

Accessing Conjugated Polymers with Precisely Controlled Heterobifunctional Chain Ends via Post Polymerization Modification of OTf Group and Controlled Pd(0)/*t*-Bu₃P-Catalyzed Suzuki Cross-Coupling Polymerization

Hong-Hai Zhang,¹ Qiao-Sheng Hu^{1*} and Kunlun Hong^{2*}

1. Department of Chemistry, College of Staten Island and Graduate Center of the City University of New York, Staten Island, New York, 10314, United States

2. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37831, United States

Qiaosheng.hu@csi.cuny.edu or hongkq@ornl.gov

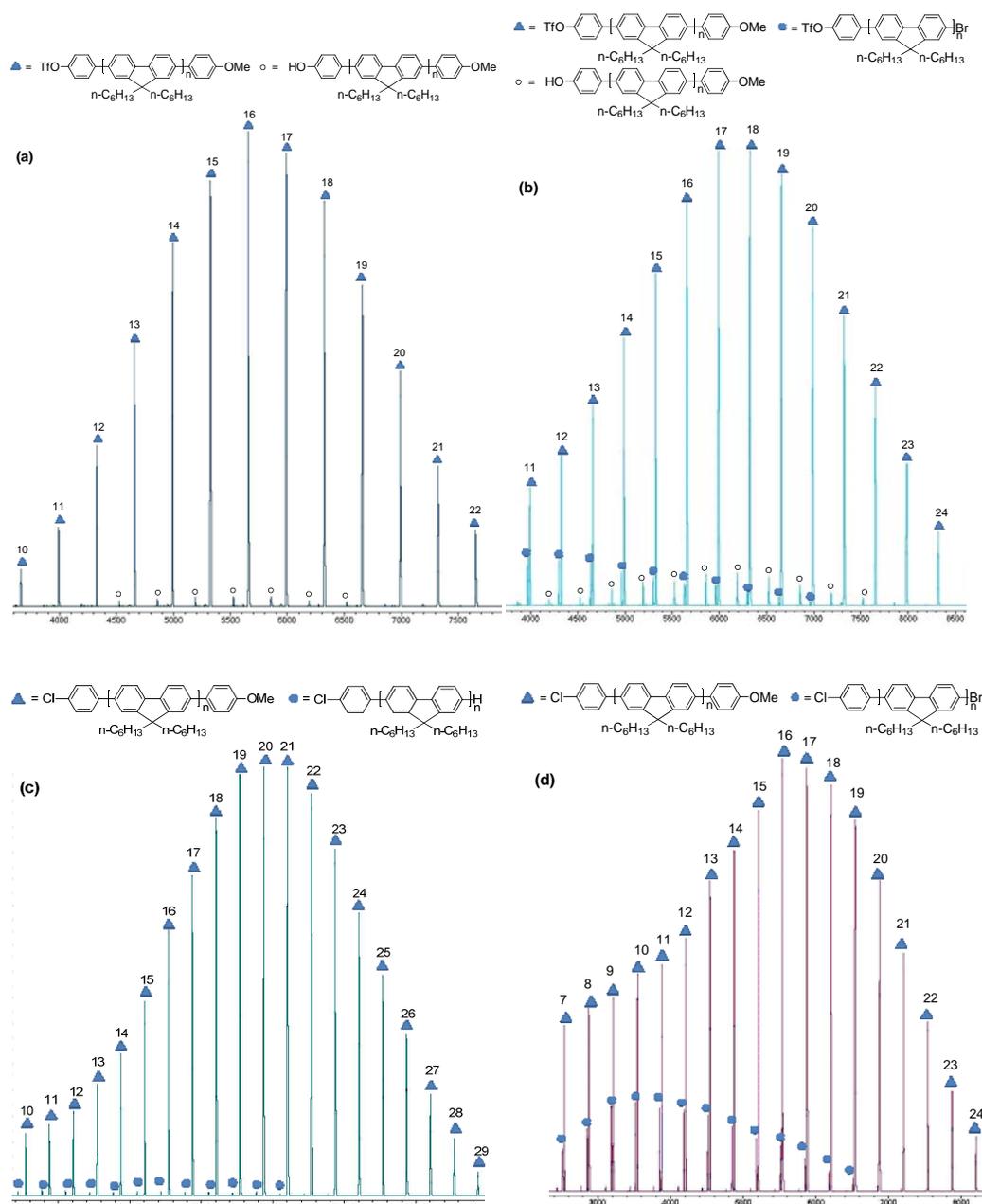
Supporting Information

General: ¹H & ¹³C NMR spectra were recorded on Varian 600 MHz NMR spectrometer. Chemical shifts were determined relative to internal (CH₃)₄Si (TMS). All yields reported refer to isolated yields unless otherwise indicated. Mn and Mw/Mn (PDI) value of polymers were measured with gel permeation chromatography (TOSOH HLC-8320GPC) using THF as eluent (1 mL/min) at 40 °C, which were calibrated with polystyrene standards. MALDI-TOF mass spectra were recorded on a Bruker Reflex III in the reflection mode with a laser (λ = 337 nm) using 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received.

2-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared in the way similar to the literature.¹ 4-Bromo-2,5-dihexyloxyphenylboronic acid was prepared according to the reported procedure but purified by recrystallization from Methanol.² 2-(5-bromo-4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the reported procedure.³ The preparation of Sphos-coordinated 2-Phenylaniline-based Palladacycle complex **1** was previously reported.⁴ THF was freshly distilled from sodium/benzophenone. *t*-Bu₃P was purchased from Sigma-Aldrich and Pd₂(dba)₃ was purchase from Stem Chemicals and used as received.

General Procedure for the polymerization of 2-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with Pd₂(dba)₃/*t*-Bu₃P/*ArX* as initiator and quenched by arylboronic acid: In a drybox under N₂ atmosphere, to 5-mL vial containing Pd₂(dba)₃ (5.5 mg, 0.006 mmol), THF (0.4 mL) and *t*-Bu₃P (48 μL, 0.5 M solution in THF) was added aryl halogen (80 μL, 0.25 M solution in THF). The mixture was stirred for 1 hour at room temperature to generate the initiator. To another vial containing 2-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-4,4,5,5-

tetramethyl-1,3,2- dioxaborolane (0.1 mmol) and THF (5.4 mL) was added 0.5 mL of K_3PO_4 solution (0.5 mL, 2 M solution in water) and the mixture was cooled to 0 °C. The solution of the in situ generated initiator was quickly injected into the solution of monomer and the resulting mixture was stirred for 25 min at 0 °C. The reaction was quenched by injecting arylboronic acid (0.4 mL, 0.25 M solution in THF) and stirred for 1 hour. The product was extracted with CH_2Cl_2 (3 x 20 mL). The organic layer was combined, washed by brine and dried with Na_2SO_4 . The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and the solution was added dropwise to methanol with stirring. The precipitate was collected by filtration, washed with methanol and water and dried under vacuum.



