Electronic Supplementary Information

Regioisomeric Donor-Acceptor-Donor Triads based on Benzodithiophene and BODIPY with Distinct Optical Properties and Mobilities

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Table of contents

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.

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 triads **D-A1-D** and **D-A2-D** were performed using hole only architecture: ITO/PEDOT:PSS/Active Layer (**D-A1-D** or **D-A2-D**)/Au. The thickness of the active layer was about ~ 150 nm. Space charge limited current (SCLC) model was used to extract hole mobilities by using Mott Gurney equation[1,2] described by

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

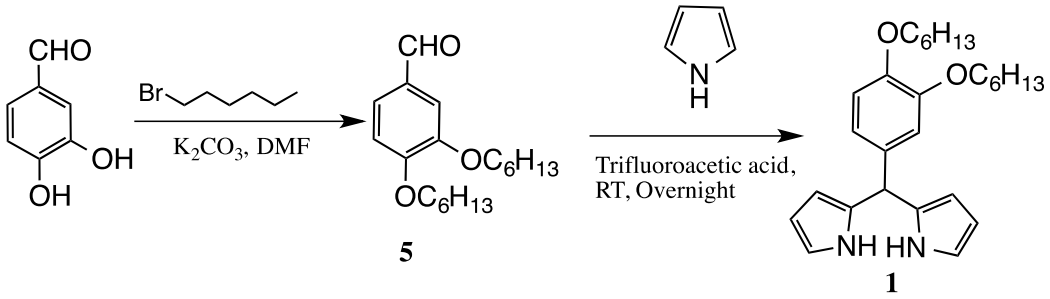
Where J is current density, d is the thickness of active layer, μ_h is hole mobility, ε_r is the relative dielectric constant of material, ε_0 is the permittivity of free space (8.85×10^{-12} Fm^{-1}), V is the applied voltage to the diode.

Quantum chemical density functional theory (DFT) calculations were performed on the coupled D-A-D triads in ground state using Gaussian09 program suite.[3] 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

Bodipy acceptors A1 and A2



Scheme S1. Synthesis of dipyrromethane compound **1**.

3,4-bis(hexyloxy)benzaldehyde (**5**)

Dimethylformamide (DMF) was added (50 mL) to a 100-mL two-neck round-bottom flask containing 3,4-dihydroxybenzaldehyde (1.50 g, 10.86 mmol), 1-bromohexane (3.6 mL, 26.06 mmol), and K_2CO_3 (5.97 g, 43.44 mmol) and the mixture was stirred for 4 h at 80 °C under nitrogen atmosphere.[4] The reaction was monitored by TLC and upon completion of the reaction, DMF was removed from the mixture under reduced pressure. The residue was dissolved in 150 mL of ethyl acetate and washed with water and saturated brine solution twice. The organic layers were collected, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (80/20, v/v) to obtain a white crystalline solid (3.2 g, 97 % yield).

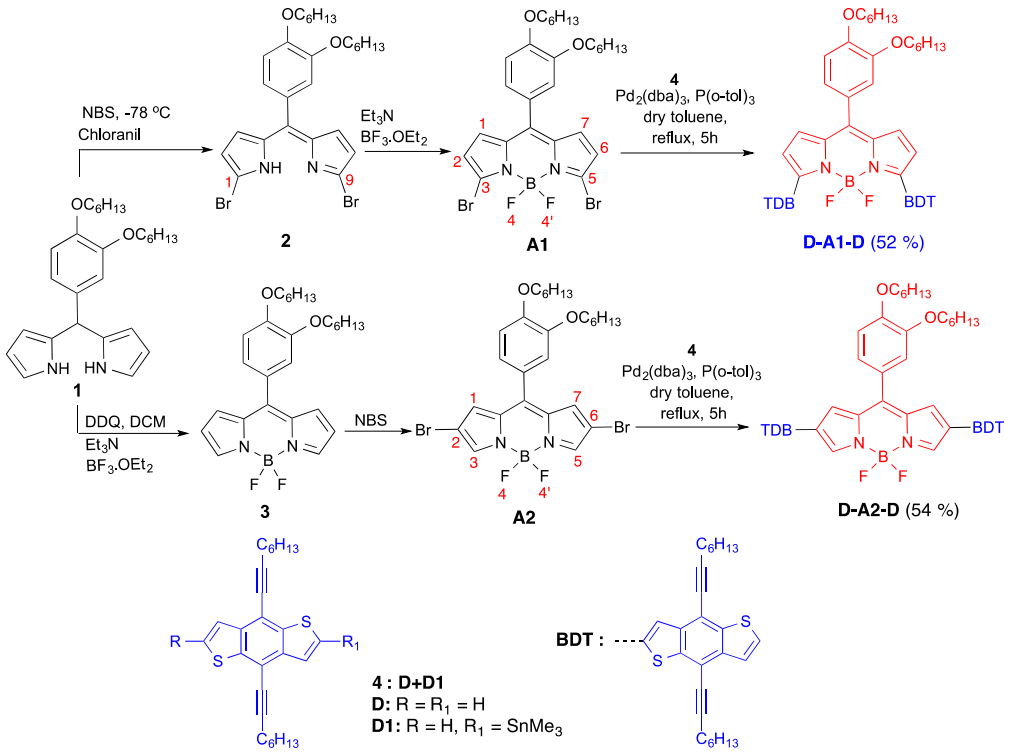
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (s, 1 H, CHO), 7.42-7.39 (m, 2 H, Ar-H), 6.95

(d, J = 8.4 Hz, 1 H, Ar-H), 4.09-4.03 (m, 4 H, α-H), 1.87-1.82 (m, 4 H, β-H), 1.49-1.33 (m, 12 H, CH_2), 0.92-0.89 (m, 6 H, ω-H).

Meso-(3,4-bis(hexyloxy))phenyldipyrromethane (**1**)

A solution of **5** (1.00 g, 3.26 mmol) was added to excess pyrrole (13.6 mL, 195.82 mmol) was stirred at room temperature and 100 µl of trifluoroacetic acid was added and stirred overnight at room temperature. Subsequently, excess pyrrole was removed in vacuo using rotary evaporator and the resulting reaction mixture was subjected to column chromatography with petroleum ether/ethyl acetate (90/10 v/v) as the eluent. The resulting dipyrromethane obtained was a pale white solid (1.20 g, 87 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 2 H, NH), 6.82-6.67 (m, 6 H, Ar-H), 6.16-6.14 (m, 2 H, Ar-H), 5.94-5.92 (m, 2 H, Ar-H), 5.40 (s, 1 H, C-H), 3.97 (t, J = 6.8 Hz, 2 H), 3.91 (t, J = 6.8 Hz, 2 H), 1.79-1.73 (m, 4 H, β–H), 1.44-1.26 (m, 12 H, CH_2), 0.92-0.87 (m, 6 H, ω-H).



Scheme S2. Synthesis of acceptors **A1**, **A2** and triads **D-A1-D** and **D-A2-D**.

Meso-(3,4-bis(hexyloxy))phenyl-3,5-dibromodipyrromethene (**2**)

Compound **1** (400 mg, 0.95 mmol) was taken in dry THF (20 mL) and N-Bromosuccinimide (NBS) (336 mg, 1.89 mmol) was added in two portions over 1 hour period at -78 °C. Subsequently, solvent was evaporated and compound dissolved in dry DCM (30 mL) followed by addition of tetrachloro-1,4-benzoquinone (chloranil) (464 mg, 1.89 mmol). Reaction mixture was stirred for 1 hour under nitrogen at room temperature. Solvent was evaporated using rotary evaporator under vacuum and a flash column was performed in DCM to obtain the brominated compound (440 mg, 80 % yield) that was used for the next step without further purification.

4,4-difluoro-8-(3,4-bis(hexyloxy))phenyl-3,5-dibromo-4-bora-3a,4a-diaza-s-indacene (**A1**)

A1: Compound **2** (274 mg, 0.47 mmol) was dissolved in dry DCM (20 mL) followed by addition of trimethylamine (Et_3N) (2.3 mL, 16.61 mmol) and boron trifluoride diethyletherate ($BF_3{\cdot}Et_2O$) (2.9 mL, 23.80 mmol) and stirred at room temperature for 1 hour. The reaction mixture was extracted using DCM (100 × 2 mL) and washed with 0.1 M KOH solution (50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The desired dibromo derivative was isolated by silica gel column chromatography using petroleum ether/dichloromethane (75/25 v/v) as eluent. The solvent was removed using rotary evaporator under vacuum and **A1** was obtained as an orange powder (210 mg, 71 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07-7.02 (m, 2 H, Ar-H), 6.96 (d, J = 8 Hz, 1 H, Ar-H), 6.86 (d, J = 4 Hz, 2 H, Ar-H), 6.53 (d, J = 4 Hz, 1 H), 4.07 (t, J = 6.8 Hz, 2 H, α-H), 4.00 (t, J = 6.8 Hz, 2 H, α-H), 1.89-1.81 (m, 4 H, β-H), 1.41-1.25 (m, 12 H, CH_2), 0.94-0.88 (m, 6 H, ω-H).

^{13}C NMR (100MHz, $CDCl_3$): δ = 14.01, 22.61, 22.62, 25.69, 25.71, 29.12, 29.22, 31.57, 31.59, 69.26, 69.62, 112.72, 112.75, 116.10, 116.13, 116.21, 122.46, 122.48, 124.21, 124.23, 124.29, 124.90, 125.65, 131.56, 131.62, 131.76, 148.87, 152.05 ppm.

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for $[M+H]^+$ $C_{27}H_{33}Br_2F_2N_2O_2B$: 625.105 found: 625.899.

Meso-(3,4-bis(hexyloxy))phenyl-4-bora-3a,4a,diaza-s-indacene (**3**)

Compound **1** (400 mg, 0.9465 mmol) was taken in dry toluene (8 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (216 mg, 0.95 mmol) was added to it and stirred for 30 mins. Subsequently, Et_3N (0.92 mL, 6.63 mmol) and $BF_3.OEt_2$ (0.82 mL, 6.63 mmol) were added to the reaction mixture and stirred for 1 h at RT. The solvent was removed in vacuo in rotary evaporator, washed with DCM (2 × 100 mL) and solvent was evaporated to obtain the crude compound. Subsequently, it was subjected to column chromatography using ethylacetate/petroleum ether (12.5 % v/v) as eluent and an orange compound, bodipy **3** was obtained (150 mg, 34 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 2 H, Ar-H), 7.16-7.12 (m, 2 H, Ar-H), 7.01-6.97 (m, 3 H, Ar-H), 6.55-6.54 (m, 2H, Ar-H), 4.09 (t, J = 6.4 Hz, 2 H, α-H), 4.02 (t, J = 6.8 Hz, 2 H, α-H), 1.90-1.81 (m, 4 H, β-H), 1.50-1.25 (m, 12 H, CH_2), 0.94-0.88 (m, 6 H, ω-H).

^{13}C NMR (100MHz, $CDCl_3$): δ = 13.99, 14.04, 22.62, 25.70, 29.15, 29.71, 31.59, 69.24, 112.67, 112.70, 116.26, 118.24, 124.36, 124.40, 126.40, 131.38, 131.43, 143.33, 148.78, 152.00

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for $[M+H]^+$ $C_{27}H_{35}BF_2N_2O_2$: 469.284 found: 469.284

4,4-difluoro-8-(3,4-bis(hexyloxy))phenyl-2,6-dibromo-4-bora-3a,4a-diaza-s-indacene (**A2**)

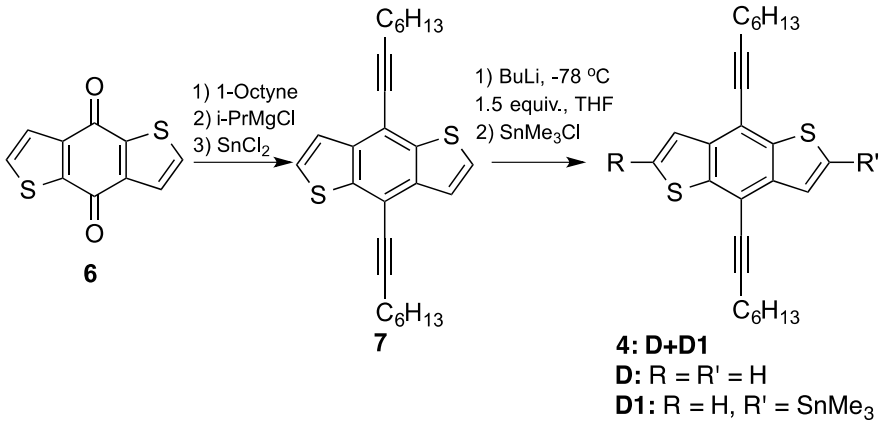
Compound **3** (128 mg, 0.27 mmol) was dissolved in 20 mL dry DCM/DMF (1/1 v/v) and NBS (117 mg, 0.65 mmol) dissolved in DCM (5 mL) was added slowly. The reaction mixture was stirred for 1 hour and subsequently the solvent was removed using rotary evaporator under vacuum. The crude product was subjected to silica gel column chromatography and compound was collected using petroleum ether/ethyl acetate (93/3 v/v). The solvent was removed using rotary evaporator in vacuo and compound **A2** was afforded as a red solid (137 mg, 80 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 2 H, Ar-H), 7.11-6.97 (m, 5 H, Ar-H), 4.10-4.02 (m, 4 H, α-H), 1.87-1.83 (m, 4 H, β-H), 1.56-1.24 (m, 12 H, CH_2), 0.91-0.86 (m, 6 H, ω-H).

^{13}C NMR (100MHz, $CDCl_3$): δ = 14.03, 22.63, 25.70, 29.08, 29.23, 29.73, 31.56, 31.62, 69.30, 69.74, 106.83, 106.86, 106.89, 112.83, 116.09, 124.69, 125.42, 131.55, 134.51, 143.25, 149.10, 152.91

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for $[M]^+$ $C_{27}H_{33}Br_2F_2N_2O_2B$: 625.105 and found: 625.872.

Benzodithiophene (BDT) donor precursor



Scheme S3. Synthetic procedure for the preparation of BDT donor and its stannylated derivative.

BDT-4,8-dione **6** was synthesized in three steps starting from thiophene-3-carboxylic acid.[5] Compound **6** was subjected to reaction by 1-octyne, isopropyl magnesium chloride (i-PrMgCl) and tin chloride ($SnCl_2$) to obtain 4,8-dioctyneBDT **7** as shown in Scheme S3.[5] The octyne chain functionalization induces solubility of these compounds in organic solvents. Subsequently, **7** was converted to the corresponding mono-/di-stannylated derivatives using butyllithium (BuLi) solution and trimethyltin chloride ($SnMe_3Cl$). Addition of one equivalent (equiv.) of BuLi and $SnMe_3Cl$ at -78 ^oC afforded only the starting material **D** without any monostannylated product **D1**. Two or excess equivs. of BuLi and $SnMe_3Cl$ led to a mixture of **D**, **D1** and distannylated BDT. The isolation of starting material **D**, **D1** and disubstituted BDT was difficult to accomplish by column chromatography owing to their negligible differences in retention factors (R_f) in hexane and their instability on silica or alumina columns. In several attempts to selectively obtain **D1**, the reactions were performed using different equivs. of BuLi (1.3-1.8 equiv.) and $SnMe_3Cl$. The reaction mixtures obtained using ~ 1.5 equiv. of BuLi and $SnMe_3Cl$ consisted of BDT and monostannylated derivative only, **4**. Donor precursor **4** was directly used for Stille

coupling reaction. Owing to significant differences in their R_f values of BDT and D-A-D triads, the separation of the products and unreacted BDT was possible by column chromatography.

