Tetrahedron 65 (2009) 5936–5944

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Photo, proton and metal ion responsive wide-rim acridane substituted calix[4]arenes

L. Grubert, H. Hennig, W. Abraham *

Humboldt-Universität zu Berlin, Institute of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany

ARTICLE INFO

Article history:
Received 7 May 2009
Received in revised form 26 May 2009
Accepted 28 May 2009
Available online 6 June 2009

Keywords:
Calixarene
Acridinium salt
Acridanes
Photoswitch
Cation receptor

ABSTRACT

Calix[4]arenes bearing acridinium and acridane substituents at the wide rim and a short glycol chain and two OH-groups at the narrow rim have been prepared. The interaction with alkali metal ions can be identified with the naked eye by the change in solution color arising from deprotonation of the OH-groups. Unlike the acridane calixarenes, the acridinium-substituted calixarene-crown-4 binds sodium ions. Due to the photoheterolysis of the acridane, calixarene sodium ions are picked up from the acetonitrile solution due to the formation of acridinium calixarene.

1. Introduction

Calixarenes[1] belong to the important category of building blocks for supramolecular assemblies[2] and molecular recognition, and are widely used as receptors for inorganic and organic cations,[3,4] anions,[5] and also neutral compounds.[6] *endo*-Cavity inclusion complexes with organic cations such as quaternary ammonium ions and the iminium and tropylium ions are assumed to be favored by cation-π-interaction and π-stacking.[7]

The introduction of switches into the calixarenes has attracted interest as a means of obtaining gated hosts.[8,9] A photoswitchable resorc[4]arene based on [4+4]cycloaddition of anthracene has been studied recently with the aid of single-molecule force spectroscopy.[10] We became interested in introducing a photoswitch into calix[4]arenes that reversibly switches between electron deficient and electron rich groups. The system 9-alkoxy acridane (9,10-dihydroacridine), which undergoes photoheterolysis in the photoexcited state to give an acridinium salt, matches these requirements.[11] The reset of the system proceeds in protic solvents by attack of the alkoxide on the acridinium ion.[11] Recently, we have synthesized calix[4]arenes with such substituents having a *1,3-alternate* conformation and glycol bridges at the aryl units, which carry the switching unit.[11] Additionally we described calix[4]arenes with four alkylated OH-groups having a *pinched-cone* conformation.[11]

Earlier investigations have shown that calix[4]arenes with four alkyloxy substituents at the narrower rim are not able to complex organic cations,[7] and therefore we sought to obtain calix[4]arenes with two alkoxy and two hydroxyl groups at the narrower rim. Herein, we report the synthesis and conformation of calix[4]arenes substituted at the wider rim with acridane and acridinium units and OH-groups at the same aryl units. We also present calix[4]arenes with a short glycol bridge exhibiting a *cone* conformation.

The *p*-hydroxyphenylacridinium subunit within the calixarene framework offers the possibility of color changes by deprotonation of the OH-groups due to the presence of a quinonoid structure. We examined the influence of bases on this process and also performed photochemical experiments to explore the reversibility of the switching process. We also present some complexation results.

2. Results and discussion

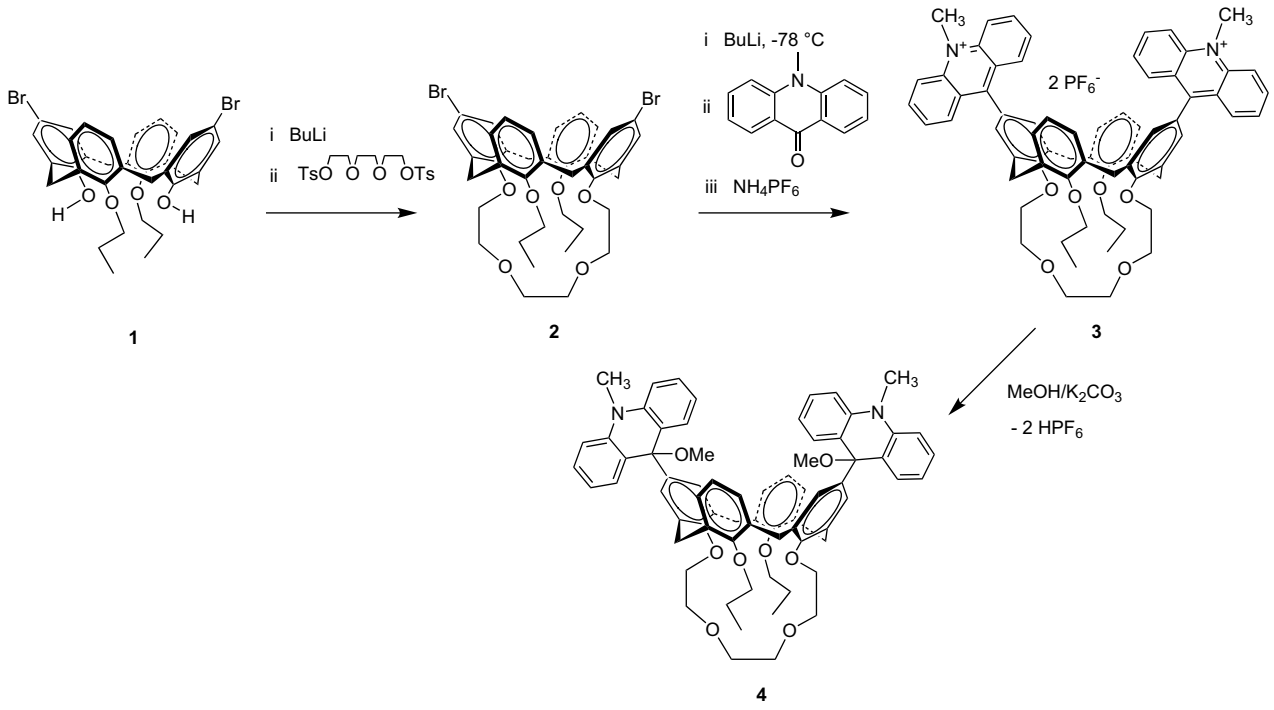
2.1. Synthesis

In contrast to results obtained with other calix-crowns,[11] the incorporation of a crown-4 at the narrow rim results in the *cone* conformation of the dibromo-compound **2** and, consequently, the yellow diacridinium compound **3** (see Scheme 1). Reaction of the acridinium ion with methanol in the presence of a base easily affords the corresponding colorless acridane compound **4**.

In order to maintain two hydroxyl groups at the narrow rim the *cone*-calix[4]arenes **7** and **8** were synthesized using the protected derivative **5** (Scheme 2).

* Corresponding author. Tel.: +49 30 2093 7348; fax: +49 30 2093 7266.
E-mail address: abraham@chemie.hu-berlin.de (W. Abraham).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.05.082



Scheme 1. Synthesis of compounds **3** and **4**.

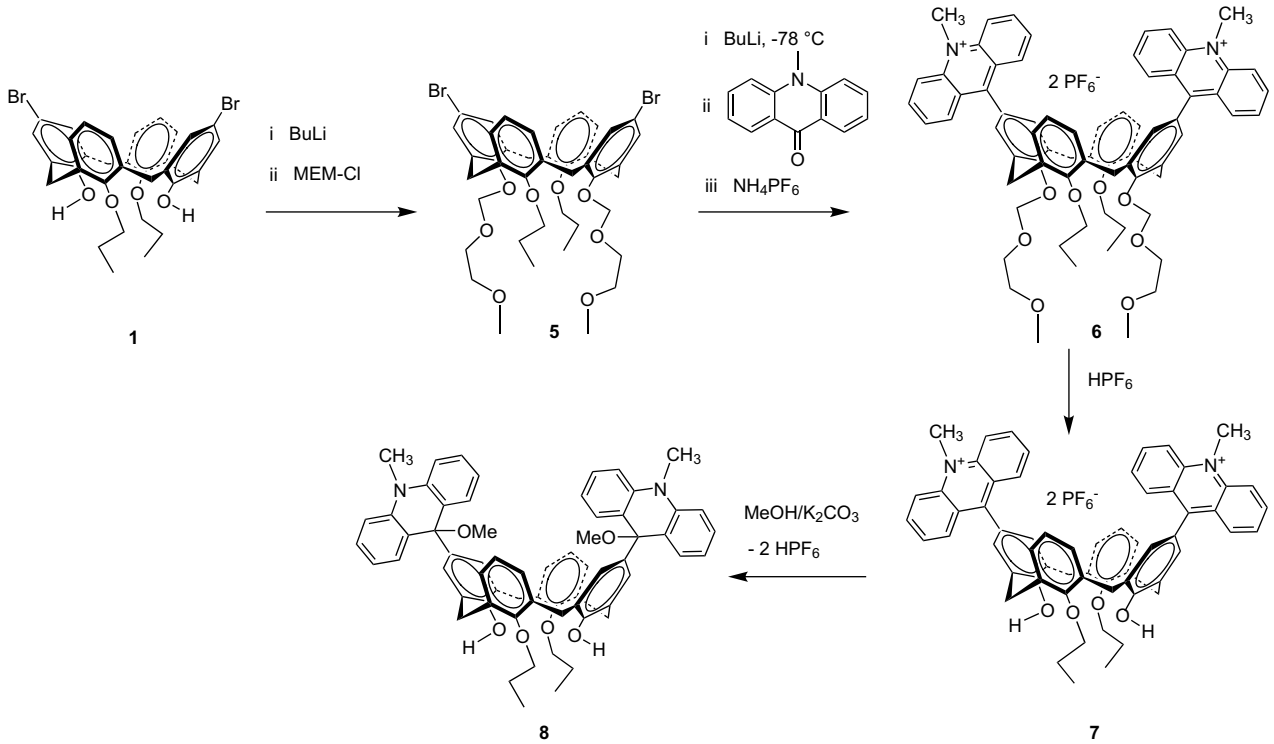
Compound **11** was synthesized as a model for the acridinium unit present in **7** (Scheme 3).

