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Emission via Aggregation of Alternating Polymers with *o*-Carborane and *p*-Phenylene−Ethynylene Sequences

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Considerable importance has been attached to polymer aggregation owing to their potential applications in adsorption, sludge treatment, drug encapsulation, and shaping the assembly of nanostructures.[1] Among them, aggregations of π-conjugated polymers are of especial interest because of their rigid polymer backbone structure, extraordinary light-gathering ability, and controllable emission property.[2] In recent years, Tang et al.[3] and Park et al.[4] have developed several material systems having aggregation-induced emission (AIE) properties; i.e., nonemissive molecules are induced to emit intensely by aggregate formation. This property possesses latent advantages for fabricating organic light-emitting diode (OLED) in the form of a thin film or by the vapor deposition technique, since the emitting ability of the dyes would drastically improve in such aggregated states.[5] Drawing on their characteristics, substantial applications of AIE have been reported, e.g., luminescent organogels, phosphorescent emissive complexes, and sensory materials including turn-on bioprobes.[6] Up-to-date research reveals that restricted intramolecular vibrational and rotational motions in aggregated state are responsible for the AIE phenomena, and its occurrence in sterically crowded molecules has been presented.[7] On the basis of these findings, we selected *o*-carborane (1,2-dicarba-dodecaborane) as a candidate of core unit for the sterically crowded environment. *o*-Carborane as an icosahedral inorganic boron cluster compound is recognized as one of carborane compounds consisting of three-center, two-electron bonds and subsequent three-dimensional delocalization of skeleton electrons (three-dimensional aromaticity) and possesses a well-known highly polarizable σ-aromatic character.[8] Therefore, it is anticipated that introduction of luminescent π-conjugated segments onto the 1,2-position in the *o*-carborane would undergo the AIE, i.e., design of polymers with alternating *o*-carborane and π-conjugated sequences. In this Communication, we report the synthesis and optical properties of AIE-active alternating polymers with *o*-carborane and *p*-phenylene−ethynylene sequences.

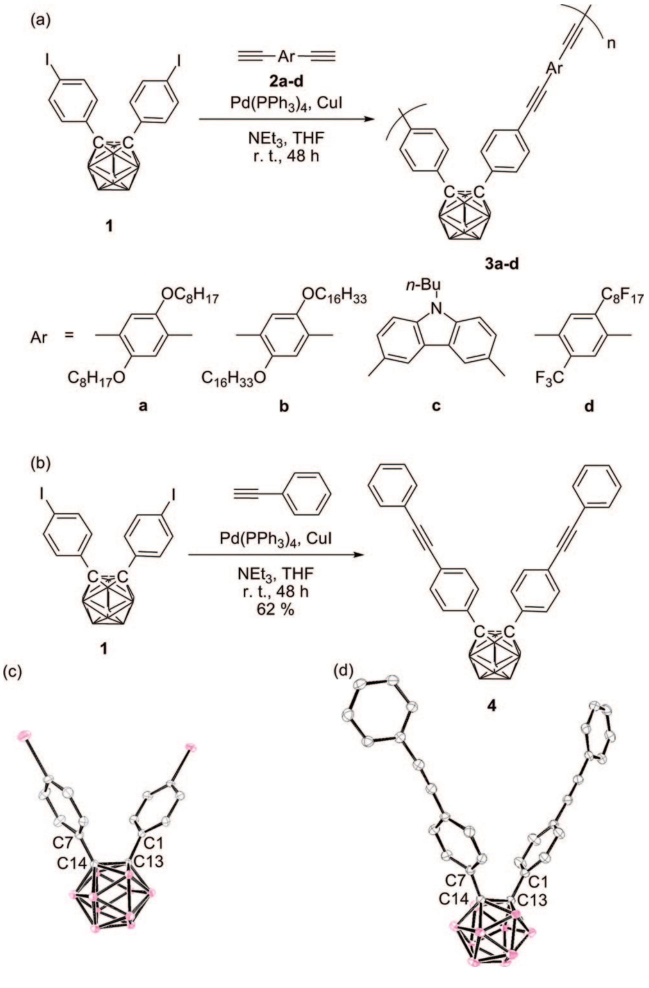

Figure 1. (a) Polymerization of **1** with diyne compounds and (b) model reaction of **1** with phenylacetylene. ORTEP drawings of (c) **1** and (d) **4**. Thermal ellipsoids are drawn at the 50% probability level.

