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pH-Induced Luminescence Changes of Chromophore-Quencher Tricarbonylpolypyridylrhenium(I) Complexes with 4-Pyridinealdazine

Mauricio Cattaneo,[a] Florencia Fagalde,[a] Néstor E. Katz,*[a] Claudio D. Borsarelli,[b] and Teodor Parella[c]

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The new chromophore-quencher tricarbonylrhenium(I) complexes $[Re(4,4'\text{-}X_2\text{-bpy})(CO)_3(PCA)]^+$, $[(4,4'\text{-}X_2\text{-bpy})(CO)_3Re(\mu\text{-PCA})Re(CO)_3(4,4'\text{-}X_2\text{-bpy})]^{2+}$, and $[(4,4'\text{-}X_2\text{-bpy})(CO)_3Re^{I}(\mu\text{-PCA})Ru^{II}(NH_3)_5]^{3+}$ (X = Ph or CO_2Me and PCA = 4-pyridinealdazine) have been synthesized as their PF_6^- salts and characterized by spectroscopic, electrochemical, and photophysical techniques. In contrast to previously reported species with X = Me or H, these complexes emit at room temperature in CH_3CN. The recovery of luminescence can thus be ascribed to the change of energy levels induced by adding electron-withdrawing substituents to the 2,2′-bipyridine ring, since the emissive $Re^{II}(X_2bpy^-)$ excited state becomes much lower in energy than the $Re^{II}(PCA^-)$ non-emissive excited state. For the mononuclear and symmetric dinuclear rhenium(I) complexes with X = CO_2Me, consecutive protonation of both the pyridinyl and imine N atoms of PCA in aqueous solution leads to unusual bell-shaped curves for both the absorption and the emission intensities vs. pH because of opposite effects on the electronic delocalization of PCA. This latter property can be employed to devise novel luminescent pH sensors of the on-off-on type. The corresponding unsymmetrical dinuclear complexes $[(4,4'\text{-}X_2\text{-bpy})(CO)_3Re^{I}(\mu\text{-PCA})Ru^{III}(NH_3)_5]^{4+}$ have been obtained in situ by oxidizing the $[Re^{I},Ru^{II}]$ precursors in CH_3CN solution. Spectral and electrochemical measurements with these complexes lead to the values of the metal-to-metal electronic coupling elements.

Introduction

Tricarbonylpolypyridylrhenium(I) complexes of the type *fac*-$[Re(\alpha\text{-diimine})(CO)_3L]^+$ (L = auxiliary monodentate ligand) have very interesting properties, such as relatively high thermal and photochemical stabilities, high redox potentials, and luminescence in the visible region that have led to their applications as light switches,[1] ion sensors,[2] intercalating agents for nucleic acids,[3] probes for biological molecules,[4] and models in fundamental studies of energy- and electron-transfer reactions relevant to solar energy conversion.[5] Tuning the physicochemical properties of these complexes by changing the nature of the diimine and/or L offers a high degree of versatility for the design of new supramolecular systems that may perform useful specific functions.[5r]

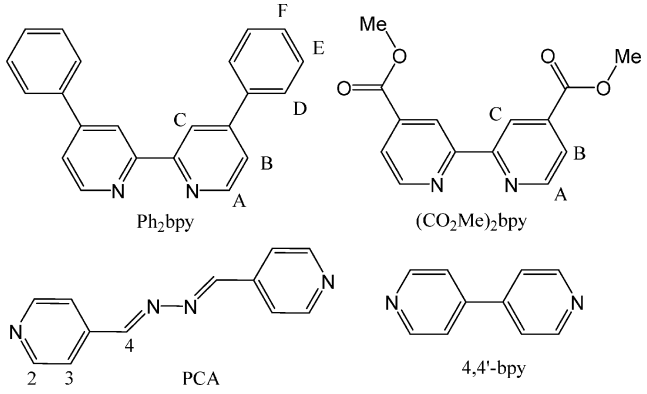
We have recently described the novel chromophore-quencher tricarbonylrhenium(I) complexes $[Re(4,4'\text{-}X_2\text{-bpy})(CO)_3(PCA)]^+$ and $[(4,4'\text{-}X_2\text{-bpy})(CO)_3Re(\mu\text{-PCA})Re(CO)_3(4,4'\text{-}X_2\text{-bpy})]^{2+}$ (bpy = 2,2′-bipyridine, X = CH_3 or H, and PCA = 4-pyridinealdazine).[6,7] Emission from the lowest-energy metal-to-ligand charge-transfer excited state ^3MLCT $[d_\pi(Re)\rightarrow\pi^*(X_2bpy)]$ is completely quenched in these complexes by the presence of PCA in the mononuclear species at room temperature in CH_3CN. Quenching of luminescence has been observed before in tricarbonylpolypyridylrhenium(I) complexes with electron-acceptor ligands (L) such as *N*-methyl-4,4′-bipyridinium (MQ^+), *N*-benzyl-4,4′-bipyridinium (BzQ^+), or *N*-(4-pyridyl)-β-(*N*-methylpyridinium-3-yl)acrylamide ($pyAm\text{-}Mepy^+$).[8] In the case of L = PCA, the emission was also found to be quenched in aqueous solution at high pH values, and when the pH was lowered until one of the imine N atoms of PCA became protonated, alteration of the ligand conjugation brought about a recovery of luminescence. We thus concluded that these complexes can be employed as luminescent pH sensors.[7]

In this work, we have prepared and studied the new complexes $[Re(4,4'\text{-}X_2\text{-bpy})(CO)_3(PCA)]^+$, $[(4,4'\text{-}X_2\text{-bpy})(CO)_3Re(\mu\text{-PCA})Re(CO)_3(4,4'\text{-}X_2\text{-bpy})]^{2+}$, and $[(4,4'\text{-}X_2\text{-bpy})(CO)_3Re^{I}(\mu\text{-PCA})Ru^{II/III}(NH_3)_5]^{3+/4+}$ (X = Ph and CO_2Me), thereby completing the previously studied series. We expected that introducing substituted bipyridines with strongly electron-withdrawing groups would have different

[a] Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán,
Ayacucho 491 (T4000INI), San Miguel de Tucumán, Argentina
Fax: +54-381-424-8169
E-mail: nkatz@fbqf.unt.edu.ar
[b] Instituto de Ciencias Químicas, Facultad de Agronomía y Agroindustrias, Universidad Nacional de Santiago del Estero, Av. Belgrano (S) 1912 (G4200ABT), Santiago del Estero, Argentina
[c] Servei de RMN, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain

effects on the emission properties. Indeed, we found that the emission is recovered at high pH values, and protonation changes in the PCA ligand can now be employed to devise novel luminescent switches of the on-off-on type. The effect of pH on the emission properties of the previously reported complex $[Re(bpy)(CO)_3(4,4'\text{-bpy})]^+$ (4,4′-bpy = 4,4′-bipyridine)[9] was also studied in order to compare the behavior of complexes containing an auxiliary ligand with one protonation site (4,4′-bpy) with that of those containing an auxiliary ligand with two protonation sites (PCA). Finally, dinuclear unsymmetrical complexes with $[Ru(NH_3)_5]^{n+}$ as electron donor (n = 2) or acceptor (n = 3) groups have been prepared and characterized in relation to intramolecular electron transfer in the Marcus inverted region.[10]

The structures of the ligands, along with the atom numbering for NMR assignments, are shown in Scheme 1; the structures of the complexes are shown in Scheme 2.

