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Article

Improvement of the Dynamic Range of pH Sensing by Using a Luminescent Tricarbonylpolypyridylrhenium(I) Complex with Three Different Protonation Sites

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The complex [Re(4,4′-$(CO_2H)_2$-bpy)$(CO)_3$(4,4′-bpy)](CF_3SO_3), **1** (4,4′-$(CO_2H)_2$-bpy = 4,4′-dicarboxyl-2,2′-bipyridine, 4,4′-bpy = 4,4′-bipyridine), synthesized and characterized by spectroscopic techniques, displays a strong dependence of its photophysical properties on pH. From both emission intensity and lifetime measurements at different pH values, three values for the protonation constants of the excited states have been determined ($pK_{a1}^* = 1.8 \pm 0.1$, $pK_{a2}^* = 3.9 \pm 0.1$, and $pK_{a3}^* = 5.6 \pm 0.1$). The unusual bell-shaped variations of these photophysical properties can be accounted for by the changes of energy level orderings induced by each protonation, as confirmed by time-dependent density functional theory (TD-DFT) calculations. Since the solubility, stability, and dynamic range of pH sensing by **1** have been improved with respect to similar tricarbonylpolypyridylrhenium(I) complexes, we conclude that **1** can be used as an efficient molecular switch of the *on-off-on* type.

Introduction

Photophysical techniques applied to pH sensing have been considerably explored in the past decade because of their importance in medical and environmental issues.[1] It has long been recognized that luminescent transition metal complexes, especially those of Os(II), Ru(II), and Re(I) with polypyridyl ligands, have great potential as pH sensors, since their photophysical properties can be judiciously tuned by modifying the structure of the surrounding ligands.[1,2] We have recently described the pH dependence of the luminescence, in aqueous solutions, of a series of tricarbonylpolypyridylrhenium(I) complexes with the ligand PCA (= 4-pyridinecarboxaldehylde azine or 4-pyridinealdazine), which has two protonation sites.[3] The observed results allowed us to envision the application of some of these complexes as *on-off-on* switches, although the dynamic range of pH sensing was rather small (about 3 units), and coordinated PCA was shown to be unstable at low pH values.

As already noted before,[1]lifetime-based detection of physicochemical properties has more advantages with respect to intensity methods, since the need for repetitive calibration is reduced. Applications of pH sensing in Analytical Chemistry using fluorescent decay time have been described in the literature.[4] Dynamic range is simply defined, following Demas et al.,[1] as the ratio of the intensity or lifetime maximum/minimum values over the whole range of pH.

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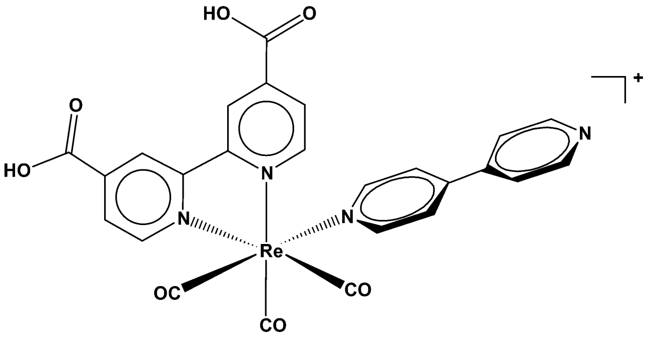
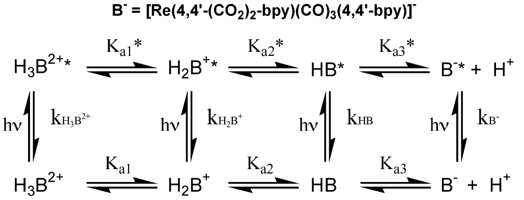
10.1021/ic802203d CCC: $40.75

