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Singlet and Triplet Excited-State Interactions and Photochemical Reactivity of Phenyleneethynylene Oligomers

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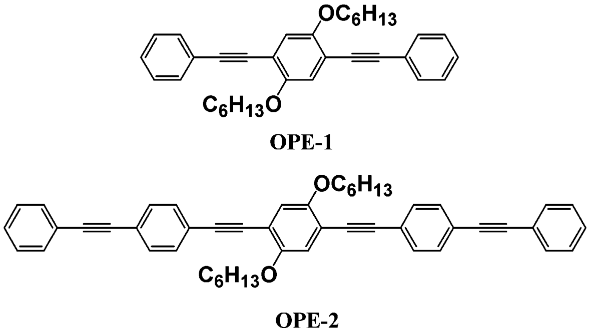
The rigid rodlike character of phenyleneethynylenes and their ability to communicate charge/excitation energy over long distances have made them useful as molecular linkers in the light energy harvesting assemblies and molecular electronics devices. These linker molecules themselves possess rich photochemistry as evident from the relatively large yields of the excited singlet (0.5−0.66) and triplet (0.4−0.5) states of two model oligomers, 1,4-bis(phenylethynyl)-2,5-bis(hexyloxy)benzene (**OPE-1**) and 1,4-bis((4-phenylethynyl)phenylethynyl)-2,5-bis(hexyloxy)benzene (**OPE-2**). In particular, the long-lived triplet excited state is capable of undergoing deactivation by self-quenching processes such as ground-state quenching and triplet−triplet (T−T) annihilation. The T−T annihilation occurs with a nearly diffusion-controlled rate ($\sim 2 \times 10^9$ M^{-1} s^{-1}), and ground-state quenching occurs with a rate constant of $\sim 6 \times 10^7$ M^{-1} s^{-1}. The electron transfer from the excited **OPE-1** and **OPE-2** to benzoquinone as characterized from the transient absorption spectroscopy illustrates the ability of these molecules to shuttle the electrons to acceptor moieties. In addition, pulse radiolysis experiments confirm the spectroscopic fingerprint of the cation radical (or "trapped hole") with absorption bands in the 500−600 nm region.

Introduction

Oligo(*p*-phenyleneethynylene)s have emerged as molecular building blocks for the design and fabrication of optoelectronic systems such as organic light emitting diodes,[1−3] solar energy conversion systems,[4−8] and chemical/biological sensors.[9−15] The rigid rodlike character of phenyleneethynylenes and their ability to communicate charge/excitation energy over long distances provide unique characteristics to design a new class of molecular systems.[4,16−20] Of particular interest are molecular electronics devices. A few prototype systems were fabricated by incorporating molecular rigid rods in semiconductor/metal hybrid systems. These include (i) single-molecule diodes by immobilizing them between both electrodes by sulfur−gold bonds,[21] (ii) nanocell electronic memories,[22] (iii) voltage-triggered conductance switching,[23−25] and (iv) photovoltaic systems by functionalization of redox/photoactive molecules on to semiconductor surfaces.[4−8] Recently Galoppini and co-workers[4−8] have investigated, in detail, the dynamics of the electron injection from excited Ru^{II}-polypyridine sensitizers to TiO$_2$ semiconductor through phenyleneethynylene bridging units. These studies suggest that the charge injection occurs over a long distance of 2.4 nm. The electronic coupling between Ru^{II}-polypyridine and the phenyleneethynylene bridging unit is quite strong and thus assists in the fast electron injection into semiconductor nanoparticles.[4] Electrochemical studies have confirmed that phenyleneethynylene bridge structures promote strong coupling between gold electrode and ferrocene, thereby promoting rapid electron transport over long distances.[16,26]

CHART 1: 1,4-Bis(phenylethynyl)-2,5-bis(hexyloxy)benzene (OPE-1) and 1,4-Bis((4-phenylethynyl)phenylethynyl)-2,5-bis(hexyloxy)benzene (OPE-2)



OPE-1

OPE-2

Although the potential applications of this class of molecules in various devices have been demonstrated, a detailed understanding of the excited-state behavior is yet to be established. Most of the physical studies published to date deal with aggregation induced emission changes.[10,13,27,28] The photophysical properties of oligomers based on the aryleneethynylene architecture, with a 2,2′-bipyridine-5,5′-diyl (bpy) metal binding unit, was reported by Schanze and co-workers.[29] The excited-state characterization indicated a composite behavior of two excited-state manifolds. Charge transfer through terthiophene end-capped poly(arylene ethynelene)s has been studied by characterizing the behavior of cations and anions in a pulse radiolysis experiment.[17] Characterization of the geometric and electronic properties of alkoxy-substituted derivatives of phenyleneethynylenes, in comparison with an unsubstituted system, (1,4-bis(phenylethynyl)benzene), was reported in an earlier paper.[30] These studies indicate that phenyleneethynylenes exist in planar and twisted conformations in their ground state due to the nearly free rotation of the arene rings along the molecular

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axis. On the other hand, these molecular rods attain a planar configuration in the excited state.

Based on the picosecond time-resolved studies, Beeby et al. concluded that 1,4-bis(phenylethynyl)benzene does not exhibit significant cumulenic/quinoidal character in its S_1 state.[31] Interestingly, recent time-resolved IR measurements indicate that an unpaired electron when conjugated in the phenyleneethynylene core is substantially delocalized over the π-system of the chromophore resulting in the formation of a partial cumulene-like structure.[32] Although there are several reports indicating that phenyleneethynylenes communicate charge as well as excitation energy over long distances, no major effort has been made to characterize the excited-state behavior and redox properties of this class of molecules. We report herein the behavior of excited singlet and triplet state as well as the redox properties of two model oligo(phenyleneethynylene)s possessing dialkoxy substitution, namely 1,4-bis(phenylethynyl)-2,5-bis(hexyloxy)benzene (**OPE-1**) and 1,4-bis((4-phenylethynyl)phenylethynyl)-2,5-bis(hexyloxy)benzene (**OPE-2**).

