

# Synthesis of Bis(diarylphosphino)dithienosilole Derivatives as Novel Photo- and Electroluminescence Materials<sup>†</sup>

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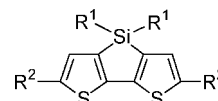
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Bis(diarylphosphino)dithienosiloles and their oxidized species were synthesized, and their optical properties were studied. They showed efficient photoluminescence (PL) in solutions as well as in the solid states, which was markedly affected by the phosphine oxidation states. The bis(diphenylphosphino) derivative exhibited reversible changes of the PL spectra in solutions upon interaction with Lewis acids. The electroluminescence properties were also examined, and a whitish-blue-green emission with a maximum luminance of ca. 130 cd/m<sup>2</sup> was observed from a double-layered device having vapor-deposited films of bis(dinaphthylphosphino)dithienosilole dioxide and *N,N'*-diphenyl-*N,N'*-di-*m*-tolylbiphenyl-4,4'-diamine as the emitting and hole-transporting electron-blocking layers, respectively.

## Introduction

Siloles (silacyclopentadienes) have been extensively studied as novel conjugated compounds. Bonding interaction between the silicon  $\sigma^*$  and butadiene  $\pi^*$  orbitals lowers the lowest unoccupied molecular orbital (LUMO) energy level, leading to the unique electronic states.<sup>1</sup> This allows numerous applications of silole-containing compounds as functional materials, such as electron-transporting materials for multilayered electroluminescence (EL) devices<sup>2</sup> and conducting polymers.<sup>3</sup> Highly photoluminescence (PL) and EL properties have also often been noted for silole derivatives.<sup>4</sup> Previously, we have introduced dithienosilole (DTS) as a novel type of silole system (Chart 1), and it has been demonstrated that the DTS derivatives exhibit enhanced conjugation compared with the corresponding silole-free bithiophenes.<sup>5</sup> For example, the UV absorption maximum of poly[4,4-bis(4-butylphenyl)dithienosilole-2,6-diyl] was at 561

Chart 1. Structure of DTS



nm in tetrahydrofuran, which was largely red-shifted from that of poly(3-hexylthiophene) (HT > 95%;  $\lambda_{\text{max}} = 458$  nm).<sup>6</sup> Recently, it was reported by Usta et al. that similar DTS–thiophene alternate polymers exhibited highly semiconducting properties, being applicable to field-effect transistors.<sup>7</sup> The extended conjugation in the DTS system is due to not only  $\sigma^*-\pi^*$  interaction but also its complete planarity. The DTS derivatives were usable as electron-<sup>8</sup> and hole-<sup>9</sup>-transporting materials for multilayered EL devices, depending on the substituents on the DTS ring. In addition, DTS derivatives often exhibit highly PL properties; e.g.,  $\Phi_{\text{em}} = 0.79$  for DTS-1 (Chart 1; R<sup>1</sup> = Ph; R<sup>2</sup> = SiMe<sub>3</sub>) in chloroform.

Recently, photophysical properties of an anthracene derivative bearing diphenylphosphino groups at the 9 and 10 positions and its oxidized species have been reported. Interestingly, the sulfide was found to be emissive, more efficiently in the crystal form than in solutions.<sup>10</sup> Aiming at developing DTS-based novel luminescence materials, we prepared bis(diarylphosphino)-substituted DTSs and their oxides and sulfide. These compounds exhibited efficient PL in solutions as well as in the solid states, which was considerably affected by the phosphine oxidation states. Bis(diphenylphosphino)dithienosilole showed chromic behaviors in response to the coexisting Lewis acids in solutions.

<sup>†</sup> This paper is dedicated to the late Professor Yoshihiko Ito, who passed away on December 23, 2006.

