

Highly Efficient Blue Photoexcitation of Europium in a Bimetallic Pt–Eu Complex

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Abstract: We report the preparation and characterization of dinuclear Pt–Ln complexes constructed from a square-planar Pt^{II} core bearing an ethynyl-terpyridine residue connected to platinum by the ethynyl bond. Complexation of the neutral Eu(hfac)₃ (hfac = hexafluoroacetylacetonate) fragment to free terpyridine (terpy) gives a stable bimetallic complex (log β = 6.7). In the crystal structure, the flat Pt≡terpy core coordinates to Eu^{III}, which is nonacoordinated with the three nitrogen atoms of the terpy

subunit and six oxygen atoms of the three hfac ligands. These atoms form a distorted monocapped square antiprism with a pseudo-*C*₂ symmetry axis passing through the nitrogen atom of the central pyridine ring and the Eu atom. Spectroscopic measurements showed that irradiation with visible light of wavelength up to 460 nm in the

¹MLCT state of the Pt subunit resulted in a quantitative energy transfer to the Eu center, which strongly luminesces in the red with an overall luminescence quantum yield of 38%. The energy-transfer process is quantitative and not sensitive to oxygen, and the complexation of Eu to the Pt metallosynthon allows the recovery of the energy lost due to triplet-oxygen quenching of the ³MLCT state observed in the uncomplexed Pt precursor.

Keywords: electrochemistry • energy transfer • europium • luminescence • platinum

Introduction

Chromophoric ligands that photosensitize lanthanide-ion luminescence are of intense current interest.^[1] Their complexes are used in significant technological applications such as fluoroimmunoassays^[2] and cellular imaging,^[3] chemosensors,^[4] optical communication,^[5] and optoelectronic devi-

ces.^[6] As population of f–f excited states by direct absorption is very inefficient, a light-harvesting ligand is essential for light emission from the metal-ion states. Such ligands commonly absorb in the UV region, although systems are known for which visible-light sensitization is effective. In particular, polyaza ligands such as 3,6-bis(2-pyridyl)tetrazine,^[7] dipyrzolytriazine,^[8] and thioxanthone^[9] appear to be very challenging for this purpose. A recent development in the search for better visible-region sensitizers was concerned with the use of phosphorescent transition-metal complexes to sensitize emission (e.g., from Yb, Nd, Er) in the near-IR region.^[10,11] Amongst these luminescent Pt^{II}(bipyridine)(diacetylide)^[12] complexes, 2,3-bis(2-pyridyl)pyrazine d–f dinuclear complexes^[13] or multimetallic edifices with a diphosphine-tethered Pt–Pt core^[14] were found to be quite effective. A particularly attractive synthetic strategy was established for the design of heterotetranuclear Pt₂Ln₂ and heterohexanuclear Pt₂Ln₄ arrays, in which phenanthroline–acetylide ligands are bound to a central and soft Pt^{II}-based core and hard lanthanide luminophores.^[14] The central chromophore tethered by bridging diphosphine ligands provide the antennae for visible-light absorption, whereas an efficient intramolecular energy-transfer (IET) process occurs, thus facilitating the sensitization of the lanthanide emission.

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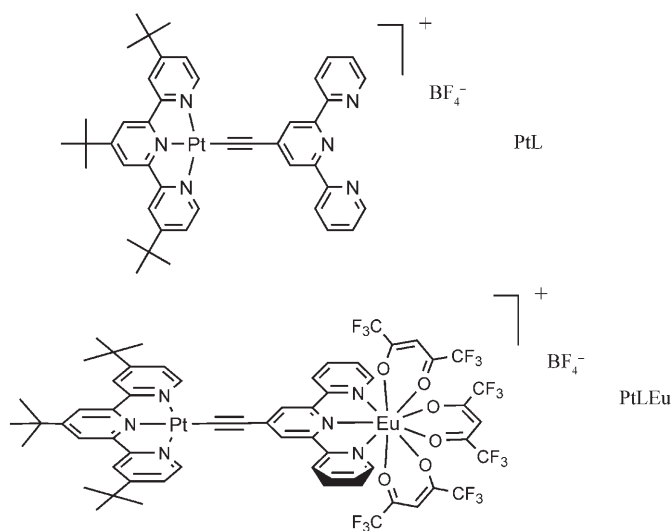
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In contrast, very few examples deal with the metallosynthesis photosensitization of lanthanide cations that emit in the visible part of the electromagnetic spectrum. Such cations, particularly Eu and Tb, display the longest excited-state lifetimes in the 4f series by reaching the millisecond timescale,^[15] which is of unique interest in time-resolved applications.^[16] At such wavelengths, excitation can be easily achieved by cheap sources such as blue light-emitting diodes (LEDs). It also avoids the need for special UV optical components and diminishes the problems inherent to photodecomposition of the samples. However, the small energy gap associated with excitation and emission in the visible domain is hardly compatible with efficient photosensitization, and only a few examples concerning Eu complexes have been reported. Thus, visible photosensitization was observed in the case of the tethered Pt–Pt core^[14] and in an ionic Ir/Eu complex.^[17] However, in both cases, the luminescence quantum yields were low at less than 2 and 7%, respectively. The lack of data for Eu sensitization in the visible region is probably due to the high energy of the triplet state required for the sensitization process of Eu,^[18] which few transition-metal complexes can indeed provide. Additionally, long-lived excited states would favor the IET process, a property well-established with tridentate terpyridine Pt^{II} complexes.^[19]

