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Luminescence Lifetime-Based Sensor for Cyanide and Related Anions

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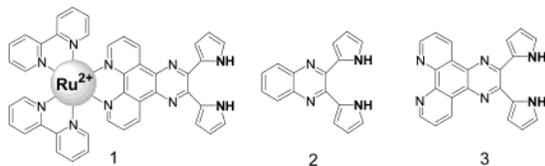
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Inorganic anions such as chloride, fluoride, and phosphate continue to be extensively used as food additives, drugs, and agricultural fertilizers. Cyanide has common industrial use as a raw material in the production of organic chemicals and polymers such as nitriles, nylon, and acrylic plastics.¹ Cyanide is also critical to the gold-extraction process.² Thus, the widespread application of cyanide raises a number of environmental concerns, particularly in terms of its retention in leach circuits, recovery, and potential for contamination.² These issues necessitate the development of sensor molecules that can adequately detect these anions in a variety of settings.

Optical sensors for anions have recently received considerable attention, focused mainly upon the supramolecular chemistry of receptor design.³ The binding event is typically monitored by changes in color, fluorescence intensity, or both from a chromophore covalently attached to the receptor.⁴ Competitive noncovalent chromophore-displacement methods have also been devised for the optical sensing of anions.⁵ Regardless of sensor function, both organic^{3a,4} and inorganic⁶ moieties have been employed as chromophores in emission intensity-based sensors for inorganic anions.

Unfortunately, the performance accuracy of sensors based on fluorescence intensity measurements can be limited by many factors including excitation source intensity fluctuations, light loss in the optical path, light scattering, and detector drift.⁷ Signal transduction utilizing emission lifetimes (lifetime-based chemical sensing) is particularly attractive, because it is unaffected by the sample's emission intensity, thereby circumventing many limitations of intensity-based methods.⁷ In this contribution, we report a new anion sensor based on a luminescent Ru(II) metal complex and 2,3-di-(1*H*-2-pyrrolyl)quinoxaline receptor (**1**),⁸ representing the first example of a direct luminescence lifetime-based sensor for anions.



The complex **1** combines the luminescence characteristics of Ru(II) diimine compounds possessing metal-to-ligand charge transfer (MLCT) excited states⁹ with the anion recognition capabilities of 2,3-di-(1*H*-2-pyrrolyl)quinoxaline, DPQ (**2**).¹⁰ The 1,10-phenanthroline-containing DPQ ligand (**3**) was prepared by condensation of 1,10-phenanthroline-5,6-diamine¹¹ with 1,2-di-(1*H*-2-pyrrolyl)ethane-1,2-dione in 75% yield. The reaction of **3** with Ru(bpy)₂Cl₂¹² followed by a treatment with NH₄PF₆ (aq) and chromatography over Sephadex LH-20 afforded **1** in 54% yield.

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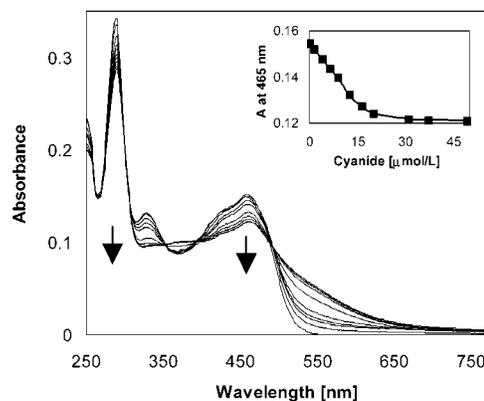


Figure 1. Changes in the UV-vis spectrum of sensor **1** (9.04 μM in CH₂Cl₂/CH₃CN (98:2)) upon the addition of cyanide (0–49.02 μM). (Inset) Binding isotherm monitored by the absorbance decrease at 465 nm.

The anion binding affinity of **1–3** was evaluated by monitoring their respective UV-vis and steady-state emission properties as a function of anion concentration. Time-resolved photoluminescence decays were also measured for **1** to test its viability as a lifetime-based sensor for anions. [Ru(bpy)₃](PF₆)₂ (**4**) served as a parallel control for all experiments that incorporated **1**. Air-equilibrated solutions were used for all measurements to appropriately simulate real-world sensing conditions. Preliminary investigations revealed that fluoride, chloride, dihydrogenphosphate, and cyanide, available as tetra-*n*-butylammonium salts, would serve as substrates for **1–3** in CH₂Cl₂/CH₃CN (98:2). An addition of fluoride, cyanide, and (to a lesser extent) phosphate to 9 μM solutions of **1–3** caused significant changes to the UV-vis and steady-state emission properties in all three receptors. For brevity, only the spectroscopic data for **1** obtained from the titration with cyanide will be discussed in detail. These results are of particular importance, given the lack of suitable emission-based cyanide sensors presently available. The UV-vis and emission titrations of **1** and **3** with various halides and polyatomic anions are reported in Supporting Information.

