Excited-State Structure and Dynamics of 1,3,5-Tris(phenylethynyl)benzene as Studied by Raman and Time-Resolved Fluorescence Spectroscopy

Tomonori Nomoto,[†,§] Haruko Hosoi,[‡] Tatsuya Fujino,[‡,||] Tahei Tahara,[‡] and Hiro-o Hamaguchi*[,†]

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Molecular Spectroscopy Laboratory, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako 351-0198, Japan

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Excited-state structure and dynamics of 1,3,5-tris(phenylethynyl)benzene (TPB) have been studied in *n*-hexane and *n*-heptane solutions. Time-resolved fluorescence spectra, fluorescence anisotropy, and lifetime of TPB were recorded with femtosecond to nanosecond time resolution. Raman depolarization ratio was also measured to elucidate a nonplanar structure of the ground state. Two fluorescence components, the short-lived component with 150 fs lifetime and the long-lived component with 10 ns lifetime, were observed. The analysis of the fluorescence anisotropy values combined with the Raman depolarization data has led to a conclusion that TPB is primarily excited to a short-lived excited singlet state with a nonplanar structure, and then it relaxes to a long-lived excited singlet state with a 3-fold axis. A rapid structural change from a nonplanar to a planar structure is suggested to take place in the process of relaxation.

Introduction

Diphenylacetylene ($C_6H_5C{\equiv}CC_6H_5$, hereafter abbreviated as DPA) is one of the fundamental aromatic molecules with a triple bond. Recently, functional molecules containing DPA moieties are attracting much attention for its characteristic properties and possible applications. For example, a variety of electroluminescent devices and molecular electronic devices containing DPA have been proposed.[1−10] For those devices, DPA or its oligomers work as molecular wires bridging molecular devices such as sensors, resistors, junctions, and logic devices.[3−10]

Light-harvesting phenylacetylene dendrimers are also arousing much interest for their high light-harvesting efficiencies.[11−19] Two types of perylene-terminated metaconjugated phenylacetylene dendrimers, called the compact type and the extended type, have been reported. They have light-harvesting tree-like structures and a perylene terminator as an energy trap connected to the center. Excitation energy transfer with high yields has been observed for both of the two kinds of perylene-terminated phenylacetylene dendrimers. The compact type shows 91−95% energy transfer yields with 2 ns lifetime in a smaller generation,[15] and the yield decreases to 54% in a large generation. On the other hand, the extended type shows higher energy transfer yields and apparently much faster intramolecular energy transfer rates.[15,16] According to the ultrafast transient bleach experiments on “nanostar”, which is a typical extended type phenylacetylene dendrimers,[17] the lifetime of the transient bleach signal is dependent on the excitation wavelength. Transient bleach signal excited at 310 nm, which corresponds to two-ring (DPA) chromophores, shows time constants of 270 fs and 1.1 ps, while that excited at 352 nm, which corresponds to linear four-ring chromophores, shows time constants of 3 and 14 ps. These results indicate different intramolecular relaxation processes dependent on excitation wavelength. Several theoretical studies have been reported to explain the energy transfer in phenylacetylene dendrimers.[20−29] A Frenkel exciton model is applied in most studies. They have explained excitation energy transfer of the extended type as the migration of exciton from the periphery toward the center.

To elucidate the energy transfer processes of large molecules like phenylacetylene dendrimers, knowledge on the excited-state dynamics of component molecules is highly important. Small component molecules are expected to show prototype dynamics of the very early stage of the energy transfer in dendrimers. 1,3,5-tris(phenylethynyl)benzene ($C_{30}H_{18}$, hereafter abbreviated as TPB, Figure 1) is one of such prototype components of metaconjugated phenylacetylene dendrimers.

TPB is also attractive in itself. DPA has large amplitude torsional motions and several closely lying excited singlet states.[30] They have unusually long lifetimes in higher excited states and markedly different structures (with a triple bond or double bond) in different excited states.[31−36] Furthermore, the ordering of the excited states is sensitive to substitution. For example, DPA and cyano-substituted DPA have different excited-state characters.[37] TPB has a structure as if three DPA are combined in one molecule. TPB has similar absorption band to DPA, indicating that some of the DPA characters remain also in TPB. Therefore its excited-state structure and dynamics are of considerable interest. There is a report on X-ray crystallography showing that TPB in crystal is nonplanar without any characteristic symmetry.[38] There are also studies on analogues of TPB such as 1,3,5-tris[[3,5-bis(1,1-dimethylethyl)phenyl]-ethynyl]benzene (*t*Bu-TPB), which is also a component of phenylacetylene dendrimer. Here, *t*Bu-TPB is a *tert*-butyl-substituted TPB at meta positions of each phenyl ring. Absorp-

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* Corresponding author. E-mail: hhama@chem.s.u-tokyo.ac.jp.

