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Enantioselective inclusion of chiral alkyl aryl sulfoxides in a supramolecular helical channel consisting of an enantiopure 1,2-amino alcohol and an achiral carboxylic acid

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Abstract—The enantioselective clathrate formation of alkyl aryl sulfoxides **4** was achieved with dissymmetric one-dimensional helical channels created in two-component hosts consisting of (1*R*,2*S*)-2-amino-1,2-diphenylethanol **1** and an achiral carboxylic acid, *p*-*tert*-butylbenzoic acid **2**, or 2-anthraquinonecarboxylic acid **3**. X-ray crystallographic analyses showed that the host framework (1*R*,2*S*)-**1**·**3** in the single crystal of a clathrate with methyl *p*-methylphenyl sulfoxide **4n** [(1*R*,2*S*)-**1**·**3**·**4n** (single)] maintained a supramolecular helical array as those of the solvent-included single crystals (1*R*,2*S*)-**1**·**3**·**EtOH**(single) and (1*R*,2*S*)-**1**·**3**·$\mathbf{H_2O}$·**THF**(single), while the guest **4n** molecules were highly disordered. Moreover, the X-ray powder diffraction pattern of (1*R*,2*S*)-**1**·**3**·**4n**(clathrate) obtained through the clathrate formation demonstrated that the molecular arrangements of (1*R*,2*S*)-**1**, **3**, and **4n** were not the same as those which appeared in (1*R*,2*S*)-**1**·**3**·**4n**(single); the channel was enlarged. These results are consistently explained by assuming the dynamic motion of the framework (1*R*,2*S*)-**1**·**3** to achieve widely applicable clathrate formation.

1. Introduction

Chirality-recognition has attracted much attention because it is a fundamental phenomenon in various chiral technologies, such as chromatographic analyses (high-performance liquid chromatography,[1] liquid chromatography,[2] gas chromatography,[3] capillary electrophoresis,[4] etc.), diastereomeric crystallization,[5] asymmetric synthesis,[6] host–guest complexation,[7] membrane separation,[8] enzymatic separation,[9] and so on. To understand such chirality-recognition phenomena and to develop new selectors/resolving agents/chiral auxiliaries/hosts, the elucidation of chirality-recognition processes is indispensable; it is very important to detect differences in thermodynamic and/or kinetic properties between stereoisomers (diastereomers and enantiomers) in chirality-recognition processes.

From the middle of the 1970s to the middle of the 1980s, chirality-recognition through clathrate formation has been reported by some pioneering groups.[10] The enantiomeric excesses of guests included in the clathrate crystals were, however, not so high due to their zero-dimensional cavities. In the second stage of chirality-recognition through clathrate formation, higher-dimensional host frameworks have been developed, such as two-dimensional sheets[11] and three-dimensional hydrogen-bonding networks,[12] which offered cavities fit for the functional group and molecular shape of the guests. This strategy has been successfully applied to the design of tailor-made hosts for racemic targets. Such a precisely designed host can realize extremely high chirality-recognition for a particular racemic guest. At the same time, however, its chirality-recognition ability dramatically deteriorates, even when racemic guests, which have a chemical structure only slightly different from that of the particular guest, are targeted. The singular chirality-recognition of a certain racemic guest by a host in clathrate formation is attributable to the inevitability that the host is designed to have only one (or a very few) global minimum with a large thermodynamical advantage on the potential surface for the clathrate formation with a

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single kind of enantiomer of the guest, owing to the intricate intermolecular interaction system of the host. Thus, clathrate formation has serious limitation in wide applicability.[13]

Recently, we developed a supramolecular host system, consisting of an enantiopure amine and an achiral carboxylic acid (the two-component salt strategy).[14] In the supramolecular assemblies, there exists a one-dimensional helical channel with a twofold screw axis in the center, originating from the topology of a hydrogen-bonding network created from ammonium cations and carboxylate anions. Through a study on the chirality-recognition of racemic 1-arylalkanols by the supramolecular host system, the supramolecular architectures have been demonstrated to be promising frameworks for enantioselective clathrate formation;[14] the helical channels offer dissymmetric cavities interactive with guest molecules. Herein, we report the application of supramolecular architectures with a one-dimensional helical channel to the enantioselective inclusion of racemic alkyl aryl sulfoxides and the behavior of the host and guest molecules in the channel, examined by X-ray crystallographic and powder diffraction analyses.

