

## Synthesis of Dithienobismoles as Novel Phosphorescence Materials

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**Summary:** Dithienobismoles having a bismole ring fused with a bithiophene system were prepared by the reactions of  $\beta,\beta'$ -dilithiobithiophenes with aryldihalo-bismuthanes, as novel phosphorescence materials.

Organic phosphorescence compounds are of current importance, because of their utility as emissive materials for high-performance organic light-emitting diodes (OLEDs), and many efforts to develop organic phosphorescence systems have been made.<sup>1,2</sup> However, most of the efficient organic phosphorescence compounds reported so far are complexes with a noble-metal or rare-earth-metal center and there is urgent need for the development of new systems without such rare-metal elements. On the other hand, oligo- and polythiophenes are currently receiving considerable attention as functional organic materials in the field of organic electronics.<sup>3</sup> The extended  $\pi$ -conjugation in these systems arising from the fairly good coplanarity of adjacent thiophene rings, and the sufficient thermal and chemical stability, allow the use of oligo- and polythiophenes as active components in organic electronic devices, such as OLEDs, thin-film transistors, sensors, and photovoltaic cells. Recently, bridging a bithiophene unit with a heteroatom at the  $\beta,\beta'$ -position to form a fused tricyclic system has been

well studied, which provides useful building blocks for the preparation of materials with even better conjugation than the parent bithiophene, not only by fixing the tricyclic units into a complete plane but also by electronic effects of the bridging atoms. Examples include dithienothiophene,<sup>4</sup> dithienopyrrole,<sup>5</sup> dithienoborole,<sup>6</sup> and dithienophosphole<sup>7</sup> and their oligomers and polymers. The unique properties and functionalities of these compounds have been demonstrated.

In this regard, we prepared dithienosiloles having a Si-bridged bithiophene system.<sup>8</sup> In the course of our studies concerning the functionalities of dithienosiloles, we found that dithienosiloles are generally highly emissive. For example, the solid-state fluorescence quantum yield of a dithienosilole with diphenylphosphino substituents is as high as 0.8 in the solid state (**DTS1** in Chart 1).<sup>9</sup> To explore further the scope of heteroatom-bridged bithiophene systems, we prepared dithienobismoles and investigated their optical properties. Bismuth is the heaviest abundant element of little environmental and biological concern, and its heavy-atom effects would lead to phosphorescence properties of the compounds.<sup>10</sup>

Dithienobismoles **DTBi1–DTBi4** were obtained in 41, 57, 30, and 20% yields, respectively, by the reactions of dilithiobithiophenes and aryldihalo-bismuthanes, as shown in Scheme 1. Their structures were verified by spectroscopic analysis as well as by elemental analysis. The solid-state structures of **DTBi2–DTBi4** were determined by X-ray diffraction studies, and the ORTEP drawing of **DTBi3** is

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(10) Only a few bismuth-containing compounds are known to exhibit phosphorescence.<sup>11,12</sup>

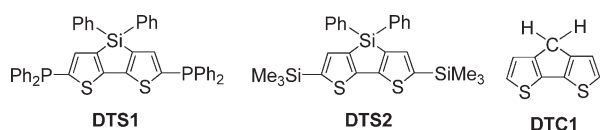
depicted in Figure 1a (for others, see Figures S-1 and S-2). Their structures possess essentially the same geometry for the dithienobismole tricyclic unit with almost complete planarity, independent of the substituents. All the bond lengths and angles are in the normal range, except for the small C(thiophene)–Bi–C(thiophene) angles of 78.3(2), 78.8(2), and 77.9(3)° for **DTBi2**–**DTBi4**, respectively, presumably due to the long Bi–C bonds. The structures were well reproduced by DFT calculations at the level of B3LYP/6-31G(d)/LANL2DZ, as presented in Figure 1b,c. These dithienobismoles are solids and are soluble in common organic solvents. **DTBi2** was stable in the solid state and could be stored for 10 months without detectable decomposition in air at room temperature, under room light, but underwent decomposition readily in a dilute solution. In fact, allowing the chloroform solution ( $10^{-5}$  g/L) of **DTBi2** to stand overnight led to the conversion of **DTBi2** to unidentified compounds (Figure S-4). Compound **DTBi1** was less stable and underwent decomposition slowly even in the solid state. In contrast, **DTBi3** and **DTBi4** were stable even in solution and no spectral changes were observed when the solutions stood for several weeks. It is likely that the methyl substituents and the benzo annulated units kinetically stabilize the bismole system.

