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Excited-State Localization in a 3-Fold-Symmetric Molecule as Probed by Electroabsorption Spectroscopy

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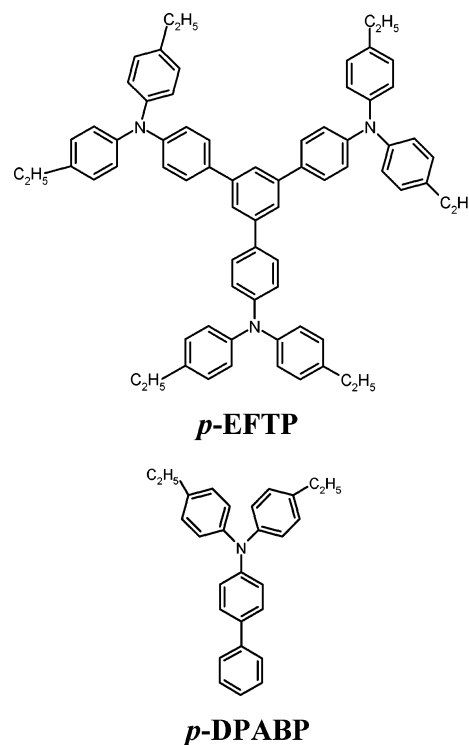
Excitation localization in a nominally 3-fold-symmetric molecule is probed using electroabsorption (Stark) spectroscopy in polymer and organic glass matrixes. The absolute value of the change in dipole moment ($|\Delta\mu|$) of this molecule, referred to as the trimer, is found to be nearly identical to that of a model compound consisting of one of its three arms within experimental error. Electronic structure calculations presented in the companion paper to this one (Liu, L. A.; Peteanu, L. A.; Yaron, D. J. *J. Phys. Chem. B* 2004, 108, 16841) reveal that the value of $|\Delta\mu|$ measured in the trimer is consistent with absorption to a state localized on a single branch of the molecule. Previously, localization on the emission time scale had been demonstrated for these particular trimers. The localization evident from the electroabsorption spectrum results from ground-state geometrical disorder in the branches that renders their excitation energies nonequivalent and reduces the overall symmetry of the molecule.

Introduction

An important feature of large multichromophoric systems such as dendrimers, aggregates, and luminescent polymers is the extent to which the excited states formed upon optical excitation are delocalized over the entire molecular framework. For such systems, strong electronic coupling between the subunits of these structures enhances a diverse set of molecular properties with important applications including long-range energy transfer in organic and biological systems,^{2–4} efficient electron and hole transport in molecular devices,^{5,6} and large optical hyperpolarizabilities.^{7–9} Alternatively, such excitations may become localized or “trapped” within particular regions of the multichromophore assembly either on the time scale of absorption or prior to decay from the excited state. Frequently studied models for symmetry breaking in organic molecules include bianthryl and triphenylmethane dyes, which are 2- and 3-fold-symmetric, respectively.

This study is concerned with a 3-fold-symmetric molecule, *p*-EFTP, and a model compound (*p*-DPABP) that constitutes a single arm of the trimeric species (Scheme 1). These molecules are referred to subsequently as the trimer and the monomer, respectively. Steady-state and time-resolved fluorescence measurements and microwave conductivity studies have shown that the excitation of *p*-EFTP gives rise to a polar excited state localized on one arm of the structure.^{10–13} Although these experiments probe the relaxed excited state of the molecule, the question remains as to whether this localization is also characteristic of the Franck–Condon region of the excited state. Consistent with localization at short times are the measurements

SCHEME 1: Trimer (Top) and Monomer (Bottom) Molecules Studied in This Work



of Latterini et al., who observed the rapid loss of polarization in femtosecond transient absorption measurements on *p*-EFTP.¹⁴ The aim of the work presented here is to use electroabsorption (Stark) spectroscopy to confirm the hypothesis that the excitation

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is localized on one arm of the trimer upon absorption by comparing the extent of charge separation or the magnitude of the change in dipole moment ($|\Delta\mu|$) in the Franck–Condon region of the trimer to that of the monomer.¹⁵

There have been a number of studies using Stark spectroscopy to probe the degree of electronic delocalization, primarily of the metal-to-ligand and ligand-to-metal charge-transfer states of organometallic complexes such as $\text{Ru}(\text{bpy})_3^{2+}$ (D_3 symmetry).^{16–19} For these systems and for the trimers studied here, the allowed optical transition is to a state of E symmetry. It has been proposed that the size of $|\Delta\mu|$ for such complexes can be correlated to the degree of localization of the transition to a single arm of the molecule, assuming that the magnitude of the ground-state dipole moment is small, as is expected for molecules of this symmetry.²⁰ Talanina et al. first made this correlation quantitative by modifying the Liptay formalism²¹ for the analysis of the Stark spectrum to consider the effect of an applied field on an absorption to a doubly degenerate state.²² These authors showed that the dipole moments of the two components of E symmetry are of equal magnitude but opposite in direction, yielding a value of zero for the overall dipole moment of the excited state.²² However, because the applied electric field used to measure the Stark effect splits the absorption spectrum, they noted that a second-derivative component appears in the electroabsorption spectrum even when one averages over all possible molecular orientations relative to the light field and the applied electric field. This signal is interpreted as a nonzero $|\Delta\mu|$ using the traditional analysis developed for nondegenerate systems.²¹

