

Chain-Growth Suzuki–Miyaura Condensation

Polymerization of Fluorene Co-Polymers

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Supporting Information

General.

Measurements.

^1H NMR (400 MHz) spectra was recorded using a Bruker Avance QNP 400. Chemical shifts are recorded in ppm (δ) either in CDCl_3 , THF (d8) or toluene (d8) with the internal references set to δ 7.250, 3.580 or 6.980 ppm, respectively. ^{13}C NMR (125 MHz) spectra was recorded using a Bruker Avance Cryoprobe ATM TCI DRX 500 or a Bruker Avance 500 BB-ATM. Chemical shifts are recorded in ppm (δ) in CDCl_3 with the internal reference set to δ 77.230 ppm. Column chromatography was preformed with Material-Harvest Silica Gel 60 (40-63 μm). M_n and M_w/M_n values of polymers were measured with gel-permeation chromatography (GPC) with UV detector using tetrahydrofuran (THF) as eluent which was calibrated with polystyrene standards, at room temperature. MALDI-TOF mass spectra were recorded on Applied Biosystems in linear mode, using 1,1,4,4,-tetraphenyl-1,3-butadiene as a matrix. Absorption spectra were recorded with Carry 400 UV/visible spectrometer, and photoluminescence spectra were measured with Cary Eclipse fluorimeter.

Materials

2,7-dibromo-9,9-dioctyl-9H-fluorene, triisopropyl borate, 1,8-diaminonaphthalene, bis(pinacolato)diboron, CsF, potassium acetate, pinacol, 1,1'-Bisdiphenylphosphino ferrocene (dppf) and THF (sealed bottle, initiator free) were purchased from Sigma-Aldrich and used as received. Phenyl-bromide, CH_2Cl_2 and CHCl_3 were freshly distilled before use and purchased from Sigma Aldrich. Bromo-pyrene, *n*-Butyllithium and DMSO were purchased from Acros and used as received. Palladium (II) acetate ($\text{Pd}(\text{OAc})_2$), $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ and 1,1'-Bis(diphenylphosphino) ferrocene-palladium(II)dichloride (PdCl_2 (dppf)) were purchased from Strem. 4,7-dibromobenzo[c][1,2,5]thiadiazole was synthesized by Cambridge Technology Display (CDT). 2,7-dibromo-9,9-dioctyl-9H-fluorene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**) was prepared according to the literature¹.

1) (7-bromo-9,9-dioctyl-9H-fluoren-2-yl)boronic acid (2)

2,7-dibromo-9,9-dioctyl-9H-fluorene (4 g, 7.30 mmol, 1 eq.) was dissolved in dry THF (50 mL) at -78°C and *n*BuLi (4.80mL of a 1.6 M solution in hexane, 7.66 mmol, 1.1 eq.) was slowly added to it. The resulting white milky solution stirred for 1 h before triisopropyl borate (1.44 g, 7.66 mmol, 1.1 eq.) was added in one portion. After another 1 h, the solution was allowed to warm to room temperature and stirred for 18 h. Water (10 mL) and 1 M HCl (10 mL) were added and the layers were separated, the organic phase was dried over MgSO_4 and the solvent was evaporated *in vacuo*. Column chromatography (silica gel 20 to 80% CH_2Cl_2 /hexane) enabled isolation of the pure product **2** as a white powder (2.32 g, 4.53 mmol, 62%). ^1H NMR (400 MHz, CDCl_3): δ 0.70 (m, 4H), 0.79-0.82 (t, 6H), 1.11-1.20 (m, 20H), 1.98-2.19 (m, 4H), 7.51-7.53 (d, 1H), 7.56 (s, 1H), 7.67-7.69 (d, 1H), 7.86-7.88 (d, 1H)< 8.23 (s, 1H), 8.32-8.34 (d, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.34, 23.17, 24.34, 25.86, 29.97, 30.60, 32.58, 40.89, 56.34, 78.00, 84.94, 120.11, 122.35, 127.01, 129.51, 130.33, 134.98, 140.89, 143.92, 150.54, 154.61. HRMS GC-MS): (*m/z*) calculated for $\text{C}_{29}\text{H}_{42}\text{BBrO}_2$ [M]⁺: 512.25012; found: 512.22011 (error: 1.987e-06).

