Chiral exciplex dyes showing circularly polarized luminescence: extension of the excimer chirality rule†

Kazuto Takaishi,* Sho Murakami, Kazuhiro Iwachido and Tadashi Ema*†

A series of axially chiral binaphthyls and quaternaphthyls possessing two kinds of aromatic fluorophores, such as pyrenyl, perylenyl, and 4-(dimethylamino)phenyl groups, arranged alternately were synthesized by a divergent method. In the excited state, the fluorophores selectively formed a unidirectionally twisted exciplex (excited heterodimer) by a cumulative steric effect and exhibited circularly polarized luminescence (CPL). They are the first examples of a monomolecular exciplex CPL dye. This versatile method for producing exciplex CPL dyes also improved fluorescence intensity, and the CPL properties were not very sensitive to the solvent or to the temperature owing to the conformationally rigid exciplex. This systematic study allowed us to confirm that the excimer chirality rule can be applied to the exciplex dyes: left- and right-handed exciplexes with a twist angle of less than 90° exhibit (−)- and (+)-CPL, respectively.

Introduction

Circularly polarized luminescence (CPL) organic dyes are recognized to be next-generation materials,1 and their development has been a recent focus of research.2 To develop CPL dyes, connecting two of the same aromatic lumino-phores, which can form an excimer (excited homodimer), to a chiral unit is one of the main approaches because these lumino-phores often emit with high quantum yields and large Stokes shifts. For example, CPL-active pyrene,3,4 perylene,4,5 anthracene,6 carbazole,7 and naphthalimide8,9,8 excimers have been reported. In contrast, exciplex (excited heterodimer) CPL dyes are still rare, although exciplex fluorescence (FL) dyes are often used in the field of materials and biological sciences.9 Exciplex CPL dyes will widen the range of application significantly due to the infinite number of combinations of two lumino-phores. Exciplex CPL dyes will widen the range of application significantly due to the infinite number of combinations of two lumino-phores; CPL dyes having desired absorption and emission wavelength ranges can be provided by the combination of different lumino-phores. In addition, information obtained from simple exciplex CPL dyes may be useful for the investigation of the conformation of complex (supra)molecules in the excited state. Yamaguchi–Meijer group has recently reported supramolecular aggregates including 0-bridged triphenyl-borane and triphenylamine moieties as the sole example of an exciplex CPL dye, although the aggregation requires a specific temperature and solvent, and the fluorophore versatility is unknown.10 A new and versatile method for creating exciplex CPL dyes that are not affected by conditions is needed. Rigid and monomolecular chiral dyes are expected to reach this goal.

In the past decade, several axially chiral binaphthyl-based CPL dyes have been reported, demonstrating that the binaphthyl is one of the most suitable skeletons for the development of CPL dyes.11 We have also developed several axially chiral CPL dyes.12 Among them, tetrapyrenyl-appended binaphthyl (R)-1 displayed pyrene-excimer CPL with a $\delta_{\text{lim}}$ value13 of +1.3 $\times$ 10$^{-2}$ and a typical FL quantum yield ($\Phi_{\text{F}}$) of 0.24 (Fig. 1a).14 The quaternaphthyl analogs showed slightly greater CPL performance.15 The CPL was based on the locally chiral intramolecular excimer, which allowed us to discover the excimer chirality rule: left- and right-handed twisted excimers exhibit (−)- and (+)-CPL, respectively. We postulated that the binaphthyl- and quaternaphthyl-based strategy might be applied to creating exciplex CPL dyes. Herein, we synthesized binaphthyls (R)-2–6 and quaternaphthyl (R,R,R)-7 possessing two kinds of well-known fluorophores alternately arranged, such as pyrenyl, perylenyl, and 4-(dimethylamino)phenyl groups,9 as the first examples of monomolecular exciplex CPL dyes in addition to CPL-active pyrene–perylenyl and pyrene–4-(dimethylamino)phenyl exciplexes (Fig. 1b). The experimental and computational studies gave us an extended rule, named the exciplex chirality rule: left- and right-handed exciplexes exhibit (−)- and (+)-CPL, respectively.
Results and discussion

