

Electronic Supplementary Information

Side Chain Engineering in π -Stacked Polybenzofulvene Derivatives Bearing Electron-Rich Chromophores for OLED Applications

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Content: Experimental details for the preparation and the characterization of the new
polybenzofulvene derivatives (pages 2-19)

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 F₂₅₄ were used for TLC. NMR spectra were recorded with a Varian Mercury-300, a Bruker DRX-400 AVANCE, a 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-(9-methyl-9*H*-carbazol-3-yl)-1-oxo-3-phenyl-1*H*-indene-2-carboxylate (2a).

In a microwave tube, a mixture of 9-methyl-9*H*-carbazole-3-boronic acid pinacol ester (140 mg, 0.456 mmol) in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing Cs₂CO₃ (450 mg, 1.38 mmol) was stirred at room temperature for 30 min. To the resulting mixture, Pd(PPh₃)₂Cl₂ (65 mg, 0.0926 mmol), PPh₃ (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 (8:2) as the eluent afforded **2a** (110 mg, yield 53%) as a dark red solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (dark red crystals, mp 177-178 °C). ¹H NMR (400 MHz, CDCl₃): 1.18 (t, *J* = 7.1, 3H), 3.89 (s, 3H), 4.22 (q, *J* = 7.1, 2H), 7.26-7.30 (m, 2H), 7.40-7.62 (m, 8H), 7.72-7.78 (m, 2H), 8.00 (s, 1H), 8.15 (d, *J* = 7.7, 1H), 8.34 (s, 1H). MS(ESI): *m/z* 480 (M + Na⁺).

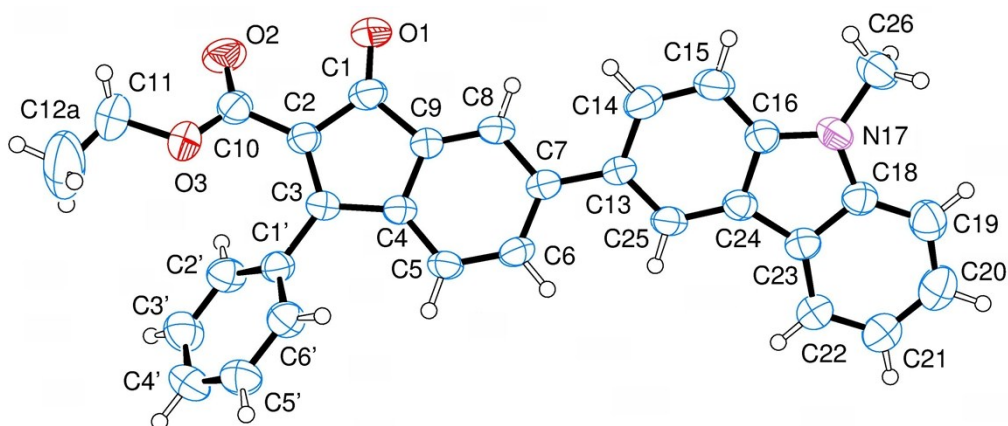


Figure ESI-1. Structure of compound **2a** found by crystallography. Ellipsoids enclose 50% probability.

Ethyl 1-hydroxy-1-methyl-6-(9-methyl-9*H*-carbazol-3-yl)-3-phenyl-1*H*-indene-2-carboxylate (3a).

To a solution of **2a** (50 mg, 0.109 mmol) in dichloromethane (5.0 mL) was added a 2M solution of $\text{Al}(\text{CH}_3)_3$ in toluene (0.22 mL, 0.44 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 $\text{Al}(\text{CH}_3)_3$ 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. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate-dichloromethane (7:2:1) as the eluent afforded indenol derivative **3a** (27 mg, yield 52%) as a yellow glassy solid. ^1H NMR (400 MHz, CDCl_3): 1.08 (t, $J = 7.1$, 3H), 1.88 (s, 3H), 3.77 (s, 1H), 3.88 (s, 3H), 4.09-4.25 (m, 2H), 7.23-7.30 (m, 2H), 7.39-7.53 (m, 8H), 7.66 (dd, $J = 7.9, 1.5$, 1H), 7.78 (dd, $J = 8.5, 1.7$, 1H), 7.96 (d, $J = 1.1$, 1H), 8.16 (d, $J = 7.7$, 1H), 8.38 (d, $J = 1.5$, 1H). MS(ESI): m/z 496 ($\text{M} + \text{Na}^+$).

Ethyl 6-(9-methyl-9H-carbazol-3-yl)-1-methylene-3-phenyl-1H-indene-2-carboxylate (6-MCBZ-BF3k).

A mixture of indenol **3a** (10 mg, 0.021 mmol) in CDCl₃ (0.80 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 1.0 mg, 0.00526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and purified by flash chromatography with CDCl₃ as the eluent to obtain a solution of pure monomer 6-MCBZ-**BF3k** in CDCl₃. ¹H NMR (400 MHz, CDCl₃): 1.07 (t, *J* = 7.1, 3H), 3.90 (s, 3H), 4.15 (q, *J* = 7.1, 2H), 6.51 (s, 1H), 6.67 (s, 1H), 7.25-7.28 (m, 1H), 7.32 (d, *J* = 7.9, 1H), 7.42-7.52 (m, 8H), 7.65 (dd, *J* = 7.9, 1.4, 1H), 7.78 (dd, *J* = 8.5, 1.8, 1H), 8.05 (d, *J* = 1.2, 1H), 8.17 (d, *J* = 7.8, 1H), 8.35 (d, *J* = 1.3, 1H). ¹³C NMR (100 MHz, CDCl₃): 13.8, 29.2, 60.1, 108.7, 108.8, 117.1, 118.9, 119.1, 120.4, 122.6, 122.9, 123.4, 125.1, 125.3, 126.0, 127.5, 128.0, 128.3, 128.7, 132.2, 134.7, 137.7, 139.8, 140.7, 141.5, 142.5, 144.1, 153.1, 165.1. MS(ESI): *m/z* 456 (M + H⁺).

Poly-[Ethyl 6-(9-methyl-9H-carbazol-3-yl)-1-methylene-3-phenyl-1H-indene-2-carboxylate] (Poly-6-MCBZ-BF3k).

A mixture of indenol **3a** (357 mg, 0.754 mmol) in CHCl₃ (stabilized with amylene, 800 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 250 mg, 1.31 mmol) was refluxed for 30 min. The reaction mixture was then cooled to room temperature and washed with a NaHCO₃ saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with CHCl₃ as the eluent to obtain a solution of pure monomer 6-MCBZ-**BF3k** in CHCl₃. The solution of the monomer was concentrated under reduced pressure and then dissolved again in CHCl₃. This procedure of dissolution/evaporation in CHCl₃ 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-MCBZ-**BF3k** (215 mg, yield 63%) as a yellow solid.

