Photoprocesses of Thiacarbocyanine Monomers, Dimers, and Aggregates Bound to Polyanions

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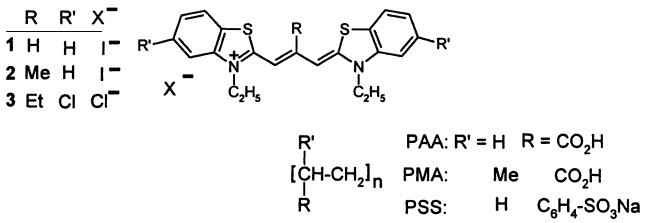
The photophysical and photochemical properties of thiacarbocyanine **1** and the methyl **2** and ethyl **3** meso derivatives in aqueous solution were studied in the presence of poly(styrenesulfonate) (PSS), poly(acrylic acid) (PAA), or poly(methacrylic acid) (PMA). When the ratio of polyanion residue to dye concentrations (*r*) is increased, a monomer/dimer equilibrium in neat water is shifted toward bound H-aggregates (high dye loading conditions), dimers, and monomers (low dye loading). The photodeactivation properties of **1**−**3** depend significantly on these ground-state equilibria. The fluorescence quantum yield (Φ_f) is strongly enhanced for low dye loading and reduced when bound aggregates and dimers are present, $r = 3-30$ and $(0.2-2) \times 10^3$, respectively. For **1** the quantum yield of trans → cis photoisomerization (Φ_{t-c}) is also reduced by aggregation. The quantum yield of intersystem crossing (Φ_{isc}) is enhanced for bound dimers, the value is largest for **3**. In the redox reactions via the triplet state of **3**, ascorbic acid and *p*-benzoquinone serve as electron donor and acceptor, respectively. The photoinduced electron transfer is less efficient for bound monomers than for bound dimers. For the three polyanions comparable effects were found; especially, the ground-state equilibria and the Φ_f, Φ_{isc}, and Φ_{t-c} values depend in a well-defined manner on the parameter *r*.

Introduction

Cyanine dyes are attractive for spectral sensitization and a variety of technical applications.[1] Because of their unique ability to form different aggregates, they can be present as monomers, dimers, and H- and J-aggregates.[2−7] A low quantum yield of intersystem crossing (Φ_{isc}) and a rather high quantum yield of trans → cis photoisomerization (Φ_{t-c}) are typical for cyanine monomers.[1,8−12] J-aggregates generally show narrow peaks at long wavelengths, whereas H-aggregates often show a broader band at shorter wavelengths.[1−3] These H-aggregates as well as the dimers are often nonfluorescent, in contrast to J-aggregates that exhibit resonance fluorescence.[2] J-aggregates strongly enhance the photosensitivity. Photoinduced electron transfer takes place in organic solvents,[11,13] as well as in J-aggregates, when the cyanines are adsorbed to a surface, e.g., silver halide microcrystals.[14] Thus, influencing aggregation−deaggregation processes in the ground and excited states is desirable.

Formation of aggregates strongly depends on the structure of the dye, the concentration, and the medium.[1,6,7,15] In particular, H- and J-aggregates are formed for cyanine dyes bound to DNA templates.[16] Aggregation of cyanine and other dyes in aqueous solution also takes place in the presence of synthetic polyelectrolytes,[17−25] such as poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), or poly(styrenesulfonate) (PSS). In contrast to PSS, a conformational transition takes place for PMA or PAA from the hypercoiled form at pH <5 to the elongated form at pH >6.[18,21] For 9-methylthiacarbocyanine (**2**) in the presence of PSS, PAA, or PMA, the photophysical properties were recently studied as a function of the ratio of polyanion residue to dye concentrations (*r*).[26]

In this paper we focus our attention on a deeper insight in the photoprocesses of cationic dyes bound to water-soluble polyanions. For this purpose 3,3′-diethylthiacarbocyanine (**1**), **2**, and the ethyl meso derivative (**3**) together with PSS, PAA, and PMA were chosen. Photoisomerization as an additional mode of registration of deactivation processes is accessible for parent **1**, i.e., in the absence of a meso substituent.[6] Moreover, a low Φ_{isc} value for the monomer is advantageous to detect excited dimer processes. These features and the water solubility make the thiacarbocyanines more accessible than many other dyes. The relative yields were determined vs *r*, being the usual measure of the concentration ratio. Plots of the ground-state absorbances at appropriate wavelengths, the fluorescence quantum yield (Φ_f) and the Φ_{isc} and Φ_{t-c} values as a function of the parameter *r* reveal specific minima and maxima.



