## Electronic Supplementary Information

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

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Content: MALDI-TOF spectra of sample MA-2 and of poly-6-BT-BF3k (page 2) Optical absorption and emission spectra of the polymers (page 3) $\mathrm{J} / \mathrm{V}$ characteristics of the polymers (page 4)

Experimental details for the preparation and the characterization of the newly-synthesized polybenzofulvene derivatives

## 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).







Figure ESI-4. J/V characteristics of poly-6-HBT-BF3k (bottom, average: $5.81 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{Vs}$ ),
poly-4'-HBT-6-MO-BF3k (middle, average: $3.95 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{Vs}$ ), and PVK (top, average: $4.84 \times 10^{-}$ $\left.{ }^{6} \mathrm{~cm}^{2} / \mathrm{Vs}\right)$.

## 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 $60 \mathrm{~F}_{254}$ 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-1H-indene-2-carboxylate (2a).

In a microwave tube, a mixture of $2,2^{\prime}$-bithiophene-5-boronic acid pinacol ester ( $137 \mathrm{mg}, 0.469$ $\mathrm{mmol})$ in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing $\mathrm{Cs}_{2} \mathrm{CO}_{3}(450 \mathrm{mg}, 1.38 \mathrm{mmol})$ was stirred at room temperature for 30 min . To the resulting mixture, $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}_{2}(65 \mathrm{mg}, 0.0926$ $\mathrm{mmol}), \mathrm{PPh}_{3}(12 \mathrm{mg}, 0.0458 \mathrm{mmol})$, and compound 1 (ref 1) ( $200 \mathrm{mg}, 0.469 \mathrm{mmol}$ ) were added in sequence. The reaction mixture was exposed to microwave in a CEM Discover apparatus (1 cycle of $10 \mathrm{~min}, \mathrm{~T}=80^{\circ} \mathrm{C}, \mathrm{W}=150, \mathrm{P}=250 \mathrm{psi}$ ) 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 $116-118^{\circ} \mathrm{C}$ ).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $1.17(\mathrm{t}, J=7.1,3 \mathrm{H}), 4.21(\mathrm{q}, J=7.1,2 \mathrm{H}), 7.01-7.05(\mathrm{~m}, 1 \mathrm{H}), 7.13-$ $7.24(\mathrm{~m}, 4 \mathrm{H}), 7.32(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.52(\mathrm{~s}, 5 \mathrm{H}), 7.58(\mathrm{~d}, J=7.7,1 \mathrm{H}), 7.84(\mathrm{~s}, 1 \mathrm{H})$.

MS(ESI): $m / z 465\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

To a solution of $\mathbf{2 a}(50 \mathrm{mg}, 0.113 \mathrm{mmol})$ in dichloromethane $(5.0 \mathrm{~mL})$ was added a 2 M solution of $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ in toluene $(0.22 \mathrm{~mL}, 0.44 \mathrm{mmol})$. 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 $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ excess was cautiously destroyed with a 1 M NaOH solution $(2.0 \mathrm{~mL})$. 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 $3 \mathrm{a}(33 \mathrm{mg}$, yield $64 \%$ ) as a brown glassy solid.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $1.06(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.83(\mathrm{~s}, 3 \mathrm{H}), 3.72(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 4.06-4.23(\mathrm{~m}, 2 \mathrm{H})$, $7.03(\mathrm{dd}, J=5.0,3.7,1 \mathrm{H}), 7.14-7.16(\mathrm{~m}, 2 \mathrm{H}), 7.19-7.24(\mathrm{~m}, 2 \mathrm{H}), 7.31(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.37-7.48$ (m, 5H), $7.52(\mathrm{dd}, J=8.0,1.6,1 \mathrm{H}), 7.81(\mathrm{~d}, J=1.3,1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): 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): $m / z 481\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