Scheme 1. Structure of $[Re(4,4'-(CO_2H)_2-bpy)(CO)_3(4,4'-bpy)]^+$



Scheme 2. Protonation Equilibria for a Four-Species Model



To improve the stability and the dynamic range of this type of pH sensors, we have looked for a complex with three protonation sites that would not decompose in strongly acidic solutions. Therefore, we have chosen as a prototype the complex $[Re(4,4'-(CO_2H)_2-bpy)(CO)_3(4,4'-bpy)](CF_3SO_3)$ ($4,4'-(CO_2H)_2$-bpy = 4,4′-dicarboxyl-2,2′-bipyridine, 4,4′-bpy = 4,4′-bipyridine), **1** (Scheme 1), and in this Article we report the variation of its spectroscopic and photophysical properties in aqueous solutions as a function of pH. The present results are compared to those of the related complex $[Re(4,4'-(CO_2H)_2-bpy)(CO)_3(PCA)]^+$, **2**, and similar ones.[5] Finally, quantum mechanical calculations of the energy levels of **1** and related compounds have been carried out to rationalize their photophysical behavior.

Experimental Section

Materials and Techniques. All used chemicals were p.a. grade. UV/vis spectra were recorded with 1 cm quartz cells on a Varian Cary 50 spectrophotometer. Luminescent spectra were taken with 1 cm fluorescence cells on a Shimadzu RF-5301 PC spectrofluorometer. pH values were determined with an Altronix TPX-1 pH meter. The luminescence decay time of complex **1** was determined by using a homemade pulsed luminescence system that included a PTI 101 Monochromator (f/4, 1200 blazes) with a photomultiplier tube Hammamatsu R928 attached to the output slit. The signals were fed to a digital oscilloscope (Tektronix TSB3032, 300 MHz) and analyzed with the program Origin Microcal 7.0. Spectra of excited states were obtained with a Luzchem m-LFP system (Luzchem, Canada), using a Nd:Yag laser (Minilite II, Continuum, U.S.A.) as an excitation source at 355 nm (10 ns FMHW, 5 mJ/pulse). Chemical Analysis for C, H, N, and S were carried out at INQUIMAE, University of Buenos Aires, Argentina, with an estimated error of ± 0.5%.

Syntheses PCA. The ligand 4-pyridinealdazine was prepared as described before.[6]

$[Re(4,4'-(CO_2H)_2-bpy)(CO)_3(4,4'-bpy)](CF_3SO_3)$, 1. A 181 mg quantity (0.50 mmol) of $[Re(CO)_5Cl]$ and 122 mg (0.50 mmol) of 4,4′-dihydroxycarbonyl-2,2′-bipyridine were heated at reflux for 1 h in 20 mL of toluene. When adding 20 mL of hexane, a red solid precipitated, which was cooled, washed with toluene and diethyl ether, and dried in vacuum. The resulting compound $[Re(4,4'-(CO_2H)_2-bpy)(CO)_3Cl]$ (241 mg, 0.438 mmol) and $Ag(CF_3SO_3)$ (113 mg, 0.438 mmol) were heated at reflux for 30 min in 40 mL of THF. The formed AgCl was filtered, and the filtrate was rotoevaporated to a minimum volume and precipitated with hexane. The ligand 4,4′-bpy (684 mg, 4.38 mmol) was then added, and the mixture was heated at reflux for 2 h in 40 mL of THF. The solvent was removed on a rotavap to give a reddish yellow oil, which was dissolved in acetone and precipitated with ether. The obtained solid was filtered, washed, and dried under vacuum. Yield, 292 mg (71%). Chem. Anal. Found: C, 38.3; H, 2.1; N, 6.9; S, 4.2. Calcd for $C_{26}H_{16}N_4O_{10}F_3ReS$: C, 38.1; H, 2.0; N, 6.8; S, 3.9. IR (KBr, cm^{-1}): 3438 (m), 3096 (w), 2927 (w), 2034 (s), 1920 (s), 1640 (m), 1619 (m), 1492 (w), 1408 (w), 1368 (w), 1277 (m), 1259 (m), 1230 (w), 1165 (w), 1069 (w), 1031 (m), 812 (w), 775 (w), 639 (m), 574 (w), 520 (w).