Experimental Section

Materials and Methods. Phenyleneethynylenes **OPE-1** and **OPE-2** were synthesized according to the published procedure.[33] Care was taken to purify these compounds using the recycling HPLC method.[30] It is difficult to separate the trace amounts of impurities present in these compounds using conventional column chromatographic or crystallization techniques. If not purified carefully these impurities interfere with the photophysical measurements. All solvents were spectrophotometric grade. 1-Pyrenecarboxaldehyde purchased from Aldrich was recrystallized before use. All experiments were performed at room temperature, and the solutions were deaerated by bubbling with nitrogen. Absorption spectra were recorded with a Shimadzu 3101 spectrophotometer. Emission spectra were recorded using an SLM 8000 photon counting spectrofluorimeter. Emission lifetimes were measured using Horiba Jobin Vyon single photon counting system, and the fluorescence decay measurements were further analyzed using the IBH software library. Pulse radiolysis experiments were performed with the 8-MeV Titan Beta model TBS-8/16-1S linear accelerator. Cyclic voltammetric experiments were carried out using a BAS 100B electrochemical analyzer. The measurements were carried out using a standard three-compartment cell consisting of a working electrode (glassy carbon), a reference electrode (saturated calomel electrode, SCE), and a counter electrode (Pt). All solutions were made in acetonitrile containing 0.05 M tetra-*n*-butylammonium perchlorate.

Laser Flash Photolysis. Nanosecond laser flash photolysis experiments were performed with a 355 nm laser pulse (5 mJ, pulse width 6 ns) from a quanta Ray Nd:YAG laser system. Femtosecond transient absorption experiments were conducted using a Clark-MXR 2010 laser system and an optical detection system provided by Ultrafast Systems (*Helios*). The source for the pump and probe pulses is the fundamental of the Clark laser system (775 nm, 1 mJ/pulse, fwhm = 150 fs, 1 kHz repetition rate). A second harmonic generator is introduced into the path of the laser beam to provide 387 nm (3.20 eV, 150 fs) laser pulses for the pump. The pump beam is attenuated to 5 μJ/pulse with a spot size of 2 mm (diameter) at the sample where it is merged with the white light incident on the sample cell with an angle <10°. After passing through the 2 mm cell, the probe is focused onto a 200 μm core fiber connected to a CCD spectrograph (Ocean Optics, S2000−UV−vis), enabling time-resolved spectra to be recorded (425−800 nm). Typically, 5000 excitation pulses are averaged to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths are assembled from the time-resolved data. All measurements were conducted at room temperature.

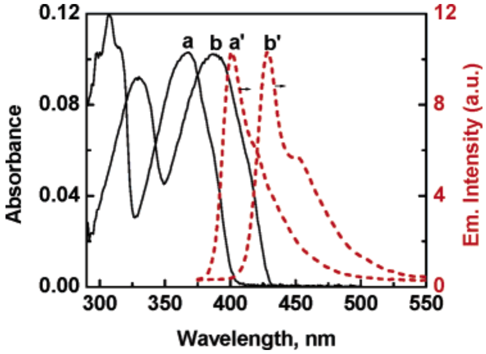

Figure 1. Absorption (−) and emission spectra (····) of (a,a′) **OPE-1** and **OPE-2** (b, b′) recorded in toluene. Emission spectra (a′ and b′) were recorded using excitation at 355 nm.

TABLE 1: Singlet-State Properties of OPE-1 and OPE-2 in Toluene

compd	λ_{S0max},[a] nm	ϵ, $M^{-1}\,cm^{-1}$	λ_f,[b] nm	τ_f,[c] ns	S_{0-0}, eV	ϕ_f[d] (λ_{exc}=355 nm)	λ_{s1max},[e] nm
OPE-1	367	3.1×10^4	401	1.43	3.16	0.66 ± 0.06	555
OPE-2	387	6.6×10^4	429	0.92	2.96	0.50 ± 0.05	638, 740

[a] Absorption maxima. [b] Emission maxima. [c] Fluorescence lifetime. [d] Fluorescence yield. [e] Absorption maxima of singlet excited state.

Results and Discussion

Absorption and Emission Characteristics. The absorption and emission spectra of **OPE-1** and **OPE-2** in toluene solutions are shown in Figure 1. The spectral characteristics are summarized in Table 1. The dialkoxy substituted phenylethynyl oligomers exhibit strong absorption in the UV and visible region (<425 nm) with two well separated absorption maxima. The unsubstituted molecule, viz., 1,4-bis(phenylethynyl)benzene, on the other hand, exhibits a single broad absorption band with a maximum around 320 nm.[34,35] Increasing the number of phenylethynyl units makes the absorption and emission bands of the molecule to shift to lower energy while retaining the overall band structures.

