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Strong NIR electrochemiluminescence from lanthanide ions sensitized with a carbon-rich ruthenium chelate†

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We report on intense electrochemiluminescence (ECL) emission from the redox switching of a series of heterobimetallic systems consisting of lanthanide complexes emitting in the near-infrared (NIR) range (Yb^{3+} and Nd^{3+}) associated with a redox-active carbon-rich ruthenium bipyridyl antenna chelate. The NIR ECL emission was achieved successfully using the same molecular scaffold. Electrochemical reactions between the antenna and the sacrificial ECL coreactant allow for the low-potential redox modulation of the NIR luminescence from Yb^{3+} and Nd^{3+} . This strategy offers interesting new insights into NIR ECL systems based on inorganic complexes.

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Introduction

Electrochemiluminescence (ECL) is the light emitted from the excited state of a dye initiated by an electrochemical reaction.^{1–3} Due to the orthogonality of the initial electrochemical trigger and the final optical readout, ECL offers several advantages such as high sensitivity and selectivity, precise control over the emission position, no use of external light sources, and no photobleaching or phototoxicity.^{4–6} It has progressively become a powerful technique for clinical diagnostics and imaging of biological entities and chemical systems.^{7–12} Nowadays, the classical ECL system, composed of tris(2,2'-bipyridyl) ruthenium(II) dye, $[\text{Ru}(\text{bpy})_3]^{2+}$, and tri-*n*-propylamine (TPA) coreactant, is a benchmark for visible range emission (615 nm).^{7,13–15} However, a major experimental effort also focusses on the development of new ECL-active dyes emitting in the NIR region to extend the potentialities of ECL technology, within the biologically transparent window.^{16–33}

The possibility of combining this feature with sharp emission bands for multiplexed ECL detection makes lanthanide-based systems particularly attractive.^{28,34–45} Indeed, lanthanide-based (Yb^{3+} , Nd^{3+} , Eu^{3+} , etc.) complexes display long-

lived, well-defined, and narrow bandwidth photoluminescence (PL) bands ranging from the visible to the NIR spectral range, with high emission efficiency, particularly attractive for biological applications.⁴⁶ For such complexes, sensitization with a chromophore able to transfer its excited state energy to one of the lanthanides is needed because direct excitation corresponds to forbidden transitions.^{36,47–50} The sensitization process can proceed *via* either electron transfer or energy transfer from an excited antenna ligand.^{51,52} In the case of NIR emitters, chromophores with visible absorption, such as tetrathiafulvalene, ferrocene,^{50,53} and metal acetylide complexes,^{49,54,55} are particularly suitable and also exhibit accessible redox events for luminescence switching.⁵⁶ Among them, ruthenium acetylide complexes, which belong to group-8 metal complexes, are attractive redox-switchable building blocks with oxidation potential similar to that of ferrocene. In addition, they exert strong ligand-mediated electronic effects owing to the substantial ligand character of the highest occupied molecular orbital (HOMO) resulting from the overlap of a metal $d(\pi)$ orbital with an appropriate π orbital of the carbon-rich ligand, leading to a major involvement of this ligand in the redox processes and a minor metal contribution.⁴⁹ In this context, it has been demonstrated that ruthenium acetylide complexes with chelating units can modulate $\text{Nd}(\text{III})$ and $\text{Yb}(\text{III})$ PL successfully by a simple redox process.^{49,54,55} However, surprisingly, to our knowledge, ECL has not been achieved so far with such a heterobimetallic scaffold in coreactant ECL and, more generally, it has not been achieved with lanthanide NIR emitters.

Herein, ECL from a series of lanthanide complexes with NIR luminescence (Scheme 1) is demonstrated by taking advantage of the redox trigger of the abovementioned and pre-

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viously synthesized carbon-rich ruthenium complexes *trans*-[Ph-C≡C-(dppe)₂Ru-C≡C-bpy-κ²N,N'-Ln(TTA)₃] (**1Ru-Ln**, where Ln = Yb and Nd, dppe = 1,2-bis-(diphenylphosphinyl) ethane and TTA = 2-thenoyltrifluoro-acetonate),^{49,55} via the coreactant ECL pathway. The excited state of the ruthenium antenna is likely generated through an electrochemical reaction with TPrA in a wide potential range, followed by the sensitization of lanthanide ions coordinated with the bipyridine ligand. The separated moiety Yb(TTA)₃(phen) (with phen = phenanthroline) named **2Yb** and the ruthenium acetylide complex (**3Ru**) were also employed for control experiments.

