Ground-State Structural Disorder and Excited-State Symmetry Breaking in a Quadrupolar Molecule

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S Supporting Information

ABSTRACT: The influence of torsional disorder around the ethynyl π-bridges of a linear D−π−A−π−D molecule on the nature of its S_1 excited state was investigated using ultrafast time-resolved infrared spectroscopy. By tuning the pump wavelength throughout the $S_1 \leftarrow S_0$ absorption band, subpopulations with different extents of asymmetry could be excited. In nonpolar solvents, the equilibrated S_1 state is symmetric and quadrupolar independently of the initial degree of distortion. Photoexcitation of distorted molecules is followed by planarization and symmetrization of the S_1 state. Excited-state symmetry breaking is only observed in polar environments, where the equilibrated S_1 state has a strong dipolar character. However, neither the extent nor the rate of symmetry breaking are enhanced in an initially distorted molecule. They are only determined by the polarity and the dynamic properties of the solvent.
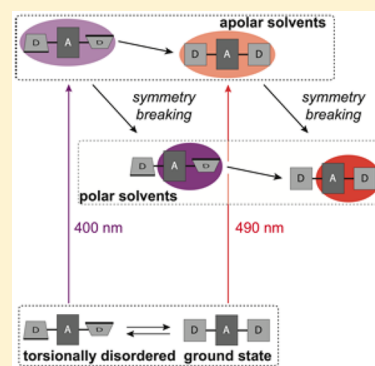
The growing interest for quadrupolar dyes with A−π−D−π−A and D−π−A−π−D motives, where D and A are electron donor and acceptor subunits, is mainly related to the quest for strong two-photon absorbers,[1−4] which are in demand for a broad variety of applications, including fluorescence imaging,[5,6] phototherapy,[7,8] or photopolymerization.[9,10] Although these molecules are centrosymmetric in the ground state, as testified by their one- and two-photon absorption spectra,[11,12] their fluorescence exhibits a pronounced solvatochromism,[13−21] similar to that observed with their single-branch D−π−A analogues. This phenomenon is explained in terms of excited-state symmetry breaking (ES-SB), i.e., by the localization of the electronic excitation on one D−π−A branch of the molecule and, thus, by a transition from a quadrupolar to a dipolar excited state.[22−24] Theoretical work by Painelli and Terenziani suggests that ES-SB is primarily triggered by antisymmetric vibrations,[22,23,25] with solvent and/or structural fluctuations leading to a subsequent stabilization of the SB state. Provided the molecule is equipped with IR marker modes localized in the D−π−A branches, ES-SB can be directly monitored using time-resolved IR (TRIR) spectroscopy.[26−29] Otherwise, ES-SB can be inferred from the decrease of the emission transition dipole moment.[30,31] Such investigations, performed with several symmetric A−π−D−π−A and D−π−A−π−D dyes, revealed that ES-SB is mainly driven by solvent fluctuations, as it takes place on the same time scale as that of solvent motion and as it does not occur in apolar solvents.[26−30] Recent investigations on platinum acetylides and ferrocene−phenyleneethynylenes pointed to the role of structural disorder in the electronic ground state as the origin of symmetry breaking in these molecules.[32,33] The change of permanent electric dipole

moment upon excitation, determined from the two-photon absorption cross section, was consistent with that calculated for molecules with a 90° twist angle of either the acetylene ligand[32] or the phenyleneethynylene chain.[33]

Whereas phenyleneethynylene oligomers exist with a relatively broad distribution of torsional angles in the ground state, their S_1 electronic excited state is more rigid because of conjugation, and thus, the amount of structural disorder is significantly smaller.[34−36] As a consequence, their $S_1 \leftarrow S_0$ absorption band is generally broad and featureless, whereas their $S_1 \rightarrow S_0$ emission band is narrower and exhibits a vibronic structure.[34−37] Additionally, the vertical S_1−S_0 transition energy varies with the torsion angle, allowing for photoselection.[38]

