Photophysical Characterization of Donor-Acceptor Systems using Ultrafast Laser Spectroscopy

Dissertation by
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In Partial Fulfillment of the Requirements
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EXAMINATION COMMITTEE PAGE

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ABSTRACT

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Amani Abdu M Alsam

In donor-acceptor systems, ultrafast interfacial charge transfer (CT), charge separation (CS) and charge recombination (CR), are among the key factors in determining the overall efficiency of the optoelectronic devices. In this regime, precise knowledge of the mechanisms of these processes on the femtosecond scale is urgently required. In this dissertation, using femtosecond transient absorption and mid-Infrared spectroscopies along with steady-state absorption and emission measurements, we are not only able to address the fundamental understanding of these ultrafast dynamical processes, but also control them at various inter- and intramolecular electron donor-electron acceptor systems.

In the photoinduced intermolecular charge transfer systems, where donor and acceptor are separated from each other, three systems have been investigated; cationic poly[(9,9-di(3,3’-N,N’-trimethylammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyl)] diiodide salt (PFN) conjugated polymer donor with 1,4-dicyanobenzene (DCB) acceptor, negatively charged porphyrin (POS) donor with positively charged (PFN) acceptor, and finally, positively charged (PFN) donor with negatively charged graphene carboxylate (GC) acceptor. Based on studying these three systems, we were able to explore some important factors and deriving forces including chemical structure, electrostatic interactions, energy band alignment, hydrogen bonding and solvents with different polarities and capabilities for hydrogen bonding
that influence the rate and efficiency of the charge transfer at the interfaces of these donor-acceptor systems. For instance, unlike the conventional understanding of the key role of hydrogen bonding in promoting the charge-transfer process, our results reveal that the hydrogen-bonding increases the spacing between the donor and acceptor units which significantly hinders the charge-transfer process.

On the other hand, in the photoinduced intramolecular charge transfer systems, where donor and acceptor are chemically attached to each other, we investigate the effects of conjugation length on photoinduced charge transfer in \( \pi \)-conjugated oligomers naphthalene diimide (NDI) end-capped oligo(phenylene ethynylene)s (PE-NDI), and poly-(phenylene ethynylene) (PPE) donor backbone with (NDI) acceptor end-caps (PPE-NDI-n) systems. The results of femtosecond transient absorption and mid-IR spectroscopies show that the charge separation occurs on the 1-10 ps time scale with the rates decreasing as oligomer length increases in PE-n-NDI system. In addition, in PPE-NDI-n system, the fluorescence quenching measurements indicate very efficient photoinduced electron transfer from the PPE backbone to the NDI end-groups, and the transfer efficiency increases with decreasing the number of units.

Finally, the new physical insights reported in this thesis provide an understanding of several key variable components involved, thus paving the way toward the exploitation of efficient charge transfer at donor-acceptor interfaces, which is the key element and urgently required for optimal optoelectronic-device performance.
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"My great thanks to Allah for all the gifts he gave me”

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<th>Full Form</th>
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<tr>
<td>A</td>
<td>acceptor</td>
</tr>
<tr>
<td>Abs</td>
<td>absorbance</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>aluminum oxide</td>
</tr>
<tr>
<td>CdSe</td>
<td>cadmium selenide</td>
</tr>
<tr>
<td>CIP</td>
<td>contact ion pair</td>
</tr>
<tr>
<td>CR</td>
<td>charge recombination</td>
</tr>
<tr>
<td>CS</td>
<td>charge separation</td>
</tr>
<tr>
<td>CT</td>
<td>charge transfer</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>methanol</td>
</tr>
<tr>
<td>CD₃OD</td>
<td>tetradeuteromethanol</td>
</tr>
<tr>
<td>D</td>
<td>donor</td>
</tr>
<tr>
<td>DCB</td>
<td>1,4 dicyanobenzene</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DPV</td>
<td>differential pulse voltammetry</td>
</tr>
<tr>
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<td>fetetraphenyl porphyrin</td>
</tr>
<tr>
<td>FI</td>
<td>free ions</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster resonance energy transfer</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>fs</td>
<td>femtosecond</td>
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<tr>
<td>Fs-TA</td>
<td>femtosecond transient absorption</td>
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<tr>
<td>GC</td>
<td>graphene carboxylate</td>
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<td>GPC</td>
<td>gel permeation chromatography</td>
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<tr>
<td>GSB</td>
<td>ground state bleach</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<tr>
<td>ICT</td>
<td>intramolecular charge transfer</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ISC</td>
<td>intersystem crossing</td>
</tr>
<tr>
<td>LIP</td>
<td>loose ion pair</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<tr>
<td>Mn</td>
<td>number-average molecular weight</td>
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<tr>
<td>Mw</td>
<td>weight-average molecular weight</td>
</tr>
<tr>
<td>ms</td>
<td>millisecond</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<td>---------</td>
<td>-------------</td>
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<tr>
<td>mm</td>
<td>millimeter</td>
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<tr>
<td>NDI</td>
<td>naphthalene diimide</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance spectroscopy</td>
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<td>NP</td>
<td>nanoparticle</td>
</tr>
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<td>ns</td>
<td>nanosecond</td>
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<td>ns-TA</td>
<td>nanosecond transient absorption</td>
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<td>OPV</td>
<td>oligo(phenylenevinylene)</td>
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<tr>
<td>PbS</td>
<td>lead sulfide</td>
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<td>PCBM</td>
<td>phenyl-C$_{61}$-butyric acid methyl ester</td>
</tr>
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<td>PDI</td>
<td>polydispersity index</td>
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<tr>
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<td>phenylene ethynylene</td>
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<tr>
<td>PET</td>
<td>photoinduced electron transfer</td>
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<tr>
<td>PFN</td>
<td>poly[(9,9-di(3,3′-N,N′-trimethylammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyl)] diiodide salt</td>
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<td>PFP</td>
<td>poly [(9,9-bis(6′-N,N,N-trimethylammonium)hexyl)-fluorenylene phenylene dibromide]</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>POS</td>
<td>Meso tetra(4-phosphonomethylphenyl) porphine tetrasodium salt</td>
</tr>
<tr>
<td>PPE</td>
<td>poly-(phenylene ethynylene)</td>
</tr>
<tr>
<td>ps</td>
<td>picosecond</td>
</tr>
<tr>
<td>QDs</td>
<td>quantum dots</td>
</tr>
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<td>R.T.</td>
<td>room temperature</td>
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<td>SnO$_2$</td>
<td>tin dioxide</td>
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<tr>
<td>SSIP</td>
<td>solvent-separated ion pair</td>
</tr>
<tr>
<td>SV</td>
<td>Stern-volmer plot</td>
</tr>
<tr>
<td>TA</td>
<td>transient absorption</td>
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<td>TCNE</td>
<td>tetracyanoethylene</td>
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<td>time-correlated single-photon counting</td>
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<td>time dependent density functional theory calculation</td>
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<td>tetrahydrofuran</td>
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<tr>
<td>TiO$_2$</td>
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<tr>
<td>TIP</td>
<td>tight ion pair</td>
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<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible</td>
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<td>ZnO</td>
<td>zinc oxide</td>
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**LIST OF SYMBOLS**

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<td>$\beta$</td>
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<tr>
<td>$\beta_{CS}$</td>
<td>charge separation distance</td>
</tr>
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<td>$E_{abs}$</td>
<td>absorption potential</td>
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<tr>
<td>$E_{em}$</td>
<td>emission potential</td>
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<td>$E_{0}$</td>
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<td>oxidation potential</td>
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<td>$E_{red}^0$</td>
<td>initial reduction potential of the acceptor</td>
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<td>reduction potential</td>
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<td>$\epsilon$</td>
<td>molar absorption coefficient</td>
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<td>$C$</td>
<td>molar concentration</td>
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<td>$k_0$</td>
<td>initial rate constant</td>
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<td>$\tau$</td>
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<td>fluorescence carrier lifetime</td>
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<tr>
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<td>carrier lifetime</td>
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\( \mu s \)  
\( \eta \)  
\( r_{DA} \)  
\( V_{OC} \)  
\( I_{SC} \)  
\( \Phi_\Delta \)  
\( \nabla \)  
\( \Phi_i \)  
\( \phi_{ISC} \)  
\( \lambda \)  
\( \lambda_{abs} \)  
\( \lambda_f \)  
\( \lambda_{T-T} \)  
\( \Delta G \)  
\( \Delta G^{0}_{CR} \)  
\( \Delta G_{CR} \)  
\( \Delta G^{0}_{CS} \)  
\( \Delta G_{CS} \)  
\( \Delta A \)  
\( \Delta E_{0,0} \)

microsecond  
electron transfer efficiency  
donor–acceptor separation distance.  
open-circuit voltage  
short-circuit current  
work functions  
nonradiative recombination  
work functions for fluorescence quantum yields  
fluorescence quantum yield  
intersystem crossing efficiency  
wavelength  
absorption wavelength  
fluorescence wavelength  
triplet-triplet absorption  
gibbs free energy  
initial charge recombination free energy driving force  
charge recombination free energy driving force  
initial charge separation free energy driving force  
charge separation free energy driving force  
change in the absorbance  
singlet excited state energy.
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Chapter 1

Introduction

1.1 Photoinduced Electron Transfer (PET) in Donor-Acceptor Systems

Inter- and intramolecular photoinduced charge transfer between donor and acceptor units is one of the most fundamental processes in nature with many potential applications in solar cells,\textsuperscript{1-3} optical devices,\textsuperscript{4} chemical and biological sensors.\textsuperscript{5-6}

In a typical donor acceptor system, the absorption of light initiates the photoinduced electron transfer from a photoexcited donor (D) to an acceptor (A) molecule, resulting in the formation of radical ions \((A^-\bullet, D'^+\bullet)\)\textsuperscript{7} as shown in Scheme 1.1:

\begin{center}
\begin{tikzpicture}
    \node (D) [cylinder, draw, fill=green!30, shape aspect=0.1, minimum height=1cm, minimum width=1.5cm] at (0,0) {D};
    \node (A) [cylinder, draw, fill=red!30, shape aspect=0.1, minimum height=1cm, minimum width=1.5cm] at (2,0) {A};
    \node (D*) [cylinder, draw, fill=green!30, shape aspect=0.1, minimum height=1cm, minimum width=1.5cm] at (4.5,0) {D'^+};
    \node (A*) [cylinder, draw, fill=red!30, shape aspect=0.1, minimum height=1cm, minimum width=1.5cm] at (6.5,0) {A'^-};
    \node (electron) at (1.5,-0.5) {Electron donor};
    \node (electron acceptor) at (3.5,-0.5) {Electron acceptor};
    \node (cation radical) at (5.5,-0.5) {Cation radical};
    \node (anion radical) at (7.5,-0.5) {Anion radical};
    \node (electron transfer) at (3,-1) {Electron Transfer};
    \draw[-latex] (D) -- (A) node [midway, above] {Electron Transfer};
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.1} General intermolecular electron transfer process in donor acceptor system.

A deep understanding of the parameters that govern electron transfer process is very crucial for many potential applications. The bimolecular photoinduced electron transfer (PET) reaction between donor and acceptor species has been among one of the most studied chemical reactions that has attracted extensive experimental investigations.\textsuperscript{8-11} As mentioned previously, absorption of visible (Vis) or ultraviolet (UV) light initiates one electron in the donor molecule to its LUMO and is then transferred to the LUMO of the acceptor molecule. As a result, the donor is oxidized to \(D'^+\), while the acceptor is simultaneously reduced to \(A'^-\), see Figure 1.1.
Figure 1. Schematic of the photoinduced electron transfer (PET) process at a typical donor-acceptor interface. Modified from references.\textsuperscript{12-13}

In particular, the aspect of charge separation (CS) was a focus in the 1960s by Weller and co-workers who determined the driving force of the charge separation ($\Delta G_{CS}$) to be dependent on the bimolecular quenching rate ($k_q$) constant, which in turn was found to vary with the diffusing rate constant ($k$).\textsuperscript{8-11} The binding ability between the reactant species is also one of the strongest driving forces of electron transfer (ET), in a donor-acceptor of the biological systems including labeled single-stranded DNA with graphene oxide (GO), and a cationic conjugated polymer (PFP).\textsuperscript{6}

The electron transfer in Marcuse theory is basically passed on the electronic coupling between the reactants donor and acceptor where an electron can move or jump from one chemical species (D) to another chemical species (A). Then the reactant (D-A) transform to the products (D$^+$-A$^-$) via transition states (D---A). The work in his theory involved with the changes in internal bond length and angles as well as solvation. The basic theory has an activation factors:

$$A = k_{et} \nu_N k_p$$  \hspace{1cm} (1)
Where $k_{et}$ is the electron transfer rate, $\nu_N$ is nuclear frequency factor, and $k_p$ is complex equilibrium.

The activation energy is formulated in terms of driving force ($\Delta G^0$) and solvent reorganization energy ($\lambda$) by applying Gibbs free energy as quadratic function of solvent reaction coordinates.

$$\Delta G^\# = \left( -\frac{(\Delta G^0 + \lambda)^2}{4\lambda} \right)$$  \hspace{1cm} (2)

Where $\lambda$ is the reorganization energy, and its equal $\lambda = \lambda_i + \lambda_0$ where $\lambda_i$ and $\lambda_0$ are the energies involve in solvation and vibration, respectively.

**Figure 1.** Potential surface energy versus nuclear configuration plot of a donor acceptor system in electron transfer reaction. $\Delta G^0$ and the $\Delta G^\#$ are the free energy change and free energy of activation respectively. Redraw from reference.\textsuperscript{14}

And the electron transfer rate can be expressed by the Marcus-Hush theory:

$$k_{et} = \frac{2\pi}{\hbar} |H_{DA}| \frac{1}{\sqrt{4\pi \lambda k_B T}} \exp \left( \frac{-\left(\Delta G^0 + \lambda\right)^2}{4\lambda k_B T} \right)$$  \hspace{1cm} (3)

Where $|H_{DA}|$ is a matrix element for electronic coupling between the D and the A.
Depending on the value of the $H_{DA}$ the electron transfer process can be referred as adiabatic (When ($|H_{DA}| >> k_BT$)), and diabatic (or non-adiabatic) (when ($|H_{DA}| << k_BT$)). For most of the cases, the $k_{ET}$ depends on the electronic coupling parameter, $|H_{DA}|$.\textsuperscript{14}

The progress of such an ultrafast process can be monitored using time-resolved experiments (see later sections). It should be noted that the energy level alignment of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of the donor and the acceptor, respectively, is of crucial importance to control the charge transfer process. Thus, the D-A systems should be selected judiciously to promote the photoinduced electron transfer between the two relevant species. Several common types of donor-acceptor systems are well studied in chemistry and materials science communities. Here, we discuss and highlight some of these donor-acceptor systems.

### 1.2 Electron Transfer Mechanisms of Bimolecular Photoinduced Electron Transfer (PET) in Donor-Acceptor Systems

The most widely used reaction scheme of a bimolecular photoinduced electron transfer process in polar solvents in a donor-acceptor system is shown in Scheme 1.2.

The first reaction mechanism is in case of high exergonic CS, where D and A diffuse to each other to form reactive complex. Then electron transfer occurs from a donor to an acceptor, forming radical ions. The closed shell ions are contact ion pairs (CIP), which are also called tight or intimate ion pairs (TIP), (where these ion pairs are very close to each other). These contact ion pairs either recombine into the neutral ground-state or solvent-separated ion pairs (SSIP), and are also called loose ion pairs (LIP) (where these ion pairs are slightly separated from each
other) which dissociate to free ions at the end of the reaction. In other words, the LIP either recombine into a neutral state or form separated free ions (FI), as can be seen in Scheme 1.2, reaction mechanism (1).

![Diagram](image)

**Scheme 1.2** Most widely used scheme of a bimolecular photoinduced electron transfer reaction in polar solvent. Charge Separation (CS), contact ion pairs (CIP), tight ion pairs (TIP), loose ion pairs (LIP) solvent-separated ion pairs (SSIP), and free ions (FI). Modified from reference.¹⁵

The second possible reaction mechanism is at a low concentration of the donor and acceptor. In this case, long distance electron transfer occurs in the system, forming loose radical ion pairs (LIP) which are separated to free ions (FI) at the end of the reaction, as shown in the reaction mechanism (2).

The third possible reaction mechanism is the formation of ground state complex at very high concentration of the donor and acceptor. In this case, ultrafast electron transfer occurs to form TIP, which recombine quickly to the ground state, as shown in the reaction mechanism (3).
1.3 Types of Photoinduced Electron Transfer (PET) in Donor-Acceptor Systems

As mentioned above, several common types of donor-acceptor systems are well studied in chemistry and materials science communities. Here, we discuss and highlight some of these donor-acceptor systems, which can undergo either inter- or intramolecular charge transfer pathways:

1.3.1 Photoinduced Intermolecular Charge Transfer in Donor and Acceptor System

Intermolecular CT occurs when the donor and acceptor are well separated from each other in the ground state, and the generated excitons need to diffuse to the interface where the charge transfer takes place. As mentioned earlier, intermolecular CT complexes are formed upon mixing a strong electron donor with a strong electron acceptor as shown in Scheme 1.2. The driving forces, including energy level alignment, electronic structure of the donor, and solvent polarity have a great impact on controlling the charge transfer rate in such (D-A) systems. Factors including electrostatic interaction and electronic coupling between the reactant donor and acceptor are also important parameters to control CT at the interface of the donor and acceptor units. It should be noted that the CT complexes generally exhibit a discrete absorption band in the near UV or visible region, which is spectrally resolved from those of A and D. In the section below, a description for intermolecular CT and the associated driving force operating behind it are given.

Depending on the nature of the species involved, intermolecular CT can be classified into various types, such as organic donor/organic acceptor, organic donor/inorganic acceptor, inorganic donor/organic acceptor, and inorganic donor/inorganic acceptor.
a) **Organic donor/Organic acceptor**

In this case, the donor and acceptor units are organic molecules with well-defined HOMO and LUMO energy levels.

Mohammed et al. have provided a general scheme by an implementation of femtosecond time-resolved IR spectroscopy for the bimolecular ET between the organic donor 3-methylperylene (MePe) and the strong electron organic acceptor tetracyanoethylene (TCNE), as shown in Figure 1.3. They found that in two different solvents, namely polar acetonitrile (ACN) and a weak solution of polar dichloromethane (CH$_2$Cl$_2$), the TIPs and LIPs can be distinguished by their respective frequency positions of the C≡N stretching bands for TCNE.$^{16}$

The donor and acceptor form a complex in the ground state that generate directly tight ion pairs (TIP) upon photoexcitation. These TIPs form a loose complex followed by separation into free ions.

It should be point out that the CR happens for TIP or LIP with different lifetimes as indicated by time-resolved transient absorption experiments. This example confirms the importance of the electronic coupling between the donor and acceptor to dictate the intermolecular CT dynamics in the system. In addition, this work provide new physical insights into the impact of the solvent on the photoinduced intermolecular CT between the donor and acceptor units.
Figure 1. General scheme for bimolecular ET between donor D and acceptor A. Solid arrows indicate charge separation (CS), charge recombination (CR), and molecular diffusion. Photoinduced local excitation (LE) to the $S_1$ state of the donor D* and charge-transfer (CT) excitation of a ground-state complex DA to TIPs are indicated by wavy lines. The solid gray lines indicate solvation or desolvation. Copyright from reference.16

Aly and co-workers have recently reported the impact of adding Pt metal into the organic donor. They found that Pt metal ions have a significant impact on the CT and CR in an organic donor/organic acceptor system.17 They used platinum oligomer (DPP-Pt(acac)) as an electron donor with porphyrin as an electron acceptor and they found by using femtosecond (fs) transient absorption (TA) spectroscopy, that turning the CT on and off is very possible by switching from an organometallic oligomer to a metal-free oligomer. In addition, they found that the metallic center in the DPP-Pt(acac) oligomer donor and the positive charge on the porphyrin acceptor are the keys to switching on and off the ultrafast CT process.
Muraoka and co-workers have investigated theoretically and experimentally the electron transfer and charge separation in PTB7, PTB1, and PTBF2 donors and PC$_{71}$BM acceptor systems. They found that the variation of dipole moments between the ground and excited states of the donor-acceptor complexes are the keys to control the charge transfer process and the solar cell efficiency. They proposed that increasing the distance between donor and acceptor and having a large amount of variation of dipole moments of the donor-acceptor complexes are a requirement for developing high-efficiency polymer/PCBM solar cells.

**b) Inorganic donor/Organic acceptor**

Inorganic donors such as semiconductor quantum dots (QDs) have also emerged as interesting case studies for photoinduced electron transfer. More specifically, understanding the dynamics of the electron transfer at the surface of the QDs, is a key component in determining the utility of these semiconducting QDs in potential applications that principally rely on the interfacial dynamics such as light-emitting diodes, p-n junctions, and photo-catalysis.

El-Ballouli et al. have explored and deciphered the impact of the size of PbS QDs on the electron transfer process to Phenyl-C$_{61}$-butyric Acid Methyl Ester (PCBM) acceptor molecules. The steady-state PL quenching and TA spectroscopy results reveal that only small-sized PbS QDs (880) with a bandgap larger than 1 eV can transfer an electron to PCBM within 120 fs upon light absorption. This observation is supported by suitable energy band alignment as shown in Figure 1.4, tuned by the quantum size effect.
Figure 1. Schematic illustrates the energy alignment for the quantum dot donor and PCBM acceptor, (top figure), and the PbS QD size dependence in tuning the electron injection at interfaces; PbS-880 (left), PbS-1470 (right) QD donors show a fast ET (more than 120 fs) in the small size QD, whereas no ET was found in the case of the larger size of the QD donor react with PCBM acceptor. Copyright from reference.20

However, the largest size quantum dots, PbS (1470), with a bandgap less than 1 eV, cannot transfer the electron to the PCBM molecular acceptor. As a result, energy alignments and quantum confinement could be one of the key prerequisites for CT to occur and control in an inorganic donor and organic acceptor system.

Another example of electron transfer at inorganic donor/organic acceptor interfaces is the inorganic CuInS$_2$/ZnS (QD) and positively charged trimethylamino-functionalized iron tetraphenylporphyrin (FeTMA) organic acceptor. In this work, Lian and co-workers have
described the use of electrostatic self-assembly driven charge transfer (CT) in this donor-acceptor system. They found that when a negatively charged colloidal CuInS$_2$/ZnS quantum dot (QD) reacts with positively charged organic acceptor (FeTMA), to photoreduce carbon dioxide (CO$_2$) to carbon monoxide (CO) in water, upon illumination with 450 nm light, the CT from QD donor into the organic acceptor exhibit different lifetimes at the interfaces (based on the size of assemblies), as indicated from time-resolved measurements. The size of assemblies formed in the mixture is controlled by the addition of K$^+$, which leads to increase the electrostatic interaction compared to the QD-to- fetetraphenyl porphyrin (FeTPP) process. These dynamics suggest that the donor-acceptor electronic coupling between the charged QD and FeTMA is smaller than that of uncharged QD and FeTPP.

**c) Organic donor/Inorganic acceptor**

Lead halide perovskites have been the focus of a great number of studies as a model system for photoinduced electron transfer in organic/inorganic donor-acceptor systems. One of the most common studies is to involve TiO$_2$ as an electron transporting layer. The mechanism of electron transfer and charge separation in such a system can be described by electron and hole injection as shown below in the equations:

First, electron injection:

\[
(e^- \ldots h^+)_{\text{perovskite}} \rightarrow e_{cb}^- (TiO_2) + h^+ (\text{perovskite}) \quad (4a)
\]

\[
h^+ (\text{perovskite}) \rightarrow h^+ (HTM) \quad (4b)
\]

Second, hole injection:

\[
(e^- \ldots h^+)_{\text{perovskite}} \rightarrow h^+ (HTM) + e^- (\text{perovskite}) \quad (5a)
\]

\[
e^- (\text{perovskite}) \rightarrow e_{cb}^- (TiO_2) \quad (5b)
\]
Exciton annihilation:

\[(e^- \ldots h^+)_{\text{perovskite}} \rightarrow h\nu\quad (\text{Emitting photon}) \tag{6}\]

\[(e^- \ldots h^+)_{\text{perovskite}} \rightarrow \nabla \quad (\text{Non-radiative}) \tag{7}\]

Back electron transfer at the TiO\textsubscript{2} surface:

\[e_{cb}^- (TiO_2) + h^+ (\text{perovskite}) \rightarrow \nabla \tag{8}\]

Back charge transfer at the HTM surface:

\[h^+ (HTM) + e^- (\text{perovskite}) \rightarrow \nabla \tag{9}\]

Charge recombination at the TiO\textsubscript{2} | HTM interface:

\[e_{cb}^- (TiO_2) + h^+ (HTM) \rightarrow \nabla \tag{10}\]

Here, \(\nabla\) represents the non-radiative recombination of the charge carriers at the interfaces.