[†] Department of Chemistry, School of Science, The University of Tokyo.

[‡] Molecular Spectroscopy Laboratory, RIKEN (The Institute of Physical and Chemical Research).

[§] Present address: Department of Chemistry, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan.

[||] Present address: Department of Chemistry, Tokyo Metropolitan University, 1-1 Mainami-Osawa, Hachioji, Tokyo 192-0397, Japan.

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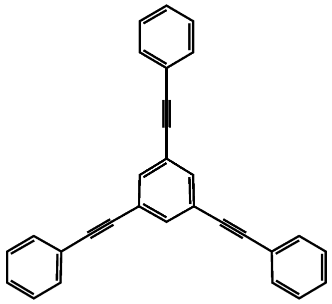

Figure 1. 1,3,5-Tris(phenylethynyl)benzene (TPB) in a D_{3h} planar structure.

tion and fluorescence spectra are reported for *t*Bu-TPB. The fluorescence lifetime is 8.4 ns with a quantum yield $\phi_{\text{fl}} = 0.26$ in dichloromethane,[15] 11.2 ns with $\phi_{\text{fl}} = 0.26$ in nondeaerated cyclohexane, and 14.9 ns with $\phi_{\text{fl}} = 0.35$ in deaerated cyclohexane.[19] On the basis of an ab initio calculation and emission spectroscopy of metaconjugated building blocks of phenylethynyl dendrons, Thompson et al. suggests a variable electron coupling between the phenylethynyl branches, which takes molecules from the weak coupling to the strong coupling as they relax on the excited surface.[20]

The aim of the present paper is to understand the structure and the excited-state dynamics of TPB. We first determine the ground-state structure of TPB using Raman spectroscopy. Then excited-state dynamics and the structure of TPB are discussed using the results from time-resolved fluorescence spectroscopy.

Experimental

1,3,5-Tris(phenylethynyl)benzene (TPB) was obtained from Alfa Aesar and used after repeated recrystallization from *n*-hexane. HPLC-grade *n*-hexane and *n*-heptane were used as solvents. All the spectroscopic measurements were carried out at room temperature.

For Raman spectroscopic measurements, the 514.5 nm from a cw Ar^+ ion laser (Spectra-Physics, Model 2670) was used for excitation. Polarization of the laser beam was purified by Glan–Taylor polarizing prisms. Raman scattering at 90° direction to the incident laser beam was collected by a camera lens, passed through a film analyzer, a depolarizer, dispersed with a triple spectrometer (SPEX Triplemate 1877) and detected by a CCD camera (Princeton Instruments, Model 7509-0001). For measurements of crystals, a different Ar^+ ion laser (Spectra-Physics, Model 160, 488 nm) was used with another CCD (Princeton Instruments LN/CCD 1100PBUVAR). A 10×10^{-3} mol dm^{-3} *n*-hexane solution of TPB was used. Depolarization ratio data were calibrated referring to those of CCl_4.

Steady-state absorption spectra were recorded on a Hitachi U-3500 spectrophotometer. Steady-state fluorescence spectra were measured with a Jasco FP-6500 spectrofluorometer. Sample concentration was 0.1×10^{-3} mol dm^{-3} in *n*-hexane. Fluorescence intensity correction was made with the quantum counter method using rhodamine B in ethylene glycol. Nanosecond fluorescence lifetime measurements were carried out using an N_2 laser (Laser Science Inc. VSL-337, 337 nm, ~4 ns), a monochromator (Nikon G250), and a photomultiplier (Hamamatsu H6780). The output signal of the photomultiplier was monitored by an oscilloscope (Tektronix TDS380P) and fluorescence time profiles were recorded. Sample concentration was 0.1×10^{-3} mol dm^{-3} in *n*-hexane.

