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A PCP-Pincer Ru^{II}–Terpyridine Building Block as a Potential “Antenna Unit” for Intramolecular Sensitization

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The redox- and photoactive mononuclear complex [Ru(PCP)(tpy–DTTANa$_4$)]Cl {PCP = [$C_6H_3(CH_2PPh_2)_2$-2,6]$^-$; tpy–DTTA^{4-} = 4′-(2,2′:6′,2′′-terpyridine)-diethylenetriamine-*N*,*N*,*N*′′,*N*′′-tetraacetate} possesses an externally directed, vacant N_3O_4 polyaminocarboxylate-type binding site that coordinates to lanthanide(III) ions to give the neutral heterodinuclear Ru^{II}–Ln^{III} complexes [Ru(PCP)(tpy–DTTA)Ln(H_2O)$_2$] (Ln = Gd^{3+}, Eu^{3+}). The photophysical properties of solutions of the mononuclear complex [Ru(PCP)(tpy–DTTANa$_4$)]Cl were investigated in MeOH/EtOH (1:4) and compared to those of the solutions of heterodinuclear complexes [Ru(PCP)(tpy–DTTA)Ln(H_2O)$_2$] (Ln = Gd^{3+}, Eu^{3+}). Rigid matrix excitation at 77 K of the ππ* level of the ruthenium chromophore in the [Ru(PCP)(tpy–DTTA)Eu(H_2O)$_2$] complex results in a weak europium(III) emission pointing to a transfer of energy from Ru→Eu as a result of the metal-to-ligand charge-transfer (MLCT) excited state of the ruthenium component to the luminescent lanthanide ion. The excited state lifetime of the europium complex is 0.2 ms in methanol solution. In deuterated solvents, the lifetime increases to 0.4 ms, which indicates that the process is solvent-dependent as a result of the strongly coordinated molecules of water that are responsible for the quenching in nondeuterated solvents.

Introduction

Luminescence exerted by lanthanides is a subject that attracts considerable interest because of their potential use as components,[1] luminescent probes[2] and sensors for light amplification and frequency conversion.[3] In particular, research efforts were devoted to the design of fluorophores containing the most emissive Eu^{III} and Tb^{III} ions. Their long-lived emission (up to ms) in the visible spectral region, positioned away from most intrinsic fluorescence of organic or biological molecules, found a wide range of applications such as probes for clinical use (e.g. fluoroimmuno assay agents) and sensors for time-resolved microscopy.[4]

The in-principal spin-forbidden luminescence of the lanthanide ions originates from transitions within the partially filled 4f orbitals.[5] Lanthanide ions with completely filled (Lu^{III}) or completely unfilled (Y^{III} and La^{III}) 4f orbitals do not show any luminescence. Characteristics of the luminescence displayed by the other ions are the line-like emission, long excited state lifetimes and the fact that the low energy of the emission is hardly affected by the environment of the ions, as the filled 5s and 5p orbitals shield the electrons in the 4f levels. In other words, the effect of the ligand field is rather small. The biggest drawback of all the lanthanide ions is their low molar absorption coefficient. A way to circumvent this problem is to use chelating ligands that are able to efficiently absorb UV and/or visible light. Upon excitation, the allowed π→π* transitions lead to the population of their excited states, which can undergo efficient energy transfer to the excited states of the lanthanide ions. Such an energy transfer in most cases occurs from the triplet-excited level of the ligands. The process is often referred to as the “antenna-effect”.

Several UV-absorbing aromatic chromophores containing nitrogen and/or oxygen donor atoms (e.g. β-diketonates,[6] phenantridine,[7] bipyridine,[8] terpyridine,[9] calix[4]arenes and *m*-terphenyl moieties[10]) as well as fluorescent dyes possessing low ππ* transitions (e.g. fluorenone dyes[11] or tetrazine[12]) were used as light-harvesting units in lanthanide complexes.

Most recently, it was demonstrated that intramolecular sensitization of lanthanide(III) ions can be achieved by

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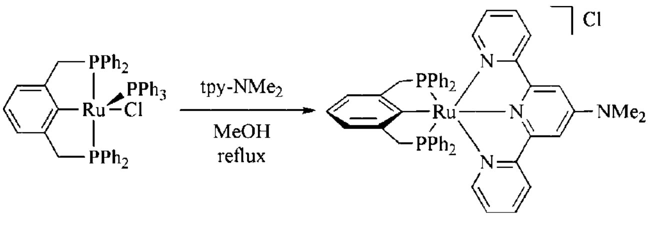
coupling a lanthanide ion to a redox-active d block fragment that possesses broad d-d and intense charge-transfer (CT) transitions in the visible spectral region to efficiently collect photonic energy.[13] Intersystem crossing (ISC), followed by a multipolar d→4f energy transfer, leads to the sensitization of the lanthanides. One of the advantages of this approach relies on the multiplicity of the lowest excited state of the metal complexes (often the triplet states) and to the long-lived excited state lifetimes (ns versus hundreds of ns or several μs) of the metal complexes. The long-lived excited states of the donor d block allow for energy transfer processes that can be rather slow relative to the systems containing organic donor chromophores. Another interesting characteristic displayed by metal complexes is the presence of CT states in the visible region that can be selectively excited to produce sensitization of the lanthanide ions. Importantly, the energy of these states depends on the energy gap between the d and π* orbitals, for a MLCT state, and they can be modulated by choosing an appropriate metal ion, by changing the chelating ligand or by fine tuning the donating properties of the hosting ligands by introduction of electron-withdrawing or -releasing substituents (i.e. changing the HOMO and LUMO energies). However, an efficient electronic energy transfer in such polymetallic edifices requires orbital overlap between the d block excited LUMO and the 4f orbitals of the lanthanides.[14] Thus, the distance between the d and f units must be short and the linker must maximize the electronic interactions. This condition is difficult to realize because the preparation of suitable bridging ligands, as well as the introduction of two different metals, often represents a chemical challenge.

