

Dual Light and Redox Control of NIR Luminescence with Complementary Photochromic and Organometallic Antennae

Hassan Al Sabea,[†] Lucie Norel,^{*,†} Olivier Galangau,[†] Hussein Hijazi,[†] Remi Métivier,[‡] Thierry Roisnel,[†] Olivier Maury,[§] Christophe Bucher,[§] François Riobé,[§] and Stéphane Rigaut^{*,†}

[†]Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France

[‡]UMR CNRS 8531-PPSM, ENS Paris-Saclay, Université Paris-Saclay, 94235 Cachan, France

[§]Univ Lyon, CNRS, Ecole Normale Supérieure de Lyon, Laboratoire de Chimie UMR 5182 46 allée d'Italie, F-69007 Lyon, France

Supporting Information

ABSTRACT: With the help of a judicious association between dithienylethene (DTE) units, an ytterbium ion, and a ruthenium carbon-rich complex, we describe (i) the efficient (on/off) switching of pure NIR luminescence with a photochromic unit absorbing in the UV range and (ii) the association of electrochemical and photochemical control of this NIR emission in a single system with nondestructive readout.

Molecule-based switching devices in which key physical properties can be modulated with an external stimulus are currently the focus of much attention, most notably to address the development of smart miniaturized devices.^{1–3}

In the particular domain of luminescence, conventional molecular switches use electric input signals to turn on and off emission activities via redox reactions centered either on the emitter or on a remote unit (electrofluorochromism).⁴ Such properties are useful for various applications in analytical chemistry, biological sensing, and the development of optical memories and displays. On the other hand, associating fluorescent dyes with photochromic units is an effective strategy to tune emission with spatially and temporally resolved light input.^{5–7} Among all photochromic molecules, dithienylethene derivatives (DTE) receive much attention due to their remarkable photoisomerization efficiency and deactivation schemes generally triggered by energy transfer from the excited state of the fluorophore (donor) to the photochromic unit (acceptor) in its conjugated state.^{5,6,8–10} Among all luminescence processes, the long-lived, narrow bandwidth NIR emission of lanthanide ions (Nd³⁺, Yb³⁺, or Er³⁺) is well suited to the development of highly sensitive signaling tools due to its noninvasive nature and fast response time.^{11–14} Achieving a reversible modulation of pure NIR emission of lanthanides stands as a major objective for both the academic and industrial sectors. Surprisingly, this has been scarcely explored, as most research efforts have been focused on systems displaying a larger emission band overlapping the visible range.^{15–17}

Concerning electromodulation, few groups have successfully modulated NIR emission of Yb³⁺ and/or Nd³⁺ sensitized with redox active species.^{18–21} Some of us used a series of ruthenium acetylide complexes displaying strong ligand-

mediated electronic effects²² that allowed the realization of several redox controlled optical switches or molecular devices.^{19,23–28} Regarding photomodulation, whereas europium luminescence has been modulated with several photochromic units,^{29–33} we recently report the first attempt to modulate Yb(III) ion emission in the NIR range thanks to a DTE functionalized ligand used as a sensitizer in its closed form. However, the resulting emission was very weak.³⁴

In this context, challenging goals remain to be reached to ensure the development of materials featuring controllable NIR properties. It includes (i) the achievement of efficient photocontrol of bright NIR luminescence and (ii) the combination of electro- and photomodulations in a single system to reach multifunctionality.³⁵ Herein, we describe both accomplishments with the dual electrochemical and photochemical control of ytterbium luminescence by taking advantage of (i) the redox switching of the carbon-rich ruthenium antenna linked to the Yb(III) ion and (ii) the photostimulation of three photochromic DTE units connected to the Yb(III) center with a β -diketonate moiety. This system stands also as a remarkable example enabling a nondestructive readout of photocontrollable luminescence.¹⁰

