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Proton-Induced Luminescence of Mono- and Dinuclear Rhenium(I) Tricarbonyl Complexes Containing 4-Pyridinealdazine

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New mono- and dinuclear rhenium(I) tricarbonyls, of formulas $[Re(bpy)(CO)_3(PCA)]^+$ (**1**), $[(bpy)(CO)_3Re^I(PCA)Re^I(CO)_3(bpy)]^{2+}$ (**2**), and $[(bpy)(CO)_3Re^I(PCA)Ru^{II}(NH_3)_5]^{3+}$ (**3**) (bpy = 2,2′-bipyridine, PCA = 4-pyridinecarboxaldehydeazine), have been synthesized as PF_6^- salts and characterized by spectroscopic, electrochemical, and photophysical techniques. These species do not emit at room temperature in CH_3CN; however, in aqueous solutions, a decrease in pH induces luminescence in all of them, due to protonation of one of the N atoms of the –C=N–N=C– chain of PCA, as indicated by the pK_a values of the ground states, obtained by absorption measurements, which are ca. 3 orders of magnitude lower than the pK_a value of the pyridine N of PCA in complex **1**. On the other hand, the values of pK_a* of the excited states, obtained by emission measurements, of complexes **1** and **2** are similar (pK_a* = 2.7 ± 0.1 at I = 0.1 M) and higher than those of the corresponding ground states. At low values of pH, chemical decomposition takes place rapidly in complex **3**, but not in **1** and **2**, supporting the possible use of these latter species as luminescent sensors of pH. The heterodinuclear complex, of formula $[(bpy)(CO)_3Re^I(PCA)Ru^{III}(NH_3)_5]^{4+}$, was obtained by bromine oxidation of the [Re^I, Ru^{II}] precursor in CH_3CN solution; from spectral and electrochemical measurements, the recombination charge-transfer reaction [Re^{II}, Ru^{II}] → [Re^I, Ru^{III}], which occurs after photoexcitation, is predicted to lie in the Marcus inverted region.

Introduction

A fundamental issue in the development of supramolecular machines based on single molecules is the synthesis of molecules capable of performing switching functions. It has already been demonstrated that luminiscence is a property suitable for switching purposes; therefore, various emissive complexes of Ru^{II}, Os^{II}, and Re^I that contain polypyridyl ligands have been employed for this purpose.[1] In particular, rhenium(I) tricarbonyl complexes have been extensively studied not only as luminescent sensors[2] but also in connection to electron- and/or energy-transfer processes that lead to applications such as solar energy conversion, CO_2 reduction, biological probes, and so on.[3] Besides, the photophysical behavior of these complexes can be tuned by adequate variations in the structures of the coordinating ligands. Numerous examples of transition-metal complexes of Ni^{II} and Cu^{II} that are the basis of light-emitting molecular devices have been discussed in a recent review.[4]

It is well-known that the lifetimes of the excited states of complexes of the type $[Re(X_2bpy)(CO)_3L]^{n+}$, where bpy = 2,2′-bipyridine, X = group acting as an electron donor or acceptor, and L = substituted pyridine, can be controlled by changing the nature of X and/or of L.[5] This is a desirable effect in designing new luminescent sensors. There are already elegant studies in the literature where platinum group metal complexes have been used as pH-sensitive luminescent sensors, usually by modifying the core ligand bpy.[6] Changes of luminescence with pH by modifying the auxiliary ligand

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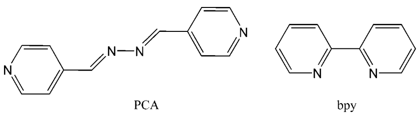
L are less frequent; therefore, we report in this work an unusual proton-induced emission of chromophore-quencher rhenium(I) tricarbonyl mono- and dinuclear complexes that contain the electron-accepting ligand L = PCA (4-pyridinecarboxaldehydeazine, also known as 4-pyridinealdazine or 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene).

In a recent study, we proved that PCA behaves as a bridging ligand connecting two metal centers in heterodinuclear and mixed-valent species with an enhanced metal–metal coupling resulting from the strongly delocalized electronic structure of PCA.[7] On the other hand, the presence of several N atoms in PCA with lone pair electrons makes this ligand a potential proton acceptor at various pH values. In the previously studied complex $[Re(Me_2bpy)(CO)_3(PCA)]^+$ (Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine), the emission from the MLCT (metal-to-ligand charge-transfer) excited state $d_\pi(Re) \rightarrow \pi^*(Me_2bpy)$ is completely quenched, in CH_3CN, by crossing to a lower lying MLCT excited state $d_\pi(Re) \rightarrow \pi^*(PCA)$.[7] In this work, we address the possibility of reviving the emission from the former MLCT excited state in the novel mononuclear species of formula $[Re(bpy)(CO)_3(PCA)]^+$ by changing the energy of the $\pi^*(PCA)$ electronic state with pH and by replacing Me_2bpy with the more electron accepting ligand bpy. Furthermore, since PCA has two different protonation sites in this complex, the proton-induced luminescence of a novel symmetric dinuclear species, of formula $[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$, which has only two equal sites of protonation, has also been studied, and constitutes one of the few examples of a dinuclear complex that could eventually be used as a luminescent sensor of pH. Finally, dinuclear asymmetric complexes, of formulas $[(bpy)(CO)_3Re^{I}(PCA)Ru^{II/III}(NH_3)_5]^{3+/4+}$, have been prepared and characterized in relation to pH-sensitive emission and intramolecular electron transfer in the Marcus inverted region.

