Electron Transfer Threshold for Spectral Sensitization of Silver Halides by Monomeric Cyanine Dyes

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The energetic requirements for electron transfer to the conduction band of silver bromide from a series of cyanine dyes have been studied using both picosecond time-resolved and steady state fluorescence techniques. The selected dyes exhibit monomeric absorption spectra in the adsorbed state and have excited state donor energies that are calculated to span a range about the conduction band edge of AgBr. Rate constants and yields for these electron transfers were extracted from the picosecond fluorescence lifetime measurements. Yields were also obtained through independent measurements of the steady state fluorescence of these dyes and were correlated with estimates of the free energy of the reaction to depict a threshold for electron transfer with respect to the conduction band of AgBr. The threshold compares well with model curves from electron transfer theory and with literature reports of photographic relative quantum yield measurements on similar monomeric systems at silver halide surfaces. This correlation supports the electron transfer model for spectral sensitization of the silver halides. Contrasts are drawn with the sharp energetic thresholds expected for aggregated dyes.

Introduction

Fluorescence lifetime techniques have been used extensively in the determination of electron transfer rates from excited dye molecules to semiconductors.[1−13] For the most part, the goal of these studies has been to study and test models for heterogeneous electron transfer, and with time-resolved fluorescence lifetime measurements now extending below the picosecond range, even activationless electron transfer reactions can be observed and analyzed. A variety of semiconductor substrates have been employed in these studies, ranging from oxides such as TiO_2, ZnO, and SnO_2 to transition metal dichalcogenides and silver halides; the solids have been used in their single-crystalline, polycrystalline, colloidal, and nano-crystalline forms. Many different classes of chromophores have been used, from inorganic to organic, with degrees of aggregation of the adsorbed molecule that have varied from monomer to blue-shifted H- and red-shifted J-aggregates.

A dye/substrate combination of particular importance is that of cyanine dyes and silver halide grains in photographic systems.[2,9,10,12] The excited state electron transfer from the cyanine dye to silver halides is considered to be the primary event in the spectral sensitization of silver halide photography with the efficacy of a dye as a spectral sensitizer, determined in large part by the rate constant for the electron transfer step.[14] This rate constant can be estimated through the use of fluorescence lifetime techniques, as has been done for many other dye/semiconductor systems. Given the advanced state of models for electron transfer, it should also be possible to compare these experimental results with rate constants calculated

from the energetics of the silver halide substrate and the excited state of the dye.

In this work, we study a series of monomeric sensitizing dyes on the surface of AgBr grains to obtain an experimental description of the energetic threshold for electron transfer from the excited dye to the solid. The threshold is a mapping of the quantum yield for electron transfer Φ_{et} as a function of the free energy ΔG of the reaction. The analysis of the threshold will make use of data from three experimental approaches: one originates from picosecond fluorescence lifetime measurements, a second comes from an independent measurement of steady state fluorescence quantum yields on the same set of dyes, and a third is data taken from the photographic literature on the yield Φ_{rel} of latent image formation as a function of ΔG. It will be shown that interpretation of the picosecond fluorescence lifetime data in terms of electron transfer theory results in a broad Φ_{et} vs ΔG threshold that agrees with the thresholds defined by the other two experimental sources.

The picosecond fluorescence lifetime data for the dyes are obtained under the same experimental conditions as previous work[9] with the monomeric cyanine dye 3,3′-diethylthiacarbocyanine iodide (**TC**) at the surface of AgBr grains. The analysis of the transients is also done in a similar manner. In the work with **TC**,[9] the application of classical Marcus theory revealed that the activation energy for electron transfer is about 90 meV and that, for the excited dye, the reorganization energy λ from electron transfer theory falls in the range of 0.3−0.4 eV. A recent fit to the same experimental data,[12] applying the quantum mechanical Jortner−Levich model, gave an uphill value of 63 meV for the standard free energy difference and 0.28 eV for the reorganization energy. The fairly large reorganization energy found for this monomeric dye implies a

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rather broad energy threshold of Φ_{et} vs ΔG for electron transfer to AgBr that may stretch over several hundred millivolts as Φ_{et} climbs from zero to unity.

