

Electronic Supplementary Information *for*

Synthesis and Characterization of Diketopyrrolopyrrole-Based Conjugated Molecules Flanked by Indenothiophene and Benzoindenothiophene Derivatives

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Characterization and instrumentation

¹H NMR and ¹³C NMR spectra were measured by a Bruker 400-MHz spectrometer in CDCl₃ (the ¹H NMR of **DPP-NaCO** was in CD₂Cl₂) at room temperature with tetramethylsilane (TMS) as internal standard. Molecular mass was characterized by a Bruker/AutoflexIII Smartbean MALDI mass spectrometer. FT-IR spectra were obtained in chloroform solvents on a BIOFTS-7 Fourier transform infrared spectrometer. Elemental analysis was carried out on a VarioEL elemental analysis system. TGA was recorded by Perkin-Elmer TGA-7 at a heating rate of 10 °C/min under N₂ and DSC was measured by Perkin-Elmer DSC7 thermal analyzer at a scanning rate of 10 °C/min under N₂. Absorption spectra were obtained on a PerkinElmer Lambda35 UV/Vis Spectrometer. Solution spectra were measured in chloroform with a concentration of 1×10⁻⁵ mol/L and films were prepared by spin-casting with chloroform as solvent. Cyclic voltamogram (CV) was obtained by a CHI660 electrochemical analyzer in a three-electrode cell with a glassy carbon working electrode, a Pt wire counter electrode and a saturated calomel electrode (SCE) reference electrode, at a scan rate of 100 mV/s in anhydrous dichloromethane solution with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The potential was calibrated by ferrocene/ferrocenium (Fc/Fc⁺), the highest occupied

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: $\text{HOMO} = - (4.80 + E_{\text{onset}}^{\text{ox}}) \text{ eV}$, $\text{LUMO} = - (4.80 + E_{\text{onset}}^{\text{re}}) \text{ eV}$. DFT calculation was carried out on the Gaussian 09 package program by means of B3LYP/6-31G. Out-of-plane X-ray diffraction (XRD) was recorded on Bruker D8 Discover thin-film diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 40 mA. In-plane XRD of the thin films were measured with a Rigaku Smart Lab with Cu K α source ($\lambda = 1.54056 \text{ \AA}$) in the air. AFM images were recorded in tapping mode on a SPI3800N (Seiko Instruments Inc., Japan).

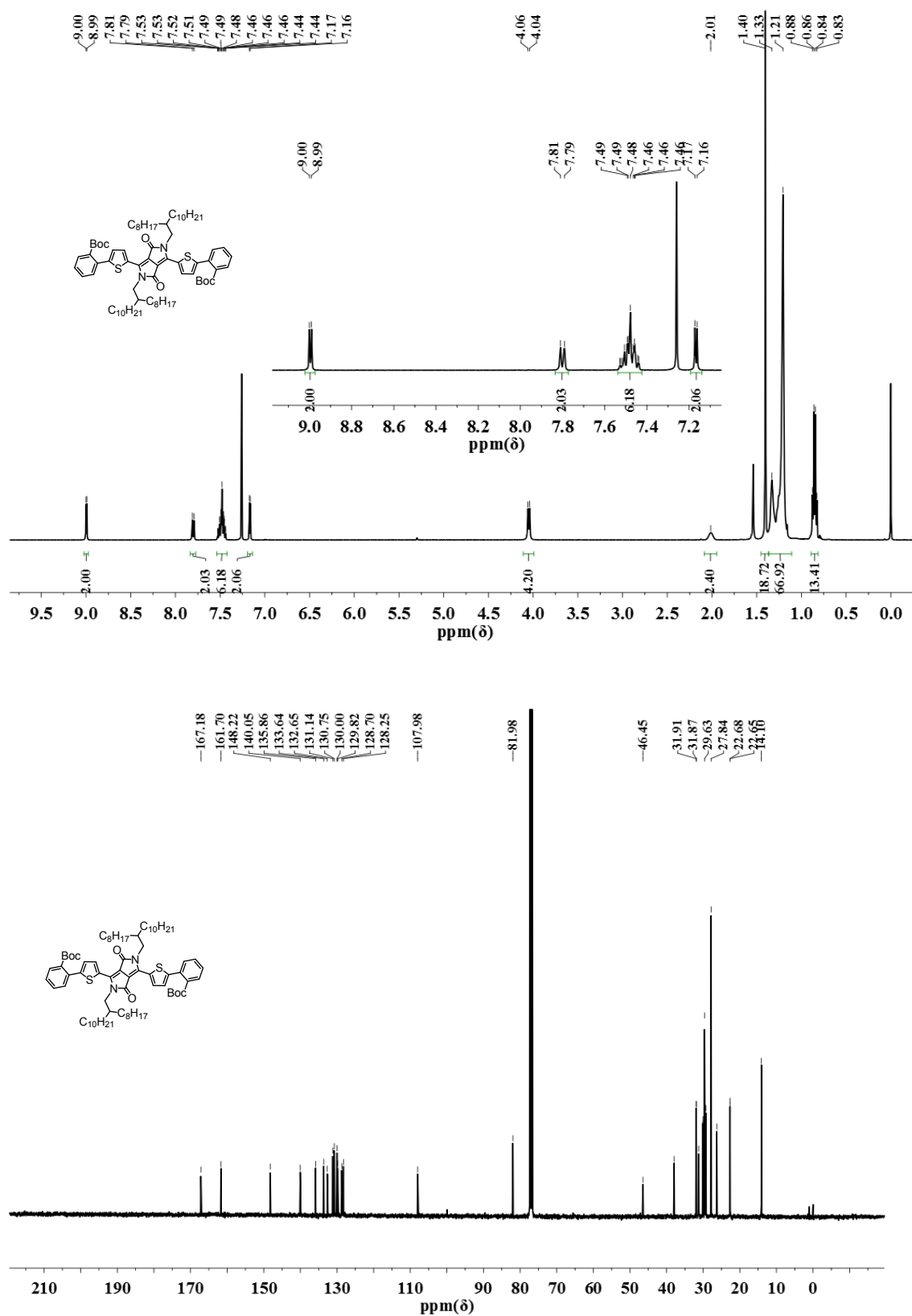


Figure S1 ¹H NMR (top) and ¹³C NMR (bottom) spectra of di-*t*-butyl 2,2'-(5,5'-(2,5-bis(2-octyldecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl)dibenzoate (**4**).

