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Use of *meso*-ternaphthalene derivatives: linear recognition of the α,ω-diamines by homoditopic receptors☆

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Abstract—The new ditopic receptors **1**–**3** consisting of a *meso*-ternaphthalene backbone and two crown ether rings have been synthesized. Hosts **2** and **3** have been shown to selectively complex and transfer the dipicrates, 1,9-diaminononane and 1,10-diaminodecane, from aqueous solution into the organic phase.

1. Introduction

In the development of host molecules with complementary functionality for selectively binding guest molecules, a number of systems in which the length of the guest molecule controls recognition have been developed. These host molecules possess two binding sites at opposite ends of their backbones.[2] In general, due to the flexibility of the molecular framework, these ditopic receptors are effective in selectively binding guest species shorter than the distance between the two binding sites. For guest molecules longer than the host inter-binding site distances, however, selective complexation is lost. To overcome this indiscriminate binding problem for longer guests, several cylindrical host molecules have been reported.[3] Due to their structural properties, each binding site is tightly connected with two or three props, cylindrical host molecules which can discriminate longer length guests. Nevertheless, vagueness remains for host molecules with a single prop connecting two binding sites.

Recently, we reported the preparation and properties of chiral ter-, quarter-, sexi-, and octinaphthalene derivatives connected at the 1,4-positions.[4] These compounds have rigid backbones due to their upright nature. *meso*-Ternaphthalene derivatives, especially, are expected to make suitable backbones in host molecules for recognizing the length of α,ω-diamines. This is hypothesized as *meso*-ternaphthalene derivatives have not only a rigid framework, but also scaffold sections which extend in the same direction as the ternaphthyl backbone. In this paper, we report the synthesis of the new ditopic receptors **1**–**3** that consist of a *meso*-ternaphthalene backbone and two crown ether rings, and detail their molecular recognition of α,ω-diamines **4** of varying lengths (Fig. 1).

2. Results and discussion

2.1. Synthesis

The synthetic pathway to hosts **1**–**3** is shown in Scheme 1. The key intermediate, ternaphthalene skeleton **8**, was synthesized by a published route as an (*R*,*S*) and (*S*,*R*) mixture.[4a] Thus, monobenzyl protected hydroxynaphthalene **5** was dimerized by oxidative coupling in the presence of phenylethylamine and copper chloride, and then subjected to methylation of two hydroxy groups, followed by deprotection of the benzyl group to afford **6** in 68% overall yield for three steps. Diol **6** was treated with 1.3 equiv. of acetyl chloride to give monoacetate **7** in 32% yield. To avoid homo coupling of valuable **7**, oxidative coupling between **7** and **5** was carried out in the presence of 5–10 equiv. of **5** to afford the key intermediate **8** in 24% yield. Compound **8** was methylated and subjected to deprotection of the acetyl group followed by reductive removal of the benzyl group to give *meso*-ternaphthalene **9** in 94% overall yield for three steps. The *meso*-ternaphthalene **9** was then converted to ditriflate **10** in 79% yield. The coupling partner **12** was prepared from the corresponding bromide **11**[5] using *n*-butyllithium and trimethylborate in 49% yield. The reaction of the triflate **10** with boric acid **12** under modified Suzuki coupling conditions[6] gave the desired host **1** in 80% yield. Simultaneous deprotection of an allylic group took place

☆ See Ref. 1

Keywords: crown ethers; molecular recognition; diamines; host–guest chemistry.