We realize, however, that a number of experimental conditions must be met in order to obtain reliable estimates of k_{et} for a dye at a solid surface through picosecond fluorescence measurements. For the study of monomeric dyes, the surface coverage of the substrate must be sufficiently low that energy transfer between neighboring dye molecules can be neglected.[8,9] Only then can the fluorescence lifetime be taken as a measure of the electron transfer rate into the solid. The incident photon flux on the sample must not be too high or the measurements will reflect the activity of a photochemically degraded dye layer.[12] In order to obtain information on the energetics of the reaction, temperature studies must be conducted over a large range so that activation energies may be determined.

Bearing these requirements in mind, we have measured the picosecond fluorescence lifetimes of this series of dyes, which have been selected to span the threshold for electron transfer to AgBr from low k_{et} to high k_{et}. The series consists of four cyanine dyes, including **TC**, on which a detailed report has already been made.[9,12] A dozen candidate molecules were screened at low surface coverage on AgBr in a search for the ideal behavior found for **TC**. However, it was not possible to find a series which met the stringent experimental conditions described above. Nevertheless, the three best-behaved dyes were selected for further analysis. Their fluorescence decay was multiexponential at room temperature, but for all of them, greater than 90% of the signal amplitude was attributable to one component of the decay. The fluorescence decays for these dyes at room temperature were used to derive their k_{et} values.

It is evident that the use of fluorescence lifetime data from these dye/AgBr combinations will yield only approximate values for k_{et}. The purpose of this exercise is to see if such k_{et} results are consistent with three other experimental observations: the broad, energetic threshold for spectral sensitization predicted by the λ of 0.3−0.4 eV found for **TC**,[9] the threshold found in independent measurements of the fluorescence quantum yields of these dyes, and thresholds reported for photographic relative quantum yields. This is found to be the case. The energetic threshold is in line with both prediction and data.

It is rare to find an experimental result on electron transfer to the conduction band of a semiconductor in such fine gradations of energy that it may be compared with theory. There have been studies in photoelectrochemical systems where pH changes have been made at oxide surfaces to shift the conduction band edge energy E_c relative to a dye.[15,16] For the complementary study where a series of dyes of varying donor abilities are studied at the surface of a solid with a fixed E_c, however, silver halide substrates are ideal. This is a consequence of the negative potential of the conduction band edge, about −1.3 eV (Ag/AgCl),[17] in combination with the use of cyanine dyes as sensitizers, which afford a fine tuning of the redox potential of the excited dye.[18]

Another significant aspect of this work is found in the practical implications for AgBr photographic systems. Heretofore, the sensitizing ability of cyanine dyes on silver halide grains was believed to be described by a sharp energy threshold that rises over a 0.1 eV range of reduction potential from little-to high-sensitizing ability.[18−20] This has served as an important screening parameter in the selection of sensitizing dyes for photographic systems. However, included within these sharp threshold data have been dyes with both J-aggregate and monomeric absorption spectra. The results of this work with electron transfer theory illustrate the contrast of the energetic

and kinetic characteristics of spectral sensitization of silver halides by monomeric dyes as opposed to those in their J-aggregated forms. A proper appreciation of the sensitizing ability of monomeric dyes can only be obtained if the data for monomers and aggregates are analyzed separately.

Experimental Section

The picosecond fluorescence lifetime experiments were performed with the same AgBr systems as in previous work[9] where detailed descriptions of the experimental procedures and transient analyses can be found. The sensitizing dyes of this study were adsorbed onto 0.82 μm (mean volume diameter) monodisperse octahedral AgBr at a dye loading of 10^{-8} mol/mol of Ag or a surface coverage θ of about 10^{-3}. The AgBr photographic emulsion was adjusted to pAg of 8.5 and to a pH of 6.4. It was prepared through a double-jet technique; the AgBr was not subject to any chemical sensitization procedures.

