Electronic Supplemental Information

Symmetry Breaking Charge Transfer Leading to Charge Separation in a Far-Red Absorbing Bisstyryl-BODIPY Dimer†

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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 spectroscopy were dried using appropriate methods. Chemical shifts are reported in parts per million (ppm) with respect to tetramethyl silane, used as the internal standard. NMR spectra were acquired at room temperature using both 400 MHz and 500 MHz spectrometers.

Mass spectrometry experiments were done using a Thermoscientific MALDI-LTQ-XL-Orbitrap mass spectrometer. UV/Vis data was obtained using either a CARY 5000 spectrometer or a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored by using a Horiba Yvon Nanolog coupled with time-correlated single-photon counting with nanoLED excitation sources. Degassed solvents were used for all luminescence and lifetime experiments. A right angle detection method was used. Differential pulse voltammograms were recorded on an EG&G PARSTAT electrochemical analyzer 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/ferrocenium redox couple was used as an internal standard. All the solutions were purged before electrochemical and spectral measurements using nitrogen gas.

Femtosecond Transient Absorption Spectroscopy. Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with a femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290-2600 nm tuning range from

Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is ±10%.

Synthesis

Ph-BODIPY (1a).

In a 250 ml round-bottomed flask wrapped in foil and under a nitrogen atmosphere at room temperature, benzaldehyde (0.162 ml, 1.58 mmol), 2-methyl pyrrole (0.30 ml, 3.48 mmol), and dry THF (48 ml) were combined. After stirring for 15 minutes, trifluoroacetic acid (53µ, 0.7 mmol) was added dropwise to the solution. After 18 hours, a solution of DDQ (346 mg, 1.5 mmol) in dry THF (64 ml) was added to the flask and stirred for an additional 8 hours. The mixture was cooled in an ice bath for 15 minutes, followed by the gradual dropwise addition of triethylamine (9.5 ml) to the solution. Subsequently, boron trifluoride diethyl etherate (9.5 ml) was added dropwise to the mixture. The reaction was warmed to room temperature and stirred under a nitrogen atmosphere for 6 hours. Afterward, THF was evaporated, and the residue was dissolved in DCM (100 ml). The resulting solution was washed with saturated sodium bicarbonate solution and DI water. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. To purify the compound, a silica column was run using hexanes/DCM (1:1, v/v) as the eluent. The desired compound was obtained as an orange solid (225mg, 48%). UV-vis (CH_2Cl_2) λ_{max} (nm): 350, 510. ^{1}H NMR (400 MHz, $CDCl_3$) 7.48 (m, 5H), 6.70 (d, *J* = 4.0 Hz, 2H), 6.26 (d, *J* = 4.0 Hz, 2H), 2.64 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) 157.55, 142.53, 134.52, 134.08, 130.42, 130.34, 129.90, 128.15, 119.36, 14.90.

Ph-bis(Phenyl) BODIPY(1)

Compound 1a (100 mg, 0.34 mmol) was dissolved in benzene (10 ml) within a 50 ml round-bottom flask (RB flask). Subsequently, benzaldehyde (0.13 ml, 1.3 mmol), piperidine (0.6 ml, 6 mmol), and acetic acid (0.6 ml, 10.4 mmol) were sequentially added to the flask. The reaction mixture turned red in color. The flask was then connected to a condenser equipped with a Dean-Stark apparatus and placed under a nitrogen atmosphere for 15 minutes. The reaction mixture was refluxed under nitrogen and monitored using UV to ensure completion. The color of the mixture gradually shifted to blue. After 48 hours, the reaction was cooled to room temperature and extracted with chloroform. The organic layer was washed with sodium bicarbonate and dried using anhydrous Na_2SO_4. The solvent was evaporated using a rotary evaporator, and the resulting product was purified over a silica column using a hexane/DCM (60:40, v/v) mixture as the eluent. The final compound was obtained as a copper-bluish solid (80 mg, 49%). UV-vis (CH_2Cl_2) λ_{max} (nm): 354, 582, 632. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.78 (s, 1H)7.67 (d, *J* = 7.5 Hz, 4H), 7.55 – 7.50 (m, 5H), 7.42 (t, *J* = 7.5 Hz, 4H), 7.37 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.33 (s, 1H), 6.94 (d, *J* = 4.5 Hz, 2H), 6.82 (d, *J* = 4.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 154.75, 139.53, 136.68, 136.42, 136.20, 134.35, 130.41, 129.80, 129.66, 129.12, 128.82, 128.29, 127.62, 119.34, 116.31. MALDI-TOF (APCI+) m/z calcd for $C_{31}H_{23}BF_2N_2$ [M+H]+ : 472.2031, 473.1955, 474.2029, 475.2062, 476.2096 ; found: 469.1872, 472.2022, 473.1981, 474.2015, 475.2049, 476.2080.

Dimer-BODIPY (2a)

The synthesis of the dimer is similar to (1a) with some modifications. Terephthalaldehyde (319 mg, 2.4 mmol) and 2-methyl pyrrole (1 mL, 12 mmol) were dissolved in dry THF (140 mL) under an N2 atmosphere in dark conditions. The resulting solution was further degassed for 15 minutes, and trifluoroacetic acid (158 µL, 2.6 mmol) was slowly added. The reaction mixture was allowed to proceed with stirring for 18 hours. DDQ (1.08 g, 4.75 mmol) in 190 mL dry THF was then added to the reaction, resulting in an immediate color change to dark red-orange. The mixture was stirred for an additional 8 hours. The reaction mixture was cooled in an ice bath for 15 minutes, and N, N-Diisopropylethylamine (28.55 mL, 164 mmol) was added all at once, leading to a color change to dark brown. Stirring was continued for 15 minutes at 0°C. Boron trifluoride diethyl etherate (28.55 mL, 231 mmol) was added dropwise. The reaction mixture was then brought up to room temperature and stirred for 6 hours. Afterward, the solvents were evaporated, and the residue was dissolved in DCM (300 mL). The resulting mixture was washed with saturated sodium bicarbonate solution, deionized water, and brine. The organic layer was dried using anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified using a silica column with a hexanes/DCM (10:90, v/v) mixture as the eluent. This yielded the desired compound as a deep red-orange solid. (400 mg, 32.4%). UV-vis (CH_2Cl_2) λ_{max} (nm):

350, 512. ^{1}H NMR (400 MHz, $CDCl_3$) 7.62 (s, 4H), 6.77 (d, *J* = 4.1 Hz, 4H), 6.31 (d, *J* = 4.1 Hz, 4H), 2.68 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.22, 140.98, 135.78, 134.30, 130.27, 130.17, 119.74, 14.99

Tetrakis(phenyl)dimer-BODIPY (2)

