

Dendrimer Analogues of Linear Molecules to Evaluate Energy and Charge-Transfer Properties

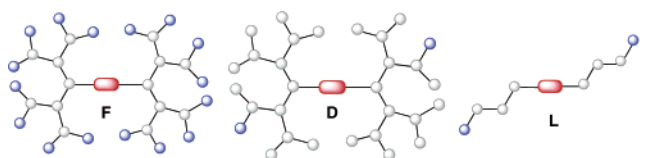
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ABSTRACT



◊ EET / CT donor ◊ EET / CT acceptor ◊ spectator moiety

We have designed and synthesized difunctionalized dendrimers containing two donors in the periphery and an acceptor at the core to serve as scaffolds for comparison with linear analogues to investigate the advantage of dendritic scaffolds for energy and charge transfer. Comparison of these dendrimers with the fully decorated dendrimers provides information on the advantage of chromophore density in energy/charge transfer from periphery to the core.

Multichromophore dendrimers provide the ability to surround a single energy acceptor with a dense periphery of energy donors. These types of structures are of interest as artificial light-harvesting systems for use in solar energy conversion devices.¹ Both conjugated² and nonconjugated³ dendrimers

have been extensively studied for this purpose. Light harvesting represents only the first step in the photosynthetic process, which also involves the creation of a long-lived charge-separated state to convert photon energy into an electrochemical potential. There have been relatively few reports on charge transfer within dendritic architectures in both conjugated⁴ and nonconjugated⁵ systems. To the best of our knowledge, there has been no study that compares dendrimers with the corresponding linear analogues in the context of intramolecular electronic energy transfer (EET) and charge transfer (CT). Such a study has the potential to provide fundamental insights into the possible advantages that dendritic architectures provide for these photoinduced processes. We utilize the combination of donors and acceptors that we have recently shown to exhibit a sequential EET and CT events in dendrimers,⁶ since these provide a unique opportunity to investigate the advantages that dendrimers

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provide in both EET and CT processes. This paper outlines the design and syntheses of the linear molecules and the corresponding dendrimer analogues for a straightforward comparison.

Comparison of dendrimers with linear analogues has been previously done in the context of their physical properties.⁷ However, similar comparison in light-harvesting dendrimers is more complicated. Classical dendrimers with the periphery fully decorated by donor moieties and a single acceptor unit at the core are represented by **F** (see the Abstract for a schematic representation; see Figure 1 for the structures of

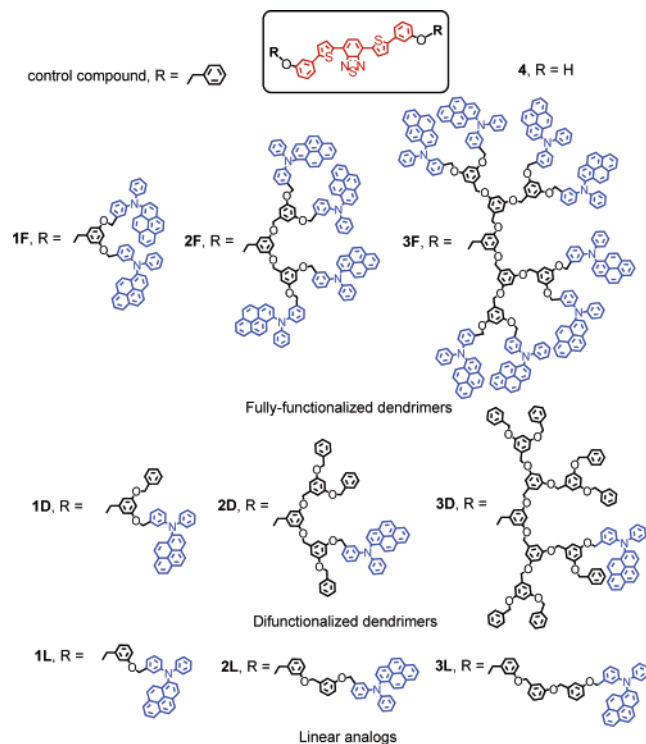


Figure 1. Structures of the **L**, **D**, and **F** molecules.

