Enhanced brightness and electron affinity of terrylenediimide with sulfone-bridged substituents on the bay region

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Note added after first publication:

This Supplementary file replaces that originally published on 11 Dec 2020. The reaction scheme for the synthesis of TDI4SF on page S6 has been updated to reflect the corrected optimized conditions.

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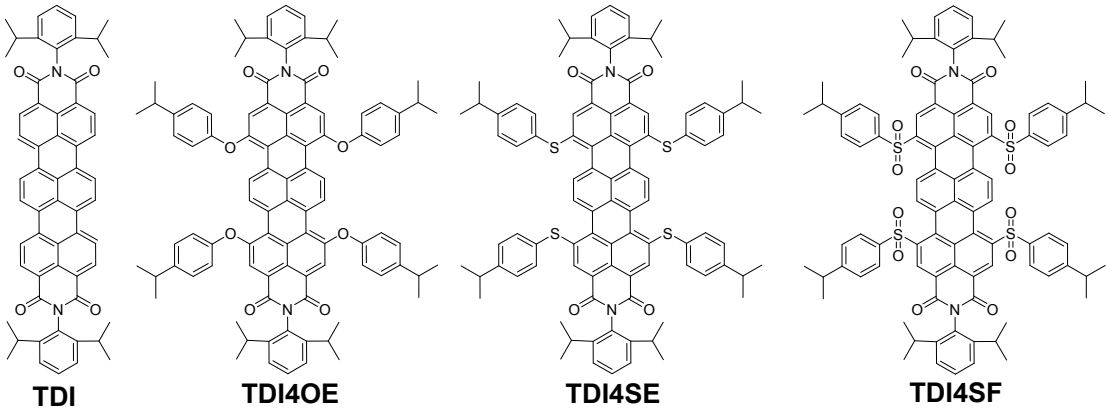
Part A: Experimental Section

1 General information on materials

The chemical reagents were purchased from J&K Scientific Ltd or Beijing zhong sheng hua teng Technology Co., Ltd. and used as received. Solvents were either employed as purchased or dried according to procedures described in the literature. Deionized water was obtained from a Milli-Q water purification system (Millipore). Phosphate buffer saline (PBS) was purchased from Life Technologies Co., Ltd.. All glassware was oven-dried prior to use when water- and/or air-sensitive reagents were used. The synthetic steps were performed under ambient atmosphere unless stated otherwise. The ^{1}H-NMR spectra were recorded at 20°C on 600 MHz NMR spectrometer (Bruker). The ^{13}C-NMR spectra were recorded at 20°C on 150 MHz NMR spectrometer (Bruker). Mass spectra were carried out using Thermo Finnigan TSQ Quantum Ultra AM EMR Mass Spectrometry or Agilent LC/MSD Ion Trap G2445D SL Mass Spectrometer. Cyclic voltammetry (CV) was performed on a CHI660b electrochemical ananlyzer with a three-electrode cell in 0.1 M tetrabutylammoniumperchlorate (Bu_4NClO_4) dichloromethane solution at a scan rate of 100 mV/s. A glass carbon disk (2-mm diameter) was used as working electrode with a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The redox potential was calibrated with ferrocene/ferrocenium (0.438 V *vs* Ag/AgCl in DCM). Energy gap (E_g) and LUMO energy levels were calculated

