Communication

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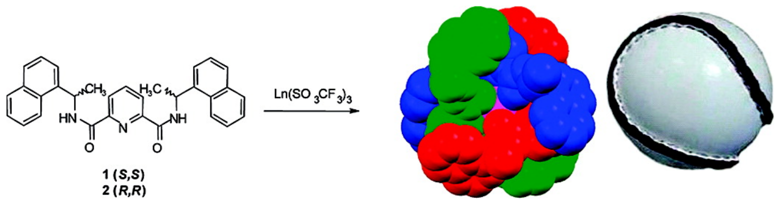

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Self-Assembly of Chiral Luminescent Lanthanide Coordination Bundles

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Supramolecular chemistry has yielded many beautiful structures of different shapes and sizes through the self-assembly of smaller complementary subunits or ligands.[1] Often these are designed to mimic the shapes, forms, and function of large macromolecules or macroscopic machineries[2] or are designed purely because of our "artistic" desire to create beautiful structures and shapes.[3,4] The use of transition-metal ions in coordination-driven self-assembly is now a well-established methodology.[5] In contrast, the use of the f or mixed d−f metal ions, in such metal-directed synthesis has been much less explored.[6,7] The lanthanide ions possess both rich coordination requirements and highly desirable luminescent properties which can be probed to elucidate the nature of the supramolecular structure, as we have recently demonstrated.[8,9] In this Communication, we demonstrate the formation of novel, highly symmetrical, coordination-driven lanthanide self-assemblies, or bundles, "The Trinity Sliotar" (sliotar is the ball used in the Gaelic (Irish) sport of Hurling (GAA)), from simple chiral pyridyldiamide ligands **1** (*S*,*S*) and **2** (*R*,*R*). Moreover, using circular polarized luminescence and X-ray crystallography, we demonstrate that the chirality of these ligands is transferred during the self-assembly to give either Δ or Λ metal stereochemistry.

The high yield synthesis of the chiral tridentate ligands **1** and **2** was achieved in a single step by reacting 2,6-pyridinedicarbonyl dichloride in the presence of triethylamine with either (*R*)- or (*S*)-1-[1-naphthyl]-ethylamine in dry THF (Supporting Information). The use of naphthalene chromophores as antennae should allow the population of the lanthanide excited states by indirect sensitization which will also help determine the solution structure of the resulting complexes.[10] Slow evaporation of **1** and **2** from CH_2Cl_2 gave suitable crystals for single-crystal X-ray diffraction studies (Supporting Information). The ligands crystallize with local C_2 symmetry with the two naphthalene antennae adopting a winglike appearance on either side of the central pyridine unit, Figure 1. Circular dichroism (CD) spectroscopy also confirmed the enantiomeric relationship of **1** and **2** (Figure S1). The lanthanide complexes were synthesized by reacting **1** or **2** with $Ln(CF_3SO_3)_3$ (Ln(III) = Tb, Sm, Eu, Nd, and Yb) in 3:1 stoichiometry in dry CH_3CN. After cooling to room temperature the Ln·**1** and Ln·**2** complexes were isolated as off-white colored solids when precipitated with diethylether (Supporting Information). The ^1H NMR spectra (400 MHz, CD_3OD) of the paramagnetic complexes showed that they all exhibit a high degree of symmetry in solution and that the spectra were identical for each set of complexes (Figure 2 and Supporting Information). The resonances are shifted because of the paramagnetic nature of the Ln(III) ions being most pronounced for Tb(III) and being least pronounced for Eu(III) (Figure S2). Such variation in NMR shifts in axially symmetric lanthanide chelates is known.[11]

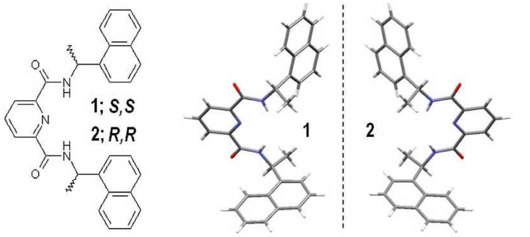

Figure 1. Ligands **1** (*S*,*S*) and **2** (*R*,*R*) and their corresponding solid-state structures, showing the enantiomeric nature of the two ligands. Solvent molecules of crystallization were omitted for clarity.

