Designing molecules in which the vectorial motions of charges can be controlled has been of significant research interest in the recent past. Covalent linear arrays of chromophores or other molecular assemblies such as liquid crystals, zeolites, polymers, peptides, and amphiphiles have all been used as components for this purpose. Significant amount of this effort also involved the use of dendrimers as the molecular architecture. The structural feature in which multiple functionalities are present in the periphery that decreases gradually as one moves towards the core renders dendrimers obvious candidates for light harvesting antenna. Most of the efforts reported in the literature are directed towards energy funneling from a chromophore in the periphery to another chromophore at the core of the dendrimer. There are relatively few reports that utilize the dendritic architecture for photoinduced charge separation, an important step in designing materials for photovoltaics. These reports focus mostly on conjugated molecular backbones. Since non-conjugated dendrimer backbones provide the possibility of independently tuning the electronic characteristics of the chromophore and the charge transfer unit and therefore carry out a systematic structure-property relationship study, we designed and synthesized dendrimers represented by the structure **1**. The excited state energies of the diarylaminopyrene units in the periphery and the benzthiadiazole unit at the core are such that an electronic energy transfer (EET) from the periphery to the core is possible. Similarly, the redox potentials of these units suggest that the diarylaminopyrene unit is capable of reducing the excited state of the benzthiadiazole core unit through a CT process.

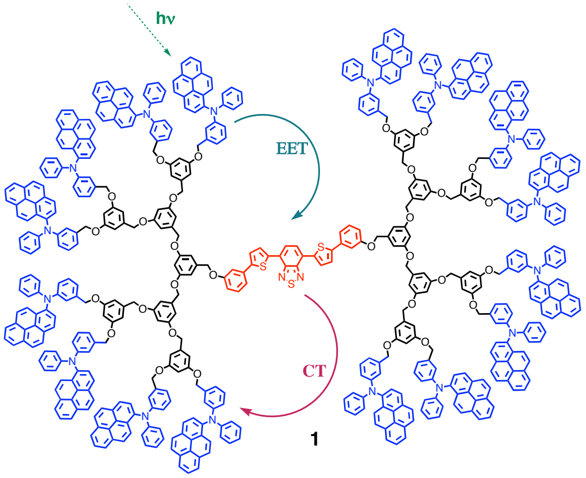

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Figure 1. Structure of a 3rd generation dendrimer that exhibits sequential EET and CT

By studying the photophysical properties of different generations of these dendrimers using steady state and time-resolved spectroscopy, we have found that: (*i*) there is a sequential EET and CT process in these dendrimers as schematically shown in Figure 1. The EET process happens at picosecond time scale, CT quenching of the core excited state happens at nanosecond time scale, and the lifetime of the charge separated state is about a microsecond. (*ii*) The EET efficiency decreases with increasing generation, as one would predict. However, the decrease is smaller than expected where the EET efficiency exhibits $1/r^3$ dependence instead of the expected $1/r^6$ dependence for Förster energy transfer. It is known that the through-space distance between two functionalities in a random coil polymer chain scales as $r^{1/2}$, where ‘r’ is the through-bond distance between the functionalities. Therefore, the observed generation dependence is attributed to the random coil nature or the backfolding of the dendrimers.

We also have been interested in investigating the inherent architectural advantages of dendrimers. In order to test this, we have synthesized the difunctionalized dendrimers exemplified by the G-3 structure **2** (Figure 2). The reasons for synthesizing dendrimers of this type include: (*i*) the relative number of donors *vs.* acceptor is not different from the linear analogs (represented by the corresponding G-3 linear analog **3** in Figure 2) and therefore isolates the number density advantage in the dendrimer from other possible architectural advantages in the comparison study. (*ii*) The relative number of donors *vs.* acceptor does not change with generation number as well. It is 2:1 in all cases.

When comparing EET efficiencies of the molecules of the type **1-3** representing the classical fully functionalized dendrimers, difunctionalized dendrimers, and linear analogs respectively, we found that: (*i*) the EET efficiency is high in all three classes of molecules with only minor differences, since the chromophores are within the Förster radius. (*ii*) A small and subtle advantage that dendrimers also provide is that a fast energy hopping process among the donor chromophores could allow for an efficient EET, since this process allows for sampling through the relative orientations between the donor and acceptor chromophores until the appropriate one is found. We have shown evidence for this possibility using anisotropy decay experiments. The possibility of multiple relative orientations between the chromophores exists, because the benzyl ether dendrimers are flexible and therefore are capable of backfolding. Considering these findings, we concluded that the advantages that dendrimers provide for EET are: (*i*) the possibility of packing a high density of chromophores within a short distance from the core. (*ii*) The possibility of decorating the periphery with different chromophores and thus the opportunity for a more complete coverage of the solar spectrum. Energy hopping possibility among the chromophores in the periphery could become very useful in this regard. Note that we have previously developed synthetic methods to realize such a possibility. (*iii*) This energy hopping process is also inherently helpful for an efficient EET to the core, even when the chromophores at the periphery are the same (as in **1**).

