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Dimesitylboryl-containing polydiphenylacetylene with a large Stokes shift, high fluorescence efficiency, and fluoride ion sensing ability

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ABSTRACT

A diphenylacetylene monomer carrying a dimesitylboryl functional group was newly synthesized and polymerized by heating the toluene solution at 80 °C, using $TaCl_5$–*n*-Bu_4Sn as a catalyst. A polydiphenylacetylene (PDPA) derivative was obtained in high yield despite the presence of the heteroatom; the polymer had an extremely high weight-average molecular weight of 1.27×10^6 $gmol^{-1}$ and readily dissolved in organic solvents. This polymer was highly resistant to heat and existed in an amorphous, glassy state at room temperature. Unlike the usual PDPA derivatives, the fluorescence (FL) maximum for this derivative appeared at 526 nm through efficient intramolecular energy transfer from the side dimesitylboryl groups to the polyene backbone upon excitation at a very short wavelength of 320 nm, indicating an extremely large Stokes shift of 206 nm. Moreover, the polymer showed considerably higher FL efficiency of 49.3% in a tetrahydrofuran solution and 19.1% in a film as compared to the usual PDPA derivatives. This polymer reacted with fluoride ions to exhibit critical changes in absorption and FL emission, which were expressed by an exponential and a Gaussian functional equation, respectively.

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1. Introduction

Fluorescent conjugated polymers have recently attracted much attention as functional materials for various sensors [1] and (bio)imaging probes [2–4] as well as active layer materials in optoelectronic devices [5]. In particular, polydiphenylacetylene (PDPA) derivatives have many advantages in practical application, such as high (photo)chemical resistance, thermal stability, mechanical strength and toughness, excellent solubility, and ability to form self-supporting membranes [6–10]. Recently, a variety of PDPA derivatives, as well as their nano- and hybrid materials, have been developed, and many efforts have been made to apply them to advanced sensors, (bio)imaging probes, and even chemomechanical actuators [11]. A typical synthetic procedure for the PDPA derivatives is as follows. A group V transition metal catalyst such as $TaCl_5$ or $NbCl_5$ is added with a Lewis base such as organosilane or organotin as a cocatalyst to be activated for polymerization, and then, the corresponding monomer is added to the catalytic system [12]. As a result, high-molecular-weight polymers can be obtained in high yield. However, two-component catalytic systems are highly reactive and very sensitive to moisture and air, which often causes accidental loss of activity. For the same reason, these catalysts are not tolerant to polar monomers with heteroatoms such as oxygen and nitrogen, and hence, the range of applicable polymerizable monomers is quite limited [13,14]. Such heteroatom-containing monomers are thought to act as catalytic poisons that induce loss of coordination bonding ability of the transition metals because of the large dipole moment and lone-pair electrons attributed to the electronegative atoms.

Among heteroatom-containing organic compounds, boron-containing compounds are of particular interest in terms of their electronic structure [15]. Triarylboranes or aryl-substituted dibenzoboroles are weak Lewis acids and the central atom, boron, has sp^2 hybridized orbitals so that the π-conjugation is extended through the vacant *p* orbital of the boron atom [16,17]. These compounds are known to react selectively with fluoride ions to interrupt the p_π-π conjugation between the boron atom and the three π-conjugated

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aromatic rings, resulting in significant changes in absorption (color-to-colorless) and fluorescence (FL) emission (FL enhancement).

Although some conjugated polymers containing a boron atom in side group have already been synthesized to date [18–22], PDPA derivatives containing a boron atom have never been synthesized before despite the unique electronic structures and photophysical properties of boron-containing organic compounds. Therefore, it is quite interesting to know if boron-containing diphenylacetylene monomers undergo polymerization smoothly in the group V transition metal catalytic system, that is, whether the monomers act as catalytic poisons or not. More importantly, if the polymerization proceeds smoothly, it would be intriguing to understand the difference between the photophysical properties of boron-containing PDPA and other derivatives without a boron atom. To address this issue, in this study, we synthesized a new diphenylacetylene monomer containing a dimesitylboryl moiety as a side group, and monitored the polymerization of the monomer and evaluated the fundamental photophysical properties of the product polymer. An extremely high-molecular-weight polymer was obtained in good yield, and it showed a large Stokes shift and considerably high FL efficiency in both solution and film states. Moreover, the polymer reacted with fluoride ions to show significant changes in absorption and FL emission. The details will be described on the basis of spectroscopic analyses and fluoride-ion titration experiments.

2. Experimental section

2.1. Materials

The monomer was synthesized by referring to the literature method [22]. Dehydrated THF was obtained from Kanto Chemical Co. Other chemicals were purchased from Tokyo Chemical Industry Co. and used without further purification. 1-(4-Bromophenyl)-2-phenylacetylene was synthesized according to the literature [23]. Poly [1-(4-trimethylsilylphenyl)-2-phenylacetylene] (SiPDPA in Fig. 1) was synthesized according to the literature method [24].