Experimental Section

The synthesis of the cyanine dyes **1**, **2**, and **3** has been described elsewhere.[27,28] Dye **2′,** where the CH_2CH_3 groups in **2** are replaced by CH_2CH_2OH, was the same as used previously.[10] The molar absorption coefficients at the maximum are $\epsilon = 9.8 \times 10^4$, 1.15×10^5, and 1.17×10^5 M^{-1} cm^{-1} for **1**, **2** (water−ethanol, 99:1), and **3** (water−ethanol, 3:1), respectively. PSS, PAA (Aldrich), rhodamine 101 (Lambda Physik), ascorbic acid, and *p*-benzoquinone (Merck) were used as commercially available. PMA was placed at our disposal by Professor A. R. Khokhlov. The molecular weight of PSS, PAA, and PMA is 0.7×10^5, 2.4×10^5, and 4.5×10^5 Da, respectively. Water was from a Millipore (milli Q) system. Aqueous dye solutions

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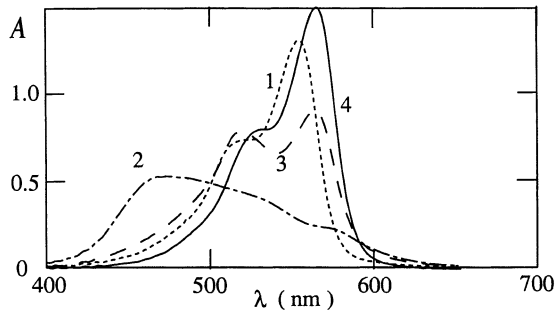

Figure 1. Absorption spectra for **1** (ground state) in neat aqueous solution (10 μM, curve 1) and in the presence of PSS for $r = 1$ (2), 30 (3), and 10^4 (4).

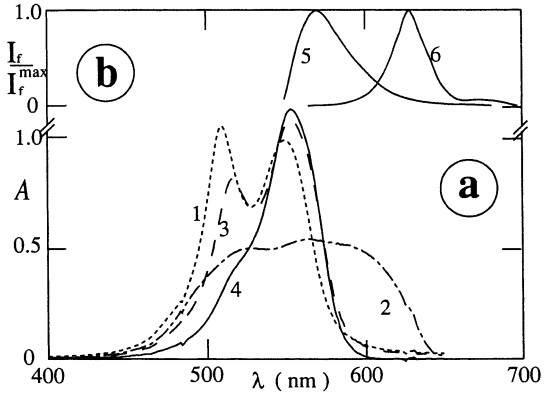

Figure 2. Spectra for **3**: (a) absorption in neat aqueous solution (10 μM, curve 1) and in the presence of PMA for $r = 1$ (2), 30 (3), and 10^3 (4); (b) fluorescence with PSS (5) and PMA (6), for $r = 1$.

(mostly 10 μM) were prepared by diluting from stock solution in ethanol (1 mM). The stock solutions of polyanions (0.1 M) were prepared, especially for isosbestic points, by dissolving them in the aqueous dye solution. Buffers were not applied because they would require changing the binding conditions at high concentration, which would be necessary to compensate for the low pH of PAA and PMA (at $r > 10^3$).

A diode spectrophotometer (HP 8453) was used for the steady-state absorption spectra, and spectrofluorometers (Spex-Fluorolog and a Perkin-Elmer LS-5) were used for fluorescence spectra. As reference, rhodamine 101 in air-saturated methanol with $\Phi_f = 1.0$,[29] $\lambda_{exc} = 500-560$ nm was used. The fluorescence decay kinetics were determined by a fluorometer (Edinburgh Instruments F900), time resolution 0.09 ns, $\lambda_{exc} = 480$ nm. For the time-resolved absorption measurements the laser setup, including the second harmonic from a Nd:YAG-laser (J. K. Lasers, $\lambda_{exc} = 530$ nm) and two transient digitizers (Tektronix 7912AD and 390AD), was the same as used previously.[13,15] Φ_{isc} was obtained from absorption difference measurements under optically matched conditions, using the quantum yield $\Phi_{t-c} = 0.25$ of **3** (20 μM) in methanol as a standard[8] and the molar absorption coefficients of the triplet ($\epsilon_{620} = 9 \times 10^4$ M^{-1} cm^{-1}) and the isomer (value for difference: $\epsilon_{578} = 1.8 \times 10^4$ M^{-1} cm^{-1}). The experimental error in τ_f, Φ_f, and Φ_{isc} is ±15%. The samples were always freshly prepared in 1 cm cuvettes prior to the measurements that refer to 24 °C.[26]

Results

Absorption Properties. The absorption spectra of **1** and **3** (10 μM) in neat aqueous solution at pH 6 are shown (curves 1 in Figures 1 and 2, respectively). The spectrum of **3** is characterized by two distinct peaks at $\lambda_D = 510$ nm and $\lambda_M = 551$ nm. These two bands are assigned to the absorption of dimer and monomer, respectively.[3] For **1** the short wavelength peak at $\lambda_M = 518$ nm is less pronounced and is present as a shoulder. The overall amount of dimer decreases on passing from **3** to **1**. The dimer band disappears completely when ethanol (10−20 vol %) is added.