Although the observation of a nonzero $|\Delta\mu|$ in a D_3 molecule is not in itself diagnostic of symmetry breaking, Liu et al. have shown that the ratio of the values of $|\Delta\mu|$ for single arm and trimeric structures such as those studied here is a sensitive measure of the extent of electronic delocalization in the trimer species. The experiments performed here provide a powerful test of the detailed predictions of their model.¹ Our measurements find that the $|\Delta\mu|$ for the single dendrimer arm (monomer) is similar in value to that of the trimer. Liu et al. predict that the ratio of the trimer $|\Delta\mu|$ to that of the monomer will be near unity for systems in which the excitation is fully localized on a single arm of the trimer and smaller ratios will be observed for more symmetric and therefore electronically delocalized trimers.¹ Our results are also consistent with the relatively weak electronic coupling that is expected between the three arms linked through meta substitution of the benzene ring at the core of the trimer structure.^{9,23,24}

Experimental Section

Materials. The preparation and purification of 5'-(4-(bis(4-ethylphenyl-amino)phenyl)- N,N,N',N'' -tetrakis(4-ethylphenyl)-(1,1':3',1''-tetraphenyl)-4,4''-diamine (abbreviated *p*-EFTP) and the biphenyl model compound, N,N -di(4-ethylphenyl)-(1,1'-biphenyl)-4 amine (abbreviated *p*-DPABP) has been reported elsewhere by Van der Auweraer et al.²⁵ For simplicity, these molecules (Scheme 1) are also referred to in the text as the trimer (*p*-EFTP) and the monomer (*p*-DBABP), respectively. Polymethyl methacrylate (PMMA) (Aldrich) was used without further purification. Polyethylene (PE) was obtained in film form. Before use, films of PE were immersed overnight in chloroform to remove additives, washed with methanol, and allowed to air dry. The PE film used has no significant absorption or emission in the wavelength range of interest. The

film thickness is typically between 20 and 50 μm . Spectroscopic-grade solvents toluene (Fisher Chemicals) and 2-methyltetrahydrofuran (MTHF, Aldrich) were used as received.

The sample preparation methods used have been detailed previously.²⁶ As compared to the room-temperature spectra in organic solvents, no new features appeared at low temperature, though for both compounds there was a slight increase in the optical density (OD) and a red shift of peak positions by 10–15 nm. These observations suggest that the extent of aggregation in the glasses and polymer films is minimal. Likewise, the observation of polarized fluorescence from the monomer (see below) suggests that at least this compound does not exhibit significant aggregation under the conditions used. Likewise, heating the polymer films to prepare samples did not alter the optical density or the absorption spectrum of either compound, indicating that no substantial thermal degradation had occurred.

Data Collection and Analysis. Instrumentation. The electroabsorption apparatus is home-built and has been previously described elsewhere.²⁷ In essence, it consists of a 150-W xenon arc lamp (Oriel), 0.3-m single monochromator (Spex), polarizer, and photodetector (UDT) that is connected to a lock-in amplifier (Stanford Research SR850). A high-voltage AC power supply (Joe Rolfe) is used to deliver between 10^5 and 10^6 V/cm to the sample via the optically transparent electrodes at a frequency of 450 Hz. The power supply also provides the reference frequency for phase-sensitive light detection via a lock-in amplifier. Steady-state fluorescence and fluorescence polarization spectra were obtained using a Fluorolog-2 instrument (Spex) with 1-nm resolution. The reported spectra are corrected for the grating and detector response.

Electroabsorption Data Analysis. The analysis of the electroabsorption data follows that in the literature for randomly oriented molecules within a rigid glass.^{21,28} This method assumes excitation to a nondegenerate excited state and, as such, is appropriate only for the monomer. Below we describe how the fitting results have been modified to account for the doubly degenerate nature of the trimer excited state using the results of Liu et al.¹

