ARTICLE

Solvent-Induced Symmetry-Breaking Charge Transfer in an Octupolar Triphenylamine Derivative Resolved with Transient Fluorescence Spectroscopy†

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The excited-state symmetry-breaking charge transfer (SBCT) dynamics in quadrupolar or octupolar molecules without clear infrared markers is usually hard to be tracked directly. In this work, on the basis of the evolution of instantaneous emission dipole moment obtained by femtosecond transient fluorescence spectroscopy, we presented a real-time characterization of the solvent-induced SBCT dynamics in an octupolar triphenylamine derivative. While the emission dipole moment of the octupolar trimer in weakly polar toluene changes little during the excited-state relaxation, it exhibits a fast reduction in a few picoseconds in strongly polar tetrahydrofuran. In comparison with the fluorescence dynamics of dipolar monomer, we deduced that the emitting state of the octupolar trimer in strongly polar solvent, which undergoes solvent-induced structural fluctuation, changes from exciton-coupled octupolar to excitation localized dipolar symmetry. In weakly polar solvent, the octupolar symmetry of the trimer is largely preserved during the solvation stabilization.

Key words: Symmetry breaking charge transfer, Solvent effect, Transient fluorescence spectroscopy, Emission dipole moment

I. INTRODUCTION

Excited-state intramolecular charge transfer (ICT) is a fundamental photophysical process in organic molecules which has directly linked or π-bridge linked electron donor (D) and electron acceptor (A) units [1, 2]. The ICT property has been proven to have a significant effect on the nonlinear optical (NLO) properties such as two-photon absorption (TPA) cross section [3, 4]. In decades, intense research efforts focus on developments in synthesis, mechanism, and application of new materials with high NLO and TPA performance [5–11].

Upon the photoexcitation of a dipolar D-A molecule, a considerable increase of electric dipole moment usually occurs in excited states. Thus, the ICT process of a dipolar molecule is highly influenced by the polarity of surrounding environment, which can be reflected by solvatochromism phenomena or changes in radiative and non-radiative rates [12, 13]. The ICT process also takes place in some molecules with specific structural symmetry, such as D-A-D-type or A-D-A-type quadrupolar, D-A3-type or A-D3-type octupolar molecules [14–18]. There is a longstanding confusion that whereas the ground-state electronic absorption spectra of quadrupolar or octupolar molecules barely exhibit solvent-polarity dependency, the emission spectra usually present a strong solvatochromism which is the spectral character of dipolar emissive S1 state, indicative of the electronic excitation asymmetrically localized on one of these arms. Researchers introduce the concept of solvent-induced symmetry breaking charge transfer (SBCT) to rationalize the reduction of structural symmetry in the relaxed S1 state [17, 19–34]. The SBCT was suggested in theory to be induced by the structural fluctuation in excited states and/or the surrounding solvent reaction field [27, 32].

A direct characterization of symmetry breaking in real time, which is a kind of excited-state structural dynamics, can be achieved by ultrafast time-resolved infrared spectroscopy [26, 30, 31]. However, for molecules lacking ideal infrared marker modes, it is hard to implement the spectral tracking of special vibrational modes from branches of symmetry molecules. Time-resolved electronic spectroscopy, such as transient absorption spectroscopy, is adept to track the electronic state evolution during SBCT, while it does not provide a direct spectroscopic signature of structural dynamics [33, 35, 36]. Recently, Vauthey and Kim et al. proposed an approach to directly tracking the SBCT in quadrupolar...
lar molecules by monitoring the instantaneous emission transition dipole moment based on transient fluorescence spectroscopy. However, an experimentally real-time tracking of the SBCT in octupolar molecules is still lacked at present, and many debates remain in this structural dynamics, especially the time scale and the solvent-polarity-dependency [17].

