

D- π -A Organic Dyes Derived from Indacenodithiophene Core Moiety for Efficient Dye-Sensitized Solar Cells

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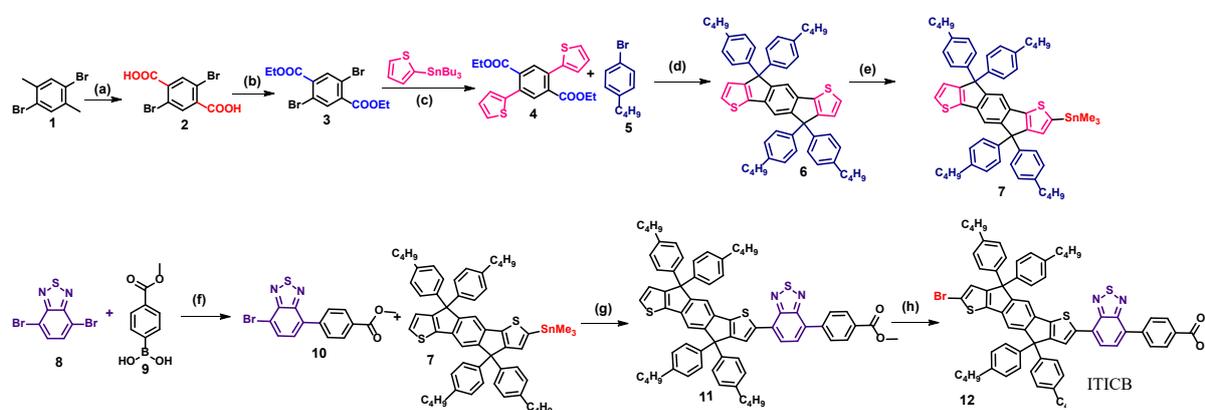
5. References:.....S**Error! Bookmark not defined.**

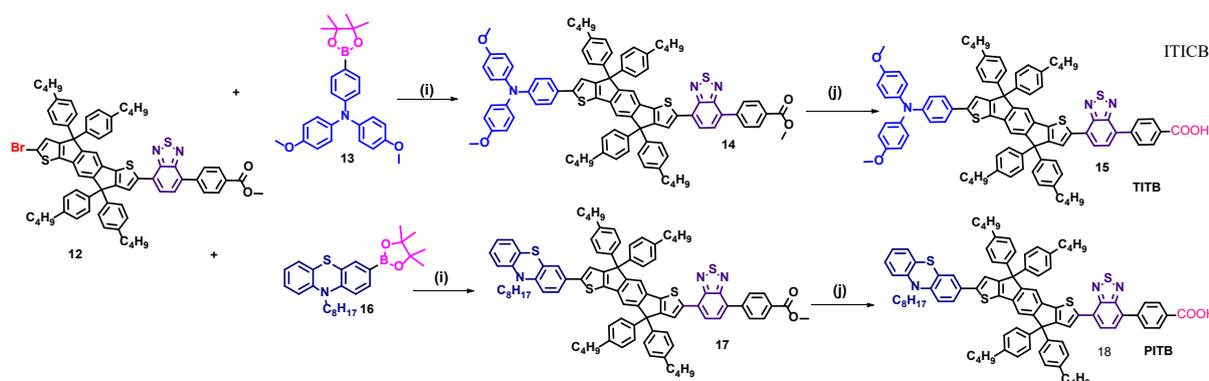
1. Materials and methods

All precursor materials were purchased directly from commercial sources and used as such without any further purification and solvents were dried under vacuum by following standard procedure. UV-vis spectrophotometer used to record absorption spectra in chloroform (CHCl_3) solution and for TiO_2 film. NMR (^1H and ^{13}C) spectra were measured with advance spectrometers at 300, 400, and 500 MHz, using tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were measured on a Shimadzu LCMS-2010 EV model with an ESI probe, and the final compounds were also characterized by using MALDI-TOF. Cyclic voltammetry was performed on CH-Instruments with a three-electrode system consisting of Ag/AgCl reference electrode, a working electrode, and a platinum wire counter-electrode. The redox electronic potentials of the dyes were measured in chloroform (CHCl_3) containing 0.1 M $\text{Bu}_4\text{NHClO}_4$ at a scan rate of 100 mV s^{-1} .

Device fabrication: The nc- TiO_2 layer was deposited on the FTO glass substrate via screen-printing and then annealed at 500°C for 30 min. After annealing, the electrodes were immersed in 2×10^{-4} M of PITB/TITB in the toluene for 3 hours (the digital photograph shown in Fig. 1). The PITB/TITB loaded electrodes were assembled with platinized FTO substrate using the surlyn polymer sheet (60 microns) and sealed at 100°C . The liquid electrolyte was prepared by adding the 0.05 M iodine, 0.1 M guanidine thiocyanate, 0.5 M 1-butyl-3-methylimidazolium iodide, and 0.5 M 4-tert-butyl pyridine in acetonitrile and injected into the device by vacuum backfilling technique. Subsequently, the performance of the device was measured under darkness and illumination of 100 mW cm^{-2} . After 3h, the power conversion efficiencies of the as-fabricated DSSCs were measured under simulated solar light conditions and in the dark (Newport, 94043A). All the mentioned solar cell performance values are the average from a sample of 10 cells.

2. Synthetic Scheme: Synthetic routes of compound **PITB** and **TITB** dyes.





Reagents and Conditions. (a) KMnO_4 , ${}^t\text{BuOH}$, 80% (b) H_2SO_4 , EtOH, 90% (c) $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-toly})_3$, THF, 80% (d) i) $-78\text{ }^\circ\text{C}$, nBuLi , THF ii) H_2SO_4 , HOAc, 45%, (e) i) $-78\text{ }^\circ\text{C}$, nBuLi , THF ii) SnMe_3Cl (f) Cs_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, Toluene:DMF (1:1), 65% (g) $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-toly})_3$, Toluene, 45% (h) NBS, CHCl_3 , 80% (i) $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , THF, $60\text{ }^\circ\text{C}$, 75%, (j) THF:MeOH, NaOH, Reflux, 4h, 65%.

3. Synthetic Procedure:

Synthesis of 2, 5-dibromo terephthalic acid (2): To a 500 mL round bottom flask was added 1, 4- dibromo-2, 5-dimethyl benzene 1 (18.0 g, 68.7 mmol), 1:1 (by volume) solution of tert-butyl alcohol and water (250 mL) and potassium permanganate (24.0 g, 151 mmol, 2.2 equiv.). The reaction mixture was refluxed for 18 hr. The mixture was allowed to cool to room temperature, HCl (12M, 30, mL) was added. The resulting precipitate was collected. The crude material was purified by recrystallization from hot ethanol to give white crystals (17.4 g, 80 %).

Synthesis of diethyl 2, 5 –dibromoterephthalate (3): Concentrated sulphuric acid (13.3 g, 6.0 mL) was added to the mixture of compound 2 (11.0 g, 34.0 mmol) and ethanol (100 mL). The mixture was stirred under reflux for 2 days. The solvent was removed by rota vapor and the residue was purified by column chromatography on silica gel eluting with dichloromethane to give a white solid. ${}^1\text{H}$ NMR (400MHz, DMSO-d_6) δ = 8.05 (s, 2H), 4.35 (q, 4H), 1.32 (t, 6H). ${}^{13}\text{C}$ NMR (125 MHz, DMSO-d_6) δ =163.995, 136.270, 135.130, 119.011, 62.270, 13.923.

Synthesis of diethyl 2,5-di(thiophene-2-yl) terephthalate (4): To a solution of 2-(tributylstannyl) thiophene (9.33 g, 25 mmol) and diethyl 2,5 dibromo terephthalate (3.80 g, 10 mmol) in THF (80 mL), tris(dibenzylideneacetone)dipalladium (0) (40 mg,) and tri-o-

tolylphosphine (80 mg) was added under nitrogen and then the mixture was stirred over night at 80 °C. After that reaction was quenched with 100 mL water and extracted with DCM. Then the combined organic solvent was washed with brine and dried over sodium sulphate. After removing the solvent, the compound was purified by column chromatography on silica gel using a mixture of DCM and hexane to get compound **4** as a light-yellow solid (3.0 g 80%). ¹H NMR (400MHz, CDCl₃) δ =7.81 (s, 2H), 7.39 (dd, j=4.9, 1.4 Hz, 2H), 7.11 (m, 4H), 4.22 (q, 4H), 1.16 (t, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.73, 140.51, 134.11, 133.47, 131.89, 127.37, 127.01, 126.51, 61.69, 13.85.

Synthesis of 4,4,9,9-tetrakis(4-butylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b] dithiophene (6): To a solution of 4-hexyl-1-bromobenzene (6.0 g, 25 mmol in THF (30 mL) at -78 °C was added n-BuLi (10 mL, 2.5 M in hexane) under nitrogen, then the mixture was kept stirring at -78 °C for 2 h. After that, a solution of compound (2.0 g, 5.2 mmol) in THF (20 mL) was added slowly and then stirred overnight at room temperature. Water was added to quench the reaction, and the mixture was extracted with dichloromethane. After the removal of solvent, the crude product was charged into a 250 mL flask, and acetic acid (100 mL) and conc. H₂SO₄ (2 mL) was added. Then the mixture was refluxed for 2 h. After adding water, the mixture was extracted with chloroform and washed with brine. The resulting crude compound was purified by silica gel to give a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ= 7.42 (s, 2H), 7.23 (d, 2H), 7.15 (d, 8H), 7.04(d, 8H), 6.99 (d, 2H), 2.55 (t, 8H), 1.58 (m, 10H), 1.29 (m, 7H), 0.87 (t, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 155.88, 153.43, 142.10, 141.32, 135.13, 128.31, 127.92, 127.41, 123.15, 117.51, 62.69, 35.27, 33.56, 29.75, 22.52, 14.01. MALDI-TOF calculated for C₅₆H₅₈S₂ (M⁺): 795.08 found: 796.18.

Synthesis of trimethyl (4,4,9,9-tetrakis(4-butylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b] dithiophene-2-yl) stannane (7): n-BuLi (1.1 mL, 2.5M in hexane) was added dropwise to a solution of compound **6** (1g, 1.1 mmol) in THF (20 mL) at -78 °C. The mixture was kept at -78 °C for 30 min. After cooling to -78 °C, trimethyl tin chloride (1.5 mL, 1M hexane) was added. The reaction was stirred overnight at room temperature and then quenched with water, extracted with hexane, and dried over sodium sulfate. After the removal of the solvent, ethanol was added to the mixture, and the precipitate was collected as a white solid (1.1 g, 82%). MALDI-TOF calculated for C₅₉H₆₆S₂Sn (M⁺): 958.26 found: 959.31.

