Electronic Supplementary Information

Highly Emissive Supramolecular Assemblies Based on π-Stacked Polybenzofulvene Hosts and a Benzothiadiazole Guest

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Content:

PLE and PL spectra of blends of the polymers with **DTBT** (page 1)

Foerster radius values (pages 1 and 2)

Experimental details for the preparation and the characterization of the newly-synthesized polybenzofulvene derivatives (pages 3-13)

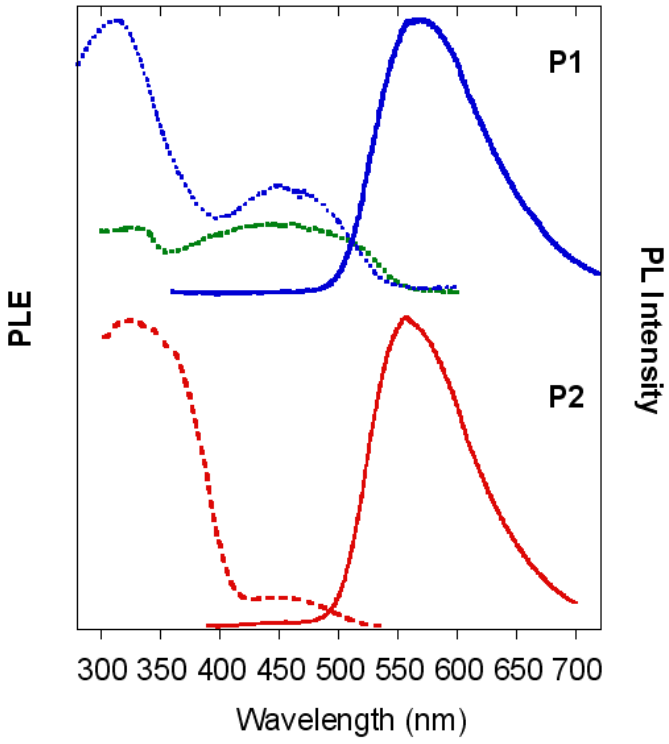

Figure ESI-1. PLE (dotted line) and PL (solid line) spectra of blends of the polymers with 5% (w/w) of **DTBT**, for poly-4'-DMFL-6-MO-**BF3k (P1**) (blue) and poly-6-DMFL-**BF3k** (**P2**) (red lines) cast films. PLE of **DTBT** cast film (green).

Foerster radius

The Foerster radius R_0 can be estimated according to the following formula:[1]

$$R_0^{\,6} = 8.79\times10^{-5}\left[k^2 n^{-4} QY_D J(\lambda)\right]$$

where k^2 is the orientation factor, assumed to be 2/3 for randomly oriented dipoles,[1] n is the refractive index of the medium (assumed to be 1.65 in poly-6-DMFL-**BF3k** (**P2**) and poly-4'-DMFL-6-MO-**BF3k (P1**) blends and 1.7 in **PVK** blends), QY_D is the quantum yield of the donor in the absence of the acceptor (0.16, 0.24 and 0.10 for **PVK**, **P2**, and **P1** matrices, respectively) and $J(\lambda)$, the spectral overlap between the donor emission and the acceptor absorbance, is obtained as follows:[1]

$$J(\lambda) = \frac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda)d\lambda}$$

where F_D is the corrected fluorescence intensity of the donor and ε_A is the molar extinction coefficient of **DTBT** (9700 M^{-1} cm^{-1}).[2]

Table ESI-1. Spectral Overlaps and R_0 Values.

Sample	$J(\lambda)$ [cm^{-1} M^{-1} nm^4]	R_0 [Å]
PVK-DTBT	1.53×10^{14}	23.7
P2-DTBT	2.57×10^{14}	27.6
P1-DTBT	2.44×10^{14}	23.6

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 AC200, 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 1-oxo-3-phenyl-6-(trifluoromethylsulfonyloxy)-1*H*-indene-2-carboxylate (2).

