

## Supporting Information

### Synthesis and photovoltaic investigation of 8, 10-bis (2-octyldodecyl) -8,10-dihydro-9H-bisthieno [2', 3': 7.8; 3'', 2'': 5.6] naphtho [2,3-d] imidazol-9-one based conjugated polymers using non-fullerene acceptor

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### Experimental part

#### Materials

Pd(PPh<sub>3</sub>)<sub>4</sub> were purchased from Sigma-Aldrich or Acros. All solvents used for synthesis were purified and dried according to standart methods. Toluene was dried and distilled over sodium/benzophenone. CHCl<sub>3</sub> and AcCN were dried with CaH<sub>2</sub> and distilled prior to use. All chemicals were reagent grade and purchased from Sigma-Aldrich and used without further purification. All chromatographic separations were carried out on silica gel (200-300 mesh).

#### Instruments and characterization methods

<sup>1</sup>H NMR spectra were collected on a Bruker AVANCE 500MHz spectrometer (CDCl<sub>3</sub> as solvent). The molecular weight characteristics of conjugated polymers were studied by gel permeation chromatography on liquid chromatograph “Shimadzu LC-20A”. The column (Phenomenex Luna - phenogel, 5 μm, 300 × 7.8) was calibrated using poly [(9,9-di-n-octylfluorenyl-2,7-diyl) -alt- (benzo [2,1,3] thiadiazol-4,8-diyl)] (F8BT) as the standard (polydispersity of samples <1.5). Chlorobenzene at T = 50°C was used as an eluent. Thermogravimetric analysis (TGA) measurement were conducted under a dry nitrogen at a heating rate of 20°C/min on a Perkin-Elmer TGA 7. UV-Vis spectra of dilute chloroform solution(10<sup>-5</sup>M) were recorded using a Hitachi U-4100 spectrophotometer. Solid film for UV-Vis analysis were obtained by spin-coating polymer solution onto quartz substrates. Cyclic voltammetry (CV) of the polymer films was performed using “μAUTOLAB type III

electrochemical analyzer operated at a scan rate of 50 mVs<sup>-1</sup>. Solvent was MeCN containing 0.1M TBAPF<sub>6</sub> as the supporting electrolyte. The potentials were measured against a Ag/Ag<sup>+</sup>(0.01M AgNO<sub>3</sub>) reference electrode. Fe/Fe<sup>+</sup> was used as the internal standard (0.36V).

### Synthesis of monomers and polymers and characterization

#### 4.3. 1.Synthesis of monomers

4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**M2**) [1] and 5,6-difluoro-4,7-bis(5-(trimethylstannyl) thiophen-2-yl)benzo[c] [1,2,5]thiadiazole (**M3**) [1] respectively, were prepared according to the procedure reported in the were prepared according to the reported procedures.

**N, N'-(1, 2-Phenylene) bis (4-methylbenzenesulfonamide) (3)**. o-Phenylenediamine 1 (540 mmol, 58.5 g) was slowly added to a solution of p-toluenesulfonyl chloride (1.080 mol, 205.9 g) in dry pyridine (500 ml) at a temperature of -10°C, then the reaction mixture was stirred at room temperature for 18 hours. Then a 15% HCl solution was added, the resulting precipitate was filtered off, dried and dissolved by heating in 1.4 L of ethanol. After complete dissolution, the solution was filtered and cooled to -10°C overnight. The precipitate was filtered off, dried and the desired product was obtained in 203 g (90%) yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.60 (d, 4H), 7.25 (d, 4H), 7.06 (m, 2H), 7.00 (m, 2H), 6.93 (br s, 2H), 2.41 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 144.22, 135.43, 130.83, 129.63, 127.55, 127.36, 126.16, 21.60 (Figure S1 and S2)

