Unravelling the Excited State Dynamics of Monofunctionalized Mono- and Di-styryl BODIPY and Perylenediimide Dyads

Kavita Rani[†], Sakshi Chawla[†], Vinita Kumari, Arijit K. De* and Sanchita Sengupta*

Department of Chemical Sciences,

Indian Institute of Science Education and Research (IISER) Mohali,

Knowledge City, Sector 81, P. O. Manauli, Punjab 140306, India

*Email: akde@iisermohali.ac.in, sanchita@iisermohali.ac.in

[†]contributed equally

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1. Materials and Methods

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

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Biospin Avance III FT-NMR400 MHz and AvanceNeo (Bruker) 500 MHz spectrometer at room temperature. Tetramethyl silane was used as an internal standard.

The high-resolution mass spectra were recorded with Waters QTOF mass spectrometer. Software used for acquiring mass spectra was Flex Control, Bruker (USA) and software used for analyzing mass spectra was Flex Analysis 3.1.

UV/Vis and near infrared (NIR) spectral measurements were carried out with Carey 5000 UV/Vis spectrophotometer using a quartz cuvette with 1 cm path length. Steady-state emission and excitation studies were carried out with Hitachi F7000 fluorescence spectrophotometer equipped with R928F photomultiplier expandable up to 900 nm.

The electrochemical measurements were recorded using CHI-610 electrochemical workstation from CH Instruments (USA), with a conventional three-electrode single-compartment cell consisting of glassy carbon as the working electrode, Ag/AgCl containing 1 M KCl solution as the reference electrode, and Pt wire as the counter electrode. Cyclic voltammetry measurements were performed at a scan rate of 100 mV/s. Tetrabutylammonium hexafluorophosphate (TBAHFP) (Alfa Aesar) (0.1 M) dissolved in pre-dried DCM was used as a supporting electrolyte. The solutions were purged with nitrogen prior to measurement. The electrochemical potential was internally calibrated against the standard ferrocene/ferrocenium (Fc/Fc^{+}) redox couple prior to each measurement.

Time-resolved fluorescence spectra were measured using time-correlated single photon counting (TCSPC) model from Fluorocube, Horiba Jobin Yvon, NJ equipped with picosecond laser diodes as an excitation source. The 510 nm and 590 nm lasers were used as a light sources for the excitation of samples and the instrument response function (IRF) was collected using Ludox (colloidal silica) solution. The width (FWHM) of IRF was ~ 250 ps and the optical pulse durations from < 70 ps were used. Highly integrated picosecond PMT modules as well as microchannel plate PMTs were used for the time resolution.

Spectroelectrochemical measurements were performed using a cell assembly (SEC-C) supplied by BAS Inc (Japan) and the assembly comprised of a Pt counter electrode, a Pt gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The absorption spectra were measured using an ocean optics set up connected in absorbance mode and using the FLAME spectrometer. Voltages were swept in the range of -2 V to +2 V, dry DCM was used as solvent and TBAHFP was used as the supporting electrolyte. The solutions were purged with nitrogen for 10 min prior to Spectro electrochemical measurements.

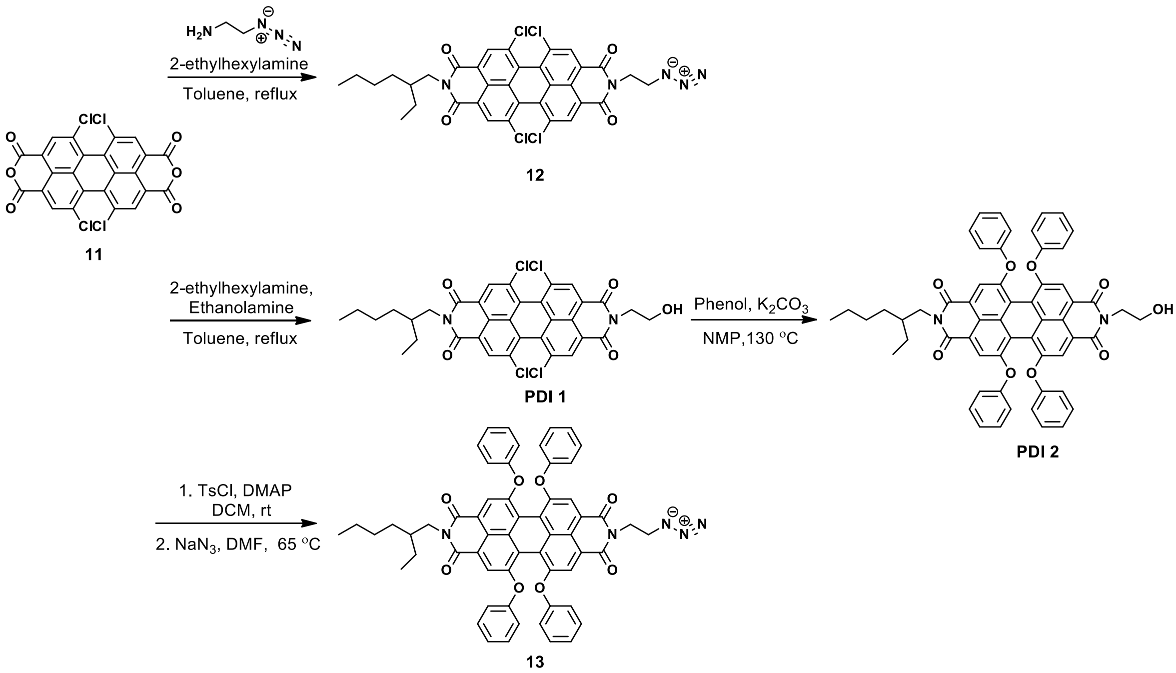
Quantum chemical density functional theory (DFT) calculations were performed on the triads **1** and **2** in the ground state using Gaussian 09 program suite.[S1] The side chains in all molecules were replaced with methyl groups in order to account for the electron-donating effect of the alkyl chain 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 the gas phase together with frequency calculations. The frontier molecular orbital (FMO) energy levels and FMO distribution were obtained from geometry optimization of the neutral ground state geometries.

Femtosecond transient absorption spectroscopy

A customized broadband femtosecond transient absorption spectrometer (TAS, Newport Corp.) was used to investigate the excited state charge transfer dynamics, the details of which may be found elsewhere.[S2,S3] Briefly, the light source is output from a commercial Ti: sapphire laser (Libra, Coherent Inc.) with a central wavelength of 800 nm, the repetition rate of 1 kHz, and pulse duration of 50 fs. The incident pulse is split into pump and probe pulses. One part of the pulse was guided into a commercial non-collinear optical parametric amplifier (NOPA, Topas White, Light conversion), which was used to tune the wavelength of the pump pulse to electronically excite the sample, the other part of the output from the amplifier is focused onto a CaF_2 crystal to generate a broadband white-light probe pulse. The transient absorption data are collected at the pump magic angle (54.7°) with respect to the vertically polarized probe to negate the anisotropic effects of the sample. The spectrally-dispersed differential signal (ΔOD) is generated by using a mechanical chopper to block every alternate pump pulse. The data is analyzed using open-source global analysis software (Glotaran, version 1.5.1) to obtain evolution-associated spectra (EAS) assuming a three-state kinetic model. The absorbance of the sample used for the TA measurements was about 0.3 at the excitation wavelength. The absorbance was recorded after the experiment to rule out any effect of photobleaching in the sample.

2. Synthesis

(a) Synthesis Procedures for Perylenediimide (PDI) compounds



Scheme S1. Synthesis of PDI subchromophores.

The detailed experimental procedures and NMR structural characterization for PDI compounds are reported elsewhere.[S4]

(b) Synthesis Procedures for Styryl-BODIPY (STBDP) compounds

Synthesis of compound 1

3,4-dihydroxybenzaldehyde (3 g, 21.72 mmol), K_2CO_3 (12 g, 86.88 mmol) were dissolved in dry dimethylformamide DMF (40 mL) under nitrogen atmosphere and 2-ethylhexylbromide (12.58 g, 65.16 mmol) was added. The reaction mixture was refluxed overnight. Subsequently, the reaction mixture was extracted with ethyl acetate, washed with brine solution and water. The organic layer was dried over sodium sulphate (Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography hexane/ethyl acetate (90 / 10). Compound **1** was obtained as a yellow oil.

Yield: 6.05 g (77 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.81 (s, 1 H), 7.40 - 7.38 (m, 2 H), 6.93 (d, J = 8 Hz, 1 H), 3.94 - 3.89 (m, 4 H), 1.81 - 1.73 (m, 2 H), 1.56 - 1.40 (m, 8 H), 1.33 - 1.29 (m, 8 H), 0.94 - 0.87 (m, 12 H).

Synthesis of compound 2

3,4-dihydroxybenzaldehyde (3 g, 21.72 mmol), K_2CO_3 (12 g, 86.88 mmol) were dissolved in dry dimethylformamide (DMF) (40 mL) under nitrogen atmosphere and 1-bromohexane (10.75 g, 65.16 mmol) was added. The reaction mixture was refluxed overnight. Then reaction mixture was extracted with ethyl acetate, washed with brine solution and water. The organic layer was dried over sodium sulphate (Na_2SO_4) and solvent was removed under reduced pressure. The crude product was purified by column chromatography hexane / ethyl acetate (90 / 10). The compound **2** was obtained as a white solid.

Yield: 5.53 g (83 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.83 (s, 1 H), 7.43 - 7.39 (m, 2 H), 6.95 (d, J = 8 Hz, 1 H), 4.10 - 4.03 (m, 4 H), 1.89 - 1.80 (m, 4 H), 1.52 - 1.44 (m, 4 H), 1.37 - 1.33 (m, 8 H), 0.91 (t, J = 8 Hz, 12 H).

Synthesis of compound 3

2,4-dimethylpyrrole (1.15 g, 12.14 mmol) and compound **1** (2 g, 5.52 mmol) were dissolved in 50 mL of dry dichloromethane (DCM) and 60 µL TFA was added to this mixture and stirred for 2 h at room temperature (RT). Tetrachloro-1,4-benzoquinone (chloranil) (1.48 g, 6.01 mmol) was added and the reaction mixture was stirred for half an hour. From the crude reaction mixture, DCM was removed under reduced pressure and obtained the intermediate compound which was further dissolved in 50 mL of dry toluene. Subsequently, triethylamine (1.67 g, 16.49 mmol) was added, the reaction mixture was stirred for 15 minutes at RT. Then $BF_3.OEt_2$ (3.90 g, 27.47 mmol) was added and reaction was stirred at 80 °C for 30 min and cooled to RT. After that reaction was quenched with 50 mL of water and stirred for 3 h. The mixture was extracted with DCM (3 × 60 mL) and combined organic layers were washed with brine solution and water (3 × 100 mL). The organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure. The crude product was purified by column chromatography with hexane / DCM (80 / 20) as an eluent to obtain the compound **3** as a red solid.[S5]

Yield: 1.28 g (40 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.96 (d, J = 8 Hz, 1 H), 6.77 - 6.75 (m, 2 H), 5.98 (s, 2 H), 3.91 (d, J = 8 Hz, 2 H), 3.82 - 3.80 (m, 2 H), 2.55 (s, 6 H), 1.82 - 1.70 (m, 2 H), 1.57 - 1.30 (m, 22 H), 0.98 - 0.89 (m, 12 H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ (ppm): 155.11, 150.20, 150.02, 143.13, 141.96, 131.73, 126.92, 121.00, 120.30, 113.70, 113.22, 71.92, 71.66, 39.62, 39.53, 30.63, 30.54, 29.20, 29.10, 23.93, 23.85, 23.02, 14.39, 14.07, 14.04, 11.23, 11.14.

HRMS (ESI): m/z calcd for $C_{35}H_{52}BF_2N_2O_2^+$ [M + H]$^+$: 581.4084; Found: 581.4106.

Synthesis of compound 4

Compound **3** (1.03 g, 1.77 mmol) was dissolved under a nitrogen atmosphere in dry DCM (30 mL) and a solution of N-iodosuccinimide (NIS) (0.40 g, 1.77 mmol) in dry DMF (5 mL) was added. The solution was stirred at RT for 24 h. Then reaction mixture was washed with saturated solution of NaCl (2 × 100 mL) and ice cold water to remove the DMF. The organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure. The crude product was purified using column chromatography hexane / DCM (70 / 30) and compound **4** was obtained as red solid.[S6]

Yield: 950 mg (76 %).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm): 6.97 (d, J = 8 Hz, 1 H), 6.75 - 6.74 (m, 2 H), 6.04 (s, 1 H), 3.92 (2 H, J = 8 Hz, 2 H), 3.84 - 3.77 (m, 2 H), 2.63 (s, 3 H), 2.56 (s, 3 H), 1.84-1.74 (m, 2 H), 1.59 - 1.44 (m, 14 H), 1.37 - 1.30 (m, 8 H), 0.98 - 0.88 (m, 12 H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ (ppm): 157.66, 154.40, 150.51, 150.38, 145.42, 143.45, 141.97, 132.33, 131.41, 126.88, 122.22, 120.36, 113.99, 113.23, 84.20, 72.20, 71.98, 39.75, 39.67, 30.76, 30.66, 29.33, 29.24, 24.08, 23.99, 23.17, 23.16, 16.86, 15.87, 14.87, 14.83, 14.23, 14.20, 11.38, 11.29.

HRMS (ESI): m/z calcd for $C_{35}H_{51}BF_2IN_2O_2^+$ [M+H]$^+$: 707.3051; Found: 707.3096.

Synthesis of compound 5

Compound **4** (548 mg, 0.776 mmol) and compound **2** (261 mg, 0.776 mmol) were dissolved in dry benzene (30 mL) and acetic acid (0.2 mL) and piperidine (0.2 mL) were added. The reaction mixture was stirred at 105 $^\circ$C for 24 h and the Dean-Stark trap was used to remove the water generated by condensation. Then the reaction mixture was extracted with DCM several times and washed with water. The organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography using hexane / DCM (60 / 40) and compound **5** was obtained as a blue viscous liquid.[S7]

Yield: 183 mg (24 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, *J* = 16 Hz, 1 H), 7.23 (d, *J* = 16 Hz, 1 H), 7.15 - 7.13 (m, 2 H), 6.97 (d, *J* = 8 Hz, 1 H), 6.86 (d, J = 8 Hz, 1 H), 6.78 - 6.76 (m, 2 H), 6.64 (s, 1 H), 4.09 - 4.01 (m, 4 H), 3.93 (d, *J* = 8 Hz, 2 H), 3.85 - 3.80 (m, 2 H), 2.67 (s, 3 H), 1.89 - 1.79 (m, 6 H), 1.61 - 1.44 (m, 20 H), 1.37 - 1.31 (m, 14 H), 0.99 - 0.90 (m, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.24, 153.22, 150.96, 150.37, 150.26, 149.36, 144.63, 142.18, 139.83, 138.38, 133.77, 131.54, 129.39, 127.08, 122.17, 120.65, 118.46, 116.71, 113.84, 113.43, 113.22, 112.45, 83.99, 72.15, 71.92, 69.57, 69.21, 39.73, 39.64, 31.76, 31.71, 30.75, 30.65, 29.40, 29.33, 29.27, 29.24, 28.86, 25.81, 24.06, 23.97, 23.18, 23.17, 22.76, 22.74, 16.80, 15.95, 15.11, 14.25, 14.22, 14.18, 14.16, 11.39, 11.30.

HRMS (ESI): m/z calcd for $C_{54}H_{79}BF_2IN_2O_4^+$ $[M+H]^+$: 995.5140; Found: 995.5196.

Synthesis of compound 6

Compound **5** (300 mg, 0.302 mmol) was dissolved in diisopropylamine (20 mL), after purging the solution with nitrogen, $Pd(PPh_3)_2Cl_2$ (10.6 mg, 0.02 mmol) and CuI (2.3 mg, 0.02 mmol) were added under nitrogen atmosphere, subsequently ethynyltrimethylsilane (TMSA) (0.09 mL, 0.60 mmol) was added and reaction mixture was refluxed for 2 h. Then solvent was removed under reduced pressure and the crude product was purified by silica column chromatography using hexane/ethyl acetate (95 / 5) and **6** was obtained as a green solid.[S6]

Yield: 133 mg (46 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, *J* = 16 Hz, 1 H), 7.22 (d, *J* = 16 Hz, 1 H), 7.14 - 7.13 (m, 2 H), 6.97 (d, *J* = 8 Hz, 1 H), 6.85 (d, *J* = 8 Hz, 1 H), 6.77 - 6.76 (m, 2 H), 6.62 (s, 1 H), 4.09 - 4.01 (m, 4 H), 3.93 (d, *J* = 4 Hz, 2 H), 3.82 (d, *J* = 4 Hz, 2 H), 2.66 (s, 3 H), 1.88 - 1.76 (m, 6 H), 1.61 - 1.46 (m, 20 H), 1.35 - 1.31 (m, 14 H), 0.99 - 0.88 (m, 18 H), 0.22 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.82, 155.15, 150.92, 150.35, 150.21, 149.37, 144.21, 142.48, 140.52, 138.16, 134.36, 132.35, 130.68, 129.44, 126.96, 122.12, 120.61, 118.29, 116.75, 114.87, 113.85, 113.43, 113.24, 112.46, 100.80, 98.12, 72.14, 71.94, 69.59, 69.23, 39.74, 39.65, 31.77, 31.72, 30.76, 30.68, 30.62, 29.84, 29.41, 29.34, 29.28, 29.25, 25.87, 25.82, 24.07, 23.99, 23.19, 23.18, 22.77, 22.75, 15.06, 14.26, 14.22, 14.19, 14.17, 13.64, 13.37, 11.39, 11.30.

HRMS (ESI): m/z calcd for $C_{59}H_{88}BF_2N_2O_4Si^+$ $[M+H]^+$: 965.6569; Found: 965.6489.

Synthesis of compound 7

Compound **6** (100 mg, 0.10 mmol) was dissolved in dry DCM (15 mL) and dry methanol (5 mL), potassium carbonate (43.0 mg, 0.31 mmol) was added and mixture was stirred for 12 h at RT. Subsequently, the reaction mixture was extracted with DCM, washed with water and dried over sodium sulphate and solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane/ethyl acetate (95 / 5), however, due to unstability of compound **7** on silica column, it could not be purified completely. After one column purification, it was obtained as bluish viscous liquid and used for the next reaction without further purification.[S8]

Yield: 26 mg (28 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (d, J = 16 Hz, 1 H), 7.23 (d, J = 16 Hz, 1 H), 7.15 - 7.13 (m, 2 H), 6.99 - 6.96 (m, 1 H), 6.86 (d, J = 8 Hz, 1 H), 6.78 - 6.76 (m, 2 H), 6.64 (s, 1 H), 4.09 - 4.01 (m, 4 H), 3.93 (d, J = 8 Hz, 2 H), 3.84 - 3.82 (m, 2 H), 3.30 (s, 1 H), 2.67 (s, 3 H), 1.89 - 1.74 (m, 6 H), 1.62 - 1.46 (m, 20 H), 1.37 - 1.32 (m, 14 H), 0.99 - 0.88 (m, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.51, 150.99, 150.36, 150.25, 149.39, 144.49, 142.60, 140.62, 138.45, 134.49, 129.40, 126.88, 122.19, 120.62, 116.73, 113.86, 113.44, 113.25, 112.48, 83.30, 72.17, 71.95, 69.59, 69.24, 39.74, 39.66, 32.07, 31.77, 31.73, 30.77, 30.67, 30.44, 29.51, 29.42, 29.34, 29.28, 29.25, 25.87, 25.82, 24.08, 23.99, 23.19, 22.84, 22.75, 15.09, 14.25, 14.21, 14.17, 13.23, 11.40, 11.29.

HRMS (ESI): m/z calcd for $C_{56}H_{80}BF_2N_2O_4^+$ $[M+H]^+$: 893.6174; Found: 893.6212.

Synthesis of compound 8

Compound **4** (500 mg, 0.71 mmol) and compound **2** (952.20, 2.83 mmol) were dissolved in dry benzene (30 mL) and acetic acid (0.2 mL) and piperidine (0.2 mL) were added. The reaction mixture was stirred at 105 $^\circ$C for 24 h and the Dean-Stark trap was used to remove the water generated by condensation. The reaction mixture was extracted with DCM, washed with water.

The organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography with hexane / DCM (50 / 50) and compound **8** was obtained as a green colour viscous liquid.[S7]

Yield: 667 mg (73 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, *J* = 16 Hz, 1 H), 7.58 - 7.52 (m, 2 H), 7.24 - 7.19 (m, 3 H), 7.16 (s, 1 H), 7.11 (s, 1 H), 6.98 (d, *J* = 8 Hz, 1 H), 6.89 (t, *J* = 8 Hz, 2 H), 6.80 - 6.78 (m, 2 H), 6.67 (s, 1 H), 4.11 - 4.03 (m, 8 H), 3.93 (d, *J* = 4Hz, 2 H), 3.83 (s, 2 H), 1.89 - 1.78 (m, 10 H), 1.59 - 1.45 (m, 26 H), 1.35 - 1.31 (m, 20 H), 0.99 - 0.89 (m, 24 H).

