

論文の内容の要旨

論文題目 Synthesis and Physical Properties of Multifunctional Disilane-bridged Arenes

(多様な機能を示すジシラン架橋芳香族化合物の創製と物性)

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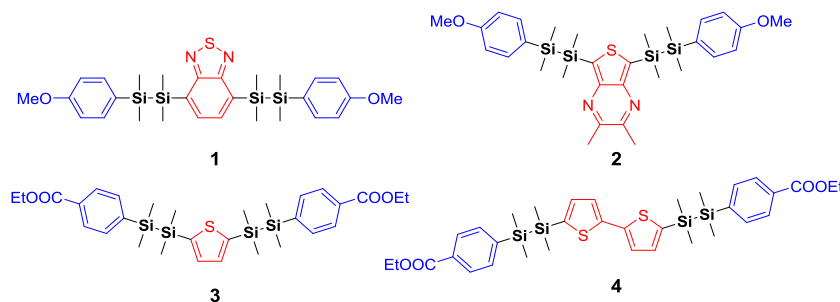
1. Introduction

Recently, π -conjugated molecules containing electron-donating and -accepting moieties (i.e. donor- π -acceptor molecules) have attracted much attention to their photonic and electronic applications (e.g. organic light-emitting diodes (OLEDs)),¹ because of their photofunctionalities arising from the intramolecular charge-transfer (ICT). On the other hand, oligosilane-arene molecules are known for luminescent materials by means of σ - π conjugation, the interaction between Si-Si σ -orbital and aryl π -orbital.² Thus, the hybridization of disilane units (the simplest oligosilane) and donor-acceptor systems leads to novel types of photofunctional materials. In my master course, disilane-bridged donor-acceptor molecules which displayed strong emission and second-order nonlinear optical properties were investigated.³ In my Ph.D. thesis, disilane-bridged donor-acceptor-donor (D-A-D) and acceptor-donor-acceptor (A-D-A) triads were designed, and their physical properties such as solid state emission were investigated. Moreover, octamethyltetrasilane[2.2]cyclophanes (hereinafter refer to as tetrasilane[2.2]cyclophanes), the hybridized molecules of cyclophanes and disilane units, were investigated for the development of OLEDs and circularly polarized luminescence (CPL) materials.

2. Disilane-bridged donor–acceptor–donor and acceptor–donor–acceptor triads: aggregation-induced emission and bright solid state emission

π -Conjugated donor–acceptor triads, such as D– π –A– π –D and A– π –D– π –A compounds, have received much attention because of their strong fluorescent properties. However, they often face quenching emission in the aggregated state due to the intermolecular π – π stacking. Meanwhile, oligosilane–arene compounds displayed effective emission in the condensed state derived from the suppression of π – π stacking. Thus, the molecules hybridized D–A–D and A–D–A triads and disilane units are desired for the strong luminescent materials in the aggregated state.

Disilane-bridged D–A–D molecules (**1** and **2**) and A–D–A molecules (**3** and **4**) were synthesized in 20–40% yield *via* Pd-catalyzed arylation of hydrosilanes (Scheme 1). D–A–D compounds displayed broad UV–vis absorption bands, and the excitation of the bands led to weak fluorescence at around 500 nm in toluene, which were assignable to ICT transition. A–D–A compounds absorbed in UV region, and they emitted at around 400 nm as blue color in low to moderate efficiency. On the other hand, these compounds showed strong solid state emission with high quantum yield (Φ_f : 0.85 for D–A–D compound **1** and 0.77 for A–D–A compound **4**). Moreover, compound **2** exhibited aggregation-induced emission according to the THF/water method, which insists that the non-radiative relaxation channels (e.g. vibration and rotation) were suppressed in the aggregated phase. Moreover, X-ray diffraction (XRD) of these compounds revealed that there is no π – π stacking in the crystal structure owing to the steric hindrance of disilane units, which suppressed the intermolecular π – π interaction. Thus, disilane-bridged D–A–D/A–D–A triads was prepared utilizing Pd-catalyzed arylation, which showed efficient solid state emission by means of the suppression of the non-radiative relaxation and the intermolecular π – π interaction.



Scheme 1. The molecular structures of prepared disilane-bridged D–A–D (**1** and **2**) and A–D–A triads (**3** and **4**).

