

Synthesis of Solution Soluble Pentacene-containing Conjugated Copolymers

Toshihiro Okamoto and Zhenan Bao*

*Department of Chemical Engineering, Stanford University,
381 North-south Mall, Stanford, California 94305.*

Supporting Materials

Characterization: ^1H and ^{13}C NMR spectra were recorded using Varian Inova 300, Merc 400 or Inova 500 in deuterated chloroform at 293 K. Size exclusion chromatography (SEC) was performed in THF solution and the molecular weights calculated using a calibration curve based on polystyrene standards. Thermal gravimetric analyses (TGA) were performed using a Mettler TOLEDO TGA/SDTA 851 $^\circ$ at a heating rate of 10 $^\circ\text{C min}^{-1}$ under a nitrogen flow (20 mL/min). Electrochemical analysis of the compounds in solution was carried out by cyclic voltammetry using a CH Instruments Electrochemical Analyzer. The experiments were performed under a stream of argon in a saturated solution of 0.05 M tetra-*n*-butylammonium hexafluorophosphate which was recrystallized from ethanol ($^n\text{Bu}_4\text{NPF}_6$, from Strem Chemicals, Inc.) as a supporting electrolyte in anhydrous *o*-dichlorobenzene. The experiments were carried out using platinum electrodes at a scan rate of 100 mVs^{-1} against Ag wire as a pseudoreference electrode at room temperature. Ferrocene was used as a reference oxidation potential for all of our compounds. We calculated HOMO levels from the onset wave oxidation potential compared to 6,13-bis(triisopropylsilylethynyl)pentacene which has a reported HOMO level of -5.20 eV.¹ UV-vis and FL spectra in *o*-dichlorobenzene were collected from a UV-vis spectrophotometer (model Cary 6000i) at room temperature using a quartz cuvette with a path length of 1 cm capped under Ar prepared inside a glove box. Optical bandgaps (HOMO-LUMO gaps) were calculated from the edge of the visible-absorption bands.

Preparation of Starting Materials: 1,4-Diethynyl-2,5-bis(octyloxy)benzene and 1,4-diethynyl-2,5-bis(2-ethylhexyloxy)benzene were synthesized in the same manner as

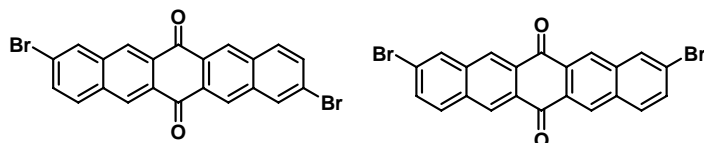
literature.²

4-Bromo-1,2-bis(dibromomethyl)benzene

To a solution of *N*-bromosuccinimide (NBS) (29.2 g, 164 mmol, 2.03 mol amt.) in carbon tetrachloride (100 mL) was added benzoyl peroxide (BPO) (638 mg, 0.0325 mol amt.), which was dried over phosphorous pentoxide under vacuum overnight, as a catalyst and corresponding *o*-xylene (15.0 g, 81.0 mmol) under argon condition. The reaction suspension was stirred and heated under reflux for 4 hs. After the reaction mixture was once cooled down to room temperature, both additional NBS (29.2 g, 2.03 mol amt.) and BPO (638 mg, 0.0325 mol amt) was added to reaction mixture which was heated up to reflux again. After overnight, the final reaction mixture was cooled down and firstly the succinimide formed was filtered off and washed with dichloromethane thoroughly. The filtrate obtained was then washed with water three times, followed by a saturated sodium thiosulfate solution and brine, dried over magnesium sulfate, filtered, and concentrated with a rotary evaporator. The resulting mixture was purified by either recrystallization from hexane or a silica gel column chromatography (hexane) to give the desired compound as a white powder in 62 % yield.

