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Relation	



Synthesis and optical properties of spirobi(dithienometallope)s and spirobi(dithienothiametalline)s

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1. Introduction

Spiro-condensed compounds with orthogonal chromophores are of interest [1]. The nonplanar structures of these compounds would hinder the close packing of the chromophores in the solid states to improve the solubility in organic solvents, the photoluminescence (PL) efficiency in the solid states, and also the thermal stability of the amorphous phase, providing the opportunity to utilize them in areas of organic electronic devices. Of those, spirobifluorene has been extensively studied as a core fragment of star-shaped molecules [2] and as a component of conjugated oligomers and polymers, and their use as organic light emitting diode (OLED) and thin film transistor (TFT) materials, and also as microporous materials has been explored [3]. Modification of the spirofluorene system by the introduction of heteroatoms has been studied. For example, it was demonstrated that silicon-cored bi(silafluorene) derivatives could be used as efficient luminescence materials [4]. Replacement of the phenylene rings of the spirobifluorene by heteroaromatic systems such as N- [5] and S-containing ones [6] has been also examined to modify the electronic states and the functionalities.

Recently, we have introduced dithienosilole (DTS) [7] and -germole (DTG) [8] derivatives as functional materials based on their PL and carrier transporting properties (Chart 1). In these compounds, the conjugation is markedly enhanced by the highly planar structures of the tricyclic systems, and also by the bonding interaction between the metal σ^* - and bithiophene π^* -orbital (σ^* - π^* conjugation), which lowers the LUMO energy levels. Currently, these DTS [9] and DTG [8,10] systems attract much attention as the donor-components of donor-acceptor type π -conjugated photovoltaic polymers. We prepared also dithienothiasilines (DTTSs) with a sulfide linkage and demonstrated the hole-transporting properties of their vapor-deposited films, being usable in multi-layered OLEDs [11]. In this paper, we report the synthesis of spiro-condensed dithienometalloles (metal = Si, Ge) and dithienothiametallines (metal = Si, Ge, Sn) [12]. To gain insight into the role of the spiro-structure and the center elements affecting the electronic states, we investigated their optical properties and carried out theoretical calculations of spiro-condensed dithienometallore models with C and Si as the center element.

2. Results and discussion

2.1. Preparation of spirobi(dithienometallore) and spirobi(dithienothiametalline) derivatives

Spiro-condensed dithienosilole and -germole (sDTS and sDTG) derivatives were obtained as shown in Scheme 1. The reactions of β,β' -dilithiated bithiophenes with 0.5 equiv of MCl_4 ($M = Si$ or Ge) afforded the corresponding spirobi(dithienometallore)s (**sDTS1**, **sDTS2**, and **sDTG1**). Bromination and iodination of **sDTS1** with Br_2 and ICl readily afforded tetrahalospirobi(dithienosilole)s **sDTS3** and **sDTS4**, respectively. Because

of the barely soluble properties of tetraiodo compound **sDTS4** in organic solvents, we employed tetrabromo compound **sDTS3** for the further transformation, leading to **sDTS2** and **sDTS5**. These spiro-condensed compounds were colorless or yellow solids and soluble in common organic solvents, except for **sDTS4**.

In contrast to the reactions with SiCl_4 and GeCl_4 , a complex mixture was obtained with SnCl_4 , from which a compound whose MALDI TOF-mass spectrum revealed the parent signal at m/z 1472 corresponding to a dimeric form of the expected tetrakis(trimethylsilyl)spirobi(dithienostannole) (**sDTSn**) was isolated in 15% yield. The ^1H and ^{13}C NMR spectra indicated the existence of two sets of 5,5'-bis(trimethylsilyl)-2,2'-bithiophene-3,3'-diyl segments in a 1:1 ratio, agreeing with the cyclic structure shown in Figure 1. Attempted X-ray single crystal structural analyses failed. However, quantum chemical calculations at the B3LYP/LANL2DZ//MOPAC/PM6 level indicated that this dimeric form is thermally stable and contains ring strain less than **sDTSn** as demonstrated by a thermodynamic equation of $2 \text{ sDTSn} = \text{ sDTSn-dimer} + 14.1 \text{ kcal/mol}$.

Spirobi(dithienothiametalline)s including a tin derivative were prepared by the reactions of bis[lithio(trimethylsilyl)thienyl] sulfide with MCl_4 as shown in Scheme 2, similarly to the preparation of sDTS and sDTG. No dimeric compound was obtained from the reaction with SnCl_4 . It seems that **sDTTSn** having a six-membered core possesses less strain than **sDTSn**. Oxidation of **sDTTS** was carried out to give its oxides **sDTTSO1** and **sDTTSO2** by selective mono- and dioxidation with *m*CPBA, similarly to that of DTTS, reported previously [11].