Chart 1. Ligands



The structures of the ligands are shown in Chart 1. The structures of the complexes are shown in Chart 2.

Experimental Section

Materials and Techniques. All used chemicals were p.a. grade. CH_3CN was distilled over P_4O_{10}. Tetrakis(*n*-butyl)ammonium hexafluorophosphate (TBAH) was purified by recrystallization over ethanol three times and dried at 150°C for 72 h. IR spectra were recorded (as KBr pellets) on a double-beam Perkin-Elmer 983G spectrophotometer. UV/vis spectra were taken on a Varian Cary 50 spectrophotometer, provided with 1 cm cells. Electrochemical measurements were carried out in CH_3CN (0.1 M TBAH) with BAS Epsilon electrochemical equipment. A standard three-electrode compartment cell was used, with Ag/AgCl (3 M KCl) as a reference electrode, Pt or vitreous C a working electrode, and Pt wire as an auxiliary electrode. All values of redox potentials, $E_{1/2}$, were referred to Ag/AgCl. Spectroelectrochemical measurements were performed in an OTTLE (optically transparent thin-layer electrolysis) type cell from BAS. Emission studies were made by using a Shimadzu RF-5301 PC spectrofluorometer, provided with 1 cm fluorescence cells. Ar was bubbled through the solutions for 15 min prior to electrochemical measurements. Chemical analyses for C, H, and N were done at INQUIMAE, University of Buenos Aires, Argentina, with an estimated error of ±0.5%. Density functional theory (DFT) calculations were performed with the GAUSSIAN 98 program package,[8] using optimization with B3LYP/6-311G bases, within a spin-restricted formalism, and energy calculations of the first 20 default states were carried out by using the time-dependent (TD) DFT method.

Syntheses. PCA. The ligand 4-pyridinealdazine was prepared as described previously.[9]

$[Re(bpy)(CO)_3(PCA)]PF_6 \cdot 4(CH_3)_2CO$ (1) and $[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)](PF_6)_2$ (2). These salts were prepared by a procedure similar to that reported in the literature.[10] In a typical experiment, $[Re(CO)_5Cl]$ (181 mg, 0.50 mmol) and 2,2′-bipyridine (78 mg, 0.50 mmol) were heated at reflux for 1 h in 20 mL of toluene. The solid obtained after cooling was collected, washed with diethyl ether, and dried in a vacuum. The resulting compound, $[Re(bpy)(CO)_3Cl]$ (222 mg, 0.48 mmol), and $Ag(CF_3SO_3)$ (124 mg, 0.48 mmol) were heated at reflux for 30 min in 40 mL of THF. The ligand PCA (151 mg, 0.72 mmol) was then added to the reaction mixture, and heating at reflux was continued for 2 h. After

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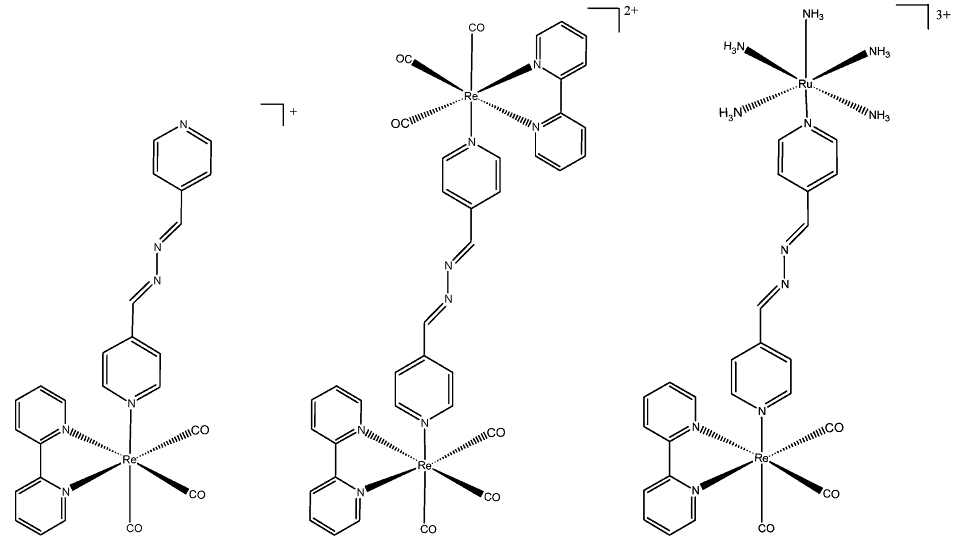
Chart 2. Complexes



Complex **1**   Complex **2**   Complex **3**

removal of AgCl by filtration, the solvent was removed on a rotary evaporator to give a red-yellow oil. The oil was dissolved in 40 mL of 3:1 (v/v) MeOH/H_2O, 1.2 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. This solid was dissolved in a minimum amount of 1:4 (v/v) acetonitrile/methylene chloride, sorbed onto a silica gel (Kiessegel 60) column, and eluted with the same solvent. The yellow fractions (the first is complex **2**, and the second is complex **1**) were evaporated to dryness, redissolved in acetone, and precipitated with diethyl ether. Data for complex **1**: yield 55 mg (11%); IR (KBr, cm^{-1}) 2032 (s), 1923 (s), 1608 (m), 1598 (w), 1469 (w), 1444 (w), 1416 (w), 1313 (w), 1239 (w), 842 (s), 767 (m), 690 (w), 646 (w), 558 (m). Anal. Found: C, 43.5; H, 3.9; N, 8.5. Calcd for $C_{37}H_{42}N_6O_7PF_6Re$: C, 43.8; H, 4.2; N, 8.3. Data for complex **2**: yield 50 mg (15%); IR (KBr, cm^{-1}) 2033 (s), 1918 (s), 1609 (m), 1471 (w), 1445 (w), 1420 (w), 1316 (w), 1242 (w), 843 (s), 768 (m), 725 (w), 646 (w), 626 (w), 559 (m). Anal. Found: C, 33.8; H, 1.8; N, 8.8. Calcd for $C_{38}H_{26}N_8O_6P_2F_{12}Re_2$: C, 33.7; H, 1.9; N, 8.3.

