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Electronic Supplementary Information

The influence of spacer units on molecular properties and solar cell performance of non-fullerene acceptors

Jingbo Zhao,[b]† Yunke Li,[b]† Jianquan Zhang,[b]† Lu Zhang,[b] Joshua Yuk Lin Lai,[b] Kui Jiang,[b] Cheng Mu,[b] Zhengke Li,[b] Chun Lam Clement Chan,[b] Adrian Hunt,[c] Subhrangsu Mukherjee,[c] Harald Ade,[c] Xuhui Huang[a,b] and He Yan[a,b]*

[a.] The Hong Kong University of Science and Technology-Shenzhen Research Institute, No. 9 Yuexing 1st RD, Hi-tech Park, Nanshan, Shenzhen 518057, China.
[b.] Department of chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong.
[c.] Department of Physics, North Carolina State University, Raleigh, NC 27695, USA.
† These authors contributed equally to this work.
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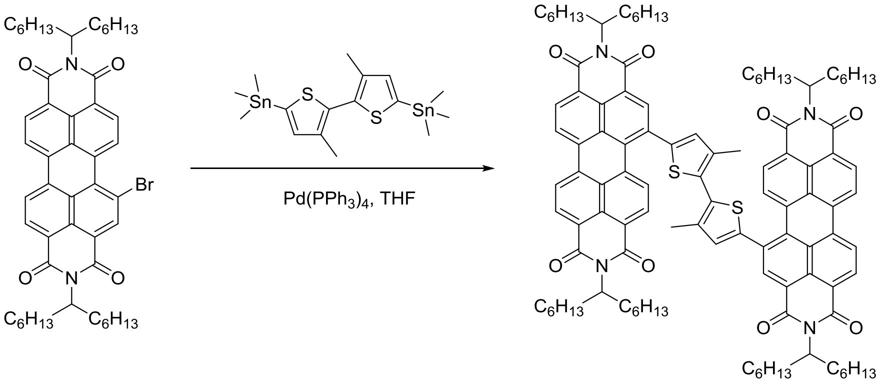
Email: hyan@ust.hk

I. Materials and Methods:

Materials. All reagents and chemicals were purchased from commercial sources and used without further purification unless stated otherwise. PDI-Br [1], 5,5'-bis(trimethylstannyl)-3,3'-dimethyl-2,2'-bithiophene [2], 5,5'-bis(trimethylstannyl)-4,4'-dimethyl-2,2'-bithiophene [3], PffBT4T-2DT [4, 5] and T$_2$-PDI$_2$ [6] were synthesized according to literature procedures.

Characterizations of new compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ^{1}H NMR and ^{13}C NMR spectra were referenced to tetramethylsilane (0 ppm) or solvent residual peak (7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR) as internal standard. Mass spectra were collected on a MALDI Micro MX mass spectrometer.

