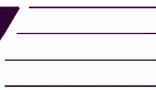


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Supporting Information

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Supramolecule Regulated Photophysics of Oligo(*p*-phenyleneethynylene)-Based Rod-Coil Block Copolymers: Effect of Molecular Architecture

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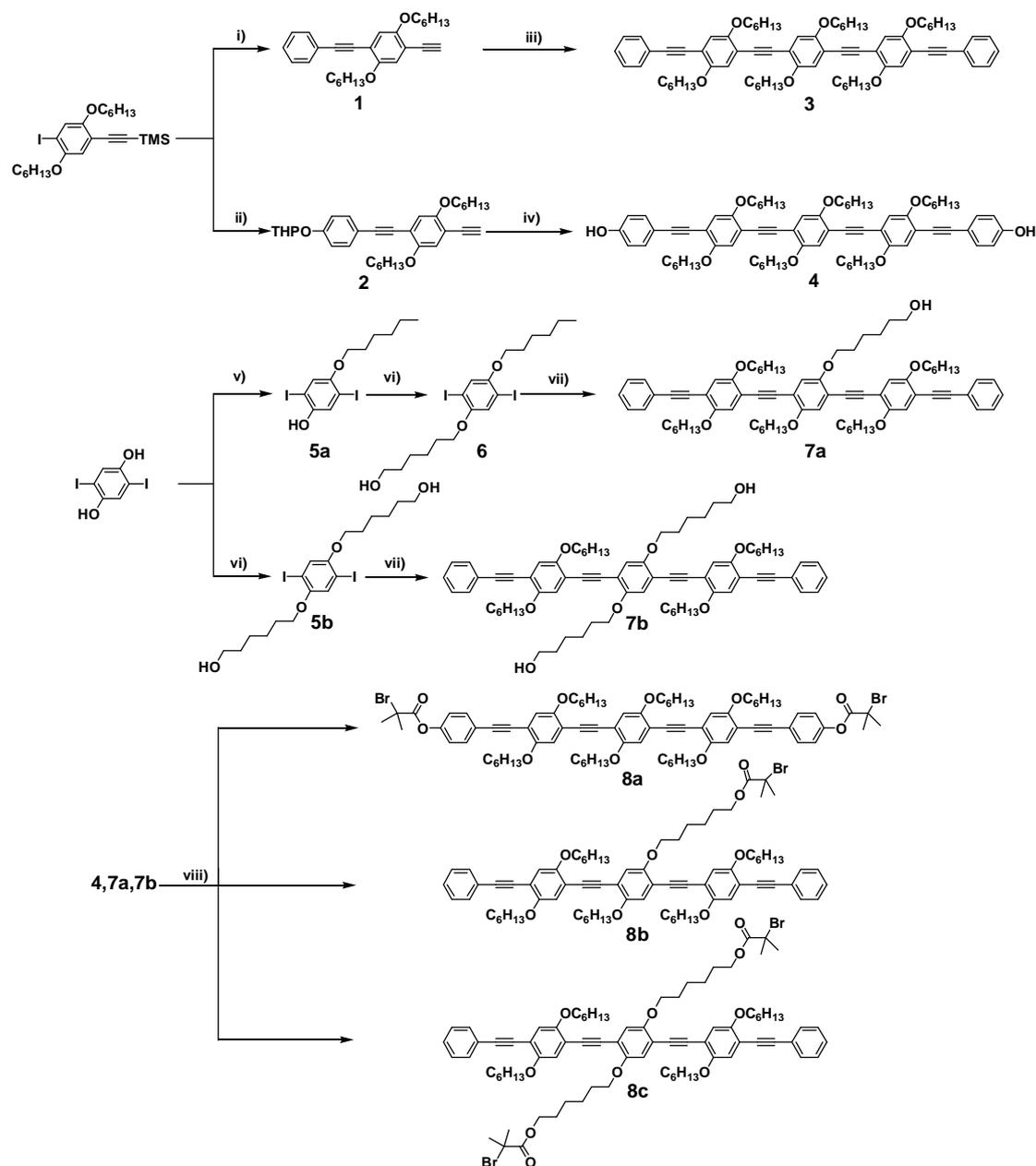
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Supporting Information

Synthesis and Characterization of Macroinitiators and OPE

The synthesis routes of macroinitiators and OPE are shown in Scheme S1. The detailed synthesis procedures and characterization of these compounds are listed below.



