

# RSC Advances

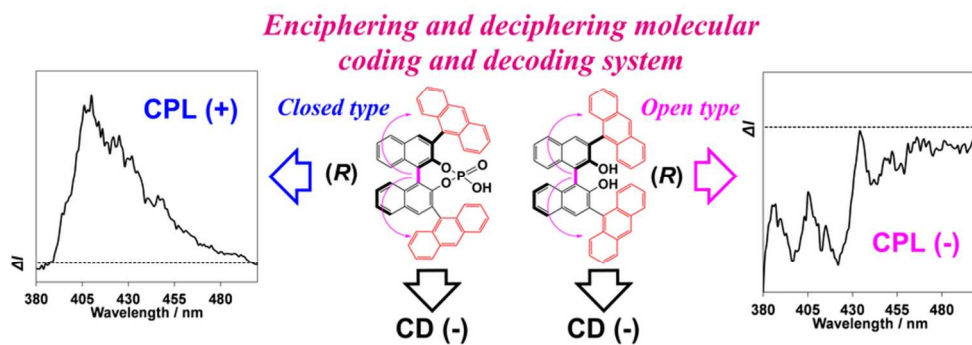


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



80x27mm (300 x 300 DPI)



## Photoexcited State Chirality Transfer. Hidden Tunability of Circularly Polarized Luminescent Binaphthyl–Anthracene Tandem Molecular Systems

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Sayaka Kitamura,<sup>a</sup> Kazuki Nakabayashi,<sup>a</sup> Takashi Wakabayashi,<sup>a</sup> Nobuo Tajima,<sup>b</sup> Michiya Fujiki,<sup>c\*</sup> and Yoshitane Imai<sup>a\*</sup>

Circularly polarized luminescent properties of C<sub>2</sub>-symmetrical binaphthyl molecular systems bearing two achiral anthracenes as luminophores were tuned by solely exploiting photoexcited-state chirality transfer from the binaphthyl to anthracenes when open- or closed-type binaphthyl structure as non-luminophore was chosen.

### Introduction

Although many organic luminophores are utilized in organic electroluminescence, lasing and optoelectronic devices, chiral luminophores exhibiting circularly polarized luminescence (CPL) with a high quantum efficiency are rarely reported.<sup>1,2</sup>

C<sub>2</sub>-symmetrical binaphthyl is one of the more prominent building blocks, facilitating the introduction of chiral motifs into achiral molecular units in the ground state.<sup>2</sup> Additionally, binaphthyl moiety itself, though a good luminogen, reveals CPL and photoluminescence (PL) signals in UV region reflecting from photoexcited chirality.<sup>2</sup> Previously, we reported that, in certain binaphthyl chromophores with rotational freedom of C–C single bond between the naphthyls, chiroptical signs in circular dichroism (CD) signals are determined solely by the dihedral angle between two binaphthyl units whilst the chromophores possess the same axial chirality.<sup>3</sup> In this case, C<sub>2</sub>-chiral binaphthyl itself acts as CPL luminophore. Chiroptical sign inversion between CD and CPL spectra was observed, depending on the degree of the rotational freedom.

This knowledge and understanding prompted us to investigate in more detail the ground- and photoexcited-state chiralities, revealed by chiroptical signs in the CPL and CD signals of binaphthyl chromophore directly connected to two achiral anthracene luminophores. A comparative study between the CD and CPL signals of tandem chiral luminophores, *e.g.*, binaphthyl with multiple achiral

luminophores, is rare to date. Actually, analysis of tandem chiral luminophores is especially difficult due to the presence of conformational freedom of C–C bonds and plural dihedral angles.<sup>2–5</sup>

Herein, we demonstrate the hidden tunable CPL properties of binaphthyl-driven luminophores connected to the two achiral anthracenes, in which marked difference in photoexcited- and ground-state chiralities are reflected by CPL and CD signals and their signs. Two types of chiral luminophore systems were designed: closed-style and open-style. The former is 3,3'-bis(9-anthracenyl)-1,1'-binaphthyl-2,2'-diyl-hydrogen phosphate (**1**, Fig. 1) and the latter is 3,3'-bis(9-anthracenyl)-1,1'-bis-2-naphthol (**2**, Fig. 1). Generally, we cannot fully predict their chiroptical properties because the chiral and achiral units are remotely positioned and these units have many rotatable C–C single bonds (Fig. 1).