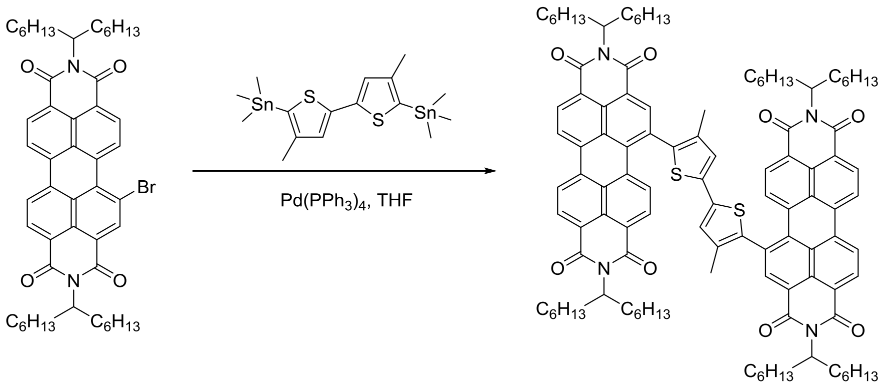


***i*-Me$_2$T$_2$-PDI$_2$.** 5,5'-Bis(trimethylstannyl)-3,3'-dimethyl-2,2'-bithiophene (46.8 mg, 0.0899 mmol), PDI-Br (150 mg, 0.180 mmol), tetrakis(triphenylphosphine)palladium(0) (5.2 mg, 0.0045 mmol) and distilled tetrahydrofuran (6 mL) were mixed in a nitrogen-filled glovebox. The mixture was heated to 110 °C for 1 h in a microwave reactor. The reaction mixture was poured into an aqueous potassium fluoride solution and stirred for 1 h. The mixture was extracted with diethyl ether. The organic layer was separated and washed with water followed by brine. Then the solution was dried over sodium sulfate and concentrated in vacuum. The residue was purified by flash column chromatography (eluent: *n*-hexane: dichloromethane = 1:2) to get the product as red solid (134 mg, 88%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.78 – 8.59 (m, 10H), 8.47 – 8.27 (m, 4H), 7.16 (s, 2H), 5.26 – 5.07 (m, 4H), 2.36 (s, 6H), 2.34 – 2.13 (m, 8H), 1.92 – 1.77 (m, 8H), 1.46 – 1.12 (m, 64H), 0.91 – 0.75 (m, 24H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 164.65, 163.71, 144.00, 139.10, 137.15, 136.45, 135.05, 134.42, 133.75, 133.52, 131.78, 131.37, 131.04, 130.12, 129.77, 129.39, 129.08, 128.20, 127.70, 123.81, 122.99, 54.97, 54.84, 32.51, 31.91, 31.87, 29.36, 29.33, 27.05, 22.73, 22.71, 15.39, 14.18.

HRMS (MALDI+) Calcd for $C_{110}H_{130}N_4O_8S_2$ (M^+): 1699.9364, Found: 1699.9357.



***o*-Me$_2$T$_2$-PDI$_2$.** 5,5'-Bis(trimethylstannyl)-4,4'-dimethyl-2,2'-bithiophene (46.8 mg, 0.0899 mmol), PDI-Br (150 mg, 0.180 mmol), tetrakis(triphenylphosphine)palladium(0) (5.2 mg, 0.0045 mmol) and distilled tetrahydrofuran (6 mL) were mixed in a nitrogen-filled glovebox. The mixture was heated to 110 ℃ for 1 h in a microwave reactor. The reaction mixture was poured into an aqueous potassium fluoride solution and stirred for 1h. The mixture was extracted with diethyl ether. The organic layer was separated and washed with water followed by brine. Then the solution was dried over sodium sulfate and concentrated in vacuum. The residue was purified by flash column chromatography (eluent: *n*-hexane: dichloromethane = 1:2) to get the product as red solid (106 mg, 69%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.81 – 8.63 (m, 10H), 8.52 – 8.40 (m, 4H), 7.15 (s, 2H), 5.30 – 5.08 (m, 4H), 2.34 – 2.13 (m, 8H), 1.99 (s, 6H), 1.94 – 1.79 (m, 8H), 1.45 – 1.12 (m, 64H), 0.91 – 0.76 (m, 24H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 164.87, 164.65, 163.83, 137.72, 137.56, 135.29, 135.03, 134.40, 132.49, 131.79, 131.03, 129.36, 129.14, 128.09, 127.40, 123.79, 123.03, 54.98, 54.87, 32.51, 31.91, 31.88, 29.36, 27.06, 22.74, 22.73, 14.73, 14.20.

HRMS (MALDI+) Calcd for $C_{110}H_{130}N_4O_8S_2$ (M^+): 1699.9364, Found: 1699.9421.

Optical characterizations. UV-Vis absorption spectra were acquired on a Perkin Elmer Lambda 20 UV/VIS Spectrophotometer. All film samples were spincast on ITO/ZnO substrates.

Electrochemical characterizations. Cyclic voltammetry was carried out on a CHI760E electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Small molecules (1.0×10^{-4} mol L^{-1}) and tetrabutylammonium hexafluorophosphate (0.1 mol L^{-1}) were dissolved in dichloromethane. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as external standards in dichloromethane or acetonitrile solutions. The scan rate is 0.1 V s^{-1}.

Hole mobility measurements. The hole mobilities were measured using the space charge limited current (SCLC) method, employing a device architecture of ITO/V$_2$O$_5$/blend film/V$_2$O$_5$/Al. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_{\mathrm{r}}\mu V^2}{8L^3}$$

Where ε_0 is the permittivity of free space, ε_{r} is the relative permittivity of the material (assumed to be 3), μ is the hole mobility and L is the thickness of the film. From the plots of $J^{1/2}$ vs V, hole mobilities can be deduced.

Electron mobility measurements. The electron mobilities were measured using the SCLC method, employing a device architecture of ITO/ZnO/blend film/Ca/Al. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_{\mathrm{r}}\mu V^2}{8L^3}$$

Where ε_0 is the permittivity of free space, ε_{r} is the relative permittivity of the material (assumed to be 3), μ is the electron mobility and L is the thickness of the film. From the plots of $J^{1/2}$ vs V, electron mobilities can be deduced.

