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Preparation and unique circular dichroism phenomena of urea-functionalized self-folding resorcinarenes bearing chiral termini through asymmetric hydrogen-bonding belts†

Osamu Hayashida,*[a,c] Jun-ichi Ito,[b] Shinji Matsumoto[b] and Itaru Hamachi[a,c]

[a] *Institute for Materials Chemistry and Engineering, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan*

[b] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan*

[c] *PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama, 332-0012, Japan. E-mail: ohaya@ms.ifoc.kyushu-u.ac.jp*

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Chiral macrocycles with eight (*R*)- and (*S*)-methylbenzylurea residues on the resorcinarene skeleton linked through a hexyl or dodecyl spacer having amide linkages have been prepared by the reactions of the corresponding octaamine derivative with (*R*)- and (*S*)-α-methylbenzylisocyanate, respectively. In chloroform, the urea-functionalized resorcinarenes with hexyl spacers form intramolecular hydrogen bonds by bundling the urea and amide residues in a cyclic fashion to give a self-folding cavitand. The urea and amide residues are cooperatively oriented in the same direction to result in asymmetric hydrogen-bonding belts. Unique circular dichroism (CD) bands are induced in the absorption wavelength ranges of the macrocyclic skeleton, caused by a chirality transmission from their chiral urea termini through hexyl spacers in the self-folded conformation. On the other hand, urea-functionalized resorcinarenes with a longer dodecyl spacer do not show such unique CD bands on the macrocycle, because of their weaker propensity for hydrogen bond formation. The characteristic CD bands of the urea-functionalized self-folding macrocycles disappeared upon complexation with anions such as chloride and bromide, reflecting breaking of the intramolecular hydrogen-bonding belts.

Introduction

Self-folding cavitands[1] are synthetic hosts in which intramolecular hydrogen bonding and solvophobic effects play important roles in maintaining their unique conformation. Rebek and co-workers reported that resorcinarene[2]-based (**2**) cavitands bearing four aromatic walls, each having two amide groups, fold into a deep open-ended cavity by means of intramolecular (C=O···HN) hydrogen bonds in non-polar solvents (Fig. 1).[3] These molecules provide an internal cavity suitable for encapsulating small, complementary organic molecules and ions as a guest. The eight amide groups provide a head-to-tail belt of hydrogen bonds along the wide rim of the resorcinarene.[3] The belt of the hydrogen-bonded amide groups makes possible two cycloenantiomers, with clockwise and counterclockwise orientations of the amide bonds (Fig. 1). In solutions at ambient temperature, the interconversion between these two conformational enantiomers occurs through the reorientation of the hydrogen-bonding arrays. A possible strategy for the development of chiral self-folding cavitands[4] is control of the formation of either of the two cycloenantiomers at the dynamic level.

On the other hand, urea moieties[5] also act as strong hydrogen-bond donors and acceptors. These have been frequently used as functional groups for the formation of supramolecular architectures.[6] For example, modifications at the wide rim of calix[4]arene with bulky urea residues resulted in supramolecular dimeric capsules, in which cationic guests such as tetraethylammonium cations were encapsulated.[6] On these grounds, we were interested in the development of chiral self-folding cavitands[4]

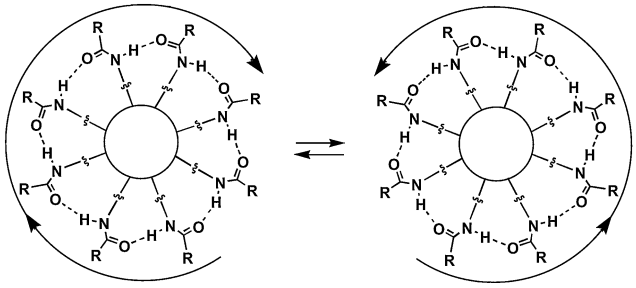

Fig. 1 Head-to-tail hydrogen-bonded belt formed cooperatively by eight amide groups of Rebek's self-folding cavitand. Interconversion of two cycloenantiomers, with clockwise and counterclockwise orientation of the amide bonds, is shown. The large circles represent the resorcinarene skeleton; R is an alkyl group.

capable of providing an asymmetric internal cavity, on the basis of a molecular design that allows the introduction of an optically active urea moiety onto each of the eight OH groups of the resorcinarene skeleton (**2**) through an alkyl spacer having an amide linkage.[7] Urea-functionalized resorcinarenes are expected to form similar intramolecular hydrogen bonds in a non-polar solvent, with the direction of the hydrogen-bonded arrays being controlled to some extent by steric hindrance of the neighboring chiral moieties, as schematically shown in Fig. 2.

In this context, we report preparation of the urea-functionalized self-folding resorcinarene derivatives as well as their unique circular dichroism (CD) spectroscopic features in chloroform. We have discovered that, in chloroform, CD bands were induced in the absorption wavelength range of the macrocyclic skeleton, which were transmitted from the remote chiral urea termini in the asymmetrically self-folded conformation.

† Electronic supplementary information (ESI) available: NMR and CD spectra of **1**, CD spectrum of **10-S**, and FAB MS spectra of 1 : 1 adducts of **1** with chloride ion and bromide ion. See http://www.rsc.org/suppdata/ob/b4/b418880b/

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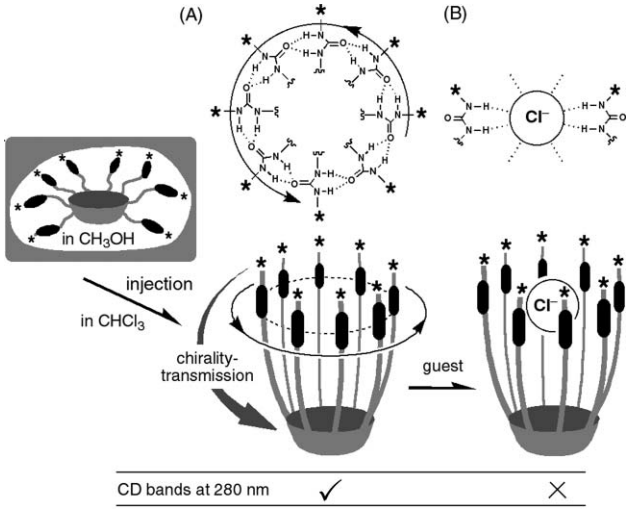
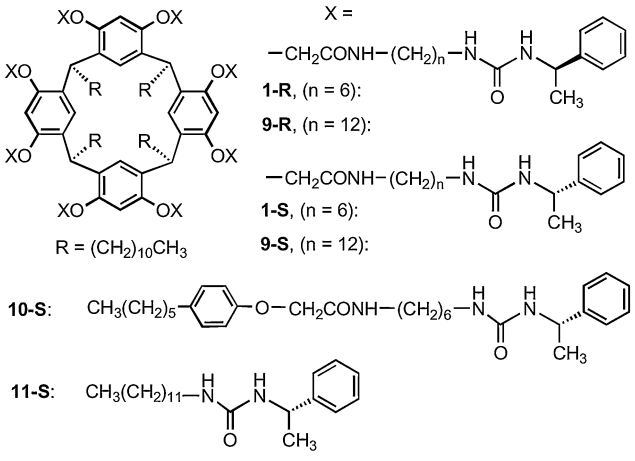


