

## ELECTRONIC SUPPORTING INFORMATION

for

New NIR Absorbing DPP-based Polymer for Thick Organic Solar Cells

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### General

All commercially available reagents were purchased from Sigma-Aldrich, Across, Tokyo Chemical Industry Co., Ltd. (TCI), and Merck. All reactions were performed under Ar unless otherwise noted. All anhydrous solvents such as THF, DMF, and toluene were either distilled over Na/benzophenone or supplied from an MBraun solvent purification system. 2,5-Bis(trimethylstannyl)selenophene and 3,6-bis(5-bromofuran-2-yl)-2,5-didecyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione were synthesized according to literature.<sup>1,2</sup> The electrochemical properties of each monomer were investigated by using a Voltalab 50 potentiostat in a three-electrode system including Indium Tin Oxide (ITO) coated glass slide as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode calibrated against Fc/Fc<sup>+</sup>. All cyclic voltammetry measurements of polymers were made by using GAMRY Reference 600 potentiostat and such measurements were performed under argon atmosphere at room temperature. The spectroelectrochemical properties of each polymer were analyzed by using Varian Cary 5000 UV-Vis spectrophotometer. HOMO and LUMO energy values were determined by taking NHE value as -4.75 eV in the formula of  $HOMO = -(4.75 + 0.3 + E_{onset}^{ox})$  and  $LUMO = -(4.75 + 0.3 + E_{onset}^{red})$ . <sup>1</sup>H and <sup>13</sup>C NMR spectra of each product were identified by using Bruker Spectrospin Avance DPX-400 Spectrometer with using either CDCl<sub>3</sub> or DMSO as the solvents. To make such analysis chemical shifts (δ / ppm) were reported relative to TMS as the internal reference. The accurate mass measurements for each novel product were made by HRMS by using Waters Synapt MS System. Silica Gel Column Chromatography with silica gel (Acros, 35–70 μm) filled in a suitable glass column was used to purify most of the products. TLC on glass plates coated with EMD silica gel 50 F254 was used to determine the best solvent system to make Silica Gel Column Chromatography and to confirm the identity of each product by either looking under ultraviolet light or staining KMnO<sub>4</sub> stain by exposing mild heating.

**GPC:** Number-average (M<sub>n</sub>) and weight-average (M<sub>w</sub>) molecular weight were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL

mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards.

**AFM:** A 5400 Agilent atomic force microscope (AFM) was used to image the active layers in tapping mode.

**TEM:** TEM images were recorded in bright field mode with a microscope operating at 300 keV (Tecnai Bio twin, FEI), using an 4k x 4k eagle CCD camera (FEI).

**Solar Cell Fabrication and Testing:** The polymers : PC<sub>71</sub>BM were dissolved in chlorobenzene with and without solvent additive, and the solutions were stirred overnight at 60 °C hotplate. We have optimized the thickness, additive ratio and blend ratio. The best devices were prepared using a polymers : PC<sub>71</sub>BM ratio of 1:3 (by weight), with an overall concentration of 30 mg mL<sup>-1</sup>. The active layers were then spin-cast from the solutions in a glove box at 400 rpm for 30 sec, resulting in a film of ~210 nm in thickness. Next, the samples were placed in a thermal evaporator for evaporation of a 5 nm thick molybdenum oxide (MoO<sub>3</sub>) layer and a 100 nm thick layer of silver, at a pressure of less than 2x10<sup>-6</sup> Torr. Following electrode deposition, samples underwent J–V testing. Solar cell J-V measurements were performed in the glovebox with a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5 G. The external quantum efficiency (EQE) measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by NIST.

