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Synthesis and properties of *S*,*R*-alternating octinaphthalenes

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ABSTRACT

(*S*,*R*,*S*,*R*,*S*,*R*,*S*)- and (*S*,*R*,*S*,*S*,*R*,*S*)-octinaphthalenes were synthesized by oxidative coupling of (*S*,*R*,*S*)-quaternaphthalene, and differences due to axis chirality of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-, (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-, (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-, and (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-octinaphthalenes were compared using the R_f values on TLC, specific optical rotations, ^{1}H NMR chemical shifts of the hydroxy groups, and CD spectra. A clear CD additivity was found in the $\Delta\varepsilon$ values of the ^1L_a transition around 290 nm, which are proportional to the difference between the numbers of *S* and *R* binaphthalene units.

1. Introduction

In the field of materials science, rod shaped molecules[1] such as oligothiophene[2] and oligophenylene[3] have received much attention due to the versatility of novel functions. We have been studying oligonaphthalenes composed of a 2,3-dioxynaphthalene unit continuously connected at the 1,4-positions.[4,5] In particular, we have investigated the construction and function of homochiral oligonaphthalenes (thus, the axial chiralities are completely controlled, either *R* or *S*) oligonaphthalenes. In homochiral oligonaphthalenes, dioxy groups are arranged in a helical shape. In contrast, in *S*,*R*-alternating oligonaphthalenes, the hydrophilic oxygen functional groups are linearly aligned on one side of the molecule, and the hydrophobic naphthalene rings are on the other side. In this paper, we describe the synthesis of chiral octinaphthalenes (including the *S*,*R*-alternating derivative), and compare their properties with those of others having different axial chiralities.

2. Results and discussion

Scheme 1 outlines the synthetic route to chiral octinaphthalenes. The central hydroxy groups of (*S*,*R*,*S*)-(+)-**1**[5f] were methylated under MeI/K_2CO_3 conditions to give (*S*,*R*,*S*)-(+)-**2** in 98% yield. Both benzyl groups on the top and bottom naphthalenes were removed with Pd/C and hydrogen (92%) followed by monobenzylation with 1.05 equiv of benzyl bromide to provide key compound (*S*,*R*,*S*)-(+)-**4** in 43% yield. Table 1 summarizes the oxidative coupling reactions of (*S*,*R*,*S*)-(+)-**4** to (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a** and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b** under various conditions (discussed below). The diastereomeric octinaphthalenes were separated by column chromatography on SiO_2. The introduction of tetraphenylporphyrin carboxylic acid ($TPPCO_2H$) under WSC/DMAP conditions afforded (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(−)-**6a** and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**6b** in good yields. These were then used to determine the absolute configuration. Compared to other diastereomeric octamers, (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a** was unstable in air or basic conditions, and gradually tarnished to red-brown. Therefore, the central hydroxy groups of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a** and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b** were protected by methyl groups in 40% and 93% yields, respectively. Due to the chemical instability of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a**, the yield of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**7a** was low.

The coupling conditions of (*S*,*R*,*S*)-(+)-**4** were optimized using ^{1}H NMR measurements (Fig. 1). Thus, the ratio of desired (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a**,(*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b**, and recovered (*S*,*R*,*S*)-(+)-**4** was estimated by integrating the corresponding central hydroxy protons for **5a**,**b** and the bottom hydroxy proton of **4**. Prior to measuring the NMR of the reaction mixture, we confirmed (1) the chemical shifts of the hydroxy protons of (*S*,*R*,*S*)-(+)-**4**,(*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a**, and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b**, which were observed near 6.22, 6.09, and 6.44 ppm, respectively, and determined (2) that the influence of sample concentration on the chemical shifts of the OH protons was negligible.

For the copper promoted oxidative coupling reaction of naphthols, several groups have reported isomerization of a newly formed axis along with a bond forming reaction.[6] We also found that the coupling reactions of chiral binaphthyls exhibited some degree of chiral

