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Aggregation of 3,4,9,10-Perylenediimide Radical Anions and Dianions Generated by Reduction with Dithionite in Aqueous Solutions

Rodrigo O. Marcon[†] **and Sergio Brochsztain***[,‡]

Centro Interdisciplinar de Investigação Bioquímica, Universidade de Mogi das Cruzes, Av. Dr. Cândido Xavier de Almeida Souza, 200, Mogi das Cruzes-SP, 08780-911, Brazil, and Universidade Federal do ABC, Rua Santa Adélia, 166, Santo André-SP, 09210-170, Brazil

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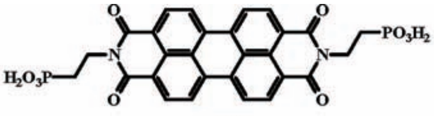
Aqueous solutions of *N,N′*-bis(2-phosphonoethyl)-3,4,9,10-perylenediimide (PPDI) were titrated with sodium dithionite, generating radical anions ($PPDI^{-\bullet}$) and dianions ($PPDI^{2-}$). In aqueous ethanol (1:1 v/v), PPDI existed as monomers and remained in the monomeric form in all reduced states. In water, on the other hand, PPDI formed dimers, which were transformed into a π-stacked aggregated form upon one-electron reduction to $PPDI^{-\bullet}$. Addition of a second electron, however, resulted in dissociation of the aggregates, giving the dianion $PPDI^{2-}$ in the monomeric form. The presence of CTAB micelles prevented the aggregation of $PPDI^{-\bullet}$ in water, indicating that the radical anions were incorporated into the micellar phase. Reduction of PPDI in ethanol solution, where the dye was aggregated, resulted in the formation of soluble mixed stacks containing both $PPDI^{-\bullet}$ and $PPDI^{2-}$. These mixed stacks stabilized the radical anion form, preventing further reduction to the dianion.

1. Introduction

The 3,4,9,10-perylenediimides (PDI) are a class of organic dyes with high thermal and photostability.[1−3] The PDI are known as one of the best n-type organic semiconductors,[4,5] which makes them very suitable for applications in optoelectronic devices, such as solar cells,[6−9] organic field-effect transistors,[10−12] and electroluminescent devices.[13,14] The remarkable properties of PDI arise from the ease of reduction, which is a common characteristic of the aromatic diimides, including the 1,4,5,8-naphthalenediimides (NDI).[15−19] Accordingly, the PDI and NDI can be easily reduced in two steps, generating first radical anions, followed by doubly reduced dianions.[14−16] The formation of radical anions by reduction of the NDI in aqueous solution with sodium dithionite has been well reported.[20,21] Surprisingly, there is much less information available on the reduction of PDI, in spite of the central role of PDI radical anions in semiconductor devices. Most of the reported studies employed electrochemical[14−16,22−25] or photochemical[26] reduction in organic solvents. Since most reported electrochemical studies were performed in organic solvents, there is a lack of information about the behavior of PDI reduced species in aqueous solutions.

In a recent report from our group on the reduction of self-assembled PDI films,[27] we observed that reduction of *N,N′*-bis(2-phosphonoethyl)-3,4,9,10-perylenediimide (PPDI), a water-soluble anionic PDI derivative (Figure 1), with sodium dithionite in aqueous solutions gave stable radical anions and dianions. Following our report, Shirman et al.[28] also reported briefly the generation of stable PDI dianions in water using dithionite reduction. However, a thorough characterization of aggregation and solvent effects on the PDI reduced species was not given in those previous accounts. In the present report we describe in detail the stepwise reduction of PPDI with dithionite in water and in aqueous ethanolic and micellar solutions. We present studies on the aggregation states of PDI radical anions and dianions in solvents of different polarity and the effect of CTAB micelles in preventing radical aggregation. A detailed spectroscopic characterization is given, including absorption maxima and molar coefficients (ε) for each species in its different aggregation states. Other authors have studied the aggregation of both cationic[29−31] and anionic[32−34] substituted PDI in water, but no attempts to obtain reduced species were mentioned in those reports.



PPDI

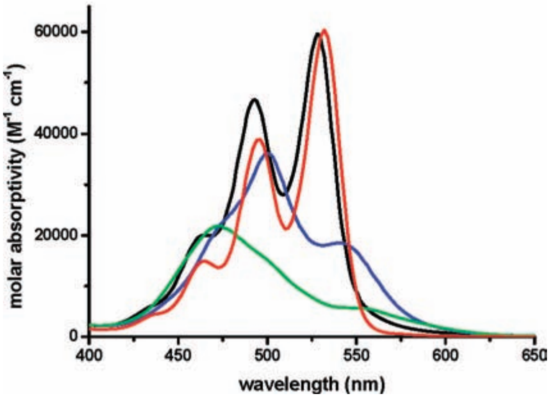


Figure 1. Absorption spectra of PPDI (2×10^{-5} M) in different solutions: water/ethanol (1:1 v/v) (black); 0.05 M CTAB (red); water (blue); ethanol (green).