The DTE-modified precursor **1o** was obtained in two steps from the known hydrogen terminated analogue lacking the β -diketonate function (Supporting Information). Then, complexation of the Yb(III) ion with 3 equiv of **1o** afforded the bis-aqua complex [Yb(**1o**)₃(H₂O)₂] (**2000**; Scheme 1). Further displacement of the water molecules with the ruthenium-bipyridine ligand **3** led to complex **4000**, in good yield (85%). This new compound was fully characterized with ¹H NMR and IR spectroscopies and HR-MS. Good quality crystals suitable for X-ray structure determination were obtained from a CH₂Cl₂/*n*-pentane biphasic mixture. **4000** crystallizes in the *P* $\bar{1}$ space group (Figure 1). This complex is rather large, and some disorder on the DTE units leads to low quality refinement. However, the model is of sufficient quality to allow confirmation of the structure and bond lengths and angles are consistent with those measured on the analogue complex [Ln(**3**)(TTA)₃] (Ln = Eu, Nd), the Ln³⁺ ion being in a slightly distorted square antiprismatic coordination polyhedron (Supporting Information).¹⁹

Received: October 21, 2019

Published: December 10, 2019



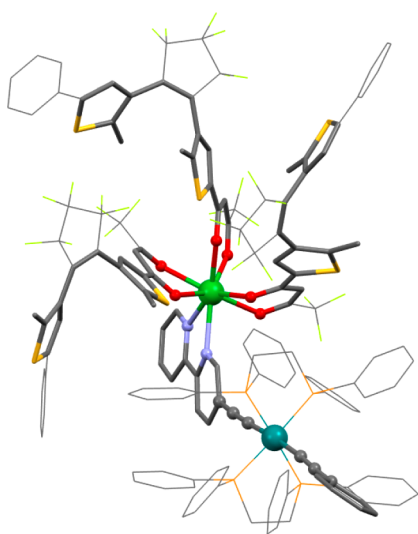
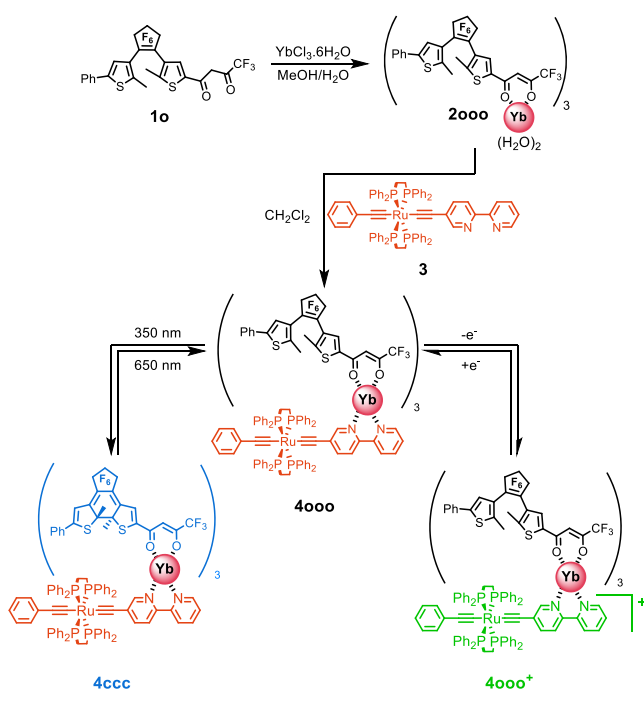
Scheme 1. Synthetic pathway to **4000** and redox/optical commutation to **4000⁺** and **4ccc**

Figure 1. Simplified view of the crystal structure of **4000** (H atoms have been omitted).

The absorption spectrum of **4000** is similar to that of $[\text{Yb}(\text{3})(\text{TTA})_3]^{18}$, with three main absorption bands observed at $\lambda_{\text{max}} = 272, 343, \text{ and } 460 \text{ nm}$ (Figure 2). The second transition is assigned to a DTE β -diketonate ligand-centered absorption overlapping with $\pi-\pi^*$ transitions centered on the bipyridyl unit. The lower energy transition at 460 nm is characteristic of the ruthenium acetylide moiety resulting from a Metal to Ligand Charge Transfer (MLCT)-type process from $\text{Ru}(d\pi)/\text{alkynyl}$ based orbitals to a π^* orbital associated with the bipyridine unit. Note that **4000** is found to be stable in solution, even in very diluted conditions (10^{-5} – $10^{-6} \text{ mol L}^{-1}$), as proven by the absence of a band centered at 400 nm for the ruthenium-based free ligand **3**. Upon irradiation of **4000** at $\lambda_{\text{irr}} = 350 \text{ nm}$, a broad absorption assigned to the formation of the