## Dehydration of indenol 3a by Method A.

A mixture of indenol 3a ( $70 \mathrm{mg}, 0.153 \mathrm{mmol}$ ) in $\mathrm{CDCl}_{3}(3.0 \mathrm{~mL})$ containing $p$-toluenesulfonic acid monohydrate (PTSA, $6.0 \mathrm{mg}, 0.0325 \mathrm{mmol}$ ) was heated to reflux for 1 h . The reaction mixture was then cooled to room temperature and washed with a saturated solution of $\mathrm{NaHCO}_{3}$. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. A solution of the residue in chloroform $(2.0 \mathrm{~mL})$ was added dropwise into ethanol $(70 \mathrm{~mL})$ 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 $80 \mathrm{mg}(0.174 \mathrm{mmol})$ of indenol 3a with $6.5 \mathrm{mg}(0.0342$ $\mathrm{mmol})$ of PTSA in 3.4 mL of $\mathrm{CDCl}_{3}$ to obtain sample MA-2 ( 52 mg ) as a yellow solid.


Figure ESI-5. ${ }^{13} \mathrm{C}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ of sample MA-2, [top trace, the structure of the Major monomeric unit ( $\mathbf{M m u}$ ) 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)-1-methylene-3-phenyl-1H-indene-2-carboxylate (6-BT-BF3k).

A mixture of indenol 3a $(50 \mathrm{mg}, 0.109 \mathrm{mmol})$ in $\mathrm{CDCl}_{3}(100 \mathrm{~mL})$ containing PTSA $(10 \mathrm{mg}, 0.0526$ mmol ) was heated to reflux for 30 min . The reaction mixture was then cooled to room temperature and washed with a $\mathrm{NaHCO}_{3}$ saturated solution. The organic layer was dried over sodium sulfate,
concentrated to a volume of 25 mL and purified by flash chromatography with $\mathrm{CDCl}_{3}$ as the eluent to obtain a solution of pure monomer 6-BT-BF3k in $\mathrm{CDCl}_{3}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $1.06(\mathrm{t}, J=7.1,3 \mathrm{H}), 4.14(\mathrm{q}, J=7.1,2 \mathrm{H}), 6.46(\mathrm{~s}, 1 \mathrm{H}), 6.66(\mathrm{~s}, 1 \mathrm{H})$, 7.01-7.05 (m, 1H), $7.17(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.20-7.27(\mathrm{~m}, 3 \mathrm{H}), 7.30(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.41-7.49(\mathrm{~m}$, $5 \mathrm{H}), 7.52-7.56(\mathrm{~m}, 1 \mathrm{H}), 7.92(\mathrm{~s}, 1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): 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): $m / z 463\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

A mixture of indenol 3a $(50 \mathrm{mg}, 0.109 \mathrm{mmol})$ in $\mathrm{CHCl}_{3}(100 \mathrm{~mL})$ containing PTSA $(10 \mathrm{mg}, 0.0526$ mmol ) was heated to reflux for 30 min . The reaction mixture was then cooled to room temperature and washed with a saturated solution of $\mathrm{NaHCO}_{3}$. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with $\mathrm{CHCl}_{3}$ as the eluent to obtain a solution of pure monomer 6 -BT-BF3k in $\mathrm{CHCl}_{3}$. The solution of the monomer was concentrated under reduced pressure and then dissolved again in $\mathrm{CHCl}_{3}$. This procedure of dissolution/evaporation in $\mathrm{CHCl}_{3}$ 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 $(5.0 \mathrm{~mL})$ was added dropwise into ethanol $(20 \mathrm{~mL})$ 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 ${ }^{1} \mathrm{H}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ of monomer 6-BT-BF3k with that of the corresponding polymer poly-6-BT-BF3k.


Figure ESI-7. Comparison of the ${ }^{13} \mathrm{C}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ 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-1H-indene-2-carboxylate (2b).