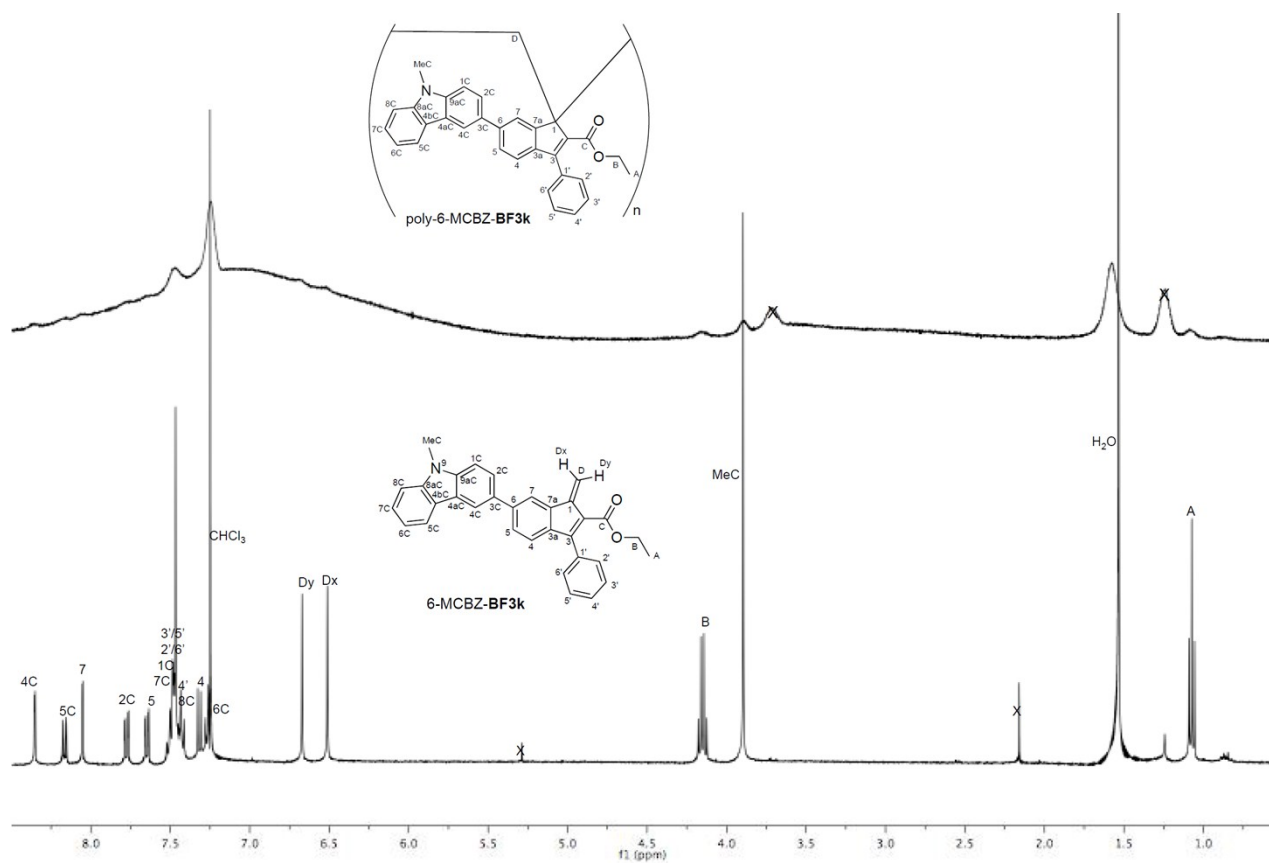


Figure ESI-2. Comparison of the ¹H NMR spectrum (CDCl₃) of monomer 6-MCBZ-BF3k with that of the corresponding polymer poly-6-MCBZ-BF3k.

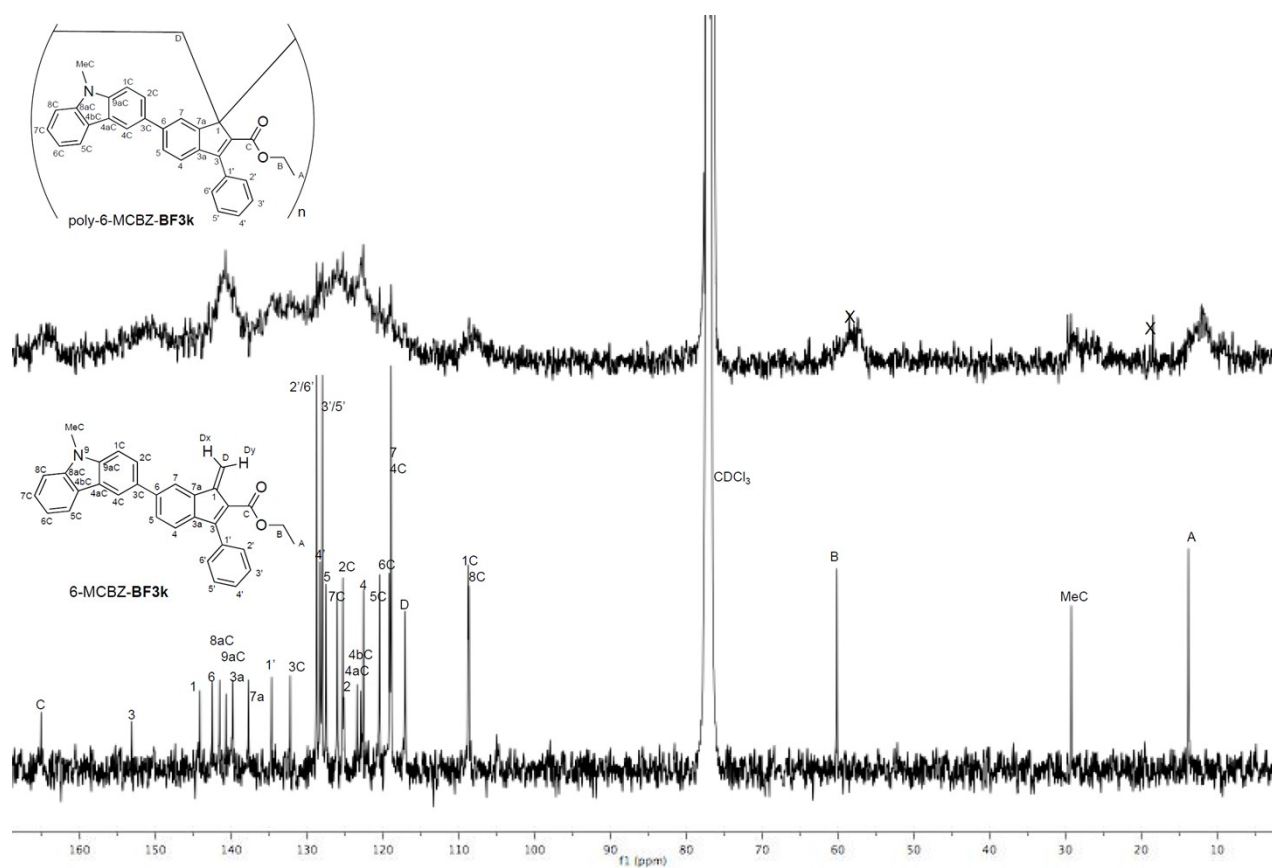


Figure ESI-3. Comparison of the ^{13}C NMR spectrum (CDCl₃) of monomer 6-MCBZ-BF3k with that of the corresponding polymer poly-6-MCBZ-BF3k.

