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Ultrafast Dynamics of Electronic Excitations in a Light-Harvesting Phenylacetylene Dendrimer

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Femtosecond degenerate pump–probe spectroscopy is used to investigate the ultrafast dynamics of electronic excitations in the nanostar dendrimer. The laser wavelength was chosen to preferentially excite the 2-ring peripheral phenylacetylene chromophores, or the 3-ring intermediate phenylacetylene chromophores. The transients reveal several components with relaxation times ranging from several hundred femtoseconds to tens of picoseconds, depending on the excitation wavelength. The experimental transients resulting from excitation of the 2-ring chromophores are interpreted in terms of Förster energy transfer, which predicts energy transfer rates that are consistent with the experimental measurements.

1. Introduction

There recently has been much interest in examining the potential of nanometer-size dendrimers for light-harvesting applications.^{1–4} The work of Moore, Kopelman, and co-workers has shown that dendrimers based on phenylacetylene chromophores exhibit highly efficient and unidirectional energy transfer properties.^{4–7} The nanostar shown in Figure 1 is an example of a dendrimer with an energy gradient.^{4,6} The nanostar has a phenylacetylene backbone with a perylene trap located at the core. The energy gradient is engineered by linking chromophore units of increasing length (2-, 3-, and 4-ring) in the direction of dendrimer periphery to the perylene trap. Substitution at the meta position on the benzene ring suppresses the π -electron conjugation and leads to localized excitations within the different chromophore segments.^{5,8} Electronic excitations at the periphery then migrate down the gradient and funnel into the perylene trap.

Questions remain regarding the time scale and mechanism for the energy transfer process in the nanostar. For example, do excitations at the periphery migrate to the perylene through each of the intermediate chromophores, or are there direct “jumps” from the periphery to the perylene trap? If the energy transfer occurs through a multistep mechanism, then what is the time scale for each of the individual steps? Using the time-correlated photon counting method, Swallen et al. have determined an ensemble-averaged trapping time on the order of 10 picoseconds for energy transfer from the lowest energy chromophore (4-ring linear segment) to the perylene trap.⁹ Somewhat longer trapping times occur starting from the periphery.⁹ While these measurements emphasize the rapid unidirectional funneling of the nanostar, the time resolution is not sufficient to resolve individual steps in the funneling process, which may be considerably faster. To our knowledge, an experimental investigation of the energy funneling process in the nanostar with femtosecond resolution has not yet been performed.

In this paper, we use degenerate femtosecond pump–probe spectroscopy to measure the dynamics of electronic excitations of impulsively excited chromophores in the nanostar. The observed transients reveal several components with time scales

that range from hundreds of femtoseconds to tens of picoseconds. The characteristics of the experimental transients depend on whether the peripheral or intermediate chromophores are initially excited.

2. Experimental Section

Laser pulses of 180 to 200 fs duration were generated in the wavelength region of 300–360 nm by nonlinear conversion of the output of a femtosecond optical parametric amplifier. The nanostar sample was provided by Professor J. Moore and dissolved in dried dichloromethane. A 3×10^{-6} molar solution was circulated through a 2 mm path length cell (o.d. \approx 0.6). The beam diameter was approximately 130 μ m at the sample, and the pump–pulse energies were in the 3–18 nJ range, yielding energy fluences from 23 to 135 μ J/cm².

3. Results and Discussion

The absorption spectrum of the nanostar in dichloromethane is shown in Figure 2. The peaks/shoulders near 310, 352, and 373 nm correspond to the vibrationless excitonic bands of the 2-, 3-, and 4-ring linear chromophores, respectively.^{5,8} The peaks/shoulders near 290 nm and 325 nm correspond to vibronic transitions of the 2-ring and 3-ring chromophores, respectively. The weak feature in the region around 450 nm is the absorption of the perylene trap. The degenerate pump–probe experiments were conducted at 310 and 352 nm, as indicated by the arrows in Figure 2. These wavelength choices preferentially excite the 2-ring or the 3-ring chromophores; highly selective excitation is prevented by the overlapping vibronic transitions associated with the next longest chromophore species. Excitation of the perylene trap is minimal due to its relatively low number density and its small absorption cross section in the wavelength range of 300–370 nm.

