Excitation Energy Transfer in Branched Dendritic Macromolecules at Low (4 K) Temperatures

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The investigation of optical excitations in branched dendritic macromolecules has drawn great interest in recent years due to their possible applications in harvesting light,[1] enhancement of nonlinear optical properties,[2] use in light-emitting diodes[3] as well as in medical applications.[4] To understand these phenomena in detail it is important to know the role of interactions among closely spaced chromophores in the branched macromolecule with well-defined geometrical order. The strength of interactions among chromophores determines the mechanism of optical excitation and the mode of energy transport among chromophores.[5]

Previous investigations, both theoretical[6] and experimental[5,7,8] have revealed that the branching center plays a key role in determining the type of interaction among chromophores and hence the modes of energy transport in dendrimers. However, all of these previous investigations were carried out at room temperature, and due to the flexibility of these large macromolecules it is important to probe the optical excitations at low temperatures. For certain energy transport mechanisms it is expected that the dynamics of energy migration at low temperature could be significantly different than room temperature results.[5,7,8] This may be due to changes in the homogeneous broadening, which decreases when the temperature is lowered. Also, at low temperature, the vibrational motion (phonons) of chromophores is suppressed, and therefore the orientation of dipoles in the rigid geometry is fairly uniform. This will lead to an increase in the number of accessible dipoles for optical excitation, which will subsequently lead to an instantaneous depolarization. From our previous reports we have found that the fluorescence anisotropy decay times and homogeneous line width (Γ) can be used to probe the interaction strength in branched macromolecules.[5] While the room temperature results did indeed show evidence of coherent interactions in the branched structures, the measurement of the energy migration at low temperature may give a clearer description of the mode of energy transport in these systems.

For our studies a dendritic core consisting of an amino distyryl-benzene (A-DSB) trimer was investigated. We selected this system as nitrogen plays an important role in determining the mode of energy transfer in dendrimers. The synthesis of this system as well as photophysical investigations at room temperature have been well documented in the literature,[5,7,9,10] and we followed these synthetic procedures. We fabricated films of the active system doped in PVB to make low temperature polymeric glass samples. To investigate the dynamics of energy transport in the branched macromolecules we utilized our femtosecond ($\sim$120 fs)[11] fluorescence upconversion setup. The experimental setup has been discussed in detail in our previous publications.[7,8] For low temperature measurements (from 298 to 4 K) an Oxford Instruments continuous flow liquid helium cryostat is utilized which is interfaced (optically and electronically) to our upconversion unit. Shown in Figure 1 is the parallel and the perpendicular fluorescence decay dynamics of A-DSB at 4 K. The fluorescence decay time is $\sim$30 ps. The fluorescence decay did
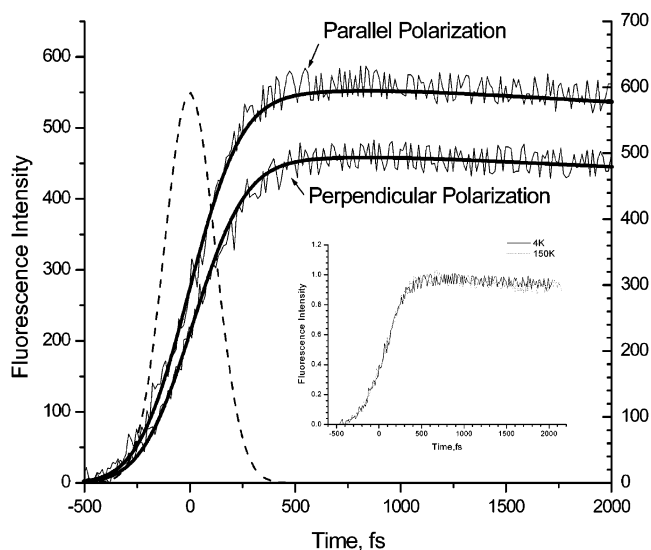

Figure 1. Fluorescence decay of A-DSB at 4 K. Fit for data (thick solid line) IRF (dashed line). The inset shows the fluorescence decay at 150 and 4 K. Excitation at 400 nm and emission detection at 480 nm.
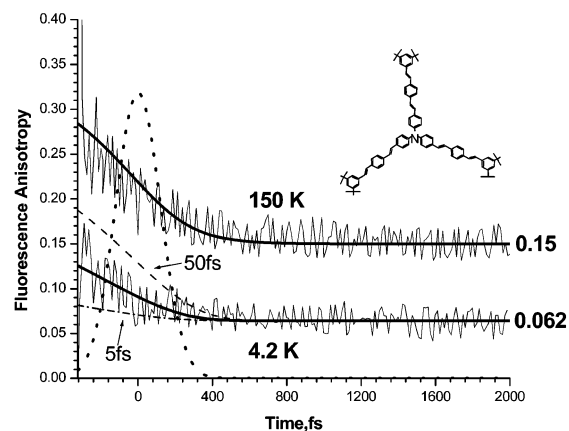