$[(bpy)(CO)_3Re^I(PCA)Ru^{II}(NH_3)_5](PF_6)_3\cdot 3H_2O$ (3). A 40 mg (0.039 mmol) sample of **1** was stirred in 10 mL of acetone under Ar for 30 min, and $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (24 mg, 0.048 mmol), prepared as described in the literature,[11] was added, followed by continuous stirring under Ar for 2 h in the dark. A 100 mL portion of diethyl ether was added to precipitate the complex. It was then redissolved in the minimum amount of acetone, and 40 mL of methylene chloride was added to reprecipitate the complex, which was filtered and washed with methylene chloride and diethyl ether. 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, evaporated to dryness, redissolved in acetone, precipitated with methylene chloride, filtered, washed with methylene chloride and ether, and dried in a vacuum over P_4O_{10}: yield 31 mg (46%). Anal. Found: C, 22.8; H, 3.0; N, 12.6. Calcd for $C_{25}H_{39}O_6N_{11}F_{18}P_3ReRu$: C, 22.9; H, 3.0; N, 11.7.

$[(bpy)(CO)_3Re^I(PCA)Ru^{III}(NH_3)_5]^{4+}$ (4). This heterodinuclear ion was generated in situ by adding bromine to an acetonitrile solution of **3**. The oxidation progress was monitored by measuring the absorbance changes in the 200−1100 nm range.

$[Re(Me_2bpy)(CO)_3(PCA)]PF_6$ (5) and $[(Me_2bpy)(CO)_3Re(PCA)Re(CO)_3(Me_2bpy)](PF_6)_2$ (6). These complexes were available from a previous work.[7]

Protonation Studies. For pK_a determinations, pH titrations by spectrophotometric and spectrofluorometric techniques were performed using Britton and Robinson's buffer, containing 0.04 M acetic acid, 0.04 M phosporic acid, and 0.04 M boric acid with variable amounts of a solution of NaOH (0.2 N). The ionic strength was fixed at 0.1 M with a solution of NaCl. The complexes were dissolved in aqueous solutions of NaCl (0.1 M), stirring for many hours until total dissolution and with a final average absorbance of ca. 0.4. Luminiscence intensity measurements were done in air-saturated solutions. Each sample was prepared just before measurement with 2 mL of buffer and 2 mL of a stock solution of the complex. Then the pH value of each fraction was determined by using an Altronix TPX-1 pH meter. Reversal of pH values of the extreme fractions was done by using a solution of HCl (3 M) or NaOH (3 M). In each titration, 12−14 points were recorded. The intensity measurements were corrected by absorbance differences.

For fitting the obtained data in complex **1**, at least two different sites of protonation of PCA must be considered, one at the pyridine N and the other at the imine N (see Chart 1). We used an analysis slightly modified with respect to that already reported for transition-metal complexes that contain the pH-sensitive ligand 5-carboxy-1,10-phenanthroline.[2] The absorbance and luminescence data were satisfactorily fitted with a three-species scheme, where B is the corresponding mononuclear nonprotonated PCA complex: In the

$$\begin{tikzcd} H_2B^{2+}* \arrow[r, shift left, "K_{a1}*"] \arrow[d, shift left, "k_{H_2B^{2+}}"] & HB^{+}* + H^+ \arrow[l, shift left] \arrow[r, shift left, "K_{a2}*"] \arrow[d, shift left, "k_{HB^+}"] & B* + 2\,H^+ \arrow[l, shift left] \arrow[d, shift left, "k_B"] \\ H_2B^{2+} \arrow[u, shift left, "h\nu"] \arrow[r, shift left, "K_{a1}"] & HB^{+} + H^+ \arrow[u, shift left, "h\nu"] \arrow[l, shift left] \arrow[r, shift left, "K_{a2}"] & B + 2\,H^+ \arrow[u, shift left, "h\nu"] \arrow[l, shift left] \end{tikzcd} \qquad (1)$$

fast exchange limit, it is assumed that the excited-state equilibria among B*, HB^{+}*, and H_2B^{2+}* are maintained. This allows for simple expressions for the observed absorbance and intensity variations as a function of the fraction of each species present. For complex **2**, only one site of protonation (that at the imine N of

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Table 1. Electronic Absorption Spectral Data, in CH_3CN, at 22 °C

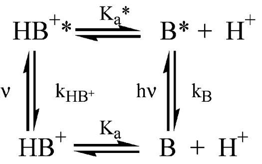
complex	λ_{max}, nm ($10^{-3}\epsilon_{max}$, $M^{-1}\,cm^{-1}$)
$[Re(bpy)(CO)_3(PCA)]^+$ (**1**)	332 (21.8), 319 (36.6), 305 (38.2), 278 (44.0)
$[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$ (**2**)	336 (31.3), 320 (46.9), 310 (41.5), 273 (44.5), 249 (41.7)
$[(bpy)(CO)_3Re^I(PCA)Ru^{II}(NH_3)_5]^{3+}$ (**3**)	563 (10.3), 333 (14.5), 319 (22.7), 305 (22.8), 275 (30.2)
$[(bpy)(CO)_3Re^I(PCA)Ru^{III}(NH_3)_5]^{4+}$ (**4**)	498 (1.5), 333 (14.5), 319 (22.7), 305 (22.8), 275 (30.2)