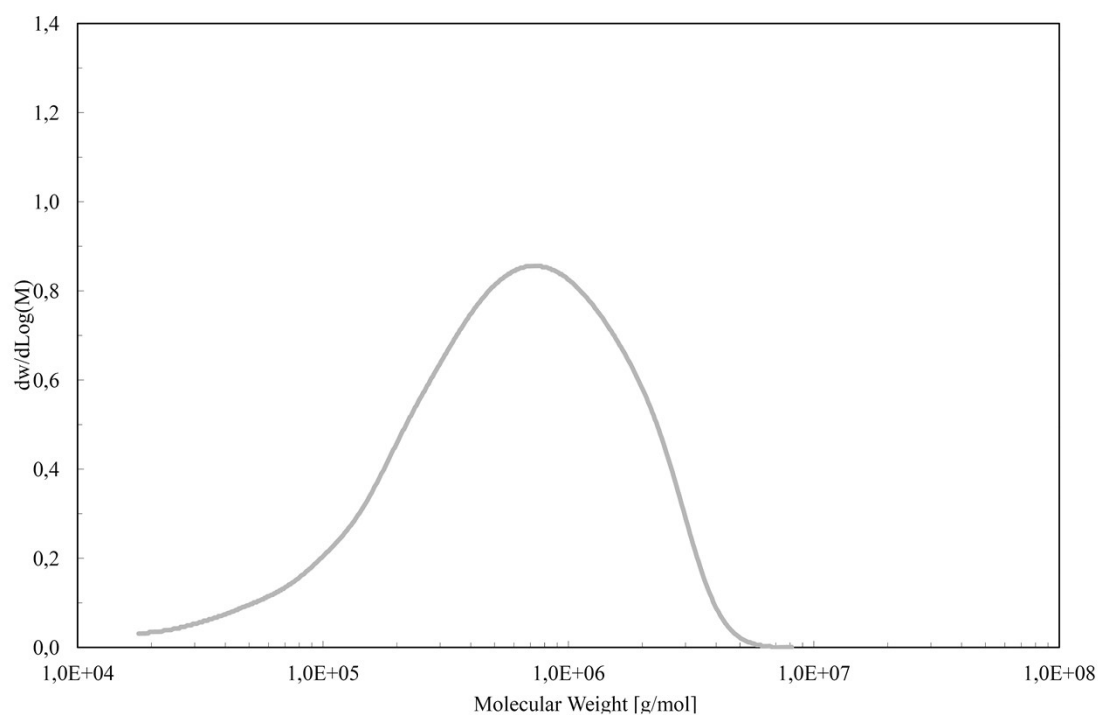


Figure ESI-4. Differential molecular weight distribution (MWD) of poly-6-MCBZ-BF3k.

Ethyl 6-methoxy-3-[4-(9-methyl-9*H*-carbazol-3-yl)phenyl]-1-oxo-1*H*-indene-2-carboxylate (5a).

In a microwave tube, a mixture of 9-methyl-9*H*-carbazole-3-boronic acid pinacol ester (80 mg, 0.260 mmol) in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing Cs₂CO₃ (250 mg, 0.77 mmol) was stirred at room temperature for 30 min. To the resulting mixture, Pd(PPh₃)₂Cl₂ (37 mg, 0.053 mmol), PPh₃ (7.0 mg, 0.027 mmol), and compound **4** (ref 1,100 mg, 0.258 mmol) were added in sequence. The reaction mixture was exposed to microwave in a CEM Discover apparatus (1 cycle of 15 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 (8:2) as the eluent afforded **5a** (110 mg, yield 87%) as a red solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (mp 195-196 °C). ¹H NMR (400 MHz, CDCl₃): 1.23 (t, *J* = 7.1, 3H), 3.87 (s, 3H), 3.91 (s, 3H), 4.24 (q, *J* = 7.1, 2H), 6.86 (dd, *J* = 8.1, 2.4, 1H), 7.18-7.31 (m, 3H), 7.44 (d, *J* = 8.1, 1H), 7.47-7.55 (m, 2H), 7.66 (d, *J* = 8.3, 2H), 7.80 (dd, *J* = 8.5, 1.7, 1H), 7.86 (d, *J* = 8.2, 2H), 8.16 (d, *J* = 7.7, 1H), 8.39 (d, *J* = 1.4, 1H). MS(ESI): *m/z* 510 (M + Na⁺).

Ethyl 1-hydroxy-6-methoxy-1-methyl-3-[4-(9-methyl-9*H*-carbazol-3-yl)phenyl]-1*H*-indene-2-carboxylate (6a).

To a stirred solution of **5a** (50 mg, 0.103 mmol) in dichloromethane (5.0 mL) was added a 2M solution of Al(CH₃)₃ in toluene (0.22 mL, 0.44 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(CH₃)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. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate-dichloromethane (7:2:1) as the eluent afforded

indanol derivative **6a** (28 mg, yield 54%) as a yellow-orange glassy solid. ¹H NMR (400 MHz, CDCl₃): 1.13 (t, *J* = 7.1, 3H), 1.80 (s, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 4.18 (m, 2H), 6.84 (dd, *J* = 8.4, 2.4, 1H), 7.15-7.20 (m, 2H), 7.28 (m, 1H), 7.40-7.55 (m, 5H), 7.80 (m, 3H), 8.16 (d, *J* = 7.7, 1H), 8.38 (d, *J* = 1.6, 1H). MS(ESI): *m/z* 526 (M + Na⁺).

Ethyl 6-methoxy-3-[4-(9-methyl-9H-carbazol-3-yl)phenyl]-1-methylene-1H-indene-2-carboxylate (4'-MCBZ-6-MO-BF3k).

A mixture of **6a** (10 mg, 0.0199 mmol) in CDCl₃ (0.80 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 1.0 mg, 0.00526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and purified by flash chromatography with CDCl₃ as the eluent to obtain a solution of pure monomer 4'-MCBZ-6-MO-BF3k in CDCl₃. ¹H NMR (400 MHz, CDCl₃): 1.13 (t, *J* = 7.1, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 4.18 (q, *J* = 7.1, 2H), 6.35 (s, 1H), 6.61 (s, 1H), 6.86 (dd, *J* = 8.4, 2.3, 1H), 7.23-7.27 (m, 2H), 7.28 (d, *J* = 2.1, 1H), 7.43 (d, *J* = 8.1, 1H), 7.48-7.54 (m, 4H), 7.79-7.82 (m, 3H), 8.16 (d, *J* = 7.6, 1H), 8.38 (d, *J* = 1.5, 1H). ¹³C NMR (100 MHz, CDCl₃): 13.9, 29.2, 55.7, 60.0, 105.9, 108.6, 108.8, 114.0, 116.5, 118.8, 119.1, 120.4, 122.9, 123.4, 125.2, 126.0, 126.6, 129.3, 131.9, 132.7, 134.6, 139.2, 140.7, 141.5, 142.0, 144.0, 153.4, 160.8, 165.1. MS(ESI): *m/z* 486 (M + H⁺).

Poly-[Ethyl 6-methoxy-3-[4-(9-methyl-9H-carbazol-3-yl)phenyl]-1-methylene-1H-indene-2-carboxylate] (Poly-4'-MCBZ-6-MO-BF3k).

A mixture of **6a** (230 mg, 0.457 mmol) in CHCl₃ (stabilized with amylene, 400 mL) containing *p*-toluenesulfonic acid monohydrate (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 NaHCO₃ saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with CHCl₃ as the eluent to obtain a solution of pure monomer 4'-MCBZ-6-MO-BF3k in CHCl₃. The solution of the monomer was concentrated under reduced

pressure and then dissolved again in CHCl_3 . This procedure of dissolution/evaporation in 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 mL) and the precipitate was collected by filtration and dried under reduced pressure to obtain poly-4'-MCBZ-6-MO-BF3k (140 mg, yield 63%) as a pale yellow solid.