2.2. Conformation

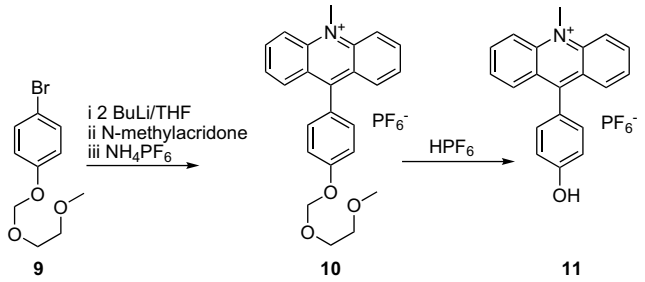
The calixarenes **2**–**4** exhibit a *pinched-cone* conformation in the solid state (see Fig. 1). Compounds **3** and **4** are also assumed to adopt a *pinched-cone* conformation in solution since the *axial* and *equatorial* protons of the methylene bridges resonate with a difference of 0.9 ppm.[7]

Compound **8** resembles the narrow rim fourfold substituted derivatives **2**–**4** (see Fig. 2).

Also, in the case of **8**, the difference of the resonances of the *equatorial* and *axial* protons of the methylene bridges is 1 ppm in $CDCl_3$ solution. We were not able to crystallize the acridinium-substituted derivative **7**. However, according to the difference of



Scheme 2. Synthesis of compound **8**.



Scheme 3. Synthesis of compound **11**.

0.82 ppm in the resonances of the methylene protons, we can assign a distorted *cone* conformation.

The crystal structure of **3** reveals that the torsion angle between the acridinium unit and the aryl group of the calixarene is 75°. Because one part of the acridinium unit points toward the cavity of the calixarenes, the proton resonances are upfield shifted compared with the resonance of protons, which are outside (see Scheme 4). Obviously, a rotation of the acridinium unit against the calixarene skeleton does not occur on the NMR time scale. A closer look at the monosubstituted calix[4]arene **12**[11] at higher resolution (600 MHz NMR) reveals that this derivative also exhibits a double set of proton signals (Scheme 4). Indeed, the split is much larger if two acridinium groups are present on the calixarene skeleton.

As acridinium compounds, the acridane calixarenes **4** and **8** exhibit a large 99° torsion angle between the acridane moiety and the aryl group of the calixarene skeleton (see Figs. 1 and 2). In these cases, however, only one set of proton resonances corresponding to the acridane units appears in the NMR spectra. Accordingly, a rapid rotation around the bond connecting the two groups in solution can be assumed.

2.3. Deprotonation of compounds 7 and 11

p-Hydroxyphenylacridinium ions such as **7** and **11** are both an acid and a pseudo acid (see Scheme 5).

A quinonoid system such as **11q** would be formed by dissociation of the ion pair giving rise to a bathochromic shift of the longest wavelength absorption band of the parent acridinium system (see Fig. 3). In fact, the addition of LiOH is accompanied by a dramatic shift in the visible absorption (λ_{max}=680 nm (**11**) and 720 nm (**7**), see Figs. 3 and 4). The reaction was performed by successive additions of aliquots of 0.01 M LiOH in water to 2.5 mL of an acetonitrile solution of **7** or **11**. Therefore, in acetonitrile solution a rather strong coordination of the cation to the phenolate unit is expected (**11s** in Scheme 5).

Surprisingly, a second absorption band around 500 nm was observed with other bases such as Et_4NOH, NaOH, KOH, and CsOH (see Fig. 5).

Qualitatively, the model compound **11** and the calixarene **7** show similar behavior. Only the ratio of the two long-wavelength absorption bands is different. Obviously, the observed color

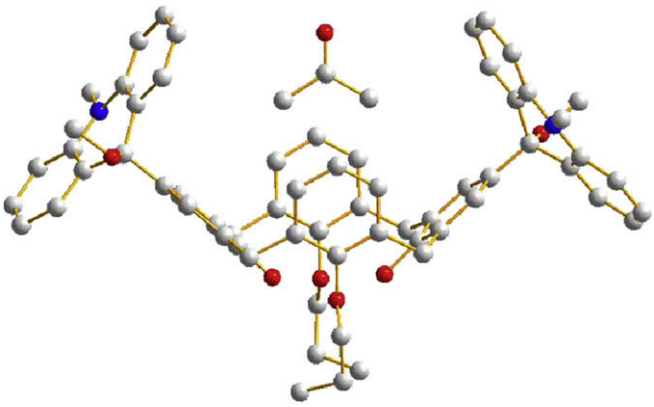
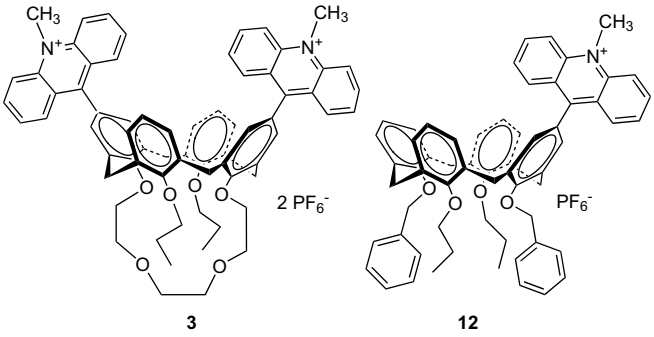
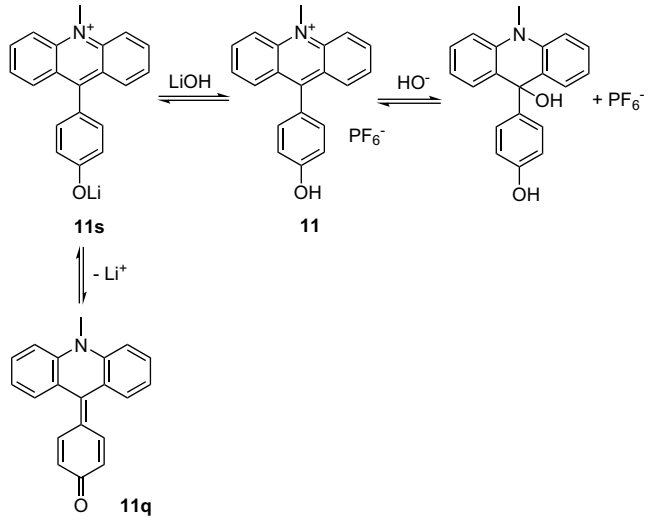


Figure 2. Structure of **8** with acetone as guest.



Scheme 4.



Scheme 5. Acid–base behavior of compound **11**.

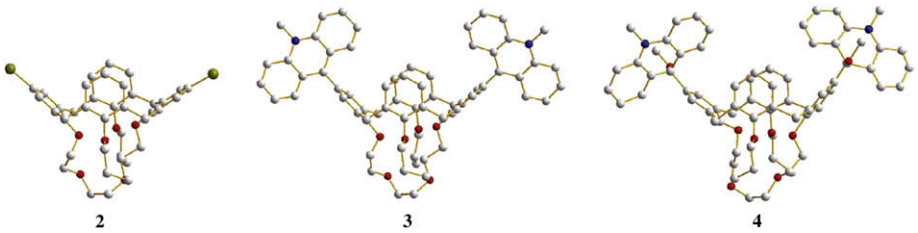


Figure 1. Crystal structures of calixarenes **2**–**4**.

