## New Fluorescent Calix Crown Ethers, Part II: Synthesis and Complex Formation in Solution and the Solid State

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New luminescent 1-aza-15-crown-5 ethers bearing a coumarin unit were synthesised leading to the cavitand-based calix crown ether **9**. The solid-state structures of crown ethers **5** and **6** and the solid-state structures of the sodium and potassium iodide complexes of crown ether **5** are presented. The association constants for the complex formation with alkali metal ions in methanol were determined. Only weak complexes were formed ( $K_{\text{Na}} = 286 \text{ M}^{-1}$ ,  $K_{\text{K}} = 392 \text{ M}^{-1}$ ). The aza-15-crown-5 ether was attached by a methylene unit to a cavitand to give the new fluorescent calix crown ether **9**. The association constants for the sodium and potassium complexes in methanol were investigated as well, and an en-

#### Introduction

Recognition phenomena are essential in biological systems. Therefore, the preparation of receptors for molecular recognition is one of the main pursuits in supramolecular chemistry.<sup>[1]</sup> One route to molecular receptors is to mimic natural receptor characteristics, but entirely artificial receptors are also of broad interest. A fundamental requirement of molecular receptors is the selective and strong binding of substrate molecules. Chemical sensing is very meaningful in the research of receptor interactions as well.<sup>[2]</sup> Crown ethers and aza-crown ethers are mature units in this context and possess selectivity and strong binding.<sup>[3]</sup> Furthermore, a variety of crown ether sensory systems are established in supramolecular chemistry.<sup>[4]</sup> Hence, crown ethers are adequate foundations upon which to build an artificial sensory

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hancement for the association constant of the sodium complex was found ( $K_{\rm Na} = 1215 \text{ M}^{-1}$ ,  $K_{\rm K} = 497 \text{ M}^{-1}$ ). Selected equilibrium structures of the complexes of **9** were examined by Kohn–Sham density functional calculations to give a detailed understanding of the interplay between the two involved building blocks. Based on these results, a sidewise cation binding of the host **9** can be assumed. These complex geometries are distinct from our findings in our previous work for a larger crown ether attached to a cavitand.

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receptor. The resorcinol-based cavitand<sup>[5]</sup> is a sophisticated host molecule and offers various functional groups to form weak interactions for complex formation.<sup>[6]</sup> The association constants of the complexes formed in solution are weak, and the selectivity is not complete.<sup>[7]</sup> Nevertheless, the cavitand provides a lipophilic cavity and an oxygen crown at the upper rim, which makes it a versatile supramolecule for recognition phenomena and possibly even substrate interactions, in particular, for extended supramolecules based on the cavitand.<sup>[8]</sup> Given the properties of these two building blocks (i.e. a crown ether and the cavitand), a modular approach to new receptor molecules is obvious.<sup>[9]</sup> In our previous work, we presented the combination of the cavitand with a fluorescent 1-aza-21-crown-7 ether.<sup>[10]</sup> The binding strength of selected alkali-metal-ion complexes was increased by at least one order of magnitude by the attached cavitand over that of the crown ether alone. Herein, we report that DFT calculations of a container-like supramolecule containing the cavitand and crown ether indicated cooperative binding interactions. In this work, we present the synthesis of luminescent 1-aza-15-crown-5 ethers 5, 6, and 7. The crown ether 7 is attached to the cavitand to form the corresponding calix crown ether 9. Complex formation with alkali metal ions in solution and the solid state were investigated. Kohn-Sham density functional (KS-DFT) calculations for different conformations of the calix crown ether complexes are presented to illustrate the interplay of the cavitand with a small crown ether.



### **Results and Discussion**

The coumaryl crown ethers **5** and **6** were synthesised analogously to the coumaryl *N*-benzylaza-21-crown-7 ether, as reported previously.<sup>[10]</sup> 2-(2-Hydroxyethoxy)ethyl toluene-4-sulfonate **2** was attached to the dihydroxy coumarin (**1**),<sup>[11]</sup> and the product was tosylated. Cyclisation by use of a primary amine gave the corresponding crown ethers. Na<sub>2</sub>CO<sub>3</sub> was used as a template for the crown ether formation (instead of a mixture of potassium and caesium carbonate). Furthermore, the yield was increased by the use of toluene (Scheme 1).<sup>[12]</sup>

The benzyl group can be removed by hydrogenation, as described previously.<sup>[10]</sup> We found that besides the cleavage of the benzyl group, hydrogenation of the coumarin double bond can also occur, although the double bond hydrogenation is slower than the removal of the benzyl group. It is difficult to achieve complete conversion to the deprotected crown ether 7 without hydrogenation byproducts. The catalytic removal of the benzyl group is a fast reaction, but the reaction rate is also very sensitive to the amount of catalyst and solvent. Some non-hydrogenation methods for the removal of a diphenylmethane group as protecting group for an amine are reported.<sup>[13–16]</sup> Therefore, we synthesised the

diphenylmethane-protected crown ether **6** to allow for easier removal without an adverse effect to the coumarin double bond. Unfortunately, none of the reported methods worked properly in our hands. Also, deprotection by the palladium-catalysed hydrogenation of **6** only progressed at a reasonable rate if stoichiometric amounts of the catalyst were used at higher temperatures (60 °C, Scheme 2).