In the Liptay formalism, the change in absorption due to the application of an external electric field is fit to the weighted sum of zeroth, first, and second derivatives of the zero-field absorption spectrum. The overall change in absorbance caused by the application of an electric field can be described by the following equation:

$$\Delta A(\tilde{\nu}) = \bar{\mathbf{F}}_{\text{eff}}^2 \left[\mathbf{a}_\chi A(\tilde{\nu}) + \mathbf{b}_\chi \frac{1}{15\hbar} \left\{ \frac{\partial}{\partial \tilde{\nu}} \left(\frac{A(\tilde{\nu})}{\tilde{\nu}} \right) \right\} + \mathbf{c}_\chi \frac{\tilde{\nu}}{30\hbar^2} \left\{ \frac{\partial^2}{\partial \tilde{\nu}^2} \left(\frac{A(\tilde{\nu})}{\tilde{\nu}} \right) \right\} \right] \quad (1)$$

The term $A(\tilde{\nu})$ represents the unperturbed absorption as a function of frequency ($\tilde{\nu}$), and $\bar{\mathbf{F}}_{\text{eff}}$ represents the field at the sample in V/cm. This effective field includes the enhancement of the applied field due to the cavity field of the matrix. The subscript χ represents the angle between the direction of the applied electric field and the electric field vector of the linearly polarized light. The expressions of \mathbf{a}_χ , \mathbf{b}_χ , and \mathbf{c}_χ are related to $|\Delta\mu|$ and $\text{Tr}(\Delta\alpha)$. It is also important to emphasize that for a sample embedded randomly in a glass, such as those studied here, the magnitude but not the sign of $\Delta\mu$ is measured.

The experiment is normally performed at two angles, $\chi = 54.7$ and 90° . When the experiment is performed at the magic

angle ($\chi = 54.7^\circ$), \mathbf{b}_χ and \mathbf{c}_χ take the simple form of eqs 2 and 3 below.

$$\mathbf{b}_{54.7} = \frac{5}{2} \text{Tr}(\Delta\alpha) \quad (2)$$

$$\mathbf{c}_{54.7} = 5|\Delta\vec{\mu}|^2 \quad (3)$$

Here the transition moment polarizability and hyperpolarizability terms, which are typically quite small, have been neglected.^{21,28}

The coefficients \mathbf{a}_χ , \mathbf{b}_χ , and \mathbf{c}_χ in eq 1 are extracted by means of a linear least-squares (LLSQ) fit of the electroabsorption signal to the sum of the derivatives of $A(\tilde{\nu})$. If the resultant fit to the absorption line shape (a single set of \mathbf{a}_χ , \mathbf{b}_χ , and \mathbf{c}_χ) is not of high quality, then this is an indication that there is more than one transition (electronic or vibronic) underlying the absorption band, each having different electro-optical properties.²⁹ The molecules studied here appear to contain more than one electronic state within their absorption bands (vide infra). Nonetheless, the fits to the electroabsorption spectra obtained using a single set of parameters were sufficiently good that no effort was made to deconvolve the absorption spectrum.

To interpret correctly the results of fitting the trimer data using the formalism described above, the parameters must be adjusted to account for the perturbation of the absorption spectrum due to the field-induced splitting of the two components of the state of E symmetry to which the excitation occurs in this molecule. (See ref 22 and the Supporting Information section of ref 1.) In the Discussion section, these modifications, derived in ref 1, are described and used to analyze the experimental findings.

Results and Discussion

Both the monomer and the trimer exhibit two overlapping absorption bands in the low-energy region (Figures 1–4, top panels). The absorption spectra of the two compounds are similar in both low-temperature glasses (Figures 1 and 2, top panels) and in polymers (Figures 3 and 4, top panels), though it appears that the lowest-energy band is red shifted $\sim 1000 \text{ cm}^{-1}$ on going from the monomer to the trimer whereas the position of the higher-energy band remains essentially fixed. This is more evident in the organic glasses than in the polymers because the absorption spectra are more highly resolved. A weak solvent effect on the positions and the intensities of these bands is seen in both compounds, as seen in Table 1 and refs 10 and 12. As expected, the trimer extinction coefficient is found to be roughly 3 times that of the monomer in all environments studied (Table 1).

Fluorescence polarization studies on the monomer in 77 K methylcyclohexane glass (not shown) and in a PMMA matrix (Figure 5) show that the degree of polarization of the emission from the low-energy band is quite high (degree of polarization, P , of ~ 0.35) but drops significantly for excitation wavelengths below 320 nm. This is consistent with the idea that at least two distinct electronic transitions having orthogonally polarized transition moments underlie the absorption envelope of this molecule. Moreover, the absorption and emission transition dipole moments of the low-energy band are essentially parallel.