Scheme S1. Synthesis of the macroinitiators and **OPE**. Reagents and conditions: i) 1-ethynylbenzene, CuI, Pd(PPh₃)₄, (iPr)₂NH/THF (2:1), room temperature. Then, THF and NaOH solution, room temperature; ii) 2-(4-ethynylphenoxy)-tetrahydro-2H-pyran, CuI, Pd(PPh₃)₄, (iPr)₂NH/THF (2:1), room temperature. Then, THF and NaOH solution, room temperature; iii) 1,4-dihexyloxy-2,5-diiodobenzene, CuI, Pd(PPh₃)₄, (iPr)₂NH/THF (2:1), room temperature; iv) 1,4-dihexyloxy-2,5-diiodobenzene, CuI, Pd(PPh₃)₄, (iPr)₂NH/THF (2:1), room temperature. Then, *p*-toluenesulfonic acid, THF/CH₃OH; v) 1-bromohexane, NaOH solution and absolute ethanol, 60 °C; vi) 6-

bromohexanol, K₂CO₃, NaI, 2-butanone, 70 °C; vii) **1**, CuI, Pd(PPh₃)₄, ((iPr)₂NH)/THF (2:1), room temperature; viii) 2-bromo-2-methylpropanoyl bromide, Et₃N, THF, room temperature.

1-Ethynyl-2,5-bis(hexyloxy)-4-(2-phenylethynyl)benzene (1): A two-necked flask was charged with 2,5-dihexyloxy-4-[(trimethylsilyl)ethynyl]iodobenzene (3.50 g, 7.00 mmol), 1-ethynylbenzene (0.715 g, 7.00 mmol), CuI (0.133 g, 0.700 mmol), and Pd(PPh₃)₄ (581 mg, 0.500 mmol). It was degassed with three vacuum-nitrogen cycles and then diisopropylamine ((iPr)₂NH) (50.0 mL) and THF (25.0 mL) were added at 0 °C. The reaction mixture was stirred at room temperature for 12 hours, and then it was subjected to water and extracted with dichloromethane. The combined organic solution was washed with water NH₄OH (50%) twice, distilled water twice and brine twice and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified using a flash silica gel chromatograph with hexane/dichloromethane (6:1) as eluent. Thus, the intermediate product, (2-(2,5-bis(hexyloxy)-4-(2-phenylethynyl)phenyl)ethynyl)trimethylsilane (3.90 g, 92.8%), was obtained, and it was dissolved in THF (30.0 mL). Then, the mixture of methanol (40.0 ml) and NaOH solution (3.00 mL, 5 N) was added to the stirred THF solution slowly. After the reaction mixture was stirred at room temperature for 1 hour, the mixture solvents were evaporated and the resulting residue was purified using a silica gel chromatograph with dichloromethane/hexane (1:6) as eluent to afford **1** (3.14 g, 95.0%) as white crystal. ¹H NMR (CDCl₃), d (ppm): 7.53 (m, 2 H), 7.34 (m, 3 H), 6.99 (m, 2 H), 4.01 (m, 4 H), 3.33 (s, 1 H), 1.82 (m, 4 H), 1.58 (m, 8 H), 1.33 (m, 4 H), 0.90 (m, 6 H); ¹³C NMR (CDCl₃), d (ppm): 154.36, 153.66, 131.81, 128.53, 123.58, 117.98, 117.04, 114.86, 112.72, 95.15, 85.92, 82.50, 80.24, 31.83, 31.77, 29.51, 29.35, 25.96, 25.83, 22.87, 22.83, 14.27; MALDI-TOF MS: *m/z*: 402.26 [*M*]⁺.

