Null Exciton-Coupled Chromophoric Dimer Exhibits Symmetry-Breaking Charge Separation

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ABSTRACT: A comprehensive understanding of the structure– property relationships in multichromophoric architectures has pushed the limits for developing robust photosynthetic mimics and molecular photovoltaics. The elusive phenomenon of null exciton splitting has gathered immense attention in recent years owing to the occurrence in unique chromophoric architectures and consequent emergent properties. Herein, we unveil the hitherto unobserved null exciton coupling assisted highly efficient photoinduced symmetry-breaking charge separation (SB-CS) in a Greek cross (+)-oriented spiro-conjugated perylenediimide dimer (Sp-PDI₂). Quantum chemical calculations have rationalized the infrequent manifestation of null exciton coupling behavior in Sp-PDI₂. Negligible contribution of long-range Coulombic and short-



range charge-transfer mediated coupling renders a monomer-like spectroscopic signature for Sp-PDI₂ in toluene. The Greek cross (+)-arranged Sp-PDI₂ possesses a selective hole-transfer coupling, facilitating the ultrafast dissociation of null excitons and evolution of the charge-separated state in polar solvents. Radical cationic and anionic spectroscopic signatures were characterized by employing femtosecond transient absorption spectroscopy. The substantial hole transfer electronic coupling and lower activation energy barrier of Sp-PDI₂ accelerated the charge separation rate. The rate of charge recombination (CR) markedly decelerated due to falling into the inverted region of the Marcus parabola, where the driving force of CR is larger than the total reorganization energy for CR. Hence, the ratio of the rates for SB-CS over CR of Sp-PDI₂ exhibited an unprecedently high value of 2647 in acetonitrile. The current study provides impeccable evidence for the role of selective charge filtering in governing efficient SB-CS and thereby novel insights towards the design of biomimics and advanced functional materials.

INTRODUCTION

The three-dimensional (3D) coalition of π -conjugated organic materials in photosynthesis, solar energy conversion, and optoelectronic devices play an imperative role in ensuring a high degree of solar energy harvesting, transport, and conversion.¹⁻⁶ Specifically, in the photosynthetic complexes, impinging solar photons are transferred into the reaction center through coherent exciton transport. The conversion of excitation energy to chemical energy at the reaction center is initiated by the symmetry-breaking charge separation process (SB-CS), which trigger the sequential electron transfer.^{7,8} The comprehensive understanding of the photophysical processes (exciton formation, energy transfer, and charge separation) in molecular dimers and its precise dependence on the spatial arrangement, π -overlap, and intermolecular distances are essential for the design of efficient and robust artificial solar energy conversion systems.⁹

Davydov¹² and Kasha^{13–15} independently worked out the molecular exciton theory in the 1960s based on intermolecular Coulombic interactions (point–dipole approximation), eventually leading to the primary classification of J-aggregates ("head-to-tail" configuration) and H-aggregates ("sandwich"

configuration). H-aggregates exhibit blue-shifted absorption bands, high charge transport character, and quenched fluorescence emission. Conversely, exciton coupling among the staggered transition dipoles (J-aggregate) exhibits a redshifted absorption peak, weak charge transport behavior, and superradiant fluorescence character.^{16,17} However, in closepacked molecular aggregates, wave functions overlap among the neighboring molecules prompting an additional shortrange charge-transfer-mediated exciton coupling ($J_{\rm CT}$).¹⁸ The magnitude and the sign of CT coupling are governed by the electron and hole transfer integral derived from the extent of orbital overlap between the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs).^{19–21} Consequently, the interference between long-

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range Coulombic coupling and short-range CT coupling defines the effective excitonic coupling in interacting chromophores. A substantial theoretical and experimental effort has been invested in understanding CT coupling and Coulombic coupling (J_{Coul}) interferences.^{22–25}

Photoinduced SB-CS is a process where a symmetrical pair of identical chromophores forms a charge-separated excited state with the hole and electron on different chromophores, i.e., $M-M + h\nu \rightarrow M^{+} - M^{-}$, upon photoexcitation.²⁶ SB-CS has found wide applications in artificial photosynthesis and optoelectronic devices owing to the minimal energy loss during the charge-separated state formation (energy loss between the exciton and charge-separated state is <100 mV for SB-CS, in contrast to the value of ~500 mV or more for charge separation in the donor-acceptor systems).²⁷⁻²⁹ The rate of SB-CS mainly depends on the strength of electronic coupling and solvent environment.^{26,30} In a weak exciton coupling regime, the electronic absorption spectra of the interacting chromophores show minor variation when compared to the noninteracting systems. Theoretically, the excited states of the molecular dimer can be represented as locally excited singlet (LE) states and charge-separated (CS) states.^{31,32} SB-CS processes in weakly coupled dyad and the triad of perylenediimide,^{30,33–35} perylene,^{26,36,37} BODIPY,^{28,38} metal-lopyrrins,^{38–40} bianthryl,⁴¹ subphthalocyanine,⁴² and terrylenediimide^{43,44} are well explored and documented in the literature. Moreover, probing SB-CS processes in film samples and polymers is an emerging research topic.⁴⁵ Strong excitoncoupled aggregates show shifted or split absorption bands and excimer formation.^{24,26,46} The excimer states can act as an exciton trap and compete with the desired products. In a strongly coupled system, the excitation energy is delocalized over the dimer molecule, and the excited state may lack the charge separation character.³⁶

An exciting class of aggregates called "null aggregates", exhibiting monomeric optical properties in the condensed state, was initially proposed by Kasha and co-workers and later by Spano and co-workers.^{15,47} Besides the theoretical predictions, innovative designs exhibiting minimal exciton coupling have been reported in recent years.⁴⁹ Xie and coworkers reported minimal excitonic coupling in a perylenediimide crystal possessing magic angle (slip angle = 54.7°) stacking.⁵⁰ Würthner and co-workers demonstrated very weak coupling in a molecular foldamer of perylenediimide (PDI) owing to the destructive interference between Coulombic and CT coupling.²⁵ Our group has devised an alternative strategy for constructing molecular aggregates with minimal excitonic interactions in a crystalline state through the orthogonal (faceto-face) stacking of chromophores at a 90° rotational angle. The first crystalline evidence for the Greek cross (+)-architecture with null exciton coupling mediated monomeric optical properties was reported in 1,7-dibromoperylene-3,4,9,10tetracarboxylic tetrabutylester.⁵¹ Yet another example of null exciton splitting was realized in a series of pentacene derivatives existing in orthogonal molecular stacks.⁵² The orthogonally cross-stacked linear and nonlinear acene dimers were found to exhibit mutually exclusive hole and electron transfer coupling.53