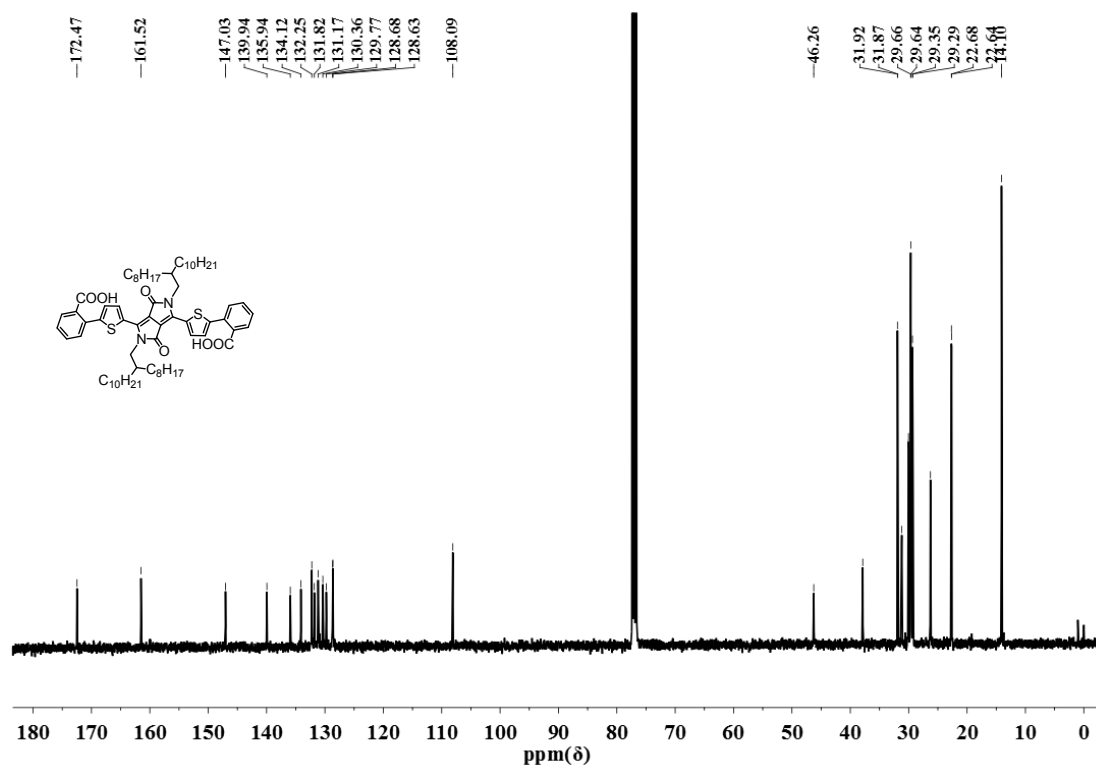
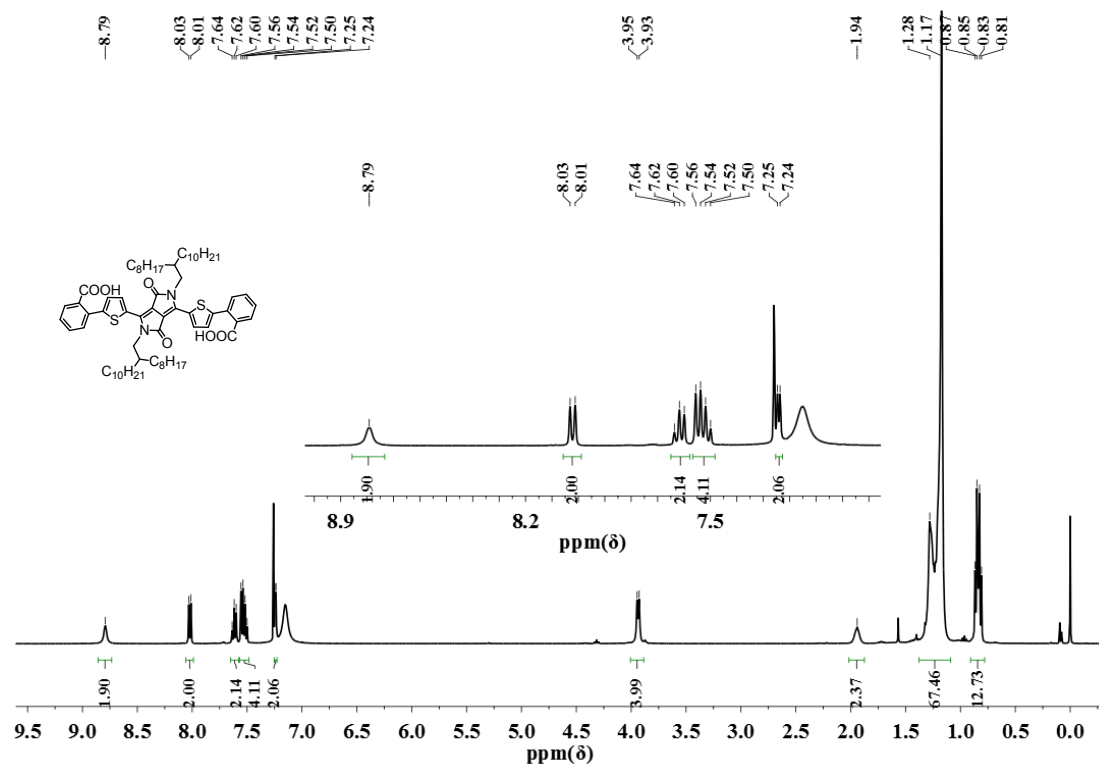


Figure S2 1H NMR (top) and ^{13}C NMR (bottom) spectra of 2,2'-(5,5'-(2,5-bis(2-octyldecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl)dibenzoic acid (5).

