Electronic Supplemental Information

Isoenergetic Symmetry Breaking Charge Separation in Far-Red Absorbing Orthogonal BODIPY Dimer – a Classic Case of No Energy Loss During the Process of Light Capture and Conversion

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Supporting Information (SI)

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Experimental section

General

All chemicals were obtained from commercial suppliers and used without further purification. Experiments involving air-sensitive conditions were conducted using conventional Schlenk methodologies as required. The Knoevenagel Condensation was performed using a Dean-Stark apparatus. Tetrahydrofuran (THF) was dried with calcium hydride (CaH_2), and anhydrous benzene was purchased from a vendor. All other solvents used for spectroscopic purposes were dried using the appropriate methods. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane, used as the internal standard. NMR spectra were acquired at room temperature using 400 MHz and 500 MHz spectrometers. Mass spectrometry experiments were done using a Thermo Scientific MALDI-LTQ-XL-Orbitrap mass spectrometer.

1.1 Optical spectral measurement

The UV-visible spectral measurements were performed using a Jasco V-770 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right-angle detection method was used.

1.2 Electrochemical experiments

Differential pulse and cyclic voltammograms were recorded on a Gamry Instruments (Reference 620) potentiostat using a three-electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferricenium redox couple was used as an internal standard. All the solutions were purged before electrochemical and spectral measurements using argon gas.

The spectroelectrochemical study used a cell assembly (SEC-C) supplied by ALS Co., Ltd. (Tokyo, Japan). This assembly comprised a Pt counter electrode, a 6 mm Pt Gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optical transmission was limited to 6 mm covering the Pt Gauze working electrode. Spectra were recorded by applying a potential of 100 mV past the potential of a given oxidation or reduction process and continuing until no additional changes were observed.

1.3 Rehm-Weller analysis

The free energy change for charge separation (ΔG_{CS}) from the singlet excited state of the donor-acceptor system was calculated using spectroscopic, computational, and electrochemical data following eqn (1)– (3).[3]

$$\Delta G_{CR} = \mathrm{E}_{\mathrm{ox}} - \mathrm{E}_{\mathrm{red}} + \Delta G_{S} \qquad (1)$$

$$-\Delta G_{CS} = \mathrm{E}_{00} - (-\Delta G_{CR}) \qquad (2)$$

$$\Delta G_{S} = \mathrm{e}^{2}/4\pi\varepsilon\ [(1/2\mathrm{R}_{+} + 1/2\mathrm{R}_{-})\Delta(1/\varepsilon_{\mathrm{R}}) - 1/\mathrm{R}_{\mathrm{CC}}\varepsilon_{\mathrm{R}}] \qquad (3)$$

where E_{00} and ΔG_{CS} correspond to the energy of the excited singlet state and electrostatic energy, respectively. The Eox and $Ered$ represent the oxidation and reduction potentials of the donor-acceptor system. The term ΔGs refers to the static Coulombic energy, calculated by using the “dielectric continuum model” according to eqn (3). The symbols ε_0, and ε_R represent the vacuum permittivity and dielectric constant of the solvent used for photochemical and electrochemical studies, respectively. R_{CC} is the center-to-center distance between pull-pull entities from computational data. R_+ and R_- are the ionic radii of the donor and acceptor.

1.4 Computational analysis

All the theoretical calculations were carried out in Gaussian 16 employing the B3LYP functional and 6-311+g(d,p) basis set at the DFT level of theory.[4] Vertical excitation energies and oscillator strengths were calculated employing time-dependent DFT (TD-DFT) at the b3lyp/6-311+g(d,p) level of theory. Multiwfn version 3.7.8 was used to perform hole-electron analyses .[5] Multiwfn uses post-processed Gaussian 16 output files generated at b3lyp/6-311+g(d,p) level of theory for the respective analyses.

1.5 Femtosecond transient absorption (fs-TA) measurement

Femtosecond transient studies were performed using an Ultrafast Femtosecond Laser Source (Astrella) by Coherent, which incorporates a diode, mode-locked Ti: Sapphire laser (Vitara), and diode-pumped intracavity doubled Nd: YLF laser (Revolution) to generate a fundamental compressed laser of 800 nm and a power output of 5.24 W. For optical detection, a Helios transient absorption spectrometer coupled with a femtosecond harmonics generator, both provided by Ultrafast Systems LLC, will be used. The source for the pump pulse is derived from the fundamental output of Astrella (compressed output 5.24 W, pulse width 91 fs, 800nm at a repetition rate of 1 kHz) by introducing 95% of the beam into the HG or OPA, while the other 5% is sent to the delay line and white light generating crystal. The beam sent through the HG or OPA is termed the pump beam as it is used to excite the sample. The beam sent through the delay line and crystal is termed the probe beam, as it shows what spectral changes occur in the sample with time. The OPA takes the 800 nm fundamental and converts it into a specific wavelength in the range of 400 – 2200 nm, which allows the excitation wavelength to be selected.

Section 2. Synthesis

The synthesis of **1a** and **1** was carried out using earlier methods with minor modifications.[1,2]

2,4-Me-Ph-BODIPY (1a).

In a 500 mL round-bottom flask wrapped in aluminum foil and maintained under a nitrogen atmosphere at ambient temperature, benzaldehyde (0.35 mL, 3.4 mmol), 2,4-methylpyrrole (0.77 mL, 7.4 mmol), and anhydrous tetrahydrofuran (THF, 100 mL) were combined. The reaction mixture was stirred for 15 minutes before the dropwise addition of trifluoroacetic acid (0.1 ml, 1.5 mmol). After stirring for 18 hours, a solution of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 780 mg, 3.4 mmol) in anhydrous THF (135 mL) was introduced, and the reaction was allowed to proceed for an additional 18 hours. The reaction mixture was subsequently cooled in an ice bath for 15 minutes, followed by the slow addition of triethylamine (10 mL) under continuous stirring. Boron trifluoride diethyl etherate (12 mL) was then added dropwise, and the reaction was stirred at room temperature under an inert atmosphere for 8 hours. Upon completion, THF was evaporated under reduced pressure, and the resulting residue was dissolved in dichloromethane DCM. The organic phase was washed sequentially with a saturated sodium bicarbonate solution and deionized water, then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product was subjected to silica gel column chromatography using hexanes/DCM (50:50, v/v) as the eluent. The target compound was obtained as an orange solid. (400 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 3H), 7.31 – 7.27 (m, 2H), 5.99 (s, 2H), 2.57 (s, 6H), 1.38 (s, 6H). ^{13}C NMR (126 MHz, cdcl3) δ 155.41, 143.15, 141.72, 134.98, 131.42, 129.12, 128.92, 127.92, 121.20, 14.59, 14.38.

