Synthesis and Properties of Spiro-double Sila[7]helicene: The LUMO Spiro-conjugation

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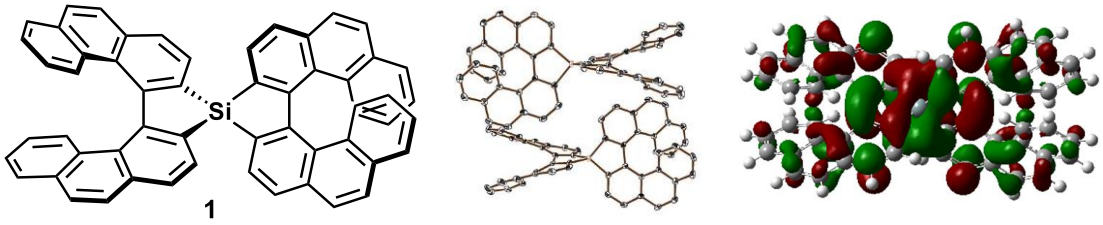
Helicenes, π-conjugated molecules with helical chirality have attracted attention from various research fields due to their unique helical structures and concomitant chiroptical properties. A class of them, doublehelicenes often have higher curved π-surface than mono-helicenes leading to unique three-dimensional structures and/or intermolecular interactions of the helicene units. Doublehelicenes and doublehelicene-like compounds synthesized until now have conjugated linkers between the two helicene units and thus the π-conjugation spreads to the entire molecule. In such fully conjugated doublehelicenes, the two helical axes corresponding to each helicene unit are approximately parallel, rendering them planar.

Here, we report the synthesis and properties of spiro-double sila[7]helicene (Figure (a), **1**) consisting of two sila[7]helicenes linked by a shared spirosilabi[fluorene] moiety. The structure was determined by single crystal X-ray analysis (Figure (b)). The enantiomers of **1** were successfully separated by HPLC. The two helicene units were symmetrically and nearly perpendicularly arranged in one molecule. The structural characteristics, optical properties, and DFT calculations were investigated for evaluating the effect of the spiro linkage of two helicene units. Notably, LUMO distribution of **1** (Figure (c)), which delocalized through the σ* orbitals of the C–Si bonds and the π* orbitals of the butadiene structure in the spirosilabi[fluorene] moiety, was found to affect the absorption properties.

(a) (b) (c)



1

Figure

(a) The structures of (*P,P*)-spiro-double sila[7]helicene (**1**).

(b) An ORTEP drawing of *rac*-**1**. triclinic $P\bar{1}$; a = 10.5082(2) Å, b = 12.1417(3) Å, c = 17.2598(5) Å, α = 91.337(2)°, β = 98.018(2)°, γ = 96.874(2)°; R_1 = 0.0979, wR_2 = 0.2187, GoF = 1.130.

(c) LUMO distribution of **1**.

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