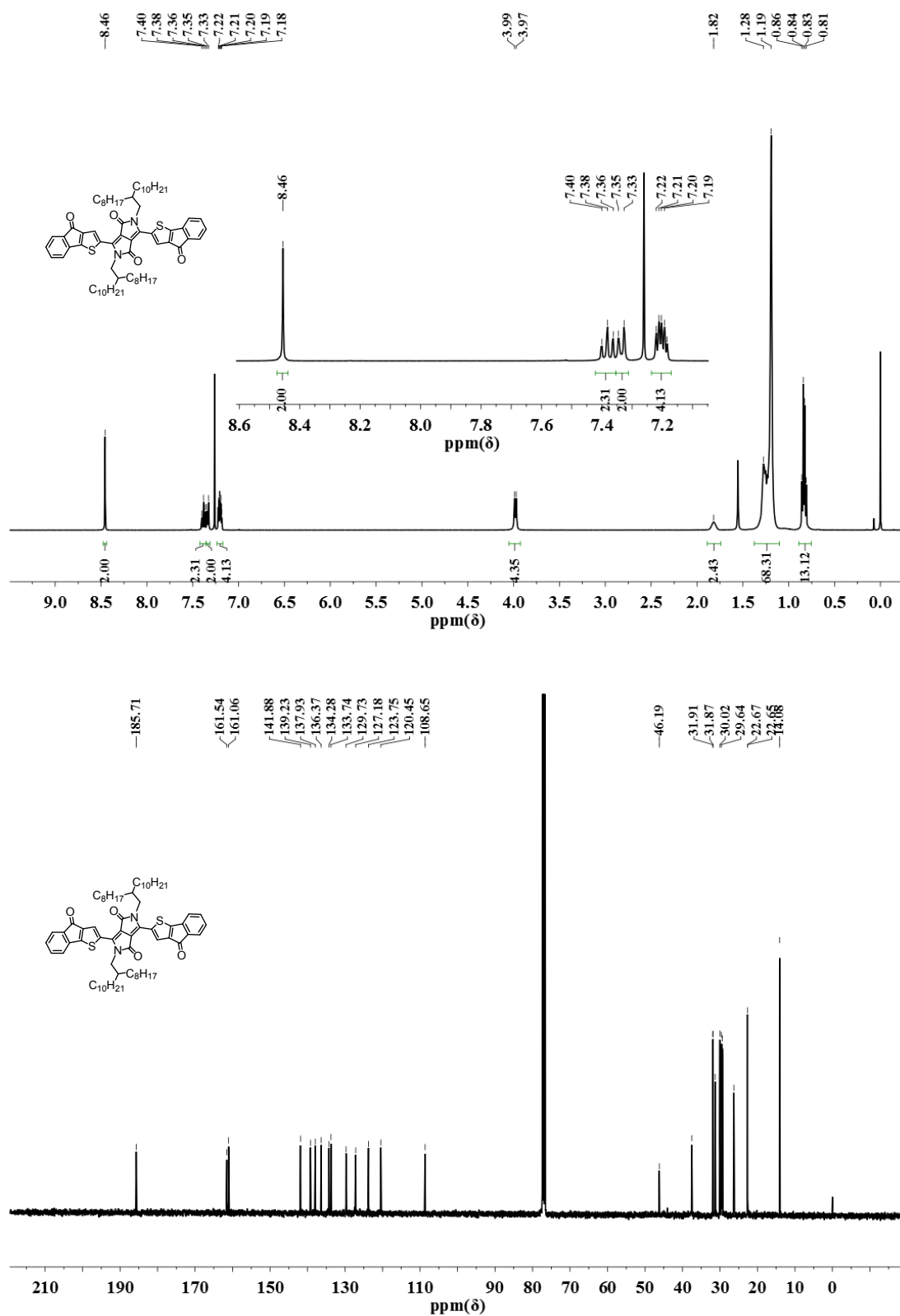


Figure S3 ¹H NMR (top) and ¹³C NMR (bottom) spectra of 2,5-bis(2-octyldodecyl)-3,6-bis(4-oxo-4H-indeno[1,2-*b*]thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (**DPP-PhCO**).

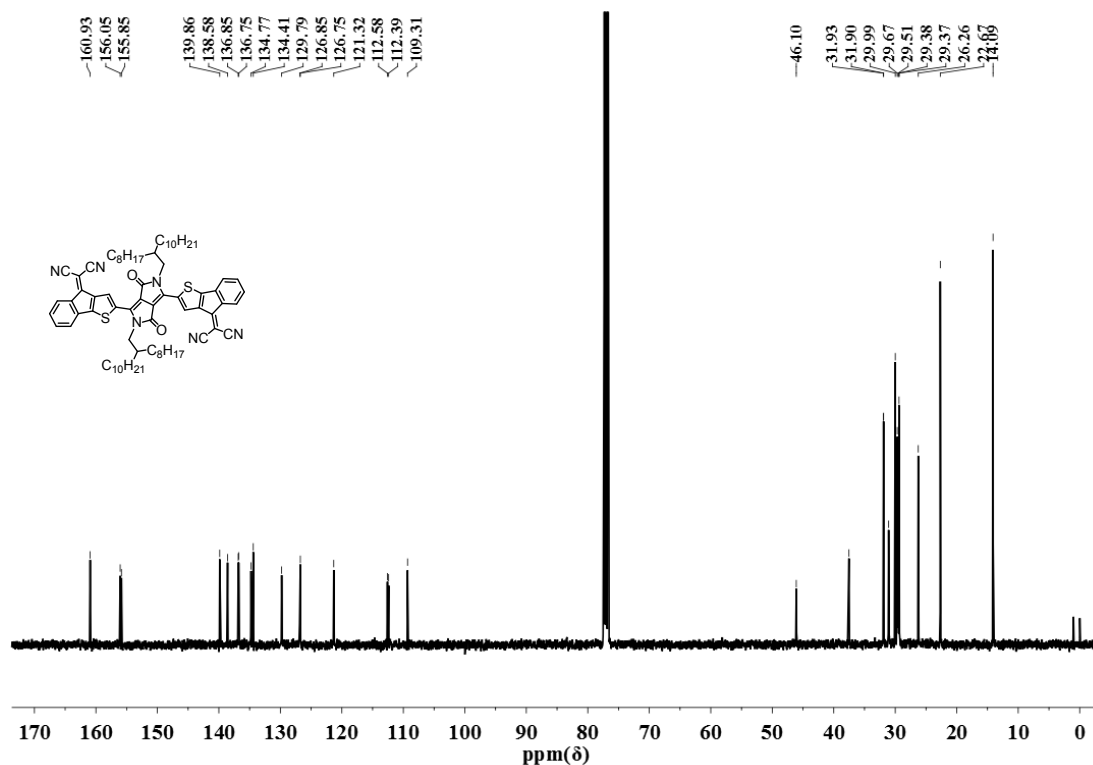
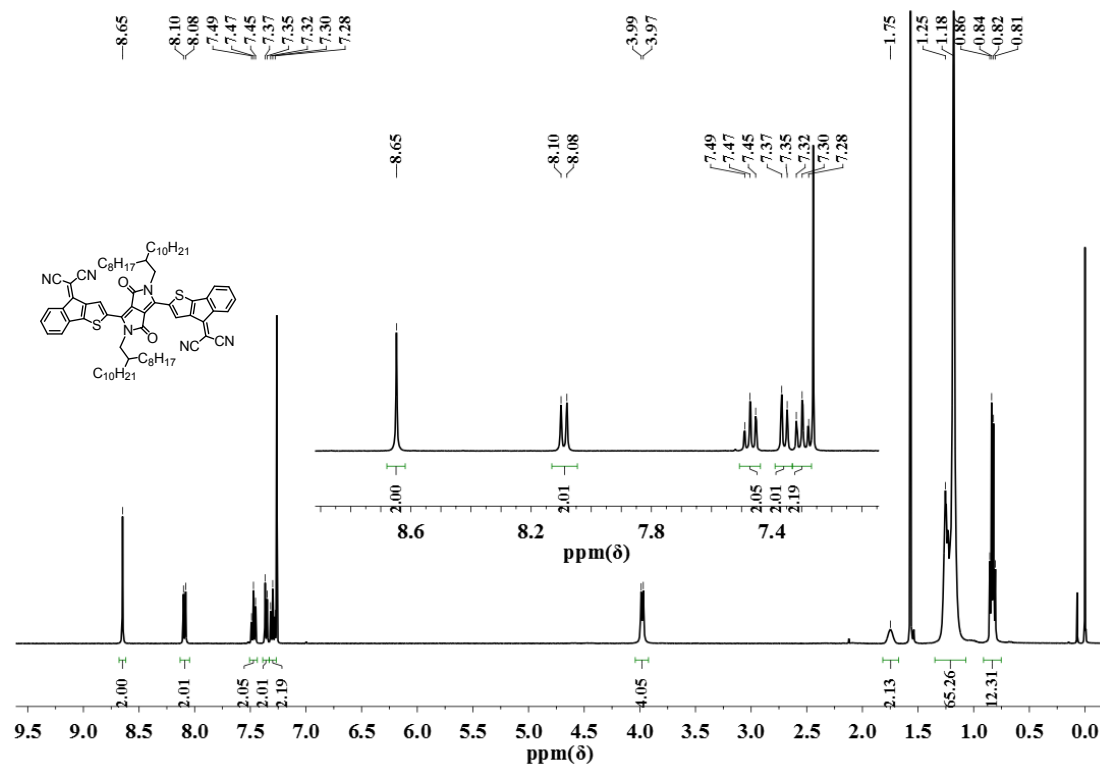


