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COMMUNICATION

Nonclassical Dual Controlling Circularly Polarized Luminescence Modes of Binaphthyl–Pyrene Organic Fluorophores in Fluidic and Glassy Media

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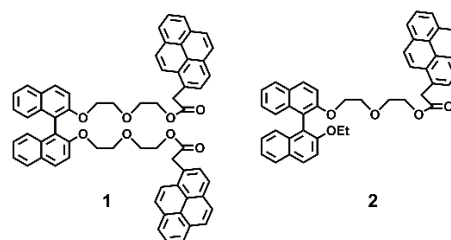
The fluorescent modes and signs of the circularly polarized luminescence of an axially chiral binaphthyl–pyrene organic fluorophore were successfully controlled by changing from a fluidic chloroform solution to a glassy poly(methyl methacrylate) solid film.

Organic fluorophores have attracted considerable attention as organic electroluminescent (EL) devices and optical sensors.¹ Although many organic fluorophores have been developed to date, there are not many chiral organic fluorophores that exhibit circularly polarized luminescence (CPL) properties with high quantum efficiency.²

In general, the maximum wavelength of CPL (λ_{CPL}) can be tuned by synthetic methods, for example, by introducing a functional substituent to the molecular backbone. In addition, the CPL sign can be controlled by switching the chirality of the starting compounds. Therefore, it would be beneficial to develop a novel facile method for controlling both λ_{CPL} and CPL sign of the chiral organic fluorophore without any synthetic methods.

Recently, we reported that the chiroptical signs of chiral binaphthyl organic fluorophores with the same axial chirality are controllable, both in the solution and solid states, (i) by controlling the dihedral angle of the binaphthyl units, (ii) by employing the neighbouring effect between the fluorescent binaphthyl units, and (iii) by manipulating their external environments, in addition to using opposite chiral counterparts.³

In this study, we investigated a non-classical approach for dual controlling the λ_{CPL} and CPL sign of chiral organic fluorophores. To that end, we used chiral binaphthyl–pyrene fluorophores, starting with a chiral binaphthyl–crown ether–bispyrene **1**[†] as the initial model (Scheme 1). Herein, we demonstrated that the dual controlling of λ_{CPL} and chiroptical sign is possible by varying the surrounding medium, e.g., by choosing a chloroform (CHCl₃) solution as the fluidic medium and poly(methyl methacrylate) (PMMA) film as the glassy solid medium.



Scheme 1 Binaphthyl–crown ether–pyrene compounds **1** and **2**.

First, we measured the solution-state unpolarized photoluminescence (PL) properties of (*R*)-**1** in CHCl₃. Fig. 1 shows that the maximum wavelength of PL (λ_{em}) is 480 nm, and the PL quantum yield (Φ_{F}) is 0.20. This feature is typical for the excimer emission of the pyrene units.

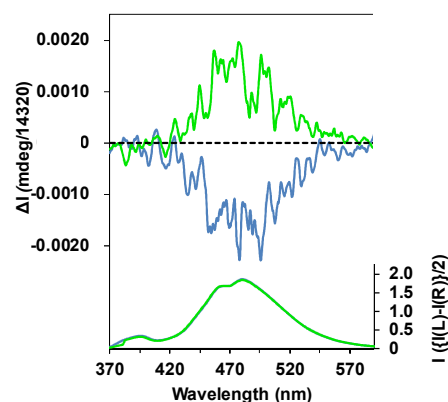


Fig. 1 CPL (upper panel) and PL (lower panel) spectra of (*R*)-**1** (blue line) and (*S*)-**1** (green lines) dissolved in CHCl₃ (1.0×10^{-3} M). $\lambda_{\text{ex}} = 340$ nm.

Next, we obtained the (chir)optical PL properties of (*R*)-**1** dispersed in PMMA film (Fig. 2, lower panel, blue line).⁵ Notably, Fig. 2 shows that the λ_{em} of (*R*)-**1** in the PMMA film shifted significantly to a shorter wavelength ($\lambda_{\text{em}} = 393$ nm) along with the

fact that the Φ_F value increased up to 0.46 due to the suppression of thermal vibrational deactivation.

