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Synthesis and Optical Properties of Stable Gallafluorene Derivatives: Investigation of Their Emission via Triplet States

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S *Supporting Information*

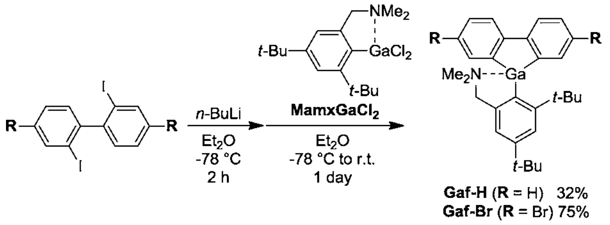
ABSTRACT: We designed and synthesized air- and moisture-stable gallafluorenes in which two benzene rings were bridged by the four-coordinate gallium atoms. The series of gallafluorenes were prepared by introducing electron-donating and -withdrawing groups through Suzuki–Miyaura coupling reactions. The gallafluorenes showed unique emissions via their triplet states in the presence of $B(C_6F_5)_3$. These emissions were obtained via the triplet exciplex of gallafluorene and $B(C_6F_5)_3$.

Fluorenes have attracted attention as building blocks for constructing highly efficient optoelectronic materials that can be used in, for example, electroluminescence displays[1] and photovoltaic cells[1a,2] because of their strong emission properties and high charge carrier ability. The introduction of a variety of heteroatoms (nitrogen,[1a,3] silicon,[1a,4] boron,[5,6] sulfur,[7] germanium,[8] etc.) into the bridgehead position leads to various inherent characteristics. Thus, the exploration of synthetic methods for fluorenes and their new functions are of great significance to comprehend their electronic structures, which may lead to applications of these materials for advanced devices.

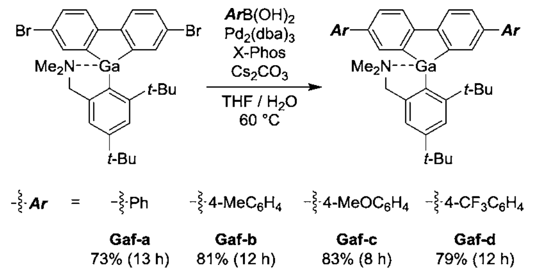
The optical and electronic properties of heterocyclic compounds containing group 13 elements are recent topics with high relevance. In particular, boron-containing heterocycles and conjugated systems have been vigorously studied in terms of antiaromaticity,[5,9] unique optical properties,[5,6e,10] and electron-carrier ability.[5,10d−f,11] To compare the electronic structures and induce other functions, replacement with heavier elements in the same periodic group often offers interesting examples.[12] Moreover, the heavy-atom-bridged compounds have great possibilities for applications as phosphorescent or electron-conducting materials. However, there have been only a few reports on dibenzoheteroles containing aluminum[13] or gallium[14] because their poor stabilities have made it difficult to evaluate the characteristics of these compounds. Although Cowley and co-workers synthesized gallafluorene and determined the structure by single-crystal X-ray diffraction (XRD) analysis,[14] the optical and electrochemical properties of gallafluorenes were not mentioned. We focused on the use of gallium as the bridging element in heterofluorenes because of the relatively higher stability of organogallium compounds than organoaluminum ones.

Herein we designed and synthesized a series of gallafluorenes with electron-donating and -withdrawing groups and investigated their optical properties. We modified their gallium atoms to increase their stabilities toward air and moisture by introducing 2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl (Mamx) as a protecting group.[15] The gallium atoms were stabilized kinetically by the *tert*-butyl groups and thermodynamically by the coordination of the nitrogen atom. Moreover, the high stabilities enabled us to study their unique optical properties. Especially in the presence of $B(C_6F_5)_3$, emissions via the triplet exciplexes[16] of the gallafluorenes and $B(C_6F_5)_3$ were observed. To the best of our knowledge, this is the first report to reveal the optical properties of gallafluorenes.

