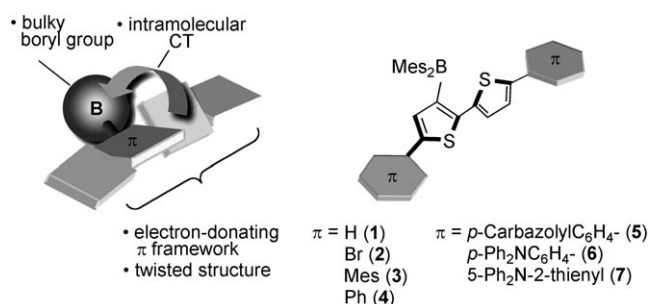


# 3-Boryl-2,2'-bithiophene as a Versatile Core Skeleton for Full-Color Highly Emissive Organic Solids\*\*

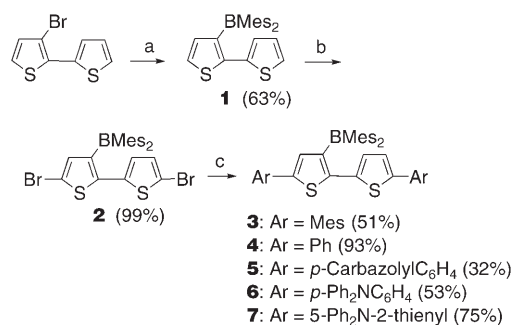
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The design and synthesis of highly emissive organic materials which can fluoresce even in the solid state is a fundamental and important requirement for various optoelectronic and photonic applications, such as organic light-emitting diodes, organic lasers, and sensors.<sup>[1]</sup> Whereas a number of molecules are known to be highly fluorescent in dilute solution, most of them tend to show a decreased fluorescence in the solid state because of certain intermolecular interactions that result in significant quenching of the emission. A problem that has to be overcome to achieve an intense solid-state emission is how to suppress the quenching processes. We recently reported the synthesis of boryl-substituted oligo(*p*-phenyleneethynylene)s and related compounds for the rational design of highly emissive organic solids.<sup>[2]</sup> While  $\pi$  systems bearing boryl groups generally have strong fluorescence in solution,<sup>[3–12]</sup> we showed that the introduction of bulky dimesitylboryl groups at the side positions of the electron-donating  $\pi$  framework is particularly effective for obtaining fluorescence quantum yields close to unity, even in the solid state. This property is attributable to two factors: First, the steric bulk of the boryl groups prevents intermolecular interaction. Second, a large Stokes shift resulting from the intramolecular charge-transfer (CT) transition from the electron-donating  $\pi$  system to the electron-accepting boron moiety diminishes the self-quenching in the condensed phase. On the basis of this design principle, we now disclose 3-boryl-2,2'-bithiophene-based  $\pi$ -conjugated materials as a new highly emissive system (Figure 1). The employment of the oligothiophene as an electron-donating  $\pi$  skeleton allows us to achieve not only an intense solid-state emission, but also full-color emissions covering a wide range—from blue (477 nm) to deep red (660 nm).

The parent compound 3-dimesitylboryl-2,2'-bithiophene (**1**) was synthesized by the lithiation of 3-bromo-2,2'-bithiophene followed by reaction with Mes<sub>2</sub>BF (Scheme 1). Dibromination of **1** with two equivalents of *N*-bromosuccinimide (NBS) produced the dibromide **2**. A series of  $\pi$ -extended derivatives **3–7** were prepared by palladium-catalyzed cou-



**Figure 1.** Schematic presentation of the molecular design of emissive organic solids and the structures of 3-boryl-2,2'-bithiophene derivatives 1–7. Mes = mesityl.



