

Supporting Information

Side Chain Linkages Control Aggregate Structure in Poly(Phenylene Ethynylene) Conjugated Polymers

Yajing Yang, Charles J. Zeman, IV, Habtom B. Gobeze and Kirk S. Schanze*

† Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

‡ Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249, United States

Yajing Yang,^{†,‡} Charles J. Zeman IV,^{†,‡,‡} and Kirk S. Schanze^{*,‡}

† Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

‡ Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249, United States

Corresponding Author

* E-mail: kirk.schanze@utsa.edu

CONTENTS

1. Synthetic Details.....	S3
1,4-Dioctyloxy-benzene.....	S3
1,4-Diiodo-2,5-dioctyloxy-benzene.....	S5
1,4-Dioctyloxy-2,5-di[2-(trimethylsilyl)ethynyl]-benzene.....	S6
1,4-Diethynyl-2,5-dioctyloxy-benzene.....	S8
1,4-Dioctyl-2,5-di[2-(trimethylsilyl)ethynyl]-benzene.....	S9
1,4-Diethynyl-2,5-dioctyl-benzene.....	S11
PPE-OC8.....	S12
PPE-C8.....	S13
2. Physical Properties of Polymers.....	S14
3. Photophysical Properties.....	S16
4. Computational Results.....	S18
5. References.....	S20

Synthetic Details

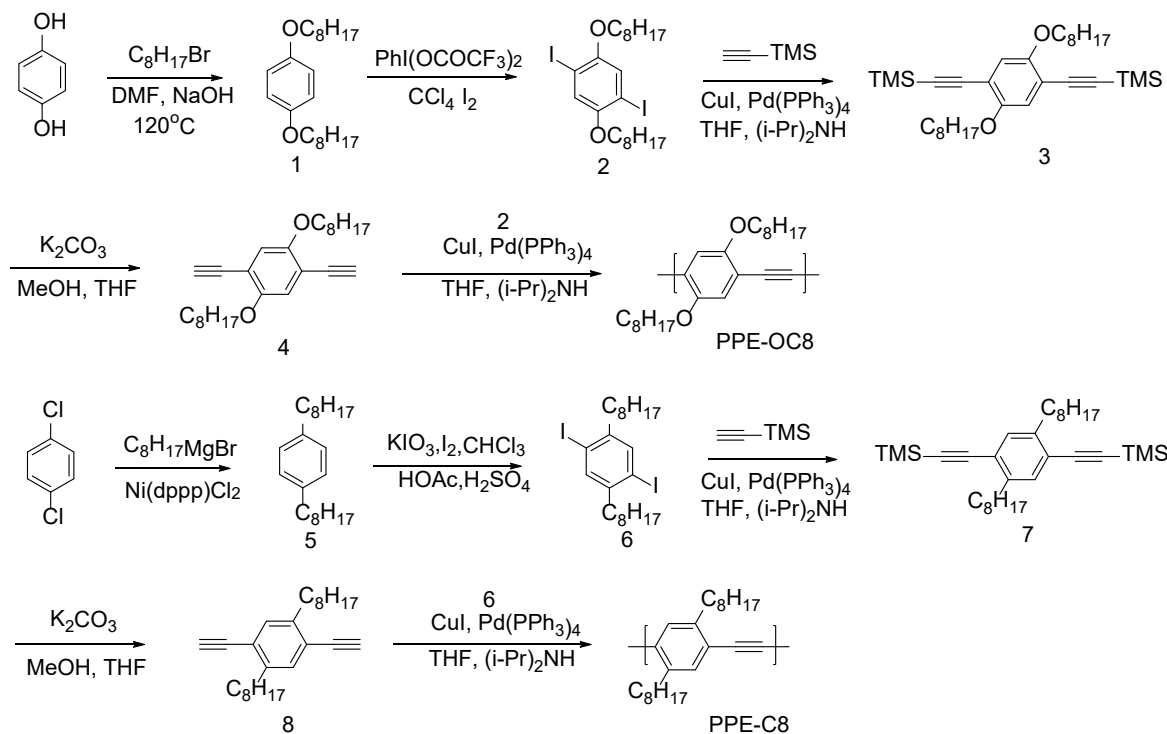


Figure S1. Synthetic procedures for PPE-OC8 and PPE-C8.

1 1,4-Dioctyloxy-benzene

1-Bromooctane (3.87 g, 20 mmol) was slowly added to a solution of hydroquinone (1.05 g, 9.5 mmol) and sodium hydroxide (0.95 g, 24 mmol) in 15 mL of dimethylformamide. The mixture was then stirred overnight at 80°C . Then the solution was cooled to room temperature. The solution was poured into cold water. The precipitate was collected by filtration. The crude product was recrystallized from ethanol and dried in a vacuum oven to give 2.56 g product (yield 82%). ^1H NMR (CDCl_3 , 500 MHz): δ = 6.82 (s, 4 H), 3.9 (t, 4 H), 1.75(m, 4 H), 1.44 (m, 4H), 1.28 (m, 16 H) 0.89 (t, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 153.13, 115.43, 68.70, 31.81, 29.41, 29.38, 29.24, 26.06, 22.65, 14.07.

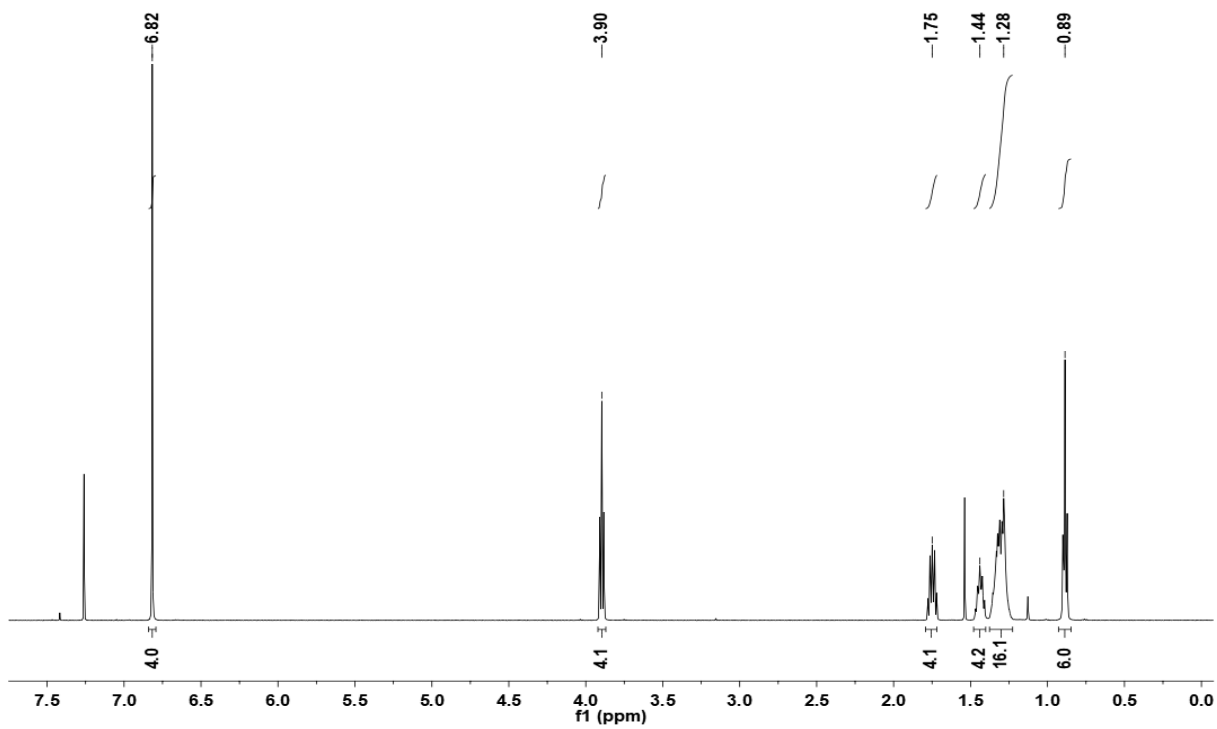


Figure S2. ¹H NMR of compound 1.

