### Electronic Supplementary Information

## Bithiophene-Based Polybenzofulvene Derivatives with High Stacking and Hole Mobility

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### **MALDI-TOF mass spectrometry**



Figure ESI-1. MALDI-TOF mass spectrum obtained with second run sample MA-2 obtained by the dehydration of indenol 3a by Method A.



Figure ESI-2. MALDI-TOF mass spectrum obtained with neat poly-6-BT-BF3k.



**Figure ESI-3.** Optical absorption and emission spectra of sample **MA-1** (top), poly-6-BT-**BF3k** (bottom left), and poly-4'-BT-6-MO-**BF3k** (bottom right) in dichloromethane solutions (blue lines) and in the solid state (black lines).



poly-4'-HBT-6-MO-**BF3k** (middle, average:  $3.95 \times 10^{-5} \text{ cm}^2/\text{Vs}$ ), and PVK (top, average:  $4.84 \times 10^{-6} \text{ cm}^2/\text{Vs}$ ).

#### **Experimental details**

**Synthesis.** Melting points were determined in open capillaries in a Gallenkamp apparatus and are uncorrected. Merck silica gel 60 (230-400 mesh) was used for column chromatography. Merck TLC plates, silica gel 60  $F_{254}$  were used for TLC. NMR spectra were recorded with a Bruker DRX-400 AVANCE, Bruker DRX-500 AVANCE, or a Bruker DRX-600 AVANCE spectrometer in the indicated solvents (TMS as internal standard): the values of the chemical shifts are expressed in ppm and the coupling constants (*J*) in Hz. An Agilent 1100 LC/MSD operating with an electrospray source was used in mass spectrometry experiments.

### Ethyl 6-(2,2'-bithiophen-5-yl)-1-oxo-3-phenyl-1*H*-indene-2-carboxylate (2a).

In a microwave tube, a mixture of 2,2'-bithiophene-5-boronic acid pinacol ester (137 mg, 0.469 mmol) in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing  $Cs_2CO_3$  (450 mg, 1.38 mmol) was stirred at room temperature for 30 min. To the resulting mixture, Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub> (65 mg, 0.0926 mmol), PPh<sub>3</sub> (12 mg, 0.0458 mmol), and compound **1** (ref 1) (200 mg, 0.469 mmol) were added in sequence. The reaction mixture was exposed to microwave in a CEM Discover apparatus (1 cycle of 10 min, T = 80 °C, W = 150, P = 250 psi) and then concentrated under reduced pressure. The residue was partitioned between ethyl acetate and water. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate-dichloromethane (7:2:1) as the eluent afforded **2a** as a dark brown solid (95 mg, yield 46%, mp 116-118 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.17 (t, *J* = 7.1, 3H), 4.21 (q, *J* = 7.1, 2H), 7.01-7.05 (m, 1H), 7.13-7.24 (m, 4H), 7.32 (d, *J* = 3.8, 1H), 7.52 (s, 5H), 7.58 (d, *J* = 7.7, 1H), 7.84 (s, 1H). MS(ESI): *m*/*z* 465 (M + Na<sup>+</sup>).

Ethyl 6-(2,2'-bithiophen-5-yl)-1-hydroxy-1-methyl-3-phenyl-1*H*-indene-2-carboxylate (3a).

To a solution of 2a (50 mg, 0.113 mmol) in dichloromethane (5.0 mL) was added a 2M solution of Al(CH<sub>3</sub>)<sub>3</sub> in toluene (0.22 mL, 0.44 mmol). After stirring the reaction mixture at room temperature for 30 min (under a nitrogen atmosphere), it was diluted with ethyl acetate (20 mL) and the Al(CH<sub>3</sub>)<sub>3</sub> excess was cautiously destroyed with a 1M NaOH solution (2.0 mL). The resulting mixture was partitioned between water and ethyl acetate and the organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography with petroleum ether-ethyl acetate (8:2) as the eluent to afford indenol derivative **3a** (33 mg, yield 64%) as a brown glassy solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.06 (t, *J* = 7.1, 3H), 1.83 (s, 3H), 3.72 (br s, 1H), 4.06-4.23 (m, 2H), 7.03 (dd, *J* = 5.0, 3.7, 1H), 7.14-7.16 (m, 2H), 7.19-7.24 (m, 2H), 7.31 (d, *J* = 3.8, 1H), 7.37-7.48 (m, 5H), 7.52 (dd, *J* = 8.0, 1.6, 1H), 7.81 (d, *J* = 1.3, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 13.8, 26.0, 60.4, 81.8, 119.5, 123.8, 124.1, 124.6, 124.8, 125.9, 127.9, 128.5, 128.7, 133.5, 135.2, 135.8, 137.3, 137.4, 140.3, 142.6, 150.6, 151.6, 165.1.
MS(ESI): *m/z* 481 (M + Na<sup>+</sup>).

