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Diastereoselective Synthesis of Chiral Diporphyrins via Intramolecular *meso*−*meso* Oxidative Coupling

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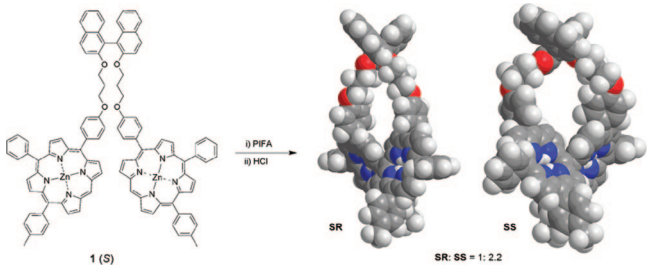
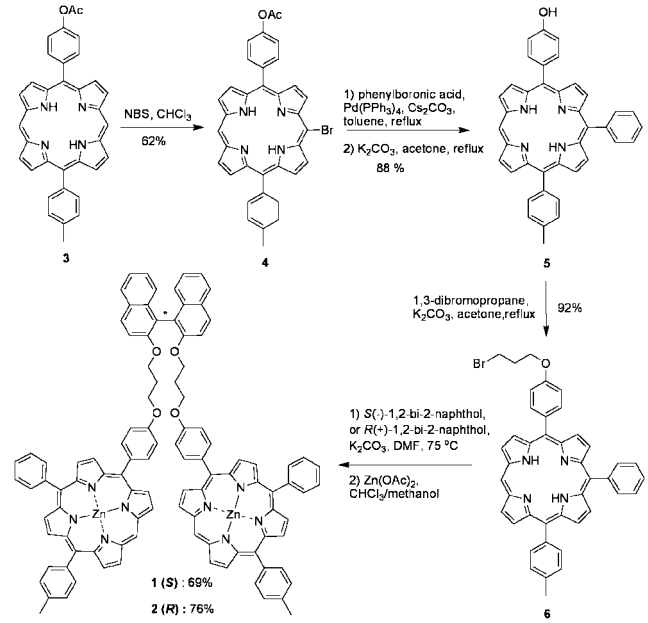


Diastereoselective syntheses of *meso*−*meso* linked diporphyrins were achieved via intramolecular chiral induction. The structures and conformations were analyzed by CD, UV, NMR, and computational calculations.

Axially chiral biaryls, which contain a rotationally hindered and thus stereogenic axis, are frequently found as key motifs in biologically active compounds, chiral auxiliaries, and chiral ligands.[1] Chiral diporphyrins, for example, have unique photoelectronic properties, and therefore have recently attracted much attention.[2,3]

In earlier publications, synthetic approaches to *meso*−*meso*, *meso*−β and β−β linked porphyrin dimers were well documented, and discussions on their stereochemical properties were also reported.[2,4] However, asymmetric syntheses of such dimers have not been investigated, and a pure diporphyrin enantiomer can only be obtained by chiral chromatography. In this paper,

SCHEME 1. The Synthesis of Intermediate Porphyrins 1 and 2



a new synthetic method is described to stereoselectively prepare *meso*−*meso* linked diporphyrins via intramolecular remote chiral induction. The axial bond between the two porphyrin moieties was formed through the *meso* atomic sites in the presence of PIFA (bis(trifluoroacetoxy)iodobenzene).[5] A chiral *S*-BINOL moiety was employed as a remote chiral auxiliary to control the chirality of the newly formed diporphyrin axial bond. The two diastereomers formed were separated by achiral column chromatography. To the best of our knowledge, this was the first example of a method in which the two atropisomers of a directly *meso*−*meso* linked chiral diporphyrin were obtained without utilizing chiral chromatography.

The synthesis was initiated with the preparation of the chiral dinaphthyl derivative **1**, which has two Zn(II)-containing porphyrin moieties (Scheme 1). This intermediate was obtained from the reactants 1,3-dibromopropane and *S*-BINOL via a Williamson ether synthesis. Then the iodine(III) reagent PIFA was utilized to promote the intramolecular *meso*−*meso* coupling reaction.[5e] During this reaction, the concentration of reactant **1** was as dilute as 0.02 mM so as to suppress the intermolecular coupling reaction. Finally, the coupling mixture was treated with HCl so as to remove the Zn(II) cation. The resulting crude

(1) For reviews, see: (a) Bringmann, G.; Mortimer, A. J. P.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5384. (b) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (c) Lloyd-Williams, P.; Giralt, E. *Chem. Soc. Rev.* **2001**, *30*, 145.