Experimentation with the tosylate and iodide salts of **TC** revealed no significant influence of the counterion upon its fluorescence lifetime. That is to be expected given the gelatin environment about the AgBr and the low-dye surface coverage θ of <0.001 used in these experiments. At the high θ of 0.2 used in photographic products, the I^- counterion influences the photographic response of the system, but that is under different experimental conditions than the one under study here and represents the results of a series of reactions, only one of which is the electron transfer from the excited dye.
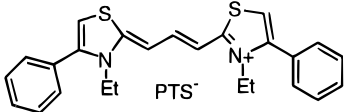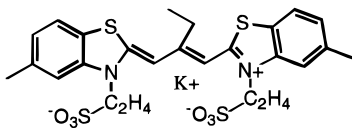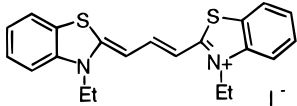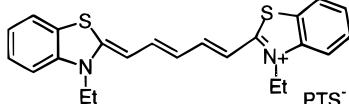
Steady state determinations of the fluorescence yield of these dye molecules on AgBr were made with the use of a SPEX Fluorolog fluorescence spectrometer at 298 K and 77 K. The emulsions were coated on the inside of an ESR tube, dried in a dessicator, and cooled in a liquid nitrogen Dewar. Previous work has shown that the electron transfer reaction for **TC** is negligible at 77 K. This was found to hold for all of these dyes. No decay in their steady state fluorescence was evident at 77 K. Therefore, the electron transfer yield Φ_{et} could be estimated through a ratio of the integrated emission intensity at 298 K to that at 77 K (*vide infra*). This ratio was obtained with corrections at each wavelength for variations in intensity of the illumination systems, sensitivity of the detection systems, and absorbances of the samples. Care must be taken in these experiments to minimize photobleaching of the dye at 298 K. The irradiance of the samples was adjusted to a level where less than a 5% decline in the fluorescence was observed over the time required for a spectral scan. These values for Φ_{et} represent a lower limit; the uncertainty, as reflected in a standard deviation, is estimated at 10% of the value of Φ_{et}.

Fluorescence lifetime measurements were made at room temperature through a procedure that has been described in earlier work[9] and can be summarized briefly. The gelatin samples containing the silver bromide grains were deposited on quartz microscope slides and dried in a dessicator before use in temperature measurements. The light source was a cavity-dumped picosecond dye laser driven by a mode-locked Ar^+ ion laser. Fluorescence decay curves were obtained with time-controlled single-photon counting which measured the apparent laser pulse width (fwhm) to be shorter than 40 ps. A procedure was developed to avoid bleaching of the sample during exposure in which the flux was maintained below 10^{-1} mW/cm^2. A description of the details of the analysis of the fluorescence decay transients can be found in prior work with **TC**.[9]

Results

The fluorescence lifetimes of the four dyes on AgBr at 298 K are given in Table 1. The lifetimes were determined in a

TABLE 1: Picosecond Fluorescence Data for Cyanine Dyes on AgBr

Dye		τ_{298} (ps)	Φ_{et}	$\Phi_{et(m)}$	k_{et} (s^{-1})	k_{fl}* (s^{-1})
1		250	.54	.35	2.2×10^{9}	2.6×10^{8}
2		180	.67	.7	3.7×10^{9}	2.3×10^{8}
3		56	.89	.9	1.6×10^{10}	3.2×10^{8}
4		480	.15	.15	2.7×10^{8}	5.8×10^{8}

* Calculated through integration of absorption spectrum.

manner similar to that reported for **TC**,[9] but they include analyses of transient decays that could be better fit to a sum of two exponentials. Whereas the **TC** transient decay could be fit with the primary component of an amplitude greater than 99%, the primary component of the decay of the other dyes fell as low as 90%. The lifetimes in Table 1 represent the primary component. The secondary component was always longer and is assumed to result from dyes adsorbed at different sites or from aggregate forms of the dye. Each type of possible adsorption site may affect a dye's photophysics or its oxidation potential in a unique way, either of which will affect its fluorescence lifetime. Dimer and aggregate formation has been found to lengthen the fluorescence lifetime of an adsorbed sensitizing dye.[8]

Under the proper experimental conditions, the rate constant for electron transfer k_{et} can, in principle, be extracted from the fluorescence lifetime τ_{fl} which is defined as

$$1/\tau_{fl} = k_{et} + k_{fl} + k_{q} \tag{1}$$

where k_{fl} is the radiative rate constant and k_{q} represents the rate of all other pathways for relaxation to the ground state, including internal conversion processes and intersystem crossing. In practice, the extraction of k_{et} from τ_{fl} measurements requires an experimental approximation to the rate constants k_{fl} and k_{q}.

Careful temperature studies[9] with **TC** on AgBr below 100 K have shown that, for an adsorbed dye, $1/\tau_{fl}$ can be fit with a value for $(k_{fl} + k_{q})$ which has negligible temperature dependence. The value of 1.8×10^{9} s^{-1} from this measurement was used as an estimate for $(k_{fl} + k_{q})$ for all of these dyes so that a value for k_{et} could be extracted from each measurement of τ_{fl}. These values for k_{et} are listed in Table 1 for each dye.