#### Dehydration of indenol 3a by Method A.

A mixture of indenol **3a** (70 mg, 0.153 mmol) in CDCl<sub>3</sub> (3.0 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 6.0 mg, 0.0325 mmol) was heated to reflux for 1 h. The reaction mixture was then cooled to room temperature and washed with a saturated solution of NaHCO<sub>3</sub>. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. A solution of the residue in chloroform (2.0 mL) was added dropwise into ethanol (70 mL) and the precipitate was collected by filtration and dried under reduced pressure to obtain sample **MA-1** (41 mg) as a yellow solid.

The same procedure was repeated with 80 mg (0.174 mmol) of indenol **3a** with 6.5 mg (0.0342 mmol) of PTSA in 3.4 mL of CDCl<sub>3</sub> to obtain sample **MA-2** (52 mg) as a yellow solid.



**Figure ESI-5.** <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of sample **MA-2**, [top trace, the structure of the Major monomeric unit (**Mmu**) is shown for comparative purposes] obtained by the dehydration of indenol derivative **3a** by **Method A** compared with that of obtained with precursor **3a**.

Dehydration of indenol 3a by Method B. Synthesis of Ethyl 6-(2,2'-bithiophen-5-yl)-1methylene-3-phenyl-1*H*-indene-2-carboxylate (6-BT-BF3k).

A mixture of indenol **3a** (50 mg, 0.109 mmol) in  $CDCl_3$  (100 mL) containing PTSA (10 mg, 0.0526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and washed with a NaHCO<sub>3</sub> saturated solution. The organic layer was dried over sodium sulfate,

concentrated to a volume of 25 mL and purified by flash chromatography with CDCl<sub>3</sub> as the eluent to obtain a solution of pure monomer 6-BT-**BF3k** in CDCl<sub>3</sub>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.06 (t, *J* = 7.1, 3H), 4.14 (q, *J* = 7.1, 2H), 6.46 (s, 1H), 6.66 (s, 1H), 7.01-7.05 (m, 1H), 7.17 (d, *J* = 3.8, 1H), 7.20-7.27 (m, 3H), 7.30 (d, *J* = 3.8, 1H), 7.41-7.49 (m, 5H), 7.52-7.56 (m, 1H), 7.92 (s, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 13.7, 60.2, 117.1, 117.6, 122.7, 123.7, 124.1, 124.5, 124.7, 125.5, 125.7, 127.9, 128.0, 128.4, 128.6, 134.1, 134.3, 137.1, 137.3, 137.7, 140.7, 143.0, 143.7, 152.6, 164.9.

MS(ESI): m/z 463 (M + Na<sup>+</sup>).

# Poly-[Ethyl 6-(2,2'-bithiophen-5-yl)-1-methylene-3-phenyl-1*H*-indene-2-carboxylate] (Poly-6-BT-BF3k).

A mixture of indenol **3a** (50 mg, 0.109 mmol) in CHCl<sub>3</sub> (100 mL) containing PTSA (10 mg, 0.0526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and washed with a saturated solution of NaHCO<sub>3</sub>. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with CHCl<sub>3</sub> as the eluent to obtain a solution of pure monomer 6-BT-**BF3k** in CHCl<sub>3</sub>. The solution of the monomer was concentrated under reduced pressure and then dissolved again in CHCl<sub>3</sub>. This procedure of dissolution/evaporation in CHCl<sub>3</sub> was repeated for 5 times, while the polymerization process was followed by TLC analysis of the residues obtained after solvent evaporations. A solution of the final residue in chloroform (5.0 mL) was added dropwise into ethanol (20 mL) and the precipitate was collected by filtration and dried under reduced pressure to obtain poly-6-BT-**BF3k** (32 mg, yield 67%) as a yellow solid.