In a microwave tube, a mixture of $5^{\prime}$-hexyl-2, ' ${ }^{\prime}$-bithiophene-5-boronic acid pinacol ester ( 177 mg , $0.470 \mathrm{mmol})$ in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing $\mathrm{Cs}_{2} \mathrm{CO}_{3}(450 \mathrm{mg}, 1.38$ $\mathrm{mmol})$ was stirred at room temperature for 30 min . To the resulting mixture, $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}_{2}(65 \mathrm{mg}$, $0.0926 \mathrm{mmol}), \mathrm{PPh}_{3}(12 \mathrm{mg}, 0.0458 \mathrm{mmol})$, and compound 1 (ref 1) ( $200 \mathrm{mg}, 0.469 \mathrm{mmol}$ ) were added in sequence. The reaction mixture was exposed to microwave irradiation in a CEM Discover apparatus ( 1 cycle of $10 \mathrm{~min}, \mathrm{~T}=80^{\circ} \mathrm{C}, \mathrm{W}=150, \mathrm{P}=250 \mathrm{psi}$ ) 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 ${ }^{\circ} \mathrm{C}$ ).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $0.89(\mathrm{t}, J=6.5,3 \mathrm{H}), 1.16(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.28-1.43(\mathrm{~m}, 6 \mathrm{H}), 1.63-$ $1.73(\mathrm{~m}, 2 \mathrm{H}), 2.79(\mathrm{t}, J=7.6,2 \mathrm{H}), 4.20(\mathrm{q}, J=7.1,2 \mathrm{H}), 6.69(\mathrm{~d}, J=3.5,1 \mathrm{H}), 7.02(\mathrm{~d}, J=3.5,1 \mathrm{H})$, $7.07(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.17(\mathrm{~d}, J=7.7,1 \mathrm{H}), 7.30(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.52(\mathrm{~s}, 5 \mathrm{H}), 7.57(\mathrm{dd}, J=7.8,1.6$, $1 \mathrm{H}), 7.83(\mathrm{~d}, J=1.1,1 \mathrm{H})$.

MS(ESI): $m / z 549\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

 (3b).To a solution of $\mathbf{2 b}(50 \mathrm{mg}, 0.095 \mathrm{mmol})$ in dichloromethane $(5.0 \mathrm{~mL})$ was added a 2 M solution of $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ in toluene $(0.19 \mathrm{~mL}, 0.38 \mathrm{mmol})$. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min , and then diluted with ethyl acetate $(20 \mathrm{~mL})$. The $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ excess was cautiously destroyed with a 1 M NaOH solution $(2.0 \mathrm{~mL})$ 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.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $0.89(\mathrm{t}, J=6.6,3 \mathrm{H}), 1.06(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.27-1.45(\mathrm{~m}, 6 \mathrm{H}), 1.63-$ $1.73(\mathrm{~m}, 2 \mathrm{H}), 1.82(\mathrm{~s}, 3 \mathrm{H}), 2.79(\mathrm{t}, J=7.6,2 \mathrm{H}), 3.70(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 4.04-4.22(\mathrm{~m}, 2 \mathrm{H}), 6.69(\mathrm{~d}, J=3.5$, $1 \mathrm{H}), 7.01(\mathrm{~d}, J=3.5,1 \mathrm{H}), 7.07(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.14(\mathrm{~d}, J=8.0,1 \mathrm{H}), 7.28(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.37-$ $7.47(\mathrm{~m}, 5 \mathrm{H}), 7.51(\mathrm{~d}, J=8.0,1 \mathrm{H}), 7.80(\mathrm{~s}, 1 \mathrm{H})$.