2-(4-(2-(4-Ethynyl-2,5-bis(hexyloxy)phenyl)ethynyl)phenoxy)-tetrahydro-2H-pyran (2): A two-necked flask was charged with 2,5-dihexyloxy-4-[(trimethylsilyl)ethynyl]iodobenzene (3.50 g, 7.00 mmol), 2-(4-ethynylphenoxy)-tetrahydro-2H-pyran (1.42 g, 7.00 mmol), CuI (0.133 g, 0.700 mmol), and Pd(PPh₃)₄ (581 mg, 0.500 mmol). It was degassed with three vacuum-nitrogen cycles and then diisopropylamine ((iPr)₂NH) (50.0 mL) and THF (25.0 mL) were added at 0 °C. The reaction mixture was stirred at room temperature for 12 hours, and then it was subjected to water and extracted with dichloromethane. The combined organic solution was washed with water NH₄OH (50%) twice, distilled water twice and brine twice and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified using a flash silica gel chromatograph with hexane/dichloromethane (5:1) as eluent. Thus, the intermediate product, (2-(2,5-bis(hexyloxy)-4-(2-(4-(tetrahydro-2H-pyran-2-yloxy)phenyl)ethynyl)phenyl)ethynyl) trimethylsilane (3.45 g, 90.0%), was obtained, and it was dissolved in THF (30 mL). Then, the mixture of methanol (40 ml) and NaOH solution (3 mL, 5 N) was added to the THF solution slowly. After the reaction mixture was stirred at room temperature for 1 hour, the mixture solvents were evaporated and the resulting residue was purified using

a silica gel chromatograph with dichloromethane/hexane (1:5) as eluent to afford **2** (3.01 g, 95.0%) as white crystal. ¹H NMR (CDCl₃), d (ppm): 7.45 (m, 2 H), 7.02 (m, 2 H), 6.96 (m, 2 H), 5.44 (t, 1 H), 4.01 (m, 4 H), 3.91 (m, 1 H), 3.64 (m, 1 H), 3.33 (s, 1H), 2.03 (m, 1 H), 1.97-1.78 (m, 17 H), 1.33 (m, 4 H), 0.90 (m, 6 H); ¹³C NMR (CDCl₃), d (ppm): 157.41, 154.38, 153.49, 133.17, 118.00, 116.91, 116.57, 116.52, 115.73, 112.29, 96.44, 95.31, 84.69, 82.34, 80.31, 69.86, 69.81, 62.27, 31.83, 31.76, 30.47, 29.52, 29.35, 25.96, 25.83, 25.36, 22.87, 22.83, 18.89, 14.28; MALDI-TOF MS: *m/z*: 503.31 [*M*+1]⁺.

Oligo(2,5-dihexyloxy-1,4-phenyleneethynylene (OPE) (3): A two-necked flask was charged with **1** (402 mg, 1 mmol), 1,4-dihexyloxy-2,5-diiodobenzene (265 mg, 0.500 mmol), CuI (19.0 mg, 0.100 mmol) and Pd(PPh₃)₄ (116 mg, 0.100 mmol). It was degassed with three vacuum-nitrogen cycles and then (*i*Pr)₂NH (26.0 mL) and THF (13.0 mL) were added at 0 °C. The reaction mixture was stirred at room temperature for 12 hours, and then it was subjected to water and extracted with dichloromethane. The combined organic solution was washed with water NH₄OH (50%) twice, distilled water twice and brine twice and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified using a silica gel chromatograph with dichloromethane/hexane (1:2) as eluent to afford **3** (421 mg, 78.0%) as light yellow crystal. ¹H NMR (CDCl₃), d (ppm): 7.53 (m, 4 H), 7.33 (m, 6), 7.01 (s, 6 H), 4.04 (m, 12 H), 1.85 (m, 12 H), 1.52 -1.34 (m, 36 H), 0.89 (m, 18 H); ¹³C NMR (CDCl₃), d (ppm): 153.85, 153.71, 131.79, 128.5, 128.47, 123.69, 117.44, 117.33, 117.28, 114.49, 114.20, 95.11, 91.75, 86.23, 69.93, 69.88, 69.81, 31.85, 29.57, 29.51, 25.99, 25.91, 22.88, 14.28; element analysis calcd (%) for C₇₄H₉₄O₆: C 82.33 H 8.78; found: C 82.56 H 8.54; MALDI-TOF MS: *m/z*: 1079.71 [*M*+1]⁺.