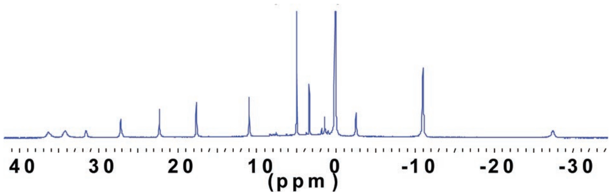

Figure 2. The ^1H NMR (400 MHz, CD_3OD) of Tb·**1** showing the high symmetry existing in solution. Tb·**2** gave an identical NMR spectrum (see Supporting Information).

The Δ and Λ chirality was also observed in the CD spectra of the complexes, where pairs of enantiomers gave rise to exciton couplings that were of equal and opposite sign (Figure S3). Moreover, the ESI mass spectra of all of these complexes were found to match closely the calculated theoretical distribution patterns for the 3:1 stoichiometry (Figure S4).

The spectroscopic data above are consistent with the formation of nine coordinate Ln(III) complexes following the self-assembly of three tridentate ligands about the metal center. The chiral nature of the assemblies as well as the verification for their bundle-type structures was confirmed by single-crystal X-ray diffraction. We were able to grow suitable crystals from CH_3OH for Tb·**2** (Figure 3), Eu·**2**, Sm·**2**, and Nd·**1** (Supporting Information), which clearly shows the coordination of the three ligands around the central Ln(III) ions that gives rise to highly symmetrical isostructural complexes. The ligands coordinate to the metal ions through the central pyridine N-atom and two flanking oxygen atoms from the carboxamide groups. Taking Tb·**2** as example shows this complex crystallizes with hexagonal symmetry within the chiral P_6322 space group. The Tb ion has overall Λ chirality as do Eu·**2** and Sm·**2**, whereas Nd·**1** has Δ chirality. Clearly, **1** (*S*,*S*) induces Δ chirality about the metal ions, whereas **2** (*R*,*R*) induces Λ chirality. The ligands wrap around the Ln ion in a helical manner so that the central pyridine unit of each ligand is sandwiched, or intercalated, in between the naphthalene units of the remaining two ligands to give a triple $\pi-\pi$ staking interaction that stabilizes the bundle. Indeed, the structure of each complex is replete with $\pi-\pi$ staking interactions as each naphthalene unit additionally interacts with its

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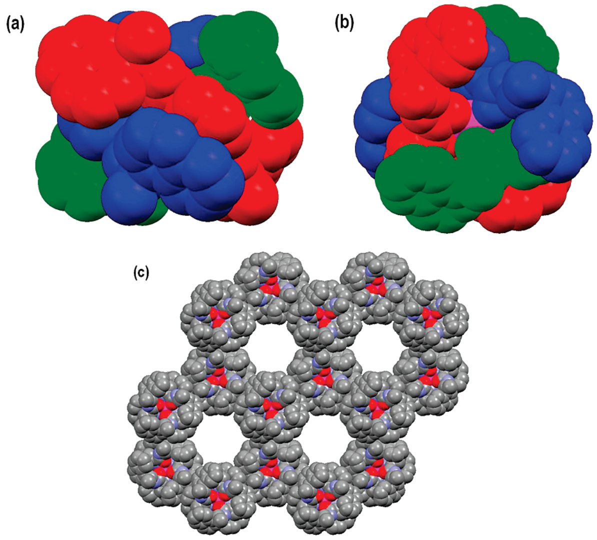

Figure 3. The X-ray crystal structure of the Tb·**2** sliotar showing the "helical" arrangement of the three ligands around Nd(III) (pink) as viewed down the crystallographic *a*-axis (a) and *c*-axis (b) and packing diagram viewed down the *c*-axis showing the channels (c). H-atoms, solvent molecules, and counter anions omitted for clarity.

nearest neighbor (i.e., each complex interacts with six others) and in so doing generates a 3D network. This packing arrangement leads to formation of ca. 1.2 × 1.3 nm channels that run down the crystallographic *c*-axis and within which the disordered triflates anions and solvent molecules reside.

