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Femtosecond Excitation Energy Transport in Triarylamine Dendrimers

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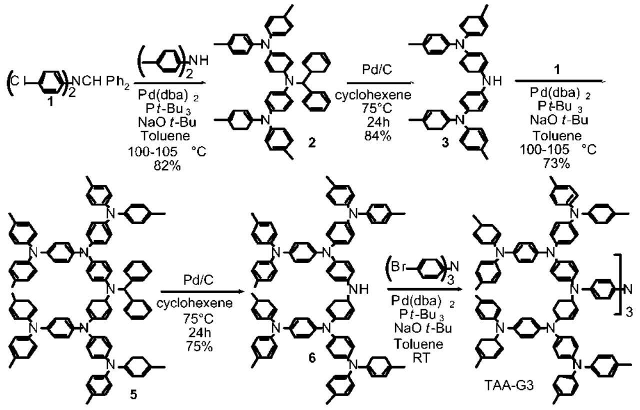
An understanding of energy transfer in organic conjugated dendrimers provides a conceptual basis for creating artificial light-harvesting and -emitting nanostructured materials.[1−3] The electronic and structural properties of the branching point within the dendrimer can influence this energy migration from branch to branch. At the limit of weak electronic interactions, energy transfer from one branch to another is incoherent, and a “hopping” mechanism operates. In this case a Forster model applies. At the other extreme, the junction between branches provides strong electronic interactions, and the energy transfer is coherent.[4,8c] The presence of weak or strong interactions in a system depends on the coupling parameter (interaction strength) and the dephasing. In many cases, the junction between branches disrupts conjugation, and the energy transport in these dendrimers can be described by following an approach that uses an exciton density matrix.[5] Experimentally, the degree of coherence in the energy-transfer process within branched molecular systems containing multiple chromophores may be evaluated using time-resolved fluorescence anisotropy.[4b,6,7] The fluorescence depolarization measurement is very useful to investigate intramolecular excitation transfer because the energy transfer is accompanied by the reorientation of the transition dipole, resulting in depolarization of the emission.

Triarylamine dendrimers containing *p*-phenylene diamine groups comprise a unique family of hyperbranched materials that are highly electron-rich and that can produce highly delocalized radical cations.[8] In contrast to unsaturated hydrocarbon dendrimers, the amine materials contain exclusively *p*-phenylene units, and these units are linked by sp^2-hybridized nitrogens. The advent of palladium-catalyzed aromatic C−N bond-formation allowed construction of modestly sized materials of this topology.[8] Here, we use improved catalysts to prepare *p*-phenylene triarylamine dendrimers of increased size. These materials, in combination with small analogues, provide a platform for understanding energy migration within a system with a strong interchromophore interaction.

Two improvements in synthetic methods allowed for the preparation of substantial quantities of a third-generation triarylamine dendrimer in analytically pure form. First, we employed diphenylmethyl protective groups on the amines to assist in deprotective hydrogenolysis of the larger structures. Benzyl and even *p*-methoxybenzyl protective groups underwent slow deprotection by hydrogenolysis or acidic conditions. Second, highly active catalysts for formation of both di- and triarylamines that are based on a 1:1 ratio of $P(t\text{-}Bu)_3$ and $Pd(dba)_2$ improved reaction yields of the C−N bond-formation and decreased reaction times.[9] Moreover, the low catalyst loadings and molecular weight of the ligand allowed for simpler purification of the materials.[6]

Scheme 1. Synthesis of Triarylamine Dendrimer



The overall strategy for preparation of second- and third-generation dendrimers is shown in Scheme 1. Reaction of ditolylamine with diphenylmethyl-protected 4,4′-dichlorodiphenylamine **1** with a 1:1 combination of $P(t\text{-}Bu)_3$ and $Pd(dba)_2$ as catalyst formed the double addition product **2** in 82% yield on a multigram scale after a standard workup and precipitation of product. Hydrogenolysis in cyclohexene solvent as the hydrogen source using 10% palladium on carbon as catalyst generated the free amine **3** in 24 h. This free amine was previously used to generate the second-generation dendrimer TAA-G2 by reaction with 0.3 equiv of tris-(4-bromophenyl)amine. In the presence of the recently developed catalyst, the free amine reacted with diphenylmethyl-protected dichlorodiphenylamine at room temperature to form after crystallization the precursor to the third-generation dendrimer. Deprotection again gave the free amine smoothly, and crystallization gave pure material in 73% yield. This free amine **6** was coupled with tribromotriphenylamine to form the three-fold symmetric TAA-G3 at room temperature in 89% isolated yield without difficulty from steric crowding.

All materials showed the appropriate MALDI mass spectra for the molecular ion and microanalytical data. With the exception of the dendrimer TAA-G3 all materials showed ^{13}C NMR signals that were resolved. ^1H and $^{13}C\{^1H\}$ NMR spectra of dendrimer TAA-G3 showed overlapping resonances for the different layers of aromatic units, but clean mass spectral data and a narrow peak in the GPC trace corresponding to a PDI (M_w/M_n) of 1.02 were obtained. Figure 1 shows the structures and absorption spectra of the triphenylamine and three triarylamine dendrimers. Two absorption maxima are clearly seen for the dendrimers, one at 320 nm and another at about 375 nm.