Fig. 2 Schematic representations for the self-folding of **1**. In chloroform, the urea moieties (black ovals) of **1** form intramolecular hydrogen bonds clockwise or counterclockwise in a cyclic fashion, the direction of which is controlled by the neighboring chiral termini. A chirality transmission from the chiral urea termini to the macrocycles through hexyl spacers results in CD bands at 280 nm, in the absorption wavelength range of the macrocyclic skeleton (A). Intermolecular hydrogen bonds with an encapsulated anion (Cl^-), resulting in the decrease and disappearance of the CD bands at 280 nm (B). Each asterisk (⋆) represents a chiral center.

Results and discussion

Molecular design and preparation

Resorcinarene (**2**) is a bowl-shaped cyclic resorcinol tetramer with four alkyl tails (R = undecyl in the present case), which are known to be oriented in the same direction.[2] We have designed self-folding macrocycles[7] bearing chiral termini by introducing (*R*)- and (*S*)-methylbenzylurea residues, respectively, onto each OH group of resorcinarene through a hexyl spacer, **1-R** and **1-S** ($n = 6$), respectively. In Fig. 3 are shown the space-filling CPK models[8] (top and side views) with estimated molecular dimensions for **1-R** in the case of a folded conformation. The bowl-shaped resorcinarene platform with four undecyl chains sustains a folded conformation in which eight branches having chiral urea termini can be spontaneously packed through intramolecular hydrogen-bonding interactions in an appropriate solvent system. Other urea-functionalized resorcinarenes having a longer (dodecyl) spacer were also designed in order to investigate the chain-length dependency of the hydrogen bond formation (**9-R** and **9-S** ($n = 12$)). The distance between the chiral urea termini and the macrocycle skeleton of **9** is about twice as long as that in **1**.



Resorcinarenes bearing eight (*R*)- and (*S*)-methylbenzylurea residues, **1-R** and **1-S**, were prepared by following the reaction sequence given in Scheme 1. An octaacid derivative of resorcinarene **4** was prepared by reaction of **2** with *tert*-butyl bromoacetate, followed by treatment with TFA. A precursor of **1**, the octaamine derivative of resorcinarene **7**, was prepared by condensation of the corresponding carboxylic acid derivative **4** with (6-aminohexyl)carbamic acid *tert*-butyl ester in the presence of the BOP reagent, followed by removal of the protecting groups. Reactions of octaamine **7** with (*R*)- and (*S*)-α-methylbenzyl isocyanate proceeded to give urea-linked resorcinarene derivatives **1-R** and **1-S**, respectively (yields 46–56%). The use of the (12-aminododecyl)carbamic acid *tert*-butyl ester in place of (6-aminohexyl)carbamic acid *tert*-butyl ester afforded the corresponding resorcinarenes bearing eight (*R*)- and (*S*)-methylbenzylurea residues with a dodecyl spacer, **9-R** and **9-S**, respectively. We also prepared the mono-urea derivative **10-S** having an *S*-configuration by using 4-hexylphenol in place of **2**, in a manner similar to that applied in the synthesis of **1-S**.

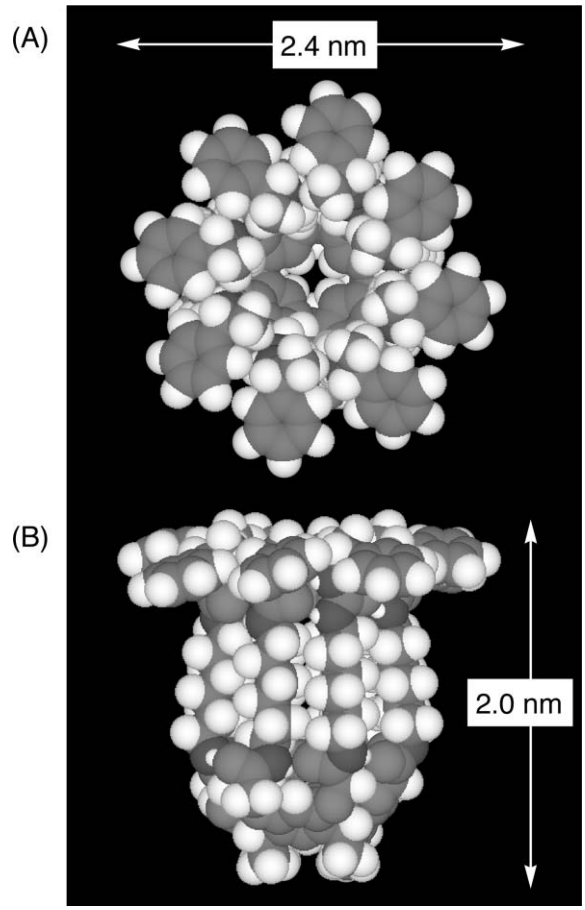
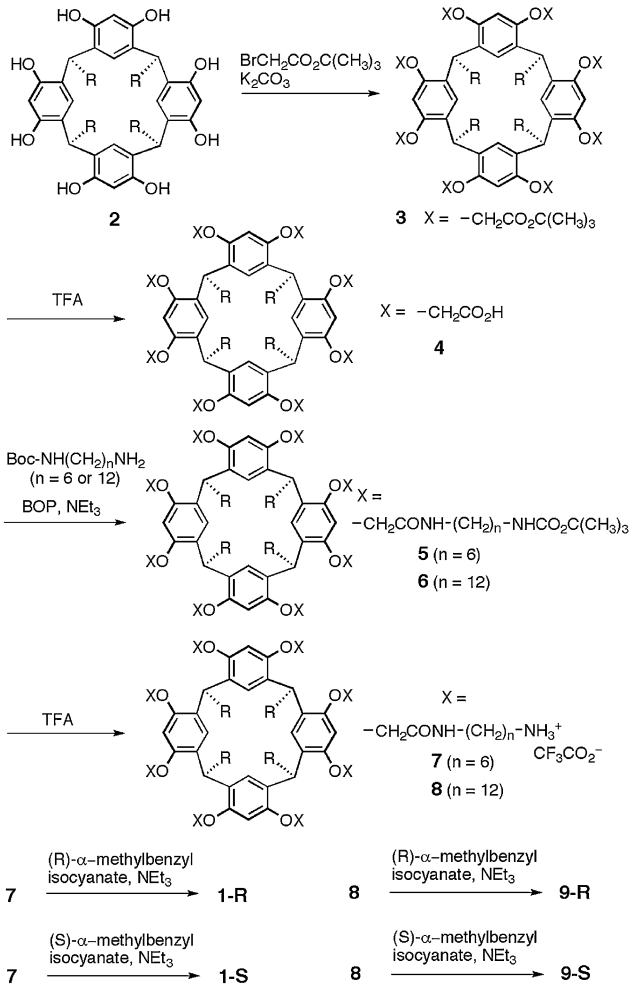


Fig. 3 A space-filling representation of **1-R**. Top view (A) and side view (B). The undecyl groups are replaced by methyl groups for clarity.