Fortunately, no reaction occurred at the coumarin double bond of 6 under palladium-catalysed hydrogenation conditions even over very long reaction times (days). At this time, we have no explanation for this result. The reaction can be accelerated by the addition of hydrochloric acid, but we were discouraged by this, because acid-catalysed cleavage of the coumarin lactone can emerge as a side reaction.

A disadvantage of the use of diphenylmethane as a protecting group is that nonvolatile components are formed, and column chromatography is needed for the isolation of the aza-crown ether. In the next step, the aza-crown ether **7** was attached to the monobenzyl-bromo cavitand **8**<sup>[10]</sup> by a nucleophilic substitution leading to the cavitand-based calix crown ether **9** (Scheme 3). The reaction was monitored by MALDI-ToF, and complete conversion was reached after 2 h. A 60% isolated yield was achieved following column chromatography.



Scheme 1. Synthesis of the luminescent crown ethers **5** and **6**. a) 2-(2-Hydroxyethoxy)ethyl toluene-4-sulfonate,  $K_2CO_3$ , DMF, 58%; b) TsCl, *i*Pr<sub>2</sub>EtN, CH<sub>2</sub>Cl<sub>2</sub>, 55%; c) Na<sub>2</sub>CO<sub>3</sub>, benzylamine, toluene, reflux 47%; d) Na<sub>2</sub>CO<sub>3</sub>, aminodiphenylmethane, toluene, reflux, 86%. R = HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>.





Scheme 2. Removal of the protecting group. a) H<sub>2</sub>, Pd/C (10%), EtOH, 50%.



Scheme 3. Synthesis of luminescent calix crown ether 9. a)  $Cs_2CO_3$ , DMF, 60%. R =  $C_{11}H_{23}$ .

Single crystals of crown ethers **5** and **6** were grown from saturated ethanol solutions. The solid-state structures are shown in Figures 1 and 2. In both crystal structures no solvent molecules are included. Crystallographic details are given in the Experimental Section.



Figure 1. Solid-state structure of luminescent crown ether **5**. Hydrogen atoms are omitted.



Figure 2. Solid-state structure of luminescent crown ether 6. Hydrogen atoms are omitted.

Crystal structures of the potassium and sodium iodide complexes of crown ether **5** were also obtained. They were grown from the metal-salt-saturated ethanol solution of **5**  by slow concentration. In accordance with the estimated complex stoichiometry in methanol solution (see below), crown ether **5** forms a 1:1 complex with sodium iodide in the solid state (Figure 3).



Figure 3. Sodium iodide complex of crown ether 5. Hydrogen atoms are omitted. Two ethanol molecules are incorporated (upper sphere).

In solution, only poor association constants were found for the sodium complex of **5** and related *N*-benzylaza-15crown-5 ethers.<sup>[3,17–20]</sup> A stronger binding of sodium ions by *N*-substituted aza-15-crown-5 ethers is reported if six oxygen atoms beside the nitrogen atom are present for binding.<sup>[21,22]</sup> This is in agreement with our findings in the solid state. Two solvent molecules (ethanol) were incorporated into the complex to increase the coordination number of the sodium ion. The coordination number is seven, including the crown ether nitrogen atom.

The longest oxygen–sodium contacts are from the crown ether oxygens attached to the coumarin (d = 2.772 and 2.561 Å). Only one is suitable for a close contact, probably by the avoided rotation due to the integrated coumarin. The nitrogen–sodium (d = 2.606 Å) distance is longer than the remaining crown oxygen–metal distances and the solvent– metal distances (d = 2.375-2.514 Å). The counterion (iodide) is far separated from the metal ion [d(I–Na) = 5.179 Å]. In the literature, only weak binding of N-benzylaza-15-crown-5 ethers with potassium ions is reported. Solid-state structures of potassium complexes of related compounds show (1:1)<sub>n</sub>, (2:2)<sub>n</sub>, and solvent-mediated 2:2 complexes rather than 1:1 stoichiometries.<sup>[17–20]</sup> The Xray structure of the potassium complexes of crown ether **5** showed an isolated 2:2 complex (Figure 4).



Figure 4. 2:2 complex of potassium iodide and crown ether 5. Hydrogen atoms are omitted. One ethanol molecule is incorporated.

Interestingly, the shortest metal-oxygen contact in the potassium iodide structure is from the carbonyl oxygen atom of the coumarin unit to the neighbouring metal centre (d = 2.753 Å). One coumarin oxygen atom is more closely coordinated than the second (d = 2.779 and 2.916 Å), as was observed in the sodium complex. The nitrogen atom takes part in the metal ion coordination, but one solvent molecule is still incorporated to increase the coordination sphere. In contrast to the sodium complex of **5**, the counterion is not far separated [d(I-K) = 3.652 Å].

The absorption and emission spectra of crown ether **5** are presented in Figure 5. The absorbance spectrum shows the typical absorption of a 7,8-substituted coumarin unit.<sup>[23,24]</sup> A local maximum of absorption at 318 nm and a smaller one at 255 nm was found, whereas the maximum of absorption in the aromatic region was at 205 nm. The fluorescence maximum was observed at 451 nm.

The absorption and emission spectra of calix crown ether 9 are shown in Figure 6. The maximum emission is slightly blueshifted compared to that of 5 (448 nm). In the absorption spectrum, a superposition of the coumarin absorbance and the absorbance of the resorcarene arenes was observed with two maxima at 317 nm and 277 nm.

