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Article

# Luminescent Ruthenium(II) Bipyridine–Calix[4]arene Complexes as Receptors for Lanthanide Cations

**Paul D. Beer,*,† Fridrich Szemes,† Paolo Passaniti,‡ and Mauro Maestri*,‡**

*Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, U.K. OX1 3QR, and Dipartimento di Chimica “G. Ciamician”, Università di Bologna, via Selmi 2, I-40126 Bologna, Italy*

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The synthesis and photophysical properties of novel luminescent ruthenium(II) bipyridyl complexes containing one, two, or six lower rim acid–amide-modified calix[4]arene moieties covalently linked to the bipyridine groups are reported which are designed to coordinate and sense luminescent lanthanide ions. All the Ru–calixarene complexes synthesized in this work are able to coordinate $Nd^{3+}$, $Eu^{3+}$, and $Tb^{3+}$ ions with formation of adducts of variable stoichiometry. The absorbance changes allow the evaluation of association constants whose magnitudes depend on the nature of the complexes as well as on the nature of the lanthanide cation. Lanthanide cation complex formation affects the ruthenium luminescence which is strongly quenched by $Nd^{3+}$ ion, moderately quenched by the $Eu^{3+}$ ion, and poorly or moderately increased by the $Tb^{3+}$ ion. In the case of $Nd^{3+}$, the excitation spectra show that (i) the quenching of the Ru luminescence occurs via energy transfer and (ii) the electronic energy of the excited calixarene is not transferred to the $Ru(bpy)_3$ but to the neodymium cation. In the case of $Tb^{3+}$, the adduct's formation leads to an increase of the emission intensities and lifetimes. The reason for this behavior was ascribed to the electric field created around the Ru calix[4]arene complexes by the $Tb^{3+}$ ions by comparison with the $Gd^{3+}$ ion, which behaves identically and can affect ruthenium luminescence only by its charge. However, especially for compounds **1** and **3**, it cannot be excluded that some contribution comes from the decrease of vibrational motions (and nonradiative processes) due to the rigidification of the structure upon $Tb^{3+}$ complexation. In the case of $Eu^{3+}$, compounds **1**, **2**, and **4** were quenched by the lanthanide addition but the quenching of the ruthenium luminescence is not accompanied by europium-sensitized emission which suggests that an electron-transfer mechanism is responsible for the quenching. On the contrary, compound **3** exhibits enhanced emission upon addition of $Eu^{3+}$ (as nitrate salt); it is suggested that the lack of quenching in the [**3**·$2Eu^{3+}$] adduct is due to kinetic reasons because the electron-transfer quenching process is thermodynamically allowed.

## Introduction

During the past decade calixarenes have gained an important place in host−guest chemistry because of their ability to form complexes with ions and neutral molecules.[1−4] In particular functionalization of the lower rim of calix[4]arenes with suitable binding groups has produced a series of powerful cation receptors whose efficiency and selectivity is related to the calixarene ring size and conformation.[4−6] The covalent attachment of calixarenes, by suitable bridges, to luminophores opens the way to new molecules capable of sensing metal ions through light emission measurements.[7] Among the luminescent molecules used for sensing or

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* To whom correspondence should be addressed. E-mail: paul.beer@chemistry.oxford.ac.uk (P.D.B.); mmaestri@ciam.unibo.it (M.M.).

† University of Oxford.

‡ Università di Bologna.

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labeling purposes[8] the Ru(bpy)$_3$ unit is one of the most extensively used[9] as it displays intense absorption bands in the near UV−visible spectral region and an intense emission band in the visible region.[10]

Encapsulation of luminescent metal ions into luminescent host molecules can lead to systems capable of exhibiting novel and unusual photophysical properties. A particularly interesting class of luminescent metal ions is the lanthanide family because of their long-lived and linelike emission bands which cover a spectral range from the near-ultraviolet to the visible and the near-infrared region.[11,12] Direct excitation of lanthanide ions, however, is difficult because of the forbidden nature of their electronic transitions.[11,12] To overcome this difficulty, the luminescent lanthanide ions are usually coordinated to ligands containing organic chromophores whose excitation, followed by energy transfer, causes the sensitized luminescence of the metal ion (antenna effect).[13] Most of the investigations in the field of luminescent lanthanide complexes have been devoted to $Eu^{3+}$ and $Tb^{3+}$ compounds,[13,14] which emit in the visible spectral region and are used as sensors[14] and as luminescent labels in fluoroimmunoassays and time-resolved microscopy.[15] Currently, however, much interest is also devoted to lanthanide ions emitting in the near-infrared (NIR) region[16−18] for both fundamental reasons and possible applications in long-range optical data transport.

Taking into account the above we report here the synthesis of new luminescent ruthenium bipyridyl complexes covalently linked to one, two, or six lower rim acid−amide-modified calix[4]arene moieties, designed to coordinate and sense luminescent lanthanide ions. The photophysical properties of these ruthenium bipyridyl−calixarene complexes together with their adducts with $Nd^{3+}$, $Eu^{3+}$, and $Tb^{3+}$ ions were investigated in detail.

## Experimental Section

**Synthesis. General Procedures.** Acylations were performed under an atmosphere of nitrogen and in dry solvents, unless otherwise specified. Methylene chloride was dried over $CaH_2$, and pyridine was kept over KOH pellets and used without distillation. The other solvents and commercial chemicals were used as received. EDC·HCl stands for *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide hydrochloride. The majority of chemicals used were purchased from Aldrich. Compounds **5**,[19] **8**,[20] and **10**,[21] solutions of "ruthenium-blue",[22] *cis*-[RuCl$_2$(bpy)$_2$],[23] and Ru(DMSO)$_4$Cl$_2$[24] were prepared according to the literature procedures. Melting points were determined in unsealed capillary tubes and are uncorrected.

**Instrumentation.** NMR spectra were recorded on Varian spectrometers operating at 500 and 300 MHz for $^1$H and at 75.4 MHz for $^{13}$C spectra. Spectra were referenced internally using the residual solvent ($CDCl_3$, $\delta$ 7.26; $CD_2Cl_2$, $\delta$ 5.34; $CD_3CN$, $\delta$ 1.95; $(CD_3)_2SO$, $\delta$ 2.49 ppm) resonances relative to $Si(CH_3)_4$. Multiplicities are indicated by one or more of the following: s (singlet); d (doublet); t (triplet); m (multiplet); br (broad).

Elemental analyses were performed by Inorganic Chemistry Laboratory (ICL) University of Oxford Microanalysis Services. Electrospray and positive ion FI mass spectra were measured on a micromass spectrometer by ICL University of Oxford Mass Spectrometry Services; MS FAB spectra were measured by the EPSRC National Mass Spectrometry Service Centre Swansea.

**2-Formyl-2,2′-bipyridine (5)**. To a solution of 4-methyl-2,2′-bipyridine[25] (8 g, 47 mmol) in diethylene glycol dimethyl ether (150 mL) was added selenium dioxide (11.5 g, 104 mmol), and the solution was mildly refluxed for 4.5 h. On cooling of the solution to 90−95 °C, water (15 mL) was added and a black solid was formed, separated, and washed twice with dioxane (2 × 15 mL);

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the filtrate was evaporated to dryness. The white solid was dissolved in $CH_2Cl_2$ (100 mL), and the solution vigorously stirred with a solution of $K_2CO_3$ (5%, 50 mL) for 15 min; the water layer was separated and reextracted with $CH_2Cl_2$ (30 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated, and the crude product was crystallized from *n*-hexane (60 mL) to afford the pure aldehyde **5** as a cream colored powder: yield 5.8 g (67%); mp 94−95 °C (lit.[19] mp 84.8−86 °C); $^1$H NMR ($CDCl_3$) $\delta$ 10.18 (s, 1H, *H*C(O)), 8.90 (d, $J = 4.8$ Hz, 1H, H$^6$), 8.84 (bs, 1H, H$^3$), 8.77 (d, $J = 4$ Hz, 1H, H$^{6'}$), 8.47 (d, $J = 8$ Hz, 1H, H$^{3'}$), 7.85 (td, $J = 7.5$ Hz, $J = 1.8$ Hz, 1H, H$^{4'}$), 7.73 (dd, $J = 4.8$ Hz, $J = 1.5$ Hz, 1H, H$^5$), 7.37 (m, 1H, H$^{5'}$); $^{13}$C NMR ($CDCl_3$) $\delta$ 191.8, 158.1, 154.9, 150.4, 149.4, 142.7, 124,5, 121.2, 120.8 ; MS-FI$^+$ *m*/*z* 184.1, [M + H]$^+$. Anal. Calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.12. Found: C, 71.50; H, 4.38; N, 15.21.

