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Photophysics of Water Soluble Perylene Diimides in Surfactant Solutions

Tingji Tang,[†] Kalina Peneva,[‡] Klaus Müllen,[‡] and Stephen E. Webber*,[†]

Department of Chemistry and Biochemistry and Center for Nano and Molecular Science, The University of Texas at Austin, Austin, Texas, 78712, and Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128, Mainz, Germany

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Our previous photophysical study of water soluble perylene diimides (WS-PDIs) has suggested that WS-PDIs are present in aqueous solution in partially aggregated form (Tang, T. J.; Qu, J. Q.; Müllen, K.; Webber, S. E. *Langmuir* **2006**, *22*, 7610−7616) In this article we present a study of the effect of surfactants (dodecyltrimethylammonium chloride (DTAC), sodium dodecyl sulfate (SDS)) on the photophysics of WS-PDIs. Adding surfactant to WS-PDI solutions is accompanied by their increased fluorescence quantum yield and lifetime and a more structured absorption spectra. We are able to demonstrate that above the surfactant critical micelle concentration (cmc) the WS-PDI moieties are molecularly dispersed and isolated from each other. Our findings are consistent with the existence of weakly interacting aggregates of WS-PDIs in pure water, which can be broken up by surfactants even below the cmc, although we cannot rule out that the observed photophysical changes arise from modifying the local environment of molecularly solubilized WS-PDIs (e.g., local polarity or modification of the molecular planarity).

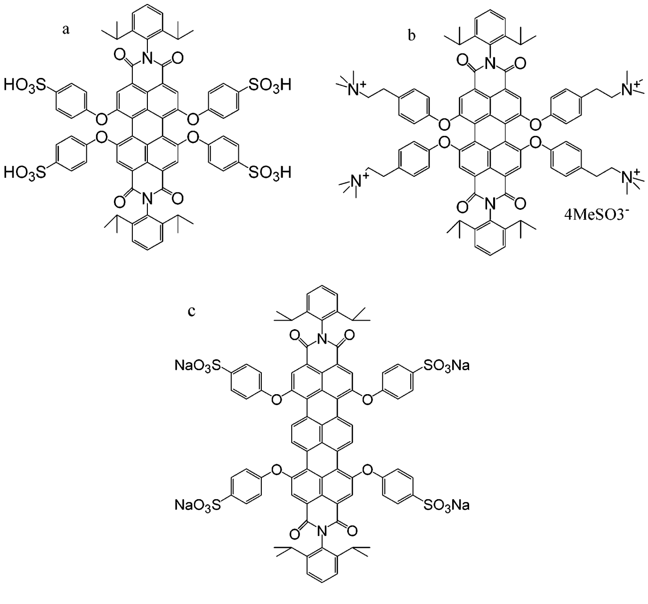
Introduction

The highly fluorescent 3,4,9,10-perylenetetracarboxylic diimide (PDI) chromophore is widely used as a commercial dye and pigment due to its outstanding chemical, thermal, and photochemical stability. Organic soluble perylene diimide (OS-PDI) molecules have drawn more and more attention because of their potential as organic semiconductors.[1,2] Due to their thermal and photostability, OS-PDI molecules have also attracted increasing interest in fabrication of single-molecule devices such as fluorescence switches, sensors, molecular wires, and molecular transistors.[3] Wasielewski et al. have studied a large variety of covalently and noncovalently assembled multichromophoric light-harvesting arrays based on the perylene diimide chromophore.[4] Li and co-workers have carried out some very important work on the self-assembly of PDI chromophores without the bay substituents of the compounds studied herein.[5]

Recently water soluble perylene diimide (WS-PDI) molecules were synthesized by Qu et al. (molecular structures are shown in Scheme 1).[6,7] The photophysics of n-PDI in water have been studied in considerable detail by Margineanu et al.,[8] where it was shown that these WS-PDI molecules are suitable for fluorescence tagging of biological systems because of the following characteristics: (1) good water solubility, (2) high fluorescence quantum yield, (3) high chemical and photostability, (4) nontoxicity, and (5) good biocompatibility. WS-PDI species also have considerable potential as elements in the self-assembly of photoactive films. In our previously published work we have explored the use of these materials to prepare thin films using the LbL (layer-by-layer)[9] or MLbL (molecular layer-by-layer)[10] approach for deposition from aqueous solution.