$[Re(4,4'-(CO_2H)_2-bpy)(CO)_3(PCA)](CF_3SO_3).2H_2O.(CH_3)_2CO$, 2. The precursor complex $[Re(4,4'-(CO_2H)_2-bpy)(CO)_3(CF_3SO_3)]$ (0.438 mmol), obtained from the first preparation, was heated at reflux for 2 h with excess of the ligand PCA (919 mg, 4.38 mmol) in 40 mL of THF. The solution was filtered and then the solvent was removed on a rotavap to give a reddish yellow oil. The oil was dissolved in acetone and precipitated with toluene. It was recrystallized with acetone and ether, filtered, washed, and dried under vacuum. Yield, 217 mg (50%). Chem. Anal. Found: C, 38.4; H, 3.2; N, 9.0. Calcd for $C_{31}H_{28}N_6O_{13}F_3ReS$: C, 38.5; H, 2.9; N, 8.7. IR (KBr, cm^{-1}): 3254 (w), 3085 (w), 2995 (w), 2025 (s), 1918 (s), 1637 (m), 1619 (m), 1560 (w), 1500 (w), 1407 (w), 1350 (w), 1280 (m), 1259 (m), 1237 (w), 1162 (w), 1061 (w), 1030 (m), 829 (w), 778 (w), 706 (w), 669 (w), 638 (m), 518 (w).

Protonation Equilibria. Titration measurements were carried out by following absorption and emission changes with pH for determining values of pK_a and pK_a*, respectively. Only one solution (approximately 30 mL) was used, with Britton and Robinson's buffer, which consists 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 with the buffer solution. Three M HCl (40−60 μL) was added in small aliquots to lower the pH up to a lowest limit of 1.5. In each titration, 25−35 points were recorded.

For fitting the experimental data corresponding to complex **1**, we consider three sites of protonation: one at the free pyridinic N of coordinated 4,4′-bpy and the other two at the carboxylate groups of coordinated $4,4'-(CO_2)_2-bpy^{2-}$, as shown in Scheme 2.

In this scheme, B^- is the nonprotonated species derived from **1**; in the fast exchange limit, we assume that the excited-state equilibria among B^-*, $HB*$, H_2B^+*, and $H_3B^{2+}*$ are maintained. This hypothesis allows for simple expressions for the observed intensity and lifetime variations as a function of each species present in solution, similar to those already reported,[1] but extended to a four-species model. In this case, we define the f variables as the fractions of excited species present, the k variables as the decay rate constants for the species, and I^{max} as the emission intensity when only that species is present. When introducing the equilibrium equations derived from Scheme 2 into these expressions, adequate fitting equations can be obtained, such as those

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already stated,[1] but extended to two additional species. The same procedure can be applied to absorbance changes with pH. Values of A^{max} and I^{max}, the absorbance and emission intensity respectively, corresponding to only one species, have been obtained from the appropriate data at the limits of the used pH range or as floating parameters. The experimental data were satisfactorily fitted by using a PSI Plot software.

Computational Procedures. Calculations were obtained using Gaussian '98.[7] The molecules were optimized using Becke's tree-parameter hybrid functional B3LYP,[8] with the local term of Lee, Yang, and Parr.[9] The basis set LanL2DZ was chosen for all atoms, and the geometry optimizations were performed in the gas phase. Non-equilibrium time dependent-density functional theory (TD-DFT)/conducting polarizable continuous model (CPCM) calculations were employed to produce a number of 40 singlet excited states in water, based on the optimized geometry in the gas phase. In the simulated absorption spectra, lowest energy bands consist of overlapping metal-to-ligand charge transfer (MLCT) transitions from d_π orbitals of Re to π^* orbitals of both polypyridyl ligands and the contribution of each ligand to the lowest unocupied molecular orbital (LUMO) follows the ordering of energy levels. To obtain the optimized structures of the intermediates species $[Re(4\text{-}(CO_2H)\text{-}4'\text{-}(CO_2)\text{-}bpy)(CO)_3(4,4'\text{-}bpyH)]^+$ and $[Re(4,4'\text{-}(CO_2)_2\text{-}bpy)(CO)_3(4,4'\text{-}bpyH)]$, we used optimizations done in $[Re(4\text{-}(CO_2H)\text{-}4'\text{-}(CO_2)\text{-}bpy)(CO)_3(4,4'\text{-}bpy)]$ and $[Re(4,4'\text{-}(CO_2)_2\text{-}bpy)(CO)_3(4,4'\text{-}bpy)]^-$ by adding a proton, respectively, at the free pyridine N of coordinated 4,4′-bpy.

