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Coherent Effects in Energy Transport in Model Dendritic Structures Investigated by Ultrafast Fluorescence Anisotropy Spectroscopy

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Abstract: Measurements of ultrafast fluorescence anisotropy decay in model branched dendritic molecules of different symmetry are reported. These molecules contain the fundamental branching center units of larger dendrimer macromolecules with either three (C_3)- or four (T_d, tetrahedral)-fold symmetry. The anisotropy for a tetrahedral system is found to decay on a subpicosecond time scale (880 fs). This decay can be qualitatively explained by Förster-type incoherent energy migration between chromophores. Alternatively, for a nitrogen-centered trimer system, the fluorescence anisotropy decay time (35 fs) is found to be much shorter than that of the tetramers, and the decay cannot be attributed to an incoherent hopping mechanism. In this case, a coherent interchromophore energy transport mechanism should be considered. The mechanism of the ultrafast energy migration process in the branched systems is interpreted by use of a phenomenological quantum mechanical model, which examines the two extreme cases of incoherent and coherent interactions.

Introduction

The nature of excitations in large molecular aggregates has been investigated in a large number of structural architectures.[1] Many of these investigations have involved aggregates of important organic chromophores. The characterization of the optical excitations in the aggregates often suggests that the excitations may be localized on specific sites of the aggregate or segments. The localization of the excitations is often directed through dipole−dipole interactions.[2] The formation of the excitation of dyads (or triads) and excimers can be explained under this context fairly well.[3] More complicated macromolecular systems such as pigments in light-harvesting photosynthetic systems have also been investigated with close attention to the nature of interactions between the pigment groups.[1b,2b,4] Much of the current interest in the nature of excitations in interacting chromophores has led investigators to revisit past work in the area of excitation of molecular crystals[5] and the excitonic character of photophysical processes.[6] The characterization of the Hamiltonian by a Frenkel exciton (excited electron and hole pair) has been applied to relatively new macromolecular architectures such as organic dendrimers.[7] Presently, the investigation of energy transfer in organic dendrimers has attracted recent attention that is motivated by the prospect of creating artificial light-harvesting and -emitting systems.[8] One of the attractive features of this approach is the controlled synthesis of dendrimers that results in a regular and well-defined architecture.[9] At the same time, the unique architecture of dendrimers allows one to bring into close proximity a number

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of optically active subunits. These two features are also very promising for creating molecular electronic devices.

The fundamental challenge in dendrimer macromolecular photophysics is the understanding of the photoexcitation energy transfer between subunits and the degree of the excitation delocalization. In most cases, the branching center in dendrimers disrupts the conjugation, thus suggesting the dendrimer molecule to be an ensemble of linear chromophores with no (or weak) charge transfer between them. If such a charge transfer is completely eliminated, and consequently the linear-segment chromophores are well separated, then their interactions are purely Coulombic. This explains the characterization of interactions in the dendrimer molecule by a Frenkel exciton Hamiltonian.[7] Recent theoretical studies on phenyl-acetylene dendrimers showed that the charge coherence between linear segments is negligibly small and that the Frenkel exciton approximation is applicable for this system.[7] There have been no other reports regarding the effect of extended conjugation on the energy migration process for other types of conjugated dendrimers (branching centers). Furthermore, even if the charge coherence between linear conjugated segments is negligible, many important questions regarding the excited-state dynamics and excitation energy transfer mechanisms in many important synthetic dendrimer systems remain unanswered. Resonance interactions between conjugated segments favor delocalized Frenkel Hamiltonian eigenstates. This leads to coherent mechanisms of excitation energy transfer, which are maintained over the duration of time during which well-defined phase relationships between segments are preserved. Interactions with the surrounding environment and with molecular nuclear motion, however, destroy this phase coherence and stabilize localized excitations. In the last case, the energy transfer between dephased fragments may then occur in a random stochastic fashion (hopping mechanism or weak interaction limit[10]). Both interactions can be significant in dendrimers, and their relative magnitudes will determine the contributions of coherent and incoherent mechanisms to the dynamics of energy transfer. This is an important issue concerning numerous promising applications of dendrimers (artificial light antennas,[8a,b] LEDs,[8c,d] nonlinear optics[8e]). Also, the question of coherence in dendrimers is an important fundamental problem. For example, it is suggested that the photophysical processes are strongly affected by geometrical confinement in dendrimers. However, neither the dephasing rate nor the resonance interaction strength has been experimentally measured for real conjugated dendritic systems. For diphenylacetylene segments connected at metapositions, the interaction strength was theoretically estimated to be about 69 cm^{-1} (347 cm^{-1} for longer segments), but this value was not independently estimated experimentally.[7]

To address the complicated problem of the excitation energy transfer dynamics in dendritic systems in a meaningful way, a simple dendritic model system (one branching center) may be investigated. In this case, each component of the branching center (each conjugated linear segment) either can be excited by another segment or can transfer the excitation energy to the other segments of the branching center. The interactions between the chromophores at a branching center are strongly influenced by the electronic and structural connectivity at the branch. The nature of these interactions can be investigated by use of fluorescence anisotropy, which is a powerful method in characterizing the energy migration in particular multichromophore systems.[4,11,12] By using fluorescence depolarization, it is possible to observe this intramolecular excitation transfer because the latter process is accompanied by the reorientation of the transition dipole resulting in depolarization of the emission. Theoretical treatments of time-resolved polarized emission from coherently excited chromophore pairs (and single molecules with degenerate electronic transitions) showed that the initial anisotropy can exceed the normally observed value for a single chromophore of 0.4, before dephasing is initiated.[11] Oscillations in optical anisotropy can be observed as a result of the beating between excitonic levels.[11,13] However, in most experiments, the observed oscillations were assigned to the vibrational wave packets formed by vibrationally impulsive excitations. To actually observe the beatings between excitonic levels for any particular system, the splitting parameter (interaction strength) should fall in a narrow window of opportunity between the limited experimental time resolution and the fast dephasing. This condition, while theoretically viable, may not be easily satisfied for many aggregated systems for which the excitonic splitting is not exactly known.