2. Results and discussion

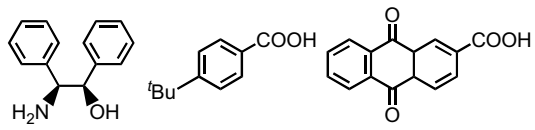
2.1. Enantioselective inclusion of alkyl aryl sulfoxides with supramolecular hosts

The combinations of enantiopure/achiral primary amines and achiral/enantiopure carboxylic acids generally afford a helical architecture with a twofold screw axis in their salt crystals. Among candidates of chiral primary amine components, enantiopure *erythro*-2-amino-1,2-diphenylethanol **1** was found to be fascinating for the construction of effective supramolecular hosts, because the two phenyl groups of **1** tend to have a *gauche* conformation in salt crystals to afford small voids, which were sometimes occupied by solvent molecules.[15] The molecular arrangement strongly indicates that the size and shape of the voids in salt crystals can be controlled by properly selecting the achiral carboxylic acid component. Moreover, in a helical architecture, there is a hydrogen-accepting site in each amine/carboxylic acid pair, and the hydroxy group of **1** offers hydrogen-donating and -accepting sites. This means that a helical architecture consisting of **1** and an achiral carboxylic acid would be able to include guests with a hydrogen-donating and/or -accepting group. In this study, we selected racemic alkyl aryl sulfoxides **4**, of which the oxygen atom has a hydrogen-accepting ability, as target guests. Since the hydroxy hydrogen atom of **1** is located a little way from the twofold screw axis of a helical architecture of **1** and an achiral carboxylic acid, large cavities are required to capture target **4** by intermolecular interaction between the hydroxy hydrogen atom of **1** and the oxygen atom of **4**. Therefore, we used *p-tert*-butylbenzoic acid **2** and 2-anthraquinonecarboxylic acid **3** as the achiral carboxylic acid components with an expectation that the bulky substituent in **2** and the large and planar aryl group in **3** would afford relatively large cavities in their helical architectures with **1**, respectively.

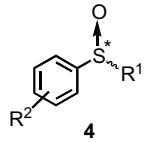
The preparation of the helical architectures and the inclusion of the guests were very easy. A solution of equimolar amounts of amino alcohol (1*R*,2*S*)-**1** and carboxylic acid **2** or **3** in methanol or ethanol was refluxed for 30 min, and then the solvent was evaporated to dryness to give the corresponding salt (host) as a crystalline powder. The host (1*R*,2*S*)-**1**·**2** or (1*R*,2*S*)-**1**·**3**, which was finely powdered, was suspended in hexane containing 4 equiv of guest **4** for 4 h with stirring to afford the (1*R*,2*S*)-**1**·**2**·**4**/(1*R*,2*S*)-**1**·**3**·**4** clathrate, which was collected by filtration and washed with hexane or toluene. The molar ratio of the included guest (the inclusion ratio) was estimated on the basis of the amount of the host by an NMR measurement of the clathrate. The enantiomeric excess (ee) of the guest, isolated from the clathrate by preparative thin layer chromatography, was determined by high-performance liquid chromatography (HPLC) on a chiral column.

