Excimer Evolution Hampers Symmetry-Broken Charge Separated State

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Section 1: Materials and Methods

All chemicals were obtained from commercial suppliers and used as received without further purification. All reactions were carried out in oven-dried glassware prior to use. Solvents were dried and distilled by standard laboratory purification techniques. TLC analyses were performed on recoated aluminum plates of silica gel 60 F254 plates (0.25 mm, Merck), and developed TLC plates were visualized under short and long-wavelength UV lamps. Flash column chromatography was performed using silica gel of 200-400 mesh employing a solvent polarity correlated with the TLC mobility observed for the substance of interest. Yields refer to chromatographically and spectroscopically homogenous substances. 1H and 13C NMR spectra were measured on a 500 MHz Bruker avance DPX spectrometer. The internal standard used for 1H and 13C NMR is tetramethylsilane (TMS). High-resolution mass spectra (HRMS) were recorded on Thermo scientific Q-exactive mass spectrometer using the Atmospheric pressure chemical ionization (APCI, positive mode) technique. Photophysical measurements of the derivatives were carried out in a cuvette of 3 mm path length. Absorption and emission spectra were recorded on Shimadzu UV-3600 UV-VIS-NIR and Horiba Jobin Yvon Fluorolog spectrometers, respectively. Lifetime measurements were carried out in an IBH picosecond time-correlated single-photon counting (TCSPC) system. The pulse width of the excitation (λexc = 478 nm) source is determined to be <100 ps, and 495 nm long-pass filter (Newport) was used to minimize the scatter arising from the laser source. The fluorescence decay profiles were de-convoluted using DAS6.3 and fitted with exponential decay, minimizing the χ2 values. Temperature-dependent (90K-250K) photoluminescence measurements were carried out using liquid nitrogen cryostat (Janis VNF-100). Dilute thin films (1% in polystyrene) of dimers (SC-SPDI2 and SC-NPDI2) were prepared from toluene solution on quartz to examine the effect of rigidification on excited-state decay dynamics.

1.1 Computational Analysis
All the calculations are carried out in Gaussian 16 employing the b3lyp functional with Grimme’s d3 dispersion and def2svp basis set at the DFT level of theory unless stated otherwise.1 Vertical excitation energies and oscillator strengths were calculated employing time-dependent DFT (TD-DFT) at the ωb97xd/def2svp level of theory. The frontier molecular orbitals (FMO) of monomers and dimers were obtained from the generated cube files of energy calculations. Hole-electron analyses were carried out using Multiwfn version 3.7.8.2 Multiwfn uses post-processed Gaussian 16 output files generated at ωb97xd/def2svp level of theory for the respective analyses. 3-pentane and hexane alkane chains in the dimers and monomers were replaced with methane group during the computation calculation in order to reduce the computational cost.

1.2 Time-Resolved Emission Spectra (TRES) Analysis
Time-resolved emission spectral (TRES) measurements followed by global analysis (GA) of the kinetic traces (at all wavelengths) were performed in an IBH picosecond time-correlated single-photon counting (TCSPC) system and glotaran2 software, respectively. The singular value decomposition (SVD) followed by the GA of the time vs. wavelength plots furnished a evolution associated spectra (EAS) based deconvolution of the temporal components in the fluorescence emission. Time-resolved emission spectral (TRES) investigation of SC-SPDI2 and SC-NPDI2 in toluene was carried out by exciting at 478 nm (DD-470L; DD-470L; pulse width <60 ps).

1.3 Electrochemistry
Cyclic voltammograms and differential pulse voltammograms were acquired on CH instruments, inc electrochemical workstation at room temperature, employing a three-electrode single-compartment cell: glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and silver wire as the reference electrode. Working and reference electrodes were polished on a felt pad with 0.05 μm Al2O3 suspension, sonicated in acetone for about 3 minutes, and dried before each experiment; the Pt wire was flame-cleaned. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAF), was previously dried under vacuum, dichloromethane was degassed prior to use, and all measurements were performed under a nitrogen atmosphere. The concentration of TBAF used was typically 100 times of the
analyte. Calibration of the instrument was performed using the ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple as an external standard and measured under the same condition before and after the measurement of samples. \(E_{\text{Fc/Fc}}\) is the potential of Fc/Fc\(^+\) vs. Ag. The energy level of Fc/Fc\(^+\) was assumed to be −4.8 eV with respect to vacuum.\(^6\) HOMO and LUMO energies were calculated using the following equation.\(^6\)

\[
E_{\text{opt}}^{\text{HOMO}} = 1240/\lambda_{\text{onset}} \quad \text{S1}
\]

\[
E_{\text{LUMO}} = -(E'_{\text{red}} + 4.8 - E_{\text{Fc/Fc}}) \text{ eV} \quad \text{S2}
\]

\[
E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{opt}}^{\text{HOMO}} \quad \text{S3}
\]

respectively, where \(E'_{\text{red}}\) are the experimentally measured reduction potentials vs. Ag. \(E_{\text{LUMO}}\) and \(E_{\text{HOMO}}\) are the corresponding to LUMO and HOMO energy levels.