4,8-Dioctynebenzo[1,2-b:4,5-b']dithiophene (**7**)

Synthesis of BDT donor precursor compound **7** was accomplished starting from thiophene-3-carboxylic acid according to the literature reported method.[5-8] The purity of the synthesized donor precursor **7** was confirmed by ^{1}H NMR and ^{13}C NMR measurement.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 5.2 H, 2H, Ar-H), 7.49 (d, J = 5.2 Hz, Ar-H, 2H), 2.63 (t, J = 6.8 Hz, 4 H, CH_2), 1.75-1.69 (m, 4 H, CH_2), 1.60-1.56 (m, 4 H, CH_2), 1.40-1.33 (m, 8 H, CH_2), 0.95-0.91 (m, 6 H, CH_3).

^{13}C NMR (100MHz, $CDCl_3$): 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.

4 (D+D1): 400 mg (0.98 mmol) of **D** was dissolved in dry THF (30 mL), the solution was cooled to -78 °C and 0.92 mL butyllithium (BuLi) (1.48 mmol, 1.5 eq.) was added dropwise while stirring under inert atmosphere. The reaction mixture was stirred at -78 °C for 1 hour following which 1.48 mL (1.48 mmol, 1.5 eq.) of trimethyltin chloride (1 M solution in hexane) was added to it. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by adding few drops of water and subsequently extracted with ethyl acetate (100 × 2 mL). The organic fractions were dried on anhydrous sodium sulphate and concentrated under vacuum by rotary evaporator. Thin layer chromatography (TLC) of the crude obtained

indicated a mixture of starting material **D** and the monostannylated derivative **D1**. The purification of the reaction mixture was attempted on silica gel column with petroleum ether as eluent, however, owing to their negligible differences in the R_f values in petroleum ether ($R_{f,\mathbf{D}}$ = 0.80, $R_{f,\ \mathbf{D1}}$=0.78), their separation could not be accomplished. Preliminary NMR analysis of the crude product **4** revealed the presence of **D** and **D1** in the ratio of 1:1.3. NMR spectra and mass spectra of the crude mixture have been shown. Donor precursor **4** was taken as such for the next step i.e., Stille coupling reaction.[9]

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for [M+H] for $C_{27}H_{35}BF_2N_2O_2$: 406.179 found: 406.368 and Calculated for [M+H] for $C_{29}H_{38}S_2Sn$: 570.152, found: 570.297

Triads D-A1-D and D-A2-D

D-A1-D: Compound **A1** (50 mg, 0.08 mmol) was dissolved in dry toluene (25 mL) and solution was degassed and purged with nitrogen for 10 minutes. Subsequently, donor precursor **4** (168 mg, 0.17 mmol)[10] was added and the reaction mixture was stirred with continued purging. Tris(dibenzylideneacetone)dipalladium (0), ($Pd_2(dba)_3$) (4 mg, 4.3 μmol) and tri(otolyl)phosphine ($P(o\text{-}tol)_3$) (7 mg, 23 μmol) were added and the reaction mixture was purged for another 15 min and then refluxed for 5 hours at 110 °C. The reaction mixture was cooled to RT and solvent was evaporated on rotary evaporator. It was then subjected to column chromatography purification using petroleum ether/ethylacetate (97/3 v/v) to isolate a dark blue amorphous solid (53 mg, 52 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 2 H, Ar-H), 7.58-7.52 (m, 4 H, Ar-H), 7.36 (t, J = 10 Hz, 2 H, Ar-H), 7.14-7.11 (m, 2 H, Ar-H), 7.03-6.96 (m, 3 H, Ar-H), 4.12 (t,

J = 6.4 Hz, 2 H, α-H), 4.06 (t, J = 6.8 Hz, 2 H, α-H), 2.65 (t, J = 6.8 Hz, 4 H, CH_2), 2.42 (t, J = 7.2 Hz, 4 H, CH_2), 2.05-1.70 (m, 12 H, CH_2), 1.41-1.25 (m, 36 H, CH_2), 0.96-0.89 (m, 12 H, CH_3), 0.71 (t, J = 7.2 Hz, 6 H, CH_3).

^{13}C (100MHz, $CDCl_3$): δ = 14.03, 20.00, 20.30, 22.53, 22.64, 25.73, 25.76, 28.66, 28.78, 28.83, 29.71, 30.24, 31.18, 31.46, 69.30, 69.61, 100.65, 103.45, 111.27, 112.83, 119.16, 121.82, 123.38, 123.99, 124.22, 124.49, 128.45, 130.33, 130.35, 134.23, 139.25, 139.97, 140.14, 147.12, 149.89, 151.36 ppm.

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for $[M]^+$ $C_{79}H_{90}BF_2N_2O_2S_4$: 1276.602 and found: 1276.680.

D-A2-D: Compound **A2** (50 mg, 0.08 mmol) was dissolved in dry toluene (25 mL) and solution was degassed and purged with nitrogen for 10 minutes. Subsequently, BDT donor precursor **4** (170 mg, 0.17 mmol)[10] was added. The solution was stirred under continuous purging and subsequently, tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) (5 mg, 5.4 μmol) and tri(otolyl)phosphine ($P(o\text{-}tol)_3$) (6 mg, 19.7 μmol) were added. The reaction mixture was purged for another 15 minutes and then refluxed for 5 h at 110 °C. It was cooled to RT and the solvent was evaporated on rotary evaporator. It was then subjected to column chromatography purification using petroleum ether/ethylacetate (95/5 v/v) to isolate a dark blue amorphous solid (55 mg, 54 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (s, 2 H, Ar-H), 7.63 (d, J = 2.4 Hz, 1 H, Ar-H), 7.55-7.48 (m, 4 H, Ar-H), 7.29 (d, J = 2.4 Hz, 2 H, Ar-H), 7.08-7.05 (m, 2 H, Ar-H), 6.59 (d, J = 8.4 Hz, 2 H, Ar-H), 4.17-4.07 (m, 4 H, CH_2), 2.68-2.61 (m, 4 H, CH_2), 1.91-1.87 (m, 4 H, CH_2), 1.41-1.20 (m, 52 H, CH_2), 0.95-0.87 (m, 18 H, CH_3).

^{13}C NMR (100MHz, $CDCl_3$): δ = 14.12, 19.97, 20.05, 22.65, 25.75, 28.67, 28.82, 29.71, 31.65, 69.29, 69.75, 111.91, 112.85, 115.96, 116.49, 117.65, 118.72, 118.99, 119.44, 123.54, 124.10, 124.48, 124.57, 127.65, 127.75, 138.94 ppm

Matrix assisted laser desorption ionization (MALDI-TOF): Calculated for $[M]^+$ $C_{79}H_{90}BF_2N_2O_2S_4$: 1276.602 and found: 1276.684.

^{1}H and ^{13}C NMR Spectra

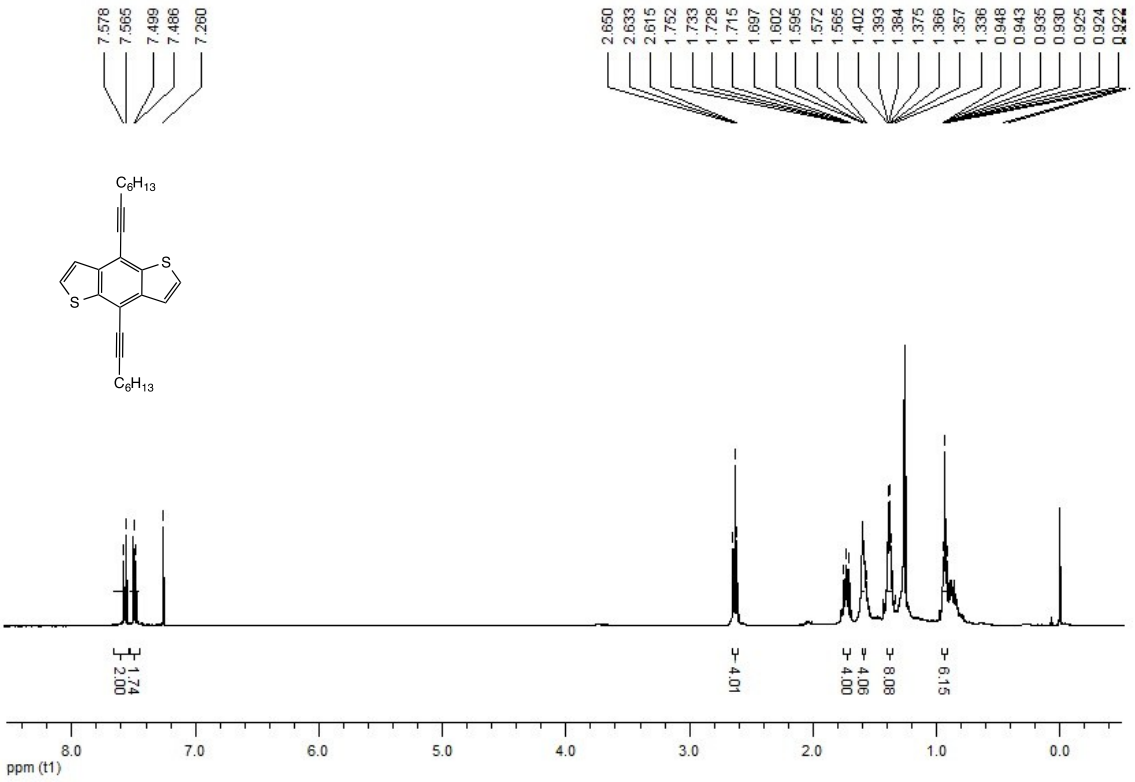


Figure S1. ^{1}H NMR (400 MHz) spectrum of BDT donor **D (7)**.

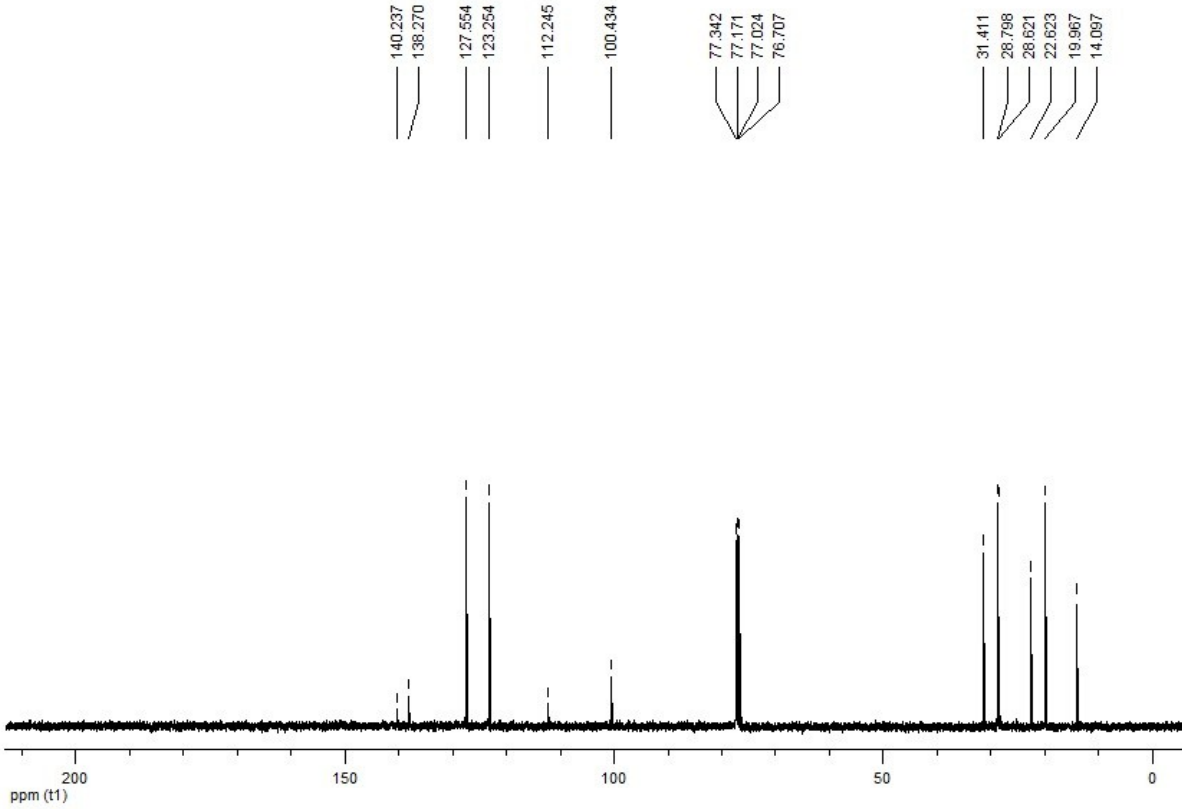


Figure S2. ^{13}C NMR (100 MHz) spectrum of BDT donor **D (7)**.

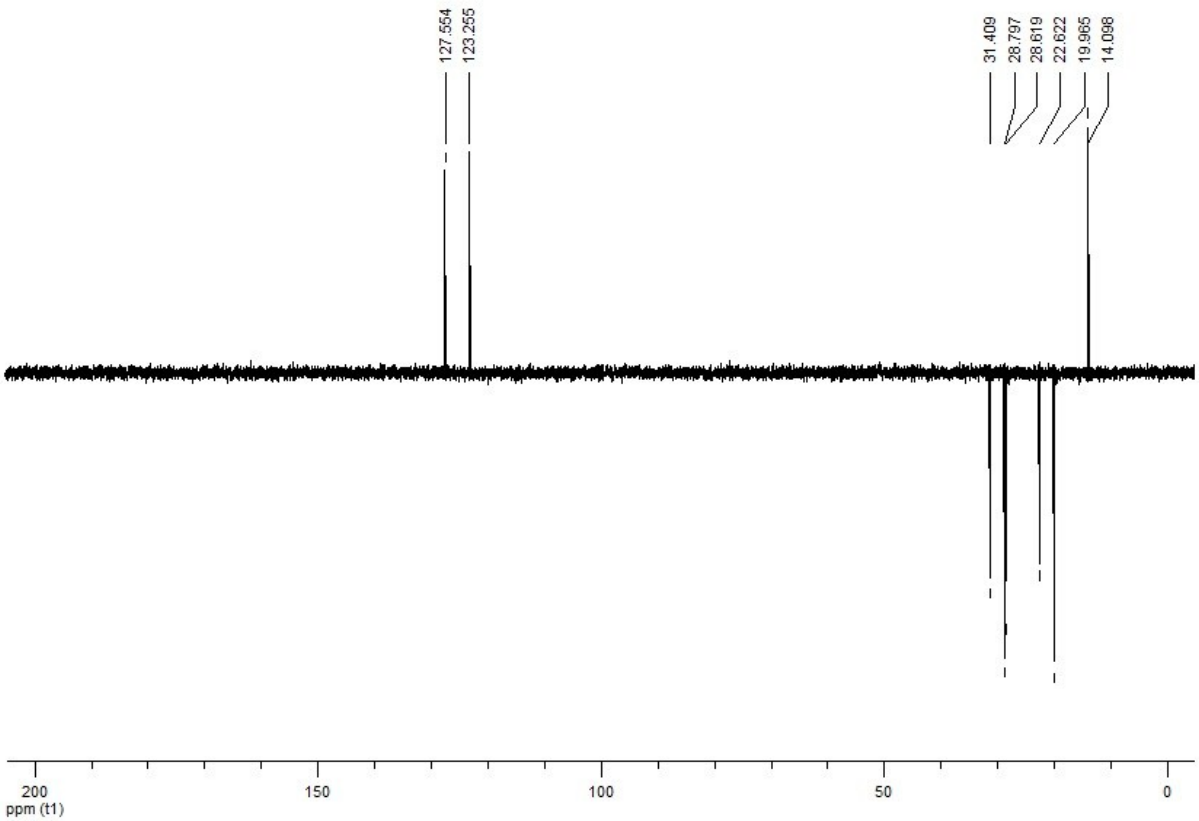


Figure S3. ^{13}C DEPT-135 (100 MHz) NMR spectrum of BDT donor **D (7)**.