**Mobility Measurements:** Mobilities were calculated with respect to the formula

$$J = \frac{9}{8} \alpha \epsilon \epsilon_0 \frac{V^2}{L^3} \exp\left(0.89\beta \frac{\sqrt{V}}{\sqrt{L}}\right)$$
 where where  $\epsilon$  is the dielectric permittivity of the polymer (generally taken to be about 3),  $\epsilon_0$  is the dielectric permittivity of free space,  $L$  is the film thickness (185 nm in this case), and  $V$  is the voltage, which is defined as  $V = V_{\text{appl}} - V_{\text{bi}}$ , where  $V_{\text{appl}}$  is the applied voltage,  $V_{\text{bi}}$  is the built-in voltage which is related to the difference in the work function of the electrodes. Hole mobility of blend films were employed with the architecture: ITO/PEDOT:PSS/Polymer/MoO<sub>x</sub>/Ag. At the same time, electron mobilities of blend films were utilized with the architecture: ITO/ZnO/Active layer/Ca/Al.

### **Synthetic Details**

**Synthesis of 3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione:** Synthesis was performed according to literature with small modifications.<sup>3</sup> Two necked 50 mL reaction flask equipped with a condenser, was subjected to 3 vacuum-argon cycles before the materials were introduced. Dry tert-amyl alcohol (25 mL) was injected into reaction flask and heated up to 75 °C. Sodium metal pieces (0.249 g, 10.7 mmol) were added in a portion wise manner until the all the sodium metals disappeared and gas evolution stopped. The temperature was raised to 120 °C and reaction was stirred overnight. 2-Furonitrile (1.00 g, 10.7 mmol) was added into reaction, the mixture was stirred for ten minutes and subsequently, diethyl succinate (0.623 g, 3.58 mmol) was added drop wise. The mixture was

stirred for 5 hours at 120 °C. The reaction was cooled to room temperature and the crude product was precipitated to a solution of hydrochloric acid (3.2 mL) and MeOH (64 mL). The product was filtered via Buchner and washed with MeOH under vacuo to give a dark-red solid. (1.73 g, 70% yield). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.21 (s, 2H), 8.05 (d, *J* = 1.4 Hz, 2H), 7.68 (d, *J* = 3.5 Hz, 2H), 6.83 (dd, *J* = 3.5, 1.7 Hz, 2H). <sup>13</sup>C NMR (100 MHz, DMSO) δ 161.1, 146.9, 143.7, 131.2, 116.8, 113.7, 107.5. NMR data is consistent with the reported literature.

**Synthesis of 3,6-di(furan-2-yl)-2,5-dioctadecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione:**

A 50 mL two-necked round bottom flask was taken under argon. 3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (0.609 g, 2.27 mmol), K<sub>2</sub>CO<sub>3</sub> (1.35 g, 9.78 mmol), dry DMF (25 mL) and a catalytic amount of 18-crown-6 were added into reaction flask. The mixture was stirred at room temperature for ten minutes and temperature was raised to 130 °C for 1 hour. 1-bromooctadecane (2.805 g, 8.401 mmol) was added into reaction portion-wise and the mixture was stirred at 130°C for 48 hours. After the reaction was completed, solvent was removed. Water was added and the product was extracted with CHCl<sub>3</sub> (300 mL). Combined organic phases dried over MgSO<sub>4</sub> and the solvent was evaporated. Column chromatography on silica gel (2:1 hexane/DCM) gave the target compound as a dark red solid (0.453 g, 25 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 3.6 Hz, 2H), 7.63 (d, *J* = 1.4 Hz, 2H), 6.69 (dd, *J* = 3.7, 1.7 Hz, 2H), 4.10 (t, *J* = 7.5 Hz, 4H), 1.73 – 1.64 (m, 4H), 1.38 – 1.19 (m, 60H), 0.87 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.9, 145.1, 144.7, 133.7, 120.1, 113.5, 106.4, 42.4, 31.9, 30.2, 29.7, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 26.9, 22.7, 14.1. HRMS calcd. for C<sub>50</sub>H<sub>81</sub>N<sub>2</sub>O<sub>4</sub>: 773.6196, found 773.6205.

**Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-dioctadecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione:**

A 50 mL two-necked flask was evacuated and filled with argon twice and previously synthesized 3,6-di(furan-2-yl)-2,5-dioctadecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (0.409 g, 0.528 mmol) and CHCl<sub>3</sub> (10 mL) was added into reaction flask under argon atmosphere. Reaction flask was covered with aluminum foil and NBS (0.280 g, 1.58 mmol) was added into reaction in one portion. Reaction was stirred for 12 hours under dark. Water was added and the mixture was extracted with CHCl<sub>3</sub> several times. Combined organic phases were dried, over MgSO<sub>4</sub>. After the solvent was removed further purification performed with column chromatography on silica gel 3:2 hexane/CHCl<sub>3</sub>) was performed to get the 3,6-bis(5-bromofuran-2-yl)-2,5-dioctadecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione as a dark purple-red solid (100 mg, 20%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 3.7 Hz, 2H), 6.63 (d, *J* = 3.7 Hz, 2H), 4.05 (t, *J* = 7.6 Hz, 4H), 1.74-1.64 (m, 4H), 1.45-1.19 (m, 60H), 0.88 (t, *J* = 6.7 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.5, 146.3, 132.5, 126.3, 122.0, 115.4, 106.4, 42.5, 31.9, 30.2, 30.2, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 26.8, 22.6, 14.0. HRMS calcd. for C<sub>50</sub>H<sub>79</sub>N<sub>2</sub>O<sub>4</sub>Br<sub>2</sub>: 929.4407, found 929.4407.

**Synthesis of poly(3-(furan-2-yl)-2,5-dioctadecyl-6-(5-(selenophen-2-yl)furan-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione) - PFDPPSe :** A 50 mL Schlenk tube under argon atmosphere 3,6-bis(5-bromofuran-2-yl)-2,5-dioctadecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (165 mg, 0.177 mmol) and 2,5-bis(trimethylstannyl)-selenophene (80 mg, 0.177 mmol), were added and the reaction was put under argon. Chlorobenzene (6 mL) was injected with a syringe and solution was degassed by bubbling the argon with cannula for 30 minutes. Then, tris(dibenzylideneacetone)dipalladium(0) (2 mol%) and tris(*o*-

