using similar lifetime values and treating them by three-dimensional vs. one-dimensional models, respectively. When similar hopping distances and diffusion coefficients are assumed, the rate of encounters are expected to be much larger in the one-dimensional model. In view of the similarity between k_2T and k_c, the natural result is a smaller predicted value of D in the one-dimensional case as is found. It is clear from these results that no completely satisfactory mode of data analysis is yet available for these polymeric systems. Additional experimental results will be needed to clarify some of the questions that the present investigation has raised. It should be noted, however, that in a system of densely populated chromophores, such as these vinyl aromatic polymers, it would be unusual to find diffusion coefficients significantly less than those obtained for small dopant molecules in polystyrene. For this reason, the one-dimensional model seems to be the less attractive alternative at this time.

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Registry No. PVK, 25067-59-8; NEC, 86-28-2.

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Fluorescence Quenching of Diphenylanthracene Covalently Bound to Poly(styrenesulfonate)

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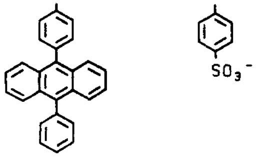
ABSTRACT: A water-soluble copolymer of styrenesulfonate and vinyldiphenylanthracene (DPA) was prepared that contained ca. 2.6 mol % DPA. The fluorescence properties of this polymer-bound chromophore were studied, with special emphasis on fluorescence quenching by the cationic quenches methylviologen (MV^{2+}) and Cu^{2+}. Both were very efficient quenchers, presumably because of electrostatic binding to the polymer coil, with an apparent quenching rate of ca. 6×10^{12} and 1.4×10^{13} M^{-1} s^{-1} for Cu^{2+} and MV^{2+}, respectively, on the basis of the initial slope of a Stern–Volmer plot. However, the quenching does not obey Stern–Volmer kinetics at higher concentrations, and the fluorescence intensity is quenched much more efficiently than the fluorescence lifetime (static quenching). For the case of MV^{2+} a weak charge-transfer (CT) complex is formed with the DPA, but in order to account for the fluorescence quenching it is necessary to postulate an additional "hydrophobic attraction" for MV^{2+} moieties to reside near a DPA without CT complexation. It is also proposed that as more MV^{2+} is attracted into the polyelectrolyte coil the DPA moieties become more protected, which is manifested by (1) a decrease in quenching efficiency and (2) a blue shift in the fluorescence excitation spectrum but with no change in the fluorescence spectrum.

Introduction

Water-soluble polymers with covalently bound hydrophobic chromophores[1-3] represent a class of microheterogeneous systems that are conceptually very similar to micelle systems in that hydrophobic materials may be solubilized in water and the chromophore may be partially protected or separated from the bulk solution. However, in the case of the polymer system the covalently bound chromophore cannot be exchanged between the elementary units and the degree of protection of the chromophore is expected to be less complete than is the case for micelles. We have proposed in an earlier paper[4] that a hydrophobic attraction can exist between an amphiphilic quencher (methylviologen) and a hydrophogic chromophore (diphenylanthracene, DPA) bound to a polyelectrolyte (deprotonated methacrylic acid). The present work explores this same phenomenon for the same quencher–chromophore pair but with a different polymer system (see Scheme I). Once again it is found that in order to un-

Scheme I



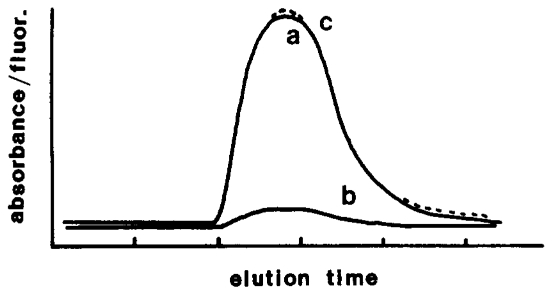


Figure 1. GPC traces of polymer sample: (a) absorption at 254 nm; (b) absorption at 365 nm; (c) fluorescence at 420 nm excited at 365 nm. Each tick mark corresponds to 5-min flow.

derstand the fluorescence quenching it is necessary to invoke a "hydrophobic interaction" between the quencher and the chromophore in addition to the formation of a weak charge-transfer complex. Additionally it is demonstrated that the local environment of the polymer-bound diphenylanthracene is heterogeneous by comparing the fluorescence excitation spectra and the absorption spectrum as a function of added methylviologen. The Cu^{2+} ion does not exhibit evidence of this microheterogeneity.