In contrast, the emission of the trimer in the same matrixes exhibits a low degree of polarization ($P < 0.1$) across the entire band (Figure 6). This suggests that the excitation is randomized over the three arms of the trimer within the time scale of fluorescence as previous studies have shown.¹³ Consistent with this finding are ultrafast measurements that show the rapid reorientation of the excitation polarization attributed to intramolecular excitation transfer among the three arms of the trimer.¹⁴

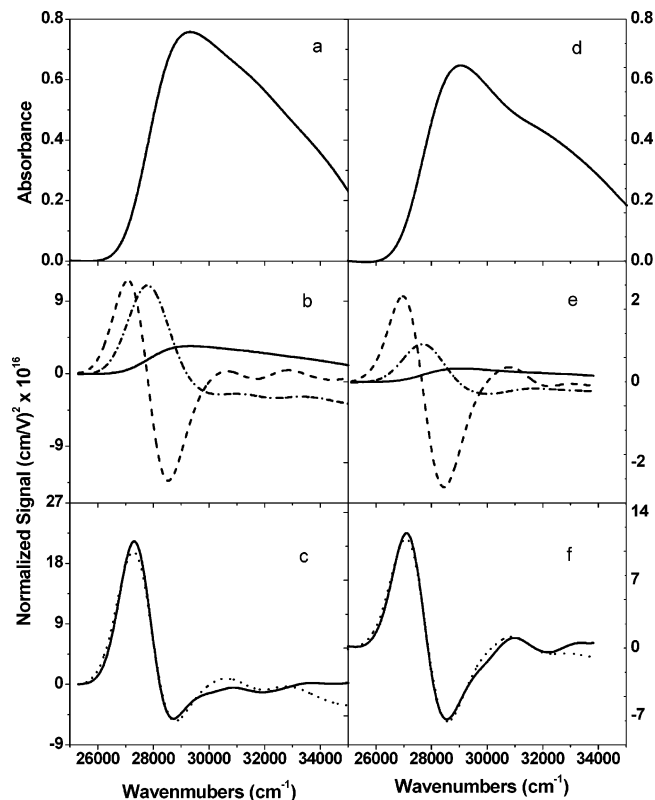


Figure 1. *p*-DPABP monomer in toluene (panels a–c) and MTHF (panels d–f) at 77 K. The absorption spectrum of the molecule is shown in panels a and d. Panels b and e contain the zeroth (—), first (---), and second (· · ·) derivatives of the absorption spectra comprising the fit to the electroabsorption spectra. Panels c and f show the electroabsorption (solid line) spectra and the fits obtained (dotted line). The normalized electroabsorption signal is $\Delta A/F^2$, where ΔA represents the field-induced change in the absorbance and F is the field strength.

Evidence that the excitation is localized on the time scale of absorption comes from the electroabsorption studies reported here. Specifically, the monomer and trimer exhibit very similar values of $|\Delta\vec{\mu}|$ in all matrixes studied (Figures 1–4, spectra obtained at $\chi = 54.7^\circ$ and Table 2) with the value for the trimer being slightly larger than that of the monomer in several matrixes. Data obtained at $\chi = 90^\circ$ (data not shown) indicate that in both the monomer and the trimer the direction of the change in dipole moment is within $10\text{--}20^\circ$ of the direction of the transition moment ($\xi = 10\text{--}20^\circ$). Despite the evidence that there is more than one electronic state having different polarizations underlying the main absorption feature (vide supra), all of the data (Figures 1–4) are adequately fit using a single set of electro-optical parameters ($|\Delta\vec{\mu}|$ and $\text{Tr}(\Delta\alpha)$). This is an indication that for both molecules $|\Delta\vec{\mu}|$ and $\text{Tr}(\Delta\alpha)$ are similar for all excited states within the bandwidth probed.

One subtlety in the comparison of the monomer and trimer is that the measured $|\Delta\vec{\mu}|$ should be scaled by the cavity field (f_c) to account for the effective field at the site of the sample. This factor represents the enhancement of the applied field due to the dielectric cavity in which the molecule is contained. The magnitude of the enhancement will depend on the size of the cavity if a realistic elliptical model for the cavity correction is used. Though the appropriate size will be different for the monomer versus the trimer, the correction is generally estimated to be $10\text{--}15\%$ in nonpolar environments such as those studied here. Therefore, this effect should not significantly affect the conclusions of this paper.