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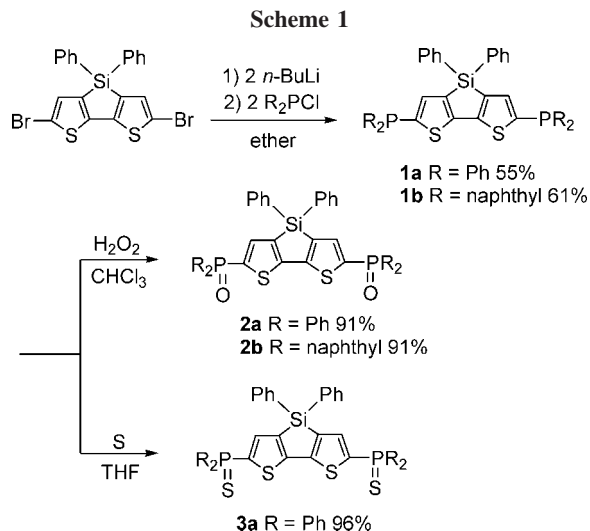
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EL properties of the present DTS derivatives in single- and double-layered devices with the structures of indium–tin oxide (ITO)/DTS/Mg–Ag and ITO/TPD/DTS/Mg–Ag, respectively, were also studied.

## Results and Discussion

**Synthesis and Optical Properties of Bis(diarylphosphino)-dithienosilole Derivatives.** 2,6-Bis(diphenylphosphino)-4,4-dithienosilole (**1a**) was synthesized by treatment of dilithiated DTS with chlorodiphenylphosphine in 55% yield, as shown in Scheme 1. Treatment of **1a** with aqueous hydrogen peroxide and sulfur afforded the corresponding oxide (**2a**) and sulfide (**3a**) in 91% and 96% yields, respectively. Bis(dinaphthylphosphino)dithienosilole (**1b**) was also obtained in moderate yield by a reaction similar to that for **1a**. However, a small amount of a byproduct was found to be formed in approximately 10% yield in this reaction, which could not be separated from **1b** by either chromatography or recrystallization. Treatment of **1b** containing the byproduct with aqueous hydrogen peroxide, followed by recrystallization of the organic products, gave the oxide (**2b**) in a pure form. These DTS derivatives were wholly characterized by spectrometric analysis (see the Experimental Section).

Table 1 summarizes the optical properties of compounds **1a–3a** and **2b**. The UV absorption maximum of **1a** appeared at 380 nm, which was red-shifted from that of DTS-2 (see Chart 1;  $R^1 = \text{Ph}$ ;  $R^2 = \text{H}$ ;  $\lambda_{\text{max}} = 345 \text{ nm}$ ; Figure 1) and silole-free bis(diphenylphosphino)bithiophene (**4a**; see Chart 2;  $\lambda_{\text{max}} = 350 \text{ nm}$ ),<sup>11</sup> indicating the effects of the phosphine substituents and the silole ring on the electronic state of **1a** and enhancing the conjugation. The emission maximum of **1a** was also at lower energy than those of DTS-2 ( $\lambda_{\text{em}} = 420 \text{ nm}$ ) and **4a** ( $\lambda_{\text{em}} = 430$  and  $460 \text{ nm}$ ).<sup>11</sup> Figure 2 represents the highest occupied molecular orbital (HOMO) and LUMO energy levels of model compounds (**1c**, **4c**, and DTS-3 in Chart 2) derived from molecular orbital (MO) calculations. The optimized geometries of compounds **1c** and **4c** possess the phosphine lone-pair orbital lying in the same plane as the adjacent thiophene ring. As can be seen in Figure 2, the lower-lying LUMO is primarily responsible for the smaller HOMO–LUMO energy gap of **1c** than those of DTS-3 and **4c**. Electronic effects of phosphino substitution on a thiophene ring, lowering the LUMO energy level, have been reported previously.<sup>11</sup> As the phosphine atoms

