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Luminescent Transition Metal Complexes as Sensors: Structural Effects on pH Response

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A series of luminescent transition metal complexes using the pH-sensitive ligand 5-carboxy-1,10-phenanthroline has been synthesized and characterized. The complexes, based on Ru(II) and Re(I), show monotonic changes in both luminescent intensity and lifetime with pH values over the range 2 < pH < 9. The impact of various structural features on both the range of pH sensitivity and dynamic response was studied using both intensity and lifetime measurements. It was possible to predictably tune the pH sensitivity range over about 1.5 pK_a units. While significant variation in the dynamic response range was observed, the correlation with structural features needs further study.

Introduction

The use of luminescent transition metal complexes as sensors continues to attract considerable interest.[1,2] In addition to the signal-to-noise advantages inherent in all luminescent measurements, transition metal complexes have some photophysical properties that make them especially attractive as sensors. These include significant Stokes shifts for easy separation of excitation and emission, emission color shifts with changes in the local environment, and relatively long lifetimes compared to their purely organic counterparts.[3] This latter attribute allows considerable simplification in the detection schemes used for lifetime-based monitoring. It is becoming clear that lifetime-based detection has significant advantages vis-à-vis intensity methods in that the lifetime methods are relatively insensitive to source variation, photobleaching of the probe material, and changes in the efficiency of the optical system. This insensitivity greatly reduces the need for repetitive calibration, a real problem for remote sensing applications.[4]

Luminescent transition metal complexes have been explored as possible sensors for oxygen concentration,[5] pH,[6] chloride[7] and CO_2 concentration,[8] and temperature.[9] The measurement of pH is important for areas ranging from cardiac critical care to acid rain pollution of streams. Because of its central importance, pH measurement via luminescent sensors has been an area of considerable study. A number of intensity-based systems using primarily organic dyes with pH-sensitive functionality have been suggested.[10] Rather fewer systems employing metal complexes have been reported. A variety of metal ions have been used in both single and multicomponent systems.[11]

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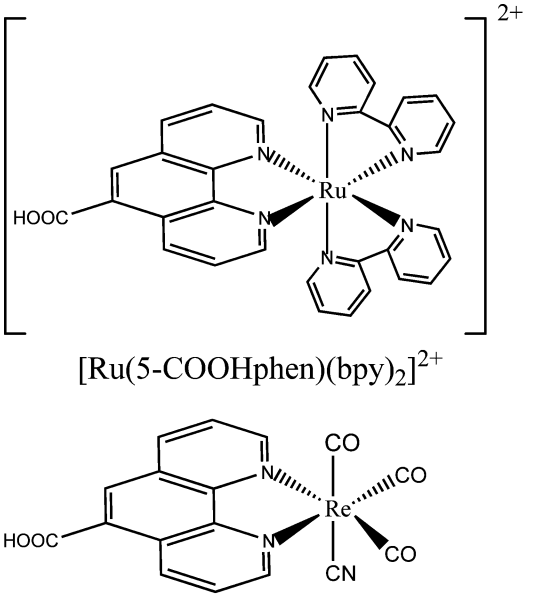
The general approach for the design of pH-sensitive luminescent metal complexes is to modify a core ligand for pH sensitivity. Typically, either a 2,2-bipyridine or 1,10-phenanthroline structure is used and an alcohol, acid, or amine function attached to provide the pH-sensitive element. Complexes based on the platinum metal ions Ru^{2+}, Os^{2+}, and Re^{+} are among the most commonly used. Complexes with these metals are normally luminescent, photochemically robust, exhibit either near UV or visible absorption, and can be "tuned" by a variety of synthetic methods.[2]

Despite the interest in and potential of pH measurement via luminescent metal complexes, there seems to be little exploration of how one can structurally manipulate the response to tune the pH response range or the dynamic range available. Further, there is a need to assess the similarities and differences in the intensity and lifetime dynamic response for these probes. This paper addresses some of these issues through the synthesis and evaluation of a series of complexes based on a simple pH sensitive ligand, 5-carboxy-1,10-phenanthroline. Various Re(I) and Ru(II) complexes were prepared with the intent of exploring the range over which both the pH response and the dynamic response could be tuned. In addition, both intensity and lifetime data are reported so that the correlation between the two detection approaches could be evaluated.

Experimental Section

Except as noted, all chemicals were obtained from Sigma-Aldrich and used without further purification. The $Ru(III)Cl_3{\cdot}xH_2O$ was obtained from Johnson Matthey Co. *cis*-$Ru(2,2'\text{-bipyridine})_2Cl_2{\cdot}2H_2O$ was purchased from Strem Chemical Co. The ligands 5-chloro-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline were purchased from GFS Chemicals. The solvents used were obtained from Fisher Chemical and were HPLC grade or better. Ligand abbreviations used in this report are (1) 2,2′-bipyridine = bpy, (2) 1,10-phenanthroline = phen, (3) 3,4,7,8-tetramethyl-1,10-phenanthroline = Me_4phen, (4) 5-carboxy-1,10-phenanthroline = 5-COOHphen, and (5) pyridine = pyr.

All the complexes were prepared by adapting well-known literature preparations.[12,13] Figure 1 shows representative complexes. Structures were verified by ^{13}C NMR, IR, and UV−vis spectra. Assignments for ^{13}C NMR spectra were facilitated by model complex spectra using 5-chloro-1,10-phenanthroline as the proxy for the 5-carboxy-1,10-phenanthroline. The model complexes were synthesized using unambiguous routes. For complexes with multiple isomers and broken symmetry, an unambiguous ^{13}C NMR assignment could not be made. Authentication for these materials was via elemental analysis supplemented with other spectral data. All complexes were purified by column chromatography and gave materials for which Thin-layer chromatography (TLC) showed only one spot with two different solvent systems. Emission purity was established by lifetime measurements, that is, a single lifetime in CH_3OH, and an acceptable excitation spectra ratio,[14] which was flat to within 3%.