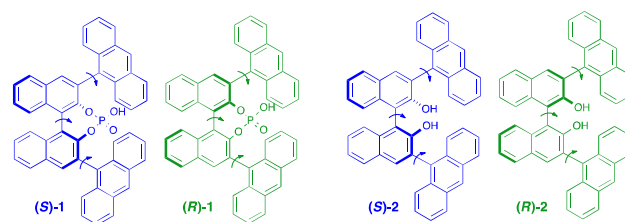


Fig. 1 C<sub>2</sub>-symmetrical binaphthyl-anthracene luminophores, closed-type **1** and open-type **2** with three rotational C–C bonds.

### Results and discussion

Firstly, the solution-state PL and CPL properties of (*R*)-**1** and (*R*)-**2** were compared to know their photoexcited chiralities in a homogeneous solution. The most probable PL phenomena of luminescent molecules containing two luminophores are the occurrence of intra-luminophore PL quenching, intra-energy transfer and excimer-like redshift emission.

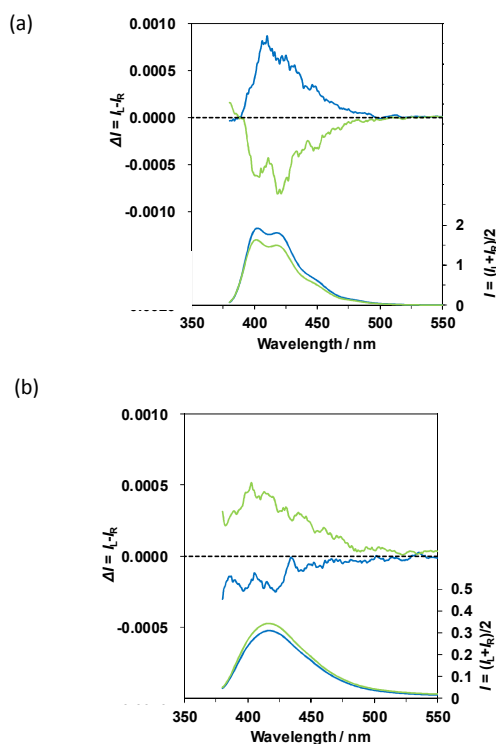
<sup>a</sup> Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.; E-mail: (Y.I.) y-imai@apch.kindai.ac.jp.

<sup>b</sup> Computational Materials Science Center, National Institute for Materials Science 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.

<sup>c</sup> Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama, Ikoma, Nara 630-0192, Japan. E-mail: (M.F.) fujikim@ms.naist.jp.

† Electronic Supplementary Information (ESI) available: Experimental details of PL, CD, and CPL spectra and theoretical calculations. See DOI: 10.1039/c000000x/.

Evidently, (*R*)-**1** and (*R*)-**2** exhibited PL from the anthracenes at a concentration of  $1.0 \times 10^{-4}$  M in *N,N*-dimethylformamide (DMF), as indicated by the blue lines in the lower panels of Fig. 2a for **1** and Fig. 2b for **2**. Although the PL maxima ( $\lambda_{em}$ ) for (*R*)-**1** and (*R*)-**2** were almost similar, *i.e.*, 422 nm of (*R*)-**1** and 419 nm of (*R*)-**2**, the absolute PL quantum yields ( $\Phi_f$ ), 0.59 for (*R*)-**1** and only 0.01 for (*R*)-**2**, were markedly different from each other. This extremely low  $\Phi_f$  value of (*R*)-**2** originates from significant ro-vibrational deactivation modes due to rotational C–C bond freedom characteristic of open-style binaphthyl in (*R*)-**2**. This is evident from a larger Stokes shift of  $\approx 30$  nm, as can be seen in Figs. 2 and 3.