TABLE 1: Solvent Effects on the Optical Properties of *p*-DPABP and *p*-EFTP

solvent	<i>p</i> -DPABP (monomer)		<i>p</i> -EFTP (trimer)		$\epsilon_{\max}^{\text{EFTP}}$
	$\lambda_{\max}^{\text{abs}}$	$\epsilon_{\max} (\text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\max}^{\text{abs}}$	$\epsilon_{\max} (\text{M}^{-1} \text{cm}^{-1})$	$\epsilon_{\max}^{\text{DPABP}}$
methylcyclohexane	331 \pm 2	24 950 \pm 3000	346 \pm 2	71 600 \pm 5000	2.87 \pm 0.05
toluene	332 \pm 2	23 500 \pm 3000	347 \pm 2	67 900 \pm 5000	2.89 \pm 0.05
toluene (77 K)	341 \pm 2	30 300 \pm 3000	360 \pm 2	88 500 \pm 5000	2.92 \pm 0.05
MTHF	333 \pm 2	25 350 \pm 3000	348 \pm 2	72 345 \pm 5000	2.85 \pm 0.05
MTHF (77 K)	344 \pm 2	29 678 \pm 3000	357 \pm 2	81 234 \pm 5000	2.74 \pm 0.05
ethylene chloride	332 \pm 2	24 450 \pm 3000	347 \pm 2	74 555 \pm 5000	2.97 \pm 0.05
acetonitrile ^a	328 \pm 2	23 950 \pm 3000	342 \pm 2	70 230 \pm 5000	2.93 \pm 0.05
chloroform	332 \pm 2	25 510 \pm 3000	348 \pm 2	73 300 \pm 5000	2.90 \pm 0.05
methanol	323 \pm 2	25 072 \pm 3000	345 \pm 2		
PMMA	326 \pm 2		341 \pm 2		
PMMA (77 K)	331 \pm 2		347 \pm 2		
PE	329 \pm 2		344 \pm 2		
PE (77 K)	340 \pm 2		350 \pm 2		

^a The acetonitrile solution of *p*-EFTP was made using a dichloroethane stock solution because of poor solubility. The absorption maxima ($\lambda_{\max}^{\text{abs}}$) are in nm, and the extinction coefficients (ϵ_{\max}) are in $\text{M}^{-1} \text{cm}^{-1}$.

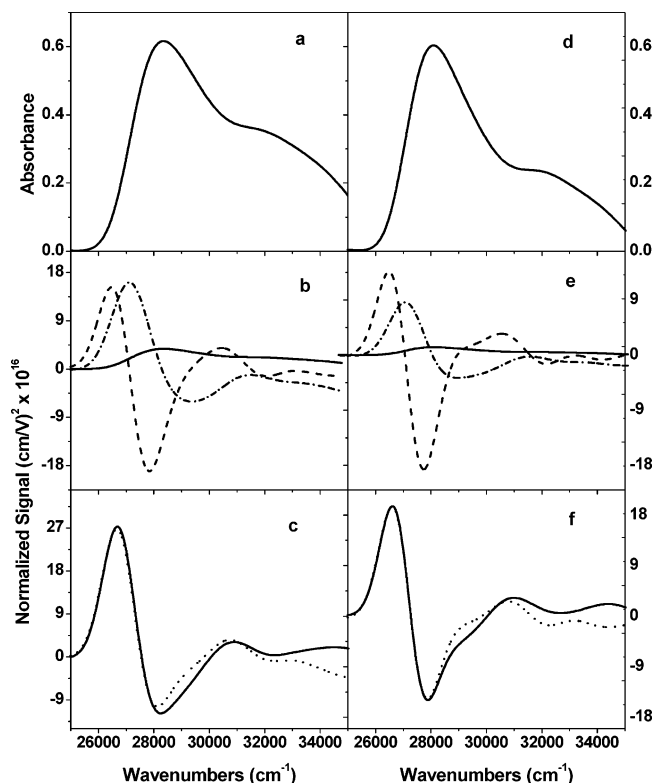


Figure 2. *p*-EFTP trimer in toluene (panels a–c) and MTHF (panels d–f) at 77 K. The absorption spectrum of the molecule is shown in panels a and d. Panels b and e contain the zeroth (—), first (— · —), and second (---) derivatives of the absorption spectra comprising the fit to the electroabsorption spectra. Panels c and f show the electroabsorption (—) spectra and the fits obtained (···). The normalized electroabsorption signal is $\Delta A/F^2$, where ΔA represents the field-induced change in the absorbance and F is the field strength.

Interestingly, the value of $|\overline{\Delta\mu}|$ reported here for the trimer is reasonably consistent with the value of the excited-state dipole moment, μ_e , (7.9 D) obtained by Verbouwe et al.¹³ for the relaxed excited state of this molecule using microwave conductivity.³⁰ In contrast, the value reported here is much smaller than the value of 27 D for the dipole moment of the fluorescence state that was previously inferred by solvent shift analysis.¹⁰ However, it is important to note that the Lippert–Mataga plots of *p*-EFTP and related molecules are clearly not linear¹⁰ and would asymptotically yield a much smaller dipole moment in nonpolar solvents.

