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A Tetrathiafulvalene-appended Calix[4]arene: Synthesis and Electrochemical Characterization

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A tetrathiafulvalene-appended calixarene derivative 3 was synthesized by the reaction of dibromide calixarene 1 with a TTF-thiolate derivative. A preliminary electrochemical study of 3 was carried out along with the X-ray structural characterization of the starting dibromide calixarene 1.

Keywords: Tetrathiafulvalene; Calixarene; X-ray structure; Cyclic voltammetry

INTRODUCTION

Important aspects of the supramolecular chemistry are strongly correlated to redox phenomena coupled to molecular recognition events. A better understanding of these systems, notably at the level of the electron transfer reactions, can be gained through the design of new molecular architectures which associate a redox phenomenon and various properties such as recognition, inclusion, or shielding effect [1–5].

Tetrathiafulvalene (TTF) is a prolifically studied redox-active candidate and has been extensively developed in the recent years in both electroconducting materials and supramolecular architectures [6–9]. On the other hand, calixarenes have been paid much attention for the last 15 years in the field of supramolecular hosts [10].

Unexpectedly, the highly organizing properties promoted by the calix[4]arene scaffold have been very poorly investigated in the peculiar case of the electroactive TTF unit. As far as we know, only one model associating a TTF moiety to the calixarene platform has been described, by J.-B. Regnouf-de-Vains *et al.* [11]. In this case, one TTF unit is located on the upper rim of the calix[4]arene moiety. Also, very recently, A. E. Kaifer *et al.* described the synthesis and the electrochemical properties of TTF-appended cavitands [12]. These results prompt us to present here the synthesis of a calix[4]arene assembly substituted on the lower rim with two TTF units, its preliminary electrochemical characterization, as well as the X-ray structure of a calix[4]arene synthetic intermediate.

EXPERIMENTAL SECTION

Instruments

^{1}H-NMR (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 related to the tetramethylsilane (TMS) signal. Mass spectra were achieved on a BRUKER BIFLEX III (maldi-Tof) spectrometer and on a JEOL JMS 700 B/ES (ESI) spectrometer. X-ray crystallographic data were collected on a STOE-IPDS diffractometer, graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å), absorption coefficient ($\mu = 1.71\,\mathrm{mm}^{-1}$), θ range for data collection ($2\theta_{\max} = 48°$). Cyclic voltammetry experiments were carried out on a potentiostat-galvanostat EG&G PARK 273A, with solvents and electrolyte of electrochemical grades. CV experiments were carried out at 298 K in a conventional three-electrode cell equipped with a Pt disk working electrode (diameter: 1 mm), a Pt wire counter electrode, and a Ag, AgCl reference electrode.

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Materials

Unless otherwise noted, solvents and starting products were commercially available and used without further purification.

Calixarene dibromide **1** and TTF derivative **2** were prepared according to the reported procedures, respectively [13–15]. A typical procedure for the synthesis of **3** is described below.

Synthesis of the Bis[(MeS)$_3$TTFS-]-substituted p-tert-butylcalix[4]arene 3

TTF derivative **2** (214 mg, 0.50 mmol) was dissolved in DMF (25 mL) and degassed with N_2 for 30 min. A solution of $CsOH,H_2O$ (84 mg, 0.50 mmol) in dry methanol (2 mL) was added in one portion, producing a darkening of the solution. After stirring for an additional 30 min, a solution of the dibromo calixarene intermediate **1** (0.25 mmol) in degassed DMF (25 mL) was added. The reaction mixture was stirred for 2 h, and the solvent was removed under reduced pressure. The resulting orange solid was dissolved in methylene chloride, washed with water several times, and dried over $MgSO_4$. Concentration *in vacuo* and purification by a silicagel column chromatography (eluent: a gradient of methylene chloride—petroleum ether binary mixture) afforded **3** as an orange solid (60% yield). ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): 7.65 (s, 2 H, OH), 7.04 (s, 4 H, ArH), 6.86 (s, 4 H, ArH), 4.27 (d, J = 13 Hz, 4 H, $ArCH_2Ar$), 4.13 (t, 4 H, OCH_2), 3.41 (t, 4 H, SCH_2), 3.34 (d, J = 13 Hz, 4 H, $ArCH_2Ar$), 2.42 (s, 6 H, SCH_3), 2.41 (s, 12 H, SCH_3), 2.31 (m, 4 H, CH_2), 1.27 (s, 18 H, $C(CH_3)_3$), 1.00 (s, 18 H, $C(CH_3)_3$). ^{13}C NMR (125.75 MHz, $CDCl_3$, ppm): 150.68, 149.42 (Ar ipso); 147.14, 141.58 (Ar para); 132.76, 127.73 (Ar ortho); 127.66, 127.39 (Ar meta); 130.89, 125.62, 125.13, 124.89 SC = CS), 111.164, 110.324 ($S_2C{=}CS_2$); 73.53 ($O\mathbf{C}H_2CH_2CH_2S$), 33.98, 33.81 ($\mathbf{C}(CH_3)_3$), 31.93 ($Ar\mathbf{C}H_2Ar$), 31.70 ($OCH_2\mathbf{C}H_2CH_2S$), 29.91 ($O\mathbf{C}H_2CH_2CH_2S$); 19.23, 19.19, 19.15 ($S\mathbf{C}H_3$). MS (Maldi tof): m/z 1476.07; HR-ESI$^+$: $C_{68}H_{84}O_4S_{16}$ Calcd: 1476.1901; found: 1476.1913.

