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Reversible Luminescence Switching of a Redox-Active Ferrocene–Europium Dyad

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Supporting Information

ABSTRACT: The copper-catalyzed cycloaddition reaction between a propargyl-appended europium complex and azidomethylferrocene yields a d–f dyad whose photophysical properties can be reversibly switched by varying the oxidation state of the ferrocene chromophore.

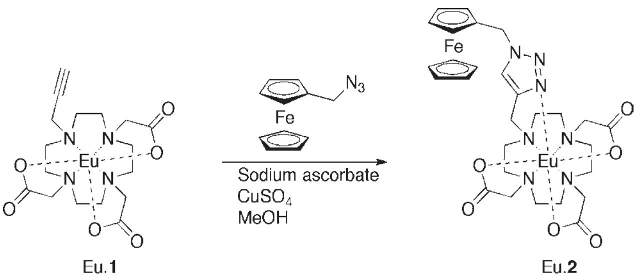
Sensitized luminescence from lanthanide complexes has been of interest for many years[1] and has begun to be widely applied in bioassays and microscopy.[2,3] The long-lived luminescence associated with luminescent lanthanide ions is readily separated from fluorescence and scattered light using time-gated techniques, meaning that very low concentrations of lanthanide probes can be observed in biological media.[4] Within the past decade or so, a number of important breakthroughs have been made in the development of lanthanide complexes that respond to changes in the concentration of a range of analytes:[5] these have been developed into ratiometric probes of ionic concentration,[6] and some show considerable promise as clinical agents for the early-stage diagnosis of tumor markers.[7]

Early studies on luminescent lanthanide complexes focused on the development and utilization of europium and terbium complexes, which emit visible light, but over the past decade or so the approach has been extended to exploit the long-wavelength emission from lanthanides such as neodymium, ytterbium, and erbium.[8−10] The low-lying emissive states of these ions can be populated using a much wider range of chromophores,[11] and much has been made of the use of transition metal complexes as antennae.[12]

We recently demonstrated that lanthanide complexes of propargyl DO3A (Ln.**1**) could be used as substrates for the copper-catalyzed ‘click’ reaction. We now report the use of this methodology to prepare a ferrocene-appended europium complex (Eu.**2**). Our synthetic strategy is shown in Scheme 1. Eu.**1** was prepared as described in the literature.[14] Reaction with azidomethylferrocene[15] (**3**) in the presence of copper(I) yielded Eu.**2**. We subsequently demonstrate that the redox characteristics of the antennae can be utilized in the reversible, high-fidelity switching of luminescence from the lanthanide center (Figure 1). While ferrocene has been used as a sensitizer for lanthanides in the past,[13] we believe that this is the first example in which its electrochemistry has been exploited as an emission switch.

The ^{1}H NMR spectrum of Eu.**2** (Figure S4) shows sharp, well-resolved signals for the ligand protons close to the lanthanide center. This can be contrasted with the broad signals observed in the NMR spectrum of Eu.**1** (Figure S5) and provides clear evidence for the rigidification of the complex by coordination of one of the triazole nitrogen atoms to the europium center.

Scheme 1. Synthesis of Eu.2



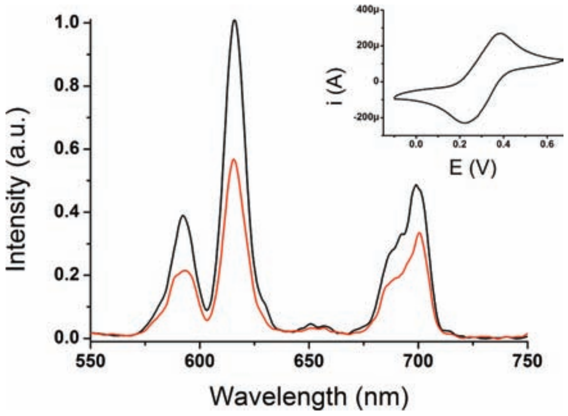


Figure 1. Emission spectrum of Eu.**2** in its reduced state (black line) and after oxidation (red line). Inset: diffusive cyclic voltammogram of Eu.**2** (2 mM in 100 mM $NaClO_4$, 100 mVs^{-1} at a Pt guaze working electrode).

