

Photophysical and electron-transfer properties of a few 2,6-dimethyl-4-arylpopyrylium derivatives[☆]

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Abstract

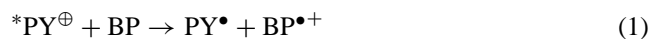
Photophysical and electron transfer properties of pyrylium salts 1–4 were investigated. The photophysical properties include absorption and fluorescence spectra, quantum yields, fluorescence lifetimes and phosphorescence spectra. Laser flash photolysis of 1–4 in degassed dichloromethane led to the formation of transients assigned to the triplets of these molecules. The quantum yields of triplet formation and the extinction coefficients of the triplet–triplet absorption were determined. Electron transfers to the excited states of 1–4 from biphenyl were studied by fluorescence quenching and laser flash photolysis. The intermediate radical ions formed in the electron transfer reactions were characterized. In the case of 1–3, only the singlet excited states were involved in electron transfer reactions, whereas, in the case of 4, the singlet as well as the triplet excited states act as electron acceptors. Involvement of the triplet in the electron transfer reactions, led to higher Φ_{ion} and lower k_{bet} values in the case of 4. Thus, suitable modification of the structure of pyrylium salts can lead to molecules with very good photoelectron transfer properties. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Sensitizers; Photoinduced electron transfer; Back electron transfer; Radical cations; Pyrylium salts

1. Introduction

2,4,6-Triphenylpyrylium (TPP) perchlorate or tetrafluoroborate has found extensive use as a sensitizer in photoinduced electron transfer (PET) reactions [1,2]. As TPP is positively charged, only charge exchange takes place when the radical cation of the donor is generated by an electron transfer process. Therefore, formation of radical ions will be enhanced and deactivation through back electron transfer will be reduced in comparison with neutral sensitizers [1]. In addition, TPP is also an efficient PET sensitizer in its triplet excited state. This allows the generation of triplet radical ion pairs and to examine the effect of spin multiplicity on the fate of these intermediates [3,4]. With respect to PET oxygenation reactions, a unique property of TPP is that it produces neither singlet oxygen nor superoxide anion [5]. Thus, TPP is a suitable sensitizer to study the reactions of radical cations with molecular oxygen [5,6]. In addition to being good sensitizers in PET reactions, pyrylium salts find potential applications as laser dyes [7,8], as Q-switches in lasers [9] and

also as phototherapeutic agents [10,11]. Although, there are several studies dealing with the photophysical and electron transfer properties of TPP and its thia analog, [12–23], practically very little is known about the electron transfer properties of other members of this group. In this paper, a detailed account of the photophysical and electron transfer properties of a few 2,6-dimethyl-4-arylpopyrylium perchlorates (1–4, Chart 1) in dichloromethane solution is presented. Our aim has been to vary the structure and correlate it to the yield of PET reactions. These studies have shown that very facile electron transfer occurs from biphenyl (BP) to the excited states of these molecules as per Eq. (1).



Using laser flash photolysis, we have characterized the pyranil radicals of 1–4 and determined their extinction coefficients. The quantum yields of radical ion formation (Φ_{ion}) were also determined. Our studies have shown that electron transfer in these cases, proceed with high Φ_{ion} values and that these derivatives can act as good sensitizers in PET reactions.

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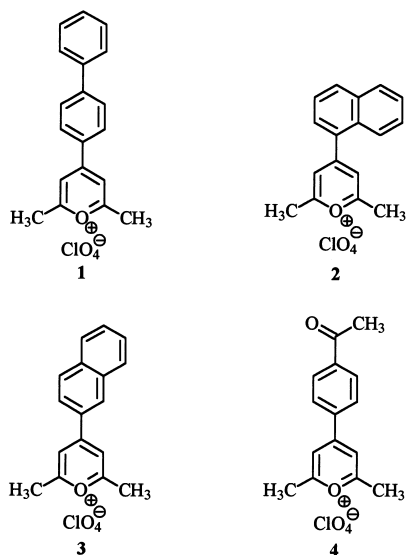


Chart 1.

2. Experimental

2.1. Materials

Pyrylium salts 1–4 used in this study were prepared by a general procedure described earlier [12].

2,6-Dimethyl-4-biphenylpyrylium perchlorate. Yield 51%; mp 180–181°C; IR (ν_{\max}): 3009, 2963, 2890, 1643, 1092 cm^{-1} ; $^1\text{H NMR}$ (90 MHz, CDCl_3), δ 3.0 (s, 6H), 7.3–8.3 (m, 11H); HRMS mol. wt. calcd for $\text{C}_{19}\text{H}_{17}\text{O}^+$ (cation) 261.1279, found, 261.1292.

