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# The origin of bisignate circularly polarized luminescence (CPL) spectra from chiral polymer aggregates and molecular camphor: Anti-Kasha's rule revealed by CPL excitation (CPLE) spectra

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#### Experimental Section

#### 1. Instrumentation

The UV-vis absorbance and CD spectra of the solution were recorded simultaneously at room temperature using a JASCO (Tokyo, Japan) J-820 spectropolarimeter equipped with Peltier controlled equipment using a square quartz (SQ)-grade cuvette with path lengths of 5 mm for **PF8T2** aggregates and 10 mm for camphor. To obtain CD/UV-vis spectra, a scanning rate of 100 nm min<sup>-1</sup>, a bandwidth of 1 nm (solution) and 5 nm (silicone grease film) and a response time of 2 sec were utilized.

CPL and PL spectra were collected on a JASCO CPL-200 spectrofluoropolarimeter using an SQ-grade cuvette with path lengths of 5 mm for **PF8T2** aggregates and 10 mm for camphor at room temperature. The optimal experimental parameters for **PF8T2** aggregates were simultaneously obtained: scanning rate: 100 nm min<sup>-1</sup>; bandwidth: 10 nm for excitation and detection; slit width for excitation: 10 nm and 2000  $\mu$ m at 390 nm and 420 nm; PMT response time: 4 sec during measurements using a single accumulation. Furthermore, this instrument was designed to obtain the **PF8T2** aggregates' CPLE spectra corresponding to their CD and CPL signals by adjusting the detection wavelength and using a bandwidth of 10 nm, a scanning rate of 20, 50, or 100 min<sup>-1</sup> and response time of 4 sec.

For camphor, the conditions used to measure the CPL, PL, CPLE and PLE spectra at room temperature were as follows: for CPL and PL measurements, path length of 10 mm and scanning rate of 20–50 nm min<sup>-1</sup> and slit widths of 2000–3000  $\mu$ m for excitation and detection; for CPLE and PLE measurements, excitation slit width of 2000  $\mu$ m at 290 nm, detection slit width of 2000–3000  $\mu$ m and PMT response time of 4-16 sec during measurements involving 4–8 accumulations. Additionally, this instrument was designed to obtain the CPLE spectra corresponding to CD signals by adjusting the detection wavelength with a bandwidth of 10 nm, a scanning rate of 100 or 10 nm min<sup>-1</sup> and a response time of 4 sec. High-resolution CPLE and PLE spectra of camphor in cyclohexane were collected under the following conditions: a scanning rate of 10 nm min<sup>-1</sup>, bandwidths of 10 nm for excitation and detection, a PMT time constant of 16 sec, and 4 accumulations. High-resolution PLE spectra of camphor in cyclohexane the following conditions: a scanning rate of 10 nm min<sup>-1</sup>, bandwidth of 10 nm for excitation and detection, a PMT time constant of 16 sec, and 4 accumulations. High-resolution PLE spectra of camphor in cyclohexane the following conditions: a scanning rate of 10 nm min<sup>-1</sup>, bandwidth of 10 nm for excitation and detection, a PMT time constant of 16 sec, and 4 accumulations. High-resolution PLE spectra of camphor in cyclohexane were also obtained using a JASCO FP6500 fluorometer under the following conditions: a scanning rate of 50 nm min<sup>-1</sup>, a bandwidth of 3 nm for excitation, a bandwidth of 5 nm for detection, a PMT time constant of 1 sec, high PMT gain, and one accumulation.

The weight-averaged molecular weight ( $M_w$ ), number-averaged molecular weight ( $M_n$ ) and polydispersity index ( $PDI = M_w/M_n$ ) were evaluated via GPC, which was performed on a Shimadzu A10 instrument with a PLgel (Varian, 10  $\mu$ m mixed-B) column and high-performance liquid chromatography (HPLC)-grade tetrahydrofuran (THF) as the eluent at 40 °C (calibrated with polystyrene standards). The aggregate sizes were analysed using DLS (detector angle of 90°, 50 accumulated scans; DLS-6000HL, Otsuka Electronics, Hirakata-Osaka, Japan) with solution viscosity data obtained with a Sekonic (Tokyo, Japan) viscometer (VM-100) at 25 °C and the  $n_D$ value of chloroform:methanol (2.1:0.9) (v/v) determined at 589 nm and 25 °C using an Atago (Tokyo, Japan) thermo-controlled DR-M2 refractometer at 25 °C.