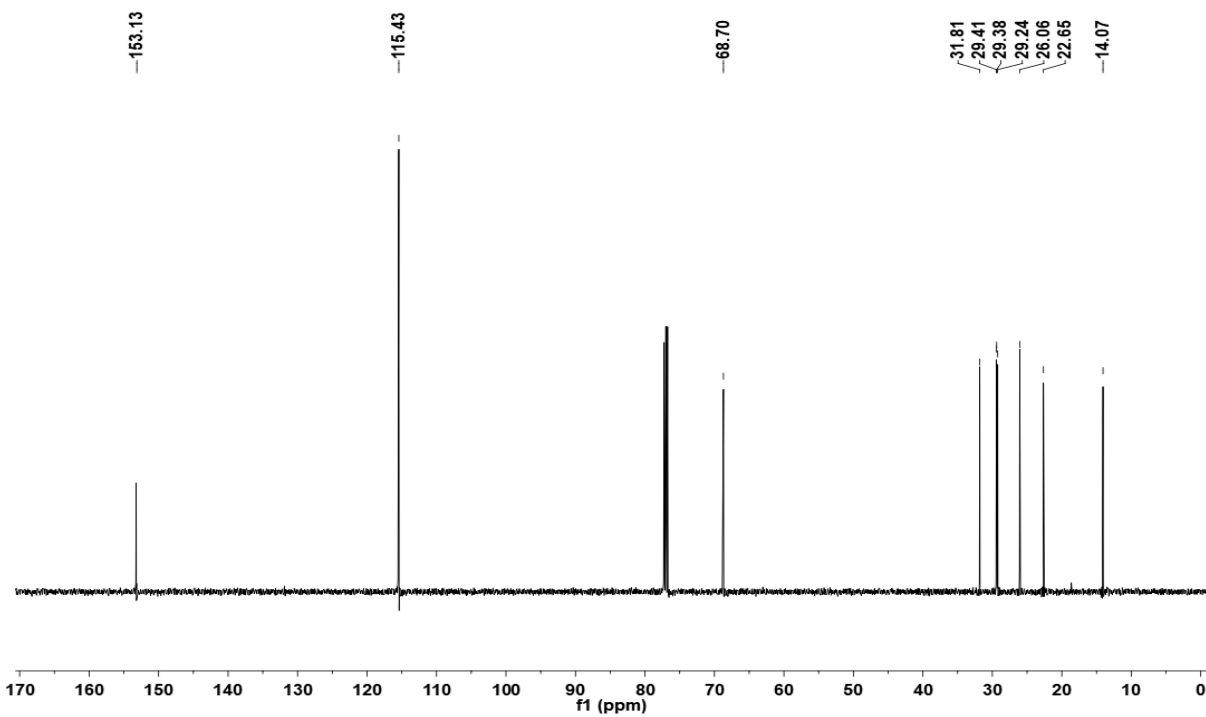


Figure S3. ¹³C NMR of compound 1.

2 1,4-Diiodo-2,5-dioctyloxy-benzene

Compound 1 (1.0 g, 3 mmol) was dissolved in 15 ml CCl_4 and degassed for about 30 min. Iodine (0.76 g, 3 mmol) and bis-(trifluoroacetoxy) iodo benzene (1.29 g, 3 mmol) were then slowly added to the solution and degassed for another 10 min. The solution was stirred for 5h under argon protection. DCM was then added to the system and washed with 5% aqueous NaHSO_3 until there was no more purple color. The solution was dried over MgSO_4 , and the solvent was removed by vacuum evaporation. The crude product was further purified by recrystallization from isopropanol to give 1.14 g white solid (yield 65%). ^1H NMR (CDCl_3 , 500 MHz): δ = 7.17(s, 2H), 3.92 (t, 4H), 1.80(m, 4H), 1.49(m, 4H), 1.29(m, 16H), 0.89 (t, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 152.91, 122.87, 86.32, 70.41, 31.77, 29.21, 29.15, 26.03, 22.65, 14.09.

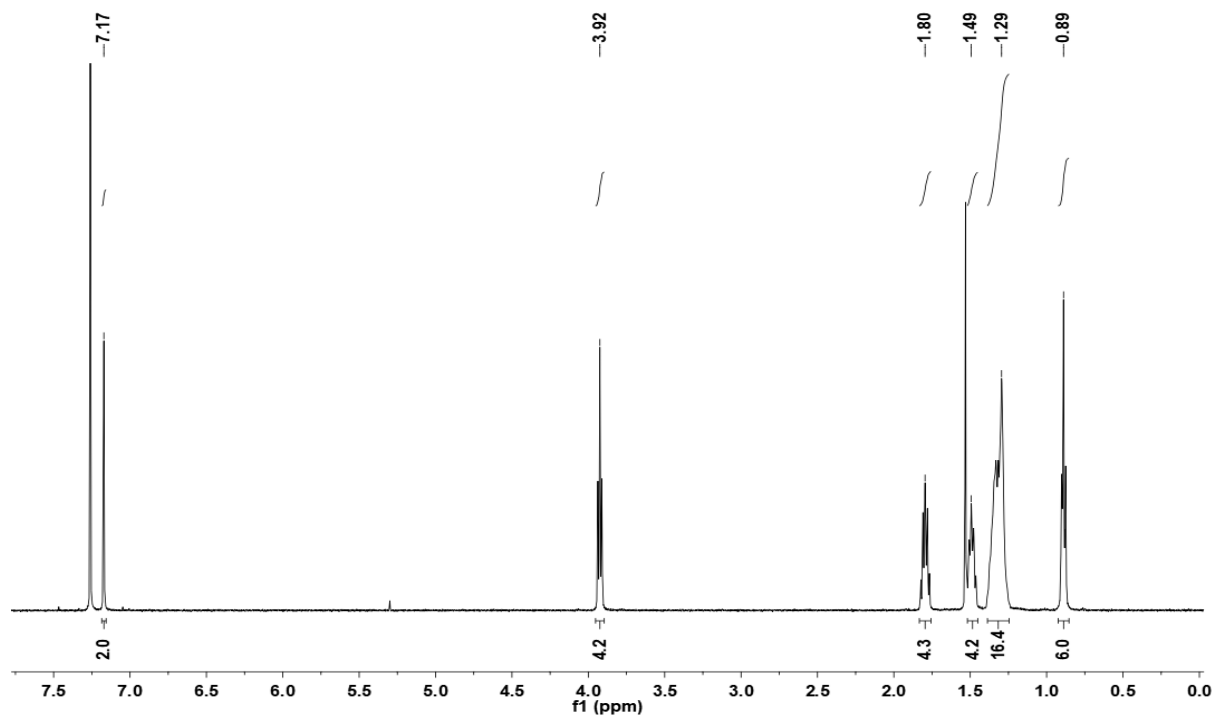


Figure S4. ^1H NMR of compound 2.

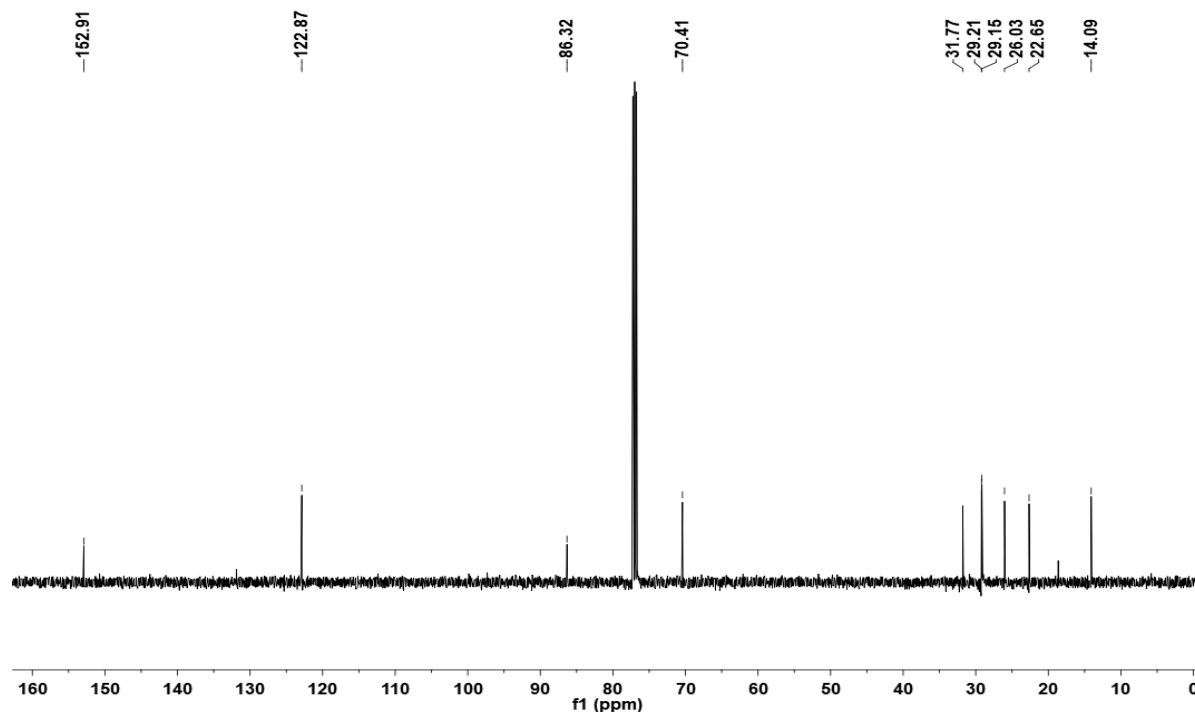


Figure S5. ^{13}C NMR of compound 2.

3 1,4-Dioctyloxy-2,5-di[2-(trimethylsilyl) ethynyl]-benzene

Compound 2 (0.3 g, 0.5 mmol) was dissolved in 15 mL 1:1 (v:v) THF:diisopropylamine and degassed for at least 30 min. CuI (4.9 mg, 0.03 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (30 mg, 0.03 mmol) were quickly added into the system and degassing was continued for 15 min. Then, trimethylsilylacetylene (0.11 g, 1.1 mmol) was added to the reaction solution and the mixture was stirred overnight at 50°C under argon protection. The reaction mixture was poured into DI water and extracted with DCM. The organic layer was washed with 1N HCl, DI water and brine several times and dried over MgSO_4 . The crude product was further purified by column chromatography using hexane and DCM (3:1) as eluent to give 0.14 g brown oil. (yield 55%). ^1H NMR (CDCl_3 , 500 MHz): δ = 6.91 (s, 2H), 3.96 (t, 4H), 1.80 (m, 4H), 1.51 (m, 4H), 1.31 (m, 18H), 0.90 (t, 6H), 0.27 (s, 18H). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 154.03, 117.28, 114.00, 101.08, 100.05, 69.49, 31.84, 29.38, 29.36, 29.28, 26.02, 22.65, 14.06, -0.05.

