

Supplementary Information

A helical array of pendant fullerenes on a helical poly(phenylacetylene) induced by non-covalent chiral interactions

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Experimental Section

Materials. Tetrahydrofuran (THF) and toluene were dried over sodium benzophenone ketyl and distilled under nitrogen onto LiAlH₄ and molecular sieves 4Å (Nacalai Tesque, Kyoto, Japan), respectively. Chloroform (CHCl₃) was dried over CaH₂ and distilled onto CaH₂ under nitrogen. Triethylamine was dried over potassium hydroxide (KOH), distilled, and stored under nitrogen over KOH pellets. These solvents were distilled again under high vacuum just before use. Anhydrous acetonitrile (water content < 0.005 vol%) and anhydrous dichloromethane (water content < 0.005 vol%) were obtained from Kanto Kagaku (Tokyo, Japan) and Aldrich, respectively. (Trimethylsilyl)acetylene was kindly supplied from Shinetsu Chemical (Tokyo, Japan). C₆₀ was obtained from Materials Technologies Research (MTR Ltd., Ohio, USA). [(Norbornadiene)rhodium(I) chloride]₂ ([Rh(nbd)Cl]₂) was purchased from Azmax (Chiba, Japan) and used as received. *N*-4-Ethynylbenzyl-3,4-fulleropyrrolidine (**1**)¹ and (4-ethynylbenzoyl)-monoaza-18-crown-6 (**2**)² were prepared according to the previously reported methods.

Polymerization. Polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere using $[\text{Rh}(\text{nbd})\text{Cl}]_2$ as the catalyst. A typical polymerization procedure is described below.

Monomer **1** (26.3 mg, 30.0 μmol) and monomer **2** (105.4 mg, 0.269 mmol) were placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and dry CHCl_3 (4.0 mL) and triethylamine (42 μL) were added with a syringe. To this was added a solution of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (0.014 M) in CHCl_3 (0.2 mL) at 30 $^\circ\text{C}$. The concentrations of the monomer and the rhodium catalyst were 0.071 M and 0.71 mM, respectively. After 22 h, the resulting polymer (poly(**1**_{0.1}-*co*-**2**_{0.9})) was precipitated into a large amount of diethyl ether, collected by centrifugation, and dried in vacuo at room temperature for 10 h (104 mg, 78.9 % yield). Copolymerization of **1** and **2** at $[\mathbf{1}] / ([\mathbf{1}]+[\mathbf{2}]) = 0.15$ was carried out in the same way. Poly(**1**_{0.1}-*co*-**2**_{0.9}) and poly(**1**_{0.15}-*co*-**2**_{0.85}) were soluble in CHCl_3 and dichloromethane. The molecular weights (M_n) of the obtained poly(**1**_{0.1}-*co*-**2**_{0.9}) and poly(**1**_{0.15}-*co*-**2**_{0.85}) were determined to be 5.1×10^4 and 6.0×10^4 , respectively, by size exclusion chromatography (SEC) analysis. As shown in Fig. S-1, the ^1H NMR spectra of poly(**1**_{0.1}-*co*-**2**_{0.9}) and poly(**1**_{0.15}-*co*-**2**_{0.85}) in CDCl_3 showed a singlet centered at 5.84 ppm, due to the main chain protons, indicating that these polymers possess a highly *cis-transoidal*, stereoregular structure.³

Spectroscopic data of poly(**1**_{0.1}-*co*-**2**_{0.9}). ν_{max} (film)/ cm^{-1} 1632 (C=O); δ_{H} (500 MHz; CDCl_3 ; 60 $^\circ\text{C}$) 3.62 (br, CH_2 (crown ether moiety), 21.6H), 4.22 (br, Ph-CH_2 , 0.2H), 5.84 (br, C=C-H, 1H), 6.2 – 8.0 (br, aromatic, 4H).

Spectroscopic data of poly(**1**_{0.15}-*co*-**2**_{0.85}). ν_{max} (film)/ cm^{-1} 1626 (C=O); δ_{H} (500 MHz; CDCl_3 ; 60 $^\circ\text{C}$) 3.62 (br, CH_2 (crown ether moiety), 20.4H), 4.22 (br, Ph-CH_2 , 0.3H), 5.84 (br, C=C-H, 1H), 6.2 – 8.0 (br, aromatic, 4H).

Copolymerization of **1** with **2** at $[\mathbf{1}] / ([\mathbf{1}]+[\mathbf{2}]) = 0.2$ was performed in the same

way, but the copolymer was precipitated in CHCl_3 during the copolymerization. The precipitated copolymer was separated by centrifugation and the supernatant was poured into a large amount of diethyl ether, collected by centrifugation, and dried in vacuo at room temperature for 10 h. However, the CHCl_3 -soluble part became insoluble in common organic solvents after isolation.

