Highly Luminescent BODIPY-Based Organoboron Polymer Exhibiting Supramolecular Self-Assemble Structure

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BODIPYs (4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacenes) and their derivatives are an important class of highly luminescent materials that have found their widespread applications in fluorescent dyes for biochemical labeling, photonic molecular systems, laser dyes, organogelators, and light-emitting devices[1] due to high quantum yields, low rates of intersystem crossing, large molar absorption coefficients, and excellent photostability.[2] The recent discovery by Ziessel et al. that several BODIPY derivatives replaced fluoride with aryl, ethynylaryl, ethynylthienyl, and so on show high stability to polar solvents and large Stokes' shifts in their emission spectra revitalized research into boron dipyrromethanes.[3] Recently, the incorporation of these boron-chelating dyes except for BODIPYs as electroluminescent chromophores into a polymer main chain[4] or side chain[5] is more attractive for applications as electroluminescent devices, organic field-effect transistors, photovoltaics, etc.[6] However, the fluorescent quantum yields (Φ_F) of their polymers were commonly low (<30%). Herein, a candidate approach is the introduction of a BODIPY unit into the polymer chain, because the Φ_F of its dye is exceedingly high as compared to those of other organoboron dyes such as boron quinolate and boron diketonate.

We designed a highly luminescent BODIPY-based monomer (**1**) (absolute quantum yield: $\Phi_F = 92\%$) with two kinds of substituents: the polymerizable bis-iodophenyl groups and the decyl group, which can be soluble in most organic solvents. Monomer **1** could be prepared from F-BODIPY having a decyl group and Grignard derivative, which was synthesized by the reaction of 1-ethynyl-4-iodobenzene and ethylmagnesium bromide, under a similar manner.[3c] The Sonogashira—Hagihara coupling reaction of **1** with diyne compounds proceeds via *p*-phenylene-ethynylene formation under mild conditions. The BODIPY-based poly(*p*-phenylene-ethynylene)s awaken our interest in not only the high luminescent properties but also supramolecular self-assembly of soluble polymers due to the rod—coil type structure; i.e., the rod and coil segments are a rigid π-conjugated polymer main chain and decyl group, respectively. Their polymers are expected to be arranged to form intriguing nanostructures by virtue of intermolecular π–π stacking.[7]

Initially, the polymerization of **1** with 1,4-diethynylbenzene (**a**) was conducted in the presence of Pd(PPh₃)₄ (5.0 mol%) and CuI (5.0 mol%) in the mixed solvents (66.7 mM: THF/NEt₃ = 2/1(v/v)) at room temperature for 24 h (Figure 1A). The soluble polymer was obtained as a deep red solid after precipitation into methanol and hexane, respectively, and the polymer yield was 87%. The ¹H NMR and IR spectra agreed well with the expected structure, and the tetracoordination state of the boron atom was confirmed by the ¹¹B NMR spectroscopy ($\delta_B = -13.8$ ppm), indicating that the polymerization proceeded without any damage
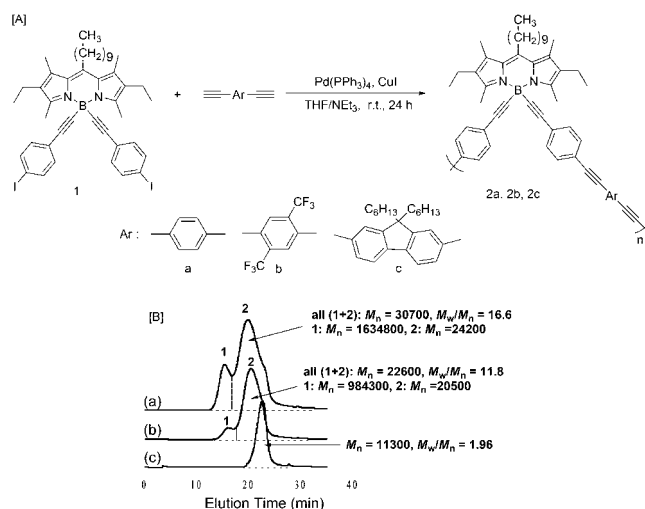

Figure 1. [A] Polymerization of BODIPY-based monomer **1** with diyne monomers and [B] SEC profiles of **2a** (a), **2b** (b), and **2c** (c).

