Marvel CPL, CPLE, and ECD Spectroscopy to Study the Origin of CD- and CPL-sign Inversion of *D-/L*-Camphor and Colloidal π-Conjugated Polymers

Michiya Fujiki[a]

[a]Devision of Materials Science, Graduate School of Science and Technology,
Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

Kasha's rule is one of the most crucial guiding principles of how photoexcited luminophores in S_n ($n =$ 1, 2, 3...) states relax radiatively and non-radiatively to the ground state (S_0). However, an open question remains yet whether the Kasha's rule is always valid for chiral luminophores. Early works of *D*- and *L*-camphors reported bisignate dual CPL characteristics at 370 nm (minor) and 450 nm (major) [1–3]. The sign of the 450-nm CPL band is opposite to that of the first Cotton CD signal at 290 nm. The origin of anomaly, so-called anti-Kasha's rule, is obscure. Nowadays, electronic circular dichroism (ECD) spectroscopy is widely utilized to characterize the S_0-state chirality of chromophores. On the other hand, circularly polarized luminescence (CPL) spectroscopy allows for direct detection S_1-state chirality of luminophores. Moreover, CPL excitation (CPLE) spectroscopy teaches directly the origin of CPL band by monitoring at a specific (+)- and (–)-sign CPL band because CPLE is an electronic band selective spectroscopy.

Herein, we applied these CPL, CPLE, and CD spectroscopy to account for the dual CPL band associated with the sign inversion between CD and CPL bands of *D*- (or *L*-) camphor [4]. With help of DFT/TD-DFT calculations, we concluded that *D*- (or *L*-) camphor adopts a planar ketone form with (+)-sign CD band at ~300 nm in the S_0 state, while camphor adopts a bent ketone form associated with (–)-sign CD band at ~350 nm in the S_1 state (Fig. 1). The former is thermodynamically stable and the latter is metastable by 12 Kcal mol^{-1}. The bent and planar ketone forms in the photoexcited *D*-camphor are responsible for the bisignate dual CPL band (Fig. 2b), while the planar form, dominant species in the S_0 state, reveals the monosignate CD band (Fig. 2a) [4]. The corresponding CPLE spectra monitored at 370 nm and 480 nm (Fig. 2c and 2d) agree well with this conclusion.

Likewise, dual CPL and couple-like CD band profiles from colloidal π-conjugated polymer (**PF8T2**) generated with helical polysilanes (**PSi-*S*** and **PSi-*R***) teach us that the colloidal **PF8T2** in the photoexcited state does not obey the convesional Kasha's rule, as shown in Fig. 3a and 3b [4].
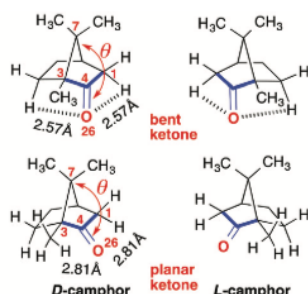

FIGURE 1. (Bottom) Planar ketone forms in the ground states and (top) bent ketone forms in the photoexcited states of *D*- and *L*-camphors, that are optimized by DFT (B3LYP, aug-ccpvDZ basis set) [4].

Our results suggest that the photoexcited chirality significantly differs from the ground state chirality owing to reorganization process of luminophores at the S_n states, that often unveils spectroscopically as (i) Stokes shift, (ii) an apparent inversion in chiroptical signs between CD at the first Cotton band and CPL