Table 2. Quantum Yields for the Emission of Complexes **1**−**3** in Water at Two pH Values (λ_{em} = 553 nm, λ_{exc} = 350 Nm)[a]

complex	pH ≅ 1.3	pH ≅ 8.5
$[Re(bpy)(CO)_3(PCA)]^+$ (**1**)	0.0095	0.0025
$[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$ (**2**)	0.0161	0.0029
$[(bpy)(CO)_3Re^I(PCA)Ru^{II}(NH_3)_5]^{3+}$ (**3**)		0.0005

[a] Corrected by solvent effects, absorbance differences, and oxygen quenching as in ref 14.

PCA) can be observed. Therefore, the scheme is simplified to a two-species one: This scheme was also used for the fitting of the



(2)

luminescence intensity of complex **1**, since neither the neutral nor the monoprotonated form emits at room temperature.

For complex **3**, since both imine N atoms can be protonated at pH ≥ 1, the scheme given in eq 1 was used to fit the absorption and emission measurements.

Values of A^{max} and I^{max}, the absorbance and emission intensity, respectively, when only one species is present, were obtained from the appropriate data at the limits of the pH range used, or as floating parameters. The experimental data were fitted by using PSI Plot software. The fits were all satisfactory, giving consistent and reasonable values of pK_a and pK_a*.

Results and Discussion

Syntheses, Solubilities, and IR Spectra. The synthetic methods used to obtain the new mono- and dinuclear rhenium tricarbonyls with PCA described in this work are slight modifications of those already described in the literature for similar complexes.[10] For the heterodinuclear rhenium−ruthenium complexes, the followed protocols have been previously developed in our laboratory.[12] The new complexes were soluble in acetonitrile; their purity was confirmed by chemical analyses, CV, and IR and UV/vis spectra. At low concentrations ($C \leq 10^{-4}$ M), all complexes are soluble in water and stable at least in neutral solutions for 2−3 days. The solubility of rhenium(I) complexes in pure water is an important property in relation to their applications in radiopharmacy.[13] Besides, the values of the carbonyl stretching frequencies, $\nu_{C\equiv O}$, shown in the IR spectra of complexes **1** and **2** (2032−2033 and 1918−1923 cm^{-1}) are almost the same as those reported for related complexes of the type *fac*-$[Re(bpy)(CO)_3(L)]PF_6$ with L = 4,4′-bpy (4,4′-bipyridine), 4-CNpy (4-cyanopyridine), and BPE (*trans*-1,2-bis-(4-pyridyl)ethene),[12] consistent with a facial configuration of carbonyl groups of local C_{3v} symmetry.

UV/Vis Spectra. Table 1 shows the electronic absorption spectral data for complexes **1**−**4** in CH_3CN. Characteristic intraligand $\pi \rightarrow \pi^*$ transitions of the bpy and PCA ligands give rise to intense UV absorptions between 200 and 300 nm.[7] The mononuclear complex **1**, $[Re(bpy)(CO)_3(PCA)]^+$, presents an intense absorption of minimum energy at λ_{max} = 332 nm that can be assigned, as observed before in the analogous complex **5**, $[Re(Me_2bpy)(CO)_3(PCA)]^+$ (λ_{max} = 330 nm),[7] to overlapping MLCTs: $d_\pi(Re) \rightarrow \pi^*(bpy)$ and $d_\pi(Re) \rightarrow \pi^*(PCA)$. In the homodinuclear Re^I-Re^I complex **2**, this same band is red-shifted to λ_{max} = 336 nm, indicating moderate interaction between both Re centers, similar to that already reported for the symmetric dinuclear complex $[(Me_2bpy)(CO)_3Re^I(PCA)Re^I(CO)_3(Me_2bpy)]^{2+}$.[7]

When comparing the UV/vis spectra of the asymmetric dinuclear complexes **3**, $[(bpy)(CO)_3Re^I(PCA)Ru^{II}(NH_3)_5]^{3+}$, and **4**, $[(bpy)(CO)_3Re^I(PCA)Ru^{III}(NH_3)_5]^{4+}$, we can readily assign the bands in the Re^I-Ru^{II} complex **3** at λ_{max} = 333 nm and λ_{max} = 563 nm to $d_\pi(Re) \rightarrow \pi^*(bpy, PCA)$ and $d_\pi(Ru) \rightarrow \pi^*(PCA)$ MLCT transitions, respectively. For the Re^I-Ru^{III} complex **4**, prepared in situ by bromine oxidation of **3**, the band at λ_{max} = 563 nm vanishes completely and the new band that appears at λ_{max} = 498 nm (value obtained by Gaussian deconvolution) can be attributed to a $Re^I \rightarrow Ru^{III}$ metal−metal charge-transfer (MMCT) transition, with some contribution from a PCA → Ru^{III} LMCT band, as discussed before for the analogous species with Me_2bpy.[7]

Luminescence Properties. The complexes studied in this work do not emit in CH_3CN solutions at room temperature, except for complex **2**, which presents a weak emission at λ_{max} = 538 nm (λ_{exc} = 336 nm), typical of $Re^{II}(diimine^-)$ complex MLCT excited states.[14] The quenching of the luminescence of complex **1** can be explained by crossing to a $[(bpy)(CO)_3Re^{II}(PCA^-)]^+$ excited state, as confirmed by flash photolysis and low-temperature emission measurements carried out in the analogous complex with Me_2bpy.[7] Since bpy is a better π-acceptor than Me_2bpy, we would expect that emission could eventually be revived at room temperature, an effect which can be observed only at low pH values, as discussed in the following section.