Initially, Sonogashira−Hagihara palladium coupling polycondensation reactions of *o*-carborane monomer **1**, which was synthesized by the reaction of decaborane (14) and bis(4-iodophenyl)acetylene in the presence of dimethyl sulfide, with diyne compounds **2a**−**d** were conducted in anhydrous THF and triethylamine solutions at room temperature for 48 h under an argon atmosphere to afford the corresponding polymers **3a**−**d** in excellent yields (Figure 1a). The crude products were reprecipitated into methanol and washed with methanol two times. The yields of the obtained polymers were high enough (**3a**: 89%; **3b**: 94%; **3c**: 92%; **3d**: 94%), and the number-average molecular weights of **3a**−**d** were 2800, 3100, 4100, and 3200, respectively. The polymerization degrees (DPs = 3.5−7.6) of polymers **3a-d** were relatively inferior to those of general poly(*p*-phenylene−ethynylene)s (PPE), probably resulting from poor reactivity in the polymerization because of high electron-withdrawing character of **1** and/or the compact polymer structure due to highly bent nature of **1**. However, the DPs should be adequate for the following measurements of optical properties due to the saturation of π-conjugation length.[9] Polymers **3a**−**d** using long alkyl chains or perfluoroalkyl chains were soluble in various organic solvents such as THF, chloroform, and so on. The structures of the obtained polymers were supported by ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectroscopies. In the ^{1}H NMR spectra, the broadening peaks assignable to the presence of *o*-carborane structure were observed at 3.50−1.70 ppm, and ^{11}B NMR spectroscopy also showed the broad peaks at around −1 to −10 ppm assignable to the borons of *o*-carborane cluster. In the IR spectrum, strong peaks due to stretching of the carbon−carbon triple bond appeared at around 2200 cm^{-1}, and those of the boron−hydrogen bond on *o*-carborane were observed at around 2600 cm^{-1}. These findings indicate that the *o*-carborane monomer **1** underwent the effective palladium-catalyzed polymerization with diyne monomers

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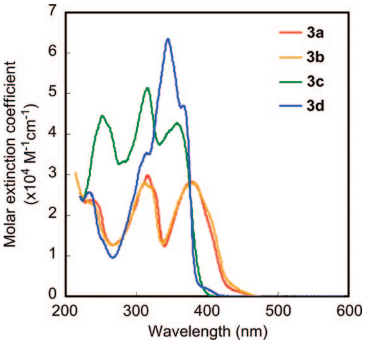

Figure 2. UV−vis spectra of polymers **3a**−**d** in THF (1×10^{-5} mol/L).

2a−**d**; i.e., the obtained polymers have expected structure with alternating *o*-carborane and *p*-phenylene−ethynylene sequences.

Structure elucidation of polymers **3a**−**d** was performed in comparison with spectroscopic data of model compound **4** by supporting ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectroscopies. Model compound **4** was synthesized by the reaction of **1** and 2 equiv of phenylacetylene via the Sonogashira−Hagihara coupling reaction (Figure 1b). Respective broad peaks at around 3.70−1.72 ppm in the ^{1}H NMR spectrum and at −1 to −10 ppm in the ^{11}B NMR spectrum were observed, similarly to ^{1}H and ^{11}B NMR spectra of **3a**−**d**. The crystallographically determined molecular structures of **1** and **4** are shown in Figure 1. Three centers and two electrons bonds of *o*-carborane are perfectly retained over the palladium coupling reaction. The bond length of C13−C14 of **4** (1.733 Å) was slightly longer than that of **1** (1.715 Å), and the dihedral angle between two phenyl rings attached to *o*-carborane is 48° in **1**, while that of **4** is 58°. These data could indicate that the C−C bond in *o*-carborane moiety and its surrounding environment are affected by the substituent on two carboranylphenyl rings.

