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Efficient Luminescence Control in Dithienylethene Functionalized Cyclen Macrocyclic Lanthanide Complexes

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TITLE RUNNING HEAD: Efficient Luminescence Control in a Dithienylethene Functionalized Cyclen Macrocyclic Lanthanide Complex

Abstract. We report the synthesis of an original ligand scaffold based on a dimethyl-cyclen platform Medo2pa with two dithienylethene units attached to each picolinate arms and the corresponding yttrium(III), europium(III) and ytterbium(III) complexes. All three compounds show reversible photochromism with high photo-conversions. Photoluminescence experiments demonstrate that this design is versatile and adapted for both europium and ytterbium emission switching when measured in frozen organic glasses at 77 K. The OFF/ON luminescence ratio are excellent in the case of europium (4 to 8 %) and still quite good in the case of ytterbium (around 13 %).

Keywords: photochromism, ytterbium(III), europium(III), dithienylethene, cyclen, azamacrocycles, luminescence, molecular switch.

Introduction

Responsive materials in which a key property can be modulated by an external stimulus in a controlled way are a great achievement in the field of molecular materials.[1-2] Among them "all-optical" systems, that are triggered by light to change their optical (absorption, emission) properties, combine fast response, remote control and a low level of technical requirements for their implementation in real life applications. Applications could be as diverse as labels for cell imaging,[3] super resolution imaging,[4] anti-counterfeiting dyes,[5-6] optical data-storage[7] and many others.

In this context, several research groups have explored the photo-modulation of lanthanide-based luminescent systems,[5, 8-16] mainly focusing on the association of photochromic compounds with the red-emitting europium(III) ion.[5, 10-16] The ubiquitous diarylethene (DAE) photochromic units,[17] on top of their excellent photo-physical properties, fatigue resistance and thermal stability of both open and closed isomers, is perfectly suited. Indeed, DAE scaffolds can be easily designed so that the closed isomers show strong absorptions around 610 nm, matching the narrow emission lines of europium(III) and then favoring emission quenching typically via an energy transfer. However, according to this strategy, a complete quenching of europium luminescence in the closed form has not been realized yet. The only total quenching of europium luminescence by a photochromic unit reported to date consist of a tris(dipicolinate)europium core decorated with three N^C chelate four coordinate organoboron T type (reversible upon heating) photoswitches.[15] Therefore, it is highly desirable to achieve a complete optical control of ON/OFF switching of europium luminescence with the P (thermally stable) photochromic DAE. Recently, some of us reported an example of partial photo-modulation in a dithienylethene (DTE) appended dipicolinic amide europium complex (Chart 1),[18] and we hypothesize that a partial lability of the metal complex could be a factor contributing to the moderate efficiency of the quenching in the closed form. At the same time, surprisingly, this previous paper showed that DTE photochromic units could actually be more versatile modulators of lanthanide luminescence than initially thought since ytterbium(III) NIR emission could be sensitized by the 580 nm absorption of the closed isomer. Based on this, two important goals remain to be achieved in this field: i) the improvement of the efficiency of europium(III) emission quenching by closed DTE system in order to reach real ON/OFF switching, and ii) the generalization and optimization of photo-modulation of ytterbium(III) ion by DTE units. These two goals thus require a better understanding of the underlying photo-physical mechanisms and the exploration of new systems combining DTE and lanthanide ions.

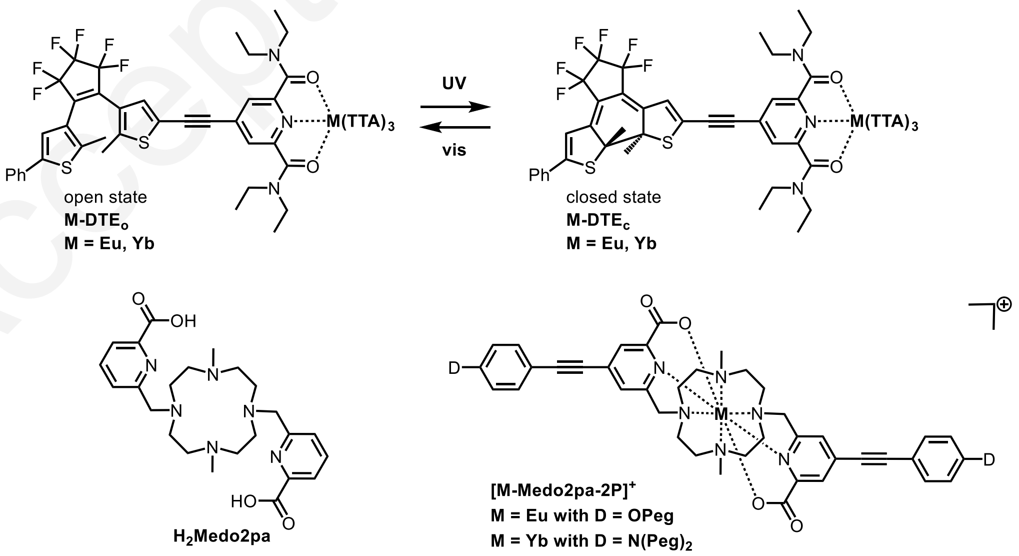


Chart 1. Previously studied systems. (top) **M-DTE** system shows versatile photo-modulation of emission of both ytterbium(III) and europium(III) ions upon switching between the open and closed state (TTA is 2-thenoyltrifluoroacetonate).[18] (middle) **Medo2pa** provides water soluble and stable lanthanide complexes and **M-Medo2pa-2P** chlorine salts enable cell imaging in the NIR range in the case of the ytterbium(III) complex.[19-20]

