PHOTOPHYSICS AND ENERGY TRANSFER OF NOVEL CONJUGATED MATERIALS
BY ULTRAFAST SPECTROSCOPY

By
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To Murat, and Asya
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In nature, life is sustained by collecting energy from the sunlight directly or indirectly. As the energy problem of the modern world climbs up, scientists are looking more ambitiously for materials that mimic nature to have superior energy-transport properties. Among various alternatives, conjugated materials have a great potential for energy-transfer applications, due to their unique physical characteristics. A fundamental knowledge of their photophysical properties is critical to be able to use these materials for light harvesting.

In this Ph.D. dissertation, we investigated photophysical properties of conjugated materials using steady-state and time-resolved spectroscopy along with anisotropy measurements. Specifically, we studied on conjugated polyelectrolytes (CPEs) which are linear polymers, conjugated polyelectrolyte dendrimers (CPE-Ds), and the ester form of CPE-Ds. In addition to the experimental work, we utilized kinetic models based on our data to interpret excited-state kinetics of these dendrimers.

CPE-Ds have desirable properties like solubility in polar solvents and well-defined, monodisperse structures. We observed that CPE-Ds and their ester forms have intramolecular energy gradients and energy transfer from periphery to core takes place...
within a few picoseconds (0.5-3.5 ps). Using time-resolved anisotropy measurements, we found out that there is a fast delocalization of energy (260-330 fs) among linear conjugated segments. The energy transfer has lower efficiency and faster rates for the CPE-Ds compared to their ester analogs. The introduction of ionic end-groups opens new channels for excited-state relaxation. These new channels originate from intra-molecular chromophore-chromophore interactions. In the ionic form, the communication between the branches of the dendrimers increases to avoid hydrophobic interactions with the solvent molecules.

CPEs are also soluble in polar solvents and capable of efficient energy-transfer to oppositely charged molecules by forming association complexes. We identified that there are two different mechanisms for energy transfer to an external dye: a prompt mechanism via strong coupling and a dynamic mechanism through exciton diffusion. We also found out that the branched side-groups suppress the aggregation tendency.

The investigation of excited-state kinetics provides crucial information about the energy-transfer efficiency and the processes affecting energy transfer. This information provides not only the identification of better candidates for applications, but also the reasoning of why some structures transport energy more efficiently.
CHAPTER 1
INTRODUCTION

Light Harvesting

Natural photosynthesis starts with the absorption of photons from the sunlight and the transfer of the energy to a reaction center. The first steps of the energy conversion involve light-matter interactions followed by the energy-transfer processes that occur in $10^{-14}$ to $10^{-10}$ seconds. Excitation energy (from photons absorbed) is transferred from one chromophore center to another before it is converted and stored for long term usage.\(^1\) The efficiency of the energy-transfer process is a very crucial factor for the overall efficiency of the energy conversion. Light-harvesting antenna complexes provide very efficient energy transport from these absorbing units to the reaction centers which has about 90% quantum yield.\(^2,3\) Cascade type of energy-transfer mechanisms and quantum coherences are found to be involved in efficient funneling of the energy.\(^4\)

There have been many studies on the light-harvesting antennas in biological systems to understand their structure and the mechanism of energy transport.\(^5-8\) These studies revealed the importance of the structural features. It is also found that, natural light-harvesting systems are not robust or inexpensive enough to be used in technological applications like solar cells,\(^9,10\) although they are extremely efficient in biological conditions.\(^6,8\) To mimic photosynthesis for such applications, there is a need for efficient light-harvesting supramolecular structures like their biological analogs. The structural features of natural pigments have been used by synthetic chemists to create artificial light-harvesting antennas.\(^11\) Different shapes of chromophore arrays including ring,\(^12-14\) windmill,\(^15-17\) or star shapes\(^18,19\) are synthesized and characterized in terms of their energy transport efficiencies. One of the most promising candidates are found to
be the dendritic arrays with their large absorption cross-sections and vectorial energy-transfer capabilities.\textsuperscript{20,21} 

Synthetic light-harvesting materials are inspired by nature in terms of their structure. They can be used for many applications such as photovoltaic cells, field-effect transistors and light emitting devices. In order to have an artificial light-harvesting system, it is essential to have a large absorption cross-section, which can be provided by a large number of chromophore units.\textsuperscript{22,23} Conjugated dendrimers readily provide this requirement which makes them one of the most promising candidates for these applications. On the other hand, non-conjugated dendrimers are also capable of funneling energy, however, there can be complications due to backfolding of flexible scaffolds since they have less rigid structures.\textsuperscript{24-30} In non-conjugated macromolecules, the backbone is light-inert only providing a scaffold for the donor and acceptor species. They are not involved in absorption of light and transport of excitation energy. Although the flexibility of the arms can be considered an advantage as it enhances the solubility, it also allows folding which can lead to intra-molecular non-radiative processes decreasing the energy-transfer efficiency. In conjugated systems, the backbone of the macromolecules acts as a vehicle for energy transfer through bond communication, which enables efficient funneling of energy. As they have more rigid structures than non-conjugated molecules, intra-molecular interactions are less likely in conjugated systems.

The aim of this dissertation is to understand energy transport mechanism and the factors affecting efficiency of energy transport in different novel conjugated materials. In this work, the connection between the structural features of the materials and the
energy transport mechanism is examined through photophysical studies. To reach a better comprehension of underlying reasons for increased or decreased energy-transfer efficiency in different systems, it is crucial to understand the energy-transfer mechanism in these systems.

**Electronic Energy Transfer**

Electronic energy transfer (EET) is an important process affecting overall energy conversion efficiency of applications like solar cells. The efficiency of EET is supposed to be very high in order to obtain better devices and it is determined by the mechanism of the energy transfer. EET mechanisms are discussed in the following section.

Excitation energy can be transferred via radiative or non-radiative processes. The radiative ET takes place by reabsorption of the emitted photons, which is depicted in equation 1-1. The acceptor (A) absorbs the photons emitted by donor molecule (D). The ET is called homotransfer if the donor and acceptor species are same type of molecules. The radiative transfer can occur even if the average distance between the donor and acceptor species is larger than the wavelengths of the absorption.\textsuperscript{31} It is not an efficient mechanism for energy transport so the emphasis of this work is on non-radiative energy transfer. The radiative transfer (or self-absorption) is avoided by using lower concentrations.

\[\text{D}^* \rightarrow \text{D} + \text{hv}\]  
\[\text{hv} + \text{A} \rightarrow \text{A}^*\]  

(1-1)

Non-radiative energy transfers result from an interaction between acceptor and donor species, which can happen if there is an overlap between the donor’s emission and acceptor’s absorption spectrum. The overlap enables coupling of the transitions, which is called resonance and gives rise to resonance energy transfer (RET).\textsuperscript{31} The
non-radiative energy transfer is depicted in equation 1-2. In this equation, donor (D) and acceptor (A) can be the same or different chemical species or they can be parts of the same molecule.

\[ D^* + A \rightarrow D + A^* \quad (1-2) \]

RET is enabled due to the presence of intermolecular interaction energy between donor and acceptor. If the total Hamiltonian is considered as the summation of the donor and the acceptor Hamiltonians and the perturbation part \((\hat{H} = \hat{H}_{\text{donor}} + \hat{H}_{\text{acceptor}} + V)\), the interaction energy can be expressed as \(\langle \psi_i | V | \psi_f \rangle\) where \(\psi_i\) and \(\psi_f\) are the wavefunctions of initial and final states, and \(V\) is the perturbation term. These wavefunctions have to be properly antisymmetrized due to quantum mechanical properties of the electrons. The wavefunctions can be written as in equation 1-3 by assuming only the two electrons are involved in the energy transfer.

\[ \psi_i = \frac{1}{\sqrt{2}} (\psi_{D^*}(1)\psi_A(2) - \psi_{D^*}(2)\psi_A(1)), \quad \psi_f = \frac{1}{\sqrt{2}} (\psi_D(1)\psi_{A^*}(2) - \psi_D(2)\psi_{A^*}(1)) \quad (1-3) \]

where the \(\psi_{D^*}\) and \(\psi_D\) are the wavefunctions of the donor in the excited and the ground state, respectively, and \(\psi_{A^*}\) and \(\psi_A\) are the wavefunctions of the acceptor. The electrons are labeled with 1 and 2.

The interaction energy is written in equation 1-4 by substituting \(\psi_i\) and \(\psi_f\) in the expression for the perturbation \(\langle \psi_i | V | \psi_f \rangle\).

\[ U = \langle \psi_{D^*}(1)\psi_A(2) | V | \psi_D(1)\psi_{A^*}(2) \rangle - \langle \psi_{D^*}(1)\psi_A(2) | V | \psi_D(2)\psi_{A^*}(1) \rangle \quad (1-4) \]

The first term of the equation is known as the coulombic term \(U_c\), while the second is referred as the exchange term \(U_{ox}\). The presence of the exchange term is a consequence of the symmetry properties of the wavefunction so it is a quantum
mechanical effect. The coulombic and exchange interaction mechanisms are depicted in Figure 1-1.

![Figure 1-1](image)

**Figure 1-1.** Schematic representation of the energy transfer. A) Coulombic mechanism. B) Exchange mechanism. CI and EE refers to coulombic interaction and electron exchange, respectively. Adapted from reference.\textsuperscript{31}

For very short ranges of distances between donor and acceptor species, there can be intermolecular orbital overlap between them. The presence of the orbital overlap gives rise to electron exchanges and charge-resonance interactions. In the case of exchange mechanism, an excited-electron of the donor is exchanged with the electron in the ground state of the acceptor directly. This mechanism contributes to energy transfer for the systems where the distance between the donor and the acceptor is shorter than 10 Å. On the other hand, the coulombic interactions can occur in both short (multipolar) and long ranges (up to 10 Å to 100 Å), in which case the energy-transfer results from the coulombic coupling between an excited-electron of the donor and an electron in the ground state of the acceptor. The energy-transfer occurs via the return of an electron of the donor from the excited-state to the ground state and excitation of electron of acceptor, simultaneously. The contribution of different mechanisms to the overall energy transfer is strongly dependent on the distance between the species and the strength of the coupling between them.
Förster classified the strength of the coupling between donor and acceptor units into three regions: strong, weak and very weak. The distinction between these regions is made by the consideration of the relative values of intermolecular interaction energy (U), the electronic energy difference between donor and acceptor (∆E), the absorption bandwidth (∆w) and the vibronic bandwidth (∆ε) which are depicted in Figure 1-2.

The interaction is in the strong category if it is much larger than the electronic energy difference between donor and acceptor, absorption bandwidth and the vibronic bandwidth (U >> ∆E, ∆w, ∆ε). In this case, the energy transfer is a coherent process, which is faster than the nuclear vibrations and vibrational relaxation. The excitation is delocalized as it oscillates back and forth between donor and acceptor.

Figure 1-2. Schematic representation of the electronic energy difference between donor and acceptor (∆E), absorption bandwidth (∆w), and the vibronic bandwidth (∆ε). Adapted from reference 31

The interaction is called weak if the interaction energy is larger than the electronic energy difference between donor acceptor, but it is smaller than the absorption bandwidth (U >> ∆E, ∆w >> U >> ∆ε). For the weakly coupled systems, the excitations are more localized than for the strongly-coupled ones. The energy transfer is slower than nuclear motions but it takes place on comparable time scales with vibrational relaxation.
The energy-transfer rate has a distance dependence $r^{-3}$ if $U$ is approximated by a
dipole-dipole interaction.

The interaction between donor and acceptor molecules is classified into very
weakly coupling if the interaction energy is much smaller than the absorption bandwidth
and the vibronic bandwidth ($U<<\Delta \varepsilon <<\Delta \omega$). The energy transfer takes place in time
scales longer than vibrational relaxation. In the case of very weak coupling, the distance
dependence is $r^{-6}$ with dipole-dipole approximation.

The non-radiative energy-transfer rate can be determined by Fermi’s Golden Rule
which states that the rate of the transition between two states is proportional to the
magnitude of the perturbation. It utilizes time dependent perturbation theory and is
applicable for very weak coupling cases. The rate-constant of the transitions ($k_{ET}$) is
given by

$$k_{ET} = \frac{2\pi}{\hbar} \langle \psi_i | V | \psi_f \rangle^2 \rho = \frac{2\pi}{\hbar} U^2 \rho$$

(1-5)

where $\rho$ is a measure of the density of interacting initial and final states and determined
the by Franck-Condon factors. The spectral overlap between emission of the donor and
absorption of the acceptor is used for determination of $\rho$ by assuming there is no
inhomogeneous broadening. The spectral overlap is given by

$$J = \int_0^\infty I_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) d\tilde{\nu}$$

(1-6)

where is $I_D(\tilde{\nu})$ is the fluorescence intensity of the donor which is area-normalized, and
$\varepsilon_A(\tilde{\nu})$ is the molar absorption coefficient of the acceptor at a given wavenumber. The
spectral overlap is calculated after normalization of the absorption spectrum of the
acceptor and emission spectra of donor to a unit area, to eliminate the effect of the
absolute values of oscillator strengths. The normalization conditions can be written as,
\begin{equation}
\int_0^{\infty} I_D(\tilde{\nu}) \, d\tilde{\nu} = 1 \tag{1-7}
\end{equation}

Once the spectral overlap is evaluated to approximate of the density of states (\(\rho\)), the energy-transfer rate can be obtained by evaluating the interaction energy and substituting in Fermi’s equation (1-5).

The interaction energy has two terms for exchange or coulombic mechanisms given in equation 1-4. Using the exchange term (\(U_{ex}\)) and the spectral overlap, Dexter’s formulation of energy-transfer rate can be obtained. As this formulation is done for exchange mechanism, it is valid for short range distances between donor and acceptor. Dexter’s energy-transfer rate is given in equation 1-8.

\[
k_{ET} = \frac{2\pi}{\hbar} K J \exp(-\frac{2r}{L})
\tag{1-8}
\]

In this equation, \(K\) is a constant, \(J\) is the spectral overlap, and \(L\) is the average Bohr radius. The most distinct feature of this mechanism is its exponential dependence on the distance. The \(K\) constant cannot be obtained from spectroscopic data so experimental characterization of this mechanism is difficult.

The coulombic term (\(U_c\)) can be used to evaluate the interaction energy term and to obtain Förster’s energy-transfer rate. In this case, the energy-transfer rate is derived for a very weak coupling limit and based on the second order perturbation treatment of electronic coupling. The matrix element of interaction between the excited state of the donor and the ground state of the acceptor contains purely electronic coupling and the point dipole-point dipole approximation is employed. The energy-transfer rate by Förster’s theory is given in the following equation:

\[
k_{ET}^{\text{Förster}} = k_d \left[ \frac{R_d}{r} \right]^6 = \frac{1}{\tau_d} \left[ \frac{R_d}{r} \right]^6 \quad \text{where} \quad R_0^6 = \frac{9000 (\ln 10) k^2 \Phi^6}{128 \pi^5 N_A n^4} \int_0^{\infty} I_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \tag{1-9}
\]
$k_d$ is the emission rate constant of the donor and $\tau_d$ is the donor lifetime in the absence of acceptor, $r$ is the distance between donor and acceptor, $R_0$ is the critical distance which is required between donor and acceptor to have equal rates for the spontaneous emission and energy transfer ($k_{ET}=k_d$, 50% energy-transfer efficiency). The sixth power dependence is an important feature revealing that RET rate strongly dependent on distance. $R_0$ is determined by using the emission spectrum of the donor and absorption spectrum of the acceptor and it is directly related to spectral overlap. $\kappa^2$ is the orientational factor, $\Phi_D^0$ is the quantum yield of the donor in the absence of acceptor, $n$ is the average refractive index of the medium in the spectral wavelength range where spectral overlap is significant. The emission spectrum the donor and the absorption spectrum of the acceptor are in wavelength scale and the emission spectrum is area-normalized. The orientational factor $\kappa$ is given by

$$\kappa = \cos \theta_{D} \cos \theta_{A} - 3 \cos \theta_{D} \cos \theta_{A} = \sin \theta_{D} \sin \theta_{A} \cos \varphi - 2 \cos \theta_{D} \cos \theta_{A}$$  \hspace{1cm} (1-10)

where $\theta_{DA}$ is the angle between donor and acceptor transition moments, $\theta_{D}$ and $\theta_{A}$ are the angles between donor/acceptor transition moments and separation vector, and the $\varphi$ is the angle between the projections of transition moments on the plane perpendicular to the line through the centers (dihedral angle).

In the literature, Förster's theory is used commonly as a routine mechanism to explain the photophysical properties and energy-transfer mechanism of conjugated systems.\textsuperscript{32-34} The theory offers very accurate calculations provided that certain conditions are met. The interactions must be in the range of very weak coupling which means that coherent energy transfer is absent. In order to have an accurate calculation for the spectral overlap, the emission and absorption spectra should not be affected by
inhomogeneous broadening and the point dipole approximation should also be valid. The point-dipole approximation is expected to be inadequate at short distances. This can be avoided calculating the resonance coulomb rate using extended transition dipole-moment densities.\textsuperscript{35}

**Conjugated Materials**

**Conjugated Dendrimers**

Dendrimers have gathered a lot of attention with their unique properties since their introduction in 1985.\textsuperscript{10,36-41} They have highly symmetric “tree-like” structures in which all bonds emerge radially from the core (the central or focal point) with a regular branching pattern. Representations of a typical dendrimer structure is given in Figure 1-3. They generally consist of three different parts: a central point called core, the branching arms (periphery), and the end-groups (termini). Each branching repeat-unit results in a new generation for the specific dendrimers. Conventionally, the dendrimers are named according to their generations.

![Dendrimer](image)

**Figure 1-3.** Schematic representation of a structure of dendrimer. Adapted from reference\textsuperscript{42}
In contrast to linear polymers, dendrimers are monodisperse in size (typically 1-10 nm) which makes them better suited for the studies on fundamental properties. The monodispersity is provided by well-defined iterative synthesis methods. Dendrimers can carry multiple functional groups as they have highly branched structures. Properties such as solubility, chemical reactivity and glass transition temperature can be tailored by modification of the end-groups. Dendrimers can have more rigid or flexible structures depending on the generation of the dendrimer, branching multiplicity of the monomer repeat units, and the number and type of bonds.

Dendritic macromolecules have globular structures with unique capabilities like core encapsulation. Encapsulation is observed in nature and inspired chemist to create similar synthetic materials. In biological systems, proteins isolate many active centers or catalytic sites to give their functions that would not be possible in bulk state. Dendrimers can also be designed in a way that the core part is isolated from the periphery to create specific nanoenvironments for certain functions. This phenomenon is called known as core encapsulation. The site isolated groups at the core can have photochemical, photochemical, electrochemical or catalytic functions.

Dendrimers are synthesized using two different strategies: divergent and convergent approaches. In the divergent approach, the growth starts from the core and evolves towards the periphery (outward). Convergent synthesis has an inward proceeding. The growth starts with the parts which will become periphery of the dendrimer. Both synthetic methods are equally applicable and complementary to each other. The choice of a synthetic-method depends on the features of the target molecule, the available specific building blocks and the chemistry employed for the
reactions. The divergent approach is better for large scale synthesis.\textsuperscript{44,58} However, it is difficult maintain the purity and structural uniformity with this approach. The convergent approach allows more structural control since purification is more straightforward and it is possible to introduce different functional groups at these steps.\textsuperscript{48,58,59} Since the surface groups are included in the very first steps of the synthesis, the solubility of the dendrons is improved. This method provides well-defined, pure and monodisperse products. However, the growth is slow with this strategy for high generations.\textsuperscript{43,45,56}

As mentioned earlier, dendrimers have gathered particular attention for light-harvesting applications among other candidates because of their superior properties such as monodispersity, well defined structure, high degree of order.\textsuperscript{42} The light-harvesting properties can be incorporated into dendritic structures by using multiple chromophoric groups. The structures of the dendrimers can be tailored to yield specific distance and the energy gap between chromophoric units so that efficient energy transport is possible.

An example of a light-harvesting dendrimer having three different chromophoric units (coumarin, fluorol 7GA, perylene) is shown in Figure 1-4. Serin et al.\textsuperscript{60} studied the photophysical properties of this dendrimer by using the steady-state spectroscopy. The absorption and emission spectra of the dendrimer consists of three distinct bands corresponding to each of the chromophores. It is possible to selectively excite different chromophore units of the dendrimer. In this system, cascade type energy transfer is observed. The overall energy-transfer efficiency upon excitation of coumarin moieties (blue) and detection of perylene core (red) emission is 95%. The high energy-transfer efficiency is the promising feature of this dendrimer as a light-harvesting antenna. The
cascade energy transfer from peripheral units to core is provided by the right choice of spectral overlap between the building blocks.\textsuperscript{14,60-62}

Another approach to create light-harvesting dendrimers is synthesizing metal containing structures, which were also investigated in the literature.\textsuperscript{63-67} Campagna et al. prepared tree-like dendrimers containing up to 22 metal centers exhibiting strong UV-VIS absorption and moderate red emission.\textsuperscript{63,64} The terminal ligands play an important role in the excited states and determine which subunit of the dendrimers is the HOMO and LUMO orbitals localized in these dendrimers. It is observed that electron transfer processes (metal based oxidation, ligand based reduction) are prominent rather than energy transfer. For energy transport purposes, the presence of metals plays a disadvantageous role by allowing additional pathways for relaxation.\textsuperscript{63,64}

The energy-transport efficiency in the conjugated dendrimers can be limited due to formation of exciplexes (excited complex) or excimers (excited dimer).\textsuperscript{68-75} New types of
species can be formed in the excited state if there is a strong interaction between chromophores. The formation of new chemical species is a reversible process after relaxation to the ground state. The presence of excimer or exciplexes can be detected in the emission spectrum as they are characterized by broad, low-energy bands. The formation of these species is more pronounced in films compared to solutions. 

Figure 1-5. Dendrimer with a cyclam core with 12 dimethoxybenzene and 16 naphthyl units. Adapted from Balzani and Suadan et al. 61,78

Saudan et al observed one of the most drastic examples of formation of intramolecular exciplex and excimer. The structure of the dendrimer is given in Figure 1-5. 78 They synthesized a dendrimer consisting of a cyclam (1,4,8,11-tetraazacyclotetradecane) core with 12 appended dimethoxybenzene and 16 naphthyl which soluble in acetonitrile and dichloromethane. They observed three different bands in the emission spectrum. The bands were assigned to naphthyl localized excited states, naphthyl excimers and naphthyl-amine exciplex. The protonation of cyclam core
affects the formation of exciplexes with the peripheral naphthyl units by engaging the nitrogen lone-pairs and causing nuclear rearrangements in the core.

Dendrimers have very useful properties and possible applications. In this work, the most emphasized application is light-harvesting, thus the energy-transfer mechanism and efficiency are the main focuses of the photophysical studies. The novel conjugated dendrimers are studied in order to understand the energy-transfer mechanism, strength of the interaction between chromophores and the processes that affect the transfer efficiency.

**Conjugated Polymers and Polyelectrolytes**

Conjugated polymers (CPs) have been subject to remarkable attention since the discovery of conducting polymers, which was recognized by the chemistry Nobel Prize in 2000. CPs are capable of transporting energy similar to dendrimers so they can also be considered for light-harvesting applications. CPs have great potential for technological applications such as light-emitting diodes (LEDs)\textsuperscript{79}, photovoltaic devices\textsuperscript{80} and sensors\textsuperscript{81} due to their ability to transport charge. Photovoltaic devices such as solar cells are receiving more consideration due to the growing demand for alternative energy resources which have lead the scientific community to search for materials cheaper than semiconductors.\textsuperscript{82} CPs are promising candidates for such applications\textsuperscript{82} since they provide good transport as charge carriers\textsuperscript{83} and they have strong absorption and high quantum yield of emission. The absorption and emission colors of CPs are tunable by modification of the backbone\textsuperscript{84,85} and this grants an advantage of using them for fabrication of LEDs.

Site-selective measurement is a the powerful technique widely used in the field of polymers to study energy transfer.\textsuperscript{86-88} In this technique, emission spectrum
measurements are done as a function of excitation wavelength which provides important information about photophysics of conjugated polymers. Site-selective laser spectroscopy was applied on poly(p-phenylenevinylene) films which supported the concept of random walk of excitations through inhomogeneously broadened states instead of a band picture involving uncorrelated electron-hole pairs. Bässler and coworkers used time-resolved site-selective fluorescence in a systematic way to investigate dispersive relaxation dynamics of a conjugated polymer film. They observed that the width and position of the fluorescence band depends on excitation energy and time. Moreover, with high-energy excitation, there is a continuous bathochromic shift in the fluorescence spectrum with time. They attributed these observations to incoherent hopping between localized states, and this method inspired other groups to further investigate energy-transfer kinetics in CPs.

Herz et al. investigated the energy-transfer kinetics in a conjugated polymer host-guest system by using site-selective excitations. They found that excitons created at the peak of the host’s density of states are very mobile and their transfer is faster than the localized excitons which are created at the low energy tail. This effect is more significant at low temperatures because at ambient temperatures there can be uphill migrations of excitons which introduces randomness in energy-transfer process; thermal phonons prevent true site-selective excitation of localized excitons. As thermal phonons are not available at low temperatures, the uphill migrations are not possible and only downhill energy migration is present. Consequently, low temperatures are employed for site-selective studies of energy-transfer processes in the literature.
Conjugated polyelectrolytes (CPEs) consist of π-conjugated backbone and the side chains decorated with ionic groups. Incorporation of ionic groups makes them water/alcohol soluble while maintaining superior photophysical properties associated with the π-conjugated backbone. Solubility in polar solvents is an important property because CPEs are easily processed into films and supramolecular assemblies from aqueous solutions. Since it is necessary to prepare films for photovoltaic applications, CPEs are good candidates for these applications.

Despite the exceptional properties of the CPs and CPEs, there are some disadvantages associated with their structures such as polydispersity and aggregation. Polydispersity is an inherited property from polymer precursors due to broad distribution of molecular weights during the synthesis. Aggregation is also a very common phenomenon among CPEs particularly if they contain aromatic rings in the backbone structure.

Aggregation is caused by self-association of molecules due to strong interactions like π-π stacking. The types of aggregates are classified according to the spectral changes concomitant with aggregation (bathochromic or hypsochromic shifts). The orientation of the transition dipole moments of the aggregated species determines the spectral features. A head to tail arrangement of the stacking results in a bathochromic shift of the spectrum and called J-type aggregation. If the transition dipole moments are in parallel (plane-plane stacking), H-aggregates are formed and characterized by a blue-shift in absorption spectra.
Figure 1-6. Schematic representation of formation of H and J aggregates.

The schematic representation of formation of H and J aggregates is given in Figure 1-6. $\mu_1$ and $\mu_2$ represent the transition dipole moments of interacting species in close proximity. The transitions having total transition dipole moment ($\mu$) greater than zero are allowed due to selection rules ($\mu = \mu_1 + \mu_2$). For this reason, $S_0$ to $S_1$ transition is not allowed in the case of H-aggregate formation and higher energy transitions ($S_0$ to $S_2$) are observed in the absorption spectra.

The energy-transfer mechanism in CPEs is affected in the presence of aggregates. The aggregation causes delocalization of $\pi$ electrons among different chains which allow inter-chain energy transport in addition to intra-chain transport along the polymers backbone. The inter-chain energy transport usually results in decreases in the quantum yield of fluorescence as excitation energy dissipates easily among the aggregates. This mechanism is undesirable for most of the applications involving light-harvesting, such as, LEDs. However, it could be useful for sensor applications if the aggregation is induced by the analytes resulting in more efficient quenching of fluorescence.
The novel structures presented in this dissertation have charged side or end-groups, which gives rise to their unique properties such as formation of association complexes with oppositely charged molecules\(^{97,98,103}\) and solubility in polar solvents\(^{84,104,105}\). Association complexes enable efficient transfer of the energy to a cationic acceptor, which results in amplified quenching of fluorescence\(^{102,106,107}\). Solubility in polar solvents is a desirable property for applications since films can be made easily from materials dissolved in polar solvents. For this reason, we explored the effects of ionic groups on the photophysical properties.

**Outline of Dissertation**

The main aim of this work is to understand the energy-transfer mechanism and features that affect energy transfer in novel conjugated polyelectrolyte dendrimers and polymers. For this purpose, steady-state and time-resolved emission spectroscopy was employed and the data was analyzed to relate photophysical properties with the mechanism of energy transfer.

Chapter 1 is the introduction of concepts that will be used throughout the dissertation. It consists of a brief literature review on dendrimers and polymers, the theoretical background on energy transfer and the anisotropy as a tool for our photophysical studies.

Chapter 2 summarizes the experimental methods used for our studies and includes a brief explanation of steady-state and time-resolved instrumentation.

Chapter 3 summarizes our findings on phenylene-ethynylene extended-dendrimers which have longer conjugation length at the core (Ph-dendrimers). The photophysical properties and energy-transfer rates of Ph-dendrimers are characterized by using model compounds. The properties of ester forms of the dendrimers are
compared to those of the ionic analogs. Time-resolved anisotropy is used to study energy delocalization and it is presented in this chapter.

Chapter 4 describes our results and analysis on thienylene-extended PE dendrimers with branched end-groups (Th-dendrimers). The photophysical properties and energy transfer of these dendrimers are characterized in this chapter. The properties are compared with model compounds which are building blocks for these dendrimers. The organic soluble ester-forms are compared with the ionic forms dissolved in polar solvents to understand effects of the introduction of polyelectrolyte characteristics on energy transfer.

CPEs with branched, highly charged side chains are investigated in Chapter 5. The aggregation and quenching properties are examined. Steady-state anisotropy and time-resolved spectroscopies are used to understand energy transfer and order in these polyelectrolytes.