DFT calculation. The geometry was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional with basis set 6-31g*. Quantum-chemical calculation was performed with the Gaussian09 package.[7] Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency. All *N*-hexylheptyl substituents were replaced with methyl groups in calculations.

GIWAXS characterization. GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source[8]. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12 °or 0.13 °, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

Solar cell fabrication and testing. Pre-patterned ITO-coated glass with a sheet resistance of ~15 Ω per square was used as the substrate. It was cleaned by sequential sonications in soap deionized water, deionized water, acetone, and isopropanol for 15 min at each step. After UV/ozone treatment for 60 min, a ZnO electron transport layer was prepared by spin-coating at 5000 rpm from a ZnO precursor solution (diethyl zinc). Active layer solutions (D/A ratio 1:1.4) were prepared in CB (polymer concentration: 6.5 mg/mL). To completely dissolve the polymer, the active layer solution should be stirred on hotplate at 110 ℃ for at least 3 hours. Before spincoating, both the polymer solution and ITO substrate are preheated on a hotplate at about 110 ℃. Active layers were spin-coated from the warm polymer solution on the preheated substrate in a N_2 glovebox at 1300 rpm to obtain thicknesses of ~90 nm. The polymer:SMA blend films were then annealed at 100 ℃ for 5 min before being transferred to the vacuum chamber of a thermal evaporator inside the same glovebox. At a vacuum level of 3×10^{-6} Torr, a thin layer (20 nm) of V_2O_5 was deposited as the anode interlayer, followed by deposition of 100 nm of Al as the top electrode. All cells were encapsulated using epoxy inside the glovebox. Device *J-V* characteristics was measured under AM1.5G (100 mW cm^{-2}) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. *J-V* characteristics were recorded using a Keithley 236 or 2400 source meter unit. Typical cells have devices area of 5.9 mm^2, which is defined by a metal mask with an aperture aligned with the device area. EQEs were characterized using a Newport EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

II. Supplementary figures and tables.

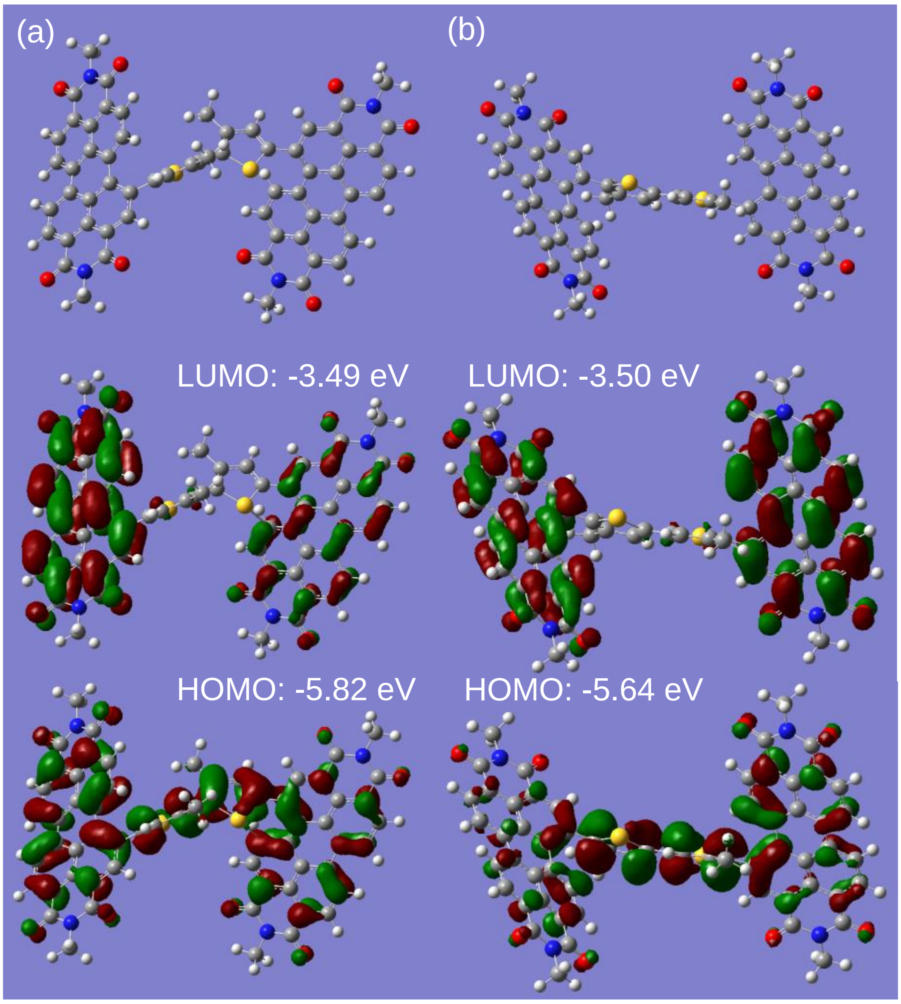


Fig. S1 DFT calculated geometry, LUMO and HOMO of (a) *i*-Me_2T_2-PDI_2 and (b) *o*-Me_2T_2-PDI_2.