(2) (a) Bringmann, G.; Rüdenauer, S.; Götz, D. C. G.; Gulder, T. A. M.; Reichert, M. *Org. Lett.* **2006**, *8*, 4743. (b) Bringmann, G.; Götz, D. C. G.; Gulder, T. A. M.; Gehrke, T. H.; Bruhn, T.; Kupfer, T.; Radacki, K.; Braunschweig, H.; Heckmann, A.; Lambert, C. *J. Am. Chem. Soc.* **2008**, *130*, 17812.

(3) (a) Shoji, Y.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 10690. (b) Peng, X.; Komatsu, N.; Kimura, T.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 15947. (c) Bhyrappa, P.; Borovkov, V. V.; Inoue, Y. *Org. Lett.* **2007**, *9*, 433. (d) Kubo, Y.; Ohno, T.; Tokita, Y. S.; Iida, T.; Ishimaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 12700. (e) Monti, D.; Venanzi, M.; Stefanelli, M.; Sorrenti, A.; Mancini, G.; Natale, C. D.; Paolesse, R. *J. Am. Chem. Soc.* **2007**, *129*, 6688. (f) Gao, G.-Y.; Ruppel, J. V.; Fields, K. B.; Xu, X.; Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2008**, *73*, 4855.

(4) (a) Kim, D.; Osuka, A. *Acc. Chem. Res.* **2004**, *37*, 735. (b) Nakamura, Y.; Hwang, I.-W.; Aratani, N.; Ahn, T. K.; Ko, D. M.; Takagi, A.; Kawai, T.; Matsumoto, T.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 236. (c) Yoshida, N.; Osuka, A. *Tetrahedron Lett.* **2000**, *41*, 9287. (d) Tsuda, A.; Furuta, H.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 10304. (e) Maeda, C.; Kamada, T.; Aratani, N.; Osuka, A. *Coord. Chem. Rev.* **2007**, *251*, 2743. (f) Ikeda, C.; Yoon, Z. S.; Park, M.; Inoue, H.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 534.

(5) (a) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed.* **1997**, *36*, 135. (b) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 176. (c) Yoshida, N.; Aratani, N.; Osuka, A. *Chem. Commun.* **2000**, 197. (d) Shi, X.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 1665. (e) Jin, L.-M.; Chen, L.; Yin, J.-J.; Guo, C.-C.; Chen, Q. Y. *Eur. J. Org. Chem.* **2005**, 3994.

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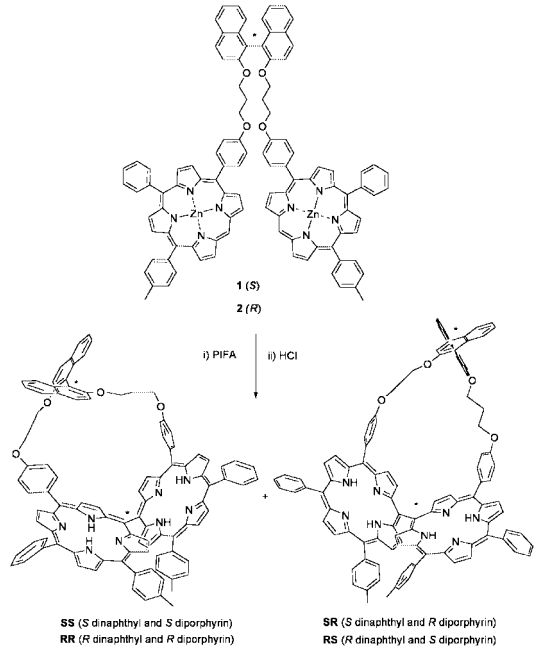
TABLE 1. Asymmetric Coupling Reaction of Diporphyrin 1 and 2 by PIFA[a]

entry	diporphyrin	PIFA (equiv)	temp (°C)	time (h)	yield[b](%)	dr[c]
1	**1**	1.2	20	0.5	54	1: 1
2	**1**	1.2	0	1	57	1: 1
3	**1**	1.2	−20	5	57	1.5: 1
4	**1**	1.2	−45	12	56	2.2: 1
5	**1**	4	−45	4[d]	58	2.2: 1
6	**2**	1.2	20	0.5	58	1: 1
7	**2**	1.2	−20	5	54	1.4: 1
8	**2**	1.2	−45	12	55	2.1: 1