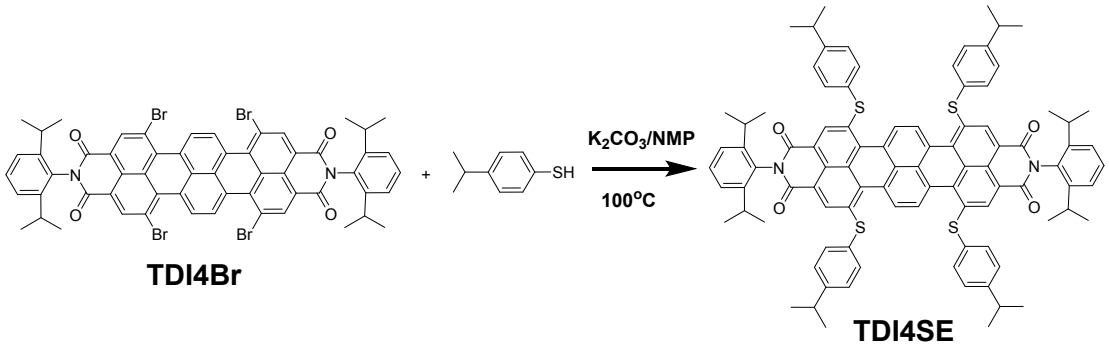
according to E_g=1240/λ_{onset} and LUMO=– (4.38+E^{onset}_{red}), respectively. UV/Vis spectra were recorded with a Shimadzu WV-2550 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301 fluorescence spectrophotometer. Fluorescence quantum yield was determined using optically matching solutions of Atto 647N (Φ = 0.35, in DCM) as the standard at an excitation wavelength of 646 nm and the quantum yield was calculated using the following equation: $\Phi s = \Phi_r (A_r F_s / As\ F_r) (n_s^2/n_r^2)$, where, s and r denote sample and reference, respectively, A is the absorbance, F is the relative integrated fluorescence intensity, and n is the refractive index of the solvent. Fluorescence microscopy images of labelled cells were obtained with spectral confocal laser scanning microscopy (Olympus Fluoview FV-1000).

2 Synthesis and characterization of TDI dyes



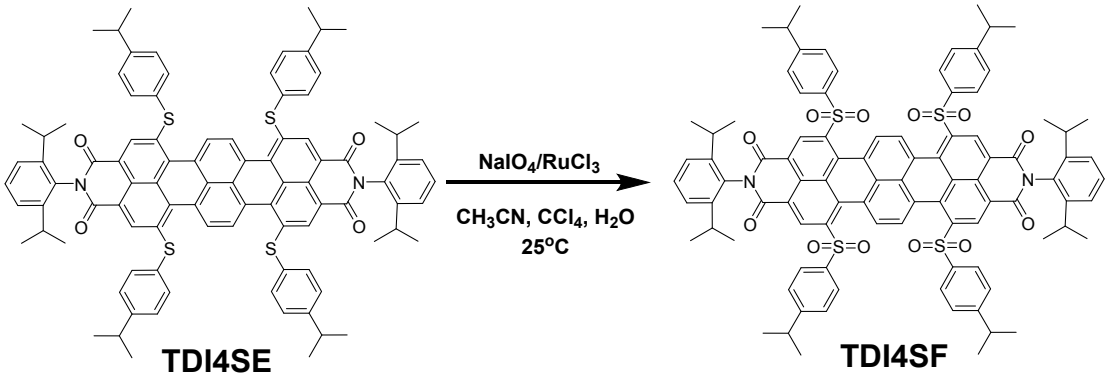
Scheme S1. Chemical structure of TDI dyes