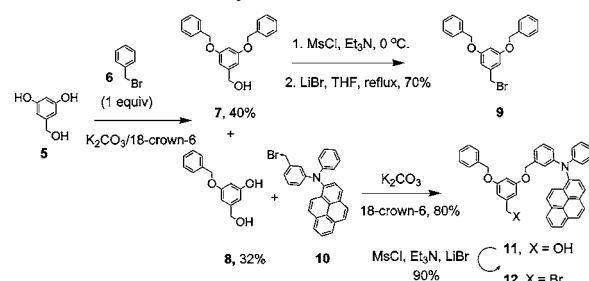
the molecules). Comparison of **F** with the linear analogue **L** accounts for the donor–acceptor distance that dendrimers and the linear oligomers provide but fails to provide the equivalent chromophore densities (number of EET/CT donors vs. acceptor). However, comparison of the dendrimer **D** with a difunctionalized periphery with the linear analogue **L** accounts for both of these factors. In other words, for this study, comparison of **D** and **L** eliminates the chromophore

density variable and directly addresses the advantages of dendritic scaffold in light harvesting. On the other hand, comparison of **F** and **D** provides information on the advantages of chromophore density in dendrimers.

We have synthesized dendrimers that contain diarylamino-pyrene-based units as the donor functionality and a benzthiadiazole-based core as the acceptor. Structures of the fully functionalized dendrimers **1F–3F**, difunctionalized dendrimers **1D–3D**, and the corresponding linear analogues **1L–3L** are shown in Figure 1. The key steps in the syntheses of dendrimers were the repetitive benzylation followed by the bromination of the hydroxymethyl group by using methanesulfonyl chloride, triethylamine, and lithium bromide as reagents. Note that in the syntheses of classical benzyl ether dendrimers, the conversion of the hydroxymethyl moiety to the bromomethyl functionality is achieved using triphenylphosphine and carbontetrabromide (or *N*-bromosuccinimide).⁸ However, when this methodology was repeated in this work, we noticed small peaks in the mass spectra that correspond to $M + 80$ and $M + 160$. This was attributed to the possible aromatic ring bromination, since the reagents above could generate bromonium ions. The presence of bromine atoms could affect our photophysical results, due to the possible heavy atom effect.⁹ By using the synthetic pathways outlined here, the formation of electrophilic Br^+ functionality is avoided, thus obviating the possibility of ring bromination.

Synthesis of difunctionalized dendrimers **D** is nontrivial because only two of the positions in the otherwise identical peripheral moieties contain the diarylamino-pyrene functionality. We used the synthetic methodologies developed in our group to achieve these molecules.¹⁰ To obtain the partially functionalized G-1 dendron **12**, we started with the reaction of 3,5-dihydroxybenzyl alcohol (**5**) with 1 equiv of benzyl bromide (**6**) (Scheme 1). This reaction afforded a mixture

Scheme 1. Synthesis of **G1–D** Dendrons



of the disubstituted dendron **7** and the monosubstituted dendron **8**. Compound **8** was used to synthesize the G-1 dendron **11** by reaction with the bromomethyl-functionalized

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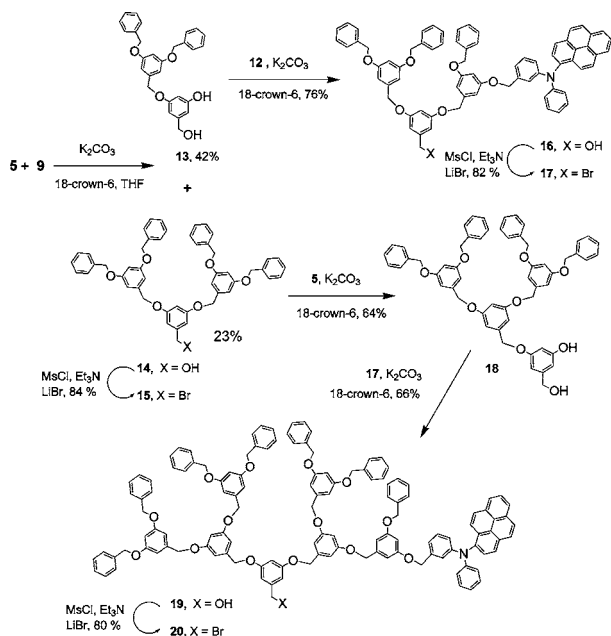
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diarylaminopyrene compound **10**, as shown in Scheme 1. Compound **11** was converted to the dendron **12** using the MsCl/Et₃N/LiBr combination.