Instruments. ^1H (500 or 300 MHz) and ^{13}C (125 or 75 MHz) NMR spectra were measured on a Varian VXR-500S or Varian Mercury-300 spectrometer using tetramethylsilane (TMS) as an internal standard. SEC measurements were performed with a Jasco PU-980 liquid chromatograph equipped with a UV detector (Jasco UV-970) and a column oven (Jasco CO-965) at 40 °C. An SEC column (Tosho-TSKgel Multipore HXL-M: 30 x 0.78 cm (i.d.)) was connected and THF containing 0.1 wt % tetra-*n*-butylammonium bromide was used as the eluent at a flow rate of 1.0 mL min⁻¹. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). IR spectra were recorded with a Jasco Fourier Transform IR-620 spectrophotometer. Absorption spectra were measured with a Jasco V-570 spectrophotometer in a 0.5 cm quartz cell. CD spectra were measured on a Jasco J-725 spectropolarimeter with a liquid nitrogen-controlled quartz cell (0.5 cm) in a cryostat.

CD Measurements. Anhydrous acetonitrile and dichloromethane were used throughout for all measurements. The concentration of copolymers was calculated on the basis of the monomer units and 0.1 or 3.0 mg mL⁻¹ for a dilute or high concentration, respectively, unless otherwise stated. A typical experimental procedure is described below. For the CD measurements at a dilute concentration, a stock solution of poly(**1**_{0.1}-*co*-**2**_{0.9}) (2.0 mg mL⁻¹) in dichloromethane was prepared in a 10 mL flask equipped with a stopcock. Stock solutions of 0.011 M of D- and L-alanine perchlorate ($\text{Ala}\cdot\text{HClO}_4$)⁴ in

acetonitrile were also prepared in two 1 mL flasks equipped with a stopcock according to the reported method.² Two hundred seventy microliter of the L- or D-Ala·HClO₄ solution followed by 1.0 mL of the poly(**1**_{0.1}-co-**2**_{0.9}) solution were transferred to a 2 mL flask equipped with a stopcock, and the solution was diluted with dichloromethane and acetonitrile to keep the poly(**1**_{0.1}-co-**2**_{0.9}) concentration at 1.0 mg mL⁻¹ and the volume ratio of acetonitrile to dichloromethane (8/2 (v/v)). The molar ratio of Ala to the monomer units of poly(**1**_{0.1}-co-**2**_{0.9}) was 2. For the CD measurements at a higher concentration, stock solutions of 0.10 M of D- and L-Ala·HClO₄ in acetonitrile were prepared in two 1 mL flasks equipped with a stopcock. Next 3.0 mg of poly(**1**_{0.1}-co-**2**_{0.9}) was placed in a 1 mL flask equipped with a stopcock. To this was added 138 μL of the L- or D-Ala solution followed by 0.8 mL of dichloromethane. The solution was then diluted with acetonitrile to keep the poly(**1**_{0.1}-co-**2**_{0.9}) concentration at 3.0 mg mL⁻¹ and the volume ratio of acetonitrile to dichloromethane (8/2 (v/v)). The molar ratio of Ala to monomer units of poly(**1**_{0.1}-co-**2**_{0.9}) was 2. The solutions were thoroughly mixed with a vibrator (Iuchi, Osaka, Japan) before measuring the absorption and CD spectra.

CD Titrations of Poly(1**_{0.15}-co-**2**_{0.85}) with L-Ala·HClO₄.** Stock solutions of L-Ala·HClO₄ (17.5 (for 1.0 equiv.), 0.82 (for 0.1 equiv.) and 0.092 (for 0.01 equiv.) mg mL⁻¹) in acetonitrile were prepared in 1, 5, and 25 mL flasks, respectively. In three 1 mL flasks equipped with a stopcock, poly(**1**_{0.15}-co-**2**_{0.85}) (3.0 mg) and 0.8 mL of dichloromethane were placed. To these flasks was added 70 (for 1.0 equiv.), 146 (for 0.1 equiv.) and 130 μL (for 0.01 equiv.) of the stock solutions of L-Ala·HClO₄, respectively and the solutions were diluted with acetonitrile to keep the poly(**1**_{0.15}-co-**2**_{0.85}) concentrations at 3.0 mg mL⁻¹. The absorption and CD spectra were then taken for each sample to determine the changes in the CD spectra (Fig. 3).

