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Chiroptical and catalytic properties of doubly binaphthyl-strapped chiral porphyrins*

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Doubly (*R*)-binaphthyl-strapped porphyrins with methylene chains were synthesized. The CD spectra showed the positive Cotton effect around the Soret bands, and several porphyrins showed CPL. In addition, we found that the chiral porphyrins were applicable to kinetic resolution of epoxide with CO_2 .

Distorted aromatic π -systems have emerged as an attractive topic because of their unique electronic states and novel functions that are not seen in planar π -molecules.¹ Strapped porphyrins were synthesized to investigate and control the porphyrin π -system, molecular recognition, and catalysis.^{2,3} Particularly, the introduction of chirality to porphyrins gave rise to fascinating properties,⁴ and several chiral strapped porphyrins were used to study their chiroptical properties and asymmetric catalytic properties. Among them, some strap bridges deform the porphyrin plane.^{2g,i,j,3g}

Recently, circularly polarized luminescence (CPL) materials have been extensively studied.⁵ Helicenes, binaphthyl derivatives, and twisted molecules have been reported to show CPL.^{6–8} Although chiral strapped porphyrins would serve as potential CPL materials, CPL of chiral porphyrins have been scarcely reported.⁹ As another recent interesting research topic, carbon dioxide (CO₂) fixation has been actively explored.¹⁰ Synthesis of cyclic carbonates from epoxides and CO₂ is one of the most efficient CO₂ fixation method, and several metalloporphyrins have been used as catalysts for the reaction.^{11–13} This reaction is applicable for the kinetic resolution of chiral epoxides using metal catalysts and organocatalysts.^{14–16}

In this work, we synthesized doubly-binaphthyl strapped chiral porphyrins 1 with methylene chains and their zinc complexes 2 (Scheme 1). The effect of the methylene chain length on the distortion of the porphyrin plane and on the chiroptical properties including CPL was investigated. In addition, the Zn(n) complexes

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were used as catalysts for the kinetic resolution of styrene oxide with CO_2 . Herein, we report the chiroptical properties and catalytic behaviors of the strapped porphyrins.

Synthetic routes to strapped porphyrins 1 and 2 are shown in Scheme 1. First, we attempted to synthesize dialdehyde 6d by the reaction of 3-(6-bromohexyloxy)benzaldehyde (3d) with (R)-BINOL. However, 6d was not obtained reproducibly. Therefore, the formyl group of 3d was once protected, and the resulting 4d was reacted with (R)-BINOL to provide 5d, which was converted into 6d and obtained in an acceptable yield by the deprotection. Next, we performed the acid-catalyzed condensation of 6d with 2 equiv. of pyrrole, which provided structural isomer 8d as a major product instead of 1d. To obtain 1d selectively, the production of 8d needed to be suppressed. Therefore, we prepared bis(dipyrromethane) 7d by treatment of 6d with excess pyrrole. The acid-catalyzed condensation of 6d and 7d selectively produced 1d with 3.7% yield. Zinc complex 2d was obtained by the reaction of 1d with Zn(OAc)₂. 1a-c and 2a-c with different methylene chain lengths were also obtained in a similar manner. Single crystals of 1d suitable for X-ray diffraction analysis were obtained via vapor diffusion of acetonitrile into a CH₂Cl₂ solution of 1d. X-ray diffraction analysis unambiguously revealed the structure of 1d (Fig. 1).[‡] Side view indicated the distorted structure, and the mean plane deviation (MPD) of the porphyrin plane was calculated to be 0.119 Å. Structural isomers 8a–d and 9a–d were also prepared for comparison.

The ¹H NMR spectra of these porphyrins exhibited down field shifts for the inner NH protons (0.01 ppm, -1.41 ppm, -1.54 ppm, and -1.92 ppm for **1a**, **1b**, **1c**, and **1d**, respectively) as compared to those of tetraphenylporphyrin (TPP) (-2.8 ppm). The ring current effect of **1a–d** was probably weakened by the distortion of the porphyrin planes. Indeed, the MPDs of the porphyrin plane of the DFT-optimized structures were calculated to be 0.301 Å, 0.241 Å, 0.170 Å, and 0.119 Å, and the calculated strain energy based on TPP were 12.5 kcal mol⁻¹, 8.1 kcal mol⁻¹, 5.1 kcal mol⁻¹, and 3.7 kcal mol⁻¹ for **1a**, **1b**, **1c**, and **1d**, respectively (ESI†).¹⁷ The strain energies for the corresponding Zn(II) porphyrins **2a**, **2b**, **2c**, and **2d** were estimated to be 12.4 kcal mol⁻¹,

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Scheme 1 Synthesis of doubly binaphthyl-strapped porphyrins 1, 2, 8, and 9.



