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Supporting Information for

Catalyst-Free One-Step Synthesis of *Ortho*-Tetraaryl Perylene Diimides for Efficient OPV Non-Fullerene Acceptors

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1. Materials and methods

General Methods. Unless otherwise stated, all of the chemicals were purchased from Aldrich Chemical and used as received. When necessary, solvents and reagents were purified using standard procedures. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova600 spectrometer. Absorption spectra were taken on a Varian Cary 50 ultraviolet-visible spectrometer. Single crystal X-ray diffraction was carried out using a Bruker Kappa Apex diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at a temperature of 100 K. Mercury software was used to process the raw data. Electrochemical measurements were performed with a Princeton Applied Research Potentiostat/Galvanostat model 263A. The electrochemical measurements were carried out in DCM solution containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, with a platinum disc, platinum wire, and silver wire as the working, counter, and pseudo-reference electrodes, respectively. A ferrocene-ferrocenium (Fc/Fc^+) redox couple was used as an internal standard (4.80 eV below the vacuum level).

Photovoltaic properties of the PDIs as electron acceptor in bulk-heterojunction solar cells were investigated with an inverted device configuration of ITO/ZnO/**PTB7-Th**:PDIs/MoO_3/Ag. ITO-coated glass substrates were cleaned stepwise in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried in an oven for several hours. Before deposition of the electron-collecting interlayer, ITO substrates were cleaned in UV azone for 5 min. Approximately 40 nm of zinc oxide was deposited as a thin film atop indium tin oxide (ITO) coated glass substrates. After being annealed at 130 °C for 30 min, the substrates were transferred into a nitrogen-filled glove box (<0.1 ppm O_2 and H_2O) for active layer coating and electrode formation. A mixture of **PTB7-Th** and PDI with a w/w ratio of 1:1, 1:1.8 or 1:2 was dissolved in chloroform with a total concentration of 20 mg/mL for spin-coating of the active layer. Finally 6 nm of molybdenum oxide and 80 nm of silver anode were evaporated at a pressure of $\sim 10^{-7}$ torr, using a shadow mask with an active area of ~ 6 mm^2. These conditions provided an active layer thickness of approximately 80-100 nm. Each parameter listed in table 1 is averaged from over 6 devices fabricated and tested under the same conditions. The best fabricating conditions of **PTB7-Th** and **PDI-2S-4Th** blend was with a w/w ratio of 1:1.8 and annealing at 125 °C/10 mins. The standard deviations are also given in the table.

The J-V characteristics were measured at 1 sun illumination (AM 1.5G, 100mW/cm^2) in a N_2-filled glovebox with a solar simulator equipped with a Xenon lamp (Newport), a Keithley 2602 Source Meter and a calibrated silicon reference cell. The power conversion efficiency (PCE) was calculated with the following equation: PCE(%) = 100*(V_{oc})*(J_{sc})*(FF)/Pinc from the open circuit voltage, V_{oc}, the short circuit current, J_{sc}, the fill factor FF and the incident powder Pinc. The external quantum efficiencies (EQE) were analyzed using a fully computerized measurement system consisting of a 300-W xenon lamp (Newport), a monochromator (Newport CS130), a chopper controller (Newport), two current preamplifiers (SRS SR570), and two lock-in amplifiers (SRS SR810).

2. Synthetic procedures

PDI-4Mes: Under nitrogen, magnesium turnings (72.0 mg, 3.0 mmol) were placed in a 50 mL round bottom flask. Anhydrous THF (10 mL) was added, followed by the addition of a catalytical amount of iodine. The 2-bromo-1,3,5-trimethylbenzene (570.0 mg, 2.8 mmol) was added dropwise to the reaction mixture that was heated to reflux until the brown color of iodine disappeared. The mixture was stirred for 3 hours and cooled to room temperature. Once the Grignard reagent formation was complete, 5 mL of mesitylmagnesium bromide solution (1.4 mmol) was added to compound **1** (100.0 mg, 0.14 mmol) in THF (10 mL) at 0°C. The resulting mixture was stirred at room temperature for 12 h and then quenched with water (5 mL). The mixture was extracted with dichloromethane (DCM) and the organic layers dried with $MgSO_4$, followed by filtration through a short silica plug. The solvent was removed in vacuo, the crude solid was collected and redissolved in fresh THF (10 mL). An additional 5 mL of mesitylmagnesium bromide solution (1.4 mmol) was added at 0°C and the resulting mixture was stirred at room temperature for 12 h then once again quenched with water (5 mL). The product was extracted into DCM, the organic layers collected and dried with $MgSO_4$. Finally, the crude product was purified by column chromatography on silica gel (DCM/Hexane, 3:2 v/v) to afford compound **PDI-4Mes** as an orange solid (63.7 mg, 38%). Mp: >260 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 8.13 (s, 4H), 7.01 (s, 8H), 4.96 (t, J = 7.6 Hz, 2H), 2.38 (s, 12H), 1.99 (m, 28H), 1.64-1.59 (m, 4H), 1.21-1.09 (m, 24H), 0.77 (t, J = 6.8 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 163.4, 162.4, 147.2, 139.1, 136.5, 133.5, 133.2, 131.0, 128.4, 127.0, 125.2, 121.9, 120.9, 54.0, 31.6, 26.4, 22.4, 21.4, 20.6, 13.8. MS (m/z): Calcd for MS: 1170.72, Found: (M^+) 1170.61. Anal. Calcd for $C_{82}H_{94}N_2O_4$: C, 84.06; H, 8.09; N, 2.39. Found: C, 84.11; H, 8.21; N, 2.28. UV-vis (DCM) λ_{max} nm (ε): 230 (180327), 265 (74941), 454 (30444), 486

(63231), and 521 (96018).