A mixture of **1** (ref 3) (1.00 g, 3.40 mmol) in dry dichloromethane (20 mL) containing TEA (1.4 mL, 10.0 mmol) was cooled at 0-5 °C, and trifluoromethanesulfonic anhydride (2.9 mL, 17.2 mmol) was added under an argon atmosphere. The resulting mixture was stirred at room temperature for 1 h and then treated with water and extracted with dichloromethane. 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 (85:15) as the eluent to afford compound **2** (1.20 g, yield 83%) as yellow crystals. An analytical sample was obtained by recrystallization from *n*-hexane-ethyl acetate by slow evaporation (yellow prisms, mp 97-98 °C). ^{1}H NMR (400 MHz, $CDCl_3$): 1.16 (t, J = 7.1, 3H), 4.21 (q, J = 7.1, 2H), 7.32 (m, 2H), 7.52 (m, 6H). MS(ESI): *m/z* 449 ($M + Na^+$).

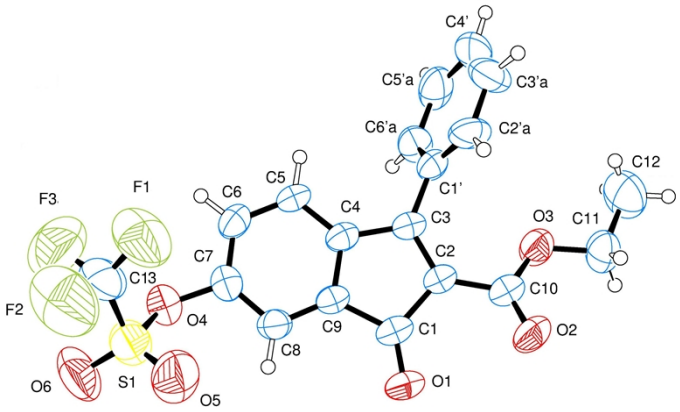

Figure ESI-2. Structure of compound **2** found by crystallography. Ellipsoids enclose 50% probability.

Ethyl 6-(9,9-dimethyl-9*H*-fluoren-2-yl)-1-oxo-3-phenyl-1*H*-indene-2-carboxylate (3).

In a microwave tube, a mixture of 9,9-dimethylfluorene-2-boronic acid pinacol ester (Aldrich, 147 mg, 0.459 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, $Pd(PPh_3)_2Cl_2$ (65 mg, 0.0926 mmol), PPh_3 (12 mg, 0.0458 mmol), and compound **8** (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. 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 **3** (120 mg, yield 56%) as a red-orange solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (red prisms, mp 162-163 °C). ^{1}H NMR (400 MHz, $CDCl_3$): 1.17 (t, *J* = 7.1, 3H), 1.54 (s, 6H), 4.22 (q, *J* = 7.1, 2H), 7.27 (d, *J* = 7.7, 1H), 7.35 (m, 2H), 7.46 (m, 1H), 7.50-7.62 (m, 6H), 7.66 (s, 1H), 7.69 (d, *J* = 7.7, 1H), 7.75 (m, 1H), 7.79 (d, *J* = 7.8, 1H), 7.94 (s, 1H). MS(ESI): *m/z* 471 ($M + H^+$).