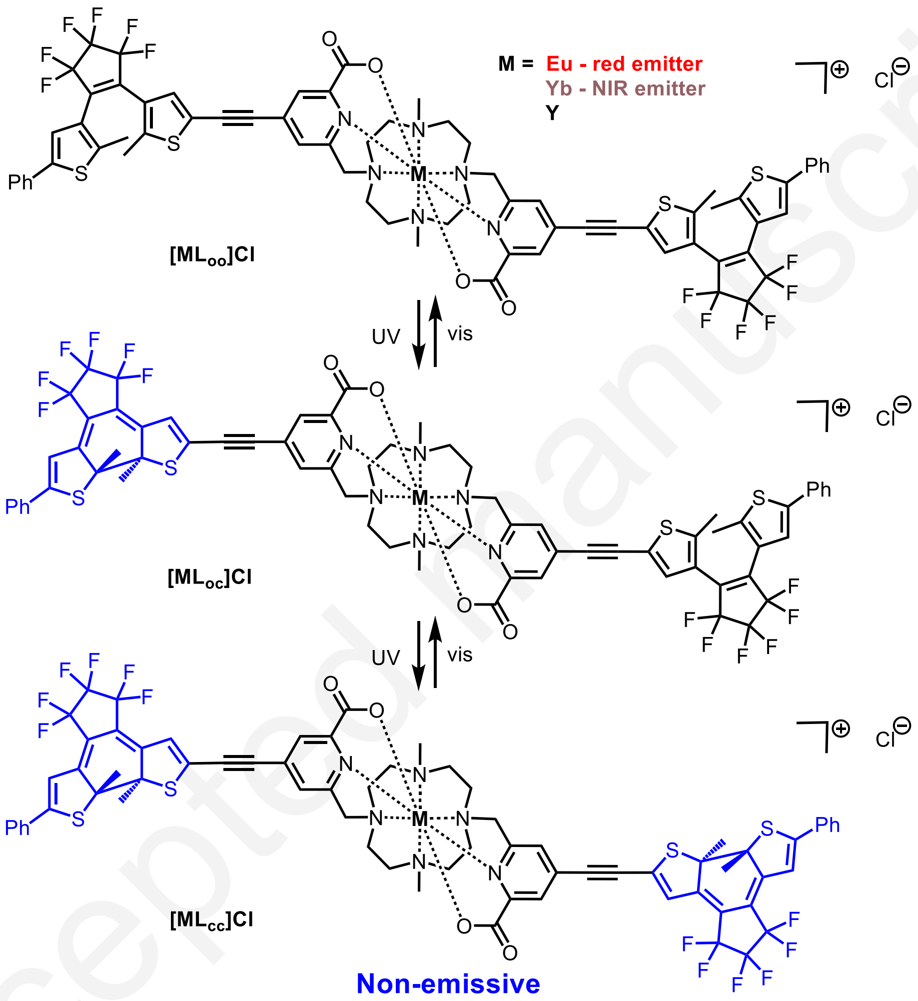


Chart 2. Targeted luminescence switches.

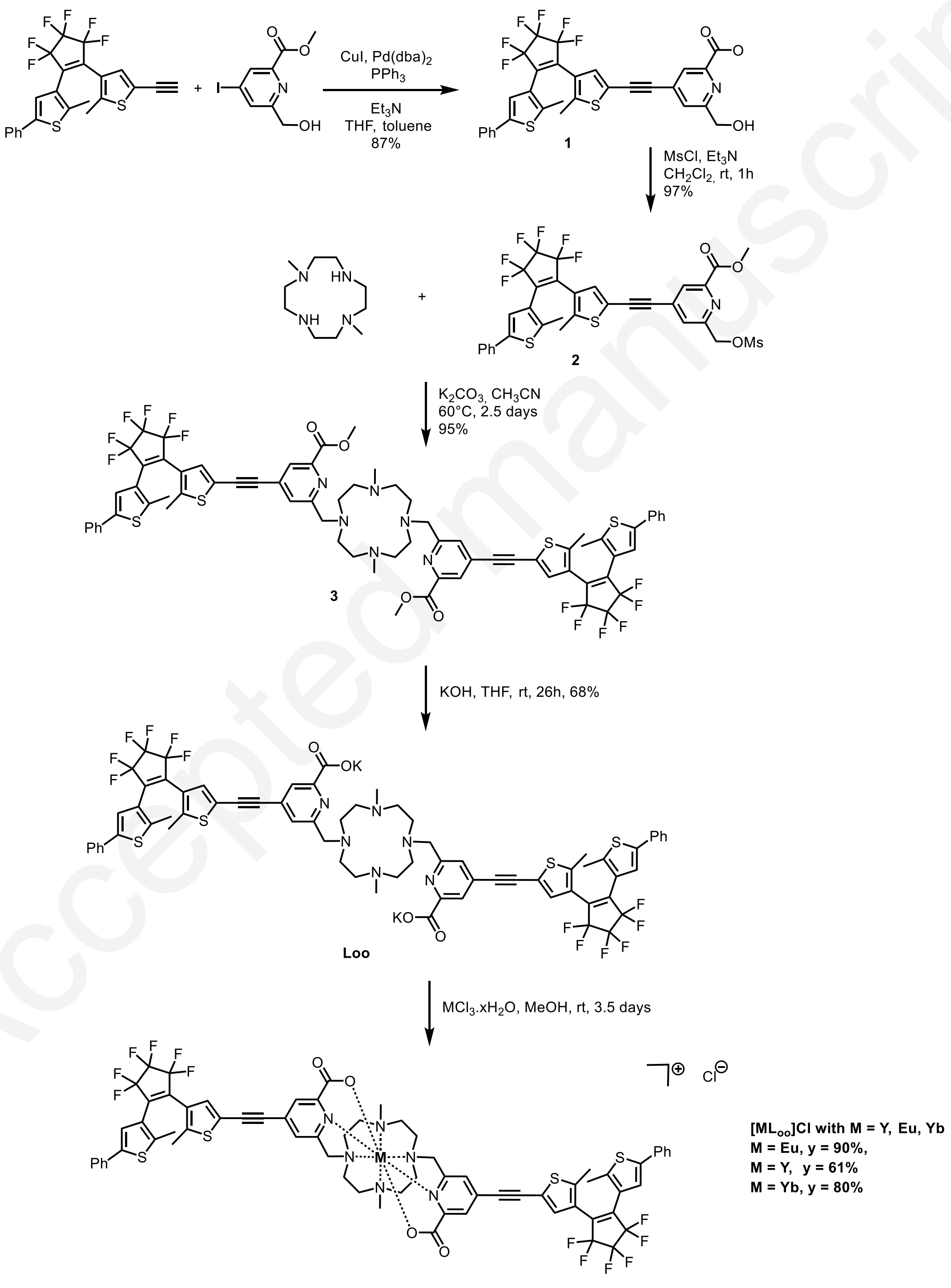
In parallel, macrocyclic lanthanide complexes have been widely studied as imaging bioprobes in general,[3, 21-22] and as luminescent systems in particular.[23-24] Among them, the cyclen based Medo2pa platform (Chart 1) has provided complexes of various lanthanide ions displaying high stability constants,[25] that are typically stable in water solutions.[26] This cyclen platform N-functionalized by two picolinate pendants and two methyl groups, when modified with two photon active conjugated antennas, provides bright luminescent europium(III) and ytterbium(III) complexes that are spontaneously internalized into live cells,[19-20] the latter remaining highly luminescent in biological media (Chart 1).[20] Based on these convincing results, and complementary to another strategy on based DTE modified acetyl acetonate ligands that we are developing in parallel,[27] we thought that the association of the Medo2pa platform with appropriate DTE units could lead to “all optical” switches with improved stability and, therefore, better switching ratio between the open and closed state, as well as to provide a new efficient ytterbium based switch in the NIR range through the closed DTE unit sensitization. We therefore targeted the synthesis of a new Medo2pa platform bearing two DTE units (on each picolinate arms) as shown in Chart 2. First motivated by the ease of synthesis, the presence of two photochromic units within the same scaffold could also be anticipated as an advantage to improve i) quenching efficiency in the case of the europium(III) complex, and ii) sensitization through the closed DTE unit in the case of the ytterbium(III) complex. In this paper, we report on the synthesis of this new ligand and of the corresponding europium(III), ytterbium(III) and yttrium(III) complexes. We study in detail the photo-switching of these three metal complexes by absorption and (^{1}H, ^{19}F) NMR spectroscopies to illustrate that a reversible and complete isomerization occurs, the two DTE units behaving independently. Our strategy is proved effective in improving the quenching efficiency of europium luminescence as shown by a residual intensity of 4-8 % of the initial one for the closed form as compared to the open one when measured at 77 K. We also show that the ytterbium complex luminescence can be modulated at 77 K although it does not exhibit any sensitization through the closed DTE.

