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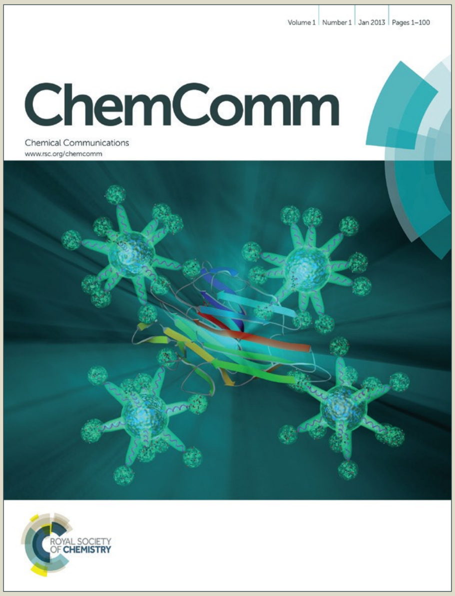

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Reversible Redox Modulation of a Lanthanide Emissive Molecular Film

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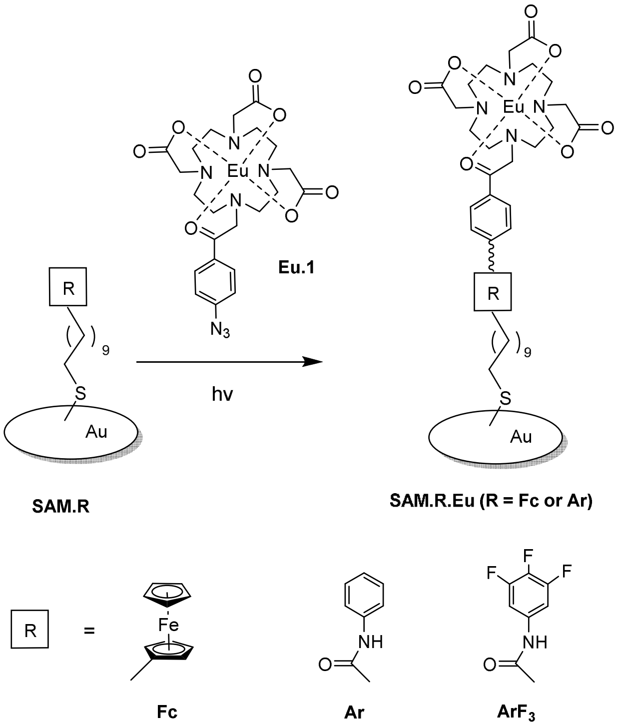
Herein we demonstrate redox switchable emission from a sensitized, europium-ferrocene containing, molecular film assembled by a novel nitrene-based strategy. Electrochemical modulation of europium emission upon switching the ferrocene moiety redox state is ascribed to the reversible generation of a quenching ferrocenium species.

The preparation of functional molecular architectures capable of exhibiting well-defined responses under specific conditions requires careful design, and offers significant new opportunities for the further development of molecular electronics,[1] molecular machines[2] and advanced sensory platforms.[3] For many applications, not least those facilitating device integration, it is desirable that such constructs should be effectively immobilised on a solid support. Consequently, the immobilisation of transducing species at interfaces for sensing/switching applications is attracting ever-increasing interest. While signal transduction within such systems may be achieved by a wide range of mechanisms, the incorporation of luminescent species offers a particularly convenient and non-destructive means to report on coordinative, electronic and conformational changes within these architectures. Accordingly, a number of sensing and switching platforms have been developed where a film's optical response is induced by changes in local conformation,[4] surface potential,[5] or the presence of analytes.[6] Redox modulation of emission affords considerable opportunities for applications in molecular electronic constructs, novel display technologies and even for incorporation as modular components in molecular machines. While there have been a number of examples of redox modulation of absorption[7] at well-defined organic molecular monolayers, examples of *luminescence* switching in such systems are extremely rare.[7b] Luminescent lanthanide species are particulary attractive in this context, offering sharp, well-defined, characteristic fingerprint emission bands, as well as long lifetimes allowing for noise and radiative scattering effects to be reduced by time gating.[8] There have, however, been surprisingly few examples of the incorporation of lanthanide luminescent species into surface bound constructs.[9]

In the current work we demonstrate the electrochemical modulation of emission from lanthanide-containing thin films on gold substrates through redox-mediated switching of a tethered ferrocene/ferrocenium moiety. After assembly of a ferrocene europium dyad at gold interfaces, electrochemical oxidation specifically leads to a reversible reduction in lanthanide phosphorescence. This constitutes, to the best of our knowledge, the first report of redox switching of lanthanide luminescence in a molecular film.