The field of heterodinuclear d/f block assemblies and the properties that can arise from metal–metal interactions is extensively reviewed.[13] Most of the systems reported to date contain low-spin d^6 pseudooctahedral chromophores (Ru^{II}, Re^{I}, Ir^{III} and Os^{II}) or square-planar Pt^{II} fragments that are connected to lanthanide ions by short heteroditopic bridging ligands (Scheme 1). The high-energy triplet level required for the sensitization of the europium(III) ions hampered the applicability of transition-metal-based antennae for photoexcitation of this lanthanide ion. However, recently De Cola and coworkers demonstrated the innovative use of cyclometallated $[Ir^{III}C_2N_4]$ chromophores to act as donors for the sensitization of a luminophoric Eu^{III} ion.[15]



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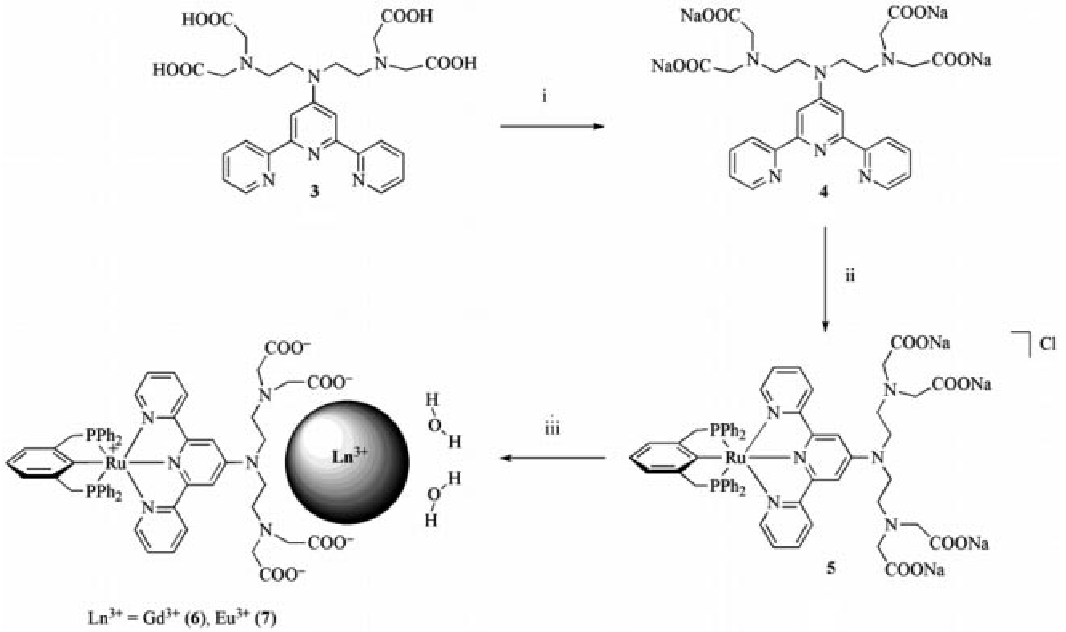
Scheme 1. Synthesis of the $[Ru(PCP)(tpy–NMe_2)]Cl$ complex.

With the aim to study the potential applicability of stable, redox and photoactive bis(ortho)cyclometallated PCP-pincer Ru^{II}–terpyridine complexes as photosensitizers for Eu^{III} ions, the synthesis of a new building block, $[Ru(PCP)(tpy–DTTANa_4)]Cl$ (vide infra; **5**, Scheme 2), was undertaken. Complex **5** contains the monoanionic, tridentate coordinating bisphosphanylaryl ligand $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$ (PCP) and the bifunctional chelator ligand $[tpy–DTTA]Na_4$ {$tpy–DTTA^{4-}$ = 4′-(2,2′:6′,2′′-terpyridine)diethylenetriamine-*N*,*N*,*N*′′,*N*′′-tetraacetate}. The rigid, chelating tpy–DTTA ligand with a N_3O_4 donor atom



Scheme 2. Synthesis of mononuclear complex **5** and heterodinuclear complexes **6** and **7**. Reagents and conditions: i) 1 N NaOH until pH = 9.5. ii) $[RuCl(PCP)(PPh_3)]$, MeOH, reflux, 2 d. iii) **5**, $LnCl_3·6H_2O$ (Ln = Gd^{3+}, Eu^{3+}), $MeOH/H_2O$, reflux, 5 h.

set was employed by Merbach and coworkers in the synthesis of heterometallic complexes [M(tpy–DTTA)$_2$Gd$_2$(H$_2$O)$_2$] (M = Fe^{2+}, Ru^{2+}) that were investigated as MRI contrast agents.[16,17] It is of special interest to this work to demonstrate that the organometallic [Ru(PCP)(tpy–DTTANa$_4$)]Cl building block is well-suited for anchoring trivalent ions such as Gd^{III} and Eu^{III} to give novel heterodinuclear complexes [Ru(PCP)(tpy–DTTA)Ln(H$_2$O)$_2$] {Ln = Gd^{3+} (**6**), Eu^{3+} (**7**)}. The luminescence properties of the prepared complexes are presented and discussed.

Results and Discussion

Synthesis of the Monomeric Complex [Ru(PCP)(tpy–DTTANa$_4$)]Cl (5)

The ligand tpy–DTTA was prepared following the four step reaction reported by Ruloff et al.[17] Reaction[18] of [RuCl(PCP)(PPh$_3$)] (**1**, Scheme 1) with an equimolar quantity of tpy–DTTA (**3**, Scheme 2) in MeOH heated at reflux afforded the desired product [Ru(PCP)(tpy–DTTA)]Cl only in low yield (< 10%). Preparation of complex [Ru(PCP)(tpy–NMe$_2$)]Cl (**2**, 63%, Scheme 1), performed under the same experimental conditions, proved unambiguously that coordination of the tpy–DTTA ligand is not hampered by the electron-donating properties of the amino substituent at the 4′-position of the tpy moiety. Synthesis of **5** involving the use of the tpy–DTTA tetrasodium salt instead of the free tetraacid was successful, which underlies the influence of the pH on the coordination properties of the tpy unit. Thus, treatment of **1** with an equimolar amount of [tpy–DTTA]Na$_4$ (**4**, Scheme 2) in refluxing methanol gave complex **5** as a dark red solid in good yield (55%). Complex **5** is stable to air and moisture and is highly soluble in water and polar solvents. The NMR spectroscopic data for **2** and **5** were as expected for their proposed six-coordinate geometry about the ruthenium centres and are similar to those of the analogous [Ru(PCP)(tpy)]Cl complex.[18]

Single-crystals of **5** suitable for X-ray analysis could not be obtained. Instead, the molecular structure of **2** was determined, which provides information concerning the effects of a 4′-NMe$_2$ substituent on both the Ru–tpy bond distances and angles.