The summary and perspectives are presented in Chapter 6. The results on Th-dendrimers are compared with Ph-dendrimers to understand effects of flexibility and band gap on the energy-transfer kinetics.
CHAPTER 2  
EXPERIMENTAL METHODS

Conjugated materials feature delocalized electronic states which give rise to useful properties like efficient electron and energy transport. These materials have been the focus of significant interest as they are very promising candidates for many applications such as LEDs, solar cells, sensors and light-harvesting systems. They are widely investigated to further understand the energy transfer, aggregation and other phenomenon that may affect their efficiency for the aforementioned applications. Our investigation of photophysical properties of novel conjugated materials (conjugated polyelectrolytes and conjugated polyelectrolyte dendrimers) involves experimental methods including steady-state and time-resolved measurements. This chapter provides information about these experimental methods.

Steady-state measurements involve the collection of absorption and emission spectra integrated over long time periods (0.5 s to 5 s). They provide important information about the nature of ground and excited states, and the energy-transfer efficiency. These measurements are used for photophysical characterization of the novel macromolecules throughout the dissertation. In Chapter 5, steady-state anisotropy and quenching measurements are used for studies on energy transfer and solvent induced aggregation.

Time-resolved emission spectra are collected using single photon counting or fluorescence up-conversion techniques. These measurements provide information about excited state dynamics which affect energy-transfer efficiency. The energy-transfer kinetics are characterized by up-conversion experiments in Chapters 3-5. The
time-resolved anisotropy is collected to investigate rotational diffusion and energy
delocalization in Chapter 4.

**Steady-State Spectroscopy**

Steady-state spectroscopy is a widely used tool to understand photophysical
processes in macromolecules. Absorption and emission spectra in the UV-visible-NIR
region of the electromagnetic spectrum provides information about electronic
transitions. Absorption spectrum probes the promotion of electrons from the ground
state to the lowest unoccupied molecular orbital (LUMO) upon absorption of photons.
The energy of the electronic transition is affected by the nature of the highest occupied
MO (HOMO) and LUMO ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, etc). In conjugated molecules, $\pi$-orbital
electrons are delocalized and the $\pi \rightarrow \pi^*$ transitions are typically in the visible region. The
greater extent of $\pi$-electron delocalization (longer conjugation) gives rise to lower
energy of $\pi \rightarrow \pi^*$ transitions and longer wavelengths for absorption bands. Thus, the
absorption bands provide information about the extent of delocalization in conjugated
macromolecules.\(^{31}\)

The emission accompanying relaxation of electrons from a singlet first excited-
state ($S_1$) to the ground state ($S_0$) is called fluorescence. Fluorescence spectrum can
probe formation of aggregates, charge transfer complexes, and or any other processes
affecting vibronic energy levels. In general, fluorescence spectra resemble absorption
spectra as the difference in vibrational level energies are similar in both the ground and
excited states (mirror image rule).\(^{111}\) However, the mirror image rule is not observed in
many cases in which nuclei have different configurations in the excited state compared
to the ground state. For example, the formation of exciplexes or excimers results in
broader fluorescence spectra which can be related to the formation of aggregates.
Anisotropy Measurements

Fluorescence anisotropy is a powerful tool to obtain information about the photophysical properties of molecules. Anisotropy is a measure of the extent of polarization of the emission upon excitation with a polarized light. It is related to the structural properties of molecules and based on the orientations of transition dipole moments of absorption and emission. Any process that changes the orientations of the transition dipole moments affects the anisotropy.

Upon illumination of a homogenous solution of fluorophores with polarized light, the excitation of those molecules whose absorption transition dipoles are orientated in the same as direction of polarization is favored. As a result, the excited fluorophores are only photo-selected portion of the population. The emitted photons also carry the information about the polarization of the incident beam provided that no process which can affect the orientation of transition dipoles takes place during the excited state lifetime (fluorescence depolarization). The depolarization can be caused by non-parallel absorption and emission transition dipoles, torsional vibrations, brownian motion and energy transfer.

The measurement of anisotropy involves excitation of the samples with linearly polarized light followed by selective detection of different polarizations of the emission from samples by using polarizers. The emission polarizer is orientated parallel the excitation beam to collect $I_\parallel$ and perpendicular to detect $I_\perp$. Anisotropy is calculated as the following:

$$R = \frac{I_\perp - I_\parallel}{I_\parallel + 2I_\perp}$$ (2-1)
In certain cases there can be more than one fluorescent species in the sample solutions. The average anisotropy is a given by addition of the anisotropy of the individual species \( r_i \) and multiplied by their population fraction \( f_i \).

\[
\bar{r} = \sum_i f_i r_i
\]  

(2-2)

This property is very useful when we consider mixture of species in a solution which can arise from processes like aggregation. Under certain conditions when it is difficult to quantify the relative concentrations of species, anisotropy can be used for quantification of relative concentrations provided that the individual anisotropies species are already known.

![Figure 2-1](image)

**Figure 2-1.** Emission intensities for a single fluorophore in a cartesian coordinate system. Adapted from reference 111

The theoretical expression for anisotropy values can be calculated by considering a single molecule and assuming the absorption and emission transition dipole moments are parallel. Consider a single fluorophore as shown in Figure 2-1, the emission intensities in parallel and perpendicular orientations are proportional to square of vector projections onto axis of observation.
For a population of many fluorophores randomly distributed in the solution, the anisotropy can be calculated as in equation 2-4 by determining average value of \( \cos^2(\theta) \).

\[
\begin{align*}
I_{||}(\theta, \phi) & = \cos^2(\theta) \quad \text{and} \quad I_{\perp}(\theta, \phi) = \sin^2(\theta) \sin^2(\phi) \\
\end{align*}
\]

(2-3)

\[
\text{where } \theta \text{ is the angle between the emission dipole and the z-axis and } \langle \cos^2(\theta) \rangle \text{ is the average value of } \cos^2(\theta) \text{ over the whole population of fluorophores. It is defined as }
\]

\[
\langle \cos^2(\theta) \rangle = \frac{\int_{\theta}^{\pi/2} \cos^2(\theta) f(\theta) d\theta}{\int_{\theta}^{\pi/2} f(\theta) d\theta}
\]

(2-5)

where \( f(\theta) d\theta \) is the probability that a fluorophore is oriented between \( \theta \) and \( \theta + d\theta \). For collinear absorption and emission transition dipole moments maximum value of \( \langle \cos^2(\theta) \rangle \) is 0.6 (random distribution around z axis) which results in maximum anisotropy of 0.4. This is the maximum theoretical anisotropy value for a randomly distributed fluorophores in solution, which can be achieved in the absence of depolarization processes.

The maximum value of 0.4 for anisotropy is calculated by assuming that the absorption and emission transition dipoles are parallel. In reality, there can be an angular displacement between them which results in decreased values for anisotropy. Thus the fundamental anisotropy can be calculated by taking into account the angular displacement (\( \beta \)) absorption and emission transition dipole moments.

\[
r_0 = 0.4 \left( \frac{3(\cos^2(\beta)-1)}{2} \right)
\]

(2-6)

The fundamental anisotropy is zero for \( \beta=54.7^0 \) and it becomes negative for larger angles with maximum negative value of \(-0.2\) for perpendicular orientation the absorption
and emission transition dipoles. The fundamental anisotropy can only be observed when there is no depolarization processes.

Rotational diffusion and energy transfer are most common depolarization processes in solutions.\textsuperscript{112-114} For small molecules, the rotations are faster than excited state lifetimes causing low anisotropies in steady-state measurements. The time dependent anisotropy of a fluorophore in the presence of rotational diffusion is given by

\[ r(t) = r_0 e^{-t/\Theta} \]  \hspace{1cm} (2-7)

\( \Theta \) is the rotational correlation time of the molecule. It depends on the size of the fluorophore, and viscosity of the solvent. The analysis of correlation times can become very complicated even in simplest systems due to presence of multiple exponential decays as there can be many processes involving in depolarization dynamics. Despite the difficulty in analysis, time-resolved anisotropy is a powerful tool which can used to study the size of molecules in addition to energy transfer and other depolarization processes.\textsuperscript{115-118}

The anisotropy measurements are done by consecutive measurements with different polarizations. However, the monochromators have different transmission efficiencies for different polarizations as the reflectivity of optics are sensitive to the polarization. Rotation of polarizers introduces a change in signal, independent of the samples being analyzed. The instrumental factors affecting the intensity of the signals should be corrected to obtain the real anisotropy values. For example, the emission intensity of vertically polarized excitation and vertically polarized detection (\( I_{vv} \), see Figure 2-2) is the product of the signal intensity when excitation and detection
polarizations are parallel (I\textsubscript{||}), and the sensitivity of the instrument for vertical polarization (S\textsubscript{V}) along with a proportionality constant for the quantum yield of the sample.

\begin{align*}
I_{VV} &= kS_V I_{||} \quad (2-8) \\
I_{VH} &= kS_H I_{\perp} \quad (2-9)
\end{align*}

The actual ratio of parallel and perpendicular intensities provides information about the anisotropy of the sample. By taking the ratio of equations (2-8) and (2-9), the actual signal intensity information can be separated from the instrumental sensitivities.

\begin{equation}
\frac{I_{VV}}{I_{VH}} = \frac{S_V I_{||}}{S_H I_{\perp}} = G \frac{I_{||}}{I_{\perp}} \quad (2-10)
\end{equation}

The G-factor is defined as the ratio of the sensitivity of the instrument for parallel and vertical polarizations. It is expected to be close to one if the transmission efficiency of the monochromator is almost identical for different polarizations. The G-factor can be obtained easily by using horizontal polarization for the excitation beam and combinations of horizontal and vertical polarizations for the detection. In both cases the signal is proportional to the I\textsubscript{\perp}.

\begin{equation}
\frac{I_{HV}}{I_{HH}} = \frac{S_V I_{\perp}}{S_H I_{\perp}} = \frac{S_V}{S_H} = G \quad (2-11)
\end{equation}

For the measurements of anisotropy four different orientations of the polarizations are collected (I\textsubscript{VV}, I\textsubscript{VH}, I\textsubscript{HV}, I\textsubscript{HH}, see Figure 2-2).

After the collection of all four orientations, the following formula is used to calculate the anisotropy, R, which accounts for the sensitivity difference of the instrument by calculation of the G factor.

\begin{equation}
R = \frac{I_{VV} - GL_{VH}}{I_{VV} + 2GL_{VH}} \quad \text{where} \quad G = \frac{I_{VH}}{I_{HH}} \quad (2-12)
\end{equation}
For time-resolved anisotropy measurements, the four polarization combinations are recorded under the instrumental settings such as excitation intensity, and acquisition time in the same way as the steady-state measurements. The correction factor G for detection efficiency is determined by using $I_{HV}(t)$ and $I_{HH}(t)$ decays. If it is not possible to collect $I_{HV}(t)$ and $I_{HH}(t)$ decays due to low signals or a low signal to noise ratio, it is possible to use the tail matching method. The tail matching method calculates the G-factor by assuming that at long time-scales (where the signal is close to zero) any difference is caused in the decays is due to the transmission efficiency of the optics. It can be used for samples which have faster rotational diffusion times than fluorescence lifetimes.

**Time-Resolved Emission Spectroscopy**

The photophysical properties and excited state dynamics of conjugated systems can be studied by time-resolved emission measurements. The energy transfer in these systems also involves very fast processes. In order to investigate such fast kinetics, it is a necessity to use an ultrafast time-resolved technique (time-resolution: $10^{-12} - 10^{-15}$ s). Time-resolved fluorescence spectroscopy methods include: streak-camera detection,
time-correlated single-photon-counting and up-conversion method. Streak-camera detection and time-correlated single-photon counting use electronic devices to obtain the time-resolved emission of a sample limiting the time resolution to the response time of the electronics. Up-conversion uses an optical gate allowing faster measurements (limit $10^{15}$ s). In our studies time-resolved emission measurements using: time-correlated single photon counting and fluorescence up-conversion.

**Time-Correlated Single Photon Counting**

Time-correlated single-photon-counting measurement (TCSPC) is based on detection of individual emitted photons. This method relies on the fact that the probability of detecting a single photon is proportional to the fluorescence intensity at a given time. The arrival times of the individual photons are measured with respect to the excitation pulse. After timing and recording a large number of individual photons, they are used to reconstruct the time-resolved decays.\(^{31}\)

Since the measurements rely on detection single photons, the ratio of the number of fluorescence photons detected must be kept much smaller than the number of exciting photons (<0.01-0.005). In order to achieve this condition, dilute solutions should be used and the optics can be tuned by using neutral density filters or apertures.

The TSCPC instruments include a pulsed excitation source ideally having a high repetition rate to ensure fast measurements with high signal to noise ratios. The optical excitation source is used to generate an electrical pulse which is used as a start input of a time to amplitude converter (TAC). Detection of individual emitted photons provides stop input for TAC. The latter generates an output pulse whose amplitude is proportional to the delay time between start and stop inputs. The height of this output pulse is analyzed by analog to digital converter and a multichannel analyzer (MCA). The
Histograms of the decays are created after many excitation and detection events and a large number of events provides better accuracy.

**Fluorescence Up-Conversion**

![Diagram](image)

Figure 2-3. The basic principles of up-conversion technique. A) Representation of sum frequency generation or up-conversion. B) Obtaining time profile by delaying the gate pulse.

In conjugated macromolecules, energy transfer takes place via an excited state relaxation the neighboring chromophores on sub-picosecond time-scale. In order to study this process, ultrafast time-resolved emission spectroscopy is employed for our investigations. The up-conversion method enables monitoring the changes in fluorescence in time within a few hundred femtoseconds.

Up-conversion is an optical gating technique based on sum frequency generation of a laser beam and fluorescence from the sample.\(^{120,121}\) It is based on monitoring the sum frequency signal as a function of the delay time between excitation and a shot gate pulse (Figure 2-3).
Sum frequency generation (SFG) or frequency mixing is a second order nonlinear optical phenomenon for which spatial and temporal overlaps are crucial.\textsuperscript{122} Phase-matching is also essential in order to have SFG because three wave mixing can exist only if the following condition is fulfilled:

\[ \mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 \tag{2-12} \]

In this equation, \( k_j \) are the wave vectors of the three waves. Phase-matching condition is satisfied when the three waves propagate collinearly and the equation can be written as follows

\[ \frac{n_1}{\lambda_1} + \frac{n_2}{\lambda_2} = \frac{n_3}{\lambda_3} \tag{2-13} \]

The refractive index of the material at the corresponding wavelength is given as \( n_i \) in this equation. The phase-matching condition cannot be met for many materials as their refractive index varies with the wavelength. On the other hand, birefringent materials can be used to satisfy this condition. By adjusting the angle between the optical axis of a birefringent crystal and the direction of propagation of the gate beam the phase matching condition can be fulfilled for desired wavelengths.

The up-conversion technique utilizes a pulsed laser which is divided into two parts. The first part excites the samples and the induced emission is collected and focused on a nonlinear crystal (NLO). The second part goes through an optical delay stage which increases or decreases the optical path. The temporal overlap is swept by delaying the gate pulse with respect to the excitation pulse (Figure 2-2). The gate beam is also focused on the nonlinear crystal and spatially overlapped with the fluorescence. The up-converted signal can be obtained when the fluorescence beam and gate pulse are present in the nonlinear crystal simultaneously.
For samples with broad emission bands, different parts of the emission spectrum can be up-converted by varying the angle of the NLO. Spectra resolution of up-converted signals can be provided by using a monochromator.

The intensity of the sum-frequency (up-converted) signal is determined by the convolution of the intensity of the gate pulse and the fluorescence, as given in the following equation.

\[ I_{\text{sum}}(\tau) = \int_{-\infty}^{\infty} I_{\text{fluo}}(t) I_{\text{gate}}(t - \tau) \, dt \quad (2-14) \]

The decays of the intensity of the up-converted signal as the gate pulse is delayed with respect to the excitation (\( \tau \) is increased) reflect the changes in the temporal response of the intensity of the fluorescence.

The time resolution of fluorescence up-conversion experiments depends on the pulse width of the short laser pulse which is used for optical gating and the pump pulse used for excitation of the samples. Therefore, the instrument response function (IRF) of the up-conversion set-up is measured by the cross-correlation of the excitation (pump) pulse and the gate pulses. The convolution of pump and gate pulses is obtained by replacing fluorescence intensity with the scattered light from the pump pulse.

**Steady-State Instruments**

Steady-state measurements are done at the material chemistry characterization laboratory (MCCL). The absorption measurements are recorded with a PekinElmer Lamda 25 UV-VIS spectrometer. The spectrometer has tungsten and deuterium lamps to provide excitation sources in both the ultraviolet and visible regions of the electromagnetic spectrum. The instrument has an accessible range of 190 nm to 1100 nm with double beam operation which provides automatic compensation for lamp
intensity variations. The emission spectra are recorded with a Jobin-Jvon Spex-Flurolog-3 instrument which has a double grating system for the excitation beam. There is a front face detection option for samples having higher optical densities to avoid self-absorption. A Xenon arc lamp is used as the light source, which provides 450 W, and a photomultiplier tube is used for detection (R928P). The excitation range of the instrument is 250 nm to 600 nm and the detection range is 300 nm to 850 nm.

The steady-state anisotropy measurements are also done at MCCL using the Spex- Fluorog-3 instrument. The lamp source used for the fluorescence measurements provides non-polarized light but by using Glan-Thompson type polarizers the unwanted polarizations are filtered. The desired excitation and detection polarizations are set by rotating the polarizers.

The measurement of fluorescence anisotropy is done by employing L-format detection (right angle detection with only one channel for detection) (Figure 2.1). Since there is only one channel for detection of emission, different orientations of polarizations are detected by consecutive measurements.

**Time-Resolved Emission Instruments**

**Time-Correlated Single Photon Counting Instrument**

TCSPC measurements are performed with a commercially available PicoQuant FluoTime 100 Compact Fluorescence Lifetime Spectrometer. The system allows laser operation rates as high as 85 MHz. The excitation source used for the measurements is a diode laser (LDH-P-C-375) which provides pulses centered at 375 nm with full width of half maximum (FWHM) smaller than 300 ps. As a part of the instrument, there are two filter wheels one of which contains neutral density filters to control the intensity of the excitation light. Long-pass or interference filters can also be used to obtain signals
from desired regions of the spectrum. A photomultiplier tube (PMT) from Hamamatsu (H5783) having a built in high voltage supply is used as the detector. The data acquisition module (PicoHarp 300) contains all the complete electronics for TCSPC and acquisition times shorter than 1 second can be achieved. With the current configuration of the instrument, instrument response functions (IRFs) as short as 200 ps can be achieved. The Picoquant instrument already has polarizers installed for the excitation and emission beams. The detection polarizer is set at the magic angle for lifetime measurements. For sub-nanosecond time-resolved anisotropy measurements the polarization is changed from vertical and horizontal combinations.

**Up-Conversion Set-up**

![Up-Conversion Set-up Diagram]

*Figure 2-4. Schematic representation of up-conversion experimental set-up*
The schematic representation of the home-made up-conversion set-up which was built by Atas et al. is given in Figure 2-4. Any changes from the original set-up is explained in details in set-up modifications section.

A portion of the output of the femtosecond laser system (50fs, 800 nm) is divided into two beams to be used as gate and pump pulses. The part of the beam which is used as the excitation source goes through an optical parametric amplifier (OPA) followed by second and fourth harmonic generation. The excitation beam is focused on the sample and the resulting fluorescence is collected by off-axis parabolic mirrors. The part of the beam which is used as the gate pulse goes through a delay stage which is used for sweeping of the temporal overlap between the fluorescence and gate pulses. Sum frequency signal is obtained when the fluorescence and gate beams are both spatially and temporally overlapped in the β-BBO crystal. This up-converted signal is collimated and dispersed on a monochromator and detected by a photomultiplier tube. The temporal evolution of the up-converted signal is scanned in time by utilizing the delay stage which is computer controlled with high precision. Each component of the up-conversion set-up is explained in details in the following sections.

**Laser source**

In order to achieve sub-picosecond time resolution for up-conversion measurements, a commercially available femtosecond laser source from Spectra-Physics is used. The laser source consists of different components including a mode-locked titanium doped sapphire (Ti:Sa) oscillator which is used as a seed beam for the Ti:Sa regenerative amplifier (Figure 2-5).

**Millenia Vs®:** It is a solid state continuous wave (CW) laser which is used as a pump beam for the mode-locked Ti:Sa oscillator. It provides high power (2-10 W) in the
visible region (532 nm). The lasing material is consists of neodymium doped yttrium vanadate (Nd: YVO$_4$). The emitted wavelength is 1064 nm which is frequency doubled by a temperature controlled lithium triborate (LBO) crystal.

**Figure 2-5.** Schematic representation of femtosecond laser system

**Ti-Sa Oscillator Tsunami®:** This laser has an active material of titanium-sapphire crystal and it is used as the seed beam for regenerative amplifier. The output of the laser is centered at 790 nm with 35 nm bandwidth and 80 MHz repetition rate. The power is in the range of 360 to 420 mW.

**Evolution X®:** It is a high power visible neodymium doped yttrium lithium fluoride (Nd:YLF) laser which is used for pumping the regenerative amplifier. This laser is pumped by AlGaAs diodes and intra-cavity frequency doubled with an LBO crystal. The Q-Switched pulses provide power greater than 6 W at 527 nm with a repetition rate of 1 kHz.

**Spitfire®:** It is the regenerative amplifier, pumped by the Evolution X® and seeded by the Tsunami® using chirp pulse amplification to produce 840 mJ centered at 790nm with 1kHz repetition rate. It consists of a pulse stretcher, cavity and compressor parts. The output of the Tsunami® is stretched by a grating scheme before it enters the cavity.
The laser cavity has a Z form and the active laser medium is Ti:Sa. The pulse is amplified by having round trips in the cavity, and pockel cells are used to release the pulse as it achieves the required energy. The compressor has a similar grating scheme as the stretcher and it is used to shorten the pulse after the cavity providing pulse widths around 50 fs.

**Optical Parametric Amplification (OPA):** The Spectra Physics OPA-800 C® is used to obtain tunable high energy femtosecond pulses over a broad wavelength range. The output wavelength range is tuned by changing the angle of the β-Barium Borate (β-BBO) crystal. In an OPA the gain is obtained from nonlinear frequency conversion processes. The high-intensity power amplification beam (ωp) is used to amplify a low energy seed beam. The seed beam is a white light continuum which is generated using a sapphire window. Signal (ωs) and idler (ωi) beam pulses are produced and amplified using β-BBO crystal. The energy conservation determines the generated wavelengths (ωp= ωs+ ωi). The gain medium is a type II β-BBO crystal so the signal and idler beams have opposite polarizations. To obtain a wider wavelength range for excitation second and fourth harmonic generation of either signal or idler beam is used after the OPA. The selection of idler or signal beam depends on the desired wavelength output. In current configuration, desired beam is separated using dichroic mirrors.

For up-conversion experiments on conjugated polyelectrolyte dendrimers, fourth harmonic generation of the OPA’s signal (310 – 380 nm) is used as the excitation pulse (Chapter 3 and 4). For the studies on conjugated polyelectrolytes (CPEs), the fourth harmonic generation of the idler output of the OPA (420 - 500 nm) is preferred for up-
conversion measurements (Chapter 5). The change from idler to signal or the opposite involves changing the orientation of the second and fourth harmonic generation crystals.

**Excitation and gate pulses**

After a fourth harmonic generation, the output beam (which is used as the excitation pulse) goes through a half-wave waveplate to provide control over the polarization of the beam before it is directed into a double-prism-compressor. The orientation of the polarization (p-polarization) is chosen such that at the Brewster’s angle, reflection losses are minimal. The prism-compressor employs UV grade isosceles fused silica prisms (CVI, IB-12.4-69.1-UV), which provide working range from UV to visible wavelengths. The first prism spatially disperses the beam and the second one adds negative group velocity dispersion (GVD) which compensates for the accumulated positive GVD as the beam goes through optics. The second pass combines all the colors together. The prism compressor improves the time resolution of overall up-conversion set-up by compressing the excitation pulse which is longer than the gate beam as it goes through more optics in the OPA. This prism compressor allows to pre-compensate the positive GVD acquired as the beam travels through the Berek Compensator, focusing lenses and the glass of the cuvette.

After the prism compressor, a Berek Polarization Compensator is used to change polarization with precision and flexibility. The Berek Compensator is set at the magic angle for time-resolved emission measurements in order to eliminate the depolarization effects on the fluorescence decays. For ultrafast anisotropy measurements, the Berek compensator is set to vertical or horizontal polarizations and the individual decays are collected. Combinations of these individual decays provide the anisotropy (see anisotropy section).
The excitation beam is focused at the focal point of the off axis parabolic using a positive lens (f = 200 mm) on a spot with 200 μm diameter (excitation volume 0.06 mm$^3$). The excitation energy is kept lower than 40 nJ/ pulse to avoid photobleaching (1.3 J/m$^2$ pulse). A homemade sample holder is used at the focal point of the parabolic mirror, for placement of the cuvette with the samples at the focal point of the parabolic mirrors. The sample holder is placed on a tool plate using pins to ensure reproducibility. The alignment of the excitation beam is done by placing a pinhole (250 μm diameter) at the sample position. The samples are placed in 2 mm pathway quartz cuvettes and the solutions are stirred by using a magnetic stirrer bar to ensure photostability.

The pair of off-axis parabolic mirrors collects and images the fluorescence after the excitation of the sample. The importance and details of the parabolic mirrors are given in the next section including modifications that has improved the alignment and efficiency of the up-conversion set-up. The fluorescence is imaged on the β-BBO crystal (β-barium Borate, type I, 0.5 mm) and overlapped with the gate beam (18 mW before the β-BBO crystal, 790 nm).

A portion of the direct output of the Spitfire laser is used as the gate beam for up-conversion experiments. The polarization of the gate beam is controlled by a waveplate and a polarizer fixed in a vertical position. The gate beam passes through a computer controlled delay stage (Physik Instrumente, M-531-DD, Resolution 0.1μm). The beam is focused right after the β-BBO crystal, using a positive lens (f= 300 mm) placed on a manually controlled translation stage. The position of the lens is varied to optimize up-conversion efficiency as long as the beam is not focused on the crystal (to avoid damage to the crystal).
Set-up modifications

Figure 2-6. The configuration of parabolic mirrors. A) Before modifications with negative mirror. B) Current configuration.

In the up-conversion set-up, a pair of off-axis parabolic mirrors collects and images the fluorescence after the excitation of the sample. The sample is placed at the foci of the first parabolic mirror. In the previous up-conversion set-up, the two off-axis parabolic mirrors had the same effective focal length (Janos-A8037-205, 6 in) and there was an additional negative lens after the second off-axis parabolic mirror (Figure 2-6). The short focal length of the parabolic mirror results in larger angles ($\theta=38\text{ mrad}$) than the acceptance angle of the $\beta$-BBO crystal ($\beta$-barium Borate, type I, 0.5 mm, acceptance angle=19 mrad). Thus, the sum frequency of only a portion of the fluorescence beam which lies within the acceptance angle was possible decreasing the overall efficiency of the set-up. The negative lens ($f=-200\text{ mm}$) was placed in order to overcome this problem by focusing the fluorescence beam at longer distance from the mirror and decreasing the solid angle at the crystal ($\Phi=20\text{ mrad}$). The crystal was also moved to the new focal point and a better conversion was achieved. In this case the distance from the center of the parabolic mirror to the $\beta$-BBO crystal was 350 mm. The negative lens was mounted on a xyz translation stage for alignment purposes. However, the presence of this lens added more dispersion (chirp) to the pulse. Moreover, it added
three additional variables (xyz) for the alignment of the set-up. In order to get rid of the negative lens, the first off-axis parabolic mirror was replaced with an off-axis parabolic mirror having shorter focal length and shorter diameter (Janos- A8037-101, 2 in) allowing to place the samples at the new foci of the parabolic mirror (2 in). The smaller solid angles (θ=18 mrad ) at the β-BBO crystal are achieved by using the configuration in Figure 2-6 B without requiring a negative lens. The position of the β-BBO crystal was changed to the foci of the second off-axis parabolic mirror which is also defined by a pinhole and makes it easier to align. Although the collection efficiency of the system is the same as before (the solid angle does not change), it is easier to minimize the pump scatter by using a smaller mirror, the GVD accumulated is smaller because there is less transmission optics and it is easier to align. The alignment is also easier as the focal point is better defined than previous configuration.

In addition, a newer spectrograph (Oriel Cornerstone™ 260 ¼ m) with better optical performance was placed. The grating blazed at 250 nm with a line intensity of 1200 mm⁻¹ (74062) (offers better wavelength resolution and better optical performance in the UV region) was used for our experiments.

**Up-converted signal**

The up-converted signals are generated by the sum frequency of the sample fluorescence and the gate beam at the β-BBO crystal. The phase-matching angle to probe the desired wavelength is achieved by rotating the β-BBO crystal with a micrometer around the vertical axis. Micrometer settings for each emission wavelength are given in Table 2-1. After the β-BBO crystal the fluorescence and gate beams are spatially separated. Irises are used to filter the fluorescence and gate beams from the

55
up-converted signal. The up-converted beam is collimated by a fused silica lens (f=150 mm) and a second positive lens (f=150 mm, fused silica) is used before the monochromator to focus the beam at the entrance slit. The monochromator entrance has a micrometer driven slit which allows 4 µM to 3 mm slit-widths and 2 to 15 mm slit-heights (Oriel 74001, 0.4 mm), and homemade output slits (0.5, or 1 mm). Background signal from fluorescence, gate and second harmonic generation of the gate beam (400 nm) are minimized by using the monochromator. Oriel Cornerstone™ 260 ¼, a fully automated, multi-grating spectrograph, is used for these purposes.

Figure 2-7. Schematic representation of pump beam incident to parabolic mirror, solid lines shows regular path, and dotted lines represent alternative pathway for alignment.

Since the up-converted signal in a typical measurement is weak and in the deep UV region (240-320 nm), the collection of the signal and the alignment of the optics is a changeling task. The alignment is done by setting the pump beam wavelength to 530 nm and creating an alternative pathway to collect the laser beam directly by the parabolic mirrors. This alternative pathway is demonstrated in Figure 2-7. For the alignment, the mirror before the sample position (M1) is taken out in which case the beam goes through M2 and M3. The sample cell is replaced by a pin hole, and the beam goes through the pin hole to arrive at the center of the parabolic mirror and the
pinhole scatter is imaged on the β-BBO crystal. The sum frequency generation of the laser beam and the gates beam is very strong and easily visualized (317 nm) and it is used to do the initial alignment. After initial alignment with this visible beam, the wavelength of the excitation beam is switched to UV and further alignment is done blindfolded monitoring the cross-correlation signal.