The dimer (200 mg, 0.4 mmol) was dissolved in benzene (21 ml), followed by the addition of benzaldehyde (0.31 ml, 3.2 mmol), piperidine (1.4 ml), and acetic acid (1.4 ml) sequentially. The mixture turned red and was brought to reflux under N_2 using a Dean-Stark apparatus. After 48 hours, the mixture's color turned blue-purplish, and the reaction completion was assessed using UV. The reaction was cooled to room temperature. Chloroform was added to the solution, and the resulting mixture was washed successively with saturated $NaHCO_3$, deionized water, and brine. The organic layer was dried over anhydrous Na_2SO_4, then the solvent was evaporated under reduced pressure. The crude product was purified using a silica column and hexane/dichloromethane (70:30, v/v) as the eluent. The desired compound was obtained as a golden-greenish solid (105 mg, 30 %). UV-vis (CH_2Cl_2) λ_{max} (nm): 360, 588 ,637. ^{1}H NMR (500 MHz, $CDCl_3$) 7.84 (s, 2H), 7.80 (s, 2H), 7.69 (s,4H), 7.68 (s, 6H), 7.45 – 7.41 (m, 12H), 7.38 – 7.35 (m, 6H), 7.00 (d, *J* = 4.4 Hz,4H), 6.90 (d, *J* = 4.4 Hz, 4H). ^{13}C NMR (126 MHz, CD_2Cl_2) 154.91, 137.09, 136.37, 136.07, 130.54, 129.68, 129.34, 128.91, 128.70, 128.51, 127.52, 118.96, 116.65. MALDI-TOF (APCI+) m/z calcd for $C_{56}H_{40}B_2F_4N_4$ [M+H]+ : 865.3521, 866.3484, 867.3448, 868.3482, 869.3515, 870.3549, 871.3582; found: 864.6458, 865.3485, 866.3462, 867.3441, 868.3468, 869.3491, 870.3492.

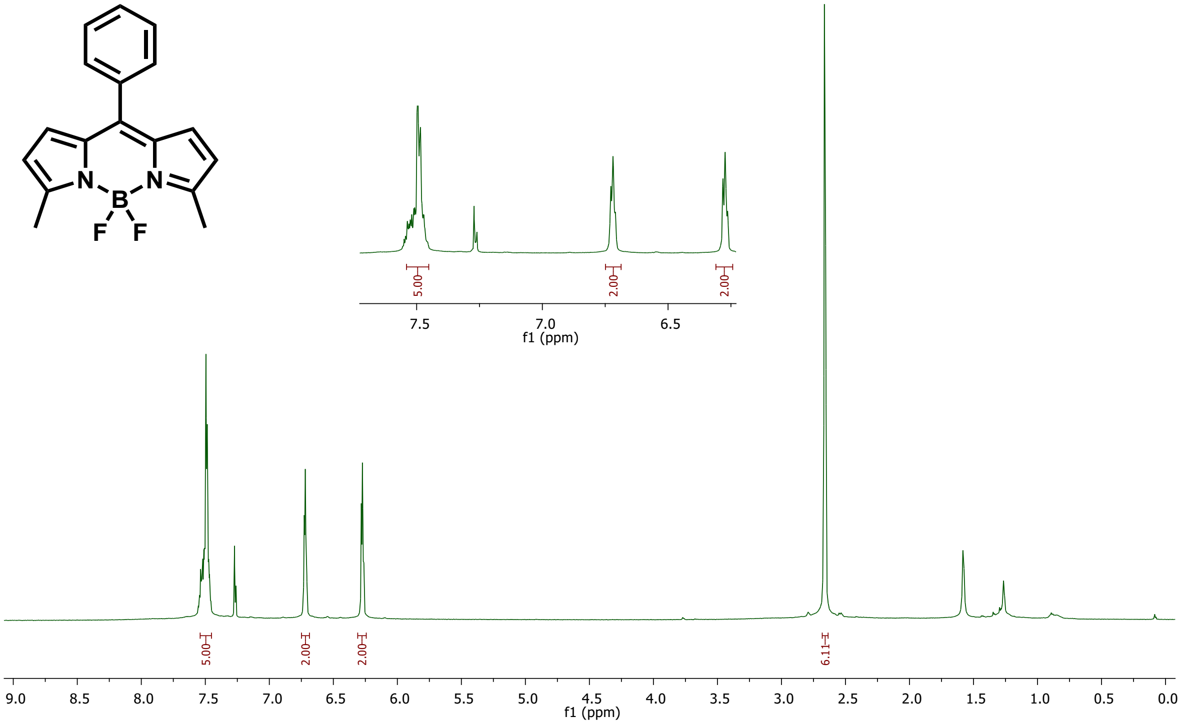


Figure S1. ^{1}HNMR spectrum of compound **1a**.

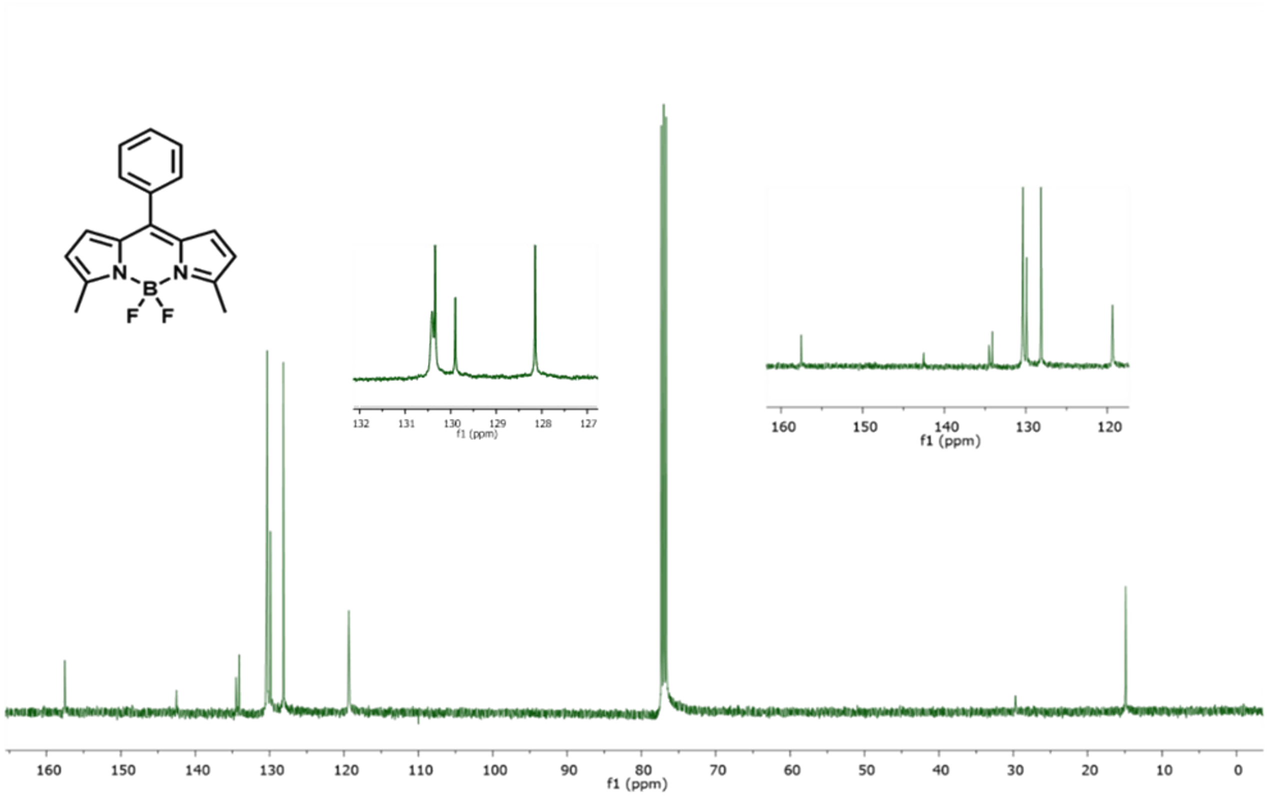


Figure S2. ^{13}CNMR spectrum of compound 1a.

