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Novel Chromogenic Pyridinium Derivatives of Calix[4]arenes,I

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Abstract: 5-(1-Pyridinio)-11,17,23-tri-t-butyl-28-hydroxy-25,26,27-trialkoxycalix[4]arene and 5,17-bis(1-pyridinio)-11,23-di-t-butyl-26,28-dihydroxy-25,27-di(ethoxycarbonyl)methoxycalix[4]arene perchlorates have been synthesized. These compounds acted as chromoionophores exhibiting optical responses in organic solvents upon complexation of Li^+, Na^+ and K^+ salts.

INTRODUCTION

Molecular design of chromogenic calix[n]arenes has attracted much attention in the past years. These ligands change their absorption (or fluorescence) spectra upon the binding of metal cations similarly to chromogenic crown ethers[1]. The coloration process taking place upon complexation thus serves as a transducer of the chemical signal to the physical one. This phenomenon plays an important role in the operation of optical sensors which have increasingly been applied in the quantitative determination of physiologically essential cations, K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}.

Recently a number of chromogenic calix[4]arene derivates have been synthesized to achieve highly selective ligands which may have great potential in the development of new metal ion sensors.

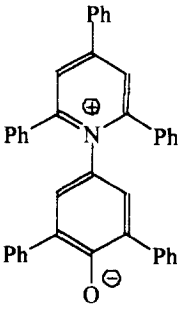
The common feature of the calixarene chromoionophores prepared till now is that the ionophoric cavity is composed of ether (linear or cyclic)[2,3], or/and $OCH_2(CO)O$[4,5,6,7,8,9,10,11] donor groups. The chromophore (fluorophore) indicator units are attached either to the end of ether/ester linkage[5,6,7,8,9] or they are in conjugation through a phenolic OH with the cation coordination sphere[2,3,4]. Direct participation of the chromophore unit in the complexation is also described.[10,11]

In the chromogenic molecules mainly (di)nitrophenylazo group[3,4] is used as coloration site although there are examples for nitrophenol[6]- and indoaniline[10,11] chromophores. The fluorogenic calixarenes generally contain anthracene[9], pyrene[5,7,8] and benzthiazole[2] fluorophore units.

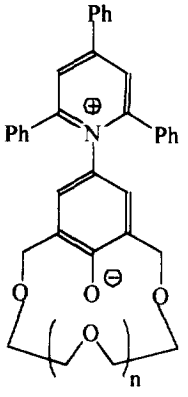
The new metal sensing calix[4]arenes due to the character of the coordination sphere composed of hard ether oxygen and/or ester carbonyl oxygen donor atoms are reported to show alkali ion (mostly sodium[6,7,8,9,10], a few of them lithium[2,4,5], potassium[3] and calcium[11]) selectivities. The optical responses

of ligands upon complexation (i.e. the change of visible or fluorescence spectra) were measured in solid-liquid two-phase extraction experiments or in homogenous solution when metal salts were added. Of the chromo(fluoro)genic calix[4]arenes several representatives possess dissociable phenolic OH located near to the ionophoric cavity.[2,3,4] In these ligands the phenol unit is substituted in p-position by chromo(fluoro)phore group, which sensitively indicates the dissociation of OH by remarkable changes in the spectra. Although phenols being weak acids require usually strong bases for dissociation (pH≥10), the metal-induced dissociation of phenolic OH in chromogenic calixarenes of that type, however, readily takes place under the assistance of weak bases.