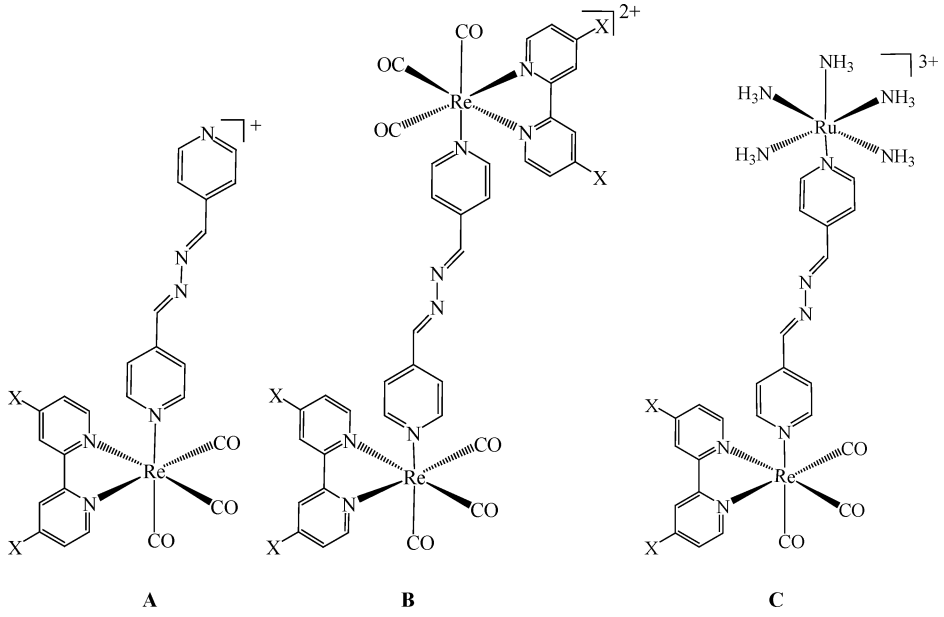


Scheme 1. Ligands.

Results and Discussion

Syntheses, Solubilities, and IR and NMR Spectral Characterizations

The synthetic methods used to obtain the new mono- and dinuclear tricarbonylpolypyridylrhenium complexes described in this work are slightly different from those previously developed in our laboratory.[6,7,11,12] All the complexes are soluble in acetonitrile, dichloromethane, and acetone and their purity was confirmed by chemical analysis, CV, and IR, NMR, and UV/Vis spectroscopy. The ester complexes are soluble in water and are stable for several days in neutral solutions at low concentrations ($\leq 10^{-4}$ M), whereas the phenyl complexes are not soluble in water, even with Cl^- as the counterion. The solubility of rhenium(I) complexes in water has a direct impact on their applications in radiopharmaceuticals.[7] The values of the carbonyl stretching frequencies (ν_{CO}) in the IR spectra of complexes **1** and **2** (2032 and 1918 cm^{-1}, respectively) are almost the same as those reported for related complexes of the type *fac*-$[Re(4,4'\text{-}X_2\text{-bpy})(CO)_3(L)]PF_6$,[6,7,11,12] whereas the values of the carbonyl stretching frequencies in the IR spectra of complexes **5** and **6** (2037 and 1927 cm^{-1}, respectively) are slightly higher than those of **1** and **2**, thereby indicating a stronger π-backbonding effect from Re to the bipyridine rings substituted with moderately strong electron-withdrawing groups, as reported previously for complexes such as *fac*-$[Re(4,4'\text{-}X_2\text{-bpy})(CO)_3(L)]PF_6$ {X = $C(O)NEt_2$, CO_2Et_2 and L = py-PTZ [10-(4-picolyl)phenothiazine]}.[13] All these values of ν_{CO} are consistent with a facial configuration of the carbonyl groups of local C_{3v} symmetry. Both the mono- and dinuclear species were completely characterized by NMR spectroscopy (see Experimental Section).



Scheme 2. **A**: Complexes **1** (X = Ph) and **5** (X = CO_2Me); **B**: Complexes **2** (X = Ph) and **6** (X = CO_2Me); **C**: Complexes **3** (X = Ph) and **7** (X = CO_2Me).

Six signals are observed for the protons of coordinated PCA in the mononuclear complexes due to coordination of only one of the pyridinyl N atoms to one rhenium center. For the dinuclear complexes, only three signals are observed for the protons of PCA due to the symmetry imposed by coordination of both pyridinyl nitrogen atoms of PCA to two rhenium centers. As a general trend, metal coordination induces slight displacements of the chemical shifts of the PCA moiety in all complexes to higher fields with respect to the values in the free ligands. Diffusion coefficients (D) were also determined to gain more insight into their overall molecular size.[14] The D values (in CD_3CN at 25 °C) of the mononuclear species **1** and **5** are 10.00×10^{-10} and 10.23×10^{-10} $m^2 s^{-1}$, respectively, and for the dinuclear species **2** and **6** 7.94×10^{-10} and 8.31×10^{-10} $m^2 s^{-1}$, respectively. These changes of 25% in the D value between the mono- and dinuclear species strongly agree with the corresponding increase in molecular weights (about 75%) and hydrodynamic radius (7.2 and 7.0 Å for the mononuclear species **1** and **5** and 9.0 and 8.7 Å for the dinuclear complexes **2** and **6**, respectively). Furthermore, the characteristic ^{15}N chemical shifts of the nitrogen atoms from the different ligands provide direct experimental evidence for the existence of an Re–N bond. Thus, the ^{15}N chemical shifts of the two pyridinyl nitrogen atoms of PCA in the mononuclear species appear at $\delta \approx +323$ (free N) and +238 ppm (N bonded to Re), whereas a single resonance appears at $\delta \approx +238$ ppm in the dinuclear complexes. Figure 1 shows the ^1H NMR spectrum of complex **2** as a representative example.

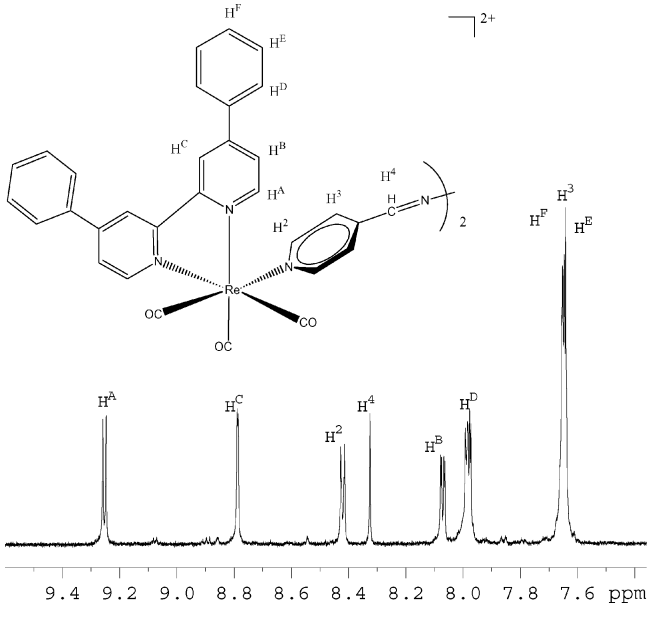


Figure 1. ^1H NMR spectrum of complex **2** in CD_3CN at 500.13 MHz.

UV/Vis Spectra

Table 1 shows the spectroscopic data for complexes **1**–**8** in CH_3CN. Characteristic spin-allowed intraligand $\pi \rightarrow \pi^*$ transitions of the polypyridyl ligands give rise to intense UV absorptions between 200 and 330 nm.[6,7,9] The mononuclear complexes **1** and **5** present minimum-energy absorptions at λ_{max} = 346 and 352 nm, respectively, which can be assigned, as observed previously in the analogous complexes $[Re(X_2bpy)(CO)_3(L)]^+$ (λ_{max} = 330–380 nm),[6,7] to overlapping metal-to-ligand charge transfers (MLCT) of the type $d_\pi(Re) \rightarrow \pi^*(X_2bpy)$ and $d_\pi(Re) \rightarrow \pi^*(PCA)$. These same bands are redshifted to λ_{max} = 350 and 355 nm, respectively, in the homodinuclear Re^I–Re^I complexes **2** and **6**, as reported previously for symmetric dinuclear complexes of the type $[(X_2bpy)(CO)_3Re(L)Re(CO)_3(X_2bpy)]^{2+}$.[6,7,9] Figure 2 shows the UV/Vis spectrum of complex **6** as a representative example. It is noteworthy that both the $\pi \rightarrow \pi^*$ transitions of X_2bpy as well as the MLCT $d_\pi(Re) \rightarrow \pi^*(X_2bpy)$ transitions are shifted to longer wavelengths when increasing the electron-accepting strength of the substituent X, as already reported for similar species.[9,13,15] On the other hand, when comparing the effect of ligands L in complexes of the type $[Re(bpy)(CO)_3L]^+$, a

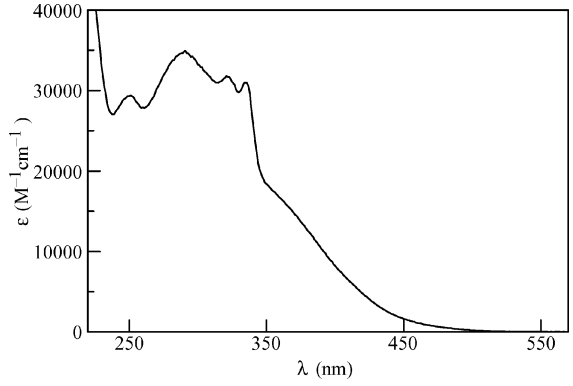


Figure 2. UV/Vis spectrum of $[\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3Re(\mu\text{-}PCA)Re(CO)_3\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}]^{2+}$ (**6**) in CH_3CN.