[a] Reaction conditions: diporphyrin (1 equiv) and PIFA reacting at the same concentration (0.02 mM) at different temperatures in CH_2Cl_2. [b] Total yields of **SS** and **SR** or **RR** and **RS**. [c] Ratios were the value of **SS**:**SR** or **RR**:**RS**, determined by UV−vis of the isolated diastereomers separated by silica gel column chromatography. [d] This reaction was terminated by $NaBH_4$/methanol.

SCHEME 2. PIFA Promoted *meso*−*meso* Coupling Reaction



product was smoothly purified by silica gel column to give two diastereomers.

As expected, the stereoselectivity was highly temperature dependent (Table 1). Whereas almost equal amounts of diastereomers **SS** and **SR** (Scheme 2) were obtained at room temperature, the ratio of **SS** to **SR** reached a value as high as 2.2:1 when the temperature decreased to −45 °C. At −78 °C, very little product was observed even when the reaction time was prolonged to 12 h. Increasing the PIFA content (up to 4 equivalence) had little effect on diastereoselectivity. For the coupling reaction of compound **2**, which was the enantiomer of compound **1**, similar results were obtained. Attempts at increasing the diastereoselectivity by using a shorter ethylene linker instead of propylene resulted in a complicated product distribution.

The resulting isomers were characterized by CD, NMR, and HR-MS. The four stereomers **RR**, **RS**, **SS**, and **SR** were distinguished mainly through their CD spectra based on previously reported results, including empirical exciton chirality methods,[6] theoretical calculations of chiral diporphyrins,[2] and Osuka's research.[7] As shown in Figure 1, each of the four

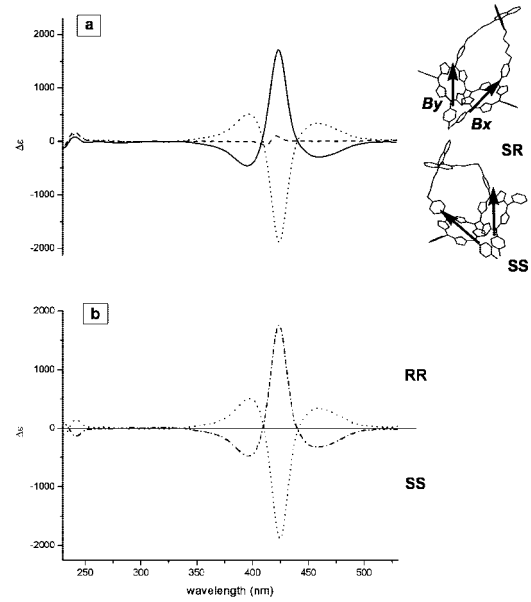


FIGURE 1. (a) The CD spectra of **1** (dash line), **SR** (full line), and **SS** (dot line). (b) The CD spectra of **SS** (dot line) and **RR** (dash-dot line).

stereomers exhibited strong Cotton effects. The CD spectrum which was positive at 240 nm, positive at 398 nm, negative at 424 nm, and positive at 460 nm was assigned as diastereomer **SS**. The other diastereomer derived from compound **1** was therefore assigned as **SR**. Both **SS** and **SR** showed positive sign at 240 nm, arising from the dinaphthyl moiety. In the Soret-band region (370−480 nm), arising from the coupling of the ***Bx*** and ***By*** transition dipole moments of the diporphyrin moiety, **SS** and **SR** showed completely opposite sign patterns. Similar results were found for **RR** and **RS** diporphyrins (Figure S4, Supporting Information). For the enantiomers **SS** and **RR**, completely opposite Cotton effects were ascribed to the absolutely contrary stereoconfiguration (Figure 1b).