Results and discussion

Since the ECL process is governed by electrochemistry and both homogeneous and heterogeneous electron-transfer reactions, the electrochemical properties of the **1Ru-Ln** series were investigated by cyclic voltammetry (CV) in a degassed CH₂Cl₂ solution containing 0.2 M TBAPF₆ as a supporting electrolyte as well as both monometallic moieties **2Yb** and **3Ru**, respectively (Scheme 1). The heterobimetallic complex **1Ru-Yb** was first studied and displays a reversible one-electron anodic wave peaking at 0.56 V vs. the Ag pseudo-reference electrode (Fig. 1a), corresponding to the reversible oxidation of the carbon-rich ruthenium antenna moiety. The **3Ru** complex, which comprised only the ruthenium acetylide center without the electron-withdrawing lanthanide center, showed the same oxidation wave (Fig. S1a†). **1Ru-Nd** exhibited the same reversible oxidation wave (Fig. S2†), confirming the attribution of this reversible one-electron transfer reaction to the ruthenium moiety.⁴⁹ The anodic peak current of the first reversible oxidation wave is slightly smaller for **1Ru-Nd** in comparison with **3Ru**. Such a difference reflects the larger size of **1Ru-Nd** compared to **3Ru**, which directly affects the corresponding diffusion coefficient. At higher anodic potentials, the CVs of **1Ru-Yb** showed an irreversible process at 1.25 V, similar to the **1Ru-Nd** complex (Fig. S2†). These results are consistent with the voltammetric behaviour reported in the literature.⁴⁹ In comparison, the lanthanide moiety (*i.e.* **2Yb**) exhibited an irre-

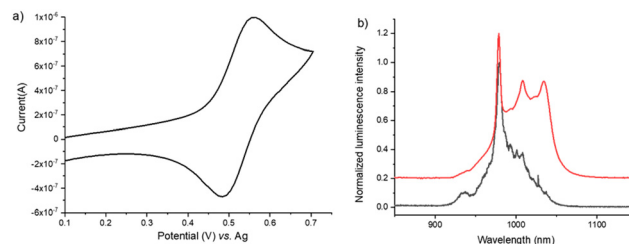
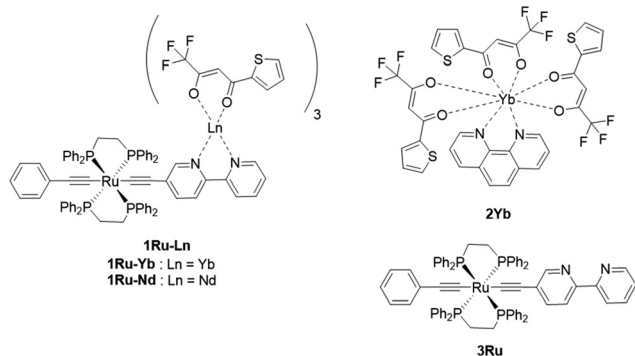


Fig. 1 (a) Cyclic voltammogram of 0.5 mM **1Ru-Yb** in a degassed CH₂Cl₂ solution with 0.2 M TBAPF₆ as a supporting electrolyte. Scan rate: 0.05 V s⁻¹. (b) Normalized ECL (black line) and photo-excited emission (red line) spectra of **1Ru-Yb**. The ECL spectrum was recorded in a CH₂Cl₂ solution containing 0.5 mM **1Ru-Yb**, 100 mM TPrA and 0.2 M TBAPF₆. A Pt disk and an Ag wire were used as the working electrode and the pseudo-reference electrode, respectively. For the sake of clarity to distinguish both spectra, the PL (λ_{exc} = 450 nm) signal was translated vertically by an increment of 0.2.

versible oxidation process with an onset potential at 1.65 V (Fig. S3†),³⁴ but we should mention that the ligand in **2Yb** was phenanthroline, whereas it was a bipyridyl ligand in **1Ru-Ln**. However, we consider that such a small structural change does not significantly affect the interpretation of the voltammetric results and that they remain valid in a first-order approximation.

