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Luminescent and Axially Chiral π-Conjugated Polymers Linked by Carboranes in the Main Chain

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ABSTRACT: Sonogashira−Hagihara polycondensations of two bis(4-iodophenyl)carborane compounds with axially chiral diyne monomers having binaphthyl unit were carried out to obtain the corresponding chiral π-conjugated polymers having *o*- or *m*-carborane segment in the main chain. The polymer structures and their optical properties were characterized by ^{1}H, ^{13}C, and ^{11}B NMR, FT-IR, UV−vis absorption, photoluminescence, and circular dichroism spectroscopies. Photoluminescence study revealed that the polymer having *m*-carborane exhibited intense blue emission in solution state, whereas polymers having *o*-carborane exhibited aggregation-induced emission (AIE). All polymers showed strong CD signals, indicating the construction of highly ordered conformation.

Introduction

π-Conjugated polymers have been paid more considerable attention for their photonic and electronic applications, such as organic light-emitting diodes, photovoltaics, organic lasers, and organic-field-effect transistors as well as other organic devices.[1] Among π-conjugated polymers, optically active π-conjugated polymers are a new class of materials potentially useful in areas of enantioselective sensing, polarized photoluminescence and electroluminescence, asymmetric electrosynthesis, and asymmetric catalysis.[2] Generally, axially chiral 1,1′-binaphthol (BINOL) and its derivatives have often employed as one of the building blocks to construct π-conjugated polymers with a main-chain chiral configuration.[3] Recently, Pu and co-workers have reported the successful synthesis of a series of novel chiral π-conjugated polymers by means of the chiral binaphthyl compounds as chiral starting materials for the construction of the main chains.[4] The chiral conjugated polybinaphthyls can express the properties of electro-optical sensors and enantioselective and molecular recognition by controlling the chiral organic groups and the linker structures at the well-defined molecular level.[5]

In this article, we present the synthesis and optical properties of novel π-conjugated polybinaphthyls connected with *o*- and *m*-carboranes. Carboranes are icosahedral clusters consisting of 10 boron atoms and 2 carbon atoms with three-center two-electron bonds and exhibit excellent thermal and chemical stabilities due to the three-dimensional delocalized electrons, i.e., three-dimensional aromaticity.[6] Various novel molecules containing carboranes have been synthesized for the purpose of heat-stable materials, boron−neutron capture therapy, or coordination chemistry.[7] However, very few researches have reported the synthesis of carborane-containing molecules exhibiting particular optical properties and electronic structures originated from the three-dimensional aromaticity.[8] In recent reports, we have investigated the alternating polymers with *p*-phenylene-ethynylene and *o*-carborane or *m*-carborane sequences, and the molecular design successfully led to the occurrence of aggregation-induced emission (AIE)[9] or highly emissive polymers in solution state.[10] In hope of combining the desirable properties of both chiral binaphthyl and carborane units into π-conjugated systems, we have developed a new kind of hybrid-type chiral π-conjugated polymer consisting of chiral binaphthyl-based poly(*p*-phenylene-ethynylene) π-conjugated backbone connected with "three-dimensionally aromatic" carboranes. To the best of our knowledge, this is the first example of the introduction of carborane groups into chiral π-conjugated polymers.

Experimental Section

Instruments. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR measurements were recorded on a JEOL JNM-EX400 instrument. ^{1}H and ^{13}C NMR spectra used 0.05% tetramethylsilane (TMS) as an internal standard, and ^{11}B NMR spectra were referenced externally to $BF_3 \cdot Et_2O$ at room temperature. Number-average molecular weight and molecular weight distribution values were estimated on a TOSOH size exclusion chromatography (SEC) system equipped with polystyrene gel column (Tosoh TSKgel G3000HXL) using an ultraviolet detector (UV-8020) and a refractive-index (RI-8020) detector at 40 °C. FT-IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Thermogravimetric analysis (TGA) was performed using a TG/DTA 6200, Seiko Instruments, Inc., with heating rate of 10 °C/min under dry air. UV−vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. Fluorescence emission spectra and absolute quantum yield by integrating sphere method were recorded on a Horiba Joban Yvon Fluoromax-4 spectrofluorometer. Dynamic light scattering (DLS) measurements were performed by an Otsuka FPR-1000 system. Atomic force microscopy (AFM) observation was conducted by using a Seiko Instrument SPA 400. Circular dichroism (CD) spectra were obtained using a JASCO J-820 spectropolarimeter with THF as a solvent. Specific rotations ($[\alpha]_{25}{}^{D}$) were measured with a Rudolph Research Analytical ATUTOPOL IV digital polarimeter.