Scheme 1. Synthesis of Gaf-H and Gaf-Br



Scheme 2. Synthesis of Gaf-a–d



The synthetic schemes for the gallafluorenes are illustrated in Schemes 1 and 2. The appropriate diiodide-substituted biphenyls were treated with *n*-BuLi followed by $(Mamx)GaCl_2$. After reaction for 1 day, the stable gallafluorenes **Gaf-H** and **Gaf-Br** were obtained (Scheme 1). The series of modified gallafluorenes **Gaf-a–d** with electron-withdrawing or -donating groups were prepared in good yields via Suzuki–Miyaura coupling with **Gaf-Br** in the presence of the catalyst formed from tris(dibenzylideneacetone)dipalladium $[Pd_2(dba)_3]$ and 2-(2′,4′,6′-triisopropylbiphenyl)dicyclohexylphosphine (X-Phos) (Scheme 2). All of the gallafluorene derivatives showed high

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durability toward common synthetic procedures such as extraction with water, column chromatography with acidic silica gels, and recrystallization under ambient atmosphere. In addition, unexpected degradation was hardly observed during the subsequent measurements of optical properties. Thus, it can be said that the gallafluorenes used in these experiments should have good resistance to environmental changes.

The molecular structure of **Gaf-H** was determined by single crystal XRD analysis (Figure 1). A small C1−C6−C7−C12 dihedral angle of 1.06° was obtained, indicating that the fluorene moiety forms a nearly planar structure. In addition, the sum of the C−Ga−C angles was 355.4°, showing that the gallium center is nearly planar rather than tetrahedral. The average Ga1−N1 bond length of 2.112 Å is significantly shorter than the sum of van der Waals' radii of gallium and nitrogen (3.42 Å). These data indicate that the gallium atom in **Gaf-H** has a four-coordinate structure. We evaluated the stability of the dative bond between the nitrogen and gallium atoms by variable-temperature NMR analysis. The spectra were subtly changed over the temperature range from 24 to 90 °C.[17] This result suggests that the nitrogen atom is strongly coordinated to the gallium atom.

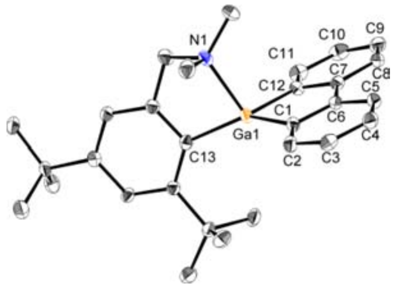

Figure 1. ORTEP drawing of **Gaf-H** (50% probability for thermal ellipsoids). H atoms have been omitted for clarity.

The optical properties of the gallafluorene derivatives **Gaf-H** and **Gaf-a−d** were investigated by UV−vis absorption and photoluminescence (PL) spectroscopy in $CHCl_3$ solution (Figure 2). **Gaf-H** showed a weak absorption peak at 282 nm assigned to the $S_0 \rightarrow S_n$ ($n = 1, 2$) transitions.[18] The absorption peaks of **Gaf-a−d** were shifted by ca. 50 nm. In the PL spectra, bathochromic shifts of the peak maxima in the spectra of **Gaf-a−d** relative to that of **Gaf-H** ($\lambda_{FL} = 369$ nm) were found. The red-shifted absorptions and emissions from **Gaf-a−d** relative to **Gaf-H** could originate from extension of the π conjugation due to the introduction of the substituents. The quantum yield of **Gaf-H** was much smaller than those of **Gaf-a−d**. The low quantum yields could be explained by two factors: First, smaller oscillator strengths of the transitions in **Gaf-H** than those in **Gaf-a−d** were obtained from theoretical calculations,[18] indicating that the synthesized gallium complexes could have intrinsically low emission properties. Second, phosphorescence was observed from the PL measurements at 77 K.[19] This result suggests that decay of the singlet excited states via intersystem crossing could occur, leading to low emissions of the gallium complexes.

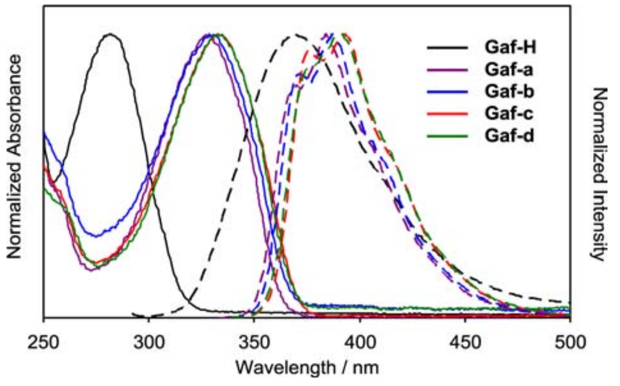

Figure 2. UV−vis absorption spectra (solid lines) and PL spectra (dashed lines, excited at λ_{max}^{abs}) of gallafluorene derivatives in $CHCl_3$ solution (**Gaf-H**, 1.0×10^{-4} M; **Gaf-a−d**, 1.0×10^{-5} M).

