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Supplementary Information

for

Rod-like Transition First or Chain Aggregation First? Ordered Aggregation of Rod-like Poly(p-phenyleneethynylene) Chains in Solution

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1. Materials and Methods

Unless otherwise noted, all commercial reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Chemical Industry Co. Ltd., or Sigma-Aldrich Co. and used as received. Column chromatography was performed on silica gel 60N (spherical, neutral) from Kanto Chemicals.

Synthesis Scheme



1,4-dioxydecanoxy-2,5-bis(trimethylsilylethynyl)benzene (1)

To a dry Et₃N solution (20 mL) of 1,4-diiode-2,5-oxydecanoxybenzene (500 mg, 1.00 mmol),^{S1} Pd(PPh₃)₄ (235 mg, 0.20 mmol), and CuI (18 mg, 0.40 mmol) was added trimethylsilylacetylene (547 mg, 3.00 mmol) under N₂, and the mixture was stirred at 60 °C for 12 h. The mixture was evaporated to dryness under reduced pressure, dissolved in CHCl₃, and passed through a plug of SiO₂. The solution was evaporated and purified by chromatography on silica gel eluted with CHCl₃/hexane (1/2) to afford **1** as a white solid. Yield: 352 mg (80%). ¹H NMR (400 MHz, CDCl₃) δ = 7.01 (s, 2H), 4.32 (t, 4H), 1.67 (m, 4H), 1.23 (m, 4H), 0.98 (m, 4H), 0.84 (m, 4H), 0.26 (s, 18H).

1,4-diethynyl-2,5-dioctyloxybenzene (2)

To a dry THF solution (50 mL) of **1** (352 mg, 0.80 mmol) was added a 1 M THF solution of tetrabutylammonium fluoride (2 mL, 2.0 mmol) at 0 °C. After stirring for 15 min, the solution was poured into water and extracted with CHCl₃. The organic layer was washed with water, dried over NaSO₄, filtered, and evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel eluted with CHCl₃/hexane (1/2) to afford **2** as a white solid. Yield: 224 mg (95%). ¹H NMR (400 MHz, CDCl₃) δ = 7.08 (s, 2H), 4.34 (t, 4H), 3.38 (s, 2H), 1.67 (m,4H), 1.23 (m, 4H), 1.01 (m, 4H), 0.79 (m, 4H).

LPPE: Poly(2,5-dioctyloxy-p-phenylene)ethynylene

To a dry Et₃N/THF solution (2.6 mL, 1/1 v/v) of 1,4-diiode-2,5-octyloxybenzene^{S2} (46 mg, 0.12 mmol) and 1,4-dioctyloxy-2,5-dioctyloxybenzene^{S2} (71 mg, 0.12 mmol) were added Pd(PPh₃)₄ (7.7 mg, 6.0 μ mol) and CuI (3.0 mg, 0.010 mmol), and the mixture was degassed by freeze-pump-thaw cycles for 3 times. After stirring at 60 °C for 24 h, the mixture was evaporated to dryness under reduced pressure, dissolved in CHCl₃, and passed through a plug of SiO₂. Further purification and fractionation were carried out by a recycling preparative SEC using CHCl₃ as an eluent.

SEC analysis: $M_{\rm n} = 5.2 \times 10^4 \text{ g mol}^{-1}$, $M_{\rm w} = 6.2 \times 10^4 \text{ g mol}^{-1}$, D = 1.2.

CPPE: Poly(2,5-oxydecanoxy-p-phenylene)ethynylene

To a dry Et_3N/THF solution (7.0 mL, 1/1 v/v) of **1** (87.8 mg, 0.33 mmol) and **2** (96.3 mg, 0.33 mmol) were added Pd(PPh₃)₄ (21 mg, 0.017 mmol) and CuI (7.4 mg, 0.034 mmol), and the mixture was

degassed by freeze-pump-thaw cycles for 3 times. After stirring at 60 °C for 24 h, the mixture was evaporated to dryness under reduced pressure, dissolved in $CHCl_3$, and passed through a plug of SiO_2 . Further purification and fractionation were carried out by a recycling preparative SEC using $CHCl_3$ as an eluent.

SEC analysis: $M_n = 1.3 \times 10^4 \text{ g mol}^{-1}$, $M_w = 2.3 \times 10^4 \text{ g mol}^{-1}$, D = 1.8.

Methods

The crude polymers were purified by recycling preparative HPLC on a Japan Analytical Industry Co. model LC-9210NEXT equipped with JAIGEL-2.5HH/-3HH columns using CHCl₃ as an eluent at a flow rate of 7.5 mL min⁻¹. Molecular weights of polymers were determined by size exclusion chromatography (SEC) in THF calibrated using polystyrene standards. SEC analysis was performed on HITACHI L-2130, L-2455, and L-2530 chromatography instruments with Shodex KF-804L/KF-805L columns using THF as an eluent at a flow rate of 1 mL min⁻¹ at 40 °C. A refractive index detector and multiwavelength photodiode array detector were used for detecting the elution peaks. Electronic absorption spectra were recorded on a JASCO V-570 spectrometer with a Unisoku CoolSpeK UV USP-203 temperature controller. Photoluminescence spectra were recorded on a HITACHI model F-2700 spectrofluorometer. ¹H NMR spectra were recorded by a JEOL model JNM-AL400 spectrometer. Chemical shifts of ¹H NMR spectra are determined relative to an internal tetramethylsilane standard (δ) and are given in parts per million (ppm).

2. Absorption and Fluorescence Spectra in Solutions



Figure S1. Electronic absorption spectra of LPPE in THF ($c = 2.1 \times 10^{-5}$ M) at a variety of temperatures varying from 233 to 253 K.



Figure S2. (a) Electronic absorption spectra of LPPE in CH₂Cl₂/MeOH mixtures ($c = 2.5 \times 10^{-5}$ M). (b) Fluorescence spectra of LPPE in CH₂Cl₂/MeOH mixtures ($c = 2.5 \times 10^{-5}$ M) upon excitation at 420 nm. Superimposed figure represents an enlarged view at the range from 2.0–3.0 eV.



Figure S3. (a) Electronic absorption spectra of **CPPE** in CH₂Cl₂/MeOH mixtures ($c = 2.2 \times 10^{-5}$ M). (b) Fluorescence spectra of **CPPE** in CH₂Cl₂/MeOH mixtures ($c = 2.2 \times 10^{-5}$ M) upon excitation at 420 nm. Superimposed figure represents an enlarged view at the range from 2.0–3.0 eV.



Figure S4. Electronic absorption (solid line) of LPPE in THF (a) $(M_w = 9.1 \times 10^3, c = 1.0 \times 10^{-5} \text{ M};$ base mol unit) and (b) $(M_w = 6.2 \times 10^4, c = 1.1 \times 10^{-5} \text{ M};$ base mol unit) at various temperature.

3. Arrhenius Plots of Oscillator Strength



Figure S5. Temperature dependence of oscillator strength. Red-dotted and blue dashed fitting lines are given by the least square method for LPPE, and by visual guide for CPPE, respectively.

4. Tacticity of CPPE



Figure S6. Schematic illustration of (a) stereoisomers of oxydodecyloxy chain-strapped monomers and (b) examples of tacticity for triad.

5. Mass spectrometry of LPPE

(a)

(b)



Figure S7. MALDI-TOF mass spectra of LPPE.

6. Supplementary References

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