**4-(Hydroxyimino)methyl-2,2′-bipyridine (6).** A mixture of **5** (0.92 g, 5 mmol), hydroxylamine hydrochloride (0.41 g, 6 mmol), and pyridine (0.56 g, 7 mmol) in ethanol (10 mL) was refluxed for 5 h. After cooling of the mixture to room temperature, water (50 mL) was added and the resulted suspension left to stand at 2−4 °C overnight. The product was separated, washed with cold water (2 × 10 mL), and dried at 50−60 °C to afford the pure oxime **6** as white powder: yield 0.9 g (90%); mp 146−147 °C; $^1$H NMR ($CDCl_3$) $\delta$ 11.16 (bs, 1H, O*H*), 8.73−8.68 (m, 3H, H$^{3,6,6'}$), 8.38 (d, $J = 8.1$ Hz, 1H, H$^{3'}$), 8.20 (s, 1H, *H*C=N), 7.89 (d, $J = 6$ Hz, 1H, H$^{4'}$), 7.44 (dd, $J = 5.1$ Hz, $J = 1.5$ Hz, 1H, H$^5$), 7,38 (t, $J = 6$ Hz, 1H, H$^{5'}$); $^{13}$C NMR ($CDCl_3$) $\delta$ 156.2, 155.8,, 149.8, 148.8, 147.6, 141.7, 137.8, 124.2, 122.1, 121.7, 118.7; MS-ES$^+$ *m*/*z* 200.1, [M + H]$^+$. Anal. Calcd for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.20; H, 4.54; N, 21.14.

**4-(Aminomethyl)-2,2′-bipyridine (7).** Oxime **6** (0.8 g, 4 mmol) dissolved in water (38 mL) and concentrated hydrochloric acid (1.6 mL) was hydrogenated on 10% Pd/C catalyst (0.7 g, Degussa) at 10 bar pressure at room temperature for 5 h. The catalyst was removed, the filtrate was concentrated to 3−4 mL and basified by addition of 50% solution of NaOH (4 mL), and the mixture was extracted three times with $CH_2Cl_2$ (60, 40, and 30 mL). The combined organic extract were dried over $K_2CO_3$ and evaporated to give the amine **7** as pale yellow oil: yield 0.56 g (75%); $^1$H NMR ($CD_2Cl_2$) $\delta$ 8.70 (d, $J = 4.8$ Hz, 1H, H$^{6'}$), 8.63 (d, $J = 5.1$ Hz, 1H, H$^6$), 8.49−8.45 (m, 2H, H$^3$, H$^{3'}$), 7.87 (t, $J = 7.6$ Hz, 1H, H$^{4'}$), 7.38−7.34 (m, 2H, H$^5$, H$^{5'}$), 4.01 (s, 2H, C*H*$_2$NH$_2$), 1.61 (br s, 2H, CH$_2$N*H*$_2$); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 156.2, 155.8, 149.8, 148.8, 147.6, 141.7, 137.8, 124.2, 122.1, 121.7, 118.7; MS−FI$^+$ *m*/*z* 186.12, [M + H]$^+$.

**4,4′-Bis(aminomethyl)-2,2′-bipyridine (11).** Dinitrile **10** (1 g, 4.8 mmol) was dissolved in a mixture of THF (20 mL) and ethanol (100 mL) in the presence of concentrated hydrochloric acid (2 mL) and was hydrogenated on 10% Pd/C (0.85 g, Degussa) under 1.2 bar pressure at 65−70 °C for 7 h. The resulting suspension was left to stand at 3−4 °C overnight. The solid phase was separated and suspended in hot 90% methanol (50 mL), and the catalyst was removed and washed with hot 90% methanol (50 mL). The filtrate was evaporated to give the crude hydrochloride as pale-pink solid. This was dissolved in water (3 mL), solid NaOH (2 g) was added under cooling by ice−water, and the mixture was extracted four times with $CH_2Cl_2$ (80 and 3 × 50 mL). The combined organic extracts were dried over $K_2CO_3$ and evaporated to give the pure diamine **11** as a white powder: yield 0.86 g (84%); mp 102−104 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 8.58 (d, $J = 5$ Hz, 2H, H$^{6,6'}$), 8.41 (s, 2H, H$^{3,3'}$), 7.31 (dd, $J = 5$ Hz, 2H, H$^{5,5'}$), 3.97 (s, 4H, C*H*$_2$NH$_2$), 1.54 (br s, 4H, CH$_2$N*H*$_2$); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 156.4, 153.8, 152.2, 149.4, 119.4, 45.7; MS-FI$^+$ *m*/*z* 215.08, [M + H]$^+$. Anal. Calcd for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.20; H, 4.54; N, 21.14.

**4,4′-Bis((methoxyacetamido)methyl)-2,2′-bipyridine (13).** To a solution of diamine **11** (0.43 g, 2 mmol) and triethylamine (0.71 g, 7 mmol) in $CH_2Cl_2$ (60 mL) was added a solution of methoxyacetyl chloride (0.48 g, 4.4 mmol) in $CH_2Cl_2$ (10 mL) and the mixture stirred at room temperature for 1 h. The reaction mixture was washed twice with water (2 × 20 mL), and the organic layer was dried over $MgSO_4$ and evaporated to give amide **13** as white powder, yield 0.7 g (97%). An analytical sample was obtained by recrystallization from ethanol: mp 154 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.63 (d, $J = 5$ Hz, 2H, H$^{6,6'}$), 8.31 (s, 2H, H$^{3,3'}$), 7.27 (d, $J = 4.8$ Hz, 2H, H$^{5,5'}$), 7.01 (br s, 2H, CH$_2$N*H*C(O)), 4.59 (d, $J = 6.3$ Hz, 4H, C*H*$_2$NHC(O)), 3.99 (s, 4H, C(O)C*H*$_2$OCH$_3$)), 3.44 (s, 6H, C(O)CH$_2$OC*H*$_3$); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.1, 156.4, 149.8, 148.5, 122.8, 120.1, 72.1, 59.5, 42.0; MS-FI$^+$ *m*/*z* 358.2, [M]$^+$. Anal. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.14; H, 6.19; N, 15.57.

**Mono(calix[4]arene)−Bipyridine (9).** A mixture of calix[4]arene monoacid **8** (0.6 g, 0.87 mmol), amine **7** (0.21 g, 1.1 mmol), and EDC·HCl (0.25 g, 1.3 mmol) in pyridine (10 mL) was stirred at room temperature for 4 h. The orange reaction mixture was poured into water (100 mL); after the mixture was stirring for 1 h, the solid was separated, washed with water, and dried at 60−70 °C. The crude product was purified by column chromatography employing silica gel 60 and $CH_2Cl_2$−ethyl acetate mixture (1:1) as eluent. The second yellow band was collected, solvents were evaporated, and the solid was crystallized from ethanol (10 mL) to give **9** as yellow crystalline product: yield 0.5 g (67%); $^1$H NMR ($CD_2Cl_2$, 500 MHz) $\delta$ 8.99 (br s, 2H, PhO*H*), 8.91 (t, $J = 6$ Hz, 1H, CH$_2$N*H*C(O)), 8.57, 8.56 (2 × s, 2H, bpy-3,3′), 8.54 (d, $J = 5$ Hz, 1H, bpy-6), 8.30 (d, $J = 8$ Hz, 1H, bpy-6′), 8.03, 8.01 (2 × d, $J = 3$ Hz, 4H, NO$_2$Ph*H*), 7.80 (td, $J = 7.5$ and 1.5 Hz, 1H, bpy-4′), 7.40 (dd, $J = 5$ and 1.5 Hz, 1H, bpy-5), 7.33 (m, 1H, bpy-5′), 7.07−7.04 (m 4H, Ph*H*), 6.95−6.91 (m, 2H, Ph*H*), 4.93 (d, $J = 6$ Hz, 2H, C*H*$_2$NHC(O)CH$_2$O), 4.65, 4.57 (2 × s, 4H, C(O)-C*H*$_2$O), 4.23, 4.20 (2 × d, $J = 13.5$ Hz, 4H, PhC*H*$_2$Ph), 3.56, 3.51 (2 × d, $J = 13.5$ Hz, 4H, PhC*H*$_2$Ph), 1.51 (s, 9H, C(C*H*$_3$)); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 168.2, 167.7, 158.8,1 56.5, 151.7, 151.6, 149.4, 149.0, 148.9, 140.5, 136.9, 131.8, 131.7, 130.3, 130.2, 128.1, 127.9, 126.7, 126.6, 124.9, 124.6, 124.0, 123.1, 120.9, 120.0, 83.6, 75.2, 73.0, 42.3, 31.4, 31.2, 28.1; MS-FAB *m*/*z* 854.0, [M + H]$^+$, 876.0, [M + Na]$^+$. Anal. Calcd for $C_{47}H_{43}N_5O_{11}$: C, 66.11; H, 5.08; N, 8.20. Found: C, 65.94; H, 4.93; N, 8.00.

