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Binaphthyl metallomacrocycles for complexation of neutral molecules

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Abstract. Binaphthyl salophen crown ethers **1** and **2**, containing an immobilized electrophilic uranyl cation, were synthesized by cyclization of dialdehyde **10** with 1,2-benzenediamine (**14**) or *cis*-1,2-cyclohexanediamine (**15**), respectively, in the presence of Ba^{2+} as a template ion and subsequent transmetallation with UO_2^{2+}. Solid complexes of urea and **1** and **2** were isolated. Molecular-mechanics calculations show that the geometry of **1** and **2** is suitable for the introduction of functional groups close to the cavity of the metallomacrocycles.

Introduction

Complexation of a substrate molecule in the active site of an enzyme is the crucial step in enzymatic catalysis. Complexation of a guest molecule by synthetic receptor molecules is the central theme of supramolecular chemistry[1]. Therefore, development of enzyme models is one of the challenging applications of supramolecular chemistry, because it opens the possibility of systematically examining the factors that contribute to enzymatic catalysis.

Although the field of supramolecular chemistry was initiated by the discovery by *Pedersen*[2] that crown ethers are able to form complexes with alkaline-metal and alkaline-earth-metal cations, it was soon discovered that crown ethers can also form complexes with neutral molecules that are able to form hydrogen bonds[3]. The complexes of simple crown ethers, *e.g.*, 18-crown-6, with neutral molecules such as urea[4a], CH_3NO_2[4b], CH_3CN[4b], and $CH_2(CN)_2$[4b,c] have rather low stabilities. Receptor molecules based on rigid hexagonal frameworks, which have a preorganized array of hydrogen-bond donors and acceptors, have been synthesized. Such host molecules are convenient for the complexation of neutral polar organic molecules, *e.g.*, urea derivatives[5a–c], amides[5c] and different heterocycles, such as methyl biotin[5b,d], uric acid derivatives[5e,f] and barbiturates[5g], in apolar solvents.

Previously, we have shown that the incorporation of an acidic group in the cavity of a crown ether of sufficient ring size renders these host molecules suitable for complexation of polar neutral organic guest molecules which contain both electrophilic and nucleophilic groups. 2-Carboxyl-1,3-xylyl crown ethers with a ring size of 27 atoms or more were found to complex urea in chloroform[6] with a stability constant[6b] of approximately $2 \cdot 10^3$ M^{-1}. The X-ray structure of the complex[6] shows that the NH_2 groups of the guest molecule are hydrogen-bonded to the ether oxygen atoms of the crown ether. X-ray crystallography also shows that the carbonyl oxygen of the guest forms a strong hydrogen bond with the acidic hydrogen of the intra-annular carboxylic acid. Using a proton as an electrophilic group has the disadvantage that complexation is pH dependent, because proton transfer to the solvent will occur if the solution is not sufficiently acidic. Therefore, a new type of crown ether was designed in which one ethylene glycol unit was replaced by a salophen moiety[7a] (Chart 1). The salophen unit is known to form very stable complexes with transition-metal cations and with several lanthanide and actinide cations[8]. If a divalent cation is complexed by the salophen unit, a neutral complex results after deprotonation of the two phenolic OH groups of this ligand.

Complexation of the uranyl cation UO_2^{2+} in the salophen unit turned out to be the proper choice[7b,c]. This cation, which has a known preference for a pentagonal bipyrimidal coordination, forms a kinetically stable complex with the salophen unit and, after accommodation of the two N and the two O donor sites of the salophen unit, still has one coordination site available, which can be occupied by either a solvent molecule or a neutral polar guest molecule[9]. It was shown that these salophen crown ethers form complexes with molecules such as formamide, acetamide, urea, DMSO, etc.[7b,c].

The low solubility of most of these salophen crown ethers could be improved by using *cis*-1,2-cyclohexanediamine instead of 1,2-benzenediamine for the cyclization reaction[10]. Investigation of the complexation behavior of these slightly modified salophen crown ethers showed that association constants with urea as high as 10^8 M^{-1} were obtained in chloroform.

The uranyl salophen unit has also been applied as an electrophilic center in cleft molecules[11]. With this immobilized metal ion, these clefts are able to complex guest molecules such as pyridine *N*-oxide, substituted pyridines,

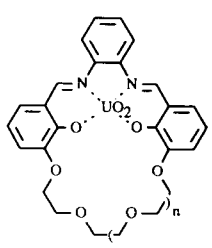
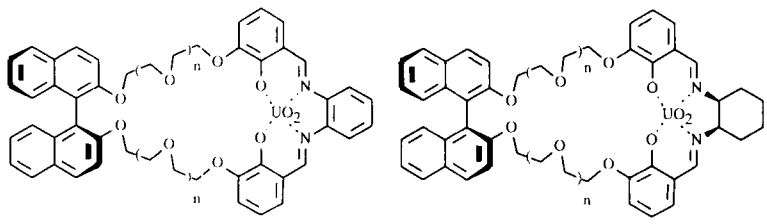


Chart 1



1 a n=1
b n=2

2 a n=1
b n=2

Chart 2

benzylamine, etc.

In order to develop the salophen crown ethers for use as potential enzyme models, we decided to replace one of the ethylene glycol units by a building block, which will allow the introduction of functional groups close to the cavity of the crown ether ring. In the present paper, we describe two routes for the synthesis of binaphthyl salophen crown ethers **1** and **2** (Chart 2). These represent a first approach towards metallomacrocycles with functional groups. It is known from the work of *Cram* et al.[12] on binaphthyl-18-crown-6 that substituents in the 3- and 3′-positions of the binaphthyl unit are just above and below the plane of the crown ether.

Complexes of **1** and **2** with small neutral guest molecules have also been studied with molecular-mechanics calculations and with ^{1}H-NMR spectroscopy. The complexing abilities of these metallomacrocycles have been examined by extraction experiments and by carrier-mediated transport of urea through a supported liquid membrane.

Results and discussion

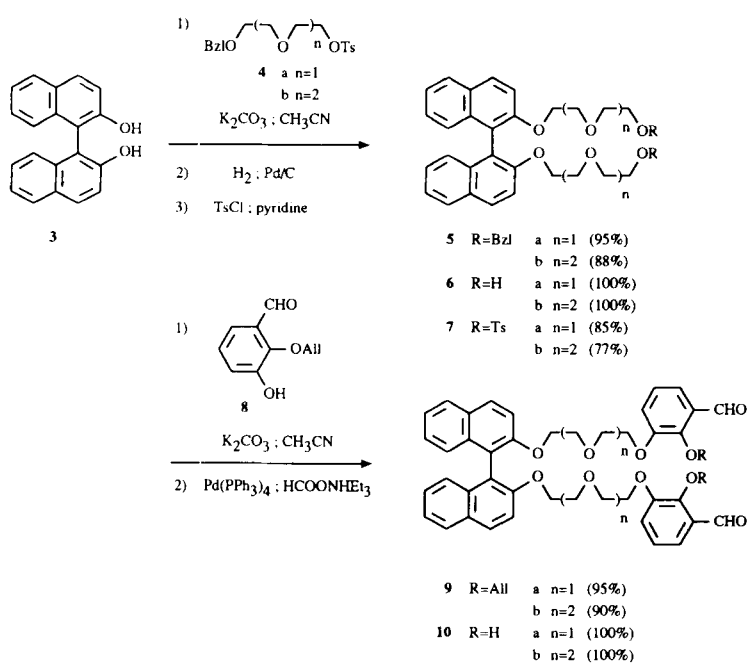
Uranyl salophen crown ethers are synthesized most conveniently[7c] if the macrocyclization, in which the Schiff bases are formed, is performed as the last step. The bis(2-hydroxybenzaldehyde) derivatives **10**, which are required for the synthesis of binaphthyl salophen crown ethers **1** and **2**, can be prepared in different ways.

Route I

In the first approach (Scheme 1), synthesis of dialdehydes **10** started with commercially available binaphthol **3**. Both phenolic OH groups of **3** were alkylated with tosylates **4**, prepared from the monobenzyl ether of di- or triethylene glycol[13] by reaction with tosyl chloride in pyridine, to give **5** in good yield (90–95%). The absence of the singlet at 5.05 ppm in the ^{1}H-NMR spectra of **5** for the phenolic OH groups of **3** showed that *O*-alkylation had occurred.

The protective benzyl ethers were cleaved quantitatively by catalytic hydrogenation with Pd/C. In the ^{1}H-NMR spectra, the characteristic singlets for the benzylic protons at 4.40 (**5a**) and 4.51 (**5b**) ppm had disappeared. Broad signals at 2.64 (**6a**) and 2.43 ppm (**6b**) for the aliphatic OH groups were observed in the ^{1}H-NMR spectra and, in the ^{13}C-NMR spectra, the CH_2OH groups showed a peak at 61.6 ppm.

It turned out that hydrogenation must be stopped as soon as debenzylation was complete according to TLC, because a by-product was formed if hydrogenation was continued overnight. Although this by-product was not completely identified, ^{1}H-NMR spectroscopy indicated that partial reduction of the binaphthyl unit had occurred (multiplets at 2.75–2.9, 2.1–2.4, and 1.5–1.8 ppm). Partial reduction of binaphthol has been reported with PtO_2 as the hydrogenation catalyst[14]. The resulting product, 5,5′,6,6′,7,7′,8,8′-octahydro[1,1′-binaphthalene]-2,2′-diol (Chart 3), was reported to show multiplets at 2.70, 2.20, and 1.66 ppm in



Scheme 1

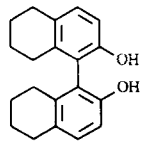


Chart 3

the ^{1}H-NMR spectrum[14].

Tosylation of diols **6** with tosyl chloride in pyridine proceeded in good yield (75–85%). The IR spectra of **6** show strong absorptions at 1355 and 1177 cm^{-1} for the sulfonate esters. Reaction of ditosylates **7** with the selectively protected 2,3-dihydroxybenzaldehyde derivative **8**[7c,15] gave the protected dialdehydes **9** in high yield (90–95%). The aldehyde group showed a singlet at 10.42 ppm in the ^{1}H-NMR spectra at 190.4 ppm in the ^{13}C-NMR spectra. In the IR spectra, a strong absorption at 1687 cm^{-1} was observed for the carbonyl group of the aldehyde.