Synthesis of methyl 4-(7-bromobenzo[c] [1,2,5] thiadiazol-4-yl) benzoate (10)¹

Synthesis of methyl 4-(7-(4,4,9,9-tetrakis(4-butylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6] dithiophene-2-yl) benzoate (11): In a 50 ml of single neck round bottom flask, a

mixture of compound **7** (0.10 g, 1 mmol) and compound **10** (0.35g, 0.9 mmol) in toluene (10 ml) added tris(dibenzylideneacetone)dipalladium (0) (1 mg) and tri-*o*-tolyl phosphine (2 mg) under nitrogen and then the mixture was stirred overnight at 80 °C. After that reaction was quenched with 10 mL water and extracted with DCM. Then the combined organic solvent was washed with brine and dried over sodium sulfate. After removing the solvent, the compound was purified by column chromatography on silica gel using a mixture of EtOAc and hexane to give the product (0.40 g, 35%). ¹H-NMR (400 MHz CDCl₃): δ=8.20(d, 2H), 8.07-7.91 (m, 5H), 7.75(d, 2H), 7.53 (s, 1H), 7.46 (s, 1H), 7.27 (d, 2H), 7.25 (d, 2H), 7.17(d, 4H), 7.10-7.06(m, 8H), 7.02 (d, 1H), 3.95(s, 3H), 2.57(t, 8H), 1.62-1.54(m, 7H), 1.40-1.25(m, 15H), 0.90(m, 12H). ¹³C-NMR (400 MHz CDCl₃): δ= 129.508, 128.694, 128.056, 127.990, 127.635, 127.514, 34.898, 33.181, 29.369, 22.132. MALDI-TOF calculated for C₇₀H₆₆N₂O₂S₃ M⁺ 1062.710 found: 1063.757.

Synthesis of methyl 4-(7-(7-bromo-(4,4,9,9-tetrakis(4-butylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6] dithiophene-2-yl) benzoate (12): In a 25 ml of a single neck round bottom flask charged with compound 11(0.040 g, 0.037 mmol) dissolved in chloroform and in another flask NBS (0.006g, 0.037mmol), dissolve in a small amount of chloroform added dropwise at 0 °C for 10 min. and left for overnight at rt. After that reaction was quenched with 10 mL water and extracted with DCM. Then the combined organic solvent was washed with brine and dried over sodium sulphate. The solvent was removed by reduced pressure and given the product (0.035 g, 82%). MALDI-TOF calculated for C₇₀H₆₅BrN₂O₂S₃ M⁺ 1141.346 found: 1142.404.

Synthesis of 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl) aniline (13)²: In a 100 ml of single neck round bottom flask a mixture of bromo triphenylamine (0.50 g 1.3 mmol), Bispinacolatodiborane (0.49 g 1.95 mmol), KOAc (0.637 g 6.5 mmol), in 1,4-dioxane (10 ml) was degassed before the addition of [PdCl₂(dppf)] (8 mg) and subsequent degassing for 30 min. the reaction was heated under argon at 80 °C overnight. After cooling to room temperature, the mixture was extracted with DCM and the organic phase was dried over anhydrous sodium sulphate. After removal of the solvent, the residue was purified by silica gel column chromatography eluted with 20% (Ethyl Acetate, Hexane) to give the product (0.40 g, 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.54 (m, 2H), 7.08 – 7.00 (m, 4H), 6.92 – 6.74 (m, 6H), 3.86 – 3.74 (m, 6H), 1.27 – 1.25 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 156.21, 151.40, 140.43, 135.78, 127.14, 126.41, 120.95, 119.56, 118.65, 114.74, 113.54, 83.54, 83.42, 55.50, 29.74, 25.06, 24.87.

Synthesis of methyl 4-(7-(7-(4-bis(4-methoxyphenyl)amino)phenyl)-4,4,9,9-tetrakis(4-butylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,66-b]dithiophen-2-yl)benzo[c]

[1,2,5]thiadiazol-4-yl)benzoate (14): In a 50 ml of one neck round bottom flask a mixture of compound 12 (0.056 g, 0.05 mmol), compound 13 (0.022 g, 0.05 mmol), K₂CO₃ (2M solution 1 mL), in THF (8 ml) was degassed for 15 min, before the addition of [Pd (PPh₃)₄] (3 mg) and subsequent degassing for 5 minutes. The reaction mixture was heated under argon at 65 °C for 24 hrs. After cooling to room temperature, the reaction was quenched with water, extracted with DCM and dried over sodium sulphate. After removal of the solvent, the crude product was purified by column chromatography with ethyl acetate/hexane and give the product (0.045 g, 65%) MALDI-TOF calculated for C₉₀H₈₃N₃O₄S₃ M⁺ 1365.636 found: 1366.702.

Synthesis of 4-(7-(7-(4-bis(4-methoxyphenyl)amino)phenyl)-4,4,9,9-tetrakis(4-butylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,66-b]dithiophen-2-yl)benzo[c]

[1,2,5]thiadiazol-4-yl)benzoic acid (15): In a 25 ml of one neck round bottom flask charged with compound 14 (0.045g 0.032mmol), dissolve into a mixture of THF: MeOH (5 mL:3.5mL) followed by addition of 1.5 mL 20% NaOH aqueous solution. The mixture was allowed to stir at 40 °C for 8h before quenching with 1N HCl (50 mL). The solution was extracted with DCM (50 x 2) and the organic phase dried over sodium sulphate. The solvent was removed under reduced pressure before purification by silica gel chromatography using DCM: Ethyl acetate=3:1 with few drops of acetic acid (2-3 drops per 100 mL) to yield dark red solid (0.025g, 57%).¹H-NMR (400 MHz CDCl₃): δ=8.21(d, 2H), 7.83(s, 10H), 7.65(d, 8H), 7.09-7.01(m, 8H), 6.84-6.81(m, 4H), 3.80(s, 6H), 2.56(m, 7H), 2.0(s,2H), 1.63-1.50(m, 7H), 1.40-1.29(m, 17H),0.88(m,12H). ¹³C NMR (101 MHz, CDCl₃) δ 159.36, 156.72, 152.14, 144.78, 140.95, 140.51, 140.29, 138.79, 136.60, 133.92, 132.58, 129.24, 128.75, 127.62, 127.53, 126.87, 126.69, 126.42, 125.89, 124.13, 123.61, 121.99, 120.46, 118.65, 116.28, 116.04, 115.80, 115.37, 112.48, 111.65, 111.19, 106.65, 101.79, 70.61, 53.74, 47.71, 39.35, 36.77, 30.76, 30.53, 29.75, 29.10, 28.83, 28.71, 24.16, 23.86, 23.14, 23.09, 14.14, 14.10, 11.15, 11.04. MALDI-TOF calculated for C₈₉H₈₁N₃O₄S₃ M⁺ 1352.841 found: 1353.907.

Synthesis of methyl 4-(7-(8,8,10,10-tetrakis(4-butylphenyl)-6-(10-octyl-10H-phenothiazine-3-yl)-8,10-dihydro-s-indaceno[1,2-b:6,7-b]dithiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)benzoate (17): In a 50 ml of one neck round bottom flask a mixture of compound 12 (0.056 g, 0.05 mmol), compound 16 (0.021 g, 0.05 mmol), K₂CO₃ (2M solution 1 mL), in THF (8 ml) was degassed for 15 min. before the addition of [Pd (PPh₃)₄] (3 mg) and subsequent degassing for 5 minutes. The reaction mixture was heated under argon at 65 °C for

24 hrs. After cooling to room temperature, the reaction was quenched with water, extracted with DCM and dried over sodium sulphate. After removal of the solvent, the crude product was purified by column chromatography with ethyl acetate/hexane and given the product (0.046g, 65%). MALDI-TOF calculated for compound **17** C₉₀H₈₉N₃O₂S₄ M⁺ 1372.321 found: 1373.567.

Synthesis of 4-(7-(8,8,10,10-tetrakis(4-butylphenyl-6-(10-octyl-10H-phenothiazine-3-yl)-8,10-dihydro-s-indaceno[1,2-b:6,7-b] dithiophen-2-yl) benzo[c] [1,2,5] thiadiazol-4-yl) benzoic acid (18): The synthesis of compound **18** is similar to compound **15**. ¹H-NMR (400 MHz CDCl₃): δ=8.30-8.24(d, 2H), 8.15-8.0(m, 4H), 7.95(t, 2H), 7.82-7.73(m, 2H), 7.67-7.60(m, 1H), 7.55(s, 1H), 7.47(s, 1H), 7.41-7.28(m, 4H), 7.24-7.16(m, 4H), 7.12-7.09(d, 10H), 4.20(m, 1H), 2.60(t, 8H), 2.40(t, 1H), 2.0(m, 2H), 1.67-1.28(m, 27H), 0.88(t, 15H). ¹³C NMR (101 MHz, CDCl₃) δ 153.93, 153.00, 144.79, 141.24, 136.82, 136.57, 135.35, 132.92, 132.47, 132.29, 129.69, 129.32, 128.16, 126.95, 126.27, 125.88, 123.64, 122.08, 118.57, 115.80, 115.36, 113.57, 112.53, 111.65, 106.32, 47.73, 36.78, 30.77, 28.83, 24.17, 23.14, 14.09, 11.04. MALDI-TOF calculated for compound **18** C₈₉H₈₇N₃O₂S₄ M⁺ 1358.89 found 1359.97.

