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**Bimolecular Excited-State Electron Transfer with Surprisingly
Long-Lived Radical Ions**

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ABSTRACT

We explored the excited-state interactions of bimolecular, non-covalent systems consisting of cationic poly[(9,9-di(3,3'-N,N'-trimethyl-ammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyl)] diiodide salt (PFN) and 1,4-dicyanobenzene (DCB) using steady-state and time-resolved techniques, including femto- and nanosecond transient absorption and femtosecond infrared spectroscopies with broadband capabilities. The experimental results demonstrated that photo-induced electron transfer from PFN to DCB occurs on the picosecond time scale, leading to the formation of $\text{PFN}^{+\bullet}$ and $\text{DCB}^{\bullet-}$ radical ions. Interestingly, real-time observations of the vibrational marker modes on the acceptor side provided direct evidence and insight into the electron transfer process indirectly inferred from UV-Vis experiments. The band narrowing on the picosecond time scale observed on the antisymmetric C-N stretching vibration of the DCB radical anion provides clear experimental evidence that a substantial part of the excess energy is channeled into vibrational modes of the electron transfer product and that the geminate ion pairs dissociate. More importantly, our nanosecond time-resolved data indicate that the charge-separated state is very long lived (~ 30 ns) due to the dissociation of the contact radical ion pair into free ions. Finally, the fast electron transfer and slow charge recombination anticipate the current donor-acceptor system with potential applications in organic solar cells.

INTRODUCTION

Conjugated polymers have become materials of interest for solar cell applications,¹⁻² optical devices,³ and chemical and biological sensors.⁴⁻⁵ Among the emerging conjugated polymers, conjugated polyelectrolytes (CPEs) consisting of conjugated main and side chains with various functional groups have been intensively investigated.⁶ By virtue of their light-harvesting properties, CPEs have also been utilized as photosensitizers in solar cells⁷⁻⁸ and fluorescent sensors.⁹⁻¹¹ The basis of the successful utilization of CPEs in optoelectronic applications is their semiconducting properties, including their large optical densities and high emission intensities for fluorescence resonance energy transfer.¹² In particular, key features of CPEs for solar cell applications are their flexibility and their simple, large-scale, and low-cost fabrication.^{1, 7} Another advantage is that the functional groups of the side chains can be ionic or polar moieties, allowing the modification of not only the solubility of the CPEs in water and other polar solvents¹³ but also their intermolecular interactions, energy levels, and redox potentials, which determine electronic coupling¹⁴ and the rate of electron transfer at the donor–acceptor interface.^{8, 15}

In solar cell devices, rapid electron transfer and separation to overcome electron-hole recombination are required for high energy-conversion efficiency.¹⁶⁻¹⁷ In this sense, the interaction, linking, and distance between the electron donor and acceptor moieties play crucial roles.¹⁸ In particular, CPEs should form strong interconnections and interpenetrations with the electron acceptor moieties to attain efficient electron or energy transfer.¹⁹ An innovative approach utilizing the electrostatic interactions between cationic CPEs with negatively charged electron acceptor moieties has therefore attracted extensive attention.^{8, 15, 20-24} For example, this approach was used to achieve strong electrostatic interactions between cationic CPEs and DNA base pairs, allowing the detection of DNA based on fluorescence quenching of the cationic CPEs.⁵ In addition, efficient energy transfer from photoexcited cationic polyfluorene, a CPE, to porphyrin demonstrated that the cationic polyfluorene can form an electrostatic assembly with small molecules and act as a photosensitizer in the assembly.²⁵⁻²⁶

Recently, polyfluorene with azide derivatives was covalently linked with graphene flakes to produce a material with low bandgaps and high charge carrier mobility.²⁷ With such features, this material has high potential to be used in solar cells. We therefore sought to explore electron or

energy transfers in non-covalent polyfluorene derivatives to determine the bimolecular electron transfer reactions of polyfluorene in the solution phase.²⁸⁻³¹ As in the case of the photoexcitation of small molecules, vertical excitation of the electron donor–acceptor system should induce electron or energy transfer.³² Knowing the rates of photoinduced electron transfer (PET), charge separation (CS), and charge recombination (CR)³⁰ is required to understand the quenching dynamics of polyfluorene as well as how electrons or energy is transferred from excited polyfluorene to molecular acceptors. Such information is critically important in developing solar cell materials based on water or organic solvent-soluble polyfluorenes²¹ and on solid-phase polyfluorenes.³³

