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Picosecond dynamics of excitations studied in three generations of new 4,4′-bis(diphenylamino)stilbene-based dendrimers

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Abstract

Picosecond fluorescence decay is observed in a new family of dendrimers constructed from 4,4′-bis(diphenylamino)stilbene repeat units. The rate of the decay is shown to depend on detection wavelength and the generation number in such a way that the energy of accepting states gradually lowers with the generation number. These observations can be consistently described in terms of the fast energy transfer from initially created localized states to more delocalized ones. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Tree-like dendritic structures based on identical branched repeat units present promising macromolecular systems for light harvesting and photochemical processing [1–3]. Dendrimers offer advantages over traditional linear polymers for photophysical studies in that they are mono-disperse macromolecules with well-defined chemical structures, whereas linear polymers are normally polydisperse with a large number of different chain lengths, thus making detailed structure–property relationships difficult to establish. Dendrimers show strong light absorption due to very large number of chromophores, which grows exponentially with generation number. Absorbed light energy can be efficiently transferred to a molecular trap in the center of a dendrimer to be used for photochemical reaction. Due to these unique properties, dendrimers are attractive candidates for incorporation in artificial photosynthetic cells.

However, the study of fundamental features of electronic excitations in dendrimers, such as degree of spatial localization and rates and direction of migration along the backbone has only just begun. In particular, it has been shown that the degree of localization is different in compact and extended phenylacetylene dendrimers [3]. The dendrimers of the first type have branches of equal length, independently of distance from the center, thus leading to complete self-similarity. Electronic states of such dendrimers are shown to be uncoupled and localized

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on a smallest segment [3]. On the other hand, the length of branches of extended dendrimers increases from periphery toward the core. Furthermore, the higher the generation number, the longer the branches adjacent to the core. This results in a more delocalized electronic wave function for higher generations [3].

Time-resolved pico- and femtosecond optical techniques have been recently applied to study relaxation processes in dendrimers [4–7]. In [4], a fast, 4 ps anisotropy relaxation time in polyphenylene dendrimer was tentatively attributed to the Förster energy transfer between neighboring chromophores. An estimated Förster radius appeared to be several times larger than the nearest-neighbor inter-chromophore distance within the dendrimer [4], making an ultrafast transfer reasonable in such systems. The problem of funneling direction in dendrimers was studied theoretically [8,9]. It was shown, that excitation can migrate either from the core to the periphery or vice versa, depending on the presence of an energy gradient of segments across the radius of dendrimer. If this gradient is absent (like in compact dendrimers) excitation will funnel from the core to periphery because of probabilistic considerations [8,9]. If, however, there is a specific low-energy trap in the center of dendrimer macromolecule and the temperature is low enough, excitation will be sooner or later trapped on it [8,9]. Efficient energy transfer from dendrimer periphery to such a specific trap was confirmed by steady-state fluorescence measurements in several systems [10–12].

In this paper we study the fast relaxation of optical excitations and the degree of their localization as a function of generation number in a new family of dendrimers build with 4,4′-bis(diphenylamino)stilbene (DPAS). These dendrimers have equal lengths of the branches (i.e. they are geometrically similar to compact ones) and do not possess any special trap group in the center.

In addition to steady-state absorption and fluorescence spectroscopy, we apply time-resolved and observation energy-selective fluorescence measurements with picosecond resolution. This approach allows us to associate a fast picosecond component in fluorescence decay kinetics with the efficient energy transfer to the low-energy states, which seem to be more delocalized than the initially created ones.

2. Experimental

Chemical structures of the parent 4,4′-bis(diphenylamino)stilbene (DPAS) molecule, a model 3-arm compound (1) and a series of 4-arm dendrimers are shown in Fig. 1. The synthesis of model compound (1), as well as G-0 dendrimer without side groups has been described in [13]. In order to maintain solubility and processibility in the G-1 and higher dendrimer generations, we have recently modified our syntheses to include n-butylthio substituents (SBu) in the para positions of each terminal phenyl ring, retaining, however, the synthetic routes similar to that previously published for the G-0 dendrimer. Complete synthetic details and characterization will be published elsewhere.

Thus, the G-0 four-arm dendrimer contains 8 SBu groups, the G-1 dendrimer 16 SBu groups and the G-2 dendrimer 32 SBu groups. The respective molecular weights of the three dendrimers are: G-0 (2,997), G-1 (5,157) and G-2 (10,878). It should be emphasized that each dendrimer is a monodisperse macromolecule with its own unique set of physical properties.