TABLE 1: Absorption Properties of Cyanine Dyes[a]

dye[b]	polyanion	λ_H[c] (nm)	r	λ_D (nm)	λ_M (nm)	A_D/A_M
1	none		0	518	554	0.57
	PSS	470	$10/100/10^3$	518	564	1.1/0.7/0.45[d]
	PAA	475	200	518	562	0.8
	PMA	490	100	523	565	1.5
2	none		0	502	540	0.6
	PSS	470	$10/100/10^4$	506	547	1.6/0.8/0.4
3	none		0	510	551	1.1
	PSS	485	$10/10^3/10^4$	517	559	1.3/0.6/0.4
	PAA	595	$100/10^4$	517	555	0.8/0.4
	PMA	595	$100/10^3/10^4$	517	555	1/0.8/0.4

[a] In aqueous solution at natural pH (neutral for PSS). [b] Dye concentration: 10 μM. [c] For $r = 2$. [d] From left to right, respectively.

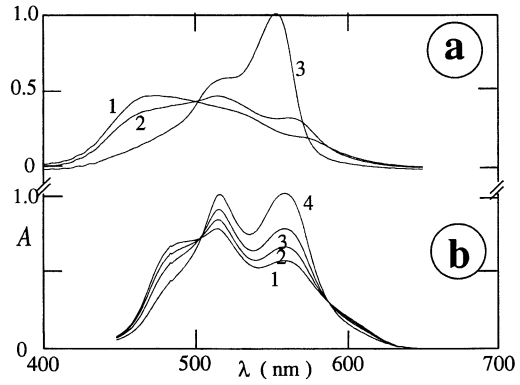

Figure 3. Absorption spectra in the presence of PSS for (a) **1**, $r =$ 0.1, 1, and 10, curves 1−3, respectively, and (b) **3**, $r = 20$, 30, 40, and 150, curves 1−4, respectively.

Generally, the ground-state properties of cyanine dyes depend on the ratio of polyanion residue to dye concentrations (r). At a low r of 0.3−30 H-aggregates (maximum λ_H) appear, whereas at a high r of 10^4, monomers are mainly present; λ_M is red-shifted by 5−10 nm with respect to λ_M in neat water. The maxima of the monomer and dimer bands and the ratio of their absorbances (A_D/A_M) are compiled in Table 1. For **2**[26] and **1** λ_H is blue-shifted and independent from the polyanion. For **3** and PSS $\lambda_H = 485$ nm, i.e., similar to the other cases, but red-shifted to $\lambda_H = 595$ nm with PAA and PMA, where contribution from a J-aggregate should not be excluded.

When the dye concentration is constant and the polyanion concentration increased from $r = 10^2$ to 10^4, the monomer band increases and the dimer band decreases (Figures 1−3). The dependences of A_M and A_D against log r are shown in Figure 4a for the **1**/PSS system together with the absorbance at λ_H (A_H). The intercepts of these plots define characteristic inflection points (midpoints for 50% change).[26] That derived from A_M and A_D is $r_3 = 300$. A second inflection point, which is due to the change from dye in bulk solution to H-aggregates bound to the polyanion, is $r_1 = 0.3$. A third value, reflecting the change from H-aggregated dyes vs dimers bound to the polyanion, is $r_2 = 20$. Another example of the dependences of A_M, A_D, and A_H on log r is shown in Figure 5a for **3** and PMA. The three r_i values for several dye/polyanion systems are listed in Table 2.

Fluorescence. The fluorescence spectrum of **1** (2−4 μM) in neat argon- or air-saturated aqueous solution (pH 6) has a

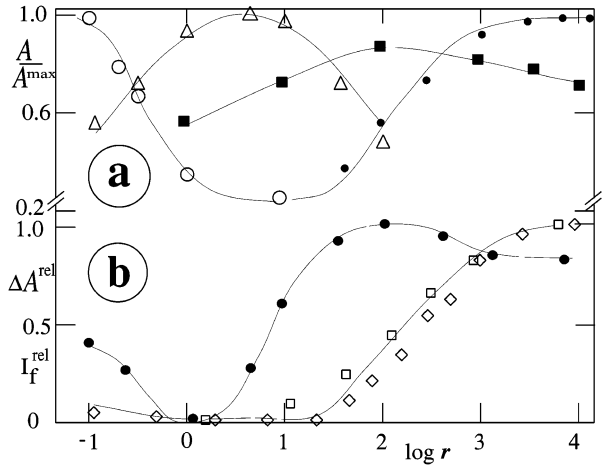

Figure 4. Dependences of (a) A_M (free (○), bound (●)), A_D (bound (■)), and A_H (△) and of (b) I_f (◇), ΔA_{t-c} (□), and ΔA_T (●) on the ratio of polyanion residue to dye concentrations (log r) for the **1**/PSS system.