$[Ru(5\text{-COOHphen})(bpy)_2]^{2+}$

$Re(5\text{-COOHphen})(CO)_3CN$

Figure 1. Structures of $[Ru(5\text{-COOHphen})(bpy)_2]^{2+}$ and $Re(5\text{-COOHphen})(CO)_3CN$.

NMR spectra were obtained using a Bruker ERX 400 MHz instrument. UV−visible spectra were obtained with a Hewlett-Packard 8452A diode array spectrometer. Corrected emission spectra were obtained using a Spex FluoroMax instrument, while IR spectra were recorded on a Midac FT-IR instrument. Lifetime measurements were made using a locally constructed apparatus utilizing an LSI−VSL nitrogen laser (3 ns pulse width) as the excitation source. The decay curves were analyzed using a Marquardt-based nonlinear least-squares fitting routine. Quantum yields were based on the accepted value of 0.042 for $Ru(bpy)_3Cl_2$ in degassed water,[15] and the appropriate refractive index corrections were applied.

Preparation of 5-Carboxy-1,10-phenanthroline. Though this ligand has a Chemical Abstracts registry number (630067-06-0) and is available in small quantities from AKos Consulting and Solutions, GmbH, to our knowledge, its synthesis has not been reported in the open literature. The pH-sensitive ligand, 5-carboxy-1,10-phenanthroline was prepared using an extension of the work of Kishnan[16] and Sullivan.[17] The 5,6-epoxy-1,10-phenanthroline was prepared by treatment of 1,10-phenanthroline with chlorine bleach

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under slightly basic conditions (pH ∼ 8.5). The epoxide was then converted to the 5-cyano-1,10-phenanthroline by stirring at room temperature with excess KCN in water. Suitable H NMR and C NMR spectra along with a gas liquid chromatography analysis confirmed the desired products and their purities. The 5-cyano-1,10-phenanthroline product was smoothly hydrolyzed in 6 M NaOH by overnight reflux. The cooled reaction mixture was extracted several times with CH_2Cl_2 to remove residual starting materials. Precipitation of the acid followed adjustment of the reaction mixture to a pH of ∼5 with 6 M HCl. The acid was recrystallized from methanol. Typical overall yields were 40% based on starting 1,10-phenanthroline. The major loss occurs in the initial epoxidation step. ^{13}C NMR (CD_3OD/ppm): 124.4_5, 124.9_6, 127.3_3, 128.2_6, 129.4_0, 137.4_1, 137.5_8, 138.5_8, 146.6_8, 146.8_3, 150.7_2, 151.5_2, 174.5_2. IR: (COOH) 1718 cm^{-1}. Anal. (as CH_3 ester) Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.32; N, 11.76. Found: C, 70.07; H, 4.19; N, 11.68 [Midwest Microlab]. Mp (ester) 149−150 °C; mp (acid) 335−337 °C (decomp).

Preparation of [Ru(bpy)$_2$(5-COOHphen)](ClO$_4$)$_2$ (1). 0.100 g of Ru(bpy)$_2$Cl$_2$·2H$_2$O (2.78×10^{-4} mol), 0.125 g of 5-COOHphen (5.56×10^{-4} mol), and 5 mL each of H_2O and C_2H_5OH were refluxed until TLC [alumina, CH_3CN/CH_2Cl_2 (1:1)] showed that all the cis starting material had reacted (usually about 4−6 h). The solvent volume was reduced to ∼2 mL, and then, the bright orange solution was dripped into a stirred saturated $NaClO_4$ solution. The product precipitate was collected via suction filtration and washed with cold water. After drying, the product was further purified by column chromatography using neutral alumina with acetone, acetone/methanol, methanol, and methanol/water as the successive eluants. The desired, bright orange luminescent complex was the last material to elute. ^{13}C NMR (CD_3OD/ppm): [bpy] 125.6_1, 125.6_7, 128.8_9, 128.9_7, 139.2_3, 139.3_5, 152.8_5, 152.9_0, 158.7_4, 158.7_8, 167.9_3; [5-COOHphen] 127.6_8, 127.9_2, 129.9_5, 130.9_7, 134.2_6, 137.4_3, 149.3_3, 150.3_4, 152.9_7, 153.6_4, 155.2_3, 158.5_3; (COOH) 167.9_3. IR: (carboxyl) 1702 cm^{-1}. UV−vis λ_{max} (CH_3OH): 452 nm. Anal. (as CH_3 ester) Calcd for $RuC_{34}H_{26}N_6O_{10}Cl_2$: C, 47.97; H, 3.06; N, 9.88. Found: C, 47.42; H, 2.98; N, 10.01 [Midwest Microlab]. *[WARNING!: perchlorates are potentially explosive and require care. Do not heat to dryness, and use small amounts.]*