On the other hand, the byproduct of the previous reaction, **7**, was used to obtain the next generation of the monofunctionalized dendron. First, the hydroxymethyl compound **7** was converted to the corresponding bromomethyl compound **9**, which was then treated with **5** to obtain a mixture of the monosubstituted **13** and disubstituted **14** dendrons. Dendron **13** was used to synthesize the monofunctionalized G-2 dendron **17** using a pathway similar to that adapted for **12**, as shown in Scheme 2. Similarly, dendron **14** was converted

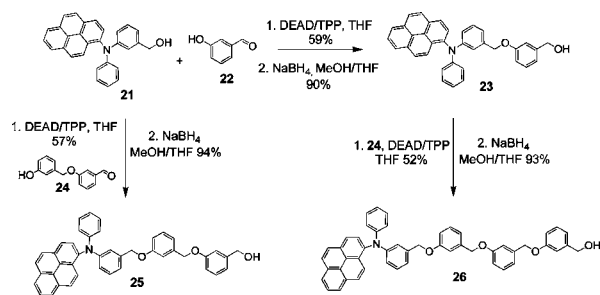
Scheme 2. Synthesis of G2-D and G3-D Dendrons



to the corresponding monofunctionalized G-3 dendron **20** (Scheme 2). Detailed experimental procedures and characterizations for all the compounds are outlined in the Supporting Information.

The linear analogues were synthesized using the Mitsunobu¹¹ reaction as the key step in the synthesis. The hydroxymethyl-functionalized diarylaminopyrene compound **21** was treated with 3-hydroxybenzaldehyde (**22**) under Mitsunobu reaction conditions to give corresponding aldehyde. The aldehyde was then reduced to the alcohol **23**, linear analogue for the G-1 dendron (Scheme 3). Reaction of **21** with the aldehyde **24**, followed by reduction afforded the G-2 analogue **25**, whereas a similar reaction sequence with the compound **23** afforded the G-3 analogue **26**. Note that these

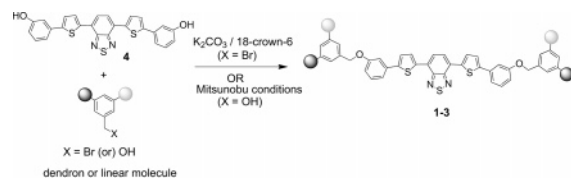
Scheme 3. Synthesis of Linear Analogues



reactions also do not involve the possibility of any heavy atom incorporation into the dendrimers. When we attempted the Mitsunobu reaction for the syntheses of the dendrimers, the yields of reactions were poor, especially at higher generation.

Finally, the targeted dendrimers **1D–3D** were accomplished by the benzylation reaction of the benzthiadiazole core chromophore **4** with the bromomethyl functionalized dendrons **12**, **17**, and **20**, respectively (Scheme 4). Similarly,

Scheme 4. Synthesis of D and L Molecules



the linear analogues **1L–3L** were obtained by a Mitsunobu reaction between **4** and the hydroxymethyl compounds **23**, **25**, and **26**, respectively, as shown in Scheme 4. The dendrons, dendrimers, linear analogues, and key compounds that lead to these molecules were characterized by ¹H and ¹³C NMR and mass spectrometry. Compounds **1D–3D** and **1L–3L** were also analyzed by elemental analysis. For consistency, we also synthesized our previously reported **1F–3F**⁶ using the same synthetic pathway. The purity of these molecules was also analyzed by elemental analysis. While recording MALDI spectra of these compounds particular attention was paid to the presence of even a small peak containing bromine at M + 80 or M + 160. No such peaks were observed even in small amounts. Additionally, the purity of the samples was also further confirmed using gel permeation chromatography.

The three families of molecules were compared using fluorescence spectroscopy. For energy transfer study, we found that, in all these cases, when the donor component of the molecules is excited at 395 nm, the emission arises mainly from the acceptor (Figure 2a,b). This indicates a high degree of energy transfer from the periphery to the core in all families. The differences in energy transfer among generations **1–3** were very similar for all three families within experimental error. We have previously estimated that the Förster radius for this combination of donor and acceptor

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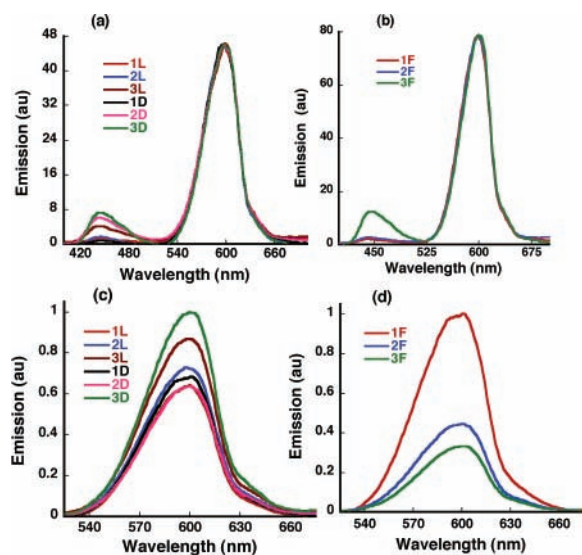