For spectroscopic and fluorescence kinetic measurements, all the compounds were dissolved in dichloromethane to a concentration 0.1 mg/ml, giving rise the maximum optical density ~ 1 in 0.2 cm thick cell.

Absorption spectra were measured with a Perkin–Elmer Lambda 900 spectrophotometer. Fluorescence spectra were measured with a Jobin–Ivon TRIAX 550 spectrometer coupled to Hamamatsu HC120-05 PMT detector and lock-in amplifier synchronized with exciting laser pulses.

Fluorescence was excited by second harmonic (395 nm) of a Coherent Mira 900 mode-locked Ti:sapphire laser, pumped with Coherent Verdi Nd:YVO_4 laser. The excitation pulses had duration of 200 fs with 76 MHz repetition rate.

Excitation laser beam was attenuated with neutral density filters and uniformly focused with an $f = 50$ mm lens onto a 1 mm diameter spot on the sample. The measured photon flux on the sample was varied between 10^6 and 10^{10} photons/(cm^2 pulse) by varying neutral density filters. The fluorescence signal was collected at small angle with a 1:1.8 relative aperture 50 mm objective lens and was focused on

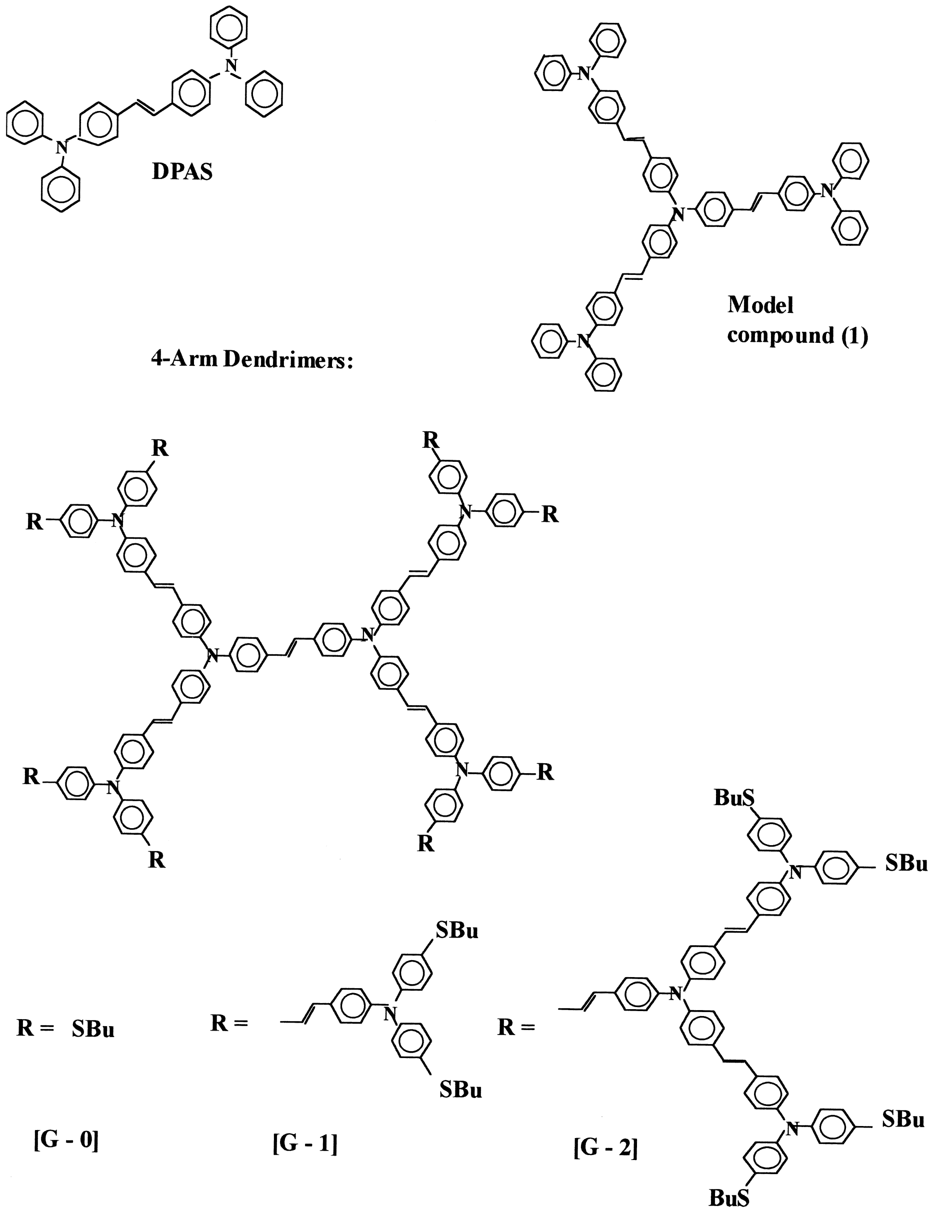

Fig. 1. Chemical structures of the molecules studied.

the entrance slit of a Hamamatsu C5680-31 synchroscan streak camera. To select particular fluorescence wavelengths, a set of interference filters (with spectral width ~ 20 nm) was used. The prompt response and time calibration of the streak camera were obtained by using a laser pulse train, obtained at the output of a Fabry–Perot etalon. In our experiment, the half width (at 1/e of the peak intensity) of the prompt response was about 2–4 ps.