PDI-4Th: Under nitrogen, magnesium turnings (72.0 mg, 3.0 mmol) were placed in a 50 mL round bottom flask. Anhydrous THF (10 mL) was added, followed by the addition of a catalytical amount of iodine. The 2-bromothiophene (450.0 mg, 2.8 mmol) was added dropwise to the reaction mixture that was heated to reflux until the brown color of iodine disappeared. The mixture was stirred for 3 hours and cooled to room temperature. Once the Grignard reagent had formed, 5 mL of thienylmagnesium bromide solution (1.4 mmol) was added to compound **1** (100.0 mg, 0.14 mmol) in THF (10 mL) at 0°C. The resulting mixture was stirred at room temperature for 12 h and then quenched with water (5 mL). The mixture was extracted with DCM and the organic layers dried with $MgSO_4$ and passed through a short silica plug. The solvent was removed in vacuo and the crude solid collected and redissolved in fresh THF (10 mL). An additional 5 mL of thienylmagnesium bromide solution (1.4 mmol) was added at 0°C and the resulting mixture was stirred at room temperature for 12 h then once again quenched with water (5 mL). The product was extracted into DCM, the organic layers collected and dried with $MgSO_4$. Finally the crude product was purified by column chromatography on silica gel (DCM/Hexane, 3:2 v/v) to afford **PDI-4Th** as an orange solid (44.1 mg, 30%). Mp: >260 ^{o}C. ^{1}H NMR(600 MHz, CD_2Cl_2, δ, ppm): 8.54 (s, 4H), 7.55 (dd, J = 5.1, 1.1 Hz, 4H), 7.24 (d, J = 2.5 Hz, 4H), 7.20 (dd, J = 5.1, 3.5 Hz, 4H), 4.97-4.93 (m, 2H), 2.15-2.10 (m, 4H), 1.68 (dd, J = 12.8, 6.6 Hz, 4H), 1.29 (dt, J = 12.4, 4.1 Hz, 24H), 0.86 (t, J = 6.9 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 163.6, 162.6, 142.6, 139.5, 132.3, 130.9, 128.1, 127.4, 127.2, 126.8, 125.6, 122.5, 55.1, 32.1, 31.7, 26.6, 22.6, 14.0. Calcd for MS: 1026.36, Found: (M^+). 1026.38. Anal. Calcd for $C_{62}H_{62}N_2O_4S_4$: C, 72.48; H, 6.08; N, 2.73. Found: C, 72.11; H, 6.42; N, 2.91. UV-vis (DCM) λ_{max} nm (ε): 234 (82135), 267 (49281), 462 (24640), 496 (41067), and 533 (51334).

PDI-2S: $Pd(PPh_3)_4$ (0.3 g, 0.36 mmol) and bis(tributyltin)sulfide (1.5 g, 2.4 mmol) were added to a solution of compound **2** (1.0 g, 1.2 mmol) in toluene under nitrogen atmosphere. The mixture was refluxed for 10 hours. The crude product was purified by column chromatography on silica gel (DCM/Hexane, 1:1 v/v) to afford compound **PDI-2S** as an orange solid. (0.64 g, 70%). Mp: >260 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 9.24 (d, J = 32.2 Hz, 4H), 5.37 (t, J = 9.1 Hz, 2H), 2.40-2.33 (m, 4H), 1.99 (t, J = 11.8 Hz, 4H), 1.47-1.26 (m, 24H), 0.84 (t, J = 7.2 Hz, 12H). ^{13}C NMR

(151 MHz, $CDCl_3$, δ, ppm): 165.2, 164.0, 141.2, 132.3, 126.2, 125.4, 123.2, 122.7, 122.5, 119.9, 55.3, 32.5, 31.8, 26.8, 22.6, 14.0. MS (m/z): Calcd for MS: 758.32, Found: (M^+). 758.30. Anal. Calcd for $C_{46}H_{50}N_2O_4S_2$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.21; H, 6.80; N, 3.22.

PDI-2S-4Mes: Mesitylmagnesium bromide solution, *vide supra* (5 mL, 1.4 mmol) was added to **PDI-2S** (100.0 mg, 0.13 mmol) in THF (10 mL) at 0°C. The resulting mixture was stirred at room temperature for 12 h and then quenched with water (5 mL). The mixture was extracted with DCM and the organic layers dried with $MgSO_4$ and passed through a short silica plug. The solvent was removed in vacuo and the crude solid collected and redissolved in fresh THF (10 mL). An additional 5 mL of mesitylmagnesium bromide solution (1.4 mmol) was added at 0°C and the resulting mixture was stirred at room temperature for 12 h then once again quenched with water (5 mL). The product was extracted into DCM, the organic layers collected and dried with $MgSO_4$. Finally, the crude product was purified by column chromatography on silica gel (DCM/Hexane, 3:1 v/v) to afford **PDI-2S-4Mes** as a yellow solid (81.1 mg, 50%). Mp: >260 °C. ^1H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.09 (s, 8H), 5.14 (t, J = 7.7 Hz, 2H), 2.43 (s, 12H), 2.14-2.08 (m, 4H), 1.98 (s, 24H), 1.75-1.69 (m, 4H), 1.19 (dtd, J = 18.2, 9.4, 3.6 Hz, 24H), 0.75 (t, J = 7.0 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 164.5, 163.1, 144.2, 143.7, 143.0, 137.3, 136.5, 133.6, 132.7, 128.8, 125.5, 120.9, 119.8, 54.6, 31.6, 26.5, 22.5, 21.4, 20.2, 13.9. MS (m/z): Calcd for MS: 1230.63, Found: (M^+). 1230.48. Anal. Calcd for $C_{84}H_{90}N_2O_4S_2$: C, 79.96; H, 7.36; N, 2.27. Found: C, 79.79; H, 7.41; N, 2.02. UV-vis (DCM) λ_{max} nm (ε): 229 (113300), 292 (54187), 424 (19704), 453 (49261), and 485 (78817).

PDI-2S-4Th Thienylmagnesium bromide solution, prepared as described above, (5 mL, 1.4 mmol) was added to **PDI-2S** (100.0 mg, 0.13 mmol) in THF (10 mL) at 0 °C. The resulting mixture was stirred at room temperature for 12 h and then quenched with water (5 mL). The mixture was extracted with DCM and the organic layers dried with $MgSO_4$ and passed through a short silica plug. The solvent was removed in vacuo and the crude solid collected and redissolved in fresh THF (10 mL). An additional 5 mL of thienylmagnesium bromide solution (1.4 mmol) was added at 0°C and the resulting mixture was stirred at room temperature for 12 h then once again quenched with water (5 mL). The product was extracted into DCM, the organic layers collected and dried with $MgSO_4$. Finally, the crude product was purified by column chromatography on silica gel (DCM/Hexane, 3:2

v/v) to afford **PDI-2S-4Th** as an orange solid (62.3 mg, 45%). Mp: >260 °C. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.61 (d, J = 5.2 Hz, 4H), 7.51 (s, 4H), 7.32-7.25 (m, 4H), 5.24 (t, J = 9.2Hz, 2H), 2.28-2.22 (m, 4H), 1.86-1.80 (m, 4H), 1.37-1.20 (m, 24H), 0.81 (t, J = 7.1 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 163.9, 162.8, 145.9, 139.7, 136.7, 136.2, 131.4, 128.1, 127.7, 125.49, 120.4, 119.9, 118.9, 55.3, 32.3, 31.7, 26.6, 22.3, 14.0. MS (m/z): Calcd for MS: 1086.27, Found: (M^+). 1086.29. Anal. Calcd for $C_{62}H_{58}N_2O_4S_6$: C, 68.47; H, 5.38; N, 2.58. Found: C, 68.36; H, 5.62 N, 2.38. UV-vis (DCM) λ_{max} nm (ε): 231 (65217), 306 (42390), 459 (22826), 492 (32609), and 525 (19565).

