

NOTE

Synthesis and characterization of an alternating copolymer with 1,2-disubstituted and 9,12-disubstituted *o*-carborane units

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INTRODUCTION

o-Carborane is a representative polyhedral boron cluster consisting of 2 adjacent carbon atoms and 10 boron atoms (Figure 1a).¹ In addition to its unique properties, such as ¹⁰B-based neutron-capturing abilities and thermal as well as chemical stability, considerable attention has recently been paid to its electron-withdrawing building block.² In particular, the incorporation of *o*-carborane into π -conjugated moieties offers interesting optoelectronic properties.^{3–8} From this viewpoint, we reported the synthesis and characterization of various *o*-carborane-based conjugated compounds and polymers that exhibited aggregation-induced emission⁹ (AIE) properties.³ In solution, intramolecular charge transfer (ICT) from the π -conjugated moieties to *o*-carborane quenches the emission, whereas in the solid and aggregation states, restricted molecular motion suppresses vibrational radiation, leading to emission.

The polymers discussed in the present study are shown in Figure 1b. Polymer **P1** ($M_n = 10\,600$ and $M_w = 22\,600$) is composed of *p*-phenylene-ethynylene and C1,C2-disubstituted *o*-carborane, which exhibits AIE.³ In polymer **P2** ($M_n = 6\,300$ and $M_w = 11\,000$), *p*-phenylene-ethynylene units are substituted at the B9 and B12 positions of *o*-carborane.¹⁰ Polymer **P2** behaves as a general emitter; in other words, bright emission is observed in solution, and no emission is observed in the solid state owing to aggregation-caused quenching. Here, the question arises of what occurs if C1,C2-disubstituted and B9,B12-disubstituted *o*-carboranes coexist in a single polymer chain. To answer this question, we prepared copolymer **P3** (Figure 1b) consisting of alternating C1,C2- and B9,B12-disubstituted *o*-carborane units. The synthesis and emission behaviors are described in detail herein.

EXPERIMENTAL PROCEDURE

Synthesis of compound 3

The mixture of Pd(PPh₃)₄ (20.0 mg, 17.0 μ mol), CuI (3.0 mg, 17.0 μ mol), compound 1 (118.0 mg, 342 μ mol), and compound 2 (480.0 mg, 718 μ mol)

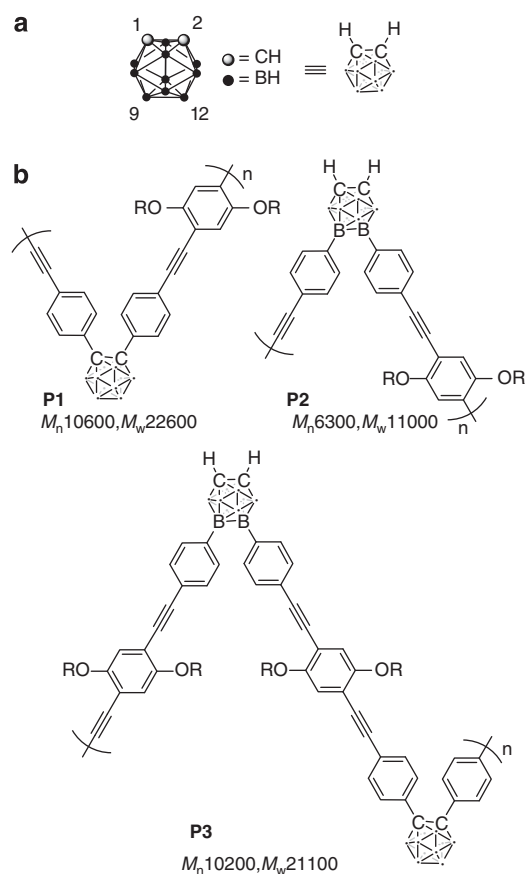


Figure 1 (a) Structure of *o*-carborane. (b) Structures of *o*-carborane-containing polymers **P1–3**.

