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Conformations and Photophysics of a Stilbene Dimer[†]

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Photophysical studies of pseudo-*p*-distyryl[2.2]paracyclophane, a model molecule of a stilbene dimer arranged in a brick-wall geometry, in tetrahydrofurane solution indicate the existence of at least two conformers in the ground state. The conformer **A** with the smallest optical gap of 3 eV has a short radiative lifetime of 3.3 ns, while the conformer **B** with an optical gap about 0.3 eV larger is much more abundant in solution and its radiative lifetime is about 10 times longer. Ab initio calculations show that the ground-state energy has a shallow minimum with respect to the torsional angle between the styryl side group and the paracyclophane core around the zero position, with the lowest energy conformation at a torsional angle of −21°. On this basis, **A** and **B** are assigned to flat and twisted conformations, respectively. Conformer **B** shows a partial decay of excited-state absorption and fluorescence with a time constant ranging from 5 to 30 ps, depending on excitation photon energy. We attribute this to isomerization of the stilbene moiety, which initially keeps conjugation in the ground state. The isomerization product is long-lived and tends to accumulate in solution.

1. Introduction

Intermolecular interactions are important in defining material properties and represent a popular research field. Pseudo-*p*-distyryl-[2.2]-paracyclophane (PPDSPc) (Figure 1) mimics a stilbene dimer with the stilbene moieties shifted along the long molecular axis in a brick-wall geometry. Stilbene is the smallest oligomer of the conjugated polymer poly(phenylenevinylene) (PPV), which is attractive material for flexible displays, photosensors, solar cells, etc.[1] Interchain interactions in polymers are essential for conductivity but also lead to the formation of intermolecular aggregates and excimers, which act as excitation traps and fluorescence quenchers.[2−9] Previous work showed that the oscillator strength of the lowest excited state of such dimers increases with the length of the molecules connected to the paracyclophane core.[10]

In this paper, we report fluorescence and transient absorption studies of PPDSPc, which show existence of conformers with different optical gap. Combining experimental findings with ab initio calculations we suggest that the flat conformation with extensive delocalization of the electronic transition is present at low concentration, while the dominating conformer has a broken conjugation in one of the stilbene moieties and it undergoes isomerization of the other stilbene moiety in the excited state.

2. Experimental Section

PPDSPc was synthesized as described elsewhere.[10] Time-resolved fluorescence was measured with a streak camera, which had an apparatus response function of about 2 ps (fwhm) using the second harmonic of a Ti:sapphire laser (pulse width about 100 fs, spectral width 0.06 eV) for excitation at 82 MHz repetition rate and detecting fluorescence in a forward direction. Transient absorption was measured in a conventional manner using an optical parametric amplifier pumped by an amplified Ti:sapphire laser system at 5 kHz for excitation and another for probe; the instrumental response function was about 120 fs. A spectral width of about 0.06 eV was determined for the probe window by a monochromator placed after the sample. Time-resolved measurements were performed on PPDSPc solutions in tetrahydrofurane at room temperature in a 1 cm cell; samples were degassed and filled with argon before measurements. Control experiments in a 2 mm rotating cell gave the same result. The ground-state absorption spectra were recorded with a Jasco V530 spectrophotometer. Time integrated fluorescence and fluorescence excitation spectra were measured with a Spex Fluorolog fluorimeter in dilute solutions with absorbance of less than 0.2 at the maximum, detecting the emitted light near the backscattering direction. Spectra were corrected for the detection sensitivity. Fluorescence quantum

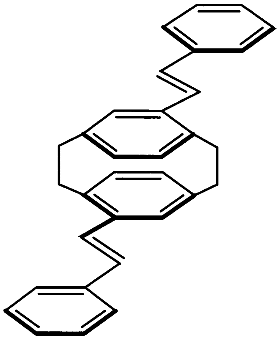

Figure 1. Chemical structure of PPDSPc.