2.2. Quantum chemical calculations and optical measurements

First, we examined quantum chemical calculations for spiro(dithienometallope)s with metal = C and Si, to estimate the effects of the core elements on their electronic states. Figure 2 depicts the HOMO and LUMO energy levels and profiles of the models, derived from DFT calculations at the B3LYP/6-31G(d,p) level [13-15]. The LUMO of **sDTS0** lies at lower energy than that of **sDTC0**, indicating that the σ^* - π^* conjugation operates even in these spiro-condensed systems, similarly to **DTS0**. On the other hand, spiro-condensation decreases the HOMO-LUMO energy gap for both **sDTC0** and **sDTS0**, relative to those of **DTC0** and **DTS0**, respectively. This is probably due to the through-space interaction between the orthogonally arranged bithiophene π -orbital in HOMO, namely spiro-conjugation [16]. In their LUMOs, the interaction through the σ^* orbital of the center atom is involved to an extent.

UV absorption and fluorescence data of the present spirobi(dithienometallope)s are listed in Table 1. Spiro-compounds **sDTS1** and **sDTG1** exhibited red-shifted absorption maxima from those of **DTS1** [7a] and **DTG1** (R = SiMe₃ and Ar = Ph in Chart 1), respectively, indicating the spiro-conjugation being operative in these systems. However, the shifts ($\Delta\lambda_{\text{max}}$ in Table 1) were similar for M = Si and Ge, showing no significant effects of the center elements on the spiro-conjugation. Although these spirobi(dithienometallope)s were photoluminescent, the quantum efficiencies were markedly lowered by spiro-condensation in both the solution and the solid states ($\Phi = 0.10$ - 0.17), compared to simple dithienometalloles **DTS1** and **DTG1**, despite our expectation (Table 1).

For the spirobi(dithienothiametalline) derivatives, UV λ_{max} shifted to shorter wavelength in the order of $M = \text{Si} > \text{Ge} > \text{Sn}$ (UV $\lambda_{\text{max}} = 321 \text{ nm}$ (3.86 eV, $\epsilon = 25,000$) for **sDTTS**, 312 nm (3.97 eV, $\epsilon = 28,300$) for **sDTTG**, and 302 nm (4.11 eV, $\epsilon = 21,000$) for **sDTTSn**), as shown in Figure 3 (a). The absorption band of **sDTTS** was at longer wavelength by 4 nm than that of **DTTS1** ($R = \text{SiMe}_3$ and $\text{Ar} = \text{Ph}$ in Chart 1) [11], due to the spiro-conjugation, but the shift was smaller than that of **sDTS1** from **DTS1**. It was also found that the electronic states were tunable by stepwise oxidation of the bridging sulfur atoms of **sDTTS**, shifting the absorption edges from 356 nm (3.48 eV) for **sDTTS** to 342 (3.63 eV, $\epsilon = 23,000$) and 329 nm (3.77 eV, $\epsilon = 20,000$) for **sDTTSO1** and **sDTTSO2**, respectively, although the maximum of **sDTTSO1** appeared at higher energy than that of **sDTTSO2** (Figure 3 (b)). No photoluminescence was detected for these spirobi(dithienothiametalline) and the oxides either in solutions or as solids.

In conclusion, spiro-condensed dithienometalloles (metal = Si and Ge) and dithienothiametallines (metal = Si, Ge, and Sn) were readily prepared by simple ring closure reactions of dilithiated bithiophene and dithienyl sulfide derivatives with metal tetrachlorides. It must be noted that the electronic states of these compounds were finely tuned by changing the center elements and step-by-step oxidation of the bridging sulfur atom of spirobi(dithienothiasiline).

3. Experimental

3.1. General

All reactions were carried out under a dry argon atmosphere. THF and ether were dried over sodium-potassium alloy and distilled immediately before use. Methylene chloride was distilled from CaH₂ and stored at 0°C until use. NMR spectra were recorded on a JEOL EX-270 or LA-400 spectrometer. EI mass spectra were measured on a Hitachi M80B spectrometer, while MALDI-TOF mass analysis was performed on a Shimadzu Kompact Muldi2 spectrometer. APPI mass spectra were measured on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. UV-vis spectra were measured on a Hitachi U-3210 spectrophotometer, and emission spectra were recorded on a Shimadzu RF5000 spectrophotometer. The solution PL quantum efficiencies were determined relative to a 9,10-diphenylanthracene solution as the standard, while those in the solid states were determined in an integration sphere attached by a Hamamatsu Photonics C7473 Multi-Channel Analyzer.