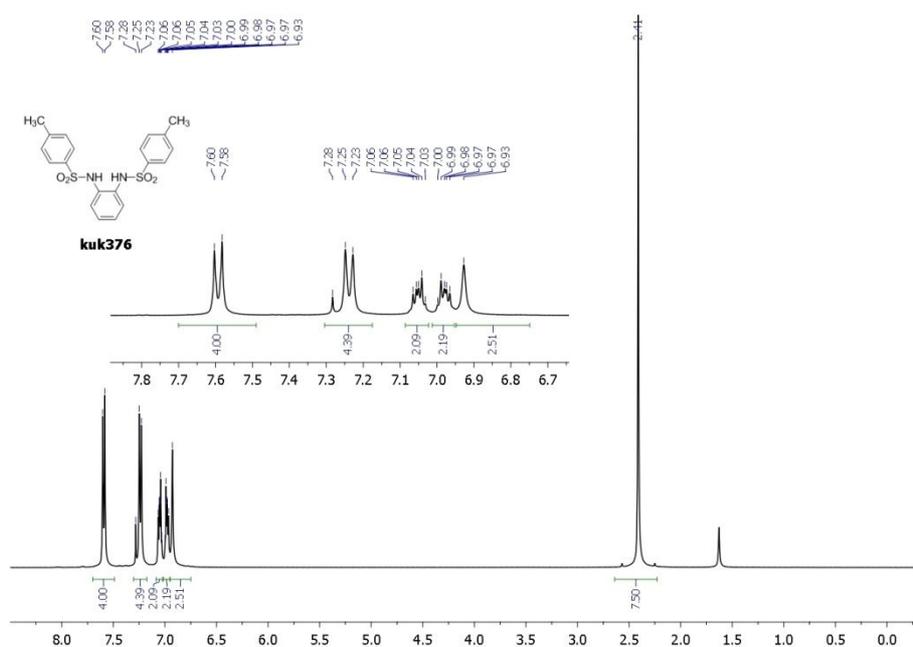


Figure S1 <sup>1</sup>H NMR of 3

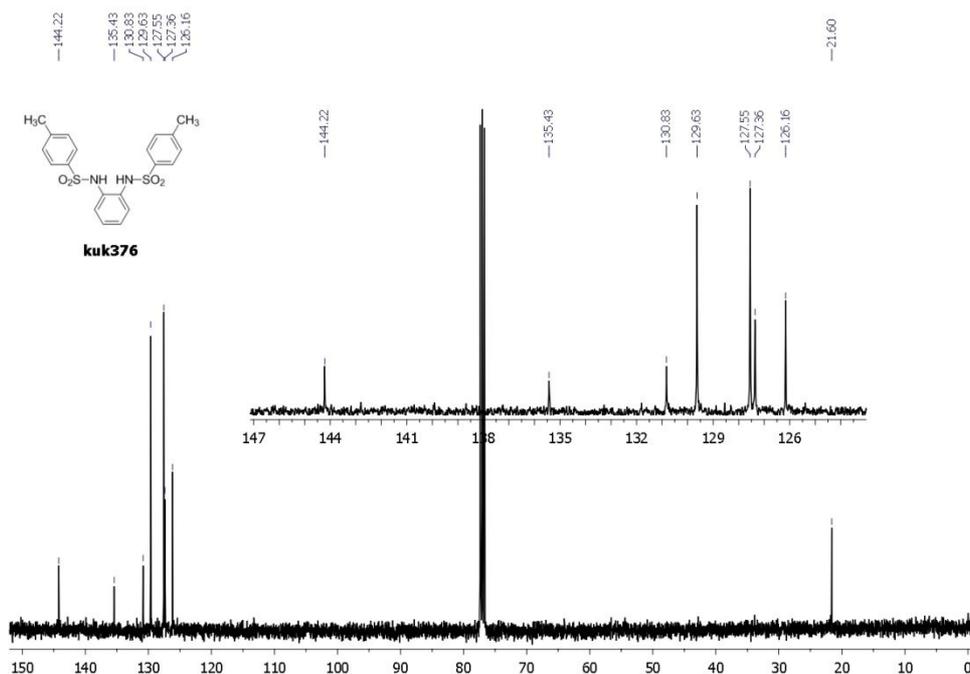


Figure S2 <sup>13</sup>C NMR of **3**

**N, N'-(4,5-Dibromo-1,2-phenylene) bis(4-methylbenzenesulfonamide) (4).** Bromine (19.2 g, 0.180 mol) was added dropwise with stirring to a suspension of substance **3** (37.5 g, 0.090 mol) and sodium acetate (15.0 g) in glacial acetic acid (150 ml), cooled to 0 ° C. After the addition was complete, the reaction mixture was stirred at 110°C for 3 hours, then cooled and poured into ice water (400 ml), then stirred for another 1 hour and ethanol (200 ml) was added. The precipitate was filtered off and 43 g (84%) of the expected product were obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.62 (d, 4H), 7.30 (d, 4H), 7.22 (s, 2H), 6.83 (s, 2H), 2.45 (s, 6H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 144.86, 134.84, 130.72, 130.02, 129.90, 127.57, 122.62, 21.64 (Figure S3)[2]

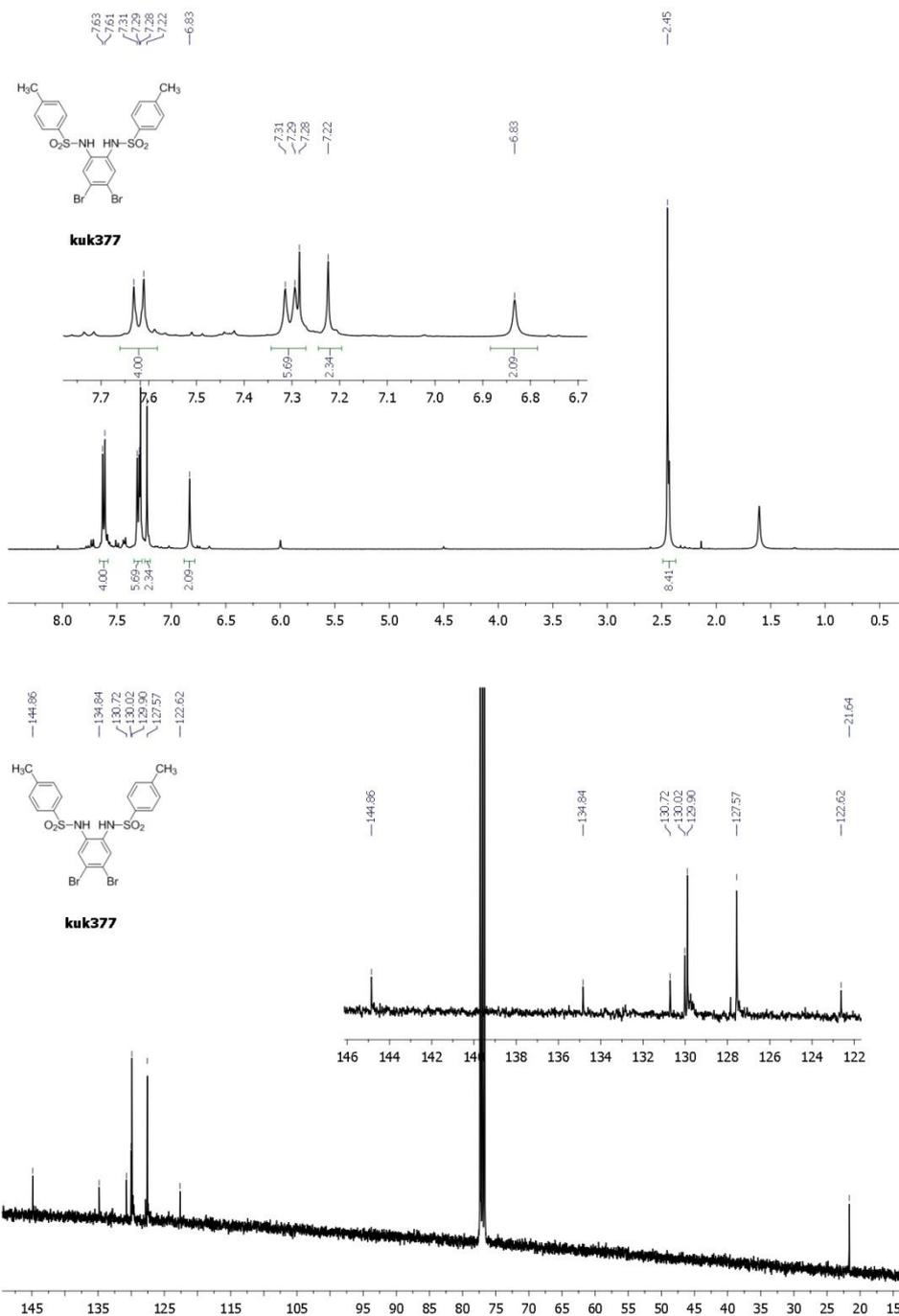


Figure S3 <sup>1</sup>H NMR and <sup>13</sup>C NMR of 4

**4,5-dibromophenylene-1,2-diamine (5).** Compound 4 (45.2 g, 78.7 mmol) was dissolved in concentrated sulfuric acid (90 ml), the solution was heated to 110 ° C and stirred at this temperature for 15 minutes. After cooling to room temperature, the reaction mixture was poured into a mixture of ice and water and neutralized with a 50% NaOH solution until the dark color of the solution disappeared and a bulk precipitate formed. The precipitate was filtered off, washed with water and dried, and the desired product was obtained in 17.9 g (88%)

yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 6.95 (s, 2H), 3.41 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 135.37, 120.48, 113.51. [Figure S4] [2].