Synthesis of TDI4SE



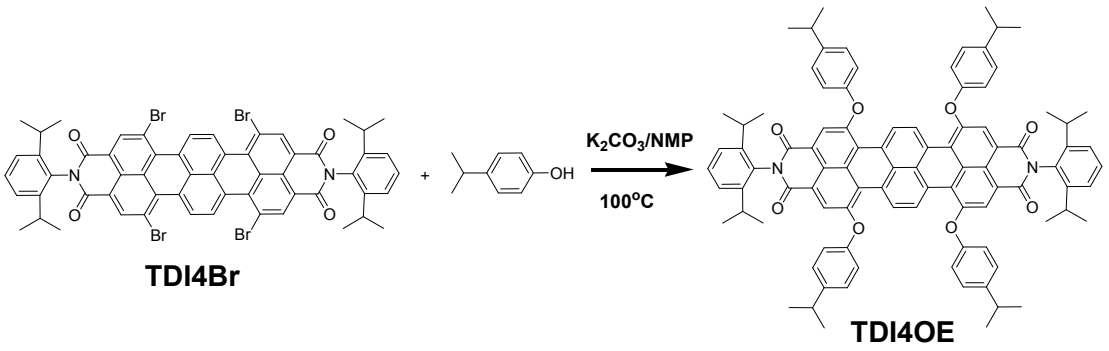
TDI4Br (100mg, 0.087mmol), anhydrous potassium carbonate (50.0 mg, 0.36 mmol), and 25 mL N-methyl pyrrolidone were added into a 50 mL of reaction flask. The mixture was stirred at 100°C under nitrogen for 36 h, and then poured into 50 mL of 2 M hydrochloric acid to precipitate the product. The crude product was washed with water to neutrality, and dried in a vacuum drying oven. Dichloromethane/Petroleum ether=1:3 was used as the eluent on a silica column to obtain 81.5 mg black solid, and the yield was 65%. ^{1}HNMR (600 MHz，$CDCl_3$) δ (ppm)：8.98 (s，4H)，8.48(s，4H)，7.48(d，J =8.4 Hz，8H)，7.44(t，J =7.8 Hz，2H)，7.30(d，J =7.8 Hz，4H)，7.24(d，J =8.4 Hz，8H)，2.90(m，4H)，2.70(m，4H)，1.23(d，J =6.6 Hz，24H)，1.13(d，J =6.6 Hz，24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.36, 150.49, 145.59, 138.50, 134.13, 133.65, 133.33, 131.10, 130.74, 129.44, 128.91, 128.70, 128.59, 128.43, 128.01, 124.64, 123.98, 120.53, 33.88, 29.07, 23.91, 23.74; MALDI-TOF MS: Calcd for $C_{94}H_{86}N_2O_4S_4$: 1435.96, found:1434.5$[M^+H]^+$.

Synthesis of TDI4SF



TDI4SE (100 mg, 0.070 mmol) dissolved in 2mL acetonitrile and 2mL carbon tetrachloride, followed by the addition of $NaIO_4$ (176.9mg, 0.836 mmol), $RuCl_3 \cdot H_2O$ (28.9 mg, 0.139 mmol) and 4mL distilled water. The resulted solution was stirred at room temperature overnight. The mixture was extracted with CH_2Cl_2, dried with Na_2SO_4. The crude product was concentrated through rotary-evaporation in vacuum and concentrated in vacuum. The crude product was further purified by column chromatography (CH_2Cl_2) to afford TDI4SF (blue solid, 77 mg, yield 71%). ^{1}H NMR (600 MHz，$CDCl_3$) δ (ppm)：9.36 (s，4H)，8.82 (s，4H)，7.97 (d，J =8.4 Hz，8H)，7.48 (t，J =7.8 Hz，2H)，7.43 (d，J =8.4 Hz，8H)，7.33(d，J =7.8 Hz，4H)，2.98(m，4H)，2.62 (m，4H)，1.23 (d，J =6.6 Hz，24H)，1.13 (d，J =6.6 Hz，24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.13, 156.49, 145.47, 141.30, 136.94, 136.33, 134.39, 133.84, 129.90, 129.04, 128.85, 127.82, 126.41, 124.20, 120.54, 38.76, 34.33, 29.72, 29.16, 28.95, 23.86, 23.49; MALDI-TOF MS: Calcd for $C_{94}H_{86}N_2O_{12}S_4$: 1563.95, found:1562.5$[M^+H]^+$

Synthesis of TDI4OE



TDI4Br (30mg, 0.026mmol), anhydrous potassium carbonate (24.0 mg, 0.174 mmol), and 10 mL N-methyl pyrrolidone were added into a 25 mL of reaction flask. The

mixture was stirred at 100°C under nitrogen for 36 h, and then poured into 50 mL of 2 M hydrochloric acid to precipitate the product. The crude product was washed with water to neutrality, and dried in a vacuum drying oven. Dichloromethane/Petroleum ether=1:3 was used as the eluent on a silica column to obtain **TDI4OE** (blue solid, 27.2 mg, 72%). ^{1}H NMR(600 MHz，$CDCl_3$) δ(ppm)：9.54(s，4H)，8.34(s，4H)，7.47(t，J =7.8 Hz，2H)，7.32(m，12H)，7.17(d，J =8.4 Hz，8H)，2.96(m，4H)，2.74(m，4H)，1.31(d，J=7.2 Hz，24H)，1.74(d，J=6.6 Hz，24H).