Time-dependent density functional theory (TDDFT) studies suggest that the dialkoxy substitution in the 2,5-position of the phenyl ring of **OPE-1** and **OPE-2** alters its central arene π-orbitals through the resonance interaction with oxygen lone pairs.[30] This results in two transitions, one from HOMO and the other from HOMO-1/HOMO-2 to LUMO. The molar extinction coefficients in toluene were estimated as 3.1×10^4 M^{-1} cm^{-1} (at 364 nm) and 6.6×10^4 M^{-1} cm^{-1} (at 387 nm) for **OPE-1** and **OPE-2**, respectively (Table 1). The absorption spectral features of **OPE**s in various solvents such as methylcyclohexane, toluene, and dichloromethane indicate no noticeable ground-state aggregation effects at concentrations ≤15 μM. The singlet excited-state energies of phenyleneethynylenes as determined from the crossover point between the normalized absorption and emission spectra were 3.16 eV for **OPE-1** and 2.96 eV for **OPE-2** (Figure 1).

West and co-workers[33] reported that phenyleneethynylenes (e.g., **OPE-1**) possess strong self-absorption/excimer formation, and the measured quantum yield is highly dependent on their concentration and excitation wavelength. In the present case we found emission spectra and lifetimes of both compounds to

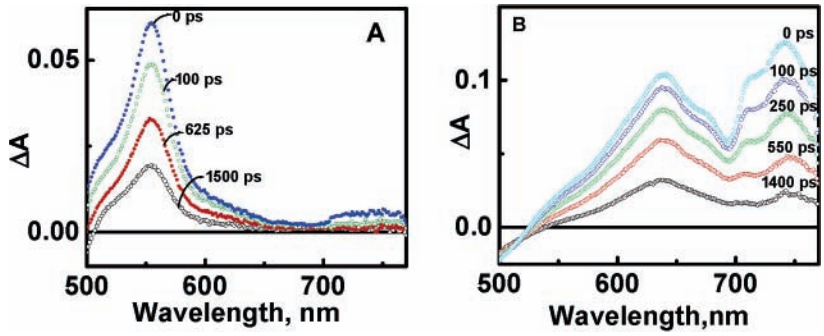

Figure 2. Time-resolved transient absorption spectra of singlet excited states of (A) **OPE-1** and (B) **OPE-2** in toluene. The spectra were recorded at different intervals following the 387 nm laser pulse excitation.

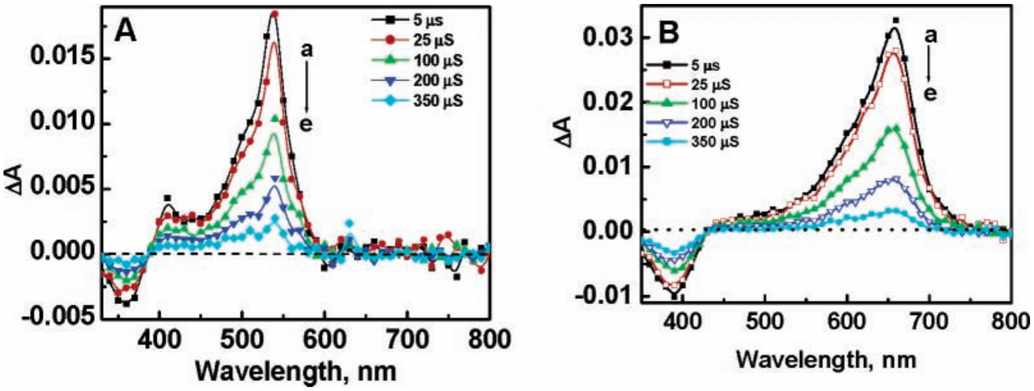

Figure 3. Transient absorption spectra of (A) **OPE-1** and (B) **OPE-2** in toluene. The difference absorption spectra were recorded (a) 5, (b) 25, (c) 100, (d) 200, and (e) 350 μs following 355 nm laser pulse excitation.

be independent of excitation wavelengths, thus confirming the existence of a single emitting species. This excited singlet behavior is in agreement with other reports presented previously.[30]

The fluorescence quantum yield was estimated, using dilute solutions of **OPE**s and integrating the emission spectra. The experiments were repeated using four different concentrations of **OPE-1** and **OPE-2**. The absorbance at the excitation wavelength 355 nm varied from 0.025 to 0.1. A solution of diphenylanthracence in cyclohexane was used as the reference (Φ=0.9).[36] In each case the sample absorbance was matched with that of the reference. The average quantum yield obtained from these measurements was 0.66 ± 0.06 and 0.5 ± 0.05 for **OPE-1** and **OPE-2**, respectively (Table 1).

Excited Singlet State. The femtosecond laser flash photolysis was employed to characterize the absorption characteristic of the excited singlet state of the **OPE-1** and **OPE-2**. The singlet state of these two oligomers was generated using 387 nm laser pulse (pulse width 150 fs) excitation. The time-resolved transient absorption spectra recorded following the laser pulse excitation of **OPE-1** and **OPE-2** are shown in Figure 2. The difference absorption spectrum of **OPE-1** showed a maximum at 555 nm, whereas a higher homologue exhibited two distinct bands (λ_{max} at 638 and 740 nm). A large bathochromic shift in the absorption maximum is observed for **OPE-2** compared to **OPE-1** suggesting lower energy S_1-S_n transitions with increasing phenylethynyl units. The lifetimes measured from the absorption decay of S_1 matched well with the lifetimes measured from the fluorescence decay (Table 1).

