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Symmetry-breaking charge separation in a null-excitonic 3-dimensional rigid nonconjugated trimer

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ABSTRACT
Photoinduced symmetry-breaking charge separation (SB-CS) has been extensively observed in various oligomers and aggregates, which holds great potential for robust artificial solar energy conversion systems. It attaches great importance to the precise manipulation of interchromophore electronic coupling in realizing efficient SB-CS. The emerging studies on SB-CS suggested that it could be realized in null-excitonic aggregates, and a long-lived SB-CS state was observed, which offers an advanced platform and has gathered immense attention in the SB-CS field. Here, we unveiled the null-exciton coupling induced ultrafast SB-CS in a rigid polycyclic aromatic hydrocarbon framework, triperyleno[3,3,3]propellane triimides (TPPTI), in which three chromophores were attached through a nonconjugated bridge. Through a combination of theoretical calculations and steady-state absorption results, we demonstrated that this nonconjugated TPPTI possesses negligible exciton coupling. Increased solvent polarity was found to significantly enhance state mixing between local excited and charge transfer states. Using transient absorption spectroscopy, ultrafast SB-CS was observed in highly polar dimethylformamide, facilitated by a selective hole-transfer coupling and a favorable charge separation free energy ($\Delta G_{CS}$). Additionally, the rate ratio between SB-CS and charge recombination was at least high to 1800 in dimethylformamide. This investigation provides profound insights into the role of null-exciton coupling in dominating ultrafast SB-CS in multichromophoric systems.

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INTRODUCTION
The photoinduced charge separation process is an indispensable step in light-harvesting in both photosynthesis and organic photovoltaics. In the bacterial photosynthetic reaction center, energy conversion is accomplished by a sequence of electron transfer (ET) and charge separation (CS) processes upon the excitation of $\pi$-stacked bacteriochlorophyll pairs.5,6 Great efforts have been devoted to designing highly efficient photoelectronic materials applied to organic photovoltaics (OPVs) to mimic this reaction. However, the power conversion efficiencies (PCE) of OPVs are significantly limited by the low open-circuit voltages ($V_{OC}$). It has been demonstrated that $V_{OC}$ is dependent on the energy offset between the highest occupied molecular orbital...
(HOMO) of the electron donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor.\textsuperscript{18–19} Notably, photoinduced symmetry-breaking charge separation (SB-CS) is a process observed in symmetrical oligomers where the charge-neutral of excited states are broken into identical multichromophores due to the formation of a charge transfer (CT) state and separate into electron/hole pairs. The implementation of materials capable of SB-CS into OPVs emerges as a promising mechanism to potentially improve the \( V_{OC} \) in OPVs.\textsuperscript{14–16} Bartynski \textit{et al.} have demonstrated that implementing SB-CS materials into OPVs could result in a high \( V_{OC} \).\textsuperscript{17}

Perylene imides and their derivatives have garnered extensive attention in OPVs due to their excellent chemical properties, including strong absorption in the visible region, a variety of functionalization sites, and robust photochemical stability.\textsuperscript{20–21} Although SB-CS has been observed in perylene imides and their derivatives,\textsuperscript{22–25} there remains a rarity of precise design rules for multichromophoric systems capable of SB-CS. The rate of SB-CS is highly sensitive to the strength of electronic coupling and solvent polarity. Strong coupling can promote ultrafast electron transfer; however, it would also accelerate other competing decay pathways, which could potentially hinder the occurrence of SB-CS.\textsuperscript{26–27} For example, the excitation of cofacial aggregates usually tends to evolve into a lower-energy excimer state, which serves as a trap state.\textsuperscript{28,29} Moreover, the photoinduced excited state does not evolve into the CS state in strongly coupled molecules due to the delocalized excitation energy. Therefore, a comprehensive understanding of the interplay between the photophysics and spatial arrangement of chromophores, as well as excitonic coupling in multichromophoric systems, is vitally important for utilizing them as advanced functional materials.\textsuperscript{30,31}

