Synthesis and Properties of a Novel Through-Space Conjugated Polymer with [2.2]Paracyclophane and Ferrocene in the Main Chain

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ABSTRACT: The novel conjugated polymer (12) which has [2.2]paracyclophane and ferrocene units in the polymer backbone was synthesized by palladium-catalyzed polycondensation of the monomer (10) with diiodoferrocene (11). The obtained polymer (12) was soluble in common organic solvents, and the structure of 12 was confirmed by ¹H NMR, ¹³C NMR, and FT-IR. The polymer showed delocalization of the π -electron via the through-space of the [2.2]paracyclophane moiety. The [2.2]paracyclophane unit was more effective for the delocalization of the π -electron than the ferrocene unit. The cyclic voltammetry measurement of 12 showed a broad oxidation potential reversibly with a E_{pa} value of 0.62 V. The electrochemical oxidation was diffusion-controlled by the linear dependence of the oxidative peak currents (*I*) on the square root of the scan rate ($v^{1/2}$), and the diffusion coefficient (*D*) of the electroactive substance was about 5.5 × 10⁻⁷ (cm²/s). On iodine doping under ambient conditions, the polymer (12) showed a maximum conductivity of 1.6 × 10⁻⁴ S/cm.

Introduction

Over the past decade, a great deal of interest has arisen in the synthesis of novel conjugated polymers¹ as a result of their intriguing properties, including electrical conductivity,² electroluminescence,³ liquid crystallinity,⁴ third-order nonlinear optical properties,⁵ and chemical sensing.⁶ The most prominent example concerns poly(p-phenylenevinylene)s, PPVs, which have led to the development of polymer-based light-emitting diodes (LEDs) used for displays and other purposes since the first report on PPVs in 1990,⁷ and poly(pphenyleneethynylene)s, PPEs,8 which are a promising candidate for the molecular wire used as an active component in polymer-based electronic and photonic devices. One of current research interests in conjugated polymers including PPVs and PPEs focuses on tuning their spectral and electrical properties. For this purpose, a number of aromatic compounds have been incorporated with the conjugated polymer backbone, and the physical properties of these compounds have been investigated in detail.

Cyclophane, especially [2.2]paracyclophane, is a very attractive molecule as an aromatic building block leading to the construction of a π -conjugated polymer.⁹ To date, many cyclophane compounds have been prepared, and their reactivity and physical properties have been investigated in detail due to their characteristic interactions between the two cofacial π -electron systems.^{9,10} Recently, we reported the first preparation and the physical properties of novel π -conjugated polymers (Chart 1)¹¹ using cyclophane derivatives as the key monomer. We found that the obtained polymers showed an extension of π -delocalization via the through-space with π - π stacking according to the UV–vis absorption spectra and that they also exhibited an intense luminescence in solution.

On the other hand, charge transfer is essential to expression of conductivity and electroluminescence, in which charge hopping between the π -conjugated sys-

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tems plays an important role. From this standpoint, Mizogami and Yoshimura reported the first synthesis of polymetacyclophane (Chart 1) by polycondensation reaction of an oxidative dimer of 8,16-dihydroxy[2.2]metacyclophane, and this polymer exhibited a conductivity of 0.25 S/cm by doping with H₂SO₄ vapor.¹² Recently, oligothiophene-substituted [2.2]paracyclophane and thiophene-containing [2.2]paracyclophane polymers were synthesized, and their redox activities were investigated by cyclic voltammetry analysis.^{13,14} Ferrocene derivatives and polymers, like those of thiophene, are also electroactive and show semiconductive behavior.¹⁵ There are a number of articles dealing with the synthesis of ferrocene-containing polymers.^{15b} In view of the interesting structure and the electronic effect, it is fascinating to incorporate a sandwich framework of ferrocene into the [2.2]paracyclophane-containing π -conjugated polymer.

In this study, we present the synthesis of the novel through-space π -conjugated polymer with alternating [2.2]paracyclophane and ferrocene units in the main chain based on PPE, and we discuss the optical properties as well as the electrochemical behaviors of the obtained polymer.