Earlier reports have indicated that phenyleneethynylenes possess fluorescence quantum yields close to unity.[33] Such an argument implies that the radiative deactivation is the only pathway for the relaxation of the singlet excited state of phenyleneethynylenes. Schmieder et al.[37] ruled out the possibility of the vibrational relaxation and intersystem crossing for the singlet excited state of an analogous molecule, 1,4-bis-(9-ethynylanthryl)benzene. The fluorescence quantum yield values observed for **OPE-1** and **OPE-2** in the present experiments are much lower than unity (0.66±0.06 and 0.5±0.05 for **OPE-1** and **OPE-2**, respectively). These observations indicate that nonradiative pathways contribute to the deactivation of the excited state. If this argument is true, we should be able to identify other deactivation pathways. For example, intersystem crossing can be monitored by the formation of long-lived triplet excited state. The residual absorption seen at 1.5 ns in the femtosecond transient studies (Figure 2) is an indication of the presence of long-lived species. The obvious question is whether these long-lived species correspond to the triplet excited state.

Triplet Excited State. To further characterize the formation of the triplet excited state, we carried out nanosecond laser flash photolysis experiments. Both phenyleneethynylenes possess a strong absorption at 355 nm which allows their direct excitation by the third harmonic of Nd:YAG laser (355 nm). The time-resolved transient spectra, recorded following 355 nm laser pulse excitation of **OPE-1** and **OPE-2**, are shown in Figure 3. The transient spectrum of **OPE-1**, recorded immediately after laser pulse excitation, showed depletion at 390 nm and an absorption at 520 nm. In the case of a higher homologue of phenyleneethynylene, the absorption of the newly formed transient is red shifted to 660 nm. The transient absorption band observed for both **OPE-1** and **OPE-2** is prompt, and the formation of this transient is completed within the 10 ns laser pulse duration. These spectral characteristics are assigned to triplet−triplet absorption based on the following observations: (i) the transient is readily deactivated by oxygen, and (ii) the transient is quenched by the addition of triplet energy acceptor such as oxazine or squaraine dyes. The spectral characteristics of the triplet excited states are summarized in Table 2.

TABLE 2: Triplet-State Properties of OPE-1 and OPE-2 in Toluene

compd	λ_{T-TMax},[a] nm	ϵ_T max, M^{-1} cm^{-1}	ϕ_T[b]	τ_T,[c] μs	k_{O2}, M^{-1} s^{1-}	k_{sq}, M^{-1} s^{1-}	$2k_{T-T}$,[d] M^{-1} s^{1-}
OPE-1	520	47 000	0.40	140	1.6×10^9	6.0×10^7	2.0×10^9
OPE-2	660	31 000	0.50	218	1.5×10^9	6.0×10^7	1.6×10^9

[a] Triplet absorption maxima. [b] Triplet yield. [c] Triplet lifetime. [d] Bimolecular rate constant for triplet−triplet annihilation.

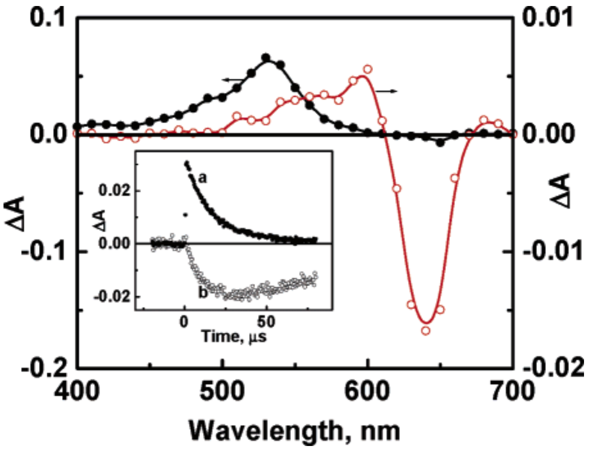

Figure 4. Energy transfer from triplet **OPE-1** to squaraine dye in methylene chloride. Transient absorption spectra were recorded following 355-nm laser pulse excitation of a solution containing **OPE-1** (10 μM) and squaraine dye (25 μM) at time intervals (●) 0 μs and (○) 50 μs. Absorption-time profile in the inset shows (a) the triplet decay of **OPE-1** at 510 nm and (b) ground-state bleaching of squaraine dye at 630 nm.

We further confirmed the identity of the long-lived transient as a triplet excited state by employing a squaraine dye, Sq (bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine) as a triplet energy acceptor. The time-resolved transient absorption spectra recorded after the 355 nm laser pulse excitation of **OPE-1** in dichloromethane solution containing a squaraine dye (25 μM) is shown in Figure 4. The transient spectrum recorded immediately after the laser pulse excitation corresponds to the triplet of **OPE-1**. The spectra recorded 50 μs after the laser pulse excitation corresponds to the triplet squaraine dye. Note that the direct excitation of the squaraine dye in dichloromethane does not produce its triplet.[38] As the triplet **OPE-1** decayed we observe an increase in the bleaching of the squaraine dye. The absorption features of the spectrum recorded at 50 μs confirm the formation of the squaraine triplet (reaction 1).

$$^3\mathrm{OPE} + \mathrm{Sq} \rightarrow \mathrm{OPE} + {}^3\mathrm{Sq}^* \qquad (1)$$

The fact that we are able to generate a squaraine triplet by the T−T energy transfer method further confirms the ability of an OPE triplet to act as a triplet energy donor to the molecule having lower triplet energy.

The extinction coefficient of the triplet excited state of phenyleneethynylenes was determined using the total depletion method.[39] The complete conversion of ground-state molecules to the triplet excited state was achieved by employing dilute solutions of **OPE** and maintaining the laser excitation intensity at which a saturation in the transient absorbance is achieved (the absorbance at the excitation wavelength was kept at 0.02). The extinction coefficient values determined by the total depletion method were 47 600 M^{-1} cm^{-1} for **OPE-1** and 31 000 M^{-1} cm^{-1} for **OPE-2** (Table 2).