Experimental Section

1. Materials. The sodium styrenesulfonate salt monomer was received as a gift from Du Pont Co. and purified by 3–4 recrystallizations from methanol, producing a white flaky solid (the original material is a light-yellow amorphous powder). The vinyldiphenylanthracene was prepared and purified as described in previous publications.[5] The polymerization was carried out in DMF (freshly distilled) by using ca. 1.0 wt % AIBN. The sample for which detailed results are presented contained 2.6 mol % diphenylanthracene and the remainder styrenesulfonate. The final polymer was purified by precipitation into hexane, dissolution into water, and extensive dialysis.

This polymer was characterized by size exclusion chromatography using a pair of Waters 300/125 Protein–Pak columns with a 0.5 M sodium acetate (aqueous) mobile phase and refractive index, absorption, and fluorescence detection. The following detection signals were found to correlate very well with each other as a function of elution volume: (1) absorption at 254 and 365 nm (absorption by phenyl plus anthracene and anthracene only, respectively) and (2) fluorescence at 420 nm excited by 365-nm light (anthracene only) (see Figure 1). This implies that the anthracene is homogeneously distributed in the polymer for all molecular weights. The molecular weight distribution is fairly broad, yielding $M_w/M_z \simeq 3.7$ and $M_w \simeq 35000$ based on dextran standards. This implies that essentially all polymers contain at least one DPA moiety. By comparison of the absorption spectrum of this polymer with a polymer with a lower doping level (ca. 0.6 mol %), we see no evidence for DPA aggregation. However, this is not easily detected for the DPA system since there is no excimer fluorescence for this species that might serve as a good test for pairwise (or higher) aggregates.

The methylviologen used as a quencher was obtained from Aldrich Chemical and recrystallized three times from methanol before use.

All solutions were prepared with distilled water and kept in the dark at ca. 5 °C. Because of the high content of sodium ions from the sodium styrene sulfonate (ca. 0.5 mM), we have not studied ionic strength effects in this system. All solutions were air-saturated. As will be seen the anthracene fluorescence lifetime is close to that expected for deaerated solutions.

2. Optical. For steady-state fluorescence a SPEX fluorimeter with a double excitation and emission (1680 Spectramate) monochromator and data acquisition via the SPEX Datamate DM1A system was used. Since the shape of the fluorescence spectrum was not changed by the addition of the quenchers (see below), the fluorescence intensity was determined by integrating the fluorescence spectrum between 400 and 550 nm (this can be done automatically on the SPEX Datamate instrument controller). As the fluorescence intensity was decreased by the addition of quencher the photomultiplier voltage had to be increased to maintain linearity in the sensitivity. Thus at various stages in the acquisition of the steady-state quenching curve, fluorescence intensities at the same quencher concentration but different photomultiplier voltages had to be scaled to each other. It was found that the reproducibility of this procedure to high degrees of quenching ($I_0/I \simeq 90$) was excellent.

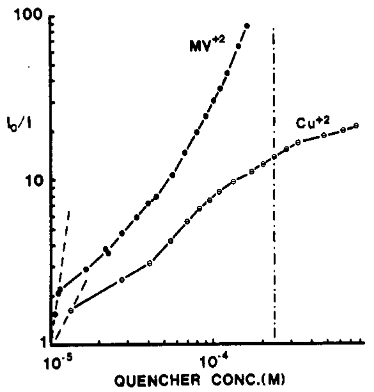


Figure 2. log–log plot of I_0/I for MV^{2+} and Cu^{2+} quenching ($[SO_3^-]_0 = 4.9 \times 10^{-4}$ M) as a function of quencher concentration. The point at which the quencher concentration is equal to $[SO_3^-]_0/2$ is indicated by the vertical line (–··–).