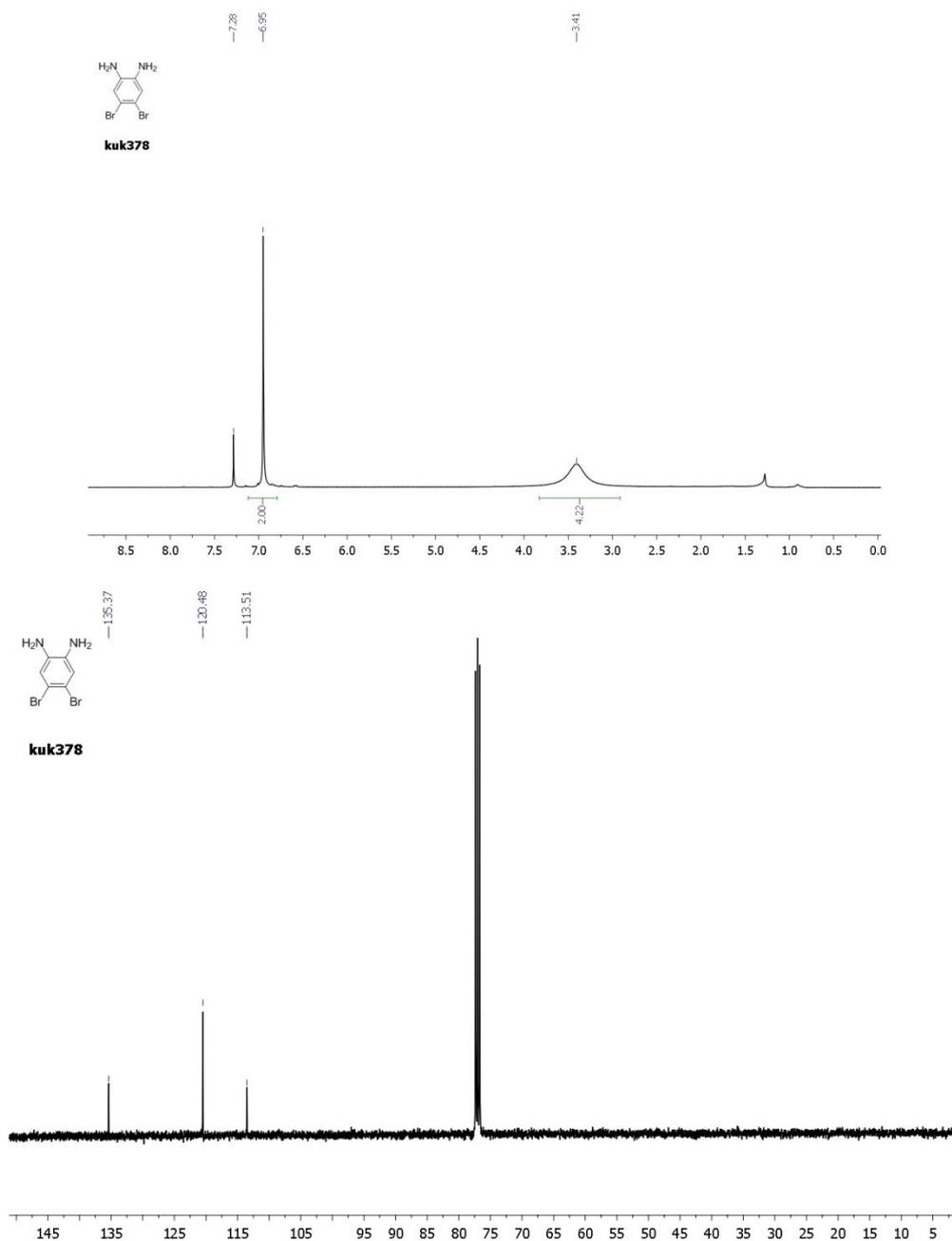
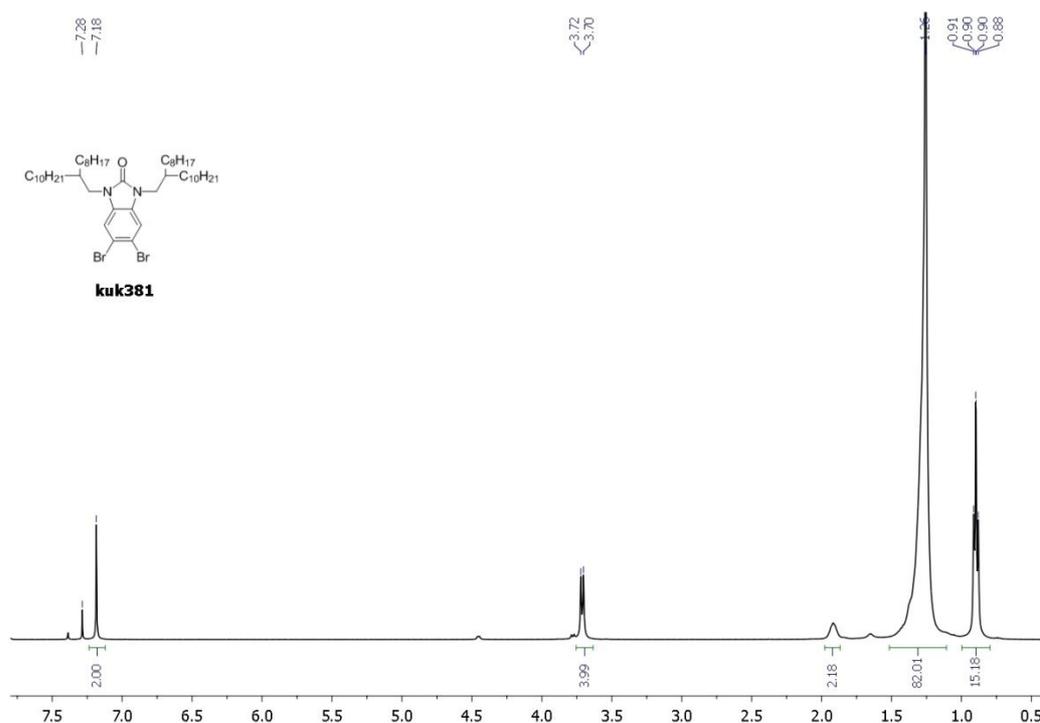


Figure S4  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of 5

**5,6-Dibromo-1H-benzo [d] imidazole-2 (3H) -one (7).** Carbonyldiimidazole (7.95 g, 49 mmol) was added to a stirred solution of diamine 5 (13.03 g, 49 mmol) in 90 ml of DMF, and the mixture was stirred for 24 hours. The solvent was evaporated in vacuo, the residue was

suspended in ethyl acetate, filtered and dried in vacuo. Received 9.136 g (64%) of insoluble in nothing substance, which was used without further purification