Though vital for optoelectronic application, a comprehensive understanding of the excited-state dynamics of very weak/ null excitonic coupled chromophores remains rare. Recently, Kim, Würthner, and co-workers reported efficient multiexciton state generation in a null exciton-coupled perylenediimide

foldamer by the large charge-transfer coupling between the chromophores.⁵⁴ Our long-standing efforts to achieve chromophoric aggregates in Greek cross (+)-arrangement (face-to-face stack) and understand the diverse photoexcited state processes in self-assembled donor-acceptor systems^{55,56} and bichromophoric systems⁵⁷⁻⁵⁹ motivated us to dwell into the realm of null exciton and its concomitant effect on ultrafast excited-state dynamics. Herein, we report the null exciton coupling in spiro-conjugated perylenediimide dimer (Sp-PDI₂), wherein two planar π -conjugated PDI chromophores are connected perpendicularly via a quaternary sp³ carbon center (edge-to-edge arrangement), exhibiting ultrafast SB-CS. Unperturbed spectroscopic features of Greek cross (+)-arranged Sp-PDI₂ in toluene evidence minimal excitonic coupling. Monomer-like spectral signatures displayed by Sp-PDI₂ can be rationalized by the interference of negligible contribution from both long-range Coulombic and short-range charge-transfer mediated couplings. The orthogonally oriented Sp-PDI₂ are found to possess a selective charge-filtering phenomenon (selectively hole-transfer coupling). Significant wave function overlap (hole-transfer coupling) among monomeric chromophores of Sp-PDI₂ facilitates efficient ultrafast SB-CS in polar solvents (THF and ACN). The rate of charge recombination (CR) processes of Sp-PDI₂ is significantly decelerated due to the low molecular reorganization energy when compared to the free energy change of CR $(\Delta G_{CR} > \lambda)$. The ratio of rates of SB-CS over CR of SP-PDI₂ is estimated as 2647, which is the most long-lived chargeseparated state obtained so far among the multichromophoric PDI derivatives (Table S1).

RESULTS AND DISCUSSION

Synthesis, Single-Crystal Structure, and Geometry Optimizations. PDI, Ref-PDI, and Sp-PDI₂ were synthesized and characterized according to the previous reports (Figure 1



Figure 1. Molecular structure of (a) PDI, (b) Ref-PDI, and (c) Sp-PDI₂. (d and e) Single-crystal X-ray structure of Sp-PDI₂. "R" represents the 3-pentyl group.

and Scheme S1).^{60,61} **Ref-PDI** is the monomer unit of Sp-PDI₂. Slow evaporation of a homogeneous solution of Sp-PDI₂ (in a 1:1 chloroform/methanol solvent) at room temperature led to good-quality crystals for single-crystal X-ray diffraction. The X-ray crystallography technique unambiguously confirmed the molecular structure of Sp-PDI₂ (Figure 1).

An sp³-hybridized spiro-carbon atom connects the two blades of **PDI** subunits to form a Greek cross (+)-architecture (edge-to-edge arrangement) with a rotational angle (θ) of 87.43° between the chromophores (CCDC number 2086823 and Table S2). Geometry optimization of **PDI**, **Ref-PDI**, and **Sp-PDI**₂ was performed at the B97D3/def2-TZVP level of theory.^{62,63} The geometrical features of **Sp-PDI**₂ are essentially the same in the vacuum, and θ was found to be 90° between the spiro-fused **PDI** units (Figure S1). As a response to the increased steric constraint of the five-membered cyclic carbon ring in the **PDI** core's bay region, a small inward bend along the long axis of the perylenediimide chromophore of **Ref-PDI** and **Sp-PDI**₂ is observed (Figure S2).

Optical Properties. The ground-state electronic properties of **Sp-PDI**₂ along with the reference compounds (**Ref-PDI and PDI**) were explored by means of steady-state absorption spectroscopy in toluene ($c_0 = 0.1-0.5 \ \mu$ M) at room temperature (Figure 2 and Figure S3). The UV-visible



Figure 2. Normalized absorption (solid black line) and emission spectra (solid red line) of Ref-PDI (top) and Sp-PDI₂ (bottom) in toluene at room temperature.

absorption spectrum of **Ref-PDI** shows characteristic spectral signatures of monomeric **PDI** dye with a 10 nm bathochromic shift (Figure S3). The absorption maximum of **Ref-PDI** observed at 533 nm ($\lambda_{max}^{Abs} = 18761.73 \text{ cm}^{-1}$) with a molar extinction coefficient (ϵ_{max}) of 95 690 M⁻¹ cm⁻¹ corresponds to the S₀-S₁ electronic transition (f = 0.72, Table S3). The dipole-allowed electronic transition of **Ref-PDI** (S₀-S₁ transition) is strongly coupled to the vinyl stretching mode

of the perylene core ($v_{c=c} \sim 1400 \text{ cm}^{-1}$), resulting in pronounced vibronic progression in the absorption spectrum at 495 nm ($\lambda_{0-0}^{Abs} = 20\ 202.02\ \text{cm}^{-1}$), 464 nm ($\lambda_{0-1}^{Abs} = 21\ 551.72\ \text{cm}^{-1}$), and 435 nm ($\lambda_{0-2}^{Abs} = 22\ 988.51\ \text{cm}^{-1}$). The A_{0-0}/A_{0-1} oscillator strength ratio, as determined by the ratio of the intensities of the 0–0 and 0–1 absorption bands, amounts to 1.74 (Table 1).

Table 1. UV-vis and Fluorescence Spectroscopic Data of
Ref-PDI and Sp-PDI ₂ Measured in Toluene at Room
Temperature

	Ref-PDI	Sp-PDI ₂
$\lambda_{\rm abs}(A_{0-0}), \ {\rm nm/cm^{-1}}$	533/18761.73	549/18214.94
$\lambda_{\rm abs}(A_{0-1}), {\rm nm/cm^{-1}}$	495/20202.02	509/19646.37
$\lambda_{\rm em}$, nm/cm ⁻¹	542/18450.18	558/17921.15
$\varepsilon_{\rm max}~{\rm M}^{-1}/{\rm cm}^{-1}$	95690	123590
A_{0-0}/A_{0-1}	1.74	1.60
$\Delta \tilde{\nu}_{\mathrm{Stokes'}} \mathrm{~nm/cm^{-1}}$	9/311.50	9/293.79
$\phi_{ ext{Fl}}$ %	97.7	90.20
$ au_{ m Fb}$ ns	4.17	6.62

In concurrence with the theoretical predictions, the UVvisible absorption spectrum of Sp-PDI₂, a Greek cross-shaped molecule with two π -conjugated perylenediimide rings embraced by a spiro-linker, reveals virtually unperturbed spectral features as compared to the Ref-PDI. Though Sp-PDI₂ exhibits a monomeric spectral signature, the absorption maximum is bathochromically shifted to 549 nm ($\lambda_{max}^{\hat{A}bs}$ = 18 214.94 cm⁻¹) with an extinction coefficient of 123 590 $M^{-1}cm^{-1}$. The observed redshift (546.79 cm⁻¹), though not insignificant, arises from the self-energy correction (ΔCT , vide *infra*).⁴⁸ A minor decrease in the ratio of the absorption band intensities $(A_{0-0}/A_{0-1} = 1.60 \text{ (Sp-PDI}_2) \text{ and } 1.74 \text{ (Ref-PDI}))$ and minimal absorption band broadening ($\Delta \tilde{v}_{1/2} = 721.35$ cm⁻¹ for Ref-PDI and $\Delta \tilde{\nu}_{1/2} = 746.17$ cm⁻¹ for Sp-PDI₂) suggest negligible exciton coupling among the orthogonally connected PDI units in Sp-PDI₂.