The signal is detected by a photo-multiplier tube (PMT) which can be either a solar blind (Hamamatsu, R7154) which has low quantum efficiency at visible wavelengths or a PMT sensitive to visible light (Hamamatsu, R928). For the detection ranges from 242 nm to 300 nm a solar blind PMT was used since it provides better performance to avoid detection of 400 nm background signal originating from second harmonic generation of the gate beam. The detection of 400 nm is avoided by using UG-11 filter, which has a cut of at 380 nm. For up-converted signals at wavelengths longer than 300 nm the quantum efficiency of the solar blind PMT decreases drastically so the R 928 PMT was used instead. The electrical signal is amplified by a Fast Preamp (SR 240) and gated and integrated with a boxcar averager (SR 250) from Stanford Systems. The electronic gate widths can be varied from 2ns to 15 μs and 10 ns width was used for the up-conversion experiments. A personal computer is used to control the delay stage and for data acquisition and storage.

Typically, 200 laser shots are averaged for each time step in a given experiment. If the samples have very low quantum yields, (CPE-Ds have quantum yields between 0.06-0.01) up to 4000 laser shots are averaged at each time-delay position. The decays reported in this work are averages of many decay scans collected consecutively (10-50 scans). These scans can take from 3 to 10 hours depending on the number of time
steps and signal to noise ratios. The power of the pump is recorded during the scans to check the stability of the laser. Each scan is compared to the previous one to make sure that there are no changes regarding samples. The steady-state spectra of the solutions are recorded before and after up-conversion experiments and if there is any change in the spectra, these scans are discarded.

Figure 2-8. Instrument response function collected by cross-correlation of gate and pump pulses. A) Pump wavelength at 316 nm B) Pump wavelength at 365 nm.

In order to obtain the instrument response function (IRF) of the up-conversion apparatus, a cross-correlation between the pump scatter and gate beams is collected. For the collection of IRF, cross-correlation is collected in the same conditions with the fluorescence measurements, for example, filters are placed in the same positions. The IRF depends strongly on the excitation wavelength as it is more difficult to compress UV pulses with the prism compressor. Two different IRFs at 316 nm and 365 nm are given in Figure 2-8. The full width of maximum of the IRF is 330 fs at 316 nm while it is 290 fs at 365 nm (corresponding to pulse widths of 317 fs and 275 fs respectively). These IRFs were obtained after optimization of the prism compressor conditions (distance between
two prisms, incident angle, and the amount of material the beam travels in the second prism) and they were used for convolution with the proposed fitting functions.

Table 2-1. Experimental conditions for different wavelength detections (\(\lambda_{\text{gate}} = 790\) nm)

<table>
<thead>
<tr>
<th>Emission (\lambda) (nm)</th>
<th>Detected (\lambda) (nm)</th>
<th>Micrometer Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>345</td>
<td>240</td>
<td>14.10</td>
</tr>
<tr>
<td>350</td>
<td>242</td>
<td>13.70</td>
</tr>
<tr>
<td>363</td>
<td>249</td>
<td>12.67</td>
</tr>
<tr>
<td>376</td>
<td>255</td>
<td>11.50</td>
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<tr>
<td>458</td>
<td>290</td>
<td>6.35</td>
</tr>
</tbody>
</table>
CHAPTER 3
ENERGY TRANSFER IN PHENYLENE ETHYNYLE EXTENDED DENDRIMERS IN ESTER AND IONIC FORMS

Since the discovery of light-harvesting phenomena in photosynthesis, there has been tremendous amount of efforts towards synthesis of artificial light-harvesting systems which steered attention towards dendrimers.\textsuperscript{42} Dendrimers gathered particular attention among other candidates because of their superior properties such as monodispersity, well defined structure, and high degree of order.\textsuperscript{42,47,61,62} The phenylene-ethynylene (PE) dendrimers consisting of all conjugated linear segments are one of the most promising candidates for light harvesting systems since they are capable of unidirectional energy transfer.\textsuperscript{124-131} The large number of chromophores in their structures increases the molar extinction coefficient while the intra-molecular energy gradients improve directionality of the energy migration. These properties make PE dendrimers well-suited for light-harvesting applications.

PE dendrimers have interesting electronic properties at the branching points. In the ground electronic-state, the meta branching breaks the conjugation giving rise to localized excitations. There are studies which have shown the presence of increased delocalization in the excited state.\textsuperscript{118,132,133} The presence of strong electronic coupling in the excited state is also supported by ab-initio calculations.\textsuperscript{132} The extent of delocalization in the excited state and electronic coupling between PE units are still under investigation for larger systems.

Moore and coworkers synthesized and characterized two families of PE dendrimers having threefold symmetry and Cayley tree topology.\textsuperscript{58,124,125,134} The first family of dendrimers consists of 2-ring PE units (diphenylethynylene) building blocks. The same building blocks (2-ring PE units) are used for creating higher generations of
the dendrimers. This family is called “compact” because of the steric effects of periphery groups.\textsuperscript{124} The compact dendrimers do not have an energy gradient since the conjugation length of the linear buildings blocks is the same for all generations. The second family of dendrimers consists of 2-, 3- or 4-ring PE units. The higher generations of the dendrimers have longer PE units at the core and shorter ones at the periphery in hierarchical manner. This family of PE dendrimers is called “extended” and has energy gradients from shorter buildings blocks to longer ones. The gradual change in conjugation length introduces a descending HOMO-LUMO gap from periphery to core.\textsuperscript{134} Devadoss and coworkers claimed that extended dendrimers act like highly photoactive antennas with discrete energy funnels.\textsuperscript{71}

PE dendrimers are only soluble in non-polar solvent due to their hydrophobic structure which limits their procesability for applications. However, it is possible to overcome this limitation by utilizing different end-groups. The end-groups can be engineered to make them soluble in polar solvents. Although there are a variety of PE dendrimer structures (symmetrical and unsymmetrical) having unique photophysical properties studied in literature,\textsuperscript{58,72,133,135-139} the energy-transfer properties in polar solvents are not well-known and they are the focus of this dissertation.

We have investigated a new family of extended dendrimers consisting of 3-ring PE units at the core and 2-ring PE units at the periphery. The longer conjugation length at the core gives rise to an energy gradient from the periphery to the core of the dendrimer. The HOMO-LUMO gaps of the 2-ring and 3-ring PE units in the PE dendrimer structures were determined experimentally by Kopelman et al.\textsuperscript{124} The 2-ring PE units have a HOMO-LUMO gap which is 3000 cm\textsuperscript{-1} larger than the 3-ring PE units.
Palma et al.\textsuperscript{140} performed MD/QM simulations to study the electronic absorption spectra. The calculated HOMO-LUMO gaps are in agreement with the experimental values observed at room temperature. They showed that the HOMO-LUMO gap is significantly affected by phenyl ring rotations.

Figure 3-1. The structures of PE dendrimers. A) Branched end-group R in ester form B) Branched end-group R in ionic form C) Second generation of compact dendrimers (Ph\textsubscript{2}PG-2/ Ph\textsubscript{2}G-2) D) Third generation of extended dendrimers (Ph\textsubscript{3}PG-3/ Ph\textsubscript{3}G-3).

Figure 3-1 shows the structures of the PE dendrimers functionalized with branched ester or ionic groups (R or R\textsuperscript{'}). These dendrimers were synthesized by our collaborators.\textsuperscript{141} PE dendrimers studied in this work are labeled according to their generation, backbone and end-groups. For example, a second generation structure
(Figure 3-1 C) is labeled as Ph$_{2-2}$PG-2, where Ph stands for phenylene and the subscripts depicts the number of phenyl rings, P stands for precursor (ester form) and G-n for the generation number. The ionic analog of the second generation is labeled as Ph$_{2-2}$G-2 to emphasize that the end-groups are no longer protected. The third generation (Ph$_{3-2-2}$PG-3/ Ph$_{3-2-2}$G-3) of the extended dendrimers has 3-ring PE units at the core and 2-ring PE units at the periphery. Our dendrimers are different from the ones studied by the Moore group in terms of the end-groups. Since the extended dendrimers presented here have branched end-groups, their solubility is higher and their tendency to form aggregates is suppressed.$^{98,103,142}$

The ionic forms of the dendrimers are obtained by deprotection of the branched end-groups making it possible to compare properties of ester precursors with ionic analogs (CPE-Ds). The photophysical properties of both forms of the dendrimers are studied by steady-state and time-resolved spectroscopy. The changes from ester to ionic forms are analyzed to gain information about interactions and aggregation. The energy transfer from periphery to core is studied by ultrafast up-conversion spectroscopy. We have collected fluorescence decays at different excitation and emission wavelengths and analyzed time-resolved data using kinetic models. We determined the energy-transfer efficiency and rates of the ester and ionic forms of the dendrimers and compared them to understand the underlying photophysical processes.

The extended dendrimers studied in this work have two parts, one acting as a donor (periphery) and the other acting as an acceptor (core). In order to estimate the properties of the donor and acceptor parts, model compounds are investigated first. The structures, steady-state and time-resolved characterizations of the model compounds
are presented in the following section. This information will be used to understand the photophysical properties of the extended dendrimers. The energy transfer studies also benefit from information provided by the results of model compounds.

**Model Compounds**

Figure 3-2 shows the structures of model compounds. Their steady-state spectra are used to assign individual bands to the core (acceptor) and periphery (donor) part of the extended dendrimers. They are also used to understand the fluorescence decays and modeling of the excited-state kinetics.

For example, the 3-ring PE unit (para-TPA, Figure 3-2 B) along with the first generation (Ph$_3$PG-1/Ph$_3$G-1, Figure 3-2 D), are used to characterize the core structure of extended dendrimers. There are two main differences between these structures. First, the backbone of the first generation dendrimer (Ph$_3$PG-1/Ph$_3$G-1) consists of three equivalent para-TPA units coupled in meta position to a central phenylene group opening the possibility of coupling between these units. Second, the first generation (Ph$_3$PG-1/Ph$_3$G-1) has alkoxy substituents and branched end-groups. We consider both structures (para-TPA and Ph$_3$PG-1/Ph$_3$G-1) as model compounds because i) the core structure of the extended dendrimers does not have the alkoxy substituents in close proximity so the effects if these groups will not be as pronounced with the extended dendrimers as it is in the Ph$_3$PG-1/Ph$_3$G-1; ii) linear para-TPA does not provide information about the possible contribution from coupling among the para-TPA groups which can also affect the absorption and emission bands of the core structure. Thus, both compounds are needed to model for the core structure photophysics.
A family of compact dendrimers was also synthesized and characterized by our collaborators and Figure 3-2 shows their structures (C, E and F). They consist of 2-ring PE units and do not have an energy gradient. They can be in either ester or ionic forms similar to extended dendrimer family. The ester forms are soluble in organic solvent and the ionic forms are soluble in polar solvent. Compact dendrimers are good approximates for the periphery part of the extended dendrimers. They are also used to understand the effects of ionic end-groups on photophysical properties. We compared
their steady-state spectra to understand the similarities and the differences between ester and ionic forms.

**Model Compounds for the Core**

The model compounds for the core part of the extended dendrimers are characterized using steady-state absorption and emission measurements. Figure 3-3 (A and B) shows the absorption and emission spectra of the Ph₃PG-1 (black) and para-TPA (green). In panels C and D, steady-state spectra of Ph₂PG-1 (black) and DPA (green) are compared to show that similar effects are also observed for 2-ring PE units. There are significant differences in the steady-state spectra of these compounds. Although the absorption spectra of Ph₃PG-1 and para-TPA have very similar shapes, the absorption spectrum of Ph₃PG-1 is significantly (12 nm) red-shifted compared to para-TPA (Figure 3-3 A). The emission spectrum of Ph₃PG-1 is broad and featureless while the emission spectrum of para-TPA shows a clear vibronic structure (Figure 3-3 B). The emission spectrum of Ph₃PG-1 is 30 nm red-shifted compared to para-TPA. The absorption maximum of DPA is 15 nm red-shifted relative to Ph₂PG-1 while the red-shift is 48 nm for the emission maximum.

The differences between absorption and emission spectra of the Ph₃PG-1/Ph₂PG-1 and para-TPA/DPA can be caused by the presence of alkoxy substituents in the para position of the end-phenyl rings for Ph₃PG-1.¹³³ These alkoxy groups enable electron donation to the PE units. The increased electron density can give rise to charge transfer character in the excited state and result in broad emission bands.

Yoshida and coworkers¹⁴⁴ synthesized oligo(p-phenylene ethynylene)s as rod shaped π conjugated systems and characterized their photophysical properties (i.e. absorption). They observed red-shifts in the absorption (6 nm) and emission (27 nm)
maxima, and an enhancement in the molar extinction coefficient of the oligomers as they are substituted with alkoxy groups in para position.\textsuperscript{144} Moreover, Kolandaivel and coworkers\textsuperscript{145} calculated substituted and unsubstituted OPEs absorption and emission spectra by using time-dependent density functional theory (TDDFT) obtaining results in good agreement with the experiments and stated that the substitution with electron withdrawing or donating groups has a significant effect on the spectrum.\textsuperscript{145}

![Figure 3-3. Steady-state spectra of model compounds. A) Absorption spectra of Ph$_3$PG-1 (black) and para-TPA (green) B) Emission spectra of Ph$_3$PG-1 (black), and para-TPA (green) C) Absorption spectra of Ph$_2$PG-1 (black) and DPA (green) D) Emission spectra of Ph$_2$PG-1 (black), and DPA (green)](image)

The 12 nm red-shift absorption spectrum of Ph$_3$PG-1 compared to para-TPA is larger than the expected red-shift due to the presence of alkoxy substitution. This larger
red-shift can be related to the rotations of the phenyl rings. It is known that the absorption spectra of PE oligomers are strongly affected by the rotation of phenylene rings.\textsuperscript{146,147} In the ground state, the energy cost for the twisting of the rings is very low (near $kT$, 0.59 kcal/mol for DPA in gas phase) and the ground-state potential is shallow. The ground-state electronic spectra of PE oligomers arise from the ensemble average of different geometries of the phenyl ring. In the excited state, the barrier for rotation is substantially larger and the geometries are more constrained to the planar configuration.\textsuperscript{147} Therefore, absorption and emission spectra are not mirror images of each other. The absorption spectrum is affected more by these rotations than the emission spectrum.

\textit{DPA/para-TPA} is a short oligomer that has no substituent groups so lower energy barriers for phenyl ring rotations are expected for this molecule. However, \textit{Ph$_2$PG-1/Ph$_3$PG-1} is expected to be more rigid than DPA/\textit{para-TPA} and the energy barrier for ring rotations are expected to be higher. Since \textit{Ph$_3$PG-1/Ph$_2$PG-1} has a more planar structure than the linear molecules, the conjugation length is increased. In other words, the red-shift in the absorption maxima of first generations of the dendrimers and linear units can arise from the difference in their flexibility. In order to approximate the absorption spectra of extended dendrimers, \textit{Ph$_3$PG-1} is preferred since the core structure is expected to be more rigid than individual \textit{para-TPA} units.

The coupling between \textit{para-TPA/DPA} units can also affect the emission spectrum of the \textit{Ph$_3$PG-1/Ph$_2$PG-1}. Moore and coworkers characterized \textit{meta}-branched compact PE dendrimers and showed localized optical excitations by steady-state spectroscopy.\textsuperscript{124,125} However, Goodson and coworkers used time-resolved
measurements to claim that there is an ultrafast energy migration, which was not evident in the steady-state measurements.\textsuperscript{108,148,149} Although, the meta-branching breaks the conjugation in the ground state, the delocalization is increased in the excited state.\textsuperscript{118,132} The presence of strong electronic coupling in the excited-state geometry is also supported by ab-initio calculations.\textsuperscript{132} We have investigated the excited-state kinetics of Ph\textsubscript{3}PG-1 by using ultrafast anisotropy measurements to understand the extent of coupling between the linear para-TPA units.

**Excitation energy delocalization**

Anisotropy decays in the femtosecond time-scale provide valuable information about the excited state kinetics. In this time-scale, the depolarization of the fluorescence signal is related to energy transfer, or delocalization. At early times, the anisotropy lost due to rotation of molecules is minor since rotational diffusion will occur on the nanosecond time-scale. Thus, it is possible to characterize other processes without interference from the rotational diffusion.

The ultrafast up-conversion instrument is used to explore the excited-state kinetics of a model compound for the core structure (Ph\textsubscript{3}PG-1). The dendrimer is dissolved in THF and excited at 340 nm while the emission is detected at 376 nm. The parallel and perpendicular fluorescence intensities and the corresponding anisotropy during the first 5 ps are given in Figure 3-4.

Parallel and perpendicular intensities are fitted with sum of exponentials and convolution of the instrument response function (FWHM: 300 fs) to improve the time resolution. The anisotropy is calculated by using the perpendicular and parallel fluorescence decays and the fittings. The data requires three exponentials ($\tau_1=0.33$ ps, $\tau_2=3$ ps, $\tau_3=720$ ps). We have characterized the longest time constant (720 ps) by using...
TCSPC measurements and in here, it is used as a fixed parameter (Table 3-1). The 3 ps time component is characterized by using up-conversion measurements (see vibrational cooling). The shortest time component (330 fs) is attributed to the fast excitation energy delocalization in the excited state of the dendrimer.

Figure 3-4. Time-resolved fluorescence decay of Ph$_3$PG-1 in THF at parallel polarization (black squares) and perpendicular polarization (red squares). The fittings with 330 fs time constant are given in solid lines. The calculated anisotropy data (blue squares) and fittings (blue line) are given in the inset.

Varnavski et.al. used similar time-resolved anisotropy measurements on PE dendrimers and observed fast energy delocalization kinetics.$^{118}$ They investigated dendrimers having two types of symmetries (C$_3$ and Td). For both dendrimers, they observed anisotropy decays on the femtosecond time-scale. The rate of the energy delocalization process was strongly dependent on the nature of the central moiety. In the case of nitrogen core, the delocalization is much faster as it enables strong coupling among the linear segments (35 fs). When the nitrogen was replaced with an adamantane core, delocalization got slower revealing weaker coupling (880 fs). Moreover, they showed the relationship between the symmetry and the residual
anisotropy of dendrimers. For example, the planar molecules having rotational symmetry higher than C\textsubscript{2} are expected to have 0.1 residual anisotropy.

The average residual anisotropy of the anisotropy decay of Ph\textsubscript{3}PG-1 is 0.12. Since the dendrimer has C\textsubscript{3} symmetry, the residual anisotropy is expected to be 0.1 if the structure is planar. Thus, anisotropy measurement indicates that Ph\textsubscript{3}PG-1 has a planar structure. Even though the dendrimer has bulky end-groups, it conserves planar structure, which is attributed to the presence of the rigid triple bonds.

Briefly, we assigned the 330fs time component of anisotropy decay to energy delocalization among the linear building block of the dendrimer. It is consistent with the previous dendrimers examined in literature.\textsuperscript{118,150,151} As the central point in the Ph\textsubscript{3}PG-1 is a phenyl ring, it enables stronger coupling than adamantane and weaker than nitrogen atom.\textsuperscript{118} We also studied the Ph\textsubscript{2,2,2}PG-3 which shows a residual anisotropy value of 0.05 indicating less planar structure (see model compounds for the periphery).

The coupling between the linear building-blocks in Ph\textsubscript{3}PG-1 makes it harder to approximate absorption properties by para-TPA. However, the alkoxy groups have drastic effects on the emission spectrum (broadening and red-shift) so their effect will be less pronounced. These groups are not directly attached to the core of extended dendrimers. Thus, para-TPA is preferred as a model compound to approximate emission spectrum of core. In conclusion, the core properties of the dendrimers are a result of the combination of the delocalization and the minor contribution from the electron donating groups.

**Vibrational cooling**

We characterized the excited-state kinetics of the model compound Ph\textsubscript{3}PG-1 by measuring the time-resolved fluorescence decays using the up-conversion technique.
At very early time scales (Figure 3-5), the fluorescence decays are detection wavelength-dependent. We collected the fluorescence decays following excitation at 316 nm and 350 nm and at each excitation wavelength, we detected emission at three different wavelengths obtaining a similar response. As the detection wavelength is scanned from high to low energy, there is a decay component which becomes a rise time at the low energy side of the spectrum. The decays are fitted by sum of exponentials with two time constants. The long time constant 720 ps is fixed by using information gathered from the nanosecond time-resolved TCSPC measurements. The fast time-component (3 ps) is obtained by simultaneously fitting the three data sets collected at different detection wavelengths (global analysis). Fractional amplitudes of each time constant are given in Table 3-3. The fractional amplitude of 3 ps time component is positive at shorter detection wavelength (363 nm and 376 nm) and it becomes negative indicating a rise in the population of detected state at longer detection wavelength (420 nm).

A vibrational relaxation process, which is completed within few picoseconds, was previously observed for organic polyphenylene and phenylene ethynylene dendrimers.\textsuperscript{70,123,152} Karni and coworkers studied a polyphenylene dendrimer using time-resolved up-conversion measurements and observed a 5 ps time constant. They attributed this time constant to a vibrational relaxation process.\textsuperscript{70} They observed that the amplitude of the 5 ps component was positive at shorter wavelengths and negative at longer wavelengths. De Belder et al attributed a varying component from 500 fs to 2 ps to intra-molecular vibrational energy redistribution in polyphenylene dendrimers.\textsuperscript{152} Atas
et al observed a 6 ps decay component in unsymmetrical PE dendrimers and attributed this component to the vibrational relaxation process coupled to solvent relaxation.\textsuperscript{123}

![Figure 3-5. Time-resolved fluorescence decays of Ph$_3$PG-1 in dissolved in THF detected at 363 nm (black), 376 nm (red) and 420 nm (blue) following excitation at A) 316 nm and B) 350 nm. Fittings are done using sum of exponentials ($\tau_1 = 3$ ps, $\tau_1 = 720$ ps).](image-url)

The 3 ps component observed in our fast kinetics is in agreement with these literature values, and we assign it to vibrational relaxation. At short wavelengths, the signal originates from hot vibrational states which decay to lower vibration levels. At longer wavelengths, we observe the emission from the lower vibrational states. The vibrational relaxation time (3 ps) is shorter compared to the published PE dendrimers.\textsuperscript{127} The first generation of the PE dendrimers (Ph$_3$PG-1) is expected to be less rigid than the higher generations. Moreover, the bulky end-groups can increase the spatial strain, which can result in increased flexibility of the core part of the dendrimer. This increased flexibility is expected to be a reason for the faster vibrational relaxation.

**Ionic analogs and H-aggregate formation**

Figure 3-6 (panel A and B) shows the absorption and emission spectra of model compounds in ester (Ph$_3$PG-1) and ionic (Ph$_3$G-1) forms. These absorption spectra are
normalized at the maximum to reveal the shifts of the absorbance wavelengths. The absorption maximum of the ionic form is significantly blue-shifted compared to the ester form (Figure 3-6 A) of the dendrimer (42 nm). The emission spectra are also normalized at the maximum and have similar shapes in both forms (Figure 3-6 B), with only a minor red-shift in the emission maximum of the ionic form compared to the ester form. The emission spectra of both forms of the dendrimers are broad and structureless which is attributed to the presence of alkoxy groups in para position of the end-phenyl-rings and coupling between linear PE units.

Figure 3-6. Steady-state spectra of first generations of dendrimers in THF (black) and in methanol (red) A) Absorption spectra of Ph$_3$PG-1 and Ph$_3$G-1 B) Emission spectra of Ph$_3$PG-1 and Ph$_3$G-1 following excitation at 310 nm C) Absorption spectra of Ph$_2$PG-1 and Ph$_2$G-1 D) Emission spectra of Ph$_2$PG-1 and Ph$_2$G-1 following excitation at 300 nm
The large hypsochromic shift (42 nm) in the Ph$_3$G-1 absorption spectrum is an indication of formation of H-aggregates. The backbone of Ph$_3$G-1 is a highly hydrophobic while the charged end-groups provide solubility in methanol. When Ph$_3$G-1 is dissolved in methanol, the environment is very hydrophilic. Formation of aggregates can allow intermolecular $\pi$-$\pi$ interactions decreasing the disfavored interactions with the solvent molecules. From the anisotropy measurements, it is known that the Ph$_3$PG-1 has a planar structure, which promotes face-to-face $\pi$ stacking.

Figure 3-6 (panel C and D) shows the absorption and emission spectra of model compounds, which consist of 2-ring PE units, in ester (Ph$_2$PG-1) and ionic (Ph$_2$G-1) forms. The absorption spectrum is blue-shifted in the ionic form compared to ester form similar to a 3-ring PE system. The emission spectrum is slightly red-shifted and broader in the ionic form. The spectral changes in the ionic form are very similar to Ph$_3$G-1 indicating the presence of H-aggregation. The first generation dendrimers of the both families of the dendrimers (2-ring PE unit and #-ring PE units) show signs of H-aggregation formation.

The formation of H-aggregates by first generation of the compact dendrimers in ionic form (Ph$_2$G-1) is also supported by dynamic light scattering measurements, which reveal increased hydrodynamic radius for Ph$_2$G-1.\textsuperscript{153} AFM images showed similar features confirming the presence of H-aggregates. We have shown that 3-ring PE dendrimer (Ph$_3$G-1) forms H-aggregates and similar to 2-ring PE dendrimers (Ph$_2$G-1). Thus, the first generations of the dendrimers in ionic form are prone to form H-aggregates due to their planar structure.
Figure 3-7 shows a cartoon representing formation of H-aggregates. In this cartoon, the lines represent 3-ring PE units while the spheres represent the end-groups. In the ester form, the dendrimers are dissolved in THF and they are well-solvated. This condition is represented by having the dendrimers apart in the cartoon (left). The condition of the ionic form in methanol is represented on the right with formation of face-to-face stacks of dendrimers.

![Figure 3-7. Representation of formation of H-aggregates](image)

We used time-resolved fluorescence measurements to study H-aggregate formation of Ph$_3$G-1 dendrimers. Figure 3-8 shows the fluorescence decays of Ph$_3$G-1 following excitation at 316 and 350 nm. The fluorescence decays show the same time-constants with different fractional amplitudes as the detection wavelength is scanned. The decays become slower at the low energy part of the spectrum (longer wavelengths). Using global analysis, it is possible to fit the decays at different emission wavelengths with three time components ($\tau_1 = 360$ ps, $\tau_2 = 20$ ps and $\tau_3 = 2$ ps). The fractional amplitudes of each time component are given in Table 3-4. The contributions of the ultrafast time components (2 ps and 20 ps) decrease at longer wavelengths. On the contrary, the contribution from the long time component (360 ps) increases at longer...
wavelengths. Slower decays at longer wavelengths are characteristic of fluorescence decays of aggregates.

It should be noted that the decays were only collected up to 500 ps with the up-conversion instrument so they do not provide complete fluorescence lifetime information. The characterization of the 360 ps is not very reliable and longer time-scale measurements are required for better characterization.

![Figure 3-8. Time-resolved fluorescence decays of Ph₃G-1 dissolved in methanol detected at 363 nm (black), 376 nm (red) and 420 nm (blue) following excitation A) at 316 nm and B) 350 nm. Fittings are done using sum of exponentials (τ₁ = 360 ps, τ₂ = 20 ps, and τ₃ = 2 ps).](image)

The fluorescence lifetime of Ph₃G-1 was also characterized in the nanosecond time-scale using TCSPC.¹⁴¹ There are two time components: 0.9 and 4.9 ns. The 900 ps component could originate from the same state as the 360 ps since it is not possible to properly characterize this constant with the up-conversion instrument. The longest time component 4.9 ns has increased contribution at longer wavelengths and it is absent in the ester form. This component might be originating from the H-aggregates.¹⁴¹ Since the aggregate emission is very slow, TCPSC measurements provide more reliable information about the aggregates. In conclusion, the presence of H-aggregates,
which is observed by steady-state spectroscopy, is also observed by time-resolved measurements.

**Model Compounds for the Periphery**

The compact CPE-Ds consists of 2-ring PE units (Figure 3-2 C-E). They do not have an energy gradient.\textsuperscript{124} They have very similar structures to extended dendrimers except for the core part. Since their properties (such as size and shape) are expected to be very similar to the periphery of the extended dendrimers, they are used to approximate of donor properties of extended dendrimers in the absence of an acceptor. These dendrimers were synthesized and characterized by Lee et. al.\textsuperscript{153}

Figure 3-9 shows the steady-state spectra of the compact dendrimers in ionic and ester forms. The absorption spectra are given in panel A and C. The absorption spectra of the ester forms have very similar shape (panel A). The molar extinction coefficient increases with increasing generation (inset). The absorption spectra of the ionic forms also have similar shapes except for the first generation (Ph\textsubscript{2}G-1). The absorption spectrum of first generation in the ionic form (Ph\textsubscript{2}G-1, Figure 3-9 C) is very broad and blue-shifted compared to ester form (see above the description of H-aggregation, Figure 3-6 C).

The similarity on the absorbance bands for all generations of PE dendrimers indicates that the excitations are localized in the ground state, which is a common feature of meta-branched PE structures.\textsuperscript{71,124,125} The monotonic increase in molar extinction coefficient is consistent with increasing number of 2-ring PE units. The intensity gain in the blue side of the spectra of the ionic forms of the dendrimers can be caused by twisting of the branches. Since hydrophilic interactions with solvent
molecules are highly unfavorable, ionic dendrimers are believed to have twisted backbones.

Figure 3-9. Steady-state spectra of first (black), second (red) and third (blue) generation of compact dendrimers A) Absorption spectra of ester forms in THF and C) ionic forms in methanol B) Emission spectra of ester forms and D) ionic forms. Insets show the molar extinction coefficient versus the number of 2-ring PE units.

