Synthesis and properties of the chiral oligonaphthalenes

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Helical oligonaphthalenes were constructed by bottom-up synthesis (repeating dimerization reactions), their absolute configurations were determined by an exciton chirality method and their functions, such as energy transfer, are also reported.

Introduction

The binaphthalene skeleton represented by 1,1′-binaphthyl-2,2′-diol (**1**)[1] and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)[2] is unique in that it is possible to construct a large chiral space and to adjust the dihedral angle according to the outside environment. Therefore, the binaphthalene skeleton has made great contributions as a catalyst in synthetic chemistry and plays useful roles in supramolecular chemistry. However, the synthesis of ternaphthalene, in which one unit of naphthalene is added to binaphthalene or higher-order oligonaphthalenes, has received little attention.[3] 1,1′-Binaphthyl-2,2′-diol (**1**) and related compounds are shown in Fig. 1. Compounds that involve consecutive axial bonds are quite rare.

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Kazunori Tsubaki received his BS (1987, under the direction of Professor Zenichi Yoshida) and his Dr Pham (1999, under the direction of Professor Kaoru Fuji) from Kyoto University. After working at Fujisawa Pharmaceutical Company as a medicinal chemist (1987–1998), he then moved to the Institute for Chemical Research, Kyoto University and was appointed as an Assistant Professor. He was promoted to Associate Professor in 2005. His research interests are in supramolecular chemistry, especially oligonaphthalene chemistry, functional dyes based on phenolphthalein and homooxacalix[3]arenes, etc.

Kazunori Tsubaki

We have studied the synthesis and functions of oligonaphthalenes that are composed of a 2,3-dialkoxynaphthalene unit and are continuously connected at their 1,4-positions. All of the axial bonds that bridge naphthalene rings are chiral, and if the axial chirality can be controlled to be either *R* or *S*, it should be possible to construct a helical oligonaphthalene.[15] Moreover, if the axial chirality can be controlled to generate an *R*,*S*-alternating pattern, a unique molecule, in which hydrophilic oxygen functional groups are located in a line on one side of the molecule and hydrophobic naphthalene rings are lined up on the other side, should be synthesized (Fig. 2). In addition, while this structure should be rigid in the rod direction,[16] it should have some degree of flexibility around the axial bonds, and it should be possible to introduce various functional groups into the scaffold of phenolic hydroxy groups.

We have been examining a bottom-up method for constructing these compounds by a repeated dimerization reaction (*i.e.* 2-mer → 4-mer → 8-mer → 16-mer →..?!).[17] With this bottom-up method, oligonaphthalenes, in which all of the axial chiralities and the type and arrangement of side chains are controlled without a molecular weight distribution, can be constructed. In this paper, we introduce our recent results regarding the synthesis and functions of homochiral (helical) oligonaphthalenes.

Synthesis of the quaternaphthalenes

Regarding the dimerization of binaphthalene derivatives, several examples (including our data) have been reported and it has been shown that an efficient transfer of chirality from the axis to the newly formed axis did not occur even if chiral binaphthalenes were used as starting materials.[6,18,19] However, to achieve appropriate reaction conditions, the oxidative coupling of chiral **13a–d**[20,21b] took place under a classical combination of copper(II) chloride and amine to give the corresponding quaternaphthalenes with high diastereoselectivities (Scheme 1 and Table 1).[21]

In the case of **13a**, low diastereoselectivities were observed for **14a** in the presence of (*RS*) or (*R*)-**15** (entries 1 and 2), and in contrast, when (*S*)-**15** was used as an amine component, (*S*,*S*,*S*)-**14a** was obtained with high selectivity along with the generation of a large amount of precipitate (entry 3). Brussee *et al.*,[22] Kočovský *et al.*,[23] and Wulff *et al.*[24] reported the asymmetric synthesis of 2,2′-binaphthol based on diastereoselective precipitation accompanied by isomerization of the axis of 2,2′-binaphthol. Thus, racemic 2,2′-binaphthol was treated with copper(II) chloride and (*S*)-amphetamine to give a large amount of precipitate: (*S*)-binaphthol