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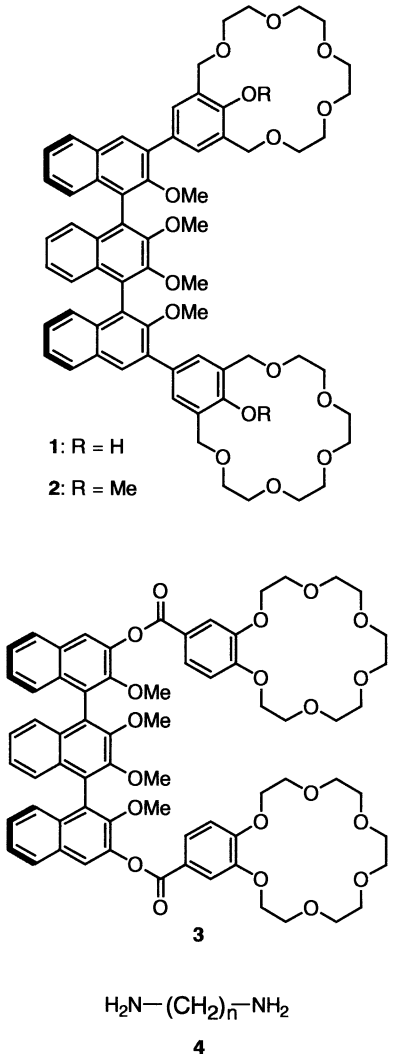
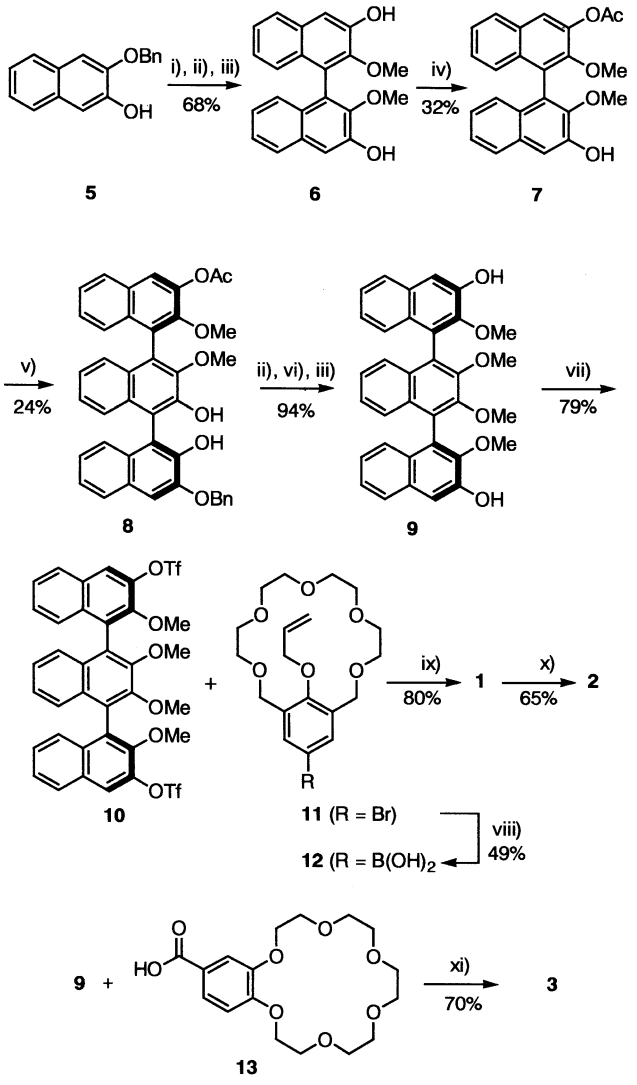


Figure 1.



Scheme 1. *Reactions and conditions*: (i) $CuCl_2$, phenethylamine; (ii) MeI, K_2CO_3; (iii) Pd/C, HCO_2NH_4; (iv) AcCl, pyridine; (v) **5**, $CuCl_2$, phenethylamine; (vi) NaOH, H_2O–THF; (vii) Tf_2O, *i*-Pr_2NEt; (viii) *n*-BuLi, $B(OMe)_3$, then H^+; (ix) $Pd(PPh_3)_4$, Na_2CO_3; (x) MeI, NaH; (xi) WSC, DMAP.

under these reaction conditions. Methylation of **1** gave **2** in 65% yield. Host **3** was synthesized by condensation between **9** and commercially available **13** in the presence of WSC and DMAP in 70% yield.

2.2. Crystal structure of hosts 1 and 2

Colorless crystals of host **1** were precipitated from toluene. The crystal structure was clarified by X-ray analysis and is shown in Fig. 2. Host **1** cocrystallized with two disordered toluene molecules, moreover, the central naphthalene ring of **1** was disordered in the opposite sense about 1/1 in the crystalline state. One likely crystal structure for the central naphthalene moiety was selected and is shown in Fig. 2. Both phenol crown ethers are projected in an identical direction from the ternaphthyl backbone, with a distance between phenolic oxygen atoms of about 15 Å. Dihedral angles between the phenol crown aromatic ring and the naphthalene ring are about 48–50°. That indicates the two phenol crown rings are slightly slanted in the solid state.

Two kinds of crystals of host **2** were obtained from acetone and acetonitrile. Host **2**, which precipitated from acetone and co-crystallized with six water molecules, also exhibits a disordered central naphthalene ring in the crystalline state. One crystal structure for the central naphthalene moiety was selected and is shown in Fig. 3. Of particular interest, four of the six water molecules observed in the crystal lattice are located in series between the two phenol crown moieties. Due to the low quality of the crystal data, the interoxygen distance between the two central water molecules, which occupancy is estimated only 0.5, is found to be too small.[7] In crystals precipitated from acetonitrile, no disorder of the central naphthyl ring was observed, however, an oxygen atom in the crown ether ring was disordered (Fig. 4). Both crystal structures are quite similar with the exception of the four water molecules being substituted by two acetonitrile molecules.

A marked difference between the crystal structures of **1** and **2** was found in the conformation of the crown rings. The two crown rings of **2** were bent over and created a cavity, while those of **1** adopted a more extended conformation.