Linear-shaped OH-functionalized OPE (4): A two-necked flask was charged with **2** (502 mg, 1.00 mmol), 1,4-dihexyloxy-2,5-diiodobenzene (265 mg, 0.500 mmol), CuI (19.0 mg, 0.100 mmol) and Pd(PPh₃)₄ (116 mg, 0.100 mmol). It was degassed with three vacuum-nitrogen cycles and then (*i*Pr)₂NH (26.0 mL) and THF (13.0 mL) were added at 0 °C. The reaction mixture was stirred at room temperature for 12 hours, and then it was subjected to water and extracted with dichloromethane. The combined organic solution was washed with water NH₄OH (50%) twice, distilled water twice and brine twice and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue (about 600 mg) was obtained and dissolved in the mixture of THF (25.0 mL) and methanol (3.00 mL). The combined solution was added *p*-toluenesulfonic acid (0.490 g, 4.45 mmol) and stirred at 60 °C for 6 hours. After cooling, the solution was diluted with dichloromethane and washed twice with water and with once half-saturated brine to remove the catalyst, and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified using a silica gel chromatograph with dichloromethane/ethyl acetate (15:1) as eluent to afford **4** (350 mg, 63.0%) as yellow crystal. ¹H NMR (CDCl₃), d (ppm): 7.44 (d, 4 H), 7.00 (s, 4 H), 6.82 (d, 4 H), 5.00 (s, 2 H), 4.05 (m, 12 H), 1.85 (m, 12 H), 1.55-1.33 (m, 36 H), 0.90 (m, 18 H); ¹³C NMR (CDCl₃), d (ppm): 153.86, 153.70, 150.71, 132.98,

121.79, 121.42, 117.43, 117.26, 114.66, 114.48, 113.88, 94.10, 91.83, 91.73, 86.21, 69.91, 69.87, 69.78, 31.83, 29.53, 29.50, 25.96, 25.91, 22.86, 14.26; MALDI-TOF MS: m/z : 1110.69 $[M]^+$.

4-(Hexyloxy)-2,5-diiodophenol (5a): A two-necked flask was charged with 1,4-diiodo-2,5-hydroquinone (3.37 g, 9.32 mmol) and degassed. The solution of sodium hydroxide (573 mg, 14.3 mmol) in the absolute ethanol (90.0 mL) was added to the flask at room temperature under a nitrogen atmosphere. The mixture solution was warmed to 60 °C with constant stirring, followed by the dropwise addition of 1-bromohexane (1.54 g, 9.32 mmol). After 10 hour of stirring under nitrogen atmosphere, the reaction mixture was cooled and filtered, and the precipitate was washed with methanol. The filtrate was concentrated to remove the solvents. Distilled water was added to the residue, and the mixture was acidified with concentrated HCl, boiled gently for 1 hour, and cooled. The resulting precipitate was collected by filtration, washed with water. The crude product was purified by column chromatography on silica gel using dichloromethane/hexane (1:5) as eluent to get the pure product **5a** (2.50 g, 60.0%). ^1H NMR (CDCl_3), δ (ppm): 7.40 (s, 1 H), 7.02 (s, 1 H), 4.91 (s, 1 H), 3.92 (t, 2 H), 0.93 (m, 3 H), 1.81 (m, 2 H), 1.52-1.34 (m, 6 H).

