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Synthesis, electrochemical and intramolecular charge-transfer properties of 'calix[4]arene-acceptor' diad and triad derivatives

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Abstract—Calix[4]arenes substituted with various acceptor moieties (naphthoquinone (NQ), tetracyanoanthraquinodimethane (TCNAQ)) have been synthesized. In these derivatives the three-dimensional structure of calix[4]arene acts as a weak electron donor (D), connected via a linear sigma spacer to one or two electroactive acceptor (A) units. The electrochemical behavior of these derivatives has been studied by cyclic voltammetry. The UV–Vis spectrum of the TCNAQ triad (A–D–A, **13**) reveals the presence of a weak intramolecular charge transfer absorption band.

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1. Introduction

Based on Aviram and Ratner's theoretical proposal[1] of molecular systems containing a covalent linkage between electron donor and acceptor units, D–σ–A ('D' represents electron donor and 'A' stands for electron-acceptor), much attention has been paid to the design and synthesis of systems with potential ability for intramolecular charge transfer. The covalent linkage between TTF and TCNQ moieties has proved to be a great challenge due to the difficult synthetic route and problems with purification.[2,3] As an alternative, systems with other acceptor groups, such as quinone,[4] C_{60},[5] pyridinium[6] and viologen[7] cations, have been studied. Recently, Bryce and co-workers[8b] reported the first readily available, analytically pure and stable TTF–σ–TCNAQ and TCNAQ–σ–TTF–σ–TCNAQ derivatives (e.g., **1** in Scheme 1) by attaching TTF (via a sigma spacer) to moderate acceptor (TCNAQ=teteracyanoanthraquinone-dimethane) moiety. Compared with TCNQ, the weaker acceptor TCNAQ adopts a 'butterfly' conformation which suppresses the rapid formation of intermolecular charge-transfer complexes during the combination reaction of TCNAQ and functionalized TTF derivatives. On the other hand, TCNAQ still has a reasonably high electron affinity.

In order to obtain improved electrically conducting materials, an increase of dimensionality has also proved to be of a priority in TTF and TCNQ chemistry. A promising strategy is to design nonplanar materials,[9] and to use spiro-conjugation.[10] For example, binaphthalene with a dihedral angle ranging from 60 to 120° as a nonplanar spacer (**3** in Scheme 1)[11] and spiro-cycle (**2** in Scheme 1)[12] as a spiro-conjugation were prepared to achieve increased dimensionality.

Calixarenes[13] have attracted widespread interest in recent years due to their unique combination of properties and structure. Their preparation is remarkably simple; they can be readily modified at both lower or upper rim; abound of conformers and well-defined hydrophobic and hydrophilic regions make calixarenes suitable hosts for neutral and ionic species. Tetranitrotetrapropoxycalix[4]arenes with electron-accepting nitro and electron-donating propoxy substituents have been used as supramolecular materials with second-order nonlinear optical properties.[14]

In the present study we report the synthesis, spectral and redox properties of novel TCNAQ diad **9**, and triads **13** (involving TCNAQ) and **16** (involving naphthoquinone, NQ), based on calyx[4]arene scaffold. In these systems, the three-dimensional calix[4]arene framework is used as a weak electron donor (phenol units) functionalized at the lower rim by different number of pendant tails bearing electron-accepting groups (TCNAQ or NQ). The properties of these new compounds have been investigated by cyclic voltammetry and UV–Vis spectroscopy.

2. Results and discussion

2.1. Synthesis and NMR spectroscopy

The synthesis of TCNAQ-containing calix[4]arene derivatives is outlined in Schemes 2 and 3. Calix[4]arene **4** was

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Keywords: Calix[4]arene-sigma-acceptor; Tetracyanoanthraquinodimethane; Napthoquinone; Intramolecular charge transfer; Cyclic voltammetry.