Table 1. UV/Vis spectroscopic data (in CH_3CN) at 22 °C.

Complex	λ_{max} [nm] (10^{-3} ε_{max} [$M^{-1} cm^{-1}$])
$[Re(Ph_2bpy)(CO)_3(PCA)]^+$ (**1**)	346 (18.6), 330 (29.1), 284 (57.6)
$[(Ph_2bpy)(CO)_3Re(\mu\text{-}PCA)Re(CO)_3(Ph_2bpy)]^{2+}$ (**2**)	350 (26.8), 330 (40.4), 284 (76.5)
$[(Ph_2bpy)(CO)_3Re^I(\mu\text{-}PCA)Ru^{II}(NH_3)_5]^{3+}$ (**3**)	560 (14.6), 350 (20.2), 330 (30.8), 283 (60.4)
$[(Ph_2bpy)(CO)_3Re^I(\mu\text{-}PCA)Ru^{III}(NH_3)_5]^{4+}$ (**4**)	496 (4.7), 350 (24.4), 330 (36.4), 281 (66.6)
$[Re\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3(PCA)]^+$ (**5**)	352 (9.2), 335 (18.8), 320 (21.8), 290 (27.0)
$[\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3Re(\mu\text{-}PCA)Re(CO)_3\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}]^{2+}$ (**6**)	355 (17.5), 335 (31.0), 321 (31.8), 291 (34.9)
$[\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3Re^I(\mu\text{-}PCA)Ru^{II}(NH_3)_5]^{3+}$ (**7**)	560 (13.6), 355 (10.9), 334 (20.9), 320 (23.3), 284 (28.8)
$[\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3Re^I(\mu\text{-}PCA)Ru^{III}(NH_3)_5]^{4+}$ (**8**)	501 (2.0), 355 (13.6), 335 (24.5), 321 (26.6), 280 (30.6)

blueshift of the (Re→bpy) MLCT band can be observed with increasing electron-withdrawing power of L; in effect, the values of λ_{max} in CH_3CN decrease in the order 4-Etpy (λ_{max} = 352 nm)[16] > 4,4′-bpy (λ_{max} = 340 nm)[9] > PCA (λ_{max} = 332 nm),[7] thus pointing to an increasing stabilization of the d_π(Re) energy levels.

With respect to the UV/Vis spectra of the unsymmetrical dinuclear complexes **3**, **4**, **7**, and **8**, we can assign the bands in the Re^{I}–Ru^{II} complexes **3** and **7** at λ_{max} = 350 and 560 nm to $d_\pi(Re)\rightarrow\pi^*(X_2bpy, PCA)$ and $d_\pi(Ru)\rightarrow\pi^*(PCA)$ MLCT transitions, respectively. For the Re^{I}–Ru^{III} complexes **4** and **8**, which were prepared in situ by oxidation of **3** and **7**, respectively, with bromine, the bands at λ_{max} = 560 nm disappear completely, and the new bands that appear at λ_{max} = 497 and 501 nm, respectively, whose values were obtained by Gaussian deconvolution, as shown in Figure 3 for complex **4**, can be assigned to $Re^{I}\rightarrow Ru^{III}$ MMCT transitions, with some contribution from $PCA\rightarrow Ru^{III}$ LMCT bands, as discussed previouly for the analogous species with Me_2bpy and bpy.[6,7]

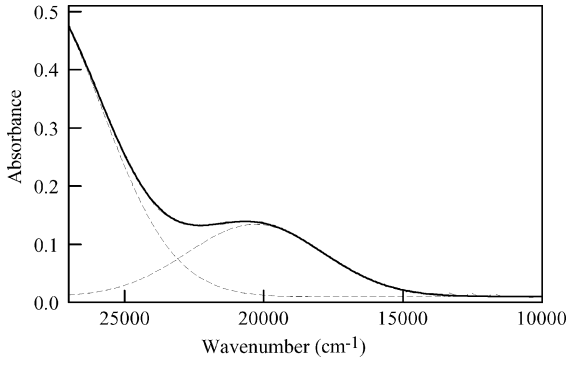


Figure 3. Gaussian deconvolution of the visible bands of the mixed-valent complex $[(Ph_2bpy)(CO)_3Re^{I}(\mu\text{-}PCA)Ru^{III}(NH_3)_5]^{4+}$ (**4**; approx. 3×10^{-5} M) obtained by Br_2 oxidation (in CH_3CN) of the dinuclear complex **3**.

Figure 4 shows the results of a controlled-potential electrolysis of complex **3** in CH_3CN at 800 mV. The results obtained are consistent with those obtained upon bromine oxidation. In effect, the $d_\pi(Ru)\rightarrow\pi^*(PCA)$ MLCT band at λ_{max} = 560 nm disappears completely, and a new MMCT band (combined with an LMCT band) appears near 500 nm. When reverting the oxidation process in the spectroelectrochemical experiment, the intensity of the $d_\pi(Ru)\rightarrow\pi^*(PCA)$ MLCT band at λ_{max} = 560 nm is not recovered completely, which is consistent with the results obtained upon Sn^{2+} reduction. We consider that, besides mere electron transfer, the formation of a *cis* isomer is possibly favored on oxidation.

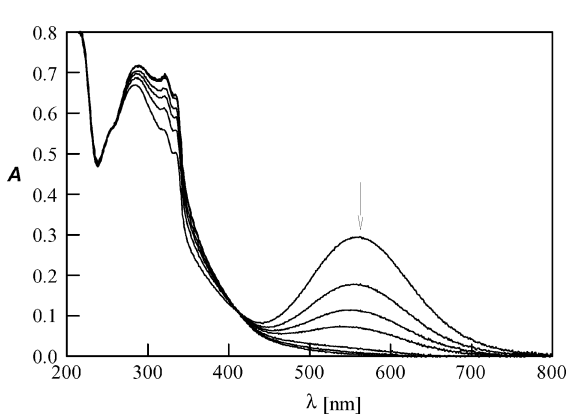


Figure 4. Controlled potential electrolysis of a CH_3CN solution of $[(Ph_2bpy)(CO)_3Re^{I}(\mu\text{-}PCA)Ru^{II}(NH_3)_5]^{3+}$ (**3**; approx. 2×10^{-5} M) at 800 mV in an OTTLE cell. The arrow indicates increasing times: t = 0, 1, 2, 3, 4, 8, and 10 min.

Photophysical Properties

In contrast to the previously reported complexes with Me_2bpy and bpy,[6,7] the complexes studied in this work emit in CH_3CN solution at room temperature. The shape and position of the emission maxima are typical of Re^{II}-(diimine$^-$) MLCT excited states.[13] Table 2 shows the data obtained at 22 °C for the emission maxima, lifetimes, and emission quantum yields for complexes **1**, **2**, **5**, and **6**. The same lifetimes were obtained both by laser flash photolysis and by pulsed luminescence decay in argon-saturated solutions, thereby indicating that the luminescence properties are not due to impurities. Furthermore, the reported chemical analyses and the spectral and electrochemical data point to a high degree of purity of the complexes under study. The observed quantum yields, which were calculated and corrected by taking into account the refractive indices of the solvents and absorbance differences, as described in the literature,[17] are much lower (by a factor of about 10^2) than those reported for related complexes with the same chromophore,[13] which can be attributed to intramolecular luminescence quenching induced by the presence of the PCA ligand.[6,7] This quenching was attributed in the Me_2bpy derivative to crossing to a neighboring $[(X_2bpy)(CO)_3Re^{II}$-$(PCA^-)]^+$ excited state, as confirmed by laser flash photolysis and low-temperature emission measurements.[6] The radiative rate constants k_r (approx. 10^3–10^4 s^{-1}), on the other hand, are lower than those expected (approx. 10^5 s^{-1}) for Re^{I} complexes of the type $[Re(bpy)(CO)_3X]$ (X = substituted pyridine).[13] Energy transfer from ^{3}MLCT (Re→bpy) to PCA to give an excited intraligand triplet state (^{3}PCA*) that decays non-radiatively to the ground state may be the cause of these low values of k_r. In support of this argument, it should be noted that changes in photophysical properties brought about by MLCT or intraligand excited states placed very close to the luminescent excited state have al-

Table 2. Photophysical data (in CH_3CN) of complexes of the type $[Re(4,4'\text{-}X_2\text{-}bpy)(CO)_3(PCA)]^+$ and $[(4,4'\text{-}X_2\text{-}bpy)(CO)_3Re$-$(\mu\text{-}PCA)Re(CO)_3(4,4'\text{-}X_2\text{-}bpy)]^{2+}$ at 22 °C.

