Tuning the Transition Electric and Magnetic Dipole Moments: [7]Helicenes Showing Intense Circularly Polarized Luminescence

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Circularly polarized luminescence (CPL) is a photophysical phenomenon, in which right- and left-handed circularly polarized lights are emitted at different intensities. Although chiral molecules with both high-emission quantum yields (Φ_f) and high dissymmetry factors (g_{CPL}) are desired for applications in sensors, bioimaging, displays, and optical communications based on circular polarization, there is a trade-off relationship between Φ_f and g_{CPL} : chiral molecules showing a high Φ_f tend to have low g_{CPL} .

A major challenge in the field of CPL is to establish the design strategy to achieve the maximum g_{CPL} value ($g_{CPL} = \pm 2$) with quantitative emission quantum yield ($\Phi_f = 1$); however, a reliable guideline to design such ideal chiral molecules is undeveloped so far. According to the theory of optical activity,¹ the g_{CPL} value is a function of (i) the magnitude ratio between the transition electric/magnetic moments ($\beta = |\mu|/|m|$) and (ii) the angle between the μ and m vectors ($\theta_{\mu,m}$), i.e., $g_{CPL} = 4\beta/(\beta^2 + 1) \cdot \cos \theta_{\mu,m}$. This equation suggests that the $|\mu|$, |m|, and $\cos \theta_{\mu,m}$ are the three key parameters for evaluating the g_{CPL} values, and the g_{CPL} value is maximized (i.e., $g_{CPL} = \pm 2$) under the conditions of (1) $|\mu|$ and |m| are the same magnitude (i.e., $\beta = |\mu|/|m| = 1$) and (2) the directions of μ and m vectors are parallel or antiparallel (i.e., $\cos \theta_{\mu,m} = \pm 1$).²

In this work, we investigated the substitution position of the [7]helicene framework so

that the $S_1 \rightarrow S_0$ transition has a large transition magnetic dipole moment (TMDM) and is partially symmetryallowed (Figure 1).³ A [7]helicene derivative (3) thus designed showed a large fluorescence emission rate ($k_{\rm f} = 0.02 \text{ ns}^{-1}$) and a large TMDM for the $S_1 \rightarrow S_0$ transition ($|m| = 2.37 \times 10^{-20} \text{ erg} \cdot \text{Gauss}^{-1}$), which are more than 10 times greater than those of unsubstituted [7]helicene ($k_{\rm f}$ = 0.001 ns^{-1} , 10^{-20} |m| = 0.045× $erg \cdot Gauss^{-1}$) (Table 1). As a result, compound **3** exhibits a large dissymmetry factor of CPL and high fluorescence quantum yield ($|g_{CPL}| = 1.3 \times 10^{-2}, \Phi_f =$ 0.17) in the solution phase.



Figure 1. Chemical structures of 1–3.

Compd	$ \boldsymbol{\mu} / 10^{-20} \mathrm{esu} \cdot \mathrm{cm}$	$ {\bm m} / 10^{-20} { m erg} \cdot { m G}^{-1}$	β	$\cos(\theta_{\mu,m})$	f^b	$g_{ m CPL,calcd}{}^c$
1	23	0.045	511	-1.00	0.0006	-0.008
2	124	0.17	729	-1.00	0.014	-0.005
3	265	2.37	112	0.50	0.058	0.018

Table 1. Electronic transition properties of 1–3.^{*a*}

^{*a*}Calculated for the (*P*)-isomers at the TD-RB3LYP/6-311G(2d,p) level. ^{*b*}Oscillator strength. ^{*c*}Dissymmetry factor calculated as follows: $g_{CPL} = 4\beta/(\beta^2 + 1) \cdot \cos(\theta_{\mu,m})$, where $\beta = |\mu|/|m|$.

The strategic substitution of electron-withdrawing (-CN) and electron-donating (-OMe) groups into a [7]helicene framework allowed us to alter the types of their frontier molecular orbitals (FMOs) (Figure 2), which is an effective approach to realize a *magnetically allowed* $S_1 \rightarrow S_0$ transition with large $|\mathbf{m}|$ values.

The large $|\mathbf{m}|$ value is a necessary condition to design chiral molecules whose $\Phi_{\rm f}$ and $g_{\rm CPL}$ are both high.³ The transition moment density analysis provides intuitive insights into the relationship between the shape of FMOs and the magnitude of |m|; the TMDM density (ρ_{total}^m) tends to be where the bonding large and antibonding natures alter between the HOMO and LUMO with large orbital overlaps (Figures 3). This finding will be a logical guideline for the further investigation of organic emitters with excellent CPL properties.



TD-B3LYP-GD3BJ/6-311g(2d,p)

Figure 2. Orbital correlation diagram and compositions of the $S_1 \rightarrow S_0$ transition for 1–3. The molecular structures were optimized in the S_1 state.



Figure 3. Transition moment density analysis of **3** calculated at the TD-B3LYP-GD3BJ/ 6-311G(2d,p) level. (a) The spatial arrangement of μ and m vectors, where length of the m is multiplied by 100 for clarity. (b) The transition electric/magnetic dipole moment densities ($\rho_{\text{total}}^{\mu}$ and ρ_{total}^{m}) correspond to the $|\mu|$ (left) and |m| (right) values, respectively.

1) J. A. Schellman, *Chem. Rev.* **1975**, *75*, 323–331. 2) *Circular Dichroism: Principles and Applications*, 2nd ed.; N. Beroba, K. Nakanishi, R. Woody, Eds.; Wiley-VCH: New York, **2020**. 3) H. Kubo, T. Hirose, T. Nakashima, T. Kawai, J.-y. Hasegawa, K. Matsuda, *J. Phys. Chem. Lett.* **2021**, *12*, 686–695.