We turned our attention toward the use of acetylide Pt^{II} complexes that display pronounced metal-to-ligand charge-transfer (MLCT) states and intriguing photophysical proper-

ties. These include strong visible absorption and intense phosphorescence, which have been exploited for the understanding of ultrafast kinetic events^[20] and the engineering of electroluminescent thin films and organic light-emitting devices (OLEDs).^[21,22] Furthermore, the kinetic robustness of Pt^{II} complexes in general has enabled their use for interactions with biomolecules^[23] and has permitted the Pt core to be retained during reactions that involve the introduction or modification of peripheral substituents.^[24,25]

Recognition of all these properties prompted us to construct a metalloligand (PtL) carrying a vacant terpyridine residue suitable for lanthanide coordination. The coordina-



Abstract in French: Un protocole de synthèse a été établi pour préparer des complexes mixtes de platine(II) et de lanthanides(III) connectés par l'intermédiaire d'un ligand constitué d'un pont acétylène. Le choix d'un site terpyridine a été privilégié pour complexer un fragment Eu(hfac)₃ et former un complexe stable ayant une constante d'association de $\log \beta = 6.7$. La structure moléculaire déterminée par diffraction aux rayons X confirme la chélation du fragment Pt≡terpy sur le centre europium en raison de la présence de ligands électro-attracteurs de type hexafluoroacétylacétonate (hfac). Le nombre de coordination du cation europium est de neuf fourni par les trois atomes d'azote de la terpyridine et les six atomes d'oxygène des ligands hfac. La sphère de coordination de l'Eu^{III} est décrite comme un antiprisme déformé mono-capé avec un pseudo axe d'ordre deux passant par la pyridine centrale et l'atome d'euporium. Les études spectroscopiques démontrent que l'irradiation dans le visible jusqu'à 460 nm, correspondant à l'absorption ¹MLCT de la sous-unité platine, est à l'origine d'un transfert quantitatif d'énergie vers les niveaux émissifs de l'euporium, donnant une émission exclusive du centre europium. Le rendement quantique de luminescence est de 38% et l'efficacité du processus n'est pas sensible à l'oxygène contrairement à la phosphorescence du complexe précurseur de platine. Les perspectives de ce travail sont présentées dans la conclusion.

tion sphere of the europium atom was fulfilled by the coordination of three bidentate hexafluoroacetylacetonate (hfac) anions, which was preferable to the thenoyltrifluoroacetate (TTA) anions to minimize the overlapping of the excitation due to the PtL fragment and that of the β -diketonate in the visible domain.^[7] This special molecular design is motivated by the possibility of obtaining very efficient IET owing to the correct balance between the energy level of the triplet state of platinum and the luminescence level of Eu. The high stability of the emergent complexes and the non-sensitivity towards oxygen are additional motivations to prepare and study these novel d–f dinuclear complexes. Until now, very few studies have addressed the problem of quenching with molecular oxygen.^[7,10a,b,12]

Results and Discussion

The PtL complex was prepared in 88% yield by reaction of [(*t*Buterpy)PtCl](BF₄) (*t*Buterpy = 4,4',4''-*tert*-butyl-2,2':6',2''-terpyridine)^[26] with 4'-ethynyl-2,2':6',2''-terpyridine^[27] in *N,N*-dimethylformamide (DMF) mediated by CuI (3 mol%) under anaerobic conditions.

The interaction of the resulting PtL complex with Eu^{III} was first studied by spectrophotometric titration in CH₂Cl₂/

CH₃OH with [Eu(hfac)₃(H₂O)₂] (Figure 1). Upon addition of the Eu^{III} complex, the ¹MLCT absorption band of the Pt^{II} complex at 409 nm was gradually displaced toward higher energy until one equivalent was added. An intense absorp-

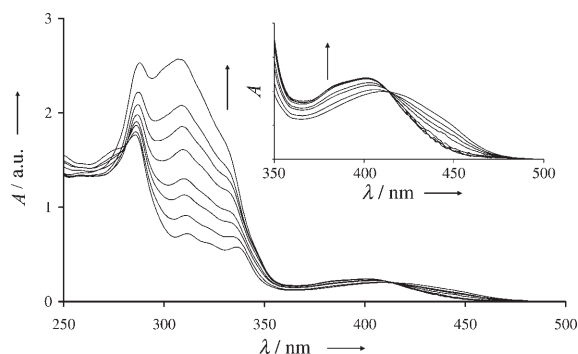


Figure 1. UV/Vis spectrophotometric titration of a 2.7×10^{-5} M solution of PtL by addition of 0, 0.17, 0.33, 0.50, 0.67, 0.89, 1.11, and 1.67 equivalents of [Eu(hfac)₃(H₂O)₂] in CH₂Cl₂/MeOH (99:1). Inset: Enlargement of the 350–500 nm region showing the isosbestic point at 411 nm.

tion band appearing concomitantly at around 320 nm was assigned to the $n \rightarrow \pi^*$ transitions of the hfac moieties. The presence of an isosbestic point at 411 nm suggests that a single equilibrium is involved. Evolution of the absorbances at different wavelengths together with evolving-factor analysis with the Specfit software^[28] also point to the formation of a single species. The titration can be readily fitted on the basis of the following equilibrium [Eq. (1)]:



Analysis of the absorbance changes provided a conditional stability constant for a 1:1 species of $\log \beta = 6.7 \pm 0.6$, in which β is given by Equation (2):

$$\beta = [\text{PtLEu}(\text{hfac})_3] / ([\text{PtL}] \times [\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]) \quad (2)$$

The high stability of the complex prompted us to isolate the PtLEu complex by mixing PtL with [Eu(hfac)₃(H₂O)₂] in dichloromethane at room temperature followed by crystallization in chloroform/cyclohexane (79% yield). The ¹H NMR spectrum of the PtLEu complex in CD₃OD showed five broad patterns for protons of the terpy unit coordinated to the Eu center spread over 12 ppm due to the paramagnetic contribution of the Eu atom. Each of these signals is from the equivalent of two protons with respect to that of the *t*Bu group. The *t*Buterpy/Pt core displays four additional patterns (each corresponding to 2H), which are loosely affected by the Eu atom. The degeneracy of the proton signals agrees with a C₂ axis that passes through the Pt and Eu atoms, as later confirmed by the X-ray molecular structure.

Slow diffusion of cyclohexane into a dilute solution of PtLEu in CDCl₃ containing trace amounts of CH₃OH afforded brown-orange single crystals suitable for X-ray dif-

fraction analysis. The molecular structure confirmed Eu-(hfac)₃ complexation to the free terpy unit of the PtL metallosynthon to form the PtLEu complex (Figure 2), the overall charge of which is balanced by the presence of a BF₄[−] anion.

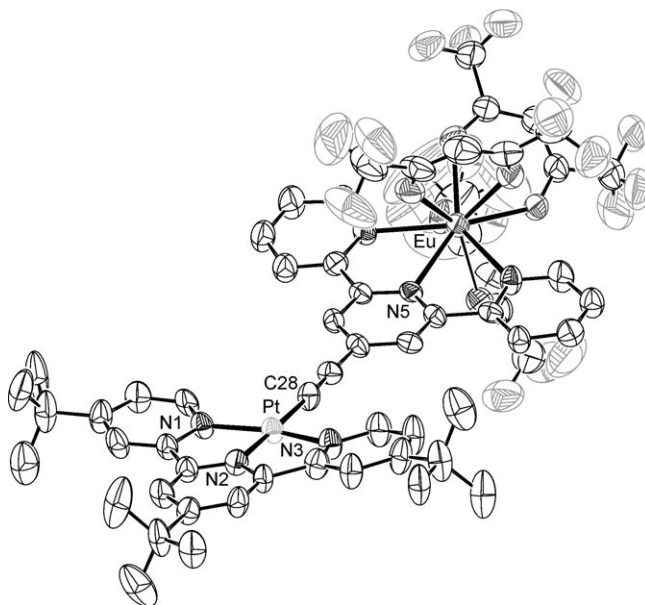


Figure 2. ORTEP view of PtLEu (ellipsoids at 50% probability), with hydrogen atoms omitted for clarity. Selected angles (°): N1–Pt–N2 = 80.7, N2–Pt–N3 = 80.5, N1–Pt–C28 = 99.4, N3–Pt–C28 = 99.5. The Eu–N5 bond length is 2.54 Å, and the average lateral pyridine N–Eu bond length is 2.52 Å; Eu–O bond lengths are 2.31–2.47 Å.

The coordination geometry of the Pt^{II} cation is distorted towards a lozenge as a result of the steric constraints of the *t*Buterpy ligand. Within the PtL moiety, the two terpy subunits display a pseudo-C₂ axis that passes through N2–Pt–C28 and the nitrogen atom of the central pyridyl ring (N5) coordinated to Eu. The Eu atom is slightly displaced from this axis with an Eu–N5–Pt angle of 164°. The Eu^{III} center is nonacoordinated with the three nitrogen atoms of the ethynyl terpyridine unit and six oxygen atoms of the three hfac ligands to form a distorted monocapped square antiprism with a pseudo-C₂ axis passing through N5 and the Eu atom (Figure 3). The asymmetric unit consists of three independent units of PtLEu (inclusive of anions and solvent), the main difference in the units being the relative orientation of the two terpy platforms. The twist angle passes from 10.4° (molecule 1) to 25.9° (molecule 2), through to 35.8° for molecule 3, which displays the greatest disorder of the hfac groups.

The crystal packing of these elongated molecules does not appear to involve significant terpy π – π stacking interactions, which may be owing to the bulk around the Eu atom, but there are numerous sub-van der Waals contacts to the aromatic rings that involve the trifluoromethyl and BF₄[−] groups as well as the CDCl₃ solvent molecules.

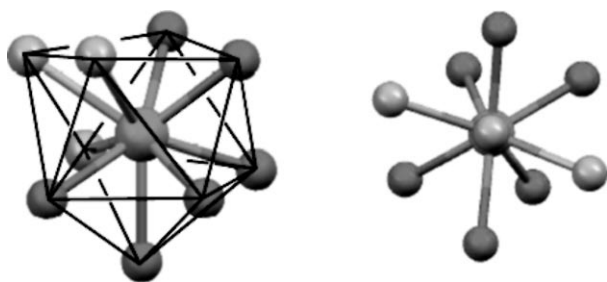


Figure 3. Left: Coordination polyhedron around Eu in the PtLEu complex. Right: View of the polyhedron along the pseudo- C_2 axis.