3 The photoluminescence quantum yields in solid film: The thin films of TDI dyes were prepared on quartz substrates via dropping 5×10^{-5} M solution on quartz substrates, and drying in vacuum. The QYs of the thin films of TDI dyes were determined using a commercial QY spectrometer (Quantaurus-QY, Hamamatsu Photonics, Hamamatsu City, Japan). Reported values are averages (n=3).

4 Cytotoxicity Test: MTT assays were performed to assess the metabolic activity of Hela cells. Hela cells were seeded in 96-well plates (Costar, IL, USA) at an intensity of 2×10^4 cells/mL. Then, the medium was replaced by the different concentration TDI4SF solution, and the cells were then incubated for 24h. After the designated time intervals, the wells were washed twice with PBS buffer and freshly prepared MTT (10 μL, 5 mg/mL) solution in culture medium was added into each well. The MTT medium solution was carefully removed after 3h incubation in the incubator. DMSO (100 μL) was then added into each well and gently shaken for 10 min at room temperature to dissolve all the precipitate formed. The absorbance of MTT at 490 nm was monitored by the ELX-800 microplate reader (ELISA Reader). Cell viability was expressed by the ratio of the absorbance of the cells incubated with **TDI4SF** solution. Each result is an average of data from six wells; 100% viability was determined using untreated cells.

5 Cell culture and Confocal imaging

Human cervical cancer cells (HeLa) were purchased from National Infrastructure of Cell Line Resource. Cells were cultured in Dulbecco's modified Eagle's medium (DMEM medium, Invitrogen Corp) supplemented with 10% FBS, penicillin (100 units/ml), and streptomycin (100 ug/ml). All cells were maintained in a humidified atmosphere of 5/95 (v/v) of CO2/air at 37 °C. The cells were passed for plated on 35 mm glass bottom poly-D-lysine coated Petri-dish for at least 24 h to enable adherence to the bottom.

For fluorescence imaging, cells were grown in DMEM on a 35 mm glass bottom culture dishes for at least 24 h to enable adherence to the bottom, and then treated and incubated with 5 μM TDI4SF (PBS with 0.1% DMSO) at 37 °C under 5% CO_2 during the time mentioned in the text. The cells were washed three times with phosphate buffered saline (PBS) and then imaged after further incubation in colorless serum-free media for 30 min. Fluorescence microscopy images of labelled cells were obtained with spectral confocal laser scanning microscopy (Olympus Fluoview FV-1000). The fluorescence intensity (FI) was the average fluorescence intensity of the cell area (at least 20 cells) from the confocal fluorescence images, which was quantified by LAS AF software.