4. ^1H , ^{13}C -NMR and MALDI-TOF Spectra:

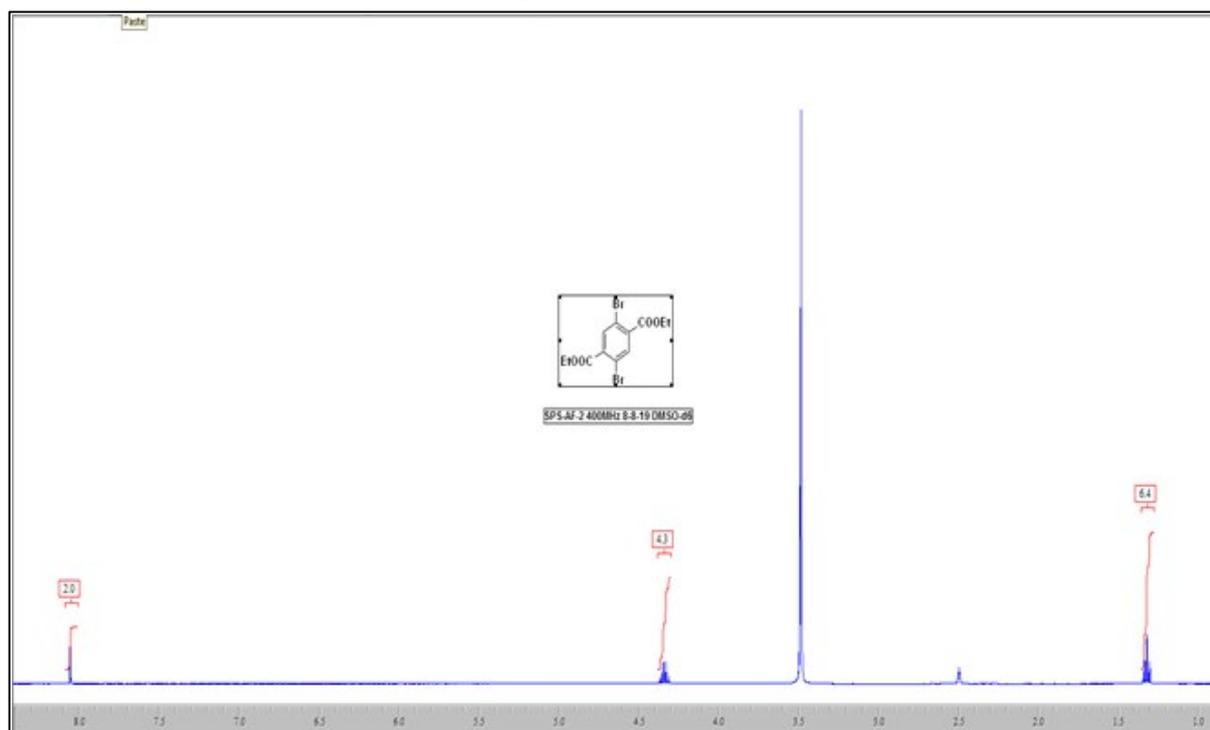


Fig. S1: ^1H -NMR spectra of compound 3

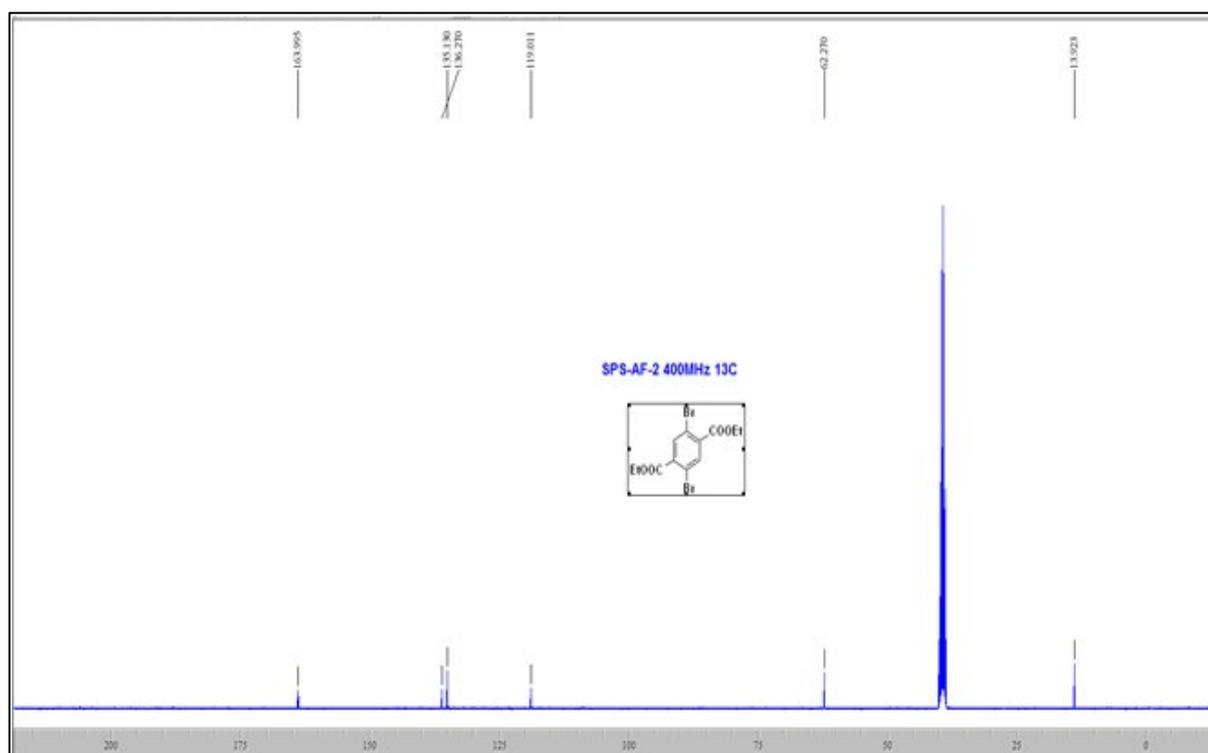


Fig. S2: ^{13}C -NMR spectra of compound 3

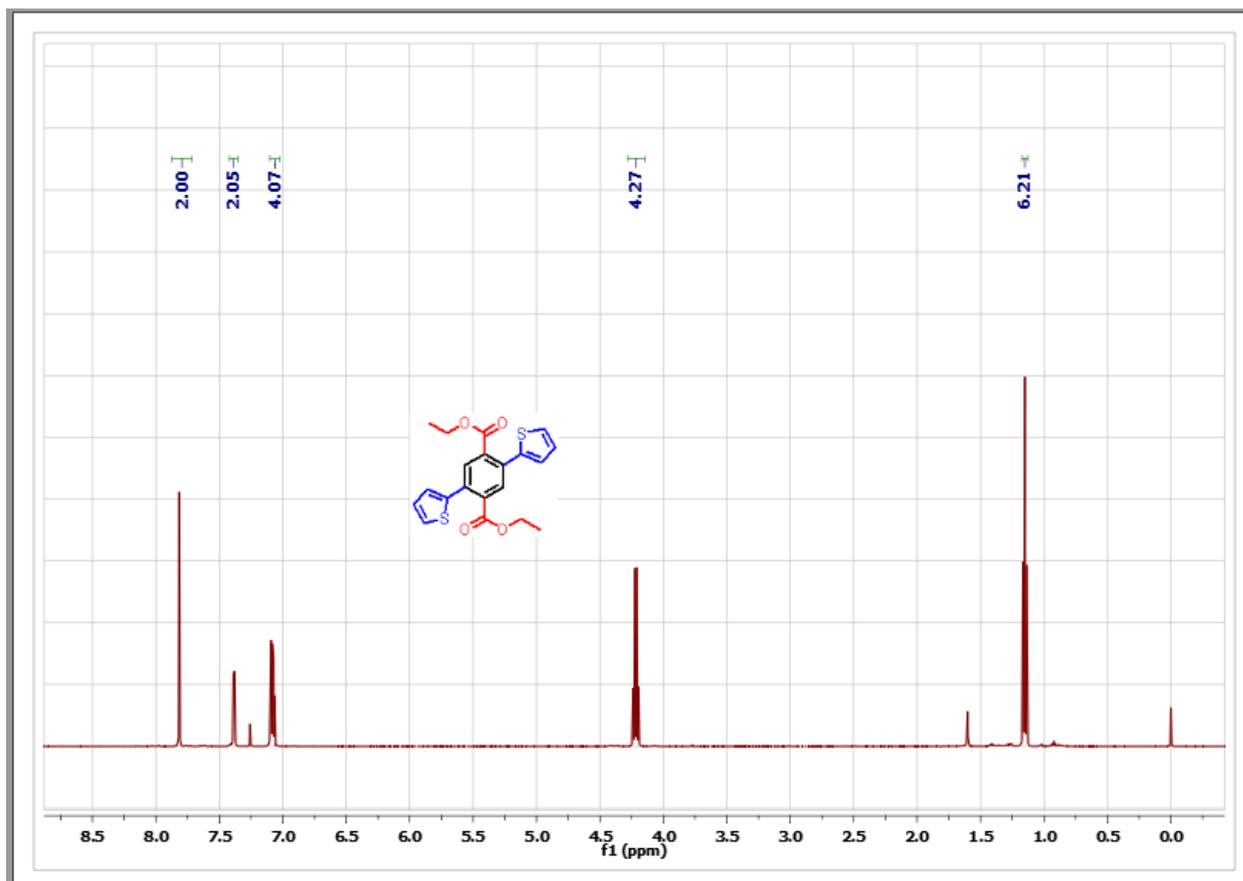


Fig. S3: ¹H-NMR spectra of compound 4

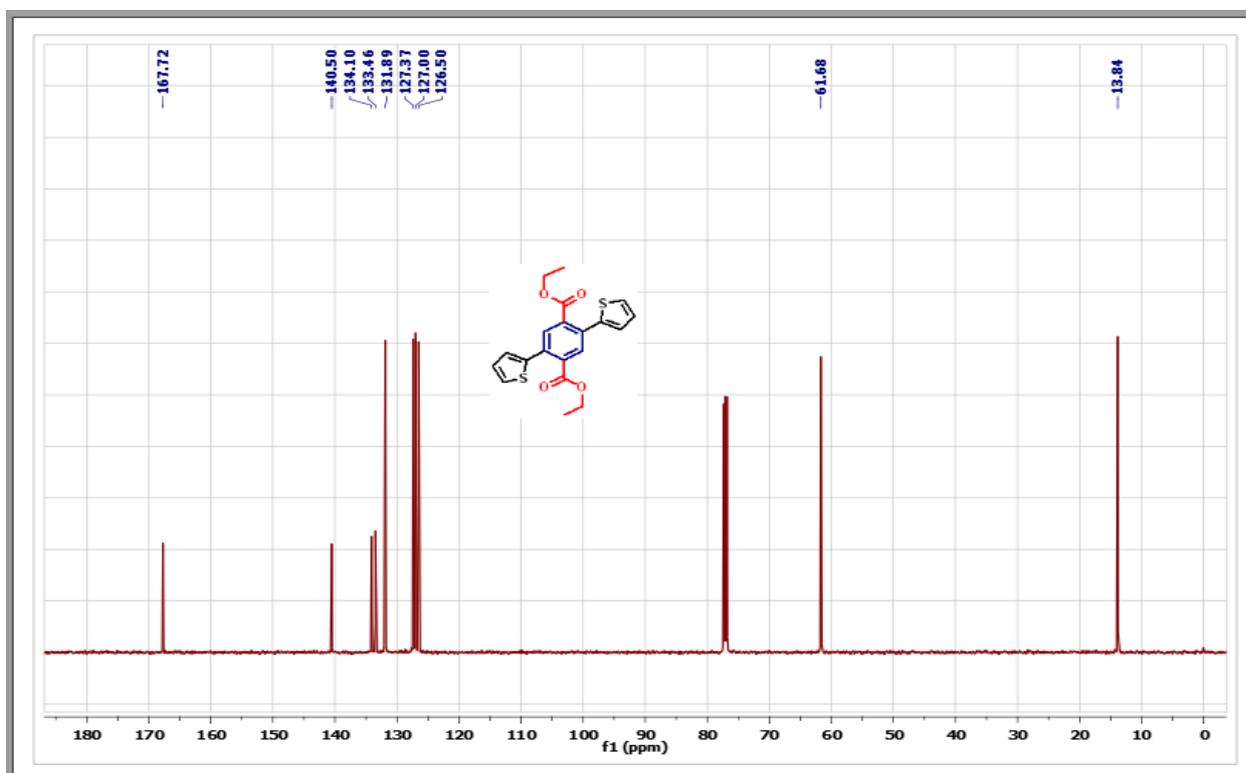


Fig. S4: ¹³C-NMR spectra of compound 4