2,6-Dimethyl-4- α -naphthylpyrylium perchlorate. Yield 28%; mp 159–160°C; IR (ν_{\max}): 3089, 2975, 2918, 1635, 1095 cm^{-1} ; $^1\text{H NMR}$ (90 MHz, CDCl_3), δ 3.0 (s, 6H), 7.3–8.1 (m, 9H); HRMS mol. wt. calcd for $\text{C}_{17}\text{H}_{15}\text{O}^+$ (cation) 235.1123, found, 235.1129.

2,6-Dimethyl-4- β -naphthylpyrylium perchlorate. Yield 40%; mp 237–238°C; IR (ν_{\max}): 3020, 2937, 2869, 1628, 1108 cm^{-1} ; $^1\text{H NMR}$ (90 MHz, CDCl_3), δ 3.0 (s, 6H), 8.0–9.0 (m, 9H); HRMS mol. wt. calcd for $\text{C}_{17}\text{H}_{15}\text{O}^+$ (cation) 235.1123, found, 235.1142.

*2,6-Dimethyl-4-(*p*-acetylphenyl)pyrylium perchlorate.* Yield 20%; mp 134–135°C; IR (ν_{\max}): 3087, 2936, 2864, 1636, 1099 cm^{-1} ; $^1\text{H NMR}$ (90 MHz, CDCl_3), δ 2.6 (s, 3H) 3.0 (s, 6H), 7.9–8.3 (m, 6H); HRMS mol. wt. calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2^+$ (cation) 227.1072, found, 227.1075.

Biphenyl used in these studies was purified by recrystallization. Spectroscopic grade solvents were used throughout and solutions for flash photolysis experiments were saturated with argon for 15 min prior to the experiments.

2.2. Measurements

All melting points are uncorrected and were determined on a Büchi Model 530 melting point apparatus. IR spectra were recorded on a Perkin Elmer Model 882 IR spectro-

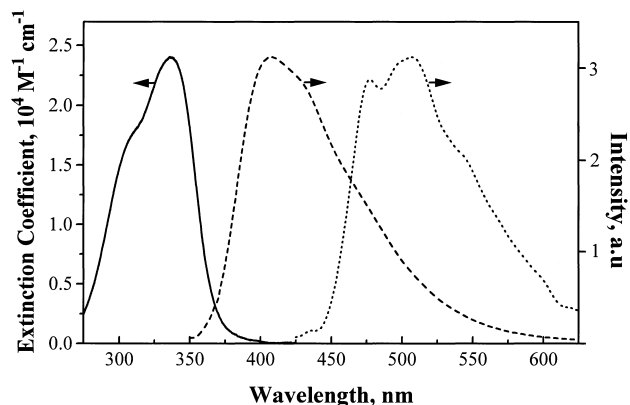


Fig. 1. Absorption (—), fluorescence (---), and phosphorescence (••••) spectra of 4. Absorption and fluorescence spectra are in dichloromethane and phosphorescence spectrum in glycerol glass at 77 K.

meter. $^1\text{H NMR}$ spectra were recorded on a JEOL EX-90 spectrometer. Mass spectra (FAB) were recorded on a JEOL JMS AX503 mass spectrometer. The absorption spectra were recorded on a Shimadzu UV-2100 or a GBC double beam UV-VIS spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog F 112X spectrofluorimeter with a right-angled geometry using 1×10^{-5} M solutions. Fluorescence quantum yields were determined using optically matched solutions and by employing a solution of quinine sulfate in 1 N sulfuric acid ($\Phi_{\text{F}} = 0.54$) as the reference. Phosphorescence spectra of the compounds in glycerol glass at 77 K were recorded on a SPEX 1934D phosphorimeter. Fluorescence lifetimes were determined using an Edinburgh Instruments FL900CD single photon counting system. Electrochemical experiments were performed with a Wenking Model POS 73 potentiostat and pulse generator. Solutions of the pyrylium salts (1×10^{-3} M) in acetonitrile, containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte were thoroughly degassed before use. A glassy carbon electrode was used as the working electrode and a platinum gauze was used as the counter electrode. Laser flash photolysis experiments were carried out by employing an Applied Photophysics Model LKS-20 Laser Kinetic Spectrometer using GCR-12 Series Quanta Ray Nd:YAG laser. The analyzing and laser beams were fixed at right angles to each other. The laser energy was 60 mJ at 355 nm.