To get additional insights into the excitonic coupling of Sp-PDI₂, steady-state fluorescence spectroscopy was performed in toluene ($c_0 = 0.1 - 0.5 \,\mu\text{M}$) at room temperature (Figure 2 and Figure S3). Photoexcitation of Ref-PDI shows a characteristic fluorescence emission spectrum with a well-resolved vibronic fine structure of PDI. The emission maximum of Ref-PDI $(\lambda_{\rm em})$ is bathochromically shifted to 542 nm (18 450.18 cm⁻¹), and a Stokes shift of 9 nm was observed. The fluorescence quantum yield of Ref-PDI is quantified as 97.7%, which is comparable to the reported value of PDI.^{33,64} Fascinatingly, the fluorescence emission spectrum of Sp-PDI₂ reveals a monomer-like spectral signature with well-resolved vibronic bands (Figure 2) with the peak maximum (λ_{em}) at 558 nm. Furthermore, high fluorescence quantum yield ($\phi_{\rm Fl}$ = 90.20%) and identical Stokes shift ($\Delta \tilde{\nu}_{\text{Stokes}} = 9 \text{ nm}$) reconfirm the exiguous exciton communication between the PDI monomers and rule out the other possible deactivation channels (Table 1).

Theoretical Investigation. Having rationalized the presence of null exciton coupling of $Sp-PDI_2$ in toluene, we explored the nature of excitonic interactions arising from relative interchromophoric orientations by employing theoretical methods. The excitonic coupling (*J*) of the $Sp-PDI_2$ was scrutinized by evaluating the contributions from both long-range and short-range effects^{20,48} (during the theoretical

calculation, the spiro-carbon atom of the DFT-optimized Sp- PDI_2 molecule was replaced by four H atoms).

The long-range Coulombic coupling between any two chromophores arises from the interaction between their transition charge distribution which is often calculated using point-dipole approximation.^{65,66} Herein, we have employed the transition charge from electrostatic potential (TrEsp) method for calculating Coulombic coupling energy (J_{coul}) between the interacting molecules.⁶⁷ The method provides a good result when the interchromophore distance is shorter than the chromophores size, where dipole–dipole approximation overestimates the exciton coupling energy. In the TrESP method, the transition electrostatic potential is fitted to atomic partial charges. The Coulomb interaction between the transition charges of the different chromophores is equal to long-range Coulombic coupling (J_{coul}) and can be efficiently calculated using eq 1:

$$J_{\text{coul}} = \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j} \frac{q_i^{(1)} q_j^{(2)}}{|r_i^{(1)} - r_j^{(2)}|}$$
(1)

Here, $q_i^{(m)}$ represents 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 ε_0 is the vacuum permittivity (Supporting Information, Section 1.2). Sp-PDI₂ shows a negligible long-range Coulombic coupling (J_{coul}) value of 3.34 cm⁻¹, reinforcing the hypothesis of minimum Coulombic coupling between orthogonally (edge-to-edge) arranged transition dipole vectors of PDI molecules (Table 2 and Figure S4).

Table 2. Experimentally and Theoretically Calculated Excitonic Coupling and Hole/Electron Transfer Integrals of Sp-PDI₂

	(eV)	(cm^{-1})
J^{a}	1.72×10^{-2}	139.13
J^{b}	0.64×10^{-4}	0.55
$J_{\rm coul}^{c}$	4.10×10^{-4}	3.34
t _e	-1.03×10^{-3}	-8.06
$t_{ m h}$	-1.47×10^{-1}	-1185.63
$J_{\rm CT}^{d}$	-3.46×10^{-4}	-2.79

^{*a*}Estimated from the intensity ratio of the A_{0-0} and A_{0-1} absorption bands in the UV–vis spectra. ^{*b*}Determined based on eq 3. ^{*c*}Calculated by the transition charge method based on eq 1. ^{*d*}Determined based on eq 2.

The charge-mediated short-range coupling stemming from the wave function overlap between neighboring molecules has a significant role in defining the effective excitonic interaction.^{17,20,48} The LUMO–LUMO and HOMO– HOMO orbital overlap, which can be substantial in the short interchromophoric distance, enables a virtual high-energy charge-transfer state between the molecules. The short-range exciton coupling energy can be calculated by eq 2^{68,69}

$$J_{\rm CT} = -2 \frac{t_{\rm e} t_{\rm h}}{E_{\rm CT} - E_{\rm S_1}}$$
(2)

where t_e and t_h represent the electron and hole-transfer integrals which depend on the LUMO–LUMO and HOMO– HOMO orbital overlap of the monomer, respectively; E_{CT} is the energy of the virtual charge-transfer state; and E_{S_1} is the energy of the local Frenkel exciton state. Equation 2 holds under the assumption that diabatic Frenkel and CT states are energetically well separated.

The net exciton coupling (J) between neighboring molecules derived from the interference between the long-range Coulombic coupling (J_{coul}) and the short-range charge-transfer mediated coupling (J_{CT}) is given by:^{68,69}

$$J = J_{\rm coul} + J_{\rm CT} \tag{3}$$

The hole and electron-transfer integral were calculated using the energy-splitting dimer method (Table 2, Figure 3a, and Figure 3b).^{70,71} Sp-PDI₂ imparts a selective hole-transfer coupling ($t_{\rm h} = -1185.63$ cm⁻¹, Figure 3b) owing to the constructive interference between the HOMO of the monomeric PDI molecule, whereas the destructive LUMO-LUMO orbital interaction of the PDI unit resulted in the minimal value of electron transfer coupling ($t_e = -8.06 \text{ cm}^{-1}$, Figure 3a). Constructive and destructive interference of the p_z orbital around the spiro-linkage is depicted in Figure 3a and Figure 3b (p_z orbitals of these four carbon atoms are close enough to interact through space). We further proceeded to calculate the J_{CT} value using eq 2. The energy difference between the charge-transfer state (E_{CT}) and the local Frenkel exciton state (E_{S_1}) for Sp-PDI₂ $(E_{CT} - E_{S_1} = 0.875 \text{ eV})$ was calculated using TheoDORE (vide infra) which is in good agreement with the recent literature.⁷² The minimal magnitude of CT coupling $(J_{CT} = -2.79 \text{ cm}^{-1})$ obtained upholds the insignificant nature of the charge-transfer coupling between the orthogonally arranged PDI units ($\theta = 90^{\circ}$) of Sp-PDI₂ (Table 2). Thus, the spiro-conjugated perylenediimide dimer exhibits null exciton coupling $(I = -0.55 \text{ cm}^{-1})$ due to negligible contributions from Coulombic and CT-mediated couplings.