Results and Discussion

We synthesized the monomer (**10**), which has a didodecyloxy-substituted phenylene spacer, because the



long alkoxy chain provides good solubility for the long and rigid π -conjugated polymer. The synthetic route is shown in Scheme 1. The synthesis of 4,16-diethynyl-[2.2] paracyclophane (4) was started from commercially available [2.2] paracyclophane (1). The iron-catalyzed electrophilic dibromination of 1 and recrystallization afforded only pseudo-*p*-dibromo[2.2]paracyclophane (2) in 25% isolated yield due to highly poor solubility.¹⁶ The PdCl₂(PPh₃)₂/CuI-catalyzed cross-coupling¹⁷ of 2 and trimethylsilylacetylene provided 3 (71%), which was then converted to compound 4 by Bu_4^nNF -promoted desilylation in 90% yield. 4-Iodo-2,5-didodecyloxy-1-[(trimethylsilyl)ethynyl]benzene (8) was prepared in a three-step reaction from hydroquinone $(\mathbf{5})$, as follows: dialkylation of 5, diiodination of 6, followed by the treatment of 7 with trimethylsilylacetylene in the presence of the Pd/Cu catalyst. Due to the fact that 2,5didodecyloxy-1,4-diiodobenzene (7) showed a high reactivity for palladium-catalyzed coupling reaction, both 2,5-didocyloxy-1,4-[bis(trimethylsilyl)ethynyl]benzene and starting compound (7) were obtained along with 8. Consequently, pure 8 was isolated in 11% yield by column chromatography. Sonogashira coupling reaction of 4 with 8 and, finally, deprotection of the trimethylsilyl group of 9 gave the desired monomer (10) in 36% yield. 1,1'-Diiodoferrocene (11) was prepared according to the published procedure.¹⁸

The procedure for the synthesis of the polymer (12) was carried out as follows (Scheme 2). The orange powder (12) was obtained in 93% yield by the treatment

Figure 1. ¹H NMR spectrum of the polymer (12) in CDCl₃.

of **10** with **11** in the presence of a catalytic amount of $PdCl_2(PPh_3)_2/PPh_3/CuI$ for 48 h under a nitrogen atmosphere after purification. The polymer (**12**) was soluble in common organic solvents such as THF, CH_2Cl_2 , CHCl₃, and toluene. The polymer (**12**) could be processed into a self-standing film, and it was thermally stable in solution and in the solid state. The molecular weight measurements were performed by gel permeation chromatography (GPC) in a CHCl₃ eluent using a calibration curve of polystyrene standards, and the polymer (**12**) was shown to have a number-average molecular weight (M_n) of 24 500, which corresponds to a degree of polymerization of about 18, with a M_w/M_n of 2.7.

This polymer was characterized by the ¹H NMR, ¹³C NMR, and IR spectra. In the ¹H NMR spectrum of **12** in $CDCl_3$ (Figure 1), the peak corresponding to the terminal alkyne protons at 3.0 ppm of the monomer (10) disappeared. The signals of the dodecyloxy side chains were dominating in the region 0.80-1.8 ppm, and the bridged methylene protons of [2.2]paracyclophane units appeared at 2.8–3.8 ppm. The methylene groups adjacent to the oxygen were found to be 4.0 ppm. The incorporated ferrocene protons appeared at 4.2 and 4.4 ppm, respectively. The signals of the aromatic protons were between 6.5 and 7.5 ppm. In the ¹³C NMR spectrum of the polymer (12), typical signals for acetylenic carbons were dominant in the region 83–95 ppm. The acetylenic moieties were also characterized by the IR spectrum, and a weak stretching vibration mode of



a carbon-carbon triple bond was observed at around 2200 cm^{-1} .

The UV-vis absorption spectrum of the polymer (12) was recorded in dilute CHCl₃ at room temperature, as shown in Figure 2. In the UV–vis absorption spectrum, absorption maxima at 306 nm ($\epsilon = 27$ 800, based on the repeating unit) and 376 nm ($\epsilon = 37\,000$, based on the repeating unit), which were ascribed to the $\pi - \pi^*$ transition of the conjugated polymer backbone, were observed. The band gap energy of 12, estimated from the absorption edge of the UV-vis spectrum, was about 2.10 eV.¹⁹ The spectrum of polymer 12 exhibited a blueshift of about 10 nm in comparison with that of polymer **13** ($\lambda_{max} = 384 \text{ nm}$,^{11a} Chart 2), indicating that a [2.2]paracyclophane unit is more effective for the delocalization of the π -electron via the through-space than the ferrocene unit. On the other hand, the model compound (17) was prepared. The synthetic procedure is outlined in Scheme 3, and the UV-vis absorption spectrum is also shown in Figure 2. The UV-vis spectrum of 17 in CHCl₃ solution was similar to that of polymer 12, with the absorption maxima at 297 and 363 nm, respectively. This result indicates the extension of π -delocalization length via the through-space of the two facing benzene rings. Furthermore, 17 showed the d-d transition band in the ferrocene moiety at around 450 nm, while 12 exhibited the broadened $\pi - \pi^*$ transition band which covered the d-d band.