Materials. All synthetic procedures were performed under an argon atmosphere. Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) and triethylamine were

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purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). Bis(4-iodophenyl)-*o*-carborane (**M1**),[9a,11] bis(4-iodophenyl)-*m*-carborane (**M2**),[10] and (*S*)-(+)-6,6′-diethynyl-2,2′-bis(octyloxy)-1,1′-binaphthyl (**S**)[12] were synthesized and characterized according to the literature.

***R*-(−)-6,6′-Diethynyl-2,2′-dioctyloxy-1,10-binaphthyl (R).** (**R**) was prepared in a similar manner as **S** using (*R*)-binaphthol as a starting material. Yield = 68%. ^{1}H NMR ($CDCl_3$): δ (ppm), 8.03 (s, 2H), 7.88 (d, 2H, J = 9.0 Hz), 7.40 (d, 2H, J = 9.0 Hz), 7.24 (d, 1H, J = 7.1 Hz), 7.06 (d, 2H, J = 8.8 Hz), 3.98−3.89 (m, 4H), 3.07 (s, 2H), 1.40−1.38 (m, 4H), 1.23−1.21 (m, 4H), 1.09−1.00 (m, 16H), 0.86 (6H, t, J = 7.3 Hz). HRMS (EI) Calcd for $C_{40}H_{46}O_2$: *m*/*z* 558.3498. Found: *m*/*z* 558.3499. Anal. Calcd for $C_{40}H_{46}O_2$: C, 85.98; H, 8.30. Found: C, 86.07; H, 8.46.

4,4″-Diiodo-*o*-terphenyl (M3). To a suspension of Mg turning (800 mg, 33.00 mmol) in 10 mL of anhydrous ether was added dropwise a solution of 4-(trimethylsilyl)bromobenzene (5.04 g, 22.00 mmol) in ether (10 mL) through a syringe under an argon atmosphere at room temperature. After 1 h stirring, the resulting Grignard reagent was transferred to a solution of 1,2-diiodobenzene (1.81 g, 5.50 mmol) and dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (29.0 mg, 0.055 mmol) in ether (10 mL) by cannula under an argon atmosphere at room temperature. The reaction mixture was refluxed for 48 h. After the mixture was cooled to room temperature, and 2 M aqueous HCl solution was added to hydrolyze it. The organic layer was washed successively with water, aqueous $NaHCO_3$ solution, and brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent under vacuum, the residue was purified by silica gel column chromatography eluted with hexane to give 4,4″-bis(trimethylsilyl)-*o*-terphenyl as a white solid (783 mg, 38%). ^{1}H NMR ($CDCl_3$): δ (ppm), 7.42 (d, J = 2.44 Hz, 4H), 7.36 (d, J = 8.28 Hz, 4H), 7.13 (d, J = 8.04 Hz, 4H), 0.24 (s, 18H). ^{13}C NMR ($CDCl_3$): δ (ppm), 141.6, 141.2, 139.2, 133.8, 128.7, 127.2, 126.5, −1.1. HRMS (EI) Calcd for $C_{24}H_{30}Si_2$: *m*/*z* 374.1886. Found: *m*/*z* 374.1890.

To a solution of 4,4″-bis(trimethylsilyl)-*o*-terphenyl (750 mg, 2.00 mmol) in carbon tetrachloride (20 mL) was added iodine monochloride (2.5 mL of 1.0 M solution in CH_2Cl_2) at −20 °C under an argon atmosphere. After the addition, the reaction mixture was stirred at 50 °C for 1 h. Aqueous $NaHSO_3$ solution was added to remove unreacted iodine monochloride. The organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed in a rotary vacuum evaporator, and the residue was chromatographed on a silica gel column chromatography eluted with hexane to give **M3** (752 mg, 78%) as a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm), 7.57 (d, J = 8.53 Hz, 4H), 7.40 (dq, J = 21.50, 2.96 Hz, 4H), 6.87 (d, J = 8.53 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm), 140.5, 140.3, 137.0, 129.4, 129.2, 127.3, 93.2. HRMS (EI) Calcd for $C_{18}H_{12}I_2$ *m*/*z* 482.9107 $[M + H]^+$. Found: *m*/*z* 482.9102 $[M + H]^+$.