In water, all complexes emit very weakly at λ_{max} = 553 nm (λ_{ex} = 350 nm), although the emission is almost completely quenched in complex **3**, probably because of autoabsorption at the emission maximum, as shown in Table 2, which contains the quantum yields of complexes **1**−**3** at extreme pH values. When the pH is decreased, the emission from the Re → bpy MLCT excited state is revived, as

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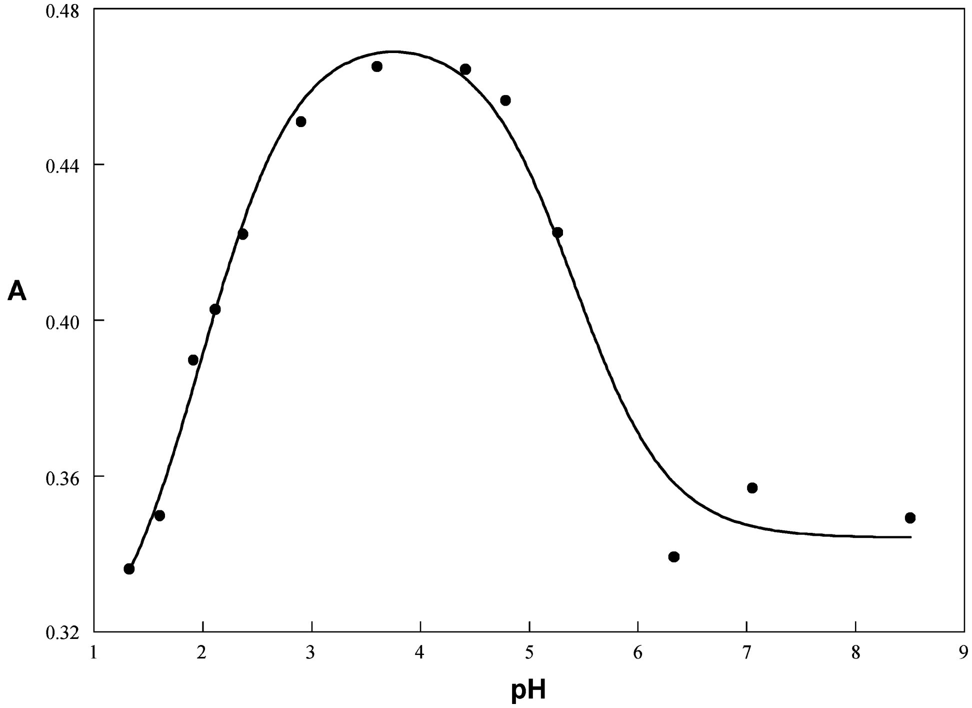

Figure 1. Variation of absorbance with pH for $[Re(bpy)(CO)_3(PCA)]^+$ in aqueous buffers at $\lambda = 330$ nm. The line indicates the best fit using a three-species model.

Table 3. Values of pK_a for Ground and Excited States of Complexes **1**−**3** ($I = 0.1$ M, $T = 22$ °C)

complex	pK_a	pK_a*
$[Re(bpy)(CO)_3(PCA)]^+$ (**1**)	$pK_{a1} = 1.98 \pm 0.13$	$pK_{a1}^* = 2.72 \pm 0.10$
	$pK_{a2} = 5.41 \pm 0.14$	
$[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$ (**2**)	$pK_{a1} = 1.53 \pm 0.31$	$pK_{a1}^* = 2.71 \pm 0.12$
$[(bpy)(CO)_3Re^I(PCA)Ru^{II}(NH_3)_5]^{3+}$ (**3**)	$pK_{a1} \cong -0.40$	$pK_{a1}^* \cong -0.18$
	$pK_{a1} = 3.98 \pm 0.30$	$pK_{a1}^* = 3.20 \pm 0.34$

disclosed by the excitation spectra and the quantum yields, increased by a factor of 4 in complex **1** and by a factor of 5 in complex **2** on going from pH ≅ 8.5 to pH ≅ 1.3. No emission is detected in complex **3** with excitation at the absorption maximum of the Ru → PCA MLCT band ($\lambda_{max} = 563$ nm).

Protonation Equilibria. Table 3 shows the data obtained from the spectrophotometric and spectrofluorometric titrations of all complexes. These results are interesting in the context of using some of the studied species as luminescent on−off switches.

The ligand PCA does not emit at room temperature in all used solvents (CH_2Cl_2, MeOH, H_2O, and MeCN). Fitting absorbance changes at $\lambda = 275$ nm, a value of pK_a = 5.19 is obtained, which compares well to that of similar pyridine compounds (e.g., pK_a = 5.9 for 1,2-bis(4-pyridyl)ethylene)[15] and corresponds to protonation of the pyridine N atoms. The other pK_a (that of the imine N) could not be determined up to pH 2 and is therefore considered to be less than 2.

When the pyridine N atoms of PCA are protonated, the $\pi \rightarrow \pi^*$ excited state decreases in energy, as shown by the experimental UV/vis absorption shift from $\lambda_{max} = 278$ nm at pH 7.4 to $\lambda_{max} = 332$ nm at pH 2.0 (with an isosbestic point at $\lambda = 304$ nm). These results are consistent with time-dependent DFT calculations of the lowest lying excited state.