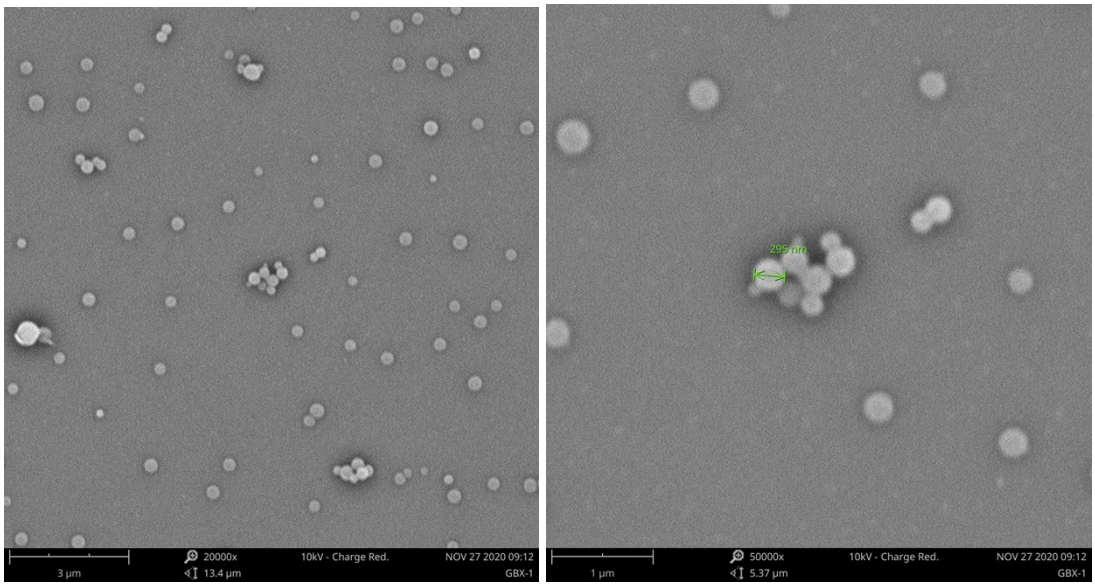


Figure S1 SEM images of TDI4SF on a Si substrate. SEM image of a sample prepared by dropping a dilute solution of water with 0.1% DMSO (5 µM) onto a silicon substrate, followed by solvent evaporation in a closed chamber saturated with an appropriate water vapor.

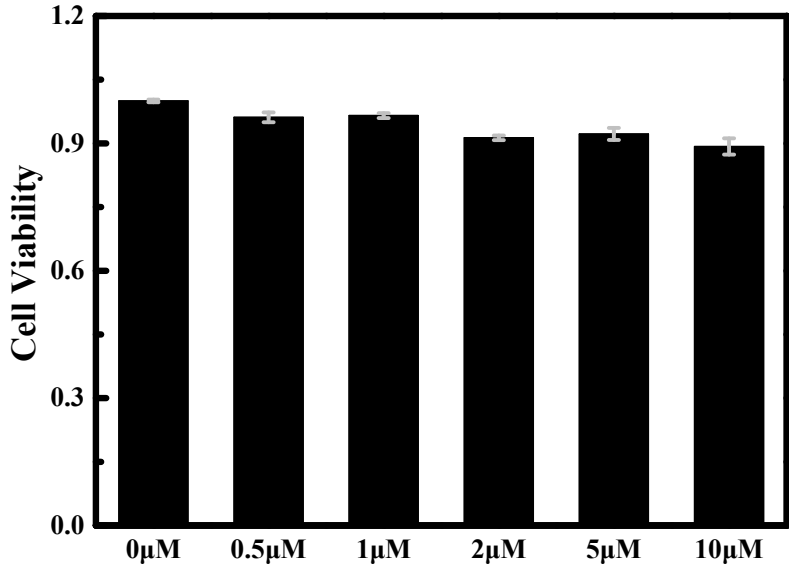


Figure S2 In vitro viability of Hela cells treated with TDI4SF solution with 24 h