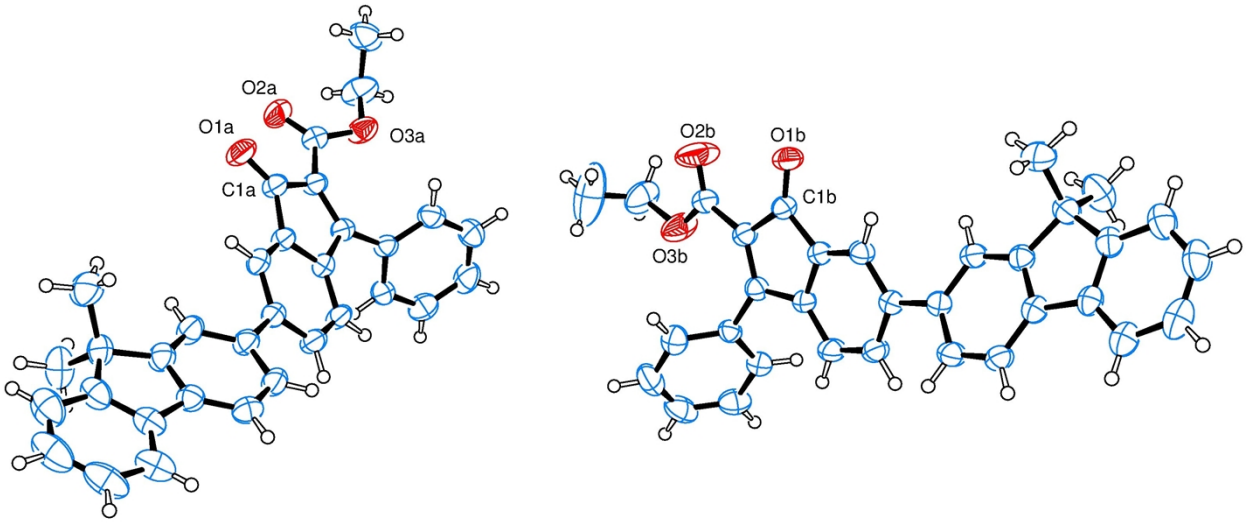

Figure ESI-3. Structure of compound **3** found by crystallography. Ellipsoids enclose 50% probability.

Ethyl 6-(9,9-dimethyl-9*H*-fluoren-2-yl)-1-hydroxy-1-methyl-3-phenyl-1*H*-indene-2-carboxylate (4).

To a solution of **3** (0.25 g, 0.531 mmol) in dichloromethane (10 mL) was added a 2M solution of $Al(CH_3)_3$ in toluene (1.1 mL, 2.2 mmol). The resulting mixture was stirred under a nitrogen atmosphere at room temperature for 30 min, and the $Al(CH_3)_3$ excess was then cautiously destroyed with a 1M NaOH solution. 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 (85:15) as the eluent to obtain indenol **4** (0.14 g, yield 54%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.07 (t, *J* = 7.1, 3H), 1.53 (s, 3H), 1.56 (s, 3H), 1.86 (s, 3H), 3.78 (s, 1H), 4.15 (m, 2H), 7.24 (d, *J* = 7.7, 1H), 7.34 (m, 2H), 7.40-7.51 (m, 6H), 7.60 (m, 2H), 7.70 (d, *J* = 1.3, 1H), 7.75 (dd, *J* = 6.3, 2.2, 1H), 7.78 (d, *J* = 7.9, 1H), 7.89 (d, *J* = 1.4, 1H). MS(ESI): *m/z* 509 ($M + Na^+$).

Ethyl 6-(9,9-dimethyl-9*H*-fluoren-2-yl)-1-methylene-3-phenyl-1*H*-indene-2-carboxylate (6-DMFL-BF3k).

A mixture of indenol **4** (18 mg, 0.037 mmol) in $CDCl_3$ (0.80 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 1.0 mg, 0.00526 mmol) was heated to reflux for 1 h. The reaction mixture was then cooled to room temperature and purified by flash chromatography with $CDCl_3$ as the eluent to obtain a solution of pure monomer 6-DMFL-**BF3k** in $CDCl_3$. ^{1}H NMR (600 MHz, $CDCl_3$): 1.07 (t, *J* = 7.1, 3H), 1.55 (s, 6H), 4.15 (q, *J* = 7.1, 2H), 6.50 (s, 1H), 6.67 (s, 1H), 7.31-7.38 (m, 3H), 7.41-7.50 (m, 6H), 7.59 (dd, *J* = 7.9, 1.5, 1H), 7.62 (dd, *J* = 7.9, 1.6, 1H), 7.68 (d, *J* = 1.4, 1H), 7.76 (m, 1H), 7.80 (d, *J* = 7.9, 1H), 7.98 (d, *J* = 1.4, 1H). MS(ESI): *m/z* 469 ($M + H^+$).

Poly-[Ethyl 6-(9,9-dimethyl-9*H*-fluoren-2-yl)-1-methylene-3-phenyl-1*H*-indene-2-carboxylate] (Poly-6-DMFL-BF3k).

A mixture of indenol **4** (180 mg, 0.37 mmol) in $CHCl_3$ (stabilized with amylene, 8.0 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 14 mg, 0.0736 mmol) was heated to reflux for 1 h. The reaction mixture was then cooled to room temperature and purified by flash chromatography with $CHCl_3$ as the eluent to obtain a solution of pure monomer 6-DMFL-**BF3k** in

$CHCl_3$. 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 ^1H NMR 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-**6-DMFL-BF3k** (121 mg, yield 70%) as a white solid.

