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Synthesis and Properties of [7]Helicene-like Compounds Fused with a Fluorene Unit

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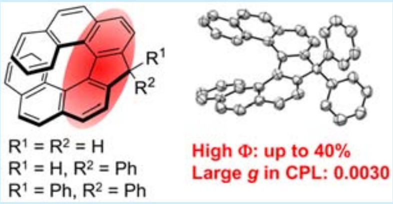
Supporting Information

ABSTRACT: [7]Helicene-like compounds with a fluorene unit were successfully synthesized using a platinum-catalyzed double cyclization reaction. Crystal structures and photophysical properties of these compounds were also studied. In particular, they were found to exhibit a high fluorescence quantum yield and a relatively large *g* value (dissymmetric factor) of circularly polarized luminescence (CPL) for small molecules.



Helicenes are *ortho*-fused polycyclic aromatic compounds with a helically twisted π-conjugated structure. Owing to their unique helical structure, they exhibit more enhanced chiroptical properties [optical rotatory power (ORP), circular dichroism (CD), circularly polarized luminescence (CPL), and so on] than common chiral organic molecules, and they have attracted much attention in materials science.[1,2] However, they generally suffer from poor fluorescence properties, a severe disadvantage in the application as luminescent materials. For example, the fluorescence quantum yield of [7]helicene **1** was reported to be 2% (Figure 1).[3] Such poor fluorescence properties should be attributed to the rapid intersystem crossing from the singlet state to the triplet state which lowers the fluorescence quantum yield.[4] Thus, it is highly desired to develop a molecular design for luminescent helicenes.

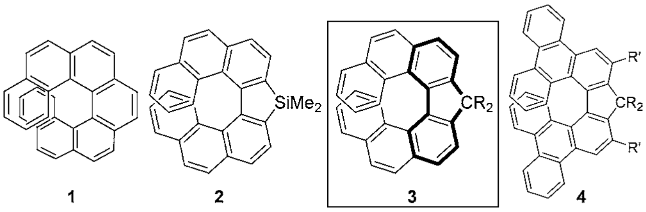


Figure 1. Structures of [7]helicene and its analogues.

Recently, we reported the synthesis of silole-fused helicene-like compound **2** (Figure 1) and found that it exhibits much higher fluorescence quantum yield than the prototypical helicenes, such as [7]helicene **1**.[5,6] Silole-fused π-conjugated compounds have been known to show a high fluorescence property.[7] Thus, the high fluorescence quantum yield of compound **2** would be ascribed to the electronic perturbation by the silole moiety. On the basis of this result, we further developed a molecular design for luminescent helicenes and helicene-like compounds, and focused on fluorene-fused compounds **3**, a carbon analogue of silole-fused [7]helicene-like compound **2**. Fluorene has been known to show much higher fluorescence quantum yield than polycyclic aromatic compounds composed of only benzene rings.[8] Accordingly, the introduction of a fluorene unit in place of a phenanthrene unit of [7]helicene **1** is expected to afford luminescent helicene-like compounds. Tanaka and co-workers have already reported [7]helicene-like compounds **4** with both fluorene and triphenylene units (Φ: up to 32%).[6a] The compounds were found to show high fluorescence property, while it is unclear whether the fluorene or triphenylene unit is required for such high fluorescence property. Herein we report the synthesis and photophysical properties of fluorene-fused helical π-conjugated compounds **3** as well as their solid state structures.