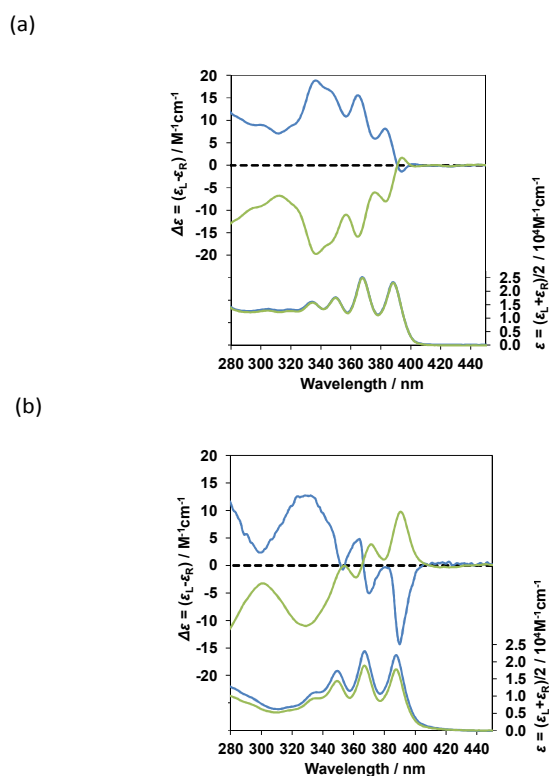


**Fig. 2** CPL (upper panel) and PL (lower panel) spectra of (a) (*R*)-**1** (blue lines) and (*S*)-**1** (green lines) and (b) (*R*)-**2** (blue lines) and (*S*)-**2** (green lines) dissolved in DMF ( $1.0 \times 10^{-4}$  M, pathlength: 2 mm).  $\lambda_{ex} = 340$  nm for **1** and 330 nm for **2**. Bandwidths for excitation/emission of highly luminescent **1** ( $\Phi_f \approx 0.59$ ) and inefficient luminescent **2** ( $\Phi_f \approx 0.01$ ) were 10 nm/10 nm in a computer controlled mode and 3000  $\mu$ m/3000  $\mu$ m in manual mode, respectively.

As expected, (*R*)-**1** and (*R*)-**2** revealed CPL signals on the order of  $|g_{em}| \approx (0.1-1.3) \times 10^{-3}$ , where the dimensionless Kuhn's anisotropy in the photoexcited state ( $g_{em}$ ) is defined as:  $g_{em} = 2(I_{L+} - I_{R+}) / (I_{L+} + I_{R+})$ , where  $I_{L+}$  and  $I_{R+}$  denote the quantum yields of the left-handed and right-handed CPL under excitation of unpolarized light, respectively. The CPL spectra of (*R*)-**1** and (*R*)-**2** in DMF are given as the blue lines of the upper panels in Fig. 2. Surprisingly, although (*R*)-**1** and (*R*)-**2** commonly possess the same axial chirality, their CPL signs are opposite; (*R*)-**1** is positive whereas (*R*)-**2** is negative. To verify whether these signs arise from unresolved artefacts, the CPL spectra of (*S*)-**1**

and (*S*)-**2** in DMF were acquired in a similar manner (Fig. 2, green lines).

