Heteroatom Chemistry
Volume 22, Number 3/4, 2011

Synthesis and Optical Properties of a Bis(diphenylphosphino)dithienosilole-digold(I) Complex

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Received 17 November 2010; revised 17 January 2010

ABSTRACT: *Treatment of 2,6-bis(diphenylphosphino)-4,4-bis(4-n-butylphenyl)dithienosilole with chloro(dimethylsulfide)gold(I) in acetone gave the corresponding digold complex as pale green solids. The complex was highly emissive and showed blue photoluminescence with the quantum efficiencies of $\Phi = 0.99$ and 0.30 for its solution and powders, respectively. The complex showed good film forming properties and its spin coating from the toluene solution afforded a thin solid film that also showed emissive properties with $\Phi = 0.08$.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:514–517, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20715

INTRODUCTION

Silole derivatives have been well studied as functional materials, such as organic semiconductors, emissive materials, and photovoltaic materials [1–3]. Applications of siloles in organic light-emitting diodes (OLEDs) as electron-transporting materials were first reported by Tamao, Yamaguchi, and coworkers [4]. The excellent electron-transporting properties of siloles are ascribed to the interaction between the silicon σ^* and the butadiene π^*-orbital (σ^*–π^* conjugation) [5], which lowers the LUMO energy level to enhance the electron affinity.

We have studied the synthesis and properties of dithienosiloles (DTSs) as a class of silole derivatives [6–11]. DTS has a silole ring fused to a bithiophene unit, which exhibits extended conjugation attributable not only to the coplanarity of the two thiophene rings fixed by the tricyclic system, but also to the σ^*–π^* conjugation, and it has been demonstrated by us and other research groups that DTS-based compounds are applicable to OLEDs, organic transistors, and organic photovoltaic cells [9]. Recently, we found that a DTS derivative with diphenylphosphino-substituents (**DTSP1**) showed good photoluminescence (PL) properties (Chart 1) [10]. Interestingly, the PL quantum yields in solutions increased about four times by oxidation of the phosphorous atoms (**DTSPO**). It was also found that a DTS-phosphine oxide compound showed electroluminescence properties, thus being applicable to OLEDs. However, they could form the films only by vapor deposition and attempted film formation by spin coating and drop-cast failed.

On the other hand, gold complexes have received much attention as the emissive materials that may be usable for organic devices, such as OLEDs, sensors, and so on [12–14]. In the hope of obtaining solution processable DTS-based materials with efficient PL properties, we prepared

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Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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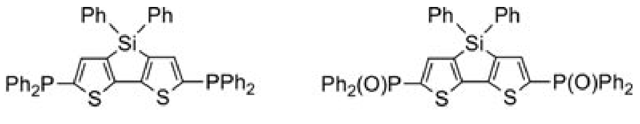
Contract grant sponsor: Shorai Foundation for Science.



DTSP1
λ_{max} = 380 nm, λ_{em} = 465 nm, Φ = 0.22 (0.79)

DTSPO
λ_{max} = 361 nm, λ_{em} = 422 nm, Φ = 0.85 (0.41)

CHART 1 Structures of emissive DTS derivatives. UV absorption and emission maxima, and quantum yields in $CHCl_3$ (solids).

bis(diphenylphosphino)dithienosilole-$(AuCl)_2$ complexes in which the intermolecular Au-Au, Au-Cl, and/or Au-S interaction would exist to facilitate the film formation.

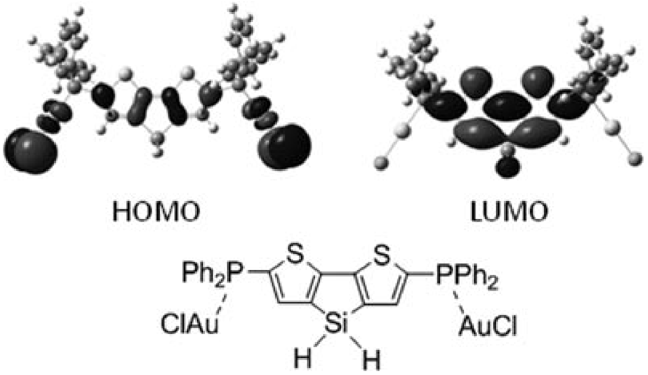
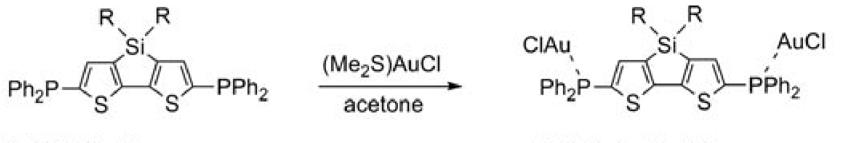


FIGURE 1 Structure of model compound, and HOMO and LUMO profiles derived from DFT calculations at B3LYP/LanL2DZ.

