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A luminescent pH sensor based on a sol–gel film functionalized with a luminescent organometallic complex

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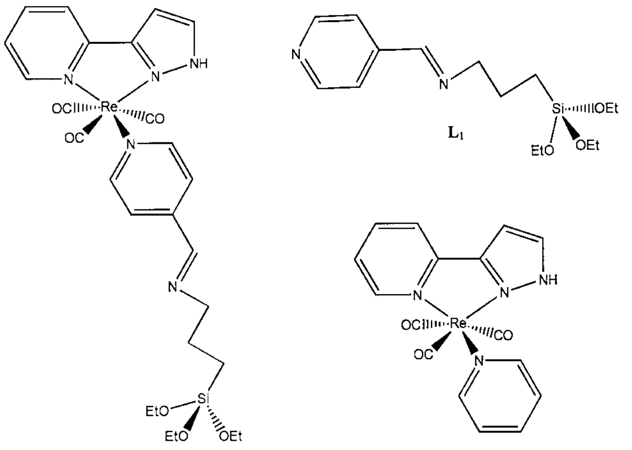
A rhenium(I) tricarbonyl complex with a 3-(pyridin-2-yl)pyrazole chromophoric ligand and a functionalized organosilane spectator ligand, [Re(py-pzH)(CO)$_3$(L$_1$)](CF$_3$SO$_3$) (**1**) [where py-pzH = 3-(pyridin-2-yl)pyrazole, L$_1$ = 3-*N*-(pyridin-4-ylmethylene)aminopropyltriethoxysilane], as well as its analog, [Re(py-pzH)(CO)$_3$(py)](CF$_3$SO$_3$) (**2**) (where py = pyridine) have been synthesized. The room temperature MLCT luminescence properties of **1** and **2** (λ_{max} at 484 and 489 nm, respectively) were found to be sensitive to the protonation–deprotonation status of the 3-(pyridin-2-yl)pyrazole ligand. Spectrofluorometric pH titration of **2** in aqueous media revealed an excited state pK_a of 7.05. Sol–gel material formed from hydrolysis of **1** was successfully spin-coated onto glass microscope slides. The result was a sol–gel based luminescent pH sensor capable of responding over a wide pH range from pH 2.3 to 12 in air. The applicability of the principle of direct perturbation of electronic factors of sensor molecules in the development of luminescent chemical sensing materials is demonstrated.

Introduction

Luminescent chemical sensing by sol–gel derived materials is an attractive area of applied research bridging material sciences and analytical chemistry.[1–6] In general, this involves incorporation of chemical sensor molecules into a sol–gel matrix. Physical entrapment[1,7–10] and functionalization of organosilane monomers by sensor molecules[11–13] are the two common approaches for such incorporation. The latter method is considered more advanced, as it eliminates the problem of dopant leaching and improves the homogeneity of sensing units in the sol–gel matrix. For the design of chemical sensors, the two commonly adopted sensing mechanisms are photoinduced electron transfer (PET) quenching and direct perturbation of electronic factors of sensor molecules. In the PET mechanism, chemical sensing involves suppression of the intramolecular non-radiative decay pathway for the luminophore in the sensor molecule, leading to enhancement of luminescence, by coordinating/binding to the analyte.[14–20] While the PET mechanism is a powerful and sensitive tool in the design of chemical sensors, its applicability is complicated by the possibility of intermolecular quenching of the luminophore by interfering agents present in the sample, *e.g.* dioxygen. Any enhancement in luminescence due to analyte binding and subsequent suppression of PET quenching may be significantly masked by such intermolecular quenching unless all interferences are carefully removed before measurement. In this context, analyte-specific direct perturbation of electronic factors of sensor molecules may be advantageous, as quenching of the luminophore is not involved and the spectroscopic properties of the luminophore/chromophore of the sensor molecule are specifically altered by the analyte. This is most easily demonstrated in optical pH sensing by indicators.[6,21] Changes in the electronic factors of indicator molecules due to protonation–deprotonation cause the corresponding changes in the spectroscopic properties.

