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Photoinduced Electron Transfer for Pyrromethene Dyes

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The photophysics and electrochemistry of pyrromethene dyes (PM), an important class of laser dyes, have been investigated. Selected dyes were found to be moderately good electron donors. Diffusion-limited fluorescence quenching (ca. 6×10^9 M^{-1} s^{-1}) is observed for the dyes having half-wave oxidation potentials <1.07 V (vs SCE) in the presence of an electron acceptor, such as methyl viologen or pyromellitic dianhydride. For pyrromethene 567, the dye radical cation and triplet state, along with the pyromellitic dianhydride radical anion and the methyl viologen radical cation, were identified using transient absorption spectroscopy. The dye radical cation, which displays a sharp absorption band at 410 nm, is found to be insensitive toward oxygen. Secondary electron transfer involving the reduction of oxygen and producing superoxide radical anion is suggested. Oxygen plays a critical role in PM dye photochemistry as it induces intersystem crossing to generate the dye triplet state and gives rise to products of oxidation.

Introduction

Since their discovery in 1966,[1] dye lasers have been used in diverse fields related to medicine and military or space applications. Their use as a spectroscopic tool in chemistry, physics, and biology has also proven to be of importance. Organic dyes offer advantages over other traditional lasing materials, such as low cost, high lasing efficiency, and broad spectral coverage from the ultraviolet to the near-infrared.[2,3] The pyrromethene (PM) family of dyes constitutes an important class of laser dyes, whose lasing action extends from 550 to 700 nm. The photophysics and lasing properties of various PM's have been investigated for dyes in fluid solution.[4−6] Pyrromethene dyes are also ideal candidates for solid-state dye lasers operating in the mid-visible region, as these dyes have been successfully incorporated into solid matrices such as poly(methacrylic acid),[7,8] sol−gel,[9] and polymer-filled nanoporous glasses[10−12] and have shown good photostability.

Novel modifications of PM structures have been made, either to move their lasing action further to the red[13] or to functionalize them so they can be attached to a polymer backbone. Trudell and co-workers[14] synthesized a methacryloxymethyl derivative of pyrromethene 567 (PM 567) that can be copolymerized with other monomers to make solid-state materials with lasing properties. These dyes are further used as molecular probes in biological systems.[15] Specifically modified derivatives of PM dyes have been studied in lipid bilayers and proteins.[16] Recently, Scott et al.[17] have devised a white-light LED that is composed in part of a cross-linked polymer hole transport layer containing pyrromethene 546.

Although the lasing action of the pyrromethene dyes has been the focus of numerous investigations,[5,18] very few studies have been directed toward understanding their photodecomposition.[19,20] Lightner and co-workers studied the products of photolysis of similar compounds such as dipyrrylmethenes and other pyrrole analogs.[21] Moreover, the electron-transfer properties of the laser dyes have received very little attention in general. To the best of our knowledge, there are only few reports that discuss electron-transfer properties of other laser dyes, such as the coumarins.[22,23] One recent report[24] describes the binding of alkali metals to an assembly comprised of modified PM dyes (electron acceptors) covalently attached to crown ether derivatives (electron donors).

The present article reports the fluorescence quenching and phototransient behavior of PM dyes (Scheme 1) involving photoinduced electron transfer.

In addition, the electrochemical properties of these chromophores are described for the first time. The dye, PM 567, has been investigated in detail in this study. Transient absorption spectroscopy has been employed to identify the PM 567 triplet state and radical cation along with the radical ions of pyromellitic dianhydride and methyl viologen associated with intermolecular electron-transfer processes. A better understanding of the electron-transfer properties of these dyes will be useful in associating redox properties and mechanism of dye photodegradation which limits laser performance.

Experimental Section

Most pyrromethene dyes used in this study were purchased from Exciton (their names derive from the approximate peak lasing wavelengths), and their purity was checked by TLC (eluent, 20% ethyl acetate/hexanes). The PM 560 was a generous gift from Professor Mark Trudell of the University of New Orleans. Spectroscopic grade acetonitrile was obtained from J.T. Baker. Ethanol (200 proof) was supplied by Pharmco. Benzophenone, obtained from Aldrich, was recrystallized from EtOH prior to use. Methyl viologen chloride salt (MV^{2+}) was (Aldrich) recrystallized from methanol. Pyromellitic dianhydride (PMDA) (Aldrich) was purified by sublimation.