The fluorescence emission was investigated in dilute $CHCl_3$ solution $(1.0 \times 10^{-5} \text{ mol/L})$ at room temperature by the excitation wavelength at 365 nm. The polymer (12) gave a highly weak fluorescence with a peak maximum at about 475 nm in the visible bluish green region. The fluorescence quantum efficiency in solution was measured relative to that of 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard, and the value was 0.04.²⁰

To evaluate the electrochemical behavior of the novel polymer examined herein, the cyclic voltammetry measurement of 12 was carried out in CH₂Cl₂ solution containing Bu₄NPF₆ (0.10 M) as a supporting electrolyte, with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. Consequently, the reversible cyclic voltammogram was obtained with a scan rate of 100 mV/s, and one broad oxidation peak was found to be 0.62 V vs Ag/Ag+ (Figure 3). The model compound (17) had a relatively sharp oxidation peak at 0.58 V (Figure 3, inset). These oxidative waves could be attributed to the typical formation of the ferrocenium corresponding to the Fe-(II)/Fe(III) and Fe(III)/Fe(II) systems. Communication between phenyleneethynylene groups including a ferrocene as a core, via the through-space of two cofacial



Figure 2. UV–vis spectra of the polymer (**12**) and the model compound (**17**) in $CHCl_3$ solution at room temperature.



polymer 13^{11a}

benzenes in [2.2]paracyclophane, causes the single broad oxidation peak,^{13c} although each redox active ferrocene unit is spaced widely. Figure 4 shows the cyclic voltammetric responses of 12 at various scan rates from 50 to 1000 mV/s. The height of the current peaks increased as the scan rate increased, and the oxidation potentials were independent of the scan rate. As shown in Figure 5, the oxidation waves were diffusioncontrolled by the linear dependence of the oxidative peak currents ($I/\mu A$) on the square root of the scan rate $(v^{1/2}/V^{1/2} s^{-1/2})$, and they demonstrated the zero intercept, which indicates the diffusion coefficient (D) of the electroactive substance is about 5.5×10^{-7} (cm²/s).²¹ In addition, *D* of the model compound (17) was 2.53×10^{-5} (cm^{2}/s) , which is larger than that of the polymer, due to the smaller molecular size and weight. Similar results were reported in detail by Yamamoto and co-workers using PPE-type conjugated polymers having a ferrocene unit in the main chain.²²



Figure 3. Cyclic voltammogram of the polymer (**12**) in CH₂-Cl₂ containing Bu₄NPF₆ as a supporting electrolyte using a Pt electrode (vs Ag/Ag⁺) at a scan rate of 100 mV/s. First and second cycles are shown. The inset shows the cyclic voltammogram of **17** in CH₂Cl₂ containing Bu₄NPF₆ (vs Ag/Ag⁺) at a scan rate of 100 mV/s.



Figure 4. Cyclic voltammogram of the polymer (**12**) in CH₂-Cl₂ containing Bu₄NPF₆ as a supporting electrolyte using a Pt electrode (vs Ag/Ag⁺) at scan rates from 50 to 1000 mV/s.



Figure 5. Plot of I(I = anodic peak current) vs $v^{1/2}$ (v = scan rate) for the titled polymer (**12**).

The electrical conductivity measurement of the polymer (**12**) by oxidatively doping with iodine vapors for 24 h under a nitrogen atmosphere exhibited a conductivity of 1.6×10^{-4} S/cm. Before doping, **12** showed a conductivity of ~ 10^{-8} , at least 4 orders of magnitude greater than that of the undoped state. On the other hand, the conductivity of polymetacyclophane was found to be 0.25 S/cm by doping with H₂SO₄.¹² The lower conductivity of **12** seems to be the reason there are not many electroactive ferrocene units in the polymer backbone, while all components are doped in polymetacyclophane.