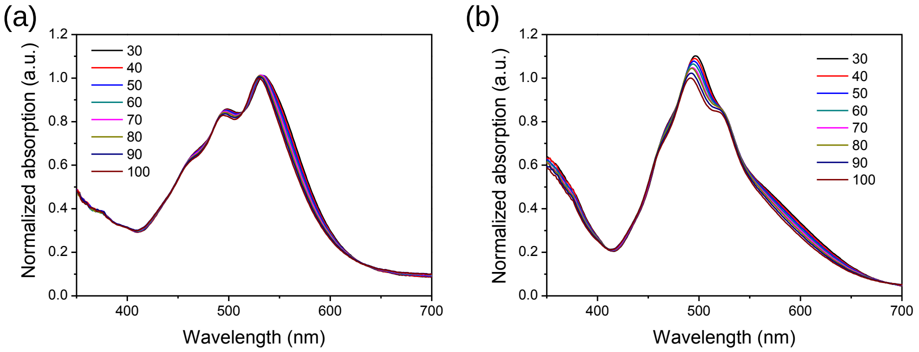


Fig. S2 UV-Vis spectra of (a) *i*-Me_2T_2-PDI_2 and (b) *o*-Me_2T_2-PDI_2 at elevated temperatures in chlorobenzene solutions. The insets indicate the temperatures (units: ℃).

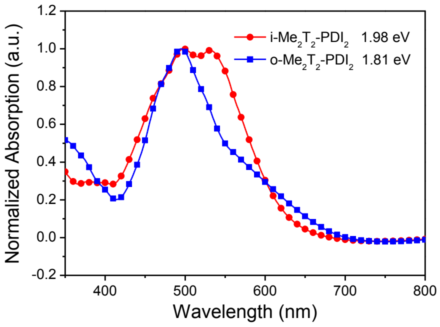


Fig. S3 Film absorption spectra of the two acceptors. The insets indicate the optical bandgaps.

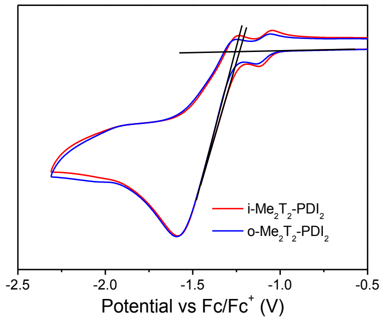


Fig. S4 Cyclic voltammograms of the two acceptors.

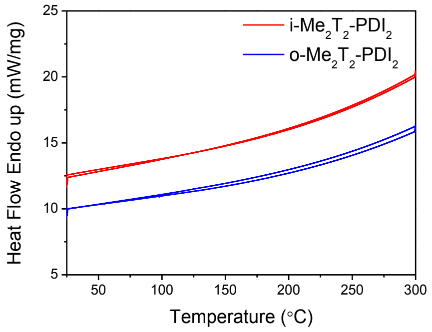


Fig. S5 DSC results of the two acceptors.

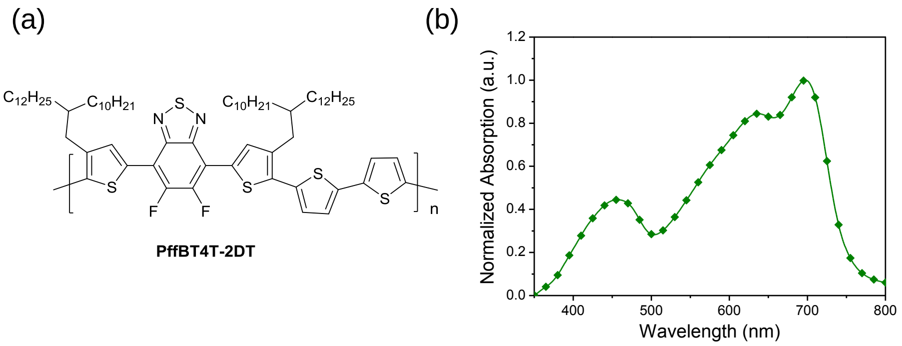


Fig. S6 (a) The chemical structure and (b) UV-Vis absorption spectrum of a PffBT4T-2DT film.