Suitable crystals of **2** were obtained from a CH$_2$Cl$_2$ solution to which *n*-hexane was slowly diffused. Figure 1 depicts the molecular structure of **2** (a selection of bond lengths and angles are given in Table 1). In the solid state of **2**, a ruthenium centre, the monoanionic *P*,*C*,*P*-coordinated bisphosphanylaryl ligand and the tridentate-coordinated tpy–NMe$_2$ ligand are present. The Ru1 atom adopts a distorted octahedral coordination environment and both the PCP-pincer and tpy–NMe$_2$ ligands are coordinated in a meridional fashion. The Ru1–C1 bond length of the PCP-pincer ligand is 2.120(2) Å, whereas the two Ru–P distances are 2.3189(6) and 2.3330(5) Å, respectively.

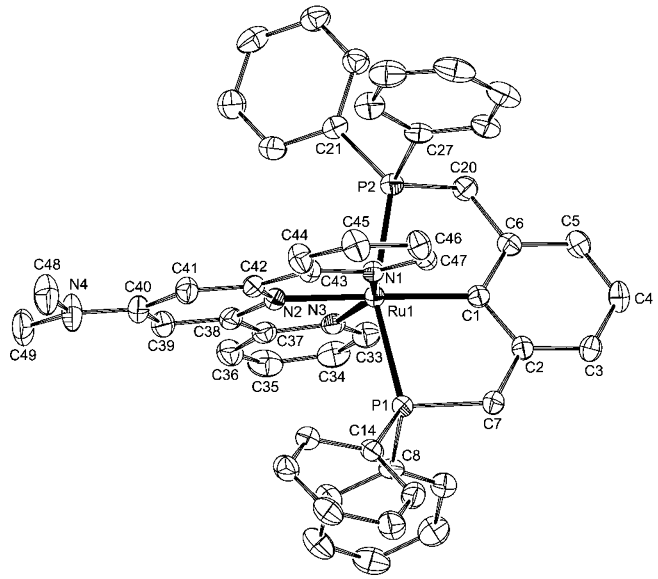


Figure 1. Displacement ellipsoid plot of **2**, drawn at the 50% probability level. Hydrogen atoms, uncoordinated chloride anions and disordered solvent molecules are omitted for clarity.

Table 1. Selected bond lengths [Å], bond angles [°] and torsion angles [°] for **2**.

Bond Lengths [Å]			
Ru1–N1	2.0886(17)	Ru1–N2	2.0292(17)
Ru1–N3	2.0899(17)	Ru1–C1	2.120(2)
Ru1–P1	2.3189(6)	Ru1–P2	2.3330(5)
N4–C40	1.361(3)	N4–C48	1.454(3)
N4–C49	1.454(3)		
Bond Angles [°]			
N1–Ru1–N3	155.85(7)	N2–Ru1–C1	178.40(7)
P1–Ru1–P2	157.35(2)	N1–Ru1–N2	78.01(6)
N2–Ru1–N3	77.86(7)	N3–Ru1–C1	101.25(7)
C1–Ru1–N1	102.84(7)	P1–Ru1–N1	89.70(5)
P1–Ru1–N2	99.37(5)	P1–Ru1–N3	93.16(5)
P1–Ru1–C1	79.32(6)	P2–Ru1–N1	91.96(5)
P2–Ru1–N2	103.07(5)	P2–Ru1–N3	94.49(5)
P2–Ru1–C1	78.29(6)		
Torsion Angles [°]			
N1–C43–C42–N2	0.0(3)	N2–C38–C37–N3	0.4(3)
C1–C2–C7–P1	23.6(2)	C1–C6–C20–P2	24.2(2)
C39–C40–N4–C48	–177.2(2)	C41–C40–N4–C49	175.8(2)

The three pyridyl groups of the tpy–NMe$_2$ ligand are almost coplanar. The N1–Ru–N3 bond angle [155.85(7)°] is slightly smaller than those observed in other Ru^{II}–tpy complexes, which show values in the range of 156.9(5) to 159.8(1)°.[19] As commonly observed for other Ru^{II}–tpy complexes, geometrical constraints of the tpy backbone makes the central Ru–N2 distance [2.0292(17) Å] shorter than those of Ru–N1 [2.0886(17) Å] and Ru–N3 [2.0899(17) Å]. Analogous to what was reported for [Ru(tpy–NMe$_2$)$_2$](PF$_6$)$_2$,[19b] the 4′-NMe$_2$ group is approximately coplanar with the central pyridine ring of the tpy moiety [torsion angle C39–C40–N4–C48 is –177.2(2)°], which points to a planar geometry of the nitrogen atom and a high degree of π-conjugation between the sp^2-hybridized atom of the NMe_2 group and with the pyridine ring. This is also apparent from the short N4–C40 distance of 1.361(3) Å and both the N4–C48 and N4–C49 bonds are 1.454(3) Å in length. Comparison of these data obtained for **2** with those reported for $[Ru(tpy\text{-}NMe_2)_2](PF_6)_2$ [C_{tpy}–NMe_2 = 1.352(14) Å; cf. 1.366(5) Å for the free tpy–NMe_2 ligand] reveals that in **2** the conjugation between the dimethylamino group and the central pyridine ring is slightly lower. This may indicate that the σ-donor capability of the cyclometallating PCP-pincer ligand in **2** is lower than that of the terpyridine ligands in $[Ru(tpy\text{–}NMe_2)_2](PF_6)_2$.[18]

Synthesis of the Heteronuclear Complexes [Ru(PCP)(tpy–DTTA)Ln(H_2O)$_2$] {Ln = Gd^{3+} (6), Eu^{3+} (7)}