Figure S4 shows that the aqueous speciation of Eu.**2** is dominated by a single isomer, though close inspection of the baseline reveals peaks corresponding to a minor isomer present in <5% abundance. For the major form, the shifts of the axial ring protons on the macrocycle are consistent with the adoption of monocapped square-antiprismatic geometry around the lanthanide center and are comparable with data in the literature for other europium complexes with similar geometries.[16]

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Having established that this process provided an effective method for preparing a ferrocene-containing d−f hybrid complex, we also used the same methodology to prepare Yb.**2** from Yb.**1**. The ^{1}H NMR spectra of Yb.**2** and Yb.**1** (Figures S6 and S7, respectively) revealed that these complexes behave very similarly to their europium-containing analogues.

Time-resolved luminescence measurements were used to define the inner-sphere solvation of the complexed lanthanide, using the equation

$$q_{Eu} = A_{Ln}(\tau_{H_2O}{}^{-1} - \tau_{D_2O}{}^{-1} - B_{Ln}) \tag{1}$$

to define q, the number of bound water molecules, from the luminescence lifetimes in H_2O and D_2O (τ_{H_2O} and τ_{D_2O}) measured in milliseconds (A_{Eu} = 1.2 ms, B_{Eu} = 0.25 ms^{-1}; A_{Yb} = 1.0 μs, B_{Yb} = 0.1 μs^{-1}).[17] The observed temporal profiles of the luminescence of Eu.**2** were fitted by iterative reconvolution with the detector response, to give lifetimes of 0.38 and 0.82 ms in H_2O and D_2O, respectively, following excitation at 340 nm. Applying eq 1 to these lifetimes gives q_{Eu} = 1.4, suggesting that the monocapped square-antiprismatic form does indeed predominate. For the ytterbium complex, the observed lifetimes, 1.0 and 5.9 μs in H_2O and D_2O, respectively, give q_{Yb} = 0.7. This smaller value is consistent with the lanthanide contraction and the change in structure across the lanthanide series commonly observed as a consequence of decreasing ionic radius.

Though ferrocene is known to act as an efficient triplet and lanthanide excited-state quencher,[18] this is likely to be efficient only at intermetallic separations where electron transfer is effective,[19] and ferrocene derivatives have also been shown to sensitize emission from europium complexes.[13a] Ferrocene also displays a well-known ligand-to-metal charge-transfer transition where the extinction coefficient is highly sensitive to the metal redox state.[20] We accordingly reasoned that this could be exploited to tune the luminescence from the lanthanide center.

Initial analyses with a 1:1 aqueous solution of ferrocene monocarboxylic acid and Eu.**1** in 100 mM sodium perchlorate confirmed not only the ability of ferrocene illumination to sensitize Eu emission but also the ability of ferrocene-centered electrochemistry to reversibly switch the process (see Supporting Information). Since this assembly is not kinetically inert, analogous experiments with the dyad Eu.**2** (Figure 1) were then carried out in a 10 mm path length quartz fluorimeter electrochemical cell (total solution volume ∼140 μL). Chronoamperometry was employed to cycle a Pt gauze working electrode between oxidative (0.6 V) and reductive (0 V) potentials for 30 and 40 min, respectively. Simultaneous luminescence analyses confirm an on/off switching with high fidelity (Figure 2).

Similarly reversible switching was observed in the case of Yb.**2** (Figure 3). Oxidation of the sample in D_2O was found to be accompanied by a change in luminescence lifetime from 5.9 μs for the reduced form to 4.4 μs for the oxidized form. This suggests that the oxidized form of ferrocene sensitizes the formation of the ytterbium $^2F_{5/2}$ excited state, but that low-lying excited states of ferrocenium can act to quench this excited state once it has formed. The efficiency of such quenching (ϕ_{quench}) is given by

$$\phi_{quench} = 1 - \tau_{red}/\tau_{ox} \tag{2}$$

In this case, ϕ_{quench} = 0.25. This is borne out closely by the ratio of the observed intensities of ytterbium-sensitized emission (Figure 3), suggesting that nonradiative quenching of the ytterbium excited state is the dominant pathway for modulating the intensity of emission.