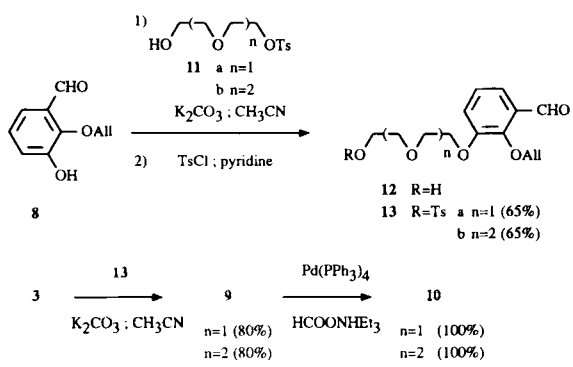
Removal of the protective allyl ethers was achieved by slight modification of the reported deallylation of oximes[16]. For practical reasons, the active catalyst $Pd(PPh_3)_4$ was added as such, instead of being generated *in situ* from $Pd(OAc)_2$ and PPh_3. For reasons of solubility, THF was added to the reaction mixture, but this did not have any significant effects on the reductive deallylation. The deallylated dialdehydes **10** were obtained in quantitative yield. In the ^{1}H-NMR spectra, no signals for the allyl ethers were observed. The 2-OH groups of **10** are present as slightly broadened singlets around 10.8 ppm in the ^{1}H-NMR spectra, indicating that they are hydrogen-bonded to the aldehyde groups. The signals for the aldehyde groups have shifted to 9.95 ppm in the ^{1}H-NMR spectra and to 196.0 ppm in the ^{13}C-NMR spectra. Absorptions for the carbon atoms bearing the phenolic OH groups are found at 147.4 ppm in the ^{13}C-NMR spectra. In the IR spectra, two absorptions are observed for the carbonyl group of the aldehyde, *viz.* at 1681 (w) for the free form and at 1656 (s) for the hydrogen-bonded form.

Route II

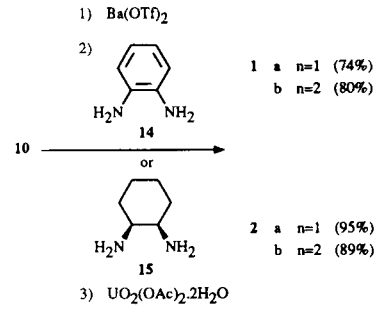
In the second approach (Scheme 2), aldehydes **10** were synthesized starting from protected 2,3-dihydroxybenzaldehyde derivative **8**[7c,15]. Alkylation of the unprotected 3-OH group of **8** with the monotosylates of di- and triethylene glycol **11**[17] in CH_3CN gave aldehydes **12**, which, after purification by some washing steps, were pure enough to be used as such. Reaction of **12** with tosyl chloride in dry pyridine at 0°C gave tosylates **13**, after purification by flash column chromatography, in 65% yield (two steps). In the IR spectra, strong absorptions are observed at 1687 cm^{-1} for the aldehyde groups and at 1356 and 1177 cm^{-1} for the sulfonate esters.

Dialkylation of binaphthol **3** with tosylates **13** gave the protected dialdehydes **9**, which were identical with the compounds prepared following the first route, in good yield (80%). Reductive deallylation gave dialdehydes **10** in quantitative yield.

If the two routes are compared, it can be concluded that they give similar results. The first approach gave aldehydes **10** in 5 steps and in approximately 65% yield, whereas the second route gave aldehydes **10** in 4 steps and approximately 50% yield.



Scheme 2

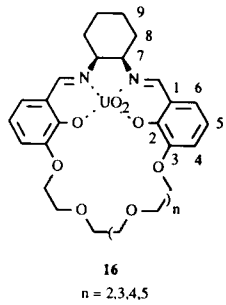


Scheme 3

Cyclization

The cyclization reactions were performed under reasonably dilute conditions (0.01 M) in THF with Ba^{2+} as a template[7a,c] (Scheme 3). Dialdehydes **10** and 2 equiv of $Ba(OTf)_2$[18] were dissolved in THF to give a complex in which the Ba^{2+} ion is coordinated to the polyether oxygen atoms and keeps the two aldehyde groups in close proximity. After addition of 1 equiv of diamine **14** or **15**, the reaction mixture was refluxed for about 30 min to effect cyclization of the linear dialdehydes by formation of the Schiff bases. At this stage, the reaction is probably still reversible. Addition of $UO_2(OAc)_2$ renders the cyclization irreversible by formation of a stable uranyl complex. Deprotonation of both phenolic OH groups of the salophen moiety occurs, with formation of acetic acid. In addition, a white precipitate of barium salts is formed. After some washing steps, the crude metallomacrocycles **1** and **2** were obtained.

The salophen crown ethers **1** were purified by precipitation from a solution in CH_2Cl_2 with cyclohexane[19]. Metallomacrocycle **1a** shows limited solubility in dry CH_2Cl_2 and $CHCl_3$. Its ^{1}H-NMR spectrum in DMSO-d_6 exhibits a singlet at 9.60 ppm for the imine protons; no signal is observed for phenolic OH groups. The carbon atoms bearing the phenoxide ions have shifted from 147.4 to 161.2 ppm in the ^{13}C-NMR spectrum. In the FAB mass spectrum, a $M + 1$ peak at m/z 1043.3 demonstrates that the uranyl cation is strongly bound by the salophen unit. In the IR spectrum, the signals at 1600 cm^{-1} (C=N) and 892 cm^{-1} (O–U–O) clearly indicate that cyclization and complex formation have occurred. Metallomacrocycle **1b** is well soluble in CH_2Cl_2. The imine protons show as a



16
n = 2,3,4,5

Chart 4

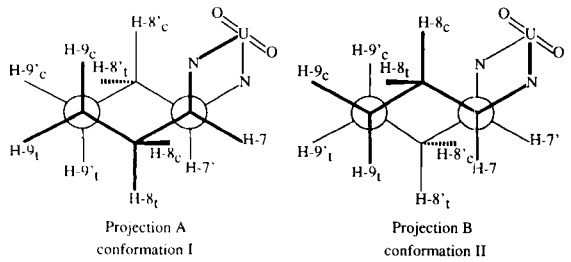


Figure 1. Newman projections of two possible conformations of the cyclohexyl ring.

singlet at 9.35 ppm in $CDCl_3$ and at 9.62 ppm in DMSO-d_6 in the ^{1}H-NMR spectrum. The FAB mass spectrum shows a $M + 1$ peak at m/z 1131.5. In the IR spectrum, absorptions for the imine bond and for the uranyl cation are observed.

Using *cis*-1,2-cyclohexanediamine **15** instead of 1,2-benzenediamine **14** for the cyclization gave metallomacrocycles **2**. In contrast to **1**, these could be purified by column chromatography on silica gel, as has been reported earlier for related compounds[10a]. In some cases, the uranyl cation was lost to a small extent during this purification step, as was evident from the ^{1}H-NMR spectra of the metallomacrocycles. The uranyl cation could easily be re-introduced by stirring a solution of the metallomacrocycle in CH_2Cl_2 with a solution of $UO_2(OAc)_2$ in water. In the FAB mass spectra, compounds **2** show a $M + 1$ peak, indicating that the uranyl cation is tightly bound. Strong absorptions are observed in the IR spectra at 1615 cm^{-1} for the imine bonds and at 897 cm^{-1} for the uranyl cations.

The cyclohexyl ring in salophen crown ethers **16**[10a] (Chart 4) can adopt two different chair conformations (Figure 1). If rapid interconversion of both conformations takes place, the atoms X and X′ (*e.g.*, C-8 and C-8′ or H-8_c and H-$8'_c$) become equivalent on the NMR time scale. This is observed for metallomacrocycles **16**[20], which show only three signals for the cyclohexyl ring in the ^{13}C-NMR spectra.

The ^{1}H-NMR spectrum of **2a** in $CDCl_3$, on the other hand, shows separate signals for every C-8 and C-8′ proton and the ^{13}C-NMR spectrum reveals signals for all six carbon atoms of the cyclohexyl ring. A possible explanation is that the chiral binaphthyl unit renders the atoms of the cyclohexyl ring diastereotopic (Figure 2). It is well known that diastereotopic atoms may have different chemical shifts in the NMR spectrum.

At higher temperatures (140°C, $CDCl_2CDCl_2$), the four signals for the different C-8 and C-8′ protons in the ^{1}H-NMR spectrum of **2a** coalesce to give two signals. The increased molecular mobility probably reduces the differences between the diastereotopic protons. The possibility that rapid rotation around the binaphthyl central bond renders the binaphthyl unit achiral on the NMR time scale is not very likely, because it is known that simple binaphthyl crown ethers are conformationally stable in diethylene glycol at 205°C for at least 6 h[21].

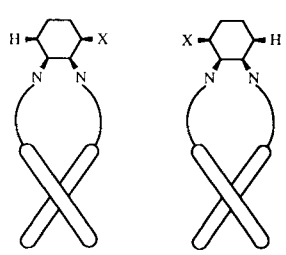


Figure 2. Diastereotopic protons H-8_c and H-$8'_c$ in the chiral binaphthyl salophen crown ethers.