1.4 Weller Analysis

The change in free energy for the charge-separation and charge recombination (\(\Delta G\)) were estimated employing the followed relations based on the Born dielectric continuum model.\(^6\)

\[
\Delta G_{\text{cs}} = e[E_{\text{ox}} - E_{\text{red}}] - E_{\text{so}} + C + S \quad \text{S4}
\]

\[
C = \frac{-e^2}{4\pi\varepsilon_0\varepsilon_s r_{\text{AD}}} \quad \text{S5}
\]

\[
S = \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r_{\text{D}}} + \frac{1}{r_{\text{A}}} \right) \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_{\text{sp}}} \right) \quad \text{S6}
\]

\[
\Delta G_{\text{cr}} = -(E_{\text{so}} + \Delta G_{\text{cs}}) \quad \text{S7}
\]

Where \(e\) is the charge of the electron, \(E_{\text{ox}}\) and \(E_{\text{red}}\) are the oxidation and reduction potentials, respectively, \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon_s\) is the static dielectric constant of the solvent, and \(\varepsilon_{\text{sp}}\) is the static dielectric constant of the solvent used for electrochemical measurements, \(r_{\text{AD}}\) is the donor-acceptor distance, \(r_{\text{D}}\) and \(r_{\text{A}}\) are the cation and anion hard-sphere radii, respectively (were approximated as \(r_{\text{AD}}^2/2\)) and \(E_{\text{so}}\) is the energy of the excited singlet (donor) state. At finite distances, the Coulombic attraction energy between(C) the radical ion-is given by a point-charge model as \((1/\varepsilon_{\text{sp}} r_{\text{AD}})\). Since SC-SPDI\(_2\) and SC-NPDI\(_2\) exhibit excimer formation in all the solvents, the optical bandgap \((E_{\text{so}}\) the precursor of SB-CS) was determined by the intersection of the normalized absorption and emission spectra of monomeric SPDI and NPDI.

1.5 Femtosecond transient absorption (fsTA) measurement

A Spectra-Physics Mai Tai SP mode-locked laser (86 MHz, 800 nm) was used as a seed for a Spectra-Physics Spitfire ace regenerative amplifier (1 kHz, 5.5 mJ). A fraction of the amplified output was used to produce a 470 nm pump pulse by TOPAS. A residual pulse of 800 nm was sent through an optical delay line inside an Exciplex pump-probe spectrometer to produce a white light continuum by employing a sapphire crystal. The white light continuum was split into two, and the streams were used as a probe and reference pulses. The femtosecond transient absorption spectra of the sample were recorded using a dual diode array detector, having a 200 nm detection window and 3.5 ns optical delay. Sample solutions were prepared in a rotating cuvette with a 1.2 mm path length. Determination of an appropriate instrument response function (IRF) is needed for accurate deconvolution of recorded transient absorption data. The IRF was determined by a solvent (10% benzene in methanol) two-photon absorption and was found to be ~110 fs at about 530 nm. A neutral density filter (80%) was used for controlling the incident flux on the sample. fsTA measurement of dimers and monomers in different solvents were recorded by photoexciting the sample with 470 nm, 200 nJ, and 100 fs pulses to moderate singlet–singlet annihilation that often arises in multi-chromophoric assemblies.\(^7\) The observed kinetic components were laser intensity-independent, ruling out the chance of singlet–singlet annihilation.

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1.6 Global Analysis
Target analyses of the fsTA spectra were performed using the Glotaran software. The procedure evaluates the instrument time response function and the group velocity dispersion of the white continuum and allows one to compute decay time constants and dispersion-compensated spectra. All the wavelengths were analyzed in target analysis concurrently, employing a target model to give evolution associated spectra (EAS). The EAS indicates that the evolution of the spectra in time does not necessarily denote a real physical/chemical species. EAS designates the spectral changes that occur with their associated time constants.

1.7 TheoDORE Analysis
The excitations of orthogonally arranged core annulated perylenediimide dimers at the DFT optimized structure were analyzed using TheoDORE. The calculations were carried out in Gaussian 16 at TD-ωb97xd/def2svp level of theory. For the dimer systems under investigation, each monomer is considered as a fragment. The parameters used to investigate the excited state characteristics are participation ratio (PR), mean position (POS) of initial orbital (hole) and final orbital (electron), and charge transfer character (CT). The magnitude of PR relates to the number of fragments participating in the excitation; hence, and ranges from 1 to 2. When the exciton localized one fragment, PR~1.0 and PR~2.0 when the exciton delocalized in both fragments. POS provides the mean position of hole and electron for a particular excitation. Charge transfer states and delocalized Frenkel states show POS = 1.5. If the Frenkel state is localized on monomer A, then POS = 1, and if localized on monomer B, POS = 2, for a dimer AB. Finally, CT is related to the total weight of configurations where initial and final orbitals are situated on different fragments. A CT value of 1 denotes the presence of a charge-separated state, and CT = 0 refers to Frenkel states. Further, electron-hole correlation plots were generated for analyzing the excitonic character for the perylenediimide dimer systems. If the shade is present only in the off-diagonal parts, the excitonic character is Frenkel. Diagonal shades refer to a CT state.
Section 2: Synthesis and Characterization

Scheme S1: Showing the synthesis scheme for monomers (SPDI and NPDI) and dimers (SC-SPDI\textsubscript{2} and SC-NPDI\textsubscript{2}).