Figure S4 ¹H NMR (top) and ¹³C NMR (bottom) spectra of 2,2'-(2,2'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydro-pyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(4H-indeno[1,2-*b*]thiophene-2-yl-4-ylidene))dimalononitrile (DPP-PhCN)

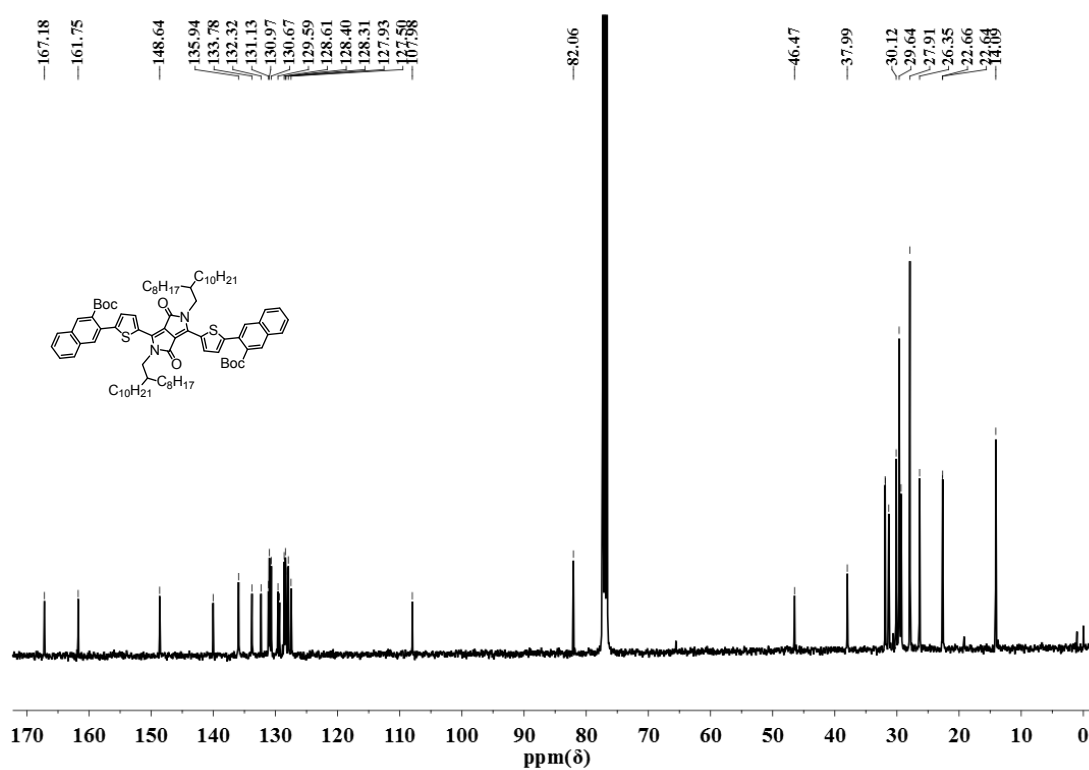
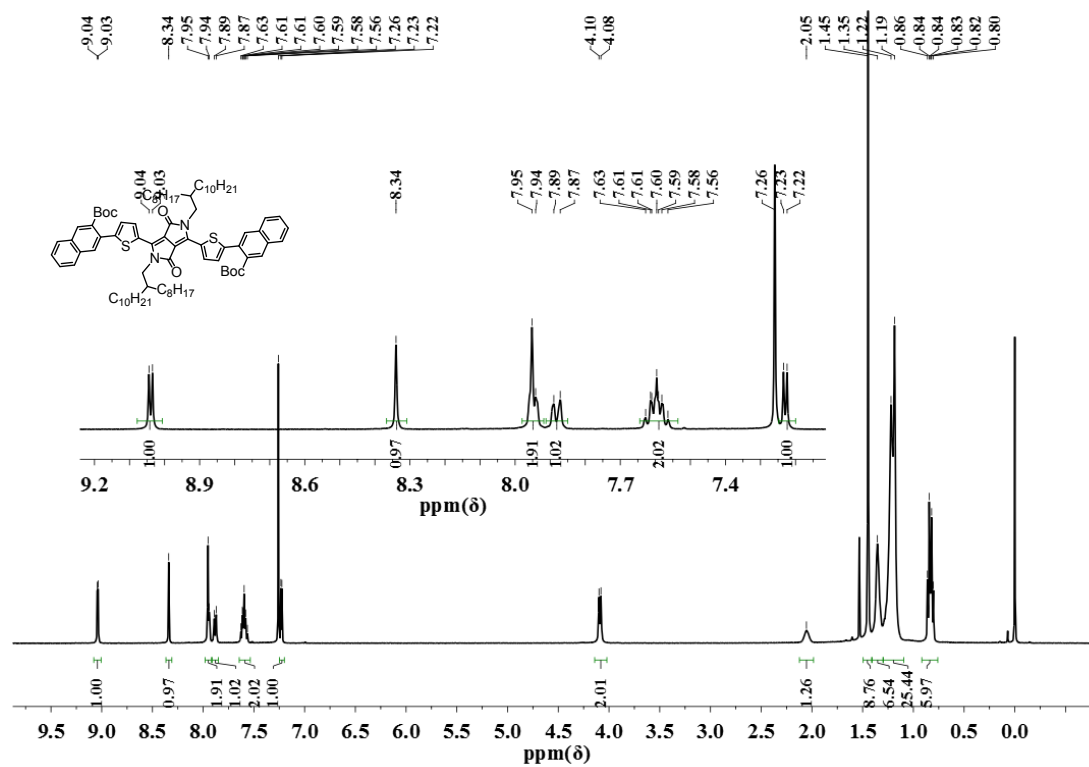


Figure S5 ¹H NMR (top) and ¹³C NMR (bottom) spectra of di-*t*-butyl 3,3'-(5,5'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl))bis(2-naphthoate) (7).