¹H NMR (300 MHz, CDCl₃): δ 7.81 (s, 1H), 7.60-7.46 (m, 2H), 7.05 (s, 1H), 7.02 (s, 1H), ¹³C NMR (75 MHz, CDCl₃) δ 139.12, 136.65, 133.55, 132.23, 131.15, 124.18, 35.40, 34.96, MS (DEI) 500 (M⁺), Anal. Calcd for C₈H₅Br₅: C, 19.19; H, 1.01; Br, 79.80. Found: C, 19.27; H, 1.00; Br, 79.70.

Dibromopentacene quinone (2,9-Dibromopentacene quinone and 2,10-dibromopentacene quinone)

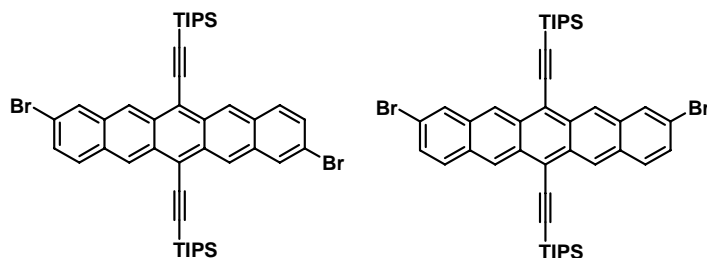


To a mixture of 4-bromo-1,2-bis(dibromomethyl)benzene (66.7 g, 133.2 mmol, 2.2 mol amt.) and 1,4-benzoquinone (6.54 g, 60.6 mmol, 1.0 mol amt.) was added sodium iodide (121.2 g, 808 mmol, 13.3 mol amt.) and anhydrous *N,N*-dimethylformamide (500 mL). The rusty red solution was stirred and heated to 60 °C for two days under argon. The reaction mixture was cooled down before quenched with cold water and filtered off, and

the collected solid was washed with water and methanol, and then dried under vacuum. The crude compound was then washed with hot methanol and hot chloroform to give 6.73 g (14.4 mmol) in 24 % yield.

MS (DEI) 466 (M^+), Anal. Calcd for $C_{22}H_{10}Br_2O_2$: C, 56.69; H, 2.16. Found: C, 56.64; H, 1.94.

Dibromo pentacene monomer (6,13-Bis(triisopropylsilylethynyl)-2,9-dibromopentacene and 6,13-Bis (triisopropylsilylethynyl)-2,10-dibromopentacene)