Charge separation and charge carrier recombination processes are closely related to the method of preparing the samples.

d) **Inorganic donor/Inorganic acceptor**

Inorganic donors such as quantum dots combined with an inorganic acceptor such as metal oxide nanoparticles, offer attractive systems to investigate the photophysics properties of inorganic donor and inorganic acceptor photoinduced charge transfer process. Tvrdy and others, in 2011 made a comprehensive study on the photoinduced electron transfer from semiconductor quantum dots donors (CdSe) with different sizes: 2.8, 3.3, 4.0, and 4.2 nm in diameter to metal oxide nanoparticles acceptors (SnO\textsubscript{2}, TiO\textsubscript{2}, and ZnO).\textsuperscript{24} The study showed that charge transfer is strongly affected by the metal oxide nanoparticles acceptors. The CdSe QD with a size of 4.2 nm diameter reacts with three different metal oxide NP acceptors. In this work, the TA measurements show that CT from CdSe QD to SnO\textsubscript{2} nanoparticle acceptor is faster
than the case of TiO$_2$, and ZnO for the same size of the QD with electron transfer rate constants of $k_{ET} = 4.62 \times 10^{11}$ S$^{-1}$, 5.07$ \times 10^{10}$ S$^{-1}$, and 1.86$ \times 10^{10}$ S$^{-1}$, respectively. This can be attributed to the difference in energy level alignment between the QDs and metal oxides as shown in Figure 1.5.

![Figure 1.5](image)

**Figure 1.5** Diagram of the relative electronic energy differences between CdSe donating species and metal oxide (MO) accepting species for all CdSe-MO combination used in this study.$^{24}$

Copyright from reference.$^{24}$

It should be noted that knowing the photophysics of electron transfer along with hole transfer in inorganic donor/inorganic acceptor is essential to develop the next generation of solar cells, light emitting diodes, and nanostructured electronic array.$^{24}$ Early this year, Dana et. al have investigated the electron and hole transfer between cesium lead bromide (CsPbBr$_3$) perovskite nanocrystals (NCs) and cadmium selenide (CdSe) quantum dots (QDs) interfaces.$^{25}$ The results of the time resolve spectroscopy show that electron and hole transfer time constant between perovskite nanocrystals and the (CdSe) quantum dots are 500 and 750 fs, respectively. They also found that the size and the energy level alignment control the injection rate at the interface of these nanocrystals.
1.3.2 Photoinduced Intramolecular Charge Transfer (ICT) in Donor-Acceptor System

The intramolecular CT is operative when the donor and the acceptor are chemically attached to each other, such as those found in other small molecules. For instance, it has been found that the solvent can strongly effect the intramolecular CT in formylperylene (FPe) small molecules.\textsuperscript{26} It was found that the ultrafast intramolecular charge transfer from the perylene unit to the formyl (CHO) group can be facilitated by hydrogen-bonding interactions between the carbonyl group oxygen of FPe and hydrogen-donating solvents in the electronically excited state.\textsuperscript{26} (see Figure 1.6).

![Molecular structures of H-bonded FPe and protonated FPe](image)

**Figure 1.6** Molecular structures of H-bonded FPe and protonated FPe\textsuperscript{a,26}

\textsuperscript{a}The dotted line shows the hydrogen-bond formation between MeOH and the carbonyl group of FPe and the H-bond networks between solvent molecules. Copyright from reference.\textsuperscript{26}

In addition, it was demonstrated that a site-specific hydrogen-bonding interaction of FPe with the protic solvent, leads to a significant stabilization of the emitting state of the FPe, as reflected in the additional spectral red shift of the emission spectra in MeOH with respect to
ACN. The large increase in the dipole moment upon excitation, is likely caused by the charge redistribution in the excited state due to charge transfer from the perylene moiety (rich electron donor) to the electron-acceptor group (CHO).\textsuperscript{26}

Furthermore, Intramolecular charge transfer (ICT) is also found in conjugated systems such as polymers or oligomers. Conjugated systems (with alternating single and multiple bonds) are chemical structures in which $\pi$-orbital bonding plays a crucial role as showing in Scheme 1.3:

\begin{center}
\begin{tikzpicture}
    \node (D) at (0,0) {$D$};
    \node (A) at (2,0) {$A$};
    \node (Ddot) at (0,1) {$D^+$};
    \node (Am) at (2,1) {$A^-$};
    \node (n) at (0,-0.5) {$D \pi A$};
    \node (n1) at (2,-0.5) {$D^+ \pi A^-$};
    \node (E) at (0,1.5) {Electron donor};
    \node (F) at (2,1.5) {Electron acceptor};
    \node (G) at (0,0.5) {Cation radical};
    \node (H) at (2,0.5) {Anion radical};
    \draw[->,thick] (D) -- (A);
    \draw[->,thick] (Ddot) -- (Am);
    \draw[->,thick] (n) -- (n1);
    \node (I) at (1,1.5) {$hv$};
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.3} General concept for the intramolecular electron transfer process in donor-acceptor system.\textsuperscript{27} Modified from reference\textsuperscript{27}

This leads to charge delocalization over the bonds participating in the conjugation and results in a decrease of the energy of the molecule and an increased stability.\textsuperscript{28}

It is worth mentioning that ICT is affected by the nature of the donor and acceptor groups (for example the energy band alignment, twisting angle between moieties), solvent (polarity, viscosity, hydrogen bonding capability) and the length of the $\pi$ system over which the charge is transferred.\textsuperscript{29}

The key issue in determining the efficiency of intramolecular CT, lies in understanding the role of the charge hoping or charge transfer through $\pi$-conjugated spacers in donor-bridge-acceptor (D-B-A) molecular assemblies, the mechanism of which remains under debate.

For example Wasielewski and co-workers have explored electron transfer across oligo(p-phenylene) bridges in a D-B-A system, featuring a perylene diimide acceptor and phenothiazine
as the donor. Albinsson and co-workers have carried out systematic investigations of electron transfer in porphyrin-based D-B-A systems, in which the bridge was a series of oligo(phenylene ethynylene)s (OPEs) with varying lengths.

1.4 Objectives and Outline

1.4.1 Objective of this Dissertation

The objective of this thesis is to investigate the photophysical properties of inter- and intramolecular electron transfer at donor-acceptor interfaces using ultrafast broadband time-resolved spectroscopy, to allow the monitoring of the evolution of charge-separated moieties in D-A systems.

1.4.2 Outline of the Dissertation

First, a detailed introduction will be given at the beginning of each chapter to explain the background, perspective and aim of the work reported.

Chapter 1 provides a broad overview of the existing knowledge available in literature, regarding photoinduced intermolecular as well as intramolecular CT in D-A systems.

Chapter 2 provides materials and techniques used in this dissertation.

Chapter 3 includes a study on bimolecular excited-state electron transfer with surprisingly long-lived radical ions using Poly[(9,9-di(3′-N,N′-trimethylammonium) propyl fluorenyl-2,7-diyi)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyi)] diiodide salt (PFN) as a donor and 1,4 dicyanobenzene (DCB) as an acceptor.

Chapter 4 includes a study on real-time observation of intersystem crossing induced by charge recombination during bimolecular electron transfer reactions in PFN and DCB system.
Chapter 5 deals with the bane of hydrogen-bond formation on the photoinduced charge-transfer process in negative porphyrin (POS) as a donor with positive PFN acceptor interface.

In chapter 6, we investigate the dynamics of the synthesized series of π-conjugated monomers/polymers OPE and study the effect of conjugation length on photoinduced charge transfer in π-conjugated oligomer-acceptor dyads.

Chapter 7 deals with charge separation in different chain length conjugated polymers (PPE).

Chapter 8 provides a study on ultrafast intermolecular charge transfer between positively charged PFN and negatively charged graphene carboxylate (GC) system.

Chapter 9 offers an overall conclusion of this work and gives prospects for future investigations.
Chapter 2

Materials and Methods

2.1 Materials

Poly[(9,9-di(3,3′-N,N’-trimethylammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyl)] diiodide salt (PFN) was purchased from Solaris Chem. Inc. and 1,4 dicyanobenzene (DCB) (98%) was purchased from Sigma-Aldrich. In all the experiments described here, high-purity dimethyl sulfoxide (DMSO; 99.9%; Sigma-Aldrich) was used as the solvent.

Meso-Tetra (4-phosphonomethylphenyl) porphine tetrasodium salt (POS) (Frontier Scientific), PFN (Solaris Chem Inc.), methanol (CH$_3$OH, 99.9%, Sigma Aldrich), N,N-dimethylformamide (DMF, 99.8%, Sigma Aldrich), acetonitrile (ACN 99.9%, Alfa Aesar), and methanol-d (CD$_3$OD 99.5+ % (isotopic), Alfa Aesar) were used as procured without further purification.

Synthesis of PE4-TIPS and PE4-NDI

Unless specified, all compounds and solvents were purchased from commercial sources (Aldrich, Acros, Strem Chemicals, et al) and used without further purification. For all palladium-catalyzed reactions, the solvents were carefully degassed with argon for 30 minutes.

Tetrakis(triphenyl phosphine) palladium (Pd(PPh$_3$)$_4$) was purchased from Strem Chemical, triisopropylsilyl acetylene and trimethylysilylacetylene was purchased from TCI. Copper(I) iodide (CuI), diisopropylamine ((i-Pr)$_2$NH), Tetra-n-butylammonium fluoride in THF (1 M), Na$_2$CO$_3$, Methanol, tetrahydrofuran (THF) and all other chemicals were purchased from either Sigma-Aldrich or Fisher Chemicals. All reagents were used without further purification unless specified.
Chart 2. 1: Synthesis steps for all PEn-NDI oligomer.\textsuperscript{36}

Compounds 1\textsuperscript{37}, 2\textsuperscript{38}, 8\textsuperscript{13} were synthesized according to references.

**Compound 3**

Compound 2 (2.33 g, 4.67 mmol) and Compound 1 (1.1 g, 3.89 mmol) were dissolved in a mixed solvent of THF (75 ml) and diisopropylamine (45 ml) and degassed with argon for 30 minutes. Pd(PPh\textsubscript{3})\textsubscript{4} (219 mg, 0.19 mmol) and Cul (74 mg, 0.39 mmol) were added under argon protection. The mixture was degassed for another 30 minutes and stirred at room temperature (R.T.) overnight, under argon protection. The mixture was filtered and the solution was evaporated under vacuum. The oil was purified by column with hexane as eluent to yield compound 3 (1.2 g, 46%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 7.67 (s, 1H), 7.44 (dd, 4H), 7.30 (s, 1H), 2.73 (t, 2H), 2.65 (t, 2H), 1.56-1.67 (m, 4H), 1.26-1.39 (m, 12H), 1.14 (s, 21H), 0.89 (m, 6H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): 11.35, 14.13, 18.70, 22.64, 29.08, 29.24, 30.23, 30.67, 31.70, 33.89, 40.25, 89.64, 92.86, 93.18, 101.20, 106.67, 122.51, 123.26, 123.40, 131.18, 132.02, 132.22, 139.54, 142.82, 144.12 ppm.\textsuperscript{36}
**Compound 4**

Compound 2 (5 g, 10 mmol) and 1-Ethynyl-4-methylbenzene (1.16 g, 10 mmol) were dissolved in mixed solvent of THF (100 ml) and diisopropylamine (50 ml) and degassed with argon for 30 minutes. Pd(PPh$_3$)$_4$ (347 mg, 0.3 mmol) and CuI (114 mg, 0.6 mmol) were added under argon protection. The mixture was degassed for another 30 minutes and stirred at R.T. overnight, under argon protection. The mixture was filtered and the solution was evaporated under vacuum. The oil was purified by column with hexane as eluent to yield compound 4 (2.2g, 45%).

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.66 (s, 1H), 7.41 (d, 2H), 7.30 (s, 1H), 7.16 (d, 2H), 2.74 (t, 2H), 2.65 (t, 2H), 1.57-1.67 (m, 4H), 1.31-1.39 (m, 12H), 0.89 (m, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 14.50, 21.93, 23.01, 29.43, 29.60, 30.61, 30.97, 32.11, 34.26, 40.62, 87.59, 94.05, 101.01, 120.70, 123.32, 129.55, 131.72, 132.56, 138.85, 139.81, 143.08, 144.41 ppm.

**Compound 5**

Compound 4 (1.9 g, 3.9 mmol) was dissolved in mixed solvents of THF (45 ml) and diisopropylamine (25 ml) and degassed with argon for 30 min. Pd(PPh$_3$)$_4$ (218 mg, 0.19 mmol), CuI (74 mg, 0.39 mmol) and trimethylsilylacetylene (0.58 g, 5.85 mmol) were added under argon protection. The mixtures were stirred at R.T. overnight, under argon protection. The mixture was filtered and the solution was evaporated under vacuum to obtain crude products. The crude products were dissolved in mixed solvents of 4 ml of methanol and 8 ml of THF, 2 ml of KOH aqueous solution (10%) was added to the reaction solution. The mixtures were stirred at R.T. for overnight. After the reaction, the organic solvents were evaporated and dissolving in 30 ml dichloromethane, followed by washing with 30 ml of water three times. The organic solution was collected and dried with Na$_2$SO$_4$. The mixture was filtered and the solution was...
evaporated under vacuum. The oil was purified by column with hexane as eluent to yield compound 5 (1.1 g, 73%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.41 (d, 2H), 7.32 (d, 2H), 7.17 (d, 2H), 3.29 (s, 1H), 2.75(dt, 4H), 2.36 (s, 3H), 1.60-1.70 (m, 4H), 1.30-1.40 (m, 12H), 0.88-0.91 (m, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.12, 21.54, 22.65, 29.16, 29.24, 30.52, 30.58, 31.70, 31.77, 33.88, 34.10, 81.30, 82.56, 87.57, 94.20, 120.35, 121.15, 123.31, 129.17, 131.38, 132.14, 133.00, 138.46, 142.07, 142.75 ppm.$^{36}$

**Compound 6 (PE4-TIPS)**

Compound 3 (0.75 g, 1.15 mmol) and compound 5 (0.49 g, 1.26 mmol) was dissolved in a mixed solvent of THF (30 ml) and diisopropylamine (20 ml) and degassed with argon for 30 minutes. Pd(PPh$_3$)$_4$ (65 mg, 0.058 mmol), CuI (22 mg, 0.115 mmol) were added under argon protection. The mixtures were stirred at R.T. for overnight, under argon protection. The mixture was filtered and the solution was evaporated under vacuum. The solid was purified by column with hexane as eluent to yield compound 6 (0.87g, 84%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.41-7.46 (m, 6H), 7.34-7.37 (m, 4H), 7.16 (d, 2H), 2.75-2.84 (m, 8H), 2.38 (s, 3H), 1.70 (dd, 8H), 1.33-1.40 (m, 21H), 1.14 (m, 16H), 0.88 (m, 12H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 11. 34, 14.13, 14.16, 18.69, 21.54, 22.63, 22.67, 29.07, 29.22, 29.28, 29.29, 30.50, 30.61, 30.67, 30.70, 31.68, 31.76, 31.78, 31.85, 33.97, 34.09, 34.19, 78.24, 81.71, 87.64, 87.82, 90.34, 92.8093.22, 93.61, 94.19, 94.86, 106.68, 120.29, 120.44, 120.96, 122.22, 122.54, 122.80, 123.08, 123.31, 123.36, 123.70, 129.17, 129.18, 131.21, 131.37, 131.41, 132.02, 132.21, 132.30, 132.45, 132.49, 133.28, 138.42, 138.57, 141.88, 141.93, 142.18, 142.32, 143.64 ppm. MALDI-MS: m/z=908.6653 [M-H]$^+$ (calcd: 908.6650).$^{36}$ $^1$H NMR and $^{13}$C NMR figures are showing in supporting information (Figure S1).
**Compound 7**

Compound 6 (0.75 g, 0.825 mmol) was dissolved in chloroform (30 ml) and degassed with argon for 30 minutes. Tetrabutylammonium fluoride solution (2 ml, 1M in THF) was added under argon protection. The mixtures were stirred at R.T. for 24 hours, under argon protection. After the reaction, the organic solvents were evaporated and dissolving in 20 ml dichloromethane, followed by washing with water (20 ml) for 3 times. The organic solution was collected and dried with Na$_2$SO$_4$. The mixture was filtered and the solution was evaporated under vacuum.

The crude products were purified by column with hexane as eluent to yield compound 7 (350 mg, 56%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.46-7.49 (m, 4H), 7.42 (d, 2H), 7.35-7.36 (m, 4H), 7.17 (d, 2H), 3.18 (s, 1H), 2.79-2.83 (m, 8H), 2.38 (s, 3H), 1.67-1.73 (m, 8H), 1.25-1.41 (m, 24H), 0.86-0.89 (m, 12H). $^{13}$C NMR (75 MHz, CDCl$_3$): 614.12, 21.59, 22.66, 29.31, 30.66, 30.70, 31.77, 31.78, 31.84, 34.18, 78.95, 83.31, 87.81, 90.56, 92.80, 93.27, 93.32, 94.22, 120.43, 121.84, 122.10, 122.52, 122.82, 123.18, 124.00, 129.17, 131.32, 131.38, 132.12, 132.21, 132.33, 132.45, 132.50, 138.43, 141.90, 141.94, 142.18, 142.35 ppm.$^{36}$

**Compound 9 (PE4-NDI)**

Compound 7 (154 mg, 0.20 mmol) and compound 8 (100 mg, 0.17 mmol) were dissolved in a mixed solvent of THF (20 ml) and diisopropylamine (12 ml) and degased with argon for 30 minutes. Pd(PPh$_3$)$_4$ (9.7 mg, 0.0085 mmol) and Cul (3.3 mg, 0.017 mmol) were added under argon protection. The mixtures were stirred at R.T. for overnight, under argon protection. The mixture was evaporated under vacuum. The crude product was purified by column with dichloromethane as eluent to yield compound 9 (174 mg, 85%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.81 (m, 4H), 7.72 (d, 2H), 7.54 (m, 4H), 7.42 (d, 2H), 7.31-7.34 (m, 6H), 7.17 (d, 2H), 4.2 (t, 2H),
2.78-2.85 (m, 8H), 2.38 (s, 3H), 1.68-1.75 (m, 10H), 1.29-1.44 (m, 34H), 0.87-0.91 (m, 15H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 14.11, 14.14, 14.15, 27.12, 28.10, 29.22, 29.30, 29.31, 30.66, 30.68, 30.71, 31.79, 31.82, 31.86, 34.19, 34.20, 41.09, 90.36, 90.42, 90.61, 92.86, 93.27, 93.63, 94.23, 120.41, 122.18, 122.51, 122.72, 122.79, 123.12, 123.63, 124.18, 126.51, 126.82, 127.03, 127.05, 128.74, 129.16, 130.98, 131.37, 131.40, 131.42, 131.70, 132.17, 132.31, 132.43, 132.49, 132.67, 134.44, 138.42, 141.88, 142.16, 142.34, 162.68, 162.84 ppm. MALDI-MS: m/z=1205.7106 [M]$^+$ (calcd: 1205.7085). $^1$H NMR and $^{13}$C NMR figures are shown in supporting information (Figure S2).

**Compound 10 (PE6-TIPS)**

Compound 3 (372 mg, 0.57 mmol) and compound 7 (215 mg, 0.286 mmol) were dissolved in a mixed solvent of THF (18 ml) and diisopropylamine (12 ml) and degassed with argon for 30 seconds to 10 minutes. Pd(PPh$_3$)$_4$ (16.5 mg, 0.014 mmol), Cul (5.4 mg, 0.028 mmol) were added under argon protection. The mixtures were stirred at R.T. overnight, under argon protection. The mixture was filtered and the solution was evaporated under vacuum. The crude product was purified by column with hexane as eluent to yield compound 10 (230mg, 63%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.53 (s, 4H), 7.47 (m, 4H), 7.44 (d, 2H), 7.39 (t, 6H), 7.19 (d, 2H), 2.79-2.85 (m, 12H), 2.39 (s, 3H), 1.70-1.75 (m, 12H), 1.28-1.44 (m, 36H), 1.16 (m, 21H), 0.88-0.91 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 11.32, 14.11, 18.67, 21.52, 22.64, 22.65, 29.28, 30.66, 31.77, 31.84, 34.19, 87.81, 90.28, 90.41, 90.53, 92.84, 93.25, 93.67, 93.76, 93.79, 94.20, 106.67, 120.42, 122.20, 122.52, 122.80, 123.11123.24, 123.33, 129.14, 131.20, 131.36, 131.42, 132.00, 132.19, 132.30, 132.35, 132.43, 132.48, 138.39, 141.87, 141.92, 142.16, 142.34 ppm. MALDI-
MS: m/z=1277.9205[M]+ (calcd: 1277.9186).\textsuperscript{36} \textsuperscript{1}H NMR and \textsuperscript{13}C NMR figures are showing in supporting information (Figure S3).

**Compound 11**

Compound 10 (250 mg, 0.20 mmol) was dissolved in THF (10 ml) and degassed with argon for 30 minutes. Tetrabutylammonium fluoride solution (1ml, 1M in THF) was added under argon protection. The mixtures were stirred at 40 °C overnight, under argon protection. After the reaction, the organic solvents were evaporated and dissolved in 20 ml dichloromethane, followed by washing with water (20 ml) three times. The organic solution was collected and dried with Na\textsubscript{2}SO\textsubscript{4}. The mixture was filtered and the solution was evaporated under vacuum. The crude products were purified by column with hexane: dichloromethane (20:1) as eluent to yield compound 11 (187 mg, 83%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.57 (s, 4H), 7.49 (m, 4H), 7.44 (d, 2H), 7.39 (dd, 6H), 7.18 (d, 2H), 3.19 (s, 1H), 2.80-2.87(m, 12H), 2.39 (s, 3H), 1.70-1.75 (m, 12H), 1.28-1.45 (m, 36H), 0.89-0.92 (m, 18H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): δ 14.14, 22.69, 29.21, 29.32, 30.66, 30.70, 31.77, 31.87, 34.15, 34.20, 78.94, 83.29, 87.82, 90.37, 90.48, 90.56, 92.88, 93.24, 93.48, 93.66, 93.85, 94.22, 120.44, 121.89, 122.21, 122.42, 122.54, 122.62, 122.82, 123.13, 123.23, 123.37, 123.95, 129.17, 131.33, 131.38, 131.44, 132.12, 132.21, 132.32, 132.40, 132.45, 132.50, 138.42, 141.88, 141.95, 142.18, 142.32, 142.38, 142.39 ppm.\textsuperscript{36}

**Compound 12 (PE6-NDI)**

Compound 8 (51.7 mg, 0.09 mmol) and compound 11 (50 mg, 0.045 mmol) were dissolved in a mixed solvent of THF (8 ml) and diisopropylamine (4 ml) and degassed with argon for 30 minutes. Pd(PPh\textsubscript{3})\textsubscript{4} (4.6 mg, 0.0045 mmol), Cul (1 mg, 0.005 mmol) were added under argon protection. The mixtures were stirred at R.T. overnight, under argon protection. The mixture
was evaporated under vacuum. The crude product was purified by column with dichloromethane as eluent to yield compound 12 (52mg, 73%). $^1$H NMR (300 MHz, CDCl$_3$): δ 8.80 (m, 4H), 7.72 (d, 2H), 7.53 (m, 8H), 7.42 (d, 2H), 7.36 (m, 6H), 7.32 (d, 2H), 7.17 (d, 2H), 4.2 (t, 2H), 2.80-2.84 (m, 12H), 2.38 (s, 3H), 1.69-1.76 (m, 14H), 1.29-1.44 (m, 46H), 0.88-0.92 (m, 21H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 14.12, 21.55, 22.67, 22.70, 27.12, 28.09, 29.23, 29.29, 29.31, 30.66, 30.69, 30.71, 31.79, 31.83, 31.86, 34.18, 41.09, 87.82, 90.35, 90.43, 90.51, 90.55, 92.86, 93.27, 93.71, 93.77, 93.87, 94.22, 120.42, 122.21, 122.50, 122.53, 122.56, 122.78, 122.81, 123.12, 123.24, 123.34, 123.57, 124.16, 126.50, 126.81, 127.04, 128.75, 129.17, 130.96, 131.38, 131.44, 131.71, 132.19, 132.30, 132.38, 132.44, 132.50, 132.67, 134.45, 138.43, 141.88, 141.93, 142.16, 142.32, 142.55, 162.65, 162.82 ppm. MALDI-MS: m/z=1573.9569 [M-H]$^+$ (calcd: 1573.9589). $^1$H NMR and $^{13}$C NMR figures are shown in supporting information (Figure S4).