**5,6-dibromo-1,3-bis (2-octyldodecyl) -2H-benzimidazol-2-one (9).** The original 5,6-dibromo-1,3-dihydro-2H-benzimidazol-2-one **7** (1 g, 3.425 mmol), 2-octyldodecyl bromide (2.25 g, 7.536 mmol), anhydrous, was placed in a 50 ml 2-necked flask K<sub>2</sub>CO<sub>3</sub> (2.37 g, 17.125 mmol) and anhydrous DMF (25 ml, distilled over CaH<sub>2</sub>), the resulting suspension was heated in an oil bath at 70 ° C with good stirring for 48 hours. After cooling, the solvent was evaporated on a rotary evaporator, the residue was dried for a long time at 90°C, suspended in a mixture of toluene (5 ml) and petroleum ether (20 ml) and applied to a column with SiO<sub>2</sub> (d = 1.5 cm, L = 20 cm). First, a fraction containing excess halide was collected using a mixture of toluene - petroleum ether = 1: 4 as eluent. After collecting all of the starting halide, chromatography was continued using a toluene - petroleum ether = 1: 2 mixture as eluent and a fraction containing the reaction product was collected. The purity of the effluent was monitored by TLC. The fractions containing the pure product were evaporated and dried on a rotary evaporator at 80-90 ° C. Received 2.1 g (72%) of the desired product as a colorless oil. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, δ ppm): 7.18 (s, 2H), 3.71 (d, 4H), 1.90 (m, 2H), 1.26 (m, 80H), 0.90 (m, 12H). <sup>13</sup>C NMR (100.13 MHz, CDCl<sub>3</sub>, δ ppm): 154.46, 130.24, 115.40, 112.14, 45.65, 36.77, 31.94, 31.34, 29.99, 29.66, 29.61, 29.56, 29.37, 26.34, 14.13 (Figure S5). Anal.Cald for C<sub>55</sub>H<sub>86</sub>Br<sub>2</sub>N<sub>2</sub>O S<sub>2</sub>: C, 66.18; H,9.93; Br,18.74; N,3.28.



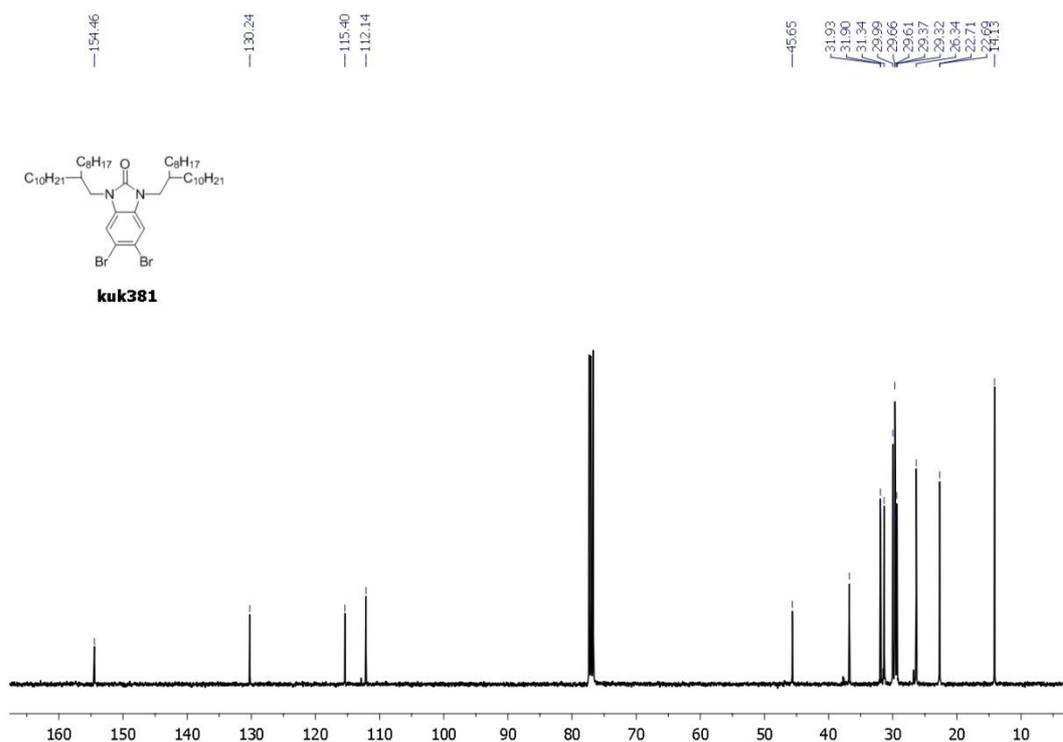


Figure S5  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of 9

**1,3-Bis (2-octyldodecyl) -5,6-di (thiophen-3-yl) -1,3-dihydro-2H-benzimidazol-2-one (11).**

In a three-necked flask (50 ml), 483 mg (0.5662 mmol) of the starting 5,6-dibromo-1,3-bis (2-octyldodecyl) -2H-benzimidazol-2-one, 0.528 g (1.416 mmol) 3- (tributylstannyl) thiophene 10, 30 ml of toluene (distilled over  $\text{P}_2\text{O}_5$  and Na), argon was passed through the solution for 30 minutes using a Teflon capillary. Then, 70 mg (0.05662 mmol) of  $\text{Pd}(\text{PPh}_3)_4$  was added and transmission continued for another 30 minutes, then the mixture was heated in an oil bath for 20 hours. After cooling, the reaction mixture was evaporated, suspended in petroleum ether and applied onto a column of  $\text{SiO}_2$  (d = 1.5 cm, L = 20 cm), chromatographed with mixtures of petroleum ether-toluene = 60:20 ---> 60:30 ---> 60 : 60 ---> 50:60, controlling the composition of the eluate by TLC (PE-toluene = 1: 1). Colorless fractions of organotin products, unreacted starting material, monosubstituted product and target product (main fraction) were sequentially collected. After evaporation and drying of the main fraction, 226 mg (46%) of a colorless oily substance was obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.22 (m, 2H), 7.05 (m, 4H), 6.80 (m, 2H), 3.80 (m, 4H), 2.01 (m, 2H), 1.20-1.50 (m, 64H), 0.90 (m, 12H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 155.09, 142.41, 129.41, 129.22, 128.53, 124.67, 122.45, 109.19, 45.57, 36.95, 31.95, 31.94, 30.09, 29.69, 29.40, 26.40, 22.73, 22.71

14.16 (Figure S6) Anal. Calcd for C<sub>55</sub>H<sub>90</sub>N<sub>2</sub>OS<sub>2</sub>: C, 76.86; H,10.56; N,3.26; S,7.46.