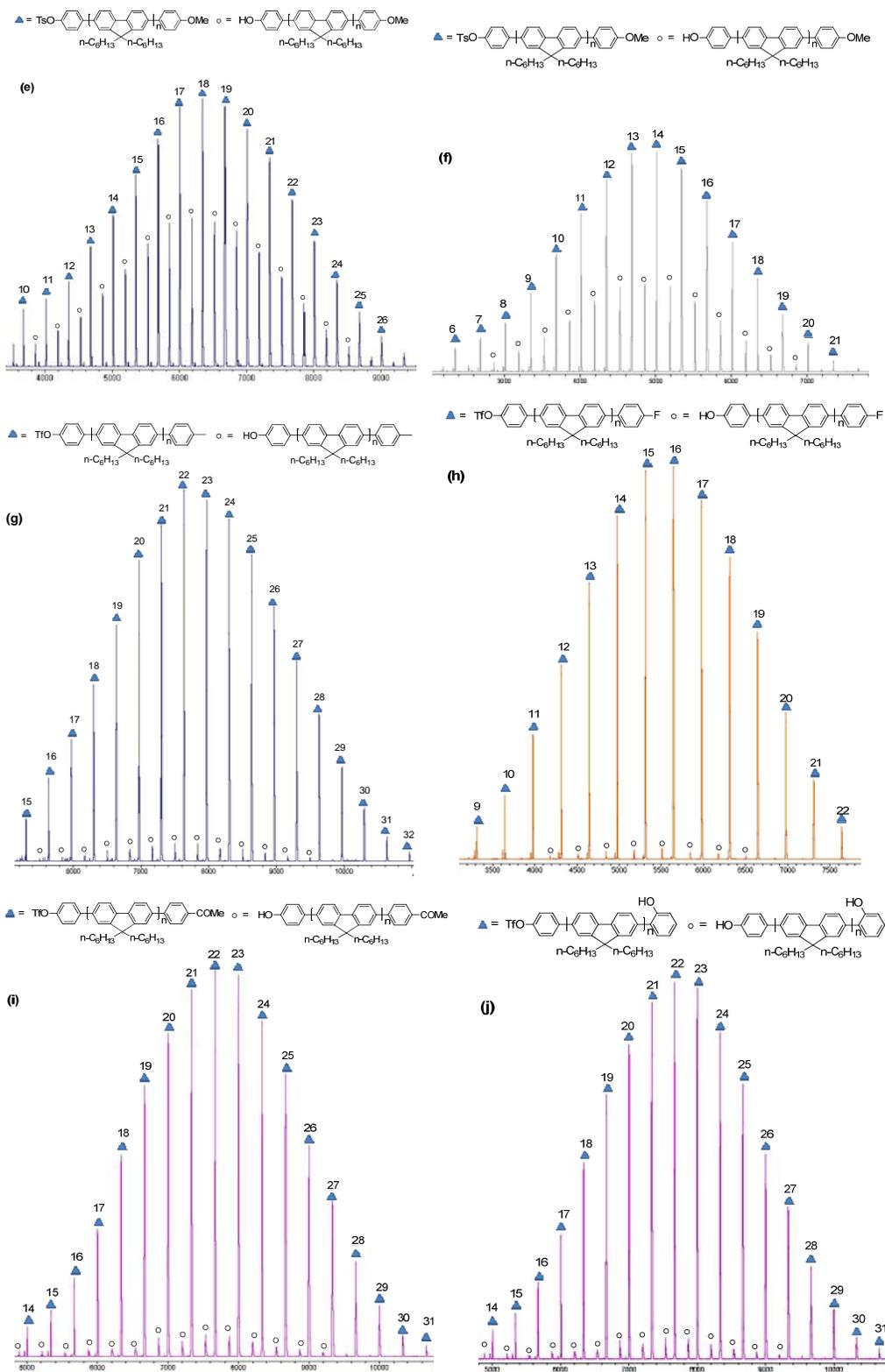
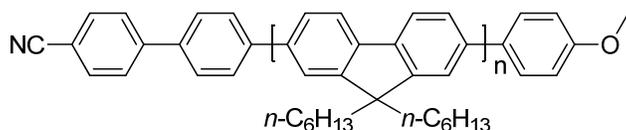


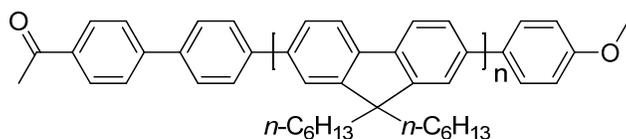
Figure S1: MALDI-TOF mass spectrum of poly(9,9-dihexylfluorene)s obtained with $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/\text{ArX}$ as initiator and quenched by different aryl boronic acid. (a) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TfOC}_6\text{H}_4\text{Br}$ as initiator, 4-methoxyphenyl boronic acid as

quenching reagent. (b) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TfOC}_6\text{H}_4\text{I}$ as initiator, 4-methoxyphenyl boronic acid as quenching reagent. (c) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-ClC}_6\text{H}_4\text{Br}$ as initiator, 4-methoxyphenyl boronic acid as quenching reagent. (d) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-ClC}_6\text{H}_4\text{I}$ as initiator, 4-methoxyphenyl boronic acid as quenching reagent. (e) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TsOC}_6\text{H}_4\text{Br}$ as initiator, 4-methoxyphenyl boronic acid as quenching reagent. (f) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TsOC}_6\text{H}_4\text{I}$ as initiator, 4-methoxyphenyl boronic acid as quenching reagent. (g) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TfOC}_6\text{H}_4\text{Br}$ as initiator, 4-methylphenyl boronic acid as quenching reagent. (h) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TfOC}_6\text{H}_4\text{Br}$ as initiator, 4-fluorophenyl boronic acid as quenching reagent. (i) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TfOC}_6\text{H}_4\text{Br}$ as initiator, 4-acetylphenyl boronic acid as quenching reagent. (j) $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-TfOC}_6\text{H}_4\text{Br}$ as initiator, 2-hydroxyphenyl boronic acid as quenching reagent.

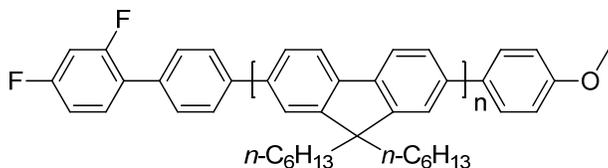
General procedure for Suzuki cross-coupling reaction between polyfluorene and arylboronic acid: In a drybox under N_2 atmosphere, to 5-mL vial containing polymer (20 mg), precatalyst **1** (3.2 mg) and aryl boronic acid (0.08 mmol) in THF (4 mL) was added K_3PO_4 solution (0.1 mL, 2 M solution in water). The mixture was stirred at 50°C for 12 hour. The product was extracted with CH_2Cl_2 (3 x 20 mL). The organic layer was combined, washed by brine and dried with Na_2SO_4 . The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and the solution was added dropwise to methanol with stirring. The precipitate was collected by filtration, washed with methanol and water and dried under vacuum.



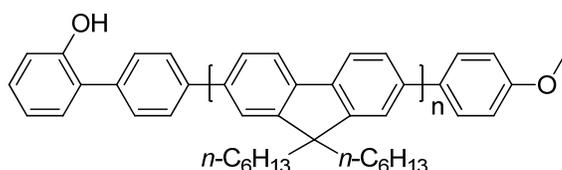
80% yield. Yellow solid. GPC: $M_n = 9\ 600$ (PDI = 1.16). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 7.77 (s, 0.21 H) and 3.88 (s, 0.13 H) are attributed to characteristic protons of the end groups.