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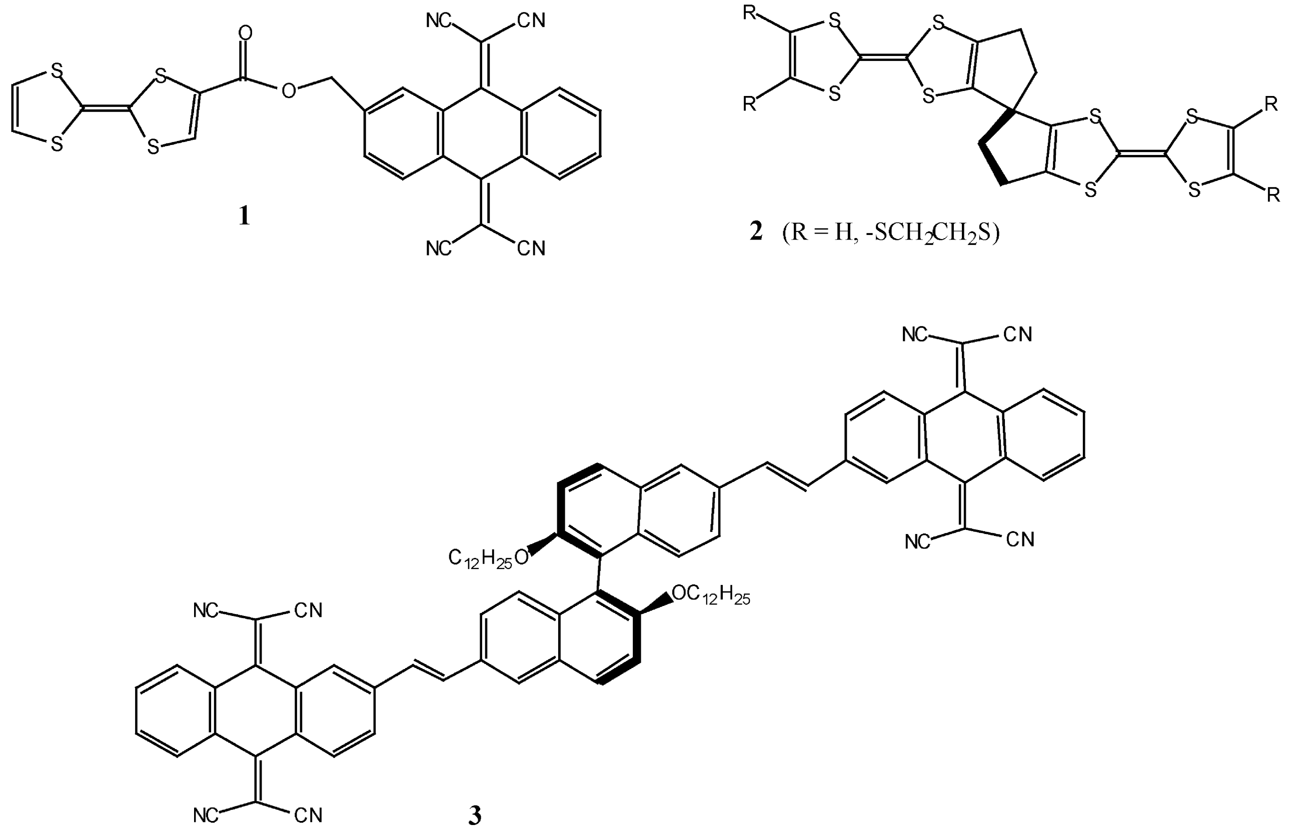