Our primary concern in this work is to track the ultrafast solvent-induced symmetry breaking in the target octupolar trimer molecule. The molecular structures of the target trimer and the monomer which is used as a reference are shown in FIG. 1. The trimer, named as 4-((E)-2-(benzo[1,2,5]thiadiazol-4-yl)vinyl)-N,N-bis(4-((E)-2-(benzo[1,2,5]thiadiazol-7-yl)vinyl)phenyl)benzenamine, is a star-shaped organic molecule containing a triphenylamine unit as an electron donor and benzo[1,2,5]thiadiazole vinylene as electron acceptors. The trimer has been proven as a promising solution-processable organic photovoltaic material [37, 38]. Different from conventional dipolar molecules as the monomer, the octupolar trimer that connects three ICT moieties has a high structural symmetry. Thus trimer is a suitable prototype to investigate the solvent-induced SBCT phenomenon. The solvent-dependent ICT delocalization/localization and structural dynamics in quadrupolar and octupolar chromophores have been deeply investigated by femtosecond transient absorption spectroscopy, while the transient absorption spectra do not provide direct evidence of the SBCT dynamics [15, 23, 39–43].

In the proposed study, the basic photophysical properties of monomer and trimer were obtained in different solvents with different polarities. Toluene and tetrahydrofuran (THF), which have different solvation strengths but similar solvation response time of a few picoseconds, are selected to provide weakly polar and strongly polar solvent environments, respectively [44, 45]. By using the femtosecond transient fluorescence spectroscopy, the solvent-dependent SBCT of trimer is directly tracked in real time.

II. EXPERIMENTS

A. Materials

The synthesis and characterization of monomer and trimer have been reported elsewhere in detail [37]. All solvents including toluene and tetrahydrofuran (THF) used in this work were analytic reagent grade and used as received.

B. Steady-state spectral measurements

Steady-state absorption spectra were measured on a UV-Vis spectrometer (U-3010, Hitachi, Japan). Steady-state fluorescence spectra were measured on a fluorescence spectrophotometer (F-4600, Hitachi, Japan). The fluorescence quantum yields of these compounds in solutions were determined by a comparative method, and the fluorescein was used as standard (0.90).

C. Transient fluorescence spectral measurements

Femtosecond time-resolved transient fluorescence spectra were measured on a femtosecond fluorescence up-conversion spectrometer (FluoMax-MP, IB Photonics). The system was pumped by a regeneratively-amplified femtosecond Ti:sapphire laser (Legend Elite, Coherent) centered at 800 nm at a repetition rate of 1000 Hz. Pulse duration was ~50 fs, with a bandwidth of ~30 nm, and an energy of ~1.0 mJ. The light beam was frequency-doubled in a BBO (type I) crystal and a dichroic mirror was used to separate the fundamental from the doubled beam (400 nm) sent for the fluorescence excitation. The remained fundamental light was time-delayed and used to gate the emission of the sample that flew in a 1-mm quartz cell. The collected fluorescence was focused onto a BBO crystal (type I) using reflective optics. The gating pulse was also focused onto the crystal overlapping with the fluorescence. The included angle between the excitation and gating beam polarization was set to the magic angle (54.7°). The up-converted signal was filtered and detected with a photomultiplier tube. The instrument response function of the system measured by gating the Raman signal from solvent was ~300 fs.

Fluorescence lifetimes were also measured on a time-correlated single photon counting (TCSPC) spectrometer (F900, Edinburgh Instruments), excited by a picosecond LED source (PLS-500, PicoQuant) at 450 nm with the FWHM of 400 ps. All experiments were done at (293±1) K.

III. RESULTS AND DISCUSSION

A. Steady-state spectra

Steady-state absorption and fluorescence spectra of monomer and trimer were measured to obtain their basic photophysical properties in two selected solvents

FIG. 1 Molecular structures of monomer and trimer.
TABLE I Photophysical properties of monomer and trimer in toluene and THF.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Monomer</th>
<th>Trimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>Monomer</td>
<td>Trimer</td>
</tr>
<tr>
<td>Lifetime/ns</td>
<td>5.7</td>
<td>6.1</td>
</tr>
<tr>
<td>QYD</td>
<td>0.42</td>
<td>0.26</td>
</tr>
<tr>
<td>$k_r/(10^7 s^{-1})$</td>
<td>7.3</td>
<td>4.3</td>
</tr>
<tr>
<td>$k_{nr}/(10^8 s^{-1})$</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>$\mu_{em}$ in FC/D</td>
<td>6.1</td>
<td>6.9</td>
</tr>
<tr>
<td>$\mu_{em}$ in relaxed $S_1$/D</td>
<td>4.3</td>
<td>3.9</td>
</tr>
</tbody>
</table>

$^a$ $\mu_{em}$ in the FC state is calculated from the transient fluorescence spectra, and $\mu_{em}$ (0.2 ps) was approximately set as $\mu_{em}$ in FC.