To examine the optical properties of the obtained polymers **3a**−**d**, the UV−vis absorption experiment was carried out in THF (Figure 2). The rigid conformation of **3a**−**d** in the ground state leads to the vibrational structure in their absorption spectra corresponding to $\pi \rightarrow \pi^*$ transition of *p*-phenylene−ethynylene linkers. The absorption maxima of **3a** and **3b** (λ_{max} = 379 and 380 nm, respectively) showed almost identical values and were bathochromically shifted in comparison with that of **3d** (λ_{max} = 345 nm), resulting from higher donating ability of alkoxybenzene unit in the *p*-phenylene−ethynylene linkers. In contrast, **3c** (λ_{max} = 358 nm) has absorption maxima at shorter wavelength than **3a** and **3b** because the 3,6-position-linked carbazole is more shorter conjugation than the 1,4-linked alkoxybenzene. The absorption maxima of **3a**−**d** were red-shifted as compared to reported the diphenyl adduct of diethynyl compounds,[10] indicating that *o*-carborane moiety acts as aromatic character for an extension of conjugated length along the polymers. For example, the maximum of **3a** was shifted to bathochromic side relative to 1,4-bis(octyloxy)-2,5-bis(phenylethynyl)benzene (λ_{max} = 366 nm). Although there are no reports on chromophores containing *o*-carborane, Tour and co-workers also reported bathochromic shift and extension of conjugation length through the *p*-carborane moieties in hybrid molecules including *p*-carborane connected with oligo-phenylene−ethynylenes (OPE).[11] Further, the spectra of **3a**−**d** exhibited a similar shape to the reported compounds, meaning no distortion in the main chain from steric hindrance between the *p*-phenylene−ethynylene linkers in spite of the introduction of *o*-carborane into the π-conjugated polymer sequences.

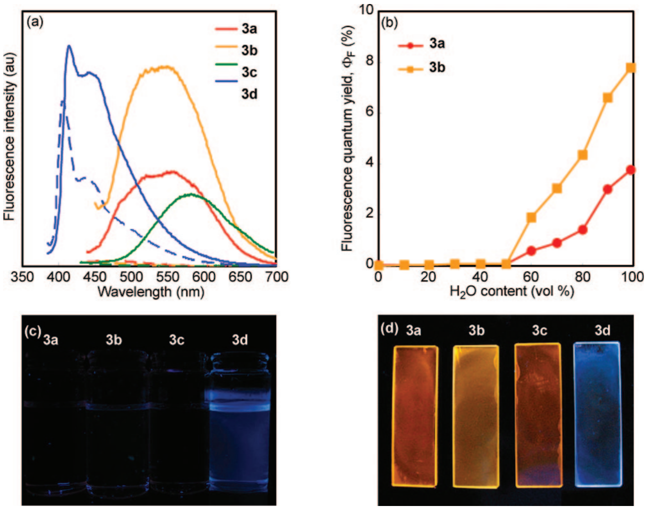

Figure 3. (a) Fluorescence spectra of **3a**−**d** in THF (1×10^{-5} mol/L, dashed line) and mixed solvent of THF/H_2O = 1/99 (v/v) (1×10^{-5} mol/L, solid line). (b) Dependence of quantum yields of **3a** and **3b** on solvent compositions of the THF/H_2O mixture and photographs of **3a**−**d** (c) in solution state and (d) in film state.