The CPL spectra of (*R*)-**1** and (*S*)-**1** adopt nearly mirror images of each other. The CPL spectra in absolute magnitude of (*R*)-**2** and (*S*)-**2** are, however, slightly different, due to unresolved reasons. The  $|g_{em}|$  value was  $\approx 4.3 \times 10^{-4}$  at 415 nm for (*R*)-**1** and (*S*)-**1**. The  $|g_{em}|$  values of (*R*)-**2** and (*S*)-**2** are  $\approx 0.7 \times 10^{-3}$  (at 415 nm) and  $\approx 1.2 \times 10^{-3}$  (at 415 nm), respectively. These results led to an idea that the CPL sign, deriving from certain chirally reorganized geometry between two remote anthracene luminophores (chirality sergeants) under the 350-nm excitation, is controllable by the choice of open- or closed-style binaphthyl unit (chirality commander). The axial chirality of binaphthyl in the ground state is not the deterministic factor in controlling photoexcited chirality. *The sergeants may not always obey a left-right hand from the commander.* Obtaining a luminophore with the opposite chirality is often difficult. Thus, the choice of the open- or closed-style chiral-gen should offer a unique opportunity to control photoexcited chirality, proven by the sign inversion of CPL signals, without any use of the counterpart chirality. This idea may contribute to the design of more elaborate chiral molecular emitters.



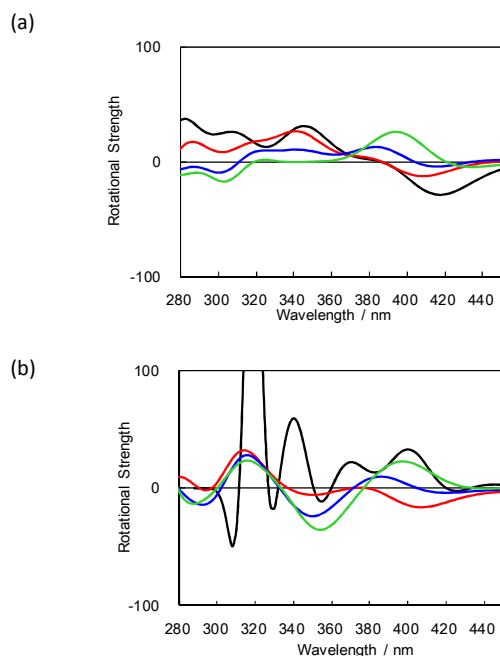
**Fig. 3** CD (upper panel) and UV-Vis absorption (lower panel) spectra of (a) (*R*)-**1** (blue lines) and (*S*)-**1** (green lines) and (b) (*R*)-**2** (blue lines) and (*S*)-**2** (green lines) in DMF ( $1.0 \times 10^{-4}$  M, pathlength: 2 mm).

For comparison, the ground-state chirality of **1** and **2** was verified by means of CD and unpolarized UV spectra in dilute

solution. CD and UV spectra of (*R*)-**1** and (*R*)-**2** in DMF were acquired as shown in Fig. 3 (indicated by blue lines).

(*R*)-**1** and (*R*)-**2** in DMF have several well-resolved CD bands in the range of 340 nm to 410 nm, arising from  $\pi$ - $\pi^*$  vibronic transitions (0-0, 0-1, 0-2, 0-3 and so on) of the two achiral anthracenes (Fig. 3). This suggests that the binaphthyl  $C_2$ -chirality efficiently transfers to the two achiral, but remote-positioned anthracene chromophores in the ground state. The CD band profiles between (*S*)-**1** and (*R*)-**1** displayed an ideal mirror image relationship. Similarly, the CD band profiles between (*S*)-**2** and (*R*)-**2** had nearly a mirror image relationship.