The use of this value of 1.8×10^{9} s^{-1} for all of the dyes requires some examination. For cyanine dyes in solution, k_{q} includes the rate constants for internal conversion and intersytem crossing which are so large that τ_{fl} for the dye is reduced to below 50 ps. These fast pathways for decay require a torsional

motion about the polymethine chain of the dye,[21] a motion which has also been found to be a prerequisite for intersystem crossing[22] and which is strongly hindered when the dye is in a medium of high viscosity or adsorbed on the surface in a planar orientation.[14] Such a restriction of torsional motion can also be effected through rigidization of the polymethine chain through bridging groups on the cyanine molecule.[23] This rigidization can increase the quantum yield for fluorescence from <0.05 to >0.7. It is the rigidization of the polymethine chain which causes this change in fluorescence yield; substituents on the molecule appear to play a secondary role. Given the similar polymethine backbone of the dyes in Table 1, we make the assumption that differences in $(k_{fl} + k_{q})$ for these dyes will be minimized when adsorbed on the surface of AgBr and that the value of 1.8×10^{9} s^{-1} for $(k_{fl} + k_{q})$ from work with **TC** should be a reasonable estimate for the other three dyes of this work. This assumption can be examined in a quantitative manner following the introduction of data obtained from steady state fluorescence measurements.

There is also a variation in k_{fl} from 2.3 to 5.8×10^{8} s^{-1} for the four dyes in Table 1, where k_{fl} is estimated through an integration of the absorption spectra of the dyes. The results are listed as k_{fl} in Table 1. However, this range in k_{fl} of $\pm 2 \times 10^{8}$ s^{-1} about 4×10^{8} s^{-1} introduces a variation of only $\pm 10\%$ in the assumed value for $(k_{fl} + k_{q})$ of 1.8×10^{9} s^{-1} because the term is dominated by a k_{q} that is many times larger than k_{fl}.

With the values for k_{et} listed in Table 1, it is possible to calculate the quantum yield Φ_{et} for electron transfer which is defined as

$$\Phi_{et} = k_{et}/(k_{et} + k_{fl} + k_{q}) \tag{2}$$

These estimates of Φ_{et} are listed in Table 1.

A second, independent measure of Φ_{et} can be derived through steady state fluorescence quantum yield measurements of the quantum yield for fluorescence Φ_{fl} for the adsorbed dye, which is defined by

$$\Phi_{fl} = k_{fl}/(k_{et} + k_{fl} + k_q) \qquad (3)$$

As mentioned above for **TC** at 77 K,[9] $k_{et} \ll (k_{fl} + k_q)$, so that $\Phi_{et(m)}$, the Φ_{et} deduced from these fluorescence yield measurements, can be extracted from the relative Φ_{fl} values at 298 and 77 K:

$$\Phi_{et(m)} = 1 - (\Phi_{fl}(298)/\Phi_{fl}(77)) \qquad (4)$$

This was done for these dyes through the fluorescence emission measurements that established the ratio of the steady state fluorescence at 298 K to that at 77 K for each dye. The silver halide samples were prepared with the same surface coverage as employed in the fluorescence lifetime measurements.

From comparison of $\Phi_{et(m)}$ and Φ_{et}, it can be seen that the assumption of 1.8×10^9 s^{-1} for $(k_{fl} + k_q)$ holds very well for dyes 2−4. Using $\Phi_{et(m)}$ and τ_{298} from Table 1 and eqs 1 and 2, one calculates values for $(k_{fl} + k_q)$ of 1.6×10^9, 1.8×10^9, and 1.8×10^9 s^{-1} for dyes 2−4, results which are in line with the assumed value of 1.8×10^9 s^{-1}. A similar derivation of k_{et} for dyes 2−4 using eqs 1 and 2 yields k_{et} values which match those in Table 1 precisely.

In contrast, the calculated $(k_{fl} + k_q)$ value for dye 1 is 2.6×10^9 s^{-1}, a figure from which a k_{et} value of 1.3×10^9 s^{-1} can be extracted for electron transfer from this dye to the AgBr. This is a factor of 2 slower than the k_{et} rate listed in Table 1. In the context of the rigidization argument above, the larger value of $(k_{fl} + k_q)$ for dye 1 could be attributed to the smaller size of its chromophore. The van der Waals forces between the dye chromophore and the AgBr surface play an important role in dye adsorption, and a smaller dye with a smaller van der Waals interaction may be less effectively immobilized on the surface.