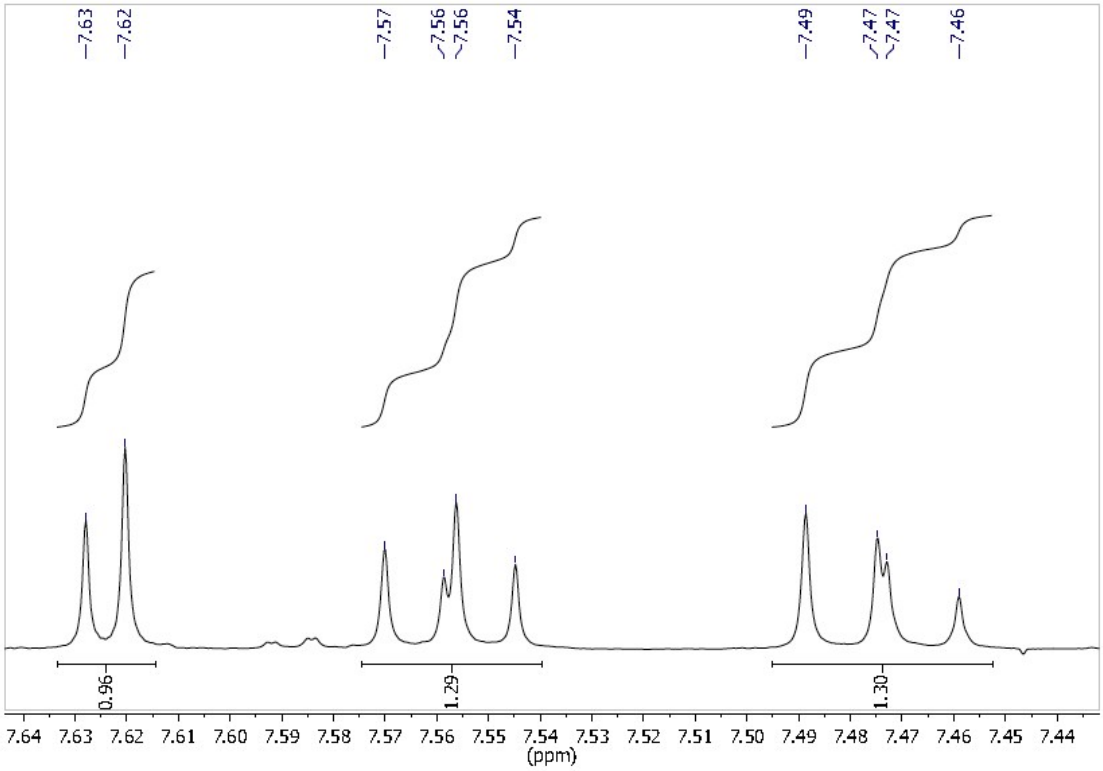


Figure S4. ^{1}H NMR (400 MHz) spectrum of **D+D1 (4)**.

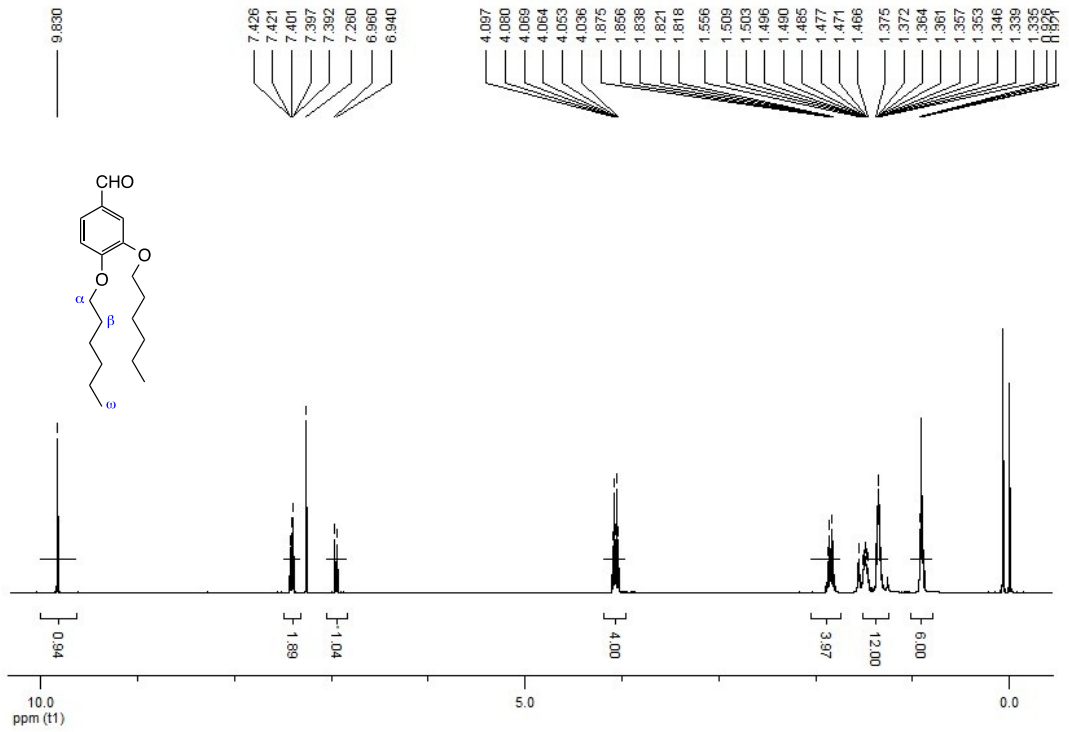


Figure S5. ^{1}H NMR (400 MHz) spectrum of compound **5**.

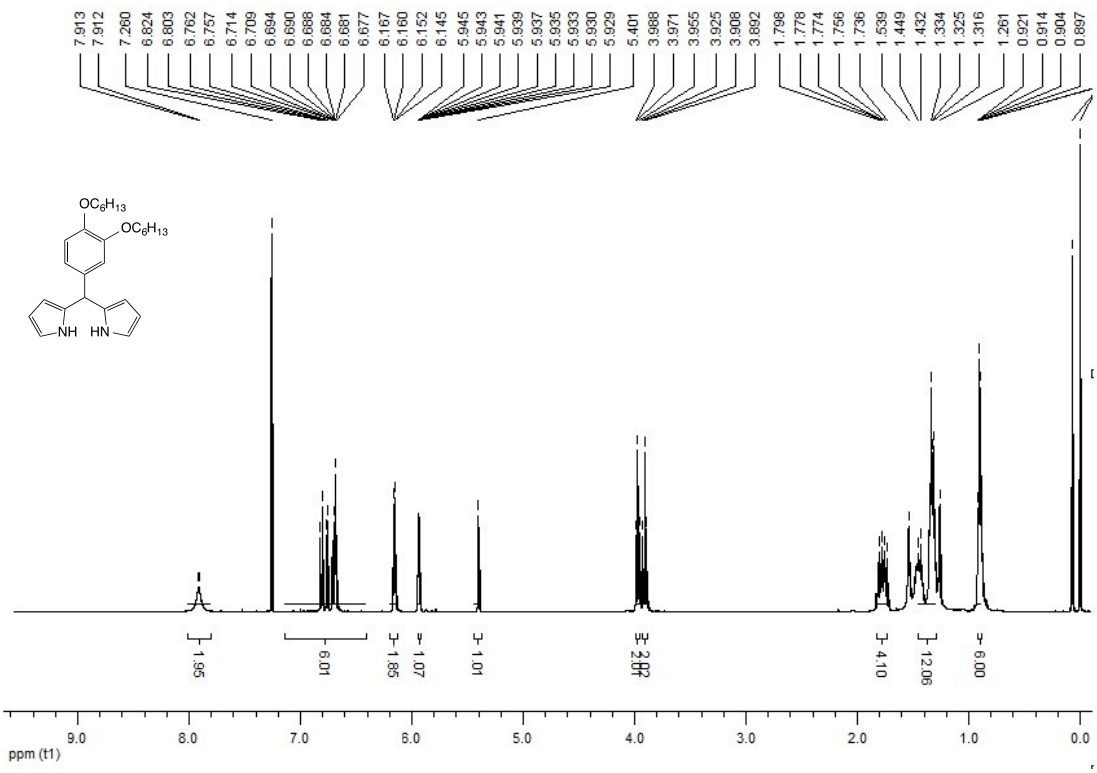


Figure S6. ^{1}H NMR (400 MHz) spectrum of compound **1**.