The steady-state emission spectra of the compact dendrimers in ester form have a single band centered at 375 nm. There is no shift in the emission spectra with increasing generation. The intensity of the emission increases monotonically with increasing generation. The emission spectra lack vibronic structure. The ionic forms of the compact dendrimers have broader emission bands compared to the ester forms. The emission maximum of Ph\textsubscript{2,2,2}G-3 is 30 nm red-shifted compared to the emission
maximum of $\text{Ph}_{2.2}\text{PG}-3$. Although the emission spectrum of the $\text{Ph}_{2.2}\text{G}-2$ (Figure3-9 D) is broader than the emission spectrum of $\text{Ph}_{2.2}\text{PG}-2$ (Figure3-9 B), the emission maxima are the same for both forms of the dendrimers.

The emission spectra of the compact dendrimers are affected by the presence of alkoxy groups in the *para* positions, becoming broad and structureless due to electronic donating effects of these groups. The monotonic increase of the emission is due to the increased number of absorbing units (concentrations of the dendrimers are 1 $\mu$M). The emission bands are even broader in the ionic form, which is an indication of chromophore-chromophore interactions. Lee at al. collected emission spectra of ionic dendrimers solutions of different concentrations and observed that the shape and the maxima of the emission bands do not depend on concentration eliminating the possibility of inter-molecular aggregation.\textsuperscript{153} Twisting of the branches can allow hydrophobic interactions between PE units, which is called intra-molecular aggregation. Thus, the intra-molecular aggregation is thought to be the reason behind the broad and red-shifted emission spectra of the second and third generation of the compact dendrimers in ionic form ($\text{Ph}_{2.2}\text{G}-2$ and $\text{Ph}_{2.2.2}\text{G}-3$).

Table 3-1 and Table 3-2 show the emission quantum yields of compact dendrimers in ester and ionic forms. The quantum yields of the ester forms of the compact dendrimers (0.34-0.38) are very high suggesting absence of aggregate formation. The quantum yield decreased following the deprotection of the ester groups, supporting the presence of aggregates, which can act as trap states. While the first generation of the ionic form of the compact dendrimers ($\text{Ph}_{2}\text{G}-1$) is prone to
intermolecular aggregation, higher generations are more likely to form intra-molecular aggregates.

The fluorescence lifetimes of the compact dendrimers were characterized by TCSPC measurements. The fluorescence decays of the ester forms reveal a single time component, which does not depend on the detection wavelength. If there was aggregate formation, we would expect more than one time component. The ionic forms of the compact dendrimers have more complicated fluorescence decays. They have two decay components also suggesting of aggregation. For the ester forms, the up-conversion measurements on the subpicosecond time-scale show no additional decay components. Similar measurements for the ionic forms of the compact dendrimers were not possible due to the very low quantum yields.

To sum up, the ester forms of the compact dendrimers do not form aggregates in THF. In the ionic form, the first generations of the compact dendrimer form H-aggregates and higher generations form intra-molecular aggregates.

**Excitation energy delocalization**

The femtosecond anisotropy decay of Ph₃PG-1 revealed fast delocalization of excitation energy among linear 3-ring PE units. Similar measurements are done on third generation of the compact dendrimers Ph₂₂₂PG-3 to gain information about energy delocalization in a larger system.

Following excitation at 316 nm, the fluorescence decay of Ph₂₂₂PG-3 is collected at 376 nm. The intensities for parallel and perpendicular polarizations are collected and they are fitted by sum of exponentials. The instrument response function is collected by the cross-correlation of pump and gate beams (FWHM=330 fs) and used for convolution of exponential function in fitting process to obtain better time resolution. Two time
constants are used for the fittings fluorescence decays. The long time constant is used as a fixed parameter was obtained from the long time-scale lifetime measurements \( \tau = 8.20 \) ps. The fast time constant, 260 fs, is attributed to energy delocalization among 2-ring PE units.

![Figure 3-10](image)

Figure 3-10. Time-resolved fluorescence data of Ph\(_{2.2.2}\)PG-3 in THF for parallel polarization (black squares) and perpendicular polarization (red squares). The fittings are done using sum of exponentials \( \tau_1 = 260 \) fs, \( \tau_2 = 8.20 \) ps and given in solid lines. The calculated anisotropy data (blue squares) and fittings (blue line) are given in the inset.

The average residual anisotropy of Ph\(_{2.2.2}\)PG-3 is 0.05 compared to the residual anisotropy of Ph\(_3\)PG-1 of 0.12. As expected, the larger dendrimer is no longer planar, since a planar molecule would have 0.1 residual anisotropy. The non-zero residual anisotropy indicates that third generation has neither perfectly spherical nor planar shape. It is expected that the bulky end-groups force the dendrimer to have a more globular structure even though the PE units are known to be very rigid.

The excitation energy delocalization is faster for Ph\(_{2.2.2}\)PG-3 than Ph\(_3\)PG-1. The third generation is larger than the first generation and many more groups can participate
in the delocalization process. The globular structure can also allow easier coupling among linear units.

**Size of compact dendrimers**

The sizes of macromolecules can be obtained by monitoring their rotational diffusion dynamics, which causes fluorescence depolarization. Anisotropy decays on the nanosecond time-scales provide rotational correlation times. The compact dendrimers have absorption bands in the UV region of the spectrum and very low quantum yields, which makes it very difficult to obtain high signal to noise fluorescence signal.\(^{143}\) It is possible to overcome the experimental obstacles by using a dye having high quantum yield as a label.

CPEs are known to form complexes with the oppositely charged dyes.\(^{97,98,103,107}\) One of the well known dye families, which has been studied thoroughly via steady-state and time-resolved measurements, is the cyanine dyes. For this reason, we chose to use 3,3′-diethyloxacarbocyanine iodide (DOC) to label the dendrimer.\(^{103}\) The dye-molecules bonded to the dendrimers have slower anisotropy decays since their rotations are restricted and correspond to the rotational diffusion dynamics of dendrimers. Figure 3-11 shows a cartoon representation of a DOC molecule (yellow ellipse) associated with a compact dendrimer.

Following the excitation of the solutions containing mixtures of DOC and compact dendrimers at 425 nm, we expect that only DOC is excited since absorption of light by the compact dendrimers at this wavelength is negligible. The fluorescence decays of DOC are collected using the TCSPC instrument and a long pass filter with a 450 nm cut off to avoid background signals from the scattered excitation beam. The anisotropy
decays are calculated using four combinations of polarization orientations (see Chapter 2 for details).

Figure 3-11. Nanosecond anisotropy decay of DOC (1 μM) in the presence of Ph$_{2,2,2}$G-3 (1 μM) in water (θ=5.63 ns) and cartoon representation of association complex formation between DOC and Ph$_{2,2,2}$G-3

Figure 3-11 shows the anisotropy decay of DOC (1 μM) in the presence of Ph$_{2,2,2}$G-3 dendrimer (1 μM). Most of the dye molecules are expected to be associated with the dendrimer since they are oppositely charged. We know from the steady-state quenching experiments that the association constant for formation of dye-CPE complex is very high.$^{153}$

The anisotropy decay of DOC is well fitted with a mono-exponential function to obtain the rotational correlation time. The correlation time is related to the volume of the rotating unit by the following equation.

$$\Theta = \frac{nV}{RT}$$  \hspace{1cm} (3-1)

Once the volume of the rotating unit is calculated, the radius of gyration can be found assuming that the macromolecule is spherical. The calculated radius of gyrations
from anisotropy decays are in agreement with the dynamic light scattering data collected by Lee.\textsuperscript{153} The radius of gyration is slightly larger compared to the DLS radii because solvated dendrimers are expected to have a larger volume (Table 3-5). In other words, calculated radii correspond to the sizes of dendrimers with a solvation sphere including the water molecules dragged during the rotations. The validity of assumption that the contribution from the free dye molecules is negligible is confirmed by varying the ratio of dendrimer to dye (2:1). As the molar ratio is changed, the calculated radius of gyrations does not change within the error margin.

**Steady-State Spectroscopy of Extended Dendrimers**

![Diagram of extended PE dendrimers](image)

Figure 3-12. The structures of extended PE dendrimers A) Ph\textsubscript{3-2}PG-2/ Ph\textsubscript{3.2}G-2 B) Ph\textsubscript{3.2}PG-3/ Ph\textsubscript{3.2}G-3

Figure 3-12 shows the structures of the extended dendrimers. The structures are labeled in the same way with the model compounds and the structures of branched end-groups are shown in Figure 3-1. The core consists of 3-ring PE units and the periphery has 2-ring PE units as building blocks. The steady-state instruments used for
our measurements are explained in detail in Chapter 2. For steady-state characterizations, either THF (for ester form) or methanol (for ionic form) is used as the solvent. The optical densities are kept below 0.1 cm$^{-1}$ and the concentrations are lower than 1 μM to avoid self-absorption. At higher concentrations (up to 30 μM), no sign of aggregation or self-absorption is observed.

**Results for the Ester Form of the Dendrimers**

Figure 3-13 shows the steady-state absorption and emission spectra of the three generations of ester form of extended dendrimers dissolved in THF. The absorption spectra were normalized at the absorption maximum of the core, which is 350 nm. The absorbance at 300 nm versus the number of 2-ring PE units is depicted in inset of the Figure 3-13 A. The emission spectra were collected following excitation at 310nm. These spectra are normalized by their absorbance at 350 nm to match the optical density of the core part of the dendrimers. The inset shows the emission intensities at the maximum versus the number of 2-ring PE units.

The absorption spectrum of Ph$_3$PG-1 was already characterized as a model compound for the core. It has the maximum absorption at 365 nm corresponding to absorption from 3-ring PE units. The absorption maxima of Ph$_{3,2}$PG-2 and Ph$_{3,2,2}$PG-3 at 312 nm are the same as in the model compounds used for periphery. When the absorbance at 312 nm versus the number of 2-ring PE units is plotted, it reveals an almost linear relationship. This monotonic increase in absorbance was previously observed in the literature for PE dendrimers having meta-substitution and it was explained by the localized excitations on individual linear building blocks.$^{71,124}$ Thus, we conclude that the presence of the bulky branched end-groups does not change the excitonic localization in the ground state of these dendrimers.
The red-edge of the absorption spectrum of the first generation (\(\text{Ph}_3\text{PG-1}\)) is lower in energy than the second and third generation. Moreover, the emission spectrum of \(\text{Ph}_3\text{PG-1}\) is red-shifted and broad whereas higher generations have sharp emission spectrum with vibronic structure. As mentioned before, these properties of \(\text{Ph}_3\text{PG-1}\) spectra are attributed to presence of alkoxy end-groups.

![Absorption and Emission Spectra](image)

**Figure 3-13.** Steady-state absorption and emission spectra of extended dendrimers. A) The absorption spectra and B) the emission spectra of \(\text{Ph}_3\text{PG-1}\) (black), \(\text{Ph}_3\text{PG-2}\) (red) and \(\text{Ph}_{3,2}\text{PG-3}\) (blue) A) Inset shows the absorption at 300 nm versus the number of 2-ring PE units and B) inset shows emission intensity at the maximum versus number of 2-ring PE units.

The emission spectra of \(\text{Ph}_{3,2}\text{PG-2}\) and \(\text{Ph}_{3,2,2}\text{PG-3}\) have very similar shapes with distinct vibronic structures. The emission is originating from the core (3-ring PE unit) of the dendrimers since the emission maximum is at 358 nm, which corresponds to 3-ring PE unit emission (see Figure 3-14 B, green curve). The intensity of emission is expected to correlate with the number of 2-ring PE units being excited if the energy transfer is very efficient. The optical density of the core is matched for all generations to eliminate the effects of concentration difference between solutions so that the increase in emission intensity is only because of the increased absorption of 2-ring PE units. However, the presence of electron donating groups complicates the comparison of the
emission intensities. The inset (Figure 3-13 B) depicts the emission intensity at the maximum versus number of PE units. It deviates from linearity, which can be due to the emission characteristics of Ph₃PG-1. The first generation has very broad emission so the comparison of emission intensities is ambiguous. In addition, it is known that the presence of electron donating group increases molar extinction coefficient complicating the normalization procedure of the emission spectra. Although these factors contribute to the deviation from linearity, it is evident that there is a gradual increase in the emission intensity as more 2-ring PE units are added to the structure with increasing generation.

Figure 3-14. Comparison of steady-state spectra of extended dendrimers with model compounds A) Absorption spectrum of Ph₃PG-1 (black), Ph₃₋₂PG-2 (red), Ph₂₋₂PG-2 (cyan), and the sum of Ph₃PG-1 and Ph₂₋₂PG-2 absorbance (dash line in magenta) B) Emission spectra of Ph₃₋₂PG-2 (red), Ph₃₋₂₋₂PG-3 (blue), and para-TPA (green)

Figure 3-14 shows the comparison of the steady-state spectra of extended dendrimers with the model compounds. The absorbance spectrum of the second generation of compact dendrimers (Ph₂₋₂PG-2) is used to model the donor (or periphery) part of the extended dendrimers while Ph₃PG-1 is used to model the core. For the
emission spectra, para-TPA is used as a model since, as it was mentioned above, the alkoxy group on Ph₃PG-1 have too much of an effect on its emission spectrum. While they are further away from the emissive core in the second and third generation of dendrimers.

Figure 3-14 A shows the steady-state absorption spectra of the absorption spectra of Ph₃PG-1, Ph₂₂PG-2, and Ph₃₂PG-2. The sum of the absorbances of the Ph₃PG-1 and Ph₂₂PG-2 is compared with the Ph₃₂PG-2 spectrum. The absorption were normalized to provide the best match to the absorption spectrum of Ph₃₂PG-2 spectrum when added. The sum represents the addition of six 2-ring PE units and three 3-ring PE units for the approximation of the second generation of extended dendrimers (Ph₃₂PG-2). This built spectrum matches well with the absorption spectrum of Ph₃₂PG-2. This behavior supports the excitonic localization in the ground state. The mismatch at the red-edge of the spectrum is caused by the alkoxy group effect on the absorption spectrum of Ph₃PG-1. Alkoxy groups do not affect the absorbance spectra of higher generations since the core part does not have these groups in para position of the phenyl rings.

Figure 3-14 B shows the comparison of emission spectra of extended dendrimers with para-TPA. Although, the emission spectra of the extended dendrimers originate from the core part, there are some differences between the emission spectra of the dendrimers and para-TPA. The emission maxima of Ph₃₂PG-2 and Ph₃₂₂PG-3 are 10 nm red-shifted, which is attributed to the presence of large electronic coupling in the emitting geometry, not present in the absorbing geometry of the PE dendrimers.¹³²,¹³³,¹³⁶
To investigate possibility of energy transfer we compare absorption and excitation spectra of $\text{Ph}_3\text{-PG-2}$ and $\text{Ph}_{3\cdot2}\text{-PG-3}$, as depicted in Figure 3-15. The excitation spectra are collected at 400 nm and they are normalized to match absorbance at 350 nm. The excitation spectrum collected at different observation wavelengths did not show any changes. The shapes of excitation and absorption spectra match well for both generations. These spectra combined with the Figure 3-14 B demonstrate the presence of energy transfer.

![Comparison of absorption (black) spectrum (black) with excitation (red) spectrum detected at 400 nm of A) $\text{Ph}_3\text{-PG-2}$ and B) $\text{Ph}_{3\cdot2}\text{-PG-3}$.](image)

Figure 3-15. Comparison of absorption (black) spectrum (black) with excitation (red) spectrum detected at 400 nm of A) $\text{Ph}_3\text{-PG-2}$ and B) $\text{Ph}_{3\cdot2}\text{-PG-3}$.

Shortreed et al. used absorption and excitation spectra to quantify the efficiency of energy transfer within the nanostar which is an extended PE dendrimer with a perylene trap. A transfer efficiency of 96% was observed from the periphery of the nanostar to its perylenic trap which they attributed to symmetric and ordered exciton funnel with a well-directed energy gradient.

The emissions of $\text{Ph}_3\text{-PG-2}$ and $\text{Ph}_{3\cdot2}\text{-PG-3}$ dendrimers are originating from the core of the macromolecules, as suggested by the model compound spectrum. The energy-transfer efficiency from periphery to core can be calculated by normalizing the
excitation and absorption spectra at a wavelength corresponding to the acceptor transition (350 nm) and comparing the intensities at the absorption maximum of the donor (315 nm). An efficient energy-transfer is observed for extended dendrimers with quantum yield of 96% for \( \text{Ph}_3 \text{PG}-2 \) and 93% for \( \text{Ph}_{3,2} \text{PG}-3 \).

The energy-transfer efficiency of \( \text{Ph}_{3,2} \text{PG}-3 \) is 3% smaller than \( \text{Ph}_{3,2} \text{PG}-2 \) which can be due to the difference in energy gradient of the third generation. The 2-ring PE units at the outer-shell of the third generation have the same conjugation length as the second generation. Thus, there is no difference in the energy gradient of \( \text{Ph}-\text{Ph}_3 \text{PG}-2 \) and \( \text{Ph}_{3,2} \text{PG}-3 \). However, the distance from periphery to core increases for the third generation, leading to decrease energy-transfer efficiency. Molecular dynamic simulations were done on the extended dendrimers in ester forms by our collaborators (Cho and Roitberg).\(^{141}\) They calculated the average distance between 2-ring PE units and 3-ring PE units by the using center of masses. For the second generation of the dendrimers in the ester the form, the average distance between these units is \( 9.0 \pm 0.2 \) Å. The distance is increased to \( 14.0 \pm 1.0 \) Å in the case of the third generation. Although, the excitation could hop among different 2-ring PE units, the increased distance between donor and acceptor parts is believed to cause the slightly lower energy-transfer efficiency for longer dendrimers.

**Results for the Ionic Form of the Dendrimers**

Figure 3-16 shows the absorption and emission spectra of ionic form of the extended dendrimers. The molar absorptivities of \( \text{Ph}_3 \text{G}-1 \), \( \text{Ph}_{3,2} \text{G}-2 \) and \( \text{Ph}_{3,2,2} \text{PG}-3 \) are plotted in panel A. Emission spectra are collected by excitation 310 nm and normalized at the emission maximum.
The spectral features of ionic dendrimers are very similar to the ester precursors with a few exceptions. The most significant differences are observed in the absorption spectrum of Ph$_3$G-1 (model compound) compared to ester form, which was already assigned to formation of H-aggregates and explained in detail above. The emission spectra of the ionic dendrimers show similar features than the ester forms, such as a broad structureless band for the first generation and vibronic structure for higher generations.

![Figure 3-16. Steady-state spectra of extended dendrimers in methanol. A) Absorption spectra and B) Emission spectra of Ph$_3$G-1 (black), Ph$_{3.2}$G-2 (red) and Ph$_{3.2}$-$_2$PG-3 (blue)](image)

The ester form of the extended dendrimers has a monotonic increase of absorption at 300 nm corresponding to an increased number of 2-ring PE units. The absorption spectra of the ionic form of the dendrimers do not have the same dependence due to the H-aggregate formation in the first generation. It is difficult to compare the molar absoprtivities at the low-energy edge of the spectrum since the absorption spectrum of the Ph$_3$G-1 is significantly blue-shifted (42 nm).

For a given generation, the absorption spectra of the ester and the ionic forms of the extended dendrimers are compared in Figure 3-17. These absorption spectra are
normalized at the maximum to reveal spectral shifts. The second-generation ionic-dendrimer is slightly red-shifted compared to the ester form (panel A) of the dendrimer. The absorption spectrum of third generation reveals a 22 nm hypsochromic shift in the ionic form compared to the ester form.

Figure 3-17. Comparison of the absorption spectra of the ester forms with the ionic forms A) \( \text{Ph}_3\text{-2PG-2} \) (black) and \( \text{Ph}_3\text{-2G-2} \) (red)  B) \( \text{Ph}_3\text{-2-2PG-3} \) (black) and \( \text{Ph}_3\text{-2-2G-3} \) (red)

Molecular dynamic simulations were also performed on the extended dendrimers in the ionic forms in water.\textsuperscript{141} The average distance between 2-ring PE units and 3-ring PE units is calculated as 9.0±0.2 Å for the second generation and 14.6±0.9 Å for the third generation. The average distance increases by a factor of 1.6 while the number of negatively charged end-groups doubles for the second generation compared to the first generation. Thus, we believe that the charge density is higher in the case of the third generation. As a result, the inter-dendrimer interactions are more likely to be suppressed since the dendrimers are expected to repel each other more effectively. The minor changes in absorption spectra \( \text{Ph}_3\text{-2G-2} \) compared to \( \text{Ph}_3\text{-2PG-2} \) can be due to changes in geometry or solvation. The third generation is not expected to have inter-
molecular interactions, as the charge density of this generation is much larger than smaller generations. The hypsochromic shift can be an indication of presence of intra-dendrimer interactions. The highly charged end-groups can cause spatial restrain and lead to interactions among peripheral units.

Comparisons of the emission spectra of the ester and ionic form of PE dendrimers are given in Figure 3-18. The second and third generations of extended dendrimers have vibronic structures in both forms. For both generations, there are 3 nm hypsochromic shifts when the ester groups are deprotected to form ionic analogs, although, the vibronic structures are slightly less pronounced.

The emission spectra of ionic forms have vibronic structure as expected which supports absence of inter-molecular aggregates. However, ester forms have sharper spectra than their ionic counterparts. This difference is attributed to intra-dendrimer chromophore-chromophore interactions in the case of ionic forms of the dendrimers.

Figure 3-18. Comparison of the emission spectra of the ester forms with the ionic forms
A) Ph\textsubscript{3,2}PG-2 (black) and Ph\textsubscript{3,2}G-2 (red) B) Ph\textsubscript{3,2,2}PG-3 (black) and Ph\textsubscript{3,2,2}G-3 (red)

Absorption and excitation spectra are used to calculate the energy-transfer efficiencies in the same way as it was performed with the ester form of the dendrimers.
Figure 3-19 shows these comparisons for the second and third generation of the ionic dendrimers. The excitation spectrum of the Ph$_3$-2G-2 is collected at 380 nm and it is normalized to match the absorbance at 350 nm showing very similar features. The excitation spectrum of the Ph$_3$-2.2G-3 is collected at 400 nm and normalized to match the absorbance at 350 nm. The spectral features of Ph$_3$-2PG-3 and Ph$_3$-2.2G-3 are very similar but the relative intensities are significantly different.

Figure 3-19. Comparison of the absorption (red) and the excitation (black) spectra of A) Ph$_3$-2G-2 and B) Ph$_3$-2.2G-3 in methanol

The energy-transfer efficiency is calculated at 313 nm: 99% for Ph$_3$-2G-2 and 61% for Ph$_3$-2.2G-3. The decrease in the energy-transfer efficiency for the third generation can be due to the increased intra-molecular interactions. Since the backbone of the dendrimers is hydrophobic, there will be a tendency for the branches to interact with each other to decrease the interactions with the polar solvents molecules. For higher generation this effect can be more drastic since the hydrophobic core is larger and the charge density is increased significantly. The intra-molecular interactions can allow non-radiative relaxation pathways, which result in lower energy-transfer efficiency from
periphery to core. \( \text{Ph}_{3}\text{G-2} \) is not as affected by these interactions since it has a lower charge density.

The longer distances between periphery and core in the longer dendrimer can also contribute to the decreased energy-transfer efficiency, although it is not thought to be a major reason since the ester forms have very similar energy-transfer efficiencies for both generations (only 3% difference).

Steady-state spectroscopy provides valuable information about the photophysical properties of the dendrimers. It is used to understand the character of the excited states and the effect of end-groups on this character. It reveals that there is not intra- or inter-dendrimer aggregation for the ester forms but the ionic analogs have more tendency to undergo chromophore-chromophore interactions. The first generation of the ionic dendrimers is prone to inter-molecular H-aggregate formation while the second and third generation are more likely to have intra-molecular interactions. These interactions can affect the energy-transfer efficiencies by opening non-radiative channels for relaxation. We will further explore these processes by time-resolved measurements. The information gathered from the steady-state measurements will be used to interpret the excited-state kinetics in order to achieve an understanding of the underlying factors affecting the properties of PE dendrimers in the ionic and ester form.

**Time-Resolved Spectroscopy of Extended Dendrimers**

The time-resolved emission measurements were collected using either the up-conversion or TCSPC techniques (for details refer to Chapter 2). The ester form of the dendrimers was dissolved in THF whereas for the ionic form, methanol was used as the solvent. For measurements using up-conversion technique, the optical densities were kept lower than 0.2 mm\(^{-1}\) with concentrations lower than 15 \(\mu\text{M}\). Lower concentrations
cannot be used because of the low efficiency of the method. At this concentration range, no sign of aggregation was observed for the ester form of the dendrimers by steady-state spectroscopy. Ionic dendrimers revealed aggregation characteristics, which were explained above.

**Results for the Ester Form of the Dendrimers**

Time-resolved fluorescence of the ester form of the extended dendrimers were characterized on three different time scales. We use the up-conversion instrument to measure i) a short time-scale up to 20 ps ii) long time-scale, up to 1000 ps, and they were also characterized by single photon counting instrument in the nanosecond regime by our collaborators. The time constants for fluorescence decays of the each generation are given in Table 3-6. The fractional amplitudes of the individual time constants are not significantly affected by the detection wavelength.

**Excitation of core**

To investigate the energy transfer observed in the steady-state experiments, we first need to understand the kinetic response of the acceptor. Very long time characterization on the nanosecond time-scale (TCSPC) performed by Feng et al. shows two time constants on the order of 1 and 5 ns (Table 3-6).

**Long time-scale:** Experiments performed with the up-conversion apparatus are shown in Figure 3.20. This figure presents the time-resolved fluorescence decays of the ester form of extended PE dendrimers collected at different detection wavelengths. Setting the laser wavelength at 350 nm results in direct excitation of the 3-ring PE units at the core. Following excitation at this wavelength, electronic energy transfer is not expected. The fluorescence decays of Ph₃₂PG-2 and Ph₃₂₂PG-3 are not completed in
this time scale. Fluorescence decays from both dendrimers show similar features such as wavelength-independent kinetics.

![Figure 3-20. Fluorescence decays of extended dendrimers following excitation at 350 nm A) Ph₃-PG-2 B) Ph₃-2-PG-3 fluorescence decays are detected at 363 nm (back), 376 nm (red) and 420 nm (blue)](image)

The fluorescence decays do not depend on detection wavelength supporting the absence of aggregation (inter- or intra-molecular interactions) in the ester form, and in accordance with our steady-state results. If present, aggregated states are expected to have longer decay times and emit at longer wavelengths as they are more delocalized and lower in energy. If there was a mixture of aggregated and non-aggregated states, the contribution of each state to emission signal would be wavelength-dependent in which case the emission would become slower at longer wavelengths. In conclusion, the kinetic behavior also supports that there is no aggregation in ester forms.

**Short time-scale:** In order to study energy transfer from periphery to core, time-resolved fluorescence was collected in a shorter time scale (up to 20 ps). At very early times, the characterization of the model compound Ph₃-PG-1 showed wavelength-
dependent kinetics, attributed to vibration cooling. This dendrimer was used to understand the excited-state kinetics in the absence of an energy gradient.

In this section, we investigated the decays at very early times (up to 5 ps) of the second and third generation PE dendrimers which have energy gradient from periphery to core due to differences in conjugation length. These experiments were done on as control experiments exciting the samples at 350 nm where only the core of the dendrimers is excited. Direct emission from the core can be observed and no energy-transfer kinetics is expected.

![Fluorescence decays of ester form of the extended dendrimers in THF upon excitation at 350 nm.](image)

Figure 3-21. Fluorescence decays of Ph$_3$2PG-2 and Ph$_3$2-2PG-2 upon excitation at 350 nm. The decays are collected at different emission wavelengths. The time-resolved kinetics are not affected by the detection wavelength. Moreover, we observe very similar kinetics for both Ph$_3$2PG-2 (Figure 3-21 A) and Ph$_3$2-2PG-3 (Figure 3-21 B). Interestingly, we do not observe significant contribution from vibrational cooling which was previously observed in the model compound for the Ph$_3$PG-1. The absence
of vibrational cooling in the higher generations of the dendrimers can be due to rigidity. The core part of the dendrimers becomes more rigid in the presence of peripheral units since these units increase the spatial restrain.

**Excitation of periphery leading to energy transfer**

![Figure 3-22](image)

Figure 3-22. Time-resolved fluorescence data of Ph$_3$$_2$PG-2 (black) and Ph$_3$$_2$PG-3 (red) in THF following excitation at 316 nm detected at A) 350 nm, and B) 420 nm

In order to observe energy transfer, dendrimers are excited at 316 nm where predominantly the 2-ring PE units at the periphery absorb (Figure 3-4 A). The fluorescence decays are collected at 350 nm (Figure 3-22 A) and 420 nm (Figure 3-22 B) for Ph$_3$$_2$PG-2 (black) and Ph$_3$$_2$PG-3 (red). The time-resolved fluorescence data show a fast-decay component at the shorter wavelength detection. This decay component becomes a rise time at the longer wavelength. Although, the general kinetic behaviors of the two dendrimers are similar, there is a difference between the second
and the third generation in terms of the rates associated with the excited states, second generation has faster $\tau$.

The difference in the kinetic behavior at different emission wavelengths indicates the presence of energy transfer. At 350 nm, the high-energy edge of the spectrum, there is a decay component because it corresponds to detection of emission from the excited state of the donor. At 420 nm, the low-energy edge of the spectrum, this component becomes a rise-time corresponding to the detection of emission from the excited state of the acceptor. A kinetic model (discussed in the following section) is considered in order to have better characterization of energy-transfer kinetics and compare the different generations.

**Results for Ionic Form of the Dendrimers**

Ionic counterparts of the PE dendrimers (CPE-Ds) are also studied using time-resolved fluorescence measurements. CPE-Ds are promising candidates for applications as they are soluble in polar solvents and easily processed into films. However, their photophysical properties and energy-transfer mechanisms are not well-known yet. The time-resolved fluorescence signals are collected using the up-conversion instrument on relatively long and short time-scales. The long time-scale data is used to characterize intermolecular interactions while the short time-scale data is used to understand energy-transfer properties.