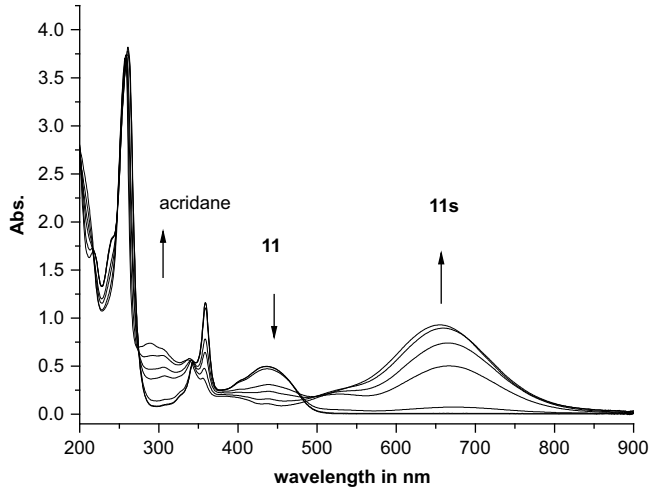


Figure 3. Absorption spectra of compound **11** (6.6×10^{-5} M in MeCN solution) recorded after addition of LiOH (0, 3.2×10^{-4}, 5.6×10^{-4}, 6.4×10^{-4}, 8×10^{-4}, 1.2×10^{-3}, 1.3×10^{-3} M).

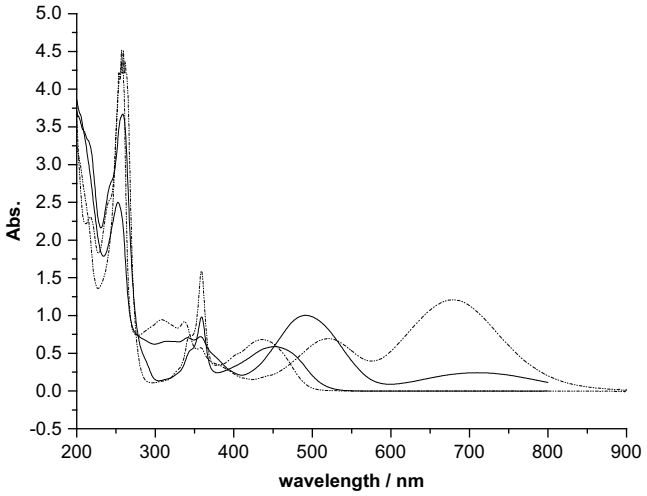


Figure 5. UV–vis spectra of compounds **7** — (MeCN, 4.8×10^{-5} M) and **11** - - (MeCN, 9.1×10^{-5} M) before and after addition of KOH (10 μL, 0.1 M=4×10^{-4} M final concentration).

changes are not a property of the calixarene scaffold with acridinium substituents, but, rather, are inherent to the *p*-hydroxyphenylacridinium moiety. By participation of the acridinium unit at the calixarene framework, the reaction with a nucleophile is much slower. The blue color of **11** is not stable due to the reaction of the primary formed deprotonated acridinium salt with nucleophiles such as OH^- or EtOH present in the solution, which forms the colorless acridane compound (see Scheme 5), but a stable blue compound was formed from calixarene **7** and LiOH (Fig. 4). We were able to record the NMR spectrum of the blue compound and found that it does not match the expected spectrum of a quinonoid compound. Both the resonances of the *N*-methyl group and of the aryl protons of the acridinium moiety are only slightly upfield shifted as compared to the original acridinium compound (see Scheme 6).

The presence of Li^+ is necessary to form the species with the uniform UV–vis absorption band at 715 nm. The base di-*iso*-propylethylamine is too weak to deprotonate the OH-groups, and no changes of the absorption spectrum of **7** can be observed. However, the addition of neutral LiBr leads to the formation of the blue salt (see Fig. 1, Supplementary data). Thus, Li ions must be strongly coordinated at the oxygen atoms at the narrow rim of the calixarene. Consequently, ^{6}Li NMR spectroscopy of the blue solution formed by addition of LiOH reveals that the Li-resonance is low-field shifted (1.6 ppm) in comparison to LiBr (0 ppm). The acetonitrile solution of Li-phenolate exhibits a Li-resonance at 2.2 ppm. Accordingly, the blue color is attributed to the increased electron donor (Li-phenolate)/acceptor (acridinium moiety) interaction. The phenolate acridinium units of the calixarene are more planar than in the parent acridinium ions. In fact, unlike the parent acridinium calixarene the deprotonated salt exhibits only a single set of proton resonances for the acridinium protons (compare Fig. 2, Supplementary data).

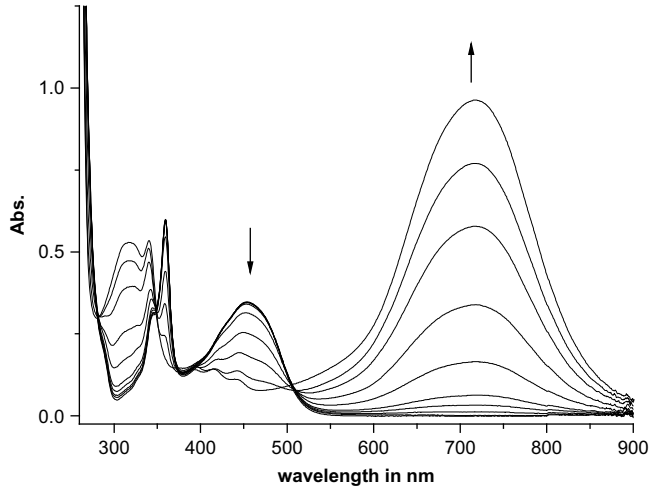


Figure 4. Absorption spectra of compound **7** (2.4×10^{-5} M in MeCN solution) recorded after successive addition of LiOH (4×10^{-6}, 1.6×10^{-5}, 2.4×10^{-5}, 3.2×10^{-5}, 4×10^{-5}, 4.8×10^{-5}, 5.6×10^{-5}, 6.4×10^{-5} M).

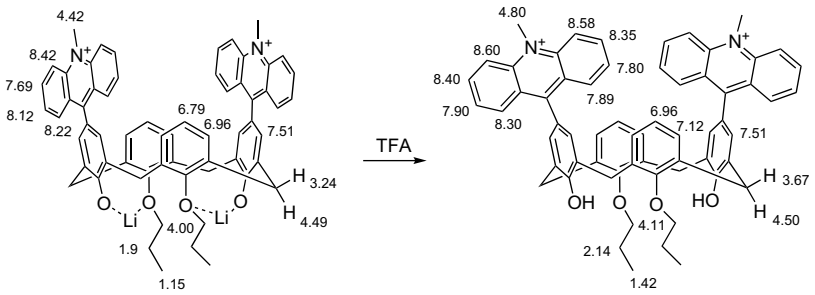
The absorption spectrum of the deprotonated species is strongly influenced by the cation of the base. With tetraethylammonium hydroxide a shorter wavelength absorption band at 490 nm is formed instead of the longer wavelength absorption band described above (see Fig. 6).

The addition of other hydroxide bases results in the formation of two species represented by the two absorption bands at 490 and 720 nm. The ratio of the two species depends on the cation used. The larger the cation, the stronger is the absorption band at 490 nm. Therefore, the nature of the cation can be identified with the naked eye by the solution color (see Fig. 7).

Using CsOH, a red solid could be separated, which was soluble in chloroform and insoluble in acetonitrile. By atomic absorption spectroscopy, no Cs ions could be detected. Therefore, we assume that this species and accordingly the absorption band at 490 nm are attributed to the quinonoid structure of **7** (Scheme 7).

Unfortunately the NMR spectrum of the solid in $CDCl_3$ solution exhibits only very broad signals, which could not be used to assign specific proton resonances of the quinonoid structure. But the position of the signals does not contradict the quinonoid structure (compare Fig. 3, Supplementary data). The NMR spectrum of the solution recorded after 6 days matches that of the corresponding acridane (Supplementary data). We were not able to crystallize the red compound.

The nucleophile OH^- attacks the deprotonated species and forms the colorless acridane, which is assignable by the absorption band at 285 nm. This reaction seems to start from the salt-like deprotonated species, because the absorption band at 715 nm is more rapidly lost than that at 490 nm (see Fig. 4, Supplementary data). However, in the case of the Li-salt, this reaction is very slow.



Scheme 6. Changes of proton resonances on going from the salt formed by addition of LiOH to the parent acridinium compound **7** by addition of trifluoroacetic acid (TFA).

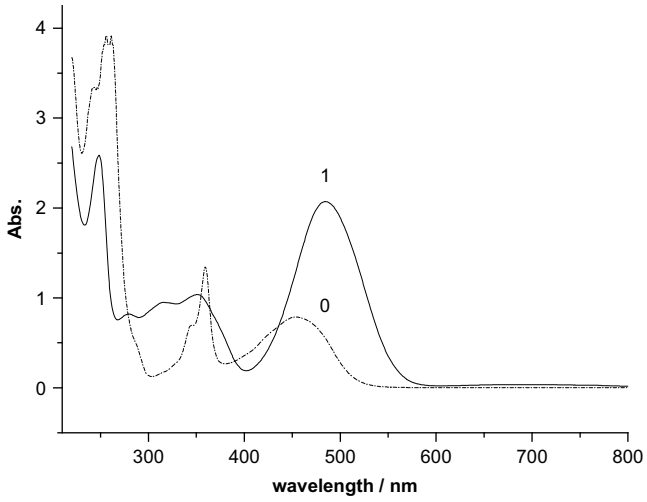
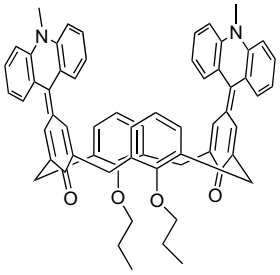


Figure 6. UV–vis spectra of **7** (0) (3.8×10^{-5} M) and absorption spectrum recorded after addition of Et_4NOH (1) (4×10^{-4} M).