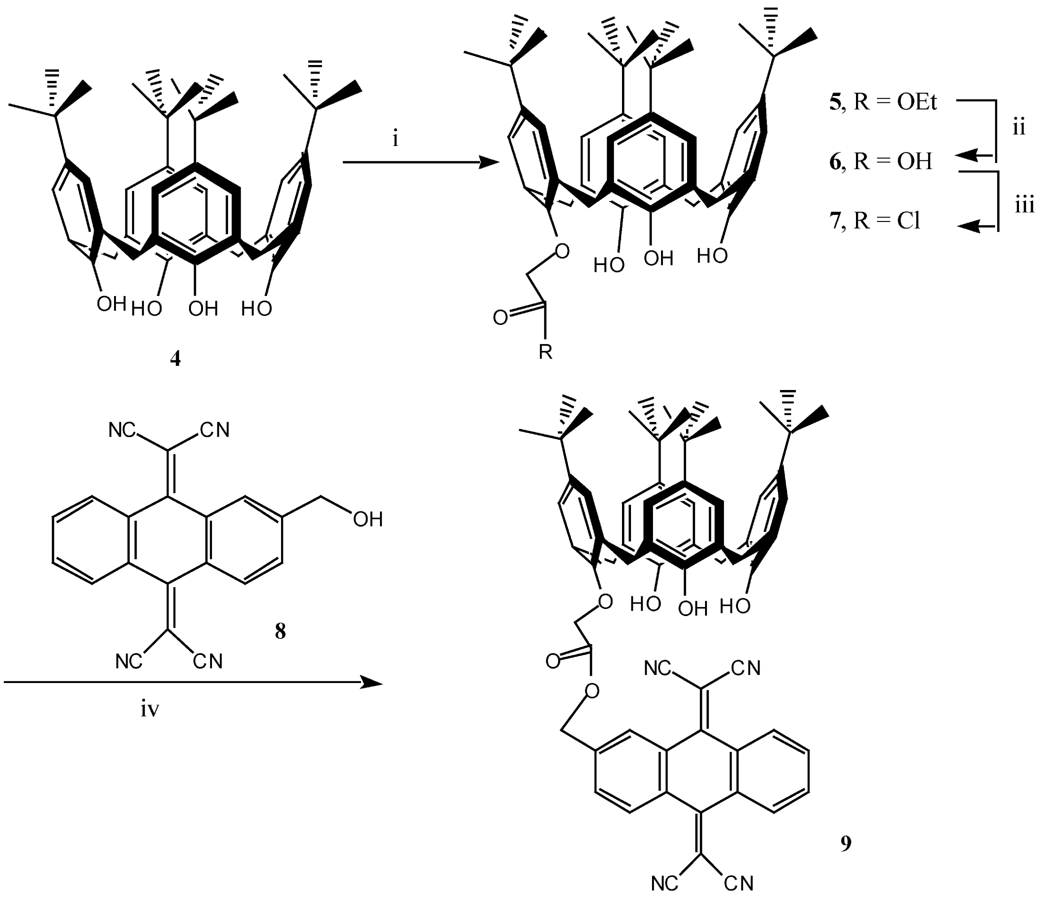
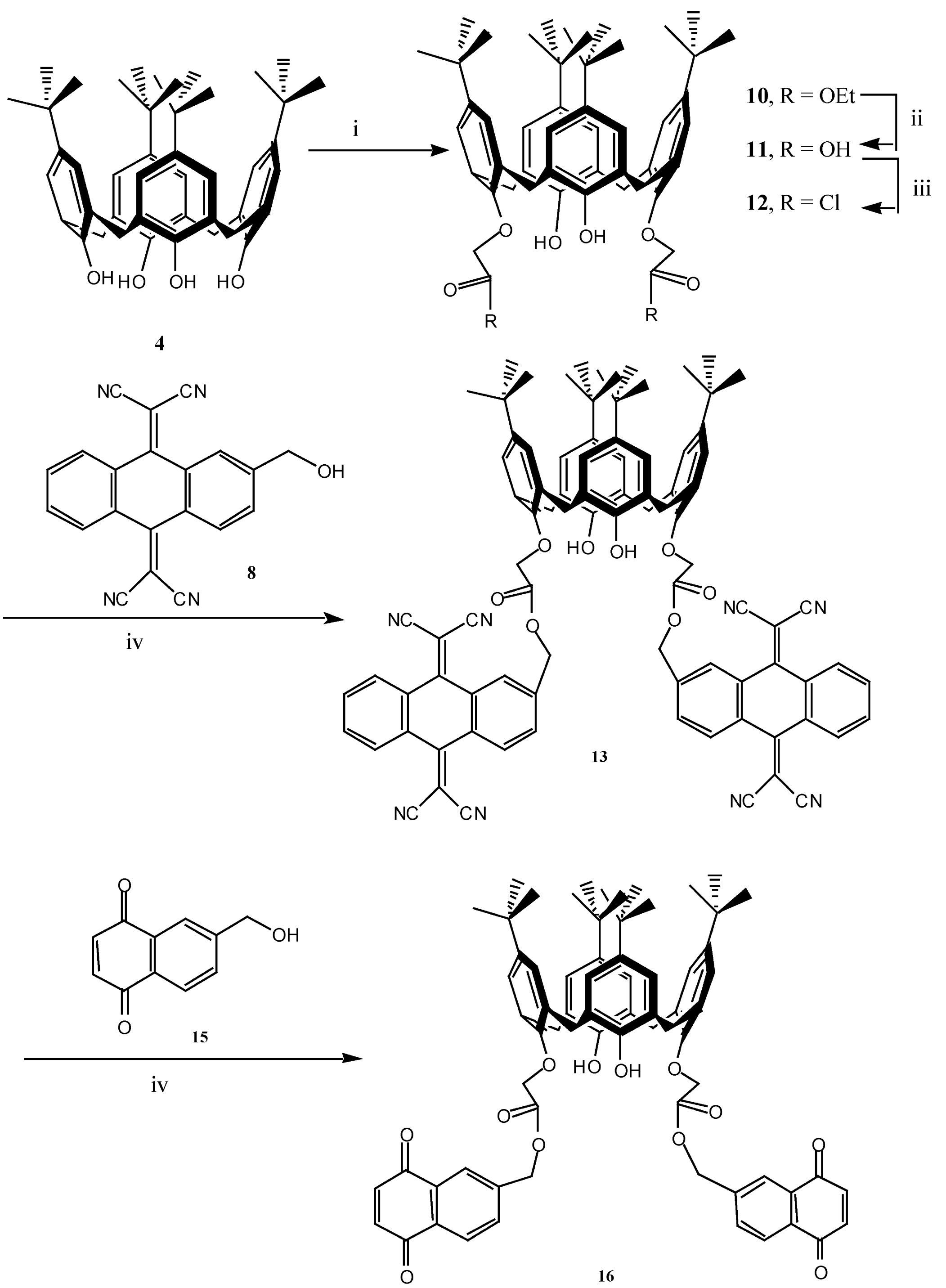