Fluorescence decays were determined with standard single-photon methods, using a PRA air-filled lamp (HWFM $\simeq$ 2.5 ns) with a double monochromator for excitation (JV Model DH-10) and emission (McPherson Model 215). The excitation and emission wavelengths were 358 and 420 nm, respectively. The instrument response curve and a trial fitting function were reconvoluted to obtain a weighted best-fit agreement to the experimental decay by using standard methods. In addition to minimizing the weighted χ^2, the weighted residuals were examined visually for randomness around zero.[6]

Results

1. Comparison of Fluorescence Quenching by Cu^{2+} and MV^{2+}. The experimental results for DPA fluorescence quenching have certain similarities that we emphasize here. The special features of MV^{2+} quenching will be discussed in the next subsection.

As might be expected with an anionic polymer and a cationic quencher, the quenching does not obey a Stern–Volmer equation.[7] This is illustrated in Figure 2 by means of a log–log plot of I_0/I vs. quencher concentration. As can be seen these two plots differ in character as the ratio of the quencher concentration to sulfonate concentration approaches 0.5 (i.e., the point of charge balance between the divalent cationic quencher and polyelectrolyte negative charge). For MV^{2+} the I_0/I curve appears to be diverging while for Cu^{2+} I_0/I appears to be saturating. We note that the initial slope of I_0/I vs. [Q] corresponds to a k_q value of ca. 1.4×10^{13} M^{-1} s^{-1} for MV^{2+} and ca. 6×10^{12} M^{-1} s^{-1} for Cu^{2+}.[8] This merely serves to illustrate how efficient the fluorescence quenching is since in this calculation the average quencher concentration is used (i.e., no account is made of the concentrating effect of the polyelectrolyte that surrounds the DPA moiety). While we have not studied the effect of ionic strength, one would expect that increasing the ionic strength of the solution would decrease the strength of the electrostatic binding of these quenchers to the polymer and hence decrease K_{SV}.

The DPA fluorescence decay is multiexponential as one might expect for a microheterogeneous system. The addition of either quencher does shorten the average fluorescence decay time up to a point, but the increase of $\langle\tau_0\rangle/\langle\tau\rangle$ (average lifetime in the absence and presence of quencher, respectively) is much less than the steady-state quenching (I_0/I) and appears to plateau. Because of the rapid decrease of fluorescence intensity with the addition

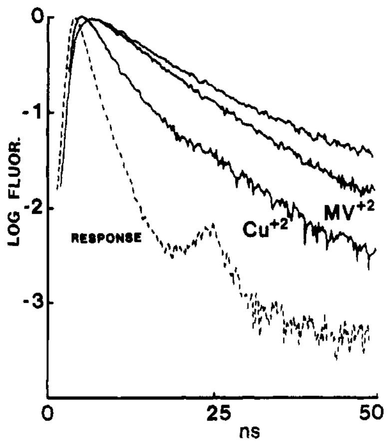


Figure 3. Fluorescence decay as a function of added quencher for Cu^{2+} and MV^{2+}. For these quencher concentrations I_0/I = 9.6 and 15.6, respectively.

Table I
Fitting Parameters for Fluorescence Decay in Figure 3[a]

sample	τ_1/A_1	τ_2/A_2	$\langle\tau\rangle$[b]
unquenched	6.4/0.770	17.4/0.230	11.3
$[MV^{2+}] = 2.2 \times 10^{-5}$	4.8/0.619	10.5/0.381	8.1
$[Cu^{2+}] = 4.0 \times 10^{-5}$	1.3/0.860	7.4/0.140	4.2

[a] Fitting function is $I(t) = a_1e^{-t/\tau_1} + a_2e^{-t/\tau_2}$ ($I(0) \equiv 1.0$). [b] $\langle\tau\rangle = \sum a_i\tau_i^2/\sum a_i\tau_i$.

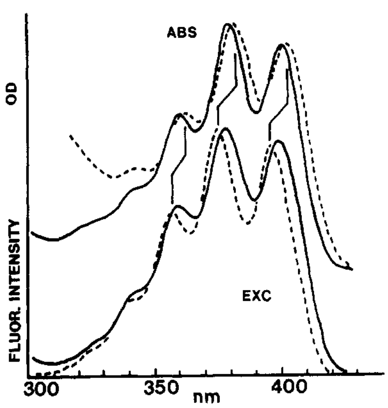


Figure 4. Absorption (top) and excitation (bottom) spectra for PSS-DPA as a function of added MV^{2+}: (—) $[MV^{2+}] = 0$; (- - -) $[MV^{2+}] = 1.07 \times 10^{-4}$ M. The line connecting the peaks of the absorption and excitation spectra for $[MV^{2+}] = 1.07 \times 10^{-4}$ M are to emphasize the shift discussed in the text. All spectra are normalized to equal maxima for ease of comparison.

