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Luminescence-based assessment of thermodynamic constants for electrostatic binding of non-luminescent dyes and atomic ions to colloidal semiconductor surfaces

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Abstract

Steady-state and time-resolved luminescence experiments were employed to study the electrostatic interaction of cationic photosensitizers and negatively charged colloidal semiconductor particles. Electrostatic adsorption of efficient photosensitizers on semiconductor surfaces is known to quench the photosensitizers' luminescence. By monitoring the quenching, either directly or competitively, thermodynamic constants for binding of both luminescent and non-luminescent ruthenium and osmium complexes to negatively charged SnO_2 particle have been determined. The function of atomic cations, such as Li^+, Na^+ and K^+, in controlling the binding of cationic dyes to colloidal SnO_2 has also been studied via competitive luminescence. From the study, semiconductor surface binding constants for these species have also been determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Binding constant; Electrostatic binding; Semiconductor surface

1. Introduction

Investigations of photo-induced charge-transfer between dye sensitizers and wide bandgap semiconductor films and particles are of considerable interest in the context of visible-region solar energy conversion (light-to-electricity conversion) via photoelectrochemical methods [1–4]. A prerequisite for efficient photosensitization is that the dye be adsorbed or otherwise attached to the semiconductor surface. Most investigations have been focused on sensitization by complexes covalently attached to the semiconductor surfaces [5–8]. Electrostatic binding of a cationic dye to a semiconductor featuring net negative surface charges also provides an interesting approach for surface sensitization. The way that dye is bound to the semiconductor surface can sometimes profoundly influence the mechanism and kinetics of the electron transfer process [9,10] and the efficiency of energy conversion [11–14]. Therefore, understanding the binding properties of photosensitizer and colloidal semiconductor is of particular importance in both fundamental studies and applications of the photosensitization systems.

We report here binding studies for systems composed of colloidal SnO_2 and electrostatically attached cationic photosensitizers of the form $Ru^{II}L_3{}^{2+}$ and $Os^{II}L_3{}^{2+}$ ($L =$ 2,2′-bipyridine or derivatives of 1,10-phenanthroline). SnO_2 is a wide bandgap (3.5 eV) semiconductor, featuring a net negatively charged surface at $pH > 4.8$ due to the ionization of SnOH groups [15]. Ruthenium(II) and osmium(II) tris(polypyridyl) dyes are typically luminescent, and the luminescence is quenched via transfer of an electron to the conduction band of the SnO_2 particle [16]. By monitoring the quenching process under steady-state illumination conditions, and assuming that direct contact between the dye and the colloidal particle is required for appreciable quenching, the binding equilibrium constant can be evaluated. Since the adsorption of $M^{II}L_3{}^{2+}$ species at colloidal SnO_2 surfaces is dominated by electrostatic interactions, screening the charge on the particle surface via competitive adsorption of another cation can alter the binding equilibrium and, consequently, the intensity of luminescence of the sensitizing dye [17]. We illustrate below how the competition and the alteration of luminescence intensity can be used to determine the binding constant of a non-luminescent dye as well as binding constants for non-chromophoric cations.

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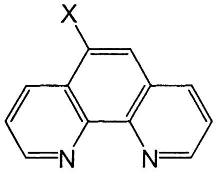
2. Experimental section

About 15% tin(IV) oxide, as a colloidal dispersion in water, was obtained from Alfa/Aesar and used as received. The counter ion was K^+. The average particle diameter, as reported by the manufacturer, was 15 nm. The pH of the colloidal dispersion was pH 9.5–10.5. The compound 1,10-phenanthroline (phen), and its derivatives, 5-methyl-1,10-phenanthroline (5-methyl-phen), 5-chloro-1,10-phenanthroline (5-chloro-phen), and 5-nitro-1,10-phenanthroline (5-nitro-phen), were purchased from GFS Chemical Co. (see drawing). $RuCl_3 \cdot H_2O$, used for synthesis of some complexes, was purchased from Aesar. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ and $Ru(phen)_3Cl_2 \cdot H_2O$ were purchased from Aldrich. All other ruthenium(II) and osmium(II) complexes were prepared by modifications to published methods [18,19].