Instrumentation and Methods. Absorption spectra were recorded on a Beckman DU-640B spectrophotometer. Steady-state and time-resolved fluorescence emission measurements were made on a PTI (Photon Technology International, Inc.)

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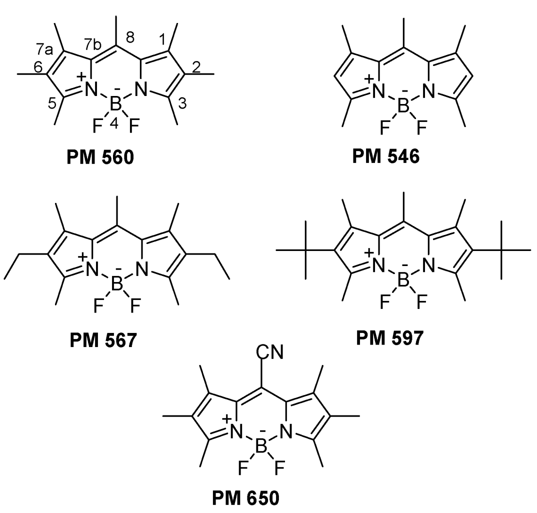
SCHEME 1



fluorimeter using Felix/TimeMaster software. Fluorescence lifetimes were recorded using a PTI dye laser source (λ_{exc} = 503 or 536 nm). Fluorescence quantum yield measurements were carried out using dilute solutions (OD < 0.2). For a typical measurement the reported fluorescence quantum yield of the same dye was used as reference. A tunable laser system (Continuum) pumped by a Q-switched Nd:YAG laser (Surelite II-10) was used as excitation source in laser flash photolysis experiments as described previously.[25] The repetition rate was 10 Hz with 20−25 mJ/pulse at 355 nm and 15−20 mJ/pulse at 532 nm. Control of the apparatus and the recording of data were performed using LabView 5.0 (National Instruments).

Benzophenone (BP) (E_T = 69.2 kcal/mol, Φ_T = 1.0)[26] was used as a photosensitizer. Sample solutions were excited at either 355 or 532 nm. All solutions were freshly prepared and deaerated by purging with argon for 30 min, as necessary. Phototransient decay data were analyzed using Igor Pro 3.12 software and fit to mono- or biexponential decay functions. All measurements were repeated several times; lifetimes were reproducible to ±10%.

Cyclic voltammograms were recorded using a model 273A potentiostat/galvanostat (EG&G Princeton Applied Research) controlled by an EG&G M270A (version 4.0) software package (scan rate = 1000 mV/s). All measurements were performed using anhydrous acetonitrile or methylene chloride, containing 2.0 mM dye and 0.1 M tetrabutylammonium hexafluorophosphate. The reference electrode (Ag/AgCl) was calibrated using 5.0 mM ferrocene (0.307 V vs SCE, 0.2 M $LiClO_4$)[27] in dry acetonitrile. Solutions were purged with argon (20 min) before making the measurements.

Results and Discussion

Electrochemistry. Oxidation potentials of PM dyes were measured in dry methylene chloride using cyclic voltammetry (Table 1). All dyes showed good reversibility as shown for PM 546, PM 567, and PM 650 in Figure 1.

Three structurally similar dyes, PM 560, PM 567, and PM 597, have similar oxidation potentials (0.88 ± 0.01 V vs SCE). By contrast, PM 546, which lacks two alkyl groups at the C2 and C6 positions, shows a ∼150 mV higher oxidation potential. The PM 650 dye is the least readily oxidized member of the group (1.17 V vs SCE), presumably due to placement of the cyano group, an electron-withdrawing substituent, at the C8 position. Except for PM 567, the pyrromethene dyes failed to show reversibility in acetonitrile, although indicating a similar trend in their oxidation potentials to that measured in methylene chloride.