**Compound 13 (PE8-TIPS)**

Compound 3 (217 mg, 0.33 mmol) and compound 11 (187 mg, 0.167 mmol) were dissolved in a mixed solvent of THF (18 ml) and diisopropylamine (12 ml) and degassed with argon for 30 minutes. Pd(PPh$_3$)$_4$ (9.6 mg, 0.0084 mmol), Cul (3.2 mg, 0.017 mmol) were added under argon protection. The mixtures were stirred at R.T. overnight, under argon protection. The mixture was filtered and the solution was evaporated under vacuum. The crude product was purified by column with hexane: dichloromethane (10:1) as eluent to yield compound 10 (170mg, 62%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.53 (s, 8H), 7.44-7.47 (m, 6H), 7.39 (m, 8H), 7.18 (d, 2H), 2.85 (m, 16H), 2.39 (s, 3H), 1.75 (m, 16H), 1.28-1.44 (m, 48H), 1.16 (m, 21H), 0.88-0.91 (m, 24H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 11.35, 14.15, 18.70, 21.57, 22.65, 22.68, 29.27, 29.32, 30.67, 30.74, 31.77, 31.81, 31.88, 34.18, 87.82, 90.29, 90.43, 90.55, 92.86, 93.27, 93.69, 93.79, 93.83, 94.22,
Compound 14

Compound 13 (120 mg, 0.073 mmol) was dissolved in THF (12 ml) and degassed with argon for 30 minutes. Tetrabutylammonium fluoride solution (2 ml, 1 M in THF) was added under argon protection. The mixtures were stirred at 40 °C overnight, under argon protection. After the reaction, the organic solvents were evaporated and dissolved in 20 ml dichloromethane, followed by washing with water (20 ml) three times. The organic solution was collected and dried with Na₂SO₄. The mixture was filtered and the solution was evaporated under vacuum. The crude products were purified by column with hexane: dichloromethane (10:1) as eluent to yield compound 14 (100 mg, 92%). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.58 (s, 8H), 7.53 (m, 4H), 7.42-7.48 (m, 10H), 7.24 (d, 2H), 3.29 (s, 1H), 2.87 (m, 16H), 2.42 (s, 3H), 1.75 (m, 16H), 1.30-1.47 (m, 48H), 0.88-0.91 (m, 24H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 13.86, 21.22, 22.68, 29.20, 29.65, 30.67, 30.67, 31.77, 31.78, 31.89, 34.09, 78.84, 83.03, 87.63, 90.28, 90.34, 92.80, 93.17, 93.38, 93.60, 93.72, 94.17, 120.27, 121.89, 122.21, 122.52, 122.53, 122.58, 122.79, 123.09, 123.23, 123.25, 123.28, 123.32, 123.90, 129.18, 131.27, 131.32, 131.41, 132.09, 132.14, 132.28, 132.35, 132.37, 132.40, 132.45, 138.73, 142.03, 142.07, 142.26, 142.45, 142.49, 142.52 ppm.

Compound 15 (PE8-NDI)

Compound 8 (50.6 mg, 0.088 mmol) and compound 14 (65 mg, 0.044 mmol) were dissolved in a mixed solvent of THF (10 ml) and diisopropylamine (4 ml) and degassed with argon for 30
minutes. Pd(PPh₃)₄ (4.6 mg, 0.0045 mmol), Cul (1 mg, 0.005 mmol) were added under argon protection. The mixtures were stirred at R.T. overnight, under argon protection. The mixture was evaporated under vacuum. The crude product was purified by column with dichloromethane as eluent to yield compound 12 (65 mg, 76%). ¹H NMR (300 MHz, CDCl₃): δ 8.81 (m, 4H), 7.73 (d, 2H), 7.54 (m, 12H), 7.43 (d, 2H), 7.36 (m, 8H), 7.33 (d, 2H), 7.17 (d, 2H), 4.18 (t, 2H), 2.78-2.85 (m, 18H), 2.38 (s, 3H), 1.68-1.75 (m, 18H), 1.29-1.44 (m, 58H), 0.87-0.91 (m, 27H). ¹³C NMR (75 MHz, CDCl₃): δ 14.13, 21.56, 22.69, 27.12, 28.11, 29.22, 29.28, 29.30, 30.66, 30.69, 30.72, 31.79, 31.80, 31.82, 31.86, 34.17, 41.10, 87.74, 90.35, 90.42, 90.51, 90.53, 92.85, 93.27, 93.68, 93.76, 93.84, 94.21, 120.43, 122.21, 122.53, 122.78, 122.81, 123.12, 123.24, 123.29, 123.35, 123.58, 124.19, 126.52, 126.84, 127.07, 128.74, 129.17, 130.99, 131.37, 131.45, 131.71, 132.18, 132.29, 132.36, 132.39, 132.45, 132.50, 132.68, 134.44, 138.43, 141.88, 141.94, 142.17, 142.32, 142.36, 142.39, 162.70, 162.84 ppm. MALDI-MS: m/z=1942.2120 [M]+ (calcd: 1942.2091). ³⁶ ¹H NMR and ¹³C NMR figures are shown in supporting information (Figure S6).

**Synthesis of PPE-NDI-n Polymers**

The polymers were synthesized under Sonogashira polycondensation reaction conditions and molecular weight was controlled using the “end-capping” strategy during polymerization reactions. In a typical reaction, Monomer 1 and Monomer 2 (1:1 molar ratio) and various amounts of End-cap 1 were added into a flask. Without the presence of mono-functionalized End-cap 1, the polymer chain will keep growing. However, the addition of End-cap 1 changed the stoichiometric balance of the functional groups and lowered the overall molecular weight.
End-cap 2 was added at the end of polymerization to ensure efficient end-capping at both chain ends (see chart below):

![Chart 2: Synthesis of PPE-NDI-n Polymers.]

### 2.2 Techniques

#### 2.2.1 Absorption and Emission Measurements

Our steady-state absorption and emission spectroscopy are recorded on a Cary5000 UV-visible spectrometer (Agilent Technologies), and on a Fluoromax-4 spectrofluorometer (Horiba Scientific). The absorption spectrometer is a high performance UV-Vis-NIR with superb photometric performance in the range of 175 nm to 3300 nm wavelength. This makes it a powerful tool, providing important information about the absorption band and materials band gap for all kind of materials such as polymers, oligomers, QDs, nanoparticles and others in both liquid and solid states.

Furthermore, our emission spectrometer offers the sensitivity in fluorescence investigations, from 210 nm to 2400 nm, which means that analyzing the emission over a wide range is possible. However, for infrared wavelength, we need to use liquid nitrogen to measure the emission as it necessitates cooling of the detector. The source used is a xenon lamp and the slits are continuously adjusted by the software to preserve maximum resolution.
Before the excitation light reaches the sample, a photodiode reference detector monitors the intensity as a function of time and wavelength to correct for any change in the output. Our emission spectrometer can be used for different kind of samples both in solid and solution state. Both absorption and emission samples typically use 2-mm cuvettes to measure for liquid, and glass for film.

2.2.2 Pump-Probe Transient Absorption (TA) Spectroscopy

The principle of pump-probe transient absorption spectroscopy involves use of a ultra-short laser pump pulse, which photo-excites the sample under study from its ground state ($S_0$) to a higher excited state ($S_n$). Next, a probe pulse is sent to monitor the changes in the excited state and follow the events in real time. **Figure 2.1** depicts the scheme for our pump-probe transient absorption system.

![Pump-Probe Concept](image)

**Figure 2.1** Schematic depiction of the basic pump-probe experimental setup: pump pulse excites the sample, and the probe is used to measure the induced changes. The variable delay between the pump and probe pulses provides the time dependence of the different absorption signal.34
It is worth mentioning that the pump pulse should be more intense than the probe pulse, because it induces the change in the molecules. However, the probe only interrogates the subsequent environment. The probe pulse should ideally not have any influence on the sample under investigation.

Time-resolved spectroscopy is a well-known technique and one of the most powerful tools, which provides information on the excited state spectra and carrier dynamic lifetime. It also helps distinguish whether the process undergoes an energy transfer or a charge transfer reaction. It can also reveal the effect of solvents (like polarity and hydrogen bond dynamics) on the CT. Moreover, it can provide information on molecular motion and the molecular environment which are not available from steady-state measurements.\(^{39}\)

In our lab, we have two kind of time-resolved spectroscopy systems for studying different regimes of ultrafast processes, namely electronic and vibrational spectroscopies.

Our electronic time-resolved spectroscopy technique involves UV-vis pump and UV-vis probe pulses. We first excite the molecules with the pump (UV-vis), and probe the \(S_1\) to \(S_n\) transition using white light. In this technique, a pump pulse excites an electronic transition to bring the molecule into the electronically excite state. Here, one can turn the probe pulse to transitions between the transient state and the higher laying state (\(A-S_1\) to \(A-S_n\)) for the reactants and (\(B-S_1\) to \(B-S_n\)) for the products, (see Figure 2.2).
For our electronic time-resolved spectroscopy, we have two main setups (Ultrafast Systems); with femtosecond (fs) and nanosecond (ns) capabilities consisting of HELIOS and EOS TA systems. In the fs-TA or HELIOS setup, the instrument produces spectral and kinetic data that are desirable for investigations of photoexcitation events with ultrafast time resolutions (120 fs and detection limits of 5.5 ns time window) throughout its broad spectral coverage and longtime window. However, for the ns-TA measurements, the EOS laser system is employed, where a broadband pump-probe sub-nanosecond TA spectrometer is designed to work with ∼1 kHz repetition rate laser, to allow the collection of broadband TA spectra over a greatly extended time regime, ranging from several ns, to hundreds of µs (ns-µs time window), following photoexcitation. In our setup, the fundamental laser is provided by a Ti:Sapphire femtosecond regenerative amplifier (Spectra-Physics Spitfire Pro 35F-XP), which produces 35 fs pulses at 800 nm with 4 mJ of energy/pulse, and a repetition rate of 1 kHz. The pump
(excitation) beam is tuned by passing 1 mJ of the fundamental ($\lambda=800$ nm) through an optical parametric amplifier (TOPAS-C stage) to tune its wavelength ($\lambda=240$-2600 nm), and selectively excite specific electronic transitions within a sample.\textsuperscript{41} Finally, a two-channel probe (probe-reference) method is used. In this method, the probe beam is split into two before passing through the sample. While one arm travels through the sample, the other is sent directly to the reference spectrometer that monitors the fluctuations in the probe beam intensity.\textsuperscript{41} As for the probe beam, a small portion of the fundamental ($\sim 60 \mu J$) is routed via a computer controlled delay line, adjustable pinholes, focusing lens, and the variable neutral density filter to a crystal for white light continuum (WLC) generation. The white probe beam is then directed towards the sample via a focusing mirror. The delay between the pump and probe pulses can be varied to allow TA measurements within 5.8 ns (HELIOS) and 400 $\mu$s (EOS) time windows.\textsuperscript{17}

The pump and probe beams are adjusted to overlap spatially and temporally on the sample. The chosen spectrometer collects the probe beam after passing through filters that reduce the white light around the Spitfire fundamental at 800 nm. The TA spectra are usually averaged until the desired signal-to-noise ratio is achieved. For both the fs- and ns-TA, only the total absorption signals obtained are recorded as shown in Figure 2.3. Finally, global analysis fitting procedures are applied to extract the kinetics of dynamical processes from the TA spectra.\textsuperscript{41}
2.2.3 Femtosecond Infrared Transient Absorption (fs-IRTA) Spectroscopy

In time-resolved vibrational spectroscopy, we used a UV/vis pump to excites the molecule, after which the populations are followed with an IR probe by the inspection of marker modes of the reactants, possible intermediates and the products in their electronic excited states (see Figure 2.4). Thus, one can follow conformational changes of the molecules under study during the course of chemical reaction.
Figure 2.4 Ultrafast time-resolved UV/vis pump-mid IR probe.\textsuperscript{40}

Since vibrational TA spectroscopy is more powerful and much more localized than electronic spectroscopy, it therefore provides microscopic information about specific functional groups, both in the donor and acceptor sites.\textsuperscript{42-46} 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.

Time-resolved infrared (IR) experiments were carried out in this thesis using a Helios-IR spectrometer with broadband capability (Ultrafast Systems, U. S. A.). The UV pump pulses at 400 nm were immediately 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 different 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 liquidnitrogen-cooled double array (2 × 32 pixels) of MCT (HgCdTe) detectors. Spectrally resolved absorbance changes in the mid-IR were recorded at a 2-7 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 \(\sim 160\) fs in semiconductor silicon.\(^{33}\)

### 2.2.4 Steady-State Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a measurement technique that allows us to record infrared spectra, helping to identify the studied chemicals at IR range in the ground state, from the nominal red edge of the visible spectrum at 700 nanometers (nm) to 1 millimeter (mm). This range of wavelengths corresponds to a frequency range of approximately 430 THz down to 300 GHz. Our steady-state IR spectra of NCs is measured on a Cary 600 series FTIR spectrometer (Agilent Technologies).\(^{35}\)

### 2.2.5 Time Correlated Single Photon Counting (TCSPC)

Time Correlated Single Photon Counting (TCSPC) is the most sensitive electronic method to measure the luminescence lifetime. It has a limited time resolution of no more than a few picoseconds (ps), which is usually determined by measuring the duration of the light pulse that is elastically scattered by the sample. Furthermore, TCSPC is a single-wavelength method. At
each given time, the fluorescence kinetics are only registered at one detection wavelength.

TCSPC has significant advantages, such as not requiring intense excitation light. The fundamental assumption of this technique is that each excitation pulse causes only one fluorescence photon to be detected. TCSPC is also completely insensitive to the stability of the laser pulse energy (even if these energies fluctuate by a factor of two, the method still works).\textsuperscript{33, 47}

In this setup, the excitation source was fs pulses at 370 nm (a few $\mu$J of pulse energy) generated from an optical parametric amplifier (Newport Spectra-Physics). The emission at 90$^\circ$ 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, U. S. A.). Detailed information on the experimental setup can be found elsewhere.\textsuperscript{47}

2.2.6 Cyclic Voltammetry (CV)

Cyclic voltammograms were acquired using Metrohm Autolab Potentiostat/galvanostat. The electrolytic cell was assembled by using a glassy carbon-working electrode, and an Ag/AgCl double membrane reference electrode containing LiCl in anhydrous ethanol as electrolytic medium. 5 $\mu$g of the polymer was dissolved in 10 mL of the supporting electrolytic solution consisting of 0.1 M tetrabutylammonium hexafluorophosphate ($\text{NBu}_4\text{PF}_6$) in anhydrous acetonitrile. The redox couple ferrocene/ferrocenium (Fc/Fc$^+$) was taken as an electrolytic reference to relate the electrochemical scale to the physical scale. For this purpose, a 0.01 M solution of ferrocene in acetonitrile containing 0.1 M $\text{NBu}_4\text{PF}_6$ as supporting electrolyte was cycled in the same experimental conditions.\textsuperscript{33}
2.2.7 Time Dependent Density Functional Theory Calculations (TDDFT)

Geometry optimization and characterization of the photophysical properties were performed with the Becke three parameters hybrid functional\(^ {48} \) and the VWN functional \( V \) for local density approximation\(^ {49} \), together with the polarizable splitvalence extended 6-31G\(^ * \) basis set.\(^ {50} \) Excitation and emission energies are obtained from extrapolation of a different number of monomers, ranging from one to seven conjugated fluorenes, to the polymer consisting of an infinite number of monomers.\(^ {51-52} \) This method is known to reproduce excellent light absorption, although it is known to over-estimate charge delocalization in the excited states and to give a smaller value for the emission energy.\(^ {53-54} \) For this reason, to model the charge transfer energy we used the \( \gamma \) tuning method.\(^ {55-57} \) In this method, \( \gamma \) is the variable to determine the distribution of the short-range and long-range interaction,\(^ {58} \) and can be obtained by minimizing equation 8.

\[
J = \left| \epsilon HOMO - |E_{gs}(N - 1; \gamma) - E_{gs}(N; \gamma)| \right|
\]  

(11)

In details, we first optimized the structure of PFN and PFN\(^ + \) at the B3LYP/6-31G\(^ * \) level, and we subsequently tuned the \( \gamma \) value at the \( \omega \)B97xd level. Then we optimized a structure with stacked PFN and DCB. Finally, the charge transfer energy of the stacked pair is calculated via TD-DFT.\(^ {34} \)

2.2.8 Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy is a powerful technique used to observe local magnetic fields around atomic nuclei helping to determine the content and purity of a material as well as its molecular structure.
H NMR (300 or 500 MHz) and $^{13}$C NMR (75.4 or 125.7 MHz) spectra were obtained on either a Varian Mercury 300 or a Varian Inova 500 spectrometer utilizing CDCl$_3$ or CD$_2$Cl$_2$ as solvents. $^1$H NMR data were recorded with residual internal CD$_2$Cl$_2$ (δ 5.32) or CDCl$_3$ (δ 7.26). $^{13}$C NMR data were recorded with references CD$_2$Cl$_2$ (δ 53.84) or CDCl$_3$ (δ 77.16). High-resolution mass spectrometry was performed with either an Agilent 6200 ESITOF or an AB Sciex 5800 MALDI TOF/TOF in the Chemistry Department at the University of Florida.

2.2.9 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) is one of the most powerful and versatile analytical techniques used to understand and predict polymer performance. It is the most convenient technique for characterizing the complete molecular weight distribution of such a material. GPC can determine several important parameters. These include number-average molecular weight (Mn) and weight-average molecular weight (Mw). The polystyrene standards with (PDI) of less than 1.2 are typically used to calibrate the GPC.

Gel Permeation Chromatography (GPC) data in this dissertation was collected on a system composed of a Shimadzu LC-6D pump, an Agilent mixed-D column, and a Shimadzu SPD-20A photodiode array (PDA) detector with THF as eluent at 1 ml/min flow rate. The system was calibrated against linear narrow dispersed polystyrene standards in THF.
Chapter 3

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

3.1 Introduction

Conjugated polymers have become materials of interest for solar cell applications,\(^1\)\(^-\)\(^2\) optical devices, 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.\(^59\) By virtue of their light harvesting properties, CPEs have also been utilized as photosensitizers in solar cells\(^60\)-\(^61\) and fluorescent sensors.\(^62\)-\(^64\) 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.\(^65\) In particular, key features of CPEs for solar cell applications are their flexibility and their simple, large-scale and low-cost fabrication.\(^1\),\(^59\) 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 solvents\(^66\) but also their intermolecular interactions, energy levels, and redox potentials, which determine electronic coupling\(^67\) and the rate of electron transfer at the donor–acceptor interface.\(^61\),\(^68\)

In solar cell devices, fast electron transfer and charge separation to overcome electron-hole recombination are required for high energy-conversion efficiency.\(^69\)-\(^70\) In this sense, the interaction, linking, and distance between the electron donor and acceptor moieties play crucial
roles.\textsuperscript{71} In particular, CPEs should form strong interconnections and interpenetrations with the electron acceptor moieties to attain efficient electron or energy transfer.\textsuperscript{72} An innovative approach utilizing the electrostatic interactions between cationic CPEs with negatively charged electron acceptor moieties has therefore attracted extensive attention.\textsuperscript{61, 68, 73-77} 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.\textsuperscript{6} 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.\textsuperscript{78-79} Recently, polyfluorene with azide derivatives was covalently linked with graphene flakes to produce a material with low bandgap and high charge carrier mobility.\textsuperscript{80} With such features, this material has high potential to be used in solar cells. We therefore sought to explore electron or energy transfers in noncovalent polyfluorene derivatives to determine the bimolecular electron transfer reactions of polyfluorene in the solution phase.\textsuperscript{81-84} This has motivated our group to investigate the bimolecular photoinduced electron or energy transfer associated with noncovalent polyfluorene assemblies in solutions. As in the case of the photoexcitation of small molecules, vertical excitation of the electron donor-acceptor system can induce electron and/or energy transfer.\textsuperscript{85} Knowing the rates of photoinduced electron transfer (PET), charge separation (CS), and charge recombination (CR)\textsuperscript{83} is required to understand the quenching dynamics of polyfluorene, as well as how electrons or energy are transferred from excited polyfluorene to molecular acceptors. Such information is critically
important in developing solar cell materials based on water or organic solvent-soluble polyfluorenes and on solid phase polyfluorenes. In this chapter, we report PET dynamics in noncovalent associations of cationic polyfluorene, namely poly[(9,9-di(3,3′-N,N′-trimethylammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyfluorenyl-2,7-diyl)] diiodide salt (PFN) with neutral electron acceptor 1,4-dicyanobenzene (DCB). The work presented in this chapter has already been published in the Journal of Physical Chemistry C in 2015. The chemical structure of PFN is shown in Figure 3.1. 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 the energy transfer process. In addition, anion radical of DCB, formed as a result of the electron transfer process, has a clear electronic and vibrational spectroscopic signatures. 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.
3.2 Results and Discussions

3.2.1 Steady-State and TCSPC Measurements

The absorption and fluorescence spectra of PFN with successive addition of DCB are shown in Figure 3.1. In the absence of DCB, the absorption spectrum of PFN has a peak centered at 403 nm and an absorption cutoff at 450 nm.

Figure 3.1 Steady-state absorption (A) and emission spectra ($\lambda_{ex} = 370$ nm, B) for the 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.\(^{33}\)
Upon successive DCB addition, only a consecutive increase was observed in the region below 350 nm (Figure 3.1 A), 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. However, selective photoexcitation of the PFN at 370 nm gave rise to a fluorescence spectrum in the visible region between 400 to 550 nm, with its maximum at 424 nm with three vibronic features at 420, 447 and 480 nm. The 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 the addition of \( \sim 0.24 \) M DCB. It should be noted that the fluorescence quenching suggests electron 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. The Stern-Volmer plot was constructed for the PFN fluorescence quenching using the equation:

\[
\frac{F_0}{F} = 1 + K_{SV} [DCB] \tag{12}
\]

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 Figure 3.1 A).\(^{89}\)

A bimolecular quenching rate constant can be calculated using

\[
K_q = \frac{K_{SV}}{t_F} \tag{13}
\]

where \( t_F \) is the fluorescence lifetime in absence of the quencher.

Fluorescence lifetime of the PFN estimated using TCSPC and a decay curve is shown in the inset of Figure 3.1 using TCSPC and found it to be 0.43 ± 0.04 ns (which is in good agreement with the
reported fluorescence lifetime of polyfluorenes). This allowed us to estimate the bimolecular quenching rate constant ($K_q$) to be $3.37 \times 10^{10}$ M$^{-1}$ s$^{-1}$. However, the quenching rate constant for a diffusion-controlled mechanism in DMSO is equal to about $3.3 \times 10^9$ M$^{-1}$ s$^{-1}$. 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.

### 3.2.2 Time-Resolved Femtosecond Spectroscopy

 Ultrafast TA spectroscopy with femtosecond temporal resolution and broadband capabilities is used to probe further the reaction mechanism of the excited-state interaction. Figure 3.2 shows TA spectra of PFN in the absence and the 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 there is overall similarity of the TA spectrum to that for free PFN, for the one measured in the presence of DCB, as shown in Figure 3.2 B, 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 Figure 3.2 C. We assigned these emerging bands at 600 nm and 430 nm to the spectroscopic signatures of PFN** and DCB** radical ions, respectively.
Figure 3.2 Transient absorption spectra using photoexcitation at 370 nm of a 150 fs laser for (A) PFN alone, (B) PFN in the presence of 0.12 M DCB, and (C) PFN in the presence of 0.24 M DCB. The band at 430 nm is in agreement with literature reports on dicyanobenzene radical anions and that at 600 nm it is in agreement with fluorene radical cations. As can be clearly seen in Figures 3.2 and 3.3, the formation of radical ions and the significant increase in the amplitude of the unrecovered GSB of PFN in the presence of DCB, provide clear indication of electron transfer and charge separation on the picosecond time scale. On the basis of 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.

**Figure 3.3** 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.33

Kinetic profiles collected from fs-TA of both GSB and ESA of PFN in the absence and presence of DCB are presented in **Figure 3.3 A, B**. 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 (**Figure 3.1 B**, ...)
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.

3.2.3 Time-Resolved Nanosecond Spectroscopy

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.