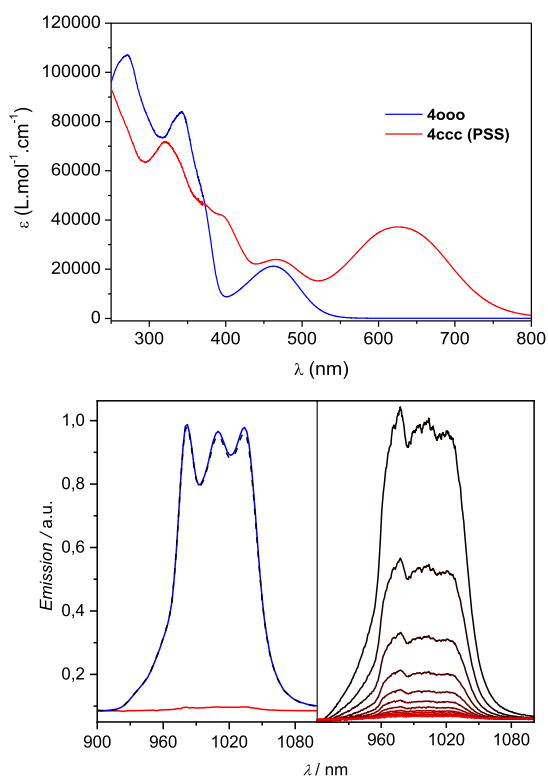


Figure 2. (Top) Evolution of the absorption spectrum of **4000** upon UV irradiation ($\lambda_{\text{irr}} = 350 \text{ nm}$) to PSS in CH_2Cl_2 . The initial spectrum was recovered after bleaching at $\lambda_{\text{irr}} = 650 \text{ nm}$. (Bottom left) Initial emission spectrum of **4000** in CH_2Cl_2 (blue), after UV irradiation ($\lambda_{\text{irr}} = 350 \text{ nm}$, red), and then bleaching ($\lambda_{\text{irr}} = 650 \text{ nm}$, dashed) with $\lambda_{\text{ex}} = 450 \text{ nm}$. (Bottom right) Emission decay upon UV irradiation. Each spectrum is recorded with a 1 s time lapse.

closed DTE ligand appears at $\lambda_{\text{max}} = 627 \text{ nm}$. The solution can be further bleached back to the pure open form under visible irradiation ($\lambda_{\text{irr}} = 650 \text{ nm}$), as attested by the quantitative recovery of the initial spectrum. Importantly, irradiation of **4000** at $\lambda = 450 \text{ nm}$ does not lead to any observable photochromic reaction. Further characterization of the photo-conversion process could not be achieved with ^1H NMR spectroscopy due to the paramagnetic nature of the complexes that requires high NMR concentration and extended irradiation time inducing degradation. In order to identify the composition of the photostationary state (PSS), the diamagnetic ytterbium analogue **6000** was synthesized from the aqua complex $[\text{Y}(\text{10})_3(\text{H}_2\text{O})_2]$ (**5000**). A similar synthesis was implemented from the PSS state (92% conversion) of ligand **1c**, the closed isomer of **10**, to achieve **6ccc** through to the aqua complex $[\text{Y}(\text{1c})_3(\text{H}_2\text{O})_2]$ (**5ccc**) (Supporting Information). A careful integration of bipyridine-based ^1H NMR signals of **6ccc** revealed in fact the presence of the **60cc** and **6ccc** forms in 27% and 73%, respectively (Figure S13), which is consistent with an initial composition of 92% in **1c**. We also found that (i) the UV-vis spectra obtained after UV irradiation of **4000** and **6000** to their respective PSS states match exactly (Figure S14) and (ii) they are identical to that recorded for **6ccc** prepared chemically from **1c**. These findings are thus consistent with the assumption that PSS after irradiation of **4000** is composed of 27% of **40cc** and 73% of **4ccc**.