Fluorescence Quenching Studies. Absorption for the selected PM dyes ($\epsilon \sim (4-7) \times 10^4$ M^{-1} cm^{-1}) lies typically in the blue-green region of the spectrum (Table 1). As expected,[2] these dyes in alcohol solution (and acetonitrile/water) display fluorescence lifetimes (τ) of 4−7 ns and high fluorescence quantum yields (Φ_f); lower emission yield and shorter lifetime were reported for PM 650. The emission of PM 567 (10 μM, λ_{exc} = 502 nm) (Figure 2) and PM 546 (4.1 μM, λ_{exc} = 480 nm) in 40% (v/v) acetonitrile/water[31] was quenched on addition of an electron acceptor, methyl viologen (MV^{2+}) (−0.69 V vs SCE).[32] For these dyes, fluorescence quenching was assigned to a diffusion-limited process ($k_q \sim 6 \times 10^9$ M^{-1} s^{-1}); $k_q = K_{sv}/\tau$, where K_{sv} and τ are the Stern−Volmer quenching constant and the singlet state lifetime of the dye, respectively. On the other hand, the quenching rate for PM 650 was found to be diminished ($k_q = 2.3 \times 10^9$ M^{-1} s^{-1}). The fluorescence emission of PM 567 (in acetonitrile) also decreases on addition of pyromellitic dianhydride (PMDA) (−0.55 V vs SCE) (Table 2).[33]

The fluorescence quenching of the PM dyes in the presence of an electron acceptor is ascribed to an intermolecular electron-transfer process. The quenching data were assessed further using the Rehm−Weller equation:[34]

$$\Delta G_{et} = nF(E_{ox} - E_{red}) - E_{00} - C \tag{1}$$

where E_{ox} and E_{red} are the half-wave oxidation and reduction potentials for the donor and the acceptor, respectively, and E_{00} denotes the excitation energy. A contribution from the Coulombic term (C = 0.1 eV), the energy of stabilization of a radical ion pair, was assumed (for quenching by PMDA) on the basis of a value typically used for polar media. Computed free energies for the intermolecular electron-transfer process are shown in Table 2.

The near-diffusion-limited quenching rates in the case of PM 567 and PM 546 are associated with favorable free energy changes (ca. −0.8 eV, 18.4 kcal/mol) for an intermolecular electron-transfer process. However, for PM 650 the driving force is reduced (−0.20 eV, 4.6 kcal/mol), a finding consistent with a reduced k_q. The approximate 4-fold enhancement in the quenching rate observed in the case of PMDA, in comparison with MV^{2+}, is perhaps related to a slightly more negative free energy change (∼ −0.2 eV). However, the intervention of a weak ground-state complex of PMDA and dye that is not readily apparent in absorption spectra cannot be ruled out, since PMDA is known to have a propensity to aggregate with polynuclear aromatic hydrocarbons.[35]

Transient Absorption Spectroscopy. Laser flash photolysis experiments were carried out using a Q-switched Nd:YAG laser. For PM 567 (λ_{exc} = 532 nm) in deaerated acetonitrile, the transient spectra showed a weak absorption between 400 and 460 nm which decays exponentially with a lifetime (τ) of 28 μs. In aerated acetonitrile, the same transient was observed showing a higher intensity (ca. 6-fold). This transient, which decays more rapidly (τ = 150 ns), is assigned as part of the PM dye triplet on the basis of the spectra observed for dye solutions having a sensitizing agent. Laser flash photolysis experiments were conducted on PM 567 using benzophenone (BP) (8.2 mM) as a triplet sensitizer (λ_{exc} = 355 nm). Transients at 710 nm and between 380 and 470 nm were observed concomitant with ground-state bleaching at 520 nm in deaerated acetonitrile (Figure 3).

TABLE 1: Photophysical and Electrochemical Properties of Selected Pyrromethene Dyes

dye	solvent	λ_{abs} (nm)	$\epsilon \times 10^{-4}$ (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_f	τ (ns)[a]	E_{ox} (V)[b]
PM 546	MeOH	493	7.9[c]	503	0.99[c]	5.6	1.07
	40% ACN/water	491	7.3	500	1.0	6.8	
PM 560	EtOH	517	5.4	534	0.70[c]	6.9	0.87
PM 567	ACN	514	7.4	530	0.85	6.5	0.89
	EtOH	518	7.2[c]	534	0.83[c]	6.6	
	40% ACN/water	515	6.3	535	0.77	6.3	
PM 597	EtOH	525	6.8[d]	557	0.77[d]	4.2	0.87
PM 650	EtOH	588	4.6[e]	606	0.54[e]	1.6	1.17
	40% ACN/water	590	3.9	612	0.20	1.2	

[a] Measured at the fluorescence maximum using a nitrogen laser pumped dye laser (λ_{exc} = 503 or 536 nm). [b] All values are ±0.01 V (vs SCE); solvent = methylene chloride. [c] Reference 28. [d] Reference 29. [e] Reference 30.