To establish a reference point for discussing the dynamics associated with the peripheral 2-ring chromophores in the nanostar, we briefly discuss the excited-state dynamics of diphenylacetylene (DPA) monomers in solution. Hirata et al.¹⁰ measured the relaxation dynamics of DPA in *n*-hexane after excitation at 295 nm. The excitation pulse initially populates the S₂ manifold, which can either return to the ground state through (mainly) nonradiative relaxation, or undergo internal

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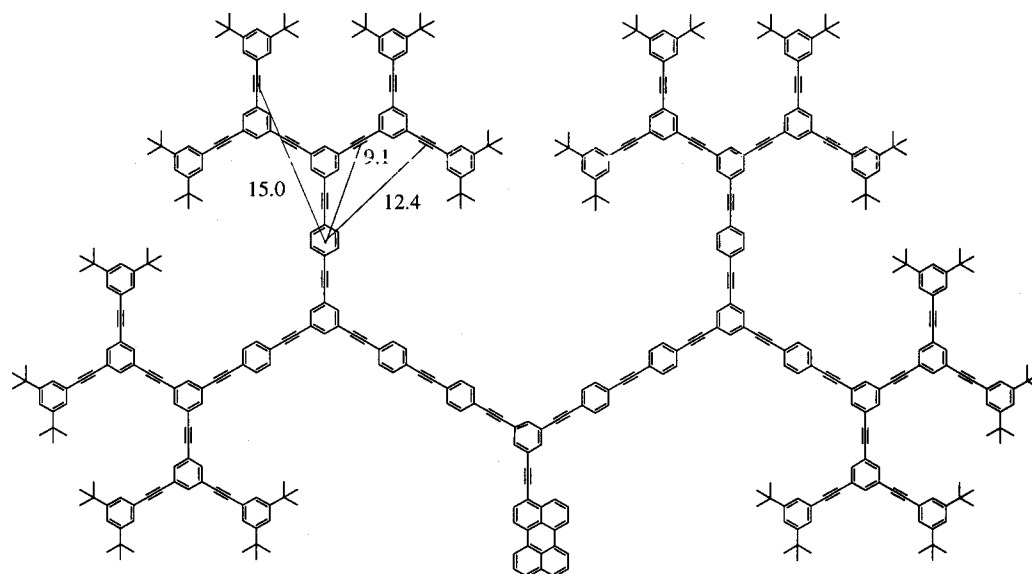


Figure 1. Chemical structure of the nanostar dendrimer. The lines indicate the chromophore couplings considered in the Förster energy transfer calculation. The numbers indicate distances in angstroms for a planar geometry.

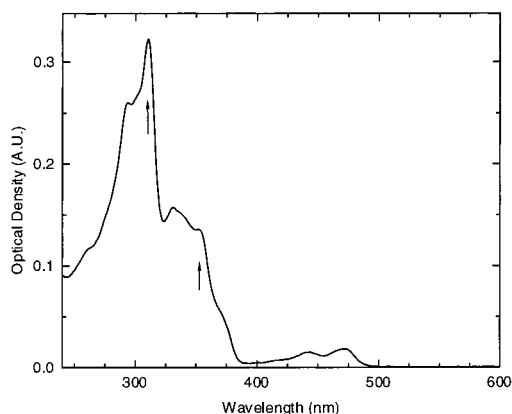


Figure 2. Absorption spectrum of the nanostar in dichloromethane. Absorption for wavelengths shorter than 400 nm correspond to the dendrimer backbone. The feature in the region around 450 nm corresponds to the perylene absorption. The arrows indicate the wavelengths used in the experiment and correspond to the vibrationless exciton energies.

conversion to the S_1 state. The S_1 state undergoes intersystem crossing to populate the T_1 state. With an instrument response of 8 ps, they estimated the lifetime of the S_2 state to be about 8 ps in *n*-hexane, and established a lifetime of 200 ps for the S_1 state.¹⁰ In our laboratory, degenerate pump–probe measurements for DPA in dichloromethane (not shown here) exhibit a biexponential decay, with a fast component corresponding to relaxation of the S_2 manifold and a slow component ($\tau > 150$ ps, amplitude $\approx 30\%$ of the signal at $t = 0$) identified with the intersystem crossing process. We determined the S_2 lifetime using two-color transient absorption. Figure 3 shows the decay of the $S_n \leftarrow S_2$ absorption following excitation at 297 nm and detection at 500 nm. The data are fit with a single-exponential decay with a 6.3 ps time constant to yield the lifetime for the S_2 manifold.