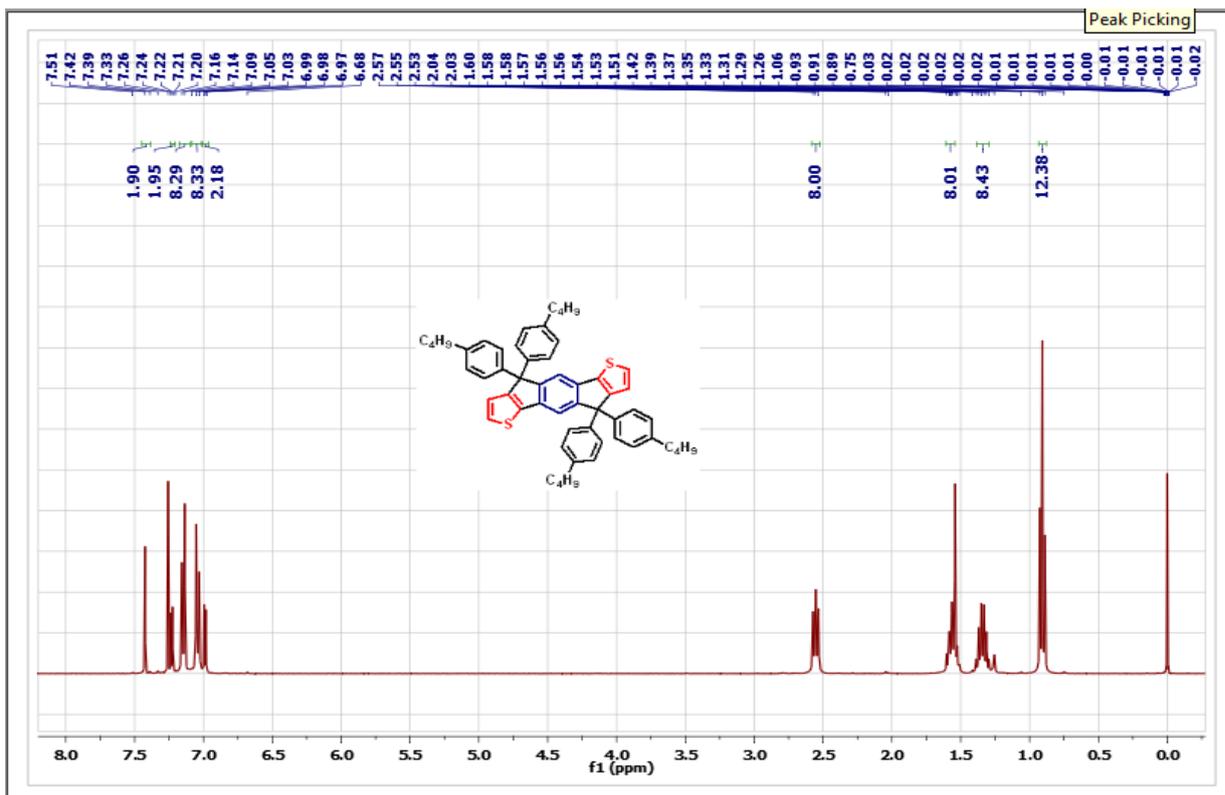


Fig. S5: $^1\text{H-NMR}$ spectra of compound 6

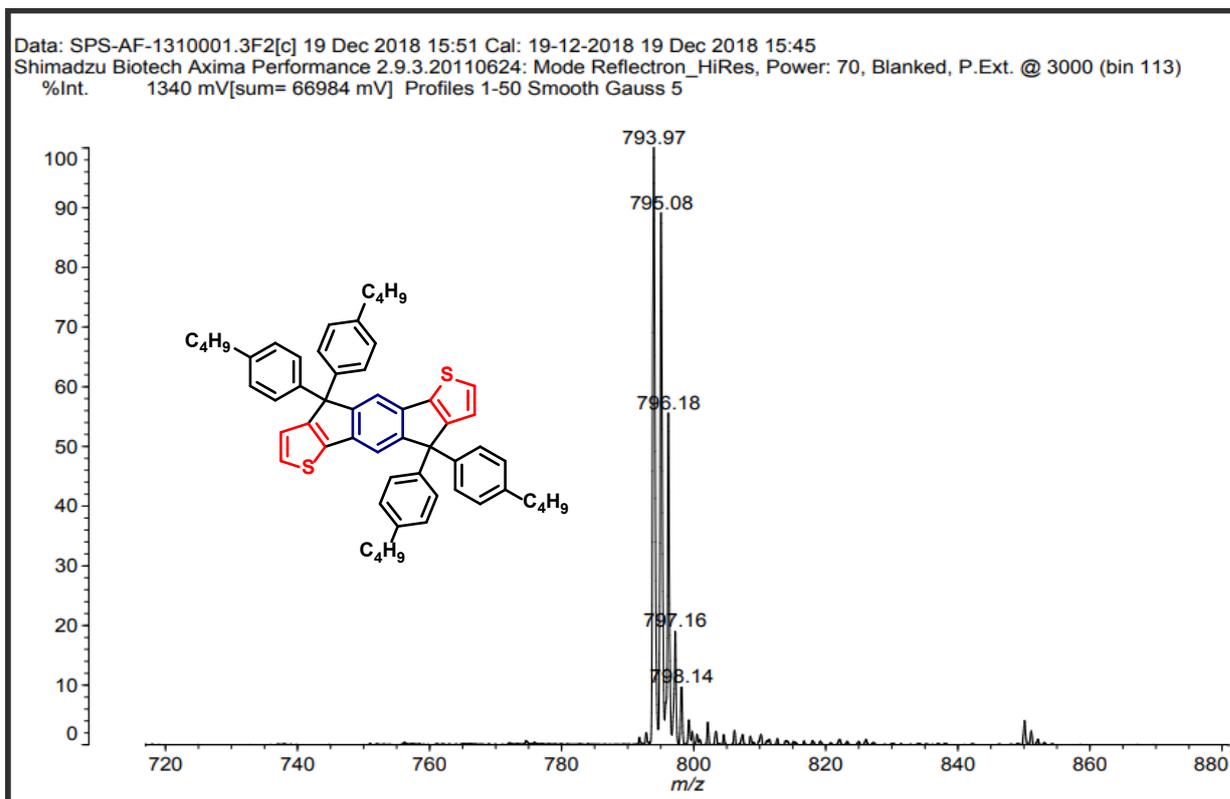


Fig. S6: MALDI-TOF spectra of compound 6

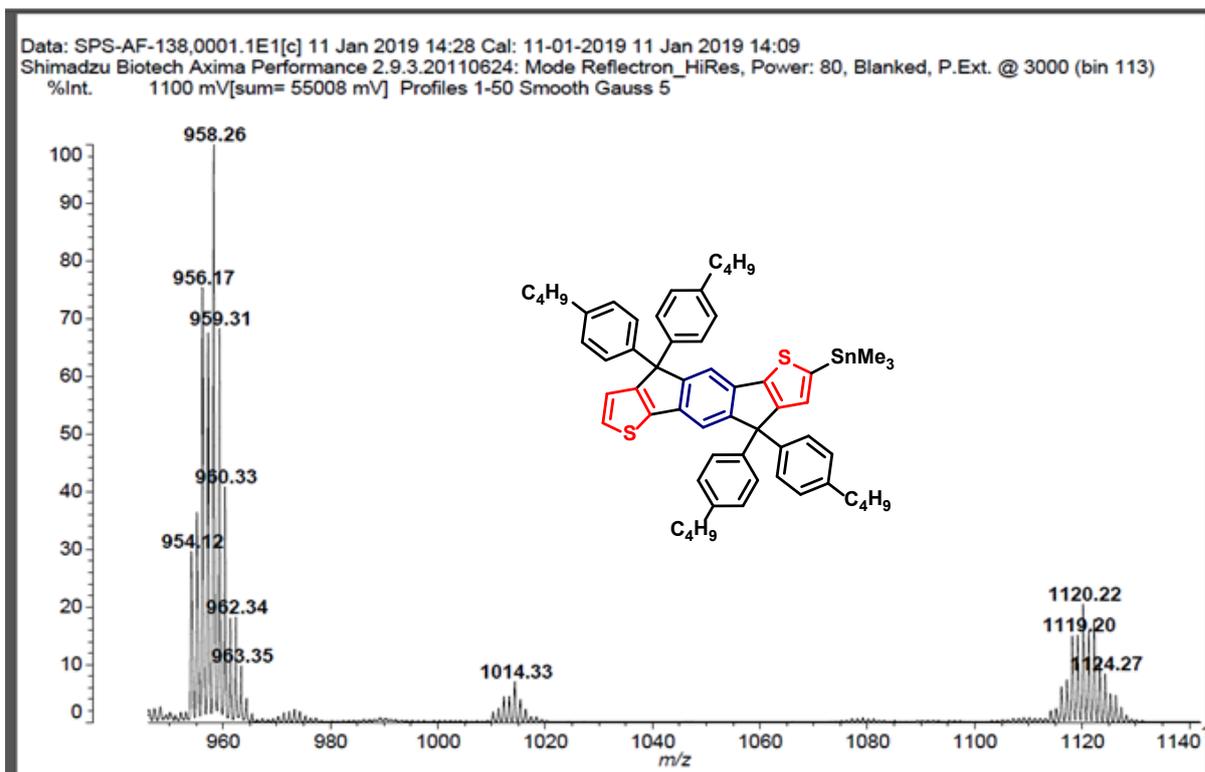


Fig. S7: MALDI-TOF spectra of compound 7

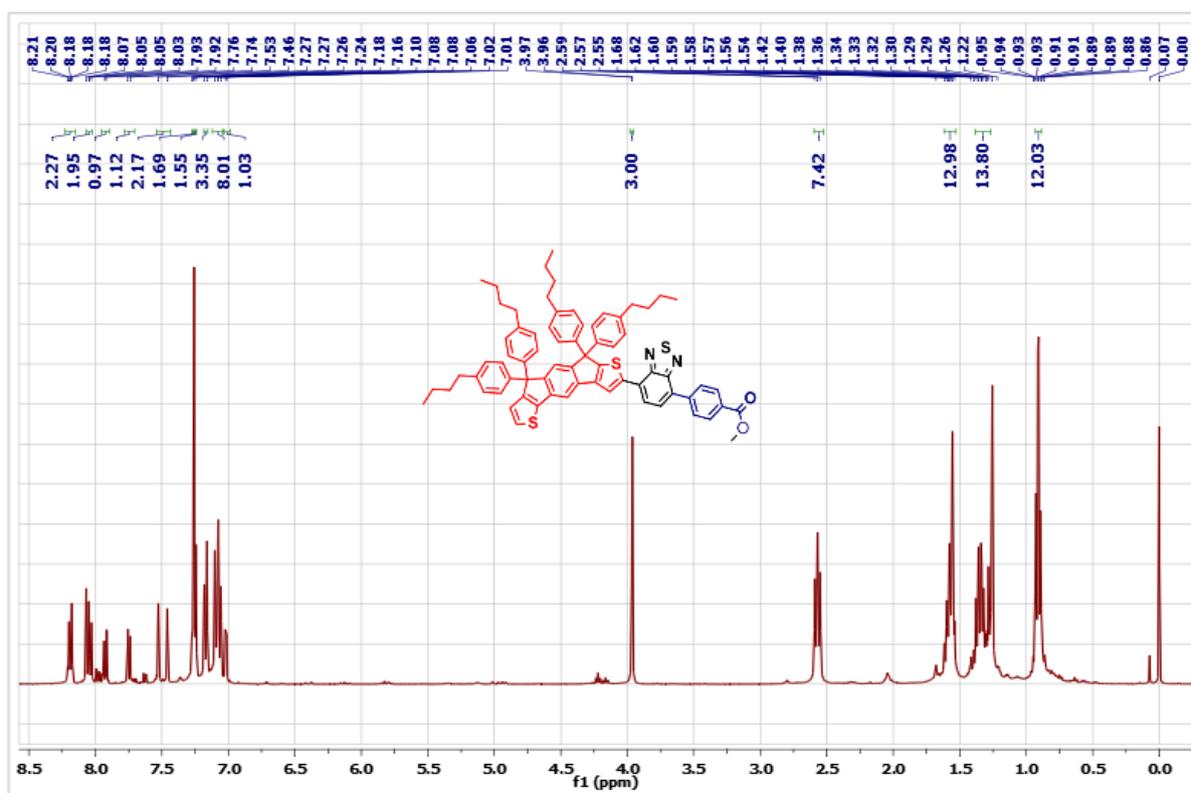


Fig. S8: $^1\text{H-NMR}$ spectra of compound 11

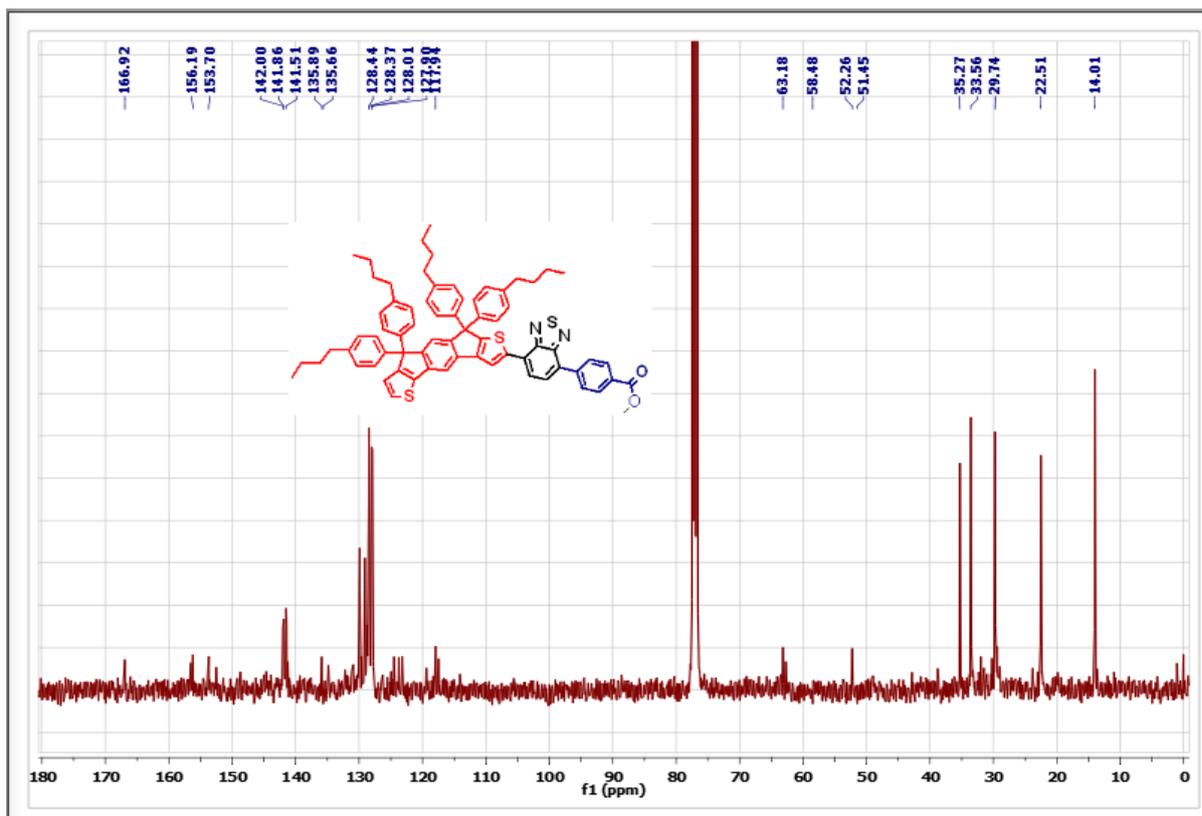