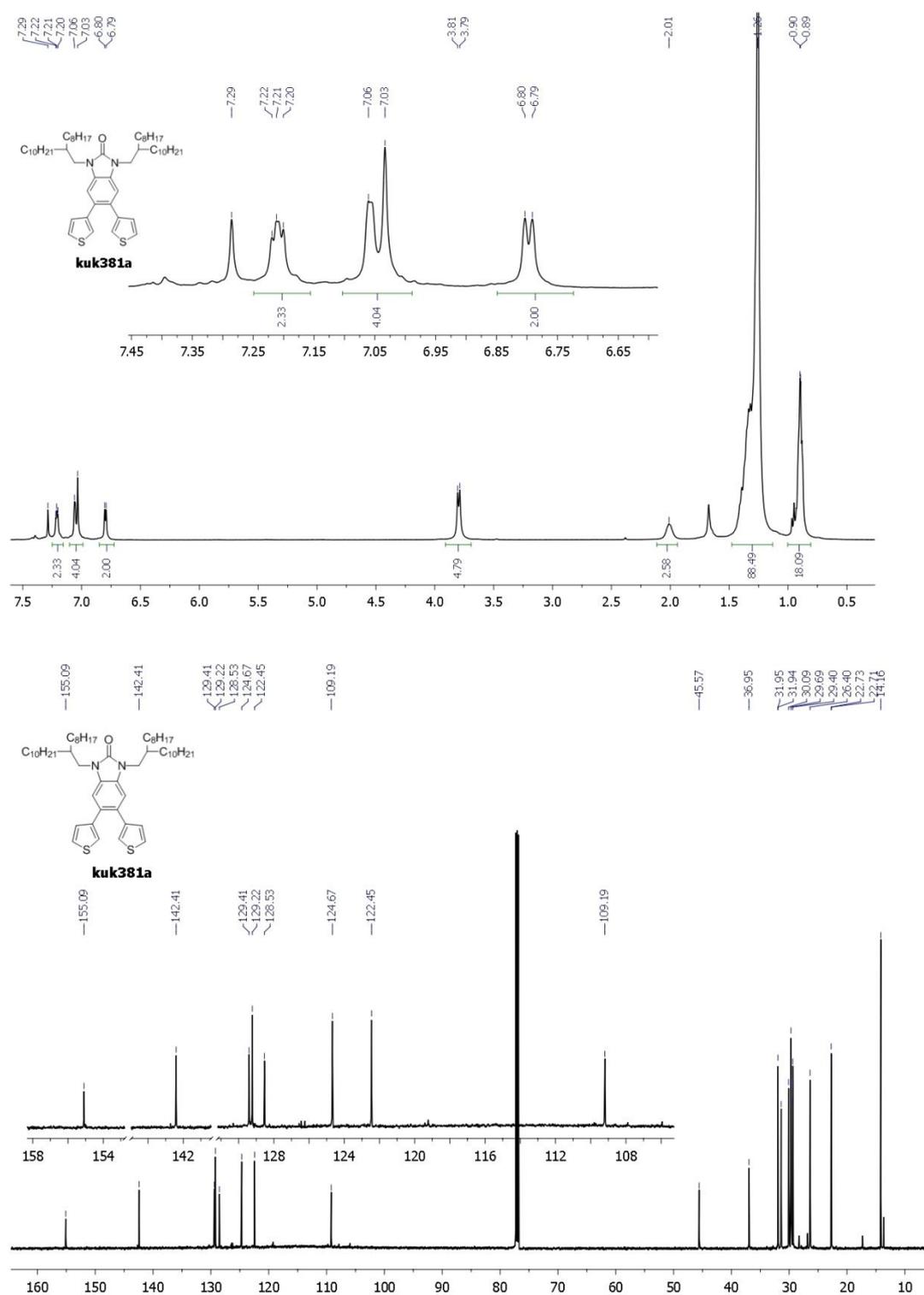
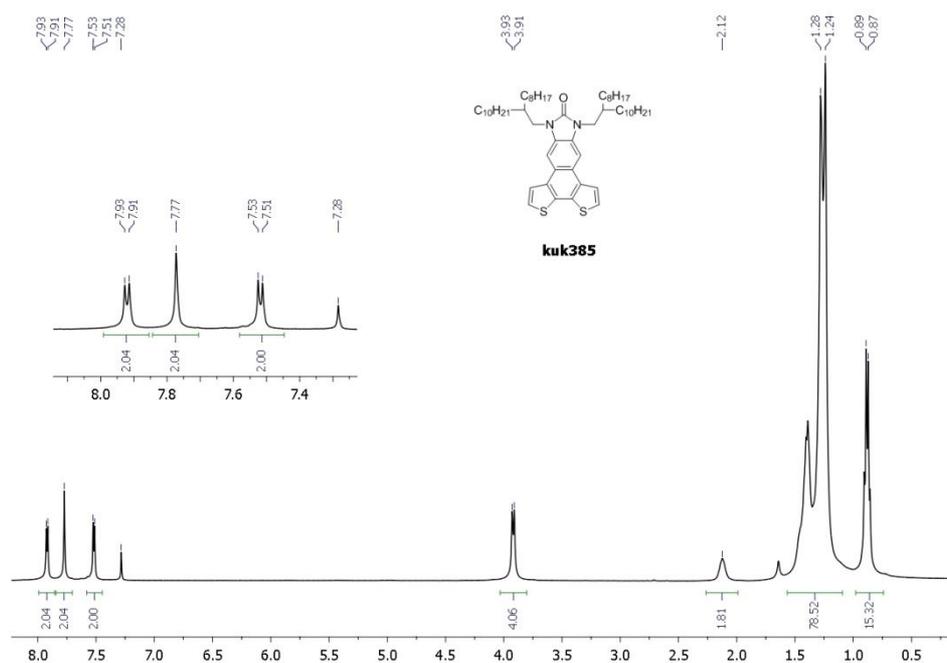


Figure S6 <sup>1</sup>H NMR and <sup>13</sup>C NMR of 11

**8,10-bis (2-octyldodecyl) -8,10-dihydro-9H-bisthieno [2', 3':7.8;3'',2'': 5.6] naphtho [2,3-d] imidazol-9-one (12).** 226 mg (0.263 mmol) of the starting 1,3-bis (2-octyldodecyl) -5,6-di (thiophen-3-yl) -1,3-dihydro-2H-benzimidazol-2-one 11 was placed in a three-necked flask.

