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Sensitized Near-Infrared Lanthanide Luminescence from Nd(III)- and Yb(III)-Based Cyclen–Ruthenium Coordination Conjugates

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The development of novel mixed lanthanide–transition-metal (f–d) based supramolecular self-assemblies made from neodymium- and ytterbium-based tetraamide-functionalized cyclen complexes bearing a single 1,10-phenanthroline moiety coordinating to a Ru^{II}-$(bipy)_2$ (bipy = bipyridine) unit is described. Excitation of the Ru(II) metal-to-ligand charge-transfer band in water gave rise to long-wavelength sensitized emission from the Yb(III) or Nd(III) centers, observed in the near-infrared.

Lanthanide luminescence is a very attractive tool for biological imaging and luminescence sensing.[1,2] Ions such as Eu(III) and Tb(III) exhibit long-lived excited-state emission lifetimes, at long wavelengths with characteristic line-like emission bands that are sensitive to the local coordination environment.[1−3] Moreover, changes in the band structure, intensity, and lifetime can be employed for analysis of biological species and structures.[4] These can also be used to gain insight into the structure of supramolecular (self-assembly) structures.[5−8] Because the above ions suffer from symmetry-forbidden f−f transitions, it is typically necessary to populate their excited states via sensitizing chromophores that absorb at shorter wavelengths.[1,2] This factor can somewhat limit their use for biological imaging.[2] This can be overcome by employing other lanthanide ions, such as Nd(III), Yb(III), and Er(III), which emit in the near-infrared (NIR) region.[2] These ions can be sensitized using visible absorbing antennae such as d-block transition-metal complexes.[5,6,9] Such complexes possess relatively long-lived metal-to-ligand charge-transfer (MLCT) excited states, which facilitate the efficiency of the sensitization process.[5,6,9−11] Even though several examples of such complexes and conjugates have recently been developed, they often suffer from low water stability, the use of acyclic ligands, and relatively long covalent distances from the lanthanide center and the sensitizing antenna.

We have recently demonstrated the self-assembly of mixed f−d metal ions, where a lanthanide ion complex was coordinated to polypyridyl antenna, giving rise to the supramolecular structure **A** (Figure 1).[12] The coordination of **A**, as a Eu(III) complex, to ions such as Fe(II) (green

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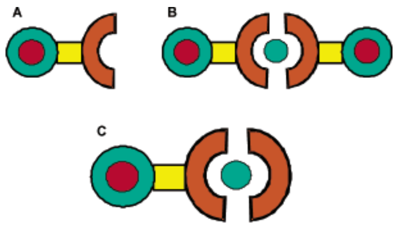
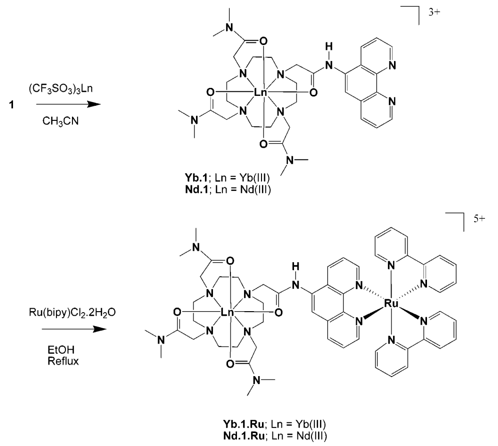


Figure 1. Schematic representation of linear self-assembly **B**, made from the cyclen-based conjugate **A** [red ball = Eu(III)] upon coordination to d metal ions such as Fe(II) (green ball) and **C**. Formation of a capped-self-assembly from **A** [red ball = Yb(III) and Nd(III)] and [Ru(bipy)$_2$Cl$_2$] [Ru-(II) = green ball].

Scheme 1. Synthesis of the Yb(III) and Nd(III) Complexes of **1** and the Corresponding Ru^{II}(bipy)$_2$ Conjugates **Yb.1.Ru** and **Nd.1.Ru**



circles) gave rise to the formation of the linear supramolecular complex **B**. In this Communication, we expand on this design principle with the aim of developing other novel mixed f−d supramolecular motifs, based on the design of **C**. These are made from cyclen−1,10-phenanthroline (phen) conjugate **1**, where the synthesis of **C** can be achieved by using NIR-emitting lanthanide ions and varieties of capped or ancillary ligands, such as Ru(bipy)$_2^{2+}$ (bipy = bipyridine). This combination allows for the sensitization of the lanthanide ions in the visible region via the MLCT and the formation of self-assemblies that can, for instance, be employed for probing the structure of nucleic acids.[2] The f−d-based **Yb.1.Ru** and **Nd.1.Ru** conjugates are the first examples of this design principle where cyclen conjugates have been employed. These give rise to short f−d metal−metal separation and consequently efficient d → f sensitized energy transfer, features that are essential for use in biological imaging and for sensing.[1,2]