To quantitatively evaluate the absolute CD magnitude, we used the dimensionless Kuhn's anisotropy factor in the ground state, defined as  $g_{\text{abs}} = \Delta\epsilon/\epsilon$ . The  $|g_{\text{abs}}|$  values of **1** and **2** were  $\approx 1.1 \times 10^{-4}$  at 394 nm (the first Cotton band) and  $\approx 7.2 \times 10^{-4}$  at 391 nm (the first Cotton band), respectively. The  $|g_{\text{abs}}|$  value of **2** is enhanced by  $\approx 7$  times, relative to that of **1**. These  $|g_{\text{abs}}|$  values and their CD signs at the first Cotton band in the ground state, however, were not identical to the corresponding  $|g_{\text{em}}|$  values and their CPL signs in the photoexcited state. The  $|g_{\text{em}}|$  value of **1** is enhanced by  $\approx 4$  times compared to the corresponding  $|g_{\text{abs}}|$  value at the first Cotton band. The  $|g_{\text{em}}|$  value of (*R*)-**2** is almost identical to the corresponding  $|g_{\text{abs}}|$  value of (*R*)-**2** at the first Cotton band, while the  $|g_{\text{em}}|$  value of (*S*)-**2** is twice relative to the  $|g_{\text{abs}}|$  value of (*S*)-**2** at the first Cotton band.



**Fig. 4** Relationship between dihedral angles  $\theta_1$  ((O)C-C-C(O)) and  $\theta_2$  ((O)C-C-C) in binaphthyl and anthracene units and the CD spectra of (*R*)-**2**. (a)  $\theta_1 = -60^\circ$ , (b)  $\theta_1 = -120^\circ$ , black curve:  $\theta_2 = +60^\circ$ , red curve:  $\theta_2 = +80^\circ$ , blue curve:  $\theta_2 = +100^\circ$ , green curve:  $\theta_2 = +120^\circ$ .

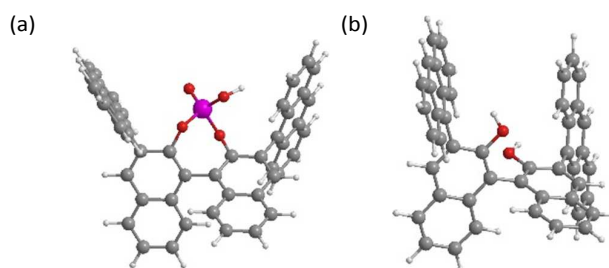
Actually, CPL signs of (*R*)-**1** and (*R*)-**2** in the photoexcited state are negative and positive, respectively, although their CD signs in the ground state are commonly negative. Evidently,

these results demonstrated that the ground state chirality and photoexcited state chirality are not solely determined by the binaphthyl chirality. Whether the open-type with C-C rotational freedom or the close-type with greatly restricted C-C rotational freedom might be critical structural factors to control ground and photoexcited chiralities. These results will bring a conceptually novel tandem molecular chromophore-luminophore system, offering hidden ground-state chirality. In other word,  $C_2$ -symmetrical binaphthyl moiety acts as non-luminescent chirality commander and two achiral luminescent anthracenes obey chirality sergeants, but do not always follow his/her hand in some case.

To theoretically clarify those differences in the CPL and CD characteristics of closed-style **1** and open-style **2**, the CD spectra of (*R*)-**2** were calculated as functions of two dihedral angles. Fig. 4 displays the calculated CD spectra of (*R*)-**2**. These spectra were simulated by varying the dihedral angle  $\theta_1$  ((O)C-C-C(O)) of the binaphthyl unit and  $\theta_2$  ((O)C-C-C) between anthracene and naphthalene of binaphthyl.

Evidently, the CD sign of (*R*)-**2** completely inverted when  $\theta_1$  altered.<sup>2c,3</sup> From a comparison between Fig. 4a ( $\theta_1 = -60^\circ$ ) and Fig. 4b ( $\theta_1 = -120^\circ$ ), this significant alteration of (*R*)-**2** might occur, depending on the ground- and photoexcited states. Moreover, these simulations indicate that the first Cotton CD sign of (*R*)-**2** is changeable by angle  $\theta_2$  between binaphthyl and anthracene ( $\theta_2 = 60^\circ$  for black curve,  $\theta_2 = 80^\circ$  for red curve,  $\theta_2 = 100^\circ$  for blue curve, and  $\theta_2 = 120^\circ$  for green curve), as given in Figs. 4a and 4b.