Synthesis of NPDI:
The synthesis of NPDI was carried out following reported procedures.\textsuperscript{10} NH-PDI (0.50 g, 0.92 mmol) and potassium carbonate (0.25 g, 1.8 mmol) were added to a round-bottom flask. Approximately 20 mL dry N,N'-dimethylformamide was added, followed by the addition of 1-bromo-hexane (0.27 g, 1.7 mmol). The reaction mixture was purged with nitrogen followed by heating at 170 °C for 1 hour. After the completion of the reaction, the reaction mixture was cooled to room temperature. The compound was extracted using water and dichloromethane. The organic phase was collected and the solvent was removed using a rotary evaporator to give a crude solid. The crude product was purified using column chromatography. The product fraction was collected and the solvent was removed in vacuo to give a red solid. **Yield**: 65%

NPDI: 1H NMR (500 MHz, CDCl\textsubscript{3}, ppm) $\delta$ = 8.91 (s, 2H), 8.87-8.84 (m, 2H), 8.82-8.76 (m, 2H), 5.30-5.21 (m, 2H), 4.80 (t, 2H), 2.46-2.34 (m, 4H), 2.20-2.12 (m, 2H), 2.11-2.01 (m, 4H), 1.45-1.28 (m, 6H), 1.03 (t, 12H), 0.87 (t, 3H)

13C NMR (500 MHz, CDCl\textsubscript{3}, ppm) $\delta$ = 133.71, 131.57, 123.59, 122.76, 120.72, 118.42, 56.77, 45.91, 30.47, 30.30, 25.81, 24.22, 21.42, 12.90, 10.47

HRMS (APCI) m/z calculated for C\textsubscript{40}H\textsubscript{42}N\textsubscript{3}O\textsubscript{4}: 628.3175, Observed: 628.3164

Synthesis of SPDI:
The synthesis of SPDI was carried out following modified reported procedures.\textsuperscript{11} Sulfur (160 mg, 4.9 mmol) was dissolved in N-methylpyrrolidone (12 mL, 70°C). Compound NO\textsubscript{2}-PDI (0.50 g, 0.62 mmol) was added under nitrogen to the round-bottom flask. The mixture was heated (130°C, ca. 75 min, until the starting material could not be detected by TLC). After the completion of the reaction, the reaction mixture was poured into water (150 mL) and the precipitate was collected by vacuum filtration followed by washing with water. The mixture is dried and purified by column chromatography. **Yield**: 52%

SPDI: 1H NMR (500 MHz, CDCl\textsubscript{3}, ppm) $\delta$ = 9.204 (d, 2H), 8.826 (d, 4H), 5.144 (m, 2H), 2.286-2.53 (m, 4H), 1.96-1.932 (m, 4H), 0.915 (t, 12H)

13C NMR (500 MHz, CDCl\textsubscript{3}, ppm) $\delta$ = 137.20, 131.57, 130.46, 125.26, 122.54, 122.16, 76.25, 75.99, 56.97, 24.11, 10.41

HRMS (APCI) m/z calculated for C\textsubscript{34}H\textsubscript{29}N\textsubscript{2}O\textsubscript{4}S\textsubscript{4}[(M+H)\textsuperscript{+}]: 561.1848, Observed: 561.1842
Synthesis of SC-NPDI2:
The synthesis of SC-NPDI2 was carried out following the reported procedures. Br-NPDI (0.37 g, 0.52 mmol) and zinc dust (170 mg, 2.6 mmol) were added to a 20 mL roundbottom flask. Approximately 40 mg of bis(dibenzylideneacetone)palladium(0) was added to the mixture. The flask was sealed under a nitrogen atmosphere and 20 mL of N’N-dimethylformamide was added. The reaction mixture was purged with nitrogen for 10 minutes and was heated to ~100 °C for 2.5 hours. After the completion of the reaction, the crude solid obtained after removing the solvent in vacuo was purified using column chromatography. A dark red solid was obtained after the initial purification. For further purification, the red solid was boiled in 100 mL of isopropanol with vigorous stirring for approximately 1 hour followed by cooling to room temperature and filtration using a Buchner funnel, resulting in a bright red solid. Yield: 38%.