To photoimage **PF8T2**, the aggregate suspension in chloroform:methanol (2.1:0.9) (v/v) was drop-cast onto a micro slide glass with a thickness of 0.9–1.2 mm, and the image was obtained directly by FOM with excitation at 365 nm using a Nikon eclipse E400 optical microscope equipped with a Canon EOS Kiss X7i digital camera.

#### 2. Chiroptical analysis

The dissymmetry factor of circular polarization at the ground state  $(g_{abs})$  was theoretically calculated as  $g_{abs} = (\varepsilon_L - \varepsilon_R)/[1/2(\varepsilon_L + \varepsilon_R)]$ , where  $\varepsilon_L$  and  $\varepsilon_R$  are the extinction coefficients for left- and right-CP light, respectively. The dissymmetry factor of circular polarization at the excited state  $(g_{CPL})$  was calculated as  $g_{em} = (I_L - I_R)/[1/2(I_L + I_R)]$ , where  $I_L$  and  $I_R$  are the output signals for left- and right-circularly polarized light under the unpolarized incident light, respectively. The parameter  $g_{abs}$  was experimentally determined using the expression,

 $\Delta \epsilon / \epsilon$  = [ellipticity (in mdeg)/32 980]/absorbance at the CD extremum,

similar to the parameter  $g_{\rm em}$ , which was calculated as

 $\Delta I/I =$  [ellipticity (in mdeg)/(32 980/ln10)]/[unpolarized total PL intensity (in volts)] at the CPL extremum.

The refractive index ( $n_D$ ) value of the cosolvent was determined as  $n_{D,ave} = x n_{D(CHCI3)} + (1-x) n_{D(MeOH)}$ , where x is the volume fraction of CHCl<sub>3</sub> in the mixture of the two solvents. The  $n_D$  values of pure CHCl<sub>3</sub> and MeOH were selected in this research.

#### 3. Computational simulations

The most stable structure of *D***-camphor**, which has a C(7)–C(4)=O(26) bond angle of 153°, as shown below, was optimized using PM6 with Gaussian09 rev. D.01 (Gaussian, Inc., Wallingford CT, 2013).<sup>S1</sup> All hydrogen atoms are omitted for clarity. A series of other unstable structures was obtained as a function of the C(7)–C(4)=O(26) bond angle based on the global minimum structure



with a planar ketone C(1)-C(4)=O(26)-C(4)geometry. These hypothetical models with the C(7)-C(4)=O(26) bond angle of **D-camphor** were further optimized using a DFT programme and the aug-cc-pVDZ basis set as a function of the C(7)-C(4)=O(26) bond angle. Subsequently, TD-DFT calculations with B3LYP and the aug-cc-pVDZ basis set were performed to obtain the UV-is and CD spectra (6 singlet transitions) with a FWHM of 0.1 eV. These simulated UV-vis and CD spectra were saved as text data sets and re-plotted using KaleidaGraph ver. 4.5 (Synergy Software,

Reading, PA 19606, USA). Two MacPro computers (2.80 GHz and 2.66 GHz clock, 8-core and 32 GB memory) were used to perform these calculations.

Ref. S1. Gaussian 09, Rev. D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

#### 4. Materials

#### 4.1. Preparation of stock solutions and dried aggregates

The stock solutions of **PSi-***R* and **PSi-***S* (details are given in the experimental section of ref 9a) were diluted in a good solvent (chloroform) and then stirred for 1 hour and kept at room temperature overnight. A similar process was used for poly[(9,9-di-octyl-fluorenyl-2,7-diyl)-*alt*-bithiophene] (**PF8T2**). In this research, **PF8T2** with an  $M_n$  of 10,300 and PDI of 2.64 (Sigma-Aldrich Japan, Tokyo, Japan) as received was utilized.

The stock solution of (1S)-(-)-camphor (*L*-camphor, Aldrich) and (1R)-(-)-camphor (*D*-camphor, Aldrich) were diluted in cyclohexane  $(1.0 \times 10^{-2} \text{ M}, \text{ Dojindo}, \text{ Kumamoto}, \text{ Japan})$  at room temperature. For confirmation, spectroscopic-grade ethanol (Wako, Osaka, Japan) was used as a solvent to dilute *L*-/-*D*-camphor at a concentration of 0.4 % wt/v (2.6 x 10<sup>-2</sup> M).