However, there is also very important information in the decay time and shape of the optical anisotropy. The anisotropy decay time combined with isotropic dynamics and steady-state spectroscopic information can be correlated with the excitation energy migration (or redistribution) time in the aggregates organized about a rotational axis.[1b,4] In the limit of incoherent interactions the anisotropy decay time is directly related to the hopping time (interaction strength) between adjacent chromophores.[4b,11a,14] In the excitonic limit this decay is associated with the transition between the excitonic states possessing different directions of transition dipoles.[1e,11,13] It is worth noting that for the aggregated systems with axial symmetry (if it is not broken after excitation) the excitonic levels with strong enough oscillator strength remain doubly degenerated with different orientation of the dipoles for each state.[2a,4b] The optical anisotropy decay associated with mutual dephasing and population exchange between these two states which is driven by interactions with random electric fields of the solvent molecules or dynamical breaking of the symmetry can be very fast.[1e,11,15,16] The anisotropy dynamics in a transition area between these two limits can be modeled either numerically[4c,13] or, with some restrictions, analytically.[17] Many parameters about the molecule itself and solute−bath interactions are required to perform such modeling. For natural photosynthetic systems, many of them have been established in the course of many years of investigations.[1b,4] For new synthetic macromolecular systems (such as dendrimers), most of the important physical quantities associated with a fast depolarization process are still to be discovered.

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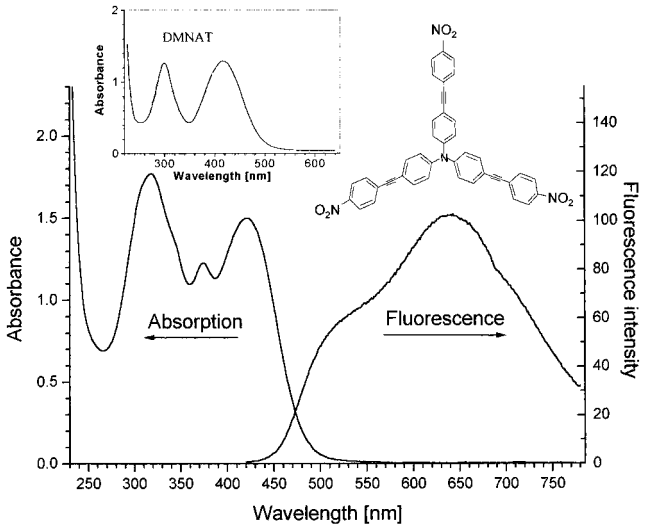


Figure 1. Absorption and fluorescence spectra of the nitrogen-cored tris-4,4′,4″-(4-nitrophenylethynyl)triphenylamine. Fluorescence excitation wavelength is 410 nm. The right inset shows the absorption spectrum of the linear model compound dimethylnitrotolane (DMNAT).[19] Molecular structure of the tris-4,4′,4″-(4-nitrophenylethynyl)triphenylamine is shown in the left inset.

In this paper, we report a femtosecond time-resolved fluorescence anisotropy study of the interchromophore energy transfer processes in model branched dendritic molecules of C_3-symmetry with a nitrogen core and T_d (tetrahedral) symmetry with a carbon and adamantane core. From the fast fluorescence anisotropy decay data, the interchromophore interaction strength and energy transfer regime have been estimated. We showed that the Förster energy transfer model can describe qualitatively the interchromophore energy migration process in adamantine-cored tetramers. However, for the triarylamine trimers, the hopping dynamics are not appropriate, and exciton (coherent) dynamics should be considered.

Results and Discussion

Synthesis and Characterization. The structure of the nitrogen-cored tris-4,4′,4″-(4-nitrophenylethynyl)triphenylamine system is shown in the inset of Figure 1. In the inset in Figure 2, the structures of the carbon-cored distrylbenzene tetramer (tetrakis(3,5-di-*tert*-*t*-butylstyrylstilbene)methane, C(^{t}BuSSB)$_4$), and adamantane-cored dystrylbenzene tetramer (tetrakis(3,5-di-*tert*-*t*-butylstyrylstilbene)methane, Ad(^{t}BuSSB)$_4$), are both shown. These model systems represent the fundamental branching units of conjugated dendrimer molecules with coordination numbers three and four. The triarylamine system is a new molecule and is easily prepared by palladium-mediated C−C bond formation. The synthesis procedure is sketched in Scheme 1. Tris-(4-iodophenyl)amine (**1**): A mixture of triphenylamine (3.0 g, 12 mmol), HgO (12.18 g, 56 mmol), and I_2 (15.24 g, 60 mmol) in EtOH (150 mL) was stirred overnight at room temperature. The solvent was removed, and the product was separated from mercuric salts with boiling toluene. The solution was filtered through the short column of Al_2O_3, and product was precipitated from hot toluene with MeOH. Yield: 6.5 g (86%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.53 (d, 6H, J = 8,4 Hz), 6.80 (d, 6H, J = 8,4 Hz). Tris-[*p*-(4-nitrophenylethynyl)phenyl]amine (**3**): To a solution of tris-(4-iodophenyl)amine (2.0 g, 3.3 mmol) in THF (30 mL) were added $PdCl_2(PPh_3)_2$ (0.022 g, 0.03 mmol),