Cyclic hydrogen-bonding belts

In view of investigations of the CPK molecular models of **1-R** (Fig. 3), all branches with urea moieties are oriented in the same direction, as mentioned above. The urea moieties linked to the chiral centers of **1-R** approach close to each other and are twisted in the same direction in a location suitable for intramolecular hydrogen bonding with its neighbors. The formation of such a hydrogen-bond network by bundling the urea and amide residues in a cyclic fashion gives a self-folding cavitand, as schematically shown in Fig. 2. When all of the urea or amide residues are oriented in the same direction, the cyclic hydrogen-bonding belts are formed cooperatively.

In general, small urea molecules at higher concentrations tend to self-assemble by hydrogen-bonding interactions in non-polar organic solvents.[9] First, the hydrogen-bonding properties of



Scheme 1 Preparation of urea-functionalized resorcinarenes (R = $(CH_2)_{10}CH_3$).

1-S in chloroform solution (1.3 mM) were evaluated by FT-IR measurements, and compared with those for the mono-urea derivative **10-S** (10 mM) in a monomeric state,[10] as a component analogue of **1-S**. The absorption frequency of the N–H deformation band of **1-S** (δ_{N-H} = 1565 cm^{-1}) is higher than for **10-S** (δ_{N-H} = 1554 cm^{-1}), whereas the C=O stretching frequency of **1-S** ($\nu_{C=O}$ = 1658 cm^{-1}) is lower than for **10-S** ($\nu_{C=O}$ = 1668 cm^{-1}) (Fig. 4), indicating the formation of intramolecular hydrogen bonds for most urea and amide residues of **1-S**. A monomeric dispersion of **1-S** was also suggested by NMR spectroscopy, without any detectable concentration dependence on the chemical shifts of urea protons of **1**, within the concentration range 0.1–2.4 mM (see ESI†). A similar property in the hydrogen-bonding properties of macrocyclic urea **1-R** was also confirmed by identical methods (δ_{N-H} = 1565 and $\nu_{C=O}$ = 1658 cm^{-1}). Kobayashi and Seki reported similar results for hydrogen bond formation in urea derivatives by identical methods.[11] A urea-functionalized resorcinarene with a longer dodecyl spacer, **9-S**, however, gave values of 1561 and 1667 cm^{-1} for the N–H deformation band and C=O stretching vibrations, respectively, indicating its weaker propensity for urea hydrogen-bonding belt formation. In the case of **9-S**, the conformational flexibility originating from the dodecyl spacer seems to be preventing the urea residues from forming strong intramolecular hydrogen bonds.

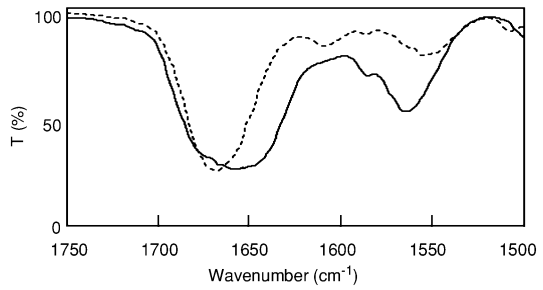


Fig. 4 FT-IR spectra of **1-S** (solid line) and **10-S** (dotted line) in chloroform at 298 K.

Circular dichroism phenomena induced by the self-folding conformation

Resorcinarenes and their derivatives show a characteristic absorption band at around 280 nm which is attributed to an electric transition moment of the resorcinol ring; the electronic absorption spectrum of **1-S** is shown in Fig. 5, as a typical example. At least in the concentration range of UV measurements, **1-S** exists in a monomeric state, as confirmed by a Beer's plot. Achiral resorcinarene derivatives such as **5** did not show any detectable CD bands in the absorption wavelength ranges of the macrocyclic skeleton. Weak absorption bands of 1-undecyl-3-(1-phenylethyl)urea **11-S** (a terminal methylbenzylurea analogue of **1-S**) on the other hand, have shorter wavelengths – 254, 260, and 267 nm in chloroform (Fig. 5).

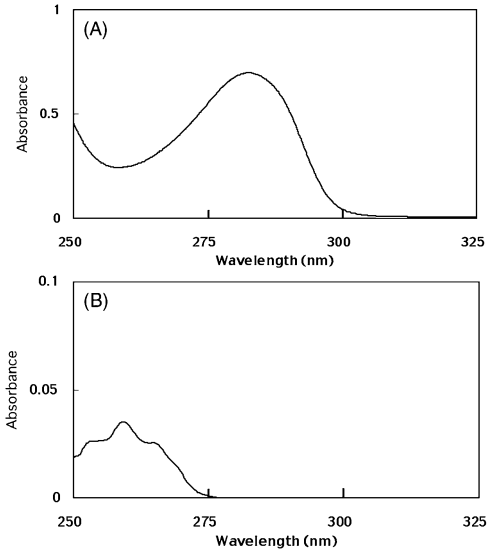


Fig. 5 UV spectra of **1-S** (A) and **11-S** (B) in chloroform.