The synthesis of **Yb.1.Ru** and **Nd.1.Ru** (see the Supporting Information) was achieved in two steps, as shown in Scheme 1, from the cyclen−phen-based ligand **1**, previously synthesized in our laboratory.[8] The Yb(III) and Nd(III) complexes of **1** were formed by refluxing the appropriate triflate salts in CH_3CN under an inert atmosphere overnight. The complexes **Yb.1** and **Nd.1** were isolated upon precipitation from diethyl ether and trituration using CH_2Cl_2. The ^1H NMR (400 MHz, D_2O) spectrum of **Yb.1** indicated that in solution the complex was formed as a mixture of complexes adopting square-antiprismatic and twisted square antiprismatic geometries (Figure S1 in the Supporting Information).[13] In contrast, the structure of **Nd.1** showed the formation of a single square-antiprismatic isomer in solution. The mixed f−d conjugates were synthesized by reacting **Yb.1** and **Nd.1** with ruthenium bis(bipyridine) bis(chloride) dihydrate in ethanol at reflux overnight. After evaporation of the solvent to dryness, the red solids were purified by trituration using diethyl ether, filtered, and washed several times with diethyl ether to yield strong-red solids, which were dried under vacuum, giving the desired products **Yb.1.Ru** and **Nd.1.Ru** (as their mixed chloride/triflate salts) in ca. 80% yields. All of the mixed f−d complexes were characterized by ^1H and ^{19}F NMR spectroscopy and matrix-assisted laser desorption ionization time-of-flight mass spectrometry. The ^1H NMR (400 MHz, D_2O) characteristic signals for the paramagnetic lanthanide ion were also observed for the bipy protons. The ^{19}F NMR (in D_2O) spectra showed a singlet at around −80 ppm and two broad peaks at −160 and −190 ppm, which were assigned to the triflate counterions.

The ground- and excited-state properties of the lanthanide complexes **Yb.1** and **Nd.1** and the mixed f−d conjugates of **Yb.1.Ru** and **Nd.1.Ru** were investigated in aqueous solution using 1 μM concentration of each complex. The absorption spectra of **Yb.1** and **Nd.1** gave a band at 285 nm ($\pi - \pi^*$ phen, Figure S2 in the Supporting Information). Excitation of this band did not give rise to NIR emission. However, upon excitation of 337 nm (see later), the long-wavelength NIR emissions were observed and assigned to the emission from the lanthanide centers. The hydration state (q) of these complexes, or the number of metal-bound water molecules, was determined by excitation at 337 nm and following the deactivation of the lanthanide excited states in H_2O and D_2O [$^2F_{5/2}$ (10 300 cm^{-1}) and $^4F_{4/3}$ (10 200 cm^{-1}) for Yb(III) and Nd(III), respectively]. On all occasions, the rise time is within the envelope of the laser pulse. For **Yb.1**, the Yb(III) luminescence decay in D_2O was fitted to a single-exponential decay with $\tau = 6.3$ μs, while in H_2O, a double-exponential decay with lifetimes of $\tau = 0.64$ and 1.86 μs was obtained.[14] From these results, we determined that **Yb.1** has indeed two q values of 0.3 and 1.3, respectively.[14] This is due to the presence of two geometrical isomers in solution, as shown by ^1H NMR, and indicates that one of the isomers has a coordinated water molecule, while the other one does not. In contrast to these results, the Nd(III) decay in **Nd.1**, in both H_2O and D_2O, was fitted to a single-exponential decay with significantly shorter lifetimes of $\tau = 323$ and 119 ns observed, respectively. From these values, a $q \sim 0$ was determined.

The absorption spectra of both **Yb.1.Ru** and **Nd.1.Ru** showed a strong transition centered at ca. 285 nm and a second transition centered with λ_{max} at ca. 450 nm corre-

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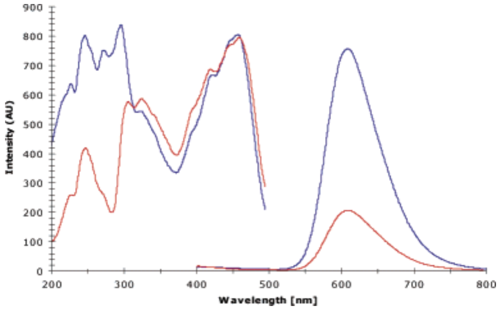

Figure 2. Excitation spectra (emission at 610 nm) and fluorescence emission spectra from the Ru(II)-based MLCT emission upon excitation at 285 nm for **Yb.1.Ru** (in red) and **Nd.1.Ru** (in blue), respectively, and probing the emission of the MLCT band (610 nm). All were recorded under identical experimental conditions.

