Synthesis, stereochemistry and chiroptical properties of naphthylphenyl-substituted optically active oligosilanes with α,ω-chiral silicon centers

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Abstract

Novel naphthylphenyl-substituted optically active oligosilanes with α,ω-chiral silicon centers were synthesized. The absolute configuration of $(1R,2R)$-1,2-dimethyl-1,2-di(1-naphthyl)-1,2-diphenyldisilane (R,R)-**3**, one of the oligosilanes, was determined by X-ray diffraction, which gave a direct evidence for the retention and inversion stereochemistry of attacking silylanion and attacked chlorosilane. The intense $\pi-\pi$ interaction of aryl substituents on chiral silicon centers enhanced by $\sigma-\pi$ conjugation with oligosilane unit made it possible to clearly assign the absolute configuration and stable conformation of the optically active oligosilanes. The disilane (R,R)-**3** showed positive exciton chirality originated from $\pi-\pi$ interactions of $^1B_{b,Np}$ transition bands of two naphthyl chromophores on the adjacent silicon atoms. Contrary to this, $(1R,3R)$-1,3-di(1-naphthyl)-1,3-diphenyl-2-trimethylsilyl-1,2,3-trimethyltrisilane (R,R)-**5**, having silylene spacer with bulky trimethylsilyl group as branched substituent between two chiral centers, showed positive exciton chirality by interaction between red-shifted $^1L_{a,Ph}$ and $^1B_{b,Np}$ on the same silicon atom. $(1R,3R)$-1,3-Di(1-naphthyl)-1,3-diphenyl-1,2,2,3-tetramethyltrisilane (R,R)-**4**, which has dimethylsilylene group between two chiral silicon centers, showed two exciton chiralities, namely, positive chirality by $^1L_{a,Ph}$ and $^1B_{b,Np}$ on the same silicon atom, and negative chirality by two $^1B_{b,Np}$ on the adjacent silicon atoms. The intensified negative Cotton effect at 234 nm was caused by overlapping of Cotton effects of two exciton chiralities.

1. Introduction

Control of stereoregularity and optical activity of polymers have been challenging topics in the field of material synthesis [1]. Optical activity can be induced by configurational or conformational chirality or by both. Most conformationally induced chirality of polymers in solution is obtained and stabilized by rigid structure [2] or bulky substituents [3] at low temperature. In many cases, tacticity plays an important role to determine the conformational states of the polymer. This is considered also true for polysilanes.

Conformation, controlled by tacticity, is one of the important factors to determine the electroptical behavior of the polysilanes [4]. Relation between induced conformation of silicon backbone and optical property has been usually studied on peralkyl poly- or oligosilanes due to the perturbation of electronic structure of silicon main chain by aryl substituents. Large optical activity is observed by incorporation of chiral alkyl substituents in the middle [5] or terminal group [6] of polysilanes, which induces ordered conformation of the main chain. σ-Conjugation properties along the polysilanes main chain permit a relatively straightforward analysis of the helix-property-functionality relationship

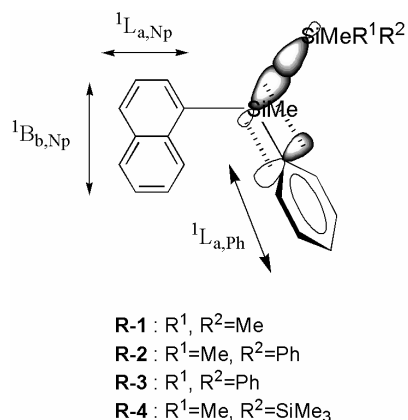* Corresponding author. Tel.: +81-761-51-1630; fax: +81-761-51-1635.
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[7]. Applications as chiral sensors [8] and chiroptical devices [9] are suggested.

Meanwhile, it has been pointed out that aryl-substituted polysilanes, with high glass transition temperature and thin film forming ability, have high potential as high hole mobility [10], photochemical hole burning [11], and electroluminescence materials [12]. Recently, conformationally optically active aryl-substituted polysilanes were reported [13]. The origins of the red-shift in electronic spectra are considered as combined effect of interaction between backbone σ and substituted phenyl π ring orbitals, and elongation of the bond length of the silicon backbone caused by steric effect of aryl substituents.

On the other hand, perfectly stereoregular polysilanes have not been synthesized yet, and there is no report on the optical activity derived from the chiral silicon centers of the main chain, either. Recently, we reported on chiroptical properties of oligosilanes with naphthylphenyl-substituted single chiral silicon center (Scheme 1) by circular dichroism (CD) exciton chirality method [14]. The $^1L_{a,Ph}$ transition of phenyl group on chiral silicon center was shifted to longer wavelength by σ–π conjugation with disilane linkage, and appeared at clearly assignable wavelength, which made it possible to determine the absolute configuration of the oligosilanes. Meanwhile, the phenyl substituents on achiral silicon center, regardless of their electronic property, did not affect the resultant CD sign because of long chromophoric distance.

Although a few optically active oligosilanes with a single chiral silicon center were reported [15], optically active oligosilanes with two or more chiral silicon centers have not been reported so far, due to synthetic difficulty. This report shows, firstly, the synthesis of these oligosilanes with two chiral silicon centers, and, secondly, the effect of π–π interaction of aromatic substituents on chiral silicon centers on chiroptical properties of the oligosilanes. These compounds are expected to act as very important model compounds for stereochemical analysis of σ–π conjugated polymers with chiral disilane units, as well as polysilanes with many chiral silicon centers.