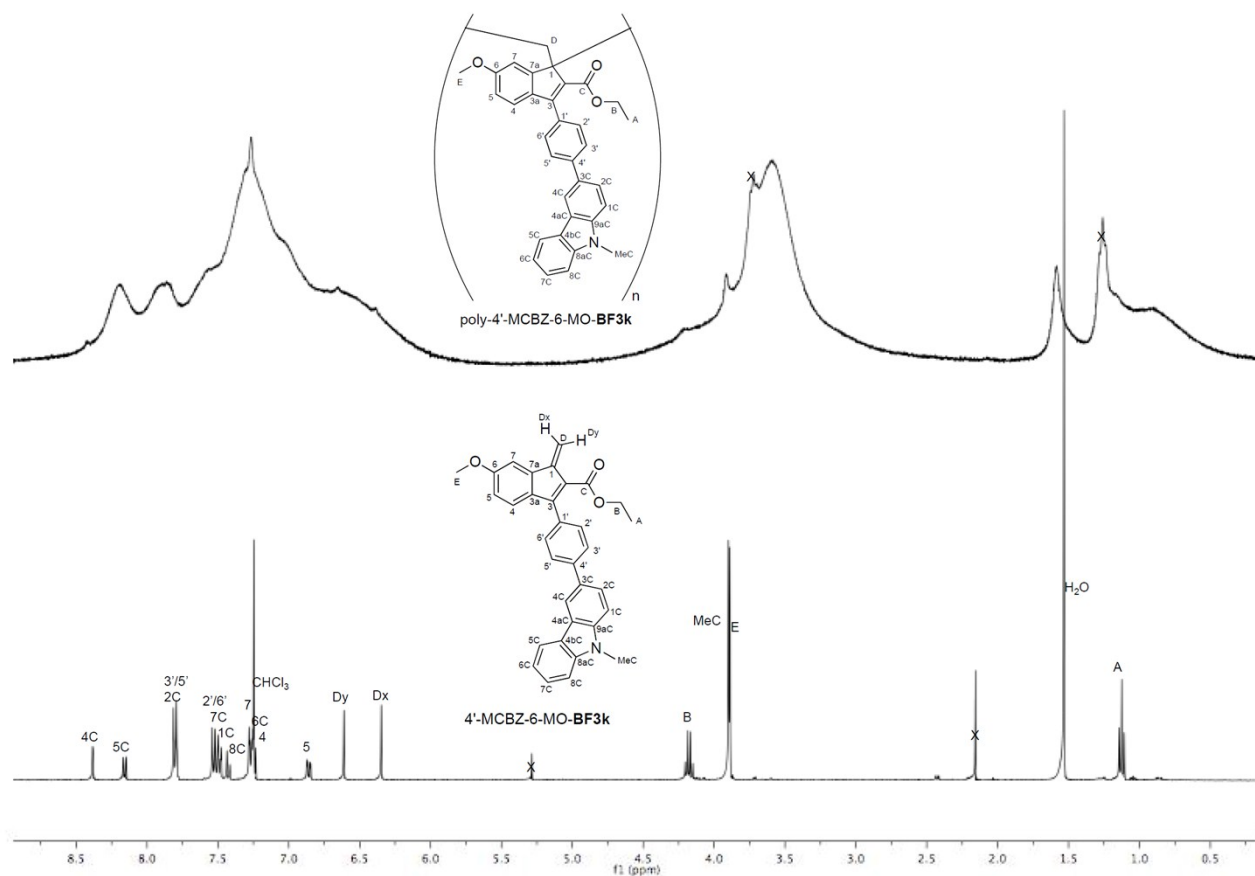


Figure ESI-5. Comparison of the ^1H NMR spectrum (CDCl_3) of monomer 4'-MCBZ-6-MO-BF3k with that of the corresponding polymer poly-4'-MCBZ-6-MO-BF3k.

ether-ethyl acetate by slow evaporation (violet prisms, mp 200-201 °C). ¹H NMR (400 MHz, CDCl₃): 1.17 (t, *J* = 7.1, 3H), 4.20 (q, *J* = 7.1, 2H), 7.05 (t, *J* = 7.3, 2H), 7.10-7.16 (m, 6H), 7.22 (d, *J* = 7.7, 1H), 7.27 (m, 4H), 7.44-7.57 (m, 7H), 7.58 (dd, *J* = 7.7, 1.6, 1H), 7.83 (d, *J* = 1.6, 1H). MS(ESI): *m/z* 544 (M + Na⁺).

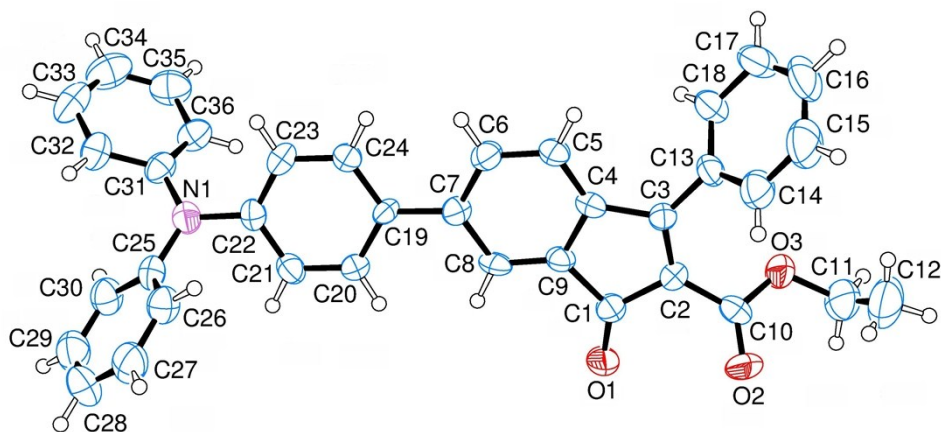


Figure ESI-7. Structure of compound **2b** found by crystallography. Ellipsoids enclose 50% probability.

Ethyl 6-[4-(diphenylamino)phenyl]-1-hydroxy-1-methyl-3-phenyl-1*H*-indene-2-carboxylate (3b).

To a solution of **2b** (60 mg, 0.115 mmol) in dichloromethane (6.0 mL) was added a 2M solution of Al(CH₃)₃ in toluene (0.23 mL, 0.46 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(CH₃)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** (41 mg, yield 66%) as a yellow glassy solid. ¹H NMR (400 MHz, CDCl₃): 1.06 (t, *J* = 7.1, 3H), 1.82 (s, 3H), 3.69 (br s, 1H), 4.01-4.27 (m, 2H), 7.04 (t, *J* = 7.3, 2H), 7.09-7.16 (m, 6H), 7.18 (d, *J* = 7.9, 1H), 7.23-7.31 (m, 4H), 7.38-7.54 (m, 8H), 7.78 (d, *J* = 1.3, 1H). MS(ESI): *m/z* 560 (M + Na⁺).

Ethyl 6-[4-(diphenylamino)phenyl]-1-methylene-3-phenyl-1*H*-indene-2-carboxylate (6-TPA-BF3k).

