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Excited States of Bromine-Substituted Distyrylbenzenes: Models for Conjugated Polymer Emission

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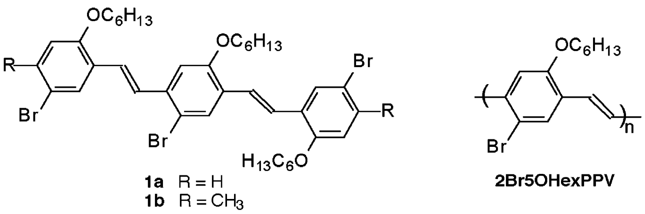
Model 1,4-bis(styryl)benzene derivatives **1a**,**b** related to poly(2-bromo-5-methoxy-1,4-phenylenevinylene) were synthesized to probe the effect of bromination on excited-state behavior of conjugated phenylenevinylene analogues. They showed solution absorption maxima at about 385 nm, without evidence of excimer formation up to 100 μM. Their fluorescence spectra showed overlapping bands at 435 and 460 nm, with quantum yields in tetrahydrofuran of 0.16 and 0.21 for **1a** and **1b**, respectively. Excited-state transients were monitored by time-resolved laser flash spectroscopy at room temperature. The triplet states were characterized by absorption maxima at about 520−530 nm with lifetimes of about 0.6 μs, much longer than would be observed for prompt fluorescence states. The quantum yields of singlet to triplet-state intersystem crossing were determined to be 0.45 and 0.28 for **1a** and **1b**, respectively. The acceleration of triplet transient decay rates under increased oxygen pressure according to the Stern−Volmer law further supports the triplet-state assignments. The relatively high yields of intersystem crossing and low yields of fluorescence are attributed to a bromine-modulated heavy atom effect that enhances intersystem crossing between excited singlet and triplet states.

Introduction

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have been intensely studied due to their potential use in technology employing organic light-emitting diodes (OLEDs).[1] Despite much recent progress in the fabrication of OLEDs, the nature of the photoexcited states and the efficiency of their generation is still not entirely clear. Photoluminescence, especially prompt fluorescence, is known to originate from the radiative decay of singlet polaronic excitons, whereas photogenerated triplet excitons in PPVs yield long-lived photoinduced optical absorptions.[2] Direct emission from triplet excitons (phosphorescence) in PPVs and related model compounds has apparently not been observed, although the presence of such excitons has been deduced by use of transient absorption,[2] photon photoelectron spectroscopy,[3] optically detected magnetic resonance,[4] and pulse-radiolysis experiments.[5] The triplet states in PPV-based OLEDs are particularly interesting, because statistically one expects three triplet microstates per singlet exciton to be generated by excitation.[6] Thus, we aimed to investigate heavy atom substitution effects on triplet-state spectroscopy of PPV oligomers.

Short chain model compounds are suitable to benchmark the PPV photophysical process in solution. The quenching of excitons in trapping sites is limited in model systems due to their finite size, easily achieved chemical purity, and the low degree of structural disorder. Furthermore, excimer formation by interchain interactions, which is common in conjugated systems,[7] should be less efficient in model oligo(phenylenevinylenes) in solution than in higher polymers.

CHART 1



1a R = H
1b R = CH_3

2Br5OHexPPV

We synthesized model compounds **1a**,**b** analogous to previously described[8] polymer **2Br5OHexPPV**, which has a push−pull pattern of hexyloxy and bromine substituent on the aryl moiety (Chart 1). Most oligomeric PPV models studied previously have only electron donor[9] ring substitution or vinylic substitution by electron-withdrawing cyano groups.[10] The presence of the bromine atom could, in principle, increase the triplet populations in photoexcited **1a**,**b** by intersystem crossing due to a heavy atom effect. We hoped, therefore, to see effects of the bromine substitution upon the optical spectroscopy. Here we describe excited-state photophysical studies of these two model compounds.

Experimental Section

Synthesis. The syntheses of **1a**,**b** are shown in Scheme 1; synthetic details for **2**−**4** are given in the Supporting Information. Horner-Emmons condensation between phosphonate ester **4** and aldehydes **2a**,**b** in the high-boiling solvent dimethoxyethane gave trans configured **1a** and **1b**. The trans configuration was confirmed by the coupling constants of the vinylic protons, $J = >16$ Hz in the ^{1}H NMR. No evidence for the cis isomer was observed by ^{1}H NMR after recrystallization.

Spectroscopy. Absorption spectra were recorded using JASCO, Ubest-55, or Shimazu UV-1600 spectrophotometers.