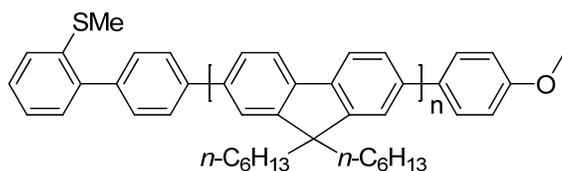
80% yield. Yellow solid. GPC: $M_n = 9\ 700$ (PDI = 1.15). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 8.07 (d, 0.11 H), 3.88 (s, 0.14 H) and 2.67 (s, 0.16 H) are attributed to characteristic protons of the end groups.



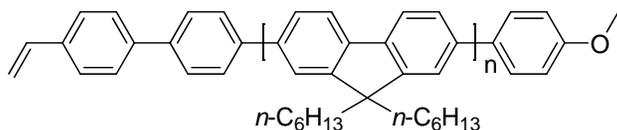
80% yield. Yellow solid. GPC: $M_n = 11\,700$ (PDI = 1.14). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.84 ~ 7.85 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 6.96 (m, 0.10 H) and 3.88 (s, 0.14 H) are attributed to characteristic protons of the end groups.



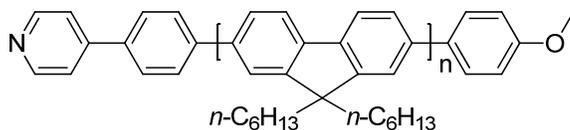
80% yield. Yellow solid. GPC: $M_n = 11\,100$ (PDI = 1.15). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.84 ~ 7.85 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 5.26 (s, 0.05 H) and 3.88 (s, 0.13 H) are attributed to characteristic protons of the end groups.



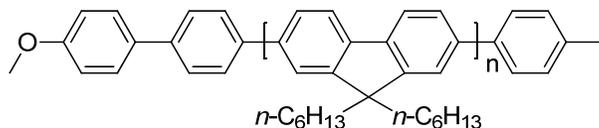
80% yield. Yellow solid. GPC: $M_n = 11\,200$ (PDI = 1.16). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.84 ~ 7.85 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 3.88 (s, 0.13 H) and 2.42 (s, 0.14 H) are attributed to characteristic protons of the end groups.



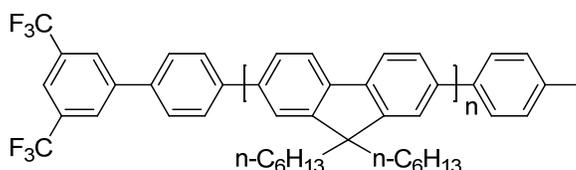
80% yield. Yellow solid. GPC: $M_n = 11\,700$ (PDI = 1.14). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.84 ~ 7.85 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 6.78 (dd, $J = 14.4$ Hz, $J = 18.0$ Hz, 0.05 H), 5.82 (d, $J = 17.4$ Hz, 0.05 H), 5.30 (d, $J = 10.8$ Hz, 0.05 H) and 3.88 (s, 0.13 H) are attributed to characteristic protons of the end groups.



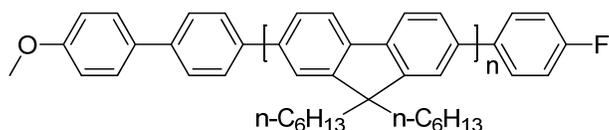
80% yield. Yellow solid. GPC: $M_n = 9\ 700$ (PDI = 1.17). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.84 ~ 7.85 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 8.70 (d, $J = 6.0$ Hz, 0.09 H) and 3.88 (s, 0.15 H) are attributed to characteristic protons of the end groups.



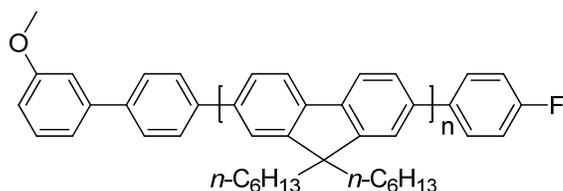
90% yield. Yellow solid. GPC: $M_n = 12\ 500$ (PDI = 1.17). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.84 ~ 7.85 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 3.88 (s, 0.10 H) and 2.43 (s, 0.10 H) are attributed to characteristic protons of the end groups.



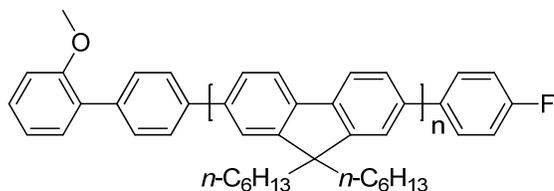
95% yield. Yellow solid. GPC: $M_n = 12\ 500$ (PDI = 1.17). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.84 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 8.08 (s, 0.07 H) and 2.43 (s, 0.11 H) are attributed to characteristic protons of the end groups.



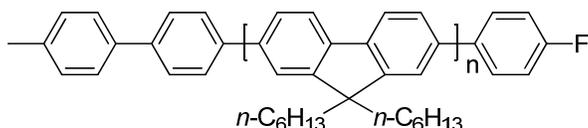
95% yield. Yellow solid. GPC: $M_n = 9\ 000$ (PDI = 1.16). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.84 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 7.26 ~ 7.37 (m, 0.09 H) and 3.90 (s, 0.14 H) are attributed to characteristic protons of the end groups.



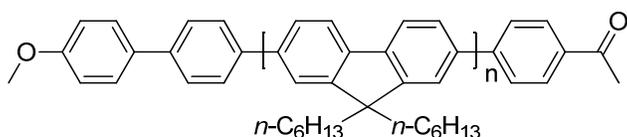
95% yield. Yellow solid. GPC: $M_n = 10\ 400$ (PDI = 1.18). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.84 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 7.26 ~ 7.37 (m, 0.10 H) and 3.90 (s, 0.16 H) are attributed to characteristic protons of the end groups.



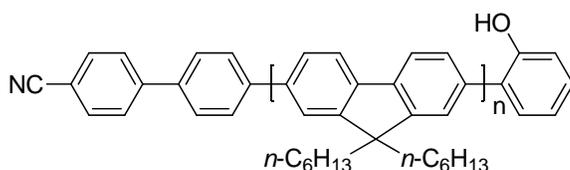
95% yield. Yellow solid. GPC: $M_n = 10\,700$ (PDI = 1.16). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.84 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 7.26 ~ 7.37 (m, 0.10 H) and 3.86 (s, 0.17 H) are attributed to characteristic protons of the end groups.



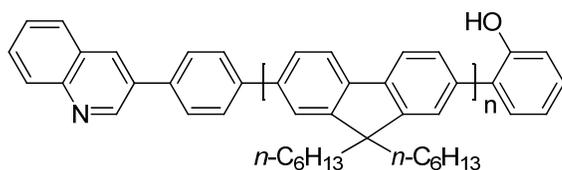
95% yield. Yellow solid. GPC: $M_n = 9\,000$ (PDI = 1.17). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.84 (m, 2 H), 7.67 ~ 7.71 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.18 (m, 12 H), 0.77 ~ 0.84 (m, 10 H); small peaks which were observed at 7.25 ~ 7.30 (m, 0.12 H) and 2.42 (s, 0.19 H) are attributed to characteristic protons of the end groups.



