

## Supplementary Information For

### Linearly polarized emission, Mesogenic polythiophenes, Self-assembly, Organic Light Emitting Diodes, Dimensional confinement.

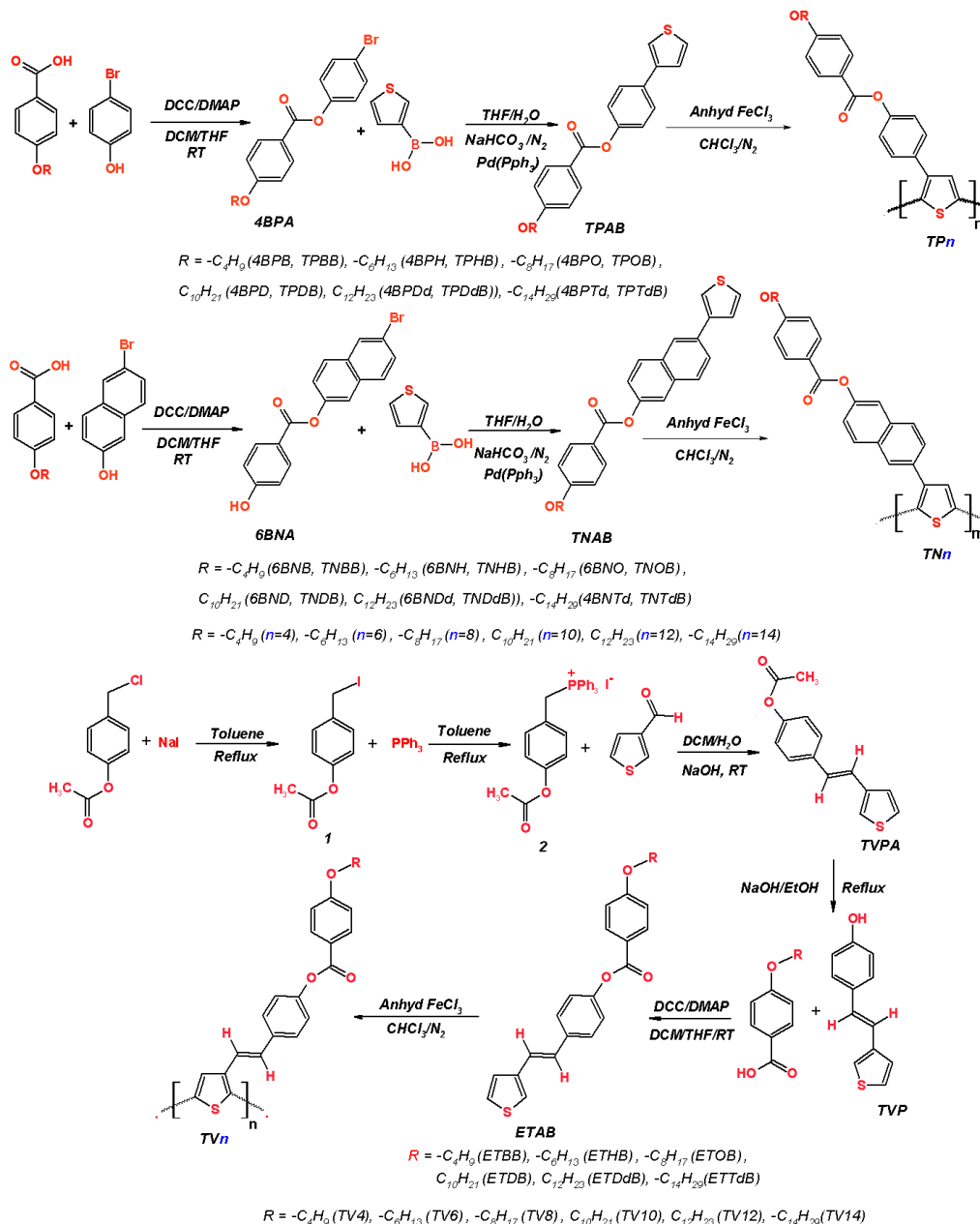
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#### Synthesis of Monomers and Intermediates.

A multistep synthetic strategy was followed to achieve the synthesis of all key intermediates, monomers and all polymers. The structural integrity of intermediates, monomers and polymers were established by <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, ESI mass spectrometry and elemental analysis. All reactions were carried out under nitrogen atmosphere unless exclusively stated. A detailed synthetic strategy for all Intermediates, monomers and polymers is outlined in **Scheme 1**. Specific procedures followed for each steps are given in the following subsections.

**Synthesis of 4-bromophenyl 4-alkoxybenzoate (4BPA).** In a representative experiment, 3g (0.0173 moles, 1.0 eq) of 4-bromophenol and 4.24 g (0.0190 moles, 1.1 eq) 4-hexyloxybenzoic acid was dissolved in minimum amount of THF. The above mixture was mixed with 50 ml of DCM under stirring for about 5 minutes in a sealed round bottom flask. About 4.27g (0.0207 moles, 1.2 eq) of N,N'-Dicyclohexylcarbodiimide (DCC) was dissolved in 10ml of DCM in a separate conical flask and added to the above mixture and stirring was continued for about a minute and 211.3mg (0.00173, 0.01 eq) of 4-dimethylaminopyridine was added and the reaction vessel was sealed. After 12 hours the reaction mixture was filtered and the filtrate was concentrated under vacuum to get the crude product which was further purified by column chromatography with hexane, ethyl acetate (1:9) as eluent. The intermediate 4-bromophenyl 4-hexyloxybenzoate 4BPH was obtained as white crystalline solid (5.61 g, yield 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.91 (t, 3H), 1.35 (m,

4H), 1.45(m, 2H), 1.80 (m, 2H), 4.03 (t, 2H), 6.95 (d, 2H) and 7.09 (d, 2H), 7.52 (d, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.15, 22.70, 25.75, 29.15, 31.64, 68.44, 114.43, 118.85, 121.16, 123.75, 132.42, 132.55, 150.20, 163.79 and 164.73.



### Scheme S1. Synthetic strategy for synthesis of Intermediates, monomers and polymers

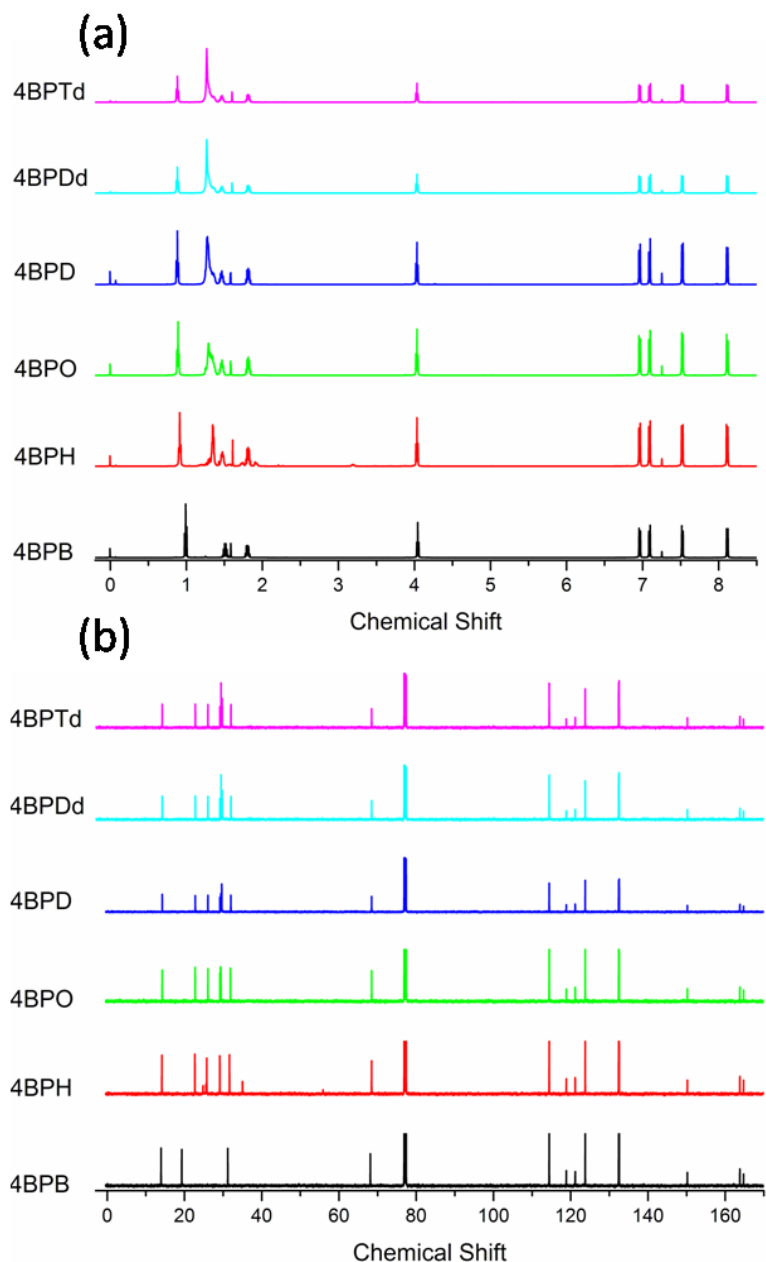
**Synthesis of 4-bromophenyl 4-alkoxybenzoate (4BPA).** In a representative experiment, 3g (0.0173 moles, 1.0 eq) of 4-bromophenol and 4.24 g (0.0190 moles, 1.1 eq) 4-hexyloxybenzoic acid was dissolved in minimum amount of THF. The above mixture was mixed with 50 ml of DCM under stirring for about 5 minutes in a sealed round bottom flask.

About 4.27g (0.0207 moles, 1.2 eq) of N,N'-Dicyclohexylcarbodiimide (DCC) was dissolved in 10ml of DCM in a separate conical flask and added to the above mixture and stirring was continued for about a minute and 211.3mg (0.00173, 0.01 eq) of 4-dimethylaminopyridine was added and the reaction vessel was sealed. After 12 hours the reaction mixture was filtered and the filtrate was concentrated under vacuum to get the crude product which was further purified by column chromatography with hexane, ethyl acetate (1:9) as eluent. The intermediate 4-bromophenyl 4-hexyloxybenzoate (4BPH) was obtained as white crystalline solid (5.61 g, yield 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.91 (t, 3H), 1.35 (m, 4H), 1.45 (m, 2H), 1.80 (m, 2H), 4.03 (t, 2H), 6.95 (d, 2H) and 7.09 (d, 2H), 7.52 (d, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.15, 22.70, 25.75, 29.15, 31.64, 68.44, 114.43, 118.85, 121.16, 123.75, 132.42, 132.55, 150.20, 163.79 and 164.73.

**4-bromophenyl 4-butoxybenzoate (4BPB)** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.99 (t, 3 H), 1.51 (m, 2 H), 1.81 (m, 2 H), 4.04 (t, 2 H), 6.96 (d, 2 H), 7.09 (d, 2 H), 7.52 (d, 2 H), 8.11 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 13.93, 19.29, 31.21, 68.12, 114.43, 118.85, 121.17, 123.75, 132.48, 150.20, 163.79 and 164.74

**4-bromophenyl 4-octyloxybenzoate (4BPO)** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.89 (t, 3 H), 1.38 (m, 11 H), 1.81 (q, 2 H), 4.03 (t, 2 H), 6.96 (d, 2 H), 7.10 (m, 2 H), 7.52 (d, 2 H) and 8.11 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.22 , 22.76 , 26.08 , 29.18, 29.43, 29.18, 31.90 , 68.45 , 114.43 , 118.85 , 121.16 , 123.75 , 132.42, 132.45, 150.19 , 163.79 and 164.74.

**4-bromophenyl 4-decyloxybenzoate (4BPD)** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.88 (t, 3 H), 1.32 (m, 13 H), 1.47 (m, 2 H), 1.81 (m, 2 H), 4.03 (t, 2 H), 6.97 (d, 2 H), 7.09 (d, 2 H), 7.52 (d, 2 H) and 8.11 (m, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.24, 22.79, 26.07, 29.18, 29.42, 29.47, 29.66, 68.45, 114.43, 118.85, 121.16, 123.75, 132.42, 132.55, 150.20, 163.79 and 164.73.