Optical properties of the present dithienobismoles **DTBi1**–**DTBi4** are summarized in Table 1. The absorption maxima of **DTBi2** and **DTBi3** are at 356 and 359 nm (Figure 2a), which are comparable to that of similarly substituted dithienosilole **DTS2** ( $\lambda_{\max}$  354 nm) but red-shifted from that of

dithienocyclopentadiene **DTC1** ( $\lambda_{\max}$  323 nm) (Chart 1). Presumably, in the dithienobismole system, a  $\sigma^*-\pi^*$  type interaction operates to lower the LUMO energy level as shown in Figure 1c, similar to the case for dithienosilole. No obvious participation of the Bi  $\sigma$ -orbital in the HOMO is observed by the DFT calculations. The UV spectrum of **DTBi4** showed four maxima, two of which were at longer wavelength than those of **DTBi1**–**DTBi3**, indicating the extended conjugation in **DTBi4**, as expected.

The present dithienobismoles exhibited clear red emission in solution under an argon atmosphere, and the spectra revealed broad bands centered at 600–640 nm (Figure 2b), together with those around 400 nm. The former disappeared in air, indicating that this emission originated from phosphorescence (Figure S-5). The phosphorescence lifetimes in  $\text{CHCl}_3$  were determined to be approximately  $\tau = 2\text{--}6\ \mu\text{s}$  for **DTBi2**–**DTBi4** (Table 1). The phosphorescence quantum yields were approximately 0.2%, as given in Table 1. Compounds **DTBi2** and **DTBi3** were also phosphorescent in the solid state (Figure 3), while only fluorescence bands were observed from the solids of **DTBi1** and **DTBi4**. It is likely that the trimethylsilyl groups in **DTBi2** and **DTBi3** prevent the molecules from being stacked to suppress the concentration quenching even in the solid state. Usually, the smaller the singlet–triplet energy splitting  $\Delta E(S_1-T_1)$  of the molecule, the higher the phosphorescence quantum yield. However, the splitting of the present dithienobismoles estimated by theoretical calculations is  $\Delta E(S_1-T_1) = 1.1\text{--}1.3\ \text{eV}$ , which is much larger than that for well-known phosphorescent metal complexes ( $\Delta E(S_1-T_1) = 0.4\text{--}0.7\ \text{eV}$ ).<sup>1</sup> Since phosphorescence is no longer observed for organic compounds with  $\Delta E(S_1-T_1)$  greater than 1 eV usually, this is indicative of the large bismuth heavy-atom effects.

Chart 1



Scheme 1. Synthesis of Dithienobismoles

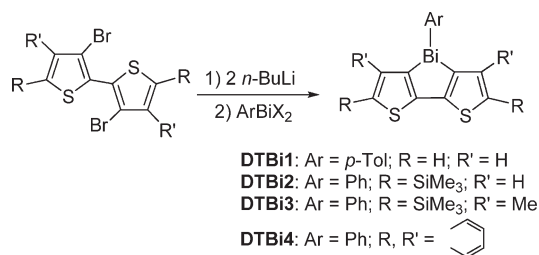
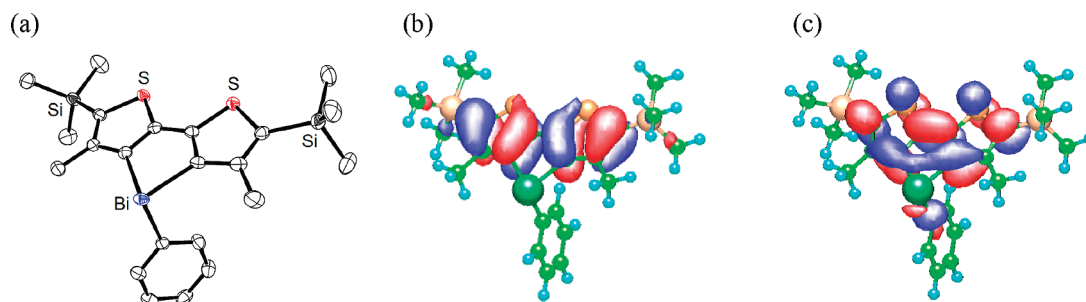