2. Results and discussion

2.1. Absolute configuration of the product between (S)-**1** and (S)-**2**

The reaction between (S)-methyl(1-naphthyl)phenylsilyllithium [16] (S)-**1** (82% ee) and (S)-methyl(1-naphthyl)phenylchlorosilane [17] (S)-**2** gave two peaks in 7:3 ratio detected by UV. CD detects only one peak (Fig. 1(a) and (b)). This indicates that the peak at 42 min is reasonably assigned to (R,S)-**3**. The (R,S)-**3** is considered to stem mainly from side-reaction of (S)-**1** with (R)-methyl(1-naphthyl)phenylsilyltrimethylstannane (R)-**SiSn** (Scheme 2, Eq.(2)), as well as from the reaction of (S)-**2** and (R)-**1** contained as the minor enantiomer in the original (S)-**1**. The reaction of pure (S)-**1** and (S)-**2** is considered to give the optically pure compound, corresponding to the first peak in Fig. 1. The first peak was separated, and elucidated as (R,R)-**3** by X-ray diffraction (XRD) as shown in Fig. 2, which confirmed retention and inversion for silicon stereocenters of silyllithium (S)-**1** and chlorosilane (S)-**2** in the nucleophilic substitution reaction [17]. This reaction mechanism is also suggested in our previous report [14].

HPLC of the products from dimethyldichrolosilane with (S)-**1** (82% ee) (Scheme 2, Eq. (4)) gave two well separated peaks in the ratio of 88:12. The second peak is not active in CD detection. Judging from the result of stereochemistry on (R,R)-**3**, it is reasonably concluded that the major product is (1R,3R)-1,3-di(1-naphthyl)-1,3-diphenyl-1,2,2,3-tetramethyltrisilane (R,R)-**4**. Selectivity in the formation of (1S,3S)-1,3-di(1-naphthyl)-1,3-diphenyl-2-trimethylsilyl-1,2,3-trimethyltrisilane (S,S)-**5** from 1,1-dichloro-1,1,2,2-tetramethyldisilane [18] and (R)-**1** (ca. 86% ee) (Scheme 2, Eq. (5)) is 92:8, a little
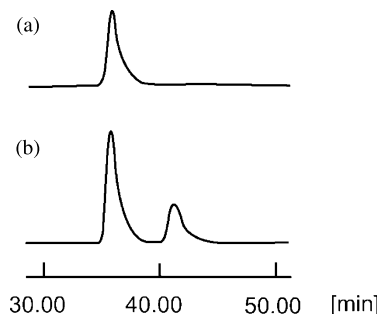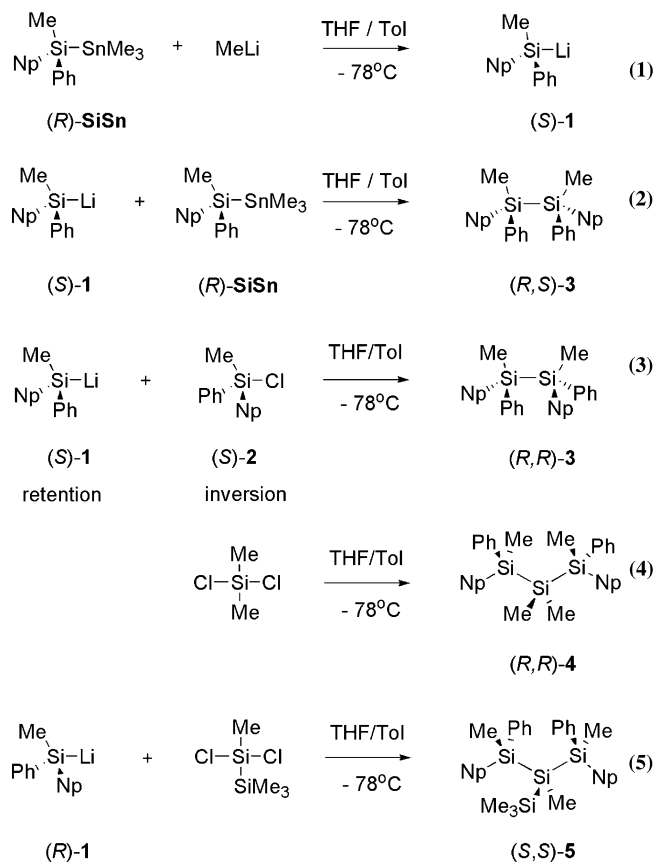
Scheme 1. Transition moments of naphthylphenyl-substituted chiral silicon center.

R-1 : R^1, R^2=Me
R-2 : R^1=Me, R^2=Ph
R-3 : R^1, R^2=Ph
R-4 : R^1=Me, R^2=SiMe$_3$

Fig. 1. HPLC of the products from (S)-**1** and (S)-**2** detected by (a) CD (b) UV.