For picosecond time-resolved fluorescence measurements, a streak camera was used.[39] The third harmonic (270 nm, 1 kHz) of the output from a mode-locked Ti:sapphire laser/regenerative amplifier system (Clark-MXR, CPA-1) was used for excitation. The magic angle setting of an analyzer (54.7° to the polarization direction of the incident light) was adopted except for the anisotropy measurements in which the parallel (0°) and perpendicular (90°) settings were used. Emitted fluorescence was wavelength resolved with a spectrometer (Chromex 500) and time-resolved by a streak camera (Hamamatsu C-2909). Time resolution of the system was estimated as ~10 ps from the observed time profile of the exciting pulse. To make a correction for sensitivity difference between the parallel and perpendicular settings of the analyzer, the obtained parallel and perpendicular intensities were normalized with the values at 4–5 ns after excitation where no anisotropy was expected. A 0.1×10^{-3} mol dm^{-3} *n*-hexane solution was measured in a 5 mm cell with a magnetic stirrer.

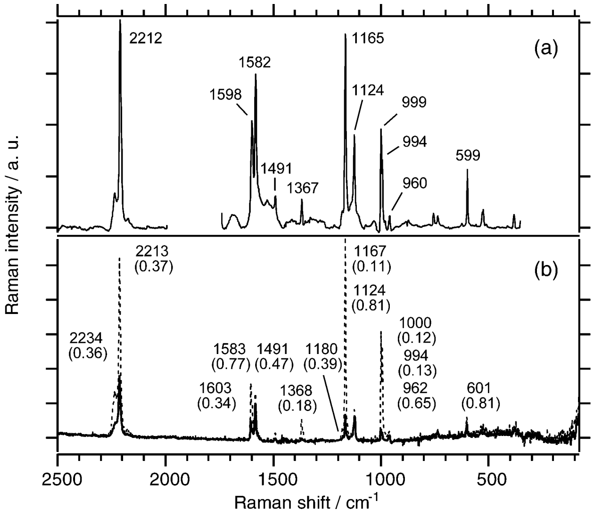

Figure 2. Raman spectrum of crystalline TPB (a) and those of an *n*-hexane solution (b). The dotted line in (b) shows the parallel and the full line the perpendicular component, respectively. The observed depolarization ratios are also given in parentheses in (b).

The fluorescence upconversion experiments were carried out with a system reported previously.[40–42] The third harmonic (280 nm, ~25 mW) of a mode-locked Ti:sapphire laser (840 nm, 78 MHz) was focused on a sample film jet of 200 μm thick. Fluorescence was collected by an ellipsoid mirror and refocused on a BBO crystal. On the same BBO crystal, a residual fundamental beam was focused. The BBO crystal was rotated to follow the phase-matching condition for upconversion. The generated upconverted signal was in the wavelength range 240–273 nm when fluorescence in the range 336–405 nm was detected. Upconverted fluorescence was filtered with a monochromator and detected by a photomultiplier. The magic-angle setup of the polarizer was used except for the anisotropy measurements. The time resolution estimated from the cross-correlation between the excitation and probe pulses by difference frequency generation was 280 fs.

Results and Discussion

Raman Spectra, Depolarization Ratios, and Structure of the Ground State TPB. The Raman spectrum of crystalline TPB and those in an *n*-hexane solution are shown in parts a and b of Figure 2, respectively. Parallel and perpendicular components are shown for the solution spectra. Each band in the parallel and perpendicular spectra was fitted by a Lorentzian or a Gaussian function and the Raman depolarization ratio $\rho = I_{\text{perpendicular}}/I_{\text{parallel}}$ was obtained from the area intensities. Two strong polarized bands are observed at 2213 cm^{-1} ($\rho = 0.37$)

and 1167 cm^{-1} ($\rho = 0.11$) in the solution spectra. They are assigned to the C≡C stretch and the C−Ph stretches, respectively. The solution Raman spectra closely resemble the crystalline spectrum, suggesting that TPB in solution takes a structure similar to that in a crystal.