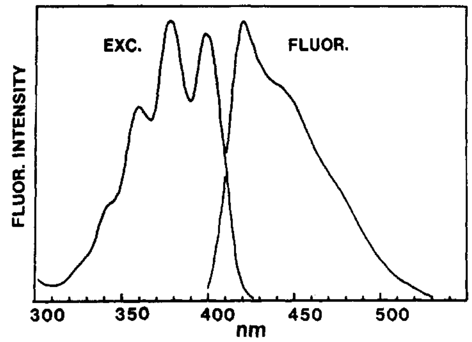


Figure 5. Excitation and fluorescence spectrum of unquenched sample.

of quencher, it is not possible to obtain a plot of $\langle\tau_0\rangle/\langle\tau\rangle$ over an appreciable range of quencher concentration. Examples of fluorescence decay data for similar additions of MV^{2+} and Cu^{2+} are presented in Figure 3. The decay parameters obtained are given in Table I. Because of the general behavior of $\langle\tau_0\rangle/\langle\tau\rangle$ relative to I_0/I, we conclude that the fluorescence quenching is almost completely static; that is, diffusional interaction of fluorophore and quenching species is unimportant, but rather the important contact between these species is present at $t = 0$ or not at all.

The absorption, fluorescence, and excitation spectra of the Cu^{2+}-quenched solution did not change as a function of Cu^{2+} concentration, implying a relatively simple static quenching scheme. The case of MV^{2+} quenching is much less simple and will be discussed separately in the next section.

2. Special Features of Fluorescence Quenching by MV^{2+}. It has been noted previously that MV^{2+} can form a charge-transfer (CT) complex with DPA when the latter is covalently bound to poly(methacrylic acid) at basic pHs (DPA-PMA),[4] and the same is found in the present case (DPA-PSS). This complexation is illustrated in Figure 4, where the absorption spectrum is observed to red-shift as MV^{2+} is added. There is a slight decrease in overall OD (not illustrated in Figure 4 because of normalization of spectra). This change in the absorption spectrum is almost identical with that found for DPA-PMA. As will be discussed later, the equilibrium constant for the MV^{2+} complexation with DPA-PSS is almost the same as that found for DPA-PMA. Also illustrated in Figure 4 is the fluorescence excitation spectra (λ_{obsd} = 420 nm). It is seen that the addition of MV^{2+} results in a *blue shift* of the excitation spectrum in direct contrast to the absorption spectrum. This implies that there is a heterogeneous environment for the individual DPA's and those that are still able to fluoresce after a significant amount of MV^{2+} has been added experience a polarity significantly different from the average DPA species in the polymer. It is possible that structural changes of the polymer are induced by the addition of MV^{2+}, which in turn results in some DPA's being protected. However, in this case one might expect the quenching to plateau, similarly to the Cu^{2+} quenching. We will come back to this point in the Discussion. It is tempting to ascribe to these remaining DPA species a more "protected" and less polar environment, but there is no direct proof for this supposition at this time. It is interesting to note that there is no change in the DPA fluorescence spectrum as a function of added MV^{2+}. See Figure 5 for a comparison of the excitation and fluorescence spectra of this system.

All of these observations demonstrate the complexity of the interaction of amphiphilic cations with hydrophobic groups covalently bound to polyanions and additionally demonstrate that some degree of "self-organization" must occur in these systems. In the Discussion we will present a simple complexation equilibrium model that rationalizes some of the quenching features observed but that leaves open the question of the detailed structure of the polyelectrolyte-DPA-quencher complex.