**Bis(calix[4]arene)−Bipyridine (12).** A mixture of calix[4]arene monoacid **8** (1.3 g, 1.9 mmol), diamine **11** (0.2 g, 0.9 mmol), and EDC·HCl (0.7 g, 3.6 mmol) in pyridine (20 mL) was stirred at room temperature for 5 h. The reaction mixture was poured into water (100 mL); after the mixture was stirred at 50 °C for 1 h, the solid was separated, washed with water (3 × 5 mL), and dried at 60−70 °C to give **12** as white powder, yield 1.36 g (97%). An analytical sample was obtained by crystallization from ethanol: $^1$H NMR ($CD_2Cl_2$, 500 MHz) $\delta$ 9.00 (br s, 2H, PhO*H*), 8.90 (t, $J = 6$ Hz, 2H, CH$_2$N*H*C(O)), 8.43 (s, 2H, bpy-3,3′), 8.41 (d, $J = 5$ Hz, 2H, bpy-5,5′), 8.04, 8.03 (2 × d, $J = 8$ Hz, 8H, NO$_2$Ph*H*), 7.36 (d, $J = 4$ Hz, 2H, bpy-5,5′), 7.07, 7.05 (2 × d, $J = 8$ Hz, 8H, Ph*H*), 6.95, 6.94 (2 × t, $J = 8$ Hz, 2H, Ph*H*), 4.92 (d, $J = 6$ Hz, 4H, C*H*$_2$NHC(O)), 4.67, 4.55 (2 × s, 8H, C(O)C*H*$_2$O), 4.23, 4.18 (2 × d, $J = 13.5$ Hz, 8H, PhC*H*$_2$Ph), 3.58, 3.51 (2 × d, $J = 13.5$ Hz, 8H, PhC*H*$_2$Ph), 1.49 (s, 18H, C(C*H*$_3$)); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.1, 156.4, 149.8, 148.5, 122.8, 120.1, 72.1, 59.5, 42.0; MS-FAB *m*/*z* 1551, [M]$^+$. Anal. Calcd for $C_{84}H_{78}N_8O_{22}\cdot 2H_2O$: C, 63.55; H, 5.21; N, 7.06. Found: C, 63.16; H, 5.27; N, 7.16.

**Tris[(bis(methoxyacetamido)methyl-2,2′-bipyridine]ruthenium Bis(hexafluorophosphate) Dihydrate (1).** A mixture of diamide **13** (0.143 g, 0.4 mmol) and $Ru(DMSO)_4Cl_3$ (60 mg, 0.12 mmol) in ethanol (15 mL) was refluxed for 5 h. After evaporation of the solvent, the dark-red crude product was purified on a Sephadex LH 20 column by employing a mixture of acetonitrile and 2-propanol (2%) as eluent. The last dark-orange band was collected, solvents were evaporated, the solid residue was dissolved in water (15 mL), and under vigorous stirring a saturated solution of $NH_4PF_6$ (0.5 g) was added. After the mixture was stirring for 0.5 h, the precipitate was separated, washed with ice−water (2 × 3 mL), and dried in vacuo over $P_2O_5$ to give the title compound as dark orange powder: yield 0.15 g (75%); $^1$H NMR ($CD_3CN$) $\delta$ 8.38 (d, $J = 1$ Hz, 3H, bpy-3,3′), 7.64 (d, $J = 6$ Hz, 6H, bpy-6,6′), 7.58 (t, $J = 6.5$ Hz, 6H, $CH_2NHC(O)$), 7.31 (dd, $J = 6$ and 2 Hz, 6H, bpy-5,5′), 4.58 (d, $J = 6.5$ Hz, 12H, $CH_2NHC(O)$), 3.94 (s, 12H, $C(O)CH_2OCH_3$), 3.41 (s, 18H, $OCH_3$); $^{13}$C NMR ($CD_3CN$) $\delta$ 171.7, 158.0, 152.6, 152.4, 127.1 123.8, 72.9, 60.1, 42.2; MS-ES$^+$ $m/z$ 588.1, $[M]^{2+}$. Anal. Calcd for $C_{54}H_{66}F_{12}N_{12}O_{12}P_2Ru\cdot 2H_2O$: C, 43.18; H, 4.70; N, 11.19. Found: C, 43.43; H, 4.83; N, 11.04.

**Procedure for De-*tert*-butylation of 9 and 12.** A solution of *tert*-butyl ester in a 1:1 (v/v) mixture of trifluoroacetic acid and $CH_2Cl_2$ (16 mL/mmol) was refluxed for 6 h. After solvent removal, the solid residue was dissolved in $CHCl_3$ (150 mL/mmol) and washed with water (30 mL/mmol); the organic phase was dried over $MgSO_4$ and evaporated to afford the free acid in quantitative yield. The $^1$H NMR spectrum taken in DMSO-$d_6$ indicated the absence of *tert*-butyl groups.

**Ruthenium Mono(calix[4]arene)−bipyridine Ligand (2).** A mixture of free acid prepared from **9** (0.17 g, 0.2 mmol) and $[RuCl_2(bpy)_2]\cdot 2H_2O$ (0.11 g, 0.21 mmol) was refluxed in a mixture of ethanol (30 mL), acetic acid (5 mL), and water (5 mL) for 16 h. The solvents were evaporated in vacuo, and the dark-orange solid was purified on Sephadex LH 20 column employing acetonitrile containing 0−5% 2-propanol as eluent. The broad orange band was collected, and solvents were evaporated to leave an orange solid, which was dissolved in $CH_2Cl_2$ (50 mL) and vigorously stirred with a solution of $NH_4PF_6$ (0.5 g) in water (5 mL) for 0.5 h. The organic layer was separated, washed with water (5 mL), and dried over $Na_2SO_4$, and after evaporation of the solvent, the product was dried in vacuo over $P_2O_5$ to give **2** as orange powder: yield 0.15 g (50%); $^1$H NMR ($CD_3CN$, 500 MHz) $\delta$ 9.27 (br s, 2H, PhO*H*), 8.64 (t, $J = 6$ Hz, 1H, $CH_2NHC(O)$), 8.56−8.50 (m, 6H, bpy), 8.24−8.20 (m, 4H, $NO_2PhH$), 8.10, 8.04 (m, 4H, bpy), 7.77−7.72 (m, 5H, bpy), 7.65 (d, $J = 6$ Hz, 1H, bpy), 7.52 (dd, $J = 6$ and 2 Hz, bpy), 7.44−7.35 (m, 5H, bpy), 7.19, 7.15 (2 × d, $J = 7.5$ Hz, 4H, Ph*H*), 6.98, 6.97 (2 × t, $J = 7.5$ Hz, 2H, Ph*H*), 5.03−4.91 (m, 2H, $CH_2$-NHC(O)), 4.72−4.63 (m, 2H, $C(O)CH_2O$), 4.37−4.26 (m, 4h, $HOC(O)CH_2O$ and $PhCH_2Ph$), 4.10, 4.06 (2 × d, $J = 13.5$ Hz, 2H, $PhCH_2Ph$), 3.74−3.61 (4 × d, $J = 13.5$ Hz, 4H, $PhCH_2Ph$); MS FAB $m/z$ 1211 $[M - 2PF_6]$, 1356 $[M - PF_6]$; TOF MS ES$^+$ $m/z$ 605.88 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{63}H_{51}F_{12}N_9O_{11}P_2Ru$: C, 50.41; H, 3.42; N, 8.40. Found: C, 50.61; H, 3.78; N, 8.73.

**Ruthenium Bis(calix[4]arene)−Bipyridine Ligand (3).** A mixture of free bis(acid) prepared from **12** (0.62 g, 0.4 mmol) and $[RuCl_2(bpy)_2]\cdot 2H_2O$ (0.22 g, 0.42 mmol) was refluxed in a mixture of ethanol (80 mL), acetic acid (10 mL), and water (10 mL) for 20 h. The solvents were evaporated in vacuo, and the dark-orange solid was purified on Sephadex LH 20 column employing acetonitrile containing 0−5% 2-propanol as eluent. The broad orange band was collected, solvents were evaporated to leave an orange solid, which was dissolved in $CH_2Cl_2$ (120 mL), and the solution was vigorously stirred with a solution of $NH_4PF_6$ (1 g) in water (15 mL) for 0.5 h. The organic layer was separated, washed with water (5 mL), and dried over $Na_2SO_4$, and after evaporation of the solvent, the product was dried in vacuo over $P_2O_5$ to give **3** as orange powder: yield 0.48 g (55%); $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 9.25 (br s, 4H, PhO*H*), 8.87 (d, $J = 8.5$ Hz, 4H, bpy-3,3′), 8.79 (s, 2H bpy-3,3′), 8.52 (br s, 2H, $CH_2NHC(O)$), 8.26 (s, 8H, $NO_2PhH$), 8.17 (m, 4H, bpy-4,4′), 7.73 (d, $J = 5.5$ Hz, 4H, bpy-6,6′), 7.61 (d, $J = 6$ Hz, 2H, bpy-6,6′), 7.56−7.52 (m, 4H, bpy-5,5′), 7.41 (br s, 2H, bpy-5,5′), 7.20−7.13 (m, 8H, Ph*H*), 6.92, 6.85 (2 × t, $J = 7.5$ Hz, 4H, Ph*H*), 4.76−4.46 (m, 12H, $CH_2NHC(O)CH_2C(O)$ and $HOC(O)$-$CH_2O$), 4.24−4.01 (m, 8H, $PhCH_2Ph$), 3.76−3.68 (m, 8H, $PhCH_2$-Ph); MS FAB $m/z$ 1852.4 $[M - 2PF_6 - 4H_2O]$. Anal. Calcd for $C_{96}H_{78}F_{12}N_{12}O_{22}Ru\cdot 4H_2O$: C, 52.06; H, 3.91; N, 7.59. Found: C, 52.13; H, 4.12; N, 7.53.

