

Simple diphenylamine based D- π -A type sensitizers/co-sensitizers for DSSCs: A comprehensive study on the impact of anchoring groups

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1. Materials and methods

General:

All the starting materials and reagents were procured from Sigma Aldrich, Alfa-aesar and Spectrochem companies. They were used without purifying further. All the solvents were dried prior to use. The reaction progress was monitored by TLC technique. The target molecules and intermediates were purified by column chromatography and recrystallization. All column chromatographic separations were carried out on Merck silica gel. ^1H and ^{13}C -NMR spectra were run on a BRUKER spectrometer in deuterated chloroform or dimethyl sulfoxide solution at 298 K. Chemical shifts (δ values) were recorded in units of ppm relative to tetramethylsilane (TMS) as an internal standard. ATR-FTIR spectra were measured with Bruker Alpha instrument equipped with a Silicon Carbide as IR source. Data acquisition was done on an attenuated total reflectance accessory made up of Zinc selenide crystal. Absorption and fluorescence spectra were measured in chloroform solution on Analytik Jena Specord S600 Spectrophotometer and JASCO FP6200, respectively. Electrochemical measurements were performed on an IVIUM VERTOSTAT electrochemical workstation. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum disc working electrode, a glassy carbon (GC) working electrode, and an Ag/AgCl was used as the reference electrode. The potentials were reported vs ferrocene as standard at a scan rate of 100 mV/s using 0.1 M tetra *n*-butyl ammonium hexafluorophosphate ($(n\text{-Bu})_4\text{N}^+(\text{PF}_6)^-$) as a supporting electrolyte in acetonitrile under Argon atmosphere. Mass spectra were recorded on Thermo Scientific-EXACTIVE (ESI-MS). The DFT calculations were performed using Turbomole, V 7.2 software package. The DSSCs were fabricated using the standard dye alone and were further co-sensitized with N3 dye in presence of chenodeoxycholic acid (CDCA) as a co-adsorbent on the TiO_2 photoanode. The Doctor Blade method was used for fabrication and its details are given in electronic supplementary information. The IPCE experiments were conducted for the fabricated devices using a spectral response measurement system (QEX10, PV Measurements). Finally, the electrochemical impedance spectroscopy (EIS) measurements were obtained over a frequency range of 100 mHz to 200 kHz at 298K with the Bio-Logic SP-150 impedance analyser under the illumination of light using a solar simulator (SOL3A, Oriel) equipped with a 450 W Xenon lamp (91160, Oriel). The applied voltage was set at the

V_{OC} of the DSSCs with AC amplitude fixed at 10 mV. The obtained plots were fitted *via* Z-Fit software (Bio-Logic). Also, IPCE (Incident photon conversion efficiency) spectra of all the fabricated DSSCs were recorded using QEX10PV measurement system.

Photoelectrochemical Measurements:

Photocurrent-voltage characteristics of DSSCs were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (100 mW/cm²). The measurement was fully controlled under Oriel IV Test Station software.

IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochromator. Calibration of incident light was performed before measurements using a silicone photodiode (IF035, PV Measurements). All the measurements were carried out without the use of anti-reflecting film.

2. Synthetic methods

(E)-2-(5-Formylthiophene-2-yl)-3-(4-(hexyl(phenyl)amino)phenyl)acrylonitrile (5)

Freshly distilled DMF (0.8 mL, 10.33 mmol) was taken in a two necked round bottomed flask to which POCl₃ was added drop-wise (0.96 mL, 10.33) at 0 °C under nitrogen. The reaction mixture was stirred for 30 minutes and to this compound **4** (4.1 g, 2.5 mmol) dissolved in dichloroethane (5 mL) was added while stirring which was allowed to stir at room temperature for 15 hours. The reaction mass was then poured into ice cold water and subsequently basified using 5 M NaOH solution. The product was extracted using ethyl acetate (3×50 mL). The organic phase was dried using anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product obtained was further purified by column chromatography on silica gel (100-200 mesh) using *n*-hexane as an eluent yielded a bright red viscous liquid as the product. Yield: 80%. ¹H NMR (CDCl₃, 400 MHz, δ ppm): 9.82 (1H, s), 7.88-7.86 (2H, d (J=8 Hz)), 7.76-7.73 (2H, d (J=12 Hz)), 7.38-7.37 (1H, d (J=4 Hz)), 7.34 (1H, s), 7.31-7.29 (2H, d (J=8 Hz)), 7.23-7.21 (2H, d (J=8 Hz)), 7.09-7.07 (1H, t (J=4 Hz)), 7.01-6.98 (2H, d (J=12 Hz)), 3.83-3.79 (2H, t (J=8 Hz)), 1.74-1.67 (2H, p),

1.32-1.24 (6H, m), 0.90-0.87 (3H, t (J=4 Hz)). **FT-IR (ATR)**, ν cm^{-1} : 3072-2733 (C-H), 2212 (C \equiv N), 1665 (C=O), 1567 (C=C); **Mass (m/z)**: 414; Obtained (M+H): 415.

4-(((E)-(5-(E)-1-Cyano-2-(4-(hexyl(phenyl)amino)phenyl)vinyl)thiophen-2-yl)methylene)amino)benzoic acid (DTP)

A mixture of compound **5** (0.5 g, 1.2 mmol) and 4-aminobenzoic acid (0.18 g, 1.3 mmol) was heated to reflux in absolute methanol for 3 hrs. The separated solid was filtered at room temperature and recrystallized from methanol to obtain bright red colour solid. Yield 77%. **¹H NMR** (CDCl₃, 400 MHz, δ ppm): 8.50 (1H, s), 8.14-8.12 (2H, d(J=8 Hz)), 7.76-7.75 (2H, d (J=4 Hz)), 7.45-7.41 (3H, m), 7.37 (1H, s), 7.30-7.27 (3H, m), 7.25 (1H, s), 7.22 (1H, s), 7.21 (1H,s), 6.74-6.72 (2H, d (J=8 Hz)), 3.74-3.71 (2H, t (J=8 Hz)), 1.73-1.67 (2H, p), 1.36-1.30 (6H, m), 0.90-0.87 (3H, t (J=8Hz)). **¹³C NMR** (CDCl₃, 100 MHz, δ ppm): 162.01, 149.92, 149.32, 145.65, 140.38, 139.91, 137.43, 136.17, 130.36, 126.51, 125.69, 125.12, 123.29, 121.78, 120.97, 120.55,116.99, 116.30, 112.64, 109.21, 92.83, 46.76, 26.07, 21.97, 20.95, 17.13, 8.92. **FT-IR (ATR)**, ν cm^{-1} : 3467 (O-H), 3026 (C-H), 2211 (C \equiv N), 1677 (C=O), 1602 (C=C), 1569 (C=N); **Mass (m/z)**: 533.21; Obtained (M+H): 534.00.

(Z)-3-(5-((E)-1-cyano-2-(4-(hexyl(phenyl)amino)phenyl)vinyl)thiophen-2-yl)-2-(4-nitrophenyl)acrylonitrile (DTN)

A few drops of piperidine was added to the mixture of 4-nitrophenylacetonitrile (0.2 g, 1.233 mmol) with compound **5** (0.5g, 1.2mmol) in dry ethanol (15 mL) under nitrogen atmosphere. The reaction mixture was refluxed for about 3 hours. The reaction mass allowed to cool to room temperature and the product was extracted using ethyl acetate (3 \times 50 mL). Organic phase was dried using anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product obtained was further purified by column chromatography on silica gel using hexanes to yield the red solid. **¹H NMR** (CDCl₃, 400 MHz, δ ppm): 8.26-8.24 (2H, d (J=8 Hz)), 7.83-7.76 (4H, dd (J=16 Hz)), 7.52 (1H, s), 7.46-7.43 (2H, t (J=8Hz)), 7.30-7.22 (4H, m), 6.75-6.73 (2H, d (J=8 Hz)), 3.75-3.72 (2H, t (J=4 Hz)), 1.72-1.68 (2H, p), 1.35-1.31 (6H, m), 0.90-0.87 (3H, t (J=4 Hz)). **¹³C NMR** (CDCl₃, 100 MHz, δ ppm):151.36, 146.91, 145.13, 145.71, 141.95, 132.02, 130.09, 127.33, 126.34, 125.78, 124.29, 122.0, 118.62, 114.03, 102.25, 52.67, 31.60, 27.35, 26.67, 22.66, 14.04. **FT-IR (ATR)**, ν cm^{-1} : 2915, 2848 (C-H), 2200 (C \equiv N), 1567, (C=C), 1503 (N=O), 1178 (C=N). **Mass (m/z)**: 558.21; Obtained (M+H): 559.12.