Kohl et al. have suggested that the WS-PDI molecules might be partially aggregated in aqueous solutions, which results in a quantum yield substantially less than unity.[7] In the present paper we attempt to answer this question by the use of surfactants. It is well-known that surfactants above their critical micelle concentration (cmc) can solubilize hydrophobic species in water, and presumably they can break up aggregates of WS-PDIs, if they exist. We note that for similar reasons Ford[11] and Marcon et al.[12] previously studied the effect of surfactants on the photophysics of several PDI dyes (without bay substituents) in aqueous solution.

SCHEME 1: Chemical Structures of n-PDI (a), p-PDI (b), and n-TDI (c)



Experimental Section

Materials. Positively and negatively charged water soluble p-PDI (CAS [817207-4-7]) and n-PDI (CAS [694438-88-5]) (Scheme 1) were synthesized by Qu et al.[6,7] We have measured

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[†] The University of Texas at Austin.

[‡] Max-Planck-Institut für Polymerforschung.

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the quantum yields of n-PDI and p-PDI to be 0.54 and 0.14 in water, respectively,[10] in good agreement with Kohl et al.[7] and Margineanu et al. for n-PDI.[8] In ref 7 the partition coefficients of n- and p-PDI between octanol and water were measured and demonstrated that p-PDI is considerably more hydrophobic than n-PDI, and it was suggested by these authors that p-PDI was more likely to form aggregates in aqueous solution. We have also carried out a few experiments with a water soluble terrylene derivative, n-TDI (which is the sodium salt of the parent tetrasulfonic acid, CAS [862852-56-0][13]), also shown in Scheme 1. In the absence of surfactants the fluorescence quantum yield of this species in water is essentially zero.[14] *N*,*N*′-Bis(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide was purchased from Aldrich for use as a fluorescence standard.

Sodium dodecyl sulfate (SDS; cmc, 8 mM) was purchased from Aldrich and recrystallized in ethanol before use. Dodecyltrimethylammonium chloride (DTAC; puriss grade ≥99%; cmc, 20 mM) was purchased from Fluka and used as received. Deionized water was used for all the aqueous solution preparations. The effects of surfactants such as SDS and DTAC on the absorption and fluorescence emission spectra of p-PDI and n-PDI were studied by diluting a stock aqueous solution of p-PDI and n-PDI with the SDS and DTAC solutions of different concentrations. Except for the dilution experiments the PDI concentrations were in the range of $(2-2.7) \times 10^{-7}$ M. All samples were stirred overnight before taking their spectra. Equivalent results were obtained by titrating the n-PDI solution with a concentrated solution of DTAC or SDS in dimethylformamide (DMF; 0.65 M; at the highest concentration of DTAC used, the volume fraction of DMF in the solution was ca. 5%; see the Supporting Information).

Instruments. UV−vis absorption spectra were obtained with an HP-8453 diode array spectrometer.

The fluorimeter used was a SPEX Fluorolog-τ2 equipped with a 450 W xenon light source, Czerny-Turner double grating excitation and emission monochromators. A photomultiplier voltage of 950 V was typically used, and the excitation and emission slit widths were set at 1/1/2/2 mm for solution samples. Emission spectra were collected in right-angle mode with $\lambda_{ex} = 540$ nm. It was verified that the absorption and excitation spectra for the model compound (*N*,*N*′-bis(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide) were identical to within a few percent, such that the differences discussed later are experimentally significant.

A time-correlated single-photon counting system (TCSPC) was used for the life time measurements. A Mira 900-D titanium−sapphire mode-locked femtosecond oscillator cavity with Optima Controller serves as the light source, whose tunable wavelength is in the range of 700−980 nm with pulse width less than 200 fs. An optical frequency doubler was coupled to extend the excitation wavelength range from 350 to 490 nm. The excitation wavelength for all experiments was 463 nm, and the right-angle mode was used for data collection. A cutoff filter was coupled to remove the excitation light from emission light before being collected on the single photon counting multiplier. The optical densities for all the samples were adjust to ca. 0.08. The data were analyzed with the PicoQuant FluoFit Version 4.0. All the fluorescence decay curves were fitted with the value of the sum of weighted residuals (χ^2), less than 1.5 in most cases.

