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Change in conformation upon complexation of double-armed terephthalamide hosts: dynamic molecular recognition of ditopic guests with strong CD signaling

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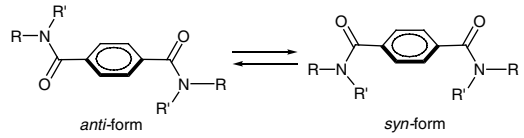
Abstract—Conformation of novel terephthalamide hosts **1** changes from anti to syn upon complexation with a bidentate guest (**2** or **3**). Chiral sense in the helical syn-form of the double-armed host molecules **1** is biased by the asymmetric centers on the chiral guest [(*R*,*R*)/(*S*,*S*)-**2a**], which can be detected by the drastic change in circular dichroism (CD) spectrum thanks to the exciton coupling of two chromophores ('arms') linked to the amide nitrogens. Asymmetric centers on the host molecule also exhibit preference for the twisting direction upon change in geometry from the anti- to syn-form. Thus, the achiral guests (**2b** or **3**) can also be detected by modulation of CD spectrum upon complexation with the chiral host [(*R*,*R*)-**1a**].

Dynamic molecular recognition is a key process not only in the biological system[1] but also in the artificial host–guest chemistry,[2] by which the guest determines the preferred conformation of the host molecule. The mechanistic understanding of the guest-induced geometrical change as well as realization of signal transduction processes of neurotransmitter by using artificial receptors have attracted great interest in the field of supramolecular chemistry. In this context, terephthalamide derivatives with proper substituents are interesting[3] since they would provide a unique prototype in designing the novel host molecules. Due to the steric hindrance, tertiary amides cannot adopt a planar geometry but adopt conformations in which the plane of amide is more or less perpendicular to the plane of aromatic ring. Hence, *N*,*N*,*N*′,*N*′-tetrasubstituted terephthalamides exist as a mixture of two kinds of interconvertible twisted conformers (syn and anti)[4,5] in terms of the relative orientation of two amide carbonyl groups (Scheme 1). In general, the anti-conformer is more stable due to the offset effect of the dipoles,[2c,5,6] whereas the syn-conformer is endowed with the suitable binding geometry for the ditopic guest molecules such as *p*-phenylene bis(ammonium)s **2** or dopamine **3** with forming the 'supramolecular cyclophane' structure (Scheme 2). When the substituents attached on the amide groups are rigid and expanded enough to prevent their coplanar arrangement in the syn-form as in the double-armed hosts **1**, this conformer adopts the helical 'arm-crossing' geometry[7] of either (*P*)- or (*M*)-configuration.



Scheme 1. Interconvertible conformers of terephthalamide derivatives with the twisted amide carbonyl groups.

We have found that the helical sense in the syn-form of host **1** is biased by the asymmetric centers of the chiral guest [(*R*,*R*)/(*S*,*S*)-**2a**], and the complexation-induced drastic change in geometry from anti to syn is accompanied by strong CD (circular dichroism) signaling due to exciton coupling of the arylethynylbenzene chromophores ('arms'). In addition, the chiral auxiliaries on the host molecules exhibit preference for the twisting direction upon change in geometry from the anti- to helical syn-form. Thus, the achiral guests (**2b** or **3**) can be also detected by the modulation of CD spectrum of

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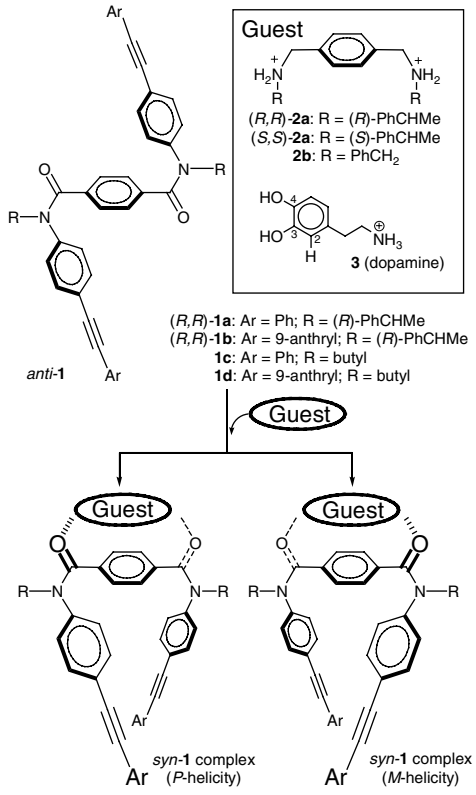

