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Towards multianalyte molecule-based sensors: reactivity and photophysical behaviour of hemilabile ligand-containing Ru(II) bipyridyl complexes

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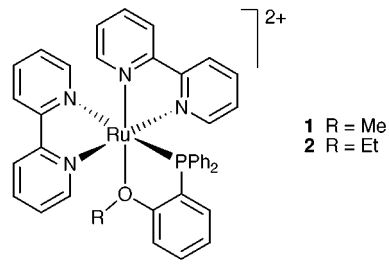
The concept of using hemilabile ligand-containing complexes as the basis for multianalyte sensors is introduced: the preparation of two such ruthenium complexes (1 and 2) and their reactivity towards a series of donor molecules is reported; differential photoluminescence and absorption responses are observed.

Molecule-based sensors are compounds designed to respond to specific analyte molecules by undergoing changes in readily-monitored physical properties. Ideally, molecule-based sensors should be sensitive to the amount and type of analyte present, while functioning in a reversible fashion. Many different and elegant strategies have been used to detect a variety of analytes, such as metal ions,[1] small anions,[2] gases,[3] biomolecules,[4] and pH.[5]

In this communication, we show how a new class of ruthenium complexes containing hemilabile ligands may be used as the basis for molecule-based sensors. Hemilabile ligands, which contain both substitutionally inert and labile moieties, provide a site for the binding of analytes to a metal center. Importantly, hemilabile ligands have been shown to allow the *reversible* binding of small molecules to metal complexes because of their chelating ability.[6] In a previous study, a rhodium carbonyl complex containing a hemilabile ligand was shown to selectively detect carbon monoxide in a mixture of gases.[3b]

In our approach, multiple analytes may be distinguished *via differences* in the response of a tailor-made complex to different analytes. Two such complexes, $[Ru(bpy)_2(PO)](PF_6)_2$ [PO = 2-(diphenylphosphino)anisole (**1**) and 2-(diphenylphosphino)-phenetole (**2**)], have been prepared and their reactions with a



series of analytes examined in solution. In these complexes, the PO ligands are hemilabile because of weak coordination of the ether moiety to the metal, and the bpy groups provide an optical handle. The absorption and emission properties of ruthenium polypyridyl complexes are well-known to be sensitive to the nature of the other ligands on the metal.[7] The bpy ligands also serve to prevent isomerization, a common occurrence with six-coordinate Ru complexes bearing hemilabile ligands.[6]

Complexes **1** and **2** were prepared† by reacting the appropriate PO ligand with 1 equivalent of $[Ru(bpy)_2(Me_2CO)_2](BF_4)_2$. Metathesis to the hexafluorophosphate salts yielded **1** and **2** as yellow powders which are soluble in polar organic solvents and stable for > 10 days in air-saturated solution. The ^{1}H NMR spectrum of **1** obtained at −80 °C (CD_2Cl_2) was unchanged from the spectrum at 25 °C; thus, either the opening-and-closing of the PO ligand does not occur on the NMR timescale, or the opening-and-closing is still fast at −80 °C. Two-dimensional ^{1}H correlation spectroscopy and NOE experiments established that the coordination of the PO ligand in **1** is bidentate.

The reactions of **1** and **2** with a variety of small molecules have been explored. The complexes react rapidly and irreversibly with one equivalent of acetonitrile, resulting in upfield shifts of the methoxy or ethoxy ^{1}H and phosphine ^{3}P NMR resonances of the hemilabile ligand. On the other hand, no reaction occurs with the oxygen donors ether, acetone and methanol.

The complexes **1** and **2** also react with sulfur donors such as ethanethiol, dodecanethiol, dimethyl sulfoxide and dimethyl sulfide. In these cases, the analyte-bound complexes are in equilibrium with the corresponding analyte-free complexes. The equilibrium is conveniently monitored by ^{1}H and ^{31}P NMR since the analyte-bound complexes also show upfield shifts of the methoxy or ethoxy ^{1}H and phosphine ^{31}P NMR resonances of the hemilabile ligand (data for reactions with **1** are shown in Table 1). The reversibility of the reaction of these analytes with **1** and **2** was established by varying the concentration of analyte in solution; this results in the expected changes in the ratios of analyte-bound to analyte-free complex as equilibrium is reestablished.

The equilibrium constant (K) is sensitive to the nature of the analyte and the hemilabile ligand. For example, of the sulfur donors examined, dimethyl sulfide binds with greatest affinity. We also observed differences in analyte affinity between **1** and **2**; for instance, all the sulfur donors bind with higher affinity to **2**. The equilibrium constant for dimethyl sulfide binding to **2** (300 ± 60 M^{-1}) is significantly higher than for binding to **1** (50 ± 10 M^{-1}). These differences suggest that sensor complexes can be designed to react specifically with certain analytes and may be used to distinguish analytes with closely related structures.

