Specific Monitoring of Excited-State Symmetry Breaking by Femtosecond Broadband Fluorescence Upconversion Spectroscopy

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Supporting Information

ABSTRACT: Most quadrupolar molecules designed for large two-photon absorption cross section have been shown to undergo symmetry breaking upon excitation to the $S_1$ state. This was originally deduced from their strong fluorescence solvatochromism and later visualized in real time using transient infrared spectroscopy. For molecules not containing clear IR marker modes, however, a specific real-time observation of the symmetry breaking process remains lacking. Here we show that this process can be resolved using broadband fluorescence upconversion spectroscopy by monitoring the instantaneous emission transition dipole moment. This approach is illustrated with measurements performed on two quadrupolar molecules, with only one of them undergoing excited-state symmetry breaking in polar solvents.

Molecules that have a large two-photon absorption cross section, $\sigma^{(2)}$, are of interest for a variety of applications that include bioimaging, photopolymerization, photodynamic therapy, and data storage.1–13 Large $\sigma^{(2)}$ values are associated with large changes of electric quadrupolar or octupolar moments upon excitation,14–16 and thus most chromophores with large $\sigma^{(2)}$ values synthesized to date contain several electron donor and acceptor (D and A, respectively) units arranged in conjugated chromophores of DA$_n$ or AD$_n$ type (where $n$ generally equals 2 or 3). The electronic ground state of these molecules is well understood due to a range of investigations that have successfully related their multipolar character, symmetry, one-photon absorption spectra and their $\sigma^{(2)}$ cross sections.17–23 For a long time, their excited states presented considerable confusion: Whereas the electronic absorption spectra of DA$_n$ and AD$_n$ molecules usually present little solvent dependence, to be anticipated for purely quadrupolar or octupolar electronic states, the fluorescence spectra display a strong solvatochromism reminiscent of a dipolar $S_1$ state.18–20,24,25 This phenomenon was rationalized using an essential-state model in which structural or solvent fluctuations break the symmetry of the excited state.26–28 A real-time observation of this symmetry breaking was lacking until recently because transient electronic absorption spectroscopy does not provide a clear spectroscopic signature of this process.29,30 However, clear real-time observation of the symmetry breaking was achieved using time-resolved IR spectroscopy to monitor specific vibrational modes located in the two branches of quadrupolar molecules.31–34 These investigations revealed that, for these molecules at least, symmetry breaking is driven by the environment, more specifically by differences in the instantaneous orientation of the solvent molecules around the two arms of the molecule and that their symmetry-breaking dynamics occur on similar time scales as those of solvent motion. The asymmetry of the instantaneous solvent orientation also plays a key role in photoinduced symmetry-breaking charge-separation processes between two identical molecules.35–41 Here, however, symmetry breaking can be easily identified by the presence of absorption bands of the resulting anionic and cationic species.

However, for quadrupolar molecules without specific IR markers, a real-time observation of symmetry breaking remains lacking. Kim et al. applied broadband fluorescence upconversion spectroscopy (FLUPS)42,43 to track the peak position of the emission spectrum.44 However, the time-dependent shift of the emission band also reports on solvent relaxation.45

Chart 1. Structures of the Two DAD Molecules Investigated

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DOI: 10.1021/acs.jpclett.7b02754
quadrupolar states are also stabilized by dipolar solvation, it is not clear whether the shift of the emission band due to solvent relaxation around the quadrupolar excited state can be unambiguously distinguished from that due to symmetry breaking from a quadrupolar to a dipolar excited state. Because both processes may occur on similar time scales, it is, in principle, not possible to distinguish between where the solvation of the quadrupole ends and the symmetry-breaking process begins, meaning that the tracking of the peak position is not specific to the observation of symmetry breaking in real-time.

