Lanthanides

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Circularly Polarized Lanthanide Luminescence from Langmuir–Blodgett Films Formed from Optically Active and Amphiphilic Eu^{III}-Based Self-Assembly Complexes**

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The development of functional nanomaterials and supramolecular systems is an active area of research, particularly for molecular recognition/sensing, catalysis, optical devices, and magnetically active compounds for switching and data storage.[1–9] While much attention has been focused on transition-metal-based supramolecular systems,[10,11] there has been a recent insurgence of lanthanide-based systems.[12–14] These ions possess rich coordination environments and unique physical properties, such as long-lived and long-wavelength emission in the visible or the NIR regions, as well as magnetic properties, which have been exploited for use in the developments of MRI contrast agents. Hence, these properties make them ideal and highly desirable candidates for the formation of functional supramolecular systems.[15,16] The development of supramolecular assemblies that can be further organized into functional devices is also of great current interest. These assemblies can be achieved by covalently attaching appropriate ligands and complexes to nanoparticles or flat surfaces, through the formation of polymers, or by forming thin films using Langmuir–Blodgett (LB) techniques.[17]

Herein we describe our efforts in bridging these two areas of research by employing lanthanide-directed synthesis (using ligands **1** and **2**) in the formation of chiral luminescent lanthanide amphiphilic complexes, and their use in the formation of LB films, the properties of which can be probed by using circularly polarized luminescence (CPL). The ligands were designed to include a terdentate coordination pocket with a closely associated sensitizing antenna (i.e. the *R*- or *S*-naphthylamine moieties) for the lanthanide ions such as Eu^{III} and Tb^{III}—an approach that has been extremely successful for the development of luminescent supramolecular self-assembly structures, such as chiral "bundles"[18] and dilanthanide triple-stranded helicates.[19–21] Additionally, a long hydrophobic hexadecyl chain was included to allow the formation of Langmuir–Blodgett films. Ligands **1** and **2** were prepared in yields of 74% and 82%, respectively, by employing EDCI·HCl peptide coupling reactions (EDCI·HCl = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride) between the *R* and the *S* isomers of precursors **3** and **4**, respectively,[18–20] and *N*-hexadecylamine (Figure 1).

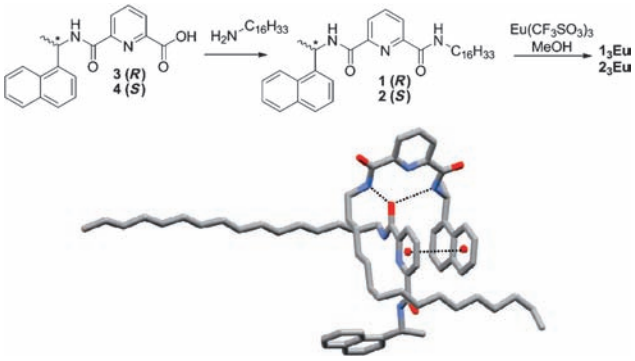

Figure 1. Synthesis of **1** (*R*), **2** (*S*), and their corresponding Eu^{III} complexes $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu. a) EDCI·HCl, 1-hydroxybenzotriazole, THF, triethylamine, room temperature. Perspective view of the crystal structure of **1**. Dashed lines indicate intermolecular interactions (N–H···O hydrogen bonding, and π···π stacking). Hydrogen atoms are omitted for clarity.

The ligands were characterized using conventional methods (see the Supporting Information), as well as by using circular dichroism (CD) spectroscopy, which confirmed that the compounds were isolated as a pair of enantiomers (see Figure S1 in the Supporting Information). Moreover, rod-shaped single crystals were obtained by the slow evaporation of a solution of the two ligands in CH_2Cl_2/CH_3CN, allowing solid-state crystal structure analysis of both. The resulting X-ray structure of **1** was determined at 108 K and is shown in Figure 1 (see also the Supporting Information). The ligand crystallized in the chiral monoclinic space group $P2_1$ and contained two crystallographically independent molecules in the asymmetric unit. One molecule has a relatively *trans*