to the tetrahedral structure in the BODIPY moiety. The SEC (a size-exclusion chromatography) trace of **2a** (eluent: THF) showed two peaks in the high molecular region as a shoulder as well as the main peak corresponding to **2a** (Figure 1B(a)). The observed shoulder peak ($M_n = \sim16$ million) implies that this polymer was arranged in supramolecular self-assembly in THF. Continuously, the synthesis of **2b** and **2c** was also performed by the polymerization of **1** with 1,4-diethynyl-2,5-bis(trifluoromethyl)benzene (**b**) and 2,7-diethynyl-9,9-dihexyl-9*H*-fluorene (**c**) under similar conditions. Figure 1B presents the SEC traces **2b** and **2c**, respectively. Analogously to **2a**, **2b** showed the shoulder peak in the high molecular weight region (Figure 1B(b)). However, the shoulder peak of **2b** decreased in comparison with that of **2a**. In contrast, the absence of an observable shoulder peak in **2c** was displayed as shown in Figure 1B(c), probably suggesting that the higher steric hindrance of the substituent in diyne monomer interferes with the construction of self-organization of **2c**. Scanning electron microscopy (SEM) was used to visualize the assemblies of the obtained polymers along with monomer after drying the THF solution on a glass plate. Surprisingly, the SEM image of **1** revealed a wide range of particle structures from μm to nm (Figure 2A), and the image of **2a** showed the presence of nm-sized particles and μm-sized fiber-like structures formed by aggregation of each particle, which was roughly 1.2 μm in diameter, as confirmed by transmission electron microscopy (TEM) (Figure 2B and E). Further, Figure 2C and D also illustrate the SEM images of **2b**
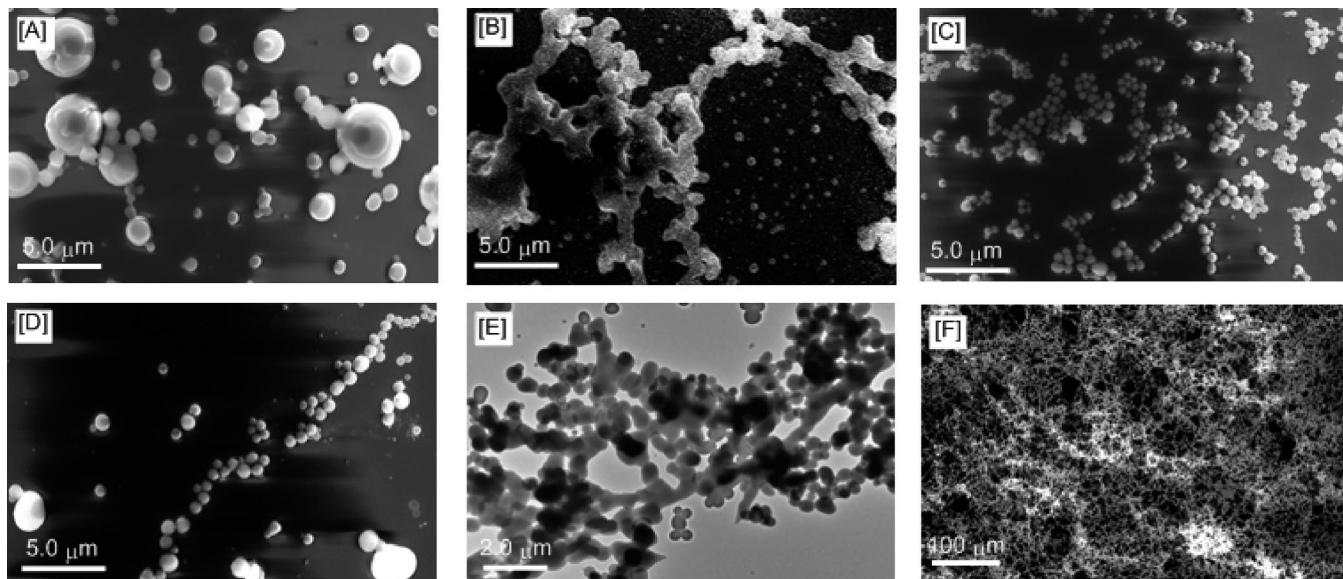
Figure 2. SEM micrographs of **1** [A], **2a** [B], **2b** [C], and **2c** [D] dried at rt for 3.0 h on a glass plate, TEM micrograph of **2a** [E] dried at rt for 5.0 h on a carbon-coated copper grid, and SEM micrograph of a dried gel of **2a** [F] from CHCl₃. The concentration of all samples except for that for sample F is 1.0 g/L of THF.