Results and Discussion

The synthetic methods used to obtain the mononuclear rhenium tricarbonyls addressed in this work are similar to those previously reported,[3] and are described in the Experimental Section. Complex **1** is highly soluble in water, an important property in relation to its applications in radiopharmacy.[10] It is also very stable in both acid and basic aqueous solutions. Slow substitution of coordinated 4,4′-bpy by OH^- occurs at pH > 10 after a period of 4 days. Titration measurements for determining the pK_a of coordinated OH^- in $[Re(4,4'\text{-}(CO_2H)_2\text{-}bpy)(CO)_3(OH)]$ gave $pK_a = 8.6 \pm 0.1$, a value similar to those measured for the corresponding hydroxo- complexes derived from the precursor species $[Re(bpy)(CO)_3(CF_3SO_3)]$ and $[Re(4,4'\text{-}(CO_2H)_2\text{-}bpy)(CO)_3(CF_3SO_3)]$. Supporting Information, Figure 1 shows the variation of the electronic spectrum with pH of the aquo-species $[Re(bpy)(CO)_3(H_2O)]^+$, obtained by dissolving the former triflate species in an aqueous buffer at low pH. It is possible to obtain similar values of pK_a's from the precursor complexes $[Re(bpy)(CO)_3(Cl)]$ and $[Re(4,4'\text{-}(CO_2H)_2\text{-}bpy)(CO)_3(Cl)]$, although the absorbance changes were much smaller in both cases, as expected when considering the higher lability of coordinated $CF_3SO_3^-$ as compared to that of coordinated Cl^-.

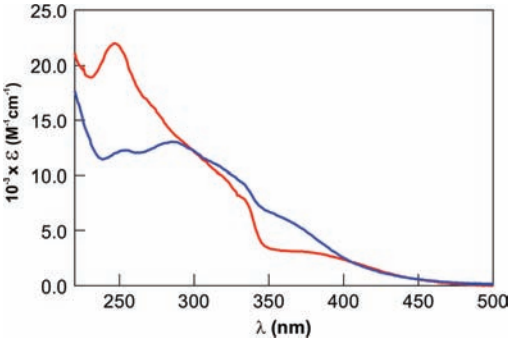

Figure 1. UV−vis spectra of $[Re(4,4'\text{-}(CO_2H)_2\text{-}bpy)(CO)_3(PCA)]^+$ (blue line) and $[Re(4,4'\text{-}(CO_2H)_2\text{-}bpy)(CO)_3(4,4'\text{-}bpy)]^+$ (red line) in CH_3CN at room temperature.

The absorption and luminescence properties of **1** and **2** are similar to those of other tricarbonylpolypyridyl-rhenium(I) complexes with PCA[3,6] and 4,4′-bpy.[5,11a–c] As shown in Figure 1, typical $\pi \rightarrow \pi^*$ intraligand transitions of 4,4′-$(CO_2H)_2$-bpy, 4,4′-bpy, and PCA give rise to intense UV absorptions between 200 and 330 nm. The broad bands at $\lambda_{max} \cong 350-370$ nm can be assigned, as observed before in analogous complexes of the type $[Re(X_2bpy)(CO)_3(L)]^+$,[11a–c,12] to overlapping MLCT transitions: $d_\pi(Re) \rightarrow \pi^*(X_2bpy)$ and $d_\pi(Re) \rightarrow \pi^*(L)$, with X = CO_2H and L = 4,4′-bpy or PCA.