2,4-Me-Ph-bis(Phenyl) BODIPY (1)

Compound 1a (100 mg, 0.3 mmol) was dissolved in benzene (10 mL) in a 50 mL round-bottom flask. Benzaldehyde (0.13 mL, 1.3 mmol), piperidine (0.6 mL, 6 mmol), and acetic acid (0.6 mL, 10.4 mmol) were sequentially introduced into the reaction mixture, resulting in a red coloration.[1, 2] The flask was equipped with a condenser fitted with a Dean-Stark apparatus and maintained under a nitrogen atmosphere for 15 minutes. The reaction mixture was then refluxed under nitrogen, and its progress was monitored via UV-Vis spectroscopy. Over time, the color of the solution transitioned from red to blue. After 48 hours, the reaction mixture was cooled to room temperature and extracted with chloroform. The organic phase was washed with a saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified via silica gel column chromatography using hexane/DCM (60:40, v/v) as the eluent. The final compound was obtained as a golden-bluish solid. (61 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.74 (s, 1H), 7.67 – 7.60 (m, 4H), 7.53 – 7.47 (m, 3H), 7.44 – 7.37 (m, 4H), 7.36 – 7.29 (m, 4H), 7.28 (s, 1H), 7.24 (s, *J* = 3.2 Hz, 1H), 6.65 (s, 2H), 1.45 (s, 6H). ^{13}C NMR (500 MHz, $cdcl_3$) δ 152.59, 142.23, 139.13, 136.56, 136.20, 135.08, 133.37, 129.11, 129.00, 128.93, 128.78, 128.37, 127.56, 119.26, 117.82, 14.65. HR-ESI-MS (+): m/z calculated for $C_{33}H_{27}BF_2N_2[M + H]^+$: 502.1229; found: 502.1229

2,4-Me-directly-linked dimer BODIPY (2a)

In a round-bottom flask, 2,4-methylpyrrole (0.93 mL, 9 mmol) was dissolved in 60 mL anhydrous tetrahydrofuran (THF) under a nitrogen atmosphere and maintained in dark conditions. The solution was degassed for 15 minutes before the slow addition of oxalyl chloride (0.13 ml, 1.5 mmol). The reaction mixture was stirred at room temperature for 12 hours. Upon completion, the reaction was cooled in an ice bath for 15 minutes, followed by the rapid addition of N,N-diisopropylethylamine 12 mL, inducing a color change to dark brown. Stirring was continued at 0°C for 15 minutes, after which boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) 12 mL was added dropwise. The reaction was then allowed to warm to room temperature and stirred for an additional ~~8~~ 6 hours. Following completion, the solvents were removed under reduced pressure, and the resulting residue was dissolved in DCM (300 mL). The organic layer was sequentially washed with saturated sodium bicarbonate solution, deionized water, and brine, then dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure, and the crude product was purified via silica gel column chromatography using a hexane/DCM (30:70, v/v) mixture as the eluent, yielding the desired compound as a deep red-orange solid. (120 mg, 16%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02 (s, 4H), 2.57 (s, 12H), 1.90 (s, 12H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 157.12, 143.85, 142.53, 130.17, 121.57, 29.70, 14.31.

2,4-Me-Tetrakis-directly-linked dimer-BODIPY (2)

The dimer (100 mg, 0.2 mmol) was dissolved in benzene (12 mL), followed by the sequential addition of benzaldehyde (0.3 mL, 2.9 mmol), piperidine (0.8 mL), and acetic acid (0.8 mL). The reaction mixture turned red and was heated to reflux under a nitrogen atmosphere using a Dean-Stark apparatus. After 48 hours, the color of the mixture changed to blue-purple, and reaction completion was monitored using UV-Vis spectroscopy. The reaction was then cooled to room temperature, and chloroform was added. The organic phase was sequentially washed with saturated sodium bicarbonate solution, deionized water, and brine. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using a hexane/dichloromethane (40:60, v/v) mixture as the eluent, yielding the desired compound as a copper-blueish solid (66 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.73 (s, 2H), 7.68 – 7.62 (m, 8H), 7.45 – 7.39 (m, 8H), 7.37 – 7.32 (m, 6H), 7.31 (s, 2H), 6.73 (s, 4H), 2.02 (s, 12H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.85, 141.49, 137.49, 136.36, 132.56, 129.98, 129.27, 128.84, 127.69, 119.02, 118.27, 14.68. HR-ESI-MS (+): *m/z* calcd for $C_{54}H_{44}B_2F_4N_4$ $[M + H]^+$: 848.2556; found: 848.2556.