and **2c**. The presence of particles of **2b** was more predominant than that of fibers of **2b**. On the contrary, the fibers of **2c** were almost not observed, possibly suggesting that the fiber-like architectures result from the steric factor of the substituents in comonomer units similarly to SEC observations. The size distributions of these aggregates in THF solution ($c = 1.0$ g/L) were in the order **1** (643.8 ± 144.3 nm) > **2a** (11.5 ± 2.0 nm) > **2b** (10.9 ± 1.5 nm) > **2c** (9.0 ± 1.9 nm) as measured from dynamic light scattering (DLS) measurement. In particular, **1** with least molecule weight constructs larger aggregates as is the SEM measurement as well (Figure S1). More surprisingly, only in CHCl₃ (2.0×10^{-2} mol/L) among various solvents such as THF, benzene, and toluene, the gelation of **2a** was observed at room temperature after 24 h (Figure S2).[8] The concentration of gelation of **2a** was checked in CHCl₃, and the concentration at more than 2.0×10^{-2} mol/L led to the efficient gelation of **2a** in CHCl₃. Therefore, we investigated the correlation between specific viscosity (cP) and time (h) in CHCl₃ (Figure S3). The viscosity increased gradually with time, and the final viscosity of gelation was very high (2.52×10^4 cP) after 24 h. The SEM image of a dried gel of **2a** represented the formation of an entangled network structure with roughly a $1.2-1.9$ μm width (Figure 2F). X-ray diffraction (XRD) of a dried gel **2a** showed a d-spacing of 3.48 Å, which is characteristic of π-stacked packing and a signal at the small angle region corresponding to an interlayer spacing of 12.63 Å (Figure S4). The dried gel can redissolve in benzene at more than 50 °C or with sonication. The ¹H NMR studies of **1** and **2a** were recorded with benzene-d_6 and CDCl₃ at room temperature. Their signals assignable to aromatic protons and methyl and methylene protons in BODIPY ligand in CDCl₃ were almost shifted upfield in benzene-d_6, indicating the inhibition of the π-stacked self-assembly by interaction between **1** or **2a** and benzene (Figures S5 and S6). These data support that the construction of supramolecular self-assembly consists of π-stacking interaction.

The UV−vis absorption and photoluminescence experiments of monomer and the obtained polymers were carried out in CHCl₃ (1.0×10^{-5} mol/L). Commonly, all compounds showed the absorption maxima at 519 nm assignable to BODIPY ligand