In the UV−vis spectra (Figure S1, Supporting Information), the Soret bands of the *meso*−*meso* linked diporphyrin isomers **SS** and **SR** were broadened and split because of the exciton coupling between the two porphyrin moieties. In addition, the UV−vis spectrum of **SR** displayed more curvatures at the inflection points (400 and 475 nm) than those of **SS**, indicating that the dihedral angle between neighboring porphyrin planes in **SS** is bigger than that in **SR**.[7,8]

To understand the stereochemical properties of the diaxial systems, the geometries of **SR** and **SS** were optimized at the B3LYP/6-31G level with no symmetry constraints, using the Gaussian 03 program.[9,10] We did not use the more convenient

(6) (a) Nakanishi, K.; Berova, N. In *Circular Dichroism: Principles and Applications*; Nakanish, K., Berova, N., Woody, R. W., Eds.; VCH: NewYork, 1994; p 361. (b) Mason, S. F. *Molecular Optical Activity and the Chiral Discriminations*; Cambridge University Press: Cambridge, UK, 1982. (c) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257.

(7) Yoshida, N.; Ishizuka, T.; Osuka, A.; Jeong, D. H.; Cho, H. S.; Kim, D.; Matsuzaki, Y.; Nogami, A.; Tanaka, K. *Chem. Eur. J.* **2003**, *9*, 58. The Cotton effects at low energy Soret bands are difficult to explain solely by invoking the exciton coupling theory.

(8) Yoshida, N.; Osuka, A. *Org. Lett.* **2000**, *2*, 2963.

(9) Geometries were optimized at the B3LYP/6-31G level with no symmetry constraints. Calculations were carried out with Gaussian 03.[10] The computational method, result, and relevant references are displayed in the Supporting Information.

(10) Frisch, M. J.; et al. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

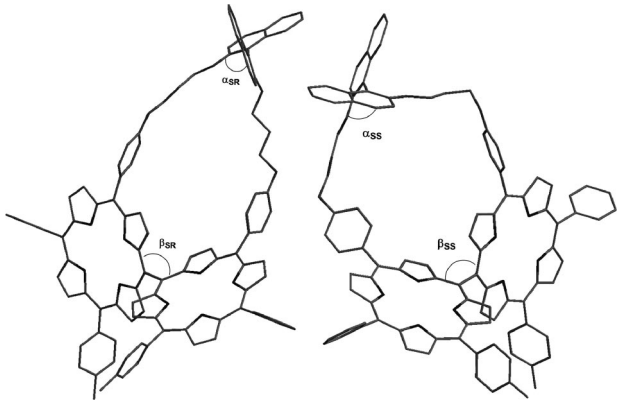


FIGURE 2. Structure of the chiral diporphyrins **SR** (left) and **SS** (right), as derived by DFT calculations (H atoms are omitted).

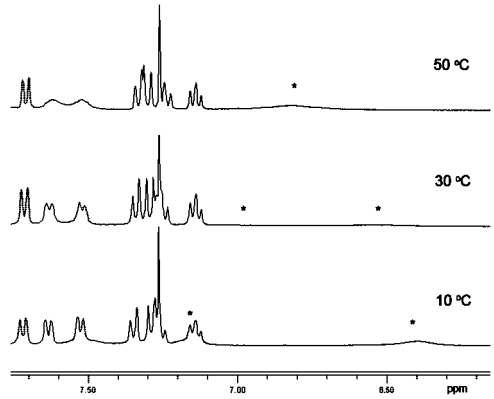


FIGURE 3. Temperature-dependent NMR study of **SS**.

Hartree−Fock theory, since it was known to artificially favor a bond-alternating geometry for porphyrins.[11] As for the global minimum structures (Figure 2), the dihedral angle of the porphyrin planes in **SS** (β_{SS}) was 70.0°, which was larger than that in **SR** (β_{SR} = 65.6°). This result was consistent with the UV−vis spectra.

Full assignments of the proton signals were achieved from a 2D-COSY spectrum. The most notable peculiarity of the stereomers is that the phenyl group protons partitioned by the porphyrin plane gave two distinct NMR signals, something that was not observed in other directly linked diporphyrins. In addition, the dinaphthyl proton signals of **SS** were upfield shifted relative to those of **SR**, owing to the stronger shielding effect of the porphyrin ring. This was consistent with the computational results, which indicated that the naphthyl ring of **SS** was right above the porphyrin with a narrower angle and a shorter distance than that of **SR**.