The maximum absorbance in the aromatic region is at 204 nm. The absorption and emission spectra of compounds **6** and **7** are given in the Supporting Information. Cation addition changed the emission spectra of **5** and **9** owing to the change of the excited-state dipole of the complexes formed (photoinduced charge transfer, PCT).<sup>[10,25]</sup> A photoinduced electron-transfer mechanism from the crown ether nitrogen atom can be ruled out, because titration of the hosts with trifluoroacetic acid does not change the emis-



Figure 5. Absorption (-) and emission (···) spectra of luminescent crown ether 5 in methanol ( $c = 1 \times 10^{-5}$  M,  $\lambda_{ex} = 317$  nm).



Figure 6. Absorption (-) and emission (···) spectra of luminescent calix crown ether **9** in methanol ( $c = 1 \times 10^{-5}$  M,  $\lambda_{ex} = 317$  nm).

sion significantly. The crown ether **5** and the calix crown ether **9** were titrated with solutions of different alkali-metal acetates to obtain association constants for complex formation by nonlinear curve fitting.<sup>[10]</sup> The determined association constants are shown in Table 1. For all titration plots, the coefficient of determination was higher than 0.99. All fluorescence spectra, titration plots, and Job plots are given in the Supporting Information. As mentioned above, only weak complexes of *N*-benzylaza-15-crown-5 ethers and alkali metal ions are formed.<sup>[21,22]</sup>

Table 1. Association constants of  ${\bf 5}$  and  ${\bf 9}$  in methanol with alkalimetal acetates at 25 °C.

| Entry | Compound | Guest           | $K \left[ \mathrm{M}^{-1}  ight]$ | $\log(K/[M^{-1}])$ |
|-------|----------|-----------------|-----------------------------------|--------------------|
| 1     | 9        | Na <sup>+</sup> | $1215\pm168$                      | 3.08               |
| 2     |          | $K^+$           | $497 \pm 33$                      | 2.70               |
| 3     | 5        | Na <sup>+</sup> | $268 \pm 26$                      | 2.43               |
| 4     |          | $K^+$           | $392\pm75$                        | 2.59               |

This was also found for crown ether **5**. The association constant of the potassium complex of **5** exceeded that of the sodium complex, but no pronounced selectivity was found. For both complexes, a 1:1 stoichiometry in solution can be estimated by the shape of the binding isotherm, and the stoichiometry was confirmed by a Job-plot analysis.<sup>[26]</sup>

Even though we found a 2:2 complex of potassium and 5 in the solid state, we exclude the formation of a 2:2 complex in solution. A 2:2 complex is not distinguishable from a 1:1 complex by a Job-plot analysis, but the involvement of the carbonyl oxygen atom and the resulting change in the electronic environment by complexation would change the photochemical properties of the formed complex dramatically. Therefore, we assume that no 2:2 complexes with participation of the carboxylic oxygen in complexation were formed. An additional argument against the appearance of a 2:2 complex in solution is the high dilution of the sample solution  $(1 \times 10^{-5} \text{ M})$ . For the alkali-metal complexes of 9, a preference for sodium ions was found. The association constant was almost five times as large as that for the sodium complex of 5. The association constant for the potassium complex of 9 was only marginally larger than that of the potassium complex of 5. In summary, the strength of the potassium complexes of hosts 5 and 9 and the sodium complex of host 5 were low, and no distinct preference was found. Only the sodium complex of host 9 was favoured. The strength of the formed complexes of N-pivot crown ethers is mainly influenced by the number of oxygen atoms involved in the complexes.<sup>[12,21]</sup> By attaching the cavitand, the number of oxygen atoms for complexation is only increased by one (see below). From the solid-state structures of the crown ether moiety (see above), it can be established that three crown oxygen atoms can develop short metal ion contacts. Hence, the calix crown ether 9 provides only a small coordination sphere. This is in good agreement with a preferential binding for sodium ions. We assume that this small coordination sphere is not able to stabilise the potassium complex in a distinct manner. Titration experiments with lithium acetate were carried out as well. Regrettably, no association constants were obtained within an acceptable experimental error. As already mentioned, the change in the excited-state dipole of a complex accounts for changes in emission spectra. The magnitude of this change is specific for the guest cation. For the lithium complexes of 5 and 9, the change was very small, leading to a large experimental error. Nevertheless, a 1:1 complex stoichiometry for the lithium complexes of 5 and 9 were assured by Job plots.

As previously reported, the combination of a larger crown ether and the cavitand can enhance the association constants for complex formation with alkali-metal acetates in a synergistic manner.<sup>[10]</sup> To evaluate the interplay of the two building blocks, we examined the sodium and the potassium complexes of 9 by structure optimisation and normal-mode analysis in the framework of KS-DFT (for details see the Experimental Section). Two different starting structures were taken into account for each guest cation: a sandwich-like arrangement of the two host building blocks and an arrangement with the metal-cation-containing azacrown ether rotated away from the calixarene moiety (sidewise conformation). The starting geometries of the crown ether moiety were taken from the X-ray structures. For the calculations, the resorcarene lower-rim n-undecyl chains were replaced by methyl groups. Figure 7 shows a ball-and-



stick representation of the equilibrium structures obtained with a sidewise arrangement. Cartesian coordinates and electronic energies are given in the Supporting Information.