Discussion

In the following we will discuss in detail the quenching results for MV^{2+} since this system demonstrates extraordinarily efficient quenching indicative of a "hydrophobic association" between MV^{2+} and DPA. The absorption spectrum in Figure 4 clearly demonstrates the formation of a CT complex between MV^{2+} and DPA. However, as will be pointed out below the extent of this complexation is much smaller than required to account for the fluorescence quenching. We will use the following three-state model, like that proposed previously for DPA-doped poly(methacrylic acid).[4] It is assumed that all MV^{2+} resides in the polyelectrolyte (denoted (MV^{2+})), but we must distinguish between MV^{2+} at sites adjacent to the DPA (denoted $(MV^{2+})_{DPA}$) and MV^{2+} forming a CT complex with the DPA (denoted $(MV^{2+}\cdot DPA)$). In each case a polymer-bound uncomplexed sulfonate is produced (denoted SO_3^-). Thus we can write the following two equilibria:[9]

$$(MV^{2+}) + DPA \underset{K_{CT}}{\rightleftharpoons} SO_3^- + (MV^{2+}\cdot DPA) \qquad (1)$$

$$(MV^{2+}) + (\ )_{DPA} \underset{K_{hyd}}{\rightleftharpoons} SO_3^- + (MV^{2+})_{DPA} \qquad (2)$$

Reaction 1 is the CT-complex formation, and reaction 2 is the preferential association of the MV^{2+} at sites adjacent to the DPA moiety. We believe that reaction 2 arises because of a hydrophobic attraction between the polyelectrolyte-bound MV^{2+} and the DPA. We do not consider any preferential formation of the CT complex between $(MV^{2+})_{DPA}$ and DPA, and we ignore any interference of $MV^{2+}\cdot DPA$ with the formation of $(MV^{2+})_{DPA}$. We will come back to this point later. The value of K_{CT} can be estimated by a variation of the Benesi–Hildebrand method,[10] in which the change in the DPA optical density is plotted as a function of added MV^{2+} and a value of K_{CT} is obtained from eq 1 that best describes this plot (see Appendix). The value of K_{CT} obtained in this fashion is 12 (±3).

Equation 2 describes the concentration of MV^{2+} species adjacent to DPA moieties. It is assumed that the $(MV^{2+}\cdot DPA)$ and $(MV^{2+})_{DPA}$ concentrations are independent (i.e., a CT-complexes DPA could also have a nearest-neighbor MV^{2+} moiety) except that the total concentration of MV^{2+} is conserved. The details of this calculation are presented in the Appendix. The probability of a DPA moiety having a nearest-neighbor MV^{2+} is given by

$$P = [(MV^{2+})_{DPA}]/(2[DPA]_0) \qquad (3)$$

The equilibrium described by eq 2 neglects the fact that there are two nearest-neighbor SO_3^- groups for each DPA. The Bernoullian probability for 0, 1, and 2 nearest-neighbor MV^{2+} quenchers is given by $(1 - P)^2$, $2P(1 - P)$, and P^2, respectively.

We assume that all quenching is static and that DPA's with one or two nearest-neighbor MV^{2+} or all DPAs CT-complexed with MV^{2+} are nonfluorescent. Thus the following can be written:

$$I/I_0 = (1 - [(MV^{2+}\cdot DPA)]/[DPA]_0) \times (1 - [(MV_{2+})_{DPA}]/2[DPA]_0)^2 \qquad (4)$$

In order to evaluate I/I_0 with this model the equilibria 1 and 2 must be solved as a function of added MV^{2+} concentration. Since K_{hyd} is not known we have evaluated I/I_0 as a function of K_{hyd} assuming $K_{CT} = 12$ and compared with the experimental data (see Figure 6). As is seen, K_{hyd} in the range 5–8 provides a reasonable fit to the experimental data. We note that in the limit $K_{CT} = 0$ (no CT complexation) and $K_{hyd} = 1$ (no hydrophobic attraction), the following expression describes the quenching (see Appendix):

$$\lim_{\substack{K_{CT}=0\\K_{hyd}=1}} (I/I_0) = (1 - [(MV^{2+})]/[SO_3^-]_0)^2 \qquad (5)$$

This quenching formula predicts much too slow a decrease of I/I_0 with added quencher.

As can be seen from Figure 6, it is essential to postulate $K_{hyd} > 1$ to fit the steady-state quenching data. However, the model proposed here does not fit the experimental data very well for $I/I_0 < 0.1$ and $[MV^{2+}]/[(SO_3^-)]_0 > 0.1$. We presume this follows from the simplifications of the model, especially the assumption that the equilibrium constant for either CT-complex formation or nearest-neighbor association is independent of $[MV^{2+}]/[(SO_3^-)]_0$. Clearly, as this ratio approaches 0.5 one would expect the configuration of the polymer coil to change (presumably coil contraction would occur), hindering the access of the quencher to the DPA. Thus it is no surprise that the experimental data in Figure 6 lie above the calculated I/I_0 curve that fits the data fairly well for $[MV^{2+}]/[(SO_3^-)]_0 < 0.1$. This idea is consistent with the blue shift of the excitation spectrum that occurs at higher MV^{2+} concentrations (Figure 4).

