Sensing Alkali and Alkaline Earth Metal Cations by Conduction Band Quenching of Dye Photoluminescence

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A new luminescence approach for sensing alkali and alkaline earth metal cations in fluid solution at room temperature is described. The approach is to utilize surface-adsorption/desorption–induced energetic shifts of a semiconductor conduction band to alter the electron transfer quenching efficiency of a photoluminescent dye. A proof-of-concept example is described based on TiO_2 nanoparticles with a surface bound Ru(II) coordination compound as the dye, $Ru(deeb)(bpy)_2(PF_6)_2$ where deeb is $4,4'-(CO_2CH_2CH_3)_2-2,2'$-bipyridine and bpy is $2,2'$-bipyridine, sensing alkali and alkaline earth metal cations in acetonitrile solution. The Ru(II) compound is highly luminescent with long excited state lifetimes in the absence of the cations but is quenched in their presence. The quenching is found to be reversible. The data demonstrate that this approach yields intensity, lifetime, and wavelength-ratiometric calcium ion sensors that are sensitive to 5×10^{-4} M concentrations.

INTRODUCTION

There is widespread interest in dye-sensitized nanocrystalline TiO_2 films for applications in solar energy conversion [1]. The most promising dyes for these solar cells are Ru(II) polypyridyl transition metal compounds. The TiO_2 films are comprised of ~20-nm anatase particles interconnected in a 10-μm mesoporous sponge-like layer deposited on a conductive glass substrate. Anatase is one of the three common crystalline forms of TiO_2, with a 3.2-eV bandgap that does not appreciably absorb visible light. In the accepted sensitization mechanism, the dye injects an electron into the semiconductor conduction band from its excited state. For Ru polypyridyl excited states, electron injection often occurs on a pico- to femtosecond time scale, k_{inj}, whereas recombination of the injected electron with the oxidized ruthenium compound occurs on a micro- to milli-second time scale [1]. Ru(II) polypyridyl compounds with carboxylic acid groups or ester groups are known to bind tenaciously to the TiO_2 surface. Under basic surface conditions, the semiconductor-dye linkage appears to be a carboxylate [1].

An important aspect of the sensitization process is that the position of the conduction band edge, E_{CB}, can be tuned in energy with respect to that of the dye. For example, in aqueous solution E_{CB} shifts positive (away from the vacuum level) by 59 mV/pH unit [2]. Therefore, with a pH-insensitive dye, conduction band quenching of the luminescent excited dye is favored as the pH is lowered (Scheme) [3]. We recently found that Li^+ adsorption to TiO_2 from acetonitrile solutions also shifts E_{CB} positive, resulting in more favorable overlap with the dye excited state donor levels and thus more favorable injection [4]. Detailed transient absorption studies of $Ru(deeb)(bpy)_2^{2+}$, where bpy is $2,2'$-bipyridine and deeb is $4,4'-(CO_2CH_2CH_3)_2-2,2'$-bipyridine, anchored to TiO_2 confirm a conduction band quenching mechanism [4]. Here we describe our initial efforts at exploiting this

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Scheme 1
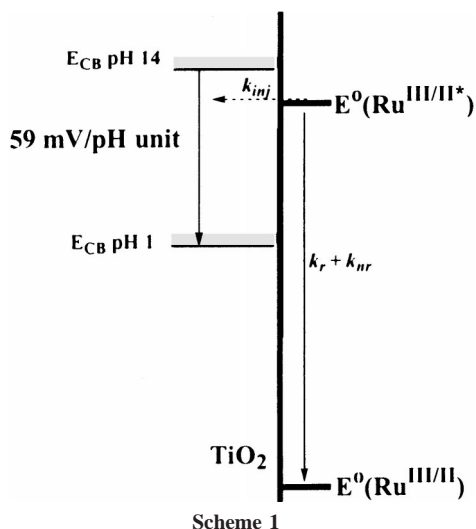
behavior for luminescent sensor applications with a specific emphasis on Ca^{2+} sensing. We describe the successful demonstration of intensity-, wavelength- ratiometric–, and lifetime-based cation sensors [5]. The possible benefits and limitations of these sensors for practical applications are also discussed.

EXPERIMENTAL SECTION

Materials

Reagents

Acetonitrile (99.5+% A.C.S.), calcium perchlorate (99%), lithium perchlorate (99.99%), sodium perchlorate (99%), and magnesium perchlorate were obtained from Aldrich. Tetra-n-butyl ammonium perchlorate (99+%) was obtained from Alfa Aesar.