(E)-3-(4-(hexyl(phenyl)amino)phenyl)-2-(5-((2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene)methyl)thiophen-2-yl)acrylonitrile (**DTB**)

To a dry 100 mL RB flask, a mixture of compound **5** (0.5 g, 1.2 mmol) and barbituric acid (0.160 g, 1.25 mmol) was added. This mixture was dissolved in 20 mL of absolute methanol and then refluxed for 10 hours under argon atmosphere. The reaction completion was monitored by TLC technique. After reaction completion, the content was cooled down to room temperature; the solid obtained was collected by filtration and dried. The product was recrystallized from methanol to yield the pure compound. Yield 85%. **¹H NMR** (DMSO-*d*₆, 400 MHz, δ ppm): 11.32, (1H, s), 11.22 (1H, s), 11.09 (1H, s), 8.38-8.36 (1H, d (J=8 Hz)), 8.18 (1H, s), 8.01-7.99 (1H, d (J=8 Hz)), 7.92-7.88 (1H, t (J=8 Hz)), 7.80 (1H, s), 7.70-7.69 (1H, J=4 Hz), 7.51-7.42 (2H, m), 7.33-7.29 (1H, t (J=8 Hz)), 7.21-7.19 (1H, t (J=4 Hz)), 6.97-6.95 (1H, d (J=8 Hz)), 6.81-6.78 (1H, d (12 Hz)), 3.92-3.88 (2H, t (J=8 Hz)), 1.64-1.59 (2H, p (J=4 Hz)), 1.36-1.25 (6H, m), 0.86-0.83 (3H, t (J=4 Hz)); **¹³C NMR** (DMSO, 100 MHz, δ ppm): 164.74, 162.87, 155.24, 150.74, 150.68, 139.09, 138.48, 135.66, 132.50, 131.23, 130.59, 128.94, 128.11, 127.44, 126.98, 125.61, 123.72, 115.96, 114.39, 103.99, 97.63, 52.23-52.10, 31.46-31.43, 27.56-27.35, 26.33-26.29, 22.52, 14.31; **FT-IR (ATR)**, ν cm⁻¹: 3171 (N-H stretch), 2918, 2845 (C-H stretch), 2211 (C \equiv N stretch), 1690, 1658 (C=O stretch), 1605 (C=C), 1174 (C-N stretch); **Mass (m/z)**: 524.12; Obtained (M+H): 525.12.

3. FTIR Spectra

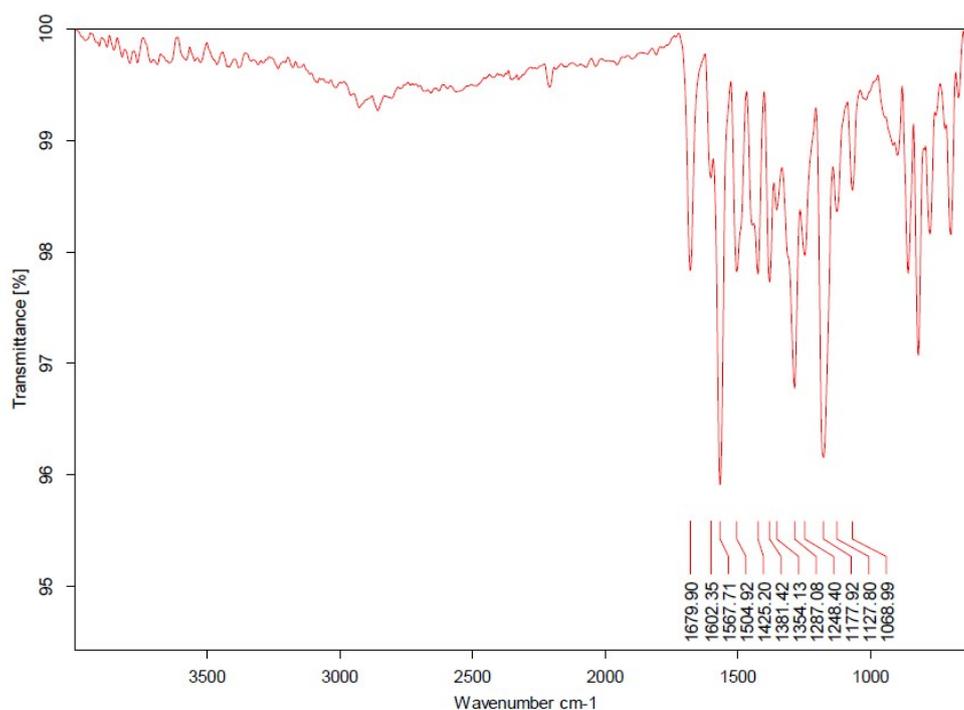


Figure S1: FT-IR spectrum of **DTB**.

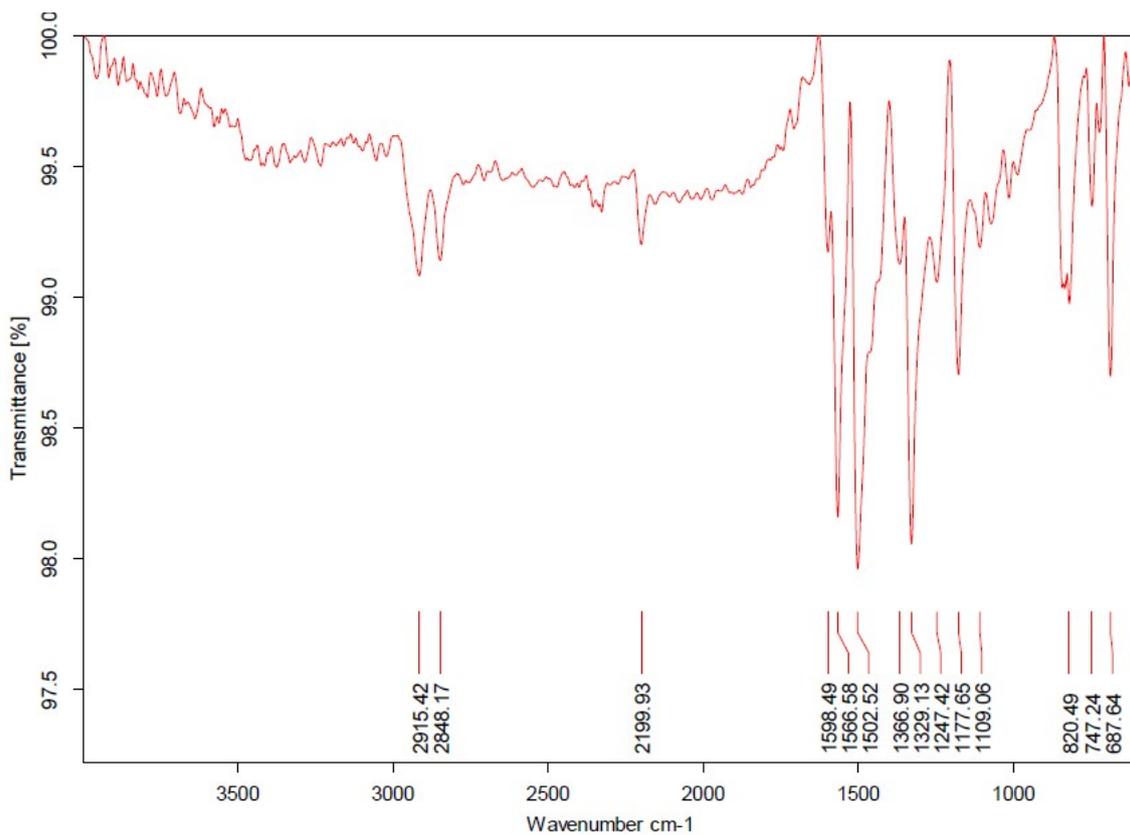


Figure S2: FT-IR spectrum of DTN.