To assign all broad ^{1}H NMR signals of **SS** and **SR**, temperature-dependent experiments were carried out (Figure 3). For **SS**, when the temperature was raised to 50 °C, the two broad signals at 6.4 and 7.1 ppm amalgamated into one peak at 6.8 ppm, and all of the other distinct phenyl group protons gave broadened NMR signals. Similar changes were observed for **SR** (Figure S8, Supporting Information). These temperature-dependent broad signals happen because of the larger extent of the isotropic intramolecular motional averaging mechanism on the static ^{1}H NMR time scale.[12]

In summary, an asymmetric method has been developed for the first time to synthesize chiral *meso*−*meso* directly linked diporphyrins. With a chirality induction process, enantiomeric pure dinaphthyl bridged diporphyrins **1** and **2** underwent an intramolecular coupling reaction to produce diastereomeric excess *meso*−*meso* directly linked diporphyrins, respectively. The diastereomeric ratios (dr) showed a systematic dependence on the reaction temperature, and could reach 2.2:1 (**SS**:**SR**) under optimum conditions. Moreover, the diastereomers are separable by achiral column chromatography, offering a convenient process for macroscopic scale preparations.

Experimental Section

Binaphthyl-Bridged Zn(II) Diporphyrin 1(*S*). Anhydrous K_2CO_3 (332 mg, 2.42 mmol) was added to a stirred solution of porphyrin **6** (62 mg, 0.090 mmol) and *S*(−)-1,2-bi-2-naphthol (11 mg, 0.039 mmol) in dry DMF. The resulting mixture was heated to 75 °C under argon for 24 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were washed with water then dried over Na_2SO_4. After concentration of the filtrate, the resulting residue was dissolved by 20 mL of chloroform. Then $Zn(OAc)_2$-saturated methanol solution (2 mL) was added and the reaction mixture was heated to reflux for 0.5 h. The reaction mixture was washed twice with water, and the organic layer was dried over Na_2SO_4 and evaporated. The product was purified by silica gel flash column chromatography with $CHCl_3$ as eluent. Purple solid was obtained after recrystallization from $CHCl_3$/methanol in 69% yield (44 mg, 0.027 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 9.73 (s, 2H), 8.96 (m, 16H), 8.16 (m, 4H), 8.05 (m, 10H), 7.92 (d, J = 7.8 Hz, 2H), 7.71 (m, 6H), 7.56 (m, 6H), 7.36 (m, 2H), 7.30 (m, 4H), 6.93 (d, J = 8.4 Hz, 4H), 4.41 (m, 2H), 4.30 (m, 2H), 3.79 (m, 4H), 2.72 (s, 6H), 2.14 ppm (m, 4H); HR-MS (ESI) m/z $[M + H]^+$ calcd for $C_{104}H_{75}N_8O_4Zn_2$ 1626.441, found 1626.439; UV/vis (in CH_2Cl_2, λ_{max}/nm, ϵ/mol^{-1} dm^3 cm^{-1}) 233 (1.64×10^5), 289 (7.07×10^4), 415 (9.01×10^5), 543 (2.61×10^4), 581 (3.20×10^3); fluorescence (CH_2Cl_2, λ_{ex} = 412 nm) λ_{em} = 424, 588, 639 nm.

Binaphthyl-Bridged Zn(II) Diporphyrin 2(R). This compound was prepared by the same procedure used for diporphyrin **1** in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.89 (s, 2H), 9.01 (m, 16H), 8.19 (m, 4H), 8.05 (m, 10H), 7.96 (d, J = 7.8 Hz, 2H), 7.72 (m, 6H), 7.60 (m, 6H), 7.39 (m, 2H), 7.33 (m, 4H), 6.97 (d, J = 8.4 Hz, 4H), 4.44 (m, 2H), 4.34 (m, 2H), 3.81 (m, 4H), 2.75 (s, 6H), 2.17 ppm (m, 4H); HR-MS (ESI) m/z $[M + H]^+$ calcd for $C_{104}H_{75}N_8O_4Zn_2$ 1626.441, found 1626.441; UV/vis (in CH_2Cl_2, λ_{max}/nm, ϵ/mol^{-1} dm^3 cm^{-1}) 232 (1.85×10^5), 289 (5.63×10^4), 416 (9.11×10^5), 542 (4.89×10^4), 580 (9.5×10^3); fluorescence (CH_2Cl_2, λ_{ex} = 412 nm) λ_{em} = 590, 637 nm.