X	Complex	λ_{em} [nm]	Φ_{em}[a]	τ [ns]
Ph	**1**	552	0.0010	690
	2	552	0.0045	865
CO_2Me	**5**	570	0.0004	132
	6	565	0.0017	187

[a] Calculated as described previously.[7,17]

ready been observed in related complexes.[18] Moreover, a recent review by Schmehl et al. gives a detailed discussion of similar systems in which reversible energy transfer between a long-lived ^{3}IL state and a ^{3}MLCT state leads to longer lived ^{3}MLCT emission.[19] In complex **2**, laser flash photolysis showed the emergence of a transient with λ_{max} = 380 nm, which is typical of the absorption of the radical anion of bpy ligands, as shown in Figure 5, together with emission bleaching at λ_{max} = 550 nm. The lifetime (τ) is 865 ns, which is about two orders of magnitude higher than the lifetime of the excited state of $[Re(Me_2bpy)(CO)_3(PCA)]^+$. These findings are consistent with formation of an $Re^{II}(Ph_2bpy^-)$ excited state. The mononuclear complex $[Re(Ph_2bpy)(CO)_3(PCA)]^+$ has a lower lifetime (τ = 690 ns) but with a similar transient spectrum. We conclude that, since Ph_2bpy is a much better π-acceptor than Me_2bpy and bpy, the energy of the emissive $Re^{II}(Ph_2bpy^-)$ excited state becomes much lower than that of the non-emissive $Re^{II}(PCA^-)$ excited state, with consequent recovery of luminescence at room temperature. As shown in Table 2, the quantum yields and lifetimes for the complexes containing $(CO_2Me)_2bpy$ are lower than those of the Ph_2bpy complexes. Luminescence in the series of complexes $[Re(4,4'\text{-}X_2\text{-}bpy)(CO)_3(PCA)]^+$ and $[(4,4'\text{-}X_2\text{-}bpy)(CO)_3Re(\mu\text{-}PCA)Re(CO)_3(4,4'\text{-}X_2\text{-}bpy)]^{2+}$ can thus be finely tuned by changing the nature of X: when X = Me or H, the emission is almost completely quenched,[6,7] whereas when X = Ph or CO_2Me, emission is partially recovered because of the less effective intramolecular quenching by PCA.

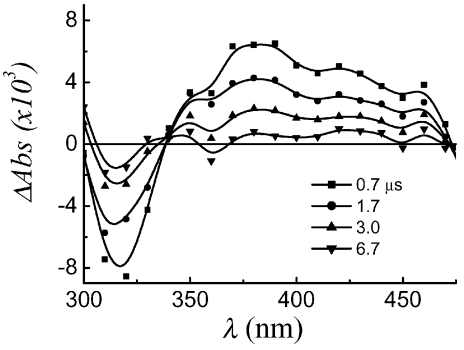


Figure 5. Transient spectra of $[(Ph_2bpy)(CO)_3Re(\mu\text{-}PCA)Re(CO)_3(Ph_2bpy)]^{2+}$ (**2**) in deaerated CH_3CN solution at 22 °C.

Protonation Equilibria

These studies were carried out with complexes **1**, **2**, **5**, and **6** since the heterodinuclear complexes **3**, **4**, **7**, and **8** have very low stability in aqueous solutions, as already reported for analogous complexes.[7] Table 3 shows the acidity constants obtained from the spectrophotometric and spectrofluorometric titrations of all the measured complexes. Complexes **1** and **2** were measured in a 1:4 mixture of CH_3CN/H_2O because of their poor solubility in water. The effect of the organic solvent could be to lower all pK_a values with respect to those in aqueous solution. In water, complexes **5** and **6** emit very weakly between λ_{max} = 565 nm at pH 8.5 and λ_{max} = 575 nm at pH 1.5 (λ_{ex} = 380 nm). When performing the experiment at constant ionic strength, a decrease in pH brings about not only an increased emission from the Re→X_2bpy MLCT excited state but also a noticeable isomerization/hydrolysis process of the PCA and $(CO_2Me)_2bpy$ ligands, which becomes enhanced at extreme pH values. Evidence for ligand isomerization has been presented before,[6,7] and evidence of ester hydrolysis emerges when comparing the final spectra, obtained after several hours, with the spectra of the corresponding complexes of carboxylic acid substituted bipyridines. On the other hand, more accurate values of the protonation constants could be obtained when the protonation studies were done with larger volumes of solution since the decomposition processes were negligible during the time taken for the measurements. This latter method has therefore been used for reporting the values in Table 3, except for the reference complex $[Re(bpy)(CO)_3(4,4'\text{-}bpy)]^+$, which proved to be very stable in aqueous solutions.

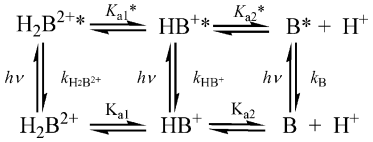
Consistent and reproducible values of pK_a for both ground and excited states could only be obtained for the mononuclear complex **5** starting from basic aqueous solutions. Both the absorbance and luminescence data can be fitted with a three-species diagram involving protonation equilibria of the ground and excited states of PCA complexes, as shown in Scheme 3. Two ground-state pK_a values were detected by fitting the UV/Vis absorptivity changes with pH at λ = 330 nm, as shown in Figure 6(a). The first of these (pK_{a1} = 2.15) corresponds to one of the imine N atoms of coordinated PCA and the second one (pK_{a2} = 5.59) corresponds to the free pyridine N atom of coordinated PCA. This latter value is 0.4 units larger than the

Table 3. Values of pK_a for the ground and excited states of complexes **1**, **2**, **5**, and **6** at 22 °C in aerated aqueous solution.

Complex	pK_a	pK_a*
$[Re(Ph_2bpy)(CO)_3(PCA)]^+$ (**1**)[a]	pK_{a1} < 1 pK_{a2} = 5.08 ± 0.23	pK_{a1}* < 1
$[(Ph_2bpy)(CO)_3Re(\mu\text{-}PCA)Re(CO)_3(Ph_2bpy)]^{2+}$ (**2**)[a]	pK_{a1} < 1	pK_{a1}* < 1
$[Re\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3(PCA)]^+$ (**5**)[b]	pK_{a1} = 2.15 ± 0.03 pK_{a2} = 5.59 ± 0.06	pK_{a1}* = 2.34 ± 0.17 pK_{a2}* = 3.33 ± 0.05
$[\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3Re(\mu\text{-}PCA)Re(CO)_3\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}]^{2+}$ (**6**)[c]	pK_a < 1	not detected
$[Re(bpy)(CO)_3(4,4'\text{-}bpy)]^{+}$[c]	pK_a = 3.70 ± 0.07	pK_{a1}* = 4.03 ± 0.05

[a] In CH_3CN/H_2O (1:4). [b] Data obtained from bulk experiments. [c] Data obtained from experiments at constant ionic strength (I = 0.1 M).

value for the free ligand, probably because of the $Re^{I}\rightarrow$PCA π-backbonding effect. Both pK_a values are very similar to those corresponding to the previously studied complex $[Re(bpy)(CO)_3(PCA)]^+$ (pK_{a1} = 1.98 and pK_{a2} = 5.41),[7] thereby indicating little influence of the nature of the substituent X on the basicity of coordinated PCA.



Scheme 3. Three-species diagram for the protonated equilibria of the ground and excited states of PCA complexes. B is the non-protonated species.