Preparation of [Ru(Me$_4$phen)$_2$(5-COOHphen)](ClO$_4$)$_2$ (2). *cis*-Ru(Me$_4$phen)$_2$Cl$_2$ was prepared from RuCl$_3$·*x*H$_2$O and a stoichiometric amount of the ligand by refluxing the materials in dimethyl formamide (DMF) with excess LiCl for 4.5 h in accordance with literature guidelines.[13] The DMF was stripped, and the deep purple complex was washed repeatedly with cold water and dried to give an amorphous solid. UV−vis and ^1H NMR spectra were consistent with the desired product. Then, 0.100 g of Ru(Me$_4$phen)$_2$Cl$_2$ (1.55×10^{-4} mol) and 0.104 g of 5-COOHphen (4.65×10^{-4} mol) in 12 mL of 95% ethanol and 4 mL of water were refluxed for 6.5 h. TLC [alumina plates, CH_3CN/CH_2Cl_2 (1:1)] showed complete reaction of the Ru(Me$_4$phen)$_2$Cl$_2$. The solvent was stripped, and the resulting solid redissolved in a minimum quantity of hot water. This solution was slowly dripped into saturated $NaClO_4$ with vigorous stirring. The orange precipitate was collected by suction filtration. This product showed three TLC spots and the desired product obtained by column chromatography with neutral alumina as the support. The initial eluant was CH_3CN with increasing amounts of CH_3OH. The desired product was the middle fraction and was the most copious. The yield was ∼50% based on the Ru(Me$_4$phen)Cl$_2$. ^{13}C NMR (CD_3OD/ppm): [Me$_4$phen] (CH_3)15.0_8, (CH_3)17.8_7, 126.1_2, 126.1_6, 126.5_5, 126.5_9, 130.5_7, 130.5_9, 130.6_0, 130.6_4, 135.7_3, 135.7_7, 135.8_5, 135.8_8, 145.5_4, 145.5_9, 145.5_7, 145.6_0, 147.6_8, 147.7_1, 147.7_6, 147.8_1, 153.3_4, 153.7_4, 153.8_1, 153.9_3; [5-COOHphen] 125.2_0, 125.2_5, 129.8_2, 131.3_9, 131.7_5, 137.5_7, 138.4_1, 139.6_7, 149.6_9, 149.7_2, 152.6_9, 154.0_3; (COOH) 171.7_2. IR: (carboxyl) 1687 cm^{-1}. UV−vis λ_{max} (CH_3OH): ∼425 nm. Anal. (as CH_3 ester) Calcd for $RuC_{46}H_{42}N_6O_{10}Cl_2$: C, 54.61; H, 4.15; N, 8.31. Found: C, 54.25; H, 4.22; N, 8.25 [Midwest Microlab].

Preparation of [Ru(5-COOHphen)$_3$](ClO)$_2$ (3). 0.100 g of RuCl$_3$·*x*H$_2$O (4.13×10^{-4} mol), 0.463 g of 5-COOHphen (2.06×10^{-3} mol, 66% excess), and 15 mL of ethanol−water solvent (3:1) were refluxed for about 6 h, at which time, TLC (alumina plates, CH_3OH/H_2O, 80:20%) showed only a single luminescent complex. The solvent was stripped and the desired complex obtained by first triturating the solid mixture with CH_3OH, in which the complex is readily soluble. This solution, after concentration, was dripped into saturated $NaClO_4$. The collected precipitate was then passed through a neutral alumina column using CH_3OH with increasing amounts of H_2O to elute the tris complex. The desired complex was the last material to elute. ^{13}C NMR (CD_3OD/ppm): 126.8_3, 127.2_5, (128.2_9, 128.3_1, 128.3_4, 128.3_6), (131.0_0, 131.0_1, 131.0_3), (131.7_6, 131.7_7, 131.7_8), 138.1_3, (138.4_2, 138.4_4), (140.3_8, 140.4_1), (149.3_1, 149.3_4), (149.4_3, 149.4_6), (153.3_5, 153.3_9), (153.6_8, 153.7_2); (COOH) 172.8_3. The complex forms two equally weighted geometric isomers. IR: (carboxyl) 1624 cm^{-1}. UV−vis λ_{max}(CH_3OH): 446 nm. Anal. (as CH_3 ester) Calcd for $RuC_{42}H_{30}N_6O_{14}Cl_2$: C, 49.70; H, 2.96; N, 8.28. Found: C, 49.25; H, 3.02; N, 8.35 [Midwest Microlab].

Preparation of Ru(5-COOHphen)$_2$(CN)$_2$ (4). 0.068 g of RuCl$_3$·*x*H$_2$O (2.90×10^{-4} mol), 0.130 g of 5-COOHphen (5.80×10^{-4} mol), and 5 mL of N,N-dimethylformamide were stirred at reflux for 4.75 h. TLC [silica gel plates, acetone/water eluant (60:40)] showed conversion of virtually all the starting material. The solvent was stripped and a slurry of the product prepared by adding a small amount of water. The solid was isolated by suction filtration and washed with small amounts of water and acetone. TLC (silica gel plates, methanol with 3×10^{-3}M HCl eluant) showed a single product. This product and 1.030 g of KCN in 30 mL of water were refluxed for 6.5 h during which the color changed to red-orange. The solvent was stripped and the residue triturated with CH_3OH, in which the complex is soluble. TLC showed several luminescent components, and these were separated by column chromatography using neutral alumina. The separation started with pure CH_3OH as an eluant and continued with increasing amounts of water up to 15%. The desired product was the most copious fraction. This complex has three isomers (1:2:1) and a very complex ^{13}C NMR spectrum. IR: (COOH) 1622 cm^{-1}, (CN) 2066 cm^{-1}. UV−vis λ_{max} (CH_3OH): ∼ 450 nm. Anal. (as CH_3 ester) Calcd for $RuC_{30}H_{20}N_6O_4$: C, 57.19; H, 3.18; N, 13.34. Found: C, 57.67; H, 3.12; N, 13.15 [Midwest Microlab].