5-X-1,10-phenanthroline; X = H, CH_3, Cl, or NO_2

Absorbance spectra were obtained by using a Hewlett Packard 8452A diode array spectrophotometer. Steady-state luminescence studies were performed on an ISA Fluorolog-3 spectrofluorimeter in air-equilibrated solutions by excitation, typically, near the absorption maximum of the photosensitizer. Luminescence lifetimes were measured by using the 473 nm output of a small dye laser pumped by a PRA model LN1000 nitrogen laser (~5 Hz, 300–700 ps pulse width) as the excitation source; the resulting emission was monitored at 605 nm. All data were collected at ambient temperature, and all the simulation work was done using SigmaPlot software (SPCC Inc.).

3. Results and discussion

3.1. Binding of luminescent dye molecules to colloidal SnO_2 particles

The adsorption of solutes from aqueous solution onto a colloidal particle surface is a process involving dynamic equilibrium [20]. Assuming equivalent, non-interacting adsorption sites, the binding equilibrium should be describable by the Langmuir isotherm, Eq. (1).

$$KC = \frac{\theta}{1-\theta} \tag{1}$$

where K is the adsorption equilibrium constant (binding constant), C the solution-phase concentration of the solute, and θ is the surface coverage, i.e. the fraction of binding sites that are occupied. To formulate the Langmuir isotherm in a form convenient for the luminescent dye/SnO_2 systems, the parameters C and θ are replaced with $C = C_T - \theta C_{sat}$ and $\theta = C_T(1 - I/I_0)/C_{sat}$, where C_T is defined as the total concentration of dye (bound and free), and C_{sat} the concentration of dye at binding saturation. In other words, C_{sat} is the solution-phase concentration corresponding to the amount of dye needed to saturate the colloidal semiconductor surface, under the hypothetical condition where all available dye is bound. The term θC_{sat}, therefore, corrects for dye solution-phase concentration depletion due to adsorption. I and I_0, respectively, are the luminescence intensities of the sensitizing dye in the presence and absence of colloidal SnO_2. With these changes, the Langmuir isotherm can be expressed as

$$K\frac{I}{I_0} = \frac{1-(I/I_0)}{C_{sat} - C_T(1-(I/I_0))} \tag{2}$$

Binding to colloidal SnO_2 has been quantified for several dyes by fitting the dye-concentration-dependent luminescence response to Eq. (2). Fig. 1 is a representative plot of I/I_0 for $Ru(bpy)_3{}^{2+}$ as a function of the total concentration of the dye. The concentration of colloidal SnO_2 particle was fixed at $0.056\,g\,l^{-1}$. The solid line, which is a best-fit curve of the data to the Langmuir isotherm, corresponds to a binding constant of $2.5 \times 10^6\,M^{-1}$ and a C_{sat} value of $6.7 \times 10^{-6}\,M$. The results obtained with other cationic dyes are reported in Table 1. The value measured for $Ru(bpy)_3{}^{2+}$ agrees within about a factor 4 with values obtained in a similar way by Mulvaney et al. [16] and Ford et al. [11,14] — albeit, for slightly different forms of the colloid and slightly different forms of the isotherm. Ford and co-workers found it necessary to include a small adsorbate–adsorbate attraction term in their isotherm; omitting this term should yield larger K values.

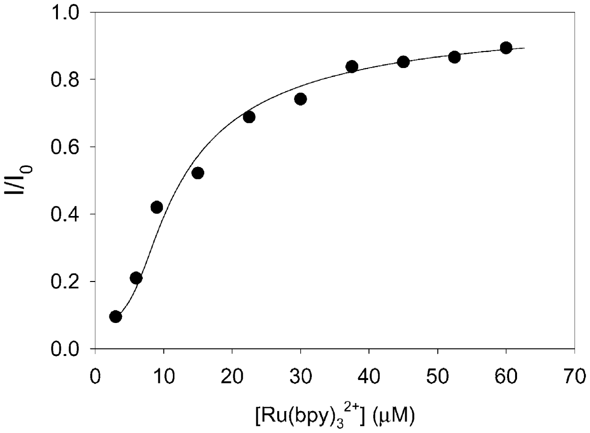


Fig. 1. Plot of I/I_0 for $Ru(bpy)_3{}^{2+}$ molecules as a function of the total concentration of the dye in the presence of $0.056\,g\,l^{-1}$ SnO_2 particle. The curve drawn is the best-fit to the Langmuir isotherm, Eq. (2).

