COMMUNICATION

Synthesis of Conjugated Polymers Containing Gallium Atoms and Evaluation of Conjugation though Four-co-ordinate Gallium Atoms

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The synthesis and analysis of the electronic states of the main-chain type-organogallium polymers are presented. We synthesized the polymers containing four-coordinate gallium atoms with organometal coupling reactions. The synthesized polymers showed good solubility in common organic solvents and enough stability for measuring a series of properties under ambient conditions. In the UV−vis absorption spectra, the electronic interaction through four-coordinate gallium atoms was suggested from the peak shifts of the polymer compared to the model compounds. Theoretical calculation of these molecules supports the extended electronic interaction through the polymer main-chain involving gallium atoms.

Conjugated polymers have been paid much attention because of their unique properties, for example luminescence properties, electrical conductivities and nonlinear optical properties, and applied for organic light-emitting diodes (OLEDs),[1] organic solar cells,[2] organic field effect transistors (OFETs),[3] nonlinear optical (NLO) devices,[4] and polymer sensors.[5] General conjugated polymers consisted of benzene rings or carbon–carbon multiple bonds in their main chains.[6] By replacing the heavier atom, further properties are often obtained. For example, polysilanes show σ-conjugation, which is geminal interaction of orbital overlap between the two neighboring Si-Si σ-bonding orbitals and vicinal interaction between sigma-bonding orbitals of nearest-neighbor and next-nearest neighbor Si atoms.[7] Siloles or silacyclopentadienes show σ*-π* conjugation by interaction between σ* orbital of two exocyclic σ-bonds on the silicon atom and the π* orbital of the butadiene moiety.[8]
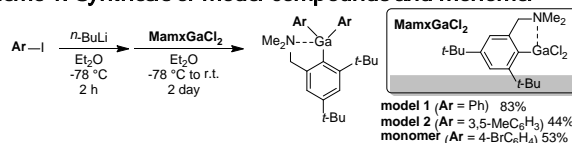
Boron atom is a 13th group element and can form a stable complex with various ligands. Versatile properties as an opto and/or electric materials have been found from the organoboron-containing conjugated molecules and polymers.[9] Therefore further functions can be expected by replacing heavier atoms in the same group.[10] However, there are only a few reports on electronic properties of organogallium compounds because of their instability to air and moisture.[11] The role of gallium atoms in the conjugation is unclear. Recently, we have reported on synthesis and optical properties of dibenzogalloles, namely
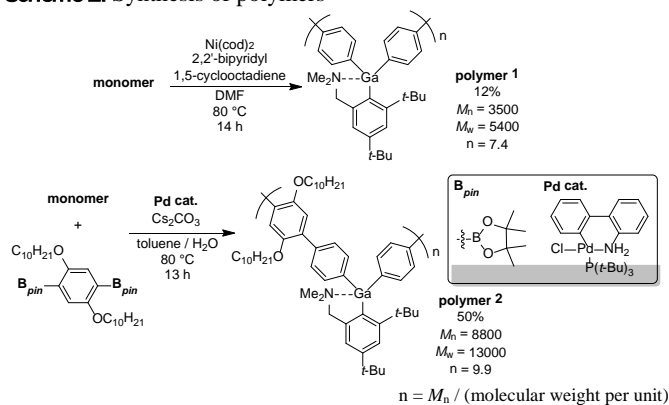
gallafluorenes. It was found that these organogallium complexes have enough stability toward air and moisture for measuring a series of optical properties.[12] However, there are still much room to explore the electronic interaction between gallium atom and the conjugation system.

In this work, we present the stable conjugated polymers including four-coordinate gallium atoms and aim to reveal the conjugation with gallium atoms experimentally. We designed gallium-containing polymers with 2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl (Mamx) groups[11b,13]. By the coordination with the amine, it was expected that the gallium polymers were stabilized to air and moisture. In addition, the conformation around the gallium atoms should be immobilized.[11a] We investigated and compared optical properties of the synthesized polymers and their model compounds. Finally, to ensure the conjugation through the gallium atoms, we performed the calculation with the model compounds and polymers with molecular and crystal orbital methods.