Section 3. Figures

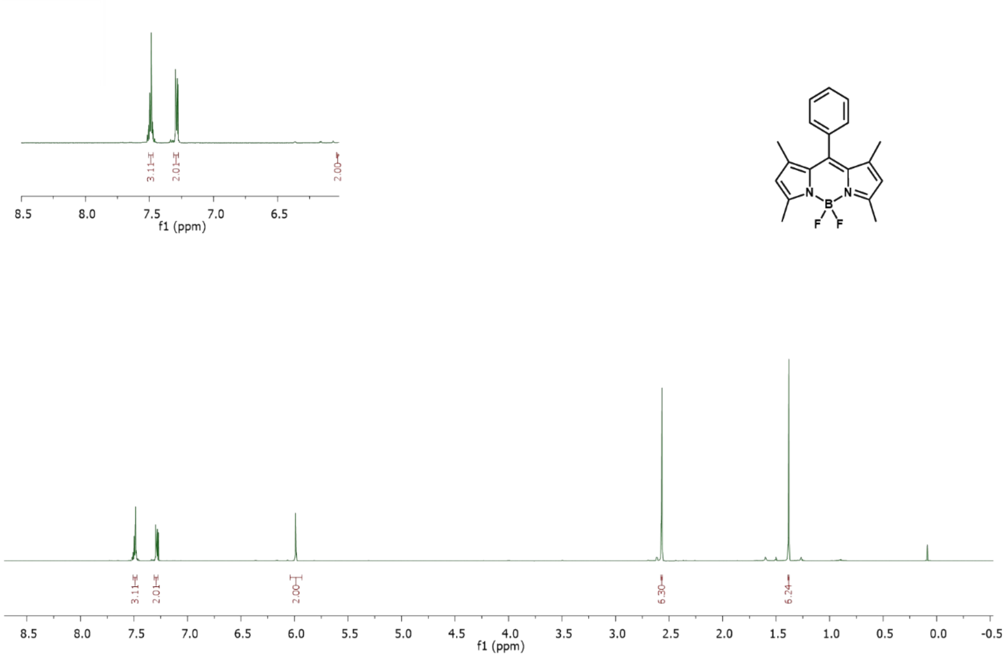


Figure S1. ^{1}H NMR of compound **1a**

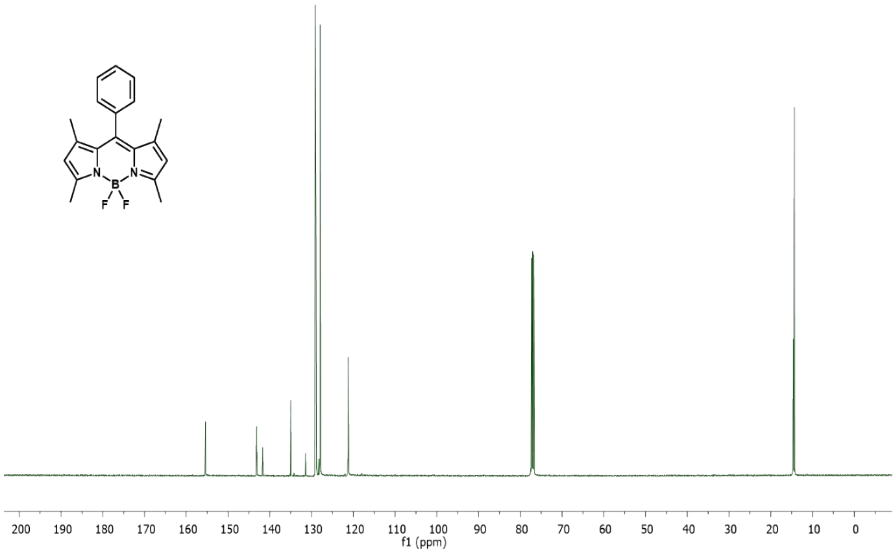


Figure S2. ^{13}C NMR of compound **1a**