3. DFT calculations

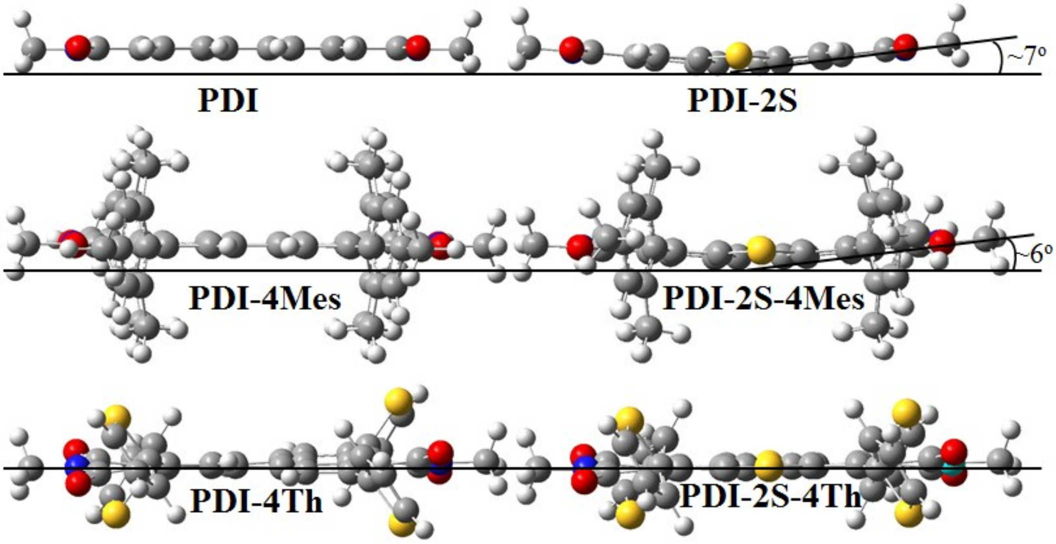

Figure S1. Side views of the optimized geometries obtained from DFT calculations at the B3LYP/6-31G level.[1]

4. Cyclic voltammograms

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[1] Frisch, M. J.; et al. Gaussian09 Revision D.01., Gaussian Inc. Wallingford CT 2009.

[2] Y. Zhong, M. T. Trinh, R. Chen, G. E. Purdum, P. P. Khlyabich, M. Sezen, S. Oh, H. Zhu, B. Fowler and B. Zhang, Nat. Commun., 2015, 6, 8242-8249.

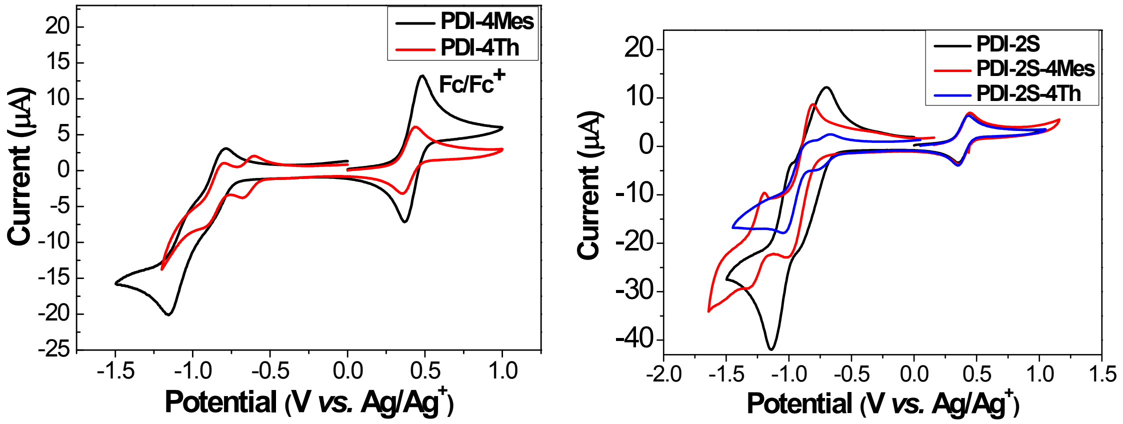

Figure S2. Cyclic voltammetry of the PDIs. (DCM/0.1 M $TBAPF_6$ vs. Ag/Ag^+ at 100 mV/s)

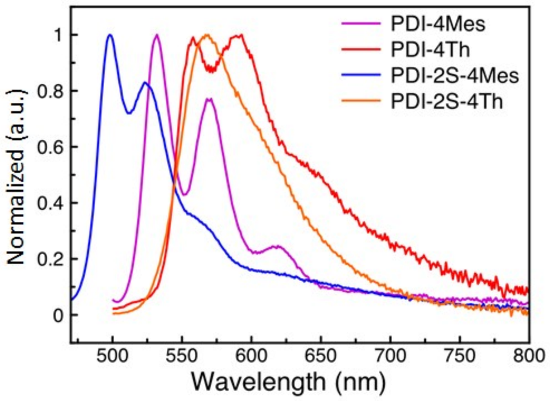

Figure S3. The photoluminescence spectra of **PDI-4Mes, PDI-4Th**, **PDI-2S-4Mes** and **PDI-2S-4Th** in DCM solutions.

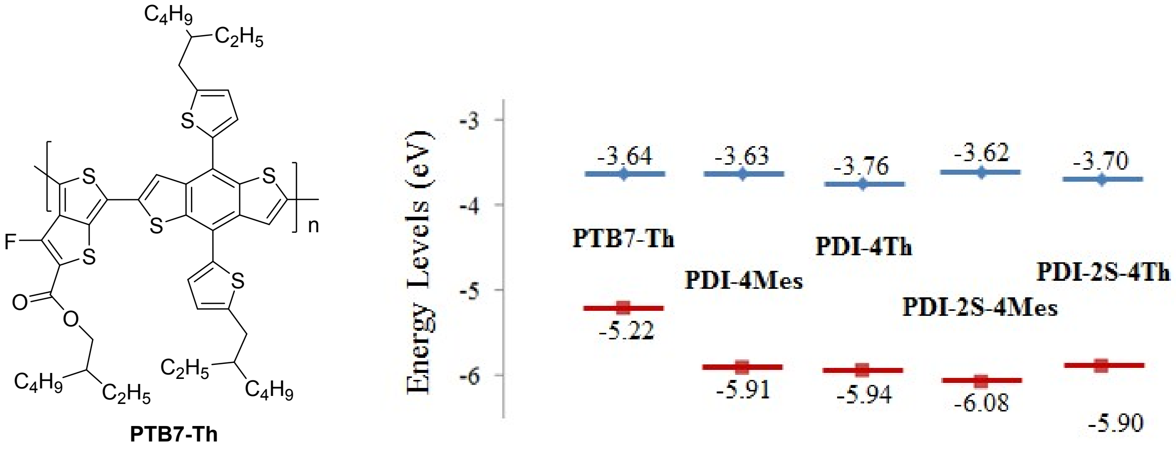

Figure S4. The chemical structure of **PTB7-Th** and the schematic of the energy levels of **PTB7-Th**, **PDI-4Mes**, **PDI-4Th**, **PDI-2S-4Mes,** and **PDI-2S-4Th**. Energy levels of **PTB7-Th** were adopted from ref. 2.