Fig. 1 X-ray crystal structure of 1d. Hydrogen atoms except for NH protons are omitted for clarity. Side view of the tetraphenylporphyrin moiety is shown. Thermal ellipsoids are at the 30% probability level.

8.1 kcal mol⁻¹, 4.9 kcal mol⁻¹, and 3.7 kcal mol⁻¹, respectively. The nucleus independent chemical shift (NICS) values were calculated to be -12.8, -13.9, -13.7, -13.3, and -14.4 at the central positions of **1a**, **1b**, **1c**, **1d**, and TPP, respectively, suggesting weakened aromaticity of **1a–d**, which is consistent with the results of NMR. The effect of distortion was also observed in the photophysical properties as shown below.



Fig. 2 (a) UV/vis absorption (left) and fluorescence (right) spectra of **1a-d** in 1,4-dioxane. (b) CD spectra (left) of **1a-d** and CPL spectra (right) of **1b-d** in 1,4-dioxane.

The UV/vis absorption and fluorescence spectra of 1 and 2 are shown in Fig. 2a, and the data are summarized with TPP and ZnTPP in Table 1. The absorption spectra of 1 showed bands at ca. 230 nm derived from binaphthyl moieties, and 420 nm and 500-650 nm as Soret and O-bands, respectively. The absorption maxima of the free-base porphyrins increased in the order: TPP < 1d < 1c < 1b < 1a. The fluorescence maxima also increased in the same order, while the fluorescent quantum yields decreased with a decrease in the methylene chain length. In particular, the molar absorption coefficient of 1a is low probably because of the weak aromaticity and/or the strong intramolecular interaction between the binaphthyl and porphyrin moieties. Zinc complexes 2a-d also showed red-shifted bands as the methylene chain length decreased. On the other hand, 8a-d or 9a-d gave almost unchanged spectra as compared with TPP or ZnTPP, regardless of the length of the methylene chain (ESI⁺).

The CD spectra of **1a-d** are shown in Fig. 2b. Notably, positive Cotton effects were observed in the porphyrin Soret region (420–450 nm), suggesting induced CD effect.¹⁸ Interestingly, the

Table 1	1 Photophysical data in 1,4-dioxane			
Compd	λ_{Soret} (nm)	$\lambda_{\rm Q} (\rm nm)$	λ_{F}^{a} (nm)	${\Phi_{ m F}}^b$
1a	430	529, 568, 601, 654	663, 724	0.030
1b	423	520, 555, 595, 648	655, 717	0.053
1c	422	518, 553, 593, 647	650, 715	0.066
1d	420	515, 550, 590, 645	649, 714	0.066
TPP	416	513, 547, 591, 648	647, 713	0.088
2a	439	573, 618	623	0.011
2b	430	562, 603	612, 660	0.026
2 c	428	559, 596	608, 655	0.026
2d	426	555, 594	602, 651	0.023
ZnTPP	423	555, 594	601, 605	0.028

^{*a*} Excited at λ_{Soret} . ^{*b*} Absolute fluorescence quantum yields.

Table 2 Kinetic resolution of styrene oxide with CO₂^a



^{*a*} Reaction conditions: styrene oxide (0.3 mmol), Zn(II) porphyrin (0.05 mol%), TBAB (0.1 mol%), CO₂ (1.7 MPa) in a 30 mL autoclave. ^{*b*} Conversion calculated from c = ee(10)/(ee(10) + ee(11)). ^{*c*} Isolated yield. ^{*d*} Determined by HPLC or GC analyses. ^{*e*} Calculated from s = ln[1 - c(1 + ee(11))]/ln[1 - c(1 - ee(11))]. ^{*f*} Reaction conditions: 2c (0.5 mol%), TBAB (1 mol%), 6 h.