1,4-Bis(6-hydroxyhexyloxy)-2,6-diiodobenzene (5b): In a round bottom flask containing 2-butanone (40.0 mL) were combined 1,4-diiodo-2,5-hydroquinone (2.06 g, 5.70 mmol), 6-bromohexanol (2.27 g, 12.5 mmol), K_2CO_3 (6.32 g, 45.8 mmol), and NaI (0.20 g, 1.29 mmol). The mixture was heated at 70 °C for 24 hours under nitrogen atmosphere. The reaction mixture was filtered and the salts washed with dichloromethane. The filtrate was washed several times with NaOH solution (0.1 N), followed by distilled water, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was recrystallized from the mixture of dichloromethane/hexane (1:3) to give pure product **5b** (2.34 g, 73.0%) as white powder. ^1H NMR (CDCl_3), δ (ppm): 7.16 (s, 2 H), 3.95 (m, 4 H), 3.68 (m, 4 H), 2.17 (s, 2 H), 1.82 (m, 4 H), 1.46-1.30 (m, 12H); ^{13}C NMR (CDCl_3), δ (ppm): 153.02, 122.97, 86.51, 70.36, 63.14, 32.89, 29.31, 26.12, 25.64.

6-(4-(Hexyloxy)-2,5-diiodophenoxy)hexanol (6): In a round bottom flask containing 2-butanone (40.0 mL) were combined **5a** (2.54 g, 5.70 mmol), 6-bromohexanol (1.14 g, 6.25 mmol), K_2CO_3 (3.16 g, 22.9 mmol), and NaI (0.100 g, 0.645 mmol). The mixture was heated 70 °C for 24 hours under nitrogen atmosphere. The reaction mixture was filtered and the salts washed with dichloromethane. The filtrate was washed several times with NaOH solution (0.1 N), followed by distilled water, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane/hexane (1:2) **6** (2.34 g, 75.0%) as white liquid. ^1H NMR (CDCl_3), δ (ppm): 7.16 (s, 2 H), 3.94 (m, 4 H), 3.67 (m, 2 H), 2.18 (s, 1 H), 1.82-1.30 (m, 16 H),

0.90 (m, 3 H); ^{13}C NMR (CDCl_3), d (ppm): 153.09, 152.96, 122.97, 122.94, 86.53, 86.50, 70.56, 70.36, 63.11, 63.00, 34.11, 33.62, 29.92, 29.31, 26.12, 25.93, 22.82, 14.28.

T-shaped OH-functionalized OPE (7a): A two-necked flask was charged with **1** (402 mg, 1 mmol), **6** (273 mg, 0.500 mmol), CuI (19.0 mg, 0.100 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (116 mg, 0.100 mmol). It was degassed with three vacuum-nitrogen cycles and then $(i\text{Pr})_2\text{NH}$ (26.0 mL) and THF (13.0 mL) were added at 0 °C. The reaction mixture was stirred at room temperature for 12 hours, and then it was subjected to water and extracted with dichloromethane. The combined organic solution was washed with water NH_4OH (50%) twice, distilled water twice and brine twice and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified using a silica gel chromatograph with dichloromethane/ethyl acetate (10:1) as eluent to afford **7a** (329 mg, 60.0%) as yellow crystal. ^1H NMR (CDCl_3), d (ppm): 7.51 (m, 4 H), 7.32 (m, 6 H), 7.01 (s, 6 H), 4.05 (m, 12 H), 3.66(m, 2 H), 2.12(s, 1 H), 1.85 (m, 12 H), 1.70-1.35 (m, 36 H), 0.90 (m, 15 H); ^{13}C NMR (CDCl_3), d (ppm): 153.78, 153.68, 153.65, 131.80, 128.58, 128.45, 123.67, 117.62, 117.35, 117.279, 114.50, 114.42, 95.18, 91.74, 91.61, 86.22, 69.86, 69.78, 66.20, 31.89, 30.95, 30.78, 29.61, 29.54, 29.38, 25.95, 25.85, 25.82, 22.84, 14.32. MALDI-TOF MS: m/z : 1094.70 $[M]^+$.