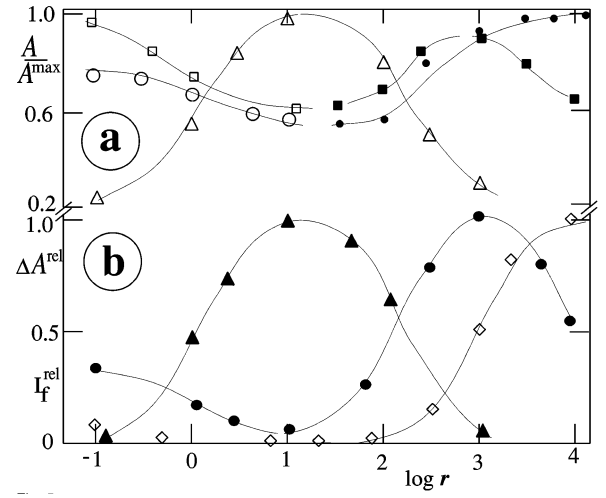

Figure 5. Dependences of (a) A_M (free (○), bound (●)), A_D (free (□), bound (■)), and A_H (△) and of (b) I_f (◇, 580 nm), I_f (J-aggregate (▲), 635 nm), and ΔA_T (●) on log r for the **3**/PMA system.

TABLE 2: Inflection Points Defining the Characteristic Ratios of Polyanion Residue to Dye Concentrations[a]

dye	polyanion	r_1		r_2	r_3	r_3[b]
1	PSS	0.3	0.3[b]	20	300	300
	PAA	1		100	1000	>1000
	PMA	20		400	4000	4000
2[c]	PSS	0.3		5	100	200
3	PSS	0.3		30	≤1000	600
	PAA	0.3		200	≥2000	≥2000
	PMA	1		200	3000	≥2000

[a] In aqueous solution at natural pH (neutral for PSS). [b] Fluorescence, otherwise absorption. [c] Taken from ref 26.

maximum at $\lambda_f = 570$ nm and those of **2** or **3** are 5−10 nm red-shifted. The quantum yield is in the 0.002−0.07 range, but much larger, up to $\Phi_f = 0.35$, in the presence of a polyanion at high concentration (Table 3). At low dye loading each λ_f value is 5−10 nm red-shifted with respect to neat aqueous solution. This is in agreement with a corresponding shift of λ_M. Such a red shift for the bound monomer with respect to the free monomers seems not to be unusual and was registered in all cases (Table 1). For the **3**/PAA and PMA systems, but not for **3**/PSS, a new fluorescence was recorded with emission peak at 630 nm (Figure 2b). This species is not observable in the absorption and fluorescence excitation spectra and is attributed to a J-aggregate.

TABLE 3: Fluorescence Properties of Cyanine Dyes[a]

dye	polyanion[b]	τ^1_f (ns)	τ^2_f (ns)	% a^1[c]	Φ_f
1	none	0.09		97	0.07
	PSS	0.7	2.0	20	0.19
	PAA	0.6	2	25	0.35
	PMA	0.6	2	23	0.29
2	none	<0.1		95	0.002
	PSS	0.3	1.6	40	0.04
	PAA	0.6	2	30	0.14
	PMA	0.5	1.7	50	0.13
3	none	<0.1		95	0.005
	PSS	0.6	2.4	30	0.12
	PAA	0.5	2.3	15	0.23
	PMA	0.5	2.3	20	0.20

[a] In air-saturated aqueous solution at natural pH (neutral for PSS). [b] At $r = (0.3-1) \times 10^4$. [c] Amplitude of the first τ^1_f component.

TABLE 4: Triplet Properties of Cyanine Dyes[a]

dye	polyanion	r	λ_T^{bl} (nm)	λ_T (nm)	τ_T (μs)	Φ_{isc}
1	none[b]	0	(560)[c]	625	55	0.005
	PSS	10	525, 570	650	11	
		10^4	(570)	620	600	0.008
	PAA	100	520, 560	640	14	
		10^4	(570)	625	130	0.012
	PMA	10		620	40	
		10^4		620	110	0.016
2[d]	none[b]	0	505, 550	535, 650	8	0.007
	PAA	10^4	535	630	≥30	0.020
3	none[b]	0	510, 565	540, 650	10	0.010
	PSS	10^4	520, 570	540, 650	5	0.014
	PAA	10^4	560	650	8	0.020
	PMA	10^4	560	630	9	0.014

[a] In argon-saturated aqueous solution at natural pH (neutral for PSS). [b] Water−ethanol 3:1, vol, otherwise 99:1. [c] Parentheses: due to isomer. [d] Taken from ref 26.

