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Luminescent *m*-Carborane-Based π-Conjugated Polymer

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ABSTRACT: A series of *m*-carborane-based π-conjugated polymers were successfully synthesized via Sonogashira−Hagihara polycondensation reaction. Diiodo-*m*-carborane monomer underwent efficient polycondensation reaction with both electron-donating and electron-accepting diyne comonomers. The wide-angle structure of *m*-carborane monomer allowed the preparation of polymers with high molecular weights (M_n = 26 600−36 400 g mol^{-1}) and good polymerization degrees (DP = 31−56). UV−vis absorption study in dilute $CHCl_3$ solution revealed π-conjugation extension of a *p*-phenylene−ethynylene segment by introducing *m*-carborane moieties into the polymer backbone. Further, the lack of C−C bond in the carborane cluster leads to polymers exhibiting intense blue emission in solution state (Φ_F = 0.11−0.26).

Introduction

Carboranes, which are icosahedral cluster compounds consisting of 10 boron atoms and 2 carbon atoms, reflect their features in the fields of medicinal chemistry and material science because of their rich boron content and high thermal or chemical stability, derived from three-center two-electron bonds and consequent three-dimensional delocalization of skeleton electrons.[1] Additionally, the especial reactivity and electron-withdrawing nature of carboranes are widely recognized as three-dimensional aromaticity.[2] Although immense positive results have been achieved from developing coordination complex, heat-resistant materials, and application for boron neutron capture therapy (BNCT),[3] very few researches have focused on synthesis of carborane-containing organic molecules exhibiting particular optical properties and electronic structures originated from the three-dimensional aromaticity. For an example, Tour et al. have presented *p*-carboranes connected with *p*-phenylene−ethynylene as carborane-wheeled nanocars and illustrated the occurrence of bathochromic absorption shift, that is, extension of π-conjugated length with the incorporation of *p*-carborane.[4] Recently, we have also investigated the alternating polymers with *o*-carborane (1,2-dicarbadodecaborane) and *p*-phenylene−ethynylene sequences, and the molecular design successfully led to unique properties such as aggregation-induced emission (AIE) in water dispersion; i.e., nonemissive polymers in the solution state are induced to emit intensely by aggregate or film formation.[5] Therein, variable C−C bond in *o*-carborane cluster effeciently quenches the photoluminescence from *p*-phenylene−ethynylene segments in solution state.[6] On the other hand, *m*-carborane, which is a structural isomer of *o*-carborane and possesses two carbon atoms on the 1,7-position, includes no variable C−C bond dissipating the excited states in the solution state. Furthermore, the substitution on 1,7-position of *m*-carborane would construct a sterically open cluster unit to achieve effective polymerization. Therefore, we selected *m*-carborane as a candidate of a carborane segment in π-conjugated systems; i.e., if *m*-carborane derivative is employed as the monomer of Sonogashira−Hagihara polycondensation, we should be able to obtain *m*-carborane-based π-conjugated polymers with luminescence in solution state and high polymerization degrees. Herein, this article deals with the synthesis and optical properties of luminescent polymers with alternating *m*-carborane and *p*-phenylene−ethynylene sequences.

Experimental Section

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 purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 1,7-Bis(4-bromophenyl)-*m*-carborane (**1**),[7] 1,4-diethynyl-2,5-bisoctyloxybenzene (**2a**),[8] 1,4-diethynyl-2,5-bishexadecyloxybenzene (**2b**),[9] 3,6-diethynyl-9,9-dihexylfluorene (**2c**),[10] and 1,4-diethynyl-2,5-bistrifluoromethylbenzene (**2d**)[11] were synthesized and characterized according to the literature.

Measurements. ^{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. The system was operated at a flow rate of 1.0 mL/min with $CHCl_3$ as an eluent after calibration with the standard polystyrene samples. Thermogravimetric analysis (TGA) was performed using a TG/DTA 6200, SEIKO Instruments, Inc., with heating rate of 10 °C/min under dry air. FT-IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. UV−vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer.