Cross-shaped OH-functionalized OPE (7b): A two-necked flask was charged with **1** (402 mg, 1 mmol), **5b** (281 mg, 0.500 mmol), CuI (19.0 mg, 0.100 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (116 mg, 0.100 mmol). It was degassed with three vacuum-nitrogen cycles and then $(i\text{Pr})_2\text{NH}$ (26.0 mL) and THF (13.0 mL) were added at 0 °C. The reaction mixture was stirred at room temperature for 12 hours, and then it was subjected to water and extracted with CH_2Cl_2 . The combined organic solution was washed with water NH_4OH (50%) twice, water twice and brine twice and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified using a silica gel chromatograph with dichloromethane/ethyl acetate (8:1) as eluent to afford **7b** (322 mg, 58%) as yellow crystal. ^1H NMR (CDCl_3), d (ppm): 7.54 (m, 4 H), 7.35 (m, 6 H), 7.01 (s, 6 H), 4.15 (t, 12 H), 3.68 (m, 4 H), 2.15 (s, 2 H), 1.85-1.35 (m, 48 H), 0.90 (m, 12 H); ^{13}C NMR (CDCl_3), d (ppm): 153.83, 153.72, 153.67, 131.78, 128.52, 128.46, 123.65, 117.63, 117.37, 117.32, 114.59, 114.36, 95.18, 91.77, 91.57, 86.18, 69.89, 69.82, 66.13, 31.85, 31.76, 30.78, 29.58, 29.50, 29.38, 26.10, 25.99, 25.92, 22.87, 14.30; MALDI-TOF MS: m/z : 1111.53 $[M]^+$.

Linear Macroinitiator (8a): To a solution of **4** (289 mg, 26 μmol) and Et_3N (373 μL , 2.60 mmol) in THF (20 mL) was slowly added 2-bromo-2-methylpropanoyl bromide (600 mg, 2.6 mmol) at 0 °C in darkness. The reaction mixture was stirred for 1 h at 0 °C and for additional 12 h at room temperature. The red solution was condensed by evaporation of most of the solvent. The residue was subjected to water and extracted with CH_2Cl_2 . The organic solution was washed with brine and dried over anhydrous sodium

sulfate. After removal of the solvent under reduced pressure, the residue was purified using a silica gel chromatograph with dichloromethane/hexane (1:4) as eluent to afford **8a** (345 mg, 94%) as light yellow crystal. ^1H NMR (CDCl_3), d (ppm): 7.57 (d, 4 H), 7.14 (d, 4 H), 7.01 (s, 6 H), 4.04 (m, 12 H), 2.07 (s, 12 H), 1.85 (m, 12 H), 1.55-1.33 (m, 36 H), 0.90 (m, 18 H); ^{13}C NMR (CDCl_3), d (ppm): 170.23, 153.86, 153.70, 150.71, 132.98, 121.79, 121.42, 117.43, 117.26, 114.66, 114.48, 113.88, 94.10, 91.83, 91.71, 86.56, 69.93, 69.88, 69.78, 55.45, 31.91, 31.85, 30.82, 29.53, 25.98, 25.90, 22.88, 14.29; element analysis calcd (%) for $\text{C}_{82}\text{H}_{104}\text{Br}_2\text{O}_{10}$: C 69.87 H 7.44; found: C 70.10 H 7.31; MALDI-TOF MS: m/z : 1408.60 $[M]^+$.

T-shaped Macroinitiator (8b): It was synthesized using the similar procedure as described for **8a**. ^1H NMR (CDCl_3), d (ppm): 7.54 (m, 4 H), 7.35 (m, 6 H), 7.01 (s, 6 H), 4.15(t, 2 H), 4.04 (m, 12 H), 1.95 (s, 6 H), 1.85-1.80 (m, 14 H), 1.70-1.35 (m, 34 H), 0.90 (m, 15 H); ^{13}C NMR (CDCl_3), d (ppm): 171.94, 153.82, 153.71, 153.69, 131.78, 128.53, 128.47, 123.65, 117.62, 117.37, 117.29, 114.59, 114.46, 95.18, 91.74, 91.62, 86.21, 69.86, 69.78, 66.20, 56.17, 55.14, 31.89, 30.95, 30.78, 29.61, 29.54, 29.38, 25.96, 25.86, 25.84, 22.85, 14.30; element analysis calcd (%) for $\text{C}_{78}\text{H}_{99}\text{BrO}_8$: C 75.28 H 8.02; found: C 75.10 H 7.99; MALDI-TOF MS: m/z : 1244.60 $[M]^+$.