We further calculated the excitonic coupling of **Sp-PDI**₂ by employing a method developed by Spano and co-workers based on the 0–0 and 0–1 absorption band intensities that show exciton–vibrational coupling (Supporting Information, Section 1.3).^{73,74} Excitonic coupling energy obtained by the method is comparable with the one obtained by eq 3 (Table 2). The marginal disparity in excitonic coupling energy could be a consequence of exciton coupling stemming from the small rotational degree of freedom around the spiro-linkage of Greek cross (+)-arranged **Sp-PDI**₂ under the experimental conditions (Figure S5).^{41,75,76} Therefore, the exciton coupling calculated by the ratio of the intensity of the 0–0 and 0–1 absorption band observed in the UV–visible absorption spectra and theoretical methods restate the null excitonic coupling between the orthogonally (edge-to-edge) arranged **PDI** chromophores.

To obtain further insight into the nature of different excited states of **Sp-PDI**₂, fragment-based excited-state analysis developed by Plasser, implemented in TheoDORE, was performed (Supporting Information, Section 1.4).^{77,78} **Sp-PDI**₂ has two nearly degenerate localized Frenkel states S₁ and S₂ with equal oscillator strengths (f = 0.79), while the degenerate S₃ and S₄ states (f = 0.06) possess pure CT state character (S₃ and S₄ states with CT = 0.82), where the hole is localized on one fragment and the electron is localized on the other. The higher-energy virtual CT state (S₃ and S₄) and local Frenkel exciton state (S₁ and S₂) are energetically well-separated, and $E_{\rm CT} - E_{\rm S_1} = 0.875$ eV is calculated for **Sp-PDI**₂ in toluene. The description is pictorially represented using an electron-hole correlation plot (Table S4 and Figure S6). Further, natural transition orbitals (NTO)⁷⁹ and hole-



Figure 3. Schematic of the **Sp-PDI**₂ molecule with the p_z orbitals around the spiro-link showing (a) destructive interference between LUMOs and (b) constructive interference between HOMOs of the PDI molecule. (c) Top: schematic of the LUMO–LUMO orbital interaction of the PDI dimer responsible for the electron transfer integral in different rotational angles. Middle: the electron and hole transfer integrals as a function of the PDI dimer responsible for hole transfer integral arranged PDI molecules. Bottom: schematic of the HOMO–HOMO orbital interaction of the PDI dimer responsible for hole transfer integral in different rotational angles (representation of HOMO and LUMO molecular orbitals of PDI molecule is restricted to the p_z orbitals that are close enough to interact through space).



Figure 4. Energy level diagram of different singlet excited states of Sp-PDI₂, depicting hole and electron transfer between the neighboring PDI molecule and corresponding isosurface of hole (blue) and electron (yellow) distribution.

electron isosurface analyses⁸⁰ of the S₀ to S_n transition (n = 1, 2, 3, and 4) of **Sp-PDI**₂ are portrayed in Figures S6, S7, and Figure 4. Localization of hole–electron distribution in one of the **PDI** monomers of **Sp-PDI**₂ is observed for S₀ \rightarrow S₁ and S₀ \rightarrow S₂ transitions. In contrast, S₀ \rightarrow S₃ and S₀ \rightarrow S₄ electronic transitions hole–electron distribution isosurfaces show that the hole and electron are localized on different **PDI** units of **Sp-PDI**₂. The excited-state characteristics of **Sp-PDI**₂ in its ground-state geometry resembles the bianthryl molecules reported in the literature, where all excited states reflect the symmetry of the molecular structure. However, transition

dipole vectors are arranged parallelly in bianthryl and orthogonally in Sp-PDI₂ (Figure S4).^{81,82}

The short-range CT-mediated exciton coupling, or superexchange coupling, $J_{\rm CT}$, represent an energy-transfer process that proceeds through a high-energy virtual CT state, as depicted in Figure 4.²⁰ In **Sp-PDI**₂, the exciton localized initially on a single PDI molecule dissociates by transferring a hole ($t_{\rm h} = -1185.63 \text{ cm}^{-1}$) to its neighbor PDI molecule, resulting in creating the higher energy CT state. Electron transfer is forbidden due to negligible electron transfer coupling $t_{\rm e} = -8.06 \text{ cm}^{-1}$. For energy transfer to the neighboring molecule ($J_{\rm CT}$), the created CT state has to decay by transferring an electron to the neighboring molecule. In contrast, because of the minimal magnitude of $t_{e^{j}}$ the CT state decay to the initial local Frenkel exciton state by the back-transfer of hole resulted in self-energy correction (Δ CT):^{20,48}

$$\Delta \text{CT} = -2 \frac{(t_e^2 + t_h^2)}{E_{\text{CT}} - E_{S_1}}$$
(4)

 Δ CT is universally negative whenever the virtual CT state is higher in energy than the local Frenkel exciton. Calculated selfenergy correction (Δ CT = -396.34 cm⁻¹) successfully accounts for the spectral absorption shift of 546.94 cm⁻¹ observed for the **Sp-PDI**₂ in toluene. Interestingly, the spectral absorption shift stemmed from Δ CT complicates Kasha's conventional classification of H- and J-aggregates.

To assess the effect of relative spatial orientation on the Coulombic and charge-transfer coupling, rotational angledependent J_{coul} , t_e , t_h , and J_{CT} were probed for orthogonally arranged **PDI** monomers of **Sp-PDI**₂ (spiro-carbon of the optimized structure was replaced by four H atoms, Figure 3c, Figure 5, Table S5, and Table S6). The **PDI** dimer with a



Figure 5. Variation of the modulus of Coulombic coupling $|J_{coul}|$ and charge-transfer coupling (J_{CT}) as a function of rotation angle (θ) between the perylenediimide monomers (for evaluating J_{CT} ; $E_{CT} - E_{S_1} = 0.875$ eV was used as a constant).

rotational angle of 90° has a $J_{\rm coul}$ value of 3.34 cm⁻¹. $J_{\rm coul}$ drastically increased to 76.90 cm⁻¹ for rotation of a **PDI** monomer with respect to the other by about an angle of 5° from the initial 90° cross-architecture. A linear increase of $J_{\rm coul}$ with the decrease of rotational angle is observed, and a maximum value of 798.59 cm⁻¹ reached at the rotational angle of 40°, indicating the relatively more robust Coulomb-coupled regime. On the other hand, the behavior of t_e , t_b , and $J_{\rm CT}$ will depend on the nodal pattern of the molecular orbitals involved. The hole transfer integral shows a significant value ($t_{\rm h} = -1185.63$ cm⁻¹) at the rotational angle of 90°, while the electron transfer integral exhibits minimal magnitude ($t_e = -8.06$ cm⁻¹), reflecting the charge filtering effect in **Sp-PDI**₂.

