Inorganic Chemistry

Formation of Enantiomerically Pure Luminescent Triple-Stranded Dimetallic Europium Helicates and Their Corresponding Hierarchical Self-Assembly Formation in Protic Polar Solutions

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ABSTRACT: Ditopic helicate ligands 1 and 2 were synthesized for the formation of dinuclear Eu^{III} luminescent chiral helical assemblies ($Eu_2 \cdot L_3$) in competitive organic and protic solvent media. Spectroscopic analysis revealed formation of the 2:3 ($Eu_2 \cdot L_3$) and 2:2 ($Eu_2 \cdot L_2$) species in methanolic solutions. Circular dichroism and circularly polarized luminescence (CPL) spectroscopy confirmed the chiral purity of the helical systems, while scanning electron microscopy imaging demonstrated the formation of hierarchical self-assemblies with spherical morphologies.

T he use of the f-block lanthanide ions (Ln^{III}) to direct the assembly of preorganized ligand constituents has recently become an active area of research.^{1–5} The development of novel Ln^{III}-directed chiral assemblies has been a major topic of our interest,⁶ with the formation of monometallic systems receiving considerable attention. Furthermore, functional Ln^{III}-directed self-assemblies can display sensing capabilities, while luminescent polymeric gels⁷ and emissive Langmuir–Blodgett films have also been generated.⁸ The formation of enantiomerically pure Ln^{III} luminescent dimetallic triple-stranded helicates have also been developed by us, e.g., A (Figure 1).^{9a} However,



Figure 1. Ditopic helicate ligands 1 and 2 and the previously reported compound A.

these have only been soluble in organic media, which has hampered our effort in exploring their applications. We foresaw that the "simple" introduction of substituents at the 4-pyridyl position of **A** could enhance both the solubility in protic solvents¹⁰ and potentially their use in the formation of solventdependent hierarchical self-assemblies. Hence, we develop **1** and **2** and explore the effects that this additional functionality has on the self-assembly process in more competitive protic solvent media and demonstrate the formation of hierarchical self-assemblies with spherical morphology in protic polar solutions.

The preparation of ligands **1** and **2** involved an initial monoprotection of chelidamic acid using benzyl bromide

(Scheme 1). Introduction of the appropriate (S)- or (R)-1-(1naphthyl)ethylamine antenna moiety was achieved via a 1ethyl-3-[3-(dimethylamino)propyl]carbodiimide/hydrochloric acid peptide coupling reaction, yielding 4/5 as orange oils. The poly(oxyethylene) chain¹¹ 6 was then grafted onto 4/5 by stirring with K₂CO₃ in anhydrous N,N-dimethylformamide at 50 °C for 72 h. Deprotection of the benzyl group was achieved by hydrogenolysis using a 10% palladium/carbon catalyst in CH₃OH under 3 atm of H₂, affording 9/10, which were then subjected to a second peptide coupling reaction, giving 1 and 2 as white solids (see the Supporting Information, SI). Complexes $Eu_2 \cdot I_3$ and $Eu_2 \cdot 2_3$ were prepared by reacting 1/2with $Eu(CF_3SO_3)_3$ in 2:3 stoichiometries in CH₃OH for 10 min at 70 °C under microwave irradiation. The products were isolated as white solids in 78% and 71% yields and characterized by ¹H NMR (see the SI), where the paramagnetic nature of Eu^{III} caused a broadening and shifting of the ¹H NMR signals in both cases. The 2:3 complexes were further evidenced by high-resolution mass spectrometry and elemental analysis. Furthermore, the characteristic red emission from Eu^{III} was clearly visible to the naked eye under UV-light irradiation (Figure 2).

The photophysical properties of Eu₂·1₃ and Eu₂·2₃ were evaluated in CH₃OH, CD₃OD, and CH₃CN (Figures S3–S8). The absorption spectra of these complexes were dominated by a band located at $\lambda_{max} = 281$ nm, with two shoulders appearing at 270 and 293 nm in CH₃OH and CD₃OD but which were less pronounced in CH₃CN. Excitation at $\lambda_{max} = 281$ nm gave rise to Eu^{III}-centered luminescence from both complexes in all three solvent systems, indicating effective population of the

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Figure 2. (Left) Isolated sample of $Eu_2 \cdot 2_3$ and its corresponding Eu emission under a UV lamp. (Right) CPL emission spectra of the $Eu_2 \cdot 1_3$ and $Eu_2 \cdot 2_3$ complexes obtained in a 75:25 CH₃OH/H₂O solution.

