Monitoring the formation of TTF dimers by Na$^+$ complexation†

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The formation of the two dimeric species [(TTF)$_2$]$^{+\bullet}$ and (TTF$^{+\bullet}$)$_2$ can be monitored by complexation of Na$^+$ on a calix[4]arene–TTF assembly.

Tetrathiafulvalene derivatives have been extensively studied for decades for their ability to generate organic materials possessing a broad range of physical properties.[1] Recently, this unit has also appeared as a powerful electroactive brick in the design of supramolecular systems,[1] in particular because of its peculiar electronic (two successive reversible oxidation steps giving rise to three stable redox states) and structural (electron-rich π-system favouring interplanar interactions) characteristics. One-electron oxidation of TTF is known to generate a paramagnetic cation-radical monomer (TTF$^{+\bullet}$) in solution at room temperature. It is only very recently that a mixed-valence cation radical ([(TTF)$_2$]$^{+\bullet}$) and a cation radical π-dimer (TTF$^{+\bullet}$)$_2$ could be observed at rt by encapsulation in 3D host structures, namely a self-assembled metalla-cage[2] and a cucurbit[8]uril[3] structure respectively. Recent developments in synthetic tetrathiafulvalene (TTF) chemistry[4] have revolutionized the possibilities of integration of this redox-system into macrocyclic, molecular and supramolecular structures, and we have been engaged for some years in the preparation of redox-responsive[5] ligands involving this unit. Some recent examples[6] associate the TTF unit and the calix[4]arene platform, which is used to promote a 3D organization of the receptor and therefore to optimize the binding of a guest.

Here, we report on the synthesis of a TTF-based redox responsive ligand built around the tetracarbonyl-*tert*-butyl calix[4]-arene scaffold, and which allows modulation of the interactions between TTF planes, upon binding of Na$^+$.

The three-dimensional cavity generated by a tetracarbonyl substitution on the lower rim of the calixarene unit is known to provide a high binding affinity for alkaline cations, in particular when tertiary amides are involved.[7] We have therefore designed the target receptor **6**, which presents four carbonyl groups. Diacid **4** is prepared by adaptation of the literature (Scheme 1).[8] The final step to **6** involves esterification of **4** with hydroxymethyl-TTF **5**.[9]

As expected from the introduction of two different substituents in alternate positions around the calixarene platform, compound **6**
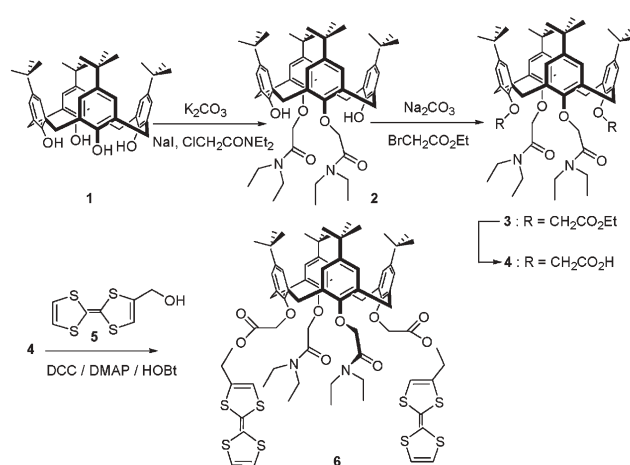
Scheme 1 Synthetic route to target calix[4]arene assembly **6**.

exists as a distorted cone as shown in the ^{1}H-NMR spectrum (ESI†),[10] which is in particular illustrated by the $\Delta\delta$ value between the two types of aromatic protons ($\Delta\delta$ = 0.50 ppm). The Na$^+$ binding ability of **6** was first evaluated by ^{1}H-NMR investigations (ESI). Introduction of aliquots of NaClO$_4$ onto **6** (CD$_3$CN–CD$_2$Cl$_2$) results in the appearance of a new set of signals and the concomitant disappearance of those of free **6**, which corresponds to the progressive formation of a 1 : 1 stoichiometric complex (**6**·NaClO$_4$). The aromatic protons now appear all identical (δ = 7.24 ppm), as a manifestation of the rigid character of the symmetrical cone which is now obtained from Na$^+$ complexation.

