CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200500878

Bis(calixcrown)tetrathiafulvalene Receptors

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Abstract: A new class of electroactive receptors has been synthesized, built by covalent association of five subunits: two calixarene platforms for spatial organization, two polyether 3D cavities for cation binding, and one electroactive TTF unit to probe the complexation event. Sodium complexation induces rigidification of the molecular assembly, as shown by ^{1}H NMR titration and single-crystal X-ray crystallographic studies on free receptor **14** and a corresponding complex with two bound sodium atoms per receptor (**15**-$(NaPF_6)_2$). The calixarene units in these receptors change from a pinched cone conformation in the free ligand to a symmetrical cone in the complex. Cyclovoltammetric studies validated the electrochemical recognition concept of these five-member assemblies.

Keywords: calixarenes · crown compounds · cyclic voltammetry · host–guest systems · receptors

Introduction

The tetrathiafulvalene (TTF) unit and its derivatives have been at the forefront of different research topics for more than thirty years. Besides the historical use as a precursor of solid-state electroconducting organic metals[1] and recent stimulating developments in exploring various other physical properties,[1,2] this electroactive unit has recently emerged as a very important redox brick in a great number of supramolecular systems,[3] such as catenanes, rotaxanes, pseudorotaxanes, and molecular shuttles, and also in dendrimer chemistry.[4] These systems benefit from the well-defined electrochemical properties of TTF derivatives, which are known to be reversibly and easily oxidized to stable $TTF^{\cdot+}$ and TTF^{2+} states.

We have been engaged for some years in the synthesis of electroactive receptors incorporating the TTF unit, designed to electrochemically sense or address the binding of a cationic guest.[5] These redox-responsive ligands are built from the covalent association of the TTF moiety with a specific binding unit. Although a broad variety of TTF derivatives have been synthesized by different groups, only in a few structures is the TTF unit associated with a rigid cavity, that is, cyclodextrin,[6] calixarene,[7] or resorcinarene[8] platforms.

In the course of our project devoted to the preparation of redox-responsive ligands, we recently illustrated the modularity of the calixarene scaffold with the synthesis of calixarene–TTF assemblies, linked either by aliphatic junctions as the first models towards redox receptors,[9] or by amide functions as molecular assemblies designed for anion recognition.[10]

More approaches to supramolecular receptors involving several cavities have been described during the past decade, in particular by covalent association of two or more calixarene units.[11] Besides their initial interest as synthetic targets with exotic geometries, such multicavity architectures may provide specific high-level host properties involving cooperative effects, otherwise not reachable with monocavity derivatives. On this basis, several types of linkers have been introduced between two or more calix[4]arene units; they range from simple aliphatic hydrocarbon chains to functionalized linkers.[11,12] Moreover, a few examples of electroactive units have been grafted to or inserted into the calixarene backbone, for example, ferrocene,[13] pyrrole,[14] thiophene,[15] *p*-quinone,[12a,16] or oligophenylenevinylene motifs.[17] In some cases, such units may allow coupling of recognition and conformational changes to redox perturbation.[11]

In the light of the structural properties of calixarenes, crown ethers, and TTF, we launched the project for con-

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Supporting information (^{1}H NMR chemical shifts of **10**–**15** (Table 1) and ^{1}H NMR titration data with Na^+ (Table 2)) for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

structing a novel family based on the above three members. Here we report on a family of double calix[4]arenes **10, 11** and their persubstituted analogues **12–15**, which are tethered by an electroactive TTF unit and have two three-dimensional (3D) cavities. To enhance the binding ability of intermediate receptors **10** and **11**, we introduced two additional metal-coordinating appendages per calixarene unit in **12–15** to give rise to 3D coordinating cavities. The calixarene scaffold is used here as a 3D promoter. Such cryptand-like behaviour is somewhat similar to what is encountered with the so-called bibracchial lariat ethers (BiBLE), in which the three-dimensional character of the cavity is promoted by a threefold substitution at the N junctions.[18]

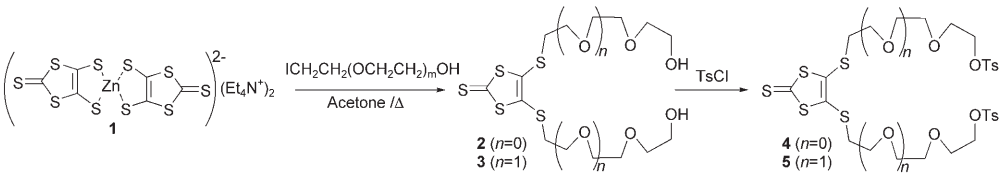
Herein we present 1) the synthesis of these novel five-unit assemblies (i.e., two calixarene platforms for spatial organization, two polyether 3D cavities for cation binding, and one electroactive TTF unit to probe the complexation event); 2) a ^{1}H NMR conformational study of **12–15** on Na^+ binding and the associated single-crystal X-ray structures of both a free receptor and a bound form incorporating two sodium cations; and 3) the electrochemical behaviour of target receptors **12–15**.

Results and Discussion

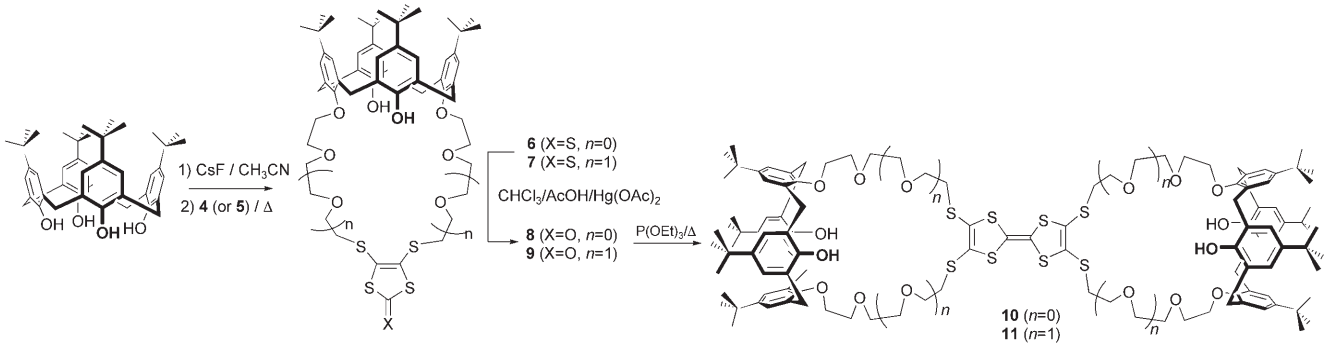
Synthesis: The synthetic route to target calix–crown–TTF assemblies **10–15** is outlined in Schemes 1–3. Thiones **2** and **3**, which incorporate two different poly(ethylene glycol) chains, were prepared in good yields from the bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol)zincate $[(TEA)_2[Zn(DMIT)_2]$ (**1**)],[19] by adapting a classical procedure,[20] and subsequently tosylated to produce **4** and **5** (Scheme 1). A key step in our strategy is the [1+1] cyclocondensation between **4** or **5** and the *p-tert*-butylcalix[4]arene molecule. This reaction was carried out in refluxing acetonitrile in the presence of cesium fluoride, used both as a weak base and as a cyclization template. In this way, calixthiones **6** and **7** were obtained in reasonable yields of 58 and 18% respectively. No evidence of any higher cyclocondensation macrocycles, oligomers, or regioisomers (only dialkylation on the 1,3-rings of the calix[4]arene moiety took place) was observed (Scheme 2).