2) 2-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine

A mixture of (7-bromo-9,9-dioctyl-9H-fluoren-2-yl)boronic acid (3 g, 5.86 mmol, 1 eq.) and 1,8-diaminonaphthalene (0.95 g, 5.98 mmol, 1.02 eq.) in toluene (50 mL) was heated for 2 h under reflux with azeotropic removal of water. After 2 h, water (10 mL) was added and the layers were separated, the organic phase was dried over MgSO_4 and the solvent was evaporated *in vacuo*. Purification of the product was carried out by a column chromatography (silica gel, 20 % CH_2Cl_2 /hexane), to obtain 3.35 g of the product (5.27 mmol, 90%). ^1H NMR (400 MHz, CDCl_3): δ 0.60 (m, 4H), 0.79-0.83 (t, 6H), 1.06-1.21 (m, 20H), 1.91-2.03 (m, 4H), 6.07 (s, 2H), 6.45-6.47 (d, 2H), 7.06-7.08 (d, 2H), 7.14-7.18 (d, 2H), 7.44-7.49 (m, 2H), 7.57-7.62 (m, 3H), 7.69-7.74 (d, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.10, 22.63, 23.65, 23.75, 29.24, 29.97, 31.81, 40.34, 55.54, 106.04, 117.86, 119.65, 121.41, 121.60, 125.51, 126.27, 127.66, 130.06, 130.38, 136.41, 139.48, 141.11, 142.23, 150.13, 153.26. HRMS (GC-MS): (*m/z*) calculatd for $\text{C}_{39}\text{H}_{48}\text{BBrN}_2$ [M] $^+$: 634.31360; found: 634.31580 (error: 3.385e-06).

3) 3-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (3)

Under a nitrogen atmosphere, a mixture of 2-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (3 g, 4.73 mmol, 1 eq.), bis(pinacolato)diboron (1.32 g 5.2 mmol, 1.1 eq.), potassium acetate (1.53 g, 15.6 mmol, 3 eq.) and PdCl_2 (dppf) (103.84 mg, 0.14 mmol, 0.03 eq.) in DMSO (65 mL) was heated at 80°C for 17 h. After cooling to room temperature, water (10 mL) was added to the mixture. After extraction with 20 mL CHCl_3 , the organic layer was washed with brine (20mL) and dried over MgSO_4 . The solvent was evaporated under vacuum. The crude product was purified by flash chromatography (silica gel, 0 to 30% CH_2Cl_2 /hexane), and 2.42 g of 3 were obtained (3.55 mmol, 75%). ^1H NMR (400 MHz, CDCl_3): δ 0.65 (m, 4H), 0.81-0.84 (t, 6H), 1.06-1.21 (m, 20H), 1.42 (s, 12H), 2.02-2.10 (m, 4H), 6.15-6.46 (s, 2H), 6.46-6.48 (d, 2H), 7.07-7.09 (d, 2H), 7.15-7.17 (t, 2H), 7.62-7.64 (d, 2H), 7.76-7.80 (t, 2H), 7.85 (s, 1H), 7.88-7.90 (d, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.05, 22.58, 23.69, 24.94, 29.20, 29.21, 29.97, 31.78, 40.27, 55.21, 83.78, 105.98, 117.75, 119.31, 119.83, 119.95, 125.54, 125.54, 127.63, 128.92, 130.38, 133.77, 136.38, 141.16, 143.15, 143.39, 150.16, 151.08. HRMS (GC-

MS): (*m/z*) calculated for C₄₅H₆₀B₂N₂O₂ [M]⁺: 682.485; found: 682.51130 (error: 3.326e-06).

4) 4-(7-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-9,9-dioctyl-9H-fluoren-2-yl)-7-bromobenzo[c][1,2,5]thiadiazole (4)

Under nitrogen atmosphere, a mixture of, 4,7-dibromobenzo[c][1,2,5]thiadiazole (1.28 g, 4.39 mmol, 1.5 eq.), 2M CsF (0.89 g, 5.86 mmol, 2 eq.) Pd(OAc)₂ (13.16 mg, 58.5 μ mol, 0.02 eq.) and dppf (32.43 mg, 58.5 μ mol, 0.02 eq.) were dissolved in 10 mL THF. (3) (2 g, 2.93 mmol, 1 eq.) was dissolved in 10 mL THF and added to the solution dropwise. After 2 d in room temperature, water (10 mL) was added to the reaction mixture, and the organic phase was extracted with CH₂Cl₂ (20 mL). Then, the organic phase was dried over magnesium sulphate and the solvent was evaporated in *vacuo*. The crude product was purified by silica by column chromatography (silica gel 0 to 30 % CH₂Cl₂/ hexane) to afford the corresponding coupling yellow product 4 in 60% yield. ¹H NMR (400 MHz, CDCl₃): δ 0.58-0.73 (m, 10H), 1.02-1.13 (m, 20H), 1.95-2.08 (m, 4H), 6.04 (s, 2H), 6.40-6.42 (d, 2H), 6.98-7.02 (d, 2H), 7.08-7.02 (d, 2H), 7.56-7.60 (m, 3H), 7.75-7.60 (m, 3H), 7.81-7.84 (m, 2H), 7.86-7.91 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 1.03, 14.08, 23.12, 25.64, 29.74, 29.10, 30.54, 32.73, 36.84, 40.77, 50.77, 53.55, 109.77, 112.63, 119.38, 120.99, 121.66, 122.68, 122.87, 123.89, 129.79, 132.17, 132.39, 135.26, 136.69, 136.89, 140.42, 141.78, 143.96, 143.88, 143.53, 150.83, 158.22, 162.10. HRMS (GC-MS): (*m/z*) calculated for C₄₅H₅₀BBrN₄S [M]⁺: 768.30056; found: 768.29782 (error: 1.215e-06).