2. Experimental Part

Sodium dithionite ($Na_2S_2O_4$) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Aldrich and used

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* To whom correspondence should be addressed. E-mail: sergio.brochsztain@ufabc.edu.br. Phone and Fax: (55) (11) 49963166.

[†] Universidade de Mogi das Cruzes.

[‡] Universidade Federal do ABC.

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as received. *N*,*N*′-Bis(2-phosphonoethyl)-3,4,9,10-perylenediimide was synthesized as previously reported and used in the form of the water-soluble disodium salt.[35] All solvents employed were of spectroscopic grade. Aqueous solutions were prepared with deionized water. UV−vis absorption spectra were registered with a Cary 50 spectrophotometer (Varian).

Titrations of PPDI with $Na_2S_2O_4$ were carried out in standard quartz cuvettes (10 mm path length) sealed with screw-caps (Hellma model 117.100), equipped with a silicone septum for argon purging with a needle. Stock solutions of sodium dithionite (typically 0.02 M in pH 8 borate buffer) were prepared freshly and used in the same day. The cuvette containing 3 mL (1 mL in the case of CTAB) of the PPDI solution (typically $[\mathrm{PPDI}] \sim 2 \times 10^{-5}$ M, diluted from a 1 mM stock solution in water) was purged with argon for 5 min. Aliquots from the $Na_2S_2O_4$ stock solution were then introduced with a needle, the solution was stirred, and the absorption spectra were recorded.

3. Results

3.1. Aggregation of Ground-State PPDI. The absorption spectra of PPDI in aqueous ethanol (50% v/v) showed a well-defined vibrational progression typical of PDI derivatives in the monomeric state (Figure 1). The longest wavelength band ($0 \rightarrow 0$ transition, $\lambda_{\max} = 528$ nm) was the most intense band, with a second maximum at shorter wavelengths ($0 \rightarrow 1$ transition, $\lambda_{\max} = 492$ nm) and a shoulder near 462 nm. In water, on the other hand, an inversion in the relative intensity of the vibrational bands was observed, indicating the dimerization of the dye.[32] The main band in water was found at 500 nm, with a lower intensity band at 540 nm. The presence of cationic CTAB micelles, however, caused the dissociation of the dimers, resulting in monomer-like spectra, very similar to those observed in aqueous ethanol (Figure 1). The main difference between the spectra was a slight red-shift in CTAB solution (ca. 4 nm). Considering that the longest wavelength transition of the PDI has a $\pi-\pi^*$ character, it can be concluded that the dye is in a more polar environment in the micellar solution than in aqueous ethanol. Therefore, PPDI must be located at the micellar interface, where the phosphonate groups can interact electrostatically with the positive CTAB head groups. In ethanol, further spectral changes were observed (Figure 1). The most intense absorption was found at 473 nm in this case, with a shoulder at 546 nm. The spectra of PPDI in ethanol can be attributed to an aggregated form of the dye, possibly consisting of soluble π-stacks, as observed for the related NDI.[20,21] The spectral data for PPDI in different solutions are summarized in Table 1.

3.2. Reduction of PPDI in Aqueous Ethanol. Having characterized the aggregation states of PPDI in different environments, we then carried out titration experiments using the reducing agent sodium dithionite, in order to study the aggregation states of PPDI in its reduced forms. Addition of $Na_2S_2O_4$ to monomeric PPDI, in aqueous ethanolic solutions, led initially to the formation of radical anions (PPDI$^{-\bullet}$), as indicated by the decrease of PPDI absorption (400−550 nm) and the concomitant increase of new absorption bands peaking at 713, 800, and 960 nm (Figure 2A, Table 1). The spectra of PPDI$^{-\bullet}$ in Figure 2A are in full agreement with literature data for PDI$^{-\bullet}$.[16,27]

TABLE 1: Absorption Maxima (Nanometers) for PPDI in the Ground State and Reduced Forms in Different Solutions[a]

solution	PPDI	PPDI$^{-\bullet}$	PPDI^{2-}
water/ethanol (1:1)	528 (59 600)	960 (26 500)	601 (20 100)
	492 (46 700)	800 (39 500)	537 (76 500)
	462 (sh)	713 (84 000)	503 (46 400)
			288 (58 800)
			275 (68 900)
			265 (50 200)
water	540 (18 500)	987 (8200)	600 (18 300)
	500 (36 200)	817 (15 400)	536 (74 500)
		730 (24 800)	506 (47000)
			286 (56700)
			274 (66900)
			264 (48900)
aqueous CTAB (0.05 M)	532 (60 300)	962 (25 000)	616 (14 500)
	496 (39 000)	800 (40 000)	550 (54 700)
	464 (sh)	716 (79 300)	514 (32 100)
			290 (38 900)
			277 (46 000)
			266 (35 600)
ethanol	546 (6500)	1002 (5300)	594 (sh)
	473 (22 000)	822 (8000)	517 (16 500)
		734 (12 300)	

[a] Values in parentheses are the molar absorptivity coefficients (ε, M^{-1} cm^{-1}). ε values were calculated using the analytical [PPDI], i.e., the extinction coefficients of dimers and aggregates are per monomer component.