**Figure S1 (a)**  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra of 4BPA intermediates.

**4-bromophenyl 4-decyloxybenzoate (4BPD)**  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ , ppm): 0.88 (t, 3 H), 1.32 (m, 13 H), 1.47 (m, 2 H), 1.81 (m, 2 H), 4.03 (t, 2 H), 6.97 (d, 2 H), 7.09 (d, 2 H), 7.52 (d, 2 H) and 8.11 (m, 2 H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  500 MHz,  $\delta$ , ppm): 14.24, 22.79, 26.07, 29.18, 29.42, 29.47, 29.66, 68.45, 114.43, 118.85, 121.16, 123.75, 132.42, 132.55, 150.20, 163.79 and 164.73.

**4-bromophenyl 4-dodecyloxybenzoate (4BPDD)** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.88 (t, 3 H), 1.32 (m, 17 H), 1.46 (m, 2 H), 1.81 (m, 2 H), 4.03 (t, 2 H), 6.96 (d, 2 H), 7.09 (d, 2 H), 7.52 (d, 2 H) and 8.11 (d, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.24, 22.80, 26.07, 29.18, 29.46, 29.68, 29.75, 32.03, 68.45, 114.44, 118.84, 121.17, 123.74, 132.42, 132.54, 150.20, 163.79 and 164.72.

**4-bromophenyl 4-tetradecyloxybenzoate (4BPTD)** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.85 (t, 3 H), 1.36 (m, 21 H), 1.46 (m, 2 H), 1.78 (m, 2 H), 4.02 (t, 2 H), 6.97 (d, 2 H), 7.06 (d, 2 H), 7.52 (d, 2 H) and 8.12 (d, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.24, 22.78, 26.09, 29.18, 29.46, 29.68, 29.75, 32.03, 32.05, 68.42, 114.41, 118.86, 121.19, 123.68, 132.45, 132.55, 150.19, 163.81 and 164.69.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of 4BPA intermediates are presented in **Figure S1**.

#### **Synthesis of 6-bromonaphthalen-2-yl 4-(alkoxy)benzoate (6BNH)**

5g (0.0224 moles, 1.0 eq) of 6-bromonaphthalen-2-ol and 5.48 g (0.0246 moles, 1.1 eq) 4-hexyloxybenzoic acid were dissolved in minimum amount of THF. The above mixture was mixed with 50 ml of DCM and stirred for about 5 minutes in a sealed round bottom flask. About 5.54g (0.0268 moles, 1.2 eq) of N,N'-Dicyclohexylcarbodiimide (DCC) dissolved in 15ml of DCM in a separate conical flask was added to the above mixture followed by 273.6 mg (0.00173, 0.01 eq) of 4-dimethylaminopyridine was added and the reaction vessel was sealed. After 24 hours the reaction mixture was filtered and concentrated in a rotary evaporator to get the crude product. which was further purified by column chromatography with hexane, ethyl acetate (1:4) as eluent. The intermediate 6-bromonaphthalen-2-yl 4-(hexyloxy)benzoate (**6BNH**) was obtained as off-white crystalline solid (7.59 g, yield 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.92 (t, 3H) , 1.36 (m, 4H), 1.48 (m, 2H), 1.82 (m, 2H), 4.04 (t, 2H), 6.99 (d, 2H), 7.36 (d, 1H), 7.57 (d, 1H), 7.65 (m, 2H) , 7.78 (d, 2H), 8.02(s, 1H) and 8.16 (d, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.15, 22.70, 25.77, 29.16,

31.65, 68.45, 76.88, 77.13, 77.39, 114.46, 118.95, 119.61, 121.37, 122.70, 128.56, 129.37, 129.92, 130.01, 132.37, 132.44, 132.52, 149.12, 163.78 and 165.08.

#### **Synthesis of 6-bromonaphthalen-2-yl 4-(butoxy)benzoate (6BNB)**

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.99 (m, 3 H), 1.52 (m, 2 H), 1.82 (m, 2 H), 4.06 (t, 2 H), 6.99 (d, 2 H), 7.37 (dd, 1 H), 7.56 (dd, 1 H), 7.67 (m, 2 H), 7.79 (d, 1 H), 8.02 (s, 1H) and <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ,ppm): 13.94, 19.30, 31.22, 68.13, 114.46, 118.95, 119.61, 121.37, 122.70, 128.56, 129.37, 129.92, 130.01, 132.44, 132.40, 132.50, 149.12, 163.01, 163.78 and 165.08.

#### **Synthesis of 6-bromonaphthalen-2-yl 4-(octyloxy)benzoate (6BNO)**

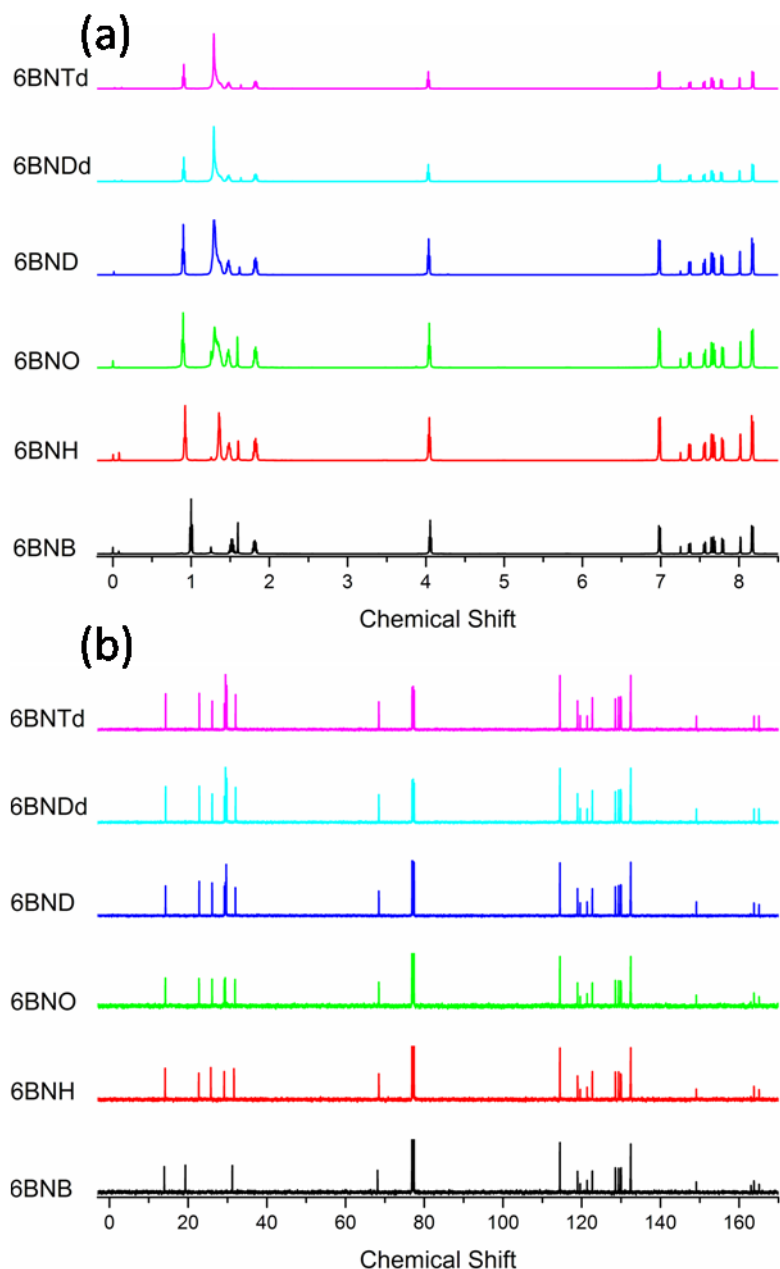
<sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.90 (t, 3 H), 1.33 (m, 8 H), 1.48 (q, 2 H), 1.82 (m, 2 H), 4.04 (t, 2 H), 6.98 (d, 2 H), 7.37 (dd, 1 H), 7.56 (dd, 1 H), 7.67 (m, 2 H), 7.79 (m, 1 H), 8.02 (s, 1 H) and 8.17 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ,ppm): 14.22, 22.76, 26.09, 29.19, 29.33, 29.43, 31.91, 68.46, 114.46, 118.94, 119.61, 121.37, 122.70, 128.56, 129.37, 129.92, 130.01, 132.37, 132.44, 132.52, 149.12, 163.78 and 165.08.

#### **Synthesis of 6-bromonaphthalen-2-yl 4-(decyloxy)benzoate (6BND)**

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.90 (t, 3H), 1.34 (m, 12 H), 1.48 (m, 2H), 1.82 (m, 2H), 4.04 (t, 2 H), 6.98 (d, 2 H), 7.37 (dd, 1H), 7.56 (dd, 1H), 7.66 (m, 2 H), 7.78 (d, 1H), 8.01 (s,1H), 8.17 (d, 7H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ,ppm): 14.26, 22.81, 26.10, 29.21, 29.49, 29.68, 32.02, 68.46, 114.46, 118.94, 119.61, 121.38, 122.70, 128.55, 129.37, 129.92, 130.00, 132.37, 132.44, 132.52, 149.14, 163.78 and 165.07.

#### **Synthesis of 6-bromonaphthalen-2-yl 4-(dodecyloxy)benzoate (6BNDd)**

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.91 (t, 3 H), 1.34 (m, 16 H), 1.48 (m, 2 H), 1.82 (m, 2 H), 4.03 (t, 2 H), 6.98 (d, 2 H), 7.37 (dd, 1 H), 7.55 (m, 1 H), 7.66 (m, 2 H), 7.78 (d, 1 H), 8.01 (d, 1 H) and 8.18 (d, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ,ppm): 14.28, 22.84, 26.11, 29.22, 29.51, 32.06, 68.45, 114.46, 118.94, 119.62, 121.39, 122.71, 128.55, 129.37, 129.92,



**Figure S2.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra of 6BNA intermediates.

132.37, 132.45, 132.51, 149.15, 163.79 and 165.05.

#### **Synthesis of 6-bromonaphthalen-2-yl 4-(dodecyloxy)benzoate (6BNTd)**

$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ , ppm): 0.89 (t, 3 H), 1.33 (m, 20 H), 1.44 (m, 2 H), 1.80 (m, 2 H), 4.01 (t, 2 H), 6.99(d, 2 H), 7.31(dd, 1 H), 7.56 (m, 1 H), 7.68 (m, 2 H), 7.79 (d, 1 H), 8.05 (d, 1 H) and 8.11 (d, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  500 MHz,  $\delta$ ,ppm): 14.25, 22.81, 26.01, 29.00,

29.45, 32.06, 32.12, 68.39, 114.38, 118.87, 119.71, 121.45, 122.64, 128.50, 129.29, 129.88, 132.32, 132.43, 132.46, 149.13, 163.68 and 165.13.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of all 6BNA intermediates are presented in **Figure S2**.

#### **Synthesis of 4-iodomethylphenyl acetate (compound 1).**

10.00g (0.0586 moles, 1.0 eq) of 4-chlorophenyl acetate was dissolved in 130ml of acetonitrile in a 500ml round bottom flask and 11.86g (0.0644, 1.1eq) sodium iodide was dissolved in 130ml of acetonitrile in a separate container. The solution of sodium iodide was added to 4-chloromethylphenyl acetate solution in the 500ml with stirring. The mixture was heated to 60 °C with stirring for about 3 hours. After 3 hours the reaction mixture was filtered off and the filtrate was concentrated in a rotary evaporator to get 4-iodomethylphenyl acetate (compound 1) as pale yellow crystalline solid. Compound 1 was redissolved in toluene and washed with 5% sodium thiosulphate solution until the pink color vanishes in the organic medium. Pure **Compound 1** obtained after washing is white crystalline solid (15.71g, yield 97%) which turns yellow and brown on standing. **Compound 1** was taken immediately for further step without any further purification owing to its quick decomposition.