⁵D₀ excited state and deactivation to the ⁵F₁ (J = 0-4) ground states, with linelike emission bands appearing at 579, 593, 614, 649, and 695 nm, respectively. Excitation spectra of $Eu_2 \cdot I_3$ and $Eu_2 \cdot 2_3$ were also recorded and displayed maximum intensity $(\lambda_{em} = 615 \text{ nm})$ at approximately 226 nm, with a broad shoulder at 281 nm again signifying successful indirect excitation. The luminescence lifetimes observed in CD₃OD and CH₃CN were best fit to a monoexponential decay, while that observed for CH₃OH was best fit to a biexponential decay, indicating the presence of more than one luminescent species (Table S1). Excited-state lifetimes of 1.39 and 1.32 ms were exhibited by the major species in CH₃OH (present in 80% and 83% for Eu₂·1₃ and Eu₂·2₃, respectively) correlating to q values of 0.2 in both cases. A relative method was used to calculate the quantum yields and efficiency of Ln^{III} sensitization (η_{sens}) for both complexes in CH₃CN and CH₃OH (see the SI). Quantum yields (Φ_{tot}) were measured for the Eu^{III}-centered emission from $Eu_2 \cdot \mathbf{1}_3$ and $Eu_2 \cdot \mathbf{2}_3$ and were found to be 3.5% and 3.2% in CH₃OH, and 4.1% and 4.4% in CH₃CN for Eu₂·1₃ and $Eu_2 \cdot 2_3$, respectively. These, in particular for CH₃CN, were slightly lower than what we had seen for chiral mononuclear ${\rm Eu}^{\rm III}$ "sliotar" complexes.^{6a,b} However, a comparison of the $\Phi_{\rm Ln}^{\rm Ln}$ values calculated for the helicate complexes $Eu_2 \cdot I_3$ and $Eu_2 \cdot 2_3$ (Table S2) and mononuclear complexes indicates that nonradiative deactivation via quenching does not play such a prominent role in reducing Φ_{tot} . It is the efficiency of the sensitization step $[\eta_{sens} (\Phi_{tot} = \eta_{isc}\eta_{et}\Phi_{Ln}^{Ln} = \eta_{sens}\Phi_{Ln}^{Ln}, where \eta_{isc}$ is the efficiency of intersystem crossing and η_{et} the efficiency of energy transfer] that is responsible for these reduced Φ_{tot} values for Eu₂·1₃ and Eu₂·2₃. Interestingly, compared to Eu₂·A₃, ^{9b} a smaller η_{sens} value was calculated for Eu₂·1₃ (27.6% for Eu₂·A₃ and 18.0% for Eu₂·1₃), indicating a less efficient antenna-to-ion energy-transfer pathway and a subsequent decrease in Φ_{tot} for Eu₂·1₃ (5.8% for Eu₂·A₃ and 4.14% for Eu₂·1₃) in CH₃CN.

The chirooptical properties of 1 (*S*,*S*) and 2 (*R*,*R*), and their corresponding helicate complexes were evaluated by circular dichroism (CD) and circularly polarized luminescence (CPL) spectroscopy. CD spectra for 1 (*S*,*S*), 2 (*R*,*R*), Eu₂· 1_3 (*S*,*S*), and Eu₂· 2_3 (*R*,*R*) were recorded in CH₃CN (Figure S9), with the latter being formed in solution upon the addition of 0.67 equiv of Eu(CF₃SO₃)₃. The enantiomeric relationship between stereoisomers 1 (*S*,*S*) and 2 (*R*,*R*) was clearly evident, with both CD spectra displaying mirror images of one another, confirming the presence of a single chiral stereoisomer in solution in each case.

CPL spectra were recorded in CH₃CN, CH₃OH, and a mixed 75:25 CH₃OH/H₂O solvent system (Figures 2 and S10). Excitation of the antenna resulted in Eu^{III}-centered chiral emission, with the ${}^{5}D_{0} \rightarrow {}^{7}F_{I} (J = 1-4)$ transition bands of the complexes being of equal magnitude and opposite sign, confirming the chiral nature of the Eu^{III} excited states. A comparison of the CPL spectra of $Eu_2 \cdot I_3$ (S,S) and $Eu_2 \cdot 2_3$ (R,R) to that of the analogous "sliotar" complexes, ^{6a,b} whose absolute configurations have been determined by X-ray crystallography, allowed us to predict the absolute configurations of Eu₂·1₃ (S,S) and Eu₂·2₃ (R,R) as $\Delta\Delta$ and $\Lambda\Lambda$, respectively. The dissymmetry factor values for the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions were calculated (Table S3), and particularly large g_{lum} values were seen for the magnetic-dipoleallowed transition $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ in all cases, with g_{lum} values of 0.17 (CH₃CN), 0.18 (CH₃OH), and 0.20 (75:25 CH₃OH/ H_2O) for $Eu_2 \cdot I_3$ (S,S).