Both complexes **1** and **2** present emission spectra in deareated CH_3CN which are typical of $Re^{II}(diimine^-)$ MLCT excited states (λ_{em} = 572 and 568 nm, respectively). Although their lifetimes are similar (τ = 183 and 189 ns, respectively), the quantum yields differ by an order of magnitude (ϕ = 0.011 and 0.0018, respectively). This difference was previously accounted for by the presence of additional radiationless deactivation pathways in PCA complexes because of intraligand n-π^* and/or π-π^* excited states lying close to the emitting ^{3}MLCT excited states.[3b]

The values for the protonation constants of the corresponding ground states can be determined by measuring the absorption changes with pH. By using the four-species model shown in Scheme 2, the values of pK_{a2} and pK_{a3} are equal within experimental error. Therefore, we have recalculated the fitting of absorbance data versus pH with a three-species model, assuming that $pK_{a2} = pK_{a3}$, as shown in Figure 2. The obtained values are $pK_{a1} = 1.7 \pm 0.1$, $pK_{a2} = pK_{a3} = 4.1 \pm 0.1$.

Figure 3 shows the variation of quantum yields versus pH for complex **1** and its fitting by using the four-species model

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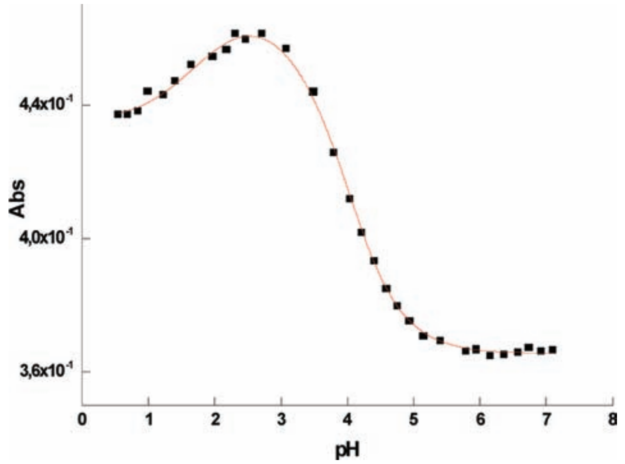

Figure 2. Variation of absorbance with pH for [Re(4,4′-$(CO_2H)_2$-bpy)$(CO)_3$(4,4′-bpy)]$^+$ ($C \cong 8 \times 10^{-5}$ M) in aqueous buffers at $\lambda = 353$ nm. The red line indicates the best fit using a three-species model.

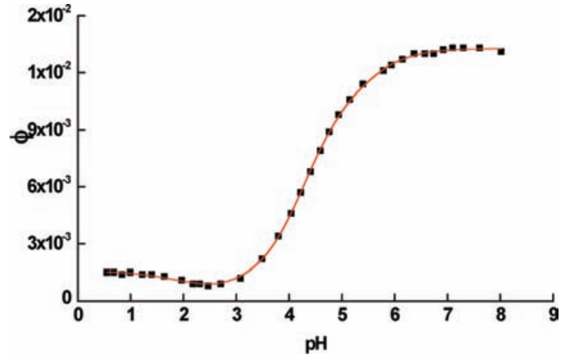

Figure 3. Variation of quantum yields with pH for [Re(4,4′-$(CO_2H)_2$-bpy)$(CO)_3$(4,4′-bpy)]$^+$ in aqueous buffers at $\lambda_{em} = 572$ nm ($\lambda_{exc} = 380$ nm). The red line indicates the best fit using a four-species model. The ϕ values were calculated using $[Ru(bpy)_3]^{2+}$as actinometer ($\phi = 0.062$ in CH_3CN).