Dynamic light scattering at 90° (Zetaplus, Brookhaven Instruments) was used to monitor all aqueous solutions for particulate formation for either n- or p-PDI, but no particles larger than ca. 10 nm (the limit of this instrument at such low concentrations) were observed. This is in contrast to the observations of Jung et al. for n-TDI in the absence of surfactant, in which case aggregates with a hydrodynamic diameter of ca. 450 nm were observed.[14]

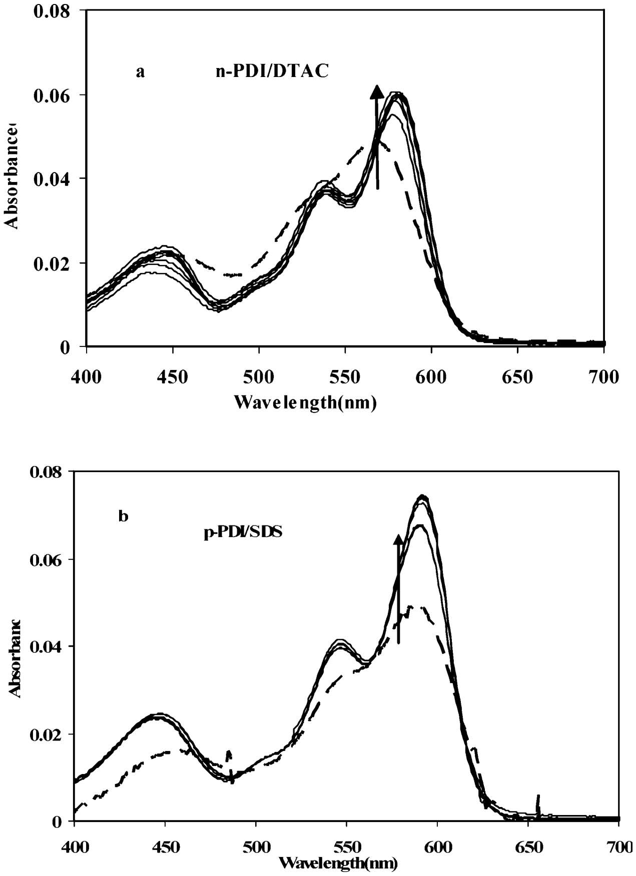

Figure 1. Absorption spectra of n-PDI with DTAC (a) and p-PDI with SDS (b) at different concentrations. Arrows indicate increasing surfactant concentration. Dashed lines: Pure aqueous solution. Solid lines: Aqueous solution with added surfactant (see inset of Figure 2 for concentrations).

Results and Discussions

Complexation of PDI and Oppositely Charged Surfactants. Adding DTAC to n-PDI (abbreviated as n-PDI/DTAC) or SDS to p-PDI (p-PDI/SDS) resulted in an increase in the extinction coefficient and a more resolved absorption spectra upon the initial addition of surfactant, well below the cmc (Figure 1). The fluorescence spectra blue shift upon addition of surfactant (see Figure 2), and there is a steady increase in the fluorescence intensity, becoming approximately constant above the surfactant cmc (see the insets in Figure 2). The excitation and absorption spectra are compared in Figure 3 for the WS-PDI in pure water and in surfactant solution above the cmc. All photophysical parameters for the various solutions studied herein are collected in Table 1. In the following we discuss some of the details of the behavior of each WS-PDI/surfactant pair.

n-PDI/DTAC. Upon complexing with DTAC the absorption spectrum of n-PDI shifts to the red by ca. 12 nm. The new emerging peak at 540 nm and the spectral shape with DTAC present is typical of PDI moieties. At the highest DTAC concentration (35 mM), $\lambda_{0-0} = 581$ nm with $\epsilon = 3.71 \times 10^4$ M^{-1} cm^{-1}, $\lambda_{0-1} = 540$ nm with $\epsilon = 2.28 \times 10^4$ M^{-1} cm^{-1} and a shoulder at 500 nm was observed. Over the whole DTAC concentration range, only one emission peak is observed, as