![Transient absorption spectra](image)

**Figure 3. 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.33
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 Figure 3.4. The dynamics at 600 nm (due to the charge recombination) were fitted to double-exponential functions with time constants of $3.58 \pm 1.40$ ns and $30.14 \pm 7.10$ ns. It is worth pointing out that the charge separation dynamics obtained from the fs-TA measurements (see Figure 3.3 C) is biphasic in nature. More specifically, the kinetic trace is fitted to a biexponent function with characteristic time constants of $23.27 \pm 4.39$ ps and $217.50 \pm 18.20$ ps. This biphasic nature is further supported by the fs-time resolved IR discussed below, where the time constants are closely related. In addition, these two time domains observed, allow the estimation of two rates for charge separation, one fast $\sim 4.3 \times 10^{10}$ s$^{-1}$, while the other is slower $\sim 4.6 \times 10^{9}$ 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.$^{11, 16, 20, 97}$ The geometry and electronic coupling between donor and acceptor molecules can greatly affect both charge separation and charge recombination rates.$^{16}$ 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. However, the slowly formed ion pairs encountering lower degree of coupling will in turn undergo 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,\(^{98-99}\) and the oxidation potential of PFN, as experimentally measured, is \(+1.09\) V. With the free energy (\(\Delta G\)) for PET given by

\[
\Delta G (eV) = E_{ox(D^+/D)} - E_{red(A/A^-)} - E_{0-0} + C \quad (14)
\]

where \(E_{ox}\) is oxidation potential of the electron donor, \(E_{red}\) is the reduction potential of the electron acceptor, \(E_{0-0} = 3.08\) eV (the singlet energy level of the donor), and \(C\) is energy released due to charge separation.\(^{89}\) This allows us to estimate \(\Delta G\) to be \(\sim -0.47\) eV, indicating a smaller yet thermodynamically feasible PET from PFN to DCB.

### 3.2.4 Time-Resolved IR Spectroscopy.

As mentioned in chapter 2, 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.\(^{43-46,100-102}\) 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 thesis, 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 3.5 A-C displays the transient mid-IR absorbance changes after 400 nm excitation. The antisymmetric C-N stretching mode of DCB\(^{**}\) radical anion at 2100 cm\(^{-1}\) is clearly observed. This confirms the anticipated PET from PFN to DCB.\(^{88}\) The radical anion of the DCB signature is formed at an early delay time as a broad transient band (see Figure 3.4). 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 Figure 3.5 A,B).

Figure 3.5 Mid-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 the time constant is given on the graph.\(^{33}\)

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. The electronic and vibrational spectroscopic results allow us to describe the reaction mechanism using the following equations:

\[ PFN + DCB \xrightarrow{400 \text{ nm}} PFN^* + DCB \] Photoexcitation \hspace{1cm} (15)

\[ PFN^* + DCB \xrightarrow{<5 \text{ ps}} (PFN^{++} + DCB^{-*}) \] Electron transfer \hspace{1cm} (16)

\[ PFN^{**} - DCB^{-*} \xrightarrow{27\text{&}196 \text{ ps}} PFN^{++} + DCB^{-**} \] Dissociation \hspace{1cm} (17)

\[ PFN^{**} + DCB^{-*} \xrightarrow{38\&30 \text{ ns}} PFN + DCB \] Charge recombination \hspace{1cm} (18)

The kinetic trace collected at 2100 cm\(^{-1}\) which corresponds to the antisymmetric C-N stretching vibration of the DCB radical anion (Figure 3.5 C) fits with double-exponential decays with characteristic time constants of 26.65 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 3.3 C). 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.\(^{11, 16, 20, 97}\)

### 3.2.5 Triplet-State Formation

As can be seen in Figures 3.2 A and 3.3 A, 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.\(^{90, 103-106}\) 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 \(\mu\)s in the absence of oxygen.\(^{107}\) 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 nanosecond to microsecond transient absorption spectroscopy tests in aerated and degassed solutions (Figure 3.6).

![Figure 3.6](image)

**Figure 3.6** 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.  

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 (Figure 3.6 A). This lifetime is three orders of magnitude longer than the singlet-state lifetime ($\sim 0.4 \, ns$) 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.\textsuperscript{90,107} Our nanosecond-microsecond TA signal in the absence of oxygen, exhibits much slower dynamics compared to the signal in the presence of oxygen (Figure 3.6 B), fully supporting the triplet nature of the long-lived component. The time constant extracted from the excited-state decay, which was 73.29 ± 10.80 μs, is in good agreement with the range reported for triplet state lifetimes.\textsuperscript{104}

3.3 Conclusion

We investigated photoinduced bimolecular electron transfer between cationic poly[(9,9-di(3,3′-N,N′-trimethylammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-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 further demonstrated 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 systems,\textsuperscript{46,108-110} 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.
Chapter 4

Real-Time Observation of Intersystem Crossing Induced by Charge Recombination during Bimolecular Electron Transfer Reactions

4.1 Introduction

In donor-acceptor systems, photoexcitation generally initiates the flow of the electron density associated with donor to acceptor units.\textsuperscript{111-112} Typically, photoinduced electron transfer (PET) results in ultrafast, radical ion pair formation (i.e., charge separation (CS)) followed by back electron transfer (i.e., charge recombination (CR)) within pico-to nanoseconds depending on the electron affinity of the acceptor and the amount of reorganization energy and also depend on the ionization potential of the PFN.\textsuperscript{113} In nature, energy conversion devices (e.g., biological photosynthetic systems) achieve better efficiency by using reaction centers associated with energy cascade structures, where photo-generated charges are prevented from recombination;\textsuperscript{114} this type of efficiency remains a challenge in artificial devices. In photosystem II of photosynthesis devices, the charge-separated ions formed in the excited singlet state and during charge recombination are prone to singlet-triplet interconversions in the charge-separated state, causing the formation of an excited triplet state.\textsuperscript{115} In organic light-emitting diodes (OLEDs), the formation of a triplet state has a significant impact on the enhancement of device performance.\textsuperscript{116-117} In this regard, numerous recent publications have reported on the important role of a triplet state in OLED applications.\textsuperscript{118-122} However, the elucidation of the formation mechanism of the triplet state, especially after charge transfer and separation, is a challenge because of the strong spectral overlap and the existence of complicated energy levels
of the transient species following optical excitation. For instance, in conjugated polymers, the
triplet state is located just \( \sim 0.7 \) eV below the excited-singlet state,\textsuperscript{123} supporting the picture of
complicated energy levels in these systems. There is a lot of evidence in the literature
identifying the successful formation of triplet-state populations by CR of excited singlet-state
radical ions in organic donor and acceptor electron interactions.\textsuperscript{97, 124-129} Longevity of charged
ions is expected to enhance the possibility of populating the triplet state via CR of excited
singlet-state charged ions.\textsuperscript{130} Moreover, CR to the triplet state is expected to be dependent on
the energy difference between the highest occupied molecular orbital (HOMO) on the donor
and the lowest unoccupied molecular orbital (LUMO) on the acceptor CR from high energetic
charge transfer state to the low lying triplet state is favored when the HOMO-LUMO offset is
low.\textsuperscript{131} Polyfluorenes and their derivatives belong to an attractive class of electroluminescent
molecules that significantly impact device performance, fabrication and charge transfer
properties.\textsuperscript{132} In the last decade, research testing the use of polyfluorene in LED devices has
emerged.\textsuperscript{119, 133-137}

Recently, in our investigation on CS and CR in a noncovalent polyfluorene-dicyanobenzene dyad
using both time-resolved electronic and vibrational spectroscopy evidences were given for the
formation of an ultrafast PET within picoseconds (ps), \(< 5 \) ps and slower CR that takes place
within nanoseconds (ns).\textsuperscript{33} Our time-resolved vibrational spectroscopic results confirmed the
dissociation of the initially formed geminate ion pairs within ps time scale. While the charge-
separated state turned out to be long lived, CR was achieved within ns. Time-resolved laser
spectroscopy has seldom been used to characterize fluorescent polymers and/or noncovalent
donors-acceptors in solutions where a triplet state has been detected as a product of CR.
Nevertheless, a recent example using fluorene-based dyads\textsuperscript{138} found that retarded CR led to recombination to the excited triplet state of the donor. In this chapter, we investigate in more detail the outcome of the charge-separated state we identified in our previous study.\textsuperscript{33} Using time-resolved laser spectroscopy, including femtosecond (fs) and nanoseconds transient absorption (fs- and ns TA) spectroscopy with broadband capabilities, we investigate the donor-acceptor system 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); see Scheme 4.1 for structures. The work presented in this chapter has already been published in the Dyes and Pigments Journal in 2017.\textsuperscript{34}

Our steady-state, fs and ns time-resolved measurements indicate the presence of PET from PFN to DCB. This observation is supported by fluorescence quenching monitored in PFN upon the addition of DCB. The formation of radical ion pairs (DCB$^-•$ and PFN$^+•$) is confirmed by fs-transient absorption (TA) measurements, where charge separation is achieved within ps. This observation was confirmed by fs time-resolved infrared spectroscopy where the cyano stretching vibration of the anion radical was monitored.\textsuperscript{33,88} Results from this study demonstrate that the triplet state is formed as a result of back ET from initially formed singlet-state ion pairs.

\textbf{Scheme 4. 1} Chemical structures of PFN and DCB.\textsuperscript{34}
4.2 Results and Discussions

4.2.1 Steady-State Absorption and Emission Measurements

The absorption and emission spectra of PFN alone and PFN upon the addition of 0.24-M DCB in dimethyl sulfoxide (DMSO) are shown in Figure 4.1 a. The absorption of free PFN in DMSO localizes at 402 nm and shows no spectral change upon the addition of DCB.

The only spectral change is observed around 350 nm due to superimposing the bulk absorption curve of DCB. PFN shows a broad-structured fluorescence spectrum extending over a range of 400-550 nm with a vibronic structure at 424, 447, and 480 nm. Successive additions of 0.24-M DCB to a solution containing a fixed concentration of PFN resulted in an observable fluorescence quenching, with its efficiency being estimated at ~78% as calculated considering the maximum quenching observed in the fluorescence spectrum of PFN. Note that this fluorescence quenching could be a result of energy or electron transfer. Because of the lack of spectral overlap between DCB absorption and PFN emission, we can confidently assign this quenching to electron transfer (ET).

Broadband TA spectroscopy was used to investigate the excited state behavior of this bimolecular ET reaction, from ps-to μs time scales.\textsuperscript{17, 110} Figure 4.1 b shows the TA spectra collected after a 5.5 ns delay upon photoexcitation for PFN alone and for PFN with 0.24-M DCB. This concentration of DCB was identified as having the highest quenching efficiency in the system. A comparison of the two TA spectra recorded for PFN in the presence and absence of DCB, provide clear evidence for the excited state interaction; see nanosecond transient absorption section.
Figure 4.1 (a) Steady-state absorption and emission ($\lambda_{\text{ex}} = 380$ nm, B) for PFN alone (black line) and PFN with 0.24-M DCB (magenta line) in DMSO. (b) TA spectra after a 370 nm photoexcitation for PFN alone (black line) and PFN with DCB (0.24-M) (magenta line).\textsuperscript{34}

4.2.2 Nanosecond Transient Absorption and Kinetics of Triplet State

While a broad excited-state TA spectrum was observed for PFN alone, a more detailed spectrum was detected in the presence of DCB; the bands emerging at 430 and 590 nm. According to previous reports, peaks at $\sim$430 and $\sim$590 nm are characteristic for DCB•• and PFN••, respectively.\textsuperscript{33, 92-96} As explained in our previous chapter, CS can be achieved in the ps domain, leading to the formation of long lived DCB•• and PFN••, whereas CR takes place within ns-to $\mu$s time scales.\textsuperscript{33} Closer evaluation of the TA spectrum obtained for PFN alone, reveals the
presence of a low optical density band at $\sim 792$ nm, that is associated with a relatively long lifetime, which becomes more predominant with time (see the inset in Figure 4.1 b). To investigate the origin of this band, ns-TA measurements were performed for two PFN solutions in the presence and absence of molecular oxygen. The kinetic traces are given in Figure 4.2.

**Figure 4.2** Nanosecond-TA spectra after a 370 nm photoexcitation in the presence of O$_2$ at room temperature for (a) PFN alone and (b) PFN in the presence of 0.24-M DCB$^{34}$.

The ns-TA decay of the PFN signal at 792 nm showed its lifetime to be $\sim 0.59 \pm 0.03$ $\mu$s in the presence of O$_2$ and $\sim 73.29 \pm 10.8$ $\mu$s in the absence of O$_2$. The sensitivity of the lifetime extracted at this wavelength in the presence of O$_2$ strongly supports our assignment of this band to T$_1$-T$_n$ absorption.$^{90,107}$ Evidence of this band when PFN is mixed with DCB is suggestive of triplet-state formation in the dyad as well, however, at a slower formation rate. Meanwhile PFN alone has a triplet-state population through intersystem crossing from an excited singlet-
state ($S_1$) population. When DCB is present, the expected involvement of electrons at singlet excited state in the fast PET (as indicated by the formation of radical ions within 5 ps), suggests that another mechanism is involved. To investigate the origin of triplet-state formation in the PFN and DCB mixture, we performed the ns-TA experiments after a 370-nm photoexcitation of PFN in the presence and absence of 0.24-M DCB. The results are shown in Figure 4.3. It is worth mentioning that in the absence of DCB, a negligible $^3$PFN is formed directly from the excited state of the neural PFN, which can be observed (see Figures 4.3 a and 4.2 a) in our earlier study. Two major differences can be observed with time in the spectral features of the TA spectra of PFN, when DCB is present.

![Figure 4.3](image)

**Figure 4.3** Kinetic traces derived from ns-TA spectra after a 370-nm photoexcitation in the presence (green) and absence of oxygen (yellow) for PFN alone and in the absence of oxygen in the presence of 0.24-M DCB (red). Inset shows the first 250 ns time window for PFN-DCB in the absence of oxygen. Fitting is indicated by blue lines and kinetic decay of PFN is rescaled for comparison purposes.
Figure 4. Kinetic traces derived from nanosecond transient absorption spectra for PFN in the presence of 0.24-M DCB at 591 nm (green) and 792 nm (red). Fitting is indicated by blue lines. One difference is the observable decrease in optical density of the radical ions (DCB−• and PFN+•) as delay time increases. The other difference is an increase in the TA spectra at 792 nm, which is assigned to PFN triplet-triplet absorption. The decay of the TA signal of the ion pair on a longer time scale is accompanied with a rise of the triplet-triplet absorption, creating an isosbestic point. The presence of an isosbestic point indicates that an equilibrium is achieved between the radical ion and the T₁-Tₙ species. Thus, CR of the radical ion pairs is likely responsible for this PFN triplet-triplet absorption. This mechanism can be confirmed by comparing kinetic traces at 591 nm for CR of PFN** with those at 792 nm for T₁-Tₙ absorption of PFN. We have performed concentration dependent experiments and similar results are observed, excluding any type of aggregation processes. On the other hand, there is a possibility that ion exchange may happen in nonpolar solvent. In this case, we used very polar solvent.
(DMSO) which can easily separate and solvate the radical ions, minimizing such an ion exchange.

By analyzing the amplitudes of the fitting data for the transient band at 591 nm (see Figure 4.4), we found that 60% of radicals show a direct recombination to the ground state and the remaining 40% undergoes intersystem crossing (ISC) to form the triplet state. The fast component is assigned as back ET to the singlet ground state \(S_0\) of the neutral form, while the long component is assigned as spin conversion of PFN\(^{**}\) into the triplet state \(^3\)PFN\(^*\).

Alternatively, when the time constant is extracted from the \(T_1-T_n\) absorption time evolution curve at 792 nm, it is found to be \(~30 \pm 2.9\) ns in strong agreement with the long component of the CR signal. Agreement between the rate of CR and the rate of \(T_1-T_n\) absorption formation of PFN provides strong support for our proposed PFN triplet-triplet formation mechanism. The triplet state formation via back ET (i.e. CR of radical ion pairs) was also reported in the literature for both polymer blended films and molecular donor-acceptor systems in solution. \(^{139-142}\) This type of CR mechanism is expected for donor-acceptor interactions where a quenching rate is close to the diffusion rate of what is in polar media \(^{143-144}\) and for those cases where energy of the charge transfer state is higher than that of \(T_1\). \(^{131}\)

Charge-transfer pairs (i.e., an electron-hole pair) have been reported to be coulombically bound for such \(\pi\)-conjugated polymers, thus confirming the feasibility of populating the triplet state through CR. \(^{145-147}\) It is worth pointing out that the contribution of triplet-triplet absorption at 591 nm in the absence of DCB, is too small and can be ignored. In other words, the kinetics trace monitored at 591 nm has a major contribution of the radical ion pair (PFN\(^{**}\) DCB\(^-\)) and hence the kinetic profile reflects mainly the recombination of the radical ion pair. Accordingly,
the decay curve at 591 nm with number of components reflects the pathways involved in the recombination of the formed radical ion pair that is given in **Scheme 4.1**, while that at 792 nm reflects only the formation of the triplet state. More importantly, the perfect match observed between the decay at 591 nm and evolution time of the triplet state strongly supports our anticipated theory of charge recombination to the triplet state.

### 4.2.3 Reaction Mechanism

The measurements we have discussed here allow us to speculate on the mechanism of PET between PFN and DCB as outlined in **Scheme 4.2**. According to this mechanism, electrons are promoted from the ground state to the excited state upon 370-nm photoexcitation that leads to the formation of a singlet excited state of PFN. With DCB present as an electron acceptor, ET proceeds from the donor PFN into the acceptor DCB in less than 5 ps, which forms free radical ions with singlet multiplicity (in this case PFN** and DCB**).
Next, the CR process proceeds either through the direct recombination route identified by CR$_1$, where electrons recombine back to the ground state (4.3 ns), or via CR$_2$, where electrons undergo intersystem crossing to populate the low-lying triplet state (34 ns). Once formed, the excited triplet state undergoes non-radiative relaxation to the ground state with a time constant of $\sim 79$ $\mu$s.

Time dependent density functional theory (TD-DFT) calculations were performed to further support the mechanism proposed in Scheme 4.2. Initially, we benchmarked the chosen TD-DFT protocol to reproduce the experimental absorption from the S$_0$ state and the experimental emission spectrum from the S$_1$ state for PFN. The calculated absorption from the S$_0$ to the S$_1$ state, 402 nm, reproduces perfectly the experimental value of 403 nm, while the calculated emission from the S$_1$ state, 457 nm, is in good agreement with the broad-structured fluorescence spectrum extending over a range of 400-550 nm with a vibronic structure at 424, 447, and 480 nm.

At this point, we performed a TD-DFT optimization of the T$_1$ state of PFN, and we estimated the energy of the charge separated PFN$^{**}$ and DCB$^{**}$ state via TD-DFT to predict the relative energy of the species reported in Scheme 4.2. According to our calculations, the S$_1$ and T$_1$ states of PFN are located 3.08 and 1.92 eV above the corresponding S$_0$ state, while the charge separated PFN$^{**}$ and DCB$^{**}$ state is located 2.80 eV above the S$_0$ state. This hierarchy of the energy levels is consistent with the mechanism proposed in Scheme 4.2.
4.3 Conclusion

In this investigation we have provided experimental evidence for intersystem crossing and triplet state formation induced by charge recombination of the radical ion pairs in bimolecular PET reaction, using fs- and ns-TA spectroscopy with broadband capabilities.

Our experimental results clearly indicate the existence of long-lived, charged ion-radical pairs forming within ps and charge recombination within ns-to μs time scales. The long-lived radical ions and the slow charge recombination from PFN to DCB generate a triplet-state population of PFN. In other words, the triplet state is populated as a potential mechanism of charge recombination between the radical ion pairs. Additionally, our proposed mechanism regarding the triplet-state formation was supported by strong agreement between the $T_1$-$T_n$ TA signal formation rate and the kinetic traces for CR.
Chapter 5

Bane of Hydrogen-Bond Formation on the Photoinduced Charge-Transfer Process in Donor-Acceptor Systems

5.1 Introduction

Photoinduced charge transfer remains one of the most important photochemical reactions in chemistry, biology, and materials science.\textsuperscript{17, 82, 88, 100, 108, 150-162} The process is usually characterized by the transfer of an electron from a photoexcited donor to an acceptor and is often driven by complex formations between the donor-acceptor moieties, especially if they carry opposite electrostatic charges. Such excited-state processes are significantly influenced by the properties of the solvents, including polarity and hydrogen-bonding interactions.\textsuperscript{163-169} Time-resolved laser spectroscopic measurements in picosecond and femtosecond time domains have been used to investigate the dynamics of hydrogen bonding in the excited singlet ($S_1$) state of ketone molecules in alcoholic solvents,\textsuperscript{164} where evolution of the excited-state properties have been observed and attributed to repositioning of the hydrogen bonds around the carbonyl group. Theoretical studies on the excited-state hydrogen bonding dynamics of fluorenone (FN) in protic (methanol) solvent reveal that intermolecular hydrogen bonds ($\text{C}=\text{O}\cdots\text{H}--\text{O}$) between fluorenone and methanol molecules are significantly strengthened in the electronically excited state upon photoexcitation of the hydrogen-bonded FN-MeOH complex.\textsuperscript{169} Furthermore, the radiationless deactivation via internal conversion can be facilitated by the hydrogen-bond strengthening in the excited state, as reflected in the reduced fluorescence quantum yield of fluorenone in polar protic solvents. Similar studies on oxazine 750 (OX750) chromophore in
protic alcoholic solvents show that selected hydrogen bonds can be transiently strengthened in the excited states to facilitate ultrafast solute-solvent intermolecular electron transfer reactions. Subsequently, charge transfer assisted by solvent dynamics has been demonstrated for formylperylene in protic solvents, indicating the role of a collective solvent network acting upon a single molecular site. Upon photoexcitation, the increase in the electronic charge density on the carbonyl group causes formylperylene to undergo charge transfer, resulting in its stronger intermolecular H-bonding with the protic solvent molecules. A shift in the femtosecond-resolved fluorescence (time dependent Stokes shift), recorded by systematically varying the composition of a binary solvent mixture involving methanol and acetonitrile (i.e., two solvents with similar polarity but differing in hydrogen-bonding capabilities), allowed the contribution of specific hydrogen-bonding interactions to the overall solvation to be ascertained thus elucidating the nature of the solvent-network-assisted charge transfer.

In this study, we explore the ultrafast interfacial charge transfer between a negatively charged anionic porphyrin (mesotetra(4-phosphonomethylphenyl) porphine tetrasodium salt) (POS) as an electron donor and a positively charged π-conjugated polymer (poly[(9,9-di(3,3’-N,N’-trimethylammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyl)] diiodide salt) (PFN) as an electron acceptor using steady-state, time-resolved experiments. The work presented in this chapter has already been published in the Journal of Physical Chemistry C in 2017. The chemical structures of the donor-acceptor components are shown in Scheme 5.1. We chose POS as the electron donor for this study because of its good thermal stability, strong
absorption of visible light, and remarkable photoelectrochemical properties, making it a desirable component of many energy-harvesting devices.$^{17,42,171-172}$ We selected PFN as the electron acceptor for this study because its solubility in aqueous and alcohol media makes it popular as a cathode in many solar cells.$^{34,48-50}$ Together, they create an interface that is a suitable donor-acceptor system worthy of systematic investigation, particularly for studying the way solvent properties can influence charge transfer. We examine the role of hydrogen bonding on the dynamics of excited-state charge transfer by choosing a pure solvent, methanol (MeOH), and two binary solvent mixtures, methanol with N,N-dimethylformamide (1:1 v/v) (MeOH:DMF) and methanol with acetonitrile (1:1 v/v) (MeOH:ACN). Results from our study stand at variance with the traditionally accepted view, which suggests that hydrogen bonding accelerates excited-state charge transfer. Instead, site-specific hydrogen bonding and geometric considerations can actually impede charge transfer, and we explore these conditions to show how hydrogen bonding can hinder photoinduced charge-transfer processes in donor-acceptor systems.

Scheme 5. 1 Chemical structure of the negatively charged porphyrin derivative (POS) and the positively charged conjugated polymer (PFN).$^{35}$
5.2 Results and Discussions

5.2.1 Steady-State Absorption and Emission Measurements

Figure 5.1 displays the steady-state absorption (left) and emission spectra (right) of ionic POS without and with successive addition of cationic PFN in each of the three solvents: MeOH, MeOH:DMF (1:1), and MeOH:ACN (1:1).

The absorption spectra of POS show the characteristic intense Soret band ($S_0$-$S_2$ transition) at ~416 nm along with the weak broad Q bands ($S_0$-$S_1$ transition) over the 480-650 nm range. Successive addition of PFN to a given concentration of POS solution in all three solvents induced a quenching of the intensity of the Soret band and a slightly detectable red shift, indicating a ground-state interaction between the two components. Moreover, the four vibronic bands in the Q region, $Q_y(1,0)$, $Q_y(0,0)$, $Q_x(1,0)$, and $Q_x(0,0)$, also displayed a slight red shift. Meanwhile, the characteristic absorption band of PFN at 391 nm increased in intensity with successive addition of PFN in all the solvents, as shown in Figure 5.1 (dotted gray line). Upon photoexcitation at 550 nm, the emission for POS shows a broad fluorescence spectrum covering the spectral range of 625-750 nm with typical shape of prophyrin fluorescence spectra, mirror image of the Q-region, where two bands are detected at 650 and 720 nm (Figure 5.1). Gradual addition of PFN (up to $7.4 \times 10^{-4}$ mg/mL) in all three solvents indicates a significant quenching of the fluorescence, which can be attributed to either electron or energy transfer.
Steady-state absorption and emission spectra of (0.01 mM) POS upon addition of PFN in MeOH, MeOH:DMF (1:1), and MeOH:ACN (1:1). The samples were excited at 550 nm.