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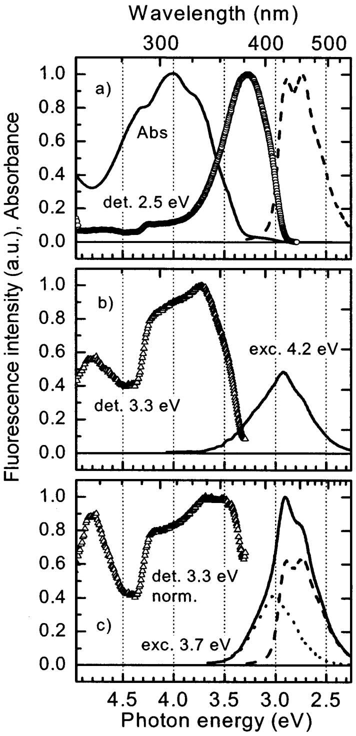

Figure 2. Steady-state spectra of the PPDSPc solution in tetrahydrofurane at room temperature: (a) absorption (solid line), time integrated fluorescence after excitation at 3.3 eV (dashed line) and excitation spectrum of the emission detected at 2.5 eV (circles); (b) fluorescence spectrum after excitation at 4.2 eV (solid line) and excitation spectrum of the emission detected at 3.3 eV (triangles); (c) fluorescence spectrum after excitation at 3.7 eV (solid line), scaled fluorescence spectrum with 3.3 eV excitation (dashed line) and difference between them (dotted line), triangles show excitation spectrum of the emission at 3.3 eV normalized to the number of absorbed photons.

efficiencies were estimated using a Coumarin 30 solution in acetonitrile as a reference, for which the fluorescence quantum yield of 0.67 has been documented.[11]

3. Results

A. Fluorescence Dependence on Excitation Photon Energy. The ground-state absorption of PPDSPc dissolved in tetrahydrofurane (Figure 2a) has a maximum at about 4 eV, and a weak absorption band is seen at the red edge of the spectrum in the region of 3−3.3 eV. Fluorescence spectra and intensity strongly depend on excitation photon energy. When excitation is in the 3 eV band, the fluorescence spectrum shows clear vibronic structure with a 0−0 vibronic peak at 2.88 eV and the fluorescence quantum yield is also constant for excitation at <3.2 eV. The distance between vibronic peaks is 0.17 eV (1370 cm^{-1}), which corresponds to the mean frequency of the stretching of single and double carbon−carbon bonds. The relative intensity of the vibronic peaks indicates a Huang−Rhys factor $S \approx 1$, similar to that of stilbene.[10] Upon tuning the excitation above 3.2 eV, the intensity of the low energy fluorescence drops quickly and a higher energy emission band grows in, which peaks at 3 eV (Figures 2b and 2c). It is very likely that vibrations with a frequency similar to that observed in the low energy spectrum are also coupled to the 3 eV emission. Then, the emission maximum at 3.03 eV would correspond to the 0−1 vibronic peak and the 0−0 transition is expected to be at 3.2 eV. The spectrally integrated fluorescence quantum yield decreases dramatically from 0.66 when exciting at 3.2 eV down to 0.07 for excitation at 3.7 eV.

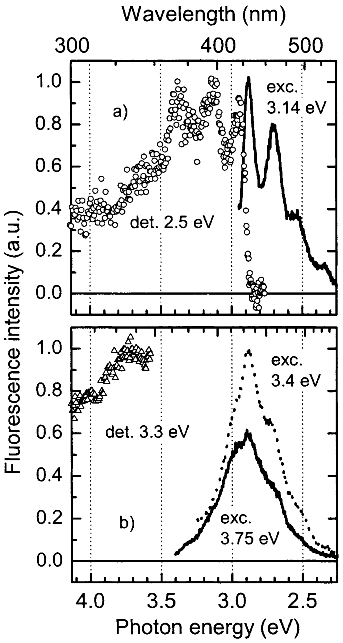

Figure 3. Low-temperature (77 K) fluorescence (lines) and fluorescence excitation spectra (symbols) of PPDSPc in dimethyltetrahydrofurane for various excitation and detection photon energies as indicated.

The fluorescence spectrum of the frozen solution at 77 K after excitation into the low energy band (Figure 3a) is almost identical to that recorded at 293 K with a 0−0 peak at 2.87 eV, only vibronic bands are somewhat narrower. The fluorescence excitation spectrum shows peaks at 2.95 eV and at 3.12 eV, which obviously correspond to the 0−0 and 0−1 vibronic peaks of the conformer with a small optical gap (later we call it conformer **A**) with the same 0.17 eV separation as observed in the fluorescence spectrum. The Stokes shift is quite small, just 0.07 eV, indicating that structural relaxation of **A** in the excited singlet state is not significant. The fluorescence dependence on excitation wavelength at 77 K is very similar to that at room temperature: when excitation is tuned above 3.3 eV, the low energy fluorescence decreases and the higher energy emission band grows in, and peaks again at about 3 eV (Figure 3b). Since extensive molecular motion is unlikely to occur in frozen solution, we concluded that the other conformer with a larger optical gap (conformer **B**) exists in the ground state and its absorption appears above 3.3 eV, as also indicated by fluorescence excitation spectra in Figures 2b and 2c.