Figure 2. Emission spectra in toluene, $\lambda_{\text{ex}} = 395$ nm, of (a) **1D**–**3D**, **1L**–**3L** and (b) **1F**–**3F**. Spectra of 1.0–3.0 μM solutions are normalized at the λ_{max} of the acceptor. Emission spectra in DMF based on relative quantum yields using ethidium bromide as a reference, $\lambda_{\text{ex}} = 490$ nm of (c) **1D**–**3D**, **1L**–**3L** and (d) **1F**–**3F**.

is approximately 48 Å. Since all these three families have the donors and acceptors within this distance, the energy transfer seems to be efficient in all cases. These results suggest that our dendrimers do not provide an inherent advantage, when one compares the **D** and **L** family of molecules. However, when one compares these molecules with the **F** family of molecules, an obvious advantage of dendritic architectures can be seen when the absorption spectra of these molecules were compared (see Figure 3, for

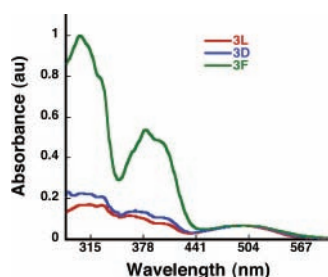


Figure 3. Absorption spectra of **3D**, **3L**, and **3F** (1.0–3.0 μM solutions in toluene normalized at 500 nm).

a comparison of donor vs acceptor in the G-3 molecules). Although the inherent energy transfer efficiencies are similar for these two types of molecules, note that the absorption crosssection of the donor component of the molecule increases with increasing generation in the case of **F** dendrimers, a feature that is obviously not available in linear molecules.

To understand the differences in CT efficiencies in these families, we directly excited the benzthiadiazole-based core

functionality at 490 nm in solvents with different dielectric constants. The fluorescence of the acceptor was quenched relative to a control chromophore that does not contain any diarylaminopyrene moieties (Figure 1). Moreover, the degree of fluorescence quenching increases with increasing solvent polarities indicating the presence of CT. An interesting divergence in generation dependence emerges when the trend in the extent of fluorescence quenching in the three families of molecules are compared. As could be seen in Figure 2c, with increasing generation, the fluorescence quenching decreases in the case of **1L**–**3L** and **1D**–**3D**. This trend is understandable because the distance between the donor and the acceptor increases with increasing generation. Therefore, the efficiency of photoinduced electron transfer is expected to decrease with generation, as observed. However, there is a discernible difference between **L** and **D** families in the third generation where linear analogues seem to provide better CT efficiency than their difunctionalized dendrimer counterparts. This might be due to the steric hindrance generated by the dendritic arms in **D**, which could result in increased donor–acceptor distance and therefore decreased CT efficiency. The generation-dependent trend is opposite in the case of **1F**–**3F**, where the fluorescence quenching increases with increasing generation (Figure 2d). In the case of the **F** dendrimers, even though the donor–acceptor distance increases with increasing generation, the number of donors also doubles with each generation, unlike the **L** and **D** molecules. The observed results indicate that doubling the number of the electron donors around the core chromophore more than compensates for the loss in charge-transfer efficiency due to increased distance in these dendrimers.

In summary, we have designed and synthesized linear versions of dendrimers that could exhibit electronic energy transfer and electron transfer upon excitation of the donor. We have synthesized dendrimer analogues of these linear molecules (difunctionalized dendrimers **D**) to investigate whether there are any architectural advantages to dendrimers in either of these photoinduced processes. Comparison of these two classes of molecules with the more classical fully functionalized dendrimers **F** suggests that dendrimers are indeed advantageous for these processes. The advantage primarily emanates from the number density of the energy or electron donors that one could decorate equidistant from the acceptor core, a feature that is not available in linear molecules. A more quantitative understanding of this structure–property relationship is likely to emerge from time-resolved spectroscopy and molecular modeling studies, which are the focus of current work in our laboratories.

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Supporting Information Available: Experimental details and characterization data for all of the compounds reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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