Results and Discussion

Complex synthesis. Synthesis of the target metal complexes **[ML$_{oo}$]Cl** (M = Y, Eu, Yb) is described in Scheme 1. The DTE-photochromic-picolinate arm **1** was obtained by Sonogashira coupling from the alkyne terminated DTE and methyl 6-(hydroxymethyl)-4-iodopicolinate[28] (see SI). Mesylation of the latter was performed under usual conditions and *trans*-dialkylation of the dimethyl-cyclen macrocycle with two equivalents of compound **2** in the presence of K_2CO_3 led to the desired di-ester **3** with an excellent yield of 95%. Saponification of compound **3** in the presence of KOH in THF led to **L$_{oo}$** as a potassium salt which was purified, thanks to a precipitation in an EtOAc/hexane mixture. The synthesis of the compounds was further performed in MeOH at pH around 7. Washings with water and precipitations in CH_2Cl_2/hexane gave the desired **[ML$_{oo}$]Cl** with yields comprised between 61% and 90%. These new compounds were fully characterized (see experimental section and SI). As characteristic features in its ^{1}H NMR spectrum, diamagnetic **[YL$_{oo}$]Cl** exhibit shielded pyridine protons chemical shifts, similarly to other yttrium(III) dimethyl cyclen complexes,[29] while the signals from the cyclen moiety become significantly broadened upon coordination (Figure S12). In the case of **[EuL$_{oo}$]Cl**, additional paramagnetic shifts (pseudo contact shifts) are observed. Typically, the photochromic moiety shows small paramagnetic shifts, of around -0.1/-0.2 ppm as compared with the yttrium(III) complex, while the pyridine protons are observed at δ = 38.4 and 25.8 ppm and the cyclen protons give broad signals down to -16 ppm as expected (Figure S21).[19] For **[YbL$_{oo}$]Cl**, in line with the greater magnetic anisotropy tensor of ytterbium(III) compared with europium(III),[30] shifts of the same sign but of greater magnitude are observed, the pyridine protons being observed at δ = 83.8 and 55.5 ppm and the cyclen ones down to δ = - 40.5 ppm (Figure S18). The paramagnetic shifts observed for the photochromic moiety are also larger with, for instance, the thiophene protons shielded to δ = 6.97 and 6.37 ppm instead of δ = 7.47 and 7.28 ppm in **[YL$_{oo}$]Cl**.

Electronic absorption spectra and photochromism of 3$_{oo}$ and [ML$_{oo}$]Cl. The absorption spectrum of **3$_{oo}$** in DCM shows several intense bands in the UV range (Figure 1) that can be assigned to local $\pi-\pi^*$ transition of the picolyl unit (275 nm) overlapping with one of the DTE open form (315 nm). Upon irradiation at 330 nm, a decrease of absorption is observed at λ_{max} =272 nm while two new bands appear at λ_{max} = 382 and 607 nm (Figure 1). The initial spectrum can be recovered by 580 nm irradiation. This is in line with the usual photochromic behavior of DTE units[18] and consistent with the above mentioned assignment of the bands. Photo-cyclisation is evidenced by the characteristic lower energy band (λ_{max} = 607 nm) ascribed to an intra-ligand (IL) transition centered on the closed DTE moiety.[17] In this system with two DTE units, isomerization proceeds through the intermediate **3$_{oc}$** compound with one closed ring. However, at intermediate photo-conversions, no shifting of the lower energy transition was observed, suggesting that the two DTE units are electronically decoupled and behave independently in that case (Figure S24).[31] The isomerization was also studied by ^{1}H NMR spectroscopy that proved that a high photo-isomerization conversion (up to 94 % of **3$_{cc}$** and 6 % of **3$_{oc}$**) can be reached in the photo-stationary state (PSS) (Figure S29). Typically, the thienyl protons chemical shifts change from δ = 7.25 and

7.31 ppm in $\mathbf{3}_{oo}$ to 6.72 and 6.43 ppm in $\mathbf{3}_{cc}$. In the NMR conditions ([c] = 1.2×10^{-3} M), the cycloreversion process is almost quantitative with the recovery of $\mathbf{3}_{oo}$ in 94 % yield accompanied by unknown species, probably coming from partial degradation upon prolonged exposure to light. This behavior is in contrast to the more diluted UV-vis experiment that displays quantitative recovering.



Scheme 2. Synthetic pathway yielding the target compounds.

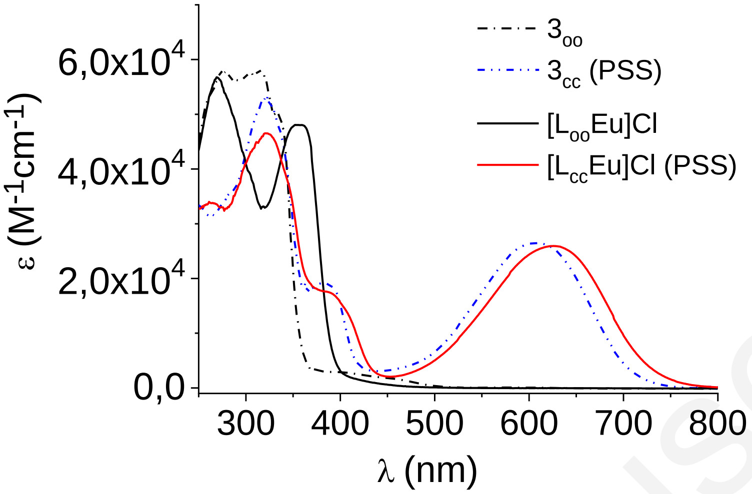


Figure 1. Electronic absorption spectra of $\mathbf{3_{oo}}$ and **[EuL$_{oo}$]Cl** in CH_2Cl_2 solutions. Upon UV light irradiation to PSS, the spectra of $\mathbf{3_{cc}}$ and **[EuL$_{cc}$]Cl** are obtained. The other compounds (Y, Yb) show similar behavior (see Table 1 and Figures S27 and S28). The initial spectra were recovered after bleaching at 580 nm.

Once the cyclen group is coordinated, clean photochromic behavior, without photo-degradation was observed as evidenced by the presence of isobestic points. The absorption spectra of the three metal complexes are very similar with two main transitions at λ_{max} = 269 nm and 350-360 nm and Figure 1 shows the representative behavior of the europium complex (the cases of Y and Yb complexes are depicted in Figures S27 and S28 respectively). Both bands are strongly modified upon UV irradiations and subsequent ring closure, and new transitions appear with λ_{max} values of 330 and 627 nm. The lower energy transition is slightly red shifted upon coordination as compared with **3cc**. Under visible light irradiation (λ_{max} = 580 nm), the cycloreversion process is triggered as attested by the quantitative recovery of the initial spectra. Further ^{1}H NMR spectroscopy monitoring of the process unambiguously shows that the photochromic process upon UV irradiation is almost complete with the reaching of a photo-stationary state composed of ca. 95 % of closed DTE units and a recovery of the initial spectra upon 580 nm irradiation, in contrast to the organic precursor. Details of the changes in the NMR spectra are highlighted in Figures 2 and S31.

compound	λ_{max}[nm], *corresponding energy* [cm^{-1}]	ε [M^{-1}.cm^{-1}]
3_{oo}	340, *29400*	40000
$3_{cc}$$^{(a)}$	382, *26200* 607, *16500*	19200 28000
[YL$_{oo}$]Cl	269, *37200* 362, *27600*	55600 48300
[YL$_{cc}$]Cl$^{(b)}$	330, *30300* 627, *15900*	42900 27800
[EuL$_{oo}$]Cl	269, *37200* 352, *28400*	53400 45300
[EuL$_{cc}$]Cl$^{(b)}$	339, *29500* 627, *16000*	39400 24700
[YbL$_{oo}$]Cl	269, *37200* 347, *28800*	57400 45300
[YbL$_{cc}$]Cl$^{(b)}$	330, *30300* 627, *15900*	46000 25900

a) Photo-stationary state after 330 nm irradiation, b) photo-stationary state after 364 nm irradiation

Table 1. Electronic absorption data for all compounds measured in DCM solutions.

