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COMMUNICATIONS

Published on Web 07/18/2003

Ultrafast Fluorescence Investigation of Excitation Energy Transfer in Different Dendritic Core Branched Structures

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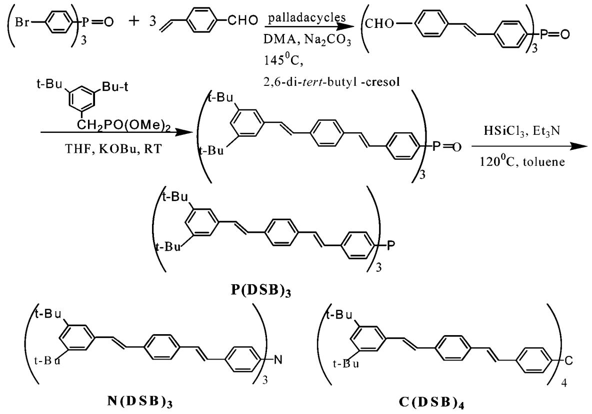
The investigation of optical excitations in branched structures continues to be an important issue as it can provide valuable information regarding the creation of new organic light-emitting and nonlinear optical materials.[1] In particular, the mechanism of energy transport in dendritic and other multichromophore architectures plays a key role in the understanding of the enhanced optical effects observed in these systems.[2] Previous reports of a nitrogen-cored dendritic system illustrated impressive energy transfer efficiencies as well as very strong electronic interactions of the participating chromophore building blocks.[3] This is explained by the very good electronic overlap of the nitrogen-cored system where the attached chromophores are situated in an almost planar (propeller) geometry. Indeed, the issues of planarity, electronic coupling, and the degree of functionality are important factors related to the excitations in dendrimers and should be investigated systematically. To investigate these questions, we have carried out the synthesis of new branching structures, all with the same building blocks (chromophores) but with different core units (C, N, and P). The dynamics and scale of energy migration are investigated in each of these model systems to determine the dominance of the key parameters for superior energy transfer efficiency.

A phosphorus-cored distyrylbenzene dendrimer ($P(DSB)_3$, G0) was synthesized for this purpose. The synthesis of a phosphorus core conjugated triaryl-dendrimer has not been reported. We initially attempted a method utilizing a Grignard reagent to react with PCl_3. Yet, the lithium/bromine exchange reaction of brominated distyrylbenzene did not occur and finally appeared to give a *tert*-butyl-substituted phosphine. Also, the direct coupling of substituted styrenes with tris(*p*-bromophenyl) phosphine ($P(C_6H_4Br)_3$) failed due to its weak activation and possible poisoning of active palladium species by an excess of the phosphine under Heck conditions.[4] However, the coupling of an oxidized phosphine ($PO(C_6H_4Br)_3$) with substituted styrenes was successful. The synthesis of the phosphorus-cored stilbene dendrimer $P(SB)_3$ suggested a similar procedure to build up an aldehyde unit containing the central phosphorus oxide. Such an aldehyde moiety reacts with a dendron containing benzylphosphonate to obtain the target macromolecules. Scheme 1 shows the complete synthetic pathway for $P(DSB)_3$. All structures are well characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectra. The ^{31}P spectrum shows a resonance at −5.5 ppm for the final phosphine dendritic macromolecule without any peak at 27 ppm for phosphine oxide. The ^{1}H NMR spectrum not only displays the appearance of the *trans*-vinyl signal (d, $J = 16.2$ Hz), but it also shows the coupling of phosphorus with aromatic protons. The coupling of phosphorus with carbons was observed from the ^{13}C spectrum. The ESI mass spectrum gave a corresponding molecular ion peak at m/z 1211 $(M + H)^+$.

Scheme 1. Synthesis of Phosphorus-Cored Distyrylbenzene Dendrimer $P(DSB)_3$, G0



The geometry of $P(DSB)_3$ is pyramidal but not trigonal planar as in triphenylamine[5a] due to the increase in size from N (1.71 Å) to P (2.12 Å) and the increase in bond length from N (N−C(aryl) 1.42 Å) to P (P−C(aryl) 1.83 Å).[6] Hence, the lone pair in $P(DSB)_3$ is in a sp^3 orbital directed from the apex of the pyramid so that the bond angle of C−P−C is less than the bond angle of C−C−C in tetrahedral tetrastilbenoidmethanes (111.3°).[5b] As a result, the $P(DSB)_3$ is more pyramidal than $C(DSB)_4$. Shown in Figure 1 are the absorption and the fluorescence spectra of three DSB systems and the DSB chromophore. The spectra of $P(DSB)_3$ are blue-shifted with respect to those for the $N(DSB)_3$ and red-shifted with respect to $C(DSB)_4$ and DSB. This phenomenon can be explained by the mesomeric effect of the three different cored systems.[7] In comparison with the trigonal planar $N(DSB)_3$, the overlap of the lone pair orbital on the larger phosphorus with the adjacent p-orbital on the smaller carbon atom is much less efficient. Therefore, the delocalization of the lone pair on phosphorus with the conjugated distyrylbenzene units is less extensive. As a result, the spectra of $P(DSB)_3$ are shifted to the blue. In contrast, there is no lone pair available from a saturated carbon atom; therefore, the spectra of $C(DSB)_4$ are similar to those of the building block DSB chromophore.

