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Synthesis and Photophysical Properties of the 4-(Biphenyl-4-yl)-2,6-bis(4-iodophenyl)pyrylium Ion

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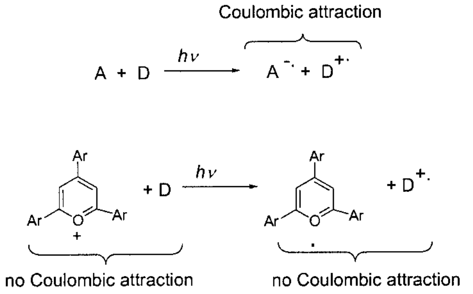
A triarylpyrylium ion containing iodo and biphenyl substituents has been synthesized and its photophysical properties measured. Compared to its parent triphenylpyrylium ion, the photophysical data recorded for 4-(biphenyl-4-yl)-2,6-bis(4-iodophenyl)pyrylium are significantly influenced by substitution. Remarkable decreases in fluorescence and phosphorescence quantum yields, a shorter singlet lifetime, and lower energies of the singlet and triplet excited states are observed.

Introduction

The 2,4,6-triphenylpyrylium ion (TP$^+$) has been the subject of an intense study aimed at determining its photophysical and photochemical properties in solution as well as in a variety of other media.[1,2] Most of the interest in TP$^+$ arises from its general use as a sensitizer for photoinduced electron transfer (PET) reactions.[1,3] TP$^+$ exhibits many features that make this ion and its derivatives unique among other PET sensitizers. TP$^+$ can act as a spin-selective photosensitizer and can promote PET reactions both from the singlet and from the triplet excited states.[1] TP$^+$ has high oxidation potentials, which are estimated to be 2.5 V and 2.0 V for the singlet and triplet excited states, respectively.[1] In addition, TP$^+$ does not generate singlet oxygen, a common interference in many PET reactions.[1]. As TP$^+$ is converted upon electron transfer into a neutral TP$^{\cdot}$ radical, no net charge separation occurs in the PET. Diffusion of the resulting geminate species out of the cage is not impeded by electrostatic attraction [Equation (1)] and thus, Coulombic interactions, which usually negatively affect charge separation, can be neglected in most TP$^+$-promoted reactions. Sulfur analogs such as 2,4,6-triphenylthiapyrylium exhibit photochemical properties that are very similar to those of the pyrylium heterocycles, but they are more stable and have higher aromaticity due to the more uniform charge delocalization through the six-membered ring and the lower electronegativity of sulfur relative to that of oxygen.[4,5]



(1)

These unique properties of TP$^+$ and its derivatives are the basis for the use of triarylpyrylium ions in technological applications such as photoinduced polymer curing, photolithography, and related photographic processes.[6] In polymer curing, the pyrylium ion acts as a photosensitizer and in the presence of suitable coinitiators it is able to generate radicals that promote polymer crosslinking. In addition, TP$^+$ derivatives have been used as chemosensors for Lewis acid cations and carboxylic acids.[7]

With this background in mind, it is of interest to develop new derivatives that can exhibit optimized properties. Most current best-selling photoinitiators contain several iodine atoms. Iodine as a substituent should promote intersystem crossing through operation of the heavy atom effect.[8–11] The longer life of triplets with respect to singlets may be responsible for the higher efficiency of iodo derivatives in photocuring.

As biphenyl is an electron-transfer mediator that has been widely used to enhance the efficiency of PET processes,[12] we consider the possibility of incorporating a biphenyl subunit in the structure of TP$^+$.

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In this work we report the synthesis and study of the properties of a triarylpyrylium derivative, namely 4-(biphenyl-4-yl)-2,6-bis(4-iodophenyl)pyrylium tetrafluoroborate ($3^+\cdot BF_4^-$), whose structure encompasses two iodo substituents and a biphenyl moiety. As expected, we have observed a large influence of these substituents on the photophysics of **3**$^+$, as compared to the photophysical properties of the parent pyrylium ion.