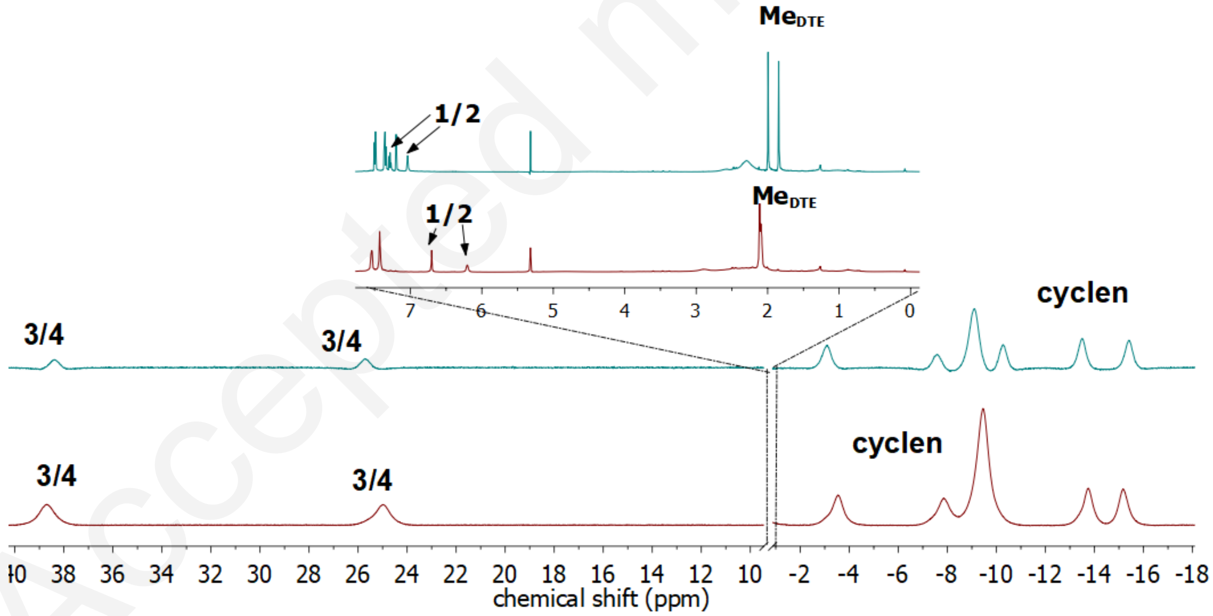


Figure 2. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) measured during the course of **[L$_{oo}$Eu]Cl** (blue line) isomerization to the PSS containing **[L$_{cc}$Eu]Cl** and **[L$_{oc}$Eu]Cl** with 95 % of overall closed DTE units (red line) upon 364 nm excitation in CD_2Cl_2..See Scheme 3 (experimental section) for numbering.

Photoluminescence of [ML$_{oo}$]Cl. We further studied the photoluminescence of all three metal complexes (M = Y, Eu, Yb). The yttrium complex serves as a reference to understand the photophysics of the ligand since no metal-based emission is expected for this compound. Thus, upon excitation at λ_{ex} = 350 nm of [**YL$_{oo}$]Cl** in an ethanol:methanol glass (77 K), a ligand-based fluorescence centered at λ_{em} = 395 nm was observed (Figure S32) with the presence of additional peaks in its tail. A time-gated measurement performed with a 1 ms delay allows us to assign unambiguously these features to a simultaneous structured phosphorescence with maximum at λ_{em} = 517 nm and a corresponding lifetime of 14 ms at 77 K (Figure S33). This phosphorescence process corresponds to a ligand-centered triplet at around 19 000 cm^{-1}. Upon continuous irradiation at 350 nm and closing of the DTE units, both fluorescence and phosphorescence progressively disappeared, and at the PSS the closed yttrium(III) complex was almost non-emissive (Figure S32). Concerning the spectroscopy of the europium(III) complex, **[EuL$_{oo}$]Cl** was studied at room temperature and at 77 K. At room temperature, excitation at 350 nm induces both emission and competitive closing of the DTE units. The spectrum is actually dominated by an intense ligand-centered emission at λ_{em} = 395 nm accompanied by a weak europium emission at 616 nm (Figure S34). In contrast, at 77 K in a methanol/ethanol organic glass, ligand centered emission is drastically decreased as compared with the sharp f-f transitions. The difference in the response of the system with temperature could be ascribed to the occurrence of thermally activated back energy transfer that is hampered at 77 K. We also observed a drastic slowing down of the closing reaction by this lowering of temperature and immobilization in an organic glass that allows one to measure the emission spectrum of pure **[EuL$_{oo}$]Cl** with an excellent resolution. Therefore, the characteristic europium(III) emission profile assigned to the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions were detected at λ_{em} = 580 (J = 0), 588, 593, 595 (J = 1), 610, 613, 622, 627 (J = 2), 646, 650 , 652, 658, 673 (J = 3), and 694, 704, 711 nm (J = 4) (Figure 4) and overall, the spectrum and particularly the crystal field splitting, is very similar to the one of a previously published europium(III) complexes with a similar Medo$_2$pa ligand for which a C$_2$ symmetry was calculated by DFT.[19] The same measurement at 77 K was performed on **[EuL$_{cc}$]Cl** (PSS state) and showed that an impressive quenching of europium luminescence occurs after closing of the DTE since only very weak emission (about 8 % of the original intensity determined by integration of the open state more intense band (J = 2), see Figure 3) was detected. It is also possible to follow the emission quenching in the glass at 77 K upon successive scans, highlighting the progressive closing of the DTE during each luminescence measurement (Figure S35). An attempt to reach the PSS was performed upon irradiation of the glass during 1000 s. A 90 % quenching was achieved after only 40 s but the complete closing was not reached at the end of the experiment where less than 4% of the initial emission was still observed. A perfect reproducibility of the behavior was observed after several re-opening were performed with white light irradiation (Figure 4).