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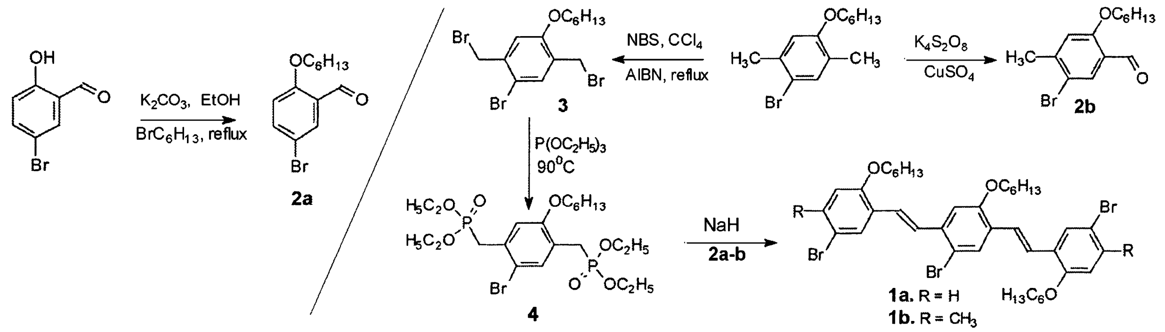
SCHEME 1



Fluorescence spectra were recorded with the correction of the wavelength-dependent instrument responses using a Hitachi F-4000 spectrofluorometer. The Φ_f values were measured relative to 9,10-diphenylanthracene in cyclohexane as external standard,[11] with correction for the refractive indices of the solvents. For all the fluorescence measurements, the optical density of the solutions were kept at OD ~ 0.2 at the excitation wavelength.

All transient absorption spectra were obtained using a kinetic spectrophotometric detection system previously described.[12] For these measurements, either 308 nm excitation pulses from an XeCl excimer laser (Lambda Physik LPX-100) or 425 nm pulses from a dye laser (Lambda Physik FL-3002; fwhm 10 ns) pumped by the 308 nm excimer laser were used. Laser energies employed were less than 10 mJ. The monitoring light was oriented perpendicular to the exciting laser beam, passed through a grating monochromator (JASCO CT-25C), and detected with a photomultiplier (Hamamatsu Photonix R928) and a storage oscilloscope (Iwatsu TS-8123). The system was computer controlled and the data analyzed using a NEC PC-9801vm Intel-chip personal computer.

Determination of Bimolecular Rate Constants for Reaction With Oxygen. Compounds **1a** and **1b** were excited at 308 nm at room temperature and their absorption decay curves monitored at 530 nm. Excited-state lifetimes were determined at various oxygen concentrations (calculated from the measured pressure). The eq $1/\tau = 1/\tau_0 + k_q[Q]$ was used to calculate the rate constants, where τ is the observed lifetime, τ_0 is the lifetime in the absence of oxygen (argon degassed), k_q is a bimolecular rate constant, and [Q] is the concentration of oxygen. The rate of decay was plotted against oxygen concentration at room temperature to yield the oxygen-quenching rate from the slope.

Results and Discussion

Steady-State Spectroscopy. The absorption spectrum of **1a** in THF (10 μM) shows intense absorption with a maximum at 385 nm [$\epsilon = 46\,000$ dm^3/(mol cm)] assigned to the $^1\pi \rightarrow {}^1\pi^*$ transition (Figure 1). The shape and width of this band remains constant over a wide range of concentrations (from 10 to 100 μM). The absence of broadening at high concentrations suggests a minimal contribution from ground-state aggregates. The lack of additional peaks at higher concentrations shows that excimers are not formed to a significant extent.

A typical fluorescence spectrum of **1a** excited at 355 nm in room-temperature tetrahydrofuran (THF, Figure 1) shows well-resolved peaks at 435 and 460 nm, the relative shapes of which remain constant over a range of concentration with no increase in low-energy emission. Fluorescence excitation spectra monitored at 435 and 460 nm appeared the same, and overlapped the absorption spectrum (see supporting material). The analogous spectra for **1b** in THF are very similar to those of **1a** under the same conditions. Therefore, we assign these fluorescence bands to the lowest excited singlet states of isolated **1a** and **1b**, corresponding to about 2.95 eV, or 285 kJ/mol above the ground state. The fluorescence quantum yields Φ_f for **1a** and **1b** were found to be 0.16 and 0.21, respectively. These were independent of excitation wavelength throughout the absorption bands, consistent with the presumption of only one emitting conformation in solution.