B. Time-Resolved Fluorescence and Radiative Lifetimes. The fluorescence spectrum taken at the time delay of 100 ps after excitation to the higher energy band at 3.4 eV (Figure 4) is very similar to the time integrated fluorescence spectrum measured with the same excitation energy. This observation suggests that relaxation processes of both conformers **A** and **B** in the excited state are basically complete within 100 ps. The spectrum taken at 4 ps time delay has slightly higher intensity of the blue side shoulder at about 3 eV, where a partial decay with a time constant of 30 ps is observed (Figure 5a). No significant dynamics is seen on the red side of the fluorescence spectrum. Fluorescence kinetics measured after excitation at 3.2 eV (not shown) were independent of detection wavelength and very similar to that at 2.7 eV observed after 3.4 eV excitation. A nondecaying transient anisotropy value of 0.32 was calculated from fluorescence kinetics with parallel and perpendicular polarizations of excitation at 3.4 eV and detection within the fluorescence band of **A** (not shown). From this, we estimate an

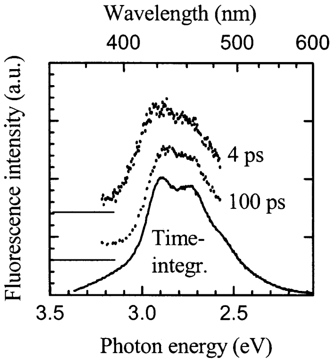

Figure 4. Fluorescence spectra of the PPDSPc solution in tetrahydrofurane at 293 K taken at 4 ps and at 100 ps time delay after excitation at 3.4 eV. The time integrated fluorescence spectrum recorded for excitation at 3.4 eV (solid line) is shown for comparison. Spectra are shifted vertically as indicated by horizontal lines.

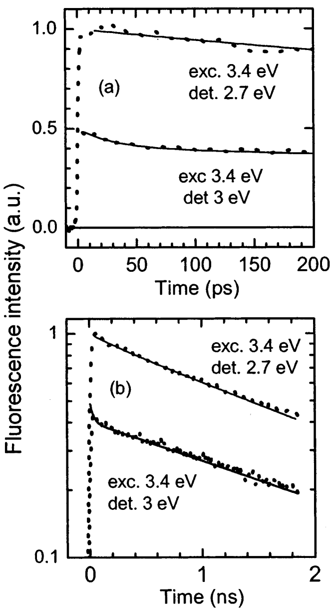

Figure 5. Fluorescence kinetics on the short (a) and long (b) time scale. Thin solid lines show biexponential decay fits with parameters in Table 1.

angle of about 20° between the transition dipole moments of the two lowest energy transitions in **A**.

On the long time scale, the fluorescence decays are basically monoexponential (Figure 5b). A decay with a time constant of about 2.2 ns dominates the kinetics on the red side of the emission spectrum and can be safely attributed to conformer **A**, which shows strong emission in this spectral region (Figure 2). At the blue side of the emission spectrum, the decay of **B** fluorescence with a time constant of 2.5 ns is more pronounced.

The fluorescence quantum yield in the case of several emissive species is a sum of the individual contributions from each of them:

$$\Phi_F = \Sigma G_i \cdot (\tau_i/\tau_{0i}) \tag{1}$$

where G_i represents generation efficiencies of each excited species, and τ_i and τ_{0i} are fluorescence and radiative lifetimes, respectively. For excitation at 3.2 eV, $\Phi_F = 0.66 \pm 0.1$ and only **A** is excited, thus its radiative lifetime is $\tau_0 = 3.3 \pm 0.5$ ns. Since the **A** fluorescence intensity normalized to the number of absorbed photons drops by a factor of 20 when tuning excitation from 3.2 to 3.7 eV (can be obtained from data in Figure 2a), then the generation efficiency of **B** excitations with 3.7 eV excitation is about 0.95. Making use of the observation that **B** fluorescence decays by 20% on a picosecond time scale (Figure 5a) and assuming that nonemissive species are not excited directly with 3.7 eV, from the measured $\Phi_F = 0.07 \pm 0.01$ at 3.7 eV excitation, we obtain $\tau_0 \approx 51$ ns for conformer **B**. It is consistent with the fact that the spectrally integrated fluorescence after excitation at 3.7 eV has about equal contributions of **A** and **B** (Figure 2b). If the 3.7 eV excitation does excite nonemissive species, τ_0 for **B** would be shorter. At this point we cannot arrive at definite conclusions on this point. Anyhow, the radiative lifetime of **B** is about 10 times longer than that of **A**.