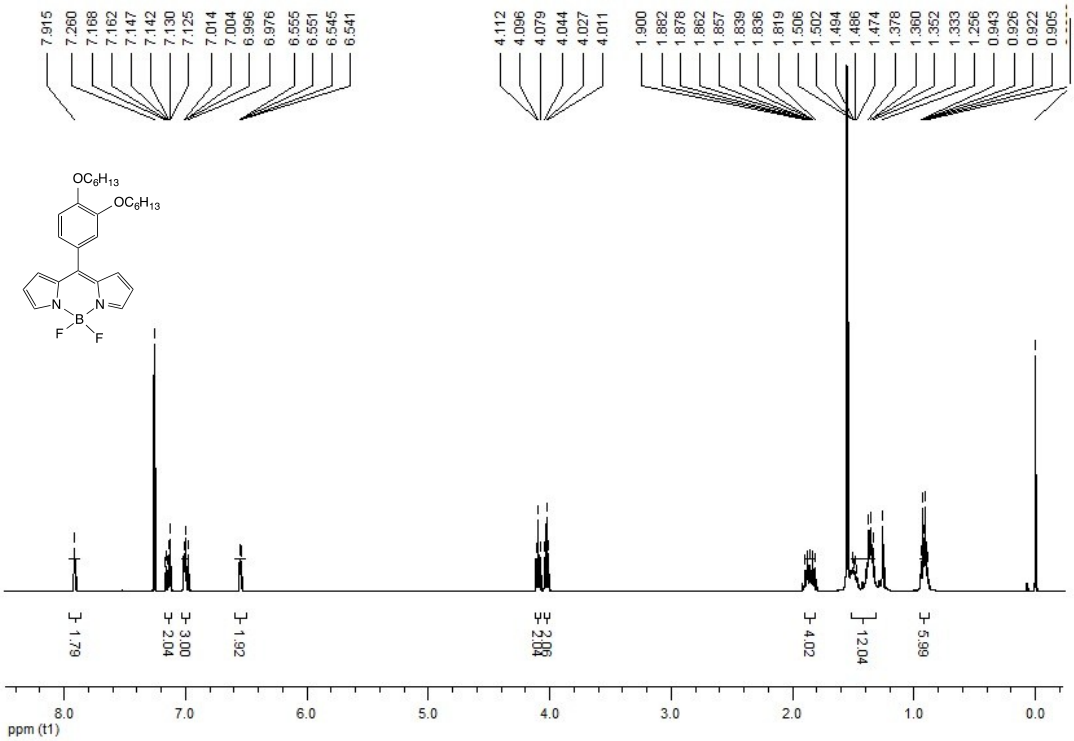


Figure S7. ^{1}H NMR (400 MHz) spectrum of BODIPY **3**

Figure S8. ^{13}C NMR (100 MHz) spectrum of BODIPY **3**

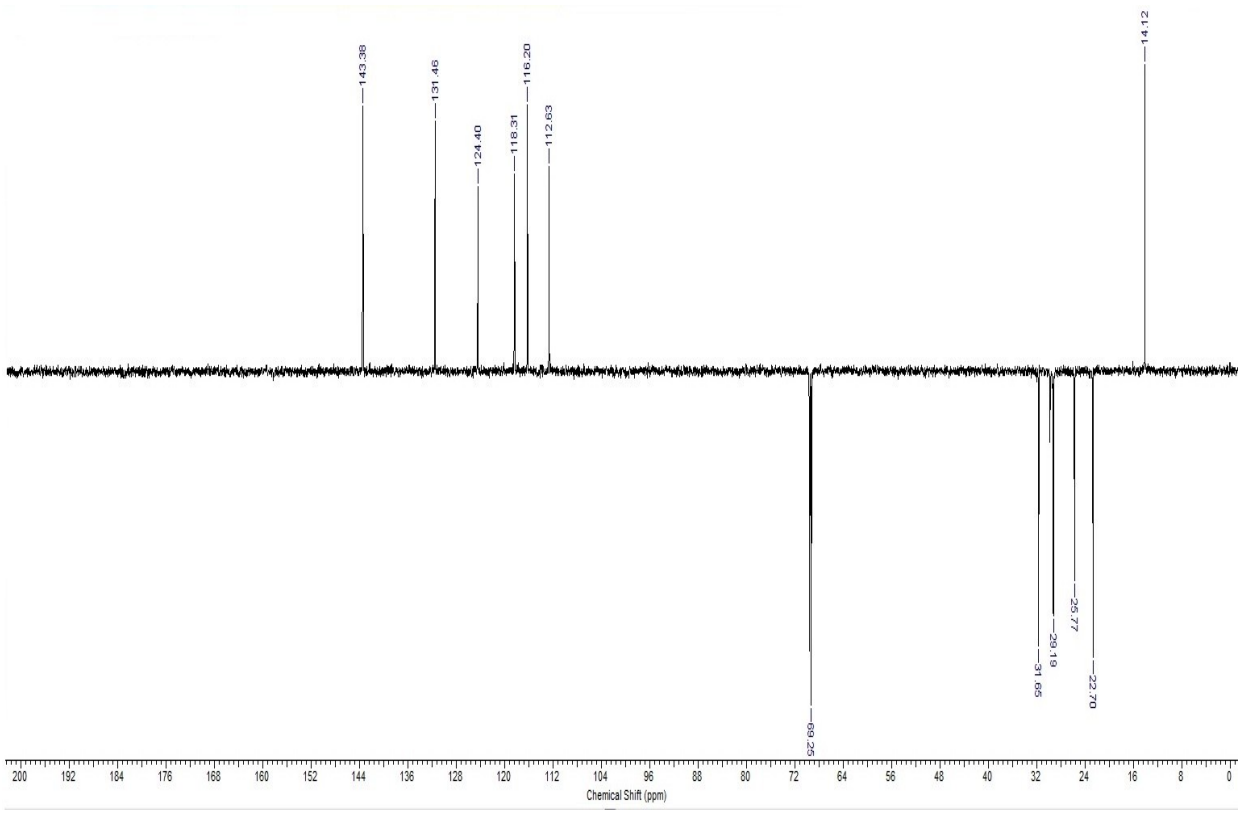


Figure S9. ^{13}C DEPT-135 NMR (100 MHz) spectrum of BODIPY **3**

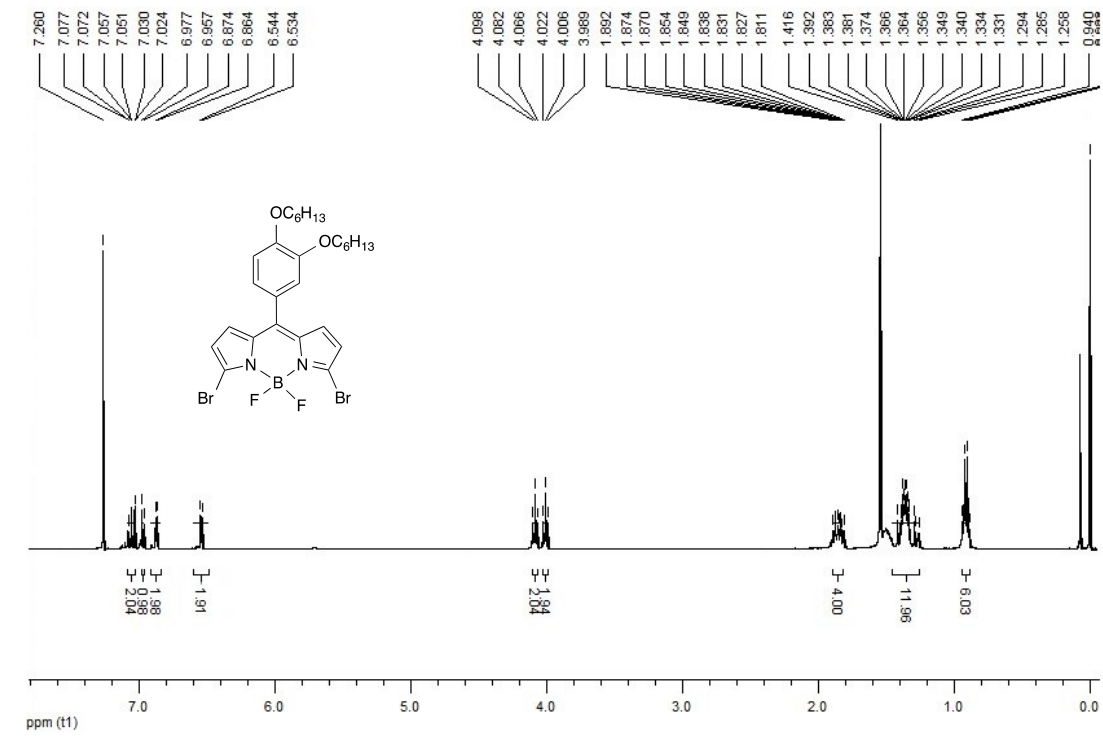


Figure S10. ^{1}H NMR (400 MHz) spectrum of BODIPY acceptor **A1**.

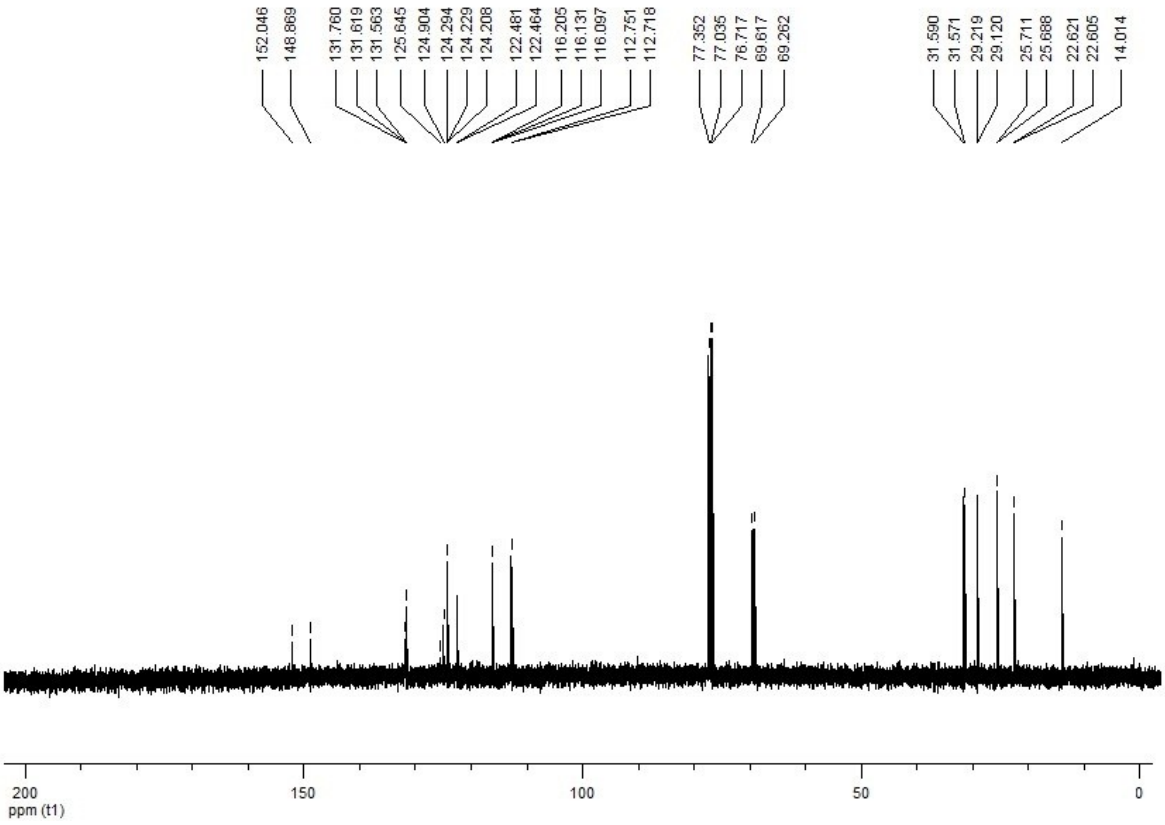


Figure S11. ^{13}C NMR (100 MHz) of BODIPY acceptor **A1**.

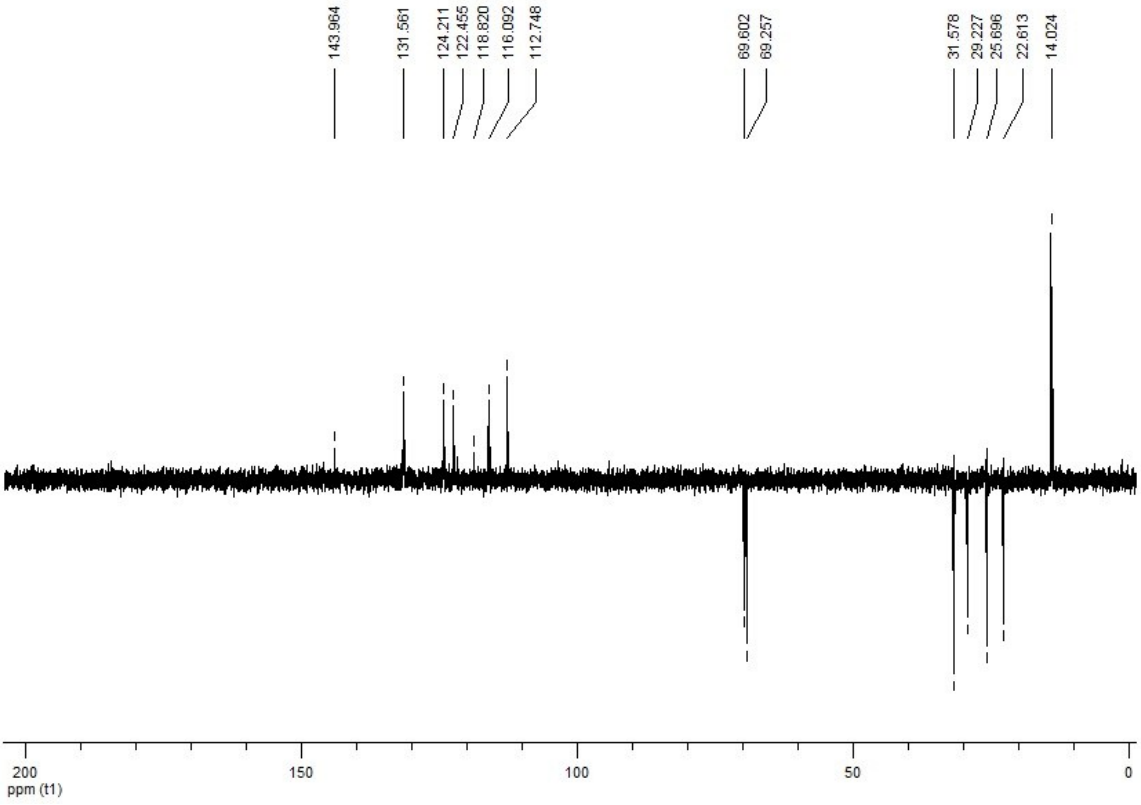


Figure S12. ^{13}C DEPT-135 NMR (100 MHz) spectrum of BODIPY acceptor **A1**.

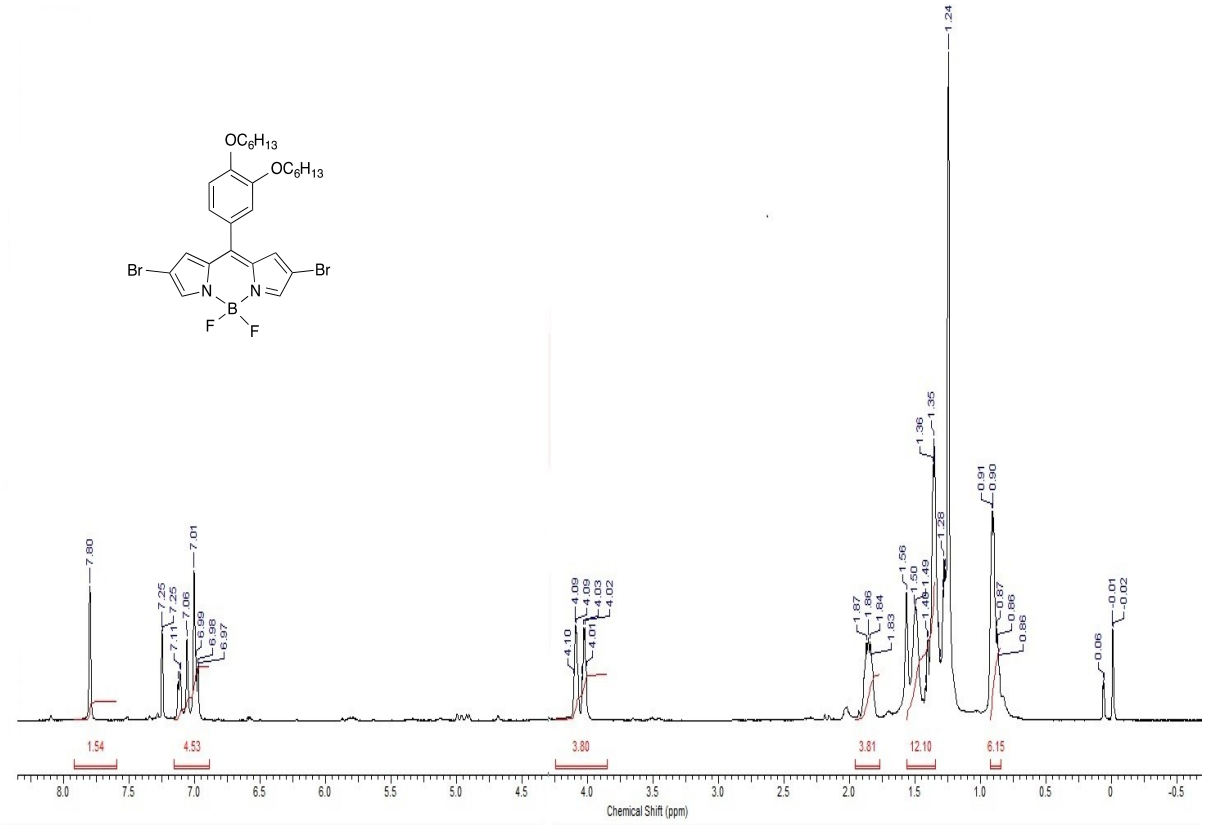


Figure S13. ^{1}H NMR (400 MHz) spectrum of BODIPY acceptor **A2**.

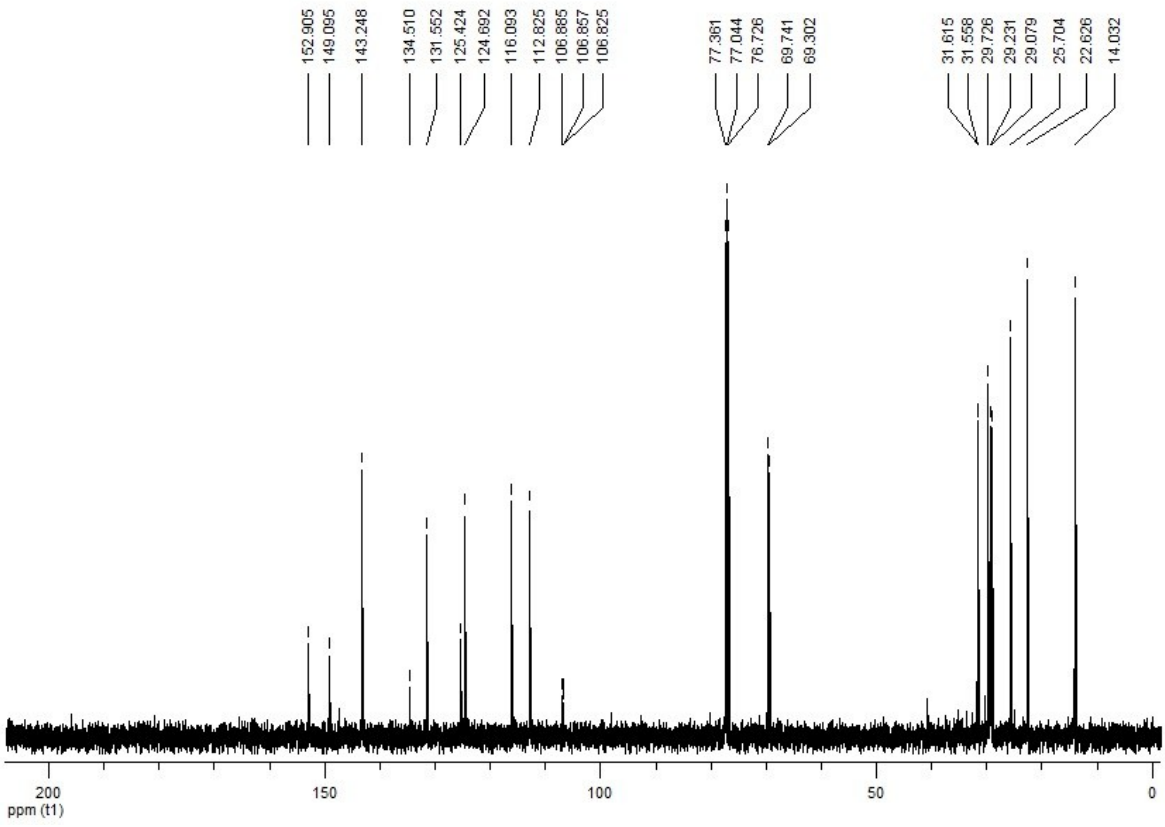


Figure S14. ^{13}C NMR (100 MHz) spectrum of BODIPY acceptor **A2**.