Preparation of Sensitized TiO_2 Films

The preparation of TiO_2 films and the attachment of the Ru(deeb)(bpy)$_2$(PF$_6$)$_2$ sensitizer have been previously described. Briefly, the hydrolysis of titanium isopropoxide in dilute nitric acid forms small TiO_2 particles which are subsequently heated under pressure and cooled to room temperature [6]. Addition of poly(ethylene) glycol yields a glue-like paste that was deposited on glass slides (VWR) and annealed in the oven at 420°C for 30 min. The cooled TiO_2 films were placed in an aqueous pH 11 solution for 30 min, air-dried, and then dried under vacuum for 30 min. The TiO_2 films were then placed in m*M*

acetonitrile solutions of Ru(deeb)(bpy)$_2$(PF$_6$)$_2$ overnight. The samples were rinsed with copious amounts of acetonitrile prior to optical studies.

Optical Studies

In all optical studies, the sensitized films were placed diagonally in a 1-cm-square fluorescence cuvette filled with acetonitrile or acetonitrile electrolyte solutions in air. UV-Vis absorbance measurements were made on a Hewlett-Packard 8453 diode array spectrophotometer. Steady-state photoluminescence measurements were carried out on a Spex Fluorolog that was calibrated with a standard tungsten-halogen lamp by procedures detailed by Spex. The cuvette in the Spex Fluorolog was positioned so that the excitation beam was incident 45 degrees to the film surface, and emitted light was monitored from the front face of the sample assembly. Time-resolved photoluminescence data were acquired in the time-domain with an N_2 dye laser excitation source and a monochromator/photomultiplier detector, similar to one that has been previously described [7].

RESULTS

Figure 1 shows the absorption spectra of Ru(deeb)(bpy)$_2^{+2}$ anchored to a mesoporous nanocrystalline TiO_2 film, abbreviated Ru/TiO_2, and immersed in neat acetonitrile. The broad absorption band centered at 460 nm is typical of metal-to-ligand charge-transfer (MLCT) excited states [8]. The total surface coverage was system-
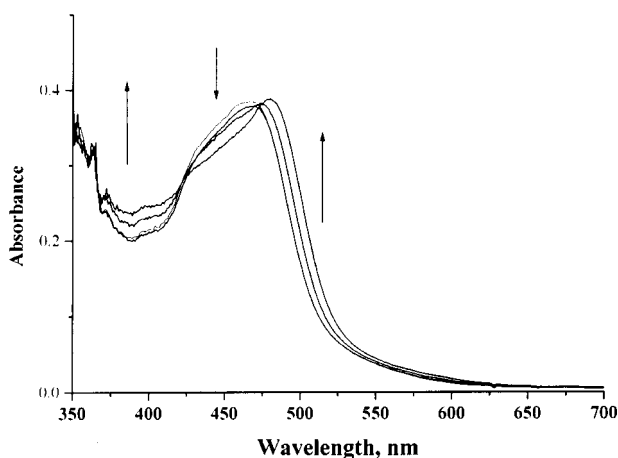

Fig. 1. Absorption spectra of Ru/TiO_2 in the presence of 0, 5.0×10^{-6}, 5.0×10^{-4}, 5.0×10^{-2} M Ca(ClO$_4$)$_2$ in acetonitrile at room temperature. The arrows indicate the spectral shifts observed as the [Ca^{2+}] concentration was increased.

atically tuned by changing the Ru concentration in the acetonitrile derivatizing solution. The absorption at the MLCT band could be routinely varied from below the detection limits to 0.6 absorbance units.

The addition of Ca^{2+} to the acetonitrile solution induces a red shift in the absorption band and a slight absorbance decrease at 460 nm (see Fig. 1). At mM and higher Ca^{2+} concentrations the appearance of two discrete MLCT bands becomes more apparent. An isosbestic point is observed at 475 nm.

Figure 2 shows the corrected photoluminescence, PL, spectra of Ru/TiO$_2$ at the indicated Ca^{2+} concentrations. The PL intensity decreases significantly with increasing [Ca^{2+}], and the PL maximum shifts to longer wavelengths. The spectral shift begins to become salient at 10^{-4} M concentrations and higher and can be utilized for ratiometric sensing. Experiments in which the solution was alternated between neat acetonitrile and Ca^{2+}/acetonitrile solutions demonstrate that the PL quenching is largely reversible. The inset shows the ratio of PL intensities measured at two selected wavelengths, 654 and 684 nm PLI$_{654}$/PLI$_{684}$, as a function of Ca^{2+} concentration. Absorbance measurements made before and after PL experiments confirmed that no significant desorption of the Ru compounds occurred.