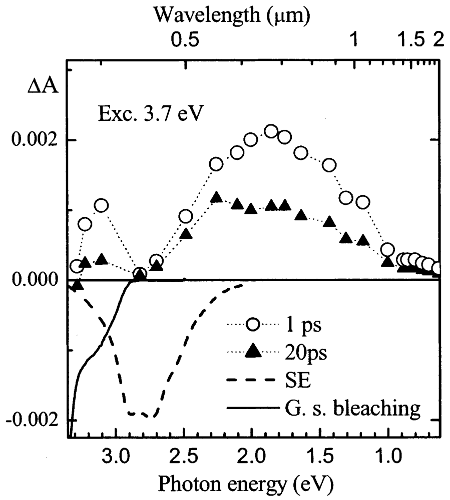

Figure 6. Transient absorption spectra taken at 1 ps (circles) and at 20 ps (triangles) time delay after excitation at 3.7 eV. Dashed and solid lines show the rough estimates of the contribution from the stimulated emission (SE) and the ground-state bleaching to the transient absorption.

The estimated radiative lifetime of 3.3 ns for **A** is rather short (only two times longer than that of stilbene), thus, the lowest energy transition carries reasonably high oscillator strength. The strong absorption band rising at >3.3 eV is dominated by conformer **B**; thus, **B** is much more abundant in solution than **A**.

C. Transient Absorption. Transient absorption spectra recorded with excitation at 3.7 eV (Figure 6) show strong excited-state absorption, extending over the visible spectral range with a maximum at about 1.8 eV. The dip in the transient absorption at around 2.8 eV is apparently due to the negative contribution of the stimulated emission (SE), which is depicted in Figure 6 as an approximate estimate from the time-integrated fluorescence spectrum. In the spectral region of ground-state absorption, the ΔA signal contains a negative contribution from ground-state bleaching. Excited-state absorption decreases by approximately a factor of 2 in the time window from 1 to 20 ps.

Transient absorption kinetics (Figure 7) show an ~400 fs rise in the spectral region of 0.6−1.2 eV and at around 3.1 eV, while the kinetics at 1.8 eV exhibit the decay on the same time scale. These spectral changes apparently are related to the combined effect of internal conversion, intramolecular vibrational redistribution (IVR), and solvation processes. These fast spectral changes of transient absorption are followed by partial decay of excited-state absorption with a time constant of 9 ps for excitation at 3.54 eV and about 5 ps for excitation at 3.7 eV.

The anisotropy of the excited-state absorption calculated from parallel and perpendicular polarizations of excitation and probe

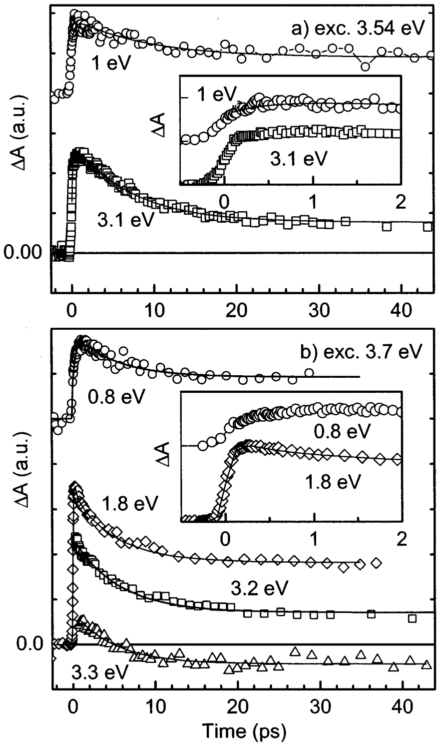

Figure 7. Transient absorption kinetics at various probe photon energies after excitation at 3.54 eV (a) and at 3.7 eV (b). Kinetics at 0.8 eV and at 1 eV are shifted vertically for clarity and the signals at 3.2 eV and at 3.3 eV are not shown for the time interval up to 1 ps, where they are dominated by solvent response. Solid lines are biexponential fits to the kinetics with parameters given in Table 1. Insets show kinetics on a short time scale.