Transient bleach signals for the nanostar are shown in Figures 4a and 4b. The induced transmission was observed to be linear over a nearly a 6-fold increase of the excitation fluence ($23\text{--}135\ \mu\text{J}/\text{cm}^2$). Excitation at 310 nm (Figure 4a) is resonant with the 2-ring chromophores at the periphery (and the 3-ring chromophore through vibronic excitation) and yields a multi-component transient bleach signal. Two decay components are

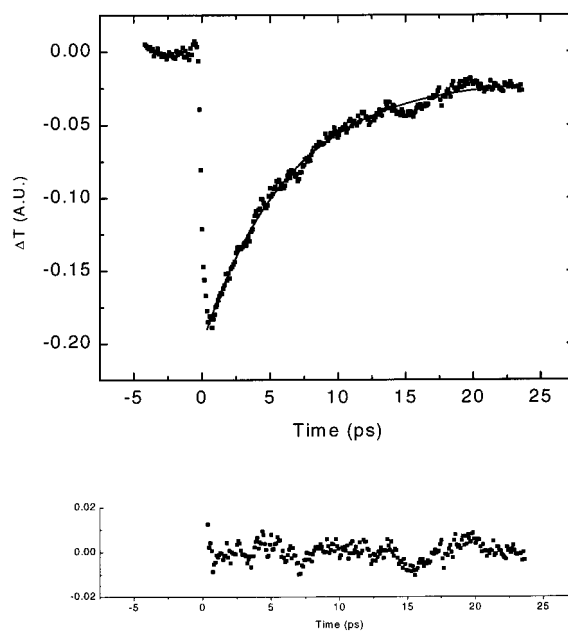


Figure 3. Two-color transient absorption of diphenylacetylene in dichloromethane. The pump wavelength is 297 nm and the probe wavelength is 500 nm. The signal, ΔT , represents the change in the probe transmission induced by the pump laser pulse. The points correspond to experimental data, and the solid line corresponds to a fit with a decay time of 6.3 ps.

evident, as well as a reproducible complex oscillatory component. The solid line is a fit based on the sum of two exponential components. The faster component decays with a time constant of 3.0 ± 0.5 ps, while the slower component decays with a time constant of 14 ± 2.5 ps. The transient bleach signal of the nanostar is qualitatively different than the corresponding transient bleach signal from the DPA monomers. Notably absent from the nanostar dynamics is the long-lived ($\tau > 150$ ps) decay due to the $S_1 \rightarrow T_1$ intersystem crossing observed for the DPA monomers. Further, the fast component in the nanostar transient is significantly shorter than the 6.3 ps lifetime of the S_2 state that we measured for DPA.

A transient bleach signal also is observed for excitation centered at 352 nm (Figure 4b), which is resonant with the intermediate 3-ring chromophores (and the 4-ring chromophores