Scheme 1. Summary of the interfaces utilised in this work, showing a schematic representation of photografting of the europium 4-azidophenacyl DO3A (**Eu.1**), followed by nitrene insertion into ferrocene and benzene terminated monolayers.

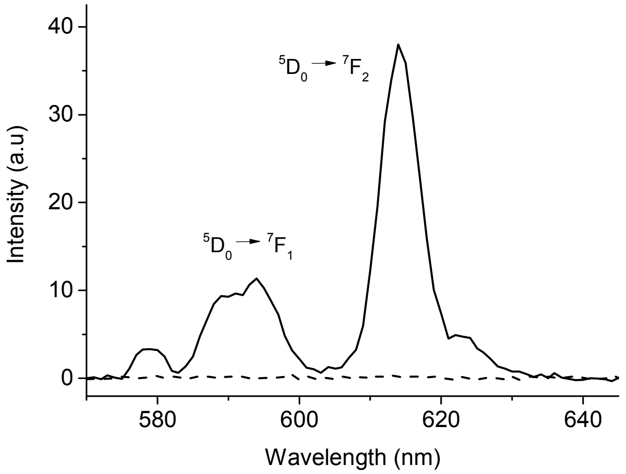


Figure 1. Emission phosphorescence (delay time = 0.1 ms) spectra (λ_{ex} = 350 nm) of europium-ferrocene dyad interfaces (**SAM.Fc.Eu**) prepared by photografting of **Eu.1** to a **SAM.Fc** film (—) and the corresponding control prepared by the same method except no exposure to light to induce photografting was undertaken (---).

The preparation of europium cyclen incorporating surface architectures (**SAM.R.Eu**) is outlined in Scheme 1. Initially, ferrocene, benzene and trifluorobenzene-terminated interfaces were prepared and characterized as summarized in the supporting information (SI 1 and SI 2). Subsequent photografting of **Eu.1**, via photogeneration of a reactive nitrene species from the aryl azide, onto the primer layers was carried out. Reactive nitrenes, generated from the photolysis of aryl azides, are well known to insert into aromatic C-H bonds[10]. The construction of ferrocene-europium interfaces (**SAM.Fc.Eu**) was observed and studied by fluorometry, ellipsometry, X-ray photoelectron spectroscopy (XPS) and electrochemistry. After photografting of **Eu.1** to the **SAM.Fc** primer layer the characteristic europium luminescence emission fingerprint was observed upon excitation through the aryl ketone antenna at 350 nm[11] (Figure 1 a) with a lifetime of 0.32 ± 0.02 ms; a value markedly lower than that of 0.60 ms determined previously[11] for the azide precursor in aqueous solution, and consistent with the proximity of a quenching gold interface.[9a] No europium emission was seen for controls prepared in the same manner in the absence of irradiation, indicating that generation of the reactive nitrene species is vital for the formation of a stable europium cyclen film. Similarly, the europium 3d XPS signature was only observed after photografting of **Eu.1** (SI 3). Voltametrically determined surface concentrations of 3.8×10^{-10} mol cm^{-2} for ferrocene at the **SAM.Fc.Eu** interfaces compare well to the theoretical value of 4.6×10^{-10} mol cm^{-2} previously suggested for a close packed monolayer of ferrocene thiol at the interface[12] indicating densely packed thiol layers are formed with little loss of electroactivity upon photografting.