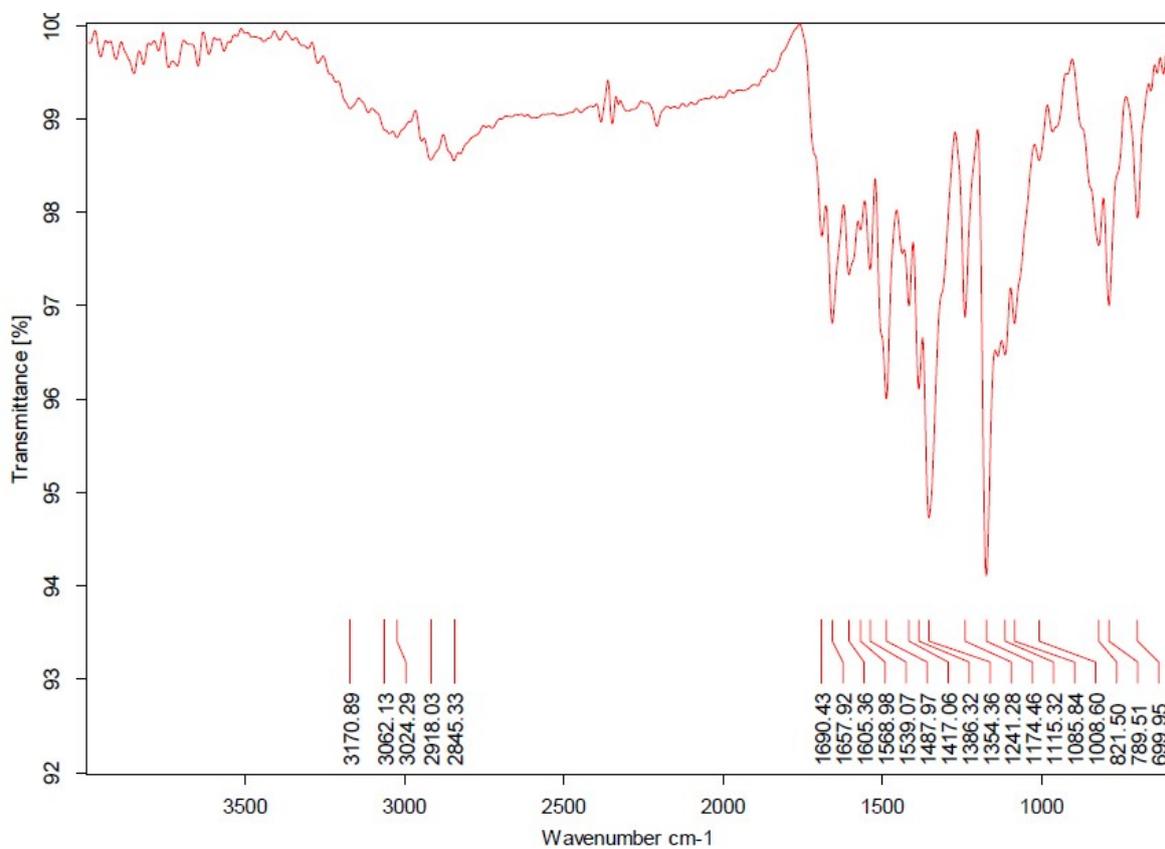


Figure S3: FT-IR spectrum of DTB.

4. ^1H -NMR spectra

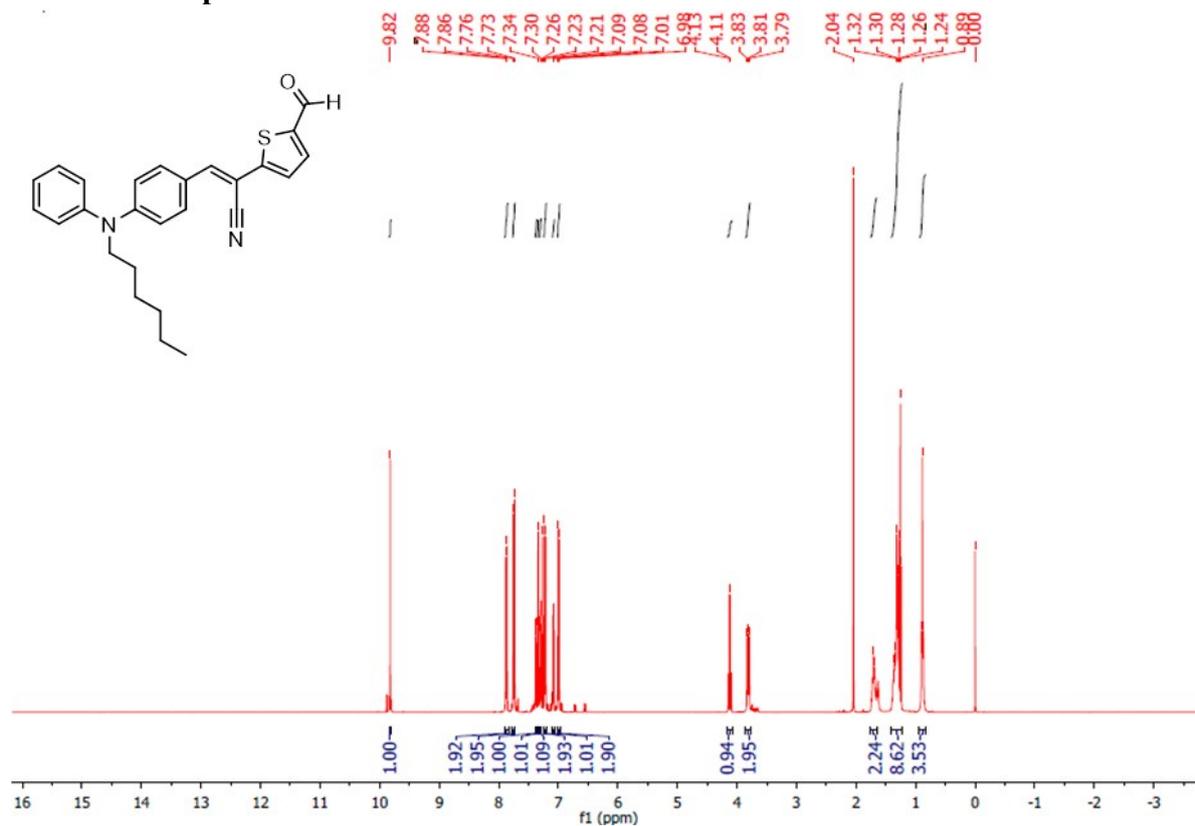


Figure S4: ^1H NMR spectrum of **compound 5** recorded in CDCl_3 .

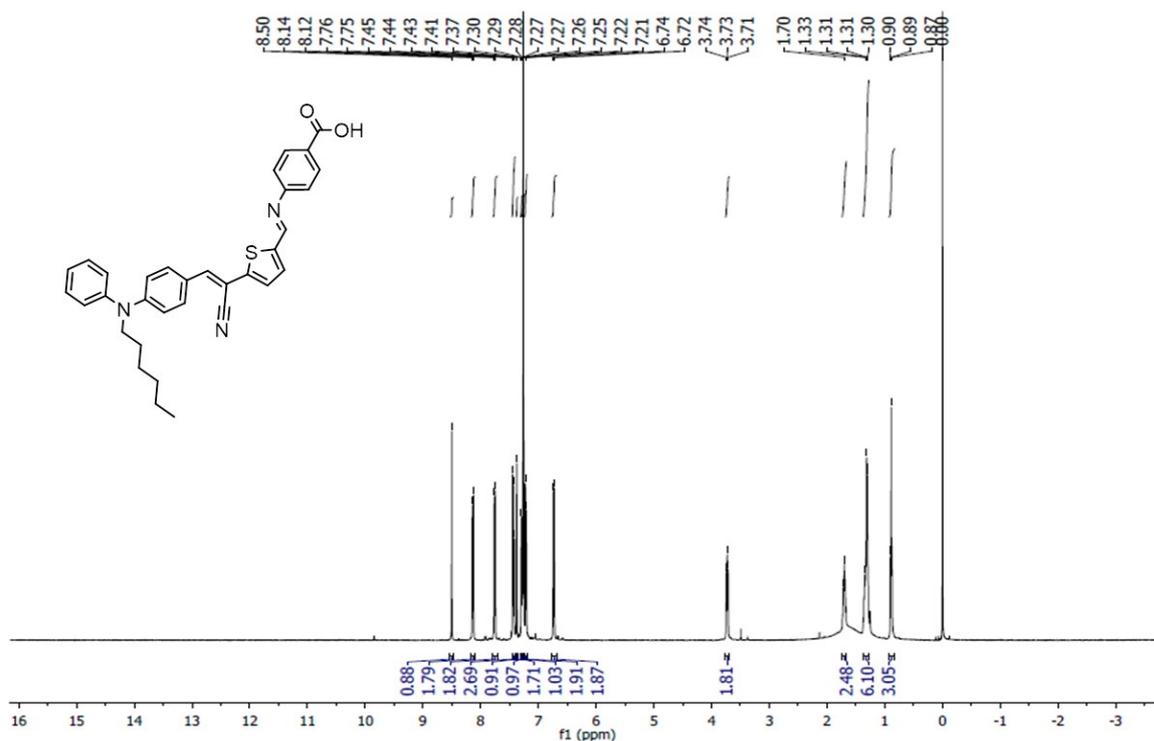


Figure S5: ^1H NMR spectrum of **DTP** recorded in CDCl_3 .