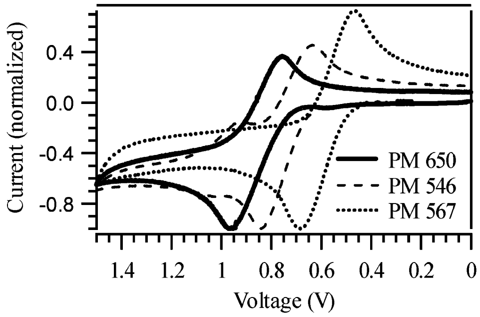


Figure 1. Cyclic voltammograms for various PM dyes (2.0 mM) in dry methylene chloride (vs Ag/AgCl; scan speed 1000 mV/s).

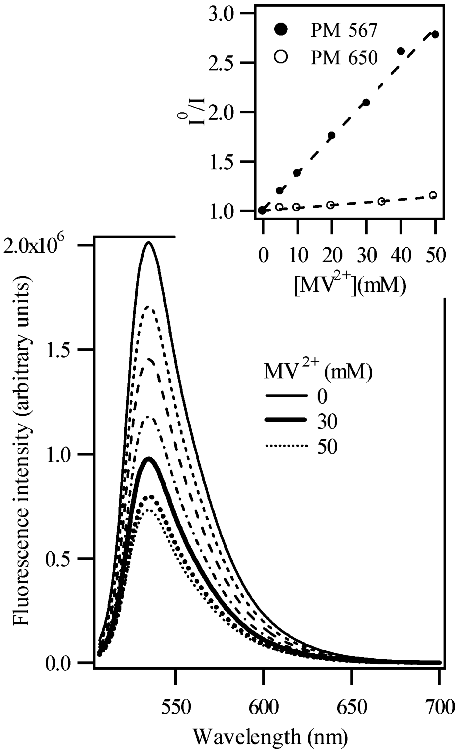


Figure 2. Quenching of the fluorescence of PM 567 (10 μM, λ_{exc} = 502 nm) by MV^{2+} in aerated 40% acetonitrile−water. Inset: Stern−Volmer plot of the data for PM 567 and similar data for PM 560.

TABLE 2: Fluorescence Quenching Data for Pyrromethene Dyes

dye	quencher	K_{sv} (M^{-1})	$k_q \times 10^{-9}$ (M^{-1} s^{-1})	E_{00} (eV)	ΔG_{et} (eV)
PM 546[a]	MV^{2+} [b]	37.2	5.9	2.50	−0.74
PM 567[c]	MV^{2+} [b]	37.2	5.5	2.37	−0.79
	PMDA[d]	144	22.	2.37	−1.0
PM 650[e]	MV^{2+} [b]	2.70	2.3	2.06	−0.20

[a] [Dye] = 4.1 μM, λ_{exc} = 480 nm. [b] Aerated 40% acetonitrile/water. [c] [Dye] = 10 μM, λ_{exc} = 502 nm. [d] Aerated acetonitrile. [e] [Dye] = 4.0 μM, λ_{exc} = 580 nm.

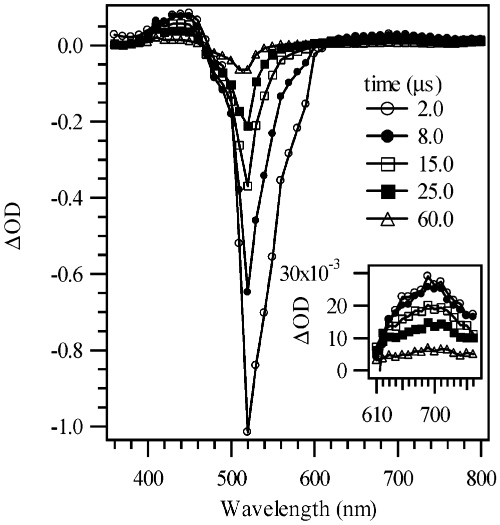


Figure 3. Transient absorption spectra obtained on flash photolysis of PM 567 (13.4 μM dye; λ_{exc} = 355 nm) in deaerated acetonitrile using BP (8.2 mM) as sensitizer. Lower inset shows expanded transient absorption spectra, 610−760 nm.