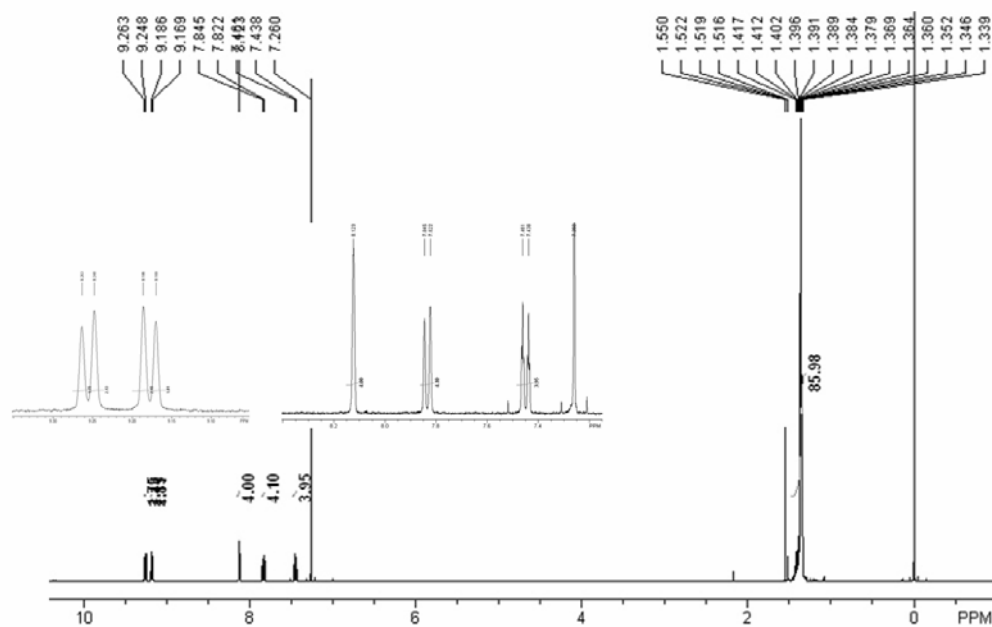


To a solution of isopropyl magnesium chloride (67.0 mmol, 67.0 mL, 1.0 M in THF solution) in THF (66 mL) was added triisopropylsilylacetylene (15.0 mL, 67.0 mmol) dropwise and then heated at 60°C for 45 min. After the mixture was cooled down to room temperature, a mixture of dibromopentacene quinones (5.0 g, 10.7 mmol) was added under a stream of nitrogen and heated at 60°C again for 19 hrs to form a brown solution. After a further cooling over 30 min, the mixture was re-heated to 60°C, after which a solution of stannyl chloride dihydrate (24.2 g, 107.3 mmol, 10 mol amt.) in 10 % hydrogen chloride solution (110 mL) was added to form a dark blue solution with two layers. The reaction mixture was concentrated under reduced pressure. The residual was extracted with dichloromethane, washed with water and brine. The resulting organic layer was dried over magnesium sulfate, filtered off and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with hexane as an eluent to give the desired product (4.72 g, 5.92 mmol) in 55% yield.

1H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 2H), 9.25 (s, 2H), 9.19 (s, 2H), 9.17 (s, 2H), 8.12 (s, 4H), 7.83 (d, 4H, $J = 9.0$ Hz), 7.45 (d, 4H, $J = 9.0$ Hz), 1.46-1.34 (m, 84H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.87, 132.79, 131.13, 130.90, 130.86, 130.62, 130.49,

130.40, 130.24, 129.82, 129.79, 127.04, 127.00, 125.61, 125.57, 120.63, 120.57, 119.02, 118.85, 118.69, 19.11, 19.09, 19.08, 11.71. MS (DEI) 796 (M^+). Anal. Calcd for $C_{44}H_{52}Br_2Si_2$: C, 66.32; H, 6.58; Br, 20.05; Si, 7.05. Found: C, 66.26; H, 6.81; Br, 20.33.

