Conjugated *p*-(tetrathiafulvalenylmethylideneamino)calix[4]arene

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2 PERKIN COMMUNICATION

The tetrathiafulvalene has been coupled *via* an imine bond to the *p*-(*tert*-butyl)calix[4]arene upper rim.

In the field of supramolecular chemistry, the calix[4]arene displays interesting behaviour as a pure entity[1] and as an organizing platform for various kinds of substituents such as acids, esters, amides and, more recently, transition metal heterocyclic complexing agents.[2] As far as we know, no specific studies have been related in this sense to the organization, around a calixarenic macrocycle, of tetrathiafulvalenyl (TTF) species. This biheterocyclic electron-donor group, well known for forming electron-conducting charge transfer complexes with electron acceptors such as tetracyanoquinodimethane (TCNQ), has been widely studied since the early seventies but, as mentioned by Becher and co-workers,[3] relatively little attention has been given to its implication in supramolecular chemistry as a building-block of supramolecular devices as well as a simply spatially organized electroactive substructure.

For this last purpose, in relation with some of our recent works dedicated to the organization of biheterocyclic chelating systems at the lower and upper rims of calix[4]arene,[2d,e,g] we describe here the synthesis and some physico-chemical properties of the first conjugated electroactive TTF-calixarene in which conjugation is maintained *via* an imine bond.

We took as a model platform the tri-*tert*-butylcalix[4]arene,[4] which was nitrated according to the literature[5] then reduced into its mono-amino analogue[6] following the procedure of Hosseini and co-workers.[7] The amine was reacted with TTF monocarboxaldehyde[8] in the presence of 3 Å molecular sieves in refluxing EtOH-free CH_2Cl_2 to give after chromatography (SiO_2, CH_2Cl_2 : hexane) the desired imine **1** (53% yield).†

Positive mode ESMS spectrum of **1** (CH_3CN as medium) displayed the proto- and sodio-charged peaks at 822.4 and 844.4 amu respectively, but accompanied by an intense peak at 821.4 amu which was attributed to the corresponding radical cation.

† **1**: Mp: 336–337 °C; $\lambda_{max}(CH_2Cl_2)$/nm 288 (ε/dm^3 mol^{-1} cm^{-1} 24 000), 320 (18 500), 456 (5150); $\lambda_{max}(CH_3CN)$/nm 286.6 (ε/dm^3 mol^{-1} cm^{-1} 25 350), 314.7 (19 225), 350.0 (sh); 437.5 (7125); $\delta_H(CDCl_3$ + TMS, 300.133 MHz, *J* values given in Hz) 1.186 (s, 9H, Bu^t) 1.235 (s, 18H, Bu^t), 3.50 and 4.26 (AB, J_{AB} 13, 8H, bridge CH_2), 6.10 (d, *J* 2.5, 2H, TTF), 6.81 (s, 1H, TTF), 6.91 (s, 2H, Ar), 7.03 (s, 2H, Ar), 7.053 and 7.095 (AB, J_{AB} 2.3, 4H, Ar), 7.97 (s, 1H, N=CH), 10.25 (s, 4H, OH); $\delta_H(CD_3CN)$ 1.178 (s, 9H, Bu^t), 1.185 (s, 18H, Bu^t), 3.59 (br s, 4H, bridge CH_2), 4.14 (br s, 4H, bridge CH_2), 6.46 (br s, 2H, TTF), 7.09 (br s + s, 1H TTF and 2H Ar), 7.18 and 7.26 (AB, J_{AB} 2.2, 4H, Ar), 7.228 (s, 2H, Ar), 8.16 (s, 1H, N=CH), 9.54 (s, 4H, OH); $\delta_C(CDCl_3$ + TMS, 50.32 MHz) 31.51, 31.65 (Me, Bu^t), 32.53 and 32.60 (bridged CH_2), 34.13 and 34.25 (C, Bu^t), 118.53 119.25, 121.91, 125.91, 126.04, 126.32 and 128.06 (4, 4′, 5′ of TTF; 3,5-Ar), 148.54 [N=C(H)], 127.14, 127.73, 128.17, 129.23, 139.12, 144.63, 144.80, 144.85, 146.36, 146.82 and 148.23 (5, 2 and 2′ of TTF; 2,6-Ar, 4-Ar, 1-Ar) (Found: C, 68.58; H, 6.35; N, 1.71; S, 15.40. Calc. for $C_{47}H_{51}NO_4S_4$ (822.19): C, 68.66; H, 6.25; N, 1.70; S, 15.60%). *m*/*z* (ESMS) negative mode 820.4 [M − H$^+$]$^-$; positive mode 821.4 [M$^{\bullet}$]$^+$, 822.4 [M + H]$^+$; 844.4 [M + Na]$^+$.