Preparation of [Re(5-COOHphen)(CO)$_3$(pyr)]ClO$_4$ (5). 0.100 g of Re(CO)$_5$Cl (2.76×10^{-4}mol) and 0.066 g of 5-COOHphen (3.04×10^{-4} mol) were refluxed for 2 h in toluene. Recrystallization from CH_3OH yields Re(5-COOHphen)(CO)$_3$Cl. ^{13}C NMR (DMSO/ppm): (5-COOHphen) 127.1_6, 127.2_8, 127.7_7, 128.8_1, 129.1_1, 132.6_4, 138.2_0, 140.9_4, 146.5_3, 147.4_3, 153.9_7, 155.4_9; (COOH) 166.6_6; (carbonyls)190.0_7, 197.7_4, 197.8_1. IR: (COOH) 1707 cm^{-1}; (COs) 1921, 1943, 2027 cm^{-1}. A total of 0.107 g of the chloro complex (2.06×10^{-4} mol) was dissolved in THF, and then, 0.046 g (2.06×10^{-4}mol) of AgClO$_4$·H$_2$O was added. The mixture was stirred at room temperature overnight in the dark. The reaction mixture was then centrifuged and the liquid carefully separated from the powdery AgCl. To the liquid was added excess pyridine, and the mixture was refluxed until TLC [alumina plates, CH_3CN/CH_2Cl_2 (20:80)] showed complete reaction of the starting material. The solvent was removed and the components of the resulting solid separated by column chromatography. A silica gel column was used with acetone as the initial eluant. The eluant was gradually enriched in CH_3OH. The desired product was eluted with a CH_3OH/H_2O mixture (85:15). ^{13}C NMR (CD_3OD/ppm): (5-COOHphen) 127.8_0, 128.0_6, 128.2_6, 130.8_2, 131.6_5, 139.8_2, 141.2_0, 141.8_0, 147.4_3, 147.6_4, 155.2_6, 155.6_0; (carboxyl) 172.1_1; (pyridine) 127.6_3, 140.9_4, 152.8_8; (carbonyl) 192.3_5, 196.3_6, 196.4_4. IR: (COOH) 1630 cm^{-1}; (COs) 1888, 1911, 2022 cm^{-1}. UV−vis λ_{max} (CH_3OH): ∼375 nm.

Preparation of [Re(5-COOHphen)(CO)$_3$CN] (6). 0.100 g of $Re(CO)_5Cl$ (2.76×10^{-4} mol) and 0.066 g of 5-COOHphen (3.04×10^{-4} mol) were refluxed for 2 h in toluene. Recrystallization from CH_3OH yields Re(5-COOHphen)$(CO)_3Cl$ (vide supra). A total of 0.107 g of the chloro complex (2.06×10^{-4} mol) was dissolved in THF, and 0.046 g (2.06×10^{-4} mol) of $AgClO_4 \cdot H_2O$ was added. The mixture was stirred at room temperature overnight in the dark. The reaction mixture was then centrifuged and the liquid carefully separated from the powdery AgCl. The liquid was stripped and the solid dissolved in a 1:1 C_2H_5OH/H_2O mixture to which was added 1.0 g of KCN. The mixture was refluxed overnight and the solvent evaporated. The obtained solid was triturated with CH_3OH to obtain the desired complex. The complex was purified via column chromatography with neutral alumina using CH_3OH with gradually increasing amounts of H_2O as the eluant. ^{13}C NMR (DMSO/ppm): (5-COOHphen) 126.0_2, 126.6_6, 127.2_1, 130.1_1, 130.2_6, 139.5_9, 139.9_9, 141.7_9, 146.0_1, 146.3_9, 153.3_7, 153.6_9;(COOH) 167.5_7; (CN) 139.7_5; (carbonyls) 191.6_8, 196.1_0, 196.1_4. IR: (CN) 2127 cm^{-1}; (COOH) 1631 cm^{-1}; (COs) 1894, 1917, 2022 cm^{-1}. UV−vis λ_{max} (CH_3OH): ∼375 nm.

pH Titrations. Stock aqueous solutions of the various complexes were made by stirring ∼100 mL of deionized water with an excess of the appropriate complex for about 4 h at room temperature. The solution was filtered through a Gelman 0.45 μm Acrodisc. The filtered stock served as the basis for both intensity and lifetime measurements.

The buffer solutions used employed H_3PO_4, KH_2PO_4, K_2HPO_4, and K_3PO_4 in varying proportions. The buffer concentration was 0.1 M. The buffer pHs were determined using a Corning model 440 pH meter. Typically, 1 mL of the stock solution of the complex and 4 mL of buffer were combined for the intensity or lifetime measurement. There was no detectable pH difference between the pure buffer solution and the test solution. The test solution was transferred to Wheaton 2 mL ampules, which are very uniform and transmit to 290 nm. The luminescence intensity and lifetime measurements were made with air-saturated solutions.

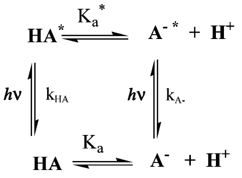
All intensity measurements were made on corrected emission spectra. The lifetimes were measured using an average of 64 traces. The composite trace was analyzed using an in-house Marquardt-based nonlinear least-squares fitting program, which fit the decays with one to three exponential terms. All the decays proved to be single exponential with the exception of one complex at pHs < 3. For Ru(5-COOHphen)$_2$(CN)$_2$, the preexponential weighted lifetime, eq 1, was used

$$\tau_{pe} = \sum (A_i / \sum A_j)\tau_i \tag{1}$$

where A_i is the preexponential for the *i*th lifetime and $\sum A_j$ is the sum of the preexponential terms. Only two exponentials were required for a satisfactory fit of Ru(5-COOHphen)$_2$(CN)$_2$ at low pH, and the decays at higher pH were single exponential. The low pH data may result from the protonation of CNs.[18]

To test specific ion effects, a limited number of both intensity and lifetime titrations were also done using a buffer system based on H_2SO_4, $KHSO_4$, and K_2SO_4. This buffer yielded results indistinguishable from those of the phosphate buffer system.

Data Fitting/Analysis. Except as noted above, all the luminescence decays observed in this study were satisfactorily fitted with a single exponential decay with no evidence of a second component. At the high buffer concentrations used, this is not unexpected and is completely consistent with the experiments being done in the rapid exchange limit. A simple kinetic scheme is then applicable.