The asymmetric characters of the octa-ureas **1-R** and **1-S** were examined by CD spectroscopy, especially in the wavelength ranges of the terminal urea residues (254, 260, and 267 nm) and the macrocyclic skeleton (280 nm). A chloroform solution of compound **1-S** showed positive CD bands at 254, 261, and 267 nm as well as a negative band at 280 nm, as shown in Fig. 6. In addition, mono-urea derivatives such as **10-S** and **11-S** show similar CD bands at 255, 261, and 268 nm with *ca.* $\frac{1}{8}$ of the intensity of **1-S** (see ESI for **10-S**†). These results suggest that the CD bands at shorter wavelengths are originally attributable to the optically active urea residues. On the other hand, the negative CD band at 280 nm indicates a remote chirality transmission from the chiral urea termini to the macrocycles through hexyl spacers; *i.e.*, the originally achiral macrocyclic skeleton of **1-S** gains induced chirality through the asymmetric cyclic hydrogen-bonding belts around the urea terminus in chloroform, as shown schematically in Fig. 2. A similar character was observed for **1-R**, which had an inverted CD spectrum (Fig. 6). No concentration dependency in the CD spectra of **1** was observed, at least within the concentration range 15–760 μM (see ESI†), indicating that **1** exists in a monomeric state. The formation of intramolecular hydrogen bonds of **1** is responsible for the unique CD phenomena, which was evidenced by the following results.

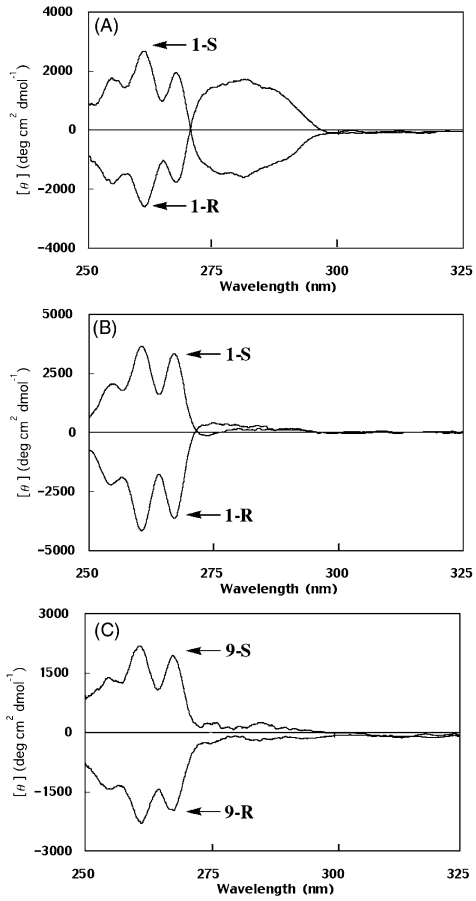


Fig. 6 CD spectra of **1-S** and **1-R** in chloroform (A) or in chloroform–methanol (3 : 97 v/v) (B). CD spectra of **9-S** and **9-R** in chloroform (C).

(i) The CD band of **1-S** at 280 nm weakened to *ca.* 42% of its original intensity in chloroform–methanol (92 : 8 v/v) and completely disappeared in chloroform–methanol (3 : 97 v/v) (Fig. 6). Methanol breaks intramolecular hydrogen bonds. (ii) Resorcinarenes having a dodecyl spacer, **9-S** and **9-R**, which were lacking effective intramolecular hydrogen-bonding belts, as mentioned above, did not show meaningful CD bands at longer wavelengths of around 280 nm (Fig. 6). The CD signal of **1** at 280 nm, which is the effect of the individual chiral urea termini on the macrocycle skeleton, arose owing to the formation of asymmetric hydrogen-bonded arrays to give a self-folded conformation.[12]

Conformational changes upon guest binding

An interesting potential use of the self-folding cavitand is as a host[13] for inclusion of guest anions. First, the guest-binding behavior of **1-S** was observed by FAB spectrometry. MS peaks for 1 : 1 adducts with Cl^- and Br^- were directly detected; *m/z* 3 568 $[M + Cl]^-$ and 3 613 $[M + Br]^-$ (see ESI†). Second, the guest-binding behavior of **1-S** for anions has been investigated by ^1H NMR spectroscopy. Upon addition of chloride (as a tetrabutylammonium salt) to a $CDCl_3$ solution containing **1-S**, the ^1H NMR signals due to the urea protons of **1-S** were sharpened with concomitant downfield shifts, showing a simple saturation behavior for the complexation, as shown in Fig. 7. These results indicate again that **1** has a self-folding cavity suitable for binding an anion, as schematically shown in Fig. 2. A similar complexation behavior for **1-S** was also confirmed with bromide. The binding constants (K) for 1 : 1 host–guest complexes were evaluated on the basis of computer-aided least-squares curve fitting methods applied to the NMR data (K = 1000 and 600 M^{-1} for chloride and bromide, respectively). On the other hand, the K value of **1-S** for the ClO_4^- ion could not

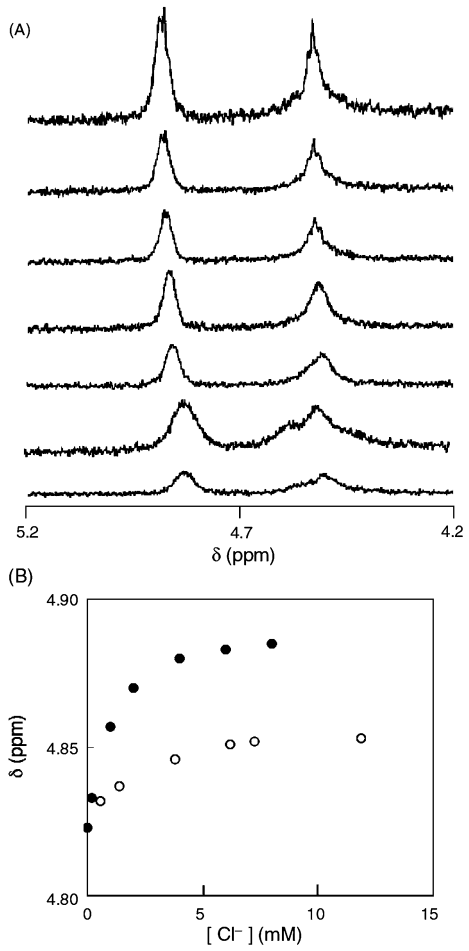


Fig. 7 Partial ^1H NMR spectra of **1-S** at 298 K in the presence of Cl^- (as a tetrabutylammonium salt): 0, 1, 5, 10, 20, 30, and 40 equiv. (from bottom to top) (A). The corresponding NMR titration curves for Cl^- (●) and Br^- (○) (B).

be evaluated due to its weak binding affinity. Most interestingly, the CD bands of **1-S** at 280 nm were weakened upon addition of chloride (Fig. 8) and bromide. The extent of change in CD bands upon complexation with guests follows the sequence: $Cl^- > Br^- \gg ClO_4^-$, reflecting the guest-binding affinities of **1-S**. These results suggested that the encapsulated guest anions disrupted the formation of intramolecular hydrogen bonds of **1-S**, as schematically shown in Fig. 2, so that the resulting complexes did not show any CD phenomena at 280 nm. Such conformation changes around the urea residues of **1** upon complexation with anions were monitored by circular dichroism measurements. A similar complexation behavior for **1-R** with these anions was also confirmed by identical methods.