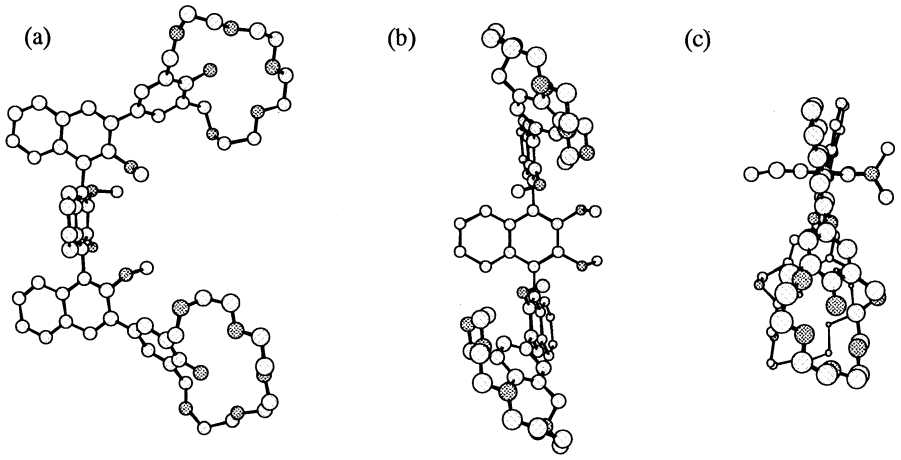


Figure 2. X-Ray structure of **1** (a, side view; b, front view; c, top view). Hydrogen atoms and two toluene molecules are excluded for clarity.

2.3. Interaction between hosts and α,ω-diamines

Since host **1** has two acidic phenol groups responsible for binding, free α,ω-diamines are suitable as guests. Interactions between host **1** and α,ω-diamines **4** were examined by the UV–Vis spectroscopic method. In spite of the addition of α,ω-diamines **4** (n=6, 8 and 10) to the host **1** solution, differences in absorption are hardly discernible in chloroform, THF, and DMSO solvents. In order to increase the acidity of the phenolic hydroxy group and stabilize the charged host–guest complex, the water containing solvent system, THF/H_2O, was used. Absorption around 375 nm, attributed to the phenolate ion, clearly increased with the addition of these diamines to host **1** in THF/H_2O (4/1). The stoichiometry of complexation was determined by Job plots. As shown in Fig. 5, Job plots indicated a 1/1 host–guest ratio for this mixed solvent system at 25°C. The association constants (K_a) and the molar absorption coefficient (ε) were determined by titration, and analyzed by the Rose–Drago method.[8] Results are summarized in Table 1. No relationship was observed between the association constants and lengths of α,ω-diamines **4**. Furthermore, the behavior of **1** and nonylamine also indicated 1/1 complexation, and its K_a of 139±13 was nearly the same as those of **1** and diamines.

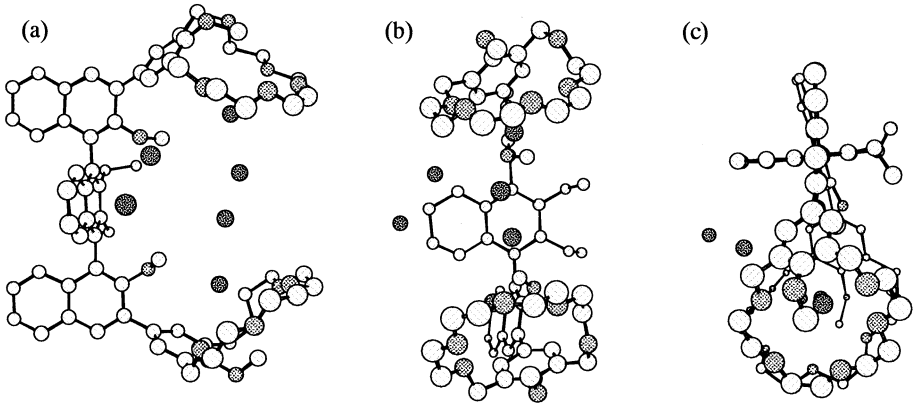


Figure 3. X-Ray structure of **2**·6H_2O (a, side view; b, front view; c, top view). Hydrogen atoms are excluded for clarity.

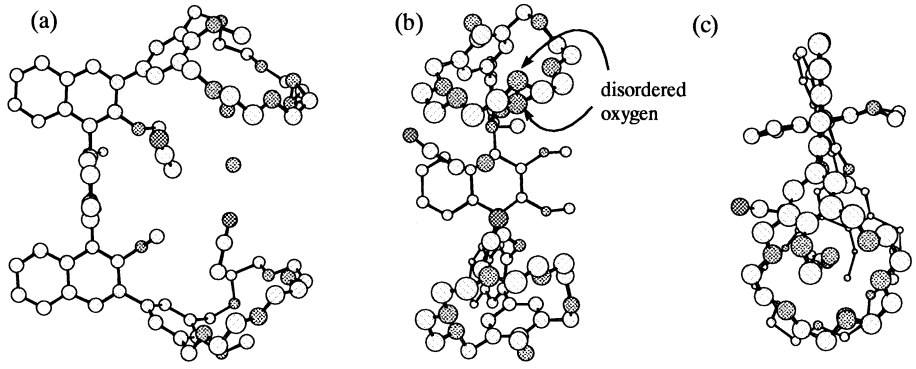


Figure 4. X-Ray structure of **2**·2H_2O·2CH_3CN (a, side view; b, front view; c, top view). Hydrogen atoms are excluded for clarity.