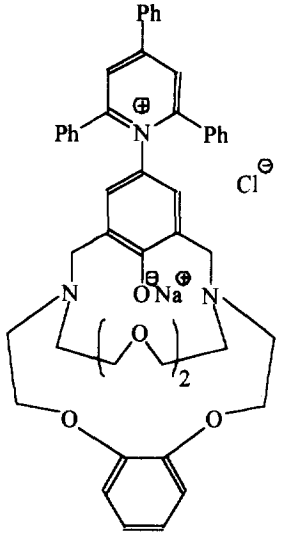
It is interesting to note that no attention was paid to pyridinium N-phenoxide betaine chromophores such as **1** (Reichardt dyes) in calixarene chemistry. It has been shown by Reichardt[13] that compound **1** has a long wavelength charge transfer (CT) absorption band. The position and intensity of this band depend on the solvent polarity (solvatochromism) and charge density of added cations (halochromism). In excited state of the betaine **1** the charge separation is reduced, therefore with increasing solvent polarity or in the presence of metal cations of increasing surface charge density hypsochromic shifts (to shorter wavelength) can be observed. Several structural variations of the reagent **1** have been published including the crown ether modified dyes **2**[14] and cryptand **3**[15]. Especially ligand **3** (prepared as the NaCl adduct) show interesting properties, solvatochromism and pronounced negative halochromism associated with highly selective Na^+ complexation in two phase extraction processes (pH≥10,5).



1



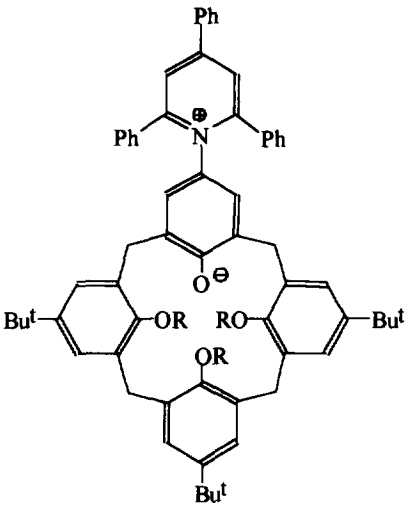
2 n=2,3,4



3

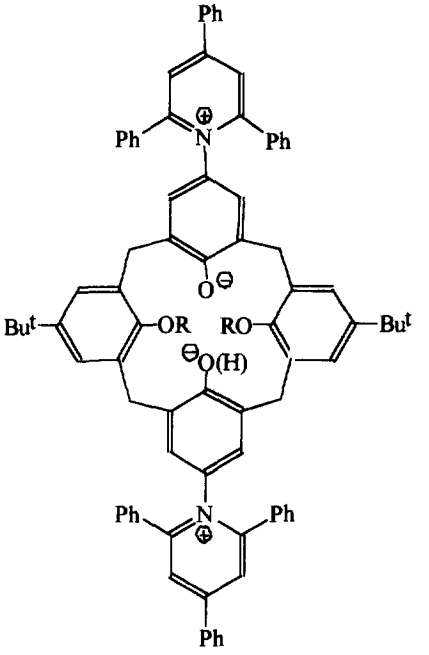
Continuing our efforts aiming at synthesizing new calixarene chromoionophores[12] we planned to introduce pyridinium unit(s) into the calix[4]arene framework supplied with various ligating functions. 25,26,27-Trimethoxy-28-hydroxycalix[4]arene containing benzthiazolyl chromo-and fluorophore group in p-position to the phenolic OH was reported to bind Li^+ in organic solvent.[2] On analogy first we prepared similar ligands with longer trialkoxide binding site whereas pyridinium moiety was attached instead of

benzthiazolyl group. In another entry ethoxycarbonyl(methoxy) donor units were introduced keeping the same chromophore structure. In both cases the pyridinium salts precursors were expected to transform into the Reichardt betaine chromophore system (**11**,**12**).



11

R= Et (a), Bu (b)