Table 1
Binding constants and saturation concentrations of some dye molecules on 0.056 g l^{-1} colloidal SnO_2

Dye molecules	K (M^{-1})	C_{sat} (M)
$Ru(bpy)_3^{2+}$	$(2.5 \pm 0.2) \times 10^6$	$(6.7 \pm 0.5) \times 10^{-6}$
$Ru(phen)_3^{2+}$	$(0.9 \pm 0.1) \times 10^6$	$(8.5 \pm 1.0) \times 10^{-6}$
Ru(5-methyl-phen)$_3^{2+}$	$(1.2 \pm 0.1) \times 10^6$	$(6.5 \pm 0.7) \times 10^{-6}$
Ru(5-chloro-phen)$_3^{2+}$	$(1.3 \pm 0.1) \times 10^6$	$(8.1 \pm 0.8) \times 10^{-6}$
$Os(phen)_3^{2+}$	$(1.8 \pm 0.2) \times 10^6$	$(6.6 \pm 0.7) \times 10^{-6}$

Despite the structural similarities, modest differences in binding constant do exist for the series of dyes (factor of 2.7 or less). We are unable to rationalize the differences on chemical grounds. The values of C_{sat}, on the other hand, are constant, within ±15% as one would expect, for a series of similarly sized and identically charged complexes.

3.2. Binding of non-luminescent dye molecules to colloidal SnO_2 particles

Equilibrium constants for the binding of non-luminescent dye molecules to colloidal semiconductor particles obviously cannot be obtained directly from emission measurements. We reasoned, however, that the desired values could be obtained indirectly via competition with a luminescent reporter dye for the available binding sites. As suggested in Scheme 1, adsorption of a non-luminescent dye on a surface initially covered with reporter dye molecules will lead to displacement of some fraction of the reporter dye, with concomitant increase in photoluminescence due to an increase in the number of reporter dye molecules present in solution. In designing such an experiment, however, it is important to avoid complications due to absorption losses (see below) and due to chemical or photochemical interactions between the luminescent and non-luminescent dyes.

For two-component adsorption — a non-luminescent dye and a reporter dye — the Langmuir isotherms can be expressed as [20]

$$K_{Non}(C_{T,Non} - \theta_{Non}C_{Non,sat}) = \frac{\theta_{Non}}{1-\theta_{Non}-\theta_{Rep}} \quad (3)$$

$$K_{Rep}C_{T,Rep}\frac{I}{I_0} = \frac{\theta_{Rep}}{1-\theta_{Non}-\theta_{Rep}} \quad (4)$$

Combining Eqs. (3) and (4), we obtain

$$\frac{K_{Non}}{K_{Rep}}\frac{C_{T,Non} - \theta_{Non}C_{Non,sat}}{C_{T,Rep}(I/I_0)} = \frac{\theta_{Non}}{\theta_{Rep}} \quad (5)$$

where

$$\theta_{Rep} = \left(1 - \frac{I}{I_0}\right)\frac{C_{T,Rep}}{C_{Rep,sat}} \quad (6)$$

and

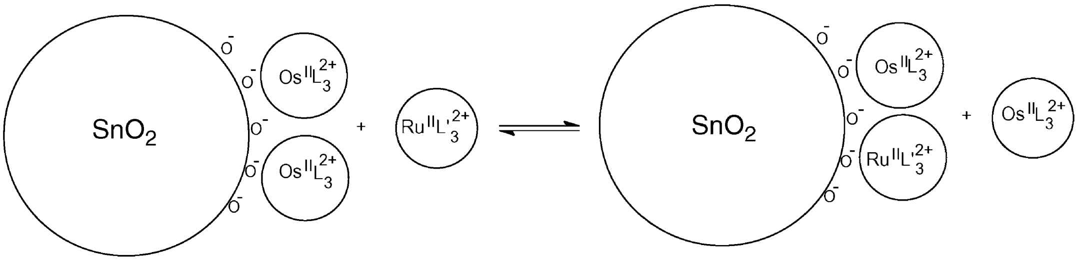
$$\theta_{Non} = \left(\frac{I}{I_0} - \frac{I'}{I'_0}\right)\frac{C_{Rep}}{C_{Rep,sat}} \quad (7)$$