Further photokinetic experiments were performed with irradiation of **4000** at 365 nm . The absorption-time profile

was analyzed numerically, based on the classical photochromic differential equations, to decipher the photochromic quantum yields (Supporting Information).³⁶ When identical ring-closure quantum yields are considered for the three successive closing reactions, calculated photokinetic curves cannot simulate the experimental profile (Figure 3a, black dashed line with $\Phi_{o \rightarrow c} =$

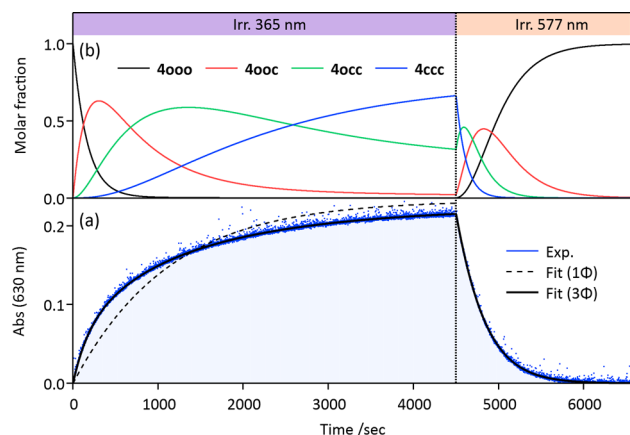


Figure 3. (a) Absorption–time profile recorded at 630 nm (blue dots) of a sample of **4000** in CH_2Cl_2 under successive irradiation at 365 nm ($380 \mu\text{W}$) and 577 nm (8.8 mW), and fitting curves involving a simple model (black dashed line: single $\Phi_{o \rightarrow c}$) and a complete model (black solid line: see text). (b) Molar fractions of the different species as a function of irradiation time (complete model).

0.065). A model involving three different quantum yields of the sequential ring closures ($4000 \rightarrow 400c \rightarrow 40cc \rightarrow 4ccc$) is necessary to fit appropriately the experimental data, with $\Phi_{000 \rightarrow 00c} = 0.16 \pm 0.01$, $\Phi_{00c \rightarrow 0cc} = 0.06 \pm 0.01$, $\Phi_{0cc \rightarrow 0ccc} = 0.03 \pm 0.01$ (Figure 3a, black solid line). The lower values of the second and third quantum yields highlight the specific behavior of this multi-DTE system:³⁷ the electrocyclization reaction efficiency is decreased by a factor 2–3 when one or two DTE units are converted to the closed form. The calculated molar fractions of all species (Figure 3b) are compatible with the NMR experiments, with 75% of **4ccc** calculated at the PSS. The ring-opening reaction was analyzed by the same method with $\lambda_{\text{irr}} = 577 \text{ nm}$, and a satisfying fit was obtained with identical values of quantum yields for all photocycloreversion reactions ($\Phi_{c \rightarrow o} = 0.006 \pm 0.002$).

The photophysical properties of **4000** were further studied (Figure 2 and Supporting Information). Upon excitation in the aforementioned MLCT transition ($\lambda_{\text{ex}} = 450 \text{ nm}$), a stable line shape emission, characteristic of the ytterbium ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition, is observed in the NIR spectral range at $\lambda_{\text{max}} = 980 \text{ nm}$ evidencing the antenna character of the ruthenium moiety. Then, emission photoswitching experiments were carried out using absorption and emission spectroscopies as monitoring techniques. These experiments revealed (i) the vanishing (to 1.4% of initial maximum intensity) of the emission signal upon UV irradiation ($\lambda_{\text{irr}} = 350 \text{ nm}$) leading to the PSS and (ii) a total recovery of the emission up to its initial intensity after visible irradiation ($\lambda_{\text{irr}} = 650 \text{ nm}$). To the best of our knowledge, this is the first example where “pure” NIR emission can be reversibly switch on and off upon stimulation of a photochromic system. We also demonstrate that excitation in the MLCT band at 450 nm provides an efficient non-destructive read out of the system state. Our design not only avoids deleterious energy transfers⁵ but also stresses the

relevance of organometallic complexes as photosensitizers, as they allow separation of MLCT excitation, photoisomerization, and emission wavelengths. The photoswitching process has also been investigated under a dynamic regime: when excitation is performed at the photocyclization wavelength ($\lambda_{\text{irr}} = 350 \text{ nm}$), using the DTE β -diketonate ligands or the bipyridine unit as sensitizers, a fast decrease of the NIR signal is observed (Figure 2 and Supporting Information). At this stage, the quenching mechanism remains speculative. However, a possible hypothesis is that the closed DTE excited triplet state lies at lower energy than that of the ${}^2\text{F}_{5/2}$ excited state of the Yb(III) ion ($10\,200 \text{ cm}^{-1}$).⁵