3. Results and discussion

Fig. 2 presents steady-state normalized absorption and fluorescence spectra of the parent bis(diphenyl-

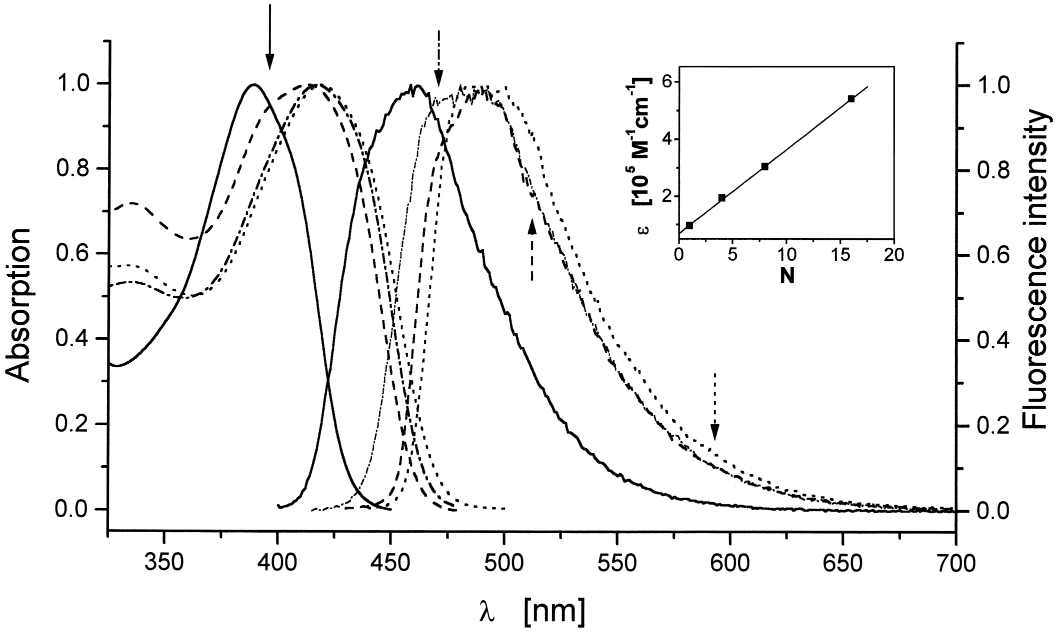

Fig. 2. Absorption and fluorescence spectra of DPAS (solid), G-0 (dashed–dotted), G-1 (dashed), and G-2 (dotted). Absorption spectrum is the left one and fluorescence spectrum is the right one in each pair. Solid arrow marks the excitation wavelength. Dashed–dotted, dashed and dotted arrows mark the positions of the acceptor states (obtained from Fig. 4, see text) for G-0, G-1, and G-2, respectively. Insert: dependence of extinction coefficient on the number *N* of DPAS groups in a dendrimer.

amino)stilbene (DPAS) molecule and G-0, G-1, and G-2 dendrimers. First of all, absorption spectra of all dendrimers are noticeably red-shifted with respect to that of the parent molecule. This can be explained by extension of conjugation length from one (in parent molecule) to two or more (in dendrimers) DPAS entities. Actual degree of conjugation length (number of DPAS chromophores) of the states responsible for the main absorption peak of dendrimers probably does not exceed 2–3, because the model compound (1) with 3 DPAS entities has almost the same position of absorption spectrum as the dendrimers. Furthermore, there is no gradual dependence of the absorption maximum position on dendrimer generation number: G-2 spectrum is only slightly red shifted with respect to that of G-0, but G-1 spectrum is even blue-shifted respectively to G-0 and G-2.