Results and Discussion

Up to now, no triarylpyrylium derivatives containing iodo substituents have been synthesized, in spite of the large influence that can be expected because of the presence of this halogen. The synthesis of pyrylium **3**$^+$ was achieved in 30% yield by treating 4-iodoacetophenone with 4-phenylbenzaldehyde in the presence of BF_3 as catalyst, as indicated in Scheme 1. Compound **3**$^+$ was characterized as its BF_4^- salt. The ^1H- and ^{13}C NMR spectra contain the expected peaks according to the proposed structure. The most salient features are the protons at the 3- and 5-positions that appear as singlets at δ = 9.35 ppm. The expected absorption corresponding to the $C{=}O^+$ stretching vibration was observed at 1623 cm^{-1} in the IR spectrum. All the above spectroscopic data are very similar to those of the parent TP$^+$.[1]

From compound **3**$^+$, the corresponding thiapyrylium **4**$^+$ could be obtained by reaction with Na_2S in acidic aqueous medium (Scheme 1). Although compound **4**$^+$ could be purified and characterized, the yield was unsatisfactory (see Experimental Section). Further studies with this sulfur analog were postponed and will be reported independently once the synthesis has been optimized.

The photophysical characterization of twice recrystallized pyrylium **3**$^+$ starts with the UV/Vis spectrum of compound $3^+\cdot BF_4^-$ (Figure 1) that shows a visible absorption band at λ_{max} = 425 nm (ε = 31200 mol^{-1} L cm^{-1}). The optical spectrum of **3**$^+$ is similar in λ_{max} and appearance to that of the parent TP$^+$ (λ_{max} = 370 and 420 nm), with minor differences. TP$^+$ has two close absorption bands that have been rationalized as arising from the orthogonal absorption of two substructures, namely, the 2,6-diphenylpyrylium and the 4-phenylpyrylium moieties acting as independent chromophores.[1] In the case of compound **3**$^+$, it seems that the two bands of TP$^+$ have merged into a single band with somewhat higher molar absorptivity. The biphenyl substructure should have shifted the band at 370 nm towards longer wavelengths because of the bathochromic effect, which brings it closer to the 420-nm band that is characteristic of the 2,6-diarylpyrylium. This higher ε value may be due to the collapse of the bands corresponding to the two chromophores in a single one and/or to the auxochromic effect of the two iodo substituents. Apparently, in compound **3**$^+$ the 4-(biphenyl-4-yl)pyrylium band is red shifted and has overlapped with that of the 2,4-bis(4-iodophenyl)-pyrylium chromophore.

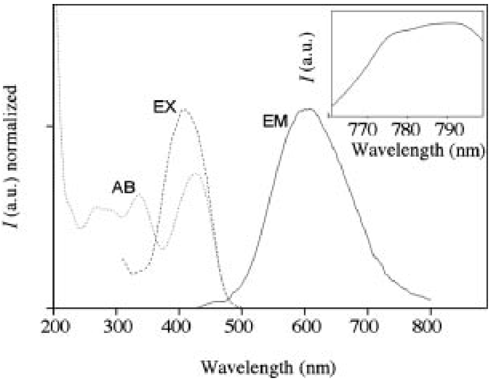
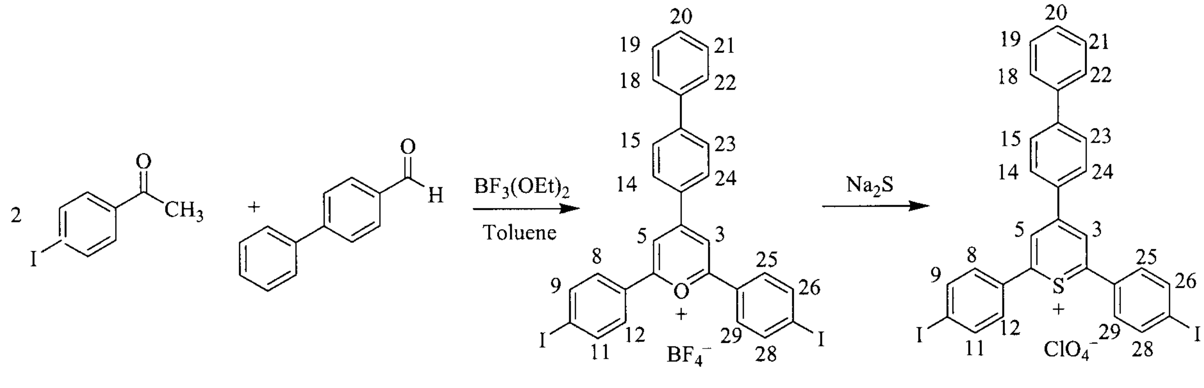


Figure 1. Absorption (AB), emission (λ_{exc} = 425 nm) (EM), and excitation (λ_{em} = 600 nm) (EX) spectra recorded for compound **3**$^+$ in acetonitrile (1×10^{-5} M). The inset shows the phosphorescence spectrum of compound **3**$^+$ recorded upon 355-nm laser excitation (1 mJ pulse^{-1}).