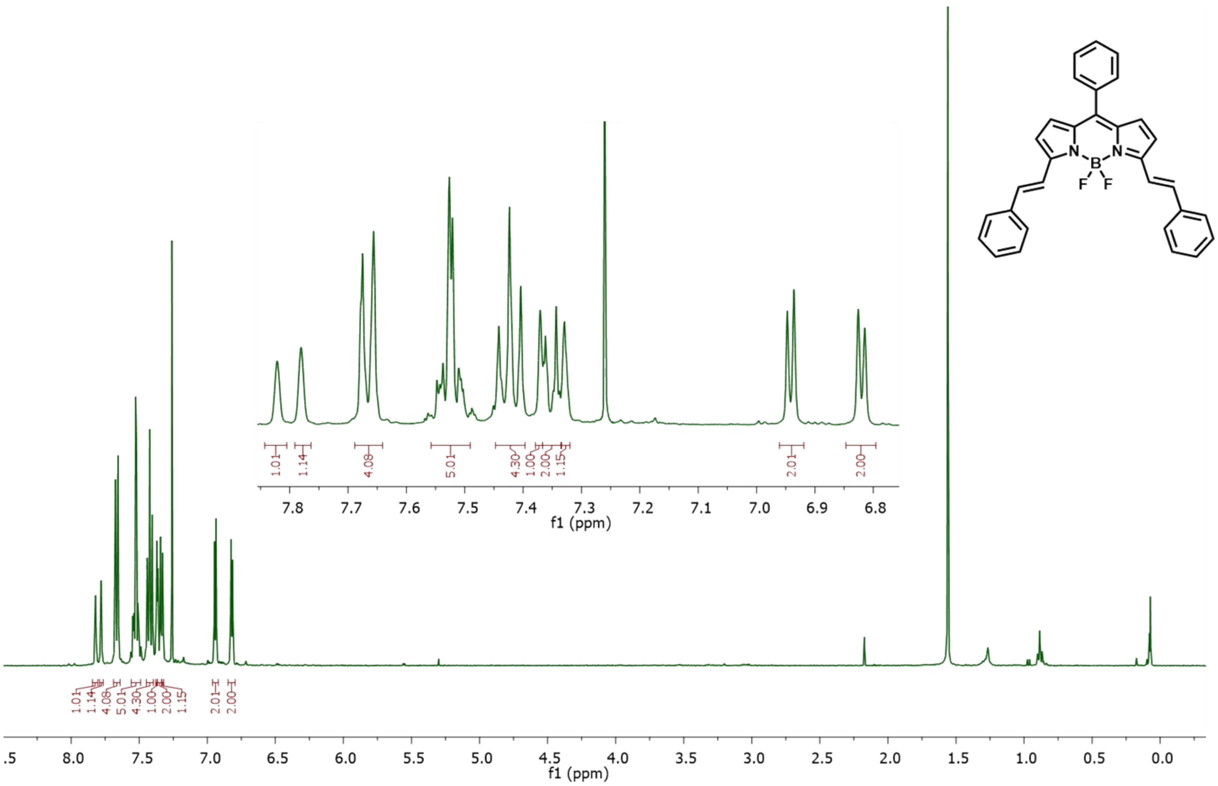


Figure S3. ^{1}HNMR spectrum of compound **1**.

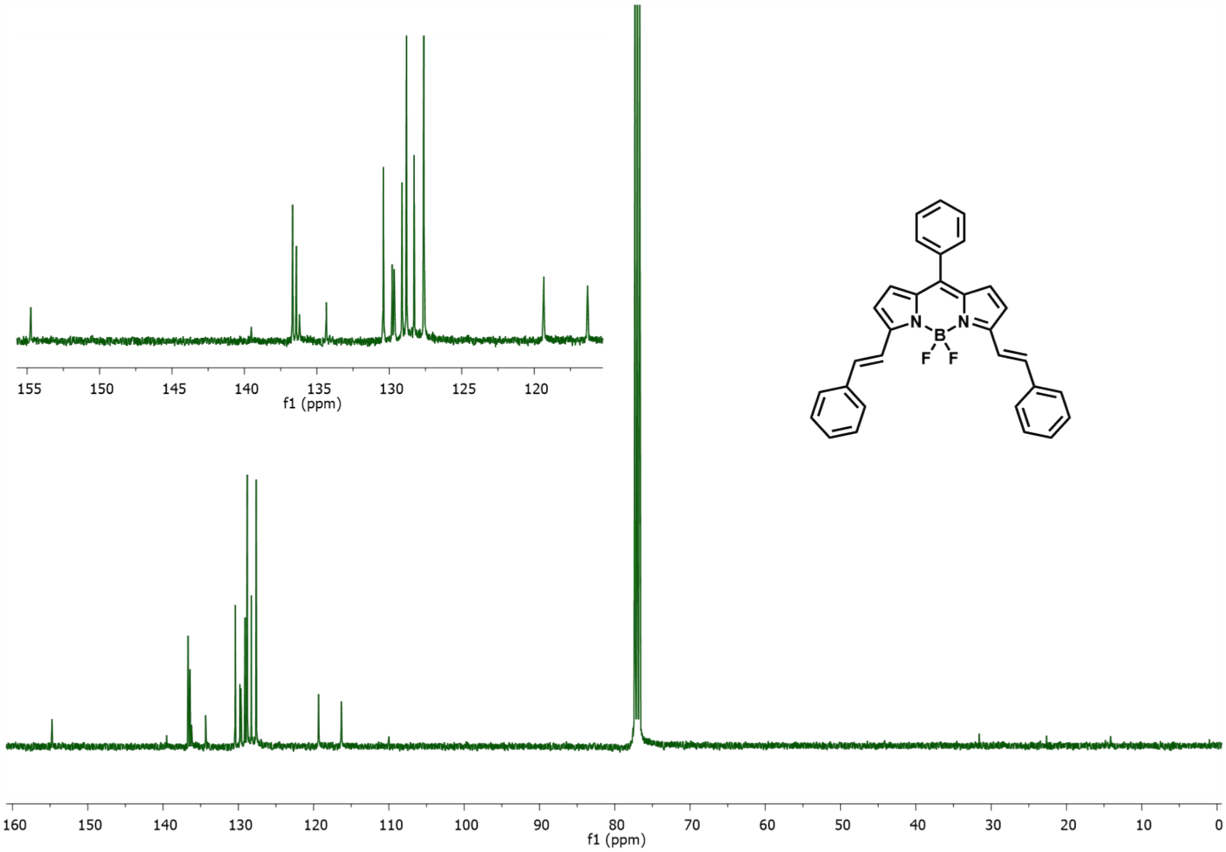


Figure S4. ^{13}CNMR spectrum of compound **1**.