The primary exciton theory was proposed by Davydov\textsuperscript{32} and Kashka\textsuperscript{33,34} and mainly referred to the long-range Coulombic coupling (\( I_{\text{Coul}} \)). Based on this theory, molecular aggregates can be divided into two categories: H-aggregates and J-aggregates. Developed by Spano and co-workers,\textsuperscript{35,36} an additional short-range charge-transfer-mediated exciton coupling (\( I_{\text{CT}} \)) should be taken into account in close-packed aggregates.\textsuperscript{37} Consequently, there exists a special aggregate called “null aggregates” in molecular aggregates, where the overall excitonic coupling strength is approximately zero (\( I_{\text{Coul}} + I_{\text{CT}} = 0 \) cm\(^{-1}\)), arising from the destructive interference between \( I_{\text{Coul}} \) and \( I_{\text{CT}} \). “Null aggregates” typically exhibit monomer-like photophysical properties, which has sparked significant interest in exciton dynamics research, particularly in the SB-CS field. Recently, Sebastian and Harirhan first unveiled null exciton coupling assisted highly efficient SB-CS in a Greek cross (\textit{+})-oriented spiro-conjugated PDI dimer (Sp-PDI\textsubscript{2}), in which the ratio of the rates for SB-CS over CR exhibited an unprecedentedly high value of 2647 in acetonitrile.\textsuperscript{38} Lin \textit{et al.} provided fundamental insights into the mechanisms of SB-CS in null-type slip-stacked PDI trimer, demonstrating that coherent vibronic coupling facilitates state mixing between Frenkel exciton (FE) and charge transfer (CT) states, thus enabling ultrafast SB-CS.\textsuperscript{39}

In this work, we reported the null exciton coupling in a rigid three-dimensional (3D) polycyclic aromatic hydrocarbon (PAH) framework, triperyleno[3,3,3]propellane trimides (TPPTI).\textsuperscript{40} This molecule is structured as three nonconjugated perylene monoimides radiating outwards like fan blades, with minimal \( \pi \)-stacking overlap, and demonstrated null-exciton coupling induced ultrafast SB-CS in polar dimethylformamide solvent. Theoretical calculations revealed that both long-range Coulombic coupling (\( I_{\text{Coul}} = 1.67 \) cm\(^{-1}\)) and short-range CT coupling (\( I_{\text{CT}} = -0.33 \) cm\(^{-1}\)) approach zero, signifying a negligible excitonic interaction due to the lack of both through-bond coupling and spatial \( \pi - \pi \) interactions. However, the absorption spectra of TPPTI in polar solvents exhibited slightly strengthened excitonic coupling and red-shifted signatures, suggesting an efficient electronic mixing between the Frenkel state and the CT state. The fluorescence spectra displayed a mirror-like feature to those of the absorption spectra, and the fluorescence quantum yields (FLQYs) showed a strong dependence on solvent polarity, which was severely quenched in dimethylformamide. Combining the femtosecond transient absorption spectroscopy (fs-TA) measurements and theoretical calculations, we unambiguously demonstrated the ultrafast formation of SB-CS governed by a selective hole-transfer coupling and attained a long-lived charge separated state in dimethylformamide (where the rate ratio between SB-CS and charge recombination is higher than 1800). We believe this report offers more insight into the structure-property relationship in null-exciton multichromophoric systems and thereby paves the way for designing novel materials capable of SB-CS.

### RESULTS AND DISCUSSION

#### Synthesis

The synthesis route of TPPTI has previously been reported by Lv \textit{et al.} in detail (see Ref. 40). The molecular structures of TPPTI and its corresponding monomer MPMI are depicted in Fig. 1(a).