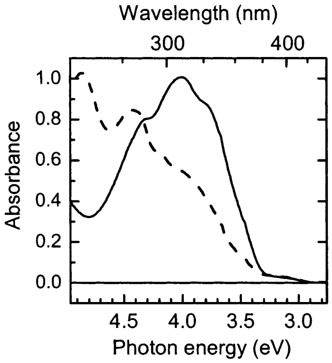

Figure 8. Ground-state absorption spectra of the PPDSPc solution in tetrahydrofurane for the fresh sample (solid line) and for the sample exposed for 2 h to the weak 3.7 eV pulsed laser radiation at 5 kHz (dashed line).

was about 0.33 in the visible spectral range and about 0.21 in near-IR, implying that the angles between the corresponding transition dipole moments are in the range of 20−35°. During the spectral evolution of the excited-state absorption the anisotropy remains constant.

We also observed that irradiation with photon energies >3.2 eV, even with the low intensity of a fluorimeter lamp, caused long-lived absorption changes of the sample in solution, but no changes occurred when irradiating with <3.2 eV. Absorption bleaching in the region of 3.3−4.2 eV (Figure 8), which corresponds to the absorption of conformer **B**, is accompanied by appearance of new absorption peaks at 4.4 eV (282 nm) and at 4.8 eV (260 nm), while the absorption of conformer **A** remains unaltered. The fluorescence intensity decreases by a similar factor as the absorbance of the exposed sample and the shape of the fluorescence spectrum excited at 3.7 eV remains unchanged. This implies that photoproducts do not have significant absorption at 3.7 eV.

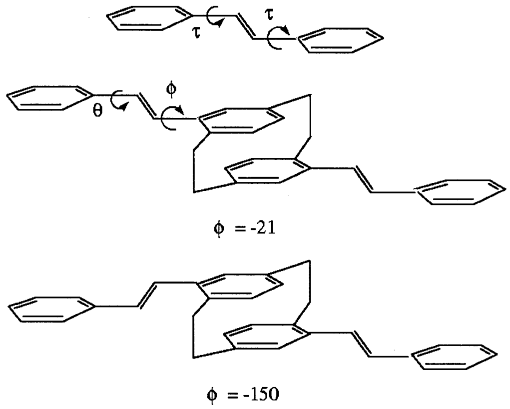

Figure 9. Scheme for defining torsional angles for stilbene and PPDSPc, and low energy conformers of PPDSPc.

4. Calculational Results

We carried out ab initio calculations to find possible stable conformers for PPDSPc and stilbene. All the calculations have been carried out at a level of Becke-3-Lee-Yang-Parr density functional theory (B3LYP) with 6-31G* basis sets and five d-functions using a suite of Gaussian 98 programs.[12] First, we have found a lowest energy conformer by geometry optimization for possible several conformers. Then, we have searched potential energy surfaces along the torsional angles for stilbene (τ) and PPDSPc (θ and ϕ) as shown in Figure 9. There are two sets of torsional angles (τ) and (τ') for stilbene, and ($\theta$and ϕ) and (θ' and ϕ') for PPDSPc. The torsional angles for the lowest energy stilbene conformer are (6°) and (−6°), while those for PPDSPc are (5°, 21°) and (−5°, −21°). We obtained the energy surface by changing one of the torsional angles, while keeping the other structural parameters constant as the optimized geometry. In searching the potential surface along the torsional angle τ for stilbene and θ for PPDSPc, it is enough to investigate from −90° to 90° due to the symmetric environment of benzene. Figure 10 shows that the torsional angles τ and θ give only one minimum, while the torsional angle ϕ gives three different local minima. Thus, the stilbene has only one minimum, while PPDSPc has three local minima. In particular, the energy difference between the two low-energy conformers of PPDSPc seems to be very small. We fully optimized the second lowest energy conformer and found that the torsional angles are (5°, 21°) and (13°, −150°). From the shape of the conformer, the lowest and the second lowest energy conformers can be called trans- and cis-conformers, respectively. The energy difference between trans- and cis-conformers is only 1.18 kcal/mol based on the full optimization. The potential barrier for the conformational change from cis to trans would be about 3 kcal/mol by rotation. However, another reaction path could be possible from cis to trans based on a recent report on the flexible pedal motion of stilbene crystal,[13] though the reaction barrier is not known yet. These results strongly support the conjecture from the experiments that there are at least two conformers for PPDSPc. The terminal styryl groups can be twisted and give two different conformers. This is quite reasonable in the following point of view: the [2,2]paracyclophane has a very rigid structure and the benzene is quite distorted due to the enforced strain energy by the side chain.[14] On the other hand, the terminal styryl group can keep the aromaticity and conjuga-