The inclusion was performed for 17 types of sulfoxides **4** by using (1*R*,2*S*)-**1**·**2** and (1*R*,2*S*)-**1**·**3** salts as hosts. The results are summarized in Table 1. Most of sulfoxides **4** examined were included in the (1*R*,2*S*)-**1**·**2** and/or (1*R*,2*S*)-**1**·**3** host

Table 1. Chirality-recognition of **4** with (1*R*,2*S*)-**1**·**2** and (1*R*,2*S*)-**1**·**3**



1 **2** **3**



4

Guest	R^1	R^2	(1*R*,2*S*)-**1**·**2** salt		(1*R*,2*S*)-**1**·**3** salt	
			Inclusion ratio[a]	ee[b] (%)	Inclusion ratio[a]	ee[b] (%)
4a	Me	H	0.88	99 (*R*)	0.92	12 (*R*)
4b	Et	H	0.68	64 (*S*)	0.44	12 (*R*)
4c	*i*Pr	H	0.45	84 (*S*)	1.00	96 (*R*)
4d	*i*Bu	H	0.25	5 (*S*)	0.87	91 (*R*)
4e	*t*Bu	H	0.41	92 (*R*)	—[c]	—
4f	Me	*o*-Me	0.75	98 (*S*)	0.88	96 (*S*)
4g	*i*Pr	*o*-Me	0.25	97 (*S*)	0.61	92 (*S*)
4h	Me	*o*-OMe	0.32	21 (*R*)	0.78	62 (*S*)
4i	*i*Pr	*o*-OMe	—[c]	—	—[c]	—
4j	Me	*m*-Me	—[c]	—	0.66	30 (*R*)
4k	*i*Pr	*m*-Me	—[c]	—	0.66	82 (*R*)
4l	Me	*m*-OMe	0.23	25 (*S*)	0.75	38 (*R*)
4m	*i*Pr	*m*-OMe	—[c]	—	0.32	75 (*R*)
4n	Me	*p*-Me	0.46	4 (*S*)	1.00	96 (*R*)
4o	*i*Pr	*p*-Me	—[c]	—	0.93	72 (*S*)
4p	Me	*p*-OMe	0.49	3 (*R*)	0.50	90 (*R*)
4q	*i*Pr	*p*-OMe	0.27	74 (*R*)	0.88	88 (*R*)

[a] The inclusion ratio (the guest/the host) was calculated on the basis of the ^{1}H NMR analysis of the clathrate crystal.

[b] The enantiomeric excess was determined by a HPLC analysis. The absolute configuration of the major enantiomer was shown in the parenthesis.

[c] Not included.

with moderate to excellent enantioselectivity, although the inclusion ratios were not necessarily 1.00, probably due to the insufficient intermolecular interaction between (1*R*,2*S*)-**1**·**2**/(1*R*,2*S*)-**1**·**3** host and guests **4**, resulting in the incomplete inclusion of **4** with (1*R*,2*S*)-**1**·**2**/(1*R*,2*S*)-**1**·**3** and/or in the volatilization of **4** during the isolation and handling of the (1*R*,2*S*)-**1**·**2**·**4**/(1*R*,2*S*)-**1**·**3**·**4** clathrates, as was observed for the inclusion of 1-arylalkanols in a similar helical architecture.[14] As can be seen from Table 1, the (1*R*,2*S*)-**1**·**3** host showed a superior chirality-recognition ability for sulfoxides **4**, compared with the (1*R*,2*S*)-**1**·**2** host. However, it is noteworthy that the (1*R*,2*S*)-**1**·**2** and (1*R*,2*S*)-**1**·**3** hosts could complementarily recognize the chirality of the sulfoxides **4**; the (1*R*,2*S*)-**1**·**2** salt showed a chirality-recognition ability for **4a**, **4b**, and **4e** with a relatively short molecular length better than did the (1*R*,2*S*)-**1**·**3** host. The results strongly indicate that the chirality-recognition ability of the present supramolecular system for alkyl aryl sulfoxides can be tuned upon properly selecting the achiral carboxylic acid component. Thus, it was clearly demonstrated that the present host system consisting of **1** and an achiral carboxylic acid could be successfully applied to the enantioselective inclusion of sulfoxides via clathrate formation.