As expected, upon excitation at λ_{max} = 425 nm, compound **3** emits fluorescence [λ_{em} = 605 nm, Φ_{fl} = 0.1 (TP$^+$ has been used as standard Φ_{fl} = 0.52)]. The excitation spectrum of this emission corresponds to that of the ground state absorption. Figure 1 also shows the corresponding fluorescence and excitation spectra. The $E_{0,0}$ of the singlet excited state was estimated as 59 kcal mol^{-1} from the wavelength corresponding to the crossing of the absorption and



3$^+$ **4**$^+$

Scheme 1.

emission spectra. The fluorescence lifetime (τ_s = 0.85 ns) was obtained by fitting the emission decay to a first order kinetics and a deconvolution procedure was used to differentiate the fluorescence decay from the lamp profile.

All of the above experimental data indicate that although observation of the fluorescence spectrum of pyrylium $\mathbf{3}^+$ apparently suggests behavior similar to that of TP^+, there are remarkable quantitative differences between these two pyrylium ions in terms of the singlet lifetime and Φ_{fl}; both values are significantly smaller for pyrylium $\mathbf{3}^+$ than for TP^+ (τ = 2.9 ns, Φ_{fl} = 0.52). These differences can probably reflect: (1) the operation of a heavy atom effect of the iodo substituents favoring intersystem crossing to the triplet excited state, (2) an increase in the radiationless decay of the singlet excited state due to the higher conformational mobility introduced by the biphenyl unit, and/or (3) the occurrence of a photochemical reaction from the singlet state. Any combination of these processes will lead to a reduction of the singlet lifetime and fluorescence quantum yield of $\mathbf{3}^+$.

In fact, the triplet excited state was easily detected by laser flash coupled with time-resolved optical spectroscopy. The transient absorption spectrum of pyrylium $\mathbf{3}^+$ upon 355-nm laser excitation shows a negative signal corresponding to the bleaching of the ground state (λ_{max} = 425 nm) and an absorption band at 700 nm decaying with a lifetime of 5 µs. Figure 2 shows the actual transient spectrum recorded 1 µs after laser excitation of $\mathbf{3}^+$. The temporal profile on the µs time scale of the triplet signal monitored at λ_{T-T} = 700 nm is also shown in Figure 2. The triplet excited state of $\mathbf{3}^+$ is shorter-lived than that of TP^+ (τ_T = 10 µs).

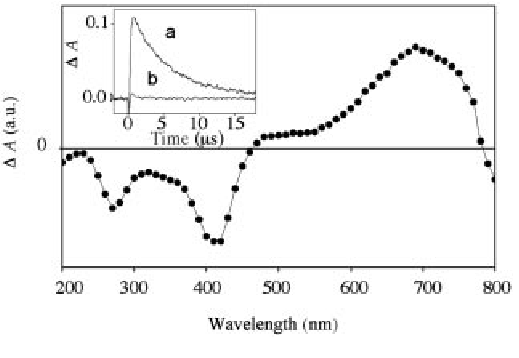


Figure 2. Transient absorption spectrum of an acetonitrile solution of compound $\mathbf{3}^+$ (2.5×10^{-5} M) recorded 1 µs after 355-nm laser excitation (20 mJ pulse^{-1}, 10 ns pulse width) under a N_2 atmosphere. The inset shows the temporal profiles for the signal monitored at 700 nm under a N_2 (a) and an air (b) atmosphere.

Observation of complete quenching of this transient by oxygen indicates that this 700-nm band corresponds to the T–T absorption band of the triplet excited state of $\mathbf{3}^+$. Considering that pyrylium is a strong electron acceptor in its singlet and triplet excited states and that biphenyl can act as an electron donor, one possibility that was envisioned but disregarded was that the transient spectrum corresponded to a charge-separated state. If this were the case, the charge-separated state would be generated mainly from the singlet that is only marginally quenched by oxygen. On the other hand, radical ions are fairly insensitive to the presence of oxygen. Thus, the complete disappearance of the transient when oxygen is present is conclusive evidence of its triplet nature and not of charge separation.