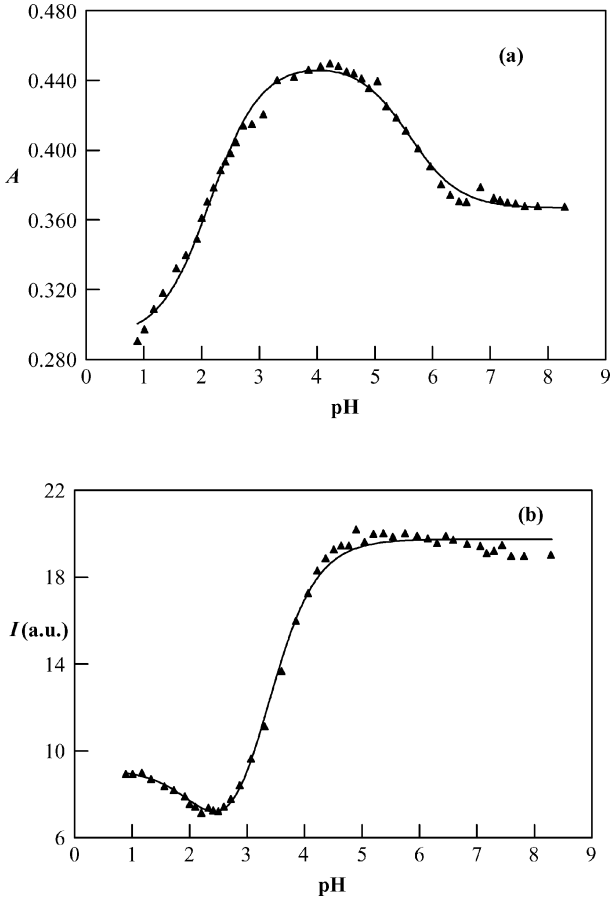


Figure 6. Variation of (a) absorbance A (at λ = 330 nm) and (b) emission intensity (at λ_{ex} = 380 nm and λ_{em} = 570 nm) for $[Re\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3(PCA)]^+$ (**5**) in aqueous buffer, with pH. The lines indicate the best fits using a three-species model in each case.

As found before in related unsubstituted bpy complexes,[7] protonation of the pyridine N atom of PCA leads to an absorbance increase at λ = 330 nm due to an increased d_π(Re)-π*(PCA) coupling. The MLCT band corresponding to this transition is expected to fall in this region.[6] Protonation of the imine N atom of PCA leads instead to an absorbance decrease at λ = 330 nm because the energy of the lowest-lying π* orbital of PCA is increased and d_π(Re)-π*(PCA) coupling is consequently diminished. The result is a bell-shaped curve which can be reproduced in an inverted way when fitting the emission intensities at different pH values. This is in contrast to similar carbonylrhenium complexes, where only sigmoid curves have been observed.[2,7] As shown in Figure 6(b), complex **5** presents two adjustable excited-state pK_a* values: the first one, pK_{a1}* = 2.34, corresponds to the imine N atom of coordinated PCA and the second one, pK_{a2}* = 3.33, corresponds to the free pyridine N atom of coordinated PCA. No better fitting could be obtained between pH = 5 and 9, and in any case the observed deviations from the fits are within the experimental uncertainties of the intensity measurements. The first basicity constant of the excited state is higher than that of the ground state (by around 0.2 pK units), as expected for tricarbonylrhenium(I) complexes,[2] but lower than that of the complex $[Re(bpy)(CO)_3(PCA)]^+$ (by around 0.4 units),[7] thereby evidencing the effect of decreasing the electron density on PCA as a result of including a more electron-accepting bipyridine ligand. Strikingly, the value of pK_{a2}* is 2.26 units lower than that of the ground state, which points to the fact that since more electron density has been delocalized in the excited state, $[(CO_2Me)_2bpy^{-}(CO)_3\text{-}Re^{II}(PCA)]^+$, to the substituted bpy ligand, less electron density is available at the remote N atom of the coordinated PCA ligand, and possibly evidencing some contribution of the pK_a of the carboxylate-substituted bpy that results from hydrolysis of the ester-substituted bpy.

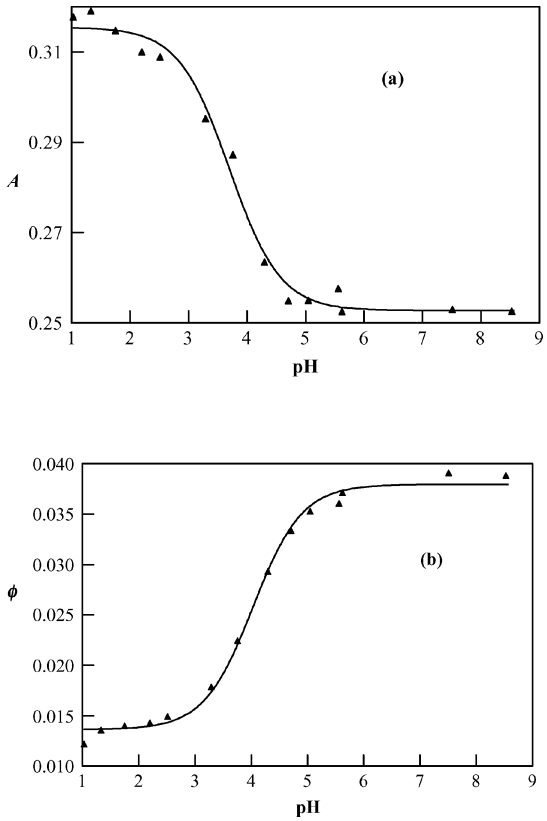


Figure 7. Variation of (a) absorbance A (at λ = 350 nm) and (b) emission quantum yield Φ_{em} (at λ_{ex} = 350 nm and λ_{em} = 552 nm) for $[Re(bpy)(CO)_3(4,4'\text{-bpy})]^+$ in aqueous buffer, with pH. The lines indicate the best fits using a two-species model in each case.

There is only one protonation site possible in the model complex $[Re(bpy)(CO)_3(4,4'\text{-bpy})]^+$, namely the free pyridyl N atom. As shown in Figure 7, a value of the ground-state pK_a of 3.70, which agrees with those reported for polypyridylruthenium complexes, is obtained by fitting absorbance changes with pH.[20] However, we obtain a pK_a^* value of 4.03 for the excited state when fitting the emission quantum yields with pH. This value is higher than that of the ground state by 0.33 units and points to much less electron density being delocalized onto the unsubstituted bpy ligand in the excited state.

We conclude that when the free pyridine N atom of coordinated PCA is protonated, the π* excited state of PCA decreases in energy, and the emission is partially quenched, as observed before for MQ^+,[8] but when the imine N atom of coordinated PCA is protonated, the π* excited state of PCA increases in energy, due to alteration of the ligand conjugation, and emission is recovered again. In effect, when decreasing the pH from 4 to 1, the band assigned to the π-π* transition of PCA at λ_{max} = 290 nm is shifted to lower wavelengths, thereby indicating a proton-induced energy increase of the π* levels of PCA. The mononuclear species **5** can therefore be used as a novel luminescent pH sensor of the on-off-on type.

Electrochemistry

Table 4 shows the electrochemical data for the studied complexes. The redox potentials for the Re^{II}/Re^{I} couple of the mononuclear Re^{I} species **1**, the Re^{I}–Re^{I} dinuclear species **2**, and the Re^{I}–Ru^{II} dinuclear species **3** are very similar, with $E_{1/2}$ values between 1.8 and 1.9 V, with some degree of irreversibility, as expected for carbonyl(diimine)rhenium(I) complexes.[6,7,11,12] The redox potentials for the Re^{II}/Re^{I} couple in complexes **5**, **6**, and **7** are higher than 2.0 V and could not be detected. The PCA ligand is reduced irreversibly at $E_{peak} \approx -0.8/-1.0$ V in all complexes except **7**. The first reduction of X_2bpy appears at $E_{peak} \approx -1.2$ V, while a second irreversible reduction at $E_{peak} \approx -1.4$ V can be attributed to an $Re^{I/0}$ couple, as reported previously for the related Me_2bpy complex.[6]

The voltammetric wave that appears in the asymmetric Re^{I}–Ru^{II} dinuclear complexes **3** and **7** at $E_{1/2}$ = 0.46 and 0.48 V, respectively, which is absent in the mononuclear rhenium complexes, can be readily assigned to the Ru^{III}/Ru^{II} couple by comparison with similar complexes.[6,7] The high ΔE_p values (92–134 mV) suggest redox-induced ligand isomerization processes, and experimental evidence of redox-induced ligand isomerization has been described previously.[6] Varying the sweep rate gave no better ΔE values at higher sweep rates. The differences between the redox potentials of both metallic couples in **3** and **7** are: $\Delta E_{1/2} = E_{1/2}(Re^{II}/Re^{I}) - E_{1/2}(Ru^{III}/Ru^{II})$ = 1.52 and 1.54 V, respectively.