Since **1Ru-Yb** exhibited a reversible electron-transfer reaction in oxidation, we used an anodic sacrificial coreactant to probe the possibility of generating its excited state rather than by an annihilation mechanism.² The role of this coreactant is to produce a highly reducing species that can populate the excited state of the dye by a sufficiently exergonic electron-transfer reaction with the oxidized species [**1Ru-Yb**]⁺. In this study, we selected the highly efficient TPrA coreactant, which is widely used to promote the ECL of the archetypical [Ru(bpy)₃]²⁺ dye and others for numerous applications in analytical chemistry and microscopy.^{11,57–60} The ECL process follows the “oxidative-reduction” mechanism occurring by simply applying an anodic potential sweep or step to oxidize both the coreactant and the dye at the electrode surface. After a fast deprotonation of the electrogenerated TPrA^{•+} cation radical, the neutral strong reductant TPrA[•] radical is produced. It reacts with the oxidized form of the dye and generates its excited state. Using such an “oxidative-reduction” pathway, we successfully recorded the ECL spectrum of **1Ru-Yb**. Fig. 1b shows the ECL spectrum (black line) and the comparison with the PL spectrum (red line) of **1Ru-Yb** previously obtained by photo-excitation with the low-energy metal-to-ligand charge transfer (MLCT) transition corresponding to transitions from Ru(dπ)/alkynyl-based orbitals to a π* orbital associated with the bipyridine unit.^{49,54} It is noteworthy that the ECL spectra were obtained using an optic fibre spectrometer equipped with a silicon-based CCD detector whose quantum efficiency vanishes drastically in the NIR range after 850 nm, explaining a well-known spectral discrepancy in comparison with that obtained with an InGaAs detector for the PL spectra (see the ESI for details on the photodetectors†).⁶¹ Overall, the same



Scheme 1 Chemical structures of complexes **1Ru-Ln** (Ln = Yb or Nd), **2Yb** and **3Ru**.



intense characteristic line shape of Yb(III) at 980 nm ($2F_{5/2} \rightarrow 2F_{7/2}$) was observed both in ECL and in PL, indicating the formation of the same excited state. Therefore, we can conclude that ECL probably proceeded through the sensitization mechanism from the Ru acetylide ligand to the Yb(III) ion with the help of an intramolecular energy transfer from the carbon-rich antenna to the metal ion (*vide infra*).

Then, we further investigated the effect of the imposed anodic potential on the ECL signal of the heterobimetallic **1Ru-Yb** complex in the presence of TPrA. ECL spectra were obtained using multistep chronoamperometric mode by applying progressively higher potential values (Fig. 2a). The ECL spectra with a sharp peak at 980 nm can be observed for potentials higher than 0.6 V. We calculated the global ECL signal by integrating the area under each ECL spectrum and plotted it as a function of the applied potential (Fig. 2b) for comparison with the current recorded during the voltammetric scan. The strength of the ECL signal was found to be correlated to the current with an onset potential of around 0.6 V and then an increase with a maximum at 1.6 V. One can see a clear correlation between the oxidation current and the ECL emission, which is self-consistent. The current intensity is mainly dominated by the oxidation of TPrA since, as classically performed in ECL studies, the coreactant concentration is largely in excess (*i.e.*, 100 mM) compared to the concentration of the dye (*i.e.*, 0.5 mM). Thus, above 0.6 V, both **1Ru-Yb** and TPrA are oxidized. This indicates that, as expected, the ECL emission of **1Ru-Yb** requires the oxidation of both TPrA and **1Ru-Yb**. However, oxidation of the Yb(III) moiety, which occurs at higher potential, is not necessary to generate the ECL emission of the complex. The maximum values of both the ECL signal and current occur at 1.6 V, after which they decrease rapidly when applying larger overpotentials. This decrease is correlated with the lower oxidation current of TPrA at potentials higher than 1.6 V. From this study, we can conclude that the oxidized carbon-rich ruthenium antenna reacts with the electrogenerated TPrA radicals directly to generate the excited state. This step is followed by intramolecular energy transfer occurring from the excited carbon-rich ruthenium antenna to

the Yb(III) ion. Interestingly, ECL can still be observed even at a high applied potential of 2 V (Fig. S4†), indicating that ECL emission of the Yb(III) complex may be generated in a wide potential range. In addition, ECL emission is visible even at potentials where the Yb(III) moiety is oxidized.