FIG. 2 Normalized absorption and emission spectra of monomer and trimer in toluene and THF.

with different polarities, toluene (dielectric constant $\varepsilon=2.38$, refractive index $n=1.497$) and THF ($\varepsilon=7.58$, $n=1.404$) [45]. As shown in FIG. 2, the lineshapes of absorption spectra of monomer and trimer are nearly identical in these two solvents. The absorption band around 450 nm is attributed to the intramolecular charge transfer (ICT) transition, while the absorption below 380 nm is attributed to the locally-excited (LE) transition [39, 46]. The red-shifted ICT state absorption in trimer, in comparison with that of monomer, indicates a higher conjugation between the electron acceptor branches which gives rise to charge delocalization in the ground state.

Fluorescence bands of both monomer and trimer shift bathochromically from the weakly polar toluene to the strongly polar THF. The significant increase of the Stokes shifts with the increasing solvent polarity indicates a solvent-induced structural reorganization from the Franck-Condon (FC) state to the relaxed $S_1$ state [41]. The feature of solvent-polarity-dependent fluorescence exists in both monomer and trimer. That is, the trimer with a symmetry structure exhibits more dipolar character in the relaxed $S_1$ state, which may correspond to a symmetry broken dipolar state.

Fluorescence lifetime of monomer and trimer in the two solvent was measured using the TCSPC technique with a time-resolution of 400 ps. As shown in Table I, monomer and trimer both exhibit a fluorescence lifetime of 4–6 ps. In combination with the measured fluorescence quantum yield (QYD), the radiative and non-radiative rate constants were calculated. From weakly polar toluene to strongly polar THF, the non-radiative rate constants ($k_{nr}$) grow significantly for both the dipolar monomer and the symmetric trimer. This fact, which is the characteristic of dipole-dipole interaction in solvent effect, also indicates that the fluorescence of trimer in THF arises from a symmetry broken CT state. The radiative rate constant ($k_r$) of trimer reduces 60% from that in toluene ($k_r=9.4\times10^7$ s$^{-1}$) to THF ($k_r=3.8\times10^7$ s$^{-1}$). It implies that trimer in THF, under the effect of intense solvent reaction field of the strongly polar solvent, readjusts its geometry in the relaxed $S_1$ state, resulting in a significant decrease in the radiative rate which is closely associated with the emission dipole moment.

B. Steady-state emission dipole moments

The steady-state emission dipole moments of monomer and trimer in the two solvents were calculated to determine the nature of the relaxed $S_1$ state. The emission dipole moment ($\mu_{em}$) is calculated following Eq.(1) [28, 29, 47],

$$\mu_{em} = 1.7857 \times 10^3 \left( \frac{1}{n^3} \right) \left( \frac{1}{f(n) \bar{\nu}_f^3} \right)^{1/2}$$

where $k_r$ is the radiative rate constant in s$^{-1}$, $n$ is the refractive index of the solvent. $f(n)$ is an effective cavity factor represented as Eq.(2),

$$f(n) = \frac{9n^2}{(2n^2 + 1)^2}$$

and $\bar{\nu}_f^3$ denotes the cube of the emission frequency following Eq.(3),

$$\bar{\nu}_f^3 = \frac{\int F(\nu) \nu^3 d\nu}{\int F(\nu) d\nu}$$

where $\nu$ is the wavenumber and $F(\nu)$ denotes the fluorescence spectrum after the correction of the instrument spectral response.
The obtained steady-state emission dipole moment represents as $\mu_{\text{em}}(S)$ in relaxed $S_1$ (D). The time-dependent instantaneous emission dipole moment is calculated following Eq. (4),

$$\mu_{\text{em}}(t) = \mu_{\text{em}}(S) \cdot \sqrt{\frac{\int_{v_2}^{v_1} F_\tau(t) \, dv}{\int_{v_2}^{v_1} F_\tau(t>200 \, \text{ps}) \, dv}}$$  

(4)

where $F_\tau(t)$ is the corrected fluorescence intensity for population decay following Eq. (5),

$$F_\tau(t) = \frac{F(t)}{\exp(-t/\tau)}$$  

(5)

Considering the timescale of dynamical processes of compounds in this work, including solvation dynamics, SBCT, and structural relaxation, 200 ps is an adequate time to use $F_\tau(t>200 \, \text{ps})$ as a normalization factor.