Scheme 2. Complexation of the double-armed host **1** with a bidentate guest to form the 'supramolecular cyclophane' structure.

chiral host (*R*,*R*)-**1a**. Here we report preparation, structure, and the detailed complexation properties of novel terephthalamide hosts **1** with hydrogen bond donors **2** and **3**.

The chiral hosts (*R*,*R*)-**1a**,**b**[8] were prepared by the Sonogashira coupling reactions [Pd(0)–CuI, Et_3N–benzene] of the chiral iodide (*R*,*R*)-**4a**, (*R*,*R*)-*N*,*N*′-bis(4-iodophenyl)-*N*,*N*′-bis(1-phenylethyl)terephthalamide, with phenylacetylene or 9-ethynylanthracene in respective yield of 92% and 76%. Hosts **1c**,**d**[8] without asymmetric centers were similarly prepared from the achiral precursor **4c**, *N*,*N*′-dibutyl-*N*,*N*′-bis(4-iodophenyl)terephthalamide, in 96% and 64% yield, respectively. Diiodides **4a**,**c**[9] were obtained easily from terephthaloyl chloride and 4-iodoaniline derivatives as reported previously.

According to the X-ray analysis[10] of achiral host **1c**, there are two crystallographically independent molecules in the crystal, both of which adopt the C_i-symmetric anti-conformation of higher stability. The central phenylene moieties and the amide planes are twisted with a dihedral angle of 40.5° or 39.8°, respectively. Fortunately, we could isolate the less stable syn-conformer upon crystallization of chiral host (*R*,*R*)-**1a**. The torsion angle between the two diphenylacetylene chromophores ('arms') is 62.6° in the syn-form of (*R*,*R*)-**1a**, whereas the corresponding angle is 180.0° by definition in the centrosymmetric anti-conformers of **1c** in the crystal (Fig. 1). In solution, the ^{1}H NMR spectra of hosts **1** exhibit a set of peaks that can be assigned to the single species. Hence, even when the less stable syn-isomer coexist in solution, the two conformers are interconverted very rapidly through the faster rotation around C_{Ar}–C_{CO} bond than the NMR time scale.

The complexation of hosts **1** with bis(ammonium) guests **2** or dopamine **3** was first investigated by ^{1}H NMR spectroscopy in 3% $CD_3CN/CDCl_3$. The association of the two components was evidenced by a significant upfield shift of the central phenylene protons for both of the host and guest molecules.[11] Such a complexation-induced chemical shift (CIS) indicates close proximity of these phenylene groups in the complex. The 1:1 stoichiometry of the host–guest complexes was confirmed by Job plots (Fig. S1). The binding constants (K_a) were determined on the basis of titration experiments (Fig. 2) and are summarized in Table 1. The similar titration curves were found in all combinations of host and