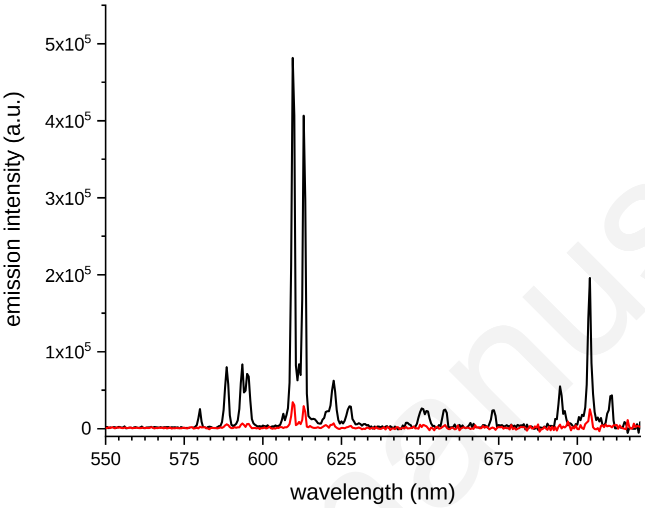


Figure 3. Emission spectra (λ_{ex} = 350 nm) of **[L$_{oo}$Eu]Cl** (black line) and **[L$_{cc}$Eu]Cl**. (red line) in ethanol: methanol (4:1) organic glass at 77K.

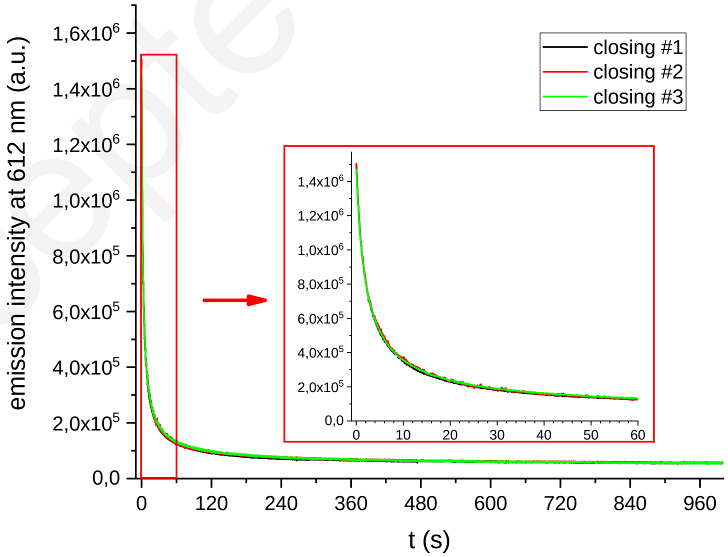


Figure 4. Emission at 612 nm (λ_{ex} = 350 nm) of **[L_{oo}Eu]Cl** while isomerizing to **[L_{cc}Eu]Cl**. in ethanol : methanol (4:1) organic glass at 77K. Two other successive measurements are performed after discoloration with white light (at RT).

Concerning **[YbL_{oo}]Cl**, no ytterbium emission was detected upon 350 nm excitation at room temperature. In contrast, in an ethanol/methanol organic glass at 77 K, the typical emission of ytterbium(III) was detected in the NIR. In order to avoid distortion of the signal due to concomitant closing, the emission was detected with a CCD camera. First, a resolved spectrum can be obtained, clearly showing the different lines expected for the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and again very similar to previously reported ytterbium(III) complexes with C_2 symmetry,[20] with the main crystal field splitting lines at 971, 996, 1025 and 1040 nm (Figure 5). In order to follow the effect of photo-isomerization on ytterbium emission, fast-acquired successive spectra were obtained, clearly showing a 10 fold quenching of luminescence due to the closing reaction (Figure S36). Note that the quenching ratio is not rendered by Figure 5 because the initial intensity actually corresponds to a system already undergoing a significant amount of closing. Rather, the ratio between the initial and final states can be obtained from integration of the fast acquired data (Figure 6), giving a 13 % ratio. Finally, we have addressed the possibility of sensitization by excitation at 600 nm, and unlike **Yb-DTE$_c$** (Scheme 1) no ytterbium emission was detected in such case.[18] For both europium and ytterbium complexes, it is unclear whether the remaining emission after closing arises from the closed species or whether a PSS composition different from the one in DCM solutions at room temperature (95 % of closed units, no remaining oo isomer) is reached due to immobilization in a frozen organic glass.

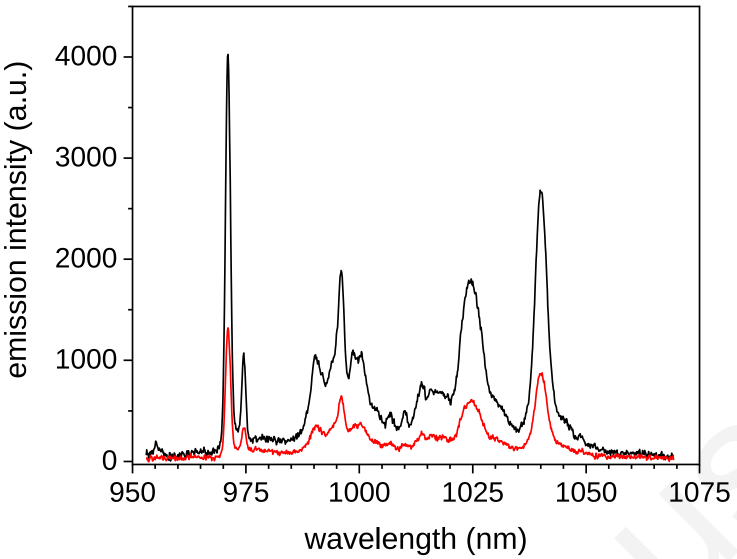


Figure 5. Emission spectra (λ_{ex} = 350 nm) of **[L_{oo}Yb]Cl** (black line) and **[L_{cc}Yb]Cl** (red line) in ethanol : methanol (4:1) organic glass at 77K.

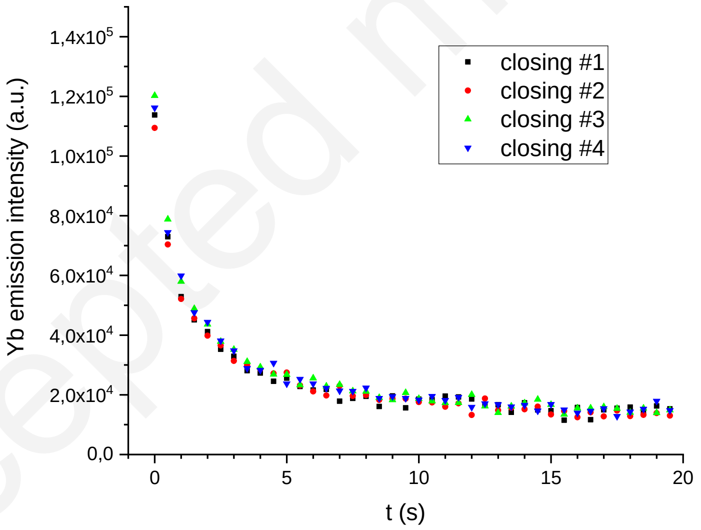


Figure 6. Emission (integrated intensity from Figure S36) at 1000 nm (λ_{ex} = 350 nm) of **[L_{oo}Yb]Cl** while isomerizing to **[L_{cc}Yb]Cl** in ethanol : methanol (4:1) organic glass at 77 K. Two other successive measurements are performed after discoloration with white light (at RT).

