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Modulation of Eu(III) and Yb(III) luminescence using a DTE photochromic ligand

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Abstract.

In this work, we show that a dithienylethene (DTE) modified dipicolinic amide ligand can be a versatile tool to modulate Eu(III) and Yb(III) luminescence using light as an external stimulus. The nature of the modulation depends on the lanthanide emitter: with the europium ion, the DTE ligand quench the red luminescence upon ring closure, whereas with the ytterbium ion, ring closure can be used to turn on the luminescence in the NIR range.

Keywords: Photochromism, ytterbium, europium, dithienylethene, luminescence, molecular switche

Introduction

Molecular-based switching devices in which key physical properties can be modulated with external stimuli are focusing much attention.¹⁻⁹ Among the chemical and physical properties that a molecule can switch, luminescence is particularly attractive to achieve smart materials as well as cell imaging.^{6, 10, 11} A typical example of such molecules is a dyad composed of photochromic and fluorescent dyes units in which the fluorescence emission is modulated by the photochromic reaction.⁴ Such a modulation has been extensively studied, and two types of quenching mechanism are possible involving intramolecular energy transfer or electron transfer.^{12, 13} However, most systems involve a photochromic unit linked to an organic or a metal-organic fluorophore which luminescence is regulated by intramolecular energy transfer. This non-radiative process occurs from the excited state of the fluorophore (donor) to the photochromic unit (acceptor), generally in its conjugated state, and requires that the acceptor characteristic absorption band overlaps the emission of the donor (FRET, Förster Resonance Energy Transfer, or Dexter energy transfer).

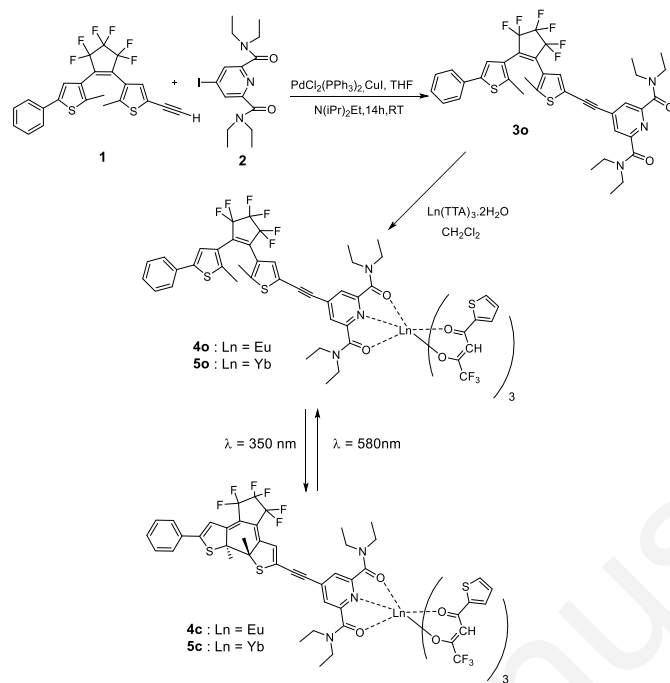
Dithienylethene (DTE) is one of the most promising photochromic systems due to its high fatigue resistance.⁶ It can be efficiently switched from a non-conjugated form to a conjugated form upon UV irradiation, and switched-back using visible light. Therefore, this unit has been used for the photoregulation of various properties including sensing,^{2, 14} NLO,¹⁵ magnetism,¹⁶ molecular conductance,¹⁷⁻²⁰ redox behavior,²¹⁻²³ NIR absorption,²⁴ optical rotation,²⁵ super resolution imaging,^{4, 26} triplet-triplet annihilation,²⁷ catalysis,²⁸ and so on. Although DTE can be a fluorescent switch itself,^{29, 30} it serves as a non-fluorescent switch to modulate the fluorescence of a neighboring fluorophore through FRET as mentioned above, including in combinations of DTE and metal centers that have opened up new perspectives for the design of metal based photoswitchable fluorescent materials.³¹⁻⁴³

Among all fluorophores, lanthanide occupy a very particular place due to their unique photophysical properties.^{44, 45, 46} Indeed, since the emission origins from the Laporte forbidden $f-f$ transitions, lanthanide complexes display long lived excited state and narrow bandwidth emission band ranging from the visible to the near infra-red spectral range (NIR), with high emission efficiency and a large (pseudo)-Stokes shift that attracts considerable interests for molecular materials and imaging applications.^{45, 47-53} Therefore, reversible modulation of this luminescence is an attractive target. Such modulation can be achieved chemically, *i.e.* with external stimulus like pH, ion or molecules,⁵⁴⁻⁵⁶ or electrochemically.⁵⁷⁻⁶³ In contrast, the modulation of europium luminescence triggered by light irradiation itself is quite rare. One can mention the elegant 30% modulation of europium luminescence promoted by the ligand field change due to a significant variation of the coordination sphere induced by photochromic ligands.⁶⁴⁻⁶⁶ In addition, few examples of intramolecular FRET were reported, also with europium complexes, containing an inorganic⁶⁷ or organic⁶⁸ photochromic unit, or embedded in a pseudorotaxane supramolecular assembly controlled by a DTE unit.⁶⁹ To the best of our knowledge, no example of modulation of the luminescence of other lanthanide emitters have been reported, especially those displaying emission in the NIR spectral range.

Herein, we describe the synthesis and the luminescence modulation of lanthanide complexes (Ln = Eu and Yb) by taking advantage of a DTE unit incorporated in a dipicolinic amide ligand. We demonstrate that depending on the lanthanide ion used, the DTE unit can be used in different ways to modulate the lanthanide luminescence intensity upon ring closure/opening reactions, including the unprecedented Yb(III) luminescence turn on.