A linear decrease in $t_{\rm h}$ as a function of θ was observed and resulted in $t_{\rm h} = 0$ at ~41°. The constructive interference between HOMOs of **PDI** at 90° is gradually transforming to destructive interference as θ reduces (Figure 3c). In contrast, $t_{\rm e}$ depicts inverted-parabolic behavior as a function of intramolecular rotational angle (θ). As the θ decreases from 90°, the electron-transfer coupling increases from $t_e = -8.06 \text{ cm}^{-1}$ to reach a maximum value of $t_e = 924.21 \text{ cm}^{-1}$ at 60° (destructive interference between LUMOs of PDI changes to constructive interference). Similarly, the rotational angle dependence of short-range CT coupling, J_{CT} , follows inverted-parabola behavior and attains a maximum at ~65° (Figure 5). At the angle of ~41°, both t_h and t_e become zero, effectively shutting off charge-transfer coupling and creating an aggregate driven solely by Coulombic couplings, i.e., an ideal Kasha aggregate.

To shed light on the solvent polarity modulated photophysical properties of null exciton-coupled Sp-PDI₂, we carried out solvent-dependent absorption and fluorescence measurements in solvents of different dielectric constants, i.e., toluene ($\varepsilon = 2.4$), tetrahydrofuran (THF, $\varepsilon = 7.6$), and acetonitrile (ACN, $\varepsilon = 37.50$) (Figures S8, S9, S10, and Table S7).⁸³ The line shapes of the absorption spectra of Sp-PDI₂ in different solvents have a strong resemblance. However, fluorescence quantum yield decreases substantially, and the fluorescence lifetime decay exhibits biexponential lifetimes as the solvent polarity increases (Figure S8 and Table S7), which indicates the existence of additional decay pathways such as SB-CS. In high-polar solvents, such as ACN, the fluorescence is almost quenched ($\Phi_{\rm Fl}$ < 1%), and biexponential emission lifetimes are observed ($\tau_{\rm Fl}^1$ = 1.63 ns (15.75%) and $\tau_{\rm Fl}^2$ = 6.87 ns (84.25%)). However, in THF, moderately polar solvent, Sp-PDI₂, exhibits considerable fluorescence emission ($\Phi_{
m Fl}$ = 24%) and the biexponential decay profile ($au_{
m Fl}^1$ = 14.2 ns (90.20%) and $au_{
m Fl}^2$ = 6.80 ns (9.80%)). The normalized emission spectrum of Sp-PDI₂ in polar solvents (Figure S9) is observed as broad and distinct from that in toluene and not exhibiting any Stokes shift, implying that the emission may have originated from newly formed states. By virtue of the orthogonal arrangement of PDI molecules and restricted rotation around the spirolinkage, the presence of emission from low-lying excimer and relaxed singlet states can be ruled out.^{33,35} The nature of the emissive states in THF and ACN has to be further explored, employing transient absorption and emission measurement (vide infra).

The rate constants (k) for SB-CS and charge recombination (CR) were calculated through the classical expression of Marcus electron transfer theory:^{84,85}

$$k = \frac{2\pi}{\hbar} \frac{V_{\rm DA}^2}{\sqrt{4\pi\lambda k_{\rm b}T}} \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_{\rm b}T}\right)$$
(5)

According to eq 5, the nonadiabatic electron transfer rate depends on the three variables that can be computed or determined experimentally. The first Marcus parameter is the Gibbs free energy change (ΔG) between the equilibrium reactant and product states; the other Marcus parameters are total reorganization energy (λ), which is the total energy required to distort the equilibrium geometry of the reactant state to the product state, and electronic coupling (V_{DA}). The magnitude of the electronic coupling matrix element indicates the coupling strength between the initial and the final state. The region in which the V_{DA} is small is commonly referred to as nonadiabatic electron transfer. The most profound feature of the Marcus theory for charge separation is the so-called inverted region effect; that is, the charge recombination

Article



Figure 6. (Top) Femtosecond transient absorption spectra of **Sp-PDI**₂ in (a) toluene, (b) THF, and (c) ACN showing the excited-state dynamics after photoexcitation. (Middle) Species associated spectra reconstructed from target analysis of the A \rightarrow GS model for toluene, the A \rightleftharpoons B \rightarrow GS model for THF, and the A \rightarrow B \rightarrow GS model for ACN, respectively, where A is ¹***Sp-PDI**₂, B is the SB-CS state, and GS is the ground state ($\lambda_{ex} =$ 440 nm). (Bottom) Relative population profiles of the excited state are fitted by kinetic models.

kinetics gets slowed down, given that the free energy changes are more significant than the reorganization energy (λ) .^{30,86}

Energetics. The feasibility of the photoinduced symmetrybreaking charge-transfer is determined with the Rehm-Weller formulation⁸⁷ based on the Born dielectric continuum model, which estimates the energy gap between the optically excited state (E_{00}) and the ion pair using the redox potentials (E_{redox}) and the Coulomb penalty for holding the charges at a fixed distance. The optical bandgap (E_{00}) was determined by the crossing points of the normalized absorption and emission spectra. The electrochemical bandgap (E_g) of Sp-PDI₂ was calculated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) with the ferrocene/ferrocenium (Fc/Fc^{+}) couples as a reference in dry CH₂Cl₂ under a nitrogen atmosphere (Figure S11 and Table S8). As previously reported,^{60,61} the Ref-PDI exhibits two distinct reversible reduction waves ($E_{1(red)} = -1.15$ and $E_{2(red)} = -1.35$ V) and one quasi-reversible oxidation wave ($E_{1(ox)} = 1.20$ V), like PDI,³³ whereas **Sp-PDI**₂ shows four consecutive redox waves $(E_{1(\text{red})} = -0.99, E_{2(\text{red})} = -1.02, E_{3(\text{red})} = -1.21, \text{ and } E_{4(\text{red})} =$ -1.33 V) and a single oxidation wave at 1.23 V. The distinct redox properties of Sp-PDI₂ conforms the electronic communication between the orthogonally arranged PDI chromophores. The near degeneracy of first and second reduction potentials (-0.99, -1.02 V) of Sp-PDI₂ can be attributed to the destructive interference between the LUMO of the PDI monomer and is consistent with the calculated t_e value (Figures S12 and S13). Thus, Rehm-Weller treatment

gives $\Delta G_{\rm CS} \approx +0.37$, -0.16, and -0.30 eV for Sp-PDI₂ in toluene, THF, and ACN, respectively. The estimated positive free energy change of charge separation ($\Delta G_{\rm CS} \approx +0.37$) in toluene would render SB-CS infeasible in nonpolar solvents (*vide infra*). Calculated $\Delta G_{\rm CS}$ in toluene seems to be a bit higher than expected which could be due to the overestimation of polarity of nonpolar solvents by the Born dielectric continuum model.⁸⁸