Scheme 1. Selected examples of D–σ–A diads and a D–σ–A–σ–D triad.



Scheme 2. (i) BrCH$_2$COOEt/CsF, DMF (67%); (ii) NaOH, EtOH/water, reflux (54%); (iii) SOCl$_2$, reflux (quant.); (iv) pyridine/CH$_2$Cl$_2$, rt (48%).



Scheme 3. (i) $BrCH_2COOEt/K_2CO_3$, CH_3CN, reflux (75%); (ii) NaOH, EtOH/water, reflux (70%); (iii) $SOCl_2$, reflux (quant.); (iv) pyridine/CH_2Cl_2, rt (36 and 48%, respectively).

converted into the corresponding monoacetate **5** and diacetate **10**, respectively, by alkylation with an excess of ethylbromoacetate. The acetates were hydrolyzed to carboxylic acids by refluxing with NaOH in ethanol, followed by acidification with 50% H_2SO_4. Compounds **6** and **11** were subsequently converted to the corresponding acid chlorides **7** and **12**. Condensation with 2-hydroxymethyl-TCNAQ (**8**) in the presence of pyridine, at room temperature, gave the desired TCNAQ diad **9** and triad **13**. Similarly, condensation with hydroxymethyl-NQ (**15**) afforded triad **16**.

Basically, calix[4]arenes exist in four conformers: cone, partial cone, 1,2-alternate and 1,3-alternate. Their structure can be easily distinguished by characteristic ^1H NMR patterns of the $ArCH_2Ar$ methylene protons. For example, cone, partial cone, 1,2-alternate and 1,3-alternate will exhibit a pair of doublets, two pairs of doublets, one singlet and a pair of doublet, and one singlet, respectively.[15] The structure of compounds **9** and **13** were characterized using ^1H and ^{13}C NMR spectroscopy. For triad **13**, the presence of two doublets of the CH_2 bridging groups (at 3.30 and 4.32 ppm) with geminal coupling constants of 13.4 Hz and

Table 1. Oxidation and reduction potentials of calix[4]arenes and related compounds[a]