The switching properties of **4000** have been further investigated using electrochemical methods coupled to either absorption or fluorescence spectroscopies. Initial cyclic voltammetry curves (CH_2Cl_2 , 0.2 M Bu_4NPF_6) revealed the existence of a single reversible wave at $E_1^\circ = 0.049 \text{ V}$ vs $\text{FcP}_2/\text{FcP}_2^+$ ($\Delta E_p = 83 \text{ mV}$) ascribed to the one-electron oxidation of the ruthenium acetylide subunit. Spectroelectrochemistry (SEC) measurements carried out in the UV/vis/NIR range then showed that the one-electron oxidation of **4000** leads to a gradual disappearance of the band centered at $\lambda_{\text{max}} = 460 \text{ nm}$ at the expense of a new broad absorption band at $\lambda_{\text{max}} = 1060 \text{ nm}$ ($\epsilon = 9500 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) (Figure S19).

In order to modulate the emission of **4000** with an electric stimulation, our investigations were carried out in a homemade SEC quartz cell mounted in a fluorimeter, with the emission recorded at $\lambda = 1025 \text{ nm}$ ($\lambda_{\text{ex}} = 450 \text{ nm}$) when scanning the electrode potential (20 mV/s) of the platinum grid between -0.1 V and 1 V . The main findings are captured in Figure 4A

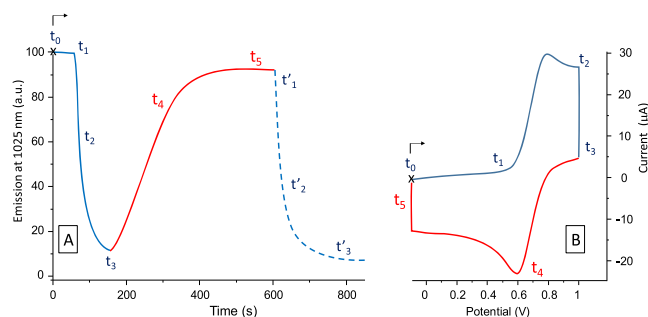


Figure 4. Emission monitoring at $\lambda = 1025 \text{ nm}$ ($\lambda_{\text{ex}} = 450 \text{ nm}$) upon oxidation (blue lines) and reduction (red lines) of **4000** in the electrochemical cell, and simultaneously measured current–potential curve showing oxidation and reduction of **4000** ($E^\circ = 0.69 \text{ V}$ vs Ag wire pseudo reference).

and B, showing the changes in the emission intensity together with the cyclic voltammetry experiment implemented at the electrode. It results that the one electron oxidation of **4000** is associated with a drastic drop in the emission intensity down to 12% of its original value ($t_1 \rightarrow t_3$ in Figure 4A and 4B). Most importantly, we found that the initial emission intensity can be almost fully recovered (93%) upon scanning the electrode potential back to the starting open circuit potential $E = -0.1 \text{ V}$ ($t_3 \rightarrow t_5$ in Figure 4A and 4B). The second oxidation cycle, shown as a dashed curve in Figure 4, led to a similar quenching down to 7% of the emission intensity. It should be mentioned that this quenching ratio stands among the very best reported to date for strategies involving electrochemical quenching of lanthanide emission.^{20,21,38–40} The simultaneous recording of the current–potential and emission responses

clearly demonstrate that the changes in emission are triggered by the reversible transformation of 4000 into 4000^+ . As previously discussed,¹⁹ extinction of NIR emission with 4000^+ can be rationalized either by the oxidation of the ruthenium acetylide moieties preventing any sensitization through an electron transfer mechanism or by the new transition at ca. 1060 nm that can afford a preferential nonradiative back-energy transfer pathway from the $^2F_{5/2}$ ytterbium excited state.

