Electronic Supplementary Information

Dual Emissive Bodipy-Benzodithiophene-Bodipy TICT Triad with Remarkable Stokes Shift of 194 nm

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Materials and Methods

All chemicals and solvents were purchased from commercial suppliers (Sigma Aldrich, SD Fine Chemicals) and used without further purification. Tetrahydrofuran (THF) was dried over sodium/benzophenone and distilled prior to use. Dichloromethane (DCM) was dried over calcium hydride and distilled prior to use. Silica gel of mesh size 60-120 was used for column chromatography.

^{1}H and ^{13}C NMR (400 and 100 MHz, respectively) spectra were recorded using a BRUKER AV 400 NMR spectrometer. For acquisition and processing, Bruker Topspin software was used. All the spectra were recorded in CDCl$_3$ with TMS as the internal standard. CDCl$_3$ was purchased from Merck (Germany).

Mass spectrometry measurements were performed on UltrafleXtreme MALDI TOF/TOF (Bruker Daltonics) instrument. Software used for acquiring mass spectra was Flex Control, Bruker (USA) and software used for analyzing mass spectra was Flex Analysis 3.1.

All spectroscopic measurements were performed at room temperature. The absorption spectra were recorded with UV/Vis/NIR Shimadzu spectrophotometer model UV 3600. Thin films for UV/Vis absorption measurements were prepared by spin coating solution of triads in chloroform (CHCl$_3$) onto cleaned and UV Ozone treated quartz substrates.

Fluorescence solution measurements were performed with Hitachi F7000 fluorescence spectrophotometer equipped with R928F photomultiplier expandable upto 900 nm. Various excitation wavelengths were used to perform the fluorescence measurements. Standard software FL Solutions was used for the measurement and analysis of the data. Absolute fluorescence quantum yield of samples were measured with quantum yield measurement set-up equipped with 60 phi integrating sphere with

sample holder and quantum yield calculation program provided with F7000 from Hitachi.

Time resolved fluorescence spectra were measured by using time correlated single photon counting (TCSPC) model from Horiba Jobin Yuvon Fluorocube -01-NL equipped with picosecond laser diodes as excitation source. The optical pulse durations from < 70ps were used. Highly integrated picosecond PMT modules as well as micro channel plate PMTs were used for the time resolution.

Electrochemical measurements were performed using Autolab PGSTAT 302N (Metrohm Autolab electrochemical instruments, Switzerland), with a conventional three electrode single-compartment cell consisting of a platinum (Pt) disk electrode as the working electrode, Ag/AgCl containing 3M KCl solution as the reference electrode, and Pt wire as the counter electrode at a scan-rate of 0.1 V/s. As a supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) (Alfa Aesar) dissolved in pre-dried DCM was used. The solutions were purged with nitrogen for 2 mins prior to measurement. The concentration of the prepared samples was ~ 0.1-0.3 mM. The electrochemical potential was internally calibrated against the standard ferrocene/ferrocenium (Fc/Fc$^+$) redox couple.

Charge carrier mobility measurements of triad **A-D-A** was performed using hole only architecture: ITO/PEDOT:PSS/Active Layer (**A-D-A**)/Au. The thickness and active area of the active layer was about ~ 110 nm and 0.09 cm^2 respectively. Space charge limited current (SCLC) model was used to extract hole mobilities by using Mott Gurney equation[1,2] described by

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$$

where J is current density, d is the thickness of active layer, μ_h is hole mobility, ε_r is the relative dielectric constant of material, ε_0 is the permittivity of free space (8.85 ×

10^{-12} Fm^{-1}), V is the voltage applied to the diode. Current density and voltage data were fitted for above equation to extract mobility values.

Quantum chemical density functional theory (DFT) calculations were performed on the coupled D-A-D triads in ground state using Gaussian09 program suite.[1] The side chains in all molecules were replaced with methyl group in order to account for the electron donating effect of the alkyl chain and at the same time reducing the computational time and cost. The studied molecules were optimized using global hybrid B3LYP functional and 6–31G (d, p) basis set in gas phase. The frontier molecular orbitals (FMO) electronic levels and FMO distribution were obtained from geometry optimization into neutral ground state geometries.

Synthesis
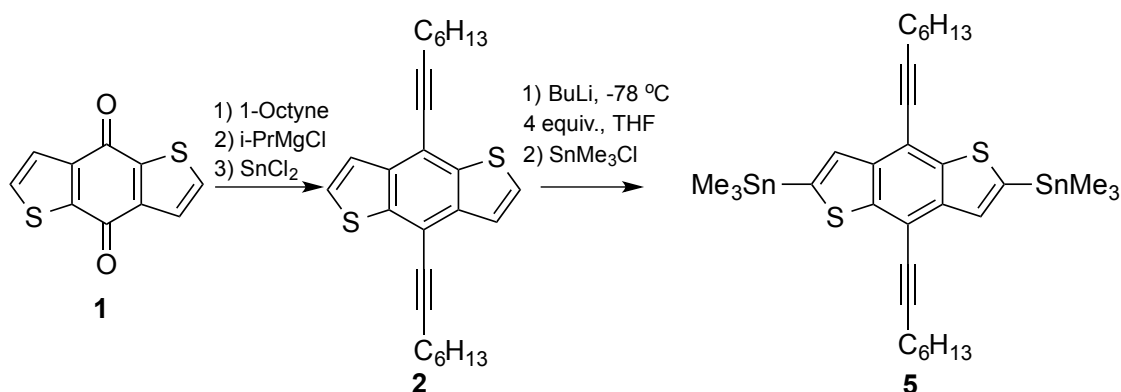
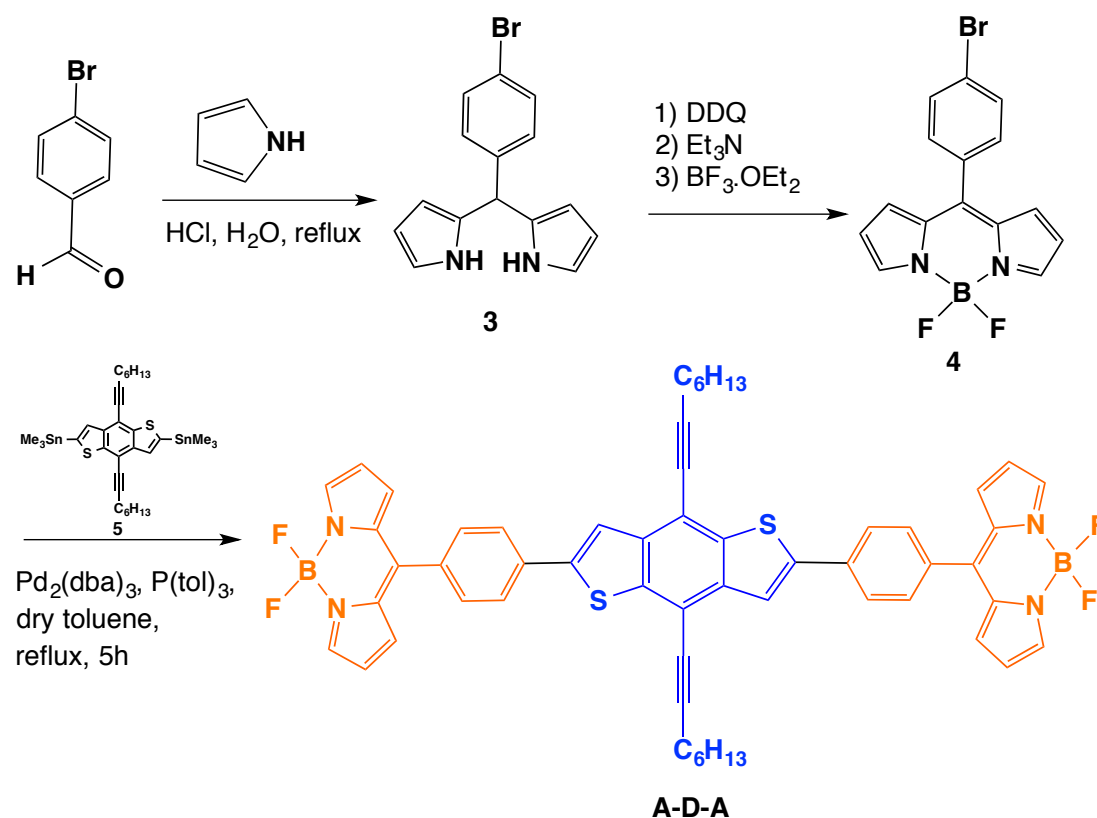**Scheme 1.** Synthesis of distannylated BDT derivative **5**.

5: Synthesis of BDT donor precursor compounds **1** and **2** were accomplished starting from thiophene-3-carboxylic acid according to the literature reported method.[2] 200mg (0.49 mmol) of **2** was dissolved in dry THF and the solution was cooled to -78°C and 1.2 ml of *n*-BuLi as a 1.6 M solution in THF (1.97 mmol) was added dropwise while stirring under inert atmosphere. The reaction mixture was stirred at -78 °C for 1 hour following which 1.97 ml of Trimethyltin chloride as a 1 M solution in hexane (1.97 mmol) was added to it. The reaction mixture was stirred overnight at room

temperature. The reaction was quenched by adding water and extracted with diethyl ether. **5** was obtained as yellow crystalline solid upon recrystallization from ethanol solution of the crude.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61 (s, 2 H, Ar-H), 2.65 (t, d = 6.8 Hz, 4 H), 1.72-1.53 (m, 18 H, CH$_2$), 0.95-0.92 (m, 6 H, CH$_3$), 0.45 (t, J = 28 Hz, 18 H, CH$_3$).

^{13}C NMR (100MHz, CDCl$_3$): δ = 9.36, 15.26, 17.92, 20.61, 23.86, 24.07, 26.69, 94.92, 105.62, 126.24, 134.31, 137.89 ppm.