A mixture of indenol **3b** (10 mg, 0.0186 mmol) in CDCl₃ (0.80 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 1.0 mg, 0.00526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and purified by flash chromatography with CDCl₃ as the eluent to obtain a solution of pure monomer 6-TPA-**BF3k** in CDCl₃. ¹H NMR (400 MHz, CDCl₃): 1.06 (t, *J* = 7.1, 3H), 4.14 (q, *J* = 7.1, 2H), 6.44 (s, 1H), 6.64 (s, 1H), 7.03 (t, *J* = 7.3, 2H), 7.11-7.18 (m, 6H), 7.23-7.32 (m, 5H), 7.41-7.56 (m, 8H), 7.90 (d, *J* = 1.2, 1H). ¹³C NMR (100 MHz, CDCl₃): 13.8, 60.1, 117.1, 118.3, 122.5, 123.1, 123.8, 124.5, 125.3, 126.8, 127.8, 128.0, 128.3, 128.7, 129.3, 134.5, 134.9, 137.6, 140.1, 140.9, 144.0, 147.5, 147.6, 152.9, 165.0. MS(ESI): *m/z* 542 (M + Na⁺).

Poly-[Ethyl 6-[4-(diphenylamino)phenyl]-1-methylene-3-phenyl-1*H*-indene-2-carboxylate] (Poly-6-TPA-BF3k).

A mixture of indenol **3b** (240 mg, 0.446 mmol) in CHCl₃ (stabilized with amylene, 400 mL) containing *p*-toluenesulfonic acid monohydrate (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 NaHCO₃ saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with CHCl₃ as the eluent to obtain a solution of pure monomer 6-TPA-**BF3k** in CHCl₃. The solution of the monomer was concentrated under reduced pressure and then dissolved again in CHCl₃. This procedure of dissolution/evaporation in CHCl₃ 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-TPA-**BF3k** (188 mg, yield 81%) as a yellow solid.

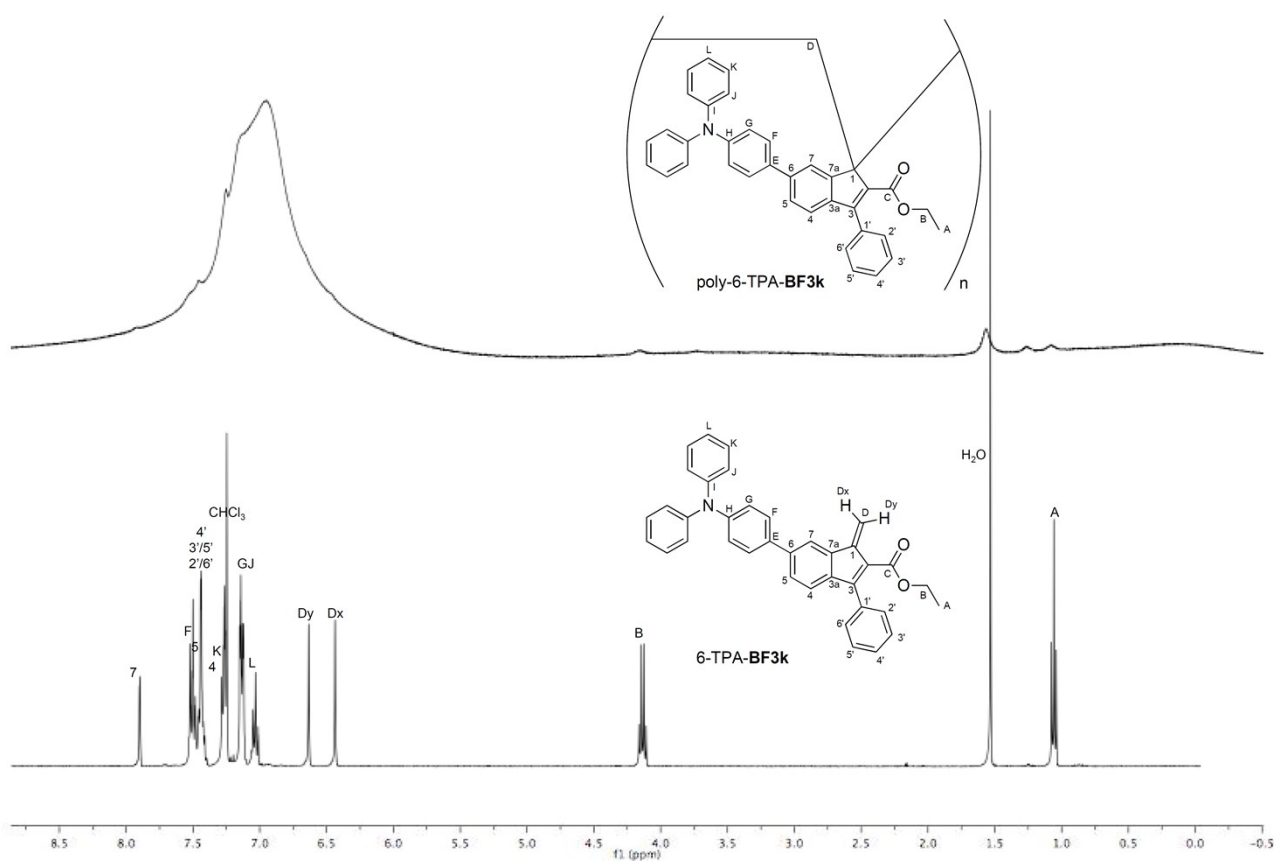


Figure ESI-8. Comparison of the ^1H NMR spectrum (CDCl_3) of monomer **6-TPA-BF3k** with that of the corresponding polymer **poly-6-TPA-BF3k**.