In conclusion, these results establish (i) the possibility to switch pure NIR luminescence with a photochromic unit absorbing in the UV range and (ii) that both electrochemical and photochemical control of luminescence can be efficiently achieved in a single system with nondestructive readout. Further studies, using spectroscopic and theoretical tools, will provide better insights in the understanding of this system as well as its extension to other lanthanide ions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.9b11318>.

Synthetic procedures and spectroscopic data. (PDF)

Crystallographic data for 4000 (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*Lucie.norel@univ-rennes1.fr

*stephane.rigaut@univ-rennes1.fr

ORCID

Lucie Norel: 0000-0001-6654-1211

Remi Métivier: 0000-0001-5612-8327

Olivier Maury: 0000-0002-4639-643X

François Riobé: 0000-0001-6746-8132

Stéphane Rigaut: 0000-0001-7001-9039

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Université de Rennes 1, the CNRS, the GDR MCM2, and the Agence Nationale de la Recherche (RuOxLux - ANR-12-BS07-0010-01) for support.

■ REFERENCES

- (1) Feringa, B. L., Ed. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001.
- (2) Erbas-Cakmak, S.; Leigh, D. A.; McTernan, C. T.; Nussbaumer, A. L. Artificial Molecular Machines. *Chem. Rev.* **2015**, *115*, 10081–10206.
- (3) Kathan, M.; Hecht, S. Photoswitchable molecules as key ingredients to drive systems away from the global thermodynamic minimum. *Chem. Soc. Rev.* **2017**, *46*, 5536–5550.
- (4) Audebert, P.; Miomandre, F. Electrofluorochromism: from molecular systems to set-up and display. *Chem. Sci.* **2013**, *4*, 575–584.
- (5) Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chem. Rev.* **2014**, *114*, 12174–12277.
- (6) Zhang, J.; Tian, H. The Endeavor of Diarylethenes: New Structures, High Performance, and Bright Future. *Adv. Opt. Mater.* **2018**, *6*, 1701278.
- (7) Klaue, K.; Garmshausen, Y.; Hecht, S. Taking Photochromism beyond Visible: Direct One-Photon NIR Photoswitches Operating in the Biological Window. *Angew. Chem., Int. Ed.* **2018**, *57*, 1414–1417.

- (8) Su, J.; Fukaminato, T.; Placial, J.-P.; Onodera, T.; Suzuki, R.; Oikawa, H.; Brosseau, A.; Brisset, F.; Pansu, R.; Nakatani, K.; Métivier, R. Giant Amplification of Photoswitching by a Few Photons in Fluorescent Photochromic Organic Nanoparticles. *Angew. Chem., Int. Ed.* **2016**, *55*, 3662–3666.

- (9) Fernández-Acebes, A.; Lehn, J.-M. Optical Switching and Fluorescence Modulation in Photochromic Metal Complexes. *Adv. Mater.* **1998**, *10*, 1519–1522.

- (10) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. A digital fluorescent molecular photoswitch. *Nature* **2002**, *420*, 759–760.

- (11) Bünzli, J.-C. G. Lanthanide Luminescence for Biomedical Analyses and Imaging. *Chem. Rev.* **2010**, *110*, 2729–2755.

- (12) dos Santos, C. M. G.; Harte, A. J.; Quinn, S. J.; Gunnlaugsson, T. Recent developments in the field of supramolecular lanthanide luminescent sensors and self-assemblies. *Coord. Chem. Rev.* **2008**, *252*, 2512–2527.

- (13) Moore, E. G.; Samuel, A. P. S.; Raymond, K. N. From Antenna to Assay: Lessons Learned in Lanthanide Luminescence. *Acc. Chem. Res.* **2009**, *42*, 542–552.

- (14) Pointillart, F.; Bourdolle, A.; Cauchy, T.; Maury, O.; Le Gal, Y.; Golhen, S.; Cador, O.; Ouahab, L. In Solution Sensitization of Er(III) Luminescence by the 4-Tetrathiafulvalene-2,6-pyridinedicarboxylic Acid Dimethyl Antenna Ligand. *Inorg. Chem.* **2012**, *51*, 978–984.