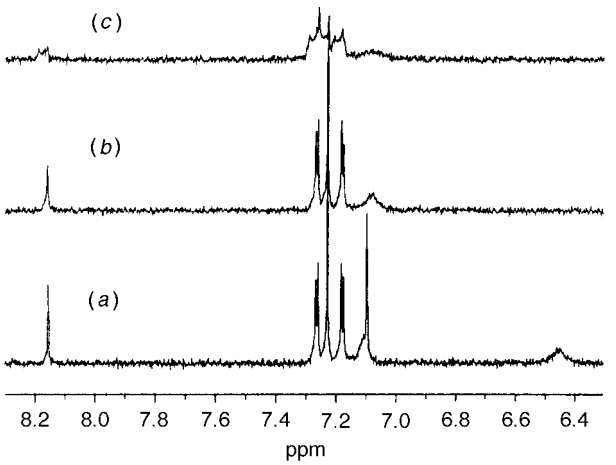

Fig. 1 ^{1}H NMR spectrum of aromatic and heterocyclic protons of **1** (CD_3CN, 300 MHz, room temp.): (*a*) alone (4.9×10^{-3} mol dm^{-3}); in the presence of: (*b*) 0.2 equiv., (*c*) 0.6 equiv. of TCNQ

^{1}H NMR analysis of **1** in $CDCl_3$ gave a well-resolved spectrum displaying notably a characteristic AB pattern for the Ar–CH_2–Ar groups, a doublet (*J* = 15 Hz) and a singlet at 6.10 and 6.82 ppm, respectively, for the TTF unit. Changing $CDCl_3$ for the more polar CD_3CN resulted in the broadening of the Ar–CH_2–Ar AB pattern and of the TTF signals; the latter and the imino proton supported a downfield shift of about 0.3 ppm. Titration of **1** by TCNQ in this solvent resulted in the rapid modification of the aromatic region (Fig. 1). After addition of 0.2 equiv. of TCNQ, the TTF resonance signals disappeared while those of the aromatic protons at 7.09 ppm and the imino group were broadened. At 0.6 equiv., the whole aromatic pattern gave a large multiplet, this was accompanied by the quasi-extinction of the imino-proton resonance signal. The *tert*-butyl and the Ar–CH_2–Ar resonance signals were not affected by this addition, suggesting that the cavity was not implied in this process. These results suggest that the expected charge transfer complex is formed in these conditions. Attempts to isolate it failed until now.

Additon of NEt_3 to **1** in CH_3CN, followed by UV–VIS spectroscopy (Fig. 2), resulted in an ipsochromic shift of the TTF transition from 437 to 412 nm with an increase of the molar absorptivity coefficient from 5700 to 11 800 dm^3 mol^{-1} cm^{-1}. The shoulder located at 350 nm, attributed to the imino-phenol group, disappeared while the band at 412 nm was formed. The latter, attributed to the imino-phenolate, joins the former *via* an isosbestic point at 358 nm and is gradually added to the close TTF band, thus explaining the high molar absorptivity coefficient at 412 nm. This titration involved exactly one equivalent of amine, leading to the conclusion that the conjugated phenolic group becomes the more acidic in the molecule, due to the increased mesomeric stabilization of the corresponding phenolate anion.