**Ruthenium Hexakis(calix[4]arene)−Tris(bipyridine) Ligand (4).** To a blue-green solution of ruthenium blue prepared from $RuCl_3\cdot 3H_2O$ (26.1 mg, 0.1 mmol) in ethanol (60% v/v, 11 mL) were added a solution of deprotected **12** (0.43 g, 0.3 mmol) in DMF (3 mL) and acetic acid (1 mL). After the solution was refluxed for 8 h, the volatile parts were removed in vacuo and the solid residue was purified by flash chromatography employing silica gel 60 for TLC and methanol containing acetic acid (2%) as eluent. The last yellow-orange band was collected, the solvents were evaporated in vacuo, and the orange residue was vigorously stirred with a mixture of $CH_2Cl_2$ and solution of $NH_4PF_6$ (0.5 g) in water (5 mL) for 0.5 h. The organic layer was separated, dried over $Na_2SO_4$, and evaporated, and the solid residue was dried in vacuo over $P_2O_5$ to give **4** as orange powder: yield 0.12 g (35%); $^1$H NMR (DMSO-$d_6$) $\delta$ 9.70 (very br s,), 8.85 (s, 6H, bpy-3,3′), 8.68 (br s, 6H, $CH_2NHC(O)$), 8.21, 8.19, 8.11 (3 × s, 24H, $NO_2PhH$), 7.77 (br s, 6H, bpy-6,6′), 7.52 (br s, 6H, bpy-5,5′), 7.20−7.10 (m, 24H, Ph*H*), 6.89−6.82 (m, 12H, Ph*H*), 4.78, 4.68, 4.48, 4.24, 4.11 (5 × br s, 60H, $C(O)CH_2O$, $CH_2NHC(O)$, $PhCH_2Ph$), 3.64 (br s, $PhCH_2Ph$), 3.38 (br s, $H_2O$); TOF MS ES$^+$ $m/z$ 2209.8 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{228}H_{186}F_{12}N_{24}O_{66}P_2Ru\cdot 12H_2O$: C, 55.60; H, 4.30; N, 6.83. Found: C, 55.45; H, 4.30; N, 7.00.

**Equipment.** Absorption spectra were recorded in acetonitrile solution on a Perkin-Elmer lambda 16 spectrophotometer. Luminescence experiments were performed in acetonitrile solution at room temperature and in butyronitrile rigid matrix at 77 K. Luminescence spectra in the visible region (400−850 nm) were obtained with a Perkin-Elmer LS50 spectrofluorimeter. NIR luminescence spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a Hamamatsu R5509-72 (spectral range 300−1700 nm) supercooled photomultiplier tube (193 K) and a TM300 emission monochromator with NIR grating blazed at 1000 nm. Luminescence lifetimes were obtained with a Edinburgh single photon counting instrument ($N_2$ lamp, 337 nm). Luminescence quantum yields were measured in air-equilibrated solutions with a Perkin-Elmer LS 50 spectrofluorometer, following the method described by Demas and Crosby[26] using $[Ru(bpy)_3]^{2+}$ ($\Phi = 2.8 \times 10^{-2}$ in aerated water).[10]

The estimated experimental error is 2 nm on the band maximum, 5% on the molar extinction coefficient, 10% on the fluorescence quantum yield, and 5% on the fluorescence lifetime. The concentrations of the ruthenium−bpy−calix(4)arene complexes were in the range $10^{-4}$−$10^{-5}$ M. Titration experiments of the complexes were performed in acetonitrile solutions with $La(NO_3)_3$.

Electrochemical experiments were carried out by employing cycling voltammetry and differential pulse voltammetry techniques

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(26) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

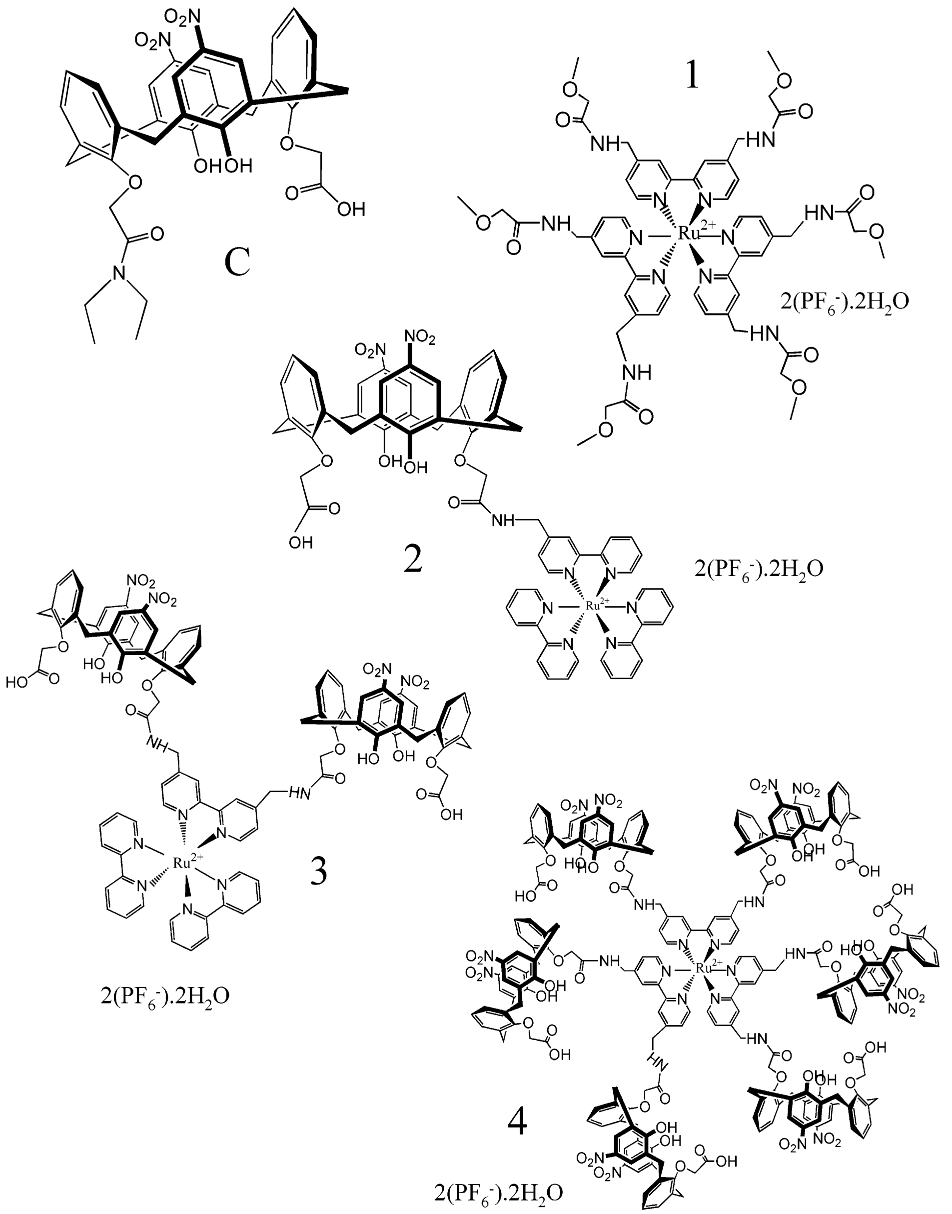


**Figure 1.** Structural formulas of the four ruthenium complexes and of a calix(4)arene reference compound.

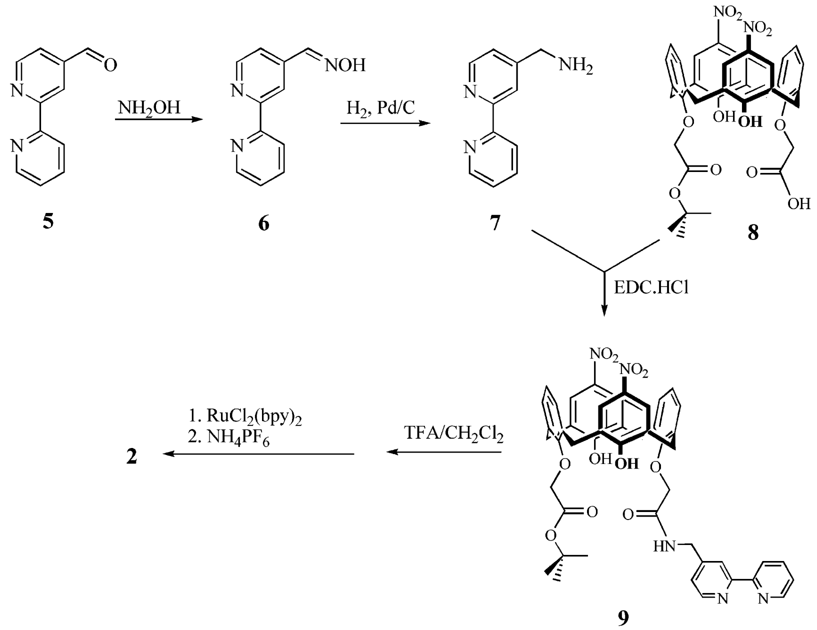
on argon-purged acetonitrile (Romil HiDry) solutions at room temperature, with an Autolab 30 multipurpose instrument interfaced to a PC. The working electrode was a glassy carbon electrode (Amel; 0.07 cm$^2$). The counter electrode was a Pt wire, separated from the solution by a frit; an Ag wire was employed as a quasi-reference electrode, and ferrocene was present as an internal standard. The concentrations of the compounds examined were 5 × $10^{-4}$ M; 0.05 M tetraetylammonium hexafluorophosphate (TEAP) was added as supporting electrolyte.