Fig. S9: ^{13}C -NMR spectra of compound 11

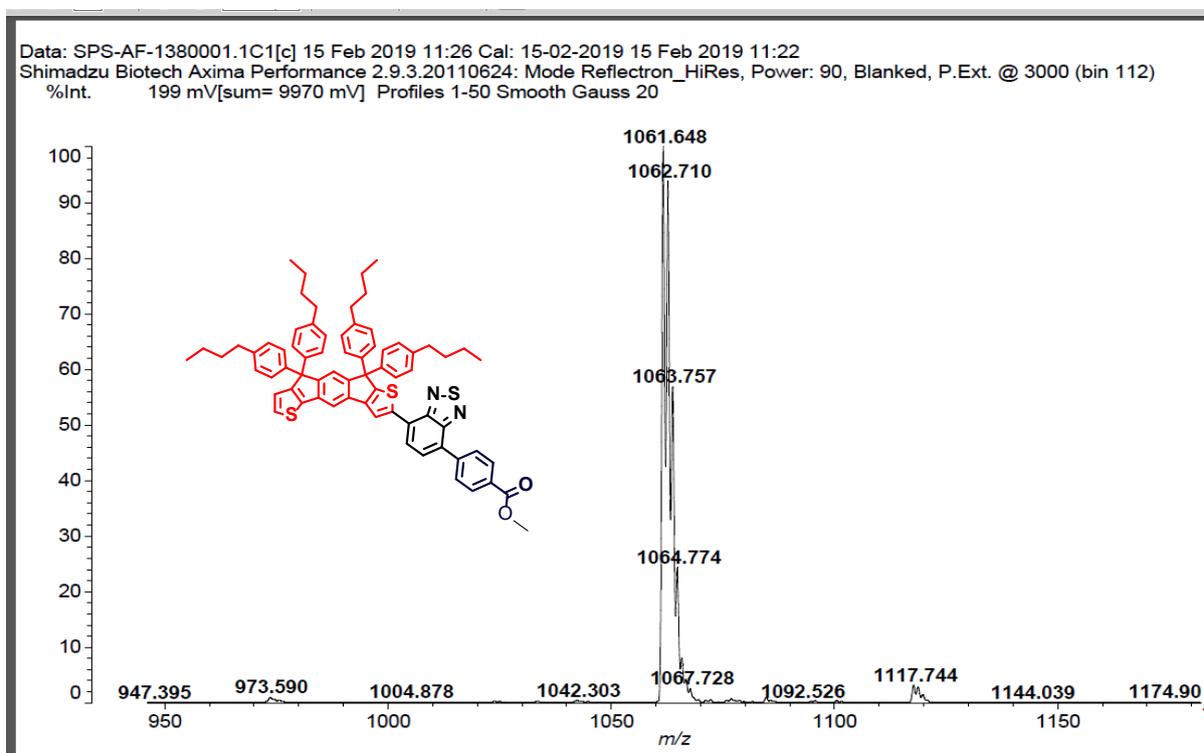


Fig. S10: MALDI-TOF spectra of compound 11

Data: SPS-AF-K0001.3J1[c] 27 Mar 2019 11:16 Cal: 27-03-2019 27 Mar 2019 10:42
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron_HiRes, Power: 80, Blanked, P.Ext. @ 3000 (bin 113)
%Int. 7.7 mV[sum= 383 mV] Profiles 1-50 Smooth Gauss 7