#### **Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl acetate (TVPA).**

About 15.71g (0.0569 moles, 1.0 eq) **Compound 1** dissolved in 90ml of toluene and 17.91g (0.0683 moles, 1.2 eq) of triphenyl phosphine predissolved in 50 ml of toluene were mixed in a round bottom flask. The above reaction mixture was refluxed with continuous stirring for 15 hours and the phosphonium salt (**compound 2**) which precipitated as white crystalline solid was filtered and dried (32.94g, yield 98%). Compound 2 was taken as such without further purification or characterization due to poor solubility in organic solvents. 12g (0.0223 moles, 1.0 eq) of **compound 2** was dispersed in 50 ml of dichloromethane along with 2.75g (0.0245 moles, 1.1eq) of thiophene-3-carbaldehyde. To the above solution 1.00 g (0.025, 1.1eq) of sodium hydroxide dissolved in 5 ml of water was added and the biphasic reaction



mixture was vigorously stirred for about 5 hours under nitrogen. After the reaction time the mixture was washed with distilled water and the organic layer was concentrated under vacuum to get crude product as a viscous oily liquid. The crude product was washed with minimum amount of methanol to get pure as white crystalline solid (2.28 g, yield 42%). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 2.3 (s, 3H) , 6.96 (d, 1H, J=14Hz), 7.99 (m, 3H), 7.28 (s, 2H), 7.34 (m, 2H), 7.48 (d, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ,ppm): 21.28, 121.90, 122.63, 123.21, 124.95, 126.37, 127.28, 135.30, 140.03, 149.99 and 169.63 . ESI mass m/z: Calculated for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>S, 244.31, found: 244.09. Elemental analysis: Calculated (%) for C<sub>22</sub>H<sub>21</sub>BrO<sub>3</sub>: C, 68.83; H, 4.95; S, 13.10. Found (%): C, 68.79; H, 4.98; S, 13.12.

#### **Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenol (TVP).**

4.0g of the TVPA was dispersed in 50ml of ethanol and refluxed after mixing with 2.63 (0.0409 moles, 2.5 eq) of sodium hydroxide dissolved in 20 ml of distilled water. The reaction mixture was refluxed for 6 hours. The dispersion of TVPA became a clear solution on refluxing. The reaction mixture was cooled after their reaction time and acidified with 3N solution of Hydrochloric acid. The acidified reaction mixture was extracted with ethyl acetate and dried over magnesium sulfate. The concentration of the organic layer yielded pure (E)-4-(2-(thiophen-3-yl)vinyl)phenol (TVP) white crystalline solid. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 6.72 (d, 2H), 6.55 (d, 1H, J=14Hz), 6.95 (d, 1H, J=14 Hz), 7.36 (d, 2H), 7.41 (m, 2H), 7.49 (m, 1H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ,ppm): 157.49, 140.84, 128.76, 128.71, 128.08, 127.23, 125.57, 122.31, 120.38, 116.09.

#### **Synthesis of 4-(thiophen-3-yl)phenyl 4-(hexyloxy)benzoate (TPHB).**

In a representative reaction 780.4 mg (0.0061 moles, 1.5 eq) of 3-thiopheneboronic acid and 1.51 g (0.004, 1 eq) 4-bromophenyl 4-hexyloxybenzoate (4BPH) were dissolved in 45ml of tetrahydrofuran at room temperature and about 18 ml of 1% sodium bicarbonate solution was added to the solution with constant stirring. The temperature of above reaction mixture was

raised to 70 °C and purged with nitrogen followed by addition of 472.1 mg (0.0004 moles, 0.1 eq) of tetrakis(triphenylphosphine)-palladium(0). After refluxing the above mixture with stirring under nitrogen for 24 hours, the organic layer was separated and concentrated under vacuum to get crude product that was brown color. The product 4-(thiophen-3-yl)phenyl 4-(alkoxy)benzoate (TPAB) was purified by column chromatography using hexane : ethyl acetate (7:3) as eluent and obtained as white fluffy solid (1.15g, yield 76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.92 (t, 3H), 1.36 (m, 4H), 1.49 (m, 2H), 1.82 (m, 2H), 4.04 (t, 2H), 6.98 (d, 2H), 7.25 (m, 2H), 7.39 (m, 3H), 7.62 (d, 2H), 8.14 (d, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.15, 22.70, 25.76, 29.17, 31.66, 68.43, 76.87, 77.13, 77.38, 114.39, 120.43, 121.56, 122.23, 126.43, 126.47, 127.57, 132.40, 133.65, 141.70, 150.30, 163.67, 165.09 and 165.91. ESI mass m/z: Calculated for C<sub>23</sub>H<sub>24</sub>O<sub>3</sub>S, 380.50, found: 380.22. Elemental analysis: Calculated (%) for C<sub>23</sub>H<sub>24</sub>O<sub>3</sub>S: C, 72.60; H, 6.36; S, 8.43. Found (%): C, 72.56; H, 6.29; S 8.39.

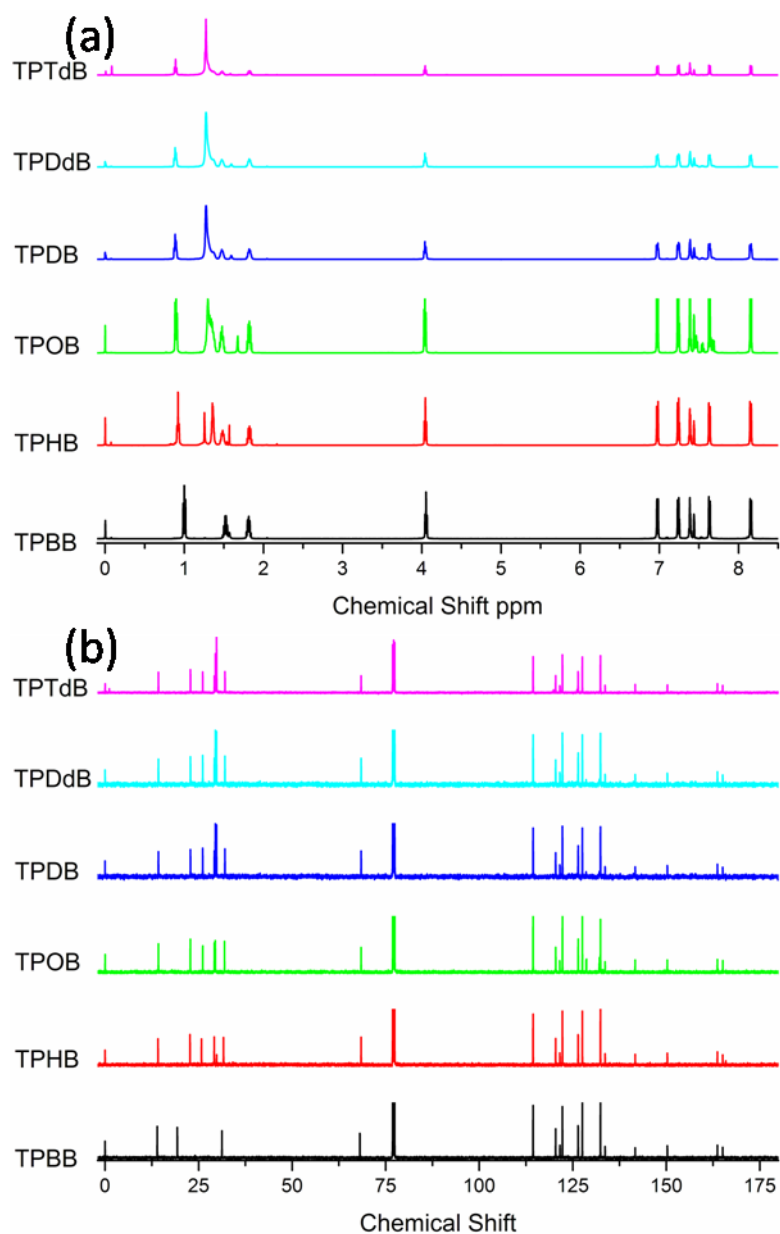
#### **Synthesis of 4-(thiophen-3-yl)phenyl 4-(butoxy)benzoate TPBB**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 1.00 (t, 3 H), 1.51 (m, 2 H), 1.81 (m, 2 H), 4.05 (t, 2 H), 6.98 (d, 2 H), 7.24 (m, 2 H), 7.39 (m, 2 H), 7.44 (d, 1 H), 7.63 (d, 2 H), 8.15 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 13.94, 19.31, 31.24, 68.10, 114.39, 120.43, 121.57, 122.23, 127.57, 132.40, 133.65, 141.70, 150.30, 163.67 and 165.09. ESI mass m/z: Calculated for C<sub>21</sub>H<sub>20</sub>O<sub>3</sub>S, 352.45, found: 353.32. Elemental analysis: Calculated (%) for C<sub>21</sub>H<sub>20</sub>O<sub>3</sub>S: C, 71.56; H, 5.72; S, 9.10. Found (%): C, 71.45; H, 5.65; S, 9.21.

#### **Synthesis of 4-(thiophen-3-yl)phenyl 4-(octyloxy)benzoate TPOB**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.90 (t, 3 H), 1.34 (m, 8 H), 1.48 (m, 2 H), 1.82 (dt, 2 H), 4.04 (t, 2 H), 6.98 (m, 2 H), 7.24 (m, 2 H), 7.39 (m, 2 H), 7.44 (t, 1 H), 7.63 (m, 2 H), 8.15 (m, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): <sup>1</sup>H NMR (Solvent) δ ppm 14.25, 22.79, 26.11, 29.21, 29.35, 29.45, 31.92, 68.43, 114.39, 120.44, 121.52, 122.25, 126.46, 127.58,

128.62, 132.41, 133.64, 141.69, 150.28, 163.67 and 165.12. ESI mass  $m/z$ : Calculated for  $C_{25}H_{28}O_3S$ , 408.55, found: 409.42. Elemental analysis: Calculated (%) for  $C_{25}H_{28}O_3S$ : C, 73.50; H, 6.91; S, 7.85. Found (%): C, 73.50; H, 6.91; S, 7.85.



**Figure S3 (a)**  $^1H$  and **(b)**  $^{13}C$  NMR spectra of TPAB monomers

#### Synthesis of 4-(thiophen-3-yl)phenyl 4-(decyloxy)benzoate TPDB

$^1H$ NMR ( $CDCl_3$ , 500 MHz,  $\delta$ , ppm): 0.89 (t, 3 H), 1.27 (m, 12 H), 1.46(m, 2 H), 1.72 (dt, 2 H), 4.03 (t, 2 H), 6.88 (m, 2 H), 7.25 (m, 2 H), 7.41 (m, 2 H), 7.47 (t, 1 H), 7.68 (m, 2 H),

8.25 (m, 2 H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  500 MHz,  $\delta$ , ppm):  $^1\text{H}$  NMR (Solvent)  $\delta$  ppm 14.35, 22.69, 26.12, 29.23, 29.36, 29.49, 31.87, 31.93, 32.03, 68.45, 114.29, 120.41, 121.60, 122.31, 126.42, 127.57, 128.61, 132.42, 133.67, 141.72, 150.29, 163.59 and 165.02. ESI mass  $m/z$ : Calculated for  $\text{C}_{27}\text{H}_{32}\text{O}_3\text{S}$ , 436.61, found: 436.55. Elemental analysis: Calculated (%) for  $\text{C}_{27}\text{H}_{32}\text{O}_3\text{S}$ : C, 74.27; H, 7.39; S, 7.34. Found (%): C, 74.19; H, 7.25; S, 7.44.