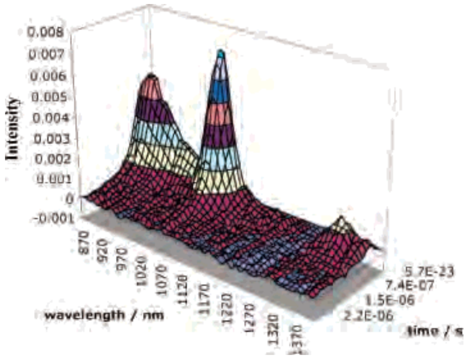

Figure 3. Time-resolved luminescence profile of **Nd.1.Ru** in H_2O, clearly showing the Nd(III) transitions at 1340 and 1055 nm.

sponding to the MLCT of the Ru center ($\epsilon = 11\ 105\ \text{mol}^{-1}\ \text{L}^{-1}$; Figure S3 in the Supporting Information). Excitation of either of these bands gave rise to an emission centered at 610 nm assigned to the Ru(II) MLCT emission in water, clearly indicating that the phen ligand sensitizes the MLCT transition (Figure 2). This characteristic d-block emission gives rise to the necessary overlap with that of the symmetry-forbidden f−f absorption bands of Yb(III) and Nd(III), allowing for the sensitization of **Yb.1.Ru** and **Nd.1.Ru** in the visible region.

The excitation spectra of both complexes were also recorded by excitation of the ligand (Figure 2). The excitation spectra revealed three principle regions at ca. 280, 337, and 460 nm, which can all be probed to investigate either the MLCT or the NIR emission. From Figure 2, it can be seen that, in the excitation spectra, the contribution from the MLCT band is the same for both dyads. However, there are significant differences observed at lower wavelengths, which can be assigned to the interactions of the coordinated phen moiety and the lanthanide ions. This was verified by recording the excitation and emission spectra of compound **2** (Figure S4 in the Supporting Information), which mimics the Ru part of **Yb.1.Ru** and **Nd.1.Ru**. Conversely, the most striking difference is seen in the MLCT emission, which is significantly more intense for **Yb.1.Ru** than for **Nd.1.Ru**, indicative of more effective sensitization (or energy-transfer overlap) by the MLCT center in **Nd.1.Ru** to the $^4F_{4/3}$ excited state of Nd(III) than in **Yb.1.Ru**. This difference was also reflected in the time-resolved measurements of the MLCT emission. For **Yb.1.Ru**, the emission exhibited a single-exponential decay with $\tau = 551$ and 377 ns in D_2O and H_2O, respectively. Similarly, for **Nd.1.Ru**, the emission exhibited a single-exponential decay of 335 ns in H_2O and 441 ns in D_2O.

The lanthanide luminescence was recorded by exciting **Yb.1.Ru** and **Nd.1.Ru** at 337 and 460 nm, respectively. Upon excitation at 337 nm (where the intensity in the excitation spectra is the same for both complexes; Figure 2), an emission was observed for **Yb.1.Ru** at 980 nm (Figure S5 in the Supporting Information). However, a significant emission, which partly overlaps with that of the Yb(III) emission, was also observed from the Ru center. Nevertheless, from the deactivation of the Yb(III) emission, we were able to determine lifetimes of 6.4 and 2.4 μs in D_2O and H_2O, respectively, which indicated that $q \sim 0$ for **Yb.1.Ru**. Similarly, excitation of **Nd.1.Ru** at 337 nm also gave rise to sensitized Nd(III) emission, occurring at 1340 nm. From these measurements, decay lifetimes of $\tau_{\text{rise time}} = 30$ ns and $\tau = 209$ ns were recorded for the Nd(III) emission (observed at 1340 nm) in H_2O and $\tau_{\text{rise time}} = 197$ ns and $\tau = 210$ ns in D_2O, which suggest $q \sim 0$. However, the most important results were observed upon excitation of **Nd.1.Ru** at the MLCT band in the visible region at 460 nm. In both cases, the NIR-based emission was clearly observed, as can be seen in Figure 3, with intense emission bands at 1340 and 1055 nm, respectively, which are clearly more intense and separated from the Ru-based emission occurring at ca. 870−990 nm. By observation of the decay at the 1340-nm transitions, lifetimes of $\tau_{\text{rise time}} = 30$ ns and $\tau = 221$ ns in H_2O and $\tau_{\text{rise time}} = 197$ ns and $\tau = 210$ ns in D_2O were seen. This clearly suggests that the Nd(III) excited state can be efficiently sensitized either by the ligand center or, more importantly, by the MLCT band; hence, this conjugate can be described as having “two channel” inputs, one at short wavelengths and one in the visible region. It also suggests that sensitization of the 377-nm band, which is mostly phen-based, would occur via the ^{3}MLCT because the decay lifetimes are the same. These results also demonstrate the formation of the supramolecular system **C**, where the nature of the capped or ancillary ligands can be used to modulate the lanthanide emission.[18]

In summary, we have developed the first examples of f−d dyads, based on the design principles laid out in Figure 1 for **C**, using the cyclen-based ligand **1**. Both complexes showed that excitation at either the ligand or the MLCT transitions gave rise to sensitized lanthanide luminescence in the NIR. Of the two complexes, the Nd(III) emission gave well-resolved and intense emission bands. We are currently in the process of making other supramolecular f−d conjugates based on this design using different ancillary ligands.

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Supporting Information Available: Synthesis and characterization of complexes (Figures S1−S17). This material is available free of charge via the Internet at http://pubs.acs.org.

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