was dissolved in tetrahydrofuran (THF) (9.0 ml) and NEt₃ (9.0 ml) at room temperature under Ar atmosphere. The reaction mixture was stirred at 50 °C under Ar atmosphere for 16 h. After cooling to room temperature, the reaction was quenched by the addition of aqueous NH₄Cl. CHCl₃ was added to the resulting mixture, and the organic layer was washed with H₂O and brine. The organic layer was dried over MgSO₄. After MgSO₄ was removed, the solvent was evaporated. The residue was purified by silica gel column chromatography with hexane/CH₂Cl₂ (v/v=2:1, R_f=0.25) as an eluent and with high performance liquid chromatography (Japan Analytical Industry LC-918R: JAIGEL-1H and 2H columns) using CHCl₃ as an eluent (flow rate: 3.80 ml min⁻¹) to obtain compound **3**, a yellow solid (273.9 mg, 192 μmol, 56%). ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J*=7.82 Hz, 4H, Ar-*H*), 7.14 (d, *J*=7.82 Hz, 4H, Ar-*H*), 6.91 (s, 4H, Ar-*H*), 3.94 (dd, *J*=9.41, 5.99 Hz, 8H, -O-CH₂-), 3.55 (s, 2H, carborane_C-*H*), 3.48-1.86 (br, 8H, B-*H*), 1.78 (s, 8H, -O-CH₂-CH₂-), 1.49-1.26 (br m, 72H, -CH₂-), 0.88 (t, *J*=6.47 Hz, 12H, -CH₃), 0.26 (s, 18H, -Si-(CH₃)₃) p.p.m. ¹³C NMR (100 MHz, CDCl₃) δ 154.0, 153.2, 132.6, 130.1, 121.7, 117.2, 116.8, 114.6, 113.36, 101.6, 99.7, 95.3, 85.7, 69.5, 69.4, 49.6, 31.9, 29.6, 29.3, 26.0, 22.7, 14.1, 0.0 p.p.m. ¹¹B NMR (128 MHz, CDCl₃) δ 5.2, -11.5, -16.5 p.p.m. high-resolution mass spectrometry (HRMS) (atmospheric pressure chemical ionization (APCI), *m/z*): [M + H]⁺ calcd for C₈₈H₁₄₁B₁₀O₄Si₂, 1426.1366; found 1426.1379.

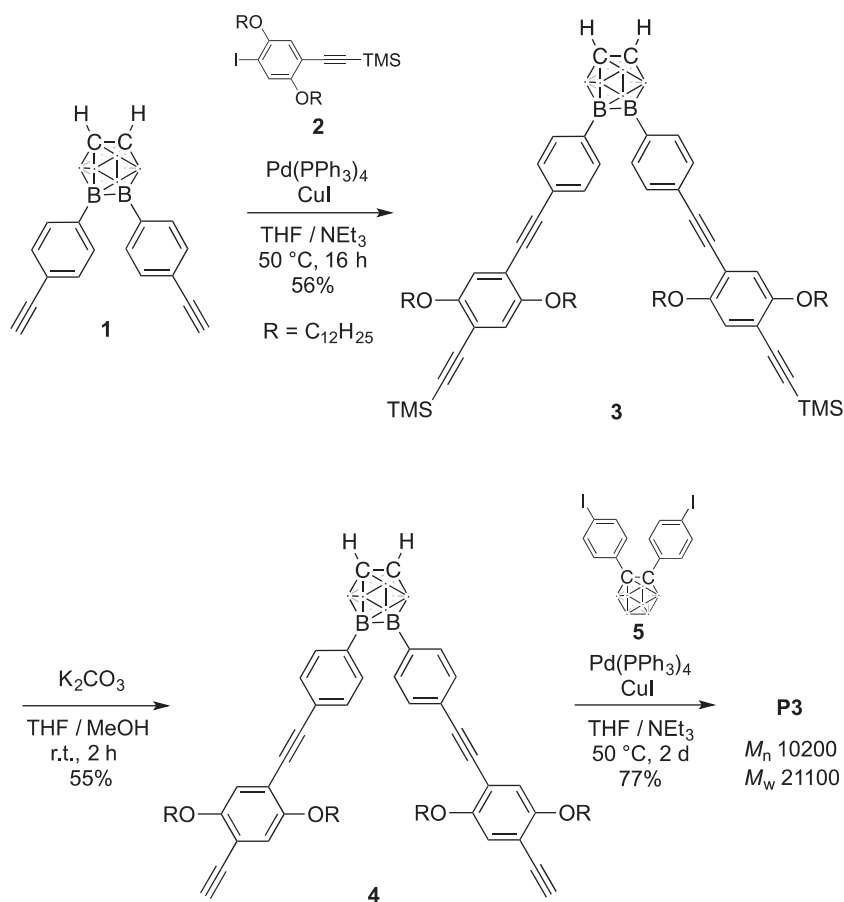
Synthesis of compound **4**

To the mixture of compound **3** (273.9 mg, 0.19 mmol) and K₂CO₃ (53.1 mg, 0.38 mmol), THF (1.9 ml) and MeOH (1.9 ml) were added at room temperature under Ar atmosphere. After stirring at room temperature for 2 h, the reaction was quenched by the addition of aqueous HCl (1.0 N) and extracted with CHCl₃ three times. The CHCl₃ solution was washed with H₂O and brine and subsequently dried over MgSO₄. After MgSO₄ was removed, the solvent was evaporated. The residue was subjected to silica gel column