3.2. Preparation of spiro-condensed dithienometallore and dithienothiametalline by ring closure

To a solution of 3,3'-dilithio-5,5'-bis(trimethylsilyl)-2,2'-bithiophene [7a], prepared by the reaction of 8.50 g (18.2 mmol) of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene and 23.0 mL (36.3 mmol) of a 1.58 M *n*-butyllithium/hexane solution in 80 mL of THF at -80°C, was added 1.54 g (9.08 mmol) of SiCl₄ at the same temperature. After being refluxed for 3 h, the mixture was hydrolyzed with water and extracted with ether. The extract was dried over anhydrous magnesium sulfate and the organic solvent was evaporated. The residue was chromatographed on a silica gel column with *n*-hexane as an

eluent to afford crude solids that were recrystallized from *n*-hexane/chloroform to give 4.80 g (82% yield) of **sDTS1** [12] as pale yellow crystals: mp > 300°C; MS *m/z* 644 (M⁺); ¹H NMR (δ in CDCl₃) 0.32 (s, 36H, MeSi), 7.07 (d, 4H, thiophene ring H); ¹³C NMR (δ in CDCl₃) 0.05 (MeSi), 136.91 (qC), 137.16 (thiophene CH), 142.14 (qC), 157.24 (qC); ²⁹Si NMR (δ in CDCl₃) -6.65 (MeSi), -33.14 (center Si). Anal. Calcd for C₂₈H₄₀S₄Si₅: C, 52.11; H, 6.25. Found: C, 52.14; H, 6.26.

Other spirobi(dithienometalloy)s and -(dithienothiametalline)s were prepared in a fashion similar to that above. Data for **sDTS2** [12]: colorless solid; mp 223-225°C; MS *m/z* 588 (M⁺); ¹H NMR (δ in CDCl₃) 0.37 (d, 24H, *J* = 3.6 Hz, MeSi), 4.53 (septet, 4H, *J* = 3.6 Hz, HSi), 7.09 (s, 4H, thiophene ring H); ¹³C NMR (δ in CDCl₃) -2.82 (MeSi), 136.96 (qC), 138.17 (thiophene CH), 138.58 (qC), 157.69 (qC). Anal. Calcd for C₂₄H₃₂S₂Si₅: C, 48.92; H, 5.47. Found: C, 49.11; H, 5.55. Data for **sDTG1**: pale yellow solid; mp >300°C; MS *m/z* 690 (M⁺); ¹H NMR (δ in CDCl₃) 0.34 (s, 36H, MeSi), 7.13 (d, 4H, thiophene ring H); ¹³C NMR (δ in CDCl₃) 0.03 (MeSi), 136.84 (thiophene CH), 138.12 (qC), 142.16 (qC), 153.83 (qC); ²⁹Si NMR (δ in CDCl₃) -6.55 (MeSi). HRMS Calcd for C₂₈H₄₀GeS₄Si₄: 690.0302. Found: 690.0273. Data for **sDTSn-dimer**: colorless solid; mp >300°C; TOF-MS *m/z* 1472 (M⁺); ¹H NMR (δ in CDCl₃) 0.30 (s, 36H, MeSi), 0.37 (s, 36H, MeSi), 6.74 (s, 4H, thiophene ring H), 7.50 (s, 4H, thiophene ring H); ¹³C NMR (δ in CDCl₃) 0.11 (MeSi), 0.22 (MeSi), 137.76 (qC), 138.67 (thiophene CH), 139.73 (thiophene CH), 139.79 (qC), 141.46 (qC), 142.74 (qC), 148.49 (qC), 154.39 (qC); ²⁹Si NMR (δ in CDCl₃) -6.75 (MeSi, two peaks may be overlapped). Anal. Calcd for C₅₆H₈₀S₈Si₈Sn₂: C, 45.70; H, 5.48. Found: C, 45.73; H, 5.50. Data for **sDTTS**: colorless solid; mp 242-244°C; MS *m/z* 708