**Scheme 1.** Reagents and conditions: a) 1. *n*BuLi, diethyl ether,  $-78^{\circ}\text{C}$ , 2. Mes<sub>2</sub>BF; b) NBS, CH<sub>2</sub>Cl<sub>2</sub>; c) for **3** and **4**: ArB(OH)<sub>2</sub>, [Pd<sub>2</sub>(dba)<sub>3</sub>] $\cdot$ CHCl<sub>3</sub>, 2-(2',6'-dimethoxybiphenyl)dicyclohexylphosphine (S-Phos), K<sub>3</sub>PO<sub>4</sub>, toluene, 50  $^{\circ}\text{C}$ ; for **5–7**: ArSnBu<sub>3</sub>, [Pd<sub>2</sub>(dba)<sub>3</sub>] $\cdot$ CHCl<sub>3</sub>, P(2-furyl)<sub>3</sub>, THF, reflux. dba = *trans,trans*-dibenzylideneacetone.

pling reactions of **2** with appropriate aryl stannanes or aryl boronic acids.<sup>[13]</sup> All of the boryl-substituted bithiophene derivatives produced are stable in air and water, and can be purified by column chromatography on silica gel. These compounds have a high thermal stability; for example, the decomposition temperatures for a 5% weight loss ( $T_{\text{d}5}$ ) of **6** and **7** are 416 and 385  $^{\circ}\text{C}$ , respectively.

During the course of the synthesis we found that the parent compound **1** shows an intense sky-blue fluorescence with a maximum wavelength of 477 nm ( $\Phi_{\text{F}}$  0.66) in THF. This long emission wavelength is remarkable considering the short  $\pi$ -conjugation length of the bithiophene unit. To demonstrate its uniqueness we first compared it to its regioisomer, 5-dimesitylboryl-2,2'-bithiophene (**8**).<sup>[6b]</sup>

Figure 2 shows the crystal structure of **1**.<sup>[14]</sup> While **8** has a coplanar bithiophene framework, the bithiophene skeleton of the 3-boryl-substituted **1** is significantly twisted with a dihedral angle of 56.0 $^{\circ}$ , which apparently arises from the

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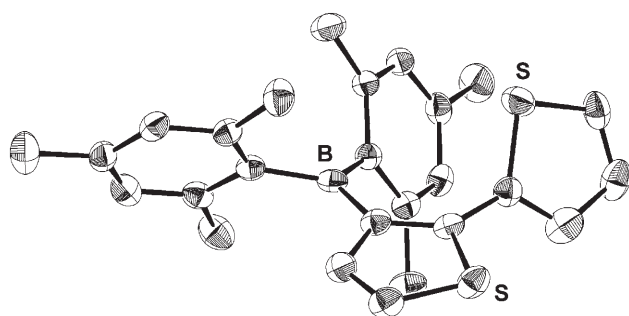


Figure 2. ORTEP drawing of **1** (50% probability for thermal ellipsoids).

steric congestion of the 3-boryl group. Despite this difference, the longest wavelength absorption maximum of both compounds are comparable (around 370 nm) in the UV/Vis spectra (Figure 3), although the molar extinction coefficient of **1** is much smaller ( $\log \epsilon = 3.65$ ) than that of **8** ( $\log \epsilon = 4.51$ ). According to TD-DFT calculations (B3LYP/6-31G(d)), the absorption bands of both **1** and **8** can be essentially assigned to the intramolecular charge-transfer transition from the highest occupied molecular orbital (HOMO) delocalized over the bithiophene moiety to the lowest unoccupied molecular orbital (LUMO) mainly localized on the boron center. In contrast to this similarity in the absorption spectra, significant differences are observed in the fluorescence properties. First, the wavelength of the emission maximum ( $\lambda_{\text{em}}$ ) of **1** is more than 40 nm longer than that of **8**. The Stokes shift of **1** exceeds 100 nm ( $5990 \text{ cm}^{-1}$ ), whereas that of **8** is only 56 nm ( $3500 \text{ cm}^{-1}$ ). This large Stokes shift is one notable characteristic of the present 3-boryl-bithiophene skeleton; presumably, it may be attributed to the change from the twisted structure to the planar structure in the excited state. Second, the lifetime of the singlet excited state ( $\tau_s$ ) of **1** (12 ns) is much longer than that of **8** (1.7 ns). According to calculations of the radiative ( $k_r$ ) and nonradiative ( $k_{\text{nr}}$ ) rate constants from the  $\Phi_F$  and  $\tau_s$  values, the  $k_r$  value ( $5.5 \times 10^7 \text{ s}^{-1}$ ) of **1** is much less than that of **8** ( $3.1 \times 10^8 \text{ s}^{-1}$ ). This finding is consistent with the transition of **1** being less-allowed, as observed in the

