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Novel Polythreaded Coordination Polymer: from an Armed-Polyrotaxane Sheet to a 3D Polypseudorotaxane Array, Photo- and Thermochromic Behaviors

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A novel coordination compound, $\{[Cd(BDC)(Bpybc)_{1.5}]\cdot 10H_2O\}_n$, obtained by the reaction of $CdCl_2$ with 1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium dichloride ($H_2BpybcCl_2$) and 1,4-benzenedicarboxylic acid (H_2BDC), contains 1D polymeric chains that are comprised of alternating rings and rods and dangling lateral arms. These 1D polymeric motifs are interlaced via rotaxane-like mechanical linkages to give 2D armed-polyrotaxane sheets, which are further mutually polythreaded via pseudorotaxane-like mechanical linkages to form a 3D polypseudorotaxane array. Notably, a sandwich-type donor−acceptor−donor stacking is formed within each ring as a consequence of both types of polythreading in this species, and photoinduced and thermal-induced reduction of bipyridinium occurs with a color change from light yellow to blue.

Interest in entangled systems is rapidly increasing not only for their potential applications as functional materials[1] but also because of their intriguing, often complicated architectures and topologies.[2] Among these, particular attention has been recently devoted to polythreaded coordination networks, which can be considered as periodic analogues of the molecule rotaxanes or pseudorotaxanes depending on the "ideal" possibility of being extricated.[3] The individual motifs in these species are not catenated but entangled together via rotaxane-like or pseudorotaxane-like mechanical linkages, which require the presence of closed loops as well as elements that can thread the loops. These two moieties may belong to the same polymeric species, such as a 1D chain of alternating rings and rods, 0D, 1D, or 2D motifs with side arms. Until now, all of the polythreaded arrays constructed from these types of motifs showed either rotaxane-like or pseudorotaxane-like mechanical links.[4−6] A polythreaded system having both polyrotaxane and polypseudorotaxane characters has not been reported so far.

Our interest focuses on the use of a flexible redox-active viologen derivative, 1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium dichloride ($H_2BpybcCl_2$),[7] as the building unit because it has been recognized that such a conformationally nonrigid species is more suited to produce these new classes of compounds[2e,5] and the incorporation of redox-active units may yield a new generation of multifunctional networks. For example, entangled systems can enable accepter (A) or donor (D) molecules grafted on different lattices to get sufficiently close and thus DA interactions may occur, rendering unusual optical or electrical properties. Herein, we report a novel polythreaded coordination network having both polyrotaxane and polypseudorotaxane characters. Notably, a sandwich-type D···A···D stacking is formed within each ring as a consequence of both types of polythreading in this species, and photoinduced and thermal-induced electron transfer occurs in the compound accompanied by a reversible color change.

Yellow prism crystals of $\{[Cd(BDC)(Bpybc)_{1.5}]\cdot 10H_2O\}_n$ (**1**) were readily prepared by diffusion of $CdCl_2$ into a mixed solution of $H_2BpybcCl_2$ and 1,4-benzenedicarboxylic acid

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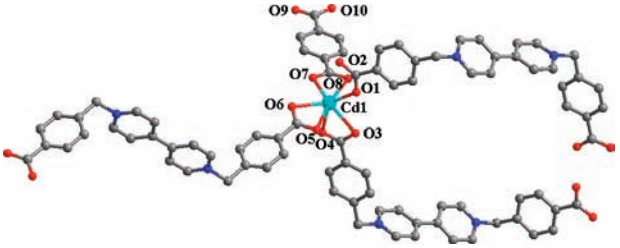

Figure 1. Coordination environment of Cd^{II} ions. All H atoms are omitted for clarity.