Part B: ^{1}H-NMR spectrum, ^{13}C NMR spectrum and MALDI-TOF spectrum

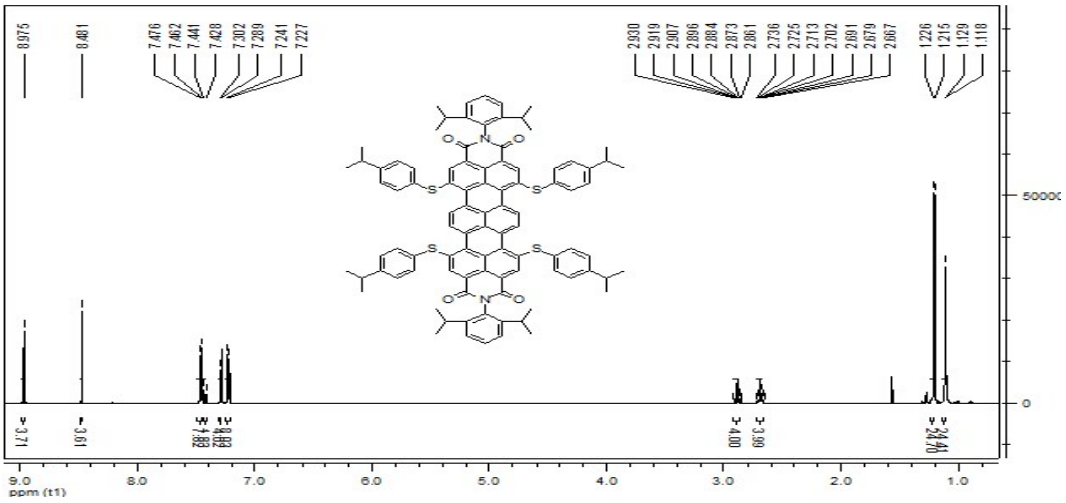


Figure S3 ^{1}H NMR (600 MHz) spectra of TDI4SE in $CDCl_3$

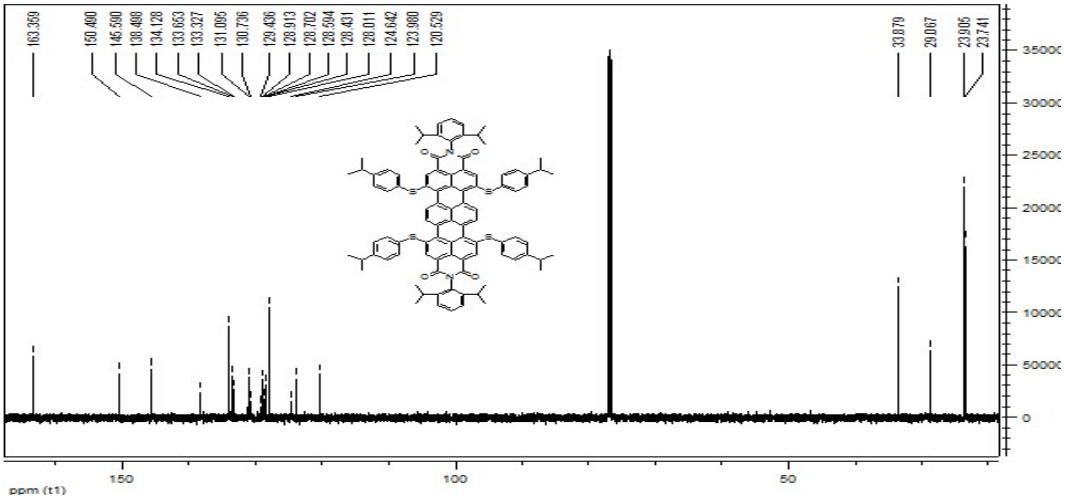