Results and Discussion

Complex synthesis. Synthesis of the new complexes **4o** and **5o** were achieved in CH₂Cl₂ with coordination of [Ln(TTA)₃.2H₂O] (**4o**: Ln = Eu, **5o**:Ln = Yb, TTA = 2-thenoyltrifluoroacetate) to the ligand **3o** in equimolar quantities.⁷⁰⁻⁷² The latter was readily achieved from precursor **1**⁷³ and **2**⁷⁴ *via* Sonogashira cross-coupling reaction in classical conditions (Scheme 1). These new compounds were fully characterized by NMR and IR spectroscopies, elemental analysis, and HR-MS. For the two lanthanide complexes **4o** and **5o**, paramagnetic shifts are observed due to the through space interactions between the observed nuclei and the 4f unpaired electrons (pseudo-contact shifts) which depend on the magnetic anisotropy of the lanthanide ion (Figures 1 and 2).⁷⁵⁻⁷⁸ We observed for **4o** that the pyridine ring and the N-ethyl protons are deshielded compared to **3o**, whereas the DTE protons (thiophene rings and methyl groups) are shielded. Coordination to the more anisotropic Yb(III) ion in **5o** leads to similar changes but with a greater amplitude: the protons of the DTE unit are shielded to 6.33 and 4.62 ppm (thiophene rings) and 0.58 and 0.28 ppm (methyl groups), whereas the protons of the dipicolinic amide ligand appear as very broad peaks in the range 6-20 ppm.



Scheme 1. Synthetic pathways yielding complexes **4o** and **5o** and isomerization process.

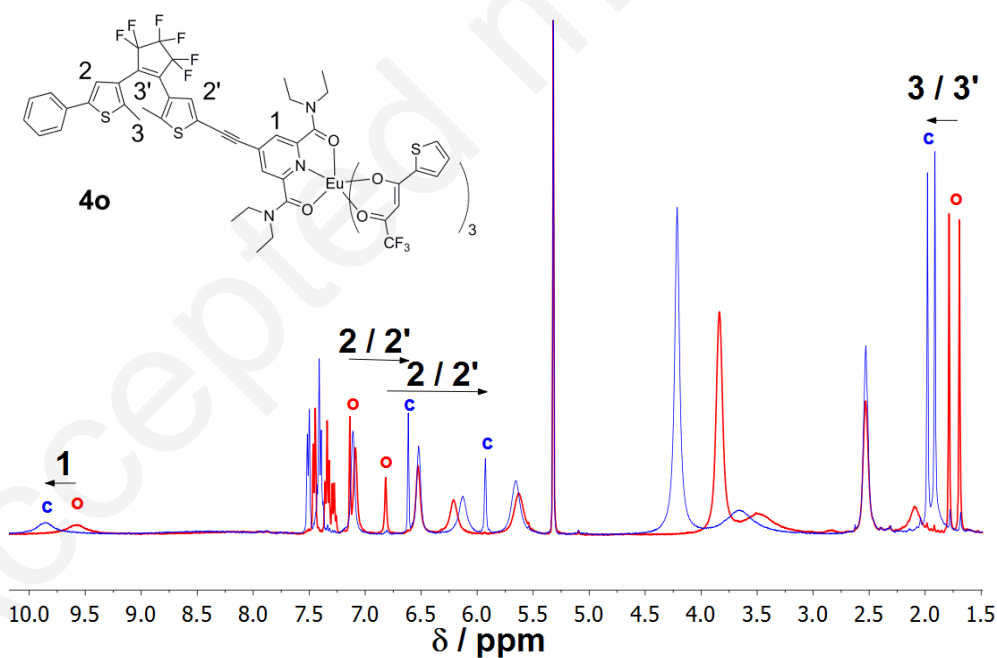


Figure 1. ^1H NMR spectrum of **4o** (red line) and of PSS (97% of **4c**, blue line) obtained from irradiation of **4o** in CD_2Cl_2 ($\lambda = 350 \text{ nm}$, 45 h, $[\text{c}] \approx 1 \times 10^{-3} \text{ mol.L}^{-1}$).

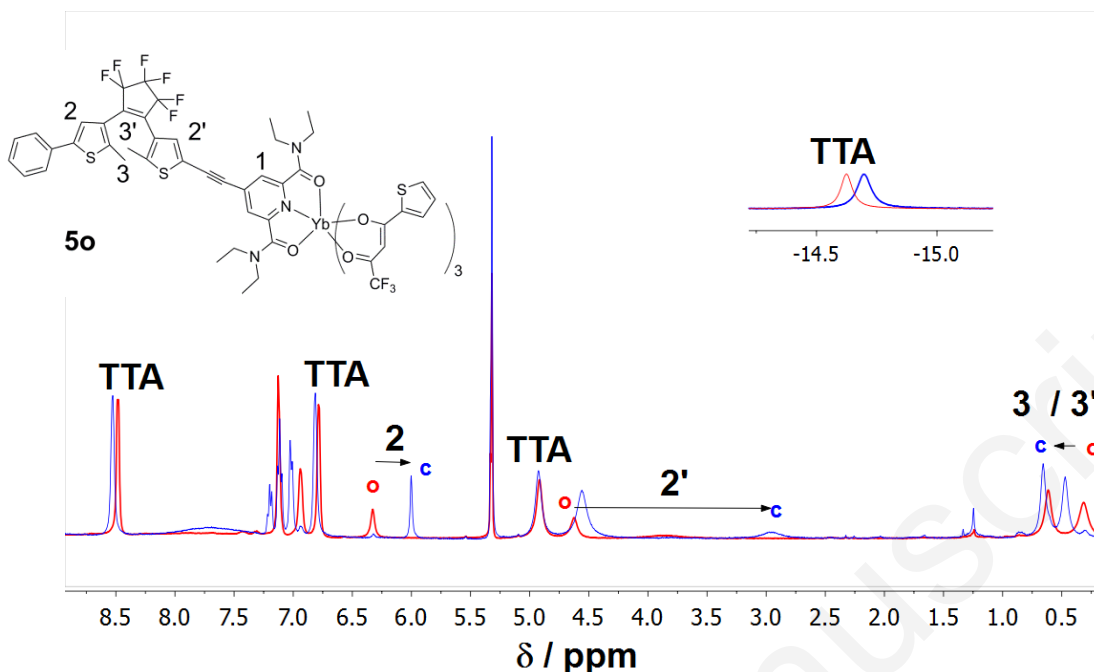


Figure 2. ^1H NMR spectrum of **5o** (red line) and of PSS (93 % of **5c**, blue line) obtained from irradiation of **5o** in CD_2Cl_2 ($\lambda = 350$ nm, 71h, $[\text{c}] \approx 1 \times 10^{-3}$ mol.L $^{-1}$).