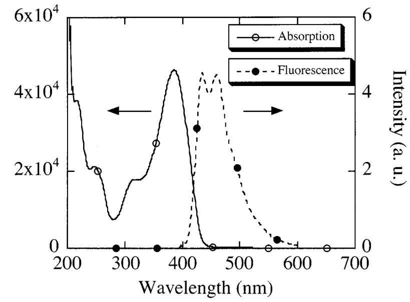


Figure 1. UV−vis absorption and fluorescence spectra of **1a** in THF (1×10^{-5} M).

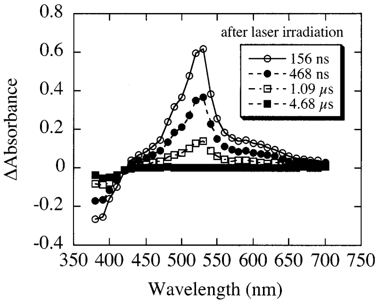


Figure 2. Triplet−triplet absorption spectra of **1a** in THF (1.1×10^{-5} M).

Triplet-State Solution Absorption Spectroscopy. The 308 nm laser excitation of **1a** in oxygen-free THF (1.10×10^{-5} M) at room temperature led to the formation of a very strong transient absorption spectra with a maximum at 530 nm (Figure 2). The transient lifetime is 0.64 μs under our experimental conditions with decayed by first-order kinetics ($k_T = 1.4 \times 10^6$ s^{-1}). Transient absorption spectra of 12.0 μM **1b** in THF under the same conditions also shows a band maximum at 530 nm (Figure 3). The transient spectrum decayed within a few nanoseconds in oxygen-saturated solutions (Figure 4). The behavior of the transient generated from **1b** is quite similar under the same conditions, with $k_T = 1.2 \times 10^6$ s^{-1} (Figure 5). The clean exponential decay observed in the oxygen-free experiments suggests that triplet−triplet bimolecular annihilation[13] is negligible under these conditions. The transients were assigned to triplet excited states of **1a** and **1b**, based on their long lifetimes

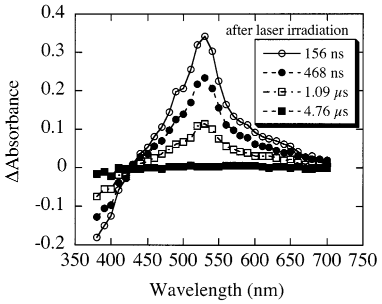


Figure 3. Triplet−triplet absorption spectra of **1b** in THF (1.2 × 10^{-5} M).

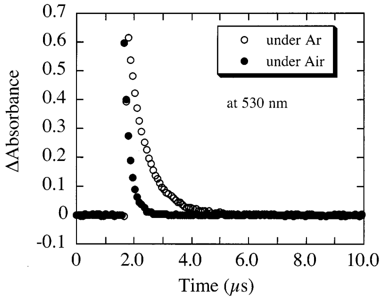


Figure 4. Kinetic profiles for triplet spectral absorption of **1a** at 530 nm in THF at room temperature.

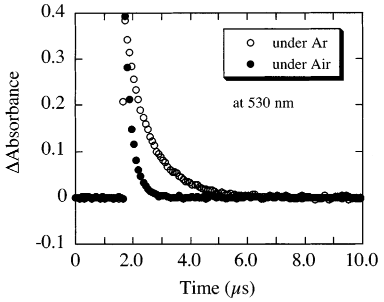


Figure 5. Kinetic profiles for triplet spectral absorption of **1b** at 530 nm in THF at room temperature.

TABLE 1: Photophysical Properties of 1a,b in Excited Triplet States[a]

properties	**1a**	**1b**
λ_{max}^T (nm)	530	530
ϵ_T (M^{-1} cm^{-1})	8200	11000
τ_T (μs)	0.64	0.50
k_T (s^{-1})	1.4×10^6	1.2×10^6
k_{O2} (M^{-1} s^{-1})	1.5×10^9	1.3×10^9
k_{et} (M^{-1} s^{-1})	1.3×10^{10}	1.1×10^{10}
Φ_{isc}	0.45	0.28

[a] λ_{max} = absorption maximum, ϵ = molar absorptivity estimated by the method of ref 17, "et" = energy transfer to benzil, "isc" = intersystem crossing.

and quenching by oxygen. After laser excitation, the solution of **1a**, displayed a good UV−vis spectral match with the original solution. Apparently, little or no chemical change occurs upon laser photoexcitation.