**Figure ESI-6.** Comparison of the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of monomer 6-BT-**BF3k** with that of the corresponding polymer poly-6-BT-**BF3k**.



**Figure ESI-7.** Comparison of the <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of monomer 6-BT-**BF3k** with that of the corresponding polymer poly-6-BT-**BF3k**.

#### Ethyl 6-(5'-hexyl-2,2'-bithiophen-5-yl)-1-oxo-3-phenyl-1*H*-indene-2-carboxylate (2b).

In a microwave tube, a mixture of 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester (177 mg, 0.470 mmol) in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing  $Cs_2CO_3$  (450 mg, 1.38 mmol) was stirred at room temperature for 30 min. To the resulting mixture, Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub> (65 mg, 0.0926 mmol), PPh<sub>3</sub> (12 mg, 0.0458 mmol), and compound **1** (ref 1) (200 mg, 0.469 mmol) were added in sequence. The reaction mixture was exposed to microwave irradiation in a CEM Discover apparatus (1 cycle of 10 min, T = 80 °C, W = 150, P = 250 psi) and then concentrated under reduced pressure. The residue was partitioned between ethyl acetate and water and the organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was

purified by flash chromatography with dichloromethane as the eluent to obtain **2b** as a dark brown solid (95 mg, yield 38%, mp 194-195 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.89 (t, *J* = 6.5, 3H), 1.16 (t, *J* = 7.1, 3H), 1.28-1.43 (m, 6H), 1.63-1.73 (m, 2H), 2.79 (t, *J* = 7.6, 2H), 4.20 (q, *J* = 7.1, 2H), 6.69 (d, *J* = 3.5, 1H), 7.02 (d, *J* = 3.5, 1H), 7.07 (d, *J* = 3.8, 1H), 7.17 (d, *J* = 7.7, 1H), 7.30 (d, *J* = 3.8, 1H), 7.52 (s, 5H), 7.57 (dd, *J* = 7.8, 1.6, 1H), 7.83 (d, *J* = 1.1, 1H). MS(ESI): *m*/*z* 549 (M + Na<sup>+</sup>).

## Ethyl 6-(5'-hexyl-2,2'-bithiophen-5-yl)-1-hydroxy-1-methyl-3-phenyl-1*H*-indene-2-carboxylate (3b).

To a solution of **2b** (50 mg, 0.095 mmol) in dichloromethane (5.0 mL) was added a 2M solution of  $Al(CH_3)_3$  in toluene (0.19 mL, 0.38 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min, and then diluted with ethyl acetate (20 mL). The  $Al(CH_3)_3$  excess was cautiously destroyed with a 1M NaOH solution (2.0 mL) and the resulting mixture was partitioned between water and ethyl acetate. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography with petroleum ether-ethyl acetate (8:2) as the eluent to obtain indenol **3b** (37 mg, yield 72%) as a brown glassy solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.89 (t, J = 6.6, 3H), 1.06 (t, J = 7.1, 3H), 1.27-1.45 (m, 6H), 1.63-1.73 (m, 2H), 1.82 (s, 3H), 2.79 (t, J = 7.6, 2H), 3.70 (br s, 1H), 4.04-4.22 (m, 2H), 6.69 (d, J = 3.5, 1H), 7.01 (d, J = 3.5, 1H), 7.07 (d, J = 3.8, 1H), 7.14 (d, J = 8.0, 1H), 7.28 (d, J = 3.8, 1H), 7.37-7.47 (m, 5H), 7.51 (d, J = 8.0, 1H), 7.80 (s, 1H). MS(ESI): m/z 565 (M + Na<sup>+</sup>).

Ethyl 6-(5'-hexyl-2,2'-bithiophen-5-yl)-1-methylene-3-phenyl-1*H*-indene-2-carboxylate (6-HBT-BF3k).

