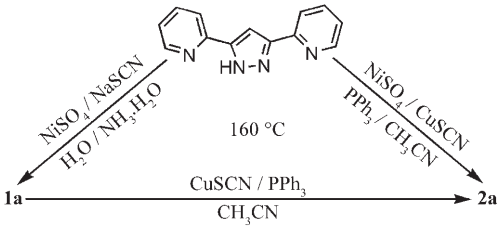
Linked historically to the discovery of the double-helical structure of DNA by Watson and Crick[1a] and the introduction of the first inorganic double-stranded helicate by Lehn et al.,[1b] artificial molecular multiple-stranded helices are at the frontier for synthetic chemists in the field of organic, inorganic, and supramolecular chemistry.[2] In the realm of coordination chemistry, artificial helical assemblies, including discrete helicates[3] and infinite helices,[4] are attracting increasing attention. The helicate series has been systematically and intensively investigated,[3a] mostly relying on intramolecular coordinative bonds to construct discrete multiple-stranded helicates. However, a potential approach is to self-assemble supramolecular multiple-helical structures using intermolecular noncovalent interactions, such as electrostatic interactions, hydrogen bonding, and π stacking.[2a,d,3a] Therefore, a judicious strategy is desired for constructing functional helical coordination polymers through transfer of intrinsic structural information from noncovalent interactions with discrete helicates.

Inspired by well-defined discrete molecular helicates,[3a] we propose herein a helix-to-helix induction strategy to fabricate supramolecular polymeric helices using helicates as templates. We have previously developed a sulfur-transformation approach[5] to construct supramolecular aggregates of anionic CuSCN/CuCN networks directed by cationic metal–bis(terpyridine) monomers.[5d] In this work, cationic cluster helicates[6] were selected to implement the helix-to-helix induction because: 1) the well-shaped cluster possesses intriguing helical character, thereby making the template effect[7,8] feasible; 2) the cluster is positively charged and should show strong electrostatic interactions with the negatively charged inorganic framework; 3) there may exist hydrogen bonding between the encapsulating inorganic components and the wrapped ligands of the cluster helicates, which carry abundant hydrogen atoms.

The ligand 3,5-bis(2-pyridyl)pyrazole (HL), synthesized through similar reactions as in our previous work,[9] reacted hydrothermally with $NiSO_4{\cdot}6H_2O$ (or $ZnSO_4{\cdot}7H_2O$) and NaSCN, yielding $[\{M(\mu\text{-}L)_3\}_2\{M_3(\mu\text{-}OH)\}](SCN)_3{\cdot}6H_2O$ ($M = Ni^{2+}$ (**1a**) or Zn^{2+} (**1b**)). Solvothermal reaction of **1a** (or **1b**) and CuSCN in the presence of PPh_3 led to coordination polymers of empirical formula $[Cu_{12}(CN)_{11}(SCN)_4]{\cdot}[\{M(\mu\text{-}L)_3\}_2\{M_3(\mu\text{-}OH)\}]$ ($M = Ni^{2+}$ (**2a**) or Zn^{2+} (**2b**)). Complex **2a** (or **2b**) could also be obtained solvothermally in acetonitrile by the one-pot reaction of CuSCN, Ni^{2+} (or Zn^{2+}) salt, HL, and PPh_3 (Scheme 1). The fact that the same polymeric



Scheme 1. Synthesis of complexes **1a** and **2a**.

helices (**2**) could be synthesized in one-pot reactions suggests that the helicate templates (**1**) may be generated and stay stable before the encapsulation of the inorganic components in the solvothermal conditions.[5c]