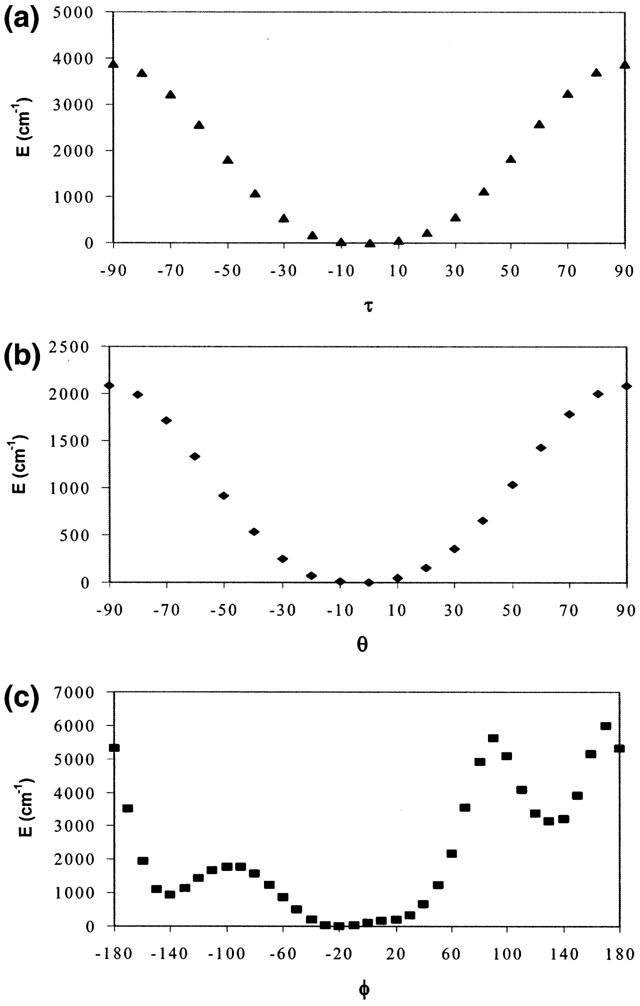

Figure 10. (a) Potential energy for the torsional angle τ of stilbene. (b) Potential energy for the torsional angle θ of PPDSPc. (c) Potential energy for the torsional angle ϕ of PPDSPc.

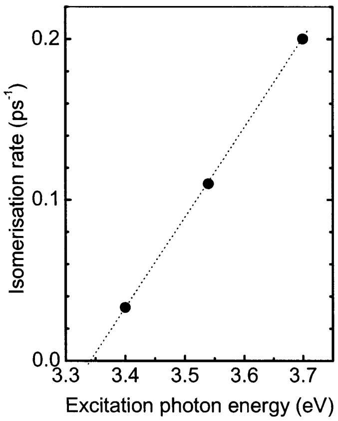

Figure 11. Dependence of isomerization rate on the excitation photon energy.

TABLE 1: Time Constants and Preexponential Factors of the Biexponential Decay Fits to the Fluorescence and Transient Absorption Kinetics. Transient Absorption Was Measured Only up to about 50 ps (Negative preexponetial factors correspond to rise components.)

probe energy (eV)	τ_1 (ps)	A_1	τ_2 (ps)	A_2	A_{long}
		Fluorescence, exc. @3.4 eV			
2.7	300 ± 20	0.05	2200 ± 100	0.95	
3.1	30 ± 5	0.20	2500 ± 100	0.80	
		Transient abs., exc. @3.54 eV			
1	0.4 ± 0.1	−0.4	9 ± 1	0.53	0.47
3.1	0.4 ± 0.1	−0.3	9 ± 0.5	0.78	0.22
		Transient abs., exc. @3.7 eV			
0.8	0.4 ± 0.1	−0.6	5 ± 0.5	0.52	0.48
	0.4 ± 0.1	0.15	5.2 ± 0.5	0.39	0.46
1.8			5.5 ± 0.5	0.70	0.30
3.2			5 ± 1	1	−0.50

tion. Hence, the single bond between the terminal styryl group and the central cyclophane does not keep the conjugation due to the broken aromaticity of the central cyclophane. This may cause different conformers along the torsional angle of ϕ.