#### **Synthesis of 4-(thiophen-3-yl)phenyl 4-(dodecyloxy)benzoate TPDdB**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ , ppm): 0.88 (m, 3 H), 1.32 (m, 17 H), 1.46 (m, 2 H), 1.81 (m, 2 H), 4.04 (m, 2 H), 6.97 (dd, 2 H), 7.24 (m, 2 H), 7.38 (m, 2 H), 7.63 (dd, 2 H), 8.15 (dt, 2 H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  500 MHz,  $\delta$ , ppm):  $^1\text{H}$  NMR (Solvent)  $\delta$  ppm 14.25, 22.81, 26.09, 29.20, 29.47, 29.70, 29.77, 32.03, 68.44, 114.39, 120.43, 121.56, 122.23, 126.43, 126.47, 127.57, 132.40, 133.65, 141.70, 150.30, 163.67 and 165.09. ESI mass  $m/z$ : Calculated for  $\text{C}_{29}\text{H}_{36}\text{O}_3\text{S}$ , 464.66, found: 465.55. Elemental analysis: Calculated (%) for  $\text{C}_{29}\text{H}_{36}\text{O}_3\text{S}$ : C, 74.96; H, 7.81; S, 6.90. Found (%): C, 74.84; H, 7.72; S, 6.82.

#### **Synthesis of 4-(thiophen-3-yl)phenyl 4-(tetradecyloxy)benzoate TPTdB**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ , ppm): 0.89 (t, 3 H), 1.31 (m, 25 H), 1.47 (m, 2 H), 1.82 (quin, 2 H), 4.04 (t, 2 H), 6.98 (d, 2 H), 7.24 (m, 2 H), 7.39 (m, 2 H), 7.44 (t, 1 H), 7.63 (d, 2 H), 8.16 (d, 2 H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  500 MHz,  $\delta$ , ppm): 14.26, 22.82, 26.10, 29.21, 29.48, 29.68, 29.71, 29.78, 32.05, 68.44, 114.40, 120.43, 121.56, 122.24, 126.43, 126.46, 127.56, 132.40, 133.65, 141.70, 150.31, 163.67 and 165.08. ESI mass  $m/z$ : Calculated for  $\text{C}_{31}\text{H}_{40}\text{O}_3\text{S}$ , 492.71, found: 493.64. Elemental analysis: Calculated (%) for  $\text{C}_{31}\text{H}_{40}\text{O}_3\text{S}$ : C, 75.57; H, 8.18; S, 6.51. Found (%): C, 75.45; H, 8.21; S, 6.62.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all TPAB monomers are given in **Figure S3**.

#### **Synthesis of (6-(thiophen-3-yl)naphthalen-2-yl)methyl 4-(decyloxy)benzoate (TNDB)**

In a representative experiment, 6-bromonaphthalen-2-yl 4-(tetradecyloxy)benzoate **6BNTd** (2.15g, 0.004 moles, 1 eq) and 3-thiopheneboronic acid (780.4 mg, 0.006 moles, 1.5 eq) were

dissolved in 45 ml of tetrahydrofuran at room temperature. 18 ml of 1% sodium bicarbonate solution was added to the above solution and the temperature was raised to 70 °C. 472.1 mg of tetrakis(triphenyl)phosphinepalladium(0) was added to the reaction mixture and nitrogen was purged with constant stirring. After reaction time of 24 hours, the organic layer was separated and washed with dilute hydrochloric acid. The crude product obtained as brown powder on concentration of the organic layer was purified by column chromatography with hexane/ethyl acetate (v/v, 7:3) as eluent. Pure **6TNDB** obtained after purification was a white fluffy solid (1.27g, yield 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.89 (t, 3 H), 1.31 (m, 12 H), 1.48 (quin, 2 H), 1.83 (quin, 2 H), 4.05 (t, 2 H), 6.99 (d, 2 H), 7.36 (dd, 1 H), 7.44 (t, 1 H), 7.53 (d, 1 H), 7.58 (d, 1 H), 7.67 (d, 1 H), 7.77 (m, 1 H), 7.85 (d, 1 H), 7.91 (d, 1 H), 8.06 (s, 1 H), 8.19 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 14.24, 22.81, 26.10, 29.21, 29.47, 29.66, 29.70, 29.77, 32.03, 68.45, 114.43, 118.70, 120.77, 121.59, 122.04, 124.74, 125.82, 126.49, 126.54, 128.31, 129.58, 131.81, 132.43, 133.03, 133.13, 142.17, 148.85, 163.71 and 165.24. ESI mass m/z: Calculated for C<sub>35</sub>H<sub>42</sub>O<sub>3</sub>S, 486.66, found: 487.53. Elemental analysis: Calculated (%) for C<sub>35</sub>H<sub>42</sub>O<sub>3</sub>S: C, 76.51; H, 7.04; S, 6.59. Found (%): C, 76.60; H, 7.16; S, 6.63.

#### **Synthesis of (6-(thiophen-3-yl)naphthalen-2-yl)methyl-4-(butoxy)benzoate (TNBB)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 1.01 (t, 3 H), 1.53 (m, 2 H), 1.82 (quin, 2 H), 4.06 (t, 2 H), 6.99 (d, 2 H), 7.36 (dd, 1 H), 7.44 (t, 1 H), 7.53 (d, 1 H), 7.58 (d, 1 H), 7.67 (d, 1 H), 7.76 (m, 1 H), 7.84 (d, 1 H), 7.91 (d, 1 H), 8.06 (s, 1 H), 8.20 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 13.95, 19.32, 31.25, 68.12, 114.43, 118.71, 120.78, 121.60, 122.05, 124.74, 125.82, 126.50, 128.32, 129.59, 131.82, 132.44, 133.04, 133.13, 142.17, 148.86, 163.71 and 165.24. ESI mass m/z: Calculated for C<sub>25</sub>H<sub>22</sub>O<sub>3</sub>S, 402.51, found: 403.39. Elemental analysis: Calculated (%) for C<sub>25</sub>H<sub>22</sub>O<sub>3</sub>S: C, 75.32; H, 6.09; S, 7.45. Found (%): C, 75.43; H, 6.14; S, 7.33.

### **Synthesis of (6-(thiophen-3-yl)naphthalen-2-yl)methyl-4-(hexyloxy)benzoate (TNHB)**

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.90 (m, 3 H), 1.34 (m, 6 H), 1.83 (dt, 2 H), 4.05 (t, 2 H), 7.00 (d, 2 H), 7.37 (d, 1 H), 7.44 (s, 1 H), 7.53 (d, 1 H), 7.58 (s, 1 H), 7.67 (s, 1 H), 7.77 (d, 1 H), 7.84 (d, 1 H), 7.90 (d, 1 H), 8.06 (s, 1 H), 8.20 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.18, 22.73, 25.79, 29.19, 31.68, 68.45, 114.44, 118.72, 120.79, 121.59, 122.06, 124.74, 125.82, 126.50, 126.55, 128.32, 129.60, 131.82, 132.45, 133.04, 133.13, 142.16, 148.86, 163.72 and 165.25. ESI mass m/z: Calculated for C<sub>27</sub>H<sub>26</sub>O<sub>3</sub>S, 430.56, found: 430.77. Elemental analysis: Calculated (%) for C<sub>27</sub>H<sub>26</sub>O<sub>3</sub>S: C, 75.32; H, 6.09; S, 7.45. Found (%): C, 75.43; H, 6.14; O, 11.11; S, 7.33.

### **Synthesis of (6-(thiophen-3-yl)naphthalen-2-yl)methyl-4-(octyloxy)benzoate (TNOB)**

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.90 (t, 3 H), 1.34 (m, 8 H), 1.48 (quin, 2 H), 1.83 (quin, 2 H), 4.05 (t, 2 H), 6.99 (d, 2 H), 7.36 (dd, 1 H), 7.44 (m, 1 H), 7.53 (d, 1 H), 7.58 (d, 1 H), 7.67 (s, 1 H), 7.77 (m, 1 H), 7.85 (m, 1 H), 7.91 (d, 1 H), 8.06 (s, 1 H), 8.19 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.23, 22.78, 26.10, 29.21, 29.34, 29.44, 31.92, 68.45, 114.43, 118.70, 120.78, 121.59, 122.04, 124.74, 125.82, 126.50, 128.31, 129.58, 131.81, 132.43, 133.03, 133.13, 142.17, 148.85, 163.71 and 165.24. ESI mass m/z: Calculated for C<sub>29</sub>H<sub>30</sub>O<sub>3</sub>S, 458.61, found: 459.42. Elemental analysis: Calculated (%) for C<sub>29</sub>H<sub>30</sub>O<sub>3</sub>S: C, 75.95; H, 6.59; O, 10.47; S, 6.99. Found (%): C, 75.87; H, 6.61; S, 7.03.

### **Synthesis of (6-(thiophen-3-yl)naphthalen-2-yl)methyl-4-(dodecloxy)benzoate (TNDdB)**

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.89 (t, 3 H), 1.28 (s, 10 H), 1.48 (quin, 2 H), 1.83 (quin, 2 H), 4.05 (t, 2 H), 6.99 (d, 2 H), 7.36 (dd, 1 H), 7.44 (t, 1 H), 7.53 (d, 1 H), 7.58 (d, 1 H), 7.67 (d, 1 H), 7.77 (m, 1 H), 7.85 (d, 1 H), 7.91 (d, 1 H), 8.06 (s, 1 H), 8.19 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.25, 22.81, 26.10, 29.21, 29.47, 29.67, 29.70, 29.75, 29.78, 32.03, 68.45, 114.43, 118.70, 120.78, 121.59, 122.04, 124.74, 125.82, 126.50, 128.31, 129.58, 131.81, 132.44, 133.03, 133.13, 142.17, 148.85, 163.71, 165.24 and 165.91. ESI

mass m/z: Calculated for  $C_{33}H_{38}O_3S$ , 514.72, found: 515.64. Elemental analysis: Calculated (%) for  $C_{33}H_{38}O_3S$ : C, 77.00; H, 7.44; S, 6.23. Found (%): C, 77.12; H, 7.36; S, 6.34.

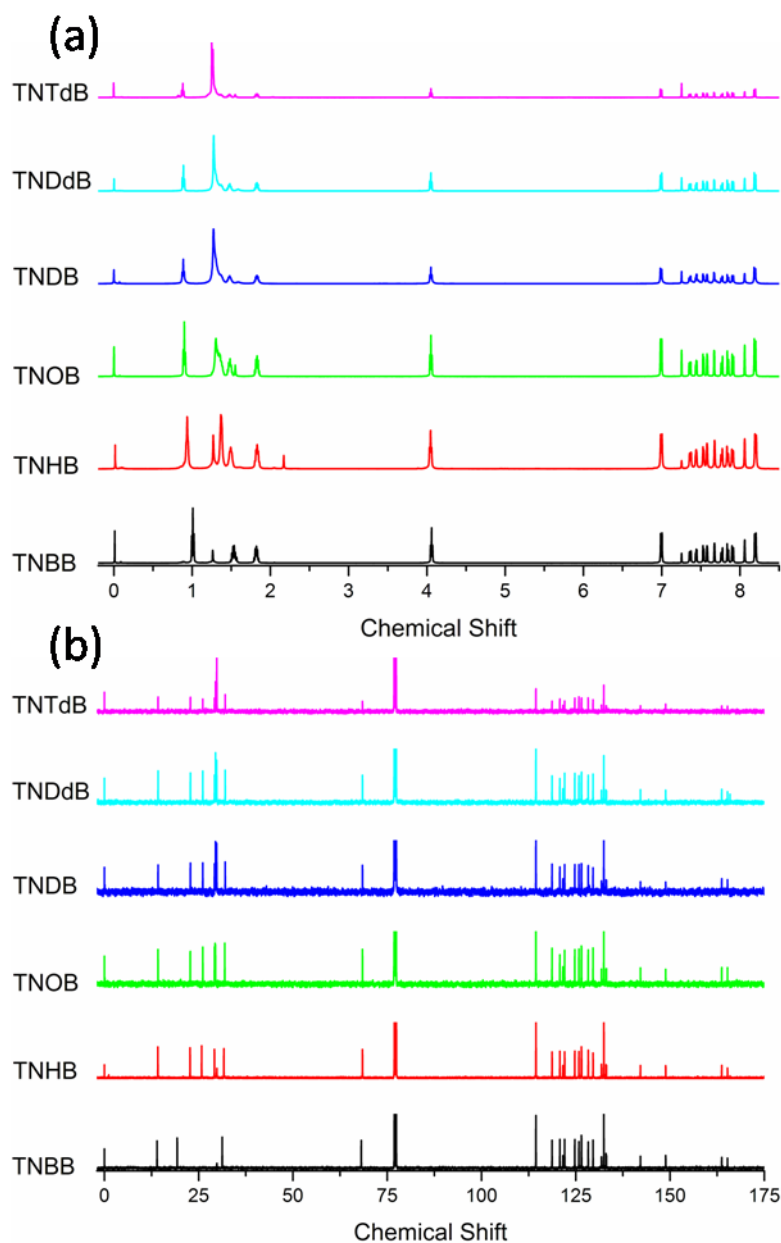
### **Synthesis of (6-(thiophen-3-yl)naphthalen-2-yl)methyl-4-(tetradecyloxy)benzoate (TNTdB)**