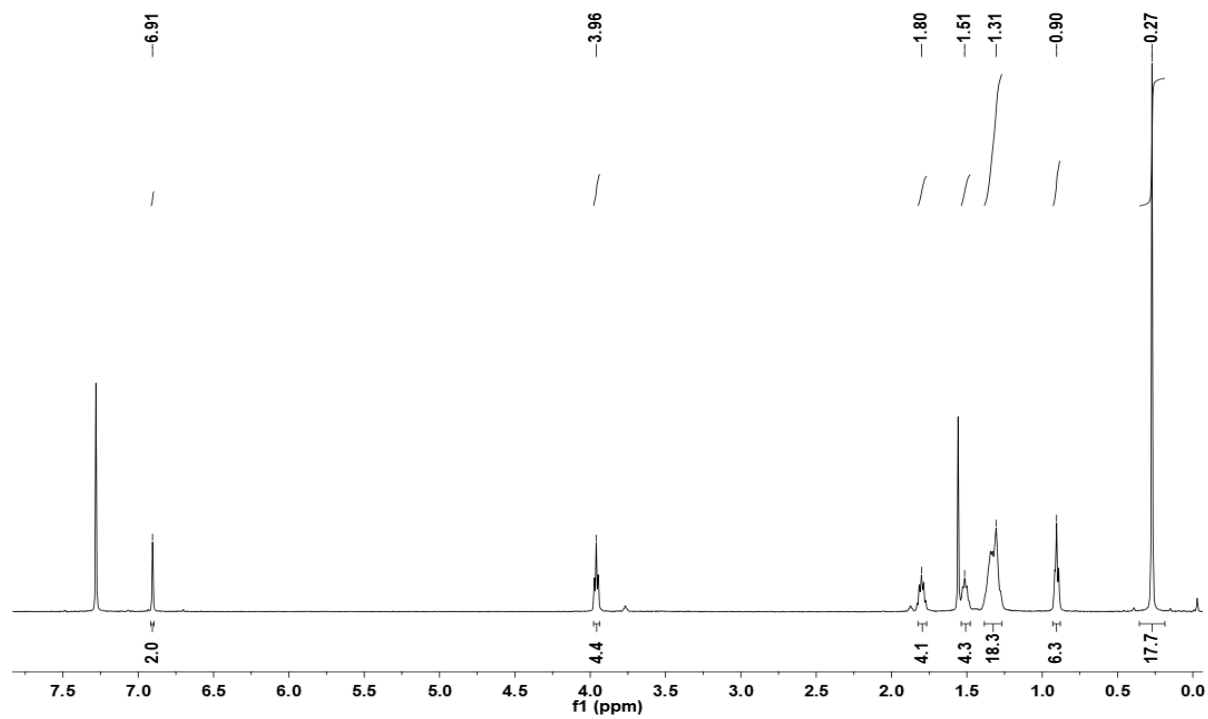


Figure S6. ¹H NMR of compound 3.

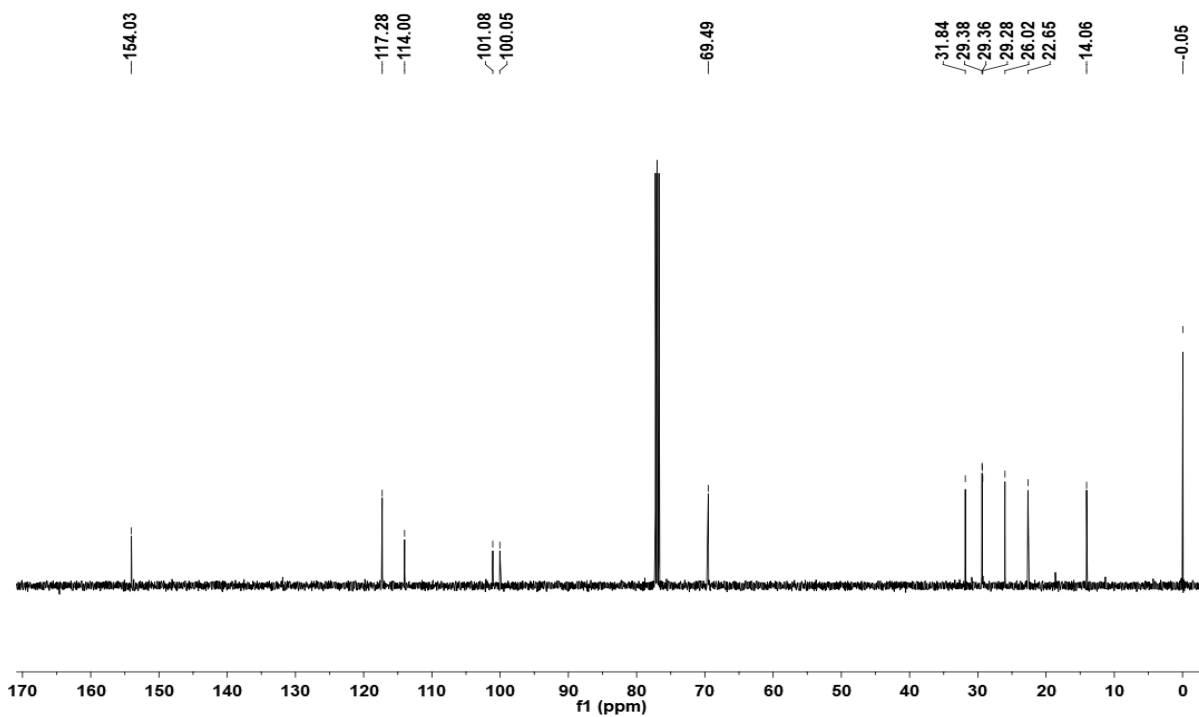


Figure S7. ¹³C NMR of compound 3.

4 1,4-Diethynyl-2,5-dioctyloxy-benzene

Compound 3 (60 mg, 0.11 mmol) and potassium hydroxide (0.34 g, 6 mmol) were dissolved in 9 mL 2:1 (v:v) THF:methanol. After 2h, TLC indicated the reaction was completed. DI water was poured into the reaction system, which was then extracted with ether several times. The organic layer was washed with DI water and brine three times, and then dried over MgSO_4 . The product was collected using vacuum evaporation to give 30.6 mg yellow solid (yield 71%). ^1H NMR (CDCl_3 , 500 MHz): δ = 6.95 (s, 2H), 3.97 (t, 4H), 3.32 (s, 2H), 1.80 (m, 4H), 1.46 (m, 4H), 1.28 (m, 20H), 0.88 (t, 4H). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 154.00, 117.81, 113.30, 82.35, 79.81, 69.70, 31.79, 29.28, 29.21, 29.13, 25.89, 22.65, 14.08.

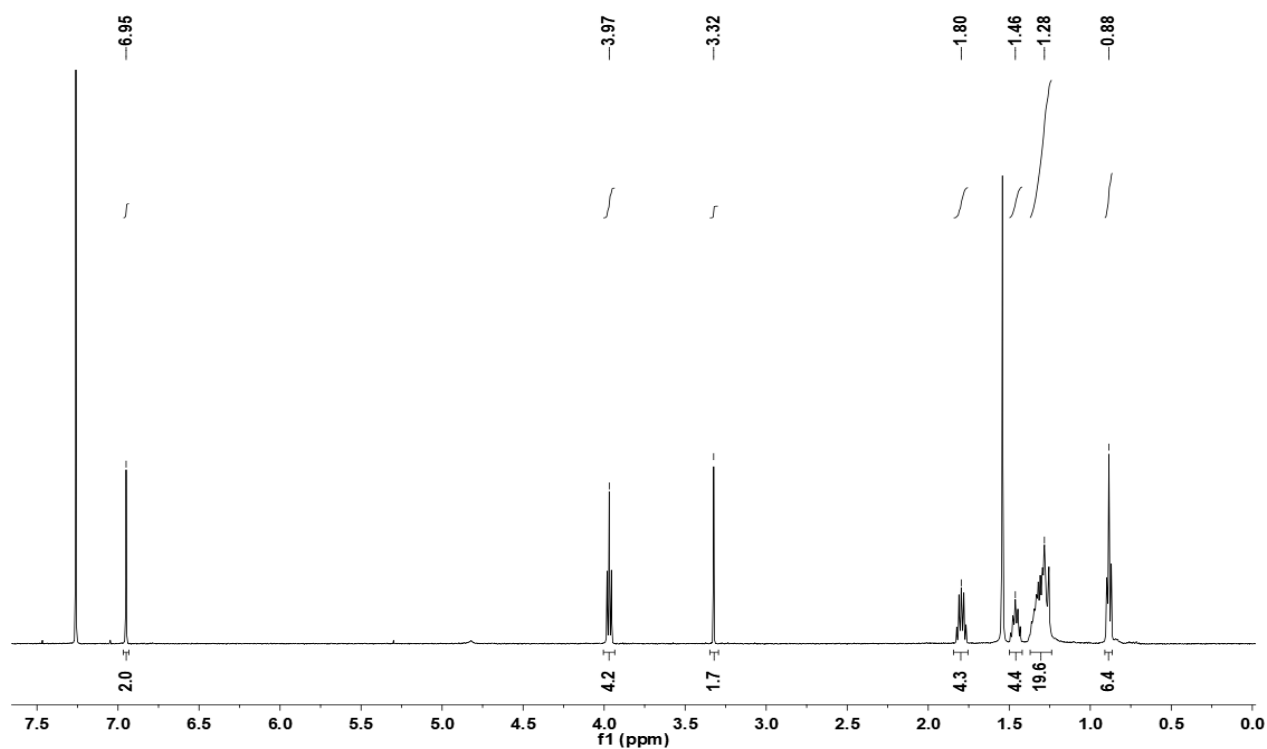


Figure S8. ^1H NMR of compound 4.