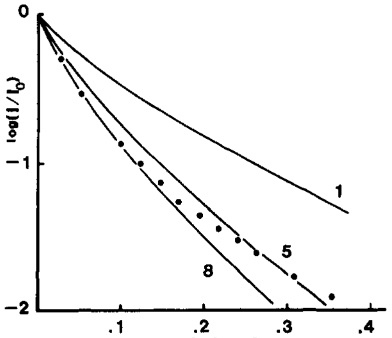


Figure 6. Plot of I/I_0 vs. $[MV^{2+}]/[SO_3^-]$ for different values of K_{hyd} for $K_{CT} = 12$ (see text).

The present results may be compared to those of Morishima et al.[11] for phenanthrene units bound to a 2-acrylamido-2-methylpropanesulfonate polymer (denoted AM) in aqueous solution. These workers used a neutral amphiphilic quencher bis(2-hydroxyethyl) terephthalate (BHET) and found no evidence for a significant hydrophobic attraction between BHET and phenanthrene when the latter was present at low loadings (ca. 2%) (strong hydrophobic attractions did exist for higher phenanthrene loadings however). Itoh, Morishima, and Nozakura[12] also studied this copolymer system using methylviologen as a quencher and observed very large Stern–Volmer constants (10^{11}–10^{12} M^{-1} s^{-1}) and CT complexation. However, the polymers used for these studies contained at least 9 mol % phenanthrene, and the results were not analyzed in terms of a hydrophobic binding model.[13] One would expect that at low loadings the AM polymer would be very similar to the present PSS–DPA system.

Summary

The photophysics and fluorescence quenching of a small mole fraction of diphenylanthracene (DPA) moieties bound to poly(styrenesulfonate) has been studied. The cationic species Cu^{2+} and MV^{2+} have been found to be extremely efficient fluorescence quenchers, with the initial slope of I_0/I corresponding to a quenching constant of 6×10^{12} and 1.4×10^{13} M^{-1} s^{-1}, respectively. However, the fluorescence quenching does not obey a Stern–Volmer quenching law at higher concentrations, and the quenching is found to be primarily static. MV^{2+} was found to form a weak charge-transfer complex with the DPA, but the size of this complexation constant is not adequate to account for the fluorescence quenching if it is assumed that the CT complex is nonfluorescent. It is postulated that preferential association of MV^{2+} at sites adjacent to DPA groups occurs through a "hydrophobic attraction", and the equilibrium constant for this association constant had been estimated to be ca. 8 ($\Delta G° = -5.2$ kJ/mol). This simple model does not fit the experimental data very well for higher loading of the polymer with MV^{2+} (i.e., for $[MV^{2+}]/[(SO_3^-)]_0 > 0.1$. Taken together with the shift observed in the excitation spectrum, these results suggest that the polymer configuration is changing with the addition of the MV^{2+}, such that the microenvironment of the polymer-bound DPA is modified. In future experiments we will explore this effect in other polyelectrolyte systems with a variety of polymer-bound chromophores.

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Appendix: Consideration of the Equilibria between MV^{2+} and DPA

We use the following symbols for the concentrations in eq 1 and 2: $[(MV^{2+})]_0 = M$, $[DPA]_0 = D$, $[SO_3^-]_0 = S$, and $[(MV^{2+}\cdot DPA)] = c$, where the subscript zero refers to the initial concentration of the species. From eq 1 we can write

$$\frac{(c)(S - M + c)}{(M - c)(D - c)} = K_{CT} \tag{A.1}$$

Under the conditions of our experiment c is much smaller than M and $S - M$, such that

$$c = (K/(K + 1))D \tag{A.2}$$

where

$$K = K_{CT}(M/(S - M)) \tag{A.3}$$

The optical density at any wavelength is given by

$$\begin{aligned} OD &= \epsilon_{DPA}(D - c) + \epsilon_C c \\ &= (OD)_0 + (\epsilon_C - \epsilon_{DPA})c \end{aligned} \tag{A.4}$$

where $(OD)_0$ is the optical density of the solution before the addition of the MV^{2+}. The observed change in OD as a function of M can be related to K_{CT} through eq A.2 and A.3. We estimate this value to be 12.