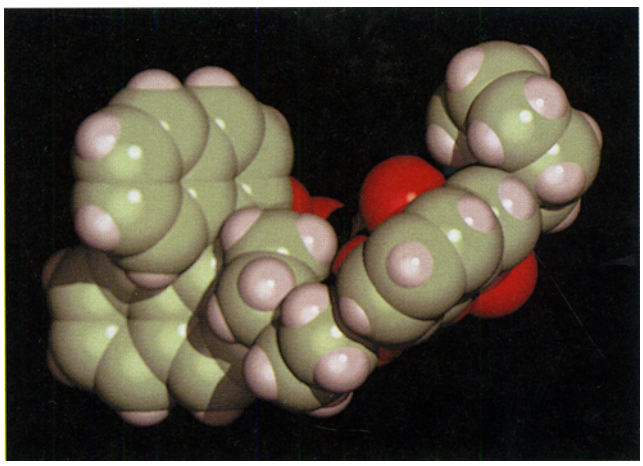


*Figure 3. Calculated structure of **2a**.*

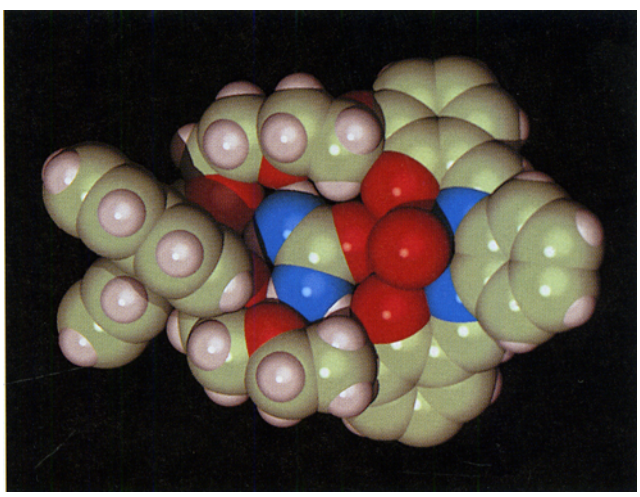


*Figure 4. Calculated structure of **1a**·urea.*

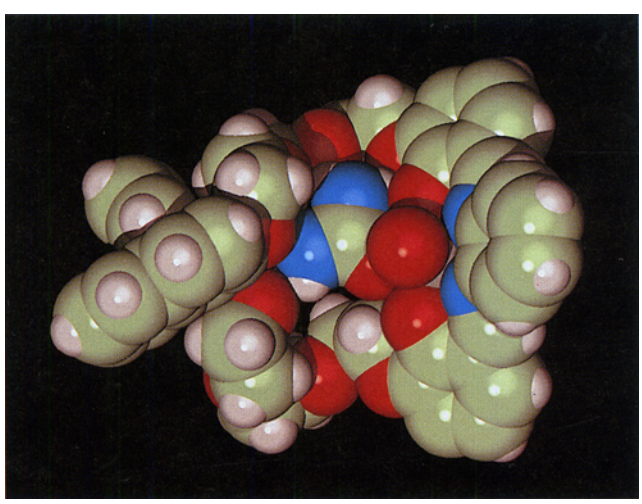


*Figure 5. Calculated structure of **1b**·urea.*

In the ^{1}H-NMR spectrum of **2b**, no evidence is observed for the non-equivalence of H-8_c and H-$8'_c$, but small differences in chemical shift may be obscured by the broadness of the peaks. In the ^{13}C-NMR spectrum on the other hand, separate signals are observed for all six carbon atoms of the cyclohexyl ring.

Another interesting phenomenon is observed in the ^{1}H-NMR spectra of macrocycles **2**, viz., "sidedness", which results from the combination of a binaphthyl unit (C_2 symmetry) with *cis*-1,2-cyclohexanediamine (C_s symmetry) in one molecule. In the development of chiral crown ethers, most attention has been paid to the use of chiral molecules with C_2-symmetry, e.g., substituted binaphthyl units[14,21] and tartaric acid derivatives[22], because both sides of the resulting crown ethers are equivalent and will show the same ability to complex a (chiral) guest. In binaphthyl salophen crown ethers **2**, however, the C_2 symmetry of the metallomacrocycles is disrupted by the presence of the *cis*-1,2-cyclohexanediamine unit (a meso compound). As a result, the two sides of the metallomacrocycle are no longer equivalent (Figure 3). This "sidedness" is clearly observed in the ^{1}H-NMR spectra of **2a** (separate doublets for H-4 and H-4′ of the binaphthyl moiety in DMSO-d_6) and **2b** (separate doublets for H-4, H-4′, and H-3 and H-3′ of the binaphthyl moiety in $CDCl_3$).

Complexation with urea

The complexing abilities of metallomacrocycles **1** and **2** were demonstrated by isolation of solid urea complexes, obtained by allowing solutions of urea in MeOH and of metallomacrocycles **1** and **2** in CH_2Cl_2 to mix by diffusion. Large changes were observed in the ^{1}H-NMR spectra of the complexes especially in the crown ether part, which reflect the increased rigidity of the polyethylene glycol chains upon complexation. In the IR spectra, the complexes show a complicated pattern for N–H stretch vibrations between 3500–3200 cm^{-1}. The urea carbonyl stretch vibration is observed at 1650–1627 cm^{-1}, proving that the guest is coordinated through the oxygen atom [ν(C=O)$_{urea}$ 1670 cm^{-1}][7c].

In the FAB mass spectra, weak "M + urea + 1" peaks are observed for the complexes (at m/z 1103.4 for **1a** · urea, at 1191.4 for **1b** · urea, and at 1109.4 for **2a** · urea) together with strong $M + 1$ peaks for the host molecules themselves. A strong signal for urea (m/z 60.032) was observed in the EI mass spectra of the complexes.

Solid–liquid extraction experiments were performed by equilibrating a 4 mM solution of metallomacrocycles **1** and **2** in $CDCl_3$ with solid urea. In all cases, ^{1}H-NMR spectra similar to those of the solid urea complexes were obtained, indicating that urea was complexed. Addition of free host to solutions of the urea complexes showed that rapid exchange on the NMR time scale occurred, because only the averaged spectra were observed.

Metallomacrocycles **1** were also used for carrier-mediated transport of urea and *N*-methylurea through a supported liquid membrane[23]. The salophen crown ethers considerably increase the flux of urea through a supported *o*-nitrophenyl *n*-octyl ether (NPOE) membrane, thereby demonstrating their ability to extract urea from an aqueous solution to the organic phase. In contrast to the salophen crown ethers **16**, which leached from the membrane, the metallomacrocycles **1** are sufficiently hydrophobic to give stable membranes. Details of carrier-mediated transport are given in Ref. 23.

The complexing abilities of macrocycles **1** and **2** were also examined by molecular-mechanics calculations by using QUANTA/CHARMm. As not all parameters for the salophen unit and for the uranyl cation were available, the structures of the two types of salophen units were taken from X-ray structure determinations[7b,10a] and kept constant during calculations by imposing constraints on the atomic positions. Interactions of the guest molecules with the uranyl cation were taken care of by imposing proper charges on the uranyl cation[24] and by using non-bonded parameters, which were determined to reproduce its hydration geometry and enthalpy[25].

For all macrocycles, reasonable starting geometries were generated by constructing the macrocycle in QUANTA's 3-D-editor, starting from the salophen units, which were taken from the X-ray structure. The guest molecules (water, formamide, acetamide, and urea) were docked by hand. Using the CHARMm force field, minimizations were performed to allow the structures to relax to minimum energy conformations.

One major problem with macrocycles **1** and **2** is their large flexibility, which makes it extremely difficult to systematically search their conformational space. It is, therefore, impossible to be certain that the structure has reached a global minimum or, instead, has converged to one (of the very many) local minima. The absolute values of the calculated steric energies should, therefore, be treated with due reserve. For all metallomacrocycles, however, the energy of complexation is observed to become more negative on going from water to formamide, acetamide, or urea. This means that, according to molecular modeling, binaphthyl salophen crown ethers **1** and **2** are able to complex these guest molecules.

From visual inspection of the calculated structures, it is clear that the sizes of the cavities of metallomacrocycles **1a** and **2a** are very suitable for the complexation of urea. This results in very ordered **1a** · urea (Figure 4) and **2a** · urea complexes. The other guests (acetamide, formamide, water) are slightly too small for the cavity, which gives rise to increasingly disordered structures. All guests are smaller than the cavities of salophen crown ethers **1b** and **2b** and this is shown in the calculated structures by a considerable amount of disorder in the crown ether part of the host molecules (Figure 5). As has been already observed for metallomacrocycles **16**[10a], the lower limit for the ring size of the salophen crown ethers, which allows complexation of small neutral guest molecules, is much more well defined than the upper limit.

The calculated structures clearly show that the 1,1′-axis of the binaphthyl unit is roughly perpendicular to the average plane of the salophen crown ether ring. This is an important feature, because this geometry will keep substituents in the 3- and 3′-positions of a functionalized binaphthyl unit close to the cavity of the host molecule.

Conclusions

Two convenient routes for preparation of dialdehydes **10** are described. These dialdehydes can be cyclized with a diamine to give salophen crown ethers **1** and **2**, after complexation of an uranyl cation. Metallomacrocycles **2** can be purified more easily than **1**, but they have lost the C_2 symmetry of the binaphthyl unit, which gives rise to more complicated NMR spectra. Both metallomacrocycles are able to complex urea. According to molecular-mechanics calculations, the binaphthyl salophen crown ethers **1** and **2** are suitable for the development of potential enzyme models, because the geometry of these metallomacrocycles places substituents in the 3- and 3′-positions of the binaphthyl unit close to the cavity of the host.

Experimental

General methods

NMR spectra were recorded on a Bruker AC 250 spectrometer in $CDCl_3$ with TMS as internal standard, if not stated otherwise.

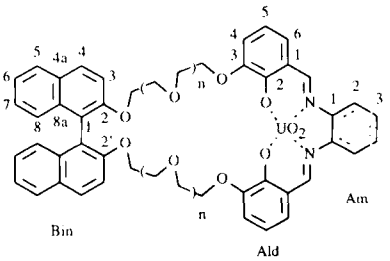


Chart 5

Assignments of the NMR spectra are according to the numbering in Chart 5[26]. Mass spectra were obtained with a Finnigan MAT 90 spectrometer. Positive-ion fast-atom-bombardment (FAB) mass spectra were obtained with *m*-nitrobenzyl alcohol as a matrix. IR spectra were recorded with a Nicolet 5 SCX FT spectrophotometer. Melting points were determined using a Reichert melting point apparatus and are uncorrected. Elemental analyses were carried out by a Model 1106 Carlo Erba Strumentazione Elemental Analyzer. CH_2Cl_2, EtOAc, and hexane were distilled before use. CH_3CN was stored over molecular sieves (4 Å) prior to use. THF was distilled from sodium/benzophenone. Other chemicals were of reagent grade and were used without purification. Column chromatography was performed with silica gel (Merck; 0.040–0.063 mm). All reactions were carried out under an argon atmosphere. 2-[2-(Phenylmethoxy) ethoxy]ethanol[13], 2-[2-[2-(phenylmethoxy)ethoxy]ethoxy]ethanol[13], 3-hydroxy-2-(2-propenyloxy)benzaldehyde[7c], 2-(2-hydroxyethoxy)ethanol mono(4-methylbenzenesulfonate)[17], and 2-[2-(2-hydroxyethoxy)ethoxy]ethanol mono(4-methylbenzenesulfonate)[17] were prepared according to published procedures. Care should be taken when handling uranyl-containing compounds because of their toxicity and radioactivity[27].