5) 4-bromo-7-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (5)

To a solution of 4-(7-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-9,9-dioctyl-9H-fluoren-2-yl)-7-bromobenzo[c][1,2,5]thiadiazole (1g, 1.55 mmol, 1 eq.) in THF (2 mL) under air, 4M HCl was added (2.32 mL, 6 eq.) at room temperature for 48 h. Afterwards, the organic phase was extracted with CH₂Cl₂ (5 mL) and dried over MgSO₄. Upon evaporating off the solvent, the crude product of (7-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)-9,9-dioctyl-9H-fluoren-2-yl)boronic acid was

obtained. 0.5 g of the crude product (0.68 mmol, 1 eq.) and 244 mg pinacol (2.06 mmol, 3eq.) were dissolved in 10 mL dry DCM. The reaction mixture was heated up to reflux with azeotropic removal of water for 2 d. The final product was purified *via* flash column chromatography (silica gel 50% DCM /hexane) to give 0.446 g (0.61 mmol, 90%) of the titled product. ¹HNMR (400 MHz, CDCl₃): δ 0.62-0.70 (m, 4H), 0.75-0.81 (t, 6H), 1.05-1.21 (m, 20H), 1.39 (s, 12H), 1.98-2.05 (m, 4H), 7.62-7.64 (d, 1H), 7.74-7.78 (m, 2H), 7.82-7.86 (m, 3H), 7.90-7.94 (m, 2H). ¹³CNMR (125MHz, CDCl₃): δ 1.03, 14.06, 22.59, 23.79, 24.96, 29.18, 29.98, 31.79, 40.11, 55.34, 83.77, 112.75, 119.33, 120.23, 123.91, 128.03, 128.10, 128.96, 132.29, 133.87, 134.60, 135.69, 141.56, 143.43, 150.49, 151.84, 153.35, 153.97. HRMS (GC-MS): (*m/z*) calculated for C₄₁H₅₄BBrN₂O₂S [M]⁺: 728.32304; found: 728.31437 (error: 1.114e-06). Anal. Calcd for C₄₁H₅₄BBrN₂O₂S: C, 67.49; H, 7.46; N, 3.84. Found: C, 67.28; H, 7.25; N, 3.41.

7) Synthesis of the initiator (6a)^{1, 2}

All the following operation was performed under glove-box atmosphere. Pd(P^tBu₃)₂ (200 mg, 0.39 mmol) and phenyl-bromide (2.04 mL, 9.80 mmol) were mixed together under argon atmosphere at 70°C for 2.5 h. The reaction mixture was then poured into cold hexane (10 mL) and stand in the fridge for another 1 h until yellow/orange precipitate was formed. The latter was collected by filtration, washed for 5 times with cold hexane (4 mL) and dried under reduced vacuum for at least 3 h, and then the yellow powder (90 mg, 50%) was stored inside a glove-box fridge. The nmr spectra are in agreement with the literature. ¹HNMR (400 MHz, Tol-*d*₈): δ 1.10-1.13 (d, 27H), 6.60-6.70 (t, 1H), 6.77-6.80 (t, 2H), 7.35-7.35 (d, 2H). ¹³CNMR (125MHz, C₆H₆-*d*₆): δ 32.12, 40.28, 124.05, 127.24, 129.07, 137.07. ³¹PNMR (121 MHz, Tol-*d*₈): δ 64.95

8) Synthesis of the initiator (6b)

All the following operation was performed under glove-box atmosphere. In similarity to the previous procedure, Pd(P^tBu₃)₂ (110 mg, 0.45 mmol) and bromo-pyrene (124.8 mg, 0.45 mmol) were mixed together with toluene under argon atmosphere at 70°C for 4 h. The reaction mixture was then poured into cold pentane (20 mL) and kept in 4°C for another 1 h until bright yellow precipitate was formed. The latter was

collected by filtration, washed 5 times with cold pentene (4 mL) and dried under reduced vacuum for at least 3 h. The yellow powder (146.6 mg, 70%) was stored inside a glove-box fridge. ^1H NMR (400 MHz, Tol- d_8): δ 1.05-1.09 (d, 27H), 7.56-7.58 (d, 1H), 7.66-7.385 (m, 3H), 7.82-7.84 (d, 1H), 7.89-7.91 (d, 1H), 7.98-8.00 (d, 1H), 8.18-8.21 (dd, 1H). ^{13}C NMR (125 MHz, Tol- d_8) ^{31}P NMR (121 MHz, Tol- d_8): δ 62.28

9) Typical polymerisation procedure.