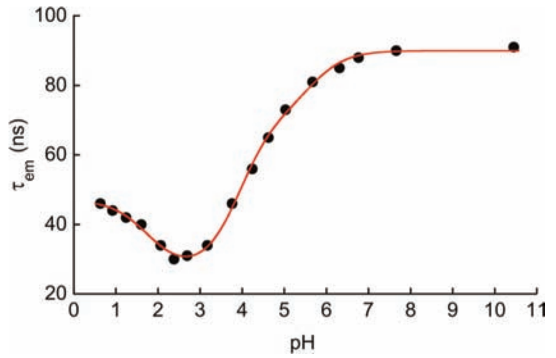

Figure 4. Variation of emission lifetime with pH for [Re(4,4′-$(CO_2H)_2$-bpy)$(CO)_3$(4,4′-bpy)]$^+$ in aqueous buffers ($\lambda_{exc} = 355$ nm; $\lambda_{em} = 575$ nm) at room temperature in air. The red line indicates the best fit using a four-species model.

(Scheme 2). Three values of pK_a* are obtained: pK_{a1}* = 1.9 ± 0.1, pK_{a2}* = 4.2 ± 0.1, and pK_{a3}* = 5.5 ± 0.1. The acidity constants can thus be better discriminated with emission measurements.

Figure 4 shows the variation with pH for the emission lifetime of complex **1** in aqueous solutions. By fitting this pH dependence again with a four-species model (Scheme 2), three values of pK_a* are obtained: pK_{a1}* = 1.8 ± 0.1, pK_{a2}* = 3.9 ± 0.1, and pK_{a3}* = 5.6 ± 0.1, which are identical, within experimental error, to those stated in the preceding paragraph, obtained from luminescence data. As expected,[1] the dynamic range of the intensity measurements was greater than the corresponding lifetime changes.

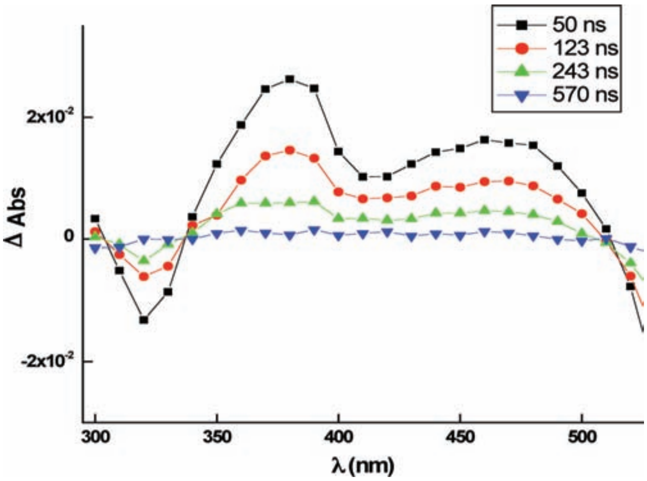

Figure 5. Transient spectra of [Re(4,4′-$(CO_2H)_2$-bpy)$(CO)_3$(4,4′-bpy)]$^+$, in CH_3CN solution at 22 °C.

Pyridine nitrogens are expected to be more basic than carboxylate groups; for example, in the complex [Ru$(bpy)_2$-(4,4′-$(CO_2H)_2$-bpy)]$^{2+}$, the values of the protonation constants for the carboxylate groups are pK_a = 2.85 and 1.75,[13] while the protonation constant of the pyridine N of 4,4′-bpy in [Ru(trpy)(bpy)(4,4′-bpy)]$^{2+}$ (trpy = 2,2′:6′,2′′-terpyridine) is pK_a = 4.3.[11d] Therefore, we assign the constants pK_{a1}* and pK_{a2}* to the carboxylate groups of substituted bpy and pK_{a3}* to the pyridine N of 4,4′-bpy.

In **2**, the absence of isosbestic points prove the existence of additional protonated species and the onset of some decomposition of PCA.[3] However, the protonation constants of the pyridinic N of coordinated PCA could be estimated as follows: pK_{a3} = 5.5 ± 0.1 and pK_{a3}* = 4.6 ± 0.1.