- (15) Bonacchi, S.; Cantelli, A.; Battistelli, G.; Guidetti, G.; Calvaresi, M.; Manzi, J.; Gabrielli, L.; Ramadori, F.; Gambarin, A.; Mancin, F.; Montalti, M. Photoswitchable NIR-Emitting Gold Nanoparticles. *Angew. Chem., Int. Ed.* **2016**, *55*, 11064–11068.

- (16) Jeong, K.; Park, S.; Lee, Y. D.; Lim, C. K.; Kim, J.; Chung, B. H.; Kwon, I. C.; Park, C. R.; Kim, S. Conjugated polymer/ photochromophore binary nanococktails: bistable photoswitching of near-infrared fluorescence for in vivo imaging. *Adv. Mater.* **2013**, *25*, 5574–5600.

- (17) Lim, H.; Seo, S.; Pascal, S.; Bellier, Q.; Rigaut, S.; Park, C.; Shin, H.; Maury, O.; Andraud, C.; Kim, E. NIR Electrofluorochromic Properties of Aza-Boron-dipyrromethene Dyes. *Sci. Rep.* **2016**, *6*, 18867–18867.

- (18) Di Piazza, E.; Norel, L.; Costuas, K.; Bourdolle, A.; Maury, O.; Rigaut, S. d-f Heterobimetallic Association between Ytterbium and Ruthenium Carbon-Rich Complexes: Redox Commutation of Near-IR Luminescence. *J. Am. Chem. Soc.* **2011**, *133*, 6174–6176.

- (19) Norel, L.; Di Piazza, E.; Feng, M.; Vacher, A.; He, X. Y.; Roisnel, T.; Maury, O.; Rigaut, S. Lanthanide Sensitization with Ruthenium Carbon-Rich Complexes and Redox Commutation of Near-IR Luminescence. *Organometallics* **2014**, *33*, 4824–4835.

- (20) Tropiano, M.; Kilah, N. L.; Morten, M.; Rahman, H.; Davis, J. J.; Beer, P. D.; Faulkner, S. Reversible Luminescence Switching of a Redox-Active Ferrocene-Europium Dyad. *J. Am. Chem. Soc.* **2011**, *133*, 11847–11849.

- (21) Molloy, J. K.; Jarjays, O.; Philouze, C.; Fedele, L.; Imbert, D.; Thomas, F. A redox active switch for lanthanide luminescence in phenolate complexes. *Chem. Commun.* **2017**, *53*, 605–608.

- (22) Costuas, K.; Rigaut, S. Polynuclear carbon-rich organometallic complexes: clarification of the role of the bridging ligand in the redox properties. *Dalton Trans* **2011**, *40*, 5643–5658.

- (23) Samoc, M.; Gauthier, N.; Cifuentes, M. P.; Paul, F.; Lapinte, C.; Humphrey, M. G. Electrochemical switching of the cubic nonlinear optical properties of an aryldiethynyl-linked heterobimetallic complex between three distinct states. *Angew. Chem., Int. Ed.* **2006**, *45*, 7376–7379.

- (24) Liu, Y. F.; Lagrost, C.; Costuas, K.; Tchouar, N.; Le Bozec, H.; Rigaut, S. A multifunctional organometallic switch with carbon-rich ruthenium and diarylethene units. *Chem. Commun.* **2008**, 6117–6119.

- (25) Tanaka, Y.; Ishisaka, T.; Inagaki, A.; Koike, T.; Lapinte, C.; Akita, M. Photochromic Organometallics with a Dithienylethene (DTE) Bridge, [Y-C≡C-DTE-C≡C-Y] (Y = {MCp*(dppe)}): Photoswitchable Molecular Wire (M = Fe) versus Dual Photo- and Electrochromism (M = Ru). *Chem. - Eur. J.* **2010**, *16*, 4762–4776.

(26) Meng, F. B.; Hervault, Y. M.; Shao, Q.; Hu, B. H.; Norel, L.; Rigaut, S.; Chen, X. D. Orthogonally modulated molecular transport junctions for resettable electronic logic gates. *Nat. Commun.* **2014**, *5*, 9.