In summary, a novel π -conjugated polymer (12) having ferrocene and [2.2]paracyclophane units in the main chain was designed, synthesized, and characterized. π -Conjugation of **12** was expanded by way of the through-space, and the [2.2]paracyclophane moiety was found to contribute more effectively than the ferrocene unit to the delocalization of the π -electron according to the UV-vis absorption analysis. Cyclic voltammetry of polymer 12 showed a single and reversible oxidative wave at 0.62 V derived from the Fe(II)/Fe(III) and Fe-(III)/Fe(II) systems. The electrochemical oxidation was diffusion-controlled by the linear dependence of the oxidative peak currents (1) on the square root of the scan rate $(v^{1/2})$, and the diffusion coefficient (D) was 5.5 \times 10^{-7} (cm²/s), as estimated by a $v^{1/2}-I$ plot. On iodine doping under ambient conditions, the polymer (12) showed a maximum conductivity of 1.6 \times 10^{-4} S/cm. The investigated polymers showed thermal stability and good film formation, and they are therefore considered promising candidates for use in electronic devices. Further studies on the preparation of cyclophane polymers containing organometallic moieties, and their application as conductive materials and their use in nonlinear optical devices, are now in progress.

Experimental Section

General. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respectively. Samples were analyzed in CDCl₃, and the chemical shift values were expressed relative to Me₄Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in CHCl₃ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in CHCl₃ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using CHCl₃ as an eluent after calibration with standard polystyrene. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F₂₅₄ plates. Column chromatography was performed with Wakogel C-300 silica gel. Elemental analysis was performed at the Microanalytical Center of Kyoto University. Cyclic voltammetry was carried out using a BAS CV-50W voltammetric analyzer with a 0.10 M CH₂Cl₂ solution containing Bu₄NPF₆ as an electrolyte, a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. Electrical conductivity was measured at room temperature with a two-probe technique using a Keithley 2400 source meter, after doping with iodine vapors for 24 h under nitrogen

Materials. THF was distilled from sodium benzophenone ketyl. NEt₃ was distilled from KOH. CH₂Cl₂ was distilled from CaCl₂. Bu₄NPF₆ was recrystallized from EtOH. [2.2]Paracy-clophane (1), hydroquinone (5), trimethylsilylacetylene, phenylacetylene, Bu^{*n*}₄NF (1.0 M in THF), dodecanol, PdCl₂(PPh₃)₂, CuI, PPh₃, K₂CO₃, KI, I₂, and KIO₄ were obtained commercially and used without further purification. 4,16-Dibromo[2.2]-paracyclophane (2),¹⁶ 1,4-didodecyloxybenzene (6),²³ 2,5-didodecyloxy-1,4-diiodobenzene (7),²³ 1,1'-diiodoforrocene (11),¹⁸

and $Pd(PPh_3)_4^{24}$ were prepared as described in the literature. All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques.

4,16-Bis(trimethylsilylethynyl)[2.2]paracyclophane (3). 4,16-Dibromo[2.2]paracyclophane (2) (3.5 g, 9.7 mmol), trimethylsilylacetylene (10 mL), PdCl₂(PPh₃)₂ (0.70 g, 1.0 mmol), PPh₃ (0.52 g, 2.0 mmol), and CuI (0.20 g, 1.0 mmol) were dissolved in 70 mL of THF-NEt₃ (v/v = 5:2). The solution was stirred at 75 °C for 2 days under a nitrogen atmosphere. Precipitated ammonium salts were filtered off, and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO₂ with hexane-CHCl₃ (v/v =2:1, $R_f = 0.15$) as an eluent to give compound **3** (2.7 g, 6.8 mmol, 81%) as a white powder. ¹H NMR (CDCl₃, 270 MHz): δ 0.31 (s, 18H), 2.80 (m, 2H), 2.97 (m, 2H), 3.14 (m, 2H), 3.57 (m, 2H), 6.44 (d, J = 7.8 Hz, 2H), 6.49 (s, 2H), 7.98 (d, J = 7.8 Hz, 2H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 0.13, 33.5, 34.0, 97.5, 105.8, 124.6, 130.1, 133.0, 137.4, 139.3, 142.6. IR (Nujol): 2146 cm^{-1} . LRMS (EI) *m*/*z* (relative intensity) = 400 (M⁺, 75), 200 (100), 185 (70). Anal. Calcd for C₂₆H₃₂Si₂: C, 77.93; H, 8.05. Found: C, 77.82; H, 8.02.