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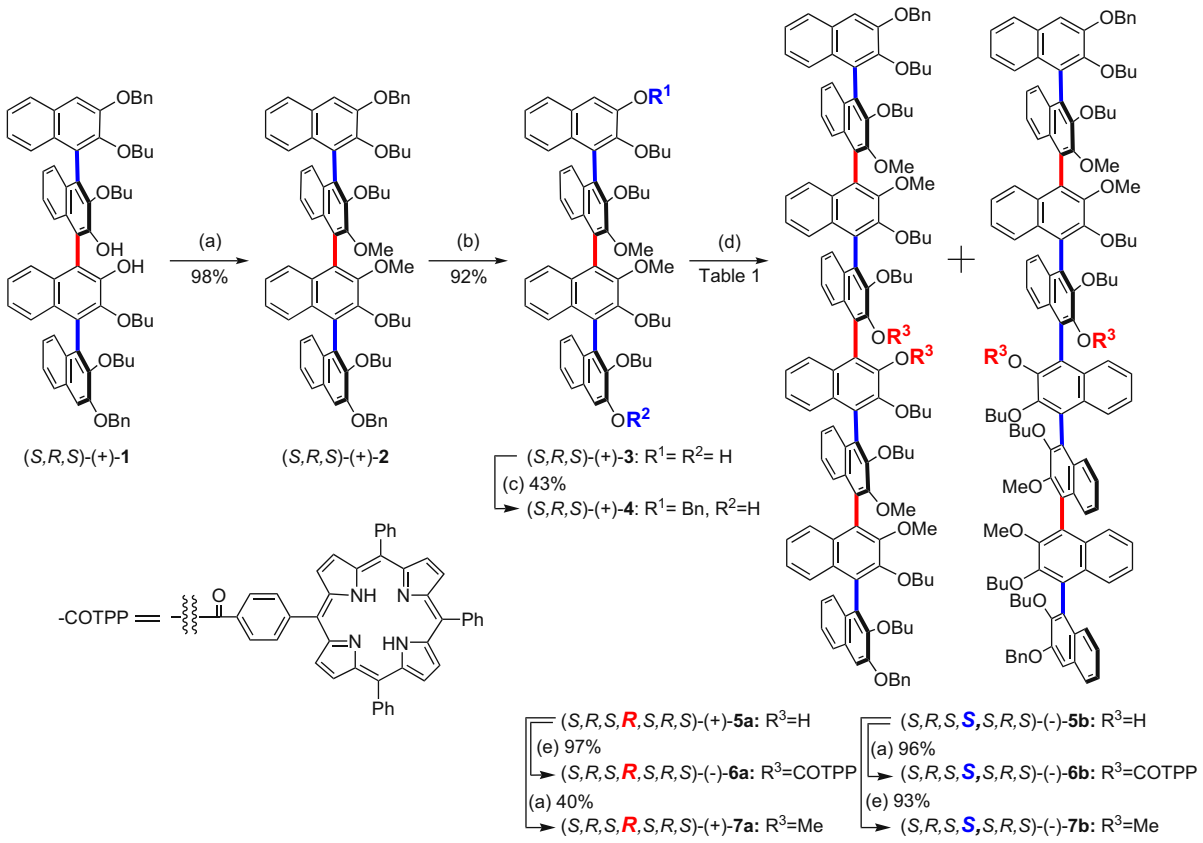

Scheme 1. Synthetic route for the octinaphthalenes. Conditions: (a) MeI, K_2CO_3; (b) Pd/C, H_2; (c) BnBr, K_2CO_3; (d) see Table 1; (e) $TPPCO_2H$, WSC, DMAP.

induction, and the substituent on the side chain controls the chirality.[5f] Thus,(1) when the all side chains were methoxy groups except top and bottom groups, the product was obtained through precipitation along with epimerization of the newly formed axis,(2) when *n*-butoxy groups or *tert*-butyl ester groups were present on the side chain, the homochiral product was generated under thermodynamic control, but (3) the kinetically controlled product was obtained for the substrate with an amide side chain. In all cases, quaternaphthalenes with homochiralities predominate over heterochiral derivatives.

Based on previous conditions, the coupling reaction was investigated under the following conditions: (*S*,*R*,*S*)-(+)-**4** (100 mg), 2.0 equiv of $CuCl_2$, and 2.5 equiv of amine in MeOH/CH_2Cl_2 (1.0 ml/1.0 ml) at 0 °C for 7 h. We initially investigated the effect of amines on the diastereoselectivity of coupling reactions of (*S*,*R*,*S*)-(+)-**4** (Table 1, entries 1–5). Despite the type of amine, (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b** prevailed over (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a**, indicating that the proximal axis from the reaction site induced the same absolute configuration at the newly formed axis ((*S*)-chirality brings (*S*)-chirality). Although the highest diastereoselectivity of *S*,*R*-alternating octinaphthalene was observed using di-*iso*-propylamine (entry 4), the reaction was too slow to apply to practical syntheses. Therefore, we chose di-*n*-propylamine as an amine (entry 5). This reaction was extremely sensitive to temperature; the reaction was negligible at −20 °C (entry 8), but at 20 °C (entry 6) the reaction proceeded smoothly without generating the desired *S*,*R*-alternating octamer, suggesting that the epimerization of the axis occurs easily and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b** is the thermodynamically favored product. A longer reaction time and