On the basis of fluorescence quenching of the ionic POS, we estimate the quenching efficiency to be ∼20%, 40%, and 50% in MeOH, MeOH:DMF (1:1), and MeOH:ACN (1:1), respectively, upon addition of $7.4 \times 10^{-4}$ mg/mL PFN. Increasing the concentration of PFN from $7.4 \times 10^{-4}$ mg/mL up to $39 \times 10^{-3}$ mg/mL considerably affected the absorption and emission spectra of POS, as shown in Figure 5.2. In the absorption spectra (left), the intensity of the Soret band ($S_0\rightarrow S_2$ transition) at ∼416 nm decreased with a clear spectral red shift in all three solvents. Concomitantly, we observed a small red shift of the broad Q bands ($S_0\rightarrow S_1$ transition) over the 480-650 nm range. In contrast, a recovery of 50% and 15% of the quenched fluorescence
intensity was observed in MeOH:DMF (1:1) and MeOH:ACN (1:1), respectively (Figure 5.2 right).

No such recovery of quenched fluorescence was observed in pure methanol.

**Figure 5.2** Steady-state measurement of (0.01 mM) POS after adding higher concentrations of PFN ($39 \times 10^{-3}$ mg/mL) in three solvents: MeOH, MeOH:DMF (1:1), and MeOH:ACN (1:1). The samples were excited at 550 nm.$^{35}$

The increased intensity in the fluorescence of POS may be attributed to either energy transfer or suppression of the twisting motion of the meso unit of the POS because of the complexation with PFN.$^{22}$ Previous fluorescence studies on a porphyrin derivative have shown that such restricted rotation of molecular moieties, for instance, in a viscous medium like glycol, helps reduce non-radiative excited state deactivation pathways, and this in turn leads to enhanced
fluorescence emission.\textsuperscript{22} In the present case, at high PFN concentrations (39 × 10^{-3} mg/mL), the enhanced electrostatic interaction between the charged donor and acceptor molecules is assumed to geometrically constrain the free twisting of the POS meso units. The effect is expected to be more pronounced in the solvent mixtures (MeOH:DMF and MeOH:ACN) which by virtue of their weaker hydrogen bonding can allow the donor and acceptor molecules to approach each other much closer, compared to pure methanol. In the low PFN concentration regime (7 × 10^{-4} mg/mL), the separation between donor and acceptor is larger. This reduced electrostatic interaction between donor and acceptor ensures that the POS meso units are no longer geometrically constrained and that charge transfer takes place. This explains the discrepancy in trend observed for the POS fluorescence quenching/recovery at low and high PFN concentration regimes. Although similar in trend, the extent of fluorescence recovery in the case of MeOH:DMF and MeOH:ACN is noticeably different (Figure 5.2). This contrast may be attributed to the difference in viscosity between DMF and ACN. Since DMF (0.90 cP) is more viscous than ACN (0.37 cP), its presence in the solvent mixture is expected to suppress the rotation of the POS meso units more effectively, leading to greater fluorescence recovery than that obtained in ACN. Note that excitation at 550 nm selectively excited POS, a wavelength where PFN has no absorption (Figure 5.1 (top panel), dotted gray curve). In addition, because of the lack of spectral overlap between the emission spectrum of POS and the absorption spectrum of PFN, we can rule out any energy-transfer processes. To confirm that the extent of twisting motion of the meso unit in POS could be responsible for enhanced fluorescence, due to the stronger complexation between POS and PFN at higher concentrations, further steady-state quenching measurements were carried out in MeOH, MeOD and MeOH:CAN, at varying
concentrations of ACN. Figure 5.3 A demonstrates that the fraction of quenching in deuterated methanol (MeOD) is higher than that in normal methanol (MeOH). Moreover, Figure 5.3 B shows that the extent of quenching in MeOH:ACN with a ratio of 20:80 is indeed higher than that for a ratio of 50:50.

Figure 5.3 Steady-state comparison for (0.01 mM) POS in (A) MeOH or MeOD alone and in (B) MeOH:ACN (50:50) and (20:80). The samples were excited at 550 nm.\(^\text{35}\)

These results suggested that weakening of the hydrogen bond environment (either by isotopic substitution of protic methanol or by increasing the concentration of the nonhydrogen-bonding solvent ACN) in the vicinity of the POS-PFN charge-transfer complex strengthened complexation between the donor-acceptor components. In contrast, in a strong hydrogen-bond environment,
the distance between the donor and acceptor is likely increased, leading to poorer quenching of 
POS and less efficient charge transfer.

5.2.2 Reaction Mechanism.

Scheme 5.2 presents the relevant mechanism found in this study. The efficiency of charge 
transfer is dictated by the hydrogen-bonding environment of the solvent media. The more 
abundant the number of methanol molecules in a solvent mixture is, the larger the separation 
between donor and acceptor molecules, and the lesser the intermolecular electrostatic 
interaction. This in turn influences the freedom of the twisting motion of the POS meso groups, 
with more flexibility resulting in more efficient excited state charge transfer.

Scheme 5.2 Mechanism of charge transfer (CT) between negatively charged anionic POS donor 
and the positively charged cationic PFN acceptor in MeOH alone or in the MeOH:ACN mixture.35

5.2.3 Fourier Transform Infrared (FTIR) Spectroscopy

To gain precise, specific information about the strengthening or weakening of a hydrogen-bond 
network, one should monitor the shift in the frequency of the infrared-vibrational marker mode
that interacts with the hydrogen-donating solvent environment. It is well-known that formation of hydrogen bonds leads to a downshift in the frequency of the vibrational marker mode.\textsuperscript{174} Since POS contains a phosphate (P≡O) functional group (with stretching frequency around 1100 cm\textsuperscript{-1}) in the meso unit of the porphyrin framework, we may use it as a convenient probe to report on the immediate solvent environment and the strength of the hydrogen bond between P≡O and the MeOH solvent. We have chosen the P≡O stretching vibration over the N-H stretch (∼3350 cm\textsuperscript{-1}) of the porphyrin ring because the latter strongly overlaps with the O-H stretch of the solvent as well as the POS hydroxyl group and thereby makes the interpretation of observed shifts very difficult.

Accordingly, Fourier transform infrared (FTIR) measurements were carried out for POS in MeOH and MeOH:ACN mixtures. Figure 5.4 shows the corresponding FTIR spectra for the POS phosphate stretch band whereby the position of the P≡O band underwent a noticeable upshift in frequency as the solvent was changed from pure MeOH to a MeOH:ACN mixture and from lower to higher concentration ACN mixtures (from 40:60 MeOH:ACN to 30:70 MeOH:ACN).
Figure 5.4 Steady-state IR spectra of (0.04 mM) POS in MeOH (black) and in MeOH:ACN (60:40) (blue) and (30:70) (red) solutions. The peaks remain unchanged over both broad and narrow scans.\textsuperscript{35}

This is consistent with the expectation that ACN weakens the hydrogen-bonding solvent network in the vicinity of the POS meso units of hydrogen bonding in the complex. Thus, FTIR results clearly reveal how the hydrogen-bonding environment is affected by the changes in the solvent media, which has implications for the observations obtained both from steady-state and from time-resolved measurements.
5.2.4 Femtosecond Transient Absorption (fs-TA) Measurements

Since it is well documented that femtosecond transient absorption (fs-TA) spectroscopy provides direct and detailed information about excited-state phenomena occurring on ultrafast time scales,\textsuperscript{155, 175} we used fs-TA to probe the real-time impact of hydrogen-bond formation on charge-transfer processes in donor-acceptor systems. Figure 5.5 depicts the recorded fs-TA spectra of POS in various media and in the presence of PFN following selective optical excitation at 650 nm.

![Figure 5.5 Femtosecond-TA spectra for (A) (0.04 mM) POS alone (top panel) and (0.04 mM) POS with (0.16 mg/mL) PFN in MeOH solvent (bottom panel), (B) (0.04 mM) POS alone (top panel) and (0.04 mM) POS with (0.16 mg/mL) PFN in MeOH:DMF (50:50) (bottom panel); both excited at $\lambda_{ex} = 650$ nm.\textsuperscript{35}](image-url)
As can be seen, the ground-state bleach (GSB) at \( \sim 420 \) nm for POS in methanol corresponds to the \( S_2 \) population\(^{176}\) and the broad but weak absorption extending over 450-580 nm corresponds to the excited-state absorption (ESA). Both GSB and ESA for POS alone show minimal observable changes over 3 ns, consistent with the long lifetimes of their excited states;\(^{177}\) however, in the POS-PFN complex, excited-state interactions were observed on faster time scales. In methanol, complexation caused the GSB band for POS to split into two peaks in the presence of PFN, with both peaks evolving in time with similar kinetics. This is in accordance with steady-state absorption results, which were accompanied by the appearance of a new broad absorption feature extending over the 500-580 nm spectral range. This new band represents formation of the POS cation radical, as reported previously in the literature\(^{47,173}\) providing strong experimental evidence for the charge transfer between POS and PFN. In MeOH:DMF, the overall trend in the excited-state spectra was similar to those observed in pure MeOH, as shown in Figure 5.5 B; for instance, the appearance of the spectral feature corresponding to the POS cation radical (450-580 nm) was also observed in the MeOH:DMF mixture. The appearance of the cation radical band is attributed solely to POS since PFN has no absorption at the wavelength of photoexcitation (650 nm).

The kinetic profiles monitored at 418 nm (corresponding to ground-state bleach) or 550 nm (corresponding to radical cation or excited-state absorption) are given in Figure 5.6 A and B, respectively. Kinetic traces obtained from the temporal evolution of the excited-state absorption (ESA) and ground state bleach (GSB) for POS alone, show similar dynamics in all three solvents and appear much slower when compared with those of the POS-PFN charge-transfer complex.
Figure 5.6 Kinetics traces for (A) ESA extracted at 550 nm and (B) GSB extracted at 418 nm for (0.04 mM) POS alone and for (0.04 mM) POS with PFN (0.16 mg/mL) in three solvents; MeOH, MeOH:DMF (1:1), and MeOH:ACN (1:1).\textsuperscript{35}

The kinetic profiles show that the GSB recovery of POS-PFN have two time constants: an ultrafast component of a few picoseconds, corresponding to charge recombination resulting from charge transfer between POS and PFN, and a relatively long nanosecond component, which likely originates from the unreacted POS. Interestingly, under the same experimental conditions, including similar solvent polarity, the kinetics of the porphyrin-PFN complex in MeOH:ACN has a much faster and larger amplitude of GSB recovery (135 ps) compared with that in pure MeOH (333 ps). This result is consistent with our conjecture that a weaker hydrogen-bonding environment (as in MeOH:ACN solvent mixture) is conducive to accelerating
the excited-state charge transfer from the POS donor to the PFN acceptor. In contrast, the stronger and more rigid hydrogen bonding network in methanol may weaken complex formation and electronic coupling between donor and acceptor, subsequently reducing the efficiency of charge transfer at their interfaces. In other words, we can assume that the presence of a strong hydrogen-bonding network hinders the POS and PFN molecules from approaching each other, forcing intermolecular separation that is detrimental for fast and efficient charge transfer.

5.2.5 Early Time Transient Absorption Spectra and Kinetics

Charge-transfer processes and the formation of radical cations can be significantly affected by the solvation of the surrounding solvent molecules.\textsuperscript{178-179} Figure 5.7 shows the early time kinetics of free POS in three solvents in the absence and presence of 0.16 mg/mL PFN following 650 nm pulsed excitation. Without PFN, the fs-TA spectrum of POS show more or less identical excited-state features with no observable change over a 1 ns time window for all three solvents studied. As stated earlier, this observation is expected because the reported excited singlet state for free-base porphyrin is fairly long-lived.\textsuperscript{22} Meanwhile, the fs-TA spectra for the assembled POS-PFN exhibit faster charge transfer and rapid formation of cation radicals on the same time scale, suggesting that charge transfer is fast in the donor-acceptor complex. However, the degree of complexation may be different from one solvent to another because of their different hydrogen-bonding capabilities.

The spectral band observed over the 480-580 nm range was attributed to the POS cation radical, as stated earlier, and the fitted-time constants of the formation were solvent dependent.
Figure 5.7 Early time absorbance and kinetics for (0.04 mM) POS alone and (0.04 mM) POS with (0.16 mg/mL) PFN in MeOH, MeOH:DMF (1:1), or MeOH:ACN (1:1); all excited at $\lambda_{\text{ex}} = 650$ nm.\(^{35}\)

The ultrafast solvent relaxation component (occurring in <100 fs) accounts for 69% and 44% of the total solvation response for ACN and MeOH, respectively.\(^{180}\) Thus, increasing the ACN content in a solvent mixture is expected to shorten the solvation time. In MeOH alone, the growth kinetics for the formation of radical ions was slightly slower than that in the mixture of MeOH:DMF or MeOH:ACN because of the slower solvation response of the surrounding environment and the weaker complex formation in the former. As can be seen, the fast kinetic traces for POS and POS-PFN complex extracted at 550 nm (Figure 5.7 lower panel) were
consistent with the formation of cation radicals of POS in MeOH, MeOH:DMF, and MeOH:ACN exhibiting time constants of 1.23, 1, and 0.3 ps, respectively. This is consistent with the idea that a rigid hydrogen-bond network in the immediate vicinity of the donor and acceptor species can hinder the charge-transfer process, leading to slower kinetics. In addition, solvation dynamics may be responsible for the different kinetic profiles observed for the radical cation formation. The fact that the kinetics of POS is largely solvent independent but that of the POS-PFN complex is not, reiterates the fact that the intervening solvent media play a decisive role in influencing the excited-state charge-transfer efficiency. Moreover, with solvent media of similar polarity (as reflected by their dielectric constants), the relative energetics of the charged species are expected to be quite similar, with the observed changes chiefly originating from the local hydrogen bonding environment. Furthermore, Coulombic interaction between the oppositely charged moieties ensures complex formation which facilitates the charge-transfer process despite the presence of bulky side groups in both POS and PFN.

5.3 Conclusion

In summary, we have explored the idea that charge transfer between donor and acceptor species can be modified and tuned by the presence of intervening solvent molecules in their immediate environment, especially when the solvent molecules can modulate the hydrogen-bonding network between donor and acceptor components. Using POS and PFN as prototype donor and acceptor molecules, and varying the hydrogen bonding tendencies of the solvent medium, we show that under specific circumstances, a stronger hydrogen-bonding network can actually hinder the ultrafast charge-transfer processes as clearly demonstrated from our steady-state and time-resolved experiments.
Chapter 6

Effect of Conjugation Length on Photoinduced Charge Transfer in $\pi$-Conjugated Oligomer-Acceptor Dyads

6.1 Introduction

Electron and energy transfer are fundamental processes involved in many important chemical and biological processes, ranging from light harvesting to energy conversion and storage. Over the past decades, significant effort has been devoted to the design and study of molecular assemblies to study electron and energy transfer processes. The knowledge gained has been applied to develop molecular-based devices such as dye-sensitized solar cells, organic solar cells, and artificial photosynthesis cells. A number of investigations have sought to understand the effect of $\pi$-conjugated spacers on electronic coupling and electron (or hole) transfer across the spacers in donor-bridge-acceptor (D-B-A) molecular assemblies. These investigations have sought to understand the role of the $\pi$-conjugated spacer in mediating charge transport. There is also the long-term goal of producing long lived radical ion pair (charge separated) states, aiming at applications to molecular electronics or artificial photosynthesis. These D-B-A systems consist of a donor (D) and acceptor (A) which are covalently linked via a molecular bridge (B).

Electron transfer dynamics in many D-B-A systems have been reported in which the bridge is a $\pi$-conjugated moiety. For example Wasielewski and co-workers explored electron transfer across oligo($\pi$-phenylene) bridges in a D-B-A system featuring a perylene diimide acceptor and phenothiazine as the donor. Albinsson and co-workers carried out systematic investigations of
electron transfer in porphyrin-based D-B-A systems in which the bridge was a series of oligo(phenylene ethynylene)s (OPEs) with varying length.\textsuperscript{31-32} Other D-B-A systems that have been explored include donor-acceptor pairs such as tetracene-pyromellitimide\textsuperscript{188} and porphyrin-C\textsubscript{60},\textsuperscript{189} and various \(\pi\)-conjugated oligomers have been used as bridges to link donor and acceptors in D-B-A systems, including oligo(phenylenevinylene) (OPV),\textsuperscript{188,190} oligo(phenylene ethynylene) (OPE),\textsuperscript{31-32,191} oligofluorene\textsuperscript{129,192-193} and oligothiophene.\textsuperscript{194} The active nature of the conjugated bridges in mediating electronic coupling is underscored by the relatively low attenuation factors (\(\beta\)) observed across these spacers,\textsuperscript{31} where the attenuation factor reflects the strength of the exponential decay of the electron transfer rate, for example

\[
k_{ET} = k_0 \exp(-\beta r_{DA}) \quad (19)
\]

where \(k_{ET}\) is the electron transfer rate constant, and \(k_0\) is the maximum rate, and \(r_{DA}\) is the donor-acceptor separation distance.

Despite considerable work on electron transfer across \(\pi\)-conjugated oligomer bridges, there has been comparatively less investigation of the effect of \(\pi\)-conjugation on intramolecular electron transfer in D-A systems where a \(\pi\)-conjugated oligomer serves as the electron donor. This is surprising, given the importance of photoinduced electron transfer from a \(\pi\)-conjugated oligomer or polymer to an acceptor as the fundamental step in the mechanism for photovoltaic response in organic solar cells. There have been multiple studies of photoinduced processes in oligomer-(fullerene) acceptor systems;\textsuperscript{195-200} however, in most cases the results are at best ambiguous due to the complex nature of fullerenes, which can act as both charge acceptors and energy acceptors, and due to their broad absorption across the visible region, make photo-selection difficult, and the low-energy fullerene triplet state.
In this chapter, we describe a detailed photophysical investigation of a series of naphthalene diimide (NDI) end capped oligo(phenylene ethynylene)s (PE-NDI, Chart 6.1). This work presented in this chapter has already been published in the Journal of Physical Chemistry A in 2017 in calibration with students under the supervision of professor Kirk at the University of Florida.

**Chart 6.1:** Chemical structures of PE$n$ and TIPS.36

These structures were designed to allow investigation of the dynamics of photoinduced charge-separation and recombination resulting from photoexcitation of the OPE chromophore, followed by photoinduced electron transfer to the NDI acceptor

\[
\text{OPE-NDI} + h\nu \rightarrow ^1\text{OPE}^+ \cdot \text{NDI} \rightarrow (\text{OPE}^{++} \cdot (\text{NDI}^{- \cdot}) \rightarrow \text{OPE} \cdot \text{NDI}
\]  

(20)

In the PE$n$-NDI series, the OPE segment length was varied from $n = 4$ to $n = 8$ phenylene ethynylene repeat units in order to examine the effect of \(\pi\)-conjugation in the donor on the dynamics of the forward and return electron transfer processes.
The naphthalene diimide acceptor was used due to its relatively low reduction potential, combined with relatively high singlet and triplet energies, which preclude OPE to NDI energy transfer from competing with electron transfer.\textsuperscript{201-202} In addition, the NDI anion radical (NDI\textsuperscript{−•}) has distinct absorption features that are easily identified by visible transient absorption spectroscopy.\textsuperscript{203}

At the outset of this investigation, we were interested in whether localization/delocalization and/or mobility of the singlet exciton and the polaron on the OPE chain (in the charge separated state) would influence the dynamics of forward or return charge transfer. Specifically, it is known that excited and charged states of π-conjugated oligomers and polymers are confined to specific segments by self-localization that occurs due to inner sphere and outer sphere relaxations. This localization may influence the electronic coupling between the donor and acceptor states, possibly resulting in interesting effects concerning the distance dependence of forward and return electron transfer reactions. The results described here reveal that photoinduced forward and back electron transfer reactions are efficient in all of the PE\textsubscript{n}-NDI series, and there are distinct variations in the observed rates with OPE segment length. The results are interpreted with a model that includes a description of the effect of singlet exciton delocalization on the rate of forward electron transfer, and a suggestion that positive polaron localization may influence the rate of return electron transfer in the charge separated state.
6.2 Results and Discussion

6.2.1 Oligomer Structures, Synthesis, and Characterization

The series of π-conjugated oligomer-acceptor dyads, PEn-NDI (n = 4, 6, 8) was synthesized that feature a conjugated oligo(phenylene ethynylene) backbone as an electron donor capped with a naphthalene diimide derivative as an electron acceptor. The naphthalene diimide derivative was chosen for its capability to serve as a strong electron acceptor and because of its characteristic radical anion absorption features. Three corresponding model oligomers end-capped with a triisopropylsilyl (TIPS) unit, PEn-TIPS (n = 4, 6, 8), were also prepared for control studies (Chart 6.1). The oligomers were mainly synthesized using Sonogashira reactions, and they were characterized by 1H NMR, 13C NMR, and high-resolution mass spectroscopy. Complete details concerning the synthesis and characterization are provided in the Appendices A. Photophysical Studies. The optical properties of the oligomers were studied by absorption and fluorescence spectroscopy in chloroform at room temperature, and the spectra of selected examples are illustrated in Figure 6.1.

In general, all the PEn-NDI oligomers show combined absorption properties from both the PEn and NDI segments; however, the absorption is dominated by the oligo(phenylene ethynylene) backbones due to their relatively larger absorption coefficients (Figure 6.1). Taking PE4-NDI as an example, as shown by Figure 6.1 A, PE4-NDI has an intense absorption band at 300-400 nm with distinct peaks at ~358 and ~378 nm. The major UV-visible absorption is attributed to the PE4 segment with superimposed features arising from the NDI moiety.
Figure 6. UV-visible absorption spectra of PEn-TIPS (black lines) and PEn-NDI (red lines); fluorescence spectra of PEn-TIPS (black dashed lines) and PEn-NDI (red dashed lines). Spectra measured in chloroform and the fluorescence spectra are normalized relative to the quantum yields. (A) PE4-TIPS and PE4-NDI. (B) PE6-TIPS and PE6-NDI. (C) PE8-TIPS and PE8-NDI. (D) Plots of fluorescence quantum yields of PEn-TIPS and PEn-NDI.\(^3\)

When conjugation length increases from PE4 to PE8, the absorption spectra of PEn-TIPS and PEn-NDI oligomers red shift and have increased molar absorptivity. Additionally, the mismatch of the emission from oligo(phenylene ethynylene) segments (see below) and absorption of the NDI moiety, ensures the minimized energy transfer in the OPE-NDI system.
All of the PEₙ-TIPS oligomers are highly emissive, and their fluorescence quantum yields (Φᵢ) decrease slightly from ∼0.85 to ∼0.76 from PE₄-TIPS to PE₈-TIPS (quinine sulfate in 0.1 M H₂SO₄ aqueous solution as standard, Φᵢ = 0.54). Similarly, the PEₙ-TIPS oligomers feature decreasing fluorescence lifetimes with increased oligomer length, with τᵢ = ∼0.82 ns down to ∼0.45 ns from PE₄-TIPS to PE₈-TIPS (Table 6.1). The significant decrease in lifetime with increasing oligomer length implies that the radiative decay rate increases with conjugation length. In stark contrast to the PEₙ-TIPS series, the PEₙ-NDI oligomers are virtually non-emissive: Φᵢ ranges from ∼0.002 to ∼0.025 from PE₄-NDI to PE₈-NDI (Figure 6.1D). Not surprisingly, the fluorescence lifetimes for all the NDI capped oligomers were below the instrument response (<100 ps).

The low fluorescence quantum yields for PEₙ-NDI oligomers indicate efficient quenching of the singlet excited state, presumably due to excited state electron transfer from the donor (OPE) to acceptor group (NDI). The electron transfer efficiency can be estimated from equation 16,

\[ \eta = 1 - \frac{\Phiᵢ (PEₙ - TIPS)}{\Phiᵢ (PEₙ - NDI)} \]  

where Φᵢ(PEₙ-NDI) is the fluorescence quantum yield for the PEₙ-NDI oligomers and Φᵢ is the quantum yield for corresponding PEₙ-TIPS oligomers. As a result, all the three PEₙ-NDI oligomers exhibit high electron transfer efficiency, ranging from 99.8% to 96.7% with increased oligomer length (Table 6.1). The highly efficient charge separation properties make the PEₙ-NDI oligomers excellent targets to investigate their charge separation and recombination kinetics and how they are influenced by the oligomer donor conjugation length.