4,16-Diethynyl[2.2]paracyclophane (4). To a solution of **3** (2.0 g, 5.0 mmol) in 50 mL of THF was added Bu^{*n*}₄NF (10 mL, 1.0 M solution in THF). The reaction mixture was stirred at room temperature for 20 h under a nitrogen atmosphere. The solution was evaporated under vacuum, and the residue was subjected to column chromatography on SiO₂ with hexane–CHCl₃ (v/v = 2:1, R_f = 0.55) as an eluent to give compound **4** (1.1 g, 4.5 mmol, 90%) as a white powder. ¹H NMR (CDCl₃, 270 MHz): δ 2.92 (m, 4H), 3.19 (m, 2H), 3.27 (s, 2H), 3.59 (m, 2H), 6.44 (d, *J* = 7.0 Hz, 2H), 6.56 (s, 2H), 7.00 (d, *J* = 7.0 Hz, 2H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 33.7, 33.8, 80.2, 83.9, 123.5, 130.6, 133.2, 137.8, 139.5, 142.6. IR (KBr): 3298, 2098 cm⁻¹. LRMS (EI) *m*/*z* (relative intensity) = 256 (M⁺, 88), 241 (35), 128 (100). Anal. Calcd for C₂₀H₁₆: C, 93.71; H, 6.29. Found: C, 93.45; H, 6.26.

4-Iodo-2,5-didodecyloxy-1-(trimethylsilylethynyl)benzene (8). 2,5-Didodecyloxy-1,4-diiodobenzene (7) (21 g, 30 mmol), trimethylsilylacetylene (3.5 g, 35 mmol), PdCl₂(PPh₃)₂ (0.70 g, 1.0 mmol), and CuI (0.20 g, 1.0 mmol) were dissolved in 120 mL of THF-Et₃N (v/v = 7.5). The solution was stirred at room temperature for 24 h under a nitrogen atmosphere. Precipitated ammonium salts were filtered off, and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO₂ with hexane-CHCl₃ (v/v =9:1, $R_f = 0.60$) as an eluent to give compound **8** (2.3 g, 3.5 mmol, 12%) as a pale yellow powder. Didodecyloxy-1,4-diiodobenzene (7) ($R_f = 0.95$) and 2,5-diiodo-1,4-bis(trimethylsilylethynyl)benzene ($R_f = 0.33$) were removed by column chromatography. ¹H NMR (CDCl₃, 270 MHz): δ 0.26 (s, 9H), 0.88 (t, J = 4.3 Hz, 6H), 1.26 - 1.31 (m, 32H), 1.51 (m, 4H), 1.79 (m, 4H)4H), 3.93 (t, J = 4.0 Hz, 4H), 6.83 (s, 1H), 7.25 (s, 1H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 0.06, 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6 (overlapping signals), 31.9, 69.8, 70.1, 87.9, 99.4, 100.8, 113.4, 116.3, 123.9, 151.7, 154.9. IR (KBr): 2162 cm⁻¹. LRMS (EI) m/z (relative intensity) = 668 (M⁺, 76), 154 (100). HRMS (FAB): calcd for $C_{35}H_{61}IO_2Si$, 668.3486; found, 668.3484. Anal. Calcd for C₃₅H₆₁IO₂Si: C, 62.85; H, 9.19. Found: C, 63.10; H, 8.94.