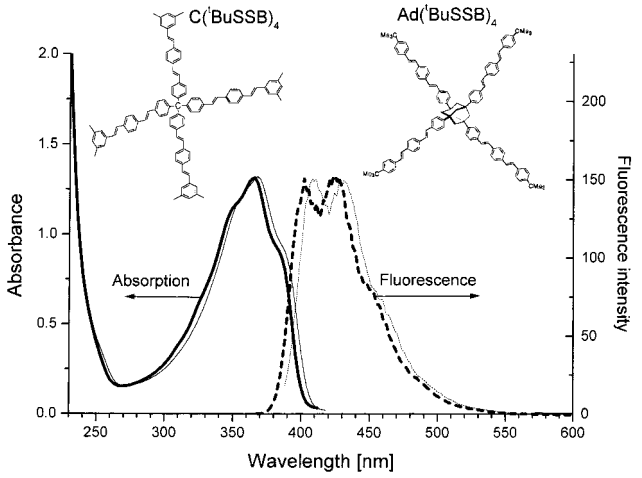
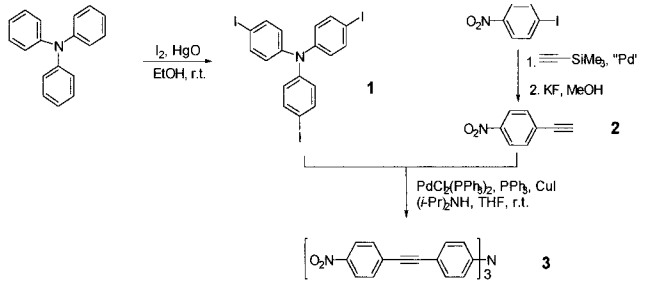


Figure 2. Absorption (solid lines) and fluorescence (dash lines) spectra of the carbon-cored distrylbenzene tetramer (tetrakis(3,5-di-*tert*-*t*-butylstyrylstilbene)methane, C(^{t}BuSSB)$_4$) (thin lines), and adamantane-cored distrylbenzene tetramer (tetrakis(3,5-di-*tert*-*t*-butylstyrylstilbene)methane, Ad(^{t}BuSSB)$_4$) (bold lines), in chloroform. Fluorescence excitation wavelength is 350 nm. Molecular structures are shown in the insets.

Scheme 1



PPh_3 (0.031 g, 0.012 mmol), CuI (0.012 g, 0.06 mmol), 4-nitrophenylacetylene (2.06 g, 12.8 mmol), and (*i*-Pr)$_2$NH (1.8 mL, 12.8 mmol). After stirring for 3 days at room temperature, the reaction mixture was diluted with toluene, the organic solution was filtered, and the solvent was removed. The residue was purified by column chromatography (ethyl acetate−petroleum ether, 1:9) to give 2 g (92%) of **3**, mp 244 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.13 (d, 6H, J = 8,1 Hz), 7.49 (d, 6H, J = 8,4 Hz), 7.65 (d, 6H, J = 8,7 Hz), 8.23 (d, 6H, J = 8,4 Hz). The synthesis and structural characteristics of the tetramer systems with four distyrylbenzene chromophores grouped around the tetrahedral adamantane or carbon core have been described previously.[18]

Continuous wave fluorescence and absorption spectra of the nitrogen-cored tris-4,4′,4″-(4-nitrophenylethynyl)triphenylamine system dissolved in chloroform are shown in Figure 1. The first absorption band peaks are at 422 nm, and two other peaks are found at 374 and 318 nm. It is important to note that the absorption spectrum of the parent molecule dimethylnitroaminotolane (DMNAT) representing the linear building block of the tris-4,4′,4″-(4-nitrophenylethynyl)triphenylamine system is similar to the spectrum of trimer (shown in the inset of Figure 1). The low-energy transition peak of the DMNAT (which has

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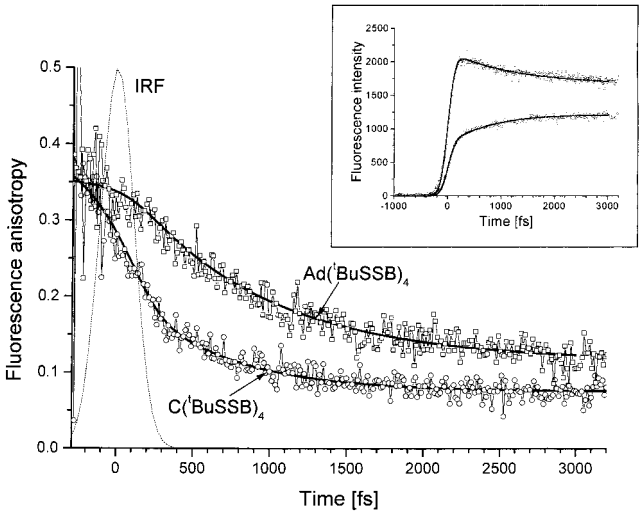

Figure 3. Time-resolved fluorescence anisotropy of tetrahedral molecules Ad(^{t}BuSSB)$_4$ and C(^{t}BuSSB)$_4$. Best fit curves are also shown (solid lines). Excitation and detection wavelengths are 385 and 480 nm, respectively. Dotted line represents the instrument response function. The perpendicular and parallel fluorescence components of the Ad(^{t}BuSSB)$_4$ are shown in the inset.

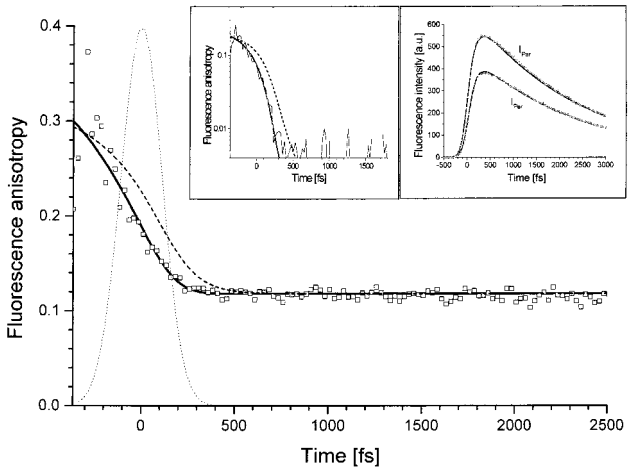

Figure 4. Time-resolved fluorescence anisotropy of tris-4,4′,4″-(4-nitrophenylethynyl)triphenylamine. Best fit curves are also shown (solid line). Dash line shows modeling of the raw anisotropy with the 100 fs single-exponential decay function. Dotted line represents instrument response function. Excitation and detection wavelengths are 410 and 550 nm, respectively. A semilogarithmic plot of the time-dependent part of the fluorescence anisotropy [$r(t) - r_{res}$] is shown in the right inset. The left inset shows the fluorescence components of tris-4,4′,4″-(4-nitrophenylethynyl)triphenylamine polarized perpendicular and parallel with respect to the excitation.