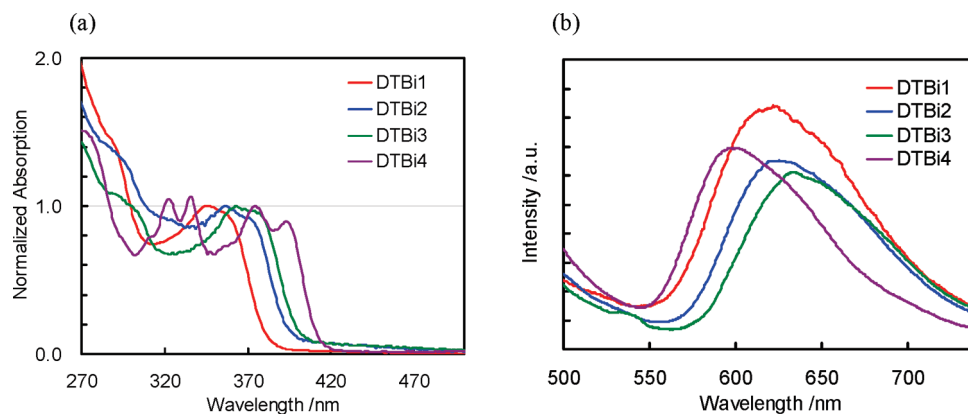
Table 1. Optical Properties of DTSi Derivatives

compd	UV–vis abs/nm <sup>a</sup>	phosphorescence $\lambda_{\text{em}}/\text{nm}$ ( $\Phi/\%$ ) <sup>b</sup>		$\tau/\mu\text{s}$ <sup>c</sup>
		in $\text{CHCl}_3$	solid	
<b>DTBi1</b>	346, 357	622 (0.2)	<sup>d</sup>	<sup>f</sup>
<b>DTBi2</b>	356, 371 <sup>c</sup>	625 (0.2)	620	5.2
<b>DTBi3</b>	359, 376 <sup>c</sup>	635 (0.2)	617	6.3
<b>DTBi4</b>	322, 336, 375, 392	601 (0.2)	<sup>d</sup>	2.1

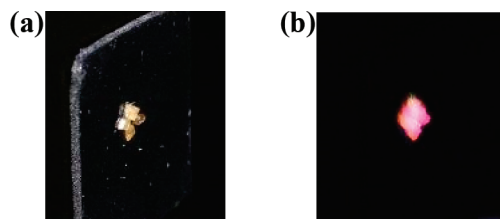
<sup>a</sup> In  $\text{CHCl}_3$ . <sup>b</sup>  $\lambda_{\text{ex}}$  380 nm; quantum efficiency ( $\Phi$ ) was determined by using a 5,10,15,20-tetraphenylporphyrinatozinc solution ( $\Phi = 3.3\%$ ) as the reference, which shows red fluorescence at 600 nm.<sup>13</sup> <sup>c</sup> Shoulder. <sup>d</sup> Not observed. <sup>e</sup> In  $\text{CHCl}_3$ ;  $\lambda_{\text{ex}}$  380 nm and  $\lambda_{\text{obs}}$  620 nm. <sup>f</sup> Not determined.



**Figure 1.** (a) ORTEP drawing of **DTBi3** with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi–C(thiophene) = 2.241(3), 2.265(3) Å; Bi–C(Ph) = 2.256(3) Å; C(thiophene)–Bi–C(thiophene) = 78.2(1)°; C(thiophene)–Bi–C(Ph) = 93.5(1), 96.9(1)°. (b) HOMO and (c) LUMO profiles of **DTBi3**, derived from DFT calculations at the level of B3LYP/6-31G(d)/LANL2DZ with ECP applied to Bi only.



**Figure 2.** (a) UV-vis absorption and (b) emission spectra of dithienobismoles ( $\lambda_{\text{ex}}$  380 nm) in  $\text{CHCl}_3$ . Emission spectra were recorded in argon.



**Figure 3.** Photos of **DTDi2** crystals in air at room temperature: (a) under room light; (b) under UV laser irradiation at 375 nm.

In conclusion, we prepared dithienobismoles and demonstrated their potential utilities as phosphorescence materials. It is noteworthy that **DTDi2** and **DTDi3** showed stable phosphorescence even in the solid state in air at room temperature. The large heavy-atom effects of bismuth in the system seem applicable to the development of novel

organic phosphorescence materials, and studies on the preparation of bismole derivatives with higher phosphorescence quantum yields are in progress.

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**Supporting Information Available:** CIF files giving crystallographic data for compounds **DTDi2**–**DTDi4**, and text, figures, and a table giving experimental details, ORTEP drawings of compounds **DTDi2** and **DTDi4**, HOMO and LUMO profiles of **DTDi1**, **DTDi2**, and **DTDi4** derived from theoretical calculations, emission spectra of **DTDi2** in chloroform as prepared and after standing for 2 weeks at room temperature in air, and emission spectra of **DTDi2** in air and under nitrogen. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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