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From Encapsulation to Polypseudorotaxane: Unusual Anion Networks Driven by Predesigned Metal Bis(terpyridine) Complex Cations

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Solvothermal reactions of CuSCN, metal (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) sulfate, and terpyridine (2,2′:6′,2″-terpyridine or 4′-*p*-tolyl-2,2′:6′,2″-terpyridine) in the presence of triphenylphosphine yielded a series of hybrid coordination compounds, in which in situ formed metal bis(terpyridine) complex cations are encapsulated by a 3D anionic network or entangled by 2D heartlike networks, forming encapsulation or poly*pseudo*rotaxane supramolecules. The complex cations play a role as template to direct the fabrication of the structures.

Supramolecular encapsulation and entanglement (e.g., catenane, knot, and rotaxane) assemblies are particularly intriguing because of the presence of independent subunits encapsulated or entangled mutually in different ways.[1−5] The ability to control the cooperative behavior of subunits within a spatial assembly is a key concern and becomes a great challenge for chemists. Metal complexes of 2,2′:6′,2″-terpyridine and its derivatives have been extensively studied for their photophysical, photochemical, and supramolecular properties and are well-known as a stable monomer cation of two terpyridine molecules chelating one transition-metal ion in a hexacoordination mode.[6] Once the bis(terpyridine) species are formed, the metal ion is coordination-saturated and incapable of further complexation. On the other hand, it is also well-known that CuSCN/CuCN can form a variety of sophisticated electronegative frameworks.[5a,b,7] A rational consideration is to employ electropositive metal bis(terpyridine) monomers as templates directing the self-assembly of electronegative CuSCN/CuCN networks. The advantage for using metal bis(terpyridine) monomer templates is the tunable sizes of terpyridine through change of the 4′-substitution groups. On the basis of the strategy, we successfully obtained two types of copper(I) *pseudo*halide anionic networks in which bis(terpyridine) monomers are encapsulated or entangled. The complexes are formulated as $[\mathrm{Cu_6(CN)_6(SCN)_2{\cdot}M(tpy)_2}]_n$ [M = Co^{2+} (**1a**), Ni^{2+} (**1b**); tpy = 2,2′:6′,2″-terpyridine] and $[\mathrm{Cu_6(CN)_8{\cdot}M'(ttpy)_2}]_n$ [M′ = Mn^{2+} (**2a**), Fe^{2+} (**2b**), Co^{2+} (**2c**), Ni^{2+} (**2d**), Cu^{2+} (**2e**); ttpy = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine].

The cation inclusion complexes with *pseudo*halide anionic networks are known;[7b−e] however, the encapsulated ion within a charged cage in extended networks like **1a** and **1b** is still rare. One example is that the cations $[\mathrm{Ln(DMF)}_x]^{3+}$ (x = 8 and 9) are encapsulated into the anionic cages of a 3D infinite $[\mathrm{Cu_6(CN)_9}]^{3-}{}_n$ network.[5a,b]

Crystals of **1a** (or **1b)** were yielded by the solvothermal reaction of CuSCN, $\mathrm{NiSO_4{\cdot}6H_2O}$ (or $\mathrm{CoSO_4{\cdot}7H_2O}$), tpy, and triphenylphosphine ($\mathrm{PPh_3}$) in acetonitrile at 180 °C (see the Supporting Information for details). Single-crystal X-ray diffraction[8] reveals that **1a** and **1b** are isostructural and crystallize in orthorhombic space group *P*2(1)2(1)2. The asymmetric unit of **1a** contains four independent Cu$^{\mathrm{I}}$ atoms and one Ni atom, in which Cu2, Cu4, and Ni reside at the twofold symmetry axis (Figure 1). Each Cu$^{\mathrm{I}}$ atom adopts a triangular coordination geometry and is coordinated by S or

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(8) Crystal data for **1a**: $\mathrm{C_{38}H_{22}Cu_6N_{14}NiS_2}$, orthorhombic, space group *P*2(1)2(1)2, M_r = 1178.77, a = 13.535(3) Å, b = 14.232(3) Å, c = 10.638(2) Å, $\alpha = \beta = \gamma = 90°$, V = 2049.3(8) Å^3, Z = 2, ρ_{calcd} = 1.910 g cm^{-3}, μ = 3.654 mm^{-1}, F(000) = 1164, T = 293(2) K; R1 = 0.0935, wR2 = 0.1890 for all data. Crystal data for **1b**: $\mathrm{C_{38}H_{22}Cu_6N_{14}CoS_2}$, orthorhombic, space group *P*2(1)2(1)2, M_r = 1178.77, a = 13.582(2) Å, b = 13.9512(19) Å, c = 10.6531(16) Å, $\alpha = \beta = \gamma = 90°$, V = 2018.6(5) Å^3, Z = 2, ρ_{calcd} = 1.940 g cm^{-3}, μ = 3.654 mm^{-1}, F(000) = 1162, T = 293(2) K; R1 = 0.1147, wR2 = 0.2152 for all data.

