High HOMO Levels and Narrow Energy Band Gaps of Dithienogalloles

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Key Word

Dithienogallole, Gallole, Fused thiophene, Heterole, Thiophene

ABSTRACT

We synthesized dithieno[3,2-*b*:2'3'-*d*]galloles containing four-coordinated gallium atoms. It was found that dithienogalloles had high stability to air and moisture and showed narrower energy-band gaps than dithienosiloles which are commodity materials in organic opto and/or electronic devices. In addition, relatively-higher HOMO levels were observed from dithienogalloles than those of other dithienoheteroles from electrochemical measurements. We experimentally and theoretically demonstrated the electron-donating properties and resonance effects of gallium atoms of dithienogalloles.

Aromatic-ring-fused thiophenes are versatile building blocks because of a wide applicability for modern organic-based electronic devices.[1] In particular, dithienoheterole and their derivatives have received much attention. Various kinds of heteroatoms such as nitrogen,[2] phosphorus,[3] bismuth,[4] sulfur,[2a,b,5] silicon,[2a,6] germanium[7] and tin[8] have been incorporated into the dithienoheterole structure, and their optical and electrochemical properties were prominently studied. It was revealed that some of these compounds had high potential as basic structures for photovoltaic cells,[2,5a,6,7] light-emitting diodes[1,6c] and field-effect transistors.[1a-c,2,5,6] Furthermore, unique electronic states originated from boron atoms such as anti-aromaticity and high reductive potentials were clarified from dithienoboroles.[9] Thereby, the introduction of group 13 elements into the dithienoheterole structures is a topic with high relevance. Indeed, the optical and electrochemical properties of heteroles of heavier group 13 elements have been presented in the most recent reports.[10] However, the high sensitivities of heteroles with heavier group 13 elements have made the investigation of their material properties challenging. Hence, to prove the uniqueness and to explore the further functional materials, the synthesis of new series of dithienoheteroles with heavier group 13 elements and understanding their characteristics are of great significance.

We have recently reported the facile synthesis and the unique optical properties of gallafluorenes. The emission via the excited triplet states and the weak electronic interaction between the aromatic units through four-coordinated gallium atoms, namely broadly-defined conjugation, were presented.[11] To establish chemistry in conjugated materials involving group 13 elements, further examples to offer the electronic effect of gallium atoms on π-conjugation systems are essential. From this stand point, herein, we demonstrate the synthesis and characterization of dithieno[3,2-b:2'3'-d]galloles. We evaluated the electronic and resonance effects of four-coordinated gallium

atoms based on the comparison with other dithienoheteroles (Figure 1) to gather the information on fundamental electronic properties of gallium-containing conjugated molecules.
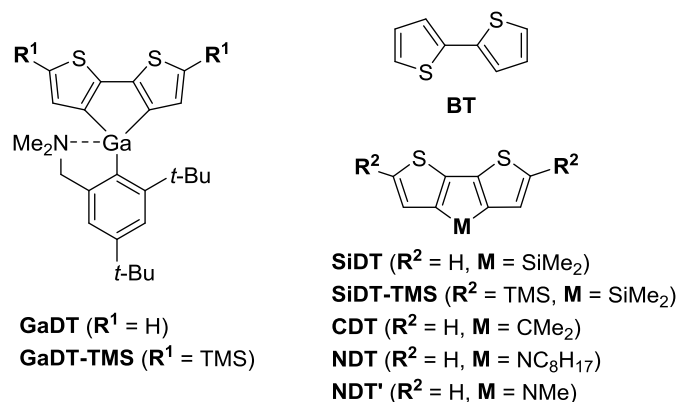

Figure 1. Chemical structures of dithienogalloles and other dithienohetelole derivatives.