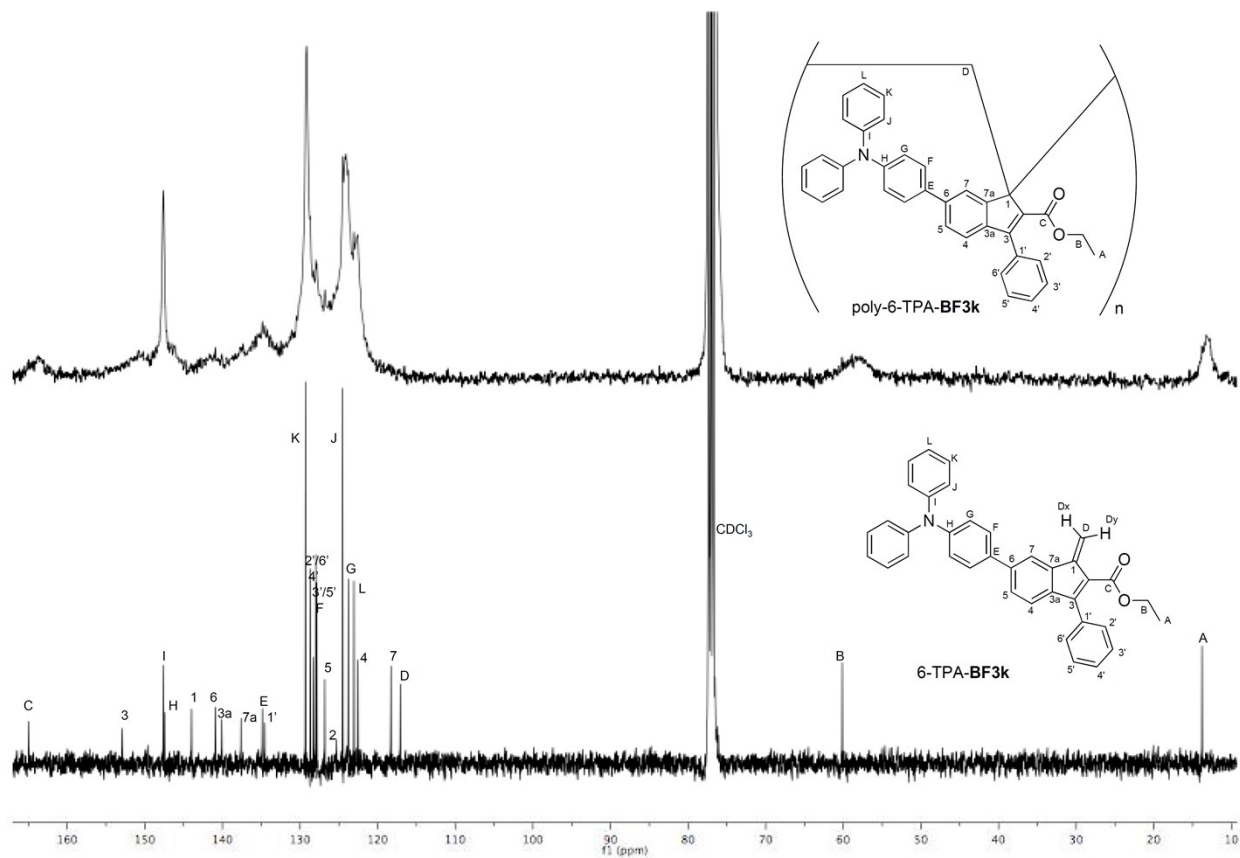


Figure ESI-9. Comparison of the ^{13}C NMR spectrum of monomer 6-TPA-BF3k with that of the corresponding polymer poly-6-TPA-BF3k.

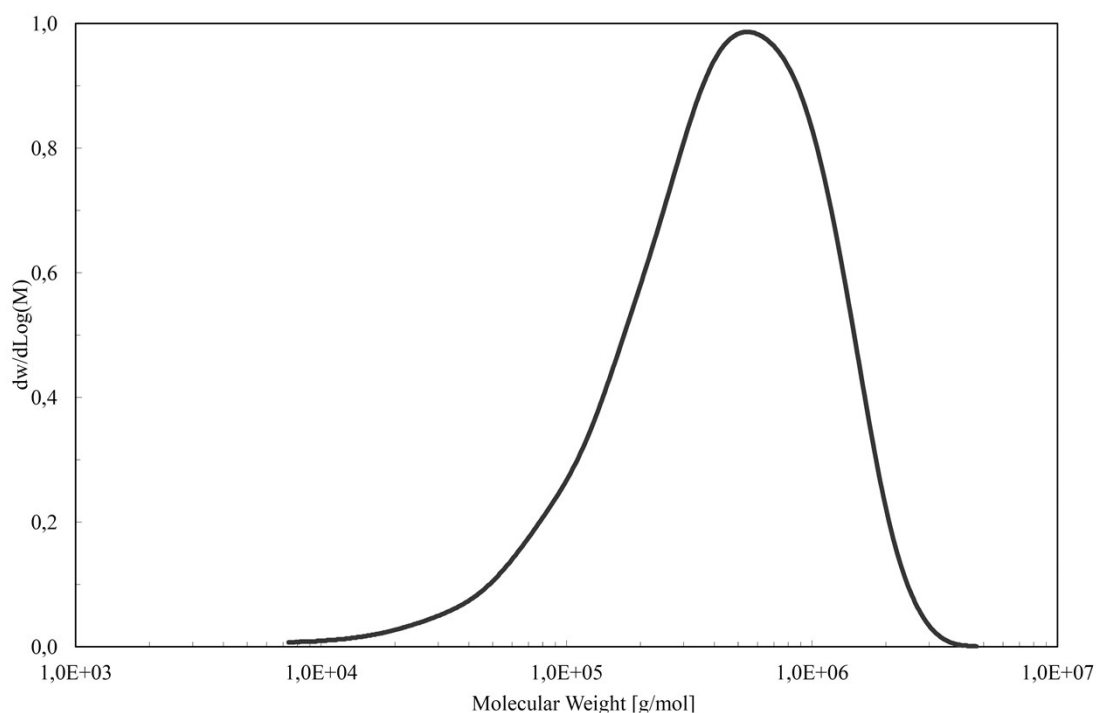


Figure ESI-10. Differential molecular weight distribution (MWD) of poly-6-TPA-**BF3k**.

Ethyl 3-[4'-(diphenylamino)biphenyl-4-yl]-6-methoxy-1-oxo-1*H*-indene-2-carboxylate (5b**).**

In a microwave tube, a mixture of 4-(diphenylamino)phenylboronic acid pinacol ester (96 mg, 0.259 mmol) in 4.0 mL of dry THF and 0.25 mL of dry MeOH containing Cs₂CO₃ (250 mg, 0.77 mmol) was stirred at room temperature for 30 min. To the resulting mixture, Pd(PPh₃)₂Cl₂ (37 mg, 0.053 mmol), PPh₃ (7.0 mg, 0.027 mmol), and compound **4** (ref 1, 100 mg, 0.258 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. 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 (9:1) as the eluent afforded **5b** (45 mg, yield 32%) as a red solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (red prisms, mp 209-211 °C). ¹H NMR (400 MHz, CDCl₃): 1.19 (t, *J* = 7.1, 3H), 3.86 (s, 3H), 4.22 (q, *J* = 7.1, 2H), 6.84 (dd, *J* = 8.2, 2.4, 1H), 7.05 (t, *J* = 7.3, 2H), 7.12-7.20

(m, 8H), 7.28 (t, $J = 7.8$, 4H), 7.53 (d, $J = 8.6$, 2H), 7.59 (d, $J = 8.2$, 2H), 7.69 (d, $J = 8.3$, 2H).

MS(ESI): m/z 574 ($M + Na^+$).

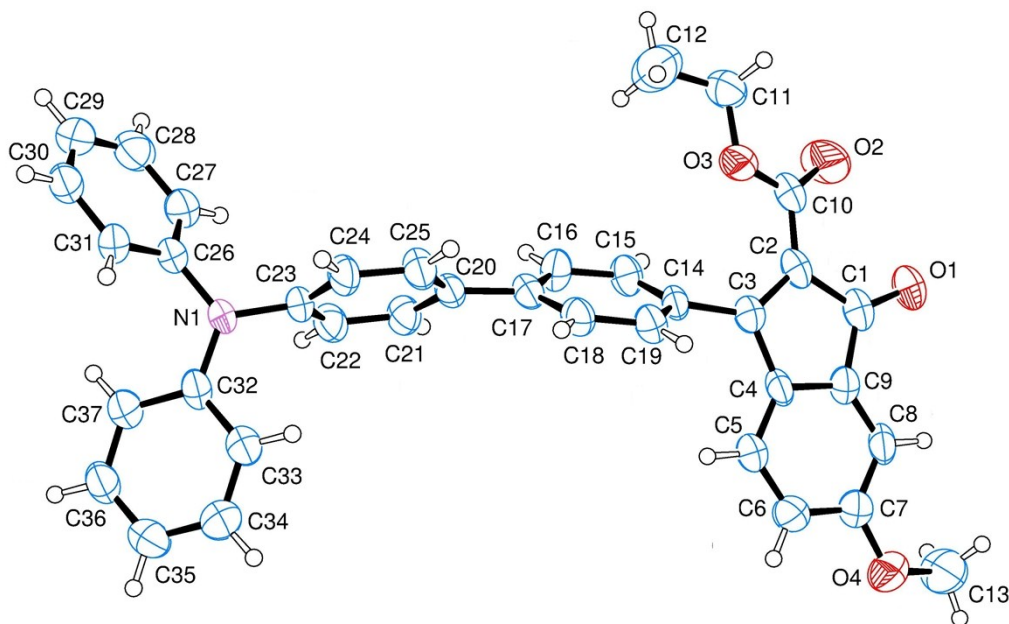


Figure ESI-11. Structure of compound **5b** found by crystallography. Ellipsoids enclose 50% probability.