General procedure for the synthesis of **4**

Tosyl chloride (22.9 g, 0.12 mol) was added to a solution of 2-[2-(phenylmethoxy)ethoxy]ethanol (19.6 g, 0.1 mol) or 2-[2-[2-(phenylmethoxy)ethoxy]ethoxy]ethanol (24.0 g, 0.1 mol) in dry pyridine (75 ml) in one portion at 0°C. The reaction mixture was stirred at this temperature for 3 h. After addition of a small amount of ice, the reaction mixture was poured into a mixture of concentrated hydrochloric acid (250 ml) and ice. The hydrochloric acid solution was extracted with CH_2Cl_2 (3×100 ml) and the combined organic phases were washed with 2N hydrochloric acid (2×100 ml). After drying over $MgSO_4$, the solvent was evaporated to give **4** as oils in nearly quantitative yield and pure enough to be used as such.

2-[2-(Phenylmethoxy)ethoxy]ethanol 4-methylbenzenesulfonate (**4a**). ^{1}H NMR: δ 7.78 (d, 2H, *J* 8.3 Hz, TsC2H); 7.3–7.2 (m, 7H, ArH); 4.52 (s, 2H, $ArCH_2O$); 4.2–4.1 (m, 2H, CH_2O); 3.7–3.5 (m, 6H, CH_2O); 2.40 (s, 3H, $ArCH_3$). ^{13}C NMR: δ 144.8 (s, TsC4); 138.0 (s, BzlC1); 132.8 (s, TsC1); 129.8 (d, TsC3); 128.3 (d, Bzl); 127.9 (d, TsCC2); 127.7, 127.6 (d, Bzl); 73.2–68.6 (t, CH_2O); 21.6 (q, $ArCH_3$). IR (KBr): 1357, 1177 (SO_2–O), 748, 699 (Bzl) cm^{-1}. MS (EI) *m* / *z* 350.119 (M^+, calcd. for $C_{18}H_{22}O_5S$ 350.119).

2-[2-[2-(Phenylmethoxy)ethoxy]ethoxy]ethanol 4-methylbenzenesulfonate (**4b**). ^{1}H NMR: δ 7.78 (d, 2H, *J* 8.3 Hz, TsC2H); 7.4–7.2 (m, 7H, ArH); 4.55 (s, 2H, $ArCH_2O$); 4.14 (t, 2H, *J* 4.8 Hz, CH_2O); 3.68 (t, 2H, *J* 4.8 Hz, CH_2O); 3.65–3.55 (m, 8H, CH_2O); 2.42 (s, 3H, $ArCH_3$). ^{13}C NMR: δ 144.8 (s, TsC4); 138.1 (s, BzC1); 132.9 (s, TsC1); 129.8 (d, TsC3); 128.3 (d, Bzl); 127.9 (d, TsC2); 127.7, 127.6 (d, Bzl); 73.1–68.6 (t, CH_2O); 21.6 (q, $ArCH_3$). IR (KBr): 1357, 1177 (SO_2–O), 749, 699 (Bzl) cm^{-1}. MS (EI) *m* / *z* 394.145 (M^+, calcd. for $C_{20}H_{26}O_6S$ 394.144).

General procedure for the synthesis of **5**

A mixture of binaphthol **3** (1.43 g, 5 mmol), tosylate **4** (11 mmol), and K_2CO_3 (1.52 g, 11 mmol) in CH_3CN (25 ml) was refluxed overnight. The reaction mixture was cooled, diluted with CH_2Cl_2 (25 ml) and filtered through Celite. After removal of the solvent, the crude products were purified by flash column chromatography to give colorless oils.

2,2′-Bis[2-[2-(phenylmethoxy)ethoxy]ethoxy]-1,1′-binaphthalene (**5a**). Eluent EtOAc/hexane 2:3; yield 95%. ^{1}H NMR: δ 7.87 (d, 2H, *J* 9.0 Hz, BinC4H); 7.80 (d, 2H, *J* 8.0 Hz, Bin C5H); 7.38 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.1 (m, 16H, ArH); 4.40 (s, 4H, $ArCH_2O$); 4.08 (t, 4H, *J* 4.9 Hz, CH_2O); 3.5–3.4 (m, 4H, CH_2O); 3.2–3.0 (m, 8H, CH_2O). ^{13}C NMR: δ 154.2 (s, BinC2); 138.2 (s, BzlC1); 134.0 (s, BinC8a); 129.3 (s, BinC4a); 129.2 (d, BinC4); 128.3 (d, Bzl); 127.8 (d, BinC5); 127.7, 127.5 (d, Bzl); 126.2 (d, BinC7); 125.5 (d, BinC8); 123.3 (d, BinC6); 120.4 (s, BinC1); 115.6 (d, BinC3); 73.0–69.2 (t, CH_2O). IR (KBr): 748, 698 (Bzl) cm^{-1}. MS (EI) *m* / *z* 642.307 (M^+, calcd. for $C_{42}H_{42}O_6$ 642.298).

2,2′-Bis[2-[2-[2-(phenylmethoxy)ethoxy]ethoxy]ethoxy]-1,1′-binaphthalene (**5b**). Eluent EtOAc/hexane 1:1; yield 88%. ^{1}H NMR: δ 7.88 (d, 2H, *J* 9.0 Hz, BinC4H); 7.81 (d, 2H, *J* 8.0 Hz, BinC5H); 7.38 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.1 (m, 16H, ArH); 4.51 (s, 4H, $ArCH_2O$); 4.07 (t, 4H, *J* 4.9 Hz, CH_2O); 3.6–3.4 (m, 12H, CH_2O); 3.25–3.0 (m, 8H, CH_2O). ^{13}C NMR: δ 154.2 (s, BinC2); 138.2 (s, BzlC1); 133.9 (s, BinC8a); 129.2 (s, BinC4a); 129.1 (d, BinC4); 128.3 (d, Bzl); 127.71 (d, BinC5); 127.65, 127.5 (d, Bzl); 126.2 (d, BinC7); 125.4 (d, BinC8); 123.6 (d, BinC6); 120.3 (s, BinC1); 115.5 (d, BinC3); 73.1–69.2 (t, CH_2O). IR (KBr): 748, 699 (Bzl) cm^{-1}. MS (EI) *m* / *z* 730.344 (M^+, calcd. for $C_{46}H_{50}O_8$ 730.351).

General procedure for the synthesis of diols **6**

Pd on carbon (10%, 0.2 g) was added to a solution of dibenzyl ether **5** (5 mmol) in a mixture of EtOAc (50 ml) and EtOH (50 ml). The reaction mixture was stirred in a hydrogen atmosphere until the starting material had disappeared according to TLC (SiO_2; EtOH/CH_2Cl_2 1:9). The hydrogen was removed and the mixture was filtered through Celite. Evaporation of the solvent gave the products as colorless oils in quantitative yield.

2,2′-[[1,1′-Binaphthalene]-2,2′-diylbis(oxy-2,1-ethanediyloxy)]bisethanol (**6a**). ^{1}H NMR: δ 7.95 (d, 2H, *J* 9.0 Hz, BinC4H); 7.87 (d, 2H, *J* 8.1 Hz, BinC5H); 7.43 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.3 (m, 2H, BinC6H); 7.25–7.2 (m, 2H, BinC7H); 7.13 (d, 2H, *J* 8.5 Hz, BinC8H); 4.2–3.95 (m, 4H, CH_2O); 3.55–3.4 (m, 8H, CH_2O); 3.25–3.1 (m, 4H, CH_2O); 2.64 (bs, 2H, OH). ^{13}C NMR: δ 154.3 (s, BinC2); 134.1 (s, BinC8a); 129.5 (s, BinC4a); 129.4 (d, BinC4); 127.9 (d, BinC5); 126.3 (d, BinC7); 125.4 (d, BinC8); 123.8 (d, BinC6); 120.6 (s, BinC1); 116.0 (d, BinC3); 72.4–69.5 (t, CH_2O); 61.6 (t, CH_2OH). IR (KBr): 3418 (OH) cm^{-1}. MS (EI) *m* / *z* 462.211 (M^+, calcd. for $C_{28}H_{30}O_6$ 462.204).

2,2′-[[1,1′-Binaphthalene]-2,2′-diylbis(oxy-2,1-ethanediyloxy-2,1-ethanediyloxy)]bisethanol (**6b**). ^{1}H NMR: δ 7.94 (d, 2H, *J* 8.9 Hz, BinC4H); 7.86 (d, 2H, *J* 8.0 Hz, BinC5H); 7.42 (d, 2H, *J* 9.0 Hz, BinC3H); 7.4–7.3 (m, 2H, BinC6H); 7.25–7.2 (m, 2H, BinC7H); 7.15 (d, 2H, *J* 8.4 Hz, BinC8H); 4.2–4.0 (m, 4H, CH_2O); 3.7–3.4 (m, 12H, CH_2O); 3.3–3.05 (m, 8H, CH_2O); 2.43 (bs, 2H, OH). ^{13}C NMR: δ 154.2 (s, BinC2); 134.1 (s, BinC8a); 129.4 (s, BinC4a); 129.3 (d, BinC4); 127.8 (d, BinC5); 126.3 (d, BinC7); 125.5 (d, BinC8); 123.7 (d, BinC6); 120.5 (s, BinC1); 115.6 (d, BinC3); 72.4–69.7 (t, CH_2O); 61.6 (t, CH_2OH). IR (KBr): 3407 (OH) cm^{-1}. MS (EI) *m* / *z* 550.262 (M^+, calcd. for $C_{32}H_{38}O_8$ 550.257).