 $\Delta \epsilon$ values at λ_{Soret} increased in the order: $\mathbf{1d} < \mathbf{1c} \approx \mathbf{1b} < \mathbf{1a}$. TD-DFT calculations indicated that the CD intensity increased with increasing distortion. $\mathbf{2a-d}$ also showed CD signals in the Soret region (ESI†), which implies that there was a chiral space around the porphyrin planes and that these Zn(π) porphyrins may be applicable to asymmetric reactions. On the other hand, **8a-d** and **9a-d** showed no appreciable CD signals in the Soret and Q regions.

Since these chiral porphyrins showed fluorescence, we measured CPL. Fortunately, **1b–d** showed CPL in the region where fluorescence was observed (Fig. 2b). The Kuhn's anisotropy factors (g_{lum}) were -6.8×10^{-4} , -8.8×10^{-4} , and -5.4×10^{-4} , for **1b**, **1c**, and **1d**, respectively.¹⁹ In contrast, CPL of **1a** was not observed. Other porphyrins showed no detectable CPL signals.

Finally, we used Zn(II) porphyrins **2a–d** and **9a–d** as chiral catalysts for the kinetic resolution of styrene oxide (**10**) with CO₂. **10** was heated at 50 °C in the presence of 0.05 mol% of each Zn porphyrin with TBAB (0.1 mol%) under CO₂ (1.7 MPa) for 24 h (Table 2). Products **10** and **11** were isolated, and their enantiomeric excesses were analysed. **2a–d** showed the *s* values of 1.2–2.7, while **9a–d** showed no enantioselectivity at all (ESI†). In addition, singly-strapped porphyrins **12** and **13** were synthesized, and Zn(II) complex **13** was used as a reference catalyst (Scheme 2). **13** recorded an *s* value of only 1.1, which indicates the importance of the double straps (entries 3 and 5). Since **2c** showed the highest *s* value, the reaction conditions were optimized, and a higher *s* value of 4.1 was recorded by using 0.5 mol% of **2c** with the reaction time of 6 h (entry 6).



Scheme 2 Synthesis of singly-binaphthyl-strapped porphyrins 12 and 13.

In summary, we have synthesized doubly-binaphthyl strapped chiral porphyrins. The structures were characterized by NMR spectroscopy and X-ray diffraction analysis. The ¹H NMR spectra, X-ray structure, and DFT-optimized structures indicated the distorted porphyrin planes. The distortion affected the photophysical properties. Notably, the free-base porphyrins **1a–d** showed strong CD signals in the Soret region, and **1b–d** showed moderate CPL. The dependence on the methylene chain length was also observed for the kinetic resolution of styrene oxide with CO₂ using the chiral Zn(π) porphyrins as catalysts. Among the Zn(π) porphyrins, **2c** showed the highest enantioselectivity of *s* = 4.1. Further investigations on the development of chiral metalloporphyrins as CPL materials and chiral catalysts are currently underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Crystal data for **1d**: formula: $2(C_{108}H_{98}N_4O_8)\cdot 3(CH_2Cl_2)\cdot 4(C_2H_3N)\cdot 2(C_2N)$, $M_w = 1830.45$, orthorhombic, space group $P2_12_12_1$ (19), a = 17.656(7), b = 24.127(9), c = 24.239(9) Å, V = 10325(7) Å³, Z = 4, $\rho_{calcd} = 1.177$, T = -180 °C, 17 869 measured reflection, 9895 unique reflections ($R_{int} = 0.0633$), flack 0.133(14), $R_1 = 0.0970$, $wR_2 = 0.3130$ (all data), GOF = 1.077.