RESULTS AND DISCUSSION

Bis(diphenylphosphino)DTS-digold(I) complexes were obtained as shown in Eq. (1). Treatment of **DTSP1** with $(Me_2S)AuCl$ in acetone readily afforded **DTSP1-Au** as crude precipitates. However, **DTSP1-Au** could not be purified by recrystallization due to its low solubility. Attempted purification of **DTSP1-Au** by repeated reprecipitation failed. To increase the solubility, we introduced *n*-butyl groups on the phenyl rings in **DTSP2**. The reaction of **DTSP2** with $(Me_2S)AuCl$ in acetone, followed by recrystallization of the resulting precipitates gave complex **DTSP2-Au** as pale green fine plate solids, which were soluble in toluene, THF, and chloroform, but insoluble in acetone, ethanol, and hexane, and melted at 236.0°C without decomposition. The structure of **DTSP2-Au** was verified by spectroscopic analysis and combustion elemental analysis. The ^1H and ^{13}C NMR spectra showed well-resolved sharp signals, indicating the absence of any considerable intermolecular interaction in the solution phase. The ^{31}P NMR signal appeared at 20.17 ppm, lowfield shifted from that of **DTSP1** [10] (−18.55 ppm).

Optical properties of **DTSP2** and **DTSP2-Au** were examined as shown in Table 1. **DTSP2** exhibited lower PL quantum efficiencies than those of **DTSP1**, both in chloroform and in the solid state. The flexible butyl groups seemed to enhance the nonradiative decay in **DTSP2**. In fact, fitting the decay curve afforded the higher nonradiative kinetic constant of $k_{nr} = 6.0 \times 10^8\ s^{-1}$ than the radiative one ($k_r = 1.7 \times 10^8\ s^{-1}$). The UV spectrum of **DTSP2-Au** in chloroform showed an absorption maximum at 369 nm, which was blue-shifted from that of **DTSP2** by 7 nm. This is probably due to the reduced contribution of the phosphorous lone pairs to the conjugation. This lowers both the HOMO and LUMO energy levels of the DTS system but affects the LUMO level primarily decreasing the HOMO–LUMO energy gap [10]. However, the degree of this blue-shift induced by the coordination to Au was smaller than that from **DTSP1** to **DTSPO** (19 nm), suggesting the interaction of the gold(I) units with the **DTSP2** system to an extent. Indeed, DFT calculations on a model compound at B3LYP/LanL2DZ showed that the Au orbital contributes to the HOMO (Fig. 1), and the time-dependent calculations at the same level indicated that the major absorption is ascribed to the HOMO–LUMO transition. The emission band of **DTSP2-Au** appeared at 432 nm, again slightly blue-shifted from that of **DTSP2**. The emission life time in chloroform was determined to be $\tau = 3.17$ ns, indicating that the emission is ascribed to fluorescence. The PL quantum yields were markedly increased by the coordination to gold to reach $\Phi = 0.99$ and 0.30, for the solution and powders of **DTSP2-Au**, respectively. Blue-colored PL from **DTSP2-Au** is shown in Fig. 2. The HOMO and LUMO energy levels of **DTSP2-Au**



(1)

DTSP1 R = Ph
DTSP2 R = 4-*n*-butylphenyl

DTSP1-Au R = Ph
DTSP2-Au R = 4-*n*-butylphenyl

TABLE 1 Optical Properties of **DTSP2** and **DTSP2-Au**

	UV abs (λ_{max}/nm)				
Compound	*In CHCl$_3$*	*Film*	*PL (λ_{em}/nm) (Φ)^a In CHCl$_3$*	*Powder*	*Film*
DTSP2	376	nd^b	449 (0.30)	483 (0.19)	nd^b
DTSP2-Au	369	374	432 (0.99)	445 (0.33)	440, 466^c (0.08)

^{a}Excited at the absorption maximum.
^{b}Not determined.
^{c}Shoulder peak.

were estimated by the work function measurement and the optical band gap to be −5.93 and −2.83 eV, respectively.