To investigate the excitation energy transfer dynamics in these branched macromolecules, we utilize time-resolved fluorescence upconversion spectroscopy. Our upconversion experimental system was described in detail in our previous publications.[8] We found that the $P(DSB)_3$ is stable to the femtosecond excitation laser pulses. Shown in Figure 2 are the fluorescence anisotropy decay dynamics of the branched dendritic macromolecules and of the DSB chromophore. The anisotropy decay dynamics of the branched DSB macromolecules are different than what is observed for the linear DSB chromophore. The DSB chromophore shows no significant anisotropy decay during this experimental time window. We have shown that the anisotropy decay times can be utilized to explain energy transfer dynamics in branched structures.[9,10]

The anisotropy decay of $P(DSB)_3$ can be fitted by a two-exponential decay function with decay time constants of 51 and 702 fs. The anisotropy decay times were found to be 37 and 960

10.1021/ja035215y CCC: $25.00 © 2003 American Chemical Society

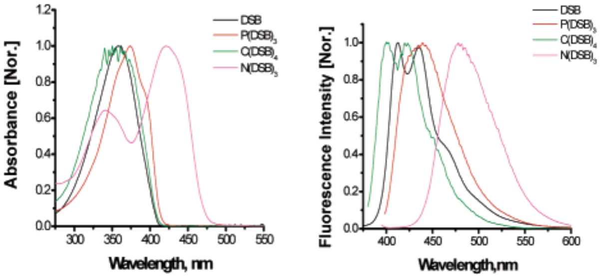


Figure 1. The normalized UV/vis and fluorescence spectra of DSB, P(DSB)$_3$, N(DSB)$_3$, and C(DSB)$_4$ in CHCl$_3$.

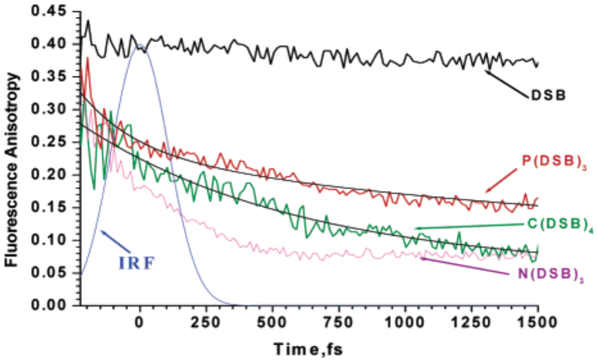


Figure 2. The fluorescence anisotropy decay for DSB, P(DSB)$_3$, N(DSB)$_3$, and C(DSB)$_4$ in CHCl$_3$. $\lambda_{ex} = 390$ nm, and $\lambda_{em} = 480$ nm. The solid lines are fits to the experimental curves.

fs for C(DSB)$_4$, and a monoexponential decay time of 57 fs was found for N(DSB)$_3$. A Förster-type incoherent energy transfer between chromophores in the C(DSB)$_4$ system was suggested as the dominant mechanism.[10] However, the fast energy migration processes observed in the N(DSB)$_3$ system suggest a coherent mechanism.[3] The presence of a slow decay component in the anisotropy of C(DSB)$_4$ and P(DSB)$_3$ before it reaches the residual value is clear evidence of the presence of weaker interactions among the DSB chromophore segments. The presence of the faster component in both C(DSB)$_4$ and P(DSB)$_3$ systems, which is comparable to the N(DSB)$_3$ decay time, may suggest that there is some contribution of coherent delocalization of excitation as well. Yet, we believe the incoherent hopping type of energy transfer dynamics dominates in both C(DSB)$_4$ and P(DSB)$_3$ systems. The difference in anisotropy decay times for C(DSB)$_4$ and P(DSB)$_3$ may suggest that the interactions among DSB chromophore segments are weaker in C(DSB)$_4$ than in P(DSB)$_3$. This can be explained by considering the geometry of the branched macromolecules. In P(DSB)$_3$, three distyrylbenzene chromophores are grouped in a fairly pyramidal arrangement around the phosphorus. This pyramidal structure of P(DSB)$_3$ may be responsible for the relatively stronger interaction among DSB segments as it holds the three DSB segments closer together than the tetrahedral structure of C(DSB)$_4$. The presence of a lone pair of electrons on P can lead to more efficient delocalization of electrons as compared to C(DSB)$_4$ where no such delocalization is possible. Yet, because of the size and geometry of P(DSB)$_3$, this increase in strength of interaction is not significant enough to push the energy transfer into the coherent regime.

The residual value of the fluorescence anisotropy (before rotational diffusion) also contains information of the arrangement of transition dipoles in a branched macromolecular system and hence gives molecular geometry information as well. As shown in Figure 2, the fluorescence anisotropy of P(DSB)$_3$ decays to a residual value of 0.140, while N(DSB)$_3$ and C(DSB)$_4$ decay to a residual value of 0.082 during the same decay time window. Theoretically, the residual anisotropy value for a planar three-fold symmetrical dipole arrangement in a branched system is 0.1.[11,12] The difference in the residual anisotropy value indicates that the dipole arrangement around the branching center of P(DSB)$_3$ deviates from planarity to a greater extent than that of N(DSB)$_3$ and C(DSB)$_4$. The pyramidal structure of P(DSB)$_3$ makes the angle between absorption and emission transition dipoles of the chromophore system smaller than that of C(DSB)$_4$. This changes the average angle between transition dipoles, which is strongly related to the structure of the branched chromophore system, and hence alters the value of the residual anisotropy.

In conclusion, we have compared the influence of the branching centers on the energy transfer dynamics in dendritic core macromolecules. This investigation provides more insight into the understanding of the energy delocalization from different cores in a dendrimer. We have shown that the geometry, structural arrangement of transition dipoles around the branching center, and the delocalization across the branching center are important in determining the mode of energy transfer in dendritic architectures.

Acknowledgment. T.G. III acknowledges the NSF (DMR-00880044) and AFOSR for support.

Supporting Information Available: Synthetic procedures of P(SB)$_3$ and P(DSB)$_3$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA035215Y