(M⁺); ¹H NMR (δ in CDCl₃) 0.25 (s, 36H, MeSi), 7.20 (s, 4H, thiophene ring H); ¹³C NMR (δ in CDCl₃) -0.05, 131.56 (qC), 139.20 (thiophene CH), 139.94 (qC), 148.13 (qC). Anal. Calcd for C₂₈H₄₀S₆Si₅: C, 47.40; H, 5.68. Found: C, 47.32; H, 5.91. Data for **sDTTG**: colorless solid; mp 256-258°C; MS *m/z* 754 (M⁺); ¹H NMR (δ in CDCl₃) 0.27 (s, 36H, MeSi), 7.09 (s, 4H, thiophene ring H); ¹³C NMR (δ in CDCl₃) -0.06 (MeSi), 133.08 (qC), 138.38 (thiophene CH), 140.53 (qC), 145.21 (qC). Anal. Calcd for C₂₈H₄₀GeS₆Si₄: C, 44.60; H, 5.35. Found: C, 44.96; H, 5.87. Data for **sDTTSn**: colorless solid; mp 275-277°C; MS *m/z* 754 (M⁺); ¹H NMR (δ in CDCl₃) 0.28 (s, 36H, MeSi), 7.22 (s, 4H, thiophene ring H); ¹³C NMR (δ in CDCl₃) 0.07 (MeSi), 137.19 (qC), 139.81 (thiophene CH), 142.10 (qC), 146.69 (qC). Anal. Calcd for C₂₈H₄₀S₆Si₄Sn: C, 42.03; H, 5.04. Found: C, 41.93; H, 5.14.

3.3. Halogenation of **sDTS1**

To a solution of 4.00 g (6.20 mmol) of **sDTS1** in 60 mL of ether, 3.69 g (24.80 mmol) of bromine was added at -80°C. After the mixture was stirred for 30 min at room temperature, the solvent was evaporated to give crude solids that were washed with *n*-hexane (50 mL × 3) to give 3.40 g (82% yield) of **sDTS3** [12]: yellow solid; mp >300°C; MS *m/z* 668 (M⁺); ¹H NMR (δ in CDCl₃) 6.87 (s, 4H, thiophene); ¹³C NMR (δ in CDCl₃) 112.85 (C-Br), 132.18 (thiophene CH), 132.22 (qC), 153.27 (qC). Anal. Calcd for C₁₆H₄Br₄S₄Si: C, 28.29; H, 0.60. Found: C, 28.53; H, 0.65. **sDTS4** was obtained in 85% yield in a fashion similar to that above using ICl instead of Br₂. Data for **sDTS4**: greenish powder; mp >300°C; APPI MS *m/z* 859.51540 (M⁺, Calcd for C₁₆H₄I₄S₄Si: 859.51383).

Anal. Calcd for C₁₆H₄I₄S₄Si: C, 22.34; H, 0.47. Found: C, 22.46; H, 0.60. Solubility of **sDTS4** in organic solvents was too low to perform its NMR analysis.

3.4. Silylation of spirobi(dithienosilole)

To a solution of tetralithiospiro(dithienosilole), prepared by the reaction of 0.40 g (0.60 mmol) of **sDTS3** and 1.90 mL (3.00 mmol) of a 1.58 M *n*-butyllithium/hexane solution in 40 mL of THF at -80°C was added 0.58 g (3.50 mmol) of PhSiMe₂Cl at this temperature. After being stirred overnight at room temperature, the mixture was hydrolyzed with water and extracted with ether. The extract was dried over anhydrous magnesium sulfate and the solvent was evaporated. The residue was chromatographed on a silica gel column with *n*-hexane/chloroform (4:1) as an eluent to afford crude solids that were recrystallized from chloroform/ethanol to give 0.27 g (50% yield) of **sDTS5** as colorless solid [12]: mp 204-205°C; TOF-MS *m/z* 893 (M+H⁺); ¹H NMR (δ in CDCl₃), 0.56 (s, 24H, MeSi), 7.04 (s, 4H, thiophene ring H); 7.33-7.38 (m, 12H, *m*- and *p*-Ph), 7.56 (dd, 8H, *J* = 7.5 and 1.9 Hz, *o*-Ph); ¹³C NMR (δ in CDCl₃) -1.31 (MeSi), 127.90 (Ph CH), 129.43 (Ph CH), 133.90 (Ph CH), 136.96 (thiophene qC), 137.54 (Ph qC), 138.37 (thiophene CH), 140.04 (thiophene qC), 157.76 (thiophene qC); ²⁹Si NMR (δ in CDCl₃) -11.73 (MeSi), -39.37 (center Si). Anal. Calcd for C₄₈H₄₈S₄Si₅: C, 64.52; H, 5.41. Found: C, 64.33; H, 5.46.