Rhenium(I) polypyridyl tricarbonyl complexes, [Re(L–L)(CO)$_3$X]$^{n+}$, are well known organometallic MLCT emitters with luminescence properties sensitive to changes in the electronic factors of the chromophoric polypyridyl ligand (L–L).[22–25] Moreover, the spectator ligand, X, provides a convenient handle for the functionalization of the complex. In fact, the rhenium(I) polypyridyl tricarbonyl moiety has been employed as a luminophore in numerous homogeneous PET chemical sensing applications.[14,26] However, its application in sol–gel based chemical sensing materials has scarcely been studied. In this work, we make use of a rhenium(I) pyridyl-pyrazolyl tricarbonyl complex containing a spectator ligand, L$_1$, with an organosilane functionality, [Re(py-pzH)(CO)$_3$(L$_1$)]$^+$ (**1**) (where py-pzH = 3-(pyridin-2-yl)pyrazole, L$_1$ = 3-*N*-(pyridin-4-ylmethylene)aminopropyltriethoxysilane), to develop a new luminescent pH sensing sol–gel material (Fig. 1) that responds to the pH of the medium by direct perturbation of the electronic factors of its pyridyl-pyrazolyl ligand.



L$_1$

[Re(py-pzH)(CO)$_3$(L$_1$)]$^+$ (**1**)　[Re(py-pzH)(CO)$_3$(py)]$^+$ (**2**)

Fig. 1 Structures of the spectator ligand L$_1$, the functionalized triethoxysilane monomer [Re(py-pzH)(CO)$_3$(L$_1$)]$^+$ (**1**) and the model analog of **1**, [Re(py-pzH)(CO)$_3$(py)]$^+$ (**2**).

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Experimental

General

Bromopentacarbonylrhenium, 3-aminopropyltriethoxysilane, trimethoxypropylsilane, pyridine-4-carbaldehyde and silver trifluoromethanesulfonate were obtained from Aldrich. 3-(Pyridin-2-yl)pyrazole was synthesized according to the literature method.[27] All solvents used were of analytical reagent grade (Riedel-de Haën and BDH). UV–Vis spectra were measured on a Hewlett Packard 8452A ultraviolet visible diode array spectrophotometer. Emission spectra were taken with an SFM 4800C spectrofluorometer. ^{1}H NMR spectra were collected using a Varian YH300 300 MHz NMR spectrometer.

Preparation of functionalized spectator ligand L$_1$: 3-*N*-(pyridin-4-ylmethylene)aminopropyltriethoxysilane

A mixture of 3-aminopropyltriethoxysilane (2.0 g, 9.0 mmol) and pyridine-4-carbaldehyde (0.97 g, 9.0 mmol) in 30 ml absolute ethanol was refluxed under nitrogen for 12 h. The mixture was cooled and the solvent removed under reduced pressure to yield L$_1$ as a pale yellow oil (2.5 g, 89%). ^{1}H NMR [CDCl$_3$, 300 MHz]: δ 8.43 (d, $J=6.0$, 2H, pyridyl-H), 8.00 (s, 1H, imine-H), 7.33 (d, $J=5.7$, 2H, pyridyl-H), 3.57 (q, $J=6.9$, 6H, ethoxy-CH$_2$), 3.41 (t, $J=6.6$, 2H, propyl-CH$_2$), 1.59 (t, $J=8.1$, 2H, propyl-CH$_2$), 0.98 (t, $J=6.9$, 9H, ethoxy-CH$_3$), 0.43 (t, $J=7.1$ Hz, 2H, propyl-CH$_2$). The resulting product was of sufficient purity for further reaction.

Preparation of Re(py-pzH)(CO)$_3$Br

Re(py-pzH)(CO)$_3$Br was synthesized from 3-(pyridin-2-yl)pyrazole and bromopentacarbonylrhenium according to the literature method for rhenium(I) polypyridyl tricarbonyl complexes.[28] A mixture of Re(CO)$_5$Br (100 mg, 0.25 mmol) and 3-(pyridin-2-yl)pyrazole (35.7 mg, 0.25 mmol) was refluxed in 20 ml of methanol under nitrogen for 16 h. Re(py-pzH)(CO)$_3$Br was obtained as yellowish orange microcrystals (85 mg, 69%) which precipitated out as the reaction mixture was cooled to 0 °C. The product was collected by filtration and was washed with cooled methanol and diethyl ether. ^{1}H NMR [acetone-*d*$_6$, 300 MHz]: δ 9.03 (t, $J=5.7$, 1H, pyridyl-H), 8.33–8.22 (m, 2H, pyridyl-H), 8.19 (d, $J=2.7$, 1H, pyrazolyl-H), 7.65 (t, $J=6.1$, 1H, pyridyl-H), 7.32 (d, $J=2.7$ Hz, 1H, pyrazolyl-H), 5.20 (s, 1H, pyrazolyl-NH).