80% yield. Yellow solid. GPC: $M_n = 9\,700$ (PDI = 1.15). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 3.88 (s, 0.12 H) and 2.67 (s, 0.12 H) are attributed to characteristic protons of the end groups.

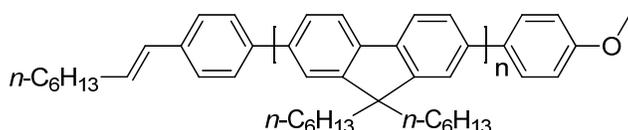


90% yield. Yellow solid. GPC: $M_n = 13\,200$ (PDI = 1.18). $^1\text{H NMR}$ (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 7.77 (s, 0.19 H), 7.04 ~ 7.06 (m, 0.10 H) and 5.33 (s, 0.04 H) are attributed to characteristic protons of the end groups.

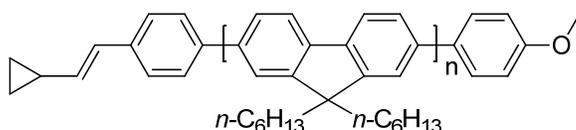


90% yield. Yellow solid. GPC: $M_n = 13\ 200$ (PDI = 1.17). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 9.28 (s, 0.04 H), 8.39 (s, 0.04 H), 8.17 (d, $J = 8.4$ Hz, 0.03 H), 7.04 ~ 7.06 (m, 0.09 H) and 5.33 (s, 0.04 H) are attributed to characteristic protons of the end groups.

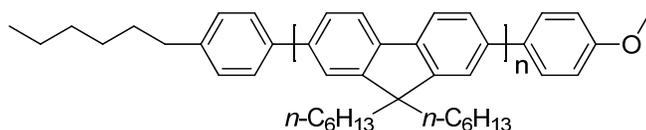
General procedure for Suzuki cross-coupling reaction between polyfluorene and alkenyl (alkyl) boronic acid: In a drybox under N_2 atmosphere, to 5-mL vial containing polymer (20 mg), $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.004 mmol) and alkenyl boronic acid (0.08 mmol) in THF (4 mL) was added K_3PO_4 solution (0.1 mL, 2 M solution in water). The mixture was stirred at 80°C for 16 hour. The product was extracted with CH_2Cl_2 (3 x 20 mL). The organic layer was combined, washed by brine and dried with Na_2SO_4 . The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and the solution was added dropwise to methanol with stirring. The precipitate was collected by filtration, washed with methanol and water and dried under vacuum.



88% yield. Yellow solid. GPC: $M_n = 12\ 800$ (PDI = 1.18). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 6.20 (d, $J = 17.4$ Hz, 0.04 H), 5.24 (d, $J = 24.0$ Hz, 0.03 H) and 3.90 (s, 0.21 H) are attributed to characteristic protons of the end groups.



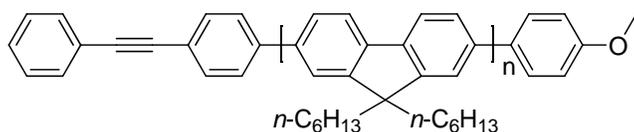
94% yield. Yellow solid. GPC: $M_n = 12\ 800$ (PDI = 1.17). ^1H NMR (600 MHz, CDCl_3 , ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 7.04 (d, $J = 9.0$ Hz, 0.13 H), 6.20 (d, $J = 17.4$ Hz, 0.04 H), 5.24 (d, $J = 24.0$ Hz, 0.04 H) and 3.90 (s, 0.17 H) are attributed to characteristic protons of the end groups. See Figure S2 for further details.



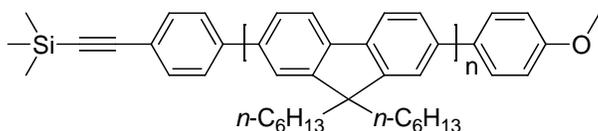
90% yield. Yellow solid. GPC: $M_n = 12\ 800$ (PDI = 1.17). ^1H NMR (600 MHz,

CDCl₃, ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 3.90 (s, 0.19 H) and 2.70 (t, $J = 9.0$ Hz, 0.11 H) are attributed to characteristic protons of the end groups. See Figure S2 for further details.

General procedure for Sonogashira cross-coupling reaction between polyfluorene and terminal alkyne: In a drybox under N₂ atmosphere, to 5-mL vial containing polymer (20 mg), Pd(CH₃CN)₂Cl₂ (0.004 mmol) and terminal alkyne (0.08 mmol) in THF (4 mL) was added Cs₂CO₃ (0.08 mmol). The mixture was stirred at 80°C for 16 hour. The product was extracted with CH₂Cl₂ (3 x 20 mL). The organic layer was combined, washed by brine and dried with Na₂SO₄. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of CH₂Cl₂ and the solution was added dropwise to methanol with stirring. The precipitate was collected by filtration, washed with methanol and water and dried under vacuum.

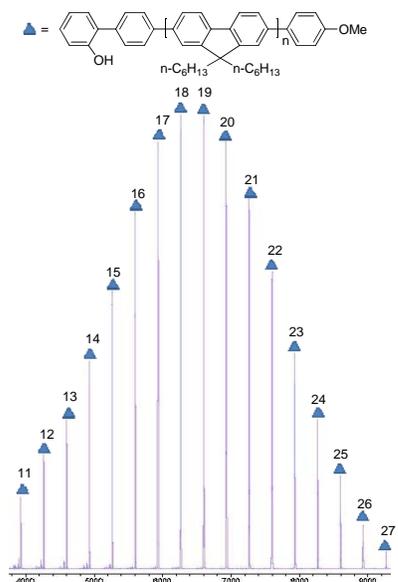
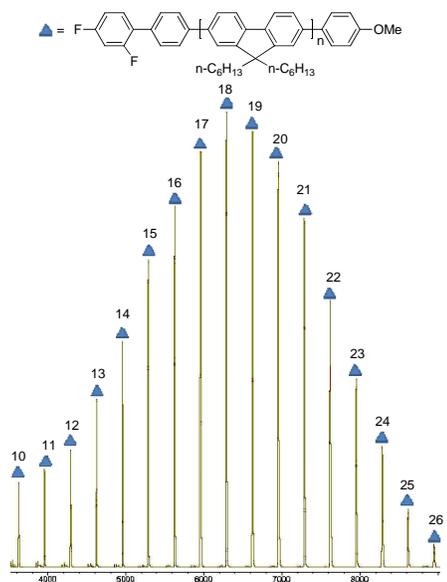
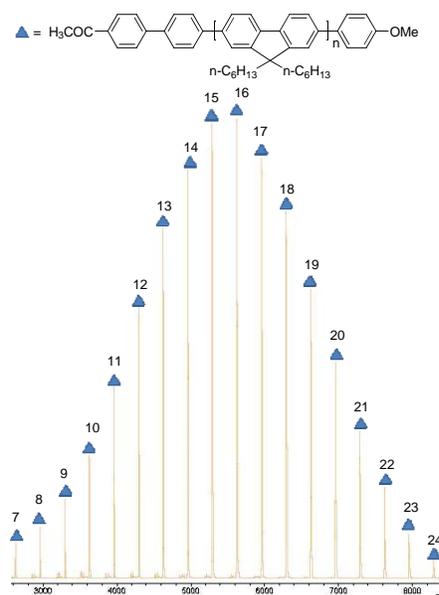
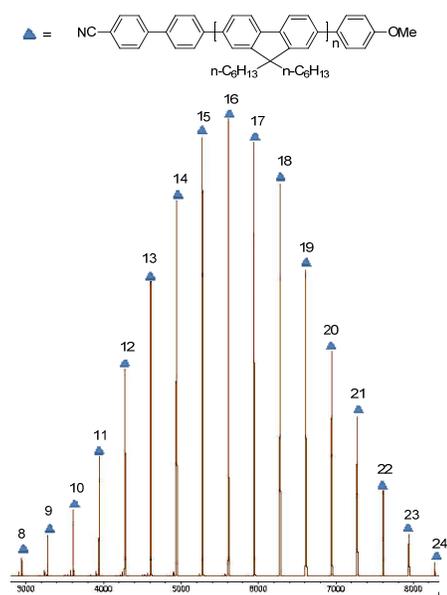