Singlet-triplet intersystem crossing is one possible pathway for the deactivation of the excited states in OPEs. In the present work, nanosecond transient absorption spectroscopy (ns-TA)
was carried out to characterize the triplet transient absorption properties for PEn-TIPS and PEn-NDI oligomers.

Table 6.1 Photophysical Properties of Oligomers.\textsuperscript{36}

<table>
<thead>
<tr>
<th>Oligomer\textsuperscript{a}</th>
<th>(\lambda_{\text{abs}}) (\text{nm})</th>
<th>(\varepsilon \times 10^5) (\text{cm}^{-1} \text{M}^{-1})</th>
<th>(\lambda_f) (\text{nm})</th>
<th>(\tau_f) (\text{ns})</th>
<th>(\Phi_f) (\text{a})</th>
<th>(\tau_T) (\mu\text{s})</th>
<th>(\lambda_{T-T}) (\text{nm})</th>
<th>(\Phi_{\Delta}) (\text{a})</th>
<th>(\eta) (\text{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{PE4-TIPS}</td>
<td>354</td>
<td>1.08</td>
<td>398</td>
<td>0.82</td>
<td>0.84</td>
<td>3.45</td>
<td>623</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>\textit{PE4-NDI}</td>
<td>362</td>
<td>1.21</td>
<td>412</td>
<td>0.0021</td>
<td></td>
<td></td>
<td></td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>\textit{PE6-TIPS}</td>
<td>372</td>
<td>1.32</td>
<td>410</td>
<td>0.51</td>
<td>0.77</td>
<td>4.17</td>
<td>696</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>\textit{PE6-TIPS}</td>
<td>381</td>
<td>1.82</td>
<td>413</td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
<td>0.984</td>
<td></td>
</tr>
<tr>
<td>\textit{PE8-TIPS}</td>
<td>377</td>
<td>2.53</td>
<td>415</td>
<td>0.45</td>
<td>0.76</td>
<td>3.13</td>
<td>712</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>\textit{PE8-TIPS}</td>
<td>382</td>
<td>2.97</td>
<td>413</td>
<td>0.025</td>
<td></td>
<td></td>
<td></td>
<td>0.967</td>
<td></td>
</tr>
<tr>
<td>\textit{NDI}</td>
<td>381</td>
<td>0.51</td>
<td>403</td>
<td>0.0018</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}All photophysical data was obtained in chloroform solutions.

\textsuperscript{b}The excitation wavelength for all fluorescence studies is 355 nm.

\textsuperscript{c}Fluorescence lifetime measured by TCSPC.

\textsuperscript{d}Quinine sulfate in 0.1 M \(\text{H}_2\text{SO}_4\) aqueous solution as standard (\(\Phi_h = 0.54\)).

\textsuperscript{e}Measured by nanosecond transient absorption spectroscopy in a mixture of THF and acetonitrile (v/v 66:34).

\textsuperscript{f}Measured in deuterated chloroform, with tertthiophene as standard (\(\Phi_d = 84\%\)).

\textsuperscript{g}Electron transfer efficiencies (\(\eta\)) were calculated as \(\eta = 1-\Phi_h(\text{PEn-NDI})/\Phi_h(\text{PEn-TIPS})\) \((n = 4, 6, 8)\).

For these experiments the optical density for all the oligomer solutions was 0.7 at the excitation wavelength (355 nm) in THF. As shown in Figure 6.2, all three of the PEn-TIPS oligomers exhibit moderately intense transient absorption (500-700 nm) that persists into the microsecond time domain.
Figure 6.2 Nanosecond transient absorption spectra of PEn-TIPS (n = 4, 6, 8). The optical densities for all the oligomers were 0.7 at 355 nm in THF. Transient absorption spectra were obtained at 20 ns after laser 10 ns pulsed excitation at 355 nm.\(^\text{36}\)

The spectra are similar to those previously assigned to the triplet state of oligo(phenylene ethynylene)s, and by analogy they are assigned to the triplet excited states of the PEn-TIPS oligomers.\(^\text{207-208}\) Interestingly, excitation of the PEn-NDI oligomers under the same conditions does not give rise to transient absorption that can be observed on time scales longer than 20 ns. The lack of a triplet absorption is consistent with rapid photoinduced charge transfer taking place from the singlet state, which quenches triplet formation (vide infra).

With \(n\) increasing from 4 to 8 for PEn-TIPS oligomers, the triplet transient absorption peak is red-shifted from 623 to 712 nm.\(^\text{208}\) At the same time, the transient absorption intensity decreases with increasing oligomer length; this finding is consistent with earlier work on OPEs showing a reduced triplet yield with increased oligomer length.\(^\text{207-208}\) The results from singlet oxygen quantum yield studies of PEn-TIPS oligomers are consistent with trends observed from
triplet-triplet transient absorption data, in particular, PE4-TIPS exhibits singlet oxygen quantum yield of 0.19, followed by 0.10 for PE6-TIPS, and 0.08 for PE8-TIPS (see Appendices A Figure S 7).

6.2.2 Energetics of Photoinduced Electron Transfer

In order to estimate the energies of the charge-separated states for the PEn-NDI oligomers, cyclic voltammetry, and differential pulse voltammetry (CV and DPV) were performed in dichloromethane.

CV and DPV data are shown in the Appendices A (Figure S8), and a tabular listing of results is provided in Table 6.2. Note that all potentials listed are relative to Fc+/Fc. The cyclic voltammetry of PE4-NDI features two reversible cathodic waves at −1.05 and −1.48 V, along with a single irreversible anodic wave at $E_{ox} \approx 1.04$ V. The other NDI capped oligomers give similar results (Table 6.2). The reduction waves are clearly due to the NDI centered one- and twoelectron processes, while the oxidation is due to the OPE segment.

The driving force for charge separation from the singlet excited states in the PEn-NDI series can be approximated by using equation 22

$$
\Delta G^0_{CS} = E^0_{ox} - E^0_{red} - \Delta E_{0,0} - \left[ \frac{e^2}{4\pi \varepsilon_0 \varepsilon R_{DA}} \right]
$$

where $E^0_{ox}$ is the oxidation potential of the donor, $E^0_{red}$ is the reduction potential of the acceptor, and $\Delta E_{0,0}$ is the singlet excited state energy. The last term is the Coulomb stabilization energy in the charge separated state, where $\varepsilon$ is the dielectric constant in the solvent (8.93 in CH$_2$Cl$_2$) and RDA is the distance between the donor and acceptor units. (The separation distances were estimated as center-to-center using structures calculated from DFT B3LYP 6-31G* structures, Figure S 9). The calculated driving forces, $\Delta G^0_{CS}$, are listed in
Table 6.2, and they range from −1.19 to −1.10 eV across the series. Note that $\Delta G^0_{CS}$ does not vary much across the series, and this is a reflection of the fact that the oxidation and reduction potentials and singlet energies do not vary much with oligomer length.

The driving force for decay of the charge separated state, $\Delta G^0_{CR}$, is estimated by equation 23:

$$\Delta G^0_{CR} = -\{ E^0_{ox} - E^0_{red} - [e^2/(4\pi\varepsilon_0 \varepsilon R_{DA})] \}$$  \hspace{1cm} (23)

where the terms are defined above. The driving force for recombination for all three PEn-NDI oligomers is estimated to range from −2.02 to −1.96 eV (Table 6.2). Taken together the thermodynamic data suggests that both charge separation and charge recombination are strongly exothermic with the latter being considerably more exothermic.

**Table 6.2** Thermodynamic Parameters for PEn-NDI Oligomers.$^3^6$

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox}/V^a$</th>
<th>$(E_{ox}/V)^b$</th>
<th>$E_{red}/V^a$</th>
<th>$(E_{red}/V)^b$</th>
<th>$\Delta E_{0,0}^c$</th>
<th>$\Delta G^0_{CS}^d$</th>
<th>$\Delta G^0_{CR}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PE4$-NDI</td>
<td>1.04</td>
<td>(0.98, 1.24)</td>
<td>−1.05, −1.48</td>
<td>(−1.05, −1.48)</td>
<td>3.20</td>
<td>−1.19</td>
<td>−2.01</td>
</tr>
<tr>
<td>$PE6$-NDI</td>
<td>1.03</td>
<td>(0.99)</td>
<td>−1.05, −1.49</td>
<td>(−1.07, −1.50)</td>
<td>3.12</td>
<td>−1.10</td>
<td>−2.02</td>
</tr>
<tr>
<td>$PE8$-NDI</td>
<td>0.96</td>
<td>(0.91)</td>
<td>−1.05, −1.51</td>
<td>(−1.05, −1.51)</td>
<td>3.12</td>
<td>−1.16</td>
<td>−1.96</td>
</tr>
<tr>
<td>$PE6$-TIPS</td>
<td>1.06</td>
<td>(0.97)</td>
<td></td>
<td>3.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Obtained from cyclic voltammetry measurements.

$^b$Obtained from differential pulse voltammetry measurements.

$^c$Zero–zero transition energy, estimated on the basis of $\Delta E_{0,0} = ((E_{abs(max)} + E_{em(max)})/2$.

$^d$Calculated from equations 22 and 23.

$^e$Calculated from equations 22-23. ($E_{ox}$ and $E_{red}$ were obtained from cyclic voltammetry measurements, Coulombic stabilization energies were calculated from Weller method, 0.05 eV for PE8-NDI, 0.06 eV for PE6-NDI, and 0.08 eV for PE4-NDI).
In order to complete the picture of the states involved in the photophysics of the PEₙ-NDI oligomers, it is necessary to pinpoint the triplet levels. Previous studies indicate that the singlet-triplet splitting (ΔEST) in phenylene ethynylene conjugated systems is ~0.75 eV. Using this value, combined with the singlet energies, we estimate that the triplet states in the PEₙ-NDI oligomers lie within the range 2.37-2.45 eV. It is important to note that the triplet states are higher in energy than the charge separated states in all of the PEₙ-NDI series.

**Scheme 6.1** below summarizes the states involve in the photophysics of the PEₙ-NDI oligomers, along with their approximate energies. The important aspect is that the charge separated state is at lower energy compared to the singlet and triplet states. Therefore, excited state decay of both states is anticipated to occur via the charge separated state.

![Scheme 6.1 Mechanism of the photoexcitation of PEₙ-NDI oligomers.](image-url)

**Scheme 6.1** Mechanism of the photoexcitation of PEₙ-NDI oligomers.³⁶
Table 6.3 Charge Separation and Recombination Dynamics in PE4-NDI Oligomers.

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<thead>
<tr>
<th>Oligomer</th>
<th>$\tau_{CS}^a$ (ps)</th>
<th>$k_{CS}^a$ (s$^{-1}$)</th>
<th>$\tau_{CR}^a$ (ps)</th>
<th>$k_{CR}^a$ (s$^{-1}$)</th>
<th>$\tau_{CS}^b$ (ps)</th>
<th>$k_{CS}^b$ (s$^{-1}$)</th>
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$^a$Lifetimes ($\tau_{CS}$ and $\tau_{CR}$) were measured from femtosecond transient absorption spectroscopy (fs-TA) in dichloromethane, and rates ($k_{CS}$ and $k_{CR}$) were calculated by $k_{CS} = 1/\tau_{CS}$ and $k_{CR} = 1/\tau_{CR}$.

$^b$Lifetimes ($\tau_{CS}$ and $\tau_{CR}$) were measured from time-resolved infrared (TRIR) spectroscopy in dichloromethane, and rates ($k_{CS}$ and $k_{CR}$) were calculated by $k_{CS} = 1/\tau_{CS}$ and $k_{CR} = 1/\tau_{CR}$.

6.2.3 Intermolecular Photoinduced Charge Transfer

Intermolecular charge transfer between the PE4-TIPS oligomers and methyl viologen (MV$^{2+}$) was studied by nanosecond transient absorption (ns-TA) to gain insight concerning the spectra of the oligomer radical cations (OPE$^{++}$). The triplet excited PE4-TIPS oligomers are expected to transfer one electron to MV$^{2+}$, forming OPE$^{++}$ and MV$^{++}$ radical cation, equation 24:

$$^1\text{PE4-TIPS}^* \rightarrow ^3\text{PE4-TIPS}^* + \text{MV}^{2+} \rightarrow \text{PE4-TIPS}^{++} + \text{MV}^{++} \quad (24)$$

Nanosecond–microsecond transient absorption was carried out on solutions of the PE4-TIPS oligomers (7.0 μM) with MV$^{2+}$ (1.0 mM) in a THF/CH$_3$CN solvent mixture (v/v 2:1).

Qualitatively similar results were obtained for all of the oligomers, and Figure 6.3 A shows the results for PE4-TIPS.
Figure 6.3 (A) Nanosecond-microsecond transient absorption spectra for PE4-TIPS (7.0 μM) with MV$^{2+}$ (1.0 mM) at 20 ns and 2 μs following 355 nm excitation (red dotted and black solid lines, respectively). (B) Eigen spectra corresponding to triplet-triplet absorption of PE4-TIPS (red solid line), PE6-TIPS (blue dashed line), and PE8-TIPS (green dotted line). (C) Eigen spectra corresponding to cation radical absorption of PE4-TIPS$^{+\cdot}$ (red solid line), PE6-TIPS$^{+\cdot}$ (blue dashed line), and PE8-TIPS$^{+\cdot}$ (green dotted line). Transient absorption carried out in a solvent mixture of THF and acetonitrile (v/v 2:1) with optical density for oligomers at 0.7 at 355 nm. Eigen spectra were obtained from principal component analysis of time resolved transient absorption spectra using SpecFit global analysis software.36
The spectra for PE6-TIPS and PE8-TIPS are in the Supporting Information (Figure S10). At early times after excitation (20 ns), the spectrum is dominated by the triplet-triplet absorption of PE4-TIPS ($\lambda \sim 610$ nm). However, over a time course of 2 $\mu$s, the triplet absorption decays, and there is a residual, blue shifted absorption remaining ($\lambda \sim 585$ nm). This absorption feature is accompanied by a narrow peak at $\lambda \sim 390$ nm. Taken together, the data suggests that the long time spectral feature is due to the products of photoinduced charge transfer, with the band in the red arising from the radical cation, PE4-TIPS$^{••}$, and the narrow peak in the near UV is due to MV$^{••}$.\textsuperscript{211} By using principal component analysis, the time-resolved absorption data for the three oligomers was analyzed to provide principal component (eigen) spectra for the short-lived and long-lived transients (e.g., assigned to $^3$PE$_n$-TIPS$^*$ and PE$_n$-TIPS$^{••}$, respectively). The resulting eigenspectra are summarized for the three oligomers in Figure 6.3 B, C. Here it is easily seen that the absorption maximum of the triplet state systematically red shifts with increasing oligomer length (compare with Figure 6.2); by contrast, the absorption of the cation radical state, PE$_n$-TIPS$^{••}$, remains approximately constant regardless of oligomer length. Importantly, the cation radical (polaron) state of the oligomers absorbs strongly in the visible region, with $\lambda \sim 575$ nm. The fact that the PE$_n$-TIPS$^{••}$ absorption is relatively constant across the series suggests that the OPE polaron is spatially confined to a segment, which is less than or equal to 4 phenylene ethynylene units.\textsuperscript{212}

Photoinduced Electron Transfer in PE$_n$-NDI Oligomers. UV-visible region femtosecond transient absorption spectroscopy was carried out to study the dynamics of photoinduced intramolecular electron transfer in the PE$_n$-NDI oligomers. The experiments were carried out in CH$_2$Cl$_2$ solution with 35 fs pulsed excitation at 350 nm. First, control experiments were carried out on the PE-
TIPS oligomers to characterize the singlet excited state absorption and dynamics (Figure S11). Here it can be seen that the singlet excited state, \(^{1}\text{PEn}-\text{TIPS}^*\), is characterized by an apparent bleach between 400-500 nm due to stimulated emission,\(^{213}\) coupled with a broad, featureless absorption that extends from the visible into the near-IR region due to excited state absorption (ESA).\(^{208, 213}\) At longer times (t > 2 ns), the absorption due to the triplet is clearly seen in the spectrum of PE4-TIPS. The excited state dynamics are shown in Figure S12, and it is seen that the \(^{1}\text{PEn}-\text{TIPS}^*\) states decay in < 1 ns, consistent with the lifetimes obtained from fluorescence decay studies (Table 6.1).

The ultrafast transient absorption spectra of the PEn-NDI oligomers are distinctly different from that of the PEn-TIPS oligomers (Figure 6.4). For each of the oligomers, the spectra are characterized by a strong band with \(\lambda_{\text{max}} \sim 580-600\) nm with a distinct narrow peak at shorter wavelength, \(\lambda \sim 480\) nm. These absorption features are clearly due to the charge separated state, PEn\(^{+}\)-NDI\(^{-}\), with the strong band in the red due to the OPE cation (OPE\(^{+}\), compare Figure 6.3 C) and the short wavelength peak due to NDI\(^{-}\).\(^{203}\) Note also that consistent with the results obtained in the bimolecular electron transfer study with MV\(^{2+}\) acceptor (Figure 6.3 C), the absorption in the 580-600 nm region that is attributed to the OPE\(^{+}\) is slightly blue-shifted in PE4-NDI compared to the other two oligomers.
Figure 6.4 (A, B, C) Transient absorption spectra for PEn-NDI series on 0-10 ps time scale after excitation. (D, E, F) Transient absorption spectra for PEn-NDI series on longer time scale (see inset). Samples were excited at 350 nm in dichloromethane. The dashed vertical line highlights NDI− absorption feature at 480 nm.36
The transient absorption dynamics of the PEN-NDI oligomers provide insight regarding the rates of charge separation and recombination.

![Diagrams showing transient absorption dynamics](image)

**Figure 6.5** (A) Visible region transient absorption dynamics of PEN-NDI monitored at 480 nm. (B) Midinfrared transient absorption dynamics of PEN-NDI monitored at 2080 cm⁻¹.³⁶

As shown in **Figure 6.5 A**, the kinetics at 480 nm (corresponding to NDI⁻⁻) exhibit a rise on the 1-10 ps time scale and then a slower decay on time scales 1-5 ns. The rise is attributed to charge separation and the decay to charge recombination, equations 25 and 26, respectively

\[
^1\text{PE}n^* - \text{NDI} \rightarrow \text{PE}n^{++} - \text{NDI}^{--} \quad (25)
\]

\[
\text{PE}n^{++} - \text{NDI}^{--} \rightarrow \text{PE}n^- - \text{NDI} \quad (26)
\]

Fits of the dynamics provide quantitative information regarding the kinetics of electron transfer (**Table 6.3**). In particular, the rates for charge separation are very fast, ranging from \(1-10 \times 10^{11}\) s⁻¹, whereas the rates for charge recombination are slower by a factor of \(~100\), ranging from \(0.8-3 \times 10^9\) s⁻¹. Note that the rates for charge separation decrease noticeably as the oligomer length increases. However, the dynamics for charge recombination are much less dependent on
oligomer length, with a modest decrease between PE4-NDI and PE6-NDI but then the rate is essentially the same for the longer two oligomers.

6.2.4 Mid-Infrared Transient Absorption Spectroscopy

Mid-infrared transient absorption spectroscopy was also applied to probe the charge transfer processes in the PEn-NDI oligomers.\textsuperscript{16, 33, 214-215} In this case, the transients were monitored at 2080 cm\textsuperscript{-1} by using a mid-infrared probe continuum combined with a mid-infrared array detector. As shown in Figure 6.6, upon laser excitation, a transient absorption band at \(\sim 2080\) cm\textsuperscript{-1} is observed to grow in on a time-scale of 3-50 ps for all the PEn-NDI oligomers and it decays in a relatively slower process within the time-scale of 1-3.5 ns. The transient absorption band at 2080 cm\textsuperscript{-1} is \(\sim 70\) cm\textsuperscript{-1} lower in frequency compared to the position of the C≡C stretch for the ground state oligomers (see spectra for PE4-TIPS and PE4-NDI in Figure S13) and is attributed to the internal acetylene vibration in radical cation (OPE\textsuperscript{**}) present in the charge separated state, an assignment that is supported by previous studies of phenylene ethynylene oligomer ion radicals.\textsuperscript{215}
Figure 6.6 (A, B, C) Mid-infrared transient absorption spectra of PEn-NDI series on short time scale. (D, E, F) Mid infrared transient absorption spectra of PEn-NDI series on longer time scale (see inset). The data were measured in CH$_2$Cl$_2$ solutions with excitation wavelength at 400 nm. The optical density of sample solutions was controlled with 1 mOD at 350 nm with a 350 μm spacer. Panels in the left column show spectra with short time delays (increasing transient absorption) while panels in the right column show spectra with longer time delays (transient absorption decay).$^{36}$

The dynamics of charge separation and recombination in the PEn-NDI oligomers were obtained by monitoring the kinetics at 2080 cm$^{-1}$, and the results are shown in Figure 6.5 B for the comparison to the kinetics obtained by monitoring the visible transient absorption (Figure 6.5 A). The rates obtained from analysis of the infrared transient absorption dynamics are
tabulated in Table 6.3, and as can be seen they are in very good agreement with the rates obtained from the visible transient absorption.

6.2.5 Rates of Electron Transfer, Structure of the Charge Separated State, and Mechanisms

The findings reported here indicate that rapid photoinduced electron transfer occurs in a family of oligo(phenylene ethynylene) oligomers that are singly end-capped with a naphthalene diimide acceptor. Forward ET (charge separation) is strongly exothermic ($\Delta G_{CS} \sim -1.1$ eV) and the rates are correspondingly large ($\sim 10^{11}$ s$^{-1}$). Return ET (charge recombination) is even more exothermic ($\Delta G_{CR} \sim -2.0$ eV), yet the rates are considerably slower, in the range of $\sim 10^9$ s$^{-1}$.

The significant difference in forward and return ET rates likely stems from several factors. First, the driving force for forward ET is comparable to the reorganization energy ($\lambda$), and as such the reaction is nearly activationless, occurring at approximately the maximum rate for a nonadiabatic ET process ($\sim 10^{12}$ s$^{-1}$). By contrast, the very large exothermicity of the charge recombination process ($-2.0$ eV) places this reaction well into the Marcus-inverted region, and this likely in part accounts for the $\sim 100$ fold decrease in the rate compared to charge separation.$^{1,50,51}$ Correlations of the rates of charge separation and recombination as a function of donor-acceptor center-to-center separation distance, provide further insight into the mechanism and distance dependence of charge transfer in the PEn-NDI series (Figure 6.7). The correlation shows that the forward ET rates decrease weakly with distance, and the correlation is consistent with a logarithmic rate decay, for example,

$$k_{CS} = k_0 \exp(-\beta r) \quad (27)$$

with $\beta_{CS} \sim 0.15$ Å$^{-1}$. By contrast, the rate for charge recombination does not decay monotonically with distance, rather it follows the sequence PE4-NDI > PE6-NDI $\sim$ PE8-NDI. Note
also that the decrease of rate between PE4-NDI and PE6-NDI is consistent with a distance dependence factor \( \beta_{CR} \sim 0.15 \text{ Å}^{-1} \), the same as the forward ET reaction but \( k_{CR} \) then is nearly constant (\( \beta_{CR} \sim 0 \)) from PE6-NDI to PE8-NDI. A similar break in distance dependence has been observed in other donor-bridge-acceptor systems, and in these cases the change has been attributed to a crossover in the ET mechanism.\(^{30,216}\)

\[ \text{Figure 6.7} \text{ Distance dependence of charge separation (A) and charge recombination (B) for PEn-NDI oligomers. (The red \bigcirc\ dot), rates measured by infrared transient absorption; (black square \blacksquare\), rates measured by visible transient absorption. In part A, dashed line (\( \beta_{CS} \)) has slope of 0.15 Å\(^{-1}\). In part B, negative sloped line is \( \beta_{CR} \sim 0.15 \text{ Å}^{-1} \).^{36} \]

As outlined below, we believe that a similar change in mechanism may occur for the return ET reactions in the PEn-NDI series.

An analysis of the variation of the rates across the PEn-NDI series must account for the fact that the thermodynamics for forward and return ET are nearly independent of the length of the OPE segment (Table 6.2). Thus, the variation in rate with length must arise from variation(s) of other factors, for example, electronic coupling, structure of the OPE polaron (cation radical state,
OPE**) and/or conformational gating. Before pursuing the discussion further, we digress briefly to consider the structure and delocalization of the singlet excited state and the charge separated states in the PEn-NDI oligomers. Previously, considerable work has explored the structure of the excited states in π-conjugated oligomers and most pertinent to this discussion is oligo(phenylene ethynylene)s. In this regard, it has been established that the effective conjugation length in the singlet excited state is approximately nine phenylene ethynylene (PE) repeating units.\textsuperscript{217-219} By contrast, less is known regarding the structure of the positive polaron state (cation radical) of OPEs. In the current study it was found that the absorption of the cation state of the OPEs does not vary significantly with oligomer length, from PE4 to PE8 (Figure 3 C). This finding suggests that the hole polaron is relatively more localized than the singlet state, perhaps effectively occupying a confined segment of \( n \leq 4 \) repeat units in the longer oligomers. With this background, we present the model shown in Scheme 6.2 to discuss and explain the trends in ET rates observed in the PEn-NDI oligomers. Excitation of PEn-NDI produces a singlet state that is delocalized over the entire oligomer. The rate of charge separation depends on the coupling between the singlet wave function on the PEn donor and the NDI acceptor.