The dependences of the fluorescence intensity at λ_f (I_f) vs r (in the $r > 10^3$ range) show increases throughout. Moreover, I_f of **1** (Figure 4b) changes in a manner similar to the amount of (free and bound) monomer. At a low ratio of $r = 0.3-30$, where H-aggregates appear, the I_f value is even lower than in neat water. On the other hand, the minimum in the cases of **3**/PAA or PMA (Figure 5b) is overlapped by the J-aggregate emission. The r_1 and r_3 values coincide with those derived from ground-state equilibria (Table 2). The fluorescence decay of **1**−**3** (2−6 μM) in neat air-saturated aqueous solution (pH 6) is essentially monoexponential with a lifetime (τ^1_f) of 0.06−0.1 ns (Table 3). The fluorescence decay of monomers of **1** and **3** in methanol is short and the yield low.[31] In the presence of a polyanion at high concentration the decay of **1**−**3** is essentially biexponential with one component having a much larger lifetime (τ^2_f).

Triplet States. The absorption spectrum of **3** (10 μM) in argon-saturated ethanol−water (1:3) just after the pulse has a main broad band with a maximum at 650 nm and a narrow band at 535 nm. The spectrum is accompanied by a photobleaching with maxima at 505 and 550 nm. The major part of the signal that decays essentially by a first-order law and is quenched by oxygen is therefore attributed to absorption of the triplet state. The absorption maxima (λ_T) and bleaching maxima (λ^{bl}_T) are listed in Table 4 together with Φ_{isc}, which is generally low. The triplet lifetime (inverse of observed rate constant: $1/k_{obs}$) is $\tau_T = 8-55$ μs.

For **3** in neat aqueous solution the amount of dimers is highest. On addition of ethanol to **3** (air-saturated) the amount of triplet is reduced to 30%. The midpoint of this dependence

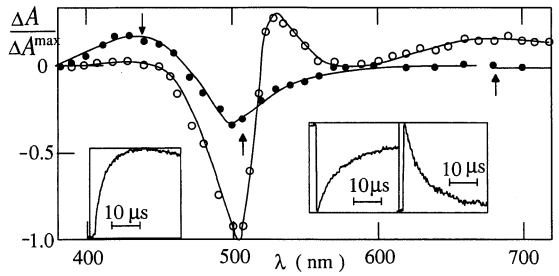

Figure 6. Absorption difference spectra for **3** (10 μM) in aqueous solution in the presence of ascorbic acid (0.25 mM) at 0.1 μs (○) and 20 μs (●). Insets: kinetics as indicated.

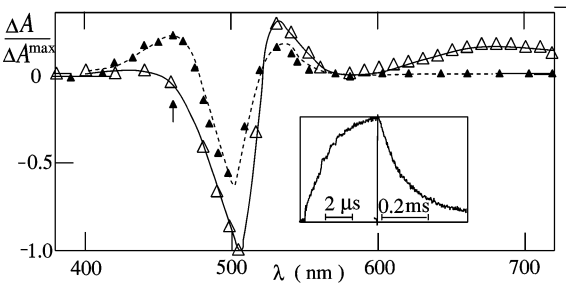

Figure 7. Absorption difference spectra for **3** (10 μM) in aqueous solution in the presence of *p*-benzoquinone (0.1 mM) at 0.1 μs (△) and 5 μs (▲). Inset: kinetics at 460 nm.

is at 1.5 M ethanol. On the other hand, the amount of dimers is reduced vs the ethanol concentration and that of free monomers enhanced; the 50% value for both effects is also at 1.5 M ethanol. These correlations of the dimer/monomer absorbances and the Φ_{isc} value demonstrate that the observed triplet state originates mainly from the dimer.

The signals from the λ_T and $\lambda^{bl}{}_T$ bands as a measure of Φ_{isc} are 1.5−3 times larger in the presence of polyanions in high concentration ($r = 10^4$) than those for the monomers in neat aqueous solution. Φ_{isc} becomes generally largest at $r = 10^2$−10^3. This dependence of the triplet yield vs r partly resembles the dependence of the amount of ground-state dimers, as shown in Figure 5b vs 5a for PMA. Similar plots are shown in Figure 4a,b for **1** and PSS. For this system the lifetime under argon is $\tau_T = 11$ μs at $r = 10$ and 0.6 ms for $r = 10^4$; the rate constant for quenching by oxygen is 4×10^9 M^{-1} s^{-1} ($r = 10$ and 10^4). For **2** and **3**/PSS, PAA, and PMA τ_T varies within the range 5−30 μs (Table 4).