36 mg (0.1315 mmol) of iodine and 70 ml of toluene (distilled over P<sub>2</sub>O<sub>5</sub>, then over Na). The resulting solution was irradiated with UV light for 5 hours while continuously passing air using a Teflon capillary. When tested by TLC (PE-toluene = 1: 1), the product rises on a par with the starting material, but its fluorescence color is different. The reaction mixture was evaporated to dryness, dissolved in hexane and applied to a column (d = 1.5 cm, L = 25 cm, SiO<sub>2</sub>-PE) and chromatographed with a mixture of petroleum ether - toluene = 1: 1. The purity of the collected fractions was monitored by TLC. After evaporation of all portions containing the pure target substance and drying at 80°C, the target substance is obtained with a yield of 50% as a colorless oil. <sup>1</sup>H NMR (400 MHz, CdCl<sub>3</sub>, δ ppm): 7.92 (d, 2H, J = 5.30 Hz), 7.77 (s, 2H), 7.52 (d, 2H, J = 5.27 Hz), 3.92 (d, 4H, 7.16 Hz), 2.12 (m, 2H), 1.50-1.10 (m, 64H), 0.88 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ ppm): 155.57, 134.18, 130.33, 129.92, 123.52, 123.16, 122.49, 101.34, 45.61, 36.77, 31.91, 31.63, 30.03, 29.66, 29.35, 26.58, 22.67, 14.10 (Figure S7). Anal. Calcd for C<sub>55</sub>H<sub>88</sub>N<sub>2</sub>OS<sub>2</sub>: C, 77.04; H,10.34; N,3.27; S,7.48.



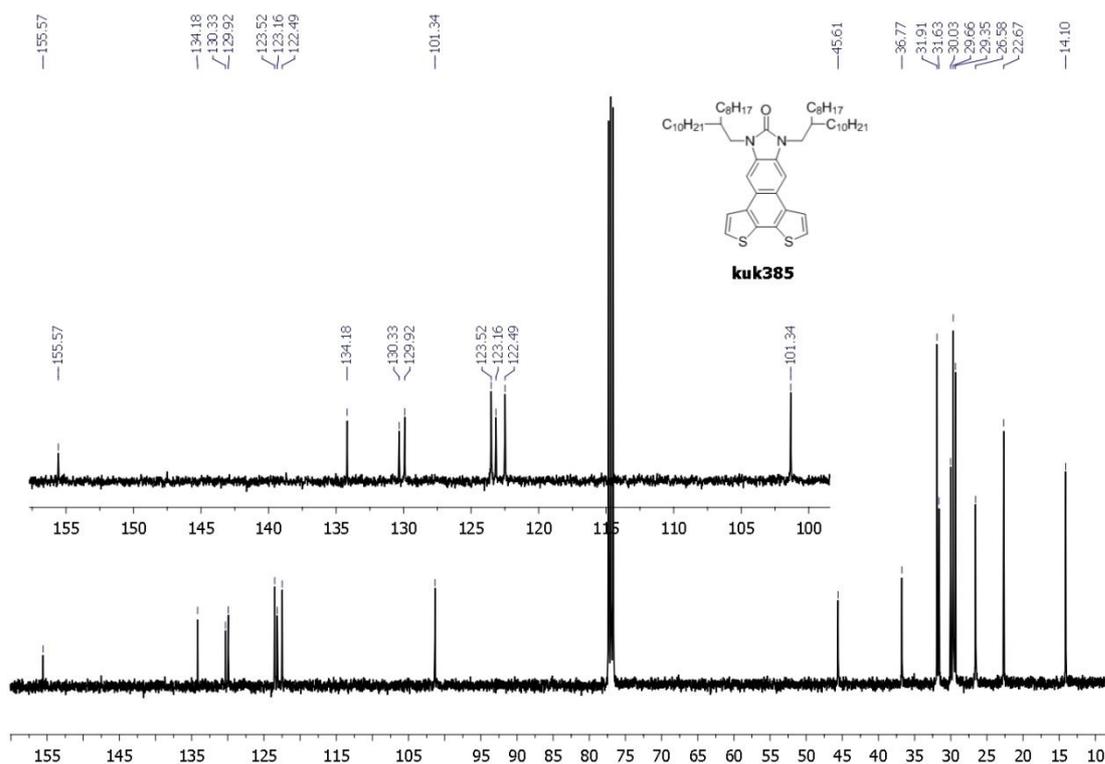


Figure S7  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of 12

**2,5-dibromo-8,10-bis (2-octyldodecyl) -8,10-dihydro-9H-bisthieno [2'3':7.8;3'',2'':5,6] naphtho [2,3-d] imidazol-9-one (M1).** NBS (0.365 g, 2.05 mmol) was added to a solution of the starting material 12 (0.837 g, 0.9761 mmol) in chloroform (distilled over  $\text{P}_2\text{O}_5$ ), and the resulting solution was stirred at room temperature overnight. The next day, a TLC test (toluene-hexane = 1: 1) showed that the process was not complete, spots of two products were observed (one of them was the product of incomplete bromination). An additional 86 mg (0.488 mmol) of NBS was added and stirring was continued for one day. The reaction mixture was evaporated under mild heating ( $35^\circ\text{C}$ ), the residue was suspended in petroleum ether and applied to a column ( $d = 1.5\text{ cm}$ ,  $L = 30\text{ cm}$ ,  $\text{SiO}_2$  - petroleum ether), chloroform-petroleum ether = 1 was used as an eluent: one. Outgoing fractions (5-8 ml each) were monitored by TLC, and the fraction containing the desired product was collected and evaporated. After evaporation, the hardened residue was dissolved in petroleum ether when heated to  $50^\circ\text{C}$  and cooled overnight in a freezer. The precipitated white substance was filtered and washed with chilled petroleum ether, dried at  $45^\circ\text{C}$  in vacuo. The target substance was obtained in the form of a white powder with a yield of 0.679 g (68.5%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.88 (s, 1H), 7.65 (s, 1H), 3.95 (d, 2H), 2.15 (m, 1H), 1.20-1.50 (m, 32H), 0.91 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CdCl}_3$ ,  $\delta$  ppm): 155.45, 133.93, 130.37, 125.31, 122.08, 112.23, 100.92,

130.01, 45.66, 36.72, 31.92, 31.60, 30.04, 29.67, 29.36, 26.55, 22.69, 14.12. Anal. Calcd for  $C_{55}H_{86}Br_2N_2OS_2$ : C, 65.07; H, 8.54; Br, 15.74; N, 2.76; S, 6.32. Found: C, 64.97; H, 8.57; Br, 16.36; N, 2.75; S, 6.17