Table 1. Ellipsometric Film Thicknesses (nm)

Primer layer[a]	Prior to photografting	After Photografting	Control[a]
SAM.Fc	2.0 ± 0.2	3.2 ± 0.3	1.9 ± 0.2
SAM.Ar	2.0 ± 0.3	3.2 ± 0.3	1.9 ± 0.3
SAM.ArF$_3$	1.9 ± 0.2	2.2 ± 0.2	-

[a] controls prepared in the same way as the photografted interfaces but in the absence of irradiation.

Construction of the **SAM.Fc.Eu** interfaces was also followed by ellipsometry, with the results summarized in Table 1. An increase in film thickness from (2.0 ± 0.2) nm to (3.2 ± 0.3) nm was observed upon photografting of **Eu.1** to the **SAM.Fc** primer layer, consistent with the attachment of a near-monolayer of aryl azide to the ferrocene terminated monolayer (the diameter of cyclen is approximately 0.9 nm[13]). Predictably, no increase in film thickness was observed in the absence of irradiation, confirming, again, film modification to be chemically specific. Comparable results were obtained for the **SAM.Ar** layers with europium luminescence emission, XPS (see supporting information SI. 4) and ellipsometric analyses confirming that photografting of **Eu.1** gave rise to a stable near-monolayer of europium cyclen on the primer SAM (Table 1). Importantly, only negligible europium emission (SI. 4a) and no statistically significant film thicknesses increase (Table 1) was observed upon the attempted photografting of **Eu.1** to the trifluoroaniline- terminated SAM (**SAM.ArF$_3$**). It has previously been shown that nitrene insertion into inert C-F bonds is not viable.[10f, 14] These irradiation and chemically specific observations are fully consistent with assembly being through nitrene insertion into aromatic C-H termini upon subjecting **SAM.Fc** and **SAM.Ar** interfaces to photografting conditions. This pathway is not available in the case of the **SAM.ArF$_3$** films. Furthermore the lack of a europium emission or film thickness change, for **SAM.ArF$_3$** interfaces subjected to photografting conditions, suggests negligible nitrene insertion into the alkyl SAM backbone, an observation likely to be associated with underlying steric restrictions within the film.

Subsequent to assembly and characterisation, spectro-electrochemical analyses were undertaken where europium luminescence emission intensity (at 616 nm, λ_{ex} = 350 nm) was monitored upon alternation of the potential between a value negative (0 V) of the Ferrocene/Ferrocenium (Fc/Fc+) redox potential (seen at 0.3 V, see Figure 2 insert) and one positive (0.7 V) of that potential. Upon electrochemical oxidation of the surface bound ferrocene to the ferrocenium, a significant decrease (~ 35 %) of the europium emission intensity is observed. Subsequent reduction back to the ferrocene species results in a return of emission intensity (Figure 2, ●). To further investigate the origins of reversible quenching, **SAM.Ar.Eu** control interfaces were analysed. These interfaces are analogous to the **SAM.Fc.Eu** surface constructs, incorporating the same europium-containing moiety at a comparable distance from the surface; crucially, however, this architecture does not incorporate a ferrocene group. The slightly lower emission intensity observed for **SAM.Fc.Eu** in comparison to the **SAM.Ar.Eu** interfaces we attribute to the weak quenching effect of the ferrocene in its reduced state[15] (an effect much less pronounced than that associated with ferrocenium).