^{13} C NMR (125 MHz, $CDCl_3$), δ (ppm): 155.31, 151.01, 150.37, 149.35, 149.30, 148.03, 144.24, 142.98, 138.57, 138.39, 137.55, 134.46, 132.64, 130.41, 129.50, 127.29, 121.97, 121.19, 120.96, 118.88, 117.36, 116.93, 113.87, 113.76, 113.70, 113.34, 113.11, 113.02, 81.29, 72.16, 71.91, 69.61, 69.58, 69.32, 69.19, 39.74, 39.66, 31.76, 31.74, 31.71, 31.69, 30.74, 30.65, 29.46, 29.43, 29.33, 29.31, 29.28, 29.22, 25.87, 25.84, 25.80, 25.79, 24.05, 23.97, 23.14, 23.13, 22.72, 22.70, 17.23, 15.06, 14.20, 14.16, 14.12, 14.11, 11.36, 11.27.

HRMS (ESI): m/z calcd for $C_{73}H_{107}BF_2IN_2O_6^+$ $[M+H]^+$: 1283.7229; Found: 1283.7251.

Synthesis of compound 9

Compound **8** (311 mg, 0.24 mmol) was dissolved in diisopropylamine (20 mL), after purging the solution with nitrogen, $Pd(PPh_3)_2Cl_2$ (8.50 mg) and CuI (2.31 mg) were added under nitrogen atmosphere, subsequently, TMSA (47.76 mg, 0.49 mmol) was added and the reaction mixture was refluxed for 2 h. Then the solvent was removed under reduced pressure and crude was purified by column chromatography with hexane/ethyl acetate (90 / 10) and **9** was obtained as a green solid.[S6]

Yield: 173 mg (57 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.33 (d, *J* = 16 Hz, 1 H), 7.65 - 7.55 (m, 2 H), 7.24 - 7.19 (m, 3 H), 7.13 (d, *J* = 8 Hz, 2 H), 6.98 (d, *J* = 8 Hz, 1 H), 6.90 (t, *J* = 8 Hz, 2 H), 6.80 - 6.78 (m, 2 H), 6.66 (s, 1 H), 4.10 - 4.03 (m, 8 H), 3.93 (d, *J* = 4 Hz, 2 H), 3.83 (d, *J* = 4 Hz, 2 H), 1.89 - 1.81 (m, 10 H), 1.61 - 1.51 (m, 26 H), 1.41 - 1.37 (m, 20 H), 1.00 - 0.92 (m, 24 H), 0.28 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 154.74, 151.00, 150.95, 150.42, 150.40, 150.27, 149.38, 149.30, 144.31, 143.55, 143.53, 138.82, 137.98, 137.97, 137.78, 134.83, 131.88, 130.61, 129.69, 127.24, 121.92, 120.97, 120.93, 118.50, 117.14, 117.11, 113.93, 113.82, 113.74, 113.48, 113.37, 113.20, 112.57, 102.98, 100.09, 72.21, 72.03, 69.73, 69.58, 69.37, 69.30, 39.78, 39.70, 31.79, 31.75, 30.79, 30.69, 29.48, 29.47, 29.36, 29.33, 29.26, 25.89, 25.88, 25.84, 24.10, 24.02, 23.20, 23.19, 22.76, 15.03, 14.25, 14.21, 14.17, 13.16, 11.40, 11.31.

HRMS (APCI): m/z calcd for $C_{78}H_{116}BF_2N_2O_6Si^+$ $[M+H]^+$: 1253.8658; Found: 1253.8652.

Synthesis of compound 10

Compound **9** (100 mg, 0.08 mmol) was dissolved in DCM (15 mL) and methanol (5 mL), potassium carbonate (33.07 mg, 0.24 mmol) was added and mixture was stirred at RT for 12h under nitrogen atmosphere. After that reaction mixture was extracted with DCM and washed with water. The crude product was purified by column chromatography by using hexane/ ethyl acetate (90 / 10) as eluent. The compound **9** was obtained as a green solid.[S8]

Yield: 57 mg (61 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (d, J = 16 Hz, 1 H), 7.59 (t, J = 16 Hz, 2 H), 7.22 (t, J = 8 Hz, 3 H), 7.13 (s, 2 H), 6.98 (d, J = 8 Hz, 1 H), 6.89 (d, J = 8 Hz, 2 H), 6.81 - 6.79 (m, 2 H), 6.66 (s, 1 H), 4.10 - 4.02 (m, 8 H), 3.94 (d, J = 8 Hz, 2 H), 3.84 (s, 2 H), 3.54 (s, 1 H), 1.89 - 1.82 (m, 10 H), 1.62 - 1.50 (m, 26 H), 1.36 - 1.31 (m, 20 H), 0.99 - 0.91 (m, 24 H).

^{13} C NMR (125 MHz, $CDCl_3$) δ (ppm): 155.04, 150.98, 150.80, 150.53, 150.34, 150.26, 149.33, 149.30, 144.48, 143.79, 138.87, 138.27, 137.51, 134.91, 131.66, 130.54, 129.58, 127.09, 121.97, 121.42, 120.93, 118.64, 117.12, 117.00, 113.89, 113.77, 113.61, 113.40, 113.35, 113.16, 111.30, 85.50, 78.69, 72.18, 71.96, 69.71, 69.68, 69.30, 69.23, 39.76, 39.67, 31.78, 31.77, 31.72, 31.71, 30.76, 30.67, 29.81, 29.50, 29.46, 29.34, 29.33, 29.30, 29.23, 25.88, 25.87, 25.82, 25.81, 24.07, 23.99, 23.16, 23.15, 22.73, 15.01, 14.21, 14.17, 14.13, 13.00, 11.37, 11.27.

HRMS (ESI): m/z calcd for $C_{75}H_{108}BF_2N_2O_6^+$ $[M+H]^+$: 1181.8263; Found: 1181.8289.

(c) Synthesis procedure for dyads 1 and 2

Synthesis of dyad 1

The compound **9** (35 mg, 0.039 mmol) and PDI **1** (28 mg, 0.039 mmol) were dissolved in tetrahydrofuran (THF) (25 mL) and the reaction mixture was purged with nitrogen, subsequently sodium ascorbate (7.3 mg, 0.037 mmol) and copper sulphate (4.7 mg, 0.019 mmol) dissolved in water were added to this mixture. Then reaction mixture was stirred for 3 days at 50 °C under nitrogen atmosphere. After 3 days, THF was evaporated under reduced pressure and reaction mixture was extracted with DCM, the organic layer was dried over sodium sulphate and solvent was removed under reduced pressure. The crude product was purified by column chromatography DCM/EA (9/1) as eluent and a pink solid compound was obtained.

Yield: 30 mg (47 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (s, 2 H), 8.55 (s, 2 H), 7.64 (s, 1 H), 7.50 (d, *J* = 16 Hz, 1 H), 7.18 (d, *J* = 12 Hz, 1 H), 7.13 - 7.11 (m, 2 H), 6.98 (t, *J* = 8 Hz, 1 H), 6.85 - 6.80 (m, 3 H), 6.62 (s, 1 H), 4.87 - 4.84 (m, 2 H), 4.73 - 4.70 (m, 2 H), 4.20 - 4.10 (m, 2 H), 4.08-4.01 (m, 4 H), 3.93 (t, *J* = 4 Hz , 2 Hz), 3.82 (t, *J* = 8 Hz, 2 H), 2.65 (s, 3 H), 1.94 (t, *J* = 8 Hz), 1.88 - 1.73 (m, 6 H), 1.60 - 1.40 (m, 16 H), 1.42 - 1.31 (m, 18 H), 0.98 - 0.85 (m, 24 H).

^{13} C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.72, 162.18, 150.74, 150.38, 150.18, 149.31, 146.47, 143.69, 141.38, 141.32, 140.72, 139.18, 137.45, 135.69, 135.37, 133.93, 133.88, 133.27, 133.24, 133.12, 131.60, 131.51, 131.45, 131.42, 130.44, 129.51, 129.16, 128.54, 127.23, 126.18, 125.31, 123.52, 123.43, 123.40, 123.10, 122.51, 121.82, 120.69, 118.09, 115.06, 113.89, 113.34, 113.28, 112.54, 72.16, 71.94, 69.59, 69.22, 47.76, 47.03, 44.73, 44.68, 39.75, 39.66, 38.11, 31.76, 31.72, 30.81, 30.77, 30.67, 29.42, 29.33, 29.29, 29.24, 28.78, 28.76, 25.86, 25.81, 24.08, 23.99, 23.18, 22.76, 22.74, 15.04, 14.25, 14.21, 14.17, 13.61, 12.96, 11.40, 11.32, 10.73, 10.71.

HRMS (ESI): m/z calcd for $C_{90}H_{105}BCl_4F_2N_7O_8^+$ $[M+H]^+$: 1600.6834; Found: 1600.6750.

Synthesis of dyad 2

The compound **11** (55 mg, 0.0465 mmol) and PDI **2** (43.8 mg, 0.0465 mmol) were dissolved in THF (25 mL) and the mixture was purged with nitrogen, subsequently, sodium ascorbate (8.7 mg, 0.0437 mmol) and copper sulphate (5.6 mg, 0.0223 mmol) dissolved in water were added to this mixture. Then reaction mixture was stirred for 3 days at 50 °C temperature. After 3 days, THF was evaporated under reduced pressure and reaction mixture was extracted with DCM, the organic layer was dried over sodium sulphate and solvent was removed under reduced pressure. The crude product was purified by column chromatography DCM/EA (4/1) as eluent and a dark green solid compound was obtained.

Yield: 43 mg (44 %).

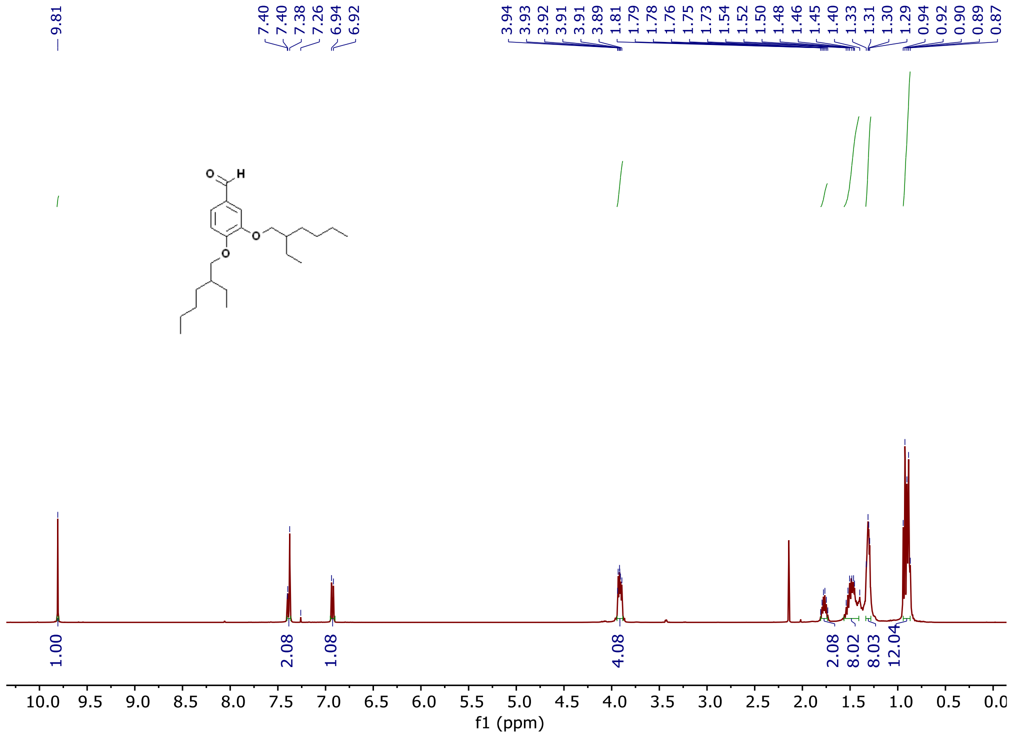
^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm): 8.10 (s, 2 H), 8.04 (s, 2 H), 7.57 - 7.53 (m, 2 H), 7.46 (d, *J* = 16 Hz, 1 H), 7.31 - 7.26 (m, 3 H), 7.22 (t, *J* = 8 Hz, 5 H), 7.15 - 7.11 (m, 3 H), 7.08 (t, *J* = 8 Hz, 2 H), 6.97 - 6.93 (m, 6 H), 6.92 - 6.89 (m, 6 H), 6.85 (s, 1 H), 6.82 - 6.76 (m, 2 H), 6.70 - 6.68 (m, 2 H), 4.74 (t, *J* = 8 Hz, 2 H), 4.62 - 4.57 (m, 2 H), 4.07 - 3.98 (m, 6 H), 3.92 - 3.88 (m, 6 H), 3.85 - 3.80 (m, 2 H), 2.04 (s, 1 H), 1.85 - 1.80 (m, 54 H), 1.75 - 1.67 (m, 6 H), 1.57 - 1.47 (m, 16 H), 1.37 - 1.25 (m, 38 H), 0.97 - 0.82 (m, 30 H).

^{13} C NMR (100 MHz, CD_2Cl_2) δ (ppm): 163.40, 163.03, 156.04, 155.72, 155.45, 150.87, 150.32, 150.17, 149.31, 149.12, 143.39, 141.15, 141.01, 139.36, 137.31, 133.03, 132.81, 132.57, 130.18, 129.94, 129.49, 127.2, 124.58, 124.01, 123.01, 121.92, 121.41, 121.08, 120.82, 120.66, 120.16, 120.11, 119.88, 119.74, 119.57, 118.08, 113.75, 113.31, 113.18, 112.90, 112.54, 71.72, 71.70, 69.51, 69.24, 69.12, 69.01, 50.06, 47.89, 40.01, 39.75, 39.63, 37.98, 31.71, 31.67, 31.65, 30.74, 30.68, 30.59, 29.44, 29.39, 29.29, 29.23, 29.15, 29.12, 28.74, 25.82, 25.76, 25.74, 24.03, 23.99, 23.91, 23.12, 23.11, 23.06, 22.69, 22.65, 14.63, 13.94, 13.90, 13.86, 13.84, 12.42, 11.10, 11.01, 10.42.

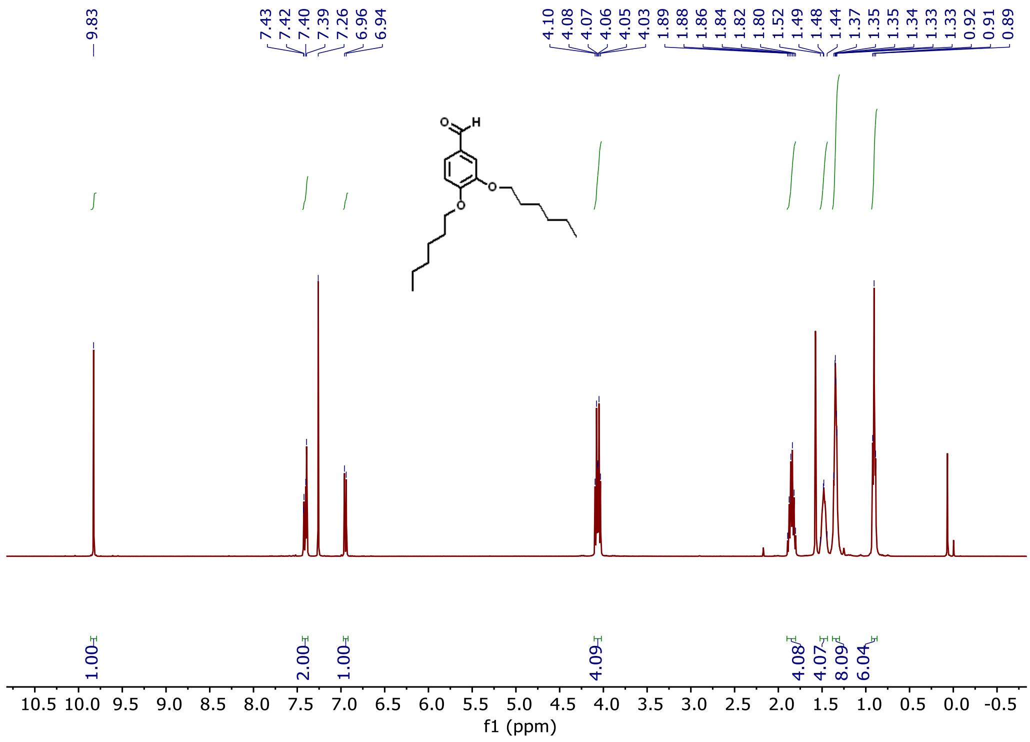
HRMS (ESI): m/z calcd for $C_{133}H_{153}BF_2N_7O_{14}^+$ $[M+H]^+$: 2121.1531; Found: 2121.1577.

3. NMR spectra

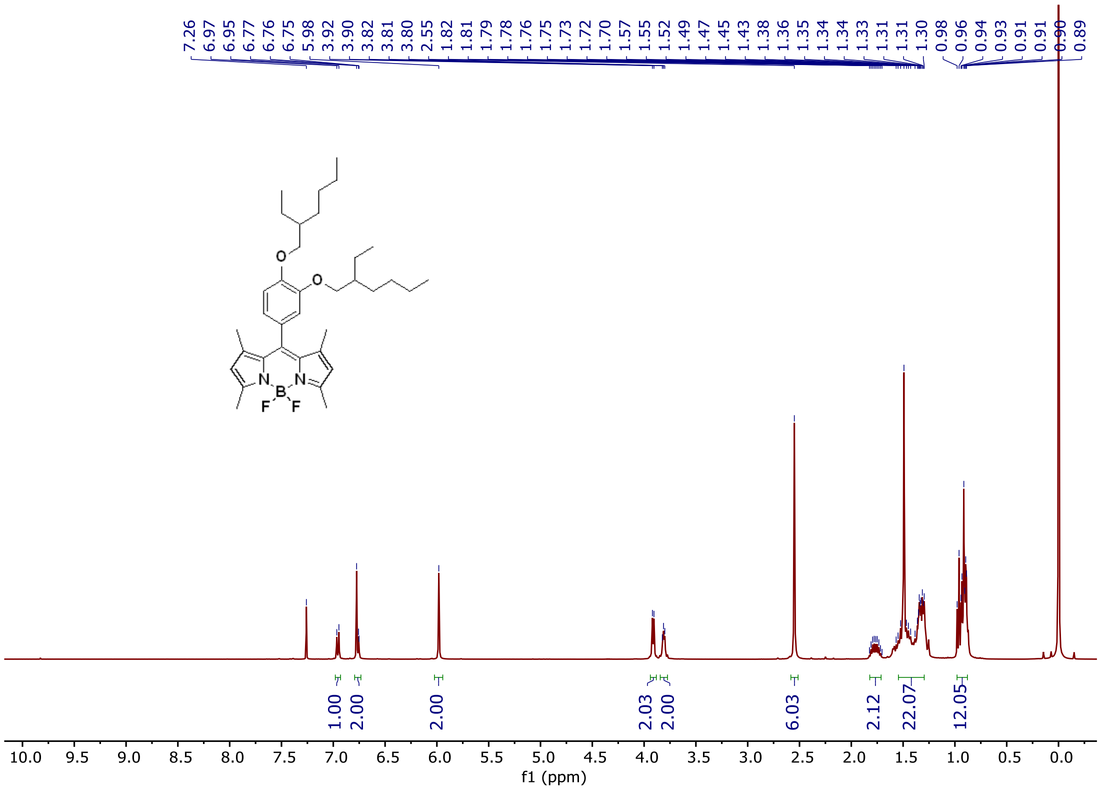
[1]H NMR spectra



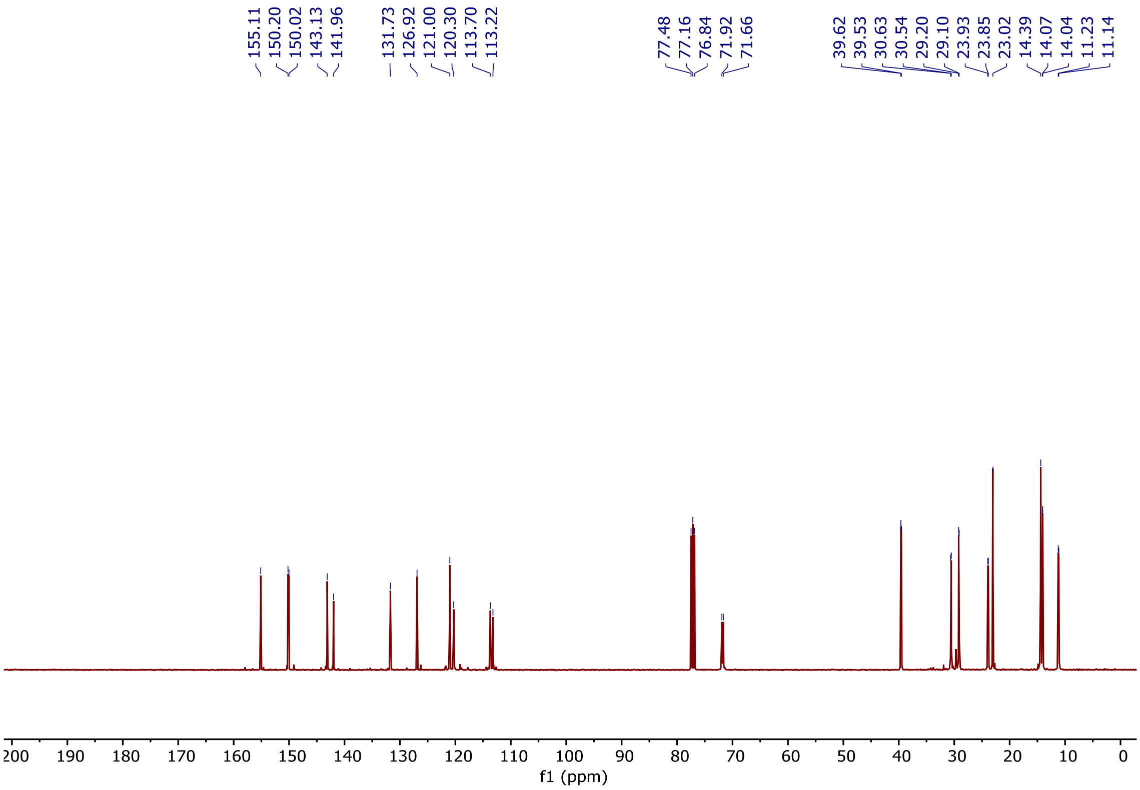
[1]H NMR spectra of compound **1** $CDCl_3$.