Figure S4 ^{13}C NMR (150 MHz) spectra of TDI4SE in $CDCl_3$

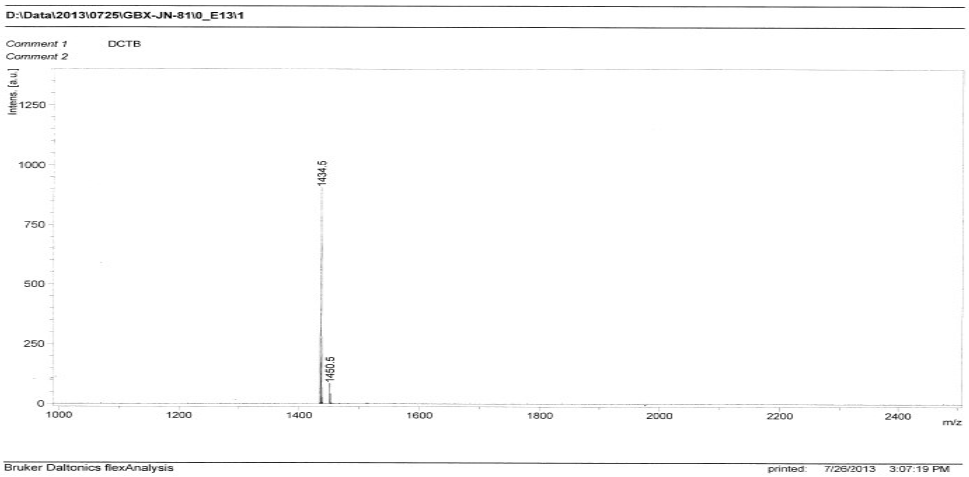


Figure S5 MS spectrum of TDI4SE

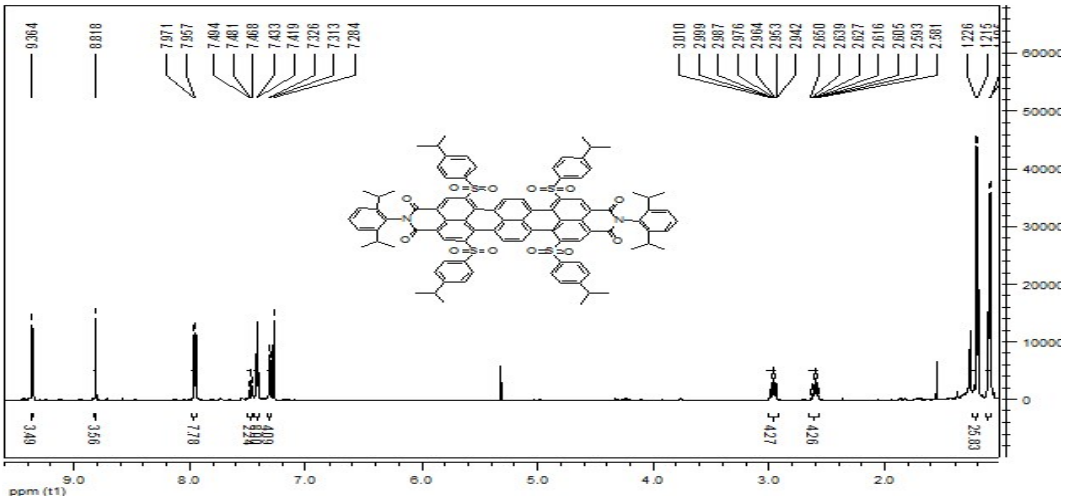


Figure S6 ^{1}H NMR (600 MHz) spectra of TDI4SF in $CDCl_3$

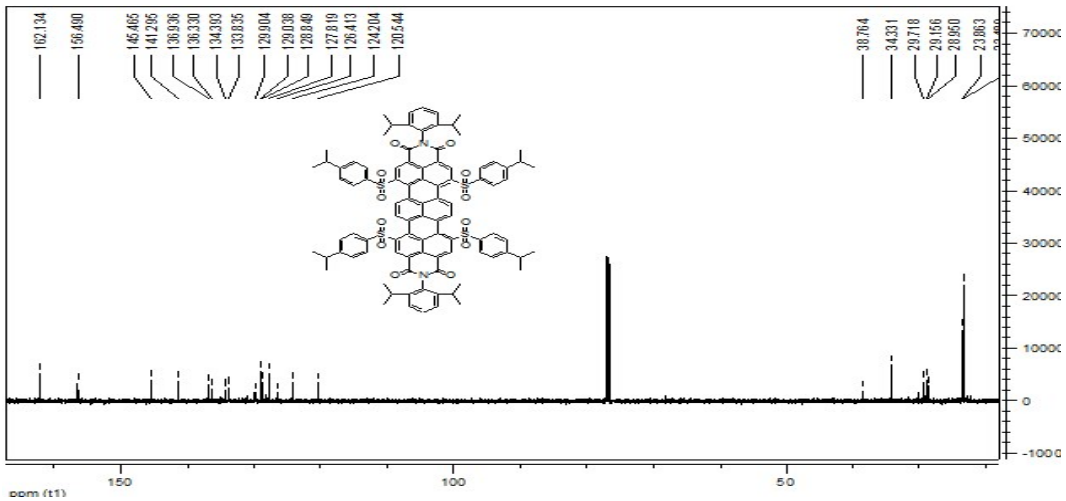