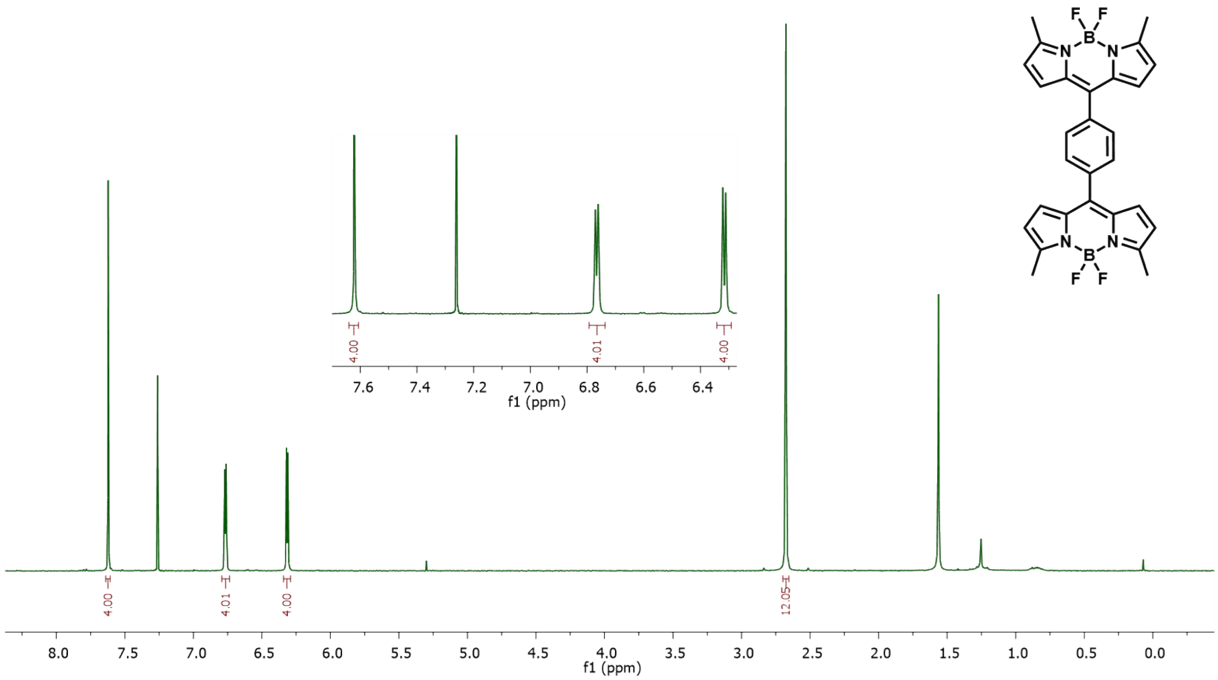


Figure S5. ^{1}HNMR spectrum of compound **2a**.

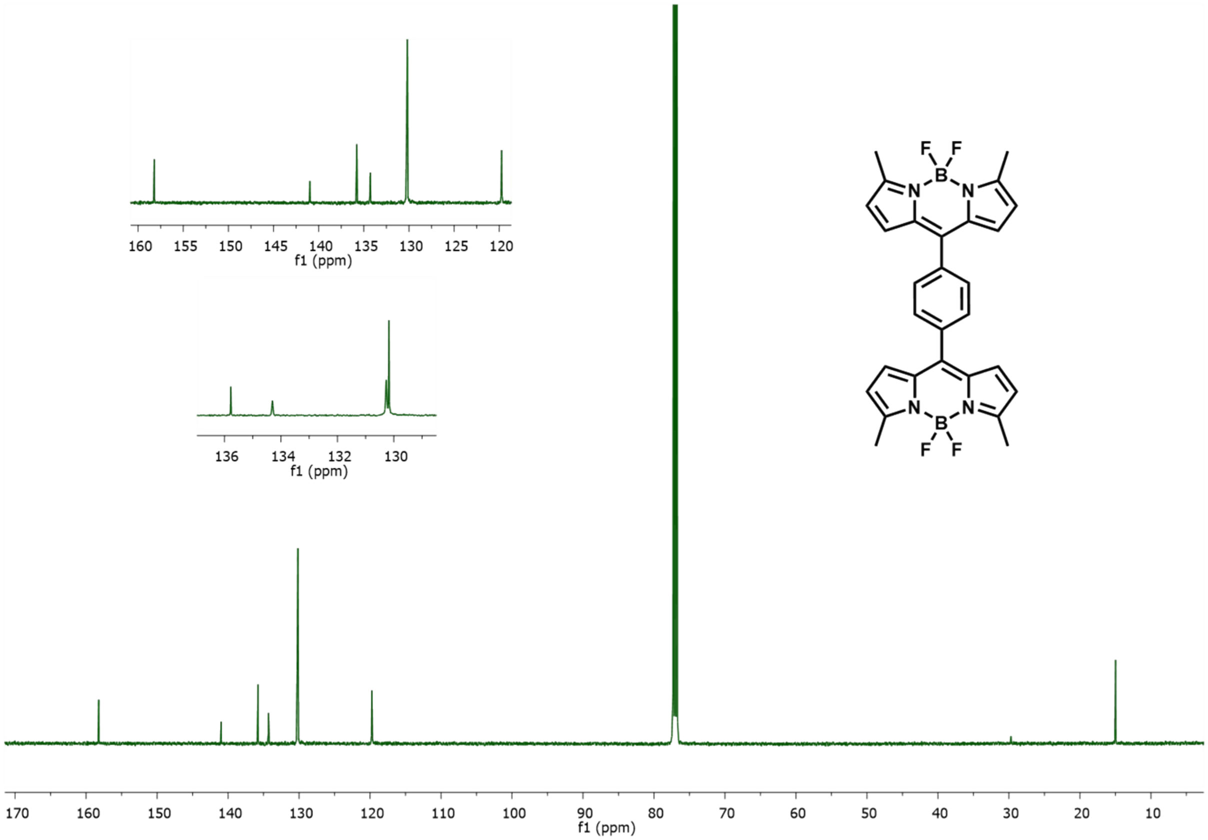


Figure S6. ^{13}CNMR spectrum of compound **2a**.