For randomly oriented systems, depolarization ratio ρ is related to the Raman scattering tensor.[43] If TPB has a planar D_{3h} structure with three equivalent phenylethynyl groups, the three C≡C stretches give rise to a totally symmetric a'_1 mode and a degenerate e' mode. The totally symmetric a'_1 mode has a Raman tensor pattern

$$a = \begin{pmatrix} c_1 & 0 & 0 \\ 0 & c_1 & 0 \\ 0 & 0 & c_2 \end{pmatrix}$$

in general.[44] If the contributions from out-of-plane electronic transitions are small (this is usually the case for a planar-conjugated system because out-of-plane electronic transitions are much weaker than in-plane transitions),

$$a_{\text{sym}} = \begin{pmatrix} c & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

where the x and y axes are in the molecular plane. In this case, $\rho = 0.125$. If there is a small contribution from out-of-plane electronic transitions, ρ becomes smaller than 0.125. The e' mode is likely to give a weak band with $\rho = 0.75$.

On the other hand, if TPB has no symmetry and the three phenylethynyl groups are independent of one another, the Raman tensor for each C≡C stretch becomes

$$a_{\text{pure}} = \begin{pmatrix} c & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

where x-axis is taken in the direction the C≡C bond. In this case, the three C≡C stretch bands are overlapped to give a single band with $\rho = 0.33$. The Raman spectra of TPB in solution (Figure 2b) show one strong polarized band (2213 cm^{-1}, $\rho = 0.37$) and a much weaker polarized band (2234 cm^{-1}, $\rho = 0.36$) in the C≡C stretch region. This observation accords more with three overlapping C≡C stretch bands with $\rho = 0.33$ than one a'_1 band ($\rho = 0.125$) with one e' band ($\rho = 0.75$). The weak polarized band at 2234 cm^{-1} can be attributed to a Fermi resonance.

The observed small depolarization ratio ($\rho = 0.11$) of the 1167 cm^{-1} band is indicative of the coupling among the three C−Ph stretches. Because C−Ph bonds are attached to the same benzene ring, they can couple with one another through the π conjugation. Then they give rise to one a'_1 mode ($\rho = 0.125$) and one e' mode ($\rho = 0.75$). The 1167 cm^{-1} band ($\rho = 0.11$) is assigned to the a'_1 mode. The nearby depolarized band ($\rho = 0.81$) at 1124 cm^{-1} may be assigned to the e' mode. There is also a weak band observed at 1180 cm^{-1} ($\rho = 0.39$) for C−Ph stretch of peripheral phenyl rings. Hence, a nonplanar structure without symmetry is most probable for the ground-state TPB. This conclusion is consistent with the fact that Raman spectrum in solution resembles that in the crystalline state in which TPB takes a nonplanar structure.

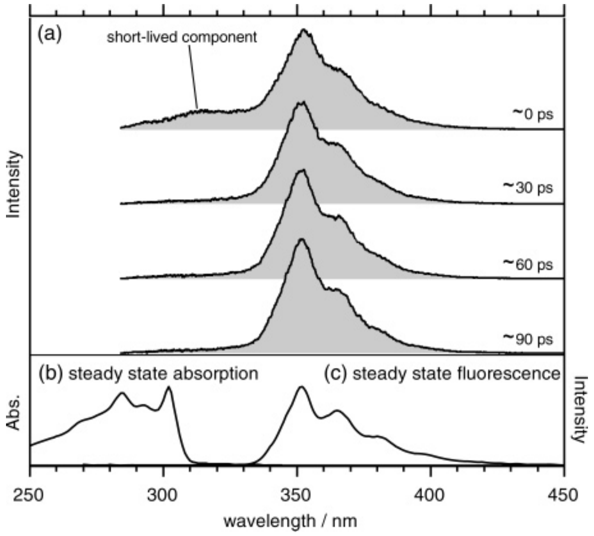

Figure 3. (a) Time-resolved fluorescence spectra of TPB in *n*-hexane, (b) steady-state absorption, and (c) steady-state fluorescence spectra of TPB in *n*-hexane.

Time-Resolved Fluorescence Spectra and the Excited-State Dynamics of TPB. The picosecond time-resolved fluorescence spectra of TPB in *n*-hexane are shown in Figure 3 together with the steady-state fluorescence and absorption spectra. Two spectral components showing different time behaviors are observed. The short-lived component is observed only at 0 ps in the wavelength range from 300 to 350 nm, which is the same range as fluorescence spectra of DPA. The long-lived component is observed in the wavelength range from 350 to 400 nm with a peak at 352 nm. This component exists in the whole time range from 0 to 90 ps. The spectral profile of the long-lived component is similar to that of the steady-state fluorescence as it should be. From a separate nanosecond fluorescence lifetime measurement, the lifetime of the long-lived component was obtained as 10 ns.