5. Discussion

The fluorescence excitation spectra of conformer **A** at 300 K (Figure 2a) and at 77 K (Figure 3a) resemble the absorption spectra of a paracyclophane-bound distyrylbenzene dimer at room temperature[10] (referred to there as compound **2a**) and at low temperature[15] (referred to there as **1**), respectively. The absence of fluorescence narrowing with site-selective excitation of this compound was attributed to increased low-frequency Franck−Condon activity in the electronically delocalized transition.[15] This similarity of the spectra and rather short radiative lifetime of conformer **A** suggests that the electronic transition in conformer **A** is at least partially delocalized over both stilbene moieties, as calculations using a collective electronic oscillator model also indicated.[10] This implies a torsional angle $\phi \approx 0°$ in this conformer. The potential surface is very shallow around the potential minimum at ϕ close to 0° (Figure 10), giving the possibility for a number of conformers. The absorption and emission of the conformer **B** are blue-shifted with respect to **A**, and **B** is more abundant, which is consistent with the potential minimum at $\phi = -21°$ and broken conjugation between the paracyclophane core and the side styryl group. Fluorescence and fluorescence excitation spectra of **B** are very similar to the fluorescence and absorption spectra of styryl[2.2]paracyclophane (compound **7** in ref 10), supporting the implications that the conjugation in **B** extends over one of the stilbene moieties and the paracyclophane core. The higher energy conformer at $\phi = -150°$ is likely to have an optical gap similar to that at $\phi = -21°$, because both are expected to have similar conjugation. This is also supported by the absence of different emission for excitation up to 4.2 eV and the discrepancy between absorption and excitation spectra at photon energies >3.7 eV (Figure 2c) can be explained by different electronic states responsible for absorption and emission.

The 30 ps decay component seen in the region of **B** fluorescence (Figure 5a) and the partial decay of excited-state absorption on a picosecond time scale (Figure 7) can be related to the bond-twisting of the stilbene moiety in **B**, which has been retaining conjugation before excitation. The resulting isomer then would have a conjugation as the styrene−benzene dimer (like compound **5** in ref 10) and its fluorescence is weak because of excitation localization basically on the paracyclophane core.[10] The time constant for isomerization decreases from 30 to 5 ps when tuning excitation from 3.4 to 3.7 eV (Table 1), so that the isomerization rate shows a linear dependence on the excitation energy (Figure 11). This indicates that vibrational relaxation of the torsional modes is not complete on the time scale of isomerization. Our observation is consistent with the results from time-resolved infrared spectroscopy, which showed that vibrational cooling of azobenzene after photoisomerization in solution occurs on the time scale of ~20 ps.[16] For comparison, the isomerization time constant of *trans*-stilbene is much longer (in the range of 30−150 ps) and independent of excitation energy,[17] while the barrierless bond-twisting of similar molecules in solution occurs on a time scale of 0.2−5 ps.[18−21] This indicates that the barrier for the excited-state isomerization of PPDSPc is low. The 4.4 eV peak in the photoproduct absorption (Figure 8) agrees well with the absorption peak of monovinyl-[2.2]paracyclophane (compound **5** in ref 10) and the peak at 4.8 eV with that of pseudo-*p*-distyryl[2.2]paracyclophane (compound **6a**, ibid.). These compounds have absorption peaks similar to those of isomer formed by twisting of the stilbene moiety after excitation of **B** as discussed above. The sample was not checked against chemical decomposition that could bring about formation of compounds **5** and **6a**; however, it is unlikely that only conformer **B** decomposes but not **A**.

6. Conclusions

The estimated radiative lifetime of 3.3 ns for the conformer **A** is just two times longer than that of individual stilbene molecules, indicating that packing the molecules in a brick-wall structure is a plausible approach to the increase of oscillator strength in molecular aggregates. However, there are difficulties achieving the brick-wall packing of stilbene molecules and one of them is a variety of conformers, which have reduced conjugation due to twisting of arene rings around double bonds of vinyl linkages. Twisted conformers have larger optical gaps and much longer radiative lifetimes; they also tend to isomerize in the excited state. The time constant for isomerization of the twisted conformer is 5−30 ps, depending on excitation energy.

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