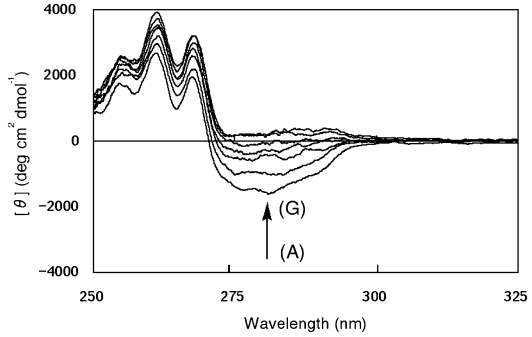


Fig. 8 CD spectra of **1-S** in chloroform in the presence of Cl^- (as a tetrabutylammonium salt): 0, 2, 7, 12, 22, 31, and 36 equiv. (from A to G).

Conclusions

Chiral self-folding resorcinarene derivatives with eight (*R*)- and (*S*)-methylbenzylurea residues linked through a hexyl spacer having amide linkages, **1-R** and **1-S**, were designed and developed. In chloroform, these urea-functionalized resorcinarenes formed intramolecular hydrogen bonds by bundling the urea and amide residues in a cyclic fashion to give a self-folding cavitand. The cooperatively oriented and hydrogen-bonded urea residues gave unique CD phenomena in the absorption wavelength ranges of the macrocyclic skeleton. In such a self-folded conformation, the formation of an asymmetric cyclic hydrogen-bonding belt is responsible for these unique CD bands, in which the information on the chirality of the termini is transferred to the absorption wavelength of the macrocycle. These characteristic CD bands for the urea-functionalized self-folding macrocycles disappeared upon complexation with anions such as chloride and bromide. Conformational changes of the urea-functionalized resorcinarenes were successfully observed by CD spectroscopy. We believe that our concept of the molecular design of urea-functionalized self-folding resorcinarenes bearing chiral termini provides a useful guidepost for developments of smart molecules having sophisticated capabilities in areas such as chiral recognition,[14] molecular informatics,[15] and catalytic performance.[16]

Experimental

General analyses and measurements

Elemental analyses were performed at the Microanalysis Center of Kyushu University. IR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer, ^{1}H and ^{13}C NMR spectra were taken on a Bruker DRX 600 spectrometer. Circular dichroism spectra were run on a JASCO J-500C spectropolarimeter, while a JEOL JMS-HX110A spectrometer and an Applied Biosystems Voyager were used for FAB and MALDI-TOF mass spectrometry, respectively.

Resorcinarene octaester (3)

A mixture of potassium carbonate (3.1 g, 22 mmol), *tert*-butyl bromoacetate (4.4 g, 22 mmol), resorcinarene **2** (1.0 g, 0.9 mmol), and dry acetone (100 ml) was refluxed for 16 h and cooled to room temperature. An insoluble material was removed by filtration, and the filtrate evaporated to dryness under reduced pressure. The residue was chromatographed on a column of silica gel (SiO_2) with EtOAc–hexane (1 : 1 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a pale yellow oil (1.8 g, 55%): δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.85 (12H, m, CH_2CH_3), 1.2–1.3 [72H, m, $CH_2(CH_2)_9CH_3$], 1.4 [72H, s, $C(CH_3)_3$], 1.83 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 4.1 (16H, s, OCH_2CO), 4.57 (4H, t, J = 7.2, CH-Ar), 6.19 (4H, s, Ar–H2), 6.58 (4H, s, Ar–H5); δ_C (125 MHz, $CDCl_3$, Me_4Si) 14.50 ($(CH_2)_{10}CH_3$), 23.1 ($(CH_2)_{10}CH_2CH_3$), 28.4 ($C(CH_3)_3$, CH), 30.2 ($(CH_2)_6CH_2CH_3$)), 32.3 ($CHCH_2CH_2CH_2$), 34.9 ($CHCH_2CH_2$), 36.1 ($CHCH_2$), 68.3 ($C(CH_3)_3$), 69.1 (OCH_2), 100.2 (Ar–C2), 127.0 (Ar–C4,6), 128.5 (Ar–C5), 154.9 (Ar–C1,3), 168.9 (CO). Anal. Calcd. for $C_{120}H_{192}O_{24}$: C, 71.39; H, 9.56. Found: C, 71.35; H, 9.56. MALDI-TOF (positive mode, matrix: dithranol): m/z calcd. for $C_{120}H_{192}O_{24}Na$: 2041.8. Found: 2040.7 $[M + Na]^+$. MS (FAB) m/z calcd. for $C_{120}H_{193}O_{24}$: 2019.8. Found: 2018.3 $[M + H]^+$.

Resorcinarene octaacid (4)

Trifluoroacetic acid (5 mL) was added to a dichloromethane (5 mL) solution of **3** (390 mg, 0.19 mmol), and the mixture was stirred for 2 h at room temperature. The solvent was then evaporated off under reduced pressure to give a white solid (290 mg, quantitative): ν_{max} (film) 1717 (acid C=O) cm^{-1}; δ_H (400 MHz, CD_3OD, Me_4Si) 0.82 (12H, m, CH_2CH_3), 1.1–1.2 [72H, m, $CH_2(CH_2)_9CH_3$], 1.74 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 4.21 [8H, d, J = 16.4, OCH_2CO (non-equivalent)], 4.46 [8H, d, J = 16.4, OCH_2CO (non-equivalent)], 4.48 (4H, t, J = 7.2, CH-Ar), 6.35 (4H, s, Ar–H2), 6.49 (4H, s, Ar–H5), 12.7 (8H, br s, COOH); δ_C (125 MHz, CD_3OD, Me_4Si) 15.0 ($(CH_2)_{10}CH_3$), 24.2 ($(CH_2)_{10}CH_2CH_3$), 29.6 (CH), 31.4 ($(CH_2)_6CH_2CH_3$)), 33.6 ($CHCH_2CH_2CH_2$), 36.1 ($CHCH_2CH_2$), 37.2 ($CHCH_2$), 68.2 (OCH_2), 102.3 (Ar–C2), 127.9, 129.8 (Ar–C4,5,6), 156.21 (Ar–C1,3), 173.34 (CO). m/z calcd. for $C_{88}H_{127}O_{24}Na$: 1568.9. Found: 1568.0 $[M - H]^-$.