5. X-ray single crystal structures

Data were collected on a Bruker Kappa Apex diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at a temperature of 100 K. Refinements were completed using the program SHELXL) 97. CCDC **PDI-4Mes**: 1504227 and **PDI-4Th**: 1504226.

6. ^{1}H and ^{13}C NMR spectra

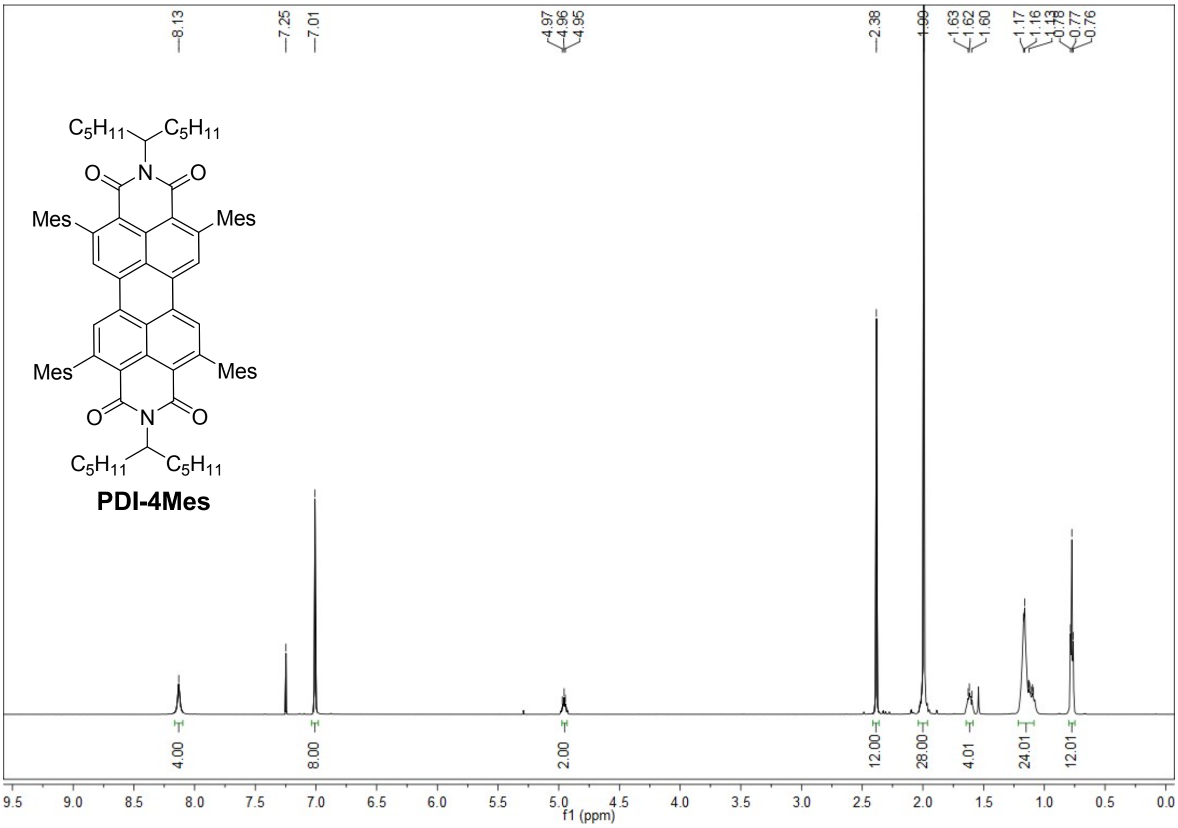

Figure S5. ^{1}H NMR of **PDI-4Mes**.

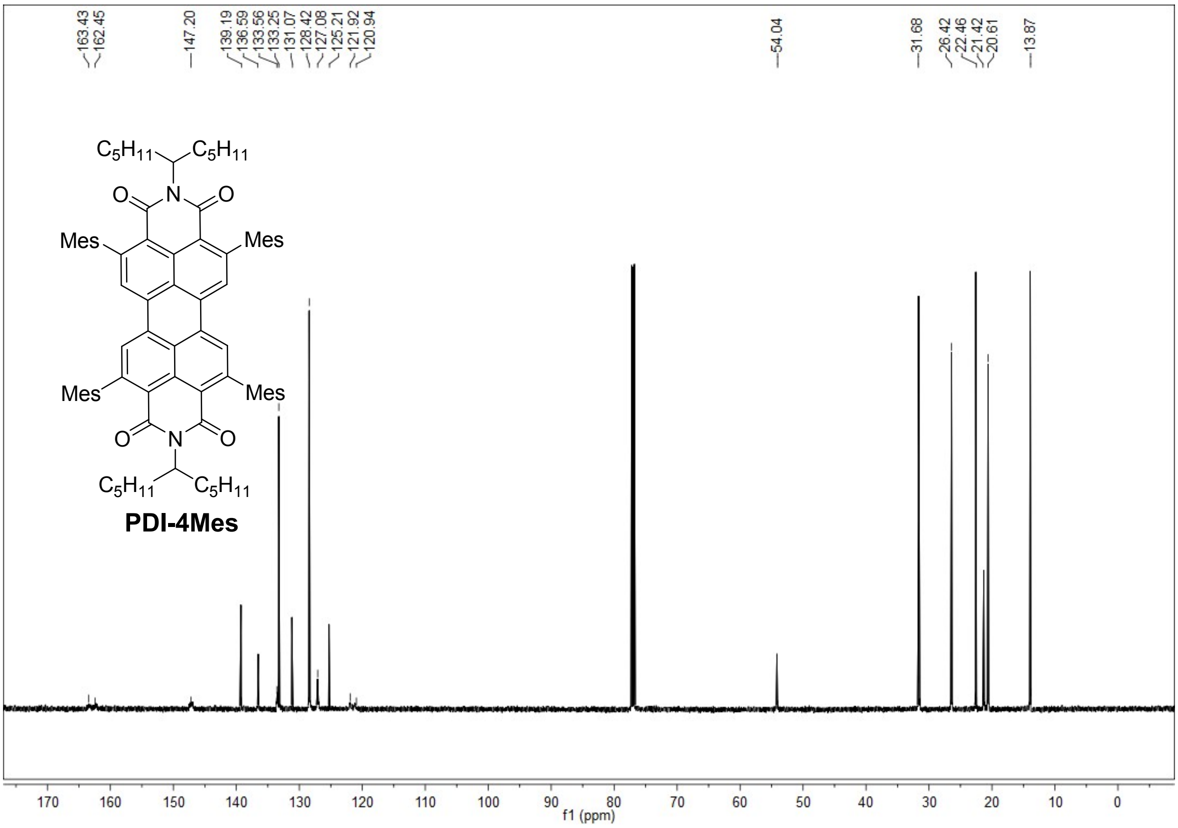

Figure S6. ^{13}C NMR of **PDI-4Mes**.