charge-transfer character[19]) is slightly shifted in the absorption spectrum from the trimer, and a small additional peak (shoulder) appears at 374 nm as well. The shift and splitting in the trimer's spectrum reflect the interaction between monomers. A relatively large Stokes shift and unresolved vibronic structure of fluorescence spectrum are correlated with the charge-transfer character of the excited state of the tris-4,4′,4″-(4-nitrophenylethynyl)-triphenylamine. The linear absorption and fluorescence spectra for both adamantane- and carbon-centered tetramer systems are shown in Figure 2. The absorption spectrum of both samples peaks at about 466−468 nm and shows weak vibronic structure. The vibrational structure is more pronounced in the fluorescence spectra revealing two distinct peaks and a red-shifted shoulder. The spectral data for tetramers are similar to those for the parent distyrylbenzene (DSB) chromophores. There are no substantial differences in optical spectra, which might suggest that interactions within the tetramer molecule are relatively weak. It is also seen from Figure 2 that both absorption and fluorescence lines of C(^{t}BuSSB)$_4$ are somewhat shifted to the red as compared to those of Ad(^{t}BuSSB)$_4$. This may be an indication of stronger interchromophore interaction in the carbon-centered system as compared to that for the adamantane-centered system which has a larger separation between branched DSB-chromophores.

The anisotropy decay result for tetramer systems is shown in Figure 3, while Figure 4 shows the fluorescence anisotropy dynamics ($r(t)$) of the triphenylamine system. The insets in both figures show the parallel and perpendicular polarized fluorescence decay profiles measured at the same wavelengths. It is clearly seen that the anisotropy decay is much faster for the nitrogen-cored trimer as compared to those of both carbon- and adamantane-centered tetramers. The best fit result for the nitrogen-core trimer system showed an anisotropy decay time of approximately 35 fs. The anisotropy dynamics contain important information about interchromophore interactions and excitation energy migration processes in branched systems.[4,11] However, there have been only a few reports concerning fast excited-state anisotropy dynamics in small symmetrical molecules. For example, pump−probe anisotropy measurements on the Q-band of magnesium tetraphenylporphyrin (MgTPP) revealed an initial anisotropy of 0.65 and a two-exponential anisotropy decay with two time constants 210 fs and 1.6 ps.[20] Very recently Jonas and co-workers performed pump−probe anisotropy measurements for the Q-band of silicon 2,3 naphthalocyanine bis(trihexylsiloxide) and observed an initial anisotropy of 0.4 that decayed to the residual value over 200 fs.[16] High anisotropy values and fast anisotropy decay results have also been obtained from pump−probe anisotropy experiments[15b] with an $[Ru(bpy)_3]^{2+}$ molecule.[15a] The anisotropy decayed from the initial value of ∼0.55 to ∼0.4 with a decay time of about 100 fs.[15a] There have been even less fluorescence time-resolved experiments which have shown these particular characteristics for symmetric molecular systems.[21,22] One experiment on the Soret band of ZnTPP showed the fluorescence anisotropy decay time of 200 fs with high initial value ≥0.7.[21] The time-dependent fluorescence anisotropy was also measured for aluminum(III) tris(8-hydroxyquinoline) (Alq_3) and was found to decay with a time constant of 2.0 ps.[22]

The process of incoherent energy transport in a C_3-symmetry system (amino-substituted phenylbenzene derivative *p*-EFTB) was reported by Latterini et al.[14] utilizing pump−probe experiments with time resolution of about 140 fs.[14] The anisotropy was found to decay in a picosecond time range (8 ps).[14] The authors attributed this slow anisotropy decay result to the incoherent hopping of the excitation between initially localized single branches.[14] It is worth noting that pump−probe anisotropy

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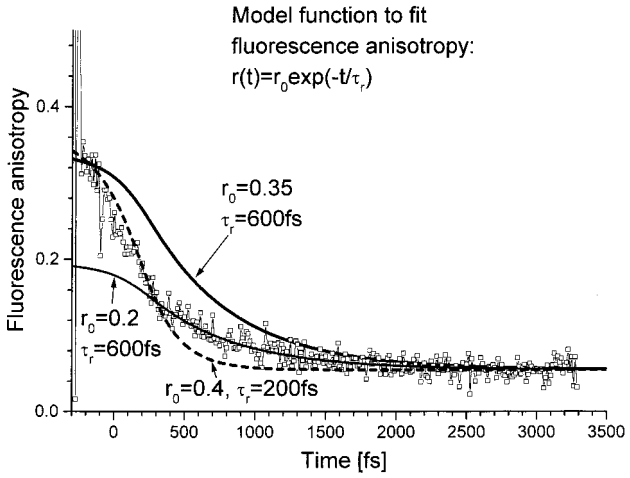

Figure 5. Simulations for the raw fluorescence anisotropy of the C(^{t}BuSSB)$_4$ using a single-exponential decay model for the anisotropy decay.