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for [M]$^+$ C$_{32}$H$_{46}$S$_2$Sn$_2$: 732.260, found: 732.029

Scheme 2. Synthesis of BDP-BDT-BDP triad **A-D-A**.

Synthesis of BDT donor precursor compound **2** was accomplished starting from thiophene-3-carboxylic acid according to the literature reported method.[2] The purity of the synthesized donor precursor **2** was confirmed by ^{1}H NMR and ^{13}C NMR measurement prior to performing the stannylation reaction (only data provided).

¹H NMR (400 MHz, CDCl₃): δ = 7.57 (d, J = 5.2 H, 2 H, Ar-H), 7.49 (d, J = 5.2 Hz, 2 H, Ar-H,), 2.63 (t, J = 6.8 Hz, 4 H, CH₂), 1.75-1.69 (m, 4 H, CH₂), 1.60-1.56 (m, 4 H, CH₂), 1.40-1.33 (m, 8 H, CH₂), 0.95-0.91 (m, 6 H, CH₃).

¹³C NMR (100MHz, CDCl₃): δ = 14.10, 19.97, 22.62, 28.62, 28.80, 31.41, 100.43, 112.25, 123.25, 127.55, 138.27, 140.24.

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for [M-H]⁺ $C_{26}H_{30}S_2$: 405.171 and found: 405.222.

3: A solution of 4-bromobenzaldehyde (1.85 g, 10 mmol) in pyrrole (3.5 ml, 50 mmol) was refluxed at 100 °C, in the presence of H_2O (20 mL) and HCl (36.5 wt.%, 70μL), for 1 hour. The product formed was extracted using ethyl acetate and then evaporating the solvent in vacuo using a rotary evaporator. The resulting reaction mixture was then subjected to column chromatography with petroleum ether/12 % ethyl acetate as the eluent. The resulting dipyrromethane was a pale white solid obtained with a yield of 78 %.

¹H NMR (400 MHz, CDCl₃): 7.92 (s, br, 1 H), 7.44 (d, J= 8 Hz, 2 H), 7.09 (d, J= 8.4 Hz, 2 H), 6.71-6.70 (m, 2 H), q (6.17, 2 H), 5.89 (s, br, 2 H), 5.44 (s, 1 H).

¹³C NMR (100MHz, CDCl₃): 43.51, 107.46, 108.60, 114.26, 117.51, 120.86, 130.51, 131.71, 131.90 ppm.

Matrix assisted laser desorption ionization (MALDI-TOF): [M-H]⁺ Calculated for $C_{15}H_{12}BrN_2$: 300.179 and found: 300.345

4: Dipyrromethane **3** (0.8 g, 2.6562 mmol) was dissolved in dry dichloromethane (DCM) and to that, DDQ (0.73g, 3.2045 mmol) was added. The color immediately changed to red. Subsequently, triethylamine (4 ml) was added to the reaction mixture after 3 hours and after further 6 hours, BF₃.OEt₂ (4 ml) was added and the reaction mixture was stirred overnight. The reaction mixture was filtered through a silica gel

column with DCM as solvent to remove the DDQ. The resulting reaction mixture was extracted with DCM and the aqueous layer was neutralized with 2N NaOH solution and organic layer washed with saturated brine solution. The organic layer was dried over sodium sulphate and solvent was removed at the rotary evaporator. The crude product obtained was subjected to silica gel column chromatography and ethylacetate (10%)/ hexane as eluent to obtain the bodipy compound **4** in 60 % yield.

^{1}H NMR 400MHz (ppm TMS, CDCl$_3$): 7.97 (s, 2 H), 7.68 (d, J= 8 Hz, 2 H), 7.44 (d, J= 8.4 Hz, 2 H), 6.90 (d, J= 4 Hz, 2 H), 6.56 (d, J= 4 Hz, 2 H).

^{13}C DEPT-135 NMR (100MHz, CDCl$_3$): δ = 118.9, 131.3, 131.9, 144.6 ppm

Matrix assisted laser desorption ionization (MALDI-TOF): [M]$^+$ Calculated for C$_{15}$H$_{10}$BBrF$_2$N$_2$: 346.970 and found: 346.790

A-D-A: Compound **4** (50 mg, 0.1385 mmol) was dissolved in dry toluene (25 mL) and solution was degassed and purged with nitrogen for 10 min. Subsequently, distannylated BDT compound **5** (51 mg, 0.0692 mmol) was added, solution was stirred and purging was continued. Pd$_2$(dba)$_3$ (2.5 mg, 0.0027 mmol) and P(o-tol)$_3$ (3.9 mg, 0.1605 mmol) were added and the reaction mixture was purged for another 15 min and then refluxed for 5 h. The Stille coupling reaction[3] mixture was cooled to RT and the solvent was evaporated on rotary evaporator. It was then subjected to column chromatography purification using DCM/petroleum ether (80/20 v/v) resulting in isolation of an orange compound with yield of 56 %.

^{1}H NMR (400MHz, CDCl$_3$): 7.97-7.94 (m, 10 H, Ar-H), 7.89-7.67 (m, 4 H, Ar-H), 7.03-7.02 (m, 4 H, Ar-H), 6.61-6.58 (m, 4 H, Ar-H), 2.06-2.01 (m, 4 H, CH$_2$), 1.82-1.78 (m, 4 H, CH$_2$), 1.40-1.25 (m, 12 H, CH$_2$), 0.89-0.86 (m, 6 H, CH$_3$).

^{13}C NMR (100MHz, CDCl$_3$): δ = 14.1, 14.2, 20.1, 22.7, 28.7, 28.9, 29.2, 29.4, 29.5, 29.7, 30.2, 31.4, 31.9, 33.8, 112.3, 114.1, 116.6, 118.7, 126.4, 128.4, 128.9, 131.3,

131.4, 135.4, 136.7, 139.3 ppm.

Matrix assisted laser desorption ionization (MALDI-TOF): $[M-H+Na]^+$

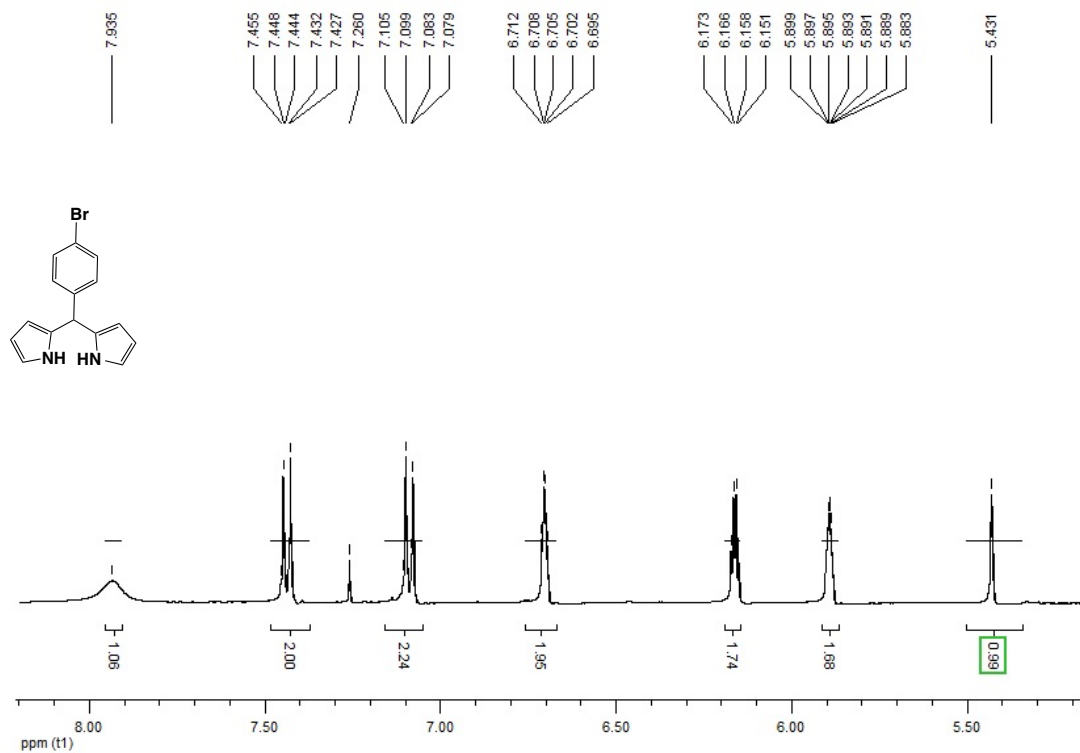Calculated for $C_{56}H_{48}B_2F_4N_4S_2Na$: 960.762 and found: 960.566
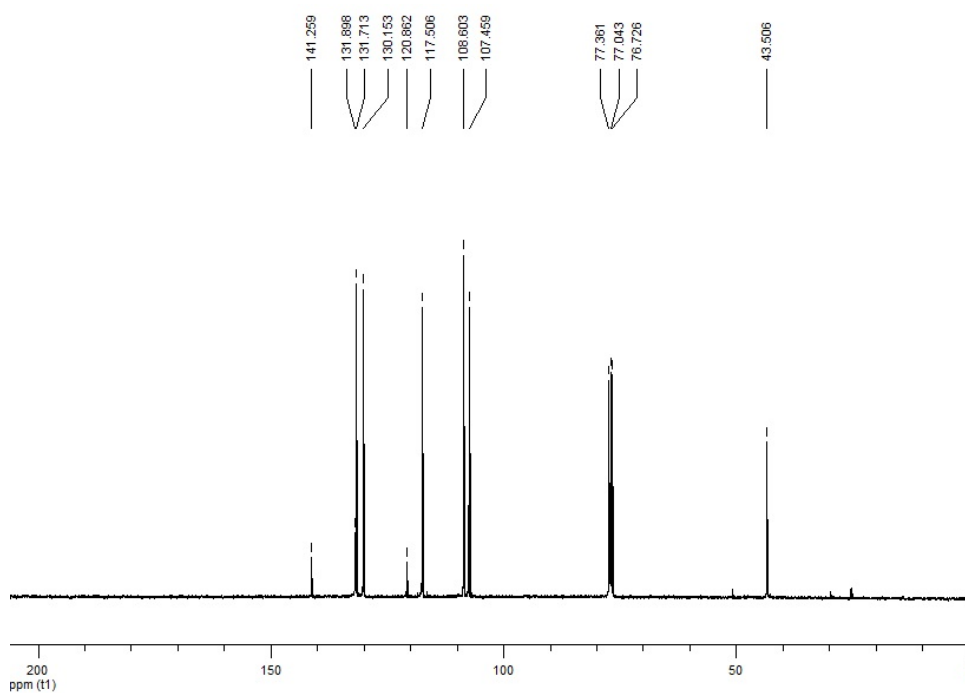

Figure S1. ^{1}H NMR (400 MHz) spectrum of DPM **3**.