#### Steady-state spectra

The steady-state absorption and fluorescence spectra of TPPTI were carried out in toluene (TOL, low polarity, \( \varepsilon = 2.38 \)), tetrahydrofuran (THF, intermediate polarity, \( \varepsilon = 7.6 \)), and dimethylformamide (DMF, high polarity, \( \varepsilon = 36.7 \)), respectively, as shown in Fig. 1(b). The steady-state absorption spectral features of TPPTI all exhibited characteristic absorption of typical perylene imide with three vibronic transitions centered at 480, 510, and 548 nm.\textsuperscript{24,25} Compared to control monomer MPMI in TOL (Fig. S1), the 0–0 absorption band of TPPTI was red-shifted by \( \sim 14 \) nm (Table S1); however, the ratio of intensities between 0–0 and 0–1 vibronic absorption bands \( I_{0,0}/I_{0,1} \) significantly increased, indicative of weak electronic coupling between MPMI subunits.\textsuperscript{25,40} As the solvent polarity increased, the absorption spectra of TPPTI became broader and red-shifted. Furthermore, the value of \( I_{0,0}/I_{0,1} \) slightly decreased, from 1.49 (TOL), 1.40 (THF), and 1.32 (DMF), as shown in Table S1. These spectral changes suggested efficient interaction between the Frenkel state and the CT state, with an increasing interplay between chromophore–solvent and chromophore–chromophore interactions from TOL to DMF.\textsuperscript{42,43}

The fluorescence spectra showed similar solvent dependence to steady-state absorption. In TOL, the fluorescence spectrum of TPPTI closely mirrored that of the absorption spectrum, displaying a well-resolved vibronic feature with a small redshift of 24 nm [Fig. 1(b)]. Besides, the fluorescence quantum yield (FLQY) was
Theoretical calculations

Geometry optimization of TPPTI was performed at the B3LYP/def2SVP level of theory (with alkyl chains replaced by methyl groups), with corresponding results shown in Figs. S3 and S4. The optimized geometry reveals that $\theta$ is 119.8° (Fig. S3), which is a potential null-exciton aggregate. The calculation results showed that the distributions of HOMO are delocalized on three units, and the distributions of LUMO are delocalized on two units. LUMO and LUMO+1 are degenerate in energy. To quantify the exciton coupling strength, time-dependent density functional theory (TDDFT) calculations were conducted with the ωB97XD functional and def2SVP basis set based on the optimized structure of TPPTI (Fig. S5). The post-treatments of excited state properties calculated from TDDFT were implemented using the Multifin 3.8 (dev) code. The hole-electron analysis results show that the first two excited states, $S_1$ and $S_2$, of TPPTI are degenerate localized Frenkel states with nearly identical oscillator strengths ($f = 1.38$), while the $S_3$, $S_4$, and $S_5$ states exhibit as “dark” states. Notably, $S_4$ and $S_5$ states are degenerate in energy and have distinct CT characters in which the partial electron distributions are localized on one MPMI fragment while the partial hole distributions are on another. Furthermore, the first high-lying CT state ($S_3$) is energetically well-separated from the Frenkel state ($S_1$), estimated to be $E_{CT} - E_{S_1} = 1.109$ eV. More accurate calculations addressed more reliably spectral trends by invoking screened range-separated hybrid (SRSH) functionals within a polarizable continuum model, where functional parameters are set according to the dielectric constant accounting for the dielectric environment.

The long-range Coulombic coupling ($J_{Coul}$) between the interacting chromophores can be approximated by the previously reported electrostatic potential (TrEsp) method using the following equation:

$$J_{Coul} = \frac{1}{4\pi\varepsilon_0} \sum_i \sum_j q_i^{(1)} q_j^{(2)} \left( \frac{r_i^{(1)} - r_j^{(2)}}{r_i^{(1)} - r_j^{(2)}} \right). \quad (1)$$

Here, $q_i^{(m)}$ is denoted as the transition charge on the $i$th atom of chromophore $m$, $r_i^{(m)}$ corresponds to the position vector of the respective transition charge, and $\varepsilon_0$ is the vacuum permittivity. The calculated result shows that there is a weak long-range Coulombic coupling ($J_{Coul}$) with a value of 1.67 cm$^{-1}$, which is attributed to a rigid 3D nonconjugated structure.