SB-CS Dynamics. To unravel the excited-state dynamics responsible for its efficient nonradiative decay, we carried out solvent-dependent femtosecond transient absorption (fsTA) measurement of Sp-PDI₂ in toluene, THF, and ACN solvents. The fsTA spectra of **Sp-PDI**₂ (optical density = 0.2 to 0.3) are shown in Figure 6. Upon photoexcitation at 440 nm, using an \sim 100 fs laser pulse, the fsTA spectra of Sp-PDI₂ in nitrogenpurged toluene solution (Figure 6a) exhibit the characteristic features of the singlet excited state of a perylenediimide chromophore (Figure S14).^{33,35} The fsTA spectra display negative ground-state bleach (GSB)/stimulated emission bands (SE) at \sim 465 to 626 nm, alongside the positive broad excited-state absorption (ESA) features are observed, with peaks at 651, 733, and 755 nm. The SB-CS process is switched off in toluene because the charge-separated state has higher energy than the excited singlet ($\Delta G_{CS} \approx +0.37$ eV). On the other hand, Sp-PDI₂ in THF ($\varepsilon_s = 7.6$, $\Delta G_{CS} \approx -0.16$ eV) shows remarkably different excited-state dynamics, as shown in Figure 6b, characterized by fast decay of the 1 Sp-PDI₂* local singlet state (GSB was seen as a negative band extending from

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Table 3. Time Constants (τ), Rate Constants ((k), Driving forces ((ΔG) , Reorganization 1	Energy (λ) , and Activation	Barrier
$(\Delta G^{\#})$ for Symmetry-Breaking Charge Separation	on (SB-CS), Back Ch	harge Transfer (BCT),	and Charge Recombination	(CR) in
Sp-PDI ₂ ^{<i>a</i>}		-	-	

solvent	$ au_{ m CS} (m ps)$	$\begin{array}{c} k_{\rm CS} \times 10^{10} \\ (\rm s^{-1}) \end{array}$	ΔG_{CS} (eV)	$\lambda_{\rm CS}$ (eV)	$ au_{ m BCT} \ (m ps)$	$k_{\mathrm{BCT}} \underset{\left(\mathrm{s}^{-1}\right)}{\times} 10^{8}$	$ au_{ m CR} \ (m ns)$	$\begin{array}{c} k_{\rm CR} \times 10^8 \\ (\rm s^{-1}) \end{array}$	${\Delta G_{ m CR}\over m (eV)^b}$	$\frac{\Delta G_{\mathrm{CR}}}{(\mathrm{eV})^c}$	$\lambda_{\rm CR} \ ({ m eV})$	$\Delta G^{\#}$ (eV)
toluene	-	-	+0.37	0.24	-	-	-	-	-2.60	-2.70	0.48	0.38
THF	2.96	33.78	-0.16	0.57	132	75.75	12.20	0.82	-2.08	-2.41	0.81	0.18
ACN	0.627	159.48	-0.30	0.96	-	-	1.66	6.02	-1.94	-2.30	1.20	0.11
a_{τ} and k	$= 1/\tau$ fr	om target fits	of visible	fsTA spec	tra ΛG	for CS and C	R from	Rehm-Weller	analysis ¹	Constrained	density	functional

" τ and $k = 1/\tau$ from target fits of visible fsTA spectra. ΔG for CS and CR from Rehm–Weller analysis. "Constrained density functional computation." λ for CS and CR calculated based on eqs 6, 7, and 8.

~465 to 585 nm, accompanied by a positive ESA band in the \sim 608–770 nm range) with the evolution of a broad new transient species characterized by positive features in the visible region at ~590, 699, and 731 nm. The newly emerging ESA signature serves as a direct measure of the SB-CS in THF; however, the characteristic signature of the PDI radical cation peak at ~730 nm is not evident in ESA as compared to the radical anion peak of PDI at ~587 nm.^{35,89} The intensity of the ESA band at ~650-750 nm is almost intact during the SB-CS, which could be due to the presence of an equilibrium between the singlet excited state and CS state. The solvation of Sp-PDI₂ by moderately polar THF reduces the energy of the CS state close to the local singlet excited state. A similar equilibrium between the excited singlet state and the SB-CS state of zinc dipyrrins, 9,9'-bianthryl, and PDI dimers was documented in the literature in weakly polar solvents.^{35,40,41}

Further, we performed fsTA measurements of Sp-PDI₂ in more polar ACN ($\varepsilon_{\rm s} = 37.50$) to probe the effect of solvent polarity on charge separation, where SB-CS is more energetically feasible, $\Delta G_{\rm CS} \approx -0.30$ eV (Figure 6c). The dynamics of the photoexcited dimers in ACN was similar to that observed in THF and displays a broad positive band (ESA) around ~657 nm and pronounced negative bands after photoexcitation at the initial time (~465–567 nm). Subsequently, these bands decay rapidly by a concomitant growth of two new absorption bands at around ~581 and ~727 nm corresponding to the spectral features of the PDI radical cation and radical anion, respectively.^{35,89}

To extract the kinetic components responsible for these transformations in the total spectra, a singular value decomposition (SVD) followed by target analysis (using A \rightarrow GS or A \rightarrow B \rightarrow GS or A \rightleftharpoons B \rightarrow GS kinetic models) of the time versus wavelength-based three-dimensional map of fsTA spectra was executed.^{90,91} Selected kinetic trace superimposed target analysis fitted curves at different wavelengths are chosen to display the fitting qualities as shown in Figures S15, S16, and S17. In the case of Sp-PDI₂ in toluene, species associated spectra (SAS) show a single principal component corresponding to the locally excited singlet state (A) $(S_1 - S_n)$ electronic transitions). The lowest singlet excited state (¹Sp-PDI₂*) does not decay entirely to the ground state (GS) within the given experimental time scale, plausibly due to the long singlet lifetime (fitted lifetime, τ_A = 6.95 ns), consistent with the fluorescence decay of Sp-PDI₂ in toluene ($\tau_{\rm Fl}$ = 6.62 ns). However, in polar solvents, THF, and ACN, species associated spectra (SAS) of Sp-PDI₂ showed two principal components that are ascribed to the locally excited singlet state (A) and the SB-CS state (B, Figure S18). The fs-TA data of $Sp-PDI_2$ in THF were fitted with a target model (A \Rightarrow B \rightarrow GS) to account for an equilibrium process between the LE state and CS state, whereas in ACN, the sequential target model (A \rightarrow B

 \rightarrow GS) was employed. The forward and backward chargetransfer rate constants $(k_{A \to B} \text{ and } k_{A \leftarrow B})$ between the locally excited state and CS states of Sp-PDI₂ in THF are $(2.96 \text{ ps})^{-1}$ and $(132 \text{ ps})^{-1}$, respectively. In ACN, the excited singlet state (A) of **Sp-PDI**₂ decays within a rate constant of $k_{A \rightarrow B} = (627)$ $(fs)^{-1}$, which initiates the ultrafast growth of a new species characterized by positive features in the visible region (\sim 565 to 775 nm). The spectroscopic signature of the newly formed species in ACN and THF persists across the entire time window of the transient absorption measurement (3.5 ns). Subsequently, these charge-separated states decay by charge recombination (CR) to the ground state with rate constants of $k_{B\to GS} = (1.66 \text{ ns})^{-1}$ and $(12.20 \text{ ns})^{-1}$ for ACN and THF, respectively, with no evidence of triplet excited state. An isosbestic point observed at ~625 and 634 nm for ACN and THF, respectively, indicates the transformation of a singlet state to the prolonged charge-separated state. The observed ultrafast transient dynamics show photoinduced intramolecular SB-CS behavior of **Sp-PDI**₂ in a polar solvent, consistent with its quenched fluorescence in polar solvents (THF and ACN). The CS and CR rate constants (k) and time constants (τ) for Sp-PDI₂ in different solvents are summarized in Table 3. The target fitted time constants of charge separation and recombination are $\tau_{\rm CS}$ = ~2.96 ps and $\tau_{\rm CR}$ = ~12.20 ns in THF, respectively, while the corresponding time constants are somewhat shorter in more polar ACN ($\tau_{\rm CS}$ = 0.627 ps and $\tau_{\rm CR}$ $= \sim 1.66$ ns).