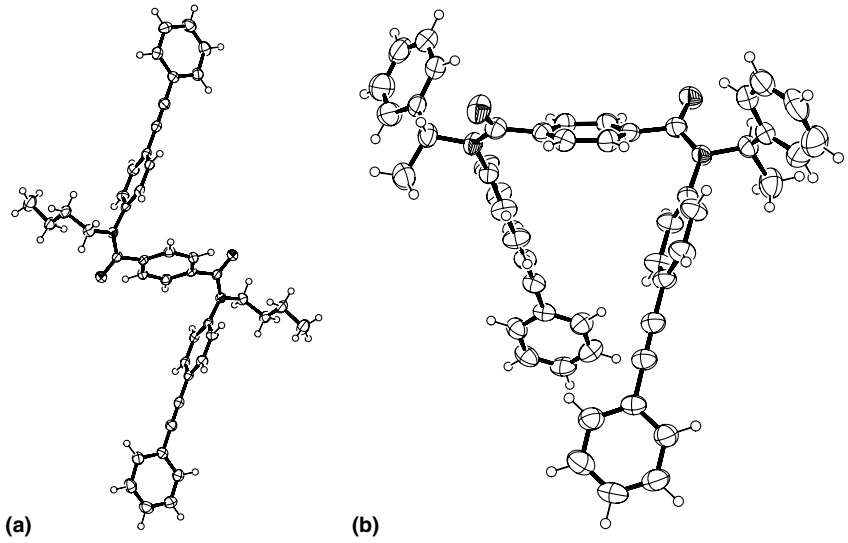

Figure 1. (a) X-ray structure of achiral host **1c** measured at −120 °C. One of the two crystallographically independent molecules is shown. (b) X-ray structure of chiral host (*R*,*R*)-**1a** measured at −40 °C.

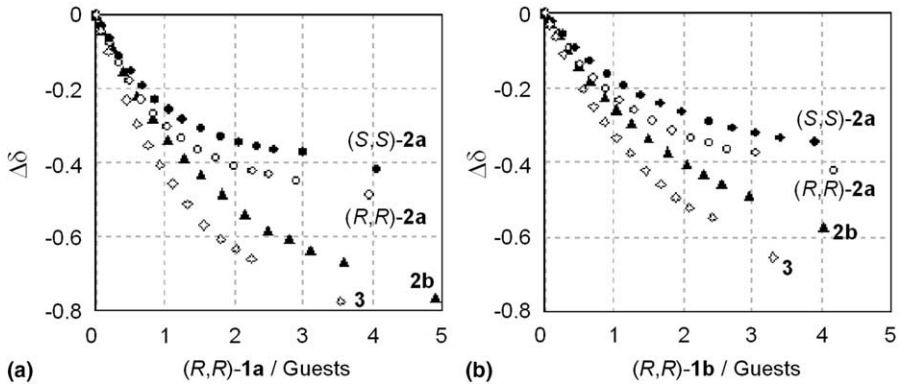

Figure 2. NMR titration curves for various guests with (a) (*R*,*R*)-**1a** and (b) (*R*,*R*)-**1b**. Protons of phenylene groups for (*R*,*R*)/(*S*,*S*)-**2a**,**2b** and that at C2 for **3** are plotted against the host/guest ratio.

Table 1. Binding constants K_a (M^{-1}) for the complexation of hosts (*R*,*R*)-**1a** and (*R*,*R*)-**1b** with guests (*R*,*R*)/(*S*,*S*)-**2a**, **2b** and **3** in 3% $CD_3CN/CDCl_3$ (v/v) at 298 K[a]

Host/guest	(*R*,*R*)-**2a**	(*S*,*S*)-**2a**	**2b**	**3**
(*R*,*R*)-**1a**	1300 (±40)	1300 (±100)	360 (±85)	640 (±90)
(*R*,*R*)-**1b**	730 (±120)	590 (±40)	270 (±40)	340 (±40)

[a] The numbers in the parentheses are the estimated errors.

guest[12] irrespective of the different spatial requirement around the central phenylene core and chromophores in the 'arms' of the hosts. Hence, it is most probable that all of the guests including dopamine **3** are bound with the host **1** through the two hydrogen bonds with forming the 'supramolecular cyclophane'[5b] structure shown in Scheme 2.

The upfield shift upon admixing was also observed for the aromatic protons in the 'arms' of the host **1**, which are located far from the binding sites. The observed CIS suggests that these chromophores of the host are shielded by each other in the complexed state by adopting the 'arm-crossing' syn-conformation.[13] Thus, the complexation of **1** with a ditopic guest is accompanied by a drastic change in geometry of the host from the anti- to syn-form (Scheme 2). The values of K_a for the bis(9-anthrylethynyl) derivative (*R*,*R*)-**1b** are slightly smaller than those for the bis(phenylethynyl) derivative (*R*,*R*)-**1a**, which can be accounted for by steric hindrance between the anthracene units in the 'arms' upon adopting the syn-conformation.