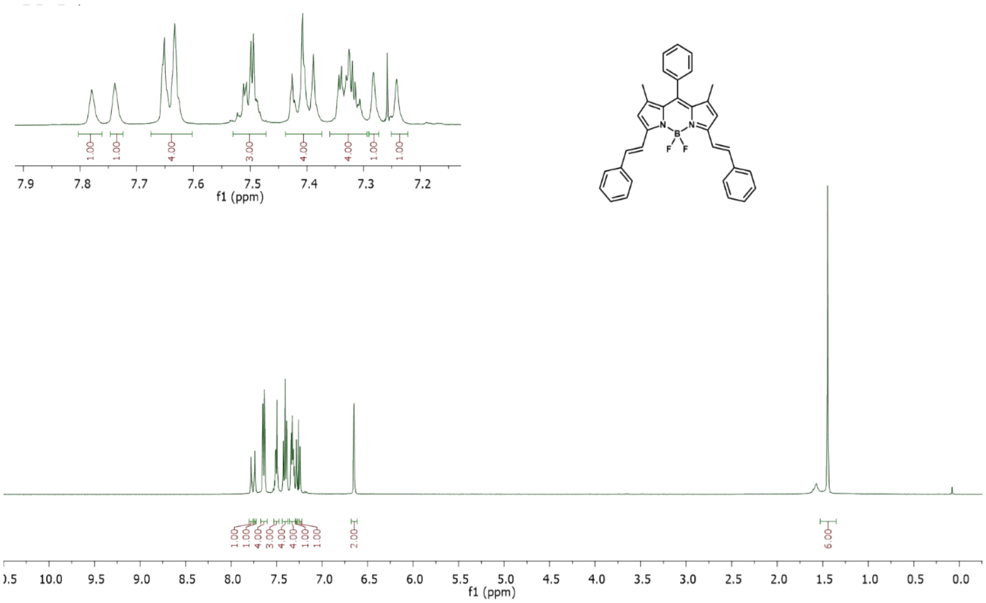


Figure S3. ^{1}H NMR of compound **1**

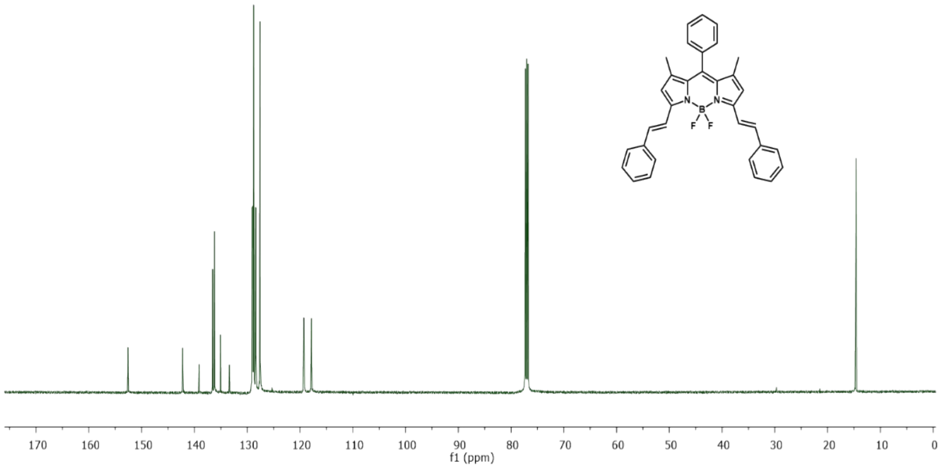
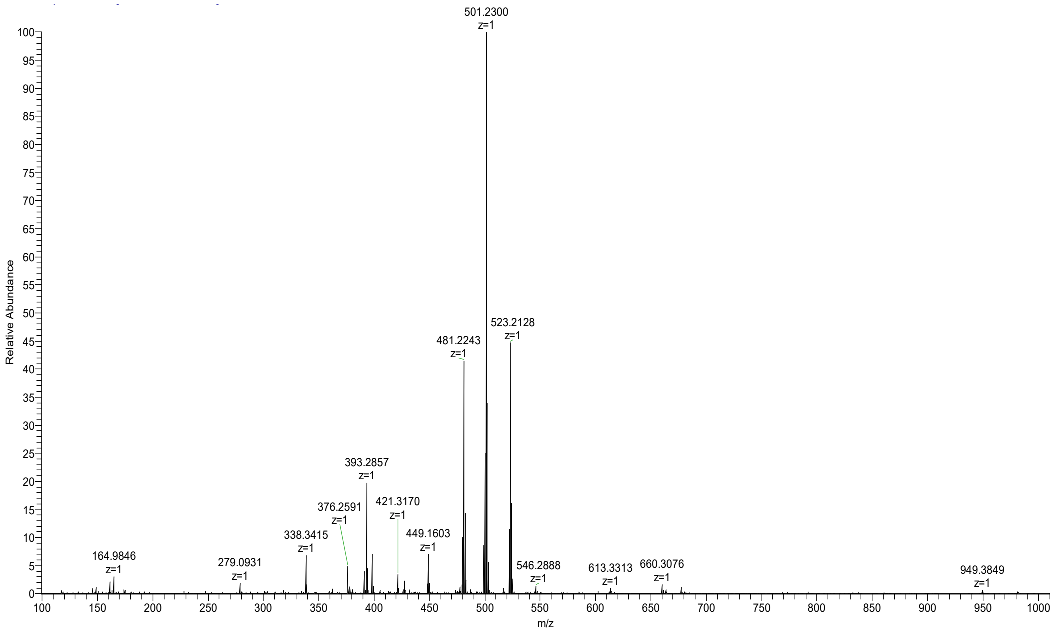