The short-range CT coupling can be derived from the wave function overlap of HOMOs and LUMOs between neighboring molecules. When the CT state is energetically well-separated from the Frenkel state, the coupling can be approximately represented as follows:

$$J_{CT} = -\frac{2\hbar t_h t_e}{E_{CT} - E_{S_1}}. \quad (2)$$

Here, $t_h$ and $t_e$ represent the effective hole and electron transfer integrals, respectively, $E_{CT}$ is the energy of the high-lying virtual CT state, and $E_{S_1}$ is the energy of the Frenkel exciton state. $t_h$ and $t_e$ can be approximated to be half of the energy splitting of the HOMO and LUMO according to Koopman’s theorem, given as...
\[ t_h = \frac{E_{\text{HOMO}} - E_{\text{HOMO-1}}}{2}, \]  
\[ t_e = \frac{E_{\text{LUMO+1}} - E_{\text{LUMO}}}{2}. \]

The hole and electron transfer integrals were calculated as \( t_h = 1210.48 \text{ cm}^{-1} \) and \( t_e = 1.21 \text{ cm}^{-1} \), respectively, where the hole transfer integral is much larger than that of the electron transfer integral. This result reveals that the rigid 3D nonconjugated TPPTI possesses a selective charge-filtering property (selective hole-transfer coupling). In this case, electron transfer is nearly forbidden; the excitons in the subunits of TPPTI are accelerated to dissociate by transferring a hole to the neighbor one, which might induce ultrafast SB-CS in polar solvents.\(^{33,58}\) The short-range CT coupling \( (J_{\text{CT}}) \) was estimated as \( J_{\text{CT}} = -0.33 \text{ cm}^{-1} \). Consequently, we could calculate the overall excitonic coupling \( (J) \), determined by the sum of long-range Coulombic coupling \( (J_{\text{Coul}}) \) and short-range CT coupling \( (J_{\text{CT}}) \), given as\(^{33,58}\)

\[ J = J_{\text{Coul}} + J_{\text{CT}}. \]

The overall excitonic coupling of TPPTI is \( J = 1.34 \text{ cm}^{-1} \), exhibiting null exciton coupling.

**Gibbs free energy change of charge separation**

To better clarify the energy barrier of the solvent-dependent CS process, we quantitatively discussed the driving force of CS according to the classical Rehm–Weller equation.\(^{35,56}\) Table 1 lists the related parameters for the free energy changes \( (\Delta G_{\text{CS}}) \) calculation in the following equation:

\[
\Delta G_{\text{CS}} = e(E_{\text{OX}} - E_{\text{RED}}) - E_{0,0} - \frac{e^2}{4\pi\varepsilon_0\varepsilon R_{\text{DA}}} - \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{R_0} + \frac{1}{R_A} \right) \left( \frac{1}{\varepsilon_{\text{Ref}}} - \frac{1}{\varepsilon_S} \right),
\]

where \( R_{\text{DA}} \) is the center-to-center distance between MPMI subunits, and \( R_0 \) and \( R_A \) are the ionic radii of MPMI, respectively, which are assumed to be half of the \( R_{\text{DA}} \) in this system and derived from DFT optimized structures (Fig. S3); \( E_{0,0} \) is the excited state energy obtained from the cross point of the normalized steady-state absorption and fluorescence spectra; \( \varepsilon_S \) is the solvent dielectric constant (TOL, 2.38; THF, 7.6; DMF, 36.7); and \( \varepsilon_{\text{Ref}} \) is the dielectric constant of the solvent used for electrochemical experiments (DCM, 8.93).\(^{35}\) The estimated \( \Delta G_{\text{CS}} \) for TPPTI in TOL, THF, and DMF are 0.193, −0.272, and −0.349 eV, respectively. These results mean that SB-CS is energetically unfavorable in nonpolar TOL due to the strongly positive \( \Delta G_{\text{CS}} \) (vide infra). Conversely, in THF and DMF, the charge separation process is thermodynamically favorable. The more negative \( \Delta G_{\text{CS}} \) in DMF would result in a larger energy difference between the LE and CS states, which could potentially facilitate the occurrence of SB-CS.

