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Single-Crystal-to-Single-Crystal Transformation in a One-Dimensional Ag−Eu Helical System

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Single-crystal-to-single-crystal transformation of one-dimensional 4d−4f coordination polymers has been investigated for the first time. More importantly, we observed the transformation of a meso-helical chain to a rac-helical chain as a function of the temperature.

Microporous coordination polymers or metal−organic frameworks have shown to be very promising for gas storage, separation, catalysis, and sensing applications.[1,2] However, d- and/or f-block coordination polymers—whose properties are sensitive to the external stimulus—have attracted much attention because of their potential applications as luminescent switches and sensors.[1] The final topology of the coordination polymers are highly influenced by several factors, including trapped guest molecules, a metal oxidation state, and coordination number changes due to the breakage and/or formation of new coordinate bonds; as a result, crystals tend to undergo single-crystal-to-single-crystal (SCSC) structural transformations.[2] However, there are only a few documented cases of SCSC transformations involving cleavage of coordination bonds; however, if such a process occurs in helical chains, one can expect the conversion of helicity in the crystals. The majority of the crystals will not survive such a dynamic process, but when the structural integrity *is* preserved, it provides valuable insight into the dynamic processes that occur during such a transformation, especially those involving the breakage/formation of chemical bonds.[3,4] However, none of these transformations have been used in generating a dynamic helical system. In this communication, we report a SCSC transformation from meso-helical structure to rac-helical chains based on Ag−Eu systems, with concomitant Mg^{2+} luminescent sensing properties.

Pyridine-2,6-dicarboxlic acid (H_2PDA), a multidentate ligand with two carboxylate groups, was designed to generate a wide variety of coordination polymers with different structural topologies. The one-dimensional coordination polymer $EuAg(PDA)_2(H_2O)_3 \cdot 3H_2O$ (**1**) was successfully obtained by cocrystallizing H_2PDA, $AgNO_3$, and $Eu(ClO_4)_3$ in a 1:1:1 ratio consisting of 15 mL of CH_3OH/H_2O at 100 °C for 48 h (Figure 1). The crystallographic measurement on **1**[5] shows that a one-dimensional meso-helical structure consists of two adjacent three-stranded single-helical P and M chains connected through Ag−O bonds (Figures 1 and 2a). Similarly, each Eu^{3+} is chelated to two PDA anions as tridentate (ONO) ligands and three water molecules that complete the nine-coordinated environments around Eu^{3+}. The tetrahedral geometry of Ag^+ was formed by four carboxyl O atoms with highly distorted square-pyramidal coordination geometry (Figure S2 in the Supporting Information).

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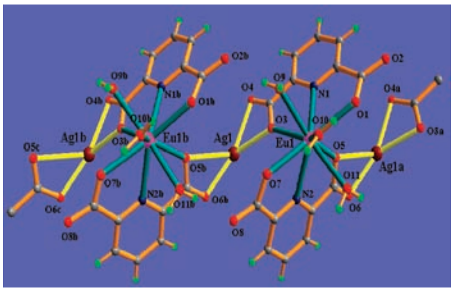

Figure 1. ORTEP diagram of complex **1**, showing the two building units and coordination environments of Eu and Ag atoms in this polymer.

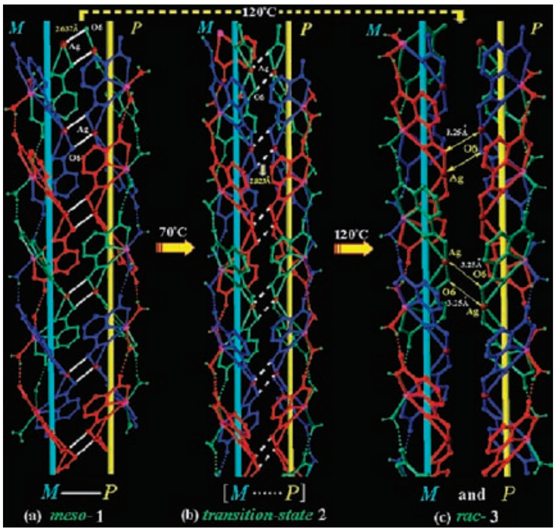

Figure 2. Three-stranded single-helical structures and temperature-driven helical conversion in compounds **1**−**3**.

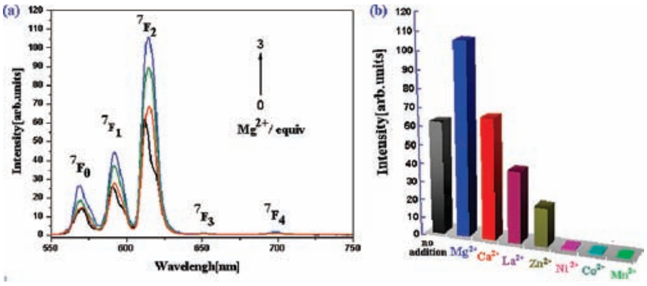

Figure 3. (a) Emission spectra of **1**−**3** in DMF (10^{-3} M) at room temperature (excited at 283 nm) in the presence of ~1−3 equiv of Mg^{2+} ions with respect to **1**−**3**: black, no addition; red, 1 equiv; green, 2 equiv; blue, 3 equiv. (b) Luminescent intensity of compounds **1**−**3** in DMF at room temperature with the addition of Mg^{2+}, Ca^{2+}, La^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+} ions (excited at 283 nm).

