Review Article

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Group 14 metalloles condensed with heteroaromatic systems

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Abstract: There has been keen interest in group 14 metalloles as building units of conjugated organic functional materials. This short review summarizes our recent work on group 14 metalloles condensed with heteroaromatic systems, including thiophene and pyridine. These condensed metalloles show interesting properties depending on both the group 14 metallole elements and the heteroaromatic systems. High planarity of the condensed systems and interaction between the element $\sigma^*$-orbital and the heteroaromatic $\pi^*$-orbital enhance the conjugation in these systems leading to their potential applications as functional materials, such as carrier transporting materials and emissive materials.

Keywords: fluorescence, phosphorescence, organic semiconductor, sensitizing dye

1 Introduction

Since Tamao and coworkers reported the use of silole derivatives as efficient electron-transporting materials for organic light emitting diodes (OLEDs) in 1996 [1], many papers have appeared to date that describe the synthesis and properties of silole derivatives [2–8]. Their applications as functional materials, such as photo and electroluminescent materials, carrier transporting materials and sensing dyes have been widely explored. The bonding interaction between the silicon $\sigma^*$-orbital and the cyclic butadiene $\pi^*$-orbital ($\sigma^*-\pi^*$ conjugation) stabilizes the silole LUMO. This interaction results in electro-accepting properties of silole and reduces the HOMO-LUMO energy gap. This is in contrast to the carbon congener, cyclopentadiene, where the presence of such orbital interaction is unclear [2, 3].

We initiated studies concerning the synthesis of thiophene-fused silole, namely dithienosilole (DTS), as the first example of siloles condensed with heteroaromatic systems, expecting that ring-condensation of electronegative silole and electron-rich thiophene would cause strong electronic interaction between these rings [9, 10]. Although such intrasystem donor-acceptor (D-A) type interaction cannot be clearly seen, DTS has enhanced conjugation ascribable to its high planarity and $\sigma^*-\pi^*$ conjugation, similar to simple siloles [11]. This review summarizes our recent work on the synthesis, properties and functionalities of DTS derivatives and related compounds.

2 Dithienosiloles

In 1998, we reported the synthesis of DTSs for the first time [9]. DTSs are typically prepared by the reactions of 3,3’-dilithio-4,4’-bis(trimethylsilyl)-2,2’-bithiophene with dichloro and difluorosilanes (Scheme 1) [9, 10]. The two trimethylsilyl groups are readily replaced with halogen atoms to allow further transformation, including oligomerization and polymerization. Simple DTS compounds that have no conjugated substituents on the thiophene rings have UV absorption bands around 350 nm, longer than those of similarly substituted bithiophene and dithienocyclopentadiene, DTC (cyclopentadithiophene, CPDT), by approximately 50 and 30 nm, respectively [10, 11]. Fig. 1 represents the HOMO and LUMO energy levels and their profiles of DTS, together with those of DTC, as derived from density functional theory (DFT) calculations. Both the HOMO and LUMO of DTS lie at lower energy levels than those of DTC. The latter is ascribable to the $\sigma^*-\pi^*$ conjugation, as observed for simple non-condensed siloles (vide supra) [2, 3]. The former arises from reduced anti-bonding interaction between the thiophene ring systems by introducing longer Si–C bonds. This is also a generally observed characteristic of siloles. Consequently, DTS has a smaller HOMO-LUMO energy gap than DTC, agreeing with the experimental data — that is, DTS usually has a UV absorption band at lower energy and its cyclic voltammogram (CV) reveals the anodic peak at slightly higher or similar potential in comparison with those of the DTC analogs. Based on the low-lying HOMO and LUMO, several DTS derivatives were applied to OLED as electron-transporting materials with good hole-
blocking properties [10, 12, 13]. In particular, a vapor deposited film of DTS-Py (Chart 1) was introduced to OLED as an electron-transporting layer, improving the device performance [12]. However, in highly conjugated systems, such as \( \pi \)-conjugated polymers, the \( \sigma^* - \pi^* \) conjugation is not efficiently operative in DTS, with minimal effect on the LUMO energy levels [11].