Figure S4. ^{13}C NMR of compound **1**



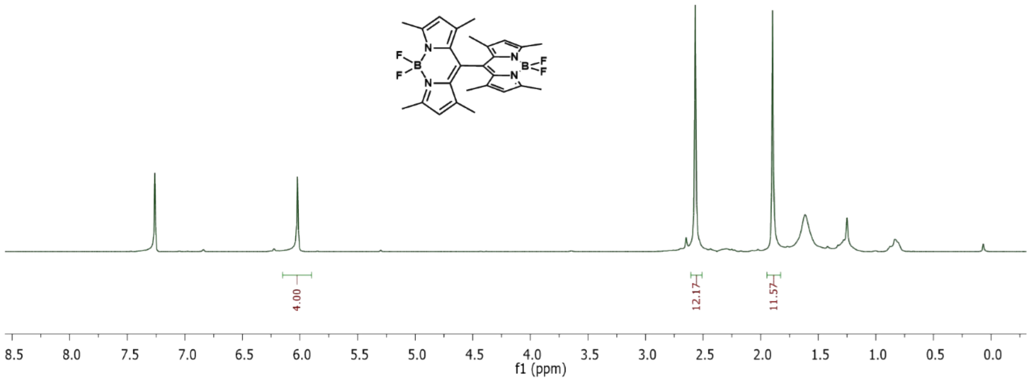


Figure S5. ESI (+) of compound **1**

Figure S6. ^{1}H NMR of compound **2a**

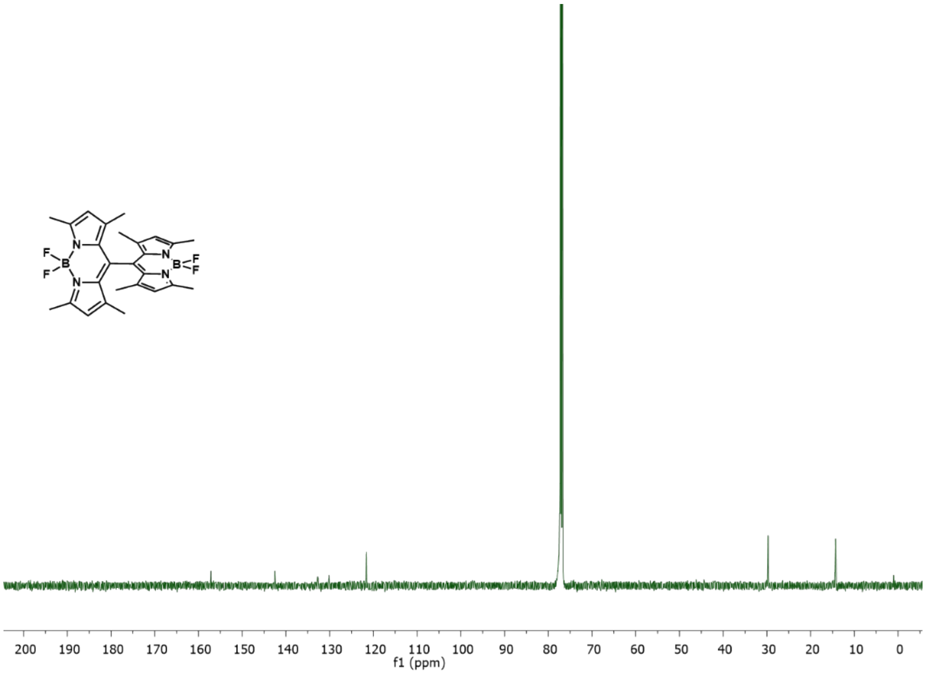


Figure S7. ^{13}C NMR of compound **2a**

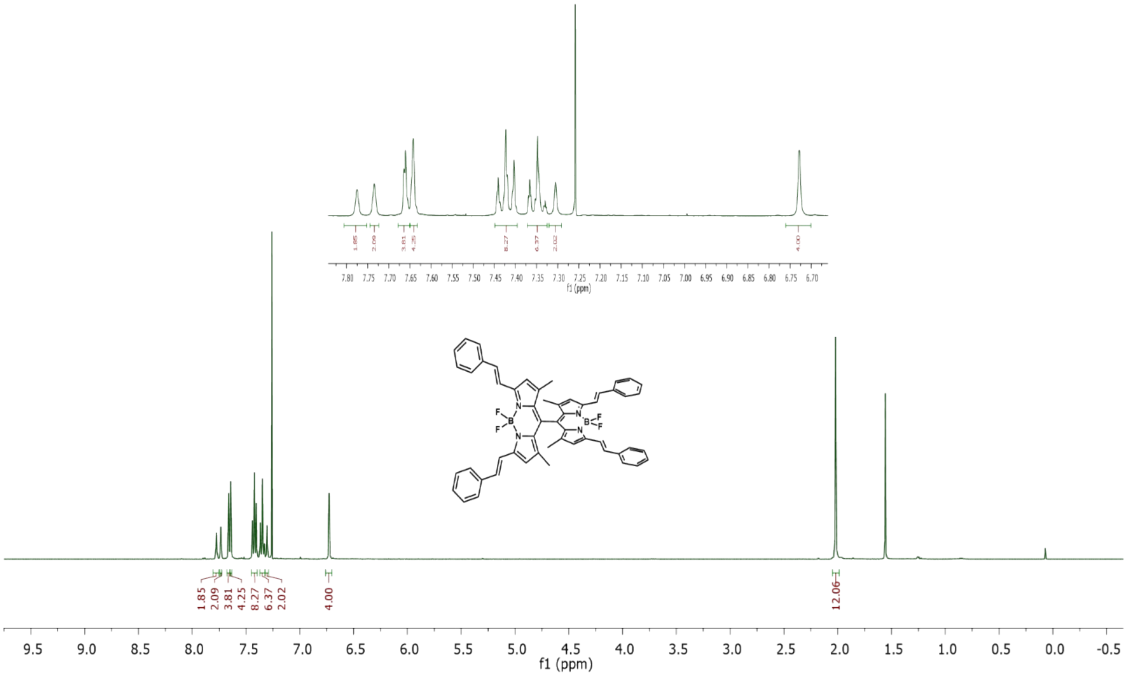


Figure S8. ^{1}H NMR of compound **2**

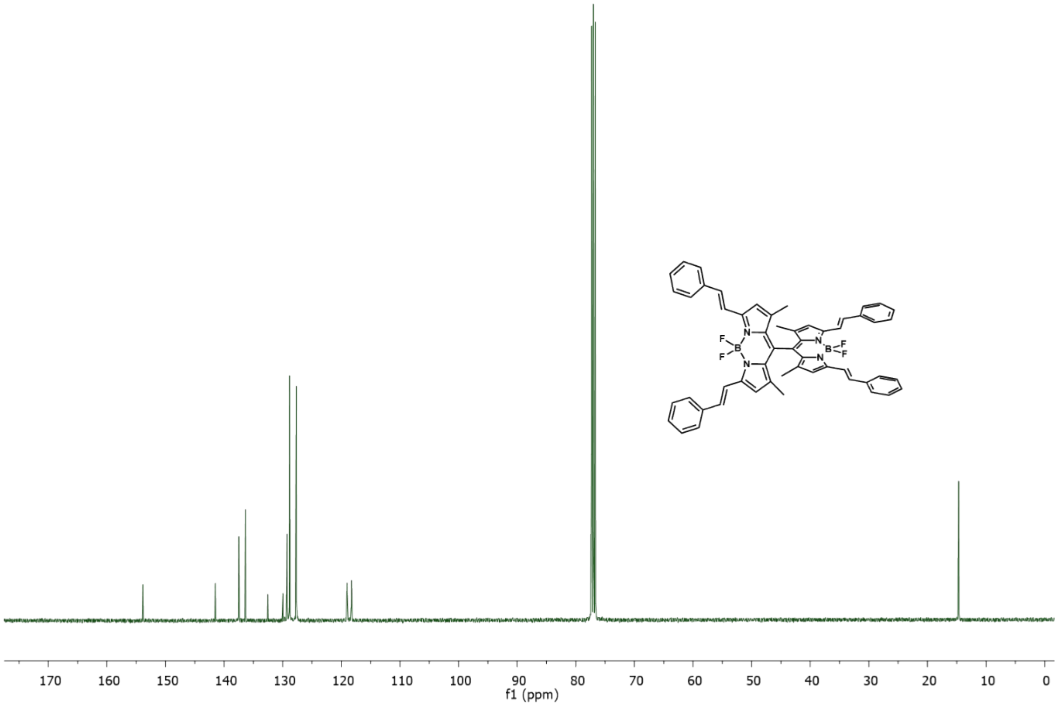