A common procedure to build the TTF skeleton involves dimerization–desulfurization of 1,3-dithiol-2-thiones in the presence of trialkyl phosphite.[21] In our case, no coupling product was observed on refluxing **6** or **7** with triethyl phosphite. This problem was solved by converting the thioxo reagents to their oxo analogues **8** and **9** with mercuric acetate in chloroform/acetic acid (Scheme 2). Refluxing **8** and **9** with $P(OEt)_3$ afforded TTF derivatives **10** and **11**, disubstituted with calix[4]crown units, in 30 and 27% yield, respectively.

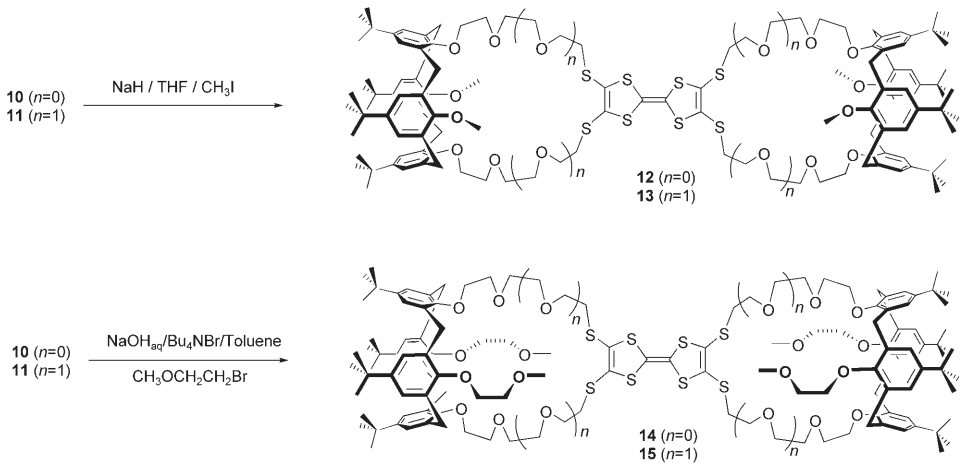
The final step to the target three-dimensional receptors **12–15** involves tetraalkylation of the free phenolic rings. The usual NaH/THF conditions and iodomethane[22] were employed to introduce four methyl groups into the lower rims of the calixarene units in **10** and **11** to produce **12** and **13** in 70 and 60% yield, respectively (Scheme 3). Attempts to prepare receptors **14** and **15** under the same conditions only afforded a mixture of mono-, di-, tri-, and tetraalkylated products when 2-bromoethyl methyl ether was employed. However, the use of phase-transfer conditions (toluene/50% aqueous NaOH/tetrabutylammonium bromide)[23] resulted in the target tetrasubstituted receptors **14** and **15** in 47 and 60% yield, respectively. Bis(calixcrown)tetrathiafulvalene



Scheme 1. Synthesis of the key 1,3-dithiol-2-thione intermediates.



Scheme 2. Synthesis of the calix–crown–TTF assemblies **10** and **11**.



Scheme 3. Synthesis of the target calix–crown–TTF assemblies **12**–**15**.

assemblies **10**–**15** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (MALDI and/or ESI).

Structural analysis: NMR study and single-crystal X-ray structures: Selected chemical shifts for calix–crown–TTF assemblies **10**–**15** are gathered in Table 1 (see Supporting Information). Both ^{1}H and ^{13}C NMR spectra indicate that the calixarene units in **10**, **11** and **14**, **15** only present in the cone conformation.[11,22b,23,24] In particular, a pair of doublets assigned to diastereotopic bridging methylene protons ($ArCH_aH_bAr$) is present in each case. This conformation is attributed to stabilization of the cone through intramolecular hydrogen bonds (H-bonds) between phenolic rings in the case of **10** and **11**,[11c,25] and to the bulkiness of the methoxyethyl substituents, which prevents interconversion between the different calixarene conformers for **14** and **15**.[26] Conversely, the methylated derivatives **12** and **13** exist as a mixture of conformers in slow exchange at room temperature on the 500 MHz timescale, as was already observed for 1,3-dimethoxy calix[4]arene crowns.[24,27] For **12** and **13**, the methyl group is not bulky enough to prevent rotation around the $ArCH_2Ar$ bridges. Therefore, Table 1 in the Supporting Information presents the chemical shifts assigned to the major conformers of **12** and **13**, which in each case correspond to the cone form.

Noteworthily, significant ^{1}H NMR spectral differences exist between the fully substituted derivatives **12**–**15** and their phenolic precursors **10** and **11.** It is known that in 1,3-bridged calix[4]arene derivatives, the degree of cone distortion can be correlated with the $\Delta\delta$ value observed between the two types of ArH protons.[28] On this basis, the calixarene cone appears essentially symmetrical for **10** and **11** ($\Delta\delta \approx 0.25$ ppm), whereas the $\Delta\delta$ values observed for **12**–**15** ($\Delta\delta \approx 0.60$ ppm) are indicative of distorted cone conformations. Such cone distortion from **10**, **11** to **12**–**15** can be ascribed to the steric requirement on *O*-alkylation, accompanied by the loss of H-bond stabilization between phenolic OH groups and O atoms located on adjacent phenoxyl moieties. Additionally, the flattening of the cone arising on alkylation is confirmed by the increase in the $\Delta\delta(ArCH_aH_bAr)$ value for **12**–**15** with respect to **10**–**11.**[29]

Slow evaporation of a solution of **14** in chloroform yielded crystals suitable for X-ray structure determination.[30] Host **14** has a crystallographic centre of symmetry at the middle of the central C=C bond of the TTF moiety (Figure 1). Each calixarene unit adopts a pinched cone conformation in the solid state, which confirms the distortion anticipated on the basis of solution NMR data. Within the same calixarene macrocycle, the phenyl rings intercept the mean plane defined by the four carbon atoms of the methyl-