band, and (iii) incomplete couplet-like dual CPL bands associated with couplet-like dual CD bands [5,6]. We assume that, in the realms of photophysics and photochemistry, anti-Kasha's rule is a common, universal concept rathar than the convesional Kasha's rule [7–10].
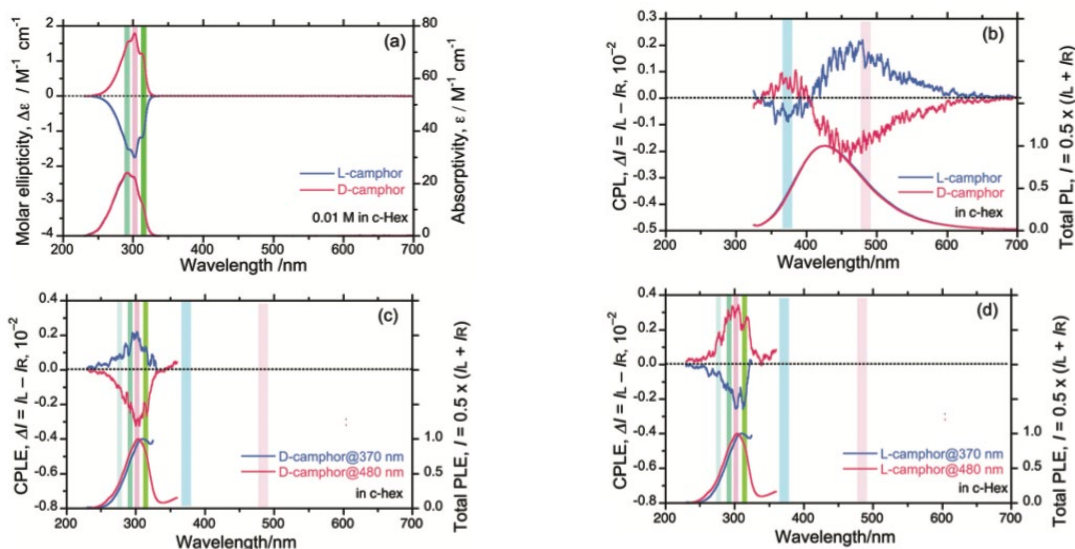

FIGURE 2. Vibronic CD spectra (a), structureless CPL spectra (b), and vibronic CPLE spectra monitored at 370 nm and 480 nm (c) and (d), respectively, of *D*- and *L*-camphors in dilute cyclohexane [4].
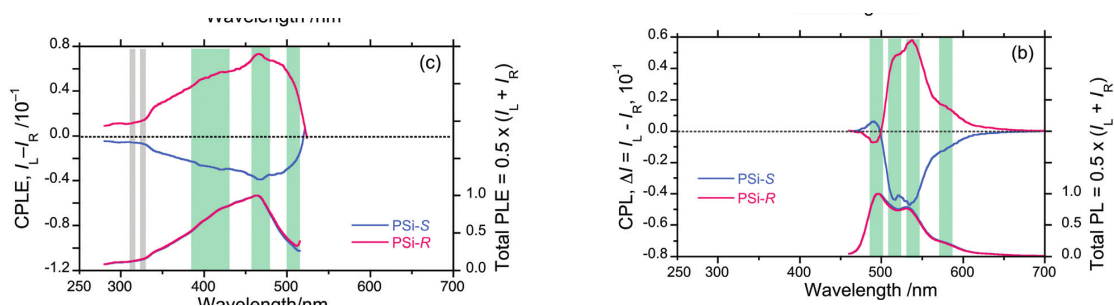

FIGURE 3. Chemical structures of optically active π-conjugated polymer (**PF8T2**) endowed with helical polysilanes (**PSi-*S*** and **PSi-*R***). (a) Couplet-like dual CD bands in the range of 350 nm and 550 nm and (b) couplet-like dual CPL bands in the range of 450 nm and 650 nm in a mixture of chloroform-methanol [4].

REFERENCES

1. H.P.J.M. Dekkers and L.E. Closs, *J. Am. Chem. Soc.*, **1976**, *98*, 2210–2219.
2. P. H. Schippers, J.P.M. van der Ploeg, and H.P.J.M. Dekkers, *J. Am. Chem. Soc.*, **1983**, *105*, 84–89.
3. G. Longhi, E. Castigilioni, S. Abbate, F. Lebon, and D.A. Lightner, *Chirality*, **2013**, *25*, 589–599.
4. S.T. Duong and M. Fujiki, *Polym. Chem.*, **2017**, *8*, 4673–4679.
5. M. Fujiki, *Symmetry*, **2021**, *13*, 199.
6. L. Wang, L. Yin, W. Zhang, X. Zhu, and M. Fujiki, *J. Am. Chem. Soc.,* **2017**, *139,* 13218–13226.
7. J. Gierschner, S. K. Behera, and S. Y. Park, *Angew. Chem. Int. Ed.* 2020 (doi.org/10.1002/anie.202009789).
8. M. Röhrs and D. Escudero, *J. Phys. Chem. Lett.*, **2019**, *10*, 5798–5804.
9. J.C. DelValle and J. Catalán, *Phys. Chem. Chem. Phys.*, **2019**, *21*, 10061–10069.
10. A.P. Demchenko, V.I. Tomin, and P.T. Chou, *Chem. Rev.*, **2017**, *117*, 13353–13381.