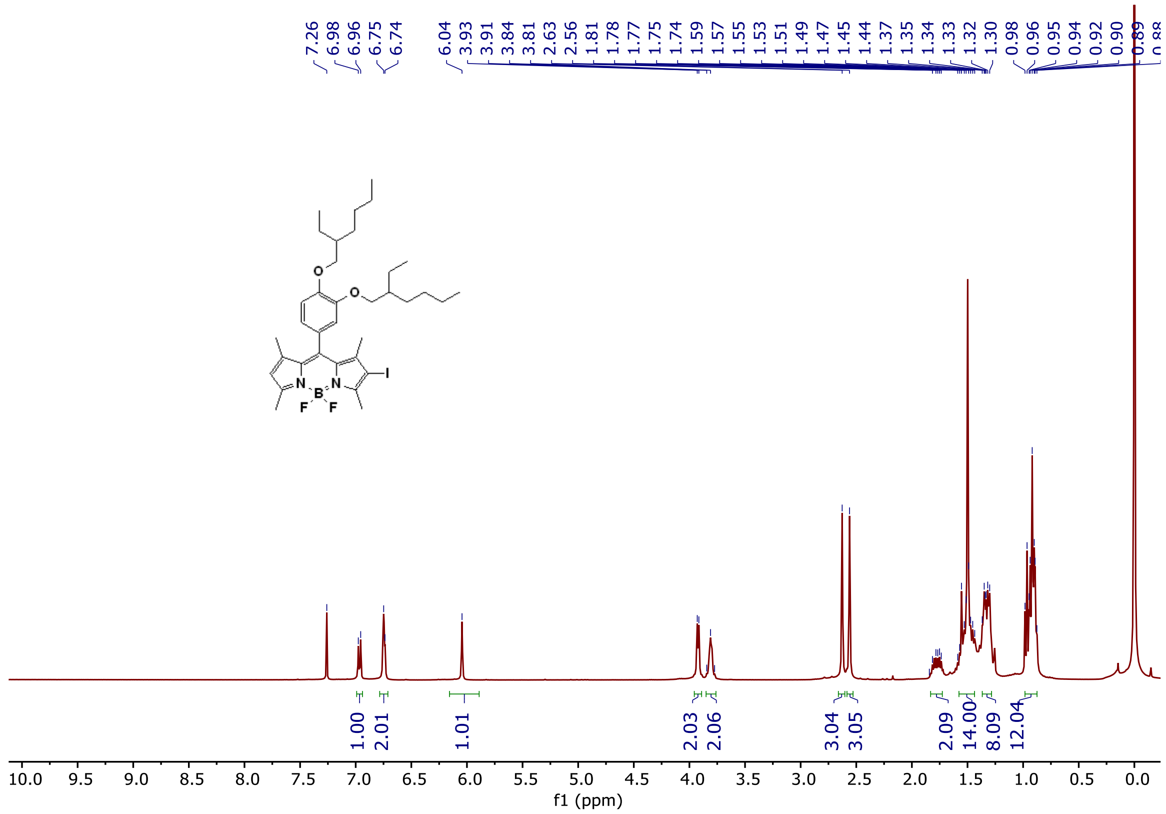
[1]H NMR spectra of compound **2** $CDCl_3$.



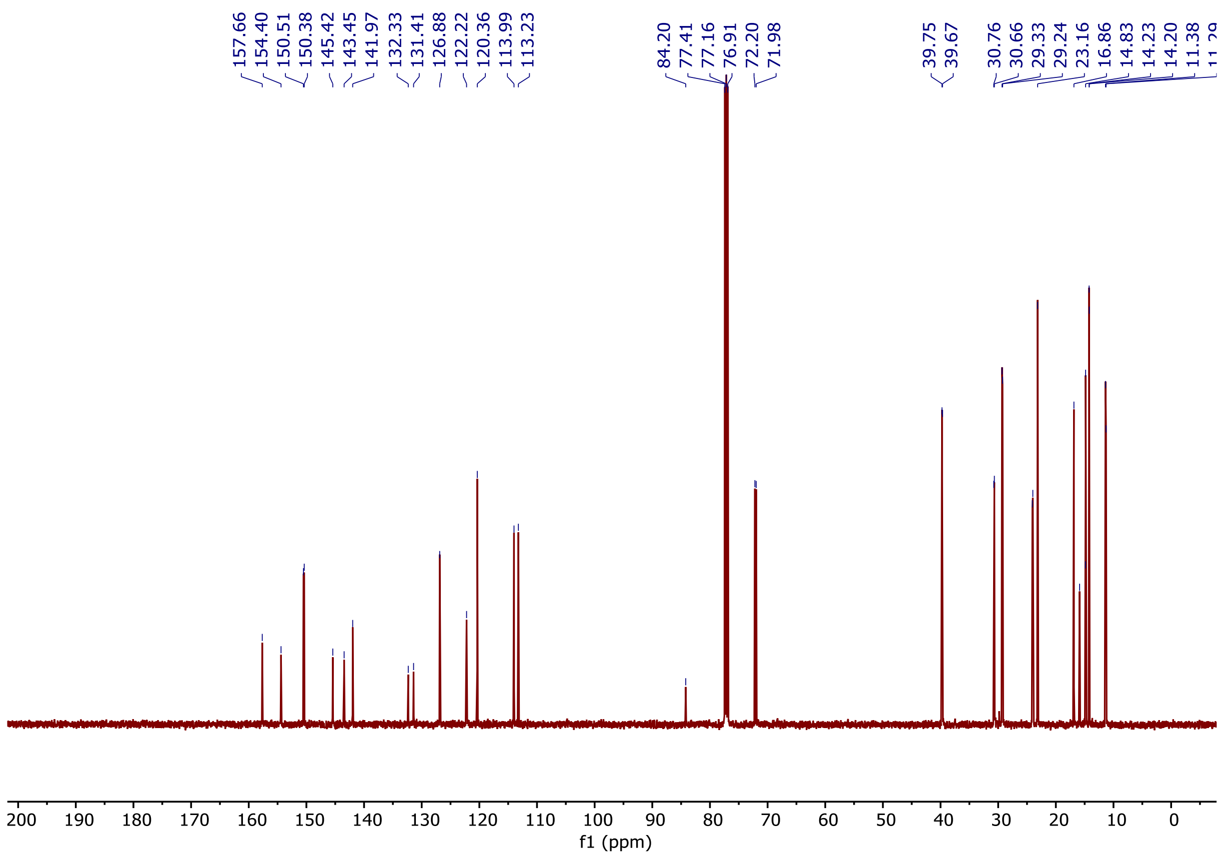
[1]H NMR spectra of compound **3** in $CDCl_3$.



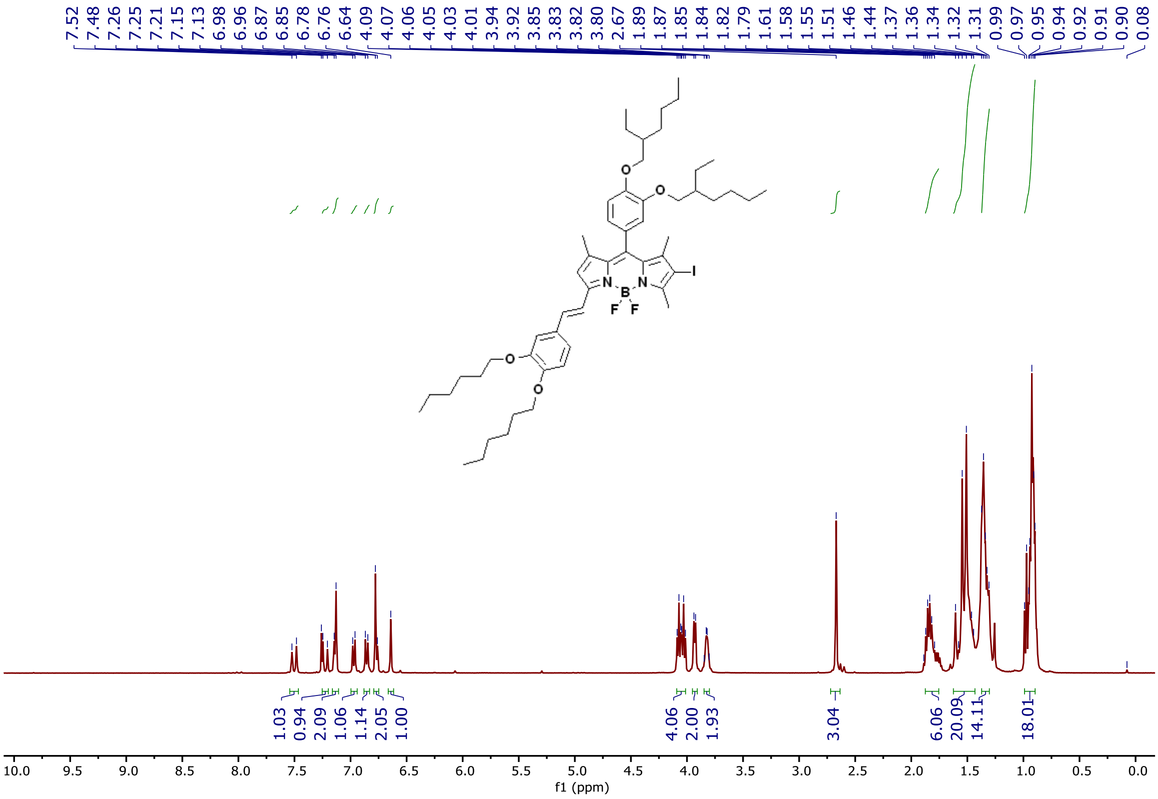
[13]C NMR spectra of compound **3** in $CDCl_3$.



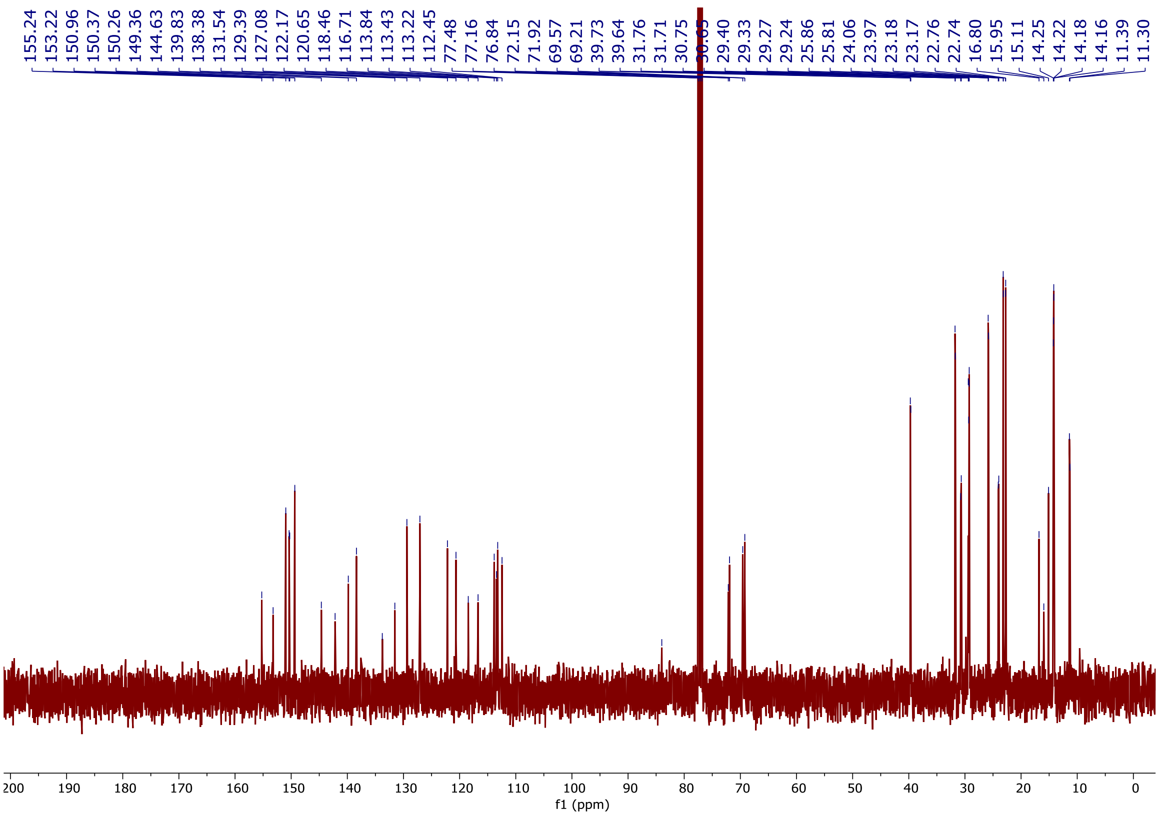
[1]H NMR spectra of compound **4** in $CDCl_3$.



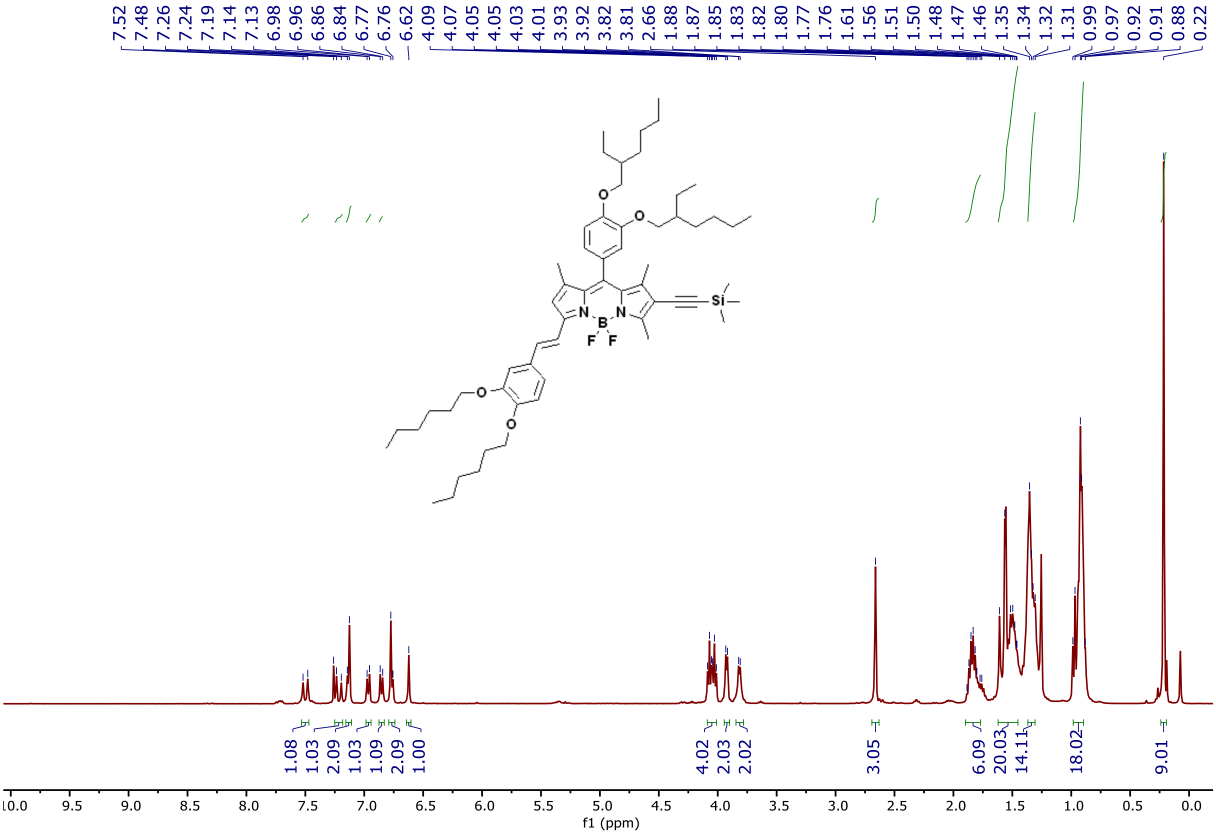
[13]C NMR spectra of compound **4** in $CDCl_3$.



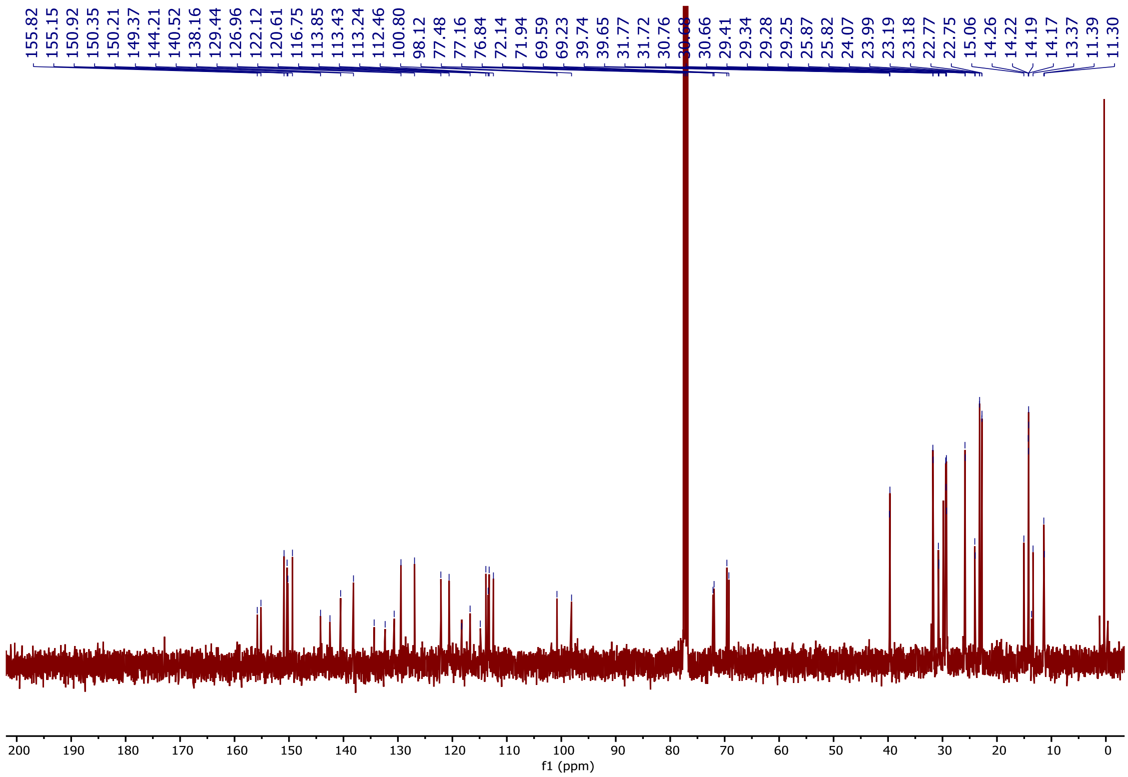
^{1}H NMR spectra of compound **5** in $CDCl_3$.