The monomer and model compounds were synthesized according to Scheme 1. Aryl iodides were treated with *n*-BuLi followed by (Mamx)GaCl₂. After reaction for 2 days, the stable monomer and model compounds were obtained. All the compounds containing gallium atoms showed unexpected degradation during the purification in an ambient atmosphere. The monomer and model compounds were stored under air for more than six months without any decomposition. The monomer was polymerized with Yamamoto coupling reaction in the presence of the Ni(cod)₂ and 2',2-bipyridine or with Suzuki–Miyaura coupling reaction with 2,5-didecyloxybenzene-1,4-diboronic acid bis(pinacol)ester as a comonomer in the presence of the palladium catalyst precursor (Scheme 2).[14] The number- and weight-average molecular weights (M_n, M_w) and degree of polymerization (n) of the products were determined by a size-exclusion
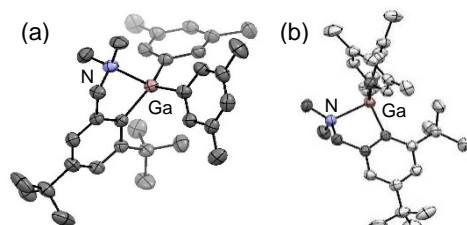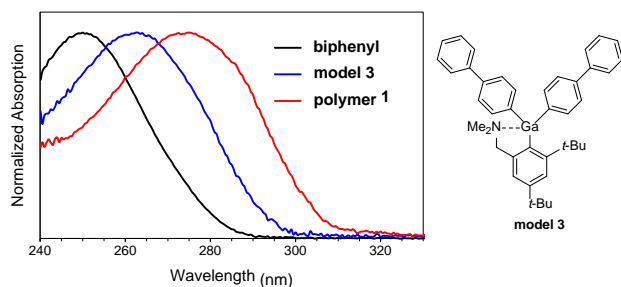
Scheme 1. Synthesis of model compounds and monomer

model 1 (Ar = Ph) 83%
model 2 (Ar = 3,5-MeC₆H₃) 44%
monomer (Ar = 4-BrC₆H₄) 53%

Scheme 2. Synthesis of polymers

n = M_n / (molecular weight per unit)

Table 1. UV−vis absorption and PL data for biphenyl, **model 3** and **polymer 1**

	$\lambda_{\text{max, abs}}^{a}$	$\varepsilon_{\text{abs, max, abs}}$ ($M^{-1}cm^{-1}$)	$\lambda_{\text{onset, abs}}$
biphenyl	250 nm	14,900	280 nm
model 3	263 nm	47,500	294 nm
polymer 1	275 nm	38,300	306 nm

^{a} Absorption maxima: 1.0×10^{-5} M in CHCl$_3$ solution.

HOMO−1 (−5.882 eV)   HOMO (−5.783 eV)   LUMO (−0.722 eV)   LUMO+1 (−0.541 eV)

Figure 3. Selected MOs of **model 3**. Hydrogen atoms are omitted for clarity.
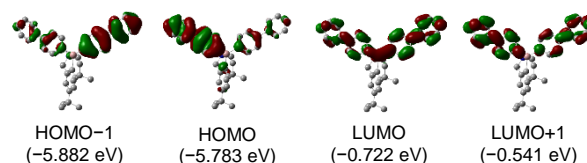
chromatography (SEC). From the profiles, **polymer 1** and **polymer 2** showed the larger molecular weights (M_n = 3,500 and 8,800, respectively) than those of the corresponding monomers. These data mean the generation of the polymeric products. From the ^{1}H NMR spectra, the polymers provided similar peaks with the corresponding monomers. The coupling polymerization progressed successfully without cleavage of bonds of gallium and carbon atoms.

The molecular structure of **model 2** was determined by a single crystal X-ray diffraction (XRD) analysis (Figure 1). The average Ga1−N1 bond length of 2.123 Å is significantly shorter than the sum of van der Waals' radii of gallium and nitrogen (3.42 Å). The Ga1−N1 bond length was compared to other reported gallium compounds with the coordination of nitrogen atoms to gallium atoms [reported Ga−N bond lengths: 2.013–2.178 Å[11a, 12, 15]]. This result represents that the gallium atom in **model 2** should have a four-coordinate structure. In addition, the sum of the C−Ga−C angles was 352.7°. It is clearly shown that the gallium center forms the nearly planar structure rather than tetrahedral one. This planarity could be favourable for extending the conjugation system through the polymer main-chain. The single crystal of **model 2** presented the fine pattern for analysis because the rotation of the benzene rings was fixed by the two methyl groups. On

the other hand, the reliable data were not obtained from the single crystals of **model 1** and **monomer** because their two benzene rings rotated and their positions wandered.