Effects of Ascorbic Acid and *p*-Benzoquinone. On addition of ascorbic acid to **3** in argon-saturated aqueous solution, the rate constant k_{obs} for triplet decay is increased. The end of the pulse spectrum is due to the above-mentioned triplet, and a new absorption difference spectrum with a maximum at 430 nm was observed (Figure 6). This is due to a radical (semi-reduced dye), produced via photoinduced electron transfer (see Discussion). The grow-in and decay kinetics at 430 and 680 nm, respectively, are nearly identical. The radical has a lifetime of 130 μs and interacts efficiently with oxygen (the rate constant is 2×10^9 M^{-1} s^{-1}). The rate constant (k_2, referring to eq 2) for quenching of triplet **3** by ascorbic acid in neat water, derived from k_{obs} vs the ascorbic acid concentration (up to 0.3 mM), is $k_2 = 4 \times 10^8$ M^{-1} s^{-1} and smaller) in a water−ethanol mixture (Table 6). On increasing the ethanol concentration (30 vol %), the radical yield (observed at 430 nm) decreases 10 times, whereas Φ_{isc} decreases to half of the initial value. In the presence of PSS or PMA, providing conditions for highest concentration of bound monomers ($r = 10^4$), the electron transfer is drastically slowed, $k_2 < 1 \times 10^6$ M^{-1} s^{-1}. In contrast, the rate constant for

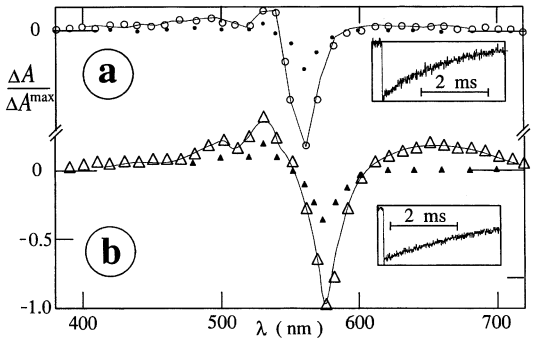

Figure 8. Absorption difference spectra for **1** (argon-saturated, 10 μM) (a) at $r = 0$ and (b) in the presence of PSS, $r = 10^4$ at 0.1 μs (open) and 2 ms (full) after the 530 nm pulse. Insets: kinetics at $\lambda^{bl} = 560$/570 nm.

TABLE 5: Maxima of the Cis Isomer, Lifetime, and Yield of 1[a]

polyanion	r	λ_c (nm)	$\lambda_c{}^{bl}$ (nm)	$\tau_{c\rightarrow t}$ (ms)	Φ_{t-c}
methanol			560	4	0.25
none	0	500, 530	560	2.0	0.15
PSS	10^4	510, 540	570	3.0	0.11
PAA	10^4	540	570	20	0.08
PMA	10^4	510, 540	570	10	0.10

[a] In aqueous solution at natural pH (neutral for PSS).

TABLE 6: Quenching Rate Constant ($\times 10^8$ M^{-1} s^{-1}) of the Triplet State of 3

medium	r		ascorbic acid	*p*-benzoquinone
water/ethanol, 3:1		monomer	1	20
PSS	10^4		<0.01	14
PAA	10^4		<0.01	17
neat water	0	dimer	4	68
PSS	10^2		0.2	57
PAA	10^2		0.4	23

electron transfer is much larger ($k_2 = (2-4) \times 10^7$ M^{-1} s^{-1}) for bound dimers ($r = 10-10^3$).

Benzoquinone quenches the triplet state of **3** in neat water with a rate constant $k_3 = 6.8 \times 10^9$ M^{-1} s^{-1} (Table 6). This is accompanied by the appearance of a new transient with absorption maxima at 465 and 530 nm (Figure 7) and assigned to another radical (semi-oxidized dye) resulting from photoinduced electron transfer. Kinetics of the triplet decay match those of the radical buildup. The lifetime of the radical is 170 μs and is not markedly influenced by oxygen. In water−ethanol (3:1) the rate constant is $k_3 = 2 \times 10^9$ M^{-1} s^{-1} and in the presence of PSS or PAA in high concentration is k_3 3−4 times smaller than in neat water. For lower concentration of PSS and PAA ($r = 10-10^3$) k_3 is higher than that for bound monomers.