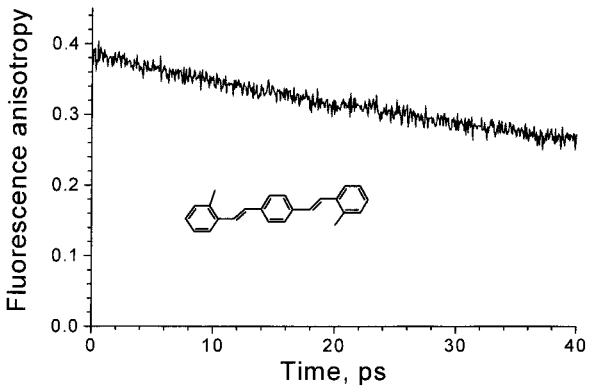

Figure 6. Time-resolved fluorescence anisotropy of the model system *p*-bis(*o*-methylstyryl)-benzene (bis-MSB). Excitation and detection wavelengths are 395 and 450 nm, respectively. The molecular structure of bis-MSB is shown in the inset.

results are complicated by a collection of contributions from ground-state bleaching, stimulated emission, excited-state absorption, and possibly pump−probe coherence coupling and perturbed free induction decay.[4a] In some cases it is difficult to account accurately for all these contributions. Fluorescence time-resolved measurements give direct information about the decay of the excited state. However, the fluorescence upconversion technique usually operates with Stokes-shifted (already relaxed) states. It complicates recovering the true early stage of the excited-state dynamics. As a result, many contradictions in time-resolved pump−probe and upconversion experimental results and interpretations of the dynamics of the optical anisotropy of symmetrical molecules still persist. For example, it has been shown theoretically that the quantum mechanical and stochastic-kinetic description of a square symmetric chromophore system (D_{4h}) requires degeneracy between two relaxation rates that may not be distinguished from each other.[23] However, experiments on square porphyrin-type molecules showed two- or even multiphase anisotropy decay with well-distinguished decay times.[20] Indeed, more experimental and theoretical efforts such as those reported here are necessary to resolve the problems with an accurate characterization of the energy transfer in multichromophore symmetrical and branched molecules.

The decay of the anisotropy for both adamantane- and carbon-centered tetramer systems (shown in Figure 3) was measured at an emission wavelength of 480 nm and excited at 385 nm. The inset shows the parallel and perpendicular polarized fluorescence decay profiles measured at the same wavelengths. The fluorescence anisotropy decays from an initial value just below 0.4 to the residual anisotropy of approximately 0.06−0.12, for the carbon and adamantane systems, respectively. The presence of a decay component in the range of ∼1 ps is clearly observed for both systems. The fluorescence anisotropy decay of adamantane-centered tetramers can be fit well with a one-exponential decay function with a lifetime of ∼880 fs and an initial value of 0.36. The carbon-centered tetramer showed a more complex decay pattern as compared to those for the adamantane-centered system and the trimers. Figure 5 shows the attempt to fit the anisotropy decay of the carbon-centered tetramer to a number of different possibilities of parameters with a single-exponential function. However, as can be seen in Figure 3, the anisotropy decay of the C(^{t}BuSSB)$_4$ fits well to a two-exponential decay function. The best fit of the decay profile gives two relaxation times, one that is 45 ± 20 fs, which is followed by another of 610 ± 50 fs.

To gain further insight into the physics behind the fast depolarization process, it is important to compare the anisotropy dynamics of the tetramers with that for a single chromophore (monomer). We measured the fluorescence anisotropy for the model system of *p*-bis(*o*-methylstyryl)-benzene (bis-MSB) representing the linear building block of the tetramers. The result is shown in Figure 6. It is clearly seen that fluorescence anisotropy dynamics of the model system of bis-MSB strongly differ from those of tetramers. Starting at the initial value close to 0.4, the fluorescence anisotropy decays with the time constant of about 100 ps, which agrees with the rotational diffusion time of the bis-MSB molecule. Comparing the anisotropy decay results for tetramers with those for the model system bis-MSB suggests that the initial ultrafast transition dipole reorientation is due to intersegment interactions in the tetramers. The residual anisotropy slowly decays to zero over 1.2 ns due to rotational diffusion of the molecule. The result of the slow decay of the residual anisotropy in tetramers is shown in Figure 7. A single-exponential best fit gave the rotational diffusion time estimate of the carbon-centered tetramer in chloroform of ∼550 ps.

The anisotropy ($r(t)$) decay result for the triphenylamine anisotropy decay measured at the emission wavelength of 450 nm and excited at 410 nm is shown in Figure 4. For the case of the triphenylamine anisotropy decay, it was possible to fit the measured profile with a single exponential as seen in Figure 4. The best fit result showed the anisotropy of the triphenylamine system decays rapidly to a residual value with a time constant of ∼35 fs. The raw initial anisotropy was below 0.4 (Figure 4); however, the best fit to the monoexponential decay gave the initial value $r(0)$= 0.47 ± 0.10. The depolarization time is shorter than the duration of the instrument response function (IRF, also shown in Figure 4). Nevertheless, even if a single-exponential depolarization process occurs on a shorter time scale then the width of IRF, most of the information about the depolarization process can be recovered. However, for a more complex anisotropy decay law, the uncertainty in determining initial anisotropy as well as the fast decay time can be substantial. The success of the fitting procedure critically

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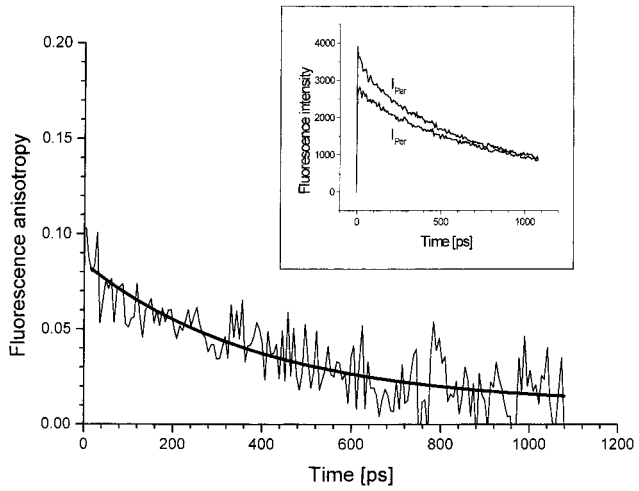

