Highly Emissive Poly(aryleneethynylene)s Containing 2,5-Diboryl-1,4-phenylene as a Building Unit

Cui-Hua Zhao,[†] Atsushi Wakamiya,[†] and Shigehiro Yamaguchi*,[†,‡]

Department of Chemistry, Graduate School of Science, Nagoya University and SORST, Japan Science and Technology Agency, Chikusa, Nagoya 464-8602, Japan

Poly(aryleneethynylene)s (PAEs) are a representative class of π-conjugated polymers,[1] whose intense fluorescence and well-developed chromicity make them attractive materials for various optoelectronic and photonic applications such as organic light emitting diodes,[2] sensors,[3] and molecular wires.[4] However, because of their high conformational rigidity, PAEs have a strong aggregation-forming tendency,[5] which generally results in a significantly decreased emission efficiency in the solid state that spoils their potential utility as light emitters. In this regard, the creation of emissive PAEs that can fluoresce even in the solid state is a current important topic in this field. Recent intensive efforts actually have succeeded in producing several fascinating emissive PAEs, in which the common strategy for attaining intense solid-state emission is to incorporate the sterically bulky side chains and insulate the π-conjugated backbone to avoid any interchain interaction.[6]

We now disclose a new type of emissive PAE materials that contain a 2,5-diboryl-1,4-phenylene as the key building unit. We envisioned that the diarylboryl groups incorporated as the side chains would not only act as bulky substituents but also affect the electronic structure through the $p_\pi-\pi^*$ conjugation between the vacant p orbital on the boron atoms with the π^* orbital of the π-conjugated backbone.[7,8] In fact, as a model study, we have recently demonstrated that diborylphenylene-based oligo(p-phenyleneethynylene)s show an intense fluorescence even in the solid state.[9] In particular, the diborylphenylene acts as a good π-electron accepting unit in the excited state, and its incorporation into the electron-donating π-conjugated skeleton results in extremely high fluorescence quantum yields. To investigate the utility of this skeleton as a versatile building unit, we now incorporated it into the PAE-type systems. To gain a sufficient solubility and obtain high-molecular-weight polymers, it is essential to introduce long alkyl chains. Therefore, we designed bis(4-hexyl-2,6-dimethylphenyl)boryl, (HDMP)$_2$B, as a new boryl group, instead of the widely used dimesitylboryl group. Herein reported are the facile synthesis of a series of boryl-substituted PAEs **P1–P5** with various comonomer units (Figure 1) as well as the elucidation of their fundamental photophysical properties both in solution and in the solid state.

A key reagent in the preparation of polymers **P1–P5** is (HDMP)$_2$BF **3**, which was obtained from 1-bromo-2,5-dimethyl-4-iodobenzene **1**[10] in two steps, as shown in Scheme 1. Thus, the Suzuki cross-coupling reaction with hexyl-9-BBN produced the alkylated **2**, which was converted to the Grignard reagent by the reaction with Mg and then reacted with BF$_3$·OEt$_2$
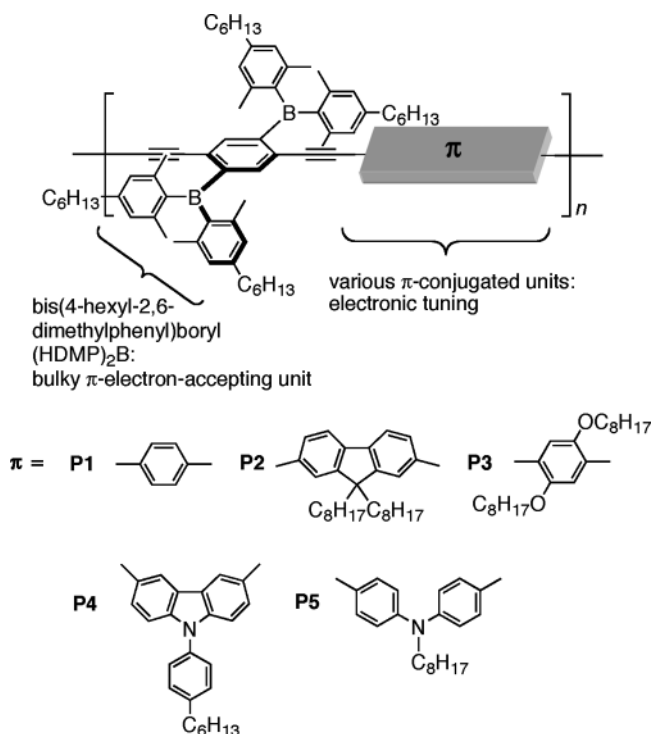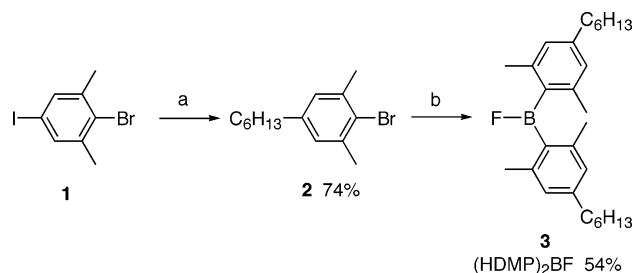
* Corresponding author. E-mail: yamaguchi@chem.nagoya-u.ac.jp.
[†] Department of Chemistry, Graduate School of Science, Nagoya University.
[‡] SORST, Japan Science and Technology Agency.