2.4. Complexation studies

The small crown moiety at the narrow rim of compounds **2**–**4** should bind small inorganic cations such as Li^+ and Na^+. Complexation studies using isothermal titration calorimetry (ITC) (Fig. 5, Supplementary data) revealed that compound **2** forms complexes with Li^+ ($K=1.23\times10^5\pm1.49\times10^4$ M^{-1}, $\Delta H=-5.16\pm0.09$ kcal mol^{-1}; $\Delta S=5.9$ cal K^{-1} mol^{-1}) and Na^+ ($K=6.73\times10^5\pm1\times10^5$ M^{-1}, $\Delta H=-10.41\pm1.25$ kcal mol^{-1}; $\Delta S=-8.3$ cal K^{-1} mol^{-1}) in acetonitrile solution. In contrast, the acridane and acridinium-substituted calixarenes **3** and **4** do not bind lithium ions. It is known that small changes in substituents at the wide or narrow rim can result in dramatic changes in binding properties.[12] Surprisingly, sodium cations are bound by the acridinium calixarene **3** and not by the corresponding acridane. The association constant of **3**/Na^+ ($9.46\times10^3\pm1.41\times10^3$ M^{-2}, $\Delta H=-7.57\pm1.34\times10$ kcal M^{-1}; $\Delta S=-7.2$ cal K^{-1} mol^{-1}) is considerably smaller than that of **2**/Na^+. Unlike the 1:1 stoichiometry of **2**/Na^+ two host molecules **3** bind one sodium ion. In all cases the complex formation is enthalpy driven.

Figure 7. Compound **7** in acetonitrile solution (4×10^{-5} M) and addition of several bases (6.6×10-5 M); from left to right: 1: without base, 2: LiOH, 3: NaOH, 4: KOH, 5: RbOH, 6: CsOH, 7: Et_4NOH.



Scheme 7. Deprotonated structure proposed for the species with the visible absorption at 490 nm.

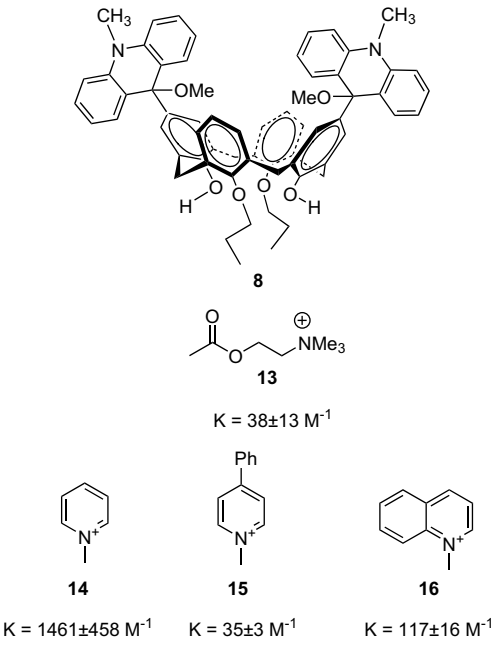
The lack of binding of Na^+ by **4** is most interesting because, in principle, the non-binding state (acridane calixarene) can be transformed into the binding state (acridinium calixarene) by photoheterolysis (see below).

Calixarenes in their *cone* conformation are able to bind organic cations in the π-basic cavity in nonpolar solvents.[5,7] Also the host **8** bearing two acridane units at the upper rim forms complexes with guests **13**–**16** in $CDCl_3$ solution with relatively small complexation constants (Scheme 8). In contrast, the corresponding acridinium-substituted calixarene does not bind these guests.

The crystal structure of **8** (Fig. 2) reveals a *pinched-cone* conformation with a cavity large enough to include guests such as **13**–**16**. Complexation constants were determined with the help of NMR titration (see Scheme 8). Because the strongest complexation induced shifts of the proton signals, the methyl groups of the guest, along with the ammonium or the iminium part of the organic cations, appear to point into the cavity.

2.5. Photoreaction

Acridanes such as **4** and **8** represent photochromic compounds because upon photoexcitation in solutions containing alcohols, acridinium methoxides formation occurs.[13] The formed alkoxide ion attacks the formed acridinium ion to restore the acridane. One percent methanol is sufficient to obtain a reversible reaction. The lifetime of the acridinium ion depends on the concentration and the nature of the alcohols and ranges between seconds and hours. Two species with lifetimes of 82 s and 785 s (ratio 2:1, Supplementary data) were observed in acetonitrile solution of **4** containing 1% methanol. A solution of **4** or **8** in acetonitrile/ethanol 4:1



Scheme 8. Guests used for complexation with host **8**.

was irradiated with a mercury lamp equipped with filter glass (λ>300 nm) for several seconds. The conversion was followed by UV–vis spectroscopy. The presence of isosbestic points indicated that the photochemical process is a unimolecular conversion (see Fig. 8). Both acridane moieties of **4** are involved. With high light intensities (HBO 500, OSRAM), more than 70% turnover is observed upon 40 s irradiation time. In general, the quantum yield of the acridane photolysis is in the range of 0.5.[13]

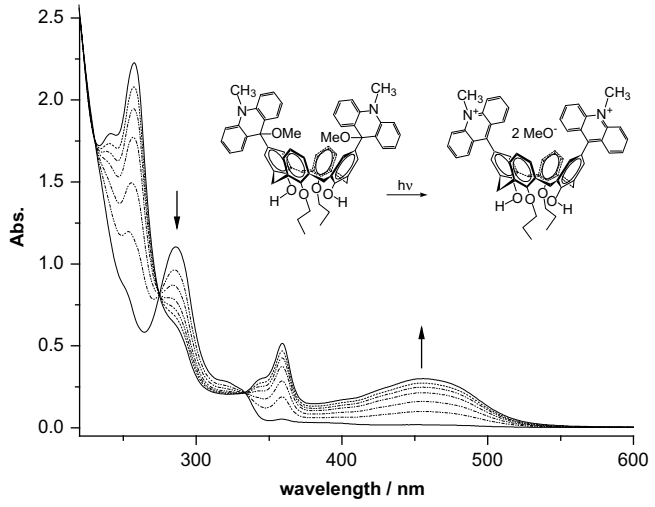


Figure 8. UV–vis spectra recorded after consecutive irradiation of a solution of compound **4** (acetonitrile/ethanol 4:1, 5.4×10^{-5} M) with light of 313 nm wavelength (3…10 s).

The kinetic trace recorded at 360 nm follows a biexponential decay (Supplementary data) with two species of the lifetime 256 s and 2250 s. The switching cycle can be repeated at least 10 times without any fading of the starting compound. Because the starting calixarene does not bind sodium ions, due to the photoreaction these ions were picked up from the solution and released during the thermal back reaction.

The photolysis of compound **8** generates, besides the acridinium compounds, a methoxide ion, which could deprotonate the OH-groups to give the quinonoid neutral compounds. But, for a successful switching cycle the presence of at least 1% alcohol is necessary (see above). In the presence of any alcohol, the back reaction giving the acridane is much faster than the formation of the quinonoid compound. Accordingly also in these cases a uniform photoreaction is observed (see Fig. 9).

Because acridinium-substituted calixarenes are formed due to the photolysis, complexes of the acridane hosts with guests would be destroyed.

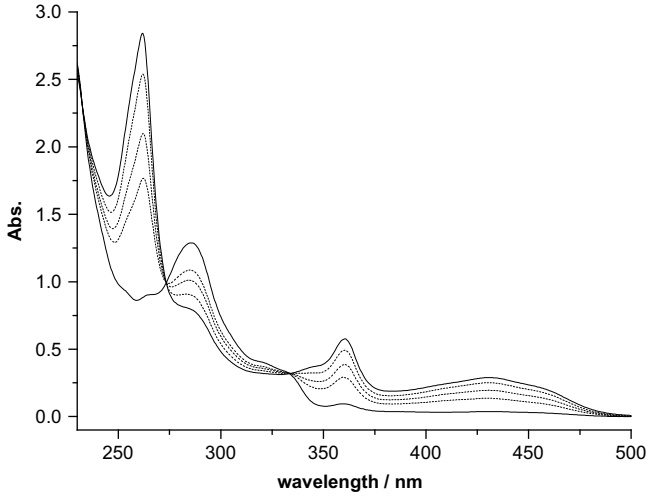


Figure 9. UV–vis absorption spectra recorded after consecutive irradiation (313 nm: 0, 0,5, 1, 2, 4, 10, 20 min) of the calixarene **8** in acetonitrile/EtOH solution (4:1, 3.0×10^{-5} M).