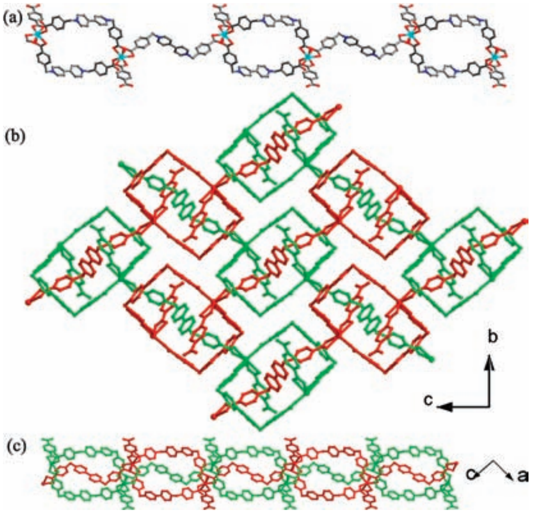

Figure 2. (a) 1D coordination polymeric chain in **1**. (b and c) Perspective views of the polyrotaxane sheet down the *a* and *b* axes, respectively. The two sets of chains along the [2, 1, −1] and [2, −1, −1] directions, polythreading with each other, are colored red and green.

(H_2BDC).[8] Single-crystal X-ray analysis of **1** reveals that a novel polythreaded coordination polymer has been formed.[9] As depicted in Figure 1, each Cd^{II} ion is coordinated by seven O atoms from four carboxylate groups that belong to one BDC and three different Bpybc ligands, respectively. The Cd−O bond lengths range over 2.207−2.598 Å. The flexible Bpybc ligand shows different conformations and coordination modes in the crystal. *trans*-Bpybc adopts a bis-bidentate chelating mode, while the coordination mode of *cis*-Bpybc is complex, with one end in a bidentate chelating mode and the other monodentate. Each BDC adopts a mono-bidentate chelating mode. An individual infinite 1D loop chain with side arms, which is formed by the connection of Cd ions and ligands, is shown in Figure 2a. The infinite chain has three elements: one is a macrocyclic $[Cd_2(Bpybc)_2]$ ring, with Bpybc in a cis conformation, that looks like a hexagonal window of approximate dimensions of 17.639 × 14.505 Å; another is a rod composed of a zigzag ligand, with Bpybc in a trans conformation, that connects the rings to form a 1D chain (Cd···Cd: 23.462 Å); yet another is a protruding arm comprising a linear ligand, with mono-bidentate BDC decorated alternately at both sides of the chain. These 1D chains are aligned in a grid in which the rods penetrate the macrocyclic rings at the intersections. Each chain is interlaced through such rotaxane interactions with an infinite number of other chains to generate a novel 2D armed-polyrotaxane layer (Figure 2b,c). It should be noted that there is no $\pi-\pi$ interaction between the aromatic rings of the "host" ring and the "guest" rod (Figure S2 in the Supporting Information). These features, including the rod-to-ring rotaxane interaction and the entangled motifs, are reminiscent of several reported polyrotaxane layers,[5] whereas we depict a new polyrotaxane architecture, in which a related form of interpenetration occurs to give a 2D armed-polyrotaxane layer. Unlike the reported motifs, the BDC ligands in **1**, grafted on the polyrotaxane layer, are just like open arms protruding from both sides of the undulated polyrotaxane layer (Figure 2c). To our knowledge, only one 1D armed-polyrotaxane chain structure based on a 1D loop chain with side arms has been reported recently;[4c] such an arm-shaped polyrotaxane layer has never been found in systems of metal−organic coordination polymers.

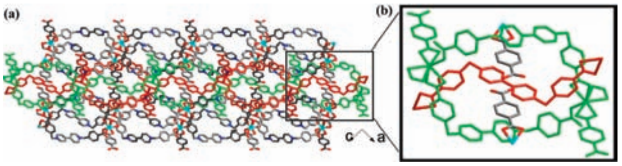

Figure 3. (a) Perspective view of the 3D polypseudorotaxane originating from mutual polythreading of three adjacent polyrotaxane sheets down the *b* axis. The middle sheet is depicted as in Figure 2c. (b) View of the sandwich-type D···A···D stacking within each hexagonal window.