3. Results and discussion

3.1. Photophysical properties

Pyrylium salts 1–4 exhibit strong absorption in the 300–450 nm region. The absorption spectrum of 4 is given in Fig. 1 and the maxima of the long wavelength absorptions along with the extinction coefficients for 1–4 are presented in Table 1. Table 1 also gives the fluorescence maxima, quantum yields and lifetimes for all these compounds. It

Table 1

Absorption maxima ($\lambda_{\max}(\text{abs})$), extinction coefficients (ϵ_{\max}), emission maxima ($\lambda_{\max}(\text{em})$), fluorescence quantum yields (Φ_F), and fluorescence lifetimes (τ_F) for pyrylium salts 1–4 in dichloromethane

Compound	$\lambda_{\max}(\text{abs})$ (nm)	ϵ_{\max} ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\max}(\text{em})$ (nm)	Φ_F	τ_F (ns)
1	402	2.8×10^4	501	0.78	3.4
2	438	1.0×10^4	554	0.22	13.4
3	430	9.0×10^3	544	0.64	16.7
4	336	2.4×10^4	405	0.03	2.0

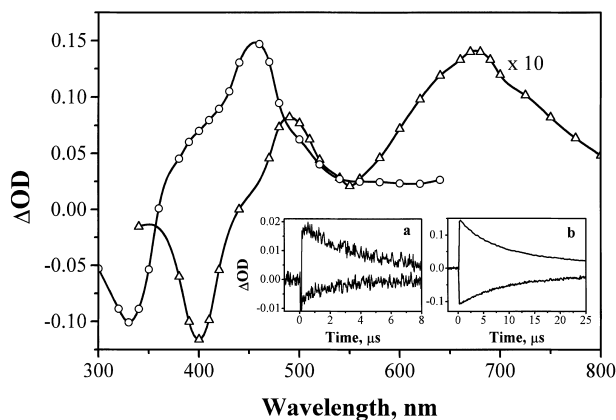


Fig. 2. Transient absorption spectra of 1 ($-\Delta-$) and 4 ($-\circ-$) in dichloromethane recorded at 100 ns after the 355 nm laser pulse. Insets show the decay profile and the bleaching recovery for (a) 1 and (b) 4.

can be seen from Table 1 that 4 exhibits very low fluorescence quantum yield compared to the other derivatives. This is attributed to the enhanced intersystem crossing in 4 due to the presence of the carbonyl group in the molecule. Thus, we expect a higher triplet yield in the case of 4. In accordance with this explanation, 4 exhibits very strong phosphorescence emission. The phosphorescence spectrum of 4 taken in glycerol glass at 77 K is shown in Fig. 1 along with its absorption and fluorescence spectra.

From the onset of the phosphorescence emission, a value of 65 kcal M^{-1} was calculated for the triplet energy of 4. Pyrylium salts 1–3 did not show any phosphorescence emission under these conditions and hence the triplet energies could not be determined in these cases. Absence of phosphorescence emission in the case of 1–3 is attributed to very poor triplet yields in these cases (wide infra).

3.1.1. Laser flash photolysis studies

Laser flash photolysis of 1–4 in dichloromethane solution saturated with argon, using the third harmonic of a Nd:YAG laser (355 nm), led to the formation of transients characterized by bleaching in the region of their ground state absorptions and transient absorptions in the 450–800 nm region. Transient absorptions in the case of 1–3 were very weak and exhibited two bands, whereas, in the case of 4 a very strong band at 460 nm was observed. Representative examples are shown in Fig. 2.

All these transients were quenched by oxygen and hence we assign them to the triplets of these compounds. The oxy-

gen quenching rate constants were determined and are presented in Table 2. For all the substrates the bleaching maxima in dichloromethane coincided with the absorption maxima. This enabled us to calculate the extinction coefficients (ϵ_T) of these absorptions by the singlet depletion method [24]. The values of extinction coefficients thus obtained were used to determine the quantum yields of triplet formation (Φ_T) by relative actinometry method [25]. An optically matched solution of benzophenone in benzene ($\Phi_T = 1$, $\epsilon_T = 7600 \text{ M}^{-1} \text{cm}^{-1}$ at 530 nm) [26] was used as the reference in these studies. The data obtained for all these compounds are summarized in Table 2. An inspection of Table 2 confirms that the Φ_T value for 4 is very high compared to those of 1–3.

3.2. Electron transfer studies

Electron transfer reactions of 1–4 were studied using BP as the electron donor. We have observed that the fluorescence of 1–4 were quenched very efficiently by biphenyl and the plots of fluorescence intensity versus BP concentration were linear in all cases. These were analyzed by the Stern-Volmer treatment. The singlet quenching rate constants (k_q^S) obtained in this way, are presented in Table 3.

Quenching of the fluorescence of 1–4 by BP occurs by an electron transfer mechanism (vide infra). The free energy change (ΔG_{el}^S) associated with the electron transfer can be calculated by the Weller Eq. (2) [27],

$$\Delta G_{el}^S (\text{kcal M}^{-1}) = 23.06[E_{\text{ox}} - E_{\text{red}} - e^2/\epsilon d] - E_s \quad (2)$$

where, E_{ox} is the oxidation potential of BP, E_{red} is the reduction potential and E_s is the singlet energy of the pyrylium salt used. The term $e^2/\epsilon d$ in Eq. (2) represents the energy gained in bringing the radical or radical ion species to an encounter distance 'd' in a solvent of relative permittivity ' ϵ '. In the present case, only charge exchange takes place in electron transfer and hence this term will be zero [1,12]. The singlet excitation energies were obtained from the absorption and fluorescence spectra of 1–4. The reduction potentials of 1–4 were measured using cyclic voltammetry. The first reduction peaks of 1–4 appeared in the -0.38 to -0.49 V (versus SCE) range. The cyclic voltammograms of these substrates did not show the reverse anodic peak. This is a very general behavior exhibited by pyrylium salts having H or CH_3 groups in position 2-or 4-of the heterocyclic