Figure 7. Calculated structures for the sidewise conformer of the potassium (top) and sodium (bottom) complex of 9. Hydrogen atoms are omitted.

For both cations (from each starting geometry), a local minimum was found: one with a complexation with a sandwich-like geometry and one sidewise to the resorcarene. For both cations, the sidewise conformer was energetically strongly favoured. Therefore, we assume that the sidewise conformer displays the global minimum in the gas phase.

For the potassium complex, the sandwich conformer was 69 kJ/mol higher in energy than the sidewise conformer. The stabilisation in the sidewise isomer occurs because shorter metal-oxygen contacts are achievable, and thereby an increased coordination number is also possible. The coordination number was six (including a K-N contact), and the K–O distances range from 273 to 283 pm [d(K-N)] =291 pm]. The sidewise-complexation isomer was also favoured over the sandwich conformer by 75 kJ/mol for the sodium complex. Shorter metal-oxygen distances [233-246 pm, d(Na-N) = 250 pm] were found for the sidewise conformation than were found for the sandwich conformer [239-249 pm, d(Na-N) = 248 pm]. The coordination number of the sidewise conformer was six. For the sandwich conformer, the coordination number was five, but one short contact (279 pm) to a methylene hydrogen atom of the cavitand was also found.

In conclusion, the sidewise conformation was strongly preferred in the gas phase for both cations due to the increased coordination number and the smaller metal–oxygen distances. Additionally, solid-state structures were examined, and the methylene units of the cavitand were pointing out of the cavity. Sandwich and sidewise conformers were calculated, and two local minima for each cation were found and confirmed by normal-mode analysis. All of these minima were remarkably higher in energy than the minima described above. The calculated structures and energies are given in the Supporting Information.

### Conclusions

We have presented the synthesis of three new fluorescent 15-crown-5 ethers (5-7) and a fluorescent calix crown ether (9). The absorption and emission properties of these compounds were also characterised. The solid-state structures of 5 and 6 were presented as well as the solid-state structures of the potassium and sodium iodide complexes of 5. For the potassium complex, we found that the coumaryl carboxyl oxygen atom participated in the formation of a 2:2 complex. The association constants and the stoichiometries for complex formation in methanol of hosts 5 and 9 with sodium and potassium acetate were determined. Host 5 formed only weak complexes. Moreover, the potassium complex of 9 was also weak. For the sodium complex of 9, an association constant almost five times larger than that for 5 was found, which showed that the interplay of the cavitand and the crown ether was stabilising. The contribution of the attached resorcarene in complex formation was investigated by KS-DFT calculations. Herein, we have shown that a sidewise-like complex conformation was favoured for both cations.

### **Experimental Section**

General Procedure for Fluorescence Titrations: A solution of the host was prepared in methanol ( $c = 1.0 \times 10^{-5}$  M). Methanol 99.9%, A.C.S. spectrophotometric grade, was purchased from Aldrich and used as received. The host solution (1.0 mL) was transferred with a transfer pipette to a PTFE-stoppered 10×4 mm half-micro quartz cuvette from Hellma. When not in use the cuvette was stored in Caro's acid. Spectra were recorded five times and accumulated. Subsequently, small amounts of alkali-metal acetate (sodium and potassium acetate 99%, Merck) solutions in methanol (1- and 5µL steps of a 0.5 M solution) were added. This led to a host/guest ratio ranging from 1:50 to at least 1:1850 at saturation concentration. The cuvette was shaken for 1 min and was allowed to equilibrate for an additional 1 min. After each addition, spectra were recorded until complex saturation was reached. Care was taken to increase the reaction volume <6%. The excitation wavelength was 317 nm, and the monochromator bandwidth was set to 6 nm for the excitation and emission monochromator for host 9 and to 7 nm for the excitation and emission monochromator for host 5. All spectra were recorded with a Perkin-Elmer LS50B luminescence spectrometer and a Perkin-Elmer Lambda 40 UV/Vis spectrometer. Integrated fluorescence intensities were used for analysis. Integrations were carried out with the software SPEKWIN32<sup>[27]</sup> from the isoemissive point to the baseline (610 nm). This approach was used for the sake of precision caused by the slight blueshift.

**Details of Calculations:** All calculations reported herein were performed with the TURBOMOLE<sup>[28]</sup> programme suite. We choose the BP86 functional [includes B88<sup>[29]</sup> gradient correction for exchange, the VWN-(V)<sup>[30]</sup> correlation functional, and the P86<sup>[31]</sup> gradient correction for correlation] combined with the TZVP basis set (triple-zeta quality, polarized for all centres). To speed up the calculations, the charge-density fitting approximation<sup>[32]</sup> was used, with the auxiliary basis sets<sup>[32]</sup> from the programmes basis set database. For the structure optimizations and normal-mode analyses, we choose the grid-type "m5". In the structure optimizations, the threshold for energy changes ( $10^{-7}$  a.u.) and changes of the root-mean-square of the gradient ( $10^{-3}$  a.u.) were chosen to give energies

of equilibrium structures consistently to  $10^{-7}$  a.u. (the same accuracy as for the electronic energy). Harmonic vibrational wavenumbers were obtained from analytic second derivatives of the energy.