Scheme 2. Synthetic routes of optically active oligosilanes (R,R)-**3**, (R,R)-**4** and (S,S)-**5**.
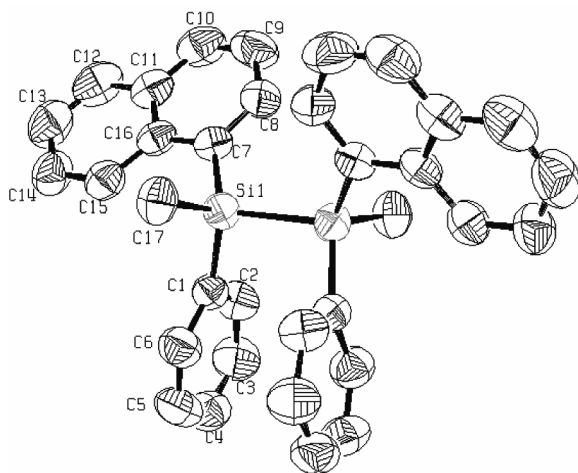

Fig. 2. Single crystal structure of (R,R)-**3**.

higher than the case of (R,R)-**4**. A little steric hindrance might be operating in the formation of (S,S)-**5**.

2.2. NMR of (R,R)-4 and (S,S)-5

In ^{1}H-NMR, two methyl groups on silicon atoms in (R,R)-**4** appeared as two singlets in the ratio of 1:1 at δ

0.35 on achiral central silicon and 0.42 ppm on chiral silicon atoms as expected. ^{29}Si-NMR showed two singlets in the ratio of 2:1 at δ −17.78 of chiral silicon and δ −45.38 of central silicon atom [19].

^{1}H-NMR of (S,S)-**5** showed basically four methyl singlets at δ −0.14 of the Me_3Si group, 0.47 of central silicon atom, 0.68 and 0.53 in the ratio of 1:1 of chiral silicon atoms. ^{29}Si-NMR showed two singlets at δ −12.72 and −14.37 of two pairs of chiral silicon atoms split by the presence of prochiral central silicon atom, a singlet of the prochiral central silicon atom at δ −84.01, and a singlet of silicon on the Me_3Si group at δ −11.28. ^{13}C-NMR of oligosilane (R,R)-**3**, (R,R)-**4**, and (S,S)-**5** showed the peaks at reasonable positions for each stereoisomer.

2.3. Spectroscopic study by UV, circular dichroism, and fluorescence

The absorption spectra of (R,R)-**3**, (R,R)-**4**, (R,R)-**5** and (S,S)-**5** in cyclohexane as non-polar solvent are presented in Fig. 3 and Table 1, which showed intense [1]$B_{b,Np}$ (ca. 227 nm) and [1]$L_{a,Np}$ transition band (ca. 287 nm) of naphthyl chromophore and broad shoulder peaks assignable to [1]$L_{a,Ph}$ transition band (ca. 240 nm) of σ−π conjugated phenyl group [20]. These results showed similar trends with naphthylphenyl-substituted oligosilanes with single chiral silicon center (Scheme 1) [14]. (R,R)-**4** and (R,R)-**5** showed more intense shoulder peak at around about 240 nm, compared with (R,R)-**3**, which can be understood as the enhanced σ−π conjuga-

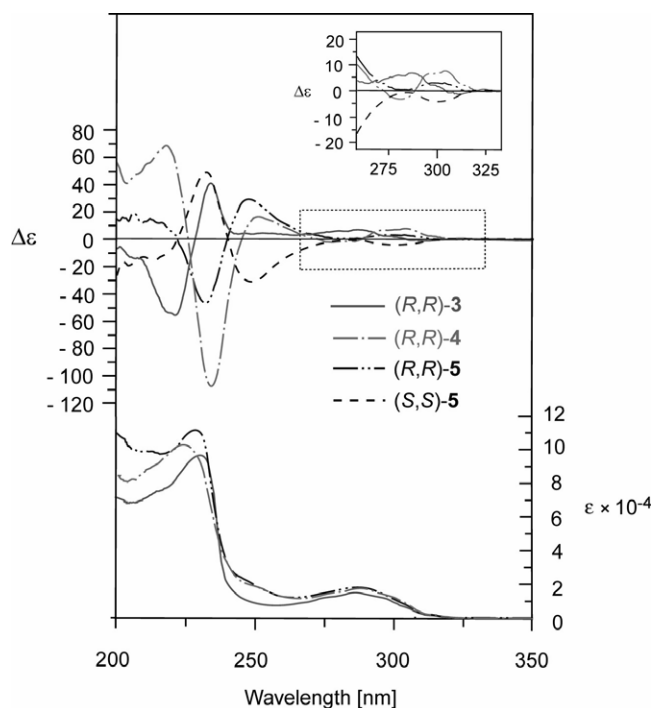Fig. 3. CD and UV Spectra of (R,R)-**3**–(R,R)-**5** and (S,S)-**5**.

Table 1
The UV, CD, and FL data of optically active oligoslianes [a]

Entry	Absorption maxima nm(ε)	CD exciton coupling $\lambda_{ext}(\Delta\varepsilon)$		Fluorescence [b]	
				λ_{max}^{LE}/nm [c]	λ_{max}^{Ex}/nm [d]
(R,R)-**3**	227.0(96 470) 286.0(15 220)	242.6(+4.2) 233.9(+40.9) 221.2(−55.7)	287.5(+6.9)	331.4, 341.0	399.0
(R,R)-**4**	224.5(103 640) 288.0(17 850)	251.2(+16.5) 234.2(−107.8) 217.6(+68.5)	304.2(+8.0) 277.2(−2.0)	332.2, 343.0	410.0
(R,R)-**5**	227.0(112 450) 287.5(18 240)	246.8(+29.3) 232.3(−46.6)	298.4(+3.5)	331.2, 340.6	405.0
(S,S)-**5**	227.0(114 150) 287.5(18 540)	248.0(−29.8) 232.2(+45.9)	300.5(−3.2)	–	–

[a] In cyclohexane at room temperature.
[b] Excitation at 287 nm.
[c] Locally excited state emission.
[d] Excimer or charge transfer.

tion effect by elongation of Si–Si σ-bond. It is interesting to note that the vibrational fine structures of $^1L_{a,Np}$ transition band around 280 nm in (R,R)-**3**–(R,R)-**5** are more broadened than those with single chiral silicon center. This change suggests the interaction of two naphthyl chromophores in the ground state [21]. Furthermore, a little blue-shift of $^1B_{b,Np}$ of (R,R)-**4** relative to that of (R,R)-**3** and (R,R)-**5** also showed the existence of an interaction between two naphthyl chromophores in (R,R)-**4** [22,23].