$^1H$ NMR ( $CDCl_3$ , 500 MHz,  $\delta$ , ppm): 0.88, (t, 3H), 1.25 (m, 19H), 1.48 (m, 2H), 1.83 (m, 2H), 4.05 (t, 2H), 6.98, (d, 2H), 7.37 (m, 1H), 7.44 (m, 1H), 7.53 (d, 1H), 7.58 (d, 1H), 7.67 (s, 1H), 7.78 (d, 2H), 7.84 (d, 1H), 7.90 (s, 1H), 8.06 (s, 1H) and 8.20 (d, 2H),  $^{13}C$  NMR ( $CDCl_3$  500 MHz,  $\delta$ , ppm): 14.24, 22.81, 26.09, 29.21, 29.47, 29.66, 29.70, 29.81, 32.03, 68.45, 114.43, 118.70, 120.77, 121.59, 122.04, 124.74, 125.82, 126.49, 126.53, 128.30, 129.57, 131.81, 132.43, 133.03, 133.13, 142.17, 148.85, 163.71, and 165.23. ESI mass m/z: Calculated for  $C_{35}H_{42}O_3S$ : 542.77 found: 542.22. Elemental analysis: Calculated (%) for  $C_{35}H_{42}O_3S$ : C, 77.45; H, 7.80; S, 5.91. Found (%): C, 76.46; H, 7.71; S, 5.96.  $^1H$  and  $^{13}C$  NMR spectra of TNAB monomers are presented in **Figure S4**.

### **Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl 4-(alkoxy)benzoate (ETHB)**

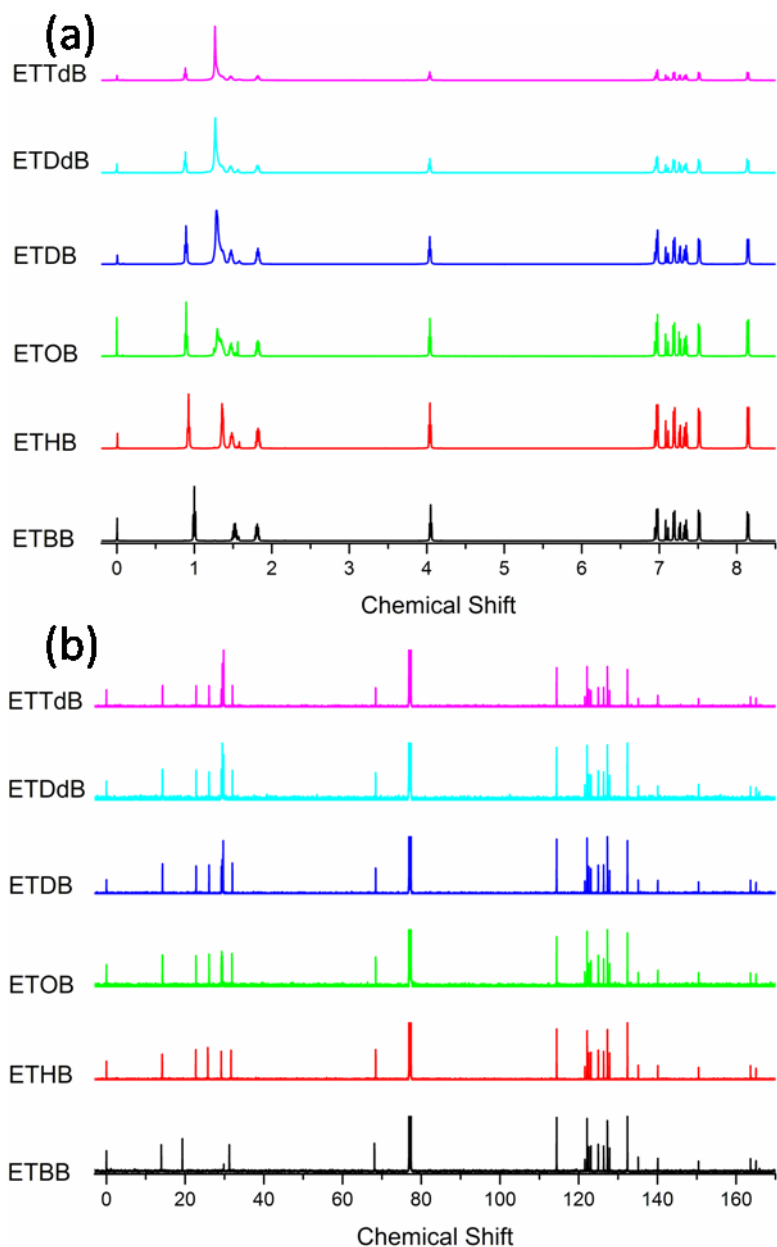
In a representative synthesis, about 1.5 g (0.0074 moles, 1.0 eq) of **TVP** and 1.97 g (0.0088 moles, 1.2 eq) of 4-hexyloxybenzoic acid were dissolved in 50 ml of dichloromethane. Ca. 1.81 g (0.0088, 1.2eq) of DCC predissolved in 20 ml of dichloromethane was added with stirring and 90.4 mg (0.0007 moles, 0.1 eq) of 4-dimethylaminopyridine was added. After 15 hours the reaction mixture was filtered and the filtrate was washed with dilute hydrochloric acid. The organic layer was then concentrated and washed with minimum amount of methanol to get white crystals of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl 4-(hexyloxy)benzoate (**ETHB**) in pure form (2.04g, yield 68%).  $^1H$ NMR ( $CDCl_3$ , 500 MHz,  $\delta$ , ppm): 0.93 (t, 3H), 1.36 (m, 2H), 1.48 (m, 2H), 1.82 (m, 2H), 4.04 (t, 2H), 6.98 (m, 3H), 7.08 (d, 1H, J=15Hz), 7.20 (d, 2H), 7.27 (m, 1H), 7.35 (m, 2H) and 7.51(d, 2H),  $^{13}C$  NMR ( $CDCl_3$  500 MHz,  $\delta$ , ppm): 14.16, 22.71, 25.77, 29.17, 31.66, 68.43, 114.39, 121.57, 122.13, 122.56, 123.09,

124.97, 126.34, 127.30, 127.85, 132.39, 135.12, 140.11, 150.46, 163.66 and 165.05. ESI mass  $m/z$ : Calculated for  $C_{25}H_{26}O_3S$ , 406.54, found: 506.58. Elemental analysis: Calculated (%) for  $C_{25}H_{26}O_3S$ : C, 73.86; H, 6.45; S, 7.89. Found (%): C, 73.79; H, 6.44; S, 7.91.



**Figure S4.** (a)  $^1H$  and (b)  $^{13}C$  NMR spectra of TNAB monomers.





**Figure S5. (a)**  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra of ETAB monomers.

#### Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl 4-(butoxy)benzoate (ETBB)

$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ , ppm): 1.00 (t, 3 H), 1.52 (sxt, 2 H), 1.81 (quin, 2 H), 4.05 (t, 2 H), 6.97 (m, 3 H), 7.10 (m, 1 H), 7.19 (d, 2 H), 7.26 (d, 1 H), 7.33 (m, 2 H), 7.51 (d, 2 H), 8.14 (d, 2 H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  500 MHz,  $\delta$ ,ppm): 13.94, 19.31, 31.24, 68.10, 114.39, 121.57, 122.13, 122.56, 123.09, 124.97, 126.34, 127.29, 127.85, 132.39, 135.12, 140.10, 150.46, 163.66 and 165.05. ESI mass  $m/z$ : Calculated for  $\text{C}_{23}\text{H}_{22}\text{O}_3\text{S}$ , 378.48, found: 378.48.

Elemental analysis: Calculated (%) for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub>S: C, 72.99; H, 5.86; S, 8.47. Found (%): C, 72.81; H, 5.90; S, 8.53.

#### **Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl 4-(octyloxy)benzoate (ETOB)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.89 (m, 3 H), 1.33 (m, 9 H), 1.47 (quin, 2 H), 1.82 (quin, 2 H), 4.04 (t, 2 H), 6.96 (m, 3 H), 7.10 (d, 1 H), 7.19 (d, 2 H), 7.26 (m, 1 H), 7.33 (m, 2 H), 7.51 (d, 2 H), 8.14 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.22, 22.77, 26.09, 29.20, 29.33, 29.44, 31.91, 68.43, 114.39, 121.56, 122.13, 122.55, 123.08, 124.96, 126.34, 127.29, 127.84, 132.38, 135.12, 140.10, 150.45, 163.66 and 165.05. ESI mass m/z: Calculated for C<sub>27</sub>H<sub>30</sub>O<sub>3</sub>S, 434.59, found: 435.07. Elemental analysis: Calculated (%) for C<sub>27</sub>H<sub>30</sub>O<sub>3</sub>S: C, 74.62; H, 6.96; S, 7.38. Found (%): C, 74.54; H, 6.79; S, 7.29.

#### **Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl 4-(decyloxy)benzoate (ETDB)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.89 (t, 3 H), 1.34 (m, 13 H), 1.47 (m, 2 H), 1.82 (quin, 2 H), 4.04 (t, 2 H), 6.96 (m, 3 H), 7.10 (m, 1 H), 7.19 (d, 2 H), 7.26 (m, 1 H), 7.33 (m, 2 H), 7.51 (d, 2 H), 8.14 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.25, 22.80, 26.09, 29.21, 29.44, 29.48, 29.67, 32.01, 68.43, 114.39, 121.56, 122.13, 122.55, 123.09, 124.97, 126.34, 127.29, 127.85, 132.39, 135.12, 140.10, 150.46, 163.66 and 165.05. ESI mass m/z: Calculated for C<sub>29</sub>H<sub>34</sub>O<sub>3</sub>S, 462.64, found: 462.51. Elemental analysis: Calculated (%) for C<sub>29</sub>H<sub>34</sub>O<sub>3</sub>S: C, 75.29; H, 7.41; S, 6.93. Found (%): C, 75.36; H, 7.35; S, 6.98.