**Intra-molecular interactions**

Second and third generation CPE-Ds do not show significant changes in their steady-state absorption spectra as ester groups become deprotected to form the ionic counterparts. For the higher generations of the dendrimers, the total charge of the end-groups increases causing repelling forces and preventing intermolecular interactions.
The increased charge density causes the dendrimers to take a globular form which was also observed for compact CPE-Ds.\textsuperscript{143}

Figure 3-23 A shows the fluorescence decays of Ph\textsubscript{3:2}G-2 at different detection wavelengths. The fluorescence decays become slower at longer wavelengths. Global analysis is used to fit the time-resolved data and the amplitude contributions are plotted in Figure 3-23 B. Feng et al. characterized the very long-time components were characterized by TCSPC (Table 3-6). On nanosecond time-scale, two time constants are obtained for fluorescence decays. The fractional amplitude contributions of the each time component are detection wavelength-dependent. The fractional amplitude of the shortest component (5 ps) decreases at longer wavelengths and the long time constant (5.2 ns) has increased fractional amplitudes at longer wavelengths.

![Fluorescence decays and fractional amplitudes of Ph\textsubscript{3:2}G-2 in methanol A) Fluorescence decays upon excitation at 316 nm and detected at 350 nm (dark yellow), 363 nm (black), 376 nm (red), 420 nm (blue) and 458 nm (cyan). Fittings are done using sum of exponentials. B) Fractional amplitudes of each time component ($\tau_1=360$ ps (black), $\tau_2=53$ ps (red) and $\tau_3=5$ ps (blue)).](image)

We do not expect inter-molecular interactions to be dominant in the second and third generation of the dendrimers since they are highly charged and repel each other.
The wavelength-dependent kinetics can be caused by other intra-molecular interactions due to globular structures. The communication between PE units at the periphery can open additional pathways for relaxation.

In conclusion, the second and third generation dendrimers are believed to be affected by intra-molecular processes. As it was observed with steady-state spectroscopy, the energy-transfer efficiency is lowered for larger dendrimers in the ionic form (61%). This decrease can be explained by the presence of additional non-radiative relaxation pathways in the ionic form that do not exist in the ester form. The non-radiative channels for relaxation are attributed to intra-molecular chromophore-chromophore interactions.

**Excitation of periphery leading to energy transfer**

![Fluorescence decay graphs](image)

Figure 3-24. Fluorescence decays of the ionic form of the extended dendrimers in methanol following excitation at 316 nm A) Ph$_{3:2}$G-2 and B) Ph$_{3:2:2}$G-3 detected at 345 nm (purple), 350 nm (dark yellow), 363 nm (black), 376 nm (red), and 420 nm (blue).

The energy-transfer properties of the ionic forms of the PE dendrimers are studied in the same way as it was done for the ester counterparts. Upon excitation at 316 nm, the fluorescence decays of Ph$_{3:2}$G-2 and Ph$_{3:2:2}$G-3 are collected at different detection
wavelengths (Figure 3-24). At this excitation wavelength, the energy is initially deposited at the periphery of the dendrimers. Within the first few picoseconds, energy-transfer kinetics are observed. At short-wavelength detection, the excited-state kinetics are dominated by the emission from excited state of the donor which is observed as a fast decay. When we move the detector to longer wavelengths the decays become slower. At the longest detected wavelength (420 nm), we observed a rise time attributed to detection of the emission from an excited state of the acceptor.

In conclusion, the fluorescence decays within the initial 5 ps show energy-transfer characteristics. The sub-picosecond time constant have positive amplitudes at short wavelengths, and negative amplitudes (rise time) at longer wavelengths. In order to obtain the energy-transfer rate constant and individual contributions of the donor and acceptor emissions to the total signals, a kinetic model is used for the fittings of the fluorescence decays.

**Kinetic Model and Energy Transfer Mechanism**

**Kinetic Model for the Ester Form**

Both time-resolved emission and steady-state measurements suggest that the excitation energy absorbed by the periphery of the ester form of the dendrimers is efficiently transferred to the core part of the molecule. Our aim is to understand the energy-transfer mechanism and the extent of electronic coupling between donor and acceptor units. The ester form of the dendrimers will be used as a platform to understand the more complicated behavior of the ionic analogs.

The time-resolved fluorescence decays at early times provide valuable information about the electronic energy-transfer kinetics. A kinetic model is used to fit the energy-
transfer data in order to extract the information about the rate constants for the corresponding processes.

A kinetic modeling program in Matlab platform is used to solve the differential equations and do least square fittings. The simplest model that could fit the time-resolved data is chosen for data analysis. It consists of a two-level system for each donor and acceptor moieties. Ground and excited state of the donor moiety (associated with the 2-ring PE units at the periphery of the dendrimers) are denoted as D and D*, respectively. Ground and excited state of the 3-ring PE units at the core are denoted as A and A*, respectively. The donor is excited by direct absorption of photons followed by energy transfer that populates the acceptor moiety with a rate constant \( k_{et} \) (energy-transfer rate constant). There can be direct emission from the excited state of the donor with a radiative decay rate constant \( k_{radD*} \) or from the excited state of the acceptor (\( k_{radA*} \)).

\[
\begin{align*}
D & \xrightarrow{hv} D^* & k_{et} & \xrightarrow{k_{radA*}} A \\
D^* & \xrightarrow{k_{radD*}} A^* & k_{radD*} & A^*
\end{align*}
\] (3-2)

The differential equations for the proposed model are solved analytically to obtain excited-state populations.

\[
D^*(t) = D^*(0) \exp\left[-(k_{radD*} + k_{et})t\right] \quad (3-3)
\]

\[
A^*(t) = \frac{k_{et}D^*(0)}{k_{radD*} + k_{et} - k_{radA*}} \left(\exp[-k_{radA^*}t] - \exp[-(k_{radD*} + k_{et})t]\right) \quad (3-4)
\]

The radiative decay times of excited states of donor (8.05 ns for Ph_{2,2}PG-2 and 8.20 ns for Ph_{2,2,2}PG-3) acceptor (0.72 ns) moieties are known from the fittings of lifetime measurements of the model compounds (see model compounds). They are used as fixed parameters in the kinetic model (\( k_{radD^*}, k_{radA^*} \)).
Since Ph$_2$-PG-2 and Ph$_2$-PG-3 have very long lifetimes (8.20 ns and 8.05 ns) compared to the energy-transfer kinetics (which takes places within 5 ps), the equations can be simplified using $k_{rad D} << k_{et}$.

$$D^*(t) = D^*(0) \exp[-k_{et}t]$$ (3-5)

$$A^*(t) = \frac{k_{et}D^*(0)}{k_{et}-k_{rad A'}} \left( \exp[-k_{rad A'}t] - \exp[-k_{et}t] \right)$$ (3-6)

The intensity of the time-resolved fluorescence signal is the product of the radiative rate constant and the population of the corresponding state, which can be written for both donor and acceptor state by:

$$I_D(t) = k_{rad D'} D^*(0) \exp[-k_{et}t]$$ (3-7)

$$I_A(t) = k_{rad A'} \frac{k_{et}D^*(0)}{k_{et}-k_{rad A'}} \left( \exp[-k_{rad A'}t] - \exp[-k_{et}t] \right)$$ (3-8)

If the donor and acceptor emission bands are well separated and the individual kinetics can be detected equation 3-7 and 3-8 can be used to directly fit time-resolved emission data. Unfortunately, and unlike the absorption bands, emission bands of donor and acceptor units of dendrimers being examined overlap as shown by the steady-state measurements of model compounds (Figure 3-3 and 3-9). The detected signals at a selected wavelength are the result of a combination of donor and acceptor intensities with different contributions (equation 3-9). The contribution of each state to the emission signal depends on detection wavelength.

$$I_\lambda(t) = C_1(\lambda) I_D(t) + C_2(\lambda) I_A(t)$$ (3-9)

$$I_\lambda(t) = G_1(\lambda)D^*(0) \exp[-k_{et}t] + G_2(\lambda) \frac{k_{et}D^*(0)}{k_{et}-k_{rad A'}} \left( \exp[-k_{rad A'}t] - \exp[-k_{et}t] \right)$$ (3-10)

where $G_1(\lambda) = C_1(\lambda) \cdot k_{rad 1}$ and $G_2(\lambda) = C_2(\lambda) \cdot k_{rad 2}$. For the fittings of time-resolved fluorescence decays at different wavelengths the equation (3-10) is used in which case
$G_1(\lambda)$, $G_2(\lambda)$ and $k_{et}$ are fitting parameters and the radiative lifetimes are kept constant (Table 3-1). More than one detection wavelength is used simultaneously for the least square fittings. The contributions ($C_1(\lambda)$ and $C_2(\lambda)$) of the individual species to the signal can be calculated by using fitting parameters ($A_1(\lambda)$ and $A_2(\lambda)$) since fitting parameters are products of radiative decay constants and contributions. The contribution of the donor and acceptor states gives information about the relative quantum efficiency of emission of the donor and the acceptor at a given wavelength at very early times after the excitation.

![Figure 3-25](image)

Figure 3-25. Time-resolved fluorescence data of the ester form of the extended dendrimers in THF following excitation at 316 nm. A) Ph$_{3-2}$PG-2 and B) Ph$_{3-2}$PG-3 detected at 350 nm (dark yellow), 363 nm (black), 376 nm (red) and 420 nm (blue). Fittings are done using analytical solutions to equation 3-2 ($k_{et}=(524 \text{ fs})^{-1}$ for Ph$_{3-2}$PG-2 and $k_{et}=(770 \text{ fs})^{-1}$ for Ph$_{3-2}$PG-3).

Figure 3-25 shows the results from the fittings using the kinetic model in equation 3-2. The fluorescence time-resolved fluorescence data detected at 350 nm are dominated by the emission from the donor, which contributes 96% to the overall signal. Although the contribution from the acceptor emission is minor at this detection wavelength, the decays are affected by acceptor kinetics since its lifetime is much shorter than lifetime of the donor. Detecting emission at 420 nm, the major contribution
to the intensity of the signal is from the excited state of the acceptor. The contributions of donor and acceptor emissions to the overall signals are given in Table 3-7.

The energy-transfer time-constants are found to be 524 fs for Ph$_{3,2}$PG-2 and 770 fs for Ph$_{3,2,2}$PG-3 (Table 3-6) by using kinetic model. The slower energy-transfer rate for the third generation is believed to be caused by longer distance between acceptor and donor units (9 Å for Ph$_{3,2}$PG-2 and 14 Å for Ph$_{3,2,2}$PG-3 from MD simulations). Energy-transfer rates in the sub-picosecond time-scale were also observed for other PE dendrimers. Kleiman et al. used pump-probe spectroscopy on PE dendrimers consisting of 2, 3, and 4 PE ring units and observed a multistep energy transfer which varies from 830 fs to 20 ps.$^{128}$ Atas et al. studied unsymmetrical PE dendrimers which have varying conjugation length (2, 3, and 4 PE ring units) and showed faster energy-transfer rates (750 fs)$^1$. The intra-molecular energy-transfer rates of our dendrimers are similar to the ones studied in literature.

The energy-transfer rate-constant can be used to calculate the energy-transfer efficiencies. The quantum yield of energy transfer is given by

$$\Phi_{ET} = 1 + \frac{1}{k_{ET} \tau_0}$$

(3-11)

where $\tau_0$ is the fluorescence lifetime of the donor in the absence of the acceptor. Using the lifetime of compact dendrimers as the donor for Ph$_{3,2}$PG-2 and Ph$_{3,2,2}$PG-3, $\Phi_{ET}$ is found to be larger than 0.99 in agreement with the steady-state measurements (0.96 for Ph$_{3,2}$PG-2 and 0.93 for Ph$_{3,2,2}$PG-3).

The energy-transfer rate-constants can be used to calculate interaction energy between donor and acceptor. In the weak-coupling limit the energy-transfer rate is given by
\[ k_{ET} = \frac{4\pi^2}{\hbar^2 c} |U|^2 \]  

(3-12)

where \( U \) (cm\(^{-1}\)) is the coupling energy and \( J \) (cm) is the spectral overlap between emission of the donor and absorption of the acceptor. The \( J \) term is a measure of the density of interacting states. It can be evaluated by using normalized absorption spectrum of acceptor \( A(\lambda) \) and normalized emission spectrum of donor \( F(\lambda) \).

\[ J = \int_{\lambda_1}^{\lambda_2} A(\lambda) F(\lambda) \lambda^2 \, d\lambda \]  

(3-13)

Figure 3-26. Spectral overlap between the emission spectrum of donor and the absorption spectrum of acceptor for the ester form of the extended dendrimers. Absorption spectrum of \( \text{Ph}_3 \text{PG}-1 \) (black) and emission spectrum of A) \( \text{Ph}_{2.2} \text{PG}-2 \) or B) \( \text{Ph}_{2.2.2} \text{PG}-3 \), the spectral overlaps are shaded.

Figure 3-26 shows the absorption spectrum of \( \text{Ph}_3 \text{PG}-1 \) (model for acceptor) and the mission spectra of \( \text{Ph}_{2.2} \text{PG}-2 \) (panel A) and \( \text{Ph}_{2.2.2} \text{PG}-3 \) (panel B) (model for donors), which are used to calculate the \( J \) values for \( \text{Ph}_{3.2} \text{PG}-2 \) and \( \text{Ph}_{3.2.2} \text{PG}-3 \) respectively. The calculated \( J \) values are given in Table 3-8. The \( J \) values for \( \text{Ph}_{3.2} \text{PG}-2 \) and \( \text{Ph}_{3.2.2} \text{PG}-3 \) are similar since emission spectra of the model compounds have very similar spectral response.
Coupling energies between core and periphery of the dendrimers are calculated by using the experimental energy-transfer rates (Table 3-6, 291 and 218 cm\(^{-1}\)). The weak-coupling limit is valid if the interaction energy is much smaller than the absorption and vibronic bandwidths. Hofkens et al. estimated vibronic bandwidths for bichromophoric dendrimers between 650 and 800 cm\(^{-1}\) by single molecule fluorescence measurements.\(^{154}\) These values are larger than the interaction energies calculated for our dendrimers approving the use of the weak coupling limit.

The interaction energies for the dendrimers presented here are larger than other symmetrical and unsymmetrical PE dendrimers measured in our group.\(^{123}\) This increase can be caused by the presence of bulky branched end-groups. The end-groups are believed to affect the planarity of the structures, which increases the coupling between linear units. The calculated interaction energy for the third generation dendrimer is smaller than the value for the second generation. It also supports that the distance between acceptor and donor units plays an important role on the energy transfer leading to slower kinetics for higher generation. The average distance from periphery to core parts of the dendrimers were calculated by molecular dynamic simulations (second generation: 9 Å, third generation: 14 Å) which shows a factor of 1.5 increase in distance for higher generation.

The energy transfer in novel PE dendrimers can be interpreted by using Förster's theory in the assumption that the coupling between acceptor and donor is very weak and the point-dipole approximation does not fail (refer Chapter 1 for details). Förster's approximations are valid if the separation between donor and acceptor is larger than the
sizes of the dipoles. We explored the validity of Förster’s approximations for our dendrimers.

We calculated the Förster radii of the dendrimers using spectroscopic data shown in Figure 3-25. The Förster radius is given by:

$$R_0^6 = 0.2108[k^2 \Phi_D n^{-4} \int_0^\infty I_D(\lambda)\epsilon_A(\lambda)\lambda^4d\lambda]$$  (3-14)

where $\kappa$ is the orientational factor ($\kappa_{avg}^2=2/3$) and $\Phi_D$ is the fluorescence quantum yield of the donor (0.36 for second and 0.38 for third generation dendrimers). $I_D(\lambda)$ is the fluorescence spectra of donor (Ph$_2$PG-2 or Ph$_2$-2-2PG-3) and $\epsilon_A(\lambda)$ is molar extinction coefficient of acceptor (Ph$_3$PG-1). The calculated Förster radii are very similar for the second and third generation of the ester forms of the dendrimers (35 and 33 Å). The energy-transfer rate constants for second and third generation are calculated by using the Förster radius and the distance values from MD simulations. The energy-transfer rate is given by $k_{et} = \frac{1}{\tau_D} \left[ \frac{R_0}{r} \right]^6$. The calculated energy-transfer rates are (2 ps)$^{-1}$ and (48 ps)$^{-1}$ are significantly slower than the experimentally observed values of (524 fs)$^{-1}$ and (770 fs)$^{-1}$. Förster approximations cannot account for the fast energy-transfer rates observed in extended dendrimers.

The point-dipole point-dipole approximation fails for dipoles in close proximity which is the case for extended PE dendrimers consisting of covalently bonded donor and acceptors.$^{127}$ In order to get better interpretation of time-resolved data the coulombic coupling should include transition dipole shapes and distribution. Ortiz et. al calculated the dipole moments for planar (11.8 D) and twisted (6.5 D) configurations of 3-ring PE units.$^{155}$ They showed that the rate constants obtained using the transition...
density cube is method is more sensitive to ring rotations than the rate constants obtained by Förster approximations.\textsuperscript{155}

In conclusion, the Förster model fails to account for the energy-transfer mechanism in extended PE dendrimers. Since the distance between donor and acceptor parts is very short (9-14 Å), the exact treatment of coulombic interaction is crucial.

**Kinetic Model for Ionic Forms**

The energy-transfer rates of ionic dendrimers are also obtained using a kinetic model in the same way as it was done for ester dendrimers. The two-state system model described in the previous section was not enough to account for the fittings of the ionic dendrimer decays. An additional relaxation pathway for the acceptor state was needed to obtain a good fit to the data. The additional relaxation pathway for ionic dendrimers had been characterized in the longer time scale (up to 1000 ps) by fluorescence decay measurements at different detection wavelengths (Figure 3-23). In the new model (3-15), T stands for a trap state, which can be formed due to intra-molecular interactions. The presence of traps results in lowered energy-transfer efficiency (61\%) and decreased quantum yields (0.02) as observed in the steady-state experiments (Figure 3-19).

\[
\begin{align*}
D & \xrightarrow{k_{uv}} D^* \xrightarrow{k_{et}} A^* \xrightarrow{k_{rad} A^*} A \\
D & \xrightarrow{k_{rad} D^*} T
\end{align*}
\]

(3-15)

The time-resolved emission detected at a different wavelength is evaluated as a mixture of donor and acceptor emission. The radiative decay times are fixed using the lifetimes obtained from the long time-scale measurements (Table 3-2). In addition to the
parameters used for $G_1(\lambda)$, $G_2(\lambda)$ and $k_{\text{et}}$, $k_i$ is fit to represents the rate constant for intra-molecular relaxation.

Figure 3-27 shows the kinetic modeling fits for Ph$_{3\cdot2}$G-2 and Ph$_{3\cdot2\cdot2}$G-3 in methanol. The contributions to the total signal from the excited state of the donor and acceptor are calculated from equation 3-9 and given in Table 3-7. The signals detected at shorter wavelengths have high contributions from the excited state of the donor similar to the ester analogs. The intra-molecular relaxation rate constant is 0.23 ps$^{-1}$ ($\tau=4.4$ ps) and it is in agreement with long time-scale measurements (5 ps) (Table 3-5).

![Fluorescence decays](image)

**Figure 3-27.** Fluorescence decays of the ionic form of extended dendrimers in methanol upon excitation at 316 nm. A) Ph$_{3\cdot2}$G-2 and B) Ph$_{3\cdot2\cdot2}$G-3 in methanol detected at 345 nm (purple), 350 nm (dark yellow), 376 nm (red) and 420 nm (blue). Fittings are done using analytical solutions to equation 3-15 ($k_{\text{et}}=(543 \text{ fs})^{-1}$ for Ph$_{3\cdot2}$G-2 and $k_{\text{et}}=(571 \text{ fs})^{-1}$ for Ph$_{3\cdot2\cdot2}$G-3, $k_i=(4.4 \text{ ps})^{-1}$).

The energy-transfer rates for ionic and ester forms of the second generation are very similar. In the case of third generation, the energy-transfer rate of the ionic form is faster than the ester form. The faster energy-transfer kinetics for Ph$_{3\cdot2\cdot2}$G-3 can be explained from the steady-state spectroscopy. We observed that the energy-transfer efficiency is decreased for Ph$_{3\cdot2\cdot2}$G-3 (61%) compared to Ph$_{3\cdot2\cdot2}$PG-3 (93%), which is believed to be because of intra-molecular interactions. In contrast to Ph$_{3\cdot2\cdot2}$G-3, the
energy-transfer efficiency of Ph$_{3}$-$_{2}$G-2 is not affected by the introduction of ionic end-groups.

Figure 3-28 shows a cartoon, which represents the energy transfer in the third generation of the ionic form of the extended dendrimer. In this representation, we consider Ph$_{3}$-$_{2}$G-3 as consisting of two shells of 2-ring PE units, an inner shell (red) and an outer shell (blue) in Figure 3-27. If we assume that the excitations deposited on the outer shell (blue arrows) cannot reach the core since that part of the molecule is more prone to intra-molecular interactions, the only part that contributing to the energy transfer is the inner PE units (red arrows). The blue arrows are more efficient than the red ones. In this case, energy transfer is expected to be faster as it is originating from closer PE units but the overall efficiency decreases. For the second generation of the dendrimer (Ph$_{3}$-$_{2}$G-2), there is only one shell which is less prone to interactions so energy transfer is completed and neither the energy-transfer rate nor the efficiency are affected by the presence of the ionic end-groups.

Figure 3-28. Schematic representation of outer and inner 2-ring PE components and energy transfer
The spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor is also calculated by using the model compounds for the ionic forms of the dendrimers. We used Ph₃PG-1 to approximate the acceptor spectrum since the ionic form is (Ph₃G-1) is prone to H-aggregate formation which is not expected to be case in higher generations. The calculated J values are given in Table 3-8. The J values for Ph₃₂G-2 and Ph₃₂₂G-3 are similar since the emission spectra of the model compounds are also very similar. However, the J value of the ionic form of the third generation is significantly smaller than the J value of the ester counterpart. The lower J value for the ionic is caused by broad emission spectra of the ionic form of the compact dendrimer, which was attributed to the presence of intra-molecular aggregation.

![Graphs showing spectral overlap between donor and acceptor](image)

Figure 3-29. Spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor for the ionic form of the extended dendrimers. Absorption spectrum of Ph₃PG-1 (black) and the emission spectrum of A) Ph₂₂G-2 or B) Ph₂₂₂G-3, the spectral overlaps are shaded.

The interaction energies (U) and the Förster radii for ionic dendrimers (21 Å Ph₃₂G-2 and 19 Å Ph₃₂₂G-2) are also calculated in the same way as it was done for the ester forms. Obtained interaction energies are much larger compared to those of ester
forms. These higher interactions energies make the very weak coupling limit approximation questionable. The calculated energy-transfer rates using steady-state data and the Förster formulation for Ph\textsubscript{3.2}G-2 and Ph\textsubscript{3.2.2}G-3 are (18 ps\textsuperscript{-1} and (610 ps\textsuperscript{-1} respectively, significantly slower than the experimental values (543 fs\textsuperscript{-1} and (571 fs\textsuperscript{-1}).

The Förster approximations are not valid in the case of ionic forms of extended dendrimers.

To sum up, energy-transfer rates for the ionic forms of the extended dendrimers are similar to their ester analogs with only a noticeable difference for \(\tau_{et}\) of Ph\textsubscript{3.2.2}G-3. The interaction energies are larger compared to ester forms and the Förster radii are smaller. The presence of ionic groups leads to intra-molecular interactions and decreases energy-transfer efficiency. The outer 2-ring PE units of the Ph\textsubscript{3.2.2}G-3 are believed to be more affected by the intra-molecular interactions due to the globular structure and the excitation localized over this part of the dendrimers is not transferred to the core leading to a decreased efficiency and faster kinetics. Although CPE-Ds are very promising candidates for applications, they have more complicated excited state kinetics compared to ester analogs. They have decreased energy-transfer efficiencies making them less suitable for light harvesting applications.
Table 3-1. Quantum yields and fluorescence decay time of the ester forms the model compounds

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>$\phi_{\text{ems}}$</th>
<th>$\tau_1$ (ns)$^a$</th>
<th>$\tau_2$ (ps)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_3$PG-1</td>
<td>1</td>
<td>0.72</td>
<td>3</td>
</tr>
<tr>
<td>Ph$_2$PG-1</td>
<td>0.34</td>
<td>9.08</td>
<td></td>
</tr>
<tr>
<td>Ph$_2$PG-2</td>
<td>0.38</td>
<td>8.05</td>
<td></td>
</tr>
<tr>
<td>Ph$_2$PG-3</td>
<td>0.36</td>
<td>8.20</td>
<td></td>
</tr>
</tbody>
</table>

a: TCPCS measurements by Lee et al.$^{153}$  
b: collected with the up-conversion instrument

Table 3-2. Quantum yields and fluorescence decay time of the ionic forms of the compact dendrimers

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>$\phi_{\text{ems}}$</th>
<th>$\tau_1$ (ns)$^a$</th>
<th>$\tau_2$ (ns)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$G-1</td>
<td>0.02</td>
<td>5.57</td>
<td>0.62</td>
</tr>
<tr>
<td>Ph$_2$G-2</td>
<td>0.02</td>
<td>6.54</td>
<td>1.54</td>
</tr>
<tr>
<td>Ph$_2$G-3</td>
<td>0.02</td>
<td>5.63</td>
<td>1.59</td>
</tr>
</tbody>
</table>

a: TCPCS measurements by Lee et al.$^{153}$

Table 3-3. Fractional amplitudes (%) of Ph$_3$PG-1 fluorescence decays (rise times in red)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Excitation at 316</th>
<th>Excitation at 365</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1$ = 3 ps</td>
<td>$\tau_2$ = 720 ps</td>
</tr>
<tr>
<td>363 nm</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>376 nm</td>
<td>13</td>
<td>87</td>
</tr>
<tr>
<td>420 nm</td>
<td>26</td>
<td>74</td>
</tr>
</tbody>
</table>

Table 3-4. Fractional amplitudes (%) of Ph$_3$G-1 fluorescence decays (rise times in red)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Excitation at 316</th>
<th>Excitation at 365</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1$ = 2</td>
<td>$\tau_2$ = 20</td>
</tr>
<tr>
<td></td>
<td>$\tau_2$ = 360</td>
<td>$\tau_1$ = 2</td>
</tr>
<tr>
<td></td>
<td>$\tau_2$ = 20</td>
<td>$\tau_2$ = 360</td>
</tr>
<tr>
<td>363 nm</td>
<td>44</td>
<td>39</td>
</tr>
<tr>
<td>376 nm</td>
<td>26</td>
<td>38</td>
</tr>
<tr>
<td>420 nm</td>
<td>13</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 3-5. Correlation times and calculated radius of gyration

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>$\Theta$ (ns)</th>
<th>Radius of Gyration (nm)</th>
<th>DLS radii (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-2</td>
<td>2.60</td>
<td>1.37</td>
<td>1.03</td>
</tr>
<tr>
<td>G-3</td>
<td>5.63</td>
<td>1.80</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Table 3-6. Quantum yields and decay times of extended dendrimers

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>$\phi_{\text{ems}}$</th>
<th>$\tau_1$ (ns)$^a$</th>
<th>$\tau_2$ (ns)$^a$</th>
<th>$\tau_3$ (ps)$^b$</th>
<th>$\tau_3$ (ps)$^b$</th>
<th>$\tau_{\text{et}}$ (fs)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_3$PG-2</td>
<td>0.84</td>
<td>5.48</td>
<td>1.04</td>
<td>24.5</td>
<td>24.5</td>
<td>524</td>
</tr>
<tr>
<td>Ph$_3$PG-3</td>
<td>0.80</td>
<td>1.85</td>
<td>0.47</td>
<td>24.5</td>
<td>24.5</td>
<td>770</td>
</tr>
<tr>
<td>Ph$_3$G-2</td>
<td>0.01</td>
<td>5.16</td>
<td>1.16</td>
<td>53</td>
<td>5</td>
<td>543</td>
</tr>
<tr>
<td>Ph$_3$G-3</td>
<td>0.03</td>
<td>6.31</td>
<td>1.16</td>
<td>36</td>
<td>5</td>
<td>571</td>
</tr>
</tbody>
</table>

a: TCPCS measurements by Feng et al.  
b: collected with the up-conversion instrument
Table 3-7. Kinetic modeling parameters

<table>
<thead>
<tr>
<th>Dendrimers</th>
<th>Wavelength (nm)</th>
<th>Signal Contribution</th>
<th>τ_{ef}(fs)</th>
<th>τ_{i}(ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Donor(%)</td>
<td>Acceptor(%)</td>
<td></td>
</tr>
<tr>
<td>Ph₃₂PG-2</td>
<td>350</td>
<td>97</td>
<td>3</td>
<td>524</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>21</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>Ph₃₂PG-3</td>
<td>350</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>363</td>
<td>15</td>
<td>85</td>
<td></td>
</tr>
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<td></td>
<td>376</td>
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<tr>
<td></td>
<td>420</td>
<td>15</td>
<td>85</td>
<td></td>
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<tr>
<td>Ph₃₂G-2</td>
<td>350</td>
<td>96</td>
<td>4</td>
<td>543</td>
</tr>
<tr>
<td></td>
<td>376</td>
<td>94</td>
<td>6</td>
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<tr>
<td></td>
<td>420</td>
<td>13</td>
<td>87</td>
<td></td>
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<tr>
<td>Ph₃₂G-3</td>
<td>345</td>
<td>98</td>
<td>2</td>
<td>571</td>
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<tr>
<td></td>
<td>376</td>
<td>95</td>
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<td></td>
<td>420</td>
<td>27</td>
<td>73</td>
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Table 3-8. Calculated coupling between core and periphery of PE dendrimers

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>J (cm)</th>
<th>U_{exp} (cm⁻¹)</th>
<th>U_{ Förster} (cm⁻¹)</th>
<th>R₀ (Å)</th>
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<tbody>
<tr>
<td>Ph₃₂PG-2</td>
<td>1.9*10⁻⁵</td>
<td>291</td>
<td>149</td>
<td>35</td>
</tr>
<tr>
<td>Ph₃₂PG-3</td>
<td>2.3*10⁻⁵</td>
<td>218</td>
<td>28</td>
<td>33</td>
</tr>
<tr>
<td>Ph₃₂G-2</td>
<td>1.4*10⁻⁵</td>
<td>333</td>
<td>58</td>
<td>21</td>
</tr>
<tr>
<td>Ph₃₂G-3</td>
<td>9.1*10⁻⁶</td>
<td>403</td>
<td>13</td>
<td>19</td>
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<tr>
<td>Symmetricalᵃ</td>
<td>9.4*10⁻⁵</td>
<td>176</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6*10⁻⁴</td>
<td>126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unsymmetricalᵃ</td>
<td>2.0*10⁻⁴</td>
<td>75</td>
<td></td>
<td>44</td>
</tr>
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</table>

ᵃ: from reference ¹²³,¹²⁷
CHAPTER 4
ENERGY TRANSFER IN THIENYLENE EXTENDED DENDRIMERS IN ESTER AND IONIC FORMS

Dendritic structures and chromophoric dendrimers have gathered a lot of attention for their light harvesting properties. Dendrimers are interesting antennae systems with molecularly well-defined architectures that can contain a rich arrangement of chromophore units. In the case of conjugated dendrimers, the band gap or low-lying electronic energy states that contribute to the light harvesting process are a function of backbone structure, and its conformation. These energies can be modified by incorporating different chemical conjugated units leading to energy gradients, thus modulating the energy transfer and energy focusing mechanisms. In these highly-branched molecules, the strength of the coupling between conjugated segments defines the mechanism of energy migration: In the presence of an energy gradient, incoherent coupling among chromophores leads to ultrafast energy transfer towards a sink.