The dependence of maximum extinction coefficient for the family of molecules under consideration on the number of side DPAS groups is shown in Fig. 2, insert. It is perfectly described by linear regression, confirming that DPAS groups are the main absorbing chromophores in the dendrimers. In contrast to absorption, fluorescence spectra of dendrimers show gradual shift to the red with increasing generation number (see Fig. 2). Continuous red shift of fluorescence spectrum with increasing generation number suggests that the energy of relaxed electronic states decreases with the size of dendrimer. One explanation could be that the bigger molecule can have wider distribution of states because of greater number of chromophores and, therefore, an excitation can reach lower states during the downwards-directed energy migration. Another possibility is the presence of more delocalized states in dendrimers of higher generations. Theoretically, the bigger the dendrimer, the more delocalized states, possessing lower energy, can be present in it. Based on symmetry considerations, these states should be centered on geometrical center of dendrimer. They could be populated during the course of energy migration from periphery to the center and could contribute to the observed fluorescence spectrum. The distinction between the two above models will be based on time-resolved measurements presented below.

Fluorescence decay kinetics for each dendrimer generation measured at different wavelengths are shown in Fig. 3. The behavior of G-0 and G-2 is similar: At high observation energies there is a very fast (10–20 ps) component. With lowering energy the decay time of this component becomes longer. G-1 dendrimer shows fast decay component only at highest observation energies ($\lambda < 500$ nm). At long wavelengths, one starts to observe rising components for this dendrimer. At 528 nm there is only one comparatively long rise time (370 ps). Further down, at 680 nm, a fast 13 ps rise component appears in addition to the slow (210 ps) one.

Similar behavior of decay kinetics as a function of detection wavelength was observed for other dendrimer system [5] and π-conjugated polymers, PPP and PPV [14,15]. The fast decay at high energies and rise components at low energies were related in [14,15] to a downward energy migration over inhomogeneously distributed polymer electronic states with subsequent population of low-lying states. Our additional measurements show that the fast component does not depend on excitation power (varied over 4 orders of magnitude) and on concentration of dendrimers in solution. It remained unchanged also if we placed a polarizer at magic angle with respect to excitation polarization after the sample. In addition, the decay of parent molecule does not depend on detection wavelength and does not show any fast component. It decays quasi-monoexponentially with lifetime $\tau_0 = 1.3 \pm 0.3$ ns, typical of stilbene molecule [16]. These observations suggest that in G-0, G-1 and G-2 dendrimers a fast energy transfer