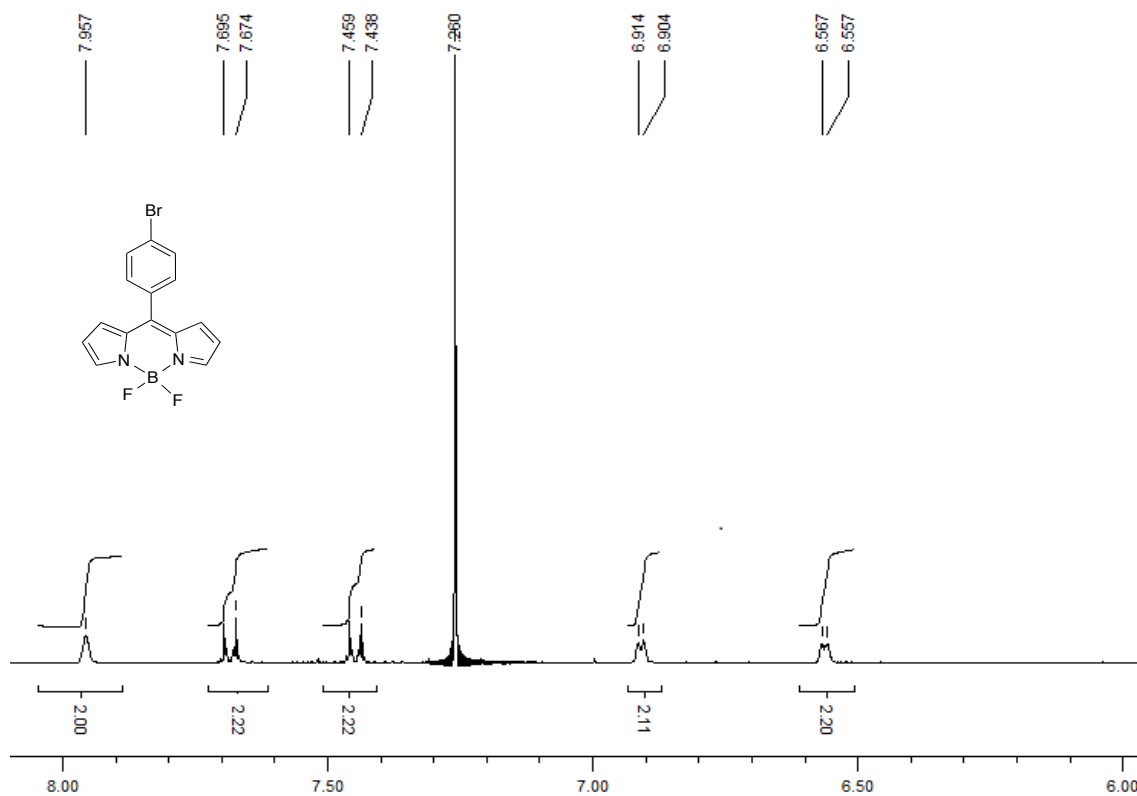**Figure S2.** ^{13}C NMR (100 MHz) spectrum of DPM **3**.
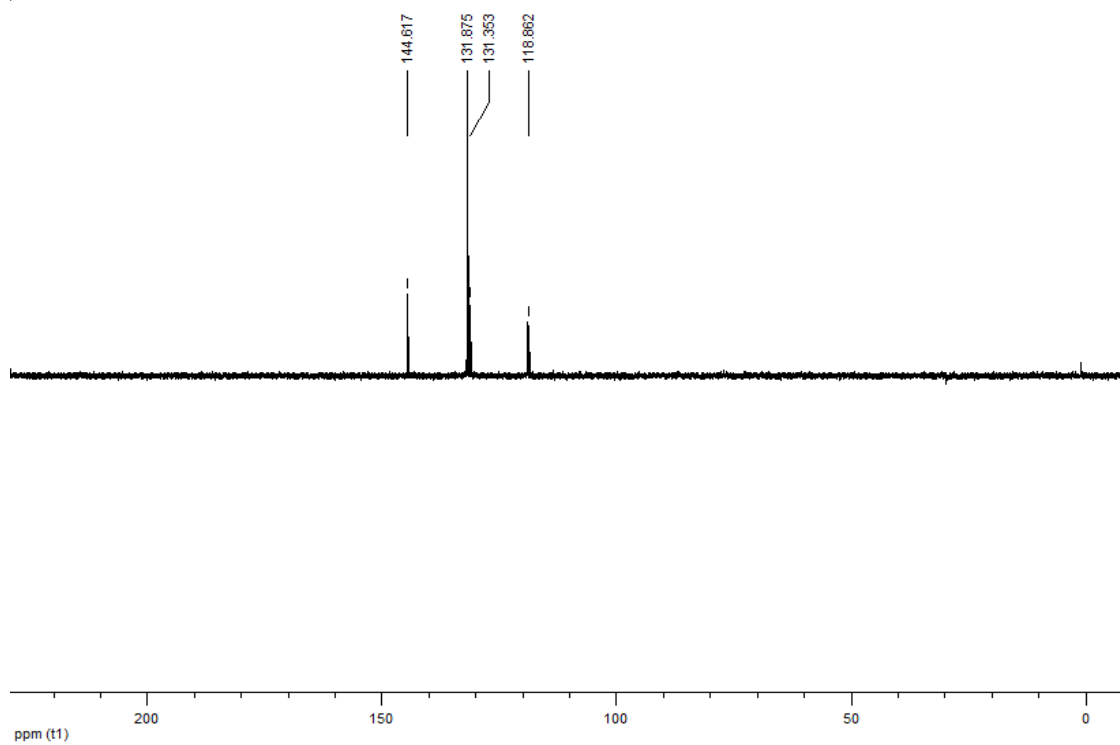
Figure S3. ^{1}H NMR (400 MHz) spectrum of BODIPY acceptor **4**.

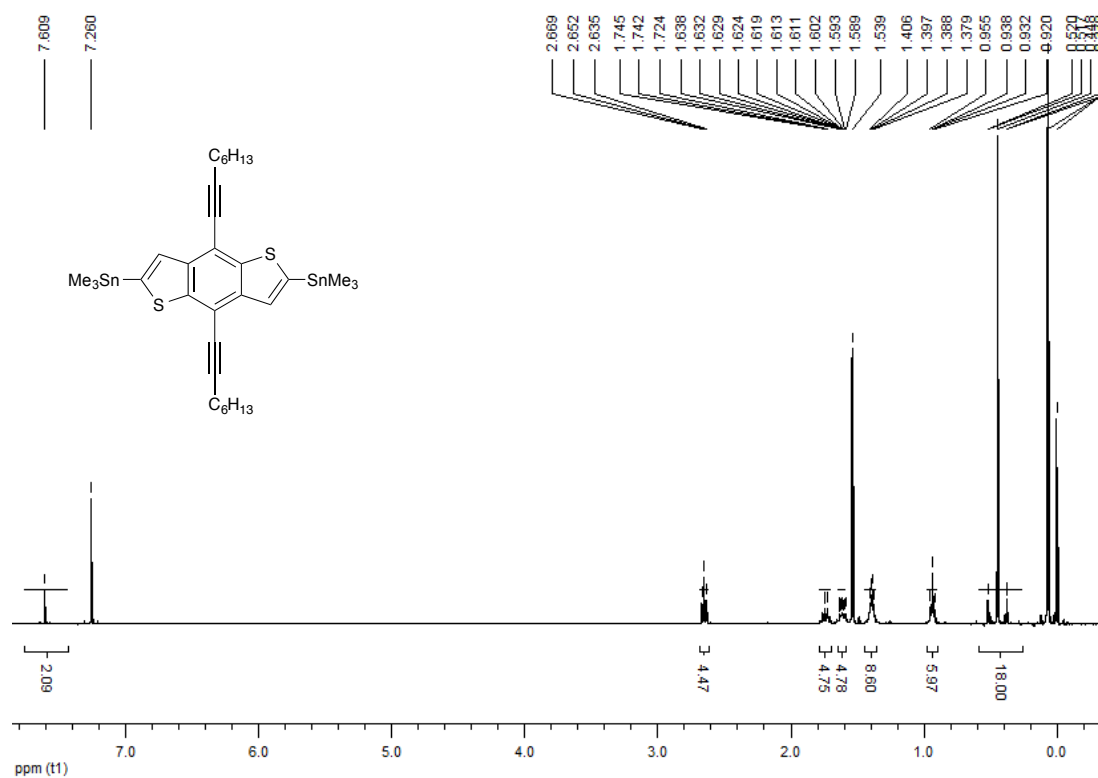**Figure S4.** ^{13}C-DEPT-135 NMR (100 MHz) spectrum of BODIPY acceptor **4**.