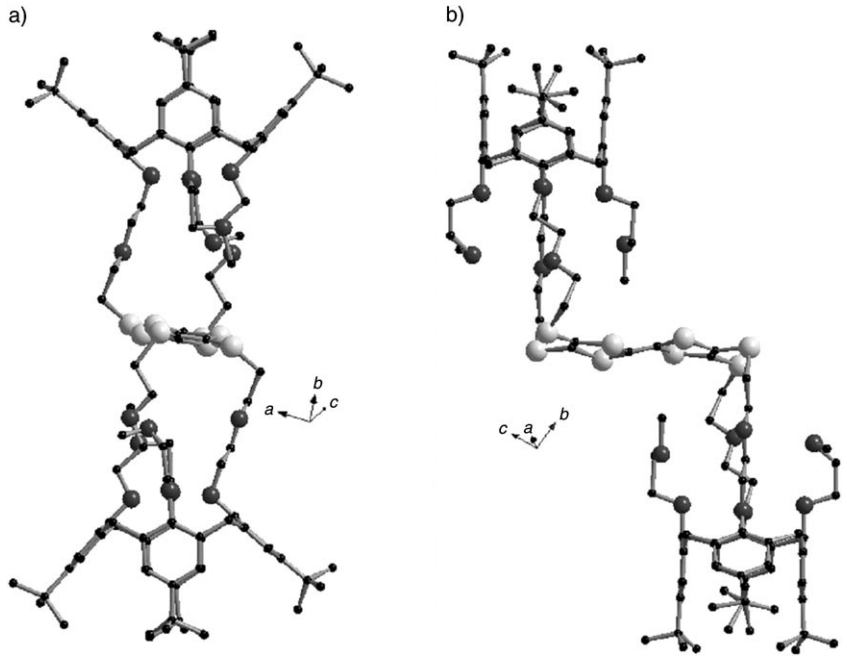


Figure 1. X-ray structure of calix–crown–TTF **14**.

ene bridges ($ArCH_2Ar$), with angles of about 68° (for phenoxyl groups linked to TTF) and about 90° (for phenoxyl groups with pendant chains). In other words, two opposite phenyl rings are perfectly parallel, whereas the other two are significantly tilted. The polyether junctions located between the TTF part and both calixarene units generate, in association with the four methoxyethyl pendant groups, two 3D cavities which are suitably organized to receive a guest metal cation. The TTF unit appears essentially planar, a requisite to retain its well-defined reversible redox properties. Finally, the two calixarene moieties are distributed on opposite sides of the TTF plane in the five-member assembly **14** (calix–crown–TTF–crown–calix).

^{1}H NMR binding study: Aliquots of sodium perchlorate in acetonitrile were added to a solution of receptors **12**–**15** in $CDCl_3/CD_3CN$ (1/1).

*Compounds **12** and **13***: Compounds **12** and **13** are conformationally flexible in solution at room temperature, and the ^{1}H NMR spectra of the free ligands show mixtures of conformers in solution, indicated in particular by the presence of inequivalent aryl residues in each calixarene unit. The signals of **12** and **13** are relatively broad until the $[Na^+]/[ligand]$ ratio reaches unity. Stabilization of just one conformation is obtained after the addition of 2.00 equivalents of Na^+. Then the spectra simplify significantly and the signals become sharper, which indicates that a tight and stable sodium complex is formed and has the cone conformation. The high symmetry of the cone in the complex is shown by the equivalence of the signals of all aryl residues. No additional changes are observed for the ^{1}H NMR signals of the sodium complexes of **12** or **13** on addition of more than 2.00 equivalents of Na^+, which indicates a 1:2 stoichiometry for these complexes. Table 2 in the Supporting Information presents some selected ^{1}H NMR chemical shifts of calix–crown–TTF assemblies **12** and **13** ($CDCl_3/CH_3CN$) before and after complexation with $NaClO_4$. The high symmetry of the calixarene cone cavity in the sodium complexes of **12** and **13** is clearly illustrated by the $\Delta\delta$ values observed for the aromatic and *tert*-butyl protons, which drop from about 0.39 (ArH) and 0.30 ppm (*t*Bu) for the free ligands in cone conformation to 0.01 ppm for each sodium complex.

*Compounds **14** and **15***: The calixarene units of free receptors **14** and **15** exclusively exist in the C_2-symmetrical cone conformation, in which the two distal aromatic units are flattened and their interconversion is relatively slow on the NMR timescale. In Table 2 in the Supporting Information, this is in particular illustrated by the large $\Delta\delta$ values for both aromatic and *tert*-butyl protons. The addition of controlled amounts of $NaClO_4$ to solutions of **14** or **15** causes the progressive appearance of a new set of signals for the bound receptor and concomitant disappearance of the free-ligand signals. An illustrative example is given in Figure 2,

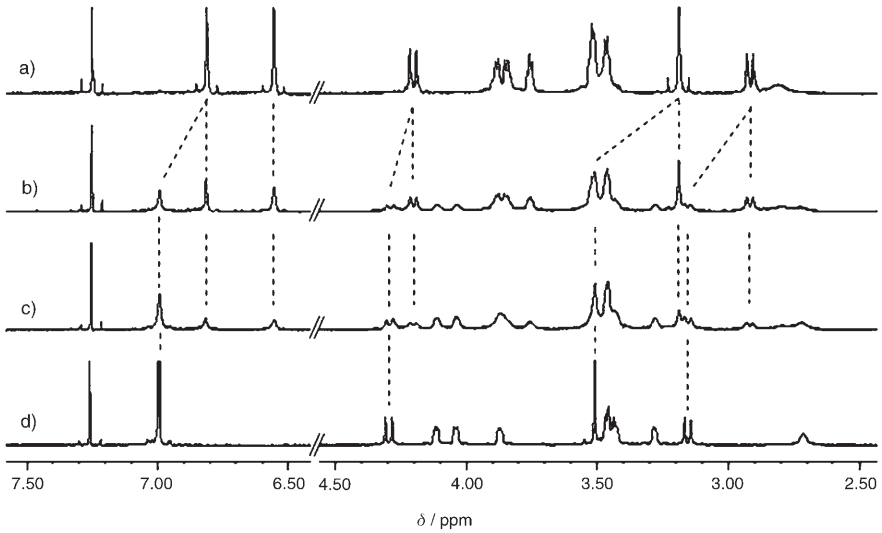


Figure 2. ^{1}H NMR spectra of **15** ($CDCl_3/CD_3CN$) in the presence of $NaClO_4$: a) $[Na^+]/[\mathbf{15}]=0.0$; b) $[Na^+]/[\mathbf{15}]=0.5$; c) $[Na^+]/[\mathbf{15}]=1.0$; d) $[Na^+]/[\mathbf{15}]=2.0$.

which shows the ^{1}H NMR spectra of **15**, without and with $NaClO_4$. Addition of sodium leads to a significant decrease in these $\Delta\delta$ values (to 0.01–0.02 ppm), which confirms the formation of symmetrical cone cavities in the sodium complexes. Moreover, sharpening of the signals is observed, which points to formation of tight and stable complexes with Na^+.