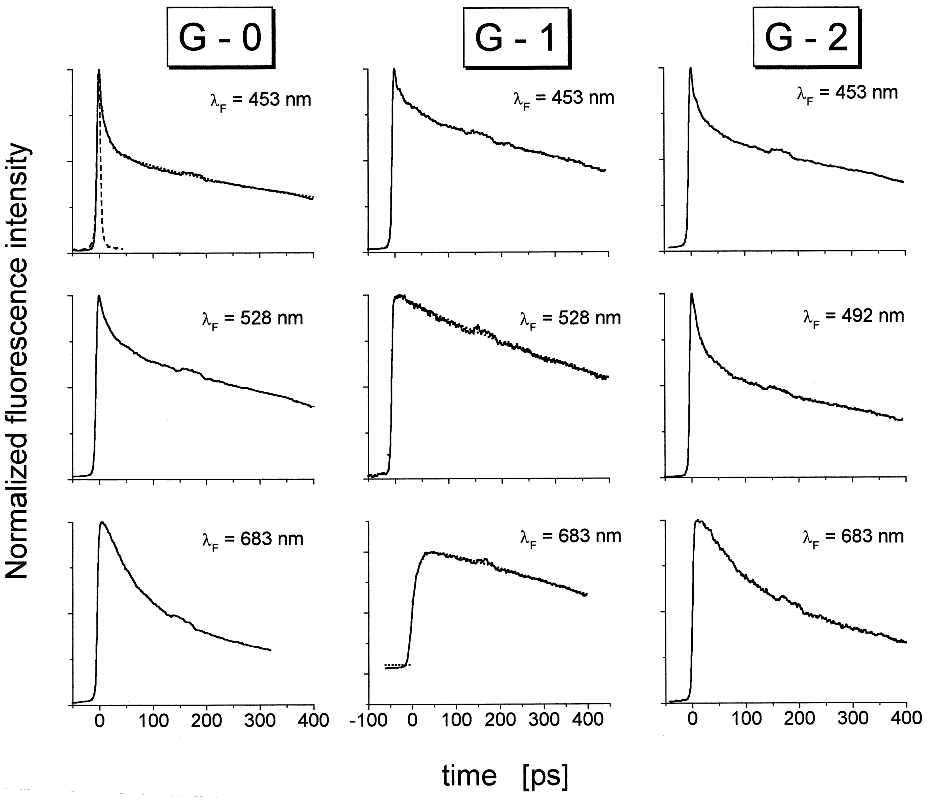

Fig. 3. Fluorescence decay kinetics measured at different detection wavelengths, λ_{fl} for G-0 (a), G-1 (b), and G-2 (c). Top left plot includes the camera response function (dashed line). Two-exponential best fit to the decay kinetics for G-0 at 453 nm and three-exponential best fits for G-1 at 528 and 680 nm are shown (dotted lines).

occurs from initially excited segments to some lower states.

The rate of fast relaxation (obtained as the reciprocal decay time of the fast component) is plotted as a function of detection energy for G-0, G-1, and G-2 dendrimers in Fig. 4.

To describe this dependence, we used a simple model [17]. It states that the rate of downward energy transfer is proportional to the fraction of integrated inhomogeneous distribution of acceptor states with energies lower than the observation frequency. This fraction is equal to error function in the case of Gaussian inhomogeneous distribution.

Fitting of our results to the error function with variable center and width is shown in Fig. 4. The most important result is that the center of Gaussian distribution of acceptor states (marked by an arrow in Figs. 2 and 4) shifts gradually to lower energies with the generation number. Note, that while the position of the inflection point of G-0 can not be defined with high accuracy, its lowest limit can be estimated to be 19650 cm^{-1}, which is still higher than corresponding points of G-1 and G-2. This suggests that the energy of acceptor state depends on the size of dendrimer molecule, which could imply the existence of more delocalized relaxed states in bigger dendrimers. Population of more delocalized states during electronic relaxation can also explain the gradual red shift of steady-state fluorescence spectrum with increasing generation. This result is very interesting because, as it was noted before, the dendrimers under consideration have equal branches at each generation level. Therefore, we can assume that it should be an interaction between different DPAS subunits within a dendrimer, giving rise to a certain delocalization of electronic wave function. The mechanism of delocalization is not clear up to now. The geometric properties of branching through N-atoms prevent neighbor stilbene groups from lying in the same plane and thus being strongly conjugated. But one can not rule out excitonic dipole–dipole interaction between them.

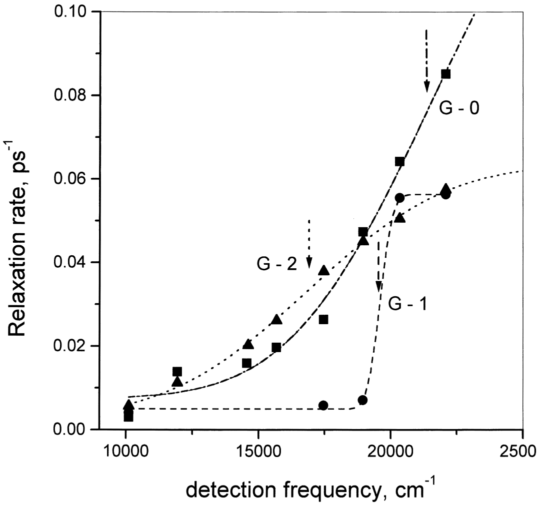

Fig. 4. Dependence of fast relaxation rate on the detection frequency for G-0 (squares), G-1 (circles) and G-2 (triangles). Error function fittings to experimental data are shown by dot–dash, dash, and dot lines, respectively.

Another unclear experimental fact is the very narrow energy distribution of acceptor states for G-1, as compared to G-0 and G-2 dendrimers (see Fig. 4). This is reflected in the very narrow spectral range where the fast component is present and the possibility to observe rising components at longer wavelengths. We can only speculate that this particular molecule has some specific geometry in solution with probably narrower distribution of isomers, than G-0 and G-2.