References

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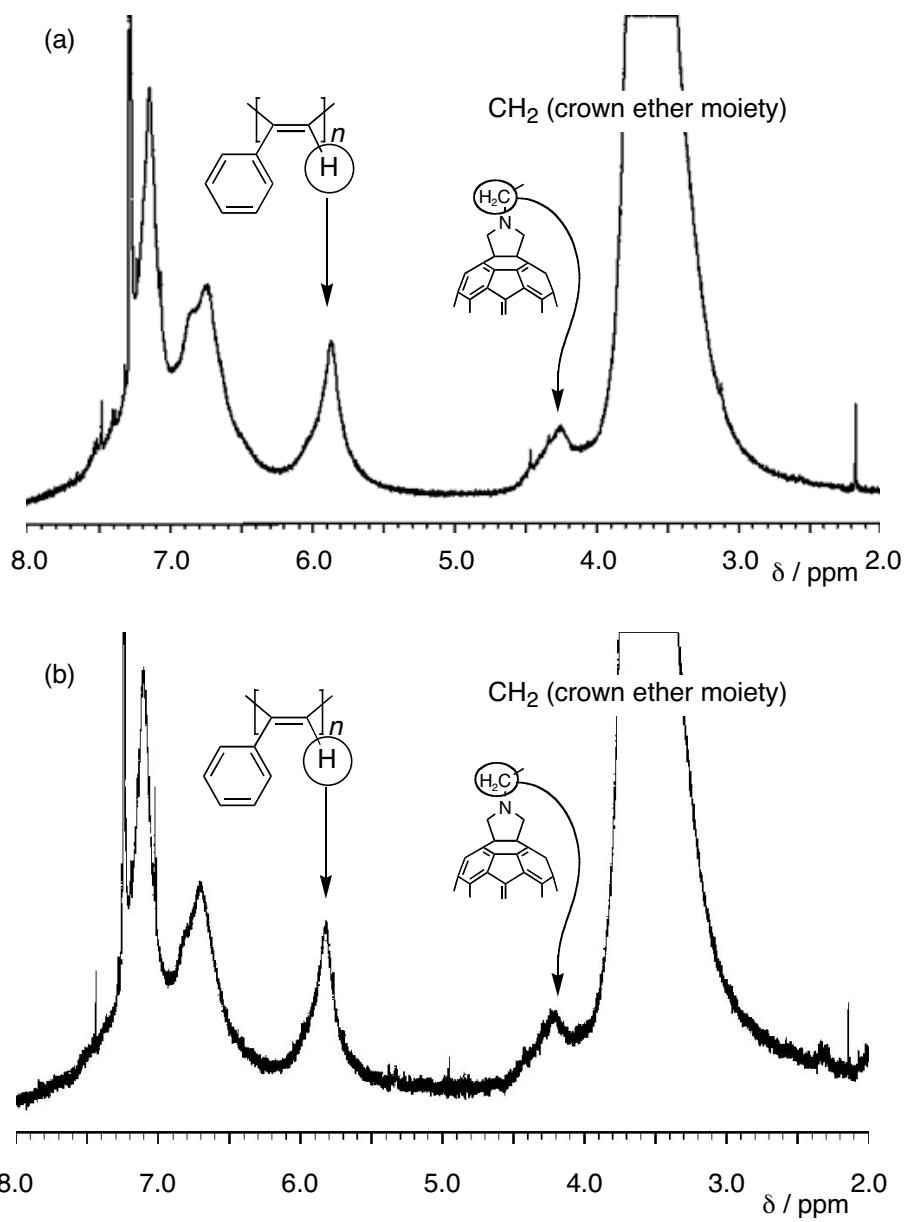


Fig. S-1 ^1H NMR (500 MHz) spectra of poly($\mathbf{1}_{0.1}\text{-co-}\mathbf{2}_{0.9}$) (a) and poly($\mathbf{1}_{0.15}\text{-co-}\mathbf{2}_{0.85}$) (b) in CDCl_3 at 60°C .