1,7-Bis(4-iodophenyl)-*m*-carborane (1). To a solution of 1,7-bis(4-bromophenyl)-*m*-carborane (1.28 g, 2.81 mmol) in diethyl ether (21 mL) was added dropwise *n*-butyllithium (1.60 M, 4.0 mL, 6.40 mmol) at −78 °C. The mixture was stirred at room temperature for 1.5 h, and then diethyl ether solution (16 mL) of 1,2-diiodoethane (1.67 g, 5.92 mmol) was added dropwise at room temperature. After stirring for 15 min at room temperature, the reaction mixture was washed with distilled water (50 mL × 2) and brine (50 mL × 2), and the combined organic phase was dried over $MgSO_4$, filtered, and evaporated to dryness in vacuo. The residual solid was purified by silica gel column chromatography using hexane as an eluent and recrystallized from chloroform/ethanol to obtain **1** as a white solid (0.65 g, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, 4H, *J* = 8.8 Hz, Ar−*H*), 7.18 (d, 4H, *J* = 8.8 Hz, Ar−*H*), 4.10−1.54 (m, 10H, B−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.6, 134.8, 129.6, 95.1, 77.2. ^{11}B

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Scheme 1. Synthetic Routes for (a) Monomer 1 and (b) Polymers P3a−d

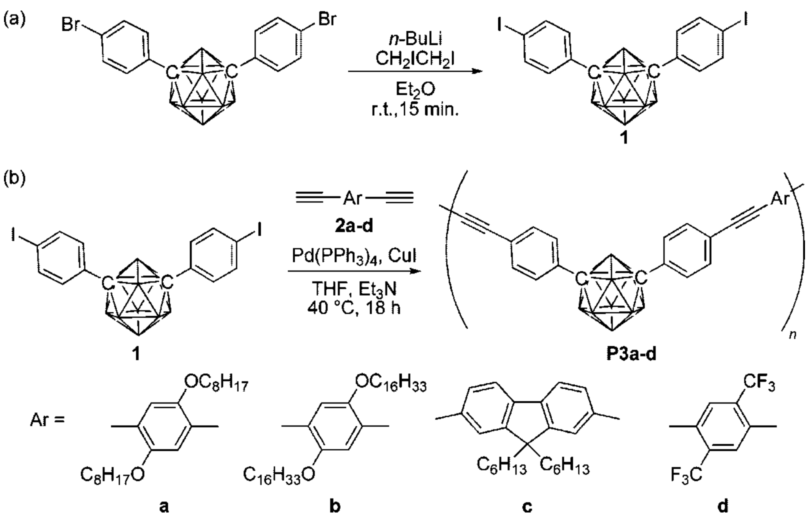


Table 1. Polymerization Results

polymer	M_n[a]	M_w[a]	M_w/M_n[a]	DP[b]	yield (%)[c]	T_{d5} (°C)[d]
P3a	26 600	42 700	1.6	39	85	326
P3b	27 600	49 600	1.8	31	91	323
P3c	36 400	51 700	1.4	54	90	387
P3d	31 200	51 100	1.6	56	93	370

[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 K/min under air.

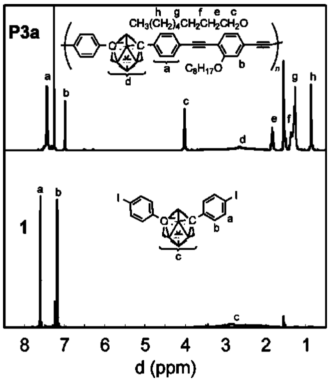


Figure 1. ^1H NMR spectra of **1** and **P3a** in $CDCl_3$.

NMR (128 MHz, $CDCl_3$): δ (ppm) −5.5, −6.5, −10.0, −11.1, −12.8, 14.2. Anal. Calcd for $C_{14}H_{18}B_{10}I_2$: C, 30.67; H, 3.31; I, 46.30. Found: C, 30.67; H, 3.30; I, 46.49. HRMS (EI) Calcd for $C_{14}H_{18}B_{10}I_2$: *m/z* 550.0428. Found: *m/z* 550.0427.