Shown in Fig. 3 are time-resolved PL decays recorded after pulsed 460 nm light excitation of Ru/TiO$_2$ as a function of Ca^{2+} concentration in acetonitrile. The transient data shows both dynamic and static quenching components as the Ca^{2+} concentration is increased. The static component corresponds to the change in the time zero amplitude. Sensitivity for just the static component
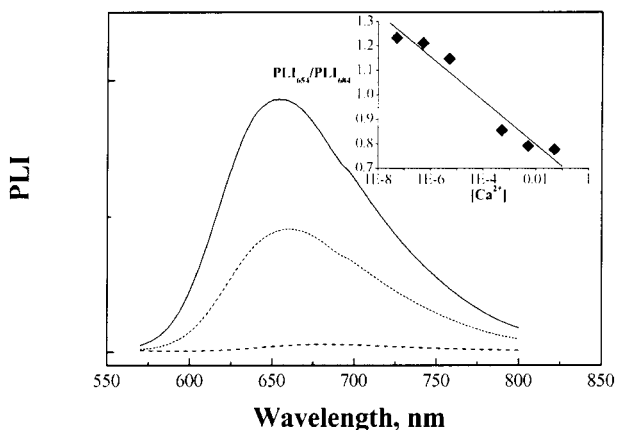
Fig. 2. Photoluminescence spectra of Ru/TiO$_2$ in the presence of 0 (solid line), 5.0×10^{-6} M (dotted line), 5.0×10^{-4} M (segmented dotted line), 5.0×10^{-2} M (dashed line) Ca(ClO$_4$)$_2$ in acetonitrile. The inset shows the photoluminescence intensity, PLI, ratios measured at 654 and 684 nm for this same data. The sample was excited with 460-nm light at room temperature.
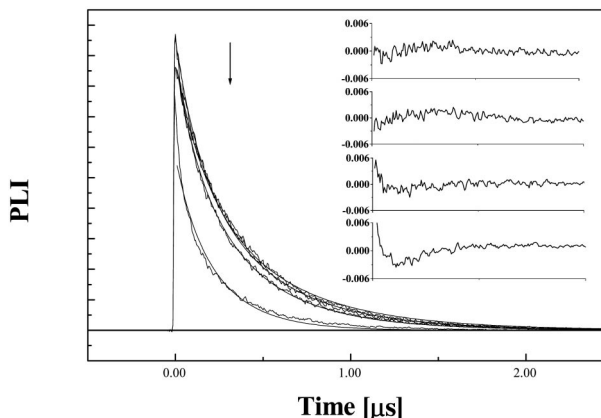
Fig. 3. Time-resolved photoluminescence decays recorded at 640 nm after pulsed 460-nm excitation of a Ru/TiO$_2$ film in acetonitrile. The arrow indicates the effect of increasing Ca^{2+} concentrations from top to bottom: 0, 5.0×10^{-6}, 5.0×10^{-4}, 5.0×10^{-2} M. Each decay shown represents an average of 80 laser pulses. Fits to a parallel first- and second-order kinetic model are superimposed on each decay. Residuals over the first microsecond are shown as an inset.

of quenching was observed at millimolar concentrations of calcium perchlorate. The traces show sensitivity to the low concentrations examined.

The PL decays in neat acetonitrile were non-exponential but were adequately fit to a parallel first- and second- order kinetic model [Eq. (1)]:

$$PLI\,(t) = \frac{C\,k_1 \exp\,(-k_1\,t)}{k_1 + k_2\,C - k_2\,C \exp\,(-\,k_1\,t)} \qquad (1)$$

where C is the excited state concentration, k_1 is the first-order rate constant, and k_2 is the observed second-order rate constant. The first-order component corresponds to unimolecular, radiative, and non-radiative decay while the deactivation of the excited state by a second-order process implies that a competitive excited state–excited state deactivation pathway exists. Efficient intermolecular energy transfer between the surface bound dyes leads to second-order equal concentration triplet-triplet annhilation processes [4]. The residuals (inset, Fig. 3), show that the quality of the fits decrease with increasing Ca^{2+} concentration. By fixing the second-order rate constant to the value obtained in neat acetonitrile, $k_2 = 2.3 \times 10^7$ s^{-1}, it was found that the first-order rate constant decreased with increasing calcium concentration (Table I).

The generality of the findings were tested with tetrabutyl ammonium (TBA$^+$), Na$^+$, Mg^{2+}, and Li$^+$ in acetonitrile and propylene carbonate. In all cases, the addition of the cations resulted in bathochromic spectral shifts, PL intensity decreases, and lifetime quenching. The sensi-

Table I. Excited State Quenching of Ru/TiO_2 with $|Ca^{2+}|^a$

$|Ca^{2+}|^b$	k_1 $(s^{-1}) \times 10^{-6c}$
0	1.9
5×10^{-6}	1.7
5×10^{-4}	2.2
5×10^{-2}	3.9

[a] All experiments performed at room temperature in acetonitrile, where Ru/TiO_2 is $Ru(deeb)(bpy)_2(PF_6)_2$ attached to anatase TiO_2.
[b] Molar $Ca(ClO_4)_2$ concentration.
[c] First-order rate constants abstracted from fits of the data in Fig. 3 to Eq. One.

tivity in propylene carbonate to 1 M concentrations was found to be $TBA^+ << Na^+ < Li^+ < Ca^{2+} < Mg^{2+}$.