Table 1
The oxidative coupling conditions of (*S*,*R*,*S*)-(+)-**4**

Entry	Amine	Ratio[a] of **4**:**5a**[b]:**5b**[c]	Temp (°C)	Time (h)
1	*iso*-Propylamine	43:14:43	0	7
2	(*S*)-1-Phenylethylamine	90:2:8	0	7
3	*n*-Propylamine	100:0:0	0	7
4	Di-*iso*-propylamine	86:7:7	0	7
5	Di-*n*-propylamine	36:25:39	0	7
6	Di-*n*-propylamine	1:0:99	20	7
7	Di-*n*-propylamine	16:20:64	0	24
8	Di-*n*-propylamine	100:0:0	−20	7
9[d]	Di-*n*-propylamine	32:28:40	0	7
10[e]	Di-*n*-propylamine	32:20:48	0	7
11[f]	Di-*n*-propylamine	81:1:18	0	7
12[g]	Di-*n*-propylamine	45:21:34	0	1.5

The reactions were carried out under following conditions: (*S*,*R*,*S*)-(+)-**4** (100 mg), $CuCl_2$ (2.0 equiv), and amine (2.5 equiv) in MeOH/CH_2Cl_2 (1.0 ml/1.0 ml).
[a] Based on ^1H NMR measurements.
[b] Compound (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a**.
[c] Compound (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b**.
[d] MeOH/CH_2Cl_2 (0.5 ml/0.5 ml).
[e] MeOH/CH_2Cl_2 (0.67 ml/1.33 ml).
[f] MeOH/CH_2Cl_2 (1.33 ml/0.67 ml).
[g] $CuCl_2$ (10.0 equiv) and di-*n*-propylamine (12.5 equiv).

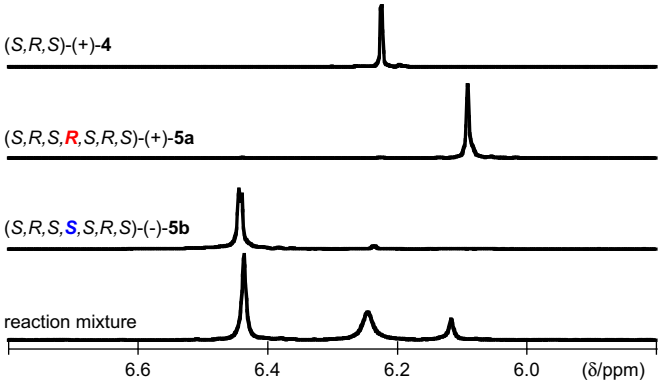

Figure 1. Partial ^1H NMR (400 MHz) spectra of oligonaphthalenes with the hydroxy groups in $CDCl_3$ at 20 °C (concentration of pure material is 2.56 mM).

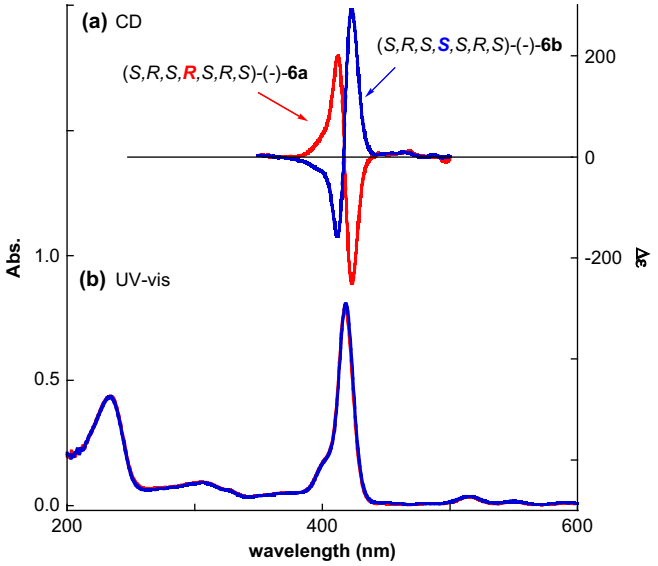

Figure 2. CD (a) and UV–vis (b) spectra of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(−)-**6a** (red) and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**6b** (blue). Conditions: CH_2Cl_2, 1.0×10^{-5} M, 25 °C, light path length=0.1 cm.

higher reaction concentration provided a high reaction conversion with a low selectivity of desired (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a** (entries 7 and 9). Even in the presence of a large excess of $CuCl_2$ (10 equiv) and di-*n*-propylamine (12.5 equiv), the diastereoselectivity did not improve (entry 12). Additionally, changing the proportion of mixed solvent was ineffective (entries 10 and 11). Hence, both thermodynamically and kinetically, the reaction provides (*S*,*R*,*S*,*S*,*S*,*R*,*S*) over (*S*,*R*,*S*,*R*,*S*,*R*,*S*) derivatives.

The absolute configuration of the binaphthalene moiety around the newly formed bond was unambiguously determined by the exciton-coupled CD method using two TPPs (tetraphenylporphyrins) as powerful excitons.[7] Figure 2 shows the UV and CD spectra of diastereomeric TPP-octinaphthalenes. The UV–vis spectra of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(−)-**6a** and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**6b** had nearly identical shapes and intensities. However, clear split Cotton effects due to chiral exciton coupling between the two TPPs were present in the CD spectra. The absolute configuration of the target axis of (−)-**6a**, which displayed negative first and positive second Cotton effects, was *R*. On the other hand, TPP ester (−)-**6b** shows positive first and negative second Cotton effects leading to the *S* absolute configuration of the newly formed axis.