chromatography with hexane/CH₂Cl₂ (v/v=3:2, R_f=0.43) as an eluent to obtain compound **4**, a yellow oil (136.2 mg, 0.11 mmol, 55%). ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, 4H, *J*=7.82 Hz, Ar-*H*), 7.15 (d, 4H, *J*=8.06 Hz, Ar-*H*), 6.94 (s, 4H, Ar-*H*), 3.96 (q, 8H, *J*=6.52 Hz, -O-CH₂-), 3.63 (s, 2H, carborane_C-*H*), 3.30 (s, 2H, -CC-*H*), 3.30-1.80 (br, 8H, B-*H*), 1.82-1.75 (m, 8H, -O-CH₂-CH₂-), 1.44-1.30 (br m, 72H, -CH₂-), 0.88 (t, 12H, *J*=6.60 Hz, -CH₃) p.p.m. ¹³C NMR (100 MHz, CDCl₃) δ 154.0, 153.2, 132.6, 130.2, 121.8, 117.6, 116.8, 115.0, 112.2, 95.4, 85.5, 82.0, 80.0, 69.6, 69.6, 49.5, 31.9, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 25.9, 22.7, 14.1 p.p.m. ¹¹B NMR (128 MHz, CDCl₃) δ 7.9, -9.5, -12.8 p.p.m. HRMS (APCI, *m/z*): [M + H]⁺ calcd for C₈₂H₁₂₅B₁₀O₄, 1283.0539; found 1283.0560.

Synthesis of copolymer **P3**

Compound **4** (38.4 mg, 30.0 μmol), compound **5** (16.4 mg, 30.0 μmol), Pd(PPh₃)₄ (0.9 mg, 4.5 μmol), and CuI (3.5 mg, 3.0 μmol) were dissolved in THF (300 μl) and NEt₃ (300 μl), and freeze-pump-thaw cycling was carried out. The mixture was stirred at 50 °C for 2 days. CHCl₃ was added to the reaction mixture. The solution was washed with 10% aqueous NH₃, H₂O and brine. The solution was dried over MgSO₄. After MgSO₄ was removed, the solvent was evaporated to afford the yellow residue, which was dissolved in CHCl₃ and reprecipitated from an excess amount of MeOH. The yellow solid was purified with high performance liquid chromatography (Japan Analytical Industry LC-918R: JAIGEL-2.5H and 3H columns) using CHCl₃ as an eluent (flow rate: 3.80 ml min⁻¹) to obtain polymer **P3**, a yellow powder (36.3 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.43 (br s, 2H, Ar-*H*), 7.28-7.20 (br m, 6H, Ar-*H*), 6.92 (br s, 2H, Ar-*H*), 3.94 (br s, 4H, -O-CH₂-), 3.79 (br s, 1H, carborane_C-*H*), 3.60-1.80 (br s, 9H, B-*H*), 1.76 (br s, 4H, -O-CH₂-CH₂-), 1.47-1.25 (br m, 36H, -CH₂-), 0.87 (br s, 6H, -CH₃) p.p.m. ¹³C NMR (100 MHz, CDCl₃) δ 154.0, 153.7, 133.1, 131.5, 130.9, 130.5, 130.3, 126.2, 122.2, 117.2, 117.0, 115.2, 113.1, 95.7, 93.2, 89.3, 86.1, 85.5, 70.0, 69.8, 50.4,



Scheme 1 Synthesis of copolymer **P3**.