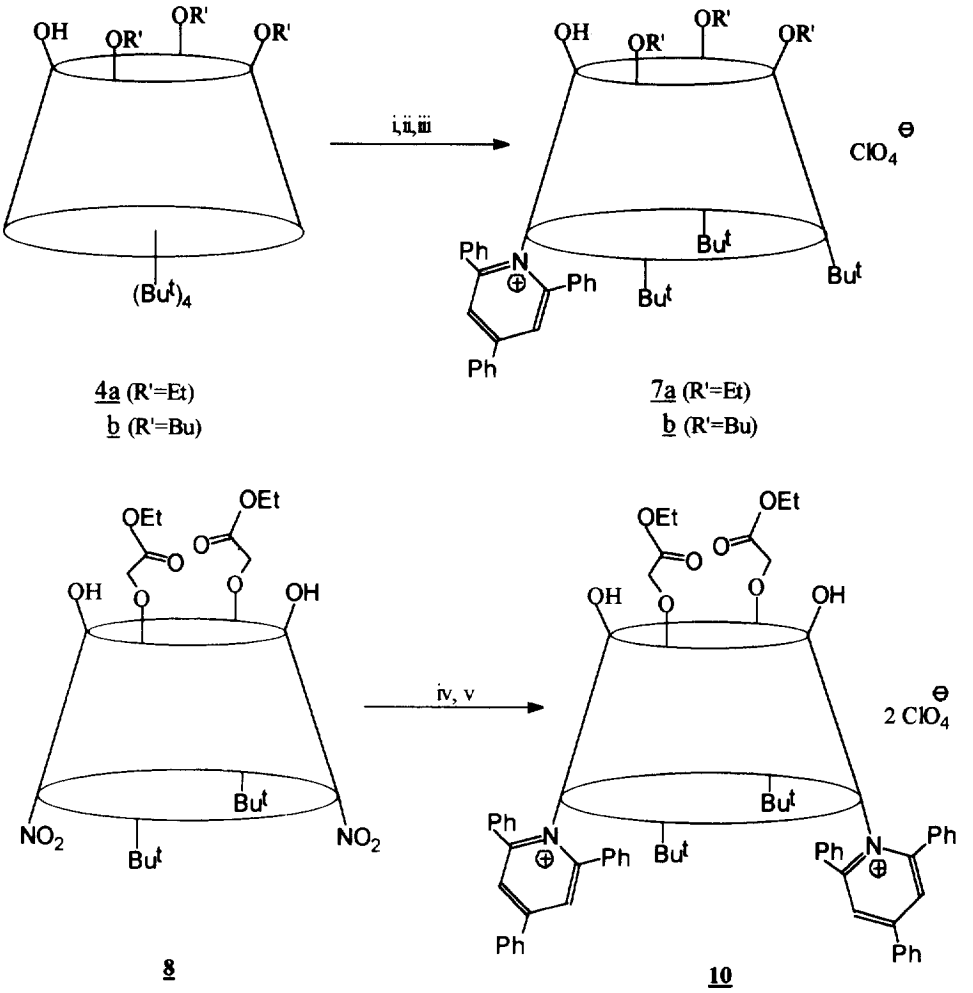
12

R= CH_2COOEt

RESULTS AND DISCUSSION

Synthesis of the ligands 7a,b and 10

Compounds **4a**,**b** were obtained in 70-80% yield by the cone-selective trialkylation of p-tert-butyl-calix[4]arene (DMF/BaO, 70°C) according to Shinkai's report[16]. The selective ipso nitration[17] of **4a**,**b** with fuming HNO_3 at -10°C then subsequent reduction of the mono-nitro compounds (**5a**,**b**) afforded the amines **6a**,**b** in 55-60% overall yields. Compounds **6a**,**b** were condensed with 2,4,6-triphenylpyrylium perchlorate (TPP) in methylene chloride in the presence of glacial acetic acid at ambient temperature resulting in the formation of pyridinium salts **7a**,**b** in 70% and 60% yield, respectively. In another entry ligand **10** was prepared similarly, starting from dinitro-diester derivative **8**[17] which was reduced in catalytic hydrogenation to diamine **9** followed by condensation with TPP furnished ligand **10** in 20% overall yield. (Since **9** was very sensitive to air, the ethanol solution was used in the next step). All ligands adopt the *cone* conformation. The synthetic approach is outlined in Scheme 1.



Scheme 1. Reagents i: HNO_3 CH_2Cl_2/AcOH (**5a,b**), ii: H_2NNH_2,/Pd(C), EtOH (**6a,b**), iii: TPP, CH_2Cl_2, iv: H_2/Pd(C), EtOH (**9**), v: TPP, EtOH, NaOAc

Unfortunately whichever literature analogy had been used to deprotonate the pyridinium salts **7a,b** and **10**, we failed to get betaines **11** and **12**.