Here, we report PET dynamics in non-covalent associations of cationic polyfluorene, namely poly[(9,9-di(3,3'-N,N'-trimethyl-ammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyl)] diiodide salt (PFN) with neutral electron acceptor 1,4-dicyanobenzene (DCB). We carefully chose DCB as an electron acceptor because of its unique optical properties including the absence of a spectral overlap with the donor to rule out the possibility of energy transfer process rat. In addition, the anion radical in DCB has clear electronic and vibrational spectroscopic signatures resulting from the electron transfer process.³⁴⁻³⁵ Steady-state absorption and emission experiments revealed efficient quenching of the PFN fluorescence upon addition of DCB. In addition, transient absorption data demonstrated that PET and charge separation from PFN to DCB occur on the picosecond time scale, leading to the formation of PFN⁺• and DCB⁻• radical ions in the UV and visible spectral range. Time-resolved infrared (IR) spectroscopy supported these data by indicating that the antisymmetric C-N stretching vibration of the DCB radical anion is evident. Additionally, band narrowing of this C-N stretching vibration of the DCB radical anion provides clear experimental evidence of the dissociation of contact-radical pairs into free ions.

EXPERIMENTAL SECTION

Materials. Commercially available PFN was purchased from Solaris Chem. Inc. and DCB (98%) from Sigma-Aldrich. In all the experiments described here, high-purity dimethyl sulfoxide (DMSO; 99.9%; Sigma-Aldrich) was used as the solvent. All chemicals were used without

further purification. The non-covalent PFN/DCB system was prepared by mixing PFN and DCB in DMSO at room temperature.

Steady-State Measurements. The steady-state absorption and emission spectra of the mixtures of PFN with and without various DCB concentrations were measured in a rectangular quartz cell with a 1-cm optical path. The absorption spectra were recorded on a Cary5000 UV-visible spectrometer (Agilent Technologies), and the emission spectra were collected on a Fluoromax-4 spectrofluorometer (Horiba Scientific). In each experiment, a fixed volume (3 mL) of the starting solution of PFN in DMSO was placed in the cell, and aliquots of the quencher dissolved in DMSO and mixed with PFN were added consecutively. The concentration of PFN was held constant at an optical density (OD) of 1.2 in the PFN/DCB system. DCB in the range of 0–0.24 M was successively added into the PFN solution. Emission spectra were collected with the excitation wavelength set at 370 nm. Both the entrance and the exit slits of the spectrofluorometer were kept the same (1 nm) in all the experiments.

Femtosecond Broadband Transient Absorption (TA) Spectroscopy. A femtosecond (fs) broadband TA spectroscopy was employed to monitor the excited state dynamics of the PFN with and without DCB after optical excitation at 370 nm. The experimental setup of the TA has been described elsewhere.³⁶⁻³⁷ Briefly, the setup consisted of white-light continuum probe pulses generated in a CaF₂ nonlinear crystal with spectrally tunable fs pump pulses (240–2600 nm; a few μ J of pulse energy) generated in an optical parametric amplifier (Newport Spectra-Physics). The pump and probe pulses were overlapped spatially and temporally into a 2-mm-thick cuvette cell containing PFN (0.4 OD) in the absence and presence of DCB (0.12 and 0.24 M). The transient absorbance change was monitored by focusing the transmitted probe light from the solution into a broadband UV-Vis detector. To cover the transient spectra in the ns- μ s time scales, we also used a nanosecond TA (Ultrafast Systems, USA) with a time resolution of 200 ps.