General procedure for the synthesis of **7**

Tosyl chloride (2.29 g, 12 mmol) was added to a solution of diol **6** (5 mmol) in pyridine (10 ml) in one portion at 0°C. The reaction mixture was stirred at this temperature for 3 h. After addition of a small amount of ice, the reaction mixture was poured into a mixture of concentrated hydrochloric acid (100 ml) and ice. The hydrochloric acid solution was extracted with CH_2Cl_2 (3×50 ml) and the combined organic phases were washed with 2N hydrochloric acid (2×50 ml). After drying over $MgSO_4$, the solvent was evaporated to give the crude products, which were purified by flash column chromatography to give pure **7** as oils.

2,2′-[[1,1′-Binaphthalene]-2,2′-diylbis(oxy-2,1-ethanediyloxy)]bisethanol bis(4-methylbenzenesulfonate) (**7a**). Eluent EtOAc/hexane 1:1; yield 85%. ^{1}H NMR: δ 7.89 (d, 2H, *J* 9.0 Hz, BinC4H); 7.81 (d, 2H, *J* 8.0 Hz, BinC5H); 7.70 (d, 4H, *J* 8.3 Hz, TsC2H); 7.35 (d, 2H, *J* 9.0 Hz, BinC3H); 7.3–7.1 (m, 10H, ArH); 4.1–3.9 (m, 4H, CH_2O); 3.63 (t, 4H, *J* 4.5 Hz, CH_2O); 3.37 (t, 4H, *J* 4.5 Hz, CH_2O); 3.05–2.85 (m, 4H, CH_2O); 2.42 (s, 6H, $ArCH_3$). ^{13}C NMR: δ 154.1 (s, BinC2); 144.6 (s, TsC4); 134.0 (s, BinC8a); 133.1 (s, TsC1); 129.7 (d, TsC3); 129.33, 129.32 (BinC4 and BinC4a); 127.9 (d, TsC2); 127.8 (d, BinC5); 126.3 (d, BinC7); 125.3 (d, BinC8); 123.8 (d, BinC6); 120.3 (s, BinC1); 115.3 (d, BinC3); 69.9–68.5 (t, CH_2O); 21.6 (q, $ArCH_3$). IR (KBr): 1355, 1177 (SO_2–O) cm^{-1}. MS (EI) *m* / *z* 770.224 (M^+, calcd. for $C_{42}H_{42}O_{10}S_2$ 770.222).

2,2′-[[1,1′-Binaphthalene]-2,2′-diylbis(oxy-2,1-ethanediyloxy-2,1-ethanediyloxy)]bisethanol bis(4-methylbenzenesulfonate) (**7b**). Eluent EtOAc; yield 77%. ^{1}H NMR: δ 7.92 (d, 2H, *J* 9.0 Hz, BinC4H); 7.84

(d, 2H, *J* 8.1 Hz, BinC5H); 7.76 (d, 4H, *J* 8.2 Hz, TsC2H); 7.40 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.1 (m, 10H, ArH); 4.1–4.0 (m, 8H, CH_2O); 3.5–3.4 (m, 8H, CH_2O); 3.15–2.9 (m, 8H, CH_2O); 2.40 (s, 6H, $ArCH_3$). ^{13}C NMR: δ 154.2 (s, BinC2); 144.7 (s, TsC4); 134.0 (s, BinC8a); 132.9 (s, TsC1); 129.8 (d, TsC3); 129.33 (s, BinC4a); 129.25 (d, BinC4); 127.9 (d, TsC2); 127.8 (d, BinC5); 126.2 (d, BinC7); 125.4 (d, BinC8); 123.7 (d, BinC6); 120.4 (s, BinC1); 115.5 (d, BinC3); 70.5–68.4 (t, CH_2O); 21.6 (q, $ArCH_3$). IR (KBr): 1355, 1177 (SO_2–O) cm^{-1}. MS (FAB) *m/z* 858.3 (M^+, calcd. for $C_{46}H_{50}O_{12}S_2$ 858.3).

General procedure for the synthesis of dialdehydes **9**

A mixture of aldehyde **8** (1.96 g, 11 mmol), ditosylate **7** (5 mmol), and K_2CO_3 (1.52 g, 11 mmol) in dry CH_3CN (50 ml) was refluxed overnight. The reaction mixture was cooled, diluted with CH_2Cl_2 (50 ml) and filtered through Celite. After evaporation of the solvent the crude products were obtained, which were purified by flash column chromatography to give colorless oils.

3,3'-[[1,1'-Binaphthalene]-2,2'-diylbis(oxy-2,1-ethanediyloxy-2,1-ethanediyloxy)]bis[2-(2-propenyloxy)benzaldehyde] (**9a**). Eluent EtOAc/hexane 2:3; yield 95%. ^1H NMR: δ 10.42 (s, 2H, CHO); 7.90 (d, 2H, *J* 9.0 Hz, BinC4H); 7.83 (d, 2H, *J* 8.0 Hz, BinC5H); 7.41 (dd, 2H, *J* 7.8 and 1.6 Hz, AldC6H); 7.39 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.1 (m, 6H, ArH); 7.06 (t, 2H, *J* 7.8 Hz, AldC5H); 6.95 (dd, 2H, *J* 8.1 and 1.6 Hz, AldC4H); 6.05–5.9 (m, 2H, $OCH_2C\underline{H}=CH_2$); 5.3–5.15 (m, 4H, $OCH_2CH=C\underline{H}_2$); 4.56 (dd, 4H, *J* 6.0 and 1.2 Hz, $OC\underline{H}_2CH=CH_2$); 4.15–4.05 (m, 4H, CH_2O); 3.65–3.5 (m, 8H, CH_2O); 3.35–3.15 (m, 4H, CH_2O). ^{13}C NMR: δ 190.4 (d, CHO); 154.3 (s, BinC2); 152.1, 151.6 (s, AldC2,3); 134.1 (s, BinC8a); 133.4 (d, $OCH_2\underline{C}H=CH_2$); 130.2 (s, AldC1); 129.4 (s, BinC4a); 129.3 (d, BinC4); 127.8 (d, BinC5); 126.4 (d, BinC7); 125.5 (d, BinC8); 123.9 (d, Ald); 123.8 (d, BinC6); 120.5 (s, BinC1); 119.7, 119.4 (d, Ald); 118.7 (t, $OCH_2CH=\underline{C}H_2$); 115.5 (d, BinC3); 74.9 (t, $O\underline{C}H_2CH=CH_2$); 70.1–68.4 (t, CH_2O). IR (KBr): 1687 (CHO) cm^{-1}. MS (EI) *m/z* 782.310 (M^+, calcd. for $C_{48}H_{46}O_{10}$ 782.309).

3,3'-[[1,1'-Binaphthalene]-2,2'-diylbis(oxy-2,1-ethanediyloxy-2,1-ethanediyloxy-2,1-ethanediyloxy)]bis[2-(2-propenyloxy)benzaldehyde] (**9b**). Eluent MeOH/CH_2Cl_2 1.5:98.5; yield 90%. ^1H NMR: δ 10.43 (s, 2H, CHO); 7.90 (d, 2H, *J* 9.0 Hz, BinC4H); 7.83 (d, 2H, *J* 8.0 Hz, BinC5H); 7.45–7.0 (m, 14H, ArH); 6.1–5.95 (m, 2H, $OCH_2C\underline{H}=CH_2$); 5.35–5.2 (m, 4H, $OCH_2CH=C\underline{H}_2$); 4.65 (d, 4H, *J* 6.1 Hz, $OC\underline{H}_2CH=CH_2$); 4.1–4.05 (m, 8H, CH_2O); 3.68 (t, 4H, *J* 4.8 Hz, CH_2O); 3.5–3.4 (m, 4H, CH_2O); 3.27 (t, 4H, *J* 4.5 Hz, CH_2O); 3.2–3.05 (m, 4H, CH_2O). ^{13}C NMR: δ 190.4 (d, CHO); 154.3 (s, BinC2); 152.2, 151.6 (s, AldC2,3); 134.1 (s, BinC8a); 133.3 (d, $OCH_2\underline{C}H=CH_2$); 130.2 (s, AldC1); 129.4 (s, BinC4a); 129.2 (d, BinC4); 127.8 (d, BinC5); 126.3 (d, BinC7); 125.5 (d, BinC8); 124.0 (d, Ald); 123.7 (d, BinC6); 120.5 (s, BinC1); 119.7, 119.5 (d, Ald); 118.8 (t, $OCH_2CH=\underline{C}H_2$); 115.6 (d, BinC3); 75.0 (t, $O\underline{C}H_2CH=CH_2$); 70.6–68.5 (t, CH_2O). IR (KBr): 1687 (CHO) cm^{-1}. MS (EI) *m/z* 870.361 (M^+, calcd. for $C_{52}H_{54}O_{12}$ 870.362).

General procedure for the synthesis of dialdehydes **10**

A solution of **9** (2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 10 μmol), and $HCOONHEt_3$ (0.88 g, 6 mmol) in a mixture of THF (20 ml), EtOH (20 ml), and H_2O (4 ml) was refluxed until the reaction was completed (2–3 h) according to TLC (SiO_2; MeOH/CH_2Cl_2 1.5/98.5). The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (100 ml) and washed with 1 N HCl (100 ml). The organic solvent was dried over $MgSO_4$ and evaporated to give the products as oils in quantitative yield.

3,3'-[[1,1'-Binaphthalene]-2,2'-diylbis(oxy-2,1-ethanediyloxy-2,1-ethanediyloxy)]bis[2-hydroxybenzaldehyde] (**10a**). Yield 100%. ^1H NMR: δ 10.80 (s, 2H, OH); 9.94 (s, 2H, CHO); 7.90 (d, 2H, *J* 9.0 Hz, BinC4H); 7.83 (d, 2H, *J* 8.0 Hz, BinC5H); 7.41 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.1 (m, 8H, ArH); 7.0–6.85 (m, 4H, AldC4,5H); 4.2–4.0 (m, 4H, CH_2O); 3.7–3.65 (m, 4H, CH_2O); 3.55 (t, 4H, *J* 4.7 Hz, CH_2O); 3.4–3.2 (m, 4H, CH_2O). ^{13}C NMR: δ 196.0 (d, CHO); 154.3 (s, BinC2); 152.1 (s, AldC3); 147.4 (s, AldC2); 134.1 (s, BinC8a); 129.4 (s, BinC4a); 129.3 (d, BinC4); 127.8 (d, BinC5); 126.3 (d, BinC7); 125.5 (d, BinC8); 124.8 (d, Ald); 123.7 (d, BinC6); 121.2 (s, AldC1); 120.6 (d, Ald); 120.5 (s, BinC1); 119.4 (d, Ald); 115.6 (d, BinC3); 70.0–68.9 (t, CH_2O). IR (KBr): 3200 (OH), 1681, 1656 (CHO) cm^{-1}. MS (EI) *m/e* 702.243 (M^+, calcd. for $C_{42}H_{38}O_{10}$ 702.247).