MS(ESI): $m / z 565\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

A mixture of indenol 3b ( $10 \mathrm{mg}, 0.0184 \mathrm{mmol}$ ) in $\mathrm{CDCl}_{3}(10 \mathrm{~mL})$ 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 $\mathrm{CDCl}_{3}$ as the eluent to obtain a solution of pure monomer 6-HBT-BF3k in $\mathrm{CDCl}_{3}$.
${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $0.89(\mathrm{t}, J=7.0,3 \mathrm{H}), 1.06(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.29-1.42(\mathrm{~m}, 6 \mathrm{H}), 1.64-$ $1.72(\mathrm{~m}, 2 \mathrm{H}), 2.79(\mathrm{t}, J=7.6,2 \mathrm{H}), 4.14(\mathrm{q}, J=7.1,2 \mathrm{H}), 6.46(\mathrm{~s}, 1 \mathrm{H}), 6.66(\mathrm{~s}, 1 \mathrm{H}), 6.69(\mathrm{~d}, J=3.5$, $1 \mathrm{H}), 7.02(\mathrm{~d}, J=3.5,1 \mathrm{H}), 7.08(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.22(\mathrm{~d}, J=8.0,1 \mathrm{H}), 7.28(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.40-$ $7.48(\mathrm{~m}, 5 \mathrm{H}), 7.52(\mathrm{dd}, J=8.0,1.6,1 \mathrm{H}), 7.90(\mathrm{~d}, J=1.3,1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): 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): $m / z 547\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

A mixture of indenol 3b ( $330 \mathrm{mg}, 0.608 \mathrm{mmol}$ ) in $\mathrm{CHCl}_{3}$ (stabilized with amylene, 600 mL ) containing PTSA ( $150 \mathrm{mg}, 0.789 \mathrm{mmol}$ ) was refluxed for 30 min . The reaction mixture was then cooled to room temperature and washed with a $\mathrm{NaHCO}_{3}$ saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with $\mathrm{CHCl}_{3}$ as the eluent to obtain a solution of pure monomer 6 -HBT-BF3k in $\mathrm{CHCl}_{3}$. The solution of the monomer was concentrated under reduced pressure and then dissolved again in $\mathrm{CHCl}_{3}$. This procedure of dissolution/evaporation in $\mathrm{CHCl}_{3}$ 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 $(40 \mathrm{~mL})$ 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 ${ }^{1} \mathrm{H}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ of monomer 6-HBT-BF3k with that of the corresponding polymer poly-6-HBT-BF3k.


Figure ESI-9. Comparison of the ${ }^{13} \mathrm{C}$ 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-1H-indene-2-carboxylate (7a).

In a microwave tube, a mixture of $2,2^{\prime}$-bithiophene-5-boronic acid pinacol ester ( $137 \mathrm{mg}, 0.469$ $\mathrm{mmol})$ in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing $\mathrm{Cs}_{2} \mathrm{CO}_{3}(450 \mathrm{mg}, 1.38 \mathrm{mmol})$ was stirred at room temperature for 30 min . To the resulting mixture, $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}_{2}(65 \mathrm{mg}, 0.0926$ $\mathrm{mmol}), \mathrm{PPh}_{3}(12 \mathrm{mg}, 0.0458 \mathrm{mmol})$, and compound 6 (ref 1) $(180 \mathrm{mg}, 0.465 \mathrm{mmol})$ were added in sequence. The reaction mixture was exposed to microwave in a CEM Discover apparatus (1 cycle of $10 \mathrm{~min}, \mathrm{~T}=80^{\circ} \mathrm{C}, \mathrm{W}=150, \mathrm{P}=250 \mathrm{psi}$ ) 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 $7 \mathbf{7 a}(97 \mathrm{mg}$, yield
$44 \%$ ) as a red solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (mp 192-193 ${ }^{\circ} \mathrm{C}$ ).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $1.21(\mathrm{t}, J=7.1,3 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 4.22(\mathrm{q}, J=7.1,2 \mathrm{H}), 6.84(\mathrm{dd}, J=$ $8.1,2.5,1 \mathrm{H}), 7.05(\mathrm{dd}, J=5.0,3.6,1 \mathrm{H}), 7.14(\mathrm{~d}, J=8.1,1 \mathrm{H}), 7.17-7.20(\mathrm{~m}, 2 \mathrm{H}), 7.22-7.26(\mathrm{~m}$, $2 \mathrm{H}), 7.34(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.56(\mathrm{~d}, J=8.3,2 \mathrm{H}), 7.72(\mathrm{~d}, J=8.3,2 \mathrm{H})$.