Absorption spectra and photochromism of 3o, 4o and 5o. The absorption spectrum of **3o** shows several intense transitions in the UV range. Upon irradiation at 350 nm, a decrease of absorption is observed at 272 nm while two new bands appear at 383 and 610 nm (Figure 3). This is consistent with the assignment of the 272 nm transition to an open-DTE centered process in **3o** and with the usual photochromic behavior of DTE units upon UV irradiation, *i.e.* ring-closure, giving rise to the lower energy band (610 nm) ascribed to an intra-ligand (IL) transition centered on the closed DTE moiety in **3c**.⁶ The isomerization was also studied by ^1H NMR that proved that a high photoisomerisation conversion (to 93% of **3c**) can be reached in the photo-stationary state (PSS) (Figure S5).

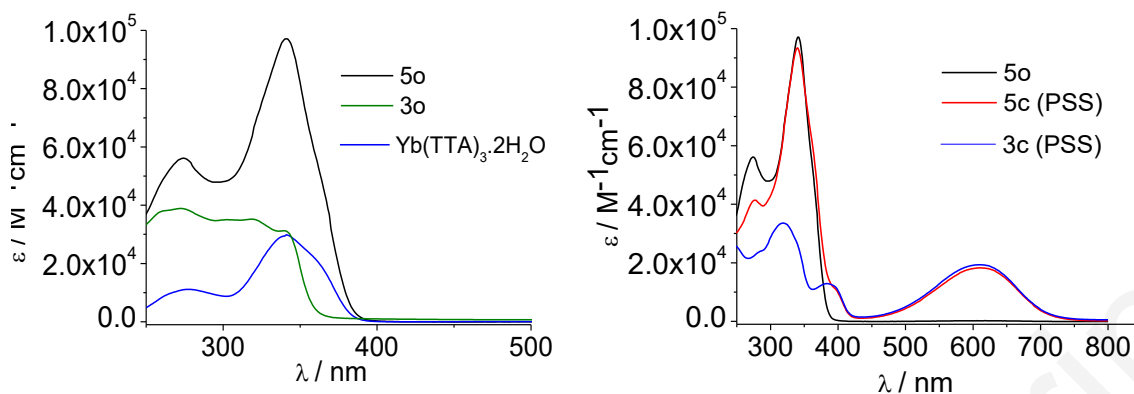


Figure 3. Absorption spectra of **3o**, **5o** and the $[\text{Yb}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}]$ precursor in CH_2Cl_2 solutions (left). Absorption spectrum of **5c**, obtained upon UV light irradiation to PSS ($\lambda = 350$ nm) of **5o** and its comparison with **3c** obtained under similar conditions (right). The Europium complex **4o** show identical behavior (Figure S6). The initial spectra were recovered after bleaching at 580 nm.

The absorption spectra of the two complexes **4o** and **5o** are identical and can be well reproduced qualitatively by the addition of the contributions from the $[\text{Ln}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}]$ ($\text{Ln} = \text{Eu}, \text{Yb}$) precursor and from **3o** (Figure 3). Therefore, the strong absorption bands at $\lambda_{\text{max}} = 342$ nm is assigned to the TTA ligand absorption overlapping with $\pi-\pi^*$ transitions of the DTE ligand. Upon irradiation of **4o** and **5o** solutions at $\lambda = 350$ nm, a broad absorption assigned to the deep blue closed isomers **4c** and **5c** appears at $\lambda_{\text{max}} = 614$ and 611 nm, respectively, as well as a shoulder at *ca.* 380 nm. These solutions can be further bleached back to the pure open forms under visible light irradiation ($\lambda = 580$ nm) as attested by the quantitative recovering of the initial spectra. It is worth noting that the absorption studies were achieved at concentrations ranking from 3.3×10^{-4} M to 2.0×10^{-5} mol.L⁻¹ with no detectable change in the spectra of both the open and closed forms of the complexes, indicating that the integrity of each complex is retained in this concentration range. Further ¹H NMR monitoring of the processes in CD_2Cl_2 ($[\text{c}] \approx 2 \times 10^{-3}$ mol.L⁻¹) with integration of the CH_3 and CH proton signals of the DTE unit unambiguously shows that the photochromic events upon UV irradiation are almost complete with the reaching of a photostationary state composed of

ca. 95 % of closed isomers, consistent with a value of 93% for **3** (Figure 1 and 2). For **4o**, the largest changes in chemical shifts upon ring closure are observed for the thiophene protons H₂ and H_{2'}, while the pyridine and ethyl protons of the amide experience a deshielding of about 0.3 ppm (Figure 1). A similar trend is observed for **5o** with a shielding of the thiophene protons down to 2.9 ppm upon ring closure due to the combination of the paramagnetic effect of Yb(III) and the increased conjugation in the closed form. In both the open and closed state, (i) the NMR signals from uncoordinated **3o** or **3c** are not detected and, (ii) well resolved signal are observed. Therefore, this is also an indication of the stability of **4o**, **4c**, **5o** and **5c** against decooordination or light-induced decooordination in this concentration range. The fact that the position of the visible absorptions is weakly influenced by the coordination of the lanthanide ion shows that there is little participation of the dipicolinic amide moiety in the DTE centred transitions as observed in related complexes.⁷³

Finally, we performed a full cycle of photoisomerization under continuous 334 and 575 nm illumination, by means of a home-made UV-visible optical set-up. The absorption spectra were recorded in real time (1.4 Hz), and the absorption time-evolution profiles were extracted at 610 nm (see Figure 4 and S7). The absorption increase as a function of time under UV light and the absorption decrease under visible light were fitted by a numerical procedure based on the photokinetic differential equations for ring-closure and ring-opening photochromic reactions (see experimental part). The quantum yields related to the photocyclization ($\phi_{\text{OF} \rightarrow \text{CF}}$) and the photocycloreversion ($\phi_{\text{CF} \rightarrow \text{OF}}$) were determined from fitting curves. Those for the cyclization of **3o** ($\phi_{\text{OF} \rightarrow \text{CF}} = 0.320$), **4o** ($\phi_{\text{OF} \rightarrow \text{CF}} = 0.177$) and **5o** ($\phi_{\text{OF} \rightarrow \text{CF}} = 0.142$) are much higher than those for cycloreversions (**3c**: $\phi_{\text{CF} \rightarrow \text{OF}} = 0.008$, **4c**: $\phi_{\text{CF} \rightarrow \text{OF}} = 0.008$ and **5c**: $\phi_{\text{CF} \rightarrow \text{OF}} = 0.007$) and consistent with the photostationary state at *ca.* 95% of closed isomer (*i.e.* 93,0%,, 95.6% and 95.4%, respectively). Such values lie in the classical ranges for diarylperfluorocyclopentene compounds.⁶