#### **Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl 4-(dodecyloxy)benzoate (ETDdB)**

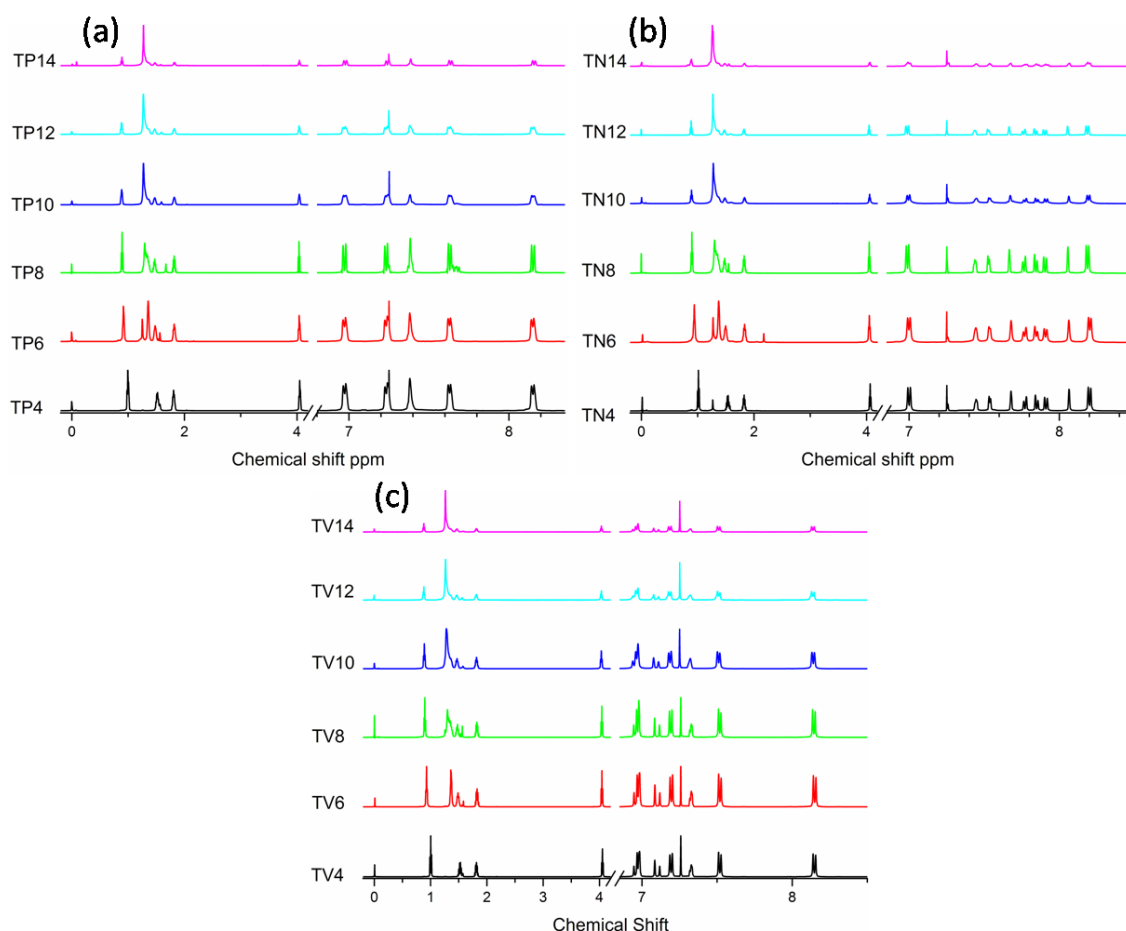
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, δ, ppm): 0.89 (t, 3 H), 1.46 (m, 2 H), 1.82 (quin, 2 H), 4.04 (t, 2 H), 6.96 (m, 3 H), 7.10 (d, 1 H), 7.19 (d, 2 H), 7.26 (m, 2 H), 7.33 (m, 2 H), 7.51 (d, 2 H), 8.14 (d, 2 H), <sup>13</sup>C NMR (CDCl<sub>3</sub> 500 MHz, δ, ppm): 14.25, 22.80, 26.09, 29.21, 29.44, 29.48, 29.67, 32.01, 68.43, 114.39, 121.56, 122.13, 122.55, 123.09, 124.97, 126.34, 127.29, 127.85, 132.39, 135.12, 140.10, 150.46, 163.66 and 165.05. ESI mass m/z: Calculated

for  $C_{31}H_{38}O_3S$ , 490.70, found: 491.61. Elemental analysis: Calculated (%) for  $C_{31}H_{38}O_3S$ : C, 75.88; H, 7.81; S, 6.53. Found (%): C, 75.81; H, 7.79; S, 6.47.

### Synthesis of (E)-4-(2-(thiophen-3-yl)vinyl)phenyl-4-(tetradecyloxy)benzoate (ETTdB)

$^1H$ NMR ( $CDCl_3$ , 500 MHz,  $\delta$ , ppm): 0.88 (t, 3 H), 1.27 (s, 20 H), 1.47 (quin, 2 H), 1.82 (quin, 2 H), 4.04 (t, 2 H), 6.96 (m, 3 H), 7.10 (m, 1 H), 7.19 (d, 1 H), 7.26 (d, 2 H), 7.33 (m, 2 H), 7.51 (d, 2 H), 8.14 (d, 2 H),  $^{13}C$  NMR ( $CDCl_3$  500 MHz,  $\delta$ , ppm): 14.25, 22.81, 26.09, 29.20, 29.47, 29.67, 29.70, 29.77, 32.04, 68.43, 114.39, 121.56, 122.13, 122.55, 123.09, 124.96, 126.34, 127.29, 127.85, 132.38, 135.12, 140.10, 150.46, 163.66 and 165.05. ESI mass m/z: Calculated for  $C_{33}H_{42}O_3S$ , 518.29, found: 518.21. Elemental analysis: Calculated (%) for  $C_{33}H_{42}O_3S$ : C, 76.41; H, 8.16; S, 6.18. Found (%): C, 76.47; H, 8.05; S, 6.21.

$^1H$  and  $^{13}C$  NMR spectra of ETAB monomers are presented in **Figure S5**.



**Figure S6.**  $^1H$  NMR spectra of (a) TPn, (b) TNn and (c) TVn polymers

**Table S1.** Gel Permeation Chromatography (GPC) data of TPn, TNn and TVn polymers.<sup>d)</sup>

Polymer	<sup>a)</sup> M <sub>w</sub>	<sup>b)</sup> M <sub>n</sub>	<sup>c)</sup> PDI
TP4	3860	1876	2.05
TP6	4120	2017	2.04
TP8	4221	1987	2.12
TP10	4234	2167	1.95
TP12	4837	2554	1.89
TP14	5170	2817	1.83
TN4	4368	2610	1.67
TN6	4742	2728	1.74
TN8	4916	2810	1.75
TN10	5287	3102	1.70
TN12	5362	3119	1.72
TN14	5761	3253	1.77
TV4	4384	2019	2.17
TV6	4578	2106	2.17
TV8	4897	2269	2.15
TV10	5217	2398	2.17
TV12	5684	2481	2.32
TV14	5871	2674	2.19

<sup>a)</sup>M<sub>w</sub>, Weight averaged molecular weight; <sup>b)</sup>M<sub>n</sub>, Number averaged molecular weight; <sup>c)</sup>PDI, Poly dispersity index; <sup>d)</sup> THF was used as mobile phase.

### General Procedure for synthesis of polymers

All polymers were synthesized by oxidative polymerization using FeCl<sub>3</sub> as oxidizing agent. In a representative synthesis, ca 500mg (0.92 mmol, 1.0 eq) of (6-(thiophen-3-yl)naphthalen-2-yl)methyl-4-(butoxy)benzoate (6TNBB) was dissolved in 15ml of dry chloroform, 747.1 mg (4.6 mmol, 4.0 eq) was suspended in dry chloroform in a 100ml round bottom flask under nitrogen atmosphere with constant stirring. The solution containing 6TNBB was added dropwise to the FeCl<sub>3</sub> suspension through 30 minutes. A constant flow of dry Nitrogen was maintained to drive out the HCl vapours formed. After addition, the flow of nitrogen was stopped and the reaction vessel was sealed and stirring was continued for 24 hours under nitrogen atmosphere. After the reaction time, the reaction mixture was filtered and evaporated

under vacuum. The residue obtained after evaporation of filtrate was washed with methanol to get polymer as precipitate. The polymers were continuously stirred with one drop ammonium hydroxide to remove excess iron.

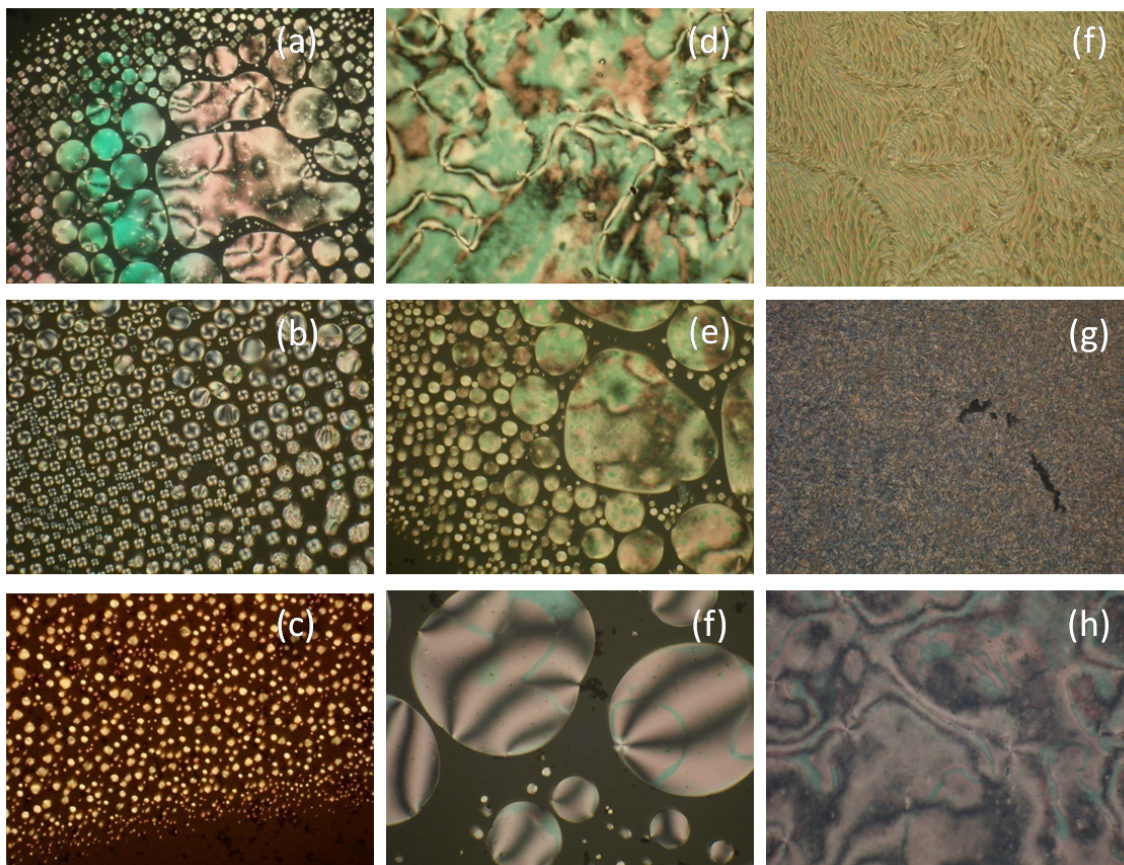
**Table S2** Spectral properties of polymers in solution and thin film state

Polymer	a) $\lambda_{\text{abs}}^{\text{sol}} (\epsilon)$	b) $\lambda_{\text{emi}}^{\text{sol}}$	c) $\lambda_{\text{exc}}^{\text{sol}}$	d) $\lambda_{\text{abs}}^{\text{TF}}$	e) $\lambda_{\text{emi}}^{\text{TF}}$	f) $\lambda_{\text{exc}}^{\text{TF}}$	g) $\Phi_{\text{PL}}^{\text{Sol}}$	h) $\Phi_{\text{PL}}^{\text{TF}}$
TP4	383(6.42x10 <sup>5</sup> )	556	383	406, 353, 271, 217	369, 446, 555	216	8.1	1.02
TP6	436(1.34x10 <sup>6</sup> )	571	436	406, 348, 266, 219	371, 449, 557	218	9.4	1.32
TP8	446(2.56x10 <sup>6</sup> )	575	446	408, 351, 275, 219	376, 443, 549	219	7.3	2.06
TP10	448(7.85x10 <sup>5</sup> )	571	448	405, 343, 265, 221	377, 445, 552	220	2.6	1.97
TP12	444(9.41x10 <sup>5</sup> )	560	444	401, 350, 267, 210	376, 449, 551	210	3.9	1.74
TP14	434(5.16x10 <sup>5</sup> )	573	434	404, 348, 264, 218	377, 445, 548	218	7.9	1.68
TN4	367(5.47x10 <sup>7</sup> )	485, 460, 429, 405	367	345, 269, 219	451, 563	219	6.2	1.05
TN6	360(8.75x10 <sup>7</sup> )	530, 454, 429, 407	360	338, 273, 211	451, 561	211	7.1	1.59
TN8	345(6.22x10 <sup>7</sup> )	517, 451, 430, 410	345	337, 269, 212	447, 551	212	4.3	4.36
TN10	340(3.89x10 <sup>7</sup> )	487, 440, 417, 396	340	333, 262, 210	446, 557	210	6.4	6.19
TN12	352(4.29x10 <sup>7</sup> )	486, 448, 428, 410	352	348, 261, 215	445, 553	215	5.2	7.25
TN14	357(5.68x10 <sup>7</sup> )	485, 453, 429, 408	357	335, 259, 210	443, 552	210	8.4	6.24
TV4	364(1.14X10 <sup>5</sup> ), 294(9.21X10 <sup>5</sup> )	428, 493	294	383, 356, 267, 215	442, 532, 560	215	1.3	5.6
TV6	363(2.87X10 <sup>4</sup> ), 294(3.18X10 <sup>5</sup> )	406, 429, 457	294	355, 270, 212	441, 556	212	3.1	4.7
TV8	395(6.12X10 <sup>4</sup> ), 294(7.19X10 <sup>5</sup> )	413, 428, 459	294	376, 348, 266, 212	448, 532, 556	212	1.1	6.1
TV10	364(2.34X10 <sup>4</sup> ), 295(9.52X10 <sup>5</sup> )	429, 495	295	351, 261, 211	445, 551	211	1.2	6.7
TV12	389(5.29X10 <sup>4</sup> ), 294(6.57X10 <sup>5</sup> )	409, 461	294	365, 266, 220	445, 561	220	1.9	9.1
TV14	371(8.75X10 <sup>3</sup> ), 295(7.42X10 <sup>5</sup> )	437, 508	295	358, 265, 214	446, 536, 560	214	12.0	12.4