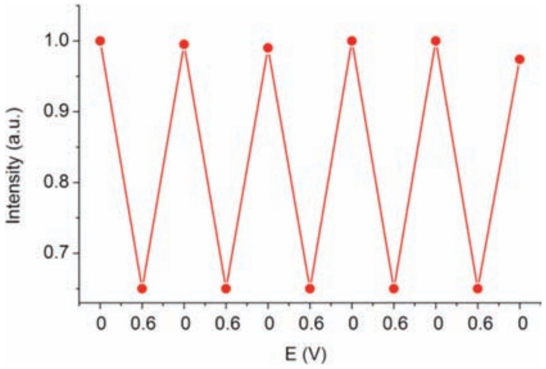

Figure 2. Reversible electrolytic switching of Eu.**2** emission (2 mM solution) at a fine Pt mesh working electrode (Pt wire counter electrode, Ag/AgCl reference electrode, in 0.1 $NaClO_4$ electrolyte).[21]

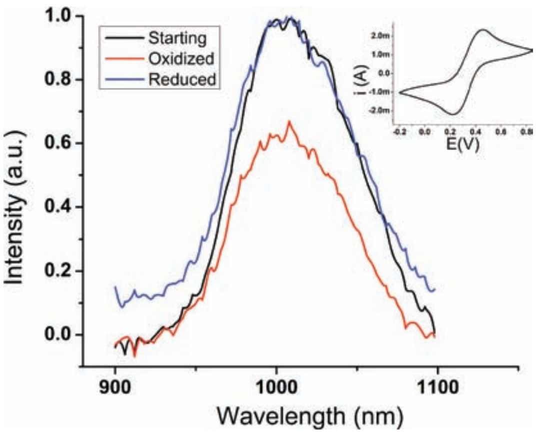

Figure 3. Emission spectrum of Yb.**2** after sequential oxidation and reduction under a 425 nm excitation light. Inset: diffusive cyclic voltammogram of Yb.**2** (2 mM in 0.1 M $NaClO_4$, 100 mV s^{-1}, Pt gauze working electrode).

It is clear that electrolytic oxidation of the ferrocene chromophore results in a significant reduction of the intensity of the lanthanide-centered emission in both cases. Triplet energy measurements on Gd.**2** at 77 K revealed that the phosphorescence spectrum of the ligand is dominated by a triazole-centered triplet state at high energy (∼23 000 cm^{-1}), while no ferrocene-centered phosphorescence could be detected.

While energy transfer in most lanthanide-containing systems has been shown to proceed via a triplet-mediated mechanism,[1a] an alternative mechanism involving the generation of an intermediate chromophore-to-lanthanide charge transfer state has been shown to provide the dominant pathway for sensitization of ytterbium where it is feasible.[22] In this case, inhibition of such a sequential double charge transfer mediated pathway upon oxidation might initially appear plausible for Yb.**2**. However, this pathway would not be expected to influence the behavior of Eu.**2** in its oxidized form, since the intermediate state in such a system would be expected to be lower in energy than $^5D_0$. Thus, it is reasonable to conclude that, in both cases, quenching of the lanthanide by ferrocenium excited states is responsible for the observed switching; such a pathway is available to all lanthanide ions (provided that the quencher state is lower in energy than the lanthanide emissive state), suggesting that redox switching can be applied to modulating lanthanide luminescence in a wide variety of applications. This area clearly merits further investigation using a wider variety of redox-active chromophores and transient absorption studies.

In summary, the click reaction offers a facile synthetic route to access d−f hybrid complexes containing ferrocene, while the incorporation of a redox-active chromophore provides the means for highly reversible electrochemical switching of lanthanide emission. We are currently working on refining these systems so that they may be exploited as devices.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and ^{1}H NMR spectra of the lanthanide complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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