As we expected, **DTSP2-Au** exhibited good film-forming properties by solution processes and a transparent thin solid film was obtained by spin coating of the toluene solution. The UV absorption and emission spectral data of the film are also summarized in Table 1. A new emission shoulder peak appeared at 466 nm as shown in Fig. 3 and the PL quantum yield of the film was determined to be $\Phi = 0.08$, much lower than that of the powders. Some intermolecular interactions concerning gold atoms would be involved in the film being responsible for the changes of the optical properties.

In conclusion, we prepared diphosphino-DTS-digold(I) complex **DTSP2-Au**. The complex formation with gold(I) remarkably enhanced PL quantum yields of **DTSP2** in the solution phase as well as in the solid state, but only slightly affected the emission λ_{max} and color. Good film-forming properties of **DTSP2-Au** by solution processes seem to allow its applications into organic electronic devices. The applications to OLEDs and sensors are being studied and will be reported elsewhere.

FIGURE 2 Emission from a chloroform solution of **DTSP2-Au** excited at 364 nm.

EXPERIMENTAL

All reactions were carried out in dry nitrogen or argon. Ether was distilled from sodium-benzophenone ketyl immediately before use. 2,6-Dibromo-4,4-bis(4-*n*-butylphenyl)dithienosilole [11] and **DTSP1** [10] were prepared as reported in the literature. Mass spectra were measured on a JEOL SX-102A spectrometer. NMR spectra were recorded on JEOL LA-400 spectrometers. UV and emission spectra were measured on Shimadzu UV-3150 and RF-5000 spectrophotometers, respectively. Emission quantum yields were determined in an integration sphere attached by a Hamamatsu Photonics C7473 Multi-Channel Analyzer. PL life time of **DTSP2-Au** was determined by monitoring the intensity at 450 nm, excited at 380 nm. The work function measurement was carried out on a Riken Keiki AC-2 photoelectron spectrometer.

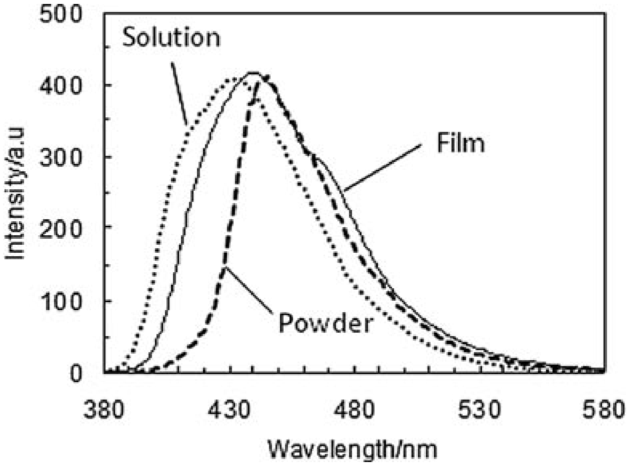


FIGURE 3 PL spectra of **DTSP2-Au**.