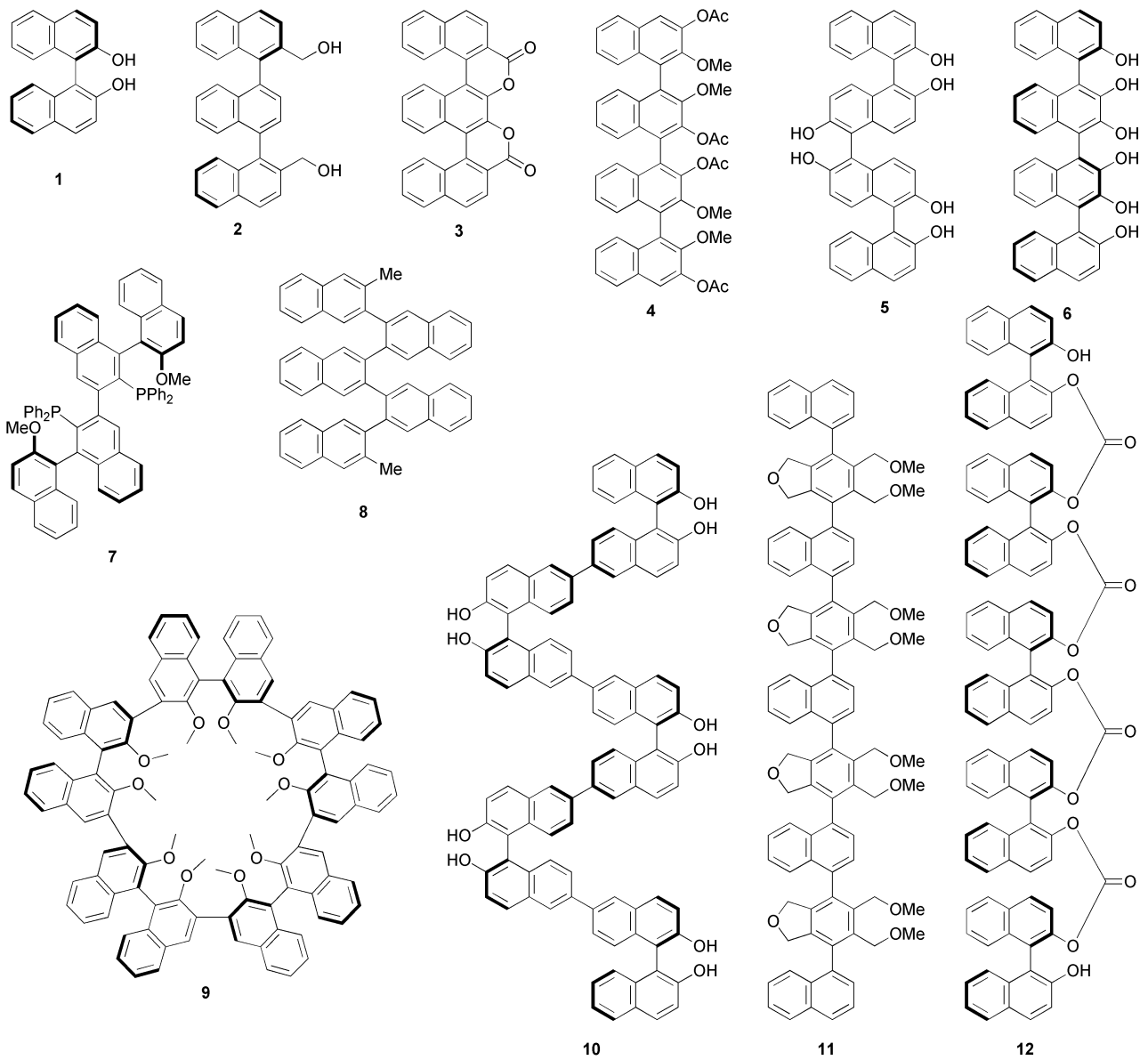


Fig. 1 1,1′-Binaphthyl-2,2′-diol and related compounds.[4–14]

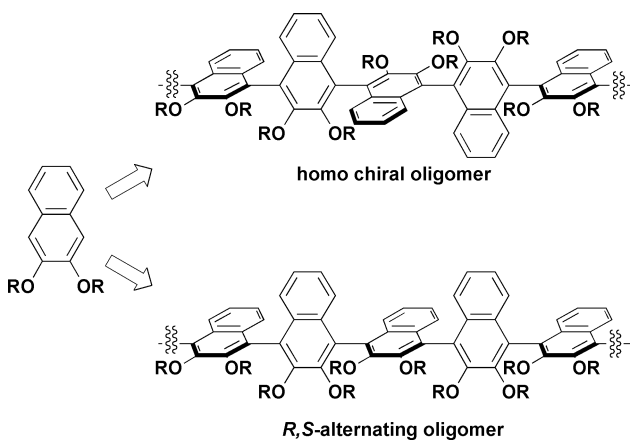
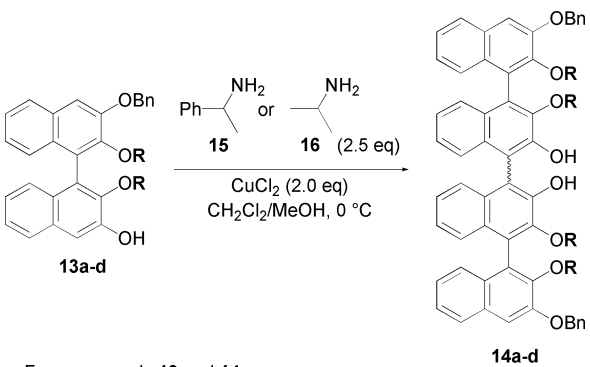


Fig. 2 Homochiral (helical) oligomer and *R*,*S*-alternating oligomer.



For compounds **13** and **14**
a: R = Me, **b**: R = *n*-Bu, **c**: R = CH_2CO_2t-Bu, **d**: R = $CH_2CON(Et)_2$

Scheme 1 Oxidative coupling of binaphthalenes **13a–d**.

Table 1 Oxidative coupling of binaphthalenes **13a–d**

Entry	Substrate	Amine	Major isomer[a]	Isolation[b]	Yield (%)[c]	De (%)[d]
1	(*S*)-**13a**	(*RS*)-**15**	(*S*,*S*,*S*)-**14a**	—	73	12
2		(*R*)-**15**		—	69	26
3		(*S*)-**15**		PF	87	75
4		(*S*)-**15**		P	58	93
5		(*S*)-**15**		F	15	17
6	(*S*)-**13b**	(*S*)-**15**	(*S*,*S*,*S*)-**14b**	—	77	62
7		(*RS*)-**15**		—	77	65
8	(*S*)-**13c**	(*R*)-**15**	(*S*,*S*,*S*)-**14c**	—	77	82
9	(*R*)-**13c**	(*RS*)-**15**	(*R*,*R*,*R*)-**14c**	—	54	79
10[e]		(*R*)-**15**		—	75	19
11		**16**		—	55	62
12	(*S*)-**13d**	(*RS*)-**15**	(*S*,*S*,*S*)-**14d**	—	96	75
13		(*R*)-**15**		—	81	75
14		(*S*)-**15**		—	89	70
15		**16**		—	94	81

[a] The absolute configuration of the major isomer was determined by transformation to the known compound or X-ray analysis. See ref. 21. [b] — = no precipitation; PF = without separation of the precipitate and filtrate; P = from precipitate; F = from filtrate. [c] Isolated yield. [d] Based on the isolated yields of corresponding diastereomers. [e] Reaction temperature = 0 °C to rt.

was obtained from the precipitate (87% yield, 91% ee) and (*R*)-binaphthol was obtained from the filtrate (13% yield, 12% ee). In the case of the homocoupling reaction of (*S*)-**13a** which has methyl groups on the side chain, high diastereoselectivity (75% de, entry 3) and the generation of precipitate were observed when only (*S*)-**15** was used as a ligand for copper. Therefore, the precipitate and filtrate were separated by filtration and each fraction was post-treated separately. As a result, (*S*,*S*,*S*)-**14a** was obtained from the precipitate with very high selectivity (58% yield and 93% de, entry 4). In contrast, (*S*,*S*,*S*)-**14a** was obtained from the filtrate as a main product with 15% yield and 17% de (entry 5). The results suggest that the induction of axial chirality in **14a** was due to diastereoselective precipitation with isomerization of the newly formed axial bond.

In substrates (**13b–d**) which possess side chains other than a methyl group, precipitation did not occur in the reaction. Moreover, high diastereoselectivities were induced by achiral isopropylamine (entries 11 and 15). Therefore, the induction of chirality in these substrates is likely caused by a pathway that is different from that of **13a**. Since the newly formed axis could be easily epimerized under the coupling reaction conditions based on the above data, conversion of the coupling reactions of **13b–d** as well as their diastereoselectivities were followed by high performance liquid chromatography (HPLC) and epimerization of the newly formed axis of the products **14b–d** under the same conditions was also monitored.