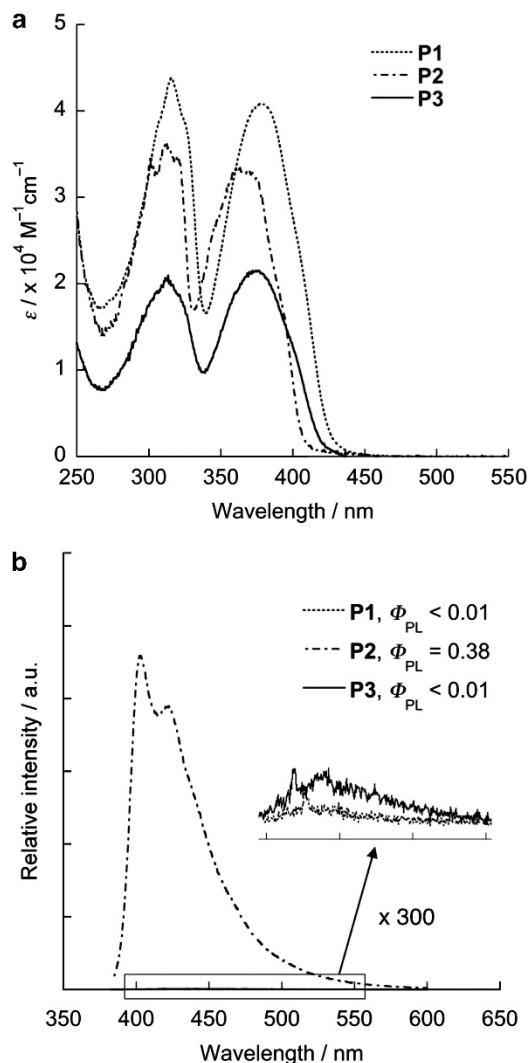


Figure 2 (a) UV/vis absorption spectra of **P1–3** in THF (1.0×10^{-5} M). (b) PL spectra of **P1–3** in THF (1.0×10^{-5} M) excited at each absorption peak top.

32.3, 30.0, 29.8, 26.4, 23.1, 14.3 p.p.m. ^{11}B NMR (128 MHz, CDCl_3) δ 5.3, –5.8, –11.8 p.p.m.

^1H , ^{13}C , and ^{11}B NMR spectra of compound **3** (Supplementary Figures S1–S3), compound **4** (Supplementary Figures S4–S6), and **P3** (Supplementary Figures S7–S9) are shown in Supplementary Information.

RESULTS AND DISCUSSION

Scheme 1 outlines the synthetic route to copolymer **P3**. The Sonogashira–Hagihara coupling¹¹ of compound **1** with compound **2** afforded the trimethylsilyl (TMS)-protected compound **3** with a 56% yield. The TMS groups of compound **3** were readily removed with K_2CO_3 to give the corresponding monomer **4** with a 55% yield. The Sonogashira–Hagihara polycondensation of monomers **4** and **5** was carried out, and the target copolymer **P3** was obtained with a 77% yield. The M_n and M_w values of **P3** were estimated to be 10 200 and 21 100, respectively. Copolymer **P3** was determined to be soluble in various organic solvents, such as THF, CHCl_3 , CH_2Cl_2 , and toluene, allowing it to be characterized by NMR spectroscopy, as shown in Supplementary Figures S7–S9.

Optical properties of the obtained polymers were investigated and the data are summarized in Supplementary Table S1. Figure 2a shows