**2-(2-Hydroxyethoxy)ethyl Toluene-4-sulfonate (2):** To a solution of diethylene glycol (66.88 g, 630 mmol) and triethylamine (32.77 g, 324 mmol) in dichloromethane (150 mL), *p*-toluenesulfonyl chloride (30.61 g, 161 mmol) was added in portions at 0 °C. The solution was stirred at this temperature for 2 h. The organic layer was washed with saturated aqueous NaHCO<sub>3</sub> solution and dried with anhydrous MgSO<sub>4</sub>. After evaporation of the solvent, the crude product was purified by flash column chromatography (SiO<sub>2</sub>, dichloromethane/methanol, 98:2) to yield a colourless oil (23.59 g, 91 mmol, 56%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 27 °C):  $\delta$  = 7.78 (d, <sup>3</sup>J = 8.2 Hz, 2 H, ArH), 7.33 (d, <sup>3</sup>J = 8.2 Hz, 2 H, ArH), 4.17 (t, <sup>3</sup>J = 5.2 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>OTs), 3.67 (t, <sup>3</sup>J = 5.2 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>OTs), 3.64 (t, <sup>3</sup>J = 5.2 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>OH), 2.42 (s, 3 H, CH<sub>3</sub>), 1.95 (s, 1 H, OH) ppm.

7,8-Bis[2-(2-hydroxyethoxy)ethoxy]-4-methyl-2H-chromen-2-one (3): K<sub>2</sub>CO<sub>3</sub> (12.54 g, 91 mmol) was suspended in a solution of 7,8-dihydroxy-4-methylcoumarin (1, 7.92 g, 41 mmol) and tosylated glycol 2 (23.56 g, 91 mmol) in N.N-dimethylformamide (200 mL). The solution was stirred under argon at 80 °C for 20 h. The solvent was removed in vacuo, and the residue was dissolved in water (400 mL). The pH was adjusted to 3 with dilute HCl. The aqueous phase was extracted with dichloromethane  $(6 \times 130 \text{ mL})$ , and the combined organic phases were dried with anhydrous MgSO<sub>4</sub>. After evaporation of the solvent, the crude product was purified by flash column chromatography (Al<sub>2</sub>O<sub>3</sub>, dichloromethane/diethyl ether/ethanol, 6:6:1) to give a yellowish oil (8.76 g, 24 mmol, 58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 27 °C):  $\delta$  = 7.25 (d, <sup>3</sup>J = 8.8 Hz, 1 H, ArH), 6.85 (d,  ${}^{3}J$  = 8.8 Hz, 1 H, ArH), 6.11 (s, 1 H, C=CH), 4.23–4.28 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.87-3.89 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.83-3.84 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.69-3.71 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>OH), 3.63-3.65 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>OH), 3.45 (t,  ${}^{3}J$  = 6.3 Hz, 1 H, OH), 3.28 (t,  ${}^{3}J$  = 6.3 Hz, 1 H, OH), 2.35 (s, 3 H, CH<sub>3</sub>) ppm.  ${}^{13}C$  NMR  $(CDCl_3, 125 \text{ MHz}, 27 \text{ °C}): \delta = 160.6, 154.5, 152.6, 147.8, 135.5,$ 119.6, 115.1, 112.4, 109.8, 73.0, 72.8, 72.6, 70.2, 69.2, 68.9, 61.6, 61.5, 18.7 ppm. HRMS (ESI): m/z calcd. for  $C_{18}H_{24}O_8$  [M + H]<sup>+</sup> 369.15439; found 369.15495. IR (ATR):  $\tilde{v}$  = 3235, 3113, 3087, 2953, 2933, 2882, 2828, 1716, 1605, 1564, 1506, 1472, 1446, 1433, 1387, 1372, 1315, 1296, 1255, 1245, 1222, 1182, 1138, 1101, 1033, 1020, 997, 935, 904, 881, 858, 847, 841, 905, 785, 775, 722, 716, 663, 651, 607, 579, 589, 531 cm<sup>-1</sup>.

7,8-Bis{2-[2-(p-tolylsulfonyloxy)ethoxy]ethoxy}-4-methyl-2H-chromen-2-one (4): A solution of chromenone 3 (8.27 g, 22 mmol) and ethyldiisopropylamine (8.71 mL, 67 mmol) in dichloromethane (100 mL) was cooled to 0 °C. p-Toluenesulfonyl chloride (12.84 g, 67 mmol) was added rapidly in portions, and the mixture was stirred at room temperature for 48 h. Additional ethyldiisopropylamine (8.71 mL, 67 mmol) and p-toluenesulfonyl chloride (12.84 g, 67 mmol) were added at 0 °C, and the mixture was stirred at room temperature for 3 d. Water (100 mL) was added, and the pH was adjusted to 3 with dilute HCl. The aqueous phase was extracted with dichloromethane  $(3 \times 50 \text{ mL})$ , and the combined organic phases were washed with saturated aqueous NaHCO3 solution and dried with anhydrous MgSO<sub>4</sub>. The crude product was purified by flash column chromatography [(i) SiO<sub>2</sub>, dichloromethane/methanol,  $100:0 \rightarrow 99:1 \rightarrow 98:2$  and (ii) Al<sub>2</sub>O<sub>3</sub>, dichloromethane/methanol, 99:1] to give a yellowish oil (8.23 g, 12.2 mmol, 55%).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 27 °C):  $\delta$  = 7.70–7.73 (m, 4 H, ArH),