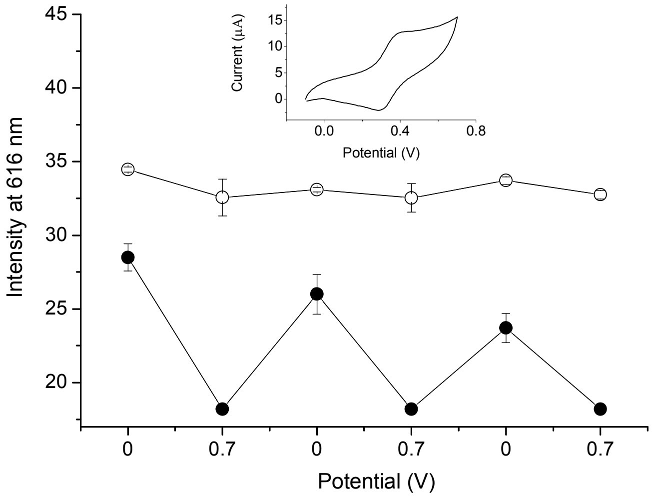


Figure 2. Intensity of europium emission (at 616 nm, $\lambda_{ex} = 350$ nm) upon alternation of potential between 0 V and +0.7 V for the ferrocene-europium dyad interface **(SAM.Fc.Eu**, ●) and (non-ferrocene incorporating) a europium control interface (**SAM.Ar.Eu**, ○). For the **SAM.Fc.Eu** interfaces oxidation of ferrocene to ferrocenium brings about a large (up to 35 %) drop in europium emission intensity. Subsequent reduction back to the ferrocene state brings about a return of emission intensity. A comparable modulation is not seen for the **SAM.Ar.Eu** control interfaces.[†] Inset: cyclic voltammogram of the europium-ferrocene thin film dyad interface shows the ferrocene couple centred at 0.35 V.

Monitoring the europium emission (at 616 nm, $\lambda_{ex} = 350$ nm) for the **SAM.Ar.Eu** interfaces while alternating the potential between 0 and 0.6 V gave only a small, statistically insignificant[#] (i.e. modulation amplitude smaller than error), modulation of emission (Figure 2, ○) indicating that the switchable redox state of ferrocene is indispensable in bringing about emission modulation in the case of the ferrocene incorporating **SAM.Fc.Eu** film (Figure 3).[16]

In summary, the first example of redox switchable lanthanide emission from a sensitized molecular film has been demonstrated. The ability to modulate emission electrochemically by controlling the status of a redox-active component within a molecular layer represents a significant development in the exploitation of such architectures within advanced sensory systems, novel display platforms and even for incorporation as modular components within larger functional molecular constructs (i.e. molecular machines).

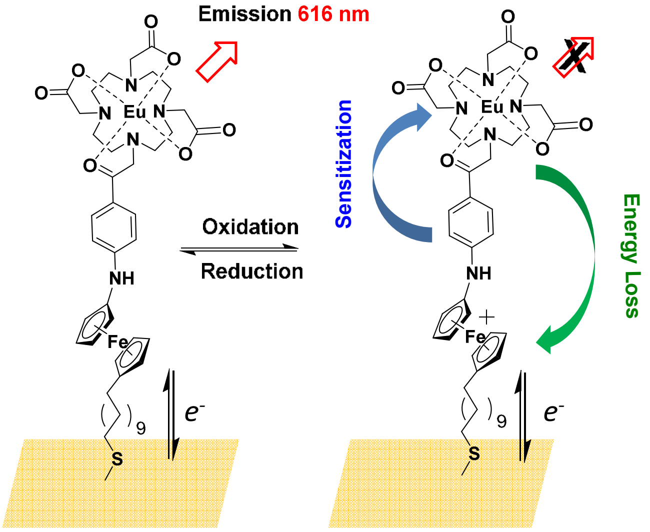


Figure 3. Electrochemical modulation of europium emission proceeds via interconversion between the ferrocene and ferrocenium redox state for the **SAM.Fc.Eu** surface bound architectures. This is assigned to the quenching of sensitized emission by the ferrocenium moiety.[16]

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Notes and reference

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† The baseline progressive decrease in emission intensity, for **SAM.Fc.Eu** interfaces, upon cycling is attributed to a growing and incomplete electrochemical reduction back to the ferrocene state upon cycling (likely to be the result of anion association with the ferrocenium[17]) and not to photobleaching, a proposal strongly supported by voltammetric analyses (SI 5.) Note that the emission intensity associated with the ferrocenium state is constant and there is no physical film loss from the interface.

The much smaller modulation observed at **SAM.Ar.Eu** interfaces could be ascribed to a field induced perturbation of molecular conformation and thus europium – gold optical coupling.

Electronic Supplementary Information (ESI) available: Experimental details, luminescence and XPS spectra of **SAM.Fc.Eu**, **SAM.Ar.Eu** and **SAM.ArF$_3$** interfaces and voltammetric analysis of **SAM.Fc.Eu** interfaces. . See DOI: 10.1039/c000000x/

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