To demonstrate photosensitization of the Eu^{III} ion by the Pt core, a titration experiment was performed in which the phosphorescence spectrum of a solution of PtL was monitored upon addition of increasing amounts of $[\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]$ (Figure 4). At 411 nm, the observed isosbestic point

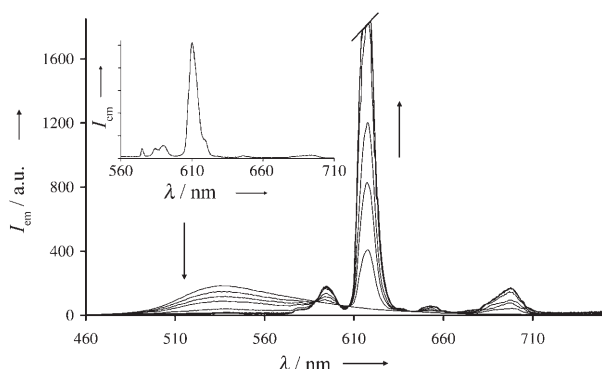


Figure 4. Luminescence spectra ($\lambda_{\text{ex}} = 411 \text{ nm}$) of a solution of PtL ($2.7 \times 10^{-3} \text{ M}$) upon addition of 0, 0.17, 0.33, 0.50, 0.67, 0.89, 1.11, and 1.67 equivalents of $[\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]$. Inset: High-resolution (2.5 \AA) phosphorescence spectrum of PtLEu in CH_2Cl_2 .

(Figure 1), absorption is exclusively due to the singlet MLCT transitions of PtL and PtLEu, so any possible sensitization that involves hfac can be excluded. Upon addition of the Eu precursor, the broad $^3\text{MLCT}$ emission of PtL centered at around 537 nm gradually disappeared, to be replaced by the typical $^5\text{D}_0 \rightarrow ^7\text{F}_j$ electronic transitions of Eu^{III} at 580 (1.4), 595 (8.7), 617 (85.6), 653 (0.7), and 698 nm (3.6% relative intensity) for $J = 0-4$, respectively, thus clearly pointing to an efficient Eu photosensitization through the $^1\text{MLCT}$ absorption of the Pt moiety. The particularly intense $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is typical of β -diketonate-ligand complexes (Figure 4, inset).^[29]

Interestingly, the excitation spectrum recorded upon europium emission at 615 nm (Figure 5) does not match perfectly with the absorption spectrum in the visible region, which corresponds to the $^1\text{MLCT}$ transition. The excitation was found to be more efficient in the low-energy end of the transition. This behavior was further confirmed by time-resolved excitation spectra of the solution in which the excitation was monitored over a period of $2 \mu\text{s}$ after a varying delay following pulsed excitation. From such spectra (Figure 5, inset),

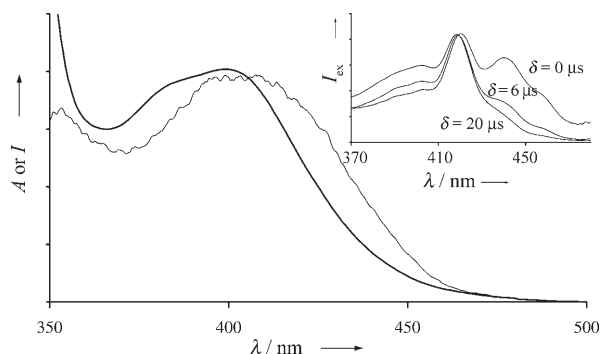


Figure 5. Absorption (bold line) and excitation ($\lambda_{\text{em}} = 615 \text{ nm}$, integration window 10 ms) spectra of PtLEu in CH_2Cl_2 . Inset: Time-resolved excitation spectra (integration window $2 \mu\text{s}$, normalized at 420 nm) recorded after 0, 6, and $20 \mu\text{s}$.

one can observe that the excitation band between 370 and 470 nm can be divided into three main regions. At low energy (440 nm), the excitation of europium is instantaneous within the time resolution of the apparatus. The excitation at about 420 nm is also rapidly obtained and displayed a maximum. At higher energy (390 nm), the excitation phenomenon took more time and only reached its maximum after 15– $20 \mu\text{s}$. Unfortunately, the time resolution of the experimental setup did not allow for a better quantitative treatment of the data, from which energy-transfer rates would have been obtained. Nevertheless, these results show that the $^1\text{MLCT}$ absorption band is composed of at least three different components originating from a vibrational substructure or from an admixture of MLCT and LLCT states, as previously found for other Pt- σ -alkyne complexes.^[30]

The luminescence decay at 616 nm ($\lambda_{\text{ex}} = 450 \text{ nm}$) was purely monoexponential with a lifetime of $(868 \pm 13) \mu\text{s}$, whereas the measured lifetime for the $[\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]$ precursor was $(401 \pm 20) \mu\text{s}$ ($\lambda_{\text{ex}} = 300 \text{ nm}$). The twofold increase in the luminescence lifetime points to a displacement of the solvent molecules from the first coordination sphere of the europium by the terpy residue, with a concomitant decrease of the nonradiative deactivation pathways associated with the CH and OH oscillators of the solvent.^[31]