When (*S*,*S*,*S*)-**14b** and (*S*,*R*,*S*)-**14b** with *n*-butyl substituents were placed under oxidative coupling conditions ($CuCl_2$–±**15**), isomerization of the central axial bond easily took place and (*S*,*S*,*S*)-**14b** was obtained as a major product from both isomers. Monitoring by HPLC revealed that isomerization of the axis of both diastereomers proceeded smoothly and reached a plateau of 70% de within 4 h, which is almost the same value as that in the homocoupling reaction of (*S*)-**13b** (Fig. 3 (1)). On the other hand, in the coupling reaction of (*S*)-**13b**, the diastereoselectivity was around 50% de at the initial stage of the reaction and gradually increased to a final value of 68% de (Fig. 3 (2)). These data indicated that the pathway for the induction of chirality in the coupling reaction of **13b** was determined by differences in the thermodynamic stabilities of the corresponding **14b**.

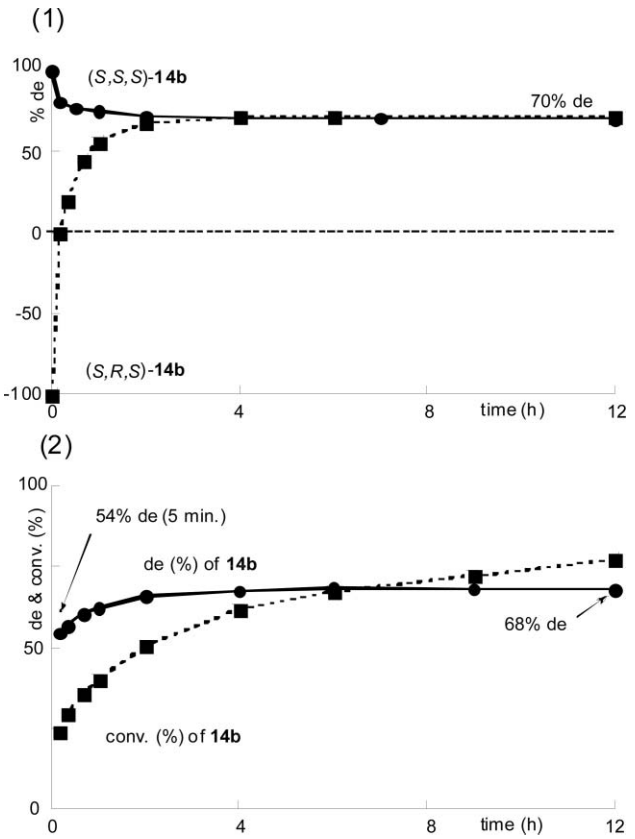


Fig. 3 Time course of the diastereoselectivities (1) with the epimerization of **14b** and (2) with the coupling reaction of **13b**. De and conversion were monitored and determined by HPLC.

The diastereoselectivity of the isomerization of quaternaphthalene (*R*,*R*,*R*)-**14c** and of the coupling reaction of (*R*)-**13c**, which has a *tert*-butoxycarbonylmethyl group on its side chain, were also examined. Although the isomerization of **14c** was slower than

that of **14b**, homochiral 4-mer (*R*,*R*,*R*)-**14c** was predominantly obtained in 70% de after equilibrium was achieved (Fig. 4 (1)). However, the diastereoselectivity of the dimerization of (*R*)-**13c** increased from 72% de at 5 minutes to 82% de at 6 h, began to fall at around 8 h and plateaued at 70% de after 25 h, which is comparable to the diastereoselectivity of the isomerization from 4-mer **14c** (Fig. 4 (2)). Overall, the diastereoselectivity of the homocoupling of **13c** was achieved through the thermodynamic stability of product **14c**, however the results suggested that the initial selectivity of the reaction under kinetic control was higher than that under thermodynamic control.

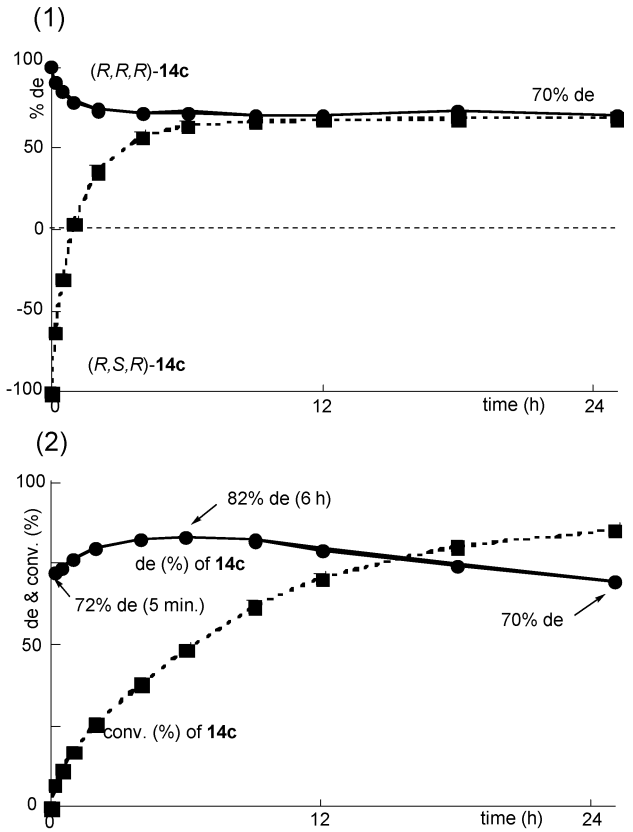


Fig. 4 Time course of the diastereoselectivities (1) with the epimerization of **14c** and (2) with the coupling reaction of **13c**. De and conversion were monitored and determined by HPLC.

In contrast to the former two cases, the direction of the isomerization of both (*S*,*S*,*S*)- and (*S*,*R*,*S*)-**14d** with a diethylaminocarbonylmethyl side chain was completely different, and heterochiral 4-mer (*S*,*R*,*S*)-**14d** was slowly obtained in about 20% de after 36 h (Fig. 5 (1)). At the early stage of the coupling reaction, homochiral (*S*,*S*,*S*)-**14d** was predominantly obtained in 74% de and this value was maintained for 12 h (when the conversion of the reaction was about 90%). Thereafter, the selectivity began to gradually fall and reached a plateau to give (*S*,*R*,*S*)-**14d** in 20% de after 88 h (Fig. 5 (2)). Thus, from a synthetic point of view, the diastereoselectivity of the coupling reaction of **13d** occurred under kinetic control.