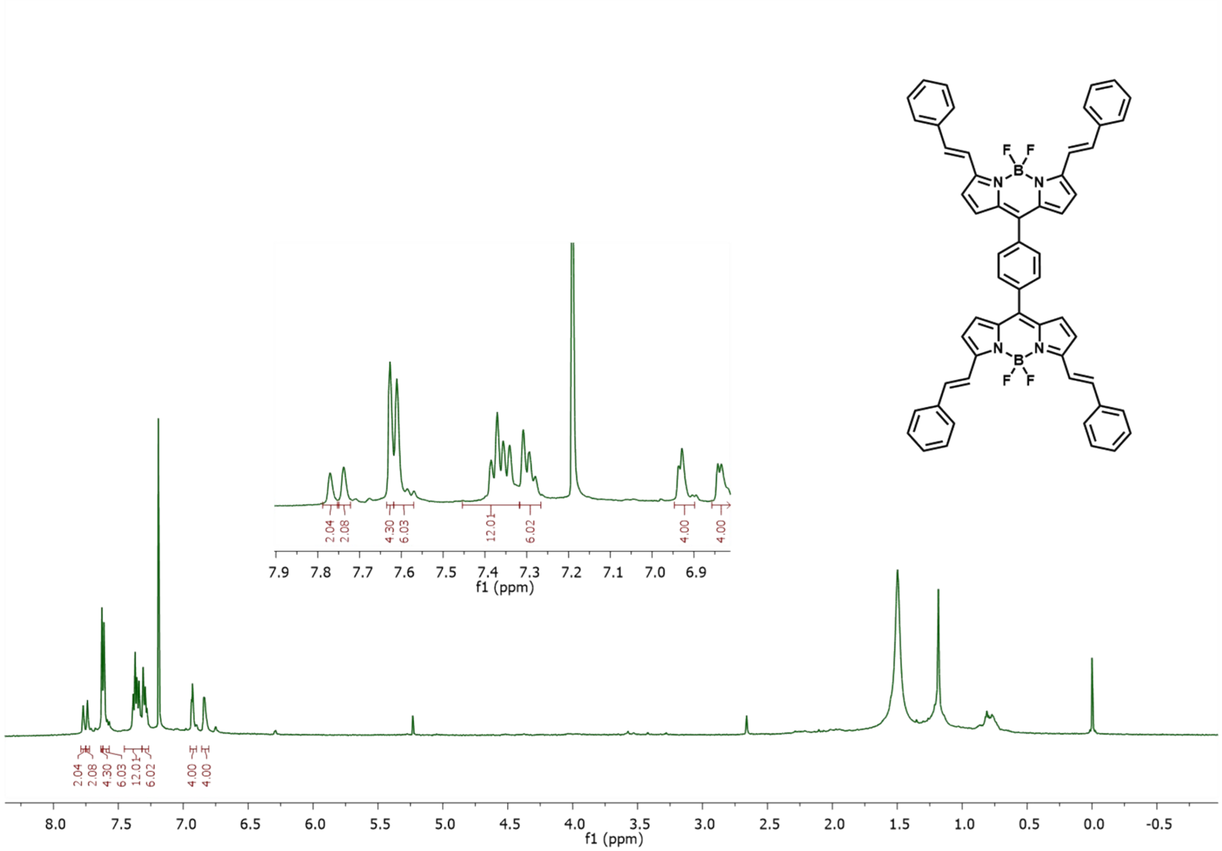


Figure S7. ^{1}HNMR spectrum of compound **2**.

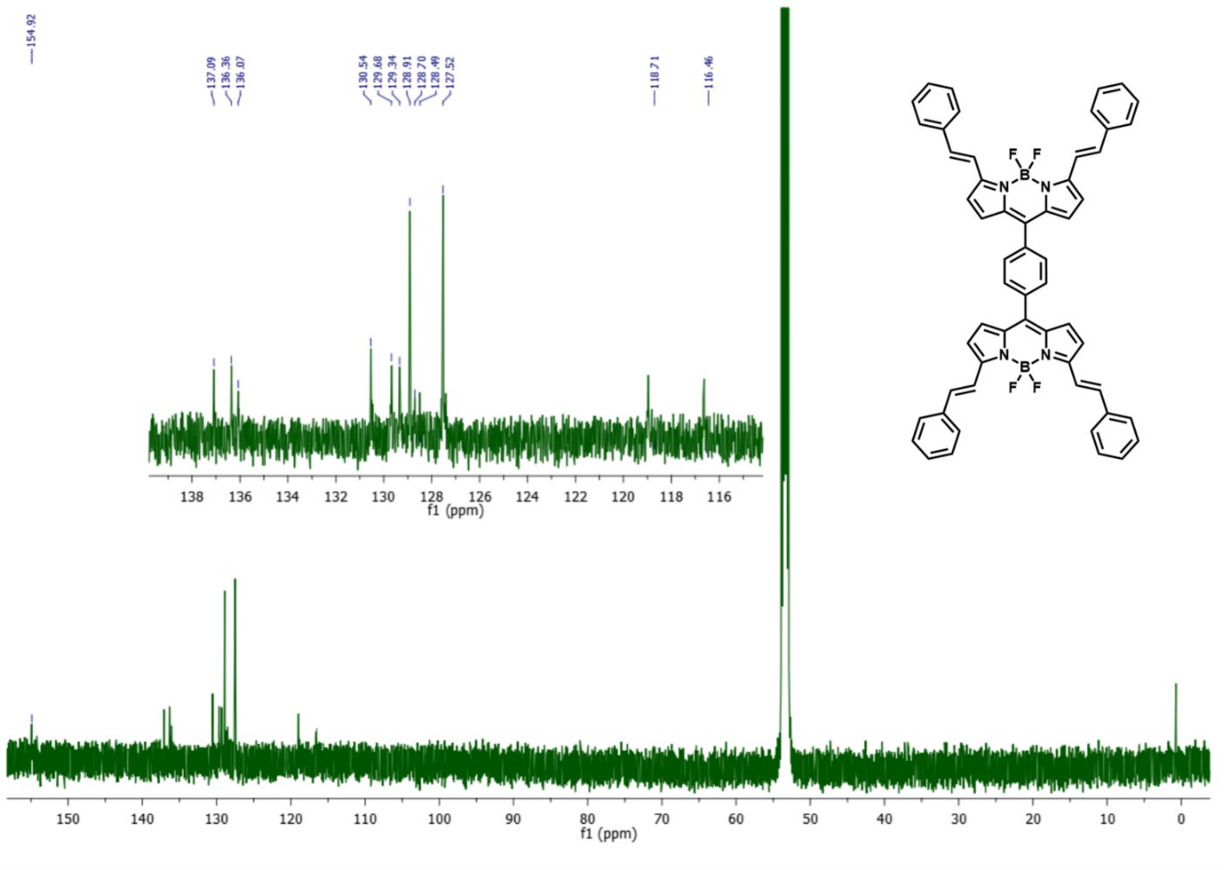


Figure S8. ^{13}CNMR spectrum of compound **2**.