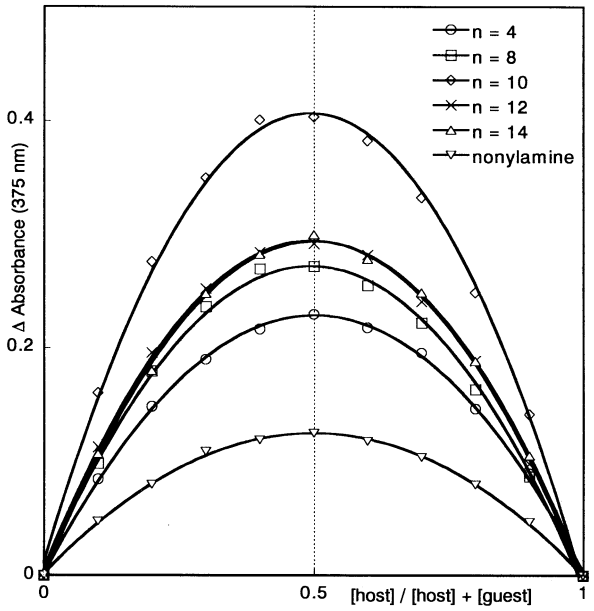


Figure 5. Job plots between host **1** and amines in THF/H_2O=4/1 at 25°C. [host]+[guest]=2.0×10^{-3} M.

Table 1. The association constants (K_a) of complexes of the host **1** with diamine **4**

Diamine **4** (n=)	K_a (M^{-1})	ε
4	326±23	1160±45
8	281±11	2050±51
10	219±7	3060±71
12	246±17	2400±11
14	168±17	2110±65

$[\mathbf{1}]_0=1.23\times10^{-3}$ M. THF/H_2O=4/1 at 25°C.

These results suggest that complexation is based on an acid–base interaction between only a single phenol crown ring of **1** and a single amino group of the α,ω-diamines **4**.[9]

Owing to the neutral binding sites of host molecules **2** and **3**, their linear recognition abilities were investigated using protonated diamines as guest molecules i.e. α,ω-diamine dipicrates. Association constants (K_a) were determined by the modified picrate liquid–liquid extraction method from H_2O to $CHCl_3$ at 25°C based on Nolte's method.[2b,10] The K_a values of complexes **2** or **3** with α,ω-diammonium dipicrates (**4**) were calculated, assuming 1/1 complex formation. Results are summarized in Table 2. Both the K_a values of hosts **2** and **3** clearly depend on the chain length of the guests. Host **2** specifically bound diamines **4** (n=9 and 10). The K_a values clearly decreased for complexes of **2** with diamines longer than 1,11-diaminoundecane and with diamines shorter than 1,8-diaminooctane, due to the rigid nature of the framework of host **2**. The K_a value for 1,11-diaminoundecane is approximately six times less than that of 1,10-diaminodecane. As judged from the two X-ray crystallographic analyses of **2** and calculations by MacroModel/MM2 (version 6.0), it might be expected that guest chain lengths from nona to undeca methylene may be accommodated. The results in Table 2 are consistent with this presumption. Host **3**, however, showed affinity for diamine dipicrate **4** (n=10). Since host **3** is linked through a flexible ester group between the receptor portions and the backbone, it should be difficult to specifically recognize longer guest chain lengths. Nevertheless, the recognition abilities of host **3** for diamine dipicrate are nearly identical to those of host **2**. A simple explanation for the relationship observed between host **3** and diamine dipicrates **4** is currently unclear. Presumably, the conformation with two benzo crown ether rings oriented parallel is exceptionally favorable for binding diamine dipicrate **4** (n=10).

Table 2. The association constants of complexes of the hosts **2** and **3** with diamine **4** dipicrate

Diamine **4** (n=)	K_a of host **2**	K_a of host **3**
6	$(6.88\pm0.50)\times10^3$	$(5.00\pm0.30)\times10^3$
8	$(4.05\pm0.27)\times10^5$	$(1.12\pm0.09)\times10^6$
9	$(6.87\pm0.21)\times10^6$	$(5.12\pm0.13)\times10^6$
10	$(6.92\pm0.28)\times10^6$	$(1.56\pm0.05)\times10^7$
11	$(1.22\pm0.18)\times10^6$	$(2.83\pm0.06)\times10^6$
12	$(2.96\pm0.10)\times10^5$	$(9.68\pm0.38)\times10^5$
14	$(4.49\pm0.26)\times10^5$	$(1.85\pm0.10)\times10^6$
16	$(1.72\pm0.11)\times10^5$	$(1.17\pm0.06)\times10^6$

$[\mathbf{2}]_{org}=1.10\times10^{-3}$ M. $[\mathbf{3}]_{org}=1.02\times10^{-3}$ M. Determined by diammonium picrate liquid–liquid extraction from H_2O to $CHCl_3$ at 25°C. The K_a values are given by $[\mathbf{2}\text{ or }\mathbf{3}\cdot\mathbf{4}^{2+}\cdot Pic_2^{2-}]org/[\mathbf{2}\text{ or }\mathbf{3}]org[\mathbf{4}^{2+}\cdot Pic_2^{2-}]org$, where [ ]org indicates the concentration in $CHCl_3$.

