[35] A smooth residual background with extremely small amplitude, a likely result of the interaction of probe electrons with positive ions in the gas sample generated by the intense laser pulses,[29] was observed in our experimental ΔI_{tot}. The background was removed by fitting a smooth curve through the zero-crossing points of the theoretical ΔI_{tot}.[29–32] The experimental ΔI_{tot} curve was smoothed by Fourier filtering[32] (9 Å low-pass) and pixel regions showing systematic abnormalities were removed.[32]

[36] I. Hargittai, M. Hargittai, *Stereochemical Applications Of Gas-Phase Electron Diffraction*, VCH, New York, **1988**.

[37] The singlet [Fe(CO)$_3$] may, in principle, be generated through subsequent loss of a CO ligand from the singlet [Fe(CO)$_4$]. However, consideration of the energetics eliminates this possibility. The total energy available following the dissociation of [Fe(CO)$_5$] into [Fe(CO)$_4$] and CO upon two-photon excitation at 620 nm (92 kcal mol^{-1}) is 33 kcal mol^{-1}, and at most about 65 % (21 kcal mol^{-1}) of this remaining energy is retained as the internal excitation of [Fe(CO)$_4$].[6, 9, 11] Since the energy gap between the singlet [Fe(CO)$_4$] and the singlet [Fe(CO)$_3$] is at least 22 kcal mol^{-1}, the available energy is not enough to liberate another CO ligand.

[38] In our previous attempt[29] to isolate the [Fe(CO)$_4$] species, 310 nm fs laser pulses were used to photolyze [Fe(CO)$_5$]. Although one photon of 310 nm just falls short of the threshold for generating [Fe(CO)$_2$], [Fe(CO)] and Fe, it was found that in fact two-photon absorption dominated. Consequently, the major products obtained were actually [Fe(CO)$_2$], [Fe(CO)], and Fe rather than [Fe(CO)$_4$] or [Fe(CO)$_3$]. In the present experiment, 620 nm photon excitation was used instead of 310 nm and the main absorption is two-photon. This excitation provides enough energy to break at most two Fe–C bonds, leaving [Fe(CO)$_4$] and [Fe(CO)$_3$] as major products.

Dual-Signaling Fluorescent Chemosensors Based on Conformational Restriction and Induced Charge Transfer**

Jesse V. Mello and Nathaniel S. Finney*

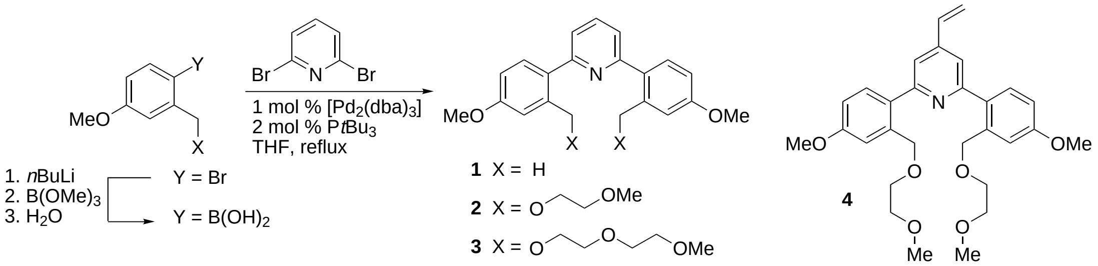
Fluorescent chemosensors provide a powerful optical method for spying on molecular recognition events. As a result, they have found practical application in cellular imaging, environmental monitoring, and biological assays.[1] Chemosensors that allow the measurement of two different emissions bands have the important feature that they permit signal ratioing, which can increase the dynamic range and provide built-in correction for environmental effects.[2] In addition, dual-channel fluorophores allow a change in perceived color as well as simple brightening, facilitating rapid visual assays.

A common feature of dual-channel fluorescent chemosensors is that substrate binding leads to enhancement of one emission channel at the expense of the other. We describe herein an exception to this generalization, in which the combination of two signaling mechanisms—conformational restriction and induction of charge transfer—allows metal binding to turn two fluorescence emission bands on independently.[3]

Biarylpyridines **1**–**4** (Scheme 1) were chosen for the present study because of their synthetic accessibility and modest fluorescence emission from the locally excited (LE) state.[4]

The unanticipated emission from an induced charge transfer (CT) state further extends the versatility of these fluorophores.[5] The emission of **1** (1×10^{-5} M in CH_3CN) is illustrative: the neutral fluorophore exhibits strong LE emission at about 345 nm; on protonation of the pyridine nitrogen atom with trifluoroacetic acid, the LE emission is completely replaced by readily visible CT emission at about 450 nm (Figure 1).