The General Procedure for the Asymmetric Coupling Reaction (Table 1). A sample of binaphthyl-bridged Zn(II) diporphyrin **1** or **2** was diluted to a certain concentration by CH_2Cl_2 then controlled to a certain temperature. After addition of different equivalences of PIFA, the mixture was stirred at a maintainable temperature for several hours. The resulting yellow-brown mixture was purified by flash column chromatography (silica gel, CH_2Cl_2/ethyl acetate = 50:1). After concentration, the residue was dissolved by $CHCl_3$ (10 mL), 1 mL of concentrated hydrochloric acid was added, and stirring was continued at room temperature for 2 h. The reaction mixture was poured into water and extracted with CH_2Cl_2, then washed with saturated sodium bicarbonate aqueous solution several times. The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography (silica gel, $CHCl_3$). Three kinds of main porphyrin were obtained: the first eluting was oligomers; the middle eluting was **SR** or **SR**, and the last was **SS** or **RR**.

(11) Almlöf, J.; Fischer, T. H.; Gassman, P. G.; Ghosh, A.; Häser, M. *J. Phys. Chem.* **1993**, *97*, 10964.

(12) (a) Davoras, E. M.; Spyroulias, C. A.; Mikros, E.; Coutsolelos, A. C. *Inorg. Chem.* **1994**, *33*, 3430. (b) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 1601. (c) Wacker, P.; Dahms, K.; Senge, M. O.; Kleinpeter, E. *J. Org. Chem.* **2007**, *72*, 6224.

SS: ^{1}H NMR (600 MHz, $CDCl_3$, rt) δ 9.07 (d, J = 4.2 Hz, 2H), 8.92 (m, 6H), 8.85 (d, J = 4.2 Hz, 2H), 8.72 (d, J = 4.2 Hz, 2H), 8.64 (d, J = 4.2 Hz, 2H), 8.39 (d, J = 7.2 Hz, 2H), 8.31 (m, 6H), 8.03 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 4.2 Hz, 2H), 7.87 (d, J = 9.0 Hz, 2H), 7.80 (m, 6H), 7.69 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 7.8 Hz, 2H), 7.50 (m, 4H), 7.32 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 7.22 (m, 2H), 7.13 (t, J = 7.2 Hz, 2H), 6.40 (s, 2H), 4.10 (m, 4H), 4.04 (m, 2H), 3.70 (m, 2H), 2.67 (s, 6H), 1.93 (m, 4H), −2.10 ppm (s, 4H); HR-MS (ESI) m/z $[M + H]^+$ calcd for $C_{104}H_{77}N_8O_4$ 1501.606, found 1501.607; UV/vis (in CH_2Cl_2, λ_{max}/nm, ϵ/mol^{-1} dm^3 cm^{-1}) 229 (2.00 × 10^5), 424 (2.68 × 10^5), 454 (2.39 × 10^5), 530 (6.59 × 10^4), 601 (3.21 × 10^4), 664 (2.27 × 10^4); fluorescence (CH_2Cl_2, λ_{ex} = 412 nm) λ_{em} = 678 nm.