Intramolecular Electron Transfer

The reorganization energy, λ, for the intramolecular electron transfer through the PCA bridge can be calculated from the Marcus–Hush equations and the experimental

Table 4. Electrochemical data (in CH_3CN) at 22 °C.[a]

Complex	Process	$E_{1/2}$ [V] (ΔE_p [mV])	E_{peak} [V]
$[\{4,4'\text{-}(Ph)_2\text{-bpy}\}(CO)_3Re(PCA)]^+$ (**1**)	$Re^{2+/+}$		1.85
	$PCA^{0/-}$		–0.98
	$Ph_2bpy^{0/-}$	–1.14 (51)	
	$Re^{+/0}$	–1.28 (94)	
$[\{\{4,4'\text{-}(Ph)_2\text{-bpy}\}(CO)_3Re\}_2PCA]^{2+}$ (**2**)	$Re^{2+/+}$		1.86
	$PCA^{0/-}$		–0.78
	$Ph_2bpy^{0/-}$		–1.18
	$Re^{+/0}$	–1.27 (97)	
$[\{4,4'\text{-}(Ph)_2\text{-bpy}\}(CO)_3Re^{I}(\mu\text{-PCA})Ru^{II}(NH_3)_5]^{3+}$ (**3**)	$Re^{2+/+}$	1.77 (166)	
	$Ru^{3+/2+}$	0.48 (134)	
	$PCA^{0/-}$		–0.95
	$Ph_2bpy^{0/-}$		–1.16
	$Re^{+/0}$		–1.31
$[\{4,4'\text{-}(MeO_2C)_2\text{-bpy}\}(CO)_3Re(PCA)]^+$ (**5**)	$Re^{2+/+}$		>2
	$PCA^{0/-}$		–0.81
	$(MeO_2C)_2bpy^{0/-}$	–0.96 (172)	
	$Re^{+/0}$		–1.32
$[\{\{4,4'\text{-}(MeO_2C)_2\text{-bpy}\}(CO)_3Re\}_2PCA]^{2+}$ (**6**)	$Re^{2+/+}$		>2
	$PCA^{0/-}$		–0.81
	$(MeO_2C)_2bpy^{0/-}$	–0.96 (172)	
	$Re^{+/0}$		–1.32
$[\{4,4'\text{-}(MeO_2C)_2\text{-bpy}\}(CO)_3Re^{I}(\mu\text{-PCA})Ru^{II}(NH_3)_5]^{3+}$ (**7**)	$Re^{2+/+}$		>2
	$Ru^{3+/2+}$	0.46 (92)	
	$PCA^{0/-}$		–0.64
	$(MeO_2C)_2bpy^{0/-}$		–1.01
	$Re^{+/0}$		–1.22

[a] All CV data were obtained at a scan rate of 200 mV s^{-1}.

data of the MMCT transition in the heterodinuclear complexes **4** and **8**[21] to be approximately 0.9 eV, a value similar to that obtained previously for the analogous complexes with Me_2bpy and bpy.[6,7] The values determined for the metal–metal electronic coupling elements ($H_{AB} = 8.8 \times 10^2$ and 6.2×10^2 cm^{-1} for the Ph and CO_2Me derivatives, respectively) are consistent with those obtained previously for mixed-valent symmetric and unsymmetrical dinuclear complexes of PCA.[6,7] These complexes might be considered as prototypes for simulating primary charge separations in the inverted region.

Conclusions

Continuing our previous studies on proton-induced luminescence of chromophore-quencher tricarbonylpolypyridylrhenium(I) complexes, we have shown in this work that quenching of luminescence in these complexes can not only be turned on and off by changing the substituents on the 2,2′-bipyridine acceptor group but also by changing the acidity of their aqueous solutions. In particular, the mononuclear complex $[Re\{4,4'\text{-}(MeO_2C)_2\text{-}bpy\}(CO)_3(PCA)]^+$ can be employed as a novel luminescent pH sensor of the on-off-on type rather than the recently reported luminescent off-on-off switches based on polypyridylruthenium complexes.[22]

Experimental Section

Materials and Techniques: All chemicals used were p.a. grade. CH_3CN was distilled from P_4O_{10}. Tetrakis(*n*-butyl)ammonium hexafluorophosphate (TBAH) was recrystallized from ethanol three times and dried at 150 °C for 72 h. IR spectra were recorded (as KBr pellets) with an FTIR Perkin–Elmer Spectrum RX-I spectrophotometer. UV/Vis spectra were recorded with a Varian Cary 50 spectrophotometer for solutions in 1-cm cells. Redox titrations were performed stoichiometrically by adding aliquots of a stock solution of Br_2 in CH_3CN which had previously been standardized by known procedures.[20] Reductions were carried out by adding solid $SnCl_2$ to CH_3CN solutions of the oxidized complexes. Electrochemical measurements were performed in CH_3CN (0.1 M TBAH) with a BAS Epsilon electrochemical equipment. A standard three-electrode compartment cell was used, with Ag/AgCl (3 M KCl) as a reference electrode, vitreous C as a working electrode, and Pt wire as an auxiliary electrode. All redox potentials ($E_{1/2}$) are referenced to Ag/AgCl. Spectroelectrochemical measurements were performed in an OTTLE (optically transparent thin layer electrolysis) type cell from BAS. Emission studies were performed with a Shimadzu RF-5301 PC spectrofluorometer in 1-cm fluorescence cells. Laser-flash photolysis (LFP) experiments were carried out with a Q-switched Nd:YAG laser (Continuum Minilite II) generating 355-nm pulses (fwhm: 10 ns; 5 mJ per pulse). The signals were recorded with a Luzchem m-LFP 112 system and fed into a transient Tektronik TDS 3032B recorder. Time-resolved luminescence detection was carried out with a home-made system composed of an *f*/4 monochromator (PTI-101, 1200 blazes) coupled with a red-extended PMT (Hamamatsu R928) placed at right angles to the excitation laser pulse. The output of the detector was fed to the Tektronix TDS3032B digital oscilloscope linked to an on-line PC for data transfer and analysis. Typically, about 100–200 laser cycles with the excitation laser operating at 15 Hz were averaged in order to obtain the decay times with a suitable signal-to-noise ratio. NMR spectra were recorded in CD_3CN with an Avance Bruker 500.13 MHz spectrometer. Full ^1H, ^{13}C, and ^{15}N chemical shift assignments were performed by collecting 2D COSY, 2D ^1H-^{13}C HSQC, 2D ^1H-^{13}C HMBC, 2D ^1H-^{15}N HMBC, and 2D NOESY (mixing time: 500 ms) experiments. Diffusion NMR coefficients were measured at 25 °C using the LEDBP pulse sequence (diffusion time: 150 ms) with sample spinning at 20 Hz to minimize convection effects.[14] Argon was bubbled through the solutions for 15 min prior to electrochemical and photophysical measurements. Chemical analyses for C, H, and N were done at INQUIMAE, University of Buenos Aires, Argentina, with an estimated error of ±0.5%.