Appending **1** with polyether metal binding domains leads to dual-channel fluorescent chemosensors that are remarkably responsive and selective given their structural simplicity. The titration of **2** (1×10^{-5} M in CH_3CN) with alkali metal and alkaline earth cations is representative (Figure 2). The addition of excess Li^+ leads to strong (5.5-fold at λ_{max}) enhancement of the emission from the LE state, and concomitant increase in quantum yield as a result of binding-induced conformational restriction.[6] In contrast, the addition of Mg^{2+} leads to a slight diminution of LE emission, but an enhancement of CT emission. Notably, the addition of Ca^{2+} leads to simultaneous enhancement of *both* emission bands (Figure 2). The K_a values for the association of **2** with Li^+, Mg^{2+}, and Ca^{2+} are 6.7×10^3 M^{-1}, 8.3×10^2 M^{-1}, and 6.7×10^2 M^{-1} respectively.[7, 8]



Scheme 1. Synthesis of biarylpyridines **1**–**4**. Compound **4** was synthesized analogously to **2** by using the 4-vinyl-substituted pyridine derivative. dba = *trans,trans*-dibenzylideneacetone.

The seemingly minor structural change from **2** to **3** leads to a significantly altered metal-binding profile. While **3** still responds to Li^+, it does so only weakly compared to **2** (I/I_0 at

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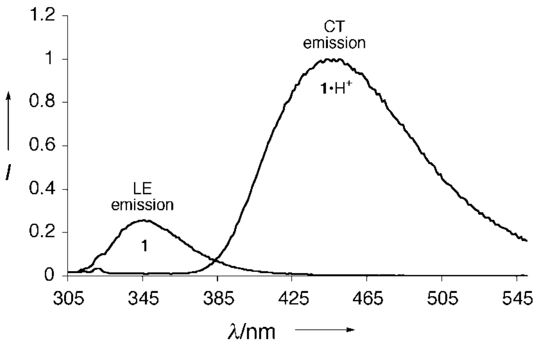

Figure 1. Emission spectra of **1**: the neutral fluorophore **1** exhibits strong LE emission at about 345 nm; the protonated form $\mathbf{1}\cdot H^+$ displays a readily visible CT emission at about 450 nm.

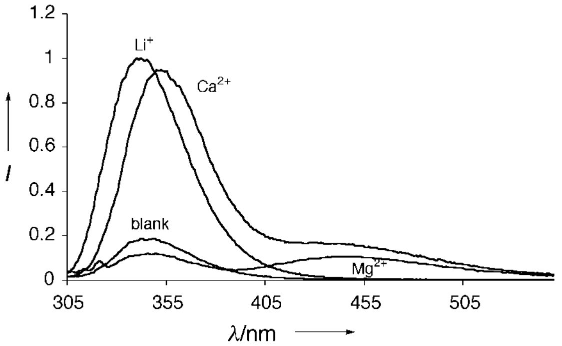

Figure 2. Curves for the titration of **2** (1×10^{-5} M in CH_3CN) with alkaline and alkaline earth cations.

$\lambda_{max} = 2.0$, $K_a = 4.0\times10^2\,\text{M}^{-1}$). Addition of Mg^{2+} again leads to a strong enhancement of CT emission, and the addition of Ca^{2+} leads to >10-fold enhancement of the LE without appreciable induction of CT.[9] The K_a value ($1.7\times10^5\,\text{M}^{-1}$) for the combination of **3** and Ca^{2+} is very high for an acyclic polyether, and is comparable to those measured for K^+ and [18]crown-6 in CH_3CN.[10]

Biarylpyridine **2** is thus capable of uniquely identifying Li^+, Mg^{2+}, and Ca^{2+} ions, while **3** can readily distinguish Mg^{2+} and Ca^{2+} ions, entirely as a result of the independent signaling from two emission channels. To our knowledge, these compounds are the first chemosensors in which both fluorophore and binding mode play a role in determining the response to a given metal ion.

Judicious selection of the excitation and emission wavelengths can further enhance the sensitivity of **2** and **3**. By selectively exciting the LE or CT state, and by surveying I/I_0 ratios at all wavelengths for which emission from **2** is $\geq 50\%$ of its maximum intensity, CT fluorescence enhancements as high as 2500-fold can be observed for Mg^{2+} and as high as 605-fold for Ca^{2+} (Table 1).

Table 1. Summary of the fluoresence emission characteristics for **2** with various alkali metal and alkaline earth cations on selective exicitation of the LE or CT state.