Figure S7 ^{13}C NMR (150 MHz) spectra of TDI4SF in $CDCl_3$

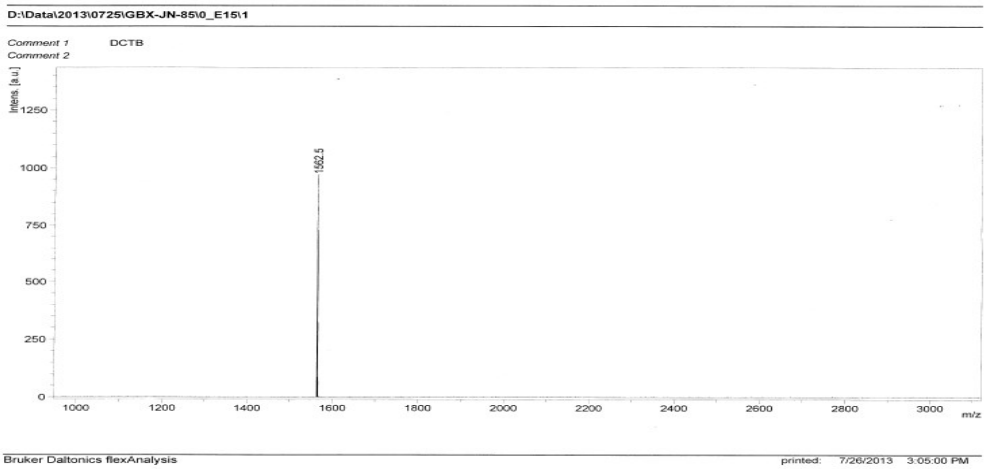


Figure S8 MS spectrum of TDI4SF

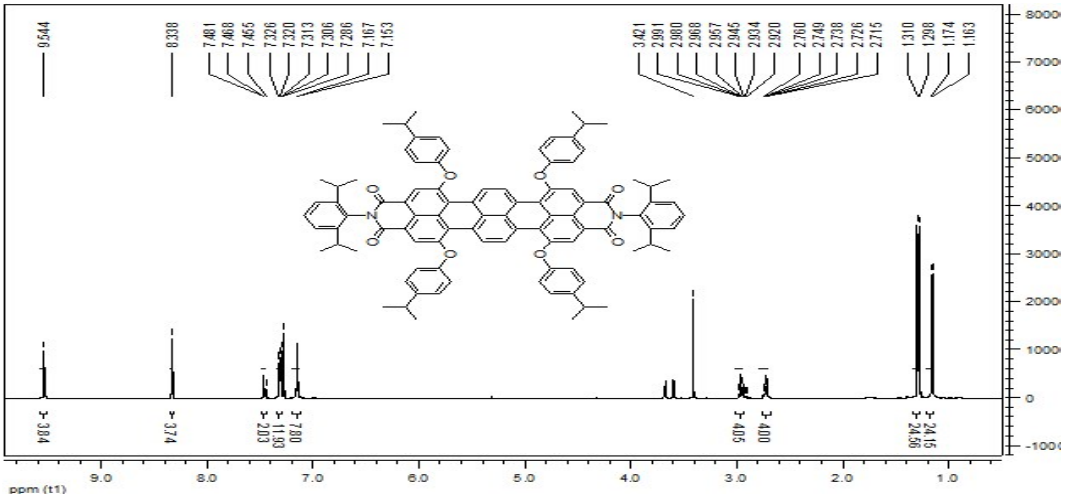


Figure S9 ^{1}H NMR (600 MHz) spectra of TDI4OE in $CDCl_3$