2.2. Structure of the (1*R*,2*S*)-1·3 framework in the clathrates

To clarify the structure of clathrates (1*R*,2*S*)-**1**·**3**·**4**, X-ray crystallographic analyses were carried out. Although we could prepare two single crystals, (1*R*,2*S*)-**1**·**3**·**EtOH**(single) and (1*R*,2*S*)-**1**·**3**·**H$_2$O**·**THF**(single), of which EtOH and H_2O/THF originated from the solvent(s) used for the recrystallization of the (1*R*,2*S*)-**1**·**3** salt, respectively, as references for the clathrates, only one kind of single crystal, (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single), was obtained among the clathrates upon recrystallization from MeOH; disappointingly, we could only determine the structure of the framework consisting of (1*R*,2*S*)-**1** and **3** in (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) due to the significant disorder of the guest (*R*)-**4n** molecules even at −173 °C. Moreover, the positions of guests also could not be determined for the other clathrates (1*R*,2*S*)-**1**·**3**·**4**, despite much effort, which resulted in only incomplete X-ray crystallographic analyses. The crystal data of (1*R*,2*S*)-**1**·**3**·**EtOH**(single), (1*R*,2*S*)-**1**·**3**·**H$_2$O**·**THF**(single), and (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) are listed in Table 2.

The crystal structures of (1*R*,2*S*)-**1**·**3**·**EtOH**(single) and (1*R*,2*S*)-**1**·**3**·**H$_2$O**·**THF**(single) are very similar to each other, as shown in Figure 1. In both single crystals, a columnar hydrogen-bonding network with a twofold screw axis in the center is formed from the ammonium cations of (1*R*,2*S*)-**1** and the carboxylate anions of **3**. However, a relatively large one-dimensional channel is constructed from (1*R*,2*S*)-**1** and **3** molecules, compared with those in the previously reported hosts.[14] The cross section of the one-dimensional channels formed in the single crystals is about 12 × 6 Å. In the channel, the space created by two anthraquinonyl groups is almost symmetrical, while the space around **1** is dissymmetrical owing to the two asymmetric centers in (1*R*,2*S*)-**1**. The hydrogen-bonding site for a guest molecule arising from the hydroxy group of (1*R*,2*S*)-**1** is located near the dissymmetrical space in the channel. The channel is filled with disordered EtOH and H_2O/THF molecules, respectively.

Table 2. Crystal data and details of the final refinement calculations for (1*R*,2*S*)-**1**·**3**·**EtOH**(single) (A), (1*R*,2*S*)-**1**·**3**·**H$_2$O**·**THF**(single) (B), and (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) (C)

	A	B	C
Chemical formula	$C_{31}H_{29}NO_6$	$C_{33}H_{33}NO_7$	$C_{99}H_{84}N_3O_{16.5}S_{1.5}$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
Z	2	2	2
a (Å)	13.863(3)	12.945(12)	13.273(5)
b (Å)	5.764(2)	5.877(5)	17.478(6)
c (Å)	17.341(6)	17.988(17)	17.503(5)
α (°)	90	90	90
β (°)	94.060(9)	94.345(4)	94.976(4)
γ (°)	90	90	90
V (Å^3)	1382.2(6)	1365.0(2)	4045(3)
Density (g cm^{-3})	1.229	1.352	1.334
Temperature (K)	296	103	100
Reflections collected	2747	8644	16,764
Reflections used in refinement	2705	4637	10,915
LS parameters	345	371	1036
GOF	0.81	1.001	0.884
R^a (F) [$I > 2s(I)$]	0.0607	0.0847	0.1086
wR^b (all F^2)	0.1406	0.2209	0.3029

[a] $R = \sum|F_o - F_c|/\sum F_o$.

[b] $wR = \left[\sum w(F_o - F_c)^2 / \sum wF_o^2\right]^{1/2}$.