Discussion

The discussion of the experimental results must take place within the constraints mentioned in the Introduction where details were given on the experimentation required to obtain accurate estimates for k_{et}. The central concern is the assurance that the measured fluorescence decay results from electron transfer to the solid. This concern is most apparent for the case of dyes with low k_{et} values, where k_q and k_{et} may be of comparable importance in the fluorescence decay and an unambiguous assignment of a decay time for electron transfer may not be possible. In this work, three dyes were studied under conditions where **TC** in earlier work[9] was found to provide reliable information. Within this uncertainty, we do not inspect the k_{et} determinations in Table 1 for their individual significance. That would require a study like that done for **TC**. Rather, we search for the collective description offered by these k_{et} values of the energetic threshold for spectral sensitization of AgBr. When correlated with the independent measurements of $\Phi_{et(m)}$, it will be shown that these k_{et} values describe a threshold consistent with the high activation energy found by applying the classical Marcus model to the electron transfer reaction of **TC**. This threshold is also found to be consistent with threshold data from relative quantum yield measurements in photographic systems.

In the electron transfer model for the spectral sensitization of silver halides, k_{et} represents the rate constant for the initial step in the sensitization of latent image formation by the dye. This rate constant can be related to the free energy change ΔG° of the reaction:[9]

$$\Delta G^\circ = E_c - qE_{D^+/D^*} \qquad (5)$$

where E_c is the energy of the silver bromide conduction band,

TABLE 2: Energetic Data for Cyanine Dyes on AgBr

dye	$qE_{D^+/D}$ (eV)	$h\nu_{oo}$ (eV)	qE_{D^+/D^*} (eV)	ΔG°_{elec} (eV)	ΔG°_{fl} (meV)
1	0.796	2.12	−1.36	−60	20
2	0.634	2.08	−1.45	−150	−6
3	0.902	2.15	−1.23	70	−93
4	0.630	1.80	−1.17	130	110

taken to be −1.3 eV vs Ag/AgCl,[17] q is the elementary charge, and E_{D^+/D^*} is the thermodynamic potential for oxidation of the excited dye molecule. Rigorously, the density of states of the conduction band goes to zero at E_c, but within kT of E_c there are sufficient acceptor states to make eq 5 an accurate approximation. More complicated analyses with multiple acceptor states can be made;[12] however, the simple approach taken here is sufficient for the issue of this work.

Using the approach of Gerischer,[24] E_{D^+/D^*} may be expressed in terms of the ground state oxidation potential of the dye $E_{D^+/D}$ and the zero−zero energy $h\nu_{00}$ in eV of the excited state of the dye:

$$qE_{D^+/D^*} = qE_{D^+/D} - h\nu_{00} \qquad (6)$$

Equations 5 and 6 have been used to calculate the free energy ΔG° for the four dyes of this work using solution measurements of $E_{D^+/D}$; the results from these calculations, termed ΔG°_{elec}, are listed in Table 2. $h\nu_{00}$ was taken to be the average of the excitation and fluorescence emission maxima. The $E_{D^+/D}$ for the dye can shift upon adsorption from solution, in the range of 100 meV,[9] an approximation that is implicit in the use of solution measures of $E_{D^+/D}$ for a surface reaction. We note that this change in $E_{D^+/D}$ contains the effects of any Coulombic interactions between dye and substrate that contribute to the free energy change of the photooxidation reaction.

Another approach in determining ΔG° uses the fluorescence lifetime data of this work and the rate expression found from prior work with **TC** where a preexponential factor of 10^{11} s^{-1} was found:[9]

$$k_{et} = 10^{11}\exp(-(\Delta G^\circ + \lambda)^2/4\lambda kT) \qquad (7)$$

ΔG° can be extracted from this expression if k_{et} and λ are known. Given values for k_{et} listed in Table 1, an estimate of ΔG°, labeled ΔG°_{fl}, has been calculated for each of the four dyes of this work using eq 5 and has been tabulated in Table 2. ΔG°_{fl} is not very sensitive to λ within the range 0.25 eV < λ < 0.5 eV, varying only 100 meV within these limits. An intermediate and commonly employed[9,16,24] value of 0.35 eV was used in these calculations. We note that the possible uncertainty in k_{et} discussed previously for dye 1, which amounts to 1×10^9 s^{-1}, translates into a small ΔG°_{fl} shift for the dye from 20 to 48 meV.