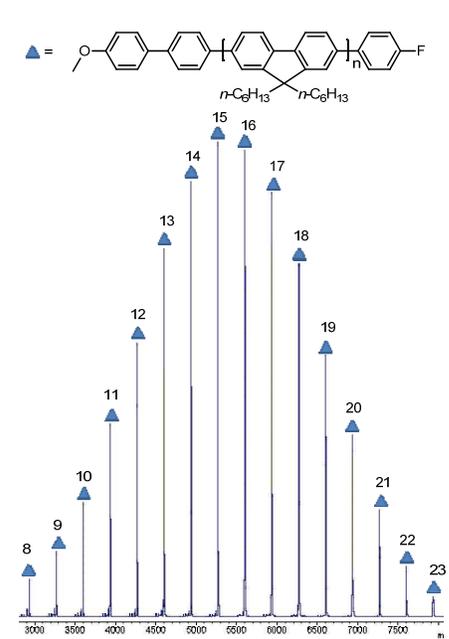
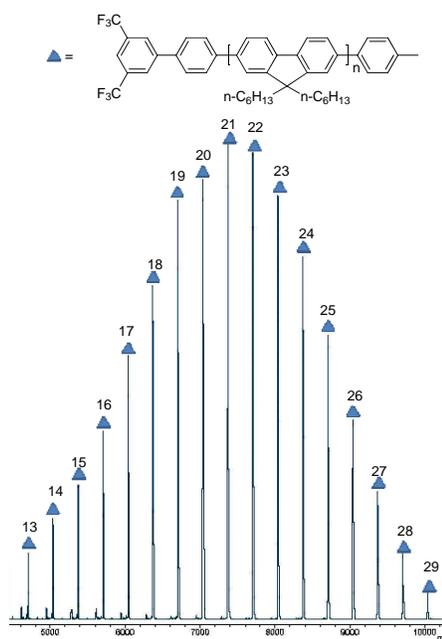
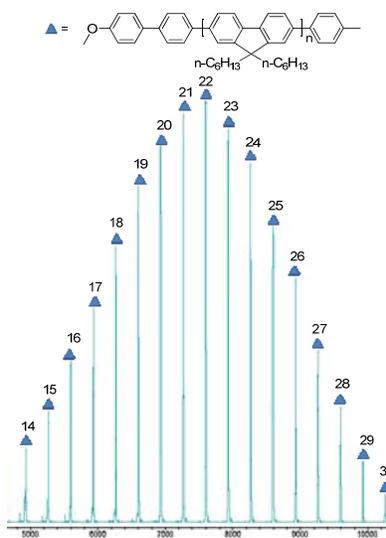
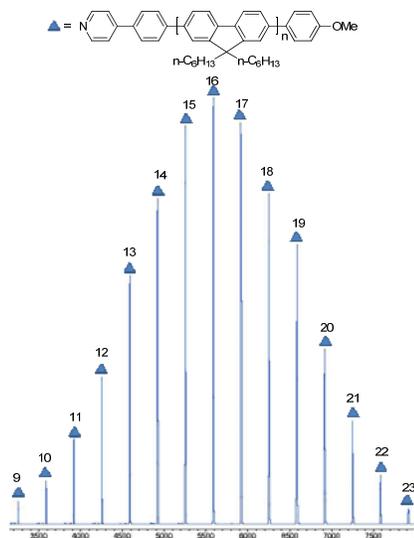
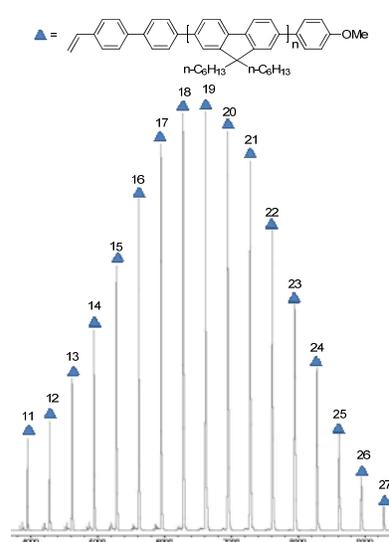
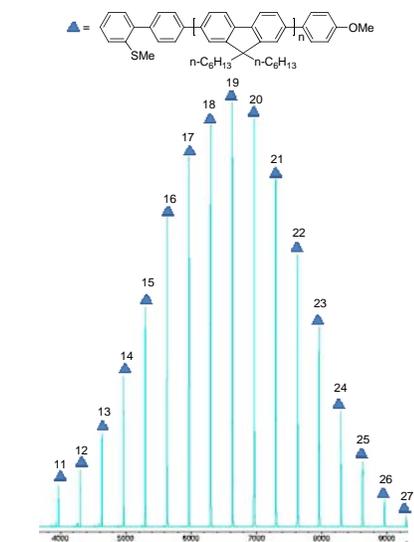
90% yield. Yellow solid. GPC: $M_n = 12\ 700$ (PDI = 1.18). ¹H NMR (600 MHz, CDCl₃, ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 7.24 ~ 7.38 (m, 0.14 H) and 3.90 (s, 0.17 H) are attributed to characteristic protons of the end groups. See Figure S2 for further details.