Table 2

Triplet–triplet absorption maxima ($\lambda_{\text{max}}^{\text{T}}$), extinction coefficients ($\epsilon_{\text{max}}^{\text{T}}$), triplet quantum yields (Φ_{T}), triplet lifetimes (τ_{T}) and oxygen quenching rate constants ($k_{\text{q}}(\text{O}_2)$) for pyrylium derivatives 1–4

Compound	$\lambda_{\text{max}}^{\text{T}}$ (nm)	$\epsilon_{\text{max}}^{\text{T}}$ ($\text{M}^{-1} \text{cm}^{-1}$)	Φ_{T}	τ_{T} (μs)	$k_{\text{q}}(\text{O}_2)$ ($\text{M}^{-1} \text{s}^{-1}$)
1	500 (680)	4.0×10^4	0.03	2.2	4.9×10^7
2	520 (680)	5.5×10^4	0.13	6.1	3.3×10^9
3	520 (680)	1.5×10^4	0.09	3.5	4.2×10^9
4	460	2.7×10^4	0.66	8.3	2.2×10^9

Table 3

Singlet energies (E_{S}), reduction potentials (E_{red}), free energies of electron transfer to the singlet state ($\Delta G_{\text{el}}^{\text{S}}$) from BP and singlet quenching rate constants (k_{q}^{S}) by BP for the pyrylium salts 1–4 in dichloromethane solution

Compound	$E_{0,0}$ (kcal M^{-1})	E_{red} (V vs. SCE)	$\Delta G_{\text{el}}^{\text{S}}$ (kcal M^{-1})	k_{q}^{S} ($\text{M}^{-1} \text{s}^{-1}$)
1	63.6	−0.44	−8.3	4.8×10^9
2	58.9	−0.49	−2.4	1.2×10^9
3	59.6	−0.47	−3.6	4.7×10^9
4	77.9	−0.38	−23.9	1.5×10^{10}

ring and is attributed to a fast dimerization of the pyranly radicals [28–30].

The oxidation potential of BP is 1.91 V versus SCE [31]. Using this value $\Delta G_{\text{el}}^{\text{S}}$ values were calculated employing Eq. (2). $\Delta G_{\text{el}}^{\text{S}}$ values along with excitation energies, reduction potentials and singlet quenching rate constants are presented in Table 3. Note from Table 3 that $\Delta G_{\text{el}}^{\text{S}}$ value for 4 is highly negative. Consequently, diffusion controlled quenching is observed in this case. For other substrates, $\Delta G_{\text{el}}^{\text{S}}$ values were only moderately negative (−2.4 to −8.3 kcal M^{-1}). These values lie in the normal region according to Marcus equation [32] and we expect the rate constants to be lower than the diffusion limited value. k_{q}^{S} obtained for 1–3 are in good agreement with these observations.

3.2.1. Laser flash photolysis studies

In order to gain a better understanding of the mechanism involved in the quenching reactions, laser flash photolysis experiments were carried out. We have observed that the quenching of the triplets of 1–3 by BP was not very efficient. This most probably is due to energetic reasons. As mentioned earlier, pyrylium salts 1–3 did not show phosphorescence emission and hence their triplet energies could not be measured accurately. For a few pyrylium salts for which triplet energies are known, a singlet–triplet gap of 10–15 kcal M^{-1} were observed [12,33]. We have assumed a singlet–triplet gap of 10 kcal M^{-1} , and calculated the free energies of electron transfer from BP to the triplet states ($\Delta G_{\text{el}}^{\text{T}}$) of pyrylium salts 1–3, using the Weller equation. $\Delta G_{\text{el}}^{\text{T}}$ values thus estimated for 1–3 were positive (1.7–7.6 kcal M^{-1}). We believe that triplet quenching in these cases were very inefficient because of the positive $\Delta G_{\text{el}}^{\text{T}}$ values associated with these quenching reactions. In contrast, very efficient triplet quenching was observed for 4. Using a triplet energy of 65 kcal M^{-1} (obtained from the phosphorescence spectrum) $\Delta G_{\text{el}}^{\text{T}} = -10.8 \text{ kcal M}^{-1}$ was calculated for this quenching reaction. Triplet quenching