One should emphasize that the decay kinetics for each dendrimer was found to be multi-exponential, at least at short wavelengths. Likewise, the rise kinetics for G-1 is multi-exponential at long wavelengths (see above), which can be explained by the distribution of population rates (cf. [15]). In this work we applied two-exponential (or three-exponential) fittings in each camera sweep range to model multi-exponential kinetic curves.

Fig. 5 shows the dependence of shortest and longest decay times on detection energy for all three generations. These times were obtained by using shortest and longest sweep ranges of the camera, respectively. One can see that at $\nu > 15625$ cm^{-1} ($\lambda < 640$ nm), which corresponds to the main fluorescence spectral range, the longest decay time falls into the range 1.2–1.6 ns, which is close to the DPAS lifetime. The presence of this long-decaying component at short wavelengths probably means that not all the initially excited segments are able to transfer their energy to lower-lying states, but some of them appear to be ‘locked’ in their sites and decay

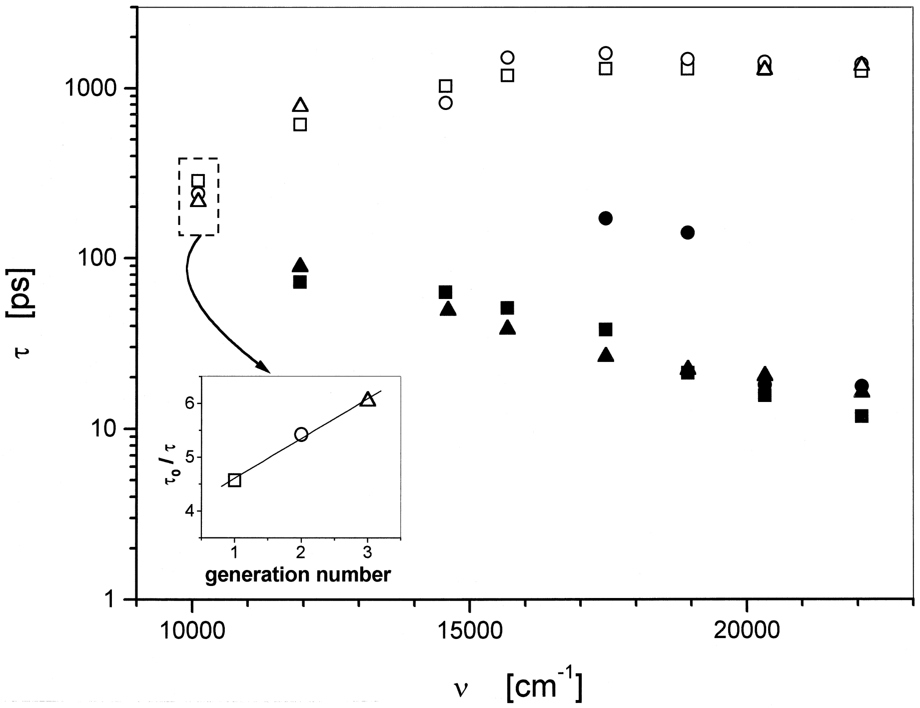

Fig. 5. Dependence of the fast (closed symbols) and slow (open symbols) decay times on detection frequency for G-0 (squares), G-1 (circles) and G-2 (triangles). Insert: dependence of superradiant factor, measured at $\lambda_F = 1000$ nm (see text for explanation) on generation number.

to the ground state. At very low-energies $\nu < 15625$ cm^{-1}, which correspond to very red tail states, the longest decay time starts to shorten, descending to 200–300 ps at $\nu \sim 10000$ cm^{-1} ($\lambda \sim 1000$ nm). This surprising result can be understood if we suppose that this time corresponds to the delocalized states mentioned above, predominantly fluorescing at these wavelengths. It is known that the longer the delocalization length of the state, the stronger is the transition to this state and, therefore, the shorter is the radiative decay (see, for example, [18] for excitonic mechanism of delocalization).