 au_{CR} obtained from target analysis can be employed to explain the fluorescence emission profile and fluorescence lifetime decay of Sp-PDI₂ in THF and ACN. In polar solvents, Sp-PDI, displays biexponential decay (Figure S8 and Table S7), and the fluorescence lifetime of the first component ($au_{
m Fl}^1$ = 1.63 and 14.2 ns for ACN and THF, respectively) is comparable with the charge recombination lifetime of **Sp-PDI**₂ (τ_{CR} = 1.66 and 12.20 ns for ACN and THF, respectively). Thus, the fluorescence emission of the first component can be assigned to emission originated from the SB-CS state \rightarrow ground state (GS) transition. Analogous radiative emissions from SB-CS to GS transition are reported for DIPYR dimers and 9,9'bianthryl and 10,10'-dicyano-9,9'-bianthryl molecules.^{38,41} Since the locally excited state of Sp-PDI₂ in polar solvents decays within a few picoseconds (627 fs and 2.96 ps in ACN and THF, respectively), the absence of a short lifetime component in the TCSPC lifetime measurements suggests the nonemissive nature of a locally excited state (Figure S8). The symmetry-breaking charge separation of Sp-PDI₂ in polar solvents results from the asymmetric distribution of polarizabilities around the Greek cross-arranged molecule. The origin of emissive second species having $\tau_{\rm Fl}^2$ = 6.87 and 6.80 ns for ACN and THF, respectively, can be explained by the presence of different microenvironments around the photoexcited molecules; i.e., a photoexcited donor/acceptor dyad undergoes charge separation in some environments, and in another microenvironment, it may not undergo the charge separation.^{92,93}

The emissive nature of the charge-separated state of **Sp**-**PDI**₂ in THF can further be substantiated by the picosecond time-resolved emission spectra (TRES) measurement, followed by global analysis (GA) of the kinetic traces (Figures S19 and S20 and Supporting Information, section 1.9). The GA of time versus wavelength plots gave a DAS-based deconvolution of the temporal components in fluorescence emission. The DAS and population profile of **Sp-PDI**₂ in THF reveal the presence of two independent emissive species ($\tau_{\rm A} = 5.8$ ns and $\tau_{\rm B} = 13.9$ ns). The spectral character of the long-lived species ($\tau_{\rm B} = 13.9$ ns) is assigned to CS \rightarrow GS emission which is red-shifted to the LE \rightarrow GS emission feature ($\tau_{\rm A} = 5.8$ ns) in THF where the microenvironmental effect does not favor the charge separation.

Evaluation Using Electron Transfer Theory. Since the nature of Sp-PDI₂ excited states is different in the diverse solvent environment (toluene, THF, and ACN), discussion of SB-CS and CR dynamics in terms of classical Marcus theory is not straightforward.^{81,82} Though SB-CS is a part of the general electron transfer reaction and realizations of electron transfer theory can be embraced to describe the dynamics of SB-CS and CR.^{26,30,94} More quantitative analysis of CS and CR kinetics requires estimation of Marcus parameters (ΔG , λ , and *V*) and the activation barrier ($\Delta G^{\#}$) of **Sp-PDI**₂. Driving forces (i.e., Gibbs free energy changes) of charge separation (ΔG_{CS}) and charge recombination $(\Delta G_{\rm CR})$ were estimated by the Weller approximation (Table 3 and Supporting Information, section 1.7).⁸⁷ The Gibbs free-energy change of charge separation with negative values shows that SB-CS is thermodynamically allowed for $Sp-PDI_2$ in both THF and ACN solvents, which agrees with the fluorescence quenching behavior. For Sp-PDI₂, in moderate polar aprotic solvent THF, the value of $\Delta G_{\rm CS}$ is -0.16 eV, and in polar solvent acetonitrile, Gibbs free energy changes of SB-CS become more negative ($\Delta G_{CS} = -0.30 \text{ eV}$); i.e., the driving forces for charge separation are more prominent with the increasing solvent polarity. In contrast, Gibbs free energy changes of CR in ACN ($\Delta G_{CR} = -1.94$ eV) are less negative than THF $(\Delta G_{\rm CR} = -2.08 \text{ eV})$; the driving forces for charge recombination are smaller with the increasing solvent polarity. From the Marcus eq 5, it is evident that the reorganization energy (λ) plays a crucial role in charge separation kinetics. Reorganization energy is composed of the solvent shell reorganization energy (λ_s) and the solute molecular structure reorganization energy upon charge separation ($\lambda_{i(CS)}$) and charge recombination $\lambda_{i(CR)}$.^{95–97} Internal reorganization energy (λ_i) was calculated by employing constrained DFT for the charge-separated state and DFT for the ground-state calculation.

$$\lambda_{i(CS)} = E_{CS}(R_{eq}^{GS}) - E_{CS}(R_{eq}^{CS})$$
(6)

The first term is the energy calculated at the optimized ground state (GS) geometry in the CS redox state, while the second term is the energies of the CS at their equilibrium geometries. This calculation provides $\lambda_{i(CS)} = 0.20$ eV.

$$\lambda_{i(CR)} = E_{GS}(R_{eq}^{CS}) - E_{GS}(R_{eq}^{GS})$$
⁽⁷⁾

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The first term corresponds to the energy calculated at the optimized CS geometry in the GS state, and the second term is the energy of the GS at their equilibrium geometries. Calculated $\lambda_{i(CR)} = 0.44$ eV (Figure S21 and Table S9, and Supporting Information, section 1.10). The solvent reorganization energy is computed using the dielectric continuum theory and depends on the radii of the donor (r_D) and acceptor (r_A), the center-to-center distance (r_{DA}), and the optical (ε_{op}) and static (ε_s) dielectric constants of the solvent as given in eq 8:⁸⁴

$$\lambda_{\rm S} = \frac{\mathrm{e}^2}{4\pi\varepsilon_0} \left(\frac{1}{2r_{\rm A}} + \frac{1}{2r_{\rm D}} - \frac{1}{r_{\rm DA}} \right) \left(\frac{1}{\varepsilon_{\rm op}} - \frac{1}{\varepsilon_{\rm s}} \right) \tag{8}$$