- (a) K. Kawasumi, Q. Zhang, Y. Segawa, L. T. Scott and K. Itami, *Nat. Chem.*, 2013, 5, 739; (b) S. Ito, S. Hiroto, S. Lee, M. Son, I. Hisaki, T. Yoshida, D. Kim, N. Kobayashi and H. Shinokubo, *J. Am. Chem. Soc.*, 2015, 137, 142; (c) Y. Hu, X.-Y. Wang, P.-X. Peng, X.-C. Wang, X.-Y. Cao, X. Feng, K. Müllen and A. Narita, *Angew. Chem., Int. Ed.*, 2017, 56, 3374; (d) N. Fukui, T. Kim, D. Kim and A. Osuka, *J. Am. Chem. Soc.*, 2017, 139, 9075.
- 2 (a) N. Yoshida, T. Ishizuka, A. Osuka, D. H. Jeong, H. S. Cho, D. Kim, Y. Matsuzaki, A. Nogami and K. Tanaka, Chem. - Eur. J., 2003, 9, 58; (b) D. I. Schuster, P. Cheng, P. D. Jarowski, D. M. Guldi, C. Luo, L. Echegoyen, S. Pyo, A. R. Holzwarth, S. E. Braslavsky, R. M. Williams and G. Klihm, J. Am. Chem. Soc., 2004, 126, 7257; (c) T. Ikeda, J. M. Lintuluoto, N. Aratani, Z. S. Yoon, D. Kim and A. Osuka, Eur. J. Org. Chem., 2006, 3193; (d) K. M. Mullen and M. J. Gunter, J. Org. Chem., 2008, 73, 3336; (e) K. Sugiyasu and M. Takeuchi, Chem. - Eur. J., 2009, 15, 6350; (f) M. Koepf, J. Conradt, J. Szmytkowski, J. A. Wytko, L. Allouche, H. Kalt, T. S. Balaban and J. Weiss, Inorg. Chem., 2011, 50, 6073; (g) Z. Zhou, M. Shen, C. Cao, Q. Liu and Z. Yan, Chem. - Eur. J., 2012, 18, 7675; (h) S. L. Gac, L. Fusaro, T. Roisnel and B. Boitrel, J. Am. Chem. Soc., 2014, 136, 6698; (i) M. Urbani and T. Torres, Chem. - Eur. J., 2014, 20, 16337; (j) Z. Zhou, Q. Liu, Z. Yan, G. Long, X. Zhang, C. Cao and R. Jiang, Org. Lett., 2013, 15, 606; (k) Z. Zhou, X. Zhou, Q. Liu, X. Zhang and H. Liu, Org. Lett., 2015, 17, 4078.
- 3 (a) J. T. Groves and P. Viski, J. Org. Chem., 1990, 55, 3628;
 (b) Y. Naruta, F. Tani, N. Ishihara and K. Maruyama, J. Am. Chem. Soc., 1991, 113, 6865; (c) J. P. Collman, Z. Wang, A. Straumanis and M. Quelquejeu, J. Am. Chem. Soc., 1999, 121, 460; (d) E. Rose, Q.-Z. Ren and B. Andrioletti, Chem. Eur. J., 2004, 10, 224;
 (e) Q. Ren, A. Wang, S. Liu and X. Ding, Chin. J. Chem., 2009, 27, 895; (f) D. Intrieri, S. L. Gac, A. Caselli, E. Rose, B. Boitrel and E. Gallo, Chem. Commun., 2014, 50, 1811; (g) A. C. Gehrold, T. Bruhn, H. Schneider, U. Radius and G. Bringmann, Org. Lett.,

2015, **17**, 210; (*h*) D. M. Carminati, D. Intrieri, A. Caselli, S. L. Gac, B. Boitrel, L. Toma, L. Legnani and E. Gallo, *Chem. – Eur. J.*, 2016, **22**, 13599.