The rate of triplet quenching by oxygen was estimated by a Stern−Volmer plot of observed rates of transient spectral decay as a function of oxygen pressure over THF at room temperature. The transient decay rates were linearly dependent on the oxygen concentration, consistent with bimolecular quenching. The quenching rate constants, k_{O_2}, were found to be 1.5×10^9 and 1.3×10^9 M^{-1} s^{-1} for **1a** and **1b**, respectively. Quenching rates on the order of 10^9 M^{-1} s^{-1} are consistent with triplet-state quenching rates previously determined for *p*-phenylenevinylene oligomers[5a] and polymers.[14,15] The kinetic results of the quenching experiments are included in Table 1, together with summaries of the photophysical studies described above. Overall, all of these transient absorption spectra were assigned to triplet-state transitions of **1a**,**b**, based on their long lifetimes and quenching behavior with oxygen.

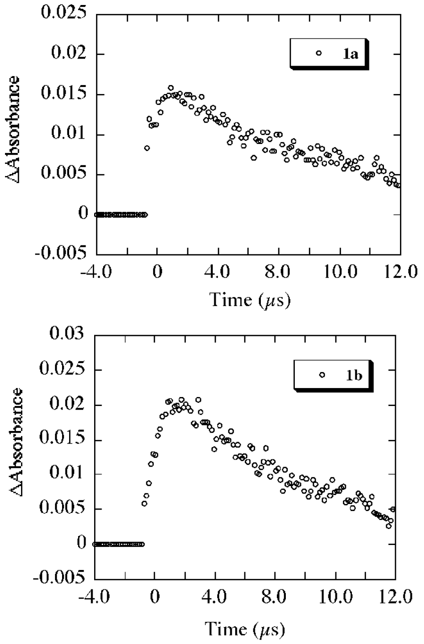


Figure 6. Buildup profiles for triplet absorption from irradiation of **1a** and **1b** in THF in the presence of benzil. See also Supporting Information for further details.

Photosensitized Triplet Formation in Solution. Triplet−triplet energy transfer is one route to generate triplet states of organic molecules. We found that we could produce the triplet states of **1** both directly and by photosensitization. Upon excitation at 308 nm, an argon-saturated 0.01−0.02 M solution of benzil in THF gave a triplet−triplet absorption at 480 nm.[16] When either **1a** or **1b** was added to a concentration of 0.01 mM, the benzil triplet absorption band at 480 nm decayed with concomitant formation of a new absorption band at about 530 nm. Figure 6 shows the buildup curve at 530 nm of the triplet absorption of **1a**,**b** in an argon saturated benzil solution (THF). These findings demonstrate triplet−triplet energy transfer from the excited triplet state of benzil to ground state **1a**,**b**, followed by formation of excited triplet state **1a**,**b**. Benzil thus is an effective triplet photosensitizer for **1a**,**b**.

The observed rate of triplet buildup was linearly dependent on the **1a**,**b** concentrations. With increasing concentration of **1a**,**b**, a corresponding increase in the amount of excited triplet state **1a**,**b** was observed. The energy transfer rate constants (k_{et}) were calculated by a Stern−Volmer plot in the same manner as described for the quenching experiments and found to be 1.3×10^{10} and 1.1×10^{10} M^{-1} s^{-1} for **1a** and **1b**, respectively. The molar extinction coefficients (ϵ_T) for the triplet spectra were estimated relative to the reported ϵ_T value of triplet benzil as a standard.[17] The ϵ_T values for **1a** and **1b** at 530 nm in THF were 8200 and 11 000 M^{-1} cm^{-1}, respectively. Given that the transients in Figures 4−6 show different rates of decay upon sensitization than upon direct excitation, it appears that the net observed behavior involves some equilibration between the triplet states of benzil and **1a**,**b**.

Quantum Yield of Intersystem Crossing. The quantum yields of intersystem crossing (Φ_{isc}) for **1a**,**b** were determined by the triplet−triplet energy transfer method using benzil as photosensitizer. By comparing the spectral intensity of **1a** or **1b** triplets formed in each experiment, it is possible to determine the triplet quantum yields relative to anthracene as a standard ($\Phi_{isc} = 0.66$) by the following[17] equation

$$\Phi_{ics} = \frac{OD \times OD_{std(s)} \times A_{std}}{OD_{std} \times OD_{(s)} \times A}\Phi_{ics(std)}$$

where $OD_{(s)}$ and OD are the respective maximal intensity of triplet absorption of **1a** or **1b** (at 530 nm) with and without sensitization by benzil. Similarly, $OD_{std(s)}$ and OD_{std} are the maximal optical intensity of anthracene triplet absorption (at 430 nm) with and without benzil, respectively. A and A_{std} are the ground-state absorption intensities at 308 nm of **1a** or **1b** and anthracene, respectively. The transient absorption spectra of **1a** or **1b** and anthracene in THF (at 10 μM) were measured with excitation at 308 nm. The same measurements using benzil as sensitizer were recorded with excitation at 425 nm. Only benzil solutions of absorption intensity ~1.0 at 425 nm were used throughout the experiments. Using the equation above, the yields of triplet formation via intersystem crossing (Φ_{isc}) were determined to be 0.45 and 0.28 for **1a** and **1b**, respectively.