If we look at the cyclization event, we notice that $\phi_{\text{OF}\rightarrow\text{CF}}$ is two times higher for **3o**. At this wavelength, its absorption coefficient is about half of that of the complexes that include the TTA contribution (see Fig 3). As the quantum yield is related to absorption coefficient, this explains that $\phi_{\text{OF}\rightarrow\text{CF}}$ of the DTE unit appears two times lower for the two complexes (about half of the light absorbed by the TTA unit does not give rise to the photoreaction). For the cycloreversion, the situation is simpler, the visible absorption involving only the DTE unit in all compounds. Overall, we conclude that the DTE unit photoreactivity is similar in **3o** and in the complexes. Then, in the light of the efficient photochromic behaviour for both complexes, we turned our interest toward the photophysical properties and their possible modulation.⁶

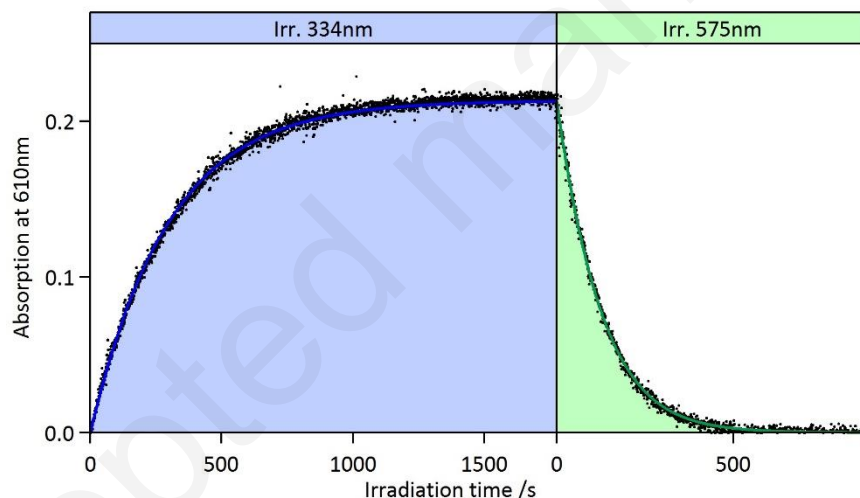


Figure 4. Continuous absorption time-evolution profile extracted at 610nm for **4o** during a full cycle of photoisomerization under continuous 334 and 575 nm illumination

Emission studies of lanthanide complexes 4 and 5. First, the emission properties of the two isomers of the europium complex (**4o** and **4c**) were studied in solution ($[c] = 10^{-5}$ - 5×10^{-6} mol.L⁻¹) using particular experimental conditions (small slit aperture) in order to prevent photoisomerization process during the luminescence measurement. For **4o**, upon excitation at $\lambda = 350$ nm, the emission features the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions characteristic of Eu(III) luminescence

at 579 (J = 0), 592 (J = 1), 612 (J = 2), 652 (J = 3), and 700 nm (J = 4) (Figure 5). The luminescence decay time of this 5D_0 state was measured to be 260 μ s (using the $^5D_0 \rightarrow ^7F_2$ transition), and the single exponential decay curve indicates that only one emitting species is present in solution. With a 350 nm excitation, the emission spectrum of **4c** is very similar but of significant lower intensity, 55-65% (*vide infra*), whereas excitation in the closed DTE centered transitions (at 550 nm) does not induce any luminescence from the Eu(III) center. These observations are confirmed with the excitation spectrum ($\lambda = 610$ nm, $^5D_0 \rightarrow ^7F_2$ transition) that is composed of a single broad band centered at 345 nm corresponding to the π - π^* transitions of the ligand **3o** and to the TTA moieties (Figure S6). A luminescence lifetime of 250 μ s was measured for **4c**. Overall the results are comparable to those observed in the pioneering example reported by Hasegawa and Kawai.⁶⁵ The absence of Eu(III) sensitization mediated by the closed DTE antenna can be easily explained by its low lying excited state (550-580 nm, 17 000-18 000 cm^{-1}) that is lower than the best accepting 5D_1 state and almost at the same energy than the 5D_0 state from the europium ion (5D_1 at 19 000 cm^{-1} and 5D_0 at 17 400 cm^{-1}). The possible sensitization of Eu(III) upon excitation at 350 nm is more surprising and could be explained by the fact that the energy transfer from the TTA in its triplet state occurs faster to the Eu(III) $^5D_{0/1}$ state than to DTE triplet state, this later photophysical process acting as non-radiative deexcitation pathway.^{65,79a}

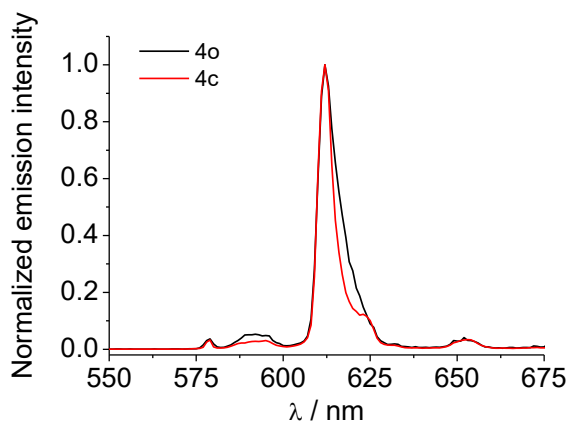


Figure 5: Normalized emission spectra of **4o** and **4c** in dichloromethane at room temp ($\lambda_{\text{ex}} = 350$ nm).