Polymerization Procedure. A typical procedure is as follows: Bis(4-iodophenyl)-*m*-carborane (**1**) (84.3 mg, 0.22 mmol), 1,4-diethynyl-2,5-bisoctyloxybenzene (**2a**) (120.7 mg, 0.22 mmol), $Pd(PPh_3)_4$ (13.4 mg, 11 μmol), and CuI (2.70 mg, 11 μmol) were placed in a 30 mL round-bottom flask equipped with a magnetic stirrer. The equipment was purged with Ar, followed by adding THF (4.4 mL) and triethylamine (2.2 mL). The reaction was carried out for 18 h at 40 °C. After cooling, the reaction mixture was diluted with $CHCl_3$ (10 mL) and washed with aqueous NH_3 solution (10%, 25 mL), distilled water, and brine. The organic layer was dried over $MgSO_4$. And then, the polymer solution was concentrated and precipitated into a large amount of methanol. The polymer was dried in vacuo to afford **P3a** as a yellow powder (126.1 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (8H, Ar−*H*), 6.99 (2H, Ar−*H*), 4.02 (4H, −O−CH_2−), 3.98−1.85 (10H, B−*H*), 1.83 (4H, −OCH_2−CH_2−), 1.37−1.25 (16H, −(CH_2)−), 0.85 (6H, −CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.7, 134.9, 131.4, 127.8, 124.2, 116.8, 113.9, 93.8, 87.6, 77.8, 69.6, 31.8, 29.4, 29.3, 26.1, 22.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −10.1. IR (KBr pellet, cm^{-1}): 2602 (ν_{B-H}), 2203 ($\nu_{C\equiv C}$). **P3b**. Yellow powder (180.6 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 (8H, Ar−*H*), 6.99 (2H, Ar−*H*), 4.00 (4H, −O−CH_2−), 3.98−1.83 (10H, B−*H*), 1.81 (4H, −OCH_2−CH_2−), 1.52 (4H, −OC_2H_4−CH_2−), 1.25 (48H, −(CH_2)−), 0.86 (6H, −CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.7, 1349, 131.4, 127.8, 124.2, 116.9, 113.9, 93.8, 87.6, 77.9, 69.6, 3.19, 29.7 (three peaks) 29.4 (two peaks), 29.3, 26.1, 22.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −10.1. IR (KBr pellet, cm^{-1}): 2604 (ν_{B-H}), 2202 ($\nu_{C\equiv C}$). **P3c**. Yellow powder (133.3 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (2H, Ar−*H*), 7.50 (12H, Ar−*H*), 3.82−1.56 (10H, B−*H*), 1.98 (4H, −CH_2−C_5H_{11}), 1.12−1.04 (12H, −(CH_2)−), 0.77 (6H, −CH_3), 0.60 (4H, −CH_2C$H_2$$C_4H_9$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.2, 140.9, 134.9, 131.5, 130.9, 127.9, 126.0, 124.2, 121.6, 120.1, 92.1, 88.6, 77.9, 55.3, 40.4, 31.5, 29.7, 23.7, 22.6, 14.0. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −10.0. IR (KBr pellet, cm^{-1}): 2603 (ν_{B-H}), 2203 ($\nu_{C\equiv C}$). **P3d**. Yellow powder (113.5 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (2H, Ar−*H*), 7.48 (8H, Ar−*H*), 3.78−1.80 (10H, B−*H*). ^{13}C NMR (100 MHz, $CDCl_3$), 136.2, 134.3, 131.8, 131.8, 128.1, 123.8, 122.7, 121.1, 97.2, 85.7, 77.6, ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −10.7. IR (KBr pellet, cm^{-1}): 2605 (ν_{B-H}), 2221 ($\nu_{C\equiv C}$).

Model Compound (4). To a solution of **1** (138.1 mg, 0.25 mmol), $Pd(PPh_3)_4$ (15.6 mg, 13 μmol), and CuI (2.40 mg, 13 μmol) in THF (2.5 mL) were added triethylamine (1.3 mL) and ethynyl-

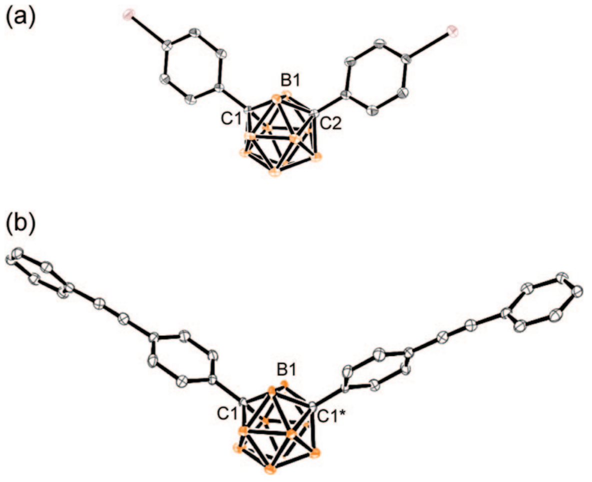


Figure 2. X-ray crystal structures of (a) **1** and (b) **4** with thermal ellipsoids drawn to the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 2. Crystallographic Data of 1 and 4