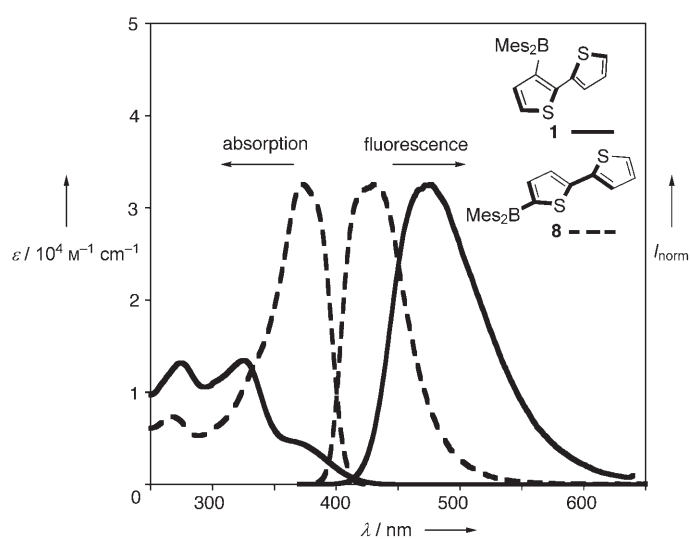


Figure 3. UV/Vis absorption and fluorescence spectra of borylbithiophenes **1** and **8** in THF.

absorption spectra. More noteworthy is that the  $k_{\text{nr}}$  value of **1** ( $2.8 \times 10^7 \text{ s}^{-1}$ ) is also less than that of **8** ( $2.8 \times 10^8 \text{ s}^{-1}$ ), thereby demonstrating the suppressed radiationless decay process in **1**, despite the larger Stokes shift in **1** than **8**. In addition to these differences, it is also worth noting that the fluorescence spectra of **1** show only a subtle solvent effect ( $\lambda_{\text{em}} = 457$  (cyclohexane), 477 (THF), 478 nm (MeOH)), which is indicative of a less-polarized excited state produced by the intramolecular charge-transfer transition,<sup>[15]</sup> unlike ordinary donor–acceptor-type  $\pi$ -electron systems.

In the present  $\pi$ -electron systems the emission comes from the singlet excited state generated by the intramolecular charge-transfer transition from the bithiophene moiety to the boron moiety, and thus the emission wavelength is highly dependent on the electron-donating ability of the  $\pi$ -conjugated framework of the bithiophene unit (Figure 4 and Table 1). Thus, the extension of the  $\pi$  conjugation with mesityl (**3**) or phenyl (**4**) groups shifts the emission maximum to 510 nm (green) and 543 nm (greenish yellow), respectively.

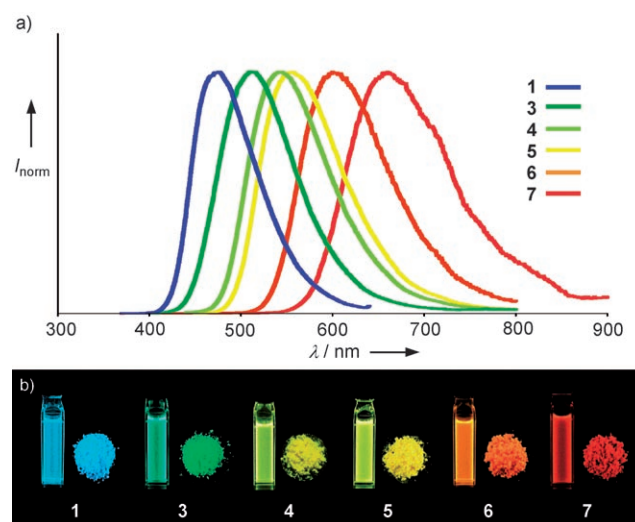


Figure 4. Fluorescence of 3-borylbithiophene derivatives **1** and **3–7**: a) Emission spectra measured in THF and b) photographs under irradiation at 365 nm.