## Results and Discussion

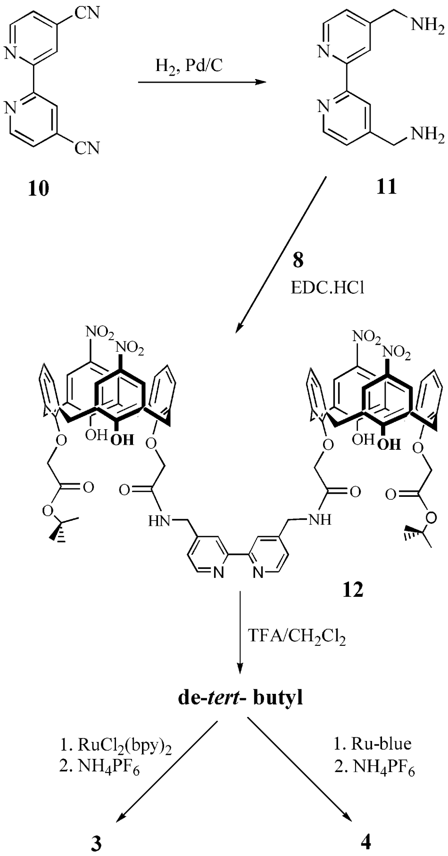
**Synthesis of Ruthenium Calix[4]arene−Bipyridine Complexes.** Calix[4]arene ligands bearing a lower rim 1,3-acid−amide functionality have been developed for the extraction of toxic metal ions including lanthanides from aqueous solutions.[20] Covalently linking this acid−amide-derivatized calix[4]arene lanthanide complexant design to the ruthenium(II) bipyridyl moiety produces the potential lanthanide sensing target receptors.

The synthetic routes used to prepare the ruthenium calix[4]arene−tris(bipyridine) complexes **1**−**4** (Figure 1) are illustrated in Schemes 1−3. 4-Formyl-2,2′-bipyridine (**5**) was prepared from 4-methyl-2,2′-bipyridine[25] by a modified literature procedure[19] employing selenium dioxide and diethylene glycol dimethyl ether as solvent. The formyl derivative **5** was converted into oxime **6** in 90% yield and reduced to amine **7** by catalytic hydrogenation on Pd/C in water and in the presence of excess HCl in 75% yield. Condensation of amine **7** with calix[4]arene monoacid **8**[20] using EDC·HCl as coupling agent in pyridine, followed by purification of the crude product on silica gel column and crystallization, afforded **9** in 67% yield. After removal of the *tert*-butyl group from the ester, by refluxing in a mixture of TFA/$CH_2Cl_2$, the resulting acid was reacted with *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II)[23] in a mixture of ethanol, water, and acetic acid. The crude product was purified on a Sephadex column and converted into the $PF_6$

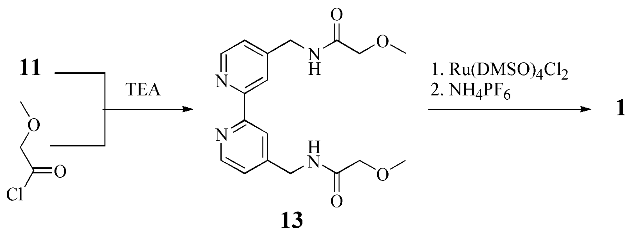
**Scheme 1.** Synthetic Route to Prepare the Mono(calix[4]arene)−Bipyridine Ligand (**9**) Used To Synthesize the Ruthenium Bipyridine−Calix[4]arene Complex **2**



**Scheme 2.** Synthetic Route To Prepare the Bis(calix[4]arene)−Bipyridine Ligand (**12**) Used To Synthesize Ruthenium Bipyridine−Calix[4]arene Complexes **3** and **4**



**Scheme 3.** Synthetic Route To Prepare the Amido−Bipyridine Ligand (**13**) Used To Synthesize the Ruthenium Bipyridine Complex **1**



salt to afford **2** in 50% yield (Scheme 1). The bis(calix[4]arene) congener **3** was prepared using analogous synthetic methodology starting from dinitrile **10**,[21] which was reduced to diamine **11** by catalytic hydrogenation on Pd/C in ethanol and in the presence of excess HCl in 84% yield. Condensation of **11** with **8** afforded bis(calix[4]arene) derivative **12** in 97% yield. After deprotection and reaction with *cis*-[$RuCl_2$-$(bpy)_2$], **3** was obtained in 55% yield. **12** was also converted into hexacalix[4]arene derivative **4** by employing ruthenium-blue[22] in 35% yield (Scheme 2). The model ruthenium tris(bipyridine) complex **1** was prepared from diamine **11** using standard synthetic procedures (Scheme 3).

All new compounds were characterized by NMR, mass spectrometry, and elemental analysis.

**Spectroscopic Characterization of the Ruthenium−Bipyridyl−Calix[4]arene Complexes and Model Compounds.** The absorption spectra of the four complexes show the typical bands at 450 and 300 nm of the tris(bipyridine)ruthenium(II) complex (see Figure 2; Table 1). The compounds carrying calixarene moieties (namely compounds **2**−**4**) exhibit an additional band at ca. 325 nm; the intensity of this band increases according to the increasing number of calixarene units bonded to the $Ru(bpy)_3$ core, as expected owing to the absorption spectrum of the free calix[4]arene (**C**) that shows an intense absorption bands at 328 nm.

The four complexes and the free calix[4]arene exhibit luminescence. The emission spectrum in butyronitrile at 77 K of the free calix(4)arene (**C**) slightly differs from the phosphorescence emission spectrum ($\lambda_{max} = 420$ nm, $\tau = 1.8$ s) reported for a similar calix[4]arene[27] showing either fluorescence ($\lambda_{max} = 390$ nm, $\tau =$ ca. 1.4 ns) or a structured phosphorescence ($\lambda_{max} = 482$ nm, $\tau = 120$ ms). The

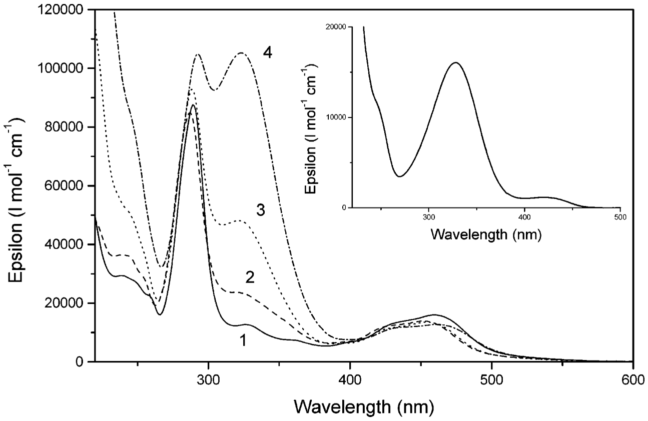


**Figure 2.** Absorption spectra of the four ruthenium complexes in $CH_3CN$. The inset shows the molar absorption coefficients of the calix(4)arene reference compound **C**.

complexes exhibit the typical luminescence spectrum of the $Ru(bpy)_3$ moiety either at room temperature or at 77 K. The characteristics of this luminescence ($\lambda_{max}$, $\Phi$, $\tau$) are reported in Table 1 and are all typical for a ruthenium $^3$MLCT excited state. Only one aspect, related to the emission spectra, is worth noting. Comparisons between the absorption and excitation spectra of complexes **2**−**4** show that the energy transfer between the excited calixarene and the $Ru(bpy)_3$ unit is very poor since the band at ca. 320 nm typical of calixarenes absorption is practically absent in the excitation spectra at room temperature. A detailed analysis of these excitation spectra (Figure 3) shows that while the energy transfer is almost negligible in compound **2** it slightly increases with the increasing number of appended calixarenes, resembling the signal amplification effect observed in luminescent dendrimers.[28]

On the contrary the excitation spectrum of compound **4** at 77 K in butyronitrile almost matches its absorption spectrum showing an almost unitary efficiency of the process that transfers electronic energy from the excited calixarene to the $Ru(bpy)_3$ unit in frozen media.

The room-temperature results can be accounted for by a competition between energy and electron-transfer processes in quenching calixarene excited states, while at 77 K only energy transfer to the ruthenium $^3$MLCT excited state occurs because of the higher energy level of electron-transfer products lacking solvent stabilization energy (solvent repolarization).

This hypothesis is supported by the redox potentials of the free calix[4]arene (**C**) ($\mathbf{C}^+/\mathbf{C} = +1.45$ V, $\mathbf{C}/\mathbf{C}^- = -1.69$ V vs SCE, both nonreversible) and Ru complex ($Ru^{3+}/Ru^{2+} = +1.26$ V; $Ru^{2+}/Ru^{+} = -1.28$ V vs SCE)[10] that compared with calix[4]arene excited-state energy ($E^{S}_{0/0} = 3.26$ eV; $E^{T}_{0/0} = 2.61$ eV) show that CT processes leading either to oxidation or reduction of the ruthenium complex are thermodynamically allowed to the singlet state of the free calix[4]arene at room temperature.