### Table 1. Driving forces \( (\Delta G_{\text{CS}}) \) for the CS process of TPPTI in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( E_{\text{OX}} ) (V)</th>
<th>( E_{\text{RED}} ) (V)</th>
<th>( R_{\text{DA}} ) (Å)</th>
<th>( E_{0,0} ) (eV)</th>
<th>( \Delta G_{\text{CS}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOL</td>
<td>0.82</td>
<td>−1.26</td>
<td>6.75</td>
<td>0.00</td>
<td>0.193</td>
</tr>
<tr>
<td>TPPTI</td>
<td>0.82</td>
<td>−1.26</td>
<td>8.75</td>
<td>2.21</td>
<td>−0.193</td>
</tr>
<tr>
<td>DMF</td>
<td>0.82</td>
<td>−1.26</td>
<td>8.75</td>
<td>2.15</td>
<td>−0.349</td>
</tr>
</tbody>
</table>

\( \Delta G_{\text{CS}} \) for TPPTI in different solvents with 490 nm excitation;

\( \Delta G_{\text{CS}} \) for TPPTI in different solvents with 490 nm excitation; corresponding data are shown in Figs. 2, S6, and S7. In nonpolar TOL [Fig. 2(a)], the fs-TA spectra of TPPTI immediately showed a negative ground-state bleaching (GSB) band at 550 nm, a positive excited state absorption (ESA) band centered at 700 nm with a shoulder at 640 nm, and an overlapped stimulated emission (SE) band after photoexcitation, attributed to the locally excited (LE) state. As the delay time carried on, the spectral shape had negligible changes apart from an unimpressive increase at 600 nm. This behavior was indicative of a relaxed LE state, which no longer represented a pure Frenkel state but retained a partial CT character due to the weak state mixing in nonpolar TOL.\(^{35,58}\) The SB-CS process is absent in nonpolar TOL because of the unfavorable \( \Delta G_{\text{CS}} \). Within the following 7 ns time window, the ESA band decayed slowly without additional spectral evolution, suggesting the presence of a long-lived emissive state, which was consistent with TCSPC results.
In the medium polar solvent THF [Fig. 2(b)], the fs-TA spectra immediately manifested as a flat LE band at around 640 and 700 nm and a prominent CT shoulder at 600 nm, which was different from the spectra in TOL. This intensity discrepancy in the CT band could be attributed to efficient mixing between LE and CT states in THF. During the first several picoseconds, the characteristic LE bands diminished, accompanied by the emergence of two ESA bands at 600 and 670 nm. These newly emerging ESA features could definitely be ascribed to the formation of the SB-CS state in THF, as evidenced by the spectroelectrochemical characterization experiments (Fig. S8); however, it retained an ESA shoulder at 670 nm. We inferred that this resulted from the incomplete SB-CS, which maintained partial CT character for TPPTI in medium THF. Over time, both the SB-CS state and CT band evolved into a long-lived state beyond the fs-TA timescale. Further insights into this behavior can be explored through nanosecond transient absorption measurements (ns-TA).

In stark contrast, the fs-TA spectra of TPPTI in strong polar DMF displayed an utterly different spectral evolution and excitonic dynamics process. As depicted in Fig. 2(c), the characteristic SB-CS state and CT band were observed at 610 and 670 nm within 0.6 ps after excitation, which highly resembled that in THF at 5 ps. The ultrafast observation of SB-CS could further indicate not only that the Frenkel state of TPPTI interacted with the CT state but also that the solvent environment dominated the extent of interactions. With the time delay increasing from 0.6 to 20 ps, the CT band decayed completely, accompanied by the emergence of a new species band ranging from 580 to 800 nm, which maintained partial CT character for TPPTI within 2.2 ps ($\tau_{\text{CS}} = 2.2$ ps), and subsequently, the SB-CS state decayed with a time constant of 3.92 ns [Figs. 4(b) and 4(e)]. However, as the solvent polarity increased to high polar DMF, three components were required for the best global fitting. The long-lived state beyond the fs-TA timescale, the partial SB-CS state was immediately observed within the instrument response after excitation, which highly resembled that in THF.

To elucidate the excited state dynamics and mechanism of SB-CS for TPPTI in different solvents, a sequential model (A) $\rightarrow$ (B) $\rightarrow$ (C) $\rightarrow$ GS was used for global fitting of the fs-TA data, as shown in Figs. 3 and 4. The kinetic traces superimposed fitting curves at selected wavelengths are shown in Fig. S7. The corresponding time constants of charge separation ($\tau_{\text{CS}}$) and charge recombination ($\tau_{\text{CR}}$) derived from global analysis are summarized in Table S3.