Additionally, one can observe a significant low-field shift (+0.31 ppm) of the singlet corresponding to the terminal OCH_3 group of the methoxyethyl appendages. This observation illustrates the complementary contribution of these pendant groups to binding of the sodium cation, besides the polyoxyethylene linkers located between the TTF and calixarene moieties.

Further binding studies were carried out with barium perchlorate. No evidence of complexation could be observed from the ^{1}H NMR data in this case, which illustrates the selectivity of receptors **14** and **15** towards Na^+ with respect to Ba^{2+}.

Crystal structure of a disodium complex of a bis(calixcrown)TTF: Single crystals for an X-ray diffraction study[31] on a sodium complex of a bis(calixcrown)TTF assembly were obtained by slow evaporation of a solution of **15** in CH_2Cl_2/CH_3CN in the presence of $NaPF_6$ (CH_3OH). As expected, two sodium atoms are bound per receptor (Figures 3

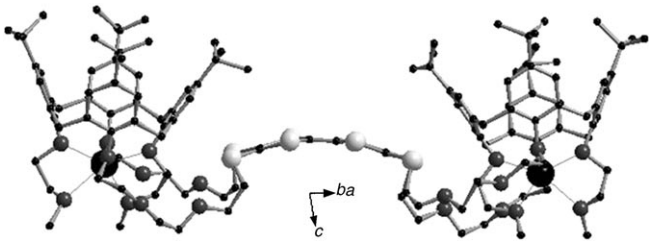


Figure 3. X-ray crystal structure of **15**-$(NaPF_6)_2(CH_2Cl_2)$ (solvent molecule and anions omitted).

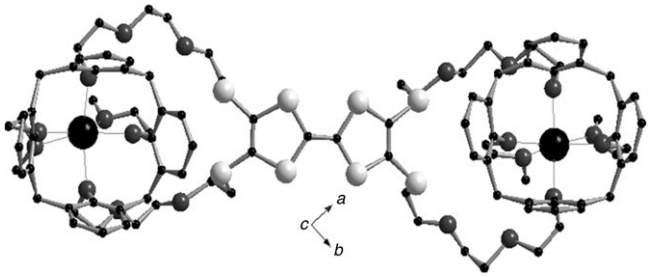


Figure 4. X-ray crystal structure of **15**-$(NaPF_6)_2(CH_2Cl_2)$ (solvent molecule, anions, and *t*Bu groups omitted).

and 4). The complex **15**-$(NaPF_6)_2$ crystallizes in the space group $P\bar{1}$ with one molecule of solvent (CH_2Cl_2). The cone conformation observed in solution by ^{1}H NMR spectroscopy for both calixarene units of **15** is also observed in the solid state. Contrary to free receptor **14**, both calixarene moieties are on the same side of the TTF plane in **15**-$(NaPF_6)_2$, with both cone axes at approximately 90° to the TTF plane. Another noticeable difference between the free receptor and the sodium complex lies in the degree of symmetry of both cones. In the complex, the four phenyl groups of each calixarene unit are tilted by 56–66° relative to the mean plane defined by the four methylene carbon atoms. Therefore, whereas the free ligand **14** shows a pinched cone conformation for both calixarene units (Figure 1), the disodium complex of **15** exhibits essentially two symmetrical cones, as anticipated from the ^{1}H NMR data, for which complexation of sodium ions results in simplification of the spectrum.

Each sodium cation of **15**-$(NaPF_6)_2$ is hexacoordinated by four phenolic oxygen atoms of the calixarene platform and two O atoms of pendant methoxyethyl fragments. Neither anion nor solvent molecule participates in metal coordination. Five Na–O distances per calixarene unit are in the range of 2.33(3)–2.51(3) Å, while the sixth, which involves one ethoxyethyl fragment, is slightly longer (2.70(4) Å). Therefore, and in opposition to X-ray data obtained for another calix[4]arene-based sodium complex incorporating methoxyethyl pendant arms,[32] the appended methoxyethyl groups of **15** clearly participate in sodium complexation, giving rise to the expected 3D cavity in which the sodium cation is isolated. To the best of our knowledge, this X-ray structure is the first example of a disodium complex in the calixcrown series; moreover, it establishes a cryptand-like binding cavity, similar to what is observed with bibracchial lariat ethers, for which the 3D character of metal binding is promoted by the added contributions of a crown ether part and two appended polyether arms.[18]

Electrochemical study: The electrochemical behaviour of bis(calix-crown)TTF assemblies **12**–**15** was investigated by cyclic voltammetry (CV) in dichloromethane/acetonitrile (1/1). Derivatives of TTF are well known to undergo two successive reversible one-electron redox processes. Compounds **12**–**15** behave similarly and exhibit the expected two successive redox processes in the usual range of potentials, that is, very similar to those of the parent $TTF(SMe)_4$ molecule. Figure 5 shows a representative example for compound **13**.

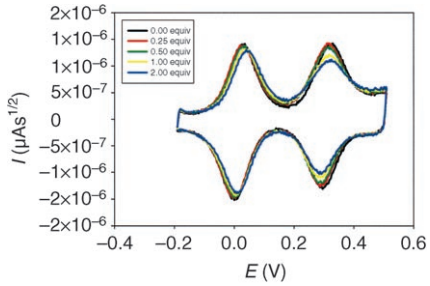


Figure 5. Deconvoluted CV of **13** (0.26 mM) in $CH_3CN/CH_2Cl_2/TBAPF_6$ (0.10 M) in the presence of increasing amounts of $NaClO_4$; Pt electrode (⌀ 1.6 mm, $v = 100$ mV s^{-1}, versus Fc^+/Fc).