Synthesis of 2–7

The synthetic routes to (R)-2 and (R,R,R)-7 are shown in Scheme 1. The condensation of bis-MOM-protected binaphthyl-tetraol (R)-8 (ref. 14) with 1-pyrenecarboxylic acid (9) gave di-pyrenyl-appended binaphthyl (R)-10. Subsequent deprotection and condensation with 3-perylenecarboxylic acid (11) afforded (R)-2 in moderate yield. Similarly, condensation of quaternaphthyl-diol (R,R,R)-12 (ref. 12b) with 11 gave (R,R,R)-13, and then deprotection and condensation with 9 afforded (R,R,R)-7. Compounds (R)-3–6 were prepared by a similar method using common intermediates (Schemes S1 and S2†).

Absorption and fluorescence properties of 2–7 and reference compounds

We next analyzed the optical properties of 2–7 (Fig. 2 and S7†). These absorption spectral shapes comprised the sum of the fluorophores16 and the binaphthyl or quaternaphthyl spectra,16,17 suggesting that in the ground state, each fluorophore is electronically isolated (Fig. 2b). The binaphthyl and quaternaphthyl skeletons absorbed light below the 350 nm wavelength; therefore, the strong CD signals with the $\Delta \varepsilon$ of over 25 were detected at around 450 nm, which indicates that the fluorophores are located in asymmetric environments (Fig. 2a). A binaphthyl (R)-17 possessing only two perylene rings, a reference compound, showed almost the same CD signals as those of (R)-2–4 (Fig. 2a and S6†), which indicates that the CD signals of...
(R)-2–4 at around 450 nm were mainly derived from the exciton coupling between the perylene rings ($g_{\text{abs}}$ = ca. –8.0 $\times$ 10$^{-3}$).

The FL spectra of 2–7 are shown in Fig. 2d. All the FL were identical with those of the typical exciplexes with the $\lambda_{\text{ex,max}}$ of ca. 530 nm. The $\Phi_\ell$ values were 0.16–0.99, which are unexpectedly high for exciplexes, probably because the movement and vibration were suppressed by the contiguous four or six large fluorophores (Table 1). For example, the $\Phi_\ell$ of 2 (0.83), 3 (0.95), 4 (0.99), 5 (0.63), and 6 (0.16) were equal or higher than those of the corresponding half model compounds 2’ (0.53), 3’ (0.92), 4’ (0.99), 5’ (0.51), and 6’ (0.06), respectively (Fig. S2†). To gain a deeper insight into excited-state characteristics, FL spectra of reference compounds, 3-methyl perylenecarboxylate (14) and two fluorophore-appended naphthalenes and binaphthyls 2 and 15–17 were measured and compared with the spectra of 2 and 7 (Fig. 3 and S3†). The FL of 14, 2’, and 15 can be regarded as perylene-monomer, pyrene–perylenexciplex, and perylene-excimer FL, respectively. The FL of 2 and 7 completely coincided with that of 2’, which indicates that the FL spectra of 2 and 7 are classified as exciplex FL that is completely free from the monomer and excimer FL. The fluorescence lifetimes of (R)-2 (16.3 ns) and (R)-6 (25.0 ns) were close to the reported lifetimes of pyrene–perylenexciplexes and pyrene–4-(dimethylamino)phenyl exciplexes, respectively. In addition, we measured the excitation spectra of (R)-2 and (R)-6, and the signals appeared in the absorption region of pyrene and perylene rings for (R)-2 and that of a pyrene ring and a 4-(dimethylamino)phenyl group for (R)-6 (Fig. S5†). These results support our assignment that they are exciplex fluorescence. In contrast, binaphthyl 16 exhibited the only perylene-monomer FL, which suggested that the two fluorophores located across the axis could not form an exciplex and that the energy transfer from the pyrene ring to the perylene ring was very fast. Binaphthyl 17 also exhibited the monomer FL without forming an excimer. These results clearly indicate that only a pair of fluorophores on the same naphthalene ring can form an exciplex efficiently and selectively. Quaternaphthyl 7 exhibited only exciplex FL due to the fast energy transfer from the outer pyrene rings to the inner pyrene rings.