**Lanthanide Complexation.** Addition of lanthanide ions (as nitrate salts) to acetonitrile solutions of the ruthenium complexes causes noticeable changes in the absorption spectrum of all the compounds carrying calixarene moieties (namely **2**−**4**). Figure 4 shows the plots obtained upon titration of a $2.5 \times 10^{-5}$ M solution of **3** with $Nd^{3+}$ in the concentration range $0-1.1 \times 10^{-4}$ M.

A common feature for cases where spectral changes have been observed is a decrease of the typical band of calixarene at ca. 325 nm with a parallel increase of a new band at ca. 390 nm as the titration with the lanthanides proceeds; this suggests the formation of adducts between the lanthanide ions and the complexes with a direct involvement of the calixarene moiety in hosting the metal cation. In agreement with this conclusion is the finding that the calix[4]arene alone (**C**) shows similar spectral changes upon addition of the three lanthanide ions.

The spectral changes obtained in all the titration experiments were treated by means of the SPECFIT[29] software, and a best-fitting procedures gave the following results.

In the case of compound **2** the spectral changes caused by the addition of the three lanthanides are consistent with an initial formation of a 2:1 (complex:$Ln^{3+}$) adduct that is then converted into a 1:1 adduct when the $Ln^{3+}$:complex ratio is greater than 0.5. The association constants of the two adducts obtained with the three ions ($Eu^{3+}$, $Tb^{3+}$, and $Nd^{3+}$) are reported in Table 2.

In the case of compound **3** the best fitting procedure (by using SPECFIT) suggests for all lanthanides an initial 1:1 and a final 1:2 (complex:$Ln^{3+}$) formation adduct, as expected owing to the two calix[4]arene acid-amine recognition sites present in **3**. The association constants are again reported in Table 2.

As far as receptor **4** is concerned, there are a large number of lanthanide complexed possible adducts; however, the UV−vis titration experiments suggest at least five $Ln^{3+}$ cations are bound by the receptor.

In the case of compound **1** addition of lanthanide ions to its acetonitrile solutions does not cause appreciable spectral changes even for lanthanide metal ion concentrations up to $10^{-3}$ M.

**Luminescence.** As we have seen before, all the complexes exhibit the typical emission spectrum of the ruthenium moiety. The addition of lanthanide ions perturbs these emission spectra to an extent that depends on the nature of the complexes as well as on the lanthanide ions.

**$Nd^{3+}$ Ion.** Addition of $Nd^{3+}$ ions decreases the luminescence intensity of the complexes. The luminescence behavior of solutions $4.9 \times 10^{-5}$ M of compound **3** at various $Nd^{3+}$ concentration is reported in Figure 5 as an example.

It can be seen that a decrease of the $^3$MLCT Ru emission at 610 nm and a parallel increase of the typical metal-centered $^4F_{3/2}$ excited-state luminescence of $Nd^{3+}$ at 1064 nm occurs as the lanthanide concentration increases. Solutions of compounds **1**, **2**, and **4** exhibit a similar behavior.

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**Table 1.** Absorption and Emission Data for the Complexes

| | abs[a] | | RT emission[a] | | | 77 K emission[b] | |
|---|---|---|---|---|---|---|---|
| compd | $\lambda$ (nm)[c] | $\epsilon$ ($M^{-1}$ $cm^{-1}$) | $\lambda$ (nm)[d] | $\tau$ (ns)[e] | $\Phi$[f] | $\lambda$ (nm)[d] | $\tau$ (ns)[e] |
| **C** | 328 | 10 500 | | | | 300 | 1.4 |
| | 420 | 680 | | | | 480 | 120 |
| $Ru(bpy)_3^{2+}$ | 452 | 14 000 | 615 | 180 (1000) | 0.028 | | |
| **1** | 459 | 16 000 | 622 | 191 (1000) | 0.016 | | |
| **2** | 452 | 13 900 | 613 | 168 (700) | 0.009 | | |
| **3** | 454 | 14 500 | 617 | 179 (860) | 0.009 | | |
| 4 | 463 | | 615 | 443 (560) | 0.028 | | |

[a] Acetonitrile; RT = room temperature. [b] Butyronitrile. [c] Wavelength of the lowest energy absorption band. [d] Uncorrected wavelength of the highest energy emission band. [e] Luminescence emission lifetime values; in parentheses the values in deaerated solutions (±10%). [f] Luminescence emission quantum yield values (±30%).

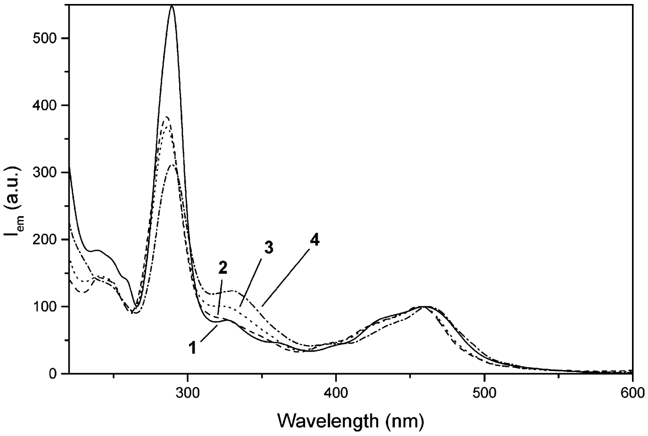

**Figure 3.** Excitation spectra of the ruthenium bipyridyl−calix[4]arene complexes ($\lambda_{em}$ = 610 nm).

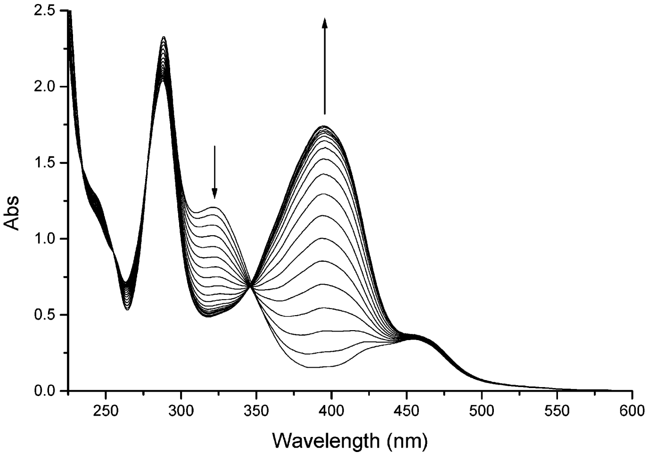

**Figure 4.** Changes in the absorption spectrum of **3** upon titration with $Nd^{3+}$ in $CH_3CN$. [**3**] = 2.5 × $10^{-5}$ M.

**Table 2.** Association Constant Values[a]

| | abs measuremnts | | | emission measuremnts | | |
|---|---|---|---|---|---|---|
| adduct | $Nd^{3+}$ | $Eu^{3+}$ | $Tb^{3+}$ | $Nd^{3+}$ | $Eu^{3+}$ | $Tb^{3+}$ |
| **1**·La | | | | 5.8 | 5.9 | 4.7 |
| **1**·2La | | | | 10.5 | 10.6 | 8.6 |
| $(\mathbf{2})_2$·La | 10.4 | 13.3 | 11.7 | 10.3 | *b* | *b* |
| **2**·La | 5.1 | 6.9 | 5.2 | 5.2 | *b* | *b* |
| **3**·La | 7.0 | 7.4 | 8.1 | 8.0 | *c* | 8.0 |
| **3**·2La | 13.1 | 13.7 | 13.4 | 13.4 | *c* | 12.5 |

[a] log *K* values for the association constants of the lanthanide adducts with the ruthenium bipyridyl−calix[4]arene complexes. [b] The low effect on the ruthenium luminescence leads to meaningful values. [c] The spectral data do not give a suitable fitting.

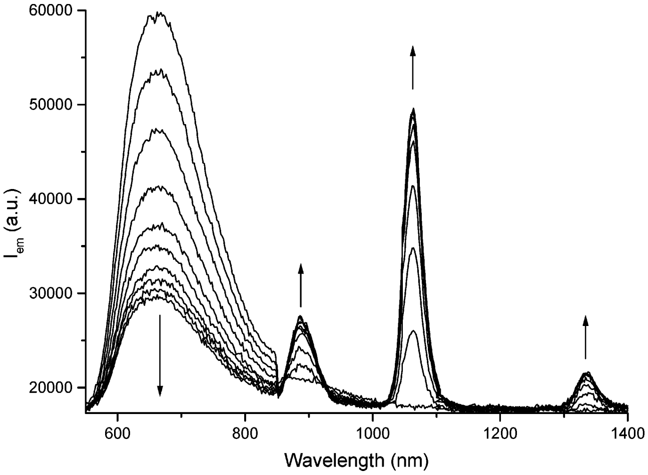

**Figure 5.** Changes in the emission spectrum of **3** upon titration with $Nd^{3+}$ in $CH_3CN$. [**3**] = 4.9 × $10^{-5}$ M.