The first redox process corresponds to reversible oxidation to a stable cation-radical state ($E_1^{1/2} = 0.04$ V versus ferrocene). The second ($E_2^{1/2} = 0.34$ V) is assigned to oxidation to the dicationic state. As shown by ^{1}H NMR studies, these calix-crown-TTF-assemblies are able to bind two equivalents of sodium cation per molecule. Therefore, we studied the electrochemical response of these compounds on progressive addition of a sodium perchlorate solution. No clear evidence of electrochemical recognition of Na^+ could be observed for bis(calixcrown)TTF assemblies **12**, **14**, and **15**. However, the CV response of receptor **13** exhibits a slight progressive positive shift of E_{pa1} (+30 mV) from zero to two equivalents of added Na^+ (Figure 5). No further variation of potential is observed for higher concentrations of $NaClO_4$, in accordance with saturation of the system. Such electrochemical recognition process can be associated with both conformational changes arising on Na^+ complexation (as shown by the ^{1}H NMR titration study) and to the electronic effect of the bound cation on the electroactive TTF unit, as is usually observed with redox-responsive ligands (the electroactive TTF unit becomes more difficult to oxidize when a positively charged guest is close).[5a,33] Interestingly, the second redox process ($E_2^{1/2}$) remains unchanged on addition of Na^+, that is, the metal complex no longer exists at this potential. This is usually attributed to repulsive electrostatic interactions between the ligand and the metal cation when the TTF moiety is positively charged.[5a,33]

Conclusion

In conclusion, we have developed a synthetic route to the first electroactive calix–crown–TTF receptors. Their binding ability for Na^+ has been studied by ^1H NMR titration, which demonstrated pronounced conformational reorganization on going from the free receptors to the sodium complexes. Two cations are coordinated per TTF-based assembly. The same observations were made in the solid-state, since X-ray structures could be solved for a free receptor and a disodium complex. Both metal cations are located in 3D pockets generated between the calixarene scaffold and the TTF redox unit. The electrochemical behaviour (cyclic voltammetry) of these five-membered assemblies (i.e., two calixarene platforms, two 3D polyether cavities, and one electroactive TTF unit) is similar to that of classical TTF derivatives, and an electrochemical response to Na^+ complexation by a bis-calixcrown–TTF assembly could be detected.

Experimental Section

Instruments: ^1H (500.13 MHz) and ^{13}C NMR (125.75 MHz) spectra were recorded on a Bruker AVANCE DRX 500 spectrometer. Chemical shifts δ are expressed in ppm relative to tetramethylsilane (TMS). Mass spectra were recorded on a Bruker BIFLEX III (MALDI-TOF) spectrometer or on a JEOL JMS 700 B/ES (ESI) spectrometer. Cyclic voltammetry (CV) experiments were carried out on a potentiostat–galvanostat EG&G PARK 273 A, with solvents and electrolyte of electrochemical grade. CV experiments were carried out at 298 K in a conventional three-electrode cell equipped with a Pt disk working electrode (∅ 1 mm), a Pt wire counterelectrode, and a reference electrode. All potentials are reported versus the ferrocinium/ferrocene redox couple, and the electrochemical response of ferrocene was recorded before and after each experiment.

X-ray diffraction study: X-ray single-crystal diffraction data were collected at 293 K on a STOE-IPDS diffractometer for **14** and on a Bruker-Nonius KappaCCD diffractometer for **15**-$(NaPF_6)_2(CH_2Cl_2)_1$, both equipped with a graphite monochromator utilizing $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structure were solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELX97 package.[34] For **14**, S and O atoms were refined anisotropically and C atoms isotropically, absorption was corrected by multiscan technique and the H atoms were included in the calculation without refinement. For **15**-$(NaPF_6)_2$-$(CH_2Cl_2)_1$, S atoms were refined anisotropically and all others atoms isotropically, absorption correction was carried out with SADABS[35] and the H atoms were included in the calculation without refinement. For both molecules, there are statistical disorders on most of the *tert*-butyl groups, which were not treated because of missing data. CCDC-278002 and CCDC-278003 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.

Materials: Unless otherwise noted, solvents and starting materials were commercially available and used without further purification. ^1H NMR titration studies were carried out by adding small volumes of concentrated solutions of the metal cation (as the perchlorate salt) in [D_3]acetonitrile to a solution of the calixarene receptor (1–3 mM) in $CDCl_3/CD_3CN$ (1/1).

1,3-Dithiol-2-thiones 2 and 3: 2-Chloroethoxyethanol or 2-[2-(2-chloroethoxy)ethoxy]ethanol (5.9 mmol) and NaI (1.33 g, 8.9 mmol) were dissolved in acetone (30 mL) and heated to reflux for 7 h. The mixture was cooled to room temperature, whereupon $(TEA)_2[Zn(DMIT)_2]$ (**1**, 0.860 g, 1.2 mmol) was added and the mixture was refluxed for 24 h. The mixture was concentrated, and the residue dissolved in CH_2Cl_2 (30 mL), washed with water (60 mL), dried with $MgSO_4$ and purified on a silica gel column to give **2** (CH_2Cl_2/AcOEt (1/2) then CH_2Cl_2/MeOH (20/1)) and **3** (CH_2Cl_2/MeOH (25/1)) as transparent red-orange oils. **2** (n = 0): Yield 80%; ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 3.75–3.59 (m, 12H; OCH_2), 3.10 (t, J = 5.9 Hz, 4H; SCH_2), 2.64 ppm (br, 2H; OH); IR (KBr): $\tilde{\nu}$ = 1790 cm^{-1}. **3** (n = 1): Yield 78%; ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 3.75–3.59 (m, 20H; OCH_2), 3.08 (t, J = 6.3 Hz, 4H; SCH_2), 2.64 ppm (br, 2H; OH)

Tosylate derivatives 4 and 5: Triethylamine (2.5 g, 25.5 mmol) dissolved in CH_2Cl_2 (5 mL) was added dropwise over 30 min to a solution of **2** or **3** (4.0 mmol) and TsCl (2.50 g, 13.1 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at room temperature under N_2 for 24 h. The organic phase was washed with water, dried over $MgSO_4$ and evaporated to yield an oily residue, which was purified by chromatography on a silica column with petroleum ether/CH_2Cl_2 (gradient) to give **4** and **5** as red-orange sticky oils. **4** (n = 0): Yield 75%; ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.79 (d, J = 8.3 Hz, 4H; ArH), 7.34 (d, J = 8.3 Hz, 4H; ArH), 4.15 (t, J = 4.8 Hz, 4H; OCH_2), 3.70–3.64 (m, 8H; OCH_2), 3.00 (t, J = 6.2 Hz, 4H; SCH_2), 2.46 ppm (s, 6H; CH_3). **5** (n = 1): Yield 72%; ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.79 (d, J = 8.3 Hz, 4H; ArH), 7.34 (d, J = 8.3 Hz, 4H; ArH), 4.15 (t, J = 4.8 Hz, 4H; OCH_2), 3.70–3.66 (m, 8H; OCH_2), 3.57 (t, J = 4.8 Hz, 8H; OCH_2), 3.05 (t, J = 6.3 Hz, 4H; SCH_2), 2.44 ppm (s, 6H; CH_3).