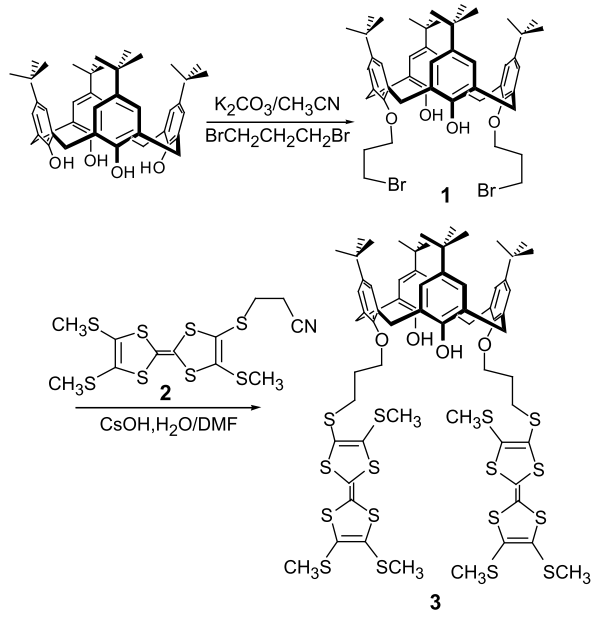
Crystallographic Structural Determination

Crystals of **1** suitable for X-ray crystallography were grown by slow evaporation from a chloroform solution of **1**. The structure was solved with the SHELX-97 software.

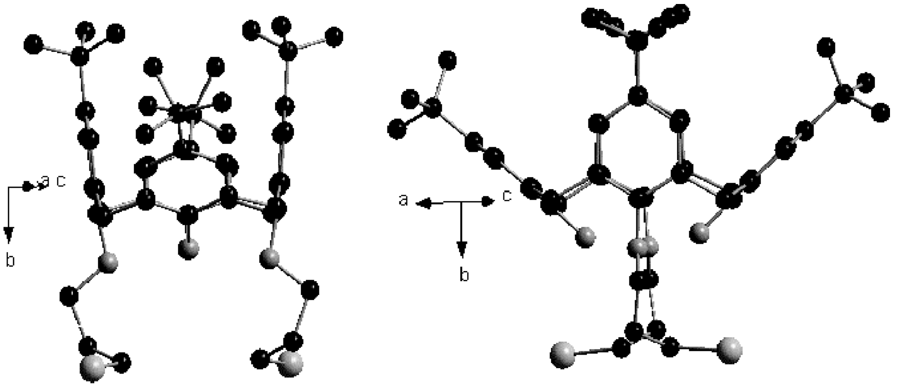
Compound **1**: $C_{50}H_{66}O_4Br_2$, $M = 890.86$, monoclinic, $a = 12.707(1)$ Å, $b = 18.852(2)$ Å, $c = 20.625(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.66(1)°$, $V = 4855(1)$ Å^3, space group I2/a, Z = 4, calculated density 1.219 g cm^{-3}, crystal dimensions (mm^3): 0.4 × 0.2 × 0.2. T = 290 K, 16820 measured reflections of which 3651 were unique ($R_{(int)} = 0.094$) and 2133 had $I/\sigma(I) > 2$. The hydrogen atoms were treated with a riding model. A statistical disorder affects one of the *tert*-butyl units, methyl groups being located on two positions with a refined occupancy rate close to 0.5. The refinements of positions and anisotropic thermal motion parameters of the non-H atoms, converge to R(F) = 0.081 (2133 reflections, 243 parameters), wR2(F^2) = 0.25 (all data), GOF on F^2 0.94, $\Delta\rho_{max} = 0.74$ e Å^{-3}. A fully completed CIF file of compound **1** has been deposited with the Cambridge Crystallographic Data Center (CCDC N° 264141).