Overall Considerations. The quantum yield of singlet-state radiative deactivation for **1a** and **1b** is low by comparison to analogues without bromine atom substitution.[18] The presence of the three bromine atoms strongly promotes radiative deactivation of singlets by intersystem crossing (ISC) into triplet manifolds. Indeed, the quantum yields of ISC for **1a**,**b** are high enough (Table 1) to be competitive with fluorescence. Efficient ISC results in higher population of the triplet states, and increased intensity of triplet manifold electronic spectroscopy. The 640 ns lifetime of triplet **1a** (Figure 2) is much longer than would be expected for singlet-state transients. Excited singlet states of less substituted phenylenevinylene derivatives exhibit prompt fluorescence with very short lifetimes ($\tau > 2$ ns), by comparison to typical triplet-state lifetimes on the order of a hundred nanoseconds to several microseconds.[19] The triplet-state absorption maxima of **1a**,**b** at 520−530 nm are similar to bands observed by laser flash photolysis for other distyrylbenzene derivatives in dilute solution.[19] In addition, the putative triplet bands of **1a**−**b** are efficiently quenched with molecular oxygen, reflecting the expected bimolecular energy transfer from triplet states to triplet oxygen. Excited-state phenylenevinylenes are known to generate singlet oxygen as a result of bimolecular quenching by triplet molecular oxygen.[14] Recently, the generation of singlet oxygen was observed from distyrylbenzene with symmetrical bromine substitution on the central aromatic ring.[20] Thus, available data very strongly support the generation of triplet states in **1a**,**b**.

We attempted to observe a direct phosphorescent state in **1a** in frozen EPA glass (ether:isopentane:ethanol = 5:5:2) at 77 K, exciting at 355 nm (Xe lamp) and employing a 100 ns time delay between excitation and detection to avoids interference of prompt fluorescence from the lowest excited singlet states. We observed a band centered around 485 nm (2.56 eV, 247 kJ/mol above ground state), with a lifetime of 39 ms, and first-order kinetic decay ($k = 26$ s^{-1}). However, the excitation spectrum associated with this emission did not match the absorption spectrum of **1a**, but was substantially blue-shifted (see Supporting Information). As a result, we felt we could not confidently assign this spectrum to direct phosphorescence from **1a**. Spin forbidden excited triplet-state emission to the ground state in conjugated polymers is very difficult to measure directly, so our difficulties in observing 77 K phosphorescence for **1a** are not unique.[21]

The relative energies of the singlet and triplet excited states in **1a**,**b** will affect their intersystem crossing rates.[22] Because the S_1-T_1 gap depends on the oligomer chain length,[23] results for **1a** cannot readily be inferred from organic conjugated high molecular weight polymers. For example, the S_1-T_1 gap for a ladder type poly(*p*-phenylene) and an analogous oligomer was found to be 0.62 eV from phosphorescence emission,[18] and an estimate of 0.6−0.7 eV for an infinite PPV chain has also been made.[24] Often, nonradiative decay processes in conjugated oligomers and polymers dominate over phosphorescence due to the long radiative lifetime of the latter process. The various decay processes not only are affected by the S_1-T_1 energy gap but may also be affected by the substituents on the chromophores.[25] Our results are consistent with this, in showing a strong heavy atom effect. The yields of fluorescent radiative decay in **1a**,**b** are low, indicating the importance of nonradiative deactivation pathways. Overall, the present studies demonstrate singlet excited-state deactivation in bromine-substituted luminescent molecules, and enhanced crossover between triplet and singlet excited-state manifolds by substitution on the emitting chromophore.

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Supporting Information Available: Synthetic procedures and characterization data for **1a**,**b** and intermediates in Scheme 1, transient decay curves at 530 nm for calculation of energy transfer from the triplet state of benzil to **1a** or **1b**, fluorescence excitation spectra of **1a** at room temperature, 77 K emission spectrum from irradiation of **1a** in EPA glass. This information is freely available for download from the Internet at http://pubs.acs.org.

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