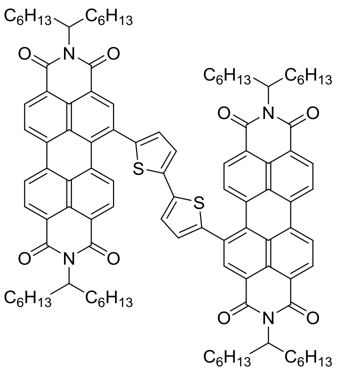


Fig. S7 The chemical structure of T_2-PDI_2.

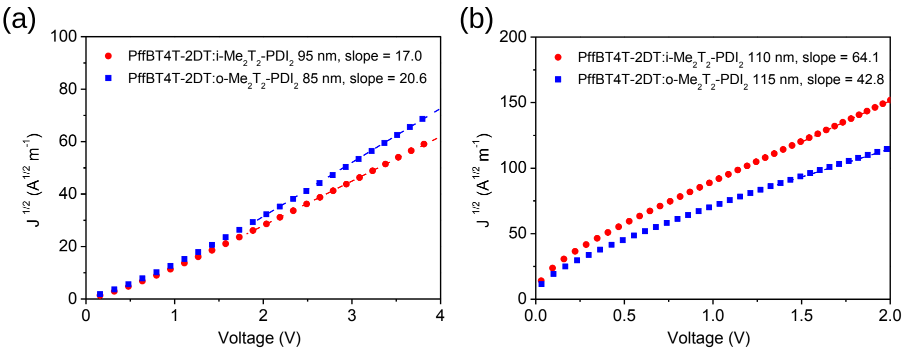


Fig. S8 $J^{1/2}$~V characteristics of (a) electron only and (b) hole only devices. Dash lines are fits.

Table S1 Hole and electron mobilities of PffBT4T-2DT:i-Me_2T_2-PDI_2 and PffBT4T-2DT:o-Me_2T_2-PDI_2 blends.

	Hole mobility [cm^2 V^{-1} s^{-1}]	Electron mobility [cm^2 V^{-1} s^{-1}]
PffBT4T-2DT:i-Me_2T_2-PDI_2	1.8×10^{-3}	8.3×10^{-5}
PffBT4T-2DT:o-Me_2T_2-PDI_2	9.3×10^{-4}	8.7×10^{-5}

Table S2 Comparison of solar cell performance based on different acceptors.

	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	PCE [%]	Reference
PffBT4T-2DT:i-Me_2T_2-PDI_2	0.91	8.0	0.56	4.1	This work
PffBT4T-2DT:o-Me_2T_2-PDI_2	0.89	6.8	0.51	3.1	This work
PffBT4T-2DT:T_2-PDI_2	0.85	6.6	0.48	2.7	This work
PffBT4T-2DT:SF-PDI_2	0.99	11.0	0.58	6.3	5
PffBT4T-2DT:$PC_{71}BM$	0.76	16.2	0.62	7.6	4