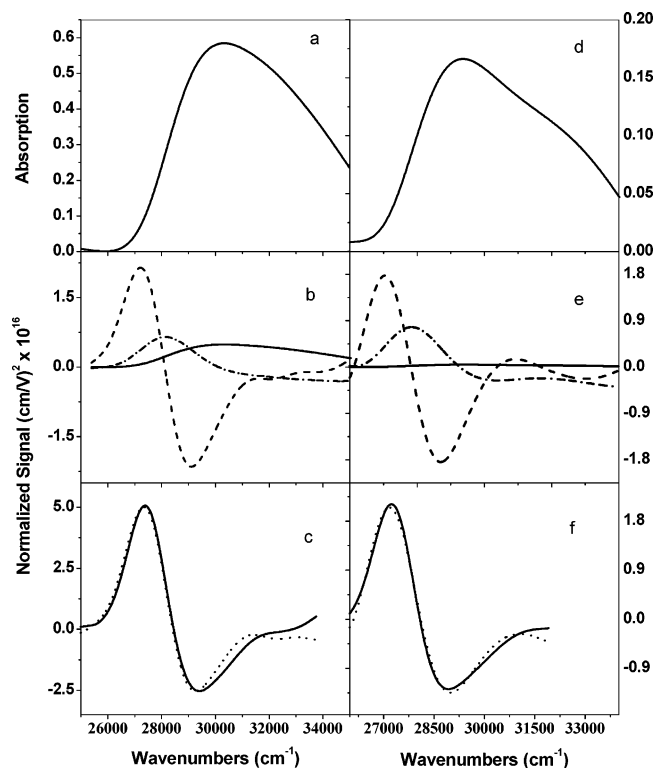


Figure 3. *p*-DPABP monomer in PMMA (panels a–c) and PE (panels d–f) at 77 K. The absorption spectrum of the molecule is shown in panels a and d. Panels b and e contain the zeroth (—), first (— · —), and second (---) derivatives of the absorption spectra comprising the fit to the electroabsorption spectra. Panels c and f show the electroabsorption (—) spectra and the fits obtained (···). The normalized electroabsorption signal is $\Delta A/F^2$, where ΔA represents the field-induced change in the absorbance and F is the field strength.

Comparing our results with those derived from microwave conductivity, we would infer that little additional charge separation or symmetry lowering occurs as the molecule evolves away from the Franck–Condon region of the excited-state potential energy surface toward its minimum. Moreover, because the microwave conductivity experiments are performed in fluid solution and those reported here are in polymers and glasses, it appears that the rigidity of the medium does not play a substantial role in the asymmetry observed as long as media of low polarity are considered.

One possible contribution to the apparent $|\overline{\Delta\mu}|$ of both compounds is the inherently asymmetric local environment of

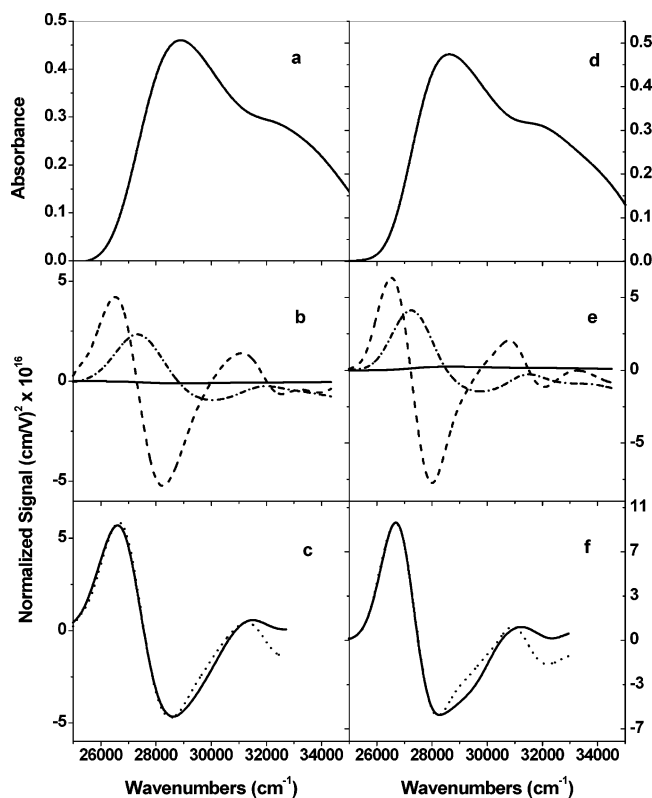


Figure 4. *p*-EFTP trimer in PMMA (panels a–c) and PE (panels d–f) at 77 K. The absorption spectrum of the molecule is shown in panels a and d. Panels b and e contain the zeroth (—), first (— · —), and second (---) derivatives of the absorption spectra comprising the fit to the electroabsorption spectra. Panels c and f show the electroabsorption (—) spectra and the fits obtained (· · ·). The normalized electroabsorption signal is $\Delta A/F^2$ where ΔA represents the field-induced change in the absorbance and F is the field strength.

