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d–f Heterobimetallic Association between Ytterbium and Ruthenium Carbon-Rich Complexes: Redox Commutation of Near-IR Luminescence

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Supporting Information

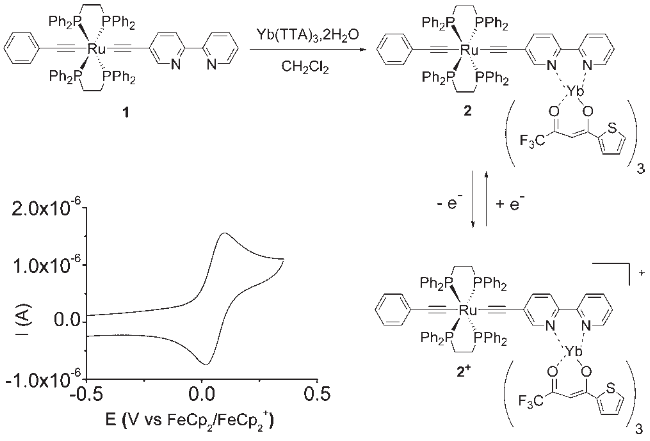
ABSTRACT: We describe how the association between an ytterbium ion and a ruthenium carbon-rich complex enables the first switching of the near-IR Yb(III) luminescence by taking advantage of the redox commutation of the carbon-rich antenna.

Molecular-based switching devices, in which key physical properties can be modulated with external stimuli, are the focus of much attention.[1] In particular, group 8 metal acetylide complexes, which display strong ligand-mediated electronic effects, are attractive redox-switchable building blocks for the realization of optical or conductive switches.[2,3] For instance, ruthenium acetylides allow the perturbation of photochromic dithienylethene (DTE) units, resulting in unique light- and electrotriggered multifunctional materials.[2a,c] Therefore, further designs with appropriate combinations of such types of organometallics with functional units should lead to redox perturbations of the resulting architectures in a more efficient way than with the ubiquitous ferrocenyl group.[3,4]

Long-lived, narrow-bandwidth luminescence of lanthanide ions ranging from the visible up to the near-IR (NIR) spectral range is attracting considerable interest in investigations of the properties of molecular materials, such as signaling systems, because of its noninvasive nature, short response time, and high sensitivity.[5,6] Indeed, the photophysical properties of these ions (i.e., lifetimes and quantum yield) can be modulated with external perturbations induced by ions or molecules.[7] In this context, NIR emitters such as Nd, Yb, and Er have been successfully sensitized using redox-active antenna ligands such as ferrocene and tetrathiafulvalene.[8] Surprisingly, however, to the best of our knowledge, redox switching or modulation of luminescence like that reported for complexes of transition metals such as Ir(III) and Re(I)[9] has never been achieved with lanthanide ions.

Herein we describe the straightforward switching of ytterbium luminescence by taking advantage of the redox commutation of a carbon-rich ruthenium antenna. Therefore, we present (i) the synthesis of a ruthenium acetylide complex coordinated to a luminescent Yb(III) unit via a bipyridyl ligand (**2**; Scheme 1) and (ii) the unprecedented redox commutation of the Yb(III) NIR emission by changing the oxidation state of the ruthenium antenna.

Scheme 1. Synthetic Pathway and CV Trace for 2 (CH_2Cl_2, 0.2 M Bu_4NPF_6, ν = 100 mV s^{-1})



The synthesis of complex **2** was readily achieved by coordination of precursor **1** to $[Yb(TTA)_3 \cdot 2H_2O]$ (TTA = 2-thenoyltrifluoroacetonate). This new compound was characterized with the help of ^1H NMR and IR spectroscopies, elemental analysis, and high-resolution mass spectrometry (see the Supporting Information). Cyclic voltammetry (CV) traces for **2** in CH_2Cl_2 solution (0.2 M Bu_4NPF_6) were recorded to study the nature of the redox properties. A reversible one-electron oxidation was observed at $E_1° = 0.059$ V vs $FeCp_2/FeCp_2^+$ (ΔE_p = 70 mV) (Scheme 1), followed by an irreversible process (E_{pa2} = 0.921 V) (Figure S3 in the Supporting Information).