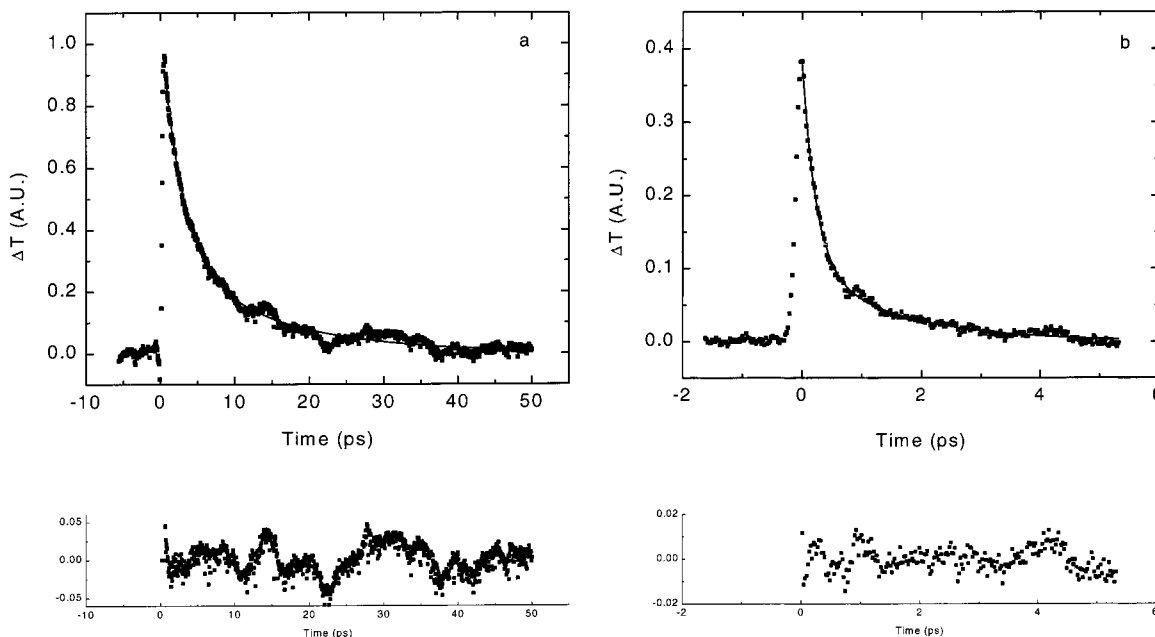


Figure 4. Transient bleach signal for the nanostar. (a) Preferential excitation of peripheral 2-ring chromophores at 310 nm. (b) Preferential excitation of intermediate chromophores at 352 nm. The signal, ΔT , represents the change in the probe transmission induced by the pump laser pulse. Solid circles correspond to experimental data and the solid line corresponds to a biexponential fit. Bottom plots show the residual. Note the different time scales in (a) and (b).

via vibronic excitation). The time scale for the relaxation dynamics is considerably faster when compared with the 310 nm excitation. The fit to the transient bleach yields a biexponential decay with time constants of 270 ± 40 fs, and 1.1 ± 0.25 ps.

The transient bleach signals probe the recovery of ground-state absorption of chromophore groups initially excited by the laser pump-pulse and can contain contributions from both population and coherence relaxation processes. In general, both intra- and interchromophore relaxation dynamics can influence the ground-state recovery. However, if the ground states of the initially excited chromophores were significantly repopulated by intrachromophore relaxation processes, then the quantum yield for energy transfer to the perylene core would be significantly less than the near unity values that have been observed.^{4,9} Thus, we conclude that the dynamics observed in these experiments are due mainly to the interchromophore events. In particular, the transient bleach signals are sensitive to the time scale for energy transfer out of the chromophore states excited at 310 or 352 nm.

Interchromophore energy transfer can be interpreted in terms of through-bond (Dexter-type) or through-space (Förster-type) mechanisms. The Dexter mechanism involves the spatial overlap between the orbitals of the donor and acceptor pair, and the energy transfer efficiency falls off exponentially with distance between the pair. Since the meta-substitution in the nanostar disrupts the π -electron conjugation between the chromophores, it is reasonable to expect that the Dexter mechanism will also be suppressed. Here, we interpret the results in terms of Förster energy transfer. In the Förster mechanism, the Coulombic interaction between donor and acceptor is the source for energy transfer. In its simplest form, the Coulombic interaction is approximated by a dipole-dipole interaction, and results in the following expression for the energy transfer rate constant:

$$k_{ET} = \frac{9000(\ln 10)\kappa^2\phi_D J}{128\pi^5 n^4 N\tau_D R^6} \quad (1)$$

TABLE 1: Orientation Factors (κ^2), Interchromophore Distances (R), Energy Transfer Rate Constants (k_{ET}), and Corresponding Time Decays (based on a planar nanostar configuration)

chromophore pairing	κ^2	R (Å)	k_{ET} (s ⁻¹)	k_{ET}^{-1} (ps)
1	2.7	9.1	1.2×10^{12}	0.83
2	1.2	12.4	8.0×10^{10}	12.5
3	2.3	15.0	5.3×10^{10}	18.8