CD spectrum of (R,R)-**3** exhibits clear positive exciton chirality with positive first and negative second Cotton effects at $\lambda_{ext} = 233.9$ nm ($\Delta\varepsilon = +41.0$) and 221.2 nm ($\Delta\varepsilon = -55.8$). Amplitude of the CD exciton coupling is proportional to the square of absorption coefficient ε, the projection angle, and the distance between the two chromophores [24]. If a disilane possess two naphthyl-phenyl-substituted chiral silicon centers, the π–π interaction between aryl substituents on two silicon atoms should be affected by change of the absorbance, the projection angle and distance between the chromophores. It can be expected to obtain more precise information on the configurational or conformational stereochemistry of the optically active disilanes by analyzing such interaction. The position of the zero line intersection flanked by two Cotton effects is almost fixed at 226–228 nm, which is close to UV absorption maximum position ($\lambda_{max} = 227.0$ nm) of $^1B_{b,Np}$ longitude transition. This positive exciton chirality is considered to originate form exciton coupling between two $^1B_{b,Np}$s on adjacent silicon chiral centers. The exciton coupling between $^1L_{a,Ph}$ and $^1B_{b,Np}$ on the same chiral silicon center, which was clearly seen as positive exciton chirality in **R1**–**R4** (Scheme 1) [14], seems to be overlapped and hidden under the intense exciton coupling between two $^1B_{b,Np}$s on adjacent silicon chiral centers,

because naphthyl chromophore has intense ε than phenyl chromophore. Broad positive Cotton effect with absorption maximum at 287 nm, apparently without exciton coupling, seems to be related to the interaction of $^1L_{a,Np}$ transition bands of two naphthyl chromophores on adjacent silicon chiral centers. However, it was difficult to obtain further information from the broad Cotton effect.

Introduction of simple dimethylsilylene group or bulky [(methyltrimethylsilyl)methyl]silylene spacer group between two chiral silicon atoms is of interest to obtain the information on the spatial interaction between the chromophores on two chiral silicon atoms. (R,R)-**5** with branched [(methyltrimethylsilyl)methyl]silylene showed a simple positive exciton chirality at around 240 nm with positive first and negative second Cotton effects, $\lambda_{ext} = 246.8$ nm ($\Delta\varepsilon = +29.38$) and 232.3 nm ($\Delta\varepsilon = -46.6$). The positive first Cotton effect originates from red-shifted $^1L_{a,Ph}$, and negative second Cotton effect from $^1B_{b,Np}$ in $^1L_{a,Ph}$ and $^1B_{b,Np}$ exciton coupling. It was shown that $^1B_{b,Np}$ is not shifted significantly by the connection with oligosilane [14]. Almost not seen exciton coupling between two $^1B_{b,Np}$ transitions in (R,R)-**5** can be understood as the result of longer chromophoric distances between two naphthyl groups caused by the existence of silylene spacer and steric hindrance of trimethylsilyl branched group. The positive exciton coupling with zero intersection at around 287 nm is considered to originate from interaction between two $^1L_{a,Np}$ transition bands on two silicon chiral centers. Corresponding (S,S)-**5** showed the mirror image of (R,R)-**5** in CD spectra.

Compared with (R,R)-**5**, (R,R)-**4** exhibits a little complex Cotton effects by the overlap of two exciton chiralities, namely, positive chirality with zero intersection at around 245 nm and negative chirality at around

226 nm. The positive exciton chirality has the positive first ($\lambda_{ext} = 251.2$ nm, $\Delta\varepsilon = +16.6$) and negative second Cotton effect ($\lambda_{ext} = 234.2$ nm), reflecting the exciton coupling between red-shifted $^1L_{a,Ph}$ and $^1B_{b,Np}$, similarly to (R,R)-**5**. The negative exciton chirality has negative first ($\lambda_{ext} = 234.2$ nm) and positive second Cotton effect ($\lambda_{ext} = 217.6$ nm, $\Delta\varepsilon = +68.5$), reflecting the exciton coupling between two $^1B_{b,Np}$s. The intensified negative Cotton effect ($\Delta\varepsilon = -107.8$) at 234.2 nm was caused by overlapping of Cotton effects of two exciton chiralities. The positive exciton chirality between two $^1L_{a,Np}$s on the two silicon chiral centers with zero intersection at around 287 nm showed more clear exciton coupling than (R,R)-**5**, which can act as a clue to predict a preferred conformation, because $^1L_{a,Np}$ has a single rotational transition moment along axis composed by α-carbon of naphthyl and chiral silicon atom, contrary to that $^1B_{b,Np}$ having orthogonal transition direction has various rotational transition moments.