As mentioned above, the pathways for the induction of chirality in the homocoupling reactions for **13a–d** were controlled by the substituent on the side chain, which did not seem to be associated

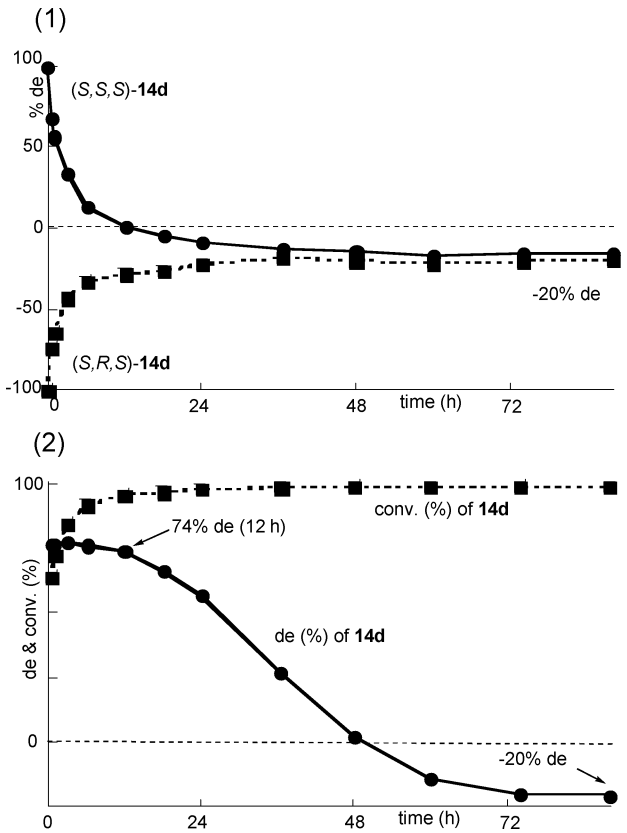


Fig. 5 Time course of the diastereoselectivities (1) with the epimerization of **14d** and (2) with the coupling reaction of **13d**. De and conversion were monitored and determined by HPLC.

with diastereoselectivity. Specifically, (1) when the side chain was a methyl group, the homochiral product was obtained through precipitation together with isomerization of the axis, (2) with *n*-butyl and *tert*-butyl ester on the side chain, homochiral 4-mer was generated under thermodynamic control, and (3) kinetically controlled product was obtained in the case of a substrate with an amide side chain. As a next step, we have been examining how many naphthalene rings can be connected using these three different pathways.

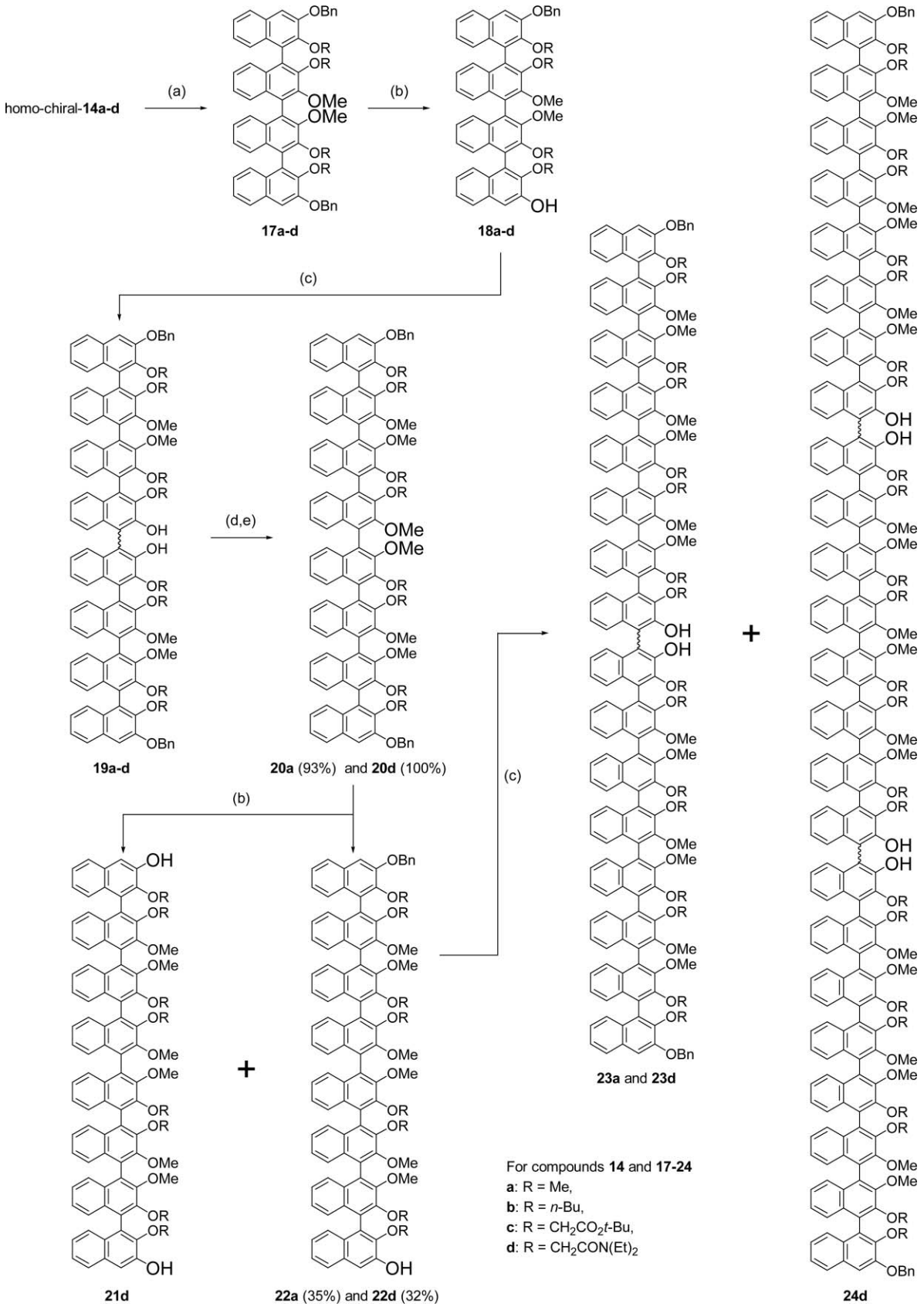
Synthesis of higher-order oligonaphthalenes

The synthetic route for higher-order oligonaphthalenes (~24-mer) starting from homochiral 4-mers **14a–d** is shown in Scheme 2.

After the central two hydroxy groups in homochiral 4-mers **14a–d** were converted to methyl ethers **17a–d** (64–100% yields), one of the benzyl ethers on the upper or lower naphthalene was removed to afford key intermediates **18a–d** for synthesis of the corresponding 8-mers **19a–d** (40–57% yields). The results with successively higher-order oligonaphthalenes are shown in Table 2.

Synthesis of higher-order oligonaphthalenes with methyl substituents (isomerization and precipitation)[21a]

In the homocoupling reaction of quaternaphthalene (*S*,*S*,*S*)-**18a**, which has methyl groups as side chains, extremely high diastereoselectivity (99% de) was observed with the generation of a large amount of precipitate to give the corresponding



Scheme 2 Synthesis of higher-order oligonaphthalenes. *Reagents and conditions*: (a) MeI, K_2CO_3 or (trimethylsilyl)diazomethane; (b) H_2, Pd/C; (c) $CuCl_2$, **15** or **16**; (d) separation of diastereomers; (e) MeI, K_2CO_3.