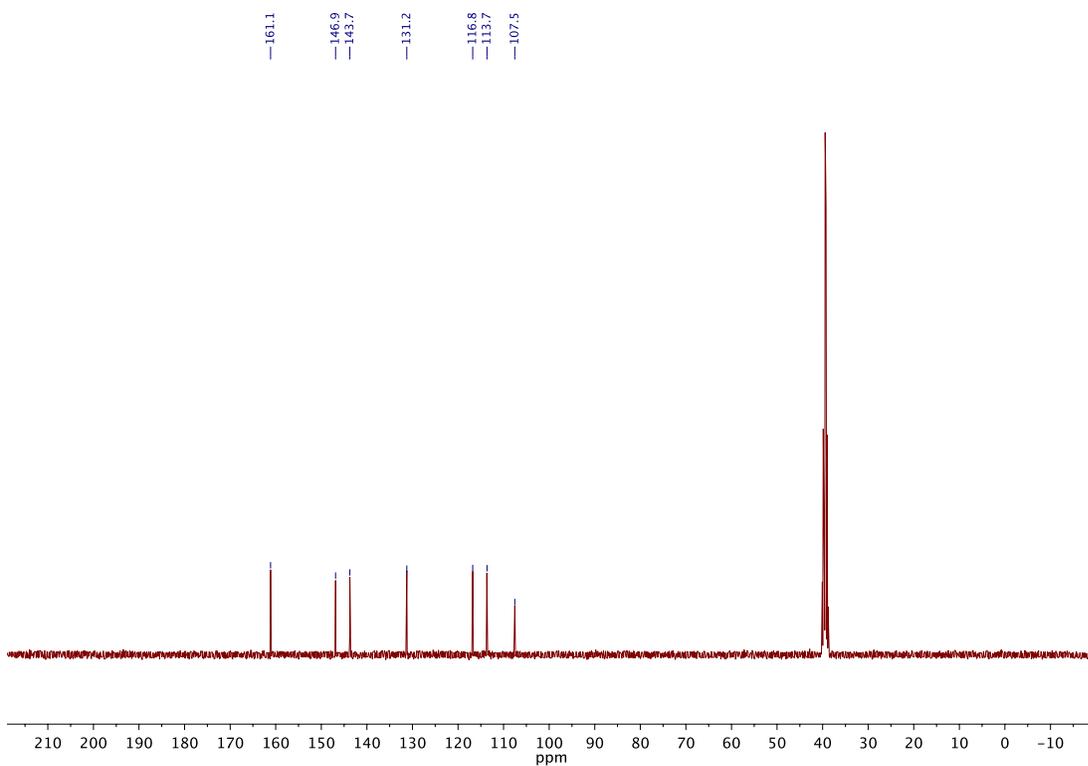
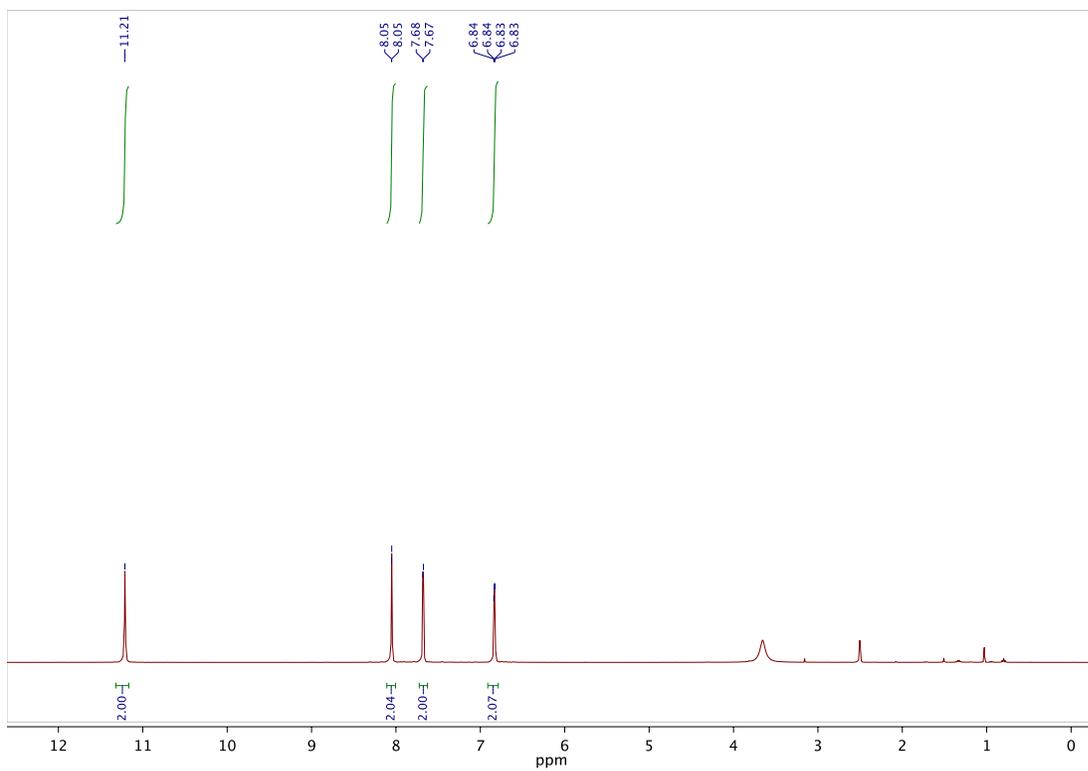
tolyl)phosphine (8 mol%) were added to the solution and Schlenk tube was put in oil bath which was heated at 90 °C. The reaction mixture was stirred at 90 °C for 5 minutes and then temperature was raised to 110 °C and stirred for 24 hours. Reaction was monitored with TLC and in 24<sup>th</sup> hour, additional catalysts tris(dibenzylideneacetone)dipalladium(0) (4 mol%) and tris(*o*-tolyl)phosphine (16 mol%) were introduced into reaction. The mixture stirred for an additional 12 hours. The reaction was cooled to room temperature and diluted with CHCl<sub>3</sub> (5 mL) and as a palladium scavenger, sodium diethyldithiocarbamate trihydrate (5.0 g) was added. The mixture was stirred for 1 hour. The resulting mixture was precipitated into cold methanol (200 mL). After filtration, the product was purified with Soxhlet extraction (methanol and hexane) and finally collected with CHCl<sub>3</sub> to give 153 mg of the target polymer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ 8.42 (br. s), 6.73 (br. s), 4.4-4.10 (br. s), 1.93-1.01 (m), 0.86 (br.s). GPC - Mn: 14.6 kDa, Mw: 50.3 kDa