Figure 7. Time-resolved fluorescence anisotropy of the tetrahedral molecule C(^{t}BuSSB)$_4$ on the long time scale (rotational diffusion). Best fit curve is also shown (solid line). The fluorescence components of the C(^{t}BuSSB)$_4$ polarized perpendicular and parallel with respect to the excitation are shown in the inset.

depends on the signal-to-noise ratio in the experimental decay curves in the vicinity of the IRF. In the case of analysis of the raw fluorescence anisotropy, this ratio drops down very quickly as we go toward the negative delays as the experimental anisotropy is associated with the ratio of two experimental values (parallel and perpendicular polarized fluorescence) which both tend to zero. This may be the cause for the many contradictory data in the literature about the raw and calculated initial anisotropies.[1e,15,16,20,21] However, the modeling of the experimental anisotropy decay showed that it could not be satisfactorily fit with an IRF-convoluted exponential with the decay times longer then 60 fs independently on the initial anisotropy $r(0)$. The result of such modeling with a 100 fs exponential decay law is shown in Figure 4. It is seen that actual decay is shorter then 100 fs. This result is similar to what was found for a distyrylbenzene trimer dendrimer, where the anisotropy also decayed to a residual value within the instrument response function of the upconversion unit (190 fs).[12] This fast depolarization may be due to the strong interactions of the three nitrotolane chromophore groups (or the three distyrylbenzene groups for the case of ref 12) around nitrogen.

It is important to note that for the isotropic (magic angle) fluorescence dynamics of the tetramers and trimers, we did not observe the same fast decay components as we observed for the anisotropy decay. This is an indication that in our case the fast dipole moment reorientation is not directly related to the processes that are responsible for isotropic fluorescence decay. A dynamic Stokes shift associated with the solvation processes is usually reflected in the isotropic fluorescence decay pattern.[24] Hence the main time scale of the solvation dynamics is different from that for the anisotropy decay, and solvation effects do not contribute substantially to the anisotropy dynamics. The residual value of the fluorescence anisotropy (before molecular rotation) contains geometrical and structural information. For a planar molecule with the rotational symmetry higher than C_2, the residual anisotropy should be 0.1.[11a,25a] In the case of the point 3-D symmetry molecule, the anisotropy should decay to zero during the relaxation process.[11b] For equilibrated systems, these values are easy to calculate just using the law of summation (additivity) of anisotropies.[25a,b] For triarylamine trimer, we observed the residual anisotropy to be 0.120 ± 0.005 which is slightly above the expected value of 0.1 for a planar molecule. The triphenylamine molecule has been reported to have a propeller-like geometry with the N−C bonds lying almost in one plane.[25b] Twisting of the phenyl rings may lead to a small inclination angle of the transition dipoles of the nitrophenylacetylene branches relative to the NC-bond plane. The inclination angle of about 9.5° could lead to the residual anisotropy of tryarylanime trimer observed in our experiments.[25c] The reasons for the nonzero (and different) residual anisotropies of carbon- and adamantine-cored tetramers are less clear. It can be suggested that there is a small amount of distorted molecules possessing high anisotropy. This could lead to a different nonzero residual anisotropy for the carbon- and adamantane-cored tetramers.

In comparing the ultafast anisotropy decays for the tetramers with that for the trimer it can be suggested that the relatively slow decay result for the tetramers corresponds to the weaker interaction (hopping) limit of the interchromophore interaction. Alternatively, the fast decay time in the case of the nitrogen-cored DSB-trimer[12] may result from a stronger interaction among the same distyrylbenzene branching chromophore groups. In a weak coupling limit (hopping regime), the energy transfer can be described by the Förster theory.[26a] To evaluate the ability of the Förster theory to describe the energy transfer between DSB-chromophores in tetramers, we compare the theoretical and measured energy transfer rates. For the case of a very weak interaction between chromophores in the macromolecule, the chromophores should behave as individual isolated molecules, and the fluorescence anisotropy decay can be described by the expression[4b]

$$r(t) = \frac{1}{10}[1 + 3e^{-t/\tau_D}], \quad \tau_D = \frac{\tau_{hopping}}{4(1 - \cos^2\theta)} \qquad (1)$$

Here $\tau_{hopping}$ is the excitation hopping time (in the absence of rotational diffusion), and θ is the angle between the transition dipoles of chromophores in a planar-symmetrical system.[4b] Similar to eq 1 for the depolarization time (rate) in planar systems, the expression for the depolarization rate in a tetrahedral molecular system can be derived:

$$\tau_D = \frac{2\tau_{hopping}}{9(1 - \cos^2\theta)} = \frac{\tau_{hopping}}{4} \qquad (2)$$

where $\theta = 109.47°$ is the tetrahedral angle between transition dipoles. The Förster rate of energy transfer between donor and acceptor separated by a distance R_{DA} is given by[26a]

$$k_t(r) = \frac{1}{T_D}\left(\frac{R_F}{R_{DA}}\right)^6 \qquad (3)$$

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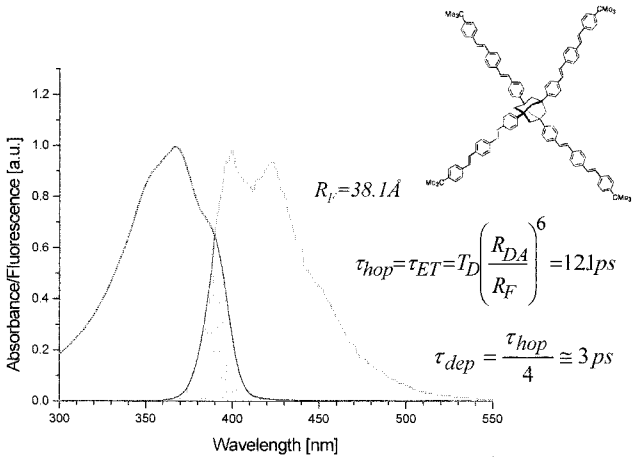