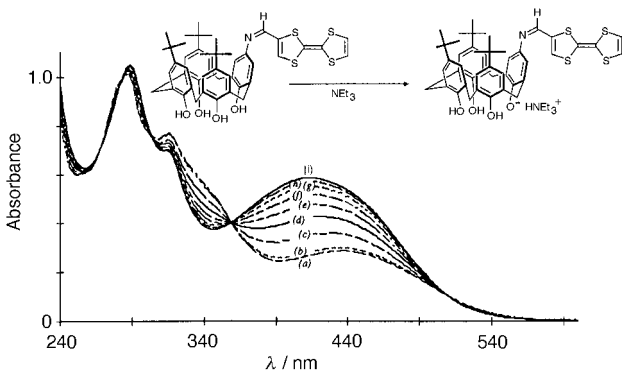

Fig. 2 UV–VIS titration of **1** by NEt_3 in acetonitrile solution: (*a*) alone (4.5×10^{-5} mol dm^{-3}); in the presence of: (*b*) 0.07, (*c*) 0.21, (*d*) 0.35, (*e*) 0.49, (*f*) 0.64, (*g*) 0.75, (*h*) 0.90 and (*i*) 1.06 equiv. of NEt_3

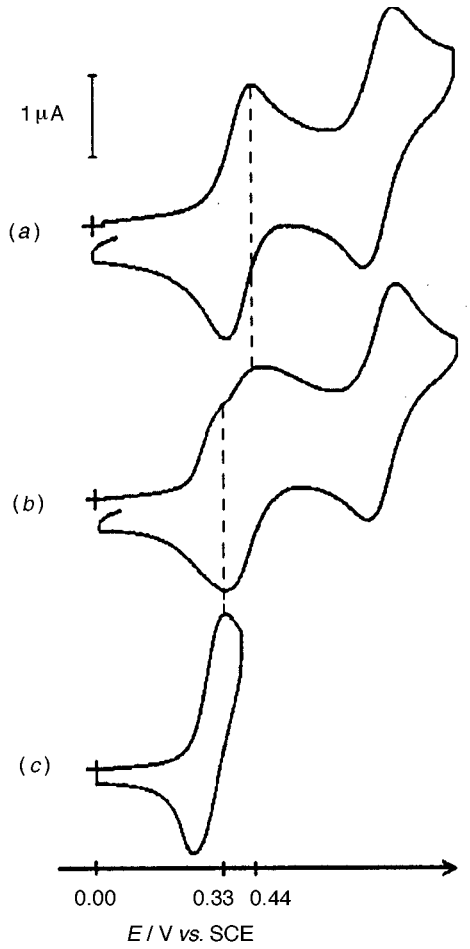

Fig. 3 Cyclic voltamogram of **1**, (*a*) alone; in the presence of (*b*) 0.5, (*c*) 1 equiv. of Et_3N

The π-donor character of this TTF-grafted calixarene was evaluated by cyclic voltametry.‡ Compound **1** exhibits two fully reversible one-electron oxidation waves in acetonitrile (Fig. 3), with peak potentials ($E_{pa}i$) slightly more positive than for TTF itself, in respect of the withdrawing character of the imino functionality (**1**: $E_{pa}1 = 0.44$; $E_{pa}2 = 0.83$ V *vs.* SCE; TTF : 0.36 and 0.72 V *vs.* SCE).

Interestingly, this good π-donating ability can be strengthened upon treatment with triethylamine. Indeed, a stepwise addition of Et_3N (0.1 equiv. portions) results in the progressive appearance of a new reversible redox system located at $E_{pa}1' = 0.33$ V, which corresponds to a 110 mV negative shift for the first oxidation potential (Fig. 3). The easier oxidizability of **1** in the presence of Et_3N is attributed to the generated phenolate anion which acts as an electron donating substituent for the conjugated TTF fragment. Note, this new redox system remains reversible from 0 to 1 equiv. of added triethylamine, with a loss of reversibility appearing for larger amounts of base.

Attempts to prepare electrogenerated cation radical salts derived from compound **1** are in progress, as well as the elaboration of its polysubstituted analogues.

‡ 10^{-3} mol dm^{-3} in acetonitrile, Bu_4NPF_6 (0.1 mol dm^{-3}), 100 mV s^{-1}, 20 °C, argon atmosphere.

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