3. Experimental

3.1. General

Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were taken at 200 or 400 MHz in $CDCl_3$ or CD_3OD with chemical shifts being reported as δ ppm from tetramethylsilane as an internal standard. FT-IR and UV spectra were obtained on a JASCO FT/IR-300 and Shimazu UV-2200, respectively.

3.1.1. Diol 6. To a suspension of $CuCl_2$ (107.6 g, 0.8 mol) in methanol (600 ml), α-phenylethylamine (129 ml, 1.0 mol) was added under nitrogen atmosphere in ice bath. After 40 min, a solution of **5** (100 g, 0.4 mol) in dichloromethane (400 ml) was added and reaction mixture was stirred for 20 h. Conc. hydrochloric acid (300 ml) was added to the reaction mixture and extracted with ethyl acetate (twice). The organic layer was washed with brine, dried over magnesium sulfate and evaporated to give pale brown solid. The precipitate was triturated with *n*-hexane/ethyl acetate to give the dihydroxy binaphthyl derivative in quantitative yield (101 g). ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.33 (s, 4H), 6.10 (s, 2H, –O*H*), 7.0–7.6 (18H), 7.77 (d, J=8.1 Hz, 2H). A mixture of the crude intermediate (50.0 g, 0.1 mol), potassium carbonate (138 g, 1.0 mol) and methyl iodide (124.5 ml, 2.0 mol) in acetone (1.0 l) was stirred for 5 h at 60°C and 2 h at room temperature. Additional methyl iodide (60 ml, 0.96 mol) and potassium carbonate (70 g, 0.51 mol) were added to the mixture. The reaction mixture was refluxed for additional 3 h and poured into water and ethyl acetate to give 2,2′-dimethoxy derivative as a pale yellow powder (37.7 g, 72%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.66 (s, 6H), 5.33 (s, 4H), 7.0–7.7 (18H), 7.80 (d, J=8.2 Hz, 2H). A mixture of the crude 2,2′-dimethoxy derivative (10.0 g, 19 mmol), ammonium formate (6.0 g, 95 mmol) and 10%

palladium on carbon (500 mg) in 1,4-dioxane (200 ml) and ethanol (100 ml) was stirred at 60°C for 4 h. Ammonium formate (6.0 g, 95 mmol) and 10% palladium on carbon (500 mg) were further added to the reaction mixture. The reaction mixture was stirred for another 4 h at 60°C. After filtration, the filtrate was evaporated and the precipitate was triturated with water and ethanol (1/1) to afford the desired diol **6** as white powder (6.18 g, 94% yield). Mp 184–186°C; IR (KBr) 3603, 3429, 3163, 1618, 1598 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.33 (s, 6H), 6.14 (brs, 2H, –OH), 7.12–7.14 (4H), 7.33–7.42 (2H), 7.49 (s, 2H), 7.77 (d, J=8.2 Hz, 2H); HRMS Calcd for $C_{22}H_{18}O_4$: 346.1205. Found: 346.1206; Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.00; H, 5.17.

3.1.2. Monoacetate 7. To a solution of **6** (57.0 g, 0.16 mol) and triethylamine (33.0 ml, 0.24 mol) in DMF (10 ml) and THF (800 ml), acetyl chloride (13.5 ml, 0.19 mol) was added dropwise at 0°C for 3.5 h. Acetyl chloride (1.1 ml, 16 mmol) was further added to the reaction mixture. The mixture was stirred for another 1 h. The reaction mixture was evaporated and the residue was partitioned between water and ethyl acetate. The organic layer was separated, washed successively with hydrochloric acid, water (two times), and brine, dried over magnesium sulfate, and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, *n*-hexane/ethyl acetate=5/1–3/1) to afford **7** as a pale yellow solid (19.8 g, 32% yield). Mp 184–186°C (triturated with *n*-hexane/ethyl acetate); IR (KBr) 3284, 1725, 1599 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.38 (s, 3H), 3.39 (s, 3H), 6.19 (brs, 1H, –O*H*), 7.0–8.0 (10H); HRMS Calcd for $C_{24}H_{20}O_5$: 388.1311. Found: 388.1305; Anal. Calcd for $C_{24}H_{20}O_5$: C, 74.21; H, 5.19. Found: C, 74.33; H, 5.17.