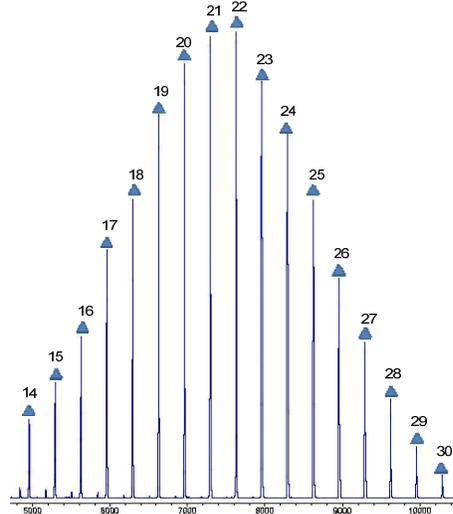
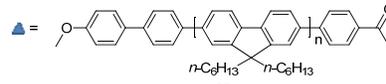
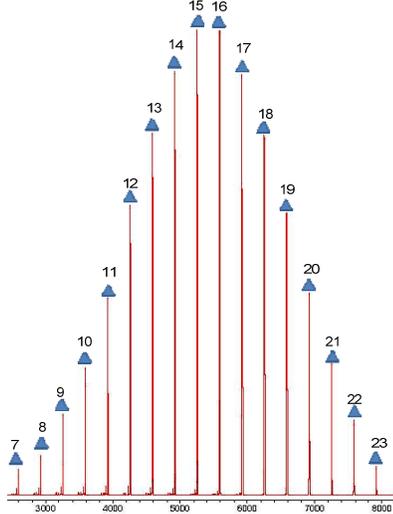
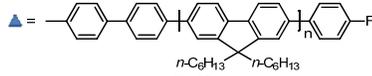
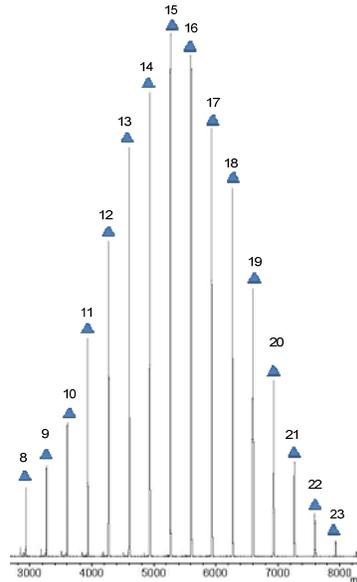
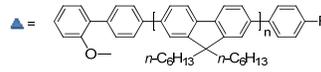
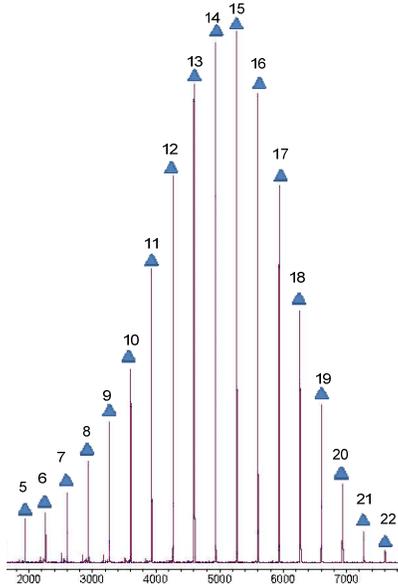
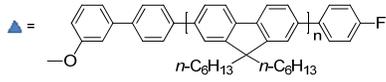


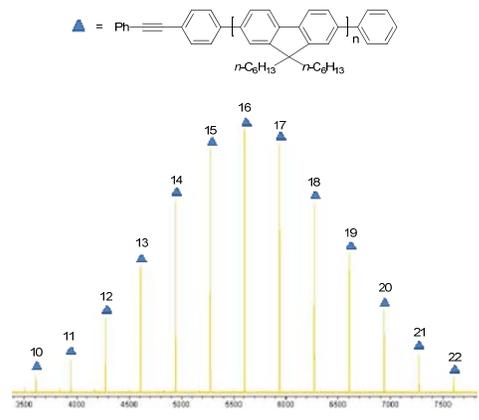
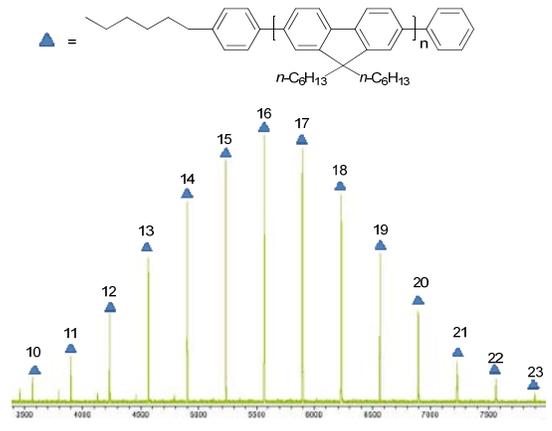
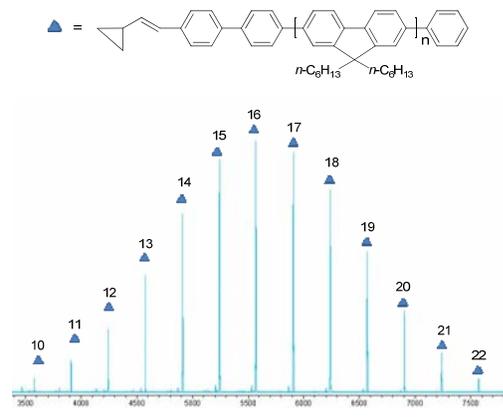
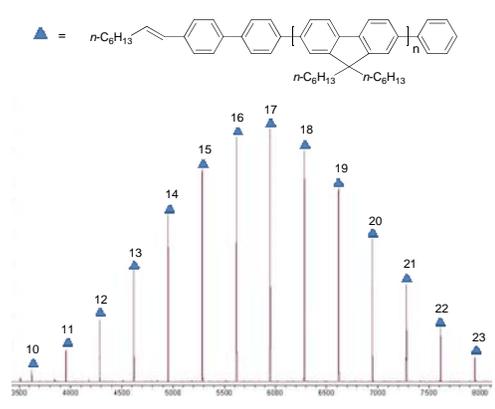
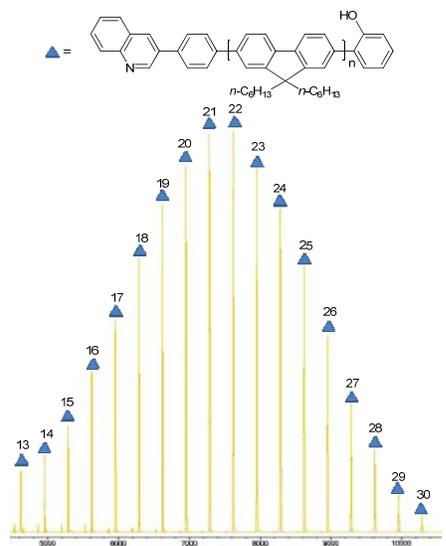
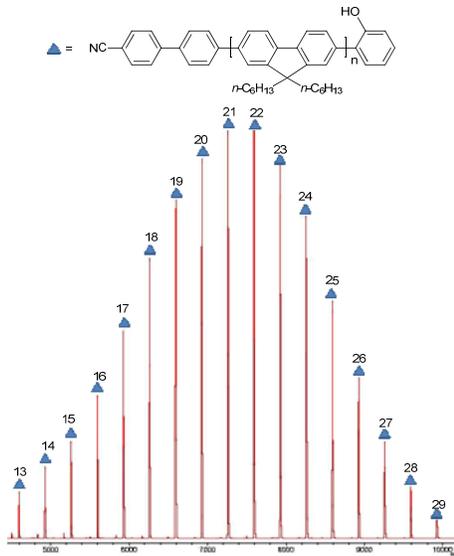
92% yield. Yellow solid. GPC: $M_n = 12\ 900$ (PDI = 1.17). ¹H NMR (600 MHz, CDCl₃, ppm): δ 7.83 ~ 7.85 (m, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.17 (m, 12 H), 0.79 ~ 0.84 (m, 10 H); small peaks which were observed at 3.90 (s, 0.18 H) and 0.52 (s, 0.48 H) are attributed to characteristic protons of the end groups. See Figure S2 for further details.