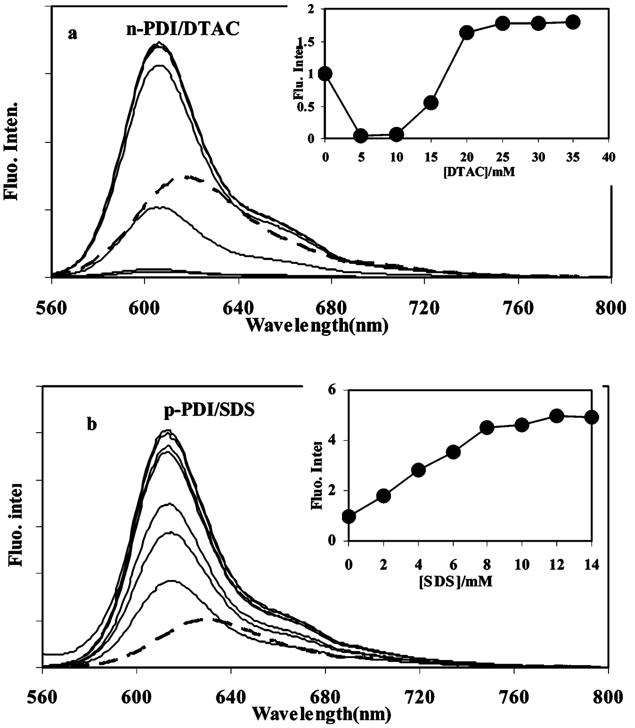

Figure 2. Fluorescence emission spectra of n-PDI (a) and p-PDI (b) mixing with DTAC and SDS surfactant solutions at different concentrations. Dashed lines: Pure aqueous solution. Solid lines: Aqueous solution with added surfactant (see inset for concentrations).

shown in Figure 2, which is typical for bay-region substituted PDIs.[7,15,16] For n-PDI/DTAC complexes there was an initial decrease in the fluorescence intensity with the addition of DTAC followed by an enhancement by a factor of ca. 1.8 above the cmc (corresponding to a quantum yield of approximately 0.96). Very similar results were obtained by adding small amounts of a concentrated DTAC/DMF solution (see Figures S1 and S2 in the Supporting Information). We presume that the strong fluorescence decrease at low DTAC concentration is due to the formation of nonfluorescent premicellar aggregates originating from the charge neutralization between the n-PDI and DTAC. It is well-known that quaternary ammonium groups in DTAC can help in stabilizing H-aggregates by forming ion pairs with sulfate groups.[17] The quantum yield of 0.96 above the cmc is the highest quantum yield reported for water soluble PDIs with four bay substitutions so far as we know. Kohl et al. did report $\Phi_{\mathrm{fl}} = 0.98$ for a cationic PDI with two bay substituents, but the analogous anionic species has a substantially smaller quantum yield ($\Phi_{\mathrm{fl}} = 0.12$).[7] The blue shift of the emission from 616 nm in water to 606 nm in the n-PDI/DTAC complex, as shown in Figure 2, suggests a less polar micelle environment.

There is a reasonably good agreement between the absorption and excitation spectra, eliminating the possibility that there coexist aggregates with strongly broadened spectra and no fluorescence and monomeric species with a well-resolved spectra and high fluorescence yield. However the agreement is not perfect as in all cases the 390−495 nm region ($S_2 \leftarrow S_0$) is weaker in the excitation spectra than in the absorption spectra. This implies that there exists an additional radiationless process from S_2 such that populating the emitting state is less efficient than direct excitation of the S_1 state.