4,16-Bis{[2,5-didodecyloxy-4-(trimethylsilylethynyl)phenyl]ethynyl [2.2] paracyclophane (9). Compound 4 (0.39 g, 1.5 mmol), 8 (2.0 g, 3.0 mmol), PdCl₂(PPh₃)₂ (0.070 g, 0.10 mmol), and CuI (0.020 g, 0.10 mmol) were dissolved in 8 mL of THF-Et₃N (v/v = 5:3). The solution was stirred at 50 $^{\circ}$ C for 24 h. Precipitated ammonium salts were filtered off, and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO2 with hexane-CHCl₃ (v/v = 1:1, R_f = 0.67) as an eluent to give compound **9** (2.0 g, 1.5 mmol, 99%) as a white powder. ¹H NMR (CDCl₃, 270 MHz): δ 0.25 (s, 18H), 0.86 (t, J = 4.7 Hz, 6H), 0.87 (t, J = 4.7 Hz, 6H), 1.25-1.36 (m, 64H), 1.53 (m, 8H), 1.81 (m, 4H), 1.91 (m, 4H), 2.89 (m, 2H), 3.00 (m, 2H), 3.30 (m, 2H), 3.76 (m, 2H), 4.03 (t, J = 4.3 Hz, 4H), 4.05 (t, J = 4.3 Hz, 4H), 6.49 (d, J = 5.4 Hz, 2H), 6.59 (s, 2H), 6.98 (s, 2H), 7.08 (d, J = 5.4Hz, 2H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 0.00, 14.1, 22.7, 26.1, 26.2, 26.6, 29.1, 29.3, 29.4, 29.5, 29.6 (overlapping signals), 31.9, 32.2, 33.8, 34.1, 69.5, 69.6, 89.2, 95.2, 99.5, 101.3, 100.8, 113.4, 114.5, 116.5, 117.3, 124.8, 130.6, 133.2, 137.1, 139.6, 142.2, 153.5, 154.1. IR (KBr): 2155 cm⁻¹. LRMS (EI) *m/z* (relative intensity) = 1338 (M⁺, 29), 154 (100). HRMS (FAB): calcd for C₉₀H₁₃₆O₄Si₂, 1336.9977; found, 1336.9973. Anal. Calcd for C₉₀H₁₃₆O₄Si₂: C, 80.78; H, 10.24. Found: C, 80.56; H, 10.00.

4,16-Bis[(2,5-didodecyloxy-4-ethynylphenyl)ethynyl]-[2.2]paracyclophane (10). To a solution of 9 (1.9 g, 1.4 mmol) in 20 mL of THF was added Buⁿ₄NF (0.50 mL, 1.0 M solution in THF). The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. The solution was evaporated under vacuum, and the residue was subjected to column chromatography on SiO₂ with hexane-CHCl₃ (v/v = 2:1, $R_f = 0.55$) as an eluent to give compound **10** (0.61 g, 0.51 mmol, 36%) as a yellow powder. ¹H NMR (CDCl₃, 270 MHz): δ 0.87 (t, J = 4.6 Hz, 12H), 1.25 (m, 64H), 1.50 (m, 8H), 1.88 (m, 8H), 2.93 (m, 4H), 3.30 (m, 2H), 3.36 (s, 2H), 3.72 (m, 2H), 4.05 (m, 4H), 4.05 (t, J = 4.3 Hz, 4H), 6.51 (d, J = 7.5 Hz, 2H), 6.60 (s, 2H), 7.03 (s, 2H), 7.10 (d, J = 7.5 Hz, 2H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 14.1, 22.7, 25.9, 26.2, 29.2, 29.3, 29.5, 29.6 (overlapping signals), 31.9, 33.8, 34.1, 69.3, 69.7, 80.1, 82.1, 89.1, 95.3, 112.3, 114.9, 117.0, 124.8, 130.6, 133.2, 137.2, 139.6, 142.2, 142.3, 153.4, 154.1. IR (KBr): 3287, 2107 cm⁻¹. LRMS (EI) m/z (relative intensity) = 1194 (M⁺, 8), 154 (100). HRMS (FAB): calcd for C₈₄H₁₂₀O₄, 1192.9187; found, 1192.9199. Anal. Calcd for C84H120O4: C, 84.51; H, 10.13. Found: C, 84.04; H, 10.09.