We designed dithienogalloles where gallium atoms were protected by Mamx groups (Mamx = 2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl).[12] According to Scheme 1, we synthesized dithienogalloles (**GaDT** and **GaDT-TMS**) through the reaction with dilithiobithiophenes and MamxGaCl$_2$. **GaDT** and **GaDT-TMS** showed stability to air and moisture and were able to be stored for at least one month under ambient atmosphere.
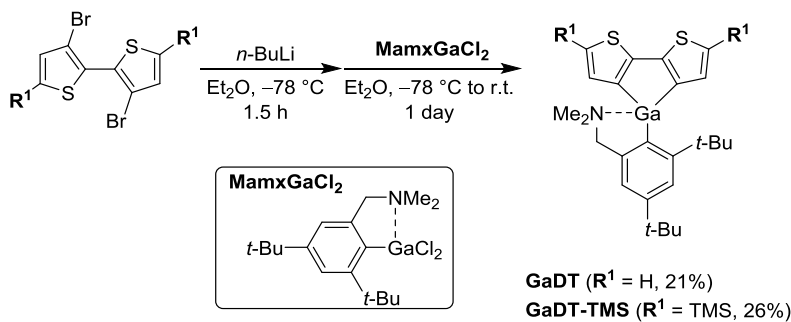
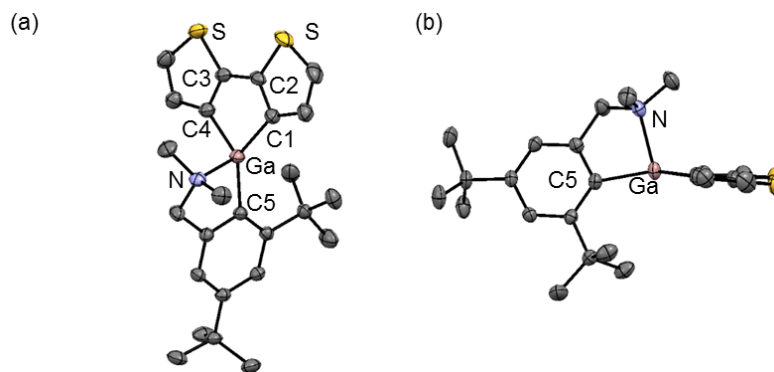**Scheme 1.** Synthesis of dithienogalloles **GaDT** and **GaDT-TMS**.

Figure 2. ORTEP drawings of (a) **GaDT** and (b) side view (30% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga–N 2.092(3), Ga–C1 1.983(3), Ga–C4 2.004(3), Ga–C5 1.971(3), C1–Ga–C4 89.95(12), C1–Ga–C5 138.92(11), C4–Ga–C5 125.63(11), C1–Ga–N 104.57(11), C4–Ga–N 105.69(11), C5–Ga–N 86.38(10), C1–C2–C3–C4 3.6(4).

The geometry of **GaDT** was determined by an X-ray diffraction analysis of single crystal as described in Figure 2. The length of Ga–N bond was 2.091 Å and comparable to well-known coordinated bond lengths of nitrogen to gallium atoms [reported Ga−N bond lengths: 2.013–2.178 Å[11,12b,13]]. The sum of C–Ga–C angles was 354.49° and similar to those of other organogallium compounds with Mamx groups [sums of C–Ga–C angles of the reported organogallium compounds: 352.7–358.6°[11,12b]]. The sum of C–Ga–N angles was 296.7° and comparable to those of reported organogallium compounds with Mamx groups [sums of C–Ga–N angles of the reported organogallium compounds: 294.9–297.3°[11,12b]]. The structure around the gallium atom was similar to the trigonal planar structure coordinated by nitrogen from upper side. The dihedral angle of C(1)–C(2)–C(3)–C(4) (3.7°) was small and the moiety of bithiophene had a planar structure.

We investigated the optical properties of **GaDT** and **GaDT-TMS** and compared to those of bithiophene (**BTH**), cyclopenta-dithiophene (**CDT**) and dithienosiloles (**SiDT** and **SiDT-TMS**). In Figure 3, their UV–vis absorption and photoluminescence spectra are represented. Optical data are listed in Table 1. The absorption band of **CDT** appeared at 316 nm, and the red-shift of the