Although our synthetic goal to prepare Reichardt dye analogue calixarenes could not be achieved we supposed that the precursor pyridinium salts **7a,b**, **10** would also behave as chromoionophores.

*Spectroscopic studies of ligand **7a,b** and **10***

UV/VIS spectra of the ligands were taken at 30 °C in chloroform, methylenechloride, acetone and ethanol, respectively. In separate experiments the spectra were recorded when excess of triethylamine, alkali salts or both had been added. The observed absorption maxima are summarized in Table1. and Table 2.

Ligand 7a and 7b. The absorption maxima of **7a** ($CHCl_3$: 306 nm, acetone: 326 nm) and **7b** ($CHCl_3$: 314 nm, acetone: 326 nm) were not affected by the addition of triethylamine (up to $[Et_3N]/[\mathbf{7a,b}]=10^3$). This implies that the basicity of Et_3N is not strong enough in these solvents to dissociate the OH group. In the absence of Et_3N, alkali salts (LiBr, $LiClO_4$, $NaClO_4$) added as solids into the solutions were not extracted and the absorption spectra remained unchanged. In the presence of Et_3N, in contrast, only LiBr caused change in the spectra of **7a,b**. The new absorption maxima 510 nm ($CHCl_3$) and 591 nm (acetone) of **7a** whereas 523 and 584 nm of **7b** indicate Li^+-selective complexation (Table 1.).

Solvent	λ_{max}(nm)					
	7a			**7b**		
	L (M^+)	L+B	L+B+Li^+	L (M^+)	L+B	L+B+Li^+
$CHCl_3$	306	306	510	313	313	523
acetone	326	326	591	326	326	584
EtOH	313	540[a]	597[a]	--	--	--

Ligand ($c=10^{-4}$ mol·dm^{-3}), Li^+:LiBr (solid, 10^{-3}M), B: Et_3N ($[B]/[L]=10^3$),
a: B= $Me_3BnN^+EtO^-$ ($[B]/[L]=10^3$)

Table 1. Spectral changes of ligands **7a,b** in different solvents, in the presence of base and LiBr.

This coloration phenomenon takes place only in dry solvents with dry salts (that is why $LiClO_4 \cdot 2H_2O$ did not cause any spectral change). It means that ligands **7a,b** form weak complexes under these conditions ($K_{diss} >> K_{ass}$) therefore only partial metal-induced dissociation can be achieved even in the presence of large excess of base. It is worth noting that λ_{max} values are higher in the more polar acetone than in chloroform with both ligands. This observation seems to be in contradiction with the negatively solvatochromic and halochromic behaviour of Reichardt dyes (pyridinium N-phenoxide betaines). which show hypsochromic shifts of the CT band with increasing solvent polarity, e.g. $\lambda_{CT}(\text{acetone}) < \lambda_{CT}(CHCl_3)$.

In order to explain this anomalous phenomenon we attempted to measure the λ_{max} of betaine **11a** formed *in situ* in ethanol. Large excess of trimethylbenzylammonium ethoxide (40% in EtOH) was added to the solution of **7a** (λ_{max}=313 nm) and the new absorption maximum appeared at 540nm is in accordance with the position of CT band of **1** (λ_{CT}=540 nm, EtOH[13]). Although partial deprotonation could only be achieved in this case, too, absorption maximum at 540 nm should be regarded as the CT band of betaine **11a**. When adding LiBr to this solution, bathochromic shift took place affording a new maximum at 597 nm ($NaClO_4$ did not affect the spectrum). It is again positive halochromism which show that tendency of the spectral changes during complexation can not be rationalized by assuming close Li^+-betaine interaction as reported in the literature. Thorough investigation of the exact structure of complex is required to explain the reverse halochromism.

Ligand 10. The optical spectrum of bis-ethoxycrbonyl(methoxy) derivative **10** was not affected either by adding excess of Et_3N or solid alkali salts, separately. When both of base and salt were added new absorption maxima appeared with each ion in the order of $Li^+ < K^+ < Na^+$ (Table 2.).