Similar tetralithiation of **sDTS3**, followed by treatment with HMe₂SiCl afforded compound **sDTS2** in 40% yield.

3.5. Oxidation of **sDTTS**

To a solution of 0.20 g (0.28 mmol) of **sDTTS** in 3 mL of CH₂Cl₂ was added 0.12 g (0.56 mmol) of 80% *m*CPBA at room temperature. The mixture was stirred overnight at room temperature, and poured into 30 ml of 10% aqueous NaHCO₃, then extracted with chloroform. The extract was dried over anhydrous magnesium sulfate and the solvent was evaporated to give crude solids that were recrystallized with *n*-hexane/chloroform to give 0.13 g (63 %) of a mixture of *cis*- and *trans*-isomers of **sDTTSO1** with respect to the two S-O bonds, as colorless solids: mp 269-272°C; MS *m/z* 740 (M⁺); ¹H NMR (δ in CDCl₃) 0.28 (s, 18H, MeSi), 0.29 (s, 18H, MeSi), 7.07 (s, 2H, thiophene ring H), 7.45 (s, 2H, thiophene ring H); ¹³C NMR (δ in CDCl₃) -0.20 (two MeSi signals are overlapped), 133.83 (qC), 133.95 (qC), 139.20 (thiophene CH), 140.51 (thiophene CH), 148.40 (qC), 148.43 (qC), 160.42 (qC), 161.22 (qC); ²⁹Si NMR (δ in CDCl₃) -4.76 (MeSi), -4.82 (MeSi), -53.05 (center Si). Anal. Calcd for C₂₈H₄₀O₂S₆Si₅: C, 45.36; H, 5.44. Found: C, 45.50; H, 5.32. Compound **sDTTSO2** was synthesized in 90% yield in a fashion similar to that above using 4 equiv of *m*CPBA: colorless solid; mp 278-280°C; MS *m/z* 772 (M⁺); ¹H NMR (δ in CDCl₃) 0.30 (s, 36H, MeSi), 7.21 (s, 4H, thiophene); ¹³C NMR (δ in CDCl₃) -0.24 (MeSi), 137.33 (qC), 139.16 (thiophene CH), 148.16 (qC), 156.94 (qC); ²⁹Si NMR (δ in CDCl₃) -4.19 (MeSi), -55.21 (center Si). Anal. Calcd for C₂₈H₄₀O₄S₆Si₅: C, 43.48; H, 5.21. Found: C, 43.44; H, 5.24.

3.6. Preparation of **DTGI**

To a solution of 3,3-dilithio-5,5'-bis(trimethylsilyl)-2,2'-bithiophene [12], prepared from the reaction of 0.47 g (1.00 mmol) of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene and 1.27 mL (2.01 mmol) of a 1.58 M *n*-butyllithium/hexane solution in 15 mL of ether at -80°C, was added 0.39 g (1.0 mmol) of Ph₂GeBr₂ dissolved in 5 mL of ether at the same temperature. After being refluxed for 1h, the mixture was hydrolyzed with water and extracted with ether. The extract was dried over anhydrous magnesium sulfate and organic solvent was evaporated. The residue was chromatographed on a silica gel column with *n*-hexane/chloroform (10:1) as an eluent to afford crude solids that were recrystallized from ethanol to give 0.29 g (54% yield) of **DTG1** as pale yellow solids: mp 135-136°C; MS *m/z* 536 (M⁺); ¹H NMR (δ in CDCl₃) 0.32 (s, 18H, MeSi), 7.26 (s, 2H, thiophene ring H), 7.35-7.40 (m, 6H, *m*- and *p*-Ph), 7.58 (dd, 4H, *J* = 7.4 and 1.5 Hz, *o*-Ph); ¹³C NMR (δ in CDCl₃) 0.11 (MeSi), 128.47, 129.66, 134.47, 134.71 (Ph), 136.30 (thiophene CH), 141.92 (thiophene qC), 142.22 (thiophene qC), 153.07 (thiophene qC); ²⁹Si NMR (δ in CDCl₃) -6.70 (MeSi). Anal. Calcd for C₂₆H₃₀GeS₂Si₂: C, 58.32, H, 5.65. Found: C, 58.30; H, 5.62.