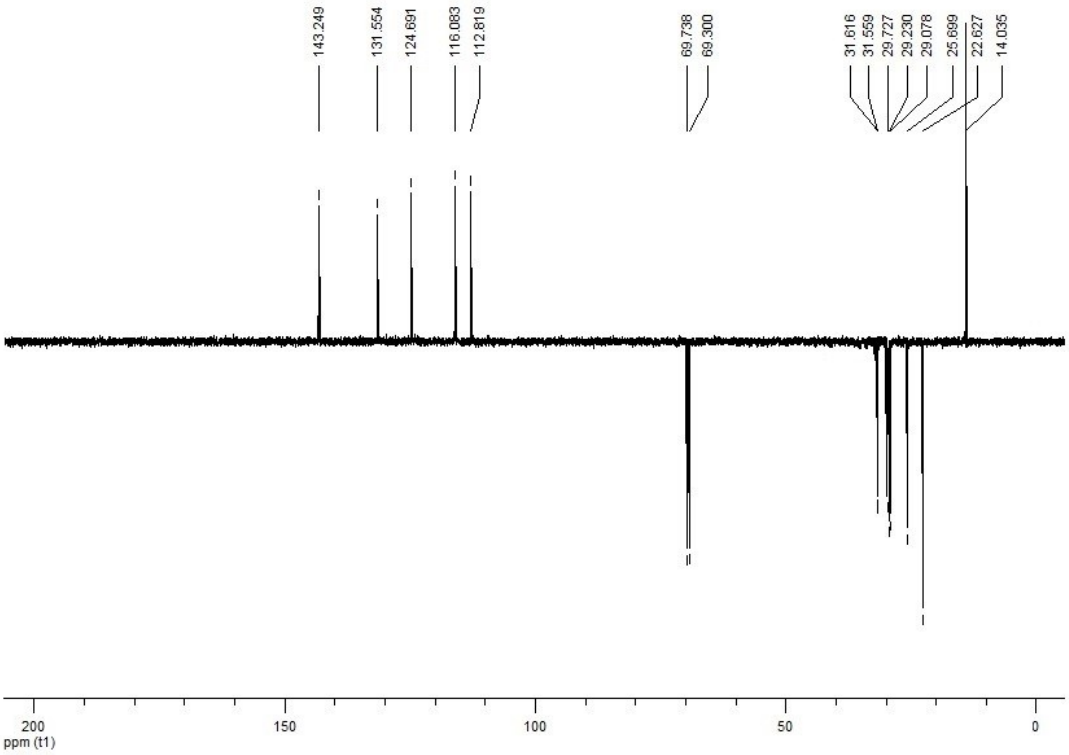


Figure S15. ^{13}C DEPT-135 NMR (100 MHz) spectrum of BODIPY acceptor **A2**.

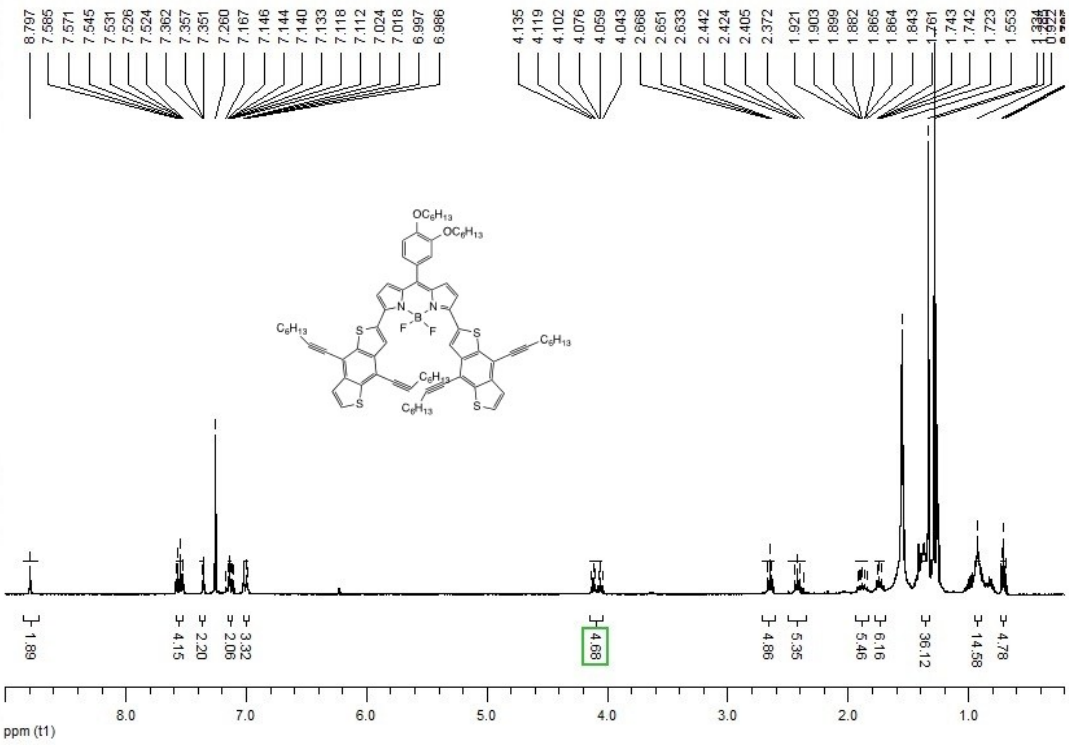


Figure S16. ^{1}H NMR (400 MHz) spectrum of triad **D-A1-D**.

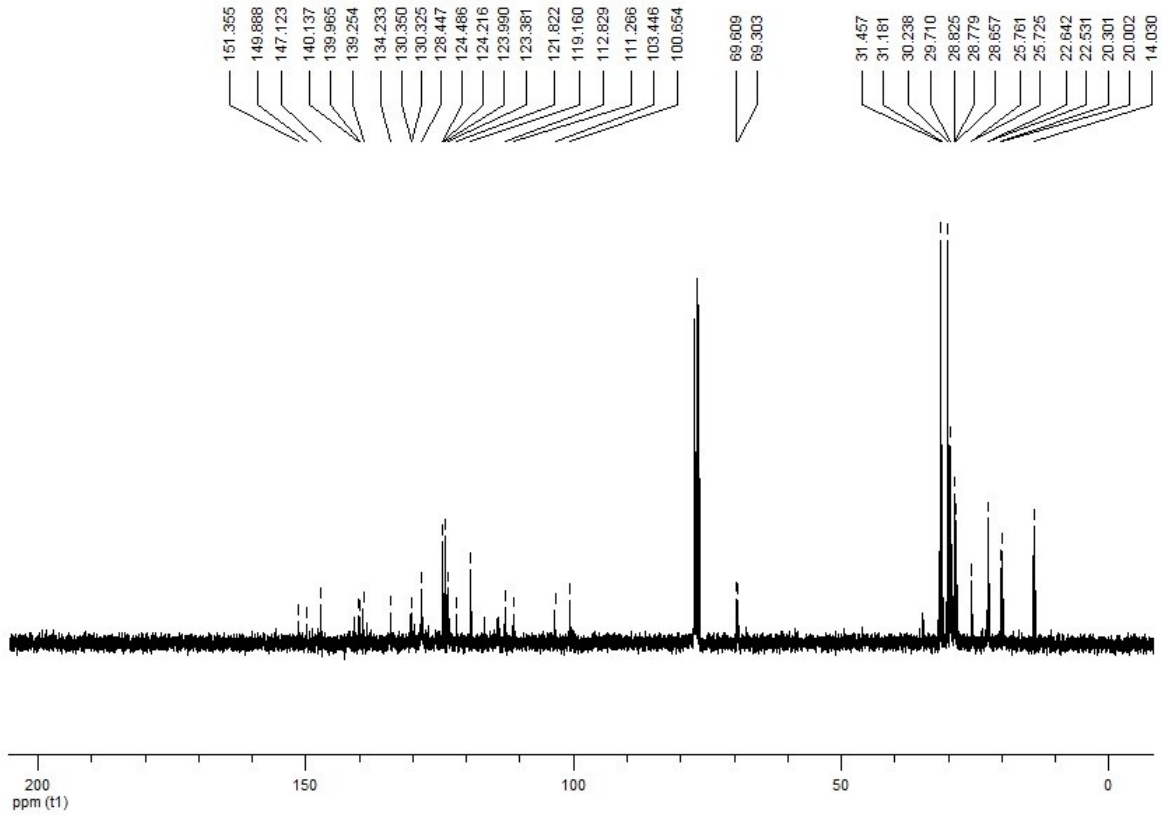


Figure S17. ^{13}C NMR (100 MHz) spectrum of triad **DA1D**.

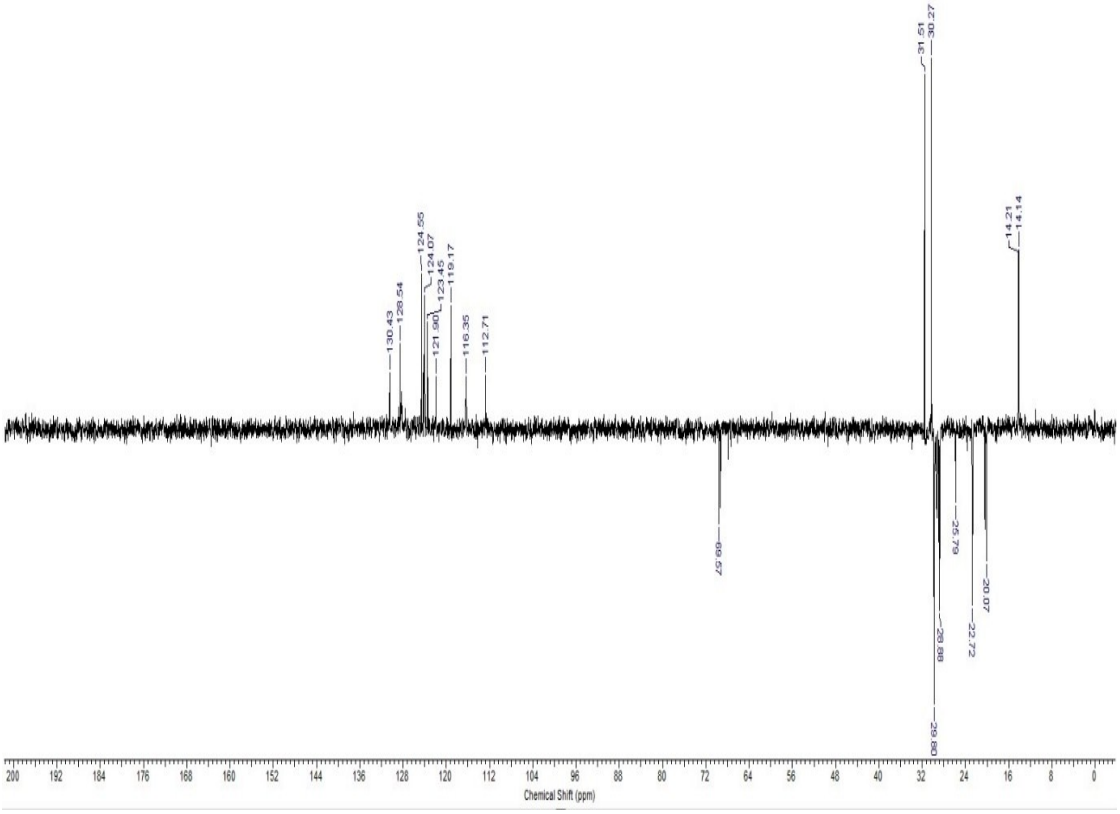


Figure S18. ^{13}C DEPT-135 NMR (100 MHz) spectrum of triad **D-A1-D**.

D-A2-D

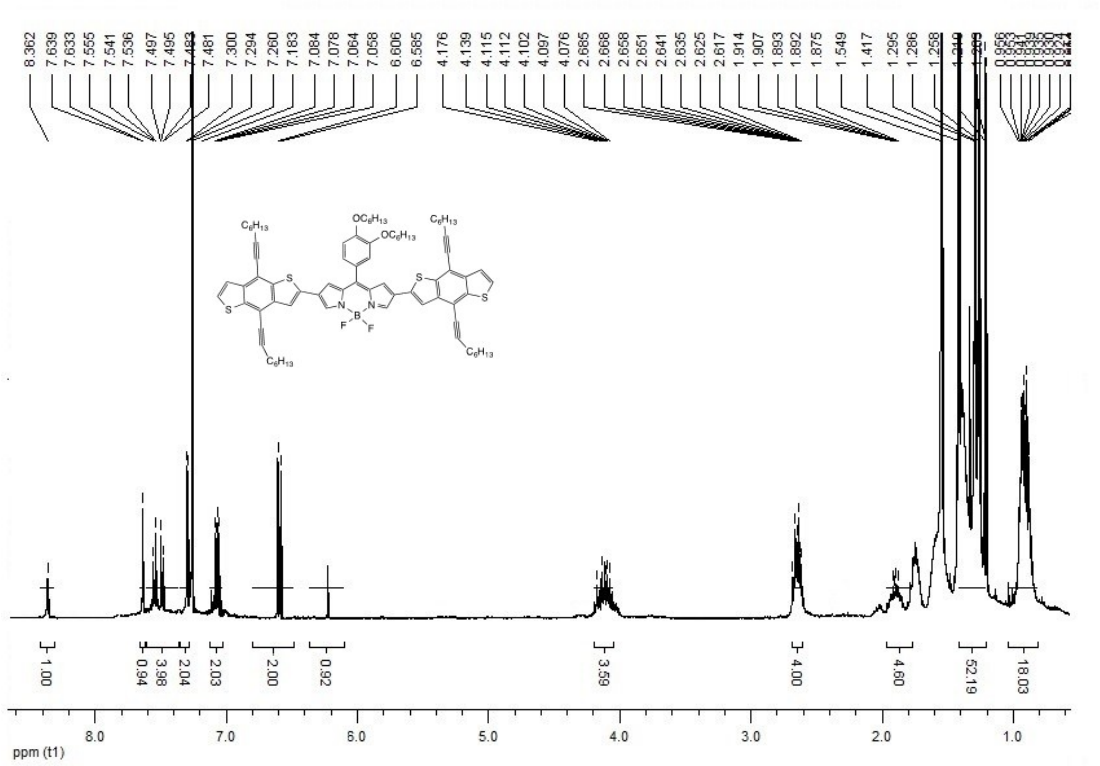


Figure S19. ^{1}H NMR (100 MHz) spectrum of triad **D-A2-D**.