We next investigated the properties of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)- and (*S*,*R*,*S*,-*S*,*S*,*R*,*S*)-octinaphthalenes as well as (*S*,*S*,*S*,*R*,*S*,*S*,*S*)- and (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-octinaphthalenes, which were synthesized in our previous studies.[5f,i] Table 2 summarizes the R_f values on TLC, $[\alpha]_D$, and ^1H NMR chemical shifts of the central hydroxy groups.

Table 2
The R_f values on TLC, $[\alpha]_D$, and ^1H NMR chemical shifts

	R_f value[a]	$[\alpha]_D$[b] (°C)	δ (ppm)[c]
(*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a**	0.19	+21 (20)	6.09
(*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b**	0.24	−2 (20)	6.44
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-(−)-**5c**	0.32	−81 (18)	6.04
(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-(−)-**5d**	0.47	−146 (18)	6.36
(*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**7a**	0.30	+29 (20)	—
(*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**7b**	0.43	−22 (20)	—
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-(−)-**7c**	0.49	−82 (20)	—
(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-(−)-**7d**	0.65	−137 (20)	—

[a] TLC on silica gel 60 F_{254} plates (0.25 mm, Merck, $CHCl_3/Et_2O$=100:1).
[b] For concentration, see Experimental section.
[c] ^1H NMR chemical shifts of the central hydroxy groups; 2.56 mM in $CDCl_3$ at 20 °C.

As the number of *R* configuration axes in octinaphthalenes increased, the R_f values decreased. Considering the polarities of each naphthalene unit, this tendency can be explained using (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**7a** as an example (Fig. 3). The dipole moments of the top naphthalene ring and that of the third naphthalene ring were parallel and coincident, and six parallel interactions were observed in this molecule. On the other hand, the six antiparallel interactions of the dipole moment occurred between every other naphthalene ring; therefore, (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-(−)-**7d** had a small polarity and showed a high R_f value. With regard to the specific optical rotation of the octinaphthalenes, as the number of *S* configuration axes increased, the specific optical rotation became more negative.

Finally, we investigated the CD and UV spectra of chiral octinaphthalenes **7a**–**d** (Fig. 4); Table 3 lists the spectral data (wavelength of maximum absorption (λ), molar absorption coefficient (ε), molar absorption coefficient per naphthalene unit (ε/unit), molar CD ($\Delta\varepsilon$), and molar CD per the difference between the numbers of *S* and *R* binaphthalene units ($\Delta\varepsilon/(S-R)$)).

Although, octinaphthalenes **7a**–**d** have similar shapes and intensities in the UV–vis spectra (Fig. 4b and Table 3, UV–vis), they display distinct differences in the CD spectra (Fig. 4a and Table 3, CD). As the number of *S* binaphthalene units increased, the intensity of the positive Cotton effect near 230 nm, which is ascribed to the positive exciton coupling between the transition moments parallel to the long axes of the naphthalene rings (^1B_b), increased with a slight red shift in wavelength of λ_1 (235 nm→239 nm). However, the intensity of the negative Cotton effect near 290 nm, which is generated by the negative exciton coupling between the transition moments parallel to the short axes of naphthalene rings (^1L_a) and those parallel to the long axes of adjacent naphthalene rings (^1B_b), increased without a shift in wavelength. As shown in Table 3, the values of $\Delta\varepsilon_2/(S-R)$ are almost constant (−6.1 to −6.3) indicating that the CDs of *S* and *R* binaphthalene units cancel each other, and the observed CD reflects the remaining chirality of the binaphthalene unit. For example, in the case of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-**7a**, the CD of three *S* and three *R* binaphthalene units cancel one another and therefore, the remaining one *S* binaphthalene unit governs the observed CD at 290 nm. The other isomer (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-**7b** has five *S* units and two *R* units, and hence the observed spectrum reflects the CD of the remaining three *S* units, i.e., three times stronger Cotton effect. The CDs of **7c** and **7d** can be similarly analyzed. The additivity correlation was thus clearly observed in the CDs of ^1L_a transition. On the other hand, the CD spectra of ^1B_b transition around 230 nm do not show any additivity correlation (Table 3).

In conclusion, we synthesized (*S*,*R*,*S*,*R*,*S*,*R*,*S*)- and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-octinaphthalenes via oxidative coupling of (*S*,*R*,*S*)-quaternaphthalene, and compared their R_f values on TLC, specific optical rotations, the ^1H NMR chemical shifts of the hydroxy groups, and CD spectra. A clear CD additivity between the intensity of the Cotton effect near 290 nm and the axial chirality of the binaphthalene units was observed. We are currently investigating the CD mechanism of these chiral oligonaphthalenes to clarify why the additivity correlation is observed for the ^1L_a transition, but not for the ^1B_b transition. Moreover, we are also studying new functions of these chiral compounds, including selective solubilization of carbon nanotubes.