Another important structural feature of **1** is that these 2D armed-polyrotaxane layers are polythreaded mutually by lateral arms into a 3D polypseudorotaxane array (Figure 3a). Three factors may play a role in the generation of mutual polythreading in **1**: (i) the remaining large void within the rod penetrated hexagonal windows of the polyrotaxane layer, (ii) the dangling BDC groups are just like open arms protruding from both sides of the layers in a slanted direction, and (iii) all of the undulated layers are interdigitated closely, with the closest distance of 6.692 Å between the center of the hexagonal rings and rods of the adjacent layer, while the effective length of each lateral arm is 9.173 Å (from the node to the baricenter of the uncoordinated carboxylate O atoms), thus providing the possibility for the ultimate realization of threading. Under this premise, the BDC lateral arms of each layer are threaded into the remaining voids of the adjacent layers in a mutual relationship. Any hexagonal window of each layer is penetrated by one bipyridinium moiety within the layer itself and two BDC molecules that belong to two adjacent layers, resulting in a novel 2D → 3D polythreaded array that originates from the entanglement of three adjacent polyrotaxane layers at the same time. Interestingly, if we regard each hexagonal window as a wheel and the paired BDC groups within the windows as a *single* rod, the nature of the entanglement in **1** can be described as polypseudorotaxane. Up to now, the polythreaded structure involving 2D components is still very

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(8) $H_2BpybcCl_2$ was synthesized by the reported procedure. A solution of $CdCl_2\cdot 2.5H_2O$ (0.05 mmol in 2.0 mL of water) was carefully layered on a mixed solution (the pH value is 7, which is adjusted by a 1 mol L^{-1} NaOH aqueous solution) of $H_2BpybcCl_2$ (24.8 mg, 0.05 mmol) and H_2BDC (8.3 mg, 0.05 mmol) in H_2O/DMSO (1.6 mL/0.4 mL) with H_2O/DMSO (1.8 mL/0.20 mL) placed between the two layers. Yellow prism crystals of **1** began to form in a few days. Yield: >45%. Elem anal. Calcd for $C_{47}Cd_1H_{54}N_3O_{20}$ (1093.36): C, 51.67; H, 4.98; N, 3.84. Found: C, 51.98; H, 4.67; N, 3.79.

(9) Crystal data for **1**: $C_{47}Cd_1H_{54}N_3O_{20}$, $M_r = 1093.36$, monoclinic, $P2_1/c$, $a = 11.986(4)$ Å, $b = 16.002(5)$ Å, $c = 25.926(8)$ Å, $\beta = 93.814(5)°$, $V = 4962(3)$ Å^3, $T = 294$ K, $Z = 4$, $D_c = 1.463$ g cm^{-3}, $\mu = 0.520$ mm^{-1}, $F(000) = 2180$, GOF = 1.043, a total of 37 482 reflections were collected, 11 126 of which were unique ($R_{int} = 0.0379$). R1 = 0.0844, wR2 = 0.2529 [$I > 2\sigma(I)$]. CCDC 708220.

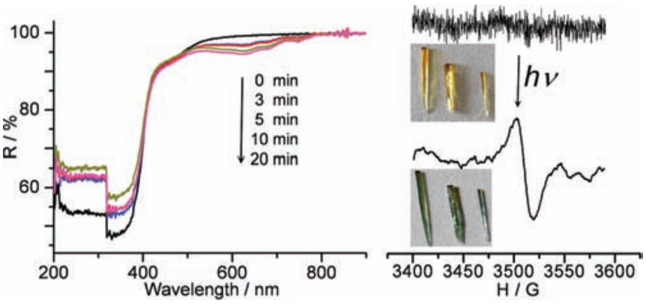

Figure 4. (left) UV−vis diffuse-reflectance spectral changes of **1** upon general fluorescent lamp irradiation. (right) Photochromism and ESR spectral changes of **1**.