![Scheme 6.2](image)

**Scheme 6.2** Mechanism of the photoexcitation in PE8-NDI system.\textsuperscript{36}
The small decrease in the forward ET rate with increasing oligomer length (β ≈ 0.15 Å⁻¹) is attributed to a decrease in the electronic coupling that occurs because the excited state wave function is more delocalized as the oligomer length increases. However, because the PEn hole polaron is more spatially confined than the singlet exciton, the distance dependence of charge recombination in the charge separated state may involve a more complicated scheme. Here we propose the possible involvement of different charge separated (CT) states that may exist in the longer oligomers. As shown in Scheme 6.2, forward ET produces an initial “geminate CT” state, where the hole polaron is localized on the OPE segment closest to the NDI acceptor. Although there clearly is a Coulombic attraction between the electron and hole in this state due to the long lifetime of the CT state, it is possible that the polaron could “hop” along the chain to form one or more distinct “separated CT” states, where the polaron has moved along the OPE segment away from the NDI acceptor. We estimate that in CH₂Cl₂ the Coulombic barrier between the geminate and separated CT states is <0.07 eV. Given that the energy barrier to hopping is relatively low, the rate of the polaron hopping is most likely controlled by fluctuations in the conformation of the OPE backbone, more specifically polaron hopping is conformationally gated by rotations of the phenylene units. Within this model, the rate of return ET may be controlled in part by conformation gating of the hole hopping which interconverts the separated CT state(s) and the geminate CT state. This could explain why the rates of return ET are comparable in the longer oligomers.
6.3 Conclusion

A series of naphthalene diimide derivative (NDI) end-capped conjugated oligomers (PEn-NDI) were prepared, where the conjugation length of oligo(phenylene ethynylene) (OPE) conjugated backbone was controlled by Sonogashira reactions. The oligomers were systematically investigated by electrochemistry and steady-state and time-resolved spectroscopy. Electron transfer is the dominant pathway for deactivating of excited states of the PEn-NDI oligomers with an efficiency >97%. Both charge separation and charge recombination are strongly exothermic ($\Delta G_{CS}^0 \sim -1.10$ and $\Delta G_{CR}^0 \sim -2.00$ eV), and the thermodynamics do not vary much across the series. By using UV-visible region femtosecond transient absorption spectroscopy and mid-infrared transient absorption spectroscopy to probe the excited-state and charge transfer dynamics, the PEn-NDI oligomers are shown to undergo charge separation on the $1-10$ ps time scale, and then a slower charge recombination on time scales $1-5$ ns. The forward CS rates decrease weakly with distance ($\beta_{CS} \sim 0.15$ Å$^{-1}$), caused by the decrease in the electronic coupling. More interestingly, a discontinuous distance dependence was observed for CR, suggesting a change in the mechanism for the return electron transfer.
Chapter 7

Charge Separation in Different Chain Length Conjugated Polymers

7.1 Introduction

Since their discovery, conjugated chromophores have been outstanding candidates for many artificial electronic device applications, such as solar cells, light emitting diodes, field effect transistors, and others.\textsuperscript{220-223} Compared to small organic molecules, conjugated polymers have many advantages, such as being more stable, easier to synthesize and more feasible for device processing. Charge transport plays an important role in these devices. For example, in bulk heterojunction solar cells, it is crucial to have fast charge separation and long-lived charge separated states in order to build high performance devices. Further, it has been proved that molecular weight can significantly affect device performance and quenching efficiency.\textsuperscript{224-227} Many works have already furthered the understanding of the effect of the molecular weight on charge transport behavior while charge recombination receives less attention.

Most of the charge recombination studies have been focused on systems containing small molecular weight molecules, due to the fact that small molecules have well-defined structures and molecular weight is mono-dispersed. Otsubo and co-workers reported charge separation and recombination studies in systems of oligothiophene-fullerene dyads.\textsuperscript{228-229} In a system consisting of tetrathiophene-fullerene, the charge separation rate was faster in highly polar solvents (on the order of $10^{10} \text{s}^{-1}$), such as THF and benzonitrile, and decreased in weaker polar solvents (on the order of $10^{9} \text{s}^{-1}$), such as anisole and toluene. The charge separation state was not observed in non-polar benzene. The chain length effect of oligothiophene on charge
separation and recombination rate was also investigated. With increasing chain length, from octathiophene-fullerene to dodecathiophene-fullerene, the charge separation rate increased while the charge recombination rated decreased. In the charge recombination, there were both fast processes which originated from direct charge recombination and slow processes which were due to indirect charge recombination after charge migration. Albinsson et al. investigated charge separation and recombination in donor-bridge-acceptor systems where donors and acceptors were porphyrin compounds.\textsuperscript{31,230} It was interesting that, in a system with a broken conjugation bridge, the singlet excited state of the donor was quenched via a singlet energy transfer mechanism and the quenching rate was independent of solvent. In contrast, when the bridge was $\pi$-conjugated, the quenching occurred via an electron transfer mechanism. Both charge separation and recombination rate in $\pi$-conjugated bridge systems decreased with increasing bridge length and the charge separation rate decreased more rapidly compared to that of charge recombination.

In this work, we reported the synthesis of a series of polymers (PPE-NDI-n) featuring a poly-(phenylene ethynylene) (PPE) (donor) backbone and naphthalene diimide derivative (NDI, acceptor) end-caps, and charge recombination studies on the polymers. This work presented in this chapter is in calibration with students under the supervision of professor Kirk at University of Florida. The polymer structure was chosen due the fact that there is no overlap of the emission spectra of PPE and absorption of NDI. Further, the NDI is almost non-fluorescent which minimizes of energy transfer. The polymer chain length was varied to study the effect of polymer molecular weight on charge transfer and recombination behaviors. Femtosecond (fs) time-resolved transient absorption (TA) spectroscopy was applied to investigate charge
recombination kinetics and the long-lived charge separation state was also studied by nanosecond TA. The results of this work provide insight on the charge recombination kinetics and charge separated state.

7.2 Results and Discussion

7.2.1 Polymer Structures, Synthesis, and Characterization

In this study, a series of polymers, PPE-NDI-n, were synthesized, that feature the same conjugated poly(phenylene ethynylene) backbone and naphthalene diimide derivative end-group substitution, but different molecular weight. The synthetic procedure was outlined in Chart 7.1. The polymers were synthesized under Sonogashira polycondensation reaction conditions and molecular weight was controlled using the “end-capping” strategy during polymerization reactions. In a typical reaction, Monomer 1 and Monomer 2 (1:1 molar ratio) and various amounts of End-cap 1 were added into a flask. Without the presence of mono-functionalized End-cap 1, the polymer chain will keep growing. However, the addition of End-cap 1 changed the stoichiometric balance of the functional groups and lowered the overall molecular weight. End-cap 2 was added at the end of polymerization to ensure efficient end-capping at both chain ends. In addition, one PPE polymer without electron acceptor was synthesized as a model compound. The synthesis of OPE-8 was reported by Mr. Junling Jiang from the Schanze group (unpublished results).
Chart 7.1. General synthesis of PPE-NDI-n polymers.

Polymer molecular weights were characterized by both GPC and $^1$H-NMR (Figure 7.1). The GPC trace shows a clear decrease in the retention time with increasing polymer molecular weight ($\text{Mn (PPE-NDI-8)} < \text{Mn (PPE-NDI-14)} < \text{Mn (PPE-NDI-22)} < \text{Mn (PPE-NDI-39)}$). In the $^1$H-NMR spectrum, both proton signals from the naphthalene diimide and polymer backbone appear. The chemical shift at 8.82 ppm was assigned to the aromatic protons on the naphthalene rings and shifts at 7.73 ppm and 6.98 ppm came from the phenyl ring next to the naphthalene unit. Aromatic protons of the PPE backbone occur at 7.38 ppm and the methylene unit which was directly connected to the phenyl ring had a chemical shift at around 2.84 ppm. Signal integration of naphthalene protons and methylene protons were used to calculate the molar ratio of naphthalene units to phenyl rings. Assuming there are two naphthalene groups on each polymer chain, the number of phenyl rings and repeat units can be determined by calculating the ratio of the signal integration at 7.38 ppm and 2.84 ppm.
Figure 7.1. GPC and NMR characterization of PPE-NDI-n. a) GPC and b) $^1$H-NMR of PPE-NDI-8 (black), PPE-NDI-14 (red), PPE-NDI-22 (blue) and PPE-NDI-39 (dark cyan).

The number of repeat units calculated from NMR differs significantly from that derived from GPC when molecular weight is high (Table 7.1).

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<td>17</td>
</tr>
<tr>
<td>$M_n$ (g/mol)</td>
<td>3700</td>
<td>3700</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$DP^c$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PPE-NDI-8</strong></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td><strong>PPE-NDI-14</strong></td>
<td>19</td>
<td></td>
</tr>
<tr>
<td><strong>PPE-NDI-22</strong></td>
<td>29</td>
<td></td>
</tr>
<tr>
<td><strong>PPE-NDI-39</strong></td>
<td>62</td>
<td></td>
</tr>
<tr>
<td><strong>PPE</strong></td>
<td>12$^d$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Narrow dispersed polystyrene was used as the standard.

$^b$ Degree of polymerization was calculated using $M_n$ obtained by GPC.

$^c$ Degree of polymerization was calculated using signal intensity integration ratio from $^1$H-NMR.

$^d$ Calculated using the $^1$H-NMR integration of the t-butyl and PPE backbone signals.
The reason might be: a) that as the molecular weight gets too large, conjugated polymers tend to form \( \pi-\pi \) stacking and aggregate in solution, shielding the NMR signal, or b) high molecular weight polymers were obtained using a reduced amount of end-caps in the reaction systems, which resulted in a decreased \(^1\text{H}-\text{NMR} \) signal of the end-cap protons and cause more error in signal integration.

### 7.2.2 Energetics and Optical Properties

The objective of this project is to investigate the charge recombination in conjugated polymers. It is essential to have the redox state information, in order to understand the excited and charge-separated state energies. The singlet excited state energy of PPE-NDI-n polymers is available from the fluorescence emission spectra. The reduction and oxidation potentials of the NDI end-caps and PPE backbone are obtained from cyclic voltammetry (CV), and the charge separated-state energy is calculated from the difference in the PPE backbone oxidation and NDI reduction potentials. Cyclic voltammetry was performed on all polymers, but reasonable results were obtained only on the shortest chain length polymer, namely, PPE-NDI-8 (Figure 7.2), due to the intrinsic difficulty of performing CV on high molecular weight polymers. However, the energetics of other PPE-NDI-n polymers should be very similar to that of PPE-NDI-8, because they have the same polymer structure and almost identical absorption and emission (Figure 7.3).
Figure 7.2 a) Energetics and b) CV of PPE-NDI-8. Cyclic voltammogram of PPE-NDI-8 in methylene chloride with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as electrolyte, vs. SCE.

The cyclic voltammogram of PPE-NDI-8 shows two quasi-reversible reduction peaks with $E_{\text{red}} = -0.61$ V and $E_{\text{red}} = -1.01$ V, along with a single irreversible oxidation peak with $E_{\text{ox}} = 1.49$ V and onset at 1.22 V (potentials vs. SCE). One thing needs to be pointed out here is that each reduction wave on the CV very likely corresponds to one electron transfer to both NDI end-caps which is supported by previous studies.\(^{202-203}\) The charge-separated state energy is calculated using:

$$E_{\text{cs}} = E_{\text{ox}} - E_{\text{red}} - 14.4/\varepsilon R_{\text{DA}}$$ \hspace{1cm} (28)

where $E_{\text{ox}}$ is the oxidation potential of the PPE backbone, $E_{\text{red}}$ is the first reduction potential of the NDI end-caps, $\varepsilon$ is the dielectric constant and $R_{\text{DA}}$ is the distance between the donor and acceptor units. The $14.4/\varepsilon R_{\text{DA}}$ term is the Coulombic stabilization energy in the charge-separated state and is estimated to be 0.05 eV for PPE-NDI-8 in DCM, assuming the average distance between the positive charge and the NDI is about the length of 4 repeat units. In the
case of PPE-NDI-8, the charge-separated state energy ($E_{cs}$) is calculated to be ~1.90 eV and the
ing singlet energy is ~2.94 eV. In PPE type conjugated polymers, the triplet state energy is found to
be 0.7 ± 0.1 eV below the singlet state.\textsuperscript{231} Thus, the triplet state energy level in PPE-NDI-n
polymers is about 2.1 ± 0.1 eV, which is within the range of reported value for PPE type
polymers (1.95 - 2.26 eV).\textsuperscript{232,233} The triplet energy level of the NDI compound has been
estimated to be 2.03 eV, using the phosphorus emission unset wavelength ($\lambda = 610$ nm).\textsuperscript{233}

\begin{table}
\centering
\caption{Energetics of PPE-NDI-8, PPE and OPE-8}
\begin{tabular}{l|cccc}
\hline
 & $E_{\text{singlet}}/eV$ & $E_{\text{red}}/V$ & $E_{\text{ox}}/V$ & $E_{cs}/eV$
\hline
OPE8\textsuperscript{a} & 2.99 & N.A. & 1.31 & N.A.
NDI-H\textsuperscript{b} & 3.21 & N.A. & -0.53 & N.A.
PPE-NDI-8 & 2.94 & -0.65 & 1.27$^{e}$ & 2.14
\hline
\end{tabular}
\end{table}

\textsuperscript{a} Taken from our group’s unpublished results.
\textsuperscript{b} Taken from Ref\textsuperscript{202}.
\textsuperscript{c} Estimated from fluorescence emission.
\textsuperscript{d} Value reported vs. SCE.
\textsuperscript{e} Calculated using the average number of $E_{\text{ox}}$(OPE8) and the onset of PPE-NDI-8 oxidation potential.

UV-visible absorption and emission spectra of the samples were measured in THF, and the
concentration of the samples was adjusted to 50 µM (based on repeating unit for polymers)
(Figure 7.3). The NDI has two major absorption peaks at 358 nm and 378 nm. The PPE backbone
has a broad absorption from 300 nm to 425 nm, with the absorption maximum at 377 nm.
Although, the PPE and NDI absorption spectra have a large overlap (300-395 nm), the
absorption of the PPE-NDI-n polymers is still dominated by the PPE backbone because the
absorption coefficient of the PPE backbone (8.8$x10^{6}$ for PPE-NDI-39) is significantly higher than
that of the NDI end-caps (~5$x10^{5}$ for NDI). The NDI does not have any absorption beyond 395
nm while the emission of the PPE backbone starts near 390 nm. The mismatch of the PPE emission and NDI absorption ensures that the energy transfer in the PPE-NDI system is minimized. In addition, the NDI is almost non-emissive in solution compared to the PPE polymer, with a quantum yield of $\phi=0.18\%$, while the quantum yield of the PPE is about 76%. Therefore, the emission of PPE-NDI-n polymers mostly comes from the PPE backbone.

Figure 7.3. UV-vis absorption and emission spectra in THF. a) UV-vis absorption of the PPE (black) and NDI (red), normalized according to the absorption coefficient. b) Fluorescence emission of the PPE (black) and NDI (red), normalized according to fluorescence quantum yields. c) UV-vis absorption and d) emission of PPE-NDI-8 (■), PPE-BDI-14 (●), PPE-NDI-22 (▲).
and PPE-NDI-39 (▼), and the signals are normalized according to the quantum yields. The excitation wavelength for all samples is 375 nm. Absorption spectra in C are offset for clarity.

In the absorption spectra of PPE-NDI-n polymers, the NDI absorption band at 362 nm can be easily identified in PPE-NDI-8 and this feature becomes less pronounced as the polymer molecular weight increases. However, despite overlapping with the PPE backbone absorbance, the NDI absorption band at 379 nm can clearly be distinguished even in longest chain length polymer. Meanwhile, the PPE backbone absorption becomes stronger as molecular weight increases, due to the fact that the molar extinction coefficient increases with molecular weight. The overall absorption spectra increasingly resemble the PPE model polymer as the molecular weight increases due to the increased contribution of the PPE backbone. Despite the changing molecular weight, the absorption maximum remains essentially the same (at 379 nm), indicating the conjugation length is saturated for all polymer samples. In many donor-acceptor molecule systems, besides the \(\pi-\pi^*\) transition band, a charge transfer absorption band can also be observed. However, it was not the case for PPE-NDI-n polymers, due to weak electronic coupling.

All polymers have almost identical emission spectra with emission maxima at 422 nm which is the same as the PPE model polymer. However, the emission intensity is significantly weaker compared PPE model due to charge transfer. Although there is only 5% NDI (molar ratio) in PPE-NDI-39, more than 80% of the emission of polymer backbone is quenched. Further, the quenching is more efficient in PPE-NDI-22 and this trend continues as NDI content increases (Table 7.3).
Table 7.3 Summary of the Photophysical Properties

<table>
<thead>
<tr>
<th>Polymers</th>
<th>NDI Content (molar %)</th>
<th>λ_{abs} (nm)</th>
<th>λ_{em} (nm)</th>
<th>ε (10^4 cm^{-1} M^{-1})</th>
<th>Lifetime at 420 nm (ns)</th>
<th>Quantum Yield</th>
<th>e-transfer Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE-NDI-39</td>
<td>4.9</td>
<td>379</td>
<td>422</td>
<td>2.25</td>
<td>0.18</td>
<td>0.15</td>
<td>80.5</td>
</tr>
<tr>
<td>PPE-NDI-22</td>
<td>8.3</td>
<td>379</td>
<td>422</td>
<td>2.14</td>
<td>0.15</td>
<td>0.093</td>
<td>87.9</td>
</tr>
<tr>
<td>PPE-NDI-14</td>
<td>12.5</td>
<td>379</td>
<td>422</td>
<td>2.16</td>
<td>0.15</td>
<td>0.044</td>
<td>94.3</td>
</tr>
<tr>
<td>PPE-NDI-8</td>
<td>20</td>
<td>379</td>
<td>422</td>
<td>2.24</td>
<td>0.13</td>
<td>0.013</td>
<td>98.3</td>
</tr>
<tr>
<td>PPE</td>
<td>0</td>
<td>380</td>
<td>422</td>
<td>2.12</td>
<td>0.38</td>
<td>0.77</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

\(^a\) With anthrathene as quantum yield standard, \(\varphi = 0.27\) in ethanol at room temperature.

\(^b\) Energy transfer efficiencies (\(\eta\)) were calculated as \(\eta = 1 - \varphi(PPE_{380-525nm})/\varphi(PPE)\), in which \(\varphi(PPE)\) was the fluorescence quantum yield of donor-only polymer PPE.

The overall energy transfer efficiency was calculated using the ratio of PPE-NDI-n polymer fluorescence quantum yields to the PPE model polymer quantum yield, and the trend is clear that charge transfer efficiency decreases with increasing \(M_n\).

7.2.3 Transient Charge Recombination Processes

Femtosecond (fs) transient absorption (TA) spectroscopy was used to characterize the intrachain charge recombination kinetics in PPE-NDI-n polymers. Figure 7.4 compares the transient spectrum of the PPE and PPE-NDI-8. The transient spectrum of PPE has negative signals (bleach) from 420 nm to 510 nm which are the combination of ground state bleaching and stimulated emission. An intense excited state absorption also is observed for \(\lambda > 510\) nm.

The transient spectrum of PPE-NDI-n is very different compared to that of PPE. The spectrum is dominated by three strong absorption bands with one at around 480 nm, which is attributed to the absorption of naphthalene diimide radical anion (NDI\(^{-}\)), and a broad band from about 570
nm to 650 nm, which is attributed to a combination of NDI radical anion and PPE radical cation (PPE**) absorptions.\textsuperscript{201, 203} The appearance of the 480 nm band clearly indicates the formation of NDI radical anion which is generated by one electron transfer from the PPE backbone to the NDI end group. In the spectrum of PPE-NDI-8, the bleaching from 420 nm to 510 nm, observed in the spectrum of the PPE, is completely covered by the NDI\textsuperscript{−} absorption.

![Figure 7.4](image.png)

**Figure 7.4.** Transient spectra of the PPE (Black Line), and PPE-NDI-8 (Red line) in DCM after 100 ps.

The time dependent transient absorption spectrum of PPE-NDI-n polymers is plotted in (Figure 7.5). As the molecular weight increases, the feature of NDI\textsuperscript{−} peak at \(~480\) nm becomes less structured due to the fact that the NDI content decreases with increasing molecular weight and the NDI\textsuperscript{−} signal intensity, which is proportional to the NDI content, decreases as well. In addition, charge transfer is less efficient in high molecular weight polymer and the bleaching signal from the PPE backbone becomes more significant. The broad peak from \(~550\) to 650 nm...
also starts to blend with the PPE excited state absorption as molecular weight increases.

Another interesting finding is that absorption signals for PPE-NDI-8 and PPE-NDI-14 decay to zero after \( \sim 5 \) ns while there are still signals at \( \sim 480 \) nm in the spectra of PPE-NDI-22 and PPE-NDI-39 which means the NDI\(^*\) lives longer in high molecular weight polymers.

**Figure 7.** 5 Femto-nanosecond time-resolved transient absorption spectra of PPE-NDI-n polymers excited at \( \lambda_{\text{ex}} = \) nm in DCM solvent.

Detailed information of charge transfer kinetics can be obtained by monitoring signals at specific wavelengths. Because the signal at 480 nm is dominated by NDI\(^*\) absorption, this wavelength was exclusively used to probe the charge separated state. In the TA spectrum, a
rise in absorbance was not observed due to polymer relaxation and reorganization and therefore, the charge transfer dynamics cannot be resolved.\textsuperscript{213, 217} In general, the decay kinetics has two components: fast component (within \(\approx 100\) ps) which is attributed to polymer structure relaxation and reorganization, and a relatively slow component (within the order of several hundred ps) reflecting the process of charge recombination. A more careful review of the charge recombination process shows that there is an increasing contribution from the slow recombination process as the molecular weight increases (Table 7.4).

**Table 7.4 Charge Recombination Kinetics**

<table>
<thead>
<tr>
<th></th>
<th>(t_1) (ps)</th>
<th>(A_1)</th>
<th>(t_2) (ps)</th>
<th>(A_2)</th>
<th>(y_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE-NDI-8</td>
<td>100.00</td>
<td>0.65</td>
<td>436.00</td>
<td>0.27</td>
<td>0.05</td>
</tr>
<tr>
<td>PPE-NDI-14</td>
<td>64.00</td>
<td>0.41</td>
<td>414.00</td>
<td>0.36</td>
<td>0.10</td>
</tr>
<tr>
<td>PPE-NDI-22</td>
<td>155.00</td>
<td>0.57</td>
<td>764.00</td>
<td>0.24</td>
<td>0.13</td>
</tr>
<tr>
<td>PPE-NDI-39</td>
<td>121.00</td>
<td>0.37</td>
<td>676.00</td>
<td>0.30</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Equation was used for fitting.

One explanation is that the holes generated by electron transfer from PPE to NDI end-groups can delocalize along the conjugated backbone and become further removed from the end NDI\(^{\bullet}\) as the polymer chain length increases. The charge recombination is driven by the Coulomb interaction between the cation and anion radicals, and the strength of which follows Coulomb’s law, which is proportional to the inverse square of the distance between the interacting charges. The distance between the cation and anion radicals increases with molecular weight as the hole delocalized further away from the NDI end-caps. Therefore, Columbic interactions decrease dramatically. The residue signals in the kinetic trace increase with molecular weight which is also consistent with the transient absorption spectrum.
A series of polymers (PPE-NDI-n) with different molecular weight were synthesized which featured the same poly-(phenylene ethynylene) (PPE) conjugated backbone and naphthalene diimide derivative (NDI) substitution at the polymer chain ends. The energetics of polymers were investigated by cyclic voltammetry and steady state absorption and emission spectroscopy. Despite the increase of molecular weight, all PPE-NDI-n polymers show similar energy levels. Yet, the fluorescence emission quantum yield measurements indicate very efficient electron transfer from the PPE backbone to the NDI end-groups, and the transfer efficiency increases with decreasing molecular weight. Femtosecond transient absorption (fsTA) analysis showed that charge recombination rate also increased with decreasing chain length.