The quantum yield of the triplet formation in toluene for **OPE-1** and **OPE-2** was determined using 1-pyrenecarboxaldehyde in acetonitrile (ϕ_T=0.78)[40] as a reference. The triplet excited state of 1-pyrenecarboxaldehyde has an absorption maximum at 440 nm with an extinction coefficient of 2.0×10^4 M^{-1} cm^{-1}. The quantum yields obtained from these experiments were 0.40 and 0.50 (error limit of 10%) for **OPE-1** and **OPE-2**, respectively. The triplet lifetimes of **OPE-1** and **OPE-2** were estimated as 140 μs and 218 μs (error limit of 5%), respectively, in dilute solutions. As will be discussed in the next section, the triplet lifetimes are dependent on the concentration of triplet as well as the ground-state dye molecules. The deactivation pathways responsible for the triplet excited state were probed at different excitation energy and ground-state concentrations.

Deactivation of the Triplet Excited State. Phenyleneethynylenes are widely used in solid-state devices. Since the triplet excited states are long-lived, they can initiate degradation via singlet oxygen generation and/or electron-transfer processes resulting from self-quenching processes. Thus, intermolecular interaction of the triplet excited state is an important factor in determining the long-term operation of optoelectronic or luminescent devices. To investigate these aspects, we looked into two types of self-quenching processes: (i) quenching of the OPE triplet by ground-state molecules and (ii) triplet−triplet annihilation.

$$^3\mathrm{OPE}^* + \mathrm{OPE} \xrightarrow{k_{sq}} 2\mathrm{OPE} + \text{heat} \qquad (2)$$

$$^3\mathrm{OPE}^* + {}^3\mathrm{OPE}^* \xrightarrow{2k_{T-T}} 2\mathrm{OPE} + \text{heat} \qquad (3)$$

The effect of the triplet excited-state quenching by the ground-state molecules (reaction 2) was probed by varying ground-state concentration of the dye molecules. The concentration of the OPE was varied from 2.5 to 45 μM while maintaining the triplet concentration around 0.3 μM. (Excitation intensity was varied such that the maximum absorbance seen after laser pulse excitation was ~0.016.) By keeping the triplet concentration in the submicromolar level we could minimize the competition from the T−T annihilation (reaction 3) during the decay of the triplet. The observed first-order decay confirms that there is no interference from the contribution of T−T annihilation (second-order decay) in the kinetic analysis. With increasing OPE concentration the triplet lifetime decreased confirming the ability of ground-state molecules to interact with the triplet excited state and influence its deactivation (Figure 5A).

Earlier studies have shown that dyes such as thionine or methylene blue undergo self-quenching with electron transfer.[41] In the present study we did not observe any long-lived transfer products thus ruling out the electron-transfer pathway in the self-quenching of OPEs. This observation parallels the diffusion-controlled ground-state quenching of triplet fullerenes.[42] The bimolecular rate constant (k_{sq}) for the quenching of triplet **OPE-1** by its ground-state molecules was determined by measuring the pseudo-first-order rate constant at various concentrations. From the linear dependence of the pseudo-first-order rate constant on the ground state, the bimolecular quenching constant of **OPE-1** and **OPE-2** in toluene were estimated as $\sim 6 \times 10^7$ M^{-1} s^{-1}. These values are low compared to the bimolecular quenching constant for molecules such as C_{60}.[42] Based on these observations we conclude that the decay of the triplet is not significantly influenced by the ground-state molecules at low (<10 μM) concentrations. However, it could be a major contributor in films where the local concentration of the dye is expected to be higher (e.g. in solid films). In cases where OPE units are used as bridging units, unintended

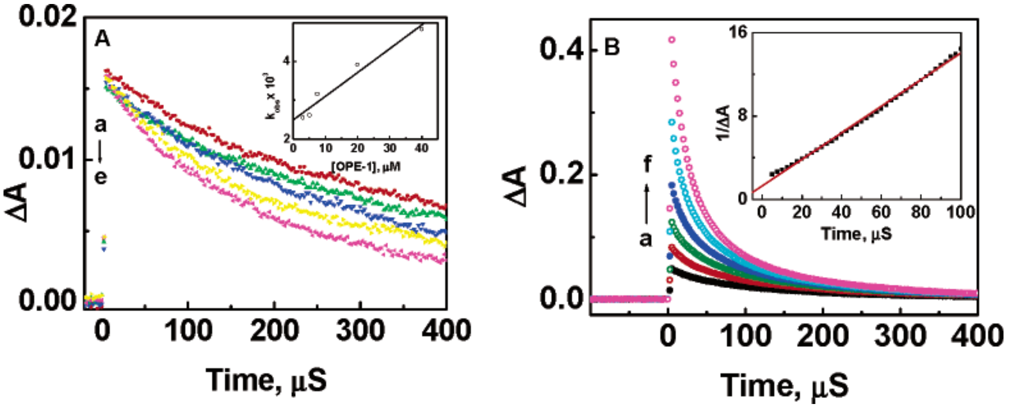

Figure 5. (A) Ground-state concentration dependence of **OPE-1** on the triplet decay at 520 nm in argon-saturated toluene solution. Concentration of **OPE-1** varied as (a) 2.5, (b) 5, (c) 10, (d) 20, and (e) 40 μM. (B) Laser-power dependence on the absorption-time profiles of **OPE-1** (7.5 μM) at 520 nm obtained by 355-nm laser flash photolysis in argon saturated toluene. The power of the laser varied from (a) 0.2, (b) 1, (c) 3, (d) 5.0, (e) 7.5, and (f) 10 mJ/pulse. Inset shows second-order fitting of the decay process at higher excitation intensity.