Preparation of PCA and 4,4′-$(MeO_2C)_2$-bpy: The ligands 4-pyridinealdazine and 4,4′-bis(methoxycarbonyl)-2,2′-bipyridine were prepared as described previously.[23,24]

Preparation of $[Re(Ph_2bpy)(CO)_3(PCA)]PF_6 \cdot H_2O$ (1) and $[(Ph_2bpy)(CO)_3Re(\mu\text{-}PCA)Re(CO)_3(Ph_2bpy)](PF_6)_2$ (2): These salts were prepared by a procedure similar to that reported in the literature.[6,7] In a typical experiment, $[Re(CO)_5Cl]$ (181 mg, 0.50 mmol) and 4,4′-diphenyl-2,2′-bipyridine (154 mg, 0.50 mmol) were heated at reflux in toluene (20 mL) for 1 h. It was cooled and then precipitated with hexane (40 mL). The solid obtained after additional cooling was collected, washed with hexane and diethyl ether, and dried in vacuo. The resulting complex $[Re(Ph_2bpy)(CO)_3Cl]$ (272 mg, 0.443 mmol) and $Ag(CF_3SO_3)$ (114 mg, 0.443 mmol) were heated at reflux in thf (40 mL) for 30 min. PCA (139 mg, 0.664 mmol) was then added to the reaction mixture and heating at reflux was continued for 2 h. After removal of AgCl by filtration, the solvent was removed in a rotary evaporator to give a yellow oil. This oil was dissolved in 80 mL of 3:1 (v:v) $MeOH/H_2O$, 2 g of NH_4PF_6 dissolved in 20 mL of water was added, and the mixture was put in the freezer. The yellow precipitate that formed was filtered and washed with copious amounts of H_2O and three times with portions of diethyl ether. This solid was dissolved in a minimum amount of 1:4 (v/v) acetonitrile/dichloromethane, adsorbed onto a silica gel (Kieselgel 60) column and eluted with the same solvent. The yellow fractions (the first is complex **2** and the second is complex **1**) were concentrated to dryness, redissolved in acetone, and precipitated with hexane. **1:** Yield: 66 mg (14%). $C_{37}H_{28}F_6N_6O_4PRe$ (951.84): calcd. C 46.7, H 2.97, N 8.83; found C 46.5, H 2.74, N 8.10. IR (KBr): $\tilde{\nu}$ = 2032 (s), 1918 (s), 1615 (m), 1542 (w), 1474 (m), 1413 (m), 1235 (w), 840 (s), 766 (m), 739 (w), 695 (w), 627 (w), 558 (m) cm^{-1}. ^1H NMR (500.13 MHz, CD_3CN, 25 °C): δ = 9.24 (d, J = 5.8 Hz, 2 H, H^A), 8.78 (d, J = 1.8 Hz, 2 H, H^C), 8.68 (dd, J = 1.6, 4.5 Hz, 2 H, H^2, 8.44 (s, 1 H, H^4), 8.42 (s, 1 H, $H^{4'}$), 8.41 (dd, J = 5.4, 1.7 Hz, 2 H, $H^{2'}$), 8.06 (dd, J = 1.8, 5.8 Hz, 2 H, H^B), 7.97 (m, 4 H, H^D), 7.68 (m, 4 H, H^3 and $H^{3'}$), 7.62 (m, 6 H, H^E and H^F) ppm. ^{13}C NMR (125.6 MHz CD_3CN, 25 °C): δ = 123.0 (C^3), 123.5 (C^C), 125.7 ($C^{3'}$), 127.0 (C^B), 128.7 (C^D), 130.5 (C^E), 132.1 (C^F), 136.2 (C), 141.4 (C), 145.0 (C), 151.6 (C^2), 153.7 (C^A), 153.8 ($C^{2'}$), 154.9 (C), 157.3 (C), 158.4 ($C^{4'}$), 161.4 (C^4), 190.0 ($C^{CO\,trans}$), 197.1 ($C^{CO\,cis}$) ppm. ^{15}N NMR (50.69 MHz CD_3CN, 25 °C; chemical shifts extracted from the ^1H-^{15}N HMBC spectrum): δ = 234.8 ($N^{A'}$), 239.3 ($N^{1'}$), 322.1 (N^1), 374.3 ($N^{5'}$), 379.7 (N^5) ppm. **2:** Yield: 48 mg (12%). $C_{62}H_{42}F_{12}N_8O_6P_2Re_2$ (1657.4): calcd. C 44.9, H 2.55, N 6.76; found C 44.8, H 2.51, N 6.37. IR (KBr): $\tilde{\nu}$ = 2032 (s), 1918 (s), 1615 (m), 1542 (w), 1474 (m), 1413 (m), 1236 (w), 840 (s), 766 (m), 739 (w), 696 (w), 627 (w), 558 (m) cm^{-1}. ^1H NMR (500.13 MHz, CD_3CN, 25 °C): δ = 9.25 (d, J = 6.0 Hz, 4 H, H^A), 8.79 (d, J = 1.7 Hz, 4 H, H^C), 8.42 (dd, J = 1.7, 5.2 Hz, 4 H, H^2),

8.32 (s, 2 H, H^4), 8.07 (dd, J = 5.6, 1.6 Hz, 4 H, H^B), 7.98 (dd, J = 5.6, 1.6 Hz, 8 H, H^D), 7.68–7.64 (m, J = 1.7, 5.2 Hz, 16 H, H^3, H^F and H^E) ppm. ^{13}C NMR (125.6 MHz CD_3CN, 25 °C): δ = 122.6 (C^C), 124.8 (C^3), 126.0 (C^B), 128.2 (C^D), 129.8 (C^F), 131.3 (C^E), 135.6 (C), 143.3 (C) 152.8 (C), 153.2 (C^2), 154.4 (C^A), 156.1 (C), 157.1 (C^4), 191.6 (C^{CO}*trans*), 196.3 (C^{CO}*cis*) ppm. The ^{1}H NMR spectrum is shown in Figure 1.

Preparation of [(Ph_2bpy)(CO)$_3$Re^I(μ-PCA)Ru^{II}(NH_3)$_5$](PF_6)$_3$·6CH_2Cl_2 (3): Complex **1** (30 mg, 0.032 mmol) was stirred in acetone (10 mL) under argon for 30 min and [Ru(NH_3)$_5$(H_2O)](PF_6)$_2$ (16 mg, 0.032 mmol), prepared as described in the literature,[25] was then added. The mixture was stirred under argon in the dark for 2 h. Diethyl ether (100 mL) was added to precipitate the complex, which was re-dissolved in a minimum amount of acetone. Dichloromethane (40 mL) and diethyl ether (40 mL) were added to re-precipitate the complex, which was filtered and washed with dichloromethane, diethyl ether, and water. It was finally dissolved in acetonitrile and purified by chromatography on Sephadex LH-20, using acetonitrile as the eluting solvent. The first, blue fraction was collected, concentrated to dryness, re-dissolved in acetone, precipitated with dichloromethane, filtered, washed with dichloromethane and diethyl ether, and dried in vacuo over P_4O_{10}. Yield: 30 mg (66%). $C_{43}H_{53}Cl_{12}F_{18}N_{11}O_3P_3ReRu$ (1919.6): calcd. C 26.9, H 2.8, N 8.0; found C 26.6, H 2.8, N 8.5.

Preparation of [(Ph_2bpy)(CO)$_3$Re^I(μ-PCA)Ru^{III}(NH_3)$_5$]$^{4+}$ (4): This heterodinuclear ion was generated in situ by adding bromine to an acetonitrile solution of **3** or by electrochemical oxidation. The oxidation progress was monitored by measuring the absorbance changes in the 200–1100 nm range.