Figure S5. ^{1}H NMR (400 MHz) spectrum of BDT donor **5**.
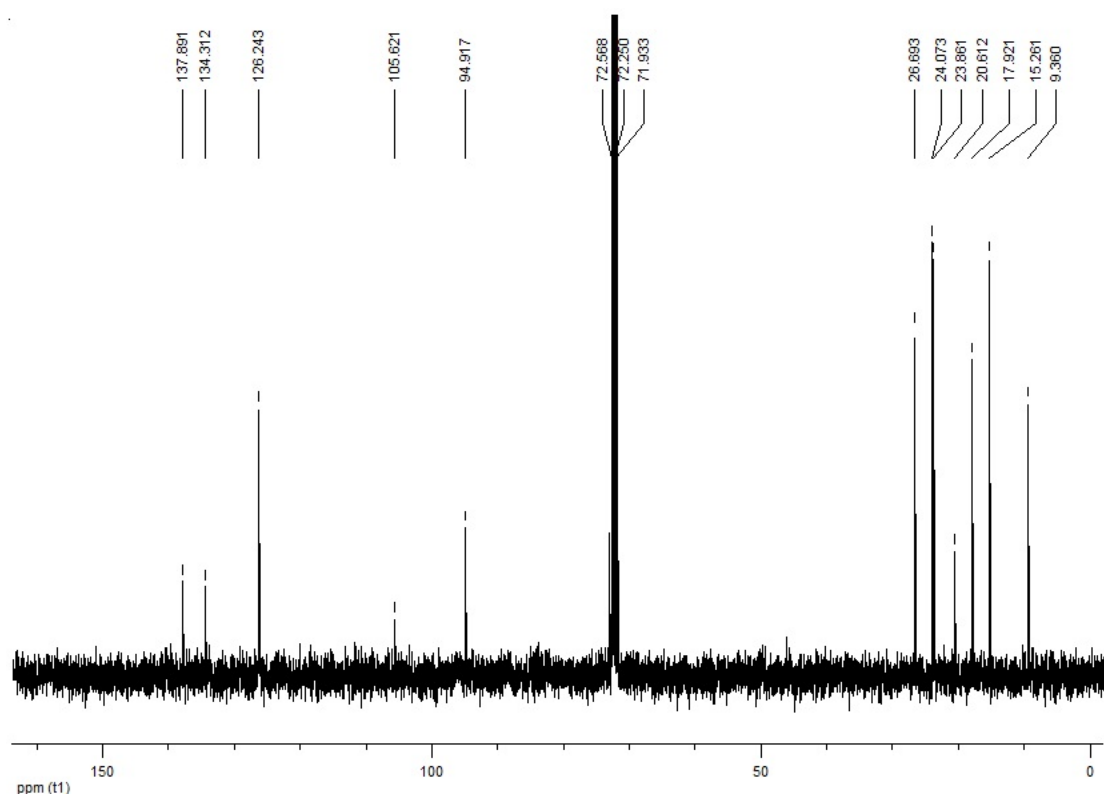
Figure S6. ^{13}C NMR (100 MHz) spectrum of donor **5**.
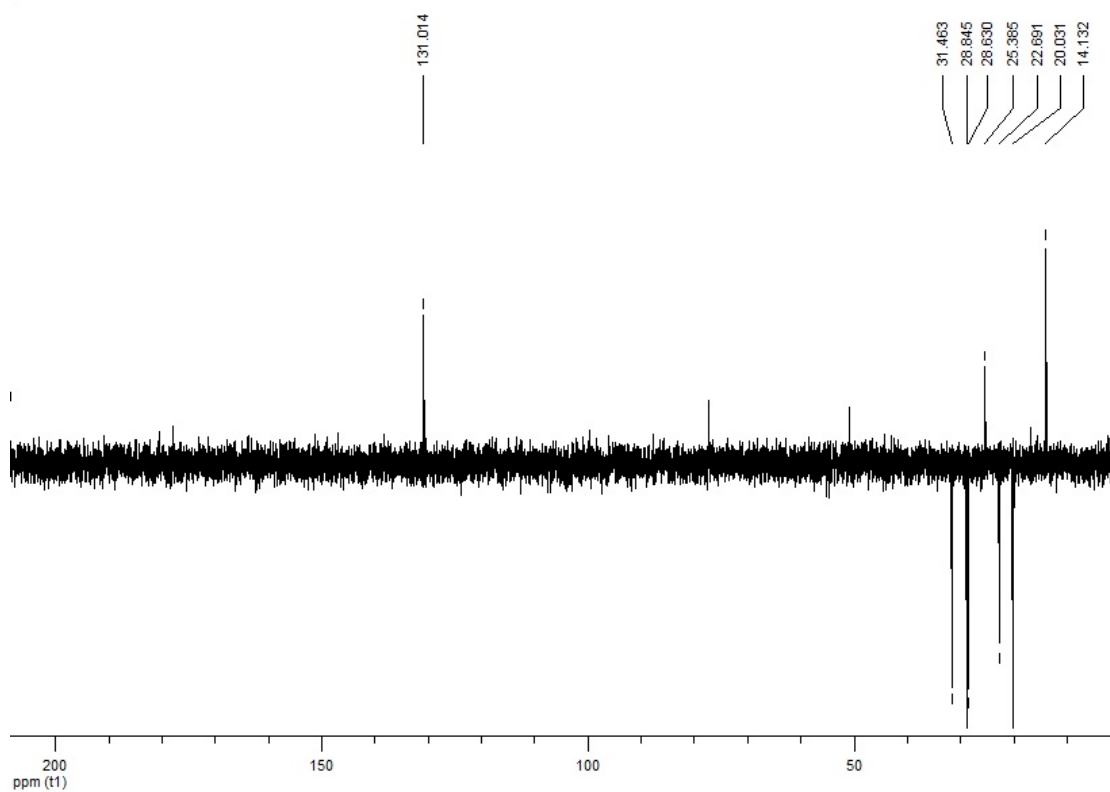
Figure S7. ^{13}C-DEPT NMR (100 MHz) spectrum of donor **5**.
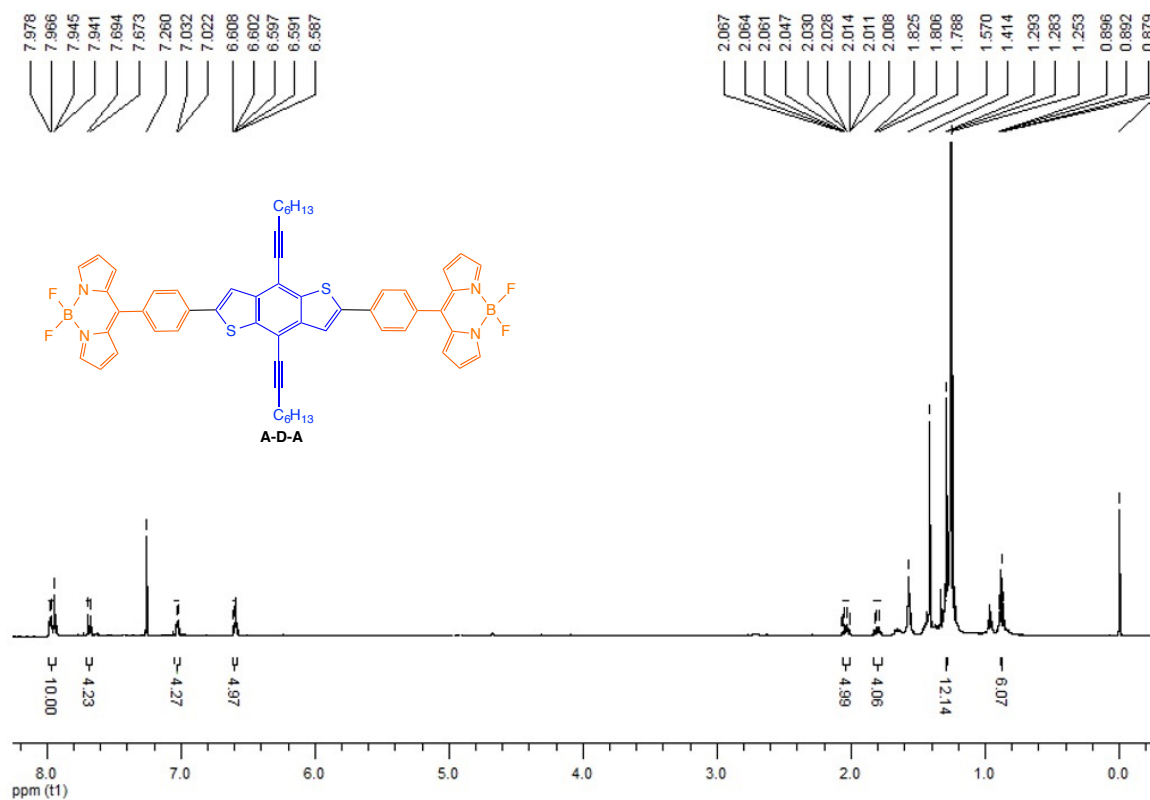
Figure S8. ^{1}H NMR (400 MHz) spectrum of triad **A-D-A**.