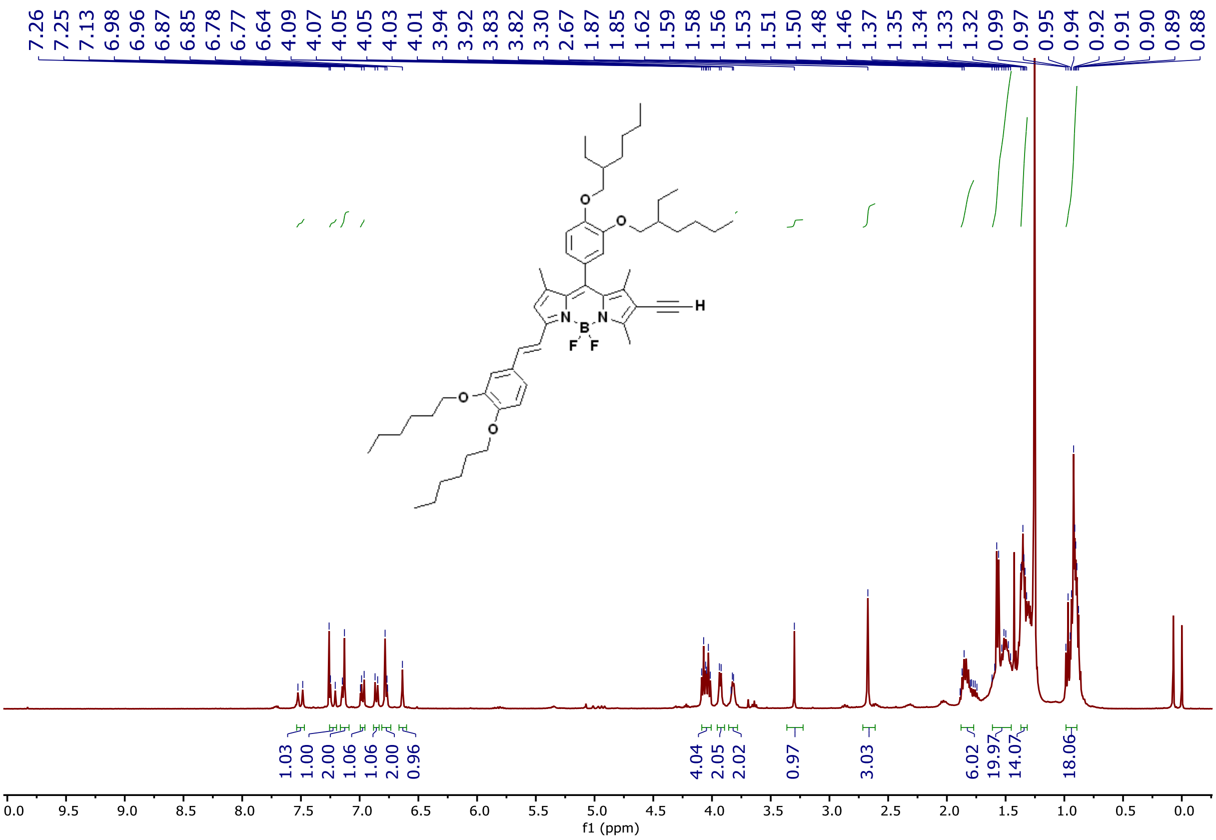
^{13}C NMR spectra of compound **5** in $CDCl_3$.



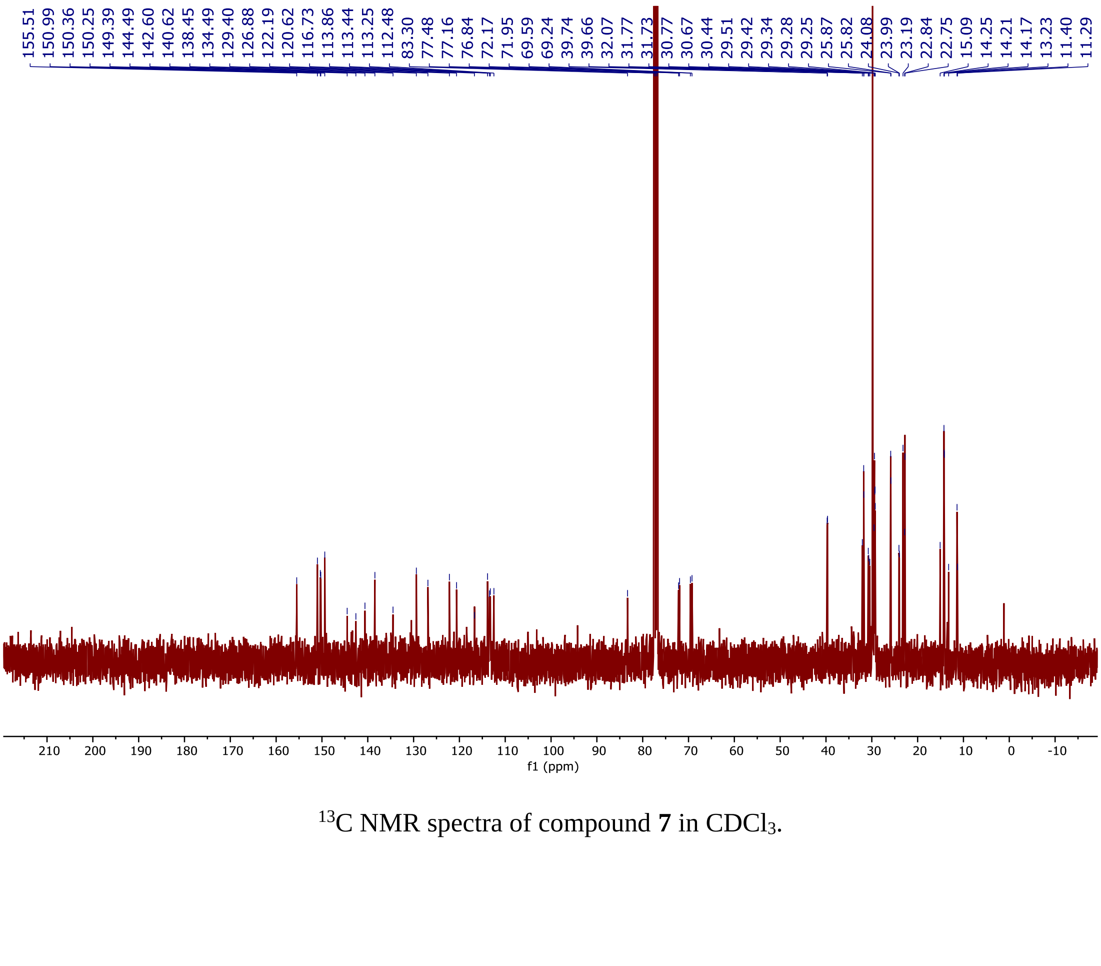
[1]H NMR spectra of compound **6** in $CDCl_3$.



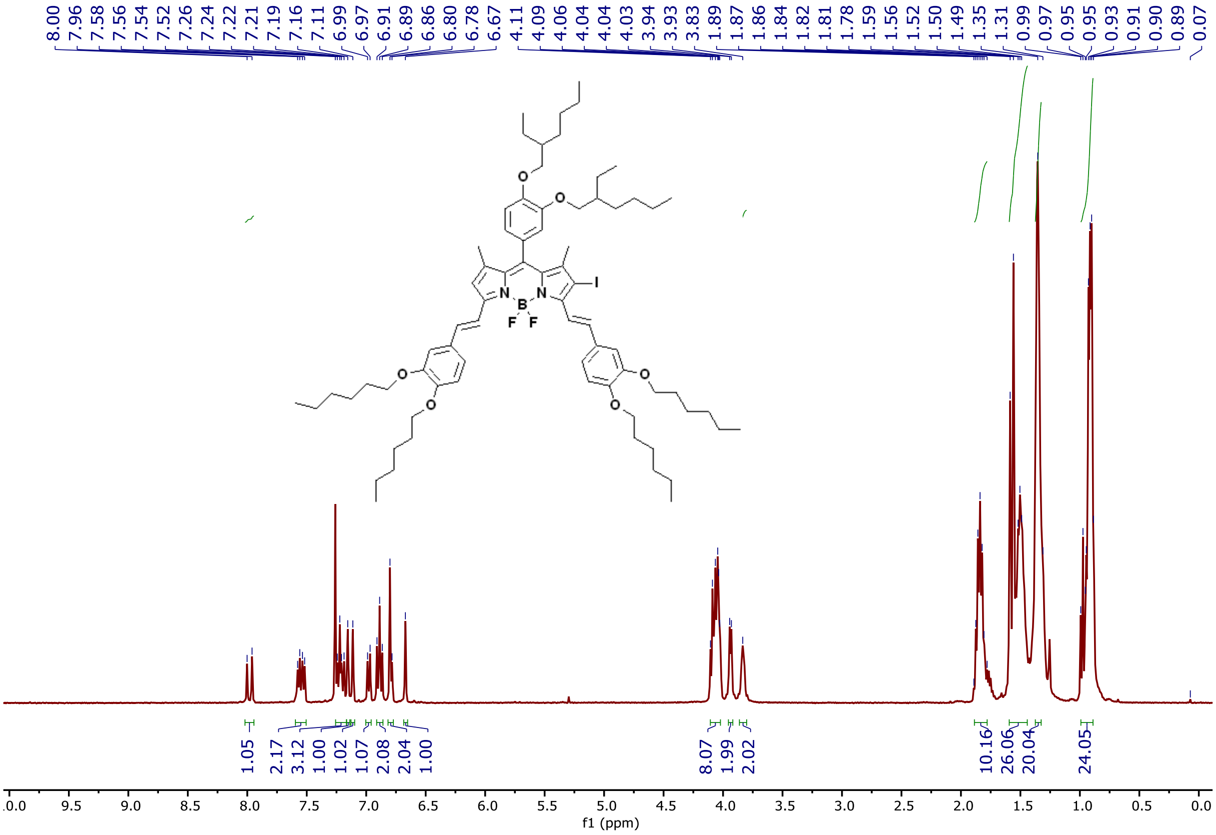
[13]C NMR spectra of compound **6** in $CDCl_3$.



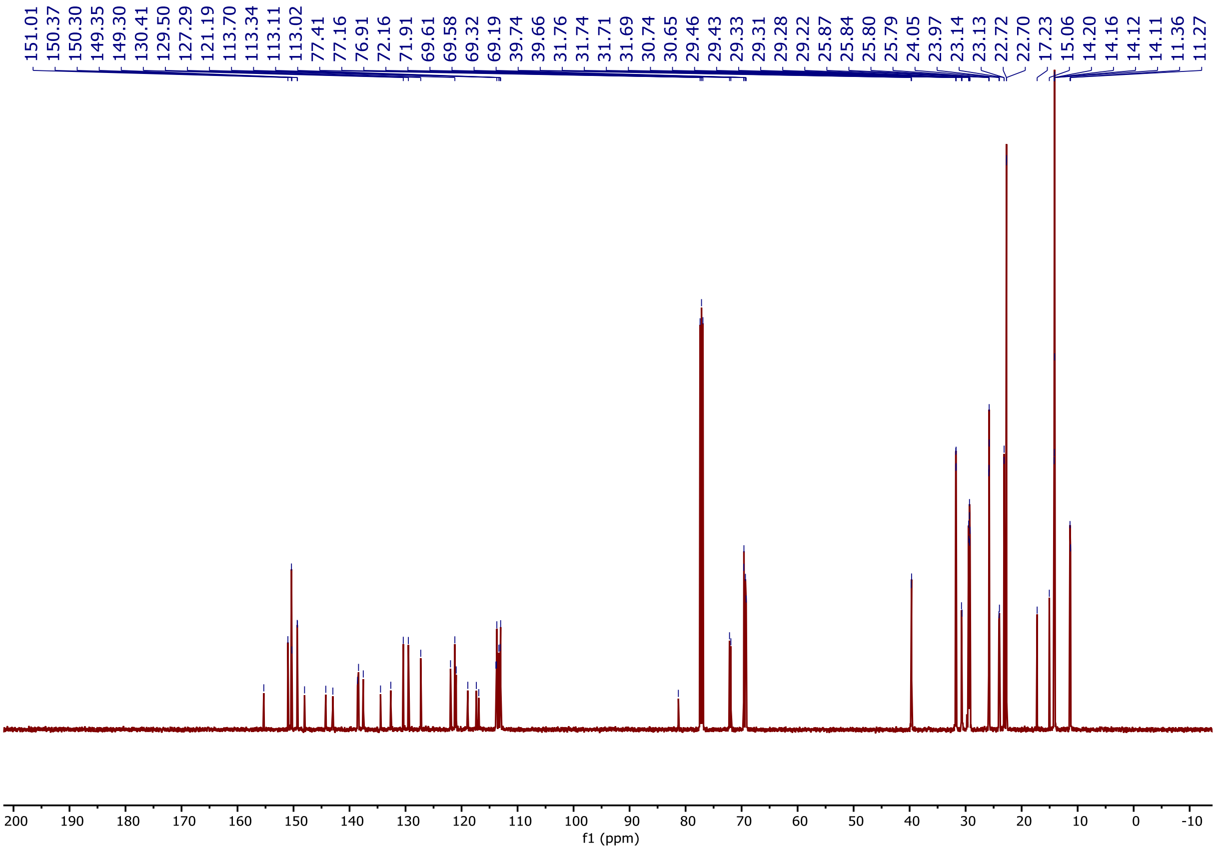
[1]H NMR spectra of compound **7** in $CDCl_3$.



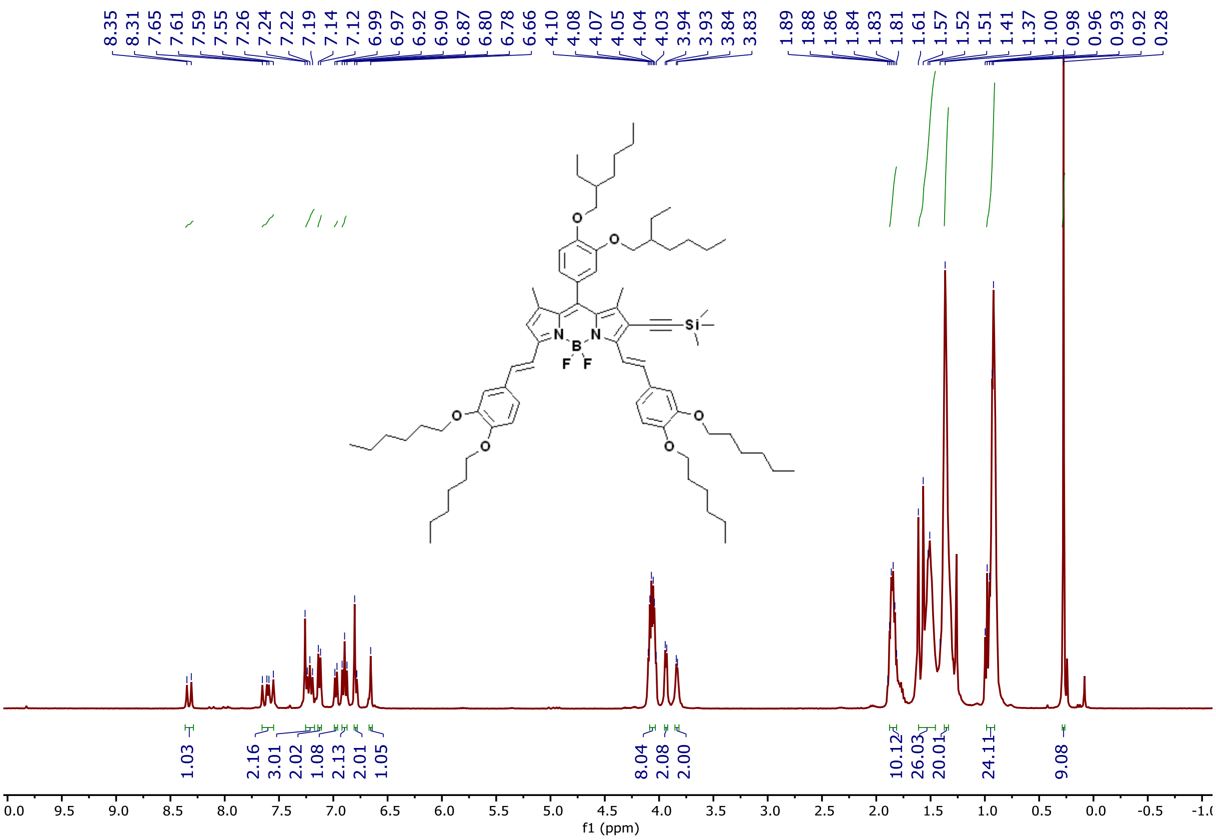
[13]C NMR spectra of compound **7** in $CDCl_3$.



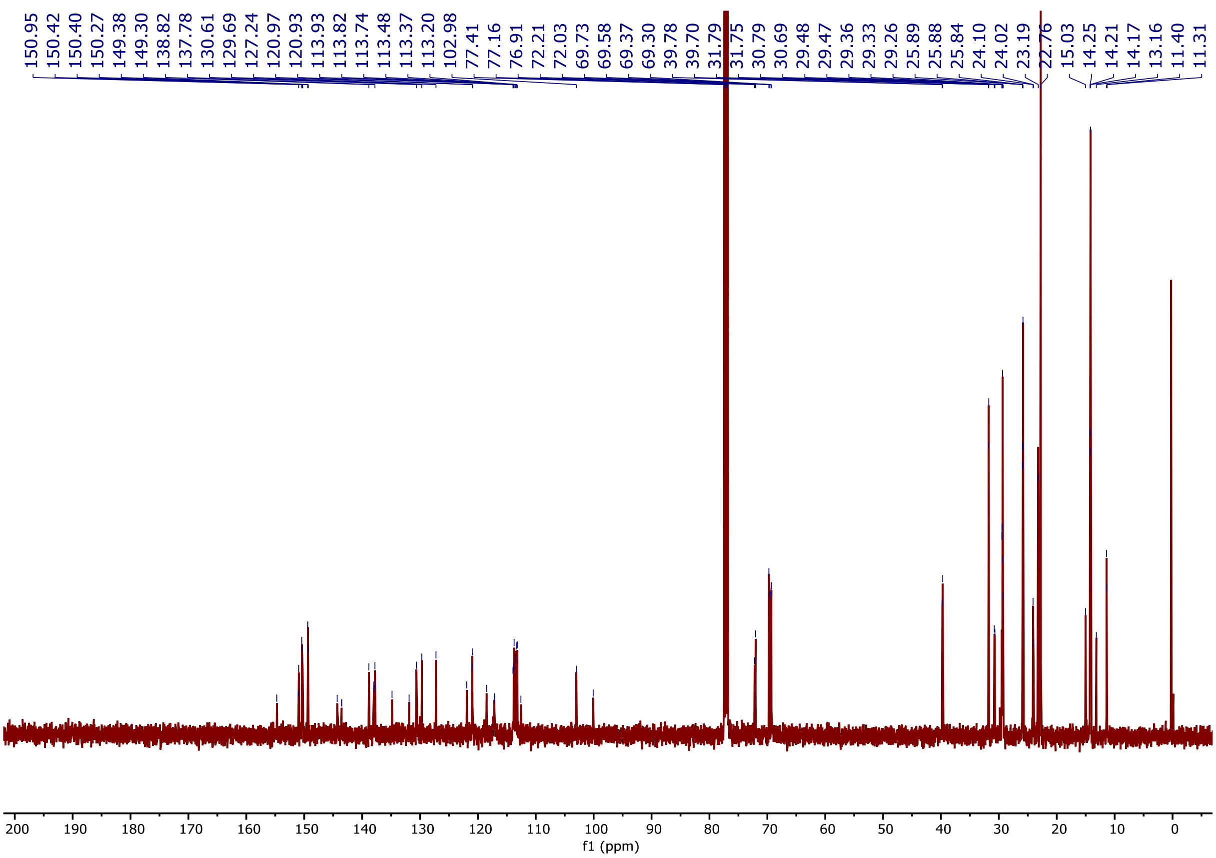
^{1}H NMR spectra of compound **8** in $CDCl_3$.



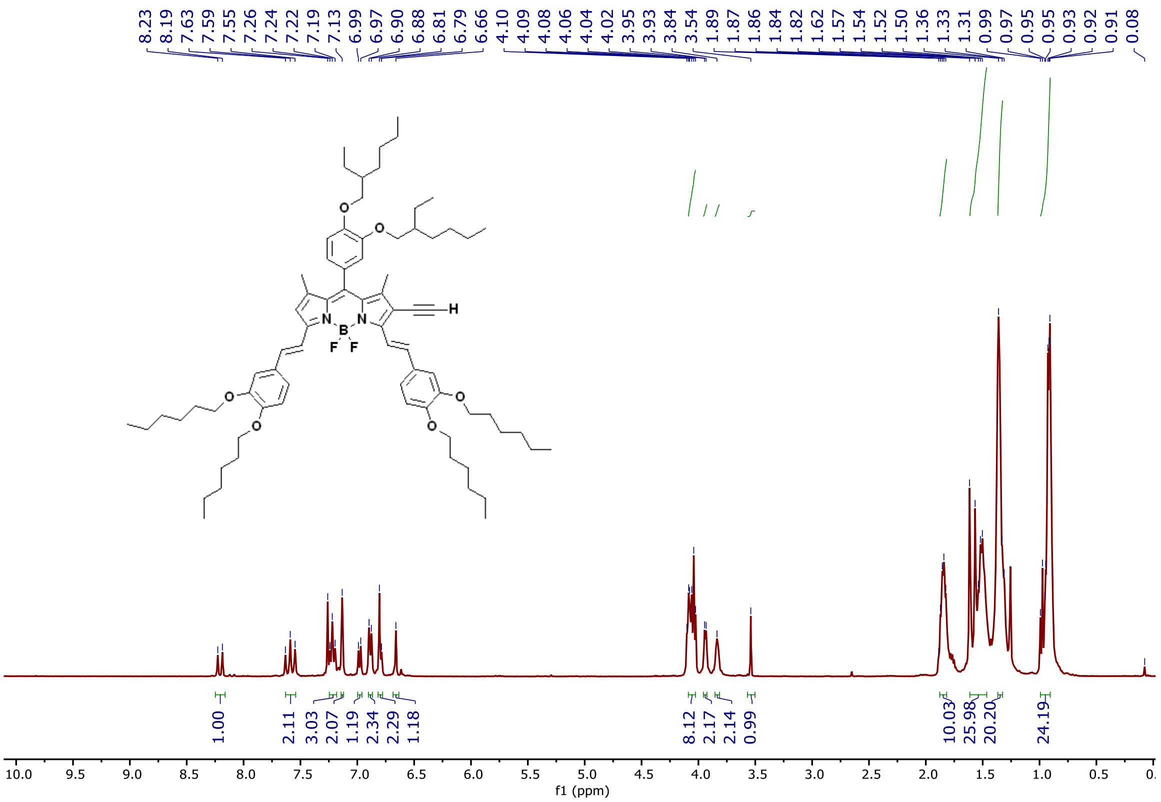
^{13}C NMR spectra of compound **8** in $CDCl_3$.