were oxidized, both the absorption and emission bands were shifted to higher energies, similar to 2,6-bis(methylthio)-4,4-diphenyldithienosilole (Chart 1;  $R^1 = \text{Ph}$ ;  $R^2 = \text{SMe}$ ), whose oxidation producing its sulfoxide and sulfone also resulted in blue shifts of the absorption bands.<sup>9</sup> Cyclic voltammograms (CVs) of the present DTS compounds showed irreversible profiles similar to simple DTSSs.<sup>5</sup> The oxidation peaks moved to higher potentials in the order of **1a** < **3a** < **2b** < **2a**. Table 2 summarizes the results of MO calculations for models **1c–3c** (see Chart 2). Two or three stable isomers were optimized for each of the compounds, with respect to the C–P bond rotation. Although the electronic states of these compounds are markedly affected by the rotation, the HOMOs of the isomers of **1c** are always at much higher energies than those of **2c** and **3c**, in accordance with the lower CV oxidation potential for **1a**. However, the red-shifted absorptions in the order of **2a** < **3a** < **1a** could not be clearly reproduced by the MO calculations. This is probably due to the effects of the substituents and solvents, which would influence the geometries of the compounds, in particular the C–P bond rotation.

The absolute PL quantum yields ( $\Phi_{\text{em}}$ ) were measured in an integrating sphere, as listed in Table 1. Interestingly, oxide **2a** exhibited much higher  $\Phi_{\text{em}}$  than **1a** in solution, while  $\Phi_{\text{em}}$  of sulfide **3a** was lower than that of **2a**. Compound **2b** was also found to be highly emissive in chloroform. On the basis of these results, we examined chromic behaviors of **1a** upon contact with Lewis acids in solutions. As can be seen in Table 1 and Figure 3, quenching of the lone pairs on phosphine atoms by interaction with Lewis acids led to blue shifts of the absorption and emission bands. In addition, the emission efficiencies were markedly enhanced by the interaction to reach the high value of  $\Phi_{\text{em}} = 0.98$  for **1a** upon treatment with  $\text{BF}_3\text{--Et}_2\text{O}$  in chloroform. This process was reversible and the original emission was recovered when methanol or ethanol was added to the solutions (Figure 4). Washing the solutions with aqueous  $\text{NaHCO}_3$  also gave rise to the original absorption and emission spectra.

It was noteworthy that compound **1a** exhibited a quite high PL efficiency of  $\Phi_{\text{em}} = 0.79$  in the solid state (Figure 5). The PL maximum of **1a** in the solid state was observed at almost the same wavelength ( $\lambda_{\text{em}} = 464 \text{ nm}$ ) as that in chloroform, indicating that no intermolecular interaction took place in the solid state. PL lifetimes of **1a** were measured under different conditions, and it was found that all of the decay curves fitted the first-order single-component simulation with parameters listed in Table 3. Presumably, sterically large phenyl groups on phosphine and silicon atoms cover the DTS fluorophore to prevent the concentration quenching even in the solid state.

**EL Properties of Bis(diarylphosphino)dithienosilole Derivatives.** We examined these compounds as single-layered EL device materials. As summarized in Table 4, the devices (ITO/DTS (90 nm)/Mg–Ag) having vapor-deposited films of the present DTS derivatives emitted whitish-blue-green light except for compound **1a**, which did not emit detectable light in the single-layered device. However, the luminance of the devices was always low, in spite of the high current density. In particular, the maximum current density of the device with **2b** was  $610 \text{ mA/cm}^2$ , while the maximum luminance of the same device was only  $0.6 \text{ cd/m}^2$ . This was probably ascribed to the low current–luminescence conversion. We then turned our attention to the use of **2b** as an emissive material in a multilayered system and fabricated a double-layered device with the structure of ITO/TPD (40 nm)/**2b** (50 nm)/Mg–Ag, in which the TPD layer was employed as a hole-transporting electron-

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Table 1. Optical Properties of DTS Derivatives 1a–3a and 2b

compd	additive in CHCl <sub>3</sub>	absorption <sup>a</sup> λ <sub>max</sub> /nm (λ <sub>edge</sub> /eV) in CHCl <sub>3</sub>	emission λ <sub>em</sub> /nm in CHCl <sub>3</sub> (powder)	Φ <sub>em</sub> in CHCl <sub>3</sub> (powder) <sup>b</sup>	CV Pa/V <sup>c</sup>
1a	none	380 (2.79)	465 (464)	0.22 (0.79)	0.8
	BF <sub>3</sub> –Et <sub>2</sub> O <sup>d</sup>	363	420	0.98	
	CF <sub>3</sub> CO <sub>2</sub> H <sup>d</sup>	364	424	0.91	
2a	none	361 (3.05)	422 (434)	0.85 (0.41)	1.5
3a	none	369 (2.99)	433 (442)	0.13 (0.47)	1.3
2b	none	363 (3.05)	425 (434)	0.71 (0.43)	1.4
DTS-2	none	345 (3.21)	420 (434)	0.29 (0.24)	1.1