3.1.3. Ternaphthalene 8. To a suspension of $CuCl_2$ (1.4 g, 10 mmol) in methanol (5.0 ml), α-phenylethylamine (1.8 ml, 14 mmol) was added under nitrogen atmosphere under ice bath cooling. After 20 min, a solution of **7** (200 mg, 0.52 mmol) and **5** (1.2 g, 5.2 mmol) in dichloromethane (20 ml) was added and the reaction mixture was stirred for 18 h at room temperature. Conc. hydrochloric acid was added to the reaction mixture and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over magnesium sulfate and evaporated to give residue. The residue was purified by column chromatography (SiO_2, dichloromethane/*n*-hexane/ethyl acetate=5/4/1) to afford **8** as colorless powder (39 mg, 24% yield) as well as (*S*,*S*) and (*R*,*R*)-**8** (42 mg, 25% yield) and binaphthyl derivative (700 mg). Mp 151–153°C (triturated with *n*-hexane/ethyl acetate); IR (KBr) 3523, 1762, 1468 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.48 (s, 3H), 3.50 (s, 3H), 5.34 (s, 2H), 6.09 (s, 2H, –O*H*), 7.1–7.6 (16H), 7.75 (s, 1H), 7.80 (d, J=7.4 Hz, 1H), 7.88 (d, J=8.0 Hz, 1H); HRMS Calcd for $C_{41}H_{32}O_7$: 636.2148. Found: 636.2178; Anal. Calcd for $C_{41}H_{32}O_7$: C, 77.34; H, 5.07. Found: C, 77.65; H, 4.94.

3.1.4. *meso*-Ternaphthalene 9. To a mixture of **8** (5.40 g, 8.5 mmol) and potassium carbonate (23.5 g, 170 mmol) in acetone (500 ml) was dropwise added methyliodide (21 ml, 340 mol) at room temperature. The mixture was refluxed for 2 h. After cooling, the reaction mixture was evaporated under reduced pressure, and the residue was poured into ethyl acetate and aqueous hydrochloric acid. The organic layer was separated and washed with water (twice) and then dried over magnesium sulfate and evaporated in vacuo to give the tetramethylether in quantitative yield, which was directly used for the next step without further purification. ^1H NMR (200 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.47 (s, 3H), 3.64 (s, 3H), 3.70 (s, 3H), 3.73 (s, 3H), 5.35 (s, 2H), 7.13–7.64 (16H), 7.74–7.92 (3H). A solution of the crude tetramethylether (0.87 g, 1.3 mmol) and 1N sodium hydroxide (3.9 ml, 3.9 mol) in THF (50 ml) was refluxed for 8 h. The solvent was evaporated under reduced pressure and the residue was partitioned between ethyl acetate and aqueous hydrochloric acid. The organic layer was washed with brine (twice), dried over magnesium sulfate and evaporated to give the alcohol (770 mg, 94%). ^1H NMR (200 MHz, $CDCl_3$) δ 3.46 (s, 3H), 3.64 (s, 3H), 3.71 (s, 3H), 3.73 (s, 3H), 5.36 (s, 2H), 7.14–7.64 (16H), 7.76–7.90 (3H), 7.92 (s, 3H). A suspension of palladium on carbon (10%, 350 mg) in EtOH (10 ml) was added to the solution of the alcohol (500 mg) in THF (15 ml). Ammonium formate (1.4 g, 22 mmol) was added the mixture and stirred for 60°C for 4 h. After the catalyst was filtered off, the filtrate was evaporated under reduced pressure, the residue was poured into ethyl acetate and aqueous hydrochloric acid. The organic layer was separated and washed with brine (twice) and then dried over magnesium sulfate and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, dichloromethane/*n*-hexane/ethyl acetate=5/4/1) to afford **9** as colorless powder (435 mg). Mp 264–266°C (triturated with *n*-hexane/ethyl acetate); IR (KBr) 3480, 1506, 1465 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.47 (s, 6H), 3.72 (s, 6H), 6.16 (s, 2H), 7.16–7.47 (10H), 7.51 (s, 2H), 7.82 (d, J=8.1 Hz, 2H); HRMS Calcd for $C_{34}H_{28}O_6$: 532.1886. Found: 532.1875; Anal. Calcd for $C_{34}H_{28}O_6$: C, 76.68; H, 5.30. Found: C, 76.66; H, 5.27.

3.1.5. Ditriflate 10. To a solution of **9** (1.50 g, 2.8 mmol) and diisopropylethylamine (2.4 ml, 14 mmol) in dichloromethane (50 ml) was dropwise added trifluoromethanesulfonic anhydride (1.9 ml, 11 mmol) under ice-bath cooling. The reaction mixture was allowed to be back to room temperature and stirred for 1 h. Further, diisopropylethylamine (1.2 ml, 7 mmol) and trifluoromethanesulfonic anhydride (1.0 ml, 6 mmol) were successively added to the solution at room temperature for 1 h. The reaction mixture was evaporated under reduced pressure, and the residue was poured into ethyl acetate and aqueous hydrochloric acid. The organic layer was separated and washed with 2% aqueous sodium hydroxide, aqueous hydrochloric acid, water and then dried over magnesium sulfate and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, dichloromethane/*n*-hexane=1/1) to afford **10** as a white powder (1.77 g, 79% yield). Mp 236–238°C (triturated with *n*-hexane/ethyl acetate); IR (KBr) 2946, 1503, 1423 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.58 (s, 6H), 3.73 (s, 6H), 7.15–7.60 (10H), 7.93 (s, 2H), 7.97 (d, J=8.0 Hz, 2H); HRMS Calcd for $C_{36}H_{26}O_{10}F_6S_2$: 796.0872. Found: 796.0901; Anal. Calcd for $C_{36}H_{26}O_{10}F_6S_2$: C, 54.27; H, 3.29. Found: C, 54.64; H, 3.48.