Figure 8. Spectral overlap between emission and absorption spectra of the Ad(^{t}BuSSB)$_4$. Förster energy transfer parameters are also shown.

where T_D is the fluorescence lifetime of the donor in the absence of acceptor, and R_F is the Förster radius, which is the critical distance between the donor and acceptor such that the energy transfer probability equals the emission probability. The spectral overlap between the absorption and emission spectrum of the Ad(^{t}BuSSB)$_4$, which is critical for the Förster radius calculation,[26a] is shown in Figure 8. The Förster radius calculation gave us the value of 38.1 Å. We estimated the distance between the centers of adjacent DSB-chromophores to be about 18 Å. Using this distance, an energy transfer time of $\tau_{\text{hopping}} = 1/k_t = 12.1$ ps was obtained. In accordance with eq 2, this should lead to a depolarization time τ_D of 3 ps. This is in qualitative agreement with our experimental anisotropy measurements with Ad(^{t}BuSSB)$_4$. The difference between calculated and experimental times could be due to the fact that the distance between DSB chromophores is comparable with the chromophore's size, and the point dipole model is not accurate in this case. Nevertheless, the order of magnitude of the Förster transfer rate is comparable with experimental results, and this is in qualitative agreement with our suggestions of a predominately hopping character of energy migration in tetramers. This result is also in qualitative agreement with the calculation performed for DSB-dimers by Mukamel et al.[27a] By using a collective electronic oscillator approach (CEO), it was shown that in the case of DSB-dimers with a paracyclophane bridge, the lowest electronic excitation is localized mostly on the DSB-unit (monomer). In the case of adamantane-cored tetramers, the distance between DSB units is larger than that in paracyclophane-based dimers, and the interaction should be even smaller. It was shown above (Figures 3 and 4) that the anisotropy decay for carbon-centered tetramers is two-exponential, opposite to single-exponential decay for adamantine-centered tetramers. Apparently, a relatively small decrease of the interchromophore separation (2.9 Å, 16% of the distance between DSB-centers) in C(^{t}BuSSB)$_4$ with respect to Ad(^{t}BuSSB)$_4$ leads to a substantial change of the anisotropy dynamics associated with interchromophore interaction. This critical distance dependence may suggest the presence of a short-range interaction of exchange (Dexter)-type[26b,c] to come into effect. Intramolecular chromophore clustering[4c] associated with small distortions can be suggested as the reason for two-exponential anisotropy decay. Fast equilibration within a cluster (for example, a strongly *exchange*-coupled dimer) leads to an initial 45 fs drop in anisotropy, while the remainder of the depolarization decays due to intercluster energy transfer.[4c] The anisotropy decay results in tetramers which are different from the dynamics of the nitrogen-centered trimers investigated in this work as well as for what was reported previously.[12] For both nitrogen-cored trimer systems, the experimental depolarization times were found to be too short (<100 fs) to be described by a Förster transfer model. The Förster transfer time for the nitrogen-cored DSB-system was calculated to be ~4 ps. This is not in agreement with the experimental anisotropy decay times.

To analyze the case of strong interactions in the triphenylamine (Figure 4), we have utilized a phenomenological model to describe the system.[17] A modest distortion of the absorption spectrum of the triphenylamine as compared to that of linear chromophore DMNAT (monomer) mentioned above suggests that the role of electron delocalization is not significant and the excitonic model can be used at least for qualitative analysis. In this particular case, the discussion of coherence of the excitations is led by using a model in which the limiting cases of Förster transfer (weak interaction) and completely delocalized excitonic states (strong interaction) are continuously connected to each other. This analysis uses the infinite temperature approximation for the extremely small phonon correlation time.[17] The interesting conclusions of this approach are that for certain limiting symmetry examples it is possible to relate the depolarization time to the ratio J/Γ of the interaction (J) and homogeneous line width (Γ).[17] For the case of N-fold symmetry (planar), they are related by[17]

$$t_{\text{dep}} = \frac{1}{\Gamma(1 - A)} \tag{4}$$

where

$$A = \frac{1}{N} \sum_{k=1}^{N} \frac{\Gamma^2}{\Gamma^2 + 16J^2 \sin^2(2\pi/N) \sin^2(2\pi k/N)}$$

Here N is the number of chromophores contributing to the energy migration process. In the weak interaction limit, it can be shown that eq 4 reduces to eq 1.[17] We have calculated the profile of eq 4 against realistic values of the homogeneous line width for the case of the trimer. The calculated curves for eq 4 versus the interaction parameter J are shown in Figure 9. From our result with the triphenylamine system, we obtained a depolarization time of approximately 35 fs. To estimate the interaction strength J and energy transfer regime, we need to know the homogeneous line width Γ. Selective excitation at a different wavelength over the absorption spectrum showed no dependence of the fluorescence spectrum on excitation wavelength. However, this steady-state result does not necessarily imply that the line is homogeneously broadened on the time scale of our experiment. Using the full line width instead of homogeneous line width would be an overestimation of Γ. A set of curves describing eq 4 for different values of homogeneous broadening Γ taken similar to the full low-energy absorption peak line width (2840 cm^{-1}, estimated by multi-Gaussian best fit analysis) is shown in Figure 9. Fortunately, several important inferences can be drawn from Figure 9 without