Surprisingly, the overall luminescence quantum yield upon $^1\text{MLCT}$ excitation increased from 20% for the PtL metallosynthon to 38% when Eu is coordinated under air-equilibrated conditions. Two hypotheses were envisaged to account for the observed luminescence increase: 1) an improvement in the $^3\text{MLCT}$ luminescence efficiency due to a better $^1\text{MLCT} \rightarrow ^3\text{MLCT}$ intersystem crossing arising from the heavy-atom effect upon lanthanide coordination, or 2) a very efficient $^3\text{MLCT} \rightarrow \text{Ln}^*$ process that is able to compete with bimolecular quenching of the $^3\text{MLCT}$ state by triplet oxygen. The first possibility was checked by UV/Vis absorption and phosphorescence titration experiments with $[\text{La}(\text{hfac})_3(\text{H}_2\text{O})_2]$ in place of Eu. The lack of an accessible excited state for La^{III} precludes energy migration and makes La^{III} a good probe to address a possible heavy-atom effect.

However, spectrophotometric titration revealed complexation behavior very similar to that of Eu with the formation of a PtLLa species (Figure 6), and luminescence measurements showed a strong quenching of the $^3\text{MLCT}$ emission

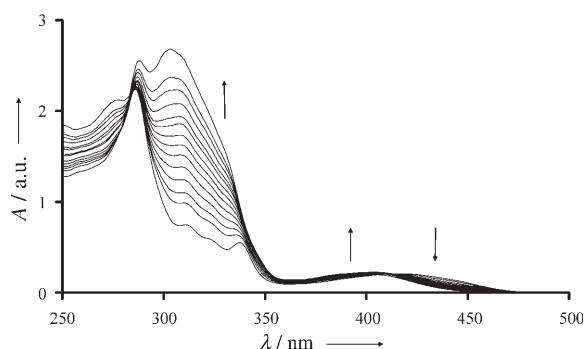


Figure 6. UV/Vis absorption titration of a $2.38 \times 10^{-5} \text{ M}$ solution of PtL containing 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.1, 2.5, 3.0, and 4.0 equivalents of $[\text{La}(\text{hfac})_3(\text{OH}_2)_2]$ in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99:1).

($\Phi = 1.9\%$) with a modest hypsochromic shift (Figure 7). Similar effects with various near-IR (NIR) lanthanide emitters were previously observed,^[12] which were tentatively ascribed to the emergence of additional vibrational modes introduced by coordination of the $\text{La}(\text{hfac})_3$ fragment that might provide nonradiative quenching pathways for the MLCT excited state.

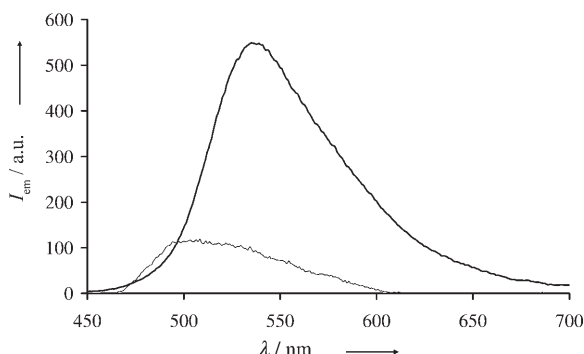


Figure 7. Fluorescence spectra of PtL in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99:1) in the absence (bold line) or presence of 4 equivalents of $[\text{La}(\text{hfac})_3(\text{OH}_2)_2]$ ($\lambda_{\text{ex}} = 411 \text{ nm}$).

Alternatively, the raising of the energy of the Pt-centered $^3\text{MLCT}$ state by coordination of the electron-withdrawing $\text{La}(\text{hfac})_3$ subunit, as observed during the titration (Figure 6), brings the triplet state close in energy to an energetically higher lying, short-lived, and nonradiative state such as the d–d state, which provides an efficient deactivation channel through a thermally activated equilibration process.

In contrast, thorough deoxygenation of a solution of PtL led to a dramatic increase in the $^3\text{MLCT}$ quantum yield to 39%. Importantly, the luminescence quantum yield of the Eu complex was almost unchanged upon deoxygenation

(<1%), thus revealing a very small quenching effect of oxygen. This observation strongly supports the hypothesis that the increase in the overall luminescence quantum yield observed upon complexation of Eu to PtL is the result of a very efficient energy transfer from the Pt-centered MLCT state to the Eu excited state. As the overall luminescence efficiency is the product of the Pt→Eu energy-transfer efficiency and the Eu-centered quantum yield, measurement of the latter would allow the determination of the former. Determination of the Eu-centered quantum yield was achieved by the method developed by Werts et al.^[29]