4,4″-Diiodo-*m*-terphenyl (M4). The procedure is analogous to that described for **M3**. 4,4″-Bis(trimethylsilyl)-*m*-terphenyl. White solid (1.16 g, 56%). ^{1}H NMR ($CDCl_3$): δ (ppm), 7.81 (s, 1H), 7.63 (s, 8H), 7.58 (d, J = 7.07 Hz, 2H), 7.52 (d, J = 6.58 Hz, 1H), 0.31 (s, 18H). ^{13}C NMR ($CDCl_3$): δ (ppm), 141.7, 141.6, 139.4, 133.9, 129.2, 126.6, 126.2, 126.2, −1.1. HRMS (EI) Calcd for $C_{24}H_{30}Si_2$: *m*/*z* 374.1886. Found: *m*/*z* 374.1884. 4,4″-Diiodo-*m*-terphenyl (**M4**). White solid (1.20 g, 83%). ^{1}H NMR ($CDCl_3$): δ (ppm), 7.78 (d, J = 8.04 Hz, 4H), 7.69 (s, 1H), 7.51 (m, 3H), 7.36 (d, J = 8.28 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm), 140.8, 140.4, 137.9, 129.5, 129.1, 126.2, 125.5, 93.3. HRMS (EI) Calcd for $C_{18}H_{12}I_2$: *m*/*z* 481.9028. Found: *m*/*z* 481.9026.