3. Conclusions

Tetra- and dialkylated calix[4]arenes exhibiting the *cone* conformation and bearing acridinium and acridane substituents at the wide rim were studied regarding their response to photoexcitation. All compounds with acridane groups at the wider rim underwent photoheterolysis to give the corresponding acridinium methoxides, which reacted back to the acridane moieties in a thermal reaction. The acridane calixarenes represent photochromic systems. Only the acridinium-substituted calix crown-4 binds sodium ions. Therefore, due to photolysis of acridane substituted calix crown-4, Na^+ ions are picked up from the solution. Only the calixarene having *p*-hydroxyphenylacridane subunits within the calixarene framework are able to bind organic cations in chloroform solution with moderate complexation constants.

The deprotonation of the *p*-hydroxyphenylacridinium subunits of the calixarene results in two different species with UV–vis absorption bands at 490 and 715 nm, respectively. The ratio of these two species depends strongly on the cation of the base. Alkali cations can be identified with the naked eye by the color of the solution.

4. Experimental part

4.1. General

Commercially available chemicals and solvents (UVASOL, Merck) were used as received unless otherwise noted; solvents were dried according to standard procedures. Column chromatographies (CC) were carried out on 200 mesh silica gel (Merck). Melting points (mp) were determined with a Boetius heating microscope. ESI mass spectroscopy was carried out on LTQ FT, Finnigan MAT (Bremen, Germany) equipped with an electrospray ion

source (Thermo Electron). NMR spectra were recorded on a Bruker DPX 300 (300 MHz), a Bruker Advance 400 (400 MHz), and a Bruker AMX 600 (600 MHz) instruments. The proton signals were attributed to the different subunits with the aid of two-dimensional NMR spectroscopy, such as C–H-COSY, H–H-COSY, and ROESY. UV–vis measurements were performed with a Shimadzu UV 2101 PC spectrometer. Irradiation of the calixarene solutions was carried out with a conventional mercury arc (HBO 500 or HBO 200) combined with a cut-off filter of 300 nm or metal interference filters. The thermal reactions were followed by UV-vis spectroscopy using the kinetics-program of the spectrometer. The absorption decay curves at the wavelength of 360 nm were analyzed by nonlinear regression fits (Origin 6.0, Microcal Software, Inc.). Transient absorption spectra between 340 and 500 nm were recorded with the UV 2101 PC spectrometer using the fastest scan mode.

4.2. Determination of stability constants

4.2.1. Binding constants

Binding studies were carried out by means of ^{1}H NMR titrations of guest solutions at usually at a concentration of 1 mmol. Increasing amounts of the host were added up to host/guest of 50:1 to 200:1 ratio (20–80% saturation). The temperature was 298 K. Upfield shifts of the resonances of different protons of the guest were monitored in order to calculate binding constants K and the upfield shift of the guests fully saturated by the host δ_{GC}.

Titration data points $\delta=f(R)$ were fitted to the equation[14]

$$\delta = \delta_G - (\Delta\delta/2)\left(b - \sqrt{b^2 - 4R}\right)$$

with $b=1+R+1/(K[H_0])$ and $R=[H]/[G]$ H=host, G=guest, $\Delta\delta=\delta_G-\delta_{GC}$

Best fit parameters K and δ_{GC} were obtained in a nonlinear least-square fitting procedure using the curve fitting program 'Sigma Plot' (Jandel Scientific Software).

Maximum errors for the K values were estimated as ±15%.

4.2.2. Microcalorimetric measurements

An isothermal calorimetry instrument VP-ITC (MicroCal) was used. The Differential Power axis (DP in $\mu cal\,s^{-1}$) of the ITC instrument was calibrated electrically using an internal electric heater. Enthalpy and equilibrium constant were determined from the titration curve using the Origin plotting software. At least three independent measurements were carried out at 298 K. Each titration experiment consisted of 70 successive injections performed. A constant volume (1 μL/injection) of the metal salt acetonitrile solution was injected into the cell (1.4255 mL) charged with the calixarene solution (acetonitrile, 2×10^{-4} M). The heat of dilution caused by the addition of the metal salt solution to the blank solution without the calixarene was determined in each run. The dilution enthalpies were subtracted from the enthalpies measured during the titration experiment.

4.2.3. X-ray crystallographic studies

Compounds **2**–**4** and **8** were obtained in monocrystalline form by slow cooling of the warm acetonitrile and acetone solution, respectively. Data were collected with a STOE-diffractometer using graphite-monochromated Mo Kα radiation (details are given in Supplementary data). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[15] The hydrogen atoms were included at calculated positions. All other nonhydrogen atoms were refined anisotropically. The X-STEP-Program was used for structure representations.

4.3. Synthesis

Compound **12** was available from previous studies.[11]

4.3.1. 11,23-Di-bromo-25,27-dihydroxy-26,28-bis-(propyloxy)calix[4]arene-crown-4 cone (**2**)

Compound **1**[16] (3.33 g, 5 mmol) was suspended in dry THF (100 mL). Buthyllithium (6.5 mL 1.6 M solution in hexane, 10.5 mmol) in dry THF (3.5 mL) was added dropwise. The solution was diluted with acetonitrile (200 mL). Triethylene glycol bistosylate (2.5 g, 5 mmol) in acetonitrile (200 mL) was added dropwise within 2 h. The solution was boiled at reflux for 6 h. The solvent was removed in vacuo. The remaining residue was dissolved in dichloromethane. The solution was washed with water, HCl (10%) and water. The solution was dried ($MgSO_4$) and evaporated in vacuo. The residue was recrystallized (acetonitrile) to provide a colorless solid (3.5 g, 90%), mp 225–228 °C. Anal. Calcd for $C_{40}H_{44}Br_2O_6$ (780.60): C, 61.55; H, 5.68; Br, 20.47. Found: C, 61.62; H, 5.62; Br, 20.37; HRMS (ESI, pos., MeOH): $[M+Na^+]^+$ calcd for $C_{40}H_{44}Br_2O_6Na$: 801.1402, found: 801.1427. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ=*calixarene*: 7.27 (s, 4H, H-10, 12, 22, 24), 6.27 (t, J=7.4 Hz, 2H, H-5, 17), 6.15 (d, J=7.4 Hz, 4H, H-4, 6, 16, 18), 4.35 (d, ^2J=15.7 Hz, 4H, H-2, 8, 14, 20), 3.12 (d, ^2J=15.7 Hz, 4H, H-2, 8, 14, 20), 3.64 (t, 4H, –O*CH*$_2$CH$_2$CH$_3$), 1.92 (q, 4H, –OCH$_2$*CH*$_2$CH$_3$), 1.12 (t, 6H, –OCH$_2$CH$_2$*CH*$_3$); *crown*: 4.09 (s, 8H), 3.76 (s, 4H). ^{13}C NMR (100 MHz, CD_3CN, TMS): δ=157.4 (C-25, 27), 154.7(C-26, 28), 138.8 (C-1, 9, 13, 21), 132.2 (C-3, 7,15, 19), 131.6 (C-10, 12, 22, 24), 127.7 (C-4, 6, 16, 18), 122.4 (C-5, 17), 114.7 (C-11, 23), 77.3 (–O*CH*$_2$CH$_2$CH$_3$), 30.3 (C-2, 8, 14, 20), 23.6 (–OCH$_2$*CH*$_2$CH$_3$), 10.9 (–OCH$_2$CH$_2$*CH*$_3$); *crown*: 74.0 (CH_2, 2C), 71.9 (CH_2, 2C), 70.2 (CH_2, 4C).

4.3.2. 11,23-Di-(N-methylacridinium-9-yl)-25,27-hydroxy-26,28-bis(propyloxy)calix[4]arene-crown-4 bis hexafluorophosphate cone (**3**)