3. Experimental

3.1. Compound (*S*,*R*,*S*)-(+)-2

A suspension of (*S*,*R*,*S*)-(+)-**1**[5f] (20.0 g, 19.2 mmol), K_2CO_3 (7.0 g, 50 mmol, 2.6 equiv), and methyl iodide (5.2 ml, 84 mmol, 4.4 equiv) in DMF (70 ml) was stirred for 3 h at 70 °C. The reaction mixture was then poured into a mixed solvent of ethyl acetate and water. The organic layer was separated and washed

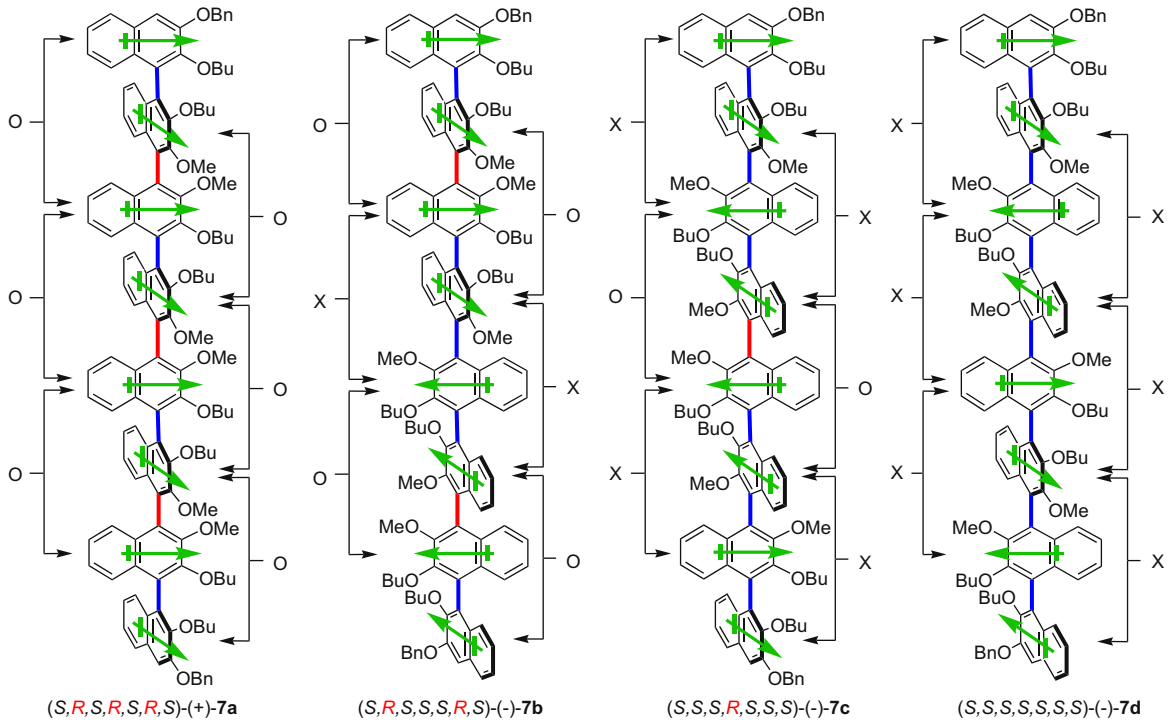

Figure 3. The dipole moments of each naphthalene units. The ○ denotes a parallel and × denotes an antiparallel between two naphthalenes.

successively with a hydrochloric acid solution, water (twice), and brine. After drying over magnesium sulfate, the solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (SiO_2 hexane/chloroform/ethyl acetate=20:3:1) to afford (*S*,*R*,*S*)-(+)-**2** (20.2 g, 98%): yellow powder; mp=131 °C; $[\alpha]_D^{20}$ +30 (*c* 0.91, $CHCl_3$); IR (KBr) 2957, 1455, 1371, 1246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.55 (t, *J*=7.2, 6H), 0.61 (t, *J*=7.2 Hz, 6H), 0.7–1.5 (m, 16H), 3.73 (s, 6H), 3.6–3.9 (m, 4H), 4.0–4.3 (m, 4H), 5.35 (s, 4H), 7.10–7.55 (m, 22H), 7.57 (d, *J*=7.8 Hz, 4H), 7.81 (d, *J*=8.2 Hz, 2H); HRMS calcd for $C_{72}H_{74}O_8$: 1066.5384. Found: 1066.5389. Anal. Calcd for $C_{72}H_{74}O_8$: C, 81.02; H, 6.99. Found: C, 80.88; H, 7.13.