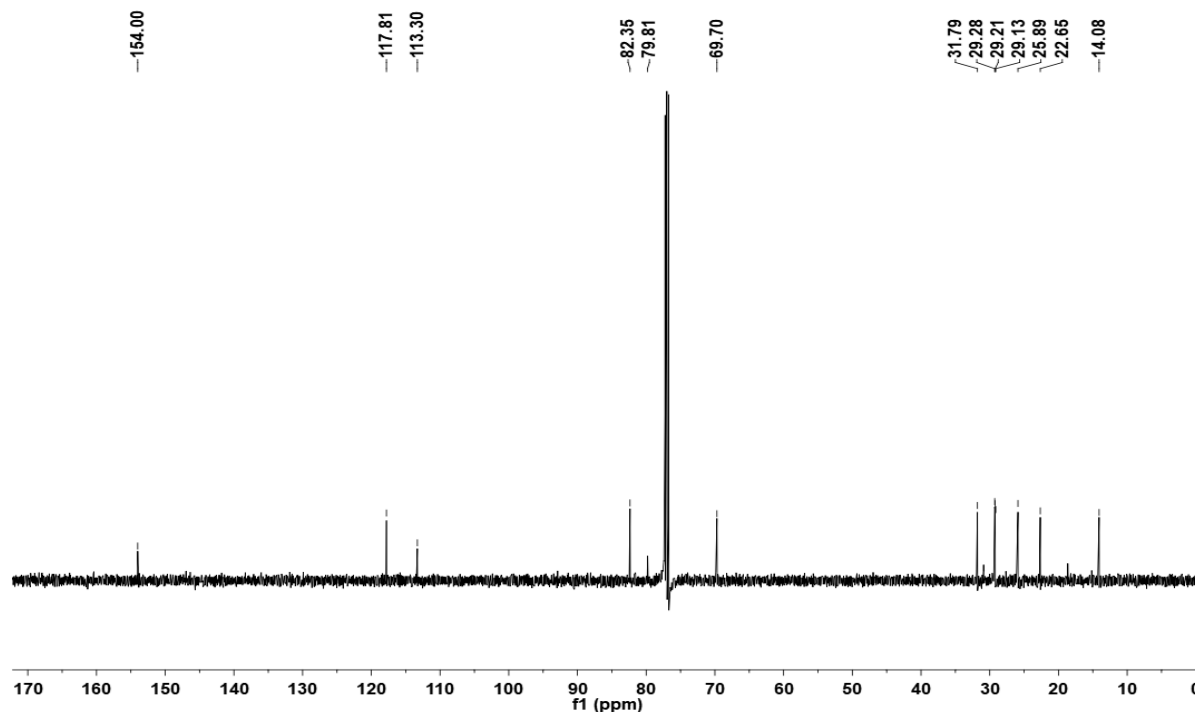


Figure S9. ^{13}C NMR of compound 4.

7 1,4-Dioctyl-2,5-di[2-(trimethylsilyl)ethynyl]-benzene

Compound 6 (1 g, 0.18 mmol) was dissolved in 15 mL 1:1 (v:v) THF:diisopropylamine and degassed for at least 30 min. CuI (17.5 mg, 0.09 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (106.2 mg, 0.09 mmol) were quickly added into the system and degassing was continued for 15 min. Then trimethylsilylacetylene (0.4 g, 4 mmol) was added to the reaction solution, and the mixture was stirred overnight at 50°C under argon protection. The reaction mixture was poured into DI water and extracted with DCM. The organic layer was washed with 1N HCl, DI water and brine several times and dried over MgSO_4 . The crude product was further purified by a flash column system using hexane and DCM (8:1) as eluent to give 0.39 g. (yield 43%). ^1H NMR (CDCl_3 , 500 MHz): δ = 7.24 (s, 2H), 2.67 (t, 4H), 1.59 (m, 2H), 1.27 (m, 22H), 0.88 (t, 6H), 0.25 (s, 18H). ^{13}C NMR (CDCl_3 , 125 MHz): δ = 142.64, 132.43, 122.54, 103.95, 98.88, 34.12, 31.88, 30.59, 29.61, 29.47, 29.29, 22.66, 14.08, -0.04.

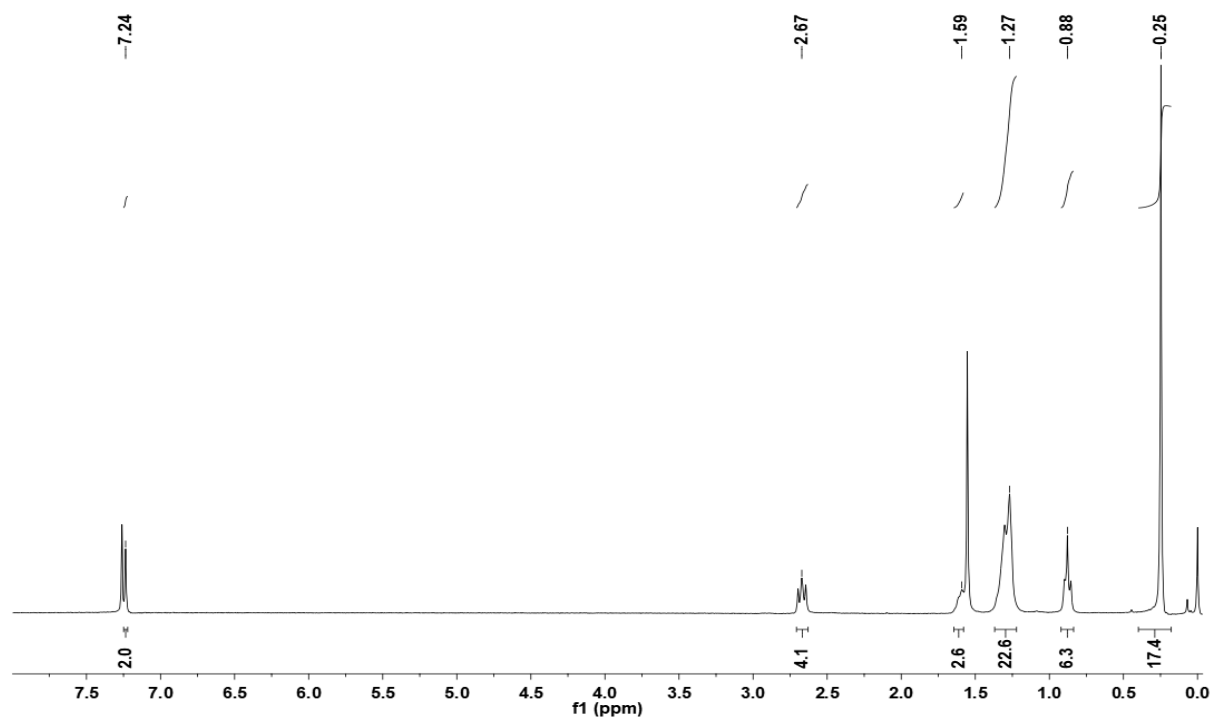


Figure S10. ¹H NMR of compound 7.

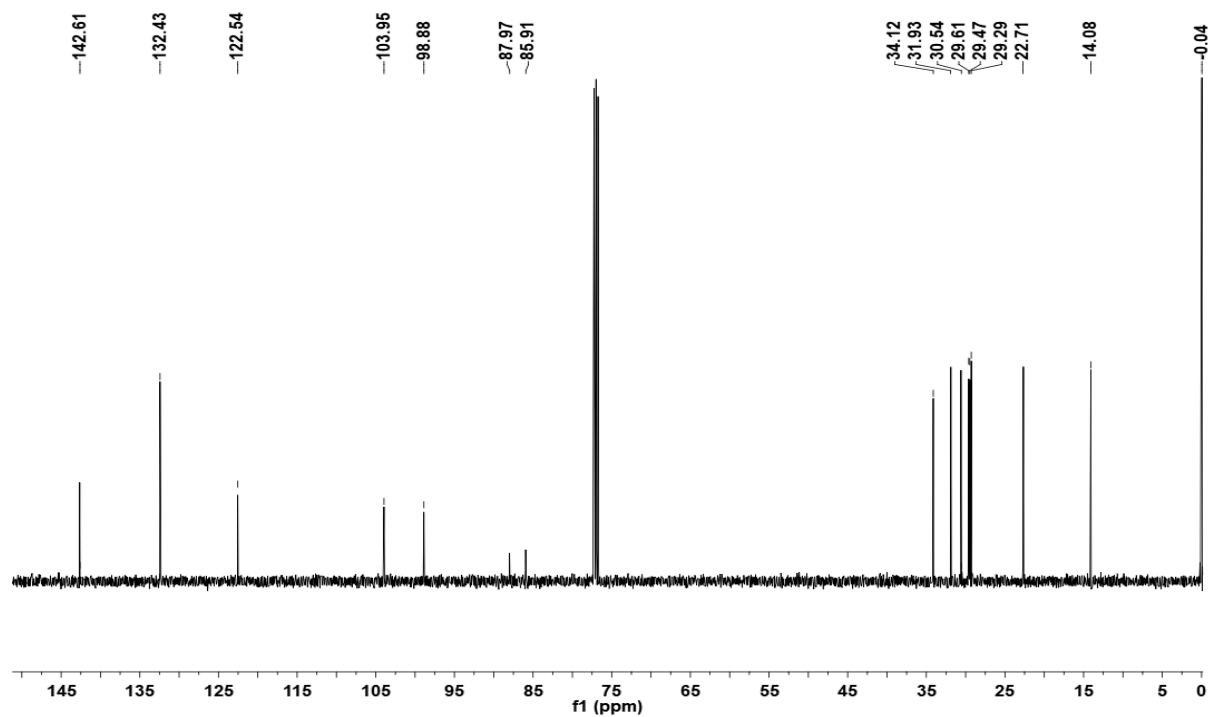


Figure S11. ¹³C NMR of compound 7.