Polymerization Procedure. A typical procedure is as follows: Bis(4-iodophenyl)-*o*-carborane (**M1**) (56.6 mg, 0.10 mmol), (*R*)-(−)-6,6′-diethynyl-2,2′-bis(octyloxy)-1,1′-binaphthyl (**R**) (55.8 mg, 0.10 mmol), $Pd(PPh_3)_4$ (5.80 mg, 0.005 mmol), and CuI (0.95 mg, 0.005 mmol) were placed in a 10 mL Pyrex tube equipped with a magnetic stirrer. And then THF (1.0 mL) and triethylamine (0.5 mL) were added as solvents. The reaction was carried out at room temperature for 48 h. After polymerization, the reaction mixture was diluted with $CHCl_3$ and washed with aqueous NH_3 solution (10 wt %), water, and brine. The organic layer was dried over $MgSO_4$ and concentrated. The residue was dissolved in a small amount of $CHCl_3$ and reprecipitated from a large amount of methanol. The polymer was dried in vacuo to obtain **P1**(**R**) as a pale yellow powder (68.1 mg, 80%). $[\alpha]^{25}_{D}$: −184.7° (c = 0.09, THF). ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.13−7.96 (2H, Ar−H), 7.95−7.80 (2H, Ar−H), 7.52−7.46 (2H, Ar−H), 7.45−7.37 (4H, Ar−H), 7.35−7.25 (4H, Ar−H), 7.23−7.13 (2H, Ar−H), 7.09−6.93 (2H, Ar−H), 4.15−3.76 (4H, $-O-CH_2-$), 3.48−1.59 (10H, B−H), 1.41−1.36 (4H, $-OCHH_2-CH_2-$) 1.25−1.17 (4H, $-OCHH_2CH_2-CH_2-$), 1.11−0.82 (16H, $-(CH_2)-$), 0.80−0.74 (6H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 156.2, 134.4, 132.6, 132.0, 131.3, 130.5, 130.1, 129.4, 129.2, 126.6, 126.0, 120.2, 117.9, 116.4, 93.5, 88.2, 85.9, 69.9, 32.4, 29.9, 29.8, 29.7, 26.3, 23.3, 14.6. ^{11}B NMR (CD_2Cl_2): δ (ppm) −3.5, −10.3. IR (KBr pellet, cm^{-1}) 2594 (ν_{B-H}), 2207 ($\nu_{C\equiv C}$). **P1**(**S**). Pale yellow powder (74.0 mg, 87%). $[\alpha]^{25}_{D}$: 117.7° (c = 0.09, THF). ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.07−7.95 (2H, Ar−H), 7.93−7.82 (2H, Ar−H), 7.52−7.47 (2H, Ar−H), 7.45−7.38 (4H, Ar−H), 7.33−7.28 (4H, Ar−H), 7.24−7.12 (2H, Ar−H), 7.07−7.00 (2H, Ar−H), 4.07−3.80 (4H, $-O-CH_2-$), 3.60−1.72 (10H, B−H), 1.40−1.36 (4H, $-OCHH_2-CH_2-$), 1.28−1.15 (4H, $-OCHH_2CH_2-CH_2-$), 1.11−0.85 (16H, $-(CH_2)-$), 0.83−0.77 (6H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 156.4, 134.5, 132.7, 132.4, 131.5, 130.7, 130.2, 129.3, 129.2, 126.7, 126.2, 120.6, 118.0, 116.5, 93.5, 88.4, 86.0, 70.1, 32.6, 30.1, 30.0, 29.9, 26.5, 23.5, 14.8. ^{11}B NMR (CD_2Cl_2): δ (ppm) −3.1, −10.2. IR (KBr pellet, cm^{-1}) 2603 (ν_{B-H}), 2206 ($\nu_{C\equiv C}$). **P2**(**R**). Pale yellow powder (75.7 mg, 89%). $[\alpha]^{25}_{D}$: −224.6° (c = 0.09, THF). ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.06−7.92 (2H, Ar−H), 7.90−7.74 (2H, Ar−H), 7.50−7.25 (10H, Ar−H), 7.23−7.10 (2H, Ar−H), 7.05−6.89 (2H, Ar−H), 4.01−3.74 (4H, $-O-CH_2-$), 3.62−1.63 (10H, B−H), 1.40−1.23 (4H, $-OCHH_2-CH_2-$), 1.21−0.79 (20H, $-(CH_2)-$), 0.79−0.59 (6H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 155.6, 134.8, 133.7, 132.4, 131.8, 130.5, 129.5, 128.5, 128.0, 125.5, 124.4, 120.2, 117.5, 115.8, 91.8, 88.0, 84.4, 69.4, 31.8, 29.3, 29.2, 29.1, 25.7, 22.8, 14.0. ^{11}B NMR (CD_2Cl_2): δ (ppm) −11.4. IR (KBr pellet, cm^{-1}) 2603 (ν_{B-H}), 2209 ($\nu_{C\equiv C}$). **P3**(**R**). White powder (62.5 mg, 79%). $[\alpha]^{25}_{D}$: −154.4° (c = 0.08, THF). ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.13−8.03 (2H, Ar−H), 8.03−7.86 (2H, Ar−H), 7.56−7.37 (10H, Ar−H), 7.37−7.26 (2H, Ar−H), 7.25−7.00 (4H, Ar−H), 4.19−3.90 (4H, $-O-CH_2-$), 1.52−0.92 (24H, $-(CH_2)-$), 0.92−0.69 (6H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 155.5, 141.4, 140.0, 137.2, 133.7, 131.9, 131.6, 131.3, 130.6, 130.1, 129.4, 128.8, 128.0, 125.5, 121.9, 119.9, 118.0, 115.9, 90.6, 89.1, 69.5, 31.9, 29.4, 29.3, 29.3, 25.8, 22.8, 14.0. IR (KBr pellet, cm^{-1}) 2204 ($\nu_{C\equiv C}$). **P4**(**R**). White powder (60.7 mg, 77%). $[\alpha]^{25}_{D}$: −259.4° (c = 0.08, THF). ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.20−8.06 (2H, Ar−H), 8.05−7.93 (2H, Ar−H), 7.93−7.79 (2H, Ar−H), 7.78−7.60 (10H, Ar−H), 7.42−7.22 (4H, Ar−H), 7.22−7.07 (2H, Ar−H), 4.15−3.96 (4H, $-O-CH_2-$), 1.51−0.93 (24H, $-(CH_2)-$), 0.79−0.59 (6H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 155.6, 141.1, 140.7, 138.0, 133.7, 132.1, 131.7, 129.4, 129.2, 128.8, 127.2, 126.4, 125.8, 125.5, 122.8, 119.9, 118.0, 115.9, 91.0, 89.0, 69.5, 31.9, 29.5, 29.3, 29.3, 25.8, 22.8, 14.0. IR (KBr pellet, cm^{-1}) 2204 ($\nu_{C\equiv C}$).

