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Facile Synthetic Route to Highly Luminescent Sila[7]helicene

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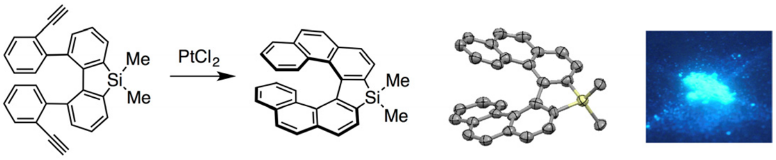
ABSTRACT



A facile synthetic route to dimethylsila[7]helicene by using a Lewis acid catalyzed double-cyclization reaction for construction of the twisted two phenanthrene moieties is described. Sila[7]helicene exhibited a high fluorescence quantum yield and a realatively large *g* value (dissymmetric factor) of circularly polarized luminencence (CPL) for small molecules.

Helicenes, which consist of *ortho*-fused aromatic rings having screw-shaped structures, are known as intriguing chiral frameworks and are intensively studied in wide ranges of areas.[1] Taking advantage of its chirality, unique optical properties such as nonlinear optical effects and circular dichroism (CD) have been well studied.[2] On the other hand, the luminescent nature of helicenes has been much less studied since the rapid intersystem crossing from the singlet state to the triplet state lowers the fluorescence quantum yield.[3] High quantum yields were only reported for helicene-like molecules in which the π-conjugation is not fully extended to the whole molecules.[4] Thus, despite their unique chiral structure, circularly polarized luminescence properties of helicenes remain rather unexplored.[4,5] Introduction of heteroatom(s) into the

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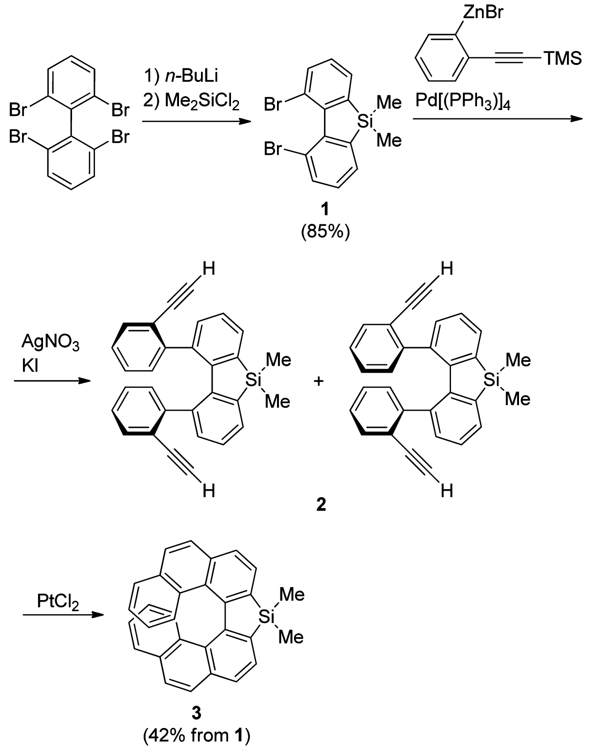
fused polycyclic frameworks adds remarkable changes to the electronic structures of helicenes, which enables fine-tuning of various physical properties. However, synthesis of such heterohelicenes still remains a challenging target despite the recent progress in photoreactions,[6] pericyclic reactions,[7] and transition-metal-catalyzed reactions.[4,8]

Introduction of silole(s), 1-silacyclopenta-2,4-diene(s), to a helicene framework would be of particular interest because of the promising high luminescent and electron-transporting properties of the silole moiety;[9] for example, silole-fused π-conjugated compounds are known to achieve high quantum yields in photoluminescence and high performance as light-emitting diode devices.[10] Thus, development of silole-fused helicenes is expected to afford characteristic optoelectronic materials, while their syntheses are currently very limited.[11] Herein we report a facile synthetic strategy toward silole-fused [7]helicene and its fundamental properties including strong luminescence.

Scheme 1. Preparation of Dimethylsila[7]helicene **3**



A sila[7]helicene **3** was prepared from an easily accessible starting material, 2,2′,6,6′-tetrabromobiphenyl[12] (Scheme 1). The biphenyl moiety was first locked with a silicon bridge, giving dibenzosilole derivative **1**. 2-Ethynylphenyl units were then introduced to **1** through a double-Negishi cross-coupling reaction and the subsequent deprotection of TMS groups by using AgNO$_3$. Owing to the coordination of Ag to ethynyl moiety, TMS group was selectively cleaved[13] and the silole moiety was left unreacted[14] in the deprotection condition to give the desired 1,9-bis-(2-ethynylphenyl)dibenzosilole **2**.[15] In order to prepare the highly twisted two phenanthrene moieties, Pt-catalyzed double cyclization of alkynes was applied.[16] We optimized reaction conditions for the double cyclization to find that the highest yield of the racemic dimethylsila[7]helicene **3** was obtained in the presence of PtCl$_2$ in 1,2-dichloroethane at 80 °C. Previously, we have reported the synthesis of oxa-, aza-, and λ^5-phospha[7]helicenes from biphenanthryl derivatives by using Pd-catalyzed carbon−heteroatom bond-formation reactions to construct highly twisted [7]helicene skeletons.[17] The present synthetic route, in which the phenanthrene moieties are constructed after the preparation of heterole moiety, gives an alternative and complementary methodology for the synthesis of heterole-fused helicenes.