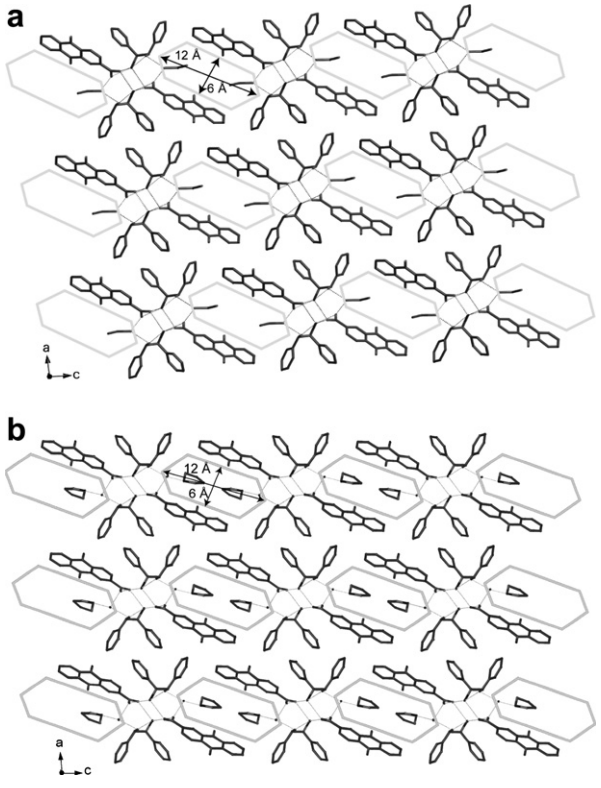


Figure 1. One-dimensional channels created in (a) (1*R*,2*S*)-**1**·**3**·**EtOH**(single) and (b) (1*R*,2*S*)-**1**·**3**·**H$_2$O**·**THF**(single).

In contrast, the *b*-axis (the column axis) of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) is about three times longer than those of (1*R*,2*S*)-**1**·**3**·**EtOH**(single) and (1*R*,2*S*)-**1**·**3**·$\mathbf{H_2O}$·**THF**-(single), although the other unit cell parameters are similar to the others; the hydrogen-bonding network composed of (1*R*,2*S*)-**1**·**3** and the cross section of the one-dimensional channel in the network of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) are very similar to those of (1*R*,2*S*)-**1**·**3**·**EtOH**(single) and (1*R*,2*S*)-**1**·**3**·$\mathbf{H_2O}$·**THF**(single). This fact implies that the framework of the (1*R*,2*S*)-**1**·**3** host in (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) is similarly constructed independent of the guest molecules, although the positions of three molecules of the guest (*R*)-**4n** in the asymmetric unit are highly disordered. The crystal structure of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) is shown in Figure 2. It is noteworthy that the positions of the sulfur and oxygen atoms in the three molecules of the sulfoxide (*R*)-**4n** are almost ordered owing to the fixation of (*R*)-**4n** by hydrogen-bonding interaction between the oxygen atom of (*R*)-**4n** and the hydroxy hydrogen atom of (1*R*,2*S*)-**1**; the O···O distances are close to each other and are in the range of 2.62–2.68 Å. However, some short contacts are observed between the disordered guest molecules. Moreover, the occupancy of the guest molecule is 0.50 for one host framework in the crystal in contrast to the fact that an inclusion ratio of 1.00 was achieved in the clathrate formation. These results strongly suggest that the structure of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) solved by the X-ray analysis does not reflect that of the actual crystal (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(clathrate) obtained through the clathrate formation; the actual crystal should shrink during single crystal formation to result in the short contacts and the forcing-out of the guest molecules.