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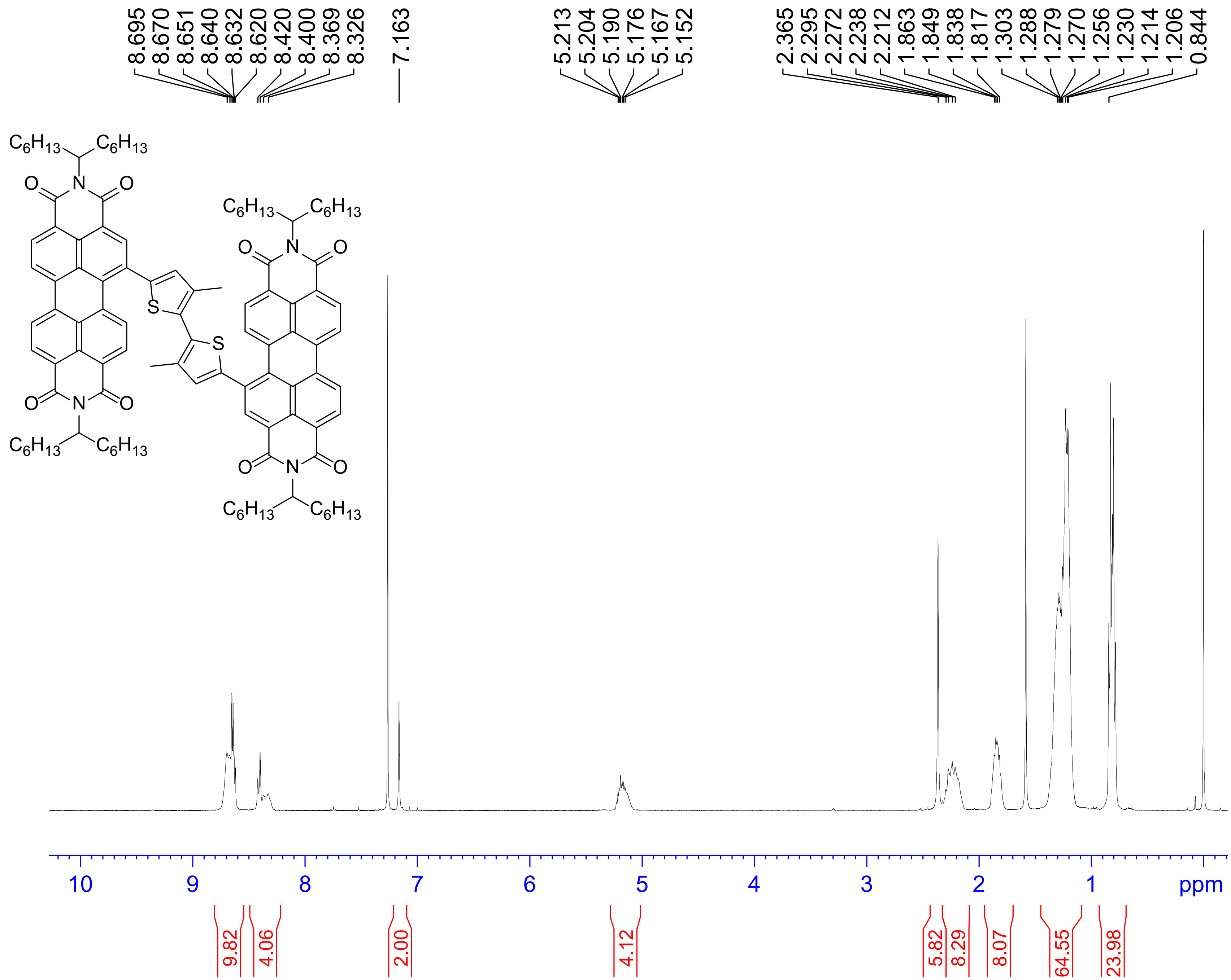

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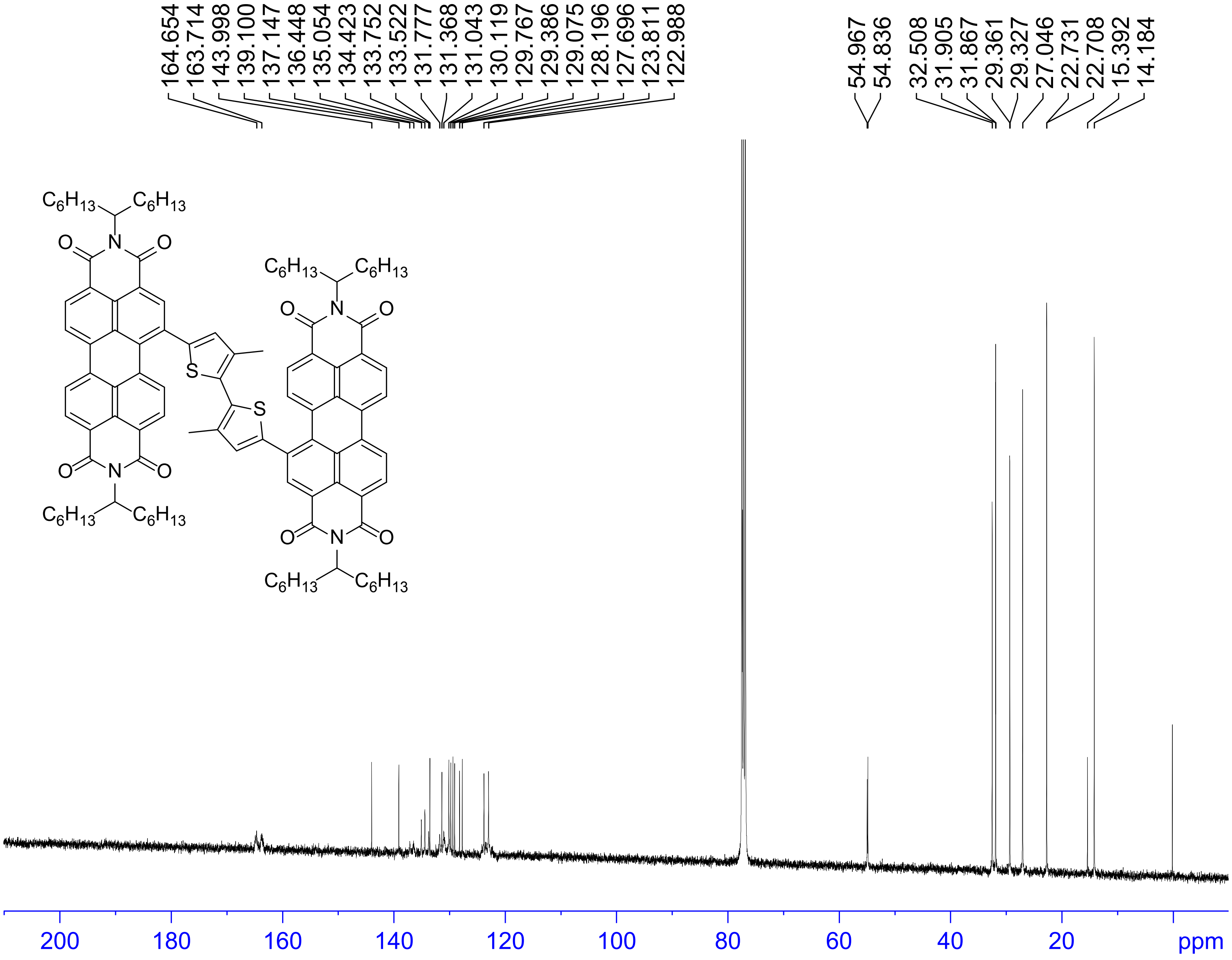