	1	4
empirical formula	$C_{14}H_{18}B_{10}I_2$	$C_{30}H_{28}B_{10}$
formula weight	548.18	496.62
crystal system, space group	monoclinic, $P2_1/n$	orthorhombic, P_{bcn}
unit cell dimensions	$a = 7.725(2)$ Å, $\alpha = 90°$	$a = 11.167(7)$ Å, $\alpha = 90°$
	$b = 15.320(4)$ Å, $\beta = 97.306(16)°$	$b = 7.445(4)$ Å, $\beta = 90°$
	$c = 16.871(6)$ Å, $\gamma = 90°$	$c = 32.828(17)$ Å, $\gamma = 90°$
volume (Å^3)	1980.5(11)	2729(3)
Z, calculated density (mg m^{-3})	4, 1.839	4, 1.209
absorption coefficient (mm^{-1})	3.171	0.063
$F(000)$	4128	1032
θ range for data collection (deg)	3.06−27.48	3.08−27.48
reflections collected (unique)	18184/4499 [R(int) = 0.0509]	22685/3132 [R(int) = 0.1845]
completeness to theta = 27.48	0.994	0.999
max and min transmission	0.7422 and 0.3636	0.9937 and 0.9814
goodness-of-fit on F^2	1.117	1.023
final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0322$, $wR_2 = 0.0861$	$R_1 = 0.0897$, $wR_2 = 0.2066$
R indices (all data)	$R_1 = 0.0367$, $wR_2 = 0.0881$	$R_1 = 0.1706$, $wR_2 = 0.2400$

[a] $R_1 = \Sigma(\Delta F/\Sigma(F_0))$; $wR_2 = (\Sigma[w(F_o^2 - F_c^2)])/\Sigma[w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]]$, where $p = [F_o^2,0]/3$.

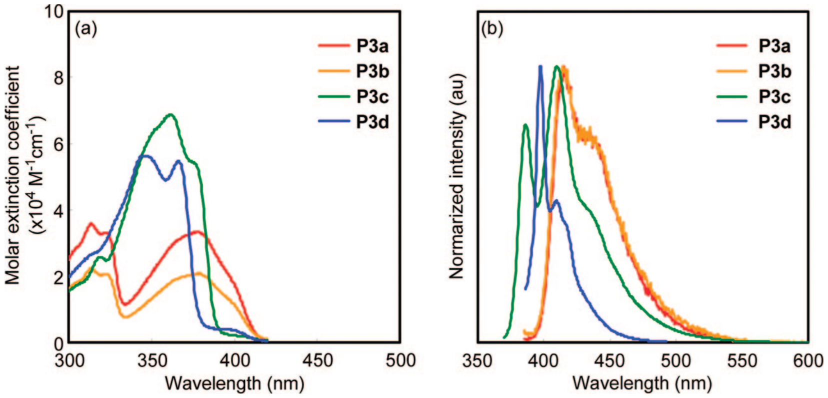


Figure 3. (a) UV−vis and (b) photoluminescence spectra of polymers **P3a−d** in $CHCl_3$ (1.0×10^{-5} M for UV−vis and 1.0×10^{-7} M for PL).

Table 3. UV−vis Absorption and Photoluminescence Properties

compound	$\lambda_{\max}$ (nm)[a]	$\varepsilon\lambda_{\max}$ (M^{-1} cm^{-1})[a]	Ex (nm)[b,c]	PL (nm)[c]	Stokes shift (nm)[c]	Φ_F[d]
P3a	314, 378	36 000	378	415	37	0.25
P3b	314, 378	22 000	378	415	37	0.25
P3c	319, 362	69 000	362	386, 410	24, 38	0.11
P3d	345, 366	56 400	366	409	43	0.22
6	313, 375	33 000	375	414	39	0.23
7	307, 365	41 000	365	403	38	0.49

[a] Measured in $CHCl_3$ (1.0×10^{-5} M) at room temperature. [b] Excited wavelength. [c] Measured in $CHCl_3$ (1.0×10^{-7} M). [d] Fluorescence quantum yields (relative to 9,10-diphenylanthracene in cyclohexane at room temperature).