Yb(III) emission is generally less intense than the Eu(III) one and requires an excitation using more power and longer integration time to get an acceptable signal/noise ratio. Therefore, measuring the full luminescence spectrum of the open isomer **5o** with excitation in the absorption band ($\lambda_{\text{ex}} = 350$ nm) was not possible owing to the fast concomitant closing of the molecule forming **5c**. In contrast, the emission spectrum of **5c** could be measured upon excitation at 350 nm and displays the characteristic ytterbium transitions ($^2F_{5/2} \rightarrow ^2F_{7/2}$) in the NIR spectral range at 980 nm (Figure 6, black line). We also found out that **5c** is also emissive upon excitation at $\lambda_{\text{ex}} = 580$ nm, in the absorption band of the closed DTE unit, in marked contrast with the Eu(III) analogous **4c**. This visible excitation of **5c** induced two competitive photophysical processes, (i) the opening of the DTE unit leading to **5o** and (ii) the emission of **5c**. Consequently, the emission is weaker but is characteristic of the Yb(III) ion (Figure 6, red line). This result can be easily explained by the position of the $^2F_{5/2}$ excited state of Yb(III) (10200 cm^{-1}) lying at much lower energy than that of Eu(III). The sensitization mechanism may proceed either directly from the DTE ligand singlet excited state^{79a} or from its corresponding triplet one.^{79b} It is worth noting that the open form **5o** does not absorb at this wavelength and does not present any emission under 580 nm excitation.

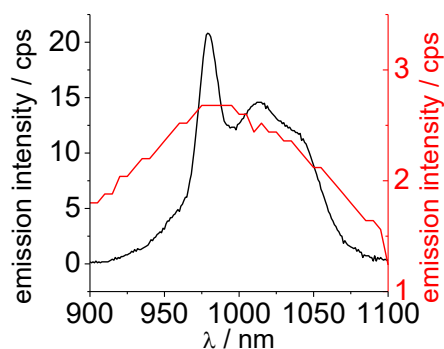


Figure 6: Emission spectra of **5c**, in dichloromethane at room temperature, upon excitation at $\lambda_{\text{ex}} = 350$ nm (black) and $\lambda_{\text{ex}} = 580$ nm (red). The difference of emission profile depending on the excitation wavelength is due to experimental parameters. Under 580 nm excitation, the emission of **5c** is low and it was necessary to use larger emission slit aperture to increase the signal/noise ratio. Consequently, resolution is lower.

Modulation of the luminescence response under irradiation in the DTE absorption bands of

4 and 5. On the basis of the above results, *in situ* modulation of luminescence was measured for both complexes. First, upon continuous irradiation of **4o** in its large absorption band at $\lambda_{\text{ex}} = 350$ nm, the luminescence decay of the europium complex was followed at $\lambda = 610$ nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition). This luminescence decay occurs simultaneously with the gradual formation of the closed form **4c** as observed by UV-visible absorption (*vide supra*). In a typical experiment displayed in Figure 7, this decay of the emission process follows a mono-exponential law with a characteristic lifetime of 10 s in these experimental conditions. In the PSS, the emission intensity reaches 65% of its initial value, whereas the optical density concomitantly measured at 600 nm is consistent with that of the above described absorption spectrum, *i.e.* with the conversion of **4o** to **4c** of *ca.* 95%. During the irradiation of **4c** at $\lambda = 560$ nm, the compound being not emissive, no emission signal is recorded. Concomitantly, compound **4o** is fully regenerated on the basis of the absorption spectrum and the initial luminescence intensity is fully recovered as well. Note that the closing process (75 s in the present experimental conditions) is faster than the opening one (300 s).

Four opening closing processes are depicted on figure 7 showing that the process is fully reversible and occurs without notable alteration.

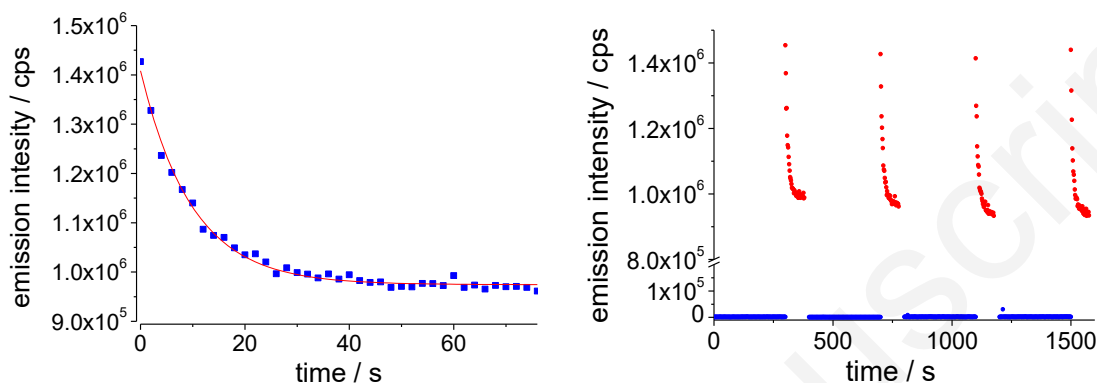


Figure 7: (left) Evolution of the emission at $\lambda = 610$ nm upon irradiation at $\lambda = 350$ nm observed at room temperature during conversion of **4o** ($[c] \approx 1 \times 10^{-5}$ mol.L $^{-1}$) to **4c**, and the mono-exponential fit (red line) with $\tau = 10$ s). (right) Representation of four opening-closing cycles: emission at $\lambda = 610$ nm upon successive irradiation at $\lambda = 560$ nm (blue) and at $\lambda = 350$ nm (red).

In the case of the ytterbium complex, the photomodulation of the NIR emission can be achieved by using an alternative sensitization pathway through the closed DTE unit. Indeed, continuous irradiation in the large absorption band of the luminescent complex **5c** in the visible range ($\lambda_{\text{ex}} = 580$ nm) gradually leads to the formation of the open form **5o**, and the decay of the luminescence emission at $\lambda = 1000$ nm (Figure 8) could be observed and monitored. When the PSS is reached, (i) the optical density measured at 580 nm in this experiment is virtually zero, consistent with the total conversion of **5c** to **5o**, and (ii) the luminescence is turned off. Upon further irradiation of **5o** at $\lambda = 350$ nm, complex **5c** is fully regenerated on the basis of the absorption spectrum, and the previous luminescence intensity is regenerated in spite of a rather low signal-to-noise ratio. Here again, the closing process (200 s in the present experimental conditions) is faster than the opening one (600 s). Three opening closing processes are depicted in Figure 8 showing that the process is fairly reversible in those experimental conditions. To the best of our knowledge, this is the very

first example of Yb(III) luminescence modulation with a photochromic unit. Note that all these modulation experiments display different kinetics than those of the quantum yield determinations owing to different effective irradiation power of the samples.