In fluorescence spectra in THF solution (Figure 3a, dashed line), **3a**−**c** with electron-donating π-conjugated linkers exhibited almost no emission, whereas **3d** with electron-withdrawing π-conjugated linker showed blue emission (λ_{em} = 405 nm, excited at 345 nm). This indicates that the electronic structure of the π-conjugated linker greatly influences the emission of the polymers with alternating *o*-carborane and *p*-phenylene−ethynylene sequences.[12] In the mixed solvent of THF/H_2O = 1/99, **3a**−**c** exhibited orange emission with large Stokes shifts (170−225 nm,) as shown in Figure 3a (solid line), derived from charge transfer between the alternating donor and acceptor segments in the polymer backbone. Actually, the emission maxima of **3a**−**c** were 559 nm (excited at 379 nm), 550 nm (excited at 380 nm), and 583 nm (excited at 358 nm), originating from aggregation-induced emission (AIE). In film state, **3a**−**c** displayed bright orange colors although no emissions of them were observed in THF solution state (Figure 3c,d). This is a signature of the restriction of tortional/vibrational motions around *o*-carborane moiety in the polymers. Indeed, model compound **4** was found to be AIE-active (λ_{max} = 294 nm, λ_{em} = 485 nm, Φ_F < 0.02% in THF and Φ_F = 12% in the mixed solvent of THF/H_2O = 1/99 (v/v)). In contrast, the blue emission of **3d** was not changed in both states probably due to the absence of charge transfer to *o*-carborane moieties, whereas Tang et al. have presented that modifying strong electron-withdrawing groups in the AIE active molecule leads to complete inactivity of the AIE.[13] Further, **3a** was also luminescent in frozen glassy matrix of 2-methyltetrahydrofuran at 77 K, meaning that any interactions between the polymer chain, e.g., π−π stacking or CH−π interaction, were unrequisite for the AIE of them (Figure S3).

To provide an effective understanding for the AIE process, we estimated the fluorescence quantum yields (Φ_F) of **3a** and **3b** in THF/H_2O mixture, using 9,10-diphenylanthracene as a reference (Figure 3b). The Φ_F of **3a** in THF solution is as low as <0.02%. The Φ_F is unchanged upon addition of H_2O up to 50 vol % but starts rapidly increase afterward. When the volume fraction of H_2O in THF/H_2O mixture increases to 99%, Φ_F rises to 3.8%, which is 220 times higher than that of the THF solution. The trajectory of the Φ_F suggests that **3a** initiates to aggregate at a H_2O fraction of >50%, and the size of the aggregates finally reached 38.0 ± 6.1 nm, measured by dynamic light scattering

(DLS), in the mixed solvent (see also Figures S4 and S5). Analogously to the AIE process for **3a**, **3b** also represented almost the same relationship of Φ_F and THF/H_2O mixture, and the final size of aggregation was 131.2 ± 18.4 nm. These results can indicate the emission behavior via aggregation of the polymers with alternating *o*-carborane and *p*-phenylene–ethynylene sequences with the large Stokes shifts, i.e., AIE effect.

In conclusion, we have demonstrated the synthesis of alternating polymers with *o*-carborane and *p*-phenylene–ethynylene having various substituents in the main chain. UV–vis absorption study in dilute THF solution revealed the extension of π-conjugation length of the *p*-phenylene–ethynylene segment via *o*-carborane moieties in the polymer backbones. Further, the obtained polymers underwent effective AIE in mixed solvent of THF/H_2O = 1/99 (v/v), and the AIE behavior was tunable by changing the electronic structures of the comonomer. Further work is currently underway to design sensory materials utilizing the AIE system of *o*-carborane.

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Supporting Information Available: Text giving typical experimental procedures, data for all new compounds, crystal packing diagram of **4**, structures for the LUMO and HOMO of **3a′** and **3d′**, fluorescence spectra of **3a** in 2-methyltetrahydrofuran (1×10^{-5} M) at 77 K, tapping mode AFM image of **3a** aggregates, histograms of diameters of **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) **3a′** (2,5-bis(octyloxy)-1,4-bis(4′,4′′-*o*-carboranylphenylethynyl)benzene) and **3d′** (2-perfluorooctyl-5-trifluoromethyl-1,4-bis(4′,4′′-*o*-carboranylphenylethynyl)benzene) were designed as the model compounds for **3a** and **3d** by using the Gaussian 03 suit of program,[14] and their electronic states were examined by theoretical calculations using density functional theory (DFT) method (B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)) to provide effective understanding for their emission behavior (see Supporting Information). The highest occupied molecular orbitals (HOMOs) of both **3a′** and **3d′** are located on the 1,4-bis(phenylethynyl)benzene moieties. The lowest unoccupied molecular orbital (LUMO) of **3a′** has a distribution from the C–C bond in *o*-carborane units, whereas that of **3d′** is still located on the 1,4-bis(phenylethynyl)benzene moiety due to its electron-withdrawing character (Figure S2). The difference on each LUMO state of them would be responsible for the emission behavior.

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