The optical properties of biphenyl, **model 3** and **polymer 1** were investigated by UV–vis absorption in CHCl$_3$ solution to examine the electronic structures at the ground state (Figure 2). **Model 3** showed the absorption peak at 263 nm and the onset of the peak at 294 nm. The top and onset of the absorption peak of **polymer 1** are 275 nm and 306 nm, respectively. Both compounds showed larger bathochromic shifts in the absorption spectra by 13 nm and 25 nm compared to that of biphenyl. In particular, **polymer 1** showed the red-shifted absorption peak relative to **model 3**. These data clearly indicate that each biphenyl unit in the polymer should electronically interact through the gallium atoms. In other words, the electronic conjugation is obtained at the ground state. The spectra of **polymer 2** and its model compound also showed similar trend.

To investigate the electronic interaction between π-units through the gallium atoms, we calculated **model 3** by the density functional theory (DFT) method at the B3LYP/6-31G(d,p) level. Figure 3 illustrates the molecular orbitals (MOs) of **model 3**. The Ga−N bond length was obtained as 2.154 Å, and the sum of the C−Ga−C angles 356.11°, signifying that the gallium center forms a planar structure. These results are in good agreement with the experimental data obtained from a single crystal XRD analysis with **model 2**. Therefore, the structure around the gallium atom of **model 2** could be applicable for estimating the structures in other model compounds and polymers. The energy gap between the HOMO (highest occupied MO) and HOMO−1 is 0.099 eV, where these two MOs are almost degenerate. In contrast, the energy gap between the LUMO (lowest unoccupied MO) and LUMO+1 0.181 eV, being larger than that between the HOMO and HOMO−1. Thus the degeneracy is rather split in the LUMO and LUMO+1. In addition, although the HOMO is localized at either biphenyl, the LUMO delocalized to the both biphenyls and the gallium atom. These results significantly support the data from the optical measurements; the conjugation involving the four-coordinate gallium atom through the polymer main-chain in the LUMO state.

For further understanding of the conjugation through the polymer main-chain, we calculated the electronic state of **polymer 1** by the crystal orbital (CO) method at the B3LYP/6-31G(d,p) level. We employed the dimer as the unit cell[16] and drew the energy band diagram with the selected COs (Figure 4). Note that all the bands stick together at the X point due to the dimer unit cell, and hence that the HO bandwidth is apparently equal to the energy gap between the HOCO and HOCO−1 at the Γ point. The LU bandwidth is comparable to that between the LUCO and LUCO+1 at the same point. The LU bandwidth
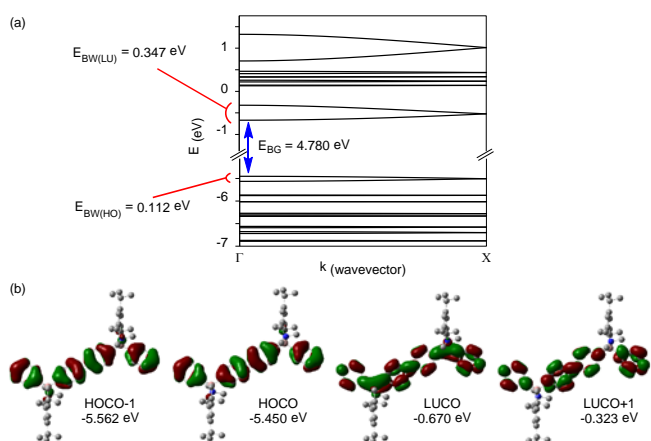

Figure 1. ORTEP drawings of (a) **model 2** and (b) side view (30% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Figure 2. UV–vis absorption spectra of 1.0×10^{-4} M biphenyl, **model 3** and **polymer 1** in CHCl$_3$ solution.

Figure 4. (a) Energy band diagram and (b) selected COs of **polymer 1**. Hydrogen atoms are omitted for clarity.

(0.347 eV) is three times larger than the HO bandwidth (0.112 eV). This result clearly indicates that the conjugation of this polymer is expanded through the main chain involving the gallium atoms in the LUCO state.

Conclusions

A series of conjugated polymers containing gallium atoms in the polymer main-chain were synthesized with conventional metal-catalyzed coupling reactions. The electronic interaction through four-coordinate gallium atoms in the main chains was observed experimentally with the optical measurements. Theoretical calculations support these data. This conjugation is less strong than π-conjugation but certainly exists. These materials are promising as a key component in the next generation of opto and/or electronic organic devices.

Notes and references

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16. This unit cell is based on the lack in screw-axis symmetry operation in the Crystal 09 program for the CO method (see Table S6 in the ESI).