Conversion of ground-state PPDI to PPDI$^{-\bullet}$ was apparently the only process taking place until approximately half of the diimide had been reduced, as judged by the decrease in the absorbance at 528 nm (Figure 2A, inset). From this point on, addition of more dithionite led to a decrease in the radical anion bands, with the increase of a new band with maxima at 503, 537, and 601 nm (Figure 2B), which can be attributed to the formation of PPDI^{2-}.[16,27] In addition to the long-wavelength absorption band, the dianion spectra also presented an intense and well-structured short-wavelength band in the range of 250−300 nm (Figure 2B, inset). When dithionite was present in excess, all the absorbance at wavelengths longer than 650 nm vanished, indicating that the dye was quantitatively reduced to PPDI^{2-}. In this condition, a broad band with maximum at 315 nm was visible (Figure 2B, inset), which can be attributed to dithionite anion, confirming that the reducing agent was indeed in excess. All the evidence, like the narrow absorption bands and high molar absorptivities (Table 1), suggests that the radical anions and dianions of PPDI exist as monomers in aqueous ethanol (see the Discussion).

3.3. Reduction of PPDI in Water. Titration of PPDI in water, where the dye was dimeric, led initially to the formation of radical anions, with maxima at 730, 817, and 987 nm (Figure 3A, Table 1), similarly to that observed in aqueous ethanol. The spectra of PPDI$^{-\bullet}$ in water, however, were broader and red-shifted relative to those in aqueous ethanol, suggesting aggregation of the anion radicals. Moreover, the reduction of PPDI to PPDI$^{-\bullet}$ in water proceeded only until ca. 30% of the dye had been reduced (Figure 3A, inset). Addition of more dithionite resulted in a decrease in the radical anion absorption, with a concomitant increase of the dianion absorption bands at 506, 536, and 600 nm (Figure 3B) and in the range of 260−300 nm (Figure 3B, inset). Quantitative conversion of PPDI to the dianion form in water was also observed in the presence of dithionite in excess, and the spectra of PPDI^{2-} were virtually identical to those observed in aqueous ethanol (Table 1).

3.4. Reduction of PPDI in Aqueous CTAB. Titration of PPDI in the presence of CTAB micelles (Figure 4) resulted in a profile very similar to that observed in aqueous ethanol, suggesting the presence of monomers in all reduction states of

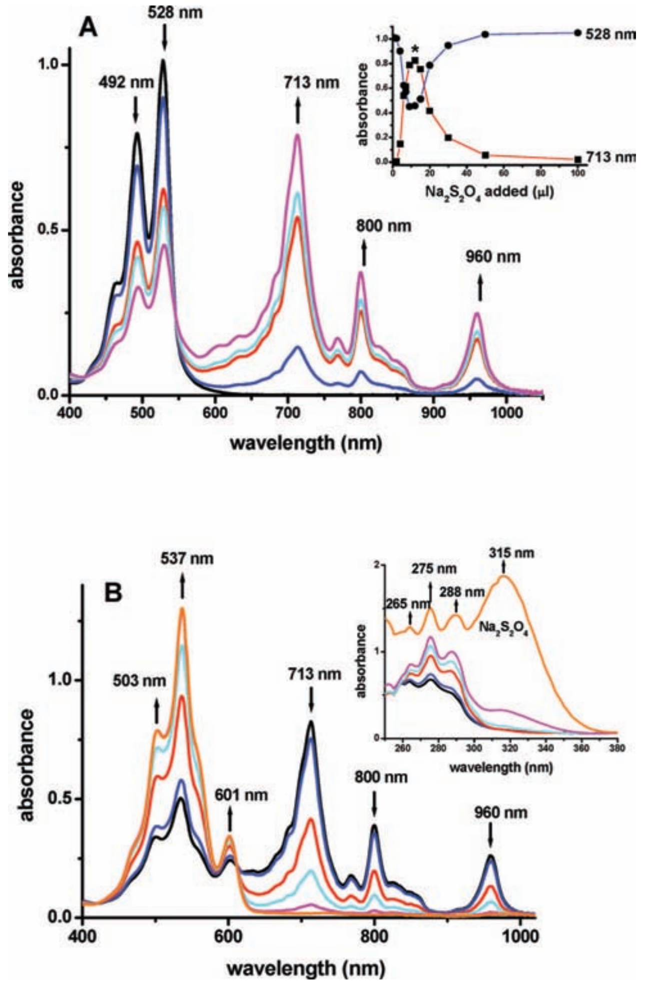

Figure 2. Absorption spectra showing the titration of a PPDI solution (3 mL, 1.7×10^{-5} M) in water/ethanol (1:1 v/v) with a stock solution of $Na_2S_2O_4$ (0.02 M in borate buffer, pH = 8). (A) Initial stage of the titration (radical anion formation). Aliquots of dithionite solution added were the following: 0 µL (black); 4 µL (blue); 6 µL (red); 7 µL (light blue); 9 µL (purple). Inset: absorbance at 528 (●) and 713 nm (■) as a function of the volume of $Na_2S_2O_4$ added. The lines are added as a guide to the eyes. (B) Final stage of the titration (dianion formation). Aliquots of dithionite solution added were the following: 12 µL (black); 15 µL (blue); 20 µL (red); 30 µL (light blue); 50 µL (purple); 150 µL (orange). Inset: short-wavelength region of the spectra.