A solution of **2** (1.17 g, 1.5 mmol) in dry THF (100 mL) was cooled to −78 °C under argon. Butyllithium (2 mL 1.6 M solution in hexane, 3.2 mmol) dissolved in THF (8 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 0.5 h. *N*-Methylacridone (0.63 g, 3.01 mmol) was added. The reaction mixture was slowly warmed to room temperature under argon. Water (1 mL) was added. The solvents were removed in vacuo. The remaining residue was dissolved in acetonitrile and treated with NH_4PF_6 (2.5 g). The solution was evaporated in vacuo. The remaining solid was washed with water and methyl-*tert*-butylether (MTBE). The crude product was purified by CC (acetonitrile/ethylacetate/cyclohexane/NH_4PF_6 400 mL/200 mL/100 mL/1 g); yellow crystals, 0.22 g (11%), mp>325 °C. Anal. $C_{68}H_{66}F_{12}N_2O_6P_2$ (1297.23); HRMS (ESI, pos., MeCN): $[M-PF_6^-]^+$ calcd for $C_{68}H_{66}N_2O_6PF_6$: 1151.4563, found: 1151.4549; $[M-2PF_6^-]^{2+}$ calcd for $C_{68}H_{66}N_2O_6$: 503.2460, found: 503.2463. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ=*acridinium*: 8.68 (d, 4H, H-5, 4), 8.41 (t, 2H, H-6), 8.37 (t, 2H, H-3), 8.08 (d, 2H, H-8), 7.90 (d, 2H, H-7), 7.77 (t, 2H, H-2), 7.73 (d, 2H, H-1), 4.84 (s, 6H, –N$^+$–CH$_3$); *calixarene*: 7.63 (s, 4H, H-10, 12, 22, 24), 7.19 (d, 4H, ^3J=7.5 Hz, H-4, 6, 16, 18), 6.94 (t, 2H, ^3J=7.5 Hz, H-5, 17), 4.67 (d, 4H, ^2J=13.0 Hz, H-2, 8, 14, 20), 4.52 (t 4H, ^3J=5.8 Hz, –O*CH*$_2$CH$_2$CH$_3$), 3.75 (d, 4H, ^2J=13.0 Hz, H-2, 8, 14, 20), 2.00 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 0.95 (t, 6H, ^3J=7.3 Hz, –OCH$_2$CH$_2$*CH*$_3$); *crown*: 4.30 (m, 8H, CH_2), 4.14 (s, 4H, CH_2). ^{13}C NMR (75 MHz, CD_3CN, TMS): δ=*acridinium*: 160.3 (C-9), 142.0 (C-10a), 141.9 (C-4a), 139.0 (C-6), 138.7 (C-3), 130.5 (C-8), 129.9 (C-1), 128.2 (C-7), 128.1 (C-2), 126.3 (C-8a), 125.7 (C-9a), 119.0 (C-5), 118.8 (C-4), 39.2 (N$^+$–CH$_3$); *calixarene*: 154.7(C-26, 28), 151.8 (C-25, 27), 136.9 (C-1, 9, 13, 21), 136.2 (C-3, 7, 15, 19), 132.1 (C-10, 12, 22, 24), 131.2 (C-11, 23), 130.0 (C-4, 6, 16, 18), 126.6 (C-5, 17), 79.8 (–O*CH*$_2$CH$_2$CH$_3$), 30.1 (C-2, 8, 14, 20), 22.3 (–OCH$_2$*CH*$_2$CH$_3$), 9.0 (–OCH$_2$CH$_2$*CH*$_3$); *crown*: 75.1 (2C, CH_2), 70.1 (4C, CH_2).

4.3.3. 11,23-Di-(9-methoxy-9,10-dihydro-N-methylacridine-9-yl)-25,27-dihydroxy-26,28-bis-(propyloxy)calix[4]arene-crown-4 cone (**4**)

A suspension of **3** (0.11 g, 0.1 mmol) in acetonitrile (9 mL) and methanol (1 mL) and K_2CO_3 (0.10 g) was stirred at room temperature for 5 h. After filtration the solvents were removed in vacuo. The residue was treated with dry chloroform (10 mL) and then filtered. The filtrate was evaporated in vacuo. After recrystallization (acetone) a colorless solid was obtained, 0.85 g, (79%), mp=192–195 °C. Anal. $C_{70}H_{72}N_2O_8$ (1069.36); HRMS (ESI, pos., MeOH): $[M+Na^+]^+$ calcd for $C_{70}H_{72}N_2O_8Na$: 1091.5186, found: 1091.5198; $[M-OCH_3^-]^+$ calcd for $C_{69}H_{69}N_2O_7$: 1037.5105, found: 1039.5122; $[M-2OCH_3^-]^{2+}$ calcd for $C_{68}H_{66}N_2O_6$: 503.2460, found: 503.2468. ^{1}H NMR (400 MHz, CD_3CN, TMS): *δ=acridane*: 7.35 (t, 4H, *J*=7.8 Hz, H-1, 8), 7.28 (d, 4H, *J*=7.8 Hz, H-2, 7), 7.16 (d, 4H, *J*=7.8 Hz, H-4, 5), 6.95 (t, 4H, *J*=7.8 Hz, H-3, 6) 3.51 (s, 6H, –N–*CH*$_3$) 3.01 (s, 6H, –O*CH*$_3$); *calixarene*: 7.09 (s, 4H, H-10, 12, 20, 24), 6.74 (d, 4H, *J*=7.5 Hz, H-4, 6, 16, 18), 6.61 (t, 2H, *J*=7.5 Hz, H-5, 17), 4.21 (d, 4H, H-2, 8, 14, 20), 3.33 (d, 4H, H-2, 8, 14, 20); *crown*: 4.01 (m, 8H,), 3.91 (s, 4H); *ether*: 4.01 (m, 4H, –O*CH*$_2$CH$_2$CH$_3$), 1.75 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 0.82 (t, 6H, ^3J=7.5 Hz, –OCH$_2$CH$_2$*CH*$_3$). ^{13}C NMR (100 MHz, CD_3CN, TMS): *δ=acridane*: 141.2 (C-4a, 5a), 129.1 (C-1, 8), 128.3 (C-3, 6), 124.3 (C-1a, 8a), 120.4 (C-2, 7), 113.1 (C-4, 5), 78.7 (C-9), 51.1 (–OCH$_3$), 33.4 (–NCH$_3$); *calixarene*: 152.3 (C-25, 27), 151.7 (C-26, 28) 147.2 (C-11, 23), 135.7 (C-1, 9, 13, 21), 134.5 132.5 (C-3, 7, 15, 19), 128.9 130.0 (C-4, 6, 16, 18), 126.6 128.2 (C-10, 12, 20, 24), 125.7 121.4 (C-5, 17), 73.8 (–O*CH*$_2$CH$_2$CH$_3$), 29.9 (C-2, 8, 14, 20), 22.1 (–OCH$_2$*CH*$_2$CH$_3$), 9.0 (–OCH$_2$CH$_2$*CH*$_3$); *crown*: 79.0 (2C, CH$_2$), 70.0 (4C, CH$_2$).

4.3.4. 11,23-Di-bromo-25,27-bis(2-methoxy-ethoxymethoxy)-26,28-bis(propyloxy)calix[4]arene (**5**)

Butyllithium (6.5 mL 1.6 M in hexane, 10.4 mmol) was added to a solution of **1** (3.33 g, 5 mmol) in THF (125 mL). After stirring for 0.5 h methoxyethoxymethyl chloride (MEM chloride, 1.25 g, 10 mmol) in THF (20 mL) was added. The solution was stirred at room temperature for 3 h. The solvent was removed in vacuo. The residue was dissolved in chloroform (100 mL) and washed with water (4×50 mL). After drying ($MgSO_4$) the solution was evaporated. The remaining solid was purified by recrystallization (*n*-hexane), 3.8 g (90%), mp 102–104 °C. Anal. Calcd for $C_{42}H_{50}Br_2O_8$ (842.66): C, 59.87; H, 5.98; Br, 18.96. Found: C, 60.12; H, 6.05; Br, 19.02; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): *δ*=7.18 (s, 4H, H-10, 12, 22, 24), 6.33 (t, ^3J=7.5 Hz, 2H, H-5, 17), 6.19 (d, ^3J=7.5 Hz, 4H, H-4, 5, 16, 18), 5.23 (s, 4H, –O*CH*$_2$O–), 4.36 (d, 4H, ^2J=13.6 Hz, H-2, 8, 14, 20), 3.95 (m, 4H, –OCH$_2$OCH$_2$*CH*$_2$OCH$_3$), 3.64 (t, 4H, ^3J=7.3 Hz, –O*CH*$_2$CH$_2$CH$_3$), 3.54 (m, 4H, –OCH$_2$O*CH*$_2$CH$_2$OCH$_3$), 3.36 (s, 6H, –OCH$_2$OCH$_2$CH$_2$O*CH*$_3$), 3.11 (d, 4H, ^2J=13.6 Hz, H-2, 8, 14, 20), 1.79 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 1.00 (t, 6H, ^3J=7.5 Hz, –OCH$_2$CH$_2$*CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): *δ*=155.1 (C-25, 27), 154.7 (C-26, 27), 138.8 (C-1, 9, 13, 21), 132.4 (C-3, 7, 15, 19), 131.4 (C-10, 12, 22, 24), 127.9 (C-4, 5, 16, 18), 122.6 (C-5, 17), 115.4 (C-11, 23), 98.9 (–O*CH*$_2$O), 76.7 (–O*CH*$_2$CH$_2$CH$_3$), 72.2 (–OCH$_2$OCH$_2$*CH*$_2$OCH$_3$), 69.7 (–OCH$_2$O*CH*$_2$CH$_2$OCH$_3$), 59.1 (–OCH$_2$OCH$_2$CH$_2$O*CH*$_3$), 31.0 (C-2, 8, 14, 20), 23.3 (–OCH$_2$*CH*$_2$CH$_3$), 10.6 (–OCH$_2$CH$_2$*CH*$_3$).