Calix-1,3-dithiole-2-thiones 6 and 7: A suspension of *p*-tert-butylcalix[4]-arene (1.520 g, 2.3 mmol) and CsF (1.778 g, 11.7 mmol) in dry CH_3CN (100 mL) was refluxed for 1 h. Then a solution of **4** or **5** (2.3 mmol) in dry CH_3CN (100 mL) was slowly added over 8 h. The mixture was refluxed for 24 h before the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ and brine was added. The organic layer was separated and dried over $MgSO_4$. The crude product obtained after evaporation of the solvent was purified by flash chromatography (gradient of CH_2Cl_2/AcOEt) to give **6** (from **4**) and **7** (from **5**) as orange powders. **6** (n = 0): Yield 58%; m.p. 97–104 °C; ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.22 (s, 2H; OH), 7.05 (s, 4H; ArH), 6.78 (s, 4H; ArH), 4.32 (d, J = 13.0 Hz, 4H; $ArCH_2Ar$), 4.12 (t, J = 4.2 Hz, 4H; OCH_2), 4.04–3.99 (m, 8H; OCH_2), 3.31 (d, J = 13.0 Hz, 4H; $ArCH_2Ar$), 3.22 (t, J = 6.2 Hz, 4H; SCH_2), 1.29 (s, 18H; $C(CH_3)_3$), 0.95 ppm (s, 18H; $C(CH_3)_3$); ^{13}C NMR (125.75 MHz, $CDCl_3$, 298 K): δ = 211.3, 150.5, 149.7, 147.0, 141.5, 137.4, 132.5, 127.8, 125.7, 125.6, 125.1, 75.5, 70.0, 36.4, 33.9, 33.8, 31.7, 31.5, 31.4, 31.3, 31.0 ppm; FTIR (KBr): $\tilde{\nu}$ = 3447.8 (OH), 1067.6 cm^{-1} (C=S); MS (MALDI-TOF): m/z: 987 [$M^{\cdot+}$]. **7** (n = 1): Yield 18%; m.p. 90–91 °C; ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.11 (s, 2H; OH), 7.05 (s, 4H; ArH), 6.75 (s, 4H; ArH), 4.34 (d, J = 13.0 Hz, 4H; $ArCH_2Ar$), 4.12 (t, J = 4.2 Hz, 4H; OCH_2), 3.97 (t, J = 4.2 Hz, 4H; OCH_2), 3.92 (t, J = 4.2 Hz, 4H; OCH_2), 3.78–3.75 (m, 8H; OCH_2), 3.29 (d, J = 13.0 Hz, 4H; $ArCH_2Ar$), 3.01 (t, J = 5.9 Hz, 4H; SCH_2), 1.29 (s, 18H; $C(CH_3)_3$), 0.92 ppm (s, 18H; $C(CH_3)_3$); ^{13}C NMR (125.75 MHz, $CDCl_3$, 298 K): δ = 211.4, 150.6, 149.7, 146.9, 141.4, 136.9, 132.5, 127.8, 125.5, 125.0, 75.8, 71.1, 71.0, 70.2, 69.9, 36.3, 33.9, 33.8, 31.7, 31.4, 31.0, 30.9 ppm; FTIR (KBr): $\tilde{\nu}$ = 3448.7 (OH), 1066.0 cm^{-1} (C=S); ESI-MS: m/z (%): 1075.35 [M^++H] (100).

Calix-1,3-dithiole-2-ones 8 and 9: A mixture of **6** (or **7**) (0.3 mmol) in a chloroform/acetic acid solution (20 mL/15 mL) and mercuric acetate (0.640 g, 2.0 mmol) was stirred under N_2 at room temperature for 6 h. The resulting white precipitate was filtered off on Celite and washed thoroughly with $CHCl_3$ (60 mL). The combined organic phases were washed with $NaHCO_3$ solution and water and then dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified on a silica gel column (CH_2Cl_2/AcOEt (5/1) to give **8** (from **6**) or **9** (from **7**) as a yellow powder. **8** (n = 0): Yield 80%; ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.31 (s, 2H; OH), 7.05 (s, 4H; ArH), 6.80 (s, 4H; ArH), 4.32 (d, J = 13.0 Hz, 4H; $ArCH_2Ar$), 4.12 (t, J = 4.7 Hz, 4H; OCH_2), 4.04 (t, J = 4.7 Hz, 4H; OCH_2), 4.00 (t, J = 6.3 Hz, 4H; OCH_2), 3.31 (d, J = 13.0 Hz, 4H; $ArCH_2Ar$), 3.18 (t, J = 6.3 Hz, 4H; SCH_2), 1.29 (s, 18H; $C(CH_3)_3$), 0.96 ppm (s, 18H; $C(CH_3)_3$); ^{13}C NMR (125.75 MHz, $CDCl_3$, 298 K): δ = 189.7, 150.5, 149.6, 147.0, 141.4, 132.6, 128.2, 127.7, 125.6, 125.1, 75.3, 70.0, 69.9, 36.1, 33.9, 33.8, 31.7, 31.5, 31.0 ppm; FTIR (KBr): $\tilde{\nu}$ = 3410.9 (OH), 1673.3 cm^{-1} (C=O); MS (MALDI-TOF): m/z: 970.06 [$M^{\cdot+}$]. **9** (n = 1): Yield 100%; m.p. 112 °C; ^1H NMR (500 MHz, $CDCl_3$,

298 K): $\delta = 7.15$ (s, 2H; OH), 7.05 (s, 4H; ArH), 6.75 (s, 4H; ArH), 4.34 (d, $J = 13.0$ Hz, 4H; $ArCH_2Ar$), 4.12 (t, $J = 4.6$ Hz, 4H; OCH_2), 3.98 (t, $J = 4.6$ Hz, 4H; OCH_2), 3.92 (t, $J = 4.2$ Hz, 4H; OCH_2), 3.77–3.74 (m, 8H; OCH_2), 3.29 (d, $J = 13.0$ Hz, 4H; $ArCH_2Ar$), 2.99 (t, $J = 4.1$ Hz, 4H; SCH_2), 1.29 (s, 18H; $C(CH_3)_3$), 0.93 ppm (s, 18H; $C(CH_3)_3$); ^{13}C NMR (125.75 MHz, $CDCl_3$, 298 K): $\delta = 189.7$, 150.6, 149.7, 146.8, 141.3, 132.4, 128.0, 127.6, 125.4, 125.0, 75.7, 71.1, 70.9, 70.1, 69.8, 53.3, 36.1, 33.8, 31.8, 31.7, 31.4, 30.9 ppm; FTIR (KBr): $\tilde{\nu} = 3398.5$ (OH), 1670.3 cm^{-1} (C=O); ESI-MS: m/z (%): 1081.7 [$M^{\cdot+}$+Na] (100); HR-ESI-MS: m/z: 1081.4442 [$M^{\cdot+}$+Na], calcd for $C_{59}H_{78}O_9S_4Na$: 1081.4426.