Single crystals of the sodium complex were formed by slow diffusion of **6** dissolved in methylene chloride to a methanol solution of sodium perchlorate. The complex crystallizes in the $P2_1/c$ group with two molecules of CH$_2$Cl$_2$ (Fig. 1).‡ A
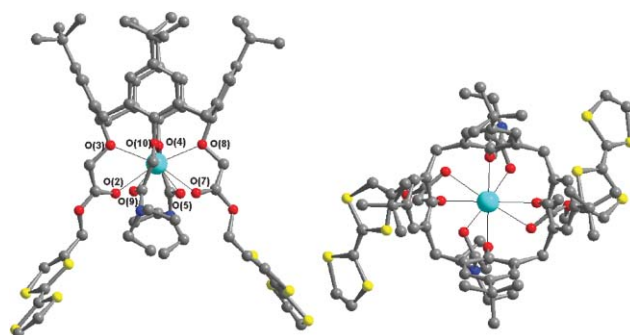
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† Electronic Supplementary Information (ESI) available: Experimental procedures and full spectroscopic data for compound **6**, ^{1}H-NMR titration and spectroelectrochemical studies of **6**. See 10.1039/b518275a
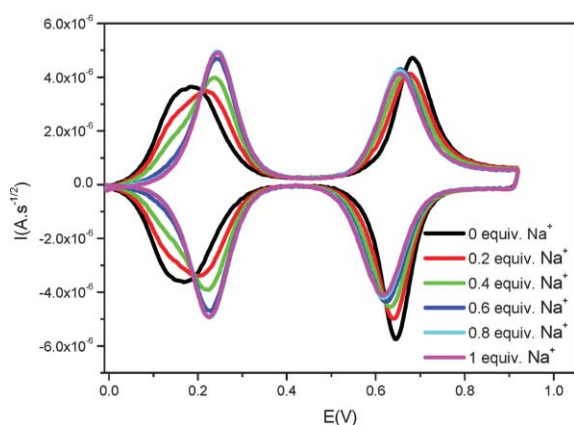

Fig. 1 X-Ray structure of **6**·NaClO$_4$(CH$_2$Cl$_2$)$_2$ (solvent and anion omitted).

Fig. 2 Deconvoluted CV of **6** (5.10^{-4} mol L^{-1}) in CH$_3$CN–CH$_2$Cl$_2$, TBAPF$_6$ (0.10 M), in the presence of increasing amounts of NaClO$_4$; Pt, diameter = 1.0 mm; $v = 100$ mV s^{-1}, *vs.* AgCl/Ag.

symmetrical cone conformation is observed in the solid state, with cone characteristics very similar to the ones observed for the previously described Na$^+$ complexes of *p-tert*-butylcalix[4]arene tetraethyl ester[11] or tetrakis(*N,N*-diethylamide),[12] which indicates that the introduction of bulky TTFCH$_2$ units on both appended esters does not perturb the binding process of Na$^+$. No short contacts are found between the two TTF units. The sodium cation occupies the centre of the cavity formed by the four pendant Ar–O–CH$_2$–C(O)–X groups, and is octacoordinated according to an antiprism mode by the four oxygen atoms from the phenate rings and the four oxygen atoms from the carbonyl groups.

As expected, cyclic voltammetry studies of compound **6** show two redox processes (E_1^{ox}, E_2^{ox}) characteristic of the TTF moiety (Fig. 2). Noticeably, the first redox wave appears broader than the second one, which is assigned to inter-TTF interactions. The second redox process ($E_2^{ox} = 0.73$ V) corresponding to the formation of **6**$^{4+}$, is thinner, in accordance with independent TTF^{2+} units subject to repulsive electrostatic interactions. A study of the through-space TTF interactions occurring upon the progressive oxidation of **6** was performed by electronic absorption spectroscopy.

Oxidation was carried out by introduction of a controlled amount of NOSbF$_6$ on to a solution of **6** in acetonitrile (Fig. 3).[13,14]
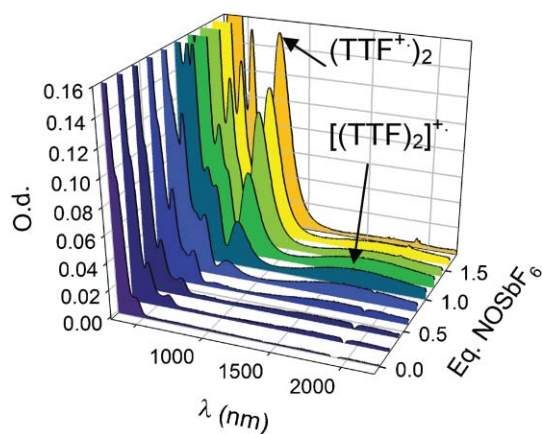

Fig. 3 Electronic absorption spectra of **6** in the presence of increasing amounts of oxidizing agent (CH$_3$CN).

Interestingly, beside the expected absorption bands corresponding to TTF$^{+•}$ (435 nm, 525 nm),[15] introduction of aliquots of NOSbF$_6$ gives rise to new bands located at 1750 nm and 765 nm, which are assigned respectively to the mixed-valence dimer [(TTF)$_2$]$^{+•}$,[2,4b,16] and to the π-dimer (TTF$^{+•}$)$_2$.[3,16b,17] As expected, the intensity of the band in the near-infrared region (1750 nm) reaches a maximum value for 1 equivalent of oxidizing agent (per mole of **6**) and then decreases, whereas the maximum absorption is observed for 2 equivalents in the case of the π-dimer ($\lambda = 765$ nm). For higher amounts of oxidizing agent (>2 equiv. related to **6**), we then observed development of the TTF^{2+} species. It is noteworthy that very few examples of oxidized-TTF dimers have been characterized in solution at room temperature, which in the case of **6** is presumably allowed by the favourable face-to-face preorganization[7b] induced by the calix[4]arene platform.