Both the protonation of 4,4′-bpy and the more basic carboxylate group of 4,4′-(CO_2)-bpy^{2-} quench the luminescence of **1** because of changes in the energy ordering of the excited states. The last protonation of the second carboxylate group of bpy produces a slight revival of its luminescence, since the lowest π^* excited-state of 4,4′-(CO_2H)-bpy becomes lower than that of 4,4′-bpyH$^+$.

Laser flash photolysis experiments of **1** and **2** showed the characteristic bands for the [Re^{II}(4,4′-$(CO_2H)_2$-bpy$^-$)$(CO)_3$-(L)]$^{+*}$ charge-separated states (L = 4,4′-bpy or PCA) at λ_{exc} = 355 nm in CH_3CN. Figure 5 shows the transient spectra for the case of L = 4,4′-bpy. The transient spectra for the case of L = PCA are very similar. On the other hand, the same transient spectra obtained at pH = 10.4, 2.33, and 0.65 indicate the formation of the same charge-separated species described above.

The unusual bell-shaped curves of Figures 3 and 4 can be interpreted by the changing of the ordering in energy levels induced by each protonation, as confirmed below by TD-DFT calculations. The dynamic range in emission quantum

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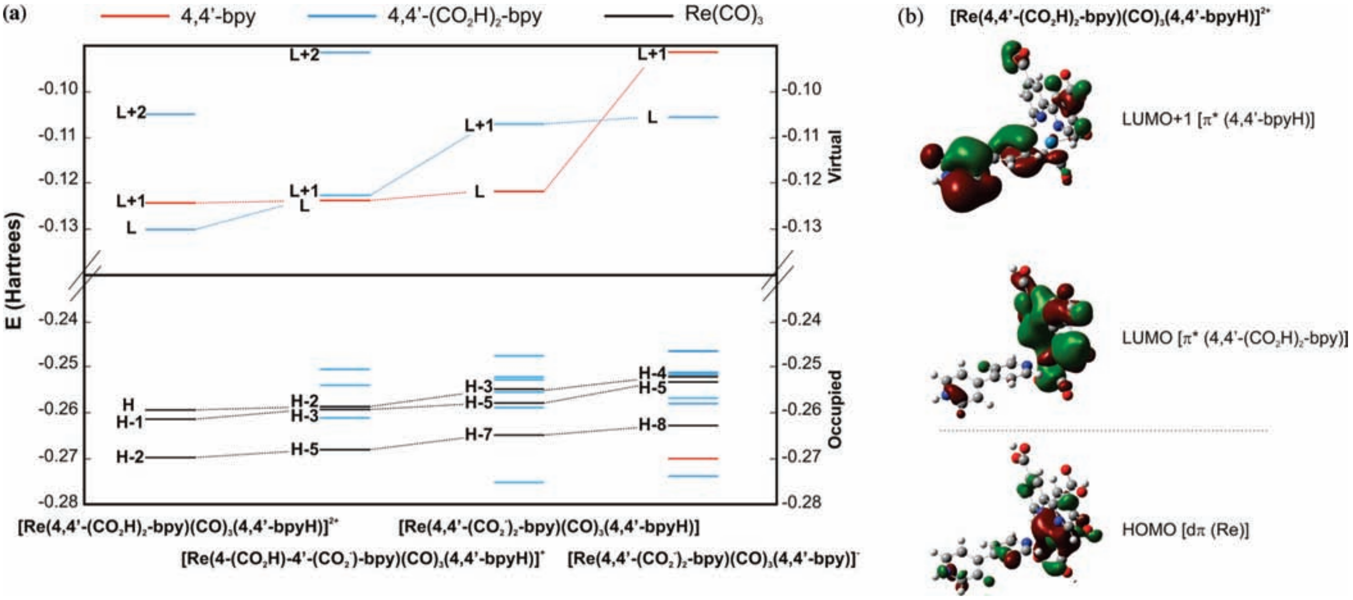