Figure 2. Fluorescence anisotropy decay of A-DSB at two different temperatures. Excitation at 400 nm and emission detection at 480 nm. Fit for data (thick solid line) IRF (dotted line). The two dashed lines represent the fits for the 4 K anisotropy decay curve for decay times of 5 and 50 fs.

not show any temperature dependence (see inset of Figure 1). Shown in Figure 2 is the temperature dependence of the anisotropy decay for the A-DSB branched macromolecular system. The decay curves for 150 and 4 K are shown. There are two important results that can be easily observed from the depolarization decay. First, the anisotropy decay times systematically decrease when the temperature is lowered. The decay times are 60 ± 25, 35 ± 20, and 20 ± 15 fs for 150, 77, and 4 K, respectively. Second, the residual anisotropy value shows a systematic decrease with decreasing temperature. The residual values are 0.15, 0.093, and 0.062 for

150, 77, and 4 K, respectively. Also shown in Figure 2 for comparison are best-fit curves for the 4 K measurement where the decay times are 5 and 50 fs. It can be seen that these curves do not fit the experimental data. From our previous investigations we found that the anisotropy decay time and residual anisotropy value both can be used to characterize the energy transport mechanism.[10] For example, for a given homogeneous line width ($\sim$2000 cm^{-1} at 298 K) a fast anisotropy decay time ($\sim$100 fs) signifies a coherent energy transport mechanism.[5,8,10] Also the trend of decreasing residual anisotropy value in a large multichromophore system may indicate a coherent mechanism.[10] The fact that both signatures (fast anisotropy decay and low residual value) are present here may suggest strong evidence for a coherent process at low temperature in these branched macromolecules.

The low temperature A-DSB anisotropy result is very interesting and may suggest the transition of the energy transport mechanism from an incoherent to a coherent mechanism as the temperature is decreased. We expect a significant decrease in the homogeneous broadening when the measurements are carried out at low temperature. This may not change the magnitude of the interaction strength (**J**) but could reflect a change in the important ratio (**J**/Γ) where a coherent energy transport mechanism should result in a large value (greater than unity) for this ratio. While changes in local motion and small torsion movements may give a small contribution to the result observed for the A-DSB, this is certainly not the only plausible mechanism. We suggest that the temperature dependence of the anisotropy decay in the dendritic core system can be understood by considering changes in both homogeneous and inhomogeneous broadening of the system at low temperature.

The influence of inhomogeneous broadening on depolarization time has been reported in the literature. For example, for a photosynthetic light-harvesting system it was shown that there is a dependence of the depolarization time and residual anisotropy value (slow component) on the inhomogeneous broadening.[12] It was concluded that the depolarization time increases when the inhomogeneous broadening is considered. Similarly, the amplitude of the slow component is systematically increasing with an increase in inhomogeneous broadening. The dependence of the depolarization time on homogeneous and inhomogeneous broadening has been discussed considering the following relationship[13] (definitions of these terms are given in the Supporting Information).

$$\tau_d = \frac{\tau_{\text{hop}}}{\left(\pi \dfrac{d}{2}\sqrt{\dfrac{2s}{d}\dfrac{\Gamma(1-d/s)}{\Gamma(1+d/2)}}\dfrac{\sigma_h}{\sigma_{\text{inh}}}\exp\{-[(E-E_0)/(0.6\sigma_{inh})]^2\}\right)^{s/d}} \quad (1)$$

This relationship suggests that with the increase the ratio of the homogeneous and inhomogeneous line widths ($\sigma_h/\sigma_{\text{inh}}$) there should be a decrease in the depolarization time. From simple estimate calculations we have found that with a change of approximately 2 in the line width ratio, the depolarization time would change by a factor of 5. Similarly, reported calculations showed a systematic decrease in the residual value of anisotropy with the decrease in inhomogeneous broadening for light-harvesting antenna systems.[12]

This type of behavior is clearly seen for A-DSB system, suggesting that for this branched structure the influence of both homogeneous and inhomogeneous broadening on the excitation energy transfer is important in explaining the dynamics of the system as the temperature is lowered toward 4 K. It should be mentioned that the relatively fast depolarization times in these upconversion measurements are a result of deconvolution procedures (see Supporting Information).

In conclusion, we have carried out low temperature (4 K) ultrafast investigations of a dendritic core organic system. We found that the anisotropy decay time and residual value decrease with decreasing temperature. The influence of both homogeneous and inhomogeneous broadening is suggested to give rise to this temperature dependence. Further studies with even larger dendritic structures as well as complimentary measurements to characterize the line widths in these systems are in progress.

Supporting Information Available: The fitting procedure and the definition of terms of eq 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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