**SC-NPDI2: 1H NMR (500 MHz, CDCl3, ppm)** \( \delta = 9.30 \) (s, 2H), 9.12 (s, 2H), 8.91 (s, 2H), 7.99 (s, 2H), 7.74-7.72 (m, 2H), 5.35-5.16 (m, 4H), 2.42-2.31 (m, 8H), 2.28-2.21 (m, 4H), 2.07-2.00 (m, 4H), 1.93-1.84 (m, 4H), 1.64-1.56 (m, 4H), 1.50-1.45 (m, 4H), 1.42-1.37 (m, 4H), 1.06-0.82 (m, 30H).

**13C NMR (500 MHz, CDCl3, ppm)** \( \delta = 139.87, 134.25, 134.03, 131.89, 129.37, 125.81, 123.94, 123.69, 122.55, 121.73, 119.08, 118.81, 56.98, 56.59, 46.12, 30.66, 30.43, 25.99, 24.02, 21.52, 13.00, 10.49, 10.22.

**HRMS (APCI) m/z calculated for C80H81N6O8 [(M+H)+]: 1253.6115,** Observed: 1253.6112

Synthesis of SC-SPDI2:
The synthesis of SC-SPDI2 was carried out following the modified procedures (Scheme 1). Br-SPDI (0.33 g, 0.52 mmol) and zinc dust (170 mg, 2.6 mmol) were added to a 20 mL roundbottom flask. Approximately 40 mg of bis(dibenzylideneacetone)palladium(0) was added to the mixture. The flask was sealed under a nitrogen atmosphere and 20 mL of N’N-dimethylformamide was added. The reaction mixture was purged with nitrogen for 10 minutes and was heated to ~100 °C for 2.5 hours. After the completion of the reaction, the crude solid obtained after removing the solvent in vacuo was purified using column chromatography. A dark red solid was obtained after the initial purification. For further purification, the red solid was boiled in 100 mL of isopropanol with vigorous stirring for approximately 1 hour followed by cooling to room temperature and filtration using a Buchner funnel, resulting in a bright red solid. Yield: 48%.

**SC-SPDI2: 1H NMR (500 MHz, CDCl3, ppm)** \( \delta = 9.61 \) (s, 2H), 9.45 (s, 2H), 8.18-8.10 (m, 4H), 5.30-4.93 (m, 4H), 2.38-2.30 (m, 4H), 2.27-2.16 (m, 4H), 2.04-1.96 (m, 4H), 1.94-1.85 (m, 4H), 1.04-0.83 (m, 24H).

**13C NMR (500 MHz, CDCl3, ppm)** \( \delta = 140.81, 138.99, 138.42, 133.30, 131.95, 131.63, 130.86, 129.04, 128.23, 126.96, 126.52, 126.36, 125.26, 124.19, 58.23, 57.87, 31.94, 29.71, 29.38, 24.98, 24.93, 22.71, 14.14, 11.47, 11.23.

**HRMS (APCI) m/z calculated for C68H55N4O8S2 [(M+H)+]: 1119.3461,** Observed: 1119.3452
### Section 3: Tables

**Table S1:** Oscillator strength for different transitions of **SPDI** calculated at TD-$\omega$B97XD/def2svp level of theory.

| Molecule | State | Oscillator Strength | Energy (eV) | Wavelength (nm) | Major Orbital Transition |
|----------|-------|---------------------|-------------|-----------------|--------------------------|
| **SPDI** | $S_1$ | 0.7381              | 2.929       | 423.4           | HOMO $\rightarrow$ LUMO  |
|          | $S_2$ | 0.1113              | 3.432       | 361.3           | HOMO-1 $\rightarrow$ LUMO|
|          | $S_3$ | 0.0023              | 4.010       | 309.2           | HOMO-3 $\rightarrow$ LUMO|
|          | $S_4$ | 0.0004              | 4.106       | 302.0           | HOMO-4 $\rightarrow$ LUMO|
|          | $S_5$ | 0                   | 4.109       | 301.7           | HOMO-5 $\rightarrow$ LUMO|
|          | $S_6$ | 0.0009              | 4.119       | 301.0           | HOMO $\rightarrow$ LUMO+2|

**Table S2:** Oscillator strength for different transitions of **NPDI** calculated at TD-$\omega$B97XD/def2svp level of theory.

| Molecule | State | Oscillator Strength | Energy (eV) | Wavelength (nm) | Major Orbital Transition |
|----------|-------|---------------------|-------------|-----------------|--------------------------|
| **NPDI** | $S_1$ | 0.7381              | 2.872       | 431.7           | HOMO $\rightarrow$ LUMO  |
|          | $S_2$ | 0.1138              | 3.282       | 377.8           | HOMO-1 $\rightarrow$ LUMO|
|          | $S_3$ | 0.0091              | 4.009       | 309.3           | HOMO-2 $\rightarrow$ LUMO|
|          | $S_4$ | 0.0003              | 4.126       | 300.5           | HOMO-4 $\rightarrow$ LUMO|
|          | $S_5$ | 0                   | 4.132       | 300.0           | HOMO-5 $\rightarrow$ LUMO|
|          | $S_6$ | 0.0001              | 4.139       | 299.6           | HOMO-3 $\rightarrow$ LUMO|
|          |       |                     |             |                 | HOMO $\rightarrow$ LUMO+2|