The introduction of electron-donating carbazolyl (**5**) or diphenylamino (**6**) groups to the terminal phenyl rings causes further red-shifts to 557 nm (yellow) and 600 nm (reddish orange), respectively, with the retention of very high quantum yields (exceeding 0.90). Moreover, the introduction of an electron-donating 5-(diphenylamino)-2-thienyl group further shifts the emission wavelength. Thus, compound **7** has a deep-red emission at 660 nm with a Stokes shift of 195 nm in THF. This example is of particular interest from the viewpoint of converting a blue excitation light into a deep-red emission. Such emitting material with a large Stokes shift of about 200 nm is rather rare among the number of red fluorescence dyes reported to date.<sup>[16–18]</sup> Notably, the Stokes shift of **7** ( $6350 \text{ cm}^{-1}$ ) is comparable to that of **1** ( $5990 \text{ cm}^{-1}$ ). This fact demonstrates that the unique property of the 3-borylbithiophene skeleton directly affects the properties of its  $\pi$ -extended derivatives.

**Table 1:** Photophysical data of 3-borylbithiophene derivatives **1** and **3–8**.

Compd		Absorption $\lambda_{\text{abs}}$ (log $\epsilon$ ) <sup>[a]</sup> [nm]	Fluorescence $\lambda_{\text{em}}$ <sup>[b]</sup> ( $\Phi_{\text{F}}$ ) <sup>[c]</sup> [nm]	Stokes shift [nm] ([cm <sup>-1</sup> ])	Lifetime $\tau$ [ns]
1	THF film <sup>[d]</sup>	371 (3.65) 386	477 (0.66) 486 (0.55)	106 (5990) 100 (5330)	12.0
3	THF film <sup>[d]</sup>	384 (3.80) 385	510 (0.92) 515 (0.87)	126 (6430) 130 (6560)	8.9
4	THF film <sup>[d]</sup>	415 (4.02) 424	543 (0.90) 552 (0.85)	128 (5680) 128 (5470)	7.5
5	THF film <sup>[d]</sup>	422 (4.26) 430	557 (0.93) 564 (0.87)	135 (5740) 134 (5530)	5.2
6	THF film <sup>[d]</sup>	449 (4.31) 456	600 (0.90) 601 (0.60)	151 (5610) 145 (5290)	5.0
7	THF film <sup>[d]</sup>	465 (4.30) 479	660 (0.38) 657 (0.30)	195 (6350) 178 (5660)	3.0
8	THF	373 (4.51)	429 (0.53)	56 (3500)	1.7

[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 errors of  $\pm 3\%$ ). [d] Spin-coated film prepared from a THF solution.

The 3-borylbithiophene derivatives **1** and **3–7** show intense fluorescence not only in solution, but also in the solid state (Figure 4b). The decrease in the  $\Phi_{\text{F}}$  value of the spin-coated film relative to that of the THF solution is within 20% for **1** and **3–5**, and about 33% and 21% even for the orange-emissive **6** and red-emissive **7**, respectively. It is also worth noting that no significant difference in the fluorescence spectra of the THF solution and the spin-coated film, in terms of both the emission maximum wavelength and the full-width at half-maximum (fwhm), is observed for all the compounds. The intense solid-state emission is a rather general property for the present 3-boryl-bithiophene-based  $\pi$  systems.

We also investigated the electrochemical properties of the present systems to evaluate their potential applicability in electronic devices. Compounds **6** and **7** not only show reversible oxidation waves by cyclic voltammetry (**6**: +0.38 V; **7**: +0.14 V, versus ferrocene/ferrocenium (Fc/Fc<sup>+</sup>)), they also show reversible reduction waves (**6**: -2.24, -2.61 V; **7**: -2.18 V; see the Supporting Information). The high reversibility in their redox process demonstrates the substantial stability of the produced charged species, and is indicative of their potential use as emissive ambipolar-transporting materials.

In summary, a series of emissive 3-boryl-2,2'-bithiophene-based  $\pi$ -electron materials have been designed and synthesized. The results show the versatility of the 3-borylbithiophene skeleton for attaining an intense solid-state emission, with the maxima ranging over the whole visible region. Notably, even a red-emitting material with an extremely large Stokes shift of 195 nm could be obtained. The present results demonstrate the generality and effectiveness of our molecular design for creating highly emissive organic solids. A further study in which these materials are utilized for optoelectronic applications is now in progress.

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