3,3'-[[1,1'-Binaphthalene]-2,2'-diylbis(oxy-2,1-ethanediyloxy-2,1-ethanediyloxy-2,1-ethanediyloxy)]bis[2-hydroxybenzaldehyde] (**10b**). Yield 100%. ^1H NMR: δ 10.81 (bs, 2H, OH); 9.96 (s, 2H, CHO); 7.91 (d, 2H, *J* 9.0 Hz, BinC4H); 7.83 (d, 2H, *J* 8.0 Hz, BinC5H); 7.41 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.05 (m, 10H, ArH); 6.89 (t, 2H, *J* 7.9 Hz, AldC5H); 4.15–4.0 (m, 8H, CH_2O); 3.69 (t, 4H, *J* 4.9 Hz, CH_2O); 3.47 (t, 4H, *J* 4.8 Hz, CH_2O); 3.28 (t, 4H, *J* 4.5 Hz, CH_2O); 3.2–3.05 (m, 4H, CH_2O). ^{13}C NMR: δ 196.0 (d, CHO); 154.3 (s, BinC2); 152.2 (s, AldC3); 147.5 (s, AldC2); 134.1 (s, BinC8a); 129.4 (s, BinC4a); 129.3 (d, BinC4); 127.8 (d, BinC5); 126.3 (d, BinC7); 125.5 (d, BinC8); 124.9 (d, Ald); 123.7 (d, BinC6); 121.3 (s, AldC1); 120.8 (d, Ald); 120.6 (s, BinC1); 119.5 (d, Ald); 115.7 (d, BinC3); 70.6–69.2 (t, CH_2O). IR (KBr): 3200 (OH), 1681, 1656 (CHO) cm^{-1}. MS (EI) *m/e* 790.295 (M^+, calcd. for $C_{46}H_{46}O_{12}$ 790.299).

General procedure for the synthesis of aldehydes **12**

A mixture of aldehyde **8** (1.78 g, 10 mmol) and K_2CO_3 (1.66 g, 12 mmol) in CH_3CN (20 ml) was heated for 5 min. After slight cooling, **11** (12 mmol) was added and the mixture was refluxed for 4 h. NaI (0.2 g) and NEt_3 (2 ml) were added and refluxing was continued for 30 min. After cooling, the reaction mixture was diluted with CH_2Cl_2 (40 ml) and filtered through Celite. The solvent was evaporated and the residue was redissolved in CH_2Cl_2 (100 ml). The organic layer was washed with 1 N hydrochloric acid (50 ml), which contained a few drops of a concentrated $NaHSO_3$ solution. The aqueous phase was extracted with CH_2Cl_2 (2×50 ml). The combined organic phases were dried over Na_2SO_4, filtered, and evaporated, giving a nearly quantitative yield of **12** as oils, which were pure enough to be used in the next step without further purification.

3-[2-(2-Hydroxyethoxy)ethoxy]-2-(2-propenyloxy)benzaldehyde (**12a**). ^1H NMR: δ 10.43 (s, 1H, CHO); 7.44 (dd, 1H, *J* 7.3 and 2.1 Hz, AldC6H); 7.17 (dd, 1H, *J* 8.1 and 2.1 Hz, AldC4H); 7.15–7.05 (m, 1H, AldC5H); 6.2–6.0 (m, 1H, $OCH_2C\underline{H}=CH_2$); 5.4–5.25 (m, 2H, $OCH_2CH=C\underline{H}_2$); 4.71–4.69 (m, 2H, $OC\underline{H}_2CH=CH_2$); 4.25–4.2 (m, 2H, CH_2O); 3.95–3.9 (m, 2H, CH_2O); 3.8–3.65 (m, 4H, CH_2O); 2.27 (t, 1H, *J* 5.7 Hz, OH). ^{13}C NMR: δ 190.4 (d, CHO); 152.2, 151.6 (s, AldC2,3); 133.2 (d, $OCH_2\underline{C}H=CH_2$); 130.3 (s, AldC1); 124.1, 119.8, 119.7 (d, AldC4,5,6); 118.9 (t, $OCH_2CH=\underline{C}H_2$); 75.2 (t, $O\underline{C}H_2CH=CH_2$); 72.6–68.7 (t, CH_2O); 61.7 (t, CH_2OH). IR (KBr): 3446 (OH), 1687 (CHO) cm^{-1}. MS (EI) *m/z* 266.113 (M^+, calcd. for $C_{14}H_{18}O_5$ 266.115).

3-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]-2-(2-propenyloxy)benzaldehyde (**12b**). ^1H NMR: δ 10.44 (s, 1H, CHO); 7.44 (dd, 1H, *J* 7.4 and 2.0 Hz, AldC6H); 7.2–7.05 (m, 2H, AldC4,5H); 6.2–6.0 (m, 1H, $OCH_2C\underline{H}=CH_2$); 5.4–5.25 (m, 2H, $OCH_2CH=C\underline{H}_2$); 4.71 (d, 2H, *J* 6.1 Hz, $OC\underline{H}_2CH=CH_2$); 4.25–4.2 (m, 2H, CH_2O); 3.95–3.9 (m, 2H, CH_2O); 3.8–3.6 (m, 8H, CH_2O); 2.49 (bs, 1H, OH). ^{13}C NMR: δ 190.5 (d, CHO); 152.1, 151.5 (s, AldC2,3); 133.3 (d, $OCH_2\underline{C}H=CH_2$); 130.2 (s, AldC1); 124.1, 119.7, 119.6 (d, AldC4,5,6); 119.0 (t, $OCH_2CH=\underline{C}H_2$); 75.1 (t, $O\underline{C}H_2CH=CH_2$); 72.5–68.5 (t, CH_2O); 61.7 (t, CH_2OH). IR (KBr): 3427 (OH), 1687 (CHO) cm^{-1}. MS (EI) *m/z* 310.144 (M^+, calcd. for $C_{16}H_{22}O_6$ 310.142).

General procedure for the synthesis of aldehydes **13**

Tosyl chloride (2.29 g, 12 mmol) was added to a solution of **12** (10 mmol) in dry pyridine (10 ml) in one portion at 0°C. The reaction mixture was stirred at this temperature for 4 h. A small amount of ice was added and the mixture was poured into a mixture of concentrated hydrochloric acid (100 ml) and ice. The hydrochloric acid solution was extracted with CH_2Cl_2 (3×50 ml) and the combined organic phases were washed with 2N hydrochloric acid (2×50 ml). After drying over $MgSO_4$, the solvent was evaporated to give the crude products, which were purified by flash column chromatography to give pure **13** as oils.

3[2-(2-Hydroxyethoxy)ethoxy]-2-(2-propenyloxy)benzaldehyde 4-methylbenzenesulfonate (**13a**). Eluent EtOAc/hexane 2:3; yield 65%. ^1H NMR: δ 10.43 (s, 1H, CHO); 7.79 (d, 2H, *J* 8.3 Hz, TsC2H); 7.44 (dd, 1H, *J* 6.7 and 2.8 Hz, AldC6H); 7.31 (d, 2H, *J* 8.2 Hz, TsC3H); 7.2–7.05 (m, 2H, AldC4,5H); 6.15–5.95 (m, 1H, $OCH_2C\underline{H}=CH_2$); 5.4–5.2 (m, 2H, $OCH_2CH=C\underline{H}_2$); 4.7–4.6 (m, 2H, $OC\underline{H}_2CH=CH_2$); 4.2–4.1 (m, 4H, CH_2O); 3.85–3.8 (m, 2H, CH_2O); 3.8–3.75 (m, 2H, CH_2O); 2.42 (s, 3H, $TsCH_3$). ^{13}C NMR: δ 190.4 (d, CHO); 152.1, 151.6 (s, AldC2,3); 144.9 (s, TsC4); 133.2 (d, $OCH_2\underline{C}H=CH_2$); 132.8 (s, TsC1); 130.2 (s, AldC1); 129.8 (d, TsC3); 127.9 (d, TsC2); 124.1, 119.7, 119.6 (d, AldC4,5,6); 118.8 (t, $OCH_2CH=\underline{C}H_2$); 75.1 (t, $O\underline{C}H_2CH=CH_2$); 69.7–68.5 (t, CH_2O); 21.6 (q, $TsCH_3$). IR (KBr): 1687 (CHO); 1356, 1177 (SO_2–O) cm^{-1}. MS (EI) *m/z* 420.124 (M^+, calcd. for $C_{21}H_{24}O_7S$ 420.124).

3-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]-2-(2-propenyloxy)benzaldehyde 4-methylbenzenesulfonate (**13b**). Eluent EtOAc/hexane 1:1;

yield 65%. ^{1}H NMR: δ 10.44 (s, 1H, CHO); 7.79 (d, 2H, *J* 8.3 Hz, TsC2H); 7.43 (dd, 1H, *J* 7.3 and 2.1 Hz, AldC6H); 7.33 (d, 2H, *J* 8.1 Hz, TsC3H); 7.2–7.05 (m, 2H, AldC4,5H); 6.15–6.05 (m, 1H, $OCH_2CH{=}CH_2$); 5.4–5.25 (m, 2H, $OCH_2CH{=}CH_2$); 4.7–4.65 (m, 2H, $OCH_2CH{=}CH_2$); 4.2–4.1 (m, 4H, CH_2O); 3.88 (t, 2H, *J* 4.7 Hz, CH_2O); 3.7–3.6 (m, 6H, CH_2O); 2.44 (s, 3H, $TsCH_3$). ^{13}C NMR: δ 190.5 (d, CHO); 152.1, 151.5 (s, AldC2,3); 144.9 (s, TsC4); 133.3 (d, $OCH_2CH{=}CH_2$); 132.9 (s, TsC1); 130.2 (s, AldC1); 129.8 (d, TsC3); 128.0 (d, TsC2); 124.1, 119.6, 119.5 (d, AldC4,5,6); 118.9 (t, $OCH_2CH{=}CH_2$); 75.1 (t, $OCH_2CH{=}CH_2$); 70.8–68.5 (t, CH_2O); 21.7 (q, $TsCH_3$). IR (KBr): 1687 (CHO), 1357, 1177 (SO_2-O) cm^{-1}. MS (EI) *m/z* 464.152 (M^+, calcd. for $C_{23}H_{28}O_8S$ 464.151).