The photophysical properties of **1** and **2** were studied in CH_2Cl_2 or MeTHF solutions (Figure 1). In addition to the intense short-wavelength absorption bands for transitions involving the 1,2-bis(diphenylphosphino)ethane (dppe) ligands and the carbon-rich ligand [intraligand (IL) transitions], the heterobimetallic complex **2** shows two main absorption bands at λ_{max} = 334 nm (ε = 50 100 L mol^{-1} cm^{-1}) and 460 nm (ε = 15 700 L mol^{-1} cm^{-1}). The first transition is assigned as a TTA ligand absorption (by comparison to the spectrum of the $[Yb(TTA)_3 \cdot 2H_2O]$ precursor) overlapping with transitions of

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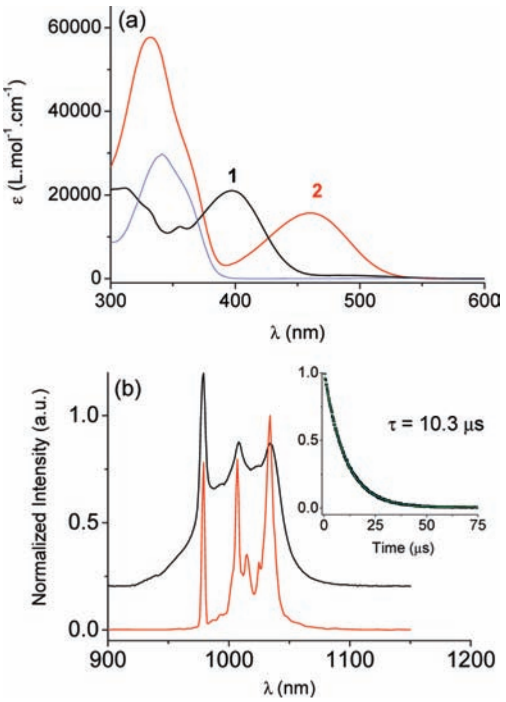

Figure 1. (a) Absorption spectra of **1** (black), [Yb(TTA)$_3$·2H$_2$O] (blue), and **2** (red) in CH$_2$Cl$_2$. (b) NIR emission of **2** (λ_{ex} = 450 nm) in MeTHF at room temperature (black) and at 77 K in a frozen organic glass (red). The inset shows the lifetime decay observed at room temperature and the monoexponential fit (green line) (λ_{ex} = 460 nm, λ_{det} = 980 nm).

$\pi-\pi^*$ character centered on the bipyridyl moieties of complex **1** (Figure 1a). On the other hand, the lower-energy transition is characteristic of the ruthenium moiety and can be described as multiconfigurational metal-to-ligand charge transfer (MLCT) excitations corresponding to transitions from Ru(dπ)/alkynyl-based orbitals to metal/ligand antibonding orbitals combined with an intraligand $\pi \rightarrow \pi^*$ character.[10,11] This band exhibits a marked bathochromic shift for **2** relative to the parent complex **1** ($\Delta\lambda$ = +62 nm) due to the enhancement of the electron-withdrawing character of the bipyridyl moieties upon complexation. Upon excitation in the aforementioned MLCT transition (λ_{ex} = 450 nm), the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission of ytterbium having a characteristic line shape was observed in the NIR spectral range at 980 nm (Figure 1b).[12] In a frozen organic glass (MeTHF, 77 K), the vibronic broadening of the transition was strongly reduced ($\omega_{1/2}$ = 27 cm^{-1}), and consequently, the emission spectrum became nicely resolved with the splitting of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition into five sublevels, a signature of the crystal-field effect. At room temperature, the Yb(III) luminescence decay of **2** (Figure 1b, inset) could be nicely fitted by a monoexponential function, indicating the presence of a single species with an excited-state lifetime of 10.3 μs. This value is in the classical range for this type of Yb(III) complex.[13]

As complex **2** presents a reversible first oxidation process, its absorption properties were investigated by means of UV−vis−NIR spectroelectrochemistry (SEC) in an optically transparent thin-layer electrochemical (OTTLE) cell (Figure 2a). While the band located at 334 nm remained unaffected, one-electron oxidation led to a decrease in the band at λ_{max} = 460 nm and to a new broad absorption band in the NIR region of the spectrum centered at λ_{max} = 1057 nm (ε = 5750 mol^{-1} L cm^{-1}), a region in which no absorption was observed for **1**$^+$ or **2**. This broad band is probably due to multiple transitions from HOMO-*n* to the SOMO resulting from the depopulation of the HOMO d$_\pi$/π orbital.[10,11] IR experiments showed an expected shift of the $\nu_{C\equiv C}$ stretching vibration from 2043 to 1907 cm^{-1} upon electron removal (Figure S4) due to the bond weakening of the acetylide linkages.[10]

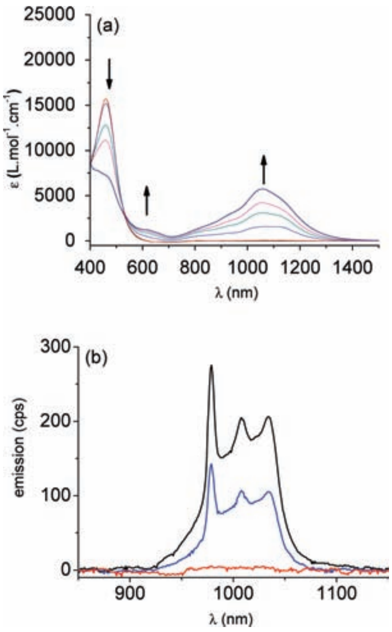

Figure 2. (a) Monitoring of the absorption spectra during the first oxidation of **2** in an OTTLE cell (CH$_2$Cl$_2$, 0.2 M Bu$_4$NPF$_6$). (b) Initial emission spectrum in CH$_2$Cl$_2$ (black), after in situ oxidation with acetylferricinium (red), and after reduction with decamethylferrocene (blue).