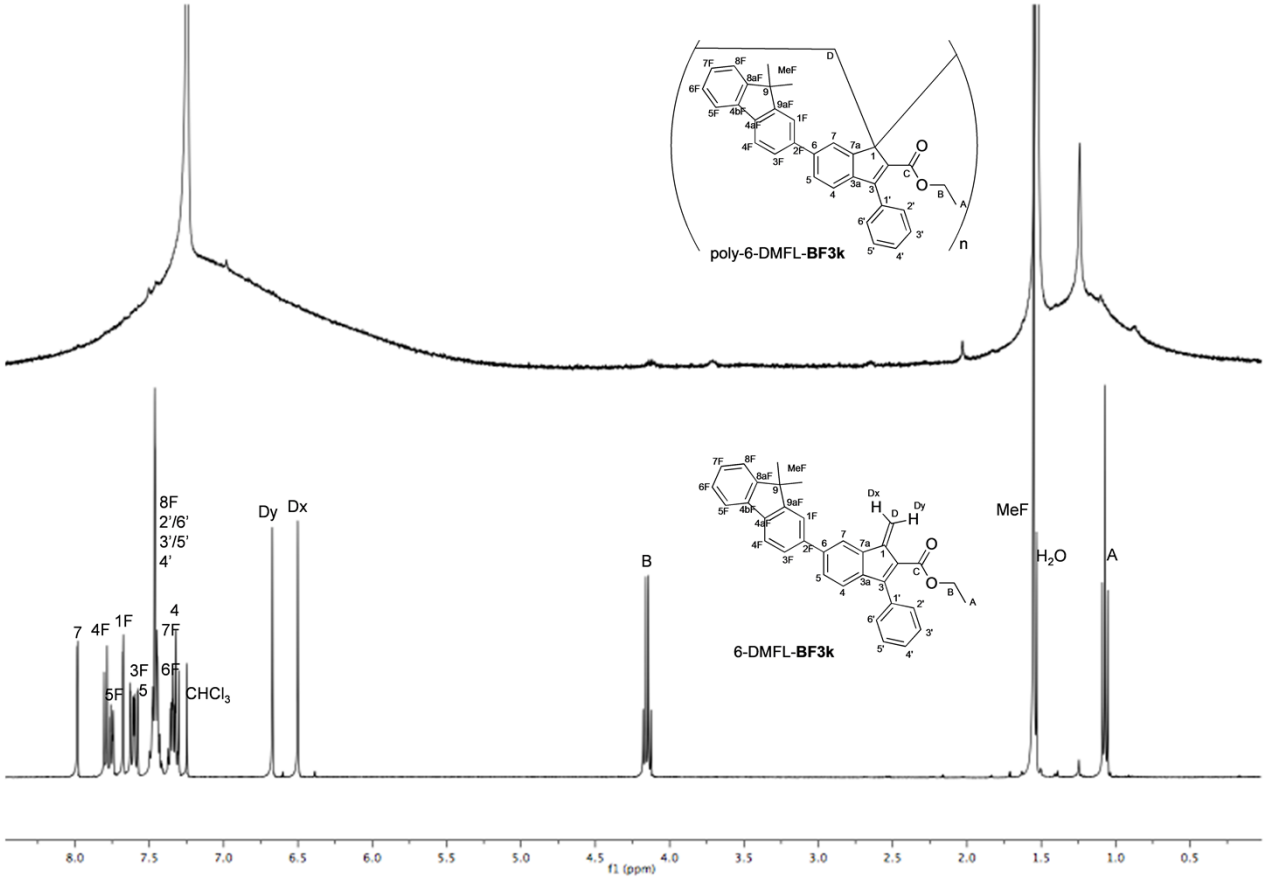

Figure ESI-4. Comparison of the ^1H NMR spectrum ($CDCl_3$) of monomer 6-DMFL-**BF3k** with that of the corresponding polymer poly-6-DMFL-**BF3k**.