It is noteworthy that Li^+ shows 22nm bathochromic shift whereas Na^+ and K^+ exhibit 20 and 54 nm hypsochromic shifts, respectively, with increasing solvent polarity. The experimental data are not enough to

explain exactly the above observations even if assuming only mono-deprotonation of the two phenolic OH groups during the coloration process.

	$10\ \lambda_{max}$ (nm)				
Solvent	L (M^+)	L+B	L+B+LiBr	L+B+NaCl	L+B+KJ
CH_2Cl_2	314	314	490	680	654
acetone	334	334	512	660	600

L:ligand ($c=10^{-4}$mol·dm^{-3}), B: Et_3N ([B]/[L]=10^3)

Table 2. Spectral changes of ligand **10** when metal salts were added

The lack of selective complexation, however, can be attributed to the not optimal coordination site for any of cations tested. The introduction of ethoxycarbonyl(methoxy) units was expected to prefer Na^+ to K^+ and Li^+ as shown by the highest λ_{max} =680 nm (even with NaCl), but the number of donor groups is not sufficient for the selective recognition.

More detailed investigation of the ligands prepared and synthesis of new calix[4]arene chromoionophores are under progress.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ at 500MHz on a Bruker DRX500 spectrometer. All δ values are reported in ppm, TMS was used as internal standard. UV/VIS spectra were taken on UNICAM UV4 spectrophotometer. FAB mass spectra were obtained using Finnigan MAT 8430 mass spectrometer (ion source temperature:25°C, matrix: m-nitrobenzyl alcohol, gas:xenon, accelerating voltage 9kV). In the positive FAB MS $[C]^+$ and $[C^2A]^+$ refer to the cationic fragments with or without ClO_4^- (A). In the negative FAB MS $[CA_2]^-$ and $[C^2A_3]^-$refer to the anionic fragments with two or three ClO_4^- (A).

Precoated silica gel plates (Merck 60 F_{254}) were used for analytical TLC. All chemicals were reagent grade and used without further purification. Compounds **4a,b**[16] and **8**[17] were prepared as described in the literature.

*11,17,23-Tri-t-butyl-25,26,27-triethoxy-28-hydroxy-5-nitrocalix[4]arene (**5a**) and 11,17,23-tri-t-butyl-25,26,27-tributoxy-28-hydroxy-5-nitrocalix[4]arene (**5b**)*

Compounds **4a,b** (2.5mmol) dissolved in a mixture of CH_2Cl_2 (20ml) and AcOH (10ml) were nitrated at -10°C with fuming (98%) HNO_3 (0.5ml, 12mmol). After 15min stirring at room temperature the reaction mixture was poured into water (100ml), the phases were separated and the organic extract was washed with water (3×30ml) ,dried ($MgSO_4$) and evaporated to dryness. The solid residue was crystallized with methanol.

5a: 1.24g (70%) pale yellow powder, mp 265-267°C ^{1}H NMR δ: 8.06 (s,2H, $ArNO_2CH$), 7.34 (s,1H,OH), 7.16 (s,2H,ArH), 6.61, 6.47(d,4H,ArH), 4.33, 3.19 (d,J=12.6Hz,4H,$ArCH_2$), 4.30, 3.40 (d,J=13.8Hz,4H,$ArCH_2$), 4.00, 3.94 (q,m,2+4H,CH_2O), 1.69, 1.51 (t,3+6H,CH_3), 1.35, 0.84 (s,9+18H,t-Bu), ^{13}C NMR δ: 31.7, 31.4 ($ArCH_2$,cone), Anal. calcd. for $C_{46}H_{59}NO_6$ (721.98): C 76.53, H 8.24, N 1.94, Found: C 76.15, H 8.20, N 1.91.