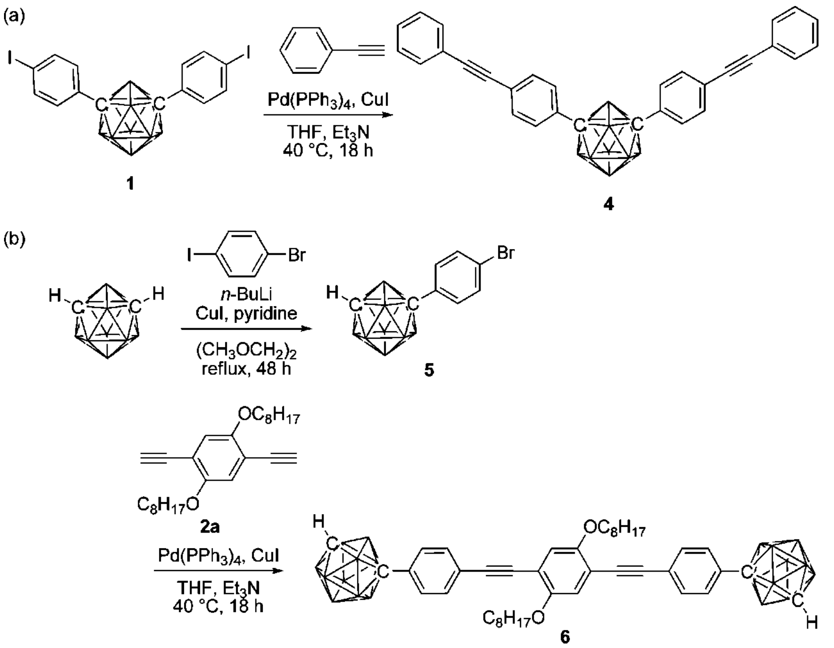
benzene (60 μL, 0.55 mmol). After the mixture was stirred for 24 h at room temperature, $CHCl_3$ (10 mL) was added and washed with aqueous NH_3 solution (10%, 25 mL), distilled water (20 mL × 2), and brine (20 mL × 2). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was chromatographed on silica gel (eluent: hexane/$CHCl_3$ = 90/10) to afford **4** as a colorless crystal (89.7 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (m, 4H, Ar−*H*), 7.45 (m, 8H, Ar−*H*), 7.34 (m, 6H, Ar−*H*), 4.00−1.60 (m, 10H, B−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 134.9, 131.7, 131.5, 128.6, 128.4, 127.9, 124.1, 122.9, 91.0. 88.2, 77.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −6.5, −10.1, −11.0. HRMS (EI) Calcd for $C_{30}H_{28}B_{10}$: *m*/*z* 498.3122. Found: *m*/*z* 498.3132.

1-(4-Bromophenyl)-*m*-carborane (5). *m*-Carborane (1.02 g, 7.09 mmol) was dissolved in 1,2-dimethoxyethane (24 mL), and *n*-butyllithium (1.60 M, 4.5 mL) was added dropwise at 0 °C. The mixture was stirred for 30 min at room temperature, and CuI (1.69 g, 8.88 mmol) was added in one portion. After stirring at room temperature for 30 min, pyridine (4.0 mL) was added and stirred for 30 min. Then, 4-bromoiodobenzene (2.11 g, 7.46 mmol) was added, and the mixture was refluxed for 48 h. After cooling to room temperature, diethyl ether (120 mL) was added and stirred for another 30 min. The mixture was filtered, and the filtrate was washed with aqueous hydrochloride solution (2.0 M, 40 mL) and distilled water (200 mL × 2). The ethereal solution was dried over $MgSO_4$, filtered, and evaporated. The residual solid was purified by silica gel chromatography (eluent: hexane/$CHCl_3$ = 4/1) to obtain **5** as a white powder (0.288 g, 14%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, 2H, J = 8.8 Hz, Ar−*H*), 7.28 (d, 2H, J = 8.8 Hz, Ar−*H*), 3.80−1.55 (m, 10H, B−*H*), 3.07 (s, 1H, carborane C−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 134.2, 131.5, 129.5, 123.2, 77.2, 55.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −3.6, −4.9, −6.3, −7.6, −10.0, −11.2, −12.9, −14.2, −16.4, −17.9. HRMS (EI) Calcd for $C_8H_{15}B_{10}Br$: *m*/*z* 300.1288. Found: *m*/*z* 300.1290.