PPDI. Initially, $PPDI^{-\bullet}$ was formed, with absorption maxima at 716, 800, and 962 nm (Figure 4A, Table 1), very close to the values in aqueous ethanol. After ca. 50% of the diimide had been reduced (Figure 4A, inset), dianion formation was observed, with maxima at 514, 550, and 616 nm and the presence of the characteristic short-wavelength spectral features (Figure 4B). The dye was quantitatively converted into $PPDI^{2-}$ in the presence of excess dithionite.

3.5. Reduction of PPDI in Ethanol. Titration of PPDI in ethanol resulted in rather different results than those observed with aqueous solvents. When π-stacks of PPDI were reduced with dithionite in ethanol, stacked radical anions were generated, as indicated by the broad and red-shifted spectra, with maxima at 734, 822, and 1002 nm (Figure 5A, Table 1). Further addition of dithionite did not lead to quantitative dianion formation. Remarkably, the absorption of the radical anion persisted even in the presence of dithionite in excess (Figure 5A, inset). However, a slight decrease in the radical anion absorption and a red-shift of PPDI absorption from 473 to 518 nm (Figure 5B) indicate that the dianion was formed at the expense of uncharged PPDI, leading to mixed stacks containing $PPDI^{-\bullet}$ and $PPDI^{2-}$. The formation of mixed stacks is supported by recent reports from our group concerning the reduction of PPDI in self-assembled thin films.[27]

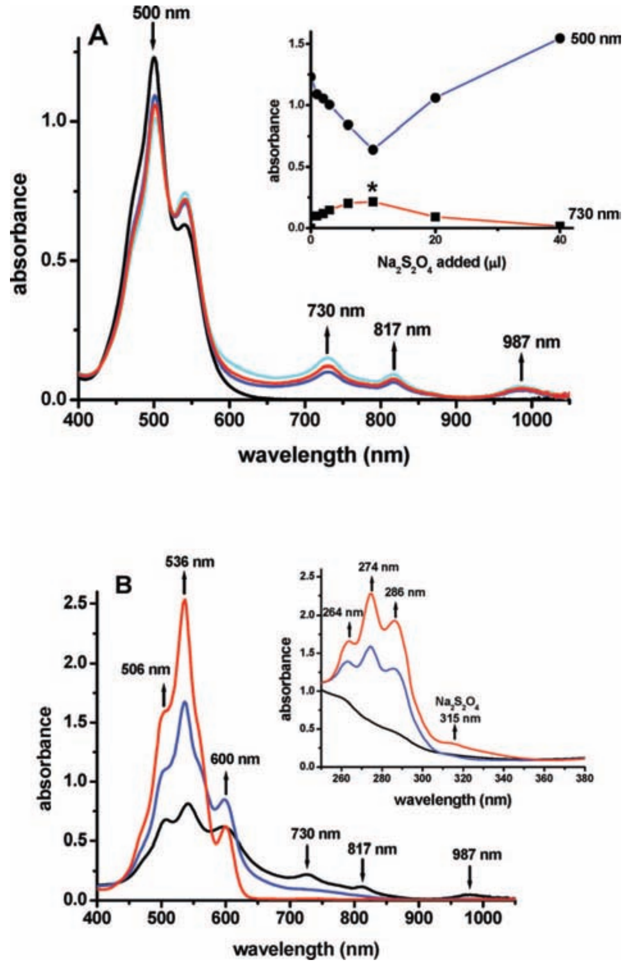

Figure 3. Absorption spectra showing the titration of a PPDI solution (3 mL, 3.4×10^{-5} M) in water with a stock solution of $Na_2S_2O_4$ (0.02 M in borate buffer, pH = 8). (A) Initial stage of the titration (radical anion formation). Aliquots of dithionite solution added were the following: 0 µL (black); 1 µL (blue); 2 µL (red); 3 µL (light blue). Inset: absorbance at 500 (●) and 730 nm (■) as a function of the volume of $Na_2S_2O_4$ added. The lines are added as a guide to the eyes. (B) Final stage of the titration (dianion formation). Aliquots of dithionite solution added were the following: 10 µL (black); 20 µL (blue); 40 µL (red). Inset: short-wavelength region of the spectra.