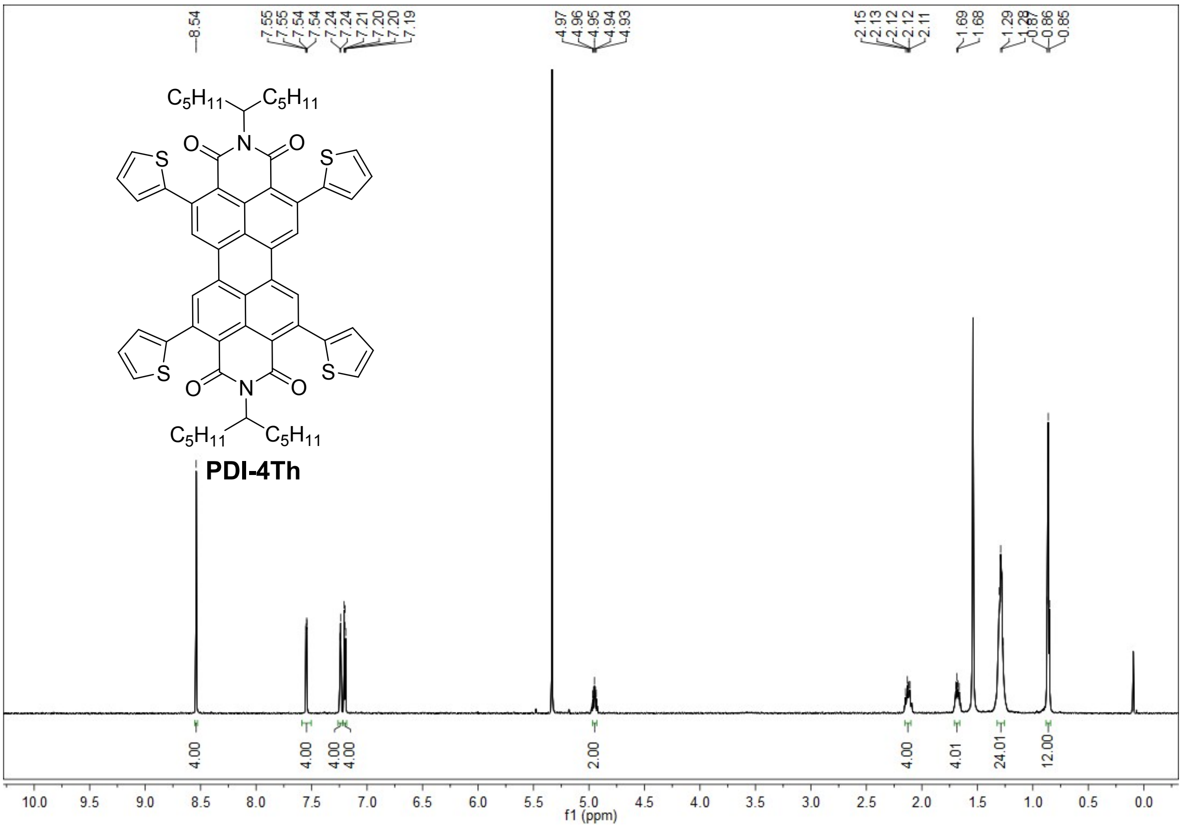

Figure S7. ^{1}H NMR of **PDI-4Th**.

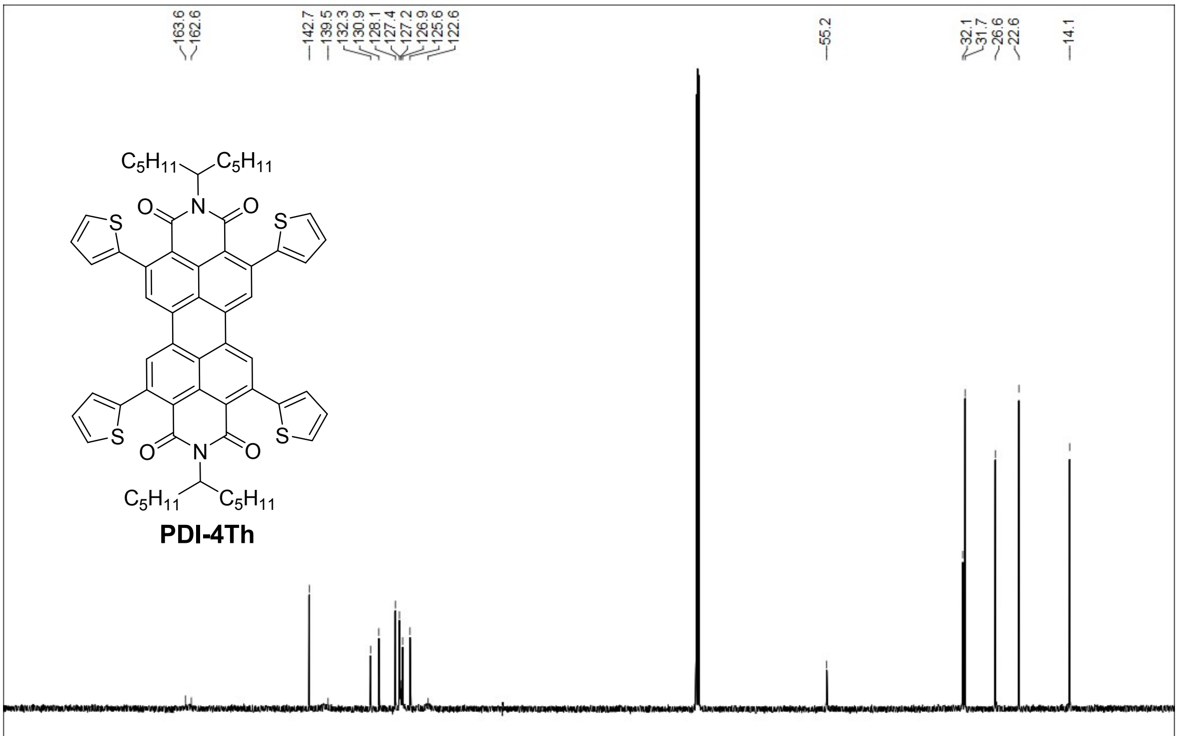

Figure S8. ^{13}C NMR of **PDI-4Th**.