We performed a series of control experiments to confirm the ECL mechanism in action. Without TPrA, no ECL signal was observed (Fig. S5a,† orange line), showing that the ECL was generated effectively *via* the coreactant pathway between the heterobimetallic ruthenium carbon-rich Yb(III) complex and TPrA radicals. In addition, under the same experimental conditions, the ECL spectrum of **2Yb** (Fig. S5b,† green line) displayed a very weak peak in the NIR range, confirming the essential role of the antenna in efficiently sensitizing the Yb(III) luminescence. Similarly, there was no ECL signal in the NIR range when using solely the ruthenium center, **3Ru** (Fig. S5b,† blue line). In addition, both PL and ECL emissions of the Ru moiety at *ca.* 675 nm are quenched by the Ln ion in **1Ru-Ln**. This is self-consistent with previously reported PL results.⁵⁵ Importantly, we have to consider that in such a coordinating environment (TPrA), partial decooordination of the Yb(III) ion may occur since the bipyridine unit shows only moderate association constants with lanthanide ions. This possible decooordination has not been considered in previous studies on ECL with lanthanide complexes. In our case, we have carefully checked the amount of decoordinated species, whose absorption spectrum is reminiscent of that of **3Ru**, with a blue shifted MLCT transition located at $\lambda_{\text{max}} = 400$ nm in comparison with that of **1Ru-Yb** at $\lambda_{\text{max}} = 450$ nm (see Fig. S6 and the ESI for details†). We could conclude that a major proportion of **1Ru-Yb**, *ca.* 66%, still exists in the ECL medium. In addition, as no significant ECL emission was observed with **2Yb**, the ECL signal observed with **1Ru-Yb** can be unambiguously ascribed to the bimetallic complex.

To probe the potential extension of the reported approach to other lanthanides, the ECL spectrum of another heterobimetallic system (Scheme 1) with Nd³⁺ (**1Ru-Nd**) was also obtained under the same experimental conditions. Fig. 3 shows the comparison of the ECL spectrum (black line) with the photo-excited luminescence spectra at room temperature (red line) and at 77 K in a frozen organic glass (blue line) of **1Ru-Nd**. The latter shows, in particular, the characteristic line sharp emission bands of the Nd(III) ion at 875 nm, 886 nm, 893 nm and 910 nm to the straightforward sensitization mechanism from the Ru acetylide ligand ($\lambda_{\text{exc}} = 450$ nm). When applying an anodic potential of 1.9 V, a sharp NIR ECL emission band appeared at 875 nm ascribed to the line shaped $^4F_{3/2}$ excited state of Nd(III), with the other transitions at 1063 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$) and 1333 nm ($^4F_{3/2} \rightarrow ^4I_{13/2}$) being, respectively, partially (broad) or totally obliterated by the silicon photodetector (*vide supra*). As in the case of the **1Ru-Yb** complex, at low potentials, a weak ECL emission can be nearly seen, which then increases and reached a maximum at a potential of 1.9 V (Fig. S7a and b†). This demonstrates that the ECL emission from the Nd(III) luminescence can also be sensitized by the excited state of the carbon-rich ruthenium

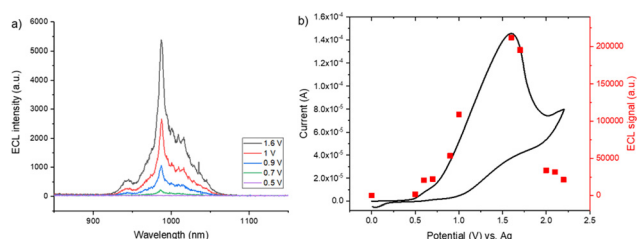


Fig. 2 (a) Evolution of the ECL spectra of **1Ru-Yb** as a function of the imposed potential. (b) Cyclic voltammogram (black line) and corresponding ECL signal (red squares) recorded in a CH_2Cl_2 solution containing 0.5 mM **1Ru-Yb**, 100 mM TPrA and 0.2 M TBAPF₆. Scan rate: 0.05 V s⁻¹. The ECL signals (red squares) have been calculated by recording the ECL spectra at different constant potentials and integrating the emission from 900 nm to 1100 nm.