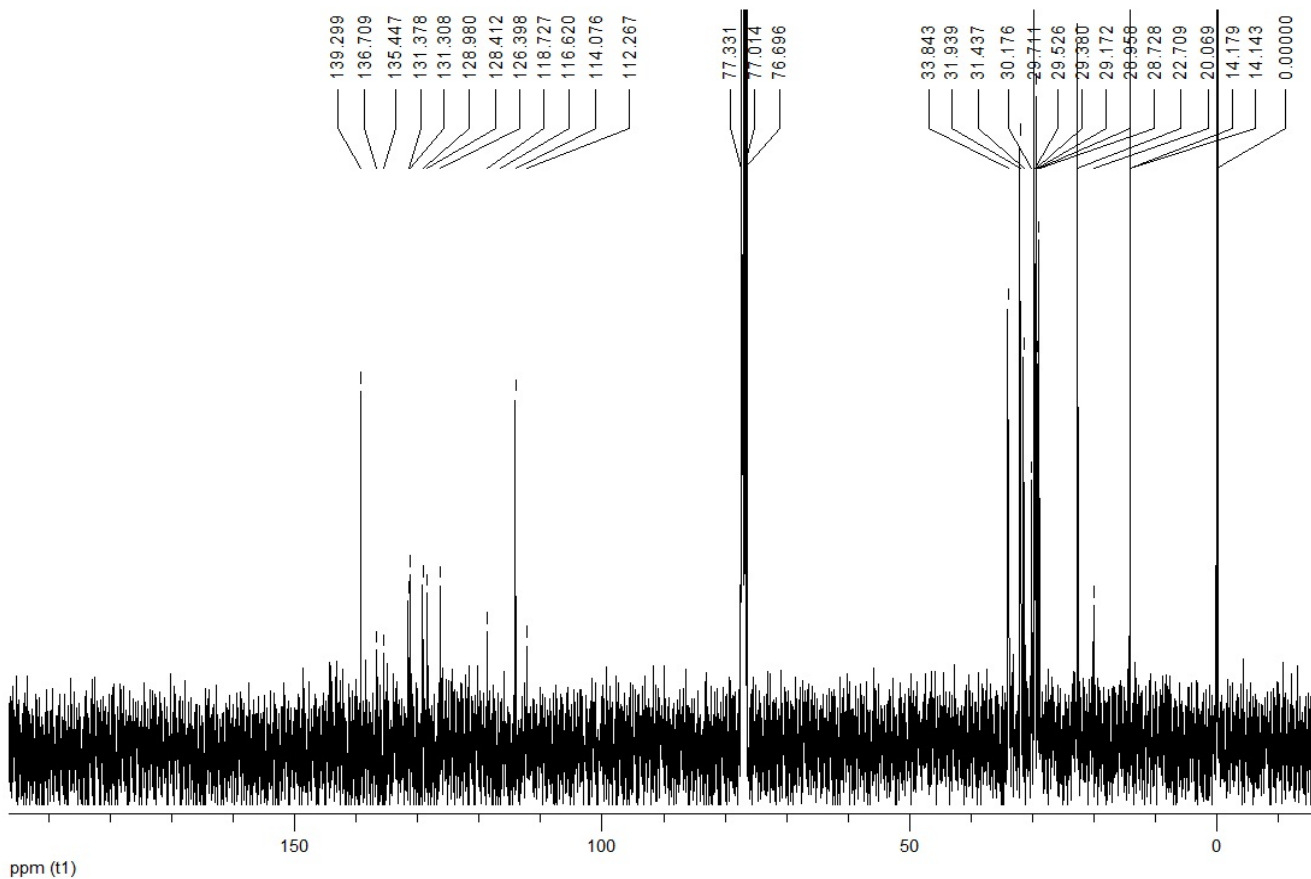
Figure S9. ^{13}C NMR (100 MHz) spectrum of triad **A-D-A**.
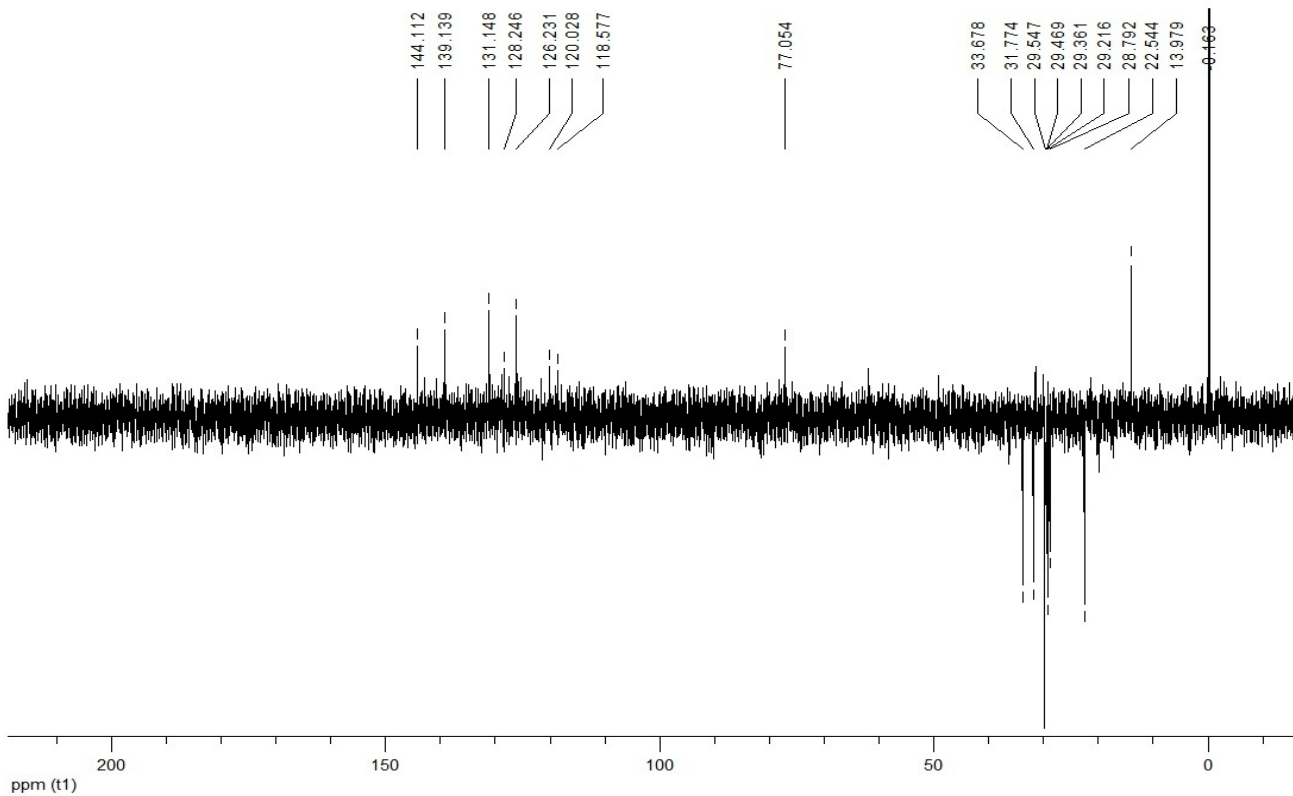
Figure S10. ^{13}C-DEPT NMR (100 MHz) spectrum of triad **A-D-A**.
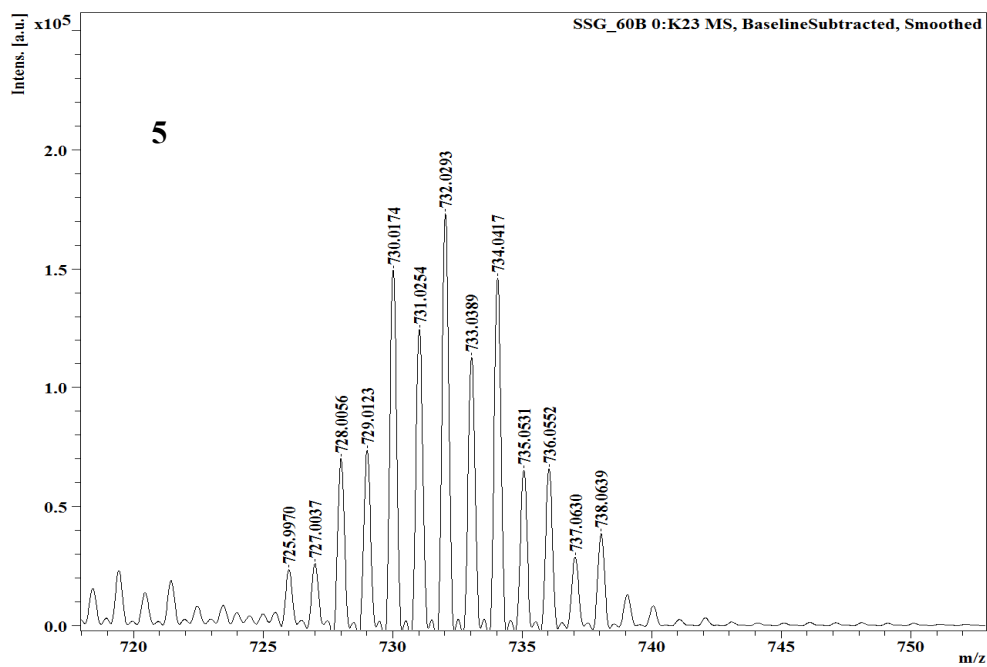
Matrix Assisted Laser Desorption Ionization (MALDI-TOF) Mass Spectrometry
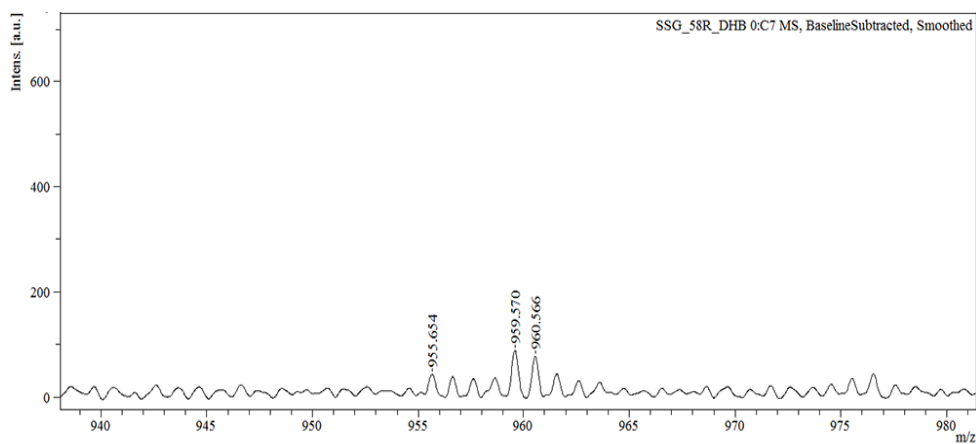