8 1,4-Di-ethynyl-2,5-dioctyl-benzene

Compound 7 (0.27 g, 0.55 mmol) and potassium carbonate (0.46 g, 3.3 mmol) were dissolved in 14 mL 1:1 (v:v) DCM:methanol. After 3h, TLC indicated that the reaction was completed. DI water was poured into the reaction system, which was then extracted with DCM several times. The organic layer was washed with DI water and brine three times, and then dried over MgSO₄. The product was further purified by column chromatography to give 0.13 g solid (yield 68%). ¹H NMR (CDCl₃, 500 MHz): δ = 7.29 (s, 2H), 3.28 (s, 2H), 2.71 (t, 4H), 1.61 (m, 4H), 1.29 (m, 21H), 0.88 (t, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ = 142.70, 132.94, 121.92, 82.27, 81.49, 33.76, 31.89, 30.44, 29.41, 29.39, 29.22, 22.66, 14.09.

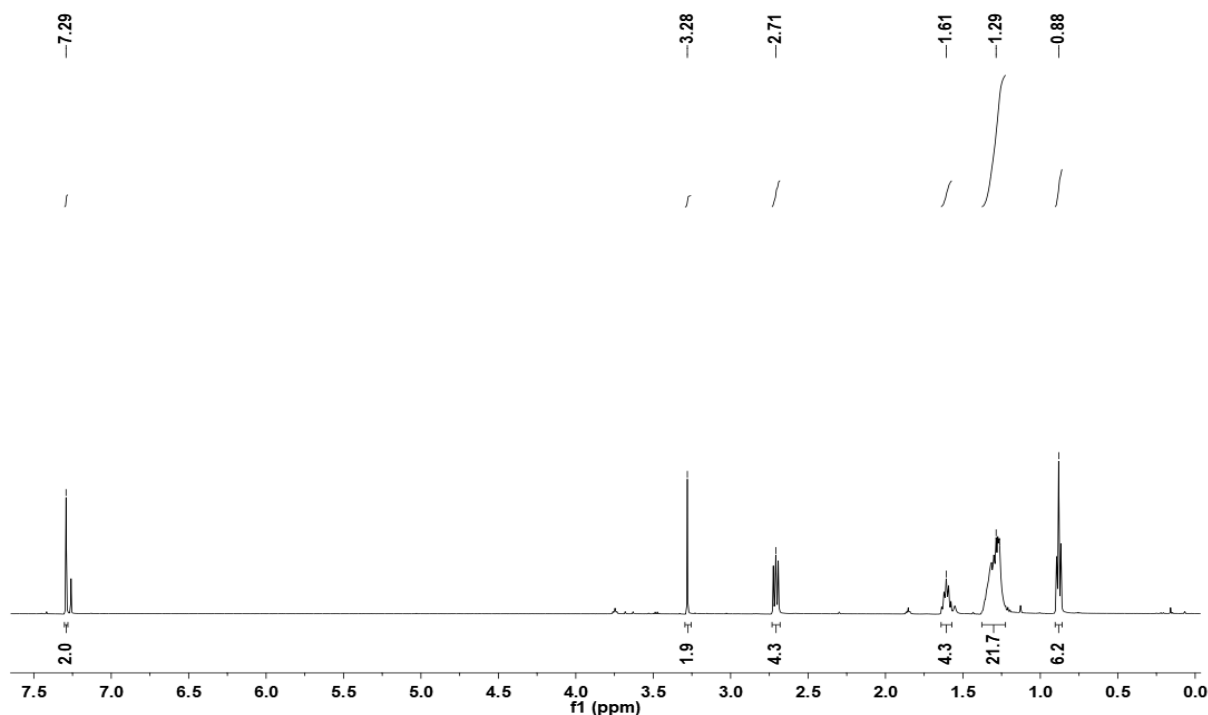


Figure S12. ¹H NMR of compound 8.

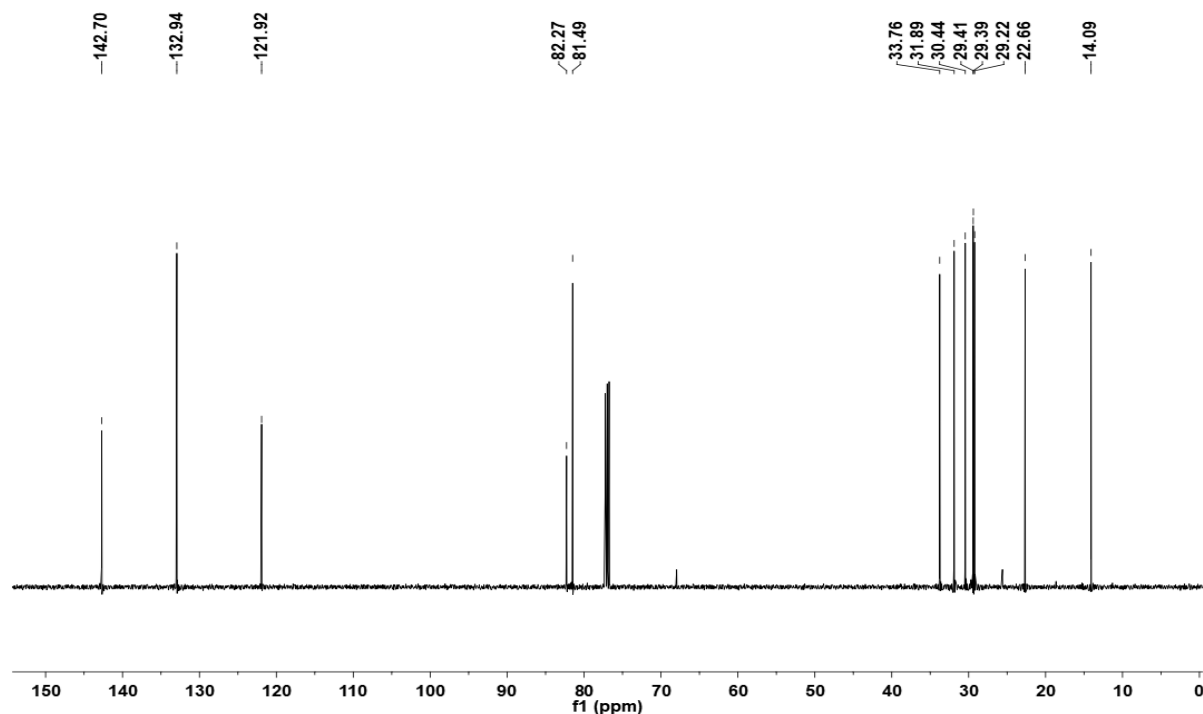


Figure S13. ^{13}C NMR of compound 8.

PPE-OC8

Compound 2 (30.0 mg, 0.05 mmol) and compound 4 (18.9 mg, 0.05 mmol) were dissolved in 9 ml 2:1 (v:v) THF:diisopropylamine and degassed for 30 min before $\text{Pd}(\text{PPh}_3)_4$ (3.0 mg, 0.0026 mmol) and CuI (0.5 mg, 0.0026 mmol) were added. The mixture was degassed for another 15 min and then stirred at 50°C for 24 hours. The solution was cooled to room temperature. The yellow solution was then poured into methanol drop by drop. The yellow precipitation started to form in methanol. The yellow polymer was collected by centrifugation. After re-dissolving in minimum amount of THF, the polymer was poured into methanol again, and repeat this cycle for three times. The final polymer was obtained after drying under vacuum. (27.7mg, yield 58%) ^1H NMR (CDCl_3 , 500 MHz): δ = 7.02 (m, 2H), 4.03 (m, 4H), 1.83 (m, 4H), 1.55 (m, 8H), 1.27 (m, 16H), 0.87 (m, 6H). GPC analysis: M_n 1.1×10^4 , M_w 2.7×10^4 , PDI 2.39.

