Design and Synthesis of Highly Emissive Helicene Derivatives Showing Excellent Chiroptical Properties Based on the Control of Electronic Transitions

Hiromu Kubo, Takashi Hirose, Kenji Matsuda

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
E-mail : kubo.hiromu.47r@st.kyoto-u.ac.jp

Helicenes have been attracting attention because of their chiroptical properties derived from the helical molecular structure. However, circularly polarized luminescence (CPL) of unsubstituted helicenes are weak due to its low fluorescence quantum yield ($\Phi_f \leq 0.02$)[1] and small rotatory strength for the $S_1 \rightarrow S_0$ transition. Based on quantum chemical calculations, we designed and synthesized 5,10-bis(2,2-dicyanovinyl)-2,13-dimethoxy-[5]helicene (**2**) and 7,12-dicyano-3,16-dimethoxy-[7]helicene (**4**) (Figure 1).

According to TD-DFT calculations, both unsubstituted [5]helicene (**1**) and [7]helicene (**3**) have symmetry forbidden $S_1 \rightarrow S_0$ electronic transitions, suggesting that these forbidden transitions are responsible for the small fluorescence quantum yields (**1**, Φ_f = 0.04; **3**, Φ_f = 0.02). By introducing substituents to **1** and **3**, the degeneracies of frontier molecular orbital energies were removed and the $S_1 \rightarrow S_0$ electronic transitions become symmetry allowed (Figure 1). As a result, both **2** and **4** showed good fluorescence quantum yields (**2**, Φ_f = 0.23; **4**, Φ_f = 0.17), which is more than 10 times larger than **1** and **3**.

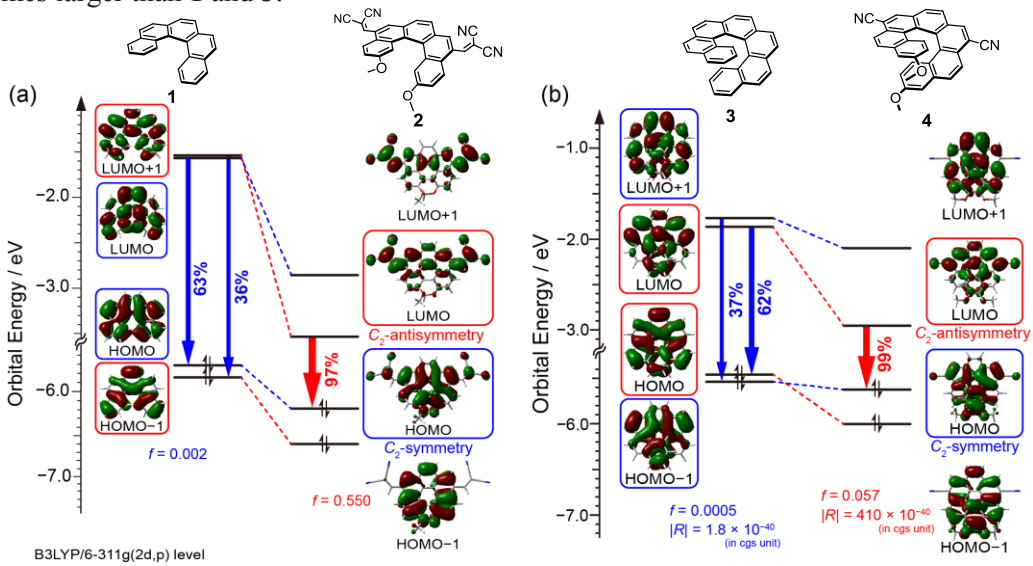

Figure 1. Orbital correlation diagram of (a) **1**, **2** and (b) **3**, **4**

In particular, compound **4** showed an excellent CPL property ($|g_{CPL}|$ = 0.016). TD-DFT calculation suggested that the large $|g_{CPL}|$ value of **4** is attributed to the large rotatory strength (R = −410 × 10^{-40} erg·esu·cm·Gauss^{-1}) for the $S_1 \rightarrow S_0$ electronic transition.[2,3]

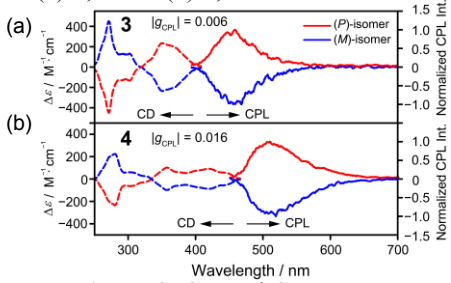

Figure 2. CD and CPL spectra of (a) **3** and (b) **4** in $CHCl_3$

[1] J. B. Birks, D. J. S. Birch, E. Cordemans, E. V. Donckt, *Chem. Phys. Lett.* **1976**, *43*, 33.
[2] H. Kubo, T. Hirose, K. Matsuda, *Org. Lett.* **2017**, *19*, 1776.
[3] H. Kubo, T. Hirose, T. Nakashima, T. Kawai, K. Matsuda, *in preparation*.