Model Compound (6). **5** (95.8 mg, 0.20 mmol), **2a** (107.9 mg, 0.36 mmol), $Pd(PPh_3)_4$ (14.0 mg, 12 μmol), and CuI (2.80 mg, 14 μmol) were dissolved in THF (1.8 mL) and triethylamine (0.9 mL) and stirred for 18 h at 40 °C. After cooling, the reaction mixture was diluted with $CHCl_3$ (10 mL) and washed with aqueous NH_3 solution (10%, 25 mL), distilled water (20 mL × 2), and brine (20 mL × 2). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residual solid was purified by silica gel chromatography (eluent: hexane/$CHCl_3$ = 4/1) to afford **6** as a yellow powder (41.2 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 (m, 8H, Ar−*H*), 6.98 (s, 2H, Ar−*H*), 4.01 (t, 4H, J = 6.3 Hz, $-OCH_2-$), 3.98−1.53 (m, 20H, B−*H*), 3.08 (s, 2H, carborane C−*H*), 1.82 (m, 4H, $-OCH_2-CH_2-$), 1.51 (m, 4H, $-OC_2H_4-CH_2-$), 1.27 (m, 16H, $-(CH_2)-$), 0.85 (t, 6H, J = 6.6 Hz, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.7, 135.0, 131.4, 127.8, 124.1, 116.9, 113.9, 93.8, 87.5, 77.9, 69.6, 55.1, 31.8, 29.4, 29.3, 26.1, 22.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −3.6, −4.8, −10.0, −11.2, −12.9, −14.2, −16.0. HRMS (EI) Calcd for $C_{42}H_{66}B_{20}O_2$: *m*/*z* 822.6924. Found: *m*/*z* 822.6913.

X-ray Crystallography Analyses. Single crystals of **1** and **4** were obtained from $CHCl_3$/methanol solution and were mounted

Scheme 2. Synthetic Route for (a) Model Compound 4 and (b) Model Compound 6



in the loop. The data were collected on a Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation operating at 50 kV and 30 mA at −180 °C with an imaging plate. A symmetry-related absorption correction was carried out by using the program ABSCOR.[12] The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. The analysis was carried out with direct methods, SHELX-97[13] and SIR97[14] using Yadokari-XG.[15] The program ORTEP3[16] was used to generate the X-ray structural diagrams.

Results and Discussion

Synthesis and Characterization. Scheme 1a illustrates the synthesis of *m*-carborane-based diiodo monomer. Two bromide groups of bis(4-bromophenyl)-*m*-carborane were smoothly lithiated by *n*-butyllithium, followed by quenching the in situ prepared bis(4-lithiophenyl)-*m*-carborane with 1,2-diiodoethane at room temperature, producing **1** in 42% yield.

Synthesis of polymers **P3a−d** is outlined in Scheme 1b. Polycondensation reactions of *m*-carborane monomer **1** were carried out with diyne compounds **2a−d** in anhydrous THF and triethylamine solutions at 40 °C for 18 h under an argon atmosphere to afford the corresponding polymers **P3a−d** in excellent yields (Table 1). In contrast to the polymers synthesized from bis(4-iodophenyl)-*o*-carborane in a similar polymerizing system,[5] size exclusion chromatography (SEC) analysis of **P3a−d** showed higher molecular weight polymers (M_n = 26 600−36 400 g mol^{-1}), presumably because of the less bent nature of *m*-carborane monomer (**1**). Thermogravimetric analysis (TGA) represented T_{d5} at 323−387 °C for **P3a−d**, meaning their thermal stability even under air. The obtained polymers were soluble in various organic solvents (e.g., THF, chloroform, and so on), enabling us to characterize the polymers by NMR spectroscopies and also to investigate the optical properties in solution. ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectroscopies of **P3a−d** gave expected shift values with the proton peaks appearing as broad multiplets (Figure 1 and Experimental Section). In the ^{1}H NMR spectra, the broaden peaks at around 3.80−1.80 ppm were assigned to the presence of *m*-carborane structure, and the ^{11}B NMR spectroscopy also showed the broad peaks at around −2 to −12 ppm which were assignable to the boron atoms of *m*-carborane cluster. In the IR spectrum, strong peaks at around 2200 cm^{-1} were attributed to the stretching of carbon−carbon triple bond, and those of boron−hydrogen bond on *m*-carborane appeared at around 2600 cm^{-1}. These results suggest that the effective palladium-catalyzed polymerization was performed with the *m*-carborane monomer **1** and diyne monomers **2a−d**; i.e., polymers with anticipated structure were successfully obtained.

Model Compound 4. To elucidate the polymer structures by supporting ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectroscopies, model compound **4** was prepared from the reaction of **1** and 2 equiv of phenylacetylene via Sonogashira−Hagihara coupling reaction (Scheme 2a). Similarly to ^{1}H and ^{11}B NMR spectra of **P3a−d**, model compound **4** exhibited respective broad signals at around 4.00−1.60 ppm in the ^{1}H NMR spectrum and −3 to −12 ppm in the ^{11}B NMR spectrum. Figure 2 shows the crystallographically determined molecular structures of **1** and **4** (see also Table 2). The existence of icosahedral cluster in **4** was confirmed without any damage on the three-center two-electron bonds in *m*-carborane. The bond lengths and bond angles of **1** and **4** were almost identical, for instance, bond lengths of C1−B1 are 1.710 and 1.705 Å, respectively, and bond angles of C1−B1−C2 (**1**) and C1−B1−C1* (**4**) are 103.3° and 102.2°, respectively. On the contrary, the bond length and bond angles of *o*-carborane derivatives varied according to the substituents on the 4-position of phenyl groups attached to the cluster.[5] These data indicate the high rigidity of cluster in *m*-carborane moiety and the sterically open structure of the two substituents.