Compounds	Conditions	Ratio of Europium based luminescence (OFF state/ON state)	reference
Eu-DTE$_o$	RT , DCM	60 %	[18]
DAE-tpy-Eu(TTA)$_3$	RT, CHCl$_3$	20 %	[14]
Host guest complex of (terpyridinyldibenzo-24-crown-8)Eu(TTA)$_3$ and DAE	RT, 1:1 CH$_3$CN/CHCl$_3$	20 %	[16]
Triangle terthiazole Eu(hfac)$_3$ complex	RT, dioxane	36 %	[10-11]
	80 K, EtOH/MeOH glass matrix	ND[a]	[10-11]
Sulfone-DTE Eu(hfac)$_3$ complex	RT, ethylacetate	60 %	[32]
(5,6-dithienyl-1,10-phenanthroline)Eu(acac)$_3$	RT, ethanol	30 %	[5]
(DTE-β-diketonate)$_3$Eu(phenanthroline)	RT, DCM	1 %	33
	RT, Film	5 %	
[L$_{oo}$Eu]Cl	77 K, ethanol : methanol (4:1)	4 – 8 %	This work
(DTE-β-diketonate)$_3$Yb(bpy-Ru-alkynyl)	RT , DCM	1.4 %	27
(DTE-β-diketonate)$_3$Yb(phenanthroline)	RT, DCM	2 %	33
	RT, film	3 %	
[L$_{oo}$Yb]Cl	77 K, ethanol : methanol (4:1)	13 %	This work

Table 2. Previously studied complexes showing reversible luminescence switching with DAE photochromic units compared with this work. TTA =2-thenoyltrifluoroacetonate, hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate, aca = acetylacetonate , tpy = terpyridine .

a. emission QY are 10 % for the open state and 7.6 % for the closed one and no photoreaction occurs.

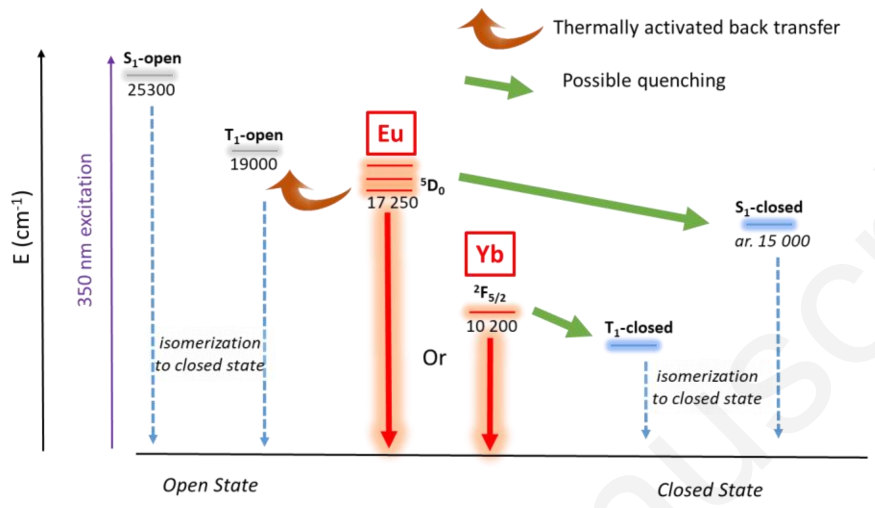


Figure 7. Tentative Jablonski diagram showing the different photophysical processes.

Discussion. Altogether, and in light with the objectives mentioned in the introduction, the results of the photoluminescence experiments deserve a few comments. First, temperature/medium dependence of the response is very spectacular for both systems and in both cases, no lanthanide based emission can be detected at room temperature, in contrast to previously published systems gathered in Table 2. In the case of europium, this is probably because of thermally activated back-transfer, hence causing ligand-centered emission as suggested by the presence of the open form ligand triplet state at 19000 cm^{-1} (see Figure 7). In the case of ytterbium, it is more likely that luminescence is inherently weak due to efficient non-radiative processes and therefore difficult to detect without causing the closing of the DTE. At 77 K in an organic glass, the non-radiative processes are drastically slowed down as well as the closing reaction and both factors favor the observation of ytterbium emission. Second, when measured in appropriate conditions, the contrast between the responses of the two states for our europium complex is much higher than in previous photoswitchable systems based on europium and diarylethene combinations (Table 2) and only one example relying on N^C chelate four coordinate organoboron photoswitches of T type previously showed better quenching ratio.[15] Provided that back transfer and non-radiative processes are reduced by further chemical engineering, our design with a macrocycle bearing two DTE units could lead to very efficient RT europium luminescence switches, more suitable for applications.[33]

Nonetheless, this design leads to the third example of efficient ytterbium luminescence photo-control reported so far. In that case, the mechanism for emission quenching does not rely on spectral overlap between the closed DTE and the lanthanide emission lines and we are currently investigating the possibility of a low lying triplet state quenching the emission in the closed state (Figure 7). We also postulate that the position of this state is not favorable to sensitization of ytterbium emission through the visible transition of the closed DTE unit unlike in **Yb-DTE$_c$**. This leaves room for improvement of ligand design in order to obtain optimized positioning of this state depending on the targeted behavior *ie* UV sensitization with quenching by a low lying state or controllable visible light sensitization.

Conclusion.

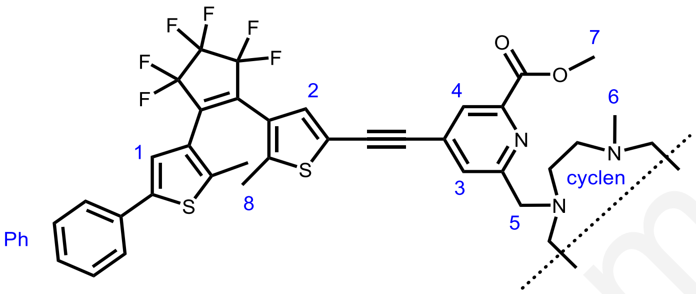
With this work, we report the synthesis of an original ligand scaffold with two DTE units attached to a cyclen based macrocycle designed for luminescence switching and the corresponding complexes of yttrium(III), europium(III) and ytterbium(III). All three metal complexes show reversible photochromism with high photo-conversions. Our design proved to be versatile and adapted for both europium and ytterbium emission switching, when measured in frozen organic glasses. The OFF/ON luminescence ratio are excellent in the case of europium compared to all previously published compounds and still quite good in the case of ytterbium, that represents the second example of such behavior. More important, our study, combined with on-going in depth photo-physical studies, will contribute to the understanding of important factors for the design of further improved molecular switches with custom switching, excitation and emission wavelengths.

Acknowledgments. We thank the Université de Rennes 1, the CNRS, the MESR, for support. H. A. S. thanks GDR MCM-2 for funding a short stay at the Laboratoire de Chimie in Lyon.

Supporting Information Available: Synthetic procedures for compounds **1** and **2**. NMR spectra and HRMS of all metal complexes. Photo-isomerization studies (absorption and NMR spectroscopy). Additional photoluminescence details.

Experimental Section.