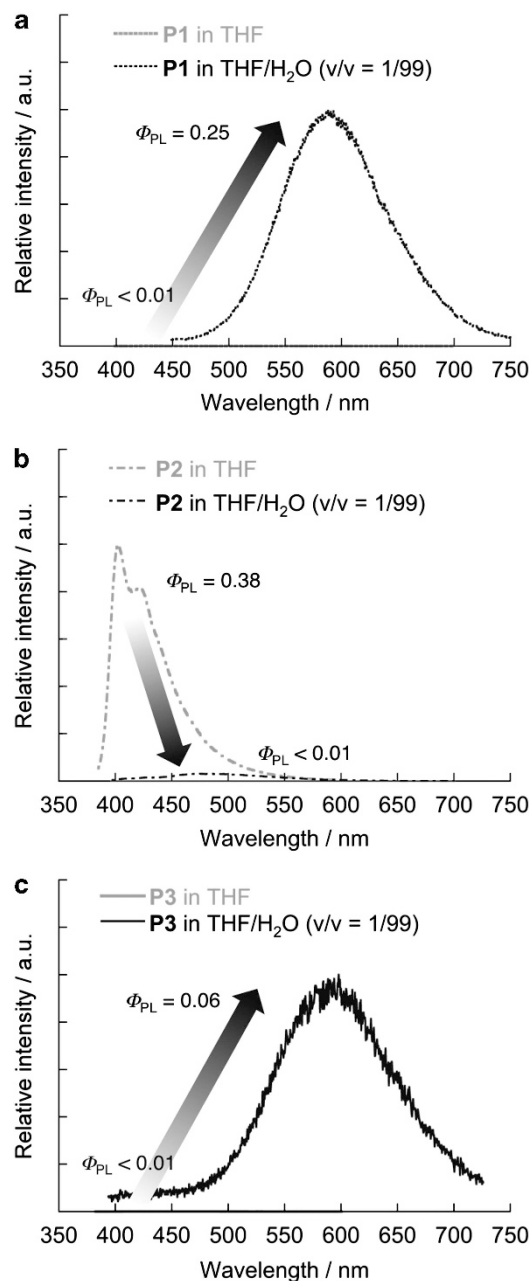


Figure 3 PL spectra of (a) **P1**, (b) **P2**, and (c) **P3** in THF (1.0×10^{-5} M) and THF/ H_2O ($v/v = 1/99$, 1.0×10^{-5} M).

the UV/vis absorption spectra of polymers **P1–3** in dilute THF (1.0×10^{-5} M). Polymer concentration was calculated using the repeating unit; therefore, the molar extinction coefficient ϵ ($\text{M}^{-1} \text{cm}^{-1}$) of **P3** was approximately half that of **P1** and **P2**. Their absorption spectra arose from the typical π – π^* transition band of a *p*-phenylene-ethynylene moiety; accordingly, the spectra were almost identical.

The photoluminescence (PL) spectra of **P1–3** in dilute THF (1.0×10^{-5} M) excited at each absorption peak maximum are shown in Figure 2b. The PL of **P1** in solution was completely quenched owing to the occurrence of ICT from the *p*-phenylene-ethynylene unit to the C1–C2 bond of the carborane cluster. The PL of **P2** in solution was observed, exhibiting a PL quantum efficiency (Φ_{PL}) of 0.38; this emission arises from the locally excited state of the

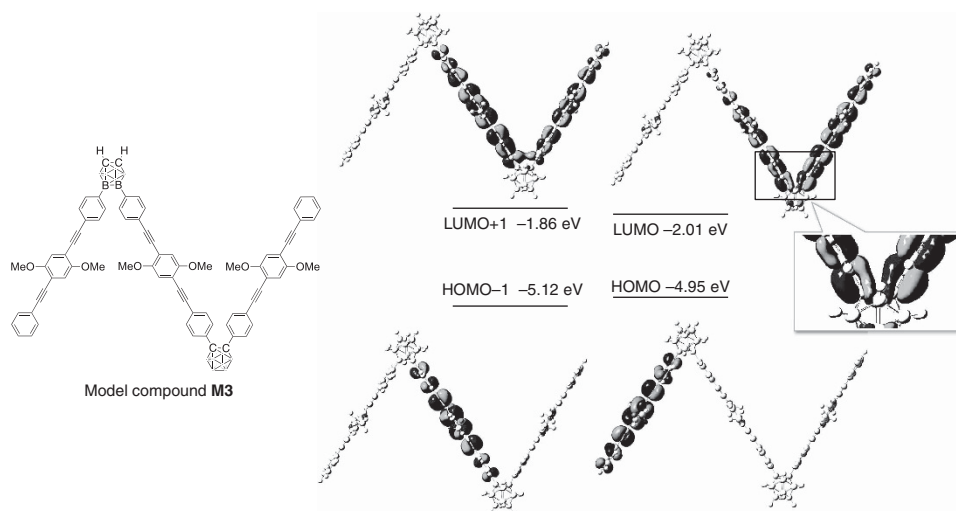


Figure 4 Molecular orbitals and energy levels of model compound **M3** calculated at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory.

p-phenylene-ethynylene moieties. As shown in Figure 2b, a PL peak corresponding to the alternating copolymer **P3** did not appear, and its Φ_{PL} was <0.01 , a behavior similar to that of **P1**. The C1,C2-disubstituted *o*-carborane unit causes ICT regardless of the presence of the B9,B12-disubstituted *o*-carborane unit in the polymer chain.