Results and Discussion

Synthesis and Characterization. The axially chiral monomers ((**R**) and (**S**)) were synthesized as previously reported.[12] The synthetic route for target axially chiral π-conjugated polymers (**P1**(**R**)−**P4**(**R**) and **P1**(**S**)) is illustrated in Scheme 1. To evaluate the difference between carborane and benzene ring, four monomers **M1**−**M4** were prepared,

Scheme 1. Synthetic Routes of Axially Chiral Polymers P1(R)−P4(R) and P1(S)

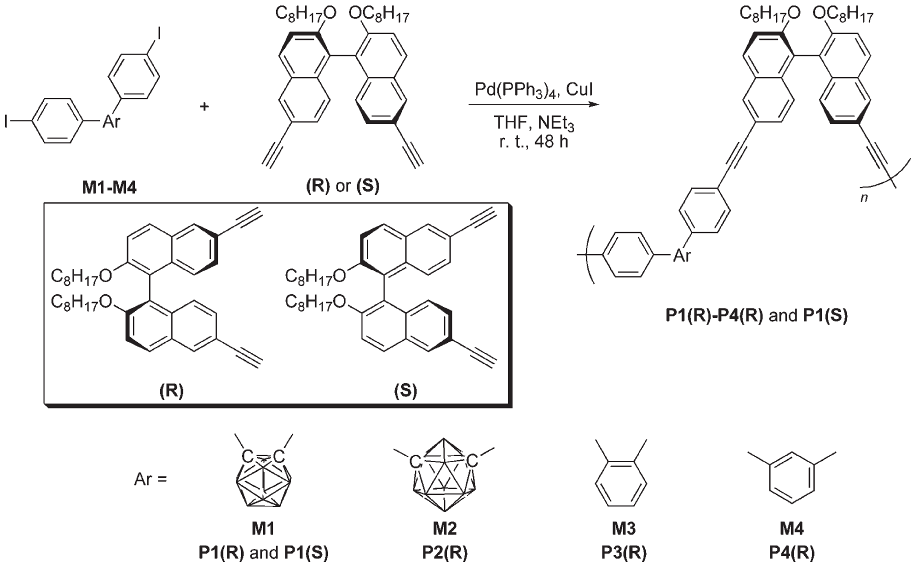

Table 1. Polymerization Results

polymer	M_n[a]	M_w[a]	M_w/M_n[a]	DP[b]	yield (%)[c]	T_{d5} (°C)[d]
P1(**R**)	3800	8400	2.2	3.8	80	404.6
P1(**S**)	3000	4200	1.4	3.5	87	412.6
P2(**R**)	29800	77500	2.6	35.0	89	365.5
P3(**R**)	2400	4100	1.7	3.1	79	350.1
P4(**R**)	8500	12000	1.4	10.8	77	349.6

[a] Estimated by SEC based on polystyrene standards in $CHCl_3$. [b] Degree of polymerization estimated by number-average molecular weight. [c] Isolated yields after reprecipitation into MeOH. [d] 5% degradation temperature given by thermogravimetric analysis (TGA) under dry air: heating rate = 10 °C/min.

i.e., bis(4-iodophenyl)-*o*-carborane (**M1**), bis(4-iodophenyl)-*m*-carborane (**M2**), 4,4′′-diiodo-*o*-terphenyl (**M3**), and 4,4′′-diiodo-*m*-terphenyl (**M4**). Sonogashira−Hagihara polycondensation reactions of monomers **M1**−**M4** were carried out with (**R**) or (**S**) in anhydrous THF and triethylamine solutions at room temperature for 48 h under an argon atmosphere to afford the polymers **P1**(**R**)−**P4**(**R**) and **P1**(**S**) in excellent yields (Table 1). The employment of meta-linked monomer **M2** and **M4** led to a polymer with higher molecular weight compared to that of *o*-carborane or *o*-terphenyl due to the less-steric hindered structure of **M1** and **M3**, meaning that the steric effect of monomers, rather than the electronic effect, is predominantly responsible for degree of polymerization. Thermogravimetric analysis (TGA) represented T_{d5} at 365.5 °C for **P2**(**R**), and **P1**(**R**) and **P1**(**S**) exhibited their T_{d5} above 400 °C, while those of **P3**(**R**) and **P4**(**R**) were at 350 °C. These results indicate that an introduction of carborane units into the π-conjugated polymer backbone steadily improved their thermal stability. The obtained polymers were soluble in common organic solvents, such as THF, $CHCl_3$, CH_2Cl_2, and so on. Their structures and purities were confirmed by ^1H, ^{13}C, and ^{11}B NMR and FT-IR spectroscopies. ^1H NMR, ^{13}C NMR, and ^{11}B NMR spectroscopies of **P1**(**R**)−**P4**(**R**) and **P1**(**S**) gave desired shift values with the proton peaks appearing as broad multiplets. In the ^1H NMR spectra, the broaden peaks at around 3.80−1.60 ppm were assigned to the presence of carborane cluster structure for **P1**(**R**), **P2**(**R**), and **P1**(**S**), and the ^{11}B NMR spectroscopy also showed the broad peaks at around −1 to −12 ppm which were attributed to the boron atoms of carborane cluster. In the IR spectrum, strong peaks at around 2200 cm^{-1} were assignable to the stretching of carbon−carbon triple bond, and those of boron−hydrogen bond on carborane appeared at around 2600 cm^{-1}. These results suggest that the effective palladium-catalyzed polymerization was performed with the carborane or terphenyl monomers **M1**−**M4** and axially chiral diyne monomers (**R**) or (**S**); i.e., polymers with anticipated structure were successfully afforded.