There have been several studies trying to uncover the coupling among the different chromophores within individual dendrimers, or to understand the changes induced by architectural differences. Several groups have also combined light-inert dendritic scaffolds incorporating chemically bonded chromophores with different electronic energies, inducing a gradient and electronic energy transfer among the chromophores. In non-conjugated dendrimers, the backbone acts essentially as a scaffold, defining the distances between donors and acceptor. Back-folding can bring a chromophore in the periphery to a close distance with the acceptor at the core. This process can lead to unsymmetrical contributions to the energy-transfer process from the individual chromophores.
branches, since the simultaneous back-folding of all branches is very unlikely due to steric effects.

The total number of chromophores in conjugated dendrimers where the backbone is composed of all photo-active units is larger for a given generation compared to non-conjugated scaffolds. For conjugated dendrimers, the potential that more chromophores will contribute to absorption and participate in intermediate steps in a gradient driven energy harvesting mechanism increases.\textsuperscript{123,125} The most common architecture for non-conjugated dendrimers consists of a periphery decorated with donor chromophores, and higher generations are required to achieve the increased absorption. On the other hand, a non-conjugate scaffold can be designed to help separate moieties after a charge separation step in those dendrimers where the harvesting is followed by a redox process which is not the focus of our research.\textsuperscript{24} Thus, all photoactive conjugated dendrimers are well-suited for energy-transfer studies.

**Thienylene Extended Dendrimers in Ester Form**

We present here steady-state and ultrafast time-resolved characterizations of the gradient-driven energy-transfer in a family of thienylene-containing dendrimers.\textsuperscript{175} While there has been considerable previous work in the area of light-harvesting chromophore dendrimers,\textsuperscript{9,39,61,62} the work presented here takes advantage of chemically modified backbones to create a dendrimer with an all-conjugated, all-photoactive backbone. The backbone includes phenylene-ethynylene units coupled to thienylene groups affording the modulation of the HOMO-LUMO transition and creating an electronic and spatial energy funnel that causes electronic energy transfer from periphery to core. The phenylene-ethynylene units in the outer arms create a rigid dendritic structure, while the addition of thienylene groups provides some structural flexibility to the core of the
dendrimer. The dendrimers we report in this work have additional dendritic chains at the end of each branch. These specific end-groups contribute to increased solubility and suppress aggregation, and open the door to future experiments on conjugated dendritic polyelectrolytes.98,103,142

Figure 4-1. Structures of the thienylene-extended phenylene-ethynylene dendrimers. First row: A) Th-PG-1, B) Th-PG-2, C)Th-PG-3, D) branched end-groups and the model compound for core E) Ph-Th-Ph

The structure of the dendrimers and their end-groups together with the model compounds are given in Figure 4-1. Phenylene-ethynylene dendrimers are vulnerable to intermolecular aggregation, which results in complicated excited-state kinetics due to π-π stacking and excimer formation (see chapter 3, Figure 3-7).71,72 To avoid the presence of intermolecular interactions, each arm is decorated with branched end-groups (Figure 4-1 D) covalently bonded. As the generation increases, the number of branched end-groups doubles. In particular for higher generation, the bulky end-groups
prevent the aggregation tendency causing less intermolecular interactions and aggregate formation.

Dendrimers are labeled according to their photoactive backbone, $Th$-$PG$-$n$, where $Th$ stands for thienylene, $P$ for phenylene-ethynylene and $G$-$n$ for the generation number. The backbone of the first generation dendrimer ($Th$-$PG$-$1$) consists of three equivalent phenylene-ethynylene-thienylene-ethynylene units coupled in meta position to a central phenylene group (Figure 4-1 A). Higher generations are branched at meta position with additional phenylene-ethynylene (PE) units, each one bonded to the branched end-chain.

In the ground state, phenylene-ethynylene units connected by meta position are only weakly-coupled and their HOMO-LUMO transition can be considered as arising from individual 2-ring PE units. Hence we can consider having 6 and 18 PE chromophore units in $Th$-$PG$-$2$ (Figure 4-1 B) and $Th$-$PG$-$3$ (Figure 4-1 C) respectively. In $Th$-$PG$-$2$ and $Th$-$PG$-$3$ we expect two distinct electronic transitions spatially localized at the core and periphery of the dendrimers. This localization of the electronic transitions creates an energy gradient from periphery to core making these novel dendrimers well suited platforms to study energy transfer.

**Steady-State Measurements**

We collected the steady-state spectra of the ester form of dendrimers with the instruments explained in Chapter 2. For steady-state characterizations, THF is used as the solvent and the optical densities are kept lower than 0.1 cm$^{-1}$. The concentrations are lower than 1 $\mu$M to avoid self-absorption. At higher concentrations steady-state spectra do not show any changes (up to 30 $\mu$M), so no sign of aggregation is observed.
Under steady-state conditions (Figure 4-2 A), Th-PG-1 presents a broad absorption band peaked at 365 nm with a shoulder at 425 nm. In order to estimate photophysical properties of this first generation dendrimers and the core of the larger dendrimers, the model compound Ph-Th-Ph (Figure 4-1 E) is investigated. The absorption spectrum of the dendritic structure is red-shifted by ~8nm indicating the presence of coupling among the three phenylene-thienylene-phenylene chromophores. When compared to the model compound (Figure 4-1 E), the emission spectrum of Th-PG-1 presents a similar red-shift, it is broader, and the vibronic structure is not as well-defined. These changes suggest that the symmetry and flexibility of the dendritic structure leads to a coupled excited state with a shallower PES (Potential Energy Surface). Additionally, Yamaguchi et al. observed a similar red-shift in absorption maximum and enhancement in molar extinction coefficient of the oligo(p-phenylene ethynylene)s as the oligomers were substituted with alkoxy groups in para position.\textsuperscript{144} Santhanamoorthi and coworkers performed TDDFT (time dependent density functional theory) calculations on substituted and unsubstituted OPEs. The calculated absorption and emission spectra show that substitution of electron donating groups have a significant effect (red-shift in the absorption) on spectrum.\textsuperscript{145} It is likely that in our systems, both effects contribute to the changes observed in the spectra.

The spectral features of PE dendrimers covered in Chapter 3 were also very similar to the thienylene extended dendrimers. The broad emission spectrum and the red-edge shift in the absorption spectrum was attributed to the presence of alkoxy groups in the \textit{para} position of the phenyl rings. The coupling among the linear units was shown by anisotropy measurements. The replacement of one of the phenyl groups with
a thiophene does not change the general features of the steady-state spectra except lowering the HOMO-LUMO gap for the core part.

Second and third generation dendrimers show an additional absorption feature, peaked at 316 nm. Compact phenylene-ethynylene dendrimers, consisting of 2-ring PE units (Figure. 3-2) are used as model compounds for the periphery part of the Th-PG-n dendrimers and their absorption spectra are given in Figure 4-2 B. From this figure, it is clear that the increased absorption at λ < 345 nm corresponds to PE units supporting the assignment of this band to the periphery components. When the absorption spectra are normalized to the maximum of the phenylene-thienylene-phenylene unit (365 nm) we observe at 316 nm, 3.2 times higher absorption for Th-PG-3 compared to Th-PG-2.
corresponding to the proportional addition of PE units to each branch.\textsuperscript{125} The linear relationship between number of PE units and absorbance increase at 316 nm is depicted in the inset of Figure 4-2 and provides evidence that the individual 2-ring units are weakly coupled in the ground state. Overall, the absorption contributions from the Ph-Th-Ph and PE components are well-separated which allows the selective excitation of the core or the periphery of the dendrimers by changing the excitation wavelength.

![Emission spectra of Th-PG-n dendrimers and model compounds. A) Th-PG-1 (black), Th-PG-2 (red) and Th-PG-3 (blue) excited at 310 nm and scaled to match the optical density of the core at 380 nm. B) normalized emission spectra of Ph\(_{2,2,2}\)PG-3 (green) and Ph-Th-Ph (black) excited at 310 nm.](image)

Figure 4-3. Emission spectra of Th-PG-n dendrimers and model compounds. A) Th-PG-1 (black), Th-PG-2 (red) and Th-PG-3 (blue) excited at 310 nm and scaled to match the optical density of the core at 380 nm. B) normalized emission spectra of Ph\(_{2,2,2}\)PG-3 (green) and Ph-Th-Ph (black) excited at 310 nm.

Interestingly, the emission from Th-PG-2 and Th-PG-3 resembles the emission from the model compound (Figure 4-1 E), with a well-defined vibronic structure and max emission at 392 nm indicating that most emission originates from the core part of the dendrimers (Figure 4-3). While the Stokes shift for the second and third generation dendrimers are 92 meV and 99 meV, respectively, for Th-PG-1 the shift is much larger.
(200 meV). This change in Stokes shift, together with the broader absorption spectrum can indicate conformational strain in the presence of the dendritic arms and coupling of the electronic excited state in the thiophene based core to low-energy (slow) torsional mode. As mentioned before the emission spectrum of Th-PG-1 presents features due to couplings that seem to vanish in the presence of the additional PE arms, an effect that is further explored with ps time-resolved experiments.

Figure 4-4. Excitation (red) and absorbance (black) spectra of Th-PG-2 (dash) and Th-PG-3 (solid). Excitation spectra were normalized to match the absorbance at 365 nm

The presence of emission from PE units in the periphery can be investigated by comparing the emission from the thienylene-containing dendrimers with that of Ph$_{2-2}$PG-3. Ph$_{2-2}$PG-3 has emission maximum at 374 nm (green line, bottom panel of Figure 4-3) and presents no vibronic progression, quite different from the Th-containing molecules. Th-PG-3 presents a small shoulder at shorter wavelengths, indicative of some unquenched emission from the excited PE units at the periphery. This shoulder
accounts for less than 2% of the integrated fluorescence. The integrated fluorescence increases linearly with the number of absorbing units revealing the presence of efficient energy transfer from periphery to core.

Highly efficient energy transfer is also supported by comparison of excitation and absorption spectrum of Th-PG-3 and Th-PG-2 (Figure 4-4). The excitation spectrum was collected at wavelengths corresponding to core emission. The energy-transfer efficiency from periphery to core is calculated by normalizing the excitation and absorption spectrum at a wavelength corresponding to the acceptor transition (365 nm) and then comparing the intensities at the donor transition wavelength (313 nm). The energy-transfer efficiency is calculated as 99% for Th-PG-3 and 93% for Th-PG-2.

**Time-Resolved Measurements**

Time-resolved emission data was collected for different combinations of excitation and detection wavelengths in the time scales of hundreds of fs to ns. By varying the excitation wavelength, it is possible to excite selectively donor and acceptor units of the dendrimers. Two key processes are observed in the traces collected for the thienylene-containing dendrimers. Depending on the excitation wavelength, we see an intramolecular relaxation pathway or energy transfer from periphery to core.

Photoluminescence decay from the core of the dendrimers can be understood by investigating the time-resolved fluorescence curves for Th-PG-1 and ThPG-3 excited at 365 nm (Figure 4-5, with fitting parameter listed in Table 4-1) where only the thiophene-containing core absorbs. The decay of the excited-state population of Th-PG-1 can be fitted with a single exponential, ($\tau_1 = 357$ ps), independent of detection (or excitation) wavelength. The presence of the thienylene groups creates a more flexible chromophore with a faster lifetime than a rigid PE based dendrimer.
Figure 4-5. Time-resolved emission of Th-PG-1 (blue) and Th-PG-3 (red) excited at 365 nm (the maximum of the core absorption) and detected at 420 nm. Th-PG-1 data is fitted with a single exponential (357 ps) while Th-PG-3 data requires a double exponential fit ($\tau_1 = 303$ ps and $\tau_2 = 44$ ps).

Upon direct excitation of the core (365 nm), fluorescence decay of the third generation dendrimers exhibits similar sub-nanosecond decay ($\tau_1 = 303$ ps) with an additional 44 ps component. The new faster component appears only in the presence of the branched arms even though, at this excitation wavelength, the periphery chromophores are not excited. Th-PG-2 shows the same behavior with the additional 44 ps decay constant following excitation and detection of the core emission. The contribution from this component is more pronounced on the high-energy side of the emission spectra suggesting a relaxation pathway associated with the twisting of the thienylene units. Intra-molecular interactions of the bulky dendritic arms can affect this twisting process. The quantum yield for emission was measured for the three dendrimers. The values obtained for the core emission of Th-PG-1 ($\Phi=0.31$) remain unchanged for the larger dendrimers (0.38 for Th-PG-2 and 0.27 for Th-PG-3) indicating
the absence of additional quenching processes due to the arms (electron transfer, or additional triplet formation).\textsuperscript{24,177}

![Figure 4-6](image)

**Figure 4-6.** Time-resolved fluorescence decay of Ph\textsubscript{2,2,2}PG-3 (black) and Th-PG-3 (red) excited at 316 nm and detected at 376 nm. Fitting parameters are listed in Table 4-2.

The second effect observed in the time-resolved emission data corresponds to the opening of energy-transfer channels from the phenylene-ethynylene units in the periphery towards the phenylene-thiylene-phenylene based energy-sink. The model compound Ph\textsubscript{2,2,2}PG-3 was investigated to understand the photophysics of the PE units within a dendritic structure in the absence of an energy acceptor. Upon excitation at 316 nm, Ph\textsubscript{2,2,2}PG-3 fluoresces following a single and slow 8 ns decay (Figure 4-5, black).\textsuperscript{71,72,156,178} Th-PG-3 has a similar periphery structure and only differs in the presence of the thienylene groups in the core, which provides a lower HOMO-LUMO transition.

Upon excitation at 316 nm its emission decays within a few hundred picoseconds (Figure 4-6, red) with no contribution from the 8 ns decay associated with the PE units.
The decay can be fitted by the same time constants observed upon direct excitation of the core (303 ps and 44 ps) with slightly different fractional amplitudes (Table 4-2). These results confirm the high efficiency of energy transfer, whereas all the observed emission detected at wavelengths longer than 385 originates from the core of the dendrimers.

Figure 4-7. Early times photoluminescence of A) Ph\textsubscript{2,2,2}PG\textsubscript{3} (blue), Th-\textsubscript{PG}-1 (green), B) Th-\textsubscript{PG}-2, and C) Th-\textsubscript{PG}-3. After illumination at 316 nm energy transfer can be monitored at selective detection wavelengths (376 nm in blue, 385 nm in red, 400 nm in orange, 420 nm in green, and 458 nm in magenta). Th-\textsubscript{PG}-1 and Ph\textsubscript{2,2,2}PG\textsubscript{3} signal rises within the IRF (black, top panel). Additional components (1.5 ps and 3.5 ps for Th-\textsubscript{PG}-2 and Th-\textsubscript{PG}-3 respectively) appear for the larger donor-acceptor dendrimers (fits in solid lines). The ultrafast contribution is negative at high emission energies and it becomes positive as detection shifts to the low energy side.

Excitation at 316 nm allows detail monitoring of energy-transfer process with minimum interference from absorption from the core. Figure 4-7 shows the early times of the fluorescence decays of model compound Ph\textsubscript{2,2,2}PG\textsubscript{3} and dendrimers Th-\textsubscript{PG}-1,
Th-PG-2, and Th-PG-3 detected at selective wavelengths. Ph$_{2.2.2}$PG-3 and Th-PG-1 (top panel) depict the emission temporal behavior of donor and acceptor components independently. For the Ph$_{2.2.2}$PG-3 dendrimer, excitation occurs directly onto S$_1$ thus emission is instantaneous (within IRF). Th-PG-1 does not show any ultrafast rise or decay activity either. Signal from Th-PG-1 is weak since at this excitation wavelength the molecule has a much smaller absorption cross-section compared to the other dendrimers. Panels B and C show emission from the 2$^{nd}$ and 3$^{rd}$ generation dendrimers. Within the first few picoseconds, a new additional kinetic component is observed with characteristic times of $\tau_{ET} = 1.5$ ps and $\tau_{ET} = 3.5$ ps for Th-PG-2, and Th-PG-3 respectively. A change in sign for this ultrafast kinetic contribution as a function of detection wavelength is a signature of energy transfer from periphery to core. Fitting parameters are listed in Table 4-2, with numbers in red corresponding to the rise in populations. For Th-PG-2, detection at 376 nm and 385 nm shows considerable emission from the donor (Table 2), with the ultrafast component observed as decay having a large contribution to the overall signal. At these detection wavelengths, the long time decay (303 ps) corresponds to the decay of the acceptor’s excited state being populated through energy transfer. As the detection wavelength is shifted to the red side of the spectrum, the donor contribution gets diminished and at 458 nm we observed mostly emission from the acceptor, where the 1.5 ps appears now as a rise time associated with the feeding of population onto this excited state. For Th-PG-3 we observed a similar behavior although the rise time contribution is already detected at 385 nm. At wavelengths further into the red side we only detect emission from the donor, which is populated with a 3.5 ps rise time and depopulated with a 303 ps lifetime.
In both systems, at very long wavelengths, the ultrafast component feeds the core unit, which in turns decays with almost a single exponential decay (only 3% contribution from the 44 ps) at wavelengths longer than 400 nm.

**Energy Transfer Mechanism**

The time scale for these processes is consistent with a Förster type mechanism. Although the building blocks of the dendrimers are conjugated, the wavefunction is not fully delocalized. The meta substitutions on the phenyl rings creates localized excitation in the periphery, which in turn are only weakly coupled to the thienylene-containing core units. Under the weak coupling limit the energy-transfer rate (inverse of time constant) can be evaluated as 

\[ k = \frac{4\pi^2}{\hbar^2 c} J |U|^2, \]

where \( U \) is the coupling and \( J \) is the vibronic spectral overlap integral (in units of cm) between energy donor and acceptor. The spectral overlap is a measure of the density of interacting initial and final states. Accurate calculation of the overlap integral employs the homogeneous vibronic bandwidths. Since the homogeneous bandwidths of the vibronic bands in the dendrimer are unknown, we rely on absorption and emission spectra to obtain an approximate \( J \) value.

The spectral density can be evaluated by using 

\[ J (cm) = \int A(\lambda) F(\lambda) \lambda^2 (nm) 10^{-7} d\lambda, \]

where a normalized absorption spectrum acceptor, \( A(\lambda) \), and a normalized emission spectra donor, \( F(\lambda) \) are used. The overlap integral for the Th-PG-3 (Th-PG-2) dendrimer is calculated by using emission spectrum of PG-3 (PG-2) as the donor and absorption spectra of Th-PG-1 as the acceptor yielding \( J \) values of \( 1.46 \times 10^{-4} \) cm (Figure 4-8 A) and \( 1.36 \times 10^{-4} \) cm (Figure 4-8 B), respectively.
Figure 4-8. Spectral overlap between emission spectrum of donor and absorption spectrum of acceptor for ester forms of the thienylene extended dendrimers. A) Absorption spectrum of Th-PG-1 (black) and emission spectrum of Ph$_2$-2PG-2 or B) Ph$_2$-2PG-3, the spectral overlaps are shaded.

Evaluation of the strength of the coupling yields values of 62 cm$^{-1}$ and 42 cm$^{-1}$ for Th-PG-2 and Th-PG-3 respectively. The interaction energy decreases as the generation increases, which is readily explained if we consider a direct coupling between the outermost PE units and the core. For the larger generation dendrimers, the distance between transition dipoles increases and thus the decrease in the coupling strength. These numbers are also consistent with similar size dendrimers where the donors consist also of PE units.$^{123,127,130}$ In those cases, additional pathways for energy transfer, as well as interactions among periphery chromophores, were observed. In the system studied here, we observe simpler kinetic decays, with slightly slower energy-transfer rates, although interaction among periphery chromophores is still a possibility that needs to be explored. Moreover, the validity of the point-dipole approximation needs to be explored. Förster type mechanism can fail to account for the fast energy-transfer rates due to point dipole approximation (refer Chapter 3).
We present a new family of dendrimers with an all-conjugated backbone and dendritic end-chains. The fast transfer kinetics yield a highly efficient light-harvester, with a 1.5 and 3 picosecond time constants for energy transfer. On the basis of steady-state spectroscopy we conclude that the electronic structure corresponds to a donor (2-ring PE units) and acceptor (Ph-Th-Ph) building blocks. The donor and acceptor are weakly coupled leading to highly efficient vectorial energy transfer. Time-resolved emission in the ps time scale suggest a Förster type mechanism with interchromophoric coupling strengths in the order of 40-60 cm\(^{-1}\). The presence of dendritic end-chains avoids intermolecular aggregation, but intra-molecular perturbations are observed in the generation 2 and generation 3 dendrimers.

**Thienylene Extended Dendrimers in Ionic Form**

The thienylene extended dendrimers (Th-dendrimers) are functionalized by ionic end-groups in a similar way as it was done for phenylene-ethynylene dendrimers. Ester groups were deprotected to form CPE-Ds. The details of the deprotection is described elsewhere.\(^{180}\) The ionic forms of the thienylene extended dendrimers have a large number of charged terminal groups (three per one terminal group) resulting in high-solubility in methanol and water. The backbone consists of branched 2-ring PE units and phenylene-thienylene-phenylene group at the core. The structure of the second generation of thienylene extended dendrimers in the ionic form (Th-G-2) is given in Figure 4-9 B. The first generation of these dendrimers has the same terminal groups resulting in only 9 ionic groups. The third generation has increased the number of ionic groups (36 ionic groups) since the number of branches increases exponentially with generation.

Unpublished data starts from here.
Figure 4-9. Structures of ionic form of the thienylene extended dendrimers. A) Th-G-1 and B) Th-G-2.

The studies on the ester form of the Th-dendrimers indicate the absence of aggregation and the presence of efficient energy-transfer. Their structures are flexible and the twisting motions of the arms affect the excited-state dynamics. The same methods are used to explore the ionic forms of the dendrimers to understand the influence of the terminal groups on flexibility, intra- and inter-molecular aggregation, excited-state kinetics and particularly energy transfer.

**Steady-State Measurements**

For steady-state characterizations, methanol is used as the solvent. The optical densities are kept lower than 0.1 cm$^{-1}$. The concentrations are lower than 1 μM to avoid self-absorption and aggregation. The solutions of Th-G-n dendrimers for steady-state characterization are prepared by diluting from a concentrated (1mM) stock solution. The stock solutions are stored in the fridge to ensure stability.
Figure 4-10 shows the steady-state absorption and emission spectra of the Th-G-n dendrimers. The absorption spectra are normalized at 350 nm (Figure 4-10 A) and depict similar features as the ester analogs (Figure 4-2 A). There are two distinct bands corresponding to absorption at 312 nm and 350 nm. The absorbance at 312 nm increases with increasing generation. The emission spectrum is broad and structureless for the first generation, with a maximum at 425 nm. The emission spectra of the second and third generation have a band at 390 nm with vibronic structure. There is a shoulder at 355 nm, which was also present in the emission spectra of the ester forms with significantly lower intensity (smaller than 2% of emission). The contribution of this shoulder to the integrated emission is higher for the ionic forms of the dendrimers (9% for Th-G-3 and 8% for Th-G-2).

![Figure 4-10. Steady state spectra of ionic form of the thienylene extended dendrimers. A) Absorption spectra and B) emission spectra of Th-G-1 (black), Th-G-2 (red) and Th-G-3 (blue) in methanol. The excitation wavelength for the emission spectra is 350 nm for Th-G-1, 310 nm for Th-G-2 and Th-G-3.](image)

The high-energy region in the absorption spectra of Th-G-2 and Th-G-3 is assigned to absorption from the 2-ring PE units at the periphery. Similar assignments were performed with the ester analogs, using the model compounds Ph$_2$G-2 and Ph$_2$-2.
The absorbance at 312 nm increases by a factor of 2.7 from Th-G-2 to Th-G-3 corresponding to the increase in the number of 2-ring PE units (factor of 3). The low-energy absorption band at 350 nm is assigned to the absorption of the core part of the dendrimers corresponding to Ph-Th-Ph building blocks (Figure 4-2 A). The presence of two distinct absorption bands for donor and acceptor allows selective excitation and it can be used to study energy transfer monitoring the time-resolved emission.

The emission spectrum of Th-G-1 is a broad and structureless with a large Stoke’s shift, which can be due to coupling of the excited state to a torsional mode and the presence of alkoxy groups in para position of the phenyl rings.\textsuperscript{144,145,172,181,182} The emission spectra of Th-G-2 and Th-G-3 have similar shapes with a maximum at 390 nm originating from the core of the dendrimer. The vibronic structure is more readily observed as the alkoxy groups and they are not directly attached to Ph-Th-Ph units. Moreover, the addition of the dendritic arms can give rise to a conformational strain which is absent in the case of Th-G-1. The small additional band at 355 nm is assigned to the direct emission from the periphery.

Figure 4-11. Comparison of the absorption spectra of the ester (black) and the ionic (red) form of the thienylene extended dendrimers. A) First generation (Th-PG-1, Th-G-1), B) second generation (Th-PG-2, Th-G-2), C) third generation (Th-PG-3, Th-G-3)
In order to have a comparison between ester and ionic form of the dendrimers, the normalized absorption spectra of Th-PG-n and Th-G-n are given in Figure 4-11. As the charged groups are introduced in the structure of the dendrimers, the absorption bands are expected to be same since the photophysical properties are defined mostly by the backbone and not the end-groups. General features of the absorption spectra of the three generations remain the same with only minor differences. The first generation of the dendrimers has a slightly broader absorption spectrum in the ionic form (Figure 4-11 A). The absorption maximum of Th-G-1 is 5nm blue-shifted with respect to the absorption maximum of Th-PG-1. For the second generation (Figure 4-10 B), a small hypsochromic shift is accompanied by broadening in the case of the ionic form. The relative ratio of donor and acceptor bands also changes after the deprotection. The absorption spectrum of Th-G-3 also has a hypsochromic shift (13 nm) in the donor band (Figure 4-11 C). The acceptor band does not show any significant changes.

Figure 4-12. Comparison of the emission spectra of the ester and the ionic form of the thienylene extended dendrimers, excitation wavelengths are given in parenthesis. A) First generation, Th-PG-1, Th-G-1 (350 nm), B) Second generation, Th-PG-2, Th-G-2 (310 nm), C) Third generation, Th-PG-3, Th-G-3 (310 nm)

There can be inter- or intra-molecular interaction between PE units giving rise to the features observed in the absorption spectra. As these dendrimers are highly
charged, they effectively repel each other, so intra-molecular interactions are expected to play a more significant role in the observed features. Moreover, the hypsochromic shifts (4 nm) are insignificant if we consider the polarity difference of the solvents. In a polar solvent, the hydrophobic backbone is expected to destabilize raising the HOMO-LUMO gap. In conclusion, the absorption spectra do not provide conclusive information about the aggregation.

In order to compare ester and ionic forms of the dendrimers, the normalized emission spectra of Th-PG-n and Th-G-n are given in Figure 4-12. The emission spectrum of the first generation is slightly broader and red-shifted for the ionic form. These features could be interpreted as a sign of aggregation, since low charge density leads to inter-molecular aggregation. As mentioned earlier, Th-G-2 has a shoulder at 355 nm that is not present in Th-PG-2. This shoulder is present in both forms for the third generation dendrimers but it has a higher contribution to the overall emission in the ionic forms. It corresponds to direct emission from the periphery indicating decreased energy-transfer efficiency.

Comparison of absorption and excitation spectra shown in Figure 4-13 is used to calculate the energy-transfer efficiencies. The excitation spectra of Th-G-2 and Th-G-3 were collected at 440 nm, which corresponds to emission from the core of the dendrimers. Spectra are normalized at 350 nm to match with the absorbance band at the periphery. Although, excitation and absorption spectra are very similar, the relative intensities of the donor and acceptor bands are significantly different. The energy-transfer efficiencies from periphery to core are calculated at 313 nm yielding 81% (Figure 4-13 A) for Th-G-2 and 65% (Figure 4-13 B) for Th-G-3. Obtained energy-
transfer efficiencies are significantly decreased compared to the ester precursors (99% and 93% respectively), which is consistent with observation of residual emission from the donor at 350 nm.