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coplanar chain configuration (straight chain), while the other forms somewhat of a square through "kinks" in the chain. The two independent molecules pack into dimers through classical NH···O hydrogen bonding and offset face to face π···π stacking (Figure 1), whereby the pyridyl group of the straight chain compound sits inside the square adopted by the bent chain compound. Complexes of **1** and **2** with Nd^{III}, Sm^{III}, Eu^{III}, Tb^{III}, Dy^{III}, Yb^{III}, and Lu^{III} were formed and studied. However, this Communication focuses only on the Eu^{III} complexes $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu ($[Eu(\mathbf{L})_3](CF_3SO_3)_3$), prepared from **1** and **2**, respectively, by reaction with $Eu(CF_3SO_3)_3$ in 3:1 stoichiometry in methanol for 10 min under microwave irradiation. The pale yellow solutions were then subjected to vapor diffusion of diethyl ether to yield white solids, which under a UV lamp gave rise to typical red emission from the Eu^{III} center. Elemental analysis confirmed the formation of the desired products $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu, whereas electrospray ionization mass spectrometry gave dominantly the *m/z* peaks for the formation of $\mathbf{1}_2$Eu and $\mathbf{2}_2$Eu.

The photophysical properties of $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu were evaluated in CH_3CN, MeOH, H_2O, and D_2O solutions (see the Supporting Information). The UV/Vis absorption spectra of these complexes were dominated by an absorption assigned to the naphthalene $\pi\rightarrow\pi^*$ antenna with $\lambda_{max} = 281$ nm, and by the $n\rightarrow\pi^*$ transition of the central pyridyl unit. Excitation of the naphthalene antennae at 281 nm gave rise on both occasions to Eu^{III}-centered luminescence, indicating effective sensitization of the $^5D_0$ excited state and subsequent deactivation to the ^7F_J states with linelike emission bands observed at 580 nm ($^5D_0\rightarrow{}^7F_0$), 595 nm ($^5D_0\rightarrow{}^7F_1$), 615 nm ($^5D_0\rightarrow{}^7F_2$), 650 nm ($^5D_0\rightarrow{}^7F_3$), and 695 nm ($^5D_0\rightarrow{}^7F_4$). The coordination numbers of $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu were evaluated by determination of the number of water molecules bound to the Eu^{III} center, the hydration state (*q*), by monitoring their excited-state decay in H_2O and D_2O, respectively, in which these complexes were only sparingly soluble. From these measurements, a *q* value of around 0 was determined for these complexes (see the Supporting Information), indicating that they were coordinatively saturated in aqueous solutions.

The formation of $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu was next observed in solution by monitoring the changes in the absorption spectra of **1** and **2** and in the evolution of the Eu^{III}-centered luminescence upon titration with $Eu(CF_3SO_3)_3$ in CH_3CN at room temperature. The latter method is an ideal way of observing the formation of these desired self-assemblies, as the population of the Eu^{III} $^5D_0$ excited state would only be observed upon sensitization from the ligands, that is, through the antenna effect. The overall changes observed in the Eu^{III} emission for **2** are shown in Figure 2A, where all of the characteristic $^5D_0\rightarrow{}^7F_{1-4}$ Eu^{III} emission bands are observed upon formation of the self-assembly complex in solution. Analyzing the emission intensities of $^5D_0\rightarrow{}^7F_{1-4}$ as a function of added Eu^{III} equivalents reveals that the emission rapidly increases to a maximum at approximately 0.35 equivalents, after which it decreases and begins to plateau after the addition of 1 equivalent of Eu^{III} (see the Supporting Information). To gain a better understanding of the formation of these species in solution, these changes were further analyzed by fitting the global luminescence changes using nonlinear regression analysis (using the software SPECFIT) to various L:Eu stoichiometries. The fitting of the changes observed in Figure 2A is shown in Figure 2B (see the Supporting Information for the fitting and the binding constants obtained for the analysis of **1**). On both occasions good fits were observed as demonstrated for the analysis of **2** in Figure 2B, for the changes in $\Delta J = 1$, 2, and 4, from which the formation of $\mathbf{2}_3$Eu in 80% yield was confirmed after addition of