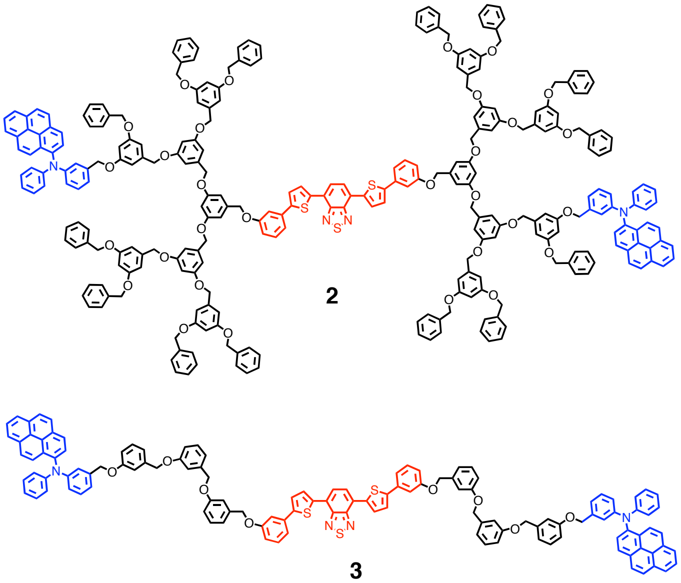

Figure 2. Structures of third generation difunctionalized dendrimer and the corresponding linear analog.

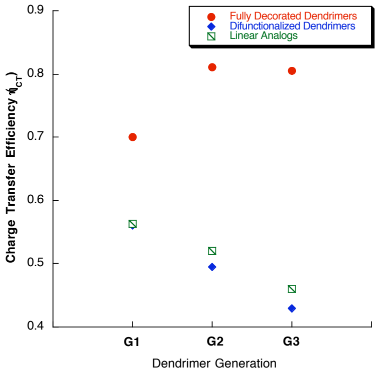

Figure 3. Plot of η_{CT} *vs*. generation for the three classes of molecules

In the case of CT, we observed that the efficiency remains high with increasing generation in the case of the fully decorated dendrimers, whereas the efficiency decreases with generation in the case of difunctionalized dendrimers and the linear analogs as shown in Figure 3. In the fully decorated dendrimers, although the distance between the donor and acceptor increases, as with other molecules, the key advantage is that the functional group density increases with generation. This combined with the fact that there is backfolding affords an opportunity for a critical number of donors to be in proximity to the acceptor at all times. However, in the case of the difunctionalized dendrimers, conformations in which the donors are significantly removed from the acceptors are possible as schematically shown in Figure 4.

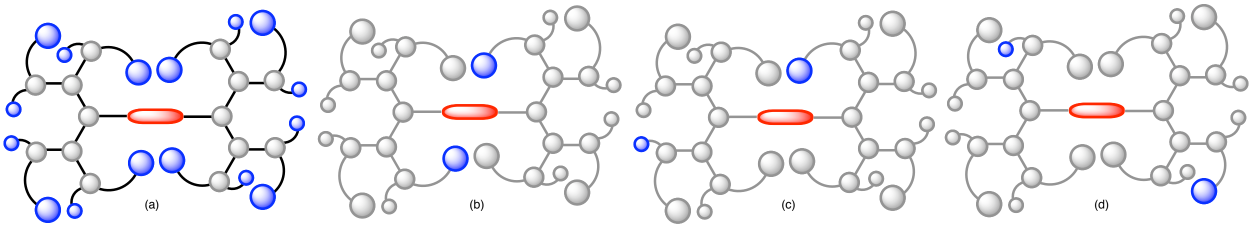

Figure 4. (a) Hypothetical conformation of a fully decorated dendrimer. (b-d) Various possible conformations of difunctionalized dendrimers similar to the one in (a). *Note*: Even when one attempts to draw the different conformations with the fully functionalized dendrimers as in (b)-(d), there would be a certain number of donor units close to the core. This could be sufficient to enhance CT efficiency in higher generations, when fully decorated.

While explaining the photophysical properties of these dendrimers, the recurring theme that is used to describe the behavior involves backfolding and the resultant spatial proximity of the peripheral functionalities and the core chromophore. This proximity results in enhanced CT efficiencies as observed above. However, it is also possible that this feature would enhance the possibility of charge recombination. Therefore, the key question becomes: is it possible to take advantage of the forward electron transfer efficiencies offered by the dendrimers, while reducing the possibility of charge recombination? In this proposal, we outline three different approaches to investigate the possibilities.

Along with one of the designs that we describe below using dendritic architectures, we plan to incorporate another strategy that we have developed to enhance the lifetime of the charge-separated state. We have shown that donor-bridge-acceptor molecules, in which the donor and acceptor are conjugated through a *meta*-connectivity exhibited longer-lived charge separated state than the corresponding *para*-linked compound. The idea behind the experiment was based on the reports that *meta*-conjugated molecules exhibit delocalization through the bridge in the excited state, while the delocalization through the bridge is poor in the ground state. In such a case, it is possible that the photoinduced forward electron transfer would be as fast as the *para*-substituted compound, while the back electron transfer would be relatively slower in the *meta*- case. This was demonstrated to be the case with the model compounds **4** and **5** shown in Figure 5.

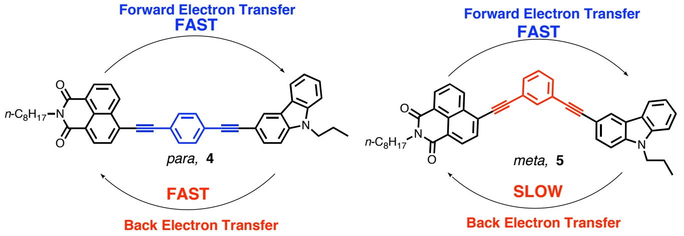

Figure 5. Model compounds to investigate the *meta*- effect for photoinduced charge separation

Publications from the DOE-Supported Grant:

Nantalaksakul, A.; Reddy, D. R.; Ahn, T.-S.; Kaysi, R.-A.; Bardeen, C. J.; Thayumanavan, S. "Dendrimer Analogues of Linear Molecules to Evaluate Energy and

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