4. Discussion

The molar absorptivity coefficients (ε) for $PPDI^{-\bullet}$ and $PPDI^{2-}$ in the different solutions can be readily obtained from the titrations in Figures 2−5. The concentration of $PPDI^{-\bullet}$ formed for each dithionite addition in the first stage of the titrations can be obtained from the decrease in the concentration of ground-state PPDI, for which ε is known, assuming that PPDI and $PPDI^{-\bullet}$ are the only species present in solution in the beginning of the titration (i.e., eq 1 is the only reaction taking place) and that $PPDI^{-\bullet}$ does not absorb significantly in the range of 400−550 nm (which is quite reasonable since the spectral shape in this region did not change in the first stage of the titration). Good linear correlations were obtained in Lambert−Beer plots for the radical anion absorption bands, as shown in Figure 6 for the most intense radical anion absorption (λ_{max} = 713−734 nm). For the doubly reduced species, ε values are readily

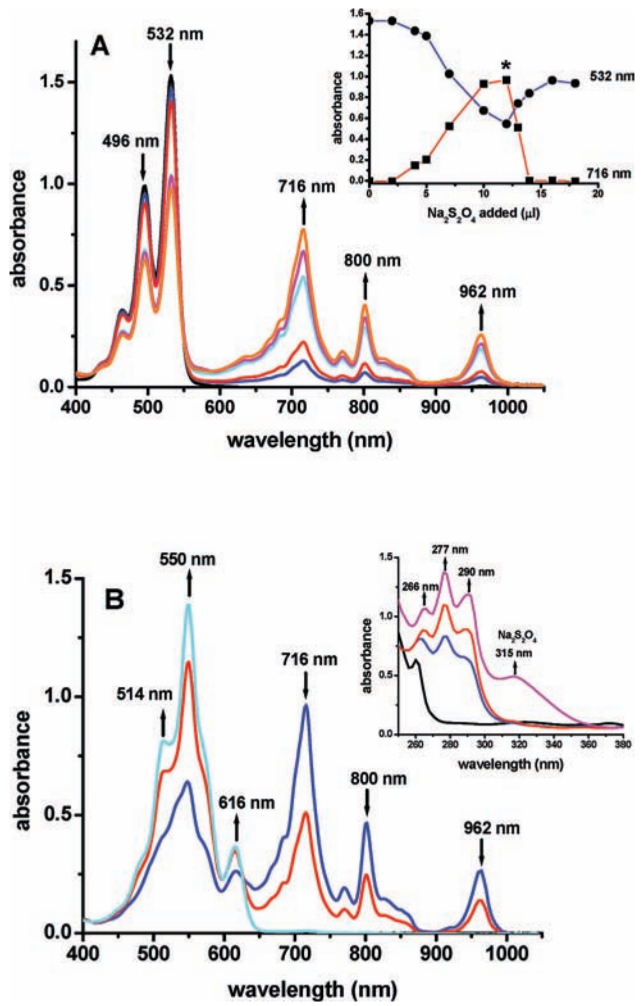

Figure 4. Absorption spectra showing the titration of a PPDI solution (1 mL, 2.5×10^{-5} M) in aqueous CTAB solution ([CTAB] = 0.05 M) with a stock solution of $Na_2S_2O_4$ (0.01 M in borate buffer, pH = 8). (A) Initial stage of the titration (radical anion formation). Aliquots of dithionite solution added were the following: 0 μL (black); 3 μL (blue); 5 μL (red); 7 μL (light blue); 8 μL (purple); 9 μL (orange). Inset: absorbance at 532 (●) and 716 nm (■) as a function of the volume of $Na_2S_2O_4$ added. The lines are added as a guide to the eyes. (B) Final stage of the titration (dianion formation). Aliquots of dithionite solution added were the following: 12 μL (blue); 13 μL (red); 14 μL (light blue). Inset: short-wavelength region of the spectra: 0 μL (black); 12 μL (blue); 13 μL (red); 18 μL (purple).