<sup>a</sup> Excited at absorption max. <sup>b</sup> Excited at 323 nm. <sup>c</sup> Oxidation peak potential vs Ag/AgCl. <sup>d</sup> A 100 M excess of the additive was added.

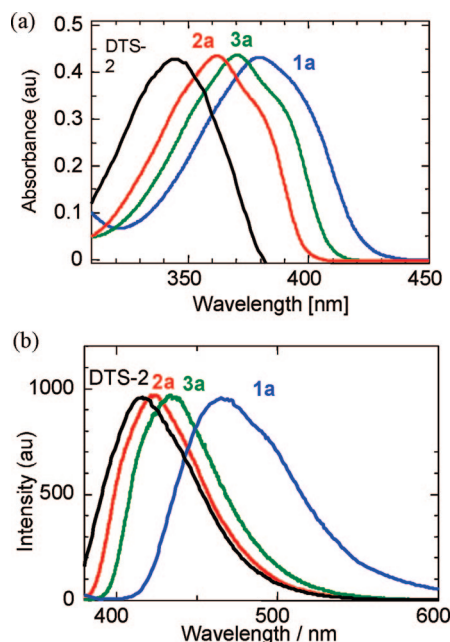


Figure 1. (a) UV absorption and (b) emission spectra of DTS derivatives in chloroform.

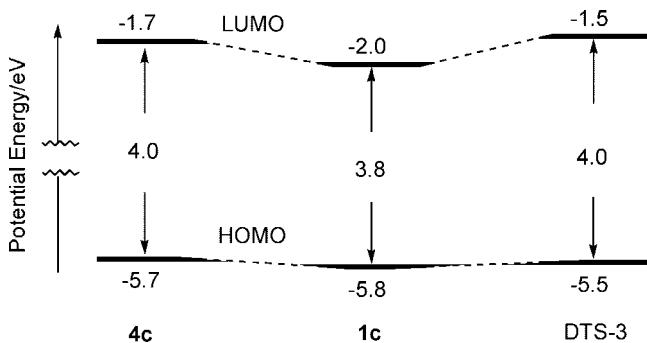
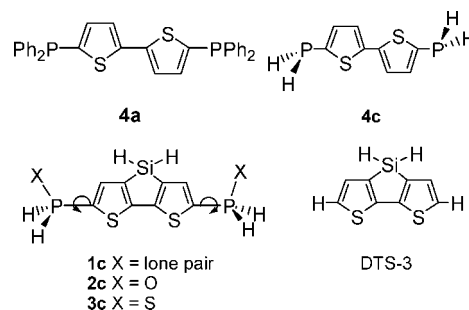


Figure 2. Relative HOMO and LUMO energy levels of the simplified model compounds, derived from MO calculations at the level of B3LYP/6-31G(d,p).

blocking layer. The maximum luminance from this device was 130 cd/m<sup>2</sup> at the applied voltage of 8 V, as shown in Figure 6. The EL spectrum showed the band at approximately 500 nm, which was red-shifted by 60–70 nm from the solid-state PL maximum of **2b**. The origin of this red shift is not yet clear. However, similar red shifts have been reported for silole-based multilayered EL devices, arising from the exciplex formation with electron- and hole-transporting materials in the interface structures.<sup>12</sup>

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Chart 2

Table 2. HOMO and LUMO Energy Levels for Model Compounds 1c–3c<sup>a</sup>

compd	C=C–P–X <sup>b</sup> dihedral angle/deg	ΔH <sup>c</sup> /kcal mol <sup>-1</sup>	potential energy/eV		
			HOMO	LUMO	ΔE/eV
1c	0	0	-5.8	-2.0	3.8
	154	3.4	-5.6	-1.8	3.8
2c	0	0.3	-6.3	-2.4	3.9
	108	0	-6.4	-2.6	3.9
	180	2.3	-6.2	-2.3	3.9
3c	0	0	-6.4	-2.6	3.8
	120	0.9	-6.3	-2.6	3.7
	180	2.7	-6.4	-2.5	3.9