Ethyl 3-[4'-(diphenylamino)biphenyl-4-yl]-1-hydroxy-6-methoxy-1-methyl-1H-indene-2-carboxylate (6b).

To a solution of **5b** (100 mg, 0.181 mmol) in dichloromethane (10 mL) was added a 2M solution of $Al(CH_3)_3$ in toluene (0.36 mL, 0.72 mmol). The resulting mixture was stirred under a nitrogen atmosphere at room temperature for 30 min, and then diluted with ethyl acetate (40 mL). The $Al(CH_3)_3$ excess was cautiously destroyed with a 1M NaOH solution (4.0 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 compound **6b** (43 mg, yield 42%) as a yellow oil. 1H NMR (400 MHz, $CDCl_3$): 1.09 (t, $J = 7.1$, 3H), 1.77 (s, 3H), 3.87 (s, 3H), 4.05-4.22 (m, 2H), 6.82 (dd, $J = 8.4$, 2.3, 1H), 7.04 (t, $J = 7.2$, 2H), 7.10-7.19 (m, 8H), 7.25-7.31 (m, 4H), 7.45 (d, $J = 8.2$, 2H), 7.53 (d, $J = 8.6$, 2H), 7.64 (d, $J = 8.3$, 2H). MS(ESI): m/z 590 ($M + Na^+$).

Ethyl 3-[4'-(diphenylamino)biphenyl-4-yl]-6-methoxy-1-methylene-1*H*-indene-2-carboxylate (4'-TPA-6-MO-BF3k).

A mixture of **6b** (10 mg, 0.0176 mmol) in CDCl₃ (0.80 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 1.0 mg, 0.00526 mmol) was heated to reflux for 30 min. The reaction mixture was then cooled to room temperature and purified by flash chromatography with CDCl₃ as the eluent to obtain a solution of pure monomer 4'-TPA-6-MO-BF3k in CDCl₃. ¹H NMR (500 MHz, CDCl₃): 1.08 (t, *J* = 7.1, 3H), 3.88 (s, 3H), 4.14 (q, *J* = 7.1, 2H), 6.34 (s, 1H), 6.61 (s, 1H), 6.84 (dd, *J* = 8.4, 2.3, 1H), 7.02-7.06 (m, 2H), 7.12-7.17 (m, 6H), 7.18-7.20 (m, 1H), 7.24-7.30 (m, 5H), 7.47 (m, 2H), 7.51-7.56 (m, 2H), 7.62-7.67 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): 13.9, 55.7, 60.0, 105.9, 114.0, 116.7, 123.0, 123.3, 123.7, 124.5, 126.0, 127.7, 129.2, 129.3, 133.1, 134.5, 139.1, 140.5, 143.9, 147.4, 147.6, 153.3, 160.7, 165.1. MS(ESI): *m/z* 572 (M + Na⁺).

Poly-[Ethyl 3-[4'-(diphenylamino)biphenyl-4-yl]-6-methoxy-1-methylene-1*H*-indene-2-carboxylate] (Poly-4'-TPA-6MO-BF3k).

A mixture of **6b** (230 mg, 0.405 mmol) in CHCl₃ (stabilized with amylene, 400 mL) containing *p*-toluenesulfonic acid monohydrate (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 NaHCO₃ saturated solution. The organic layer was dried over sodium sulfate, concentrated to a volume of 25 mL and purified by flash chromatography with CHCl₃ as the eluent to obtain a solution of pure monomer 4'-TPA-6-MO-BF3k in CHCl₃. The solution of the monomer was concentrated under reduced pressure and then dissolved again in CHCl₃. This procedure of dissolution/evaporation in CHCl₃ 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'-TPA-6-MO-BF3k (180 mg, yield 81%) as a yellow solid.

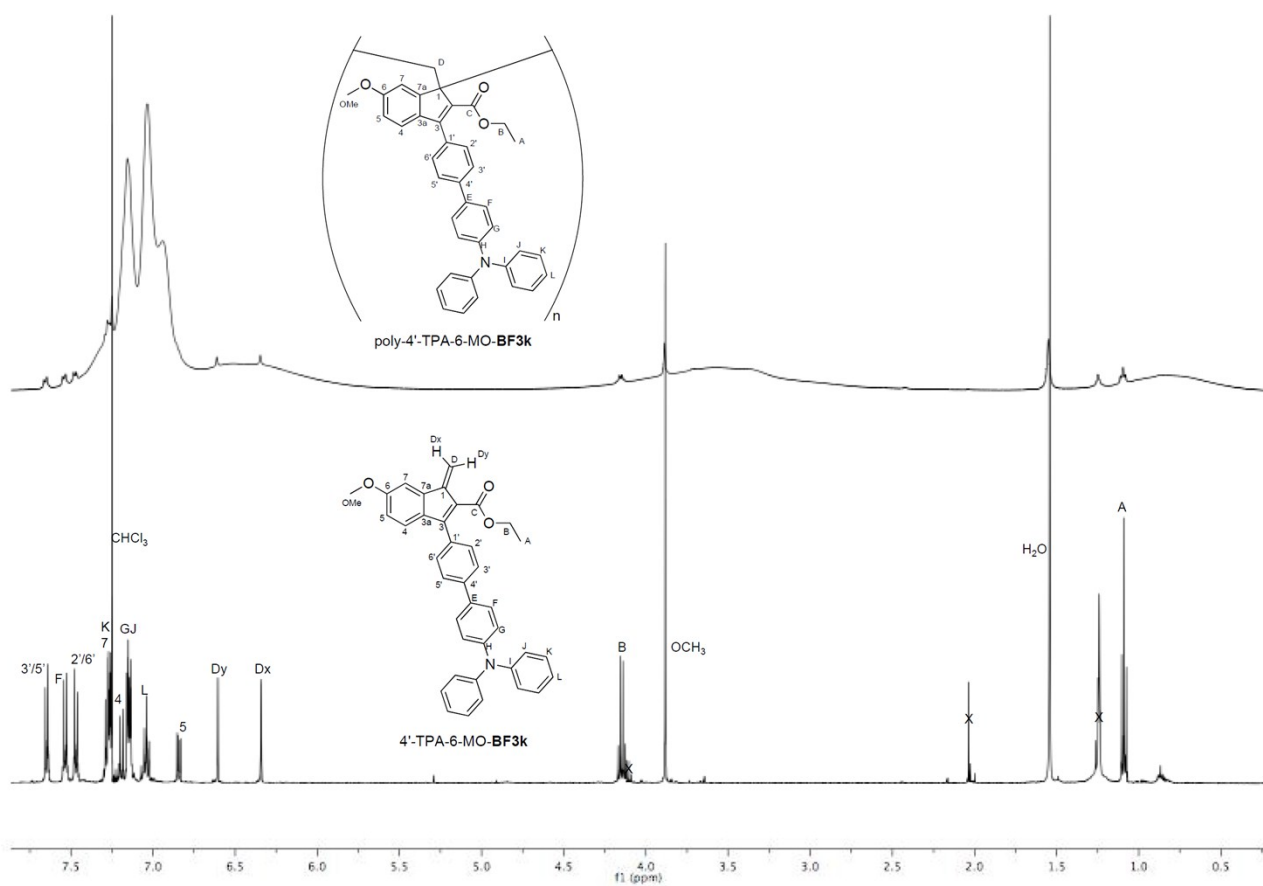


Figure ESI-12. Comparison of the ¹H NMR spectrum (CDCl₃) of monomer 4'-TPA-6-MO-BF3k with that of the corresponding polymer poly-4'-TPA-6-MO-BF3k.

