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Highly Emissive Organic Solids Containing 2,5-Diboryl-1,4-phenylene Unit

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Boron-containing π-electron materials have attracted increased attention because of their unique properties stemming from the $p_\pi-\pi^*$ conjugation between the vacant p orbital on the boron atom with the π^* orbital of the π-conjugated framework.[1] The extensive studies on the organoboron compounds have demonstrated their potential uses for various photonic and optoelectronic applications, such as nonlinear optics,[2,3] two-photon excited emitters,[4] organic light-emitting diodes,[5,6] and fluorescent sensors.[7−9] Most of the reported systems either contain the boron atoms in the main chain or attach the boryl groups at the terminal positions of the π-conjugated framework (Figure 1a and b). We now disclose a new type of boron-based π-electron compounds, in which the boryl groups are introduced at the side positions (Figure 1c). As a π-electron-accepting core unit, we chose 2,5-bis(dimesitylboryl)-1,4-phenylene and designed novel donor−acceptor−donor (D−A−D) type quadrupolar π systems **1**−**4** (Figure 1d), in which the electron-donating amino groups were introduced at the terminal positions of the oligo(phenyleneethynylene) (OPE) or oligo(phenylenevinylene) (OPV) skeletons. We envisioned that the extension of the $p_\pi-\pi^*$ conjugation along the short axis of the π-conjugated framework as well as the incorporation of the bulky boryl groups at the side positions would lead to unique properties.[10] In fact, we found that these compounds showed intriguing intense fluorescence properties in the solid state.

The boryl-substituted OPEs **1**−**3** were prepared based on the Sonogashira reaction of appropriate diboryldiethynylbenzenes with aryl halides. The synthesis of the OPV derivative **4** was accomplished via a dilithiation of a dibromo-substituted distyrylbenzene derivative followed by treatment with dimesitylfluoroborane. All the compounds are stable to air and water and have high thermal stability. The decomposition temperature for a 5% weight loss (T_{d5}) of **1** is 373 °C. Among the compounds, the structure of **1** was determined by X-ray crystallography. This molecule has a significantly twisted main chain, in which the dihedral angle between the central and terminal benzene rings is 47.5°. This nonplanar structure arises from the steric hindrance of the bulky dimesitylboryl groups at the side positions.

The absorption and fluorescence spectra of the boryl-substituted OPE **1** are shown in Figure 2. In cyclohexane, **1** shows a moderately intense absorption band at 432 nm ($\log \epsilon = 4.30$). The TDDFT calculation (B3LYP/6-31G(d)) indicates that this band is assignable to the intramolecular charge transfer (CT) transition from the HOMO delocalized over the OPE framework to the LUMO localized on the diborylphenylene unit. Apparently, the vacant p orbitals on the boron atoms substantially contribute to this LUMO (Figure 3). In the fluorescence spectrum, despite the highly twisted structure, **1** exhibits a very intense emission at 536 nm with a quantum yield (Φ_F) of 0.99. It is worth noting that this emission band is strongly dependent on the solvent. A significant red shift is observed from 536 nm in cyclohexane to 601 nm in THF and 627 nm in methanol, whereas only a subtle solvent dependence is observed in the absorption maxima ($\lambda_{max} = 432$ nm in cyclohexane and 437 nm in THF). This result confirms that the diborylphenylene in the D−A−D system can work as the π-electron-accepting unit only in the excited state.

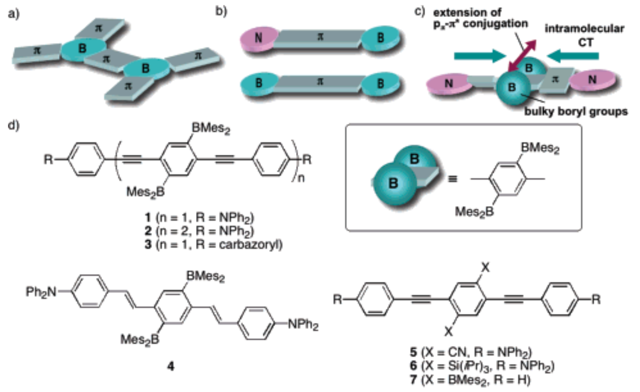

Figure 1. Schematic representation of organoboron π systems containing boron atoms or boryl groups (a) in the main chain, (b) at the terminal positions, and (c) at the side positions and (d) structures of **1**−**7**.

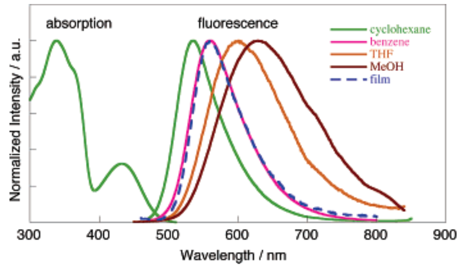

Figure 2. Absorption and fluorescence spectra of **1**.

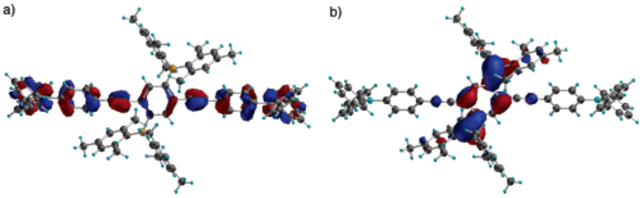

Figure 3. Pictorial presentation of (a) HOMO and (b) LUMO of **1** calculated at the B3LYP/6-31G(d) level using its crystal structure.