A mixture of indenol **3b** (10 mg, 0.0184 mmol) in  $\text{CDCl}_3$  (10 mL) containing PTSA (3.0 mg, 0.0158 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and purified by flash chromatography with  $\text{CDCl}_3$  as the eluent to obtain a solution of pure monomer 6-HBT-**BF3k** in  $\text{CDCl}_3$ .

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 0.89 (t, J = 7.0, 3H), 1.06 (t, J = 7.1, 3H), 1.29-1.42 (m, 6H), 1.64-1.72 (m, 2H), 2.79 (t, J = 7.6, 2H), 4.14 (q, J = 7.1, 2H), 6.46 (s, 1H), 6.66 (s, 1H), 6.69 (d, J = 3.5, 1H), 7.02 (d, J = 3.5, 1H), 7.08 (d, J = 3.8, 1H), 7.22 (d, J = 8.0, 1H), 7.28 (d, J = 3.8, 1H), 7.40-7.48 (m, 5H), 7.52 (dd, J = 8.0, 1.6, 1H), 7.90 (d, J = 1.3, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.8, 14.1, 22.6, 28.7, 30.2, 31.6, 60.2, 117.0, 117.6, 122.7, 123.4, 123.9, 124.1, 124.9, 125.4, 125.5, 128.0, 128.3, 128.6, 134.2, 134.3, 134.6, 137.7, 140.5, 142.2, 143.7, 145.7, 152.8, 164.9.

MS(ESI): m/z 547 (M + Na<sup>+</sup>).

## Poly-[Ethyl 6-(5'-hexyl-2,2'-bithiophen-5-yl)-1-methylene-3-phenyl-1*H*-indene-2-carboxylate] (Poly-6-HBT-BF3k).

A mixture of indenol **3b** (330 mg, 0.608 mmol) in CHCl<sub>3</sub> (stabilized with amylene, 600 mL) containing PTSA (150 mg, 0.789 mmol) was refluxed for 30 min. The reaction mixture was then cooled to room temperature and washed with a NaHCO<sub>3</sub> saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with CHCl<sub>3</sub> as the eluent to obtain a solution of pure monomer 6-HBT-**BF3k** in CHCl<sub>3</sub>. The solution of the monomer was concentrated under reduced pressure and then dissolved again in CHCl<sub>3</sub>. This procedure of dissolution/evaporation in CHCl<sub>3</sub> was repeated for 5 times, while the polymerization process was followed by TLC analysis of the residues obtained after solvent evaporations. A solution of the final residue in chloroform (10 mL) was added dropwise to ethanol (40 mL) and the precipitate was collected by filtration and dried under reduced pressure to obtain poly-6-HBT-**BF3k** (210 mg, yield 66%) as a yellow solid.



**Figure ESI-8.** Comparison of the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of monomer 6-HBT-**BF3k** with that of the corresponding polymer poly-6-HBT-**BF3k**.



**Figure ESI-9.** Comparison of the <sup>13</sup>C NMR spectrum of monomer 6-HBT-**BF3k** with that of the corresponding polymer poly-6-HBT-**BF3k**.

### Ethyl 3-[4-(2,2'-bithiophen-5-yl)phenyl]-6-methoxy-1-oxo-1*H*-indene-2-carboxylate (7a).

In a microwave tube, a mixture of 2,2'-bithiophene-5-boronic acid pinacol ester (137 mg, 0.469 mmol) in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing  $Cs_2CO_3$  (450 mg, 1.38 mmol) was stirred at room temperature for 30 min. To the resulting mixture, Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub> (65 mg, 0.0926 mmol), PPh<sub>3</sub> (12 mg, 0.0458 mmol), and compound **6** (ref 1) (180 mg, 0.465 mmol) were added in sequence. The reaction mixture was exposed to microwave in a CEM Discover apparatus (1 cycle of 10 min, T = 80 °C, W = 150, P = 250 psi) and then concentrated under reduced pressure. The residue was partitioned between ethyl acetate and water. The organic layer was dried with over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate (8:2) as the eluent afforded **7a** (97 mg, yield

44%) as a red solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (mp 192-193 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.21 (t, *J* = 7.1, 3H), 3.87 (s, 3H), 4.22 (q, *J* = 7.1, 2H), 6.84 (dd, *J* = 8.1, 2.5, 1H), 7.05 (dd, *J* = 5.0, 3.6, 1H), 7.14 (d, *J* = 8.1, 1H), 7.17-7.20 (m, 2H), 7.22-7.26 (m, 2H), 7.34 (d, *J* = 3.8, 1H), 7.56 (d, *J* = 8.3, 2H), 7.72 (d, *J* = 8.3, 2H). MS(ESI): *m/z* 495 (M + Na<sup>+</sup>).