**Table S3:** Oscillator strength for different transitions of **SC-SPDI$_2$** calculated at TD-$\omega$B97XD/def2svp level of theory.

| Molecule | State | Oscillator Strength | Energy (eV) | Wavelength (nm) | Major Orbital Transition |
|----------|-------|---------------------|-------------|-----------------|--------------------------|
| **SC-SPDI$_2$** | $S_1$ | 0.6818              | 2.906       | 426.6           | HOMO $\rightarrow$ LUMO  |
|          | $S_2$ | 0.6179              | 2.929       | 423.3           | HOMO $\rightarrow$ LUMO+1|
|          | $S_3$ | 0.3322              | 3.388       | 365.9           | HOMO-2 $\rightarrow$ LUMO|
|          | $S_4$ | 0.0106              | 3.426       | 361.9           | HOMO-3 $\rightarrow$ LUMO+1|
|          | $S_5$ | 0.0007              | 3.621       | 342.4           | HOMO-1 $\rightarrow$ LUMO|
|          | $S_6$ | 0.0050              | 3.622       | 342.3           | HOMO $\rightarrow$ LUMO+1|
Table S4: Oscillator strength for different transitions of SC-NPDI$_2$ calculated at TD-ωB97XD/ def2svp level of theory.

| Molecule | State | Oscillator Strength | Energy (eV) | Wavelength (nm) | Major Orbital Transition |
|----------|-------|---------------------|-------------|-----------------|--------------------------|
| SC-NPDI$_2$ | S$_1$ | 0.6211             | 2.826       | 438.7           | HOMO → LUMO LUMO-1 → LUMO+1 |
|          | S$_2$ | 0.6466             | 2.866       | 432.5           | HOMO → LUMO+1 HOMO-1 → LUMO |
|          | S$_3$ | 0.3330             | 3.240       | 382.6           | HOMO-2 → LUMO HOMO-3 → LUMO+1 |
|          | S$_4$ | 0.0189             | 3.286       | 377.3           | HOMO-3 → LUMO HOMO-2 → LUMO+1 |
|          | S$_5$ | 0.0013             | 3.585       | 345.9           | HOMO-1 → LUMO HOMO → LUMO+1 |
|          | S$_6$ | 0.0170             | 3.595       | 344.9           | HOMO → LUMO HOMO-1 → LUMO+1 |

Table S5: Summary of redox potentials and HOMO/LUMO calculations of SC-SPDI$_2$ and SC-NPDI$_2$ (CH$_2$Cl$_2$, 298 K, ε$_S$ = 8.93).

| Compound | $b^1E_{1\text{(red)}}$ (v) | $b^2E_{2\text{(red)}}$ (v) | $b^3E_{3\text{(red)}}$ (v) | $b^4E_{4\text{(red)}}$ (v) | $\lambda_{\text{onset}}$ (nm) | $E_{\text{opt}}$ (eV) | HOMO (eV) | LUMO (eV) | $E_00$ (eV) |
|----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|----------------|-----------|-----------|-----------|
| SC-SPDI$_2$ | -0.536                      | -0.616                      | -0.812                      | -0.920                      | 527.00                      | 2.35           | -6.10     | -3.74     | -2.48     |
| SC-NPDI$_2$ | -0.772                      | -0.820                      | -1.056                      | -1.184                      | 551.95                      | 2.25           | -5.85     | -3.60     | -2.34     |

$E_{\text{red}}^\prime$ is the reduction potential vs. Ag and $E_{\text{red}}$ is the reduction potential vs. Fc/Fc$^+$. | |

Table S6: Time constants for the different excited processes as observed from the fsTA measurements of SC-SPDI$_2$ and SC-NPDI$_2$ in different solvents.

| Solvent | Process               | SC-NPDI$_2$  | SC-SPDI$_2$  |
|---------|-----------------------|--------------|--------------|
| TOL     | FE→Ex*                | 23.6±0.2 ps  | 11.3±1.0 ps  |
|         | Ex*→Ex               | 0.79±0.02 ns | 1.12±0.02 ns |
|         | Ex→Triplet/GS        | 7.87±0.02 ns | 8.10±0.01 ns |
|         | FE→SB-CS             | 2.7±0.02 ps  | 1.5±0.1 ps   |
| ACE     | SB-CS→Ex             | 1.66±0.02 ns | 2.01±0.05 ns |
|         | Ex→Triplet           | 3.82±0.04 ns | 5.89±0.01 ns |
|         | FE→SB-CS             | 1.4±0.01 ps  | 0.9±0.1 ps   |
| ACN     | SB-CS→Ex             | 0.71±0.02 ns | 0.84±0.02 ns |
|         | Ex→Triplet           | 2.30±0.04 ns | 5.81±0.03 ns |