peak position was observed compared to that of **BDT**. It is likely that higher planarity of the bithiophene unit induces these changes. The red-shifted absorption band of **GaDT** was observed at 342 nm relative to not only that of **CDT** but also **SiDT** (338 nm). These data mean that **GaDT** has a narrower energy band gap than **CDT** and **SiDT**. The σ*–π* conjugation of their silole moieties in **SiDT** is responsible for the narrower energy band gap. Similarly, **GaDT-TMS** showed the narrower energy band gap than **SiDT-TMS**. The decrease of energy band gap of dithienosiloles compared to **CDT** are caused by σ*–π* conjugation of their silole moieties.[6] These facts suggest that the decrease of the band gaps of dithienogalloles should be attributed to the fixed-conformation of the bithiophene units as well as the electronic effect of the four-coordinated gallium atoms.
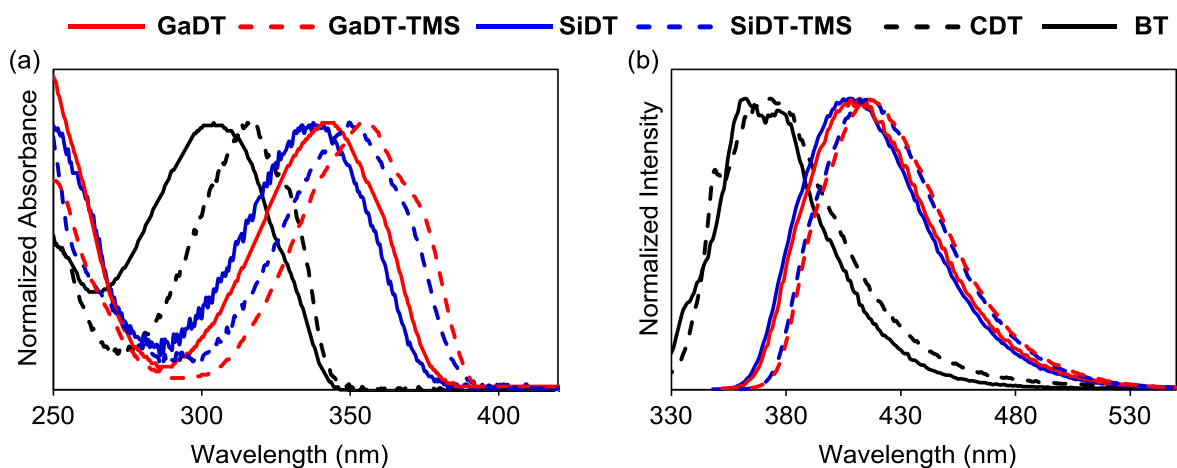

Figure 3. (a) UV−vis absorption and (b) photoluminescence (excited at $\lambda_{max,abs}$) spectra of 1.0×10^{-5} M **GaDT** (solid red), **GaDT-TMS** (dashed red), **SiDT** (solid blue), **SiDT-TMS** (dashed blue), **CDT** (dashed black) and **BT** (solid black) in THF.

Table 1. UV−vis absorption and photoluminescence data for dithienoheteroles[a]

	$\lambda_{max,abs}$ (nm)[b]	$\lambda_{onset,abs}$ (nm)[c]	$\lambda_{max,FL}$ (nm)[d]	$\Phi_F{}^e$	$\tau_{1/2}$ (ns)[f]
GaDT	342	377	412	0.52	5.63 (100%) ($\chi^2 = 1.09$)
GaDT-TMS	355	390	416	0.89	3.74 (100%) ($\chi^2 = 1.04$)
SiDT	338	374	408	0.54	5.20 (100%) ($\chi^2 = 0.98$)
SiDT-TMS	350	385	416	0.76	3.82 (100%) ($\chi^2 = 0.81$)
CDT	316	344	373	0.05	< 0.05
BT	304	343	362	0.13	< 0.05

[a]Optical measurements were performed for 1.0×10^{-5} M in THF solution. [b]Absorption maxima. [c]Onset wavelength of absorption bands. [d]Fluorescence maxima excited at $\lambda_{max,abs}$. [e]Absolute quantum yield. [f]Photoluminescence decay analyses were performed upon 375 nm (292 nm for **CDT** and **BT**) excitation by a UV diode laser.