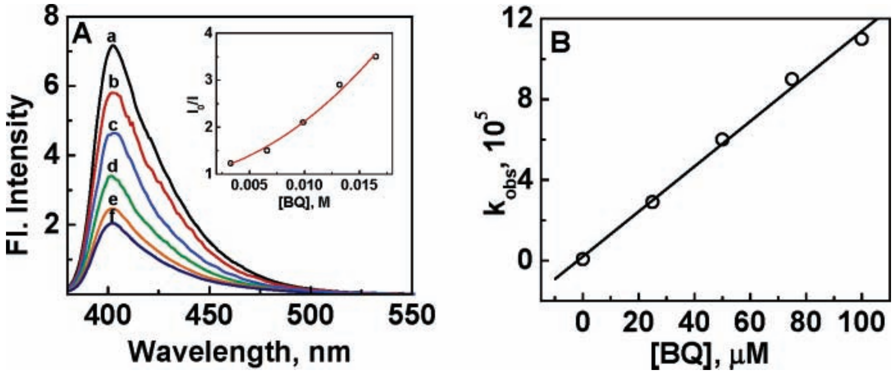

Figure 6. (A) Fluorescence quenching of **OPE-1** by BQ at concentration levels of (a) 0, (b) 3.3, (c) 6.6, (d) 9.9, (e) 13.2, and (f) 16.5 mM in acetonitrile. λ_{ex} = 375 nm. (Optical density at 375 nm kept as 0.1.) Inset shows the modified Stern−Volmer fit (expression 5) for the fluorescence quenching data. (B) Dependence of pseudo-first-order decay rate constant of triplet of **OPE-1** on benzoquinone concentration.

excitation may influence the course of electron transfer. However, if an ultrafast process such as charge injection into the semiconductor particle competes, the influence of the self-quenching process is likely to be less significant during the deactivation of the excited state.

The triplet lifetime was also sensitive to the initial triplet concentration. The triplet lifetime decreased as we increased the intensity of the excitation laser pulse. Figure 5B shows the decay profiles of the ^{3}OPE1* at different laser intensities. At low excitation intensity, the triplet decays via a first-order process, but as the initial triplet concentration increases, a second-order process dominates. At triplet OPE concentrations of 5 μM or greater, the majority of the decay is dominated by the second-order T−T annihilation process (reaction 3). The inset in Figure 5B shows the linear dependence of 1/Δ*A* versus time confirming the simple second-order decay involving the same species (reaction 3). The bimolecular rate constants ($2k_{T-T}$) as determined from the slope and initial concentration of the triplet **OPE-1** and **OPE-2** were 2 × 10^9 and 1.6 × 10^9 M^{-1} s^{-1}, respectively. Despite the high excitation intensity we did not observe any long-lived products indicating the absence of irreversible degradation pathways.

Electron-Transfer Interactions in the Excited State. Interactions of the excited OPE with electron donors and acceptors are another important aspect that can shed light onto the photochemical behavior of these molecular linkers. An OPE class of linker molecules is capable of transporting electrons across the acceptor and donor moieties. It is assumed that there is no chemical change associated with the linker molecules in such systems since the excitation is mainly centered around one of the attached moieties. Cyclic voltammetric experiments carried out in acetonitrile indicate an oxidation potential of 1.1 and 1.2 V versus SCE for **OPE-1** and **OPE-2**, respectively (Figure S1 in Supporting Information). These values are in agreement with the oxidation potential values (0.8−1.1 V vs SCE) reported for a series of terthiophene end-capped poly(arylene ethynelene)s.[17] Comparison of these oxidation potentials suggests that the end groups can play an important role in modulating the hole trapping capability of the phenyleneethylene molecules. Both **OPE-1** and **OPE-2** are quite resistant to reduction and exhibit relatively large reduction potentials. The reduction potentials for these two compounds are ≤ −2.0 V vs SCE (Figure S2 in Supporting Information).

We characterized the oxidation of OPE by initiating electron transfer with benzoquinone (BQ) in a polar solvent such as acetonitrile using laser excitation. Quinone molecules often serve as good electron acceptors for excited chromophores. Both singlet and triplet excited states of two OPEs are readily quenched in the presence of benzoquinone.

$$^1\mathrm{OPE}^* + \mathrm{BQ} \rightarrow \mathrm{OPE}^{+\bullet} + \mathrm{BQ}^{\bullet-} \qquad (4)$$

The interactions between the singlet excited OPE and BQ were monitored from fluorescence measurements. The fluorescence spectra of **OPE-1** recorded at different concentrations of BQ are shown in Figure 6A. The Stern−Volmer plot of I_o/I against the quencher concentration yields a nonlinear curve. These results suggest that both static and dynamic quenching processes are involved in the deactivation of **OPE-1**.