Currently, DTS has been extensively studied as a building unit of conjugated polymers. In 2006, Marks and coworkers reported the applications of alternating copolymers of dihexylthienoisoilole with thienylene and bithio-phenylene (pDTS-T and pDTS-2T in Chart 1) as semiconducting materials of p-type organic thin film transistors (TFT) with good mobility [14]. A little later, an excellent photovoltaic polymer was prepared by Yang et al., which was composed of bis(2-ethylhexylidithienoisisoilole and benzothiadiazole alternating units (pDTS-BT) [15]. A bulk hetero-junction polymer solar cell (BHJ-PSC) based on a blend film of pDTS-BT and PC\(_{71}\)BM was reported to achieve a photo-current conversion efficiency of 5.1%, which was higher than that reported for a similar cell based on the DTC-based analogous polymer [16]. These two excellent findings triggered a wide variety of subsequent studies concerning the use of DTS-based conjugated polymers as optoelectronic device materials [4, 7, 8, 11]. We have recently demonstrated that disilanobithiophene (DSBT) is also applicable as a component of \( \pi \)-conjugated photovoltaic polymers, as shown in Chart 2 [17–20]. A blend film of a DSBT-containing conjugated polymer (pDSBT-BT) with PC\(_{71}\)BM was applied to BHJ-PSC with higher voltage and thereby with higher photo-current conversion efficiency (6.38%) [17], compared to the similar pDTS-BT-based cell reported by Yang et al. [15]. This is primarily ascribable to appropriate twisting of the bithiophene unit of DSBT, which lowers the HOMO energy level of the polymer. It is well known that the lower-lying HOMO of the polymer basically leads to a higher voltage from the polymer-based cell.

The interesting use of DTS-containing polymers as OLED materials has been explored As mentioned above, we have demonstrated that vapor-deposited films of DTS derivatives, including DTS-based conjugated oligomers, are useful as electron-transporting layers of OLEDs. However, the introduction of DTS units into polymeric systems
enables their use as hole-transporting materials and emissive materials, as summarized in the previous review [11]. DTSs are types of bithiophene units and thus essentially possess hole-affinity and are usable as hole-transporting materials.

The rigid tricyclic systems lead to highly photoluminescence (PL) properties of the DTS-based compounds. Phosphorous-substituted DTSs are highly emissive and one of those derivatives (DTS-P in Chart 3) shows aggregation enhanced emission with a higher PL efficiency ($\Phi = 0.79$) in the solid state than that in the solution phase ($\Phi = 0.22$) [20]. This is likely due to the sterically bulky phosphorous substituents that cover the DTS chromophore to avoid concentration quenching. DTS-PO was applied as a blue-green colored electro luminescent material in OLEDs. A gold complex DTS-PAu was prepared, showing efficient blue-colored PL in the solid state ($\Phi = 0.33$). This complex has a higher PL efficiency in solution ($\Phi = 0.99$) [21]. Boryl-substituted DTSs also show highly PL properties in solid states (Fig. 2) [22]. Bis(dimesitylboryl)-DTS (DTS-B) shows sensing properties, responding to fluoride anion in the solution phase. Its UV-vis absorption spectra change clearly upon contact with fluoride anions, likely ascribable to the B-F complex formation.

![Chart 3. Highly PL DTS-based compounds.](chart3.png)

Efficient conjugation in DTS allows the use of the DTS-2,6-diyl system as an effective linker ($\pi$) of the donor-$\pi$-acceptor (D-$\pi$-A) type compounds. The D-DTS-A compounds with methylthio as the donor and perfluorotolyl or dimesitylboryl as the acceptor (S-DTS-Ft and S-TDS-B) have red-shifted emission maxima as compared with those of the corresponding symmetric A-DTS-A (DTS-Ft and DTS-B) compounds. However, the absorption bands of D-DTS-A compounds are at slightly higher energies than those of the A-DTS-A compounds (Fig. 2) [22]. The observed larger Stocks-shifts for the D-DTS-A compounds are likely ascribable to the photo-induced intramolecular charge transfer (ICT). We also prepared several DTS-containing conjugated oligomers [23]. They show PL properties where the PL color is finely controllable by tuning the conjugation length (Fig. 3).