In the mononuclear complex **1**, fitting of the UV/vis absorptivity changes with pH at $\lambda = 330$ nm gives a bell-shaped curve, as shown in Figure 1, from which two ground-state pK_a values can be determined. The first one, $pK_{a1} = 1.98$, is ca. 3 orders of magnitude lower than that of the pyridine N of the free ligand and thus corresponds to one of the imine N atoms of coordinated PCA. The second one, $pK_{a2} = 5.41$, corresponds to the free pyridine N of coordinated PCA and is increased 0.2 unit with respect to the free ligand value, probably because of π-back-bonding effects of Re^I.

What is more interesting is the emission of complex **1**, which is almost undetectable at pH 8.6 and is revived by a factor of 4 at pH 1.4. As shown in Figure 2, fitting the emission intensity changes with pH gives $pK_{a1}^* = 2.72$, corresponding again to the imine N of coordinated PCA. The basicity of the excited state is higher by 0.74 unit than that of the ground state, as expected for rhenium(I) tricarbonyls.[2] The value of pK_{a2}^* could not be determined, probably because the decrease in energy of the $Re^{II}PCA^-$ MLCT excited state induced by pH quenches almost completely the emission from the $Re^{II}bpy^-$ MLCT excited state. However, when the imine N is protonated, the π* excited state of PCA increases in energy, due to suppression of intraannular conjugation. The $Re^{II}bpy^-$ MLCT excited state then becomes lowest in energy, and emission is revived in complex **1**.

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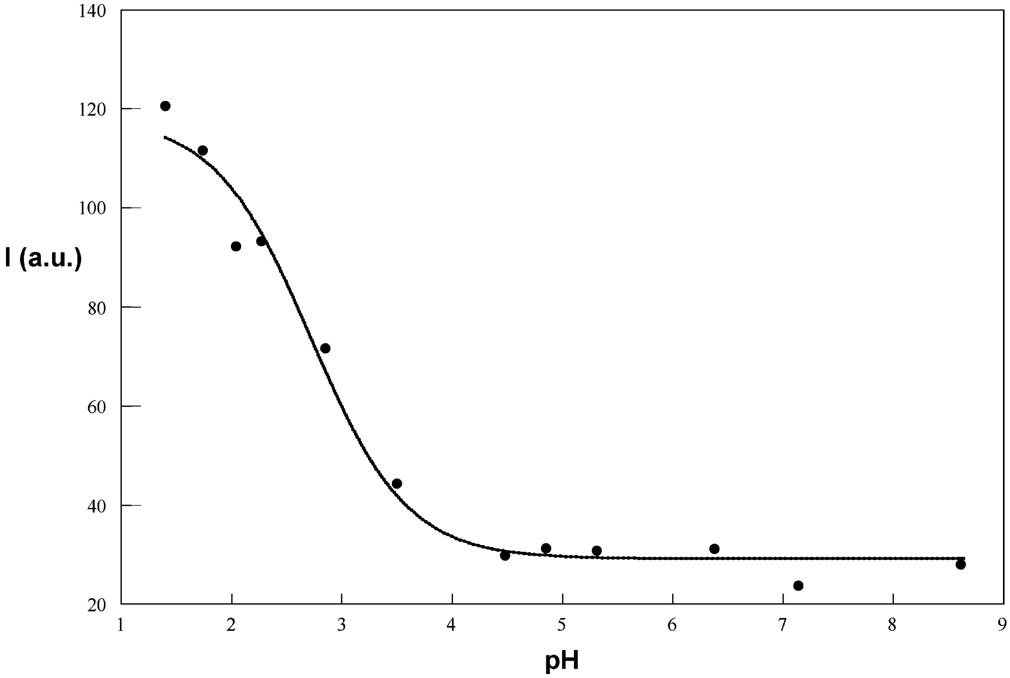

Figure 2. Variation of emission intensity with pH for $[Re(bpy)(CO)_3(PCA)]^+$ in aqueous buffers at $\lambda_{ex} = 350$ nm. The line indicates the best fit using a two-species model.

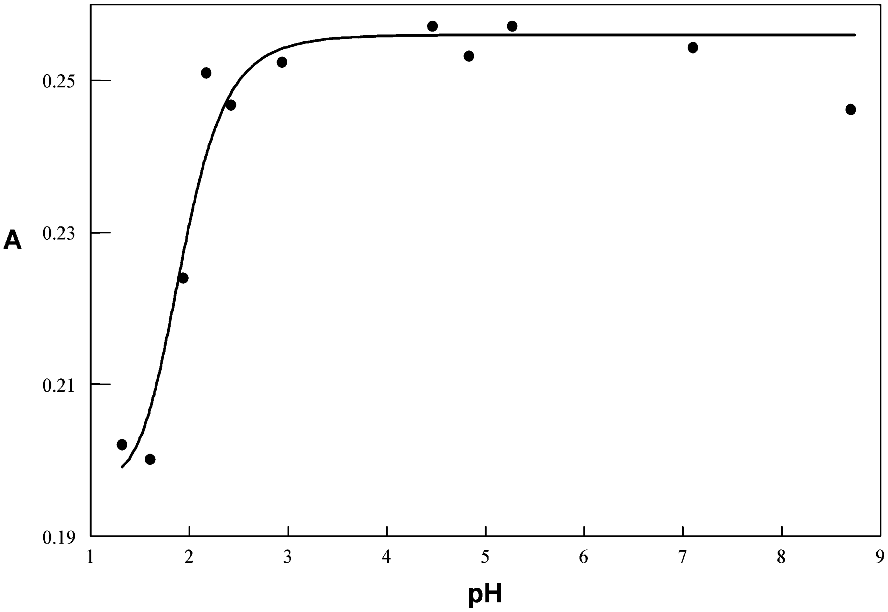

Figure 3. Variation of absorbance with pH for $[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$ in aqueous buffers at $\lambda = 319$ nm. The line indicates the best fit using a two-species model.