FE: Frenkel exciton, Ex*: Unrelaxed excimer, Ex: Relaxed excimer, SB-CS: Symmetry-Breaking Charge Separation
Table S7: Energy ($\Delta E$), oscillator strength (f), mean position (POR), participation ratio (PR) of initial orbital (hole) and final orbital (electron) and charge transfer character (CT) of singlet states in SC-SPD\(_2\) in the FC geometry.

| State | $\Delta E$ (eV) | f    | POS | PR | CT   |
|-------|----------------|------|-----|----|------|
| S\(_1\) | 2.906          | 0.682 | 1.5 | 2  | 0.026 |
| S\(_2\) | 2.929          | 0.618 | 1.5 | 2  | 0.019 |
| S\(_3\) | 3.388          | 0.332 | 1.5 | 2  | 0.023 |
| S\(_4\) | 3.426          | 0.011 | 1.5 | 2  | 0.028 |
| S\(_5\) | 3.621          | 0.001 | 1.5 | 2  | 0.937 |
| S\(_6\) | 3.622          | 0.005 | 1.5 | 2  | 0.937 |

Table S8: Energy ($\Delta E$), oscillator strength (f), mean position (POR), participation ratio (PR) of initial orbital (hole) and final orbital (electron) and charge transfer character (CT) of singlet states in SC-NPD\(_2\) in the FC geometry.

| State | $\Delta E$ (eV) | f    | POS | PR | CT   |
|-------|----------------|------|-----|----|------|
| S\(_1\) | 2.826          | 0.621 | 1.498 | 2 | 0.038 |
| S\(_2\) | 2.867          | 0.647 | 1.502 | 2 | 0.017 |
| S\(_3\) | 3.24           | 0.333 | 1.5  | 2 | 0.021 |
| S\(_4\) | 3.286          | 0.019 | 1.499 | 2 | 0.018 |
| S\(_5\) | 3.585          | 0.001 | 1.501 | 1.971 | 0.947 |
| S\(_6\) | 3.595          | 0.017 | 1.499 | 1.971 | 0.927 |

Table S9: Energy ($\Delta E$), oscillator strength (f), mean position (POR), participation ratio (PR) of initial orbital (hole) and final orbital (electron) and charge transfer character (CT) of singlet states in SC-SPD\(_2\) in the relaxed foldamer geometry.

| State | $\Delta E$ (eV) | f    | POS | PR | CT   |
|-------|----------------|------|-----|----|------|
| S\(_1\) | 2.094          | 0.082 | 1.5  | 2 | 0.375 |
| S\(_2\) | 2.684          | 0.627 | 1.5  | 2 | 0.058 |
| S\(_3\) | 2.788          | 0    | 1.5  | 2 | 0.873 |
| S\(_4\) | 3.114          | 0.019 | 1.5  | 2 | 0.419 |
| S\(_5\) | 3.145          | 0.405 | 1.5  | 2 | 0.27 |
| S\(_6\) | 3.228          | 0.064 | 1.5  | 2 | 0.094 |

Table S10: Energy ($\Delta E$), oscillator strength (f), mean position (POR), participation ratio (PR) of initial orbital (hole) and final orbital (electron) and charge transfer character (CT) of singlet states in SC-NPD\(_2\) in the relaxed foldamer geometry.

| State | $\Delta E$ (eV) | f    | POS | PR | CT   |
|-------|----------------|------|-----|----|------|
| S\(_1\) | 1.938          | 0.063 | 1.5  | 2 | 0.394 |
| S\(_2\) | 2.613          | 0.464 | 1.5  | 2 | 0.203 |
| S\(_3\) | 2.756          | 0.141 | 1.5  | 2 | 0.731 |
| S\(_4\) | 2.932          | 0.213 | 1.5  | 2 | 0.212 |
| S\(_5\) | 3.149          | 0.216 | 1.5  | 2 | 0.483 |
| S\(_6\) | 3.684          | 0.01  | 1.501 | 2 | 0.307 |
Section 4: Figures

**Figure S1**: Optimised structures of core annulated perylenediimide monomers a) **SPDI** and b) **NPDI** showing the in-plane bend in the perylene core.

**Figure S2**: Optimised structures of core annulated perylenediimide monomers a) **SPDI** and b) **NPDI** showing the C-S and C-N bond lengths.

**Figure S3**: Normalised absorption spectra of sulphur annulated (**SPDI**) and nitrogen annulated (**NPDI**) perylenediimide monomers compared to unsubstituted **PDI**.
Figure S4: Optimized geometries of the dimers a) SC-SPDi₂ and b) SC-NPDi₂ in the excited state showing the π-stacked foldamer-like geometry viewed from two different axis. The centroid to centroid distance (d) and the torsional/dihedral angles (φ) between the chromophores are also indicated in the figure.

Figure S5: Molecular structure of di-PDI.