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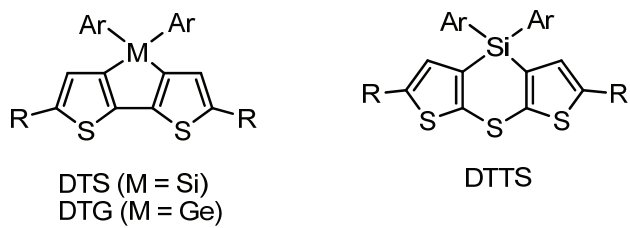
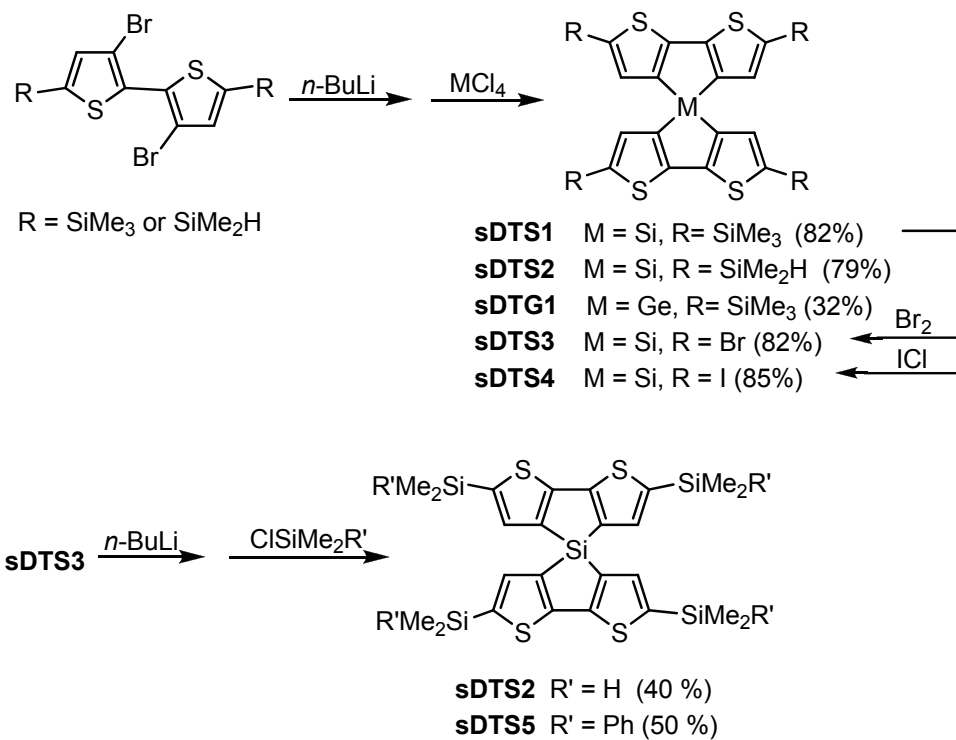
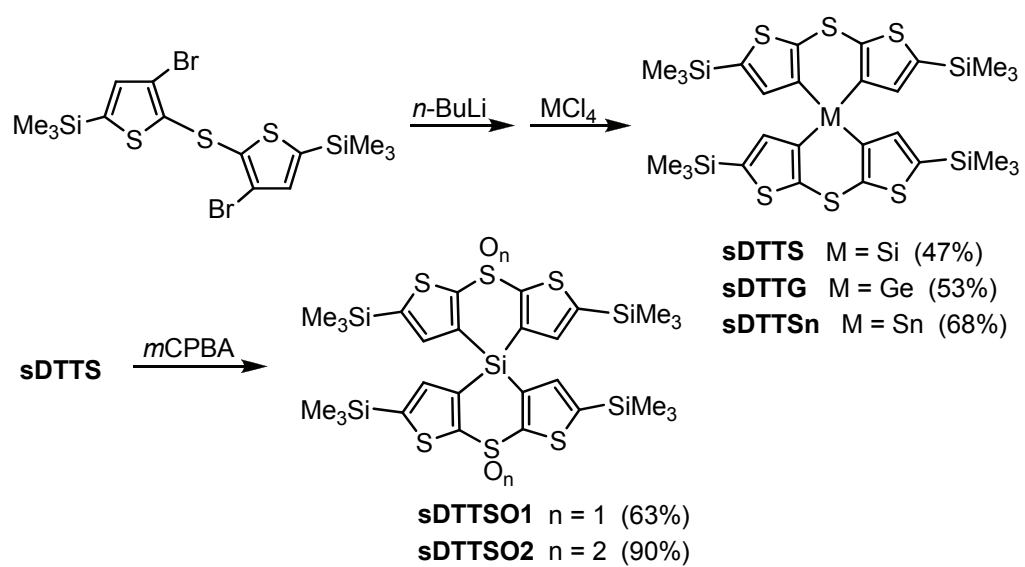


Chart 1. General structures of DTS, DTG, and DTTS.