Bis(calix-crown)tetrathiafulvalenes 10 and 11: A suspension of **8** or **9** (0.30 mmol) in freshly distilled triethyl phosphite (5 mL) under N_2 was heated to reflux for 7 h. After cooling to room temperature, cold methanol (50 mL) was added and the yellow precipitate which appeared was washed with methanol and purified by a column chromatography on silica gel to give pure **10** (CH_2Cl_2) (from **8**) or **11** (CH_2Cl_2/AcOEt 10/1) (from **9**) as an orange powder. **10** ($n = 0$): Yield 27%; m.p. 170°C; ^1H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 7.44$ (s, 2H; OH), 7.05 (s, 4H; ArH), 6.83 (s, 4H; ArH), 4.34 (d, $J = 13.0$ Hz, 4H; $ArCH_2Ar$), 4.13–4.08 (m, 8H; OCH_2), 3.96 (t, $J = 6.4$ Hz, 4H; OCH_2), 3.31 (d, $J = 13.0$ Hz, 4H; $ArCH_2Ar$), 3.14 (t, $J = 6.4$ Hz, 4H; SCH_2), 1.28 (s, 18H; $C(CH_3)_3$), 0.98 ppm (s, 18H; $C(CH_3)_3$); ^{13}C NMR (125.75 MHz, $CDCl_3$, 298 K): $\delta = 150.6$, 149.6, 146.9, 141.3, 132.6, 128.6, 127.8, 125.5, 125.0, 110.2, 75.3, 70.2, 69.2, 65.8, 35.4, 33.9, 33.8, 31.7, 31.5, 30.8 ppm; FTIR (KBr): $\tilde{\nu} = 3413.2$ cm^{-1} (OH); MS (MALDI-TOF): m/z: 1909 [$M^{\cdot+}$]; HR-ESI-MS: m/z: 1931.7979 [$M^{\cdot+}$+Na], calcd for $C_{110}H_{140}O_{12}S_8Na$: 1931.8008. **11** ($n = 1$): Yield 27%; m.p. 108°C; ^1H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 7.26$ (s, 2H; OH), 7.04 (s, 4H; ArH), 6.78 (s, 4H; ArH), 4.35 (d, $J = 13.0$ Hz, 4H; $ArCH_2Ar$), 4.12 (t, $J = 4.4$ Hz, 4H; OCH_2), 3.99 (t, $J = 4.4$ Hz, 4H; OCH_2), 3.92 (t, $J = 4.6$ Hz, 4H; OCH_2), 3.76 (t, $J = 4.6$ Hz, 4H; OCH_2), 3.70 (t, J = 6.2 Hz, 4H; SCH_2), 3.29 (d, J = 13.0 Hz, 4H; $ArCH_2Ar$), 2.99 (t, $J = 4.1$ Hz, 4H; SCH_2), 1.29 (s, 18H; $C(CH_3)_3$), 0.93 cm^{-1} (s, 18H; $C(CH_3)_3$); ^{13}C NMR (125.75 MHz, $CDCl_3$, 298 K): $\delta = 150.5$, 149.7, 146.8, 141.3, 132.5, 128.1, 127.8, 125.4, 124.9, 110.2, 75.7, 70.9, 70.8, 70.1, 69.7, 35.5, 33.8, 33.7, 31.6, 31.4, 30.9, 30.8 cm^{-1}; FTIR (KBr): $\tilde{\nu} = 3432.99$ cm^{-1} (OH); MS (MALDI-TOF): m/z: 2085.9 [$M^{\cdot+}$+H]; HR-ESI-MS: m/z: 2084.9150 [$M^{\cdot+}$], calcd for $C_{118}H_{156}O_{16}S_8$: 2084.9159.

Tetramethylated bis(calixcrown)tetrathiafulvalenes 12 and 13: Iodomethane (0.25 mL, 4.00 mmol) was added to a solution of **10** or **11** (0.04 mmol) and NaH (0.051 g, 1.3 mmol) in dry THF (10 mL). The mixture was stirred for 24 h at room temperature under N_2. The reaction was quenched with water (1 mL) and the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with water (30 mL), and the organic phase was separated and dried over $MgSO_4$. The residue was purified by chromatography on silica gel (petroleum ether/THF 10/2) to give **12** (from **10**) and **13** (from **11**). **12** ($n = 0$): Yield 70%; m.p. 186°C; ^1H NMR (500 MHz, $CDCl_3$, 298 K), cone conformer: $\delta = 7.10$ (s, ArH), 6.46 (s, ArH), 4.36 (d, $J = 12.5$ Hz, $ArCH_2Ar$), 4.07 (s, OCH_3), 3.13 (d, $J = 12.5$ Hz, $ArCH_2Ar$), 1.32 (s, $C(CH_3)_3$), 0.82 (s, $C(CH_3)_3$); other conformers are observed: $\delta = 7.18$ (s, ArH), 7.00 (s, ArH), 6.92 (s, ArH), 6.69 (s, ArH), 3.41 (s, OCH_3), 3.10 (s, OCH_3), 1.55 (s, $C(CH_3)_3$), 1.42 (s, $C(CH_3)_3$), 1.26 (s, $C(CH_3)_3$), 1.09 ppm (s, $C(CH_3)_3$). The ^1H NMR spectrum is simplified on addition of 2 equivalents of $NaClO_4$ (**12**/$NaClO_4$ complex, which only exists in a cone conformation): ^1H NMR (500 MHz, $CDCl_3/CD_3CN$ 1/1 + 4 equivalents $NaClO_4$, 298 K): $\delta = 7.26$ (s, 8H; ArH), 7.25 (s, 8H; ArH), 4.19 (d, $J = 12.5$ Hz; 8H; $ArCH_2Ar$), 4.13 (t, 8H; $ArOCH_2$), 4.07 (t, 16H; CH_2OCH_2), 3.92 (s, 12H; OCH_3), 3.47 (d, $J = 12.5$ Hz, 8H; $ArCH_2Ar$), 3.28 (t, 8H; SCH_2), 1.18 (s, 36H; $C(CH_3)_3$, 1.17 ppm (s, 36H; $C(CH_3)_3$); FTIR on free **12** (KBr, cm^{-1}): $\tilde{\nu} = 2962$, 2867, 1482, 1121; MS (MALDI-TOF): m/z: 1965.11 [$M^{\cdot+}$]; HR-ESI-MS: m/z: 1987.8717 [$M^{\cdot+}$+Na], calcd for $C_{114}H_{148}O_{12}S_8Na$: 1988.8666. **13** ($n = 1$): Yield 60%; m.p. 105–115°C; ^1H NMR (500 MHz, $CDCl_3$, 298 K), cone conformer: $\delta = 7.11$ (s, ArH), 6.44 (s, ArH), 4.37 (d, $J = 12$ Hz, $ArCH_2Ar$), 4.00 (s, OCH_3), 3.04 (d, $J = 12$ Hz, $ArCH_2Ar$), 1.05 (s, $C(CH_3)_3$), 0.81 ppm (s, $C(CH_3)_3$); other conformers are observed: $\delta = 7.22$ (s, ArH), 7.04 (s, ArH), 6.90 (s, ArH), 6.59 (s, ArH), 3.29 (OCH_3) 2.95 (OCH_3), 1.43 ($C(CH_3)_3$), 1.33 ppm ($C(CH_3)_3$). The ^1H NMR spectrum is simplified on addition of 2 equivalents of $NaClO_4$ (**13**/$NaClO_4$ complex, which only exists in a cone conformation): ^1H NMR (500 MHz, $CDCl_3/CD_3CN$ 1/1 + 4 equivalents $NaClO_4$, 298 K): $\delta = 7.26$ (s, 8H; ArH), 7.25 (s, 8H; ArH), 4.26 (d, $J = 12$ Hz, 8H; $ArCH_2Ar$), 4.14 (t, 8H; $ArOCH_2$), 4.04 (t, 16H; CH_2OCH_2), 3.80 (t, 8H; CH_2OCH_2) 3.93 (s, 12H; OCH_3), 3.74 (t, 16H; CH_2OCH_2), 3.46 (d, $J = 12$ Hz, 8H; $ArCH_2Ar$), 3.06 (t, 8H; SCH_2), 1.19 (s, 36H; $C(CH_3)_3$), 1.18 ppm (s, 36H; $C(CH_3)_3$); FTIR on free **13** (KBr): $\tilde{\nu} = 2960$, 2867, 1482, 1120 cm^{-1}; MS (MALDI-TOF): m/z: 2143.48 [$M^{\cdot+}$]; HR-ESI-MS: m/z: 2163.9658 [$M^{\cdot+}$+Na], calcd for $C_{122}H_{164}O_{16}S_8Na$: 2163.9683.