A third look at the problem can be obtained through construction of model curves for the relation between Φ_{et} and ΔG°. This can be done through the use of eqs 2, 5, 6, and 7. Three such curves are given in Figure 1 for $1/k_{fl} = 3000$ ps and $\tau_q = 1/k_q$ of 10, 100, and 1000 ps.

Examination of the model curves in Figure 1 reveal that as τ_q increases from 10 to 1000 ps, the Φ_{et} vs ΔG° curves shift to more positive energies. For a dye with a given ΔG°, the curves illustrate how Φ_{et} is determined by the rate of the competing quenching reactions of the excited state. As τ_q increases, Φ_{et} increases, an effect which is more pronounced for dyes with a more positive ΔG°.

The steady state fluorescence $\Phi_{et(m)}$ values of Table 1 for each dye are plotted in Figure 1 for the two methods of
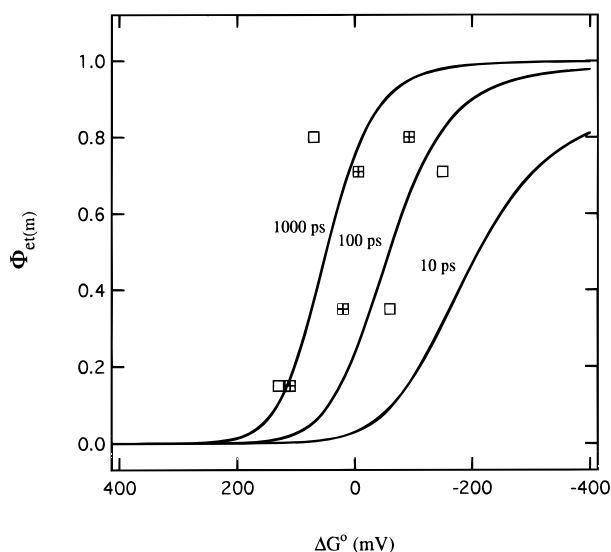
Figure 1. Using eqs 2, 5, 6, and 7, these model curves show the dependence of the quantum yield for electron transfer Φ_{et} on the free energy of the reaction ΔG°. Three model curves are given for τ_q values of 10, 100, and 1000 ps. The Φ_{et} values from Table 1 for the four dyes are also plotted as a function of the ΔG°_{elec} and ΔG°_{fl} values from Table 2.

estimating ΔG°, each of which is obtained independently of $\Phi_{et(m)}$. It can be seen in Figure 1 that the data plotted using ΔG°_{elec} fall about the τ_q curves for 100 to 1000 ps as ΔG_{elec} changes from 0.15 to -0.2 eV. We believe that the scatter of these points results from the use of solution values of $E_{D^+/D}$ to describe the $E_{D^+/D}$ of dyes on the surface. The $E_{D^+/D}$ values for a dye in solution are known to carry over well to the dye in the adsorbed state. For example, it is well established[18−20] that the absolute yield Φ_{abs} for latent image formation in dye-sensitized silver halide grains is a steep function of the solution reduction potential of the dye. Φ_{abs} is controlled by the tendency of the adsorbed dye to be reduced in the dark by an electron from the silver halide conduction band (*vide infra*). Dyes with the more positive $E_{D^+/D}$ have the greater tendency to capture electrons from the silver halide. However, the carryover is not exact. There is a random scatter of ± 100 mV in range for the dozens of data points needed to describe the threshold for Φ_{abs}. A variation of this magnitude is consistent with results from the analysis[9] of picosecond fluorescence data for **TC** where a shift in a negative direction of 30−130 mV in $E_{D^+/D}$ is evident upon adsorption, and also with reports of potentiometric titrations[25] of a pentamethine dye on AgBr where a change of -0.14 V was measured.

Although these ΔG°_{elec} points of Figure 1 do not describe a well-defined threshold for electron transfer from cyanine dyes to AgBr, they do indicate the ΔG region where such a threshold would be found. A better definition of a threshold is found with the use of ΔG°_{fl} values obtained from picosecond fluorescence lifetime measurements. As shown in Figure 1, $\Phi_{et(m)}$ increases monotonically in a smooth fashion as ΔG°_{fl} falls from 0.15 to -0.13. As previously noted, the assumption about $(k_{fl} + k_q)$ in deriving k_{et} for these dyes does cause some uncertainty in the ΔG°_{fl} value for dye 1. Nevertheless, the independent correlation of ΔG°_{fl} with $\Phi_{et(m)}$ does depict a threshold that falls within the region spanned by ΔG°_{elec} and between the model curves from electron transfer theory for τ_q = 100 ps and τ_q = 1000 ps.