(2)

In the fast exchange limit, it is assumed that the excited-state equilibrium between HA* and A^{-}* is maintained.[19] Under these conditions, only a single decay is seen, characterized by a single observed lifetime, τ_{obs}, which implies a single observed decay rate constant k_{obs}. This allows for very simple expressions for the observed intensity and lifetime variations as a function of the fraction of each species present:

$$\text{Intensity:} \qquad I_{obs} = f_{HA} I_{HA}{}^{max} + f_A I_A{}^{max} \tag{3}$$

$$\text{Lifetime:} \qquad k_{obs} = f_{HA} k_{HA} + f_A k_A \tag{4}$$

where the *f* variables are the fractions of HA* and A^{-}* present, I^{max} is the emission intensity when only that species is present, and the *k* variables are the decay rate constants for the species. The fraction of each species present will depend on the pH and pK_a* of the excited state of the complex. When this dependence is incorporated into eqs 3 and 4, one obtains

$$I_{obs} = I_{HA}{}^{max}(1 + 10^{pH - pK_a*})^{-1} + I_A{}^{max}[1 - (1 + 10^{pH - pK_a*})^{-1}] \tag{5}$$

$$k_{obs} = 1/\tau_{obs} = k_{HA}(1 + 10^{pH - pK_a*})^{-1} + k_A[1 - (1 + 10^{pH - pK_a*})^{-1}] \tag{6}$$

In the rapid exchange limit, these expressions are rigorously correct and make no assumptions regarding the excitation wavelength; only the limiting intensities or decay rates are required. Values for the I^{max} and *k* variables were obtained from the appropriate data at the limits of the pH range used where both the intensity and lifetimes had reached a constant value. Fitting the experimental data using a Marquardt approach required only a single floating parameter, pK_a*, the pK_a of the excited state. The fact that, with one exception (vide supra), all decays could be fit with a single exponential suggests this simple model is adequate. The experimental data were fitted with either eq 5 or 6 using PSI Plot software. The fits were all satisfactory, gave internally consistent values of pK_a (i.e., intensity vs lifetime), and provided chemically reasonable values.

Results and Discussion

The ligand is pH-sensitive, as shown in Figure 2. There is little change in the absorbance with pH but significant changes of both λ_{max} and intensity in the emission. The anionic form is the stronger emitter. A determination of the apparent pK_a using the integrated emission gave a value of

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(19) Vos, J. G. *Polyhedron* **1992**, *11* (18), 2285−2299.

Table 1. Selected Emission Photophysical Properties for the Complexes in Organic Solvents[a]

metal complex[b]	emission λ_{max} (nm)	lifetime τ(air) μs CH_3OH	lifetime τ(Ar) μs CH_3OH	O_2 $k_q \times 10^{-9}$ M^{-1} s^{-1}	φ
$[Ru(5\text{-}COOHphen)(bpy)_2](ClO_4)_2$ (**1**)	608[c] 614[d]	0.19_9	0.74_8	1.8_0	0.13[d]
$[Ru(5\text{-}COOHphen)(Me_4Phen)_2](ClO_4)_2$ (**2**)	614[c] 608[d]	0.16_2	1.75_3	2.7_7	0.11[c]
$[Ru(5\text{-}COOHphen)_3](ClO_4)_2$ (**3**)	593[c] 604[d]	0.16_7	0.67_0	2.2_5	0.056[c] 0.060[d]
$Ru(5\text{-}COOHphen)_2CN_2$ (**4**)	634[c] 660[e]	0.15_7	1.87_6	2.8_6	0.050[e]
$[Re(5\text{-}COOHphen)(CO)_3(pyr)]ClO_4$ (**5**)	556[c] 578[d]	0.43_9	1.85_2	0.86_0	0.068[c] 0.054[d]
$Re(5\text{-}COOHphen)(CO)_3CN$ (**6**)	566[c] 568[d]	0.24_4	1.68_8	1.7_4	0.18[c]

[a] 0.4 mM KOH. [b] Complexes are present as the anionic form of the acid function ($-COO^-$). [c] Solvent = CH_3OH. [d] Solvent = CH_3CN. [e] Solvent = $CH_3SO_2CH_3$.

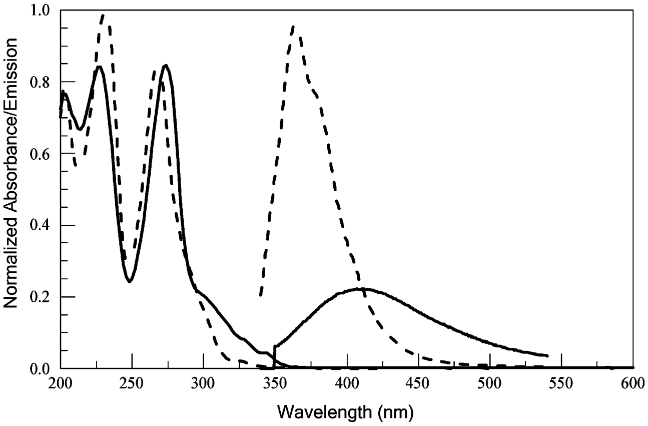

Figure 2. Absorption and emission spectra for 5-carboxy-1,10-phenanthroline in aqueous buffer at pH = 1.17 (—) and pH = 10.53 (- - -). Normalized to pH = 1.17.

