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Ultrafast polarized fluorescence dynamics in an organic dendrimer

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The excited state relaxation processes of a nitrogen-cored distyrylbenzene-stilbene (A-DSB) dendrimers and the analogous linear model compound (bis-MSB) were investigated by polarized fluorescence upconversion spectroscopy. The fluorescence anisotropy (FA) of A-DSB was found to decay to a value close to zero in less than 200 fs after excitation. For the model compound bis-MSB the FA initial value was close to 0.4 and showed a relatively slow decay (82 ps) corresponding to overall rotational diffusion of the molecule. The results are interpreted in terms of fast transition dipole reorientation during relaxation of the excited states of the branched molecules. © 2000 American Institute of Physics.

Recently there has been an increasing amount of attention devoted to the study of dendrimers, which are highly branched macromolecular systems.1,2 Their unique branched architecture affords them many properties, which are distinctively different from those of their linear analogs.3,4 Along with the synthesis and chemical properties, the photophysics of these systems is attracting rising interest in connection with their applications as artificial antenna systems.5,6 However, the origin of electronic excitations and specific mechanism of intramolecular energy transport in dendrimers is not well understood.4,6,7 The branching centers such as benzene (with a meta-position linkage)5,8 or nitrogen1 can cause a disruption of the π-electron conjugation of linear building blocks. In this case the optical excitation creates the electron-hole pairs localized on small segments.4 However, these localized electron-hole pairs can contribute to either collective optical excitations (excitons)4 or to the incoherent hopping6 due to intersegment interactions. Each step of the incoherent energy migration in a branched system should lead to the reorientation of the transition dipole moment and depolarization of the emission. The hopping time τhopping can be related to the mutual orientation of the dipoles in dendrons θ and the depolarization time τdepolar (in a simple case of a planar system) as

\[ \tau_{depolar} = \frac{\tau_{hopping}}{4(1 - \cos^2 \theta)}. \]  

A more general description of fast depolarization in a symmetrical branched molecular system is the relaxation of a superposition of degenerate states with different orientations of transition dipoles. An analysis of the fluorescence anisotropy associated with two-fold and three-fold degenerate states with different orientations of the transition dipole has been given by Wynne and Hochstrasser.10 Other manifestations of coherent effects in anisotropy optical experiments were also theoretically analyzed.11–13 In this letter we report the time-resolved polarized inherent fluorescence of dendrimers with ~200 fs time resolution.

The structure of the nitrogen-cored distyrylbenzene-stilbene (A-DSB) is shown in Fig. 1(a). Three distyrylbenzene chromophores are grouped in a tetrahedral arrangement around the nitrogen and there is a lone electron pair. The dendrons are based on metapositioned stilbene units. The molecules of zero (G0) and the second (G2) generations are shown in Figs. 1(a) and 1(b). The linear absorption spectrum is shown in the inset of Fig. 2. It shows two prominent features with maxima at 410 and 320 nm. The first feature corresponds to the absorption of DSB chromophores and the second can be assigned to the stilbene units. The structure of a nonlinear optical dendrimer also used in this study is depicted in Fig. 1(c). Synthesis and spectroscopic features of all the structures have been described elsewhere.8,14 The p-bis(-methylstyril)-benzene [bis-MSB] chromophore was used as a model compound for investigations of intermolecular interactions in A-DSB. Solutions in chloroform were used in this study.

Femtosecond upconversion spectroscopy was employed to resolve temporally the polarized fluorescence. Optical arrangement for the upconversion experiments has been described previously.14–16 The sample was excited with laser pulses delivered by a frequency doubled output of the Ti:sapphire laser (Tsunami, Spectra Physics). The laser with an average pulse width of 100 fs tuned at 790–860 nm and a repetition rate of 82 MHz. The polarization of the excitation

FIG. 1. The structure of A-DSB dendrimers for zero G0 (a) and second G2 (b) generations. (c) The structure of CZD4NS2.
The fluorescence isotropic decay of A-DSB on the picosecond time scale was found to be nonexponential and strongly dependent on the emission wavelength (Fig. 2). The effect of fluorescence rise time is clearly detected in the “red” regions of the fluorescence spectrum. This fluorescence time behavior can be assigned either to intramolecular interactions in the dendrimer (excimer formation, energy transfer) or to local relaxation processes in the chromophore (conformational changes, solvent rearrangement). The long-scale decay pattern (not shown) was found to be almost mono-exponential with the decay time of about 1 ns. The fluorescence dynamics detected at 515 nm were found to be the same for both generations when excited at 395 nm.