In photoluminescence spectra, the emission bands of **GaDT** and **GaDT-TMS** also appeared in the red-shifted wavelength regions at 412 nm and 416 nm compared to **CDT** (373 nm). Their wavelengths were similar to those of **SiDT** (408 nm) and **SiDT-TMS** (416 nm), respectively. The absorption and emission bands of dithienogalloles were slightly effected by solvents (Figures S11 and S12 in the Supporting Information). These facts suggest that the emission bands of **GaDT** and **GaDT-TMS** are mainly attributed to π–π* transitions. In addition, the red-shifts of emission bands should be caused by the electronic effect of the gallium atoms, as described in the previous section of the absorption spectra. The short emission lifetimes in nanosecond orders represent that these emissions were fluorescence. Moreover, **GaDT** and **GaDT-TMS** showed high quantum yields similarly to **SiDT** and **SiDT-TMS**. Particularly, the quantum yield of **GaDT-TMS** was 0.89. This tendency was observed in the case of dithienostannoles.[8a] New emission bands of **GaDT** and **GaDT-TMS** hardly appeared at 77K (Figure S13 in the Supporting Information). This result

means that intersystem crossing hardly proceeded in the synthesized dithienogalloles. Thereby, high quantum yields could be obtained. These data propose that dithienogallole units are promising to be used as fluorescence emitting materials.
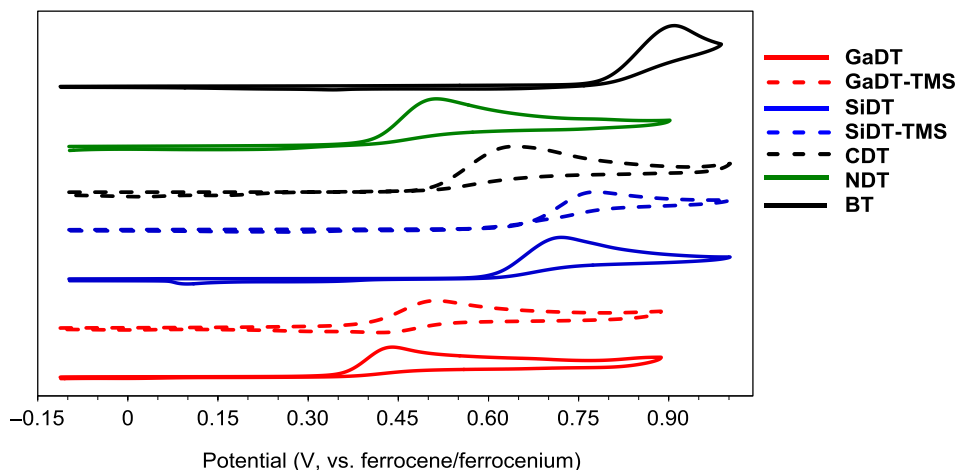

Figure 4. Cyclic valtammograms of 1.0 mM **GaDT** (solid red), **GaDT-TMS** (dashed red), **SiDT** (solid blue), **SiDT-TMS** (dashed blue), **CDT** (dashed black) **NDT** (solid green) and **BT** (solid black) in CH_3CN/CH_2Cl_2 (6:1) solution containing NBu_4PF_6 (0.10 M) using a Pt working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode, and a ferrocene/ferrocenium external standard at room temperature with a scan rate of 0.05 Vs^{-1}.

Table 2. Results of CV measurements, energy levels of frontier orbitals for dithienoheteroles.[a]

| | E_g [b] | E_{cp}^{ox} [c] | E_{onset}^{ox} [d] | E_{HOMO} [e] | E_{LUMO} [f] |
	(eV)	(V)	(V)	(eV)	(eV)
GaDT	3.29	0.44	0.36	−5.16	−1.87
GaDT-TMS	3.18	0.51	0.40	−5.20	−2.02
SiDT	3.32	0.72	0.61	−5.41	−2.09
SiDT-TMS	3.22	0.78	0.66	−5.46	−2.24
CDT	3.60	0.64	0.50	−5.30	−1.70
NDT	3.91	0.51	0.41	−5.21	−1.30
BT	3.62	0.91	0.80	−5.60	−1.98

[a]CV measurements were carried out in CH_3CN/CH_2Cl_2 (6:1) solution containing NBu_4PF_6 (0.10 M) using a Pt working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode, and a ferrocene/ferrocenium external standard at room temperature with a scan rate of 0.05 Vs^{-1}. [b]E_g were estimated from the onset wavelength of absorption spectra of dithienoheteroles. [c]Oxidation potential at the peak top of oxidation wave of dithienoheteroles. [d]Oxidation potential at the onset of oxidation wave of dithienoheteroles. [e]$E_{HOMO} = -(4.8 + E_{onset}^{ox})$. [f]$E_{LUMO} = E_{HOMO} + E_g$.