Detailed temperature studies[9] have shown that electron transfer from **TC** to AgBr is a thermally activated process with a preexponential factor in eq 3 of 10^{11} s^{-1}. In analogy to **TC**, the k_{et} values of Table 1 reveal that the electron transfer from

the other three monomeric dyes to AgBr are seen to be thermally activated processes as well, since k_{et} for each is less than 10^{11} s^{-1}. This appears to hold even though the estimates of ΔG°_{elec} for the electron transfer is as negative as -150 mV. However, the Φ_{et} for these reactions is still high because the rates of competing reactions are low. This competition was controlled in these experimental systems through the intentional use of a low surface coverage of the AgBr by the dye.

These electron transfers from cyanine dyes can induce latent images on the silver halide grains in photographic films. As a result, the developed latent image, i.e., the optical density of the developed film, can be used as another measure of Φ_{et}. A measure of Φ_{et}, termed Φ_{rel}, has been devised to measure the efficacy of sensitizing dyes adsorbed on the silver halide grains that are used in photographic films[14] and also exhibits an energetic threshold for spectral sensitization such as is shown in Figure 1. Φ_{rel} is an indirect measure. The formation of the latent image on a silver halide grain results from a sequence of reactions, and the electron transfer to the silver halide conduction band represents only the first step. It is indirect because it requires the use of a correction factor owing to the ability of unoxidized, adsorbed dye on silver halides to capture electrons from the conduction band:

$$e_{cb}^- + D \rightarrow D^- \tag{8}$$

These electrons trapped at the surface as reduced dye D^- can be siphoned off in deleterious side reactions that reduce the efficiency of latent image formation. O_2 and oxidized dye can serve in this role. The reaction of eq 6 can occur because of the negative potential of -1.3 eV (Ag/AgCl) for the conduction band edge of AgBr.[17] Most cyanine dyes have a reduction potential E_{D/D^-} positive of this edge and can be reduced by electrons from the silver halide conduction band with a recombination free energy change $\Delta G_{rec} = (E_c - E_{D/D^-})$.

The quantitative expression for Φ_{rel} is given as[14]

$$\Phi_{rel} = 400 E_{400} A_{400}/(\lambda E_\lambda A_\lambda) \tag{9}$$

where E_λ is the photon flux at a wavelength λ absorbed by the dye that is required to attain a specified optical density in the developed film; A_λ is the percent absorption of light at wavelength λ by the dye. The correction for the recombination reaction of eq 9 is accomplished through the normalization of the exposure at wavelength λ by the corresponding terms E and A at 400 nm for the intrinsic absorption of the silver halide at 400 nm.

There are a number of Φ_{rel} measurements in the literature[18−20] that have been made at a high dye coverage θ of the silver halide of 0.2−0.3. This is the coverage employed in photographic products and is necessary to obtain a high optical density for the sensitizing dye.[14]

The transition from the low θ data of 0.001 in Figure 1 from this work to the high θ data of 0.2 used in practical photographic systems can be found in measurements of Φ_{rel} that have been reported by Muenter.[26] In that work, attention was given to the value of Φ_{rel} for a dye as a function of surface coverage θ for cyanine dyes that adsorb to give spectra of monomeric form. The data from ref 26 are plotted in Figure 2 for both cubic AgBr and AgCl emulsions as a function of ΔG°_{elec} for the reaction and are compared with the model curves from Figure 1. Values of Φ_{rel} were reported for θ = 0.01, 0.02, and 0.09. The data do describe a rough threshold similar to the thresholds of Figure 1, and they also decline with increasing θ. The values of E_{D^+/D^*} for the ΔG°_{elec} of this graph were remeasured with second-