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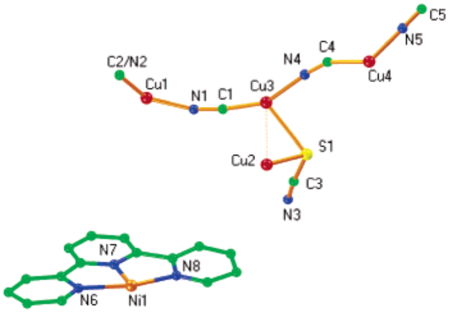

Figure 1. Asymmetric unit of **1a**.

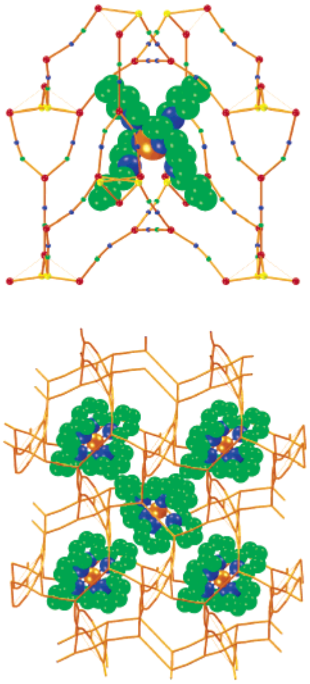

Figure 2. Structure of **1a**: anionic CuSCN−CuCN cage with encapsulated $[Ni(tpy)_2]^{2+}$ cations (top); 3D CuSCN−CuCN network (golden bar) with guest $[Ni(tpy)_2]^{2+}$ ions (bottom). Atom colors: Cu, red; N, blue; C, green; S, yellow, Ni, golden.

N/C donors from SCN^- or CN^- anions, respectively. The Ni atom is coordinated by six N atoms from two chelating tpy ligands [Ni−N 2.006(7)−2.113(8) Å] to furnish an octahedral geometry.

The crystal structure of **1a** is composed of a 3D anionic host $\{[Cu_6(CN)_6(SCN)_2]^{2-}\}_n$ network and guest bis(tpy) cations $[Ni(tpy)_2]^{2+}$. As shown in Figure 2, the nanosized guest $[Ni(tpy)_2]^{2+}$ (about 11.2 Å in length and 11.1 Å in width) is encapsulated in a large CuCN−CuSCN electronegative irregular cage, which contains 24 Cu atoms and 18 CN^- and 8 SCN^- linkages. Although the size of the CuCN−CuSCN cage of 10.6 × 13.5 × 14.2 $Å^3$ is larger than the size of $[Ni(tpy)_2]^{2+}$, the width of the largest window of the cage (ca. 8.5 Å) is narrower than the length or width of $[Ni(tpy)_2]^{2+}$. This indicates that the $[Ni(tpy)_2]^{2+}$ monomers, as templates, are assembled prior to the fabrication of the cage. Consequently, the $[Ni(tpy)_2]^{2+}$ guests are isolated and encapsulated by the extended inclusion network. So far, mixed CuCN−CuSCN complexes have been rarely documented.[9] The 3D mixed copper(I) *pseudo*halide (CuCN−CuSCN) network is unique.

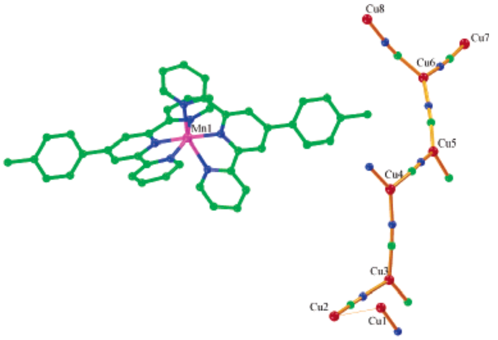

Figure 3. Asymmetric unit of **2a**.

To examine the influence of the template sizes on copper(I) *pseudo*halide networks, a longer ligand 4′-*p*-tolyl-2,2′:6′,2″-terpyridine (ttpy) was chosen. Under the same conditions, solvothermal reactions of ttpy and $M'SO_4$ resulted in crystals of **2a**−**e** (see the Supporting Information for synthetic details), which have been characterized as isostructural complexes. The structures crystallize in monoclinic space group $c2/c$.[10] The asymmetric unit of **2a** contains eight independent Cu^I atoms linked by CN^- and one Mn^{2+} atom chelated by two ttpy ligands (Figure 3).