Here, we explore the effect on ES-SB of torsional disorder and structural asymmetry in the ground state of an organic D−π−A−π−D type molecule. Such asymmetry can be expected to result in a slightly unbalanced electronic distribution on the two A−π−D branches already in the ground state. We want to find out whether this effect could lead to ES-SB already in apolar environments or accelerate ES-SB in polar solvents. For this, we study the dye **1**, which consists of a central benzothiadiazole electron acceptor flanked by two alkoxyphenyls, acting as electron donors, linked through −C≡C− bridges,[39] as well as its single-branch dipolar analogue, **2** (Chart 1). We perform TRIR measurements on these two compounds in the −C≡C− stretching region in solvents of varying polarity (Table S1,

Chart 1. Structure of Dye 1 and of Its Single-Branch Analogue 2
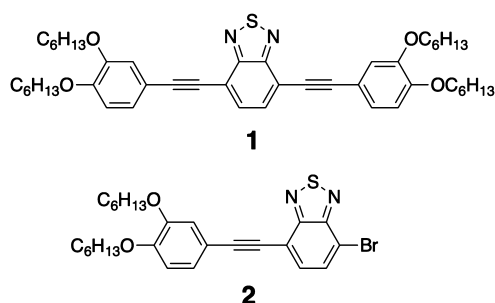
Supporting Information (SI)) using different pump wavelengths. By exciting on the red edge of the $S_1 \leftarrow S_0$ absorption band, we expect to monitor ES-SB in mostly planar dyes, whereas distorted molecules are predominantly excited at shorter wavelength. We find that no ES-SB occurs in apolar solvents, independently of whether the molecule is planar or not in the ground state. In fact, ground-state distorted molecules become more symmetric in the S_1 state upon planarization. In polar solvents, ES-SB occurs independently of the degree of the ground-state distortion, and its dynamics remain the same.

The electronic absorption and fluorescence spectra of **1** in solvents of varying polarity are depicted in Figure 1, whereas
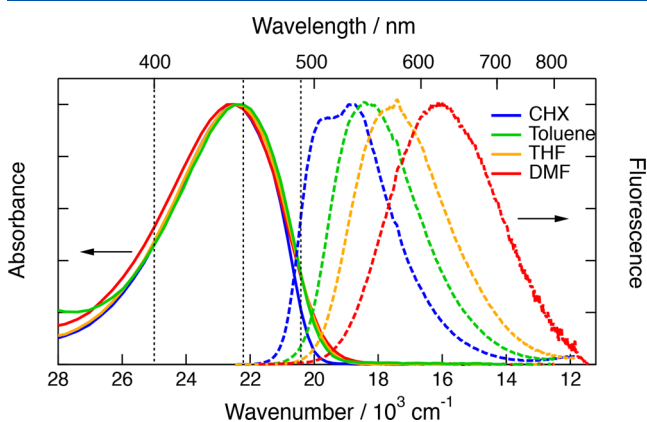

Figure 1. Electronic absorption and fluorescence spectra of **1** in various solvents. (The vertical dashed lines represent the excitation wavelengths. CHX: cyclohexane, THF: tetrahydrofuran, DMF: dimethylformamide.)

those measured with the dipolar analogue **2** are shown in Figure S1. The lack of a mirror-image relationship is evident in cyclohexane (CHX), with the absorption band significantly broader than the emission band (3900 vs 3100 cm^{-1}). The solvent dependence of the absorption spectrum is negligible, whereas fluorescence exhibits a significant solvatochromism,[39] with the band maximum downshifting by about 2700 cm^{-1} by going from CHX to DMF. This solvent dependence is almost as large as that of 3300 cm^{-1} recorded with the single-arm **2** in the same solvents and is indicative of a dipolar character of the S_1 state of **1** in polar solvents, hence, a symmetry-broken state. The shape of the S_1-S_0 absorption and emission bands and the absence of a mirror-image relationship point to a structurally disordered ground state and a more rigid excited state. This is confirmed by quantum-chemical calculations at the density functional level of theory (see SI for details), which predict a planar optimized structure of **1** in both the S_0 and the S_1 states,[39]

and a significantly lower barrier for torsion in the ground than in the excited state (Figure S2). Indeed, the dihedral angle between the D and A planes of **1** in the ground state can vary freely by ±40° at room temperature, whereas in the excited state, the potential along the torsional coordinate is steeper, and the dihedral angle is confined within ±20°. Consequently, red-edge excitation is predicted to interact with planar molecules, whereas shorter wavelengths should excite distorted molecules, which should then planarize in the S_1 state.