Optical Properties. The UV−vis absorption and photoluminescence spectra of **P3a−d** in $CHCl_3$ are shown in Figure 3. The vibrational structure in the absorption spectra of **P3a−d** corresponding to $\pi-\pi^*$ transition of *p*-phenylene−ethynylene linkers indicates the rigid conformation of them in the ground states.[17] The absorption maxima of **P3a** and **P3b** (λ_{max} = 314 and 378 nm) exhibited identical values and were red-shifted compared to those of **P3d** (λ_{max} = 345 and 366 nm) because of higher donating ability of the alkoxybenzene unit in the *p*-phenylene−ethynylene linkers. The absorption maxima of **P3a−d** were bathochromically shifted in comparison with the reported diphenyl adduct of diethynyl compounds (**2a−d**),[17] meaning that *m*-carborane unit partially acts as an aromatic character to extend the conjugated length along the polymer

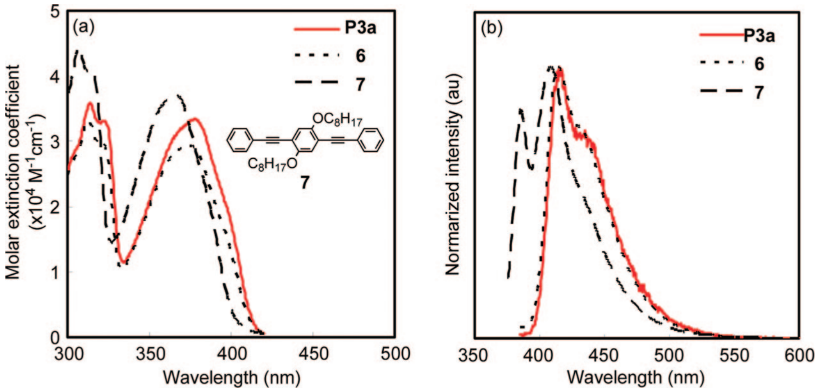


Figure 4. (a) UV−vis and (b) photoluminescence spectra of polymer **P3a**, model compounds **6** and **7** in $CHCl_3$ (1.0×10^{-5} M for UV−vis and 1.0×10^{-7} M for PL). The inset shows the molecular structure of model compound **7**.

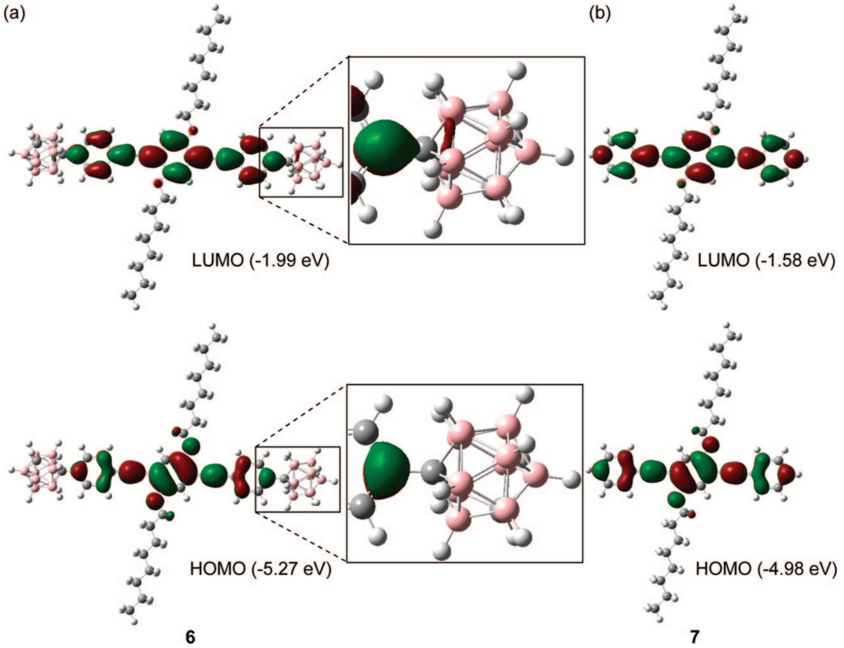


Figure 5. Structures and molecular orbital diagrams for LUMO and HOMO of **6** and **7** (B3LYP/6-31G(d)//B3LYP/6-31G(d)).