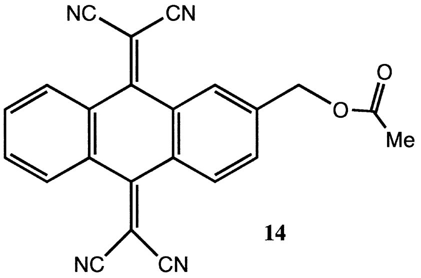
Compound	$-E^{(1)}_{1/2}$	$-E^{(2)}_{1/2}$	E_p(ox)
9	0.34	—	1.52
13	0.33	—	1.39
14	0.34	—	—
10	—	—	1.56
5	—	—	1.57
15	0.70	1.27	—
16	0.69	1.56	1.35

[a] Concentration of substrates: 1 mM; electrolyte: 0.1 M Bu_4NClO_4/CH_2Cl_2; working electrode: glassy carbon; scan rate: 100 mV/s; reference electrode: Ag/AgCl.

31.8 ppm in ^{13}C NMR, is clear evidence for a *cone* conformation.[16] In contrast, the ^{1}H NMR spectrum of the monoalkylated diad **9** is more complicated and quite different from its precursors **5** or **6**. The chemical shifts of 3.25–3.55 ppm are attributed to four bridging methylene equatorial protons, four doublets with integration of 1:1:1:1 and coupling constants of 13.4, 13.5, 14.3, 13.5 Hz, respectively. This information shows that the four methylene groups are nonequivalent, having different chemical environments. This is also proved by the four carbon signals at 32.78, 32.99, 33.98 and 33.99 ppm observed in the ^{13}C NMR spectrum. On the other hand, the four bridging methylene axial protons exhibit poorly defined signals and there are multiple signals for the methylene protons adjacent to the benzene rings. Dynamic ^{1}H NMR was also used to confirm the structure. When the temperature increased to 353 K, the bridging methylene axial protons also gave four doublets with coupling constants of 13.4, 13.9, 13.4, 14.3 Hz. The precise reason for such phenomena is unclear, although it may be due to steric interactions between the calix[4]arene moiety and the TCNAQ side chain, which may lead to a spatial distortion of the four phenyl units. Apparently, triad **16** is also in the *cone* conformation because its H NMR spectrum shows one pair of AB doublets.

2.2. Electrochemical properties by cyclic voltammetry

The electrochemical behavior of the redox-active compounds, namely diad **9** and triads **13** and **16** have been studied at room temperature, by cyclic voltammetry (CV) and compared with related derivatives, such as calix[4]arene derivatives 5 and 10, acetoxymethyl-TCNAQ (**14**) and naphthoquinone derivative (**15**). The results are summarized in Table 1 and a typical CV is shown in Figure 1.



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Upon scanning anodically, diad **9** exhibits one well defined irreversible oxidation wave at 1.52 V (vs. Ag/AgCl), attributed to the oxidation of the phenol units of calix[4]arene. The measured value of oxidation potential of **9** is slightly less positive (1.52 vs. 1.57 V) than those of calix[4]arene **5**, indicating that there is only a small influence of the chemically linked TCNAQ moiety on the oxidation of the phenol units, but in opposite to the expected direction (any kind of interaction between the phenol units and the TCNAQ electron acceptor moiety should result in a higher oxidation potential). The cathodic scan affords one quasi-reversible wave at $E_{1/2}=-0.33$ V, similar to the value obtained for acetoxymethyl TCNAQ **14**. It seems that there is no effect of the covalently bonded calix[4]arene unit on