The transient absorption near 450 nm and at 710 nm are therefore attributed to the dye triplet, a conclusion consistent with a previous report.[36] It appears that the transient absorption extending from 380 to 470 nm is actually comprised of two species. One of them absorbs at 450 nm with a decay time (21 μs) similar to that of the transient at 710 nm. The other species absorbs at 410 nm and decays more slowly (τ = 30 μs). The appearance of the weaker absorption at 410 nm (dye radical cation) in the absence of oxygen (deaerated solvent) is probably due to self-quenching via oxidation−reduction involving the dye triplet as observed for other dyes, such as eosin Y.[37] Oxygen present in the aerated solvent appears to facilitate the formation of the dye triplet (higher triplet yield, Figure 4) by inducing intersystem crossing from the dye singlet state (S_1) → (T_1). This mechanism involves formation of an exciplex from dye singlet and ground-state triplet oxygen, which dissociates to give the dye triplet and triplet oxygen ($^3\Sigma$).[38] The dye triplet further undergoes energy transfer with ground-state oxygen ($^3\Sigma$) to generate singlet oxygen ($^1\Delta$), which is most likely responsible for the photodegradation of the dye in aerated solvents (Scheme 2).[19]

On laser flash photolysis (direct excitation) of PM 567 in deaerated acetonitrile in the presence of an electron acceptor, PMDA (6.0 mM), a sharp transient absorption band at 410 nm along with a broad transient which peaks near 670 nm was