### Table 1 Luminescence and conformational properties of 2–7

| Compd       | $\Phi_\ell$ | Experimental $g_{\text{lum}}$ ($10^{-3}$) | Theoretical $g_{\text{lum}}$ ($10^{-3}$) | Twist of exciplex |
|-------------|------------|----------------------------------------|-----------------------------------------|------------------|
| (R)-2       | 0.83       | +1.0                                   | +0.49                                   | Right-handed     |
| (R)-3       | 0.95       | –1.6                                   | –0.91                                   | Left-handed      |
| (R)-4       | 0.99       | –2.7                                   | –0.93                                   | Left-handed      |
| (R)-5       | 0.63       | –1.1                                   | –2.7                                    | Left-handed      |
| (R)-6       | 0.16       | –1.8                                   | –3.6                                    | Left-handed      |
| (R,R,R)-7   | 0.89       | +1.3                                   | +0.32                                   | Right-handed     |

*Conditions: CH$_2$Cl$_2$, 10 $\times$ 10$^{-5}$ M for 2–6 and 6.7 $\times$ 10$^{-6}$ M for 7, 20 °C, $l$ = 1 cm. Absolute fluorescence quantum yield. TD DFT calculations were carried out at the CAM-B3LYP/6-31G(d,p) level.

### CPL properties

To our delight, compounds 2–7 displayed clear CPL with $g_{\text{lum}}$ values between 1.0 $\times$ 10$^{-3}$ and 2.7 $\times$ 10$^{-3}$ (Fig. 2c and Table 1). This result suggests that the binaphthyl-based strategy is a versatile method for providing exciplex CPL dyes. Interestingly, compounds (R)-2 and (R,R,R)-7 exhibited (+)-CPL and (R)-3–6 exhibited (−)-CPL, as the variation in the CPL sign has previously been observed for excimer CPL dyes (vide infra). Among compounds 2–7, compound 4 exhibited the highest $g_{\text{lum}}$ value (2.7 $\times$ 10$^{-3}$) in addition to the $\Phi_\ell$ value (0.99). The CPL properties were not very sensitive to the solvent or to the temperature (10 to 90 °C) owing to the conformationally rigid exciplex, which is one of the main advantages of monomolecular dyes (Fig. 4). Both the $g_{\text{lum}}$ and $\Phi_\ell$ values of quaternaphthyl 7 ($g_{\text{lum}}$ of 1.3 $\times$ 10$^{-3}$ and $\Phi_\ell$ of 0.89) were slightly higher than those of corresponding binaphthyl 2 ($g_{\text{lum}}$ of 1.0 $\times$ 10$^{-3}$).

![Fig. 3 FL properties of reference compounds 2′ and 14–17. The $\lambda_{\text{ex,max}}$ values are given in parentheses.](image)