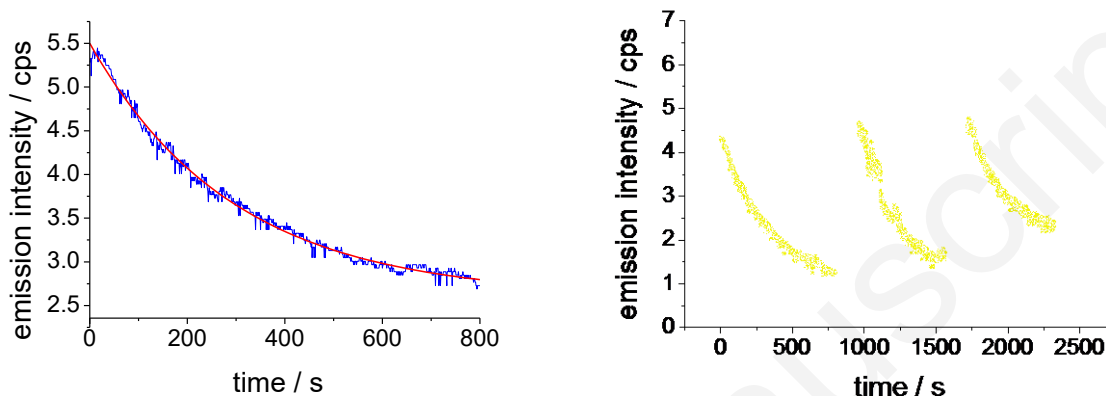


Figure 8: (left) Evolution of the emission at $\lambda = 1000$ nm upon irradiation at $\lambda = 580$ nm at room temperature leading to conversion of **5c** ($[c] \approx 1 \times 10^{-5}$ mol.L $^{-1}$) to **5o** and the mono-exponential fit (red line) with $\tau = 10$ s. (right) Representation of three opening-closing cycles: monitoring of emission at $\lambda = 1000$ nm upon irradiation at $\lambda = 580$ nm (opening), the signal being not measured during the closing process (irradiation at $\lambda = 350$ nm). Integration time was 1s for each data points.

Conclusion.

Herein, we reported the design of an original DTE based ligand and its coordination to Ln(TTA)₃ moieties (Ln = Eu, Yb). The complexes were fully characterized by NMR, mass spectrometry and elemental analysis. The photochromic behavior of the ligand and related complexes has been unambiguously established by NMR and absorption spectroscopies under irradiation. The luminescence of the lanthanide ions can be successfully modulated, thanks to the photochromic properties of the DTE ligand, both in the visible (Eu) and in for the first time in the NIR (Yb) spectral ranges. In the case of Eu,(III) a partial quenching of luminescence is observed upon closing the DTE unit under 350 nm excitation. On the other hand, in the case of Yb(III), excitation of the close DTE at 595 nm induced the ring opening reaction and the decrease of the NIR emission.

Importantly, this work shows that it is possible to modulate Yb(III) luminescence using the ubiquitous DTE photochromic unit, and further chemical engineering with photochromic molecules should be possible to achieve improved switching processes.

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Supporting Information Available: NMR spectra, isomerization studies. This material is available free of charge via the Internet at <http://pub.acs.org>.

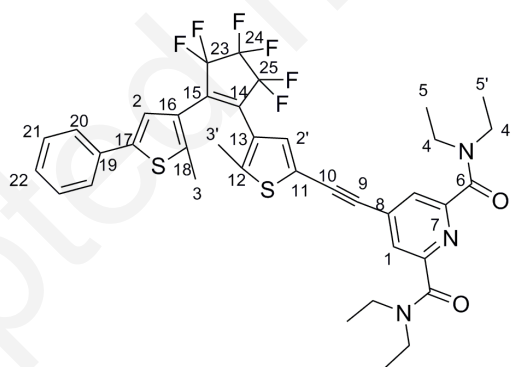
Experimental Section.

General comments: The reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were dried and distilled under argon using standard procedures. 4-iodo-2,6-bis(diethylcarbamoyl)pyridine,⁷⁴ and compound **1**,⁷³ were prepared as previously reported. YbCl₃·6H₂O (99.998%) and EuCl₃ (99.99%) were purchased from ALDRICH and ALFA INORGANICS while Yb(TTA)₃·2H₂O and Eu(TTA)₃·2H₂O were prepared according to the literature.⁸⁰ All the reactions and handling involving DTE compounds were carried out in the dark. NMR spectra were recorded on a Bruker AVANCE I 500 MHz spectrometer or a Bruker AVANCE III 400 MHz spectrometer. IR spectra were recorded on a IFS 28 Bruker spectrometer using KBr pellets or ATR. High resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest) on a ZabSpecTOF (LSIMS at 4 kV) spectrometer Bruker MicrO-Tof-Q II.