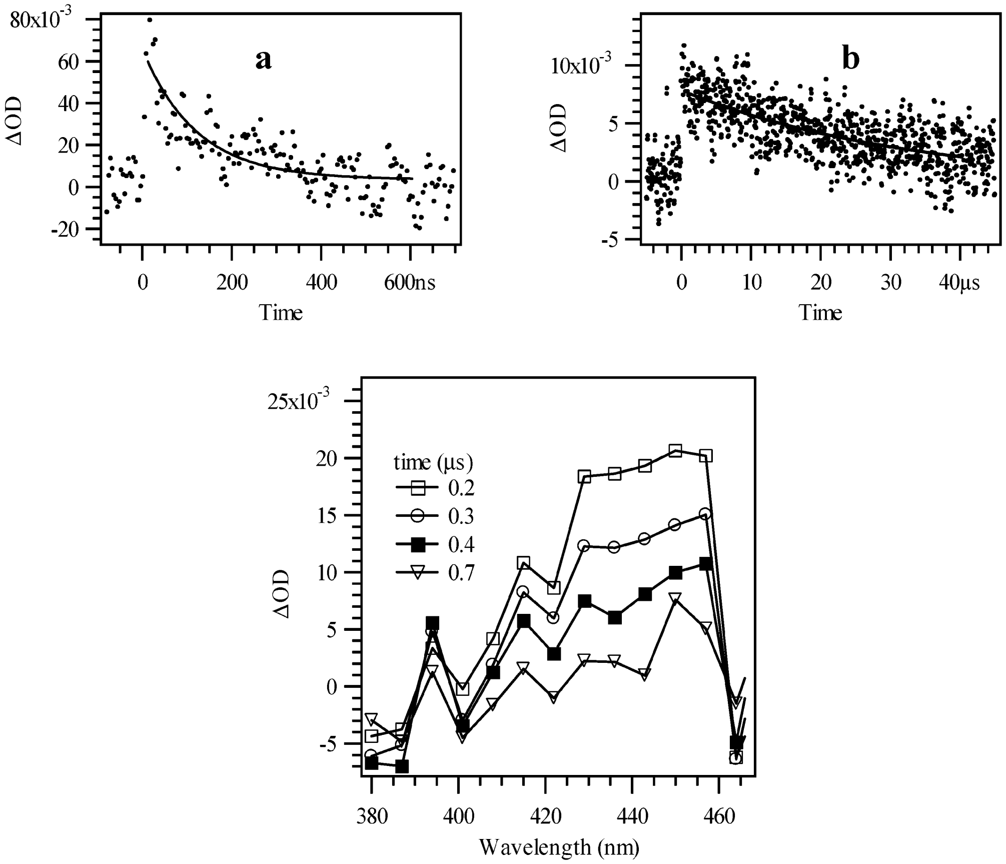


Figure 4. Transient absorption spectra obtained on flash photolysis PM 567 in aerated acetonitrile (55 μM dye; λ_{exc} = 532 nm). Insets a and b show decay of the dye triplet (440 nm) in aerated and deaerated acetonitrile, respectively.

SCHEME 2: Photochemistry of PM 567 in Aerated Solvents and in the Presence of an Electron Acceptor (A)

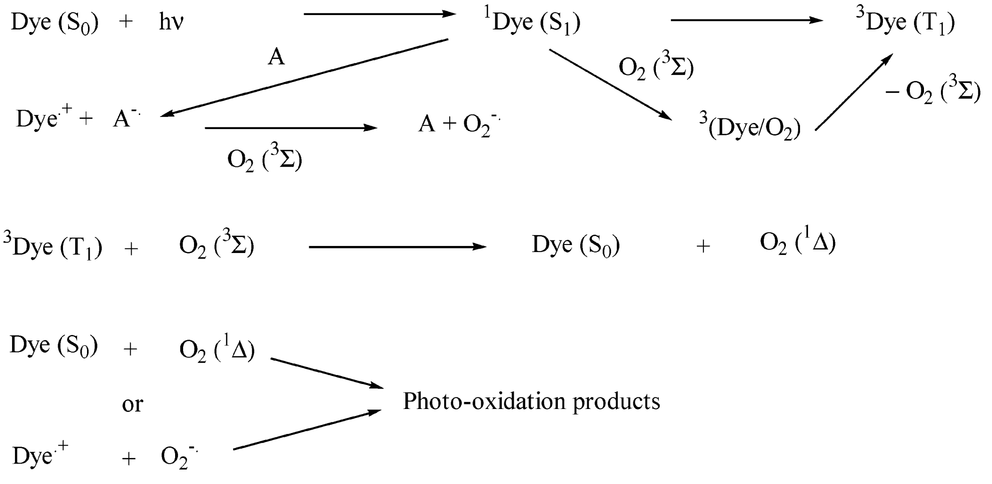


TABLE 3: Transient Decay Data from Flash Photolysis of PM 567 (Direct Excitation)[a]

medium	dye triplet[b] τ, (μs)	dye radical cation,[c] $\tau_{1/2}$, (μs)	quencher radical ion, $\tau_{1/2}$, (μs)
CH_3CN	28.		
CH_3CN + PMDA		240	190
40% CH_3CN/water + MV^{2+}		260	480

[a] PM 567 = 50 μM; λ_{exc} = 532 nm; deaerated samples. [b] Transient decay at 440 nm. [c] Transient decay at 410 nm.

observed. The decay profiles of these transients are reported as $\tau_{1/2}$ (half-life) values (Table 3). The band at 410 nm (Figure 5) has $\tau_{1/2}$ = 240 μs, whereas the species that absorbs between 600 and 700 nm, the PMDA radical anion,[35] gives a similar value $\tau_{1/2}$ = 190 μs (Figure 6). A second-order plot for decay of the transient at 670 nm is shown in Figure 7; a second-order rate constant, 5.1 × 10^9 M^{-1} s^{-1}, is obtained and associated with the intermolecular (reverse) electron transfer between photogenerated $PM^{\bullet+}$ and acceptor ($PMDA^{\bullet-}$) radical ions.

Similar transients having different half-lives were observed when the experiment was conducted using aerated solvent (for the transient at 410 nm, $\tau_{1/2}$ = 1.0 ms, and for 670 nm, $\tau_{1/2}$ = 47 μs).