The polymerization of the both of the monomers F8BT and F8 by initiation with 2a or 2b, was followed by the same protocol. Under argon atmosphere, monomer (30 mg, 0.50 mmol), 18-crown-6 ether (350 mg, 1.31 mmol) and CsF (84 mg, 0.55 mmol) were dissolved in anhydrous THF (stabilizer free, 5.2 mL) and 0.78 mL water (1:15 THF:water). The reaction flask was cool down to 0°C and the polymerization was initiated by fast injection of the monomer solution into the initiator flask (2.5 μmol , 1 mM), which was also cooled down to 0°C. After 3 h (for Pyr-pF8 polymer) or 24 h (for Pyr- pF8BT polymer) the reaction was quenched with a mixture of 1:1 2M HCl:methanol. The precipitate was collected by filtration, washed with water and dried under a vacuum oven for 24 h to give either pF8BT as a dark orange/red powder or pF8 in a light yellow color powder. The residue was dissolved in THF and filtrated in order to be analyzed by NMR, THF GPC and MALDI-TOF mass spectrum to determine PDI and M_n .

Ph-pF8BT (7a):

M_n = 7379, PDI=1.27 (crude GPC, PS standards). MALDI-TOF mass spectrum is shown and discussed in the main text. Yield: 83% ^1H NMR (400 MHz, CDCl_3 , Figure 3S): δ 0.77 (m, 10H), 1.13 (m, 20H), 2.02(m, 4H), 7.91-7.96 (m, 4H), 8.01 (s, 2H), 8.07 (d, 2H). The small peaks that are marks with stars in Figure S3 are attributed to the phenyl at the initiator end, as has been seen before.^{1,3}

UV spectrum of the polymer is shown in Figure S8b.

Pyr-pF8BT (7b):

$M_n = 7,379$, PDI=1.30 (crude GPC, PS standards). MALDI-TOF mass spectrum is shown and discussed in the main text. Yield: 87% ^1H NMR (400 MHz, CDCl_3 , Figure S7): δ 0.78 (m, 10H), 1.14 (m, 20H), 2.01(m, 4H), 7.92-7.96 (m, 4H), 7.96-8.01 (s, 2H), 8.07-8.09 (d, 2H). The small peaks that are marks with stars in Figure S7 are attributed to the pyrene at the initiator end.

UV spectrum of the polymer is shown in Figure S8b.

Ph-pF8 :

$M_n = 13,359$, PDI=1.48 (crude GPC, PS standards). Yield: 88%

^1H NMR (400 MHz, CDCl_3): δ 0.82 (m, 10H), 1.14 (m, 20H), 2.13 (m, 4H), 7.64 (s, 2H), 7.70 (d, 2H), 7.85 (d, 2H). Small peaks at 7.35-7.55 ppm are attributed to the phenyl group at the initiator end, as has been seen before.^{1,3}

UV spectrum of the polymer is shown in Figure S8a.

Pyr-pF8 (9):

$M_n = 9,556$, PDI=1.41 (crude GPC, PS standards). MALDI-TOF mass spectrum is shown and discussed in the main text. Yield: 90% ^1H NMR (400 MHz, CDCl_3): δ 0.79 (m, 10H), 1.12 (m, 20H), 2.10 (4H), 7.66-7.69 (m, 4H), 7.82-7.83 (d, 2H). The small peaks that are marks with stars in Figure S5 are attributed to the pyrene at the initiator end.

UV spectrum of the polymer is shown in Figure S8a.

10) A) The number average molecular weight (M_n) values from MALADI-TOF measurements were calculated by using the relative intensities as the number of polymer chains (N_i). The following equation was used:

$$M_n = \frac{\sum M_i N_i}{\sum N_i}$$

where N_i is the number of molecules of molecular weight M_i .

B) The weight average molecular weight (M_w) was calculated by using the following equation:

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$$

where N_i is the number of molecules of molecular weight M_i

C) Polydispersity index was calculated by dividing weight average molecular weight (M_w) by the number average molecular weight (M_n), i.e.

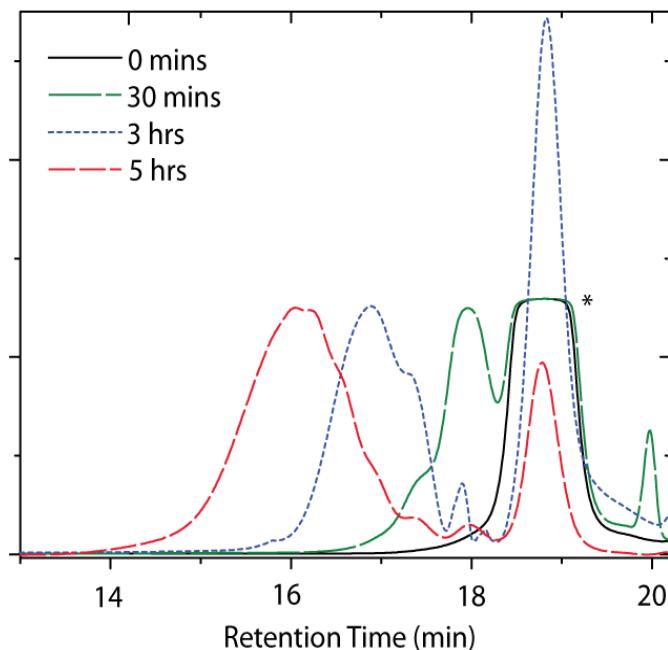


Figure S1. Crude GPC profiles (collected at 314nm) of Ph-pF8BT (**7a**) which were taken while the polymerization took place at different time, without removing the monomer from the mixture; obtained by the polymerization of **5** with 5 mol% of **6a** in a mixture of THF and 2M CsF at 0°C at $[5]_0/[6a]_0=20$. As can be expected from a chain-growth, the concentration of the monomer decreases while the polymer peak shifts in a unimodal fashion to high MW.