The coordination geometry of the Ln(III) centers was further evaluated in solution by determining the hydration state, *q*, (or the number of metal-bound water molecules)[12] of the Tb(III) and Eu(III) complexes by measuring the decay of the excited states in both H_2O and D_2O, upon excitation at the naphthalene antennae. For these complexes, the *q*-value was determined to be ~0 (Eu·**1**: $\tau_{H_2O} = 1.67$ ms, $\tau_{D_2O} = 3.50$ ms, $q = 0.08$. Eu·**2**: $\tau_{H_2O} = 1.66$ ms, $\tau_{D_2O} = 3.60$ ms, $q = 0.06$) indicating that the complexes retain coordinative saturation in aqueous solution and that no appreciable ligand dissociation occurred. These measurements also demonstrated that these complexes were luminescent (Figure S5) where the characteristic lanthanide emission for the Tb(III) (See Supporting Information) and the Eu(III) complexes ($\Phi_{Eu\cdot\mathbf{1}} = 0.08$; $\Phi_{Eu\cdot\mathbf{2}} = 0.063$) was observed at long wavelengths (in the green and red, respectively) with narrow line-like emission bands.[9,13] Here, all six chromophores could potentially funnel their excited-state energies to the lanthanide ions (see excitation spectra for Eu(III) and Tb(III) in Figure S6). This was also found to be the case for the Sm(III) complexes for the activation of the ${}^4G_{5/2} \rightarrow {}^6F_{11/2}$, which demonstrates that the naphthalene units are effective sensitizing antennae for Sm(III) (Figure 4). Indeed, these complexes were also luminescent in the solid state (Figure S7).

The enantiomeric nature of the complexes was also evident from their circularly polarized luminescence (CPL) spectra[14] as shown for **1**·Sm and **2**·Sm indicating that the metal ion is sitting in a chiral environment (Figure 4). As expected, the CPL signals were of equal and opposite sign; moreover, the magnitude of the dissymmetry factors ($2\Delta I/I$) are very large (being 0.28 and 0.50 for the 600 and 560 nm bands, respectively)[6a] and confirm that the complexes are homochiral in solution. Analysis of the CPL signals for Eu·**1**and Eu·**2** (Figure S8) showed the same results and that both ions gave rise to chiral luminescence where each ion reported the chiral nature of the local environment and that all of the ${}^5D_J \rightarrow {}^7F_J$ were all clearly visible, with the hyper sensitive $\Delta J = 2$ transition being particularly intense. In summary, we have developed novel chiral lanthanide luminescent self-assemblies, *The Trinity Sliotar*. We are currently exploring their supramolecular chemistry and other systems in greater detail.

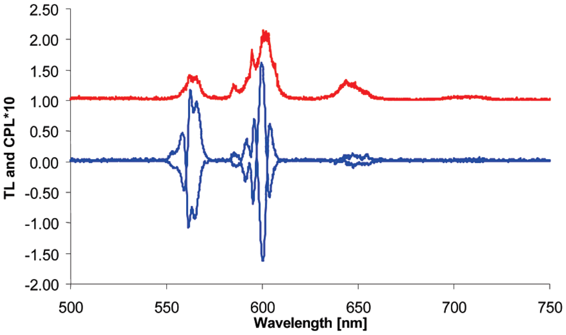

Figure 4. The luminescence emission spectra of the Sm(III) complex Sm·**1** (in red) and the circular polarized emission spectra of Sm·**1** (in blue) and Sm·**2** showing the chiral emission from the Sm(III) ion.

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Supporting Information Available: Synthesis; X-ray, crystallographic, and ESMS data; Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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