Figure S9. ^{13}C NMR of compound **2**

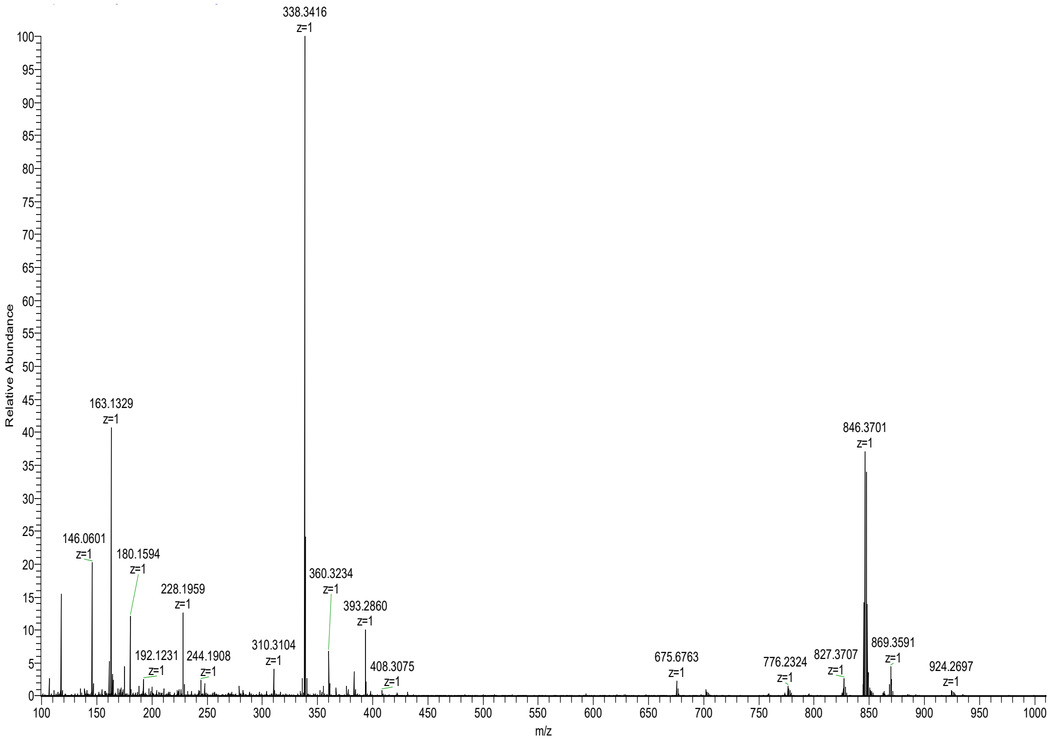


Figure S10. ESI (+) of compound **2**

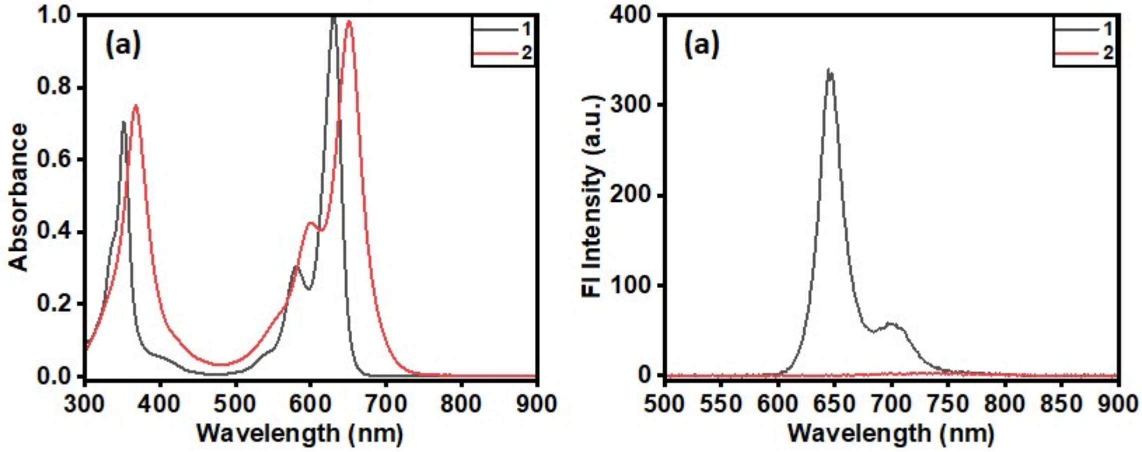


Figure S11. (a) Ground state absorption and (b) emission spectra of **1** and **2** in DCB.

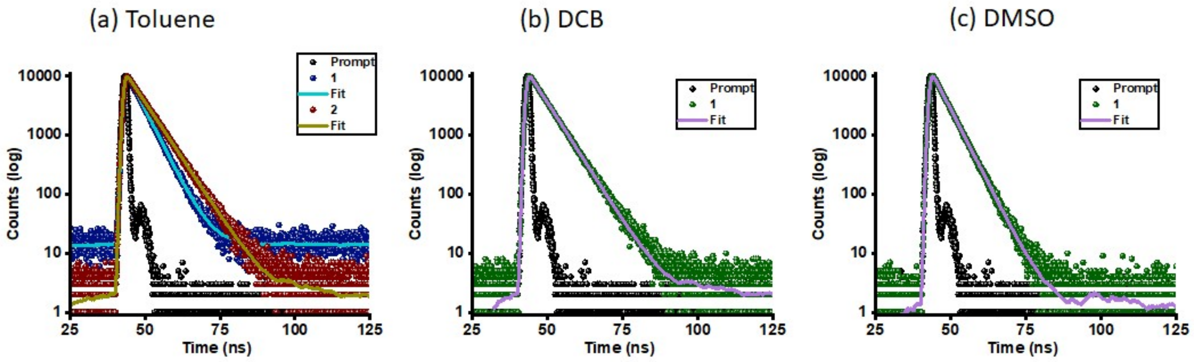


Figure S12. TCSPC emission decay curves of the indicated compounds in various solvents.