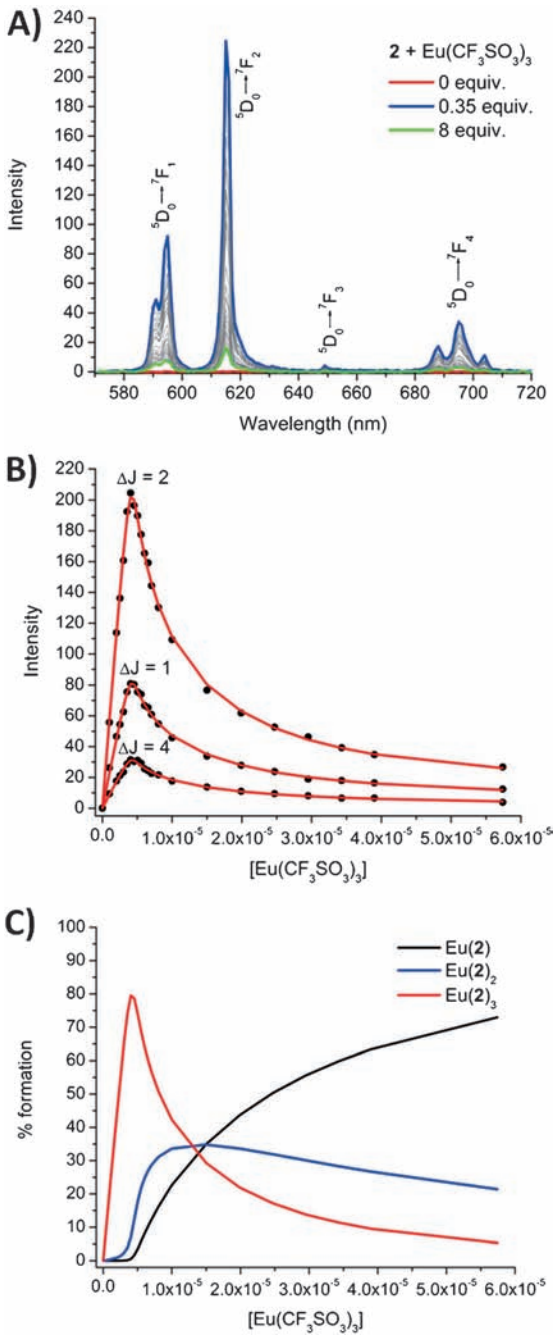

Figure 2. A) The overall changes in the Eu^{III} phosphorescence spectra upon titrating **2** with $Eu(CF_3SO_3)_3$ (0 to 10 equivalents) in MeCN at room temperature. B) Experimental binding isotherms for the changes in the Eu^{III} luminescence spectra upon titrating **2** with $Eu(CF_3SO_3)_3$ in MeCN at room temperature, and their corresponding fit by SPECFIT (——). C) Speciation-distribution diagram obtained from the fit.

0.3 equivalents Eu^{III}, with binding constants of $\log\beta = 19.9$-($\pm$0.2). Concurrently, the analysis for **1** showed similar luminescent behavior, and the self-assembly $\mathbf{1_3Eu}$ was formed with a comparable binding constant $\log\beta$ of 20.4-($\pm$0.2). On further addition of Eu^{III}, the equilibrium for both systems was displaced towards that of a species with the stoichiometry $[Eu(\mathbf{L})_2]$, which, after the addition of around 0.5 equivalents of Eu^{III}, were formed in 35 and 45% yields, respectively, and with binding constants of $\log\beta = 13.3$ ($\pm$0.2) and 14.1 ($\pm$0.2). On yet further addition of Eu^{III}, these equilibriums were displaced towards a new species, $[Eu(\mathbf{L})]$, which became the predominant species after the addition of 1.5 equivalents of Eu^{III}.

The solution formation of $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu was also observed by monitoring the changes in the absorption spectra, and by fitting the resulting global changes using nonlinear regression analysis. In particular, the changes in the absorbance bands at 207, 223, and 281 nm were analyzed (see the Supporting Information). These changes gave rise to similar results as those obtained from the analysis of the changes in the Eu^{III} emission: the formation of the $[Eu(\mathbf{L})_3]$ was confirmed after addition of 0.3 equivalents of Eu^{III} in around 85% yield with a binding constant of $\log\beta = 20.9$-($\pm$0.3). Similarly, analysis of the changes observed for **1** gave a $\log\beta$ value of 20.5($\pm$0.3). Moreover, the formation of the $[Eu(\mathbf{L})_2]$ species at around 0.5 equivalents of Eu^{III} was also confirmed in 45 and 35% yields for **1** and **2**, respectively, with $\log\beta$ value of 13.8, while upon further addition of Eu^{III} resulted in the formation of the 1:1 stoichiometry $[Eu(\mathbf{L})]$.