X-ray crystallographic analysis[10] reveals that **1a** and **1b** as well as **2a** and **2b** are isostructural, and therefore only **1a** and **2a** are discussed in detail. The structure of the triple-stranded helicate **1a** can be viewed as a $[Ni_3(\mu\text{-}OH)]^{5+}$ cluster core wrapped by two terminal $[Ni(\mu\text{-}L)_3]^-$ units,[6b] and the whole tricationic helicate is balanced by SCN^- ions. In the crystal packing left-handed (Figure 1, middle-up) and right-handed (Figure 1, middle-down) triple-stranded helicate enantiomers are present, resulting in a racemate. In the structure of **2a**, the cationic $[\{Ni(\mu\text{-}L)_3\}_2\{Ni_3(\mu\text{-}OH)\}]^{3+}$ cluster helicates are entrapped by the anionic $[\{Cu_{12}(CN)_{11}(SCN)_4\}^{3-}]_\infty$ encapsulating network, which is generated in situ by the sulfur transfer reaction from CuSCN to PPh_3.[5d] The anionic infinite network contains 1D tubes constructed by two intertwined copper–pseudohalide (mixed CuSCN/CuCN) helical strands along the *c* axis, which are templated by cluster helicates with approximate dimensions $16.1 \times 14.6 \times 12.2$ Å^3 (Figure 1, left and right). Careful examination indicates that the copper–pseudohalide components self-assemble along the helical paths constructed by the ligands wrapped around the cluster cores to form double-helical strands, resulting in the same helicity as the entrapped templates. Furthermore, the hydrogen bonding between the guest helicates and the host network stabilizes the template effect

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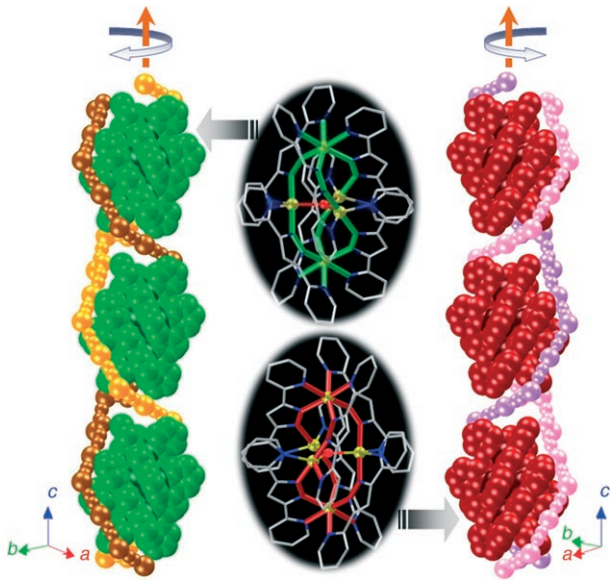

Figure 1. Side views of the cluster helicates **1a** (middle, left-handed helicates in green and right-handed helicates in red) and the double-helical strands in **2a** templated by cluster helicates (left: left-handed helical strands in gold and yellow; right: right-handed helical strands in purple and pink); in helicate structures: Ni yellow, O red, N blue, C gray, H atoms are omitted.

(Figure S4 in the Supporting Information; Cu···H 2.623–2.810 Å). The left-handed and right-handed double-helical strands in **2a** are alternately arranged to form a 3D anionic framework by sharing irregular copper–pseudohalide components (Figure 2a). The whole framework of **2a** can be topologically simplified by regarding the irregular components as ladder chains (Figure S7 in the Supporting Information, and Figure 2b). Notably, the helicity of the template is recognized to produce the outer helices with the same handedness, suggesting remarkable chirality transfer[11] from the template helicates (see the Supporting Information).

The intrinsic structural information encoded in discrete helicates (e.g. in **1a**), which is responsible for their self-assembly, includes central metal ions with appropriate coordination numbers and geometries, flexible covalent organic ligand strands, and coordination bonds that enable the ligands to wrap around the metal centers to form helicates.[3a] In this work, the cationic cluster helicates take the place of metal ions, and provide the dominant structural information in the self-assembly of the supramolecular helix. Unlike organic ligands, for which such chirality transfer can be hindered through steric constraints, the inorganic copper–pseudohalide components, with their flexible arrangement and unique encapsulating capability, interact closely with the helicate clusters and thus adopt the complementary structural information in the assembly of the polymeric helical framework. The intermolecular noncovalent interactions between the helicates and the copper–pseudohalide components respond to the stereochemical induction of the double helices in **2a**, resembling the effect of the intramolecular coordination bonds in the assembly of discrete helicates. The electrostatic interactions and hydrogen bonding furnish additional stabilization for the construction of the coordination polymers (Scheme S1 in the Supporting Information).