We found that formation of these dimers can be tuned by Na$^+$ complexation. First, as shown on the deconvoluted cyclic voltammogram in Fig. 2, the progressive addition of sodium perchlorate to calix-TTF receptor **6** is accompanied by a decrease of the intensity of the first redox wave (E_1^{ox}) (free **6**) and the concomitant appearance of a new reversible redox system at a more positive potential ($E'_1{}^{ox} = E_1^{ox} + 60$ mV), attributed to the **6**·Na$^+$ complex. Additionally, a striking peculiarity of this system lies in the thinner shape of the first redox wave for the **6**·Na$^+$ complex ($E'_1{}^{ox}$) relative to the free receptor (E_1^{ox}), which can be attributed to the conformational changes occurring upon complexation as anticipated from NMR data, where the rigidity which is induced by Na$^+$ coordination precludes any interactions between both TTF units. The same reason (conformational reorganization) is invoked to explain the slight decrease observed for the second reversible redox potential value, which also indicates that the complex still exists for this potential.

Starting from a solution containing **6** and 1 equivalent of NOSbF$_6$ (*i.e.* corresponding to the optimum ratio for the mixed-valence dimer [(TTF)$_2$]$^{+•}$), we observed in the electronic spectra (Fig. 4) that introduction of controlled amounts of NaClO$_4$ leads to the progressive disappearance of the NIR band (1750 nm), till 1 equivalent of sodium is added, and to the concomitant
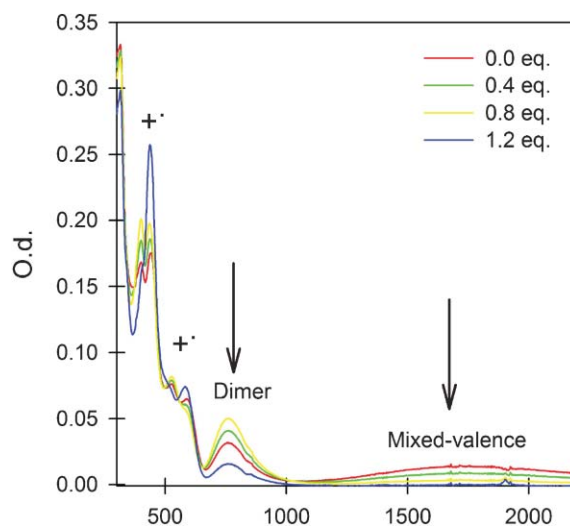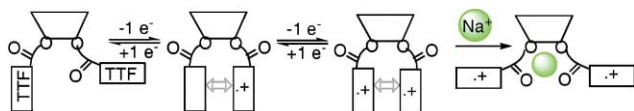

Fig. 4 Electronic absorption spectra of a mixture of **6** and NOSbF$_6$ (1 : 1) in the presence of increasing amounts of NaClO$_4$ (0–1.2 equivalents).

Scheme 2 Mode of action of **6** in the presence of an oxidizing agent and Na⁺ guest.

restoration of the usual absorption bands related to individual TTF cation-radical species (435 and 525 nm).[18] The sequence involved is therefore represented in Scheme 2. As seen in the solid-state (X-ray data) and as observed from NMR titrations for neutral **6** with Na⁺, the complexation of one sodium cation per calixarene receptor induces the formation of a rigid Na-complex, for which no more interactions exist between the two TTF units.

In conclusion, we have presented a receptor built around the calix[4]arene scaffold, which connects electroactive tetrathiafulvalene units to a 3D-binding pocket formed from a tetracarbonyl network. The good binding ability of this system for Na⁺ is demonstrated by solution NMR spectroscopy as well as by CV, and the X-ray structure of the corresponding sodium complex is provided. The preorganization of the two TTF units in this system offers a unique opportunity to observe the oxidized dimers $[(TTF)_2]^{+\bullet}$ and $(TTF^{+\bullet})_2$ in solution at room temperature. Disappearance of these dimers can be monitored by a conformational rigidification induced by complexation of Na⁺ in the cavity. Immobilization of such systems on a surface is under study.[5b]

Notes and references

‡ Crystallographic data for **6**·NaClO₄(CH₂Cl₂)₂: C₇₆H₉₄Cl₅N₂Na₁O₁₄S₈, $M = 1716.25$, yellow plate, $0.61 \times 0.42 \times 0.09$ mm³, monoclinic, space group $P2_1/c$, $a = 18.840(4)$ Å, $b = 27.549(3)$ Å, $c = 20.013(3)$ Å, $\beta = 116.78(2)°$, $V = 9273(3)$ Å³, $Z = 4$, $\rho_{calc} = 1.229$ g cm⁻³, $\mu(Mo-K_\alpha) = 0.396$ mm⁻¹, $F(000) = 3600$, $\theta_{min} = 2.13°$, $\theta_{max} = 17.98°$, 18991 reflections collected, 6174 unique ($R_{int} = 0.22$), restraints/parameters = 0/619, $R1 = 0.1730$ and $wR2 = 0.4029$ using 3213 reflections with $I > 2\sigma(I)$, $R1 = 0.2703$ and $wR2 = 0.4766$ using all data, GOF = 1.490, $-0.667 < \Delta\rho < 1.049$ e Å⁻³. CCDC 284182. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518275a

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