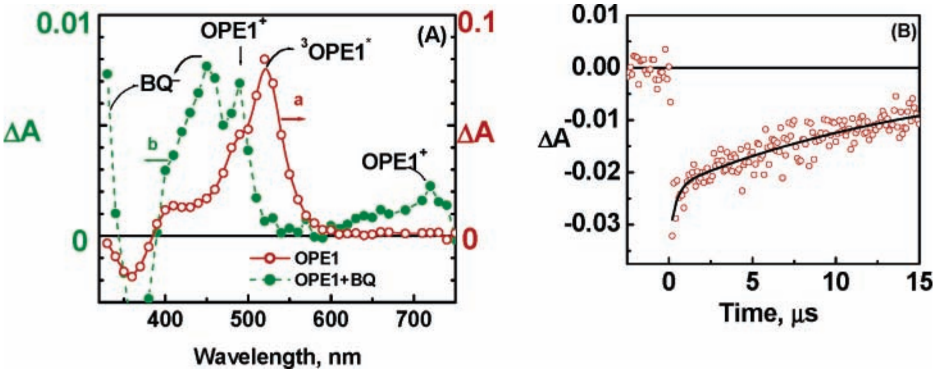

Figure 7. (A) Transient absorption spectra of **OPE-1** (10 μM) in the (a) absence (○) and (b) presence (●) of benzoquinone (100 μM) in acetonitrile. The spectra were recorded 20 μs after the laser pulse excitation. (B) Absorption-time profile of **OPE-1** recorded at 375 nm in the presence of BQ.

The quenching constant for the diffusion-controlled process (k_q) was determined from the modified Stern−Volmer expression 5.

$$I_0/I = 1 + (K + k_q\tau_f)[Q] + Kk_q\tau_f\,[Q]^2 \qquad (5)$$

I_0 and I represent the fluorescence intensities in the absence and presence of BQ, respectively, [Q] is the quencher concentration, τ_f is the fluorescence lifetime of OPE in the absence of BQ, k_q is the diffusional quenching constant, and K represents the equilibrium constant for the formation of complex between phenyleneethynylenes and benzoquinones. The expression 5 which accounts for both static and diffusion-controlled processes is illustrated in detail in the Supporting Information. The diffusional quenching constants for **OPE-1** and **OPE-2** estimated from this analysis were 5.3×10^{10} and 8.4×10^{10} M^{-1} s^{-1}, respectively.

We also probed the interaction of BQ with the triplet excited OPEs. The decay of the triplet absorption at different concentrations of BQ was followed at their corresponding absorption maximum. We observed only a diffusion-controlled quenching of the triplet excited OPE by BQ. (It is assumed that the associated complex of OPE-BQ does not produce any triplet as rapid quenching dominates in the singlet excited state. The uncomplexed fraction of OPE produces triplet excited state at the end of the pulse.) The pseudo-first-order decay of the triplet excited state was monitored at different concentrations of BQ. The bimolecular quenching rate constant (k_q) was determined from the dependence of the pseudo-first-order rate constant on the BQ concentration (expression 6).

$$k_{obs} = 1/\tau_T + k_q[Q] \qquad (6)$$

k_{obs} is the observed rate constant in the presence of quencher, [Q] is the quencher concentration, and τ_T is the lifetime of the triplet excited state in the absence of the quencher. The bimolecular quenching rate constants estimated from the slope of the plot in Figure 6B were 1.1×10^{10} M^{-1} s^{-1} and 1.3×10^{10} M^{-1} s^{-1} for **OPE-1** and **OPE-2**, respectively.

If the excited-state quenching process proceeds via photoinduced electron transfer, we should be able to observe the electron transfer products, namely the radical cation of **OPE-1** and the radical anion of BQ using nanosecond laser flash photolysis (reaction 7).

$$^3\mathrm{OPE}^* + \mathrm{BQ} \rightarrow \mathrm{OPE}^{+\bullet} + \mathrm{BQ}^- \qquad (7)$$

The transient absorption spectra recorded after 355 nm laser excitation of **OPE-1** in deoxygenated solution of acetonitrile are shown in Figure 7. In the absence of BQ, the triplet excited state of **OPE-1** is the only species formed when subjected to laser pulse excitation. In the presence of BQ, the difference absorption spectrum recorded immediately after laser pulse excitation matches the spectrum of **^{3}OPE-1***. The spectrum recorded 20 μs after the laser pulse excitation exhibits two broad peaks, one around 450 nm and the other around 490 nm. In addition we also observe bleaching at 375 nm. The transient absorption band at 450 nm corresponds to the absorption of the BQ radical anion,[43] and the bleaching at 375 nm corresponds to the ground-state recovery of **OPE-1**. We attribute the 490 nm absorption and the broad absorption in the near-IR to the formation of the cation radical of **OPE-1**.

Two distinct steps in the recovery of 375 nm can be seen in the absorption−time profile presented in Figure 7B. The initial fast recovery matches the triplet decay of **^{3}OPE1***, and the slower recovery represents the recombination of electron-transfer products (reaction 8).

$$\mathrm{OPE}^{+\bullet} + \mathrm{BQ}^- \rightarrow \mathrm{OPE} + \mathrm{BQ} \qquad (8)$$

Pulse Radiolytic Oxidation of Phenyleneethynylenes. Pulse radiolysis has been found to be a convenient method to probe the formation and recombination kinetics of charges generated in poly(phenylenevinylene)[44] and terthiophene end-capped poly(arylene ethynelene)s.[17] These studies enable the determination of the mobility of holes as well as the characterization of cations and anions. We performed pulse radiolysis experiments in methylene chloride to further establish the oxidative properties of OPEs. The radiolysis of chlorinated hydrocarbons such as methylene chloride produces an oxidizing radical such as $\mathrm{RCl}^\bullet$ which in the presence of oxygen forms an oxidizing species, $\mathrm{RClOO}^\bullet$. These species are quite stable in the submillisecond time scale and are capable of undergoing charge transfer with an added substrate (reaction 9).