#### References:

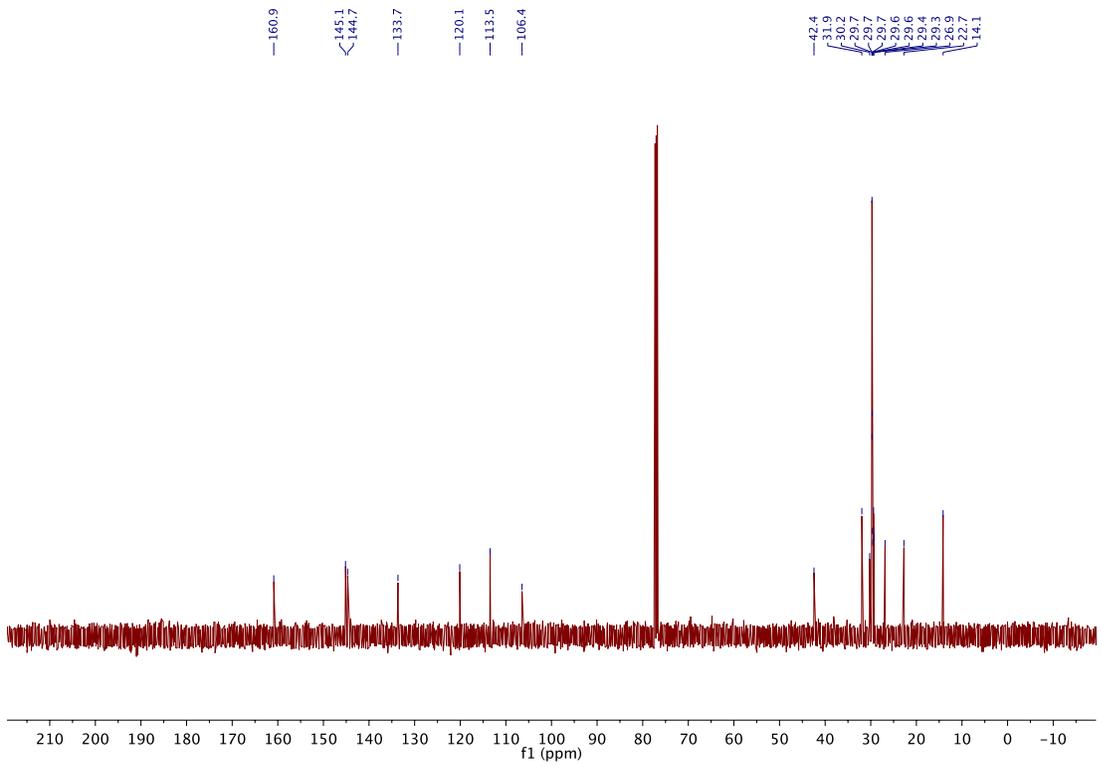
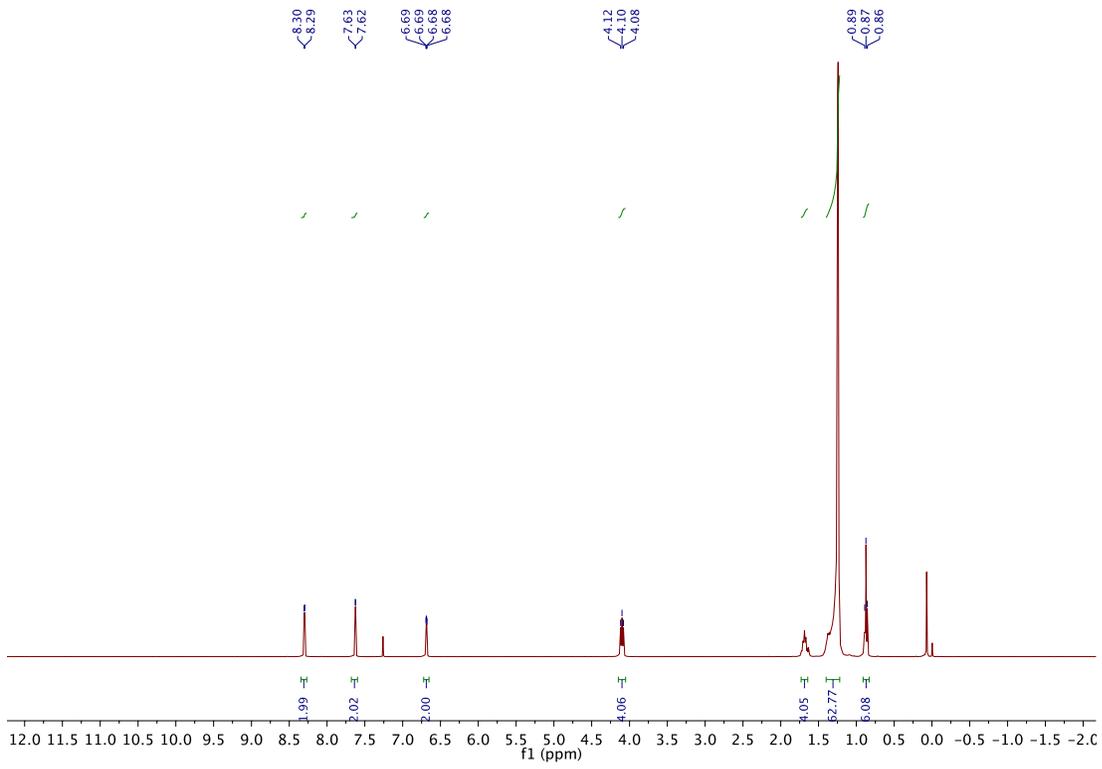
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3. Y. N. Li, P. Sonar, S. P. Singh, W. J. Zeng and M. S. Soh, *J Mater Chem*, 2011, **21**, 10829.