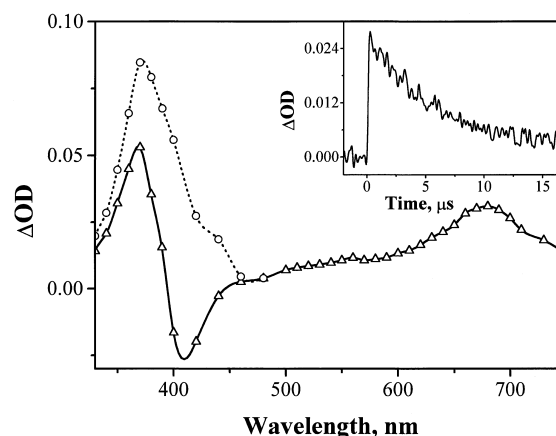


Fig. 3. Transient absorption spectrum (−Δ−) of 1 ($2 \times 10^{-5} \text{ M}$) in the presence of BP (0.1 M) at 100 ns following the laser pulse. Inset shows the decay of the transient at 680 nm. The corrected spectrum of the radical is also shown (−O−).

rate (k_{q}^{T}) of $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained in this case from a plot of the pseudo-first-order decay rates versus BP concentration. The value of k_{q}^{T} obtained was very close to the diffusion-controlled value.

In order to characterize the transients involved in these electron transfer reactions, transient absorption spectra were recorded in the presence of BP (0.1 M). Under these conditions, more than 90% of the singlets will be quenched leading to the formation of biphenyl radical cation ($\text{BP}^{\bullet+}$) and the corresponding pyranly radicals (PY^{\bullet}). Figs. 3–5 show the transient absorption spectra of 1–3 recorded in the presence of BP. All these spectra showed the well-known transient absorption due to $\text{BP}^{\bullet+}$ at 680 nm [31]. Correspondingly, the absorptions in the 380–450 nm region were assigned to the pyranly radicals formed as a result of electron transfer according to Eq. (1).

It can be seen from Figs. 3–5 that the pyranly radicals absorb in the 380–450 nm region. The pyrylium salts also absorb in this region and as a result the observed transient

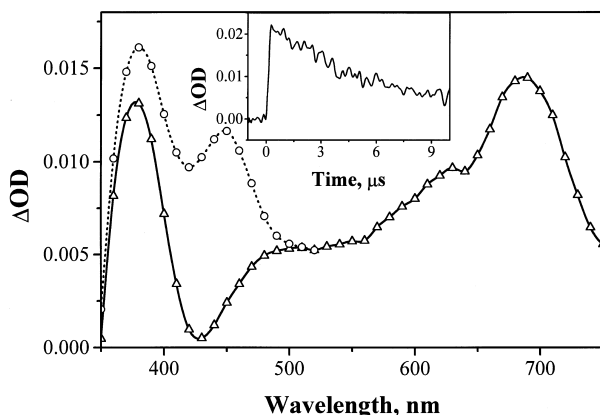


Fig. 4. Transient absorption spectrum ($-\Delta-$) of 2 (2×10^{-5} M) in the presence of BP (0.1 M) at 100 ns following the laser pulse. Inset shows the decay of the transient at 680 nm. The corrected spectrum of the radical is also shown ($-\circ-$).

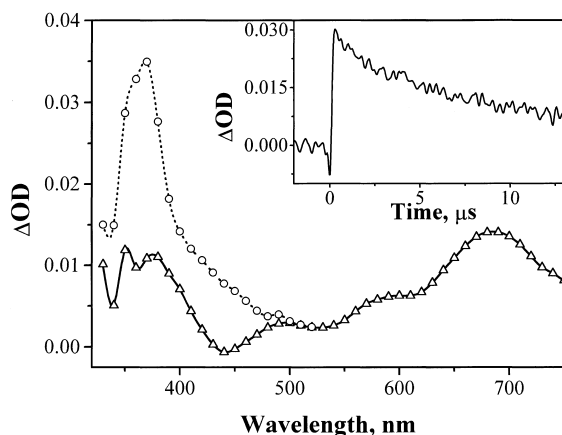


Fig. 5. Transient absorption spectrum ($-\Delta-$) of 3 (2×10^{-5} M) in the presence of BP (0.1 M) at 100 ns following the laser pulse. Inset shows the decay of the transient at 680 nm. The corrected spectrum of the radical is also shown ($-\circ-$).

absorption is a superposition of the radical absorption and the ground state bleaching due to the pyrylium salts. In such cases, the actual spectra of the radicals can be obtained using Eq. (3) [24].

$$\epsilon_{\text{PY}\bullet} = \frac{\Delta\text{OD}_{\text{obsd}}}{l[\text{PY}\bullet]} + \epsilon_{\text{PY}^+} \quad (3)$$

In Eq. (3), $\epsilon_{\text{PY}\bullet}$ is the actual extinction coefficient of the radical absorption, ϵ_{PY^+} is the extinction coefficient of the pyrylium salt, $\Delta\text{OD}_{\text{obsd}}$ is the observed difference absorption, ' l ' is the optical path length and $[\text{PY}\bullet]$ is the concentration of the pyranil radicals formed in the electron transfer reaction. Eq. (3) assumes that no other species absorb in this region. This assumption is valid in the present case because the absorption due to the $\text{BP}^{\bullet+}$ is far removed from the 350–450 nm region where the correction is attempted. (It should be mentioned here that $\text{BP}^{\bullet+}$ has an absorption in the short wavelength region. In our control experiments with triphenylpyrylium/BP system this band appeared at 330 nm.