On the basis of the relative contributions of the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($J=0-4$) transitions and by neglecting the weak emission arising from transitions to the $^7\text{F}_5$ and $^7\text{F}_6$ levels (a contribution of <3% of the total emission),^[29] the radiative lifetime of Eu in the complex, τ_r , and the metal-centered luminescence quantum yield of Eu, Φ_{Eu} , can be calculated by using Equations (3) and (4):^[29,34]

$$1/\tau_r = A_{\text{MD},0} n^3 (I_{\text{tot}}/I_{\text{MD}}) \quad (3)$$

$$\Phi_{\text{Eu}} = \tau_{\text{obs}}/\tau_r \quad (4)$$

in which $A_{\text{MD},0}$ is the spontaneous emission probability for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition in vacuo (14.65 s^{-1}), n is the refractive index of the medium (1.425 for CH_2Cl_2), $I_{\text{tot}}/I_{\text{MD}}$ is the ratio of the total area of the corrected Eu emission spectrum to the area of the magnetic-dipole-allowed $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, and τ_{obs} is the observed luminescence lifetime. This gives a very short radiative lifetime of 2.06 ms, which leads to an Eu-centered quantum yield of 42%. By using the value of the measured luminescence quantum yield of Eu upon $^1\text{MLCT}$ excitation (38%; Table 1), the sensitization efficiency was found to be quantitative (>99%) within the limits of experimental error. This is in perfect agreement with the observation that complexation of Eu not only leads to $^3\text{MLCT}$ quenching as a result of the formation of the Eu

Table 1. Photophysical and electrochemical properties of PtL and PtLEu in CH_2Cl_2 .

	Absorption λ_{max} [nm] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$])	Emission E [cm^{-1}]	Φ [%] ^[c]	E_{red}^0 [V] (ΔE [mV]) ^[f]
PtL	409 (7620)	18 690 ^[a]	20 ^[d]	−0.96 (80)
	335 (21 650)			
	311 (26 420)		39 ^[e]	−1.43 (80)
	285 (65 640)			
PtLEu	401 (9440)	16 180 ^[b]	38 ^[d]	−0.94 (80)
	308 (75 400)		38 ^[e]	−1.46 (70)
	287 (78 930)			−1.73 (90)

[a] $^3\text{MLCT}$ emission. [b] $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition on Eu. [c] Relative estimated error $\pm 15\%$. [d] Air-equilibrated solution with rhodamine 6G^[32] as reference for PtL and $[\text{Ru}(\text{bipyridine})_3]\text{Cl}_2$ ^[33] for PtLEu. [e] Degassed with nitrogen. [f] Potentials determined by cyclic voltammetry in deoxygenated CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) at a solute concentration of 1.5 mM and at room temperature. Potentials were standardized versus ferrocene (Fc) as internal reference and converted into the SCE (saturated calomel electrode) scale based on the assumption that $E_{1/2}(\text{Fc}/\text{Fc}^+) = +0.38 \text{ V}$ ($\Delta E_p = 60 \text{ mV}$) versus SCE. The error in half-wave potentials is $\pm 15 \text{ mV}$ at a scan rate of 200 mV s^{-1} . All waves were the result of a one-electron process.

excited state, it is also able to compete with the diffusion-controlled deactivation of triplet oxygen. An energy diagram with the main energy levels sketched is provided in Figure 8.

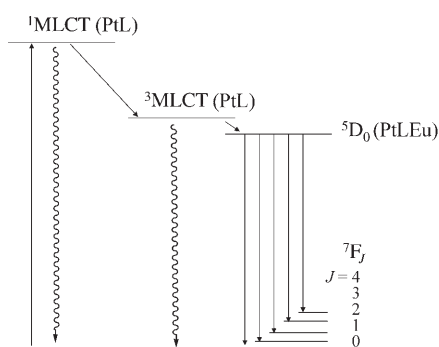


Figure 8. Schematic representation of the main energy levels involved in the energy-transfer processes.

Finally, confirmation of the strong affinity of $[\text{Eu}(\text{hfac})_3]$ for the metalloligand was given by cyclic voltammetry in CH_2Cl_2 containing a background electrolyte. For PtL, two reversible reduction processes that peaked at -0.96 and -1.43 V were observed (Figure 9). The first wave is due to

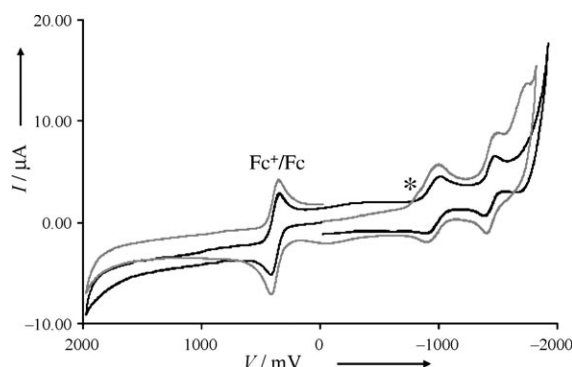


Figure 9. Cyclic voltammogram of PtL (black) and PtLEu (gray) in dichloromethane containing 0.1 M TBAPF_6 at room temperature, scan rate 200 mVs^{-1} . Fc was used as internal reference with a platinum wire as the pseudoreference electrode. * = Shoulder due to the presence of trace amounts of water from the precursor complex.