The magnitudes of the emission dipole moments in relaxed $S_1$ state of monomer are 4.3 D in toluene and 3.9 D in THF as shown in Table I. As a dipolar chromophore, the relaxed $S_1$ state of monomer displays little difference in solvents with different polarities. However, the emission dipole moments of trimer are calculated to 5.6 D in toluene and 3.7 D in THF. The remarkably reduced emission dipole moment in polar THF suggests that the origin of the emitting state has changed. These facts all support that the lowest emitting state of trimer is a solvent-induced symmetry-broken charge transfer state. Nevertheless, emission dipole moments derived from steady-state spectral parameters cannot describe the dynamics of structural relaxation.

C. Transient fluorescence spectra

To obtain a time-resolved spectral insight into the ultrafast solvent-induced symmetry breaking process, we conducted transient fluorescence spectral measurements of monomer and trimer in toluene and THF. The range of time detecting is from sub-picosecond to 1.5 ns. The transient fluorescence spectra of monomer and trimer in toluene and THF up to 100 ps are shown in FIG. 3.

Transient fluorescence spectra of both monomer and trimer show rapid spectral evolution in toluene and THF. In the initial 20 ps, the fluorescence band shows an obvious shifting to the low frequencies, accompanied by a decay of peak area. Afterwards, the spectral shape remains unchanged and the amplitude decays exponentially to zero on the 4–6 ns timescale, matching well with the fluorescence lifetime measured by TCSPC (Table I). For quantifying the spectral evolution, the total fluorescence intensity kinetics and peak position kinetics of monomer and trimer were analyzed within 40 ps as shown in FIG. 4(a, b) and Table II.
As shown in FIG. 4(a), from toluene to THF, the total fluorescence intensity kinetics of trimer shows more significant change than that of monomer. For trimer in toluene, the total fluorescence intensity loses 22% of its magnitude in the initial 20 ps, less than that of monomer in toluene. This is attributed to the preserved structural symmetry of trimer in toluene that weakens the solvation-induced energy dissipation. However, in more polar THF, both monomer and trimer lose more than 50% of their magnitude in the initial 20 ps. It suggests that trimer loses its structural symmetry and the S\textsubscript{1} state of trimer undergoing electron localization relaxes to a dipolar state, which shows more significant dipole-dipole interaction in the solvation process. The fluorescence spectrum of trimer in THF exhibits a ~1800 cm\textsuperscript{-1} frequency downshift together with the reduction in fluorescence intensity. By contrast, the frequency downshift is much less for trimer in toluene (~1200 cm\textsuperscript{-1}), whose emission state is regarded as a symmetry-preserved state.
D. Instantaneous emission dipole moments

Vauthey et al. have proven that the dynamic Stokes shift of the fluorescence band does not directly reflect the symmetry breaking [29]. The instantaneous $\mu_{em}$, which can be calculated from transient fluorescence spectra, is a sensitive indicator of excited-state symmetry breaking. FIG. 4(c, d) shows the absolute and normalized instantaneous emission dipole moment $\mu_{em}$ of monomer and trimer in toluene and THF calculated from the transient fluorescence spectra, respectively. Through the kinetics of instantaneous emission dipole moment, the emission dipole moment in the FC state can be calculated which reflects the emission properties of the initially formed exciton coupled state. For trimer in toluene and THF, the $\mu_{em}$ in the FC state are calculated to 6.9 D and 5.9 D, respectively, which change slightly with the increasing solvent polarities. Consequently, we can infer that the exciton-coupled state of trimer in polar THF, which is induced by the FC excitation, preserves the structural symmetry as that of its ground state. The $\mu_{em}$ of trimer in THF loses 38% of its magnitude as it approaches 3.9 D during the following 10 ps, while the $\mu_{em}$ of trimer in toluene only loses 18%.