## Ethyl 3-[4-(2,2'-bithiophen-5-yl)phenyl]-1-hydroxy-6-methoxy-1-methyl-1*H*-indene-2carboxylate (8a).

To a stirred solution of 7a (50 mg, 0.106 mmol) in 5.0 mL of dichloromethane was added a 2M solution of Al(CH<sub>3</sub>)<sub>3</sub> in toluene (0.21 mL, 0.42 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min, and then diluted with ethyl acetate (20 mL). The Al(CH<sub>3</sub>)<sub>3</sub> excess was cautiously destroyed with 2.0 mL of a 1M NaOH solution and the resulting mixture was partitioned between water and ethyl acetate. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography with petroleum ether-ethyl acetate-dichloromethane (8:2) as the eluent to obtain indenol derivative **8a** (23 mg, yield 44%) as a brown glassy solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.11 (t, J = 7.1, 3H), 1.77 (s, 3H), 3.70 (br s, 1H), 3.87 (s, 3H), 4.08-4.24 (m, 2H), 6.82 (dd, J = 8.4, 2.4, 1H), 7.04 (dd, J = 5.1, 3.7, 1H), 7.11 (d, J = 8.4, 1H), 7.15 (d, J = 2.3, 1H), 7.17 (d, J = 3.8, 1H), 7.20-7.25 (m, 2H), 7.30 (d, J = 3.8, 1H), 7.42 (d, J = 8.4, 2H), 7.67 (d, J = 8.3, 2H).

MS(ESI): m/z 511 (M + Na<sup>+</sup>).

Ethyl 3-[4-(2,2'-bithiophen-5-yl)phenyl]-6-methoxy-1-methylene-1*H*-indene-2-carboxylate (4'-BT-6-MO-BF3k).

A mixture of **8a** (6.5 mg, 0.0133 mmol) in CDCl<sub>3</sub> (13 mL) containing PTSA (3.0 mg, 0.0158 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and washed with a saturated solution of NaHCO<sub>3</sub>. The organic layer was dried over sodium sulfate, concentrated to a volume of ca. 2 mL and purified by flash chromatography with CDCl<sub>3</sub> as the eluent to obtain a solution of pure monomer 4'-BT-6-MO-**BF3k** in CDCl<sub>3</sub>.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 1.11 (t, *J* = 7.1, 3H), 3.88 (s, 3H), 4.16 (q, *J* = 7.1, 2H), 6.35 (s, 1H), 6.62 (s, 1H), 6.84 (dd, *J* = 8.4, 2.1, 1H), 7.04 (dd, *J* = 5.0, 3.7, 1H), 7.15-7.19 (m, 2H), 7.20-7.24 (m, 2H), 7.26 (d, *J* = 2.3, 1H), 7.30 (d, *J* = 3.8, 1H), 7.42-7.46 (m, 2H), 7.66-7.69 (m, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.9, 55.7, 60.1, 105.9, 114.0, 116.9, 123.2, 123.5, 123.7, 124.0, 124.5, 124.7, 125.0, 127.9, 129.4, 133.9, 134.0, 134.3, 137.0, 137.3, 139.1, 142.7, 143.8, 153.0, 160.8, 164.9.

MS(ESI): *m*/*z* 493 (M + Na<sup>+</sup>).

### Poly-[Ethyl 3-[4-(2,2'-bithiophen-5-yl)phenyl]-6-methoxy-1-methylene-1*H*-indene-2carboxylate] (Poly-4'-BT-6-MO-BF3k).