To gain a further insight into energy transfer (energy migration) processes in A-DSB dendrimer molecules we investigated the fluorescence anisotropy dynamics in G0 and G2. The result for G2 is shown in Fig. 3. Raw fluorescence anisotropy $R(t)$ was calculated from the decay curves for the intensities of fluorescence polarized parallel $I_{\text{par}}(t)$ and perpendicularly $I_{\text{per}}(t)$ to the polarization of the excitation light according to the equation

$$R(t) = \frac{I_{\text{per}}(t) - G^* I_{\text{par}}(t)}{I_{\text{par}}(t) + 2 G^* I_{\text{per}}(t)}.$$  

(2)

The factor $G$ accounts for the difference in sensitivities for the detection of emission in the perpendicular and parallelly polarized configurations. We obtained this factor from our test measurements of fast rotational diffusion of perylene in solution. It is clearly seen from Fig. 3(a) that the fluorescence anisotropy decays to a small residual value of about 0.05 within the instrument response function duration (200 fs) and remains almost unchanged on the picosecond time scale [Fig. 3(b)]. The initial spike at about zero delay is relatively small and comparable in duration with the time resolution of our system to be reliably analyzed quantitatively. Qualitatively, it reflects the fact that the initial decay of $R(t)$ is short compared to time resolution of our upconversion setup (~200 fs). The fluorescence anisotropy dynamics of the dendrimer CZD4NSC2 and of bis-MSB are also shown in Fig. 3 for a comparison. It is clearly seen that initial values of $R(t)$ for last two cases are in the range 0.3–0.4, close to the limiting value of 0.4. It should be noted that in our previous work no signs of interchromophore interaction was found for CZD4NSC2. The $R(t)$ decay times of 600 ps (CZD4NSC2) and 82 ps (bis-MCB) are most probably connected with overall rotational diffusion of these molecules. For G0, G2 there were no visible signs of molecular overall rotation as the fluorescence anisotropy dropped to a very small residual value within the time interval of ~200 fs, which is much shorter than a reasonable time of rotational diffusion.

It is clearly seen from Fig. 3(a) that the fluorescence
anisotropy dynamics are very similar for G0 and G2 indicating that the fast fluorescence depolarization process is associated with the dendrimer core and not sensitive to presence of the stilbene chromophore. The dendrimer core (G0) is a star-like molecule consisting of three DSB segments bonded to a central nitrogen atom. The interaction between branches could lead either to the formation of coherent excitonic states\textsuperscript{10} or hopping-type\textsuperscript{19} relaxation of excitations localized on one DSB branch. Both relaxation mechanisms between excitonic states\textsuperscript{10,13} and incoherent hopping\textsuperscript{19} may lead to fast fluorescence depolarization due to the star-like organization of the branches. Indeed, for the linear polymeric system poly(S-119) we found no fast depolarization with interacting side chain chromophores.\textsuperscript{16}

From further experimental investigations we did not observe any detectable change in the fluorescence anisotropy decay pattern with excitation wavelength variation in the range 380–410 nm (see arrows in Fig. 2). This clearly proves that the fast depolarization is not associated with an energy transfer from the stilbene dendrons to the core. Also the suggestion of simultaneous excitation of two different energy levels with different polarizations\textsuperscript{20} in G0 resulting in an anisotropy value of zero can be ruled out on the basis of these experiments.

It may be suggested as well that the fluorescence anisotropy of G0 is nearly zero because of an irreversible relaxation to a state with the transition dipole oriented at about 55° (magic angle) with respect to the initially excited one. This case is physically similar to the process of energy transfer between branches suggested in our manuscript. However, this simple two-state model is not reasonably applicable to our particular symmetrical geometry. For example in the A-DSB system a more realistic angle of 60° (120°) and for the case of one irreversible step the fluorescence anisotropy (FA) should be negative (−0.05). However, our results show a positive value close to what is expected for multistep equilibration process in a symmetrical molecule with three branches.

In conclusion, fast fluorescence depolarization within 200 fs was found for the A-DSB dendrimer. For the model system bis-MSB representing the linear building block of the dendrimer a FA decay time of 82 ps was obtained which agrees with the rotational diffusion of bis-MSB. These results demonstrate the ultrafast transition dipole reorientation due to intersegment interactions in A-DSB dendrimer suggesting energy transfer rate of \(~1.7\times10^{12}\) s\(^{-1}\) in case of hopping mechanism. The anisotropy results of CZD4NSC2 support our previous conclusions concerning the lack of detectable excited state interchromophore interactions in this particular dendrimer. Time-dependent fluorescence anisotropy measurement showed to be a powerful method for the evaluation of the intramolecular interactions in the A-DSB organic dendrimer.

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