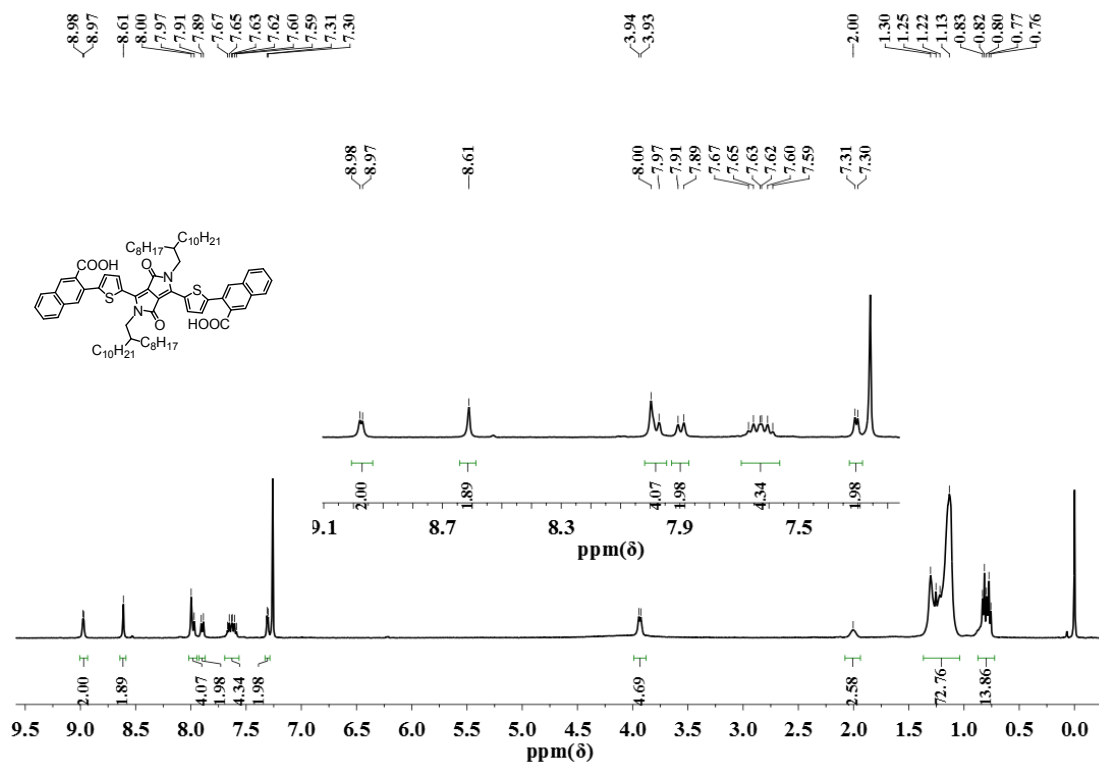


Figure S6 ¹H NMR spectra of 3,3'-(5,5'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydro-pyrrolo[3,4-c]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl))bis(2-naphthoic acid) (8).

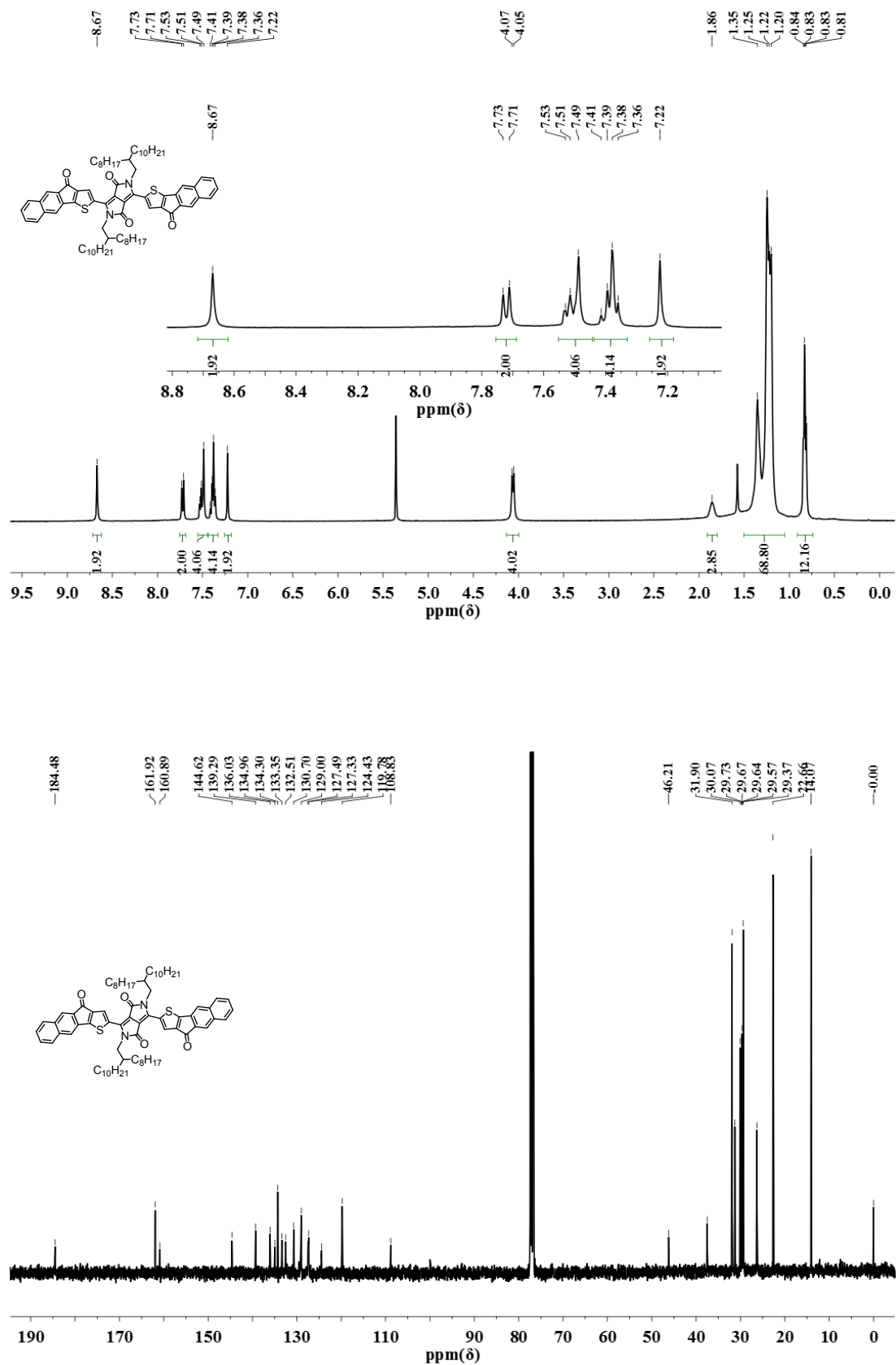


Figure S7 ¹H NMR (top) and ¹³C NMR (bottom) spectra of 2,5-bis(2-octyl-dodecyl)-3,6-bis(4-oxo-4H-benzo[5,6]indeno[1,2-*b*]thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (**DPP-NaCO**)