The solid-state structure of (*P*)-sila[7]helicene **3** was unambiguously determined by X-ray crystallographic analysis (Figure 1). Enantiomerically pure (*P*)-**3** and (*M*)-**3** were obtained via optical resolution of *rac*-**3** by using preparative HPLC on chiral stationary phase. The enantiopure **3** with the shorter HPLC retention time was confirmed to be (*P*)-**3** by the refinement of the Flack parameter with data collected by using Cu Kα radiation

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(14) Conventional deprotection condition of TMS with K$_2$CO$_3$, Bu$_4$NF, or LiOH led to the cleavage of one of the silicon−carbon bond to give the ring-opened products.

(15) NMR spectra of the obtained compound **2** indicated that it was a mixture of *cis*- and *trans*-conformers. All attempts for separation of these two conformers were unsuccessful.

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(see Figures S1 and S2, Supporting Information). The degree of twist of **3** was evaluated by the sum of five dihedral angles [∠C(1)−C(2)−C(3)−C(4), ∠C(2)−C(3)−C(4)−C(5), ∠C(3)−C(4)−C(5)−C(6), ∠C(4)−C(5)−C(6)−C(7), and ∠C(5)−C(6)−C(7)−C(8)]. The sum value was found to be 99.5°, which is comparable to the largest value among those of the related hetero[7]-helicenes (Figure S5a, Supporting Information).[17b] This is due to the large angles between the two double bonds of silole induced by large atomic diameter of silicon. Such a large angle causes a large overlap between the two terminal benzene rings of the phenanthrene moieties and therefore a strong steric repulsion (Figure S5b, Supporting Information). The highly twisted structure of **3** was reflected in its high tolerence to racemization. In fact, thermal racemization does not occur even at 220 °C in *o*-dichlorobenzene in sealed tube.

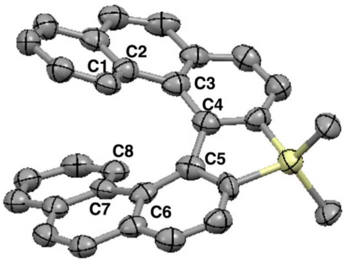

Figure 1. X-ray crystallographic structure of (*P*)-sila[7]helicene **3** (ORTEP drawing with 50% probability).

Optical properties of the obtained sila[7]helicene **3** were investigated with UV−vis absorption and photoluminescence (PL) spectroscopy (Figure 2a). The longest absorption maximum of **3** was 412 nm, which is longer than phenanthrene (293 nm) and dibenzosilole (286 nm), suggesting the effective delocalization of π-electrons over the molecule. The absorption edges of **3** was 431 nm, which is similar to that of λ^5-phospha[7]helicene (432 nm)[17b] and red-shifted compared to the related aza- and oxa-[7]helicenes (425 nm for aza[7]helicene and 409 nm for oxa[7]helicene).[14] Upon excitation at 320 nm, compound **3** exhibited a strong blue luminescence with λ_{max} = 450 nm. The fluorescence quantum yields of **3** were notably high for helicene derivatives (23% in CH_2Cl_2 and 17% in the solid state), which is a very desirable feature for applications in circularly polarized luminescent materials.[18] Electrochemical properties were also investigated with differencial pulse voltammetry to show two oxidation waves at 1.15 and 1.34 V (vs. Fc/Fc^+), which are attributed to the oxidation of the two phenanthrene moieties (Figure S3, Supporting Information).

Chiroptical properties were also investigated. Specific rotation of enantiopure sila[7]helicene (*P*)-**3** showed $[\alpha]_D$ of +2980 (c = 0.10, $CHCl_3$). The values are larger than those of the related oxa- and aza[7]helicenes, but smaller than λ^5-phospha[7]helicenes, roughly reflecting the degree of twist. Circular dichroism (CD) of (*P*)-**3** was revealed to show a large positive signal around 340 nm, followed by a small negative shoulder (∼300 nm) and a large negative signal (∼250 nm) (Figure 2b). Such a tendency in the CD spectrum is similar to those of λ^5-phospha[7]helicenes.[17] Time-dependent density functional theory (TD-DFT) calculations at the M06/6-31G(d) level of theory were carried out, and the intense signal around 340 nm was assigned to a mixed π−π* transition of HOMO−1 to LUMO (42%) and HOMO to LUMO+1 (48%) (Figure 2b and Figure S4, Supporting Information).