Figure S11. MALDI-TOF mass spectra for **5**.

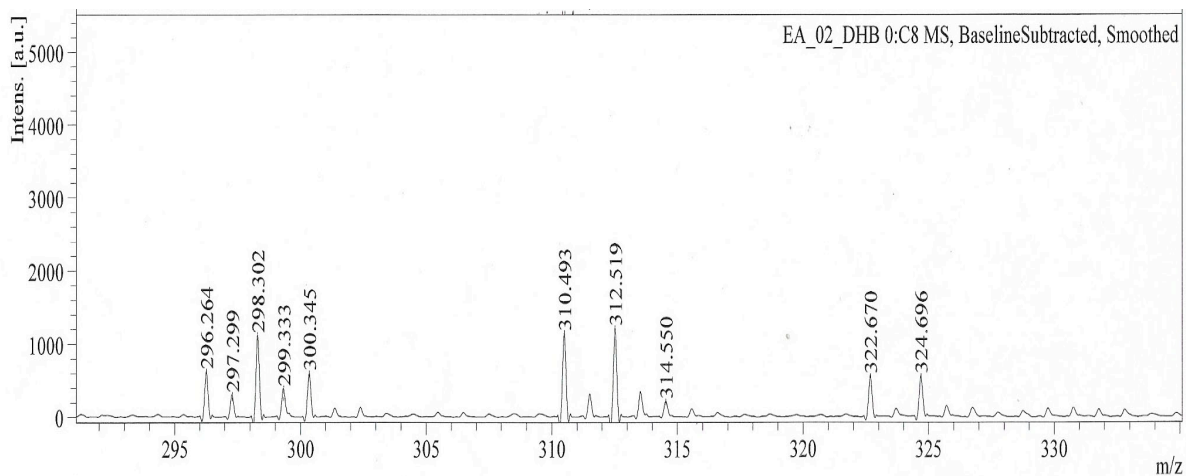**Figure S12.** MALDI-TOF mass spectra for **A-D-A**.

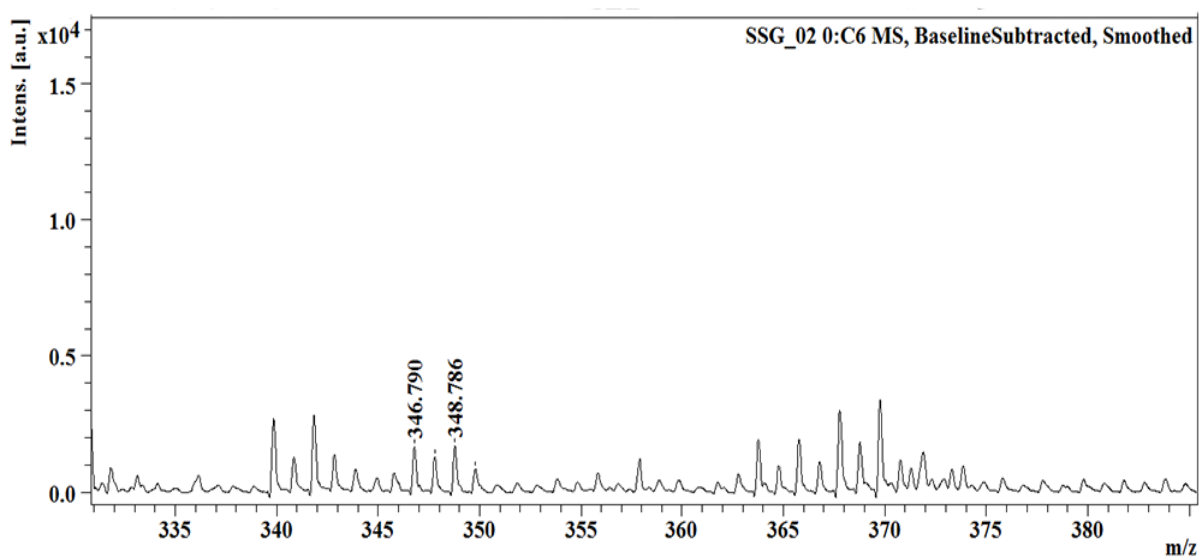**Figure S13.** MALDI-TOF mass spectra for **3**.

Figure S14. MALDI-TOF mass spectra for **4**.
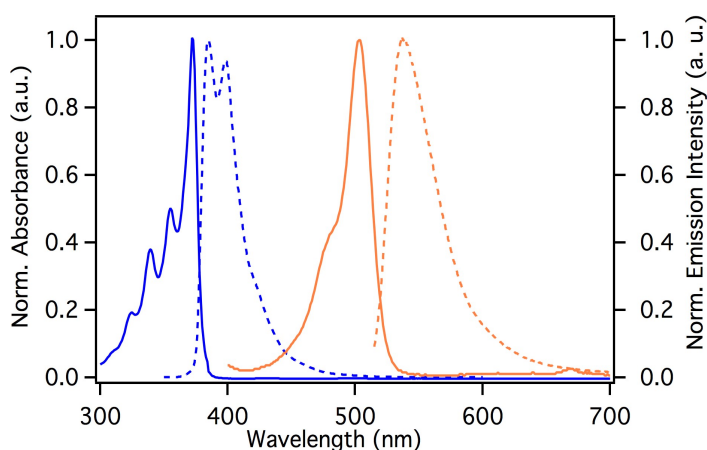
Absorption and fluorescence

Figure S15. Absorption and Fluorescence emission spectra of donor **5** (blue) and acceptor **4** (orange) in dichloromethane.
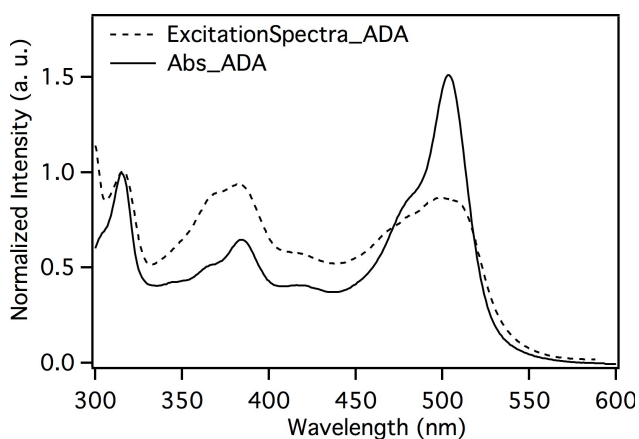

Figure S16. Fluorescence excitation spectra and absorption spectra of **A-D-A** normalized at 315 nm and excitation recorded at emission wavelength of 600 nm.
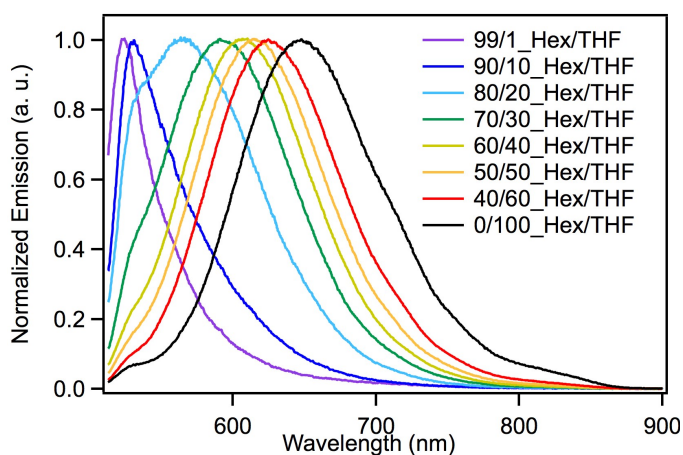

Figure S17. Solvent dependent emission spectra of **A-D-A** showing gradual hypsochromic shift in emission upon increasing the percentage of hexane (0 to 99 vol %) in THF; indicating formation of a twisted intramolecular charge transfer (TICT) state.
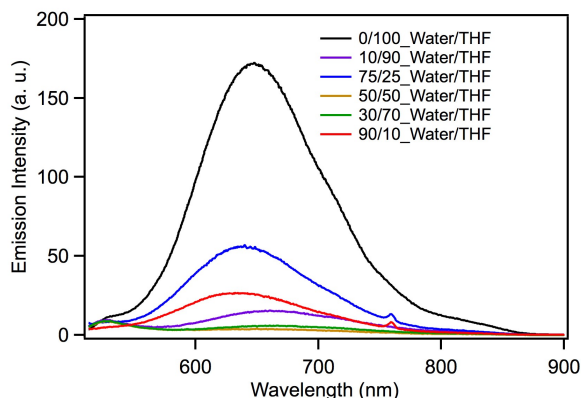
Figure S18. Emission spectra of ADA in water/THF mixtures (0 to 90 vol %) in THF; indicating aggregate induced emission state in these co-solvents.
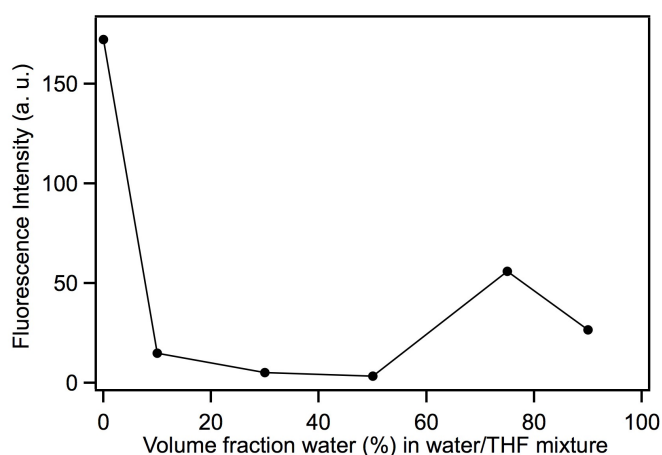
Figure S19. Variation of fluorescence intensity with increasing volume fraction of water (0 to 90 vol %) in water/THF mixtures; indicating aggregate induced emission state in the co-solvents.