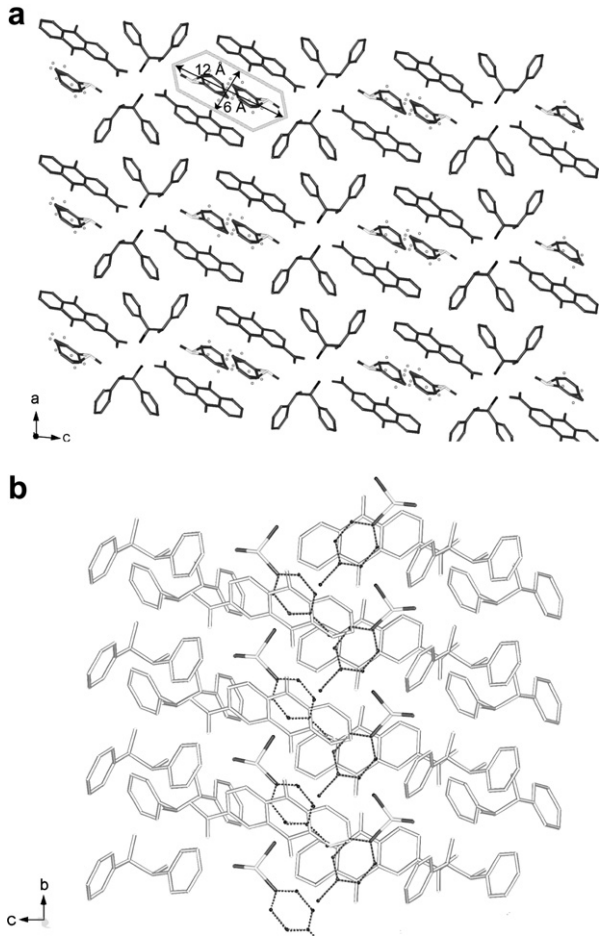


Figure 2. Crystal structure of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single). (a) Top view and (b) side view. The occupancy of the disordered guest is 0.5. Dotted line shows the predicted positions of the guest.

In the next stage, we investigated the X-ray powder diffraction (XRPD) patterns of the clathrates. As shown in Figure 3, the XRPD pattern of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) is largely different from that of the powdery crystal (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(clathrate), meaning that the molecular arrangements in (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) and (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(clathrate) are different from each other. Then, we tried to estimate the unit cell of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(clathrate) from its XRPD pattern using DICVOL in the DASH program package.[16] As a result, the calculation gave unit cell parameters with reasonable χ^2 values; 14.145 Å for the *a*-axis, 6.002 Å for the *b*-axis, 19.242 Å for the *c*-axis, and 92.13° for b. The *a* and *b* axes are slightly longer than those of (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single), while the *c*-axis is obviously longer by ca. 2 Å. This result would imply that the framework (1*R*,2*S*)-**1**·**3** can flexibly change its size depending on the shape of a guest to possess several local minima on the potential surfaces for the clathrate formation, including a minimum observed for the frameworks in (1*R*,2*S*)-**1**·**3**·**EtOH**(single), (1*R*,2*S*)-**1**·**3**·$\mathbf{H_2O}$·**THF**(single), and (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single), upon sliding the anthraquinonyl groups facing each other.

Most likely owing to the high flexibility of the (1*R*,2*S*)-**1**·**3** framework, the 'dynamic inclusion' of guests was realized to make the (1*R*,2*S*)-**1**·**3** host applicable to a wide variety of sulfoxides **4** regardless of the substituent on the phenyl group and the α-alkyl group as shown in Table 1. The chirality-recognition by the dynamic host (1*R*,2*S*)-**1**·**3** is rather similar to that by chiral stationary phases for HPLC, which achieve dynamic chirality-recognition owing to their moderately controlled structures with mobility.[17]

3. Conclusions

We designed a large dissymmetric one-dimensional channel in supramolecular two-component hosts by using (1*R*,2*S*)-2-amino-1,2-diphenylethanol **1** and an achiral carboxylic acid, such as *p*-*tert*-butylbenzoic acid **2** and 2-anthraquinonecarboxylic acid **3**, and found that various kinds of alkyl aryl sulfoxides **4** were included in the (1*R*,2*S*)-**1**·**2**/(1*R*,2*S*)-**1**·**3** hosts with moderate/excellent enantioselectivities to give the corresponding clathrates. The X-ray crystallographic analyses of one of the clathrates [(1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single)], as well as (1*R*,2*S*)-**1**·**3**·**EtOH**(single) and (1*R*,2*S*)-**1**·**3**·$\mathbf{H_2O}$·**THF**(single) including solvent(s) for the recrystallization of the (1*R*,2*S*)-**1**·**3** salt revealed that a supramolecular helical hydrogen-bonding network was commonly constructed by (1*R*,2*S*)-**1** and **3**. Although the molecular arrangement (1*R*,2*S*)-**1**·**3**·(*R*)-**4n** could not be directly determined by X-ray crystallographic analysis due to the transformation of the crystal structure during single