The theoretical equilibrium structures of **1**<sup>2c</sup> and **2** were shown in Fig. 5. (*R*)-**1** had  $\theta_1 = -56^\circ$  and  $\theta_2 = +98^\circ$  and  $+102^\circ$  (Fig. 5a), while (*R*)-**2** had  $\theta_1 = -59^\circ$  and  $\theta_2 = +77^\circ$  and  $+94^\circ$  (Fig. 5b). These equilibrium structures suggest that the first Cotton CD bands around  $\approx 400$  nm of (*R*)-**1** and (*R*)-**2** have commonly a negative sign.



**Fig. 5** Theoretically optimized structures of (a) (*R*)-**1** and (b) (*R*)-**2**.

Although chirally oriented conformations between anthracene and binaphthyl units of **1** and **2** in the ground state are very similar, their photoexcited-state chiralities might be very different, as proven by inversion in CPL signs whilst the same sign in the first Cotton CD bands is evident both experimentally and theoretically. These simulated CD spectra infer that sign inversion of CPL spectra between **1** and **2** originates from the considerable changes in  $\theta_1$  and  $\theta_2$  angles in the ground and photoexcited states.

At the moment, our theoretical explanation is qualitative and very speculative because no further consideration of

electron-phonon couplings in the ground and photoexcited states. In a previous paper, we showed dihedral angle dependent sign inversion in CD spectrum and redshift/blueshift in UV spectra of hypothetical binaphthyl moiety as a model of (R)-1.<sup>2c,3</sup> For comparison, the current simulation tells us of how two dihedral angles  $\theta_1$  and  $\theta_2$  significantly alter their CD spectra and wavelength dependent signs of (R)-2.

Previously, chiral  $\pi$ -conjugated molecular assemblies showed chiroptical (CD and CPL) inversion, that is significantly dependent on the nature of good non-polar (chloroform) or poorer non-polar (dichloroethane) solvents in the dark condition.<sup>1c</sup> In this case, CD sign at the first Cotton band (a longer wavelength edge) is identical to CPL sign at the first Cotton band (a shorter wavelength edge). The chiroptical properties may have *passive* function.

Aiming at designing more elaborate *active* function, e.g., photon-induced chirality in the photoexcited state, followed by spontaneous relaxation process to restore the ground-state chirality,<sup>4-7</sup> the choice of the opposite and/or same signs in the ground-state and photoexcited-state molecular chiralities can be exploited as advanced security systems for future global communication.<sup>4</sup> As prototype molecules,<sup>2-5</sup> the binaphthyl chirality transfer to achiral luminophores may offer unique enciphering and deciphering molecular coding and decoding system<sup>4</sup>: one is the positive-sign CD and negative-sign CPL signals from luminophores with the same chirality, whilst the other is the negative-sign CD and negative-sign CPL signals of luminophores with the same chirality. The present knowledge and understanding of our chiral tandem molecules should stimulate to design various sophisticated organic molecular systems, enabling physically and chemically controlled active and passive CPL functions in future.<sup>2,7</sup>

## Experimental

### General methods

Compounds (R)-1, (S)-1, (R)-2 and (S)-2 were purchased from Sigma-Aldrich Japan (Tokyo, Japan). Chloroform (CHCl<sub>3</sub>) and N,N-dimethylformamide (DMF) used for crystallisation and optical measurements was purchased from Wako Pure Chemical Industries (Osaka, Japan).

### Measurement of the CPL and photoluminescence spectra

Photoluminescence (PL) spectra and absolute PL quantum yields in DMF were obtained with an absolute PL quantum yield measurement system (Hamamatsu Photonics C9920-02, Hamamatsu, Japan) under air atmosphere at room temperature. The DMF solutions of (R)-1 and (R)-2 (1.0×10<sup>-4</sup> M, pathlength 10 mm) were excited at 350 nm.