To obtain more information on the change in geometry of the host upon complexation,[14] admixing of achiral host **1c** with chiral guests (*R*,*R*)/(*S*,*S*)-**2a** was followed by an examination of the CD spectrum.[16] Upon the gradual addition of (*R*,*R*)-**2a** (3 equiv) to a solution of **1c** (1.23×10^{-4} M) in CH_2Cl_2, a pair of positive (λ_{ext} 314 nm; $\Delta\varepsilon$ +16.5) and negative (285; −7.78) Cotton effects were observed in the wavelength region around 260–350 nm (Fig. 3). Such a bisignated CD signal with $\Delta\varepsilon = 0$ at the absorption maximum (295 nm) must come from the exciton coupling of the diphenylacetylene chromophores, thanks to adopting the syn-form with a helical 'arm-crossing' geometry. The observed positive couplet ($\Delta\varepsilon > 0$ for $\lambda > 295$ nm) indicates that the chiral sense of the syn-form of **1c** in the complex with (*R*,*R*)-**2a** is biased in favor of *P*-helicity.[19] Similarly, complexation of **1c** and (*S*,*S*)-**2a** resulted in the strong couplet but with an inverse sign, indicating formation of the complex with *M*-helicity in major. In the complexation of an achiral host and a chiral guest, the preferred rotating

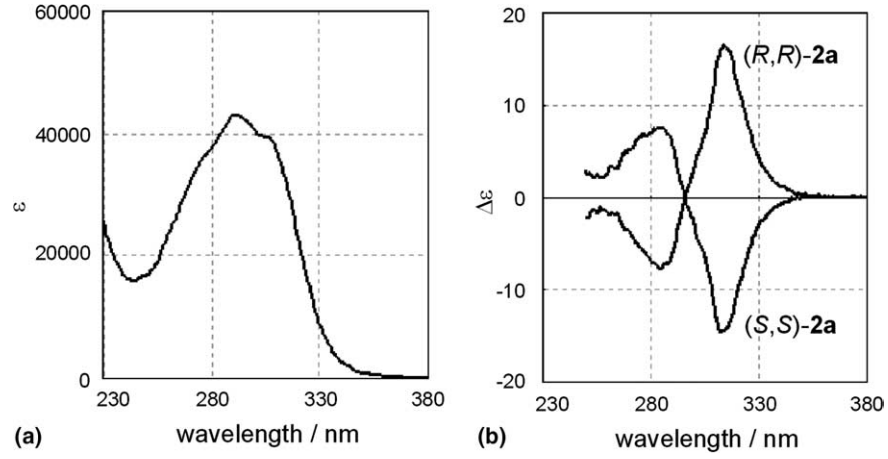

Figure 3. (a) UV spectrum of achiral host **1c**. (b) CD spectra obtained upon complexation of **1c** (1.23×10^{-4} mol dm^{-3}) with 3 equiv of (*R*,*R*)-**2a** and (*S*,*S*)-**2a** in CH_2Cl_2.

direction of amide groups was determined by the asymmetric centers of the guest. Since the CD signals of guests themselves are very weak [λ_{ext} 268 nm, $\Delta\varepsilon$ +0.61; 261, +0.68; 255, +0.51 for (*S*,*S*)-**2a**], the above mentioned complexations demonstrate the successful execution of 'chiroptical enhancement'.

To investigate if this sensing system based on the complexation-induced change in geometry could be applied to modulation of chiroptical properties,[9] complexations of the chiral host (*R*,*R*)-**1a** with chiral guests (*R*,*R*)/(*S*,*S*)-**2a** were planned. The free host (*R*,*R*)-**1a** with a phenethylamine-type chiral auxiliary on both amide units exhibits the negative Cotton effect over the whole absorption region in the CD spectrum (Fig. S2), resulted by the direct interaction between the chiral auxiliary and the diphenylacetylene chromophore. If the complexation with chiral guests (*R*,*R*)/(*S*,*S*)-**2a** induces change in geometry from the anti- to helically-biased syn-form, the CD spectrum of (*R*,*R*)-**1a** would be modulated drastically by the additional contribution from the exciton coupling between two diphenylacetylene chromophores.