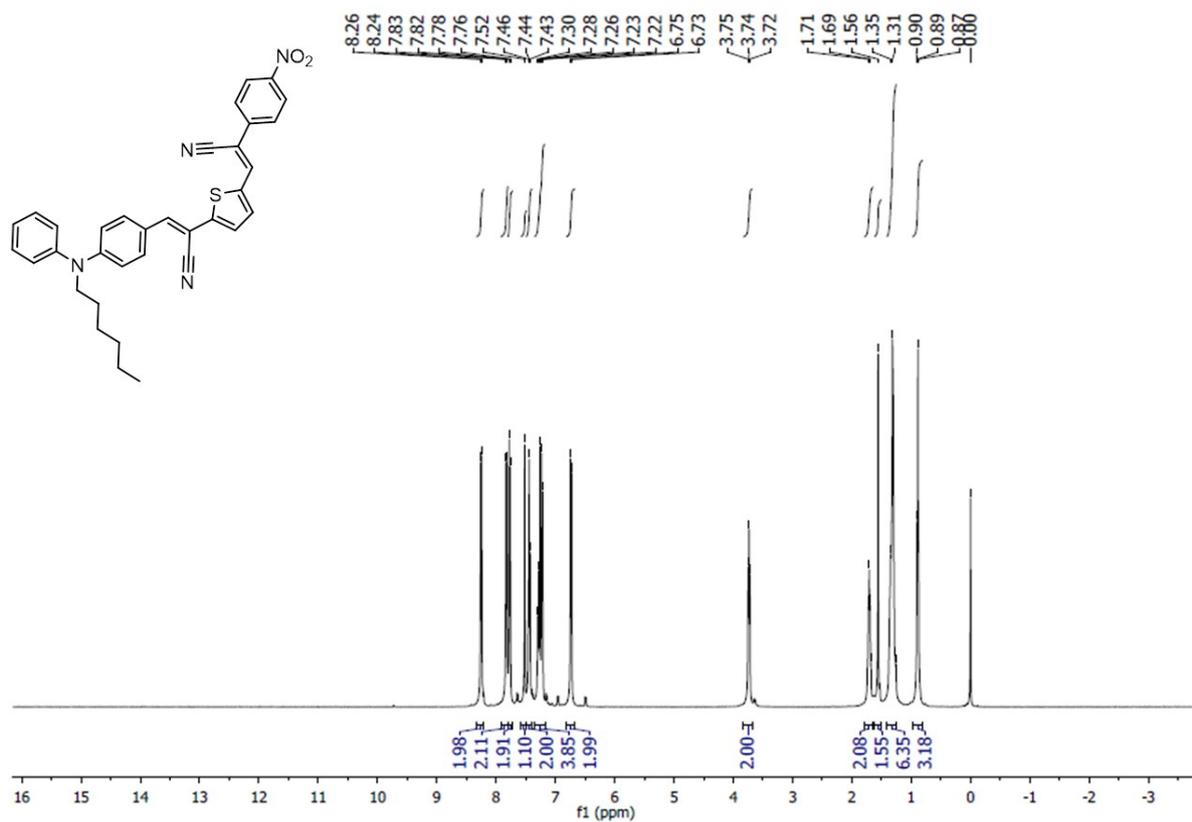


Figure S6: ¹H NMR spectrum of DTN recorded in CDCl₃.

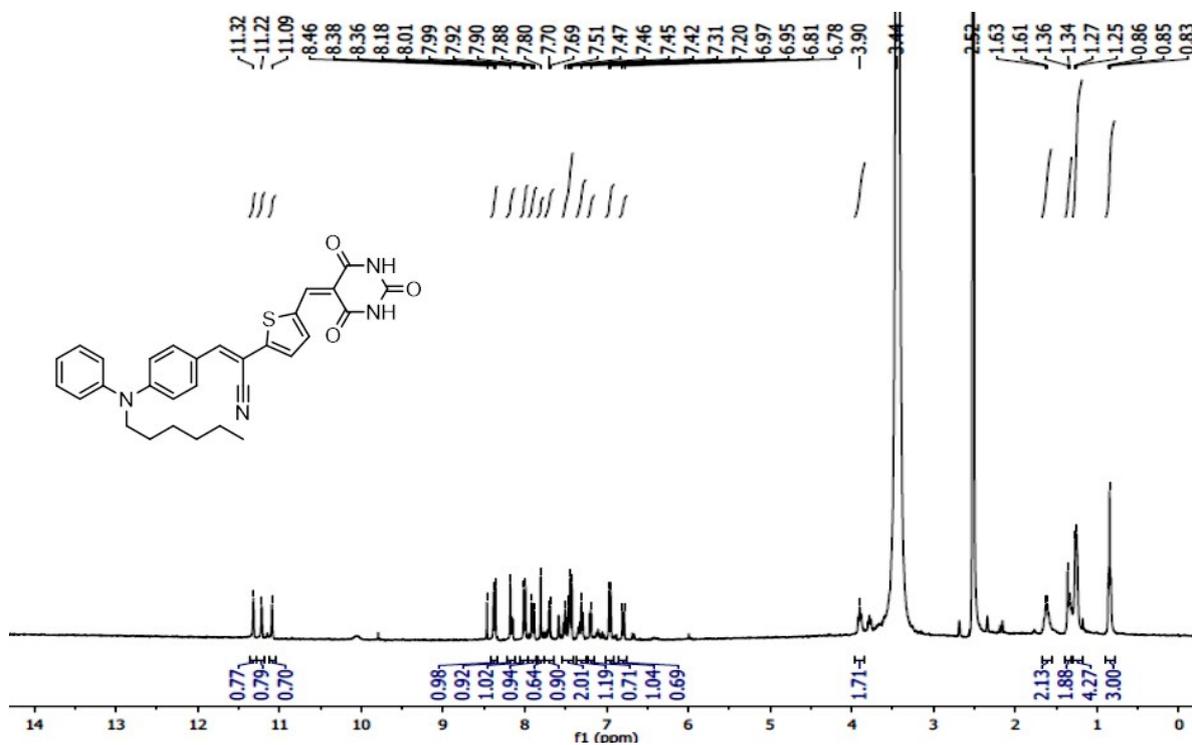


Figure S7: ¹H NMR spectrum of DTB recorded in DMSO-d₆.

5. ^{13}C -NMR Spectra

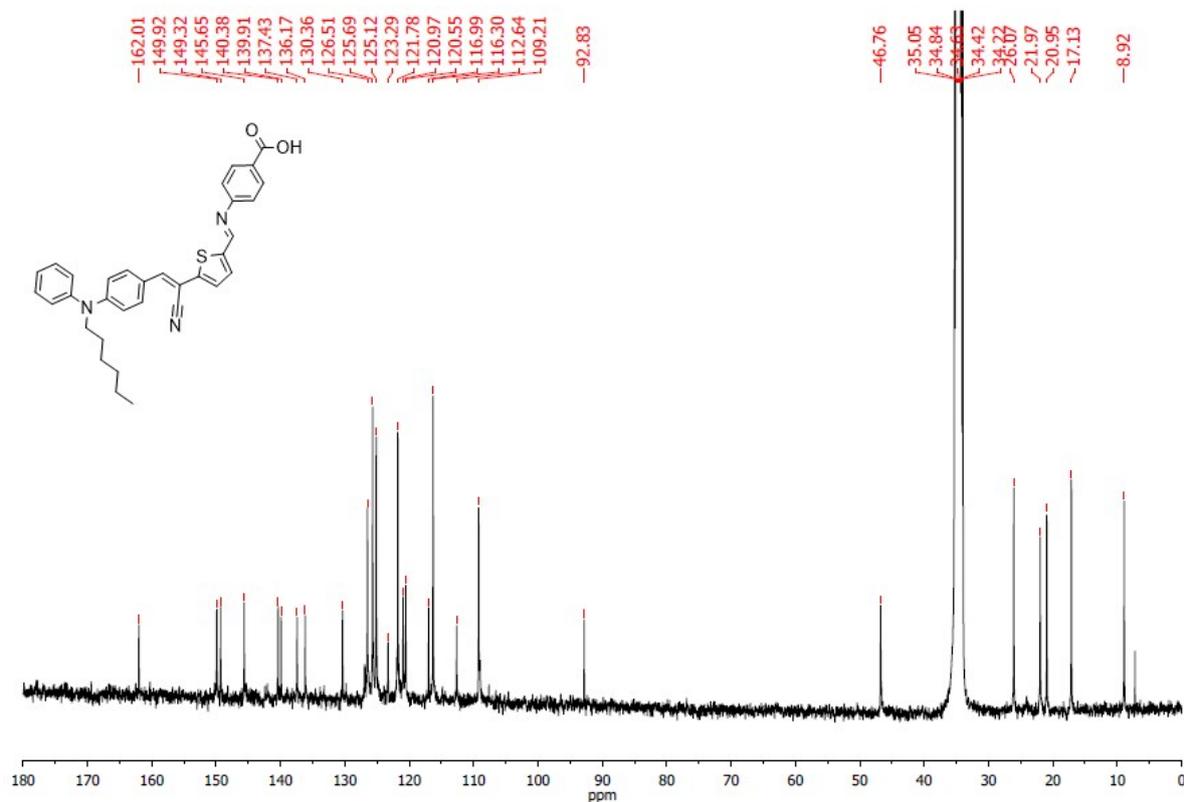


Figure S8: ^{13}C NMR spectrum of DTP recorded in CDCl_3 .