The fluorescence lifetime is 4.78 ns for n-PDI in water (in good agreement with ref 8) and is extended to 6.91 ns in 35 mM DTAC. The fluorescence decay of n-PDI is monoexponential in all environments we studied (see Table 1). (Fluorescence decay curves are in the Supporting Information, Figure S3.)

p-PDI/SDS. For p-PDI/SDS, a similar development of a more structured absorption spectra was observed upon addition of surfactant with a 5 nm red shift relative to that of p-PDI in water. In this case there was a more dramatic increase in the molar extinction coefficient, as can be judged from Figure 1b, suggesting a more extensive dissociation of p-PDI aggregates formed in water. The plot of fluorescence intensity versus SDS concentration (in Figure 2b inset) shows a monotonic increase (in contrast to n-PDI/DTAC), ultimately leveling off above the cmc with an increase by a factor of ca. 4 (quantum yield is 0.42 after correcting for the optical density (OD) change at 540 nm). The fluorescence emission spectra showed a blue shift of 14 nm relative to that in water, as shown in Figure 2. The relationship between the absorption and excitation spectra (Figure 3) is very similar to the n-PDI/DTAC system.

We observed double exponential fluorescence decay curves both for p-PDI in water and p-PDI/SDS complexes. The average lifetime of the p-PDI/SDS complex is significantly shorter than that of p-PDI in water, decreasing from 3.36 to 0.73 ns (see Table 1). It seems likely that the multiexponential decay is originating from multiple structural aggregates of p-PDI formed in water or in the presence of SDS. The behavior of the p-PDI/SDS decay is puzzling. We suggest that the fast decay component is from aggregates which in the presence of SDS have a finite fluorescence quantum yield.

Complexation of WS-PDI and the Same Charged Surfactants. Besides studying complexation of WS-PDI moieties with oppositely charged surfactant molecules, we also examined how a surfactant with the same charge affects the photophysics of the corresponding WS-PDI. Once again the absorption spectra responded to small additions of surfactant (below the cmc), while the fluorescence changed continuously up to the cmc.

n-PDI/SDS. The absorption strength for n-PDI/SDS changed very little with increased SDS concentration, but there was a 12 nm red shift in the absorption spectrum (see Figure 4a and Table 1), the fluorescence spectra had almost no shift compared to pure water (Figure 5a) and the fluorescence intensity increased relatively little over the investigated concentration range (inset of Figure 5a), with a change in the quantum yield from 0.54 in pure water to 0.59 in 14 mM SDS. A monoexponential fluorescence decay with a lifetime of 6.03 ns was observed for n-PDI/SDS ([SDS] = 14 mM), which is slightly longer than the fluorescence lifetime of n-PDI in water and shorter than n-PDI/DTAC (see Table 1). These results suggest that the incorporation of n-PDI into the SDS micelle is possible but the environment is not appreciably different than in pure water. Certainly the spectroscopic perturbations we observe for n-PDI/SDS are less typical of micelle incorporation than in p-PDI/DTAC discussed next.

p-PDI/DTAC. The change in the absorption spectrum of p-PDI upon mixing with DTAC is presented in Figure 4b. This case is totally different than n-PDI/SDS. Stronger and more structured absorption spectra were observed with a slight red shift at higher DTAC concentrations. The molar extinction coefficient of the S_0−S_1 transition for p-PDI/DTAC at 35 mM increased to 62 900 M^{-1} cm^{-1} from 32 800 M^{-1} cm^{-1} in pure water. The fluorescence is slightly blue-shifted and becomes much stronger in the presence of DTAC (Figure 5b). The fluorescence intensity changes very little above the cmc (ca. 20 mM). Interestingly, the fluorescence increase in this case is even higher than that for the p-PDI/SDS complexes, with a final