Table 4

Absorption maxima ($\lambda_{\text{max}}^{\text{PY}\bullet}$), extinction coefficients ($\epsilon_{\text{max}}^{\text{PY}\bullet}$), rate of back electron transfer (k_{bet}) and quantum yields of formation (Φ_{ion}) for the pyranil radicals generated in the PET reactions of 1–4 with BP

Compound	$\lambda_{\text{max}}^{\text{PY}\bullet}$ (nm)	$\epsilon_{\text{max}}^{\text{PY}\bullet}$ ($\text{M}^{-1} \text{cm}^{-1}$)	k_{bet} ($\text{M}^{-1} \text{s}^{-1}$)	Φ_{ion}
1	370	4.0×10^4	9.5×10^{10}	0.36
2	380 (450)	1.6×10^4 (1.2×10^4)	1.3×10^{11}	0.30
3	370	3.6×10^4	9.5×10^{10}	0.26
4	385	4.7×10^4	5.9×10^{10}	0.71

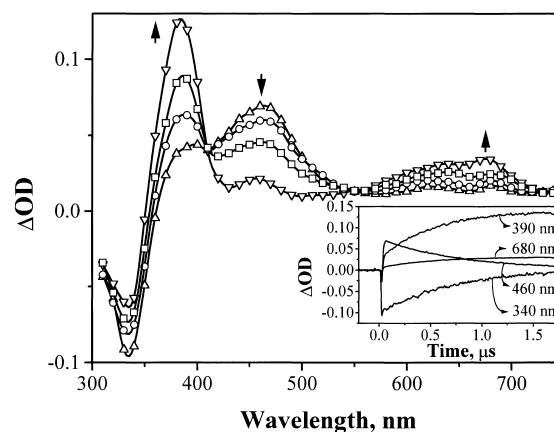


Fig. 6. Transient absorption spectra at ($-\Delta-$) 0.1, ($-\circ-$) 0.25, ($-\square-$) 0.5 and ($-\nabla-$) 1.0 μs following the 355 nm laser pulse excitation of 4 (2×10^{-5} M) in the presence of biphenyl (1×10^{-4} M) in dichloromethane. Inset shows the growth of the transients at 390 and 680 nm, decay at 460 nm and bleaching recovery at 340 nm.

Unlike the 680 nm band, this short-wavelength band is very narrow and showed negligible absorption above 350 nm. Hence any error arising from neglecting this absorption is negligible. The concentration of the pyranil radicals could not be directly measured from these experiments. However, according to the stoichiometry of Eq. (1), $[\text{PY}\bullet] = [\text{BP}^{\bullet+}]$ and hence $[\text{BP}^{\bullet+}]$ can be substituted in Eq. (3). Since the absorptions due to $\text{PY}\bullet$ and $\text{BP}^{\bullet+}$ are far removed and non-interfering, $[\text{BP}^{\bullet+}]$ can be directly calculated from the observed difference absorption and known extinction coefficient ($\epsilon = 1.45 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$) [31] at 680 nm. The corrected absorption spectra of the radicals are presented along with the transient absorption spectra in Figs. 3–5. The absorption maxima and the extinction coefficients of these radicals are listed in Table 4.

Transient absorption spectrum of 4 recorded in the presence of BP (0.1 M), also showed absorption at 680 nm due to $\text{BP}^{\bullet+}$. A second absorption observed at 385 nm was assigned to 4^\bullet . In this case, however, we have observed that the triplets were also quenched by BP. In order to see whether triplet quenching also leads to electron transfer, we have recorded the transient absorption spectrum of 4 in the presence of 1×10^{-4} M BP. The singlets are relatively unaffected and triplets are efficiently quenched at this concentration of BP. The transient absorption spectra obtained at different time intervals following the laser pulse are shown in Fig. 6. At early times the spectrum obtained corresponds to the

triplet absorption spectrum. The absorption due to the triplet at 460 nm decays with concomitant growth of absorption at 680 nm (due to $\text{BP}^{\bullet+}$) and at 385 nm (due to 4^\bullet). Isosbestic points were observed at 410 and 550 nm. The decay of the triplet matched with the growth of the radical absorptions. All these factors clearly suggested that quenching of the triplet of 4 by BP also occurs by an electron transfer mechanism and directly leads to the formation of $\text{BP}^{\bullet+}$ and 4^\bullet .