A mixture of **8a** (175 mg, 0.358 mmol) in CHCl<sub>3</sub> (stabilized with amylene, 350 mL) containing PTSA, (100 mg, 0.526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and washed with a saturated solution of NaHCO<sub>3</sub>. The organic layer was dried over sodium sulfate, concentrated to a volume of ca. 25 mL and purified by flash chromatography with CHCl<sub>3</sub> as the eluent to obtain a solution of pure monomer 4'-BT-6-MO-**BF3k** in CHCl<sub>3</sub>. The solution of the monomer was concentrated under reduced pressure and then dissolved again in CHCl<sub>3</sub>. This procedure of dissolution/evaporation in CHCl<sub>3</sub> was repeated for 5 times while the polymerization process was followed by TLC analysis of the residues obtained after solvent evaporations. A solution of the final residue in chloroform (5.0 mL) was added dropwise to ethanol (20 mL) and the precipitate was collected by filtration and dried under reduced pressure to obtain poly-4'-BT-6-MO-**BF3k** (140 mg, yield 83%) as a yellow solid.



**Figure ESI-10.** Comparison of the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of monomer 4'-BT-6-MO-**BF3k** with that of the corresponding polymer poly-4'-BT-6-MO-**BF3k**.



**Figure ESI-11.** Comparison of the <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of monomer 4'-BT-6-MO-**BF3k** with that of the corresponding polymer poly-4'-BT-6-MO-**BF3k**.

# Ethyl 3-[4-(5'-hexyl-2,2'-bithiophen-5-yl)phenyl]-6-methoxy-1-oxo-1*H*-indene-2-carboxylate (7b).

In a microwave tube, a mixture of 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester (177 mg, 0.470 mmol) in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing  $Cs_2CO_3$  (450 mg, 1.38 mmol) was stirred at room temperature for 30 min. To the resulting mixture, Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub> (65 mg, 0.0926 mmol), PPh<sub>3</sub> (12 mg, 0.458 mmol), and compound **6** (ref 1) (180 mg, 0.465 mmol) were added in sequence. The reaction mixture was exposed to microwave in a CEM Discover apparatus (1 cycle of 10 min, T = 80 °C, W = 150, P = 250 psi) and then concentrated under reduced pressure. The residue was partitioned between ethyl acetate and water. The organic layer was dried with over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash

chromatography with petroleum ether-ethyl acetate (9:1) as the eluent gave **7b** as a red solid (120 mg, yield 46%, mp 145-148 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.89 (t, J = 6.9, 3H), 1.20 (t, J = 7.1, 3H), 1.28-1.43 (m, 6H), 1.63-1.74 (m, 2H), 2.80 (t, J = 7.6, 2H), 3.85 (s, 3H), 4.22 (q, J = 7.1, 2H), 6.70 (d, J = 3.5, 1H), 6.83 (dd, J = 8.1, 2.4, 1H), 7.03 (d, J = 3.5, 1H), 7.09 (d, J = 3.8, 1H), 7.13 (d, J = 8.1, 1H), 7.17 (d, J =2.4, 1H), 7.30 (d, J = 3.8, 1H), 7.55 (d, J = 8.3, 2H), 7.69 (d, J = 8.3, 2H). MS(ESI): m/z 579 (M + Na<sup>+</sup>).

### Ethyl 3-[4-(5'-hexyl-2,2'-bithiophen-5-yl)phenyl]-1-hydroxy-6-methoxy-1-methyl-1*H*-indene-2-carboxylate (8b).

To a stirred solution of **7b** (50 mg, 0.0898 mmol) in dichloromethane (5.0 mL) was added a 2M solution of Al(CH<sub>3</sub>)<sub>3</sub> in toluene (0.20 mL, 0.40 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min, and then diluted with ethyl acetate (20 mL). The Al(CH<sub>3</sub>)<sub>3</sub> excess was cautiously destroyed with a 1M NaOH solution (2.0 mL) and the resulting mixture was partitioned between water and ethyl acetate (20 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure and the residue was purified by flash chromatography with petroleum ether-ethyl acetate (8:2) as the eluent to give indenol derivative **8b** (37 mg, yield 72%) as a yellow glassy solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.89 (t, J = 6.9, 3H), 1.11 (t, J = 7.1, 3H), 1.29-1.44 (m, 6H), 1.63-1.73 (m, 2H), 1.77 (s, 3H), 2.80 (t, J = 7.6, 2H), 3.71 (s, 1H), 3.87 (s, 3H), 4.06-4.25 (m, 2H), 6.70 (d, J = 3.6, 1H), 6.82 (dd, J = 8.4, 2.4, 1H), 7.02 (d, J = 3.5, 1H), 7.09 (d, J = 3.8, 1H), 7.11 (d, J = 8.4, 1H), 7.15 (d, J = 2.4, 1H), 7.27 (d, J = 3.8, 1H), 7.40 (d, J = 8.2, 2H), 7.66 (d, J = 8.2, 2H). MS(ESI): m/z 595 (M + Na<sup>+</sup>).