Metal ion	Excitation band	I/I_0 (LE)	I/I_0 (CT)
Li^+	LE	8.5	–
Mg^{2+}	CT	–	2505
Ca^{2+}	LE	6.5	134
Ca^{2+}	CT	–	605

Addition of a 4-vinyl substituent to the pyridine ring (**4**) sufficiently red shifts the LE emission that both LE and CT bands are visible. This visible emission allows $\mathbf{4}\cdot Li^+$, $\mathbf{4}\cdot Mg^{2+}$, and $\mathbf{4}\cdot Ca^{2+}$ to be readily distinguished by eye (Figure 3), and **4** thus combines the sensitivity of fluorescence with the convenience and aesthetic appeal of a colorimetric assay.[11]

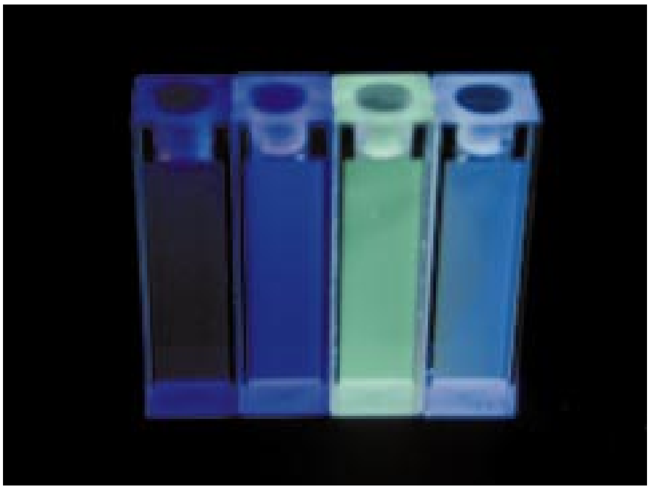

Figure 3. Visible emission observed from samples of **4** and various alkali metal and alkaline earth cations. Left to right: no metal, $\mathbf{4}\cdot Li^+$, $\mathbf{4}\cdot Mg^{2+}$, and $\mathbf{4}\cdot Ca^{2+}$.

In a development that bodes well for the construction of combinatorial libraries of chemosensors,[12] analogs of **4** immobilized on polystyrene resin exhibit similar emission upon UV irradiation. Elaboration of these solid-phase fluorescent chemosensors, as well as further photophysical characterization of **1**–**4**, will be reported in the near future.

Experimental Section

Fluorescence spectra were obtained on a Photon Technologies International QuantaMaster 2000 spectrophotometer, using excitation and emission slit widths of 5 nm. Fluorescence spectra were obtained using 10^{-5} M solutions of **1**–**4** in spectroscopic grade CH_3CN. No efforts were made to exclude H_2O or air. Metal solutions were prepared by dissolution of the appropriate perchlorate salt in spectroscopic grade CH_3CN. Fluorescence titrations were carried out by the addition of small volumes (5–30 μL) of metal solution to 2.50 mL of 10^{-5} M fluorophore in a quartz cuvette; the solutions were allowed to equilibrate to full fluorescence response between aliquot additions. All liquid transfers were carried out with Eppendorf Reference pipettes.

Compounds **1**–**4** were prepared by similar methods; the preparation of **2** is representative (see Scheme 1). 2-(2-Methoxyethoxy)methyl-4-methoxyphenylboronic acid (1.52 g, 6.33 mmol, 2.20 equiv), 2,6-dibromopyridine (0.68 g, 2.88 mmol, 1 equiv), CsF (2.89 g, 19.01 mmol, 6.60 equiv), and tris(benzylidineacetone)dipalladium (0.03 g, 0.03 mmol, 0.01 equiv) were cooled to −78 °C in dry THF (25 mL) under N_2. $PtBu_3$ (1.21 mL, 0.05 M in THF, 0.06 mmol, 0.02 equiv) was added,[13] and the solution degassed by repeated evacuation/N_2-flush cycles. The solution was warmed to room temperature, then heated to reflux for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (100 mL) then washed with H_2O (2 ×) and saturated NaCl (1 ×). The organic layer was dried over $MgSO_4$, concentrated, and chromatographed on silica gel (30% THF–hexanes) to afford **2** (1.29 g, 2.76 mmol, 96%) as a pale yellow highly viscous oil. **2**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (t, 1H, $J = 7.8$ Hz), 7.49 (d, 2H, $J = 8.4$ Hz), 7.42 (d, 2H, $J = 7.6$ Hz), 7.19 (d, 2H, $J = 3.2$ Hz), 6.91 (dd, 2H, $J = 8.6$, 2.6 Hz), 4.73 (s, 4H), 3.86 (s, 6H), 3.55 (m, 8H), 3.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.6$, 157.7, 137.6, 136.3, 132.5, 131.2, 121.5, 113.5, 113.2, 71.9, 71.1, 69.5, 59.1, 55.4; FTIR (neat film): $\tilde{\nu}$ = 2888 (w), 1614 (s), 1445 (s), 1241 (w), 1100 (w), 811 (s) cm^{-1}; HRMS (MALDI): *m*/*z*: calcd for $C_{27}H_{34}NO_6$ [$M+H^+$] 468.2381; found 468.2370; TLC R_f (55% EtOAc/Hex) 0.20.