where $C_{T,Non}$ and $C_{T,Rep}$ are, respectively, the total concentrations of the non-luminescent dye and luminescent (reporter) dye, I the luminescence intensity in the system of the reporter dye in the presence of the non-luminescent dye + colloidal, I_0 the luminescence intensity of the dye mixture in the absence of colloid, I' and I'_0 are the corresponding luminescence intensities of reporter dye with and without SnO_2, respectively. Substituting for θ_{Non} and θ_{Rep} in Eq. (5), we obtain

$$\frac{K_{Non}}{K_{Rep}}\frac{(C_{T,Non}/C_{T,Rep}) - ((I/I_0)-(I'/I'_0))(C_{Non,sat}/C_{Rep,sat})}{I/I_0} = \frac{(I/I_0)-(I'/I'_0)}{1-(I/I_0)} \quad (8)$$

Fig. 2 shows visible-region absorption spectra for a pair of dyes chosen to test the scheme: $Os(phen)_3^{2+}$ (a luminophore) and Ru(5-nitro-phen)$_3^{2+}$ (a non-luminescent dye). The far-red absorbing osmium complex was deemed attractive as a reporter because it could be excited without loss due to absorption by the ruthenium dye, and because its emissive excited state is too low to engage in energy transfer with the ruthenium dye (a potential additional emission quenching mechanism). Indeed, adding Ru(5-nitro-phen)$_3^{2+}$ to a solution containing $Os(phen)_3^{2+}$ (but lacking SnO_2) has no effect upon the luminescence intensity of the latter, based on 630 nm excitation. In other words, I_0 and I'_0 (Eqs. (5)–(8) are equivalent for this system.

On the other hand, adding Ru(5-nitro-phen)$_3^{2+}$ to a solution initially containing $Os(phen)_3^{2+}$ and colloidal SnO_2 does induce increases in $Os(phen)_3^{2+*}$ luminescence. Fig. 3



Scheme 1.

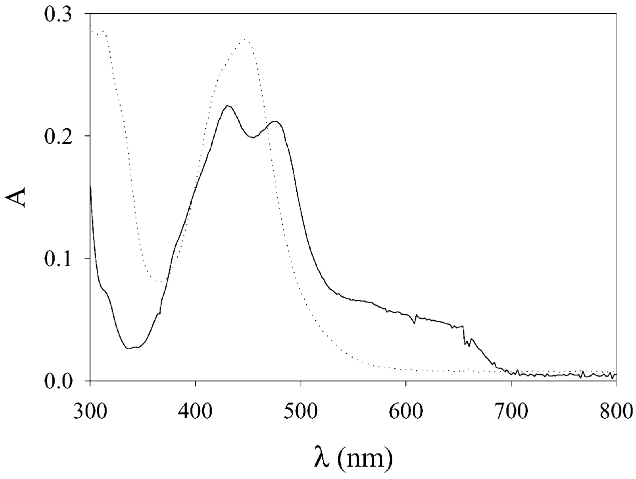


Fig. 2. Absorption spectra of $1.5 \times 10^{-5}\,M^{-1}$ $Os(phen)_3^{2+}$ (solid line) and $Ru(5\text{-nitro-phen})_3^{2+}$ (dotted line) aqueous solutions.

shows a plot of I/I_0 versus the ratio of $Ru(5\text{-nitro-phen})_3^{2+}$ concentration to $Os(phen)_3^{2+}$ concentration, $C_{T,Non}/C_{T,Rep}$. The solid line in the plot represents a fit of the experimental data to Eq. (8). From the fit, the ratio of the binding constants of the two dyes on the colloidal SnO_2 particle, K_{Non}/K_{Rep}, is 1.1. From the known value of K_{Rep} ($=K_{Os}$, Table 1), the SnO_2 binding constant for $Ru(5\text{-nitro-phen})_3^{2+}$ is $2.1 \times 10^6\,M^{-1}$.

Finally, as a test of the reliability of the method, $Ru(phen)_3^{2+}$, whose binding constant is known from direct emission measurements (Table 1), was used in place of $Ru(5\text{-nitro-phen})_3^{2+}$ in the above experiment. The binding constant obtained based on changes in $Os(phen)_3^{2+}$ emission was $0.8 \times 10^6\,M^{-1}$, a value that agrees well with the value obtained from the direct measurement ($0.9 \times 10^6\,M^{-1}$).