In Figure 4 and Table 2, we describe the results of cyclic voltammograms (CV) and the energy levels of frontier molecular orbitals of dithienoheteroles estimated from the measurement results. In all the dithienoheteroles, the oxidation waves and their peaks were observed. **GaDT** showed the onset of oxidation wave at 0.36 V and lower oxidation potential than **CDT** (0.50 V) and dithienopyrrole (**NDT**, 0.41 V), which have electron-donating carbon or nitrogen atoms at the bridgehead of cyclopentadithiophenes. These data indicate that the highest occupied molecular orbital (HOMO) level of **GaDT** was higher than other dithienoheteroles. The oxidation potential of **GaDT-TMS** was elevated by the trimethylsilyl groups compared to **GaDT**. Nevertheless, the value of the onset of the oxidation wave of **GaDT-TMS** was 0.40 V and similar level with that of **NDT**. These facts indicate that the four-coordinated gallium atoms would show strong electron-donating properties toward the bithiophene units. We estimated the energy band gaps E_g of dithienoheteroles from the onsets of the UV–vis absorption bands, the energy levels of HOMOs based on $E_{HOMO} = -(4.8 + E_{onset}^{ox})$,[14] and the energy levels of lowest unoccupied MO (LUMO) based on $E_{LUMO} = E_{HOMO} + E_g$. The HOMO levels of **GaDT** (−5.16 eV) and **GaDT-TMS** (−5.20 eV) were higher than or comparable to that of **NDT** (−5.20 eV). In contrast, the LUMO levels of **GaDT** (−1.87 eV) and **GaDT-TMS** (−2.02 eV) were almost similar to those of **BT** (−1.98 eV) and **CDT** (−1.70 eV), and lower than that of **NDT** (−1.30 eV). These results suggest that the electron-donating characteristics of the gallium atoms critically affect the energy levels of HOMOs. The electron-donating properties of the gallium atoms less significantly influence to LUMOs.
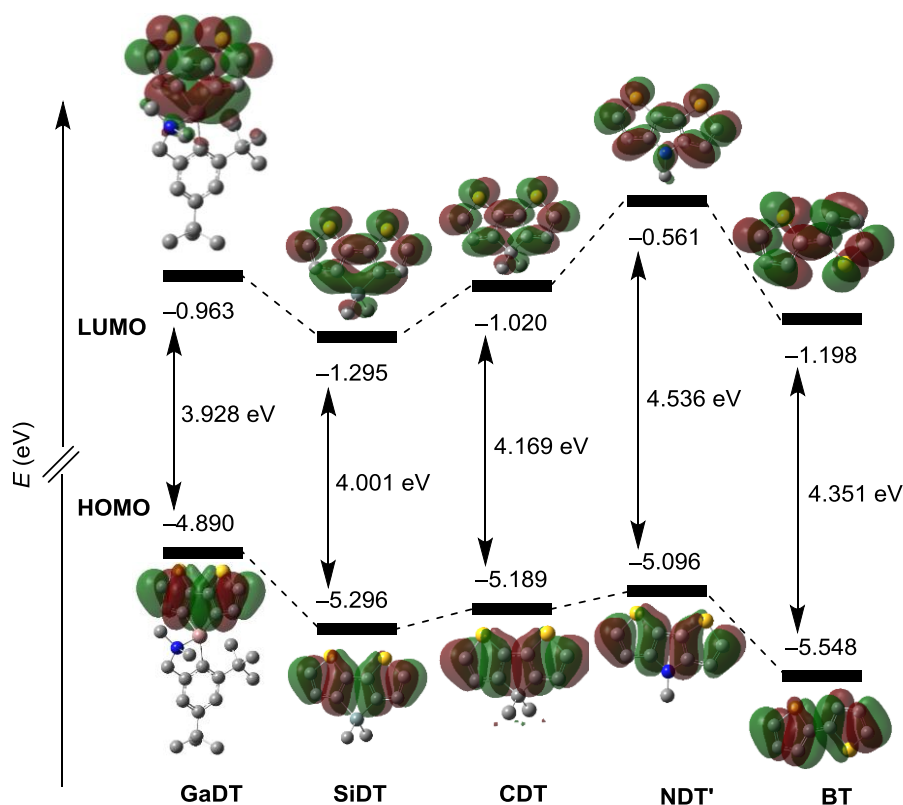
Figure 5. Energy diagram and frontier orbitals of **GaDT**, **SiDT**, **CDT**, **NDT'** and **BT** calculated by the DFT method (B3LYP/6-31G(d,p)//B3LYP/6-311+G(2df) levels for gallium atoms and B3LYP/6-31G(d,p) levels for others. Hydrogen atoms are omitted for clarity.