4.3.5. 11,23-Di-(N-methylacridinium-9-yl)-25,27-bis(2-methoxy-ethoxymethoxy)-26,28-bis(propyloxy)calix[4]arene bis hexafluorophosphate (**6**)

A solution of **5** (2.11 g, 2.5 mmol) in dry THF (150 mL) was cooled to −78 °C under argon. Butyllithium (3.13 mL 1.6 M solution in hexane, 5.01 mmol) dissolved in THF (8 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 0.5 h. *N*-Methylacridone (1.05 g, 5.02 mmol) was added. The reaction mixture was slowly warmed to room temperature under argon. Water (1 mL) was added. The solvents were removed in vacuo. The remaining residue was dissolved in acetonitrile (mL) and treated with NH_4PF_6 (2.5 g). The solution was evaporated in vacuo. The remaining solid was washed with water and MTBE. The crude product was purified by CC (acetonitrile/ethylacetate/cyclohexane/NH_4PF_6 400 mL/200 mL/100 mL/1 g); yellow crystals, 0.96 g (36%), mp 208–210 °C. Anal. $C_{70}H_{72}N_2O_8P_2F_{12}$ (1359.25); HRMS (ESI, pos., MeCN): $[M-PF_6^-]^+$ calcd for $C_{70}H_{72}N_2O_8PF_6$: 1213.4931, found: 1213.4913; $[M-2PF_6^-]^{2+}$ calcd for $C_{70}H_{72}N_2O_8$: 534.2644, found: 534.2645. ^{1}H NMR (400 MHz, CD_3CN, TMS): *δ=acridinium*: 8.51 (d, *J*=9.0 Hz, 2H, H-5), 8.41 (ddd, ^3J=9 Hz, ^3J=8 Hz, ^4J=1 Hz, 2H, H-6) 8.20 (dd, ^3J=8.8 Hz, ^4J=1 Hz, 2H, H-8), 7.91 (ddd, ^3J=9 Hz, ^3J=8 Hz, ^4J=1 Hz, 2H, H-7), 7.83 (d, *J*=9.0 Hz, 2H, H-4), 7.00 (dt, ^3J=9 Hz, ^4J=1 Hz, 2H, H-3), 6.22 (t, *J*=8 Hz, 2H, H-2), 5.89 (dd, ^3J=8 Hz, ^4J=1 Hz, 2H, H-1) 4.56 (s, 6H, –N$^+$–*CH*$_3$); *calixarene*: 7.17 (d, *J*=7.3 Hz, 4H, H-4, 5, 16, 18), 6.77 (t, *J*=8 Hz, 2H, H-5, 17), 6.74 (s, 4H, H-10, 12, 22, 24), 5.31 (s, 4H, –O*CH*$_2$O–), 4.67 (d, 4H, ^2J=13.3 Hz, H-2, 8, 14, 20), 4.20 (m, 4H, –O*CH*$_2$CH$_2$CH$_3$), 4.06 (m, 4H, –OCH$_2$OCH$_2$*CH*$_2$OCH$_3$), 3.62 (m, 4H, –OCH$_2$O*CH*$_2$CH$_2$OCH$_3$), 3.55 (d, 4H, ^2J=13.3 Hz, H-2, 8, 14, 20), 3.35 (6H, –OCH$_2$OCH$_2$CH$_2$O*CH*$_3$), 2.25 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 1.06 (t, 6H, –OCH$_2$CH$_2$*CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) *δ=acridinium*: 140.9, 139.7, 138.6 (C-6), 136.2, 135.5 (C-3), 134.9, 130.6 (C-8), 129.2 (C-1), 127.7 (C-7), 125.4 (C-2), 124.6, 123.3, 117.9 (C-5), 116.7 (C-4), 38.2 (–N$^+$–*CH*$_3$); *calixarene*: 132.1 (C-10, 12, 22, 24), 128.9 (C-4, 5, 16, 18), 123.0 (C-5, 17), 99.8 (–O*CH*$_2$O–), 76.7 (–O*CH*$_2$CH$_2$CH$_3$), 71.4 (–O*CH*$_2$CH$_2$OCH$_3$), 69.4 (–OCH$_2$*CH*$_2$OCH$_3$), 57.8 (–OCH$_2$CH$_2$O*CH*$_3$), 30.6 (C-2, 8, 14, 20), 22.9 (–OCH$_2$*CH*$_2$CH$_3$), 9.2 (–OCH$_2$CH$_2$*CH*$_3$).

4.3.6. 11,23-Di-(N-methylacridinium-9-yl)-25,27-hydroxy-26,28-bis(propyloxy)calix[4]arene bis hexafluorophosphate (**7**)

Compound **6** (0.30 g, 0.22 mmol) dissolved in acetonitrile (25 mL) was treated with HPF_6 (0.2 mL) and water (0.4 mL) under stirring for 1 h. After evaporating the solution, the remaining solid was washed with water (5 mL) and MTBE (10 mL). The remaining solid was purified by CC (acetonitrile/ethylacetate/cyclohexane/NH_4PF_6 400 mL/200 mL/100 mL/1 g), 0.195 g (75%), orange solid, mp=325 °C. Anal. $C_{62}H_{56}$ $F_{12}N_2O_4P_2$ (1183.03); HRMS (ESI, pos., MeCN): $[M-PF_6^-]^+$ calcd for $C_{62}H_{56}N_2O_4PF_6$: 1037.3882, found: 1037.3869; $[M-2PF_6^-]^{2+}$ calcd for $C_{62}H_{56}N_2O_4$: 446.2120, found: 446.2117. ^{1}H NMR (600 MHz, $(CD_3)_2CO$, TMS): *δ=acridinium*: 8.80 (d, 2H, ^3J=7.2 Hz, H-5), 8.77 (d, 2H, *J*=7.2 Hz, H-4), 8.42 (t, 2H, ^3J=7.2 Hz, H-6), 8.39 (t, 2H, ^3J=7.2 Hz, H-3), 8.31 (d, 2H, ^3J=8.4 Hz, H-8), 8.11 (d, 2H, ^3J=8.4 Hz, H-1), 7.93 (t, 2H, ^3J=8.4 Hz, H-7), 7.84 (t, 2H, ^3J=8.4 Hz, H-2), 5.00 (s, 6H, –N$^+$–CH$_3$); *calixarene*: 9.38 (s, 2H, OH), 7.53 (s, 4H, H-10, 12, 22, 24), 7.08 (d, 4H, ^3J=7.5 Hz, H-4, 6, 16, 18), 6.80 (t, 2H, ^3J=7.5 Hz, H-5, 17), 4.48 (d, 4H, ^2J=13.0 Hz, H-2, 8, 14, 20), 4.08 (t 4H, ^3J=5.8 Hz, –O*CH*$_2$CH$_2$CH$_3$), 3.67 (d, 4H, ^2J=13.0 Hz, H-2, 8, 14, 20), 2.13 (m, 4H, –OCH$_2$*CH*$_2$CH$_3$), 1.40 (t, 6H, ^3J=7.3 Hz, –OCH$_2$CH$_2$*CH*$_3$). ^{13}C NMR (75 MHz, CD_3CN, TMS): *δ=acridinium* 161.9, 155.0, 151.9, 141.4, 138.3 (C-6), 138.1 (C-3), 133.5, 130.5 (C-8), 130.0 (C-1), 128.4, 127.3 (C-7, 2), 125.8 (C-8a, 9a), 118.2 (C-5), 118.1 (C-4); *calixarene* 131.0 (C-10, 12, 22, 24), 129.1 (C-4, 6, 16, 18), 125.9 (C-5, 17), 123.8 (C-11, 23), 78.5 (–O*CH*$_2$CH$_2$CH$_3$), 38.3 (–N$^+$–CH$_3$), 30.3 (C-2, 8, 14, 20), 23.1 (–OCH$_2$*CH*$_2$CH$_3$), 10.1 (–OCH$_2$CH$_2$*CH*$_3$).