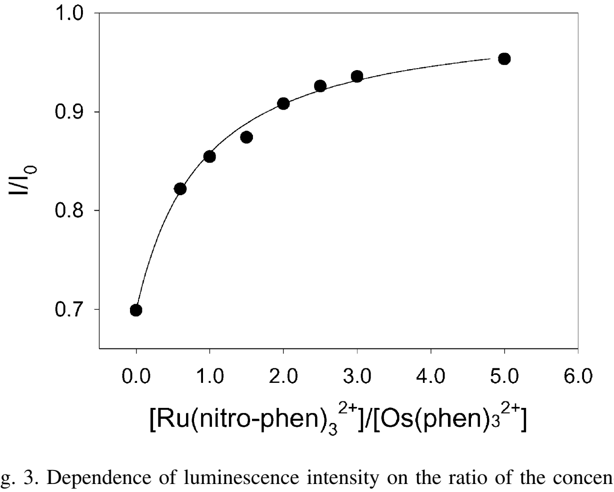


Fig. 3. Dependence of luminescence intensity on the ratio of the concentration of added $Ru(5\text{-nitro-phen})_3^{2+}$ to that of $Os(phen)_3^{2+}$. The concentration of $Os(phen)_3^{2+}$ and colloidal SnO_2 are fixed at 1.5×10^{-5} M and $0.056\,g\,l^{-1}$, respectively. The curve is the best-fit to Eq. (8).

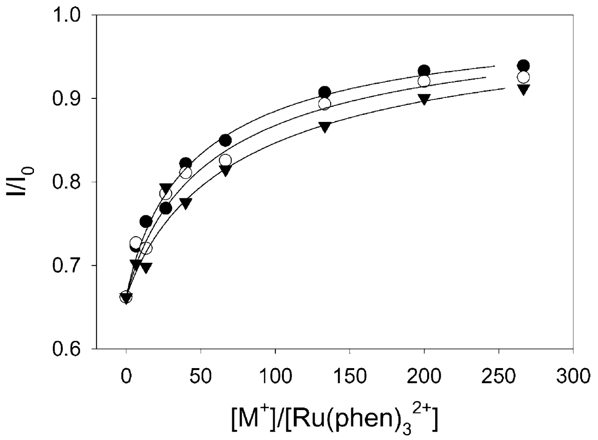


Fig. 4. Dependence of luminescence intensity on the ratio of the concentration of added K^+ (●), Na^+ (○), and Li^+ (▼) to that of $Ru(phen)_3^{2+}$. The concentration of $Ru(phen)_3^{2+}$ and colloidal SnO_2 are fixed at 1.5×10^{-5} M and $0.056\,g\,l^{-1}$, respectively. The curves are the best-fit to the Langmuir isotherm, Eq. (8).

3.3. Effect of alkali metal cations on the binding of RuL_3^{2+} to colloidal SnO_2

When simple metal cations, such as Li^+, Na^+ and K^+, are introduced to the sol of SnO_2 and $Ru(phen)_3^{2+}$, the sensitizer emission increases dramatically. This is attributed to the fact that the added cations decrease the zeta potential of the semiconductor particle, thereby leading to decreased adsorption of the ruthenium complex and hence to smaller quenching yield. Equivalently, the metal cations can be viewed as competing with the dye for the available anionic binding sites on the colloidal semiconductor particle surface. Fig. 4 shows the effect of Li^+, Na^+ and K^+ on the luminescence intensity of $Ru(phen)^{2+*}$. The solid curves are best-fits of experimental data to the Langmuir isotherm (Eq. (8)). A factor of 2, correction was included in the analysis to account for the fact that two alkali metal ions are likely required to displace one doubly-charge complex. The binding constants for Li^+, Na^+ and K^+ with colloidal SnO_2 are found to be 2.0, 3.0, and 3.4% of that of $Ru(phen)_3^{2+}$, that is, 1.8×10^4, 2.8×10^4 and $3.2 \times 10^4\,M^{-1}$, respectively. The binding constants are ordered inversely with hydrated ion radii, as expected if binding differences are determined chiefly by Coulombic effects.

An attempt to extend the study to Ca^{2+} was only partially successful. Addition of the cation, even in small amounts, caused large increases in dye luminescence, implying that the added cation competes exceptionally well for adsorption sites. The observed binding was so strong, however, that only a lower-limit estimate of the binding constant could be derived: $K_{Ca} > 4.5 \times 10^6\,M^{-1}$.