![Fig. 4 (a) CPL spectra of (R)-4 in various solutions at 20 °C and (b) VT CPL spectra of (R)-4 in toluene. Conditions: 1.0 $\times$ 10$^{-5}$ M, $l$ = 1 cm, $\lambda_{\text{ex}}$ = 355 nm.](image)
structure, which is reminiscent of the sergeants-and-soldiers
steric and dipole repulsions lead to the conformationally rigid
from each other via dipole repulsions, (2) adjacent
groups are oriented in the opposite directions due to steric and
induced by the following mechanisms, (1) adjacent carbonyl
groups was metastable conformers, in which the direction of one or more
perhaps due to the steric repulsion (Fig. 5a and c). Other
metastable conformers, in which the direction of one or more
carbonyl groups was flipped from the most stable structures,
were significantly unstable (ΔE of 2.5–7.0 kcal mol⁻¹ for 2 and
2.8–5.4 kcal mol⁻¹ for 3, Fig. S11 and S12†). These characteristics were also seen in 4 (2.9–5.9 kcal mol⁻¹), 5 (1.5–
5.4 kcal mol⁻¹), 6 (1.5–5.6 kcal mol⁻¹), and 7 (4.1–
19.4 kcal mol⁻¹) (Fig. S13–S16†), suggesting that the most stable
structures are conformationally-rigid. The especially large ΔE
values of 7 support that higher rigidity leads to a higher |g_lum|
value. In contrast, the ΔE value of two conformers of naphtha-
lene 2’, whose carbonyl groups were oriented in the same and
opposite directions, was small (0.8 kcal mol⁻¹, Fig. S17†). These results suggest that the local chirality of fluorophores in 2–7 are
induced by the following mechanisms, (1) adjacent carbonyl
groups are oriented in the opposite directions due to steric and
dipole repulsions, (2) adjacent fluorophores are directed away
from each other via steric repulsion, and (3) the cumulative
steric and dipole repulsions lead to the conformationally rigid
structure, which is reminiscent of the sergeants-and-soldiers
effect.† Prior to analyzing the excited-state structures directly
concerned with CPL properties, the orientations of the lowest
energy transition dipole moment of each fluorophore moiety
were theoretically determined using the corresponding methyl
esters (Fig. S8†). The ester group affected the alignment of the
transition moment slightly, and therefore this tilt was used in
the following analyses. The excited-state structures of 2 and 3
were optimized, and the pyrene–perylene exciplexes were surely
obtained (Fig. 5b and d). It is noteworthy that the exciplex
moieties of 2 and 3 adopted a right- and left-handed chirality,
respectively. Theoretical CPL signs of the exciplexes are (+) for 2
and (−) for 3, which are identical with the experimental signs
(Table 1). This relationship between the twist direction and CPL
sign was also found to be applicable to 4–7. These results
allowed us to find an empirical rule named the exciplex chirality
rule: left- and right-handed exciplexes exhibit (−)- and (+)-CPL,
respectively (Fig. 1b). That is, importantly, the excimer chirality
rule can be extended to exciplexes.
relationship between the twist angle and CPL sign of exciplexes

Finally, we investigated the relationship between the CPL sign and the twist pattern/angle of exciplexes in more detail. The sign of CPL of the model exciplex consisting of 1-methyl pyrene-2-carboxylate and 3-methyl pyrene-2-carboxylate was calculated for every 15° change in the twist angle (Fig. 6a and Table S1†). As a result, interestingly, the sign was clearly inverted every 90°: (−)-CPL for 0–90° and 180–270° and (−)-CPL for 90–180° and 270–360°. The model pyrene–pyrene exciplex regioisomers and pyrene–4-(dimethylamino)phenyl exciplex showed almost the same tendency (Tables S3–S6†). Moreover, an unsubstituted pyrene–pyrene exciplex had the same result, which indicates generality (Fig. 6b and Table S2†).

Conclusions

We have developed CPL-active pyrene–pyrene and pyrene–4-(dimethylamino)phenyl exciplexes using the axially chiral binaphthyl or quaternaphthyl skeletons as the first example of a monomolecular exciplex CPL dye. The CPL were insensitive to conditions such as solvent and temperature. The method improved FL intensity as a bonus. We found that the left- and right-handed exciplexes with a twisted narrow angle exhibited (−)- and (−)-CPL, respectively. CPL based on this relationship may be a powerful tool for the determination of absolute configurations and conformations of multiple aromatics in the excited state. CPL-active exciplexes will enable new applications and promote chiroptical sciences. Development of other exciplex CPL dyes using this method is being studied in our laboratory.

Data availability

All experimental supporting data and procedures are available in the ESI†.