The preparation of the lanthanide(III) complexes was straightforward. Reaction of stoichiometric amounts of **5** with the corresponding $LnCl_3·6H_2O$ salt in a MeOH/H_2O mixture afforded the NaCl-free complexes [Ru(PCP)(tpy–DTTA)Ln(H_2O)$_2$] {Ln = Gd^{3+} (**6**), Eu^{3+} (**7**)} as red coloured solids in good yields after several washings with cold water. Both complexes, characterized by elemental analysis, are soluble in MeOH and DMSO and insoluble in THF, chlorinated solvents, aliphatic and aromatic solvents. In agreement with the results obtained with the analogous complex [Ru(tpy–DTTA)$_2$Gd(H_2O)$_2$],[16] the solubility of **6** and **7** in water is very low. In water, **6** and **7** precipitate as light orange flocculent solids that can be recovered by centrifugation and redissolved in MeOH. A straightforward explanation for their low solubility is that the lipophilic phenyl substituents on the phosphorus centres of the PCP-pincer ligand may favour the formation of aggregates that resemble those of reverse micelle-type architectures in which the {PCP–Ru–tpy} units are at the core and the {DTTA–Gd} units are at the periphery. At the periphery of these aggregates, one carboxyl group of a $[DTTA]^{4-}$ unit may bridge a second lanthanide ion of another molecule forming an oligomeric/polymeric insoluble material. The coordinated water molecules complete the coordination sphere around each lanthanide ion leading to a nine-coordinate metal centre. Importantly, the X-ray structure of the complex $[\{C(NH_2)_3\}_3Gd(TTAHA)]·9H_2O$ {H_6TTAHA = [*N*-tris(2-aminoethyl)amine-*N′*,*N′*,*N′′*,*N′′*,*N′′′*,*N′′′*-hexaacetate]}[20] revealed that two pendant arms of the tripod $[TTAHA]^{6-}$ ligand and the N-donor atoms are coordinated by the donor set N_3O_4 to Gd^{3+}. The eighth and ninth coordination sites are occupied by carboxylate oxygens belonging to the “free” pendant arm of a neighbouring complex.[20] They can be replaced by two water molecules when the complex is dissolved in water.[20]

Because the NaCl containing complexes are soluble in water, it is clear that in the presence of salt such aggregates are not formed. Coordination of the Cl^- ion may compete with the coordination of the carboxyl groups (Scheme 2). Owing to the negative charge on the oxygen centres, the N_3O_4 pocket is able to bind the Na^+ cation, which results in the breakdown of the insoluble aggregates. This cooperative ion–cation bonding can be a result of the “excess” coordinating ability of the DTTA unit. Recently, Merbach and coworkers discovered that gadofullurene aggregates, whose formation may be ascribed to hydrophobic forces, can be disgregated by the addition of NaCl in aqueous solutions of $Gd@C_{60}[C(COOH)_2]_{10}$ and $Gd@C_{60}(OH)_x$ ($x \approx 27$).[21] Intercalation of the salt results in the separation of the molecules and inhibits the interactions.[21]

Interestingly, the solubility of the aggregates in water could not be improved by adding excess NaCl to aqueous solutions of NaCl-free **6** and **7**. More detailed studies are required to understand the factors that determine the solubility properties of these complexes.

Coordination of the lanthanide ions to the $[DTTA]^{4-}$ unit in **6** and **7** was investigated by infrared (IR) spectroscopy in KBr matrix. Table 2 reports the data for the bands that are most sensitive to the coordination of the lanthanide ions to the polyaminocarboxylate pendant arms of the $DTTA^{4-}$ unit. The IR spectroscopic data indicate that O_4-chelation of the $[DTTA]^{4-}$ unit occurs in both complexes. The asymmetric vibration mode, $\nu_{as}(CO)$, of the carboxylato groups is shifted to a higher wavenumber by ca. 30 cm^{-1} upon lanthanide coordination relative to the $\nu_{as}(CO)$ vibration mode in parent complex **5**, which demonstrates that the carboxylato oxygens in **6** and **7** are coordinated to the lanthanide ion.[22] The symmetric vibration mode, $\nu_s(CO)$, also shifts to higher wavenumbers upon coordination relative to that of **5**.

UV/Vis Absorption Spectroscopy

The electronic spectra of mononuclear **5** and heterodinuclear **6** and **7** were recorded in MeOH at room temperature (Figure 2). Absorption maxima (λ_{max}) and molar absorption coefficients (ε_{max}) are summarized in Table 2. Data for complexes **2** and [Ru(PCP)(tpy)]Cl[18] are included for comparison. The UV/Vis spectra of all complexes exhibit bands

Table 2. Infrared spectral and absorption data.

Compound	$\nu_{as}(CO)^{[b]}$ [cm^{-1}]	$\nu_s(CO)^{[b]}$ [cm^{-1}]	$\lambda_{max}^{[c]}$ [nm] ($\varepsilon_{max} \times 10^{-4}$ [$M^{-1}cm^{-1}$])
[Ru(PCP)(tpy)]Cl[a]	–	–	275 (3.7), 305 (3.9), 479 (0.8)
2	–	–	285 (1.6), 467 (0.4)
5	1583.80_{vs}	1408.36_s	285 (1.6), 465 (0.2)
6	1630.89_s	1434.53_w	285 (1.7), 460 (0.3)
7	1607.25_{vs}	1434.43_s	285 (1.6), 465 (0.3)

[a] Measured at 298 K in MeCN.[15] [b] Infrared data (vs: very sharp; s: sharp; w: weak). [c] Measured at 298 K in MeOH unless otherwise specified.

in the UV region characteristic of the $\pi \rightarrow \pi^*$ transition of the chelating ligands.[23] In the visible region, less intense, broad absorption bands are observed, which are assigned to singlet metal-to-ligand charge-transfer (^{1}MLCT) transitions from the dπ(Ru) orbitals to the π^* orbitals of the tpy ligand.[23] The electronic spectra of **6** and **7** show only minor changes relative to **5**, which proves that the lanthanide ions do not substantially affect the electronic properties of the {(PCP)Ru(tpy)} moiety. The UV/Vis spectra of **5**–**7** recorded in water display similar spectroscopic features, but it must be noted that they tend to precipitate because of their low solubility in aqueous media. ^{1}H NMR spectroscopic analysis in CD_3OD of the precipitated solid obtained from an aqueous solution containing **7** proved, however, that the collected Ru–Eu complex is indeed **7**.