Photoisomerization. Besides the minor T−T absorption difference spectrum, a long-lived transient with maxima at $\lambda_c = 500$ and 530 nm and bleaching maximum at $\lambda^{bl}{}_c = 560$ nm was established concomitant with the pulse for **1** in neat air-saturated aqueous solution (Figure 8). The transient spectrum is characteristic for an isomer formed by trans → cis photoisomerization[10] because the decay is insensitive toward oxygen. Both processes match the kinetics of intersystem crossing and thermal cis → trans isomerization. The subsequent (first-order) recovery for **1** has a lifetime ($\tau_{c\rightarrow t}$) of 2 ms. Note that in polar media meso substituents are known to shift a monomeric equilibrium from the trans to cis isomer.[6,7,10,31]

For **1** in the presence of PSS with $r = 10$ the quantum yield of trans → cis photoisomerization becomes 10 times less intense. The plot of Φ_{t-c} shows that on increasing r further, the yield

increases again (Figure 4b) and $\tau_{c\rightarrow t}$ is longer than in neat water (Table 5). Decay of the observed isomer of the bound monomer also for PAA and PMA at $r = 10^4$ follows a first-order law. A too low Φ_{t-c} value for **2** and **3** in aqueous solution as well as in the presence of PSS, PAA, and PMA ($r = 10^2-10^4$) makes an investigation of the trans → cis photoisomerization nearly impossible under our conditions.

Discussion

Ground-State Equilibria. The thiacarbocyanine dyes are present in aqueous solution as an equilibrated mixture of monomers and dimers (M and D, respectively). The dynamic behavior of the dye molecules is changed due to interactions between the polymer (P) and the dye. Higher aggregates (H−P) are formed at $r = 0.2-2$ (high dye loading), dimers (D−P) are formed on increasing the concentration of polyanion residues, and at even higher r (10^4, low dye loading) monomers (M−P) are present. Monomer, dimers, and H-aggregates bound to polyanions are also present in an equilibrium that depends on r. This follows from analysis of absorption spectra showing well-defined isosbestic points (Figure 3), which proves the existence of the partial equilibria M/D ⇌ H−P, H−P ⇌ D−P, and D−P ⇌ M−P.

For high dye loading the inflection point r_1 is due to H−P aggregate formation at the expense of the monomer and dimers in bulk solution; r_2 is due to the change from H−P to D−P bound dimers, and r_3 for low dye loading is due to bound monomers M−P at the expense of D−P. These partial equilibria are illustrated:

(1)

Excited Singlet States. The fluorescence properties of cyanines are strongly influenced by changing the meso substituent.[3−7,30,31] The binding of dye molecules to polyelectrolytes gives rise to changes in the dye excited-state properties. The essentially monoexponential decay in neat air-saturated aqueous solution is due to fluorescence of the free monomer. The Φ_f values of cyanine dyes are smaller than in organic solvents.[8,9] Interestingly, the fluorescence excitation spectra of **1** or **3** have no peak, which may be correlated with aggregates bound to the polyanion (at $r = 1-5$). This is in agreement with the decrease of Φ_f vs r in the range $r = 0.1-10$ for several cases (Figures 4b and 5b) and the result that dimers and H-aggregates of thiacarbocyanines exhibit a low Φ_f value.[2,6] The observation of resonance fluorescence for **3** in the presence of PAA (at $r = 1$) and PMA (Figures 2b and 5b) is typical for J-aggregates. The lack of a narrow and intense absorption band, which usually characterizes the J-aggregates,[3,14] is probably due to a low concentration of J-aggregates and also masked by an intense and wide absorption band centered at 595 nm. A related case of a derivative of **3** and polyallylamine has been reported recently.[32] The 5-fold fluorescence enhancement of the bound monomer for **1**, 20−70-fold for **2** and 30−50-fold for **3,** is due to hindered deactivation modes with respect to the free monomer. The decay of the bound monomer is therefore slower, resulting in a long-lived component (τ^2_f in Table 3) of 2−3 ns. The two components in the fluorescence decay kinetics are probably due to different microenvironments for dye encapsulation that are exposed differently to an aqueous and interfacial phase.[18]

Effect of Structure on the Radiationless Deactivation. For free monomers of **1**−**3** Φ_{isc} is small (Table 4) and similar to that for **2′** in aqueous solution.[8] For bound monomers Φ_{isc} is enhanced as a consequence of a longer lived fluorescence in comparison with that for free monomers. The triplet lifetime of bound monomer for **1** and **2** is shorter than that of the free monomer (Table 4). Φ_{isc} for **3** in neat water is also low, but twice as high as in a water−ethanol mixture (3:1). The dependence of the triplet yield vs r (Figure 5b) resembles the dependence of the amount of bound dimers. The reason for the maximum at $r = 10^2-10^3$ is the enhancement of Φ_{isc} for dimers. A possible reason for this is the singlet−triplet splitting, which has been established for the related cyanines.[6] The triplet lifetime of bound dimers for **1** and **2** is shorter than that for bound monomers (Table 4). For H-aggregates of **1**−**3** the T−T absorption was not observed due to low Φ_{isc}.