SR: ^{1}H NMR (400 MHz, $CDCl_3$, 10 °C) δ 9.07 (d, J = 4.8 Hz, 2H), 8.95 (m, 6H), 8.75 (d, J = 4.8 Hz, 2H), 8.54 (d, J = 4.8 Hz, 2H), 8.49 (d, J = 4.8 Hz, 2H), 8.43 (m, 6H), 8.20 (d, J = 7.2 Hz, 2H), 7.94 (d, J = 7.2 Hz, 2H), 7.81 (m, 10H), 7.72 (m, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.52 (s, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.28 (m, 6H), 7.25 (m, 4H), 6.56 (s, 2H), 4.39 (m, 2H), 4.00 (m, 4H), 3.99 (m, 2H), 2.66 (s, 6H), 1.98 (m, 2H), 1.90 (m, 2H), −2.16 ppm (s, 4H); HR-MS (ESI) m/z $[M + H]^+$ calcd for $C_{104}H_{77}N_8O_4$ 1501.606, found 1501.605; UV/vis (in CH_2Cl_2, λ_{max}/nm, ϵ/mol^{-1} dm^3 cm^{-1}) 229 (1.97 × 10^5), 421 (2.49 × 10^5), 454 (2.09 × 10^5), 528 (5.81 × 10^4), 601 (2.59 × 10^4), 663 (1.69 × 10^4); fluorescence (CH_2Cl_2, λ_{ex} = 412 nm) λ_{em} = 679 nm.

RR: ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.06 (d, J = 4.4 Hz, 2H), 8.92 (m, 6H), 8.84 (d, J = 4.4 Hz, 2H), 8.71 (d, J = 4.4 Hz, 2H), 8.63 (d, J = 4.4 Hz, 2H), 8.39 (d, J = 7.2 Hz, 2H), 8.30 (m, 6H), 8.02 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 4.4 Hz, 2H), 7.87 (d, J = 9.2 Hz, 2H), 7.81 (m, 6H), 7.69 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 7.2 Hz, 2H), 7.49 (m, 4H), 7.29 (m, 4H), 7.26 (m, 2H), 7.12 (m, 4H), 6.41 (s, 2H), 4.11 (m, 6H), 3.72 (m, 2H), 2.67 (s, 6H), 1.93 (m, 4H), −2.10 ppm (s, 4H); HR-MS (ESI) m/z $[M + H]^+$ calcd for $C_{104}H_{77}N_8O_4$ 1501.606, found 1501.605; UV/vis (in CH_2Cl_2, λ_{max}/nm, ϵ/mol^{-1} dm^3 cm^{-1}) 230 (1.85 × 10^5), 424 (2.70 × 10^5), 455 (2.41 × 10^5), 528 (5.92 × 10^4), 600 (2.45 × 10^4), 664 (1.46 × 10^4); fluorescence (CH_2Cl_2, λ_{ex} = 412 nm) λ_{em} = 679 nm.

RS: ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.05 (d, J = 4.4 Hz, 2H), 8.93 (m, 6H), 8.73 (d, J = 4.8 Hz, 2H), 8.52 (d, J = 4.4 Hz, 2H), 8.48 (d, J = 4.4 Hz, 2H), 8.42 (m, 6H), 8.18 (m, 2H), 7.93 (d, J = 6.8 Hz, 2H), 7.81 (m, 10H), 7.70 (m, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.47 (m, 4H), 7.39 (d, J = 8.8 Hz, 2H), 7.26 (m, 6H), 7.24 (m, 4H), 6.55 (s, 2H), 4.36 (m, 2H), 3.97 (m, 4H), 3.84 (m, 2H), 2.65 (s, 6H), 1.97 (m, 2H), 1.88 (m, 2H), −2.13 ppm (s, 4H); HR-MS (ESI) m/z $[M + H]^+$ calcd for $C_{104}H_{77}N_8O_4$ 1501.606, found 1501.605; UV/vis (in CH_2Cl_2, λ_{max}/nm, ϵ/mol^{-1} dm^3 cm^{-1}) 230 (1.86 × 10^5), 422 (2.50 × 10^5), 455 (2.15 × 10^5), 528 (5.58 × 10^4), 600 (2.34 × 10^4), 661 (1.34 × 10^4); fluorescence (CH_2Cl_2, λ_{ex} = 412 nm) λ_{em} = 680 nm.

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Supporting Information Available: Experimental procedures of the intermediates, ^{13}C NMR data of chiral compounds, copies of ^{1}H NMR, ^{13}C NMR, and HR-MS spectra of new compounds, CD spectra of **2**, **RR**, and **RS**, temperature dependence NMR study of **SR**, and the global minimum structure of **SS** and **SR**. This material is available free of charge via the Internet at http://pubs.acs.org.

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