4-Iodo-2,5-didodecyloxy-1-(phenylethynyl)benzene (14). Compound 7 (7.0 g, 10 mmol), phenylacetylene (1.1 g, 11 mmol), PdCl₂(PPh₃)₂ (0.36 g, 0.50 mmol), and CuI (0.10 g, 0.50 mmol) were dissolved in 80 mL of THF-Et₃N (v/v = 3:1). The solution was stirred at 40 °C for 24 h under a nitrogen atmosphere. Precipitated ammonium salts were filtered off, and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO₂ with hexane-CHCl₃ (v/v = 2:1, $R_f = 0.50$) as an eluent to give compound 14 (2.6 g, 3.8 mmol, 38%) as a white solid. Didodecyloxy-1,4-diiodobenzene (7) ($R_f = 0.95$) and 2,5-diiodo-1,4-bis-(phenylethynyl)benzene ($R_f = 0.20$) were removed by column chromatography. ¹H NMR (CDCl₃, 270 MHz): δ 0.88 (t, J = 6.4 Hz, 6H), 1.26-1.32 (m, 32H), 1.52 (m, 4H), 1.82 (m, 4H), 3.95 (t, J = 6.8 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 6.90 (s, 1H), 7.29 (s, 1H), 7.32 (m, 3H), 7.53 (m, 2H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.6 (overlapping signals), 31.9, 69.8, 70.0, 85.5, 87.4, 93.9, 94.1, 113.5, 115.8, 123.4, 123.7, 128.2, 131.5, 149.3, 151.7, 154.3. IR (Nujol): 2212 cm⁻¹. LRMS (EI) m/z (relative intensity) = 672 (M⁺, 96), 336 (100), 210 (81). HRMS (FAB): calcd for C₃₈H₅₇IO₂, 672.3403; found, 672.3401. Anal. Calcd for C38H57IO2: C, 67.84; H, 8.54. Found: C, 68.12; H, 8.52.

2,5-Didodecyloxy-1-(trimethylsilylethynyl)-4-(phenylethynyl)benzene (15). Compound 14 (2.6 g, 3.8 mmol), trimethylsilylacetylene (3.0 mL), PdCl₂(PPh₃)₂ (0.14 g, 0.20 mmol), PPh₃ (0.10 g, 4.0 mmol), and CuI (0.040 g, 0.20 mmol) were dissolved in 35 mL of THF–NEt₃ (v/v = 5:2). The solution was stirred at 40 °C for 24 h under a nitrogen atmosphere. Precipitated ammonium salts were filtered off, and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO₂ with hexane-CHCl₃ (v/v =2:1, $R_f = 0.48$) as an eluent to give compound **15** (1.0 g, 1.6 mmol, 42%) as a pale yellow solid. ¹H NMR (CDCl₃, 270 MHz): δ 0.27 (s, 9Ĥ), 0.88 (t, J = 6.4 Hz, 6H), 1.25 (m, 32H), 1.52 (m, 4H), 1.81 (m, 4H), 3.98 (t, J = 6.4 Hz, 2H), 3.99 (t, J = 6.8 Hz, 2H), 6.94 (s, 1H), 6.96 (s, 1H), 7.33 (m, 3H), 7.52 (m, 2H). $^{13}\mathrm{C}$ NMR (CDCl_3, 67.5 MHz): δ –0.05, 14.1, 22.7, 26.0, 29.3, 29.4, 29.6 (overlapping signals), 31.9, 69.4, 69.5, 85.8, 94.8, 99.9, 101.1, 113.5, 114.2, 116.7, 117.1, 123.4, 128.2, 131.5, 131.6, 153.4, 154.1. IR (Nujol): 2154 cm⁻¹. LRMS (EI) m/z (relative intensity) = 642 (M^+ , 100), 291 (83). HRMS (FAB): calcd for C43H66O2Si, 642.4832; found, 642.4835. Anal. Calcd for C43H66O2Si: C, 80.31; H, 10.34. Found: C, 80.01; H, 10.53.

2,5-Didodecyloxy-1-ethynyl-4-(phenylethynyl)benzene (16). To a solution of **15** (0.90 g, 1.4 mmol) in 25 mL of THF was added Buⁿ₄NF (0.50 mL, 1.0 M solution in THF). The reaction mixture was stirred at room temperature for 16 h under a nitrogen atmosphere. The solution was evaporated under vacuum, and the residue was washed with MeOH to give pure 16 (0.73 g, 1.3 mmol, 92%) as a pale yellow solid. ¹H NMR (CDCl₃, 270 MHz): δ 0.88 (t, J = 6.4 Hz, 6H), 1.25 (m, 32H), 1.51 (m, 4H), 1.82 (m, 4H), 3.35 (s, 1H), 3.99 (t, J = 6.0Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 6.98 (s, 1H), 6.99 (s, 1H), 7.34 (m, 3H), 7.53 (m, 2H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 14.1, 22.7, 25.9, 26.0, 29.1, 29.3, 29.4, 29.6 (overlapping signals), 31.9, 69.4, 69.5, 80.0, 82.2, 85.7, 94.9, 112.4, 114.6, 116.7, 117.7, 123.3, 128.3, 131.5, 131.6, 153.4, 154.1. IR (Nujol): 3280, 2106 cm⁻¹. LRMS (EI) *m*/*z* (relative intensity) = 570 (M⁺, 100), 234 (82). HRMS (FAB): calcd for $C_{40}H_{58}O_2$, 570.4437; found, 570.4440. Anal. Calcd for C₄₀H₅₈O₂: C, 84.15; H, 10.24. Found: C, 84.04; H, 10.33.