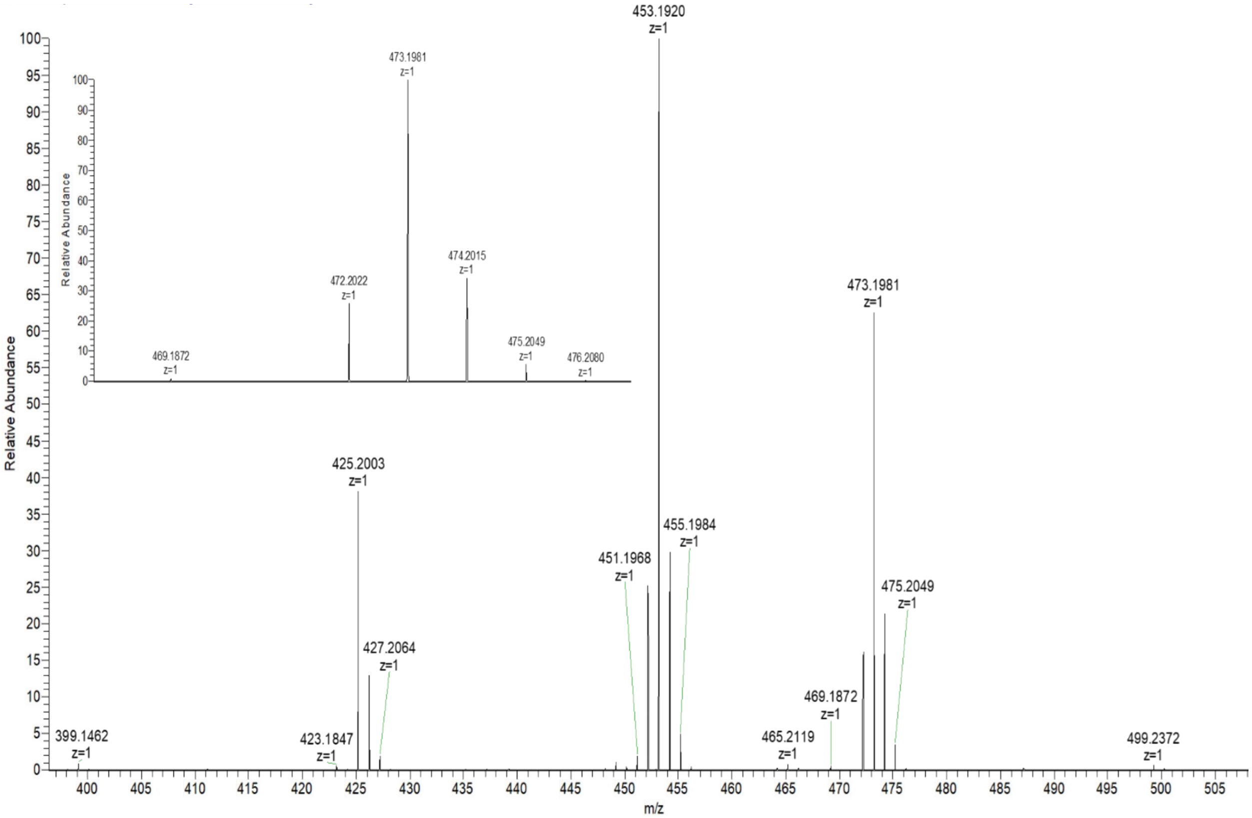


Figure S9. MALDI-TOF-Mass spectrum of compound 1

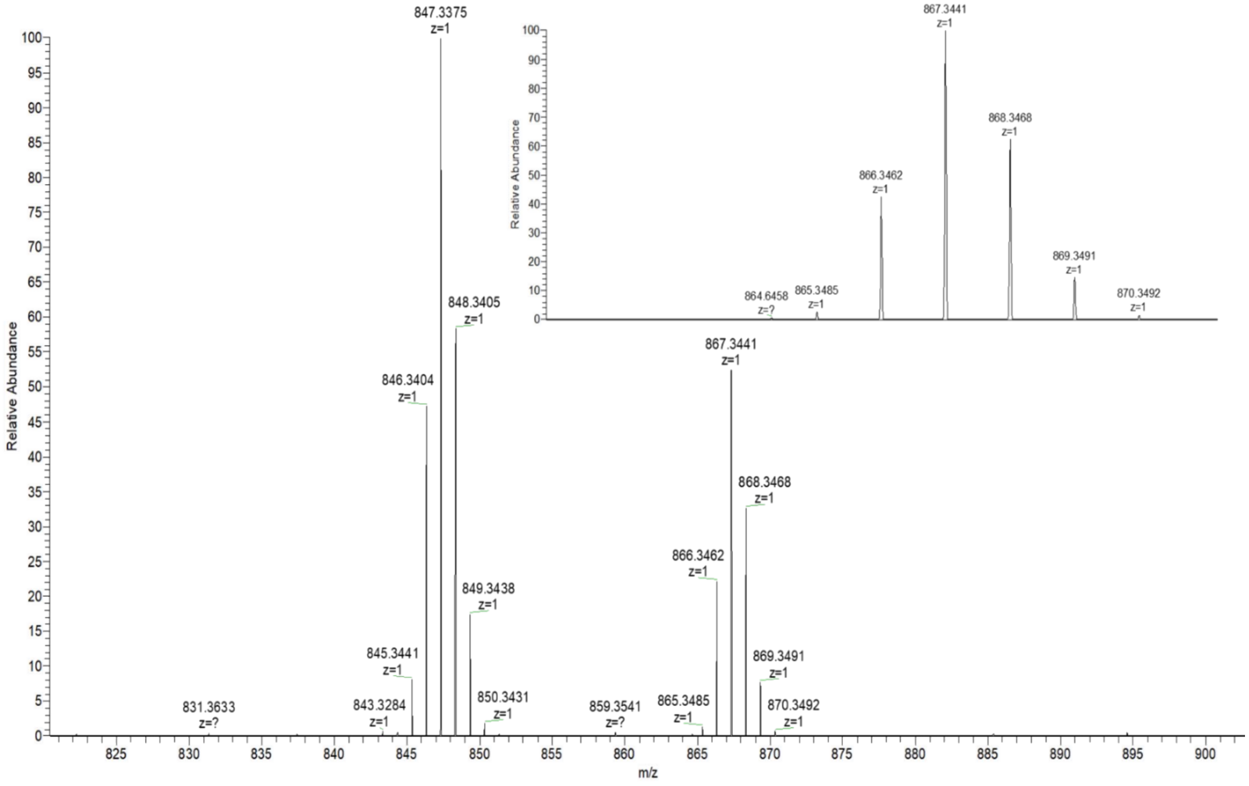


Figure S10. MALDI-TOF-Mass spectrum of compound 2

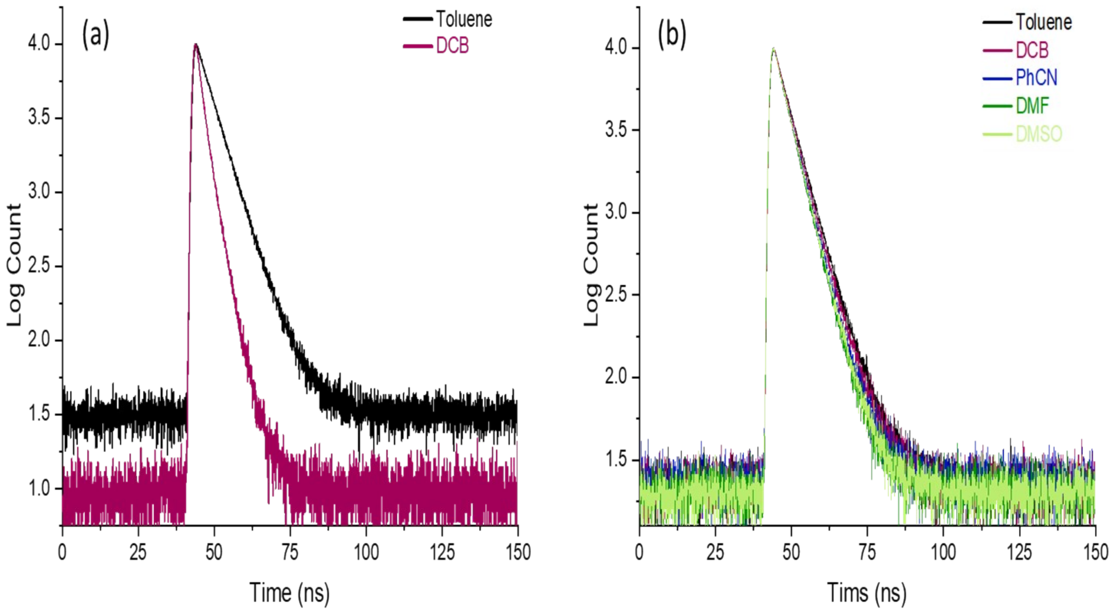


Figure S11. Emission decays of (a) dimer **2** and (b) compound **1** in different solvents following excitation at 495 nm.

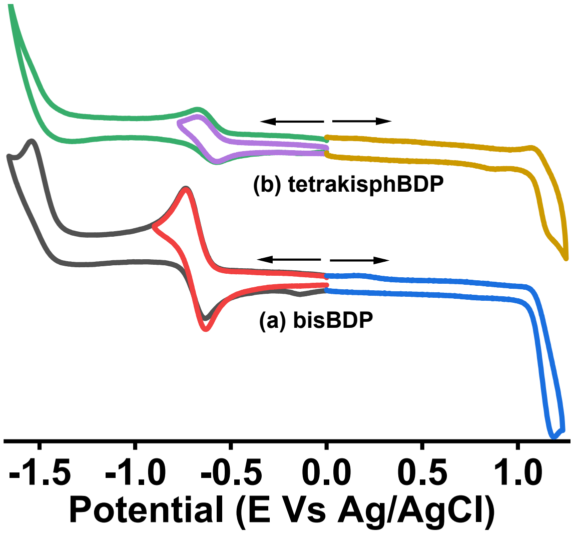