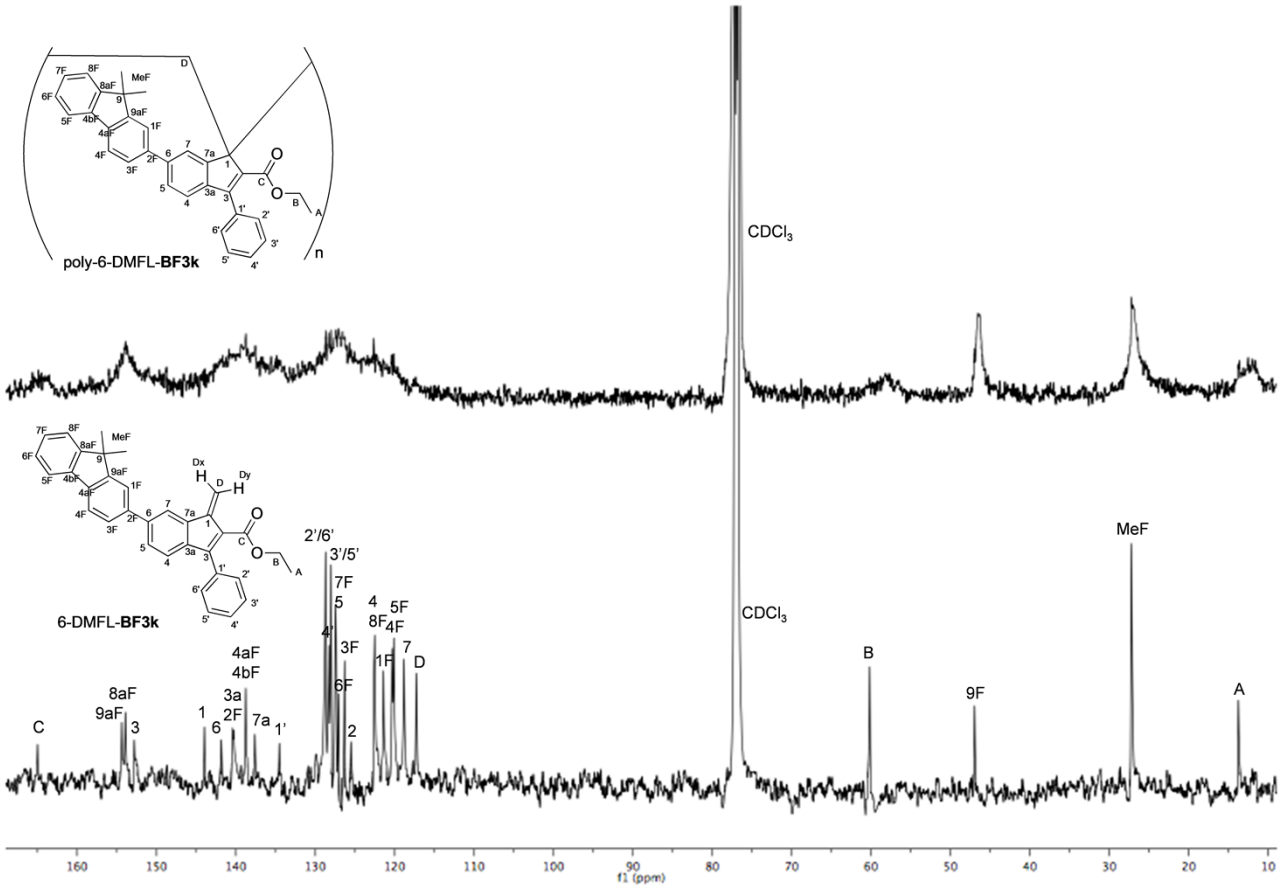

Figure ESI-5. Comparison of the ^{13}C NMR spectrum of monomer 6-DMFL-**BF3k** with that of the corresponding polymer poly-6-DMFL-**BF3k**.

Ethyl 3-(4-bromophenyl)-2-(3-methoxybenzyl)-3-oxopropanoate (6).