reduction of the *t*Buterpy ligand, whereas the second is tentatively assigned to metal-centered^[35] or double reduction of the *t*Buterpy ligand by electron pairing in the same orbital, as previously hypothesized in more-complex architectures.^[36] Interestingly, both reduction processes remained little affected by addition of increasing amounts of $[\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]$. At 1:1 stoichiometry, a new wave was found at -1.70 V. This additional reduction appeared at a similar potential in an authentic sample of PtLEu and is not centered on the Eu(hfac) fragment (reduction potential < -2.70 V in *o*-dichlorobenzene) but on the ethynyl terpy unit bonded to the acidic Eu center. Previous studies by Richter and Bard revealed that reduction of Eu^{III} in strongly acidic complexes

also occurs at very anodic potentials.^[37] A similar wave at -1.73 V was found with $[\text{La}(\text{hfac})_3(\text{H}_2\text{O})_2]$, which excludes definitely the reduction of europium in this potential range. Clearly, the *t*ButerpyPt≡ fragment was little affected by the lanthanide center, whereas the ethynyl terpy fragment was easier to reduce by 400 mV with respect to uncomplexed terpy (-2.1 V under standard conditions). These observations allow us to conclude that both metallofragments are kept independent, an observation in line with the minor variation of the MLCT absorption band observed upon titration of PtL by Eu or La salts.

Conclusions

The key feature of the present molecular design is the grafting of a square-planar Pt(*tert*-butylterpy) unit onto an ethynyl terpy ligand suitable for complexation of Ln^{III} . The deep-orange PtLEu complex exhibits four interesting features: 1) relative ease of synthesis and high stability of the resulting heterodinuclear complex; 2) strong luminescence of the Eu center due to quantitative energy transfer from visible-light irradiation up to 460 nm; 3) a luminescence quantum yield of 38% independent of the presence of oxygen with a lifetime of 868 μs ; 4) redox behavior of the terpy/Pt unit that is insensitive to binding of the neutral Ln^{III} species. Although these properties remain restricted to display in organic solvents, the strong sensitization of Eu^{III} in the visible domain (up to 460 nm) by the use of a phosphorescent Pt(terpy) complex paves the way for the design and engineering of smart labels for luminescence microscopy and biomaterial labeling.^[16]

Experimental Section

Materials and Methods

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at room temperature on Bruker Advance 300 or AC 200 spectrometers. Chemical shifts (δ) are reported in ppm relative to solvent residual-proton signals.^[38] IR spectra were recorded as KBr disks on a Nicolet 210 spectrometer. UV/Vis absorption spectra were recorded on a Uvikon 933 (Kontron Instruments) spectrophotometer. Emission spectra were recorded on a Perkin-Elmer LS 50B spectrofluorimeter equipped with an R928 (Hamamatsu) photomultiplier. Spectra were recorded in the phosphorescence mode with 0- μs delay and 10-ms integration windows at 20 Hz. Europium luminescence lifetimes ($\pm 5\%$) and high-resolution europium emission spectra (2.5 \AA) were obtained on a PTI QuantaMaster spectrofluorimeter. Luminescence quantum yields were measured by using the procedure described by Haas and Stein.^[39] Fast atom bombardment (FAB, positive mode) mass spectra were recorded on a ZAB-HF-VB analytical apparatus with *meta*-nitrobenzyl alcohol (*m*-NBA) as matrix. Chromatographic purification was performed with 0.040–0.063-mm silica gel (Merck). Thin-layer chromatography (TLC) was performed on silica-gel plates (Merck) coated with a fluorescence indicator.

Syntheses

PtL: $[(t\text{Buterpy})\text{PtCl}](\text{Cl})$ ^[26] (0.163 g, 0.244 mmol) was dissolved in a mixture of DMF (3 mL) and triethylamine (1 mL), and 4-ethynyl-2,2':6',6''-terpyridine^[27] (0.063 g, 0.244 mmol) was then added. The solution was vigorously degassed by bubbling with argon. The addition of CuI (1.0 mg,

0.005 mmol) to the yellow solution resulted in an instantaneous color change to red. After the mixture was stirred at room temperature overnight, the deep-yellow solution was concentrated to 1 mL, filtered over celite, and added dropwise to an aqueous solution (10 mL) of NaBF₄ (1.200 g). The complex was recovered by filtration over paper and washed with water (3 × 100 mL), and the red solid obtained was dried under high vacuum. Purification was achieved by column chromatography with alumina as the solid support and methanol (0–1 %) in dichloromethane as the mobile phase. Ultimate recrystallization by slow evaporation of dichloromethane from a solution of dichloromethane/hexane afforded PtL (0.202 g, 88 %). UV/Vis (CH₂Cl₂): λ (ϵ) = 410 (7600), 336 (21700), 311 (27100), 285 nm (66200 M⁻¹cm⁻¹); FTIR (KBr): $\tilde{\nu}$ = 3338 (m), 2960 (m), 2122 (m, $\nu_{C\equiv C}$), 1614 (s), 1582 (s), 1563 (s), 1466 (s), 1392 (m), 1261 (m), 880 (m), 792 cm⁻¹ (m); ¹H NMR (200.1 MHz, CDCl₃): δ = 9.12 (d, ³J = 6.0 Hz, 2H), 8.97 (s, 2H), 8.96 (s, 2H), 8.89 (d, ³J = 8.0 Hz, 4H), 8.69 (dm, ³J = 4.8 Hz, 1H), 8.61 (d, ³J = 8.0 Hz, 1H), 8.47 (s, 2H), 7.87 (td, ³J = 8.0 Hz, ⁴J = 1.9 Hz, 1H), 7.75–7.55 (m, 2H), 7.35–7.35 (m, 1H), 1.65 (s, 9H), 1.52 ppm (s, 18H); ¹³C{¹H} NMR (100.6 MHz): δ = 169.3, 169.1, 168.3, 167.7, 162.5, 158.9, 158.5, 156.1, 155.2, 154.2, 153.9, 150.9, 149.1, 125.2, 124.5, 124.3, 123.9, 123.5, 122.9, 122.6, 121.4, 30.8, 30.4, 37.9, 36.6 ppm; MS (ESI, CH₂Cl₂): m/z (%) = 852.4 (100) [M–BF₄]⁺; elemental analysis: calcd (%) for C₄₄H₄₅N₆O₆PtBF₄ (M_r = 939.75): C 56.24, H 4.83, N 8.94; found: C 55.75, H 4.62, N 8.63.