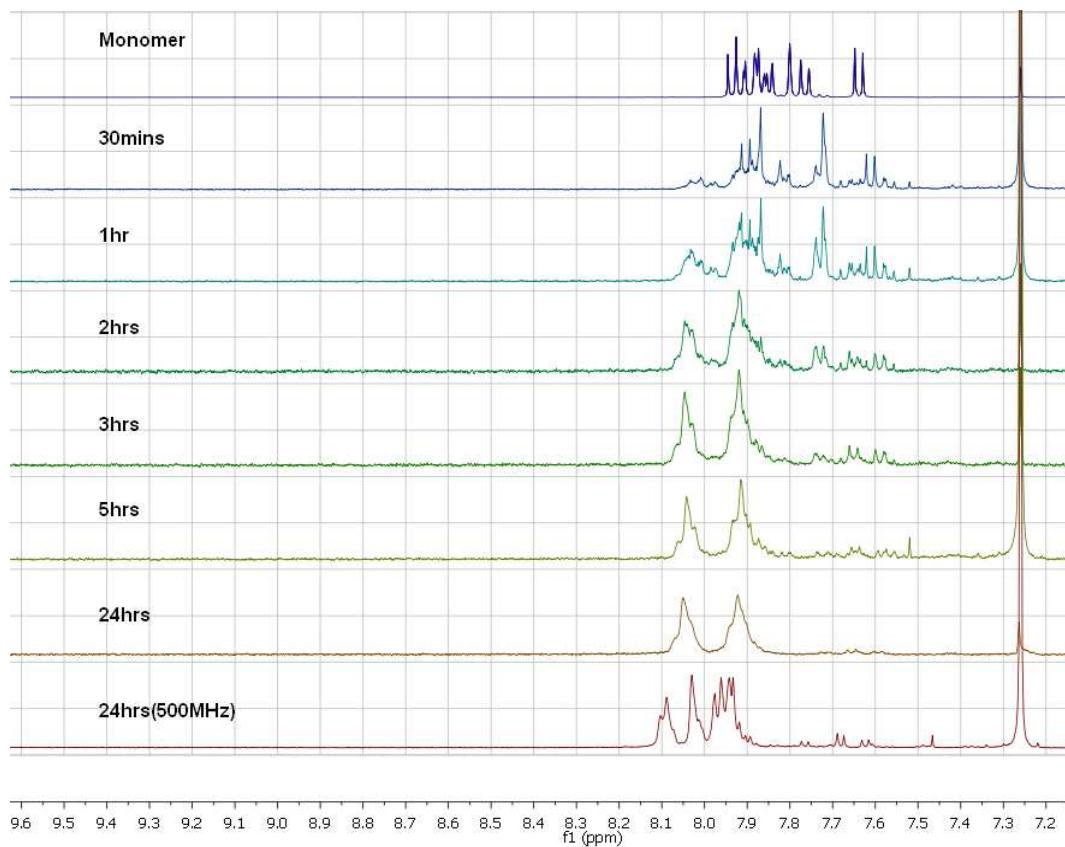


Figure S2. ¹H NMR spectra (in CDCl₃) of polymer **7a** obtained by the polymerization of **5** with 5 mol% of **6a** in a mixture of THF and 2M CsF at 0°C after 24 hours. The samples were taken at regular time intervals during the polymerization, precipitated, and re-dissolved in CDCl₃. All the spectra were measured with 400MHz machine except the last one which was measured with 500 MHz machine to obtain higher resolution.