MS(ESI): $m / z 495\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

 carboxylate (8a).To a stirred solution of $\mathbf{7 a}(50 \mathrm{mg}, 0.106 \mathrm{mmol})$ in 5.0 mL of dichloromethane was added a 2 M solution of $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ in toluene $(0.21 \mathrm{~mL}, 0.42 \mathrm{mmol})$. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min , and then diluted with ethyl acetate ( 20 mL ). The $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ excess was cautiously destroyed with 2.0 mL of a 1 M 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.
${ }^{1} \mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl}_{3}$ ): $1.11(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.77(\mathrm{~s}, 3 \mathrm{H}), 3.70(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 4.08-$ $4.24(\mathrm{~m}, 2 \mathrm{H}), 6.82(\mathrm{dd}, J=8.4,2.4,1 \mathrm{H}), 7.04(\mathrm{dd}, J=5.1,3.7,1 \mathrm{H}), 7.11(\mathrm{~d}, J=8.4,1 \mathrm{H}), 7.15(\mathrm{~d}, J$ $=2.3,1 \mathrm{H}), 7.17(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.20-7.25(\mathrm{~m}, 2 \mathrm{H}), 7.30(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.42(\mathrm{~d}, J=8.4,2 \mathrm{H}), 7.67$ (d, $J=8.3,2 \mathrm{H}$ ).

MS(ESI): $m / z 511\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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 $8 \mathbf{~}(6.5 \mathrm{mg}, 0.0133 \mathrm{mmol})$ in $\mathrm{CDCl}_{3}(13 \mathrm{~mL})$ containing PTSA ( $3.0 \mathrm{mg}, 0.0158 \mathrm{mmol}$ ) was heated to reflux for 30 min . The reaction mixture was then cooled to room temperature and washed with a saturated solution of $\mathrm{NaHCO}_{3}$. The organic layer was dried over sodium sulfate, concentrated to a volume of ca. 2 mL and purified by flash chromatography with $\mathrm{CDCl}_{3}$ as the eluent to obtain a solution of pure monomer 4'-BT-6-MO-BF3k in $\mathrm{CDCl}_{3}$.
${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $1.11(\mathrm{t}, J=7.1,3 \mathrm{H}), 3.88(\mathrm{~s}, 3 \mathrm{H}), 4.16(\mathrm{q}, J=7.1,2 \mathrm{H}), 6.35(\mathrm{~s}, 1 \mathrm{H})$, $6.62(\mathrm{~s}, 1 \mathrm{H}), 6.84(\mathrm{dd}, J=8.4,2.1,1 \mathrm{H}), 7.04(\mathrm{dd}, J=5.0,3.7,1 \mathrm{H}), 7.15-7.19(\mathrm{~m}, 2 \mathrm{H}), 7.20-7.24$ $(\mathrm{m}, 2 \mathrm{H}), 7.26(\mathrm{~d}, J=2.3,1 \mathrm{H}), 7.30(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.42-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.66-7.69(\mathrm{~m}, 2 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): 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): $m / z 493\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

A mixture of $\mathbf{8 a}(175 \mathrm{mg}, 0.358 \mathrm{mmol})$ in $\mathrm{CHCl}_{3}$ (stabilized with amylene, 350 mL ) containing PTSA, ( $100 \mathrm{mg}, 0.526 \mathrm{mmol}$ ) was heated to reflux for 30 min . The reaction mixture was then cooled to room temperature and washed with a saturated solution of $\mathrm{NaHCO}_{3}$. The organic layer was dried over sodium sulfate, concentrated to a volume of ca. 25 mL and purified by flash chromatography with $\mathrm{CHCl}_{3}$ as the eluent to obtain a solution of pure monomer 4'-BT-6-MO-BF3k in $\mathrm{CHCl}_{3}$. The solution of the monomer was concentrated under reduced pressure and then dissolved again in $\mathrm{CHCl}_{3}$. This procedure of dissolution/evaporation in $\mathrm{CHCl}_{3}$ 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 $(5.0 \mathrm{~mL})$ 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 ${ }^{1} \mathrm{H}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ 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 ${ }^{13} \mathrm{C}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ 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-1H-indene-2-carboxylate