Figure 1. Structures of diborylphenylene-containing PAEs **P1–P5**.

Scheme 1

Reagents and conditions: (a) hexyl-9-BBN, PdCl$_2$(dppf), NaOH, THF, rt; (b) i, Mg (1.2 mol amt), THF, reflux; ii, BF$_3$·OEt$_2$ (0.5 mol amt), −78 °C to Rt.

Scheme 2
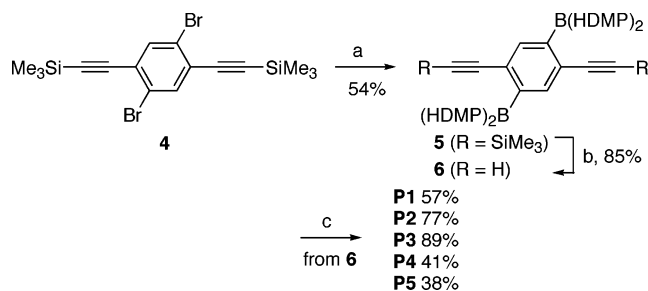
Reagents and conditions: (a) i, *n*-BuLi (2.1 mol amt), −78 °C, 1 h; ii, (HDMP)$_2$BF (2.1 mol amt), THF, −78 °C to rt; (b) TBAF (20 mol amt), rt.; (c) diiodoarene, Pd(PPh$_3$)$_4$, CuI, 10/1 toluene/(*i*-Pr)$_2$NH, 60 °C, 4 days.

(0.5 mol amount). Kugelrohr distillation produced the pure **3** in a moderate yield as colorless oil.

With this diarylfluoroborane in hand, we next synthesized 1,4-diethynyl-2,5-diborylbenzene **6**, as shown in Scheme 2. Thus, the dilithiation of the 1,4-dibromo-2,5-bis(trimethylsilyl-ethynyl)benzene **4**[11] with *n*-BuLi, followed by the treatment with

Table 1. Structural Characteristics and Photophysical Properties of Boryl-Substituted PAEs P1−P5 and Their Model Compound 7

compd	M_n (g·mol^{-1})[a]	PDI[a]	DP[a]	benzene			film[b]		
				λ_{abs}/nm[c] (log ϵ)[d]	λ_{em}/nm[e]	Φ_F[f]	λ_{abs}/nm[c]	λ_{em}/nm[e]	Φ_F[f]
P1	57 700	3.0	59	432 (4.45)	487	0.85	433	489	0.62
P2	41 400	2.7	32	436 (4.57)	499	0.87	440	504	0.36
P3	52 100	2.2	42	468 (4.40)	525	0.95	489	527	0.54
P4	12 600	1.8	10	432 (4.20)	523	0.98	437	529	0.44
P5[g]	16 100	1.2	13	452 (4.33)	567	0.96	454	562	0.51
7				400 (sh) (3.94)	477	0.14	400 (sh)	473	0.37