Preparation of [Re(py-pzH)(CO)$_3$(L$_1$)](CF$_3$SO$_3$) (1)

A mixture of Re(py-pzH)(CO)$_3$Br (50 mg, 0.1 mmol) and silver trifluoromethanesulfonate (26 mg, 0.1 mmol) was refluxed in 20 ml of THF under nitrogen for 2 h. The resultant solution was then filtered into a 10 ml THF solution containing 31 mg (0.1 mmol) of L$_1$ and further refluxed for 6 h under nitrogen. The solvent was then removed under reduced pressure to yield [Re(py-pzH)(CO)$_3$(L$_1$)](CF$_3$SO$_3$) as a yellowish orange hygroscopic oil (66 mg, 75%). ^{1}H NMR [CDCl$_3$, 300 MHz]: δ 9.10 (d, $J=5.4$, 1H, pyridyl-H), 8.45–8.29 (m, 4H, pyridyl-H), 7.93 (s, 1H, imine-H), 7.85 (d, $J=2.4$, 1H, pyrazolyl-H), 7.36–7.29 (m, 1H, pyridyl-H), 7.25 (d, $J=5.5$, 2H, pyridyl-H), 6.98 (d, $J=2.5$, 1H, pyrazolyl-H), 3.55 (q, $J=6.8$, 6H, ethoxy-CH$_2$), 3.42 (t, $J=6.5$, 2H, propyl-CH$_2$), 1.66 (t, $J=7.5$, 2H, propyl-CH$_2$), 1.05 (t, $J=6.8$, 9H, ethoxy-CH$_3$), 0.50 (t, $J=6.6$ Hz, 2H, propyl-CH$_2$). MS (FAB$^+$, *m*-NBA): *m*/*z* 726 (M$^+$). The product was used in sol–gel preparation without further purification.

Preparation of [Re(py-pzH)(CO)$_3$(py)](CF$_3$SO$_3$) (py = pyridine) (2)

The preparation was similar to that of [Re(py-pzH)(CO)$_3$(L$_1$)](CF$_3$SO$_3$) except that pyridine (50 mg) was used instead of L$_1$. The product [Re(py-pzH)(CO)$_3$(py)](CF$_3$SO$_3$) was obtained after the solvent was removed under reduced pressure as a yellowish brown solid (54 mg, 84%). ^{1}H NMR [acetone-*d*$_6$, 300 MHz]: δ 9.12 (d, $J=5.1$, 1H, pyridyl-H), 8.48–8.30 (m, 2H, pyridyl-H), 8.16 (t, $J=7.7$, 1H, pyridyl-H), 7.98–7.83 (m, 2H, pyridyl-H), 7.81 (d, $J=2.7$, 1H, pyrazolyl-H), 7.78 (t, $J=5.7$, 1H, pyridyl-H), 7.64 (t, $J=6.3$, 1H, pyridyl-H), 7.34 (m, 2H, pyridyl-H), 6.92 (d, $J=2.7$ Hz, 1H, pyrazolyl-H), 3.75 (s, 1H, pyrazolyl-NH). MS (FAB$^+$, *m*-NBA): *m*/*z* 495 (M$^+$).

Preparation of the sol–gel material

[Re(py-pzH)(CO)$_3$(L$_1$)](CF$_3$SO$_3$) (50 mg, 0.06 mmol) was dissolved in 6 ml of absolute ethanol under rapid stirring. Trimethoxypropylsilane (1.24 g, 6 mmol) was then added followed by 0.33 g of water and two drops of conc. HCl. The mixture was stirred for 1.5 h at room temperature. A thin film of the sol was then deposited onto activated glass slides (Polyscience)[29] by a spin-coating procedure.[30] The coated glass slides were allowed to stand at room temperature for 3 days, at 100 °C for 12 h, then at 120 °C under vacuum for 24 h before examination.

Spectroscopic measurement

The luminescence properties of the sol–gel coating were measured by placing a coated glass slide into buffered aqueous solutions of known pH in an ordinary 1 cm pathlength spectrofluorometric curvette so that the slide was at 45° to the incident excitation beam of the spectrofluorometer. All measurements were carried out at room temperature (18 ± 1 °C) in air.