4.3.7. 11,23-Di-(9-methoxy-N-methylacridine-9-yl)-25,27-hydroxy-26,28-bis(propyloxy)calix[4]arene (**8**)

The suspension of **7** (0.050 g, 0.48 mmol) and $KHCO_3$ (0.05 g) in acetonitrile (4 mL) and methanol (1 mL) was stirred for 5 days. The product precipitated and was filtrated together with $KHCO_3$. The solid was washed with water until the water was neutral. The solid was dried and recrystallized from acetonitrile, 0.037 g (75%), mp=148 °C (dec). Anal. $C_{64}H_{62}N_2O_6$ (955.22); HRMS (ESI, pos., MeOH): $[M-2MeO^-]^{2+}$ calcd for $C_{62}H_{56}N_2O_6$: 446.2120, found:

446.2127. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ=*acridane*: 7.28 (t, ^3J=8.3 Hz, 4H, H-3, 6), 7.21 (dd, ^3J=7.8 Hz, ^4J=1.5 Hz, 4H, H-1, 8), 7.03 (d, ^3J=8.3 Hz, 4H, H-4, 5), 6.70 (dt, ^3J=7.8 Hz, ^4J=1.5 Hz, 4H, H-2, 7), 3.54 (s, 6H, N^+–CH_3); *calixarene*: 8.28 (s, 2H, –OH), 7.00 (s, 4H, H-10, 12, 22, 24), 6.73 (d, ^3J=8.0 Hz, 4H, H-4, 6, 16, 18), 6.66 (t, ^3J=8.0 Hz, 2H, H-5, 17), 4.21 (d, ^2J=13,1 Hz, 4H, H-2, 8, 14, 20), 3.88 (t, ^3J=6.3 Hz, 4H, –O$CH_2CH_2CH_3$), 3.25 (d, ^2J=13,1 Hz, 4H, H-2, 8, 14, 20), 2.90 (s, 6H, –OCH_3), 1.98 (m, 4H, –$OCH_2CH_2CH_3$), 1.26 (t, 6H, ^3J=7.6 Hz, –$OCH_2CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ=*acridane*: 141.2 (C4a, 5a), 130.0(C-1, 8), 128.2 (C-3, 6), 125.0 (C-1a, 8a), 120.0 (C-2, 7), 112.0 (C-4, 5), 78.9 (C-9), 51.1 (–OCH_3), 33.5 (–NCH_3); *calixarene*: 152.0 (C-26, 28), 151.8 (C-25, 27), 138.0 (C-1, 9, 13, 21), 133.4 (C-3, 7, 15, 19), 129.9 (C-11, 23), 128.9 (C-4, 6, 16, 18), 127.4 (C-10, 12, 22, 24), 125.4 (C-5, 17), 78.1 (–O$CH_2CH_2CH_3$), 31.7 (C-2, 8, 14, 20), 23.5 (–$OCH_2CH_2CH_3$), 11.0 (–$OCH_2CH_2CH_3$).

4.3.8. 9-[4-(2-Methoxy-ethoxymethoxy)-phenyl]-N-methylacridinium hexafluorophosphate (**10**)

A solution of 1-Bromo-(2-methoxy-ethoxymethoxy)-phenyl]-benzene (**9**)[17] (2.61 g, 10 mmol) in dry THF (100 mL) was cooled to −78 °C under argon. Butyllithium (3.15 mL 1.6 M solution in hexane, 5.04 mmol) dissolved in THF (6 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 0.5 h. *N*-Methylacridone (2.1 g, 10.1 mmol) was added. The reaction mixture was slowly warmed to room temperature under argon. Water (1 mL) was added. The solvents were removed in vacuo. The remaining residue was dissolved in acetonitrile (50 mL) and treated with NH_4PF_6 (2.5 g). The solution was evaporated in vacuo. The remaining solid was washed with water and MTBE. The crude product was purified by CC (acetonitrile/ethylacetate/cyclohexane/NH_4PF_6 400 mL/200 mL/100 mL/1 g); yellow crystals, 2.27 g (44%), mp 128–130 °C. Anal. $C_{24}H_{24}F_6NO_3P$ (519.43); HRMS (ESI, pos., MeCN): $[M-PF_6^-]^+$ calcd for $C_{24}H_{24}NO_3$: 374.1756, found: 374.1754. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ=8.57 (d, 2H, ^3J=9.3 Hz, H-4, 5) 8.36 (t, 2H, ^3J=9.3 Hz, H-3, 6), 8.09 (d, 2H, ^3J=8.8 Hz, H-1, 8), 7.84 (t, 2H, ^3J=8.8 Hz, H-2, 7), 7.46 (d, 2H, ^3J=8.7 Hz, –C_6H_4OMEM), 7.37 (d, 2H, ^3J=8.7 Hz, –C_6H_4OMEM), 5.42 (s, 2H, –OCH_2O–), 4.80 (s, 3H, –N^+–CH_3), 3.85 (m, 2H, –$OCH_2CH_2OCH_3$), 3.56 (m, 2H, –O$CH_2CH_2OCH_3$), 3.30 (s, 3H, –$OCH_2CH_2CH_3$). ^{13}C NMR (100 MHz, (CD_3CN, TMS): δ=161.5, 158.6, 141.3, 138.3 C-3, 6), 131.5 (*o*-C_6H_4OMEM), 130.0 (C-1, 8), 127.4 (C-2, 7), 126.0, 125.9, 118.1 (C-4, 5), 116.2, (*m*-C_6H_4OMEM), 93.07 (–OCH_2O–), 71.04 (–O$CH_2CH_2OCH_3$), 67.8 (–$OCH_2CH_2OCH_3$), 57.6 (–$OCH_2CH_2CH_3$), 38.4 (–N^+–CH_3).

4.3.9. 9-(4-Hydroxy-phenyl)-N-methylacridinium hexafluorophosphate (**11**)

A solution of HPF_6 (1 mL) in water (4 mL) was added to a stirred solution of **10** (1.0 g) in acetonitrile (50 mL). The solution was evaporated in vacuo. The remaining solid was washed with water (10 mL) and MTBE (20 mL). The remaining solid was purified by CC acetonitrile/ethylacetate/cyclohexane/NH_4PF_6 400 mL/200 mL/100 mL/1 g); 0.73 g (87%), yellow solid, mp186–188 °C. Anal. $C_{20}H_{16}F_6NOP$ (431.32); HRMS (ESI, pos., MeCN): $[M-PF_6^-]^+$ calcd for $C_{20}H_{16}NO$: 286.1232, found: 286.1240. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ=9.20 (s, 1H, –OH), 8.55 (d, 2H, ^3J=9.3 Hz, H-4, 5) 8.34 (t, 2H, ^3J=9.3 Hz, H-3, 6), 8.13 (d, 2H, ^3J=8.8 Hz, H-1, 8), 7.83 (t, 2H, ^3J=8.8 Hz, H-2, 7), 7.37 (d, 2H, ^3J=8.7 Hz, –C_6H_4OH), 7.16 (d, 2H, ^3J=8.7 Hz, –C_6H_4OH), 4.78 (s, 3H, N^+–CH_3). ^{13}C NMR (100 MHz, (CD_3CN, TMS): δ=162.0, 158.6, 141.3, 138.2 (C-3, 6), 131.8 (*o*-C_6H_4OH), 130.2 (C-1, 8), 127.2 (C-2, 7), 126.0, 124.0, 118.0 (C-4, 5), 115.4, (*m*-C_6H_4OH), 38.3 (–N^+–CH_3).

Acknowledgements

Financial support provided by Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supplementary data

UV–vis, NMR spectra as well as crystallographic data are available in Supplementary data. Transient decay curves are given in supplement information. Supplementary data in the form of a CIF have been deposited with the Cambridge Crystallographic Data Centre (CCDC 730189 for **2**, CCDC 730186 for **3**, CCDC 730188 for **4**, and CCDC 730187 for **8**). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.05.082.

References and notes

1. Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, England, 1989; *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer: Dordrecht, 1991; Pochini, A.; Ungaro, R. In *Comprehensive Supramolecular Chemistry*; Vögtle, F., Ed.; Pergamon: Oxford, 1996; Vol. 2, pp 103–142; Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713–1734.
2. Wang, L.; Vysotsky, M. O.; Bogdan, A.; Bolte, M.; Böhmer, V. *Science* **2004**, *304*, 1312.
3. Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 3102.
4. Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley-VCH: Chichester, 2000.
5. Abraham, W. *J. Inclusion Phenom. Macrocycl. Chem.* **2002**, *43*, 159.
6. Gutsche, C. D.; Alam, I. *Tetrahedron* **1988**, 4689.
7. Orda-Zgadzaj, M.; Wendel, V.; Fehlinger, M.; Ziemer, B.; Abraham, W. *Eur. J. Org. Chem.* **2001**, 1549.
8. Deng, G.; Sakaki, T.; Kawahara, Y.; Shinkai, S. *Tetrahedron Lett.* **1992**, *33*, 2163.
9. Husaru, M.; Gruner, T.; Wolff, W. D.; Habicher; Salzer, R. *Tetrahedron Lett.* **2005**, *46*, 3377.
10. Schäfer, C.; Eckel, R.; Ros, R.; Mattay, J.; Anselmetti, D. *J. Am. Chem. Soc.* **2007**, *129*, 1488.
11. Grubert, L.; Abraham, W. *Tetrahedron* **2007**, *63*, 10778.
12. Casnati, A.; Pochini, A.; Ungaro, R.; Bocchi, C.; Ugozzoli, F.; Egberink, R. J. M.; Strujk, H.; Lugtenberg, R.; de Jong, F.; Reinhoudt, D. N. *Chem.—Eur. J.* **1996**, *2*, 436.
13. Abraham, W.; Buck, K.; Orda-Zgadzaj, M.; Schmidt-Schäffer, S.; Grummt, U.-W. *Chem. Commun.* **2007**, 3094.
14. Macomber, R. S. *J. Chem. Educ.* **1992**, *69*, 375–378.
15. Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.
16. Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767.
17. Chuang, C.-L.; dos Santos, O.; Xu, X.; Canary, J. W. *Inorg. Chem.* **1997**, *36*, 1967.