Here we propose a different approach, also based on FLUPS, to visualize excited-state symmetry breaking in quadrupolar molecules. Instead of tracking the temporal evolution of the S1 → S0 transition energy, we look at how the size of the S1 → S0 transition dipole moment, μem = |μem|, changes with time. The one-photon and two-photon absorption spectra of DA, or AD, molecules can be qualitatively well explained in terms of an excitonic model, where each DA branch is a chromophoric unit with a local transition dipole, μDA. In the case of a linear two-branch molecule, the transition to the lowest singlet excitonic state is one-photon allowed, but two-photon forbidden, and the size of its dipole moment, μDA, is approximately $\sqrt{2}\mu_{DA}$. Similarly, the transition to the S2 state is one photon forbidden but two-photon allowed. According to this model, the dipole moment for the S1 → S0 emission should be equal to μDA as long as the S1 state remains symmetric and the excitation is equally distributed over the two branches of the molecule. However, in the case of a complete symmetry breaking with the excitation entirely localized on one branch, the emission transition dipole should be reduced to μem ≈ μDA/√2. Therefore, time resolving μem can be anticipated to be a viable approach for monitoring symmetry breaking in real time.

To test this idea, we have measured the time dependence of the emission transition dipole moment of two molecules, 1 and 2 (Chart 1), using FLUPS. These molecules were developed for applications in two-photon induced polymerization and are composed of a central thiophene core flanked by two triphenylamines with either methoxy (1) or fluorine (2) substituents, conferring to the end-cap units a very different electron-donating strength. As a consequence, 1 is expected to have much stronger DAD character than 2 and thus excited-state symmetry breaking is only expected for 1.

Although these two molecules are not strictly linear, the relative intensities of their S1 ← S0 and S2 ← S0 bands in the one- and two-photon absorption spectra are fully consistent with those expected for linear quadrupolar molecules according to the excitonic model (Figure S6). The solvent dependence of their stationary absorption and emission spectra is shown in Figure 1a,b. Whereas the S1 ← S0 absorption band is broad and structureless in all solvents, the fluorescence band in nonpolar solvents is far from mirror image and exhibits a distinct vibrational progression. Such an absence of mirror-image relationship is typical of conjugated polyaryl molecules and can be explained by the strong increase in the barrier for torsion around the single bonds between the aryl subunits upon excitation. Consequently, the large width of the absorption band arises from torsional disorder in the ground state, whereas the structured fluorescence band in nonpolar solvents is far from mirror image and exhibits a distinct vibrational progression. Such an absence of mirror-image relationship is typical of conjugated polyaryl molecules and can be explained by the strong increase in the barrier for torsion around the single bonds between the aryl subunits upon excitation.
However, this difference in the most polar solvents, indicative of symmetry breaking. For details), and their ratio $\mu_{\text{em}}/\mu_{\text{abs}}$ is plotted versus the shift of the fluorescence band maximum relative to hexane, $\Delta \nu_{2}$ and $\Delta f$ in Figure 1c,d. Whereas this ratio remains between 0.9 and 1.1 for 2 in all solvents investigated, it is markedly smaller for 1 in the most polar solvents, indicative of symmetry breaking. However, this difference between 1 and 2 is not much greater than the error on $\mu_{\text{em}}/\mu_{\text{abs}}$ (±0.1). This error arises mostly from the difficulty to determine the absorption coefficient accurately when a limited amount of compound is available.52

These problems can be largely avoided by determining the temporal evolution of $\mu_{\text{em}}$. Figure 2 shows FLUPS spectra recorded at different time delays after excitation of 1 in cyclohexane and DMSO as well as of 2 in DMSO. Both molecules exhibit very similar fluorescence dynamics in cyclohexane: during the first 20 ps, the emission band narrows and shifts to lower frequencies and its vibrational structure develops (Figure 2a and Figure S14). These changes are assigned to the planarization of the molecules in the $S_1$ state.49–51 Afterward, the spectral shape remains unchanged and the amplitude decays exponentially to zero on the 500 ps time scale, in good agreement with the fluorescence lifetime, $\tau_F$, determined by time-correlated single photon counting (TCSPC, Table S1).

The time evolution of $\mu_{\text{em}}$ was determined by first dividing the FLUPS signal by $e^{-t/\tau_F}$ to correct for the population decay and by $\tilde{\nu}$, where $\tilde{\nu}$ is the wavenumber,46 and second by calculating the square-rooted area of the resulting spectra (see the SI for details).