Time Correlated Single Photon Counting (TCSPC) Setup. In this setup, the excitation source was fs pulses at 370 nm (a few μ J of pulse energy) generated from an optical parametric amplifier (Newport Spectra-Physics). The emission at 90° geometry was collected under magic-angle polarization and detected by a Halcyone MC multichannel fluorescence spectrometer with a temporal resolution of 150 ps (Ultrafast Systems, USA). Detailed information on the experimental setup can be found elsewhere.³⁸

Cyclic Voltammograms Setup. Cyclic voltammograms were acquired using Metrohm Autolab Potentiostat/galvanostat. The electrolytic cell was assembled by using a glassy carbon working electrode a platinum and a Ag/AgCl double membrane reference electrode containing LiCl in anhydrous ethanol as electrolytic medium. 5 μg of the polymer was dissolved in 10 ml of the supporting electrolytic solution consisting of tetrabutylammonium hexafluorophosphate (NBu_4PF_6) 0.1 M in anhydrous acetonitrile. The redox couple ferrocene/ferrocenium (Fc/Fc^+) was taken as electrolytic reference to relate the electrochemical scale to the physical scale. For this purpose a 0.01 M solution of ferrocene in acetonitrile containing NBu_4PF_6 0.1 M as supporting electrolyte was cycled in the same experimental conditions.

Femtosecond Infrared Transient Absorption (TA) (fs-IR-TA). Time-resolved IR experiments were carried out using a Helios-IR spectrometer with broadband capability (Ultrafast Systems, USA). The UV pump pulses at 400 nm were straightforwardly obtained by the second harmonic of a 120 fs Ti:sapphire regenerative amplifier operating at 1 kHz (Newport Spectra-Physics). The tunable mid-IR probe pulses were generated by difference frequency mixing of the signal and idler pulses from a near-infrared optical parametric amplifier. Probe and reference pulses, split off by a ZnSe wedge, were spectrally dispersed in a grating spectrometer and recorded simultaneously in a single-shot detection unit using a liquid-nitrogen-cooled double array (2×32 pixels) of MCT (HgCdTe) detectors. Spectrally resolved absorbance changes in the mid-IR were recorded at a $2\text{--}7\text{ cm}^{-1}$ spectral resolution. The change in absorbance of the probe was then calculated by normalization with respect to the transmission of the reference pulses and by comparison between excited and unexcited cases on two subsequent laser shots. The time resolution in these UV pump/IR probe experiments was estimated to be ~ 160 fs in semiconductor silicon.

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of PFN with successive addition of DCB are shown in Fig. 1. In the absence of DCB, the absorption spectrum of PFN has a peak centered at 403 nm and an absorption cutoff at 450 nm. Upon successive DCB addition, only a consecutive increase was observed in the region below 350 nm (Fig. 1A), due to the absorption of DCB in this spectral range. This indicates that, upon the electron acceptor addition, the electronic structure of PFN is not really affected, excluding the possibility of the presence of strong ground-state

complex between the donor-acceptor components. On the other hand, selective photoexcitation of PFN at 370 nm gave rise to a fluorescence spectrum in the visible region between 400–550 nm with its maximum at 424 nm with two vibronic features at 447 and 480 nm. Successive addition of DCB resulted in strong quenching of the PFN emission, indicating an excited state interaction between PFN and DCB. An estimated 78% quenching of the PFN was observed upon addition of ~0.24 M DCB. It should be noted that the fluorescence quenching suggests electron and/or energy transfer from the excited PFN to the DCB quencher. However, we ruled out the energy transfer mechanism on the basis of the lack of spectral overlap between the absorption of DCB and the emission of PFN. We constructed a Stern-Volmer plot for the PFN fluorescence quenching using the equation $F_0/F=1+K_{SV}[DCB]$, where F_0 and F are the fluorescence intensity of PFN in absence and presence of DCB, respectively, K_{SV} is the Stern-Volmer constant and $[DCB]$ is given in M (see Fig. 1A).³⁹ A bimolecular quenching rate constant can be calculated using $K_q=K_{SV}/t_F$, where t_F is the fluorescence lifetime in absence of the quencher. We also measured the fluorescence lifetime of the PFN as shown in the inset of Fig. 1 using TCSPC and found it to be 0.43 ± 0.04 ns (which is in good agreement with the reported fluorescence lifetime of polyfluorenes)⁴⁰. This allowed us to estimate the quenching rate to be $3.37 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. On the other hand, the quenching rate constant for a diffusion-controlled mechanism in DMSO is equal to about $3.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.⁴¹ This means that our estimated rate is almost one order of magnitude higher than the diffusion-controlled rate constant and hence the quenching for PFN is expected to be static in nature. This finding is fully supported by our time-resolved measurements as discussed below.