Preparation of [Re{4,4′-(MeO_2C)$_2$-bpy}(CO)$_3$(PCA)]PF_6·H_2O (5) and [(4,4′-(MeO_2C)$_2$-bpy)(CO)$_3$Re(μ-PCA)Re(CO)$_3${4,4′-(MeO_2C)$_2$-bpy}](PF_6)$_2$ (6): [Re(CO)$_5$Cl] (181 mg, 0.50 mmol) and 4,4′-bis-(methoxycarbonyl)-2,2′-bipyridine (136 mg, 0.50 mmol) were heated at reflux in toluene (20 mL) for 1 h. Precipitation was achieved by adding hexane (20 mL) to the cooled solution. The red solid obtained after additional cooling was collected, washed with hexane and diethyl ether, and dried in vacuo. The resulting complex [Re{4,4′-(MeO_2C)$_2$-bpy}(CO)$_3$Cl] (280 mg, 0.485 mmol) and Ag(CF_3SO_3) (114 mg, 0.443 mmol) were heated at reflux in thf (40 mL) for 30 min. PCA (153 mg, 0.728 mmol) was then added to the reaction mixture and heating at reflux was continued for 2 h. After removal of AgCl by filtration, the solvent was removed in a rotary evaporator to give an orange oil. This oil was dissolved in 40 mL of 3:1 (v/v) MeOH/H_2O, 2 g of NH_4PF_6 dissolved in 10 mL of water was added, and the mixture was put in the freezer. The yellow precipitate that formed was filtered and washed with copious amounts of H_2O and three times with portions of diethyl ether. It was then dissolved in a minimum amount of 1:4 (v/v) acetonitrile/dichloromethane, adsorbed onto a silica gel (Kieselgel 60) column and eluted with the same solvent. The yellow fractions (the first is complex **6** and the second is complex **5**) were concentrated to dryness, redissolved in acetone, and precipitated with hexane. **5:** Yield: 107 mg (24%). $C_{29}H_{24}F_6N_6O_8PRe$ (915.72): calcd. C 38.0, H 2.6, N 9.2; found C 37.9, H 2.1, N 9.0. IR (KBr): $\tilde{\nu}$ = 2037 (s), 1927 (s), 1735 (s), 1616 (m), 1560 (w), 1440 (m), 1408 (m), 1327 (m), 1308 (m), 1266 (m), 1232 (m), 1134 (w), 981 (w), 843 (s), 785 (w), 766 (m), 722 (w), 644 (w), 558 (m) cm^{-1}. ^{1}H NMR (500.13 MHz, CD_3CN, 25 °C): δ = 9.40 (dd, J = 5.7, 0.7 Hz, 2 H, H^A), 8.91 (dd, J = 1.6, 0.7 Hz, 2 H, H^C), 8.70 (dd, J = 1.7, 4.5 Hz, 2 H, H^2), 8.45 (s, 1 H, H^4), 8.42 (s, 1 H, $H^{4'}$), 8.30 (dd, J = 5.2, 1.6 Hz, 2 H, $H^{2'}$), 8.22 (dd, J = 1.6, 5.6 Hz, 2 H, H^B), 7.69 (dd, J = 1.7, 4.5 Hz, 2 H, H^3), 7.64 (dd, J = 1.6, 5.2 Hz, 2 H, $H^{3'}$), 4.02 (s, 6 H, Me) ppm. ^{13}C NMR (125.6 MHz CD_3CN, 25 °C): δ = 54.3 (C of Me), 123.0 (C^3), 125.3 (C), 125.7 ($C^{3'}$), 129.0 (C^B), 141.4 (C), 142.7 (C), 145.0 (C), 151.6 (C), 153.8 (C), 153.8 ($C^{2'}$), 156.1 (C^2), 157.6 ($C^{4'}$), 158.3 (C), 161.4 (C^4), 164.4 (C) ppm. ^{15}N NMR (50.69 MHz CD_3CN, 25 °C; chemical shifts extracted from the ^{1}H-^{15}N HMBC spectrum): δ = 248.0 ($N^{A'}$), 237.2 ($N^{1'}$),322.9 (N^1), 373.0 ($N^{5'}$), 375.5 (N^5) ppm. **6:** Yield: 48 mg (12%). $C_{46}H_{34}F_{12}N_8O_{14}P_2Re_2$ (1585.2): calcd. C 34.9, H 2.2, N 7.1; found C 34.7, H 2.1, N 6.8. IR (KBr): $\tilde{\nu}$ = 2037 (s), 1927 (s), 1735 (s), 1618 (m), 1560 (w), 1440 (m), 1408 (m), 1327 (m), 1307 (m), 1266 (m), 1232 (m), 1134 (w), 981 (w), 843 (s), 785 (w), 766 (m), 722 (w), 644 (w), 558 (m) cm^{-1}. ^{1}H NMR (500.13 MHz, CD_3CN, 25 °C): δ = 9.37 (dd, J = 5.6, 0.6 Hz, 4 H, H^A), 8.88 (dd, J = 1.7, 0.6 Hz, 4 H, H^C), 8.27 (dd, J = 1.7, 5.2 Hz, 4 H, H^2), 8.27 (s, 2 H, H^4), 8.20 (dd, J = 5.6, 1.6 Hz, 4 H, H^B), 7.57 (dd, J = 1.7, 5.2 Hz, 4 H, H^3), 4.00 (s, 12 H, Me) ppm. ^{13}C NMR (125.6 MHz CD_3CN, 25 °C): δ = 54.2 (C^{Me}), 125.3 (C^C), 125.7 (C), 129.0 (C), (C), 142.7 (C), 144.6 (C^3), 153.9 (C^2), 156.0 (C^A), 157.5 (C^4), 158.5 (C), 164.4 (C), 191.6 (C^{CO}*trans*), 196.3 (C^{CO}*cis*) ppm. ^{15}N NMR (50.69 MHz CD_3CN, 25 °C; chemical shifts extracted from the ^{1}H-^{15}N HMBC spectrum): δ = 250.5 ($N^{A'}$), 238.1 (N^1), 377.6 (N^5) ppm.

Preparation of [{4,4′-(MeO_2C)$_2$-bpy}(CO)$_3$Re^I(μ-PCA)Ru^{II}(NH_3)$_5$]-(PF_6)$_3$·CH_2Cl_2 (7): Complex **5** (50 mg, 0.056 mmol) was stirred in acetone (10 mL) under argon for 30 min, and [Ru(NH_3)$_5$-(H_2O)](PF_6)$_2$ (28 mg, 0.056 mmol), prepared as described in the literature,[25] was added. The mixture was stirred continuously under argon in the dark for 2 h. Diethyl ether (100 mL) was then added to precipitate the complex, which was redissolved in a minimum amount of acetone. Dichloromethane (60 mL) and diethyl ether (60 mL) were added to re-precipitate the complex, which was filtered and washed with dichloromethane, diethyl ether, and water. It was finally dissolved in acetonitrile and purified by chromatography on Sephadex LH-20 using acetonitrile as the eluting solvent. The first, blue fraction was collected, concentrated to dryness, redissolved in acetone, precipitated with dichloromethane, filtered, washed with dichloromethane and diethyl ether, and dried in vacuo over P_4O_{10}. Yield: 55 mg (71%). $C_{31}H_{39}Cl_2F_{18}N_{11}O_7P_3ReRu$ (1470.8): calcd. C 25.3, H 2.7, N 10.5; found C 25.1, H 2.7, N 10.8.

Preparation of [{4,4′-(MeO_2C)$_2$-bpy}(CO)$_3$Re^I(μ-PCA)Ru^{III}-(NH_3)$_5$]$^{4+}$ (8): This heterodinuclear ion was generated in situ by adding bromine to an acetonitrile solution of **7** or by electrochemical oxidation. The oxidation progress was monitored by measuring the absorbance changes in the 200–1100 nm range.

Preparation of [Re(bpy)(CO)$_3$(4,4′-bpy)]PF_6 (9): This complex was available from previous studies.[11]

Protonation Studies: For pK_a determinations, pH titrations by spectrophotometric and spectrofluorometric techniques were performed with two kinds of experiments. In the first one, Britton and Robinson's buffer, which consists of a mixture of 0.04 M acetic acid, 0.04 M phosphoric acid, and 0.04 M boric acid with variable amounts of a solution of 0.2 M NaOH, was used, and the ionic strength was fixed at 0.1 M with a solution of NaCl. The complexes were dissolved in aqueous solutions of 0.1 M NaCl and stirred for about 5 h until the filtered solution showed a final average absorbance of about 0.4. Each sample was prepared just before measurement with 2 mL of buffer and 2 mL of a stock solution of the complex. The pH value of each fraction was then determined with a Metrohm pH-meter. Reversal of the pH values of the extreme fractions was done by adding 3 M HCl or 3 M NaOH. In each titration, 12–15 points were recorded. In the second experiment, the ionic strength was not regulated. Only one solution (approx. 30 mL) was used, with Britton and Robinson's buffer, which con-

sists of 0.02 M acetic acid, 0.02 M phosphoric acid and 0.02 M boric acid with a small amount of 3 M NaOH solution up to pH = 10. The complex was dissolved by adding a drop of acetonitrile and rapidly mixing with the buffer solution. 3 M HCl (40–60 μL) was added to lower the pH to 1.5. In each titration, 40–50 points were recorded. Both methods gave consistent results. Luminescence and absorption measurements were performed with air-saturated solutions. We used a previously reported technique to fit the obtained data for all complexes.[7] The experimental data were fitted with the PSI Plot software. The fits were all satisfactory, giving consistent and reasonable values of pK_a and pK_a*.

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