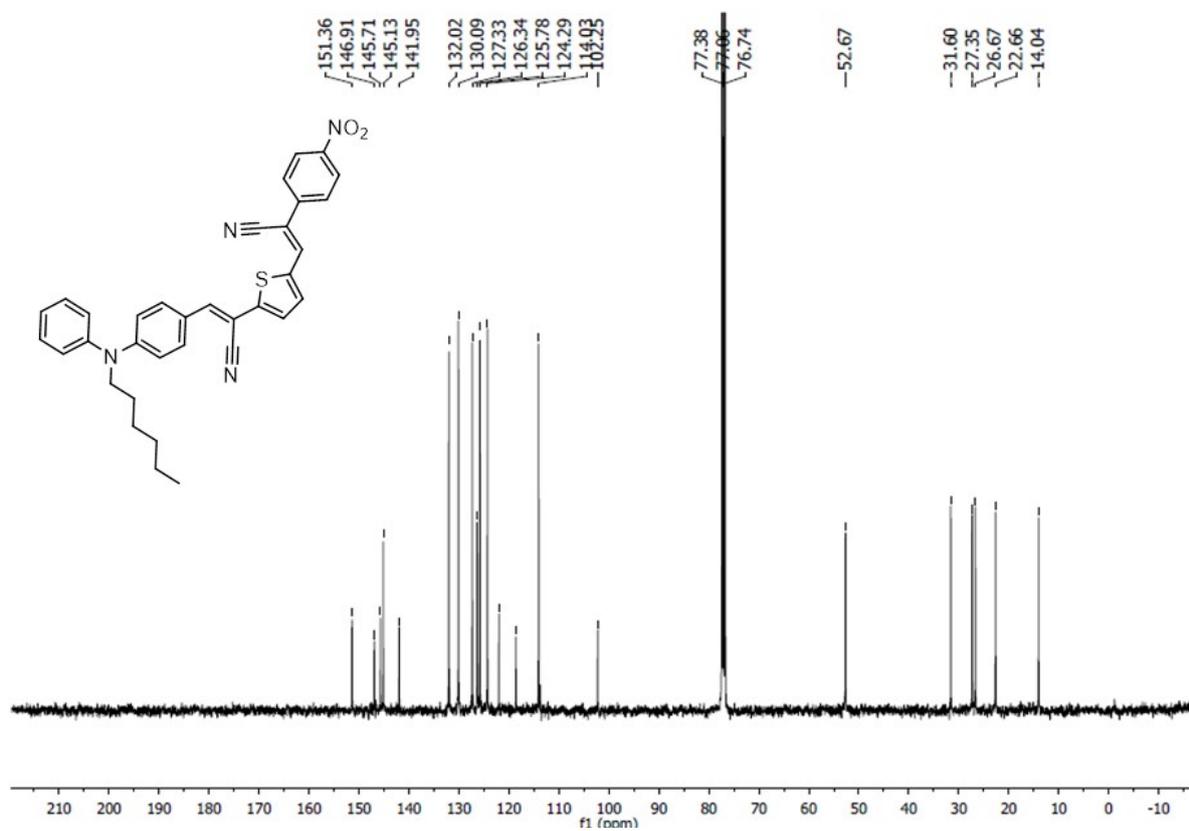


Figure S9: ^{13}C NMR spectrum of DTN recorded in CDCl_3 .

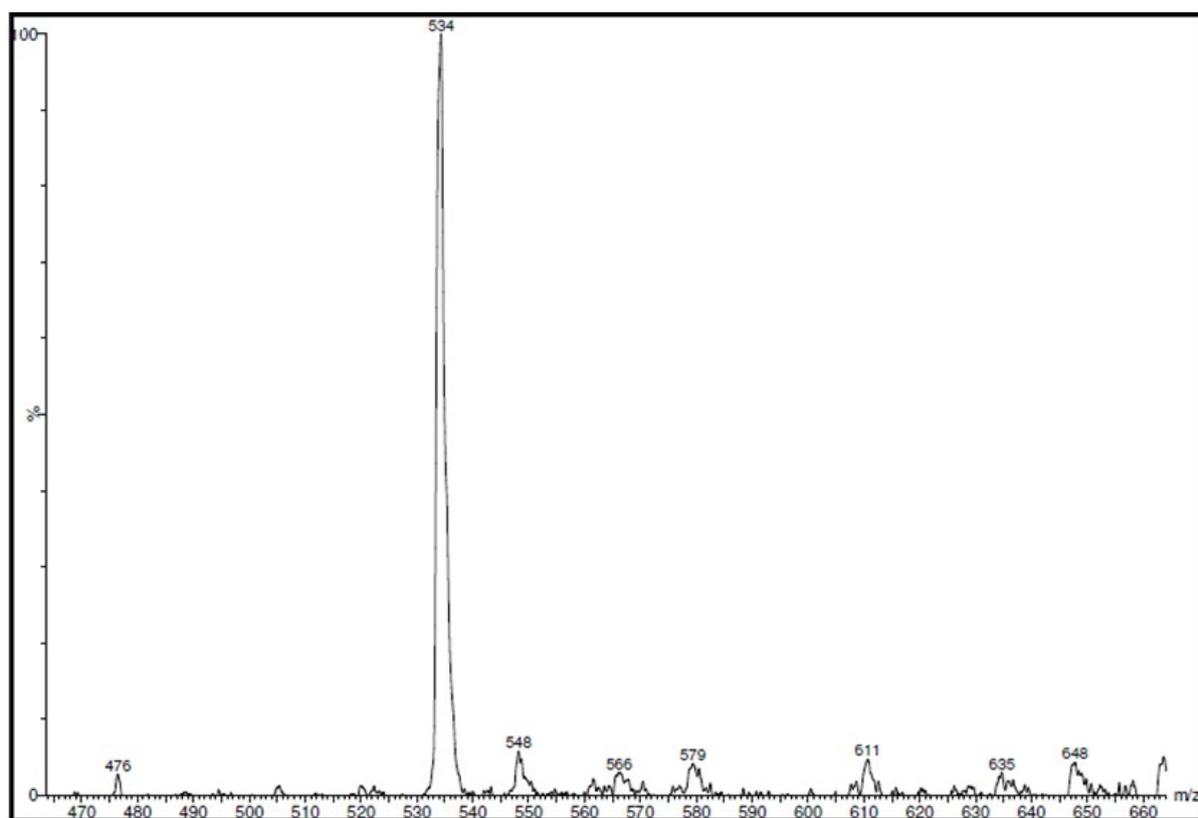


Figure S12: Mass spectrum of DTP.