<sup>a</sup> Derived from MO calculation at the level of B3LYP/6-31G(d,p).  
<sup>b</sup> For **1c**, the angle was estimated assuming that the lone-pair orbital lies in the middle of the P–H bonds. <sup>c</sup> Relative heat of formation of the rotation isomers.

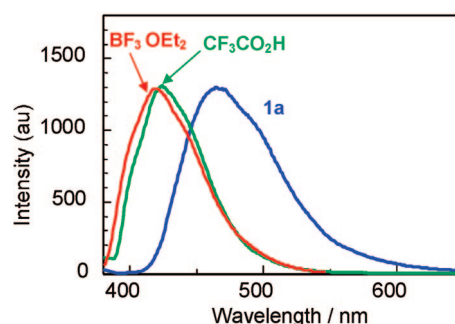
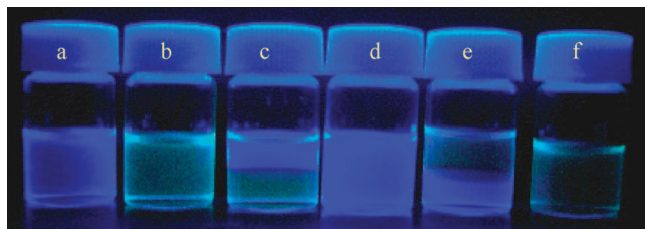


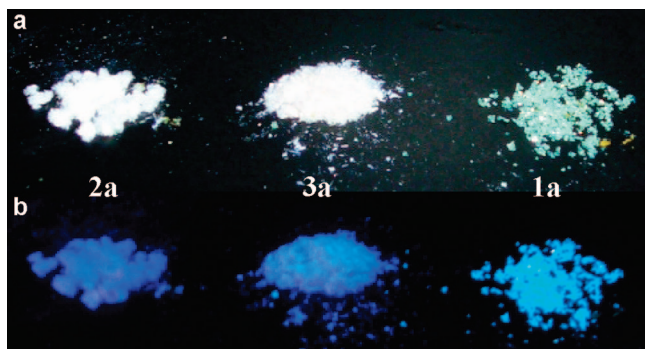
Figure 3. Emission spectra of **1a** in the presence and absence of Lewis acids in chloroform.

In conclusion, we prepared bis(diarylphosphino)dithienosilole derivatives that showed efficient PL properties. In particular, compound **1a** was found to be highly emissive even in the solid state with Φ<sub>em</sub> = 0.79. Compound **1a** exhibited interesting chromic behaviors, in response to the coexisting Lewis acids, in solutions. Although EL properties of the vapor-deposited films of these compounds in the single-layered devices were not as good as we expected from their efficient PL properties, oxide **2b** was found to be potentially useful as the multilayered EL materials.





**Figure 4.** Photograph of chloroform solutions irradiated at 365 nm of (a) **2a**, (b) **1a**, (c) **1a** upon the addition of  $\text{BF}_3\text{-Et}_2\text{O}$ , with the upper part being emissive, (d) **1a** +  $\text{BF}_3\text{-Et}_2\text{O}$ , after swirling, (e) **1a** +  $\text{BF}_3\text{-Et}_2\text{O}$  upon the addition of methanol, with the upper part being nonemissive, and (f) **1a** +  $\text{BF}_3\text{-Et}_2\text{O}$  after swirling with methanol.