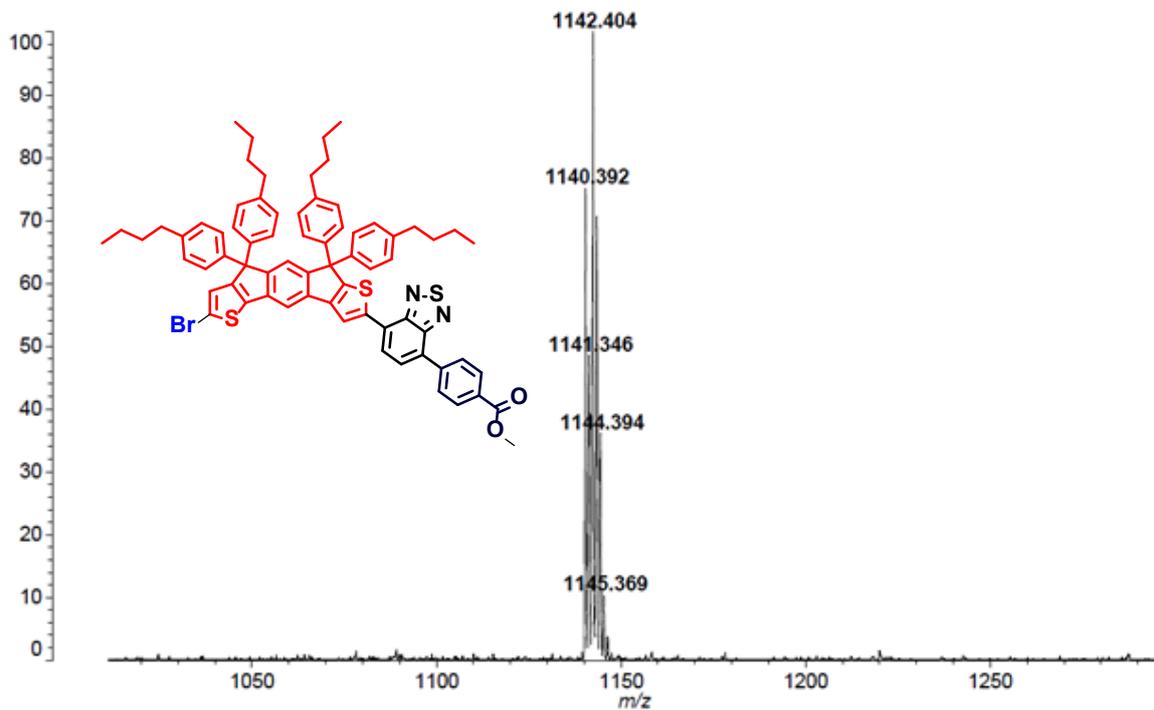


Fig. S11: MALDI-TOF spectra of compound 12

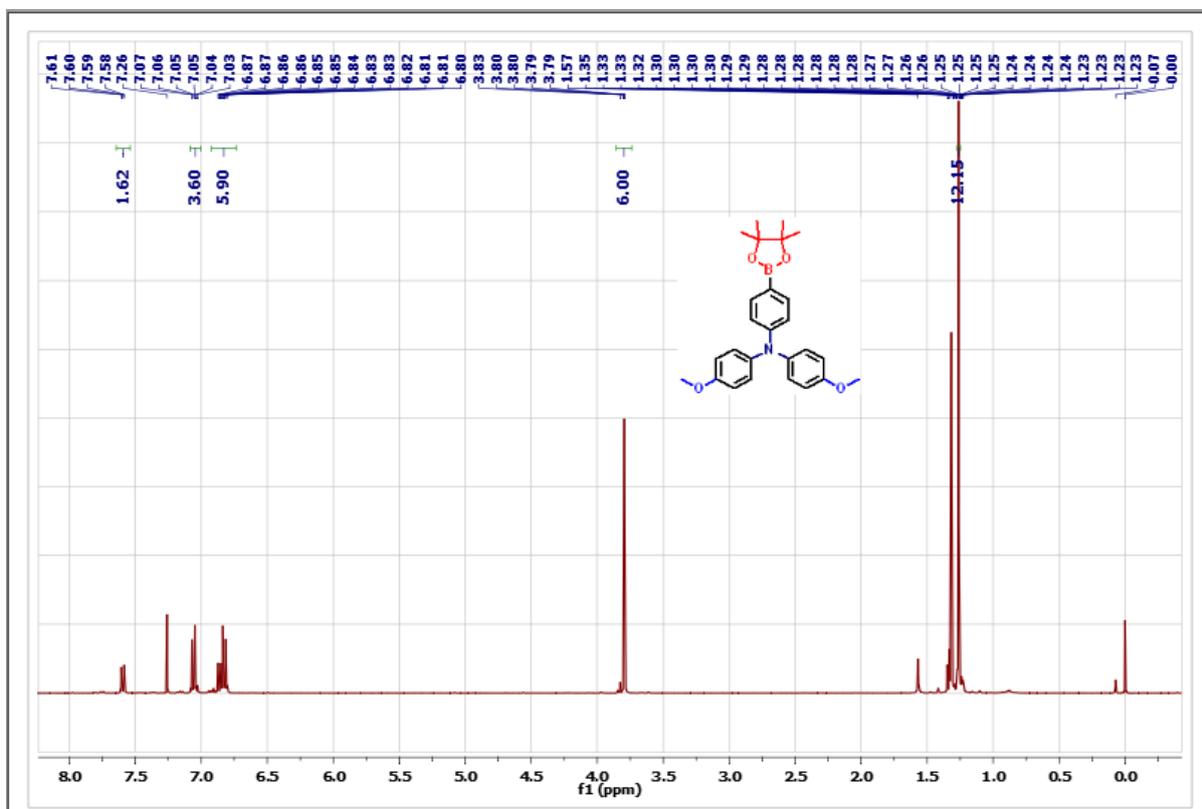


Fig. S12: ^1H -NMR spectra of compound 13

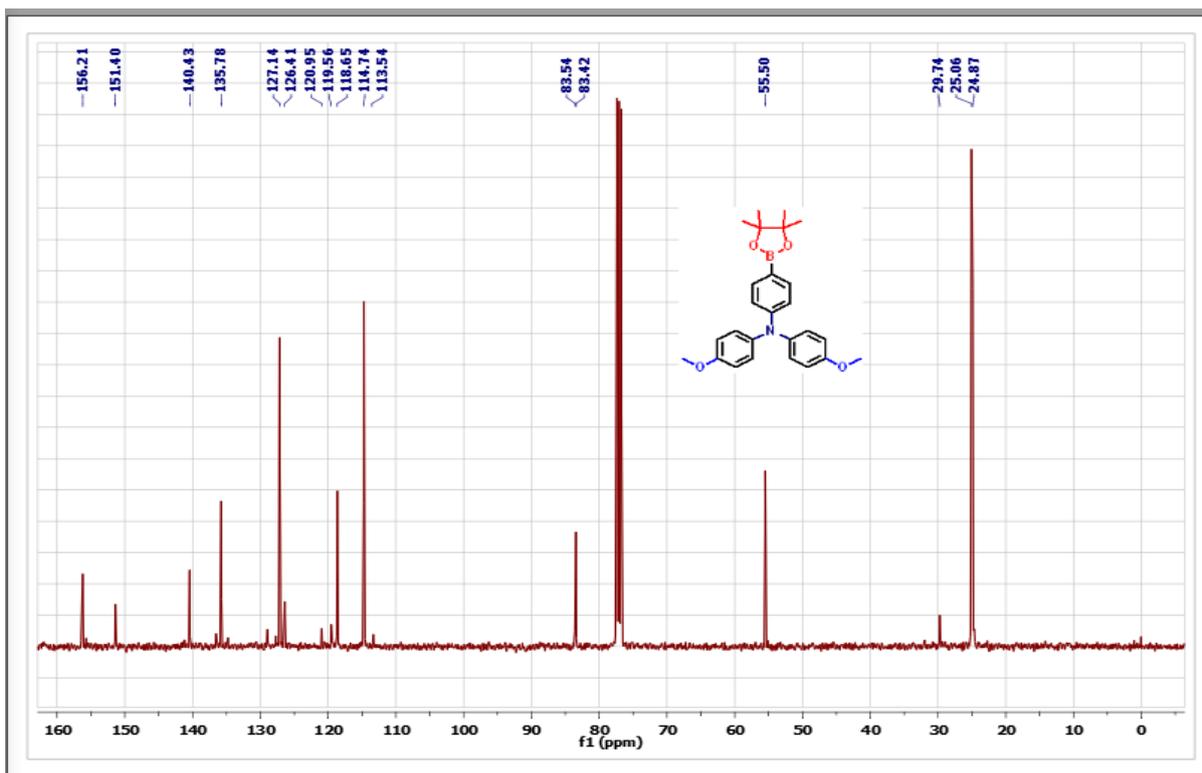


Fig. S13: ^{13}C -NMR spectra of compound 13

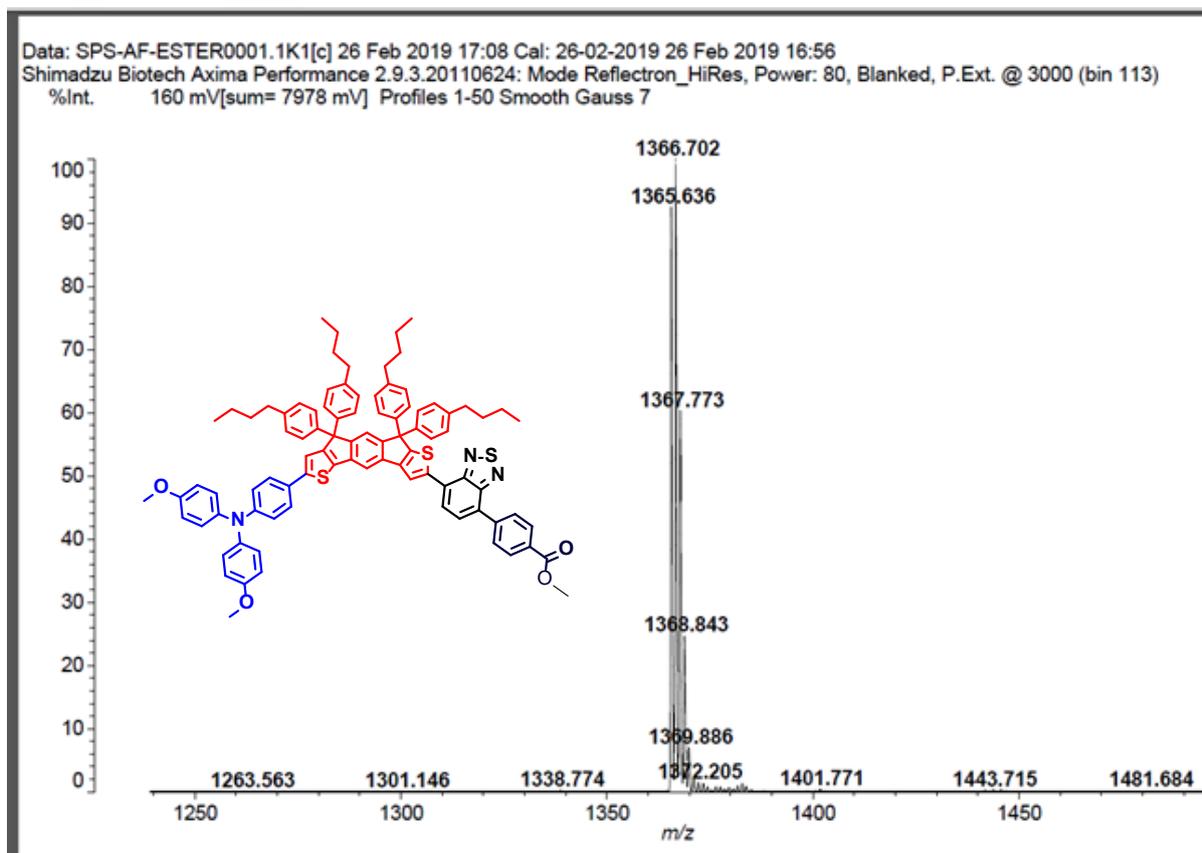


Fig. S14: MALDI-TOF spectra of compound 14

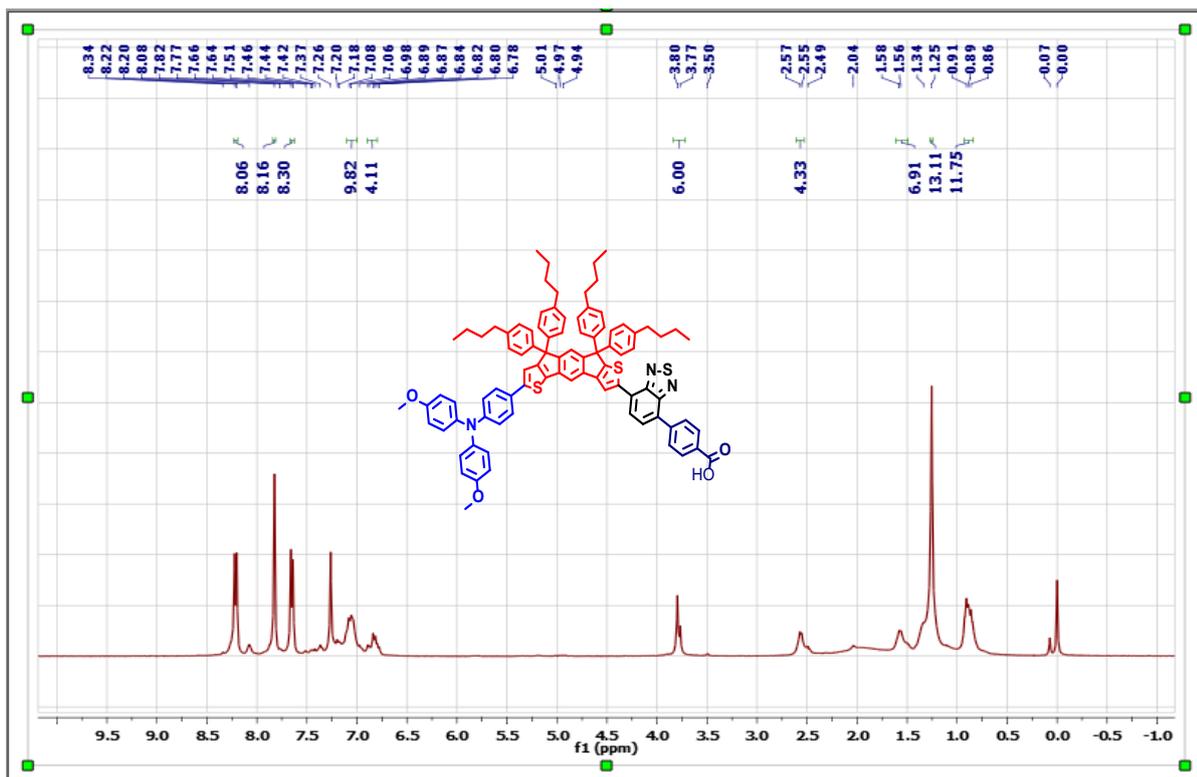


Fig. S15: ^1H -NMR spectra of compound 15