7.22–7.27 (m, 5 H, ArH), 6.84 (d,  ${}^{3}J$  = 8.8 Hz, 1 H, ArH), 6.09 (s, 1 H, C=CH), 4.08–4.16 (m, 8 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.70–3.81 (m, 8 H, OCH<sub>2</sub>CH<sub>2</sub>O), 2.37 (s, 6 H, CH<sub>3</sub>), 2.34 (s, 3 H, CH<sub>3</sub>) ppm.  ${}^{13}$ C NMR (CDC1<sub>3</sub>, 125 MHz, 27 °C):  $\delta$  = 160.5, 154.5, 152.6, 144.8,144.7, 135.6, 132.8, 129.8, 127.9, 119.6, 112.4, 109.8, 72.9, 70.6, 69.6, 69.5, 69.3, 68.9, 68.8, 68.6, 43.0, 21.6, 18.7 ppm. HRMS (ESI): *m*/*z* calcd. for C<sub>32</sub>H<sub>36</sub>O<sub>12</sub>S<sub>2</sub> [M + H]<sup>+</sup> 677.17209; found 677.17162. IR (ATR):  $\tilde{v}$  = 3090, 3064, 2946, 2924, 2873, 2363, 2328, 1723, 1601, 1563, 1507, 1448, 1384, 1352, 1296, 1244, 1174, 1136, 1094, 1038, 1016, 964, 919, 815, 772, 705, 690, 663, 582, 554 cm<sup>-1</sup>.

7-Benzyl-16-methyl-2,3,5,6,8,9,11,12-octahydrochromeno[7,8-b]-[1,4,10,13,7]tetraoxaazacyclopentadecin-18-one (5): In a solution of chromenone 4 (1.02 g, 150 mmol) and benzylamine (0.16 g, 150 mmol) in toluene (150 mL), Na<sub>2</sub>CO<sub>3</sub> (1.59 g, 14.99 mmol) was suspended. The mixture was refluxed under argon for 6 d. The reaction mixture was cooled to room temperature, and the solid was filtered off. Methanol (4 mL) was added to the filtrate, and the mixture was stirred at 50 °C for 40 min. The solvent was evaporated in vacuo, and the crude product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, ethyl acetate/cyclohexane, 45:55) to give a colourless solid (0.31 g, 0.7 mmol, 47%). The crown ether can be recrystallised from ethanol. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 27 °C):  $\delta$ = 7.17–7.25 (m, 6 H, ArH), 6.83 (d,  ${}^{3}J$  = 8.8 Hz, 1 H, ArH), 6.10 (s, 1 H, C=CH), 4.28 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 4.18 (m, 2 H, OCH<sub>2</sub>-CH<sub>2</sub>O), 3.91 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.83 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.72 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.69 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.66 (s, 2 H, PhCH<sub>2</sub>), 2.80–2.83 (m, 4 H, NCH<sub>2</sub>), 2.35 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 27 °C):  $\delta$  = 160.6, 155.0, 152.6, 148.0, 139.3, 135.2, 128.8, 128.1, 126.8, 119.5, 114.7, 112.2, 108.6, 73.1, 70.4, 70.1, 69.4, 69.0, 68.9, 60.6, 54.1, 53.9, 29.2, 18.7 ppm. HRMS (ESI): m/z calcd. for C<sub>25</sub>H<sub>29</sub>NO<sub>6</sub> [M + H]<sup>+</sup> 440.20676; found 440.20660. IR (ATR):  $\tilde{v}$  = 3084, 3061, 3026, 2961, 2867, 2247, 1725, 1646, 1604, 1562, 1507, 1495, 1448, 1439, 1384, 1367, 1360, 1297, 1241, 1203, 1177, 1129, 1096, 1045, 1028, 962, 911, 871, 849, 801, 772, 730, 699, 664, 646, 554 cm<sup>-1</sup>.

7-(Diphenylmethyl)-16-methyl-2,3,5,6,8,9,11,12-octahydrochromeno-[7,8-b][1,4,10,13,7]tetraoxaazacyclopentadecin-18-one (6): To a solution of chromenone 4 (1.02 g, 1.51 mmol) and aminodiphenylmethane (0.3 g, 1.64 mmol) in toluene (150 mL), Na<sub>2</sub>CO<sub>3</sub> (1.6 g, 151 mmol) was added. The mixture was refluxed for 8 d, and additional aminodiphenylmethane (0.16 g, 0.87 mmol) was added. The mixture was refluxed for 2 d, and the solid was filtered of. The filtrate was concentrated in vacuo, and the crude product was purified by flash column chromatography (SiO<sub>2</sub>, ethyl acetate/ cyclohexane 7:3) to give a colourless solid (667 mg, 1.29 mmol, 86%). The crown ether can be recrystallised from ethanol. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 27 °C):  $\delta$  = 7.11–7.43 (m, 11 H, ArH), 6.84 (d,  ${}^{3}J$  = 8.8 Hz, 1 H, ArH), 6.12 (s, 1 H, C=CH), 4.80 (s, 1 H, Bnz), 4.29 (dd,  ${}^{3}J = 4.4$  Hz,  ${}^{3}J = 4.4$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 4.17  $(dd, {}^{3}J = 3.8 Hz, {}^{3}J = 3.8 Hz, 2 H, OCH_{2}CH_{2}O), 3.86 (dd, {}^{3}J =$ 4.4 Hz,  ${}^{3}J$  = 4.4 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.78 (dd,  ${}^{3}J$  = 3.8 Hz,  ${}^{3}J$ = 3.8 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.74 (t,  ${}^{3}J$  = 5.6 Hz, 2 H, OCH<sub>2</sub> CH<sub>2</sub>O), 3.64 (t,  ${}^{3}J$  = 6.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 2.80–2.90 (m, 4 H, NCH<sub>2</sub>), 2.36 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 27 °C):  $\delta$  = 160.7, 155.0, 152.7, 148.0, 142.6, 135.2, 128.4, 128.3, 126.9, 119.5, 114.8, 112.3, 108.7, 73.1, 71.3, 70.2, 70.0, 69.3, 69.0, 52.2, 52.0, 18.7 ppm. HRMS (ESI): *m/z* calcd. for C<sub>31</sub>H<sub>33</sub>NO<sub>6</sub> [M + H]<sup>+</sup> 516.23806; found 516.23808. IR (ATR):  $\tilde{v} = 3024, 2925,$ 2865, 1724, 1602, 1562, 1502, 1448, 1383, 1295, 1240, 1126, 1093,  $1024, 907, 850, 727, 705 \text{ cm}^{-1}$ .