(27) Mulas, A.; He, X.; Hervault, Y.-M.; Norel, L.; Rigaut, S.; Lagrost, C. Dual-Responsive Molecular Switches Based on Dithienylethene–RuII Organometallics in Self-Assembled Monolayers Operating at Low Voltage. *Chem. - Eur. J.* **2017**, *23*, 10205–10214.

(28) Qi, H.; Gupta, A.; Noll, B. C.; Snider, G. L.; Lu, Y.; Lent, C.; Fehlner, T. P. Dependence of Field Switched Ordered Arrays of Dinuclear Mixed-Valence Complexes on the Distance between the Redox Centers and the Size of the Counterions. *J. Am. Chem. Soc.* **2005**, *127*, 15218–15227.

(29) Mei, J. F.; Lv, Z. P.; Lai, J. C.; Jia, X. Y.; Li, C. H.; Zuo, J. L.; You, X. Z. A novel photo-responsive europium(III) complex for advanced anti-counterfeiting and encryption. *Dalton Trans* **2016**, *45*, 5451–5454.

(30) Cheng, H.-B.; Zhang, H.-Y.; Liu, Y. Dual-Stimulus Luminescent Lanthanide Molecular Switch Based on an Unsymmetrical Diarylperfluorocyclopentene. *J. Am. Chem. Soc.* **2013**, *135*, 10190–10193.

(31) Hasegawa, Y.; Nakagawa, T.; Kawai, T. Recent progress of luminescent metal complexes with photochromic units. *Coord. Chem. Rev.* **2010**, *254*, 2643–2651.

(32) Cheng, H.-B.; Hu, G.-F.; Zhang, Z.-H.; Gao, L.; Gao, X.; Wu, H.-C. Photocontrolled Reversible Luminescent Lanthanide Molecular Switch Based on a Diarylethene–Europium Dyad. *Inorg. Chem.* **2016**, *55* (16), 7962–7968.

(33) Sun, J.-K.; Cai, L.-X.; Chen, Y.-J.; Li, Z.-H.; Zhang, J. Reversible luminescence switch in a photochromic metal–organic framework. *Chem. Commun.* **2011**, *47*, 6870–6872.

(34) He, X.; Norel, L.; Hervault, Y.-M.; Métivier, R.; D'Aléo, A.; Maury, O.; Rigaut, S. Modulation of Eu(III) and Yb(III) Luminescence Using a DTE Photochromic Ligand. *Inorg. Chem.* **2016**, *55*, 12635–12643.

(35) Zhu, W.; Song, L.; Yang, Y.; Tian, H. Novel Bisthienylethene Containing Ferrocenyl-Substituted Naphthalimide: A Photo- and Redox Multi-Addressable Molecular Switch. *Chem. - Eur. J.* **2012**, *18*, 13388–13394.

(36) Nakatani, K.; Piard, J.; Yu, P.; Métivier, R. In *Photochromic materials: preparation, properties and applications*, 1st ed.; Tian, H., Zhang, J., Eds.; Wiley-VCH: 2016; pp 1–45.

(37) Fihey, A.; Perrier, A.; Browne, W. R.; Jacquemin, D. Multiphotochromic molecular systems. *Chem. Soc. Rev.* **2015**, *44*, 3719–3759.

(38) Yano, M.; Matsuhira, K.; Tatsumi, M.; Kashiwagi, Y.; Nakamoto, M.; Oyama, M.; Ohkubo, K.; Fukuzumi, S.; Misaki, H.; Tsukube, H. ON-OFF switching of europium complex luminescence coupled with a ligand redox process. *Chem. Commun.* **2012**, *48*, 4082–4084.

(39) Sato, T.; Higuchi, M. An alternately introduced heterometallo-supramolecular polymer: synthesis and solid-state emission switching by electrochemical redox. *Chem. Commun.* **2013**, *49*, 5256–5258.

(40) Kanazawa, K.; Nakamura, K.; Kobayashi, N. Electrochemical luminescence modulation in a Eu(III) complex-modified TiO₂ electrode. *J. Mater. Chem. C* **2015**, *3*, 7135–7142.