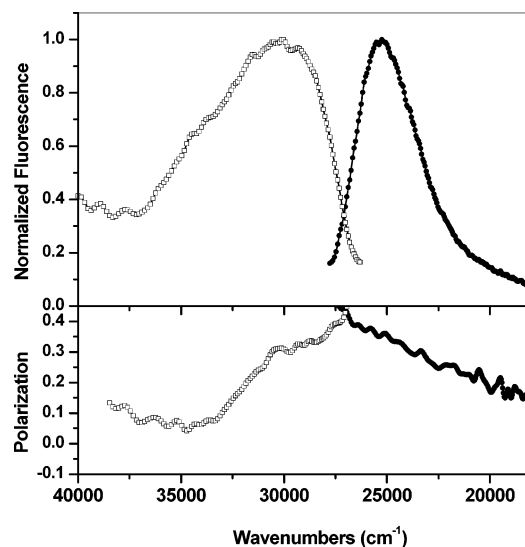


Figure 5. Fluorescence excitation (□) and emission spectra (●) of the monomer in a PMMA matrix. The excitation spectrum was collected at 394 nm, and the emission spectrum was obtained with excitation at 344 nm. The bottom panel contains a plot of the depolarization ratio, P , as a function of wavelength for both spectra that uses the same legend.

a polymer or glass matrix in which the measurements are made. Interactions of the disordered local dipoles with $\text{Tr}(\Delta\alpha)$ of these molecules could induce in them a measurable $|\Delta\mu|$. Although this is certainly a contributing factor, we note that the values of $\text{Tr}(\Delta\alpha)$ for the systems measured in this work are relatively

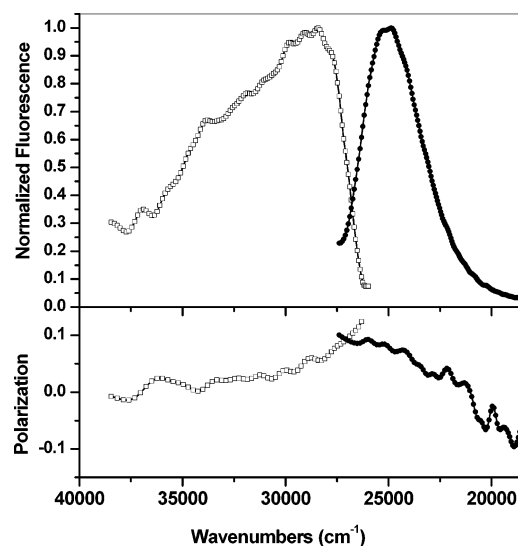


Figure 6. Fluorescence excitation (□) and emission spectra (●) of the trimer in a PMMA matrix. The excitation spectrum was collected at 400 nm, and the emission spectrum was obtained with excitation at 350 nm. The bottom panel contains a plot of the depolarization ratio, P , as a function of wavelength for both spectra that uses the same legend.

TABLE 2: Electroabsorption Results for *p*-EFTP and *p*-DPABP in Various Matrixes^a

matrix	<i>p</i> -DPABP (monomer)			<i>p</i> -EFTP (trimer)		
	$\lambda_{\text{max}}^{\text{abs}}$	$ \Delta\mu $	$\text{Tr}(\Delta\alpha)$	$\lambda_{\text{max}}^{\text{obs}}$	$ \Delta\mu $	$\text{Tr}(\Delta\alpha)$
toluene (77 K)	341	5.7 ± 0.5	108 ± 15	360	6.5 ± 0.5	171 ± 15
MTHF (77 K)	344	6.0 ± 0.5	96 ± 15	357	7.7 ± 0.5	171 ± 15
PE (300 K)	329	5.4 ± 0.5	132 ± 15	343	6.0 ± 0.5	99 ± 15
PE (77 K)	340	6.2 ± 0.5	135 ± 15	350	7.3 ± 0.5	177 ± 15
PMMA (300 K)	326	5.5 ± 0.5	69 ± 15	345	6.8 ± 0.5	96 ± 15
PMMA (77 K)	331	6.9 ± 0.5	66 ± 15	347	7.1 ± 0.5	123 ± 15

^a Absorption maxima ($\lambda_{\text{max}}^{\text{abs}}$) are in nm, dipole moments are in D, and the traces of the polarizabilities are in Å³.

small, suggesting that the asymmetry in the local fields would have to be quite large (on the order of 10^7 V/cm) to affect the observed $|\Delta\mu|$ values substantially.

The second and most likely dominant effect is that packing and/or intramolecular steric forces cause the symmetry of the trimer to be lowered sufficiently to localize the excitation on one arm. The effects of this type of disorder were considered in detail in ref 1, and the main results are summarized briefly here for comparison to experiment. A symmetric trimer structure was built from three identical energy-minimized monomer structures arranged around a central benzene core. Numerous disordered structures were constructed as well using three distinct monomer arms that had been generated by randomly varying their internal dihedral angles over a physically reasonable range. The degree of disorder (D) of each nonsymmetric trimer was then defined as the difference in energy between the arms having the highest and the lowest excitation energies.