Scheme 1. Synthesis of spirobi(dithienometalloy)s.



Scheme 2. Synthesis of spirobi(dithienothiametalline) derivatives.

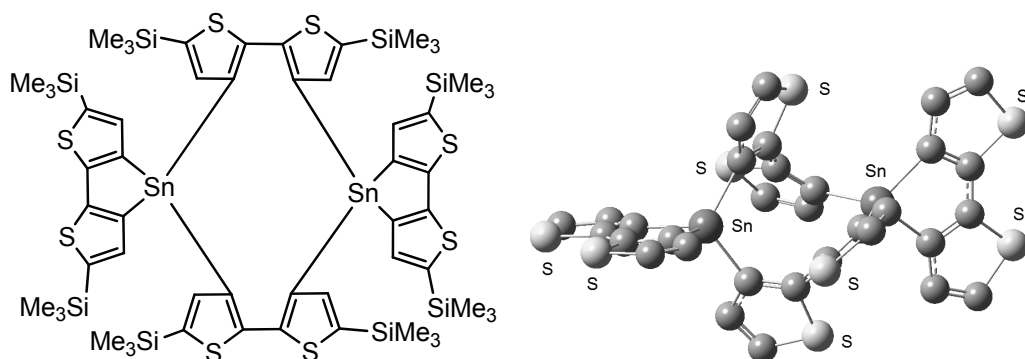


Figure 1. Chemical structure of **sDTSn-dimer** and its optimized geometry derived from MOPAC/PM6 calculations on Gaussian09 Program (hydrogen atoms and trimethylsilyl groups are omitted for clarity).

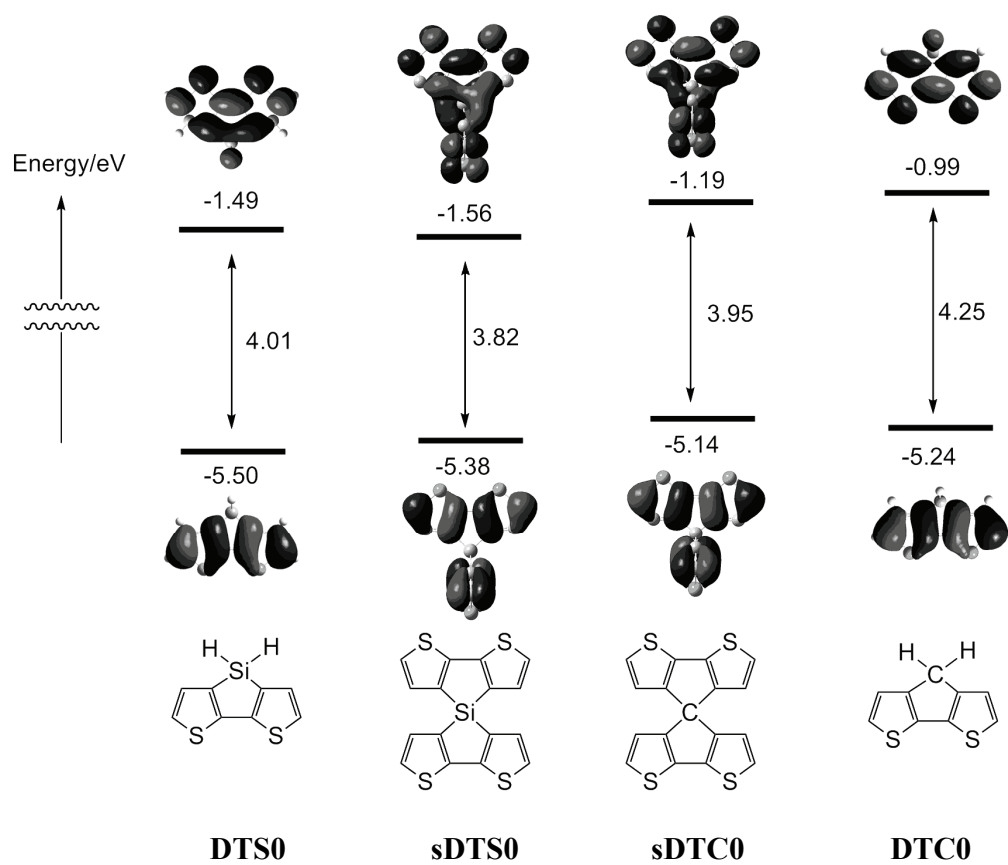


Figure 2. HOMO and LUMO profiles and relative energy levels for model compounds, derived from DFT calculations at B3LYP/6-31G(d,p) level.