We used ultrafast TA spectroscopy with femtosecond temporal resolution and broadband capabilities to probe further the reaction mechanism of the excited-state interaction. Figure 2 shows TA spectra of PFN in the absence and presence of two different concentrations (0.12 and 0.24 M) of DCB after photoexcitation at 370 nm. As can be seen, excitation of the PFN alone immediately results in ground-state bleaching (GSB) at around 390 nm, stimulated emission (SE) at 420, 448, 475 nm, and a broad excited-state absorption (ESA) band centered at 580 nm. Although this spectrum is similar to that from free PFN TA measured in the presence of DCB, as shown in Fig. 2B, there are two emerging bands in the 420–620 nm range with peaks clearly centered at 430 and 600 nm. These two bands became stronger as the DCB concentration

increased as can be seen in Fig. 2C. We assigned these emerging bands at 600 and 430 nm to the spectroscopic signatures of $\text{PFN}^{+\bullet}$ and $-\text{DCB}^{\bullet-}$ radical ions, respectively. The band at 430 nm is in agreement with literature reports on dicyanobenzene radical anions⁴²⁻⁴⁴ and that at 600 nm is in agreement with fluorene radical cations.⁴⁵⁻⁴⁶ As can be clearly seen in Figures 2 and 3, the formation of radical ions and the significant increase in the amplitude of the un-recovered GSB of PFN in the presence of DCB provide clear indication of electron transfer and charge separation on the picosecond time scale. Based on this observation and the data recorded using fs-time resolved IR spectroscopy (see below), we excluded the possibility of charge recombination on the picosecond time scale with almost all the contact radical ions undergoing charge dissociation into free ions.

Kinetic profiles collected from fs-TA of both GSB and ESA of PFN in the absence and presence of DCB are presented in Fig. 3A & 3B. More specifically, analysis of the dynamic traces of PFN in the absence of DCB demonstrates that up to 90% of the GSB recovery and ESA takes place at a time constant of 440 ± 32 ps, indicating the excited-state lifetime of PFN, which is in good agreement with the fluorescence lifetime recorded during our TCSPC experiments (Fig. 1B, inset). Yet, there is a long tail in the ESA decay and complete GSB recovery is not reached within our time window of 5.50 ns. To explore the nature and dynamics of this slow component, we carried out nanosecond-microsecond transient absorption experiments in the absence and presence of oxygen (see below).

The kinetics of the transient spectra at 380 nm and 550 nm, which are attributed to GSB and the radical cation, indicate clearly that the percentage of the unrecovered signal back to the initial state increased with increasing DCB concentration, further supporting the efficiency of the charge separation and subsequently the formation of free ions. To fully characterize the dynamics of the formed radical ions including the recombination process, we extended the time window for the TA measurements to the nano- and microsecond time scales. The recorded spectra are presented in Fig. 4. The dynamics at 600 nm (due to the charge recombination) were fitted to double-exponential functions with time constants of 3.58 ± 1.40 ns and 30.14 ± 7.10 ns. It is worth pointing out that the charge separation dynamics obtained from the fs-TA measurements (see Figure 3C) is biphasic in nature. More specifically, the kinetic trace is fitted to a bi-exponent function with characteristic time constants of 23.27 ± 4.39 ps and 217.50 ± 18.20 ps. This