Table 2 Oxidative coupling of oligonaphthalenes **18a–d**, **22a** and **22d**

Entry	Substrate	Amine	Product[a]	Yield (%)[b]	De (%)[c,d]
1	(*S*,*S*,*S*)-**18a**	(*S*)-**15**	(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19a**	84	99
			(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**19a**	1.5	
2	(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**22a**	(*S*)-**15**	(*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**23a**	70	79
			(*S*,*S*,*S*,*S*,*S*,*S*,*S*,*R*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**23a**	8	
3	(*S*,*S*,*S*)-**18b**	(*RS*)-**15**	(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19b**	50	83
			(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**19b**	5	
4	(*S*,*S*,*S*)-**18c**	(*RS*)-**15**	(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19c**	45	80
			(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**19c**	5	
5[25]	(*S*,*S*,*S*)-**18d**	**16**	(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19d**	50	46
			(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**19d**	19	
6[25]	(*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**22d**[g]	**16**	(*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**23d**	11[e]	4
			(*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*)-**23d**	12[e]	
			(*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**24d**	9[f]	—
			(*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*)-**24d**	7[f]	—
			(*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*)-**24d**	25[f]	—

[a] The absolute configuration of the major isomer was determined by transformation into a known compound and then by comparing the amplitude in the circular dichroism (CD) spectrum of the corresponding diastereomers using the pyrene or tetraphenylporphyrin (TPP) method. [b] Isolated yield. [c] Based on the isolated yields of the corresponding diastereomers. [d] The reaction conditions were not optimized. [e] Yield was calculated after methylation of two hydroxy groups. [f] Yield was calculated based on diol **21d**. [g] Including 6% of (*R*,*R*,*R*,*R*,*R*,*R*)-**21d**.

8-mer **19a** in which seven axes were controlled to be *S*. After removal of the diastereomeric minor isomer (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**19a**, the two hydroxy groups at the center of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19a** were methylated, and deprotection of one benzyl group on the top or bottom naphthalene gave the coupling precursor (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**22a**. The dimerization of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**22a** proceeded smoothly with the formation of a precipitate to give the corresponding (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**23a** in high yield (78%) as well as high diastereoselectivity (79% de). Since 16-mer **23a** showed extremely poor solubility, experiments with further higher-order oligonaphthalenes with methyl substituents were abandoned.

Synthesis of higher-order oligonaphthalenes with *n*-butyl or *tert*-butyl ester substituents (thermodynamically controlled product)[21b]

Homocoupling of (*S*,*S*,*S*)-**18b** and (*S*,*S*,*S*)-**18c** also proceeded with high diastereoselectivity to give homochiral 8-mer (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19b** (55% yield, 83% de) and (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19c** (50% yield, 80% de). Since undesired lactonization between a hydroxy group and a *tert*-butyl ester moiety gradually took place, further attempts to obtain higher-order oligonaphthalene derivatives were discontinued. Regarding oligonaphthalene with an *n*-butyl side chain, the synthesis of further higher-order oligonaphthalenes starting from (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**19b** is now under investigation.

Synthesis of higher-order oligonaphthalenes with amide substituents (kinetically controlled product)[26]

A series of oligonaphthalenes with diethylaminocarbonylmethyl groups was examined. Oligonaphthalenes with an amide side chain are highly polar compared to other compounds with an *n*-butyl side chain or methyl side chain, and consequently purification and/or isolation was more difficult. Moreover, the reactivity of the homocoupling reaction decreases as the number of naphthalene units increases. Therefore, the coupling reactions of these substrates pose an inherent dilemma: when the conversion is raised by extending the reaction time, the diastereoselectivity decreases to give hetero-chiral oligonaphthalenes as the major diastereomer.

Homochiral-**18d** was treated with $CuCl_2$–**16** to give homochiral-**19d** in 69% yield and 49% de.[25] After separation of the corresponding (*R*,*R*,*R*,*S*,*R*,*R*,*R*)-**19d** by column chromatography, the central hydroxy groups of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**19d** were methylated, and subsequent deprotection of one benzyl group on the top or bottom naphthalene gave the coupling precursor (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**22d**. Since it was extremely difficult to separate **20d**, **21d**, and **22d**, the fraction of **22d** included about 6% of diol (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**21d**. When this mixture was used without further separation for the next oxidative dimerization reaction, a 16-mer (two kinds of diastereomer) that was the usual homocoupling product and an unexpected 24-mer (three kinds of diastereomer) that was due to the condensation of three components that included two axial bonds of unknown chirality, were obtained. After separation of the 16- and 24-mer products by gel permeation chromatography (GPC), two diastereomers of 16-mer were methylated and could be separated by recycling preparative HPLC into (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)- and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**23d**. In addition, 24-mers could also be separated by recycling preparative HPLC into three chiral 24-mers: (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-, (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)- and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**24d**.

Determination of the absolute configuration of oligonaphthalenes

When we considered two hydroxy groups that existed over newly formed axial bonds of unknown chirality, the absolute configuration of the axis was determined by introducing two excitons into the scaffolding hydroxy group and measuring the Cotton effect in the circular dichroism (CD) spectrum. The pyrene ring with absorption at about 350 nm was selected as an exciton. Since it was impossible to introduce 1-pyrenecarboxylic acid directly into the phenolic hydroxy group due to steric hindrance, two 1-pyrenebutyric acids were condensed to the hydroxy group.

The chirality of the target axis was then determined from the positivity/negativity in the CD spectrum at around 350 nm that was due solely to the pyrene ring.[21] However, since there is a separation between the axis and excitons, this method is not conclusive (Fig. 6).

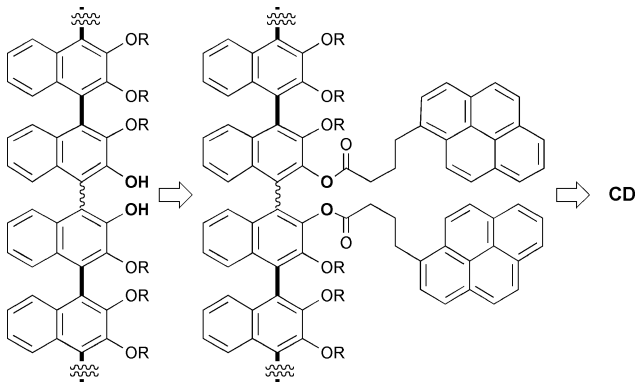


Fig. 6 Determination of absolute configuration based on the introduction of two pyrene rings.