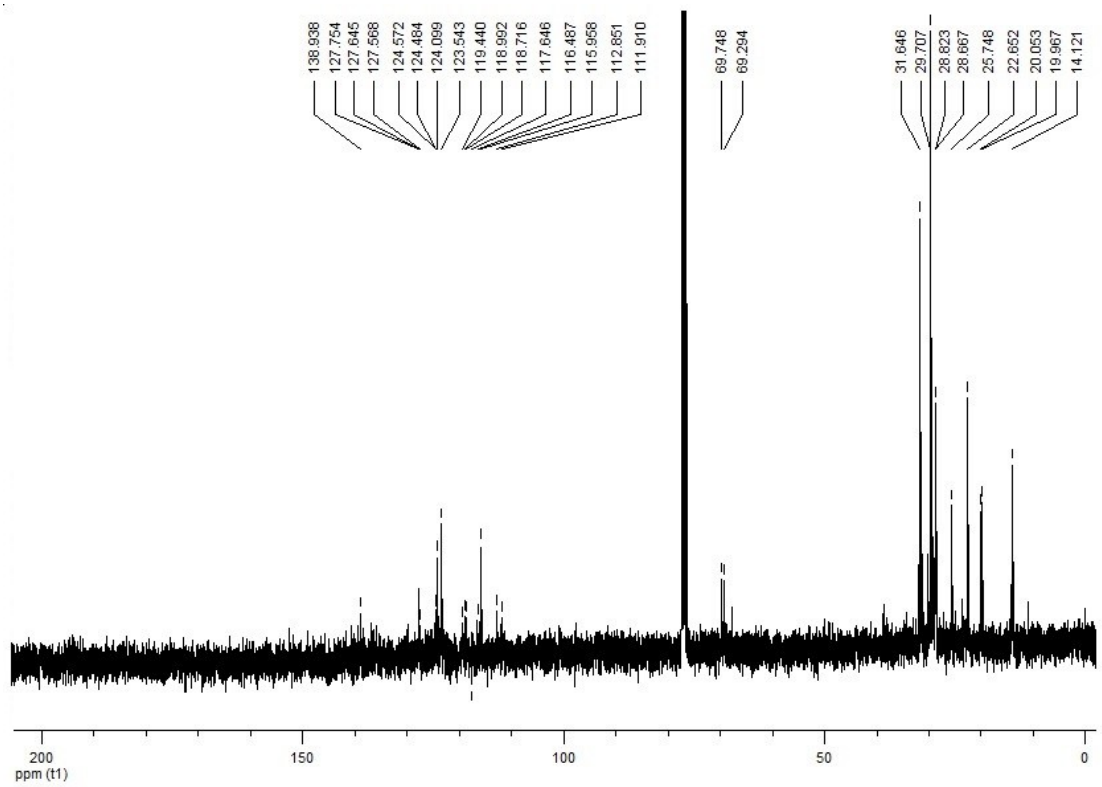


Figure S20. ^{13}C NMR (100 MHz) spectrum of triad **D-A2-D**.

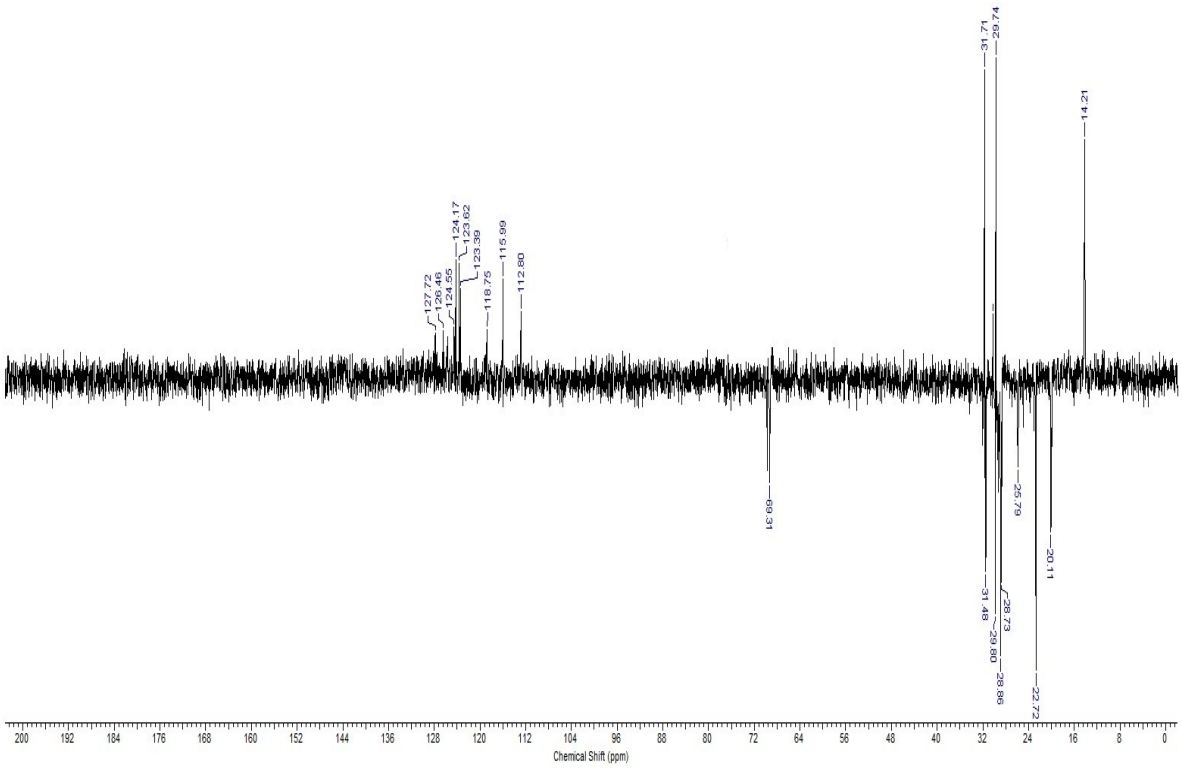


Figure S21. ^{13}C DEPT-135 NMR (100 MHz) spectrum of triad **D-A2-D**.

Matrix Assisted Laser Desorption Ionization (MALDI-TOF) Mass Spectrometry

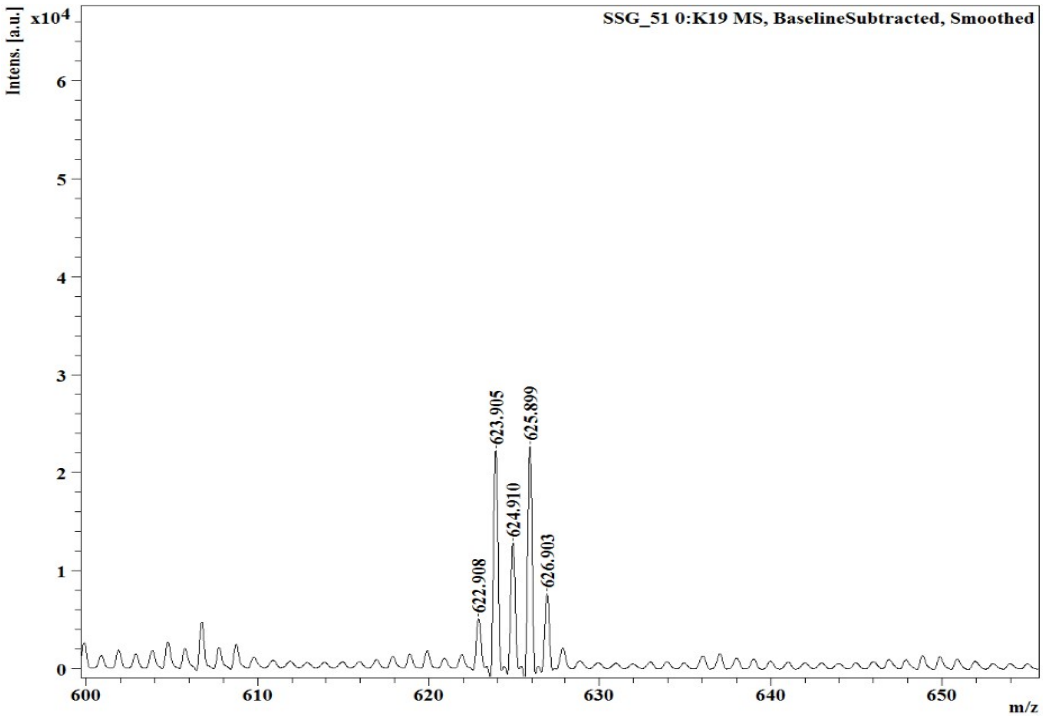


Figure S22. MALDI-TOF mass spectrum of **A1**.

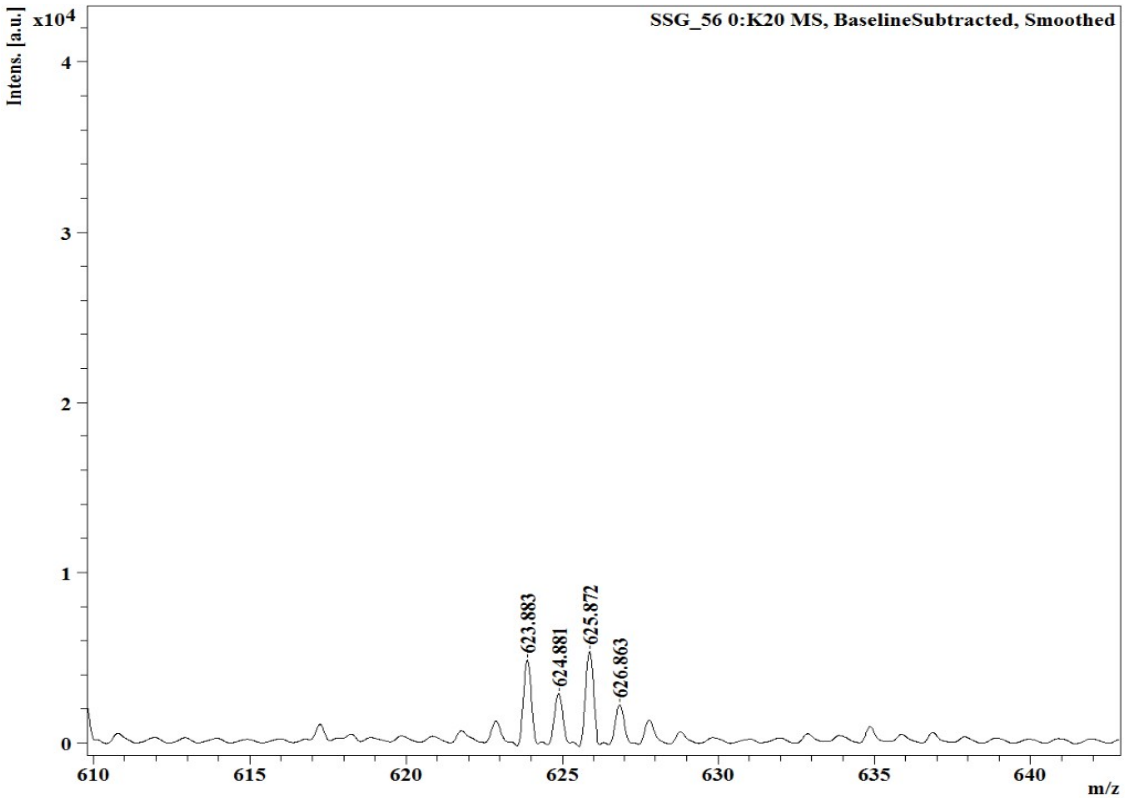


Figure S23. MALDI-TOF mass spectrum of **A2**.