- 4 (a) G. Reginato, L. D. Bari, P. Salvadori and R. Guilard, Eur. J. Org. Chem., 2000, 1165; (b) X. Peng, N. Komatsu, S. Bhattacharya, T. Shimawaki, S. Aonuma, T. Kimura and A. Osuka, Nat. Nanotechnol., 2007, 2, 361; (c) Y. Shoji, K. Tashiro and T. Aida, J. Am. Chem. Soc., 2010, 132, 5928; (d) T. Ema, N. Ura, K. Eguchi, Y. Ise and T. Sakai, Chem. Commun., 2011, 47, 6090; (e) T. Ema, N. Ura, K. Eguchi and T. Sakai, Bull. Chem. Soc. Jpn., 2012, 85, 101; (f) G. Liu, Y. Saito, D. Nishio-Hamane, A. K. Bauri, E. Flahaut, T. Kimura and N. Komatsu, J. Mater. Chem. A, 2014, 2, 19067; (g) Y. Wang, X. Wen, X. Cui, L. Wojtas and X. P. Zhang, J. Am. Chem. Soc., 2017, 139, 1049; (h) F. Burg, M. Gicquel, S. Breitenlechner, A. Pöthig and T. Bach, Angew. Chem., Int. Ed., 2018, 57, 2953.
- 5 For recent reviews, see: (a) H. Maeda and Y. Bando, *Pure Appl. Chem.*, 2013, **85**, 1967; (b) 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, **21**, 13488; (c) J. Kumar, T. Nakashima and T. Kawai, *J. Phys. Chem. Lett.*, 2015, **6**, 3445; (d) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai and K. Maeda, *Chem. Rev.*, 2016, **116**, 13752; (e) H. Tanaka, Y. Inoue and T. Mori, *ChemPhotoChem*, 2018, **2**, 386.
- 6 (a) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi and K. Tanaka, J. Am. Chem. Soc., 2012, 134, 4080; (b) K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya and K. Tanaka, J. Am. Chem. Soc., 2014, 136, 5555; (c) T. Matsuno, Y. Koyama, S. Hiroto, J. Kumar, T. Kawai and H. Shinokubo, Chem. Commun., 2015, 51, 4607; (d) Y. Yamamoto, H. Sakai, J. Yuasa, Y. Araki, T. Wada, T. Sakanoue, T. Takenobu, T. Kawai and T. Hasobe, Chem. - Eur. J., 2016, 22, 4263; (e) K. Dhbaibi, L. Favereau, M. Srebro-Hooper, M. Jean, N. Vanthuyne, F. Zinna, B. Jamoussi, L. D. Bari, J. Autschbach and J. Crassous, Chem. Sci., 2018, 9, 735.
- 7 (a) H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori and T. Kawai, J. Am. Chem. Soc., 2011, 133, 9266; (b) T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, Chem. Asian J., 2012, 7, 2836; (c) 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; (d) K. Takaishi, T. Yamamoto, S. Hinoide and T. Ema, Chem. Eur. J., 2017, 23, 9249; (e) F. Meng, Y. Sheng, F. Li, C. Zhu, Y. Quan and Y. Cheng, RSC Adv., 2017, 7, 15851; (f) K. Takaishi, R. Takehana and T. Ema, Chem. Commun., 2018, 54, 1449; (g) K. Takaishi, M. Yasui and T. Ema, J. Am. Chem. Soc., 2018, 140, 5334.
- 8 (a) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh and Y. Chujo, J. Am. Chem. Soc., 2014, 136, 3350; (b) M. Saikawa, T. Nakamura, J. Uchida, M. Yamamura and T. Nabeshima, Chem. Commun., 2016, 52, 10727; (c) A. Ushiyama, S. Hiroto, J. Yuasa, T. Kawai and H. Shinokubo, Org. Chem. Front., 2017, 4, 664; (d) T. Ikai, Y. Wada, S. Awata, C. Yun, K. Maeda, M. Mizuno and T. M. Swager, Org. Biomol. Chem., 2017, 15, 8440.
- 9 (a) T. Harada, N. Kajiyama, K. Ishizaka, R. Toyofuku, K. Izumi, K. Umemura, Y. Imai, N. Taniguchi and K. Mishima, *Chem. Commun.*, 2014, **50**, 11169; (b) M. Morisue, T. Yumura, R. Sawada, M. Naito, Y. Kuroda and Y. Chujo, *Chem. Commun.*, 2016, **52**, 2481; (c) R. Watanabe, N. Hara, Y. Imai, M. Hasegawa, S. Ishioka, Y. Mazaki and K. Sugiura, *ChemistrySelect*, 2018, **3**, 3576.
- For reviews of CO₂ fixations, see: (a) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, Angew. Chem., Int. Ed.,

2011, **50**, 8510; (b) Y. Tsuji and T. Fujihara, Chem. Commun., 2012, **48**, 9956; (c) N. Kielland, C. J. Whiteoak and A. W. Kleij, Adv. Synth. Catal., 2013, **355**, 2115; (d) C. Maeda, Y. Miyazaki and T. Ema, Catal. Sci. Technol., 2014, **4**, 1482; (e) B. Yu and L.-N. He, ChemSusChem, 2015, **8**, 52; (f) A. Tilili, E. Blondiaux, X. Frogneux and T. Cantat, Green Chem., 2015, **17**, 157; (g) Q. Liu, L. Wu, R. Jackstell and M. Beller, Nat. Commun., 2015, **6**, 5933; (h) K. Sekine and T. Yamada, Chem. Soc. Rev., 2016, **45**, 4524.