biphasic nature is further supported by fs-time resolved IR discussed below where the time constants are closely related. In addition, these two time domains observed allows the estimation of two rates for charge separation one fast $\sim 4.3 \times 10^{10} \text{ s}^{-1}$ while the other is slower $\sim 4.6 \times 10^9 \text{ s}^{-1}$. The two observed components suggest the occurrence of two types of donor-acceptor ion pairs with different associated couplings, in accordance with previous reports on other donor-acceptor systems.⁴⁷⁻⁵⁰ The geometry and electronic coupling between donor and acceptor molecules can greatly affect both charge separation and charge recombination rates.⁴⁹ Hence, it is expected that the strong electronically coupled ion pairs will undergo fast charge recombination either to the neutral molecule or to the less coupled ion pairs. On the other hand, the slowly formed ion pairs encountering lower degree of coupling will in turn undergoes charge recombination over a longer time window to the neutral molecule. One possible explanation for the long-lived charge separated ions is the localization of the charges on the molecular acceptor or/and PFN which can be stabilized by the high solvent polarity of DMSO.

However, it is noteworthy that the reduction potential of DCB is -1.64 V vs. SCE,⁵¹⁻⁵² and the oxidation potential of PFN, as experimentally measured, is +1.09 V. With the free energy (ΔG) for PET given by: $\Delta G \text{ (eV)} = E_{\text{ox(D}^+/\text{D)}} - E_{\text{red(A/A}^-)} - E_{0-0} + C$, where E_{ox} is oxidation potential of the electron donor, E_{red} is the reduction potential of the electron acceptor, $E_{0-0} = 3.08 \text{ eV}$ (the singlet energy level of the donor and C is energy release due to charge separation).³⁹ This allows us to estimate ΔG to be $\sim -0.47 \text{ eV}$ indicating a smaller yet thermodynamically feasible PET from PFN to DCB.

Time-resolved IR spectroscopy

Since vibrational spectroscopy is more powerful and much more localized than electronic spectroscopy, it thus provides microscopic information about specific functional groups both in the donor and acceptor sites.⁵³⁻⁵⁹ In addition, vibrational transitions have smaller bandwidths (narrower vibrational IR absorption lines) than electronic transitions, leading to less spectral overlapping of the different transient bands in vibrational spectroscopy compared with those in electronic spectroscopy. This increases the chances of finding spectral regions where different lines do not overlap. In this study, we used the C-N stretching vibration of the DCB anion radical as a specific marker mode to follow the electron transfer in real time. Figure 5A-C displays the transient mid-IR absorbance changes after 400 nm excitation. The antisymmetric C-N stretching

mode of $\text{DCB}^{\bullet-}$ radical anion at 2100 cm^{-1} is clearly observed. This confirms the anticipated PET from PFN to DCB.³⁵ The radical anion of the DCB signature is formed at an early delay time as a broad transient band (see Fig. 4). As time goes by (a few hundreds of picoseconds), the band shows a slight spectral upshift along with narrowing and an increase in the signal intensity (see Fig. 5A&5B). The band narrowing on a time scale of picoseconds observed on the antisymmetric C-N stretching vibration of the DCB radical anion provides clear experimental evidence that a substantial part of the excess energy is channeled into vibrational modes of the electron transfer product and also that the geminate ion pairs dissociate.³⁵ The electronic and vibrational spectroscopic results allow us to describe, the reaction mechanism using the following equations:

The kinetic trace collected at 2100 cm^{-1} which corresponds to the antisymmetric C-N stretching vibration of the DCB radical anion (Fig. 5C) fits with double-exponential decays with characteristic time constants of 26.65 ps and 196 ps. This biphasic nature of the dynamics for the charge separation is in good agreement with the dynamics of the excited-state absorption of the DCB radical anion collected at 435 nm (see Figure 3C). Again, the biphasic nature of the formation of the charge separated ions can be understood in term of different degrees and/or different geometries of charge transfer complexes.⁴⁷⁻⁵⁰