![Figure 4-13. Excitation (red) and the absorbance (black) spectra of A) Th-G-2 and B) Th-G-3. Excitation spectra are normalized to match the absorbance at 350 nm and detected at 440 nm.](image)

The decreased energy-transfer efficiency can be caused by formation of intra-molecular aggregates. In methanol (a hydrophilic solvent), the highly hydrophobic backbone of the dendrimers is expected to have a tendency to interact with each other to decrease interactions with the molecules of solvent. These intra-molecular interactions can open non-radiative decay channels resulting in lower energy-transfer efficiency. The energy-transfer efficiency for the third generation is significantly lower than for the second generation due to an increase in the intra-molecular aggregation because of higher charge density (by a factor of 2).

To sum up, the steady-state spectroscopy of ionic forms of the thiophene containing dendrimers reveals is intra-dendrimer aggregation accompanied by lower energy-transfer efficiency. The chromophore-chromophore interactions may open new
non-radiative channels for relaxation. The ionic dendrimers are further examined by time-resolved measurements.

**Time-Resolved Measurements**

The time-resolved fluorescence is collected by up-conversion or TCSPC methods (details in Chapter 2). For up-conversion measurements, the optical densities are kept below 0.2 mm\(^{-1}\) with concentrations lower than 15 μM. Lower concentrations cannot be used due to low signal-to-noise ratios.

The fluorescence lifetimes of the ionic forms of TH-dendrimers were characterized by Lee using TCSPC measurements.\(^{180}\) TH-G-1 fluorescence decays with two time components (0.39 and 1.30 ns) whereas the lifetime of the ester counterpart had only one time component (0.36 ns). The additional lifetime (1.30 ns) can originate from the emission of aggregated states. Table 4-3 shows the lifetimes of the each generation of ionic forms. Three time components are observed for TH-G-2 and TH-G-3. The fractional amplitudes of the observed time constants are significantly affected by the detection wavelength indicating presence of aggregate emission. In addition to the time constants observed in the TCSPC measurement, faster decays are characterized by up-conversion measurements.

The up-conversion technique is used to collect fluorescence decays of the ionic forms of the thiophene containing dendrimers in the picosecond to subpicosecond time-scales. Again, the measurements were done in two time-windows, i) in a relatively short time-scale up to 20 ps to study energy-transfer and ii) in a longer time-scale, up to 500 ps, to observe intra- or inter-molecular interactions.

The fluorescence decays of the ionic forms of these dendrimers are collected following excitation at 350 nm. At this excitation wavelength, we reached directly to the
core and no energy transfer is expected. Instead, direct emission from the core is observed and the data presents different kinetics depending on the detection wavelength.

Figure 4-14 shows the fluorescence decays of Th-G-1 (panel A) and Th-G-2 (panel B). In addition to the 390 ps decay characterized by TCSPC measurement (Figure 4-14 A), the first generation fluorescence decays with a short time constant (9 ps at 420 nm), which becomes slower (17 ps at 445 nm) at longer wavelengths. The steady-state measurements on Th-G-1 indicated aggregate-formation, the 9-17 ps time constant can arise from the population of aggregated states. At longer wavelengths, the detection of aggregated emission increases and the slower decay-time can be an indication of an unresolvable rise time. Instead of observing the excited-state population of aggregate increasing, we detect a combination of emission from unaggregated combined with emission from aggregates.
The time-resolved emission of Th-G-2 reveals similar behavior (Figure 4-14 B). There is a short time constant (7 ps), whose fractional amplitude is wavelength-dependent. At high-energy detection, there is a significant contribution from this decay, which can be due to an intra-molecular relaxation process. In the case of Th-PG-2, the 44 ps time constant was assigned to torsional motions. For the ionic Th-G-2, this time constant can become faster since the PE units are believed to be in closer proximity. The same constants are also observed for fluorescence decay of Th-G-3. In conclusion, the excited-state kinetics in the absence of energy transfer are characterized by selective excitation of the core at 350 nm and detection of direct emission. The 7 ps time-constant is assigned to intra-molecular relaxation processes for Th-G-2 and Th-G-3.

![Graph](image)

*Figure 4-15.* Time-resolved fluorescence data of Th-G-2 (black) and Th-G-3 (red) following excitation at 316 nm. The decays are detected at A) 376 nm (red) and B) 420 nm (blue).
Energy-transfer kinetics are studied by excitation at the periphery of the dendrimers (316 nm) and detection of the emission at selective wavelengths. The fluorescence decays of Th-G-2 and Th-G-3 are given in Figure 4-15. At shorter wavelength (376 nm), both generations show an ultrafast decay (Figure 4-15 A). Detection at 420 nm yields a rise in the signal in the same time-scale (Figure 4-15 B).

The wavelength-dependent kinetics was also observed in the Th-PG-2 and Th-PG-3 series and it is a signature of the energy transfer for both Th-G-2 and Th-G-3 dendrimers similar to ester counterparts. Third generation has slower decay and rise time-constant compared to the second generation, and in agreement with the results for the ester forms of the dendrimers.

**Kinetic Model and Energy-Transfer Mechanism**

Time-resolved fluorescence and steady-state measurements on ionic forms of the dendrimer reveal that the excitation energy absorbed by the periphery is transferred to the core with low efficiency due to intra-molecular interactions. In order to reach a better understanding of the mechanism of energy-transfer and the processes that affect the efficiency, a kinetic model is used for data analysis of time-resolved data at early times.

From the spectra model compounds (Figure 4-3), it is known that the emission signals of the donor and the acceptor moieties of dendrimers are not very well separated. The kinetic model program is modified to allow simultaneous contributions from the signals from different states. The simplest kinetic model which provides good fits to the experimental data is given by

\[
D \overset{h\nu}{\longrightarrow} D^* \overset{k_{gt}}{\longrightarrow} A^* \overset{k_{rad}}{\longrightarrow} A
\]

(4-1)
The donor state (denoted by D) is the 2-ring PE units at the periphery. The donor is excited to form D* by absorption of photons and it can relax by a radiative decay ($k_{\text{rad D}^*}$), or undergo energy transfer with a rate constant $k_{\text{et}}$ to populate the excite state of the acceptor ($A^*$) which resides in the Ph-Th-Ph unit at the core. Photons can be emitted from the excited state of the acceptor ($A^*$) by radiative decay (constant $k_{\text{rad A}^*}$) or the acceptor can relax to a trap state due to intra-molecular aggregation (T) with a rate constant $k_i$. The presence of trap states results in lower energy-transfer efficiency and decreased quantum yields observed in steady-state spectroscopy (Figure 4-13). The trap state can also have a radiative contribution, but emission from this state is not taken into account for the fittings since it is in a longer time-scale and does not affect the decays at early times (see lifetimes Table 4-3).

The proposed model is solved analytically to obtain time dependent populations of the excited states of the donor and acceptor. The radiative decay-times for the donor and acceptor are known from the lifetime measurements of the model compounds (Table 3-2). They are used as fixed parameters in this model ($k_{\text{rad D}^*}$, $k_{\text{rad A}^*}$). The integrated equations for the proposed kinetic model (Equation 4-1) are given in Equation 4-2 and Equation 4-3.

$$D^*(t) = D^*(0) \exp \left[ - (k_{\text{rad D}^*} + k_{\text{et}}) t \right]$$  \hspace{1cm} (4-2)

$$A^*(t) = \frac{k_{\text{et}} D^*(0)}{k_{\text{rad D}^*} + k_{\text{et}} + k_i - k_{\text{rad A}^*}} \left[ \exp \left[ - k_{\text{rad A}^*} t \right] - \exp \left[ - (k_{\text{rad D}^*} + k_{\text{et}} + k_i) t \right] \right]$$  \hspace{1cm} (4-3)

The lifetime of the excited state of donor is obtained from Ph$_{2,2,2}$G-3 or Ph$_{2,2}$G-2 (2.93 ns and 2.96 ns respectively) whereas the lifetime of Th-PG-1 is used as the acceptor (Table 4-1). Since the lifetime of the excited-state of the donor is very long compared to the lifetime of the acceptor (357 ps) and the energy-transfer time-scale

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From the time-resolved data (Figure 4-15), the equations can be simplified using $k_{\text{rad} D*} \ll k_i$.

\[ D^*(t) = D^*(0) \exp[-k_{\text{et}} t] \]  \hspace{1cm} (4-4)

\[ A^*(t) = \frac{k_{\text{et}} D^*(0)}{k_{\text{et}} + k_i - k_{\text{rad} A*}} (\exp[-k_{\text{rad} A} \cdot t] - \exp[-(k_{\text{et}} + k_i) t]) \]  \hspace{1cm} (4-5)

In an up-conversion measurement, the fluorescence signal is detected as a function of time. This signal is the product of the radiative rate constant and the population of the emissive state being detected as given by

\[ I_D(t) = k_{\text{rad} D*} D^*(0) \exp[-k_{\text{et}} t] \]  \hspace{1cm} (4-6)

\[ I_A(t) = k_{\text{rad} A*} \frac{k_{\text{et}} D^*(0)}{k_{\text{et}} + k_i - k_{\text{rad} A*}} (\exp[-k_{\text{rad} A} \cdot t] - \exp[-(k_{\text{et}} + k_i) t]) \]  \hspace{1cm} (4-7)

In principle, the individual fluorescence decays of the excited states of the donor and acceptor can be fit using equation 4-6 and 4-7, if the emission bands of the donor and acceptor are well separated. The steady-state measurements on model compounds for the donor and acceptor reveal that emission band of these species overlap (Figure 4-3). Although the selective excitation of the donor and acceptor species is possible, selective detection of the donor or the acceptor without any contribution from the other is very unlikely. Instead, the signal detected at a given wavelength is the summation of contributions from acceptor and donor emission, which in turn depend on detection wavelength.

\[ I_\lambda = C_1(\lambda) I_D(t) + C_2(\lambda) I_A(t) \]  \hspace{1cm} (4-8)

\[ I_\lambda = G_1(\lambda) D^*(0) \exp[-k_{\text{et}} t] + G_2(\lambda) \frac{k_{\text{et}} D^*(0)}{k_{\text{et}} + k_i - k_{\text{rad} A*}} (\exp[-k_{\text{rad} A} \cdot t] - \exp[-(k_{\text{et}} + k_i) t]) \]  \hspace{1cm} (4-9)

where $C_1(\lambda)$ and $C_2(\lambda)$ contributions of the donor and acceptor species to the fluorescence signal and $G_1(\lambda)$ and $G_2(\lambda)$ are fitting parameters. The time-resolved
emission data at different detection wavelengths are fitted by equation (4-9). The
parameters $A_1(\lambda)$, $A_2(\lambda)$ and $k_{el}$ are allowed to be changed in the least square fittings,
the $k_i$ and the radiative decay times are characterized by longer time-scale
measurements and used as fixed parameters. The contributions provide information
about the relative quantum efficiency of emission of the donor and acceptor at a given
wavelength right after the excitation of the dendrimers.

The kinetic model fits to the experimental data are given in Figure 4-16. At high-
energy detection (363 nm), the excited-state of donor contributes more than 98% of the
total signal and dominates the decay characteristics. Although the acceptor state has a
minor contribution at this wavelength, the observed kinetics are greatly affected by the
acceptor temporal behavior since its lifetime is much shorter than that of the donor. At
longer wavelengths (420 nm), acceptor emission has the major contribution to the
overall signal. The contributions of donor and acceptor populations to the emission
signal at each detection wavelength are given in Table 4-5.

![Figure 4-16](image)

Figure 4-16. Time-resolved fluorescence data of A) Th-G-2 and B) Th-G-3 in methanol
following excitation at 316nm and detected at 363 nm (black), 376 nm (red),
and 420 nm (blue). Fittings are done using kinetic model in equation 4-1 ($k_i= (7 \text{ ps})^{-1}$ for Th-G-2 and $k_{el}= (690 \text{ fs})^{-1}$ for Th-G-3, $k_2= (1.2 \text{ ps})^{-1}$).
Table 4-5 presents the rate constants for energy transfer ($k_{et}$) for Th-G-2 and Th-G-3 obtained from the kinetic model. The energy-transfer rate-constant for Th-G-2 and Th-G-3 are found to be (690 fs)$^{-1}$ and (1.2 ps)$^{-1}$. The third generation dendrimer has a slower energy-transfer rate, $\tau$, which was also observed with the ester analogs. The slower energy-transfer rate is attributed to longer distances from periphery to core. Moreover, both generations of ionic dendrimers have faster energy-transfer rates (0.69 fs and 1.2 ps) compared to the ester counterparts (1.5 ps and 3.5 ps).

The faster energy-transfer rates can be explained in two possible scenarios, which can also be acting simultaneously. Previous studies on compact CPE-D-s reveal that a globular form in the polar solvents as the dendrimers are deprotected from the ester precursors. It is claimed that dendrimers shrink or collapse to avoid hydrophilic interactions with solvent molecules. If this is also the case for our thienylene extended dendrimers, there can be shorter distances between core and periphery in the ionic analogs. If the energy-transfer process can be explained by Förster theory, the energy-transfer rate has a power six dependence on the distance between donor and acceptor in the weak-coupling limit. Thus, distance is the one of the most important factors affecting the energy-transfer rate in the weak coupling limit.

The faster rate can also be related to the energy-transfer efficiency. The energy-transfer efficiency is decreased for ionic analogs of Th-dendrimers as shown in Figure 4-13. The PE units in the outer part of the Th-dendrimers can be part of intra-molecular aggregates leading to a lower efficiency of energy transfer. Therefore, the energy transfer originates mostly from the closer PE units, giving rise to faster rates.
Figure 4-17. Spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor for the ionic form of the thienylene extended dendrimers A) Absorption spectrum of Th-PG-1 (black) and emission spectrum (red) of Ph$_2$G-2 or B) Ph$_2$G-3, the spectral overlaps are shaded.

The interaction energies between donor and acceptor are calculated using equations (3-12). Table 4-16 shows the calculated interaction energies and J values. The J values are calculated by using spectra overlap between model compounds for the donor and acceptor (Figure 4-17). The calculated interaction energy for Th-G-2 (145 cm$^{-1}$) is much larger the value obtained for Th-PG-2 (62 cm$^{-1}$). The third generation has also larger interaction energy in the ionic form (132 cm$^{-1}$) versus the organic form (42 cm$^{-1}$). The interaction energy increases as the dendrimers are deprotected from ester forms and dissolved in polar solvents, although, they are still much smaller than the vibronic bandwidth (650 cm$^{-1}$),$^{154}$ so we conclude that we are still in the weak coupling limit.

In conclusion, the energy transfer of Th-dendrimers in the ionic forms are much faster than their ester analogs, which can be due to the collapse of the dendrimer structure and stronger interaction between periphery and core. The energy-transfer
efficiency is decreased due to intra-molecular interactions. The excitations localized over the outer parts of the dendrimers are believed to relax to trap states and not reach the core part leading to lower efficiencies and faster rates.

Table 4-1. Fractional amplitudes of fluorescence decays of Th-PG-n (λ=365 nm)

<table>
<thead>
<tr>
<th>Dendrimers</th>
<th>λ_{det}</th>
<th>α₁</th>
<th>α₂(44 ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th-PG-1</td>
<td>420</td>
<td>1  (357 ps)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>458</td>
<td>1  (357 ps)</td>
<td></td>
</tr>
<tr>
<td>Th-PG-2</td>
<td>385</td>
<td>0.72 (303 ps)</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>0.93 (303 ps)</td>
<td>0.07</td>
</tr>
<tr>
<td>Th-PG-3</td>
<td>385</td>
<td>0.73 (303 ps)</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>0.97 (303 ps)</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 4-2. Fractional amplitudes of fluorescence decays of Th-PG-n (λ=316 nm). Numbers in red correspond to rise times.

<table>
<thead>
<tr>
<th>Dendrimers</th>
<th>λ_{det}</th>
<th>α₁ (303 ps)</th>
<th>α₂ (44 ps)</th>
<th>α_{EET}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th-PG-2</td>
<td>376</td>
<td>0.14</td>
<td>0.23</td>
<td>0.63 (1.5 ps)</td>
</tr>
<tr>
<td></td>
<td>385</td>
<td>0.19</td>
<td>0.34</td>
<td>0.47 (1.5 ps)</td>
</tr>
<tr>
<td></td>
<td>458</td>
<td>0.83</td>
<td>0.02</td>
<td>0.15 (1.5 ps)</td>
</tr>
<tr>
<td>Th-PG-3</td>
<td>376</td>
<td>0.27</td>
<td>0.54</td>
<td>0.19 (3.5 ps)</td>
</tr>
<tr>
<td></td>
<td>385</td>
<td>0.35</td>
<td>0.43</td>
<td>0.22 (3.5 ps)</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.64</td>
<td>0.03</td>
<td>0.33 (3.5 ps)</td>
</tr>
<tr>
<td></td>
<td>435</td>
<td>0.71</td>
<td>0.03</td>
<td>0.26 (3.5 ps)</td>
</tr>
<tr>
<td>Ph_{2,2,2}PG-3</td>
<td>376</td>
<td>1 (8.2 ns)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-3. Lifetime and quantum yields of Th-G-n dendrimers

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>ϕ_{ems}</th>
<th>τ₁ (ns)</th>
<th>τ₂ (ns)</th>
<th>τ₃ (ns)</th>
<th>τ₄ (ps)</th>
<th>τ_{et} (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th-G-1</td>
<td>0.23</td>
<td>0.39</td>
<td>1.30</td>
<td>9-17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Th-G-2</td>
<td>0.14</td>
<td>0.32</td>
<td>0.98</td>
<td>3.06</td>
<td>7</td>
<td>0.69</td>
</tr>
<tr>
<td>Th-G-3</td>
<td>0.10</td>
<td>0.32</td>
<td>1.19</td>
<td>3.64</td>
<td>7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a: collected by Lee\textsuperscript{180} b: collected with the up-conversion instrument

Table 4-4. Fractional amplitudes of fluorescence decays of Th-G-n (λ_{exc}=350 nm)

<table>
<thead>
<tr>
<th>Dendrimers</th>
<th>λ_{det}</th>
<th>α₁</th>
<th>α₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th-G-1</td>
<td>420</td>
<td>0.41 (390 ps)</td>
<td>0.59 (9 ps)</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>0.47 (390 ps)</td>
<td>0.53 (17 ps)</td>
</tr>
<tr>
<td>Th-G-2</td>
<td>376</td>
<td>0.46 (320 ps)</td>
<td>0.54 (7 ps)</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>0.89 (320 ps)</td>
<td>0.11 (7 ps)</td>
</tr>
<tr>
<td>Th-G-3</td>
<td>420</td>
<td>0.87 (320 ps)</td>
<td>0.13 (7 ps)</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>0.89 (320 ps)</td>
<td>0.11 (7 ps)</td>
</tr>
</tbody>
</table>
Table 4-5. Kinetic Model Parameters

<table>
<thead>
<tr>
<th>Dendrimers</th>
<th>Wavelength</th>
<th>Signal Contributions</th>
<th>(\tau_{el}(\text{ps}))</th>
<th>(\tau_\ell(\text{ps}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Donor</td>
<td>Acceptor</td>
<td></td>
</tr>
<tr>
<td>Th-G-2</td>
<td>363 nm</td>
<td>0.98</td>
<td>0.02</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>376 nm</td>
<td>0.97</td>
<td>0.03</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>420 nm</td>
<td>0.25</td>
<td>0.75</td>
<td>7</td>
</tr>
<tr>
<td>Th-G-3</td>
<td>363 nm</td>
<td>0.99</td>
<td>0.01</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>376 nm</td>
<td>0.96</td>
<td>0.04</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>420 nm</td>
<td>0.13</td>
<td>0.87</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-6. Calculated couplings between core and periphery of Th-\textit{PG}-\textit{n} and Th-G-\textit{n}

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>(J) (cm)</th>
<th>(U) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th-\textit{PG}-2</td>
<td>1.46*10(^{-4})</td>
<td>62</td>
</tr>
<tr>
<td>Th-\textit{PG}-3</td>
<td>1.36*10(^{-4})</td>
<td>42</td>
</tr>
<tr>
<td>Th-G-2</td>
<td>5.48*10(^{-5})</td>
<td>145</td>
</tr>
<tr>
<td>Th-G-3</td>
<td>4.00*10(^{-5})</td>
<td>132</td>
</tr>
</tbody>
</table>
Conjugated polyelectrolytes (CPEs) are conjugated polymers (CPs) functionalized with ionic side chains such as sulfonate (SO$_3^-$), carboxylate (CO$_2^-$), phosphonate (PO$_4^-$), or ammonium (NR$_3^+$). These ionic groups make the polymer soluble in polar solvents including water. Solubility in polar solvents is an important property because CPEs are easily processed into films and supramolecular assemblies from aqueous solutions. Thus, CPEs are preferable subtypes of CPs for LED and solar cell applications. CPEs are amphiphilic as they have ionic side-groups and hydrophobic backbone, which increase their tendency to form aggregates. Formation of aggregates increases the complexity of the system since aggregates allow interchain energy-transfer mechanisms. In this chapter, I present energy-transfer and photophysical properties of CPEs with dendritic side chains, which are synthesized in hope for reducing aggregation and make it possible to focus on intrachain energy-transfer mechanisms.

CPEs have extraordinary quenching efficiency, referred to as “amplified quenching” or “superquenching” in the literature. The increased quenching efficiency is a favorable property for sensors as it enables better sensitivity for the analytes. The mechanism of amplified quenching captured great interest, since it involves very efficient energy transfer and in some cases electron transfer. In order to understand the mechanism of amplified quenching, there are two main aspects. First, formations of ion-pair complexes enable ultrafast energy and/or electron transfer directly between the polymer and the quencher molecule. Second, energy as excitons or electrons can be transported along the polymer chain (intrachain mechanism) or within aggregates (interchain mechanism).
When investigating energy transfer in CPEs an additional aspect to consider is interchain mechanism in the presence of aggregation. In the presence of aggregates, the polymers $\pi$ electron density can be delocalized among different conjugated segments enabling the energy transfer between these segments.\textsuperscript{142} Interchain energy migration is a very fast and efficient process and has a variable contribution to the overall energy transfer which depends on concentration of the polymer.\textsuperscript{190}

In this chapter, the main interest is on intra-chain mechanism of energy transfer so it is crucial to prevent aggregation to decrease the contribution from interchain mechanism. It is known that CPEs dissolved in polar solvents tend to self-assemble into aggregates,\textsuperscript{34,101} with the degree of aggregation depending on the charge density of the polymer. CPEs being investigated here have highly charged branched side-groups in an attempt to diminish aggregation.\textsuperscript{191}

The structure of the novel CPEs with highly charged branched side chains, which were synthesized by our collaborators, are given in Figure 5-1.\textsuperscript{104} The polymer exhibits two branched ionic side-groups, each consisting of triad of carboxylate groups yielding six negatively charged groups per repeating unit. The bulky and charged side-groups are expected to decrease hydrophobic interactions ($\pi$-stacking) by increasing the electrostatic repulsion, and improving solubility in polar solvents.\textsuperscript{104} The different arylene units in the backbone enable tuning of the HOMO-LUMO gap. CPEs are named according to the arylene groups in their backbone structures and the side-groups. The structure in Figure 5-1 A is labeled as PPE$^d$CO$_2$ as PPE stands for poly(phenylene ethynylene)backbone and the subscript $d$ used to distinguish branched or dendritic side-groups. The abbreviation BDT is used for benzathiadiazole group of the second CPE.
being investigated. BDT-PPE$_d$CO$_2^-$ has a benzathiadiazole group instead of a second phenyl ring. Briefly, the difference between PPE$_d$CO$_2^-$ and BDT-PPE$_d$CO$_2$Na polymers lies in their backbone that makes their colors and other photophysical properties different.

![Figure 5-1. Structures of conjugated polyelectrolytes (CPEs). A) PPE$_d$CO$_2^-$ and B) BDT-PPE$_d$CO$_2^-$.](image)

The absorption and emission spectra of CPEs with dendritic side-groups are given in Figure 5-2. CPEs having the same backbone but linear side-groups were synthesized and characterized by Zhao et al.$^{84}$ The CPEs with dendritic side-groups are found to be similar to CPEs with linear side chains$^{84}$ except for the hypsochromic shift in the absorption spectrum (15-22 nm). This is attributed to less coplanarity or increased twisting in the backbone due to increased charge density.$^{104}$ On the other hand, this hypsochromic shift is not observed in the emission spectrum. The lack of energy difference in emission bands indicates that in excited-state geometry the same delocalization lengths as CPEs with linear side-groups are recovered.$^{104}$
The presence of BDT group in the backbone has an important influence on the photophysical properties of the CPEs. BDT groups act as an electron acceptor and increase the charge transfer character of the lowest excited state of the BDT-PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−}. The emission spectrum BDT-PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−} presents a broad featureless band due to the charge transfer character. Similar effects were observed by Zhao et al. when phenyl ring was replaced by BDT in polyelectrolytes with linear side-groups.\textsuperscript{84} The steady-state absorption and emission spectra indicates that the optical properties of the CPEs are mainly determined by the conjugated backbone and they are slightly modified by the side-groups.

PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−} and BDT-PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−} are soluble in polar solvents including water and methanol, and their aggregation tendency is found to be minimal in methanol.\textsuperscript{104} The polyionic side-groups induce torsional strain, which minimizes coplanarization and π-stacking. The electrostatic repulsion among the dendritic side-groups suppresses aggregation tendency. These polyelectrolytes are chosen for studying the intrachain energy-transfer mechanism because of their decreased tendency for aggregation.
In previous studies, it was observed that the aggregation state of the CPEs strongly depends on protonation or deprotonation of the ionic side-groups.\textsuperscript{100,192} At low pH conditions, some of the carboxylate groups can be protonated and the electrostatic repulsion among the side-groups can be decreased which results in aggregation.\textsuperscript{104} Aggregation can be probed by absorption, emission or excitation spectra.

![Figure 5-3](image)

Figure 5-3. Steady-state excitation spectra of 1 \( \mu \)M PPE\textsuperscript{dCO\textsubscript{2}} in methanol detected at 450 nm (black), 500 nm (red), 550 nm (green), 575 nm (blue) and 600 nm (purple) A) stored at room temperature B) after addition of a small aliquot of NaOH to prevent aggregation

Hardison et al. used steady-state excitation spectra to detect aggregation in CPE solutions.\textsuperscript{142} Excitation spectra detected at different emission wavelengths were found to be more sensitive technique than absorption and emission spectra for detection of mixtures of aggregates and isolated CPE chains. As an example, excitation spectrum of PPE\textsuperscript{dCO\textsubscript{2}} prepared from a stock solution (1mM) in water (by diluting in methanol to yield 1 \( \mu \)M) is collected after a couple of hours at room temperature (Figure 5-3 A). The excitation spectra collected at different wavelengths indicates presence of aggregation. The excitation spectra collected at longer wavelengths are red-shifted and broader compared to excitation spectra collected at shorter wavelengths. At long detection
wavelengths, the aggregated states are probed. If the polyelectrolyte solution is prepared by adding small aliquot of NaOH, the aggregation effects are not observed in the excitation spectra even couple of days after preparation of the solutions (Figure 5-3 B). Thus, it is important to control protonation state of the polyelectrolytes to suppress aggregation. The excitation spectrum is a sensitive tool to probe aggregation, which is also used confirm that the samples used for the time-resolved studies are not aggregated.

**Steady-State Measurements**

**Quenching Experiments**

The amplified quenching properties of CPEs with dendritic side-groups are investigated by using fluorescent dye molecules as energy-transfer acceptors. The quenching efficiency is affected by many factors including aggregation and stability of the complex formed between CPE and quencher. The effect of side chains on quenching efficiency is investigated by using oppositely charged cyanine dyes. The quenching efficiency is expected to increase with increasing overlap between emission spectrum of the CPE and absorption spectrum of dye.

Quenching experiments are done microtitrating a 1 μM of CPE solution in methanol (containing 100 equivalents of NaOH) with a solution of an cationic acceptor while recording the emission spectrum.

The Stern-Volmer equation is used for quantitative evaluation of quenching efficiency. The efficiency is calculated by plotting the concentration of the quencher versus the ratio of intensity of emission in presence (I) and absence of the quencher (I₀) and K_{SV} values are calculated from the slopes of the linear fits.
In order to examine the effect of the spectral overlap on the quenching efficiency, three different dyes in a cyanine dye family are used. DOC (3-3’-Diethyloxacarbocyanine Iodide), DODC (3-3’-Diethyloxadacarbocyanine Iodide) and DOTC (3-3’-Diethyloxadacarbocyanine Iodide) have very similar structures (Figure 5-4 A-C) with different conjugation lengths yielding monotonically red-shifted spectral features. The spectral overlaps of the three dyes are depicted by shaded areas in Figure 5-4. The spectral overlap decreases gradually from DOC to DOTC with values listed in Table 5-1.

![Figure 5-4](image)

Figure 5-4. Structures of cyanine dyes A) DOC B) DODC and C) DOTC, steady-state absorption (dashed) and emission (solid) spectra of PPE\textsuperscript{20}CO\textsubscript{2} (in black) and cyanine dyes (in red). The spectral overlaps are shaded by D) yellow (DOC), F) magenta (DODC) and G) blue (DOTC).

Figure 5-5 shows the steady-state emission spectra as the cyanine dyes are added to the polyelectrolyte solution. The intensity of polymer emission is quenched as the sensitized emission increases revealing an isosbestic point in the case of DOC. The sensitized emission from DOTC is not observed due to instrumental detection limits. Stern-Volmer constants are given in Table 5-1. Although DOC has a greater spectral
overlap it presents a smaller Stern-Volmer constant indicating less efficient quenching. The energy transfer does not follow the same trend as the spectral overlap, which means that an additional mechanism gives rise to efficient energy transfer. On the other hand, ionic association between polymer and dye plays a significant role in the energy transfer. As the complex is formed, there can be better hydrophobic interactions between the longer carbon chain dyes and the polymer PPE backbone (Figure 5-4 for structures).

![Figure 5-5](image)

**Figure 5-5.** Steady-state emission spectra of PPE\textsuperscript{d}CO\textsubscript{2} with increasing concentration of A) DOC, B) DODC, and C) DOTC. The insets are show Stern-Volmer plots.