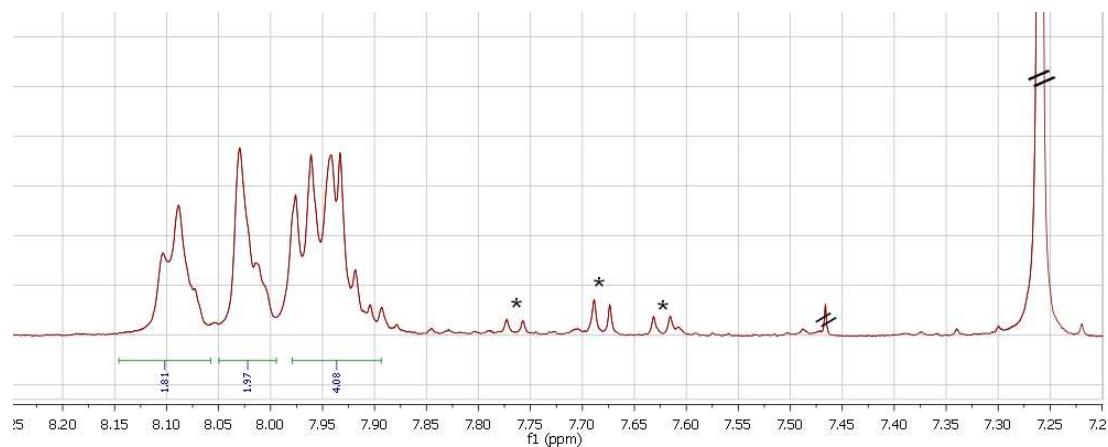


Figure S3. ¹H NMR spectrum (in CDCl₃) of polymer **7a** obtained by the polymerization of **5** with 5 mol% of **6a** in a mixture of THF and 2M CsF at 0°C after 24 hours. The small peaks at 7.56-7.73ppm which are marked with stars are attributed to the phenyl group at the initiator end, as has been seen before.^{1,3}

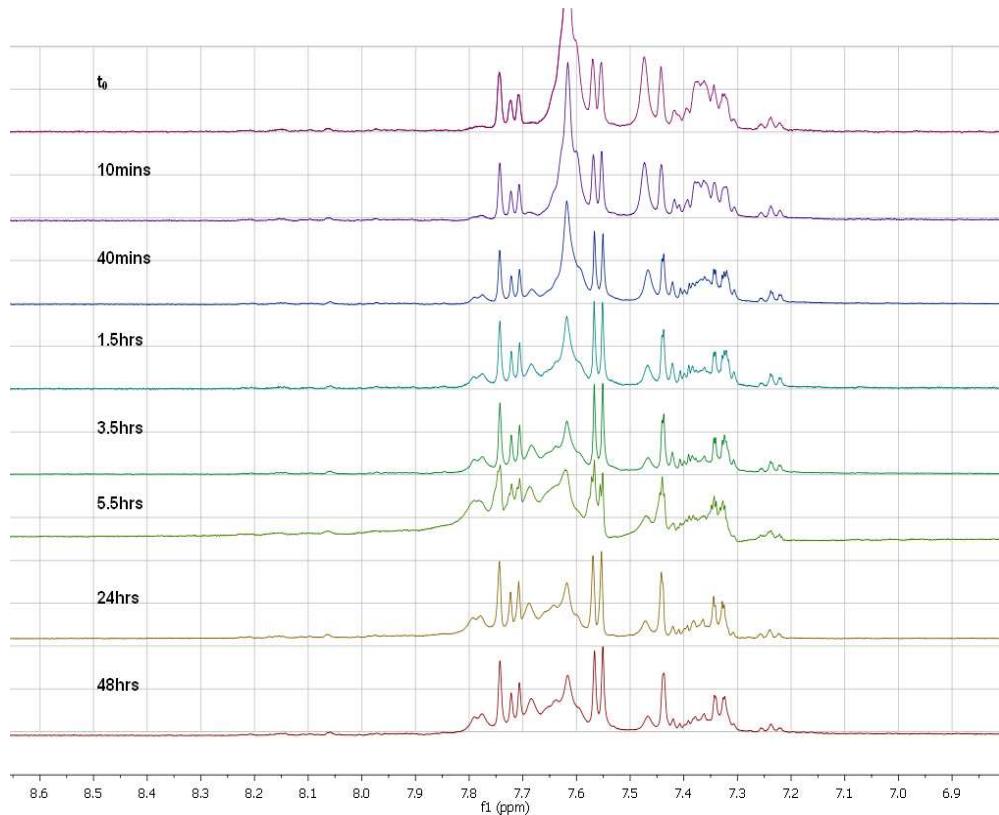


Figure S4. ^1H NMR spectra (in THF, d_8) of polymer Pyr-F8 (**9**) obtained by the polymerization of monomer **8** with 5 mol% of **6b** in a mixture of THF and 2M CsF at 0°C . The polymerization was carried out in a NMR tube in-situ in order to follow the reaction kinetic for 2 days.