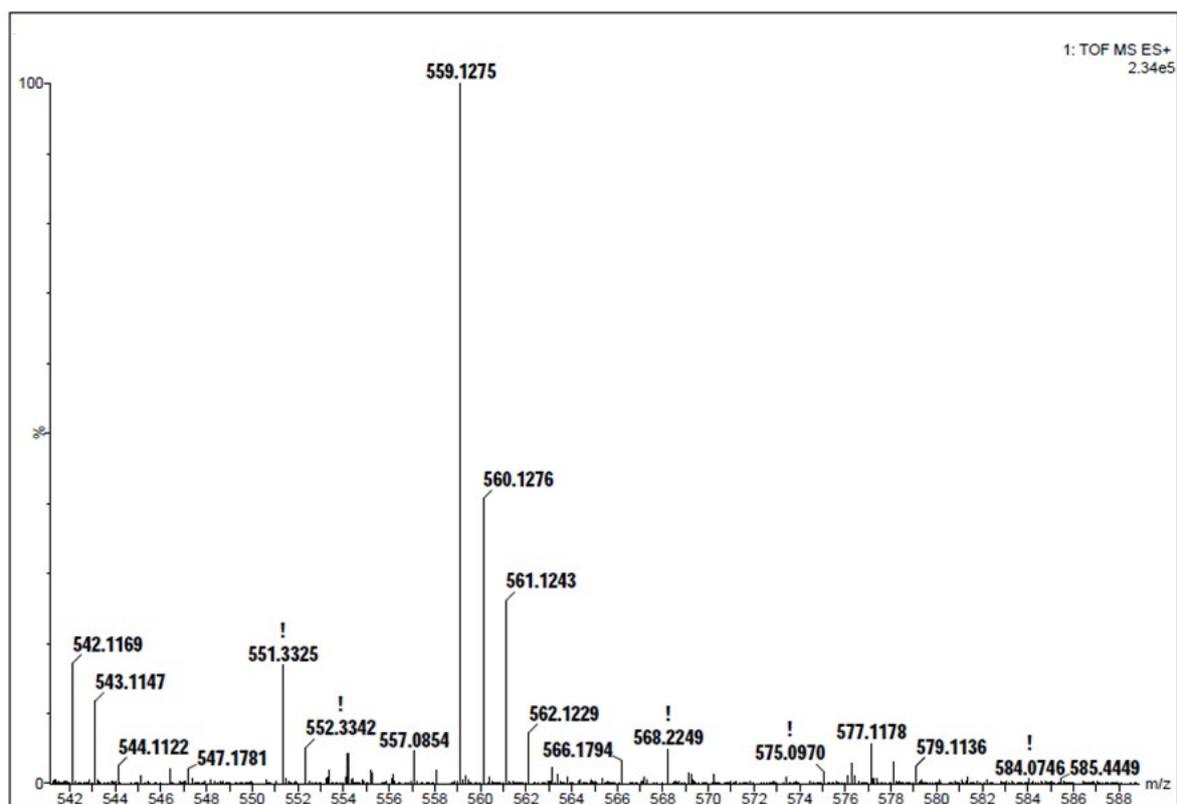


Figure S13: Mass spectrum of DTN.

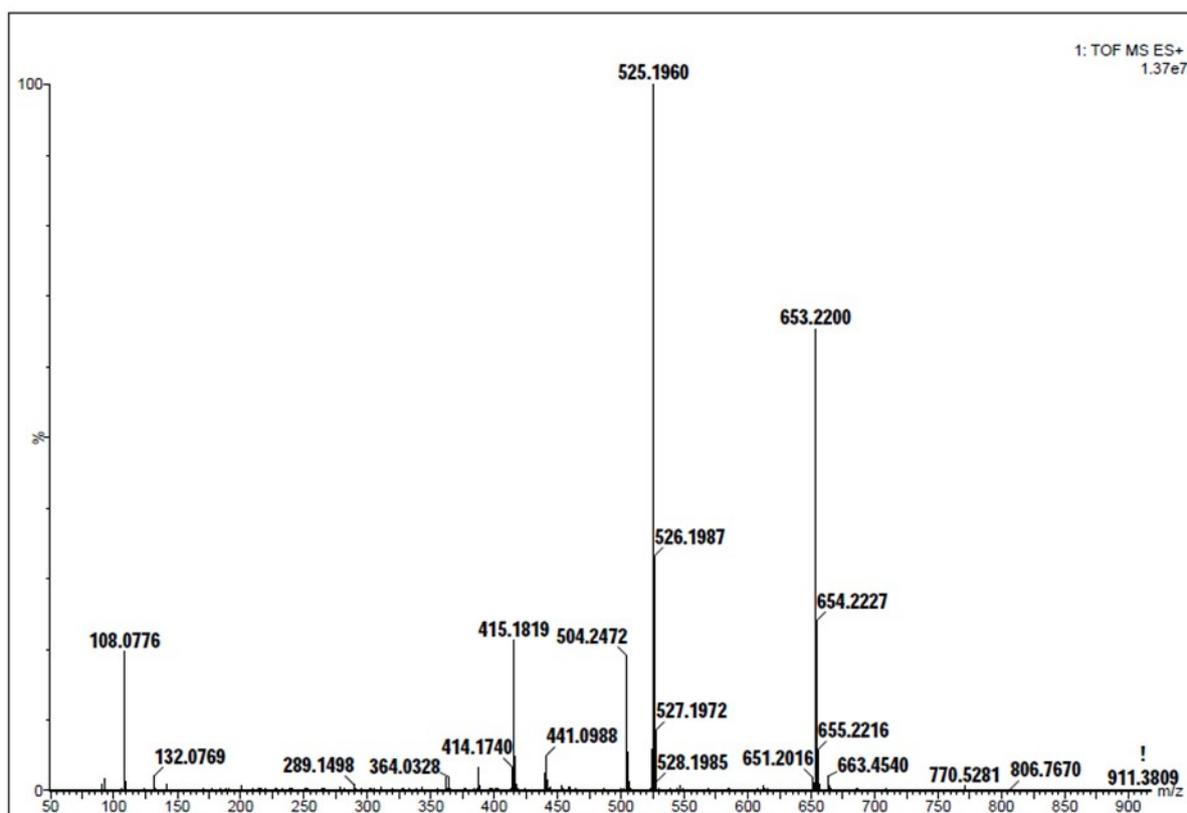


Figure S14: Mass spectrum of DTB.

7. DOS plots

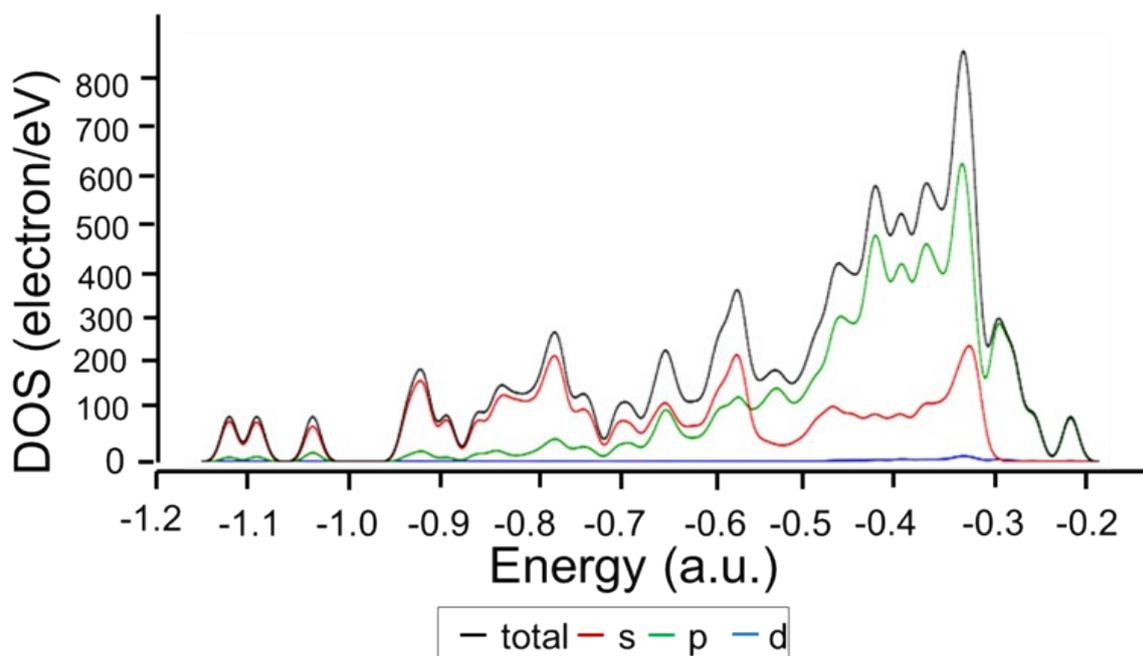


Figure S15: DOS plot of DTP.