Here, κ^2 is the orientation factor of the dipole moments, ϕ_D and τ_D are the donor quantum yield and lifetime in the absence of the acceptor, R is the interchromophore distance, n is the refraction index of the solvent ($n_{CH_2Cl_2}=1.42$), N is Avogadro's number, and J is an overlap integral of the donor emission spectrum with the acceptor absorption spectrum. There is likely to be considerable uncertainty in the estimation of k_{ET} due to uncertainties in knowing κ , R , and J in the nanostar. Nevertheless, we estimate k_{ET} by considering the coupling of the 2-ring chromophores connected to a single 3-ring chromophore (see Figure 1). Because the 2-ring chromophore assembly resembles a G2 phenyl-terminated monodendron, the donor quantum yield and lifetime in eq 1 are estimated by using values for the G2 phenyl-terminated monodendron corresponding to structure **9** in ref 4 ($\phi_D = 0.31$; $\tau_D = 7.6 \times 10^{-9}$ s). The overlap integral J is calculated using the emission spectrum of the G2 phenyl-terminated monodendron and the absorption spectrum¹¹ of a free 3-ring chromophore (1,4 bis-phenylethynyl benzene) in dichloromethane, yielding a value of 2.8×10^{-14} cm⁶/mol. The R values are determined by estimating the distance between the middle ring of the 3-ring chromophore and the center of the acetylenic bond of a 2-ring chromophore.¹² The values of the interchromophore distances (R), orientation factor (κ^2), and energy transfer rate constant (k_{ET}), for a planar configuration of the donor-acceptor pair are collected in Table 1. We find that k_{ET}^{-1} ranges between 0.83 and 18.8 ps, depending on the 2-ring chromophore considered (see Figure 1). An upper limit would correspond to an adjacent (bonded) donor-acceptor pair, for which $\kappa^2 = 2.7$, $R = 9.1$ Å, and k_{ET} takes a value of $1.2 \times$

10^{12} s^{-1} (0.83 ps). Our data for the 310 nm excitation show that both components of the transient are slower than this limiting case. The calculation based on eq 1 gives rough qualitative agreement with the experimental data, which is encouraging given the uncertainties and approximations mentioned above. A more quantitative prediction of the energy transfer rate in the nanostar will need to address disorder in the orientation factors and interchromophore distances, which are introduced by both the “globular shape” of large generation phenylacetylene dendrimers in solution, and an increase in the rotational flexibility near the dendrimer periphery. Further, it may be necessary to more accurately treat the electronic coupling between donor and acceptor. For example, when the chromophore size is comparable to the interchromophore separation, such as for the case of adjacent chromophores, the dipole approximation may not hold, and a more accurate treatment of the full Coulomb interaction may be necessary.¹³

If there is a stepwise relaxation process, then the excitation of the 3-ring chromophore at 352 nm will result in energy transfer to the 4-ring chromophore. As noted above, the relaxation time scale observed for excitation at 352 nm is considerably faster than for excitation at 310 nm. The subpicosecond relaxation can be attributed in part to a larger electronic coupling of the 3-ring and 4-ring chromophores.¹⁴ The faster relaxation may also be an indication of a better overlap between the emission spectrum of the donor and absorption spectrum of the acceptor combined with a more rigid structure in the inner regions of the dendrimer, yielding a more favorable orientation factor, κ^2 . As mentioned above, since the 3-ring and 4-ring chromophores are adjacent, a more accurate treatment of the full Coulomb interaction may be required to predict the observed energy transfer rate.

Several issues warrant further exploration: First, the complex oscillatory component that is observed for excitation at 310 nm needs to be explained. Second, while excitation at 310 nm contains some vibronic excitation of the 3-ring chromophore, we do not observe a subpicosecond component in the transient shown in Figure 4a. Finally, we have interpreted the experimental transients in terms of interchromophore energy transfer; however, we cannot rule out the possibility that coherence effects¹⁴ in the nanostar also contribute to the transients, especially at early times.

4. Conclusions

We have used degenerate pump–probe spectroscopy to investigate the ultrafast dynamics of electronic excitations in the nanostar dendrimer. The experiment provides a measure of

the time scale for energy transfer out of the initially pumped chromophores. A simple application of the Förster model predicts energy transfer rate constants that are in rough qualitative agreement with the experimental results corresponding to the excitation of the 2-ring chromophores. A more complete picture of the energy transfer dynamics would be realized using a multicolor femtosecond probe that follows the “single frequency” pump. In this manner the nature of the entire funneling process from the periphery to the core can be measured directly. Recently, more sophisticated theoretical models have been developed to describe the energy transfer dynamics in chromophore aggregates,^{13,14} and these may help to provide a better understanding of the nanostar dynamics.

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