General procedure for the alkylation of binaphthol **3** *with tosylates* **13**. *Formation of aldehydes* **9**

A mixture of binaphthol **3** (1.43 g, 5 mmol), tosylate **13** (10 mmol), and K_2CO_3 (1.38 g, 10 mmol) in dry CH_3CN (50 ml) was refluxed overnight. The reaction mixture was cooled, diluted with CH_2Cl_2 (50 ml), and filtered through Celite. After evaporation of the solvent the crude products were obtained, which were purified by flash column chromatography to give **9** as colorless oils in 80% yield [eluent $EtOAc/CH_2Cl_2$ 5:95 (**9a**) and 15:85 (**9b**), respectively].

General procedure for the cyclization of dialdehydes **10**. *Formation of the binaphthyl salophen crown ethers* **1** *and* **2**

A solution of dialdehyde **10** (2.5 mmol), $Ba(OTf)_2$ (2.18 g, 5.0 mmol), and either 1,2-benzenediamine **14** (270 mg, 2.5 mmol) or *cis*-1,2-cyclohexanediamine **15** (285 mg, 2.5 mmol) in THF (250 ml) was refluxed for 30 min. After cooling slightly, $UO_2(OAc)_2 \cdot 2H_2O$ (1.59 g, 3.75 mmol) was added and refluxing was continued for about 30 min. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (200 ml) and washed with water (2×100 ml), an aqueous solution of Na_2SO_4 (50 ml), and water again (100 ml). After drying over $MgSO_4$ and evaporation of the solvent, the crude products were obtained, which were purified by precipitation (**1**: $CHCl_3$/cyclohexane) or by flash column chromatography followed by precipitation (**2**: eluent $MeOH/CH_2Cl_2$ 3:97, CH_2Cl_2/cyclohexane).

[4,5,7,8,29,30,32,33-Octahydro-10,14:23,27-dimethenobenzo[z]dinaphtho[2,1-h:1′,2′-j][1,4,7,12,15,18,25,28]hexaoxadiazacyclotetratriacontine-45,46-diolato(2⁻)-N¹⁶,N²¹,O⁴⁵,O⁴⁶]dioxouranium (**1a**). Yield 74%; m.p. 228–230°C. Anal. calcd. for $C_{48}H_{40}N_2O_{10}U \cdot 0.5C_6H_{12} \cdot 1.25H_2O$ (M_r 1107.513): C 55.31, H 4.41, N 2.53; found: C 55.49, H 4.29, N 2.66%. Karl Fisher titration calcd. for 1.25 H_2O: 2.03; found: 2.05. ^{1}H NMR: (DMSO-d_6) δ 9.61 (s, 2H, HC=N); 7.95–7.85 (m, 4H, BinC4,5H); 7.8–7.75 (m, 2H, AmH); 7.6–7.5 (m, 4H, BinC3H + AmH); 7.45–7.42 (m, 2H, AldC6H); 7.38–7.32 (m, 2H, Bin6H); 7.3–7.24 (m, 2H, Bin7H); 7.2–7.17 (m, 2H, AldC4H); 7.05 (d, 2H, *J* 8.2 Hz, BinC8H); 6.60 (t, 2H, *J* 7.8 Hz, AldC5H); 4.4–3.3 (m, 16H, CH_2O). ^{13}C NMR: (DMSO-d_6) δ 166.5 (HC=N); 161.2 (s, AldC2); 154.4 (s, BinC2); 150.3 (s, AldC3); 146.7 (s, AmC1); 133.2 (s, BinC8a); 129.5 (d, BinC4); 129.1 (s, BinC4a); 128.7 (d, AmC3); 128.1 (d, AldC6); 128.0 (d, BinC5); 126.2 (d, BinC7); 124.6 (d, BinC8); 124.5 (s, AldC1); 123.6 (d, BinC6); 120.2 (d, AmC2); 119.9 (d, AldC4); 119.7 (s, BinC1); 116.6 (d, BinC3); 116.0 (d, AldC5); 70.1–68.8 (t, CH_2O). IR (KBr): 1600 (C=N); 892 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1043.4 ($M^+ + 1$, calcd. 1043.3).

[4,5,7,8,10,11,32,33,35,36,38,39-Dodecahydro-13,17:26,30-dimethenobenzo[f₁]dinaphth[2,1-k:1′,2′-m][1,4,7,10,15,18,21,24,31,34]octaoxadiazacyclotetracontine-51,52-diolato(2⁻)-N¹⁹,N²⁴,O⁵¹,O⁵²]dioxouranium (**1b**). Yield 80%; m.p. 163–165°C. Anal. calcd. for $C_{52}H_{48}N_2O_{12}U \cdot C_6H_{12} \cdot 2.25H_2O$ (M_r 1255.716): C 55.48, H 5.18, N 2.23; found: C 55.73, H 4.71, N 2.36%. Karl Fisher titration calcd. for 2.25 H_2O: 3.23; found: 3.23. ^{1}H NMR: (DMSO-d_6) δ 9.62 (s, 2H, HC=N); 8.02 (d, 2H, *J* 9.1 Hz, BinC4H); 7.91 (d, 2H, *J* 7.8 Hz, BinC5H); 7.8–7.75 (m, 2H, AmH); 7.61 (d, 2H, *J* 9.1 Hz, BinC3H); 7.58–7.5 (m, 2H, AmH); 7.46–7.18 (m, 8H, AldC4,6H + BinC6,7H); 6.93 (d, 2H, *J* 8.2 Hz, BinC8H); 6.63 (t, 2H, *J* 7.8 Hz, AldC5H); 4.3–3.1 (m, 24H, CH_2O). ^{13}C NMR: (DMSO-d_6) δ 165.5 (d, HC=N); 161.1 (s, AldC2); 154.0 (s, BinC2); 150.3 (s, AldC3); 146.8 (s, AmC1); 133.4 (s, BinC8a); 129.3 (d, BinC4); 128.9 (s, BinC4a); 128.7 (d, AmC3); 127.9 (d, AldC6 and BinC5); 126.2 (d, BinC7); 124.6 (d, BinC8); 124.5 (s, AldC1); 123.4 (d, BinC6); 120.3 (d, AmC2); 119.6 (s, BinC1); 119.4 (d, AldC4); 116.0 (d, BinC3 and AldC5); 69.9–68.6 (t, CH_2O). ^{1}H NMR: ($CDCl_3$) δ 9.34 (s, 2H, HC=N); 7.91 (d, 2H, *J* 9.0 Hz, BinC4H); 7.83 (d, 2H, *J* 8.0 Hz, BinC5H); 7.54–7.41 (m, 4H, AmH); 7.43 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.15 (m, 8H, ArH); 7.10 (d, 2H, *J* 7.9 Hz, BinC8H); 6.63 (t, 2H, *J* 7.8 Hz, AldC5H); 4.4–3.3 (m, 24H, CH_2O). ^{13}C NMR: ($CDCl_3$) δ 165.6 (d, HC=N); 162.4 (s, AldC2); 154.3 (s, BinC2); 150.2 (s, AldC3); 147.1 (s, AmC1); 134.1 (s, BinC8a); 129.4 (s, BinC4a); 129.3 (d, BinC4); 129.1 (d, AldC6); 128.9 (d, AmC3); 127.8 (d, BinC5); 126.2 (d, BinC7); 125.4 (d, BinC8); 124.9 (s, AldC1); 123.9 (d, BinC6); 120.4 (s, BinC1); 119.7 (d, AmC2); 116.9 (d, AldC5); 115.6 (d, BinC3); 70.9–69.8 (t, CH_2O). IR (KBr): 1602 (C=N), 903 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1131.5 ($M^+ + 1$, calcd. 1131.4).

[cis-4,5,7,8,16a,17,18,19,20,20a,29,30,32,33-Tetradecahydro-10,14:23,27-dimethenobenzo[z]dinaphtho[2,1-h:1′,2′-j][1,4,7,12,15,18,25,28]hexaoxadiazacyclotetratriacontine-45,46-diolato(2⁻)-N¹⁶,N²¹,O⁴⁵,O⁴⁶]dioxouranium (**2a**).

Eluent: $MeOH/CH_2Cl_2$ 3:97; yield 95%; m.p. 206–208°C. Anal. calcd. for $C_{48}H_{46}N_2O_{10}U \cdot 1H_2O$ (M_r 1066.975): C 54.03, H 4.53, N 2.63; found: C 53.86, H 4.67, N 2.57%. Karl Fischer titration calcd. for 1 H_2O: 1.69; found: 1.46. ^{1}H NMR: ($CDCl_3$) δ 9.28 (s, 2H, HC=N); 7.9–7.8 (m, 4H, BinC4,5H); 7.4–7.1 (m, 12H, ArH); 6.66 (t, 1H, *J* 7.7 Hz, AldC5H); 6.64 (t, 1H, *J* 7.7 Hz, AldC5′H); 4.75–4.55 (m, 2H, AmC1); 4.7–3.4 (m, 16H, CH_2O); 2.7–2.55 (m, 1H, AmC2H); 2.4–2.2 (m, 1H, AmC2H); 2.15–1.95 (m, 1H, AmC2H); 1.95–1.6 (m, 5H, AmC2,3H). ^{13}C NMR: ($CDCl_3$) δ 167.9, 167.6 (d, HC=N); 162.0, 161.7 (s, AldC2,2′); 154.43, 154.36 (s, BinC2,2′); 149.9 (s, AldC3); 134.2 (s, BinC8a); 129.7, 129.5, 129.4 (BinC4,4′ and BinC4a); 127.9 (d, AldC6 and BinC5); 126.4 (d, BinC7); 116.6, 116.5 (d, AldC5,5′); 116.3, 115.8 (d, BinC3,3′); 74.0, 69.1 (d, AmC1,1′); 71.7–69.8 (CH_2O); 28.5, 26.9 (t, AmC2,2′); 23.1, 20.4 (t, AmC3,3′); IR (KBr): 1615 (C=N), 897 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1049.2 ($M^+ + 1$, calcd. 1049.4).