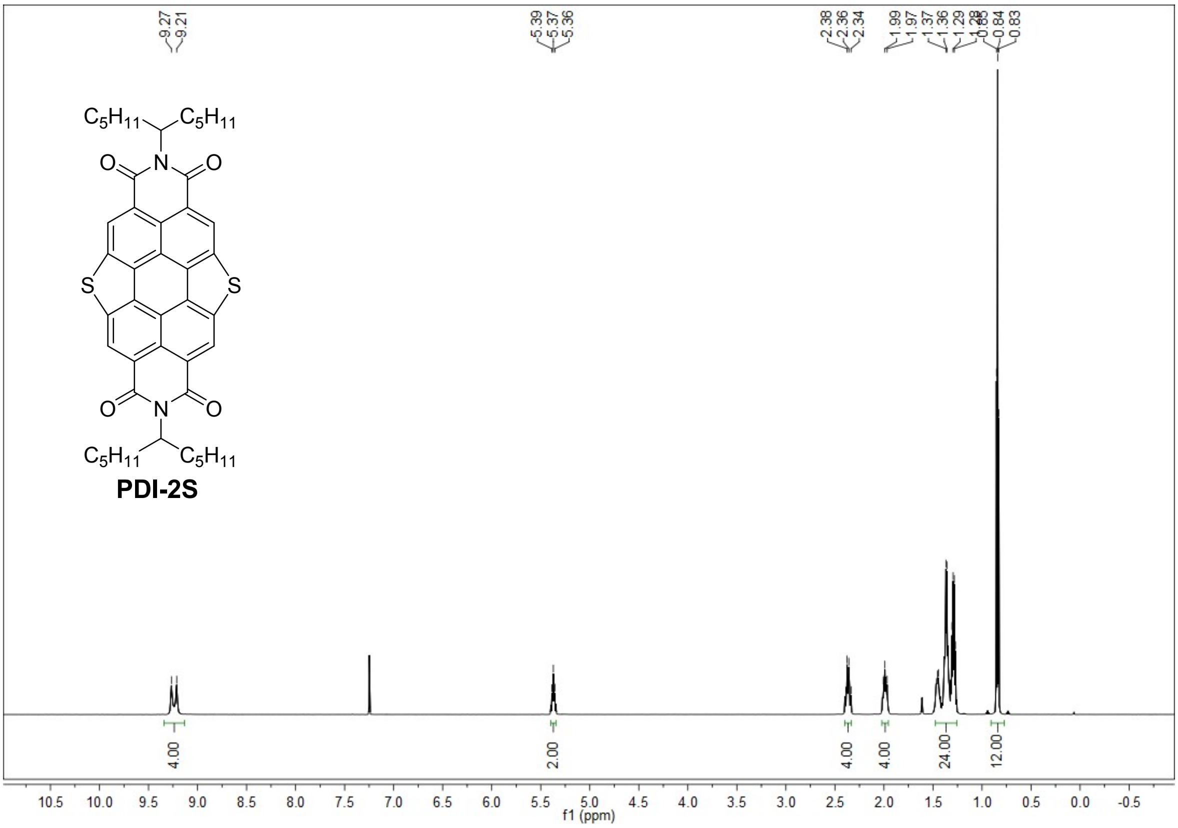

Figure S9. ^{1}H NMR of **PDI-2S**.

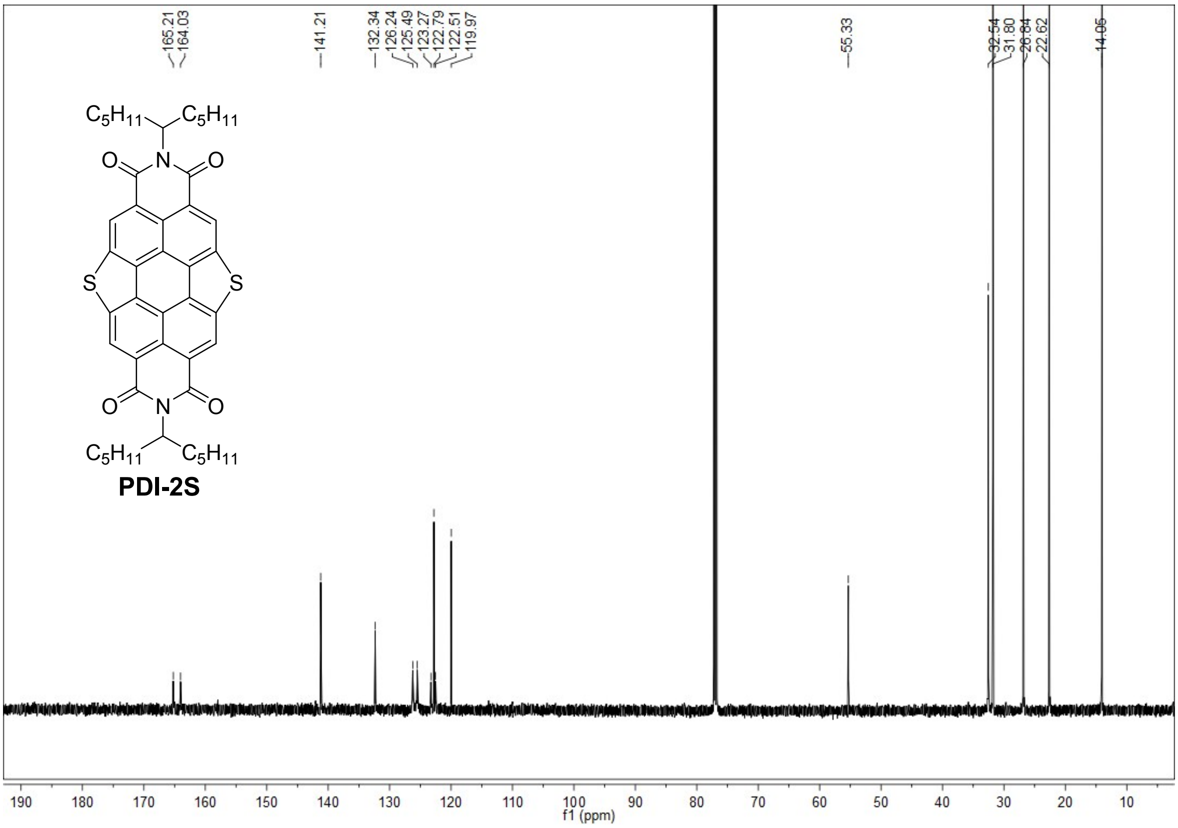

Figure S10. ^{13}C NMR of **PDI-2S**.