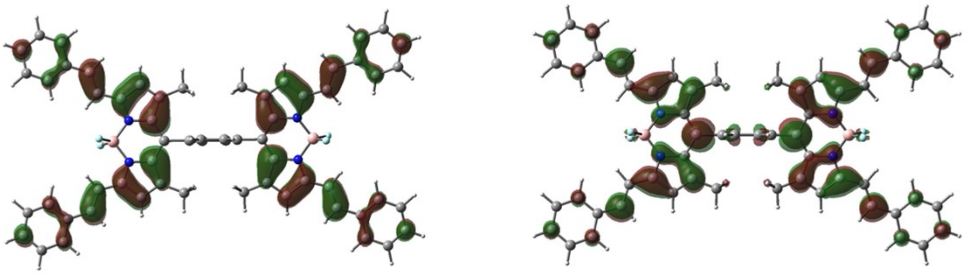
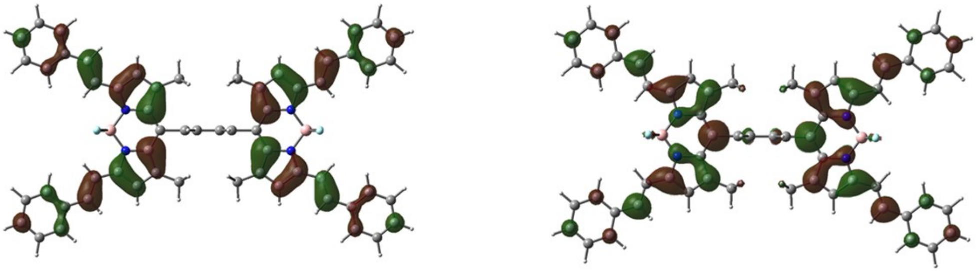


Figure S12. Cyclic voltammograms of (a) compound **1** and (b) compound **2** in DCB containing 0.1 M TBAClO$_4$.



HOMO: MO241 = -5.30 eV

LUMO: MO242 = -3.08 eV



HOMO: MO241 = -5.40 eV

LUMO: MO242 = -3.17 eV

Figure S13. Frontier HOMO and LUMO of dimer **2** in vacuo (top) and in DMSO (bottom).