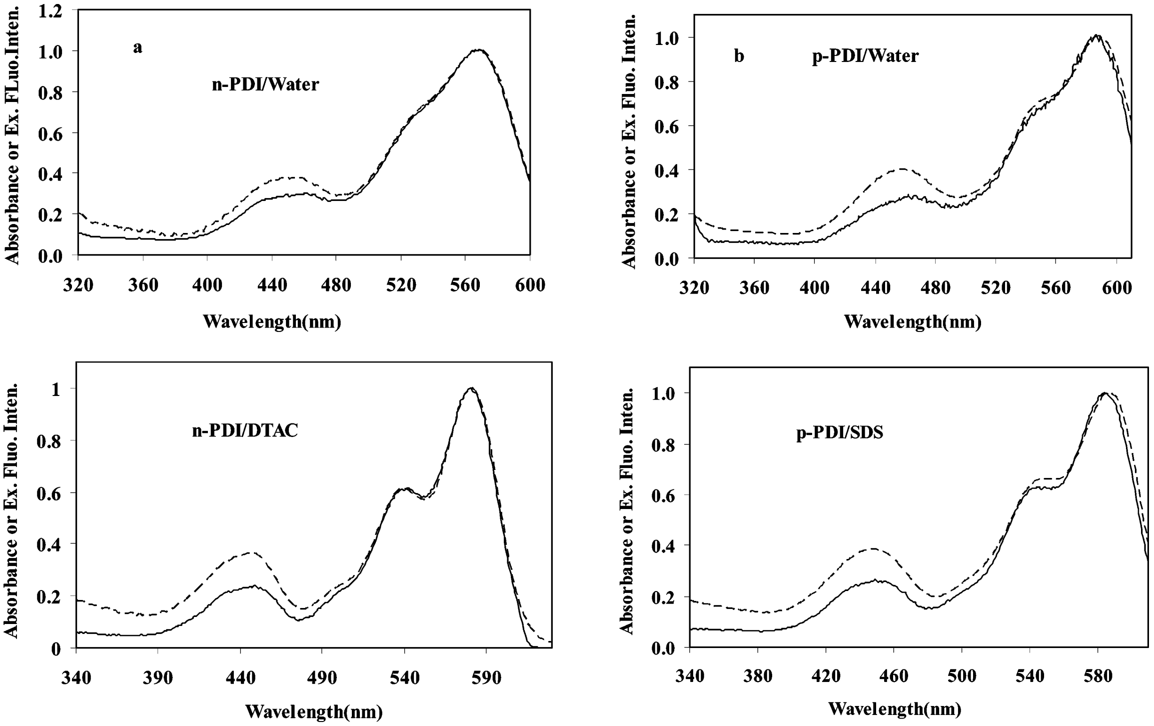

Figure 3. (a) Comparison of the absorption (dashed lines) and excitation (solid lines) spectra for n-PDI in pure water or n-PDI/DTAC (35 mM). The maximum absorbance for the excitation spectra is about 0.1 with $\lambda_{EM} = 610$ nm. (b) Comparison of the absorption (dashed lines) and excitation (solid lines) spectra for p-PDI in pure water or p-PDI/SDS (14 mM). The maximum absorbance for the excitation spectra is about 0.1 with $\lambda_{EM} = 610$ nm.

TABLE 1: Photophysical Characteristics of n-PDI and p-PDI in Different Media

	media	$\lambda_{0,0}$(abs) (nm)	$\lambda_{0,0}$(fluor) (nm)	ϵ^{max} (M^{-1} cm^{-1})	Φ_F [a]	τ [b] (ns) {k_r (10^{-9} s^{-1})}[f]
n-PDI	water	568	618	29 700	0.54	4.78 {0.113}
	DTAC[d]	581	606	37 100	0.96	6.91 {0.139}
	SDS[e]	580	617	30 200	0.59	6.03 {0.098}
p-PDI	water	587	628	32 800	0.14	6.35 (0.52); 0.13 (0.48); 3.36 [c] {0.042}
	DTAC[d]	593	622	62 900	0.52	5.61 (0.75); 0.78 (0.25); 4.40 [c] {0.118}
	SDS[e]	592	614	49 700	0.42	5.20 (0.04); 0.54 (0.96); 0.73 [c] {0.575}

[a] The quantum yield (Φ_F) was measured relative to the standard PDI compound *N*,*N*′-bis(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide in dichloroethane, for which $\Phi_F = 1$ is assumed. [b] Values in parentheses are the preexponential factors in a biexponential fit. [c] The average fluorescence lifetime by weighing the preexponential factors. [d] At 35 mM. [e] At 14 mM. [f] $k_r = \Phi_F/\tau$ (τ is the average lifetime in the case of nonexponential fluorescence decay).

quantum yield of 0.52. Two fluorescence lifetimes were observed for p-PDI/DTAC, suggesting different local environments for individual p-PDI moieties, but the average lifetime for p-PDI/DTAC is about 4.40 ns, longer than 3.36 ns in pure water.