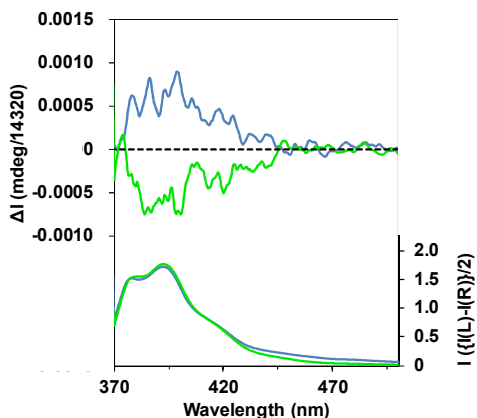


Fig. 2 CPL (upper panel) and PL (lower panel) spectra of (*R*)-**1** (blue lines) and (*S*)-**1** (green lines) dispersed in PMMA film. $\lambda_{\text{ex}} = 340$ nm.

As expected, (*R*)-**1** exhibited CPL signals in CHCl_3 and PMMA film (Figs. 1 and 2). The wavelength of CPL changed in conjugation with that of PL. The degree of CPL was evaluated by Kuhn's anisotropy factor (g_{em}) in the photoexcited state, which is defined as $g_{\text{em}} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R denote the quantum yields of the left-handed and right-handed CPL under unpolarized-light excitation, respectively. The absolute g_{em} values ($|g_{\text{em}}|$) are $\sim 7.8 \times 10^{-4}$ in CHCl_3 solution and $\sim 3.6 \times 10^{-4}$ in PMMA film. Surprisingly, (*R*)-**1** exhibits the opposite CPL signs depending on the fluidic and glassy states: negative (−) in the CHCl_3 solution, and, conversely, positive (+) in the PMMA film. To further confirm this finding, we measured the CPL spectra of (*S*)-**1** in both the states (Figs. 1 and 2). Indeed, the CPL spectra of (*R*)-**1** and (*S*)-**1** are in a nearly mirror-image relationship. Thus, both λ_{CPL} and CPL signs of chiral organic fluorophores are tunable by altering CHCl_3 solution and a PMMA film, as well as the chirality of **1**.

To clarify these phenomena, we compared these data to the previously reported CPL spectrum of (*R*)-2,2'-diethoxy-1,1'-binaphthyl, which lacks a pyrene unit, in both the states.^{3a} The binaphthyl fluorophore emitted at 365 and 373 nm in CHCl_3 solution and PMMA film, respectively. In addition, the CHCl_3 λ_{em} value of (*R*)-**1** did not change as the concentration decreased, remaining at 480 nm (1.0×10^{-3} , 1.0×10^{-4} , and 1.0×10^{-5} M). These observations confirm that this CPL of (*R*)-**1** in the PMMA film results from the pyrene unit, and indicate that this CPL is a special characteristic of the PMMA-film state of (*R*)-**1**.

Kano, Shishido, and co-workers originally reported the CPL properties of chiral pyrene excimers in γ -cyclodextrin.⁶ Intense excimer-origin $|g_{\text{em}}|$ was of the order of $\sim 10^{-2}$ at 474 nm. Since the $|g_{\text{em}}|$ value of (*R*)-**1** is significantly smaller than that of the pyrene dimer system reported previously, the chiral environment of pyrene unit in **1** is weak. The excimer-origin CPL of (*R*)-**1** in CHCl_3 can be attributed to the long-distance intramolecular interaction between the remote positions of two pyrenes in the chiral binaphthyl backbone.

To elucidate the cause of this CPL inversion phenomenon, the circular dichroism (CD) and UV spectra of (*R*)-**1** were measured in CHCl_3 solution and PMMA film. Several UV bands ranging from 310 to 370 nm, characteristic of the $\pi \rightarrow \pi^*$ transition of the pyrene or binaphthyl units in **1** were observed (Figs. 3 and 4). As expected by CPL spectra, the CD Cotton bands of (*R*)-**1** and (*S*)-**1** (Figs. 3 and 4) are in a nearly mirror-image relationship. Although the CD spectra of **1** in CHCl_3 are almost identical to those in PMMA film, the $|g_{\text{CD}}|$

value of the first Cotton CD band of **1** was: $|g_{\text{CD}}| = \sim 3.8 \times 10^{-5}$ at 344 nm in CHCl_3 , but $\sim 7.8 \times 10^{-5}$ at 343 nm in PMMA film. The first Cotton CD bands (345 nm) in CHCl_3 are a half of those (343 nm) in PMMA. The CD amplitude in the film was evaluated as follows: $g_{\text{CD}} = ((\text{Abs(L)} - \text{Abs(R)})/(\text{Abs(L} + \text{Abs(R)}))/2$.