To monitor the excited-state dynamics of planar molecules, TRIR measurements with **1** and **2** were first performed upon red-edge excitation. Figure 2 shows TRIR spectra in the
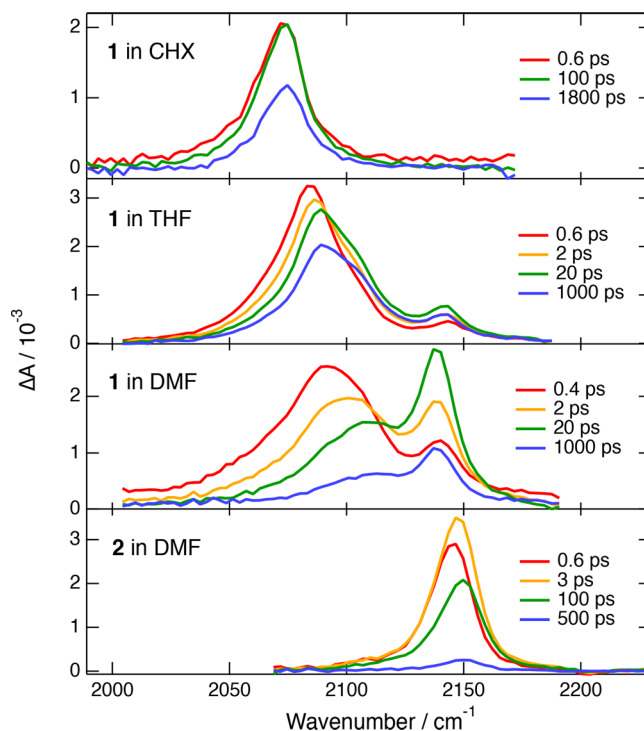

Figure 2. TRIR spectra measured after 490 nm excitation of **1** in solvents of increasing polarity and after 450 nm excitation of **2** in DMF.

−C≡C− stretching region recorded at various time delays after 490 nm excitation of **1** in solvents of increasing polarity. In CHX, the spectra are dominated by a single excited-state absorption (ESA) band around 2075 cm^{-1}. Apart from a <3 cm^{-1} upshift and slight narrowing on its low-frequency side over the first 10 ps, its shape remains essentially constant over time, and its intensity decays on the ns time scale. This band is frequency downshifted by more than 120 cm^{-1} relative to the −C≡C− stretching vibration of **1** in the ground state that can be observed as a weak negative band at about 2205 cm^{-1} (e.g., Figure S9) and in the stationary IR absorption spectrum (Figure S3). From its frequency and lifetime similar to that of fluorescence (Table S2),[39] it can be assigned to the antisymmetric −C≡C− stretching mode of **1** in the S_1 state. The presence of a single −C≡C− stretching ESA band points to an S_1 state that remains symmetric and quadrupolar during its whole lifetime.[26,27] In the medium polar THF, substantial spectral dynamics can be observed during the first 5−10 ps. The earliest spectra are dominated by an intense band at 2083 cm^{-1} (ESA1) similar to that in CHX but upshifted by about 10 cm^{-1}. Additionally, a much weaker band is visible around 2140 cm^{-1} (ESA2). Within a few ps, ESA1 upshifts by approximately 6 cm^{-1} and decreases

by ~20%, whereas the relative intensity of ESA2 increases by a factor of about 3. Afterward, the shape of the spectrum remains almost unchanged over the entire time window of the experiment. Finally, in the highly polar DMF, the earliest spectrum resembles the late spectra in THF and evolves in <5 ps to a spectrum dominated by the initially weak ESA2 with a broad shoulder around 2110 cm^{-1}. After ~10 ps, the spectral shape remains unchanged. All TRIR data were analyzed globally assuming a series of successive exponential steps with increasing time constants.[40] The resulting evolution-associated difference-absorption spectra (EADS) and time constants are depicted in Figure S4 and listed in Table S5.