The faster decay of the PMDA radical anion in aerated solvent is due to its electron-transfer reaction with oxygen ($E_{red} = -0.57$ V vs SCE) similar to that reported by Eriksen and co-workers

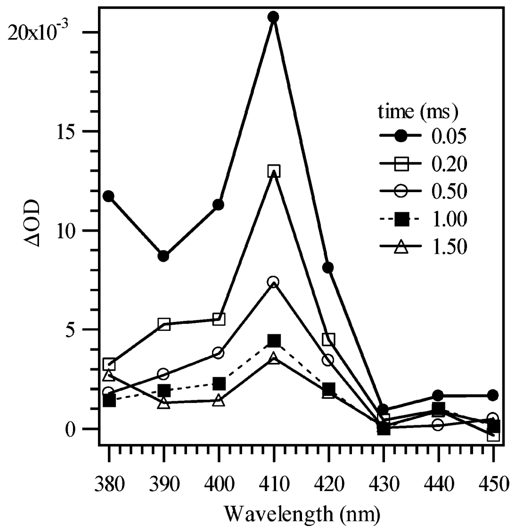


Figure 5. Time-resolved spectra obtained on flash photolysis of PM 567 (55 μM dye; $\lambda_{exc} = 532$ nm) in deaerated acetonitrile in the presence of PMDA (6.0 mM).

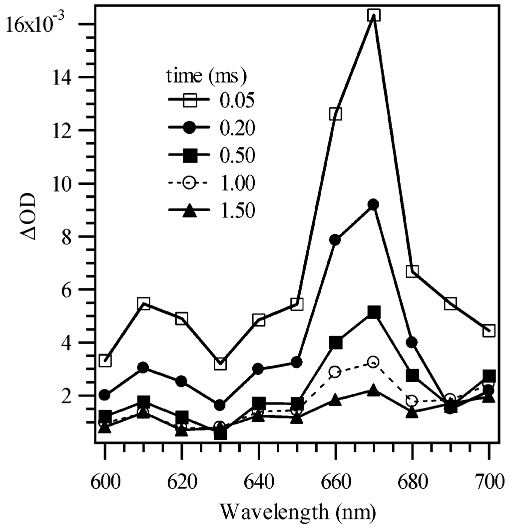


Figure 6. Time-resolved spectra assigned to the PMDA radical anion on laser photolysis of PMDA (6.0 mM) in deaerated acetonitrile in the presence of PM 567 (55 μM dye; $\lambda_{exc} = 532$ nm).

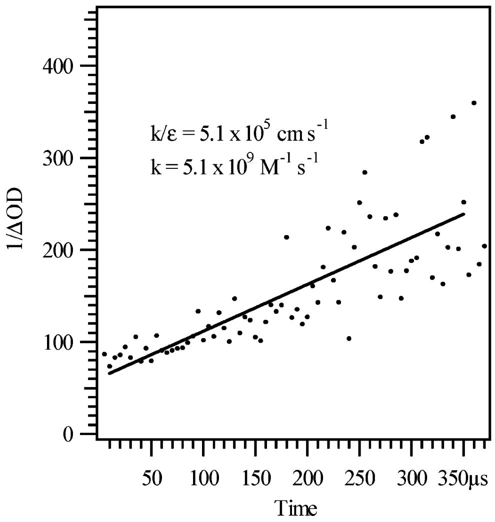


Figure 7. Plot of reciprocal absorbance monitored at 660 nm (PMDA radical anion) vs time. The extinction coefficient for PMDA radical cation is assumed to be 10 000 M^{-1} cm^{-1}.[35]

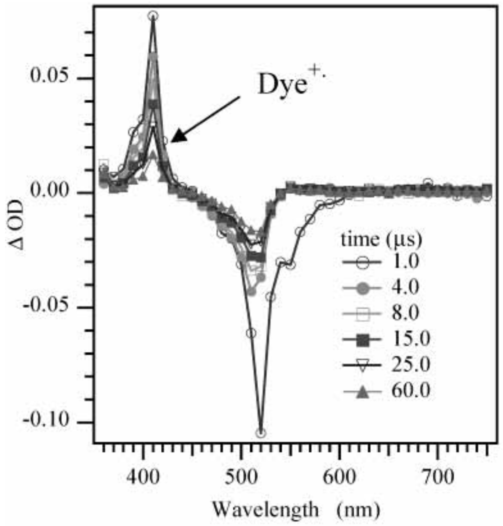


Figure 8. Transient absorption spectra obtained on laser photolysis of PM 567 (13.4 μM; $\lambda_{exc} = 355$ nm) in aerated acetonitrile using BP (8.2 mM) as sensitizer.