Triplet-state formation

As can be seen in Figures 2A and 3A, the TA signal of the free PFN exhibits a very long-lived component that is longer than the time window of the fs-TA of 5.5 ns. Several reports on fluorene-based materials indicate that there is triplet state formation with a broad absorption spectrum over the 400-900 nm range.^{40, 60-63} More specifically, triplet-triplet absorption for poly(dioctylfluorene) has a broad excited-state absorption with a maximum at 750 nm and a lifetime of 108 μ s in the absence of oxygen.⁶⁴ The long component detected in our fs-TA results may thus be attributed to the triplet-triplet absorption. To confirm such a possibility, we ran nano-microsecond transient absorption spectroscopy tests in aerated and degassed solutions (Fig. 6). The dynamic profile of PFN exhibits excited state decay with a time constant of $0.59 \pm 0.03 \mu$ s in the presence of oxygen (Fig. 6A). This lifetime is three orders of magnitude longer than the singlet-state lifetime (~ 0.4 ns) measured by fluorescence and transient absorption experiments, indicating the triplet state formation. This triplet nature of the signal was further confirmed by measurements in a degassed solution given that the dynamics of triplet states of fluorene-based materials are highly sensitive to oxygen.^{40, 64} Our nanosecond-microsecond TA signal in the absence of oxygen exhibits much slower dynamics compared to the signal in the presence of oxygen (Fig. 6B), fully supporting the triplet nature of the long-lived component. The time constant extracted from the excited-state decay, which was $73.29 \pm 10.80 \mu$ s, is in good agreement with the range reported for triplet state lifetimes.⁶¹

CONCLUSION

In conclusion, we investigated photo-induced bimolecular electron transfer between cationic poly[(9,9-di(3,3'-N,N'-trimethyl-ammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctylfluorenyl-2,7-diyl)] diiodide salt (PFN) and 1,4-dicyanobenzene (DCB) using a combination of time-resolved electronic and vibrational spectroscopies along with steady-state absorption and fluorescence experiments. The electronic spectroscopy experiments provided clear evidence of an excited-state interaction, as inferred from the extensive photoluminescence quenching and the ultrafast formation of the cationic and anionic species of PFN and DCB, respectively. The time-resolved IR spectroscopy demonstrated further that we were capturing excited-state electron transfer from PFN to DCB given the antisymmetric C-N stretching vibration of the DCB radical

anion. In addition, the band narrowing of this antisymmetric C-N stretching vibration provided clear experimental evidence that the geminate ion pairs dissociated into free ions. Interestingly, unlike many other CT systems⁶⁵⁻⁶⁸, the electron transfer from PFN to DCB in our system is ultrafast and the CR is very slow, anticipating an improved donor–acceptor system with potential applications in organic solar cells.

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Fig. 1. Steady-state absorption (A) and emission ($\lambda_{ex}=370$ nm, B) for PFN-DCB system. The concentrations used are given on the graph. The inset gives the PFN structure, Stern-Volmer plot and the time correlated single photon counting (TCSPC) kinetic profile collected using excitation at 370 nm of PFN. The red line shows the fitting profile.

Fig. 2. Transient absorption spectra using photoexcitation at 370 nm of a 150 fs laser for (A) PFN alone, (B) FPN in the presence of 0.12 M DCB, and (C) FPN in the presence of 0.24 M DCB.

Fig. 3. Kinetic traces derived from femtosecond transient absorption spectra for PFN in the absence (red) and presence of 0.24 M DCB (green). Fitting is indicated by blue lines.

Fig. 4. Transient absorption spectra for PFN in the presence of DCB (0.24 M) recorded using photoexcitation at 370 nm of a 150 fs laser. Inset: the dynamic at 600 nm and the time constant.

Fig. 5. IR-Transient absorption spectra for PFN+DCB (0.24 M) recorded at excitation of 400 nm visible pulses produced by second harmonic generation of the laser system collected at (A) 5.01 ps, (B) 667 ps delay time, and (C) dynamics at 2100 cm^{-1} . The fitting is shown with a blue line and time constant is given on the graph.

Fig. 6. Transient absorption spectra for PFN recorded using photoexcitation at 370 nm of a 150 fs laser with a nanosecond-to-microsecond time delay in the presence (A) and the absence (B) of oxygen. Insets show the dynamics and triplet lifetimes monitored at 785 nm; fitting is indicated by blue lines.

TOC graphic