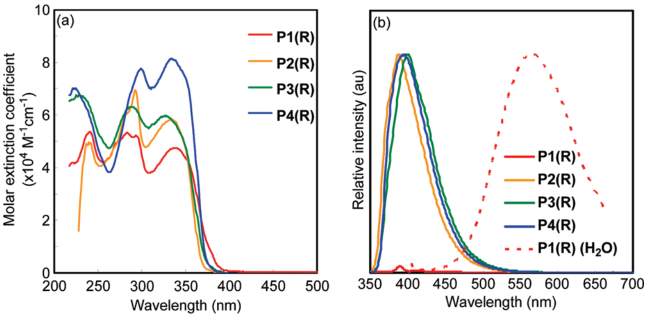

Figure 1. (a) UV−vis spectra of polymers **P1**(**R**)−**P4**(**R**) in THF (1 × 10^{-5} mol/L) and (b) photoluminescence spectra of **P1**(**R**)−**P4**(**R**) in THF (1 × 10^{-5} mol/L, solid line) and **P1**(**R**) in mixed solvent of THF/H_2O = 1/99 (v/v) (1 × 10^{-5} mol/L, dashed line).

Optical Properties. To investigate the optical properties of the obtained polymers **P1**(**R**)−**P4**(**R**), a UV−vis absorption experiment was carried out in THF (Figure 1a and Table 2). The vibrational structure in their absorption spectra corresponds to $\pi \rightarrow \pi^*$ transition of *p*-phenylene-ethynylene-type linkers due to their rigid polymer backbone in the ground state. The absorption maxima of **P1**(**R**)−**P4**(**R**) (λ_{max} = 338, 338, 326, and 334 nm, respectively) showed identical values and high molar extinction coefficient values (ε = 47 000−81 500 M^{-1} cm^{-1} per unit). The absorption maxima (239, 292, and 335 nm) and vibrational structures of **P2**(**R**) were almost identical to those of **P1**(**R**), meaning that their electronic structure and π-conjugation length were comparable.

In fluorescence spectra (Figure 1b, solid line), **P2**(**R**)−**P4**(**R**), with electron-donating axially chiral linkers, exhibited intense blue luminescence (λ_{max} = 388, 399, and 393 nm; Φ_F ∼ 0.50) in THF solution state with modest Stokes shift (53−73 nm). The employment of *m*-carborane cluster, which

Table 2. UV−Vis Absorption and Photoluminescence Properties of P1(R)−P4(R) in Solution State

polymer	λ_{max} (nm)^a	$\varepsilon\lambda_{max}$ (M^{-1} cm^{-1})^a	Ex (nm)^b	PL (nm)	Stokes shift (nm)	Φ_F^{c}
P1(R)	241, 283, 338	47 000	338			< 0.0001^a
in THF/H$_2$O = 1/99 (v/v)			338	566^d	228	0.05^d
P2(R)	239, 292, 335	58 100	335	388^a	53	0.50^a
P3(R)	229, 288, 326	59 700	326	399^a	73	0.50^a
P4(R)	221, 299, 334	81 500	334	393^a	69	0.48^a

[a] Measured in THF (1.0×10^{-5} M) at room temperature. [b] Excited wavelength. [c] Absolute fluorescence quantum yields. [d] Measured in THF/H$_2$O = (1/99) (v/v) (1.0×10^{-5} M) at room temperature.