CD and CPL analysis of $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu in CH_3CN confirmed the enantiomeric nature of these complexes (see the Supporting Information). The CD spectra of $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu were significantly different to those of **1** and **2**, respectively, particularly for the naphthalene transitions. Importantly, both systems gave rise to Eu^{III}-centered CPL spectra upon excitation of the naphthalene antennae; all $^5D_0 \rightarrow {}^7F_{1-4}$ transitions were observed, clearly demonstrating that the Eu^{III} ion was sitting within a chiral environment, where the handedness of the ligand dictated the handedness of the chiral emission (CPL) from the metal ion. This is evident from Figure S15 (Supporting Information), which shows a negative band for the $\Delta J = 1$ transition and a positive band for $\Delta J = 2$ nm for $\mathbf{1_3}$Eu; however, these bands were found to be of opposite signs for $\mathbf{2_3}$Eu, confirming their formation as an enantiomeric pair. Comparison of these CPL spectra with those obtained previously in our laboratory using the symmetrical and chiral dinaphthalene amide analogue of **3** and **4**, for which the crystal structures of the 3:1 complexes are known,[18] allowed us to assign the absolute stereochemistry of these self-assemblies as Δ and Λ using **1** and **2**, respectively. Moreover, from these spectra, the luminescence dissymmetric factor g_{lum} was determined,[22a] which for $\mathbf{1_3}$Eu gave $g_{lum} = -0.177$ and 0.106 for the $\Delta J = 1$ and 2 transitions, respectively (being $g_{lum} = 0.176$ and -0.102 for $\mathbf{2_3}$Eu). The former transition is close to that determined for the Eu^{III} complex of the aforementioned symmetric analogue of **3** ($g_{lum} = 0.28$),[18] while, for the $\Delta J = 2$ transition, g_{lum} was almost five times smaller ($g_{lum} = 0.50$).[18] This result might reflect the unsymmetical nature of $\mathbf{1_3}$Eu, as the $\Delta J = 2$ transition is highly sensitive to the change in the local coordination environment of Eu^{III} ion.[22]

Having formed $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu and analyzed their luminescent properties in solution, we investigated the self-assembling properties of $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu at the air–water interface by forming Langmuir films. Only a small number of examples of Langmuir–Blodgett films made from kinetically and thermodynamically stable lanthanide complexes have been reported.[23–38] Furthermore, only a few examples of CPL Langmuir–Blodgett films have been made,[28] and, to the best of our knowledge, no examples of CPL lanthanide emitting Langmuir–Blodgett films have been reported. The Langmuir films of $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu were identified by monitoring the pressure–area isotherms, where the exponential increase in surface pressure indicated transition from liquid-expanded phases to liquid-condensed and solid phases (Figure 3).[39]

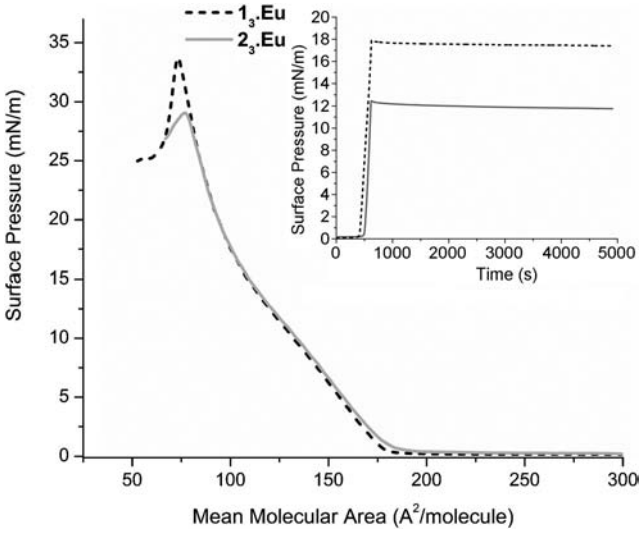

Figure 3. Pressure–area isotherms; inset shows pressure–time profiles for Langmuir films of $\mathbf{1_3}$Eu (-----) and $\mathbf{2_3}$Eu (——).

These films were seen to collapse at 34 mN m^{-1} for $\mathbf{1_3}$Eu and at 29 mN m^{-1} for $\mathbf{2_3}$Eu, corresponding to areas of 75 $\pm$ 5 Å^2. These areas are approximately those expected for three alkyl chains (ca. 66 Å^2 per molecule),[40,41] and are in agreement with the complexes remaining intact at the air–water interface with supramolecular organization of $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu as monolayers. Excellent stability properties were exhibited by films of both complexes with no pressure decrease observed on keeping the films at the liquid-condensed phase for an extended period of time (>1 hour; Figure 3 inset). The $\mathbf{1_3}$Eu and $\mathbf{2_3}$Eu films were transferred onto quartz slides, and the formation of Langmuir–Blodgett monolayers was confirmed. The monolayers were transferred with high transfer ratios (TR $\approx$ 1) on the emersion of the quartz support. The exact structural nature of these films is currently under investigation; however, we can assume that the polar Eu^{III} coordination sphere is orientated towards the water phase and the hexadecyl chains pointing out, as attempts to transfer these films by immersion was unsuccessful.