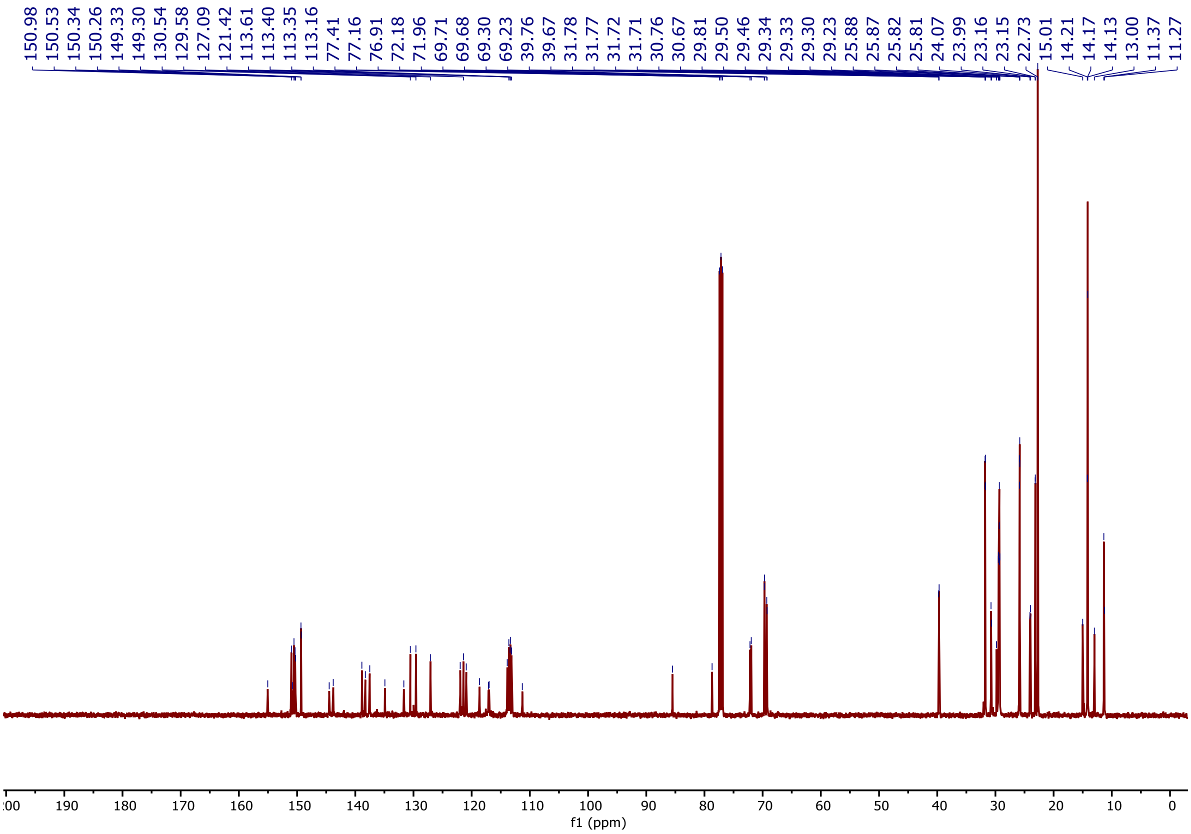
[1]H NMR spectra of compound **9** in $CDCl_3$.



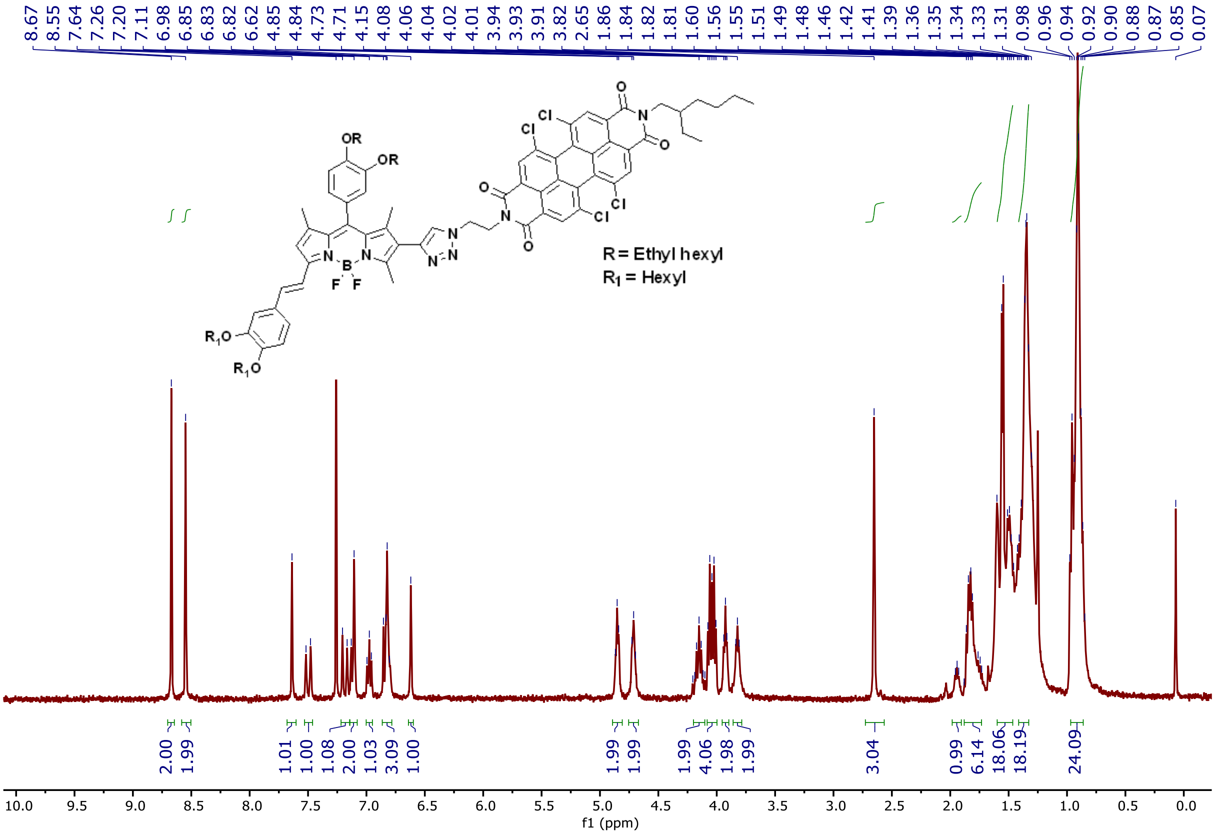
[13]C NMR spectra of compound **9** in $CDCl_3$.



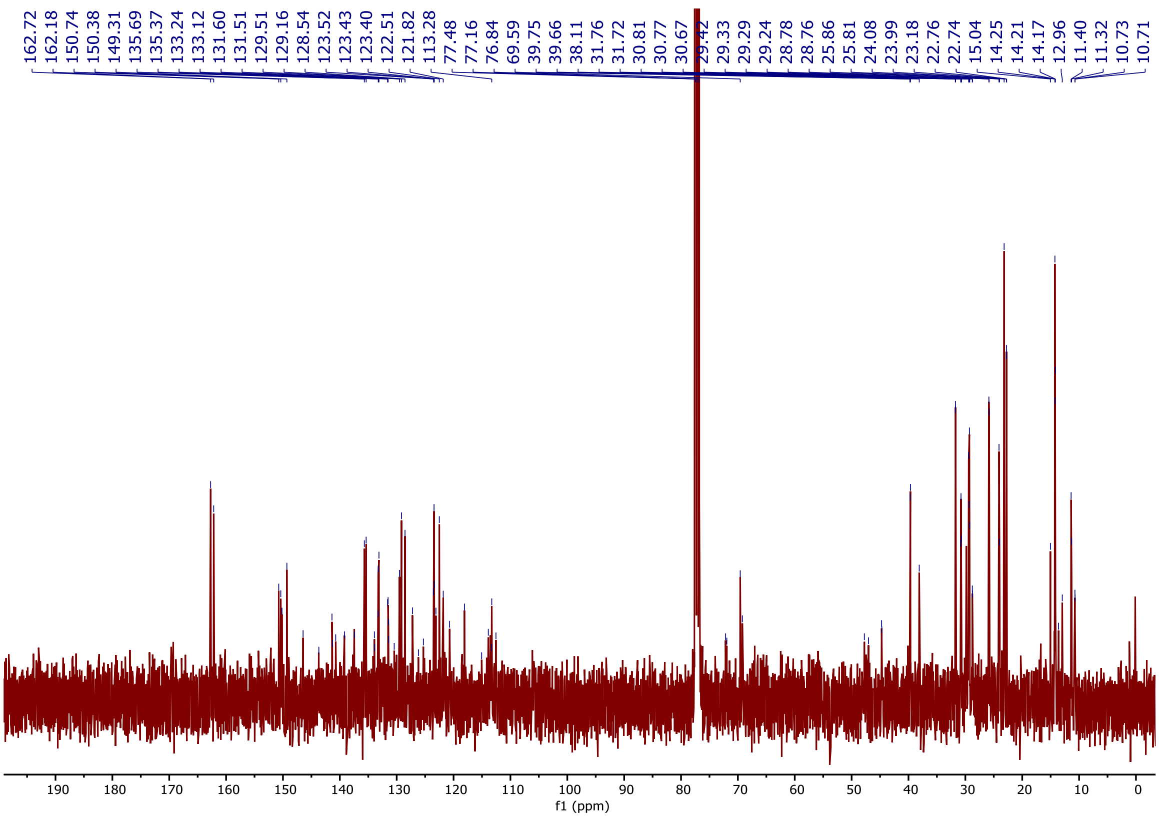
[1]H NMR spectra of compound **10** in $CDCl_3$.



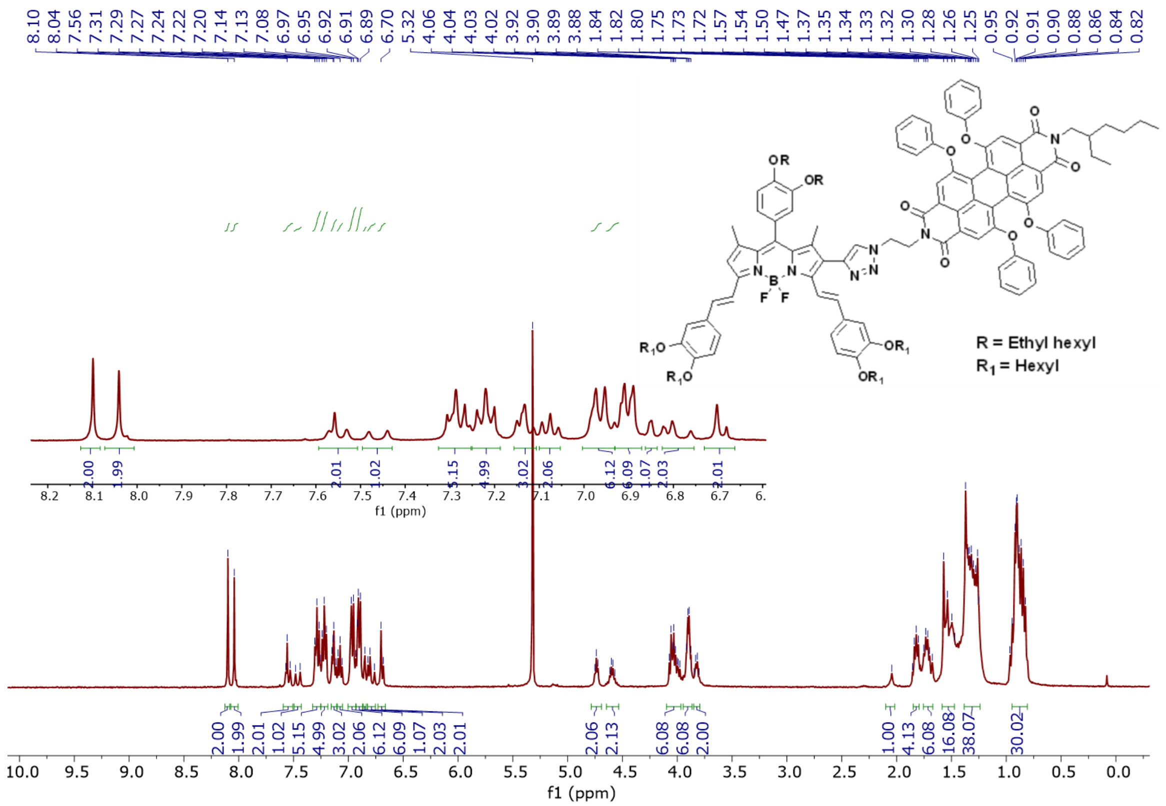
[13]C NMR spectra of compound **10** in $CDCl_3$.



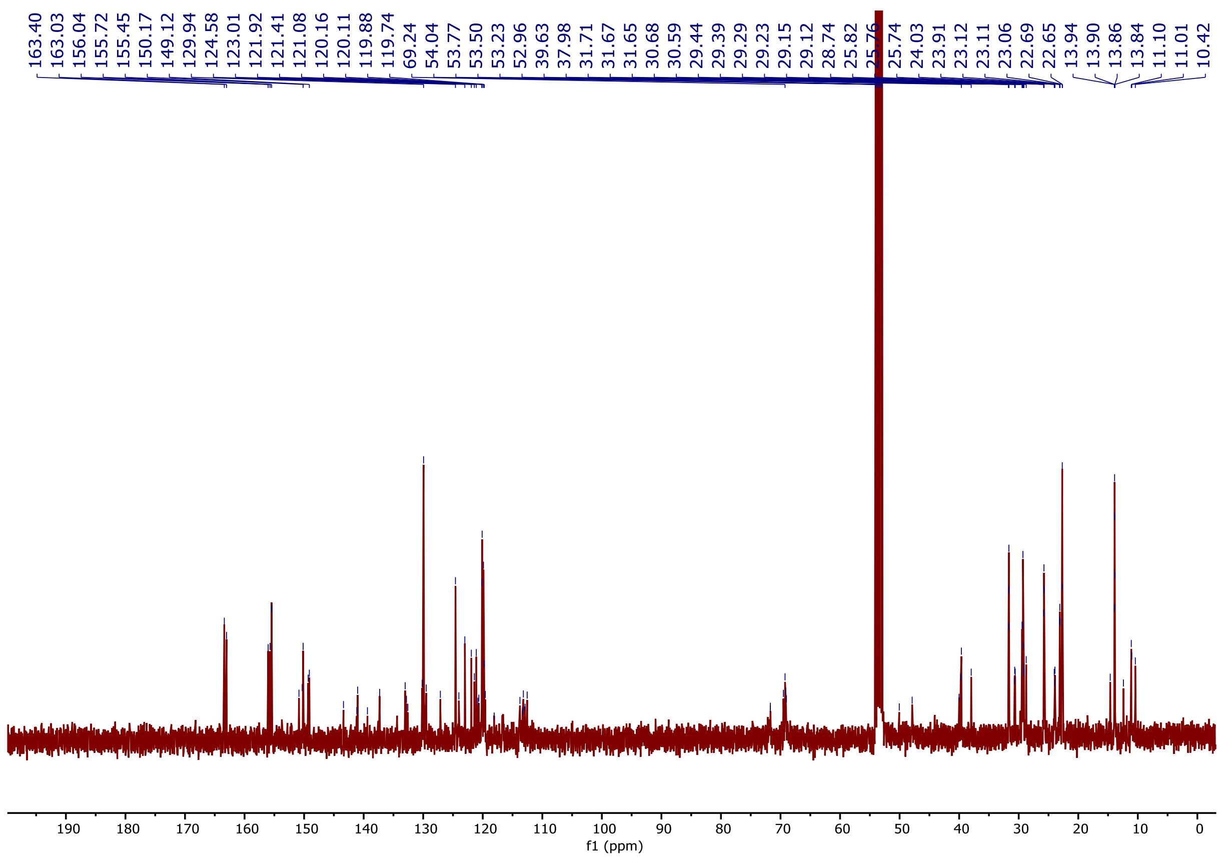
[1]H NMR spectra of dyad **1** in $CDCl_3$.



[13]C NMR spectra of dyad **1** in $CDCl_3$.



^{1}H NMR spectra of dyad **2** in CD_2Cl_2.



^{13}C NMR spectra of dyad **2** in CD_2Cl_2.

4. Photophysical study

4.1. Steady-state fluorescence experiment

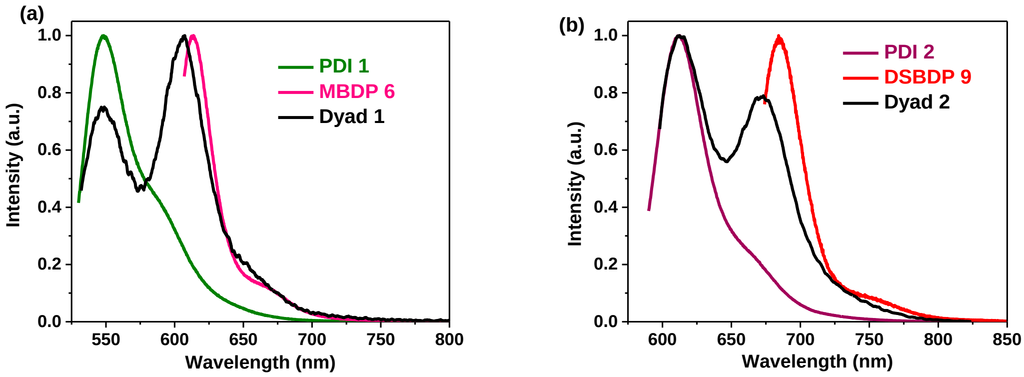


Figure S1. Normalized fluorescence spectra of (a) PDI **1** (λ_{ex} = 520 nm), MSBDP **6** (λ_{ex} = 597 nm), dyad **1** (λ_{ex} = 524 nm) and (b) PDI **2** (λ_{ex} = 580 nm), DSBDP **9** (λ_{ex} = 663 nm) and dyad **2** (λ_{ex} = 588 nm) in chloroform ($CHCl_3$) (c ~ 2×10^{-6} M).

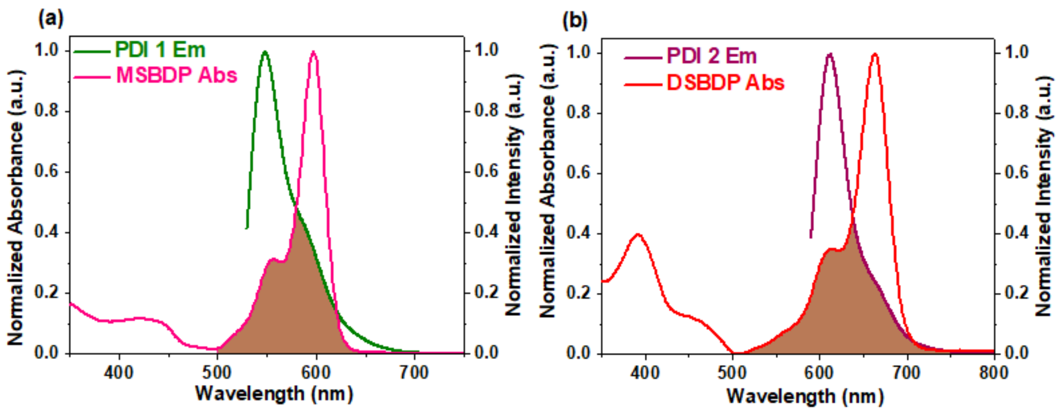


Figure S2. Overlap of UV/Vis absorption and fluorescence spectra of (a) MSBDP **6** and PDI **1** and (b) DSBDP **9** and PDI **2** in $CHCl_3$ (c ~ 10^{-6} M).