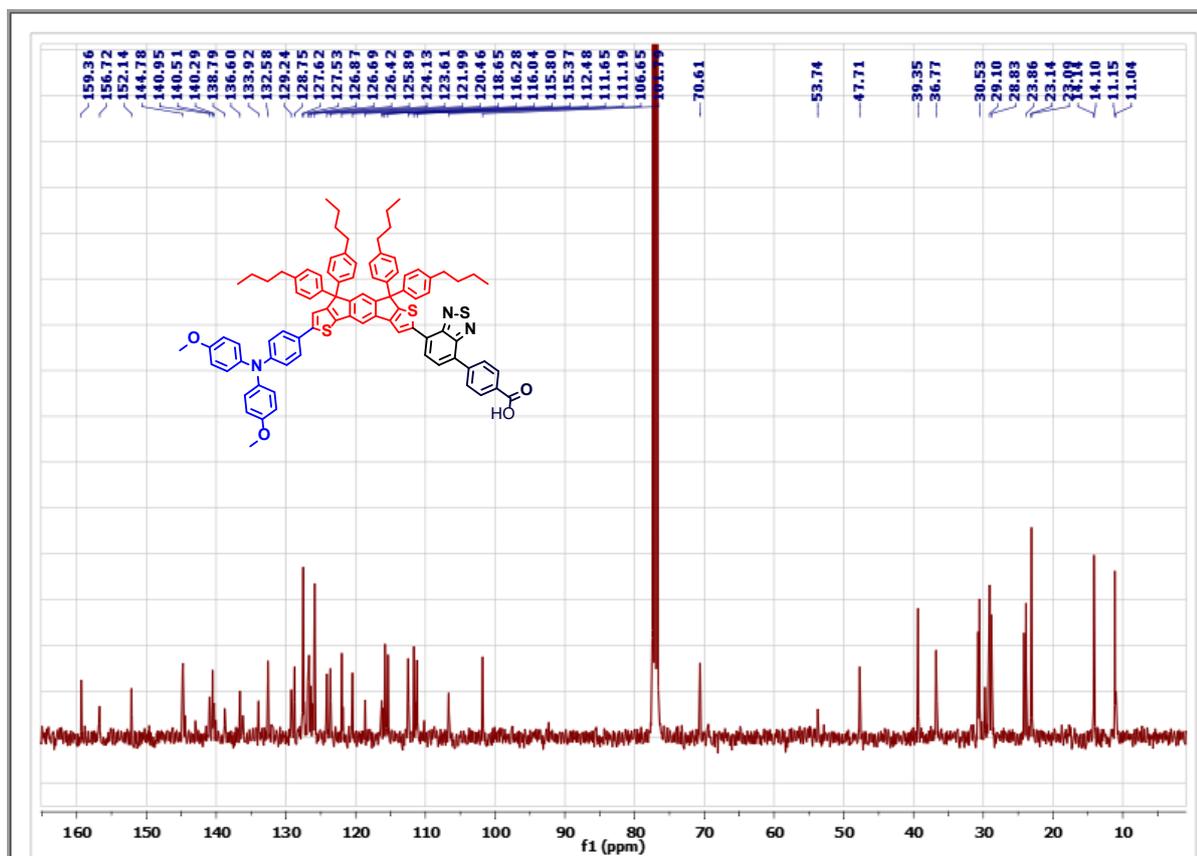


Fig. S16: ^{13}C -NMR spectra of compound 15

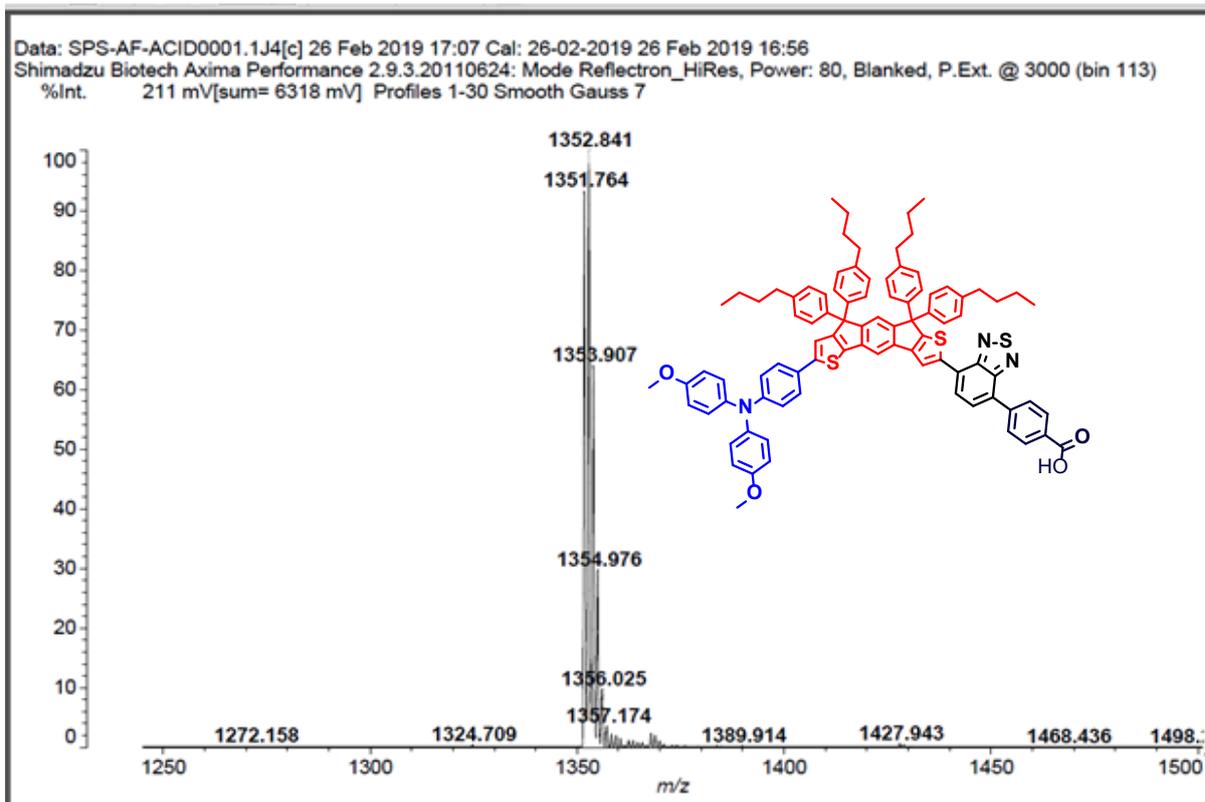


Fig. S17: MALDI-TOF spectra of compound 15

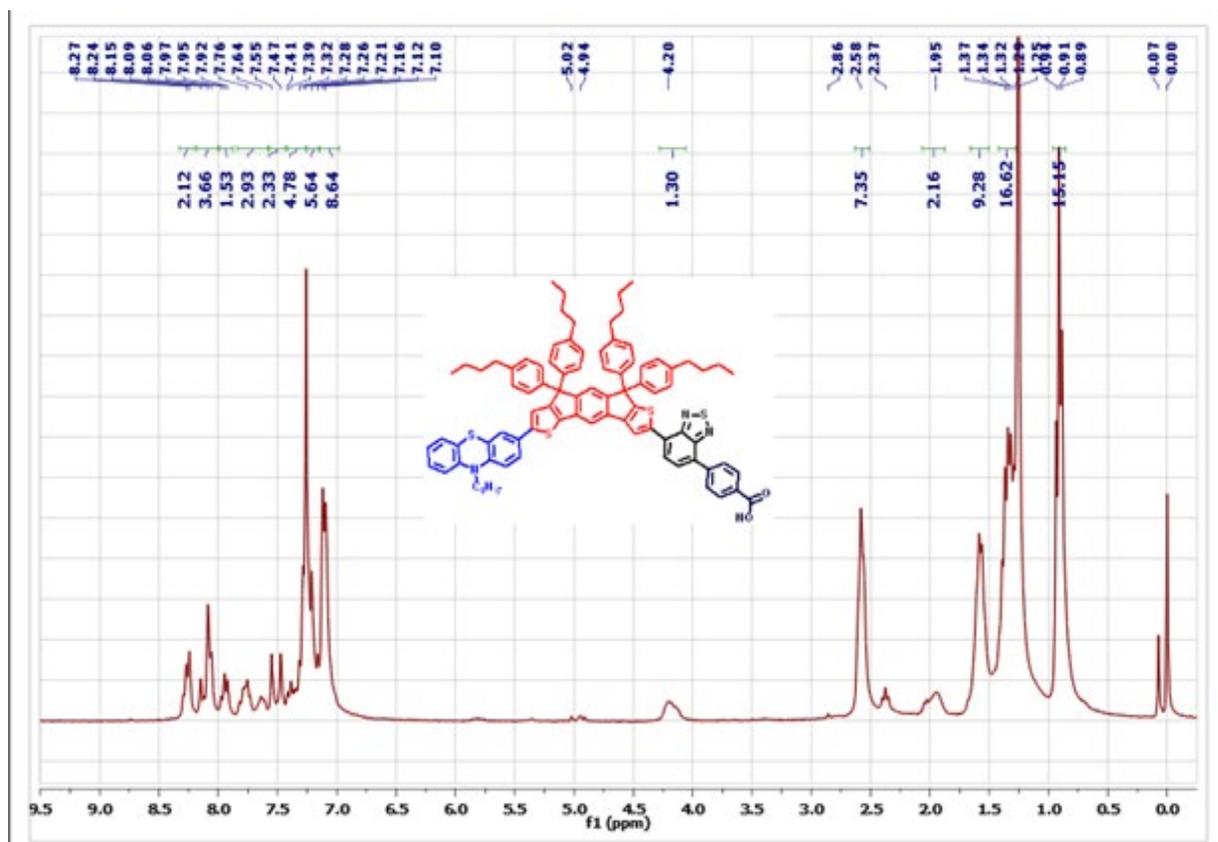


Fig. S18: ¹H-NMR spectra of compound 18

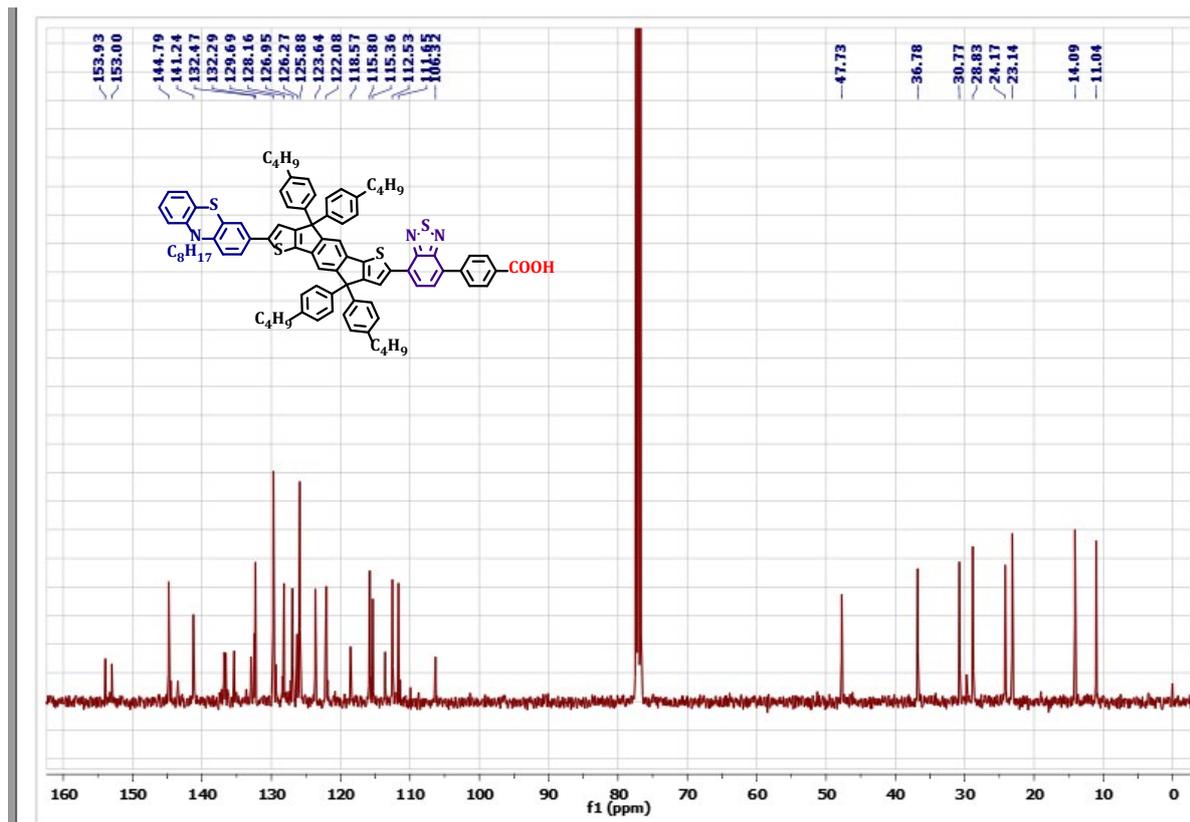


Fig. S19: ¹³C-NMR spectra of compound 18

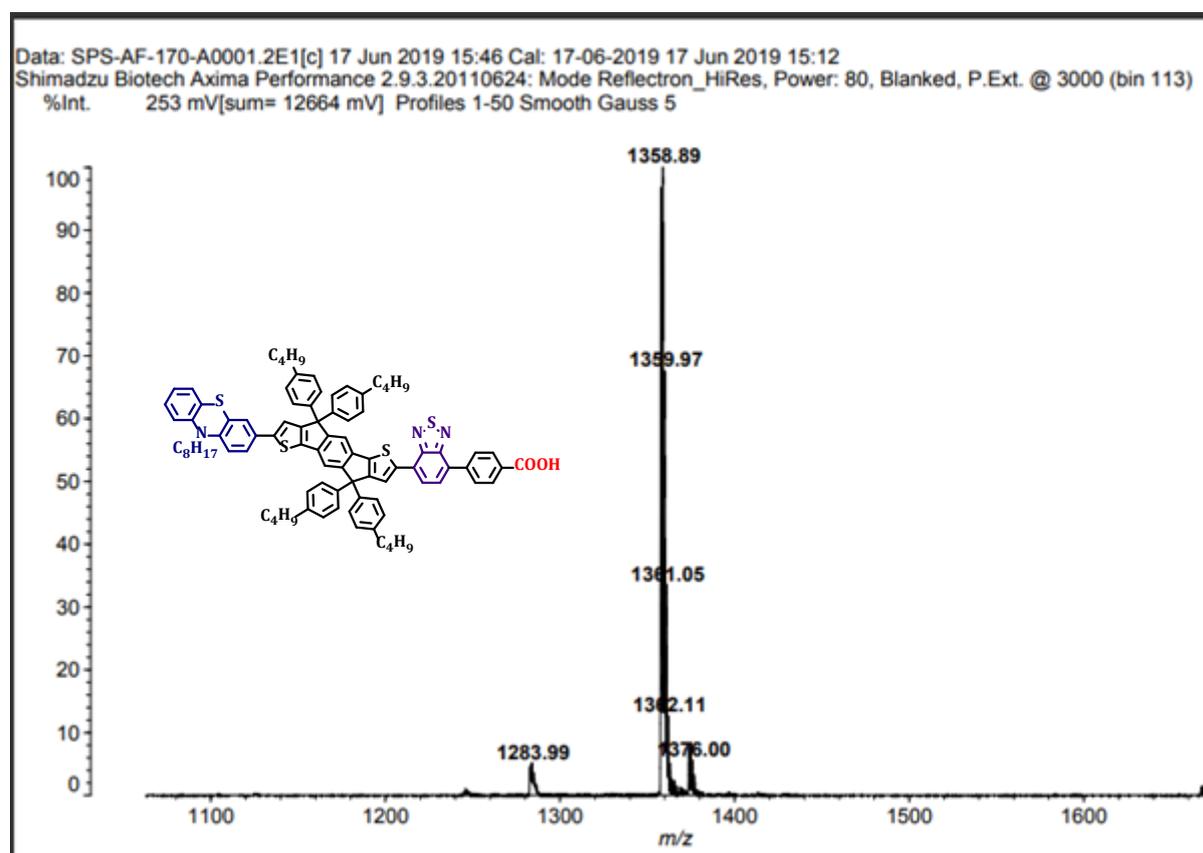


Fig. S20: MALDI-TOF spectra of compound 18