^1H NMR of **TIPSEBr₂P**



^{13}C NMR of **TIPSEBr₂P**

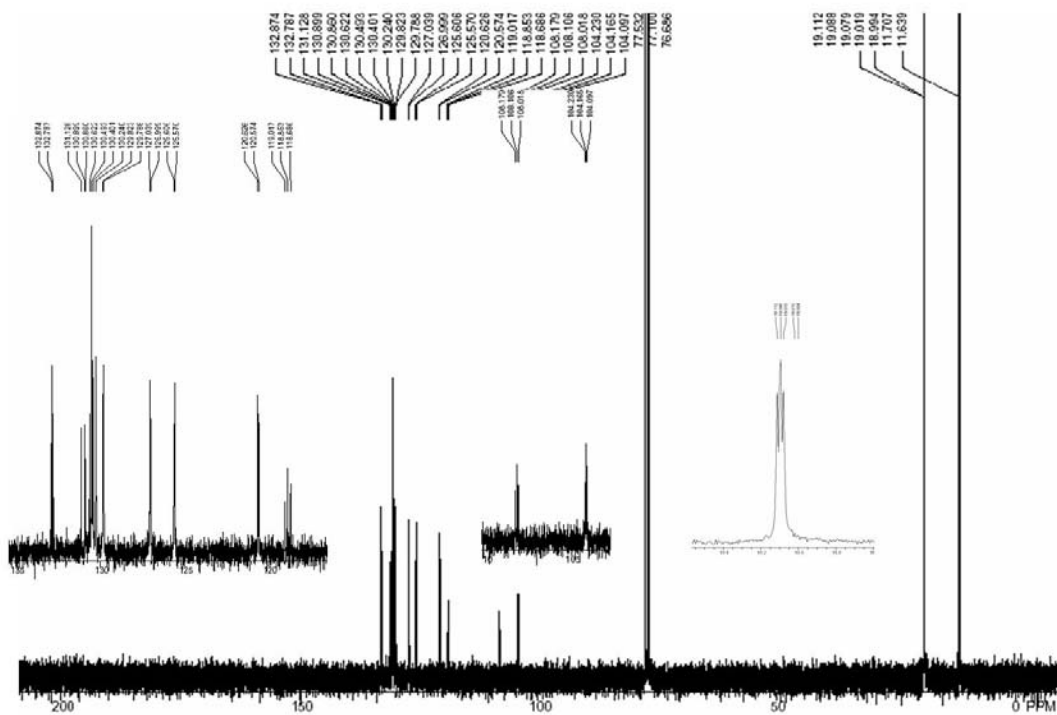


Figure 1S. ^1H NMR (top) and ^{13}C NMR (bottom) spectra of **TIPSEBr₂P**

Stability test of TIPSEBr₂P at 70 °C under degassed toluene-diisopropylamine (2 : 1).

Condition: TIPSEBr₂P (50 mg), dry toluene (3.0 mL) and diisopropylamine (1.5 mL) were placed in 25 mL Schlenk tube with a stirring bar. The tube was degassed five times and then heated at 70 °C for 3 days. As compared to starting material and product after 3 days,

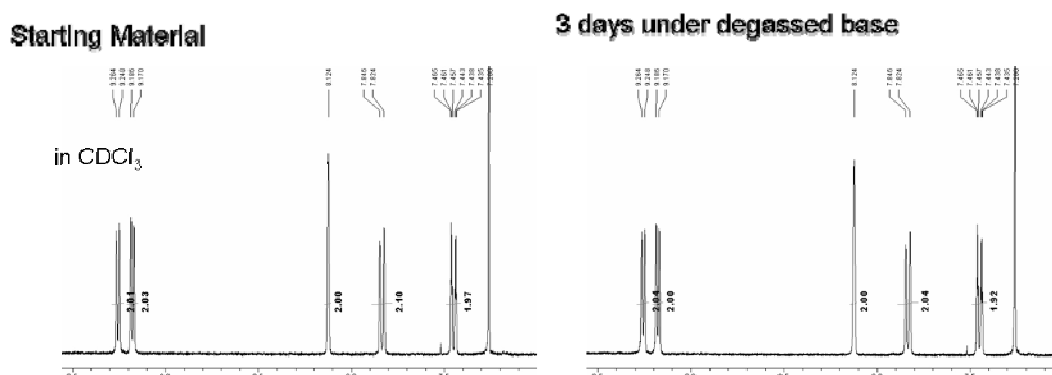
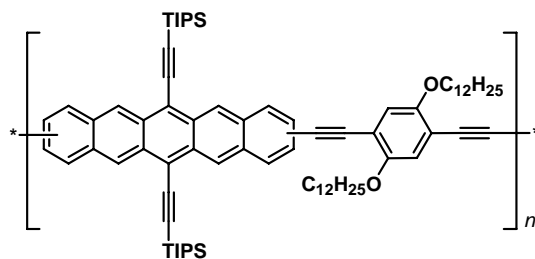


Figure 2S. ¹H NMR spectra of TIPSEBr₂P just after sampling (left) and 3 days later (right).