(Figure 3A). The maxima, corresponding to a π→π* transition, of the obtained polymers (**2a**: $\lambda_{max} = 348$ nm, **2b**: $\lambda_{max} = 370$ nm, and **2c**: $\lambda_{max} = 372$ nm) are red-shifted as compared to those of **1** ($\lambda_{max} = 265$ nm), and the molar absorption coefficients of the polymers (**2a**: $\epsilon = 18.9 \times 10^4$ M⁻¹ cm⁻¹, **2b**: $\epsilon = 12.5 \times 10^4$ M⁻¹ cm⁻¹, and **2c**: $\epsilon = 14.8 \times 10^4$ M⁻¹ cm⁻¹) are also higher than that of **1** ($\epsilon = 11.5 \times 10^4$ M⁻¹ cm⁻¹), indicating the extension of π-conjugation along the polymer main chain. Notably, the absorption coefficient of **2a** was slightly higher than those of other polymers, resulting from the formation of a regular aggregate such as fiber and network structures in CHCl₃ as considering the above morphologic studies. In the fluorescence spectra in CHCl₃ (Figure 3B), all compounds showed almost the same emission maxima at ~532 nm, which was excited at absorption maxima of both 519 nm corresponding to BODIPY ligand moiety and the λ_{max} corresponding to the π→π* transition moiety of each compound. This result means that their emissive sources consist of the BODIPY ligand moieties.[9] The absolute fluorescence quantum yields of the obtained polymers, which excited at λ_{max} corresponding to π→π* transition moiety of each compound, were barely smaller than that of **1** ($\Phi_F = 92\%$) (excited at 519 nm), actually, **2a**: $\Phi_F = 80\%$, **2b**: $\Phi_F = 71\%$, and **2c**: $\Phi_F = 85\%$. The high Φ_F of their polymers were in the order **2c** > **2a** > **2b**, probably originating from the energy transfer efficiency of each comonomer.[10] Their values were high enough as compared with general poly(p-phenylene-ethynylene)s[11] and could clearly indicate high energy transfer efficiency from π-conjugated linkers to BODIPY moieties. The Φ_F of a wet gel **2a**, which was prepared in CHCl₃ at 2.0×10^{-2} mol/L for 24 h, was 37% (excited at 348 nm), indicating that decrease in the Φ_F of the gel originates from collisional quenching of the excited state by π−π stacking.[12] Further, the emission intensity and Φ_F of **2a** have been observed in THF/benzene mixed solvents. The values in 100% benzene solution were higher than those in 50% THF/benzene and 100% THF solutions with decreasing π-stacking, implying that **2a** self-assembles into aggregates (Figure S7).[13] In the film state, the emission spectra of the polymers were red-shifted compared with those for the solution state; especially, a dramatic bathochromic shift of **2a** was observed due to a higher degree of ordering in the polymer than those of
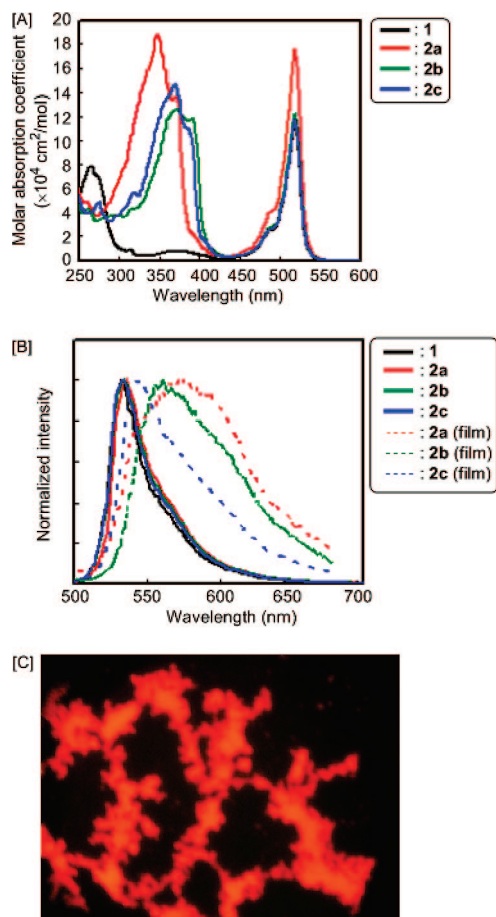
Figure 3. [A] UV−vis spectra of **1**, **2a**, **2b**, and **2c** in CHCl₃ (1.0 × 10⁻⁵ mol/L), [B] normalized emission spectra of **1**, **2a**, **2b**, and **2c** in CHCl₃ (1.0 × 10⁻⁵ mol/L), and [C] fluorescence micrograph of **2a** dried at rt for 5.0 h from THF solution (1.0 g/L) on a glass plate.

other polymers, probably originating from regulated fiber and network formation. Furthermore, the aggregate of fibers in THF was directly observed by fluorescence microscopy (Figure 3C). The bundles of the fibers gave a strong red fluorescence, which comes from the aggregated particle.

In conclusion, we have demonstrated the first example of highly fluorescent organoboron polymers with supramolecular self-assembled particle, fiber, and network structures by incorporating BODIPY dye into a common π-conjugated polymer, i.e., poly(*p*-phenylene-ethynylene). More detailed experiments are underway to determine the role of conjugation and side chain

lengths of monomers in controlling self-assembly to research potential device uses in the development of semiconductors and organic light emitting diodes.

Supporting Information Available: Text giving typical experimental procedures, data for all new compounds, DLS of all compounds, photograph of gelation of **2a**, the relationship between specific viscosity and time of **2a**, ¹H NMR spectra of **1** and **2a** in CDCl₃ and benzene-*d*₆, XRD profile of a dried gel **2a**, and UV and fluorescence spectra of **2a** in THF/benzene mixed solvent. This material is available free of charge via the Internet at http://pubs.acs.org.

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