3.1.6. Boric acid 12. To a solution of **11** (3.00 g, 6.9 mmol) in dry THF (30 ml) was dropwise added *n*-butyllithium

Table 3. Crystal and experimental data for host **1** and host **2**

	Host **1** (Fig. 2)	Host **2** (Fig. 3)	Host **2** (Fig. 4)
Recrystallizing solvent	Toluene	Acetone	Acetonitrile
Formula	$C_{66}H_{72}O_{16}$ (toluene)$_2$	$C_{68}H_{76}O_{16}$ (H_2O)$_6$	$C_{68}H_{76}O_{16}$ (H_2O)$_2$ (acetonitrile)$_2$
Formula weight	1305.55	1257.41	1267.46
Crystal size (mm^3)	0.30×0.20×0.10	0.30×0.10×0.06	0.30×0.15×0.10
	Triclinic	Triclinic	Triclinic
Space group	*P*-1 (#2)	*P*-1 (#2)	*P*-1 (#2)
a (Å)	10.334 (3)	15.470 (3)	15.172 (1)
b (Å)	33.582 (5)	17.862 (3)	17.771 (2)
c (Å)	10.303 (2)	14.362 (6)	14.481 (1)
α (deg.)	94.77 (2)	107.58 (2)	106.29 (1)
β (deg.)	95.61 (2)	109.74 (2)	109.718 (9)
γ (deg.)	94.31 (2)	65.75 (1)	65.694 (7)
V, Å^3	3533 (1)	3343 (1)	3348 (7)
Z	2	2	2
d_{calcd} (g cm^{-3})	1.227	1.263	1.257
μ (cm^{-1})	6.87	7.82	7.39
Unique ref. no.	11,738	11,401	11,427
R_1	0.083	0.089	0.089
Rw	0.101	0.115	0.129
Goodness of fit	2.79	3.11	3.45

(1.54N in *n*-hexane solution, 5.4 ml, 8.3 mmol) at −78°C under argon atmosphere. The reaction mixture was stirred for 2.5 h. This reaction mixture was added to a solution of trimethyl borate (2.4 ml, 20 mmol) in dry THF at −78°C. The reaction mixture was allowed to be back to room temperature and stirred for 30 min. 1N aqueous hydrochloric acid was added to the solution and extracted with ethyl acetate. The organic layer was washed with water and dried over sodium sulfate and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, chloroform/methanol=10/1) to afford **12** (1.37 g, 49% yield); IR (KBr) 3400, 2871, 1604 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.38–3.78 (16H), 4.20 (d, *J*=10.5 Hz, 2H), 4.85–5.10 (2H), 5.03 (d, *J*=10.5 Hz, 2H), 5.26 (d, *J*=10.5 Hz, 1H), 5.55 (d, *J*=15.8 Hz, 1H), 6.24 (m, 1H), 7.67 (s, 2H); The molecular ion peak was not detected by EI and FAB mass spectrometer. EI MS *m/z*: 352 $(M+H-B(OH)_2)^+$, 311, 158, 119. Because of the compound **12** is labile to stock for long time, so **12** was quickly used for the next step.

3.1.7. Host 1. To a solution of **10** (432 mg, 1.1 mmol) and $Pd(PPh_3)_4$ (27 mg, 0.02 mmol) in toluene (10 ml), 2 M Na_2CO_3aq (0.77 ml) and **12** (306 mg, 0.38 mmol) in methanol (10 ml) were added. The reaction mixture was refluxed for 5 h. The reaction mixture was poured into ethyl acetate and 1N aqueous hydrochloric acid. The organic layer was separated, washed with water, dried over sodium sulfate and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, chloroform/methanol=20/1) to afford **1** as a white powder (346 mg, 80% yield). For determination binding constants, **1** was further purified by recrystallization (chloroform–hexane) mp 236–238°C; IR (KBr) 2865, 1490, 1354, 1236, 1111 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (s, 6H), 3.68–3.79 (38H), 4.76 (s, 8H), 7.16 (m, 2H), 7.27 (m, 2H), 7.36 (m, 4H), 7.45 (m, 2H), 7.58 (s, 4H), 7.93 (d, *J*=8.3 Hz, 2H), 7.97 (s, 2H), 8.23 (brs, 2H); HRMS Calcd for $C_{66}H_{72}O_{16}$: 1120.4821. Found: 1120.4788; Anal. Calcd for $C_{66}H_{72}O_{16}\cdot H_2O$: C, 69.58; H, 6.55. Found: C, 69.64; H, 6.56.