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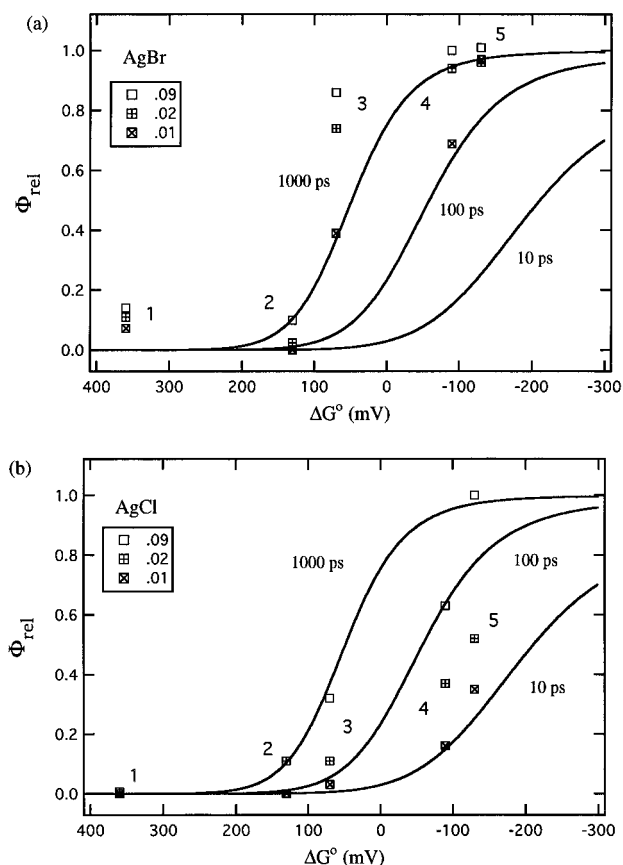
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Figure 2. (a) Φ_{rel} for five dyes with different $\Delta G°_{elec}$ for sensitization of AgBr from ref 26 are shown to follow the form of the model curves controlled by eq 2. As Θ increases from 0.01 to 0.02 to 0.09, Φ_{rel} declines as the concentration quenching from neighboring dye molecules increases and k_q climbs. (b) The corresponding measurements are shown for an AgCl substrate.

harmonic techniques to obtain reversible potentials for the dyes. For simplicity, E_c was taken to be the same for AgBr and AgCl.

According to Muenter,[26] this decrease in Φ_{rel} with increasing θ conforms to the branching ratio of the Φ_{et} curves described by eq 2, owing to an increase in dye−dye interactions on the surface that made τ_q smaller. This type of quenching behavior has been studied in silver halides[27] and also found in measures of the photooxidation yield of cyanine dyes at ZnO electrodes.[28] However, it is not always found. For xanthene dyes at molecular organic crystals, only a weak dependence on θ was found for the yield for electron transfer.[29] For the less perfect semiconductor surfaces, however, the adsorption of the dye may occur on different surface sites as the θ increases, and this may influence k_q as well.

Extrapolating the results of the work of ref 26 in Figure 2 to the high $\theta = 0.2$ level used in practical photographic applications, one predicts an energy threshold for electron transfer with a shallow slope extending over several hundred meV. This prediction contrasts with reports[18−20] of Φ_{rel} at $\theta = 0.2$ for a series of sensitizers that include both J-aggregated cyanine dyes and dyes with monomeric spectra. In these studies, which correlate Φ_{rel} with $E_{D/D}-$, it has been observed that Φ_{rel} rises from zero to unity within 0.1 eV. Analyzed in a manner analogous to the monomer models of this work, a sharp threshold for electron transfer to AgBr is expected for J-

aggregate dyes since the reorganization energy λ of a J-aggregate is small, about 50 meV.[12] In the literature reports on Φ_{rel},[18−20] however, a sharp threshold has been reported for monomeric dyes as a function of $E_{D/D}-$, implying that the Φ_{rel} data for the monomeric dyes are not fully normalized by the procedure of eq 9; the reduction reaction of eq 8 still determines the value of Φ_{rel}.[30]

It is evident that an energetic threshold for $\Phi_{et(m)}$ can be defined if ΔG_{fl} values from electron transfer theory are used. This threshold falls where estimates of ΔG_{elec} from solution measurements indicate it should be found and also at ΔG values where the Φ_{rel} threshold determinations of Figure 2 are found. However, in order to obtain a sharp energetic threshold for monomeric dyes, as was found in the ΔG_{fl} correlation of Figure 1 at high τ_q, it is evident that one must work with θ values much lower than are practical for photographic systems. As θ is increased to 0.2 and higher in practical applications, complicated quenching processes are introduced into the system which obscure the energetics of the underlying electron transfer from the excited dye to the silver halide.

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