Since (R,R)-**3**, (R,R)-**4**, and (R,R)-**5** are acyclic structures, the resulting CD spectra will represent an average of the spectra reflecting the contribution of each individual conformation [25]. Three possible rotational conformation of (R,R)-**3** is exemplified in Fig. 4. Among three conformers, conformer (a) is considered to be the most stable and preferred, because of the least steric hindrance between two naphthyl and two phenyl groups. Namely, in conformer (a), two naphthyl groups are in gauche relation, but are apart from two phenyl groups in another gauche relation. On the other hand, in both conformers (b) and (c), two naphthyl and two phenyl groups constitute a contiguous gauche relation. It will be reasonable to consider that (a) is the preferred rotational conformer of (R,R)-**3**.

Amplitude of exciton coupling between two $^1B_{b,Np}$s of (R,R)-**3** increased as decreasing temperature (Fig. 5), which might indicate the increase of the population of conformer (a). A little shoulder peak appeared at around 240 nm by decreasing the temperature is considered as the positive Cotton effect of the positive exciton coupling between $^1L_{a,Ph}$ and $^1B_{b,Np}$ on the same chiral silicon center, which was hidden under the intense exciton coupling between two ^1B_bs at higher temperature.
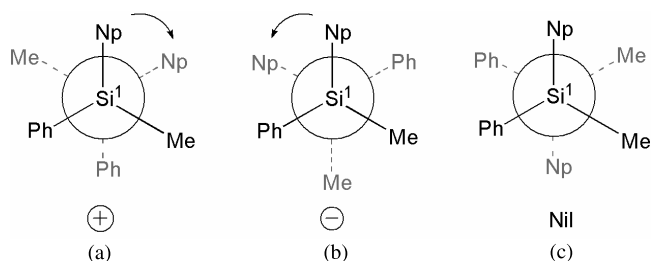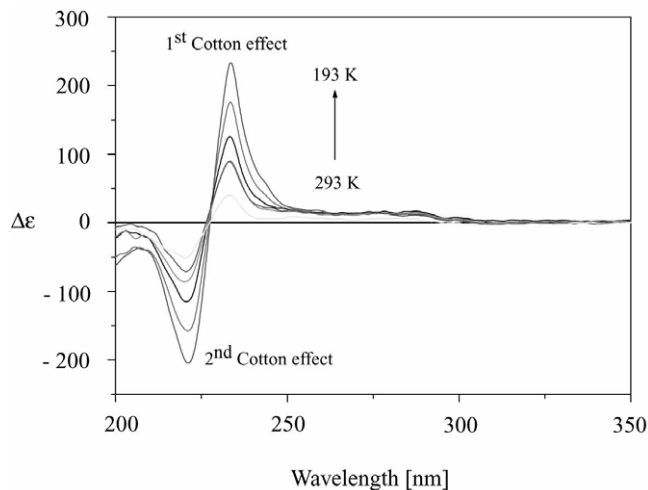

Fig. 5. The VT CD spectra of (R,R)-**3** in isooctane.

The information on interaction between aryl chromophores can be obtained from fluorescence study shown in Fig. 6 and Table 1. Fluorescence (FL) properties excited at 287 nm of (R,R)-**3**, (R,R)-**4**, and (R,R)-**5** appeared as locally excited monomer emissions at around 331 and 341 nm, and as broad bands with a maximum at 399, 410, and 405 nm, respectively. The broad bands seems to be mainly attributed to intramolecular excimer fluorescence as well known in the structure having two parallel aromatic groups separated in adequate distance [23]. The (R,R)-**4** with silylene spacer group showed the strongest excimer emission, suggesting high concentration of stacked conformation of naphthyl chromophores. (R,R)-**5** showed weak excimer fluorescence, which can be understood from the constrained conformation by the steric hindrance of branched trimethylsilyl group which hampers the parallel stacking of the naphthyl chromophores. (R,R)-**3** showed relatively weak exciton fluorescence. Although,
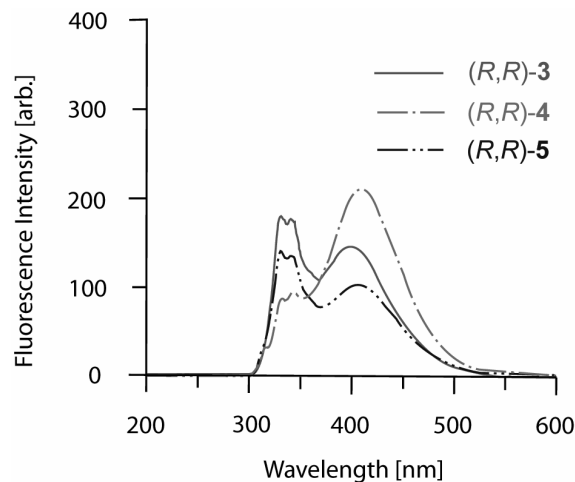

Fig. 4. Possible rotational conformation of (R,R)-**3**. (The arrow indicates the sign of $^1L_{a,Np}$–$^1L_{a,Np}$ transition band.)

Fig. 6. Fluorescence spectroscopies of (R,R)-**3**–(R,R)-**5** in cyclohexane at room temperature.

1,2-dinaphthyldisilane were shown to exhibit more intense excimer fluorescence than 1,3-dinaphthyltrisilane recently, which was explained as the result of having longer silicon–silicon bond length than carbon analogues [21], our trisilane (R,R)-**4** showed more intense excimer emission than disilane (R,R)-**3**, and which are consistent with Hirayama's rule [26]. This tendency is well matched with FL behavior of pyrene-substituted oligosilane as reported [21a,21b].