16-Methyl-2,3,5,6,8,9,11,12-octahydrochromeno[7,8-*b*][1,4,10,13,7]tetraoxaazacyclopentadecin-18-one (7): To a solution of crown ether 6 (72 mg, 0.14 mmol) in ethanol (40 mL), Pd/C (10%, 68 mg) was added. Hydrogen was discharged into the solution for 25 min, and the solution was heated to 60 °C for 2 h. The reaction was monitored by MALDI-ToF. After complete conversion, the catalyst was filtered off, and the solvent was removed in vacuo. The crude product was filtered through basic alumina (CHCl<sub>3</sub>/MeOH, 1:1) and purified by flash column chromatography (Al<sub>2</sub>O<sub>3</sub>, CHCl<sub>3</sub>/MeOH, 98:2) to give a colourless solid (25 mg, 0.07 mmol, 50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 27 °C):  $\delta$  = 7.24 (d, <sup>3</sup>J = 8.8 Hz, 1 H, ArH), 6.84 (d,  ${}^{3}J$  = 8.8 Hz, 1 H, ArH), 6.11 (s, 1 H, C=CH), 4.33 (t,  ${}^{3}J$ = 3.8 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 4.17 (t,  ${}^{3}J$  = 3.8 Hz, 2 H, OCH<sub>2</sub>-CH<sub>2</sub>O), 3.88 (t,  ${}^{3}J$  = 4.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.78 (t,  ${}^{3}J$  = 4.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.73 (t,  ${}^{3}J$  = 4.7 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O),  $3.67 (t, {}^{3}J = 4.7 Hz, 2 H, OCH_{2}CH_{2}O), 2.88-2.80 (m, 4 H, NCH_{2}),$ 2.36 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 27 °C):  $\delta$  = 160.7, 154.7, 152.8, 148.0, 135.0, 119.4, 114.7, 112.2, 108.3, 73.2, 69.8, 69.6, 68.5, 68.2, 68.1, 48.3, 47.8, 18.8 ppm. HRMS (ESI): m/z calcd. for C<sub>18</sub>H<sub>24</sub>NO<sub>6</sub> [M + H]<sup>+</sup> 350.15981; found 350.15959. IR (ATR):  $\tilde{v} = 3317, 2926, 2871, 1728, 1604, 1508, 1449, 1385, 1298,$  $1098 \text{ cm}^{-1}$ .

Cavitand 9: A mixture of aza-crown ether 7 (18 mg, 0.05 mmol), cavitand 8<sup>[10]</sup> (76 mg, 0.06 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (43 mg, 0.13 mmol) in dry N,N-dimethylformamide (6 mL) was stirred under argon at 80 °C for 2 h. The solvent was removed in vacuo, and the precipitate was dissolved in chloroform and washed with water. The aqueous phase was extracted twice with chloroform, and the combined organic phases were concentrated. The crude product was purified by flash column chromatography (Al<sub>2</sub>O<sub>3</sub>, CHCl<sub>3</sub>/MeOH, 99:1) to give the calix crown ether as a colourless solid (45 mg, 0.03 mmol, 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 27 °C):  $\delta$  = 7.26 (d, <sup>3</sup>J = 8.8 Hz, 1 H, ArH, coumarin), 7.09 (s, 3 H, ArH), 7.04 (s, 1 H, ArH), 6.83 (d,  ${}^{3}J$  = 8.8 Hz, 1 H, ArH, coumarin), 6.46 (s, 1 H, ArH), 6.43 (s, 2 H, ArH), 6.12 (s, 1 H, CH, coumarin), 5.80 (d, <sup>3</sup>J = 7.5 Hz, 2 H, OCH<sub>2</sub>O), 5.72 (d,  ${}^{3}J$  = 7.5 Hz, 2 H, OCH<sub>2</sub>O), 4.70  $(t, {}^{3}J = 8.2 \text{ Hz}, 4 \text{ H}, \text{ArCHAr}), 4.43 (d, {}^{3}J = 6.9 \text{ Hz}, 2 \text{ H}, \text{OCH}_{2}\text{O}),$ 4.30 (d,  ${}^{3}J = 6.9$  Hz, 2 H, OCH<sub>2</sub>O), 4.29 (t,  ${}^{3}J = 4.6$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 4.17 (t,  ${}^{3}J$  = 3.8 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.89 (t,  ${}^{3}J$ = 3.5 Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.82 (t,  ${}^{3}J$  = 4.1 Hz, 2 H, OCH<sub>2</sub>-CH<sub>2</sub>O), 3.73 (t,  ${}^{3}J$  = 5.4, 4 H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.47 (s, 2 H, ArCH<sub>2</sub>), 2.84-2.74 (m, 4 H, NCH2CH2), 2.36 (s, 3 H, CH3, coumarin), 2.28-2.08 (m, 8 H, CHCH<sub>2</sub>), 1.48–1.16 (m, 72 H, CH<sub>2</sub>), 0.86 (t,  ${}^{3}J$  = 6.9 Hz, 12 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 27 °C):  $\delta$ = 160.6, 155.0, 1554.8, 154.7, 154.3, 152.6, 148.0, 138.4, 138.3, 138.1, 138.0, 135.2, 123.7, 120.6, 120.5, 119.7, 119.6, 116.5, 116.3, 114.8, 112.3, 108.6, 99.6, 99.5, 73.1, 70.2, 69.8, 69.0, 68.8, 53.0, 52.9, 48.6, 36.6, 36.3, 31.9, 30.1, 29.9, 29.8, 29.7, 29.4, 27.9, 27.87, 22.7, 18.8, 14.1 ppm. HRMS (ESI): m/z calcd. for C<sub>95</sub>H<sub>135</sub>NO<sub>14</sub> [M + H]<sup>+</sup> 1514.99553; found 1514.99984. IR (ATR):  $\tilde{v} = 2920, 2851,$ 1724, 1605, 1491, 1456, 1296, 1094, 1020, 965 cm<sup>-1</sup>.