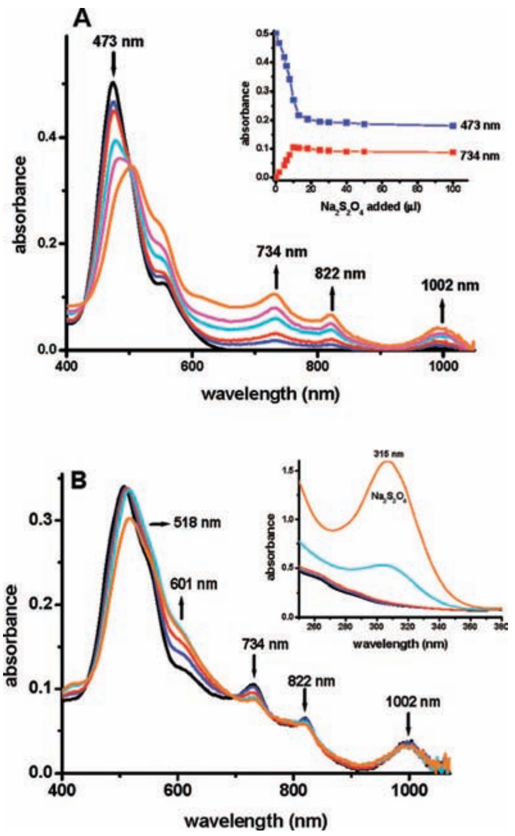

Figure 5. Absorption spectra showing the titration of a PPDI solution (3 mL, 2.2×10^{-5} M) in ethanol with a stock solution of $Na_2S_2O_4$ (0.02 M in borate buffer, pH = 8). (A) Initial stage of the titration (radical anion formation). Aliquots of dithionite solution added were the following: 0 μL (black); 2 μL (blue); 4 μL (red); 6 μL (light blue); 8 μL (purple); 10 μL (orange). Inset: absorbance at 473 (blue squares) and 734 nm (red squares) as a function of the volume of $Na_2S_2O_4$ added. The lines are added as a guide to the eyes. (B) Final stage of the titration (dianion formation). Aliquots of dithionite solution added were the following: 12 μL (black); 16 μL (blue); 25 μL (red); 50 μL (light blue); 150 μL (orange). Inset: short-wavelength region of the spectra.

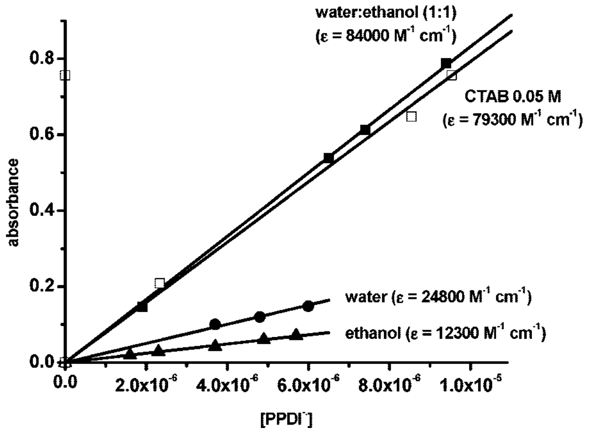

Figure 6. Lambert–Beer plots for $PPDI^{-\bullet}$ in different solutions: (■) water/ethanol (1:1) at $\lambda_{max} = 713$ nm; (□) aqueous CTAB (0.05 M) at $\lambda_{max} = 716$ nm; (●) water at $\lambda_{max} = 730$ nm; (▲) ethanol at $\lambda_{max} = 734$ nm. The lines represent linear regressions of the experimental data.

obtained from the absorption spectra in the presence of excess dithionite, since the diimide is quantitatively reduced to the dianion (except in ethanol).

The absorption maxima and ε values for PPDI, $PPDI^{-\bullet}$, and $PPDI^{2-}$ in the different solutions are summarized in Table 1. Parts A and B of Figure 7 show absorption spectra of the radical anion and dianion, respectively, in the different solutions, given in molar absorptivity scale. It can be clearly seen in Figure 7A that PPDI radical anion is monomeric in aqueous ethanol, as indicated by the narrow absorption bands with high ε values (>80 000 M^{-1} cm^{-1}). In water and ethanol, on the other hand, $PPDI^{-\bullet}$ is highly aggregated, as evident from the broad bands with low ε, which are red-shifted relative to the monomer bands. The most intense absorption of PPDI radical anions, for instance, was shifted from 713 nm in aqueous ethanol (monomer) to 730 nm in water and 734 nm in ethanol. The longest wavelength absorption band of $PPDI^{-\bullet}$ in the near-IR (NIR) region was the most sensitive to the aggregation state, being shifted from 960 nm in the monomer to 987 nm in water and 1002 nm in ethanol (Figure 7A). The ε values for $PPDI^{-\bullet}$ in water and in ethanol were much lower than the values for the monomer (less than one-third), suggesting the formation of extended aggregates or π-stacks, since the molar absorptivity of a dimer would be at least half of that of the monomer. In the presence of CTAB micelles, however, the aggregates of $PPDI^{-\bullet}$ dissociate, resulting