To determine the lifetime of the short-lived component as well as the rise time of the long-lived component, the fluorescence time profile of TPB in *n*-heptane was measured at six different wavelengths, 336, 350, 365, 380, 395, and 405 nm, by the fluorescence upconversion method (Figure 4). These time profiles were fitted with Gaussian-convoluted exponential functions. The Gaussian function corresponded to the response function of the system, which was determined from the cross-correlation between the excitation and gate pulses (full width at half-maximum 280 fs). The lifetime of the long-lived component was fixed to 10 ns. We fitted the six time profiles by assuming that the lifetime of the short-lived component is equal to the rise time constant of the long-lived component. The fitting reproduces the experimental profiles very well (the solid lines in Figure 4), indicating that the short-lived component is a precursor of the long-lived component and that the time constant of the conversion from the former to the latter is 150 fs. The obtained excited-state lifetimes are quite different from DPA (8 ps and ∼200 ps in *n*-hexane[31]), and hence the excited-state character of long-lived component is also expected to be different from DPA itself.

Fluorescence Anisotropy of TPB and Structural Relaxation in the Excited State. To gain further insights into the excited-state dynamics, fluorescence anisotropy of TPB in *n*-hexane was measured with subpicosecond and picosecond time resolution. Figure 5a shows the anisotropy change in the first few picoseconds after photoexcitation measured by the fluorescence upconversion method. Fluorescence was monitored at 365 nm where both the short- and long-lived components were observed (Figure 5b). The initial value of anisotropy is about 0.3, and then it decreases rapidly to become 0.1 and stays constant after 1 ps. As in the case of previous section, the time

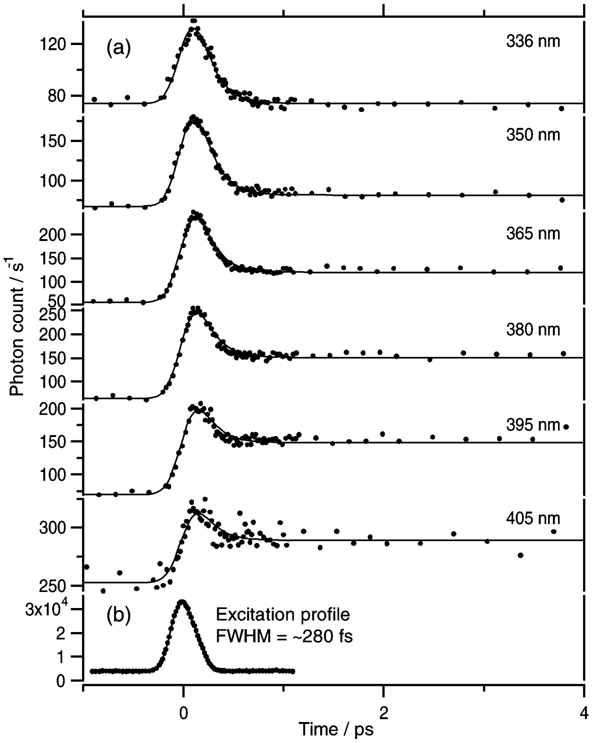

Figure 4. (a) Fluorescence time profiles of TPB measured in *n*-heptane at 336 nm, 350, 365, 380, 395, and 405 nm. The dots are observed data and solid lines are fitting curves. (b) Response function obtained from the measured cross correlation function between the excitation and gate pulses.