**Crystal Structure Determination:** CCDC-681208, -681209, -681210 and -681211 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. **Crystal Data for 5:** C<sub>25</sub>H<sub>29</sub>NO<sub>6</sub>, M = 439.49, triclinic, a = 8.6458(2), b = 9.2239(2), c = 14.9930(3) Å, a =85.0614(11),  $\beta = 79.7561(12)$ ,  $\gamma = 73.8471(12)^\circ$ , V = 1129.31(4) Å<sup>3</sup>, T = 200 K, space group  $P\overline{1}$ , Z = 2,  $\mu$ (Mo- $K_a$ ) = 0.092 mm<sup>-1</sup>, 28810 reflections measured, 5152 unique ( $R_{int} = 0.030$ ), which were used in all calculations. The final *R* values were R(F) = 0.0439 for 4181 reflections with  $I > 2\sigma I$  and  $wR(F^2) = 0.1250$  for all data. **Crystal Data for the NaI Complex of 5:** C<sub>29</sub>H<sub>41</sub>INNaO<sub>8</sub>, M = 681.52, triclinic, a = 10.2040(9), b = 11.2107(4), c = 15.6238(9) Å, a =69.016(4),  $\beta = 81.114(6)$ ,  $\gamma = 67.451(5)^\circ$ , V = 1540.86(17) Å<sup>3</sup>, T =

100 K, space group  $P\bar{1}$ , Z = 2,  $\mu$ (Mo- $K_a$ ) = 1.101 mm<sup>-1</sup>, 54491 reflections measured, 7086 unique ( $R_{int} = 0.0529$ ), which were used in all calculations. The final R values were R(F) = 0.0277 for 6111 reflections with  $I > 2\sigma I$  and  $wR(F^2) = 0.0500$  for all data. Crystal Data for the KI Complex of 5:  $C_{54}H_{70}I_2K_2N_2O_{14}$ , M = 1303.12, triclinic, a = 9.4336(2), b = 10.4674(2), c = 16.6494(3) Å, a =96.5195(10),  $\beta = 102.1135(10)$ ,  $\gamma = 114.9612(10)^{\circ}$ , V =1418.91(5) Å<sup>3</sup>, T = 100 K, space group  $P\bar{1}$ , Z = 1,  $\mu$ (Mo- $K_{\alpha}$ ) = 1.319 mm<sup>-1</sup>, 48599 reflections measured, 8279 unique ( $R_{int}$  = 0.035), which were used in all calculations. The final R values were R(F) = 0.0418 for 7143 reflections with  $I > 2\sigma I$  and  $wR(F^2) =$ 0.1029 for all data. Crystal Data for 6:  $C_{31}H_{33}NO_6$ , M = 515.58, triclinic, a = 9.1103(3), b = 10.5503(3), c = 14.7398(4) Å, a =80.423(2),  $\beta = 75.997(2)$ ,  $\gamma = 84.560(2)^\circ$ ,  $V = 1353.27(7) \text{ Å}^3$ , T =200 K, space group  $P\bar{1}$ , Z = 2,  $\mu$ (Mo- $K_{\alpha}$ ) = 0.087 mm<sup>-1</sup>, 26984 reflections measured, 4748 unique ( $R_{int} = 0.055$ ), which were used in all calculations. The final R values were R(F) = 0.0672 for 3240 reflections with  $I > 2\sigma I$  and  $wR(F^2) = 0.2135$  for all data.

**Supporting Information** (see also the footnote on the first page of this article): Absorption and emission spectra of compounds 6 and 7, all titration plots, Job plots, and cartesian coordinates for all calculated structures.

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