The Eu^{III}-directed self-assembly of 1 and 2 was then evaluated by a series of spectroscopic measurements in situ in order to establish their ability to form the 2:3 helicate in solvents of varying competitiveness. Measurements entailed titrations of 1×10^{-5} M solutions of either 1 or 2 against increasing $[Eu(CF_3SO_3)_3]$ and then analysis of the changes in the absorption, fluorescence, and Eu^{III}-centered emission of the resulting solutions. Studies were performed in CH₃CN, CH₃OH, and CH₃OH/H₂O solvent systems (50:50 and 80:20). Studies carried out in CH₃CN for both ligands were comparable to the changes observed in CH₃OH (Figures S11-S14). The absorption spectrum of ligand 2 recorded in CH₃OH was shown to consist of two characteristic bands, as was observed in CH₃CN [λ_{max} = 226 and 281 nm (ε = 16981 M^{-1} cm⁻¹)], which presented a less hyperfine structure than was observed in CH₃CN. The overall changes in the absorption spectrum of ligand 2 upon the addition of $Eu(CF_3SO_3)$ in CH₃OH (Figure S17) shows a loss in the hyperfine structure of the band centered at λ = 281 nm, while an enhancement in absorption was observed at $\lambda_{max} = 250 \text{ nm}$ up until the addition of ~1 equiv of Eu^{III}, with subsequent additions resulting in an absorption plateau. The changes observed are much less pronounced in CH₃OH because of the enhanced competitive nature of the environment.

A gradual enhancement in the characteristic linelike emission bands located at 595, 615, and 695 nm is depicted (Figure 3), which corresponds to electronic deactivation from



Figure 3. Overall changes in the Eu^{III}-centered phosphorescence spectra upon titration of 2 $(1 \times 10^{-5} \text{ M})$ against Eu $(CF_3SO_3)_3$ $(0 \rightarrow 5 \text{ equiv})$ in CH₃OH at room temperature.

the Eu^{III 5}D₀ excited state to ⁷F_J states (where J = 1, 2, and 4). The binding isotherm graph (Figure 2, inset) demonstrates that, upon the addition of $0 \rightarrow 0.6$ equiv of Eu^{III}, a rapid increase in the emission intensity was observed, similarly for that seen in CH₃CN, followed by a sharp decrease up until the addition of ~1 equiv of Eu^{III}. Additional aliquots of Eu^{III} result in an eventual plateau in the luminescence intensity because initially the Eu₂·2₃ species is formed, after which Eu₂·2₂ becomes the dominant species in solution. The fluorescence emission spectrum of 2 was also recorded in CH₃OH (Figure S18), showing the band centered at $\lambda_{max} = 400$ nm experiencing a moderate quenching effect after the addition of ~0.65 equiv of Eu^{III} (47% and 56% for 1 and 2 in CH₃OH, respectively). The overall changes in the absorption, fluorescence, and Eu^{III}-centered phosphorescence spectra following the titration of 1 with $Eu(CF_3SO_3)_3$ in CH_3OH were also investigated, where an identical behavior was displayed (Figures S15 and S16).

The results were analyzed by fitting the global changes using the program *SPECFIT* (Figures S19–S26 and Table S4). The speciation distribution diagram obtained from fitting the absorption spectra of **1** in CH₃OH (Figure S23a) showed the presence of three absorbing species in solution including ligand **1** and the 2:2 and 2:3 species. The predominant species in solution is the Eu₂·**1**₃ dimetallic triple-stranded helical species, with it being formed in approximately 54% at 0.6 equiv of Eu^{III} (log $\beta_{23} = 25.7 \pm 0.3$). The Eu₂·**1**₂ species is formed in approximately 98% yield upon the addition of 3 equiv of Eu^{III} (log $\beta_{22} = 19.8 \pm 0.1$). Similar results were displayed following fitting of the changes in the absorption spectra of ligand **2** and luminescence titration data.