The expected value for the ratio of the change in dipole moment of the trimer ($|\Delta\mu_{\text{T}}|$) to that of the monomer ($|\Delta\mu_{\text{M}}|$) was found to depend on the magnitude of D . The two extreme limits of disorder with their corresponding predicted values of $|\Delta\mu_{\text{T}}|$ are as follows: (1) zero disorder, in which the trimer structure is symmetric and the two E states are degenerate ($|\Delta\mu_{\text{T}}| = 1/\sqrt{2}|\Delta\mu_{\text{M}}|$) and (2) large disorder such that D is much greater than the coupling energy between the branches ($|\Delta\mu_{\text{T}}| = |\Delta\mu_{\text{M}}|$).¹ For the zero-disorder case, the excitation

would be considered to be delocalized over the trimer structure, with complete localization being achieved in the large disorder limit. For a more detailed discussion of these limits and of intermediate disorder cases, see ref 1.

These predicted ratios can be compared to the experimental results obtained by analyzing the monomer and trimer electroabsorption data in the same way using the formalism outlined in the Experimental Section of this paper. We find experimentally that $|\Delta\mu_T|$ is equal to or in some cases slightly larger than $|\Delta\mu_M|$, within experimental error. Therefore, we conclude that the trimers studied here are symmetry broken because of the degree of disorder in their constituent arms, causing a complete localization of the excited electronic state to a single arm upon photon absorption.

As noted above, an important factor in determining whether excitation will become localized in a given trimer is the magnitude of the coupling energy among its branches, denoted J . For example, Mukamel and co-workers estimated that the energy splitting arising from interactions between the three arms of a trimeric dendrimer composed of phenylacetylene units is sufficiently small (-69 cm^{-1}) that very weak perturbations are sufficient to localize the excitation.³¹ In contrast, Beljonne et al.⁹ calculate a much larger coupling between the arms of a benzene ring with octopole substitution ($\sim 300\text{ cm}^{-1}$), which is similar to what is calculated for the benzene-cored dendrimer studied here ($\sim 400\text{ cm}^{-1}$).¹ Despite the fact that the calculated interaction energies between the arms of the trimer are fairly substantial, our experimental results indicate that the localization of the excitation to a single arm nonetheless occurs on an ultrafast time scale.¹ The calculations of Liu et al. indicate that the trimer excitation becomes localized when the difference in excitation energies between the lowest- and highest-energy arm of the trimer is $\sim 4J$ or $\sim 1600\text{ cm}^{-1}$.¹ This value is consistent with the estimated experimental inhomogeneous width of the absorption spectrum of the trimer, which is $\sim 3200\text{--}4000\text{ cm}^{-1}$ ($0.4\text{--}0.5\text{ eV}$) fwhm.³² Interestingly, this degree of disorder is somewhat larger than the $\sim 0.24\text{ eV}$ that is predicted from a thermal distribution of conformers of the arms of the trimer at room temperature.¹

Recently, several femtosecond fluorescence depolarization studies have identified a number of dendritic compounds that exhibit a high degree of polarization anisotropy at early times, which then falls off within 100 fs.^{33–35} This early-time decay was interpreted as evidence for excitonic delocalization across the three arms of the structure. These systems also exhibit a slower (several ps) decay component arising from incoherent hopping among the arms.^{33–35} One structural factor that appears to promote strong coupling of the dendrimer arms is having an amino group at the trimer core rather than a benzene group as the molecules studied here possess. This is evident from steady-state absorption and fluorescence studies as well as from computation.³⁶ In fact, the calculated J values for such systems are roughly a factor of 5 larger than otherwise similar benzene-cored structures.⁹ Follow-up experiments on analogous amino-cored molecules are in progress to determine whether the predicted high degree of delocalization at early times is manifested in the electroabsorption spectrum. In addition, the possibility that the degree of delocalization within the molecule is altered as it moves away from the Franck–Condon region and toward its excited-state minimum, as has been suggested in ref 37, will be investigated by comparing the results of electroabsorption and electrofluorescence measurements on these systems.

Conclusions

Using electroabsorption, it has been shown that the nominally C_3 -symmetric molecule *p*-EFTP exhibits a change in dipole moment on excitation ($|\Delta\mu|$) that is very similar to that of a model compound (*p*-DPABP) consisting of a single arm of the dendrimer structure. Comparing this result to the predictions of theory demonstrates that localization of the excitation to a single arm of the trimer occurs upon absorption. Electronic structure calculations presented in ref 1 suggest that the energetically favorable lowering of symmetry due to rotations of the phenyl groups is sufficient to produce the observed localized state upon excitation despite a fairly large electronic coupling between the arms of the trimer.

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References and Notes

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