Figure 1 presents the changes in the UV-vis spectrum of **1** as a function of CN⁻ concentration. The low-lying MLCT absorption and the high-energy π-π* ligand-based absorptions decrease monotonically throughout the addition, with saturation observed toward the end of the titration. A low-energy absorption feature concomitantly grows in with increasing CN⁻ concentration. These absorption features are likely a result of anion binding with the metal complex through the DPQ receptor. In control experiments with [Ru(bpy)₃]²⁺ the addition of CN⁻ did not have a marked effect on the absorption spectrum at the low concentrations used in the titration.¹³

Figure 2 presents the quenching of the steady-state photoluminescence spectrum of **1** measured throughout the cyanide titration. In all luminescence experiments, the excitation wavelength corre-

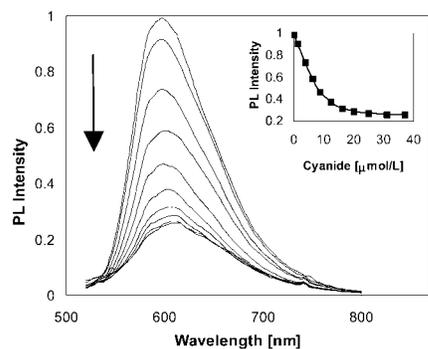


Figure 2. Changes in photoluminescence intensity of sensor **1** ($9.04 \mu\text{M}$) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (98:2) upon the addition of cyanide ($0\text{--}38.79 \mu\text{M}$). (Inset) Binding isotherm monitored by the integrated luminescence intensity. $\lambda_{\text{ex}} = 493 \text{ nm}$ (isosbestic point in UV-vis spectra).

Table 1. Affinity Constants^a for Compounds **1**, **2**,^{10b} and **3** (mol^{-1}) and Anionic Substrates in 2% Acetonitrile in Dichloromethane at 22°C

| anion | Ru ²⁺ sensor (1) | DPQ (2) | ligand (3) |
|---|--------------------------------------|------------------|---------------------|
| F ⁻ | 640 000 | 18 200 | 68 000 |
| CN ⁻ | 428 000 | 220 | 3 450 |
| Cl ⁻ | 1 700 | 50 | < 500 |
| H ₂ PO ₄ ⁻ | 14 000 | 60 | 1 620 |

^a Anions used in this assay were in the form of their tetrabutylammonium salts. Fits were performed using single reciprocal plots and 1:1 stoichiometry being obtained from Job plots.

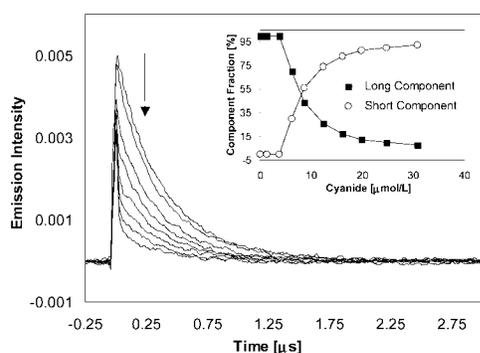


Figure 3. Changes in the time-resolved PL decay of sensor **1** ($9.04 \mu\text{M}$) upon the addition of cyanide ($0\text{--}32 \mu\text{M}$), obtained with 458 nm excitation. (Inset) Shifts in fractional intensity of the two lifetime components obtained from biexponential analysis. See text for details.

sponds to the isosbestic point found at 493 nm , Figure 1. The emission spectrum red-shifts with increasing CN^- concentration from 594 to 610 nm , indicating a lowering in energy of the excited state and enhancement of nonradiative decay.^{6c} The inset in Figure 2 shows the isotherm for the luminescence intensity titration of **1** by CN^- . Table 1 summarizes all of the emission data-derived binding constants measured for **1**–**3** toward different anions. Compound **1** clearly possesses the strongest binding affinity for F⁻ and CN^- . In all cases the binding constants are substantially enhanced (orders of magnitude) in **1** relative to **2**^{10b} and **3**. We believe this to be caused by the Ru(II) center, which makes the DPQ-ligand electron-deficient, thereby rendering the pyrrolic NHs of **1** more available for hydrogen bonding to the anions.

Figure 3 presents the luminescence lifetime quenching of **1** as a function of the cyanide concentration. Prior to the cyanide addition, **1** exhibited a single-exponential lifetime ($\tau = 377 \pm 20 \text{ ns}$) in our solvent mixture. During the first three cyanide additions, the intensity decays could be adequately fit to a single exponential model; however, the lifetime shortened minutely to $341 \pm 20 \text{ ns}$

($[\text{CN}^-] = 6.20 \mu\text{M}$). At higher CN^- concentrations, the intensity decays exhibited complex kinetics that adequately fit a sum of two exponentials. Both exponential components remained effectively constant, ranging from 320 to 370 ns (long τ) and 13 to 17 ns (short τ). The short component lies near our IRF, and thus these lifetimes may in fact be shorter. Importantly, the average lifetimes shorten as a function of the CN^- concentration since the fractional intensity shifts from an initial dominant long lifetime component to the short lifetime component as the CN^- concentration increases, Figure 3 inset. These data suggest that there are at least two distinct luminescent species, consisting of anion-bound **1** (short τ) and free **1**, the sum of which results in the observed lifetime quenching in Figure 3. Fortunately, the shift in fractional intensity makes **1** a suitable lifetime-based sensor for anions.

In summary, we have prepared the first sensor based on the direct observation of anion-induced luminescence lifetime changes. The proof-of-concept experiments described here suggest that metallo-complexes such as **1** open up the possibility for producing novel materials and approaches to anion sensing.

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Supporting Information Available: Experimental procedures for the preparation of **1** and **3**, Job plots and titration results (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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