General comments: Reagents were purchased from ACROS Organics and from ALDRICH Chemical Co. Cyclen was purchased from Chematech (Dijon, France). Dimethyl-Cyclen was synthesized as previously described.[26] The solvents were freshly distilled prior to use and according to the standard methods. NMR spectra (^{1}H, ^{19}F and ^{13}C) were recorded at the core facilities of the University of Brest, with Bruker Advanced 500 (500 MHz) or Bruker AMX-3 300 (300 MHz) spectrometers or at the Centre Régional de Mesures Physiques de l'Ouest on a Bruker Avance III HD 500 (500 MHz). The HR-MS analyses were performed at the Institute of Analytic and Organic Chemistry, ICOA in Orléans. Elemental Analysis were performed at Centre Régional de Mesures Physiques de l'Ouest. All experiments were performed in the dark.



Scheme 3. Numbering used for NMR assignment.

Compound 3. A solution of dimethyl-cyclen (60 mg, 0.3 mmol) and K_2CO_3 (165 mg, 1.2 mmol, 4 eq) in CH_3CN (7.5 mL) was stirred at room temperature for 30 min. To this solution was added dropwise a solution of compound **2** (447 mg, 0.63 mmol, 2.1 eq) in CH_3CN (11.4 mL). The reaction mixture was stirred at 60 °C for 2.5 days before evaporation of solvents to dryness. The residue was taken up in $CHCl_3$ and the residual salts were filtered off. The filtrate was evaporated to dryness to give a brown oil which was dissolved in the minimum amount of ethyl acetate. A large amount of hexane was added and the formation of a dark precipitate was observed. The precipitate was filtered and the filtrate was evaporated and dried under vacuum to give compound **3** (410 mg, 0.29 mmol, 95 %) as an orange oil. Rf (CH_2Cl_2/MeOH, neutral alumina) = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 2H, H4), 7.96 (s, 2H, H3), 7.53 (d, J = 7.6 Hz, 5H), 7.38 (t, J = 7.6 Hz, 5H), 7.30 (d, J = 7.2 Hz, 2H), 7.26 (s, 2H), 3.95 (s, 6H, H_7), 3.87 (s, 4H, H_5), 2.66 (br s, 8H, CH_2 cyclen), 2.63 (brs, 8H, CH_2 cyclen), 2.13 (s, 6H, 2* H_6), 1.92 (s, 6H, 2* H_8), 1.90 (s, 6H, 2* H_8).

^{19}F NMR (282 MHz, $CDCl_3$) δ -107.52, -107.69, -129.29. ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 165.4 (C=O), 162.3, 147.2, 144.9, 142.6, 141.3 (Cq), 137.1 (t, *J* = 23 Hz, $\underline{C}CF_2$), 134.9 (t, *J* = 23 Hz, $\underline{Cq\text{-}}CF_2$), 133.2 (Cq), 132.8, 132.2 (Cq), 129.1, 128.1, 127.9, 125.6 (CH), 125.5, 125.4 (Cq), 124.7, 122.1 (CH), 120.2 (Cq), 116.0 (tt, $^1J_{C\text{-}F}$ = 255 Hz, $^2J_{C\text{-}F}$ = 23 Hz, external CF_2), 110.9 (tquint, $^1J_{C\text{-}F}$ = 270 Hz, $^2J_{C\text{-}F}$ = 25 Hz, central CF_2), 91.7, 86.5 (alkyne), 61.0 (CH_2-pico), 56.1, 53.9 (CH_2 cyclen), 52.9 ($COOCH_3$), 44.3 (CH_3 cyclen), 14.54, 14.49 (C_8). ESI-HR-MS (positive, MeOH) *m/z* calcd. for $[C_{72}H_{63}F_{12}N_6O_4S_4]^+$: 1431.3597, found: 1431.3598, $[M+H]^+$; calcd. for $[C_{72}H_{62}F_{12}N_6NaO_4S_4]^+$: 1453.3416, found: 1453.3420, $[M+Na]^+$; calcd. for $[C_{72}H_{64}F_{12}N_6O_4S_4]^{2+}$: 716.1835, found: 716.1842, $[M+2H]^{2+}$.

L_{oo}. A solution of compound **3** (100 mg, 69.8 µmol) and KOH (1M, 4.37mL) in THF (8.73 mL) was stirred at room temperature for 26 h. Phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were dried over $MgSO_4$ and solvents were evaporated to dryness. The residue was dissolved in the minimum of ethyl acetate and a large amount of hexane was added. The precipitate was filtered and taken up in $CHCl_3$ to give **L_{oo}** (70 mg, 47.3 µmol, 68 %) as an orange oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.52 (d, *J* = 7.5 Hz, 4H), 7.37 (t, *J* = 7.5 Hz, 4H), 7.33 (s, 2H), 7.31 – 7.23 (m, 4H), 7.09 (s, 2H), 4.12 - 2.16 (H of the cyclen), 1.94 (s, 6H, 2* H_8), 1.92 (s, 6H, 2* H_8), 1.81 (s, 6H, 2* H_6). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 170.3, 157.3, 144.4, 142.6, 141.4 (Cq), 137.0 (t, *J* = 23 Hz, $\underline{C}CF_2$), 135.2 (t, *J* = 23 Hz, $\underline{C}CF_2$), 133.2 (Cq), 132.5 (CH), 131.1 (Cq), 129.1, 128.0, 125.6 (CH), 125.5, 125.3 (Cq), 125.1, 124.5, 122.2 (CH), 120.9 (Cq), 116.0 (tt, $^1J_{C\text{-}F}$ = 255 Hz, $^2J_{C\text{-}F}$ = 25 Hz, external CF_2), 110.9 (tquint, $^1J_{C\text{-}F}$ = 270 Hz, $^2J_{C\text{-}F}$ = 25 Hz, central CF_2), 92.2, 85.3 (alkyne), 62.1 (CH_2 pico), 51.1 (CH_2 cyclen), 43.2 (CH_3 cyclen), 14.7 (C_8), 14.5 (C_8). ESI-HR-MS (positive, MeOH) *m/z* calcd. for $[C_{70}H_{59}F_{12}N_6O_4S_4]^+$: 1403.3284, found: 1403.3296, $[M+H]^+$; calcd. for $[C_{70}H_{60}F_{12}N_6O_4S_4]^{2+}$: 702.1678, found: 702.1688, $[M+2H]^{2+}$ with M referring to the conjugated diacid of L_{oo}.