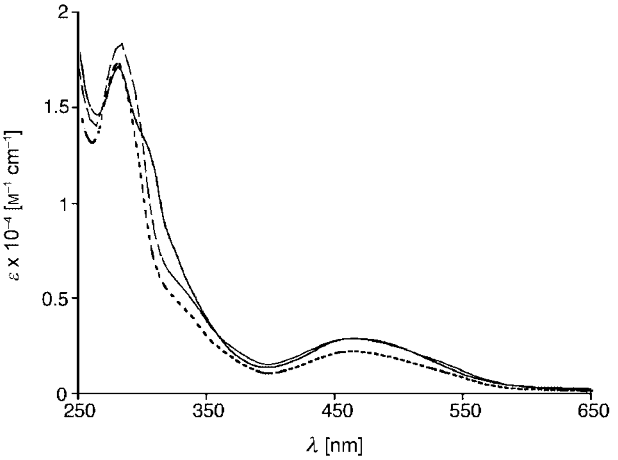


Figure 2. UV/Vis absorption spectra of mononuclear complex **5** (-----) and heterodimetallic complexes **6** (– – –) and **7** (——) measured in MeOH at 298 K.

Emission Properties

The emissive properties of **5**–**7** were investigated in MeOH/EtOH (1:4) both at room temperature and in rigid matrix at 77 K. Emission and lifetime data recorded at 77 K are summarized in Table 3. Similar to that observed for [Ru(PCP)(tpy)]Cl and other Ru^{II}–tpy complexes,[24] **5** does not show emission at room temperature. This is not surprising as it is well-established that for Ru^{II}–tpy complexes at room temperature, a fast and efficient excited-state deactivation by nonradiative processes occurs, which is related to the population of the nonemitting metal-centred (^{3}MC) state that results from the low energy gap between the luminescent ^{3}MLCT level and this state. However, **5** does not emit even at 77 K. Such a lack of emission at low temperature, contrary to what was observed for Ru–tpy analogues, could be due to the functionalization of the central pyridine ring of the tpy ligand in **5** with a tertiary amino group bearing the chelating polyaminocarboxylate units. In fact, the 4′-amino substituent is an excellent electron donor and could act as an efficient quencher both at room and low temperatures. This effect is reduced, however, once the polyaminocarboxylate unit coordinates to a lanthanide cation because the lone pair of electrons on the nitrogen atom could be involved in the coordination. In fact, at both room and low temperature, complexes **6** and **7** exhibit ruthenium-based ^{3}MLCT emission at 650 and 670 nm, respectively, which is independent of the excitation wavelength. These results indicate that the coordination of the lanthanide ions indeed also involves the nitrogen atom of the amino group, which removes any possible quenching pathway. However, it cannot be excluded that some contribution to the intensity of the ruthenium-based emission also comes from the rigidification of the structure upon lanthanide ion complexation. The emission spectrum of Ru^{II}–Gd^{III} complex **6** recorded at room temperature and at 77 K shows, aside from the ruthenium-based component, a structureless band at 440 nm (2.8 ns) and at 560 nm (200 µs). These bands were assigned on the basis of their excited lifetime to the fluorescence and phosphorescence of the ligand, respectively. It is well-known that Gd^{III} promotes intersystem crossing from the singlet excited state to the corresponding triplet state (by large spin-orbit coupling induced by the heavy atom effect) and that there are no energy levels of the lanthanide ion (the energy of the lowest excited states of Gd^{III} is at 32 200 cm^{-1}) that can accept energy from the triplet state of the ligand or from the {(PCP)Ru(tpy–DTTA)} unit. The excitation energy of the ligand-centred $\pi\pi^*$ triplet excited state (^{3}LC) of **6**, found at 17 857 cm^{-1}, is still energetically suitably placed to act as a sensitizer for the luminescent $^5D_0$ of Eu^{III} (17 000 cm^{-1}) (Figure 3, top), which allows a thermodynamically favoured energy transfer from the antenna chromophore to the lanthanide. As a result, upon excitation at 270 nm the spectrum of **7** exhibits straight lines of modest intensity that are due to transitions between the first excited state $^5D_0$ and the ground state multiplet $^7F_{1-2}$ of the Eu^{3+} ion (Figure 4).

Analogously, excitation of Ru^{II}–Eu^{III} complex **7** into the ^{1}MLCT transition of the {(PCP)Ru(tpy–DTTA)} unit at 460 nm (21 739 cm^{-1}) produces emission from the $^5D_0$ excited state of Eu^{III} (17 000 cm^{-1}) and from the ruthenium ^{3}MLCT. The latter state, located around 14 925 cm^{-1}, is well below the $^5D_0$ level of europium. Thus, it can be excluded that the europium-based emission is due to an energy transfer from this state. These findings suggest that the europium emission may partly be quenched by a Eu→Ru back-energy transfer. The most likely mechanism for the sensitization of the europium ion is a partial energy transfer from the ^{1}MLCT state. This mechanism would involve the direct population (upon excitation at 460 nm) of the ^{1}MLCT state, fast intersystem crossing to the triplet state of the ligand, which from the Ru–Gd complex was estimated to lie between the ruthenium ^{1}MLCT and the $^5D_0$ state of the europium and finally, energy transfer to the emitting lanthanide ion (Figure 3, bottom). It is interesting to note that the two excitation wavelengths (270 and 460 nm) lead to a different emission ratio between the ruthenium and the europium centres. A detailed analysis of the emissions suggests that despite the direct excitation into the ruthenium ^{1}MLCT (460 nm), the ruthenium versus europium intensity is lower

Table 3. Emission maxima ($\lambda_{em.}$) and lifetimes (τ) recorded at 77 K for complexes **6** and **7**.

Compound	^{3}LC	Ru^{II}	Eu^{III}		
	$\lambda_{em.}$ [cm^{-1}][a] (τ [μs])[c]	$\lambda_{em.}$ [cm^{-1}][a,b] (τ [ns])[d]	$\lambda_{em.}$ [cm^{-1}][a,b]	τ [ms][e]	τ [ms][f]
6	560(200)	650 (23.5)	–	–	–
7	–	670 (34.1)	612	0.2	0.4

[a] Emission data recorded in MeOH/EtOH (1:4); $\lambda_{exc.}$ = 270 nm. [b] Emission data recorded in MeOH/EtOH (1:4); $\lambda_{exc.}$ = 460 nm. [c] Lifetime data recorded in MeOH/EtOH (1:4); $\lambda_{exc.}$ = 270 nm. [d] Lifetime data recorded in MeOH/EtOH (1:4); $\lambda_{exc.}$ = 460 nm. [e] Measurement performed in MeOH; $\lambda_{exc.}$ = 611 nm. [f] Measurement performed in dry CD_3OD; $\lambda_{exc.}$ = 611 nm. LC = ligand centred.