Ethyl 3-[4-(5'-hexyl-2,2'-bithiophen-5-yl)phenyl]-6-methoxy-1-methylene-1*H*-indene-2carboxylate (4'-HBT-6-MO-BF3k). A mixture of **8b** (10 mg, 0.0175 mmol) in CDCl<sub>3</sub> (10 mL) containing PTSA (3.0 mg, 0.0158 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and washed with a NaHCO<sub>3</sub> saturated solution. The organic layer was dried over sodium sulfate and purified by flash chromatography with CDCl<sub>3</sub> as the eluent to obtain a solution of pure monomer 4'-HBT-6-MO-**BF3k** in CDCl<sub>3</sub>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 0.89 (t, J = 7.0, 3H), 1.11 (t, J = 7.1, 3H), 1.29-1.34 (m, 4H), 1.35-1.42 (m, 2H), 1.65-1.71 (m, 2H), 2.80 (t, J = 7.6, 2H), 3.88 (s, 3H), 4.15 (q, J = 7.1, 2H), 6.35 (s, 1H), 6.61 (s, 1H), 6.69 (d, J = 3.5, 1H), 6.84 (dd, J = 8.4, 2.3, 1H), 7.02 (d, J = 3.5, 1H), 7.09 (d, J = 3.8, 1H), 7.17 (d, J = 8.4, 1H), 7.26 (d, J = 2.4, 1H), 7.27 (d, J = 3.8, 1H), 7.41-7.45 (m, 2H), 7.65-7.68 (m, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.9, 14.1, 22.6, 28.8, 30.2, 31.6, 55.7, 60.1, 105.9, 114.0, 116.9, 123.2, 123.4, 123.9, 124.0, 124.9, 129.4, 133.7, 134.1, 134.3, 134.7, 137.6, 139.1, 142.0, 143.8, 145.7, 153.0, 160.8, 164.9.

MS(ESI): m/z 555 (M + H<sup>+</sup>).

### Poly-[Ethyl 3-[4-(5'-hexyl-2,2'-bithiophen-5-yl)phenyl]-6-methoxy-1-methylene-1*H*-indene-2carboxylate] (Poly-4'-HBT-6-MO-BF3k).

A mixture of **8b** (250 mg, 0.436 mmol) in CHCl<sub>3</sub> (stabilized with amylene, 360 mL) containing PTSA (100 mg, 0.526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and washed with a NaHCO<sub>3</sub> saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with CHCl<sub>3</sub> as the eluent to obtain a solution of pure monomer 4'-HBT-6-MO-**BF3k** in CHCl<sub>3</sub>. The solution of the monomer was concentrated under reduced pressure and then dissolved again in CHCl<sub>3</sub>. This procedure of dissolution/evaporation in CHCl<sub>3</sub> was repeated for 5 times while the polymerization process was followed by TLC analysis of the residues obtained after solvent evaporations. A solution of the final residue in chloroform (10 mL) was added dropwise to ethanol

(40 mL) and the precipitate was collected by filtration and dried under reduced pressure to obtain poly-4'-HBT-6-MO-**BF3k** (180 mg, yield 74%) as a yellow solid.



**Figure ESI-12.** Comparison of the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of monomer 4'-HBT-6-MO-**BF3k** with that of the corresponding polymer poly-4'-HBT-6-MO-**BF3k**.



**Figure ESI-13.** Comparison of the <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of monomer 4'-HBT-6-MO-**BF3k** with that of the corresponding polymer poly-4'-HBT-6-MO-**BF3k**.

### References

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