Figure S20. Fluorescence emission spectra of **T1** (left) and **T2** (right) in solvents of varied polarity acetonitrile (ACN), ethanol (EtOH), dichloromethane (DCM), chloroform (CF), chlorobenzene (CB) and toluene (Tol) at the excitation wavelength of 380 nm.

Figure S21. Solvent dependent emission spectra of **T1** showing a very gradual hypsochromic shift in emission upon increasing the percentage of hexane (0 to 99 vol %) in THF; indicating formation of a twisted intramolecular charge transfer (TICT) state.
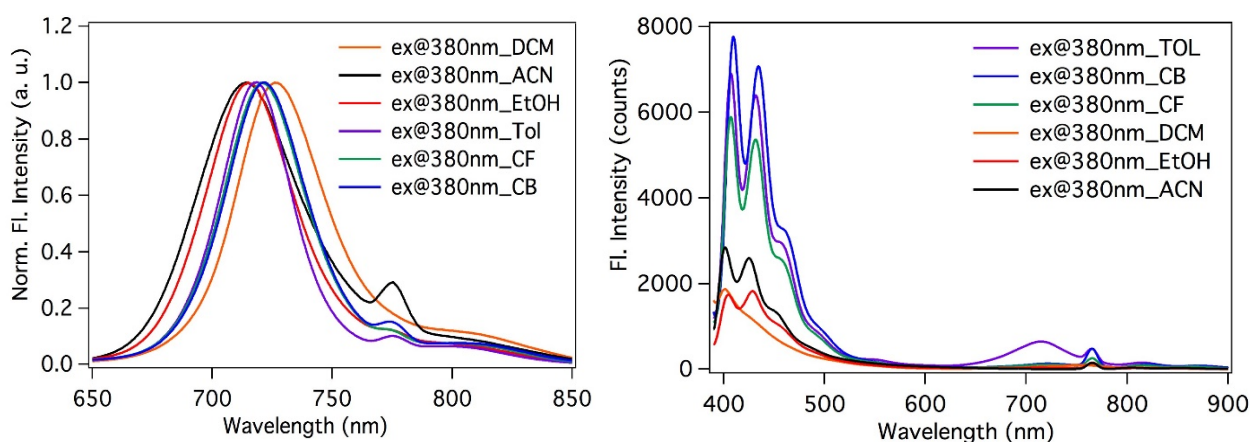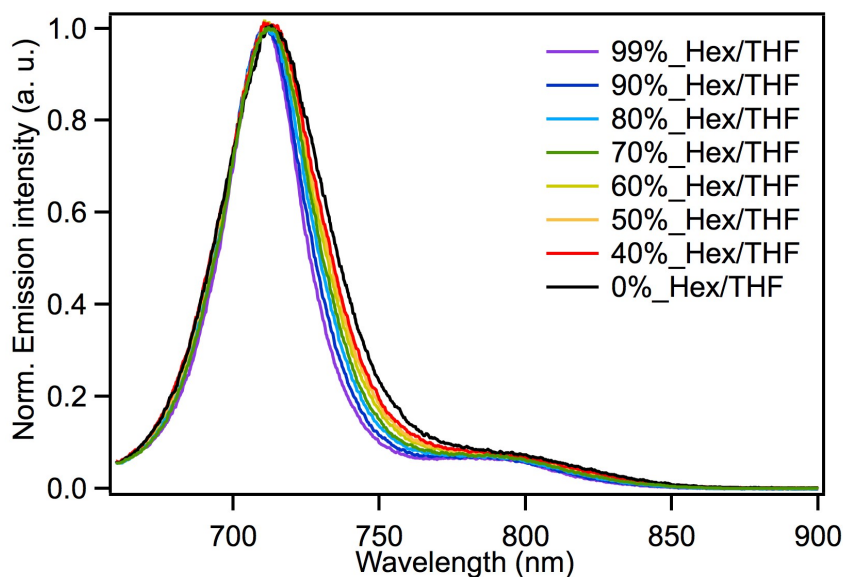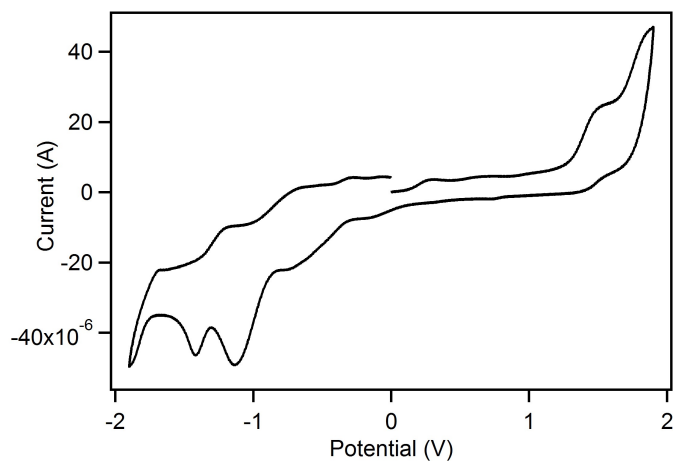

Fig. S22. Cyclic voltammogram of **A-D-A** in CH_2Cl_2; Scan rate of 100 mV/s; supporting electrolyte: 0.1 M Tetrabutylammonium hexafluorophosphate.

Table S1. Redox properties of compounds **ADA** based on cyclic voltammetry.

Compound	E_{ox}^{onset} (V)	HOMO (eV)	E_{red}^{onset} (V)	LUMO (eV)	E_g^{CV} (eV)	DFT calcd. HOMO (eV)	DFT calcd. LUMO (eV)
ADA	+1.10	-5.86	-0.87	-3.89	1.97	-3.21	-5.34

Fluorescence quantum yields by absolute method

Absolute quantum yield of the compound was measured using an integrating sphere set-up as reported protocol using Hitachi F7000 Fluoroscence Spectrometer.[11] In order to calibrate the setup, firstly a solution of quinine bisulphate (QBS) (1×10^{-5} M) was prepared in 0.5 M sulphuric acid (H_2SO_4) as standard and its quantum yield was determined using integrating sphere set-up. In order to calculate absolute quantum yield of QBS, blank and sample (1×10^{-5} M QBS) signals were recorded by placing them in the sample holder of the integrating sphere and exciting at 351 nm.

The absorbed photon flux (F_{abs}) and the emitted photon flux (F), separating the measured spectra of the sample and the blank into an excitation and an emission region were obtained as shown in Figure S23.
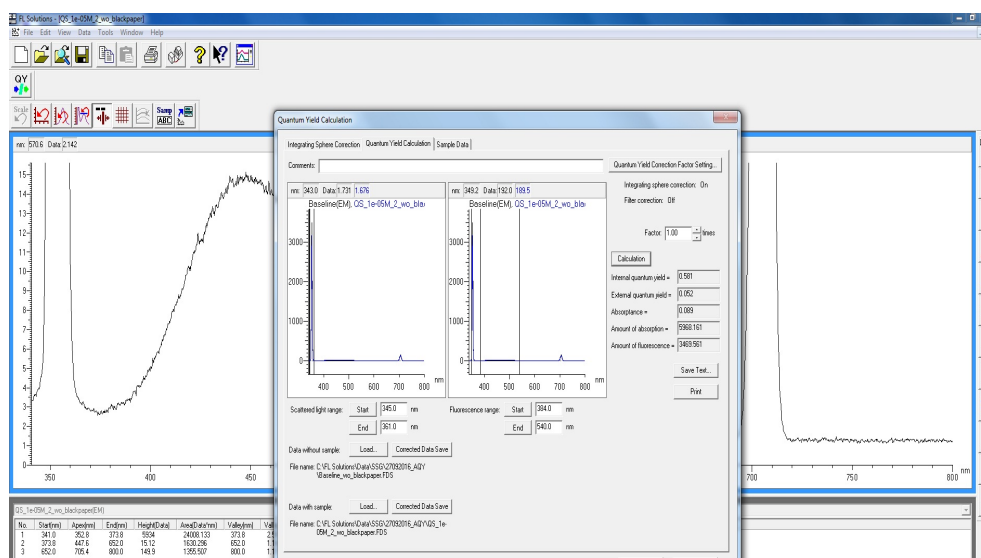
Figure S23. Screenshot of quantum yield calculation by using integrating sphere measurement for the 1×10^{-5} M QBS sample using Hitachi F7000 spectrophotometer.

Subsequently, the following two parameters were calculated i.e., 1) absorbed photon flux (F_{abs}) from the integrated difference of the spectrally corrected signals of the blank and the sample in the spectral range of the excitation and (2) the emitted photon flux (F) from the integrated difference of the spectrally corrected sample and blank

signals in the spectral region of the emission according to equations S1 and S2, where blank measurements are indicated with the index b, and sample measurements are indicated with the index s, respectively. The absolute fluorescence quantum yield was calculated as a ratio of the photon flux emitted from the sample and the absorbed photon flux (equation S3). Quantum yield values were obtained using the software provided by Hitachi for the calculation of quantum yield.

$$F = \int_{\lambda_{em}} \frac{I_x(\lambda_{em}) - I_b(\lambda_{em})}{s(\lambda_{em})} \lambda_{em} d\lambda_{em} \quad \dots\dots\dots\dots\dots\dots(S1)$$

$$F_{abs} = \int_{\lambda_{ex}} \frac{I_b(\lambda_{ex}) - I_x(\lambda_{ex})}{s(\lambda_{ex})} \lambda_{ex} d\lambda_{ex} \dots\dots\dots\dots\dots(S2)$$

$$\phi_f = \frac{F}{F_{abs}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(S3)$$

Using our integrating sphere set-up, ϕ_f values of 0.60 ± 0.01 were obtained for QBS solution (1×10^{-5} M) at 296 K. The ϕ_f value for 1×10^{-5} M QBS solution is comparatively larger than the value of 0.546 reported by Melhuish[12] for a solution of infinite dilution. The quantum yield values for 1×10^{-5} M QBS varies from 0.54 - 0.60[13-15] depending upon the methods used. Therefore, the value of 0.60 that we have obtained for standard QBS are in good agreement with the ϕ_f values of QBS obtained by integrating sphere. Followed by measurement of standard QBS, we measured the absolute quantum yields of 1×10^{-5} M solutions of triad **A-D-A** in DCM upon excitation at 383 nm and the values are summarized in table S2.