The dried aggregates were prepared by removing the CHCI<sub>3</sub>-MeOH cosolvent in a stream of dry nitrogen gas flow at room temperature. The aggregates were dispersed in a silicone grease (Dow-Corning-Toray). The aggregates-containing grease was coated onto a quartz substrate (22 mm in diameter).

#### 4.2. Hetero-aggregation of PSi and PF8T2

Spectroscopic-grade chloroform (Dojindo) as a good solvent and spectroscopic-grade methanol (Dojindo) and spectroscopic-grade ethanol (Wako) as poor solvents were added to produce an optically active hetero-aggregate in the SQ-grade cuvette (path length: 10 mm). A preliminary experiment revealed that the optimized volume ratios were 2.1:0.9 and 2.2:0.8 corresponding to each **PSi-***R*/-*S* helicity transfer; the total volume of chloroform:methanol was fixed at 3.0 mL. The molar ratio of the polymers dissolved in the chloroform was tuned according to the experimental requirements. **PF8T2** dissolved in chloroform was added to the cuvette, followed by dissolved **PSi-***R* ( $M_n = 23,900$ , PDI = 1.64) or **PSi-S** ( $M_n = 20,400$ , PDI = 1.32) to produce a well-mixed complex; then, methanol was normally added. Subsequently, CD-UV-vis, CPL-PL and CPLE spectroscopic data were collected within several minutes after the completion of the hetero-aggregate, **PF8T2** hetero-aggregates with **PSi-***S* in CHCl<sub>3</sub>-MeOH cosolvent (2.2:0.8 (v/v)) were evaluated using a 5,5'-diphenyl-3-dimesitylboryl-2,2'-bithiophene (**BT3**) ( $\Phi_{PL} = 90$  % in THF)<sup>S2</sup> as a secondary reference<sup>S3</sup> for a green emitter.

Ref. S2. A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2007, 23, 4273–4276. Ref. S3. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, Heidelberg, 3rd edn, 2006.



Fig. S1. GPC charts monitored at (a) 325 nm of PSi-S/-R and (b) 370 nm of PF8T2.





**Fig. S3.** (a) The  $g_{abs}$  value of **PF8T2** hetero-aggregate with **PSi-S/-R** (1/1) at  $\approx$  500 nm as a function of the refractive index (n<sub>D</sub>) in 3.0 mL of MeOH-CHCl<sub>3</sub> cosolvent and (b) magnified plots. (c) The  $g_{abs}$  value of **PF8T2** hetero-aggregate with **PSi-S/-R** (1/1) at  $\approx$  500 nm as a function of the refractive index (n<sub>D</sub>) in 3.0 mL of EtOH-CHCl<sub>3</sub> cosolvent and (d) magnified plots.



**Fig. S4.** (a) Raw CD/UV-vis and (b) CPL/PL spectra of **PF8T2** hetero-aggregate with **PSi-S/-***R* (1/1) produced in CHCl<sub>3</sub>:MeOH = 2.2:0.8 (v/v).



**Fig. S5.** CD/UV-vis spectra of **PF8T2** hetero-aggregate with **PSi-***S*/-*R* (1/1) produced in CHCl<sub>3</sub>:EtOH = 2.1:0.9 (v/v).



**Fig. S6.** Normalized PL spectra excited at 420 nm and PLE spectra monitored at 430 nm and 570 nm of **PF8T2** hetero-aggregate with (a) **PSi-R** and (b) **PSi-S** (1/1). PLE spectra of **PF8T2** hetero-aggregate with **PSi-R** (1/1) monitored at (c) 550 nm, 560 nm, 570 nm and 580 nm; and (e) 420 nm, 430 nm and 440 nm. PLE spectra of **PF8T2** hetero-aggregate with **PSi-S** (1/1) produced in CHCl<sub>3</sub>:MeOH = 2.2:0.8 (v/v) monitored at (d) 560 nm, 570 nm, and 580 nm; and (f) 420 nm, 430 nm and 440 nm. The final concentration was  $10^{-5}$  M. The spectra were obtained with a JASCO FP6500 spectrofluorimeter.