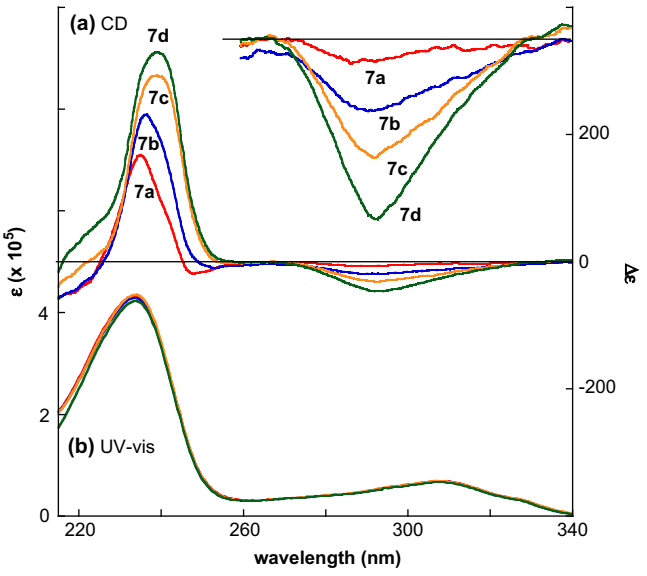

Figure 4. CD (a) and UV–vis (b) spectra of octinaphthalenes **7a**–**d**. Conditions: Dioxane/CH_2Cl_2=200:1, 20 °C, light path length=1.0 cm.

3.2. Compound (*S*,*R*,*S*)-(+)-3[5e]

A suspension of dibenzyl ether of (*S*,*R*,*S*)-(+)-**2** (150 mg, 0.141 mmol) and 10% Pd/C (7.5 mg) in THF (5 ml) was stirred at room temperature for 21 h under a H_2 balloon. The Pd/C was removed by filtration, and the solvent was evaporated in vacuo to afford crude of (*S*,*R*,*S*)-**3** as a white powder (124 mg, 99% yield). Crude (*S*,*R*,*S*)-(+)-**3** was directly used for the next step without further purification.

3.3. Compound (*S*,*R*,*S*)-(+)-4

A mixture of (*S*,*R*,*S*)-(+)-**3** (20.0 g, 23.2 mmol), benzyl bromide (2.9 ml, 24.4 mmol, 1.05 equiv), and K_2CO_3 (3.85 g, 24.4 mmol, 1.05 equiv) in DMF (200 ml) was stirred for 22 h at 70 °C. The reaction mixture was poured into a mixed solvent of ethyl acetate and water. The organic layer was separated and washed successively with a hydrochloric acid solution, water (twice), and brine. After drying over magnesium sulfate, the solvent was evaporated in vacuo to give a residue, which was

Table 3
UV–vis and CD data of octinaphthalenes **7a**–**d**

UV–vis	λ_1 (nm)	ε_1	ε_1/unit[a]	λ_2 (nm)	ε_2	ε_2/unit[a]
(*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**7a**	234	431,000	53,900	308	69,200	8650
(*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**7b**	234	429,000	53,600	307	68,700	8590
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-(−)-**7c**	234	435,000	54,400	307	68,700	8590
(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-(−)-**7d**	234	434,000	54,300	306	66,000	8250

CD	λ_1 (nm)	$\Delta\varepsilon_1$	$\Delta\varepsilon_1/(S-R)$[b]	λ_2 (nm)	$\Delta\varepsilon_2$	$\Delta\varepsilon_2/(S-R)$[b]
(*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**7a**	235	+168	+168	293	−6.3	−6.3
(*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**7b**	236	+231	+77	292	−19	−6.3
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-(−)-**7c**	239	+293	+59	292	−31	−6.2
(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-(−)-**7d**	239	+330	+47	293	−43	−6.1

Conditions: Dioxane/CH_2Cl_2=200:1, 20 °C, light path length=10 mm.
[a] Unit: number of naphthalene units.
[b] (*S*−*R*): number of *S* binaphthalene units−number of *R* binaphthalene units.

purified by column chromatography (SiO_2, hexane/chloroform/ethyl acetate=15:1:1) to afford (*S*,*R*,*S*)-(+)-**4** (9.7 g, 43%), over-reacted (*S*,*R*,*S*)-(+)-**2** (4.1 g 17%), and recovered (*S*,*R*,*S*)-(+)-**3** (5.6 g, 28%).