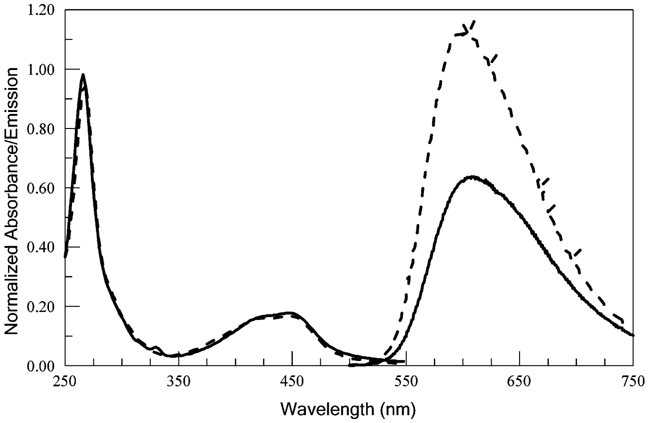

Figure 3. Absorption and emission spectra for $[Ru(5\text{-}COOHphen)_3](ClO_4)_2$ in aqueous buffer at pH = 1.17 (- - -) and pH = 9.07 (—). Normalized to pH = 9.07.

pK_a(apparent) ~ 5.76. A direct pH titration with NaOH yielded a value of 5.65. The former is the excited-state value, while the latter is for the ground state. The value of ~5.7 can be compared with values for benzoic acid, pK_a ~ 4.19, and for 4-pyridine carboxylic acid, pK_a ~ 4.96.[20] The impact of the heteroatoms can clearly be seen in the comparison of the benzoic and pyridine carboxylic acids' pK_a values. Thus, while a shift in pK_a for 5-COOHphen compared to its hydrocarbon analogue is expected, its magnitude is somewhat surprising in light of the lesser aromatic character of the 5 and 6 positions of 1,10-phenanthroline.

Table 1 shows selected photophysical properties of the various complexes in organic solvents. To ensure a single form of the carboxyl group, anionic, the solutions were 0.4 mM in KOH. The majority of the measurements are made with CH_3OH as the solvent, but some measurements with CH_3CN are provided for comparison. The Ru−cyano complex had very limited solubility in common organic solvents, and the measurements were made in dimethyl sulfoxide. The Ru(II) complexes all have the metal-to-ligand charge-transfer (MLCT) absorption in the 410−450 nm region, while the Re(I) MLCT absorption peak is less crisp but falls in the 340−375 nm region.

The Re(I) complexes' emissions show some solvatochromism, as does the Ru(II) cyano complex. The quantum yields, φ, are typical for these types of complexes and are somewhat solvent-dependent. All the complexes were bright enough to provide good signal-to-noise, even at μM concentrations. The susceptibility to oxygen quenching, as shown by the k_q values, is near diffusional for most of the complexes studied. Unfortunately, the high k_q values coupled with the rather long lifetimes lead to significant oxygen quenching in air-saturated solutions. However, the lower solubility of oxygen in water, ~0.265 mM for air-saturated water,[21] compared to those of most organic solvents ameliorates the problem somewhat.

As shown in Figure 3 for the $[Ru(5\text{-}COOHphen)_3](ClO_4)_2$ complex, which is typical, the absorption spectra of both the Ru(II) and Re(I) complexes were virtually unaffected by pH in the range studied (i.e., $1.1 < pH < 9.5$). For all complexes, the emission intensity was a function of pH. The emission λ_{max} was very slightly sensitive to pH, the $[Ru(Me_4phen)_2(5\text{-}COOHphen)](ClO_4)_2$ complex showing the largest $\Delta\lambda_{max}$ ~ 15 nm in the pH region studied. The other complexes all had $\Delta\lambda_{max}$ values < 8 nm. Like the pure ligand, the

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(20) *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990; pp 8−35, 8−36.

(21) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 89.

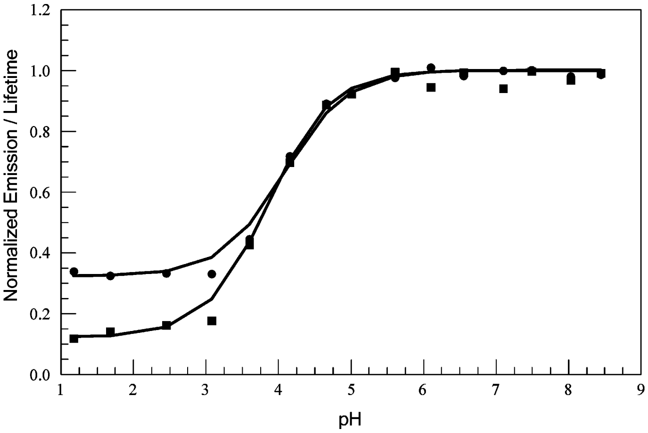

Figure 4. Normalized variation of emission intensity and lifetime with pH for $[Ru(Me_4phen)_2(5\text{-}COOHphen)](ClO_4)_2$ in aerated aqueous buffers: intensity (■); lifetime (●). (—) Best-fit line using two-species model.

deprotonated form of the complex was the stronger emitter and longer-lived species for all the complexes studies.

The pH response of a typical complex is shown in Figure 4. The normalized results for both intensity and lifetime variation are shown for $[Ru(Me_4phen)_2(5\text{-}COOHphen)](ClO_4)_2$. The general shape of the curves, with plateaus at low and high pH, was true for all the complexes studied. This allowed easy assignment of the required maximum/minimum values for both intensity and lifetime for the fitting to eqs 5 and 6. In all cases, the dynamic range of the intensity measurements was greater than the corresponding lifetime variation. The best fit line using the simple two-species model described in the Experimental section is shown also. We estimate that the pK_a derived from our fitting procedure has error limits of ±7%. Using this criterion, the pK_a values for both intensity and lifetime fits were within experimental error of each other. A summary table, Table 2, shows the best fit pK_a values, dynamic ranges, and useful pH ranges for the various complexes investigated. By dynamic range, we imply simply the ratio of either intensity or lifetime maximum/minimum values over the pH range examined, that is, either $I(\text{pH} = 8.44)/I(\text{pH} = 1.17)$ or $\tau(\text{pH} = 8.44)/\tau(\text{pH} = 1.17)$, where the I and τ values are taken at pHs that are on the two observed limiting plateaus.