[a] Determined by GPC in THF with polystyrene as a standard. [b] Spin-coated from cyclohexane solution. [c] Only the longest absorption maxima are shown. [d] Per monomer unit. [e] Excited at the longest absorption maxima. [f] Absolute quantum yield determined by a calibrated integrating sphere system within ± 3% errors. [g] After purification by a preparative GPC.
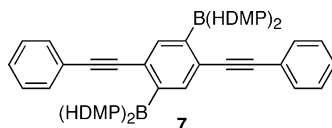
3, produced the diborylated **5** in a 54% yield. The further desilylation in the presence of an excess amount of TBAF gave **6** in an 85% yield. The use of excess fluoride ion was essential to complete this reaction, probably due to the trapping of fluoride ions by the boryl groups that retards the desilylation. The Pd-(0)-catalyzed Sonogashira coupling reaction of **6** with a variety of diiodoarenes produced the boryl-substituted PAEs **P1−P5** in moderate to good yields.

All the obtained polymers are stable to air and water and are highly soluble in the common organic solvents such as THF, chloroform, toluene, and even in cyclohexane. For instance, the solubility of **P1** in chloroform is ca. 45 mg/mL. Considering this result as well as the facile synthesis of **3**, the (HDMP)$_2$B group will be a useful and versatile group to prepare the soluble polymeric organoboron materials.

We estimated the molecular weights of the polymers by the GPC measurements using polystyrene as standards, although this method tends to overestimate the molecular weights for the rigid rod polymers.[12] The number-averaged molecular weights (M_n) for the polymers vary from 1.26×10^4 to 5.77×10^4 and the degrees of polymerization (DP) are in the range from ca. 10 to 59 (Table 1). The less efficient polymerization with bis(*p*-iodophenyl)amine is probably due to the presence of strong electron-donating amino groups on the aryl halides that typically has a detrimental effect on cross-coupling reactions.[13] Although the molecular weights are not significantly

high in some cases, all the produced polymers show a good film-forming ability, and the uniform thin films could be readily spin-coated from their solutions.

The photophysical properties of the boryl-substituted polymers **P1−P5** in benzene and in the solid state (spin-coated films obtained from cyclohexane solutions) are summarized in Table 1, together with the data of a model compound **7** (Table 1) for comparison.

To illustrate the effect of the polymerization, we first compared the photophysical properties of **P1** with those of its model compound **7** (Figure 2). In the absorption spectra in benzene, **P1** has an intense band at 432 nm (log ϵ = 4.45 per monomer unit), which is assigned as the intramolecular charge transfer (ICT) transition from the π-conjugated backbone to the diborylphenylene moiety. This absorption band is largely red-shifted compared to the corresponding absorption in **7**, which only shows a weak shoulder peak at ca. 400 nm (log ϵ = 3.94), demonstrating the effect of the π-conjugation extension in the polymeric form. In the fluorescence spectra, **P1** exhibits an intense bluish-green emission with a slightly broad emission band, unlike the sharp emissions of other conventional PAEs. The emission maximum wavelength of **P1** at 487 nm is comparable to that of **7**, indicative of the similar nature of the excited state between **P1** and **7**. However, notably, the polymer **P1** has a much higher quantum yield (Φ_F = 0.85 in benzene) than that of **7** (Φ_F = 0.14 in benzene). This difference is mainly ascribed to the difference in the radiative rate constant (k_r) from
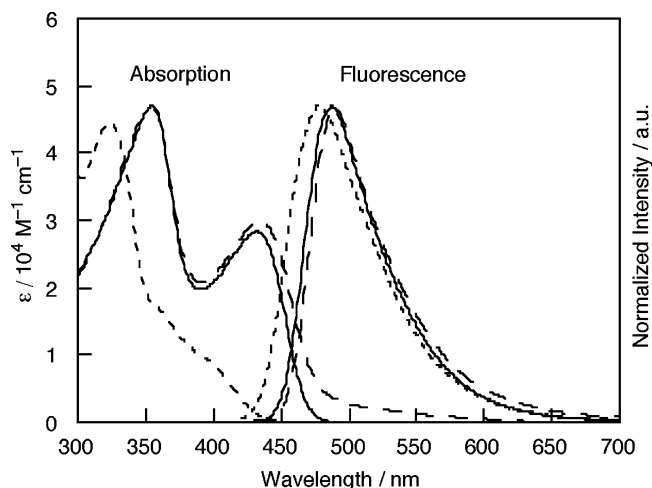
Figure 2. Absorption and fluorescence spectra of **P1** and **7:** solid line, **P1** in benzene; dashed line, **P1** in spin-coated film; dotted line, **7** in benzene. For the absorption spectrum of **P1** in spin-coated film, its intensity was normalized with that in benzene.
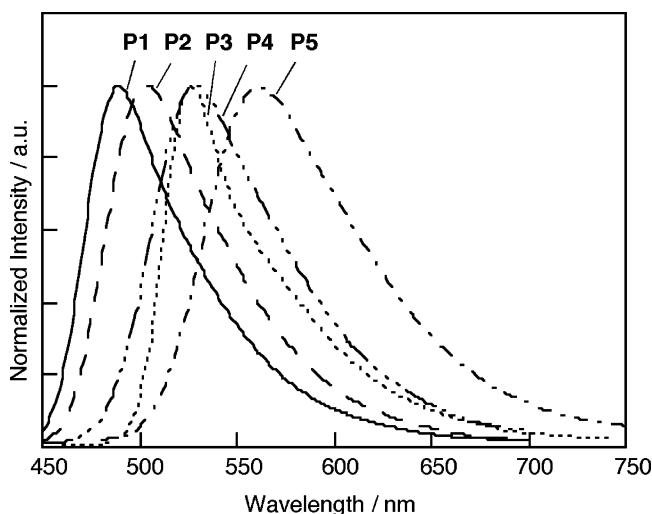
Figure 3. Fluorescence spectra of spin-coated films of **P1−P5**.