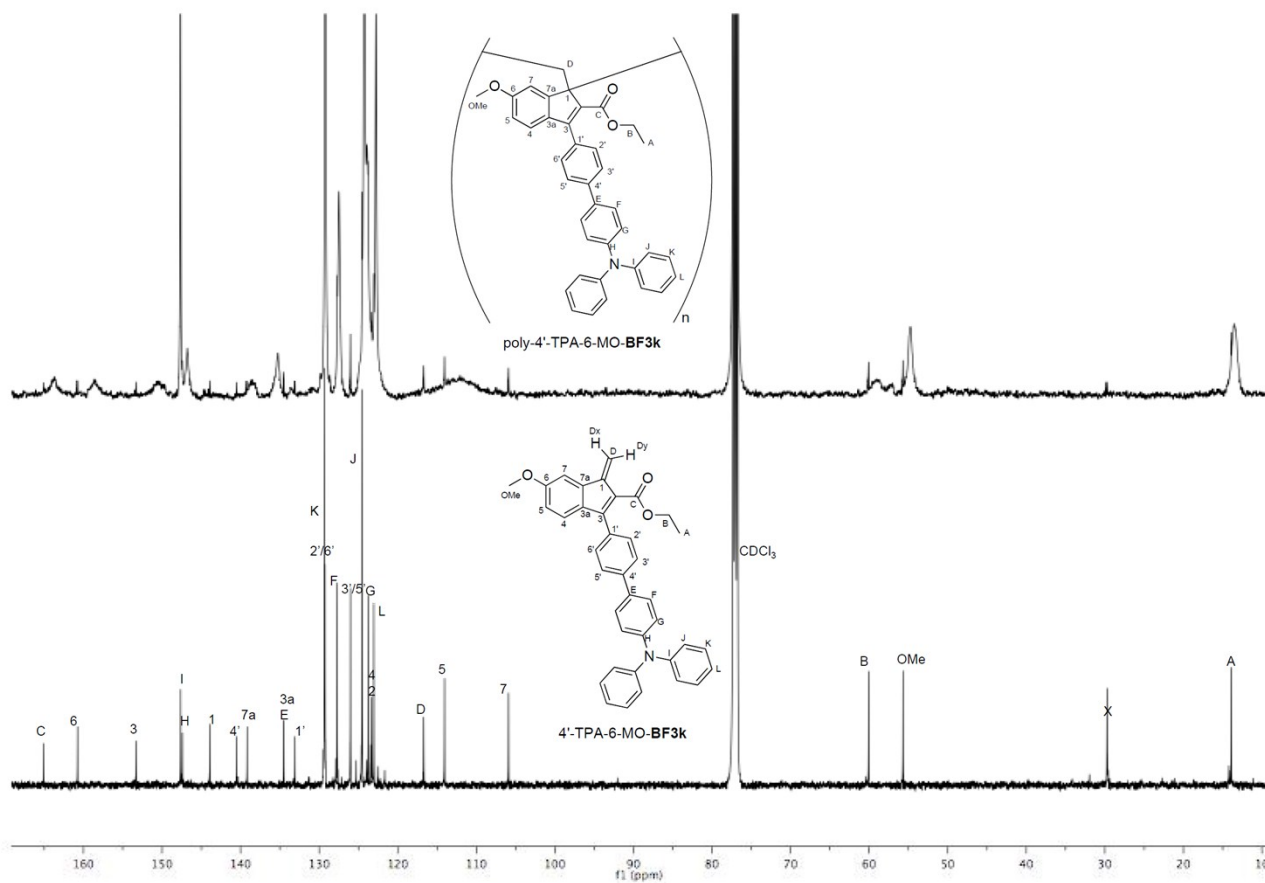


Figure ESI-13. Comparison of the ^{13}C NMR spectrum of monomer $4'-\text{TPA-6-MO-BF3k}$ with that of the corresponding polymer $\text{poly-4'-TPA-6-MO-BF3k}$.

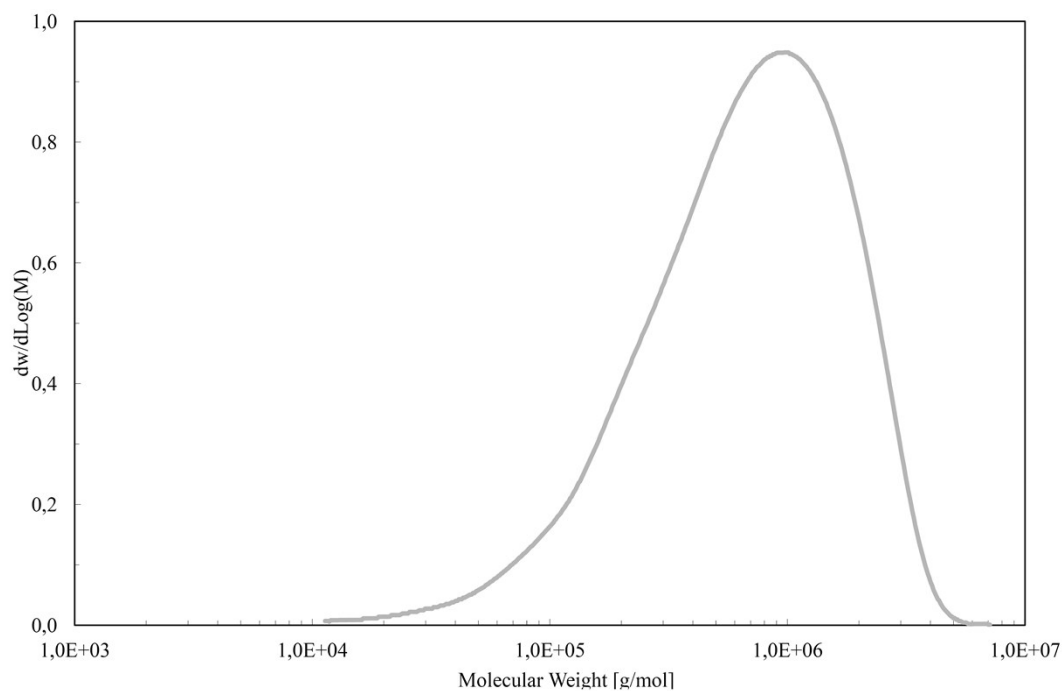


Figure ESI-14. Differential molecular weight distribution (MWD) of $\text{poly-4'-TPA-6-MO-BF3k}$.

References

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