Fluorene-fused [7]helicene-like compounds **3** were successfully synthesized by employing fluorenone-fused [7]helicene-like compound **5** as a common precursor. Compound **5** was prepared via a similar synthetic route for silole-fused compound **2** (Scheme 1).[5] First, 2,2′,6,6′-tetrabromobiphenyl[9] was transformed into 4,5-dibromofluorenone **6**[10] in 78% yield. Then, 2-ethynylphenyl units were introduced by Negishi cross-coupling reaction and the following deprotection under a basic condition. Although the resulting fluorenone **7** was indicated to be a mixture of isomers, it was used for further reaction without

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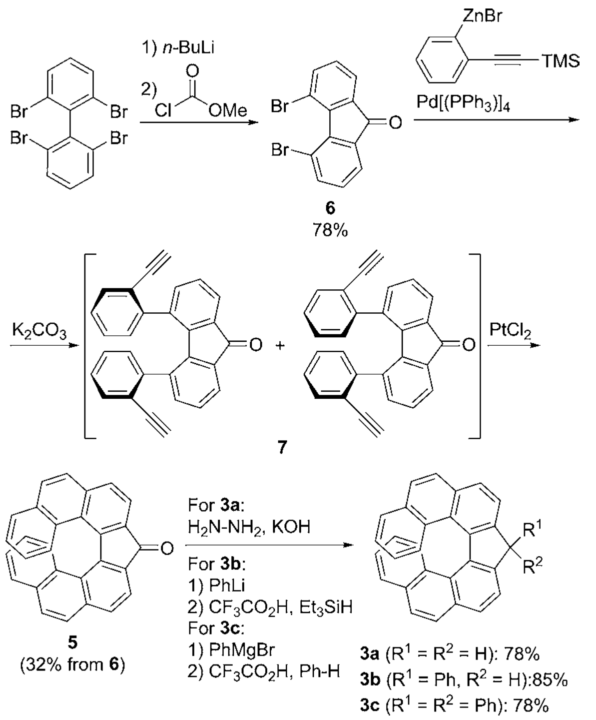
Scheme 1. Preparation of Fluorene-Fused [7]Helicene-like Compounds 3



separation. The double cyclization of fluorenone **7** was achieved by using a platinum catalyst[11] to afford the common precursor **5** in 32% yield (from **6**). With the common precursor **5** in hand, fluorene-fused [7]helicene-like compounds **3** were synthesized. Reduction of **5** readily afforded the compound **3a**. An aryl substituent can be also introduced on the fluorene unit. Thus, monophenyl derivative **3b** was obtained by the reaction of **5** with PhLi and the subsequent reduction of the resulting fluorenol (85% yield for two steps). In addition, the diphenyl derivative **3c** was synthesized by the reaction with PhMgBr followed by electrophilic substitution (78% yield for two steps). Enantiopure isomers of each compound **3** can be obtained through optical resolution by using preparative HPLC on a chiral stationary phase.

The solid-state structures of [7]helicene-like compounds **3** and **5** were determined by X-ray crystallographic analysis (Figure 2). Single crystals of *rac*-**5**, *rac*-**3b**, and enantiopure **3a** and **3c** were successfully obtained. The sums 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)], which should reflect the degree of molecular twist, are 82.8° for **5**, 86.9° for **3a**, 80.9° for **3b**, and 90.8° for **3c**. These values are smaller than those of the related [7]helicene-like compounds **4** with both fluorene and triphenylene units.[6a] The central five-membered ring of compound **3b** possesses tetrahedral geometry and one phenyl substituent. Such a structural feature is similar to that of phosphole-fused [7]helicene-like compound which forms the one-dimensional columnar stacking with the aid of its dipole moment.[12] However, unlike the phosphole-fused one, compound **3b** did not form such a one-dimensional columnar stacking. (*P*)- and (*M*)-**3b** form a racemic dimer through the face-to-face interaction between their fluorene moieties, and the dimers are arranged in a herringbone pattern (Figure S15).