Notes and references

1 For applications of CPL dyes: (a) C. Wagenknecht, C.-M. Li, A. Reingruber, X.-H. Bao, A. Goebel, Y.-A. Chen, Q. Zhang, K. Chen and J.-W. Pan, Nat. Photonics, 2010, 4, 549–552; (b) R. Carr, N. H. Evans and D. Parker, Chem. Soc. Rev., 2012, 41, 7673–7686; (c) R. Singh, K. N. N. Unni, A. Solanki and Deepak, Opt. Mater., 2012, 34, 716–723; (d) M. C. Heffern, L. M. Matosziuk and T. J. Meade, Chem. Rev., 2014, 114, 4496–4539; (e) A. T. Frawley, H. V. Linford, M. Starck, R. Pal and D. Parker, Chem. Sci., 2018, 9, 1042–1049; (f) M. Li, S.-H. Li, D. Zhang, M. Cai, L. Duan, M.-K. Fung and C.-F. Chen, Angew. Chem., Int. Ed., 2018, 57, 2889–2893; (g) D.-W. Zhang, M. Li and C.-F. Chen, Chem. Soc. Rev., 2020, 49, 1331–1343; (h) Z. Jiang, J. Wang, T. Gao, J. Ma, Z. Lü and R. Chen, ACS Appl. Mater. Interfaces, 2020, 12, 9520–9527; (i) G. Albanò, G. Pescitelli and L. Di Bari, Chem. Rev., 2020, 120, 10145–10243; (j) Z.-L. Tu, Z.-P. Yan, X. Liang, L. Chen, Z.-G. Wu, Y. Wang, Y.-X. Zheng, J.-L. Zuo and Y. Pan, Adv. Sci., 2020, 7, 2000804; (k) E. MacKenzie and R. Pal, Nat. Chem. Rev., 2021, 5, 109–124; (l) K. Dhabiba, L. Abella, S. Meunier-Della-Gatta, T. Roisnel, N. Vanuythe, B. Jamoussi, G. Pieters, B. Racine, E. Quesnel, J. Autschbach, J. Crassous and L. Favereau, Chem. Sci., 2021, 12, 5522–5533.

Acknowledgements

This work was supported by JSPS KAKENHI Grant No. 21K05022, the Kyoto Technoscience Center, the Okayama Foundation for Science and Technology, and the Konica Minolta Science and Technology Foundation. The computations were performed using RCCS, Okazaki, Japan.
For selected examples: (a) H. Maeda, Y. Bando, K. Simonura, I. Yamada, M. Naito, H. Tsumatorii and T. Kawai, *J. Am. Chem. Soc.*, 2011, **133**, 9266–9269; (b) H. Langhals, A. Hofer, S. Bernhard, J. S. Siegel and P. Mayer, *J. Org. Chem.*, 2011, **76**, 990–992; (c) E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A. R. Agarabetea, M. J. Ortíz, B. G. Vo, G. Muller and S. de la Moya, *J. Am. Chem. Soc.*, 2014, **136**, 3346–3349; (d) C. Katakami, S. Kanno, A. Torii, N. Hara, Y. Imai, T. Taniguchi, K. Monde, Y. Okabayashi, T. Hosokai, K. Kuramochi and K. Tsubaki, *J. Org. Chem.*, 2018, **83**, 14610–14616; (e) X. Yang, J. Han, Y. Wang and P. Duan, *Chem. Sci.*, 2019, **10**, 172–178; (f) Z.-B. Sun, J.-K. Liu, D.-F. Yuan, Z.-H. Zhao, X.-Z. Zhu, D.-H. Liu, Q. Peng and C.-H. Zhao, *Angew. Chem., Int. Ed.*, 2019, **58**, 4840–4846; (g) R. Takishima, Y. Nishii and M. Miura, *Org. Lett.*, 2021, **23**, 1349–1354; (h) Y. Nojima, M. Hasegawa, N. Hara, Y. Imai and Y. Mazaki, *Chem.–Eur. J.*, 2021, **27**, 5923–5929; (i) J. Hong, S. Kim, G. Park, Y. Lee, H. Kim, S. Kim, T.-W. Lee, C. Kim and Y. You, *Chem. Sci.*, 2021, **12**, 8668–8681.