It should be emphasized that our purpose was not to create the ultimate pH sensing complex but, rather, to explore the impact of several structural parameters that might allow tuning of the complexes' pH-sensitive range, enhance the dynamic response, and allow the comparison of intensity and lifetime responses. We examine the impact of various structural features on these responses in the paragraphs below.

The pK_a of the pure ligand is near the ideal range for many applications, particularly those involving physiological and natural water uses. As expected, complexation with the metal ions, Lewis acids, resulted in a significant pK_a shift toward lower values. The positive metal ion center can stabilize the charge on the ligand following loss of a proton, and this facilitates dissociation of the COOH to give the anionic form. We expected to be able to tune the pK_a somewhat by altering the formal charge on the metal ion center. To some degree, this goal was realized, though clearly, other factors are at work.

Comparing complexes **1** and **4** (see Table 2 for definitions of complexes **1**−**6**), the formal charge on the Ru(II) ion goes from 2+ to 0 while the pK_a goes from 3.0 to ~4.1. Some, but not all, of the increase in pK_a can be attributed to a decrease in the Lewis acid character of the metal ion with decreased formal charge. A similar change is seen in the Re(I) series where complex **5** has a formal 1+ charge while that of **6** is 0. The pK_a again increases with reduced formal charge from 3.4 to 3.9, but the effect is less dramatic than in the Ru(II) series. Even when the formal charge remains the same, electron donating substituents can increase the pK_a. Complexes **1** and **2** are quite similar, except that the spectator ligands are considerably more electron rich in **2**. This change results in a ΔpK_a of about +1.

We expected that because (1) the emission measurements were corrected for variation in the absorbance, (2) the change in the absorbance of the complexes on going from an acidic to a basic environment was minimal, and (3) the shifts in λ_{max} with pH for any particular complex were very modest, that the pK_a determined by intensity and lifetime methods should be equivalent. Within our experimental uncertainty, this is borne out by Table 2. None of the excursions is great enough to warrant causal speculation.

One could infer, on the basis of these examples, that for −OH- and −COOH-based pH-sensing ligands, that (1) the pK_a of the complex will be lower than that of the pure ligand, (2) the complex pK_a can be tuned by choice of both formal charge and spectator ligands, and (3) the structural tuning range is on the order of 1−1.5 pK_a units. Thus, electronic tuning of the response does work and, usually, in the intuitively predicted direction. However, the range of tweaking by modest structural changes is limited.

Table 2. pH-Dependent Emission Properties in Air-Saturated Aqueous Buffer Solutions

	intensity		lifetime		
metal complex	pK_a (I)	dynamic range (I)	pK_a (τ)	dynamic range (τ)	useful pH range
$[Ru(bpy)_2(5\text{-}COOHphen)](ClO_4)_2$ (**1**)	3.0	~2	N.A.[a]	~1.2	2−5
$[Ru(Me_4phen)_2(5\text{-}COOHphen)](ClO_4)_2$ (**2**)	4.0	9.3 10.8[b]	3.6	4.9 8.4[b]	3−6
$[Ru(5\text{-}COOHphen)_3](ClO_4)_2$ (**3**)	3.5	1.7	3.5	1.3	2.5−5.5
$Ru(5\text{-}COOHphen)_2CN_2$ (**4**)	4.4	4.8	3.8	5.4	3−6.5
$[Re(5\text{-}COOHphen)(CO)_3(pyr)](ClO_4)_2$ (**5**)	3.4	1.8	3.1	1.5	2.5−5.5
$Re(5\text{-}COOHphen)(CO)_3CN$ (**6**)	3.9	5.6	3.4	4.0	3−6

[a] Not applicable. [b] Ar purged.

Table 3. Limiting Lifetimes for Complexes at pH = 2.45 and 7.49 in Purged Aqueous Solutions

metal complex	τ (pH = 2.45) (μs)	τ (pH = 7.49) (μs)	dynamic range
$[Ru(5\text{-}COOHphen)(bpy)_2](ClO_4)_2$ (**1**)	0.67_3	0.81_7	1.2_1
$[Ru(5\text{-}COOHphen)(Me_4Phen)_2](ClO_4)_2$ (**2**)	0.16_7	1.40_0	8.4_0
$[Ru(5\text{-}COOHphen)_3](ClO_4)_2$ (**3**)	0.98_3	1.47_0	1.5_0
$Ru(5\text{-}COOHphen)_2CN_2$ (**4**)	0.16_3	1.03_3	6.3_3
$[Re(5\text{-}COOHphen)(CO)_3(pyr)]ClO_4$ (**5**)	0.52_3	0.79_0	1.5_1
$Re(5\text{-}COOHphen)(CO)_3CN$ (**6**)	0.17_2	0.71_4	4.1_5

Another important parameter for a pH sensor is the dynamic range of the observed property with changing pH. We show the limiting lifetimes at the low and high pH plateaus for the complexes under deoxygenated conditions in Table 3. The dynamic range, as measured by the lifetimes, is also included. In all cases, the lifetimes obtained were single exponential with the exception already noted. At the limiting pHs chosen, the lifetimes were invariant over several pH units.