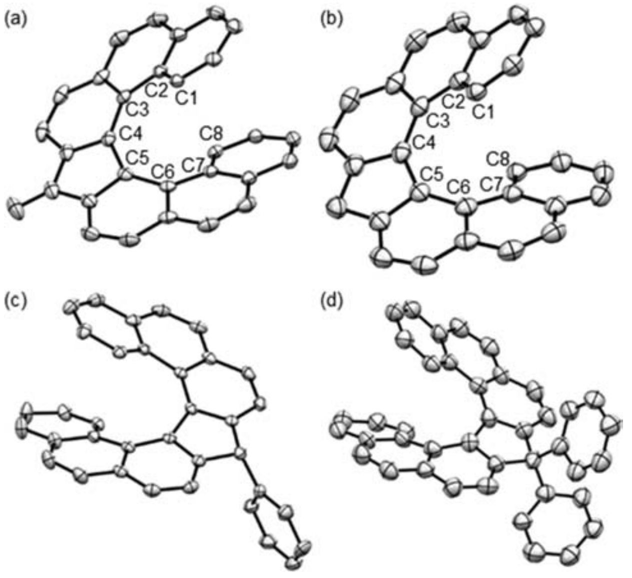


Figure 2. X-ray crystallographic structure of [7]helicene-like compounds (a) **5**, (b) **3a**, (c) **3b**, and (d) **3c** (ORTEP drawing with 50% probability. All hydrogen atoms are omitted for clarity).

Photophysical properties of [7]helicene-like compounds **3** were evaluated by ultraviolet−visible (UV−vis) absorption and photoluminescence (PL) spectroscopies. Their spectra are shown in Figure 3a, and their photophysical data are summarized in Table 1. All of compounds **3** showed similar absorption spectra with the longest absorption maximum at ~400 nm, while the molar absorption coefficients of them are slightly different. On the basis of the TD-DFT calculations

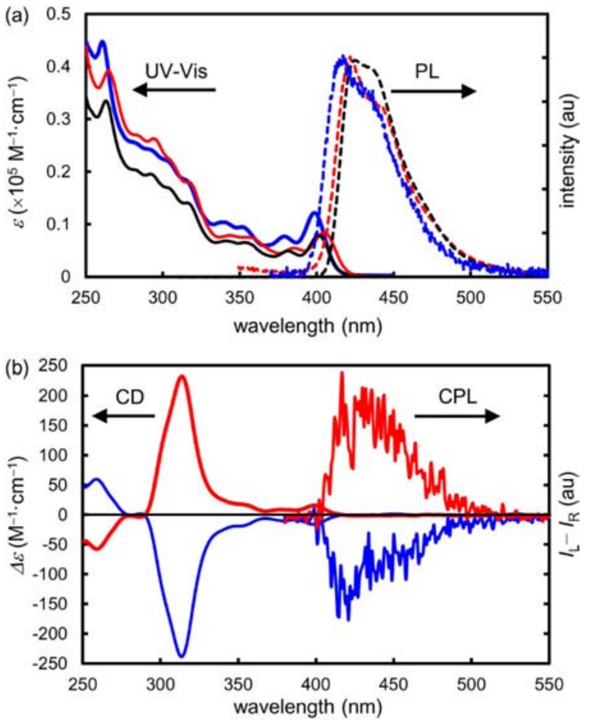


Figure 3. (a) UV−vis absorption and fluorescence spectra of **3a**−**3c** (**3a**, blue; **3b**, black; **3c**, red) in CH$_2$Cl$_2$ and (b) CD and CPL spectra of **3a** in CH$_2$Cl$_2$ (CD, 5.1 or 6.8 × 10^{-6} M for each enantiomer; CPL, 1.0 × 10^{-5} M for each enantiomer, Ex at 320 nm).