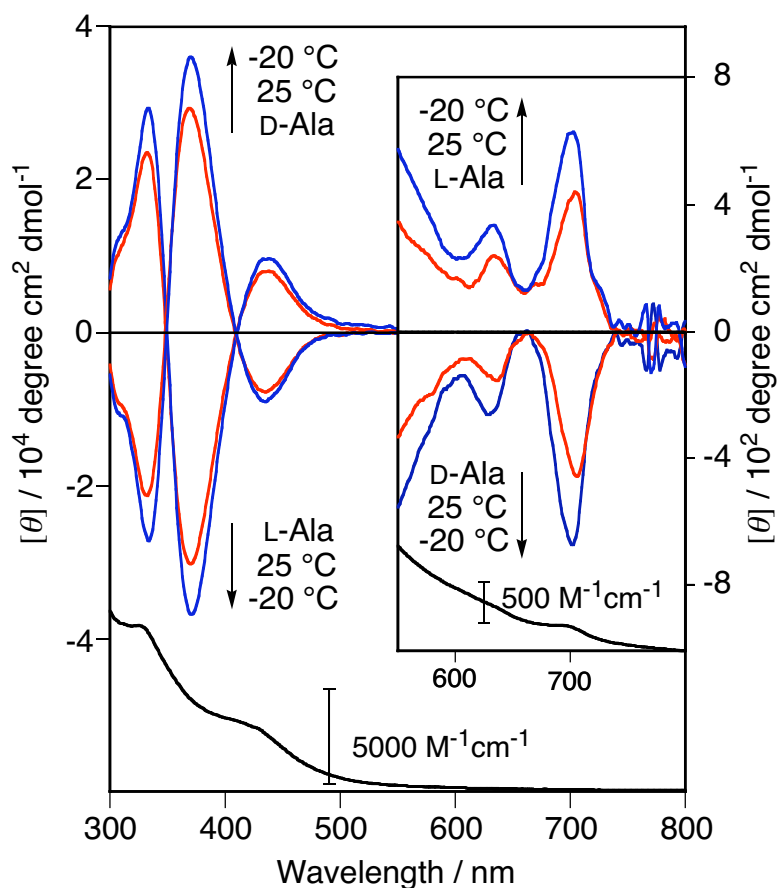


Fig. S-2 CD spectra of poly($\mathbf{1}_{0.15}\text{-co-}\mathbf{2}_{0.85}$) with L- and D-Ala·HClO₄ ($[\text{Ala}\cdot\text{HClO}_4] / [\text{poly}(\mathbf{1}_{0.15}\text{-co-}\mathbf{2}_{0.85})] = 2$) in dichloromethane–acetonitrile (8/2, v/v) at 25 and -20 °C at a dilute concentration ($[\text{poly}(\mathbf{1}_{0.15}\text{-co-}\mathbf{2}_{0.85})] = 0.1 \text{ mg mL}^{-1}$). Absorption spectrum of poly($\mathbf{1}_{0.15}\text{-co-}\mathbf{2}_{0.85}$) with L-Ala·HClO₄ at 25 °C is also shown. The inset shows the corresponding CD and absorption spectra in the fullerene region at a higher concentration (3.0 mg mL^{-1}). The molar concentrations were calculated based on the monomer units and fullerene units (inset).

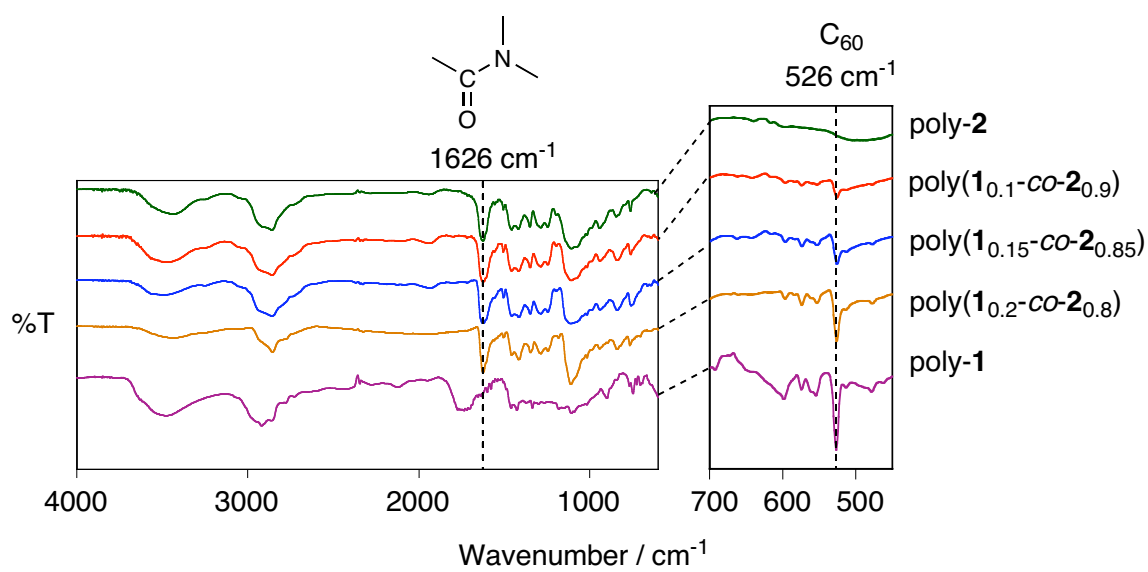


Fig. S-3 FT-IR spectra of poly-1, poly-2 and poly(1_m-co-2_n).