Compound (*S*,*R*,*S*)-(+)-**4**: yellow solid; mp=74 °C; $[\alpha]_D^{20}$ +37 (*c* 0.92, $CHCl_3$); IR (KBr) 3434, 2957, 1441, 1376, 1245 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.5–0.65 (m, 9H), 0.71 (t, *J*=7.4 Hz, 3H), 0.7–1.5 (m, 16H), 3.5–4.2 (m, 8H), 3.72 (s, 3H), 3.72 (s, 3H), 5.36 (s, 2H), 6.22 (s, 1H), 7.1–7.5 (m, 19H), 7.58 (d, *J*=7.3 Hz, 2H), 7.81 (d, *J*=8.2 Hz, 1H), 7.82 (d, *J*=7.8 Hz, 1H); HRMS calcd for $C_{65}H_{68}O_8$: 976.4914. Found: 976.4879. Anal. Calcd for $C_{65}H_{68}O_8 \cdot 0.5H_2O$: C, 79.16; H, 7.05. Found: C, 79.03; H, 7.02.

3.4. Compounds (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-5a and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-5b

To a solution of $CuCl_2$ (83 mg, 0.61 mmol) in methanol (3.0 ml), *iso*-propylamine (65 μl, 0.77 mmol) was added under an argon atmosphere in an ice bath. After 1 h, a solution of (*S*,*R*,*S*)-(+)-**4** (300 mg, 0.31 mmol) in dichloromethane (3.0 ml) was added, and subsequently stirred for 10 h. The reaction mixture was poured into a mixed solvent of 0.1 M hydrochloric acid solution, and chloroform. The organic layer was washed with a sodium hydrogen carbonate solution, water, and brine. It was then dried over sodium sulfate and evaporated to give a residue, which was purified by column chromatography (SiO_2, hexane/chloroform/ethyl acetate=8:3:1 then chloroform/diethyl ether=100:1) to successively afford to (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a** (50 mg, 17%) and (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-**5b** (203 mg, 68%).

Compound (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a**: yellow solid; mp=276 °C; $[\alpha]_D^{20}$ +21 (*c* 0.75, $CHCl_3$); IR (KBr) 3513, 2956, 1596, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.57 (t, *J*=7.3 Hz, 6H), 0.6–0.7 (m, 12H), 0.72 (t, *J*=7.3 Hz, 6H), 0.8–1.5 (m, 32H), 3.70–4.35 (m, 16H), 3.78 (s, 6H), 3.81 (s, 6H), 5.37 (s, 4H), 6.09 (s, 2H), 7.15–7.65 (m, 42H), 7.82 (d, *J*=8.2 Hz, 2H); MS (FAB^+) *m*/*z* 1951 (M^+). Anal. Calcd for $C_{130}H_{134}O_{16} \cdot 2CHCl_3$: C, 74.70; H, 6.55. Found: C, 74.92; H, 6.44.

Compound (*S*,*R*,*S*,*S*,*R*,*S*)-(−)-**5b**: yellow solid; mp=118 °C; $[\alpha]_D^{20}$ −2 (*c* 0.90, $CHCl_3$); IR (KBr) 3504, 2956, 1441, 1375, 1237 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.58 (t, *J*=7.8 Hz, 6H), 0.6–1.6 (m, 50H), 3.70–3.90 (m, 8H), 3.78 (s, 6H), 3.81 (s, 6H), 4.0–4.3 (m, 8H), 5.38 (s, 4H), 6.44 (s, 2H), 7.1–7.65 (m, 42H), 7.83 (d, *J*=8.2 Hz, 2H); MS (FAB^+) *m*/*z* 1951 (M^+). Anal. Calcd for $C_{130}H_{134}O_{16} \cdot 2CHCl_3$: C, 74.70; H, 6.55. Found: C, 75.04; H, 6.31.

3.5. Compound (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(−)-6a

To a solution of (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-**5a** (25 mg, 0.013 mmol) in CH_2Cl_2 (2.0 ml), $TPPCO_2H$ (42 mg, 0.064 mmol), WSC·HCl (192 mg, 0.13 mmol), and DMAP (31 mg, 0.27 mmol) were added and stirred at room temperature for 19 h. The reaction mixture was quenched with water, extracted with chloroform, washed successively with a 0.1 M hydrochloric acid solution, water, and brine. It was then dried over $MgSO_4$ and evaporated to give a residue, which was purified by recycling preparative HPLC (Japan Analytical Industry Co., Ltd. LC-908) connected to JAIGEL-1H (20×600 mm) and JAIGEL-2H (20×600 mm) under a 3.5 ml/min of flow rate with $CHCl_3$ detected by UV (254 nm) and RI (refractive index) to afford (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(−)-**6a** (40 mg, 97%): purple solid; mp=227 °C; $[\alpha]_D^{20}$ −2645 (*c* 0.053, $CHCl_3$); IR (KBr) 2955, 1743, 1586, 1440, 1347, 1244 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ −2.84 (s, 4H), 0.4–1.6 (m, 56H), 3.80–4.00 (m, 16H), 3.73 (s, 6H), 3.74 (s, 6H), 5.39 (s, 4H), 7.20–8.90 (m, 108H); MS (FAB^+) 3232 $(M+H)^+$. Anal. Calcd for $C_{208}H_{182}O_{18}N_8 \cdot CHCl_3$: C, 79.16; H, 5.74; N, 3.34. Found: C, 79.32; H, 5.90; N, 3.38.