 (7b).In a microwave tube, a mixture of $5^{\prime}$-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester ( 177 mg , $0.470 \mathrm{mmol})$ in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing $\mathrm{Cs}_{2} \mathrm{CO}_{3}(450 \mathrm{mg}, 1.38$ $\mathrm{mmol})$ was stirred at room temperature for 30 min . To the resulting mixture, $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Cl}_{2}(65 \mathrm{mg}$, $0.0926 \mathrm{mmol}), \mathrm{PPh}_{3}(12 \mathrm{mg}, 0.458 \mathrm{mmol})$, and compound $6(\mathrm{ref} 1)(180 \mathrm{mg}, 0.465 \mathrm{mmol})$ were added in sequence. The reaction mixture was exposed to microwave in a CEM Discover apparatus ( 1 cycle of $10 \mathrm{~min}, \mathrm{~T}=80^{\circ} \mathrm{C}, \mathrm{W}=150, \mathrm{P}=250 \mathrm{psi}$ ) 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 ${ }^{\circ} \mathrm{C}$ ).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $0.89(\mathrm{t}, J=6.9,3 \mathrm{H}), 1.20(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.28-1.43(\mathrm{~m}, 6 \mathrm{H}), 1.63-$ $1.74(\mathrm{~m}, 2 \mathrm{H}), 2.80(\mathrm{t}, J=7.6,2 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 4.22(\mathrm{q}, J=7.1,2 \mathrm{H}), 6.70(\mathrm{~d}, J=3.5,1 \mathrm{H}), 6.83$ (dd, $J=8.1,2.4,1 \mathrm{H}), 7.03(\mathrm{~d}, J=3.5,1 \mathrm{H}), 7.09(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.13(\mathrm{~d}, J=8.1,1 \mathrm{H}), 7.17(\mathrm{~d}, J=$ $2.4,1 \mathrm{H}), 7.30(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.55(\mathrm{~d}, J=8.3,2 \mathrm{H}), 7.69(\mathrm{~d}, J=8.3,2 \mathrm{H})$.

MS(ESI): $m / z 579\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

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

## 2-carboxylate ( 8 b ).

To a stirred solution of $\mathbf{7 b}(50 \mathrm{mg}, 0.0898 \mathrm{mmol})$ in dichloromethane $(5.0 \mathrm{~mL})$ was added a 2 M solution of $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ in toluene $(0.20 \mathrm{~mL}, 0.40 \mathrm{mmol})$. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min , and then diluted with ethyl acetate ( 20 mL ). The $\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}$ excess was cautiously destroyed with a 1 M NaOH solution $(2.0 \mathrm{~mL})$ and the resulting mixture was partitioned between water and ethyl acetate $(20 \mathrm{~mL})$. 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 $\mathbf{8 b}$ ( 37 mg , yield $72 \%$ ) as a yellow glassy solid.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $0.89(\mathrm{t}, J=6.9,3 \mathrm{H}), 1.11(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.29-1.44(\mathrm{~m}, 6 \mathrm{H}), 1.63-$ $1.73(\mathrm{~m}, 2 \mathrm{H}), 1.77(\mathrm{~s}, 3 \mathrm{H}), 2.80(\mathrm{t}, J=7.6,2 \mathrm{H}), 3.71(\mathrm{~s}, 1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 4.06-4.25(\mathrm{~m}, 2 \mathrm{H}), 6.70$ $(\mathrm{d}, J=3.6,1 \mathrm{H}), 6.82(\mathrm{dd}, J=8.4,2.4,1 \mathrm{H}), 7.02(\mathrm{~d}, J=3.5,1 \mathrm{H}), 7.09(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.11(\mathrm{~d}, J=$ $8.4,1 \mathrm{H}), 7.15(\mathrm{~d}, J=2.4,1 \mathrm{H}), 7.27(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.40(\mathrm{~d}, J=8.2,2 \mathrm{H}), 7.66(\mathrm{~d}, J=8.2,2 \mathrm{H})$. MS(ESI): $m / z 595\left(\mathrm{M}+\mathrm{Na}^{+}\right)$.