The stable conformation of (R,R)-**3** responsible for CD spectra can be supposed as the conformer (a) shown in Fig. 7 [27], which well coincides with its single crystal structure by XRD (Fig. 2). This conformation explains the positive exciton chirality between two $^1B_{b,Np}$s and the positive Cotton effect caused by the interaction between two $^1L_{a,Np}$s of adjacent chiral silicon atoms.

Determination of relative orientations and stable conformers of trisilane, (R,R)-**4** and (R,R)-**5** is less straightforward due to having more conformational freedom than (R,R)-**3**. The positive exciton coupling of (R,R)-**5** at around 240 nm can be considered as the result of adopting a positive screw sense between $^1L_{a,Ph}$ and $^1B_{b,Np}$ on the same chiral silicon center, similarly to the stable conformation of **R1**–**R4**. The positive screw sense between $^1L_{a,Ph}$ and $^1B_{b,Np}$, which became visible by the decreased interaction between two $^1B_{b,Np}$ transitions, suggests that conformer (c) of Fig. 7 is the conformation responsible for CD spectra of (R,R)-**5** and has longer chromophoric distance of two naphthyl groups than (R,R)-**3**. The positive exciton coupling between $^1L_{a,Ph}$ and $^1B_{b,Np}$ transition on the same chiral silicon center are increased by decreasing temperature, which supports the increase of the expected conformation (Fig. 7(c)).

It has been also observed that 1,3-interactions give rise to larger exciton coupling than 1,2 interactions, and which was explained due to the possibility of ring stacking conformer having more shorter interchromophoric distances when the chromophores are separated by a three-carbon (silicon) chain [25,28]. Despite that the conformer having two naphthyl groups in parallel might be the minor conformer by steric hindrance, the extreme proximity of the two parallel naphthalene chromophores seems to importantly contribute to

strengthen the exciton couplings at the 225 and 287 nm, as reported in literatures [20,25]. VT CD spectra of (R,R)-**4** showed increased exciton coupling between two $^1B_{b,Np}$s as temperature decreases (Fig. 8). The conformer (b) in Fig. 7 is considered responsible for CD spectra of (R,R)-**4**, which has adequate chromophoric distance being capable of interacting for two naphthyl groups [27].

3. Conclusion

Optically active naphthylphenyl-substituted oligosilanes with α,ω-chiral silicon centers, (R,R)-**3**, (R,R)-**4**, (R,R)-**5** and its enantiomer (S,S)-**5** were successfully synthesized. The absolute configuration of (R,R)-**3** was confirmed by XRD and reaction mechanism. The disilane (R,R)-**3** showed positive exciton chirality originated from the intense π–π interactions by $^1B_{b,Np}$ transition bands of two naphthyl chromophores on the adjacent silicon atoms, and its stable conformation is consistent with the conformation of single crystal data. The (R,R)-**5**, having bulky trimethylsilyl branched-silylene group between two chiral centers, showed positive exciton chirality by interaction between red-shifted $^1L_{a,Ph}$ and $^1B_{b,Np}$ on the same silicon atom due to

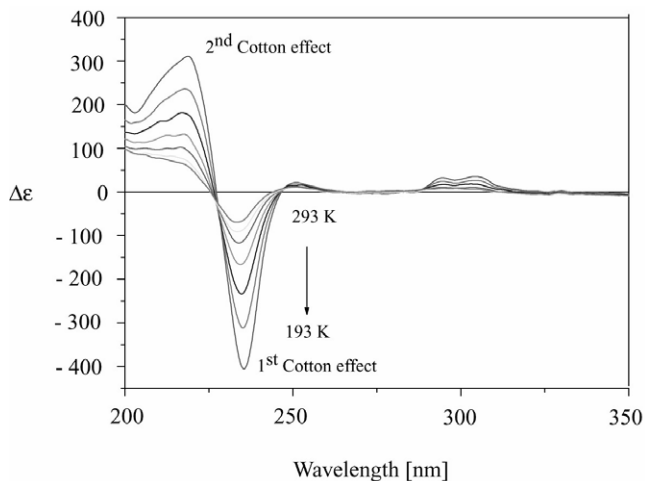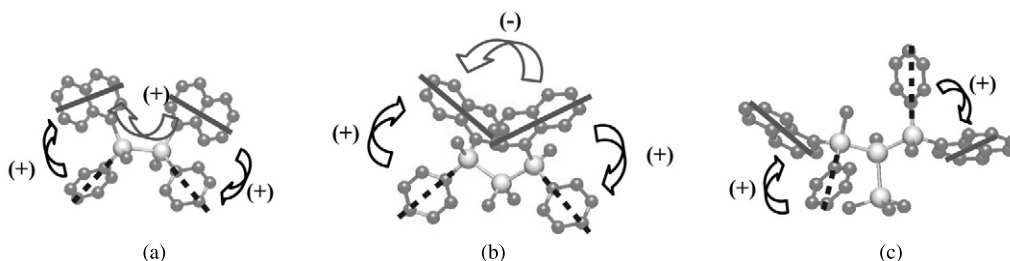Fig. 8. The VT CD spectra of (R,R)-**4** in isooctane.