Sp-PDI₂ is a rigid organic molecule for which theoretically calculated low internal reorganization energy ($\lambda_{i(CS)} = 0.20 \text{ eV}$ and $\lambda_{i(CR)} = 0.44 \text{ eV}$) is reasonable.³⁰ Thus, the total reorganization energy for the charge recombination (λ_{CR}) process would be 1.20 eV for ACN, which is approximately 0.74 eV lower than $-\Delta G_{\rm CR}$. The charge recombination of **Sp**-**PDI**₂ in ACN falls under the inverted region (where $-\Delta G_{CR}$ > $\lambda_{\rm CR}$), whereas in THF, the total reorganization energy ($\lambda_{\rm CR}$ = 0.81 eV) is 1.27 eV lower than $-\Delta G_{CR}$ (2.08 eV), pushing the system into the deeper inverted region compared to ACN (Table 3). This could rationalize the slow charge recombination of Sp-PDI₂ in moderately polar THF (τ_{CR} = 12.20 ns) than more polar solvent ACN (τ_{CR} = 1.66 ns). Several research groups unequivocally established the presence of an inverted region in charge recombination kinetics.^{99–102} Theoretically calculated ΔG_{CR} for different solvents is in good agreement with the magnitude estimated by Weller analysis (Table 3 and Supporting Information, section 1.10).

Another factor controlling the $k_{\rm CS}$ and $k_{\rm CR}$ is the electronic coupling matrix element (V). This term is used to quantify the mixing of two states or, more intuitively, the electronic communication between the electron/hole donor and acceptor. Theoretically calculated charge-transfer integrals provide an estimation of effective electronic coupling (V). The magnitude of hole transfer coupling ($t_{\rm h} = -0.147$ eV) is significantly higher than that of electron transfer coupling ($t_e = -0.001 \text{ eV}$), facilitating the excited state SB-CS of **Sp-PDI**₂ in polar solvents via hole transfer (Figure S22). The effective hole transfer electronic coupling ($V_{CS} = -0.147 \text{ eV}$) can explain the origin of the significantly accelerated charge separation rate in THF and ACN. Calculated electronic coupling of CR (V_{CR} = -0.018 eV) is much lower than CS ($V_{CS} = -0.147$ eV), supporting the decelerated CR processes over the CS of Sp- \mathbf{PDI}_2 in THF and ACN. Since the $2V < \lambda$, SB-CS in \mathbf{Sp} - \mathbf{PDI}_2 falls under a weak coupling regime.¹⁰³ A remarkable feature of Marcus theory is the relation between the kinetic barrier of charge-transfer and the reaction thermodynamics. When the reaction is more exergonic in nature, the barrier for electron transfer reduces. The activation barrier for the SB-CS is calculated by eq 9:

$$\Delta G^{\#} = \frac{(\Delta G_{\rm CS} + \lambda)^2}{4\lambda} \tag{9}$$

The reorganization energy has a strong effect on $\Delta G^{\#}$. The estimated activation barrier in different solvents is given in Table 3.

The ultrafast charge separation of **Sp-PDI**₂ in ACN ($k_{CS} = 159.48 \times 10^{10} \text{ s}^{-1}$) compared to the THF ($k_{CS} = 33.78 \times 10^{10} \text{ s}^{-1}$) solvent stems from the low activation energy for a

nonadiabatic reaction. $\Delta G^{\#}$ for the more polar ACN solvent has amounted to 0.11 eV, and moderate polar THF is 0.18 eV. Estimated Marcus parameters and activation barriers are given in Table 3. The potential energy surfaces are shown schematically in Figure 7.



Figure 7. Schematic potential energy diagrams for SB-CS of **Sp-PDI**₂ in different solvents.

Chemical redox titration experiments using cobaltocene and antimony pentachloride were performed to confirm the chargeseparated state features of **Sp-PDI**₂ observed in the femtosecond transient absorption spectroscopy. Upon addition of reducing agent cobaltocene (CoCp₂), a decrease in the neutralstate absorption band is accompanied by the appearance of new bands at ~715 nm (Figure S23). On the other hand, partial oxidation of **Sp-PDI**₂ with antimony pentachloride (SbCl₅) results in positive features at ~574 nm (Figure S24).

CONCLUSIONS

To conclude, we report the unequivocal evidence for the prolonged SB-CS state ($k_{CS}/k_{CR} = 2647$ in ACN) (Table S1) in a null exciton-coupled spiro-conjugated perylenediimide dimer (Sp-PDI₂). Single-crystal structure examination of Sp-PDI₂ confirms the Greek cross (+)-shaped molecule with two π -conjugated perylenediimide chromophores linked by an sp³hybridized carbon atom. The monomer-like steady-state absorption spectrum and photoexcited-state properties of Sp-PDI₂ in toluene advocate negligible exciton coupling among the orthogonally arranged PDI molecules. The interference between the theoretically calculated negligible contributions of $J_{\rm coul}$ and $J_{\rm CT}$ resulted in null exciton coupling of an edge-toedge arranged perylenediimide dimer possessing orthogonal orientation of transition dipoles. Sp-PDI2 imparts selective hole-transfer coupling owing to the constructive and destructive interaction between the HOMOs and LUMOs of PDI molecules, respectively. The fragment-based excited-state

analysis of Sp-PDI₂ exhibited localized Frenkel exciton in the first two degenerate excited states $(S_1 \text{ and } S_2)$ and chargetransfer (CT) character in the degenerate S_3 and S_4 states. The rotational angle-dependent Coulombic and charge-transfer coupling calculations provided significant values for lower rotational angles, manifesting impeccable evidence for the ability of Greek cross (+)-architecture in lowering excitonic coupling. The solvent-dependent fsTA measurement of Sp-PDI₂ demonstrated the SB-CS in polar solvents. The charge separation reactions of Sp-PDI₂ in polar solvents are in the Marcus normal region ($\Delta G_{CS} < \lambda$), and k_{CS} values follow the expected quadratic dependence on ΔG_{CS} ; i.e., k_{CS} increases with increment in CS driving forces. The lower activation barrier ($\Delta G^{\#}$) for CS in ACN than THF further supported that k_{CS} (ACN) > k_{CS} (THF). The CR reactions of **Sp-PDI**₂ lie far into the Marcus inverted region $(\Delta G_{\rm CS} > \lambda)$. Solventdependent studies demonstrate the rate of CR in polar solvents following the order ACN > THF, with CR becoming slower at higher driving forces. The current work integrates two fundamental concepts of photophysics, null exciton splitting and symmetry-breaking charge separation, as an innovative strategy to generate an efficient long-lived chargeseparated state. Greek cross (+)-arrangement of Sp-PDI₂ can be considered as an ideal system that highlights the explicit correlation between the relative orientation of the chromophoric system and its orbital interaction in dictating complex excited-state dynamics. Further efforts are underway to achieve a more prolonged charge-separated state in near-orthogonal arranged PDI dimers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c05793.

Experimental and computational methods, CCDC number, tables, and figures (PDF)

Accession Codes

CCDC 2086823 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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