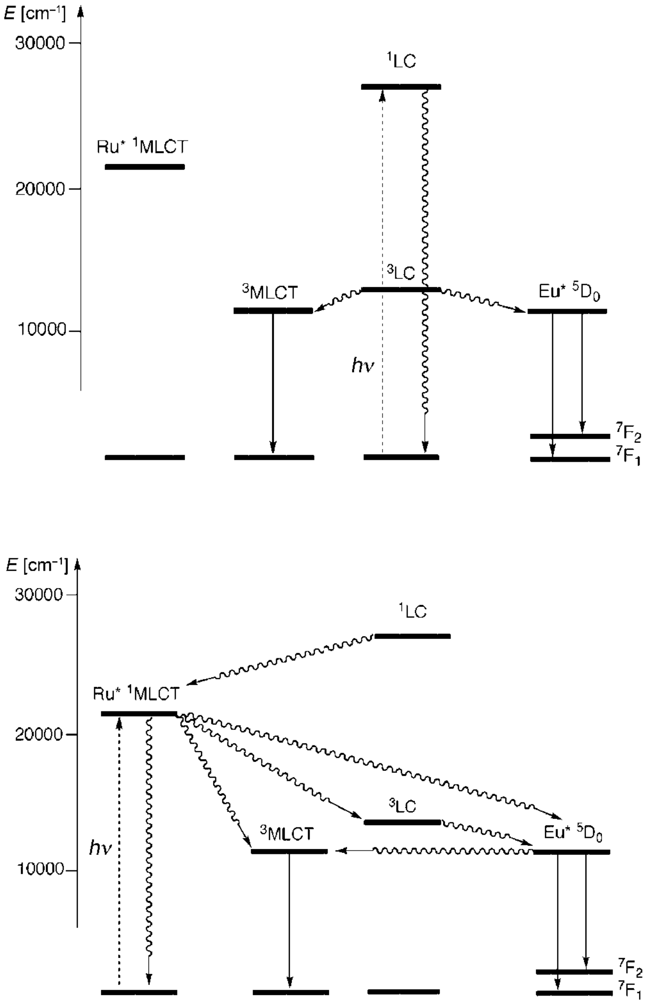


Figure 3. Energy diagram that accounts for the most important pathway for excited state deactivation of Ru^{II}–Eu^{III} complex **7**. Top: excitation at 270 nm. Bottom: excitation at 460 nm. All radiative processes are represented with solid lines whereas the nonradiative ones are wavy.

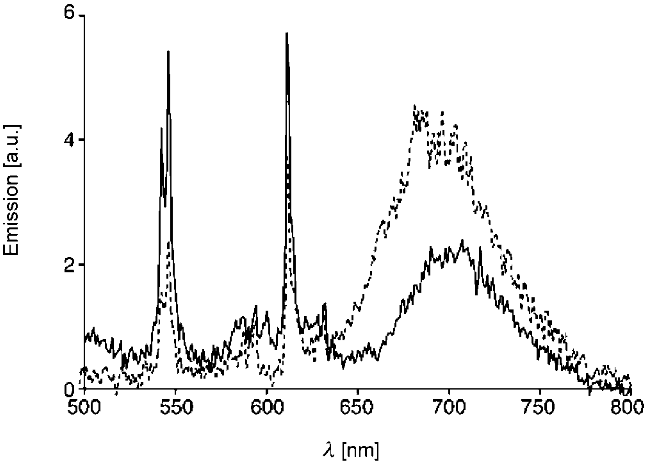


Figure 4. Emission spectral profile of Ru^{II}–Eu^{III} complex **7** measured in MeOH/EtOH (1:4) at 77 K at $\lambda_{exc.}$ = 270 nm (– – –) and at $\lambda_{exc.}$ = 460 nm (——).

than upon excitation into the ligand-centred singlet state (270 nm). These results agree with the hypothesis that upon population of the singlet ^{1}MLCT (or even of the ^{3}MLCT) state, energy transfer to the $^5D_0$ of the europium is favoured more than from the ligand-localized excited states. Further support of sensitization, most likely from the ^{1}MLCT, comes from the excitation spectra at low temperature. The excitation spectrum of **7** in MeOH/EtOH (1:4) at 77 K almost matches its absorption spectrum. The observed shift of the ^{1}MLCT band from 460 to 400 nm is attributed to the rigid matrix, which prevents relaxation of the excited state observed at room temperature in polar solvents.

To gain more information about the quenching of the Eu^{III} luminescence by its chemical environment, the lifetimes in MeOH and dry CD_3OD were measured (Table 3). Monoexponential decay of the europium emission was observed in both cases. The lifetime of europium determined at 611 nm in MeOH (τ = 0.2 ms) doubled by a factor of two when the measurements were performed in dry CD_3OD (τ = 0.4 ms). This solvent effect indicates that the emission intensity of the Eu^{III} ion is sensitive to the number of coordinated water molecules and points to a slow exchange between the solvent and the strongly bound water molecules. The number of water molecules coordinated to the europium centre was calculated with the use of the empiric Horrocks equation[25] ($q = A\ [1/\tau(H_2O)\ -1/\tau(D_2O)]$; A = 1.05 ms; uncertainty of ±0.5), which takes into account the quenching by the OH oscillators in the second coordination sphere. The estimated value of 2.5 molecules is in very good agreement with the structure of complex **7** depicted in Scheme 2, which is based on elemental analysis results. The water molecules coordinated to the lanthanide ion may exert a quenching effect on the lifetime of the Eu^{3+} emission.

The Ru- and Eu-centred quantum yields (Φ) for both complexes were rather low and hardly measurable, with reference to commonly used standards.