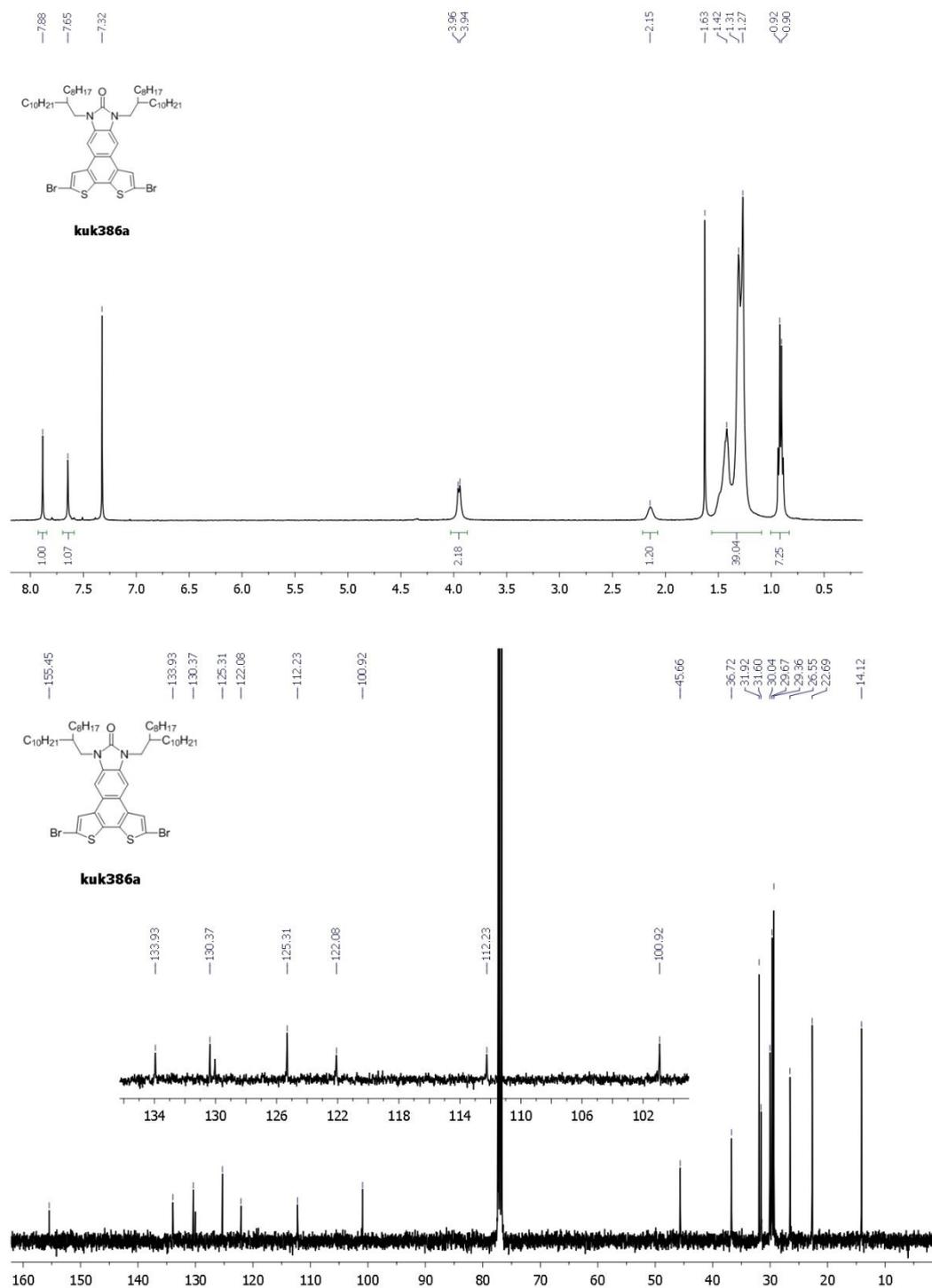


Figure S8  $^1H$  NMR and  $^{13}C$  NMR of M1

### 4.3.2. Synthesis of polymers

**Synthesis of Poly ((8,10-bis(2-octyldodecyl)-8,10-dihydro-9Hdithieno [3',2':5,6; 2'',3'':7,8] naphtha [2,3-d]imidazol-9-one-2,5-diyl)-alt-(thiophene-2,5-diyl)-alt-(benzo [c][1,2,5]thia diazole-4,7-diyl)) (P104).** The polymerization was performed by a Stille coupling reaction. Aromatic dibromide M1 (0.5076g, 0.5mmol) and distannile M2(0.3130g, 0.5mmol) were dissolved in 14ml of toluene and the solution was flushed with argon for 20 min, Pd(Ph<sub>3</sub>P)<sub>4</sub>(27 mg, 0.023mmol) was added under argon into the solution and the mixture was flushed with argon for 20min. Then reaction mixture was heated to reflux for 48h. After cooling to room temperature the mixture was slowly poured into methanol (400mL). The polymer was collected by filtration and then purified via Soxlet extraction by washing sequentially with methanol, hexane and chloroform for 20h. Polymer was obtained from the chloroform fraction by rotary evaporation to yield the final polymer P104 as a dark solid, with a yield 92%. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, δ/ppm): 8.60-6.51 (10H, Ar), 4.10-0.25 (82H, Alif) Anal. Calcd. (%) for C<sub>69</sub>H<sub>92</sub>N<sub>4</sub>OS<sub>5</sub>: C 71.83, H 8.04, N 4.86, S13.47; Found: C 71.44, H 8.00, N4.71, S13.03

**Synthesis of Poly((8,10-bis(2-octyldodecyl)-8,10-dihydro-9H-dithieno[3',2':5,6; 2'',3'':7,8] naphtho[2,3-d]imidazol-9-one-2,5-diyl)-alt-(thiophene-2,5-diyl)-alt-(5,6-difluorobenzo [c] [1,2,5] thiadiazole-4,7-diyl)) (P105).** A mixture of M1 (0.5076g, 0.5mmol), and M2 (0.3310g, 0.5mmol) in toluene was used to synthesize P104 according to the procedure described above for P105. The title polymer was obtained as black solid with a yield of 90%. <sup>1</sup>H NMR(500MHz, CDCl<sub>3</sub>,δ/pppm): 8.92-6.50 (8H, Ar), 4.00-0.25(82H, Alif). Anal. Calcd. (%) for C<sub>69</sub>H<sub>90</sub>N<sub>4</sub>F<sub>2</sub>OS<sub>5</sub>: C 69.65, H7.62, N4.71, F3.19, S13.47; Found: C 69.33, H7.49, N 4.41, F3.10, S13.09