By comparison, the TRIR spectra recorded with the single-branch dye **2** in DMF after 450 nm excitation exhibit a single −C≡C− stretching band located around 2148 cm^{-1}, close to the position of ESA2 measured with **1** in THF and DMF (Figure 2). The same band is observed in the TRIR spectra of **2** in CHX and THF (Figure S5). Consequently, the transient spectra recorded with **1** in DMF after ~10 ps point to an S$_1$ state with the electronic excitation almost entirely located on one A−π−D branch.[26,29] By contrast, the earliest spectrum, dominated by an ESA band like that in apolar solvents, suggests a more even distribution over both branches. Therefore, the increase of ESA2 reflects ES-SB occurring on a similar time scale as solvent motion.[41] In the medium polarity THF, ESA2 remains significantly smaller than ESA1, indicating a much less pronounced ES-SB. The presence of this band in the earliest spectra in THF and DMF suggests that inertial solvent motion suffices to introduce an initial asymmetry, which increases within a few picoseconds as solvent relaxes further by diffuse motion.

Similar TRIR measurements were carried out upon excitation at 450 and 400 nm to monitor the excited-state dynamics of structurally disordered molecules. Figure 3 shows the EADS obtained from the global analysis of the TRIR spectra recorded with **1** in CHX upon 400 nm excitation (original data in Figure
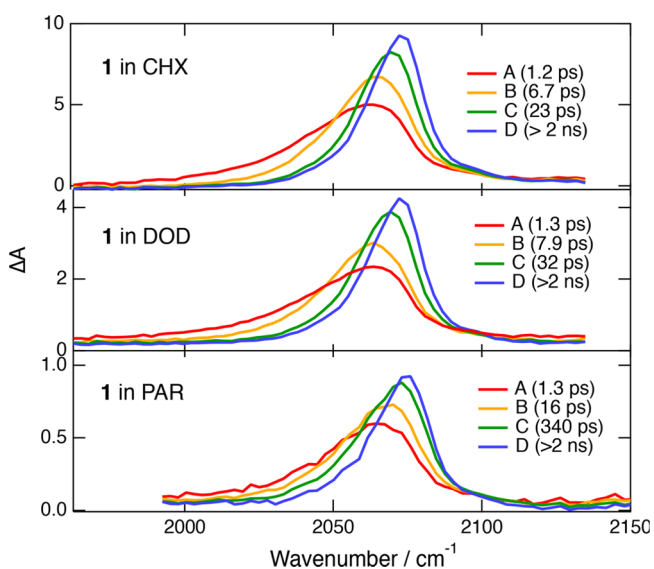
Figure 3. Evolution-associated difference-absorption spectra (EADS) and time constants obtained from a global analysis of the TRIR data measured upon 400 nm excitation of **1** in solvents of increasing viscosity, assuming a scheme with four successive exponential steps (A→B→C→D→, CHX: cyclohexane, DOD: dodecane, PAR: paraffin oil).

S6). Like for red-edge excitation, the TRIR spectra exhibit a single ESA band. However, it is initially much broader, especially on the low-frequency side. Within about 30−40 ps, it narrows, upshifts, and increases to reach the same shape and position as upon red-edge excitation. A similar effect, but of smaller amplitude, is observed after 450 nm excitation (Figure S6). In principle, short-wavelength irradiation can result in the excitation of planar molecules with the excess energy deposited in Franck−Condon active vibrational modes or in the excitation of distorted molecules with less vibrational energy. To determine whether the observed spectral dynamics originate from vibrational relaxation or reflect planarization in the S$_1$ state, TRIR measurements at different pump wavelengths were repeated in apolar solvents of increasing viscosity, namely, dodecane (DOD, η = 2.5 cP) and paraffin oil (PAR, $\eta \approx 100$ cP). The ESA band exhibits similar spectral dynamics as in CHX upon 400 and 450 nm excitation (Figures 3 and S7−S8). The early stage of these dynamics, associated mostly with the narrowing of the low-frequency side of the band, occurs on the 1−10 ps time scale independently of viscosity. On the other hand, the slower stage of the spectral dynamics, mostly associated with the frequency upshift and increase of band intensity, slows down significantly with increasing viscosity, going from ~20 ps in CHX to more than 300 ps in PAR. Previous investigations on the solvent dependence of vibrational cooling did not report on any direct influence of viscosity.[42−47] Consequently, the late, viscosity-dependent stage of the spectral dynamics can be safely assigned to structural relaxation, namely, planarization of dye **1** in the S$_1$ state. Quantum-chemical calculations predict a 5 cm^{-1} upshift of the antisymmetric −C≡C− stretching frequency of **1** in the S$_1$ state upon planarization from a dihedral angle of 40° (Table S4). On the other hand, the early, viscosity-independent dynamics can be attributed to vibrational cooling,[48,49] although an additional contribution related to the planarization of weakly distorted molecules cannot be excluded.