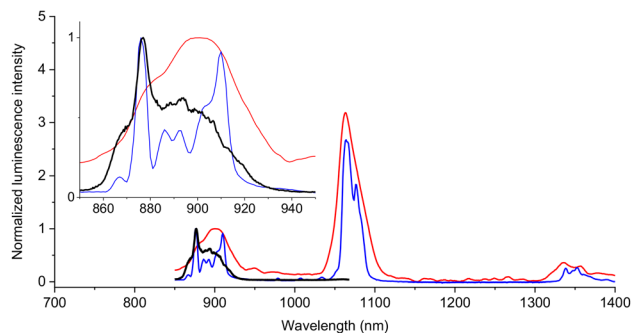
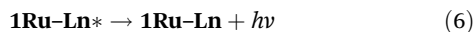
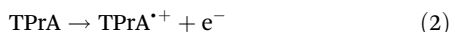
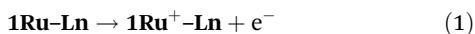


Fig. 3 Comparison of the normalized ECL (black line) and PL emission spectra of **1Ru-Nd** at room temperature (red line, $\lambda_{\text{exc}} = 450$ nm) and at 77 K in frozen organic glass (blue line) with the same experimental conditions as in Fig. 2. The ECL spectra of **1Ru-Nd** were recorded at an imposed potential of 1.9 V. The inset shows a zoomed-in view of the 850–950 nm area.

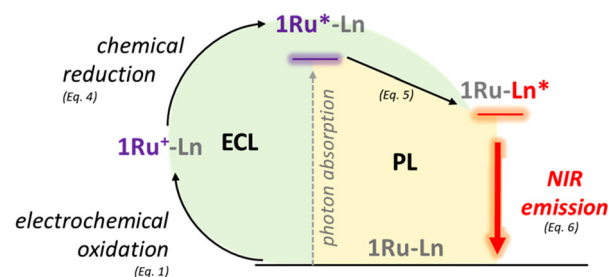
antenna generated through the electro-excited process in the presence of TPrA.

To summarize, we demonstrated that ECL emission is possible in the NIR range with Ln ions from this series of heterobimetallic **1Ru-Ln** complexes that can be generated efficiently in oxidation. The ECL mechanism of **1Ru-Ln** follows the “oxidative-reduction” pathway^{7,62} via the Ru antenna and can be described as follows:



with P being an iminium product.

Both the dye and coreactant are oxidized directly at the electrode surface (eqn (1) and (2)), which is not possible in the case of **2Yb**. After deprotonation (eqn (3)), the neutral TPrA radical reacts exergonically with the oxidized dye and forms the excited state of the ruthenium moiety (eqn (4)), which sensitizes the Nd(III) or the Yb(III) lanthanide centers (eqn (5)) via energy transfer, while an electron transfer process is also likely with the Yb(III) center (i.e. $\mathbf{1Ru^*-Yb^{III}} \rightarrow \mathbf{1Ru^+-Yb^{II}} \rightarrow \mathbf{1Ru-Yb^{III*}}$ for eqn (5)).^{63,64} Finally, from the lanthanide-centered excited state, the characteristic sharp luminescence in the NIR range is emitted (eqn (6)). Scheme 2 shows a qualitative energy diagram based on the excited state energy levels and ECL/PL processes.



Scheme 2 Energy diagram based on the excited state energy levels and the ECL and PL processes.

Conclusion

Our study demonstrated strong ECL signals originating from a series of heterobimetallic complexes comprising a ruthenium acetylide antenna conjugated to an NIR emissive lanthanide (Yb and Nd) unit via a bipyridyl ligand. The characteristic ECL emissions of the lanthanides in the NIR spectral range were achieved by populating first the excited state of the ruthenium acetylide moiety by the coreactant “oxidative-reduction” pathway, which transfers its energy to the lanthanide moiety. The electrochemical control of ECL emission using such chemically engineered heterobimetallic complexes can attract considerable interest for imaging or other analytical applications.

Data availability

The data supporting this article have been included as part of the ESI† and are available upon request to the authors.

Conflicts of interest

There are no conflicts to declare.

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