The viewpoint was then changed from a target axial bond of unknown chirality to the whole oligonaphthalene, and powerful excitons were introduced into the top and bottom naphthalenes. Although the amplitude of exciton coupling is in inverse proportion to the square of the distance between excitons,[27] the intensity of CD could be detected by introducing powerful excitons. Tetraphenylporphyrin (TPP) was used as an exciton that shows large absorption.[28] Bis(TPP)-oligonaphthalenes **25a–28a** were synthesized from the corresponding dihydroxy groups on the top and bottom naphthalenes and TPP carboxylic acid using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (WSC·HCl) (Fig. 7).

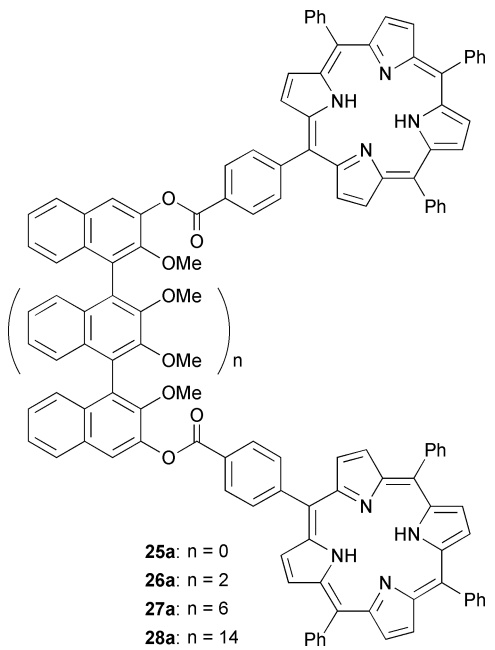


Fig. 7 Oligonaphthalenes with two TPPs **25a–28a**.

If the average dihedral angle of each naphthalene is 90°, the target axis of unknown chirality can be determined from the data in the CD spectrum that reflects the torsion of the whole molecule which includes an axis of unknown chirality (Fig. 8).[29]

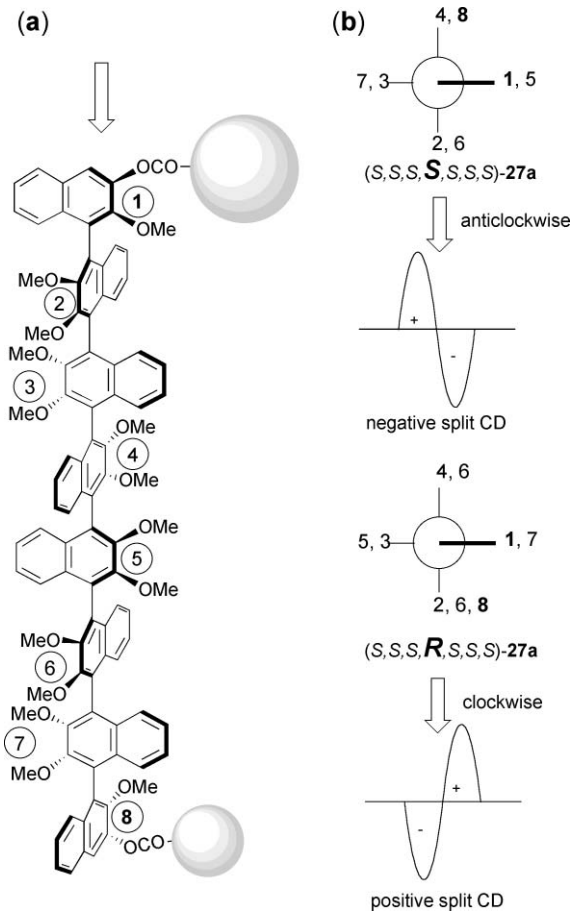


Fig. 8 Application of the exciton chirality method to oligonaphthalenes with two TPPs. (a) Structure of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**27a**. (b) Top-view of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**27a**. Each side chain is helically arranged every 90° in a clockwise direction. The two TPPs are oriented in an anticlockwise direction, which leads to a negative exciton-coupled CD spectrum.

Our assumption was valid, and we could determine the chirality of the target axis from the shape of the split type CD spectrum of the Soret band, as shown in Fig. 9.

Moreover, the amplitude of the CD was almost in inverse proportion to the square of the distance between each TPP on 4-mer, 8-mer, and 16-mer. A clear split Cotton effect was observed on 16-mers, in which the distance between the scaffolding oxygen and oxygen of the top and bottom naphthalene is about 66 Å. This is the longest example of an exciton–exciton interaction, and exceeds the longest exciton interaction (about 50 Å) that has been reported to date.[28b]

To determine the absolute configuration of diastereomeric 24-mers with two unknown axes, the above long-range CD method could not be used. Therefore, a more concise method to determine the absolute configuration of oligonaphthalenes was examined. Surprisingly, TPP carboxylic acid could be directly introduced into two phenolic hydroxy groups that existed over the newly-formed and chirality-unknown axial bond. Therefore,

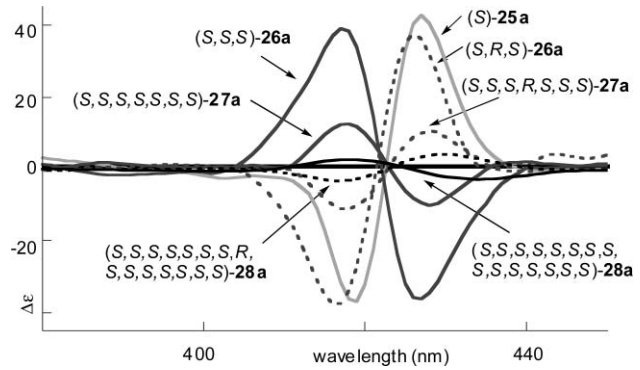


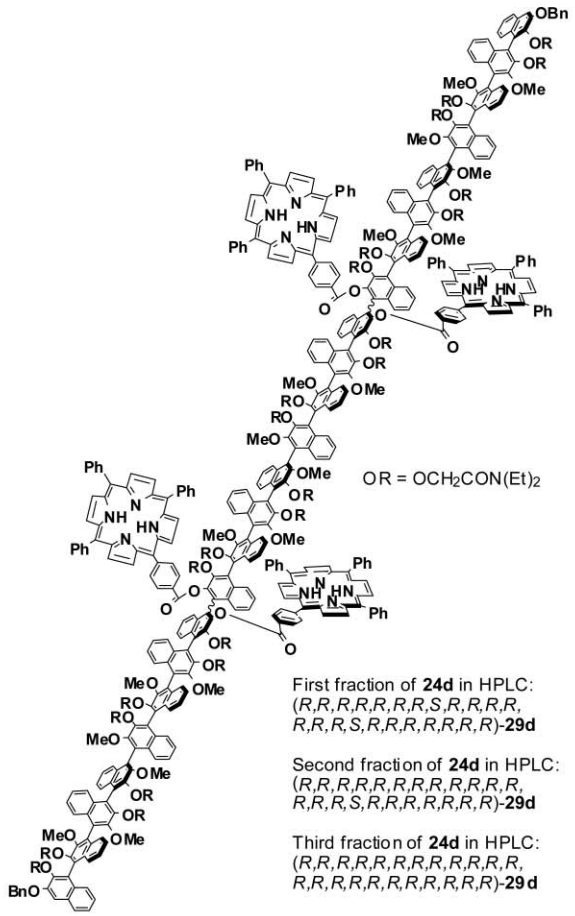
Fig. 9 CD spectra of **25a–28a**. Conditions: $CHCl_3$, 1×10^{-5} M, 25 °C, light path length = 1 mm.