The reaction of DTS with tetracyanoethylene in DMF provides DTS-TCNE, as presented in Scheme 2 [24]. The DTS unit is involved in this system as an electro-donor, forming a D-A system with the strongly electro-accepting tricyanoetheny group. DTS-TCNE exhibits excellent film forming properties and its spin-coating and vapor-deposition provide fine thin solid films. Interestingly, the films undergo quick color change upon exposure to an organic solvent vapor — such as ethanol, acetone, and hexane, as illustrated in Fig. 4 — and thus is potentially useful for sensing volatile organic compounds (VOCs). This process is reversible and a short contact with a chloroform vapor recovers the original color. The mechanism of the color changes is not clear yet, but XRD analysis of the film showed a slight shift of the diffraction peak position accompanying the color change. This seems to indicate that the packing mode of the molecules in the film changes when exposed to organic solvent vapors. Attachment of a MeS or thienyl donor unit on DTS of DTS-TCNE red-shifts the UV absorption maxima, indicating possible color tuning of this type of VOC-sensing materials by modifying the chemical structure (S-DTS-TCNE and T-DTS-TCNE) [25]. They also show clear solvatochromism, as presented in Fig. 5. DTS-linked D-A
type systems have also attracted much attention as excellent photo-sensitizing dyes for dye-sensitized solar cells (DSSCs). Indeed, a high photo-current conversion of 10.3% was achieved based on a DTS-containing dye by Wang and coworkers (Chart 4) [26].

As derivatives of DTS, dithienothiasilines (DTTS) and a DTTS-based polymer (pDTTS-S) were prepared and their hole-transporting properties have been studied in an OLED system (Chart 5) [27]. Spiro-condensed DTS (sDTS) shows p-type semi-conducting properties in its vapor-deposited film, and is potentially usable as an active material for TFT. Although the mobility of the sDTS film was not yet very high ($1.4 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), it seems interesting that such a bithiophene derivative with limited π-conjugation exhibits TFT activity [28]. Spiro-condensed dithienothiasiline derivatives (sDTTS) were also prepared [29].

### 3 Dithienogermole

Dithienogermole (DTG) was first prepared and polymerized to form photovoltaic polymers in three independent groups at similar times (Chart 6) [30–33]. Following these original works, DTG has been extensively studied as a building unit of photovoltaic π-conjugated polymers, similarly to DTS. Quantum chemical calculations of DTG suggest that DTG should have essentially the same electronic structure as that of DTS. However, replacing DTS units of photovoltaic polymers by DTG sometimes improves the cell performance. Enhanced intermolecular interaction for the DTG-containing polymers in film states raises the photocurrent [34].
Another advantage in the use DTG in the place of DTS owes to its chemical stability. DTS is less stable and treatment of DTS with an alkali solution in THF/water leads to the cleavage of Si–C (thiophene) bonds, forming Si–OH and H–C (thiophene) bonds. In contrast, DTG remains unchanged under the same conditions [35]. This chemical stability permits the preparation of DTG-containing oligo and polysilsesquioxanes under alkali conditions, as shown in Scheme 3 [36]. The polyhedral oligosilsesquioxanes with DTG units at the corners (DTG-POSS) have moderately high PL properties ($\Phi = 0.54$), similar to the corresponding DTG monomer. Each DTG chromophores of DTG-POSS are oriented to dispersed directions from the POSS core and are thus electronically separated from each other, despite the accumulation of eight DTG units in a molecule. The random polysilsesquioxane (DTG-PSQ1) is obtained as a solid film. This film has a low PL efficiency ($\Phi = 0.02$), in contrast to DTG-POSS. The interaction of DTG chromophores in the DTG-PSQ1 polymeric system appears to cause concentration quenching. In contrast, copolymerization of the DTG monomer with methyltrimethoxysilane successfully provides highly emissive films of DTG-PSQ2. The PL efficiencies of the copolymers depend strongly on the monomer ratios; a maximal value of $\Phi = 0.33$ was achieved with DTG monomer/methyltrimethoxysilane = 1/99. Incorporation of carrier conducting carbazole units in the polysilsesquioxane provides a film (DTG-PSQ3) that exhibits electroluminescence properties in OLEDs.