Figure 3 indicates that the time evolution of $\mu_{\text{em}}$ in cyclohexane is the same for both molecules and consists of an initial increase by ~5% during the first 20 ps to a value that remains constant within the entire 0 to 1 ns time window of the experiment. This rise coincides with the initial spectral dynamics attributed to planarization and is interpreted as arising from the same process. This corroborates with quantum-chemical calculations that predict an increase in the transition dipole moment upon decreasing the dihedral angle between the central thiophene and an adjacent phenyl unit (Figures S28 and S29).

In DMSO, the fluorescence spectrum of 2 exhibits a ~1000 cm$^{-1}$ frequency downshift together with changes in the vibrational envelope during the first 10–15 ps after excitation. This is followed by an exponential decay on the 1 ns time scale, in agreement with the TCSPC fluorescence lifetime (Figure 2c). The initial spectral dynamics can be ascribed to both planarization and solvent relaxation. The time dependence of $\mu_{\text{em}}$ shows the initial rise assigned to planarization and then remains constant (Figure 3). By contrast, the fluorescence spectrum of 1 undergoes a significantly larger frequency shift of the fluorescence spectrum of 1 is marked to steady state value at long times. Note the change of linear axis at 100 ps.

**Figure 2.** Transient emission spectra recorded at different time delays after excitation of 1 in (a) cyclohexane and (b) DMSO and (c) 2 in DMSO.

**Figure 3.** Time dependence of $\mu_{\text{em}}$ of (a) 1 in cyclohexane, propanol (PrOH), THF, and DMSO and (b) 2 in cyclohexane and DMSO. All traces are normalized to steady state value at long times. Note the change of linear axis at 100 ps.

Condon $S_1$ state. The absorption maximum shows a good correlation with the function $f(n^2) = 2(n^2 - 1)/(2n^2 + 1)$, where $n$ is the refractive index, indicating that the absorption solvatochromism is dominated by dispersion interactions (Figure S2). By contrast, the fluorescence solvatochromism is much more pronounced. Whereas a plot of the emission maximum of 2 versus the polarity function $\Delta f = 2(\epsilon - 1)/(2\epsilon + 1) - f(n^2)$, where $\epsilon$ is the static dielectric constant, is approximately linear, that for 1 shows a slope that increases with $\Delta f$ (Figure S3). This can be explained by an increasing permanent dipole moment of the $S_1$ state with solvent polarity, suggesting a breaking of the symmetry of the $S_1$ state of 1 but not 2 in polar solvents.

Both $\mu_{\text{em}}$ and $\mu_{\text{abs}}$ were calculated from these spectra (see SI for details), and their ratio $\mu_{\text{em}}/\mu_{\text{abs}}$ is plotted versus the shift of the fluorescence band maximum relative to hexane, $\Delta \nu_{2}$ and $\Delta f$ in Figure 1c,d. Whereas this ratio remains between 0.9 and 1.1 for 2 in all solvents investigated, it is markedly smaller for 1 in the most polar solvents, indicative of symmetry breaking. However, this difference between 1 and 2 is not much greater than the error on $\mu_{\text{em}}/\mu_{\text{abs}}$ (±0.1). This error arises mostly from the difficulty to determine the absorption coefficient accurately when a limited amount of compound is available.52

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downshift, \( \sim 1500 \text{ cm}^{-1} \), and a fast partial decrease in intensity before decaying with the 2.47 ns lifetime recorded by TCSPC (Figure 2b). Figure 3 reveals that this initial decrease in intensity is associated with a \( \sim 10\% \) reduction of \( \mu_{\text{em}} \). This decay of \( \mu_{\text{em}} \) can be reproduced with a biexponential function with 4.3 and 38 ps components of similar amplitude. This decrease in the transition dipole moment can be assigned to a change of the nature of the emitting state and hence to symmetry breaking. The fast decay component most probably reflects symmetry breaking brought about by solvation, in agreement with previous reports using time-resolved IR spectroscopy.\(^{31-34}\) However, the 38 ps component exceeds by far the time scale of solvent motion\(^{45}\) and could originate from structural relaxation occurring upon partial localization of the excitation on one branch, that is, upon redistribution of the electronic density on the two donor subunits. This slower process appears not only as a partial intensity decay of the emission band but also as a small, \( \sim 1000 \text{ cm}^{-1} \), red shift. Symmetry breaking of 1 in polar solvents is further confirmed by similar measurements in PrOH, where \( \mu_{\text{em}} \) also decays but only by \( \sim 5\% \). This weaker decrease of \( \mu_{\text{em}} \) can be explained by a smaller extent of symmetry breaking of the excited state due to the lower polarity of this solvent. In the less polar THF, the solvent reaction field is apparently too weak for symmetry breaking to take place because no significant decrease in \( \mu_{\text{em}} \) is observed.