$$\mathrm{RClOO}^\bullet + \mathrm{OPE} \rightarrow \mathrm{RClOO}^- + \mathrm{OPE}^{\bullet+} \qquad (9)$$

The transient absorption spectra of the radical cation of two phenyleneethynylenes, **OPE-1** and **OPE-2**, recorded following the pulse radiolysis of O_2 saturated methylene chloride are shown in Figure 8. The difference absorption spectrum of **OPE-1**$^{\bullet+}$ exhibits split bands at 470 and 510 nm (trace a). In the case of **OPE-2**$^{\bullet+}$ (trace b), the bands are red shifted to 520 and 570 nm. The red shift in the absorption with a longer oligomer is similar to the absorption shift observed with ground-state and excited-state absorption bands. Earlier studies have reported visible and infrared absorption bands for the terthiophene end-capped poly(arylene ethynelene)s.[17,44] The visible band in the 550−600 nm region is characteristic of a cation radical of an ethynelene based oligomer or polymeric based molecules and

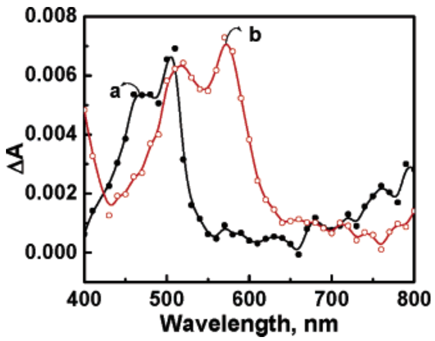

Figure 8. Transient absorption spectra of pulse radiolytically generated cations of (a) **OPE-1** and (b) **OPE-2** in methylene chloride. The spectra were recorded following the pulse radiolysis of O_2 saturated CH_2Cl_2 solution containing ~0.1 mM of phenyleneethynylenes.

represents the hole trapping properties of the phenylenethynelene class of molecules.

It is interesting to note that the absorption peak at 500 nm matches with the long time absorption of $OPE^{\bullet +}$ seen in the case of photochemical oxidation of OPE (Figure 7A). The small difference in the position of the absorption maximum (~10 nm) is attributed to the difference in the solvent polarity. The ease of cation radical formation in the photochemical and radiolytic studies indicates the ability of phenylenethynelenes in capturing the positive charge (or ‘holes”) and thus promotes the propagation of charges along the molecular chain.

Excited Interaction with an Electron Donor, *N*,*N*-Dimethylaniline. As observed in our electrochemical studies, OPEs are difficult to reduce ($E_{red} \leq -2.0$ V). For **OPE-1** the reduction potential of singlet excited-state amounts to 0.96 V vs SCE (The value is obtained from E_{red} and E_s values.). The electron donor such as *N*,*N*-dimethylaniline with its oxidation potential (0.78 V vs SCE)[45] is capable of undergoing electron transfer with singlet excited **OPE-1**. We have separately carried out quenching experiments with both the OPEs. The emission of both of these compounds is efficiently quenched by *N*,*N*-dimethylaniline (DMA). The quenching rate constants for both **OPE-1** and **OPE-2** as estimated from Stern−Volmer plot were 1.24×10^{10} and 2.0×10^{10} M^{-1} s^{-1}, respectively (see Figures S3 and S4 in the Supporting Information).

When we repeated the quenching experiments with the triplet excited state, we failed to observe any interaction with DMA. Even at concentrations as high as 10 μM of DMA, the triplet lifetime remain unchanged. Based on the quenching at higher DMA concentrations (<1 mM) we estimate the triplet quenching rate constant to be of the order of $\leq 10^6$ M^{-1} s^{-1} (see Figure S5 in the Supporting Information). The low reactivity of the triplet toward DMA indicates that the triplet excited state is not energetic enough to act as an electron acceptor.

The effect of DMA on the deactivation of the singlet excited state of **OPE-1** was also studied using the femtosecond laser flash photolysis. In the presence of DMA, the absorption of singlet excited state at 555 nm disappeared, and the absorption of the triplet at 520 nm evolved (Figure S6 in the Supporting Information) during the monitoring time of 1.5 ns. In addition, our efforts to identify electron-transfer products in the transient absorption measurements were not conclusive.

Concluding Remarks

By using transient absorption spectroscopy, we have characterized singlet and triplet excited states of two phenyleneethynylene oligomers (**OPE-1** and **OPE-2**). Unlike the previously published reports[33] these two model compounds show significant yields (≤0.4) of triplet excited state. We have confirmed the presence of the triplet excited state by characterizing a long-lived transient that is capable of transferring energy to an acceptor. Furthermore the long-lived triplet is reactive and undergoes one-electron oxidation with molecules such as benzoquinone. Because of the tail absorption of the phenyleneethynylene oligomer band in the visible, one can anticipate formation of triplet excited states during the visible excitation of the light harvesting assemblies that contain similar linker molecules. Hence caution should be taken while interpreting the results of the electron transfer/transport processes in systems that employ phenyleneethynylene as linker molecules. The excited-state interactions such as self-quenching and T−T annihilation processes also play an important role in the development of polyphenyleneethynylene based light emitting devices. A longer lifetime of the triplet excited state makes the device performance sensitive to the physical and chemical properties of the surrounding media and significantly affects the long-term stability.[46] The excited-state properties presented should provide a further basis for the fundamental understanding of the phenyleneethynylene oligomer linker molecules and the photoinduced electron transfer in light harvesting assemblies and light emitting devices.

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Supporting Information Available: Figures of cyclic voltammograms, fluorescence quenching plots, and transient spectra and derivation of eq 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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