Having formed Langmuir–Blodgett films of $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu, we next evaluated their photophysical properties by recording their UV/Vis absorption, phosphorescence, and excitation spectra (see the Supporting Information). The UV/Vis absorption spectra matched those seen for these complexes when recorded in solution, and the phosphorescence excitation spectra ($\lambda_{em} = 620$ nm) of both films structurally matched the absorption spectra. However, the fluorescence emission from these films was poor, as had been the case when the fluorescence emission of $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu was recorded in solution. However, upon excitation of the antenna, both monolayers exhibited time-delayed lanthanide luminescence (Figure 4). The Eu^{III} emission bands observed

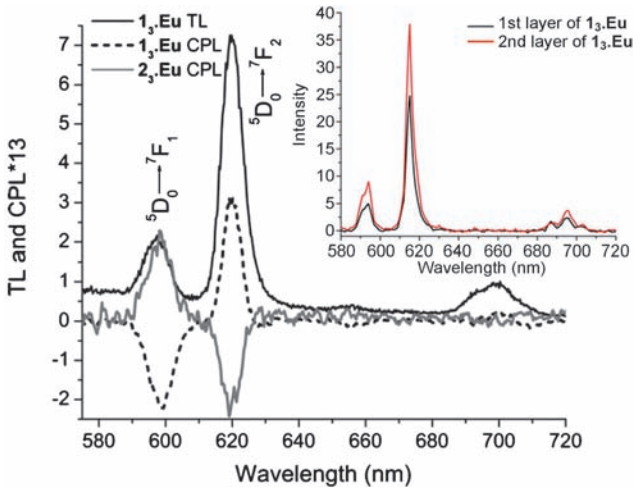

Figure 4. Total luminescence from $\mathbf{1}_3$Eu (black) and CPL spectra from monolayers of $\mathbf{1}_3$Eu (blue) and $\mathbf{2}_3$Eu (red) on quartz slides. Inset: The Eu^{III}-centered emission recoded of the Langmuir–Blodgett films after one and two emersions of $\mathbf{1}_3$Eu.

at 593, 615, and 695 nm were particularly intense as had been seen in solution. These films were stable under ambient conditions over a period of many months. Furthermore, multiple layers of these films could be transferred onto a quartz slide, as demonstrated as an inset in Figure 4 for $\mathbf{1}_3$Eu, where the emission from a slide following the deposition of the second monolayer gave rise to enhanced Eu^{III}-centered luminescence. The excited-state decay of Eu^{III}-centered emission was also determined and found to be similar to that seen in H_2O (see the Supporting Information).

The enantiomeric relationship between the monolayers of $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu was also probed by CD and CPL spectroscopy. Unfortunately, we were unable to record the CD spectra of these monolayers, most likely because of the low concentration. However, and more importantly, as can be seen in Figure 4, both films gave rise to Eu^{III}-centered CPL. The films gave spectra of equal and opposite signs for $\Delta J = 1$, 2, and 4; these were most pronounced for the $\Delta J = 1$ and 2 transitions (as was seen in solution for $\mathbf{1}_3$Eu and $\mathbf{2}_3$Eu), the former being magnetic-dipole-allowed and as such gave rise to large circular polarization. These results thus clearly confirm that the films formed are chiral and that the Eu^{III} centers again report the nature of the chiral environment of the local environment. From these spectra, the dissymmetric factor for $\mathbf{1}_3$Eu was determined as $g_{lum} = -0.161$ and 0.068 for $\Delta J = 1$ and 2, respectively. This slight difference from the solution results above is most likely related to the formation of the Langmuir–Blodgett films in which the packing of the molecules could have had an effect on the local coordination of the lanthanide ion or that this may be due to the effect of the solid surface.

In conclusion, we developed novel, chiral, europium-directed luminescent self-assemblies. These amphiphilic molecules were studied in solution, as well as used in the formation of stable self-assembled monolayers at the air–water interface. By transferring these monolayers onto quartz slides to form Langmuir–Blodgett films, we were able to generate Eu^{III} luminescent monolayers and probe, for the first time, the chiral emission from such films using CPL. These self-assemblies represent the first examples of lanthanide CPL emitting amphiphilic self-assemblies, an exciting area of research we are currently investigating.

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