for 9,10-dicyanoanthracene radical anion.[39] The depleted concentration of PMDA radical anion leads to a slower rate of decay for the dye radical cation. Additional confirmation of these assignments follows from data for the radical cation (410 nm) on laser flash photolysis of PM 567 in the presence of 20 mM MV^{2+} (in either aerated or deaerated 40% acetonitrile/water (v/v)). The dye radical ion is accompanied by the radical cation of methyl viologen ($MV^{\bullet+}$),[40] which appears at 395 nm (where it overlaps with transient absorption of dye radical cation) and 600 nm (broad absorption). The laser flash photolysis results from dye singlet quenching have been summarized in Table 3.

Laser flash photolysis experiment conducted on PM 567 in *aerated* acetonitrile in the presence of BP (8.2 mM) as a triplet sensitizer ($\lambda_{exc} = 355$ nm) shows the ground-state bleaching of the dye at 520 nm and a strong absorption at 410 nm (Figure 8). No absorption bands corresponding to dye triplet were observed after 1.0 μs. This further confirms that the transients at 450 and 710 nm observed in a *deaerated* environment are indeed that of the dye triplet.

The bleach recovery profile was biexponential; for the major component $\tau = 0.2$ μs (90%), and for the minor long-lived component $\tau = 27$ μs (10%). The initial rapid recovery of ground-state bleaching is associated with energy transfer between the dye triplet and ground-state oxygen, whereas the slower component may be due to an electron-transfer process between the dye triplet and triplet oxygen. The latter process might be also possible due to reaction between the dye triplet and singlet oxygen, which is more energetic than ground-state oxygen by 22.1 kcal mol^{-1} [38] and has an inherently long lifetime ($\tau = 30$ μs) in acetonitrile.[41] The $^1\Delta$ species would be generated from energy transfer from ^{3}BP to ground-state oxygen. One or both of these mechanisms produce the transient absorption at 410 nm. Table 4 summarizes transient data for PM 567 observed on dye photolysis in the presence of the triplet sensitizer.

It is evident from the laser flash photolysis experiments that oxygen plays a pivotal role in the photochemistry of PM dyes. Oxygen enhances triplet formation and in turn the formation of singlet oxygen. It has been reported[19] that the photostability of pyrromethene dyes increases significantly in the absence of oxygen. For photolysis of PM 567, the oxidation-cleavage product, 3-ethyl-2-methylmalemide, has been identified. The mechanism proposed involves the addition of oxygen to the

TABLE 4: Transient Decay Data from Laser Flash Photolysis of PM 567 in the Presence of a Triplet Sensitizer[a]

media	dye triplet[b] (μs)	radical cation[c] (μs)	bleach recovery 520 nm (μs)
CH_3CN[d]	<0.2	0.75 (0.5), 22 (0.5)[e]	0.62 (0.9), 27 (0.1)
CH_3CN[f]	21	30[g]	9.7 (0.8), 61 (0.2)

[a] [PM 567] = 13 μM; $\lambda_{exc} = 355$ nm; sensitizer = benzophenone (8.2 mM). [b] Transient decay at 450 or 710 nm. [c] Transient decay at 410 nm. [d] Aerated solution. [e] Numbers in parentheses correspond to the weighted average of each lifetime. [f] Deaerated solution. [g] Weak shoulder.

bridging carbon−carbon double bond (C8 and C7b). Pyrrole and its analogs, the parent ring in PM dyes, are also known to undergo photooxidation in the presence of oxygen.[42,43] The PM 650 dye, which has less reducing capability, is shown to have the greatest resistance to attack by activated oxygen species.[19]

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Note Added after ASAP Posting. This article was posted ASAP on 9/17/2003. Changes were made in the third paragraph of the Results and Discussion section and the sixth column of Table 1 to represent fluorescence quantum yield as Φ_f. The correct version was posted on 9/24/2003.

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