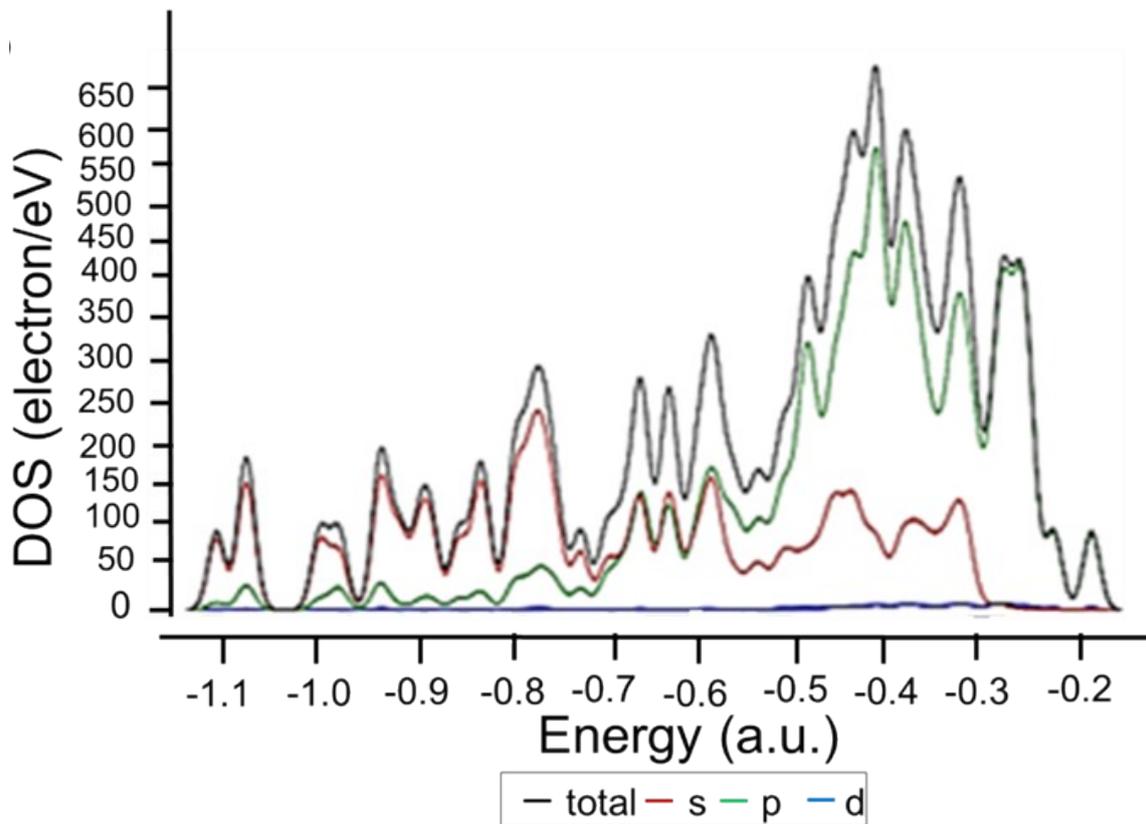


Figure S16: DOS plot of DTN.

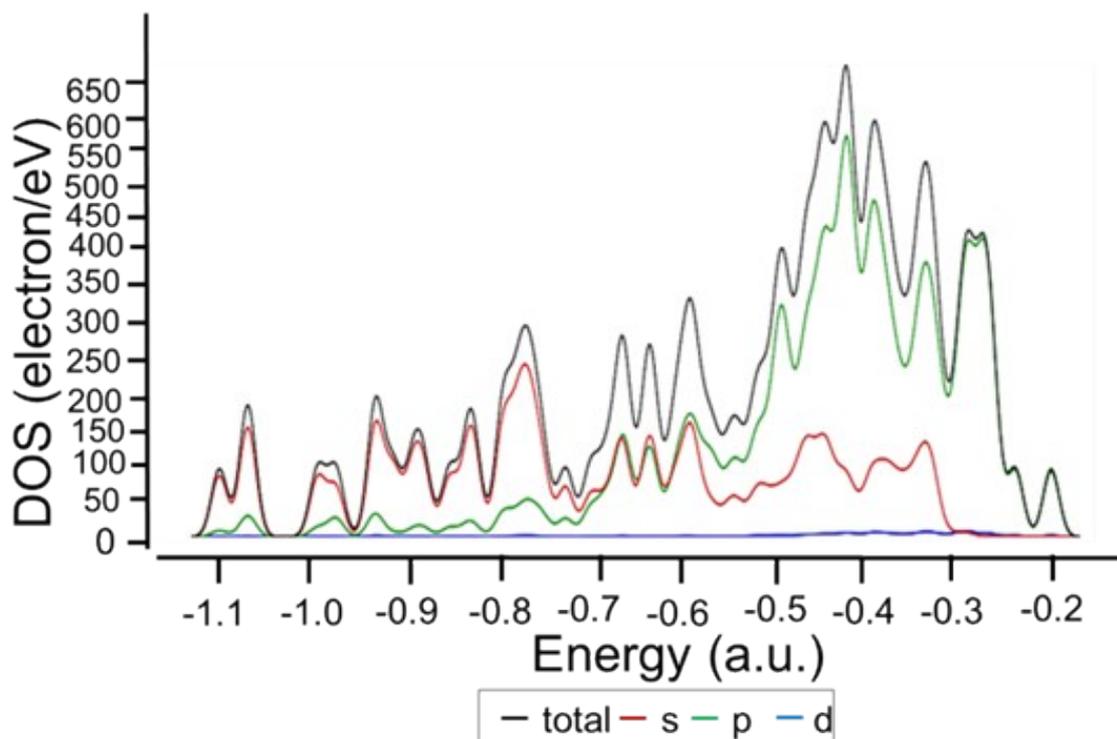


Figure S17: DOS plot of DTB.

8. Cyclic Voltammograms

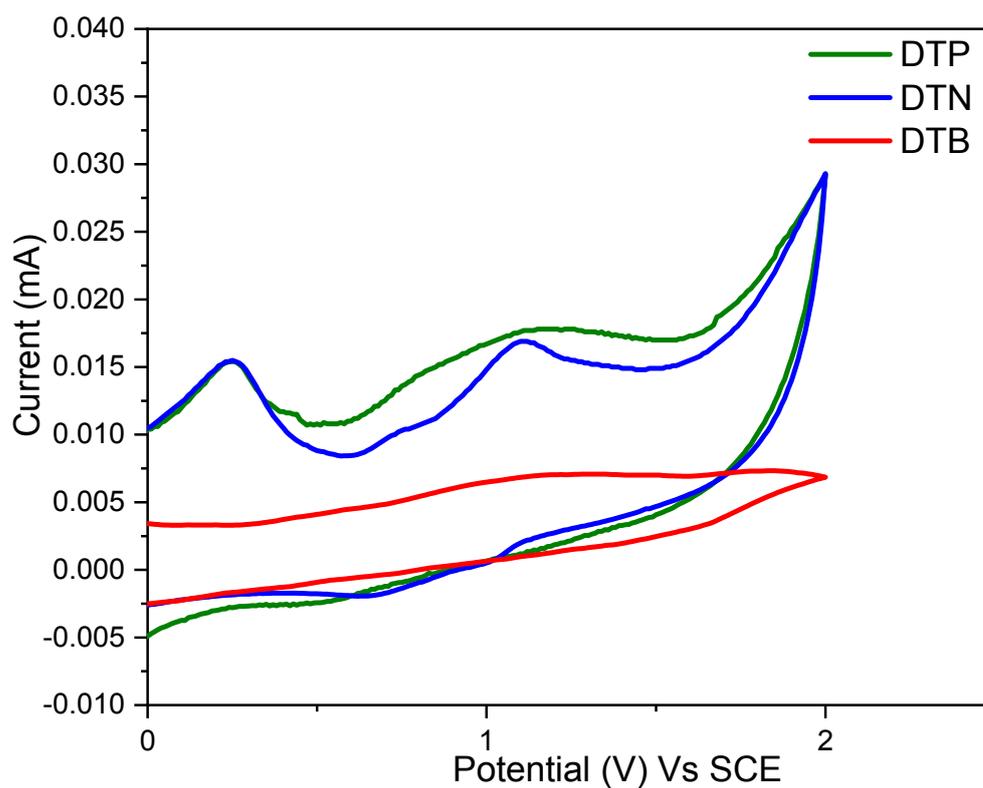


Figure S18: Cyclic voltammograms of **DTP**, **DTN** and **DTB**.