$[YL_{oo}]Cl$. To a solution of compound **L_{oo}** (60 mg, 41 µmol) in MeOH (HPLC grad, 10 mL) was added $YCl_3.6H_2O$ (37 mg, 122 µmol, 3 eq). The pH was controlled at 7 and the reaction mixture was stirred at room temperature for 3.5 days. Solvents were evaporated to dryness and water was added to the residue. Water was then filtered on cotton and the solid kept on the cotton was dissolved with CH_3CN (HPLC grad). CH_3CN was evaporated to dryness and the residue was dissolved in the minimum of CH_2Cl_2. A large amount of hexane was added and the precipitated was filtered, washed with hexane and dried under vacuum to yield **[YL$_{oo}$]Cl** (38 mg, 25 µmol, 61%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 253K) δ : 8.10 (s, 2H), 7.61 (s, 2H), 7.55 (d, *J* = 7.5 Hz, 4H), 7.46 (s, 2H), 7.40 (t, *J* = 7.2 Hz, 4H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.29 (s, 2H), 4.68 (d, *J* = 13.3 Hz, 4H), 4.49 (br s, 2H), 4.05 (d, *J* = 15.2 Hz, 2H), 3.17 (br s, 2H), 3.05 (d, *J* = 10.7 Hz, 2H), 2.89 (d, *J* = 11.8 Hz, 2H), 2.80 (s, 2H), 2.70 (d, *J* = 10.5 Hz, 2H), 2.24 – 2.12 (m, 2H), 2.04 (s, 6H, 2* H_6), 1.92 (s, 6H, 2* H_8), 1.89 (s, 6H, 2* H_8). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 168.2 (C=O), 152.6, 146.5, 142.7, 141.3 (Cq), 137.6 (m, <u>Cq</u>-CF_2), 137.3 (Cq), 134.8 (m, <u>Cq</u>-CF_2), 134.4 (C2), 133.1 (Cq), 129.0, 128.1 , 125.9 (Ar), 125.8 (Cq), 125.6 (Ar), 125.3 (Cq), 122.0 (C1), 119.1 (Cq), 115.9 (tt, $^1J_{C\text{-}F}$ = 255 Hz, $^2J_{C\text{-}F}$ = 25 Hz, external CF_2), 110.9 (tquint, $^1J_{C\text{-}F}$ = 270 Hz, $^2J_{C\text{-}F}$ = 25 Hz, central CF_2), 91.3, 90.2 (Cq alkyne), 54.2 (CH_2 cyclen), 46.1 (CH_3 cyclen), 14.64 (C_8), 14.58 (C_8). ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -110.55, -110.78, -132.34. ^{89}Y NMR (HMBC ^{1}H/^{89}Y, $CDCl_3$) *δ* 250.9. ESI-HR-MS (positive, MeOH) *m/z* calcd. for $[C_{70}H_{56}F_{12}N_6O_4S_4Y]^+$: 1489.2107, found: 1489.2114, $[M+H]^+$; calcd. for $[C_{70}H_{57}F_{12}N_6O_4S_4Y]^{2+}$: 745.1090, found: 745.1102, $[M+2H]^{2+}$.

[YbL$_{oo}$]Cl. Compound **L$_{oo}$** (60 mg, 0.041 mmol) was dissolved in 13 mL of methanol and $YbCl_3.6H_2O$ (24 mg, 0.061 mmol) was then added. After stirring at room temperature for 3.5 days, the solvent was evaporated under vacuum. Water was added and the resulting suspension was filtered. The solid was then extracted with acetonitrile. After evaporation of the solvents, the crude solid was dissolved in the minimum amount of dichloromethane and precipitated in hexane yielding **[YbL$_{oo}$]Cl** as a white bluish solid (51 mg, 80 %). ^{1}H NMR: (500 MHz, CD_2Cl_2) δ 83.88 (2H, H_3/H_4), 55.60 (2H, H_3/H_4), 27.35 (2H, H_{cyclen}), 20.29 (2H, H_{cyclen}), 15.43 (2H, H_{cyclen}), 10.47 (2H, H_{cyclen}), 7.35-7.22 (10H, H_{ph}), 6.97 (2H, H_2), 6.37(2H, H_1), 1.60-1.50 (12H, CH_3), -2.53 (2H, H_{cyclen}), -7.12 (2H, H_{cyclen}), -15.92 (2H, H_{cyclen}), -30.94 (6H, H_6), -40.64(2H, H_{cyclen}). EA C 49.07; H 3.78; S 6.52; N 4.41, Calcd for $C_{70}H_{56}ClF_{12}N_6O_4S_4Yb.5H_2O$ C 49.46; H 3.91; S 7.54; N 4.94 ESI-HR-MS (positive, MeOH) *m/z* calcd. for $[C_{70}H_{56}YbF_{12}N_6O_4S_4]^+$: 1574.2456, found: 1574.2437, $[M+H]^+$; calcd. for $[C_{70}H_{57}YbF_{12}N_6O_4S_4]^{2+}$: 787.6277, found: 787.6295, $[M+2H]^{2+}$.

[YbL$_{cc}$]Cl was obtained upon UV irradiation (see SI). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 84.99(2H, H_3/H_4), 53.37 (2H, H_3/H_4), 27.44 (2H, H_{cyclen}), 21.74 (2H, H_{cyclen}), 14.92 (2H, H_{cyclen}), 11.24-9.50 (2H, H_{cyclen}), 7.42-7.33 (10H, H_{ph}), 6.51 (2H, H_2), 5.65 (2H, H_1), 1.76-1.70 (12H, CH_3), -2.24 (2H, H_{cyclen}), -6.44 (2H, H_{cyclen}), -16.34(2H, H_{cyclen}), -32.25(6H, H_6), -38.40(2H, H_{cyclen}).

[EuL$_{oo}$]Cl. Compound **L$_{oo}$** (46 mg, 0.031 mmol) was dissolved in 10 mL of methanol (HPLC grad) and $EuCl_3.6H_2O$ (28 mg, 0.076 mmol) was then added. After stirring at room temperature for 3.5 days, the solvent was evaporated under vacuum. Water was added and the resulting suspension was filtered. The solid was then extracted with acetonitrile (HPLC grad). After evaporation of the solvents, the crude solid was dissolved in the minimum amount of dichloromethane and precipitated in hexane yielding **[EuL$_{oo}$]Cl** as a pale yellow solid (44 mg, 90 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 38.43(2H, H_3/H_4), 25.75(2H, H_3/H_4), 7.49 (d, 4H, H_{ph}), 7.36 (t, 4H, H_{ph}), 7.28 (t, 4H, H_{ph}), 7.20 (2H, H_2), 7.04 (2H, H_1), 2.59-2.34 (10H, H_5 + 6H_{cyclen}) 1.99 (6H, 2* H_8), 1.85 (6H, 2* H_8), -3.09 (2H, H_{cyclen}), -7.56 (2H, H_{cyclen}), -9.13 (6H, H_6), -10.28 (2H, H_{cyclen}), -13.52 (2H, H_{cyclen}), -15.45 (2H, H_{cyclen}). EA C 50.94; H 3.81; S 7.39; N 4.76, Calcd for $C_{70}H_{56}ClF_{12}N_6O_4S_4Eu.4H_2O$ C 50.62; H 3.88; S 7.72; N 5.06. ESI-HR-MS (positive, MeOH) *m/z* calcd. for $[C_{70}H_{56}EuF_{12}N_6O_4S_4]^+$: 1553.2261, found: 1553.2264, $[M+H]^+$; calcd. for $[C_{70}H_{57}EuF_{12}N_6O_4S_4]^{2+}$: 777.1167, found: 777.1178, $[M+2H]^{2+}$.

[EuL$_{cc}$]Cl was obtained upon UV irradiation (see SI), ^{1}H NMR (500 MHz, CD_2Cl_2) δ 38.68 (2H, H_3/H_4), 24.96 (2H, H_3/H_4), 7.55-7.43 (10H, H_{ph}), 6.70 (2H, H_2), 6.20 (2H, H_1), 2.89 (10H, H_5 + 6H_{cyclen}), 2.11-2.09 (12H, CH_3), -3.52 (2H, H_{cyclen}), -7.91 (2H, H_{cyclen}), -9.50 (8H, 6H_6 and 2H_{cyclen}), -13.79 (2H, H_{cyclen}), -15.11 (2H, H_{cyclen}).

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