this method was used to determine the chiralities of the three diastereomers of 24-mers. Compounds **29d**, in which four TPPs were introduced into the four hydroxy groups of the corresponding 24-mers **24d**, were prepared with a large excess of TPP carboxylic acid and WSC, and CD spectra were measured (Fig. 10). Among the three TPP 24-mers, the 24-mer (the first fraction of **24d** in recycling HPLC) with a large positive Cotton effect was *R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R* the 24-mer (the second fraction of **24d** in recycling HPLC) that showed a weak intensity of CD was determined to be *R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R* and the 24-mer (the third fraction of **24d** in recycling HPLC) with a large negative CD should be *R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*.

Energy transfer from oligonaphthalene skeleton to pyrene rings[30]

Using the systematically synthesized oligonaphthalenes, the quantum yields and energy transfer from the oligonaphthalene skeleton to the pyrene rings on the side chains were examined (Fig. 11). First, oligonaphthalenes with methyl side chains (**30**, **17a**, **20a** and **31a**) were selected as basic compounds among a variety of derivatives, and UV–vis and fluorescence spectra were measured (Fig. 12). In the UV spectra of **30**, **17a**, **20a**, and **31a**, as the number of naphthalene units increased, the absorption maximum at around 300 nm shifted slightly to the longer wavelength, and the intensity of absorption increased.

On the other hand, with regard to the absorption at around 240 nm, a red shift was not observed. The above phenomena were interpreted to indicate that the absorption at 240 nm is a transition of the longer direction of naphthalene (perpendicular to the axes of oligonaphthalenes), while the absorption at about 300 nm is considered to be a transition of the shorter direction of naphthalene (parallel to the axes of oligonaphthalenes). Thus, neighboring naphthalene rings have some interactions through the transition at around 300 nm. Next, in the fluorescence spectra of oligonaphthalenes excited at 310 nm, λ_{max} values at around 310 nm were also shifted to a longer wavelength. However the degree of the red shift was smaller than that in the UV spectrum. As a result, the Stokes' shift value decreased as the number of naphthalene units increased.



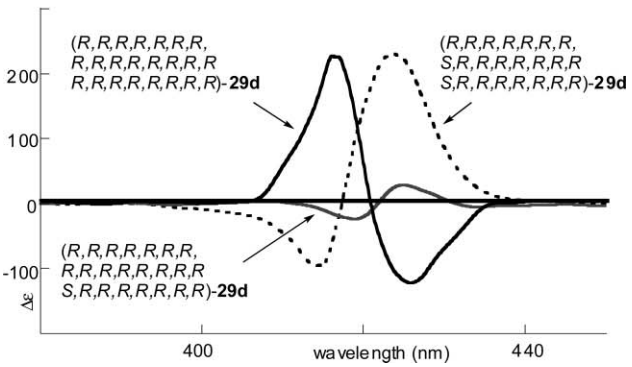


Fig. 10 TPP-24-mers **29d** and their CD spectra. Conditions: CH_2Cl_2, 1×10^{-5} M, 25 °C, light path length = 1 mm.

The quantum yields of the oligonaphthalenes depended on the number of naphthalene units: 20% (2-mer), about 60% (4-mers), and about 80% (8-mers and 16-mer). This tendency in the quantum yields is thought to reflect the fact that nonradiative transition is suppressed as the molecule becomes more rigid.

The UV spectra of oligonaphthalenes **32–35** with two pyrene rings on the central scaffolding hydroxy groups are the sum of absorption of the oligonaphthalene skeletons (**30**, **17a**, **20a**, and **31a**) and double the absorption of a methyl 1-pyrenebutyrate (**36**) side chain (Fig. 13). These results indicate that the interaction of the naphthalene ring and the pyrene ring is negligibly small in the ground state (Fig. 13, lower spectrum).

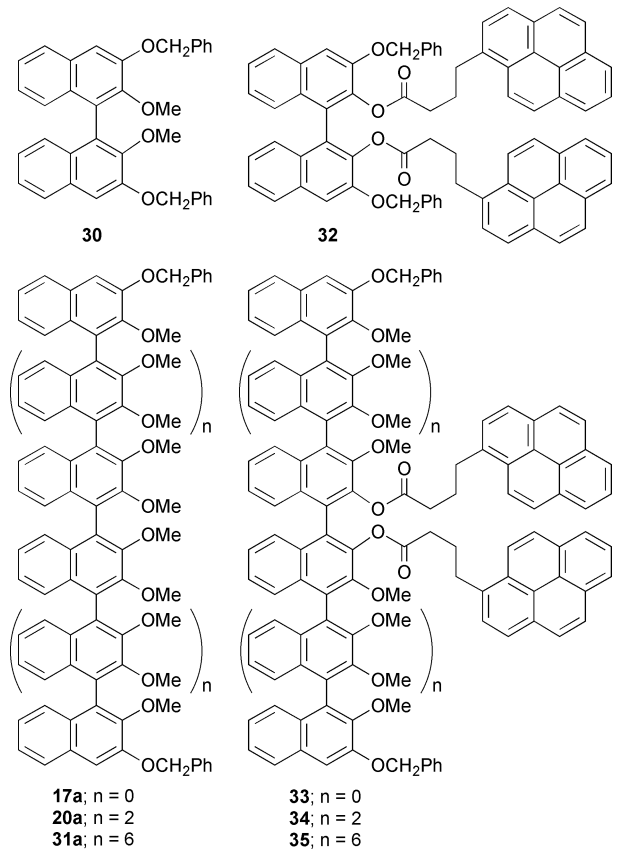


Fig. 11 Oligonaphthalenes with methyl groups and their pyrene adducts.