Table S2. Absolute quantum yields of standard QBS, triad **ADA** and model compounds **D** and **A**.

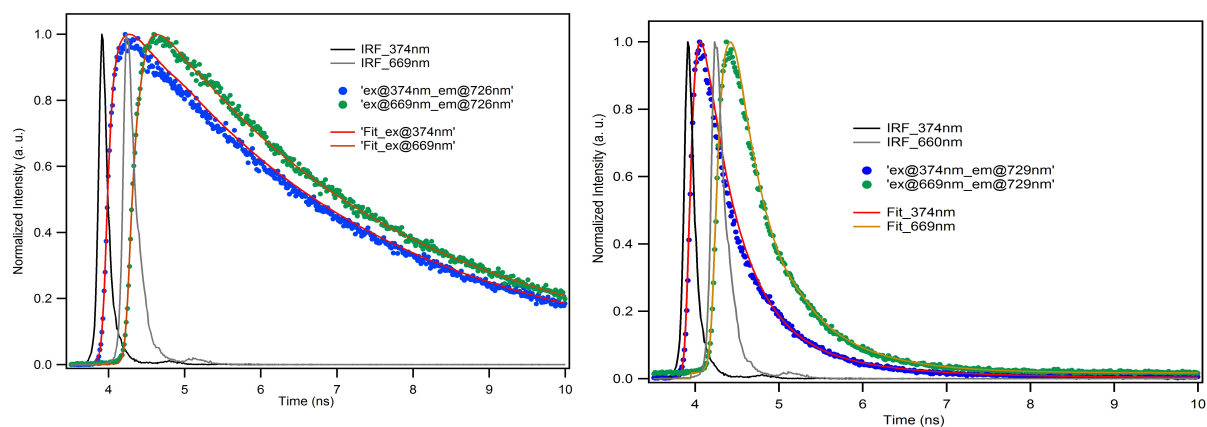| Compound	ϕ_f values obtained in three measurements			ϕ_f
QBS	0.609	0.581	0.607	0.609 ± 0.015
A-D-A	0.030	0.038	0.035	0.035 ± 0.004

Fluorescence Lifetimes

Figure S24. Fluorescence lifetime decay collected by using a single photon counting technique at different wavelengths in chloroform samples of (left) **T1** and (right) **T2**.
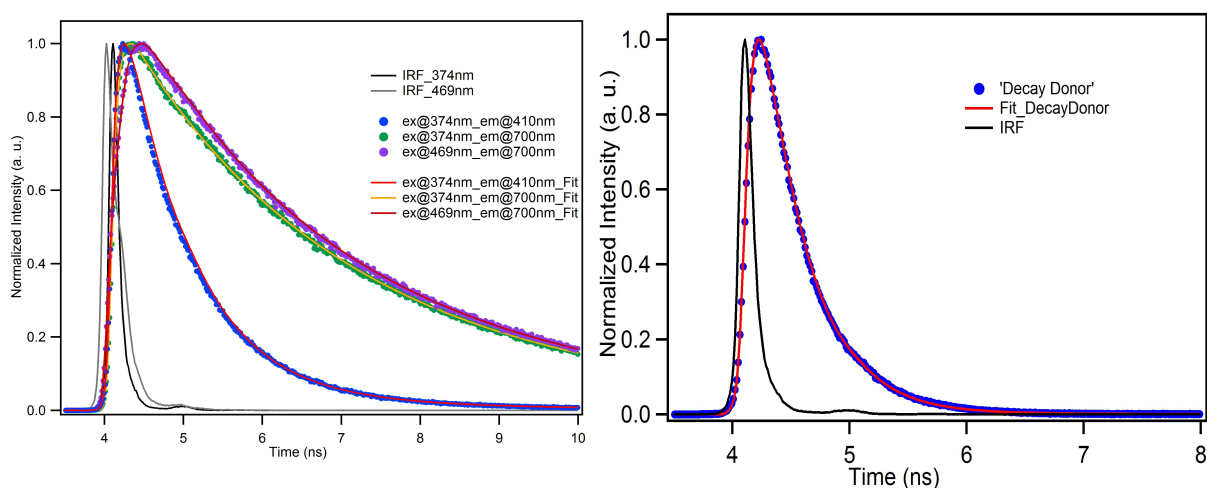

Figure S25. Fluorescence lifetime decay collected by using a single photon counting technique at different wavelengths in chloroform samples of (left) **A-D-A** and (right) donor **D**.

Table S3. Fluorescence Lifetimes of triads A-D-A, T1 and T2.

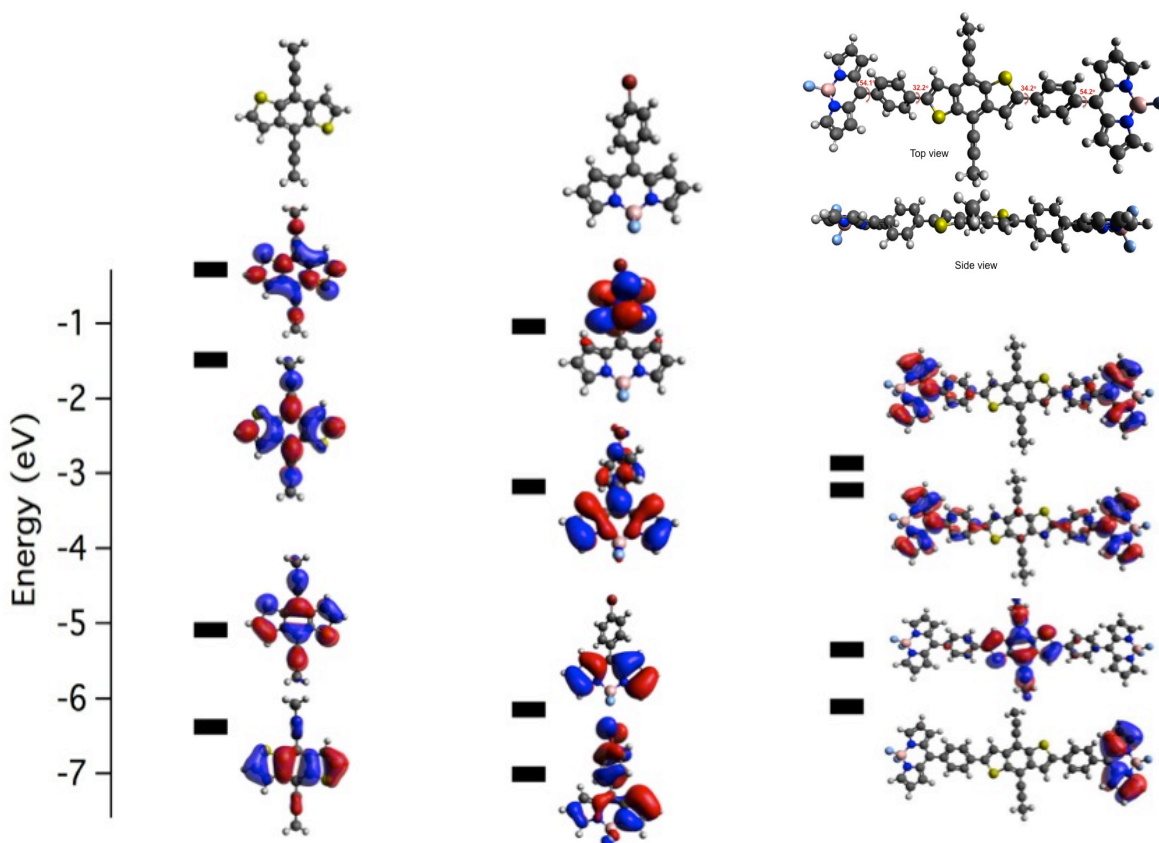| Compounds	λ_{ex} = 374 nm	λ_{ex} = 469 nm
A-D-A	λ_{em} = 410 nm τ_1 = 0.79 ns B1 = 0.104 (86.7 %) τ_2 = 2.85 ns B2 = 4.45e^{-03} (13.3 %) χ^2= 1.10	λ_{em} = 700 nm τ_1 = 1.61 ns B1 = 0.016 (14.21 %) τ_2 = 3.40 ns B2 = 4.68e^{-02} (85.79 %) χ^2= 1.13
	λ_{em} = 700 nm τ_1 = 1.95 ns B1 = 2.84e^{-02} (18.07 %) τ_2 = 3.41 ns B2 = 7.37e^{-02} (81.93 %) χ^2= 1.27	
T1	λ_{em} = 726 nm τ_1 = 2.31 ns B1 = 1.19e^{-02} (9.2 %) τ_2 = 3.42 ns B2 = 0.08 (90.88 %) χ^2= 1.07	λ_{ex} = 669 nm λ_{em} = 726 nm τ_1 = 3.16 ns B1 = 5.58 e^{-03} (72.11 %) τ_2 = 3.82 ns B2 =1.78e^{-02} (27.89 %) χ^2= 1.16
T2	λ_{em} = 729 nm τ_1 = 0.46 ns B1 = 0.132 (76. 46 %) τ_2 = 1.37 ns B2 = 1.38 e^{-02} (23. 54%) χ^2= 1.17	λ_{ex} = 669 nm λ_{em} = 729 nm τ_1 = 0.22 ns B1 = 6.99 e^{-02} (32.91 %) τ_2 = 0.71 ns B2 = 4.57 e^{-02} (67.02 %) χ^2= 1.12

Fig S26. DFT (B3LYP/6-31G(d,p)) calculated FMO energy levels of **BDT**, **4** and **A-D-A**; orbital plots have isovalue of 0.02.

References

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