The quantum yield of triplet formation of $\mathbf{3}^+$ was determined to be $\Phi_{triplet}$ = 0.13 by using a solution of TP^+ ($\Phi_{triplet}$ = 0.48) as reference. This quantum yield of intersystem crossing was unexpectedly low considering the value of intersystem crossing reported for TP^+ and the role of iodo substituents. These low Φ_{fl} and $\Phi_{triplet}$ values can be due either to the operation of an important radiationless relaxation pathway from the singlet state or the occurrence of a photochemical reaction from the singlet excited state. Decay of the triplet excited state was accompanied with concomitant recovery of the ground state absorption with the same kinetics. This indicates that the triplet excited state of $\mathbf{3}^+$ decays mainly to the ground state without undergoing any photochemical reaction.

The triplet excited state emits weak phosphorescence in the red part of the optical spectrum at room temperature. The phosphorescence spectrum of pyrylium $\mathbf{3}^+$ is also shown in the inset of Figure 1. λ_{phos} was measured to be 780 nm, although we noticed that this apparent maximum could only be due to the reduced response of our photomultiplier in the infrared region. On the basis of the onset of this emission, the energy of the triplet excited state for $\mathbf{3}^+$ was estimated as 39 kcal mol^{-1}. Room-temperature phosphorescence has a quantum yield too low to be determined with some accuracy ($\Phi_{phos} \approx 0$).

The reduction potential of the singlet and triplet excited states of pyrylium $\mathbf{3}^+$ was estimated by determining by cyclic voltammetry the reduction potential of compound $\mathbf{3}^+$ (E_{red} = –0.21 V vs. SCE) in the ground state and applying the Rehm-Weller equation. According to this, the reduction potentials are –2.3 and –1.4 V for the singlet and triplet excited states of $\mathbf{3}^+$, respectively. The value for the reduction potential from the singlet state is similar to that reported for TP^+, indicating that this reduction potential is mainly governed by the pyrylium core and that substitution of phenyl by iodo in the periphery of the heterocyclic ring has only a marginal effect on the localization of the abstracted electron. We notice, however, that because of the low triplet energy, the reduction potential of $\mathbf{3}^+$ is significantly lower than that of TP^+.

Fluorescence and laser flash photolysis demonstrate that singlet and triplet excited states of $\mathbf{3}^+$ can be quenched by typical electron donors such as tertiary amines and bromides. The bimolecular quenching rate constants for the quenching of the triplet excited state of $\mathbf{3}^+$ by triethanolamine (TEOA) ($k_q = 8.9\times10^9$ M^{-1} s^{-1}) and tetrabutylammonium bromide (TBAB) ($k_{q1} = 3.4\times10^{10}$ M^{-1} s^{-1}), calculated from the kinetic data obtained for concentrations lower than 1×10^{-5} M, have been calculated. This quenching process gives rise to a new transient species attributable to the corresponding pyrylium radical $\mathbf{3}^{\cdot}$. Figure 3 shows the optical spectrum (λ_{max} = 400 nm) and the temporal profile of $\mathbf{3}^{\cdot}$ (τ = 4.2 µs). Detection of $\mathbf{3}^{\cdot}$, together with the calculated singlet oxidation potential, shows that **3**$^+$ is also a powerful PET photosensitizer.

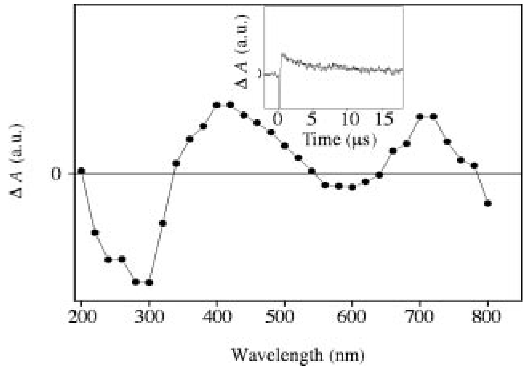
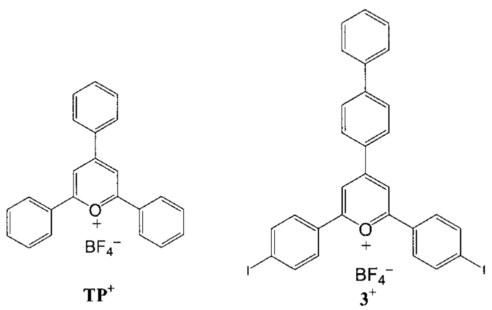


Figure 3. Transient absorption spectrum of an acetonitrile solution of compound **3** (2.5×10^{-5} M) after the addition of triethanolamine (2.5×10^{-4} M) recorded 1.3 µs after 355-nm laser excitation. The inset shows the decay monitored at 440 nm.