2.2. Synthesis of poly[1-(4-dimesitylborylphenyl)-2-phenylacetylene] (BPDPA in Fig. 1)

2.2.1. 1-(4-dimesitylborylphenyl)-2-phenylacetylene (**1**)

A 200 mL three-necked flask was equipped with a three-way stopcock, dropping funnel, and magnetic stirring bar. After the flask was flushed with dry nitrogen, 1-(4-bromophenyl)-2-phenylacetylene (1.03 g, 4 mmol) in dry THF (22 mL) was introduced at −78 °C. Then, a hexane solution of *n*-butyllithium (3.25 mL, 1.6 M, 5.2 mmol) was added dropwise, and the reaction mixture was left for 1 h at −78 °C. A solution of dimesitylfluoroborane (1.40 g, 5.2 mmol) in dry THF (11 mL) was added dropwise, and stirring was continued for 1 h; then, the mixture was gradually warmed to room temperature. The reaction was quenched by the addition of a small amount of water. The solution was concentrated to 50% volume on a rotary evaporator and extracted with diethyl ether. The ethereal solution was washed with brine and dried over anhydrous magnesium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (eluent: hexane) to obtain the desired product (1.61 g, 94%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.41 (m, 2H), 7.39 (s, 4H), 7.27–7.20 (m, 3H), 6.71 (s, 4H), 2.20 (s, 6H), 1.89 (s, 12H). Anal. Calcd for $C_{32}H_{31}B$: C, 90.14; H, 7.33; B, 2.54. Found: C, 90.22; H 7.48. The ^{1}H NMR spectrum was represented in Fig. S1.

2.2.2. BPDPA

Polymerization was carried out under dry nitrogen using the following conditions: $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM, in toluene, at 80 °C, for 24 h. The polymerization procedure was as follows. A monomer solution was prepared in a two-necked flask by mixing **1** (256 mg, 0.6 mmol) and toluene (1.50 mL). Another two-necked flask was charged with $TaCl_5$ (21.5 mg, 0.06 mmol), *n*-Bu_4Sn (39 μL, 0.12 mmol), and toluene (1.5 mL), and the catalyst solution was aged at 80 °C for 15 min. Then the monomer solution was added to the catalyst solution, and the mixture was stirred at 80 °C for 24 h. Polymerization was quenched by adding a small amount of methanol. The reaction mixture was diluted with toluene and poured into methanol with stirring to precipitate the polymer as a yellow solid. The polymer was isolated by filtration and dried. The polymer yield was determined by gravimetry. Yield: 40%. Size exclusion chromatography (SEC; eluent: THF, PSt calibration): $M_n = 7.71 \times 10^5$, $M_w = 1.27 \times 10^6$ ($M_w/M_n = 1.64$). The ^{1}H NMR and SEC results were represented in Fig. S2 and S3, respectively.

2.3. Measurement

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the prepared copolymers were evaluated by using SEC (Waters, Alliance, 2000), HPLC-grade THF as an eluent at 40 °C, and a refractive index (RI) detector. The setup was calibrated with polystyrene standards of known molecular weights. Nuclear magnetic resonance (NMR) spectra (500 MHz, $CDCl_3$) were collected on an AVANCE III 500 NMR spectrometer (Bruker). Ultra violet-visible (UV–Vis) absorption spectroscopy was performed on a JASCO V-650 spectrophotometer. The FL emission spectra were recorded on a JASCO FP-6500 spectrofluorometer. Differential scanning calorimetry (DSC, TA Instruments Q2000) was performed in a pure nitrogen atmosphere at heating and cooling rates of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was conducted using TA Instruments Q500. X-ray diffraction (XRD) measurements (PANalytical X'Pert PRO-MPD) were performed at room temperature at the Korea Basic Science Institute (Daegu). The samples were mounted directly into the diffractor, and the experiment was performed using Cu Kα (1.54 Å) radiation, at 40 kV and 25 mA. The relative FL emission quantum yields of the polymer solutions were determined relative to a quinine sulfate solution in 1 N H_2SO_4 when excited at 365 nm ($A_{re} = 0.546$), and those of the polymer films were obtained relative to 9,10-diphenylanthracence in a poly (methyl methacrylate), PMMA matrix ($\Phi_{re} = 0.83$) [25,26]. The reference film was obtained by spincoating the toluene solution of PMMA (20 wt%) and 9,10-diphenylanthracence (2.0×10^{-4} M) onto a glass slide. The quantum yields of polymer films were determined with the equation of $\Phi_s = \Phi_r (A_rF_s/A_sF_r)$, where Φ is the quantum yield, F is the measured integrated fluorescence emission intensity, A is the absorbance at λ_{max}. The subscript ‘r’ refers to the reference with a known quantum yield and ‘s’ denotes the sample.

2.4. Determination of Stern-Volmer constants and binding constants

Stern-Volmer constants of BPDPA were determined from Stern-Volmer equation [27], $I_0/I = 1 + K_{sv} [F^-]$, where I_0 is FL intensity in absence of added F^- ion, K_{sv} is Stern-Volmer constant. Binding constants of BPDPA with F^- were determined from Benesi-Hildebrand equation [28], $1/(A–A_0) = 1/\{K_a (A_{max}–A_0)[F^-]\} + 1/(A_{max}–A_0)$, where A_0 is the absorbance in absence of added F^- ion, K_a is binding constant, A_{max} is absorbance in presence of added $[F^-]_{max}$. The K_a values could be determined from the slope and intercept of the plot of $1/(A–A_0)$ *vs.* $1/[F^-]$.

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