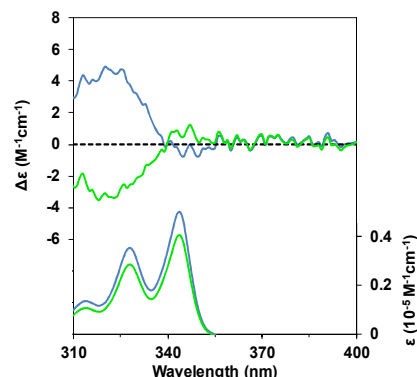


Fig. 3 CD (upper panel) and UV (lower panel) absorption spectra of (*R*)-**1** (blue lines) and (*S*)-**1** (green lines) dissolved in CHCl_3 (1.0×10^{-5} M).

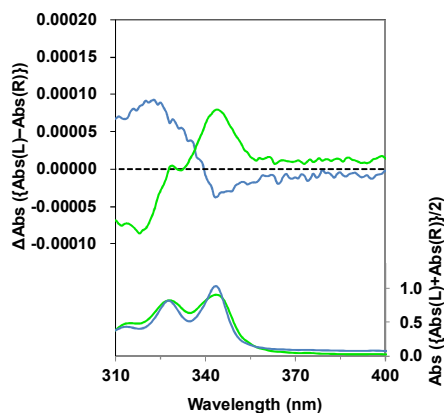


Fig. 4 CD (upper panel) and UV (lower panel) absorption spectra of (*R*)-**1** (blue lines) and (*S*)-**1** (green lines) dispersed in PMMA.

For comparison, a chiral binaphthyl-crown ether-pyrene, **2**, with one pyrene unit was newly synthesized, and its CPL and PL spectra were compared in CHCl_3 solution and PMMA film. (*R*)-**2** was prepared from chiral 2'-ethoxy-1,1'-binaphthalene-2-ol.⁷ Compound **2** exhibited efficient PL in CHCl_3 and PMMA. Fig. 5 shows that λ_{em} is 393 nm in CHCl_3 and PMMA film.

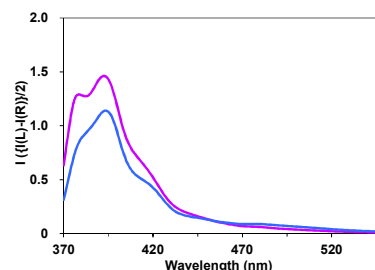


Fig. 5 PL spectra of (*R*)-**2** in CHCl_3 (1.0×10^{-3} M, blue line) and PMMA (purple line). $\lambda_{\text{ex}} = 340$ nm.

Although this PL results from the pyrene monomer only,⁸ (*R*)-**2** does not exhibit any detectable CPL signals regardless of CHCl_3 solution

and PMMA film. From these results, in CHCl_3 solution, a closer approach between photoexcited two pyrene moieties is possible by reorganization of the pyrenes in (*R*)-**1**. On the other hand, in PMMA film, although a dinote intramolecular pyrene interaction produce chiral environment of pyrene units, a closer intramolecular pyrene excimer is inhibited because of PMMA glassy solid. The intramolecular reorientational mode of two pyrene units is difficult to occur upon photoexcitation. That is, it is thought that in PMMA film, CPL of (*R*)-**1** is a monomer-like excimer CPL. This also is a reason for the increase in fluorescence quantum yield (Φ_F) in PMMA film.

Conclusions

Chiral fluorophore **1** exhibited PL in CHCl_3 solution and PMMA film. The CPL profiles and their signs were controllable by selecting a fluidic CHCl_3 solution and glassy PMMA film. This finding may offer the choice of fluidic solution and glassy solid to control the CPL/PL characteristics of multiple fluorophore molecules in addition to chiral pyrene-based fluorophores.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details of synthesis method of chiral **2** and measurements of PL, CD and CPL spectra. See DOI: 10.1039/c000000x/.