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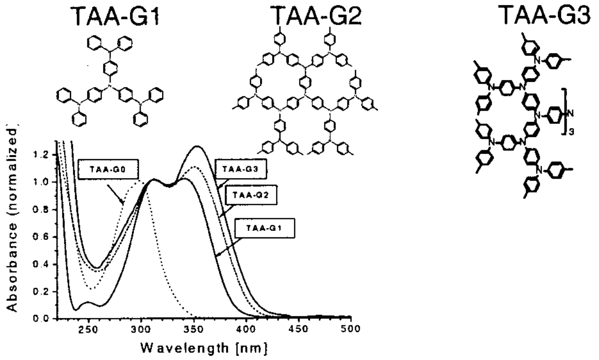

Figure 1. Absorption spectra of the TAA molecule and the three triarylamine dendrimer systems in THF. The peak at 320 nm (which was consistent for all dendrimer systems) was normalized to unity to illustrate the red-shift and increase in amplitude of the longer-wavelength peak.

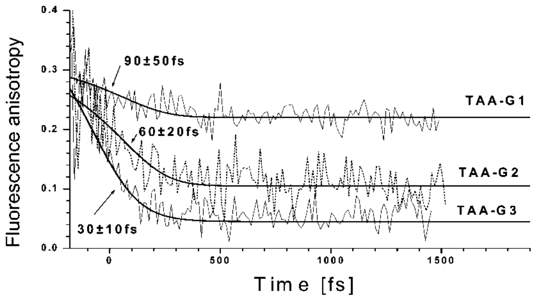

Figure 2. The fluorescence anisotropy decay for the three dendrimer systems in THF. The excitation wavelength is 390 nm, and emission wavelength is 480 nm. The scale extends to 1.5 ps so that the ultrafast decay can be well illustrated. The residual anisotropies for TAA-G1, TAA-G2, and TAA-G3 are 0.22,0.105, and 0.045, respectively.

The absorption spectra of the dendrimers are shifted to the red with respect to the absorption line of the triarylamine (TAA) NPh_3, which is the basic building block of the dendrimers. Comparison of the spectra of the three dendrimers also shows that the longer-wavelength component increases in intensity and wavelength maximum as the generation number increases (Figure 1). Such a trend was not observed for analogous spectra of dendrimers with weak intersegment interactions.

This red-shifted absorption is associated with a state that is delocalized over most of the dendrimer.[2] Using the Frenkel exciton model, we compared absorption spectra for triarylamine dendrimers with absorption spectra calculated for dendrimers with negligible charge coherence between linear segments.[4a] This model qualitatively describes the observed red-shift of the absorption line and the appearance of two absorption bands in the spectra of the dendrimers compared to the basic building block. However, this model predicts that the splitting between the two most intense excitonic absorption lines would be constant, instead of increasing with the generation number (Figure 8 in ref 5a). Thus, the observed dependence of the splitting between levels on the generation number (Figure 1) can be attributed to electronic coherence between the branches that is not considered in the excitonic model.[5a]

To probe the energy migration processes in the dendrimer systems we utilized ultrafast fluorescence anisotropy measurements. The upconversion system used in our experiments is described in detail elsewhere.[10] To avoid air oxidation and subsequent photodecomposition of the molecules upon laser excitation, the sample preparation and loading were carried out under a nitrogen atmosphere. Figure 2 shows the anisotropy decay results for the three dendrimers of Figure 1, TAA-G1, TAA-G2, and TAA-G3. The fluorescence anisotropy of all three dendrimers decayed to a residual value within ~100 fs. The value of the residual anisotropy decreases with an increase in generation number. The systematic decrease of the residual value can be associated with the increase of the number of accessible dipole orientations in a nonplanar geometry.[11] This fast decay of anisotropy and the systematic decrease in the residual value of anisotropy indicates a fast energy delocalization via a coherent excitonic mechanism between dipoles that are oriented in different directions.

The fast energy transfer may be considered in terms of the formation of coherent domains (intramolecular chromophore clustering).[6] Equilibration within a cluster leads to an initial fast decay in the value of the anisotropy, while the remainder of the depolarization decay is due to incoherent intercluster energy transfer.[6]

An important feature of this chromophore clustering is that anisotropy dynamics occurs on two time scales, with the slower decay component reflecting incoherent hopping. The anisotropy decay for all three generations of the dendrimer showed no evidence of such a second slow component in the time range ≥150 fs. Thus, the presence of the fast component of the anisotropy decay for each of the dendrimers could be explained by the coherent domains extending over large portions of the each dendrimer, including the largest TAA-G3. The most striking features of these results are the decrease in the residual anisotropy and the persistence of a fast component with increasing generation. These features may be a consequence of strong interactions over relatively large molecular distances in the branched system.

In summary, we provide the first systematic investigation of energy migration due to a coherent excitonic mechanism in a family of homogeneous dendrimers. The fast anisotropy decay to smaller residual value with the increase in generation is an indication of the exciton delocalization in multichromophore-branched systems.

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Supporting Information Available: Synthetic procedures, NMR data and steady-state fluorescence spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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