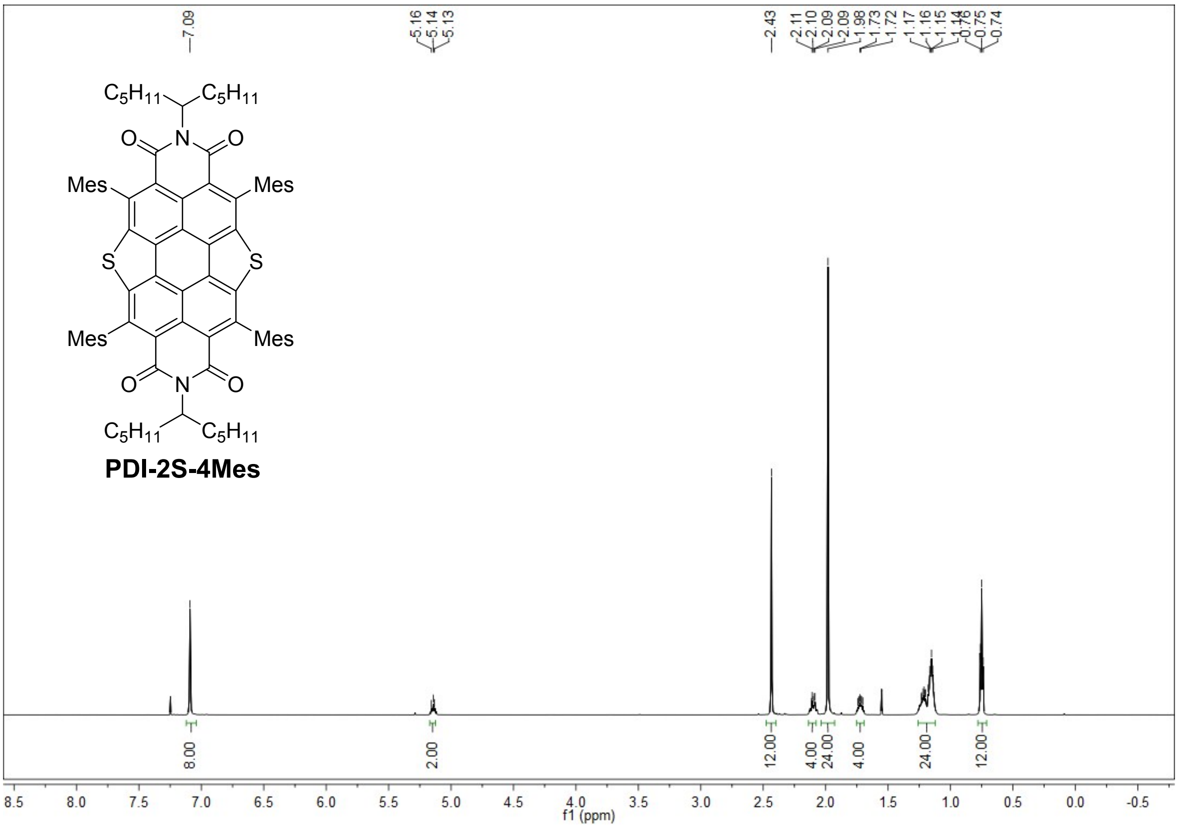

Figure S11. ^{1}H NMR of **PDI-2S-4Mes**.

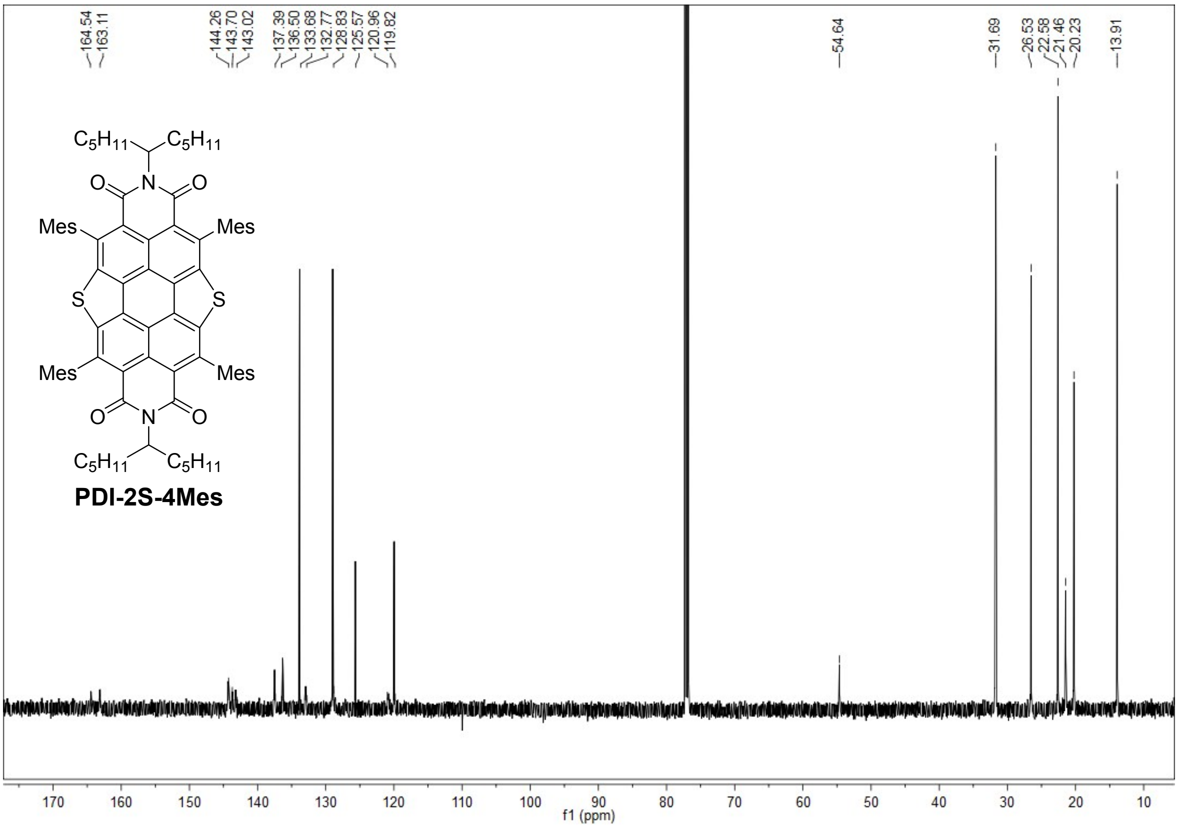

Figure S12. ^{13}C NMR of **PDI-2S-4Mes**.