To a mixture of ethyl 3-(4-bromophenyl)-3-oxopropanoate (**5**, Aldrich, 2.00 g, 7.38 mmol), NaI (1.64 g, 10.9 mmol), and $NaHCO_3$ (1.84 g, 21.9 mmol) in dry DMF (40 mL) was added 3-methoxybenzylchloride (Aldrich, 1.16 g, 7.41 mmol). The resulting mixture was stirred at 50 °C for 7 h and then quenched with a saturated solution of NH_4Cl. The reaction mixture was extracted with 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 (9:1) to obtain compound **6** (2.67 g, yield 92%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): 1.11 (t, J = 7.1, 3H), 3.28 (m, 2H), 3.73 (s, 3H), 4.08 (m, 2H), 4.55 (t, J = 7.3, 1H), 6.70-6.77 (m, 3H), 7.15 (t, J = 7.3, 1H), 7.57 (d, J = 8.6, 2H), 7.79 (d, J = 8.5, 2H). MS(ESI): *m/z* 413, 415 ($M + Na^+$).

Ethyl 3-(4-bromophenyl)-6-methoxy-1*H*-indene-2-carboxylate (7).

Compound **6** (2.67 g, 6.82 mmol) was amalgamated and mixed with polyphosphoric acid (25 g) at room temperature for 1 h. The reaction mixture was then cautiously treated with water and extracted with 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 (9:1) as the eluent to obtain indene derivative **7** (1.84 g, yield 72%) as a white crystalline solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (colorless prisms, mp 125-126 °C). ^{1}H NMR (400 MHz, $CDCl_3$): 1.15 (t, J = 7.1, 3H), 3.80 (s, 2H), 3.85 (s, 3H), 4.12 (q, J = 7.1, 2H), 6.84 (dd, J = 8.5, 2.3, 1H), 7.09 (d, J = 2.0, 1H), 7.11 (d, J = 8.5, 1H), 7.28 (d, J = 8.3, 2H), 7.57 (d, J = 8.3, 2H). MS(ESI): m/z 395, 397 ($M + Na^+$).

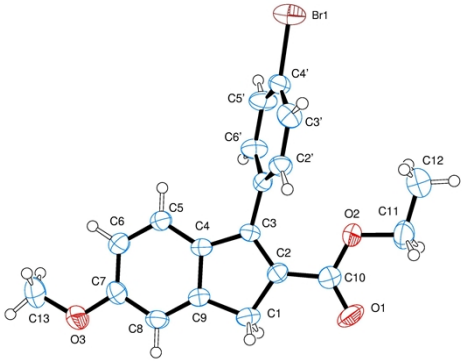

Figure ESI-6. Structure of compound **7** found by crystallography. Ellipsoids enclose 50% probability.

Ethyl 3-(4-bromophenyl)-6-methoxy-1-oxo-1*H*-indene-2-carboxylate (8).

A mixture of **7** (1.84 g, 4.93 mmol) in 1,4-dioxane (80 mL) containing SeO_2 (4.97 g, 44.7 mmol) was heated at reflux overnight. The reaction mixture was then treated with a saturated solution of $NaHCO_3$ and extracted with 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 **8** (1.60 g, yield 84%) as a red

solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (red prisms, mp 153-154 °C). ^{1}H NMR (400 MHz, $CDCl_3$): 1.19 (t, J = 7.0, 3H), 3.86 (s, 3H), 4.19 (q, J = 7.1, 2H), 6.81 (dd, J = 8.2, 2.4, 1H), 7.02 (d, J = 8.1, 1H), 7.17 (d, J = 2.3, 1H), 7.39 (d, J = 8.4, 2H), 7.62 (d, J = 8.4, 2H). MS (ESI): m/z 409, 411 ($M + Na^+$).

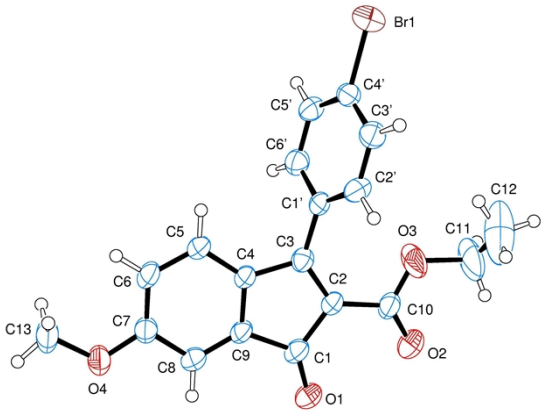

Figure ESI-7. Structure of compound **8** found by crystallography. Ellipsoids enclose 50% probability.