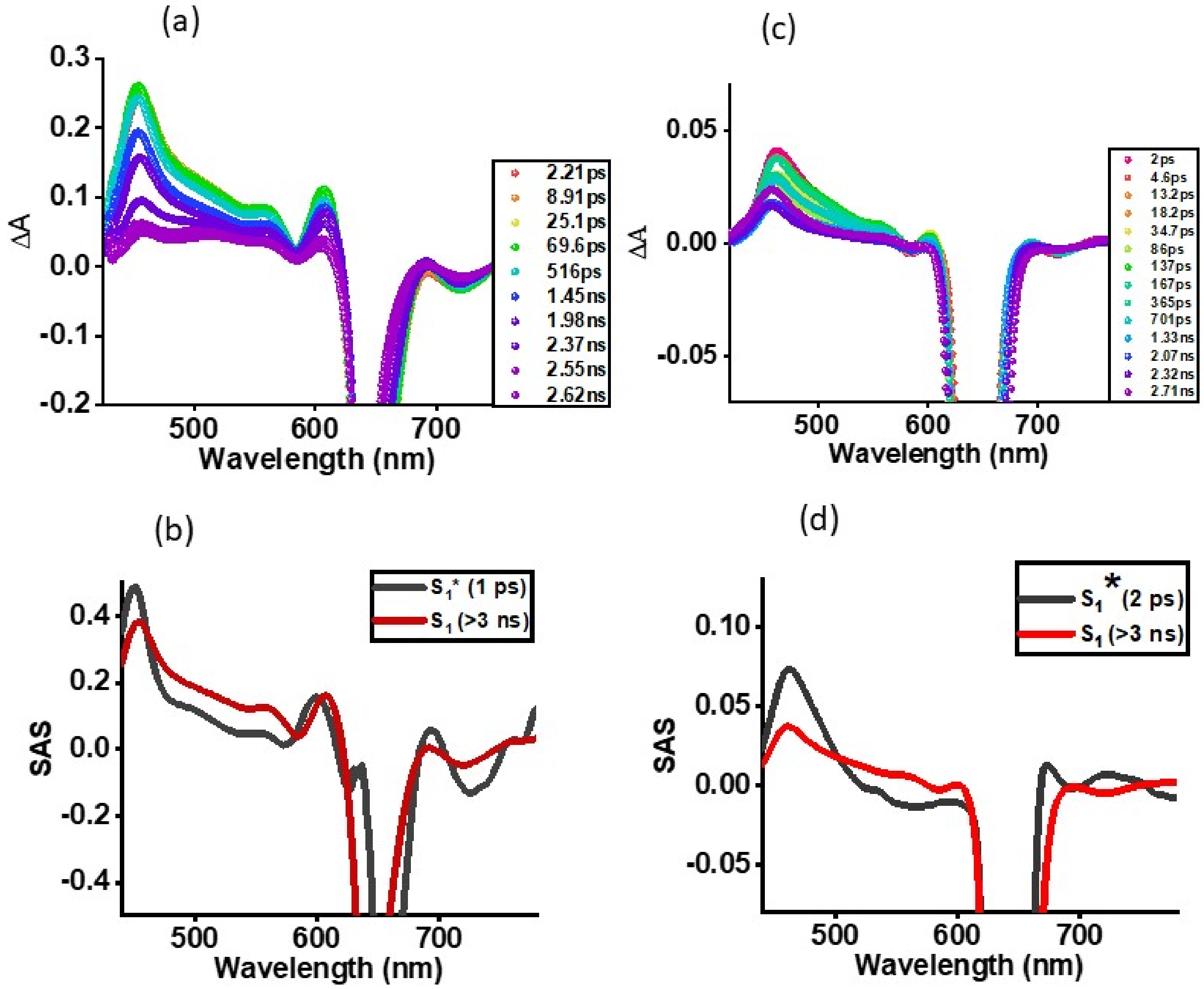


Figure S14. Femtosecond transient absorption spectra at the indicated delay times of **1** in (a) PhCN and (c) DCB (λ_{ex} = 648 nm). Species associated spectrum from Glotaran analysis is shown beneath for each spectrum.

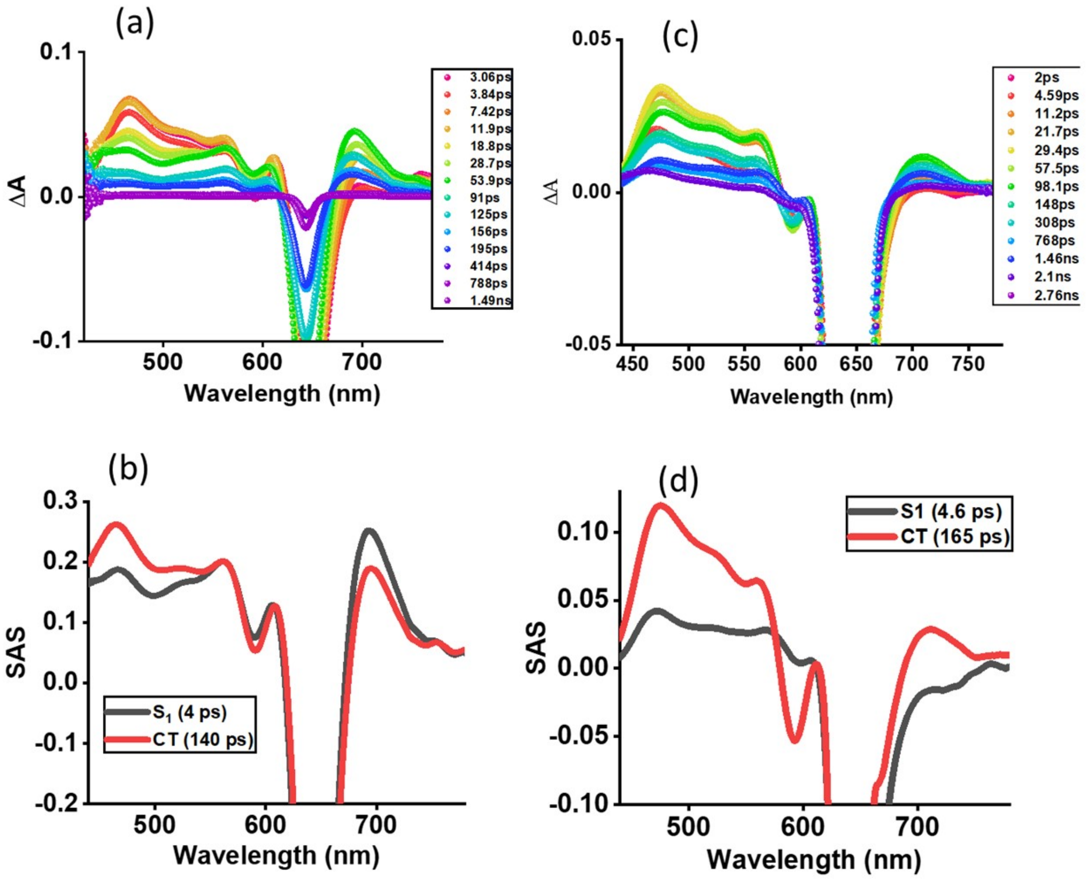


Figure S15. Femtosecond transient absorption spectra at the indicated delay times of **2** in (a) PhCN and (c) DCB (λ_{ex} = 648 nm). Species associated spectrum from Glotaran analysis is shown beneath for each spectrum.

Table S1. The natural transition orbitals (NTOs) for **2** in DMSO.

```
 Excited State   1:      Singlet-A      1.9718 eV  628.78 nm  f=0.0266  <S**2>=0.000
      240 -> 242         0.55330
      241 -> 243         0.43964
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2984.43273388
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-B      1.9720 eV  628.71 nm  f=0.0006  <S**2>=0.000
      240 -> 243         0.43166
      241 -> 242         0.55954

 Excited State   3:      Singlet-B      2.0334 eV  609.75 nm  f=0.0279  <S**2>=0.000
      240 -> 243         0.56099
      241 -> 242        -0.43361

 Excited State   4:      Singlet-A      2.0639 eV  600.74 nm  f=2.0372  <S**2>=0.000
      240 -> 242        -0.44150
      241 -> 243         0.55451

 Excited State   5:      Singlet-B      2.9457 eV  420.90 nm  f=0.5101  <S**2>=0.000
      238 -> 243         0.36480
      239 -> 242         0.52035
      240 -> 245        -0.20976
      241 -> 244         0.21825
```

HOMO in Red, **LUMO in Blue**

Table S2. Electronic coupling, *H* between the BODIPY entities of **2**.

Solvent	v_{max} (10^4 cm^{-1})	$\Delta v_{1/2,}$ (10^5cm^{-1})	ε (10^5 M^{-1}cm^{-1})	r_{DA} (Å)	H (10^3 cm^{-1})
Toluene	1.557	2.94	1.78	17.1	34.4
DCB	1.546	2.78	1.77	17.1	33.2
PhCN	1.555	2.70	1.31	17.1	28.3
DMSO	1.562	2.70	1.42	17.1	29.5