3. Multifunctional tetrasila[2.2]cyclophanes exhibiting conformational variation, electroluminescence, and circularly polarized luminescence

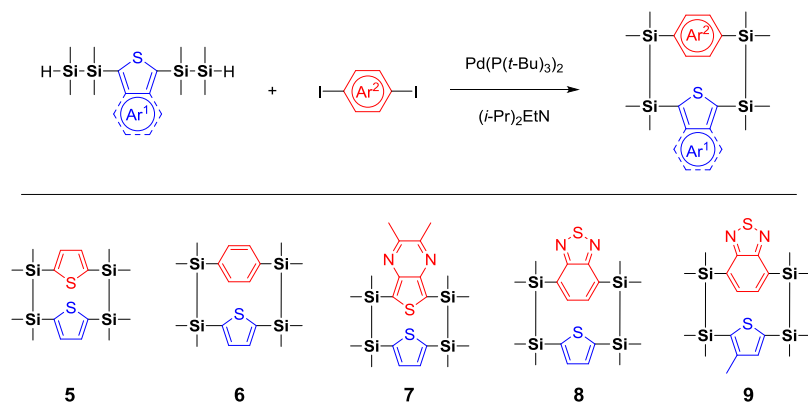
Organic molecules comprising electron donor and acceptor units (D– π –A) have attracted much attention because of their potential applications such as OLED materials. On the other hand, circularly polarized luminescence (CPL), which is derived from the difference in emission between right- and left-circularly polarized lights from chiral luminophore, has also received much attention because it has a potential use of 3D display devices.⁴

To develop functional organic molecules for OLED and CPL materials, I designed the disilane-modified cyclophanes, named tetrasila[2.2]cyclophanes. These molecules have the planar chirality derived from a cyclophane-typed structure and emissive properties arising from σ – π conjugation, which can lead to chiroptical properties (e.g. CPL). In this research, the systematic synthesis of tetrasila[2.2]cyclophane derivatives and their various functionalities were investigated.

The desired compounds **5–9**, including unsymmetrical structures, were synthesized *via* Pd-catalyzed arylation of hydrosilanes in up to 21% yield as shown in Scheme 2. According to variable temperature (VT) NMR, Si-CH₃ of compound **5** at low temperature (220 K) led two sharp signals, while at higher temperature (over 310 K) these peaks were coalesced. This result insists that the molecular inversion of **5** occurred above 310 K. The inversion barrier was estimated to 15 kcal/mol. In the case of compound **8**, four sharp peaks of Si-CH₃ did not change with the temperature, which insisted that no inversion of **8** occurred below 323 K due to high inversion barrier. These results indicated that molecular inversion of tetrasila[2.2]cyclophanes can be controlled by the bulkiness of substitutes.

Cyclic hosts that entrap small organic molecules strongly in solution are important for tuning the physical properties of guest molecules. Here, in order to control the inversion motions of **5**, the complexation of macrocycle [Ag₂L]²⁺ and **5** was performed (Figure 1). The NMR titration indicated that **5** bound to [Ag₂L]²⁺ in a 1:1 ratio with over 10¹⁰ M⁻¹ association constant. XRD analysis suggested that Ag⁺ ions and **5** were in η²-typed Ag-π coordination geometries in the complex, which allowed the strong interaction between **5** and [Ag₂L]²⁺. Moreover, VT-NMR result of **5** ⊂ [Ag₂L]²⁺ complex indicated that Si-CH₃ peaks from included **5** did not coalesce below 323 K, suggesting that the thiophene ring rotation in the cavity was restricted owing to the steric hindrance and strong Ag-π interaction between them. Thus, the molecular inversion of **5** could be controlled by the inclusion with macrocycles.

The optical properties of donor-acceptor typed tetrasila[2.2]cyclophane (**7**, **8**) were investigated, and the detailed optical data were summarized in Table 1. They displayed a broad absorption band and emitted at around 500 nm, which can be assigned to ICT transition based on DFT calculation. The emission quantum yield of compound **8** in the solid state (Φ_f = 0.49) was higher than that in the solution state (Φ_f = 0.05). According to XRD analysis, there was no π-π stacking in the crystalline state of compound **8**, indicating that the intermolecular π-π interaction was suppressed in the solid state to improve the emission efficiency of **8** in the solid phase.



Scheme 2. The synthetic scheme and molecular structures of tetrasila[2.2]cyclophane derivatives (**5–9**).

