

## STRATEGIC IMPROVEMENT OF THE EMISSION PROPERTIES BY CONTROLLING THE SYMMETRY AND ENERGY LEVELS OF THEIR MOLECULAR ORBITALS

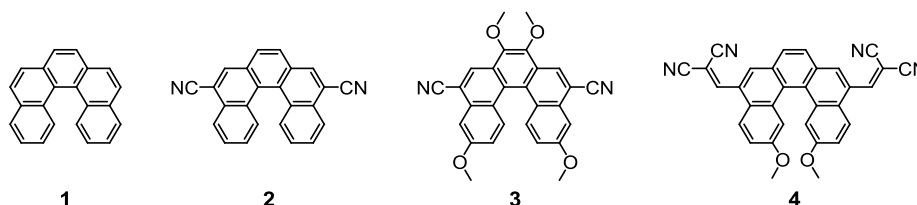
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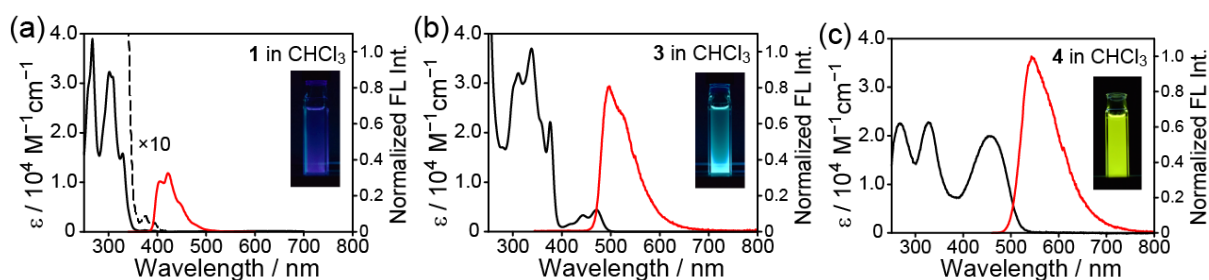
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Helicenes are *ortho*-fused polycyclic aromatic compounds with helically twisted molecular orbitals (MOs) that have attracted attention. Owing to their structures, helicenes are promising candidates for chiroptical organic dyes with strong circular dichroism (CD), and circular polarized luminescence (CPL) properties. However, the fluorescence quantum yield of unsubstituted carbohelicenes is usually very low, i.e.,  $\Phi_f < 0.05$  for  $[n]$ helicenes ( $n \geq 5$ ).<sup>[1]</sup>

Recently, we have reported that the photochemical reactivity of [5]helicenes can be efficiently suppressed by removing the degeneracy of their frontier MOs by introducing substituents.<sup>[2]</sup> Inspired by this study, we envisioned that the emission properties could also be controlled by removing the degeneracy of the MOs. We synthesized **1–4** (Figure 1) and the absorption and fluorescence spectra of **1–4** were recorded in CHCl<sub>3</sub> (Figure 2).