Notably, even in the solid state, **1** shows an intense fluorescence. In the spin-coated film, **1** shows an emission at 562 nm and retains a high quantum yield of 0.90, as determined by the calibrated integrating sphere system. It is also interesting to note that the emission spectrum is almost identical to that in benzene in terms of not only the maximum wavelength (559 nm in benzene), but also the fwhm, indicative of a comparable environment arisen in

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Table 1. Photophysical Properties of **1**, **5**, and **6**

compd		λ_{abs}/nm[a]	λ_{em}/nm[b]	Φ_F[c]	τ/ns
1	benzene	442	559	0.98	5.4
	film[d]	447	562	0.90	1.3/6.9 (37/63)[e]
5	benzene	465	520	0.98	2.2
	film[d]	489	575	0.29	0.4/3.0 (85/15)[e]
6	benzene	389	430	0.92	1.0
	film[d]	395	434	0.39	0.2/0.7 (93/7)[e]

[a] Only the longest absorption maxima are shown. [b] Excited at the longest absorption maxima. [c] Absolute quantum yield determined by a calibrated integrating sphere system within ± 3% errors. [d] Spin-coated from THF solution. [e] Amplitudes of two lifetimes are given in the parentheses.

the solid state and in the dilute benzene solution. A similar fluorescence property was also observed for the powder of **1**.

To elucidate the effect of the diborylphenylene skeleton, we compared the photophysical properties of **1** with those of **5** and **6**, which have electron-accepting cyano groups or neutral bulky triisopropylsilyl (TIPS) groups, respectively, in place of the dimesitylboryl groups (Table 1).

The dicyanophenylene skeleton also behaves as the π-electron-accepting unit mainly in the excited state, similar to the diborylphenylene unit. Thus, **5** exhibits large solvatochromism in the fluorescence spectra (λ_{max} = 482 nm in cyclohexane, 602 nm in THF), while in the absorption spectra only a slight blue shift is observed (λ_{max} = 464 nm in cyclohexane, 454 nm in THF). The most notable fact is that although **5** shows an intense fluorescence in benzene (Φ_F = 0.98), in the spin-coated film, the Φ_F of **5** significantly decreases to 0.29, in sharp contrast to the retained high Φ_F of **1**. This demonstrates the importance of a sterically bulky skeleton for attaining the intense solid-state emission, which can prevent the intermolecular interaction and hence the nonradiative energy migration through the Dexter mechanism. On the other hand, although compound **6** contains the bulky TIPS groups, the emission of it still significantly decreases from a Φ_F of 0.92 in benzene to a Φ_F of 0.39 in the solid-state. It is worth noting that the Stokes shift of **6** in the film is 2275 cm^{-1}, which is much smaller than those for **1** (4578 cm^{-1}). This result suggests that the electron-accepting character of diborylphenylene skeleton also plays an important role for the intense solid-state emission, possibly because it gives rise to the intramolecular CT transition with a large Stokes shift, which suppresses the self-quenching through the Förster mechanism.

The diborylphenylene skeleton as a bulky electron-accepting unit can satisfy both the steric and electronic demands for the intense solid-state emission. This effect can also be confirmed by the time-resolved photoluminescence study. All of **1**, **5**, and **6** show biexponential decays from the singlet excited states in the films. Whereas in **5** and **6**, the shorter-lived excited states, mainly dominated by the nonradiative process, are major components, in the boryl-substituted **1**, the major contribution is the longer-lived excited state, which is comparable to that in solution. As a consequence, **1** can retain the high Φ_F even in the solid state.

The intense solid-state fluorescence is a general characteristic for the present boryl-substituted π systems. All of the other derivatives **2**−**4** retain the high quantum yields of 0.73−0.86 in the films (Table 2). In contrast, compound **7**, without the electron-donating groups at the terminal positions, has a moderate Φ_F, again suggesting the importance of the intramolecular CT for the intense emission. In addition, by choosing appropriate terminal amino groups or π-conjugated frameworks, the emission color is widely tunable from green for the carbazolyl derivative **3** to reddish orange for the OPV derivative **4**.

Table 2. Photophysical Properties of Boryl-Substituted Compounds in the Spin-Coated Films

compd	λ_{abs}/nm[a]	λ_{em}/nm[b]	Φ_F[c]
1	447	562	0.90
2	442	555	0.86
3	400 (sh)	504	0.85
4	471	596	0.73
7	400 (sh)	476	0.43

[a] Only the longest absorption maxima are shown. [b] Excited at the longest absorption maxima. [c] Absolute quantum yield determined by a calibrated integrating sphere system within ± 3% errors.

While several intensely fluorescent compounds with the Φ_F close to unity in solution are known to date, only a few are in the solid state.[11] Development of such materials is a very fundamental subject for realizing many new optoelectronic applications, such as organic lasers. The present results not only disclose a new class of emissive organoboron materials, but also provide a firm direction in the design of emissive organic solids. The diborylphenylene skeleton is a unique skeleton for the emissive D−A−D systems, in terms of the high electron-accepting ability as well as the steric bulkiness. We believe that the present simple idea, incorporating the boryl groups as the side groups, will be the basis of further rational designs for functional emissive materials.

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Supporting Information Available: Experimental procedures, X-ray crystal data for **1**, theoretical calculation of **1**, photophysical data including the absorption and emission spectra of **1**, **5**, and **6**, and complete list of ref 2e. This material is available free of charge via the Internet at http://pubs.acs.org.

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