5b: 1.5g (75%) pale yellow powder, mp 168-170°C ^{1}H NMR δ: 8.06 (s,2H,ArNO$_2$CH), 7.28 (s,1H,OH) 7.16 (s,2H,ArH), 6.60, 6.46(d,4H,ArH), 4.34, 3.19 (d,J=12.6Hz,4H,ArCH$_2$), 4.30, 3.39 (d,J=13.8Hz,4H, ArCH$_2$), 3.90-3.76 (m,6H,CH$_2$O), 2.24, 2.00-1.80 (m,2+4H,OCH$_2$CH$_2$) 1.65-1.30 (m,6H,CH$_2$CH$_3$), 1.04, 1.01 (t,3+6H,CH$_3$), 1.35, 0.83 (s,9+18H,t-Bu), ^{13}C NMR δ: 31.7, 31.5 (ArCH$_2$,cone), Anal. calcd. for $C_{52}H_{71}NO_6$(806.14): C 77.48, H 8.88, N 1.74, Found: C 77.25, H 8.81, N 1.70.

*11,17,23-Tri-t-butyl-25,26,27-triethoxy-28-hydroxy-5-aminocalix[4]arene (**6a**) and 11,17,23-tri-t-butyl-25,26,27-trimethoxy-28-hydroxy-5-aminocalix[4]arene (**6b**)*

Compounds **5a,b** (1mmol) was dissolved in EtOH (30ml) Pd(C) (0.2g) and $H_2NNH_2 \cdot H_2O$ (0.6ml) were added and refluxed for 2h. The catalyst was filtered while hot, washed with EtOH (10ml) and the combined filtrate was evaporated in vacuo. The remaning solid was recrystallized from EtOH.

6a: 0.55g (80%) white crystals, mp199-201°C ^{1}H NMR δ: 7.13 (s,2H,ArH), 6.56, 6.54 (d,4H,ArH), 6.47 (s,2H,ArH), 4.84 (s,1H,OH), 4.36, 3.17 (d,J=12.6Hz,4H,ArCH$_2$), 4.31, 3.13 (d,J=13.2Hz,4H, ArCH$_2$), 4.01, 3.86 (q,2+4H, CH$_2$O), 3.20 (bs,2H,NH$_2$), 1.72, 1.47 (t,3+6H,CH$_3$), 1.33, 0.87 (s,9+18H,t-Bu), ^{13}C NMR δ: 32.1, 32.0 (ArCH$_2$,cone), Anal. calcd. for $C_{46}H_{61}NO_4$ (691.99): C 79.84, H 8.88, N 2.02, Found: C 79.52, H 8.83, N 2.05.

6b: 0.65g (83%) white crystals mp 166-168°C ^{1}H NMR δ: 7.11 (s,2H,ArH), 6.55, 6.53 (d,4H,ArH), 6.47 (s,2H,ArH), 4.82 (s,1H,OH), 4.34, 3.17 (d,J=12.6Hz,4H,ArCH$_2$), 4.31, 3.12 (d,J=13.2Hz,4H, ArCH$_2$), 3.90, 3.76 (m,2+4H,CH$_2$O), 3.30 (b,2H,NH$_2$), 2.29,1.85-1.78 (m,2+4H,OCH$_2$CH$_2$), 1.62-1.35 (m,6H,CH$_2$CH$_3$), 1.03, 0.99 (t,3+6H,CH$_3$), 1.32, 0.87 (s,9+18H,t-Bu), ^{13}C NMR δ: 31.7, 31.4 (ArCH$_2$, cone),Anal. calcd. for $C_{52}H_{73}NO_4$ (776.15): C 80.47, H 9.48, N 1.80, Found: C 80.20, H 9.42, N 1.78.

*11,17,23-Tri-t-butyl-25,26,27-triethoxy-28-hydroxy-5-[1-(2,4,6-triphenylpyridinio)]calix[4]arene (**7a**) and11,17,23-tri-t-butyl-25,26,27-tributhoxy-28-hydroxy-5-[1-(2,4,6-triphenylpyridinio)]calix[4]arene (**7b**) perchlorates*

Compounds **6a,b** (0.5mmol), TPP (0.2g, 0.5mmol) and AcOH (0.3ml) dissolved in CH_2Cl_2 (20ml) were stirred at ambient temperature for 12h. The solvent was removed in vacuo, the residue was recrystallized from EtOH.