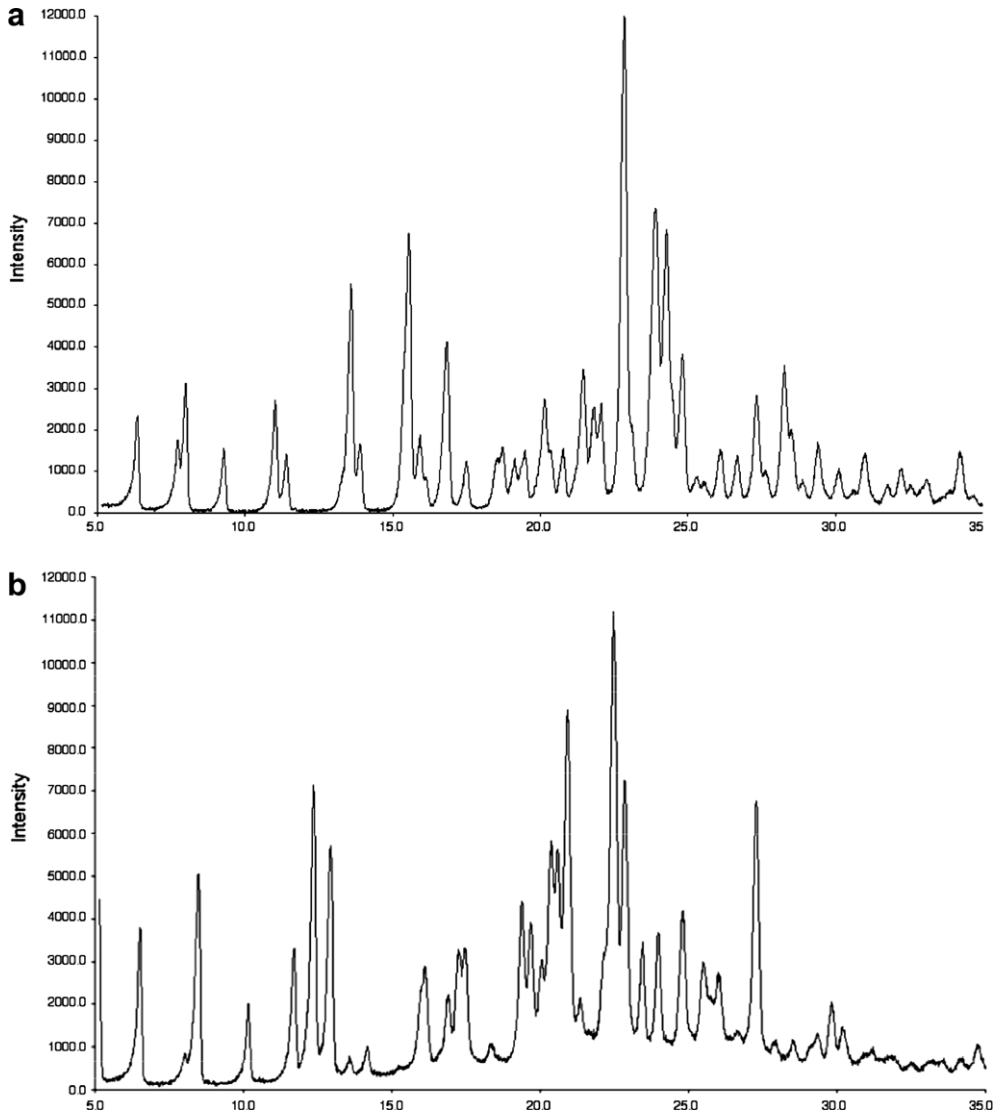


Figure 3. XRPD patterns of (a) (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(clathrate) afforded through the clathrate formation and (b) (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(single) obtained by recrystallization from MeOH.

crystal formation, the prediction of a possible unit cell for (1*R*,2*S*)-**1**·**3**·(*R*)-**4n**(clathrate) on the basis of its XRPD pattern indicated that the unit cell was enlarged in the inclusion process, suggesting dynamic inclusion behavior.