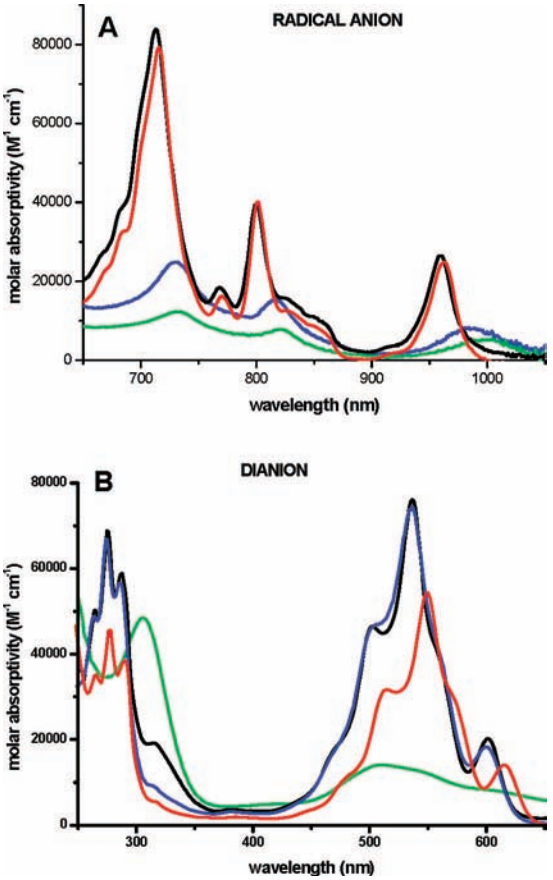

Figure 7. (A) Absorption spectra of PPDI$^{-\bullet}$ in water/ethanol (1:1) (black), 0.05 M CTAB (red), water (blue), and ethanol (green). (B) Absorption spectra of PPDI^{2-} in water/ethanol (1:1) (black), 0.05 M CTAB (red), water (blue), and ethanol (green).

in an absorption spectra almost identical to that of monomeric PPDI$^{-\bullet}$ in aqueous ethanol (Figure 7A), showing that the radical anion was present in the micellar phase, with individual PPDI$^{-\bullet}$ molecules residing in different micelles.

The absorption spectra of the doubly reduced form of PPDI shows that the dianion was monomeric in aqueous ethanol, as well as in water and in CTAB solution (Figure 7B), as seen from the narrow absorption bands and high ε values (>50 000 M^{-1} cm^{-1}). In ethanol, on the other hand, the dianion remains in the aggregated form.

The characterization of the different aggregation states of PPDI and its reduced forms in different solutions lead to the following conclusions about the titrations in Figures 2−5. In aqueous ethanol (Figure 2) and in micellar CTAB solution (Figure 4), monomeric PPDI was reduced to give monomeric PPDI$^{-\bullet}$, and then monomeric PPDI^{2-}. In water, PPDI dimer was reduced giving π-stacked PPDI$^{-\bullet}$. Further reduction leads to monomeric PPDI^{2-}. Thus, electrostatic repulsion between the doubly charged dianions in water is strong enough to cause dissociation of the aggregates, giving monomeric PPDI^{2-}. In ethanol, in contrast, π-stacking interactions are predominant, and the dye forms stacks that remain in all the reduction states. The persistence of radical anion absorption even in the presence of excess dithionite in ethanol (Figure 5) indicates the stabilization of PPDI$^{-\bullet}$ through the formation of mixed stacks, as suggested previously for the NDI.[20,21] From the absorption spectra in Figure 5, it can be deduced that stacks with the composition PPDI$^{-\bullet}$/PPDI^{2-} in the approximate ratio 1/2 were formed. More details about the formation of mixed stacks of PPDI in ethanol and in self-assembled thin films are given elsewhere.[27]

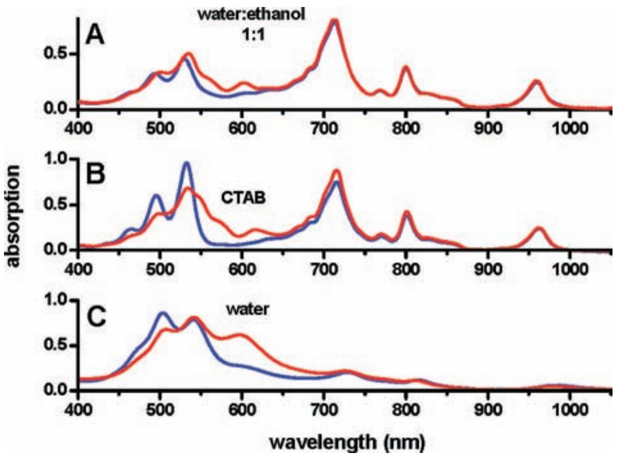

Figure 8. Absorption spectra taken near the turning point of PPDI titrations (marked with a star in the insets of Figures 2A, 3A, and 4A). The concentrations of PPDI and dithionite are given in Figures 2, 3, and 4. (A) Titration in water/ethanol (1:1) after the addition of 9 (blue) and 12 μL (red) of the dithionite stock solution. (B) Titration in aqueous CTAB solution after the addition of 9 (blue) and 11 μL (red) of the dithionite stock solution. (C) Titration in water after the addition of 6 (blue) and 10 μL (red) of the dithionite stock solution.

The titrations can be divided in two main parts, as seen by the profiles in the insets of Figures 2A, 3A, and 4A. In the beginning of the titrations, ground-state PPDI was reduced by dithionite giving PPDI$^{-\bullet}$, according to eq 1, resulting in an increase in radical anion absorption and a decrease in ground-state absorption. In the second part of the titrations, PPDI$^{-\bullet}$ was reduced by dithionite giving PPDI^{2-}, i.e., eq 2 predominated. In this stage of the titration a decrease in radical anion absorption was observed, concomitant with an increase in dianion absorption.