RESULTS AND DISCUSSION

The calixarene **3** appended with two TTF moieties was synthesized as outlined in Scheme 1. Dibromide **1** was obtained from alkylation of *p-tert*-butylcalix[4]arene with an excess 1,3-dibromo propane in acetonitrile in the presence of potassium carbonate [13,14]. The dibromo calixarene intermediate was then treated by the highly nucleophilic thiolate derivative [(MeS)$_3$TTFS$^-$] obtained from deprotection of **2** [15] by cesium hydroxide monohydrate. The target system **3** was obtained as an orange solid and purified by silicagel chromatography (60% yield). The low yield is attributed to by-side reactions of the dibromide **1** under basic conditions, as detected by TLC. Calixarene **3** exists in the cone conformation, as indicated by the ^{1}H-NMR analysis, which presents a reasonably simple spectrum as expected for a C_2 symmetry. A pair of doublets is attributed to bridging diastereotopic methylene protons ($ArCH_a\ H_bAr$) presenting a $\Delta\delta(H_b–H_a)$ value of 0.93 ppm. Both aromatic protons Ar—H and ^{t}Bu protons present a Δδ values of 0.18 and 0.27 ppm,



SCHEME 1 Synthesis of the calix[4]arene-[TTF(SMe)$_3$]$_2$ assembly **3**.



(a) (b)

FIGURE 1 X-ray crystal structure of the dibromide calix[4]arene **1**.

respectively, which means that the cavity is almost symmetrical [16,17]. The ^{13}C NMR peak (31.93) confirms the cone conformation of **3** [18–20]. Further confirmation of the structure was obtained from Maldi-tof and high resolution mass spectrometries [ESI$^+$ (m/z 1476.1913)].

Single crystals of **1** suitable for X-ray analysis were grown from a chloroform solution, and show unambiguously the cone conformation adopted by the calixarene scaffold (Fig. 1).

The electrochemical properties of **3** were investigated by cyclic voltammetry (CV) in a dichloromethane-acetonitrile (1/1, v/v) mixture.

The TTF derivatives (e.g. the parent TTF(SMe)$_4$ system) are well-known to undergo two successive one-electron redox processes leading respectively to cation-radical and dication species. It is worth noting that the calix[4]arene-(TTF)$_2$ assembly **3** is characterized by three reversible redox waves as shown in Fig. 2(a) (CV). This behavior is even more easily observable in the corresponding deconvoluted CV (Fig. 2(b)) and is attributed to the splitting of the first oxidation step of electroactive TTF units into two peaks [21], characteristic of a through space interaction between the two donor moieties. From this point of view, a significant different behaviour is observed for system **3** compared to TTF-appended cavitands [12] for which no interaction is detected between the redox units which behave independently. This certainly results from the higher conformational flexibility in **3**, which allows the TTF units to spatially interact. Finally, the molecular assembly **3** is oxidized to the corresponding stable tetracation $\mathbf{3}^{4+}$ through two independent one e$^-$ oxidations, and no deposition of the polycationic species is noticed (Fig. 2), contrary to observations made with other poly-TTF systems [12,22].

In conclusion, a calixarene-TTF assembly has been synthesized. Such architecture constitutes a suitable model to study the conformation and the multi-electron redox activity of such assemblies. Further studies towards recognition applications are under investigation.

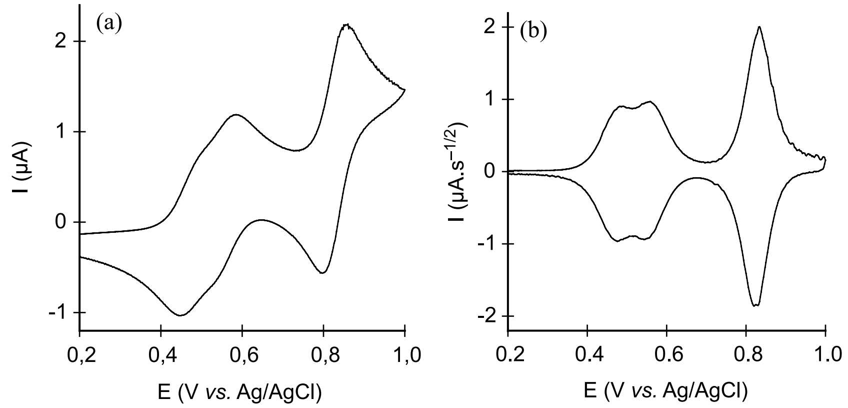


FIGURE 2 2 CV study of **3** (0.5×10^{-3} M) in CH_2Cl_2/CH_3CN, Bu_4NPF_6 (0.2 M), v = 0.1V/s, Pt (ϕ 1×10^{-3} m), vs Ag/AgCl : a) CV; b) deconvoluted CV.

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