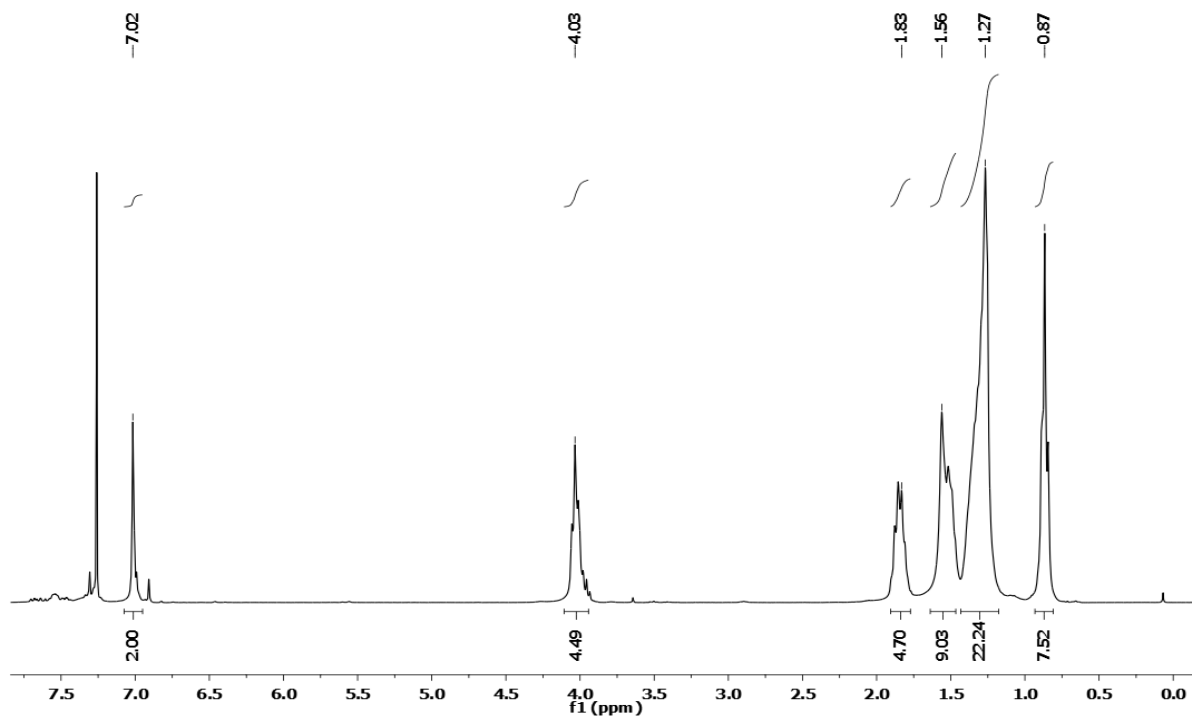


Figure S14. ^1H NMR of PPE-OC8.

PPE-C8

Compound 6 (50.0 mg, 0.09 mmol) and compound 8 (31.6 mg, 0.09 mmol) were dissolved in 9 ml 2:1 (v:v) THF:diisopropylamine and degassed for 30 min before $\text{Pd}(\text{PPh}_3)_4$ (5.2 mg, 0.0045 mmol) and CuI (1.0 mg, 0.0045 mmol) were added. The mixture was degassed for another 15 min and then stirred at 50°C for 24 hours. The solution was cooled to room temperature and then poured into methanol drop by drop. The yellow precipitation was collected by centrifugation. After re-dissolving in minimum amount of THF, the polymer was poured into methanol again, and repeat this cycle for three times. The final polymer was obtained after drying under vacuum. (21.7 mg, yield 27%) ^1H NMR (CDCl_3 , 500 MHz): δ = 7.36 (m, 2H), 2.76 (m, 4H), 1.66 (m, 4H), 1.28 (m, 26H), 0.87 (m, 6H). GPC analysis: M_n 2.7×10^4 , M_w 6.6×10^4 , PDI 2.41.

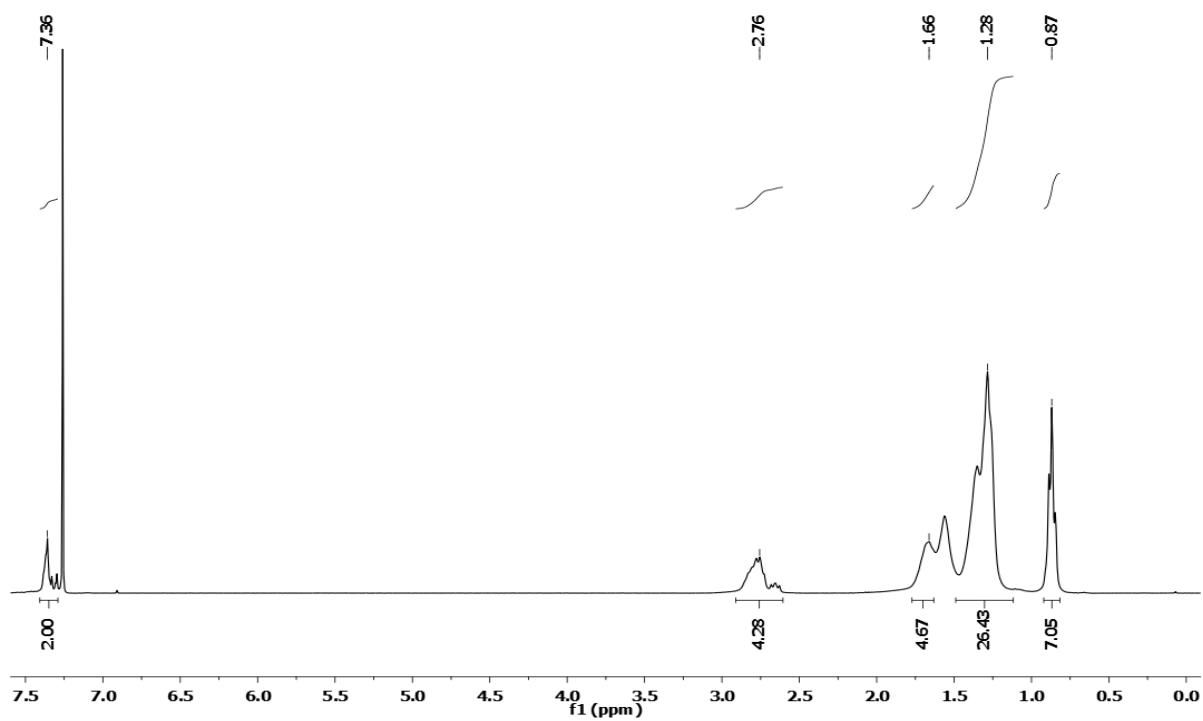


Figure S15. ^1H NMR of PPE-C8.

Physical Properties of Polymers

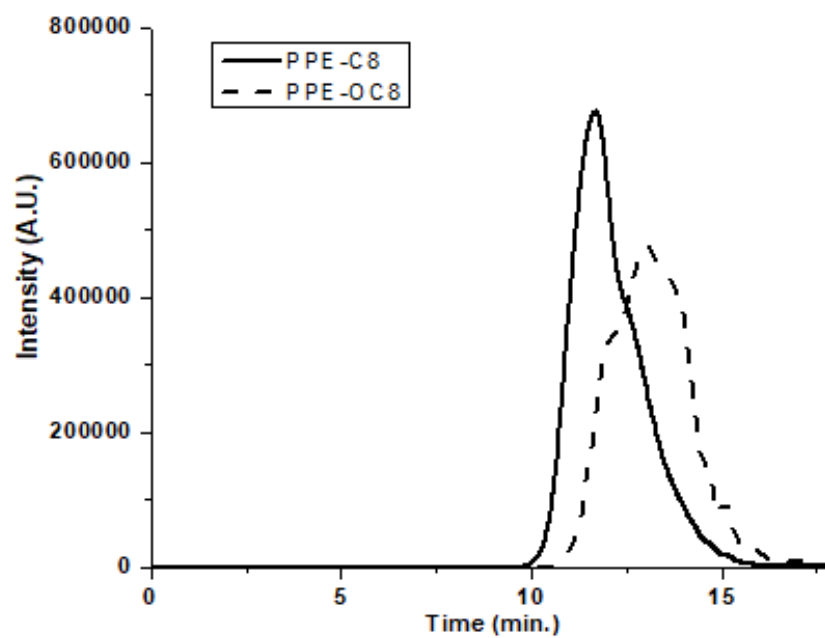


Figure S16. GPC analysis for PPE-C8 and PPE-OC8.

Table S1. Molecular information for two polymers.

	M_n	M_w	PDI	DP
PPE-C8	2.7×10^4	6.6×10^4	2.41	83
PPE-OC8	1.1×10^4	2.7×10^4	2.39	31

Table S2. Solubility parameters for solvents and polymers.

(cal/cm ³) ^{1/2}	HX	THF	CHCl ₃	DCM	ACN	MeOH	H ₂ O	PPE-C8 ^a	PPE-OC8
δ	7.3	9.1	9.3	9.7	11.9	14.5	48	10.0	9.5

^aThe density used to calculate the solubility parameter for both polymers is the density of polymer MEH-PPV.