Perturbation of aromaticity by protonation has already been noted when using pH-sensitive ligands in ruthenium polypyridyl complexes.[16]

Similar effects are displayed when the pH titrations of the dinuclear complex **2** are analyzed. In this case, only protonation of the imine N atoms of PCA is feasible, since both pyridine N atoms of PCA are already coordinated to Re atoms (see Chart 2). This behavior is reflected in the sigmoid fitting curve for experimental absorption data, shown in Figure 3, in contrast to the bell-shaped fitting curve of complex **1** (Figure 1). The obtained value of pK_a (=1.53) is lower by 0.4 unit than that of the mononuclear species.

There is also here a revival of emission at low pH. As shown in Figure 4, fitting the luminescence intensity data with a two-species model gives $pK_a^* = 2.71$, which is identical to that of complex **1**, although the emission intensity amplification factor in going from pH 8.7 to pH 1.3 is almost 5-fold, 25% higher than that of complex **1**. This is one of the few examples of a dinuclear species with an increased luminescence at low pH values.

The spectra of acidic solutions of PCA and complexes **1** and **2** change slightly only after 1 day. Basic solutions remain unaltered for several days. Therefore, these systems seem promising as luminescent pH sensors, especially the dinuclear species **2**.

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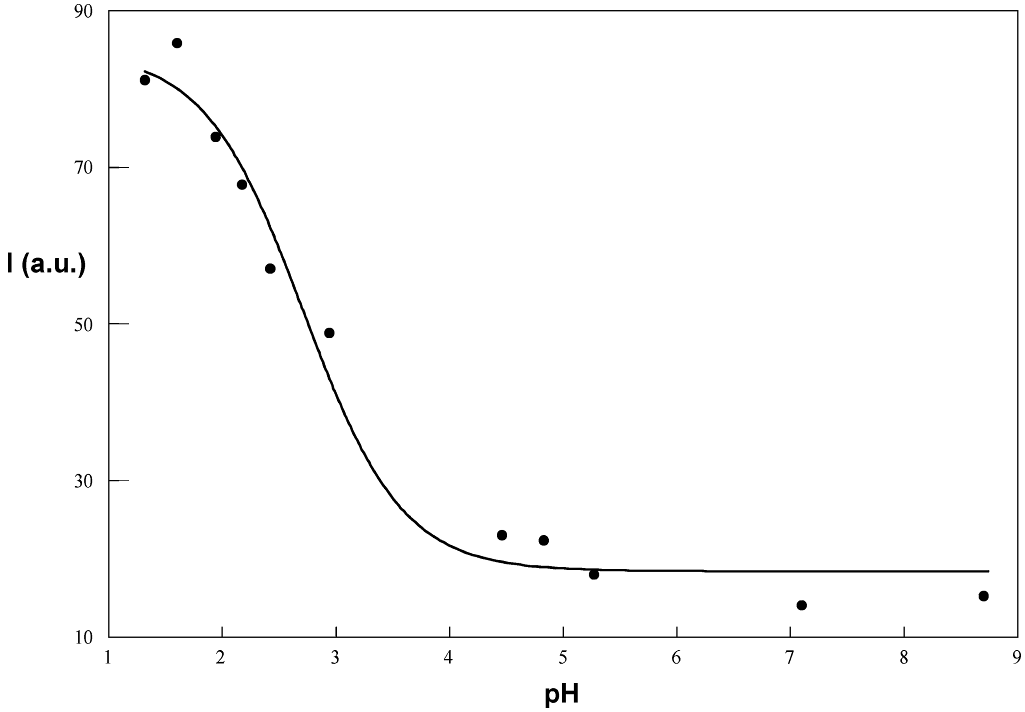

Figure 4. Variation of emission intensity with pH for $[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$ in aqueous buffers at $\lambda_{ex} = 350$ nm. The line indicates the best fit using a two-species model.

In the dinuclear asymmetric complex **3**, changes of the MLCT $d_\pi(Ru) \rightarrow \pi^*(PCA)$ band give additional information on the protonation of PCA. Fitting absorption changes with pH at $\lambda = 558$ nm with a two-species model gives two values of pK_{a1} (3.98 and −0.40) which can be attributed to successive protonations of the imine N atoms of PCA. These values are increased with respect to those obtained for complexes **1** and **2**, which can be attributed to a π-back-bonding effect from Ru^{II} to PCA.[7] Similar values of pK_{a1}* (3.20 and −0.18) are obtained when the emission intensity changes with pH of complex **3** are fitted with a two-species model. Unfortunately, rapid decomposition occurs (on a time scale of minutes) in these acidic solutions, so all these acidity constants may be in error. We have not characterized the decomposition products, but a possible pH-induced intramolecular electron transfer from PCA to Ru^{II} may be responsible for these irreversible changes, as already reported for 4,4′-azobispyridine-bridged complexes of ruthenium(II) ammines.[17] Complex **3** cannot therefore be used as a luminescent sensor. Nonetheless, in acetonitrile solutions, this complex is fairly stable, and its heterodinuclear derivative **4** can be used as a model for molecular photoconverters, as described in the last section (vide infra).