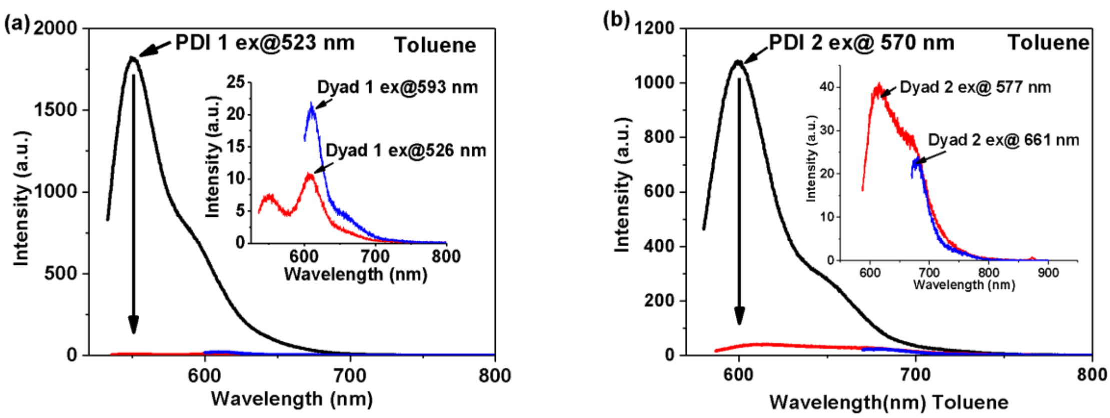


Figure S3. Fluorescence spectra of (a) PDI **1**, **6** and dyad **1** and (b) PDI **2**, **9** and dyad **2** in toluene (c ~ 2×10^{-6} M).

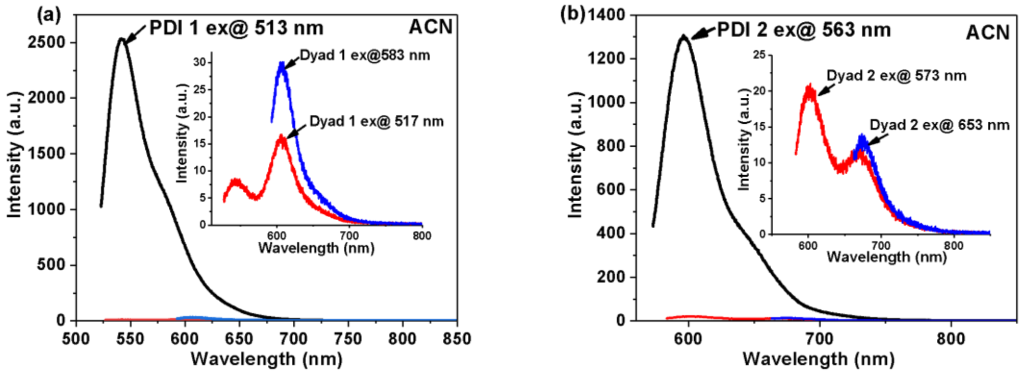


Figure S4. Fluorescence spectra of (a) PDI **1**, **6** and dyad **1** and (b) PDI **2**, **9** and dyad **2** in acetonitrile (ACN) (c ~ 2×10^{-6} M).

4.2. Solvatochromism study

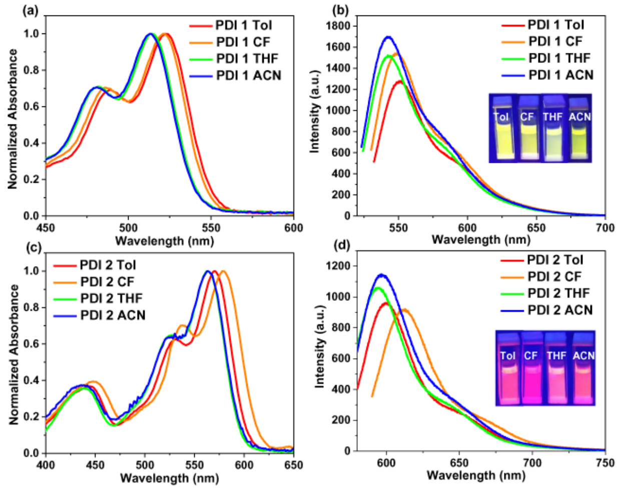


Figure S5. Solvatochromism study of PDI **1** and PDI **2** (c ~ 2×10^{-6} M). Tol (Toluene), CF (Chloroform), THF (Tetrahydrofuran), ACN (Acetonitrile) (Inset show images of compounds under UV light; λ_{ex} = 365 nm).

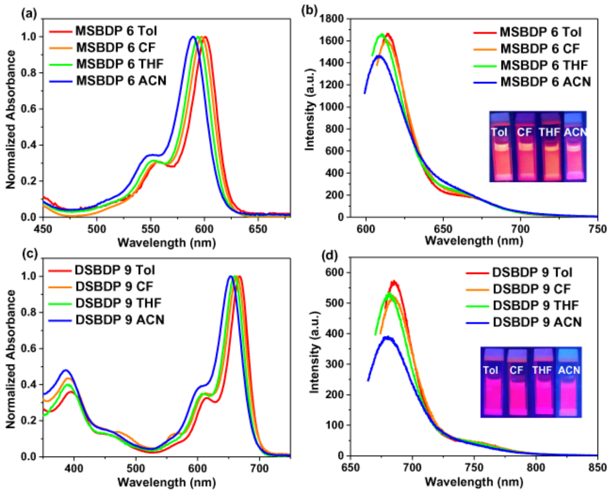


Figure S6. Solvatochromism study of MSBDP **6** and DSBDP **9** (c ~ 2×10^{-6} M) (Inset show images of compounds under UV light; λ_{ex} = 365 nm).

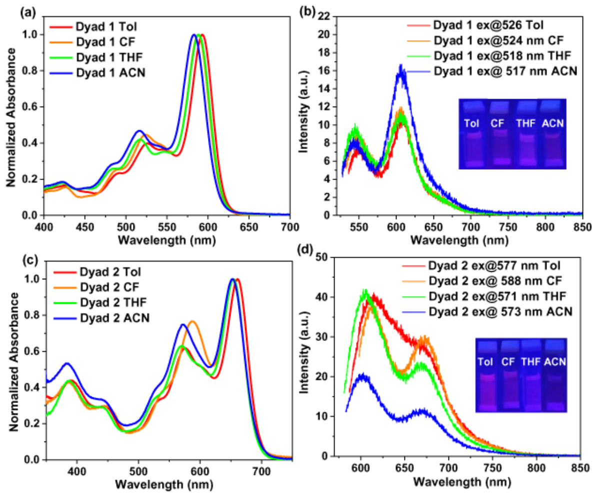


Figure S7. Solvatochromism study of dyads **1** and **2** ($c \sim 2\times10^{-6}$ M) (Inset show images of compounds under UV light; λ_{ex} = 365 nm).

Solvatochromism investigation of dyads **1** and **2** along with reference compounds PDI **1**, PDI **2**, MSBDP **6** and DSBDP **9** were carried out in four different solvents i.e., toluene, $CHCl_3$, THF and ACN, the absorption and emission maxima are reported in Table S1. For reference compounds PDI **1**, PDI **2**, MSBDP **6** and DSBDP **9**, weak negative solvatochromism was observed with increase in solvent polarity from toluene to acetonitrile (Figure S5, S6). Likewise, for dyads **1** and **2**, very little changes were observed in UV/Vis absorption spectrum in different polarity solvents which indicates that regardless of whether electronic interactions are available among PDI and STBDP, they are exceptionally feeble in the ground state (Figure S7). Moreover, in the fluorescence spectra for dyad **1**, similar fluorescence intensities were observed in toluene, chloroform and THF, however in acetonitrile intensity was comparatively high and for dyad **2**, almost similar fluorescence intensities were observed in toluene, chloroform and THF, but in acetonitrile, fluorescence intensity was quenched compared to other solvents.

Table S1. Absorption and emission maxima of dyads **1** and **2** and corresponding reference compounds in different solvents.

Compound	Toluene		$CHCl_3$		THF		ACN	
	λ_{abs} (nm)	λ_{em} (nm)	λ_{abs}(nm)	λ_{em} (nm)	λ_{abs} (nm)	λ_{em} (nm)	λ_{abs}(nm)	λ_{em} (nm)
PDI 1	522	551	520	550	514	543	513	543

PDI 2	570	600	580	612	564	595	563	597
MSBDP 6	601	614	597	613	594	610	590	608
DSBDP 9	668	685	663	683	659	680	654	680
Dyad 1	526, 593	552, 610(λ_{exc} = 526 nm) 611 (λ_{exc} =593 nm)	524, 588	550, 607 (λ_{exc} =524 nm) 607 (λ_{exc} =588)	517, 588	548, 607 (λ_{exc} =517 nm) 608(λ_{exc} =588)	516, 583	542, 607 (λ_{exc} = 516 nm) 607(λ_{exc} =583)
Dyad 2	576, 661	615, 673(λ_{exc} = 576nm) 678(λ_{exc} =661)	588, 654	613, 673 (λ_{exc}= 588 nm) 676(λ_{exc} =654)	571, 654	606, 672 (λ_{exc}=571 nm) 678(λ_{exc} =654)	573,653	603, 668(λ_{exc}= 573 nm) 678(λ_{exc}= 653)

4.3.Concentration dependent study in different solvents

The concentration dependent UV/Vis absorption spectra of dyads **1** and **2** as well as reference compounds were performed in three different solvents as for solvatochromism study except acetonitrile (ACN) because in ACN compounds were dissolved partially (Figure S8-S10). The concentration dependent spectra of $c \sim 10^{-4}$ M samples were recorded with 1 mm path length cuvette while the other samples are recorded with 1 cm path length cuvette.

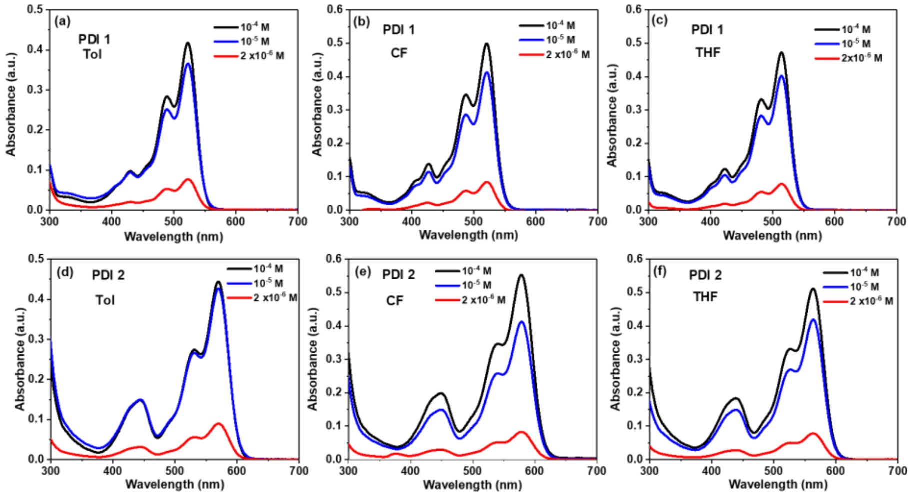


Figure S8. Concentration dependent study of study of PDI **1** and PDI **2**.

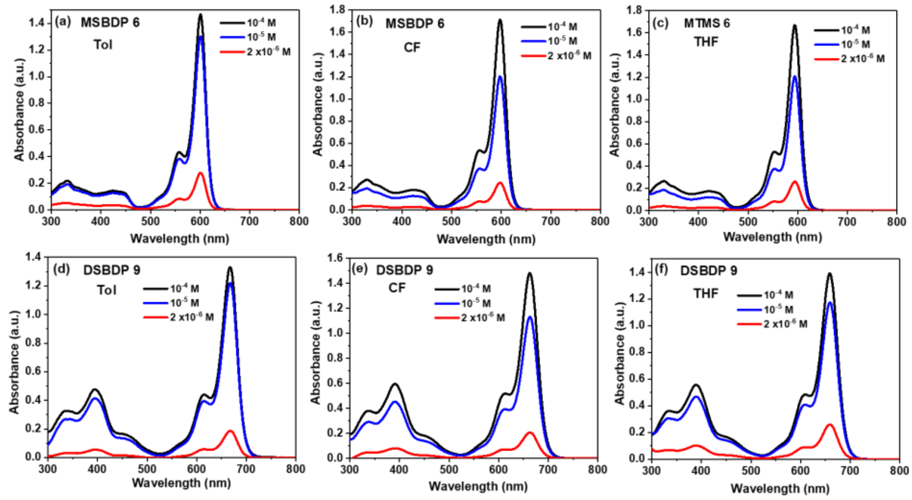


Figure S9. Concentration dependent study of study of MSBDP **6** and DSBDP **9**.

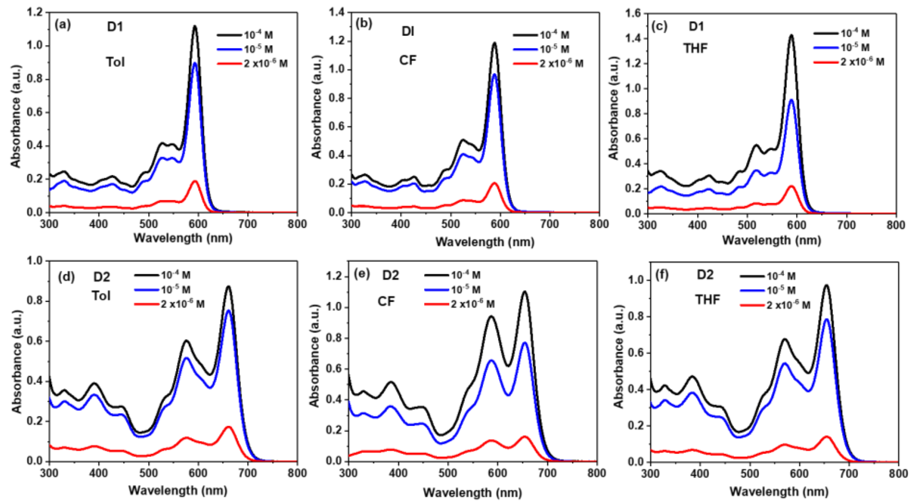


Figure S10. Concentration dependent study of study of dyad **1** and dyad **2**.

From these experiments, we didn't observe broadening in spectral features up to ~10^{-4} M concentration which indicates that there is no formation of aggregation.

4.4. Fluorescence spectra of MSBDP and DSBDP at 530 nm

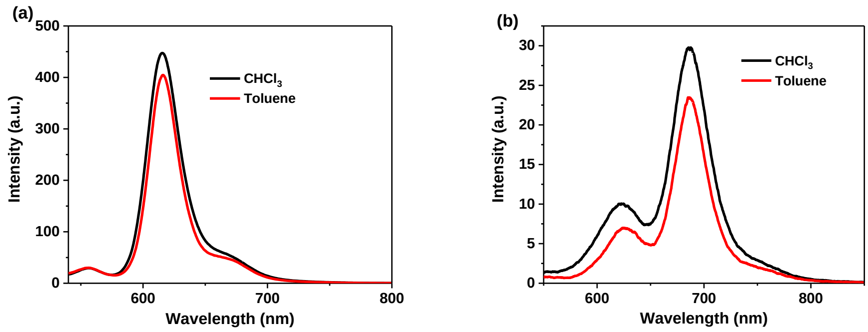


Figure S11. Fluorescence spectra of (a) MSBDP **6** and (b) DSBDP **9** in $CHCl_3$ and Toluene (*c* ~ 10^{-6} M) (λ_{exc} = 530 nm).

4.5.Fluorescence quantum yield

Table S2. Relative quantum yields of PDI **1**, PDI **2**, dyads **1** and **2** by using relative method in $CHCl_3$.

Compound	**Absorbance**			**Integrated fluorescence intensity**			**Quantum Yield** $\Phi = \Phi_R(I / I_R)(A_R / A)(\lambda_{ex.R} / \lambda_{ex})(n^2 / n_R^2)$		**ETE = 1- Φ_D/Φ_{DA}**
	1	2	3	1	2	3	ϕ_i	ϕ_{avg}	
PDI 1	0.0223	0.0317	0.0589	182.30	260.20	510.16	1.02 1.02 1.03	~ 1	
PDI 2	0.0258	0.0383	0.0542	92.92	135.52	175.30	0.80 0.83 0.78	~ 0.81	
Dyad 1	0.0165	0.0175	0.0260	1.970	2.107	2.867	0.015 0.015 0.013	~ 0.014	~99 %
Dyad 2	0.0180	0.0294	0.0401	6.179	9.816	13.413	0.075 0.077 0.080	~ 0.077	~90 %
Rhodamine 6G (ethanol)	0.0295	0.0474	0.0617	276.90	443.77	602.31		0.95 (reported)[S9]	

Lumogen® F Red 305 (in $CHCl_3$)	0.0315	0.0394	0.0454	135.19	160.11	178.19		0.96 (reported)[S10]	

4.6. Fluorescence lifetime

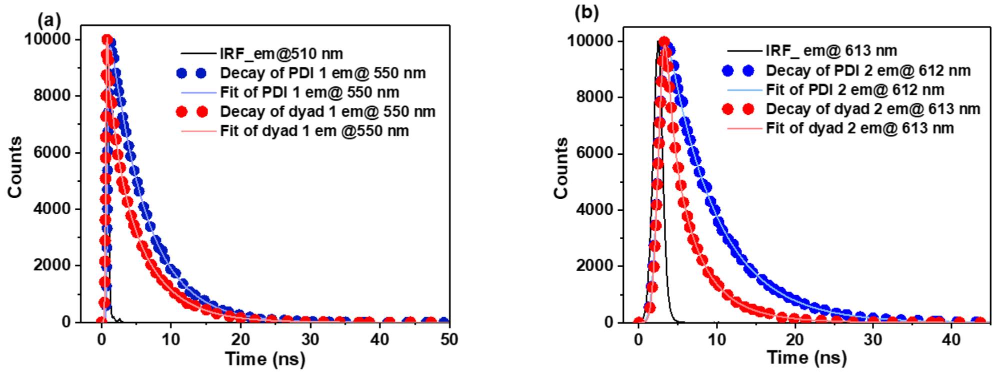


Figure S12. Fluorescence lifetime decay collected using TCSPC of (a) PDI **1**, dyad **1** at excitation wavelength of 510 nm in $CHCl_3$ and b) PDI **2**, dyad **2** at excitation wavelength of 590 nm in $CHCl_3$.

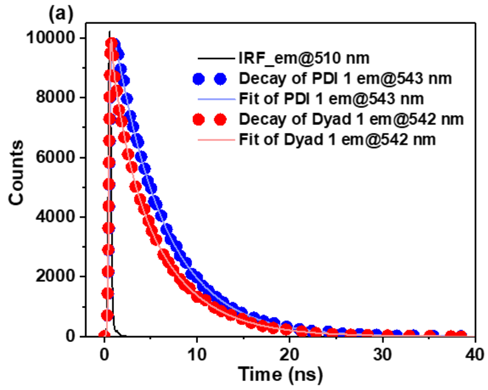


Figure S13. Fluorescence lifetime decay collected using TCSPC at different excitation wavelengths of (a) PDI **1**, dyad **1** at excitation wavelength of 510 nm in ACN.

Table S3. Fluorescence lifetime analysis of **PDI 1**, **PDI 2**, dyad **1** and dyad **2** at different excitation and emission wavelengths in toluene, $CHCl_3$ and ACN.

Compound	**Solvent**	**λ_{exc} (nm)**	**λ_{em} (nm)**	**$\tau_1(\alpha_1)$(ns)**	**$\tau_2(\alpha_2)$(ns)**	**$\tau_3(\alpha_3)$(ns)**	**τ_{avg}(ns)**	**χ^2**	**ETE = 1- τ_D/τ_{DA}**
PDI **1**	Toluene	510	551	5.25 (1.00)	-	-	5.25	1.01	
	$CHCl_3$	510	550	5.12 (1.00)	-	-	5.12	1.00	
	ACN	510	543	5.39 (1.00)	-	-	5.39	1.03	

PDI **2**	Toluene	560	600	6.41 (1.00)	-	-	6.41	1.16	
	$CHCl_3$	590	612	6.33 (1.00)	-	-	6.33	1.03	
	ACN	560	596	6.92 (1.00)	-	-	6.92	1.13	
Dyad **1**	Toluene	510	552	1.59 (0.11)	5.11 (0.31)	0.12 (0.57)	1.85	1.01	~65%
	$CHCl_3$	510	550	1.38 (0.09)	5.03 (0.26)	0.09 (0.65)	1.50	1.09	~70 %
	ACN	510	542	1.32 (0.10)	5.29 (0.36)	0.09 (0.55)	2.06	1.00	~62 %
Dyad **2**	Toluene	590	615	0.48 (0.41)	2.75 (0.41)	4.54 (0.17)	2.12	1.17	~67%
	$CHCl_3$	590	613	2.46 (0.25)	0.42 (0.56)	0.09 (0.55)	1.76	1.06	~62 %
	ACN	590	603	-	-	-	n.d.	-	-

5. Electrochemical studies and the free energy change calculations for photoinduced electron transfer

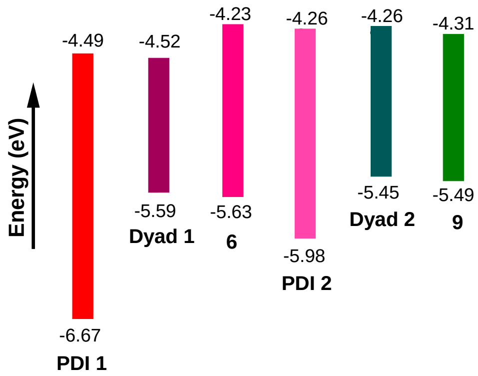


Figure S14. Alignment of frontier molecular orbital energy levels (in eV) obtained from CV measurements for PDI **1**, Dyad **1**, MSBDP **6**, PDI **2**, Dyad **2,** and DSBDP **9**.