[^0]A mixture of $\mathbf{8 b}(10 \mathrm{mg}, 0.0175 \mathrm{mmol})$ in $\mathrm{CDCl}_{3}(10 \mathrm{~mL})$ containing PTSA $(3.0 \mathrm{mg}, 0.0158 \mathrm{mmol})$ was heated to reflux for 30 min . The reaction mixture was then cooled to room temperature and washed with a $\mathrm{NaHCO}_{3}$ saturated solution. The organic layer was dried over sodium sulfate and purified by flash chromatography with $\mathrm{CDCl}_{3}$ as the eluent to obtain a solution of pure monomer $4^{\prime}$ -HBT-6-MO-BF3k in $\mathrm{CDCl}_{3}$.
${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $0.89(\mathrm{t}, J=7.0,3 \mathrm{H}), 1.11(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.29-1.34(\mathrm{~m}, 4 \mathrm{H}), 1.35-$ $1.42(\mathrm{~m}, 2 \mathrm{H}), 1.65-1.71(\mathrm{~m}, 2 \mathrm{H}), 2.80(\mathrm{t}, J=7.6,2 \mathrm{H}), 3.88(\mathrm{~s}, 3 \mathrm{H}), 4.15(\mathrm{q}, J=7.1,2 \mathrm{H}), 6.35(\mathrm{~s}$, $1 \mathrm{H}), 6.61(\mathrm{~s}, 1 \mathrm{H}), 6.69(\mathrm{~d}, J=3.5,1 \mathrm{H}), 6.84(\mathrm{dd}, J=8.4,2.3,1 \mathrm{H}), 7.02(\mathrm{~d}, J=3.5,1 \mathrm{H}), 7.09(\mathrm{~d}, J=$ $3.8,1 \mathrm{H}), 7.17(\mathrm{~d}, J=8.4,1 \mathrm{H}), 7.26(\mathrm{~d}, J=2.4,1 \mathrm{H}), 7.27(\mathrm{~d}, J=3.8,1 \mathrm{H}), 7.41-7.45(\mathrm{~m}, 2 \mathrm{H}), 7.65-$ 7.68 (m, 2H).
${ }^{13} \mathrm{C}$ NMR (125 MHz, $\mathrm{CDCl}_{3}$ ): 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): $m / z 555\left(\mathrm{M}+\mathrm{H}^{+}\right)$.

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

A mixture of $\mathbf{8 b}\left(250 \mathrm{mg}, 0.436 \mathrm{mmol}\right.$ ) in $\mathrm{CHCl}_{3}$ (stabilized with amylene, 360 mL ) containing PTSA ( $100 \mathrm{mg}, 0.526 \mathrm{mmol}$ ) was heated to reflux for 30 min . The reaction mixture was then cooled to room temperature and washed with a $\mathrm{NaHCO}_{3}$ saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with $\mathrm{CHCl}_{3}$ as the eluent to obtain a solution of pure monomer 4'-HBT-6-MO-BF3k in $\mathrm{CHCl}_{3}$. The solution of the monomer was concentrated under reduced pressure and then dissolved again in $\mathrm{CHCl}_{3}$. This procedure of dissolution/evaporation in $\mathrm{CHCl}_{3}$ 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
$(40 \mathrm{~mL})$ 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 ${ }^{1} \mathrm{H}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ 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 ${ }^{13} \mathrm{C}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ of monomer 4'-HBT-6-MO-BF3k with that of the corresponding polymer poly-4'-HBT-6-MO-BF3k.

## References

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[^0]:    Ethyl 3-[4-(5'-hexyl-2,2'-bithiophen-5-yl)phenyl]-6-methoxy-1-methylene-1H-indene-2carboxylate (4'-HBT-6-MO-BF3k).