3.6. Compound (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-6b

TPP ester (−)-**6b** was similarly synthesized: 98% yield; purple solid; mp=232 °C; $[\alpha]_D^{20}$ −3872 (*c* 0.43, $CHCl_3$); IR (KBr) 2954, 1744, 1597, 1348, 1243 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ −2.81 (s, 4H), 0.59 (t, *J*=7.3 Hz, 6H), 0.59 (t, *J*=7.3 Hz, 6H), 0.66 (t, *J*=7.3 Hz, 6H), 0.66 (t, *J*=7.3 Hz, 6H), 0.8–1.6 (m, 32H), 3.6–4.1 (m, 14H), 3.84 (s, 6H), 3.84 (s, 6H), 4.39 (m, 2H), 5.38 (s, 4H), 6.75–7.0 (br, 2H), 7.3–7.9 (m, 62H), 8.15–8.25 (m, 14H), 8.35 (d, *J*=8.0 Hz, 4H), 8.42 (brs, 4H), 8.55 (m, 4H), 8.72 (m, 4H), 8.9–9.0 (m, 8H); MS (FAB^+) *m*/*z* 3232 ($M+H^+$). Anal. Calcd for $C_{220}H_{190}N_8O_{18} \cdot 2CH_2Cl_2$: C, 78.34; H, 5.74; N, 3.29. Found: C, 78.35; H, 5.72; N, 3.33.

3.7. Compound (*S*,*R*,*S*,*R*,*S*,*R*,*S*)-(+)-7a

Compound (+)-**5a** was methylated with K_2CO_3 and methyl iodide in DMF to yield (+)-**7a**: 40% yield; yellow solid; mp=n.d. (decomp.); $[\alpha]_D^{20}$ +29 (*c* 0.75, $CHCl_3$); IR (KBr) 2935, 1453, 1375, 1244 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.49 (t, *J*=7.3 Hz, 6H), 0.56 (t, *J*=7.3 Hz, 6H), 0.63 (t, *J*=7.3 Hz, 6H), 0.64 (t, *J*=7.3 Hz, 6H), 0.7–1.5 (m, 32H), 3.6–4.2 (m, 16H), 3.70 (s, 6H), 3.71 (s, 6H), 3.74 (s, 6H), 5.30 (s, 4H), 7.10–7.55 (m, 32H), 7.52 (d, *J*=7.6 Hz, 4H), 7.76 (d, *J*=8.2 Hz, 2H); MS (FAB^+) *m*/*z* 1979 (M^+). Anal. Calcd for $C_{132}H_{138}O_{16} \cdot H_2O$: C, 79.33; H, 7.06. Found: C, 79.21; H, 7.11.

3.8. Compound (*S*,*R*,*S*,*S*,*S*,*R*,*S*)-(−)-7b

Compound (−)-**7b** was similarly prepared from (−)-**5b**: 93% yield; yellow solid; mp=128 °C; $[\alpha]_D^{20}$ −22 (*c* 1.17, $CHCl_3$); IR (KBr) 2934, 1442, 1375, 1238 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.5–0.8 (m, 18H), 0.7–1.5 (m, 32H), 3.6–4.2 (m, 16H), 3.78 (s, 6H), 3.78 (s, 6H), 3.78 (s, 6H), 5.37 (s, 4H), 7.10–7.55 (m, 32H), 7.59 (d, *J*=7.3 Hz, 4H), 7.82 (d, *J*=7.8 Hz, 2H); MS (FAB^+) *m*/*z* 1979 (M^+). Anal. Calcd for $C_{132}H_{138}O_{16} \cdot H_2O$: C, 79.33; H, 7.06. Found: C, 79.34; H, 7.05.

3.9. Compound (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-(−)-7c

Compound (−)-**7c** was similarly prepared from the corresponding precursor: 97%; white solid; mp=112 °C; $[\alpha]_D^{20}$ −82 (*c* 1.08, $CHCl_3$); IR (KBr) 2956, 1442, 1375, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.55 (t, *J*=7.3 Hz, 6H), 0.69 (t, *J*=7.3 Hz, 6H), 0.6–1.6 (m, 44H), 3.6–4.2 (m, 16H), 3.83 (s, 6H), 3.85 (s, 6H), 3.86 (s, 6H), 5.38 (s, 4H), 7.1–7.55 (m, 38H), 7.60 (d, *J*=7.3 Hz, 4H), 7.82 (d, *J*=7.8 Hz, 2H); MS (FAB^+) *m*/*z* 1979 (M^+). Anal. Calcd for $C_{132}H_{138}O_{16} \cdot 1.5H_2O$: C, 78.97; H, 7.08. Found: C, 79.00; H, 7.12.

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