For dyad **1**

Standard oxidation potential of donor in DCM; $E^{o}_{D^{+\cdot}/D}$ = +0.95 V

Standard reduction potential of acceptor in DCM; $E^{o}_{A/A^{-\cdot}}$ = -0.36 V

The average radii of the donor r_D and the acceptor r_A were estimated from the Connolly molecular surfaces volume of the respective moieties calculated with MM2 using the Chem3D Pro software.[S11]

Average radii of donor; R_A= 4.35 Å

Average radii of acceptor; R_A= 4.93 Å

Center to center distance of donor and acceptor segment, R_{cc}=15.89 Å

For dyad **2**

Standard oxidation potential of donor in DCM; $E^{o}{}_{D^{+\cdot}/D}$ = +0.8 V

Standard reduction potential of acceptor in DCM; $E^{o}{}_{A/A^{-\cdot}}$ = -0.66 V

Average radii of donor; = R_D= 4.35 Å

Average radii of acceptor; R_A= 5.27 Å

Center to center distance of donor and acceptor segment, R_{cc}=16.12 Å

Table S4. Calculated driving force for charge separation (ΔG_{CS}), and charge recombination (ΔG_{CR}) process for Dyad **1** and Dyad **2** in toluene, chloroform and acetonitrile.

Compound	**Solvent**	**E₀₀ (eV)**	ΔG^0_{CS} **(eV)**	ΔG^0_{CR} **(eV)**
Dyad **1**	Toluene	2.065	-0.13	-1.90
	Chloroform	2.079	-0.61	-1.42
	Acetonitrile	2.089	-1.01	-1.03
Dyad **2**	Toluene	1.860	-0.09	-1.91
	Chloroform	1.866	-0.28	-1.55
	Acetonitrile	1.880	-0.57	-1.25

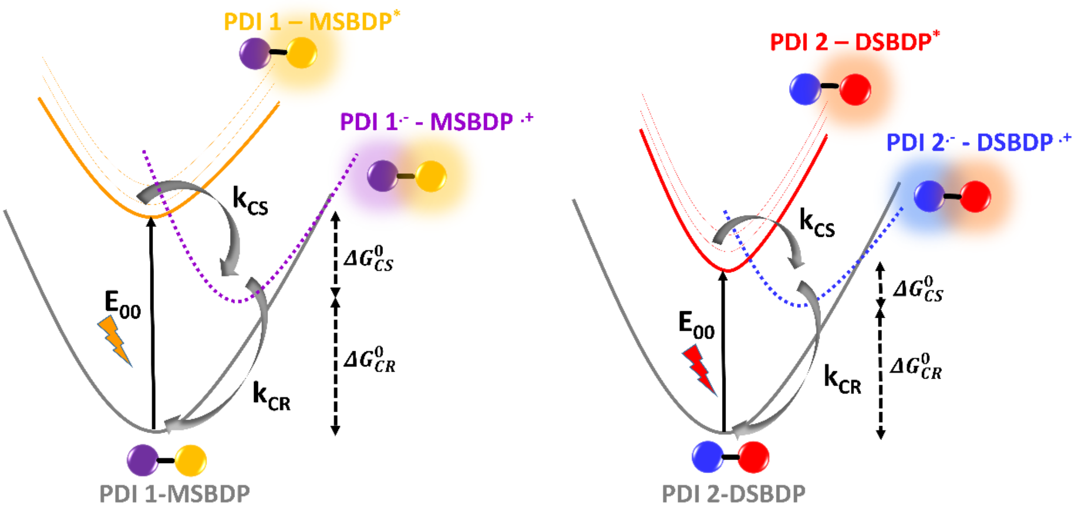


Figure S15: Schematic diagram of the potential energy surfaces for the ground state D-A (grey), vibrationally hot D-A* state (orange: dyad **1**; red: dyad **2**), and charge-separated state (violet: dyad 1; blue: dyad 2). E_{00} is the energy corresponding to the first excited singlet state.

Excitation of electron donor moiety (MSBDP/DSBDP) in the dyad produces the vibrationally hot locally excited state (MSBDP*-PDI 1/DSBDP*-PD1 2) of the dyad. The formation of this charge-separated state (CSS) opens up the CR channel involving back electron transfer from the charge-separated state to the ground state MSBDP-PDI **1**/DSBDP-PDI **2**.

6. **Computational studies**

The ground state geometries of dyads **1** and **2** were optimized by the density functional theory (DFT) method using B3LYP exchange-correlation functional and 6-31G(d, p) basis set (Figure S16). These DFT calculations uncovered that HOMO and HOMO-1 molecular orbitals are located completely on styryl-BODIPY for two dyads **1** and **2**. But, for dyad **1**, LUMO and LUMO+1 orbitals are located on the PDI unit while for dyad **2**, LUMO is on the PDI unit and LUMO+1 is on the styryl-BODIPY unit. The presence of HOMO on STBDP and LUMO+1 on PDI suggests their electron rich and deficient character respectively, and the charge transfer character of these dyads **1** and **2**.

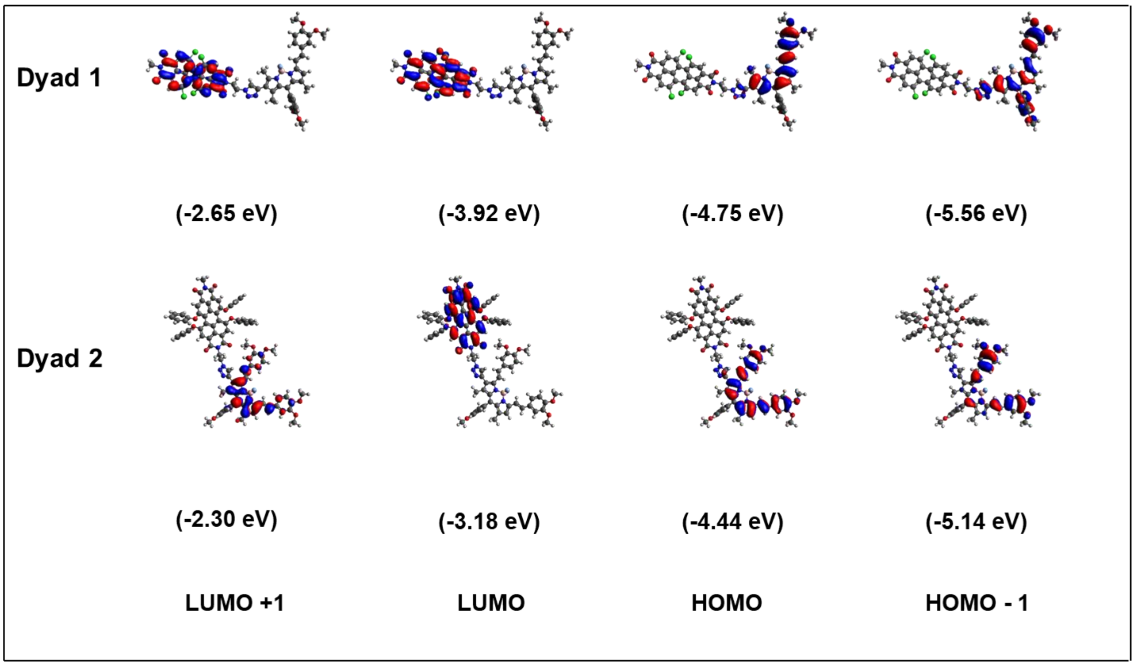


Figure S16. Frontier Molecular Orbitals (FMOs) of dyads **1** and **2** as obtained by DFT method at B3LYP 6-31G (d,p) level.

Table S5. FMO energy levels calculated using B3LYP/6-31G(d,p) calculations.

Compound	**HOMO-1 (eV)**	**HOMO (eV)**	**LUMO (eV)**	**LUMO+1 (eV)**
Dyad **1**	-5.56	-4.75	-3.92	-2.65
Dyad **2**	-5.14	-4.44	-3.12	-2.30

Table S6. First three frequencies obtained from frequency calculations for dyads **1** and **2**.

Compound	First three frequencies
Dyad **1**	2.58
	3.67
	5.41
Dyad **2**	1.81
	4.35
	5.36

7. **Transient absorption studies**

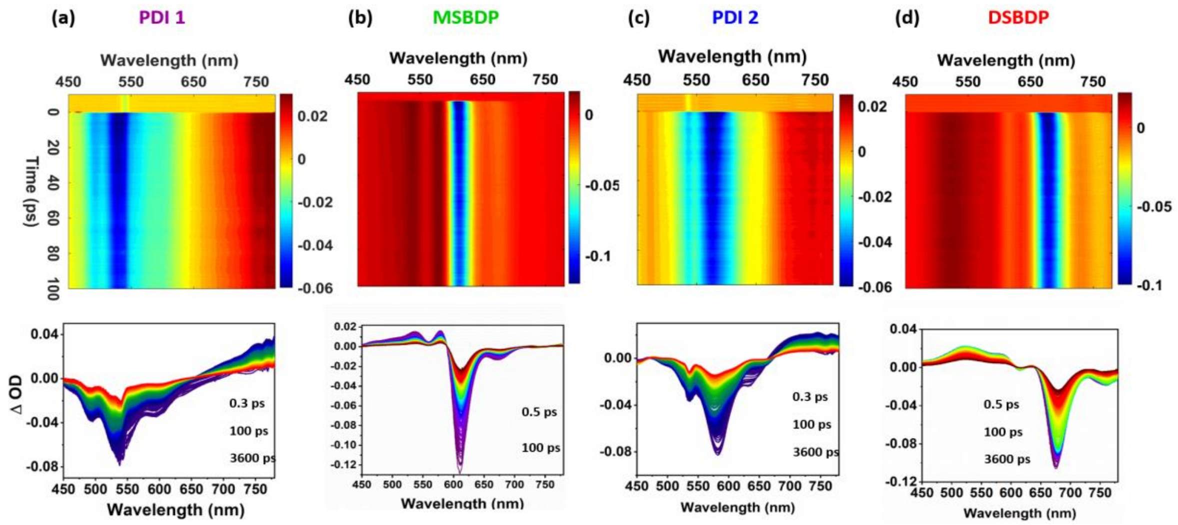


Figure S17: 2D contour maps for transient absorption spectra at varying probe for (a) PDI **1** (λ_{pump} = 537 nm), (b) MSBDP **6** (λ_{pump} = 590 nm), (c) PDI **2** (λ_{pump} = 530 nm), and (d) DSBDP **9** (λ_{pump} = 650 nm) in toluene.

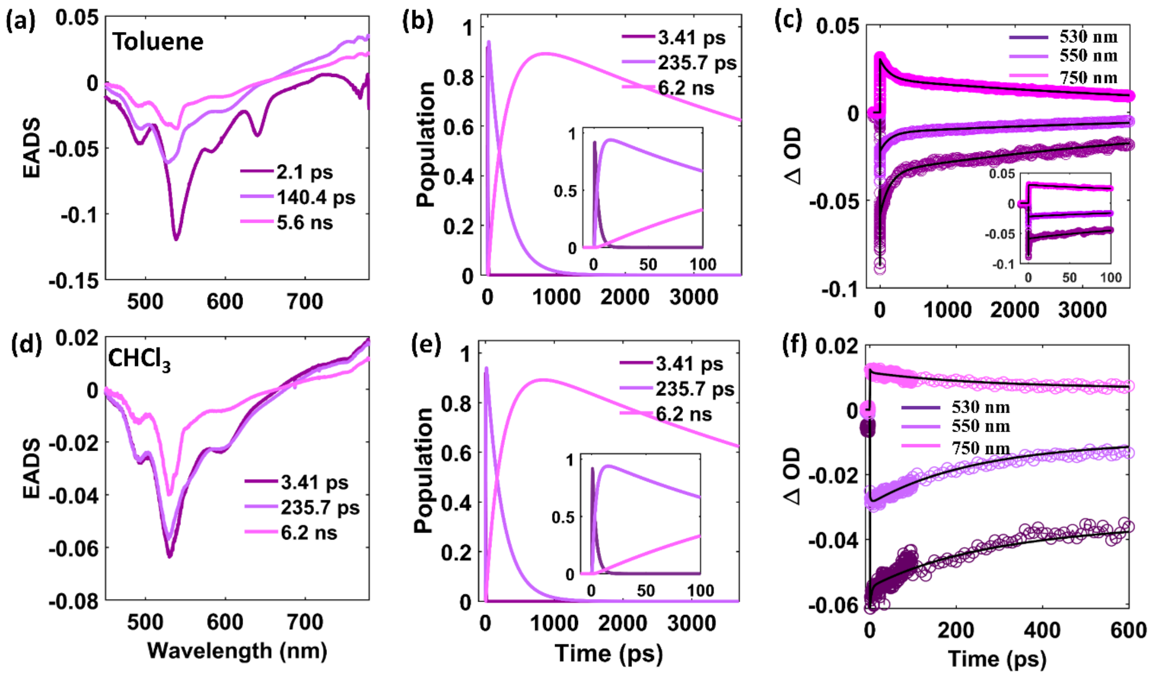


Figure S18: Evolution associated difference spectra (EADS) obtained from global fitting of the data to a sequential model (left panel) together with the corresponding population kinetics (middle panel), and kinetic traces at selected wavelengths along with fits (right panel) for PDI **1** following 537 nm excitation in toluene (a to c) and in chloroform (d to f).

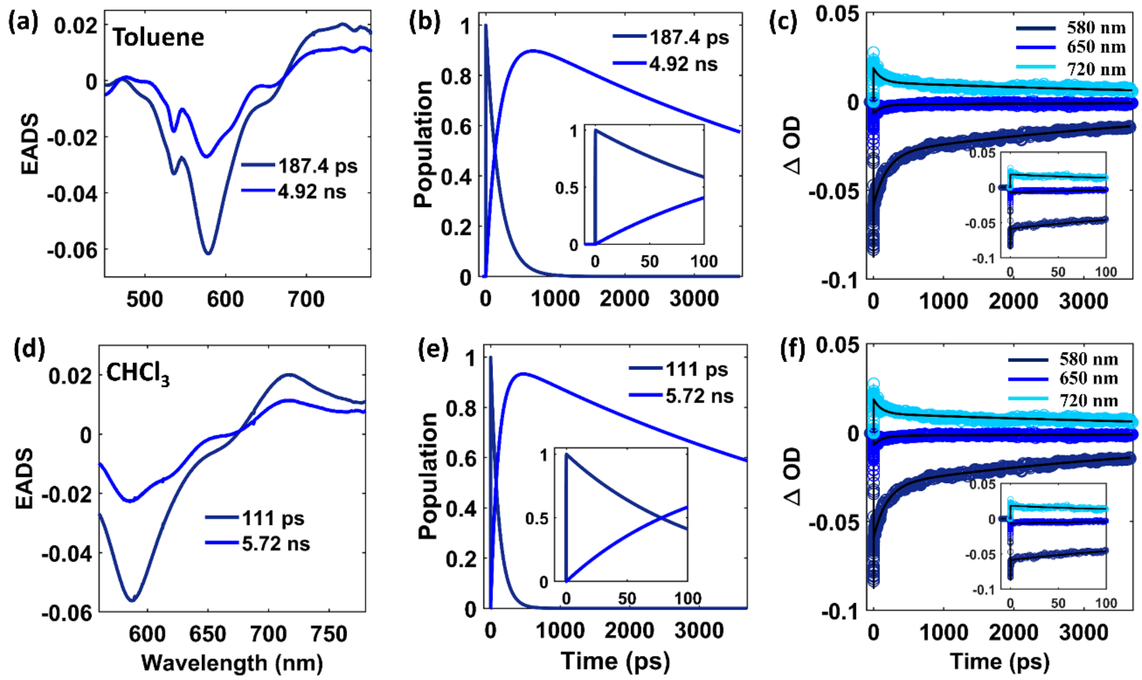


Figure S19: Evolution associated difference spectra (EADS) obtained from global fitting of the data to a sequential model (left panel) together with the corresponding population kinetics (middle panel), and kinetic traces at selected wavelengths along with fits (right panel) for PDI **2** following 530 nm excitation in toluene (a to c) and in chloroform (d to f).

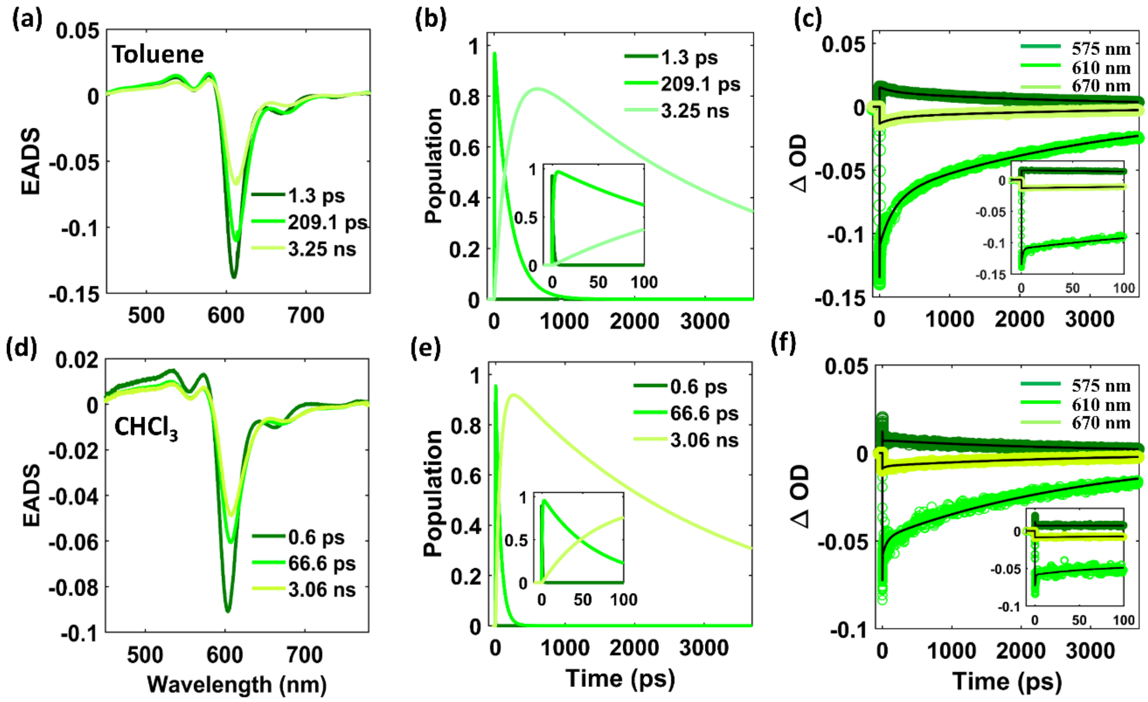


Figure S20: Evolution associated difference spectra (EADS) obtained from global fitting of the data to a sequential model (left panel) together with the corresponding population kinetics (middle panel), and kinetic traces at selected wavelengths along with fits (right panel) for MSBDP **6** following 590 nm excitation in toluene (a to c) and in chloroform (d to f).

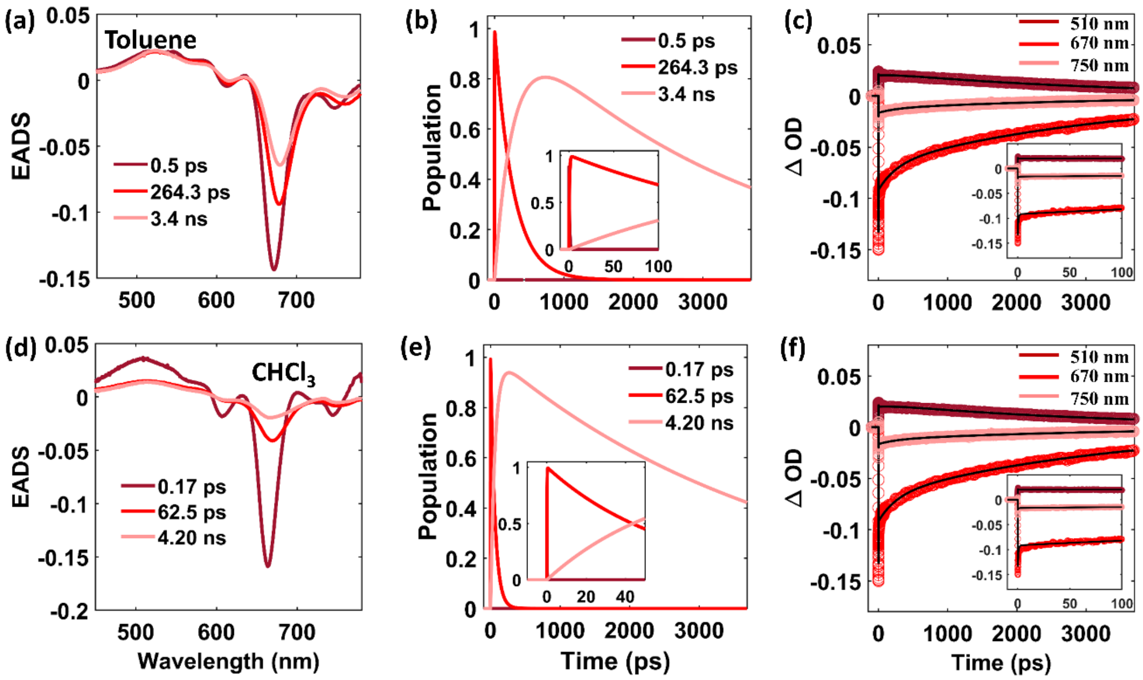


Figure S21: Evolution associated difference spectra (EADS) obtained from global fitting of the data to a sequential model (left panel) together with the corresponding population kinetics (middle panel), and kinetic traces at selected wavelengths along with fits (right panel) for DSBDP **9** following 650 nm excitation in toluene (a to c) and in chloroform (d to f).