The luminescence redox switching experiment could not be performed in situ using electrochemical stimulus for practical reasons,[14] and therefore, oxidation was probed chemically by successive addition of equimolar amounts of an oxidant (acetylferricinium, $E°$ = 0.270 V vs FeCp$_2$/FeCp$_2$$^+$) and a reductant (decamethylferrocene, $E°$ = −0.590 V vs FeCp$_2$/FeCp$_2$$^+$) in the fluorescence cell under an inert atmosphere. Monitoring using absorption and emission spectroscopies after oxidation showed (i) the expected decrease of the absorption band at λ_{max} = 460 nm with the appearance of the new broad band around 1060 nm (Figure S5), which is a clear signature of the formation of **2**$^+$ in solution, and (ii) the nonemissive behavior of **2**$^+$ (Figure 2, red trace). The subsequent chemical reduction process regenerated **2**, as underlined by the recovery of the Yb(III) NIR luminescence at up to 53% of its original intensity (Figure 2, blue trace).

Since Yb(III) sensitization can proceed via either electron transfer from an electroactive ligand[15] or energy transfer from an antenna ligand,[16] the extinction of the NIR luminescence in **2**$^+$ can be rationalized either by the oxidation of the ruthenium acetylide moieties (preventing any sensitization by the electron-transfer mechanism) or by the appearance of the new excited states at ~1060 nm. These low-lying excited states can either prohibit the Yb sensitization or afford a preferential nonradiative energy back-transfer pathway from the $^2F_{5/2}$ Yb excited state;

both photophysical processes would trigger ytterbium luminescence quenching. Notably, in contrast to the SEC experiments, the chemical redox switching was not fully reversible.[17] The absorption spectra also showed a limited reversibility consistent with the emission spectra under these conditions, with a recovery of ∼60% of the vanished absorbance at $\lambda_{max} = 460$ nm upon oxidation (Figure S5).[18] Thus, the lack of full luminescence reversibility is due to the poor stability of $\mathbf{2}^+$ under the experimental luminescence conditions (high dilution: OD < 0.1, $C < 10^{-6}$ mol L^{-1}, addition of reactants),[19] which probably allows the well-known hydrolysis of the acetylide ligand to a carbonyl adduct.[10] Indeed, a characteristic vibrational stretching band was observed at 1983 cm^{-1} via IR monitoring of the chemical switching experiment (Figure S5).

In conclusion, these results clearly establish a proof of concept of the redox switching of the ytterbium NIR luminescence. Further spectroscopic and theoretical studies to obtain a better fundamental understanding of this lanthanide system are currently in progress. This work also shows that with an accurate choice of building units, access to original organometallic assemblies with targeted physical properties is possible. In addition, further functionalization of the trans ligand offers an enhanced potential of this system for increasing functionality and/or the introduction of anchoring moieties for future integration into molecular devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) It is worth mentioning that **1** is nonemissive and that the NIR emission of **2** is accompanied by a very weak emission around 550 nm. In addition, at the 450 nm excitation wavelength, the $Yb(TTA)_3 \cdot 2H_2O$ precursor does not absorb, unambiguously establishing the ruthenium-antenna-mediated sensitization process.

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(14) These reasons include the following: (i) the use of an OTTLE cell leads only to oxidation of the compound near the grid in the optical path, and light scattering in the cell would lead to the observation of the luminescence of the remaining neutral species away from the grid in the cell; (ii) bulk electrolysis in a two-compartment cell would lead to an electrolysis time for (almost) complete conversion that would be incompatible with the stability of the product (as described later in the manuscript).

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(17) All of the experiments were carried out under inert conditions using Schlenk techniques. The SEC experiments showed a reversibility of 95−100% on the basis of the absorption intensities recovered at the end of the experiments and the presence of no features other than those of the parent material.

(18) It should be noted that we cannot exclude a contribution of the decomposition product at this wavelength. Nevertheless, it is expected to be modest at this wavelength because of the degradation of the conjugated pathway (see later in the manuscript).

(19) It is noteworthy that the absorption spectrum did not show the presence of the band at 398 nm characteristic of uncomplexed ligand, which unambiguously indicates that no dissociation occurs in dichloromethane under high-dilution conditions.

■ NOTE ADDED AFTER ASAP PUBLICATION

Scheme 1 was incomplete in the version of this Communication published ASAP April 4, 2011. The corrected version was reposted April 6, 2011.