These data sets were obtained using an achiral spectrofluorimeter (JASCO FP6500). The measurement conditions were as follows. In the PLE experiments monitored at 550 nm, 560 nm, 570 nm and 580 nm: bandwidth for excitation: 1 nm; bandwidth for detection: 3 nm: PMT: high sensitivity; PMT response time: 1 sec; data interval: 1 nm: and one scan collected at a rate of 100 nm min<sup>-1</sup>. In the PLE experiments monitored at 420 nm, 430 nm, and 440 nm: bandwidth for excitation: 3 nm; bandwidth for detection: 5 nm: PMT: high sensitivity; PMT response time: 1 sec; data interval: 1 nm; and one scan collected at a rate of 100 nm min<sup>-1</sup>.



**a.** PL spectra of 5,5'-diphenyl-3-dimesitylboryl-2,2'bithiophene (**BT3**) in THF (2.0x10<sup>-5</sup> M).



**c.** PL spectra of **PF8T2** homo-aggregate (8.0x10<sup>-6</sup> M) in CHCl<sub>3</sub>-MeOH (2.2/0.8 (v/v)). *Abs* = 0.210 at 420 nm.  $\Phi_{PL} = (0.9) \times (0.196/0.210) \times (3089.08/8612.82) \times (1.414^2/1.407^2)$ 



**e.** PL spectra of **PF8T2** hetero-aggregate  $(4.0 \times 10^{-6} \text{ M})$  with **PSi-***R* in CHCl<sub>3</sub>-MeOH (2.2/0.8 (v/v)). *Abs* = 0.185 at 420 nm.  $\Phi_{PL} = (0.9) \times (0.196/0.185) \times (2961.20/8612.82) \times (1.414^2/1.407^2)$ 



**b.** PL spectra of **PF8T2** in CHCl<sub>3</sub> ( $4.0x10^{-6}$  M). *Abs* = 0.193 at 420 nm. *Abs* = 0.196 at 420 nm.  $\Phi_{PL}$  = (0.9) × (0.196/0.193) × (6737.95/8612.82) × (1.4441^2/1.4072^2).



**d.** PL spectra of **PF8T2** hetero-aggregate  $(4.0 \times 10^{-6} \text{ M})$  with **PSi-S** in CHCl<sub>3</sub>-MeOH (2.2/0.8 (v/v)). *Abs* = 0.195 at 420 nm.  $\Phi_{PL} = (0.9) \times (0.196/0.195) \times (3158.88/8612.82) \times (1.414^2/1.407^2)$ 

Compd	Solvent(s)	Quantum yield ( $\Phi_{PL}$ )
BT3	THF	0.90
PF8T2	CHCI <sub>3</sub>	0.75
PF8T2 homo-aggregate	CHCl <sub>3</sub> -MeOH (2.2/0.8 (v/v))	0.30
PF8T2-PSi-S (1:1) hetero-aggregate	CHCl <sub>3</sub> -MeOH (2.2/0.8 (v/v))	0.34
PF8T2-PSi-R (1:1) hetero-aggregate	CHCl <sub>3</sub> -MeOH (2.2/0.8 (v/v))	0.33

**Fig. S7.** Quantum yields and their raw PL spectral data of **BT3** in CHCl<sub>3</sub>, **PF8T2** in CHCl<sub>3</sub>, **PF8T2** homo-aggregate in CHCl<sub>3</sub>-MeOH (2.2/0.8 (v/v)), **PF8T2** hetero-aggregate with **PSi-S** in CHCl<sub>3</sub>-MeOH (2.2/0.8 (v/v)) and **PF8T2** hetero-aggregate with **PSi-R** in CHCl<sub>3</sub>-MeOH (2.2/0.8 (v/v)).



**Fig. S8.** CD/UV-vis spectra of **PF8T2** hetero-aggregate with (a) **PSi-S** and (b) **PSi-R** (1/1) produced in CHCl<sub>3</sub>:MeOH = 2.1:0.9 (v/v) followed by UV-light irradiation. (c) CPL/PL spectra (excited at 420 nm) of **PF8T2** hetero-aggregate with **PSi-S**/-*R* before and after 600 sec of UV-light irradiation at 313 nm.



**Fig. S9.** Hetero-aggregate  $g_{abs}$  values of **PF8T2** (1.0 x  $10^{-5}$  M) and **PSi-S/-R** (1.0 x  $10^{-5}$  M) prepared in CHCl<sub>3</sub>:MeOH = 2.1:0.9 (v/v) as a function of the duration of UV-light irradiation at 313 nm.