The fluorescence quenching can also occur via electron transfer processes. To probe this effect methyl viologen (MV\textsuperscript{2+}, a known electron transfer divalent quencher) is used as a quencher for both PPE\textsuperscript{d}CO\textsubscript{2} and BTD-PPE\textsuperscript{d}CO\textsubscript{2}. Both of the polymers show very efficient quenching with large Stern-Volmer constants (Table 5-2). As the quencher is added to the CPE solutions, the absorption spectrum shifts to red and becomes narrower. These changes are attributed to quencher-induced polymer aggregation, which was also observed with other CPEs.\textsuperscript{97,99,102,103,106,110} Polyvalent quencher molecules enable ionic bridging between chains of polyelectrolytes and formation of interchain excimer like states. Increased efficiencies of quenching are due to lower radiative rates for the aggregated states compared to intrachain excitons.

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The Stern-Volmer plot for PPE$^d$CO$_2^-$ is superlinear even in very dilute concentration ranges indicating presence of both static and dynamic quenching mechanisms. In order to take into account the dynamic quenching mechanism and statics mechanism, the following form of the Stern-Volmer equation is used for the superlinear fitting.

$$\frac{I_0}{I} = (1 + K_{SV}[Q]) \exp(V_q N_a[Q])$$

The equation utilizes a model in which quenching is possible if the acceptor molecule is located within a sphere called sphere of effective quenching ($V_q$). The Stern-Volmer equation for this distribution is calculated by using a Possion distribution for the probability of having a quencher within the active sphere. In this model, the fluorophore and the quencher cannot change their positions relative to each other during the excited-state lifetime. The high efficiency of quenching for PPE$^d$CO$_2^-$ with MV$^{2+}$ is due to induced aggregation, which enables quenching of inter-chain excitons and enlarges the sphere of effective quenching. The BTD-PPE$^d$CO$_2^-$ features linear Stern-Volmer plots over the same concentration range with very high association constant ($9.5 \times 10^7$).
Figure 5-7. Steady-state quenching of $\text{PPE}^\text{d} \text{CO}_2^-$ (in black) with HMIDC. A) Absorption (dashed) and the emission (solid) spectra of $\text{PPE}^\text{d} \text{CO}_2^-$ (in black) and HMIDC (in red). B) Emission spectrum of $\text{PPE}^\text{d} \text{CO}_2^-$ with increasing HMIDC concentration (from black to orange), the inset shows corresponding Stern-Volmer plot.

Quenching experiments is also done by using the HMIDC (1,1',3,3',3',3'-Hexamethylindodicarbocyanine Iodide) as an acceptor since it was also used for quenching studies on CPEs with linear side-groups. The absorption spectrum of HMIDC overlaps well with the emission spectrum of the $\text{PPE}^\text{d} \text{CO}_2^-$ (shaded area in Figure 5-7) allowing energy transfer from polyelectrolyte to the dye. Figure 5-7 B shows the decrease in emission band from the polyelectrolyte (425 nm) and the simultaneous increase of sensitized emission from the dye (675 nm) with increasing concentration of the quencher.

The Stern-Volmer plot $\text{PPE}^\text{d} \text{CO}_2^-$ and HMIDC is given in the inset of Figure 5-7. At high concentrations of the quencher (up to 40 μM), upward Stern-Volmer plots (super-linear) are observed which indicates presence of both static and dynamic mechanisms of quenching. Thus, for characterization of Stern-Volmer constants, the quencher concentration range is kept low to maintain linearity (up to 8 μM). $K_{SV}$ is found to be 7.2
$10^4$ M$^{-1}$ which is higher than expected if the quenching was only diffusion controlled (dynamic quenching). This high value of $K_{sv}$ is attributed to a complex formation between polymer and charged dye. In comparison with CPEs with linear side chain (PPESO3, $K_{sv}$=1.1 x $10^6$ M$^{-1}$), Stern-Volmer constant is smaller which is expected since the side-groups of the CPEs suppress the aggregation. However, the ionic strengths is also increased due to addition of NaOH to decrease aggregation. The efficiency of CPE's fluorescence quenching is known to be affected by ionic strength.$^{105,193,194}$ In a higher ionic strength medium, the quenching efficiency is lowered. Thus, the decreased $K_{sv}$ values cannot be attributed to only suppressed aggregation.

**Anisotropy Experiments**

In addition to quenching experiments, anisotropy measurements were carried out to gain information about rotational diffusion and energy transfer, which are related to rigidity and aggregation. The details of steady-state anisotropy measurements are explained in Chapter 2.

Figure 5-8 shows the steady-state excitation and emission anisotropy of PPE$^d$CO$_2^-$ (1µM CPE with 100 equivalents of NaOH) are plotted as a function of wavelength. The excitation anisotropy is detected from 300 nm to 420 nm by detecting the emission at 450 nm. The emission anisotropy is collected in the range of 420 nm to 575 nm following excitation at 400 nm.

The effect of solvation on the anisotropy signal is examined. The absorption and emission spectra of PPE$^d$CO$_2^-$ are given in panel B to remind which transitions are observed in the corresponding wavelength region.
Figure 5-8. Steady-state anisotropy of PPE\(^{6}\)CO\(_{2}^{-}\) in methanol (black), methanol water mixtures, 3:1 (red), 1:1 (green), 1:3 (blue), water (cyan). A) Excitation anisotropy detected at 450 nm and emission anisotropy following excitation at 400 nm B) Absorption (solid) and emission spectra (dash).

In methanol (black), anisotropy is 0.17±0.02. The excitation anisotropy is almost flat except a gradual increase at longer wavelengths. Smaller values of anisotropy for excitation wavelengths further away from detection are typical for many fluorophores. The same electronic transition, which is longest-wavelength absorption band, has the highest anisotropy since the dipole moments are nearly collinear. The anisotropy experiments are repeated introducing water as a solvent. The increasing population of water in the methanol-water mixtures results in increased anisotropy caused by formation of aggregates with ordered structure. It is known from previous studies on CPEs with linear side chains (PPECO\(_{2}\)) that CPEs have a tendency to form compact aggregates in water since they are not as well solvated as in methanol.\(^{102}\) The difference in solvation between water and methanol are less pronounced in CPE with dendritic side chains compared to linear side chains.\(^{104}\)
For large dendrimers, where the loss of anisotropy due to molecular rotations is minimal, the energy transfer becomes a factor affecting the anisotropy along with aggregation. It is possible to observe affects of energy transfer on anisotropy by using an external quencher molecule. The memory of the initial polarization orientation can be preserved during the energy-transfer process. Thus, anisotropy is a powerful tool to study energy transfer.

Energy transfer from PPE\textsuperscript{d}CO\textsubscript{2}Na to HMIDC is studied by using steady-state excitation and emission anisotropy measurements. The anisotropy measurements were done on solutions of i) pure PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} (10 μM containing 100 eq NaOH) ii) HMIDC (22.5 μM ), and iii) their mixture (Figure 5-9). There are two forms of emission detected emission $\lambda<600$ nm that arises from direct excitation of PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} and emission $\lambda>600$ nm that can follow direct excitation of HMIDC or be sensitized following excitation of PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-}.

In Figure 5-9, the excitation anisotropy (panel A) and the corresponding excitation spectra (panel B) are depicted. The excitation spectra and anisotropy of pure solution of PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} is shown in green and the mixture (PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} and HMIDC) is shown in red. The excitation spectra are collected at 450 nm, where only PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} emits. The signals correspond to direct emission from the polymer. While the intensity of the excitation spectrum is slightly decreased in the presence of HMIDC, the anisotropy remains the same for both solutions ranging from 0.17 to 0.27. The excitation anisotropy of the mixture is also collected by setting detection wavelength to 675 nm where only HIMIDC emits (black). In the range where the PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} absorbs (350 – 450 nm), sensitized emission is detected and the anisotropy starts at 0.1. When excitation wavelength is at
low-energy edge of the absorption spectrum (450 nm), the maximum anisotropy is observed (0.23), then the anisotropy goes down to 0.03 for direct excitation of HMIDC at 550-600 nm. The anisotropy results for the pure solution of HMIDC gives the same answer as the direct emission from the mixture (blue).

![Figure 5-9](image)

Figure 5-9. Steady-state anisotropy measurements. A) Excitation anisotropy, B) excitation spectra, C) emission anisotropy, and D) emission of spectra of pure PPE$^d$CO$_2^-$ in methanol (green), pure HMIDC (blue) and their mixture by detection of direct emission (red), or sensitized emission (black).

The emission anisotropy (panel C) and the corresponding emission spectra (panel D) of PPE$^d$CO$_2^-$, HMIDC and their mixtures are also given in Figure 5-9. The emission spectra of pure PPE$^d$CO$_2^-$ and the mixture are collected by excitation of PPE$^d$CO$_2^-$ at 400 nm (green and black). The intensity of the emission is decreased in the case of mixture but the anisotropy value is constant ($r= 0.21\pm0.01$) in the region of polymer emission (425-550 nm) and only slightly reduced ($r= 0.16\pm0.03$) when the sensitized emission anisotropy (650-750 nm) is measured. In both cases, the anisotropy is lower than the anisotropy of sensitized emission.

Steady-state anisotropy of HMIDC is very low by itself since it is a small molecule and prone to loss memory of the orientation of polarization by rotational diffusion.
However, the anisotropy obtained in the case of sensitized emission is increased as the polarization information of PPE$^d$CO$_2$ is transferred through the coupling of the transition dipoles. Stern-Volmer constant for quenching of PPE$^d$CO$_2^-$ with HMIDC indicates they form ionic complex with very large association constant (7.2x10$^4$). In the mixture solutions of PPE$^d$CO$_2$ and HMIDC, there are tightly-bound dye molecules to the polyelectrolyte and the free ones. When we detect the sensitized emission, the signal is originating from the tightly-bound dye molecules. The rotational motion of these molecules is expected to be restrained compared to the free population in solution resulting in decreased depolarization due to rotational diffusion.

The sensitive anisotropy measurements can also be used to quantify the relative population of bonded and free dye molecules in the solution. Under the assumption that the anisotropy information is transferred completely to HMIDC and losses are only due to the presence of free dye molecules, the averaged anisotropy can be written as

\[ \bar{r} = f_1 r_{\text{free}} + f_2 r_{\text{bonded}}. \]

In this case, the average anisotropy as a product of population ratio and individuals anisotropies of free and bonded dyes. The anisotropy of the free HMIDC is approximated by using the pure dye solution ($r_{\text{free}} = 0.003$), and the bonded ones are approximated by using pure PPE$^d$CO$_2^-$ ($r_{\text{bonded}} = 0.23$). The average anisotropy is approximated by using the value of the emission anisotropy of the mixture ($r_0 = 0.12$). The bonded dyes are found to be the 45% of the quencher population. By using the Stern-Volmer constant, which is equal to the association constant for complex formation, the percentage of bonded molecules is found to be 42%. The discrepancy can be caused by additional factors, which is not taken into account for our calculations such as inter and intra chain transport of energy within the polyelectrolyte chains. The
anisotropy measurements provide not only a qualitative probe for energy transfer but also a quantitative tool for population analysis.

**Time-resolved Measurements**

In order to investigate further the mechanism of energy transfer from the polyelectrolyte to the cyanine dye, the time-resolved emission of were PPE$^{d}$CO$_2^-$ and HMIDC solutions were collected by the up-conversion method. As shown before, the absorption and emission bands of PPE$^{d}$CO$_2^-$ and HMIDC are well separated, while the overlap between emission of PPE$^{d}$CO$_2^-$ and absorption of HMIDC enables energy transfer ($J=6.9 \times 10^{14} \text{M}^{-1}\text{cm}^{-1}\text{nm}^4$).

For this experiments, the concentration of PPE$^{d}$CO$_2^-$ in methanol is kept (10 μM and contains 100 eq of NaOH) while the concentration of the HMIDC is varied to yield different the quenching efficiencies (from 0% to 95%). The quenching efficiency is calculated by the following formula, $f_q = (1 - I/I_0) \times 100$, where $I_0$ and $I$ are the steady-state emission intensities in the absence and presence of HMIDC, respectively. The solutions are excited at 420 nm to ensure excitation of only PPE$^{d}$CO$_2^-$. Figure 5-10 shows time-resolved fluorescence collected at 450 nm, where the signal originates from PPE$^{d}$CO$_2^-$.  

In order to compare the relative intensities of the fluorescence decays, they are collected at identical detection settings and experimental conditions. The measurements are done consecutively and the laser power is recorded continuously. The steady-state spectra are recorded before, after and during the measurements to ensure photostability. It is clear from the time-resolved measurements that the initial amplitude of the fluorescence decays is reduced with the addition of HMIDC (static quenching).
and the decays become faster with increasing concentration of HMIDC (dynamic component).

In order to have a better observation of the changes in the decay kinetics, Figure 5-10 B shows the fluorescence intensity of PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} and HMIDC mixtures over the fluorescence intensity of pure PPE\textsuperscript{d}CO\textsubscript{2} in methanol. From the decays of these ratios, we can see that 25% quenched-solution is almost constant while the other solutions of (50-95% quenched-solutions) have an additional dynamical component.

![Fluorescence decays](image)

Figure 5-10. Fluorescence decays of quenched solution of PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{-} in methanol and their ratios to pure solutions. A) Fluorescence decays following excitation at 420 nm and detected at 450 nm. In the absence of quencher (black), after addition of HIMDC, 20% (red), 50% (green), 90% (blue) and 95% (cyan) quenched solutions. B) The ratio of fluorescence intensity in the presence of quencher to the fluorescence intensity of pure solution. The fluorescence decays are fitted using sum of exponentials ($\tau_1=1.21$ ps, $\tau_2=11$ ps, $\tau_3=200$ ps).

The features observed in the fluorescence decays indicate presence of two different regimes for energy transfer. At very early times (within the 200 fs time resolution of the instrument), the fluorescence is quenched significantly. This fast mechanism is called prompt quenching by Kleiman and coworkers.\textsuperscript{103} On longer time scale (ps), there is a time dependent component, which depends on the concentration
of the quencher. The dynamic component indicates presence of an additional energy-transfer process, which can be attributed to the diffusion of exciton on CPE chain before it encounters an HMIDC binding site. For the fittings of the fluorescence decays sum of exponentials was used. The fitting parameters for the data set in Figure 5-10 are given in Table 5-3. The fluorescence decays of PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−} and HMIDC solutions have three time components (τ\textsubscript{1} = 1.21 ps, τ\textsubscript{2} = 11 ps, τ\textsubscript{3} = 200 ps). The fractional amplitude of the shortest time (1.21 ps) component increases with increasing concentration of HMIDC while the longest time component (200 ps) have smaller fractional amplitudes at higher concentrations of HMIDC.

The reduction in initial amplitude of fluorescence due to prompt quenching provides information about contribution of prompt mechanism to the overall quenching at steady state. For example, 90%-quenched solution at steady state (green) has 40% contribution from prompt quenching mechanism and 40% of the quenching occurs via dynamic mechanism. The CPEs linear side chains (PPESO3) have higher contributions from prompt quenching mechanism (60% contribution in the case of 90%-quenched solution) to overall quenching than PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−}.\textsuperscript{98,103} Moreover, the dynamic quenching mechanism is faster for PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−} (almost completed in 10 ps) than the PPESO3 (in 20 ps). All these differences between PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−} and PPESO3 energy-transfer characteristics reveal the importance end-groups. We believe that the end-groups determine distribution of conjugation lengths within the CPE chain affecting exciton diffusion rates.

The energy-transfer kinetic from PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−} to HMIDC can be further investigated by detecting of sensitized emission at 675 nm (Figure 5-11). The steady-state
quenching efficiency of the solutions used for these experiments are 75% and 90%. The time-resolved fluorescence of HMIDC shows an instantaneous rise followed by and additional rise component on picosecond time-scale. This is consistent with prompt transfer followed by excitation diffusion on the CPE chain towards HMIDC site.

Figure 5-11. Fluorescence decays of HMIDC in the presence of PPE$^{d}$CO$_2^-$ following excitation at 400 nm and detected at 675 nm. The steady-state quenching efficiency of solutions are 75% (blue) and 90% (cyan). The fittings are done using sum of exponentials.

The rise time of the HMIDC emission is characterized with sum of exponentials, where one of the components is 290 ps lifetime of HMIDC. While the natural lifetime is used as a fixed parameter, the rise time is optimized. Results from these fittings with amplitude fractions are given in Table 5-4. The acceptor kinetics are also fit by sum of exponential functions.

The presence of rise time confirms the energy transfer from PPE$^{d}$CO$_2^-$ to the HMIDC. The prompt energy transfer takes place within the instrument response function. The rise time for 75%-quenched solution is found to be longer than 90%-

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quenched solution. For higher HMIDC concentration, the quenching sites are more closely spaced so it can take shorter time for excitons to encounter a quenching site.

Although, the general behavior of PPE\textsuperscript{d}CO\textsubscript{2} is similar to CPEs with linear side chains, the contributions of dynamic and prompt mechanisms differ significantly. The side-groups are believed to be affecting the energy-transfer kinetics considerably, albeit in an indirect manner. Their characteristics determine the conjugation length of the CPEs by allowing or restricting the twisting of PE units. The distribution of the conjugation lengths is known to be an important factor in the exciton diffusion rate. Briefly, the energy-transfer kinetics are affected by not only aggregation but also the confirmations of the PE units. The dendritic side chains are found to suppress aggregation but they also affect distribution of different conjugation lengths causing faster dynamic quenching.

Table 5-1. Stern-Volmer constants for cyanine dyes with PPE\textsuperscript{d}CO\textsubscript{2}\textsuperscript{−}

<table>
<thead>
<tr>
<th>Quencher</th>
<th>J (M\textsuperscript{−1}cm\textsuperscript{−1}nm\textsuperscript{4})</th>
<th>R\textsubscript{0} (Å)</th>
<th>Stern-Volmer Constant (M\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>2.0 x 10\textsuperscript{15}</td>
<td>40</td>
<td>1.7 x 10\textsuperscript{5}</td>
</tr>
<tr>
<td>DODC</td>
<td>1.2 x 10\textsuperscript{15}</td>
<td>37</td>
<td>1.3 x 10\textsuperscript{5}</td>
</tr>
<tr>
<td>DOTC</td>
<td>4.6 x 10\textsuperscript{14}</td>
<td>34</td>
<td>2.4 x 10\textsuperscript{5}</td>
</tr>
<tr>
<td>HMIDC</td>
<td>6.9 x 10\textsuperscript{14}</td>
<td>34</td>
<td>7.2 x 10\textsuperscript{4}</td>
</tr>
</tbody>
</table>

Table 5-2. Stern-Volmer constants for MV\textsuperscript{2+}

<table>
<thead>
<tr>
<th>CPE\textsuperscript{d}CO\textsubscript{2}−</th>
<th>V\textsubscript{d}N\textsubscript{a}</th>
<th>Stern-Volmer Constant (M\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPE\textsuperscript{d}CO\textsubscript{2}−</td>
<td>3.7 x 10\textsuperscript{7}</td>
<td>3.0 x 10\textsuperscript{6}</td>
</tr>
<tr>
<td>BTD-PPE\textsuperscript{d}CO\textsubscript{2}−</td>
<td>9.5 x 10\textsuperscript{7}</td>
<td>9.5 x 10\textsuperscript{7}</td>
</tr>
</tbody>
</table>

Table 5-3. Fractional amplitudes (%) of fluorescence decays of PPE\textsuperscript{d}CO\textsubscript{2}− in the presence of HIMDC.

<table>
<thead>
<tr>
<th>F\textsubscript{q}</th>
<th><a href="%C2%B5M">HIMDC</a></th>
<th>α\textsubscript{1} (τ\textsubscript{1}= 1.21 ps)</th>
<th>α\textsubscript{2} (τ\textsubscript{2}= 11 ps)</th>
<th>α\textsubscript{3} (τ\textsubscript{3}= 200 ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>16</td>
<td>28</td>
<td>55</td>
</tr>
<tr>
<td>0.25</td>
<td>22.5</td>
<td>20</td>
<td>24</td>
<td>55</td>
</tr>
<tr>
<td>0.50</td>
<td>45</td>
<td>26</td>
<td>33</td>
<td>45</td>
</tr>
<tr>
<td>0.90</td>
<td>150</td>
<td>48</td>
<td>32</td>
<td>20</td>
</tr>
<tr>
<td>0.95</td>
<td>337</td>
<td>57</td>
<td>30</td>
<td>13</td>
</tr>
</tbody>
</table>
Table 5-4. Fractional amplitudes (%) of fluorescence decays of HIMDC in the presence of PPE\textsuperscript{d}CO\textsubscript{2}. Fractional amplitudes for rise times are given in red.

<table>
<thead>
<tr>
<th>$F_q$</th>
<th>[HIMDC] (μM)</th>
<th>$\alpha_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$\alpha_2$ (ps)</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>70</td>
<td>0.26</td>
<td>8.3</td>
<td>0.74</td>
<td>290</td>
</tr>
<tr>
<td>0.90</td>
<td>150</td>
<td>0.25</td>
<td>4.1</td>
<td>0.75</td>
<td>290</td>
</tr>
</tbody>
</table>
CHAPTER 6
CONCLUSION

In nature, photosynthesis is a key process that utilizes solar energy to maintain life. Photosynthesis starts with collection of solar energy and transportation of the energy to chemical reaction centers. The scientists believe that the promising solution to current energy problem is mimicking the nature. Since the first step in energy conversion is collection and transportation of light energy, efficient light harvesters are required for synthetic systems. \(\pi\)-conjugated materials are one of the most promising candidates for light-harvesting applications. It is important to understand the energy-transfer properties of these materials to design better candidates for applications.

Two different types of novel \(\pi\)-conjugated systems are studied in this work: conjugated polyelectrolytes (CPEs), which are linear polymers and CPEs with dendritic structures (CPE-Ds). These materials consist of conjugated backbones and branched end- or side-groups. These groups provide better solubility, and suppressed aggregation. Photophysical studies are performed for characterization of intra-molecular and intermolecular energy transfer in these systems.

Intra-molecular energy transfer is explored in two different families of extended dendrimers by using time-resolved and steady-state measurements. The first family we worked on consists of all phenylene-ethynylene (PE) backbone and branched end-groups. The second family of extended dendrimers contains a thiophene at the core instead of one of the phenyl rings (Th-dendrimers). Both families have two available forms, ester (soluble in non-polar solvents) and ionic forms (soluble in polar solvents). The ester form of the dendrimers is deprotected to obtain ionic forms (CPE-Ds).
Solubility in polar solvents is a desirable property since it is easier process them into films for prospective applications.

The first family of CPE-Ds investigated in this dissertation consists of 3-ring PE units at their core and 2-ring PE units at their periphery (Ph-dendrimers). The longer conjugation length of PE units at the core provides a lower band gap compared to the peripheral branches. There is an intra-molecular energy gradient giving rise to intra-molecular energy transfer.

We used model compounds to understand properties of Ph-dendrimers. The model compounds for periphery of dendrimers consist of 2-ring PE units and three generations of these dendrimers are available. Since the conjugation length is the same for core and periphery of these dendrimers, there is no intra-molecular energy gradient (compact). The model compounds for the core part the extended dendrimers are para-TPA and first generation of extended dendrimers. The absorption and emission spectrum of model compounds were used to approximate steady-state spectra of donor and acceptor moieties of extended dendrimers. The model compounds provide good matches for the overall properties of extended dendrimers. They revealed that the excitations are localized at meta branching points in ground-state geometry but there is a fast energy delocalization in the excited state. There is a strong coupling between PE units having the same conjugation length. The ionic forms of the model compounds were also studied to understand effects of charged end-groups on photophysical properties. The first generation of the ionic forms of the model compounds showed formation of H-aggregates. Higher generations of the compacts dendrimers suffer from intra-molecular aggregation.
Th-dendrimers consist of the same periphery with Ph-dendrimers, but the core structure is different from Ph-dendrimers. The same compounds (compact dendrimers) are used as a model for the periphery. Ph-Th-Ph and the first generation of the Th-dendrimers are used as model compounds for the core structure. The presence of the thiophene groups at the core lowers the band gap of the core compared to Ph-dendrimers and increases the energy gradient.

The excited-state kinetics of Th-dendrimers in ester form are affected by the twisting of periphery which is observed as a 44 ps time-component in fluorescence decays. The fractional amplitude of this time-component depends on the detection wavelength. The ester forms of the Ph-dendrimers do not have similar time-constant that has wavelength-dependent contributions. The twisting of the branches is not observed by fluorescence decays for Ph-dendrimers. We believe that thiophenes at the core structures make Th-dendrimers more flexible.

Fluorescence decays of ionic forms of the Th- and Ph-dendrimers (CPE-Ds) depend on the detection wavelength in pico to nanosecond time-scale. Global analysis is used for determination of the time-constants of the fluorescence decays at different detection wavelengths. The longer time-components have increased fractional amplitudes at longer wavelengths, which is an indication of aggregation. We believe that there are two different types of aggregates formation for CPE-Ds. The first generation of the dendrimers (model compounds for core) forms inter-molecular H-aggregates and the higher generations have tendency for intra-molecular aggregation. H-aggregate formation is more distinct for the first generation of Ph dendrimers (42 nm blue-shift in absorption spectrum). The absorption spectra of the first generation of the Th-
dendrimers is not significantly blue-shifted compared to the ester form. We attributed this behavior to less planar structure of the first generation of Th-dendrimers. In the presence of thiophene groups, the face to face π stacking is not favored. However, the higher generations of the Th-dendrimers is believed to be more prone to intra-molecular aggregation than Ph-dendrimers since they have more flexible structures.

We investigated intra-molecular energy-transfer kinetics of CPE-Ds and the ester forms by ultrafast up-conversion spectroscopy. The fast energy-transfer kinetics yield a highly efficient light-harvester in the ester forms. In the sub-picosecond time-scale, excitation of core results in fluorescence decays having different kinetics at different detection wavelengths. At the blue-edge of the emission spectrum, there is a fast decay-time, which becomes a rise time at the red-edge of the spectrum. This component is attributed to energy transfer from core to periphery. We used kinetic models to analyze energy-transfer data. At very early times after the excitation (up to 5 ps), the individual contributions of excited state of donor and acceptor states to the total fluorescence signals are calculated. The contributions of excited state of donor are very high at short wavelengths and they decrease at longer wavelengths.

The rate-constants for energy transfer are obtained for ionic and ester forms of the Th and Ph-dendrimers. They are given in Figure 6-1 A. The rate-constants for ester forms are shown in red, and ionic forms are shown in blue. They are labeled according to their generation (Ph-2: Ph_{3,2}-PG-2(red)/ Ph_{3,2}-G-2(blue)). Th-dendrimers have slower energy-transfer rates than the Ph-dendrimers, which is attributed to weaker coupling between periphery and core. The weaker coupling is also reflected in calculated
interaction energies (Figure 6-1 B). Th-dendrimers have considerably lower interaction energies than the Ph-dendrimers.

![Figure 6-1. Comparison of different families of dendrimers in ester and ionic forms. A) Comparison of energy-transfer rates and B) calculated interaction energies of Ph- and Th-dendrimers. The ester forms are shown in red and ionic forms are shown in blue.]

The energy-transfer rates of the third generations of the dendrimers are slower than the second generations. The same trend is observed for both Th- and Ph-dendrimers in ionic and ester forms. This behavior is attributed to the longer distances from periphery to core for higher generations.

When we compare the energy-transfer rate-constants of the ester and ionic forms, ionic forms have faster rates than the ester forms. The rate-constants of the ionic forms of the Th-dendrimers affected more drastically by introduction of charged end-groups. Both of the second and third generations have significantly faster energy-transfer rates compared to their ester analogs. For the Ph-dendrimers, the second generation has similar rates for both forms. The drastic effects of ionic end-groups on Th-dendrimers are probably due to their flexible structure. Since they are more flexible than Ph-dendrimers, intra-molecular aggregation can be more dominant, which causes collapse of dendrimers and shortening of the distance from periphery to core. The shorter
distances allow larger coupling between the donor and acceptor in the ionic forms compared to ester analogs.

Linear CPEs are very efficient energy transporting materials but they are polydisperse (different conjugation lengths due to twisting, coiling, and etc.) so their photophysical properties and excited-state kinetics are complicated. The energy transfer and photophysical properties of linear CPEs having branched highly charged end-groups were studied by using steady-state and time-resolved spectroscopy including anisotropy. The tendency for aggregation found to be less than the CPEs with linear side-groups. The suppressed aggregation is attributed to increased repulsion of side-groups. They are capable of amplified quenching and have potential for sensor applications. In water, they form more ordered aggregate structures. The existence of energy transfer to external dye is shown by steady-state anisotropy experiments. The quenching occurs via two mechanisms prompt energy transfer, which is very fast, and a dynamic mechanism. The dynamic component is assigned to exciton diffusion within the dendrimer before it reaches a quenching site.

The well-defined and monodisperse CPE-Ds provide a platform to study intra-chain and inter-molecular energy and electron transfer mechanisms in more complex systems like conjugated polyelectrolytes which were previously investigated. However, it is observed that even dendrimer structures in the ionic form shows complicated behaviors than the ester forms. The presence of the ionic side chains are believed to decrease tendency towards inter-molecular aggregation, but it causes new channels to open up via intra-molecular interaction. Oligomers can be better candidates to be used
as a platform to study energy-transfer mechanisms, since they do not have globular structures.
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BIOGRAPHICAL SKETCH

Sevnur Komurlu was born in Bolu, Turkey where she spent her youth until she started university. After graduating from Izzet Baysal Anatolian High School, she was accepted to the Chemistry Department of Bilkent University (Ankara, Turkey) with a comprehensive scholarship in 2001. She participated a summer internship at the University of Dortmund (Germany) in 2005, to work with Prof. Peter Eilbracht. She graduated with high honors (ranked 1st in the chemistry) in May 2006. With intense physical chemistry background and special interest in photophysics, she came to the University of Florida Chemistry Department in Fall 2006 to begin doctoral studies. Soon after she joined the group of Professor Valeria Kleiman to study energy transfer in conjugated systems.