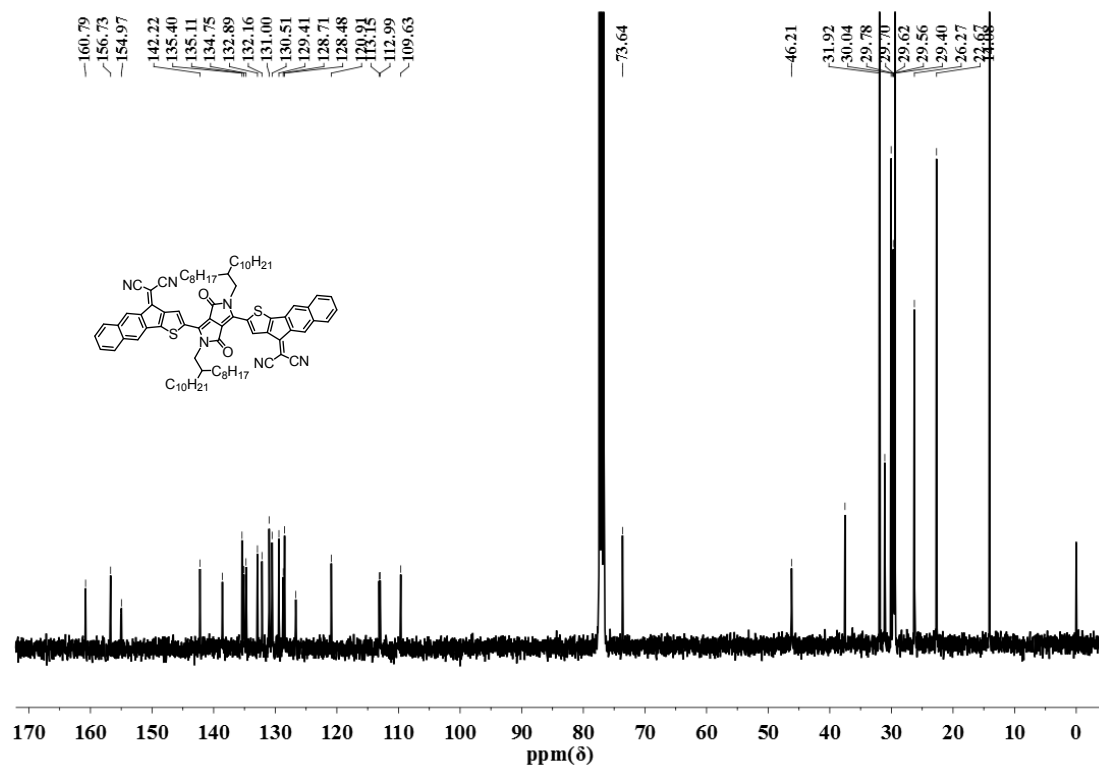
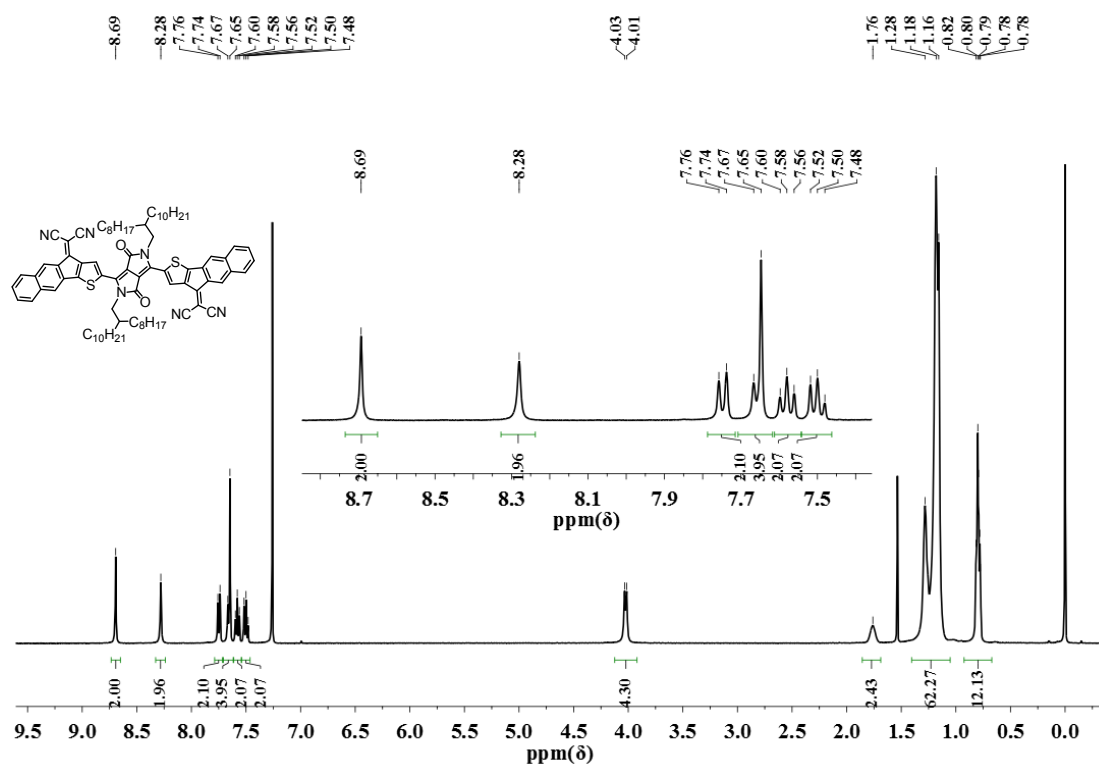
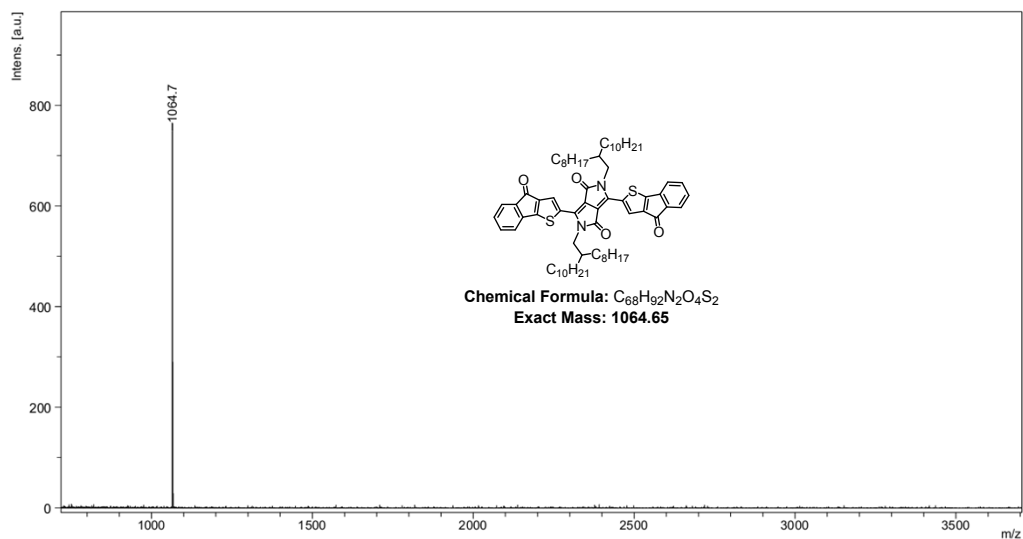