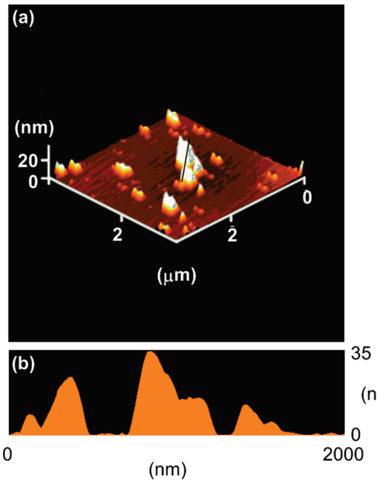

Figure 2. (a) Tapping mode AFM image of **P1(R)** aggregates and (b) the cross-section image of (a), cast from the dispersion in THF/H$_2$O = 1/99 (v/v).

includes no C−C bond, leads to a polymer (**P2(R)**) with as high luminescence as polymers containing terphenyls (**P3(R)** and **P4(R)**), analogously to the published work.[10]

The emission spectra of **P1(R)** (Figure 1b, solid red line) showed almost no emission (Φ_F < 0.0001). Similarly, alternating polymers with *o*-carborane and *p*-phenylene-ethynylene sequences exhibited no luminescence in solution states and characteristic aggregation-induced emission (AIE) behavior because of variable C−C bond in carborane cluster.[9a,13] In other words, intramolecular charge transfer from electron-donating *p*-phenylene-ethynylene units to the antibonding orbital of C−C bond in *o*-carborane cluster resulted in nonradiative quenching process. **P1(R)** also showed the AIE phenomenon in the mixed solvent of THF/H$_2$O = 1/99 (v/v), and the emission of **P1(R)** (λ_{max} = 566 nm Φ_F = 0.05 and 0.05, respectively) was associated with large Stokes shifts (228−229 nm). The size of the **P1(R)** aggregates was determined as 37.0 ± 7.3 nm measured by dynamic light scattering (DLS), in the mixed solvent, and the observation by tapping-mode atomic force microscopy also revealed the existence of **P1(R)** polymer particles with 30−40 nm diameter (Figure 2).

UV−vis absorption and photoluminescence spectra in film state of **P1(R)**−**P4(R)** were measured to estimate steric effect of carborane on optical properties (Figure 3 and Table 3). Introduction of carborane moieties to the main chain of axially chiral π-conjugated polymers (**P1(R)** and **P2(R)**) resulted in less red shift of the spectra (1−3 nm) upon the film fabrication. On the contrary, polymers consisted of terphenyls (**P3(R)** and **P4(R)**) showed larger bathochromic shift (14−29 nm) probably due to unexpected excimer formation and consequent energy dissipation. **P3(R)** and **P4(R)** also showed bathochromically shifted spectra in emission (20−30 nm), whereas those of **P2(R)** exhibited shoulder peak at the wavelength of emission maximum in solution state. These results clearly indicate that the carborane unit effectively prevents the approximation and stacking of π-conjugated main chains thanks to the icosahedral framework.

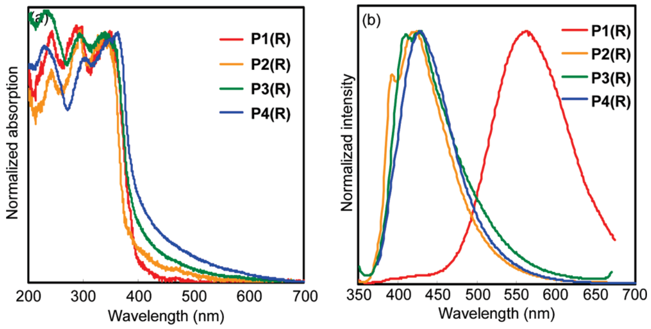

Figure 3. (a) UV−vis spectrum of polymer **P1(R)**−**P4(R)** and (b) photoluminescence spectrum of **P1(R)**−**P4(R)** in film state.