Routine UV-vis irradiations were performed in UV cells or NMR tubes with a LS series Light Source of ABET technologies, Inc (150 W xenon lamp), with single wavelength light filters “350FS 10-25” and “580FS 20-25”. For quantum yield measurements, photochromic reactions were induced in situ by a continuous irradiation Hg–Xe lamp (Hamamatsu, LC8 Lightningcure, 200 W) equipped with narrow band interference filters of appropriate wavelengths (Semrock FF01-335/7-25 for $\lambda_{irr} = 335$ nm; FF01-575/25-25 for $\lambda_{irr} = 575$ nm). The irradiation power was

measured using a photodiode from Ophir (PD300-UV). The photochromic quantum yields were determined by probing the sample with a xenon lamp during the course of the light irradiation. Absorption changes were monitored by a CCD camera from Princeton Instruments mounted on a spectrometer (Roper Scientific). Kinetic profiles were analyzed by means of a Runge–Kutta-based Igor-implemented (Wavemetrics) homemade software.⁸¹

The luminescence spectra were measured using a Horiba-Jobin Yvon Fluorolog-3® spectrofluorimeter, equipped with a three slit double grating excitation and emission monochromator with dispersions of 2.1 nm/mm (1200 grooves/mm). The steady-state luminescence was excited by unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° for diluted solution measurements by a red-sensitive Hamamatsu R928 photomultiplier tube. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Near infra-red spectra were recorded at an angle of 90° using a liquid nitrogen cooled, solid indium/gallium/arsenic detector (850-1600 nm) through a RG830 -2 mm- filter. Selective excitation at 350 nm requires the use of a CG400 filter in order to perfectly suppress the second harmonic excitation (700 nm) localized in the closed DTE absorption band.



[C₆H₅–(C₁₅S₂F₆H₈)–C≡C–*m,m*–(CON(CH₂CH₃)₂)₂–C₅H₄N] (**30**). In a Schlenk tube, compound **1** (394 mg, 0.84 mmol), 4-iodo-2,6-bis(diethylcarbamoyl)pyridine (**2**) (424 mg, 1.05 mmol), PdCl₂(PPh₃)₂ (36.9 mg, 0.05 mmol) and CuI (20 mg, 0.11 mmol) were dried under vacuum for 30 minutes. Then, well degassed THF (100 mL) and diisopropylethylamine (0.29 mL, 1.68 mmol) were added. The reaction mixture was left under stirring at room temperature for 14 hours. Then, the solvents were evaporated to obtain a crude product that was purified by column chromatography using ethyl acetate and pentane (1/1) as eluent, to obtain **30** as a yellow powder (480 mg, 76 %). ¹H NMR (400 MHz, CD₂Cl₂, 297 K): δ 7.61 (s, 2H, H₁), 7.57-7.55 (m, 2H, *o*-C₆H₅), 7.41-7.38 (m,

3H, *m*-C₆H₅+H₂), 7.37-7.34 (m, 1H, *p*-C₆H₅), 7.28 (s, 1H, H₂), 3.53 (q, 4H, ³J = 7.0 Hz, H₄ or H₄'), 3.33 (q, 4H, ³J = 7.0 Hz, H₄ or H₄'), 2.00 (s, 3H, H₃ or H₃'), 1.99 (s, 3H, H₃ or H₃'), 1.23 (t, 6H, ³J = 7.0 Hz, H₅ or H₅'), 1.14 (t, 6H, ³J = 7.0 Hz, H₅ or H₅'). ¹³C NMR (125.76 MHz, CD₂Cl₂, 297 K): δ 167.6 (s, C₆), 154.7 (C₇), 146.1 (s, C₁₃), 143.0 (s), 142.1 (s, C₁₆), 137.6 (m) and 135.6 (m), 133.7 (s, C₂'), 133.6 (s), 133.1 (s), 129.4 (s, C₂₁), 128.4 (s, C₂₂), 126.0 (s, C₂₀), 125.7 (s, C₁₂ or C₁₈), 124.9 (s, C₁), 122.6 (s, C₂), 120.5 (s, C₁₁), 116.5 (m), 111.5 (m), 91.0 (s, C₉), 87.7 (s, C₁₀), 43.6 (s, C₄ or C₄'), 40.4 (s, C₄ or C₄'), 14.8 (s, C₃ or C₃'), 14.7 (s, C₃ or C₃'), 14.5 (s, C₅ or C₅'), 12.92 (s, C₅ or C₅'). IR (KBr) (ν, cm⁻¹): 2209 (s) (ν_{C≡C}), 1638(s) (ν_{C=O}). Elemental analysis for [C₃₈H₃₅N₃O₂F₆S₂]_{0.1}CH₂Cl₂: C 60.93, H 4.66 (Calcd: C 60.83, H 4.72). HR-MS ESI(*m/z*): 766.1968 ([M+Na]⁺, calcd 766.19671), 744.2123 ([M+H]⁺, calcd 744.21477).

Data for 3c: ¹H NMR (400 MHz, CD₂Cl₂, 297 K): δ 7.62-7.44 (m, 7H, C₆H₅ + H₁), 6.72 (s, 1H, H₂'), 6.58 (s, 1H, H₂), 3.50 (q, 4H, ³J = 7.1 Hz, H₄ or H₄'), 3.30 (q, 4H, ³J = 7.1 Hz, H₄ or H₄'), 2.21 (s, 3H, H₃ or H₃'), 2.20 (s, 3H, H₃ or H₃'), 1.21 (q, 6H, ³J = 7.1 Hz, H₅ or H₅'), 1.12 (q, 6H, ³J = 7.1 Hz, H₅ or H₅').

[C₆H₅—(C₁₅S₂F₆H₈)—C≡C—*m,m*-(CON(CH₂CH₃)₂)₂-C₅H₄N-Eu(TTA)₃] (4o). In a Schlenk tube, compound **3o** (51 mg, 0.069 mmol) and Eu(TTA)₃·(H₂O)₂ (58.4 mg, 0.069 mmol) were dried under vacuum for 30min and dissolved in dichloromethane (5 mL). This solution was stirred at ambient temperature for 16 hours. The mixture was taken to dryness under vacuum to yield to a green powder (106 mg, 100 %). ¹H-NMR (400.16 MHz, CD₂Cl₂, ppm): δ 9.58 (br. s, 2H, H₁), 7.26-7.46 (m, 5H, C₆H₅), 7.14 (s, 1H, H₂' or H₂), 7.09 (br. s, 3H, H_{TTA}), 6.82 (s, 1H, H₂' or H₂), 6.53 (br. s, 3H, H_{TTA}), 6.21 (br. s, 3H, H_{TTA}), 5.63 (br. s, 4H, H₄ or H₄'), 3.84 (br. s, 6H, H₅ or H₅'), 3.51 (br. s, 4H, H₄ or H₄'), 2.53 (br. s, 6H, H₅ or H₅'), 2.1 (s, 3H, H_{TTA}-methine), 1.79 (s, 3H, H₃' or H₃), 1.69 (s, 3H, H₃' or H₃). ¹³C NMR (125.77 MHz, CD₂Cl₂, 297 K): δ 167.9 (C₆), 145.9 (C₇), 142.9, 141.8, 135.1, 133.5, 129.4, 128.4, 127.3, 125.9, 125.6, 125.3, 124.4, 122.5, 119.9, 90.1, 46.4 (C₄), 16.5 (C₅), 14.6 (C₃ or C₃'), 14.4 (C₃ or C₃'). Most of the quaternary carbon could not be observed as well as C₄' and C₅'. IR (KBr) (ν, cm⁻¹): 2212(s) (ν_{C≡C}), 1608(s) (ν_{C=O}). Elemental analysis for [10C₆₂H₄₇N₃O₈F₁₅S₅Eu]·6CH₂Cl₂: C 46.97, H 3.04 (Calcd: C 46.69, H 3.02). HR-MS ESI(*m/z*): 1582.0837 ([M⁺Na]⁺, calcd: 1582.08374).