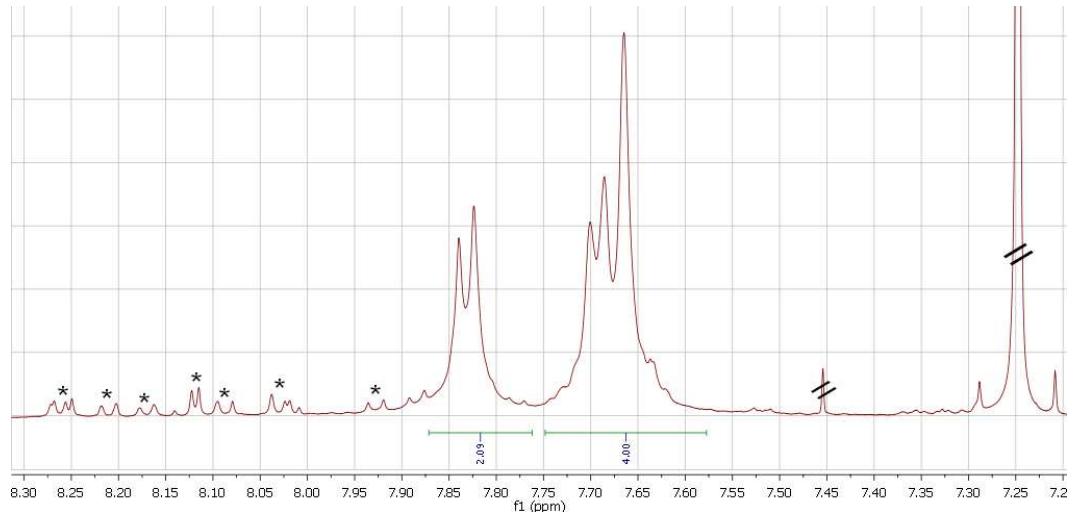


Figure S5. ^1H NMR spectrum (in CDCl_3) of polymer **9** obtained by the polymerization of **8** with 5 mol% of **6b** in a mixture of THF and 2M CsF at 0°C after 3 hours. The small peaks which are attributed to the pyrene group at the initiator end.

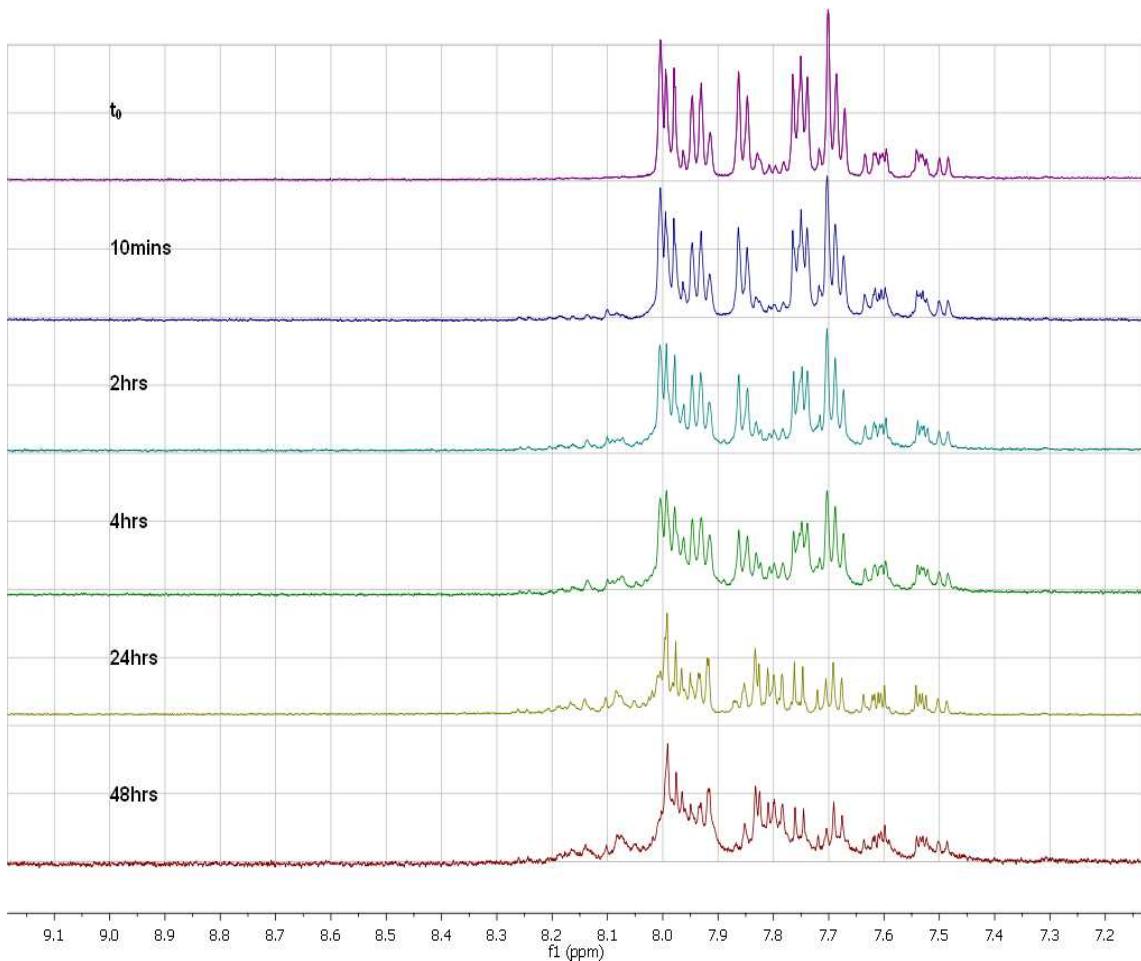


Figure S6. ^1H NMR spectra (in THF, d_8) of polymer **7b** obtained by the polymerization of **5** with 5 mol% of **6b** in a mixture of THF and 2M CsF at 0°C. The polymerization was carried out in a NMR tube in-situ in order to follow the reaction kinetic for 2 days.