7a: 0.37g (70%) yellow crystals mp246-248°C (dec) ^{1}H NMR δ: 7.80-7.20 (m,17H,ArH), 7.15, 7.05 (s,2+2H,ArH), 6.58, 6.11 (d,4H,ArH), 6.11 (s,1H,OH), 4.31, 3.17 (d,J=12.5Hz,4H,ArCH$_2$), 4.03, 3.09 (d,J=14.2Hz,4H,ArCH$_2$), 4.00, 3.78 (m,2+4H,CH$_2$O), 1.62, 1.39 (t,3+6H,CH$_3$), 1.35, 0.84 (s,9+18H,t-Bu), ^{13}C NMR δ: 30.9, 30.7 (ArCH$_2$,cone), Anal. calcd. for $C_{69}H_{76}ClNO_8$ (1082.82): C 76.54, H 7.07, N 1.29, Found: C 76.02, H 6.99, N 1.22. Positive FAB MS, *m/z (%)*: 982 (100) $[C]^+$, negative FAB MS, *m/z (%)*: 1180 (100) $[CA_2]^-$

7b: 0.35g (60%) pale yellow powder mp>300°C ^{1}H NMR δ: 7.95 (s,2H,PyH), 7.82-7.25 (m,15H,ArH), 7.14, 7.05 (s,2+2H,ArH), 6.58, 6.09 (d,4H,ArH), 6.23 (s,1H,OH), 4.32, 3.17 (d,J=12.5Hz,4H,ArCH$_2$), 4.03, 3.07 (d,J=14.2Hz,4H,ArCH$_2$), 3.90, 3.75-3.65 (m,2+4H,CH$_2$O), 2.12, 1.90-1.75 (m,1.72,2+4H,OCH$_2$CH$_2$), 1.50-1.33 (m,6H,CH$_2$CH$_3$), 1.00, 0.97 (t,3+6H,CH$_3$), 1.34, 0.83 (s,9+18H,t-Bu), ^{13}C NMR δ: 32.2, 31.7 (ArCH$_2$,cone), Anal. calcd. for $C_{75}H_{88}ClNO_8$ (1166.98): C 77.19, H 7.60, N 1.20, Found: C 76.65, H 7.51, N 1.15. Positive FAB MS, *m/z (%)*: 1066 (100) $[C]^+$, negative FAB MS, *m/z (%)*: 1264 (100) $[CA_2]^-$

11,23-Di-t-butyl-25,27-diethoxycarbonyl(methoxy)-26,28-dihydroxy-5,17-bis[1-(2,4,6-triphenylpyridinio)]calix[4]arene diperchlorate (10)

Compound **8**[17] (0.8g, 1mmol) was reduced in EtOH (50ml) over Pd(C) (0.2g) catalyst at room temperature under a continuous flow of H_2 for 20h. Catalyst was filtered and the solution of **9** was stirred under argon with TPP (0.8g, 2mmol), NaOAc (0.5g) at ambient temperature for 3d. (Caution: isolation of bis-aminophenol **9** should be avoided because of rapid oxidation to coloured materials.) The reaction mixture was then evaporated in vacuo and the remaining brownish solid was boiled with EtOH (50ml) and filtered while hot to give 0.35g (22%) of **10** as yellow powder. Mp 318-319°C ^{1}H NMR δ: 7.92 (s,4H,ArH), 6.96-7.70 (m,35H,ArH,OH), 4.28 (s,4H,CH_2OCO), 4,17 (q,4H,CH_2O), 3.94, 3.07 (d,J=14Hz,8H,$ArCH_2$), 1.19 (t,6H,CH_3), 0.87 (s,18H,t-Bu), Anal. calcd. for $C_{90}H_{84}Cl_2N_2O_{16}$ (1520.56): C 71.09, H 5.57, N 1.84, Found: C 70.45, H 5.50, N 1.79. Positive FAB MS, *m/z (%)*: 1419 (100) $[C^2A]^+$, negative FAB MS, *m/z (%)*: 1617 (70) $[C^2A_3]^-$

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