Generally, DTGs can be prepared by the reactions of dichlorogermanes with dilithiobithiophenes in higher yields than the DTS congeners. This is ascribable to longer and thus more flexible Ge–C bonds than Si–C bonds, which makes the ring formation easier by reducing the ring strain. In addition, Ge–Cl bonds are less polar and less reactive than Si–Cl bonds and the ring forming reactions proceed in a milder fashion for DTGs than that for DTSs. Reflecting the lower reactivity of Ge–Cl bonds, 4,4-DTG dichlorides (DTG-Cl) are readily prepared from the reactions of tetrachlorogermane with dilithiobithiophenes as shown in Scheme 4 [37]. This contrasts with similar reactions of tetrachlorosilane that always provide the respective spiro-compounds as the major products. Dichlorides DTG-Cl undergo numerous transformation by reacting with nucleophiles and reducing agents, as shown in Scheme 4 [38]. Wurtz type coupling of DTG-Cl with sodium gives the corresponding polygemanes pDTG.
We also prepared dithienostannnole (DTSn) derivatives \textbf{DTSn1} and \textbf{DTSn2} (Chart 7) [39]. Interestingly, \textbf{DTSn1} shows crystallization-enhanced emission, whereas \textbf{DTSn2} does not. \textbf{DTSn1} has a much higher PL quantum yield as crystals ($\Phi = 0.556$), emitting blue light, than those in the solution and amorphous phases with $\Phi = 0.009$ and 0.028, respectively. It should be also noted that the $\sigma^*-$*$\pi$ interaction is operative in DTSn, although the degree of the $\sigma^*-$*$\pi$ interaction seems to be minimized to an extent in comparison to DTS and DTG.

![Scheme 4. Preparation and reactions of DTG dichlorides.]

\begin{center}
\includegraphics[width=\textwidth]{scheme4.png}
\end{center}

\textbf{Chart 7.} Dithienostannnole.

\section{4 Dipyridinosilole and germole}

Silole and germole (\textbf{DPyS1}, \textbf{DPyS2}, and \textbf{DPyG1}) condensed with electro deficient bipyridyl were prepared (Scheme 5) [40]. These dipyridinosilole and germole exhibit pronounced electro deficiency compared to bipyridyl, which arises from the $\sigma^*-$*$\pi$ conjugation. Their PL properties were first studied at room temperature, to reveal much less efficiency ($\Phi < 0.02$) than those of DTS and DTG derivatives (\textit{vide supra}). However, they are phosphorescent at low temperature even as solids. Quantum efficiency of the solid state phosphorescence of \textbf{DPyG1} at 77K is $\Phi = 0.22$, whereas those of \textbf{DPyS1} and \textbf{DPyS2} are less than 0.01. It is speculated that the heavy atom effects of germanium of \textbf{DPyG1} enhance the phosphorescent properties.

![Scheme 5. Synthesis and reactions of dipyridinosilole and dipyridinogermole.]

\begin{center}
\includegraphics[width=\textwidth]{scheme5.png}
\end{center}

Viologen derivatives are known as electro-deficient compounds that exhibit reversible electrochromic properties on cathodes [41]. \textbf{DPyG1} was treated with methyl iodide to form a viologen derivative (\textbf{DPyG1-Me}) with pronounced electro-deficient properties, as compared with the corresponding germole-free simple viologen. \textbf{DPyG} is useful also as a ligand and its copper complex (\textbf{DPyG1-Cu}) shows clear room temperature phosphorescence in the solid state as well as in solution [42]. Spiro(dipyridinogermole)(dithienogermole)s, \textbf{sDPyDTG}, \textbf{sDPyDTG-Br}, and \textbf{sDPyDTG-2T} were also prepared from DTG-Cl [43]. Of these, \textbf{sDPyDTG-2T} shows excellent photo-sensitizing properties for singlet oxygen generation [44]. Generation of singlet oxygen is of current interest because of potential applications to photo catalytic systems and photo dynamic therapies. Spiro-condensed dipyridinogermole-dithienogermole is a new system for the singlet oxygen generation. The germanium heavy atom effects, enhancing the intersystem crossing between the photo-excited singlet state and the triplet state, seem to be responsible for the sensitizing properties.

Siloles and germoles condensed with benzothiophene (\textbf{BBTS}) [45], indole (\textbf{DIS}) [45] and benzofuran (\textbf{BBFS} and \textbf{BBFG}) [46] have been synthesized (Chart 8). Bis(benzofurano)metalloles \textbf{BBFS} and \textbf{BBFG} undergo in-
interesting reversible [2+2] dimerization upon crystallization from a certain solvent. The dimers revert to the monomers quantitatively when dissolved in organic solvents, as shown in Scheme 6.

Chart 8. Benzoheterole-condensed silole and germole.

Scheme 6. Dimerization of BBFS and BBFG.

5 Summary

Many types of group 14 metalloles that are condensed with heteroaromatic systems have been prepared. These exhibit interesting properties based on both the metallole elements and the heteroaromatic systems leading to applications as functional materials, such as carrier transporting materials, photo and electro luminescent materials, and sensitizing dyes. There remain other potential combinations of the metalloles and heteroaromatic systems and further studies to develop new systems based on these combinations are in progress.

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References

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