Maldi-tof Profiles:









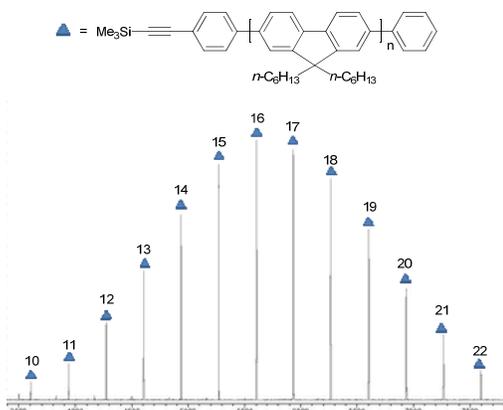
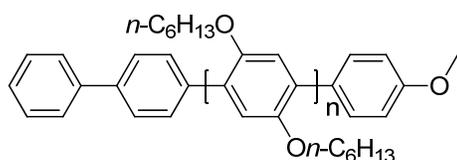
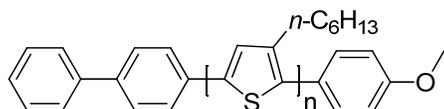


Figure S2: MALDI-TOF mass spectrum of poly(9,9-dihexylfluorene)s obtained by cross-coupling between OTf functionalized poly(9,9-dihexylfluorene)s and different boronic acid or terminal alkyne

General procedure for Suzuki cross-coupling reaction between different polymers and aryl boronic acid: In a drybox under N_2 atmosphere, to 5-mL vial containing polymer (20 mg), precatalyst **1** (3.2 mg) and aryl boronic acid (0.08 mmol) in THF (4 mL) was added K_3PO_4 solution (0.1 mL, 2 M solution in water). The mixture was stirred at 50 °C for 12 hour. The product was extracted with CH_2Cl_2 (3 x 20 mL). The organic layer was combined, washed by brine and dried with Na_2SO_4 . The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and the solution was added dropwise to methanol with stirring. The precipitate was collected by filtration, washed with methanol and water and dried under vacuum.



66% yield. Yellow solid. GPC: $M_n = 4\,400$ (PDI = 1.18). 1H NMR (600 MHz, $CDCl_3$, ppm): δ 7.10 (s, 2 H), 3.92 (s, 4 H), 1.67 ~ 1.68 (m, 4 H), 1.27 ~ 1.36 (m, 12 H), 0.87 (s, 6 H); small peaks which were observed at 7.43 (t, $J = 8.4$ Hz, 0.27 H), 7.34 (t, $J = 9.0$ Hz, 0.14 H), 7.01 (d, $J = 3.6$ Hz, 0.29 H) and 3.90 (s, 0.41 H) are attributed to characteristic protons of the end groups.



63% yield. Yellow solid. GPC: $M_n = 8\,700$ (PDI = 1.26). 1H NMR (600 MHz, $CDCl_3$,

ppm): δ 6.99 (s, 1 H), 2.81 (t, $J = 9.0$ Hz, 2 H), 1.26 ~ 1.45 (m, 8 H), 0.91 ~ 0.93 (m, 3 H); small peaks which were observed at 7.37 ~ 7.41 (m, 0.10 H) and 3.90 (s, 0.10 H) are attributed to characteristic protons of the end groups.

Maldi-tof Profiles:

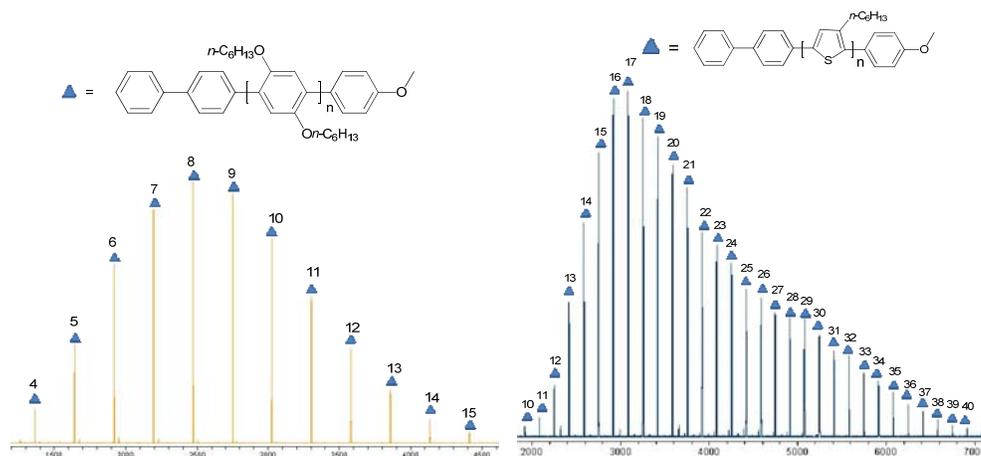


Figure S3: MALDI-TOF mass spectrum of different polymers obtained by cross-coupling between corresponding OTf functionalized polymer and different boronic acid or terminal alkyne.

Molecular Weight–Conversion Relationship Study for Polymerization with $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-BrC}_6\text{H}_4\text{OTf}$ as the Initiator: In a glovebox under N_2 atmosphere, to a 5-mL vial containing $\text{Pd}_2(\text{dba})_3$ (5.5 mg, 0.006 mmol), THF (0.4 mL), $t\text{-Bu}_3\text{P}$ (48 μL , 0.5 M solution in THF) was added 4-bromophenyl trifluoromethanesulfonate (80 μL , 0.25 M solution in THF). The mixture was stirred for 1 hour at room temperature to in situ generate the initiator. In another vial containing 2-(7-Bromo-9,9-dihexyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53.9 mg, 0.1 mmol) and THF (5.4 mL) was added 0.5 mL of K_3PO_4 solution (2 M solution in water). The mixture was cooled to 0 $^\circ\text{C}$. The solution of initiator was quickly injected into the solution of monomer and the resulting mixture was stirred at 0 $^\circ\text{C}$. A small aliquot (0.3 mL) of the organic phase of the reaction mixture was sampled at 5, 10, 15, 20, 30 min. Each aliquot was quenched with 6 N HCl solution and extracted with CH_2Cl_2 . The separated organic layer was evaporated under reduced pressure to get a residue. Half of the residue was dissolved in CDCl_3 to determine the conversion of monomer by ^1H NMR (conversions of 27%, 54%, 77%, 90% and 98% were observed for 5, 10, 15, 20 and 30 min, respectively). The other half of the residue was dissolved in THF and the solution was filtered. The filtrate was analyzed by GPC to determine the M_n and M_w/M_n values of the polymers. The M_n (M_w/M_n) values of each polymer initiated by $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-BrC}_6\text{H}_4\text{OTf}$ for 5, 10, 15, 20 and 30 min were 3000 (1.16), 7400 (1.14), 9500 (1.16), 11300 (1.19) and

12500 (1.18) respectively.