The PL behaviors of **P1–3** in the aggregation state were investigated, and the PL spectra in THF/H₂O (*v/v* = 1/99) are shown in Figure 3. Polymers **P1** and **P3** exhibited orange AIE at ~ 590 nm. The Φ_{PL} of **P1** and **P3** were estimated to be 0.25 and 0.06, respectively; the difference in Φ_{PL} values arose from that of the aggregates. In both cases, the ICT from *p*-phenylene-ethynylene to the C1–C2 bond of carborane occurred, and the restricted C1–C2 bond vibration in the aggregates suppressed the radiationless decay, which led to emission. To verify the restricted molecular motion, we obtained the PL spectra of **P1** and **P3** in a frozen glassy matrix (in 1.0×10^{-5} M 2-Me-THF at 77 K), as shown in Supplementary Figure S10. Despite the dilute conditions, a clear AIE was observed by freezing the molecular motion. These results indicate that constrained molecular motion is the main cause of AIE in the present system.

Further evaluation of the electronic state of copolymer **P3** was carried out using density functional theory (DFT) calculations for model compound **M3** at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory; the results are shown in Figure 4. DFT calculations were facilitated by using the –OMe group instead of the –OC₁₂H₂₅ group. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **M3** were mainly located on the *p*-phenylene-ethynylene moieties. In the HOMO/HOMO–1, two orbitals were degenerated. The LUMO/LUMO + 1 consisted of the orbitals of the C-substituted *p*-phenylene-ethynylenes, and the HOMO/HOMO–1 consisted of those of the B-substituted *p*-phenylene-ethynylenes. It should be noted that an apparent overlap of the orbitals was observed between the σ^* antibonding orbital of the C1–C2 bond and the π^* antibonding orbital of the adjacent phenylene unit in the LUMO. This σ^* – π^* conjugation causes the AIE of carborane dyes consisting of C1,C2-disubstituted *o*-carborane^{7,12–14} as well as a decrease in the LUMO level. Supplementary Figure S13 shows the HOMO/LUMO and energy levels of model compounds **M1** and **M2**, which consist of C1,C2- and B9,B12-disubstituted *o*-carborane, respectively. The HOMO level of

M3 was slightly higher than those of **M1**, owing to the weakly inductive electron-donating effect of the B9,B12-disubstituted *o*-carborane unit.¹⁵

The results of thermogravimetric analysis (TGA) of **P1–3** under dry air are shown in Supplementary Figure S11A; all polymers decomposed at ~ 300 °C. The TGA curve of **P3** under dry N₂ exhibited a decomposition behavior similar to that under air. The ceramic yield of **P3** under N₂ was estimated to be 51%, which was almost identical to the weight percentage of the main chain (57%). Therefore, the decomposition of alkyl chains followed by phenylene-ethynylene moieties started at ~ 300 °C. The ceramic yield of **P3** under air (71%) was larger than that of **P3** under N₂ (51%), implying that the ash after pyrolysis includes boron oxide species such as B₂O₃. It has been reported that carborane-B and aryl-C bonds were thermally stable up to 580 °C¹⁶ and that rearrangement occurs without decomposition; in contrast, the C–C bond cleavage of carborane-C and aryl-C bond occurs at ~ 300 °C.¹⁷ These reports support that, in the case of the *o*-carborane polymers, the introduction of 9,12-boron atoms in the main chain enhanced the ceramic formation. Differential scanning calorimetry (DSC) was carried out for **P1–3** under dry N₂. All polymers exhibited ambiguous glass transition peaks (T_g); therefore, they were estimated by dynamic DSC (DDSC) curves. The T_g of **P1–3** appeared at ~ 60 °C, and crystallization peaks were observed from 170 to 195 °C without melting peaks in the first scan (Supplementary Figure S12). No peaks were observed in the second scan.

In summary, a copolymer consisting of alternating C1,C2-disubstituted and B9,B12-disubstituted *o*-carborane units was synthesized and characterized. The optical properties of the copolymer were investigated by comparison with C1,C2-disubstituted and B9,B12-disubstituted *o*-carborane polymers. The results of PL analysis and DFT calculations indicated that the copolymer exhibited AIE properties via ICT to the C1–C2 bond of the *o*-carborane cluster, as was the case for the C1,C2-disubstituted *o*-carborane polymer. In addition, the copolymer also displayed the thermal behavior possessed by the B9,B12-disubstituted *o*-carborane polymer. The PL and thermal behaviors could be controlled by the choice of the substituted position in the π -electron systems. Further investigations on the development of carborane-based heat-resistant light-emitting materials are currently underway.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)