Figure 6. (a) KS molecular orbital ordering of $[Re(4,4'-(CO_2)_2-(bpy)(CO)_3(4,4'-bpy)]^-$ and its different protonated forms, calculated with a TD-DFT/B3LYP/CPCM method. (b) Forms and approximate descriptions of the frontier orbitals for the fully protonated form.

yields and lifetimes is near 13 and 5, respectively, making complex **1** a promising luminescent pH sensor of the *on-off-on* type over a 0−8 pH range. The presence of three protonation sites has thus considerably improved the dynamic range of pH sensing compared to previously reported rhenium and ruthenium complexes.[1,14]

To support the previous reasoning, we resorted to TD-DFT/CPCM calculations of **1** and its acid−base derivatives, with water as a solvent. The computational details are given in the Experimental Section. It is now a common practice to use these methods to calculate molecular orbital energies and electronic properties of both ground and excited states.[15] We have recently demonstrated that PCA has an unoccupied π^* orbital near the lowest energy unoccupied π^* orbital of bpy; this fact is the origin of additional radiationless pathways in PCA complexes.[16] In contrast, complexes with 4,4′-bpy have high emissive quantum yields because their unoccupied π^* orbitals are higher in energy than those of bpy.[16]

Figure 6a shows the orbital ordering determined for the protonated species derived from $[Re(4,4'-(CO_2)_2-bpy)-(CO)_3(4,4'-bpy)]^-$. Figure 6b shows the forms and approximate descriptions of the frontier orbitals for the fully protonated form $[Re(4,4'-(CO_2H)_2-(bpy)(CO)_3(4,4'-bpyH)]^{2+}$, which are similar to those of the other species. The colored lines relate equivalent orbitals for each ligand. The two LUMOs are mostly π^* orbitals of 4,4′-bpy (red) and $4,4'-(CO_2)_2-bpy^{2-}$ (blue). In the totally deprotonated complex (pH > 5), the π^* orbital of 4,4′-bpy is higher in energy than that of $4,4'-(CO_2)_2-bpy^{2-}$, resulting in luminescence with the highest quantum yield. After protonation at the pyridinic N of 4,4′-bpy, the π^* level of $4,4'-bpyH^+$ becomes lower in energy than that of $4,4'-(CO_2)_2-bpy^{2-}$, leading to quenching of emission from the excited ^{3}MLCT state. The following protonation, assigned to one of the two carboxylate groups of $4,4'-(CO_2)_2-bpy^{2-}$, lowers the energy of the π^* level of the substituted bpy, but its value is still higher than that of $4,4'-bpyH^+$. However, when the second carboxylate group of bpy is protonated, the ordering of both π^* levels is inverted, and consequently the complex recovers some of the original luminescence. Although the electronic transitions normally involve combinations of different frontier orbitals, our calculations disclose that the lowest allowed transitions can be assigned to Re → bpy MLCTs, with electronic density largely localized in HOMOs corresponding to d_π(Re) orbitals and LUMOs corresponding to π^* (4,4′-bpy) and $\pi^*(4,4'-CO_2H)_2$-bpy) orbitals, even when considering that emission occurs from triplet excited states. These assignments follow previous TD-DFT studies in similar tricarbonylpolypyridylrhenium(I) complexes.[15d] Our computational results thus agree very well with the photophysical properties discussed above and summarized in Figures 3 and 4.

Conclusions

We conclude that the dynamic range of pH sensing can be dramatically improved if we change the energy ordering of emissive and non-emissive excited states in tricarbonylpolypyridylrhenium(I) complexes by using a species with three potential protonation sites, such as complex **1**. This compound is also very soluble and quite stable in aqueous solutions; it can be used as an efficient *on-off-on* switch in molecular devices.

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Supporting Information Available: Variation of absorbance with pH for $[Re(bpy)(CO)_3(H_2O)]^+$ in aqueous buffered solutions (Suppl. Figure 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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