rare; only several examples assembled from 2D coordination motifs have been reported.[10] **1** represents the first polythreaded species having both polyrotaxane and polypseudorotaxane characters. Different from the reported polythreaded systems, in which hydrogen-bonding or $\pi-\pi$ interaction is the major driving force that stabilizes the whole entanglement,[10] a charge-transfer (CT) interaction occurs between the electron-rich BDC species and the electron-deficient bipyridinium unit and can be expected to make a contribution to the stabilization of the polythreaded array in **1**. As evidenced by the structural data, the dihedral angle of the two pyridinium rings of Bpybc serving as the "guest" rod is 0°. The molecular plane of this bipyridinium unit and two BDC side arms are almost parallel to each other with a skew angle of 1.24° and an interplanar distance of 3.46 Å, forming a sandwich-type D···A···D stacking within each hexagonal window (Figure 3b). This stacking structure is consistent with some observations in CT complexes formed from viologen derivatives and organic donors.[11] In addition, the appearance of a shoulder peak around 455 nm besides the local band of Bpybc and BDC below 420 nm in UV−vis diffuse-reflectance spectra provides further evidence for the formation of a CT complex (Figure 4).

1 exhibits interesting photo- and thermochromic behaviors. In fact, **1** is rather photosensitive; it turns blue upon exposure to strong sunlight under air within 2 min; color reversion can be completely accomplished in several minutes in the dark. This photochromic behavior has been characterized by UV−vis diffuse-reflectance spectroscopy and electron spin resonance (ESR) measurements (Figure 4). After coloration, a new broad adsorption peak appears at 630 nm, which is similar to that of a methyl viologen radical.[12] ESR studies before and after irradiation show that the yellow one is ESR-silent while the blue one is ESR-active, giving a single resonance at $g = 2.0058$. The spin density of a powdered sample irradiated by UV light for 10 min, using a 1,1-diphenyl-2-picrylhydrazyl radical as a reference, is about 2.95×10^{17} spins mol^{-1}. Thus, the spectral change can be ascribed to the reduction of Bpybc molecules to blue Bpybc$^{\bullet -}$ radicals. The other important observation is the thermal generation of free radicals. A simple outgassing of **1** at room temperature develops a slight blue tint visually, indicating the spontaneous generation of some Bpybc$^{\bullet -}$ radicals. Upon heating under vacuum (below 100 °C), the intensity of the color greatly increases. With decreasing temperature under air, apparently the radicals decay. This cycling can be repeated several times without noticeable loss in its ability to generate free radicals. As far as we are aware, few viologen compounds show both photo- and thermochromic responses,[13] and no viologen-based coordination complex has been reported to show such chromic behavior up to now. For the photoinduced reduction of Bpybc in **1**, two possible electron donors are BDC anion or the benzenecarboxylate group of Bpybc. From the structural data, it can be found that no $\pi-\pi$ interaction exists between the bipyridinium and benzenecarboxylate group of adjacent Bpybc's, and the nearest carboxylate O atom of Bpybc is located at a distance of 4.17 Å from the pyridinium N atom, which is much larger than the general values for the interactions between viologen and donor species.[14,15] By contrast, one bipyridinium and two BDC units form a sandwich-type D···A···D stacking with π planes approximately parallel to each other, and the carboxylate O atom is approximately perpendicular to the N atom of each pyridinium ring with an O8−N3−C39 angle of 91.36° and a O···N distance of 3.57 Å. Such geometry and distance are favorable for interaction between a donor unit and a bipyridinium acceptor;[15,13c] thus, an electron transfer from BDC to bipyridinium moieties is considered. Interestingly, the discoloration of the photogenerated radicals in **1** is much more rapid than that observed in a single Bpybc zwitterionic salt. The photogenerated radicals in the latter can survive a long time in air (more than 1 month). This observation suggests that the chromic behavior of viologen derivatives can be effectively manipulated by molecular assembly.

In summary, employment of the flexible redox-active Bpybc ligand has permitted the synthesis of an unprecedented polythreaded network that has both polyrotaxane and polypseudopolyrotaxane structural features. Notably, a sandwich-type D···A···D stacking within each ring is formed as a consequence of both types of polythreading in this species, and photoinduced and thermal-induced reduction of bipyridinium occurs with a color change from yellow to blue.

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Note Added after ASAP Publication. There was an error in Figure 4 in the version published ASAP January 23, 2009; the corrected version was published ASAP February 9, 2009.

Supporting Information Available: IR spectrum, powder X-ray diffraction patterns, thermogravimetric analysis, and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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