Near the turning point, however, where radical anion concentration reached its maximum (indicated by a star in the insets of Figures 2A, 3A, and 4A), the presence of the three species was observed simultaneously, and addition of dithionite converted ground-state PPDI directly into PPDI^{2-}, with little change in radical anion concentration (Figure 8). This result can be explained by the disproportionation reaction between two PPDI$^{-\bullet}$ (eq 3). Thus, when dithionite is added near the turning point of the titrations, PPDI$^{-\bullet}$ is formed through eq 1, but reacts further through eq 3, giving as a net result the conversion of PPDI into PPDI^{2-} (eq 4).

$$\mathrm{PPDI} + \mathrm{e}^- \rightarrow \mathrm{PPDI}^{-\bullet} \tag{1}$$

$$\mathrm{PPDI}^{-\bullet} + \mathrm{e}^- \rightarrow \mathrm{PPDI}^{2-} \tag{2}$$

$$2\mathrm{PPDI}^{-\bullet} \rightleftharpoons \mathrm{PPDI} + \mathrm{PPDI}^{2-} \tag{3}$$

$$\mathrm{PPDI} + 2\mathrm{e}^- \rightarrow \mathrm{PPDI}^{2-} \tag{4}$$

The equilibrium constant for disproportionation (K_d = [PPDI] [PPDI^{2-}]/[PPDI$^{-\bullet}$]^2), which is a measure of radical anion stability, can be estimated from the absorption spectra at the titrations turning point, since ε is known for the three species, allowing the estimation of equilibrium concentrations. The estimated values for K_d in different solvents are given in Table 2. Disproportionation constants are usually determined by electrochemistry, using the difference between the first and second redox potentials,[36] but unfortunately electrochemical reduction of PDI in aqueous solvents has not yet been achieved

TABLE 2: Disproportionation Constants (K_d) for $PPDI^{-\bullet}$ in Different Solvents

solvent	K_d
H_2O/EtOH (1:1)	0.13
CTAB	0.40
H_2O	0.20
EtOH	0.85

(all the reported studies were performed in organic solvents, to our knowledge).

It can be noted from eq 3 that radical anion stability is inversely proportional to the K_d values. The data in Table 2 show, therefore, that the stability of $PPDI^{-\bullet}$ is lower in the micellar solution than in homogeneous solutions. This phenomenon, which has been also observed with viologen derivatives,[36] can be attributed to the distribution of the disproportionation products (PPDI and $PPDI^{2-}$) in different environments, decreasing the rate of the comproportionation (eq 3, from right to the left). In the case of ethanol, the higher K_d values obtained are not in agreement with the high radical stability seen in Figure 5, since $PPDI^{-\bullet}$ persists even in the presence of excess dithionite. This apparent discrepancy is because eq 3 is an oversimplified model and does not take in account the extra stabilization obtained by the formation of mixed π-stacks, where the lone electron of $PPDI^{-\bullet}$ can be delocalized over the whole stack, as reported for the NDI.[20,21]

When the concentration of dithionite is taken in account in the titrations of Figures 2−4, a lack of correspondence between the equivalents of reducing agent added and the amount of $PPDI^{-\bullet}$ formed can be noticed. In a typical experiment, addition of an aliquot of 2 μL from a 0.02 M dithionite stock solution to 3 mL of PPDI solution should result in an increment of 13 μM in the $[S_2O_4^{2-}]$. Therefore, this aliquot would be expected to form 26 μM of $PPDI^{-\bullet}$ (since each $S_2O_4^{2-}$ is capable of donating 2 e^-). The amount of $PPDI^{-\bullet}$ that was actually formed was 1 order of magnitude lower than the expected. These results suggest that the dithionite stock solutions used in the titrations were actually more diluted than the value calculated from the weighed amount. This finding is quite reasonable, since dithionite is unstable and reacts with atmospheric oxygen. Even though the experiments were carried out in sealed cuvettes under argon atmosphere, there is always a residual amount of oxygen dissolved in the solutions that will react with part of the dithionite aliquot.

5. Conclusions

In this work, we showed that the use of dithionite as a reducing agent allowed a detailed study on the behavior of PDI radical anions and dianions in aqueous solutions. We showed that the aggregation of PDI reduced species can be controlled by solvent effects and by the presence of micelles. In the case of PPDI, a mixture of water and ethanol (1:1) was the best solvent for the dye in all its redox states. Bulk water or ethanol, on the other hand, induced extensive aggregation of the radical anions, which was prevented by the presence of CTAB micelles in water. A strict control over the aggregation states of PDI reduced species is essential for their applications in photonics and electronics. For semiconductor applications, such as in the synthesis of nanowires, a highly stacked form is desired. For biological applications, such as in photodynamic therapy of cancer, the dye should be preferentially in the monomeric state, favoring the transposition of biological membranes. In this regard, it is worth mentioning a recently published work by Baram et al. that describes the assembly/disassembly of PDI-based nanofibers controlled by the reduction state of the PDI.[37]

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