The increase of the $Nd^{3+}$ emission at 1064 nm cannot be due to direct excitation of the lanthanide, as this would increase with increasing $Nd^{3+}$ concentration, because of the negligible molar absorption coefficient of the lanthanide (close to, or lower than, 1 $M^{-1}$ $cm^{-1}$ [11,12]) compared to that of the $Ru(bpy)_3$ unit at the excitation wavelength (452 nm, $\epsilon$ = 14000 $M^{-1}$ $cm^{-1}$ [10]). Therefore, the NIR luminescence observed in fluid solution at 298 K in the $Nd^{3+}$ titration of the four complexes has to derive by sensitization from the excited $Ru(bpy)_3$ unit. This is evidence that the intimate quenching occurs via an energy transfer mechanism. This was an expected result since energy transfer between ruthenium complexes and neodymium ions has been observed[30] and can occur because of a good overlap between the donor emission and the acceptor absorption bands.[10−12]

The quenching of the ruthenium complexes emission when treated as a dynamic process with the Stern−Volmer equation leads to bimolecular quenching constants exceeding the diffusion limit with compounds **2**−**4**. In the case of compound **1**, the $Nd^{3+}$ concentration needed to quench the emission of the ruthenium moiety at first sight seems consistent with a dynamic quenching process with an almost diffusion-controlled bimolecular quenching constant (8 × $10^9$ $M^{-1}$ $s^{-1}$). Actually, bimolecular quenching constants much lower than the diffusion controlled limit are expected in energy transfer processes because of the poor availability of

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(30) Klink, S. I.; Keizer, H.; vanVeggel, F. C. J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4319.

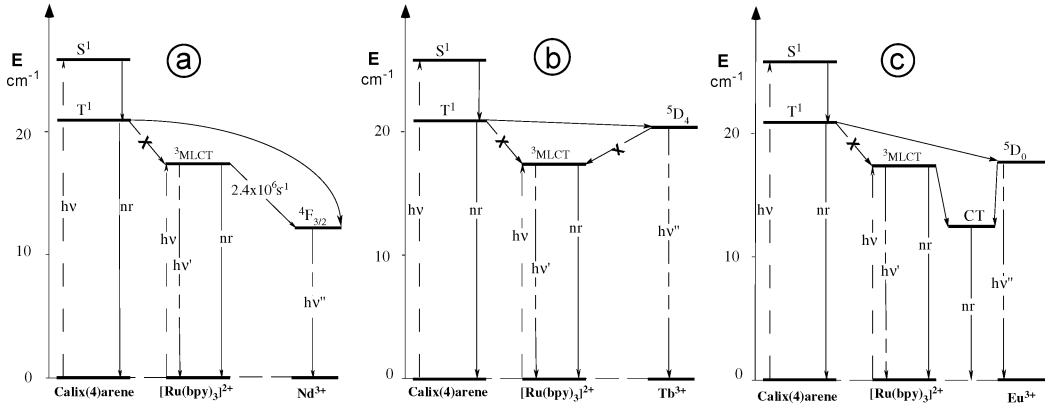

**Figure 6.** Energy level diagram accounting for the photophysical behavior of the lanthanide adducts with the ruthenium bipyridyl−calix[4]arene complexes: (a) $Nd^{3+}$; (b) $Tb^{3+}$; (c) $Eu^{3+}$.

the inner lanthanide f orbitals.[31] In agreement with this expectation we have found that the $[Ru(bpy)_3]^{2+}$ complex is dynamically quenched by $Nd^{3+}$ ions with a bimolecular quenching constant of $3 \times 10^7$ $M^{-1}$ $s^{-1}$. Thus, the high quenching constant found for the luminescence quenching of the ruthenium complexes by $Nd^{3+}$ ions is due to some sort of static quenching within an adduct formed by $Nd^{3+}$ and the complexes. Therefore, the quenching observed in the titrations of the four complexes with $Nd^{3+}$ ions must originate from an association of the metal cation and the calixarene moieties of the complexes as already suggested by the changes in the absorption spectra during the $Nd^{3+}$ titration of compounds **2**−**4**. The best-fitting procedure by using SPECFIT on the luminescence spectra obtained upon titrations of the four complexes with $Nd^{3+}$ ions gives the results reported in Table 2 that qualitatively agree with the results obtained by the fitting of the absorption spectral data.

It was shown that in the case of compound **1** the addition of $Nd^{3+}$ leads to an initial formation of a 1:1 (**1**:$Nd^{3+}$) complex that is then converted to a final 1:2 adduct as the $Nd^{3+}$:complex ratio increases. These two adducts, although not spectrophotometrically observable, most probably involve the amide-carbonyl groups linked to the bipyridines of **1**.

In the case of compound **2** titrated with $Nd^{3+}$ ions the initial formation of a 2:1 (**2**:$Nd^{3+}$) adduct is followed by a conversion to a 1:1 adduct. Lifetime measurements performed on the Ru emission support this kinetic behavior. In fact, whereas the fluorescence decay of the complex is monoexponential ($\tau° = 170$ ns), a more complex decay pattern is observed after addition of the metal ion ($Nd^{3+}$). For example, in a solution containing $4.5 \times 10^{-5}$ M of **2** and $2.5 \times 10^{-5}$ M $Nd^{3+}$, a multiexponential decay was observed with two main component (168 and 115 ns). With increase of the $Nd^{3+}$ concentration up to $6 \times 10^{-5}$ M, the fluorescence decay becomes again (almost) monoexponential ($\tau° = 120$ ns). On the basis of these results, we can confidently assign the 120 ns emission lifetime to the 1:1 adduct and evaluate the rate constant for the energy transfer process ($^3$MLCT(Ru) → $^4F_{3/2}$(Nd)) within this adduct ($k_{en} = k_1 - k_0 = (1/120 - 1/170) \times 10^9 = 2.4 \times 10^6$ $s^{-1}$).

In the case of compound **3** the best-fitting procedure (by using SPECFIT) suggests an initial 1:1 and a final 1:2 (**3**:$Nd^{3+}$) formation adduct.

In the case of compound **4** a complicated luminescence behavior again prevents one from obtaining straightforward results most probably owing to simultaneous equilibria between several species.

**Excitation Spectra.** As observed for the "free" ruthenium calix[4]arene complexes carrying the calixarene moieties (compounds **2**−**4**), even in the case of the adducts **2**/$Nd^{3+}$, **3**/$Nd^{3+}$, and **4**/$Nd^{3+}$, the excitation spectra based on the 610 nm (ruthenium) emission show that a band is missing when compared with the respective absorption spectra; in this case the missing band is the band at 390 nm typical of the lanthanide-engaged calixarene moiety. On the contrary, this band is markedly present in the excitation spectrum of the **2**/$Nd^{3+}$ adduct on the basis of the 1064 nm neodymium emission.

This result shows that the energy transfer from the excited calixarene once again does not occur toward the $Ru(bpy)_3$ unit while it occurs toward the neodymium ion. The reasons for this behavior may lie in the fact that only the $Nd^{3+}$, owing to its proximity to calixarene, can give the fast energy transfer process needed to compete with the intrinsic decay of calixarene excited states.

On the basis of the results, mainly obtained for compound **2**, we can build the excited-state energy diagram reported in Figure 6a for the adducts between $Nd^{3+}$ and the ruthenium bipyridyl complexes.

**$Tb^{3+}$ Ion.** Contrary to what was observed for the $Nd^{3+}$ ions, the addition of $Tb^{3+}$ to solutions of the four ruthenium calix[4]arene complexes increases the emission intensity of the ruthenium bipyridine moiety.

The greater effect is shown by compounds **1** and **3**; for example, in the case of complex **1** a 35% increase of the ruthenium luminescence occurs upon addition of 4 equiv of $Tb^{3+}$ ions. A parallel increase (192 ns vs 265 ns) of the $^3$MLCT (Ru) emission lifetime is observed. Similar behavior was observed in bichromophoric systems where two, close in energy, excited states are in equilibrium;[32] the equilibrium has the effect of increasing the emission intensity and lifetime of the shortest living excited state as we observe in our

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[31] Sabbatini, N.; Indelli, M. T.; Gandolfi, M. T.; Balzani, V. *J. Phys. Chem.* **1982**, *86*, 3585.

system. Nevertheless, in our case the two excited states ($^5D_4$ of $Tb^{3+}$ at ca. 2.5 eV and $^3$MLCT of $Ru^{2+}$ at 2.13 eV) are too far in energy (ca 0.4 eV) to be in thermal equilibrium, thus excluding this mechanism from occurring.

To find an explanation about the nature of the interaction that causes the $Tb^{3+}$-induced luminescence (and lifetime) increase of the four Ru complexes, we looked to the absorption and emission behavior of complexes **1** and **3** upon addition of $Gd^{3+}$ ion.

The results of these experiments show that (i) the absorption spectra of the two complexes change as in the other cases of lanthanide addition in agreement with the formation of $Gd^{3+}$ adducts and (ii) the luminescence intensity and lifetime of the ruthenium moiety of the two complexes increases in a manner very similar to that observed in the case of the $Tb^{3+}$ addition.