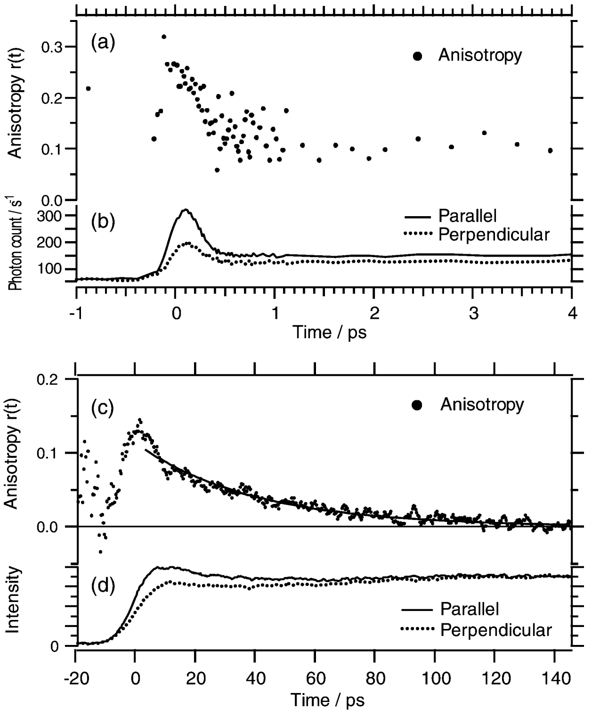

Figure 5. Anisotropy and parallel/perpendicular fluorescence time profile of TPB. (a) and (b) were obtained by fluorescence upconversion in *n*-heptane, and (c) and (d) by a streak camera in *n*-hexane.

profiles of the parallel and perpendicular components were fitted using a Gaussian convoluted biexponential function with two adjustable lifetime parameters and a fixed response function. Then the anisotropy time profile was calculated from the deconvoluted time profiles of the parallel and perpendicular components. The anisotropy decay time thus determined was ~150 fs, which agrees well with the lifetime of the short-lived fluorescence component. This fact indicates that the short-lived component shows an initial anisotropy as large as $r = 0.3$, while the initial anisotropy of the long-lived component is equal to 0.1. The anisotropy of the long-lived component was also studied in the 0−140 ps time region by the streak camera system (Figure 5c−d). The observed initial anisotropy is $r = 0.1$ and is in harmony with the upconversion measurement. Anisotropy decreases to zero with a 40 ps time constant, showing that the rotational correlation time of the long-lived component in *n*-hexane is 40 ps.

Fluorescence anisotropy is defined as,

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \tag{1}$$

where the denominator corresponds to the total intensity of fluorescence from a emitting dipole.[45] It is associated with the angle θ between the absorbing and emitting transition dipole moments with the following equation, if the effect of molecular rotation is neglected.

$$r = 0.4\,\frac{3\cos^2\theta - 1}{2} \tag{2}$$

If the absorbing and emitting transition dipoles are in the same direction ($\theta = 0°$), the anisotropy value becomes 0.4. The observed anisotropy value, $r = 0.3$, of the short-lived component, is close to 0.4. It is highly likely that, because of insufficient time-resolution of the experiment, the observed initial anisotropy is contaminated with the smaller value (0.1) from the long-lived component. In fact, a similar value is also reported for DPA substitutes by Thompson et al.[19] We conclude that the short-lived component arises from the absorbing and emitting transition dipoles in the same direction. In other words, the emission takes place only from the same DPA unit that is photoexcited. The observed small anisotropy, $r = 0.1$, for the long-lived component needs more consideration. If we apply $r = 0.1$ to eq 2, θ is calculated to be 45°. However, the angle 45° between the absorbing and emitting transition moments is highly unlikely because all the phenylethynyl groups are attached to the meta positions of the central benzene ring, making the angle 120° with one another. If there are three different states around the lowest excited state with the absorption dipole angle of 0° (the lowest state), 120° and −120° from the emission transition dipole, and if they are equally excited and relax to the lowest state, the anisotropy value is

$$r = (r(\theta = 0°) + r(\theta = 120°) + r(\theta = -120°))/3 = 0.1$$

This is also unlikely because the fluorescence spectrum and the lifetime of the long-lived state is quite different from that of DPA, while the absorption spectrum is very similar to that of DPA.

An alternative to account for the anisotropy value $r = 0.1$ is to consider the participation of a degenerated state. If TPB has a 3-fold axis, degenerated excited states are available for the fluorescence process. For a degenerate excited state, emission can take place both with *x* and *y* polarizations (Figure 6). In this case, signals from the *x*-polarized transition dipole ($\mu_{x\ \mathrm{em}}$) and the *y*-polarized transition dipole ($\mu_{y\ \mathrm{em}}$) are mixed to give the anisotropy expressed as,

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \frac{(I_{x\parallel} - I_{x\perp}) + (I_{y\parallel} - I_{y\perp})}{(I_{x\parallel} + 2I_{x\perp}) + (I_{y\parallel} + 2I_{y\perp})} \tag{3}$$