Results and discussion

The room temperature solution emission properties of complex **2** in a protic solvent (methanol) are shown in Fig. 2. In the absence of base, emission from the dπ(Re$^{\text{I}}$)$\rightarrow\pi^*$(py-pzH) MLCT excited state is observed at 489 nm. The apparent blue shift in the excited state energy compared to known polypyridyl Re(I) complexes ($\lambda_{\max}$ usually >500 nm)[31,32] is consistent with other MLCT systems involving bidentate pyrazole ligands[33,34] and can be explained by the better π-

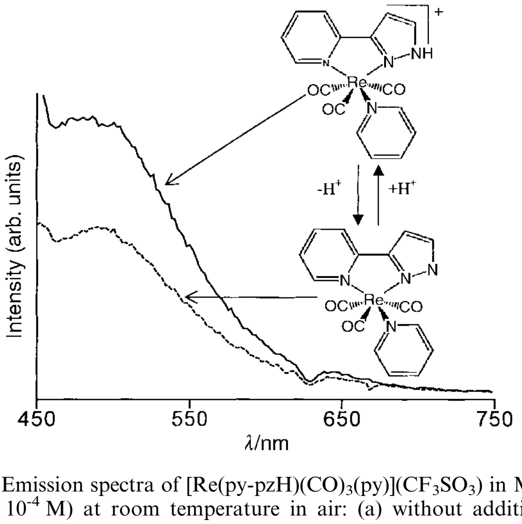

Fig. 2 Emission spectra of [Re(py-pzH)(CO)$_3$(py)](CF$_3$SO$_3$) in MeOH (1.68×10^{-4} M) at room temperature in air: (a) without addition of NEt$_3$ (——), and (b) with the addition of one equivalent of NEt$_3$ (·········). Excitation at 350 nm.

accepting properties of the py-pzH ligand compared to polypyridyl ligands, which tends to stabilize the dπ(Re^I) level and causes an increase in the MLCT band energy.[33,35] It is well known that significant differences in electronic properties exist between pyrazole and pyrazolyl ligands.[35] Thus, conversion of the chromophoric 3-(pyridin-2-yl)pyrazole ligand to 3-(pyridin-2-yl)pyrazolyl by deprotonation of the pyrazolyl-NH should substantially affect the luminescence properties of the rhenium(I) tricarbonyl luminophore. Upon addition of triethylamine, the intensity of the MLCT luminescence of **2** is reduced. Emission intensity can be restored by addition of trifluoroacetic acid. Such a reversible change in luminescence properties is attributed to the perturbation of electronic factors of the chromophoric py-pzH ligand by protonation–deprotonation. Such perturbation of luminescence properties is also observed in aqueous media. Fig. 3 shows the change in luminescence properties of **2** during spectrofluorometric pH titration in aqueous media. From the titration data, the excited state pK_a of the coordinated 3-(2-pyridyl)pyrazole is found to be 7.05 (Fig. 4).

Complex **1** is an analog of **2** with the spectator ligand, py, replaced by a functionalized organosilane, L_1, obtained from a condensation reaction between pyridine-4-carbaldehyde and 3-aminopropyltriethoxysilane. A durable functionalized sol–gel material is formed from co-hydrolysis of **1** with a 100-fold excess of an inert organosilane, trimethoxypropylsilane. A convenient spin-coating process produces a sol–gel film in the form of a transparent pale yellow film on the supporting glass slides which bind tightly to the glass surface and cannot be removed unless physically scratched. The films are stable in aqueous solution and other common organic solvents. Possible leakage of the bound rhenium(I) complex from the sol–gel material has been examined by submerging the glass-supported sol–gel film into 1.5 ml of water, methanol, acetonitrile and chloroform. Changes in spectroscopic properties of the solutions during a course of 5 days were followed by UV–vis absorption and spectrofluorometric studies. No detectable leakage was observed. The sol–gel material retains the luminescence properties of **2**. Room temperature MLCT luminescence is observed at 484 nm (shifted to 478 nm at high pH) which also display sensitivity towards the protonation–deprotonation status of the 3-(2-pyridyl)pyrazole ligand. Fig. 5 shows the responses of the sol–gel material towards different pH values in aqueous media. In fact, the material acts as a luminescent pH sensor with a wide active range from 2.3 to 12. Comparing the spectrofluorometric titration data of the sol–gel material (shown in the inset of Fig. 5) with that of model complex **2**, a more gradual pH dependence and a slight decrease in the apparent excited state pK_a value (5.80) are observed. While these could be caused by the replacement of the pyridine spectator ligand in **2** by L_1 in **1**, it is also possible that excited state pK_a of the 3-(2-pyridyl)pyrazole moiety in **1** is perturbed by the local environment of the sol–gel matrix. Minor variations in pore size and other textural characteristics of the sol–gel matrix may result in a collection of pH sensing units with slightly different pK_a values distributed throughout the material. The overall pH response of the material is thus the sum of the responses from these sensing units and, as a result, becomes more gradual than that of the homogeneous molecular sensor **2**. All measurements were carried out in oxygen saturated aqueous media and dissolved oxygen does not seem to affect the responses. No detectable deterioration in the luminescent pH response is observed when the material is allowed to age, either in air or submerged in aqueous media, for eight weeks.