Ethyl 3-[4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl]-6-methoxy-1-oxo-1*H*-indene-2-carboxylate (9).

In a microwave tube, a mixture of 9,9-dimethylfluorene-2-boronic acid pinacol ester (Aldrich, 83 mg, 0.259 mmol) in 4.0 mL of dry THF and 0.5 mL of dry MeOH containing Cs_2CO_3 (250 mg, 0.77 mmol) was stirred at room temperature for 30 min. To the resulting mixture, $Pd(PPh_3)_2Cl_2$ (37 mg, 0.053 mmol), PPh_3 (7.0 mg, 0.027 mmol), and compound **8** (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 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 **9** (88 mg, yield 68%) as a red solid. An analytical sample was obtained by recrystallization from ethyl acetate by slow evaporation (red prisms, mp 167-168 °C). ^{1}H NMR (400 MHz, $CDCl_3$): 1.21 (t, J = 7.0, 3H),

1.54 (s, 6H), 3.87 (s, 3H), 4.23 (q, *J* = 7.1, 2H), 6.85 (dd, *J* = 8.2, 2.4, 1H), 7.18 (m, 2H), 7.35 (m, 2H), 7.46 (m, 1H), 7.64 (m, 3H), 7.70 (s, 1H), 7.78 (m, 4H). MS(ESI): *m/z* 523 ($M + Na^+$).

Ethyl 3-[4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl]-1-hydroxy-6-methoxy-1-methyl-1*H*-indene-2-carboxylate (10).

To a solution of **9** (110 mg, 0.219 mmol) in dichloromethane (10 mL) was added a 2M solution of $Al(CH_3)_3$ in toluene (0.44 mL, 0.88 mmol). The resulting mixture was stirred under a nitrogen atmosphere at room temperature for 45 min, and the excess of $Al(CH_3)_3$ was cautiously destroyed with a 1M NaOH solution. 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 **10** (55 mg, yield 49%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.12 (t, *J* = 7.1, 3H), 1.55 (s, 6H), 1.79 (s, 3H), 3.72 (s, 1H), 3.88 (s, 3H), 4.17 (m, 2H), 6.83 (dd, *J* = 8.4, 2.3, 1H), 7.15 (m, 2H), 7.34 (m, 2H), 7.44-7.52 (m, 3H), 7.64 (d, *J* = 7.9, 1H), 7.71-7.76 (m, 4H), 7.81 (d, *J* = 7.8, 1H). MS(ESI): *m/z* 539 ($M + Na^+$).

Ethyl 3-[4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl]-6-methoxy-1-methylene-1*H*-indene-2-carboxylate (4'-DMFL-6-MO-BF3k).

A mixture of **10** (10 mg, 0.0194 mmol) in $CDCl_3$ (0.70 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 1.0 mg, 0.00526 mmol) was heated to reflux for 1 h. The reaction mixture was then cooled to room temperature and purified by flash chromatography with $CDCl_3$ as the eluent to obtain a solution of pure monomer 4'-DMFL-6MO-**BF3k** in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$): 1.12 (t, *J* = 7.1, 3H), 1.54 (s, 6H), 3.89 (s, 3H), 4.17 (q, *J* = 7.1, 2H), 6.35 (s, 1H), 6.61 (s, 1H), 6.85 (dd, *J* = 8.4, 2.3, 1H), 7.20 (d, *J* = 8.4, 1H), 7.27 (d, *J* = 2.2, 1H), 7.35 (m, 2H), 7.45 (m, 1H), 7.51 (m, 2H), 7.64 (m, 1H), 7.71-7.78 (m, 4H), 7.80 (d, *J* = 8.0, 1H). MS(ESI): *m/z* 499 ($M + H^+$).

Poly-[Ethyl 3-[4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl]-6-methoxy-1-methylene-1*H*-indene-2-carboxylate] (Poly-4'-DMFL-6MO-BF3k).