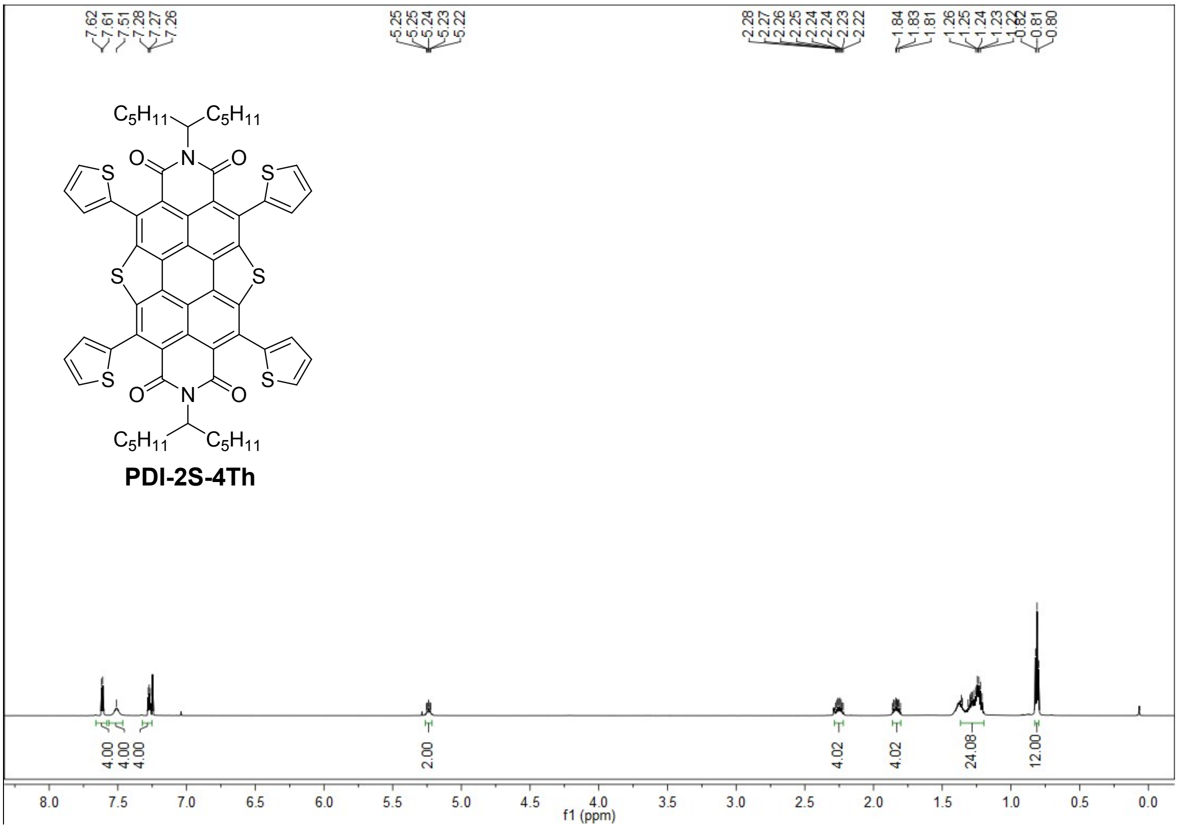

Figure S13. ^{1}H NMR of **PDI-2S-4Th**.

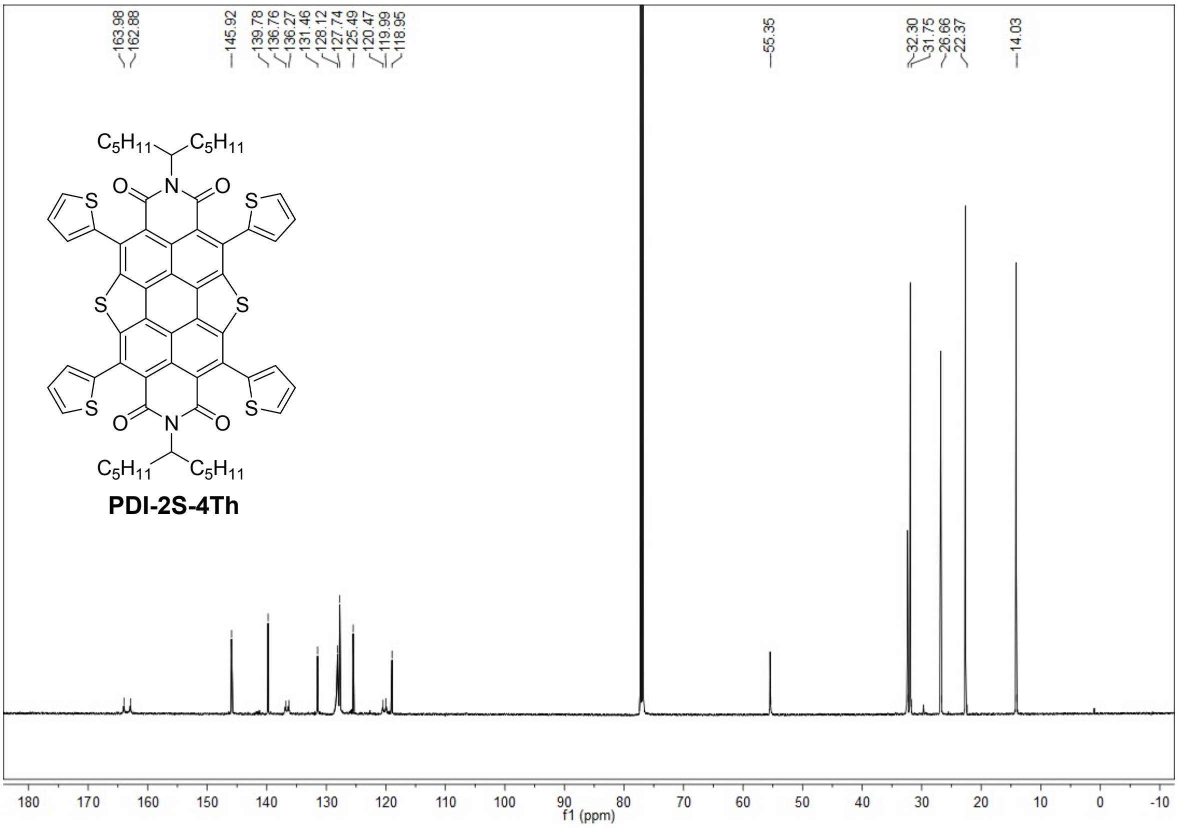

Figure S14. ^{13}C NMR of **PDI-2S-4Th**.