For meso substituents **2** and **3** the bleaching related to trans → cis photoisomerization is less efficient because the equilibrium is shifted from the trans to cis isomer.[6,10,12,31] Therefore, these measurements are restricted to **1**, where the overlap of cis absorption with T−T absorption is low and Φ_{t-c} of thiacarbocyanine iodide (free monomer of **1**) in methanol is 0.25[8] and 0.15 in water (Table 5). The yield of the cis isomer for bound monomers of **1** is smaller than that for free monomers and Φ_{t-c} correlates with Φ_{isc} (Figure 4b). The reason for the minimum in this plot of Φ_{t-c} vs r is stacking of the aggregates and dimers, resulting in sterical hindrance. Because trans → cis photoisomerization in the singlet state and intersystem crossing are competing, the enhancement of Φ_{isc} for bound dimers is due to the hindrance of isomerization. The deactivation processes of free monomers in the excited singlet state are essentially internal conversion with low Φ_f, Φ_{isc}, and Φ_{t-c}, whereas those of excited bound monomers are even lower in Φ_{isc} and Φ_{t-c}, but display a larger Φ_f value (Table 3). In the deactivation processes of excited bound dimers Φ_{isc} is enhanced at the expense of Φ_{t-c}.

Electron Transfer. To study electron transfer of excited dimers, ascorbic acid as electron donor and *p*-benoquinone as electron acceptor were applied for **3**. The observed neutral radical ($M^{\bullet}$) in aqueous solution in the presence of ascorbic acid is formed as a result of electron transfer from the triplet state of cationic dye $^{3*}M^+$.

$$^{3*}M^+ + \text{donor} \rightarrow M^{\bullet} + \text{donor}^{\bullet+} \qquad (2)$$

The rate constant for quenching (k_2) of the dimer triplet for **3** in aqueous solution is 4 times higher than that for the monomer in water−ethanol (3:1) and much higher than that for both bound dimers and monomers (Table 6). The former could reflect different reactivities of monomer and dimer in the triplet state, whereas the low k_2 for bound dimers and the even lower values for bound monomers are due to hindrance for penetration of ascorbic acid into the polyanion microdomain or, more likely, due to Coulombic repulsion.

Quenching of the **3** triplet by *p*-benzoquinone as acceptor via electron transfer leads to formation of dication radicals ($M^{\bullet 2+}$).

$$^{3*}M^+ + \text{acceptor} \rightarrow M^{\bullet 2+} + \text{acceptor}^{\bullet-} \qquad (3)$$

The rate constant k_3 is highest for free dimers and only 1.5−5 times smaller for bound dimers as well as for free and bound monomers (Table 6). *p*-Benzoquinone quenches the triplet state of the free dimer 3 times more efficiently than that of the free monomer, which may reflect a higher reactivity of the dimer

triplet in oxidation of **3**. The rate constant for triplet quenching of the bound monomers and dimers by the uncharged quinone is larger than that by (negative) ascorbate ions. This is probably due to more hydrophobic properties of the former, which promotes an access to the bound monomers or dimers in the polyanion microdomain.

Variation of Polyanion. Interactions of cyanines have been reported for PSS,[21,22] PAA,[17,21] and PMA.[17−19] The deactivation processes for dyes bound to PSS take place at neutral pH, whereas for PAA and PMA at low dye loading the acidity increases with *r*. Some photophysical effects of chromophores with PMA or PAA have been ascribed to a conformational transition from the hypercoiled to the elongated form at pH <5 and >6, respectively.[18,21] For example, the decrease of fluorescence at neutral pH has been explained by ejection of the bound pyrene into the aqueous phase.[33] However, due to the water solubility of thiacarbocyanines, this would not play the major role. A minor influence of proton concentration on the results is concluded from the similarity of the Φ_f and Φ_{isc} values at low loading and comparable r_3 values (Tables 1−6) for PSS at pH 6 on one hand and for PAA or PMA at pH 3−4 on the other.

Conclusion

PSS, PAA, and PMA interact with cationic thiacarbocyanine dyes promoting monomers, dimers, and H- and J-aggregates. The ratio between these forms depends on the relative concentrations *r*. The photophysical and photochemical properties of the dyes in the presence of polyanions reflect an equilibrium between free and bound monomer, dimers, and H-aggregates. Strong enhancement of fluorescence and moderate enhancement of intersystem crossing are characteristics for bound dyes. Free and bound dimers in the triplet state yield radicals in the redox reaction with ascorbic acid and *p*-benzoquinone. The combination of cationic dye and polyanion offers an elegant way to deposit chromophores in largely varying proximities to each other.

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