- 11 For recent reviews of the synthesis of cyclic carbonates form epoxides and CO₂, see: (a) C. Martín, G. Fiorani and A. W. Kleij, ACS Catal., 2015, 5, 1353; (b) J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, Green Chem., 2015, 17, 1966; (c) M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann and F. E. Kühn, ChemSusChem, 2015, 8, 2436; (d) X.-D. Lang and L.-N. He, Chem. Rec., 2016, 16, 1337; (e) J. Hasegawa, R. Miyazaki, C. Maeda and T. Ema, Chem. Rec., 2016, 16, 2260; (f) R. R. Shaikh, S. Pornpraprom and V. D'Elia, ACS Catal., 2018, 8, 419.
- 12 (a) T. Aida and S. Inoue, J. Am. Chem. Soc., 1983, 105, 1304;
 (b) W. J. Kruper and D. V. Dellar, J. Org. Chem., 1995, 60, 725;
 (c) R. L. Paddock, Y. Hiyama, J. M. McKay and S. T. Nguyen, Tetrahedron Lett., 2004, 45, 2023; (d) D. Bai, S. Duan, L. Hai and H. Jing, ChemCatChem, 2012, 4, 1752; (e) Y. Qin, H. Guo, X. Sheng, X. Wang and F. Wang, Green Chem., 2015, 17, 2853; (f) X. Jiang, F. Gou, F. Chen and H. Jing, Green Chem., 2016, 18, 367.
- 13 (a) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, Chem. Commun., 2012, 48, 4489; (b) T. Ema, Y. Miyazaki, T. Taniguchi and J. Takada, Green Chem., 2013, 15, 2485; (c) T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J. Hasegawa, J. Am. Chem. Soc., 2014, 136, 15270; (d) C. Maeda, T. Taniguchi, K. Ogawa and T. Ema, Angew. Chem., Int. Ed., 2015, 54, 134; (e) C. Maeda, J. Shimonishi, R. Miyazaki, J. Hasegawa and T. Ema, Chem. – Eur. J., 2016, 22, 6556; (f) C. Maeda, S. Sasaki and T. Ema, ChemCatChem, 2017, 9, 946.
- 14 For the examples of metal salen derivatives, see: (a) X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang and R. Zhang, J. Am. Chem. Soc., 2004, 126, 3732; (b) R. L. Paddock and S. T. Nguyen, Chem. Commun., 2004, 1622; (c) A. Berkessel and M. Brandenburg, Org. Lett., 2006, 8, 4401; (d) W. Yamada, Y. Kitaichi, H. Tanaka, T. Kojima, M. Sato, T. Ikeno and T. Yamada, Bull. Chem. Soc. Jpn., 2007, 80, 1391; (e) W.-M. Ren, G.-P. Wu, F. Lin, J.-Y. Jiang, C. Liu, Y. Luo and X.-B. Lu, Chem. Sci., 2012, 3, 2094; (f) M. North, S. C. Z. Quek, N. E. Pridmore, A. C. Whitwood and X. Wu, ACS Catal., 2015, 5, 3398.
- 15 For the examples of organocatalysts, see: (a) S. Liu, N. Suematsu, K. Maruoka and S. Shirakawa, *Green Chem.*, 2016, **18**, 4611; (b) T. Ema, M. Yokoyama, S. Watanabe, S. Sasaki, H. Ota and K. Takaishi, *Org. Lett.*, 2017, **19**, 4070.
- 16 During the preparation of this manuscript, Jing and co-workers reported chiral Co(II) porphyrins for asymmetric cycloaddition of CO_2 to epoxides, see: X. Fu, X. Jing, L. Jin, L. Zhang, X. Zhang, B. Hu and H. Jing, *Chin. J. Catal.*, 2018, **39**, 997.
- 17 M. J. Frisch, et al., Gaussian 09 (Revision E.01), Gaussian, Inc., Wallingford CT, 2013.
- 18 (a) M. Caricato, A. Delforge, D. Bonifazi, D. Dondi, A. Mazzanti and D. Pasini, Org. Biomol. Chem., 2015, 13, 3593; (b) M. Agnes, A. Nitti, D. A. Vander Griend, D. Dondi, D. Merli and D. Pasini, Chem. Commun., 2016, 52, 11492.
- 19 g_{lum} defined as $2(I_L-I_R)/(I_L+I_R)$ was calculated as an average value in the range of $\lambda_F\pm 5$ nm.