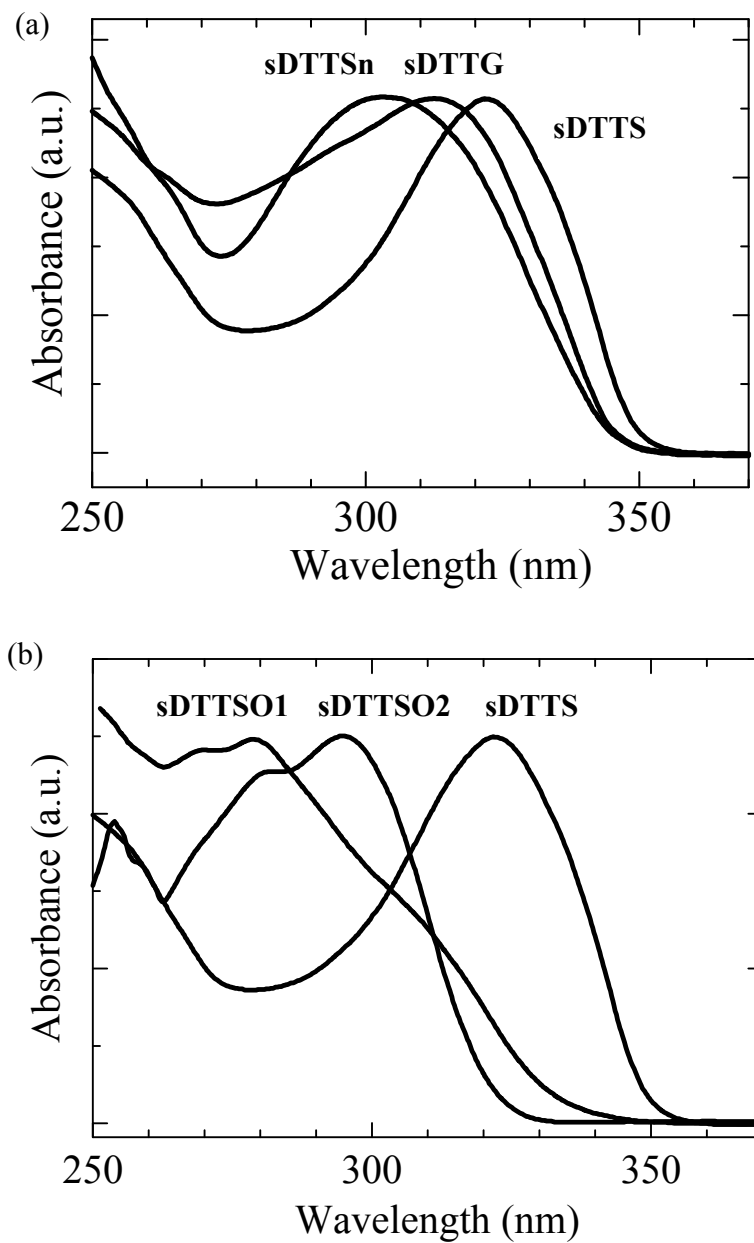


Figure 3. UV spectra of spirobi(dithienothiametalline)s (a) and spirobi(dithienothiasiline) oxides (b).

Table 1

Optical properties of dithienometalloles

Compound	UV abs λ_{\max}/nm (/eV), ϵ	$\Delta\lambda_{\max}/\text{nm}$ (/eV) ^a	Emission $\lambda_{\text{em}}/\text{nm}$	
	in THF		in THF (Φ)	as solids (Φ)
sDTS1	366 (3.39), 25 900	10 (0.9)	435 (0.17)	439 (0.06)
sDTS2	366 (3.39), 21 200		434 (0.10)	438 (0.07)
sDTS5	368 (3.37), 24 100		436 (0.10)	443 (0.07)
sDTG1	358 (3.46), 26 000	8 (0.8)	421 (0.09)	421 (0.05)
DTS1 ^b	356 (3.48), 10 200		425 (0.69)	- ^c
DTG1	350 (3.54), 8 100		409 (0.71)	- ^c

^a $\Delta\lambda_{\max} = (\lambda_{\max} \text{ of sDTM1} - \lambda_{\max} \text{ of DTM1})$.^b See reference 7a.^c Not measured.