A mixture of **10** (330 mg, 0.639 mmol) in $CHCl_3$ (stabilized with amylene, 20 mL) containing *p*-toluenesulfonic acid monohydrate (PTSA, 23 mg, 0.121 mmol) was heated to reflux for 1 h. The reaction mixture was then cooled to room temperature and purified by flash chromatography with $CHCl_3$ as the eluent to obtain a solution of pure monomer 4'-DMFL-6MO-**BF3k** in $CHCl_3$. 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 ^{1}H NMR 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'-DMFL-6MO-**BF3k** (192 mg, yield 60%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.4-1.7 (br m, 9H), 2.5-4.5 (br m, 7H), 5.7-8.0 (br m, 14H).

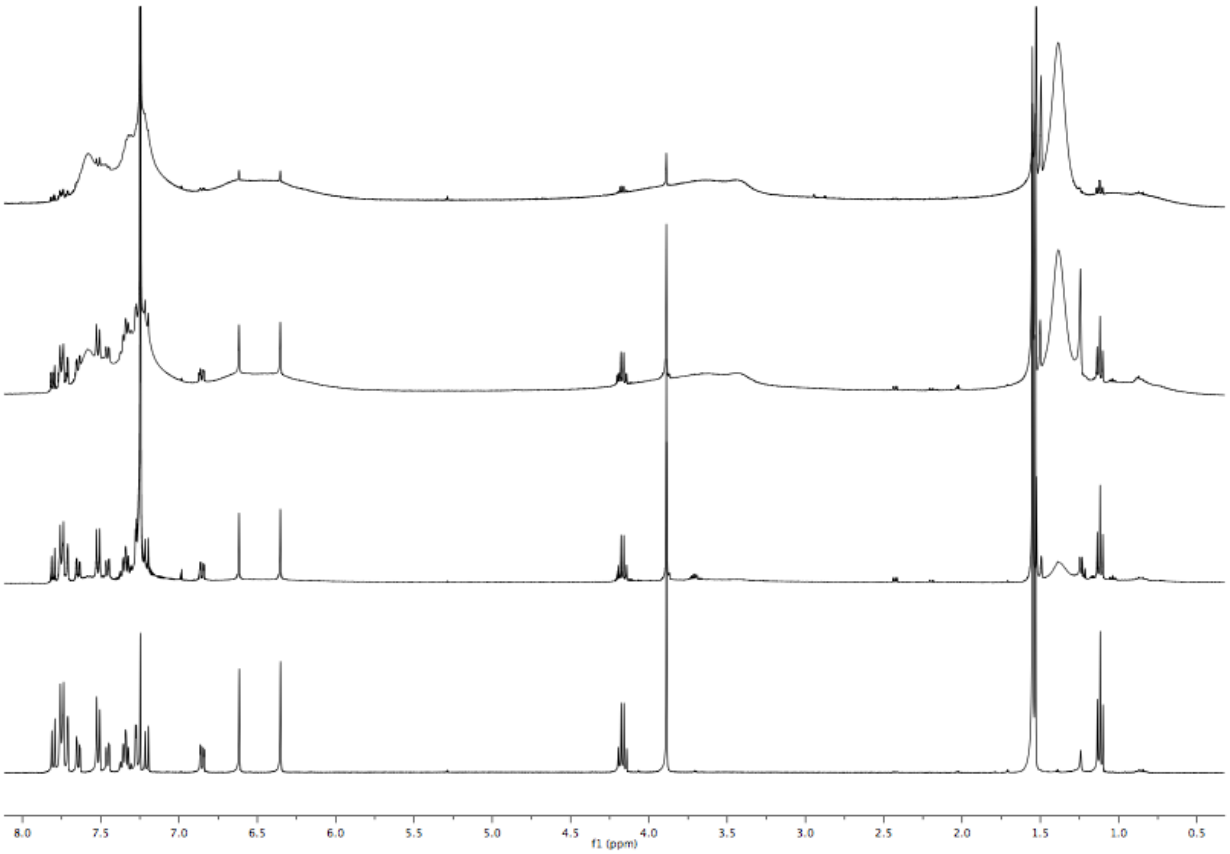

Figure ESI-8. Comparison of the ^{1}H NMR spectrum ($CDCl_3$) of monomer 4'-DMFL-6-MO-**BF3k** (bottom trace) with that of the corresponding polymer poly-4'-DMFL-6-MO-**BF3k** at the various stages of the spontaneous polymerization.

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