Table S7. The kinetic parameters for excited-state relaxation of constituent chromophores PDI **1**, PDI **2**, MSBDP **6** and DSBDP **9** in toluene and chloroform obtained using global analysis of TA data.

Compound	λ_{pump} (nm)	Solvent	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
PDI **1**	537	Toluene Chloroform	2.1 3.41	140.4 235.7	5599 6285
PDI **2**	530	Toluene Chloroform	-- --	187.4 111.5	4927 5724
MSBDP **6**	590	Toluene Chloroform	1.30 0.60	209.1 66.6	3254 3063
DSBDP **9**	650	Toluene Chloroform	0.50 0.17	264.3 62.5	3346 4256

7. Comparison with other literature examples

A comparison table for all the reported cassettes and antenna based on styryl-BODIPY is provided in table S8. It is evident that the majority of the examples show a design of cassettes where the chromophores are attached through the styryl pendant or through meso-positions of the styryl-BODIPY. The present work is the only example with monofunctionalization at *β*-position and connection of additional chromophores through only one *β*-position.

Table S8: Energy/electron transfer cassettes reported on styryl-BODIPY with other chromophores.

S. No.	Composition of LH systems	Energy/electron transfer	References
1.	Dyads **1** and **2** containing **PDI** and **Mono Styryl-** or **Distyryl-BODIPYs**: Connected through **monofunctionalization at *β*-position** via **non-conjugated** spacer	Ultrafast charge transfer from mono styryl or distyryl BODIPY to PDI followed by slow charge recombination In **toluene** dyad **1 (**τ_{CS} ~ 157 ps and τ_{CR} ~ 838 ps) and dyad **2** (τ_{CS} ~ 257 ps and τ_{CR} ~ 1032 ps) In **chloroform** dyad **1 (**τ_{CS} ~ 2.19 ps and τ_{CR} ~ 35.2 ps) and dyad **2** (τ_{CS} ~ 14.6 ps and τ_{CR} ~ 127.8 ps).	This work
2.	Electron donor-acceptor dyads of **phenoxazine** connected at **meso** position of **distyryl-BODIPY** in conjugation	For **BDP**-1 charge separation (from phenoxazine to distyryl-BODIPY) and charge recombination take 109 ps and 2.3 ns and possessed the long triplet state lifetime (τ_T = 333 μs) in **toluene** and in **ACN (**τ_{CS} ~ 0.79 ps and τ_{CR} ~ 3.5 ps). In **BDP**-2 **(**τ_{CS} ~ 1.2 ps and τ_{CR} ~ 1.6 ns) CS faster than **BDP**-1 (τ_{CS} ~ 109 ps) in toluene and in the polar solvent **ACN**, **(**τ_{CS} ~ 0.3 ps and τ_{CR} ~ 1.6 ps) results similar to those of **BDP**-1 were obtained.	*Chem Phys Chem* 2020, **21**, 1388–1401
3.	**Distyryl-BODIPY** and **BODIPY** based triads, pentads and hexads connected through **styryl arms** and **two *β*-positions** via triazole linkers	Efficient energy transfer from BODIPY to distyryl-BODIPY (ETE ~ 98 %).	*Chem. Eur. J.* 2019, **25**, 14959 – 14971
4.	Vertically positioned **Distyryl-BODIPY**–**aluminum(III) porphyrin–fullerene supramolecular** triads	In supramolecular triad, (Ph_2-BDP)-$AlPorF_3$←Im-C_{60}, energy transfer (k_{EnT} = 1.00 × 10^{10} s^{-1}) from $^1AlPorF_3$* to ^{1}(Ph_2-BDP)* and electron transfer from $^1AlPorF_3$* to C_{60} (k_{CS} = 3.35 × 10^9 s^{-1}), followed by hole shift (k_{HS} = 1.00 × 10^9 s^{-1}) to Ph_2-BDP in **toluene**.	*Nanoscale*, 2018, **10**, 20723–20739
5.	**Distyryl-BODIPY** and **squaraine** based triads connected through **meso** position of STBDP via triazole linkers (non-conjugate spacer)	Quantitative FRET (k = 3.3 x 10^{11} s^{-1}) from **SQ** to **Styryl-BDP** moiety in **toluene** and in **ACN** FRET followed by PET (k = 5.9 x 10^{10} s^{-1}) from **Styryl-BDP** to **SQ**.	*Dye. Pigment.*, 2017, **147**, 560-572
6.	Supramolecular conjugate comprised of **distyryl-BODIPY** connected to electron donors **triphenylamine** or **phenothiazine** through **styryl arms** (**conjugate spacer**) and electron acceptor **fullerene** through **meso** position	Femtosecond transient absorbance studies provided evidence for the occurrence of ultrafast charge separation and relatively slow charge recombination in these donor–acceptor systems, followed by population of the ^{3}BODIPY* as evident from nanosecond transient absorption studies in **benzonitrile**. **2** (k_{CS} = 2.2 × 10^{11} s^{-1}); (k_{CR} = 8.2 × 10^8 s^{-1}), **3** (k_{CS} = 3.1× 10^{11} s^{-1}); (k_{CR} = 2.3 × 10^8 s^{-1}), **4** (k_{CS} = 4.1 × 10^{10} s^{-1}); (k_{CS} = 3.3 × 10^8 s^{-1}).	*Phys.Chem.Chem.Phys.*, 2016, **18**, 18187-18200
7.	An asymmetric triad composed of **blue BODIPY**, **green BODIPY** connected to **meso** position of **distyryl-BODIPY**	Efficient EET from the blue BODIPY to green BODIPY ~99% and green BODIPY to red BODIPY ~ 91%.	*Chem. Commun.*, 2015, **51**, 11382-11385

8.	**2,6-diiodo BODIPY** dyads with **mono-** or **distyryl-BODIPY** connected through **meso** position via triazole linkers	Ultrafast FRET was observed from iodinated BODIPY to mono- or distyryl-BODPY (k_{FRET} = 5.02×10^{10} s^{-1}) and triplet energy transfer was efficient (Φ_{TTET} = 92 %) and fast process (k_{TTET} = 5.2×10^{4} s^{-1}).	*J. Phys. Chem. A*, 2015, **119**, 6791−6806
9.	Unsymmetrical triad of **distyryl-BODIPY**, **diketopyrrolopyrole** and **triphenyl amine** through phenyl-alkyne-phenyl or phenyl-alkyne-thienyl (**conjugate spacer**) units at **meso** position	Quantitative energy transfer from the DPPPh to the DSBDP moiety, as confirmed by the excitation spectrum and charge transfer process between the triphenylamine and the DPP module.	*J. Org. Chem*. 2015, **80**, 6737−6753
10.	Dyads B-1 and B-2 containing **BODIPY** or **monostyryl-BODIPY** connected through the **meso** position of **diiodo monostyryl** (B-1) or **distyryl-BODIPY** (B-2) via triazole linker	The intramolecular energy transfer was calculated as 66 % for B1 and 46% for B2.	*J. Org. Chem.* 2014, **79**, 10240−10255
11.	Cassettes containing **BODIPY** and **mono styryl-BODIPY** connected through biphenyl linker at **meso** positions	Through-bond energy transfer from BODIPY to mono styryl-BODIPY (TBET efficiencies ~99 %).	*J. Org. Chem*. 2014, **79**, 6315−6320
12.	Dyads of **diiodo mono styryl** or **diiodo distyryl-BODPY** (as energy acceptor) with rhodamine (as energy donor) connected through **meso** position	Intramolecular singlet energy transfer (56.3% and 53.2%) from rhodamine to iodo STBDP followed by generation of triplet excited state localized on STBDP.	*J. Mater. Chem. C*, 2014, **2**, 3900–3913
13.	Triads and tetrads of **BODIPY**, **C60 meso** linked to **distyryl-BODIPY** through phenylene bridge	Intramolecular energy transfer ~92 % from antenna to C60 followed by generation of triplet excited state due to ISC effect of $C_{60.}$	*Chem. Eur. J.* 2013, **19**, 17472 – 17482
14.	Dendritic light harvester composed of **BODIPY** connected through **styryl arms** of **tetra styryl-BODIPY** via triazole linkers	Efficient energy transfer (~90 %) from BODIPY to tetra styryl-BODIPY (based on reduced emission lifetimes of the donor moieties).	*Org. Lett*., 2012, **14**, 3636-3639
15	Tweezers containing **zinc porphyrin** rings connected through **styryl arms** of **distyryl-BODIPY** by triazole rings **(non-conjugate linker)**	Efficient EET from the ZnP to the distyryl-BODIPY in **toluene** (BDP β-Por_2, $k_{ENT} = 8.5 \times 10^{11}$ s^{-1}; BDP meso-Por_2, $k_{ENT} = 3.1 \times 10^{11}$ s^{-1}) and in **benzonitrile** energy transfer from ZnP to DSBDP (BDP β-Por_2, $k_{ENT} = 6.5 \times 10^{11}$ s^{-1}; BDP meso-Por_2, $k_{ENT} = 1.3 \times 10^{11}$ s^{-1}) as well as additional electron transfer occurred from DSBDP to ZnP in (BDP β-Por_2, $k_{CS}= 9.2 \times 10^{9}$ s^{-1}; BDP meso-Por_2, $k_{CS}= 1.2 \times 10^{9}$ s^{-1}).	*J. Phys. Chem. A* 2012, **116**, 3889−3898
16.	Dyads of **distyryl-BODIPY** and **C_{60}** connected through **meso**	Energy transfer from the distyryl-BODIPY antenna to the C_{60} unit and in turn the backward	*Org. Lett*., 2012, **14**, 2594-2597

	position or **styryl arms** of **styryl-BODIPY**	triplet state energy transfer from C_{60} to the distyryl-BODIPY antenna.	
17.	Artificial light harvesting antennae **1** and **2** based on **BODIPY** and **distyryl-BODIPY** attached to carbohydrate platform through **meso** position	Ultrafast energy transfer take place from BODIPY to distyryl-BODIPY (**1**, rate constant ~ 4 x 10^{12} s^{-1}; **2**, rate constant ~ 8 x 10^{10} s^{-1} from transient spectrum).	*Chem. Commun.*, 2012, **48**, 10550–10552
18.	Zn^{2+}ion guided **self - assembly** of **distyryl-BODIPY** and **BODIPY** dyes	Based on the emission data an energy transfer efficiency of 82% was calculated from BODIPY to distyryl-BODIPY.	*Org. Lett.*, 2012, **14**, 5286-5289
19.	Through bond energy transfer cassettes based on **coumarin** with **distyryl-BODIPY**, connected through conjugated phenyl liker at **meso** position	On excitation of coumarin, energy transfer from coumarin to distyryl-BODIPY (~96 % to 98 % energy efficiencies and antenna effect ~ 3 to 5.5 fold).	*J. Mater. Chem.*, 2011, **21**, 13168–13171
20.	Unimolecular solar concentrator based on BODIPY, monostyryl and distyryl BODIPY connected through **styryl arms** of DSBDP	Efficient energy transfer ~90 – 97 % has been found from BODIPY to monostyryl-BODIPY to distyryl-BODIPY.	*Angew. Chem. Int. Ed.*, 2011, **50**, 10907 – 10912
21.	**Silicon(IV) phthalocyanines (Pc)** substituted axially with two **mono styryl-BODIPY** moieties (through **meso** position)	Quenching of Pc-part fluorescence was due to a PET process from MSBDP to Pc. The lifetime of the charge-separated state was determined to be 1.7 ± 0.1 ns in toluene.	*Chem. Commun.*, 2009, 1517–1519
22.	Energy transfer cassettes of **BODIPY** and **distyryl-BODIPY**, connected through **meso** and **styryl arms**	Efficient energy transfer from BODIPY to distyryl-BODIPY.	*Tetrahedron Letters*, 2009, **50** 1738–1740
23.	Light harvesting system composed of **BODIPY**, **monostyryl-BODIPY** and **distyryl-BODIPY** dyes connected through **meso** positions via triazole linkers	Highly efficient energy transfer (~ 99 %) from BODIIPY or mono styryl-BODIPY to distyryl-BODIPY.	*Org. Lett.*, 2008, **10**, 29-32

8. Coordinates of geometry optimized structures

Coordinates of geometry optimized structure of dyad 1

C -8.40791 -1.18164 -0.35371

N -8.01438 0.14494 -0.17661

B -6.54089 0.64473 -0.10757

C -6.08494 -1.94561 -0.22514

C -7.45897 -2.21667 -0.38325

C -4.30839 -0.63127 0.09011

C	-3.82720	-1.96318	-0.01795
C	-4.93807	-2.79993	-0.21872
C	-9.84713	-1.20632	-0.43569
C	-10.26316	0.10494	-0.31158
C	-9.11933	0.93293	-0.14984
C	-9.04959	2.35931	0.04237
C	-10.77474	-2.37402	-0.59829
C	-3.52905	0.62610	0.30129
C	-4.88290	-4.28526	-0.41727
C	-7.92327	-3.62552	-0.56589
F	-6.21674	1.38049	-1.24116
F	-6.36614	1.42558	1.04072
C	-8.11554	-4.44922	0.55888
C	-8.55501	-5.76298	0.41703
C	-8.80751	-6.28060	-0.88116
C	-8.61171	-5.46145	-1.99032
C	-8.17498	-4.13887	-1.83422
N	-5.64790	-0.63021	-0.03371
O	-9.23097	-7.57297	-0.92405
O	-8.77187	-6.62840	1.44379
C	-2.42313	-2.35799	0.06715
C	-10.11687	3.18666	-0.07119
C	-10.13064	4.63143	0.11797
C	-11.35753	5.31987	-0.03176
C	-11.44876	6.69543	0.13468
C	-10.28410	7.43645	0.46275
C	-9.06977	6.76324	0.61015
C	-8.99138	5.38168	0.44063
O	-10.45970	8.77674	0.60775
O	-12.59157	7.42791	0.00838
C	11.29452	1.06579	-0.28163
C	9.93589	0.69212	-0.10869

C	9.59462	-0.69303	0.04069
C	10.56206	-1.62677	-0.36460
C	11.88998	-1.24780	-0.63098
C	12.27114	0.07447	-0.52644
C	11.66307	2.42753	-0.20750
C	10.70518	3.38214	0.06642
C	9.34760	3.02238	0.14093
C	8.91950	1.70416	-0.08526
C	7.53583	1.24853	-0.26786
C	7.21719	-0.05519	0.23966
C	8.25737	-0.98606	0.57122
C	5.85836	-0.42744	0.41582
C	5.54071	-1.61342	1.11571
C	6.55321	-2.38332	1.65213
C	7.89852	-2.06417	1.39685
C	6.50154	1.94212	-0.91731
C	5.16241	1.52297	-0.82939
C	4.83353	0.38920	-0.11377
C	3.41015	0.00379	0.03961
N	3.14832	-1.15181	0.79295
C	4.12690	-2.01038	1.32882
C	13.69652	0.44479	-0.73017
N	14.00667	1.81017	-0.62491
C	13.08345	2.83154	-0.36442
O	3.81109	-3.02129	1.93594
O	2.49408	0.64706	-0.45423
O	14.55393	-0.39041	-0.97477
O	13.45107	3.99341	-0.27601
C	15.40437	2.22777	-0.79619
C	1.73666	-1.50407	1.00328
C	1.17113	-2.29421	-0.18937
N	-0.25746	-2.51556	-0.04267

N	-0.71523	-3.64433	0.54605
N	-2.01254	-3.55333	0.61190
Cl	9.08237	-3.00879	2.26831
C	-1.28682	-1.68615	-0.35449
Cl	10.16799	-3.29751	-0.69238
Cl	6.80689	3.29356	-1.98247
Cl	8.25361	4.28442	0.65540
C	-9.48648	-8.14721	-2.19563
C	-13.78719	6.74168	-0.32105
C	-8.51213	-6.17626	2.76405
C	-9.32749	9.56701	0.93500
H	-11.28983	0.44361	-0.30813
H	-8.07390	2.75229	0.30154
H	-10.61334	-3.13812	0.16728
H	-10.64565	-2.86963	-1.56497
H	-11.81122	-2.03252	-0.52780
H	-2.58398	0.41185	0.80513
H	-4.10819	1.33202	0.89721
H	-3.30696	1.11477	-0.65571
H	-3.85147	-4.60705	-0.55994
H	-5.48519	-4.60016	-1.27267
H	-5.26676	-4.82328	0.45609
H	-7.91510	-4.04504	1.54362
H	-8.79640	-5.84311	-2.98717
H	-8.02787	-3.51546	-2.71032
H	-11.08000	2.75277	-0.33590
H	-12.24393	4.74848	-0.28254
H	-8.17164	7.31564	0.85859
H	-8.03013	4.89436	0.55995
H	12.62725	-1.99340	-0.90341
H	11.00694	4.41323	0.20667
H	6.30155	-3.24510	2.25872

H	4.37769	2.09693	-1.30753
H	15.99400	1.33739	-0.99754
H	15.75393	2.72464	0.11086
H	15.47844	2.93419	-1.62515
H	1.18067	-0.57453	1.12794
H	1.67485	-2.10431	1.90977
H	1.64286	-3.27637	-0.25308
H	1.34342	-1.74620	-1.11838
H	-1.13647	-0.74374	-0.85612
H	-9.80431	-9.17249	-2.00220
H	-8.58583	-8.16015	-2.82284
H	-10.28595	-7.61539	-2.72766
H	-14.56573	7.50411	-0.37234
H	-14.05586	6.00255	0.44504
H	-13.71150	6.23711	-1.29317
H	-8.74003	-7.01882	3.41796
H	-9.15105	-5.32565	3.03415
H	-7.46074	-5.89056	2.89469
H	-9.68941	10.59378	1.00189
H	-8.55329	9.50607	0.15957
H	-8.89332	9.27289	1.89906

Coordinates of geometry optimized structure of dyad 2

C	9.65991	2.20680	-0.19916
N	9.49220	0.84275	-0.42796
B	8.19405	0.04274	-0.10923
C	7.27126	2.46532	0.27008
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C	5.74549	0.82307	0.28969
C	5.05656	2.05128	0.55476
C	6.00529	3.07862	0.54861
C	11.05096	2.52179	-0.40148
C	11.66699	1.33528	-0.75233

C	10.69366	0.30131	-0.76319
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C	11.76107	3.83818	-0.28331
C	5.27932	-0.54482	0.20633
C	5.70992	4.53749	0.73329
C	8.78297	4.47230	0.39539
F	7.88264	-0.78872	-1.19591
F	8.36324	-0.71460	1.04056
C	8.96478	4.93442	1.71223
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C	9.21421	7.21038	0.89734
C	9.03132	6.74757	-0.40336
C	8.81990	5.38505	-0.65396
N	7.06198	1.09952	0.09573
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C	12.05785	-1.68578	-1.28738
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C	13.63741	-3.50644	-1.81852
C	13.94827	-4.82117	-2.13992
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C	11.28448	-4.03796	-1.75646
O	13.29335	-7.03587	-2.59062
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C	-10.70986	-2.02401	-0.30519

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C	-8.36808	0.83494	-0.94190
C	-7.11453	1.30995	-0.35622
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C	-6.55836	-1.05301	0.21909
C	-4.84143	0.71363	0.39350
C	-3.86032	-0.27408	0.63410
C	-4.19123	-1.61238	0.55041
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C	-8.70183	-5.94768	3.94521
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H	9.94034	-1.66926	-1.15036
H	11.58440	4.31611	0.68428
H	11.43776	4.55168	-1.04717
H	12.83800	3.68539	-0.39760
H	5.94019	-1.19745	-0.35142

H	4.63395	4.70316	0.77438
H	6.14078	5.13947	-0.07060
H	6.13036	4.91645	1.67024
H	8.93321	4.21965	2.52545
H	9.05072	7.44166	-1.23487
H	8.67903	5.04307	-1.67437
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H	-9.05959	5.71866	-5.73162
H	-10.58373	3.84241	-1.39250
H	-11.70340	5.84281	-2.34170
H	-10.94564	6.79065	-4.51204

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