main chains. For example, the maximum of **P3a** was shifted to the bathochromic side relative to 1,4-bis(octyloxy)-2,5-bis(phenylethynyl)benzene (λ_{max} = 366 nm). Although no chromophores containing *m*-carborane were reported, π-conjugated molecules including *o*-carborane or *p*-carborane showed similar bathochromic shifts and extension of conjugation length through the carborane moieties.[4a,5] Further, the spectra of **P3a−d** exhibited a shape similar to those of the reported compounds, indicating that an introduction of *m*-carborane into the π-conjugated polymer sequences caused no distortion in the main chain from steric hindrance between the *p*-phenylene−ethynylene linkers. **P3a−d** showed intense blue emission in the solution state (Figure 3b), and their relative quantum yields ranged from 0.11 to 0.25 (Φ_F, 9,10-diphenylanthracene in cyclohexane as a standard; Table 3) as compared to *o*-carborane derivatives ($\Phi_F < 0.0001$) exhibiting no luminescence in solution states.[5] The lack of variable C−C bond in *m*-carborane cluster successfully leads to the construction of luminescent polymers. The emission maxima of **P3a−d** gave 24−43 nm Stokes shift values consistent with the reported poly(*p*-phenylene−ethynylene)s, (PPE)s.

To investigate the optical properties of the obtained *m*-carborane-based π-conjugated polymers, model compounds **6** and **7** were prepared via similar reaction to polymerization method (Scheme 2b and Figure 4a inset). UV−vis absorption and photoluminescence experiments of **P3a**, **6**, and **7** were carried out in $CHCl_3$ (Figure 4). The absorption and emission maxima of **P3a** were red-shifted to 378 and 415 nm, respectively, as compared to those of **7** at 365 and 403 nm, respectively. Introduction of the *m*-carborane moiety into the main chain of π-conjugated polymer extended the conjugation length along the polymer main chain due to the aromatic character of *m*-carborane. However, in comparison with model compound **6** (1,4-bis(octyloxy)-2,5-bis(4-*m*-carboranylphenylethynyl)benzene), **P3a** exhibited barely bathochromical shift and photoluminescence spectra. These results indicate the absence of efficient π-delocalization between two adjacent *p*-phenylene−ethynylene linkers, while *m*-carborane groups electronically interacted with each linker.

To provide a more effective understanding for the optical properties, the electronic states of **6** and **7** were examined by the theoretical calculation using the density-functional theory (DFT) at the B3LYP/6-31G(d)/B3LYP/6-31G(d) level of the theory with Gaussian 03 suit program (Figure 5).[18] The highest occupied molecular orbital (HOMO) of both molecules are mainly located on the *p*-phenylene−ethynylene moieties. In contrast, the lowest unoccupied molecular orbital (LUMO) of **6** has a small contribution from *m*-carborane moieties, whereas that of **7** is localized on the same position as its HOMO. The contribution to LUMO of **6** from *m*-carborane moieties is restricted within surrounding of carbon atoms in the cluster, assuming that the extension of π-conjugation in the obtained polymers is almost independent of the *m*-carborane cluster units. Further, the HOMO−LUMO gap of **6** (3.28 eV) was narrower than that of **7** (3.40 eV). These data support that the lowered LUMO level of **6** leads to the red shift in UV−vis absorption by the *m*-carborane group[4,19] and shows the applicability of *m*-carborane-based π-conjugated polymers for an electron transporting material.

Conclusion

In summary, we report on the successful syntheses of a series of *m*-carborane-based π-conjugated polymers. Both electron-donating and electron-accepting diyne comonomers underwent efficient polycondensation reaction with the *m*-carborane monomer, resulting in high polymerization degrees. Study on UV−vis absorption in dilute $CHCl_3$ solution showed π-conjugation extension of the *p*-phenylene−ethynylene segment by introducing *m*-carborane moieties into the polymer backbone. The suitable molecular design leads to polymers exhibiting intense blue emission in solution state, contrary to the alternating polymers with *o*-carborane and *p*-phenylene−ethynylene sequences. The luminescent properties, low molecular orbital energy, and the solution processability of the polymers could be advantageous for various device applications, in particular, n-type semiconductors and light-emitting diodes.

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Supporting Information Available: Cif files for **1** and **4** containing crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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