Both the analyte-free and analyte-bound complexes are luminescent at 77 K in 2:1 ethanol–acetone. The emission spectrum of **1** contains a band with λ_{max} at 600 nm (Fig. 1A), and the spectrum of **2** is similar; these complexes are both weak red emitters by eye. Addition of CH_3CN to **1** or **2** results in a dramatically more intense, blue-shifted (bright yellow) emission, as shown in Fig. 1B for **1**. Addition of DMSO and

Table 1 Data for **1** and analyte-bound **1**

Analyte	^{1}H NMR $\delta(OCH_3)^a$	^{31}P NMR $\delta(PO)^a$	K/M^{-1} ^{a,b}	λ_{max}/nm (ε/ M^{-1} cm^{-1})^c
—	3.71	50.9	—	412 (6900)
CH_3CN	3.14	39.9	—	410 (6900)^d
CH_3CH_2SH	3.23	37.4	7 ± 1	410 (6090)^{d,e}
$CH_3(CH_2)_{11}SH$	3.23	37.4	8 ± 2	410 (6040)^{d,e}
DMSO	2.97^f	37.7^f	0.8 ± 0.1^f	418 (5900)^{d,e}
	3.11^g	29.7^g	0.1 ± 0.02^g	
DMS	2.70	32.8	50 ± 0	410 (6040)^{d,e}

^{a} In CD_2Cl_2; ^{b} > 3 h equilibration time; ^{c} in acetone; ^{d} upon addition of 1000 equiv. of analyte, 5 min equilibration time; ^{e} pseudo-ε intended to show relative intensity of absorption band only; ^{f} major product; ^{g} minor product.

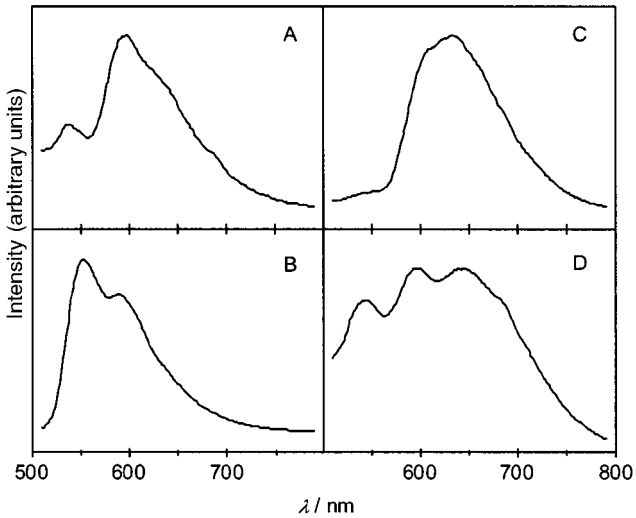


Fig. 1 Emission spectra of complexes at 77 K in 2:1 ethanol–acetone. (A) **1**; (B) **1** with 100 equiv. acetonitrile added; (C) **1** with 100 equiv. DMSO added; (D) **1** with 100 equiv. dodecanethiol added.

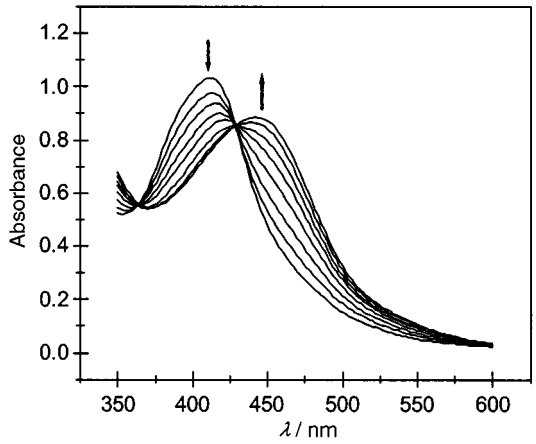


Fig. 2 Visible absorption spectra of **1** in acetone (1.47×10^{-4} M) upon addition of DMSO (0–13 000 equiv.).

dodecanethiol to **1** or **2** also results in shifts in the emission spectra (Fig. 1C and D), but minimal changes in intensity.

Certain analytes also react with **1** and **2** to yield colour changes. For example, of the analytes tested, only DMSO results in a significant colour change with **1** and **2** (Fig. 2 shows this effect for **1**). In this case, the concentration-dependent red shift of the visible absorption spectrum may be used to ascertain the amount of the analyte in solution. It may also be used to distinguish DMSO from related species that do not result in an absorption shift, such as other sulfur donors that produce only very slight colour changes.

These results show that emission characteristics, in combination with absorption, may be used to identify and quantify analytes by reaction with complexes such as **1** and **2**. Selectivity, sensitivity, and room temperature luminescence output are currently being optimized by varying the structures of the hemilabile ligand and ancillary ligand set. Studies are ongoing to incorporate these complexes into thin films to enable the development of solid-state sensors.

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Notes and references

† Synthesis of **1** and **2**: one equivalent of the appropriate PO ligand[8] was added to a deaerated acetone solution of $[Ru(bpy)_2(Me_2CO)_2](BF_4)_2$,[9] and the mixture was heated to reflux for 12 h. Filtration and removal of solvent *in vacuo* followed by metathesis to the PF_6 salt afforded **1** or **2** as a yellow powder in 85–90% yield. For **1**: ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): δ 8.55 (m, 2H), 8.30 (d, ^3J(H,H) = 5.6 Hz, 2H), 8.13 (m, 2H), 8.01 (d, ^3J(H,H) = 7.7 Hz, 1H), 7.95 (d, ^3J(H,H) = 7.6 Hz, 1H), 7.92–7.36 (m, 15H), 7.33 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,P) = 4.9 Hz, 1H), 7.24 (m, 1H), 7.17 (m, 1H), 6.97 (m, 2H), 6.39 (m, 2H), 3.71 (s, 3H, CH_3O); ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ 50.9 (s, PO), −143.8 (septet, ^1J(P,F) = 711 Hz, PF_6). Elemental analysis: calcd. for $C_{39}H_{33}F_{12}N_4OP_3Ru$: C, 47.05; H, 3.34; N, 5.63; found: C, 47.30; H, 3.39; N, 5.70%.

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