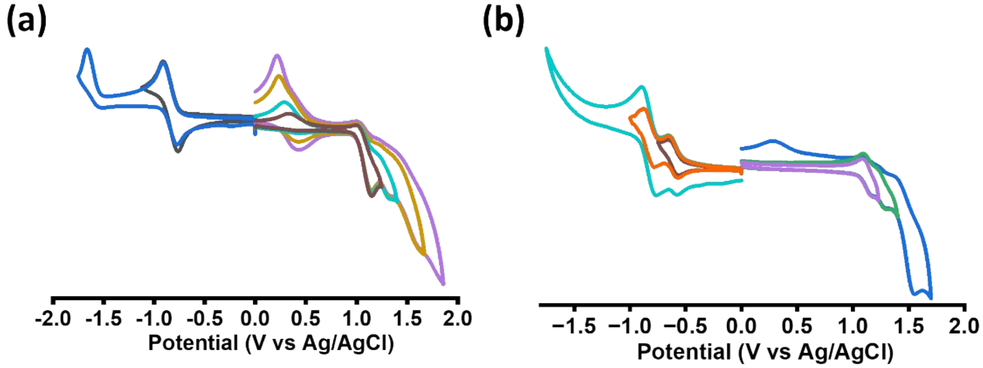


Figure S13. CVs of the compounds studied for

(a) monomer **1** and (b) dimer **2** in *o*-DCB.

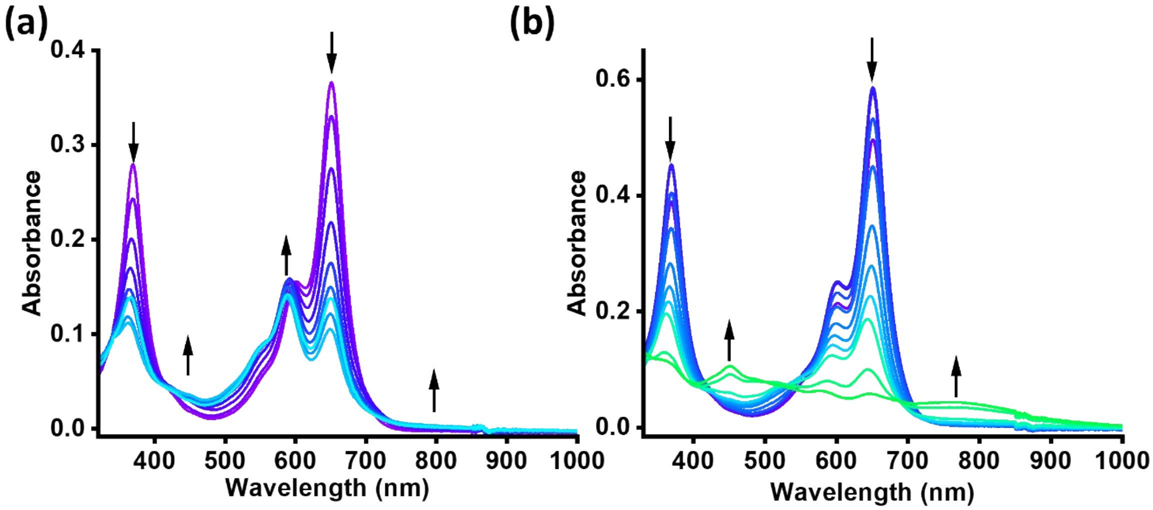


Figure S14. Spectral changes monitored during the (a) first oxidation and (b) reduction for dimer **2**.

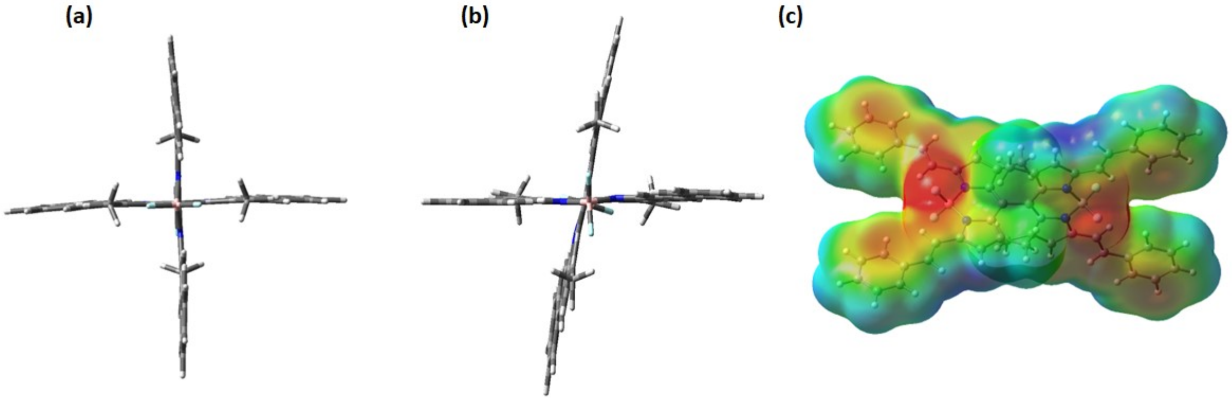


Figure S15. (a) Ground state, (b) first excited state optimized geometries, and (c) ESP map for the dimer **2**.