**Figure 7.6** Transient kinetics from $\lambda=480$ nm for all PPE-NDI-n polymers.
Chapter 8

Ultrafast Excited-State Electron Transfer at Polyfluorene-Graphene Carboxylate Interfaces

8.1 Introduction

π-conjugated polymers have become new materials of interest for solar cell applications,\textsuperscript{1-2} optical devices,\textsuperscript{4} chemical sensors\textsuperscript{5} and biological sensors.\textsuperscript{59} As discussed in chapter 3, among the emerging conjugated polymers, conjugated polyelectrolytes (CPEs) consisting of a conjugated main chain and side chains with various functional groups have been intensively investigated.\textsuperscript{61} As a result, in this chapter, we report a deeper understanding of photoinduced electron transfer (PET) in π-conjugated polymers (PFN) used in chapter 3 but this time, we react it with negatively charged graphene carboxylate (GC).

In this study, we report PET in non-covalent associations of cationic polyfluorene, namely poly[(9,9-di(3,3′-N,N′-trimethyl-ammonium) propyl fluorenyl-2,7-diy1-alt-co-(9,9-dioctyl-fluorenyl-2,7-diy1)] diiodide salt (PFN) and negatively charged graphene carboxylate (GC). GC was selected because (i) its opposite charge would provide strong electrostatic interactions with PFN, and (ii) it is one of the strong electron acceptor moieties to several porphyrin derivatives, resulting in ultrafast and efficient electron transfer.\textsuperscript{47,235} This non-covalent PFN-GC system is of interest because it gives a good model of PET in the polyfluorene electrostatically interacted with the electron acceptor.

Steady-state absorption and emission spectroscopies revealed the strong affinity of PFN on the GC surface and efficient quenching of the PFN fluorescence. By associating the fluorescence
lifetimes of PFN by GC, we demonstrated that the quenching mechanism of the PFN/GC systems is static. This finding is supported by femtosecond time-resolved absorption spectra, which reveals ultrafast electron transfer from the photoexcited PFN to GC (in 22.4 ps time scales). One advantage of the present cationic polyfluorene is, therefore, the control over the electrostatic interactions and electron transfers in non-covalent polyfluorene/quencher systems in solution. Furthermore, side chains of the polyfluorene can easily be modified in the future to construct new non-covalent associations based on polyfluorene.

8.2 Results and Discussions

8.2.1 Steady-State Absorption and Emission Measurements

The absorption and fluorescence of PFN with the successive addition of GC are shown in Figure 8.1 A. In the absence of the GC, the absorption spectrum of PFN has a maximum peak at 402 nm, with a shoulder at 387 nm and absorption cutoff at 450 nm. Upon successive addition of GC, the absorption spectrum of PFN is shifted upward with the GC concentration. This upward shift is demonstrated for the whole range of the recorded wavelength, and it is mainly originating from the absorption contribution of GC. Thus, in general, the spectra of the mixtures are the superposition of the absorptions of the PFN and the electron acceptors. This indicates that, upon the electron acceptor addition, the electronic structure of the PFN is unaffected or, in other words, the ground state interactions between the PFN and the electron acceptors do not form the CT complex formation.
Figure 8.1 Steady-state (A) absorption and (B) emission spectra for PFN and FPN-GC associations in DMSO.

Excitation at 380 nm gives rise to a fluorescence spectrum of the PFN in the visible region in the range of 400-550 nm centered at 424 nm with two vibronic shoulders at 447 and 485 nm. Successive addition of GC results in the quenching of the PFN emission. Approximate 97% quenching of the PFN was observed upon the addition of 0.12 mg/mL of GC, indicating that the strong negatively charged GC acceptor is largely effective for the enhanced fluorescence quenching of PFN. Note that the fluorescence quenching suggests electron or energy transfer from the excited PFN to the quencher. Because the fluorescence intensity for all of the PFN peaks was decreasing at the proportional scales, resulting in the consistent spectral shape of the emission without any new emission band, we can safely conclude that there is no energy transfer process from the photoexcited PFN to the electron acceptors.

The key difference of the fluorescence quenching behavior of the PFN by GC is revealed by the fluorescence lifetime of PFN-GC system at different concentrations of the quencher (as shown in Figure 8.2).
Figure 8.2 Time correlated single photon counting (TCSPC) kinetic profile collected using excitation at 380 nm of PFN-GC (concentrations indicated on graph). Inset showing the fluorescence of the solutions used for the TCSPC measurements.

The results show static quenching for PFN-GC system which is in agreement with Stern-Volmer results as showing in (Figure 1).

In the PFN and GC system, the same fluorescence lifetime PFN in the absence and presence of GC clearly suggests that the quenching in PFN and GC systems proceeds according to a static mechanism. In contrast, the fluorescence lifetime PFN in the presence of GC is shorter than that in the absence of GC, supporting the dynamic nature of the interaction. The different quenching mechanisms are considered to give different rates of the PET process; where the rate of PET for quenching through static mechanism in the PFN-GC systems should be much faster than that in the PFN-DCB due to dynamic mechanism in the PFN and DCB.
systems, (see chapter 3). In addition to the driving force of the electron transfer process,\textsuperscript{24} in the earlier case, the rate constant depends on the electronic coupling,\textsuperscript{67} whereas in the latter case the rate constant should be determined by diffusion of the electron donor and acceptor moieties.\textsuperscript{83} This issue is further evaluated by ultrafast TA spectroscopy, which provides detailed information on the photoexcitation dynamics.

\textbf{8.2.2 Femtosecond Transient Absorption Spectra Measurements}

\textbf{Figure. 8. 3} shows TA spectra of PFN in the absence and presence of two different concentrations (0.03 and 0.12 mg/mL) of GC after photoexcitation at 370 nm. As shown in \textbf{Figure. 8. 3 A}, excitation of the PFN alone immediately results in ground state bleach (GSB) at 410 nm, stimulated emission (SE) at 424 nm, and broad excited state absorption (ESA) band centered at 580 nm. Both the GSB recovery and ESA decay are dominated by slow dynamics and the GSB is recovered on the same time scales with the ESA decay without any spectral shift and new emerging band.
Figure 8.3 Transient absorption spectra for (A) PFN alone, (B) FPN in the presence of 0.03 mg/mL GC, and (C) FPN in the presence of 0.12 mg/mL GC.

8.2.3 Femtosecond Transient Absorption Kinetics

As presented in Figure 8.4, the kinetics of the GSB recovery and ESA decay can be adequately described by a single exponential fit with a time constant of 2.8 ps. This indicates that the excited $S_1$ state of PFN has a long lifetime in a few hundreds ps time scales and it decays directly into the ground state through CR process. In the presence of 0.03 and 0.12 mg/mL GC (see Figure 8.3 B, C), the transient spectral feature of PFN-GC associations is basically similar to those of PFN alone. New absorption bands which can be assigned to the existences of
PFN**-GC* radical ion pairs are not clearly observed. However, faster GEB recovery is observed, and the results shown in Figure 8.4 for the kinetics of ESA at 600 nm and GSB at 410 nm for different GC concentrations reveal that the kinetics of GSB recovery and ESA decay are GC concentration-dependent. Exponential fits to the data shown in Figure 8.4 suggest that the kinetics of the GSB recovery and ESA decay are biexponential with two time constants. The rapid GSB recovery and ESA decay of the PFN in a few ps may presumably be due to a contribution from the ultrafast PET from the excited PFN to GC as well as CR recovering the PFN ground state. This is supported by the inspection of the kinetics in Figure 8.4, in which the amplitude of the fast component increases systematically with the GC concentration (50 % and 60% for 0.03 and 0.12 mg/mL GC addition, respectively). The ultrafast PET and CR processes indicate the strong interactions and electronic couplings of PFN on the GC surface. The ultrafast CR process is the reason for the absence of PFN**-GC* radical ion pairs in the spectra. This is also consistent with the trend of the static mechanism of the fluorescence quenching. In comparison with other bimolecular systems based on the electrostatic interactions of GC, we found that rate of PET process from the PFN to GC is in agreement with those observed in porphyrins and GC systems (within few tens of ps). Accordingly, we draw a mechanism scheme for this intermolecular CT in PFN-GC system, which is showing in Figure 8.5.
Figure 8.4 Kinetic traces extracted from TA spectra (in Figure 8.2) for PFN in the absence and presence of 0.03 and 0.12 mg/mL GC.

Accordingly, Table 8.1 shows kinetics lifetimes of the CT and CR of PFN alone and PFN with two different concentrations of GC as showing below:

8.2.4 Reaction Mechanism

We believed that the slow component of GSB recovery and ESA decay of the PFN in a few hundreds ps is related to the relaxation of free or uncomplexed PFN, which decreases subsequently in the presence of GC as indicated by the lower amplitudes of the slow component with GC concentration.
Finally, it may be noted that the PET events is the reduction of the strong electron acceptor moieties by PFN. We consider that it is facilitated by the energy-level alignment between the PFN and GC to induce favorable energetics for the charge transfer process. However it is noteworthy that although the reduction potential of GC (-1.02 V vs. SCE) is lower than that of DCB (-1.64 V vs. SCE), relating to smaller driving force from PFN to GC, the PET from PFN to GC is much faster than that from PFN to DCB. Here, we consider the key role of the opposite charge on GC to achieve strong electrostatic interactions, enhancing the electronic coupling and the rate of the PET process between PFN and GC due to a close distance of the electron donor and acceptor. Using the electrostatic interactions, we can control the rate of the ultrafast PET in the non-covalent associations of the cationic polyfluorene.
8.3 Conclusion

In conclusion, we have investigated bimolecular donor-acceptor systems, namely positively charged PFN and negatively charged GC containing carboxylate groups in DMSO, by the steady state absorption and fluorescence spectra. The mechanism of the fluorescence quenching was evaluated by monitoring the fluorescence lifetime using the TCSPC technique in the absence and presence of the quencher. We found that the quenching mechanism in PFN and GC is static, suggesting the strong electrostatic interactions facilitated by the opposite charge on PFN and GC. This is supported by the dynamic quenching mechanism of PFN-DCB system. The photoexcitation dynamics of PFN-GC systems were further investigated using femtosecond broadband TA spectroscopy. TA absorption spectra of PFN in the absence and presence of different GC concentrations reveal the ultrafast PET and CR processes (within few tens of ps) in the non-covalent PFN-GC systems. This finding is consistent with the trend of the static mechanism of the fluorescence quenching. In comparison, the PFN-GC systems PET process is in 2.8 ps time scales, suggesting a diffusion-controlled PET process.
Chapter 9

Conclusions and Outline of the Dissertation

9.1 Conclusions

In all donor-acceptor systems, including organic and inorganic interfaces, understanding the charge transfer (CT), charge separation (CS), and charge recombination (CR) at different interfaces is extremely important to enhance any further photovoltaics applications. As a result, this dissertation covered very important photophysical properties for a very well-known chemical reaction processes like inter and intra molecular charge transfer processes.

In chapter 1 we give a brief introduction about photoinduced charge transfer process, and most used mechanism system for donor-acceptor reactants. We also showed different types of donor/acceptor reactions interfaces with different molecules (organic and inorganic) along with several examples for each of them.

In chapter 2 materials used in this dissertation were giving in detail and a list of extremely important instruments used in this dissertation were discussed in more detail, flowing and providing the importance of using each of them to investigate the photophysical properties in donor and acceptor systems.

In chapter 3 we explored the excited-state interactions of bimolecular, noncovalent systems consisting of cationic poly[(9,9-di(3,3′-N,N′-trimethylammonium) 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 photoinduced electron transfer from PFN to DCB occurs on the picosecond time scale, leading to the formation of PFN•• and DCB•• 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.

Figure 9.1 Schematic diagram showing the transient absorption spectra for (DCB•• - PFN••) radical ions in the excited state using pump-probe transient absorption system.33
In chapter 4 we extended our study to investigate the real-time probing of intersystem crossing (ISC) and triplet-state formation after photoinduced electron transfer (ET) which is a particularly challenging task that can be achieved by time-resolved spectroscopy with broadband capability. Here, we examine the mechanism of charge separation (CS), charge recombination (CR) and ISC of bimolecular photoinduced electron transfer (PET) between poly[[9,9-di(3,30-N,N′-trimethyl-ammonium) propyl fluorenyl-2,7-diyl)-alt-co-(9,9-dioctyl-fluorenyl-2,7-diyl)] diiodide salt (PFN) and dicyanobenzene (DCB) using time-resolved spectroscopy. PET from PFN to DCB is confirmed by monitoring the transient absorption (TA) and infrared spectroscopic signatures for the radical ion pair (DCB• - PFN•). In addition, our time-resolved results clearly demonstrate that CS takes place within picoseconds, followed by CR within nanoseconds. The ns-TA data exhibit the clear spectroscopic signature of PFN triplet-triplet absorption, induced by the CR of the radical ion pairs (DCB• - PFN•). As a result, the triplet state of PFN (3PFN*) forms and subsequently, the ground singlet state is replenished within microseconds.

In chapter 5 we controlled the ultrafast dynamical process of photoinduced charge transfer at donor-acceptor interfaces, which remains a major challenge for physical chemistry and solar cell communities. The process is complicated by the involvement of other complex dynamical processes, including hydrogen bond formation, energy transfer, and solvation dynamics occurring on similar time scales. In this study, we explore the remarkable impact of hydrogen-bond formation on the interfacial charge transfer between a negatively charged electron donating anionic porphyrin and a positively charged electron accepting π-conjugated polymer, as a model system in solvents with different polarities and capabilities for hydrogen bonding using femtosecond transient absorption spectroscopy. Unlike the conventional understanding
of the key role of hydrogen bonding in promoting the charge-transfer process, our steady-state and time-resolved results reveal that the intervening hydrogen-bonding environment, and consequently, the probable longer spacing between the donor and acceptor molecules significantly hinders the charge-transfer process between them. These results show that site-specific hydrogen bonding and geometric considerations between donor and acceptor can be exploited to control both the charge-transfer dynamics and its efficiency not only at donor-acceptor interfaces but also in complex biological systems as illustrated in Figure 9.2.

**Figure 9.2** Schematic diagram shows hydrogen bonds driving force for the intermolecular CT in POS-PFN system using two different solvents, Methanol and mixture of Methanol with Acetonitrile.$^{35}$

In chapter 6, a series of $\pi$-conjugated oligomer-acceptor dyads were synthesized that feature oligo(phenylene ethynylene) (OPE) conjugated backbones end-capped with a naphthalene diimide (NDI) acceptor, (Figure 9.3). The OPE segments vary in length from 4 to 8 phenylene ethynene units (PEn-NDI, where $n = 4, 6$ and 8). Fluorescence and transient absorption
spectroscopy reveals that intramolecular OPE → NDI charge transfer dominates the
deactivation of excited states of the PEn-NDI oligomers. Both charge separation (CS) and charge
recombination (CR) are strongly exothermic ($\Delta G^0_{\text{CS}} \sim -1.1$ and $\Delta G^0_{\text{CR}} \sim -2.0$ eV). The driving
forces do not vary much across the series because the oxidation and reduction potentials and
singlet energies of the OPEs do not vary much with their length. Bimolecular photoinduced
charge transfer between model OPEs that do not contain the NDI acceptors with methyl
viologen was studied, and the results reveal that the absorption of the cation radical state
($\text{OPE}^{**}$) remains approximately constant ($\lambda \sim 575$ nm) regardless of oligomer length. This finding
suggests that the cation radical (polaron) of the OPE is relatively localized, effectively occupying
a confined segment of $n \leq 4$ repeat units in the longer oligomers. Photoinduced intramolecular
electron transfer dynamics in the PEn-NDI series was investigated by UV-visible femtosecond
transient absorption spectroscopy with visible and mid-infrared probes. Charge separation
occurs on the 1-10 ps time scale with the rates decreasing slightly with increased oligomer
length ($\beta_{\text{CS}} \sim 0.15 \text{ Å}^{-1}$). The rate for charge-recombination decreases in the sequence PEn-NDI >
PE6-NDI > PE8-NDI. The discontinuous distance dependence in the rate for charge
recombination may be related to the spatial localization of the positive polaron state in the
longer oligomers.

![Diagram](image)

**Figure 9.** Schematic diagram illustrating the effect of length on the CT in intramolecular
charge transfer in PEn-NDI system.\textsuperscript{36}
In chapter 7, another series of polymers (PPE-NDI-n) with different molecular weight were synthesized which featured the same poly-(phenylene ethynylene) (PPE) conjugated backbone and naphthalene diimide derivative (NDI) substitution at the polymer chain ends. The energetics of polymers was investigated by cyclic voltammetry and steady state absorption and emission spectroscopy. Despite the increasing of molecular weight, all PPE-NDI-n polymers show similar energy levels. However, the fluorescence emission quantum yield measurements indicate a very efficient electron transfer from the PPE backbone to the NDI end-groups, and the transfer efficiency increases with decreasing molecular weight. Femtosecond transient absorption (fsTA) analysis showed that the charge recombination rate also increased with the decreasing chain length.

Finally, in chapter 8, the interactions, fluorescence quenching, and photoexcitation dynamics 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 negatively charged graphene carboxylate (GC) has been studied by steady state and time-resolved femtosecond transient absorption (TA) spectroscopy with broadband capabilities. The steady-state fluorescence of PFN is quenched with high efficiency by GC acceptor. Fluorescence lifetime measurements revealed that the quenching mechanism of PFN by GC is static. Here, the quenching mechanisms are well proven by TA spectra of PFN-GC systems. In PFN and GC systems, the PET and CR processes are ultrafast (within few tens of ps) related to static interactions. The advantage of the present cationic polyfluorene is the control over the
electrostatic interactions and electron transfers in non-covalent polyfluorene quencher systems in solution.

Figure 9.4 Schematic showing the ultrafast intermolecular CT in PFN and GC system.

9.2 Outlook of the Dissertation

Photoinduced electron transfer is one of the most important chemical reactions in physical chemistry and solar cells communities. Therefore, the profound understanding of such dynamical processes in donor-acceptor systems will be essential to provide an important dynamical information to help in optimizing the optoelectronic devices. We next hope to extend these experiments to different levels and study the solid form of the photophysical properties for all donor and acceptor interaction and apply them into different applications.
REFERENCES


86. Srinivasan, M. V.; Ito, M.; Kumar, P.; Abhirami, K.; Tsuda, N.; Yamada, J.; Shin, P.-K.; Ochiai, S., Performance Evaluation of an Organic Thin-Film Solar Cell of PTB7:PC71BM with


A. Supporting Information

Figure S1 $^1$H NMR and $^{13}$C NMR for compound 6 (PE4-TIPS). $^{36}$
Figure S2 $^1$H NMR and $^{13}$C NMR for compound 9 (PE4-NDI).
Figure S3 $^1$H NMR and $^{13}$C NMR for compound 10 (PE6-TIPS).
Figure S4 $^1$H NMR and $^{13}$C NMR for compound 12 (PE6-NDI).
Figure S5 $^1$H NMR and $^{13}$C NMR for compound 13 (PE8-TIPS).
Figure S6 $^1$H NMR and $^{13}$C NMR for compound 15 (PE8-NDI).
Figure S7. Singlet oxygen quantum yields of PEn-TIPS oligomers (n = 4, 6, 8), measured in deuterated chloroform under 10 mins of purging with oxygen, and reported relative to terthiophene as standard (ΦΔ= 84%).36,239
**Figure S8** Electrochemistry studies. CV (black line) and DPV (red dashed line) of A) PE4-NDI, B) PE6-NDI, and C) PE8-NDI in DCM solution containing 0.1 M TBAPF6 with scan rate of 100 mv/s, using the three-electrode setup consisting a platinum microdisk (2 mm²) working electrode, a platinum wire auxiliary electrode, and a silver wire reference electrode. Potentials are referenced to a Ferrocene/Ferrocenium standard. ³⁶
**Figure S9** Center-to-center separation distances for PEn-NDI oligomers ($n = 4, 6, 8$) using structures calculated from DFT B3LYP 6-31G*.$^{36}$
Figure S10 A) Nanosecond-microsecond transient absorption spectra for PE6-TIPS in the presence of MV$^{2+}$ (1.0 mM) at $\tau=20$ ns (black dashed line) and $\tau=2000$ ns (red solid line), B) Nanosecond-microsecond transient absorption spectra for PE8-TIPS in the presence of MV$^{2+}$ (1.0 mM) at $\tau=20$ ns (black dashed line) and $\tau=2000$ ns (red solid line). Photolysis experiments of PEn-TIPS and paraquat (MV$^{2+}$, 1.0 mM) were carried out in a mixture of THF and acetonitrile (v:v 2:1), with the optical density for oligomers were controlled at 0.7 at 355 nm. Transient absorption spectra used for principal component analysis were obtained at 20 ns after laser illumination at 355nm.$^{36}$
Figure S11. Ultrafast time-resolved transient absorption spectra for A) PE4-TIPS, B) PE6-TIPS and C) PE8-TIPS. The samples were measured in dichloromethane solution, excited at 380 nm with data collected in timescale of 1 ps - 5 ns.\textsuperscript{36}
**Figure S12** Transient absorption decay kinetics for PEn-TIPS oligomers (n = 4, 6, 8) in dichloromethane solution monitored at 650 nm. The samples were excited at 380 nm with data collected in range of 5 ns. The amplitudes are normalized at $\tau = 0$.\(^{36}\)

**Figure S13.** Ground-state FTIR spectra for PE4-TIPS and PE4-NDI. The FTIR spectra were measured in KBr solid film.\(^{36}\)
Figure S14. Solvent dependent CS/CR studies of PE6-NDI by TRIR. A) Transient IR absorption spectra of PE6-NDI at $\tau = 0$ ps and $\tau = 21$ ps in variable solvent systems, B) Kinetics monitoring at 2080 cm$^{-1}$ of PE6-NDI in variable solvent systems. The experiments were conducted in three solvents: dichloromethane, mixture of dichloromethane and acetonitrile (v:v 60:40), and mixture of dichloromethane and methanol (v:v 60:40).\textsuperscript{36}

Table S1. Charge Separation/Recombination Kinetics for PE6-NDI from TRIR.\textsuperscript{36}

<table>
<thead>
<tr>
<th></th>
<th>$\tau_{CS}$ (ps)</th>
<th>$k_{CS}$ (s$^{-1}$)</th>
<th>$\tau_{CR}$ (ps)</th>
<th>$k_{CR}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{DCM}</td>
<td>4.4</td>
<td>$2.3 \times 10^{11}$</td>
<td>1123.0</td>
<td>$8.9 \times 10^{8}$</td>
</tr>
<tr>
<td>\textit{DCM/ACN}</td>
<td>4.9</td>
<td>$2.0 \times 10^{11}$</td>
<td>540.3</td>
<td>$1.9 \times 10^{9}$</td>
</tr>
<tr>
<td>\textit{DCM/MeOH}</td>
<td>5.6</td>
<td>$1.8 \times 10^{11}$</td>
<td>213.6</td>
<td>$4.7 \times 10^{9}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The CS/CR lifetimes were extracted from kinetics traces in Figure S14.

\textsuperscript{b}The CS/CR rates were calculated with equations: $k_{CS}=1/\tau_{CS}$ and $k_{CR}=1/\tau_{CR}$. 
B. List of Publications and Conferences

a) This thesis is based on the work contained in the following papers


b) Conference Contributions

[1] **Amani A. Alsam** et al., *(Poster presentation).* King Abdullah University of Science and Technology Solar Future Symposium *(KSC)*, *(Thuwal, Saudi Arabia, Fall 2014).*

[2] **Amani A. Alsam** et al., *(Poster presentation).* *Bimolecular Excited-State Electron Transfer with Surprisingly Long-Lived Radical Ions.*
King Abdullah University of Science and Technology Solar Cells Conference *(KSC)*, *(Thuwal, Saudi Arabia, Fall 2015).*

[3] **Amani A. Alsam** et al., *(Poster presentation).* *Bimolecular Excited-State Electron Transfer with Surprisingly Long-Lived Radical Ions.*
Materials Research Society Conference *(MRS)*, *(Boston, United State, 2015).* *With certification*

[4] **Amani A. Alsam** et al., *(Poster presentation).* *Hydrogen Bonding Can be a Bane for the Charge Transfer Process.*
The 4th Saudi International Nanotechnology Conference *(SINC)*, *(Dhahran, kingdom of Saudi Arabia, 2016).* *With certificate.*

[5] **Amani A. Alsam** et al., *(Poster presentation).* *Bimolecular Excited-State Electron Transfer with Surprisingly Long-Lived Radical Ions.*
King Abdullah University of Science and Technology Solar Cells Conference *(KSC)*, *(Thuwal, Saudi Arabia, Fall 2016).*

Frontiers in Theoretical and Applied Physics *(FTAPS)*, *(Sharjah, United Arab Emirates, February 2017).* *With certificate.*
[7] **Amani A. Alsam et al.**, (Participation), King Abdulla University of Science and Technology Research Conference, Synergistic Approaches in Solar Energy Conversion (KSC), *(Thuwal, Saudi Arabia, February 2018).*