Figure S8 ^1H NMR (top) and ^{13}C NMR (bottom) spectra of 2,2'-(2,2'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydro-pyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(4H-benzo[5,6]indeno[1,2-*b*]thiophene-2-yl-4-ylidene))dimalononitrile (**DPP-NaCN**)

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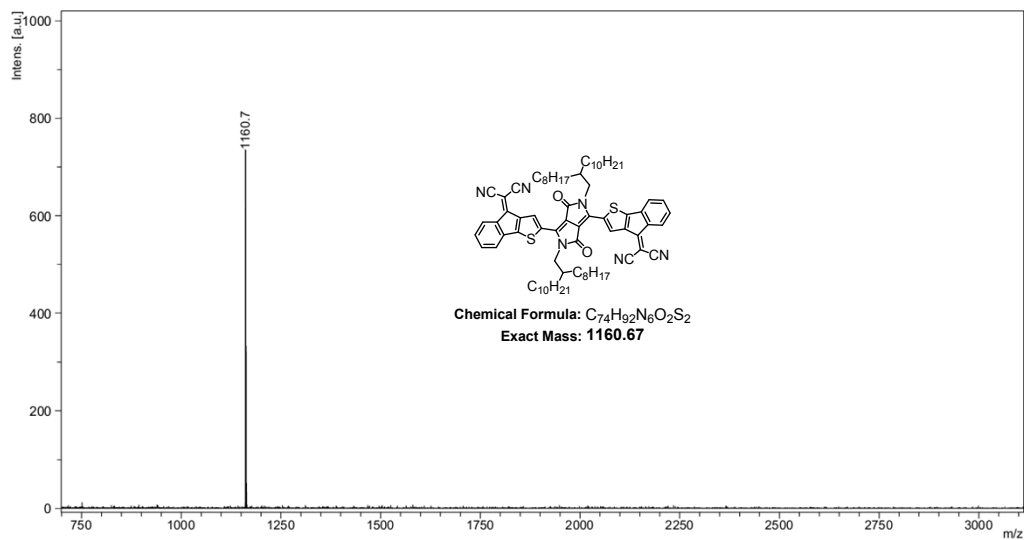
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Figure S9. MALDI-TOF MS spectrum of **DPP-PhCO**.

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Figure S10. MALDI-TOF MS spectrum of **DPP-PhCN**.

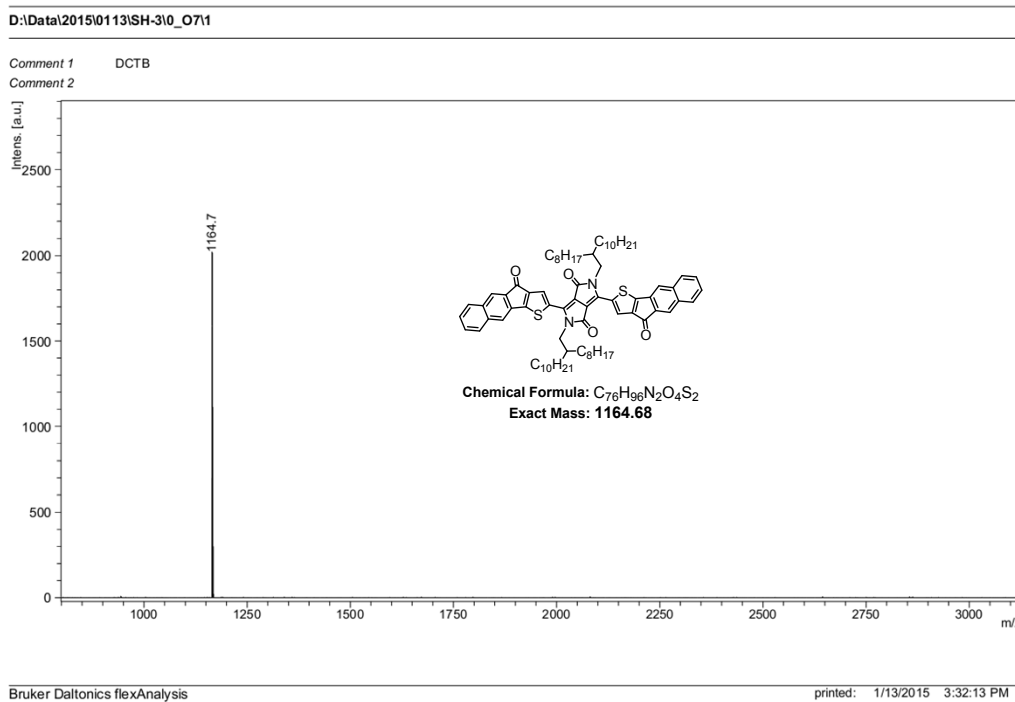


Figure S11. MALDI-TOF MS spectrum of **DPP-NaCO**.