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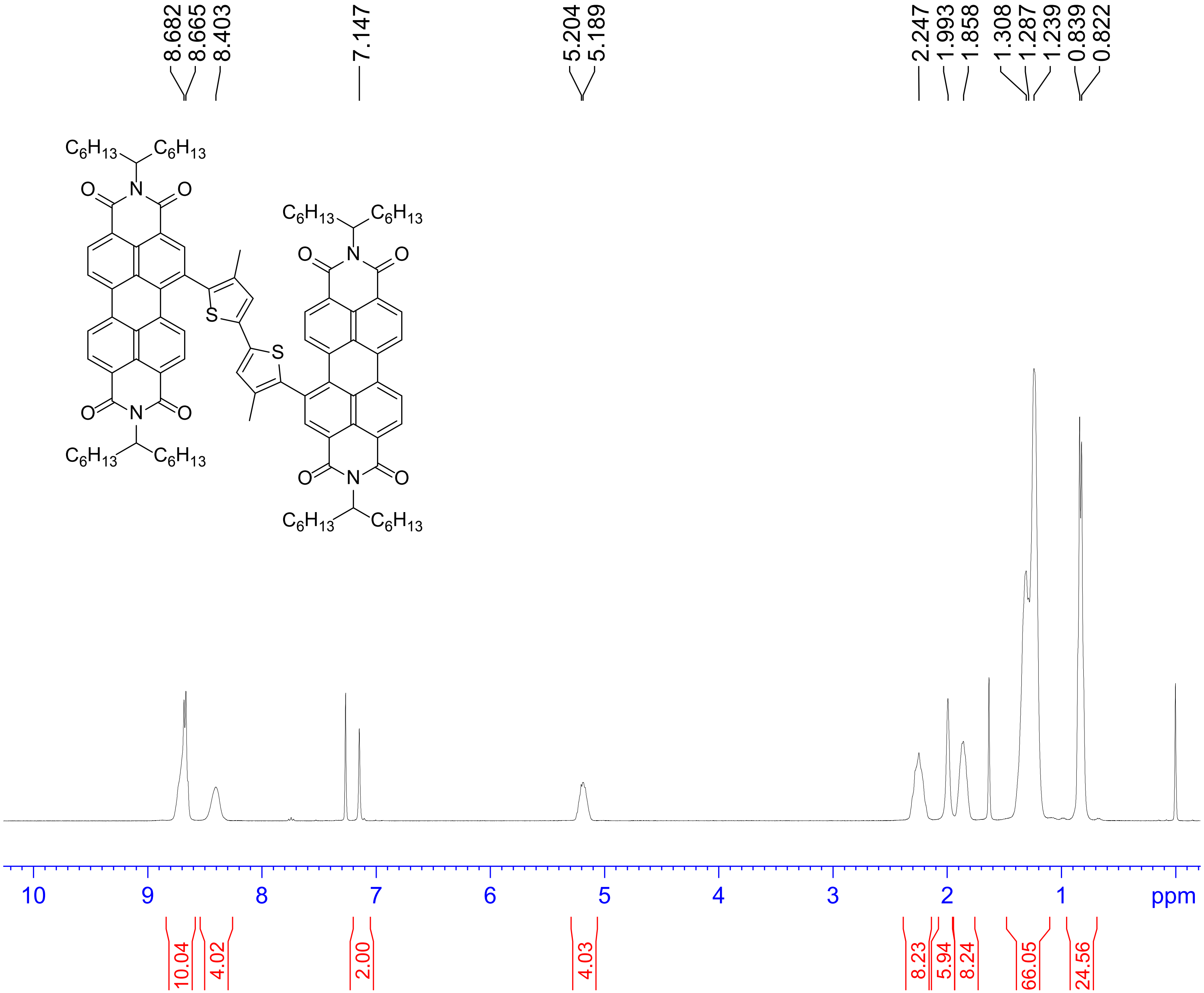