The $Gd^{3+}$ ion, owing to the very high energy of its excited states, can only affect the ruthenium luminescence by means of its electric charge. Thus, it seems correct, in view of the very similar results, to ascribe to the electric field created around the ruthenium−calix[4]arene complexes by the $Tb^{3+}$ ions the reason for this behavior. Moreover it cannot be excluded, especially for compounds **1** and **3**, that some contribution to the emission intensity increase upon addition of $Tb^{3+}$ ions comes from the rigidification of the structure consequent to the lanthanide complexation. The stiffening of the ruthenium−calix[4]arenes structure, which in compound **3** can be due to the electrostatic repulsion between the metal cations that keeps far away the two $Tb^{3+}$ ions and the $Ru^{2+}$ moiety, leads to a decrease of the vibrational motions responsible of the excited-state deactivation (nonradiative processes).

In this way, the adduct formation, decreasing the nonradiative processes, leads to a longer $^3$MLCT excited-state lifetime with a consequent increase of its emission intensity.

The excitation spectra centered on the emission wavelength of $Ru(bpy)_3$ unit of the $Tb^{3+}$/ruthenium−calix[4]arenes adducts (**2**·$Tb^{3+}$, **3**·$Tb^{3+}$, and **4**·$Tb^{3+}$) do not show the band at 390 nm typical of the lanthanide-engaged calixarene moiety showing that also in this case the energy transfer from the excited calixarene toward the $Ru(bpy)_3$ unit does not occur.

On the contrary, the excitation spectra of the same compounds centered on the emission wavelength of the $Tb^{3+}$ exhibit sensitization of the lanthanide ion showing that also in this case the energy transfer from the excited calixarene toward the $Tb^{3+}$ unit occurs.

The excited-state energy diagram summarizing the results obtained for the adducts between $Tb^{3+}$ and ruthenium−bipyridyl−calix[4]arene complexes is reported in Figure 6b.

**$Eu^{3+}$ Ion.** Addition of $Eu^{3+}$ ions to solutions of the four complexes has a conflicting effect on the ruthenium luminescence. In fact, in the case of compounds **1**, **2**, and **4**, the emission intensity is quenched while it is increased in the case of compound **3**. As we will see later on, while the emission quenching can be rationalized, it is more difficult to find an explanation for the emission increase of the ruthenium luminescence.

As far as compounds **1**, **2**, and **4** are concerned, the luminescence of the ruthenium moiety is decreased to an extent which depends on the specific compound and, contrary to what happens for the $Nd^{3+}$ ion, the quenching is not accompanied by a parallel increase of europium emission. The lack of the sensitized emission from the $Eu^{3+}$ ion, while excluding the energy transfer, suggests the electron-transfer mechanism is responsible for the observed luminescence quenching. In fact the electron-transfer mechanism has a thermodynamically allowed $\Delta G$ ca. −0.5 eV, as the europium ion is rather easy to reduce ($E° = -0.35$ V vs NHE[12a]), the $Ru(bpy)_3$ moiety is easy to oxidize ($E° = 1.26$ V vs SCE[10]), and 2.1 eV [10] is the energy content of the Ru $^3$MLCT excited state. This conclusion is also supported by the observation of europium-sensitized emission from frozen solutions of Ru−calix[4]arenes (**2**) and $Eu^{3+}$ (1:1). At 77 K the energy of the electron-transfer products ($Ru^{3+}/Eu^{2+}$) increases, because of the lack of stabilization energy due to solvent repolarization, not allowed in frozen media.

Even in this case the quenching (via electron transfer) of the ruthenium luminescence cannot be due to a dynamic mechanism, but it occurs via a static quenching within the adducts formed by association of the $Eu^{3+}$ ion with the Ru−calixarene complexes. As in the previous case (see absorption measurements), the association involves the calixarene moieties in the case of compound **2** and **4** or the amide-carbonyl groups linked to the bipyridines in **1**.

As observed for the neodymium case the excitation spectra of the **2**·$Eu^{3+}$ and **4**·$Eu^{3+}$ adducts centered on the 610 nm emission of the Ru moiety do not show the band at 390 nm typical of the lanthanide-engaged calixarene moiety suggesting that also in this case the energy transfer from the excited calixarene toward the $Ru(bpy)_3$ unit does not occur.

The excited-state energy diagram of Figure 6c summarizes the results obtained for the $Eu^{3+}$ adducts with ruthenium−bipyridyl−calix[4]arene complexes **1**, **2**, and **4**.

Concerning compound **3** as we have seen, the emission of the Ru moiety increases upon addition of $Eu^{3+}$ as nitrate salt and reaches a maximum of about +35% at $[Eu^{3+}]/[\mathbf{3}]$ ratio > 2. Searching explanations for this unexpected behavior we have found (i) the SPECFIT treatment of luminescence titration data does not give a satisfying fitting, (ii) the emission lifetime of the $^3$MLCT excited state of **3** increases upon europium nitrate addition, (iii) the addition of $Eu^{3+}$ as a triflate salt practically does not affect the ruthenium luminescence, (iv) the CV of compound **3** shows a reversible oxidation wave at +1.30 V vs SCE due to ruthenium tris-bipy moiety oxidation, (v) upon addition of 2.5 equiv of europium nitrate the ruthenium oxidation occurs at +1.28 V while an irreversible, broad reduction wave appears at ca. −0.40 V due to an irreversible reduction process of the europium ion, and (vi) the electrochemical behavior of compound **2** is identical with that of compound **3** either without or with the europium nitrate.

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(32) McClenaghan, N. D.; Barigelletti, F.; Maubert, B.; Campagna, S. *Chem. Commun.* **2002**, 602 and references therein.

These results show that (i) the luminescence spectra obtained in the titration of **3** with europium nitrate are not rationalized by the kinetic scheme obtained in the best fitting on the basis of the absorption spectra of the same titration, (ii) the luminescence behavior strongly depends on the europium counterion, and (iii) the thermodynamics of the system is practically that estimated on the basis of known data and it is not substantially modified either by the binding of the calix[4]arenes to the Ru(bpy)$_3$ moiety or by the complexation of the Eu$^{3+}$ ion. Thus, the electron-transfer process between the Eu$^{3+}$ ion and the excited Ru(bpy)$_3$ moiety still remains thermodynamically allowed and if it does not occur is only due to kinetic reasons. Most probably the specific geometry/conformation of the [**3**·2Eu$^{3+}$] adduct, where the nitrate plays a very important role, is such to render very inefficient the electron-transfer (*Ru → Eu) quenching process so that it cannot substantially compete with the intrinsic decay rate of the Ru $^3$MLCT excited state. To the peculiar structure of the [**3**·2Eu$^{3+}$] adduct may contribute the rigidity imparted to the adduct by the electrostatic repulsion between the metal cations that keeps far away the europium and the ruthenium units. These factors together with the shielding effect of interposed nitrate anions may lead to a decrease of the electronic interaction term[33] with a consequent reduction of the rate constant of the quenching process. In such a hypothesis, lacking the electron-transfer quenching, the system behaves like in the case of Tb$^{3+}$ addition where the adduct's formation, via charge effect and/or rigidification of the structure of the ruthenium complex, decreases the nonradiative processes and, consequently, increases the emission intensity and lifetime of the $^3$MLCT excited state.

## Conclusion

All the Ru−calix[4]arene complexes synthesized in this work are able to coordinate lanthanides ions (namely Nd$^{3+}$, Eu$^{3+}$, and Tb$^{3+}$ ions) with formation of adducts of variable stoichiometry. The association constants depend on the nature of the complexes as well as on the nature of the lanthanide cation. The adduct formation affects the ruthenium luminescence, which is strongly quenched by Nd$^{3+}$ ion, increased (more or less) by the Tb$^{3+}$ ion, and moderately quenched (**1**, **2**, and **4**) or increased (**3**) by the Eu$^{3+}$ ion.

In the case of Nd$^{3+}$, the excitation spectra show that (i) the quenching of the Ru luminescence occurs via energy transfer and (ii) the electronic energy of the excited calixarene is not transferred to the Ru(bpy)$_3$ but to the neodymium cation.

In the case of Tb$^{3+}$, the adduct's formation leads to an increase of the emission intensities and lifetimes. The reason for this behavior was ascribed to the electric field created around the Ru−calix[4]arene complexes by the Tb$^{3+}$ ions by comparison with the Gd$^{3+}$ ion which behaves identically and can affect ruthenium luminescence only by its charge. However, especially for compounds **1** and **3**, it cannot be excluded that some contribution comes from the decrease of vibrational motions (and nonradiative processes) due to the rigidification of the structure upon Tb$^{3+}$ complexation.

In the case of Eu$^{3+}$ addition to solutions of **1**, **2**, and **4**, the quenching of the ruthenium luminescence is not accompanied by europium-sensitized emission, which suggests that an electron-transfer mechanism is responsible for the quenching. Addition of Eu$^{3+}$ (as nitrate salt) to solutions of **3** leads to the formation of the [**3**·2Eu$^{3+}$] adduct in which the lack of quenching is due to kinetic reasons as the electron-transfer quenching process is thermodynamically allowed (Figure 6c).

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(33) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (c) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991; Chapter 2.