Conclusions

The present work demonstrates that the inert organometallic building block [Ru(PCP)(tpy–DTTANa$_4$)]Cl is able to coordinate gadolinium(III) and europium(III) ions to give the heterodimetallic complexes [Ru(PCP)(tpy–DTTA)-Ln(H$_2$O)$_2$] (Ln = Gd^{3+}, Eu^{3+}) in good yield. Study of the photophysical properties shows that coordination of the Gd^{III} cation to the mononuclear [Ru(PCP)(tpy–DTTA)]$^{3-}$ anion is accompanied by population of the triplet-excited state of the ligand and by an increase in the intensity of the ruthenium-based emission from the ^{3}MLCT state. It was shown that the Ru–Eu complex exhibits sensitized visible emission upon excitation of the ππ* level and the {(PCP)-Ru(tpy–DTTA)} chromophoric unit at 470 nm, though only in rigid matrix at 77 K. The efficiency of energy transfer from Ru^{II} to Eu^{III} upon excitation into the ^{3}LC and ^{1}MLCT states was not determined because of the low intensity of the signals. However, emission lifetimes of the Eu^{III} luminescence, measured in CH$_3$OH and dry CD$_3$OD solutions were found to be 0.2 and 0.4 ms, respectively, which confirms the presence of water coordinated to the metal ion.

The short lifetime of the Eu^{III} luminescence was rationalized on the basis of a nonefficient d→f energy transfer and quenching by the coordinated water molecules. Sensitization of the Eu^{III} luminescence combined with the stability of the organometallic {(PCP)Ru(tpy–DTTA)} unit in polar solvents and water encourage studies directed at the optimization of the properties (e.g. water solubility and thermodynamic stability under physiological conditions) of this class of complexes in order to produce efficient systems with properties suitable for practical applications, for example in bioassays. Notably, the complexes presented in this work are neutral. This is an important factor to take into account because positively or negatively charged molecules may lead to nonspecific binding in biological media.

Experimental Section

General: All the experiments were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. Pentane and Et$_2$O were distilled from sodium with benzophenone as an indicator. CH$_2$Cl$_2$ was dried with CaH$_2$. MeOH was dried with magnesium and used freshly distilled. Compounds **1**,[26] 4′-dimethylamino-2,2′:6′,2′′-terpyridine,[19b] and **3**[17] were prepared according to literature procedures. All other reagents that were used are commercially available. ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra were recorded at 298 K with a Varian AC200 or Varian Inova 300 spectrometer. Chemical shifts are reported relative to the residual solvent signal (^{1}H and ^{13}C NMR spectra) or are externally referenced to 85% H$_3$PO$_4$ solution in water (^{31}P NMR spectra). Elemental microanalysis of mononuclear complexes **2** and **5** were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Müllheim a. d. Ruhr, Germany. Elemental microanalysis of heterodinuclear complexes **6** and **7** were performed by Prof. Dr. H. Malissa and G. Reuter GmbH, Analytische Laboratorien, Lindlar, Germany.

Electronic Spectroscopic Measurements: UV/Vis absorption spectra were obtained with a Varian Cary 5000 spectrophotometer. Steady-state luminescence was measured in EtOH/MeOH (4:1) and in deuterated methanol at 77 K by using a Jobin Yvon Horiba Fluorolog 3 spectrofluorometer equipped with a Xe arc light source, a Spex R928P photomultiplier tube detector and double excitation and emission monochromators. Emission spectra were corrected for source intensity and detector response by using standard correction curves. For nanosecond time resolved lifetime measurements, a NanoLED-17 laser (sets at 295 nm) working with a maximum repletion rate of 1 MHz and a pulse <750 ps was used as an excitation source. The TBX Picosecond Photon Detection Module was used as the detector. Estimated errors are as follows: band maxima, ±2 nm; relative luminescence intensity, ±20%; lifetimes, ±10%.

X-ray Crystal Structure Determination of 2: [C$_{49}$H$_{43}$N$_4$P$_2$Ru]Cl + disordered solvent, Fw = 886.33 (Derived values do not contain the contribution of the disordered solvent molecules), red plate, 0.36×0.21×0.09 mm^3, monoclinic, $C2/c$ (no. 15), a = 34.5027(3), b = 10.6866(1), c = 24.4514(3) Å, β = 93.4702(4)°, V = 8999.10(16) Å^3, Z = 8, D_x = 1.308 g/cm^3 (Derived values do not contain the contribution of the disordered solvent molecules), μ = 0.52 mm^{-1} (Derived values do not contain the contribution of the disordered solvent molecules). 67258 Reflections were measured with a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied (0.77–0.95 correction range). Number of unique reflections: 10287 (R_{int} = 0.0717). The structure was solved with automated Patterson Methods[27] and refined with SHELXL-97[28] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. The crystal structure contains large voids (907.4 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation by using the SQUEEZE routine of the PLATON program,[29] which resulted in 328 electrons/unit cell. 516 parameters were refined with no restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0332/0.0809. $R1/wR2$ [all refl.]: 0.0508/0.0874. S = 1.081. Residual electron density between –0.65 and 0.51 e Å^{-3}. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[29] CCDC-634988 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Ru(PCP)(tpy-NMe$_2$)](Cl) (2): A solution of **1** (0.46 g, 0.5 mmol) in MeOH (15 mL) was added to a solution of 4′-NMe$_2$-2,2′:6′,2′′-terpyridine (0.14 g, 0.5 mmol) in MeOH (5 mL). The reaction mixture was heated at reflux for 2 d. Subsequently, the solvent was evaporated in vacuo to give a red solid residue, stable to air and moisture, which was dissolved in CH$_2$Cl$_2$ (5 mL). Addition of pentane/Et$_2$O (1:5) caused the precipitation of **2** as a red powder that was collected by filtration, washed with hexane and dried in vacuo. Yield: 0.29 g, 63%. ^{1}H NMR (300.1 MHz, CD$_2$Cl$_2$): δ = 8.25 [d, $J_{H,H}$ = 7.0 Hz, 2 H, tpy(3, 3′′)], 7.88 [s, 2 H, tpy(3′, 5′)], 7.47 [m, 2 H, tpy(4, 4′′)], 7.21 [d, $J_{H,H}$ = 6.0 Hz, 2 H, tpy(6, 6′′)], 7.13 (m, 3 H, ArH), 7.08 (vt, $J_{H,H}$ = 7.65 Hz, 4 H, *para*-H PPh$_2$), 6.93 (vt, $J_{H,H}$ = 7.8 Hz, 8 H, *ortho*-H PPh$_2$), 6.60 (m, 8 H, *meta*-H PPh$_2$), 6.42 [t, $J_{H,H}$ = 6.0 Hz, 2 H, tpy(5, 5′′)], 3.98 (vt, $J_{H,P}$ = 4.0 Hz, 4 H, CH$_2$-P), 3.5 (s, 6 H, N-CH$_3$) ppm. ^{13}C NMR (75.5 MHz, CD$_2$Cl$_2$): δ = 182.2 (d, $^3J_{C,P}$ = 17.2 Hz, C$_{ipso}$), 158.44, 154.3, 154.0, 153.1, 147.6 (vt, $J_{C,P}$ = 9.1 Hz, C-2,6), 134.4, 133.6 (vt, *ortho*-C PPh$_2$), 133.5 (vt, *meta*-C PPh$_2$), 130.6, 129.4 (dvt, $^1J_{C,P}$ = 74.8 Hz, ^{vt}J = 4.5 Hz, C$_{quat.}$ PPh$_2$), 129.2 (s, *para*-C PPh$_2$), 125.9, 122.7, 122.6 (s, C-4), 121.8 (vt, $^{vt}J_{C,P}$ = 7.9 Hz, C-3,5), 42.2 (vt, CH_2-P), 40.9 (s, N-CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ = 43.4 (s, CH_2-P) ppm. $C_{49}H_{43}ClN_4P_2Ru$ (886.4): calcd. C 66.40, H 4.89, N 6.32; found C 66.33, H 5.04, N 6.25.