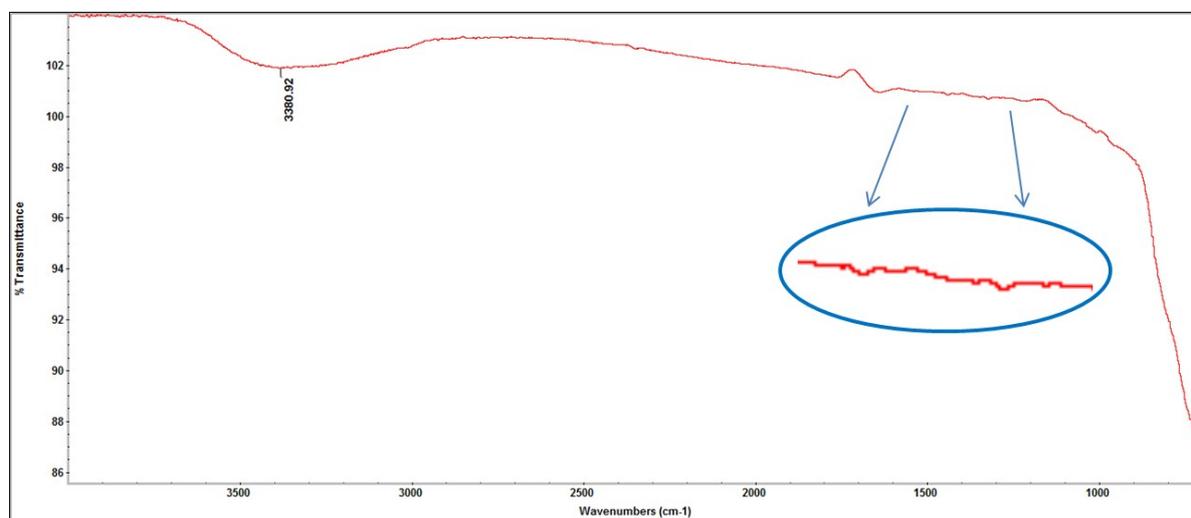


Figure S19: FTIR spectra of **DTN** adsorbed on TiO₂ surface

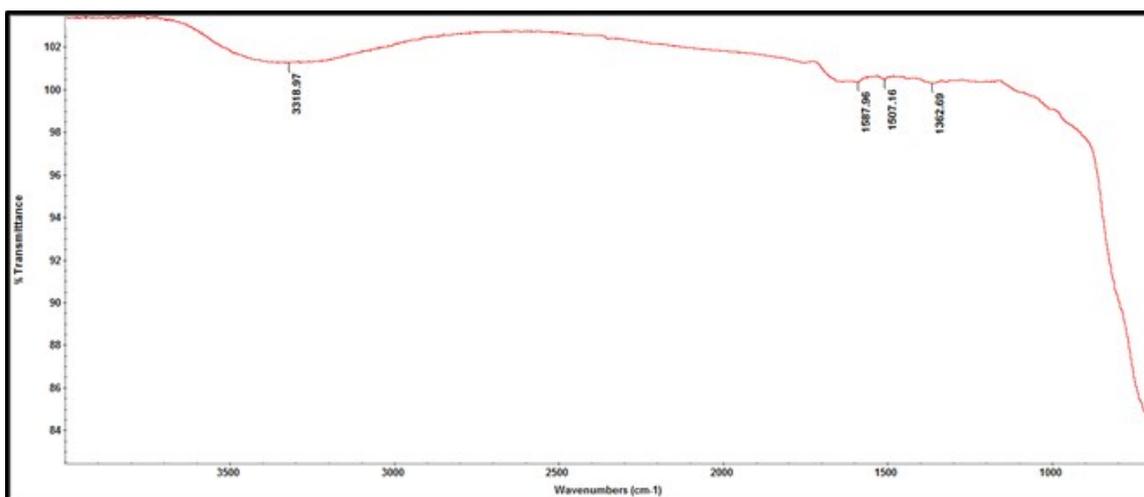


Figure S20: FTIR spectra of **DTB** adsorbed on TiO₂ surface

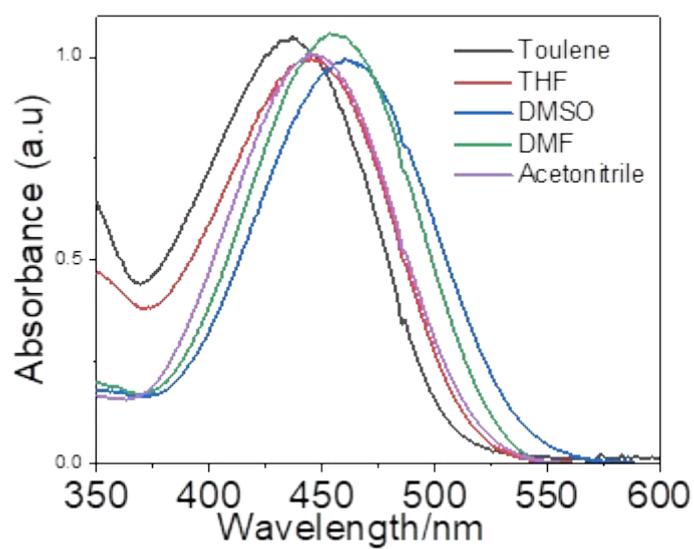


Figure S21: Absorbance spectra of **DTN** in solvents different polarity

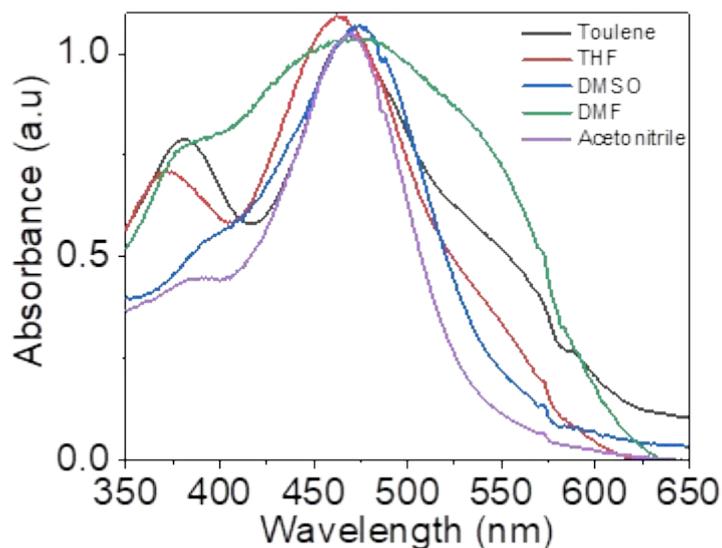


Figure S22: Absorbance spectra of **DTB** in solvents different polarity

9. Device fabrication procedure

TiO₂ Electrode Preparation and Device Fabrication:

Etched Fluorine doped tin oxide (2.2 mm thickness, sheet resistance of 8 Ω/cm^2 , TEC, Pilkington)) substrates were cleaned with detergent, water, acetone and ethanol, sequentially. These substrates were then immersed in 40 mM of TiCl₄ solution (Wako Pure Chemical Industries, Ltd) for 30 min at 70 °C, followed by rinsing with water and ethanol. The substrates were held at 500 °C for 30 min to allow formation of TiO₂ crystals to serve as the seed layer. Using a screen-printer, a layer of compact TiO₂ paste (Solaronix, Ti-Nanoxide D/SP) is printed onto the substrate (active area, 0.18 cm²) using squeegee printing setup. The printed film is allowed for drying at 350 °C for 10 min and curing at 500 °C for 30 min. Next, after drying the electrodes, scattering layer (5 μm thick) TiO₂ particles (Solaronix, Ti-Nanoxide R/SP) were printed onto the already deposited TiO₂ layer. The TiO₂ electrodes were heated under an air flow at 350 °C for 10 min, followed by heating at 500 °C for 30 min. After cooling to room temperature, these substrates were finally immersed in 40 mM of TiCl₄ solution for 30 min at 70 °C to fill up the defective “pin-holes”, followed by rinsing with water and ethanol. The electrodes were heated again at 500 °C for 30 min and left to cool to 80 °C before dipping them into the dye solution. The dye solutions (0.3 mM) were prepared in 10 mL 1:1:1 acetonitrile, *tert*-butanol and dimethyl sulfoxide. Chenodeoxycholic

acid (CDCA) was added at a concentration of 10 mM. The electrodes were immersed in the dye solutions and then kept at 25 °C for 20 hours to adsorb the dye onto the TiO₂ surface.

To prepare the counter electrode, pre-cut TCO glasses were washed with water followed by 0.1 M HCl in EtOH, and sonication in acetone bath for 10 min. These washed TCO were then dried at 400 °C for 15 min. Thin layer of Pt-paste (Solaronix, Platisol T/SP) on TCO was printed and the printed electrodes were then cured at 450 °C for 10 min. The dye sensitized TiO₂ electrodes were sandwiched with Pt counter electrodes and the electrolyte (Solaronix, Iodolyte HI-30) was then injected into the cell, while the two electrodes were held together with the clips.