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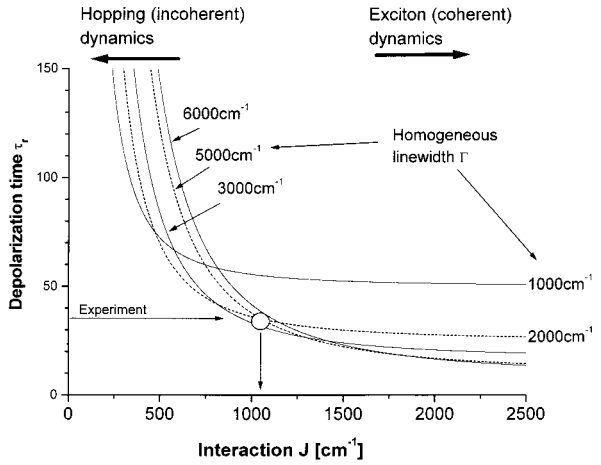

Figure 9. Theoretical dependence of depolarization time τ_r on the interchromophore interaction J for a C_3-three-chromophore molecular system. The arrow shows the depolarization time obtained from experiment for the trimer system.

exact knowledge of Γ. First, it is clearly seen that within the frame of this model it is impossible to have a anisotropy decay time of 35 fs and to reside in the Förster regime (small interaction) for any homogeneous broadening smaller than the full line width. Here, coherence must be taken into account. Actually, the experimental anisotropy decay time falls at the curvature of the plot of eq 4 and may be interpreted as a crossover region between incoherent (hopping) dynamics and the existence of excitonic interactions. Extrapolation of the 2000−3000 cm^{-1} curves to find the estimated interaction strength corresponds to a magnitude close to 1000 cm^{-1}. It is worth noting that the appearance of a small peak (shoulder) at 374 nm in the trimer's absorption spectrum (see Figure 1) could also be an indication of excitonic coupling in the trimer. These results strongly suggest that coherent interactions are essential in describing the energy migration in the trimer branched chromophore system.

In this paper, we have characterized the interactions between branch chromophore units in model dendritic systems. The three- and four-fold symmetry model branching centers showed different excitation dynamics probed by time-resolved fluorescence anisotropy. The fluorescence anisotropy of the triarylamine system decayed to a residual value with a time constant of 35 fs, while the tetramer systems showed a more complex decay with at least two decay components for the carbon-centered tetramer. The slower components of the anisotropy decay for the tetramer system may be inferred as the result of weaker chromophore interactions and can qualitatively be described by a Förster model. For the triarylamine system, theoretical modeling showed the energy migration to be at the crossover region between coherent and incoherent type as estimated by a phenomenological model. These results give stronger evidence for the significance of coherence in energy transport by strong interchromophore interactions in branched fluorescent macromolecules of various symmetries. The nature and magnitude of the interaction strengths in these branched structures are very important for applications in light emission and light harvesting. If the migration time around a single branching center is very fast (for the case of nitrogen-cored trimers), this would result in an ultrafast energy transfer time in organic dendrimers based on these branching units.

Experimental Section

Steady-State Spectra. Steady-state absorption spectra were recorded with a Hewlett-Packard 8452A diode array spectrometer. Fluorescence spectra were taken with Shimadzu RF-1501 or SPEX spectrofluorometers.

Time-Resolved Fluorescence Anisotropy Measurements. Femtosecond upconversion spectroscopy was employed to resolve temporally the polarized fluorescence. The optical arrangement for our upconversion experiments has been described previously.[12a,28] The sample solution was excited with a frequency-doubled light from a mode-locked Ti-sapphire laser (Tsunami, Spectra Physics). This produces pulses of approximately 100 fs duration in a wavelength range of 385−430 nm. The polarization of the excitation beam for the anisotropy measurements was controlled with a Berek compensator. The sample cuvette was 1 mm thick and was held in a rotating holder to avoid possible photodegradation and other accumulative effects. The horizontally polarized fluorescence emitted from the sample was upconverted in a nonlinear crystal of β-barium borate using a pump beam at about 800 nm that was first passed through a variable delay line. This system acts as an optical gate and enables the fluorescence to be resolved temporally with a time resolution of about 200 fs (pump-excitation 790/395 nm cross correlation function had a fwhm of 190 fs). Spectral resolution was achieved by dispersing the upconverted light in a monochromator and detecting it by using a photomultiplier tube (Hamamatsu R1527P). The excitation average power was kept at a level below 0.5 mW. In this excitation intensity regime, the fluorescence dynamics were found to be independent of the excitation intensity for all investigated solutions.

Fitting Procedures for Fluorescence Anisotropy. Raw fluorescence anisotropy $R(t)$ was calculated from the decay curves for the intensities of fluorescence polarized parallel $I_{par}(t)$ and perpendicular $I_{per}(t)$ to the polarization of the excitation light according to the expression $R(t) = (I_{par} - GI_{per})/(I_{par} + 2GI_{per})$. The factor G accounts for the difference in sensitivities for the detection of emission in the perpendicular and parallel polarized configurations. It was measured using perylene in methanol as a reference. In the real experiment, the G-factor has been found to be essentially in unity (1.02 ± 0.02). The initial dynamics of fluorescence anisotropy for the triarylamine system were found to be very fast, completing within the duration of the instrument response function. To make a reasonable estimation of the fluorescence anisotropy decay time, we performed Impulse Reconvolution[29] assuming for triarylamine the one-exponential decay law for anisotropy decay with time constant τ_a and the residual value of τ_r. Difference ($I_{par} - GI_{per}$) and isotropic ($I_{par} + 2GI_{per}$) decay curves were fitted to the result of the convolution of the instrument response function with an exponential model to minimize the reduced χ^2 value.[30] The minimum value was obtained by the Marquardt nonlinear least-squares method. The quality of the fit was monitored by values of the reduced χ^2 as well as by inspection of the residuals and autocorrelation function. Numerical modeling of the raw fluorescence anisotropy for different sets of isotropic and anisotropic parameters was also performed and compared with the experiment.

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