[Ru(PCP)(tpy–DTTA)Na_4](Cl) (5): Ligand **3**·7.5H_2O (0.083 g, 0.12 mmol) was dissolved in distilled H_2O (10 mL). Under vigorous stirring, 1 N NaOH was added drop wise until the pH of the solution was 9.5. Evaporation of water gave **4** as a white crystalline solid that was transferred into a Schlenk flask, dried in vacuo and stored under a nitrogen atmosphere prior to use. Subsequently, **1** (0.09 g, 0.1 mmol) and **4** were stirred under a nitrogen atmosphere in dry MeOH (20 mL) and heated at reflux for 2 d. The solvent was then removed in vacuo until a small residue remained. Addition of Et_2O caused the precipitation of **4** as a red solid that was isolated by centrifugation, washed with hexane and cold water and dried in vacuo. Yield: 0.07 g, 55%. ^1H NMR (300.1 MHz, CD_3OD): δ = 8.68 [d, $J_{H,H}$ = 4.41 Hz, 2 H, tpy(6, 6′′)], 8.56 [d, $J_{H,H}$ = 7.71 Hz, 2 H, tpy(3, 3′′)], 8.48 [d, $J_{H,H}$ = 7.9 Hz, 2 H, tpy(5, 5′′)], 8.06 [s, 2 H, tpy(3′, 5′)], 7.98 [t, $J_{H,H}$ = 9.2 Hz, 2 H, tpy(4, 4′′)], 7.02 (m, 3 H, Ar), 7.07 (vt, $J_{H,H}$ = 7.41 Hz, 4 H, *para*-H PPh_2), 6.92 (vt, $J_{H,H}$ = 7.42 Hz, 8 H, *ortho*-H PPh_2), 6.63 (m, 8 H, *meta*-H PPh_2), 4.00 (br. s, 4 H, CH_2-P), 3.73 (br. m, 4 H), 3.65 (s, 8 H), 3.57 (br. m, 4 H) ppm. ^{13}C NMR (75.5 MHz, CD_3OD): δ = 182.9 (d, $^3J_{C,P}$ = 17.2 Hz, C_{ipso}), 177.97 (m, COO^-), 158.4, 156.7, 156.6, 154.6 (vt, C-2,6), 152.9, 148.9, 147.6, 137.48, 134.7, 133.7 (vt, *ortho*-C PPh_2), 131.8 (vt, *meta*-C PPh_2), 129.1 (dvt, $^1J_{C,P}$ = 74.8 Hz, $C_{quat.}$ PPh_2), 128.8 (s, *para*-C PPh_2), 125.7, 123.9, 123.1, 122.5 (s, C-4), 121.5 (vt, C-3,5), 105.76, 61.3, 42.4 (m, CH_2-P) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ = 43.4 (s, CH_2-P) ppm. IR (KBr): $\tilde{\nu}$ = 1583.8 $(CO)_{as}$, 1408.4 $(CO)_s$ cm^{-1}. $C_{59}H_{53}ClN_6Na_4O_8P_2Ru$ (1264.5): calcd. C 56.04, H 4.22, N 6.65; found C 55.85, H 4.15, N 6.57.

[Ru(PCP)(tpy–DTTA)Gd$(H_2O)_2$] (6): $GdCl_3$·6H_2O (0.06 g, 0.16 mmol) and complex **5** (0.2 g, 1.6 mmol) were stirred together in a solution of MeOH/H_2O (2:2) (20 mL) for 5 h at 70 °C. Subsequently, the volume was concentrated in vacuo. Addition of Et_2O caused the precipitation of **6** as an orange solid, which was collected by centrifugation, washed several times with cold water and dried in vacuo. Yield: 0.18 g, 89%. IR: $\tilde{\nu}$ = 1615.9 $(CO)_{as}$, 1434.5 $(CO)_s$ cm^{-1}. $C_{59}H_{57}GdN_6O_{10}P_2Ru$ (1330.4): calcd. C 53.27, H 4.32, Gd 11.82, N 6.32, P 4.66, Ru 7.60; found C 53.11, H 4.48, Gd 11.60, N 6.34, P 4.53, Ru 7.64.

[Ru(PCP)(tpy–DTTA)Eu$(H_2O)_2$] (7): Complex **7** was prepared by applying the synthetic procedure described for complex **6**. Compound **5** (0.2 g, 0.18 mmol) in MeOH/H_2O (2:2) (20 mL) reacted with $EuCl_3$·6H_2O (0.06 g, 0.18 mmol). Yield: 0.19 g, 83%. IR: $\tilde{\nu}$ = 1607.2 $(CO)_{as}$, 1434.4 $(CO)_s$ cm^{-1}. $C_{59}H_{57}EuN_6O_{10}P_2Ru$ (1325.1): calcd. C 53.48, H 4.34, Eu 11.82, N 6.34, P 4.67, Ru 7.63; found C 53.84, H 4.04, Eu 11.85, N 6.25, P 4.59, Ru 7.32.

Supporting Information (see footnote on the first page of this article): Excitation spectrum of **7**.

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