[cis-4,5,7,8,10,11,19a,20,21,22,23,23a,32,33,35,36,38,39-Octadecahydro-13,17:26,30-dimethenobenzo[f₁]dinaphth[2,1-k:1′,2′-m][1,4,7,10,15,18,21,24,31,34]octaoxadiazacyclotetracontine-51,52-diolato(2⁻)-N¹⁹,N²⁴,O⁵¹,O⁵²]dioxouranium (**2b**). During the cyclization MeOH (125 ml) was added to maintain a homogeneous reaction mixture. Eluent $MeOH/CH_2Cl_2$ 3:97; yield 89%; m.p. 154–157°C. Anal. calcd. for $C_{52}H_{54}N_2O_{12}U \cdot 0.5C_6H_{12} \cdot 2.25H_2O$ (M_r 1219.664): C 54.16, H 5.33, N 2.30; found: C 54.12, H 5.17, N 2.28%. Karl Fischer titration calcd. for 2.25 H_2O: 3.33; found: 3.39. ^{1}H NMR: ($CDCl_3$) δ 9.24 (s, 2H, HC=N); 7.89 (d, 1H, *J* 9.0 Hz, BinC4H); 7.88 (d, 1H, *J* 9.0 Hz, BinC4′H); 7.82 (d, 2H, *J* 8.1 Hz, BinC5,5′H); 7.43 (d, 1H, *J* 9.0 Hz, BinC3H); 7.42 (d, 1H, *J* 9.0 Hz, BinC3′H); 7.35–7.05 (m, 10H, ArH); 6.64 (t, 2H, *J* 7.7 Hz, AldC5H); 4.65–4.55 (m, 2H, AmC1); 4.45–4.3 (m, 6H, CH_2O); 4.05–3.25 (m, 18H, CH_2O); 2.5–2.3 (m, 2H, AmC2H); 2.0–1.85 (m, 2H, AmC2H); 1.85–1.55 (m, 4H, AmC3H). ^{13}C NMR: ($CDCl_3$) 167.6, 167.5 (d, HC=N); 161.1 (s, AldC2); 154.3 (s, BinC2); 150.0 (s, AldC3); 134.1 (s, BinC8a); 129.23, 129.21, 129.18 (BinC4,4′ and BinC4a); 127.9, 127.8 (d, AldC6 and BinC5); 126.2 (d, BinC7); 125.4 (d, BinC8); 124.5 (s, AldC1); 123.5 (d, BinC6); 121.6 (d, AldC4); 120.2, 120.1 (s, BinC1,1′); 116.4 (d, AldC5); 115.3, 115.2 (d, BinC3,3′); 71.6, 71.2 (d, AmC1,1′); 70.7–69.6 (t, CH_2O); 27.8, 27.6 (t, AmC2,2′); 21.8, 21.6 (t, AmC3,3′). IR (KBr): 1614 (C=N), 898 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1137.1 ($M^+ + 1$, calcd. 1137.4).

General procedure for the synthesis of urea complexes.

A solution of **1** or **2** (0.05 mmol) in CH_2Cl_2 (5 ml) was covered with a solution of urea (30 mg, 0.5 mmol) in MeOH (15 ml). After standing for some days at room temperature, the precipitated complexes were obtained by filtration, washing with MeOH, and drying *in vacuo*.

***1a** · urea* M.p. 227–230°C. Anal. calcd. for $C_{48}H_{40}N_2O_{10}U \cdot CH_4N_2O \cdot 0.5H_2O$ (M_r 1111.976): C 52.93, H 4.08, N 5.04; found: C 52.94, H 4.02, N 4.97%. ^{1}H NMR: (DMSO-d_6) δ 9.61 (s, 2H, HC=N); 7.95–7.85 (m, 4H, BinC4,5H); 7.8–7.75 (m, 2H, AmH); 7.6–7.5 (m, 4H, BinC3H + AmH); 7.45–7.42 (m, 2H, AldC6H); 7.38–7.32 (m, 2H, Bin6H); 7.3–7.24 (m, 2H, Bin7H); 7.2–7.17 (m, 2H, AldC4H); 7.05 (d, 2H, *J* 8.2 Hz, BinC8H); 6.60 (t, 2H, *J* 7.8 Hz, AldC5H); 5.43 [bs, 4H, $(H_2N)_2C{=}O$]; 4.4–3.3 (m, 16H, CH_2O). IR (KBr): 1645, 1627 (C=O), 1603 (HC=N), 901 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1103.4 (M^+ + urea + 1, calcd. for $[C_{48}H_{40}N_2O_{10}U + CH_4N_2O + 1]$ 1103.3), 1043.3 ($M^+ + 1$, calcd. 1043.3); (EI) *m/z* 60.032 (urea$^+$, calcd. for CH_4N_2O 60.032).

***1b** · urea.* M.p. 181–185°C. Anal. calcd. for $C_{52}H_{48}N_2O_{12}U \cdot CH_4N_2O \cdot 2H_2O$ (M_r 1227.106): C 51.88, H 4.60, N 4.57; found: C 51.66, H 4.33, N 4.42%. ^{1}H NMR: δ 9.34 (s, 2H, HC=N); 7.95–7.85 (m, 4H, BinC4,5H); 7.55–7.4 (m, 4H, AmH); 7.38 (d, 2H, *J* 9.0 Hz, BinC3H); 7.35–7.1 (m, 10H, ArH); 6.60 (t, 2H, *J* 7.8 Hz, AldC5H); 4.8–2.9 (m, 24H, CH_2O). IR (KBr): 1636 (C=O), 1603 (HC=N), 900 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1191.4 (M^+ + urea + 1, calcd. for $[C_{52}H_{48}N_2O_{12}U + CH_4N_2O + 1]$ 1191.4), 1131.5 ($M^+ + 1$, calcd. 1131.4); (EI) *m/z* 60.032 (urea$^+$, calcd. for CH_4N_2O 60.032).

***2a* · *urea*.** M.p. 220–225°C. Anal. calcd. for $C_{48}H_{46}N_2O_{10}U \cdot CH_4N_2O \cdot H_2O$ (M_r 1127.001): C 52.22, H 4.65, N 4.97; found: C 52.32, H 4.61, N 4.89%. ^{1}H NMR: δ 9.27 (s, 2H, HC=N); 7.94 (d, 2H, *J* 8.9 Hz, BinC4H); 7.88 (d, 2H, *J* 8.2 Hz, BinC5H); 7.55–7.1 (m, 12H, ArH); 6.65–6.55 (m, 2H, AldC5H); 4.7–4.55 (m, 2H, AmC1H); 4.55–3.3 (m, 16H, CH_2O); 2.6–2.45 (m, 2H, AmC2H); 2.0–1.55 (m, 6H, AmC2,3H). IR (KBr): 1650 (C=O), 1616 (HC=N), 894 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1109.4 (M^+ + urea + 1, calcd. for $[C_{48}H_{46}N_2O_{10}U + CH_4N_2O + 1]$ 1109.4), 1049.4 (M^+ + 1, calcd. 1049.4); (EI) *m/z* 60.032 (urea$^+$, calcd. for CH_4N_2O 60.032).

***2b* · *urea*.** M.p. 171–174°C. Anal. calcd. for $C_{52}H_{54}N_2O_{12}U \cdot CH_4N_2O \cdot 0.5H_2O$ (M_r 1206.131): C 52.78, H 4.93, N 4.65; found: C 52.80, H 5.12, N 4.58%. ^{1}H NMR: δ 9.26 (s, 2H, HC=N); 7.9–7.8 (m, 4H, BinC4,5H); 7.4–7.05 (m, 12H, ArH); 6.62 (t, 1H, *J* 7.7 Hz, AldC5H); 6.60 (t, 1H, *J* 7.8 Hz, AldC5'H); 4.8–2.9 (m, 26H, CH_2O + AmC1H); 2.7–2.55 (m, 1H, AmC2H); 2.45–2.25 (m, 1H, AmC2H); 2.1–1.55 (m, 6H, AmC2,3H). IR (KBr): 1644 (C=O), 1619 (HC=N), 898 (O–U–O) cm^{-1}. MS (FAB) *m/z* 1137.4 (M^+ + 1, calcd. 1137.4); (EI) *m/z* 60.032 (urea$^+$, calcd. for CH_4N_2O 60.032).

Calculations

Molecular-mechanics calculations were performed with CHARMm and the graphical QUANTA interface[28]. Force-field parameters were taken from CHARMm, except the electrostatic[24] and the non-bonded parameters[25] for the uranyl cation, which were determined to reproduce the experimental hydration geometry and enthalpy. The coordinates of the salophen units were taken from published structures[7b,10a] and were kept constant by imposing constraints on the atomic positions. With molecular-mechanics calculations, steric minima of the complexes were determined. Minimizations were terminated at *RMS* < 0.0001.

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[19] Attempts to purify metallomacrocycles **1** by column chromatography were unsuccessful. The use of silica gel as the stationary phase led to partial decomposition of the salophen units. Alumina and Florisil strongly adsorbed the macrocycles. Reversed-phase chromatography (RP18) did not give satisfactory separation. Modification of silica gel with (acet-3-amino)propyl chains gave a reversed-phase material that strongly adsorbed the metallomacrocycles when using a reasonably apolar solvent (CH_2Cl_2).
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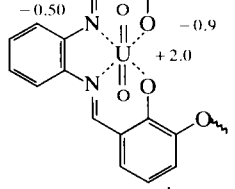
[24] Charges used on the uranyl salophen unit: charges on U, =O, and O$^-$ were fixed at +2.0, 0.0, and −0.9 respectively. The other charges were calculated with QUANTA's charge templates.



[25] $E_{min} = -1.00$ kcal·mol^{-1} and $R_{min} = 1.50$ Å were used for calculation of the van der Waals interactions.
[26] As most of the molecules described in this paper have C_2 symmetry, the equivalent atoms (') are not assigned explicitly, except for **2**, which has no C_2 symmetry.
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