The occurrence of a photochemical reaction from the singlet excited state of **3**$^+$ in acetonitrile was determined by monitoring the decrease of the long-wavelength absorption band at 425 nm upon steady state irradiation. Φ_{reaction} was found to be 0.47. 1,3,5-Triaryl-2-penten-1,5-dione arising from the photochemical hydrolytic ring aperture was observed as one reaction product due to the traces of water present in the acetonitrile solvent. This photochemical behavior is analogous to that observed for parent TP$^+$ that undergoes photohydrolysis in the presence of water.

With these Φ values, the quantum yield for internal conversion from the singlet excited state of **3**$^+$ to its ground state can be estimated to be the difference from unity, which is 0.3. Figure 4 provides a summary of the photophysical and photochemical parameters of **3**$^+$ compared to those of TP$^+$. Taking into account all of the data, the reduced ISC efficiency of **3**$^+$ might also be related to the larger singlet-triplet energy gap (20 kcal mol^{-1}) relative to TP$^+$ (12 kcal mol^{-1}).



TP$^+$

$E_S = 65$ kcal/mol
$E_T = 53$ kcal/mol
$\tau_S = 2.9$ ns
$\tau_T = 10$ µs
$\Phi_{fl} = 0.52$ (465 nm)
$\Phi_{ISC} = 0.48$

3$^+$

$E_S = 59$ kcal/mol
$E_T = 39$ kcal/mol
$\tau_S = 0.85$ ns
$\tau_T = 5$ µs
$\Phi_{fl} = 0.1$ (605 nm)
$\Phi_{triplet} = 0.13$

Figure 4. Summary of the photophysical and photochemical parameters of **3**$^+$ compared to those of TP$^+$.

It was anticipated that the low reduction potential of this derivative and the ease of triplet formation could make possible the observation of electroluminescence in this compound. We have performed a preliminary test of the electroluminescence activity by constructing an OLED cell by using a transparent indium-tin oxide (ITO) conductive electrode as anode, a submicrometric layer of compound **3**$^+$ as emitter, and an aluminum plate as cathode. Even with this unoptimized cell, we have been able to detect electroluminescence upon connecting the cell to 5 V DC.

Conclusion

By appropriate substitution on the aryl rings with iodo and biphenyl moieties, a new 2,4,6-triarylpyrylium ion has been designed and synthesized. Compound **3**$^+$ shares common features with its parent TP$^+$, such as a strong oxidation potential from the singlet state, and it can be used as a PET photosensitizer, but the photophysical constants are significantly influenced by substitution. Thus, **3**$^+$ exhibits lower Φ_{fl} and Φ_{triplet}, shorter τ_s and undergoes efficient photohydrolysis. Preliminary tests of compound **3**$^+$ as a photoinitiator have shown encouraging results for polymerization of styrene-based oligomers. An electroluminescent cell has been constructed with this pyrylium ion.

Experimental Section

Synthesis of 3$^+$: To a solution of 4-phenylbenzaldehyde (0.35 g, 1.9 mmol) in toluene (4 mL), 4-iodoacetophenone (1.04 g, 4.2 mmol) and boron trifluoride (0.6 mL, 4.2 mmol) were sequentially added. The mixture was stirred at 90 °C for 24 h under an argon atmosphere. The solvent was then evaporated under vacuum, and the dark orange solid was purified by washing with ether until the extracts were completely free of starting materials. Compound **3**$^+$ (0.42 g, 30%) was obtained as an orange solid. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 7.60 (d, $J_{H,H}$ = 7.2 Hz, 3 H, 19-H, 21-H, 20-H), 7.88 (d, $J_{H,H}$ = 6.9 Hz, 2 H, 18-H, 22-H), 8.14 (d, $J_{H,H}$ = 8.7 Hz, 2 H, 15-H, 23-H), 8.25 (dd, $J_{H,H}$ = 2.4 and 8.7 Hz, 4 H, 8-H, 12-H, 25-H, 29-H), 8.45 (dd, $J_{H,H}$ = 2.7 and 8.7 Hz, 4 H, 9-H, 11-H, 26-H, 28-H), 8.73 (d, $J_{H,H}$ = 8.4 Hz, 2 H, 14-H, 24-H), 9.35 (s, 2 H, 5-H, 3-H) ppm. ^{13}C NMR (300 MHz, CD$_3$–CO–CD$_3$): δ = 126.7, 127.4, 128.7, 129.4, 130.2, 138.8, 154.4 ppm. IR (liquid film): $\tilde{\nu}$ = 1623 cm^{-1}. UV (acetone solution): $\lambda_{\max}$ = 425 nm (ε = 31200 mol^{-1} L cm^{-1}). $C_{29}H_{19}OI_2 \cdot BF_4 \cdot (H_2O)_2$ (723.61): calcd. C 45.82, H 3.05; found C 45.34, H 2.80.