The CPL and PL spectra in DMF solution were measured using a JASCO CPL-200 spectrofluoropolarimeter (Tokyo, Japan) at room temperature. The instrument used a scattering angle of 0° under excitation of unpolarised, monochromated incident light. DMF solutions of 1.0×10<sup>-4</sup> M were excited at 350 nm. Bandwidths for excitation and emission for the high

$\Phi_F$  (R)-1 and (S)-1 were 10 nm/10 nm, respectively. However, to obtain good S/N ratio CPL spectra, bandwidths for the (R)-2 and (S)-2 should be 3000  $\mu\text{m}$ /3000  $\mu\text{m}$ , respectively, due to the extremely low  $\Phi_F$  value. Pathlength was commonly 2.0 mm to keep 63–70% transmittance under the 350-nm excitation. Scanning speed for CPL/PL measurement was 50 nm min<sup>-1</sup> with time constant 8 sec of PMT during acquisitions of 4–8 times.

### Measurement of CD and UV-Vis absorption spectra

The circular dichroism (CD) and UV-Vis absorption spectra of (R)-1, (S)-1, (R)-2 and (S)-2 in DMF solution (1.0×10<sup>-4</sup> M) were measured using a JASCO J-820 spectropolarimeter at room temperature. The pathlength is 2 mm.

### Theoretical calculations

The geometry of (R)-2 was optimised using the hybrid density functional theory (B3LYP functional).<sup>8</sup> The excitation energies and rotational strengths of the geometry-optimised molecules were calculated using the time-dependent density functional theory (TD-DFT)<sup>9</sup> with the B3LYP functional. In all the calculations, the cc-pVDZ basis set was used.<sup>10</sup> The program Gaussian03<sup>11</sup> was used for quantum chemical calculations.

## Conclusions

We compared CD and CPL spectra of open- and close-types of chiral binaphthyl moieties linked to achiral anthracene luminophores in DMF. The CPL sign due to anthracene luminophores was efficiently controlled by the choice of open- or closed-style units with the scenario of binaphthyl chirality transfer to the achiral luminophores.

## Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research (No. 15K05489) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, a MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2014-2018, and the KDDI Foundation.

## Notes and references

- (a) J. Shinar, *Organic Light-Emitting Devices*, Springer, New York, Berlin, Heidelberg, 2004; (b) K. Müllen and U. Scherf, *Organic Light-Emitting Devices*, Wiley-VCH, Weinheim, 2006; (c) A. Satrijo, S. C. J. Meskers and T. M. Swager, *J. Am. Chem. Soc.* 2006, **128**, 9030-9031; (d) C. Jeanne and R. Regis, *Dalton Trans.* 2008, 6865-6876; (e) S. Kappaun, C. Slugovc and J. M. Emil, *Int. J. Mol. Sci.* 2008, **9**, 1527-1547; (f) G. Lakhwani, R. A. J. Janssen and S. C. J. Meskers, *J. Phys. Chem. A* 2009, **113**, 10891-10894; (g) K. Milan and O. Franc, *Acc. Chem. Res.* 2009, **42**, 235-248; (h) W.-Y. Wong and C.-L. Ho, *J. Mater. Chem.* 2009, **19**, 4457-4482; (i) M. Wolffs, N. Delsuc, D. Veldman, N. V. Anh, R. M. Williams, S. C. J. Meskers, R. A. J. Janssen, I. Huc and A. P. H. J. Schenning, *J. Am. Chem. Soc.*