In nonpolar TOL, because of the absence of the SB-CS process, two components were required for the best global fitting, where state A represented the LE state and state B was the relaxed LE state with partial CT character. The photoinduced LE state underwent a vibrational relaxation process within 5.6 ps, transforming into a relaxed LE state, and the latter exhibited as a long-lived emissive state of 3.55 ns [Figs. 4(a) and 4(d)], consistent with the fluorescence lifetime in TOL ($\tau_{\text{FL}} = 4.1$ ns). However, in polar solvents, the evolution-associated spectra (EAS) of two transient components were quite different from those in TOL. In THF, the two species were denoted as the mixed LE and CT states (A) and SB-CS state (B). The mixed states underwent a rapid charge separation process within 2.2 ps ($\tau_{\text{CS}} = 2.2$ ps), and subsequently, the SB-CS state decayed with a time constant of 3.92 ns [Figs. 4(b) and 4(e)]. However, as the solvent polarity increased to high polar DMF, three components were required for the best global fitting. The lifetime of the relaxed LE state, and the latter exhibited as a long-lived emissive state. Although the time constant of charge recombination in DMF was five times shorter than that in TOL, unexpectedly, the ratio of the rates between SB-CS and CR was at least more than 1800, indicating a long-lived charge separated state in this null-exciton type molecule. Additionally, the formation of a triplet state was observed within the nanosecond timescale, and the decay time constant would be obtained in the following ns-TA measurements.

**Triple formation mechanism**

Perylene monoimide typically exhibits an extremely low intrinsic triplet yield (<1%) due to minimal spin–orbit coupling. However, the ns-TA measurements provided explicit evidence for the triplet formation of TPPTI in three solvents (Fig. S10). The lifetime for the long-lived triplet state was approximately several microseconds, though not precisely quantifiable due to the low yield. Notably, there was no evidence that singlet fission contributed to the triplet formation pathway within this timescale. Given the observation of the SB-CS (CT) state in different solvents, we inferred that the triplet states most likely originated from the intersystem crossing (ISC) process. Previous studies have shown that there are two main mechanisms for ISC, spin–orbit charge transfer intersystem crossing (SOCT-ISC) and radical-pair intersystem crossing (RP-ISC). In this case, SOCT-ISC might be the dominant mechanism for the triplet formation due to the large dihedral angle (120°) of TPPTI between MPMI subunits. The large dihedral angle (120°) could generate sufficient orbital angular momentum to induce a
spin flip. Additionally, the strength of solvent polarity perturbed the extent of state mixing between LE and CT states, resulting in a subtle discrepancy in triplet yields in three solvents, as evidenced by the ns-TA measurements.

CONCLUSIONS

In conclusion, we reported a prolonged SB-CS state \( k_{CS} / k_{CR} > 1800 \) in DMF) in a null-excitonic nonconjugated triperyleno[3,3,3]propellane trimides (TPPTI). The increased intensity ratio \( I_{0-0} / I_{0-1} \) in the steady-state absorption spectrum and monomer-like fluorescence spectrum of TPPTI in TOL suggested its negligible exciton coupling among these fan blade arranged MPMI subunits. This result was also corroborated by the theoretically calculated exciton coupling strength, which affirmed the null exciton behavior of TPPTI. Calculations further revealed that the null-exciton type of TPPTI possesses a selective hole-transfer coupling, which could facilitate ultrafast SB-CS in polar solvents. The solvent polarity was found to significantly influence the extent of state mixing between LE and CT states, resulting in the observation of a solvent-polarity dependent SB-CS. Furthermore, the solvent polarity governed the progression of charge separation, where the mixed CT state in nonpolar TOL could not separate into radical ions while the SB-CS process was almost complete in high polar DMF. Furthermore, the rate of the SB-CS process was dramatically accelerated in DMF, driven by a more negative \( \Delta G_{CS} \) and a selective hole-transfer coupling. Our findings demonstrated that this 3D nonconjugated structure could be considered an ideal system for studying the interplay between null exciton coupling and complex excited-state dynamics.

SUPPLEMENTARY MATERIAL

The supplementary material includes time-resolved spectra, global fitting, photosensitization experiments, and spectroelectrochemistry experiments.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.