

## Synthesis and Optical Properties of Dithienostiboles

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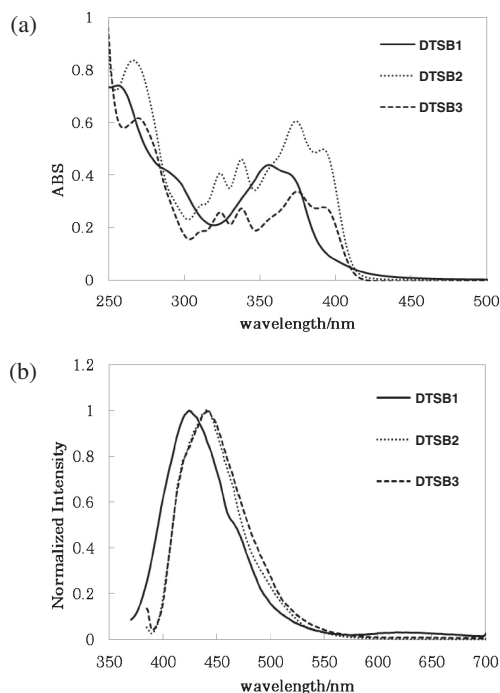
(Received June 28, 2012; CL-120692; E-mail: jo@hiroshima-u.ac.jp)

Dithienostiboles having a stibole ring fused with a bithiophene system were prepared by the reactions of  $\beta,\beta'$ -dilithiobithiophene derivatives with aryldichlorostibines. Their optical properties were examined with respect to the UV absorption and emission spectra. DFT calculations on a model were also carried out to understand the electronic states.

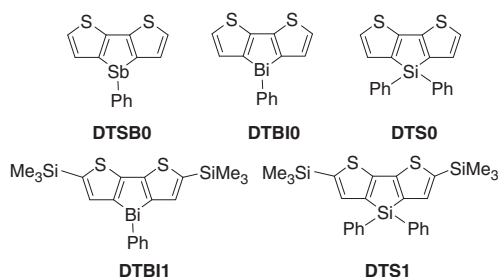
Heteroatom-bridged bithiophenes are useful building blocks for the synthesis of functional  $\pi$ -conjugated materials. In these systems, the bithiophene unit is sterically fixed to be planar by the bridge, enhancing the conjugation. The introduction of heavy elements, such as phosphorus,<sup>1</sup> silicon,<sup>2–5</sup> and germanium,<sup>5,6</sup> as the bridge is of particular interest, which often leads to the even more enhanced conjugation by its electronic effects. For example, silicon-bridged dithienosiloles (DTSs) show red-shifted UV absorption maxima from those of the carbon analogues, due to the bonding interaction between the bithiophene  $\pi^*$  and silicon  $\sigma^*$  orbitals, which lowers the LUMO energy levels.<sup>2</sup> Recently,  $\pi$ -conjugated polymers and oligomers with DTS units have been extensively studied as active materials for organic thin film transistors and solar cells. Similar studies on germanium-bridged dithienogermales have been also carried out.<sup>5,6</sup> In 2010, we reported the first synthesis of dithienobismoles (DTBIs) with bismuth as the bridging element.<sup>7</sup> Interestingly, these DTBIs have low-lying LUMO, like DTSs, and exhibit red-colored phosphorescence even in the solid states under ambient conditions, in air at room temperature, probably ascribed to the bismuth heavy atom effects. In the course of our studies concerning electronic effects of the bridging heavy elements, we prepared antimony-bridged dithienostiboles (DTSBs) and examined their electronic states with respect to the UV absorption and emission spectra, as well as by DFT calculations on a model molecule.<sup>8</sup>

The reactions of  $\beta,\beta'$ -dilithiobithiophene derivatives with aryldichlorostibines afforded the corresponding dithienostiboles (**DTSB1**–**DTSB3**) as shown in Scheme 1.<sup>10</sup> They were yellow or green solids and could be purified by gel permeation chromatography or recrystallization. Figure 1 depicts UV absorption and emission spectra of the DTSBs and the data are summarized in Table 1, together with those of the related compounds reported previously. As shown in Figure 1, **DTSB1** exhibited the UV absorption and emission bands around 350 nm, which was little shifted from those of **DTS1**<sup>3</sup> and **DTBI1**<sup>7</sup> (Chart 1 and Table 1).