**Figure 5.** Photographs of DTS derivatives (a) under room light and (b) upon irradiation at 365 nm.

**Table 3. PL Decay Parameters for 1a**

conditions	$\tau/\text{ns}$	$k_r/\text{ns}^{-1}$	$k_{nr}/\text{ns}^{-1}$	$\chi^2$
in $\text{CHCl}_3$	2.2	0.10	0.35	1.6
with $\text{BF}_3\text{-Et}_2\text{O}$ in $\text{CHCl}_3$	2.9	0.33	0.01	1.3
powder	3.9	0.20	0.05	2.9

**Table 4. Performance of Single-Layered EL Devices with DTS Derivatives<sup>a</sup>**

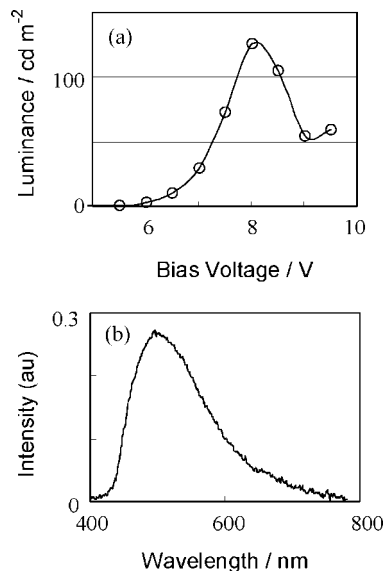
compd	max luminance/ $\text{cd m}^{-2}$ (applied voltage/V) <sup>b</sup>	max current density/ $\text{mA cm}^{-2}$ (applied voltage/V) <sup>b</sup>
<b>2a</b>	5.4 (15)	320 (16)
<b>3a</b>	4.6 (18)	200 (19)
<b>2b</b>	0.6 (11)	610 (11)

<sup>a</sup> ITO/DTS (90 nm)/Mg-Ag. <sup>b</sup> Applied voltage resulting in the maximum value.

## Experimental Section

**General Procedures.** All reactions were carried out in dry nitrogen. Ether was distilled from a sodium-potassium alloy, and benzonitrile was distilled from  $\text{P}_2\text{O}_5$ . Time-of-flight mass spectrometry (TOF-MS) spectra were measured on a Shimadzu Kompact Multi2 spectrometer. NMR spectra were measured on a JEOL model LA-400 spectrometer. UV absorption and emission spectra were recorded on Shimadzu model UV3150 and F4500 spectrophotometers, respectively. Emission quantum yields were determined in an integrating sphere fitted with a Hamamatsu Photonic Multi-Channel Analyzer C7473. The hydrolytic workup mentioned below involves hydrolysis of the reaction mixture with water, separation of the organic layer, extraction of the aqueous layer with chloroform, drying of the combined organic layer and extracts over anhydrous magnesium sulfate, and evaporation of the solvent, in this order.

**Synthesis of Bis(phosphino)dithienosiloles.** To a solution of 3.37 g (6.69 mmol) of 2,6-dibromo-4,4-diphenyldithienosilole in 55 mL of ether was added 8.47 mL (13.4 mmol) of a 1.58 M



**Figure 6.** (a) Luminance-voltage plots for the double-layered EL device with the structure of ITO/TPD/**2b**/Mg-Ag. (b) EL spectrum from the device at the applied voltage of 8 V.

*n*-butyllithium/hexane solution at  $-80^\circ\text{C}$ , and the mixture was stirred for 3 h at room temperature to complete the dilithiation. The resulting mixture was again cooled to  $-80^\circ\text{C}$ , and a solution of 2.40 mL (13.4 mmol) of chlorodiphenylphosphine in 10 mL of ether was added to the mixture. After hydrolytic workup, the residue was subjected to silica gel column chromatography using chloroform/hexane (1:1) as the eluent to give a crude solid, which was then recrystallized from chloroform/ethanol to give 2.64 g (55% yield) of **1a** as a yellow solid: mp  $239.0\text{--}239.2^\circ\text{C}$ ; TOF-MS  $m/z$  714 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 7.38–7.52 (m, 26H), 7.61 (d, 2H,  $J_{\text{H-P}} = 6.5$  Hz, thiophene ring H), 7.72 (dd, 4H,  $J = 8.0$  and 1.2 Hz, *o*-SiPh);  $^{13}\text{C}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 128.3 (d,  $J_{\text{C-P}} = 19$  Hz), 128.5, 128.8, 130.4, 131.2, 132.9 (d,  $J_{\text{C-P}} = 20$  Hz), 135.3, 137.8 (d,  $J_{\text{C-P}} = 8$  Hz), 139.6 (d,  $J_{\text{C-P}} = 32$  Hz), 140.4 (d,  $J_{\text{C-P}} = 33$  Hz), 141.1 (d,  $J_{\text{C-P}} = 8$  Hz), 156.5. Anal. Calcd for  $\text{C}_{44}\text{H}_{32}\text{P}_2\text{S}_2\text{Si}$ : C, 73.92; H, 4.51. Found: C, 73.72; H, 4.56.