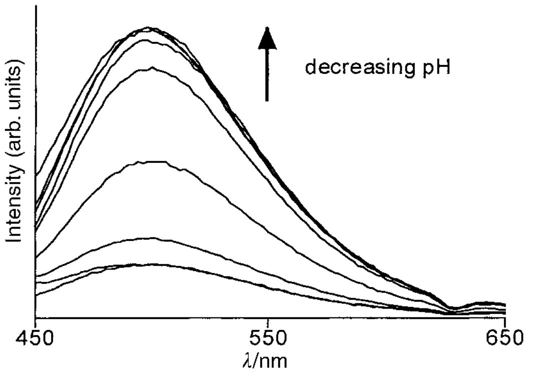

Fig. 3 Changes in the emission properties of [Re(py-pzH)(CO)$_3$(py)](CF$_3$SO$_3$) in water (1.66 × 10^{-5} M) with respect to pH at room temperature in air. Excitation at 350 nm. The pH values for the curves shown, in descending order of intersection with the intensity axis at 450 nm, are: 2.3, 3.1, 3.9, 5.0, 6.0, 6.8, 7.8, 9.2, and 12.0.

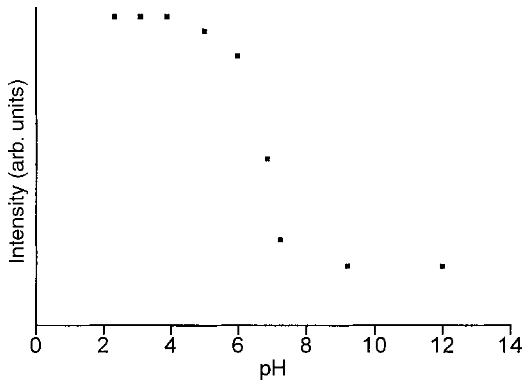

Fig. 4 Variation of emission intensity of [Re(py-pzH)(CO)$_3$(py)](CF$_3$SO$_3$) in water (1.66 × 10^{-5} M) at 500 nm with respect to pH. The excited state pK_a of the 3-(2-pyridyl)pyrazole ligand of [Re(py-pzH)(CO)$_3$(py)](CF$_3$SO$_3$) was found to be 7.05.

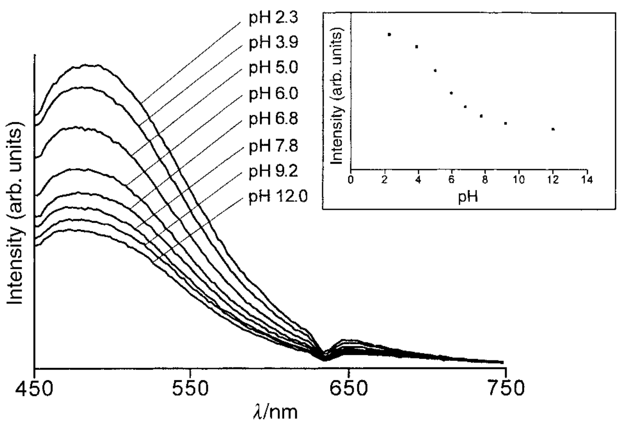

Fig. 5 Variation of the emission properties of the [Re(py-pzH)(CO)$_3$(L$_1$)]$^+$ derivatized sol–gel thin film as a function of pH in aqueous media at room temperature in air. The variation of the emission intensity at 484 nm with respect to pH is shown in the inset.

Conclusion

The synthetic convenience of functionalizing an organosilane with a rhenium(I) tricarbonyl luminophore has been demonstrated. With 3-(2-pyridyl)pyrazole as the chromophoric ligand on the rhenium(I) tricarbonyl luminophore, a luminescent pH sensor is produced. Direct perturbation of the electronic factors of the 3-(2-pyridyl)pyrazole ligand by the pH of the medium provides the basis for pH sensing. Sol–gel thin films of the functionalized organosilane supported on soda glass slides can be fabricated by spin-coating. The sol–gel thin film retains the pH sensitivity of the functionalized monomer and displays luminescence responses over a wide pH range. Dissolved oxygen does not seem to affect the responses of the pH sensor to the extent found in PET sensors.[20] Further development of the principle of direct perturbation of electronic factors of luminophores in functionalized sol–gel materials for the chemical sensing of other analytes, *e.g.* metal ions, is in progress.

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