Upon the gradual addition of chiral guest **2a** to a solution of (*R*,*R*)-**1a** (1.71×10^{-4} M) in CH_2Cl_2, continuous and drastic changes in CD spectra were actually observed with an isosbestic point at 295 nm. When (*R*,*R*)-**2a** (4 equiv) was used, the Cotton effect at the longer wavelength was increased (λ_{ext} 322 nm; $\Delta\varepsilon$ +10.2) whereas ellipticity decreased in the shorter wavelength region (275; −29.8) (Fig. S3). In contrast, when (*S*,*S*)-**2a** (4 equiv) was added, increase (312; −59.6) and decrease (286; −3.70) were observed in the inversed region. To estimate the net changes by complexation, the difference of $\Delta\varepsilon$ values before and after complexation was calculated ($\Delta\Delta\varepsilon = \Delta\varepsilon_{complex} - \Delta\varepsilon_{host}$). As shown in Figure 4, the difference CD spectra ($\Delta\Delta\varepsilon$ vs λ) are very similar in shape to those for the achiral-**1c**·(*R*,*R*)/(*S*,*S*)-**2a** complexes shown in Figure 3b. Although the complexes in question, (*R*,*R*)-**1a**·(*R*,*R*)-**2a** and (*R*,*R*)-**1a**·(*S*,*S*)-**2a**, are a diastereomeric pair, their difference CD spectra look as if they are a pair of mirror images. These results indicate that the complexations between (*R*,*R*)-**1a** and (*R*,*R*)/(*S*,*S*)-**2a** are also accompanied by the change in geometry from the extended anti to the helical syn-form and that the induced helicity by (*R*,*R*)- and (*S*,*S*)-**2a** is *P* and *M* in major, respectively.[20]

In this way it was proven that the rotating direction of amide groups during the anti- to syn-form could be controlled predominantly by the asymmetric centers of the chiral guests (*R*,*R*)/(*S*,*S*)-**2a** even when the chiral auxiliaries are attached on the amide nitrogens of the host. According to the binding studies, the diastereomeric pair, (*R*,*R*)-**1a**·(*R*,*R*)-**2a** and (*R*,*R*)-**1a**·(*S*,*S*)-**2a**, are formed nearly with the same association constants. So that, the chiral recognition of (*R*,*R*)/(*S*,*S*)-**2a** by (*R*,*R*)-**1a** is not realized in terms of the binding strength due to a small difference in stability between the complexes of (*P*)- and (*M*)-helicity. However, nearly the mirror–image relationship for the difference CD spectra indicates that the present system provides the successful example for the 'stereospecific modulation of chiroptical properties' of the host (*R*,*R*)-**1a** by the chiral guests (*R*,*R*)/(*S*,*S*)-**2a**.

It is shown in the previous section that the host (*R*,*R*)-**1a** can adopt the syn-form of both (*P*)- and (*M*)-helicity in the complexes, whose chiral sense is determined by the asymmetric centers of guests (*R*,*R*)/(*S*,*S*)-**2a** but not by the chiral auxiliaries on the host. However, (*R*,*R*)-**1a** may still have an intrinsic preference for rotating direction upon complexation. To investigate the possibility that the achiral guest such as dopamine can be detected by CD spectra by using such directional preference of (*R*,*R*)-**1a** itself, further complexation studies were conducted for the chiral host (*R*,*R*)-**1a** with achiral guests.

Upon the gradual addition of **2b** or dopamine **3** (4 equiv) to a solution of (*R*,*R*)-**1a** (1.84×10^{-4} mol dm^{-3}) in CH_2Cl_2, the CD spectra showed the drastic changes (λ_{ext} 312 nm, $\Delta\varepsilon$ −44.0; 286, −8.94 for **2b**; and 312, −45.3; 285, −12.5 for dopamine **3**, respectively) similar to the case of (*R*,*R*)-**1a**·(*S*,*S*)-**2a** complex with *M*-helicity in major (Fig. 5). These results clearly show that the chiral auxiliaries on the host exhibit their own preference: the syn-conformer of (*R*,*R*)-**1a** is favored with *M*-helicity. In this manner, the double-armed host enables detection