Using eq 2 of the text and the same notation for concentrations as above, defining $[(MV^{2+})_{DPA}] = m$, and noting that the initial concentration of $()_{DPA}$ is $2[DPA]_0 = 2D$ (i.e., two nearest neighbors of each DPA moiety) yield

$$\frac{(m)(S - M - 2D + c + m)}{(M - m)(2D - m)} = K_{hyd} \tag{A.5}$$

Note that $2D$ must be subtracted from S since $[()_{DPA}] + [SO_3^-] = S$. This was not necessary in eq A.1 because all polymer-bound MV^{2+} moieties are considered equivalent with respect to the formation of a CT complex for the purpose of this model. The maximum value of c and m is D and $2D$, respectively, which is significantly smaller than M or $S - M$. Consequently (A.5) can be written

$$\frac{(m)(S - M)}{(M)(2D - m)} = K_{hyd} \tag{A.6}$$

with a solution

$$P = m/2D = K'/(1 + K') \tag{A.7}$$

where

$$K' = K_{hyd}M/(S - M) \tag{A.8}$$

In eq A.7 we have identified P, the probability of a given DPA moiety having a neighboring MV^{2+}, as $m/2D$. There are two limiting cases:

$$\lim_{K_{hyd}\to 1} P = M/S \tag{A.9}$$

$$\lim_{K_{hyd}\to \infty} P = 1 \tag{A.10}$$

In the first case there is no hydrophobic attraction that favors the juxtaposition of MV^{2+} and DPA, such that P is just the SO_3^- site occupation ratio. In the second case the adjacent sites of the DPA's are completely occupied so long as $M > 2D$ (which is our assumption in solving eq A.5). The calculations based on eq A.7 are in good agreement with solution of the full quadratic derived from eq A.5.

In calculating the fluorescence quenching we assume that the only fluorescent species are those DPA's neither engaged in a CT complex nor with a nearest-neighbor MV^{2+}. The probability that a DPA is not complexed is $(1 - c/D)$, and of those DPA's not complexed the probability that neither neighboring site contains a MV^{2+} is $(1 - P)^2$, so the fluorescence quenching is described by

$$I/I_0 = (1 - c/D)(1 - P)^2 \tag{A.11}$$

$$I/I_0 = (1/(K + 1))(1/(K' + 1))^2 \tag{A.12}$$

where K and K' are defined in eq A.3 and A.8. If $K_{CT}M$ and $K_{hyd}M$ are much larger than $S - M$, then

$$I_0/I = K_{CT}K_{hyd}^2(M/(S - M))^3 \tag{A.13}$$

which diverges as $M \rightarrow S$. In this case the full quadratic equation would have to be solved.

In the limit $K_{CT} = 0$ and $K_{hyd} = 1$ (no preferential association adjacent to DPA moieties) eq A.12 yields

$$\lim_{\substack{K_{CT}=0 \\ K_{hyd}=1}} (I/I_0) = (1 - M/S)^2 \tag{A.14}$$

References and Notes

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(6) These methods have become routine; see, for example: O'Connor, D. V.; Phillips, D. *Time Correlated Single-Photon Counting*; Academic: New York, 1984. Demas, J. N. *Excited State Lifetime Measurements*; Academic: New York, 1983.

(7) This is in contrast to the very similar copolymer of methacrylic acid and pyrene pendent or end groups reported by Chu and Thomas[2] in which the Stern–Volmer equation is evidently obeyed.

(8) These quenching rate constants are larger than observed for pyrene–poly(methacrylic acid)[2] or $Ru(bpy)_3^{2+}$ electrostatically attracted to poly(methacrylic acid) (Chu, D. Y.; Thomas, J. K. *J. Phys. Chem.* **1985**, *89*, 4065).

(9) While similar in physical model, the approach presented here is slightly different from that of ref 4 in mathematical approach.

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(13) The quenching was studied over a small range of values of I_0/I such that only the initial slope was measured. Determination of the hydrophobic attraction in this system might be difficult because of the relatively obtrusive absorption of the CT complex.