Table 1. Photophysical Data of [7]Helicene-like Compounds 3

	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	$\Phi_{solution}$ (%)[c]	$[\alpha]_D^{25}$[d]	g_{lum}[e]
3a	400	417	39	2722	3.0×10^{-3}
3b	401	425		1536	
3c	408	421	40	3057	2.5×10^{-3}
[7]helicene	435	476	2		

[a] In CH_2Cl_2 (**3a**, 6.8×10^{-5} M; **3b**, 5.6×10^{-5} M; **3c**, 4.2×10^{-5} M). [b] In CH_2Cl_2 (**3a**, 3.0×10^{-6} M, Ex at 360 nm; **3b**, 5.6×10^{-6} M, Ex at 300 nm; **3c**, 4.2×10^{-6} M, Ex at 340 nm). [c] Absolute quantum yield determined by a calibrated integrating sphere system. [d] In $CHCl_3$, c = 0.1. [e] In CH_2Cl_2 (**3a**, 1.0×10^{-5} M, Ex at 320 nm; **3c**, 1.0×10^{-5} M, Ex at 320 nm).

[B3LYP/6-31G(d)], the longest absorption band of each compound is derived from the $S_0 \rightarrow S_1$ transition dominated by the HOMO−LUMO (π−π*) transition (Table S8). The calculated $S_0 \rightarrow S_1$ transition energies of compounds **3** (**3a**, 381 nm; **3b**, 385 nm; **3c**, 392 nm) agree well with the trend of the experimental values in absorption spectra. These results indicate that the substituents on the cyclopentadiene unit have little effect on electronic structure of the helical π-conjugated core. The absorption spectra of them were slightly blue-shifted compared to that of [7]helicene **1**, while they are significantly red-shifted compared to those of fluorene and phenanthrene. Accordingly, the π-conjugation is well extended over the whole molecule despite their helically twisted structures. In addition, the longest absorption maximum of them is slightly red-shifted compared to that of compounds **4** despite the prediction that compounds **4** possess more extended π-conjugation induced by the triphenylene units.[6a] This phenomenon may be attributed to a smaller twist of compounds **3** than compounds **4**, resulting in more effective π-conjugation along helical structure. In the PL spectra, each [7]helicene-like compound **3** exhibited an emission maximum of ~420 nm with a very small Stokes shift. It is noteworthy that fluorescence quantum yields of **3** were quite high (up to 40%) among the reported helicenes and slightly higher than those of [7]helicene-like compounds **4**.[6a] Accordingly, the introduction of the fluorene unit was revealed to be important for high fluorescent property.

Chiroptical properties were also investigated. Specific rotation of enantiopure **5** and **3a**−**3c** showed $[\alpha]_D^{25}$ of 2086, 2722, 1536, and 3057 (c = 0.10, $CHCl_3$), respectively. The order of the specific rotation of **5** and **3a**−**3c** are identical to the order of the molecular twist estimated by X-ray analysis. Circular dichroism (CD) of one enantiomer of compound **3a** was revealed to show a small positive signal around 400 nm, a large positive signal (~315 nm), and a large negative signal (~250 nm) (Figure 3b). Such a trend in CD spectrum is similar to that of silole-fused [7]helicene-like compound **2**. As shown in Figure 3b, enantiopure **3a** exhibited CPL activities. The dissymmetric factor g (normalized difference in emission of right-handed and left-handed circularly polarized light) was determined to be 3.0×10^{-3}. This value is comparable to that of silole-fused compound **2**[5] and lower than those of the related fluorene-fused compound **4**,[6a] the highest g value ever reported for [7]helicene-like compounds.

In conclusion, we have synthesized a series of fluorene-fused helicene-like compounds and examined their optical properties. The obtained compounds exhibited bright blue fluorescence (Φ: up to 40%) with g_{lum} values around 3.0×10^{-3}. Introduction of a fluorene substructure into a helicene framework would be the key for such a high fluorescence property and provide a promising molecular design for emissive helicenes and helicene-like compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01708.

Experimental procedures, ^1H and ^{13}C NMR spectra, theoretical calculation results, the packing structure of 3b (PDF)

Crystallographic data for **3a** (CIF)

Crystallographic data for **3b** (CIF)

Crystallographic data for **3c** (CIF)

Crystallographic data for **5** (CIF)

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Notes

The authors declare no competing financial interest.

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