- 2009, **131**, 4819-4829; (j) K.-L. Chan, P. Sonar and A. Sellenge, *J. Mater. Chem.* 2009, **19**, 9103-9120; (k) F. Laquai, Y.-S. Park, J.-J. Kim and T. Basche, *Macromol. Rapid Commun.* 2009, **30**, 1203-1231; (l) C. Wang, J. Zhang, K. Ryu, A. Badmaev, L. G. D. Arco and C. Zhou, *Nano Lett.* 2009, **9**, 4285-4291; (m) M.-K. Wei, C.-W. Lin, C.-C. Yang, Y.-W. Kiang, J.-H. Lee and H.-Y. Lin, *Int. J. Mol. Sci.* 2010, **11**, 1527-1545; (n) G. Duran-Sampedro, A. R. Agarrabeitia, I. Garcia-Moreno, L. Gartzia-Rivero, S. de la Moya, J. Bañuelos, I. López-Arbeloa and M. J. Ortiz, *Chem. Commun.* 2015, **51**, 11382-11385; and references cited therein.
- 2 (a) T. Kawai, K. Kawamura, H. Tsumatori, M. Ishikawa, M. Naito, M. Fujiki and T. Nakashima, *ChemPhysChem.* 2007, **8**, 1465-1468; (b) H. Tsumatori, T. Nakashima and T. Kawai, *Org. Lett.* 2010, **12**, 10, 2362-2365; (c) T. Amako, T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *Tetrahedron* 2013, **69**, 2753-2757; (d) T. Amako, T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *RSC Adv.* 2013, **3**, 6939-6944; (e) B. A. S. Jose, J. Yan and K. Akagi, *Angew. Chem. Int. Ed.* 2014, **53**, 10641-10644; (f) E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, B. G. Vo, G. Muller and S. de la Moya, *J. Am. Chem. Soc.* 2014, **136**, 3346-3349; (g) J. Kumar, T. Nakashima, H. Tsumatori and T. Kawai, *J. Phys Chem. Lett.* 2014, **5**, 316-321; (h) Y. Kitayama, T. Amako, N. Suzuki, M. Fujiki and Y. Imai, *Org. Biomol. Chem.* 2014, **12**, 4342-4346; (i) Y. Kitayama, K. Nakabayashi, T. Wakabayashi, N. Tajima, M. Fujiki and Y. Imai, *RSC Adv.* 2015, **5**, 410-415; (j) T. Amako, K. Nakabayashi, A. Sudo, M. Fujiki and Y. Imai, *Org. Biomol. Chem.* 2015, **13**, 2913-2917; (k) Y. Kono, K. Nakabayashi, S. Kitamura, R. Kuroda, M. Fujiki and Y. Imai, *Tetrahedron* 2015, **71**, 3985-3989.
- 3 (a) T. Kinuta, N. Tajima, M. Fujiki, M. Miyazawa and Y. Imai, *Tetrahedron* 2012, **68**, 4791-4796; (b) T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *Chem. Asian J.* 2012, **7**, 2836-2841.
- 4 T. Amako, K. Nakabayashi, N. Suzuki, S. Guo, N. A. A. Rahim, T. Harada, M. Fujiki and Y. Imai, *Chem. Commun.* 2015, **51**, 8237-8240.
- 5 N. Taniguchi, K. Nakabayashi, T. Harada, N. Tajima, M. Shizuma, M. Fujiki and Y. Imai, *Chem. Lett.* 2015, **44**, 598-600.
- 6 M. Fujiki, Y. Donguri, Y. Zhao, A. Nakao, N. Suzuki, K. Yoshida and W. Zhang, *Polym. Chem.* 2015, **6**, 1627-1638.
- 7 For a recent review, see. E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz and S. de la Moya, *Chem. Eur. J.*, 2015 (DOI:10.1002/chem.201501178).
- 8 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652.
- 9 M. E. Casida, *Recent Advances in Density Functional Methods*, Vol 1, D. P. Chong (ed), World Scientific, Singapore, 1995.
- 10 (a) T. H. Dunning, Jr. *J. Chem. Phys.* 1989, **90**, 1007-1023; (b) D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* 1993, **98**, 1358-1371.
- 11 GAUSSIAN03, Rev.C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L.
- Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford, CT, 2004.