The viscosity-dependent dynamics upon short-wavelength but not red-edge excitation confirm that a photoselection of molecules with different amounts of torsional disorder can be achieved with **1**. These results in nonpolar solvents reveal that excitation of distorted molecules at 400 nm does not favor ES-SB. On the contrary, because of planarization, dye **1** is more symmetric in the excited than in the ground state. Independently of the excitation, its relaxed S$_1$ state is quadrupolar and symmetric, at least from the point of view of the electronic distribution.

To find out whether torsional disorder enhances or accelerates ES-SB in polar environments, TRIR measurements upon 400 nm excitation of **1** were also performed in THF and DMF (Figures S9−S10). At early time, ESA1 is significantly broader on its low-frequency side compared to 490 nm excitation (Figures S11−12). However, the relative areas of ESA1 and ESA2 do not differ significantly. The TRIR spectra corresponding to the relaxed S$_1$ state are identical at both 400 and 490 nm excitation within the limit of error (Figure 4A,B). Figure 4C,D reveals that the rise of ESA2 intensity with time, which reflects ES-SB, is independent of the excitation wavelength in both THF and DMF. One can thus conclude that torsional disorder neither enhances nor accelerates ES-SB in **1** in polar environments.

In summary, our results reveal that, although a significant fraction of the ground-state population of **1** is nonsymmetric, the whole relaxed S$_1$-state population is symmetric and quadrupolar
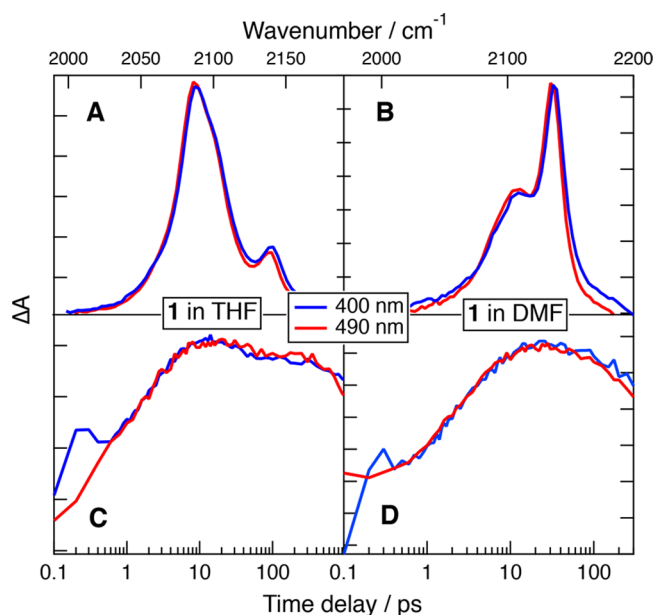
Figure 4. (A,B) Comparison of TRIR spectra at long time delay (>100 ps) and (C,D) of the temporal evolutions of the intensity at the maximum of ESA2 measured with **1** upon 400 and 490 nm excitation in polar solvents.

in nonpolar environments. This "symmetry building" is due to the steepness of the excited-state potential along the torsional coordinate, which favors planarization. Because of this, any effect due to structural disorder in ground-state asymmetry is suppressed. A polar environment is clearly required for ES-SB to take place. Starting from a distorted structure does not increase the extent of ES-SB nor make it faster. The amount of ES-SB is only determined by the polarity of the solvent, whereas the ES-SB dynamics are controlled by solvent motion. Similar behavior can be expected for other organic A−π−D−π−A and D−π−A−π−D molecules with ethynyl or phenylethynyl π-bridges. These results provide strong evidence of the critical role of the environment and of a minor effect of structural distortions on the excited-state symmetry breaking in this type of molecules at least.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b01024.

Experimental details, quantum-chemical calculations, stationary electronic and IR spectra, additional TRIR spectra and results from data analysis (PDF). All the data can be downloaded from http://doi.org/10.5281/zenodo.2635474.

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Notes

The authors declare no competing financial interest.

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