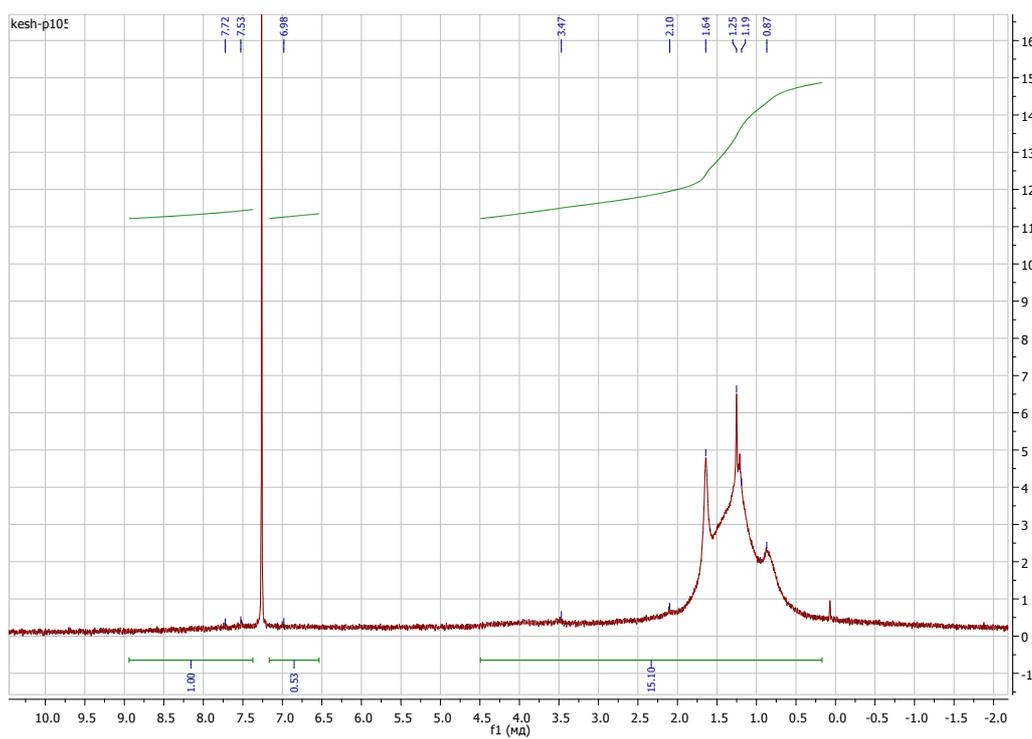
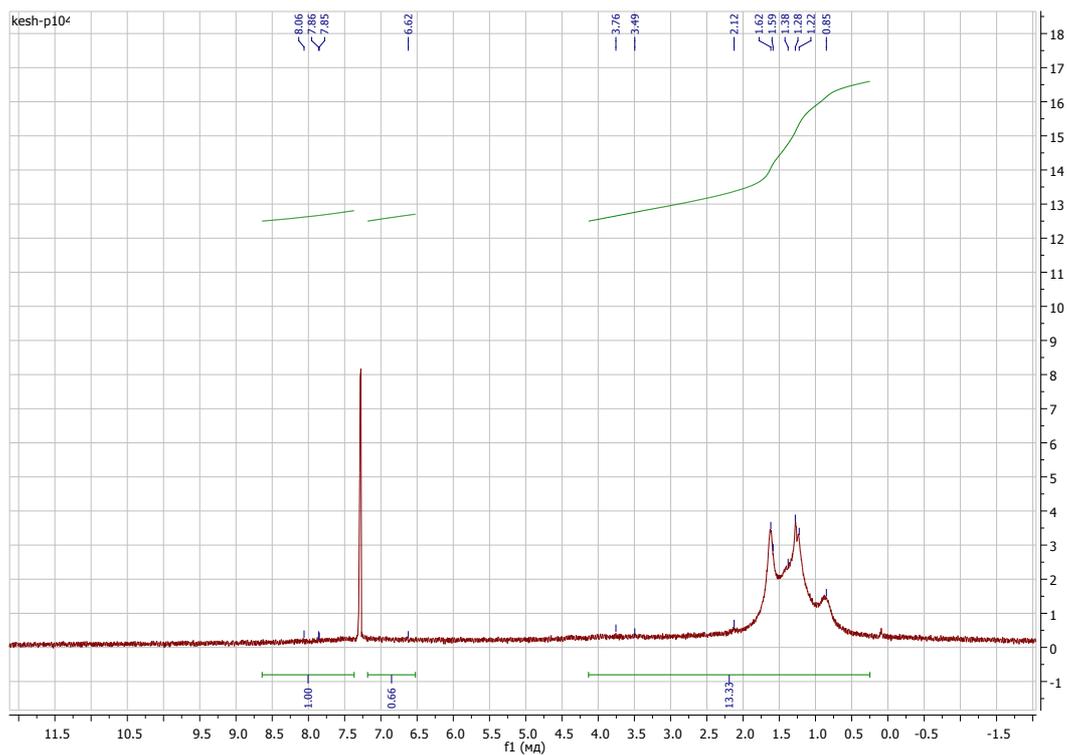


Figure S9  $^1\text{H}$  NMR spectra of polymers **P104** and **P105** in  $\text{CDCl}_3$

## Device fabrication and characterization

Polymer solar cells were fabricated with a conventional device structure of ITO/PEDOT:PSS/Polymer (**P104** or **P105**):ITIC-F/PFN/Al. The ITO glass substrates were cleaned in a ultrasonic bath with detergent, de-ionized water, acetone, and isopropyl alcohol, sequentially and dried in vacuum oven at the temperature of 50° C for overnight. A thin layer (about 40 nm) of PEDOT:PSS was then spin coated on the onto the ITO glass at 3500 rpm and annealed at 110 c for 20 min. The mixers of **P104** or **P105**/PC<sub>71</sub>BM or ITIC-F in different weight ratios were dissolved in chloroform solution and stirred for overnight and spin coated on top of the PEDOT:PSS layer for form the active BHJ layer of about 85-90 nm and dried in atmospheric environment. For solvent vapor annealing (SVA) treatment, optimized thin films were placed in the petri-disc in the THF environment for 40 s and then dried at room temperature. PFN solution (methanol with some traces of acetic acid) was then spin coated as electron transport layer. Finally, aluminum (Al) electrode was thermally evaporated under 1x10<sup>-5</sup> Pa and device area was 16 mm<sup>2</sup> was defined by a shadow mask. The current -voltage characteristics were measured with a Keithley 2400 source meter unit under stimulated 100 mW/cm<sup>2</sup> irradiation for a solar simulator. The incident photon to current conversion efficiency spectra was recorded using a IPCE measurement unit (Bentham make).

1. Hu, H, Terthiophene-Based D-A Polymer with an Asymmetric Arrangement of Alkyl Chains That Enables Efficient Polymer Solar Cells, *J. Am. Chem. Soc.* 2015, 137, 14149-14157
2. J. Shao, J. Chang and Ch Chi, Linear and Star-shaped Pyrazine containing acene dicaboximides with high electron affinity. *Org. Biomol. Chem.*, 2012, 10, 7045–7052.