Figure S6: Potential energy curve of the dimers a) SC-NPDi₂ and b) SC-SPDi₂ in the ground state with varying torsional angles.
Figure S7: a) Time-resolved emission spectra (TRES, $\lambda_{ex} = 478$ nm) of SC-SPDI$_2$ in TOL, b) Evolution associated spectra (EAS), c) the relative population profiles of SC-SPDI$_2$ in TOL and d) normalized evolution associated spectra. The orange (A, EAS$_A$) and green (B, EAS$_B$) colored spectrum and decay profiles correspond to emission from the unrelaxed (Ex*) and relaxed (Ex) excimer states.

Figure S8: a) Time-resolved emission spectra (TRES, $\lambda_{ex} = 478$ nm) of SC-NPDI$_2$ in TOL, b) Evolution associated spectra (EAS), c) the relative population profiles of SC-NPDI$_2$ in TOL and d) normalized evolution associated spectra. The orange (A, EAS$_A$) and green (B, EAS$_B$) colored spectrum and decay profiles correspond to emission from the unrelaxed (Ex*) and relaxed (Ex) excimer states.
Figure S9: Comparison between the steady-state emission spectra (top) with the time-resolved emission spectra (bottom) of a) SC-SPDI₂ and b) SC-NPDI₂ recorded in TOL. The highlighted region in the spectra represents the emission maximum.

Figure S10: Steady-state UV-vis absorption spectra along with emission spectra (recorded at 90K and 297K) of a) SC-SPDI₂ and b) SC-NPDI₂ in TOL.

Figure S11: a) Emission spectra of SPDI at room temperature and SC-SPDI₂ at 90K and b) Emission spectra of NPDI at room temperature and SC-NPDI₂ at 90K in TOL.

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Figure S12: Comparison of time-resolved emission spectra with steady-state emission spectra at different temperatures for a) SC-SPDI$_2$ and b) SC-NPDl$_2$ in TOL.

Figure S13: a) Absorption spectra and excitation spectra of SC-SPDI$_2$ in toluene and polystyrene matrix respectively, b) Emission spectra of SC-SPDI$_2$ in toluene, c) Absorption spectra and excitation spectra of SC-NPDl$_2$ in toluene and polystyrene matrix respectively, d) Emission spectra of SC-NPDl$_2$ in polystyrene matrix and toluene
**Figure S14:** Solvent-dependent absorption and emission spectra of a) SC-NPDI$_2$ and b) SC-SPDI$_2$.

**Figure S15:** Normalised absorption and emission spectra of (a, b) SPDI and (c, d) NPDI in different solvents.
Figure S16: Normalised excitation spectra of a) SPDI, b) NPDI, c) SC-SPDI₂ and d) SC-NPDI₂ collected at emission maximum in different solvents.

Figure S17: Solvent-dependent normalized emission spectra of a) SC-SPDI₂ and b) SC-NPDI₂.
Figure S18: Fluorescence decay profiles of a) SC-SPDI$_2$ and b) SC-NPDI$_2$ in different solvents. The fluorescence decay profile of SC-NPDI$_2$ in ACN is biexponentially fitted. The second component is assigned to scattering contribution as SC-NPDI$_2$ has very low fluorescence quantum yield in ACN (<0.1%).

Figure S19: Fluorescence decay profiles of (a) SPDI and (b) NPDI in different solvents.
Figure S20: (a, c) Cyclic voltammetry data and (b, d) differential pulse voltammograms of SC-SPDI\textsubscript{2} and SC-NPDI\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2}. (Tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte, scan rate 100 mV s\textsuperscript{-1}. Fc/Fc+=ferrocene/ferrocenium couple).

Figure S21: Energy level diagram with the frontier molecular orbitals of SPDI and SC-SPDI\textsubscript{2}. 

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Figure S22: Energy level diagram with the frontier molecular orbitals of NPDI and SC-NPDI$_2$.

Figure S23: Femtosecond transient absorption spectra (top), evolution associated spectra (EAS, middle) and population profiles (bottom) of SPDI in different solvents.
Figure S24: Femtosecond transient absorption spectra (top), evolution associated spectra (EAS, middle) and population profiles (bottom) of NPDI in different solvents.

Figure S25: Global analysis fits for selected fsTA wavelengths of SC-SPDI₂ (λ_\text{ex} = 470 nm) in toluene to A→B→C→D kinetic model. Fits are shown as solid lines. Evolution associated spectra (EAS, b) and population profiles (c) of SC-SPDI₂ in toluene.
Figure S26: Femtosecond transient absorption spectra (top), Evolution associated spectra (bottom) of SC-NPDI2 in toluene.

Figure S27: Global analysis fits for selected fsTA wavelengths of SC-NPDI2 (λ<sub>ex</sub> = 470 nm) in toluene to A→B→C→D kinetic model. Fits are shown as solid lines. Evolution associated spectra (EAS, b) and population profiles (c) of SC-NPDI2 in toluene.
Figure S28: Comparison between the steady-state emission spectra (top) with the evolution associated spectra (bottom) of a) SC-SPDI$_2$ and b) SC-NPDI$_2$ recorded in TOL.