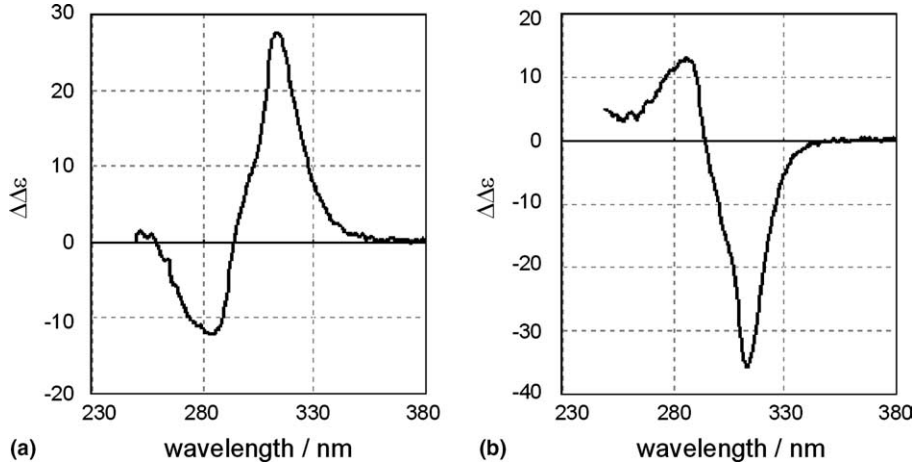

Figure 4. Difference CD spectra of chiral host (*R*,*R*)-**1a** before and after addition of 4 equiv of chiral guest (a) (*R*,*R*)-**2a** and (b) (*S*,*S*)-**2a**.

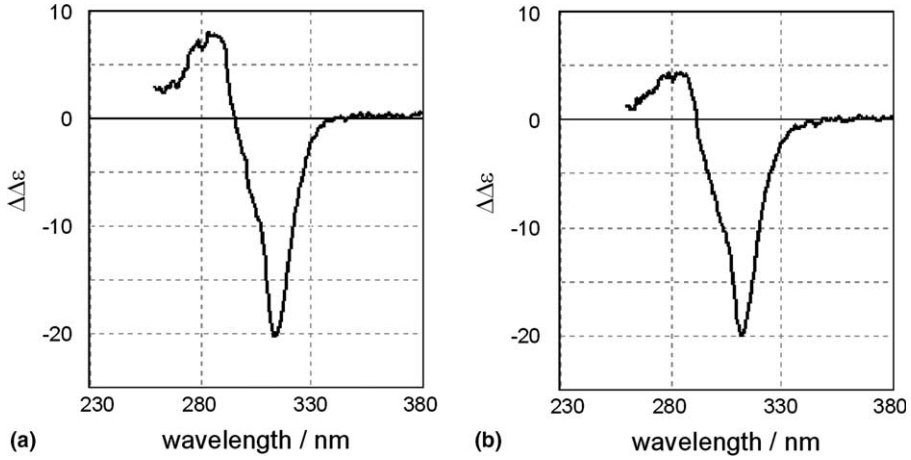

Figure 5. Difference CD spectra of chiral host (*R*,*R*)-**1a** before and after addition of 4 equiv of achiral guest (a) **2b** and (b) dopamine **3**.

of achiral guests such as dopamine by drastic changes in CD spectrum.

This work has revealed that the newly designed terephthalamide derivatives **1** can act as host molecules for dynamic molecular recognition. They provide the prototype for the novel sensory system for the bidentate guests with CD spectral detection, thanks to the dynamic and helically-biased geometrical change from the anti- to syn-form upon complexation.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 287899-287900. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Supplementary data

Selected physical and spectral data for new compounds, Job plots (Fig. S1), CD spectrum of guest-free (*R*,*R*)-**1a** (Fig. S2), and CD spectral changes upon complexation of (*R*,*R*)-**1a** with (*R*,*R*)-**1a** (Fig. S3) are available in pdf format. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.01.022.