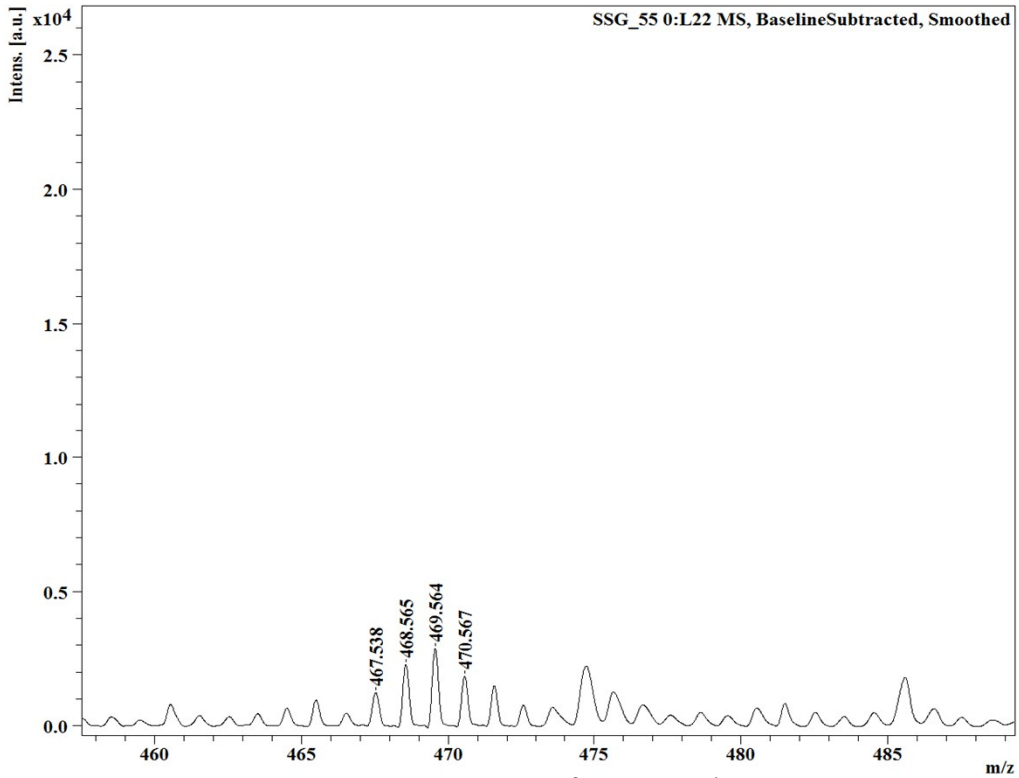


Figure S24. MALDI-TOF mass spectrum of compound **3**

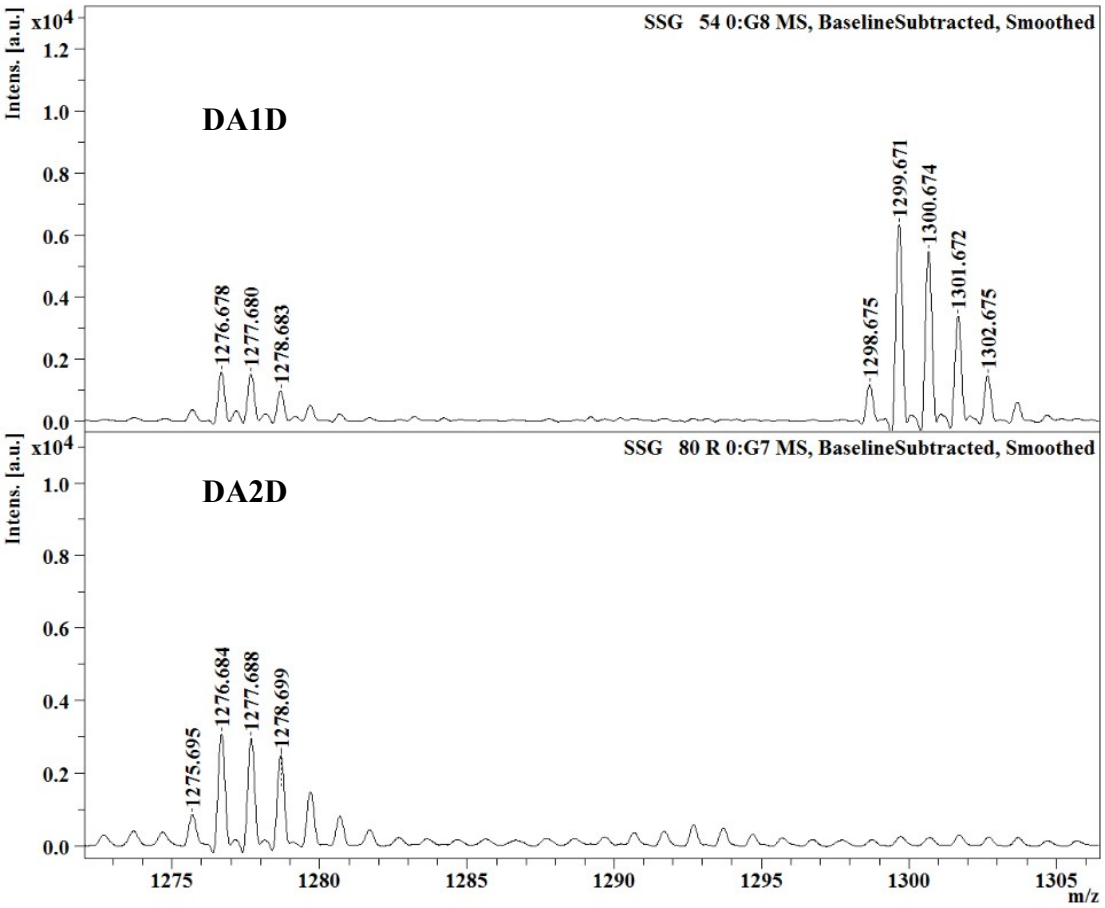


Figure S25. MALDI-TOF mass spectrum of triads **DA1D and DA2D**

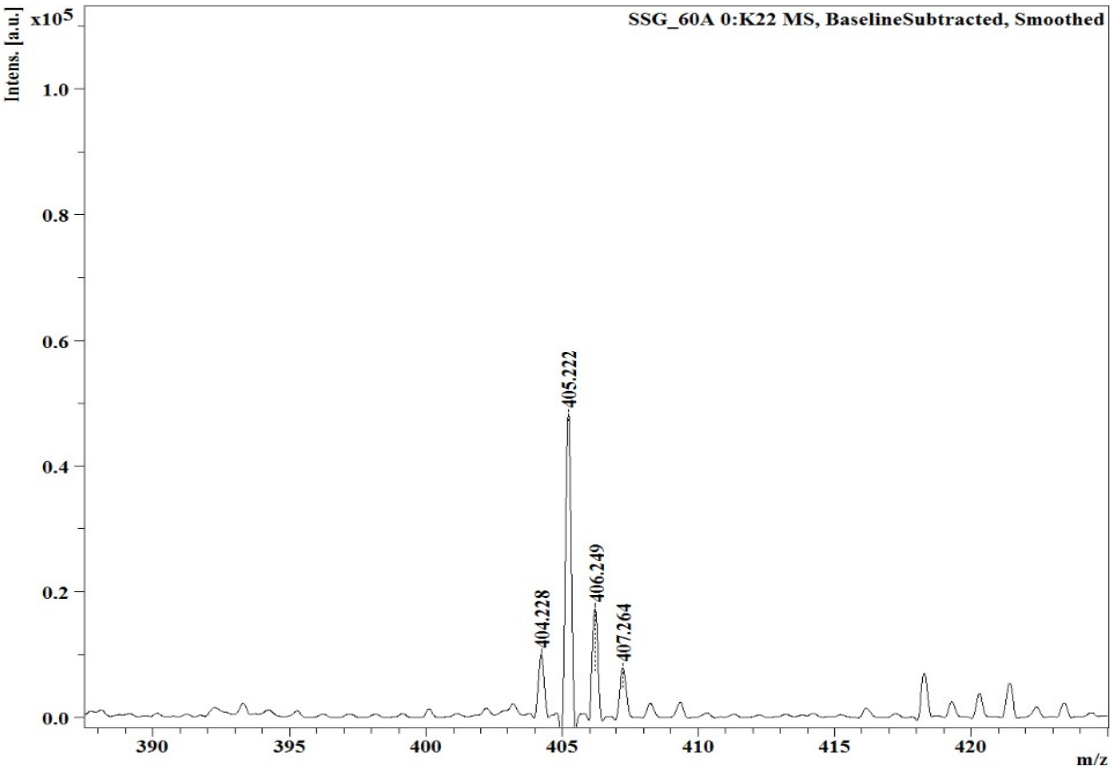


Figure S26. MALDI-TOF mass spectrum of donor **D, 7**

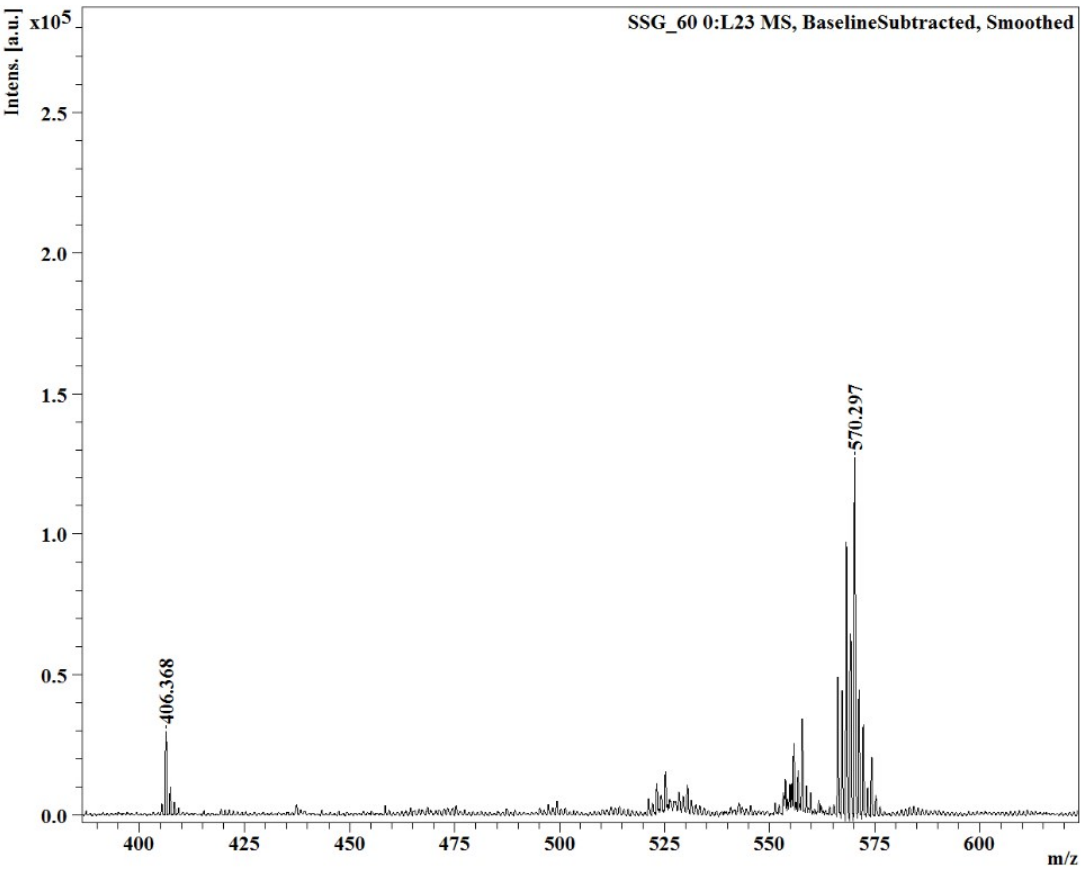


Figure S27. MALDI-TOF mass spectrum of **D**+**D1 (4)**

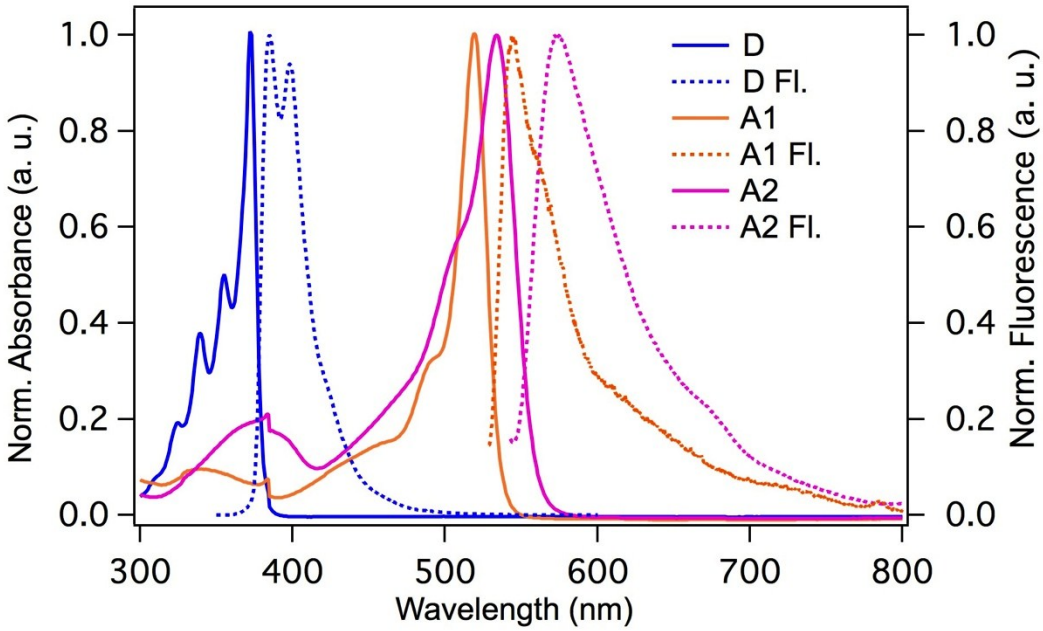


Figure S28. UV/Vis absorption and fluorescence emission spectra of model compounds **D**, **A1** and **A2** in DCM at c ~10^{-5} M.

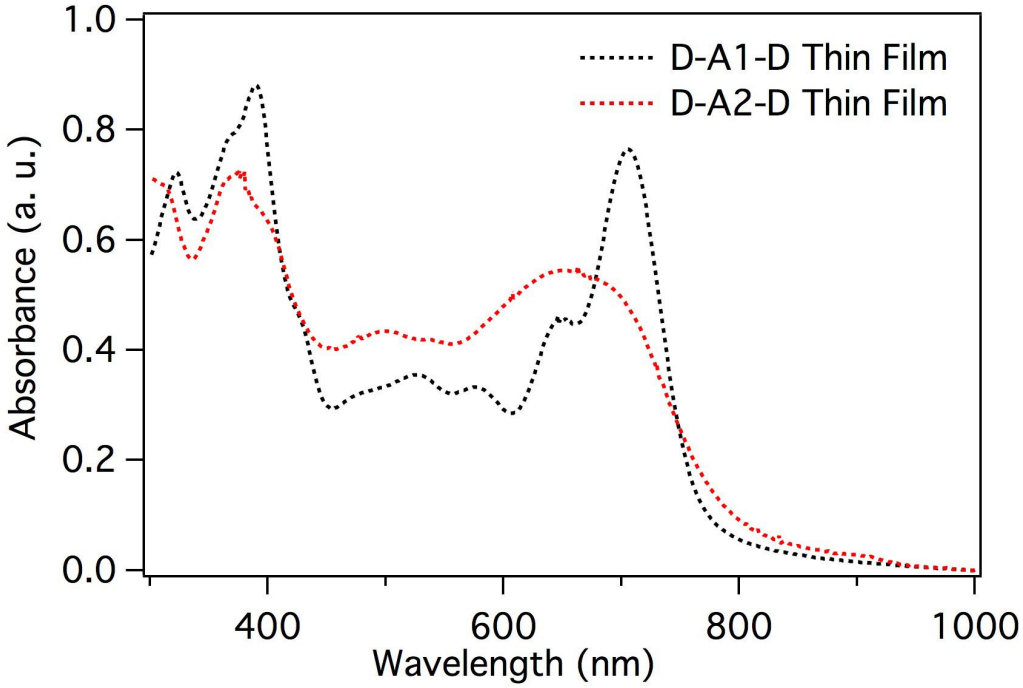


Figure S29. UV/Vis absorption spectra of thin films of **D-A1-D** and **D-A2-D** of thickness ~ 150 nm prepared from chloroform.