Fig. 7. Expected conformation responsible for CD spectra. (a) (R,R)-**3**, (b) (R,R)-**4**, (c) (R,R)-**5**. (Solid line: $^1B_{b,Np}$, Dot line: $^1L_{a,Ph}$ transition moments, hydrogen bonds are omitted.)

constrained conformation. The (R,R)-4, which has dimethylsilylene group, showed intense negative and positive exciton chiralities. The intense negative chirality is considered to originate from π–π interaction of $^1B_{b,Np}$ transition bands of two naphthyl groups taking parallel arrangement on two chiral centers, which also supported a little blue shift in UV absorption band and intense excimer in FL. These π–π interaction of aryl substituents on chiral silicon centers enhanced by σ-π conjugation made it possible to clearly correlate with the absolute configuration and stable conformation of the optically active oligosilanes.

4. Experimental

4.1. General

The ^1H (500 MHz), ^{13}C (125.7 MHz), ^{29}Si (99.3 MHz) NMR spectra were obtained in $CDCl_3$ on a Varian 500 MHz Unity INOVA spectrometer. Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.26 for ^1H), $CDCl_3$ (δ 77.00 for ^{13}C), and tetramethylsilane (δ 0.00 for ^{29}Si). Specific optical rotations $[\alpha]_D^{25}$ were measured with a JASCO DIP-370S digital polarimeter. Optical purities of optically active oligosilanes were measured with a JASCO high performance liquid chromatography (HPLC) on a Daicel CHIRALCEL OD® column (0.46 cm φ × 25 cm, cellulose triscarbamate derivate) with n-hexane as an eluent at a flow rate of 0.4 ml min^{-1} at 35 °C. High-resolution mass spectra (HRMS) were taken on a Bruker DALTONICS Bio-Apex 70 E. The pure stereoisomers of optically active oligosilanes (R,R)-3, (R,R)-4, (R,R)-5 and its stereoisomer (S,S)-5 were purified by a JASCO HPLC on a Daicel CHIRALCEL OD® column (2.0 cm φ × 25 cm, cellulose triscarbamate derivate) with n-hexane as an eluent, and all showed above 99% ee enantiomer purity. UV spectra were recorded on JASCO-Ubest V-570 UV/VIS/NIR spectrophotometer. VT CD spectra were measured with a JASCO J-720 spectropolarimeter equipped with a liquid nitrogen-controlled quartz cell (path length = 5 mm) in a cryostat, at temperatures range from 293 to 193 K, and the CD intensities observed were corrected for a volume contraction. Scanning conditions were as follows: scanning rate = 100 nm min^{-1}, bandwidth = 1 nm, response time = 1 s. The solution temperature in the cryostat was monitored directly by immersing a thermocouple into the solution. FL spectra were measured with a JASCO FL-6500 spectrophotometer. All samples for UV, CD and FL are obtained and measured for 10^{-5} M solution in cyclohexane at room temperature, and samples for VT CD are measured in isooctane solution.

4.2. Synthesis

The synthetic route to (1R,2R)-1,2-di(1-naphthyl)-1,2-diphenyl-dimethyldisilane (R,R)-3, (1R,3R)-1,3-di(1-naphthyl)-1,3-diphenyl-1,2,2,3-tetramethyltrisilane (R,R)-4, and (1S,3S)-1,3-di(1-naphthyl)-1,3-diphenyl-2-trimethylsilyl-1,2,3-trimethyltrisilane (S,S)-5 is shown in Scheme 2. The starting optically active (R)-methyl(1-naphthyl)phenylsilyltrimethylstannane (R)-SiSn (82% ee) and (S)-SiSn (86% ee) were prepared as following the literature [16].

4.2.1. (1R, 2R)-1,2-Dimethyl-1,2-di(1-naphthyl)-1,2-diphenyldisilane [(R,R)-3]

The optically active silyllithium (S)-1 was prepared from (R)-SiSn (82% ee, 0.5 mmol) in toluene (10 ml) and THF (10 ml) solution of methyllithium (1.0 mmol) at −78 °C under argon atmosphere. To the solution, a (S)-methyl(1-naphthyl)phenylsilylchloride (S)-2 (> 99% ee, 1.0 mmol) in toluene (10 ml) was added. Purification by silica-gel column chromatography (8:2 hexane–toluene) by preparative GPC (THF eluent) afforded (R,R)-3 (40% ee, 53.2% yield). $[\alpha]_D^{25} = +21.30°$ (c 1.00, CHCl$_3$); ^1H-NMR: δ 7.84 (d, 2H, J = 8.5), 7.80 (d, 2H, J = 8.0), 7.70 (t, 4H), 7.36–7.23 (m, 14H), 7.00 (t, 2H) (Aromatic), 0.84 (s, 6H, SiMePhNp); ^{13}C-NMR: δ 137.26, 137.10, 136.36, 135.26, 134.85, 133.40, 130.13, 129.22, 128.80, 128.70, 127.83, 125.35, 125.32, 125.11 (Aromatic), −2.35 (SiMePhNp); ^{29}Si-NMR: δ −19.88 (SiMePhNp); HRMS: m/z 494.1968. Calc. for $C_{34}H_{30}Si_2$: 494.1886.