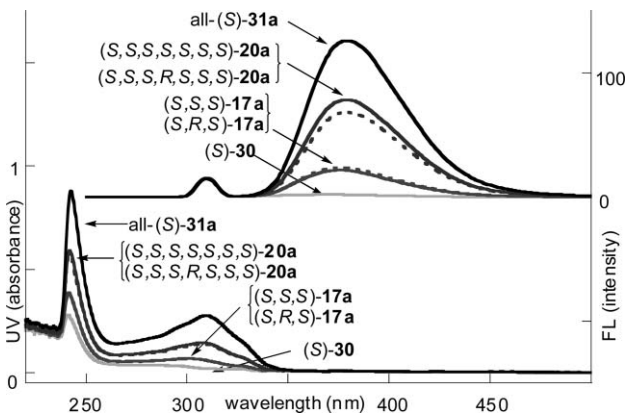


Fig. 12 (Upper) FL spectra of **30**, **17a**, **20a** and **31a**. Conditions: $CHCl_3$, 2×10^{-7} M, 25 °C, light path length = 10 mm, λ_{ext} = 310 nm. (Lower) UV–vis spectra of **30**, **17a**, **20a** and **31a**. Conditions: $CHCl_3$, 2×10^{-6} M, 25 °C, light path length = 10 mm.

Since methyl pyrenebutyrate (**36**) does not show absorption at around 310 nm, the absorption in this area for **32–35** originates only in the oligonaphthalene skeletons. Furthermore, the absorption of pyrene is overlapped from 320 nm to 360 nm with the fluorescence of oligonaphthalenes excited at 310 nm. As mentioned above, energy transfer may occur from the naphthalene rings (donor) to the pyrene rings (acceptor). In fact, when the naphthalene ring of **32–35** was excited at 310 nm, the fluorescence from pyrene rings (381, 399 nm from monomer, and 480 nm from excimer) was observed instead of that from the oligonaphthalene

Table 3 Quantum yields of oligonaphthalenes **30**, **17a**, **20a**, **31a** and **32–35**

Oligonaphthalene (–OMe)	Φ_{fl} [a]	Oligonaphthalene (–OPy)	Φ_{fl} [a]
(*S*)-**30**	0.20	(*S*)-**32**	0.18
(*S*,*S*,*S*)-**17a**	0.57	(*S*,*S*,*S*)-**33**	0.23
(*S*,*R*,*S*)-**17a**	0.62	(*S*,*R*,*S*)-**33**	0.24
(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20a**	0.83	(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**34**	0.24
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**20a**	0.76	(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**34**	0.25
All-(*S*)-**31a**	0.82	All-(*S*)-**35**	0.21

[a] The fluorescence quantum yields were determined by using a solution of quinine sulfate in 1 N H_2SO_4 as the reference standard (Φ_{fl} = 0.546).

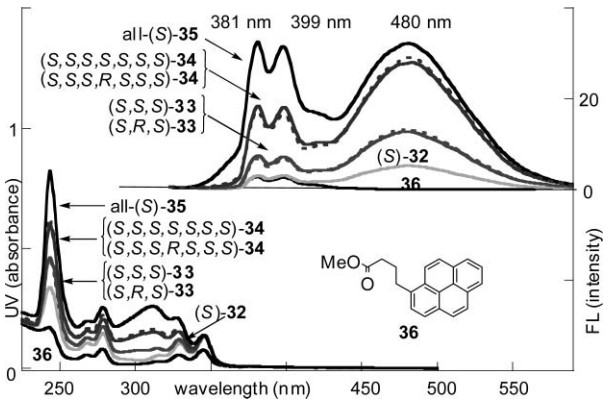


Fig. 13 (Upper) FL spectra of **32–36**. Conditions: $CHCl_3$, 2×10^{-7} M, 25 °C, light path length = 10 mm, λ_{ext} = 310 nm. (Lower) UV–vis spectra of **32–36**. Conditions: $CHCl_3$, 2×10^{-6} M, 25 °C, light path length = 10 mm.

skeleton. The quantum yields of the energy transfer of pyrene derivatives are summarized in Table 3.

Unlike in the series of oligonaphthalenes with a methyl side chain, the quantum yields of **32–35** with two pyrene rings were between 20–25%, regardless of the number of naphthalenes. Initially, we expected that the through-space energy transfer (Förster type) may occur from a randomly excited naphthalene ring to the pyrene ring. In this case, since energy transfer is in inverse proportion to the sixth power of the distance between the donor and acceptor, even if a naphthalene far from the pyrene was excited, the energy transfer from that excited naphthalene to the pyrene could be ignored. Therefore, the quantum yield of the energy transmission was expected to decrease as the number of oligonaphthalene units increased. However, the results indicate that a direct through-space energy transfer from a discrete naphthalene unit, which is excited by light (310 nm) irradiation, to the pyrene units did not occur, but rather reflects the following three steps: (1) an effective and fast through-bond energy transfer from an excited naphthalene unit to an adjacent naphthalene unit occurs. (2) Next, a through-space energy transfer (Förster type) from the naphthalene with a pyrene side chain to a pyrene unit eventually occurs. (3) Finally, monomer and/or eximer emission from a pyrene unit occurs. Thus, the nearly constant energy transfer quantum yields (20–25%) indicate that (1) the total energy transfer efficiency is determined by the second step, and (2) the intensity of the fluorescence emission from the pyrene groups (acceptor) increases in proportion to the number of naphthalene (donor) units. This interpretation is supported by the fact that the excitation wavelength (310 nm) is

the transition moment of a shorter direction of a naphthalene unit (perpendicular to the axes of oligonaphthalenes) (Fig. 14).

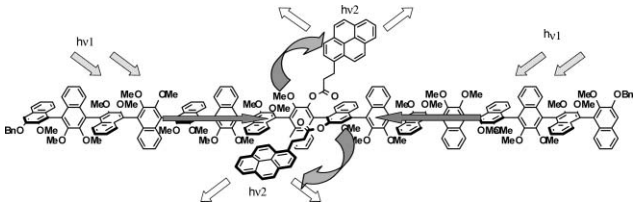


Fig. 14 Proposed energy transfer process from naphthalenes to pyrenes.

Conclusion

Homochiral oligonaphthalenes with various kinds of side chains were precisely constructed through a repeated dimerization reaction (bottom-up synthesis). After various trial-and-error processes, the absolute configuration of the newly formed axial bond could be determined by introducing two TPPs into the hydroxy groups over the target axis and by measuring the CD spectrum of the Soret band. In a 16-mer with two TPPs on the top and bottom naphthalenes, very long-range exciton interactions (about 66 Å) were detected. Optically active (helical or *R*,*S* alternating) oligonaphthalenes should be extremely unique skeletons that can be used to create more sophisticated functions by introducing various functional groups into the side chains. We are currently studying the development of specific oligonaphthalenes with interesting functions.[31]

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