Unlike the 3D structure in **1a**, the crystal structure of **2a** contains 2D anionic $\{[Cu_6(CN)_8]^{2-}\}_n$ networks, entangling the bis(ttpy) complexes $[Mn(ttpy)_2]^{2+}$ (Figure 4, top). Interestingly, the $\{[Cu_6(CN)_8]^{2-}\}_n$ network in **2a** consists solely of heartlike rings, as shown in Figure 4 (middle). Each heartlike ring sharing common sides with neighboring rings is composed of 10 Cu^I atoms and 10 CN^- linkers, of which two Cu^I atoms are coordinated by two CN^- and the other eight Cu^I atoms are coordinated by three CN^- linkers (one from neighboring rings). Topologically, the network with heartlike rings can be identified as a 2D (8, 3) net when the 3-connected Cu^I atoms are treated as nodes and both CN^- anions and 2-connected Cu^I atoms are treated as linkers. Although 3D (8, 3) uniform networks have been found,[11] most reported CuCN networks are described as belonging

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[9] Kovbasyuk, L. A.; Babich, O. A.; Kokozay, V. N. *Polyhedron* **1997**, *16*, 161.

[10] Crystal data for **2a**: $C_{52}H_{34}Cu_6MnN_{14}$, monoclinic, space group $C2/c$, M_r = 1291.11, a = 35.514(5) Å, b = 18.574(3) Å, c = 16.238(3) Å, $\alpha = \gamma = 90°$, β = 103.746(2)°, V = 10404(3) $Å^3$, Z = 8, $F(000)$ = 5144, T = 200(2) K; R1 = 0.0841, wR2 = 0.1846 for all data. Crystal data for **2b**: $C_{52}H_{34}Cu_6FeN_{14}$, monoclinic, space group $C2/c$, M_r = 1292.02, a = 35.495(6) Å, b = 18.290(3) Å, c = 16.306(3) Å, $\alpha = \gamma = 90°$, β = 103.554(2)°, V = 10291(3) $Å^3$, Z = 8, T = 200(2) K; R1 = 0.0976, wR2 = 0.1776 for all data. Crystal data for **2c**: $C_{52}H_{34}Cu_6CoN_{14}$, monoclinic, space group $C2/c$, M_r = 1295.10, a = 35.528(2) Å, b = 18.4842(11) Å, c = 16.2804(10) Å, $\alpha = \gamma = 90°$, β = 103.5750(10)°, V = 10392.9 $Å^3$, Z = 8, $F(000)$ = 5160, T = 293(2) K; R1 = 0.0806, wR2 = 0.1280 for all data. Crystal data for **2d**: $C_{52}H_{34}Cu_6NiN_{14}$, monoclinic, space group $C2/c$, M_r = 1294.88, a = 35.514(3) Å, b = 18.5884(15) Å, c = 16.2731(13) Å, $\alpha = \gamma$ = 90°, β = 103.660(2)°, V = 10438.8(15) $Å^3$, Z = 8, $F(000)$ = 5168, T = 293(2) K; R1 = 0.0783, wR2 = 0.1311 for all data. Crystal data for **2e**: $C_{52}H_{34}Cu_7N_{14}$, monoclinic, space group $C2/c$, M_r = 1299.71, a = 35.529(4) Å, b = 18.5537(18) Å, c = 16.2503(16) Å, $\alpha = \gamma$ = 90°, β = 103.894(4)°, V = 103.7330(10) $Å^3$, Z = 8, $F(000)$ = 5168, T = 200(2) K; R1 = 0.0558, wR2 = 0.1162 for all data.

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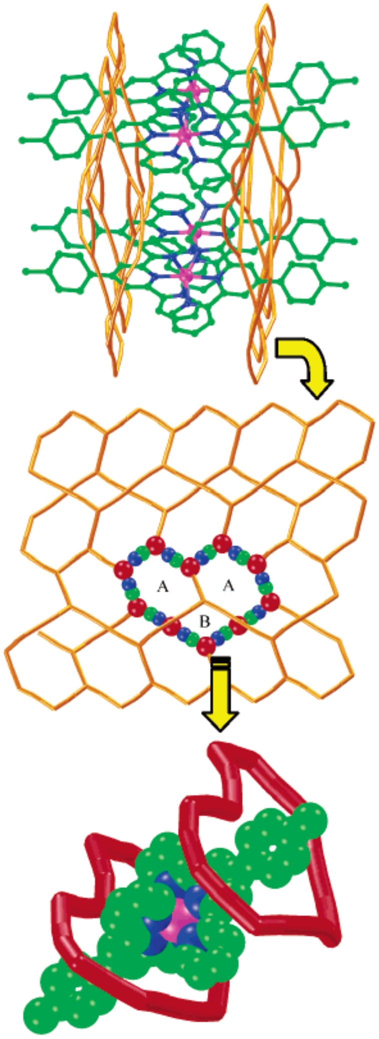