Figure S29: Femtosecond transient absorption spectra, Evolution associated spectra (EAS, bottom) of SC-SPDI$_2$ in acetone.
Figure S30: Global analysis fits for selected fsTA wavelengths of SC-SPDI$_2$ ($\lambda_{ex} = 470$ nm) in acetone to $A \rightarrow B \rightarrow C \rightarrow D$ kinetic model. Fits are shown as solid lines. Evolution associated spectra (EAS, b) and population profiles (c) of SC-SPDI$_2$ in acetone.

Figure S31: Global analysis fits for selected fsTA wavelengths of SC-SPDI$_2$ ($\lambda_{ex} = 470$ nm) in acetonitrile to $A \rightarrow B \rightarrow C \rightarrow D$ kinetic model. Fits are shown as solid lines. Evolution associated spectra (EAS, b) and population profiles (c) of SC-SPDI$_2$ in acetonitrile.
Figure S32: UV-vis absorption changes of SPDI in ACN upon the addition of a) antimony pentachloride (SbCl$_5$) and b) cobaltocene (CoCp$_2$).

Figure S33: UV-Vis absorption spectra for the electrochemical reduction of a) SPDI and b) NPDI.

Figure S34: UV-vis absorption changes of NPDI in ACN upon the addition of a) antimony pentachloride (SbCl$_5$) and b) cobaltocene (CoCp$_2$).
Figure S35: Femtosecond transient absorption spectra (top), Evolution associated spectra (EAS, bottom) of SC-NPDI$_2$ in a) acetone and b) acetonitrile.

Figure S36: Global analysis fits for selected fsTA wavelengths of SC-SPDI$_2$ ($\lambda_{ex} = 470$ nm) in acetone to A$\rightarrow$B$\rightarrow$C$\rightarrow$D kinetic model. Fits are shown as solid lines. Evolution associated spectra (EAS, b) and population profiles (c) of SC-NPDI$_2$ in acetone.
**Figure S37:** Global analysis fits for selected fsTA wavelengths of SC-SPDI$_2$ ($\lambda_{ex} = 470$ nm) in acetone to $A \rightarrow B \rightarrow C \rightarrow D$ kinetic model. Fits are shown as solid lines. Evolution associated spectra (EAS, b) and population profiles (c) of SC-NPDI$_2$ in acetonitrile.

**Figure S38:** fsTA spectra highlighting the change in intensities of 0-0 and 0-1 vibronic bands for SC-SPDI$_2$ and SC-NPDI$_2$ in different solvents.
Figure S39: (Top) Nanosecond transient absorption spectra of SC-SPDI$_2$ in (a) TOL, (b) ACE and (c) ACN showing the excited-state dynamics after photoexcitation in N$_2$ atmosphere. (Bottom) Evolution associated spectra were reconstructed from global analysis of the A → GS model in all solvents.

Figure S40: (Top) Nanosecond transient absorption spectra of SC-NPDI$_2$ in (a) TOL, (b) ACE and (c) ACN showing the excited-state dynamics after photoexcitation in N$_2$ atmosphere. (Bottom) Evolution associated spectra were reconstructed from global analysis of the A → GS model in all solvents.
Figure S41: Nanosecond transient absorption spectra of SC-SPDI₂ in a) ACN, b) ACE, c) TOL and of SC-NPDI₂ in d) ACN, e) ACE, f) TOL after O₂ purging.

Figure S42: Comparison between the EAS from fsTA measurements (top) and nTA spectra (bottom) for a) SC-NPDI₂ and b) SC-SPDI₂.
Figure S43: Schematic potential energy surface of SC-SPDi₂ in TOL summarising the excited state dynamics.

Figure S44: Schematic potential energy surface of SC-SPDi₂ in ACE and ACN summarising the excited state dynamics.
**Figure S45**: Schematic potential energy surface of SC-NPDi₂ in TOL summarising the excited state dynamics.

**Figure S46**: Schematic potential energy surface of SC-NPDi₂ in ACE and ACN summarising the excited state dynamics.
Figure S47: Molecular structures of the dimers and the corresponding PR and CT values for the transition to the first singlet excited state along with the electron-hole correlation plots (a,b) SC-SPDI$_2$ and (c,d) SC-NPDI$_2$.

Figure S48: Hole and electron isosurfaces for the first six singlet excited state transitions and the corresponding electron-hole correlation plots of SC-NPDI$_2$ in the near-orthogonal geometry.
**Figure S49**: Hole and electron isosurfaces for the first six singlet excited state transitions along with the corresponding electron-hole correlation plots of SC-SPDI$_2$ in the near-orthogonal geometry.

**Figure S50**: Hole and electron isosurfaces for the first six singlet excited state transitions along with the corresponding electron-hole correlation plots of SC-NPDI$_2$ in the foldamer geometry.
Figure S51: Hole and electron isosurfaces for the first six singlet excited state transitions along with the corresponding electron-hole correlation plots of SC-SPDi2 in the foldamer geometry.

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