Resorcinarene octaBoc-amine having a hexyl spacer (5)

A solution of *N*-1-*tert*-butoxycarbonyl-1,6-diaminohexane hydrochloride (1.0 g, 3.96 mmol) and triethylamine (0.56 ml, 3.96 mmol) in dry *N*,*N*-dimethylformamide (DMF, 5 ml) was added dropwise to a solution of **4** (520 mg, 0.33 mmol), benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP, 1.76 g, 3.96 mmol), and triethylamine (0.37 ml, 2.64 mmol) in dry DMF (3 mL) under nitrogen at room temperature. The resulting mixture was stirred for 12 h at room temperature. EtOAc (100 ml) was added to the reaction mixture, and the mixture was then washed with 10% aqueous citric acid (25 ml), saturated aqueous sodium chloride (25 ml) and 5% aqueous sodium hydrogen carbonate (25 ml), in that order. After being dried ($MgSO_4$), the solution was evaporated to dryness under reduced pressure. The residue was chromatographed on a column of silica gel (SiO_2) with EtOAc–hexane (5 : 2 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a white solid (0.4 g, 41%): ν_{max} (film) 1681 (amide C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.81 (12H, m, CH_2CH_3), 1.2 [104H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_2$], 1.3–1.4 [72H, s $C(CH_3)_3$], 1.73 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.8–2.9 (16H, m, $CH_2CONHCH_2CH_2$), 3.0 [16H, m, $CH_2CONH(CH_2)_4CH_2$], 3.1 [32H, m, $CH_2CONH(CH_2)_5CH_2$, $CH_2CONHCH_2(CH_2)_6$], 4.25 (16H, s, OCH_2CO), 4.66 (4H, m, CHAr), 6.37 (4H, s, Ar–H2), 6.56 (4H, s, Ar–H5), 6.7 and 7.5 (16H, m, NH); δ_C (125 MHz, $CDCl_3$, Me_4Si) 15.9 ($(CH_2)_{10}CH_3$), 24.4 ($(CH_2)_{10}CH_2CH_3$), 28.4 (CH), 30.3 ($C(CH_3)_3$), 31.4, 31.6 ($(CH_2)_6CH_2CH_3$, $OCONHCH_2(CH_2)_4$), 31.9 ($CHCH_2CH_2CH_2$), 33.7 ($CHCH_2CH_2$), 37.5 ($CHCH_2$), 40.9 ($OCONHCH_2$), 42.2 ($OCONH(CH_2)_5CH_2$), 71.0 (OCH_2), 80.7 ($C(CH_3)_3$), 100 (Ar–C2), 128.3, 129.4 (Ar–C4,5,6), 156.0 (CO), 157.9 (Ar–C1,3), 169.6 (CO). Anal. Calcd. for $C_{176}H_{304}N_{16}O_{32}\cdot H_2O$: C, 66.59; H, 9.72; N, 7.06. Found: C, 66.58; H, 9.63; N, 7.16. MALDI-TOF (positive mode, matrix: dithranol): m/z calcd. for $C_{170}H_{304}N_{16}O_{32}Na$: 3179.4. Found: 3180.0 $[M + Na]^+$. MS (FAB) m/z calcd. for $C_{176}H_{304}N_{16}O_{32}Na$: 3179.4. Found: 3178.6 $[M + Na]^+$.

Resorcinarene octaamine having a hexyl spacer (7)

Trifluoroacetic acid (4 mL) was added to a solution of **5** (400 mg, 0.13 mmol) in dichloromethane (5 mL), and the mixture stirred for 2 h at room temperature. After the solvent was evaporated off under reduced pressure to give a white solid (430 mg, quantitative): δ_H (400 MHz, CD_3OD, Me_4Si) 0.8 (12H, m, CH_2CH_3), 1.2 [104H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_2$], 1.4–1.5 (16H, m, $CH_2CONHCH_2CH_2$), 1.5–1.6 [16H, m, $CH_2CONH(CH_2)_4CH_2$], 1.79 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.8 (16H, m, CH_2NH_3), 3.1–3.3 (16H, m, $CH_2CONHCH_2$), 4.2 (16H, s, OCH_2CO), 4.66 (4H, t, J = 7.2, CHAr), 6.42 (4H, s, Ar–H2), 6.70 (4H, s, Ar–H5); δ_C (125 MHz, CD_3OD, Me_4Si) 13.5 ($(CH_2)_{10}CH_3$), 22.8 ($(CH_2)_{10}CH_2CH_3$), 26.1 (CH), 29.9 ($(CH_2)_6CH_2CH_3$, $OCONHCH_2(CH_2)_4$), 32.1 ($CHCH_2CH_2CH_2$), 35.0 ($CHCH_2CH_2$), 36.1 ($CHCH_2$), 39.1 ($OCONHCH_2$), 39.6 ($OCONH(CH_2)_5CH_2$), 68.9 (OCH_2), 114 (Ar–C2), 116 (Ar–C5), 122 (Ar–C4,6), 154.6 (Ar–C1,3), 169.7 (CO). MALDI-TOF (positive mode, matrix: dithranol): m/z calcd. for $C_{136}H_{24}N_{16}O_{16}$: 2356.5. Found: 2655.6 $[M + H]^+$. MS

(FAB) *m/z* calcd. for $C_{136}H_{241}N_{16}O_{16}$: 2356.5. Found: 2355.6 $[M + H]^+$.

Resorcinarene bearing (*R*)-methylbenzylurea residues (1-R)

(*R*)-α-Methylbenzyl isocyanate (78 mg, 0.53 mmol) and triethylamine (0.10 ml, 0.7 mmol) were added to compound **6** (140 mg, 0.04 mmol) dissolved in dry dichloromethane (10 mL), and the mixture was stirred for 12 h at room temperature. After the solvent was evaporated to dryness under reduced pressure, the residue was chromatographed on a column of silica gel (SiO_2) with chloroform–methanol (9 : 1 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a white solid (83 mg, 56%): ν_{max} (FT-IR) 1658 (C=O), 1565 (NH) cm^{-1}; δ_H (600 MHz, $CDCl_3$, Me_4Si) 0.86 (12H, m, CH_2CH_3), 1.23–1.28 [104H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_2$], 1.3–1.4 [56H, m, $CH_2CONHCH_2CH_2$, $CH_2CONH(CH_2)_4CH_2$, CH_3CH], 1.75 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.0 (8H, m, CH_3CH), 3.0 (16H, m, $CH_2CONHCH_2$), 3.2 (16H, m, $CH_2CONH(CH_2)_5CH_2$), 4.46, 4.81, 5.7–6.4 (36H, m, OCH_2CO, CH-Ar, NHCONH), 7.15, 7.2 (48H, m, Ar–H); δ_C (125 MHz, $CDCl_3$, Me_4Si) 14.1 ($(CH_2)_{10}CH_3$), 22.7 ($(CH_2)_{10}CH_2CH_3$), 23.4 ($CHCH_3$), 26.5 (CH), 28.8–30.2 ($(CH_2)_6CH_2CH_3$), $OCONHCH_2(CH_2)_4$), 31.9 ($CHCH_2CH_2CH_2$), 34.4 ($CHCH_2CH_2$), 36.5 ($CHCH_2$), 39.1 ($OCONHCH_2$), 39.7 ($OCONH(CH_2)_5CH_2$), 49.5 ($CHCH_3$), 68.5 (OCH_2), 125.8, 126.8, 128.4, 145.0 (Ph), 129.9 (Ar–C2), 152.8 (Ar–C5), 155.1 (Ar–C1,3), 158.4, 168.0 (CO). MALDI-TOF (positive mode, matrix: dithranol): *m/z* calcd. for $C_{208}H_{312}N_{24}O_{24}Na$: 3555.8. Found: 3559.5 $[M + Na]^+$. MS (FAB) *m/z* calcd. for $C_{208}H_{313}N_{24}O_{24}$: 3533.9. Found: 3533.0 $[M + H]^+$. Anal. Calcd. for $C_{208}H_{312}N_{24}O_{24}\cdot 3H_2O$: C, 69.55; H, 8.94; N, 9.37%. Found: C, 69.68; H, 8.86; N, 8.99%.