Note that the shortest and longest decay times converge at very low energies (see Fig. 5), giving rise to quasi-monoexponential decay. It is intriguing that the time τ of this decay gradually decreases with generation number. If we suppose that this time is mainly determined by radiative process, then this result gives us another support in favor of the increase of delocalization length with generation number. Mukamel and co-authors [19] have shown that the superradiant factor of a dendrimer, defined as the ratio of its radiative decay rate to that of monomer, scales as the generation number squared. This result has been obtained for a quasi-planar dendrimer within the framework of Frenkel exciton model. In our case the dependence of superradiant factor (obtained as a ratio τ_0/τ) on generation number, see Fig. 5, insert, is much weaker and close to linear. This can be explained by several reasons. First of all, our dendrimers do not have planar structure that prevents strong interaction between spatially separated segments (either via π-electron conjugation or dipole–dipole Frenkel interaction). In addition, we do not know the exact value of fluorescence quantum efficiency for the delocalized states. The measurement of this value seems to be a very complicated task because the delocalized states are populated indirectly via energy transfer and the fluorescence of these states is very weak. Therefore, further studies are needed to refine the nature of electronic delocalization in these new dendrimers.

4. Conclusions

Very fast (picosecond) excited-state relaxation is observed in a new family of dendrimers built with bis(diphenylamino)stilbene group. The rate of this relaxation is shown to depend on the observation wavelength and the generation number. The distribution of the acceptor energy gradually shifts downwards with the generation number. These observations can be consistently described in terms of the fast energy transfer from initially created localized states to more delocalized ones. The degree of delocalization apparently increases with the generation number.

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References

[1] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Sol. Energy Matter. Sol Cells 38 (1995) 159.
[2] G.M. Stewart, M.A. Fox, J. Am. Chem. Soc. 118 (1996) 4354.
[3] R. Kopelman, M. Shortreed, Z.Y. Shi, W. Tan, Z. Xu, J.S. Moore, J.S. Bar-Haim, J. Klafter, Phys. Rev. Lett. 78 (1997) 1239.
[4] J. Hofkens, L. Latterini, G. De Belder, T. Gensch, M. Maus, T. Vosch, Y. Karni, G. Schweitzer, F.C. De Schryver, A. Hermann, K. Müllen, Chem. Phys. Lett. 304 (1999) 1.
[5] Y. Karni, S. Jordens, G. De Belder, G. Schweitzer, J. Hofkens, T. Gensch, M. Maus, F.C. De Schryver, A. Hermann, K. Müllen, Chem. Phys. Lett. 310 (1999) 73.
[6] Y. Karni, S. Jordens, G. De Belder, J. Hofkens, G. Schweitzer, F. De Schryver, A. Hermann, K. Müllen, J. Phys. Chem. B 103 (1999) 9378.
[7] O. Varnavski, A. Leanov, L. Liu, J. Takacs, T. Goodson III, J. Phys. Chem. 104 (2000) 179.
[8] A. Bar-Haim, J. Klafter, R. Kopelman, J. Am. Chem. Soc. 119 (1997) 6197.
[9] A. Bar-Haim, J. Klafter, J. Phys. Chem. B 102 (1998) 1662.
[10] C. Devadoss, P. Bharathi, J.S. Moore, J. Am. Chem. Soc. 118 (1996) 9635.
[11] M.R. Shortreed, S.F. Swallen, Z.-Y. Shi, W. Tan, Z. Xu, C. Devadoss, J.S. Moore, R. Kopelman, J. Phys. Chem. 101 (1997) 6318.
[12] D.-L. Jiang, T. Aida, J. Am. Chem. Soc. 120 (1998) 10895.
[13] E.H. Elandaloussi, C.W. Spangler, Polymer Preprints 39 (1998) 1055.
[14] R.F. Mahrt, T. Pauck, U. Lemmer, U. Siegner, M. Hopmeier, R. Hennig, H. Bässler, E.O. Göbel, P. Haring Bolivar, G. Wegmann, H. Kurz, U. Scherf, K. Müllen, Phys. Rev. B 54 (1996) 1759.
[15] R. Kersting, B. Mollay, M. Rusch, J. Wenisch, G. Leising, H.F. Kauffmann, J. Chem. Phys. 106 (1997) 2850.
[16] I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, 2nd. Ed. Academic, New York, 1971.
[17] J.M.A. Koedijk, T.M.H. Creemers, F.T.H. den Hartog, M.P. Bakker, S. Völker, J. Lumin. 53 (1995) 55.
[18] M. Kasha, in: B. di Bartolo (Ed.), Spectroscopy of the Excited State, Plenum, New York, 1976, p. 337.
[19] E.Y. Polyakov, V. Chernyak, S. Tretiak, S. Mukamel, J. Chem. Phys. 110 (1999) 8161.