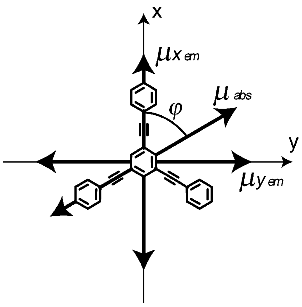

Figure 6. Molecular coordinate and absorption (μ_{abs}) and emission transition dipoles ($\mu_{x\text{ em}}$, $\mu_{y\text{ em}}$). All dipoles are in the $x-y$ plane. The angle φ is made by the x-axis and the absorption transition dipole.

where $I_{x\|} + 2I_{x\perp} = I_{y\|} + 2I_{y\perp} =$ const, because the two emitting transition dipoles are equivalent. When the absorbing transition dipole (μ_{abs}) is in the $x-y$ plane, this formula is reduced to,

$$r = \frac{1}{2}\left(0.4\,\frac{3\cos^2\varphi - 1}{2} + 0.4\,\frac{3\cos^2(90° - \varphi) - 1}{2}\right) = 0.1 \tag{4}$$

where φ is the angle between the x-axis and the direction of the absorbing dipole moment. It is clear that the anisotropy in this case is 0.1 irrespective of the value of the angle φ. Thus, the observed anisotropy $r = 0.1$ of the long-lived component is well explained if we assume that the emission originates from a degenerate excited state.

For TPB to have a degenerate excited state, it must have a 3-fold axis. Because the ground-state TPB is nonplanar without symmetry, conversion to a symmetrical structure must take place in the excited state so that emission from a degenerate state is possible. The observed ultrafast anisotropy decay is in a good harmony with this structural relaxation. First, one of the three independent phenylethynyl groups of the asymmetrical nonplanar TPB is photoexcited. The emission from the same phenylethynyl group gives rise to the short-lived component. The anisotropy value 0.3 is consistent with the same asymmetrical nonplanar structure as in the ground state (Franck–Condon principle). It then relaxes in 150 fs to an excited-state that emits the long-lived component with $r = 0.1$. This state must be associated with a symmetrical structure with a 3-fold axis. In other words, photonically produced TPB in an asymmetrical nonplanar structure relaxes in 150 fs to a symmetrical structure with a 3-fold axis. The strong coupling among the three phenylethynyl groups is more consistent with a planar D_{3h} structure with full conjugation of π electrons. Thompson et al.[19] proposed a variable exitonic coupling between three phenylethynyl branches in the excited state.

For a planar D_{3h} structure of TPB, E', A_1', and A_2' excited singlet states are the possible lowest excited state because the HOMO and LUMO are both of e'' symmetry. The E' state is a one-photon allowed degenerated state, and the A_1' and A_2' states are intrinsically one-photon forbidden. For planar molecules with 3-fold axis (e.g., benzene, triphenylene), a degenerated state is not likely to be the lowest excited singlet state.[46−50] For triphenylene, the lowest excited singlet state is A_2' and it becomes vibronically allowed via vibronic coupling with an e' vibration.[50] Hence it is most probable that the long-lived fluorescence is emitted also from an A_2' state of D_{3h} symmetry which borrows intensity from an allowed E' state through an e' vibration. In this case, the A_2' state itself does not have electronic degeneracy but the emission state is doubly degenerate through the degenerate e' vibration. In other words, there are two x and y polarized transition dipoles from the vibronically allowed A_2' state, which results in the anisotropy value of 0.1.

Conclusion

We have measured Raman and time-resolved fluorescence spectra in order to understand the excited-state structure and dynamics of TPB. The observed Raman depolarization ratio suggests a nonplanar structure of the ground state with nonequivalent phenylethynyl moieties. Two fluorescence components, the short-lived component with 150 fs lifetime and the long-lived component with 10 ns lifetime, were observed. The short-lived component is assigned to an excited singlet state localized to one phenylethynyl moiety with a nonplanar asymmetrical structure. The long-lived component is assigned to an A_2' state with a planar D_{3h} structure, which is vibronically allowed through an e' vibration. Structural relaxation from a nonplanar asymmetrical structure to a planar D_{3h} structure takes place in 150 fs. This ultrafast structural relaxation is highly likely to play a role in the early stage of the energy transfer in the metaconjugated phenylacetylene dendrimers.

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