Interestingly, **1** is the cleavage of interchain Ag−O coordination bonds that simultaneously induce the conversion of the helical arrangement (meso to rac) when crystals are heated to 120 °C, and to our surprise, the single crystals retained their structural integrity during this process (Figure S3 in the Supporting Information). When the single crystals of **1** were heated at 70 °C for 5 h, pale-yellow crystal **1** kept its original appearance and resulted in crystal **2**.[5] The X-ray structure determination revealed that both crystals **1** and **2** crystallized in the same monoclinic space group $P2_1/n$; however, the cell volume decreased 170 Å^3, stemming from the departure of two uncoordinated water molecules in **2**. As observed in **1**, P and M helical chains in **2** also appear in pairs; however, because of the increased molecular movement as a result of heating of the crystal, the distance and orientation of the two helical chains (P and M) are quite noticeable when the bond distance of O6−Ag is increased from 2.635 Å in **1** to 2.832 Å in **2**, accompanied by a reduction of the O6−Ag−O6 bond angles from 100° to 96° (Figure 2b).

As the temperature rose to 120 °C after 2 h, pale-yellow crystal **2** became yellow crystal **3**.[5] The X-ray single-crystal diffraction shows that it has monoclinic space group $C2/c$. A comparison of the unit cell dimensions shows that the crystal volume was reduced by 11% from **1** to **3**. Because the temperature rose further, the remaining uncoordinated water molecules were removed, but also because of intensive heat movement, the two helical chains (P and M) were further separated, in which the distance of O6−Ag became 3.251 Å, resulting in the formation of **3** containing P-helical and M-helical chains with a 2_1 screw axis but crystallizing as a racemate (Figure 2c). Alternatively, compound **3** is also directly obtained by heating a single crystal or bulk crystals of **1** at 120 °C for 5 h under a vacuum. Meanwhile, powder X-ray diffraction (PXRD) patterns also indicate the structural transformation of **1** to **3** (Figure S3 in the Supporting Information). The single crystals of **2** are stable unless heated to 120 °C; the same is also true for **3**.

As noted earlier, d- and f-block coordination polymers known to exhibit luminescent properties, and therefore emission properties of **1**−**3**, were measured in solution. The emission spectra of **1**−**3** at room temperature in an *N*,*N*-dimethyloformamide (DMF) solution excited at 283 nm exhibit the same characteristic transition of the Eu^{3+} ion: $^5D_0$−^7F_J (J = 0, 1, 2, 3, and 4 Hz). The symmetry-forbidden emission $^5D_0$−$^7F_0$ at 581 nm can be found in **1**−**3**, indicating that the Eu^{III} ion occupies sites with low symmetry and without an inversion center (Figure 3a).[6] Interestingly, the emission intensity of three compounds increased gradually upon the addition of 1−3 equiv of Mg^{2+} ($MgCl_2$) with respect to **1**−**3**. To further understand this phenomenon, the same experiments were performed for the introduction of Ca^{2+} ($CaCl_2$), La^{3+} ($LaCl_3$), Zn^{2+} ($ZnCl_2$), Ni^{2+} ($NiCl_2$), Co^{2+} ($CoCl_2$), and Mn^{2+} ($MnCl_2$) into the system (Figure 3b). The presence of 3 equiv of Ca^{2+} in a DMF solution slightly increases the luminescent intensity, but the effect was not as good as that of the Mg^{2+} ion. When 1−3 equiv of La^{3+} and Zn^{2+} were added to the DMF solution of **1**−**3**, the luminescent intensity decreased. Other transition metals, such as Ni^{2+}, Co^{2+}, and Mn^{2+}, almost quenched their luminescence. These results suggest that complexes **1**−**3** show selectivity toward Mg^{2+} and Ca^{2+} and they can be considered as selective luminescent probes for these metals.

To further support our evidence of the existence of a helical character in solution control experiments, in which the same amount of $MgCl_2$ was added to a solution of $H[Eu(PDA)_2(H_2O)_2]\cdot 4H_2O$[7] in DMF, however, the luminescent intensity did not change significantly (Figure S4 in the Supporting Information). These results indicate that **1**−**3** do not

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[7] $H[Eu(PDA)_2(H_2O)_2]\cdot 4H_2O$ was obtained by the following literature procedure: (a) Brayshaw, P. A.; Hall, A. K.; Harrison, W. T. A.; Harrowfield, J. M.; Pearce, D.; Shand, T. M.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Eur. J. Inorg. Chem.* **2005**, *6*, 1127–1141. (b) Alsaadi, B. M.; Rossotti, F. J. C.; Williams, R. J. P. *J. Chem. Soc., Chem. Commun.* **1977**, *15*, 527–529.

decompose into discrete rare-earth units and retain their one-dimensional chain structure in DMF. Considering the carboxylic O atoms and the coordinated water molecules located on Eu^{3+}, this may create a favorable coordination environment for Mg^{2}. Another possible mechanism for changes in the luminescent properties is due to the result of a change in symmetry at the metal ion through the loss of bound water molecules; however, to confirm our hypothesis, several experiments failed to obtain the corresponding single crystals of **1**−**3** with incorporated Mg^{2+}.

In summary, we have demonstrated for the first time the temperature-driven and conversion of three luminescent Eu−Ag polymers **1**−**3** with different helical characters. Upon removal of the uncoordinated water molecules, the structural characteristics observed in **1**−**3** reveal not only the first example of a temperature-driven SCSC transformation from a meso-helical chain to a rac-helical chain but also a promising luminescent probe for various metals with a remarkable "on−off" switch of emission. Further experiments are in progress to confirm the luminescent properties of complex **1**−**3** in the solid state and solution using various spectroscopic techniques and also indicate a possible mechanism for the change in emission.

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Supporting Information Available: Crystal data in CIF format, synthesis, PXRD, and additional Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.