Figure 4. Structure of **2a**: 2D $\{[Cu_6(CN)_8]^{2-}\}_n$ networks (golden) entangling $[Mn(ttpy)_2]^{2+}$ ions (N, blue; C, green; Mn, purple; top); 2D $\{[Cu_6(CN)_8]^{2-}\}_n$ network containing heartlike rings (one heart ring is highlighted: Cu, red; N, blue; C, green; middle); two heartlike rings (red) and one $[Mn(ttpy)_2]^{2+}$ ion (bottom).

to a (6, 3) net rather than a (8, 3) net.[12] To our knowledge, the 2D (8, 3) coordination network is unprecedented.

From a top view of the 2D network, each ring is partly overlapped by an upper or lower ring, forming two *pseudo*hexagon areas (A, Figure 4, middle) and a *pseudo*-quadrangle area (B). Careful examination finds that $[Mn(ttpy)_2]^{2+}$ acting as a double-headed arrow strikes into area A of the heartlike rings from adjacent 2D networks, forming a romantic image of Cupid's arrow and lovers' hearts (Figure 4, bottom). The size of area A (10.1 × 8.2 Å) is smaller than the widest side of the bis(ttpy) complex (11.1 × 11.2 Å); therefore, the guest bis(ttpy) complexes are not simply located in the hole like small guest molecules but embedded into the heartlike ring of the CuCN networks, forming a poly*pseudo*rotaxane assembly. The distance between the two hearts is about 8.2 Å, whereas the length of $[Mn(ttpy)_2]^{2+}$ is about 21.7 Å. As a consequence, both tolyl groups of ttpy strike into the two hearts. Meanwhile, each heart unit in the 2D CuCN network is struck by two $[Mn(ttpy)_2]^{2+}$ ions (Figure S1 in the Supporting Information).

Our original intention is to enlarge the cage size of the copper(I) *pseudo*halide network by employing larger templates. However, the resulting CuCN networks are 2D and could not encapsulate the guest complexes like **1a** and **1b**. Instead, a poly*pseudo*rotaxane assembly was obtained. It may be too difficult to assemble a cage large enough to encapsulate the whole bis(ttpy) monomer (21.7 Å in length), which is about twice as long as the bis(tpy) one (11.2 Å in length; Figure S2 in the Supporting Information). Despite failure in the construction of a cage, the phenomenon still indicates that the size influence of the monomers on the networks is significant and that the templates did play a crucial role in the structure direction of the final anionic networks.

Another feature of **1a**, **1b**, and **2a**−**e** is the spontaneous assembly of bis(terpyridine) monomers and the generation of CuCN by in situ decomposition of CuSCN. Experiments showed that the S atom was transferred from CuSCN to PPh_3, yielding PPh_3S.[13] In our previous work, we have found that, under certain solvothermal conditions, reactions of CuSCN and organic ligands in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) afforded 1,2-bis(diphenylthiophosphinyl)ethane ($dppeS_2$) and CuCN complexes.[14] In the present work, only **2c** can be successfully synthesized directly from CuCN. In situ generation of CuCN by slow decomposiition of CuSCN may favor the assembly of the supramolecular networks. Therefore, the strategy of in situ yielding of CuCN from CuSCN may be important for the synthesis of these compounds.

In summary, we developed a convenient way to fabricate encapsulation and poly*pseudo*rotaxane assemblies by changing predesigned bis(terpyridine) complexes. The S atom transfer from CuSCN to phosphine, yielding new CuCN complexes, may be a general route to constructing novel CuCN frameworks, which may not be obtained directly by using CuCN as the starting reactant. The work provides an avenue for preparing new hybrid functional materials.

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Supporting Information Available: Crystallographic data (CCDC 632692−632698) in CIF format and experimental details and supplemental figures in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Colorless blocklike crystals of PPh_3S were collected in the filtrate of the complexes. Crystal data at 293 K: triclinic, $a = 9.6789(9)$ Å, $b = 11.2470(11)$ Å, $c = 14.5873(14)$ Å, $\alpha = 88.987(2)°$, $\beta = 80.291(2)°$, $\gamma = 77.910(2)°$, $V = 1530.2(3)$ Å^3.

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