**Bis(triisopropylsilylethynyl)pentacene-bis(dodecyloxy)diethynylbenzene
Copolymer 1**

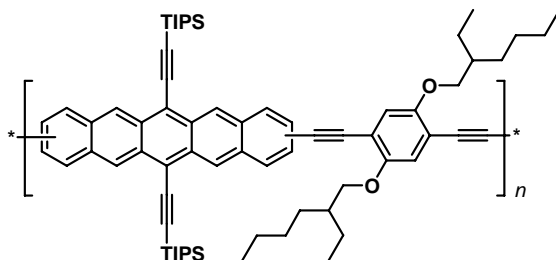


Dry toluene (6.3 mL) was placed in a 25 mL Schlenk tube with a stirring bar. The flask was evacuated and back-filled with argon five times, followed by the addition of Pd(PhCN)₂Cl₂ (2.9 mg, 0.00753 mmol, 0.06 mol amt.), CuI (1.0 mg, 0.0050 mmol, 0.04 mol amt.), P^tBu₃ in toluene (1.0 M, 15 μL, 0.0151 mmol, 0.12 mol amt.), degassed diisopropylamine (41.5 μL, 0.301 mmol, 2.4 mol amt.), TIPSEBr₂P (100 mg, 0.1255 mmol) and diethynyl (68.3 mg, 0.138 mmol, 1.1 mol amt.) under argon atmosphere. The mixture was stirred at room temperature for 46 h. The reaction mixture was poured into

methanol (200 mL) to form a black precipitate which was collected and then washed with methanol thoroughly. The resulting polymer was washed with acetone, followed by hexane. Finally, the polymer was dissolved in hot ODCB and filtered off with a syringe filter (0.25 μm pore size) to give a dark green solution which was precipitated from methanol to give black solids in 62 % yield.

^1H and ^{13}C NMR of Polymer **1** could not be measured due to bad solubility. GPC: $M_n = 11,344 \text{ g mol}^{-1}$, polydispersity index (PDI): 2.21. UV-vis (*o*-dichlorobenzene): $\lambda_{\text{max}} = 671 \text{ nm}$. Anal. Calcd for $(\text{C}_{78}\text{H}_{106}\text{O}_2\text{Si}_2)_n$: C, 82.77; H, 9.44. Found: C, 80.31; H, 9.11.

Bis(triisopropylsilylethynyl)pentacene-bis(2-ethylhexyloxy)diethynylbenzene Copolymer 2



Dry toluene was placed in a 25 mL Schlenk tube with a stirring bar. The flask was evacuated and back-filled with argon five times, followed by the addition of $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ (2.9 mg, 0.00753 mmol, 0.06 mol amt.), CuI (1.0 mg, 0.0050 mmol, 0.04 mol amt.), P^tBu_3 in toluene (1.0 M, 15 μL , 0.0151 mmol, 0.12 mol amt.), degassed diisopropylamine (41.5 mL, 0.301 mmol, 2.4 mol amt.), $\text{TIPSEBr}_2\text{P}$ (100 mg, 0.1255 mmol) and diethynylphenyl (52.8 mg, 0.138 mmol, 1.1 mol amt.) under an argon atmosphere. The mixture was stirred at room temperature for 6 h. The reaction mixture was poured into methanol (300 mL) to give a black solid which was collected and then washed with methanol and acetone thoroughly. Finally, the polymer was dissolved in chloroform and filtered off with a syringe filter (0.25 μm pore size) to give a dark green solution which was precipitated from methanol to give black solids in 47 % yield.

^1H NMR (500 MHz, CDCl_3) : δ 9.25-9.22 (m, 4H), 8.22-8.8.15 (m, 2H), 7.97-7.92 (m, 2H), 7.52-7.45 (m, 2H), 7.17 (s, 2H), 4.08-3.8 (m, 4H), 3.48 (br), 1.95-1.2 (m, 60 H), 1.16-0.82 (m, 12 H). ^{13}C NMR (75 MHz, CDCl_3) : δ 155.34, 154.15, 153.93, 138.96, 132.83, 132.19, 131.90, 131.86, 131.31, 131.15, 131.07, 128.88, 128.38, 128.32, 127.02, 126.57, 121.14, 120.54, 118.81, 118.75, 117.38, 116.77, 116.62, 114.09, 107.94, 107.74,