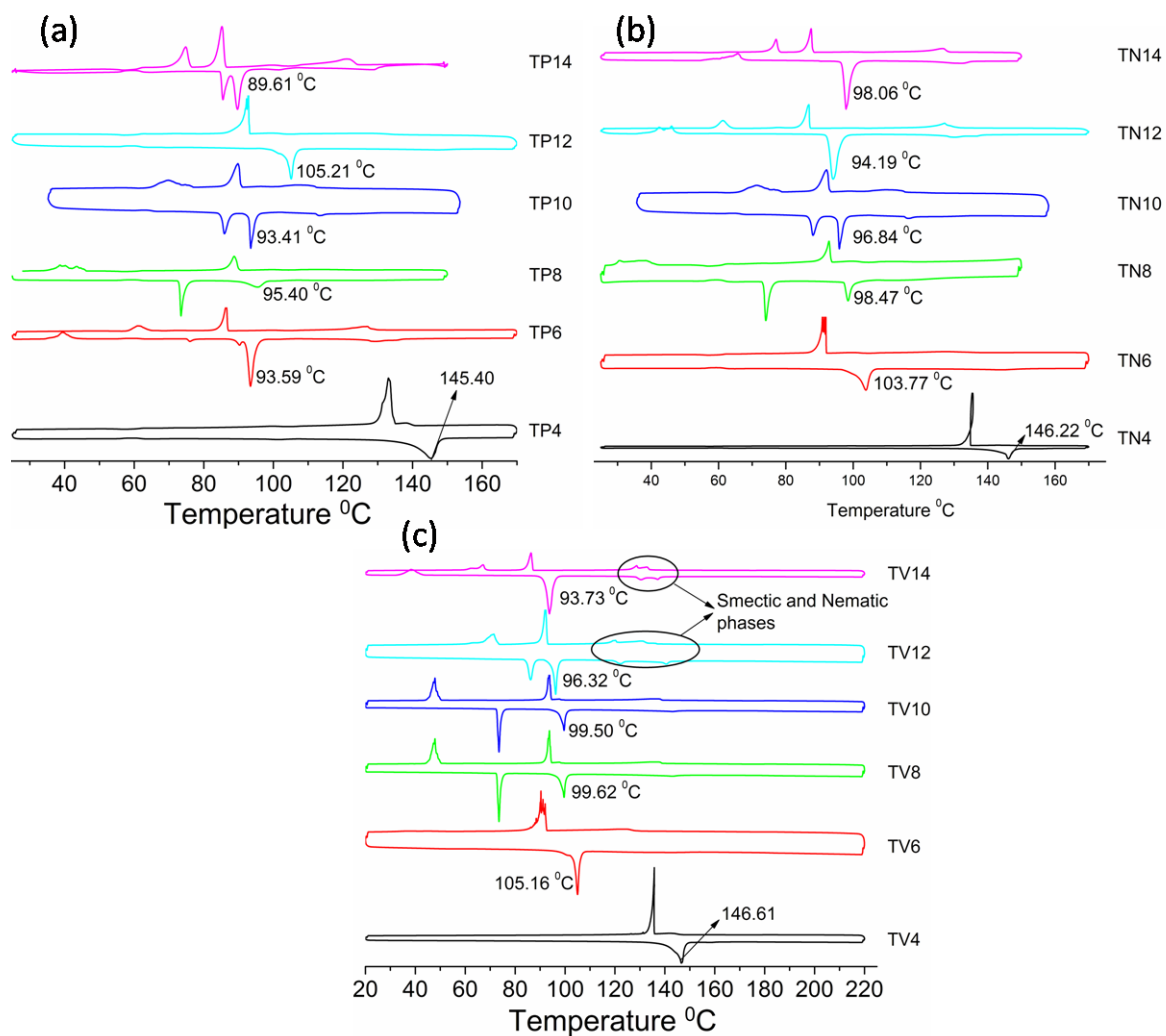
a)  $\lambda_{\text{abs}}^{\text{sol}}$ , Absorption maxima in THF solution in nm,  $\epsilon$ , extinction coefficient in dL g<sup>-1</sup> cm<sup>-1</sup>; b)  $\lambda_{\text{emi}}^{\text{sol}}$ , Emission maxima in THF solution in nm; c)  $\lambda_{\text{exc}}^{\text{sol}}$ , Excitation wavelength in solution emission; d)  $\lambda_{\text{abs}}^{\text{TF}}$ , Absorption maxima in spun thin film; e)  $\lambda_{\text{emi}}^{\text{TF}}$ , Emission maxima in spun thin film; f)  $\lambda_{\text{exc}}^{\text{TF}}$ , Excitation wavelength in thin film emission; g)  $\Phi_{\text{PL}}^{\text{Sol}}$ , Quantum yield in THF solution relative to quinine sulfate in %; h)  $\Phi_{\text{PL}}^{\text{TF}}$ , Absolute quantum yield in spun thin film in %.

The precipitated polymer was subjected to soxhlet extraction using methanol to obtain the pristine polymer as a reddish brown powder. The polymers were characterized by gel

permeation chromatography and  $^1\text{H}$  NMR spectroscopy. **Scheme S1** shows the synthesis of all polymers and monomers along with the name designations. The  $^1\text{H}$  NMR spectra of all polymers are presented in **Figure S6**. The polymers were characterized by gel permeation chromatography for molecular weight. The GPC data of polymer are presented in **Table S1**.



**Figure S7** Optical polarizing micrograph of (a) TP12 at 139 °C (b) TP10 at 122 °C (c) TP4 at 141.5 °C (d) TN12 at 130.2 °C (e) TN10 at 120 °C (f) TN4 at 151.3 °C (g) TV12 at 131.6 °C (h) TV10 at 135.4 °C and (i) TV4 at 145.8 °C.



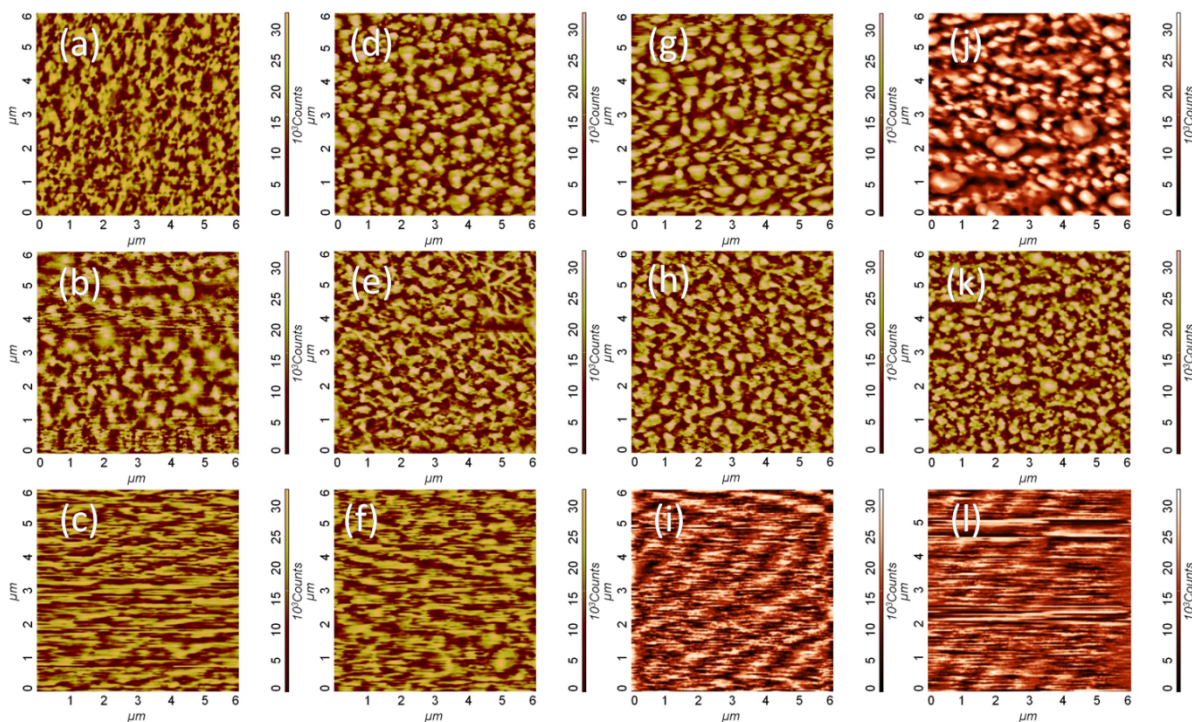
**Figure S8** Differential Scanning Calorimetry (DSC) traces of polymers.