For the Me_2bpy derivatives **5** and **6**, the absorption and emission changes induced by protonation, and the corresponding values of pK_a and pK_a*, are very similar to those reported for **1** and **2**, although the luminescence intensity amplifications observed at low pH values are smaller by a factor of 2. Work is now going on in our laboratory to increase the luminescence intensity at low pH even more by using more electron accepting substituted bipyridines; thus, we hope that better luminescent sensors of pH can be designed.

Table 4. Electrochemical Data in CH_3CN, at 22°C[a]

complex	process	$E_{1/2}$ (V) (ΔE_p, mV)	E_{peak} (V)
$[Re(bpy)(CO)_3(PCA)]^+$ (**1**)	$Re^{2+/+}$	1.82 (176)	
	$PCA^{0/-}$		−0.98
	$bpy^{0/-}$	−1.21 (83)	
	$Re^{+/0}$		−1.46
$[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$ (**2**)	$Re^{2+/+}$		1.95
	$PCA^{0/-}$	−0.80 (59)	
	$bpy^{0/-}$	−1.16 (102)	
	$Re^{+/0}$		−1.36
$[(bpy)(CO)_3Re^I(PCA)Ru^{II}(NH_3)_5]^{3+}$ (**3**)	$Re^{2+/+}$	1.81 (161)	
	$Ru^{3+/2+}$	0.45 (127)	
	$PCA^{0/-}$		−0.88
	$bpy^{0/-}$		−1.23
	$Re^{+/0}$		−1.46

[a] All CV data were obtained at $v = 200$ mV/s.

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 $E_{1/2} \approx 1.8-2.0$ V, with some degree of irreversibility, as expected for rhenium(I) carbonyl diimine complexes.[7,12] The ligand PCA is reduced irreversibly at $E_{1/2} \approx -0.8-1.0$ V in all complexes, except in **2**. The first reduction of bpy appears at $E_{1/2} \approx -1.2$ V, while a second irreversible reduction at $E_{1/2} \approx -1.4$ V can be attributed to a $Re^{I/0}$ couple.[18] As reported before for the related Me_2bpy complex,[7] PCA is more electron accepting than bpy, due to the electronic delocalization induced by the

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−C═N−N═C− chain of this ligand. When protonated at pH ≅ 1, the corresponding wave of PCA is shifted negatively, as expected for a decrease in the driving force for the intraligand hopping process.

The voltammetric wave that appears in the asymmetric $Re^{I}-Ru^{II}$ dinuclear complex **3** at $E_{1/2} = 0.45$ V, absent in complexes **1** and **2** , can be readily assigned to the Ru^{III}/Ru^{II} couple, by comparison with similar complexes.[7] However, the high value of ΔE_p (=127 mV) points to a redox-induced ligand isomerization, similar to that already reported[7] for the dinuclear complex $[(NH_3)_5Ru(PCA)Ru(NH_3)_5]^{4+}$. The results obtained by spectroelectrochemistry are consistent with those obtained by bromine oxidation followed by Sn^{2+} reduction: when the oxidation process is reverted, the $d_\pi(Ru) \rightarrow \pi^*(PCA)$ MLCT band at $\lambda_{max} = 563$ nm is displaced to $\lambda_{max} = 536$ nm, and the intensity is diminished, as shown by Supporting Information Figure S1. Besides mere electron transfer, the formation of a *cis*-isomer is favored on oxidation. The difference between the redox potentials of both metallic couples in **3** is $\Delta E_{1/2} = E_{1/2}(Re^{II}/Re^{I}) - E_{1/2}(Ru^{III}/Ru^{II}) = 1.36$ V.

Intramolecular Electron Transfer. From the Marcus−Hush equations and the experimental data of the MMCT transition in the heterodinuclear complex **4**,[19] the reorganization energy λ for the intramolecular electron transfer through the PCA bridge can be calculated as $\lambda \cong 0.9$ eV, a value similar to that obtained before for the analogous complex with Me_2bpy.[7] Since $\lambda < -\Delta G°$ (=1.36 eV) for the reverse electron-transfer process $[Re^{II}, Ru^{II}] \rightarrow [Re^{I}, Ru^{III}]$, we predict that this back-reaction will fall in the Marcus inverted region.[20] The determined value of the donor−acceptor coupling element, $H_{AB} = 5.7 \times 10^2$ cm^{-1}, is consistent with what was discussed before on the enhancement of metal−metal interaction in mixed-valent symmetric and asymmetric dinuclear complexes of PCA.[7] This complex is then another example of a prototype for simulating primary charge separation in the inverted region.

Conclusions. Following our previous studies on the significant electronic communication between metal centers in homo- and heterodinuclear rhenium(I) tricarbonyls, brought about by the bridging ligand PCA,[7] we have now found that a decrease in pH induces luminescence in all of them, due to protonation of one of the N atoms of the −C═N−N═C− chain of PCA, as indicated by the obtained values of pK_a and pK_a^*, ca. 3 orders of magnitude lower than the pK_a value for the pyridine N of PCA in the mononuclear precursor complex $[Re(bpy)(CO)_3(PCA)]^+$. This latter species and the dinuclear symmetric complex $[(bpy)(CO)_3Re(PCA)Re(CO)_3(bpy)]^{2+}$ can be used as luminescent sensors of pH. On the other hand, light excitation, in CH_3CN, of the dinuclear asymmetric complex $[(bpy)(CO)_3Re^{I}(PCA)Ru^{III}(NH_3)_5]^{4+}$ provides another example of a charge recombination step that falls in the Marcus inverted region.

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Supporting Information Available: Spectroelectrochemistry of complex **3** in CH_3CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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