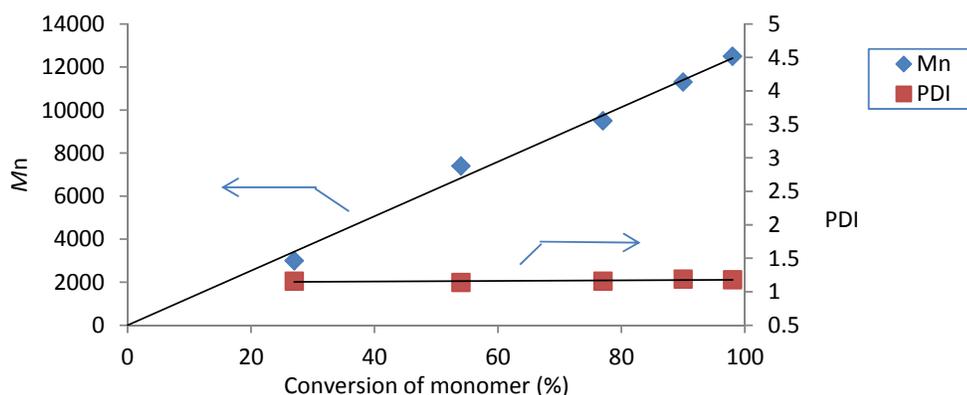


Figure S4 molecular weight–conversion relationship with $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-BrC}_6\text{H}_4\text{OTf}$ as the initiator.

The polymerization of 2-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with different amounts of initiator ($\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-BrC}_6\text{H}_4\text{OTf}$, 6, 3 and 2 mol % loading for $\text{Pd}_2(\text{dba})_3$, with the ratio of $\text{Pd}_2(\text{dba})_3 : t\text{-Bu}_3\text{P} : p\text{-BrC}_6\text{H}_4\text{I}$ to be 1 : 4 : 1.67) was performed in a manner similar to the general procedure described in the [General Procedure for the polymerization of different monomers initiated by $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-BrC}_6\text{H}_4\text{OTf}$] except different initiator loadings. The polymer yields were 85%, 65% and 63% respectively and M_n (PDI) were found to be 9600 (1.16), 19400 (1.17) and 30000 (1.19), respectively. A linear relationship was observed for the molecular weight of polymer with the initiator loading.

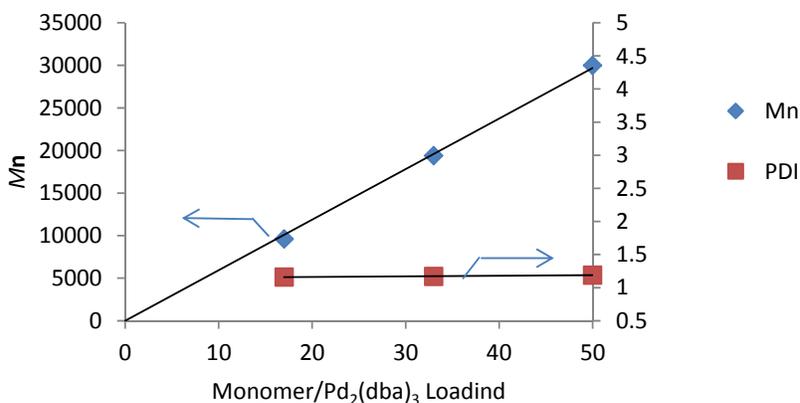


Figure S5 M_n and PDI values of polyfluorene produced by different amount of initiator $\text{Pd}_2(\text{dba})_3/t\text{-Bu}_3\text{P}/p\text{-BrC}_6\text{H}_4\text{OTf}$.

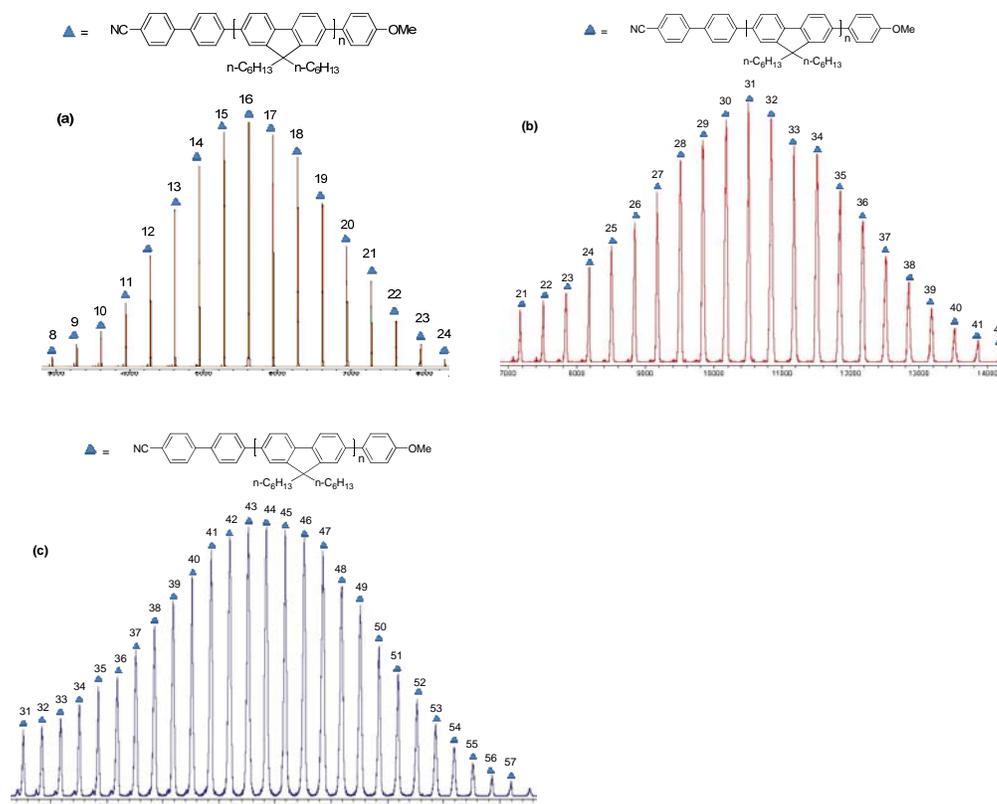


Figure S6: MALDI-TOF mass spectrum of poly(9,9-dihexylfluorene)s with different molecular weight (a) 6%Pd₂(dba)₃/24%*t*-Bu₃P/20%OTfC₆H₄Br as initiator, 4-methoxyphenyl boronic acid as quenching reagent, then modified OTf group with (4-cyanophenyl)boronic acid. (b) 3%Pd₂(dba)₃/12%*t*-Bu₃P/10%OTfC₆H₄Br as initiator, 4-methoxyphenyl boronic acid as quenching reagent, then modified OTf group with (4-cyanophenyl)boronic acid. (c) 2%Pd₂(dba)₃/8%*t*-Bu₃P/7%OTfC₆H₄Br as initiator, 4-methoxyphenylboronic acid as quenching reagent, then modified OTf group with (4-cyanophenyl)boronic acid.

Reference:

1. (a) Manickam, G.; Schluter, A. D., *Synthesis* **2000**, 442-446; (b) Zhang, X.; Tian, H.; Qin, L.; Wang, L.; Geng, Y.; Wang, F., *J. Org. Chem.* **2006**, *71*, 4332-4335.
2. Moy, C. L.; Kaliappan, R.; McNeil, A. J., *J. Org. Chem.* **2011**, *76* (20), 8501-8507.
3. Lee, J.; Ko, S.; Bao, Z. *Macromol. Rapid Commun.* **2012**, *33*, 938-942.
4. Zhang, H. H.; Xing, C. H.; Tsemo, G. B.; Hu, Q. S. *ACS Macro. Lett.* **2013**, *2*, 10-13.