Synthesis of 4$^+$: Na$_2$S·9H$_2$O (5.9 g, 2.8 mmol) dissolved in water (10 mL) was slowly added to a solution of **3**$^+$ (2.0 g, 2.8 mmol) in acetone (30 mL). After stirring for 5 h at room temperature, the solution was cooled to 0 °C, and HClO$_4$ (10% in water) was cautiously added. The mixture was stirred at 0–5 °C for 3 h. The resulting dark-orange solid (0.11 g, 5%) was filtered under reduced pressure and purified by washing with ether. Sulfur exchange was confirmed by IR and UV/Vis spectroscopy. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 7.60 (m, 3 H,19-H, 21-H, 20-H), 7.87 (d, $J_{H,H}$ = 7.8 Hz, 2 H, 18-H, 22-H), 8.10 (d, $J_{H,H}$ = 8.7 Hz, 2 H, 15-H, 23-H), 8.14 (dd, $J_{H,H}$ = 1.5 and 8.7 Hz, 4 H, 8-H, 12-H, 25-H, 29-H), 8.24 (dd, $J_{H,H}$ = 1.5 and 8.7 Hz, 4 H, 9-H, 11-H, 26-H, 28-H), 8.60 (d, $J_{H,H}$ = 8.7 Hz, 2 H, 14-H, 24-H), 9.51 (s, 2 H, 5-H, 3-H) ppm. ^{13}C NMR (300 MHz, [D$_6$]acetone): δ = 126.6, 127.7, 128.2, 129.7, 130.2, 139.0, 142.1 ppm. IR (liquid film): $\tilde{\nu}_{\max}$ = 1592 cm^{-1}. UV (acetone solution) λ_{max} = 450 nm. $C_{29}H_{19}SI_2{\cdot}ClO_4{\cdot}2H_2O$ (752.26): calcd. C 44.87, H 2.99, S 4.13; found C 43.33, H 2.49, S 4.01.

Photophysical Measurements: All the measurements were carried out at room temperature. UV/Vis absorption spectra were recorded with a Perkin–Elmer λ35 spectrophotometer. Fluorescence spectra and lifetimes were recorded with an Edinburgh Analytical Instruments FL900 spectrophotometer. Laser flash photolysis experiments were carried out in a Luzchem ns laser flash system using the third (355 nm, 20 mJ/pulse) harmonic of a Surelite Nd:YAG laser for excitation (pulse $\leq$10 ns) and a 175 W ceramic Xenon (Cermax) lamp, perpendicular to the laser beam, as a probing light. Two fiber optics (Fiberoptic Lightsource) were used to probe the sample and collect the absorption data. The signal from the monochromator/photomultiplier detection system was captured by a Tektronix TDS 3032B digitizer. Laser system and digitizer are connected to a PC through GPIB and serial interfaces that controlled all the experimental parameters and provided suitable processing and data storage capabilities. The software package has been developed in the LabVIEW environment from National Instruments and compiled as a stand-alone application. Fundamentals[13] and details[14] of similar time-resolved laser setups has been published elsewhere. The samples contained in a Suprasil quartz 0.7 × 0.7 cuvette were capped with a septum and purged with N_2 for at least 15min before laser experiments. Steady state irradiation was carried out with the pulsed 355-nm laser light.

Preparation of Electroluminescent Cells: Before preparation of the cell, ITO glass was cleaned by ultrasonic irradiation in an acetone bath. The aluminum counter electrode was also polished before use. Compound **3**$^+$ was spin coated on the ITO from a chloroform solution at 500 rpm. After solvent evaporation in the open atmosphere, a double-sided adhesive tape was used to hold the two electrodes in place in order to avoid short-circuit.

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