**Figure 1.** Molecular structure of [5]helicene **1–4**.



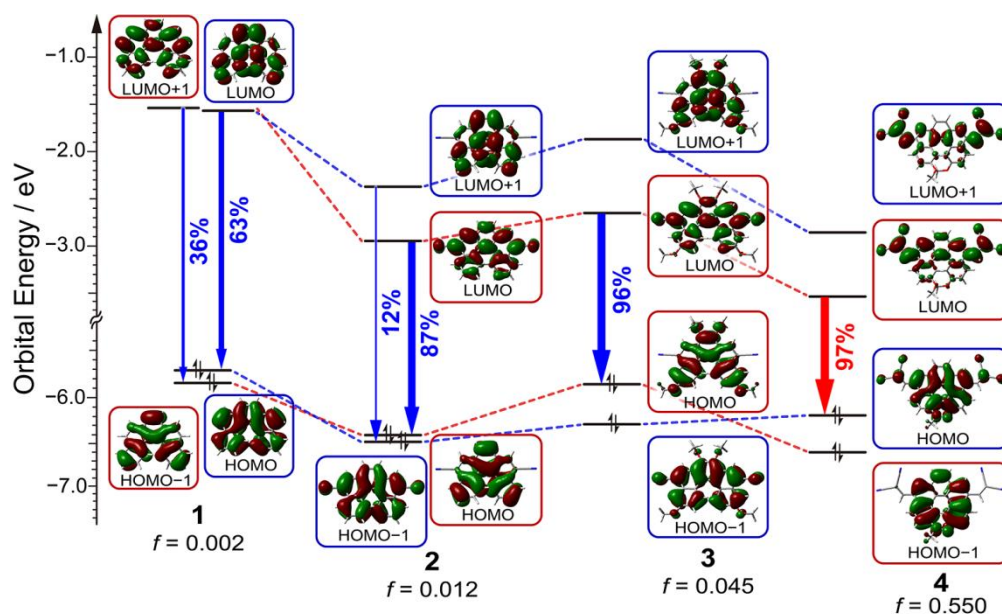
**Figure 2.** Absorption (black) and normalized fluorescence (red) spectra of (a) **1**, (b) **3**, and (c) **4** in chloroform. For clarity, the dashed line in panel (a) shows the spectrum line magnified by a factor of 10.

Unsubstituted [5]helicene **1** exhibits a very weak absorption band at 393 nm. Such a weak absorption band at the longest wavelength is related to the symmetry-forbidden  $S_0 \rightarrow S_1$  transition. TD-DFT calculation suggested that the  $S_1 \rightarrow S_0$  transition of **1** is symmetry-forbidden ( $f = 0.002$ ), which is the likely reason for the low emission quantum

yield of **1** ( $\Phi_f = 0.04$ ).

According to the TD-DFT calculations for **2**, the orbital degeneracy of LUMO and LUMO+1 was efficiently removed. In addition, in case of **3**, the HOMO energy level was efficiently separated from the HOMO-1 upon introducing methoxy groups. Despite both the HOMO and the LUMO are orbitals with  $C_2$ -antisymmetry, the oscillator strength of the  $S_1 \rightarrow S_0$  transition increased upon removing the orbital degeneracy of [5]helicene from  $f = 0.002$  (**1**) to  $f = 0.012$  (**2**) and  $f = 0.044$  (**3**) (Figure 3). We designed **4**, which bears 2,2-dicyanovinyl groups at the 5- and 10-positions and methoxy groups at the 2- and 13-positions. According to the TD-DFT calculations, the  $S_1 \rightarrow S_0$  transition of **4** consists predominantly of the HOMO-LUMO transition (97%), in which the HOMO ( $C_2$ -symmetric) and LUMO ( $C_2$ -antisymmetric) have different orbital symmetry. The calculated oscillator strength of **4** ( $f = 0.55$ ) was more than one order of magnitude larger than that of **3** ( $f = 0.045$ ).

The observed fluorescence emission rate constant of **4** ( $k_f = 0.15 \text{ ns}^{-1}$ ) was much larger than that of **1** ( $k_f = 0.002 \text{ ns}^{-1}$ ). As a result, we achieved a [5]helicene derivative exhibiting a high fluorescence quantum yield ( $\Phi_f = 0.23$ ), which is in a marked contrast to unsubstituted [5]helicene **1** ( $\Phi_f = 0.04$ ).



**Figure 3.** Orbital correlation diagram and composition of the  $S_1 \rightarrow S_0$  transition for **1–4**. The blue and red frames represent the MOs with  $C_2$ -symmetry and  $C_2$ -antisymmetry, respectively. The blue and red arrows represent symmetry-allowed and symmetry-forbidden transitions between MOs of different or identical symmetry, respectively.

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### References:

- [1] J. B. Birks, D. J. S. Birch, E. Cordemans, E. V. Donckt, *Chem. Phys. Lett.* **1976**, *43*, 33.
- [2] N. Ito, T. Hirose, K. Matsuda, *Org. Lett.* **2014**, *16*, 2502.
- [3] H. Kubo, T. Hirose, K. Matsuda, *Submitted*.