In the case of the electron transfer quenching of 1–4 by BP, the yields of radical products Φ_{ion} were estimated by relative actinometry method. Optically matched solutions of benzophenone in benzene (reference compound) and of pyrylium salts (1–4) in dichloromethane containing BP (0.1 M), were saturated with argon and subjected to flash photolysis at 355 nm. Φ_{ion} values were then calculated from the ΔOD values using Eq. (4).

$$\Phi_{\text{ion}} = \Phi_{\text{T}}^{\text{R}} \frac{\Delta\text{OD}_{\text{BP}^{\bullet+}}^{\text{R}} + \epsilon_{\text{T}}^{\text{R}}}{\Delta\text{OD}_{\text{T}}^{\text{R}} \epsilon_{\text{BP}^{\bullet+}}} \quad (4)$$

In Eq. (4), ΔOD 's are the end-of-pulse absorbance changes, ϵ 's are the extinction coefficients and R stands for the reference compound benzophenone. Φ_{ion} values thus estimated are presented in Table 4.

The radicals generated by electron transfer decayed almost completely at longer time scales. Since long-lived absorptions due to product formation were not observed, it was assumed that the decay occurred by back electron transfer according to Eq. (5),



where, k_{bet} is the rate of back electron transfer. In all these cases, decay of the radicals followed second order kinetics. Observation of second order kinetics suggested that the species are present as free and/or loose ion pairs and not as contact ion pairs, in which case first-order kinetics would be anticipated [34]. Monitoring the decay of the $\text{BP}^{\bullet+}$ absorption at 680 nm, the decay rates were calculated. Values of rate constants (k_2/ϵ) thus obtained were in the range $(4\text{--}9) \times 10^6 \text{ cm s}^{-1}$. The back electron transfer rates (k_{bet}) were obtained by substituting for ϵ and these are presented in Table 4. Notice that $k_{\text{bet}} > k_{\text{diff}}$ in all these cases suggesting that the radicals may be present as loose radical pairs and not as free radical ions.

An inspection of Table 4 shows that k_{bet} values are in the range $(5.9\text{--}13.0) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. k_{bet} values obtained for 1–3 were comparable to those reported in the literature for other pyrylium salts and an order of magnitude slower compared with the back electron transfer rates observed in dicyanonaphthalene/BP system studied under comparable conditions [12]. Φ_{ion} values obtained for 1–3 were also higher compared to those reported for a few 2,6-dimethyl-4-alkylphenylpyrylium salts and similar cationic sensitizers [12,35,36]. This is attributed to the stabilization of the pyranil radicals in these cases. According to EPR spectra and quantum mechanical calculations,

pyranil radicals exhibit higher spin density at position 4-of the heterocyclic ring [37]. Based on these results it was suggested that, if the 4-position is substituted with groups that can stabilize the odd electron by delocalization, the pyranil radicals would be more stable. Higher yield of the radicals of 1–3 in these reactions suggested that these radicals are more stable compared to their 4-alkylphenyl analogs.

Our studies have shown that 4 exhibited excellent properties as a PET sensitizer. This is reflected in the low value of k_{bet} and very high value of Φ_{ion} . This property is attributed to the higher triplet yield of 4 compared to 1–3 and also to TPP. It is well established that electron transfer involving triplet excited states leads to efficient separation of ion pairs. This is a consequence of the fact that recombination in the geminate triplet radical pair to regenerate the starting materials is spin forbidden and this leads to lower k_{bet} values and higher Φ_{ion} values [38–40].

4. Summary and conclusions

Absorption, emission and laser flash photolysis studies of pyrylium salts 1–4 were carried out. Pyrylium salts 1–3 showed higher fluorescence quantum yields, whereas, presence of a carbonyl group leads to enhanced intersystem crossing resulting in higher triplet yields in the case of 4. It was observed that the fluorescence of these molecules were efficiently quenched by electron donation from biphenyl. Using laser flash photolysis technique, we have characterized the radical ions formed in these electron transfer reactions and determined their extinction coefficients and quantum yields of formation. Our studies have shown that these sensitizers, especially 4, can have good potential for use as a sensitizer in PET reactions. These studies also show that modification of the structure of pyrylium salts can lead to molecules with very good photoelectron transfer properties.

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References

- [1] M.A. Miranda, H. Garcia, Chem. Rev. 94 (1994) 1063.
- [2] S.L. Mattes, S. Farid, in: A. Padwa (Ed.), Organic Photochemistry, vol. 6, Dekker, New York, 1983, p. 233.
- [3] R. Akaba, H. Aihara, H. Sakuragi, K. Tokumaru, J. Chem. Soc. Chem. Commun. (1987) 1262.