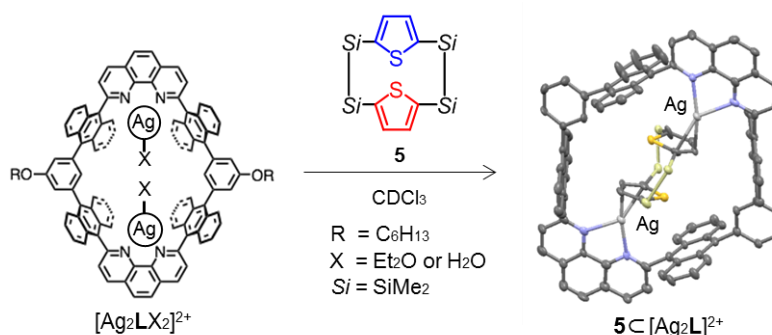


Figure 1. The synthetic scheme of **5** and macrocycle [Ag₂L]²⁺ and ORTEP drawing of **5** ⊂ [Ag₂L]²⁺ (30% probability ellipsoids). Side alkyl-chains of L, counter anions, methyl groups of **5**, solvent molecules, and hydrogen atoms are omitted for clarity.

For the application of these compounds, OLED containing emissive tetrasila[2.2]cyclophane (**8**) was fabricated with vapor deposition (structure: ITO/ α -NPD/dPVBi:**8** (3%)/BCP/LiF/Al). The **8**-doped OLED shows a green electroluminescence at around 495 nm, similar to the corresponding photoluminescence spectra in the solid phase (490 nm), with the acceptable external quantum efficiency (η_{ext} : ca. 0.4%).

Finally, I developed a planar chiral tetrasila[2.2]cyclophane for a CPL material. Tetrasila[2.2]cyclophanes containing thiophene and thiaziazole moieties are suitable for chiroptical materials because of emissive properties and no racemization by the inversion. Thus, I designed compound **9** as a CPL-active molecule, which had a planar chirality and donor-acceptor moieties. Planar chiral (*S*)-**9** and (*R*)-**9** were synthesized by Pd-catalyzed reaction, and separated with a chiral column. Their absolute configurations were determined by XRD. Figure 2 shows the emission (total luminescence, TL) of *rac*-**9** and CPL spectra of (*S*)-**9** and (*R*)-**9** in cyclohexane. Emission spectra of compound **9** displayed the broad band at 500 nm as ICT transition, similar to compound **8**. (*S*)-**9** and (*R*)-**9** showed clear CPL signals in opposite directions with acceptable CPL efficiency as single organic molecules ($|g_{\text{lum}}| = \text{ca. } 2 \times 10^{-3}$ at 500 nm). Thus, utilizing Pd-catalyzed reaction, tetrasila[2.2]cyclophane derivatives with various properties (e.g. molecular motion, inclusion into host molecule, solid state emission, electroluminescence, and CPL) was developed.

4. Conclusion

In my Ph.D. thesis, several types of disilane-bridged arenes, “disilane-bridged D–A–D/A–D–A triads and tetrasila[2.2]cyclophanes”, were investigated. These compounds were prepared *via* Pd-catalyzed arylation of hydrosilanes. They displayed various physical properties and functionalities such as efficient solid state emission, molecular inversion in solution, inclusion into a macrocycle, electroluminescence, and chiroptical properties. The investigation of disilane-bridged molecules with multiple functionalities in this research is expected to contribute to the development of silicone-based novel functional materials.

References

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Table 1. Optical properties of **7** and **8** at r.t.

	in cyclohexane			in the solid state	
	λ_{abs} (nm)	λ_{em} (nm)	Φ_{f}	λ_{em} (nm)	Φ_{f}
7	400	489	0.42	483	0.25
8	370	490	0.05	490	0.49

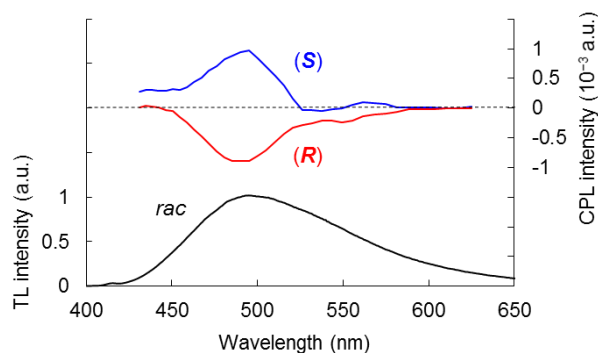


Figure 2. TL spectrum of *rac*-**9** (black line) and CPL spectra of (*S*)-**9** (blue line) and (*R*)-**9** (red line) in cyclohexane. TL: $I_L + I_R$. CPL: $I_L - I_R$. $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$. I_L and I_R : Emission intensity of left and right circularly polarized light.