For the further comprehension of the electronic interaction between the gallium atoms and the bithiophene units, we carried out density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. All the geometries of dithienoheteroles were optimized at the B3LYP/6-31G(d,p) levels, and the transitions and energy states were calculated at the B3LYP/6-311+G(2df) levels for gallium atoms and the B3LYP/6-31G(d,p) levels for others using the optimized geometries. The calculated frontier molecular orbitals and energy diagrams of dithienoheteroles in the S_0 ground states are illustrated in Figure 5 and Figure S14 in the Supporting Information. The results of the optimization of their structures and the contributions of energy transitions are described in Tables S5–S18 in the Supporting Information. Accordingly, the HOMO of **GaDT** is

localized only on the bithiophene units, while the LUMO is distributed on the bithiophene unit and gallium atom. The allowed transition at 334 nm for **GaDT** is mainly attributed to the excitations from HOMO to LUMO as observed in other dithienoheteroles. In addition, the HOMO–LUMO band gap of **GaDT** is −3.928 eV and narrower than that of **SiDT** (−4.001 eV). The energy level of HOMO of **GaDT** is −4.890 eV and higher than those in other dithienoheteroles. On the other hand, the energy level of LUMO of **GaDT** is −0.963 eV and similar to that of **CDT** (−1.020 eV) and lower than that of **NDT'** (−0.561 eV). These calculation results show good qualitative agreements with the energy levels of the frontier orbitals and HOMO-LUMO band gaps obtained from optical and electrochemical measurements. The localization of HOMO only on the bithiophene unit suggests that the increase of HOMO level should be caused by the electron-donating property of the four-coordinated gallium atom. The LUMO level of **GaDT** should be lowered and stabilized by the delocalization of molecular orbital involving gallium atom compared to that of **NDT'**. This stabilization of the LUMO level was elucidated in our previous work.[11b] In other words, the increase of HOMO levels results from the inductive effect of the four-coordinated gallium atom. Furthermore, the stabilization of LUMO level is attributed to the resonance effect of the gallium atom. Therefore, the narrower HOMO–LUMO band gap of **GaDT** is accomplished.

In conclusion, we synthesized air- and moisture-stable dithieno[3,2-*b*:2'3'-*d*]galloles not only for the creation of functional materials but also for the fundamental investigation on electronic effects of the four-coordinated gallium atoms. From single crystal X-ray structure analysis, the gallium atom of the synthesized dithienogallole had a four-coordinated structure, and the geometry of the gallium atom was similar to the trigonal planar structure coordinated by nitrogen from upper side. The optical and electrochemical measurements and theoretical calculation results revealed the increasing of HOMO levels by the electronic-donating effects of the four-coordinated gallium

atoms and the stabilization of LUMO levels by the gallium-containing conjugation. Consequently, the narrower HOMO–LUMO band gaps of dithienogalloles than those of dithienosiloles were observed. In addition, the high quantum yield of **GaDT-TMS** was obtained. Dithienogalloles and their derivatives could be promising compounds for organic electronic devices.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

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