Data for 4c: ¹H NMR (400 MHz, CD₂Cl₂, 297 K): δ 9.85 (s, 2H, H₁), 7.38-7.52 (m, 5H, C₆H₅), 7.11 (brs, 3H, H_{TTA}), 6.62 (s, 1H, H₂'), 6.52 (brs, 3H, H_{TTA}), 6.13 (brs, 3H, H_{TTA}), 5.93 (s, 1H, H₂

), 5.66 (brs, 4H, H₄ or H_{4'}), 4.21 (brs, 6H, H₅ or H_{5'}), 3.66 (brs, 4H, H₄ or H_{4'}), 2.53 (brs, 6H, H₅ or H_{5'}), 1.98-1.91 (3H, H_{TTA-methine}), 1.98(s, 3H, H₃ or H_{3'}), 1.91 (s, 3H, H₃ or H_{3'}). IR (KBr) (ν , cm⁻¹): 2202(s) ($\nu_{C\equiv C}$), 1610(s) ($\nu_{C=O}$).

[C₆H₅-(C₁₅S₂F₆H₈)-C≡C-*m,m*-(CON(CH₂CH₃)₂)₂-C₅H₄N-Yb(TTA)₃] (5o). In a Schlenk tube, **3o** (51.5 mg, 0.069 mmol) and Yb(TTA)₃·(H₂O)₂ (60.4 mg, 0.069 mmol) were dried under vacuum for 30 min and dissolved in dichloromethane (5 mL). This solution was stirred at ambient temperature for 16 hours. The mixture was taken to dryness under vacuum to yield a light green powder (109 mg, 95 %). ¹H-NMR (400.16 MHz, CD₂Cl₂, ppm): δ 8.48 (br. s, 3H, H_{TTA}), 7.12 (br. s, 3H, C₆H₅), 6.92 (br. s, 2H, C₆H₅), 6.79 (br. s, 3H, H_{TTA}), 6.33 (br. s, 1H, H₂), 4.92 (br. s, 3H, H_{TTA}), 4.62 (br. s, 1H, H_{2'}), 0.58 (s, 3H, H_{3'} or H₃), 0.28 (s, 3H, H_{3'} or H₃), -14.61 (br. s, 3H, H_{TTA-methine}), additional broad features are observed for H₁, H_{4/4'} and H_{5/5'}. ¹³C NMR (125.77 MHz, CD₂Cl₂, 297 K): δ 149.4, 143.3, 141.6, 140.3, 137.8, 135.80 (m), 134.3, 133.8, 132.4, 130.0, 128.6, 127.8, 127.7, 125.9, 124.9, 124.0, 122.8, 121.1, 116.3, 115.0, 114.4, 112.2, 110.0, 107.7, 90.7(m), 87.7, 83.6, 46.9 (br. s, C₄ or C_{4'}), 45.7 (br. s, C₄ or C_{4'}), 24.0 (br. s, C₅ or C_{5'}), 22.5 (br. s, C₅ or C_{5'}), 12.7 (C₃ or C_{3'}), 12.6 (C₃ or C_{3'}). IR (KBr) (ν cm⁻¹): 2212(s) ($\nu_{C\equiv C}$), 1606(s) ($\nu_{C=O}$). Elemental analysis for [C₆₂H₄₇N₃O₈F₁₅S₅Yb]·CH₂Cl₂: C 45.35, H 2.95 (Calcd: C 45.44, H 2.97). HR-MS ESI(*m/z*): 1359.1227 ([M-TTA]⁺, calcd: 1359.1226).

Data for 5c: ¹H NMR (400 MHz, CD₂Cl₂, 297 K): δ 8.53 (brs, 3H, H_{TTA}), 7.01-7.22 (m, 5H, C₆H₅), 6.82 (brs, 3H, H_{TTA}), 5.99 (brs, 1H, H₂), 4.93 (brs, 3H, H_{TTA}), 4.56 (brs, 4H), 2.96 (brs, 1H, H_{2'}), 0.66 (s, 3H, H_{3'} or H₃), 0.47 (s, 3H, H_{3'} or H₃) -14.70 (s, 3H, H_{TTA-methine}). IR (KBr) (ν , cm⁻¹): 2201(s) ($\nu_{C\equiv C}$), 1605(s) ($\nu_{C=O}$).

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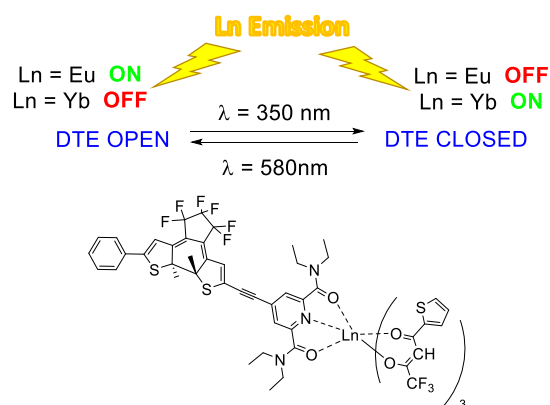
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SYNOPSIS TOC



The dithienylethene (DTE) modified dipicolinic amide ligand can be a versatile tool to modulate Eu(III) and Yb(III) luminescence. The nature of the modulation, turning on or quenching, depends on the lanthanide emitter.