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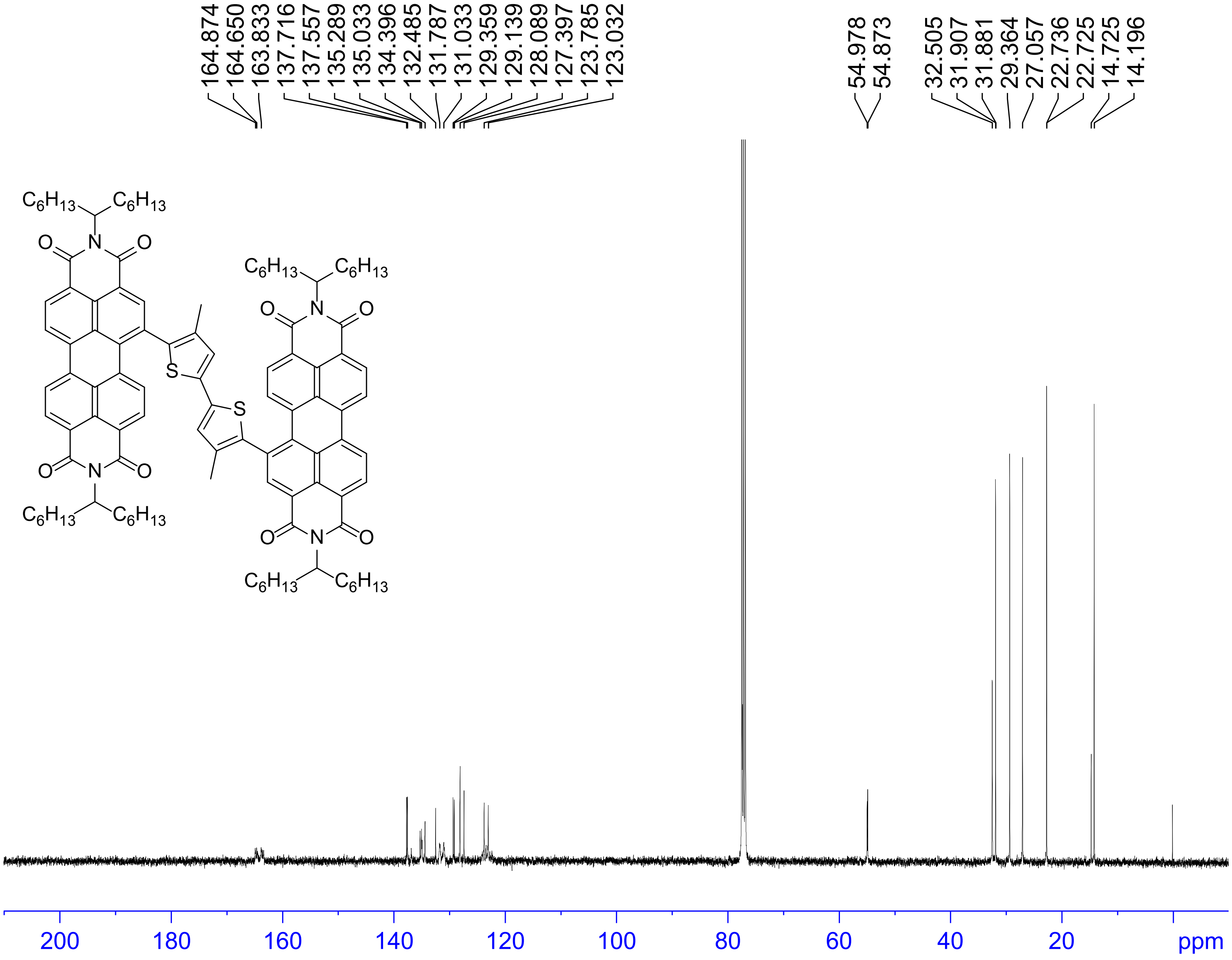

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