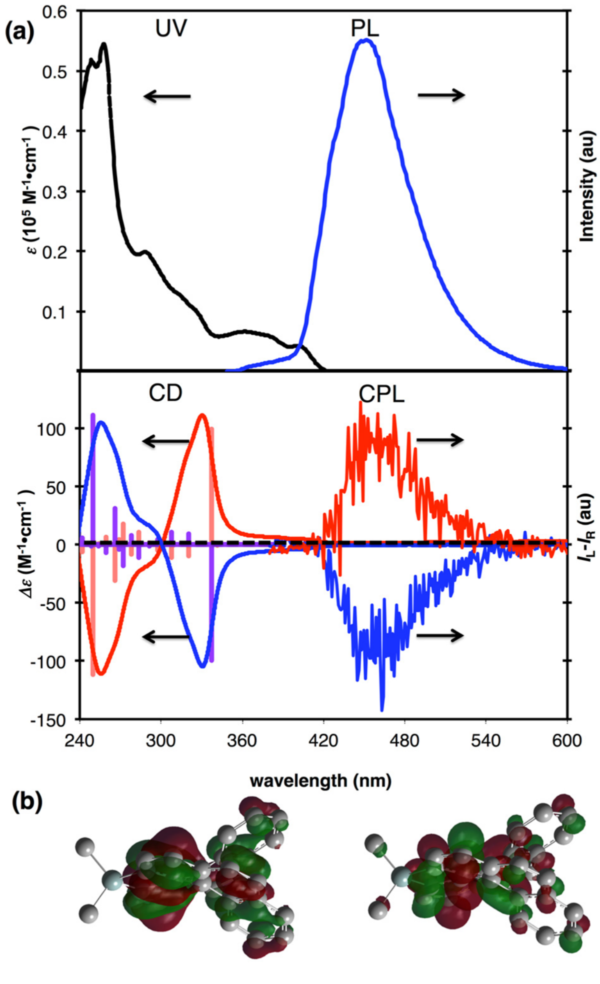

Figure 2. (a) UV (c = 4.2 × 10^{-5} M), PL (c = 4.2 × 10^{-6} M), CD (c = 4.8 × 10^{-6} M), and CPL (c = 6.8 × 10^{-6} M) spectra of sila[7]helicene **3** (CH_2Cl_2 solution). Blue lines in CD and CPL spectra: (*M*)-isomer. Red lines: (*P*)-isomer. The blue and red bars show the calculated CD spectra. (b) HOMO and LUMO orbitals of (*P*)-**3**.

Finally, we measured CPL properties of the enantiopure **3** in solution. As shown in Figure 2a, enantiopure sila[7]helicene (*P*)-**3** and (*M*)-**3** demonstrated CPL activities (excited at 320 nm), and their CPL spectra are mirror

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images of each other. The dissymmetric factor *g* (normalized difference in emission of right-handed and left-handed circularly polarized light)[19] was determined to be 3.5×10^{-3} for 470 nm. Recently, carbon-bridged 1,1′-bitriphenylenes, carbo[7]helicenes, have been reported to exihibit the highest *g* value ($g = 3.0-3.2 \times 10^{-3}$) among small organic molecules in nonaggregated state and/or without host matrix ever reported.[4] Accordingly, sila[7]helicene is also classified into the chiroptical organic molecules with a high *g* value and a high fluorescence quantum yield. The *g* value of **3** (3.5×10^{-3}) is in the same order as those of other hetero[7]helicenes ($\sim 1.5 \times 10^{-3}$) such as λ^5-phospha-[7]helicene, oxa[7]helicene, and aza[7]helicene. It is suggested that the dissymmetric factor derives mainly from the helical biphenanthryl moiety while the heterole moiety plays essential roles in the luminescent properties. However, these hetero[7]helicenes showed much lower quantum yield in photoluminescence. Thus, the strong emission and large absolute *g* value were endowed to sila[7]helicene owing to the combination of silole moiety and the distorted helical structure.

In conclusion, we developed an easily accessible synthetic route to provide silole-fused [7]helicene via a Lewis acid catalyzed double cyclization reaction. The incorporation of silole to the helicene framework resulted in a high luminescence quamtum yield, and characteristic chiroptics properties. The quantum yield of **3** is the second highest value for helicenes,[4] demonstrating the importance of this molecular design. Especially, solid state luminescent is notably high in helicene derivatives ($\Phi = 17\%$).[20] Furthermore, considering the possible extension of the synthetic approach (incorporation of other elements and easy derivatization), it can be concluded that our approach is promising to open up new aspects in chiroptics materials.

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Supporting Information Available. Experimental procedures, crystallographic data, differential pulse voltammogram, and molecular orbitals of **3**, the degree of twist of the related hetero[7]helicenes, ^{1}H and ^{13}C NMR spectra, and X-ray data for **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] No Φ values in solid states are reported from Tanaka et al.

The authors declare no competing financial interest.