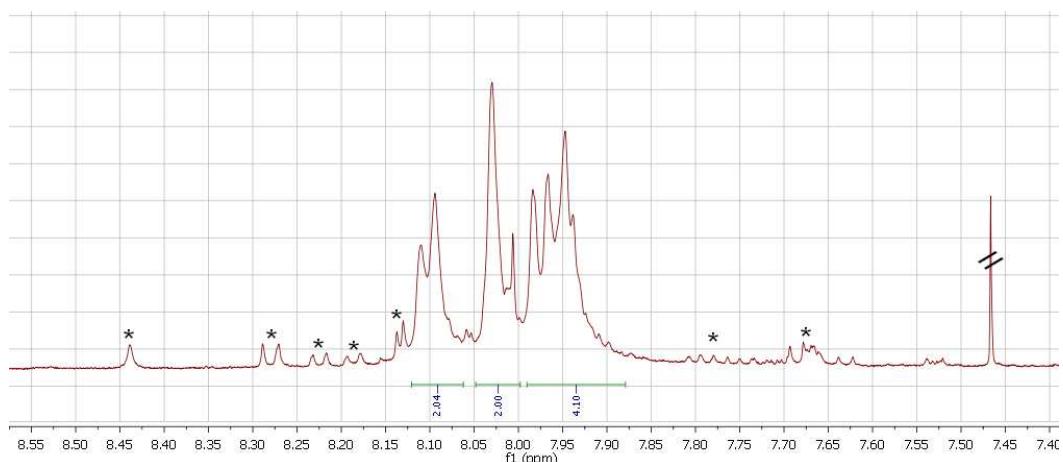


Figure S7. ^1H NMR spectrum (in CDCl_3) of polymer **7b** obtained by the polymerization of **5** with 5 mol% of **6b** in a mixture of THF and 2M CsF at 0°C after 24 hours. The small peaks which are marked with stars are attributed to the pyrene group at the initiator end.

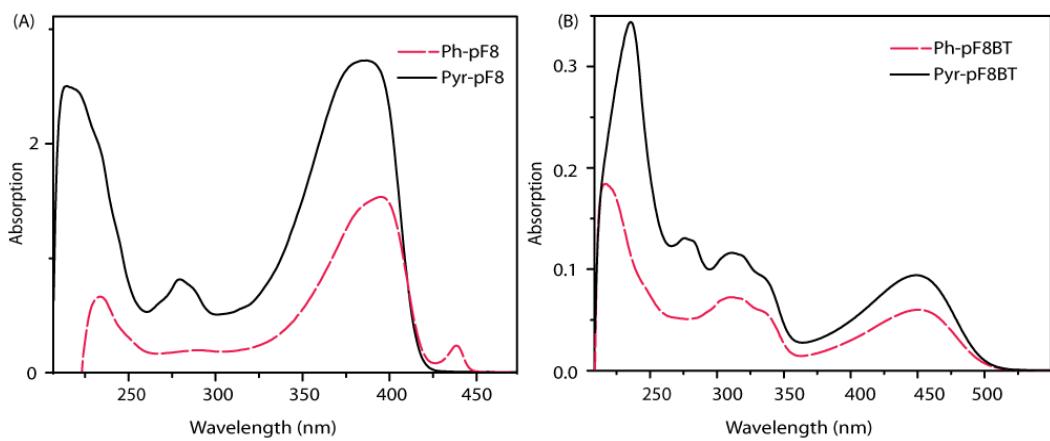


Figure S8. Absorption spectra of polymers Ph-pF8, Pyr-pF8 (9), Ph-pF8BT (7a), and Pyr-pF8BT (7b). All the polymers have the same concentration (3.4×10^{-5} M in THF) and approximately the same Mn of 7,700 and 7,500 Da for pF8 and pF8BT, respectively. A) The measured absorption coefficients for Ph-pF8 and Pyr-pF8 are $\epsilon^{395\text{nm}} = 45 \times 10^3$ and $\epsilon^{386\text{nm}} = 81 \times 10^3$ cm/M, respectively. The 9 nm blue shift of Pyr-pF8 band-gap and the intensity increase are shown. B) The calculated absorption coefficients for Ph-pF8BT and Pyr-pF8BT are $\epsilon^{451\text{nm}} = 2 \times 10^3$ and $\epsilon^{451\text{nm}} = 3 \times 10^3$ cm/M, respectively. No measurable shift in the wavelength peak was observed.

1. Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *Journal of the American Chemical Society* **2007**, *129*, 7236-+.
2. Stambuli, J. P.; Incarvito, C. D.; Buhl, M.; Hartwig, J. F. *Journal of the American Chemical Society* **2004**, *126*, 1184-1194.
3. Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angewandte Chemie-International Edition* **2009**, *48*, 2695-2698.