Compound **1b** was prepared in a fashion similar to that above, using chlorodi-1-naphthylphosphine instead of chlorodiphenylphosphine in 61% yield as a pale-yellow solid, after purification by silica gel column chromatography, followed by recrystallization from chloroform/hexane: mp  $266.0\text{--}268.2^\circ\text{C}$ ; TOF-MS  $m/z$  914 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 7.15 (t, 4H,  $J = 5.7$  Hz), 7.27–7.58 (m, 24H), 7.84 (t, 8H,  $J = 9.6$  Hz), 8.41 (dd, 4H,  $J = 7.7, 3.6$  Hz). This sample contained a small amount of an unidentified byproduct in approximately 10%.

**Synthesis of Phosphine Oxides 2a and 2b.** To a solution of 0.600 g (0.834 mmol) of **1a** in 30 mL of chloroform was added slowly at room temperature 13.5 mL of a 10% aqueous solution of  $\text{H}_2\text{O}_2$ . After being stirred for 2 h and hydrolytic workup, the residue was recrystallized from chloroform/ethanol to give 0.564 g (91% yield) of **2a** as a colorless solid: mp  $>300^\circ\text{C}$ ; TOF-MS  $m/z$  746 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 7.32–7.56 (m, 22H), 7.66 (d, 2H,  $J_{\text{H-P}} = 6.6$  Hz, thiophene ring H), 7.72–7.79 (m, 8H, *o*-PPh);  $^{13}\text{C}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 128.4, 128.6 (d,  $J_{\text{C-P}} = 13$  Hz), 129.9, 130.9, 131.8 (d,  $J_{\text{C-P}} = 13$  Hz), 132.3, 132.9 (d,  $J_{\text{C-P}} = 81$  Hz), 135.4, 137.0 (d,  $J_{\text{C-P}} = 139$  Hz), 139.5 (d,  $J_{\text{C-P}} = 11$  Hz), 143.3 (d,  $J_{\text{C-P}} = 11$  Hz), 156.6 (d,  $J_{\text{C-P}} = 7$  Hz). Anal. Calcd for  $\text{C}_{44}\text{H}_{32}\text{P}_2\text{S}_4\text{Si}$ : C, 67.84; H, 4.14. Found: C, 67.87; H, 4.02.

Compound **2b** was obtained from **1b** in a fashion similar to that above in 91% yield as a colorless solid after purification by recrystallization from chloroform/hexane: mp  $>300^\circ\text{C}$ ; TOF-MS  $m/z$  946 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 7.30–7.54 (m, 26H), 7.71 (d, 2H,  $J_{\text{H-P}} = 6.8$  Hz, thiophene ring H), 7.90 (d, 4H,  $J = 8.0$

Hz), 8.02 (d, 4H,  $J = 8.2$  Hz), 8.83 (d, 4H,  $J = 8.5$  Hz);  $^{13}\text{C}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 124.4 (d,  $J_{\text{C-P}} = 15$  Hz), 126.6, 127.5, 127.6 (d,  $J_{\text{C-P}} = 6$  Hz), 128.3, 128.8 (d,  $J_{\text{C-P}} = 3$  Hz), 130.0, 130.4 (d,  $J_{\text{C-P}} = 71$  Hz), 133.1 (d,  $J_{\text{C-P}} = 12$  Hz), 133.6 (d,  $J_{\text{C-P}} = 2$  Hz), 133.76 (d,  $J_{\text{C-P}} = 16$  Hz), 133.77, 133.9, 135.3, 137.1 (d,  $J_{\text{C-P}} = 107$  Hz), 139.8 (d,  $J_{\text{C-P}} = 8$  Hz), 143.3 (d,  $J_{\text{C-P}} = 11$  Hz), 157.0 (d,  $J_{\text{C-P}} = 7$  Hz). Anal. Calcd for  $\text{C}_{60}\text{H}_{40}\text{O}_2\text{P}_2\text{S}_2\text{Si}$ : C, 76.09; H, 4.26. Found: C, 76.38; H, 4.42.