3.4. Time-resolved luminescence studies

To understand further the nature of the quenching, time-resolved luminescence experiments were carried out.

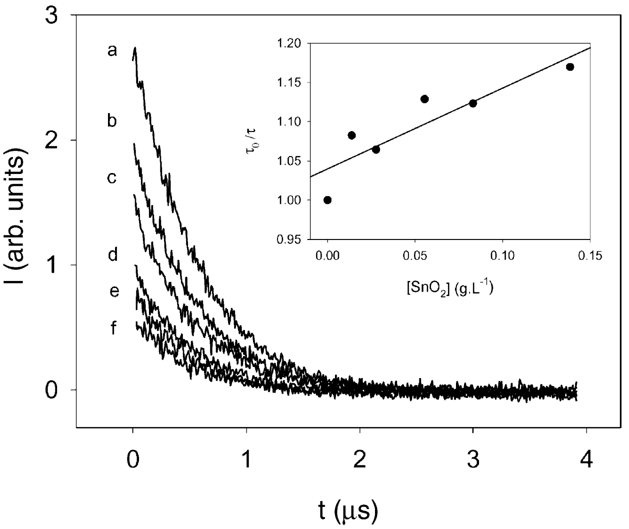


Fig. 5. Time-resolved luminescence spectra of 1.5×10^{-5} M $Ru(phen)_3{}^{2+}$ in the presence of (a) $0\,g\,l^{-1}$; (b) $0.014\,g\,l^{-1}$; (c) $0.028\,g\,l^{-1}$; (d) $0.056\,g\,l^{-1}$; (e) $0.083\,g\,l^{-1}$; and (f) $0.14\,g\,l^{-1}$ colloidal SnO_2. Inset is the corresponding plot of τ_0/τ vs. the concentration of SnO_2 particles. The line is the best-linear fit of the data.

We were interested in particular in determining whether: (a) free, as opposed to adsorbed, dye molecules could inject into SnO_2, for example, via diffusional collisional encounters, and (b) sufficient quenching occurs in this fashion to interfere with luminescence-based evaluations of non-luminescent species. Time-resolved luminescence responses from a series of sols containing a fixed concentration of $Ru(phen)_3{}^{2+}$ (1.5×10^{-5} M) and differing concentrations of colloidal SnO_2 are shown in Fig. 5. The overall luminescence intensity decreases, as expected, with the addition of the colloid. The emission decay data indicate the existence of bound/statically-quenched and free populations of $Ru(phen)_3{}^{2+}$.[1] For the lowest colloid concentration, the population of free dye has essentially the same lifetime, τ, as observed in the absence of SnO_2, while the lifetime of the strongly quenched population (dye molecules bound to particles) is too short to be resolved in this way. Ultrafast transient absorbance measurements, to be reported elsewhere, yield lifetimes of ca. 1–2 ns. Fitting the $Ru(phen)_3{}^{2+*}$ decay data obtained at higher SnO_2 concentrations reveals slight, but detectable decreases in excited-state lifetime for the free population. The data are summarized in Fig. 5 (inset) in the form of a Stern–Volmer plot: τ_0/τ versus the concentration of SnO_2, where the dye lifetime in the absence of the colloid, τ_0, is 566 ns. One interpretation of the plot is that dynamic quenching indeed is possible, but with sufficiently low efficiency (Stern–Volmer quenching constant $\cong 1\,g\,l^{-1}$) to be of only marginal significance in comparison to the static quenching pathway. A similar conclusion was reached by Ford et al. for $Ru(bpy)_3{}^{2+*}$ with antimony-doped tin oxide [11,14]. In any case, if the dynamic quenching interpretation is correct, then even less interference would be expected for the shorter lived $OsL_3{}^{2+}$ excited states.