107.56, 104.41, 104.35, 95.99, 88.37, 88.32, 72.31, 72.11, 72.04, 39.75, 39.66, 39.48, 39.39, 30.90, 30.85, 30.71, 30.67, 29.35, 29.29, 29.25, 29.20, 24.27, 24.22, 24.10, 24.04, 23.25, 23.22, 23.21, 19.17, 19.14, 19.12, 14.29, 14.26, 14.23, 11.76, 11.49, 11.44, 11.32, 11.26. GPC: $M_n = 23,921 \text{ g mol}^{-1}$, polydispersity index (PDI): 2.42. UV-vis (*o*-dichlorobenzene): $\lambda_{\text{max}} = 674 \text{ nm}$. Anal. Calcd for $(\text{C}_{70}\text{H}_{88}\text{O}_2\text{Si}_2)_n$: C, 82.62; H, 8.72. Found: C, 81.16; H, 8.66.

UV-vis and FL spectra of Polymer 1 and 2 in *o*-dichlorobenzene

Both samples of polymer 1 and 2 were prepared and sealed inside a glove box at room temperature.

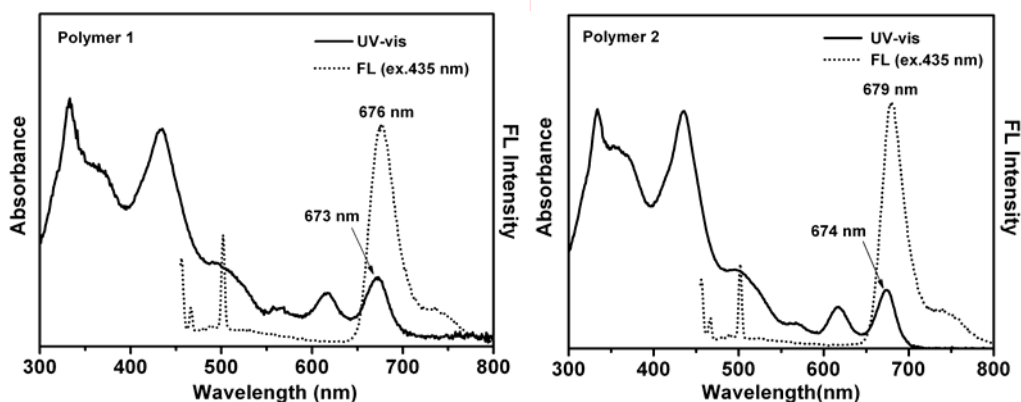


Figure 3S. UV-vis and FL spectra of polymer 1 (left) and 2 (right) at room temperature in *o*-dichlorobenzene

Stability test: polymer 2 vs TIPSEP

Measurement Condition: The time-dependent UV-vis measurement of copolymer 2 (top-left) was carried out under dry *o*-dichlorobenzene as compared to that of TIPSEP (top-right). The degradation ratio of copolymer 2 and TIPSEP based on the initial absorbance at longest peak was calculated and plotted together with linear fit lines.