Resorcinarene bearing (*S*)-methylbenzylurea residues (1-S)

This compound was prepared by reaction of **6** with (*S*)-α-methylbenzyl isocyanate in a manner similar to that applied to the synthesis of **1-R**. The crude product was purified by silica gel chromatography with chloroform–methanol (9 : 1 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a white solid (69 mg, 46%): ν_{max} (FT-IR) 1658 (C(O), 1565 (NH) cm^{-1}; δ_H (600 MHz, $CDCl_3$, Me_4Si) 0.86 (12H, m, CH_2CH_3), 1.23–1.28 [104H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_2$], 1.3–1.4 [56H, m, $CH_2CONHCH_2CH_2$, $CH_2CONH(CH_2)_4CH_2$, CH_3CH], 1.75 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.0 (8H, m, CH_3CH), 3.0 (16H, m, $CH_2CONHCH_2$), 3.2 (16H, m, $CH_2CONH(CH_2)_5CH_2$), 4.46, 4.81, 5.7–6.4 (36H, m, OCH_2CO, CHAr, NHCONH), 7.15, 7.2 (48H, m, Ar–H); δ_C (125 MHz, DMSO-d_6, Me_4Si) 13.2 ($(CH_2)_{10}CH_3$), 21.8 ($(CH_2)_{10}CH_2CH_3$), 22.5 ($CHCH_3$), 25.6 (CH), 28.5–29.9 ($(CH_2)_6CH_2CH_3$), $OCONHCH_2(CH_2)_4$), 31.0 ($CHCH_2CH_2CH_2$), 33.5 ($CHCH_2CH_2$), 35.6 ($CHCH_2$), 38.2 ($OCONHCH_2$), 38.9 ($OCONH(CH_2)_5CH_2$), 48.6 ($CHCH_3$), 67.8 (OCH_2), 124.9, 125.9, 127.5, 144.2 (Ph), 129.0 (Ar–C2), 151.9 (Ar–C5), 154.2 (Ar–C1,3), 157.6, 167.2 (CO). MALDI-TOF (positive mode, matrix: dithranol): *m/z* calcd. for $C_{208}H_{312}N_{24}O_{24}Na$: 3555.8. Found: 3563.9. $[M + Na]^+$ MS (FAB) *m/z* calcd. for $C_{208}H_{313}N_{24}O_{24}$: 3533.9. Found: 3532.8 $[M + H]^+$. Anal. Calcd. for $C_{208}H_{312}N_{24}O_{24}\cdot 3H_2O$: C, 69.65; H, 8.94; N, 9.37%. Found: C, 69.81; H, 8.80; N, 9.12%.

Resorcinarene octaBoc-amine having an undecyl spacer (6)

This compound was prepared by reaction of **4** with *N*-1-*tert*-butoxycarbonyl-1,6-diaminododecane hydrochloride in a manner similar to that applied to the synthesis of **5**. The crude product was purified by silica gel chromatography with EtOAc–hexane (5 : 2 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a white solid (840 mg, 78%): δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.81 (12H, m, CH_2CH_3), 1.2 [200H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_8$], 1.3–1.4 [72H, s, $C(CH_3)_3$], 1.73 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.8–2.9 (16H, m, $CH_2CONHCH_2CH_2$), 3.0 [16H, m, $CH_2CONH(CH_2)_8CH_2$], 3.1 [16H, m, $CH_2CONH(CH_2)_8CH_2$], 4.25 (16H, s, OCH_2CO), 4.66 (4H, t, $J = 6.8$, CHAr), 6.37 (4H, s, Ar–H2), 6.56 (4H, s, Ar–H5). Anal. Calcd. for $C_{244}H_{400}N_{16}O_{32}$: C, 70.25; H, 10.53 N, 5.85. Found: C, 70.17; H, 10.28. N, 5.61. MALDI-TOF (positive mode, matrix: dithranol): *m/z* calcd. for $C_{244}H_{400}N_{16}O_{32}K$: 3868.8. Found: 3862.1 $[M + K]^+$.

Resorcinarene octaamine having an undecyl spacer (8)

This compound was prepared by reaction of **7** with trifluoroacetic acid in a manner similar to that applied to the synthesis of **6** to give a white solid (380 mg, quantitative): δ_H (400 MHz, CD_3OD, Me_4Si) 0.8 (12H, m, CH_2CH_3), 1.2 [200H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_8$], 1.4–1.5 (16H, m, $CH_2CONHCH_2CH_2$), 1.5–1.6 [16H, m, $CH_2CONH(CH_2)_{10}CH_2$], 1.79 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.8 (16H, m, CH_2NH_3), 3.1–3.3 (16H, m, $CH_2CONHCH_2$), 4.2 (16H, s, OCH_2CO), 4.66 (4H, t, $J = 6.8$, CHAr), 6.42 (4H, s, Ar–H2), 6.70 (4H, s, Ar–H5).