Normalized $\mu_{em}$ kinetic traces (shown in FIG. 4(d)) provide a visual comparison of the structural evolution trend of monomer and trimer in toluene and THF. The time constants of emission dipole moment change ($\tau_{em-dipole}$) are fitted as listed in Table II. The time constants of fluorescence peak shifting ($\tau_{peak-shift}$) are also fitted for reference. In comparison with monomer, the trimer in toluene exhibits a smaller change of $\mu_{em}$ in amplitude. Considering that there is no specific solute-solvent interaction between two compounds and selected solvents, the solvent reorganization dynamics obtained by transient fluorescence spectra reflects not only the solvation response on narrow sense but also the charge transfer characteristics and structural relaxation of solute molecules in excited states [12, 13, 41]. It is obvious that trimer has a smaller electric dipole moment in $S_1$ than that of monomer without considering the symmetry-breaking-induced excited electronic localization. Thus, the kinetics of instantaneous emission dipole moment indicates that trimer in toluene preserves its structural symmetry with slow solvent-coupled relaxation. For trimer, the rate constant of $\mu_{em}$ reduction increases significantly from 2.74 ps in toluene to 1.43 ps in THF, showing an identical variation of those of monomer.

These results all point to the fact that the octupolar trimer shows more character of dipolar molecule through structural relaxation when it comes to a more polar solvent environment. The declining emission dipole moment for trimer in polar THF provides direct evidence for the solvent-induced SBCT dynamics. SBCT results in an increasing dipole moment along the excited-state relaxation in the ICT state of trimer in THF, leading to a faster solvent-coupled relaxation reflected in its transient fluorescence dynamics. As a result of the solvent-induced symmetry broken, the relaxed ICT state of trimer in THF should be characterized as an electronic localization state. The symmetry breaking dynamics deduced from the transient fluorescence spectra also reflects the electronic localizing process among the branches of trimer in the excited state.

E. Solvent-induced symmetry breaking process

In combination with the discussion above, the overall solvation and solvent-induced SBCT dynamics of the multibranched chromophore in solvents with different polarities can be schematically summarized as shown in FIG. 5. In weakly polar toluene, trimer with octupolar character exhibits weaker solvent coupling compared with that of monomer with dipolar character. The preserved symmetry of trimer in excited state induces excitation delocalized over the three branches. However, as a consequence of the solvation effect of polar THF, trimer with octupolar character loses its high structural symmetry in few picoseconds which is directly characterized by transient fluorescence spectroscopy. The structural relaxed $S_1$ state of trimer in THF exhibits a dipole molecule which is analogous to the monomer with a simple D-A structure. Accompanied by excited-state symmetry breaking process, the excitation energy localization takes places during the structural relaxation from the FC state to the structural-stabilized $S_1$ state [39, 40].

Furthermore, we made a comparison between the time constants of emission dipole moment change and those of stimulated emission peak shifting ($\tau_{SE-shift}$) obtained from femtosecond transient absorption spectra reported in our previous work [39]. Theoretically, the stimulated emission dynamics obtained from transient absorption and the transient fluorescence dynamics spectra are corresponding to identical physical processes. While in transient absorption spectra, stimu-
lateral emission spectra cannot be well separated as a result of its spectral overlapping with excited-state absorption and ground-state bleaching. Thus, there are small differences between fitted $\tau_{\text{SE-shift}}$ and $\tau_{\text{em-dipole}}$. In addition, although $\tau_{\text{SE-shift}}$ and $\tau_{\text{em-dipole}}$ exhibit same tendency when discussing the symmetry breaking dynamics of monomer and trimer in selected solvents with different polarities, only the $\tau_{\text{em-dipole}}$ directly reflects the structural symmetry changes.

IV. CONCLUSION

In summary, we have demonstrated the solvent-induced symmetry-breaking charge transfer in an octupolar trimer chromophore by steady-state and femtosecond transient fluorescence spectroscopy. Steady-state spectra indicate that the trimer chromophore preserves its structural symmetry upon photoexcitation in weakly polar toluene, while its relaxed emission state is symmetry-broken in strongly polar THF. Through the use of transient fluorescence spectroscopy and analyzing the dynamics of instantaneous emission dipole moment, the solvent-induced symmetry breaking and the excitation localization process are tracked in real time. In strongly polar THF, the octupolar chromophore undergoes structural relaxation in $\sim$1.4 ps, which contributes to the stabilization of dipolar symmetry-broken emission state; while the octupolar symmetry of the trimer is largely preserved in weakly polar toluene during the solvation stabilization. These findings presented in this work will provide an unambiguous view of the fundamental solute-solvent interaction and solvent-induced structural fluctuation, especially the symmetry breaking and excitation energy redistribution in multibranch chromophores.

V. ACKNOWLEDGMENTS

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