**Synthesis of Phosphine Sulfide 3a.** A mixture of 0.600 g (0.834 mmol) of **1a** and 67.2 mg (2.10 mmol) of sulfur in 60 mL of THF was stirred at room temperature for 3 days. After hydrolytic workup, the residue was subjected to silica gel preparative thin-layer chromatography with chloroform/hexane as the eluent to give 0.624 g (96% yield) of **3a** as a pale-green solid: mp  $> 300$  °C; TOF-MS  $m/z$  780 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 7.35–7.58 (m, 22H), 7.70 (d, 2H,  $J_{\text{H-P}} = 7.7$  Hz, thiophene ring H), 7.76–7.82 (m, 8H, *o*-PPh);  $^{13}\text{C}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 128.4 (d,  $J_{\text{C-P}} = 13$  Hz), 128.6, 129.8, 130.8, 131.7 (d,  $J_{\text{C-P}} = 8$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2$  Hz), 133.4 (d,  $J_{\text{C-P}} = 89$  Hz), 135.4, 137.7 (d,  $J_{\text{C-P}} = 87$  Hz), 139.8 (d,  $J_{\text{C-P}} = 8$  Hz), 142.9 (d,  $J_{\text{C-P}} = 11$  Hz), 157.1 (d,  $J_{\text{C-P}} = 7$  Hz). Anal. Calcd for  $\text{C}_{44}\text{H}_{32}\text{O}_2\text{P}_2\text{S}_4\text{Si}$ : C, 70.76; H, 4.32. Found: C, 70.79; H, 4.35.

**CV Measurements.** CVs were measured on 2 mM benzonitrile solutions of the substrates containing 100 mM  $\text{LiClO}_4$  as the supporting electrolyte. Pt wires were used as the working and counter electrodes, and  $\text{Ag}/\text{AgCl}$  was used as the reference electrode. The current–voltage curves were recorded at room temperature on a Hokuto Denko HAB-151 potentiostat/galvanostat.

**Optical Measurements.** UV spectra were recorded for a  $4 \times 10^{-5}$  M chloroform solutions. The usual PL measurements including decay analysis and determination of the absolute efficiencies were carried out for  $4 \times 10^{-6}$  M chloroform solutions. For the chromic studies of **1a**, a 100 M excess of  $\text{BF}_3\text{-Et}_2\text{O}$  or  $\text{CF}_3\text{COOH}$  was added to a  $4 \times 10^{-5}$  M chloroform solution of the substrate. After UV and PL measurements, aqueous  $\text{NaHCO}_3$  was added to the solution containing the additive and the mixture was shaken vigorously. The organic layer was separated and dried over

anhydrous magnesium sulfate. UV and PL spectra of the resulting solution were consistent with those of **1a** in the absence of the additive.

**MO Calculations.** The density functional theory calculations were carried out using the *Gaussian03* program package.<sup>13</sup> The Becke three-parameter Lee–Yang–Parr hybrid functional<sup>14–17</sup> was employed with the 6-31G(d,p) basis set. Simplified models are used in which all substituents on the silicon and phosphorus atoms are replaced by hydrogen atoms.

**EL Device Fabrication.** Organic layer(s) of the EL device was (were) prepared by vacuum deposition at  $2 \times 10^{-5}$  Torr on an ITO-coated glass substrate (Nippon Sheet Glass Co.). Then a layer of magnesium–silver alloy with an atomic ratio of 10:1 was deposited as the top electrode (200 nm). The emitting area was  $0.5 \times 0.5 \text{ mm}^2$ .

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