Tetrakis(methoxyethyl)bis(calix-crown)tetrathiafulvalenes 14 and 15: A mixture of calixarene **10** or **11** (0.1 mmol), 2-bromoethyl methyl ether (0.198 mL, 2.1 mmol) and Bu_4NBr (0.006 g) in a two-phase solution (toluene (5 mL)/NaOH (50%, aq, 1 mL)) was vigorously stirred at 100°C for 6 h. After the mixture had been cooled, water (10 mL) was added and the organic phase was separated and washed with 1N HCl and water. The toluene solution was dried over $MgSO_4$ then evaporated to dryness. The solid residue was washed with MeOH and purified by column chromatography on silica gel to afford **14** (CH_2Cl_2/THF 60/1) or **15** (CH_2Cl_2, CH_2Cl_2/AcOEt (10/1), toluene/acetone (10/1)) as an orange solid. **14** ($n = 0$): Yield 50%; m.p. 162°C; ^1H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 7.11$ (s, 8H; ArH), 6.45 (s, 8H; ArH), 4.37 (d, $J = 13$ Hz, 8H; $ArCH_2Ar$), 4.20 (br t, 16H; $ArOCH_2$), 3.88–3.76 (m, 24H; CH_2OCH_2), 3.47 (s, 12H; OCH_3), 3.11 (d, $J = 13$ Hz, 8H; $ArCH_2Ar$), 3.05 (br t, 8H; SCH_2), 1.34 (s, 36H; $C(CH_3)_3$), 0.81 ppm (s, 36H; $C(CH_3)_3$); ^{13}C NMR (125.75 MHz, $CDCl_3$, 298 K): $\delta = 154.3$, 151.8, 154.2, 144.3, 135.6, 131.9, 127.8, 125.4, 124.6, 110.0, 74.1, 72.1, 71.7, 69.7, 69.7, 69.3, 58.7, 34.9, 34.0, 34.0, 33.5, 31.7, 31.5, 30.7 ppm; FTIR (KBr): $\tilde{\nu} = 1123$ cm^{-1}; MS (MALDI-TOF): m/z: 2140.67 [$M^{\cdot+}$]; HR-ESI-MS: m/z: 2163.9690 [$M^{\cdot+}$+Na], calculated for $C_{122}H_{164}O_{16}S_8Na$: 2164.9715. **15** ($n = 1$): Yield 60%; m.p. 108–112°C; ^1H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 7.00$ (s, 8H; ArH), 6.54 (s, 8H; ArH), 4.44 (d, $J = 13$ Hz, 8H; $ArCH_2Ar$), 4.18 (t, $J = 2.8$ Hz, 8H; $ArOCH_2$), 4.13 (t, $J = 4.8$ Hz, 8H; $ArOCH_2$), 3.60 (t, $J = 4.9$ Hz, 8H; SCH_2), 3.80 (m, 40H; CH_2OCH_2), 3.45 (s, 12H; OCH_3), 3.10 (d, $J = 13$ Hz, 8H; $ArCH_2Ar$), 1.25 (s, 36H; $C(CH_3)_3$), 0.89 ppm (s, 36H; $C(CH_3)_3$); FTIR (KBr): $\tilde{\nu} = 2961$, 1480, 1123 cm^{-1}; MS (MALDI-TOF): m/z: 2318.60 [$M^{\cdot+}$], 2341.52 [$M^{\cdot+}$+Na].

Acknowledgement

The "Conseil Régional des Pays de la Loire" is gratefully acknowledged for postdoctoral fellowships (B.T.Z. and M.J.B) as well as the "Programa Europa XXI"CAI-DGA-CONSID + I (M.J.B.). M.J.B. thanks the CNRS for a three-month position of associated researcher. The SCAS of the University of Angers is thanked for spectroscopic characterization. M.S. thanks the Institut Universitaire de France (IUF) for its financial support.

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[31] Crystal data for **15**-$(NaPF_6)_2(CH_2Cl_2)_1$: $C_{131}H_{182}Cl_2F_{12}Na_2O_{20}P_2S_8$, $M_r = 2740.07$, yellow plate, $0.23 \times 0.22 \times 0.015$ mm, triclinic, space group $P\bar{1}$, $a = 12.580(3)$, $b = 23.707(4)$, $c = 26.164(6)$ Å, $\alpha = 84.93(2)$, $\beta = 80.85(2)$, $\gamma = 86.36(2)°$, $V = 7664(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.187$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.249$ mm^{-1}, $F(000) = 2900$, $\theta_{min} = 2.10°$, $\theta_{max} = 20.00°$, 40916 reflections collected, 12959 unique ($R_{int} = 0.17$), restraints/parameters 3/761, $R1 = 0.2376$ and $wR2 = 0.5268$ for 5929 reflections with $I > 2\sigma(I)$, $R1 = 0.3565$ and $wR2 = 0.5845$ for all data, GOF 1.821, $-0.870 < \Delta\rho < 1.918$ e Å^{-3}.

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Received: July 25, 2005
Published online: January 18, 2006