1,1'-Bis{[2,5-didodecyloxy-4-(phenylethynyl)phenyl]ethynyl}ferrocene (17). Compound 11 (0.22 g, 0.50 mmol), 16 (0.57 g, 1.0 mmol), Pd(PPh₃)₄ (0.12 g, 0.10 mmol), and CuI (0.020 g, 0.10 mmol) were dissolved in 7 mL of THF-NEt₃ (v/v = 5.2). The solution was stirred at 50 °C for 48 h under a nitrogen atmosphere. Precipitated ammonium salts were filtered off, and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO2 with hexane-CHCl₃ (v/v = 2:1, $R_f = 0.27$) as an eluent to give compound 17 (0.46 g, 0.34 mmol, 67% based on 11) as a red solid. ¹H NMR (CDCl₃, 270 MHz): δ 0.88 (m, 12H), 1.25 (m, 64H), 1.54 (m, 8H), 1.83 (m, 8H), 3.94 (t, J = 6.2 Hz, 4H), 4.00 (t, J = 6.2 Hz, 4H), 4.36 (s, 4H), 4.58 (s, 4H), 6.92 (s, 2H), 6.97(s, 2H), 7.33 (m, 6H), 7.52 (m, 4H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 14.1, 22.7, 26.0, 26.1, 29.3, 29.5, 29.6 (overlapping signals), 31.9, 66.7, 69.5, 71.5, 73.0, 82.8, 86.1, 93.0, 94.6, 113.3, 114.4, 116.6, 116.7, 123.5, 128.1, 128.3, 131.5, 153.4, 153.6. IR (KBr): 2212 cm⁻¹. HRMS (FAB): calcd for $C_{90}H_{122}O_4Fe$, 1322.8693; found, 1322.8676.

Polymerization. A typical procedure is as follows. A mixture of 10 (119 mg, 0.10 mmol), 11 (44 mg, 0.10 mmol), PdCl₂(PPh₃)₂ (7.2 mg, 0.010 mmol), PPh₃ (5.2 mg, 0.020 mmol), CuI (2.0 mg, 0.010 mol), NEt₃ (2.0 mL), and THF (4.0 mL) was placed in a 50 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under a nitrogen atmosphere. The reaction was carried out at 50 °C for 48 h with stirring. After the reaction mixture was cooled, precipitated ammonium salts were filtered off and washed with THF. The filtrate was concentrated and poured into MeOH (50 mL) to precipitate the polymer. The resulting polymer (12) was filtered, washed with MeOH, and dried in vacuo to give 128 mg (0.093 mmol, 93%) as an orange powder. ¹H NMR (CDCl₃, 270 MHz): δ 0.82 (br s, 12H), 1.20 (br s, 64H), 1.49 (br s, 8H), 1.88 (m, 8H), 1.83 (m, 8H), 2.84 (br, 4H), 3.25 (br, 2H), 3.72 (m, 2H), 4.00 (br, 8H), 4.21 (br s, 4H), 4.42 (br, 4H), 6.46 (m, 2H), 6.55 (br s, 2H), 7.00 (m, 6H). ¹³C NMR (CDCl₃, 67.5 MHz): δ 14.1, 22.7, 26.0, 26.2, 29.0, 29.4, 29.5 (overlapping signals), 31.9, 33.8, 34.1, 69.8, 70.0, 71.2, 72.3, 74.1, 83.3, 89.4, 92.5, 95.0, 113.7, 116.2, 117.0, 124.9, 128.3, 134.1, 137.1, 139.6, 142.2, 153.4, 153.6. IR (film): 2200, 832 cm⁻¹.

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