#### NMR Data

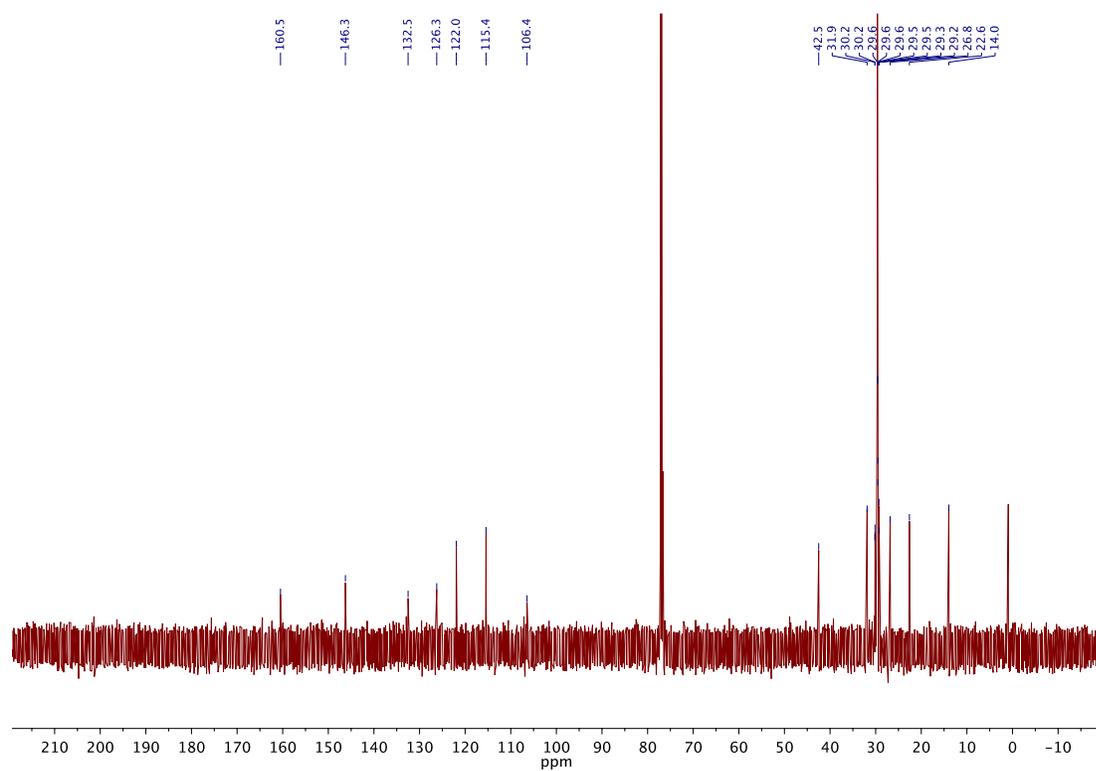
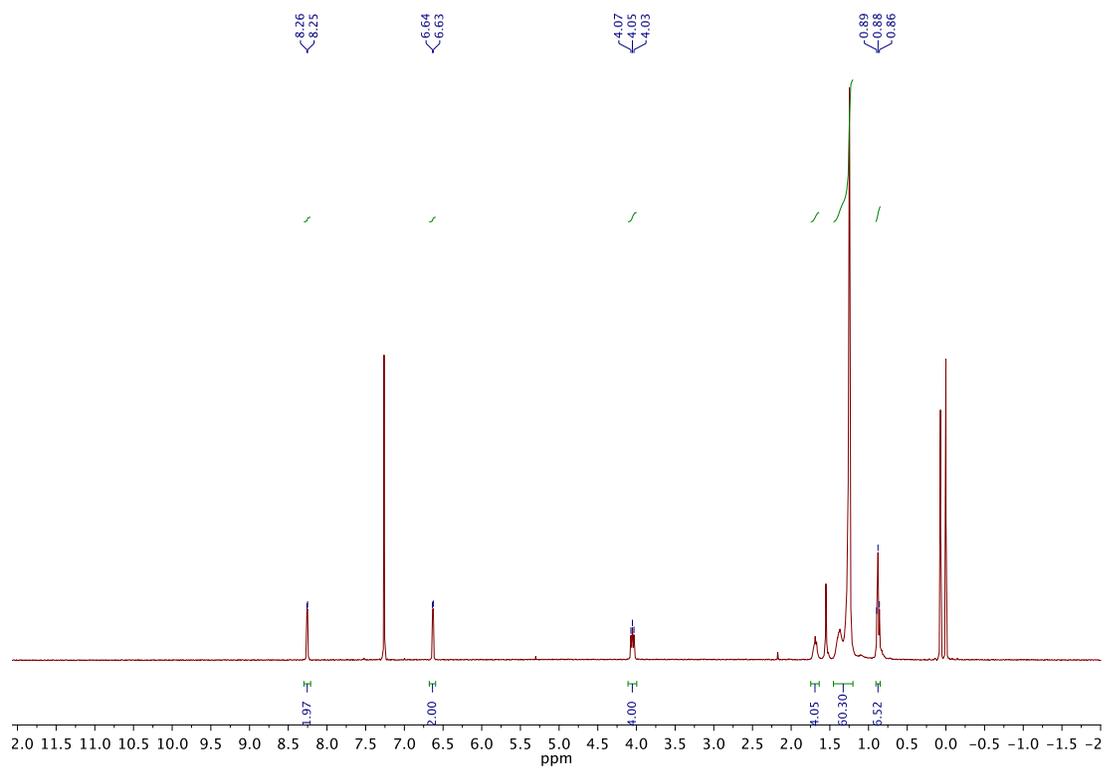
**3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione**



**3,6-di(furan-2-yl)-2,5-dioctadecyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione**



# 3,6-bis(5-bromofuran-2-yl)-2,5-dioctadecyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



**Poly(3-(furan-2-yl)-2,5-dioctadecyl-6-(5-(selenophen-2-yl)furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) - PFDPPSe**