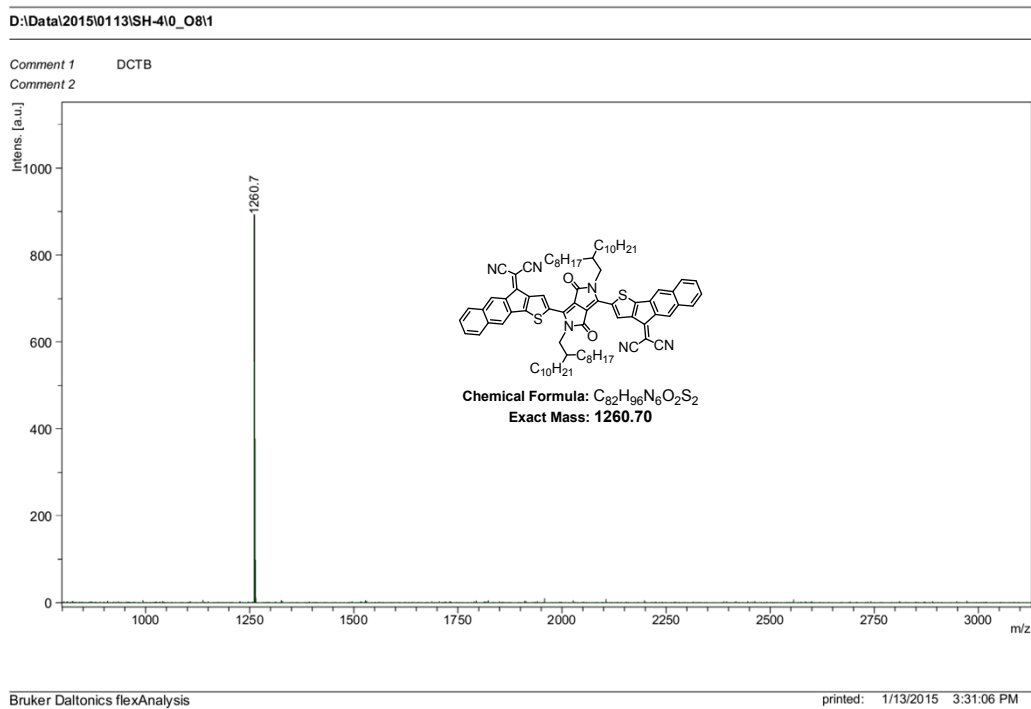


Figure S12. MALDI-TOF MS spectrum of **DPP-NaCN**.

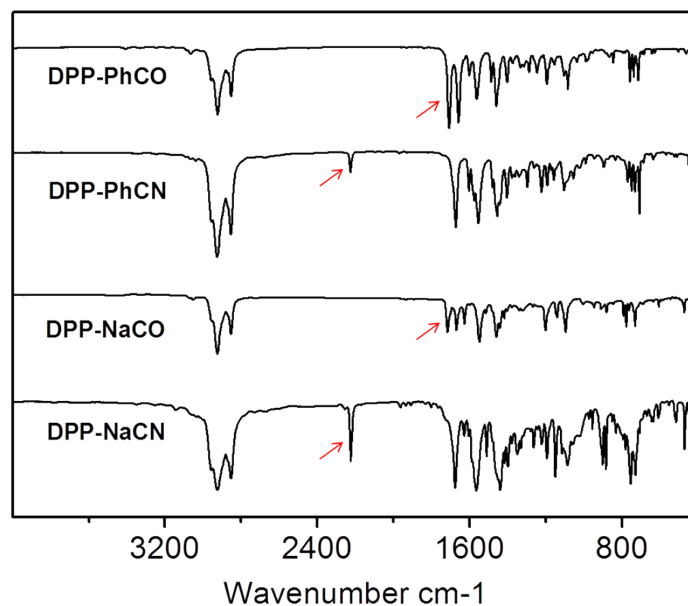


Figure S13. Infrared (IR) absorption spectra of **DPP-PhCO**, **DPP-PhCN**, **DPP-NaCO** and **DPP-NaCN**.

OTFT fabrication and measurement

Bottom-gate/top-contact (BG/TC) OTFTs were fabricated on heavily *n*-doped Si wafers with 300 nm thickness of SiO₂ as the gate dielectric layer, which was modified with octadecyltrichlorosilane (ODTS) according to literature.^[1] The active layer was spin-coated at 1000 rpm in ambient conditions from *o*-xylene solution with a concentration of 0.9 wt%. Then Au source and drain electrodes were evaporated under vacuum with a shadow mask (channel length $L = 100 \mu\text{m}$, channel width $W = 3 \text{ mm}$). OTFT devices were tested with two Keithley 336 units under ambient conditions.

[1] Y. Zhang, C. Kim, J. Lin and T.-Q. Nguyen, *Adv. Funct. Mater.*, 2012, **22**, 97.

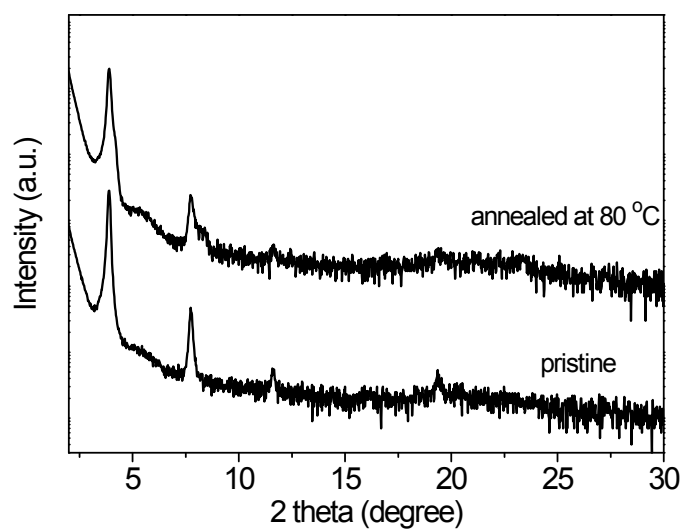


Figure S14. Out-of-plane XRD patterns of pristine and thermally annealed films of **DPP-Ph**. The thermal annealing was done at 80 °C for 10 min.

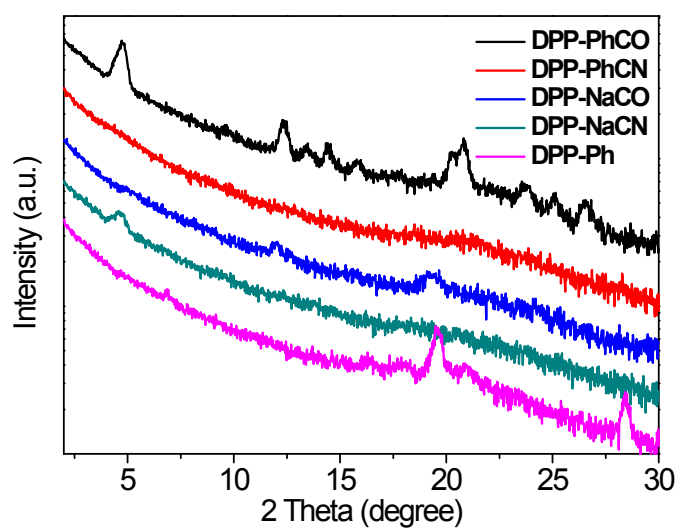


Figure S15. In-plane XRD patterns of pristine **DPP-Ph** films and thermally annealed films of **DPP-PhCO**, **DPP-PhCN**, **DPP-NaCO** and **DPP-NaCN**. The thermal annealing was done at 150 °C for **DPP-PhCO**, **DPP-NaCO** and **DPP-NaCN** and at 80 °C for **DPP-PhCN**.