3.1.8. Host 2. Sodium hydride (60% mineral oil suspension, 71 mg, 1.8 mmol) was added to a solution of host **1** (200 mg, 0.18 mmol) in DMF (10 ml) under ice-bath cooling. After 10 min, methyl iodide (0.22 ml, 3.6 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was poured into ethyl acetate and 1N aqueous hydrochloric acid. The organic layer was separated, washed with water, dried over sodium sulfate and evaporated in vacuo. The residue was purified by recrystallization from acetone to afford **2** as colorless crystal (130 mg, 65%). Mp 239–240°C; IR (KBr): 2871, 1487, 1389, 1352, 1236, 1096, 1019 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.19 (s, 6H), 3.48–3.54 (16H), 3.61–3.63 (8H), 3.68–3.69 (8H), 3.77 (s, 6H), 4.23 (s, 6H), 4.69 (s, 8H), 7.18–7.20 (2H), 7.28–7.31 (2H), 7.38–7.39 (4H), 7.41–7.49 (2H), 7.71 (s, 4H), 7.97 (d, *J*=8.3 Hz, 2H), 8.01 (s, 2H); FAB HRMS (NBA): calcd for $C_{68}H_{76}O_{16}Na$, 1171.5031 found 1171.5060; Anal. Calcd for $C_{68}H_{76}O_{16}\cdot 3/2H_2O$: C, 69.43; H, 6.77, found C, 69.11; H 6.47.

3.1.9. Host 3. A solution of **9** (100 mg, 0.19 mmol), carboxybenzo 18-crown-6 (**13**) (160 mg, 0.45 mmol), WSC (144 mg, 0.75 mmol) and DMAP (5 mg, 0.04 mmol) in dry dichloromethane (10 ml) was stirred for 12 h at room temperature. The reaction mixture was poured into ethyl acetate and 1N aqueous hydrochloric acid. The organic layer was separated, washed with water and brine, dried over sodium sulfate and evaporated in vacuo. The residue was purified by recrystallization from acetone to afford **3** as a white powder (160 mg, 70% yield). Mp 237–238°C; IR (KBr): 2884, 1735, 1599 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (s, 6H), 3.70 (s, 6H), 3.71–3.85 (24H), 3.90–4.00 (8H), 4.23–4.26 (8H), 6.94 (d, *J*=8.6 Hz, 2H), 7.19–7.22 (2H), 7.28–7.30 (2H), 7.36–7.42 (4H), 7.46–7.50 (2H), 7.75 (d, *J*=2.2 Hz, 2H), 7.87 (s, 2H), 7.91 (d, *J*=8.6 Hz, 2H), 7.92 (d, *J*=8.6 Hz, 2H); FAB HRMS (NBA): calcd for $C_{68}H_{72}O_{20}Na$, 1231.4514, found 1231.4481; Anal. Calcd for $C_{68}H_{72}O_{20}\cdot 1/2H_2O$: C, 67.04; H, 6.04, found C, 66.85; H 5.90.

3.1.10. 1,14-Tetradecanediamine dipicrate. A solution of

1,14-tetradecanediamine (270 mg, 1.2 mmol) in MeOH (2.0 ml) was added to a solution of picric acid (576 mg, 2.5 mmol) in water (30 ml) at 80°C. The reaction mixture was left standing overnight to give a yellow solid. The crude solid was recrystallized from MeOH–H_2O to give pure 1,14-tetradecanediamine dipicrate (386 mg, 44%). Mp 142–144°C (from MeOH–water); IR (KBr): 1645, 1556, 1328 cm^{-1}; ^1H NMR (CD_3OD, 200 MHz) δ 1.24–1.38 (20H), 1.64 (m, 4H), 2.91 (t, J=7.7 Hz, 4H), 8.76 (s, 4H); Anal. Calcd for $C_{26}H_{38}N_8O_{14}\cdot 1/2H_2O$: C, 44.89; H, 5.65; N, 16.11 found C, 44.63; H 5.63; N, 15.94.

3.1.11. 1,16-Hexadecanediamine dipicrate. This compound was synthesized in a similar manner as above. Mp 154–155°C (from MeOH–water); IR (KBr): 2920, 1614, 1326, 1274 cm^{-1}; ^1H NMR (CD_3OD, 200 MHz) δ 1.24–1.40 (24H), 1.64 (m, 4H), 2.91 (t, J=7.4 Hz, 4H), 8.76 (s, 4H); Anal. Calcd for $C_{28}H_{42}N_8O_{14}\cdot 3/4H_2O$: C, 46.18; H, 6.02; N, 15.39 found C, 46.33; H 6.04; N, 15.07.

3.2. X-Ray structural determinations of hosts 1 and 2

Crystal data and experimental conditions are summarized in Table 3. In Figs. 2 and 3, the central naphthalene ring was disordered in an opposite sense. Therefore, an imaginary portion was adopted instead for that naphthalene ring and that structure was refined by full-matrix least-squares refinement.

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