DISCUSSION

The spectral features for Ru/TiO_2 in acetonitrile are typical of MLCT excited states and are consistent with previous work [4,8]. The TiO_2 surface hydrolyzes the ethyl esters and the carboxylate groups bind to the semiconductor surface. The carboxylate substituents are only slightly electron donating and the $Ru \rightarrow bpy$ and $Ru \rightarrow dcb$, where dcb is $4,4'-(CO_2^-)$-bpy, absorption bands overlap [4]. The addition of Ca^{2+} to the acetonitrile solution results in a red shift of the MLCT absorption band that is reasonably attributed to stabilization of the $Ru \rightarrow dcb$ charge transfer band. It is unclear whether the Lewis acidic Ca^{2+} interacts directly with the carboxylate groups or if its interactions with the TiO_2 surface indirectly induces the observed spectral shift.

The PL intensity Ru^*/TiO_2 is reversibly quenched by the addition of Ca^{2+}. Based on previous transient absorption studies, the quenching mechanism is reasonably attributed to excited state electron transfer to the TiO_2 conduction band [4]. The injected electron is known to recombine with the oxidized dye on a millisecond or faster time scale such that no net chemistry occurs [1]. The fact that Ca^{2+} quenching is not observed in the absence of TiO_2 supports this conclusion. That is, the addition of Ca^{2+} to an acetonitrile solution of $Ru(deeb)(bpy)_2^{+2}$ does not alter the absorption or emission properties. The PL quenching is detectable at 5×10^{-4} M. The red shift that accompanies the PL quenching has been exploited for ratiometric sensing. Although the spectral shift is relatively small, it is easily measurable and a calibration curve over a wide dynamic range of concentrations can be obtained. This circumvents the well-documented difficulties associated with luminescence intensity–based sensors [5].

Time-resolved PL decays of Ru/TiO_2 are adequately described by a parallel first- and second-order kinetic model. Previous work has shown that efficient intermolecular energy transfer across the semiconductor surface, $Ru^*/TiO_2 + Ru/TiO_2 \rightarrow Ru/TiO_2 + Ru^*/TiO_2$ occurs [4,9]. Energy transfer can translate two excited states proximate to one another that can then subsequently react by a second-order triplet–triplet annihilation process. Therefore the second-order component can be minimized by utilizing low irradiances and surface coverages. The first-order rate constant arises from parallel radiative and non-radiative decay processes. In the presence of Ca^{2+} an alternative relaxation pathway exists and the first-order rate constant decreases monotonically with increased Ca^{2+}, indicating that these materials are useful as lifetime-based sensors.

In addition to dynamic quenching of the excited state, a significant static component was observed that was most prominent between 5×10^{-4} and 0.05 M Ca^{2+}. The static component is partially due to the ground state absorption and PL spectral changes, but some underlying static process(es) must be invoked to explain the magnitude of the effect. A model consistent with this observation and literature reports [4], is that the static component arises from electron injection from "hot" vibrational excited states. Interfacial electron transfer from Ru excited states is known to be a fast process, typically occurring on a femto- to pico-second time scale [10]. Injection from hot vibrational excited states effectively decreases the intersystem crossing yield and is manifest as a static component. When injection occurred from the emissive state, the excited state lifetime should decrease to the reciprocal injection rate, and only dynamic components are observed. An alternative explanation is that the static component arises from surface heterogeneity and that only those Ru compounds proximate to a surface adsorbed Ca^{2+} are able to inject electrons into the semiconductor. This model is not favored because efficient energy migration across the semiconductor surface is known, and such a model would lead to energy transfer limited interfacial electron injection, contrary to what is observed.

CONCLUSIONS

Semiconductor conduction band quenching of dye photoluminescence has been investigated for applications in cation sensing. Proof-of-concept intensity, lifetime, and wavelength-ratiometric calcium ion sensors have been realized. The further development of this approach for real-world sensors seems very worthwhile. The extension

to aqueous solution for biological applications can in principle be achieved with alternative phosphonate dye-semiconductor linkages [11]. A single semiconductor nanoparticle, rather then the mesoporous thin films described herein, may be directly coupled to fiberoptics for remote and *in situ* sensing [4]. Finally, arrays of luminescent dye molecules with different excited state reduction potentials may be used to simultaneously sense multiple cations.

ACKNOWLEDGMENT

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