The dynamic range shown in Table 3 for the lifetimes represents the upper limit in the absence of oxygen quenching. Comparing the intensity dynamic range with the lifetime range, in most cases, the intensity range is greater. This may be due, in part, to an increase in k_r, the radiative rate constant, on going from the protonated to deprotonated complex. The emission intensity can be related to the expression for the quantum yield, $\varphi = k_r/(k_r + \sum k_{nr})$, where $\sum k_{nr}$ represents the sum of all nonradiative decay paths. For the complexes used in this study, $\varphi \sim 0.1$, so that $\sum k_{nr} \gg k_r$. Thus, a 2-fold increase in k_r with no change in $\sum k_{nr}$ will translate into an almost 2-fold change in intensity. The lifetime, however, is given by $\tau = 1/(k_r + \sum k_{nr})$. Hence, a 2-fold change in k_r will only increase the lifetime on the order of 10%. Further, if only $\sum k_{nr}$ changes, the intensity and lifetime measurements would be expected to have comparable dynamic ranges. To test this suggestion, we make use of the fact that the corrected integrated emission spectrum is related to the quantum yield, $\varphi = IE_cK$, where φ is the quantum yield, IE_c is the corrected integrated emission, and K is a collection of constants. From this and the relation $\varphi/\tau = k_r$, we can estimate the ratio of the radiative rate constants for the two forms of the complex (i.e., acid and anion). For complex **3**, the ratio k_r(anion)/k_r(acid) = 1.26, while for complex **5**, the value is 1.19. While not huge, the values do suggest that the radiative rate constants for the two forms are different for both the Ru(II) and Re(I) complexes, and this plays a role in the resulting different dynamic ranges for intensity and lifetime measurements.

Both environmental and structural features can impact luminescent sensor dynamic range. The most common environmental factor is the presence of oxygen. The quenching of the excited states by oxygen is expected to reduce the dynamic range for both intensity and lifetime techniques. For all the complexes studied, the lifetimes of the acid forms were typically 100−250 ns in air-saturated solutions. The anionic forms exhibited lifetimes in the 400−800 ns range under the same conditions. The Stern−Volmer quenching constant for oxygen quenching, K_{sv}, can be expressed as $k_q\tau_o$, where k_q is the bimolecular O_2 quenching rate constant, which is expected to be the same for both the acid and anionic forms, and τ_o is the species' lifetime in the absence of quenching. Because of the longer lifetimes of the anionic forms, the impact of oxygen quenching falls most heavily on this form and results in a compressed dynamic range. When the low and high pH lifetimes are similar (i.e., small dynamic range), the difference between the air-saturated and purged dynamic ranges is not expected to be large. We have found, however, that when this type of sensor is embedded in a polymer support, the effective K_{sv} for oxygen quenching can decrease substantially.[22] This has the salutary effect of enhancing the dynamic range for the supported sensors in selected polymers.

Structural factors are also important in determining the dynamic ranges observed. Complex **1** was the first complex tested, and its dynamic range was a disappointment. Indeed, the change in lifetime with pH was so muted that we did not feel a valid pK_a could be extracted from our data. However, as shown in Figure 5, the MLCT emission for $Ru(bpy)_3^{2+}$ is lower in energy than that for $Ru(5\text{-}COOHphen)_3^{2+}$. This suggests that, in the mixed ligand complex, the MLCT emission involves the bpy's and the effects of pH on the 5-COOHphen are significantly muted as it is a spectator ligand. As appealing as this suggestion is, the dismal dynamic range of complex **3** suggests that other factors are also in play. It was hoped, with the same three pH-sensitive ligands, that complex **3** would exhibit both a broader range of pH sensitivity and a wide dynamic range. In fact, neither of these goals was realized. The reasons that **3** underperforms relative to both complexes **1** and **2** are not obvious. Indeed, complex **3** is one of the poorest pH sensors in all attributes.

At this point, it is not possible to unambiguously point to specific structural features that will enhance the dynamic range of a complex to pH changes. Both complexes **4** and **6**

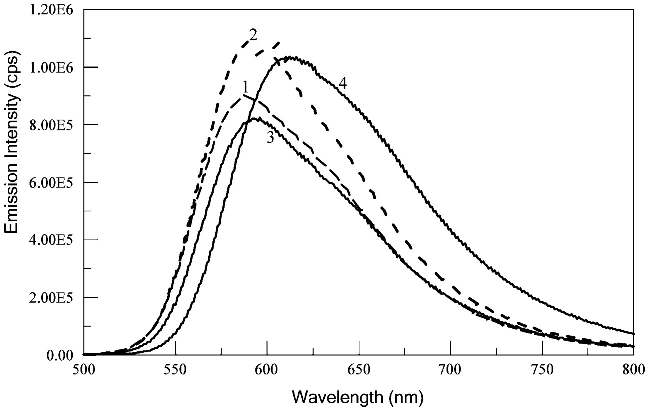

Figure 5. Emission spectra for various Ru(II) complexes in CH_3OH: 1 (— — —) $[Ru(Me_4phen)_3](ClO_4)_2$; 2 (- - - -) $[Ru(phen)_3](ClO_4)_2$; 3 (—) $[Ru(5\text{-}COOHphen)_3](ClO_4)_2$; 4 (—) $[Ru(bpy)_3](ClO_4)_2$.

are formally neutral with CN ligands and have similar, good dynamic ranges. That there is likely an additional protonation step for **4** due to the CNs muddies the interpretation for this complex, however. Complex **2**, while formally 2+, has a dynamic range that is also quite good. It seems reasonable to expect that the greater the change in the electronic distribution between the protonated and deprotonated forms, the greater the change in intensity or lifetime with pH. Thus, structural features that enhance the energy difference between the two forms should also enhance the dynamic range. The reduction in formal metal ion charge—complexes **4** and **6**—and the electron donating substituents of the ancillary ligands—complex **2**—should enhance the difference between the protonated and deprotonated forms by raising the energy of the deprotonated form. While we can rationalize the observed results for these few examples, more work is clearly needed in this area.

The better of the simple complexes reported here have a useful pH range of about 2.5 pH units with a typical dynamic range of 4.5. Depending on the experimental error of the intensity or lifetime measurement, resolution to 0.02 pH units should be possible in the pH range of maximum change. This resolution should be satisfactory for many of the possible pH sensor applications of these luminescent complexes.

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Supporting Information Available: Additional information regarding the derivation of expression for intensity and lifetime acid−base equilibrium fast exchange limit−single exponential decay. This material is available free of charge via the Internet at http://pubs.acs.org.

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