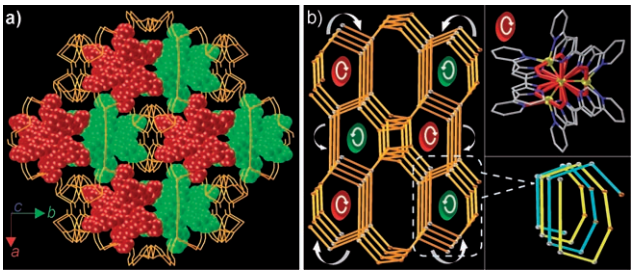

Figure 2. a) Top views of the overall framework of **2a**; left-handed helicates are shown in green, right-handed ones in red; the 3D anionic framework is shown in yellow. b) Topological representation of **2a**. Left- and right-handed helicates are simplified to green and red cylinders, respectively. The white rectangle (dashed line) highlights the left-handed double-helical strands. The white arrows suggest the helical-sense preferences of the wrapped double helices assisted by the template triple helicates.

Besides the helix-to-helix induction and the resulting coordination polymers, the cluster helicates embedded in the host framework offer fascinating possibilities for exploring functional coordination materials.[3,6] In this work, the complexes were functionalized by varying the metal ions in the cluster helicates from Ni^{2+} (**1a** and **2a**, which exhibits magnetic exchange) to Zn^{2+} (**1b** and **2b**, which is photoluminescent). The magnetic properties of **1a** and **2a** were measured in the temperature range 5–300 K. For **1a**, the $\chi_M T$ value at 300 K is 5.27 $cm^3 K mol^{-1}$, and this value rapidly decreases upon further cooling. The magnetic data can be fitted to the Curie–Weiss law with $\theta = -52.4$ K, thus indicating intramolecular antiferromagnetic coupling between the Ni^{2+} atoms.[12a] The trigonal-bipyramidal model[12b] was applied to perform a quantitative analysis, and the best-fit parameters obtained are $J_1 = -10.1$ cm^{-1}, $J_2 = -14.5$ cm^{-1}, $J_3 = -3.24$ cm^{-1}, and $g = 2.20$ (Figure S9 in the Supporting Information). For **2a**, the $\chi_M T$ value at 300 K is 3.88 $cm^3 K mol^{-1}$, which is much smaller than the calculated spin-only value of 5.0 $cm^3 K mol^{-1}$. Thus, the quantitative analysis could not be performed while the Curie–Weiss fitting indicated antiferromagnetic coupling ($\theta = -36.9$ K, Figure S10 in the Supporting Information). Photoluminescent measurements indicate that complexes **1b** and **2b** both exhibit strong blue-purple luminescence with emission maxima at 384 nm and 394 nm upon excitation at around 256 nm, respectively (Figure S11 in the Supporting Information). Compared to the emission from the ligand, with a maximum at 375 nm, the emission peaks of **1b** and **2b** show slight red shifts, and the emission of the complexes is tentatively attributed to the intraligand π–π* charge transfer modified by inter- and intramolecular interactions (see the Supporting Information).

In conclusion, we have developed a helix-to-helix induction strategy to generate coordination polymers containing double-helical strands templated by triple-stranded cluster helicates. This work successfully demonstrates the extension of molecular helicates to supramolecular helices by taking advantage of their intrinsic structural information, and offers a new protocol for synthesizing compounds that are of

interest for their fascinating structures as well as their potential properties.

Experimental Section

1a: A mixture of $NiSO_4{\cdot}6H_2O$ (0.0263 g, 0.10 mmol), HL (0.0266 g, 0.12 mmol, synthesized by a procedure similar to that in reference [9]), NaSCN (0.0324 g, 0.40 mmol), aqueous ammonia (25%, 1 mL), and H_2O (8 mL) was stirred for 1 min in air, then transferred to a 15-mL teflon-lined reactor, and sealed. The reactor was heated in an oven at 160°C for 72 h and then slowly cooled to room temperature at a rate of 5°C h^{-1}. Light-blue, blocklike crystals were collected and dried in air (75% yield). Elemental analysis (%) calcd for **1a**: C 48.06, H 3.9, N 18.68; found: C 48.00, H 4.116, N 18.68.

1b: Complex **1b** was prepared analogously to complex **1a**, except that $NiSO_4{\cdot}6H_2O$ was replaced by $ZnSO_4{\cdot}7H_2O$ (0.0287 g, 0.10 mmol). Pale-yellow, flakelike crystals were collected and dried in air (72% yield). Elemental analysis (%) calcd for **1b**: C 47.32, H 3.65, N 18.40; found: C 47.45, H 3.82, N 18.28.