Cross-shaped Macroinitiator (8c): It was synthesized using the similar procedure as described for **8a**. ^1H NMR (CDCl_3), d (ppm): 7.54 (m, 4 H), 7.35 (m, 6 H), 7.01 (s, 6 H), 4.15 (t, 4 H), 4.04 (m, 12 H), 1.96 (s, 12 H), 1.90-1.80 (m, 14H), 1.70-1.35 (m, 34 H), 0.90 (m, 12 H); ^{13}C NMR (CDCl_3), d (ppm): 171.92, 153.84, 153.74, 153.67, 131.79, 128.53, 128.49, 123.65, 117.64, 117.39, 117.32, 114.59, 114.36, 95.18, 91.77, 91.59, 86.18, 69.89, 69.80, 66.14, 56.15, 55.12, 31.85, 30.97, 30.78, 29.58, 29.50, 29.38, 26.00, 25.89, 25.82, 22.87, 14.30; element analysis calcd (%) for $\text{C}_{82}\text{H}_{104}\text{Br}_2\text{O}_{10}$: C 69.87 H 7.44; found: C 69.70 H 7.30; MALDI-TOF MS: m/z : 1408.50 $[M]^+$.

MALDI-TOF Spectra of Macroinitiators and OPE

The matrix-assisted laser desorption ionization-time-of-flight mass spectra (MALDI-TOF MS) of **3** and the macroinitiators are depicted in Figure S1, showing the successful synthesis of **3** and the macroinitiators.