Table 3. UV−Vis Absorption and Photoluminescence Properties of P1(R)−P4(R) in Film State

polymer	λ_{max} (nm)^a	shift value (nm)^b	Ex (nm)^c	PL (nm)	Stokes shift (nm)	Φ_F^{c}
P1(R)	243, 287, 339	1	339	562	223	0.23
P2(R)	242, 294, 338	3	338	393, 424	55	0.09
P3(R)	231, 296, 340	14	340	410, 430	70	0.05
P4(R)	229, 302, 363	29	363	428	65	0.06

[a] Measured in THF (1.0×10^{-5} M) at room temperature. [b] Bathochromic shift value compared to solution state in THF. [c] Absolute fluorescence quantum yields. [d] Measured in THF/H$_2$O = (1/99) (v/v) (1.0×10^{-5} M) at room temperature.

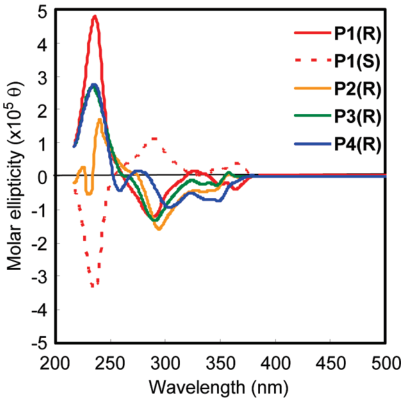

Figure 4. CD spectra of polymers **P1(R)**−**P4(R)** and **P1(S)** in THF (1×10^{-5} mol/L).

To characterize the chiroptical properties of the obtained polymers, we evaluated the circular dichroism (CD) spectra and specific rotations ($[\alpha]^{25}_D$) of the polymers. Figure 4 illustrates the CD spectra of **P1(R)** ($[\alpha]^{25}_D$ = −184.7°),

Table 4. Specific Rotation and CD Spectral Data of P1(R)−P4(R) and P1(S)

	$[\alpha]^{25}_{D}$ (deg)	λ_{max} (nm)	$[\theta]_{max}$
P1(R)	−184.7	236	4.81×10^5
		289	-1.22×10^5
		349	-2.57×10^4
		364	-3.94×10^4
P1(S)	117.7	236	-3.43×10^5
		289	1.14×10^5
		349	2.80×10^4
		364	4.04×10^4
P2(R)	−224.6	231	-5.45×10^4
		240	1.70×10^5
		294	-1.58×10^5
		335	-4.69×10^4
P3(R)	−154.4	234	2.68×10^5
		290	-1.31×10^5
		346	-2.61×10^4
P4(R)	−259.4	235	2.77×10^5
		259	-4.34×10^4
		275	1.55×10^4
		304	-9.25×10^4
		349	-7.31×10^4

P1(S) ($[\alpha]^{25}_{D}$ = 117.7°), **P2(R)** ($[\alpha]^{25}_{D}$ = −224.6°), **P3(R)** ($[\alpha]^{25}_{D}$ = −154.4), and **P4(R)** ($[\alpha]^{25}_{D}$ = −259.4). **P1(R)** and **P1(S)** have two strong mirror Cotton effects at 236 and 289 nm (Table 3). These two peaks are caused by the axially chiral binaphthyl units. These data indicate that **P1(R)** and **P1(S)** have opposite regulated highly ordered structure such as right- and left-handed helical conformation. **P2(R)−P4(R)** also exhibited an adequate negative Cotton effect at around 300 nm and the longest maximum of molar ellipticity at 340−350 nm. This finding suggests that the highly ordered structure of binaphthol unit induces chirality on the aromatic rings of diphenylcarboranes or terphenyls.

Conclusion

In summary, we have demonstrated the synthesis of *o*- and *m*-carborane-based chiral π-conjugated polymers by Sonogashira−Hagihara polycondensation reaction of bis(4-iodophenyl)-carborane compounds with axially chiral diyne monomers having binaphthyl unit. The emission behavior of the polymers containing *o*-carborane was in contrast with that of the polymer containing *m*-carborane; in solution state, only polymer having *m*-carborane was luminescent, whereas polymers having *o*-carborane exhibited aggregation-induced emission (AIE). The studies of specific rotation and CD spectra suggest that the polycondensation of bis(4-iodophenyl)carborane compounds with axially chiral diynes efficiently proceeded via introduction of chirality in the polymer backbone. Further detailed investigation on the chiroptical properties and regioregular control of these polymers is on going.

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