Preparation of **DTSP2**. To a solution of 2.0 g (3.2 mmol) of 2,6-dibromo-4,4-bis(4-*n*-butylphenyl)dithienosilole in 30 mL of ether, 6.5 mL of a 1.57 M *n*-BuLi solution in hexane was added dropwise at −80°C and the mixture was allowed to warm to room temperature and stirred for 1 h. To this, 1.2 mL (6.5 mmol) of chlorodiphenylphosphine was added and the resulting mixture was stirred for 3 h. After hydrolysis with water, the organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extract were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was subjected to silica gel column chromatography eluting with chloroform/hexane to give 0.63 g (24% yield) of **DTSP2**: mp 51.0–55.0°C; FAB-MS *m/z* 826 (M^+); ^{1}H NMR (in $CDCl_3$) δ0.91 (t, 6H, J = 7.24 Hz, CH_3), 1.26–1.42 (m, 4H, CH), 1.49–1.63 (m, 4H, CH_2), 2.60 (t, 4H, J = 7.91 Hz, CH_2Ph), 7.17 (d, 4H, J = 7.59 Hz, *m*-phenylene), 7,31–7.43 (m, 20H, Ph), 7.47–7.54 (m, 6H, phenylene and DTS ring); ^{13}C NMR (in $CDCl_3$) δ13.93, 22.37, 33.42, 35.74 (*n*-Bu), 127.99 (phenylene), 128.40 (*p*-Ph), 128.43 (d, $J_{\text{P-C}}$ = 6.7 Hz, *m*-phenyl), 128.82 (phenylene), 132.97 (d, $J_{\text{P-C}}$ = 19.3 Hz, *o*-Ph), 135.42 (phenylene), 137.91 (d, $J_{\text{P-C}}$ = 8.1 Hz, *i*-Ph), 139.62 (d, $J_{\text{P-C}}$ = 32 Hz, DTS), 140.20 (phenylene), 141.69 (d, $J_{\text{P-C}}$ = 8.2 Hz, DTS), 145.48 (DTS), 156.42 (DTS); Anal calcd for $C_{52}H_{48}P_2S_2Si$: C, 75.51; H, 5.85, found: C, 75.39; H, 5.65.

Preparation of **DTSP1-Au** *and* **DTSP2-Au**. A mixture of 0.10 g (0.12 mmol) of **DTSP2** and 71 mg (0.24 mmol) of chloro(dimethylsulfide)gold(I) in 2 mL of acetone was stirred at room temperature for 5 h. The resulting precipitate was collected and recrystallized from ethanol/chloroform = 1/1 to give 20 mg (20% yield) of **DTSP2-Au** as pale green solids: mp 236.0°C; FAB-MS *m/z* 1255 (M^+-Cl for ^{35}Cl); ^{1}H NMR (in $CDCl_3$) δ0.94 (t, 6H, J = 6.77 Hz, CH_3), 1.37 (m, 4H, CH_2), 1.60 (m, 4H, CH_2), 2.64 (t, 4H, J = 7.72 Hz,CH_2-Ph), 7.22 (d, 4H, J = 7.72 Hz, phenylene), 7.47–7.63 (m, 24H), 7.76 (d, 2H, $J_{\text{H-P}}$ = 8.71 Hz, DTS); ^{13}C NMR (in $CDCl_3$) δ13.95, 22.47, 33.39, 35.79 (Bu), 125.68 (phenylene), 128.82 (phenylene), 129.34 (d, $J_{\text{P-C}}$ = 11.9 Hz, *m*-pPh), 129.46 (d, $J_{\text{P-C}}$ = 65.5 Hz, *i*-Ph), 131.51 (d, $J_{\text{P-C}}$ = 60.2 Hz, DTS), 132.28 (d, $J_{\text{P-C}}$ = 2.2 Hz, *p*-Ph), 133.50 (d, $J_{\text{P-C}}$ = 14.1 Hz, *o*-Ph), 135.46 (phenylene), 142.42 (d, J = 14.8 Hz, DTS), 144.47 (d, J = 11.1 Hz, phenylene), 146.40, 157.42, 157.47 (DTS); ^{31}P NMR (in $CDCl_3$ from H_3PO_4) δ20.17; Anal calcd for $C_{52}H_{48}Au_2Cl_2P_2S_2Si$: C, 48.34; H, 3.74, found: C, 48.04; H, 3.44.

DTSP1-Au was prepared in a similar fashion to that mentioned above. However, attempted recrystallization was unsuccessful and repeated reprecipitation from chloroform/ethanol and chloroform/hexane did not affect the purity. Data for **DTSP1-Au** after reprecipitation: UV (in $CHCl_3$) λ_{max} 369 nm; PL λ_{em} 433 nm, Φ 0.92 (in $CHCl_3$); λ_{em} 433 nm, Φ 0.28 (solid); ^{1}H NMR (in C_6D_6) δ6.83–7.11 (m, 20H), 7.19–7.25 (m, 6H), 7.44 (dd, J = 8.0 and 1.2 Hz, 4H, *o*-Ph), 7.48 (br d, J = 8.0 Hz, 2H, DTS).

ACKNOWLEDGMENT

We thank Dr. Yousuke Ooyama of Hiroshima University for the fruitful discussion on the optical properties of **DTSP2-Au**.

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