Photophysics Study upon Mixing the PDI/Surfactant Complexes. *n-PDI/p-PDI.* On the basis of the above experiments, it is reasonable to believe that isolated p-PDI and n-PDI molecules were incorporated into the core of SDS and DTAC micelles, respectively. From our previous work we know that mixing p-PDI and n-PDI aqueous solutions results in strong fluorescence quenching, presumably via aggregation.[10] There was no fluorescence quenching upon mixing p-PDI/SDS and n-PDI/SDS or n-PDI/DTAC and p-PDI/DTAC. Likewise the absorption spectrum upon mixing p-PDI/SDS and n-PDI/SDS is identical with the average absorption spectrum of p-PDI/SDS and n-PDI/SDS (see Supporting Information, Figure S4).

p-PDI/n-TDI. While our main emphasis is on the properties of the n- and p-PDI compounds, we also carried out some experiments with n-TDI. Adding DTAC to n-TDI solutions modified the absorption spectrum and increased the fluorescence quantum yield to ca. 3% (see Supporting Information, Figure S5), similar to the observations of Jung et al. for n-TDI mixed with CTAB.[14] Mixing n-TDI with p-PDI in the absence of surfactant resulted in the total quenching of p-PDI fluorescence, but in the presence of DTAC no fluorescence quenching occurred (see Figure S6 in the Supporting Information).

These experiments demonstrate that the n-PDI/p-PDI or n-TDI/p-PDI moieties are "protected" by surfactant micelles from the strongly favored heteroassociation.

Dilution Experiments. Our primary objective in the experiments reported herein is to ascertain if our WS-PDIs are associated in pure water, and if so, can the addition of surfactants break up dimers or higher aggregates? The most obvious experiment to do is to dilute these solutions and look for nonlinearities in either the absorption strength or fluorescence intensity as a function of concentration. The accuracy of our UV−vis spectrometer allows accurate measurements of optical density down to approximately 0.01 absorbance units, limiting the lowest concentration that can be measured to approximately 3×10^{-7} M. Fluorescence is considerably more sensitive, allowing reasonable signal/noise down to ca. 10^{-9} M. In these experiments the dilution was carried out either with pure DI water or with the oppositely charged surfactant (35 mM DTAC or 14 mM SDS, both above the cmc). In all cases there was no obvious break in the curves down to the lowest concentration

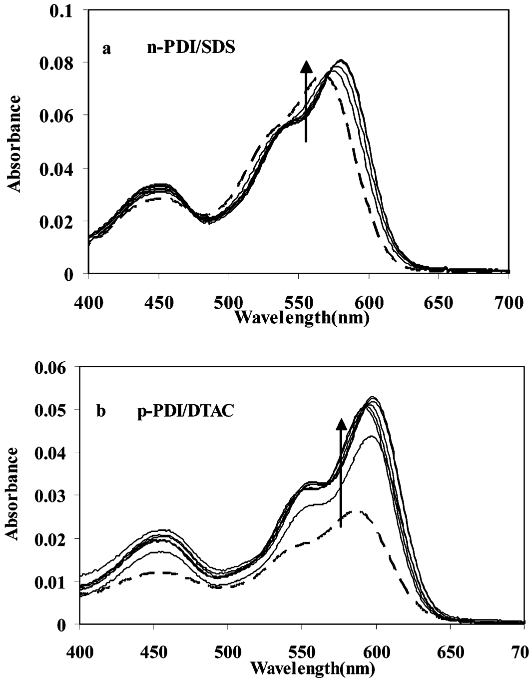

Figure 4. Absorption spectra of n-PDI with SDS (a) and p-PDI with DTAC (b) at different concentrations Arrows indicate increasing surfactant concentration. Dashed lines: Pure aqueous solution. Solid lines: Aqueous solution with added surfactant (see inset of Figure 5 for concentrations).