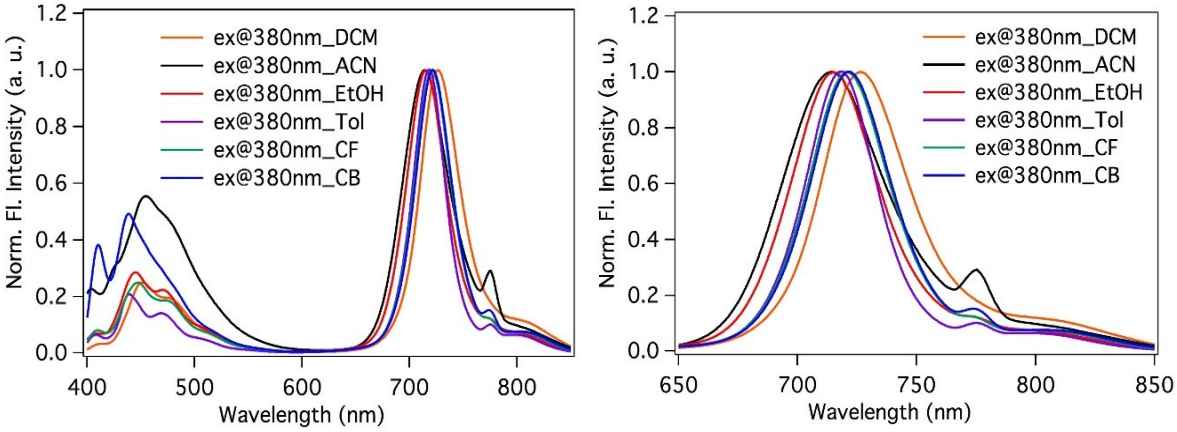


Figure S30. Fluorescence emission spectra of **D-A1-D** (left) in solvents of varied polarity acetonitrile (ACN), ethanol (EtOH), dichloromethane (DCM), chloroform (CF), chlorobenzene (CB) and toluene (Tol) at excitation wavelengths of 380 nm, and (right) magnified view showing negative solvatochromism.

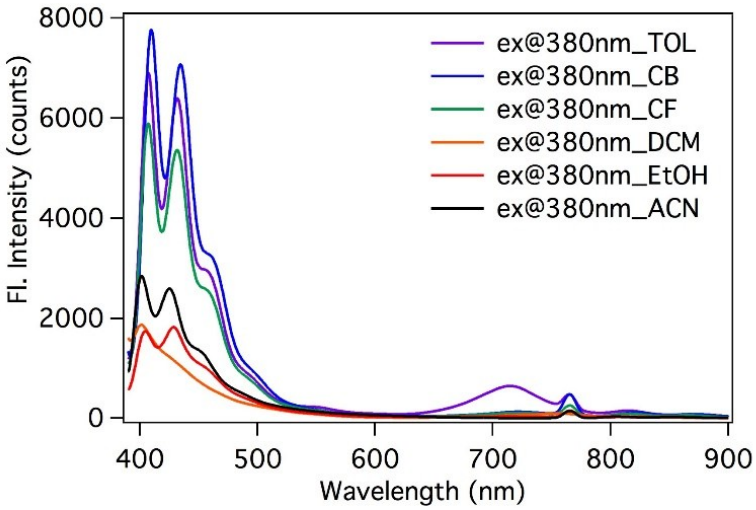


Figure S31. Fluorescence emission spectra of **D-A2-D** in solvents of varied polarity ACN, EtOH, DCM, CF, CB and Tol at excitation wavelength of 380 nm.

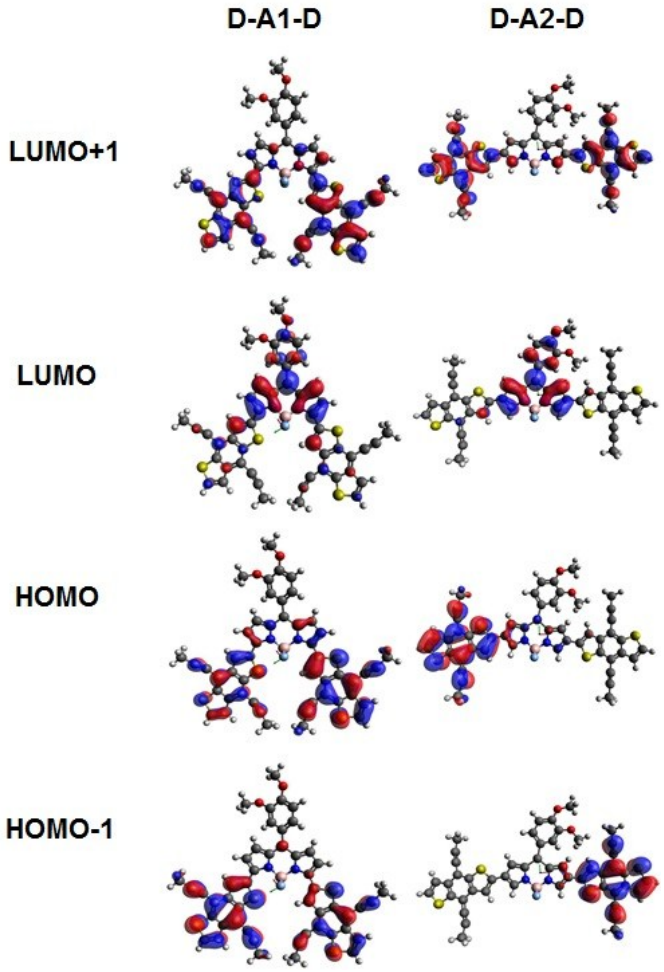
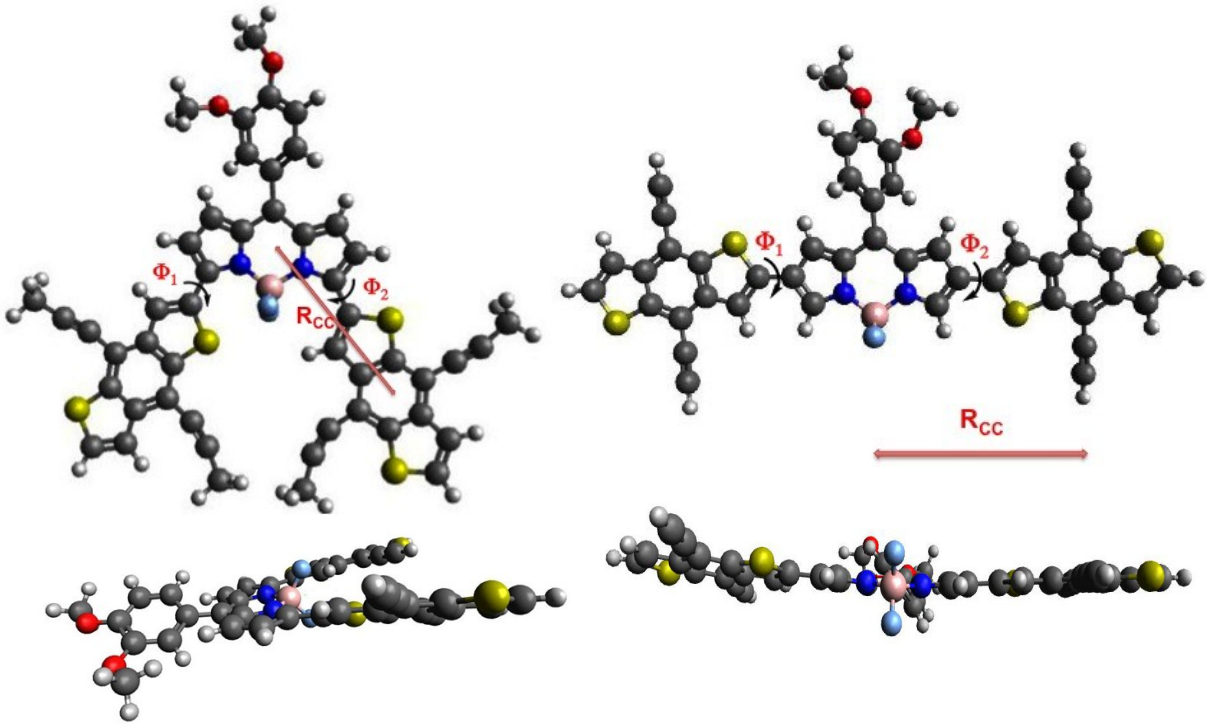


Figure S32. DFT calculated frontier molecular orbital (FMO) plots of **D-A1-D** and **D-A2-D**, orbital plots have isovalue of 0.02.

Table S1. Frontier molecular orbital energy levels of triads **D-A1-D** and **D-A2-D** calculated by B3LYP/6-31G(d,p) method.

Compound	HOMO (eV)	LUMO (eV)	HOMO-1 (eV)	LUMO+1 (eV)	$E_g^{calcd.}$ (eV)
D-A1-D	-5.03	-3.06	-5.34	-2.81	1.97
D-A2-D	-5.26	-3.10	-5.44	-2.98	2.16



D-A1-D **D-A2-D**

Figure S33. Geometry optimized structures of triads **D-A1-D** and **D-A2-D** in top view (upper) and side view (lower) with indicated torsion angles Φ_1 and Φ_2 and centre-to-centre distances R_{CC}.

Table S2. Torsion angles and centre-to-centre distances of **D-A1-D** and **D-A2-D** obtained from geometry optimized structures.

Compound	Φ_1 (°)	Φ_2 (°)	R_{CC} (Å)
D-A1-D	14.4	27.2	7.58
D-A2-D	2.5	11.1	8.90

Absolute fluorescence quantum yield

Absolute quantum yield of DA1D And DA2D 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 S34.

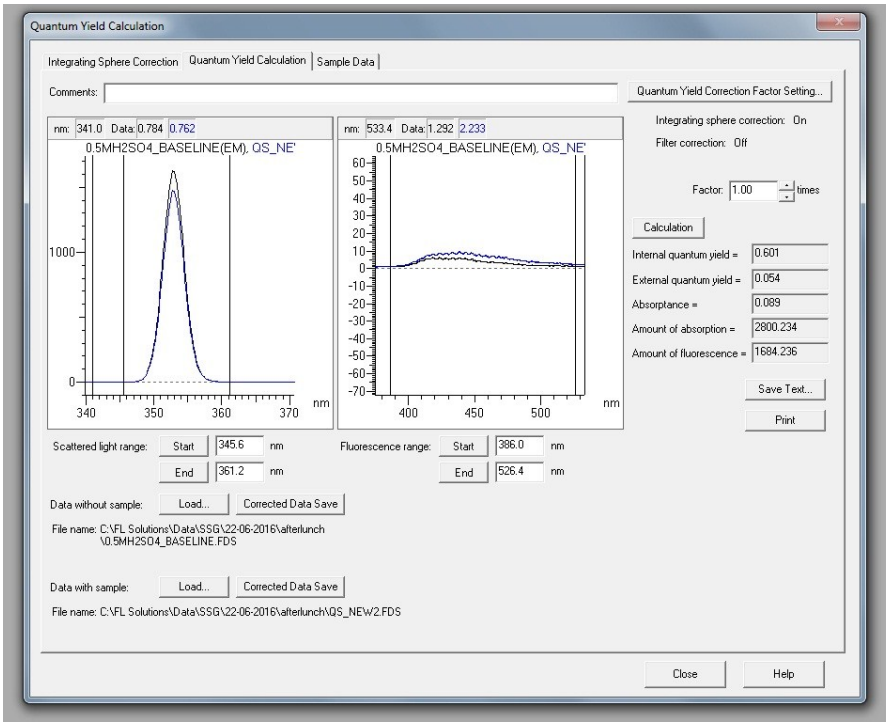


Figure S34. Screenshot of quantum yield calculation by using integrating sphere measurement for the 1×10^{-5} M QBS sample using Hitachi F7000 spectrophotometer.

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.

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

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

$$\Phi_f = \frac{F}{F_{abs}} \quad \text{.....(S3)}$$

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 triads **D-A1-D** and **D-A2-D** in DCM and the values are summarized in table S3.

Table S3. Absolute quantum yields of standard QBS and triads **D-A1-D** and **D-A2-D** obtained by using integrating sphere set-up.

Compound	ϕ_f values obtained in three different measurements			ϕ_f
QBS	0.610	0.590	0.601	0.600 ± 0.010
D-A1-D	0.123	0.107	0.080	0.107 ± 0.022
D-A2-D	0.039	0.047	0.021	0.039 ± 0.013

Charge carrier mobilities

Table S4. Average SCLC mobilities of **D-A1-D** and **D-A2-D** performed on six devices.

Compound	Mobility ($cm^2V^{-1}s^{-1}$)
D-A1-D	7.01 ± 0.47 (x 10^{-5})
D-A2-D	3.63 ± 0.98 (x 10^{-4})

D-A1-D **D-A2-D**

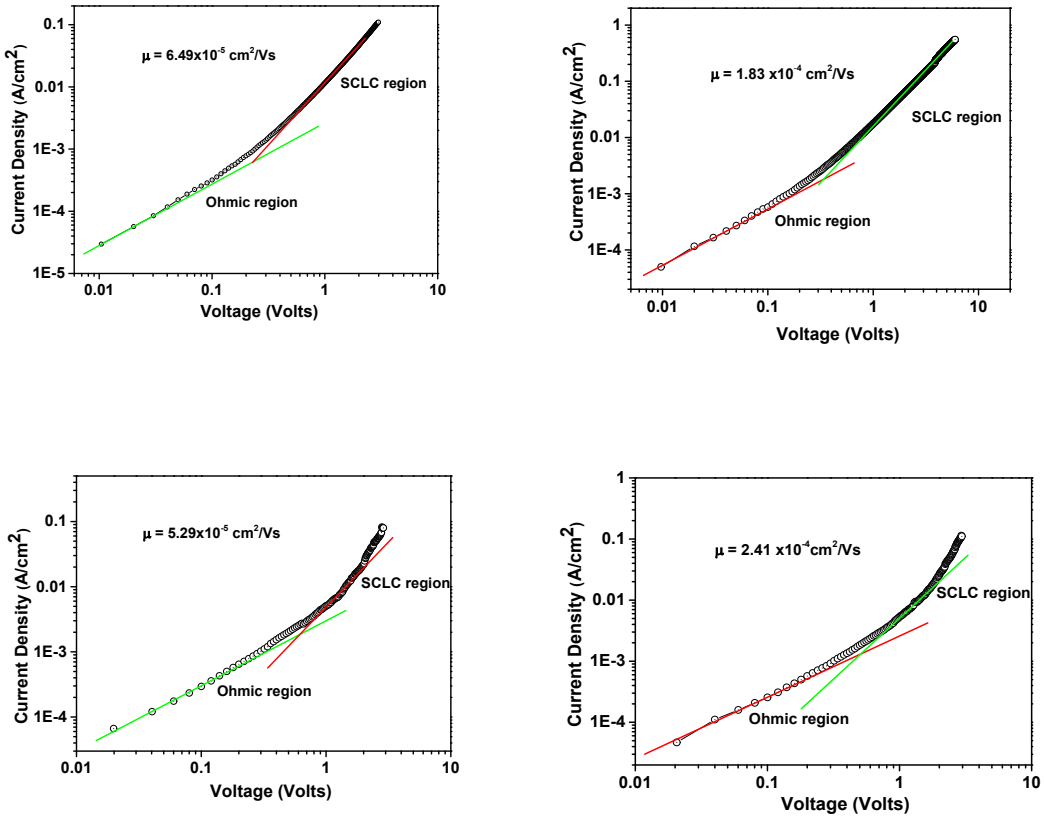


Figure S35. Typical current–voltage curve obtained for **D-A1-D** and **D-A2-D** at room temperature. The two straight lines, with slopes of 1 and 2, represent ideal ohmic and SCLC behaviour, respectively.

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10 Calculation of mmol. was performed based on the fact that **4** contains **D** and **D1** in the ratio of 1:1.3. So, the mmol. reported is that for **D1** only, in **4** that reacts with **A1** or **A2**.

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