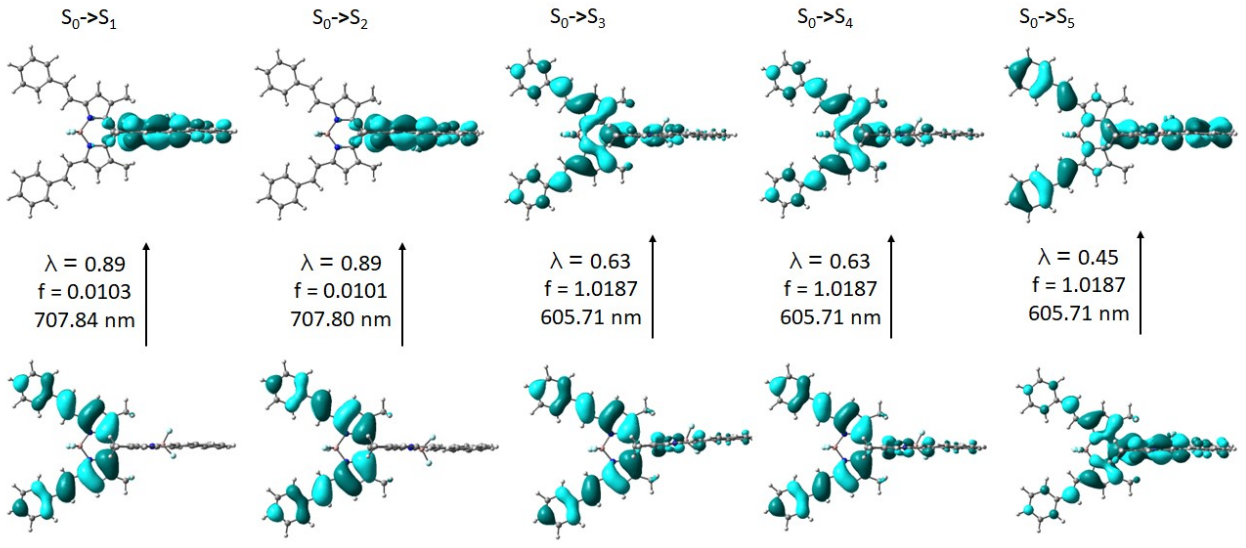


Figure S16. NTOs analysis of the first five excited states for dimer **2** in DMSO.

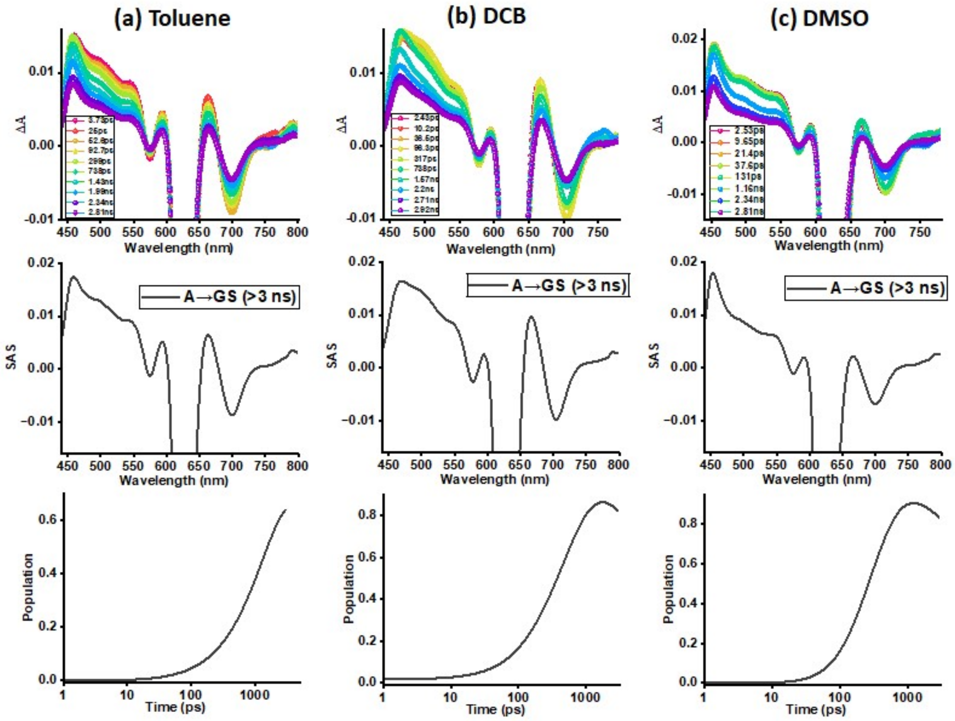


Figure S17. Fs-TA absorption spectra at the indicated delay times of monomer **1** in (a) Toluene, (b) DCB, and (c) DMSO, along with SAS spectra (middle row) and population decay curves (bottom row).

Section 4. Tables

Table S1. Excited-state properties for various transitions of the dimer calculated at the B3LYP/6-311G(df,pd) level of theory with SCRF (IEFPCM, solvent = dimethyl sulfoxide).

Electronic Transition	**Oscillator strength**	**Energy (eV)**	**Wavelength (nm)**	**Main Transition Orbital**	**$\Delta\mu$ (Debye)**	**%CT/LE**
$S_0 \rightarrow S_1$	**0.1184**	**1.7440**	**710.93**	**HOMO-1→LUMO+1** **HOMO→LUMO**	**7.1**	**72/28**
$S_0 \rightarrow S_2$	**0.1159**	**1.7442**	**710.84**	**HOMO-1→LUMO** **HOMO→LUMO+1**	**7.1**	**72/28**
$S_0 \rightarrow S_3$	**1.1235**	**1.8532**	**669.01**	**HOMO-1→LUMO** **HOMO→LUMO+1**	**~0**	**0/100**
$S_0 \rightarrow S_4$	**1.1251**	**1.8534**	**668.94**	**HOMO-1→LUMO+1** **HOMO→LUMO**	**~0**	**0/100**
$S_0 \rightarrow S_5$	**1.4117**	**2.8675**	**432.37**	**HOMO-3→LUMO+1** **HOMO-2→LUMO**	**~0**	**0/100**

References

1. Y. Dong, A. Elmali, J. Zhao, B. Dick and A. Karatay, *ChemPhysChem*, 2020, **21**, 1388-1401.
2. Z. Wang, A. Toffoletti, Y. Hou, J. Zhao, A. Barbon, B. Dick, *Chem. Sci.,* 2021*,***12***,* 2829-2840.