**Fig. S10.** DLS data of hetero-aggregates of (a) **PSi-***R*-induced **PF8T2** (1/1) and (b) **PSi-***S* induced **PF8T2** (1/1) before and after UV-light irradiation at 313 nm for 600 sec (14  $\mu$ W cm<sup>-2</sup>). The hetero-aggregates were prepared in CHCl<sub>3</sub>:MeOH = 2.1:0.9 (v/v).



**Fig. S11.** FOM images of hetero-aggregates of **PSi-***R*-induced **PF8T2** (1/1) (a) before and (b) after UV-light irradiation at 313 nm for 600 sec (14  $\mu$ W cm<sup>-2</sup>). The hetero-aggregates were prepared in CHCl<sub>3</sub>:MeOH = 2.1:0.9 (v/v).



**Fig. S12.** The dynamic force mode (DFM) images (tapping mode AFM) of hetero-aggregates of **PSi-***R*-induced **PF8T2** (1/1) prepared in CHCl<sub>3</sub>:MeOH = 2.1:0.9 (v/v). The DFM images with Al-coated cantilever were captured using a SPA 400 SPM unit with a SII SPI 3800 probe station (Hitachi High-Tech Science Corporation (Tokyo, Japan)). The sample was deposited onto a HOPG substrate (IBS-MikroMasch, Sofia, Burgaria; the Japanese vendor is Tomoe Engineering Co. (Tokyo, Japan)) by dropping the **PF8T2-PSi-***R* aggregate.



Fig. S13. A revisited Jablonski diagram explaining the bisignate CD, CPL and CPLE spectra of PF8T2 aggregates.



**Fig. S14.** (a) CD/UV-vis and (b) CPL/PL spectra (excited at 290 nm) of *D-I-L*-camphor. CPLE/PLE spectra monitored at 370 nm and 460 nm of (c) *D*-camphor and (d) *L*-camphor. Solvent: ethanol (Wako, spectroscopic grade); path length: 1 cm; 0.4 % wt/v (=  $2.6 \times 10^{-2}$  M).



**Fig. S15.** PLE spectra monitored at 370 nm, 500 nm and 520 nm of (a, b) *D*-camphor and (c, d) *L*-camphor. Concentration:  $1 \times 10^{-2}$  M in cyclohexane (cHex) (Dojindo, spectroscopic grade); path length: 1 cm; detection and excitation bandwidths: 5 and 3 nm, respectively; PMT sensitivity: high; PMT response time: 1 sec; 50 nm min<sup>-1</sup>; 0.5 nm interval; one scan conducted with a JASCO FP6500 spectrometer at room temperature.

Green zones in spectra (a) and (c) are magnified in spectra (b) and (d). At least three well-resolved weak vibronic bands (grey bars) are present, regardless of the detection wavelength (i.e., 500 nm or 520 nm). Thus, a broad structureless PL band at approximately 450-600 nm should be associated with these weak vibronic bands.



**Fig. S16.** CPLE/PLE spectra monitored at 370 nm and 500 nm of (a, b) *D***-camphor** and (c, d) *L***-camphor**. Solvent: Cyclohexane (Dojindo, spectroscopic grade; path length: 1 cm; concentration:  $1x10^{-2}$  M; detection and excitation bandwidths: 10 nm; PMT response time: 16 sec; 10 nm min<sup>-1</sup>; 0.5 nm interval; 4 scans. Bold solid lines of CPLE spectra are numerically smoothed by 19 points of raw data.



**Fig. S17.** CD/UV-vis spectra of *D***-***I***-***L***-camphor** in (a) ethanol (0.4 % wt/v) and (b) cyclohexane (Dojindo, spectroscopic grade,  $1.0 \times 10^{-2}$  M). Bandwidth: 1 nm; data sampling interval: 0.2 nm; path length: 1 cm. The shape and resolution of CD and UV spectra depend strongly on the nature of the solvent. However, cut-off wavelengths for cyclohexane and ethanol exist at approximately 210-220 nm.



**Fig. S18.** CD and UV-vis data of *D***-camphor** at the  $1^{st}$  Cotton band as a function of the C(7)-C(4)=O(26) angle (DFT and TD-DFT with B3LYP and the aug-ccpvDZ basis set).





**Fig. S19.** Simulated CD/UV-vis spectra of *D***-camphor** as the C(7)-C(4)=O(26) bond angle from a planar to a bent structure (TD-DFT with B3LYP and the aug-ccpvDZ basis set; full-width at half-maximum: 0.1 eV).