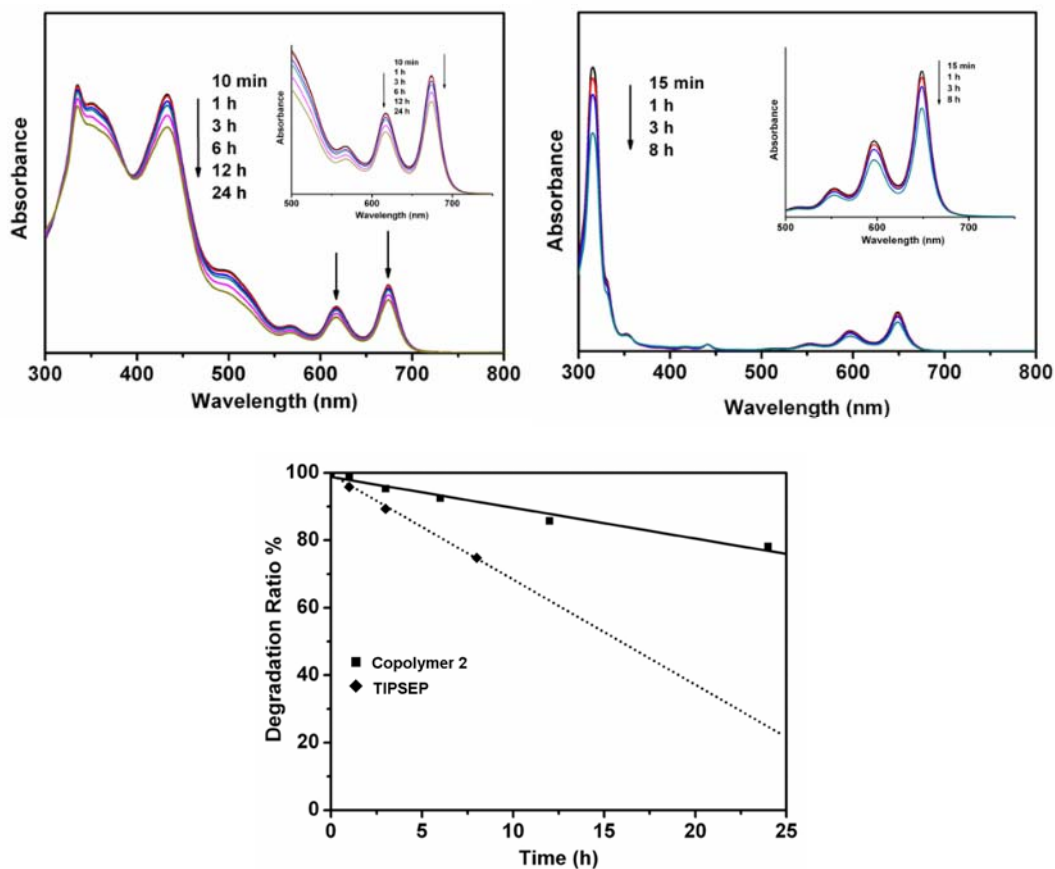


Figure 4S. Stability test of copolymer **2**(upper-left) vs **TIPSEP** (upper-right).
Degradation ratio of **2** was plotted as compared with **TIPSEP**

Thermal stability (TGA and DSC)

The thermal stability of the polymers in solid state was studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a stream of nitrogen. The degradation temperature for both copolymers was around 400 °C, slightly higher than that of **TIPSEP** (~380 °C). According to DSC results, neither polymer showed any thermal transitions between 25 and 350 °C. These results indicate that these pentacene copolymers have good thermal stability in the solid state.

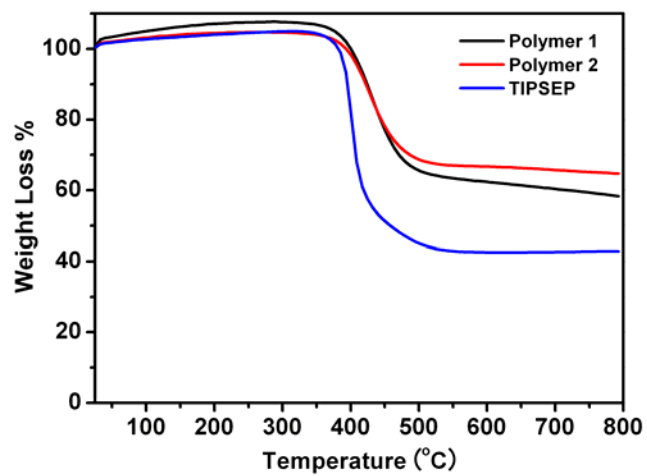


Figure 5S. TGA of polymer **1** and **2** vs **TIPSEP**

References

- (1) Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609.
- (2) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157.