**Table S3** Differential scanning calorimetry (DSC) data of polymers.<sup>g)</sup>

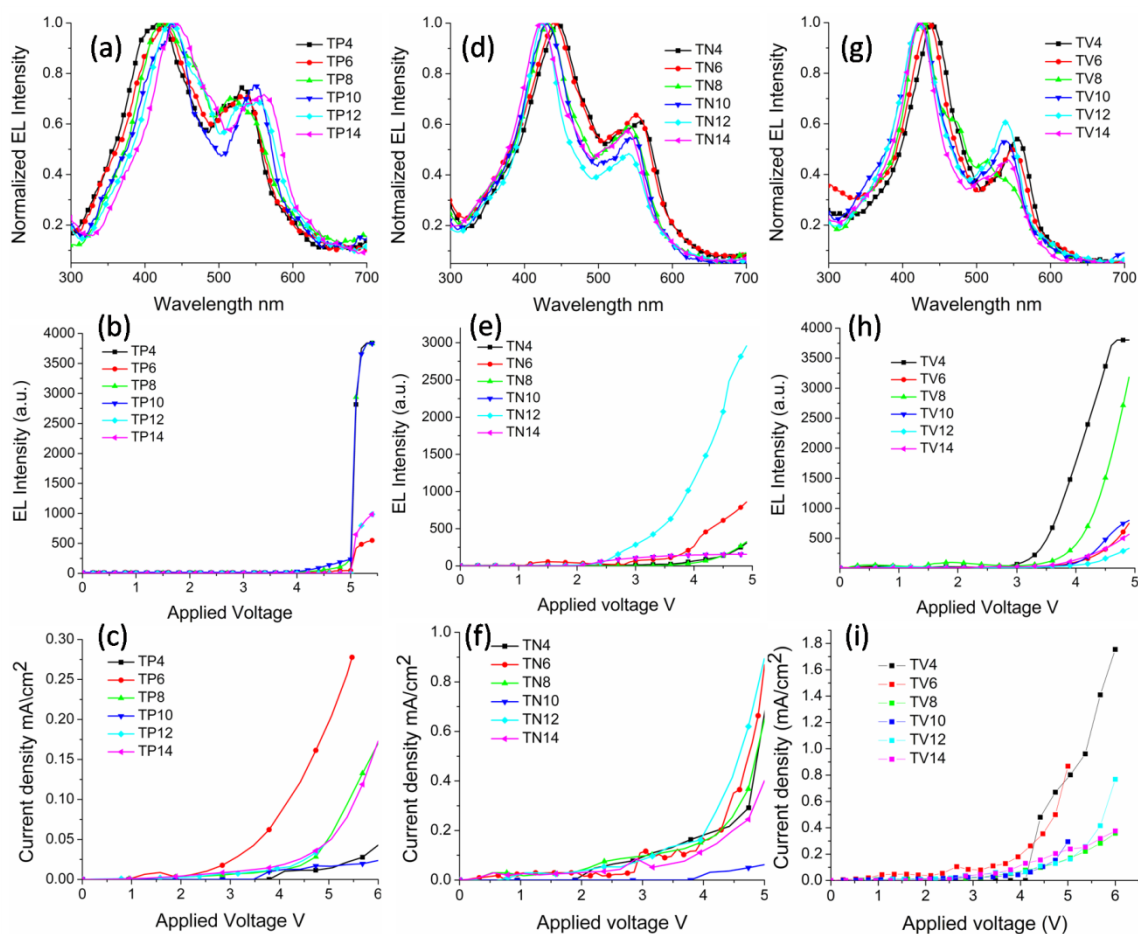
Polymer	Heating			Cooling		
	<sup>a)</sup> Mp	<sup>b)</sup> Sm-N	<sup>c)</sup> N-I	<sup>d)</sup> N-Cr	<sup>e)</sup> N-Sm	<sup>f)</sup> I - N
TP4	145.40	-	-	133.02	-	141.74
TP6	93.59	-	141.55	86.40	-	130.25
TP8	93.41	-	141.27	90.33	-	121.50
TP10	99.2	-	142.35	89.61	-	123.29
TP12	105.21	-	154.15	92.79	-	139.06
TP14	89.61	-	142.61	84.21	-	124.43
TN4	146.2	-	160.08	136.49	-	152.30
TN6	103.7	-	157.37	92.22	-	139.51
TN8	98.4	-	127.07	92.54	-	118.84
TN10	96.8	-	123.96	91.88	-	120.07
TN12	94.2	-	140.07	86.50	-	132.11
TN14	98.06	-	136.25	87.32	-	129.28
TV4	146.61	-	161.85	135.76	-	147.38
TV6	105.16	-	153.79	92.25	-	130.57
TV8	99.62	-	153.17	93.62	-	139.57
TV10	99.50	126.78	145.97	93.92	121.57	137.21
TV12	99.32	133.42	141.71	92.25	129.86	135.79
TV14	93.73	128.13	135.33	86.11	134.78	129.79

<sup>a)</sup>Mp, Melting point; <sup>b)</sup>Sm-N, smectic phase to nematic transition temperature; <sup>c)</sup>N-I, Nematic phase to isotropic phase transition temperature; <sup>d)</sup>N-Cr, temperature of crystallization on cooling; <sup>e)</sup>N-Sm, Nematic to smectic transition temperature; <sup>f)</sup>I - N, Temperature of reappearance of phase; <sup>g)</sup> All samples were heated at 10 °C/ minute and all temperatures are given in °C.

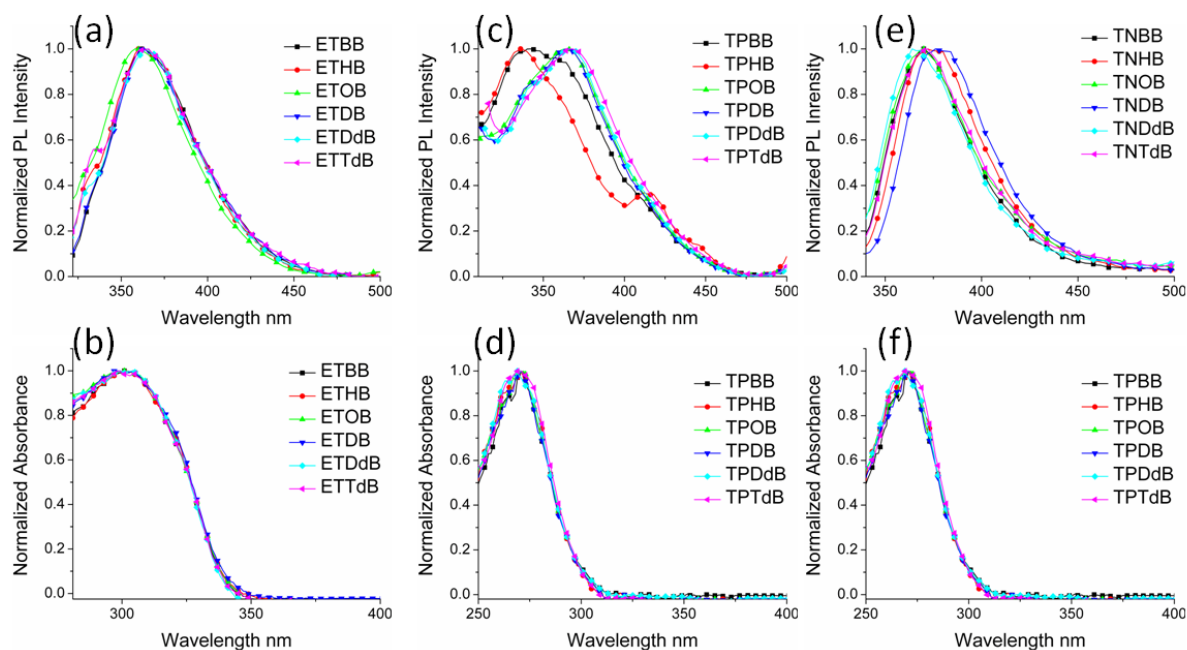


**Figure S9** AFM micrograph of (a) TP4, (b) TN4, (c) TV4, (d) TP6, (e) TN6, (f) TV6, (g) TP8, (h) TN8, (i) TV8, (j) TP10, (k) TN10 and (l) TV10 thin films spin coated on ITO substrate.

TP<sub>n</sub> polymers showed more spherical shaped aggregates and TN<sub>n</sub> polymers showed mostly lamellar structures in AFM micrograph. However, all TV<sub>n</sub> polymers showed directionally oriented thin film morphology which is in agreement with high charge carrier mobility. In case of TV8 and TV10 the 1D orientation of lamellae started to appear but, is somewhat disturbed. The disturbed ordering in TV8 , TV10 and TV14 are attributed to side chain effects.



**Figure S10** EL spectra of (a) TPn polymers at 6.5V (d) TNn polymers at 6.7 V (f) TVn polymers at 7V, Luminescence-Voltage (L-V) characteristics of (b) TPn polymers (e) TNn polymers (g) TVn polymers and Current density-Voltage characteristics (J-V) of (c) TPn polymers (f) TNn polymers and TVn polymers.



**FigureS11** Emission spectra of (a) ETAB monomers, (c) TPAB monomers, (e) TNAB monomers; Absorption spectra of (b) ETAB monomers, (d) TPAB monomers and (f) TNAB monomers in THF solution at concentration of  $4.95 \times 10^{-3} \text{ g dl}^{-1}$

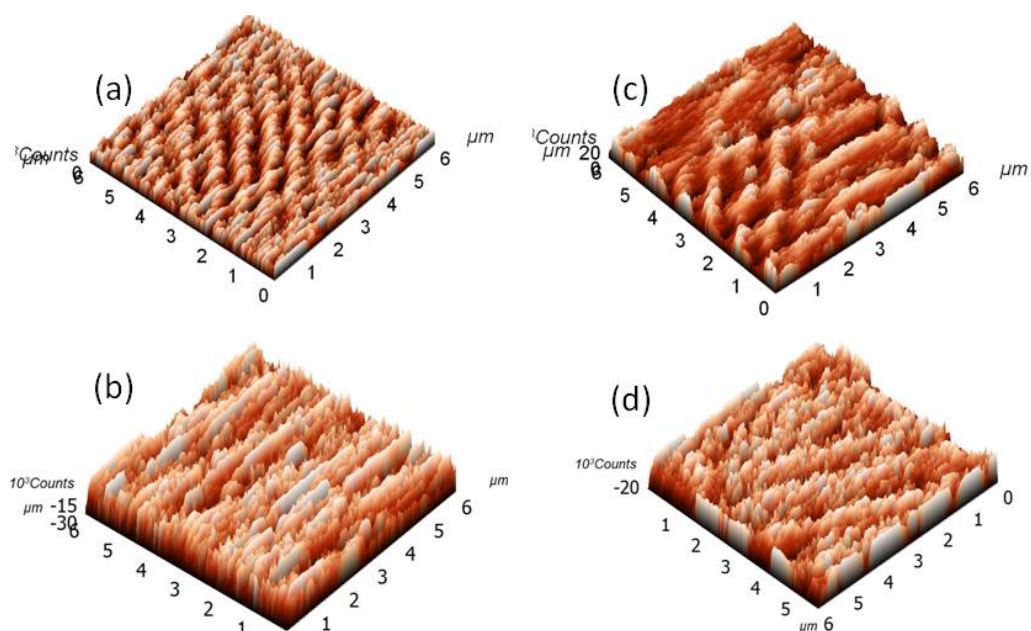
**Table S4** Spectral properties of monomers in solution state

Polymer	<sup>a)</sup> $\lambda_{\text{abs}}^{\text{sol}}$ ( $\epsilon$ )	<sup>b)</sup> $\lambda_{\text{emi}}^{\text{sol}}$
TPBB	271(0.95 $\times 10^3$ ),	341
TPHB	268(0.81 $\times 10^3$ )	335, 415
TPOB	269(0.82 $\times 10^3$ )	366
TPDH	268(0.79 $\times 10^3$ )	367
TPDdB	269(0.71 $\times 10^3$ )	367
TPTdB	270(0.53 $\times 10^3$ )	368
TNBB	262(1.36 $\times 10^3$ ), 293(0.55 $\times 10^3$ )	370
TNHB	266(1.18 $\times 10^3$ ), 295(0.47 $\times 10^3$ )	371
TNOB	264(0.99 $\times 10^3$ ), 298(0.36 $\times 10^3$ )	370
TNDB	264(1.18 $\times 10^3$ ), 302(0.39 $\times 10^3$ )	376
TNDdB	262(1.00 $\times 10^3$ ), 298(0.38 $\times 10^3$ )	368
TNTdB	261(1.00 $\times 10^3$ ), 294(0.38 $\times 10^3$ )	372
ETBB	300(0.85 $\times 10^3$ )	364
ETHB	302(0.81 $\times 10^3$ )	360
ETOB	299(0.28 $\times 10^3$ )	359
ETDB	299(0.83 $\times 10^3$ )	362
ETDdB	302(0.55 $\times 10^3$ )	364
ETTdB	299(0.51 $\times 10^3$ )	365

<sup>a)</sup> $\lambda_{\text{abs}}^{\text{sol}}$ , Absorption maxima in THF solution in nm,  $\epsilon$ , extinction coefficient in  $\text{dl g}^{-1} \text{ cm}^{-1}$ ;  
<sup>b)</sup> $\lambda_{\text{emi}}^{\text{sol}}$ , Emission maxima in THF solution in nm (excitation at respective  $\lambda_{\text{abs}}^{\text{sol}}$  values) .

It is clear from FigureS11 and Table S4 that the polymers have a longer absorption edge and longer emission wavelength indicating that the polymers have a longer conjugation length than monomers. However the difference in the absorption maxima of polymers and monomers in TN and TV series did not show very significant variation. The above fact can

be attributed to the several conformations of the polymer chains and entanglement of different polymer chains.



**Figure S12** 3D AFM micrograph of (a) TV12 (b) TV8 (c) TV14 and (d) TV10.