Resorcinarene bearing (*R*)-methylbenzylurea residues (9-R)

This compound was prepared by reaction of **8** with (*R*)-α-methylbenzyl isocyanate in a manner similar to that applied to the synthesis of **1-R**. The crude product was purified by silica gel chromatography with chloroform-methanol (9 : 1 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a white solid (130 mg, 65%): ν_{max} (FT-IR) 1667 (C=O), 1561 (NH) cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.83 (12H, m, CH_2CH_3), 1.17–1.24 [200H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_8$], 1.3–1.4 [56H, m, $CH_2CONHCH_2CH_2$, $CH_2CONH(CH_2)_{10}CH_2$, CH_3CH], 1.91 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.0 (8H, m, CH_3CH), 3.0 (16H, m, $CH_2CONHCH_2$), 3.2 (16H, m, $CH_2CONH(CH_2)_{11}CH_2$), 4.42, 4.76, 6.8 (36H, m, OCH_2CO, CHAr, NHCONH), 7.1–7.2 (48H, m, Ar–H); δ_C (125 MHz, $CDCl_3$, Me_4Si) 14.5 ($(CH_2)_{10}CH_3$), 23.1 ($(CH_2)_{10}CH_2CH_3$), 23.8 ($CHCH_3$), 27.4 (CH), 29.9 ($(CH_2)_6CH_2CH_3$), $OCONHCH_2(CH_2)_4$), 32.3 ($CHCH_2CH_2CH_2$), 35.0 ($CHCH_2CH_2$), 37.5 ($CHCH_2$), 39.8 ($OCONHCH_2$), 40.7 ($OCONH(CH_2)_5CH_2$), 50.2 ($CHCH_3$), 69.0 (OCH_2), 126.3, 127.4, 128.9, 140 (Ph), 128 (Ar–C2), 151, 154 (Ar–C5), 154.2 (Ar–C1,3), 157.6, 167.2 (CO). MS (FAB) *m/z* calcd. for $C_{256}H_{409}N_{24}O_{24}$: 4207.1. Found: 4205.9 $[M + H]^+$. Anal. Calcd. for $C_{256}H_{408}N_{24}O_{24} \cdot H_2O$: C, 72.76; H, 9.75; N, 7.99%. Found: C, 72.70; H, 9.64; N, 7.75%.

Resorcinarene bearing (*S*)-methylbenzylurea residues (9-S)

This compound was prepared by reaction of **8** with (*R*)-α-methylbenzyl isocyanate in a manner similar to that applied to the synthesis of **1-S**. The crude product was purified by silica gel chromatography with chloroform–methanol (9 : 1 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a white solid (200 mg, 98%): ν_{max} (FT-IR) 1667 (C=O), 1561 (NH) cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.83 (12H, m, CH_2CH_3), 1.17–1.24 [200H, m, $CH_2(CH_2)_9CH_3$, $NHCH_2CH_2(CH_2)_8$], 1.3–1.4 [56H, m, $CH_2CONHCH_2CH_2$, $CH_2CONH(CH_2)_{10}CH_2$, CH_3CH], 1.91 [8H, m, 4H, $CH_2(CH_2)_9CH_3$], 2.0 (8H, m, CH_3CH), 3.0 (16H, m, $CH_2CONHCH_2$), 3.2 (16H, m, $CH_2CONH(CH_2)_{11}CH_2$), 4.42, 4.76, 6.8 (36H, m, OCH_2CO, CHAr, NHCONH), 7.1–7.2 (48H, m, Ar–H); δ_C (125 MHz, $CDCl_3$, Me_4Si) 14.5 ($(CH_2)_{10}CH_3$), 23.1 ($(CH_2)_{10}CH_2CH_3$), 23.8 ($CHCH_3$), 27.4 (CH), 29.9 ($(CH_2)_6CH_2CH_3$), $OCONHCH_2(CH_2)_4$), 32.3 ($CHCH_2CH_2CH_2$), 35.0 ($CHCH_2CH_2$), 37.5 ($CHCH_2$), 39.8 ($OCONHCH_2$), 40.6 ($OCONH(CH_2)_5CH_2$), 51.0 ($CHCH_3$), 66.1 (OCH_2), 126.2, 127.3, 128.9, 145 (Ph), 128 (Ar–C2), 156, 154 (Ar–C5), 156.2 (Ar–C1,3), 158.7, 168.1 (CO). Anal. Calcd.

for $C_{256}H_{408}N_{24}O_{24}\cdot 2H_2O$: C, 72.45; H, 9.75; N, 7.95%. Found: C, 72.36; H, 9.64; N, 7.69%.

Mono-urea derivative bearing (*S*)-methylbenzylurea residues (10-S)

This compound was prepared by using 4-hexylphenol in place of **2** in a manner similar to that applied to the synthesis of **1-S**. The crude product was purified by silica gel chromatography with chloroform–methanol (9 : 1 v/v) as eluent. The product fraction was evaporated to dryness under reduced pressure to give a white solid (12 mg, 7%): ν_{max} (FT-IR) 1668 (C=O), 1554 (NH) cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.84–0.87 (3H, t, J = 12, CH_2CH_3), 1.0–1.4 [10H, m, $CH_2(CH_2)_3CH_3$, $NHCH_2CH_2(CH_2)_2$, CH_3CH], 1.4–1.5 [47H, m, $CH_2CONHCH_2CH_2(CH_2)_2CH_2$], 1.5–1.6 (2H, m, $CH_3(CH_2)_3CH_2$), 2.6 (2H, t, J = 16, $CH_3(CH_2)_4CH_2$), 3.0–3.2 (2H, m, $CH_2CONHCH_2$), 3.3 (2H, m, $CH_2CONH(CH_2)_5CH_2$), 4.4 (2H, s, OCH_2CO), 4.7–4.8 (2H, m, urea NH), 6.6 (1H, m, amide NH), 6.8–7.1 (4H, m, CH_2ArO), 7.4 (5H, m, $ArCHCH_3$); δ_C (125 MHz, $CDCl_3$, Me_4Si) 14.5 ($(CH_2)_5CH_3$), 23.6 ($(CH_2)_4CH_2CH_3$), 24.5 ($CHCH_3$), 29.8 ($(CH_2)_2CH_2CH_3$), $OCONHCH_2(CH_2)_4$), 32.7 ($ArCH_2CH_2$), 36.1 ($ArCH_2$), 39.5, 40.8 ($OCONHCH_2$, $OCONH(CH_2)_5CH_2$), 51.3 ($CHCH_3$), 68.5 (OCH_2), 115.5 (Ar–C2,6), 126.7, 128.3, 129.7, 130.6, 145.3 (Ph, Ar–C3,5), 137.7 (Ar–C4), 156.2 (Ar–C1), 158.7, 169.5 (CO). MS (HI) m/z calcd. for $C_{29}H_{44}N_3O_3$: 481.7. Found: 482.3 $[M + H]^+$. Anal. Calcd. for $C_{29}H_{44}N_3O_3$: C, 72.31; H, 9.00; N, 8.72%. Found: C, 72.19; H, 8.87; N, 9.09%.

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