Figure 3 shows the PL spectrum of 10 mM **Gaf-H** in benzene solution after the addition of an equivalent amount of $B(C_6F_5)_3$ (**B**). The optical properties are listed in Table 1. A new emission band with a peak at 575 nm appeared upon addition of **B**. The lifetime of this new emission was 1.33 μs. In contrast, the lifetimes of **Gaf-H** and **B** are <5 ns. The ^{1}H NMR spectra of **Gaf-H** were less significantly changed upon addition of **B**. In a 0.5 mM solution in benzene, the absorption spectrum of the mixture of **Gaf-H** and **B** was similar to the sum of the absorption spectra of the two components.[20] These data show that a weak interaction between **Gaf-H** and **B** occurs. In other words, the interaction that induced the new emission band should take place mainly in the excited state. After oxygen was bubbled through the mixture of **Gaf-H** and **B**, the emission band at 575 nm disappeared. These results suggest that this emission band originates via their triplet excited states.

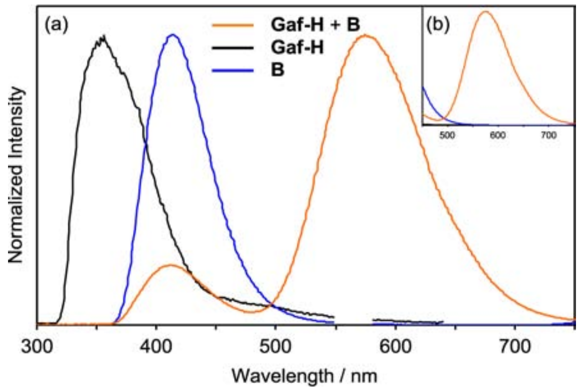

Figure 3. (a) PL spectra of 10 mM **Gaf-H** + **B** (orange), **Gaf-H** alone (black), and **B** alone (blue) in benzene solution excited at 282 nm. (b) PL spectrum obtained with a cutoff filter below 400 nm.

Table 1. PL Spectral Data for Gallafluorene Derivatives and B in Benzene Solution (10 mM Gaf-H, λ_{ex} = 282 nm; 1 mM Gaf-a−d, λ_{ex} = 360 nm)

	λ_{PL} (nm)	$\tau_{1/2}$ (μs)	χ^2
Gaf-H	575	0.152 (4.3%) 1.33 (95.7%)	1.17
Gaf-a	635	12.5	0.99
Gaf-b	654	5.38	0.95
Gaf-c	684	5.34	1.01
Gaf-d	581	0.047 (0.9%) 0.221 (99.1%)	0.91

Moreover, at lower concentrations (<0.2 mM), this long-lifetime emission was not obtained. In addition, the emission was undetectable in relatively polar solvents such as $CHCl_3$ and CH_2Cl_2. These data suggest that this emission band could be caused by formation of the triplet exciplex[16] between **Gaf-H** and **B**.

The mixtures of the gallafluorene derivatives **Gaf-a–d** and **B** showed weak emission bands at around 600 nm (Table 1). As the gallafluorene derivative was substituted with more electron-donating groups, the emission band showed more bathochromic shifts by 100 nm. The energy band gaps were narrowed by the introduction of electron-donating groups. These results also support the triplet exciplex formation with **B**.

In summary, we have reported the synthesis and optical properties of a series of gallafluorenes with various functional groups. The formation of four-coordinated gallium atoms stabilized the gallafluorenes toward air and moisture. In addition, the gallafluorene derivatives showed unique emissions via their triplet states, particularly in the presence of $B(C_6F_5)_3$. We are continuing to survey their optical and electronic characteristics. These gallafluorenes have promise to be key materials for fabricating highly functional optoelectronic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectral data for all new compounds, crystallographic data for **Gaf-H** (CIF), and results of theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) See Figure S14 in the Supporting Information.

(18) See Table S2 in the Supporting Information.

(19) See Figure S20 in the Supporting Information.

(20) See Figure S22 in the Supporting Information.