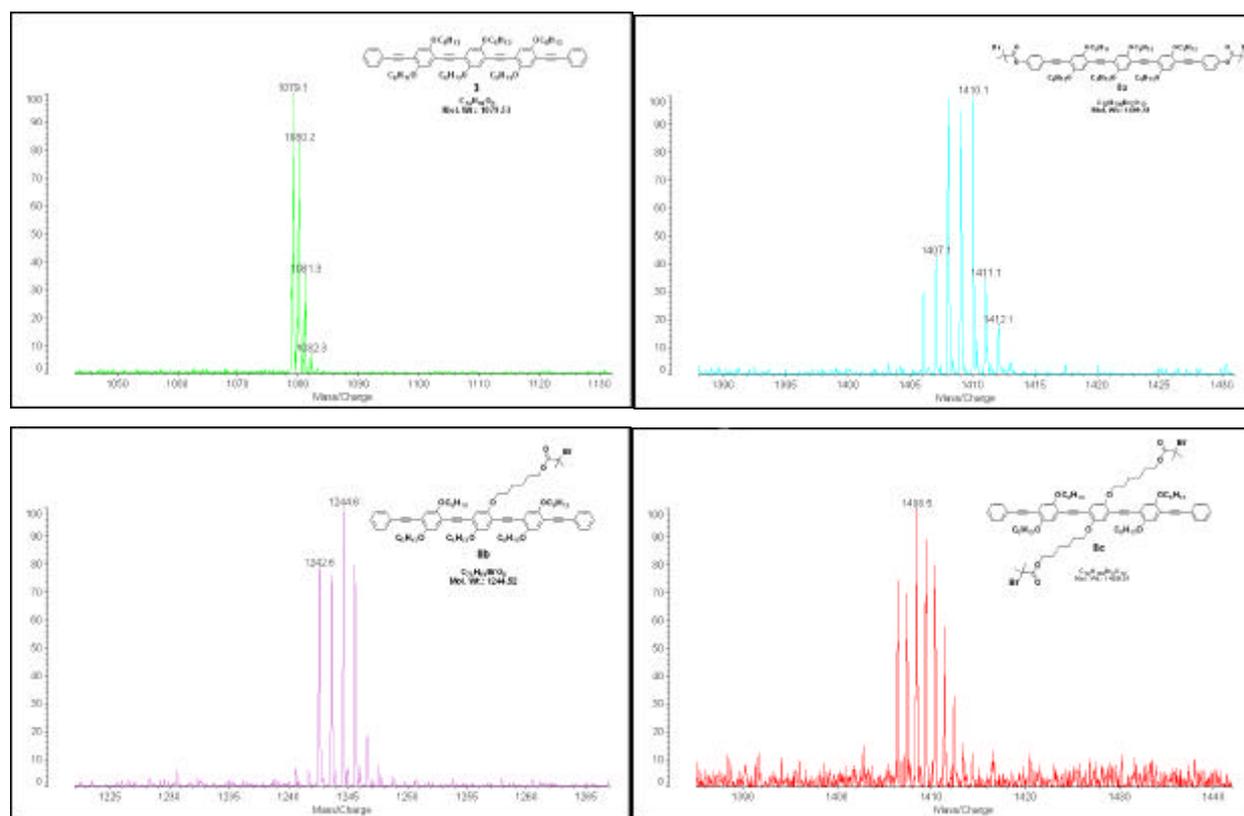


Figure S1. MALDI-TOF MS of **3** and the macroinitiators.

NMR Spectra of the Block Copolymers

The ^1H and ^{13}C NMR spectra of P_T are illustrated in Figure S2, which are identical to the spectra of P_C due to the similar chemical structure.

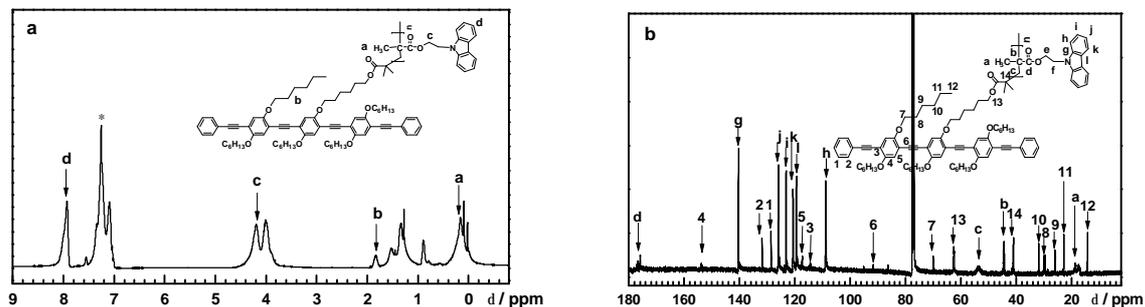


Figure S2. ^1H (a) and ^{13}C (b) NMR spectra of P_T .

Optical properties of Macroinitiators and OPE (3)

The absorption and emission spectra of macroinitiators and **3** are shown in Figure S3.

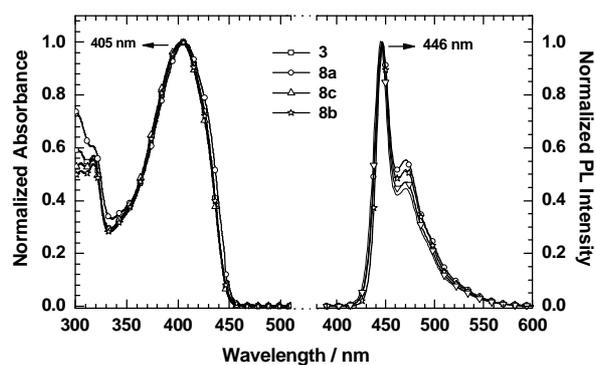


Figure S3. Normalized UV-vis absorption and PL emission spectra of **3** and the macroinitiators in tetrahydrofuran (10^{-6} mg/mL). The excitation wavelength of the PL emission spectra is 405 nm.