- (a) P. G. Coble, *Chem. Rev.*, 2007, **107**, 402; (b) T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011; (c) S.-C. Lo and P. L. Burn, *Chem. Rev.*, 2007, **107**, 1097; (d) K. Walzer, B. Maennig, M. Pfeiffer and K. Leo, *Chem. Rev.*, 2007, **107**, 1233; (e) J. Grate, *Chem. Rev.*, 2008, **108**, 726; (f) F. Jakle, *Chem. Rev.*, 2010, **110**, 3985; (g) J. E. Kwon and S. Y. Park, *Adv. Mater.*, 2011, **23**, 3615; (h) C. Zhang, Y. S. Zhao and J. Yao, *New J. Chem.*, 2011, **35**, 973; (i) Lauren E. Kreno, Kirsty Leong, Omar K. Farha, Mark Allendorf, Richard P. Van Duyne, and Joseph T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; and references cited therein.
- (a) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger and N. J. Turro, *J. Am. Chem. Soc.*, 2001, **123**, 11899; (b) J. E. Field, G. Muller, J. P. Riehl and D. Venkataraman, *J. Am. Chem. Soc.*, 2003, **125**, 11808; (c) H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori and T. Kawai, *J. Am. Chem. Soc.*, 2011, **133**, 9266; (d) R. Tempelaar, A. Stradomska, J. Knoester and F. C. Spano, *J. Phys. Chem., B*, 2011, **115**, 10592; (e) Y. Nakano and M. Fujiki, *Macromolecules*, 2011, **44**, 7511; (f) N. Nishiguchi, T. Kinuta, Y. Nakano, T. Harada, N. Tajima, T. Sato, M. Fujiki, R. Kuroda, Y. Matsubara and Y. Imai, *Chem. Asian J.*, 2011, **6**, 1092; (g) J. Liu, H. Su, L. Meng, Y. Zhao, C. Deng, J. C. Y. Ng, P. Lu, M. Faisal, J. W. Y. Lam, X. Huang, H. Wu, K. S. Wong and B. Z. Tang, *Chem Sci.*, 2012, **3**, 2737; (h) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi and K. Tanaka, *J. Am. Chem. Soc.*, 2012, **134**, 4080; (i) H. Oyama, K. Nakano, T. Harada, R. Kuroda, M. Naito, K. Nobusawa and K. Nozaki, *Org. Lett.*, 2013, **15**, 2104; (j) J. Kumar, T. Nakashima, H. Tsumatori and T. Kawai, *J. Phys. Chem. Lett.*, 2014, **5**, 316; (k) T. Shiraki, Y. Tsuchiya, T. Noguchi, S.-i. Tamaru, N. Suzuki, M. Taguchi, M. Fujiki, and S. Shinkai, *Chem. Asian J.*, 2014, **9**, 218; (l) X. Jiang, X. Liu, Y. Jiang, Y. Quan, Y. Cheng and C. Zhu, *Macromol. Chem. Phys.*, 2014, **215**, 358; (m) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 3350; (n) S. Abbate, G. Longhi, F. Lebon, E. Castiglioni, S. Superchi, L. Pisani, F. Fontana, F. Torricelli, T. Caronna, C. Villani, R. Sabia, M. Tommasini, A. Lucotti, D. Mendola, A. Mele and D. A. Lightner, *J. Phys. Chem. C*, 2014, **118**, 1682 and references cited therein.
- (a) T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *Chem. Asian J.*, 2012, **7**, 2836; (b) T. Amako, T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *RSC Adv.*, 2013, **3**, 6939; (c) T. Kimoto, T. Amako, N. Tajima, R. Kuroda, M. Fujiki and Y. Imai, *Asian. J. Org. Chem.*, 2013, **2**, 404 and references cited therein.
- E. J. Jun, H. N. Won, J. S. Kim, K.-H. Lee and J. Yoon, *Tetrahedron Lett.*, 2006, **47**, 4577.
- Chiral **1** or **2**-doped PMMA films were prepared by drop-casting tetrahydrofuran (THF) solutions, in which the PMMA concentration was fixed at 0.1 g/mL, onto quartz plates. Chiral **1** (or **2**) was added to the PMMA/THF solutions at concentrations of 0.01 mol/L. PMMA films were prepared using a spin coater at 3000 rpm.
- K. Kano, H. Matsumoto, S. Hashimoto, M. Sisido and Y. Imanishi, *J. Am. Chem. Soc.*, 1985, **107**, 6117.
- ¹H NMR (acetone-*d*₆, 400 MHz) δ 8.08-8.26 (m, 7H), 8.03 (t, *J* = 7.8 Hz, 1H), 7.87-7.96 (m, 4H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.11-7.32 (m, 4H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 4.32 (s, 2H), 3.95-4.02 (m, 4H), 3.84-3.87 (m, 2H), 3.32 (t, *J* = 4.6 Hz, 2H), 3.09-3.19 (m, 2H), 0.94 (t, *J* = 6.9 Hz, 3H).
- Excimer PL of (*R*)-**2** was observed at 507 nm in 1.0×10^{-2} M in CHCl_3 .

Graphical Abstract