4. Experimental

4.1. General procedure for the inclusion of 4 with (1*R*,2*S*)-1·2/(1*R*,2*S*)-1·3

Finely powdered (1*R*,2*S*)-**1**·**2** or (1*R*,2*S*)-**1**·**3** (0.2 mmol) was suspended in hexane (1 mL) containing 4 equiv of **4** for 4 h with stirring to afford the corresponding (1*R*,2*S*)-**1**·**2**·**4**/(1*R*,2*S*)-**1**·**3**·**4** clathrate, which was collected by filtration and washed with a small amount of hexane or toluene. The molar ratio of the included guest **4** was estimated on the basis of the amount of (1*R*,2*S*)-**1**·**2**·**4**/(1*R*,2*S*)-**1**·**3**·**4** by an NMR measurement of the clathrate. The ee of the guest **4**, isolated from the clathrate by preparative thin layer chromatography, was determined by HPLC on a chiral column. The column used as well as the conditions is listed in Table 3.

4.2. Single crystal X-ray crystallographic analysis

The X-ray intensities were collected with a Rigaku MERCURY CCD system or a Bruker APEX II CCD area detector by using Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by the direct method with the SHELXL-97 program[18] and refined by the full-matrix least-squares procedure for all non-hydrogen atoms anisotropically. All hydrogen atoms were generated geometrically. The absolute configuration of the included sulfoxide **4n** was determined on the basis of the known absolute configuration of **1**. CCDC 657007–657009 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Table 3. Conditions for the HPLC analyses

Guest	Column[a]	Solvent[b] (v/v)	Flow rate (mL/min)	Retention time (min)
4a	OB-H	8:2	1.0	$t_1(S) = 10.3$, $t_2(R) = 17.9$
4b	OB-H	8:2	1.0	$t_1(S) = 8.5$, $t_2(R) = 18.0$
4c	OB-H	8:2	1.0	$t_1(S) = 6.4$, $t_2(R) = 9.9$
4d	OB-H	8:2	0.8	$t_1(S) = 7.8$, $t_2(R) = 11.3$
4e	AS-H	8:2	0.7	$t_1(S) = 11.6$, $t_2(R) = 17.5$
4f	OB-H	8:2	1.0	$t_1(S) = 8.6$, $t_2(R) = 21.9$
4g	OB-H	8:2	1.0	$t_1(S) = 7.2$, $t_2(R) = 14.6$
4h	OB-H	8:2	1.0	$t_1(S) = 9.1$, $t_2(R) = 17.7$
4i	OB-H	8:2	1.0	$t_1(S) = 5.5$, $t_2(R) = 9.7$
4j	OB-H	8:2	1.0	$t_1(S) = 7.5$, $t_2(R) = 11.0$
4k	OB-H	8:2	0.8	$t_1(S) = 6.6$, $t_2(R) = 8.0$
4l	OB-H	8:2	0.8	$t_1(S) = 15.0$, $t_2(R) = 23.7$
4m	OB-H	9:1	0.8	$t_1(S) = 11.8$, $t_2(R) = 14.1$
4n	OB-H	8:2	1.0	$t_1(S) = 8.0$, $t_2(R) = 18.0$
4o	OB-H	8:2	1.0	$t_1(S) = 6.7$, $t_2(R) = 12.6$
4p	OB-H	8:2	1.0	$t_1(S) = 15.1$, $t_2(R) = 33.7$
4q	OB-H	8:2	0.8	$t_1(S) = 9.3$, $t_2(R) = 16.3$

[a] Daicel Chiralcel.
[b] A mixture of hexane/2-propanol.

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.3. X-ray powder diffraction (XRPD)

X-ray powder diffractions were collected with a Rigaku RINT2000 diffractometer with a Cu Kα X-ray tube, operated at 40 kV and 100 mA at room temperature, between 5° and 40° in a $2\theta/\theta$-scan mode with a step of 0.01° in 2θ. Samples were not rotated during the data collection.

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