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[4] Quantum yields were determined by standard methods (J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed., Kluwer, New York, **1999**). The quantum yields of **2** and **3** are 0.027 and 0.024, respectively, using tryptophan in H_2O as a standard ($\phi = 0.13$). We estimate values of ϕ to be accurate to $\pm 25\%$. The excitation maximum for the LE state is 290 nm; the excitation maximum for the CT band is 345 nm.

[5] For a review of fluorescent chemosensors based on induced charge transfer, see: B. Valeur, I. Leray, *Coord. Chem. Rev.* **2000**, *205*, 3–40.

[6] As detailed in our previous analysis of biphenyl-derived fluorescent chemosensors,[3] we reason as follows: no changes are observed in the UV spectrum upon complexation of Li^+, suggesting that the excitation probability (Einstein *A* coefficient), and thus the emission probability (Einstein *B* coefficient) and the rate of radiative decay (k_r), remain constant; the energetic separation of the S_1 and S_0 potential energy surfaces is sufficient (> 60 kcal mol^{-1}) to preclude internal conversion ($k_{ic} \approx 0$); increased quantum yield must thus arise from decreased intersystem crossing (ISC); k_{ISC} is known to increase with dihedral angle, and binding-induced conformational restriction thus leads to reduction in k_{ISC}.

[7] Association constants were determined by nonlinear least-squares fitting of lg[metal] versus I/I_0 plots. Curve fitting was carried out with the Prism3 software package (Graphpad, Inc., San Diego, CA). The reported K_a values have 95% confidence limits of ± 0.1 lg K_a units. In all cases reported here curve fitting is consistent with the formation of 1:1 metal/ligand complexes.

[8] Titration of **2**–**4** with Na^+ or K^+ does not lead to appreciable change in fluorescence emission.

[9] Both **2** and **3** respond slowly to Mg^{2+}. In the case of **3**, the hysteresis is severe enough to make K_a determination impractical. We tentatively ascribe the differences in the responses of **2** and **3** to coordination of Li^+ and Ca^{2+} by the distal oxygen atoms of the ether chain, although details of these interactions remain to be elucidated.

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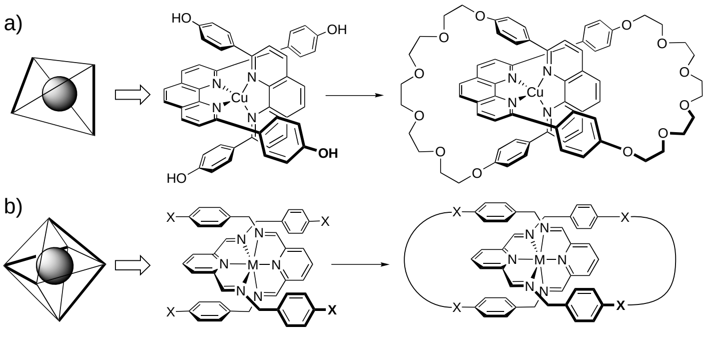
Benzylic Imine Catenates: Readily Accessible Octahedral Analogues of the Sauvage Catenates**

David A. Leigh,* Paul J. Lusby, Simon J. Teat, Andrew J. Wilson, and Jenny K. Y. Wong

Historically, one of the triumphs of coordination chemistry has been its application to the synthesis of mechanically interlocked molecular architectures, that is catenanes, rotaxanes, and knots.[1–10] In 1984 Sauvage et al. used the preferred tetrahedral geometry of Cu^I to organize appropriately derivatized phenanthroline ligands into a fixed mutually orthogonal orientation, whereupon a double macrocyclization reaction gave the [2]catenate in 27% yield (Scheme 1a).[2]



Scheme 1. Synthesis of catenates by orthogonalization of coordinated ligands about metal templates with a) tetrahedral and b) octahedral coordination preference. M in (b): Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}.

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