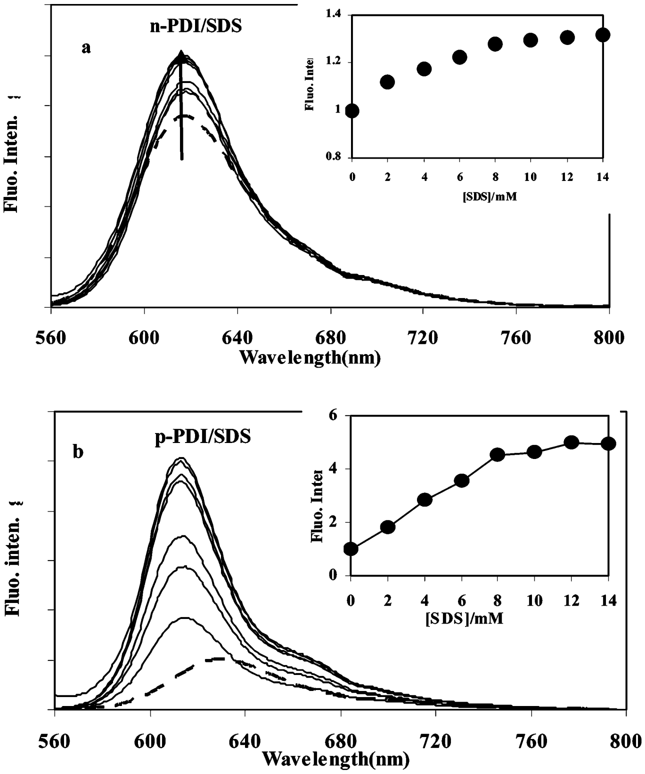

Figure 5. Fluorescence emission spectra of n-PDI (a) and p-PDI (b) mixing with SDS and DTAC surfactant solutions at different concentrations, respectively. Arrow indicates the increasing of surfactant concentrations. Dashed lines: Pure aqueous solution. Solid lines: Aqueous solution with added surfactant (see inset for concentrations).

range studied (see Supporting Information Figure S7). The fact that there was good linearity in the surfactant solution is consistent with our expectation that all aggregates would be broken up and individual WS-PDI moieties are solubilized. However the fact that there was no significant nonlinearity in the case of pure water suggests one of two contradictory conclusions: (1) There are no aggregates in pure water, in which case our observed surfactant effects are "environmental effects", which does not seem likely to us, or (2) the association constant for the dimers or aggregates exceeds 10^{+7} M^{-1}. Ford has reported an association constant of this magnitude for the dianion (which does not have any bay substituents).[18] Thus we suggest that aggregates (perhaps dimers) persist in water to the lowest concentration we have studied but the geometry of these aggregates is such that there is only moderate photophysical interaction (with concomitant fluorescence quenching) between the chromophores.

Summary

Water soluble perylene diimides (WS-PDI) have been incorporated into SDS or DTAC surfactant solution of either the opposite charge (e.g., n-PDI/DTAC or p-PDI/SDS) or the same charge (e.g., n-PDI/SDS or p-PDI/DTAC). The more structured absorption spectra, increased fluorescence quantum yield and lengthened lifetime upon complexing with surfactant suggests that PDI aggregates were broken up and individual WS-PDI moieties solvated by the surfactant moieties even below the cmc. The fact that there was no fluorescence quenching upon mixing p-PDI/SDS and n-PDI/SDS or n-PDI/DTAC and p-PDI/DTAC further demonstrates that the PDI moieties are well-solublized and isolated from each other by the surfactant micelles.[19] A similar result was obtained for mixing n-TDI/DTAC and p-PDI/DTAC solutions. It is perhaps surprising that these micelles are so efficient in preventing the strongly favored electrostatic and $\pi-\pi$ stacking between n-PDI and p-PDI in water.

Our interpretation of these results is based on surfactant solvation and deaggregation. On the basis of our dilution experiments, we conclude that the association constant for same-charged WS-PDI exceeds 10^7 M^{-1}. However we cannot dismiss the possibility that the surfactant is exerting a local "environmental effect" on the WS-PDI moieties. The photophysics of these bay-substituted perylene diimides is strongly affected by the nonplanarity of the aromatic ring which could be modified by the associated surfactant.[20] Margineanu et al. have suggested that the fluorescence yield of n-PDI is reduced by hydrogen-bonding of the charged groups to water because of the additional vibrational coupling modes this would bring into play.[8]

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Supporting Information Available: Absorption and emission spectra, fluorescence decay and fitting curves, and graphs of absorbance and fluorescence intensity vs concentration. This material is available free of charge via the Internet at http://pubs.acs.org.

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