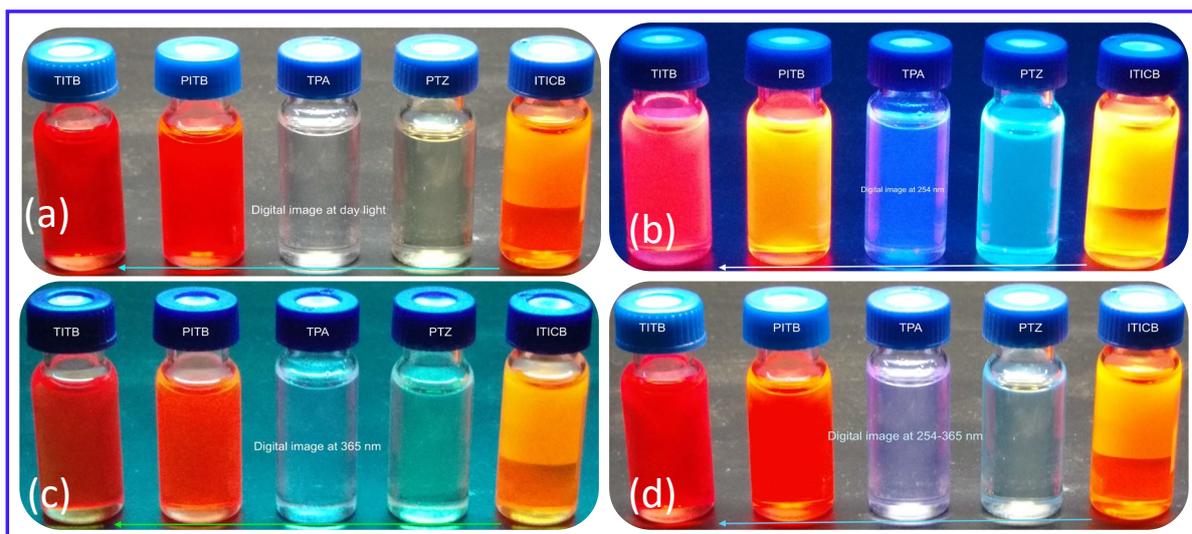


Fig. S21: Digital photographs of ITICB, PTZ, TPA, PITB and TITB with different wavelengths of light.

5. References:

1. M.-C. Tsai, C.-L. Wang, C.-W. Chang, C.-W. Hsu, Y.-H. Hsiao, C.-L. Liu, C.-C. Wang, S.-Y. Lin and C.-Y. Lin, *J. Mater. Chem. A*, 2018, **6**, 1995–2003.
2. K. M. Omer, S.-Y. Ku, J.-Z. Cheng, S.-H. Chou, K.-T. Wong and A. J. Bard, *J. Am. Chem. Soc.*, 2011, **133**, 5492–5499.