For selected papers: (a) K. Takashi, M. Yasui and T. Ema, *J. Am. Chem. Soc.*, 2018, **140**, 5334–5338; (b) K. Takashi, S. Hinoide, T. Matsumoto and T. Ema, *J. Am. Chem. Soc.*, 2019, **141**, 11852–11857; (c) K. Takashi, K. Iwachido and T. Ema, *J. Am. Chem. Soc.*, 2020, **142**, 1774–1779; (d) K. Takashi, T. Matsumoto, M. Kawataka and T. Ema, *Angew. Chem., Int. Ed.*, 2021, **60**, 9968–9972.

The disssymmetry factor $g_{\text{fum}}$ is defined as $2(I_L – I_R)/(I_L + I_R)$; $I_L$ and $I_R$ represent the intensity of the left and right CPL, respectively.

A Yanagisawa, T. Satou, A. Izumiseki, Y. Tanaka, M. Miyagi, T. Arai, K. Yoshida, S. T. Chau, J. P. Lutz, K. Wu and A. G. Doyle, *Chem.–Eur. J.*, 2009, **15**, 11450–11453.

H NMR signals of some compounds were probably due to the slow movement of the contiguous large fluorophores. The purities of these compounds were confirmed by recycle HPLC analysis (Fig. S1†).

(a) C.-H. Zhang, Z.-B. Chen and Y.-B. Jiang, *Spectrochim. Acta, Part A*, 2004, **60**, 2729–2732; (b) M. Aleksić and J. R. Heldt, *J. Lumin.*, 2007, **126**, 665–676.

K Tsubaki, H. Tanaka, K. Takashi, M. Miura, H. Morikawa, T. Furuta, K. Tanaka, K. Fuji, T. Sasamori, N. Tokitoh and T. Kawabata, *J. Org. Chem.*, 2006, **71**, 6579–6587.

(a) C. D. Borsarelli, J. J. Costa and C. M. Previtali, *Langmuir*, 1993, **9**, 2895–2901; (b) H. Kashida, M. Komiyama and H. Asamura, *Chem. Lett.*, 2006, **35**, 934–935; (c) J. N. Wilson, J. Gao and E. T. Kool, *Tetrahedron*, 2007, **63**, 3427–3433; (d) J. Chiba, S. Takeshima, K. Mishima, H. Maeda, Y. Nanai, K. Mizuno and M. Inouye, *Chem.–Eur. J.*, 2007, **13**, 8124–8130.

(5)-2 and (R)-2 showed clear mirror images, which indicate that the effects of linearly polarized emission could be ignored (Fig. S4†).

Mori group has proposed a related quantity value named circular polarization luminosity index, $A_{\text{CPL}}$, which is defined as $f \times g_\text{fum}/2$: Y. Nagata and T. Mori, *Front. Chem.*, 2020, **8**, 448.
21 DFT calculations were performed using Gaussian16, revision C.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2019, for the full citations, see ESI†

22 A. G. Crawford, A. D. Dwyer, Z. Liu, A. Steffen, A. Beeby, L.-O. Pålsson, D. J. Tozer and T. B. Marder, J. Am. Chem. Soc., 2011, 133, 13349–13362.

23 M. M. Green, M. P. Reidy, R. J. Johnson, G. Darling, D. J. O’Leary and G. Wilsin, J. Am. Chem. Soc., 1989, 111, 6452–6454.

24 The CPL sign of the exciplex including 4-methyl pyrene carboxylate with a $\theta$ of 225–255° was minus, possibly because the transition dipole moment deviates from the long axis of the pyrene ring due to the ester group attached on an orthogonal side (Fig. S8†).