the singlet excited state. Thus, according to the calculation from the Φ_F and the lifetime (τ_s) of the excited state (**P1**, 1.8 ns; **7**, 2.6 ns), the k_r of **P1** (4.7×10^8 s^{-1}) is much higher than that of **7** (5.4×10^7 s^{-1}). This can be rationalized by considering that the π-conjugation extension enhances the oscillator strength of the transition and hence accelerates the radiative process.

It is also worth noting that the polymer **P1** maintains a bright fluorescence in the thin film, whose quantum yield ($\Phi_F = 0.62$) is even higher than that of **7** ($\Phi_F = 0.37$). Both the absorption and fluorescence spectra of the **P1** thin film are almost identical to those in benzene (Figure 2). These results prove the absence of aggregates in the ground state as well as excimers/exciplexes in the excited state, suggesting the effectiveness of the incorporation of the diborylphenylene skeleton into PAE systems for preventing interactions between the conjugated backbones.

The intense fluorescence is a general characteristic for the present boryl-substituted PAE π-conjugated systems. All of the other diborylphenylene-containing PAEs **P2**−**P5** display intense fluorescence in benzene with quantum yields ranging from 0.87 to 0.98. When going from a solution to a thin film, no obvious change was observed either in absorption or fluorescence spectra (see Supporting Information). More importantly, all of the polymers still retain a strong fluorescence ($\Phi_F = 0.36-0.54$) in the solid state. In addition, the fluorescence properties of these polymers are highly dependent on the electronic nature of the combined comonomer units (Figure 3). With an increase in the electron-donating ability of the comonomer units, the emission maxima gradually shifted to a longer wavelength from 504 nm for the 2,7-disubstituted fluorene-containing **P2** to 567 nm for the 4,4′-disubstituted-*N*-octyl-diphenylamine-containing **P5**, suggesting the possible emission color tuning by choosing the appropriate comonomer units.

In conclusion, we have synthesized a series of new poly-(aryleneethynylene)s containing diarylboryl groups as the side chains. Their excellent solution processability proves the significant utility of the newly prepared diarylboryl group, (HDMP)$_2$B, for producing the soluble polymeric organoboron materials. All the produced polymers showed an intense emission not only in solution but also in the solid state. This study clearly demonstrates the utility of the 2,5-diboryl-1,4-phenylene skeleton as a useful building block for emissive π-conjugated materials.

Supporting Information Available: Experiment procedures, absorption and emission spectra of **P1**−**P5**. This material is available free of charge via the Internet at http://www.pub.acs.org.

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MA0702997