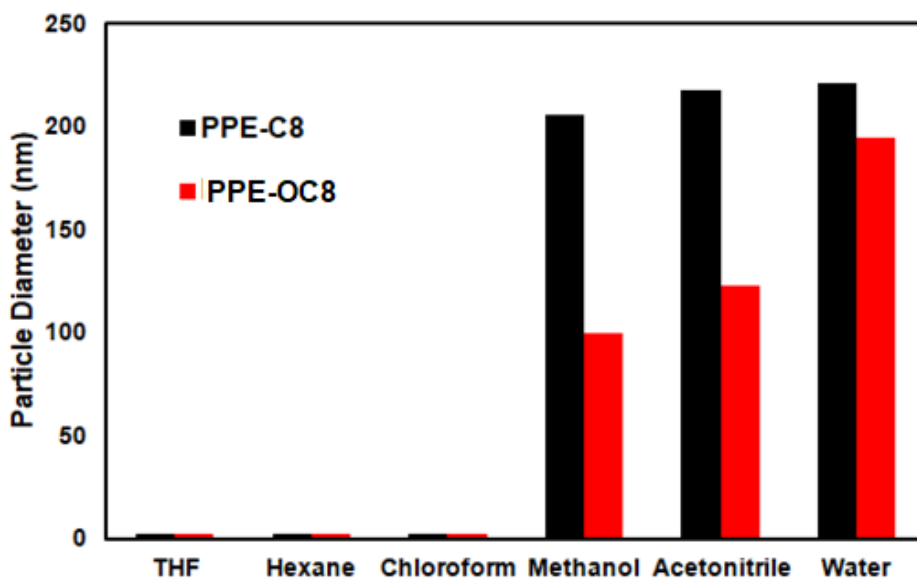


Figure S17. Results of DLS measurements for PPE-C8 and PPE-OC8 in different solvent environments (polymer concentration is 10 μ M).

Photophysical Properties

Table S3. Radiative and non-radiative decay rates for PPE-C8 and PPE-OC8 in THF and MeOH.

Sample	Solvent	τ_f (ns)	k_r (ns ⁻¹)	k_{nr} (ns ⁻¹)
PPE-C8	THF	0.36	0.72	2.05
	MeOH	0.93	0.14	0.93
	H ₂ O	0.52	0.23	1.12
PPE-OC8	THF	0.50	1.56	0.44
	MeOH	0.18	0.12	5.41
	H ₂ O	0.22	0.14	4.53

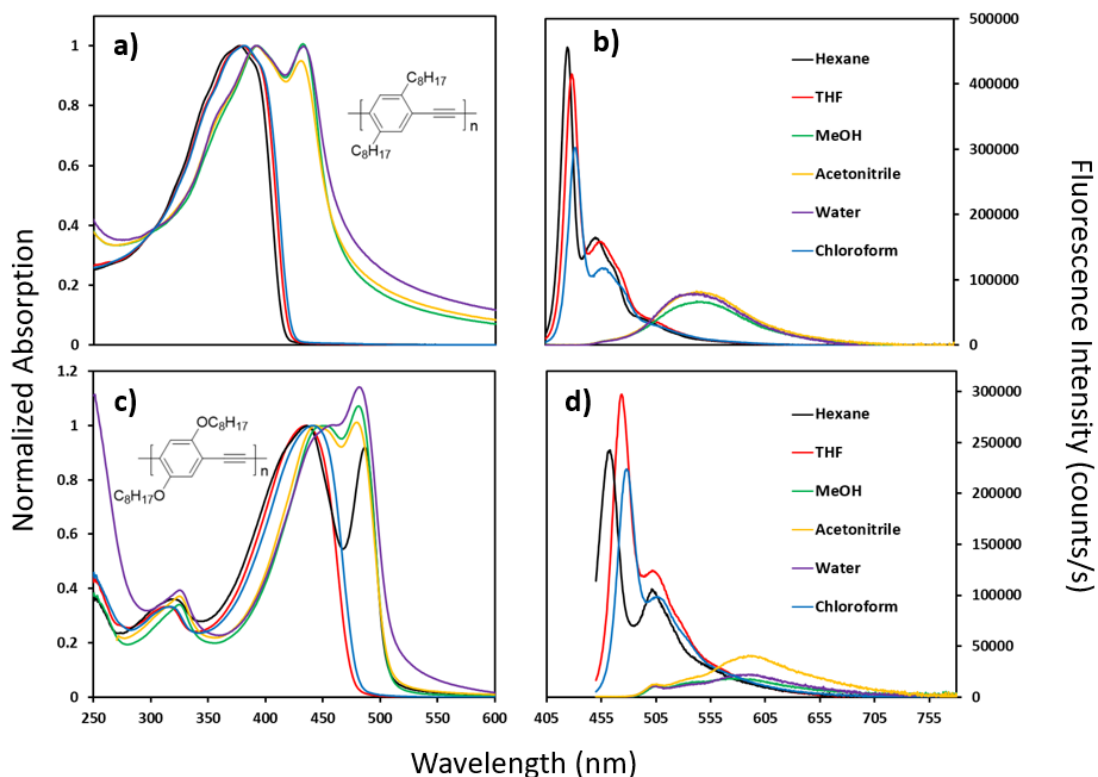


Figure S18. Normalized UV-Visible absorption and absolute emission spectra under different solvent conditions where the fluorescence intensity is weighted by the optical density of the absorbing sample at the excitation wavelength. The spectra shown are a) absorption of PPE-C8, b) emission of PPE-C8, c) absorption of PPE-OC8, and d) emission of PPE-OC8.

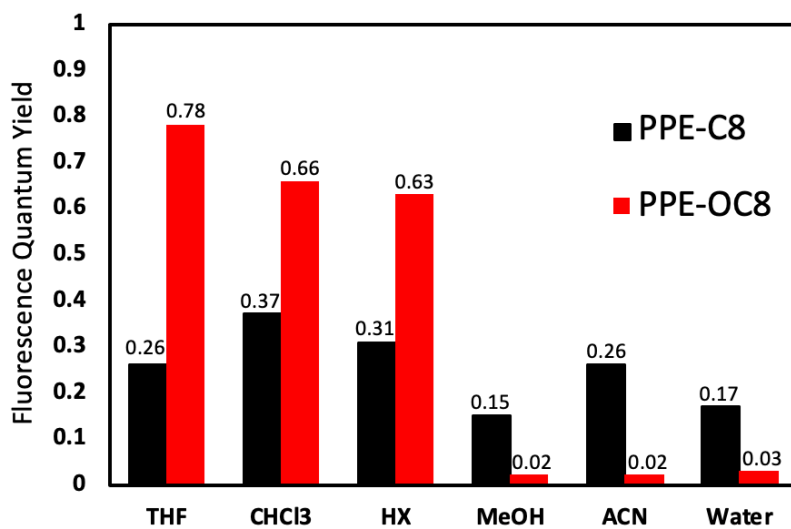


Figure S19. Quantum yield measurements for PPE-C8 and PPE-OC8 in different solvents.

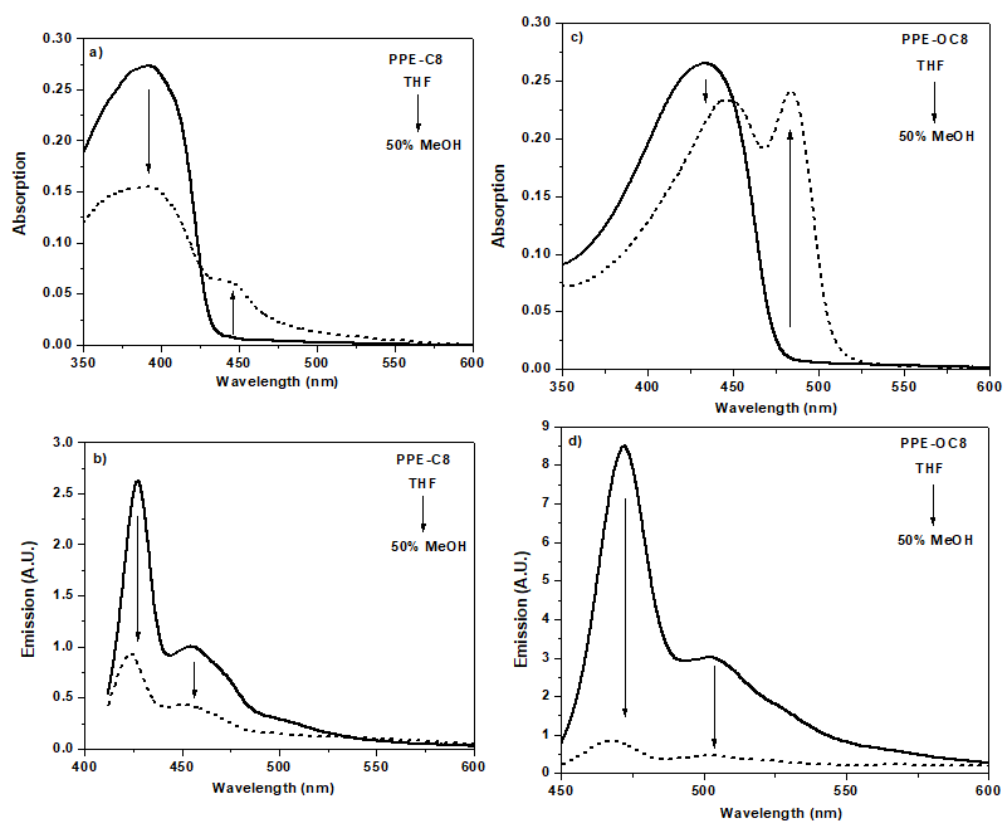


Figure S20. Absorption and emission spectra for a), b) PPE-C8 and c), d) PPE-OC8 in different percentages of THF in MeOH solvent mixture.