4. Conclusions

In the absence of added electrolyte, $ML_3{}^{2+}$ complexes adsorb strongly to colloidal tin oxide: binding constants ranging from 0.9×10^6 to $2.5 \times 10^6\,M^{-1}$ are obtained via analyses of binding-induced luminescence quenching. Time-resolved luminescence measurements confirm that quenching is associated chiefly with colloidal particle interactions with bound, rather than freely diffusing, dye molecules. In the presence of roughly 100-fold excess of univalent/univalent electrolyte (chloride salts of Li^+, Na^+, or K^+), binding is inhibited and dye-luminescence quenching is attenuated, consistent with previous observations [17]. The change in luminescence is attributed to competitive binding and displacement of the dye from the available negatively charged surface binding sites by the alkali metal cations. A non-interacting two-component competitive adsorption analysis, based on luminescence from the displaced dye, has been derived and used to determine binding constants for the otherwise spectrally inaccessible alkali cations. The values obtained correlate inversely with hydrated ion radii, as expected if simple Coulombic interactions are primarily responsible for the differences in binding strength. Extension of the scheme to Ca^{2+} indicates exceptionally strong binding, too strong to be reliably quantified. The competitive analysis has also been used to determine the binding constant for a non-luminescent dye molecule. The combined results should be of value in ongoing studies of light-induced interfacial electron transfer reactivity and in studies of dye sensitization involving related photoelectrochemical systems.

Acknowledgements

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References

[1] A. Hogfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49.
[2] S. Ferrere, B.A. Gregg, J. Am. Chem. Soc. 120 (1998) 843.

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[1] The observation of apparently non-interacting bound and free dye populations is consistent with estimated dye-desorption rates. The equilibrium adsorption constant, *K*, necessarily equals the ratio of the corresponding forward and reverse rate constants: *k*(adsorption)/*k*(desorption). Assuming that adsorption is essentially barrierless and, therefore, diffusion controlled, a reasonable estimate for *k*(adsorption) is $2 \times 10^9\,M^{-1}\,s^{-1}$. Using $K \cong 1 \times 10^6\,M^{-1}$, *k*(desorption) is $\sim 2 \times 10^3\,M^{-1}\,s^{-1}$ for $Ru(phen)_3{}^{2+}$. Establishing dynamic equilibrium between bound and free dye molecules, therefore, should require a few hundred microseconds — short on the time-scale of steady-state luminescence measurements, but long compared with excited-state lifetimes.

[3] J. Desilvestro, M. Grätzel, L. Kavan, J. Moser, J. Am. Chem. Soc. 107 (1985) 2988.

[4] B.A. Parkinson, M.T. Spitler, Electrochim. Acta 37 (1992) 943.

[5] D. Kuciauskas, M.S. Freund, H.B. Gray, J.R. Winkler, N.S. Lewis, J. Phys. Chem. B 105 (2001) 392.

[6] K. Vinodgopal, X. Hua, R.L. Hadlgren, A.G. Lappin, L.K. Patterson, P.V. Kamat, J. Phys. Chem. 99 (1995) 10883.

[7] S.G. Yan, J.T. Hupp, J. Phys. Chem. 100 (1996) 6867.

[8] C. Nasr, S. Hotchandani, P.V. Kamat, J. Phys. Chem. B 102 (1998) 4944.

[9] X. Dang, J.T. Hupp, J. Am. Chem. Soc. 121 (1999) 8399.

[10] D.A. Gaal, J.T. Hupp, J. Am. Chem. Soc. 122 (2000) 10956.

[11] W.E. Ford, M.A.J. Rodgers, J. Phys. Chem. 98 (1994) 3822.

[12] H. Frei, D.J. Fitzmaurice, M. Grätzel, Langmuir 6 (1990) 198.

[13] J. Moser, S. Punchiheua, P.P. Infelta, M. Grätzel, Langmuir 7 (1991) 3012.

[14] W.E. Ford, J.M. Wessels, M.A.J. Rodgers, Langmuir 12 (1996) 3449.

[15] A. Carre, F. Roger, C. Varinot, J. Colloid Interf. Sci. 154 (1992) 174.

[16] P. Mulvaney, F. Grieser, D. Meisel, Langmuir 6 (1990) 567.

[17] I. Willner, J.-M. Yang, C. Laane, J.W. Otvos, M. Calvin, J. Phys. Chem. 85 (1981) 3277.

[18] P.C. Alford, M.J. Cook, A.P. Lewis, G.S.G. McAuliffe, V. Skarda, A.J. Thomson, J. Chem. Soc., Perkin Trans. II (1985) 705.

[19] J.N. Braddock, T.J. Meyer, J. Am. Chem. Soc. 95 (1973) 3158.

[20] P.W. Atkins, Physical Chemistry, 4th Edition, Oxford University Press, London, 1990, pp. 885–890.