2a: One-pot synthesis: A mixture of CuSCN (0.0729 g, 0.60 mmol), $NiSO_4{\cdot}6H_2O$ (0.0263 g, 0.10 mmol), HL (0.0266 g, 0.12 mmol), PPh_3 (0.1049 g, 0.40 mmol), and acetonitrile (9.0 mL) was stirred for 1 min in air, then transferred to a 15-mL teflon-lined reactor, and sealed. The reactor was heated in an oven at 160°C for 72 h and then slowly cooled to room temperature at a rate of 5°C h^{-1}. Dark-green, blocklike crystals were collected and dried in air (63% yield). Stepwise synthesis: The solvothermal reaction of **1a** (0.1920 g, 0.10 mmol), CuSCN (0.0729 g, 0.60 mmol), PPh_3 (0.1049 g, 0.40 mmol), and acetonitrile (9.0 mL) yielded the same dark-green, blocklike crystals under conditions similar to those mentioned above. Elemental analysis (%) calcd for **2a**: C 38.40, H 1.89, N 18.79; found: C 38.56, H 1.92, N 18.72.

2b: One-pot synthesis: Complex **2b** was prepared analogously to complex **2a**, except that $NiSO_4{\cdot}6H_2O$ was replaced by $ZnSO_4{\cdot}7H_2O$ (0.0287 g, 0.10 mmol). Pale-green, blocklike crystals were collected and dried in air (58% yield). Stepwise synthesis: The solvothermal reaction using conditions similar to those for **2a**, except that **1a** was replaced by **1b** (0.1954 g, 0.10 mmol), yielded the same green, blocklike crystals. Elemental analysis (%) calcd for **2b**: C 37.99, H 1.87, N 18.58; found: C 37.67, H 1.97, N 18.65.

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[10] Crystal data for **1a**: $C_{81}H_{67}N_{27}Ni_5O_7S_3$, tetragonal, space group $I\bar{4}$, $M_r = 1920.35$, $a = 16.9518$, $b = 16.9518$, $c = 30.4260$ Å, $V = 8743.363$ Å^3, $Z = 4$, $\rho_{calcd} = 1.459$ g cm^{-3}, $\mu = 1.198$ mm^{-1}, $T = 173(2)$ K; $R_1 = 0.0681$, $wR_2 = 0.1470$. Crystal data for **2a**: $C_{93}H_{55}N_{39}O_1S_4Ni_5Cu_{12}$, monoclinic, space group $C2/c$, $M_r = 2919.03$, $a = 22.8664$ (9), $b = 23.3568(10)$, $c = 19.6974(8)$ Å, $\beta = 95.2840(10)°$, $V = 10475.4(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.851$ g cm^{-3}, $\mu = 3.400$ mm^{-1}, $T = 173(2)$ K; $R_1 = 0.0755$, $wR_2 = 0.1384$. Crystal data for **2b**: $C_{93}H_{55}N_{39}O_1S_4Zn_5Cu_{12}$, monoclinic, space group $C2/c$, $M_r = 2952.33$, $a = 22.8420(9)$, $b = 23.4045(9)$, $c = 19.8531(8)$ Å, $\beta = 95.9120(10)°$, $V = 10557.1(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.857$ g cm^{-3}, $\mu = 3.618$ mm^{-1}, $T = 173(2)$ K; $R_1 = 0.0688$, $wR_2 = 0.1383$. Crystal data for **1b** is not shown because of the disorder of the anion and solvent molecules and the quality of the data. Since **1a** and **1b** are isostructural, we carried out the data refinement of **1b** using Squeeze in Platon, which gave the main framework of **1b**. The molecular formula of **1b** is ascertained from elemental analysis, thermogravimetric analysis, and IR spectroscopy, and is suggested to be $C_{81}H_{67}N_{27}Zn_5O_7S_3$, $M_r = 1953.80$. Data collection was performed on a Bruker Smart Apex CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) by using frames of 0.3° oscillation ($4.56 \le 2\theta \le 50°$). The structure was solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on F^2 by using the SHELXTL program (G. M. Sheldrick, SHELXLT 6.10, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, **2000**). The TWIN instruction of SHELXTL was used for **2a**,**b**. The C and N atoms of the CN^- ligands are indistinguishable, and they are assigned randomly as C or N atoms. The hydrogen atoms were located from difference maps and refined with isotropic temperature factors (see the Supporting Information for crystallographic details). CCDC-

664496, 664497, 664498, and 664499 contain 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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