These results confirm that the temporal variation of \( \mu_{\text{em}} \) offers direct access to the symmetry breaking dynamics of the excited state and is a valuable alternative to time-resolved IR spectroscopy, especially for molecules such as those investigated here that do not contain vibrational markers localized on the two DA branches. Moreover, the amplitude of this change of \( \mu_{\text{em}} \) reflects the extent of symmetry breaking. Because planarization of 1 and 2 should give approximately the same \( \sim 5\% \) increase in transition dipole in all solvents, the actual decrease in \( \mu_{\text{em}} \) upon symmetry breaking of 1 in DMSO should be \( \sim 15\% \). This value indicates that here symmetry breaking does not lead to a full localization of the excitation on one DA branch. If this were the case, then \( \mu_{\text{em}} \) should decrease by \( \sim 40\% \) according to quantum-chemical calculations of 1 and of its single-branch analogue (see SI for details) and by 30\% according to the above-mentioned excitonic model.

We now consider whether symmetry breaking can be directly inferred from the dynamic Stokes shift of the fluorescence band. Figure 4 compares the changes of \( \mu_{\text{em}} \) and of the peak position measured after excitation of 1 and 2 in various solvents. If the dynamic Stokes shift were a measure of the symmetry-breaking process, then the decrease in \( \mu_{\text{em}} \) should be well-correlated with the change of peak position. As is shown by Figure 4, this is evidently not the case. For 2 in DMSO, there is a \( \sim 1000 \text{ cm}^{-1} \) shift of the emission band but no change of \( \mu_{\text{em}} \). Equally, the \( \sim 800 \text{ cm}^{-1} \) band shift of 1 in THF is not accompanied by a significant variation of \( \mu_{\text{em}} \) apart from that associated with planarization. The latter process leads to an increase in \( \mu_{\text{em}} \) with frequency downshift, as better seen in cyclohexane. For 1 in DMSO, \( \mu_{\text{em}} \) decreases in parallel with the frequency downshift of the emission. However, in PrOH, \( \mu_{\text{em}} \) remains constant during an initial \( \sim 600 \text{ cm}^{-1} \) band shift and only decreases during a further \( \sim 400 \text{ cm}^{-1} \) shift.

Although the Stokes shift is the largest when symmetry breaking takes place, it does not only reflect this process. This confirms our initial argument that the fluorescence shift does not allow one to distinguish between where quadrupolar solvation ends and symmetry breaking begins.

In conclusion, we could show that the instantaneous \( \mu_{\text{em}} \) is a sensitive reporter of symmetry breaking in the excited state and that this process can be specifically monitored in real time using broadband fluorescence upconversion spectroscopy. Additionally, our results reveal that the temporal shift of the fluorescence band cannot be used as a specific reporter on symmetry breaking and that its magnitude is not a well-suited guide for judging in which solvents symmetry breaking occurs. Such information can, in principle, be deduced from the \( \mu_{\text{em}}/\mu_{\text{abs}} \) ratio. However, the error on the absolute magnitude of \( \mu_{\text{abs}} \) is usually large when having limited amount of compound, and thus monitoring its temporal change of \( \mu_{\text{em}} \) is by far more reliable.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b02754.

Description of the experimental procedures. Lineshape analysis of the steady-state spectra and transition dipole moment calculations. Comparison of one- and two-photon absorption spectra. Details of FLUPS data analysis. Additional FLUPS data. Quantum-chemical calculations. (PDF)

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ACKNOWLEDGMENTS

We thank the Fonds National Suisse de la Recherche Scientifique (project no. 200020-165890) as well as the University of Geneva for financial support.

REFERENCES