4.2.2. (1R,3R)-1,3-Di(1-naphthyl)-1,3-diphenyl-1,2,2,3-tetramethy-trisilane [(R,R)-4]

The (S)-1 was prepared from (R)-SiSn (82% ee, 1.49 mmol) in toluene (15 ml) and THF (15 ml) solution of methyllithium (1.0 mmol) at −78 °C under argon atmosphere. To the solution, a dichlorodimethylsilane (0.86 mmol) in toluene (5 ml) was added. Purification by similar procedure with (R,R)-3 afforded (R,R)-4 (76% ee, 28.7% yield). $[\alpha]_D^{25} = +71.20°$(c 1.00, CHCl$_3$); ^1H-NMR: δ 7.84 (t, 4H), 7.77 (d, 2H, J = 8.0 Hz), 7.43 (t, 2H), 7.35 (d, 2H, J = 6.75 Hz), 7.28–7.16 (m, 14H) (Aromatic SiPh, SiNp), 0.43 (s, 6H, SiMePhNp), 0.35 (s, 6H, SiMe$_2$); ^{13}C-NMR: δ 138.29, 137.13, 135.36, 134.76, 133.35, 129.83, 129.34, 128.82, 128.57, 127.80, 125.35, 125.18 (Aromatic, SiNp, SiPh), −2.42 (2C, SiMePhNp), −3.12 (2C, SiMe$_2$); ^{29}Si-NMR: δ −17.76 (SiMePhNp), −45.35 (SiMe$_2$); HRMS: m/z 552.2137. Calc. for $C_{36}H_{36}Si_3$: 552.2125.

4.2.3. (1S,3S)-1,3-Di(1-naphthyl)-1,3-diphenyl-2-trimethylsilyl-1,2,3-trimethyl-trisilane[(S,S)-5]

The (R)-1 was prepared from (S)-SiSn (86% ee, 1.48 mmol) in toluene (15 ml) and THF (15 ml) solution of methyllithium (1.7 mmol) at −78 °C under argon

atmosphere. To the solution, a 1,1-dichloro-tetramethyl-disilane (0.85 mmol) in toluene (5 ml) was added. Purification by similar procedure with (R,R)-**3** afforded (S,S)-**5** (84% ee, 5.5% yield). ^{1}H-NMR:δ 7.85–7.77 (m, 6H), 7.55 (d, $J = 7$ Hz, 1H), 7.48 (d, $J = 6.5$ Hz, 1H), 7.44–7.36 (m, 4H), 7.32–7.18 (m, 8H), 7.12-7.04 (m, 4H)(Aromatic), 0.68, 0.53 (6H, Si*Me*PhNp), 0.46 (3H, Si*Me*), −0.14 (9H, Si*Me*$_3$); ^{13}C-NMR: δ 139.16, 138.67, 137.11, 136.87, 136.32, 135.72, 135.54, 134.91, 134.88, 134.45, 129.99, 129.95, 129.54, 129.32, 128.85, 128.71, 128.45, 127.87, 127.61, 125.35, 125.28, 125.05, 124.77 (Aromatic), 0.50 (Si*Me*(Si*Me*$_3$)), −0.41, −0.67 (1:1, Si*Me*PhNp), −8.20(Si*Me*); ^{29}Si-NMR: δ −11.24 (Si-Me(*Si*Me$_3$)), −12.72, −14.34 (*Si*MePhNp), −83.98 (*Si*Me); HRMS: *m/z* 610.2483. Calc. for C$_{38}$H$_{42}$Si$_4$: 610.2364. (R,R)-**5**: $[\alpha]_D^{25} = +54.24°$ (c 0.91, CHCl$_3$)

4.3. X-ray crystallography of (R,R)-3

The single crystals were obtained by recrystallization from hexane. Measurement: Rigaku RAXIS-RAPID Imaging Plate, $T = 293$ K. The structure was solved using direct and Fourier methods. 2546 reflections measured with θ in the range 3.26–68.24°, 2546 unique reflections; 2083 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; H atoms were refined on a riding model in their ideal geometric positions; Flack parameter 0.03(6); $R = 0.0561$, and $wR = 0.1499$. SHELXL-97 computer programs were used.

4.3.1. Crystal data for (R,R)-3

(1R,2R)-1,2-Dimethyl-1,2-di(1-naphthyl)-1,2-diphenyldisilane: C$_{34}$H$_{30}$Si$_2$, $M = 494.76$, $a = 14.1319(1)$, $b = 7.2966(7)$, $c = 13.5420(10)$ Å, $V = 1396.97(17)$ Å^3, orthorhombic, space group $P2_12_12$ (no. 18), $Z = 2$, $D_c = 1.176$ g cm^{-3}, μ(Cu-K$_\alpha$) = 1.291 mm^{-1}, $\lambda = 1.54180$.

5. Supplementary material

CCDC 198197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www: http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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[27] We performed a semi-empirical molecular orbital (MO) calculations using MOPAC 2000/ PM3 method to assess the most stable conformation of (R,R)-**3**, (R,R)-**4**, and (R,R)-**5**. In calculating the most stable conformer of the oligosilans, the main chain Si–Si bond angle was rotated with simultaneous adjustment of the positions of phenyl and naphthyl groups and rotating angle of Si–phenyl and Si–naphthyl bonds. In the case of (R,R)-**3** and (R,R)-**5**, the conformers shown in Fig. 7(a) and (c) were shown lowest optimization energy. The lowest optimization energy of (R,R)-**4** was shown in the conformer having the longest distance between two naphthyl chromophores, similar to (R,R)-**5**, but which may not contribute as responsible to CD spectra due to chromophoric distance and nil position of two $^1B_{b,Np}$ transition moments.

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