To understand the electronic states of DTSB, we carried out DFT calculations on a model molecule **DTSB0** at the level of B3LYP/LanL2DZ.<sup>10</sup> The HOMO–LUMO energy gap of **DTSB0** is almost the same as those calculated for **DTS0**<sup>3</sup> and **DTBI0**<sup>7</sup> at the same level, as listed in Table 2, in accordance with the optical

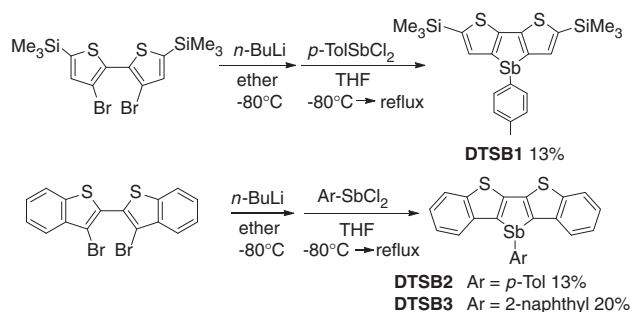


**Figure 1.** (a) UV absorption and (b) emission spectra of DTSBs in chloroform.



**Chart 1.** Bridged bithiophenes.

data. However, both the HOMO and LUMO of **DTSB0** are at slightly lower energies than those of **DTBI0**, similar to **DTS0**. Figure 2 shows the HOMO and LUMO profiles of **DTSB0** that indicate the interaction between the bithiophene  $\pi^*$  and the antimony vacant orbital, possibly Sb–C  $\sigma^*$  or Sb vacant atomic orbital in the LUMO to stabilize it, as generally observed for DTBI and DTS. No evident interaction between bithiophene  $\pi$  and the antimony orbital is seen in the HOMO.



Scheme 1. Synthesis of DTSBs.

Table 1. Properties of bridged bithiophenes

Compound	UV abs $\lambda_{\max}/\text{nm}$	Emission <sup>c</sup> $\lambda_{\max}/\text{nm}$	Mp/ <sup>o</sup> C
<b>DTSB1</b>	355	420, 625	117.5 <sup>d</sup>
<b>DTSB2</b>	266, 323, 337, 374	437	204.7 <sup>d</sup>
<b>DTSB3</b>	269, 323, 338, 374	443	248.5 <sup>d</sup>
<b>DTBI1</b> <sup>a</sup>	356	400, 625	114–116 <sup>e</sup>
<b>DTS1</b> <sup>b</sup>	356	425	158–156 <sup>e</sup>

<sup>a</sup>Ref. 7. <sup>b</sup>Ref. 3. <sup>c</sup>Excited at the absorption  $\lambda_{\max}$ . <sup>d</sup>Determined by DSC.

<sup>e</sup>Determined by visual observation.

Table 2. HOMO and LUMO energy levels of dithienometalloles, derived from DFT calculations at B3LYP/LanL2DZ

Compound	HOMO/eV	LUMO/eV	LUMO–HOMO/eV
<b>DTSB0</b>	–5.67	–1.77	3.90
<b>DTBI0</b>	–5.59	–1.69	3.90
<b>DTS0</b>	–5.65	–1.76	3.89

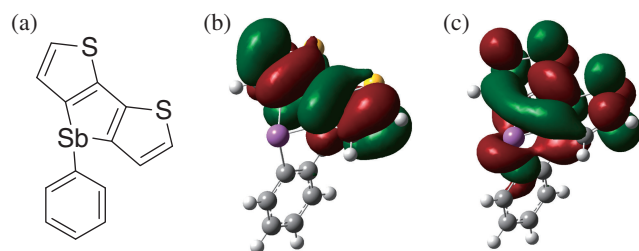


Figure 2. (a) Structure, and (b) HOMO and (c) LUMO profiles of DTSB0, derived from DFT calculations.

Dithienostiboles **DTSB2** and **DTSB3** showed red-shifted absorption and emission maxima from those of **DTSB1**, reflecting the expanded  $\pi$  conjugation. No remarkable substituent effects on the optical properties are observed for **DTSB2** and **DTSB3**. Emission spectra of the present DTSBs exhibited maxima at 420–443 nm with quantum efficiencies of 1–2%, similar to DTBI1.<sup>7</sup> The solid-state emission was investigated for **DTSB3** that showed a broad band at  $\lambda_{\max} = 461$  nm, red-shifted by about 30 nm from that in chloroform, suggesting intermolecular interaction in the solid states. Interestingly, a broad band centered at 625 nm was also observed for **DTSB1** both in the solution phase and the solid states, similar to the phosphorescence peak of DTBI1. However, this peak was too weak to investigate its origin in detail. The present DTSBs were stable in the solid states and could be

handled under ambient conditions. However, they were photoactive and irradiation of the THF solutions in argon for 1 h with a low-pressure UV lamp (254 nm) resulted in the complete decomposition of the DTSBs. Although we have not yet obtained experimental data to discuss the detailed mechanism, naphthalene and bi(benzothiophene) were detected in the photolyzed solution of **DTSB3** in 10 and 5% yields, respectively, suggesting the photochemical cleavage of the Sb–C bonds.

In conclusion, we prepared DTSBs as the first compounds with a stibole core fused with two or more heteroaromatic rings.<sup>8</sup> The optical and computational studies indicated that they possess the expanded conjugation with low-lying HOMO and LUMO, like DTS. Taking the widely accepted utilities of heteroatom-bridged bithiophenes into account, DTSB would show interesting functionalities and studies concerning the synthesis of DTSB-containing  $\pi$ -conjugated functional materials are under way. Such antimony–heteroaromatic compounds seem to be also of interest in biological aspects.<sup>9</sup>

This work was partly supported by MEXT KAKENHI (No. 24102005).

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- 10 Supporting Information including experimental and computational details is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.