- [4] R. Akaba, K. Ohshima, Y. Kawai, A. Negishi, H. Sakuragi, K. Tokumaru, *Tetrahedron* 32 (1991) 109.
- [5] R. Akaba, S. Aihara, H. Sakuragi, K. Tokumaru, *J. Chem. Soc. Perkin Trans. 2* (1991) 291.
- [6] A. Seilmeier, B. Kopainsky, W. Kaiser, *Appl. Phys.* 22 (1980) 355.
- [7] S. Tripathi, V. Wintgens, P. Valat, V. Toscano, J.F. Kossanyi, F. Bos, *J. Luminescence* 37 (1987) 149.
- [8] B. Kopainsky, W. Kaiser, K.H. Drexhage, *Opt. Commun.* 32 (1980) 451.
- [9] M.R. Detty, P.B. Merkel, *J. Am. Chem. Soc.* 112 (1990) 3845.
- [10] M.R. Detty, P.B. Merkel, R. Hilf, S.L. Gibson, S.K. Powers, *J. Med. Chem.* 33 (1990) 1108.
- [11] N. Manoj, R. Ajithkumar, K.R. Gopidas, *J. Photochem. Photobiol. A: Chem.* 109 (1997) 109.
- [12] R. Akiko, M. Kamata, K. Akiko, K.-I. Mogi, Y. Kuriyama, H. Sakuragi, *J. Phys. Org. Chem.* 10 (1997) 861.
- [13] N. Manoj, K.R. Gopidas, *J. Photochem. Photobiol. A: Chem.* 85 (1995) 53.
- [14] N. Manoj, K.R. Gopidas, *Chem. Phys. Lett.* 267 (1997) 567.
- [15] Z. Lin, G.B. Schuster, *J. Org. Chem.* 59 (1994) 1119.
- [16] Y. Chen, S.-K. Wu, *J. Photochem. Photobiol. A: Chem.* 102 (1997) 203.
- [17] R. Akaba, Y. Niimura, T. Fukushima, Y. Kawai, T. Tajima, T. Karugemi, A. Negishi, M. Kamata, H. Sakuragi, K. Tokumaru, *J. Am. Chem. Soc.* 114 (1992) 4460.
- [18] P. Ramamurthy, F. Morlet-Savary, J.P. Fouassier, *J. Chem. Soc. Faraday Trans.* 89 (1993) 465.
- [19] P. Ramamurthy, S. Parret, F. Morlet-Savary, J.P. Fouassier, *J. Photochem. Photobiol. A: Chem.* 83 (1994) 205.
- [20] F. Galindo, M.A. Miranda, *J. Photochem. Photobiol. A: Chem.* 113 (1998) 155.
- [21] S.S. Jayanthi, P. Ramamurthy, *J. Phys. Chem.* 101 (1997) 2016.
- [22] S.S. Jayanthi, P. Ramamurthy, *J. Phys. Chem. A* 102 (1998) 511.
- [23] C. Ecoffet, D. Markovitsi, P. Millie, C. Jallabert, H. Strzelecka, M. Veber, *J. Chem. Soc. Faraday Trans.* 89 (1993) 457.
- [24] I. Carmichael, G.L. Hug, *J. Phys. Chem. Ref. Data* 15 (1986) 1.
- [25] H. Lutz, E. Breheret, L. Lindquist, *J. Phys. Chem.* 77 (1973) 1758.
- [26] R. Bensasson, E.J. Land, *J. Photochem. Photobiol. Rev.* 3 (1978) 163.
- [27] D. Rehm, A. Weller, *Isr. J. Chem.* 8 (1970) 259.
- [28] J. Klima, J. Volke, J. Urban, *Electrochim. Acta* 36 (1991) 73.
- [29] F. Pragst, R. Ziebig, U. Seydewitz, D. Driesel, *Electrochim. Acta* 25 (1980) 341.
- [30] V. Wintgens, J. Pouliquen, J. Kossanyi, M. Heintz, *Nouv. J. Chim.* 10 (1986) 345.
- [31] I.R. Gould, D. Ege, J.E. Moser, S. Farid, *J. Am. Chem. Soc.* 112 (1990) 4290.
- [32] R.A. Marcus, *Annu. Rev. Phys. Chem.* 15 (1964) 155.
- [33] V. Wintgens, J. Pouliquen, J. Kossanyi, *Nouv. J. Chim.* 9 (1985) 229.
- [34] O. Ito, *Res. Chem. Intermed.* 23 (1997) 389.
- [35] A. Samanta, K.R. Gopidas, P.K. Das, *Chem. Phys. Lett.* 167 (1990) 165.
- [36] A. Samanta, K.R. Gopidas, P.K. Das, *J. Phys. Chem.* 97 (1993) 1583.
- [37] C. Hacquard, A. Rassat, *Mol. Phys.* 30 (1975) 1935.
- [38] J. Olmsted III, T.J. Meyer, *J. Phys. Chem.* 91 (1987) 1649.
- [39] E. Haselbach, E. Vauthey, P. Suppen, *Tetrahedron* 44 (1988) 7335.
- [40] D. Mauzerall, in: M.A. Fox, M. Channon (Eds.), *Photoinduced Electron Transfer, Part A*, Elsevier, Amsterdam, 1988, p. 228.