PtLEu: A solution of [Eu(hfac)₃·2H₂O]^[40] (0.066 g, 0.080 mmol) in dichloromethane (5 mL) was added dropwise to an anhydrous solution of PtL (0.064 g, 0.068 mmol) in dichloromethane (10 mL) under argon at room temperature. No obvious color change was observed after one night of stirring. After the mixture was evaporated to dryness, the bright-orange solid was dissolved in chloroform, and the solution was filtered over cotton wool and celite, mixed with methanol (a few drops), and overlaid with cyclohexane. The resulting crystals were collected after two weeks of standing and dried under high vacuum (0.092 g, 79 %). UV/Vis (CH₂Cl₂): λ (ϵ) = 401 (9500), 332 (53400), 308 (75400), 286 nm (78900 M⁻¹cm⁻¹); FTIR (KBr): $\tilde{\nu}$ = 3400 (m), 2980 (m), 2110 (m, $\nu_{C\equiv C}$), 1646 (s), 1593 (s), 1401 (m), 1242 (m), 1189 (m), 1129 cm⁻¹ (m); ¹H NMR (200.1 MHz, CD₃OD): δ = 12.01 (br s, 2H), 10.38 (br t, 2H), 9.16 (d, ³J = 6.2 Hz, 2H), 8.52 (br s, 2H), 8.48 (br s, 1H), 8.34 (br s, 2H), 7.96 (br t, ³J = 8.2 Hz, 2H), 7.87 (d, ³J = 6.2 Hz, 2H), 7.46 (br t, ³J = 8.2 Hz, 2H), 7.45 (t, ³J = 8.2 Hz, 2H), 6.70 (br d, ³J = 6.3 Hz, 2H), 1.58 (s, 9H), 1.49 ppm (s, 18H); MS (ESI, CH₃OH): m/z (%) = 1628.3 (60), 1627.3 (90), 1626.3 (100) [M–BF₄]⁺ (Eu/Pt isotropic profile); elemental analysis: calcd (%) for C₃₉H₄₈N₆O₆PtBF₂₂Eu·2CHCl₃ (M_r = 1712.87 + 2 × 119.38): C 37.54, H 2.58, N 4.31; found: C 37.37, H 2.41, N 4.19.

X-ray Structure Analysis for PtLEu

MoK α radiation, numerical absorption correction with HKL2000,^[41] solution and refinement with SHELXL-97.^[42] Six heavy-atom positions in half of the unit cell (space group $P\bar{1}$) were derived from the Patterson calculation and then refined anisotropically. All the light atoms for two of the three independent molecules in the asymmetric unit were located in difference Fourier maps, but the *tert*-butyl and hexafluoroacetylacetonato groups were treated with restraints on bond lengths and anisotropic displacement parameters. Owing to the large disorder of the groups coordinated to the Eu atom of the third molecule, most of the F atoms were generated from the respective pivot carbon atom by the AFIX command and refined isotropically with constrained IDP (including the case of one pivot carbon atom). One of the hexafluoroacetylacetonato groups was modeled over two positions with equal occupancy (0.5) around a pivot oxygen atom O1–O24. Only one BF₄[–] counterion (of three) displayed some disorder over two different positions for two F atoms with partial occupancies.

Six CDCl₃ molecules were located in difference Fourier maps, although two of them were with half occupancy and one was with large disorder modeled over two positions with equal occupancies.

At the end of the refinement, the residual density (<2.6 e[–] Å^{–3}) was found in relation to the solvent-accessible voids in the unit cell (172 Å³) that could accommodate either a cyclohexane or two to three methanol solvent molecules, but the SQUEEZE^[43] routine used to estimate the

contribution of disordered solvent to the structure factors did not improve the model refinement.

C₅₉H₄₈EuF₁₈N₆O₆Pt·BF₄·1.67CDCl₃: T = 150 K, triclinic, space group $P\bar{1}$, Z = 6, Z' = 3, a = 20.618 (3), b = 23.490 (17), c = 27.826 (8) Å, α = 105.24 (2), β = 109.39 (2), γ = 104.68 (2)°, V = 11374(9) Å³, μ (MoK α) = 2.943 mm^{–1}, $2\theta_{\max}$ = 25.5°, 40078 independent reflections collected with $I/\sigma(I)$ > 2, R_{int} = 0.033, R_{σ} = 0.0551, 2959 parameters, $R1$ ($I/\sigma(I)$ > 2) = 0.072, $R1$ (all data) = 0.111, $wR2$ = 0.209, GOF = 1.080, max. residual electron density = 2.58 e Å^{–3}.

CCDC-631662 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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