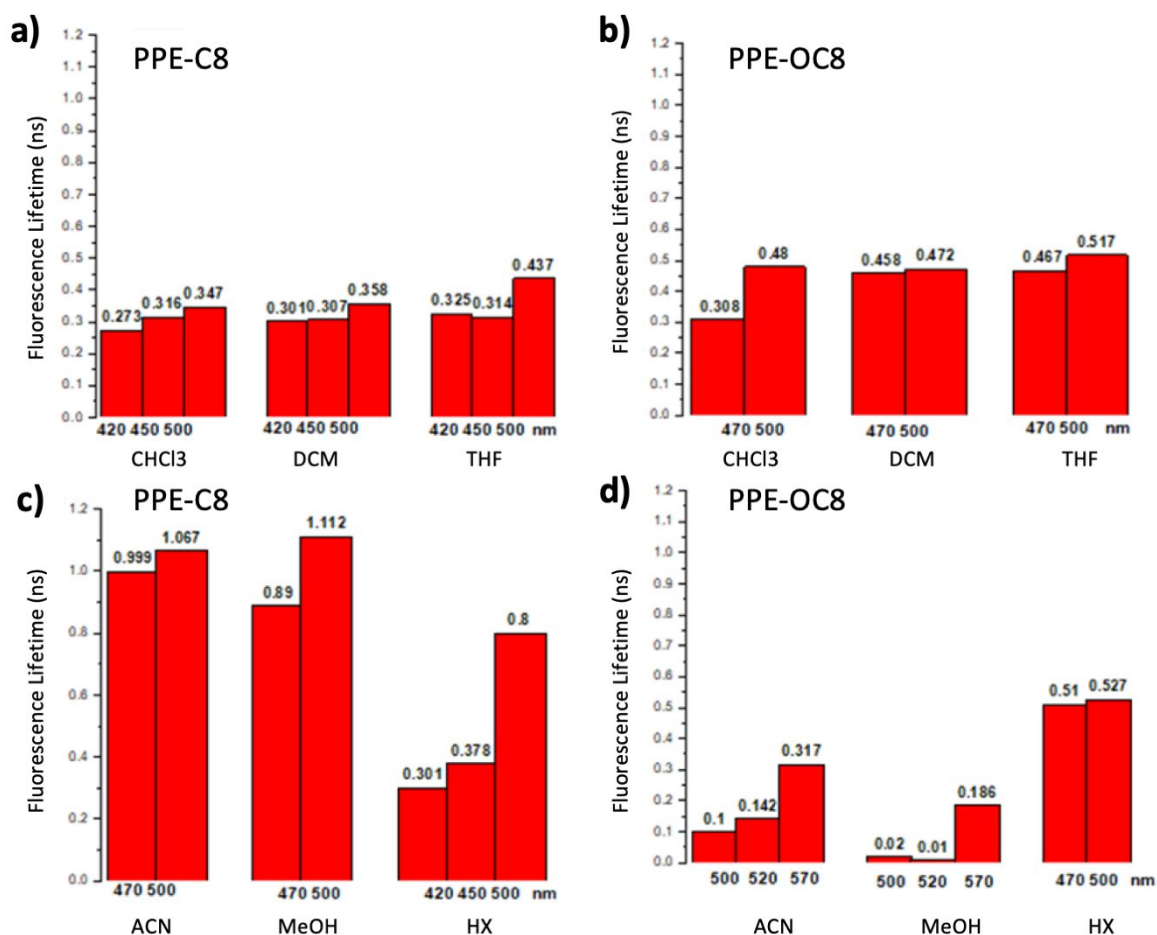


Figure S21. Fluorescence lifetimes of PPE-C8 and PPE-OC8 in different solvents from monitoring emission at different wavelengths. Results generally show longer fluorescence lifetimes when monitoring at longer wavelengths.

Computational Results

Shown here is a complete set of the results from molecular dynamics simulations of PPE-C8 and PPE-OC8 in different solvents. The figures show a 2x2 image of a periodic cell so that a total of 4 polymer chains (100 repeat units)³ are present in each image. Solvent molecules are hidden for easy identification of aggregation, which presents itself here as various degrees of phase separation.

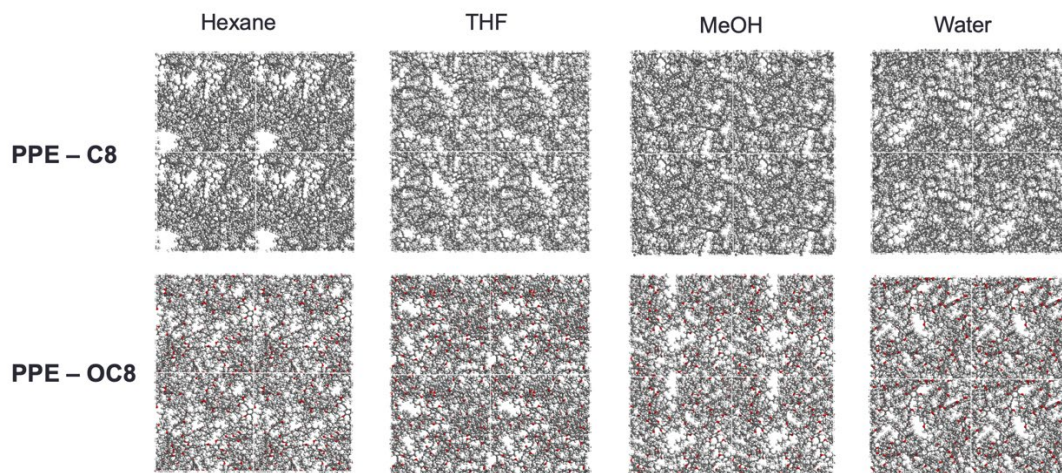


Figure S22. Randomly generated simulation cells (initial conditions).

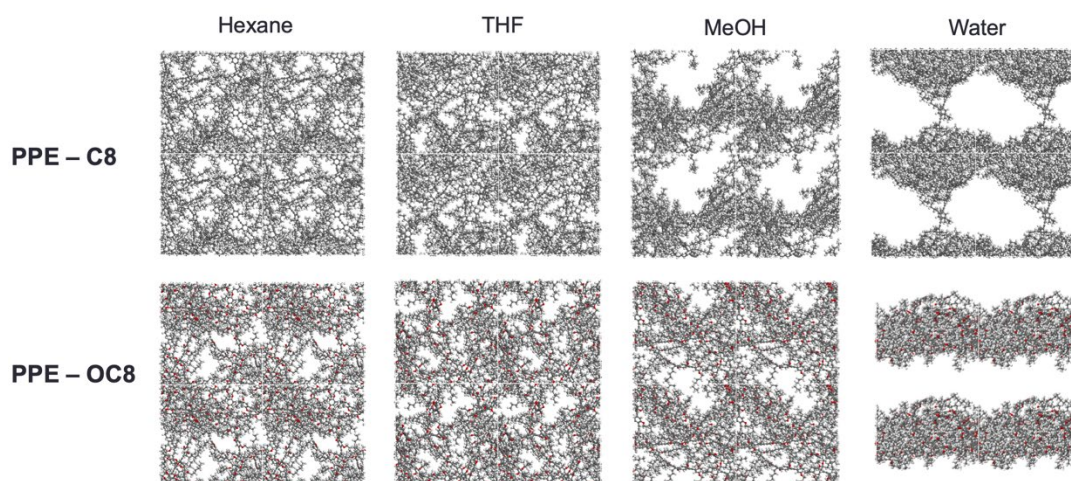


Figure S23. Annealed cells.

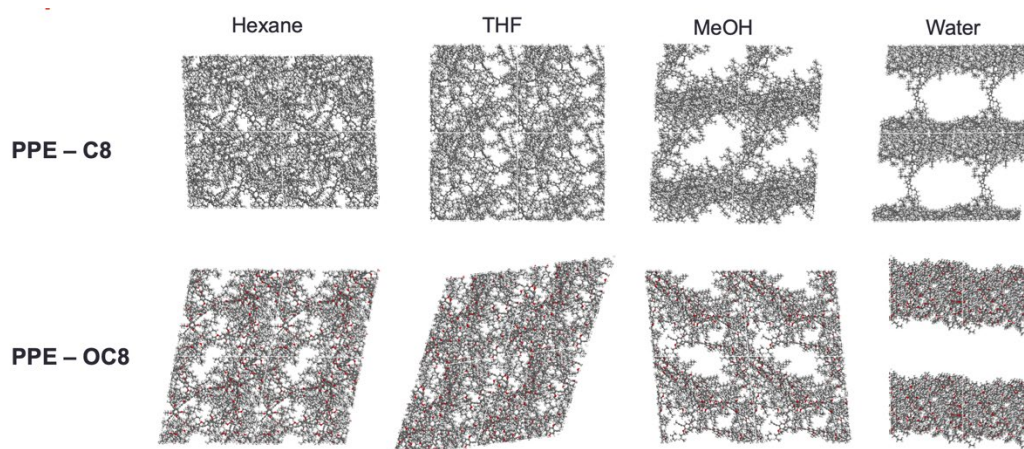


Figure S24. Fully equilibrated cells. Cell angles change due to NPT statistics.

References

- (1) Feng, L.; Zhu, C.; Yuan, H.; Liu, L.; Lv, F.; Wang, S., Conjugated polymer nanoparticles: preparation, properties, functionalization and biological applications. *Chem. Soc. Rev.* **2013**, *42* (16), 6620-6633.
- (2) Tuncel, D.; Demir, H. V., Conjugated polymer nanoparticles. *Nanoscale* **2010**, *2* (4), 484-494.