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7. The alkyl and aryl groups of *tert*-benzamides occupy the *s-cis* and *s-trans* position, respectively, relative to the carbonyl oxygen (Ref. 4).
8. Spectral properties of new compounds are given in the Supporting information.
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10. *Crystal data of* ***(R,R)*****-1a**: MF $C_{52}H_{40}N_2O_2$, FW 724.89, trigonal, $P3_121$, $a = b = 9.0892(11)$, $c = 43.007(6)$ Å, $V = 3077.0(7)$ Å^3, D_c ($Z = 3$) = 1.174 g cm^{-3}, $T = 233$ K, $\mu = 0.71$ cm^{-1}, $R = 4.69\%$, GOF = 0.956. All molecules in the crystal adopt the syn-conformation with (*M*)-helicity. *Crystal data of* **1c·(CHCl$_3$)$_2$**: MF $C_{46}H_{42}Cl_6N_2O_2$, FW 867.57, triclinic, *P*-1, $a = 8.948(4)$, $b = 16.196(9)$, $c = 16.213(9)$ Å, $\alpha = 64.806(9)$, $\beta = 89.224(9)$, $\gamma = 89.329(8)°$, $V = 2125.8(19)$ Å^3, D_c ($Z = 2$) = 1.355 g cm^{-3}, $T = 153$ K, $\mu = 4.44$ cm^{-1}, $R = 12.98\%$, GOF = 0.996. All molecules in the crystal adopt the centrosymmetric anti-conformation. Relatively large *R* value is due to disorder of the heavy atoms of solvent.

11. The chemical shifts of 7.133 ppm for free (*R*,*R*)-**1b** and 7.320 ppm for free **2b** were changed into 7.047 and 7.113 ppm, respectively, upon admixing in 3% $CD_3CN/CDCl_3$ (10^{-3} mol dm^{-3} each).
12. Different curvatures in the titration curves may be related to the variable orientation of the guest phenylene ring relative to the host phenylene moiety in the complexes. The benzene core of dopamine **3** is located on the host with T-shaped geometry through the hydrogen bonding with the ammonium proton and the hydroxy proton at C3, since the aromatic proton on C2 is the most shielded in the complex. The hydroxy group at C4 does not play a role in binding with **1**.
13. The 'arm-crossing' syn-form is also present in the uncomplexed state as the metastable conformer. According to the VT-NMR experiment of (*R*,*R*)-**1b**, the upfield shifts of the resonances were observed exclusively for the protons assigned to the anthracene units upon raising the temperature from −65 °C (8.64, 8.48, 8.05 ppm) to 25 °C (8.54, 8.37, 7.96 ppm) in $CDCl_3$, indicating the increasing population of the less stable syn-conformer at higher temperatures. Both forms interconvert so rapidly that the syn/anti ratio or energy barrier for interconversion could not be determined.
14. Only marginal changes in UV spectrum upon complexation are accompanied with complexation. Fluorescence can be another output signal for sensitive detection in the sensory systems (Ref. 15). Although the fluorescence of anthracene-based host **1d** (1.4×10^{-5} M) is quenched gradually upon addition of guest (*S*,*S*)-**2a** [70% at 0.5 equiv and 50% at 1.0 equiv], the excimer-type emission was not observed in the longer-wavelength region. So that, it is still unclear whether decrease in fluorescence intensity of host **1d** upon addition of guest (*S*,*S*)-**2a** is due to complexation-induced change in geometry or by the outer-sphere energy transfer from **1d*** to (*S*,*S*)-**2a**.
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16. Studies by using CD spectrum (Ref. 17) were carried out for only (*R*,*R*)-**1a** and **1c** containing diphenylacetylene chromophores, for which the exciton coupling between the chromophores can be directly related with the helicity of the syn-form. The lower-energy absorption of (*R*,*R*)-**1a** and **1c** is assigned to that of diphenylacetylene chromophore with the transition moment along the longitudinal direction (Ref. 18).
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20. In the crystal of host (*R*,*R*)-**1a**, all molecules adopt less stable syn-conformation, and their chiral sense is completely regulated as *M*-helicity. The solid-state CD spectrum (KBr) of the guest free host (*R*,*R*)-**1a** is similar in shape to that of (*R*,*R*)-**1a**·(*S*,*S*)-**2a** complex in solution, thus confirming that the host in this complex adopts the syn-conformation with *M*-helicity.