The self-assembly of 1 and 2 in CH₃OH/H₂O (50:50 and 80:20), in a constant ionic strength, and in a 2-[4-(2hydroxyethyl)piperazin-1-yl]ethanesulfonic acid buffered solution was also instigated. No obvious changes occurred in the absorption spectra of 1 and 2 (Figures S27-S32), suggesting little, slow, or no conformational changes in solution upon interaction with Eu^{III}. In contrast, significant luminescence changes indicated complexation and subsequent Eu^{III} sensitization. The trend observed in CH₃CN and CH₃OH was not observed in this more competitive environment, making nonliner regression analysis of these data inconclusive. Therefore, a number of kinetic measurements were conducted where the system was allowed to reach a state of equilibrium. However, the overall changes in the luminescence spectra after 14 h compared to measurements carried out after 5 min successions (Figures S33-S37) were shown to be identical, indicating that the self-assembly processes between Eu^{III} and 1/2 in such a highly competitive media give rise to the formation of identical species, which could involve other selfassembly processes that are not seen in CH₃CN/CH₃OH. While we were unable to structurally analyze these, Law and co-workers^{3e} have elegantly been able to structurally characterize the formation of 4:4 cage systems using chiral picolinate ligands, indicating the possibility of other higher-order systems being formed in situ in the case of 1 and 2.

The assembly of $Eu_2 \cdot I_3$ into higher-order architectures was next investigated using scanning electron microscopy (SEM). Prior to this, the stability of both $Eu_2 \cdot I_3$ and $Eu_2 \cdot 2_3$ complexes (synthesized) was measured by monitoring the Eu^{III}-centered emission exhibited from the solid dissolved in 80:20 CH₃OH/ H₂O. Gratifyingly, no significant decrease in the emission was obvious, indicating that both complexes remain intact and stable (Figure S37). In a 50:50 solution, however, a precipitate appeared after a short period of time. Samples of $Eu_2 \cdot I_3$ (0.2%, w/v) in these media were drop-cast onto silica plates and dried in air before the morphologies of the resulting samples were analyzed using SEM. While a thin film was observed from CH₃CN, samples drop-cast from CH₃OH and CH₃OH/H₂O mixtures all demonstrated the formation of hierarchical selfassemblies, displaying microsphere morphologies. Spherical aggregates produced from CH₃OH (Figure 4) were typically monodispersed, displaying a mean particle size of 0.681 μ m. In a similar manner, using $Eu_2 \cdot A_3$, spherical aggregates were also generated from CH₃OH, with a somewhat smaller mean particle size of 0.531 μ m (Figure S41). In contrast, while also generating monodisperse aggregates, those formed from $Eu_2 \cdot 1_3$ in CH₃OH/H₂O mixtures displayed a dramatic decrease in the



Figure 4. (Left) SEM image of $Eu_2 \cdot I_3$ complex microspheres dried on silicon plates [c = 0.2% (w/v) in CH₃OH]. (Right) Corresponding particle size distribution diagram calculated from SEM images using *ImageJ* software.

particle size as the H₂O content was increased: 0.438 and 0.079 μ m for 80:20 and 50:50 mixtures, respectively. Furthermore, less uniformity was observed for the spherical aggregates obtained from the solvent system containing the higher H₂O content. Ligand 1 was drop-cast from CH₃OH and analyzed by SEM; however, amorphous aggregates that were neither uniformly distributed nor monodisperse were observed (Figure S42). These results were fully reproducible and highlight the significance that the nature and solvent polarity can have in influencing the resulting morphologies and uniformities of the hierarchical structures.

In summary, ligands 1 and 2 and their corresponding enantiomericaly pure dimetallic 2:3 complexes were photophysically evaluated, with solution studies confirming the formation of self-assembled species in CH₃CN and CH₃OH. Investigation into the use of Eu₂·1₃ to generate hierarchical self-assembled aggregates demonstrated that, in CH₃CN, only thin films were formed, while in CH₃OH and CH₃OH/H₂O mixtures, the exclusive formation of monodisperse spherical aggregates was observed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00058.

Synthesis and characterization of 1, 2, $Eu_2 \cdot 1_3$, and $Eu_2 \cdot 2_3$, Figures S1–S37 and Tables S1–S4 including the photophysical investigations for each system as well as tables containing binding constants, calculations of quantum yields, and additional SEM images (PDF)

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Notes

The authors declare no competing financial interest.

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