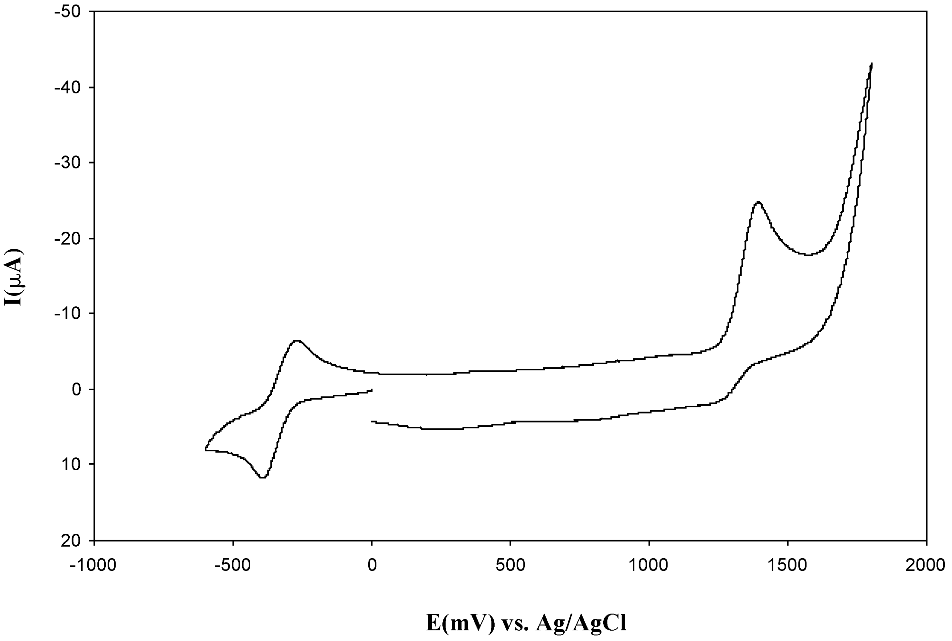

Figure 1. Cyclic voltammogram of triad **13** in 0.1 M $But_4ClO_4-CH_2Cl_2$ solution, at glassy carbon (GC); Scan rate: 100 mV/s. (Only small variations were obtained upon using Pt instead of GC or replacing the solvent by acetonitrile.).

the reduction of the TCNAQ moiety. The voltammogram of triad **13** shows a similar pattern to that of diad **9**, with a quasi-reversible couple $E_{1/2}=-0.34$ V, but with an irreversible oxidation wave at significantly less positive potential, 1.39 V. Here there is a clear influence of the chemically linked TCNAQ unit on the oxidation of the phenol units (again, opposite to the anticipated direction) but no influence of the calixarene moiety on the reduction of the TCNAQ units. As for triad **16**, with two planar NQ moieties, this compound gives an irreversible oxidation wave at 1.35 V, similar to the behavior of triad **13**, but two quasi-reversible redox couples at −0.69 and −1.56 V. Apparently, there is no effect upon reduction at the first redox couple compared with **15**. However, there is an effect on the second redox wave that becomes more negative by 290 mV. This is again in the opposite direction to what would have been expected, because if any kind of interaction (e.g., hydrogen bonding) exists between the anion radical of the NQ moiety in **16** and the phenol units of the calixarene framework, then the second reduction step should be less negative, namely, easier to reduce.

In summary, it seems that no significant change was detected in the reduction of diad **9** and triad **13** with respect to **14**; however, an effect was found in the case of the second reduction step of **16**, compared with **15**. Both triads **13** and **16** show better donor ability than **5** and **10**, exhibiting shifts in the oxidation potentials of the phenol units to less positive potentials by almost 170 mV compared with the 'free' calixarene derivatives (**5** and **10**); a smaller variation (~40 mV) is observed in diad **9**. The reason(s) behind this unexpected phenomenon, where acceptor units attached covalently to calix[4]arene skeleton cause the phenol units to be oxidized more easily, is not clear at this stage.

Previously it has been concluded by controlled potential coulometric analysis[8a,17] that the number of electrons involves in the reduction of TCNAQ is 2. Therefore, it is reasonable to also assume that the reduction wave in the CV of **9** corresponds to two-electron transfer process leading to the corresponding dianion. Similarly, the reduction of **13** consists of four electrons, yielding the corresponding tetraanion. The presence of only one single four-electron reduction wave in **13** indicates that both tetracyano-9,10-anthraquinodimethane moieties behave independently and that each is simultaneously reduced to its dianion. This behavior suggests that the calix[4]arene 'holds' the two TCNAQ units spatially separated preventing any possible interaction between them. Similar observations have also been found in other TCNAQ triad systems with different spacers.[11,18] The case of naphthoquinone derivatives **15** and **16** is different. They both exhibit two redox couples, formally involving 1e transfer each, to electro-generate the corresponding anion radical and dianion. However, the ratio of the current amplitudes between the two reduction processes is not equal to unity because of fast disproportionation of the anion radical, making the ratio usually greater than unity in favor of the first redox couple, depending on scan rate.[19]

As mentioned above, calixarene derivatives are widely used in supramolecular chemistry for the construction of various receptors for charged or neutral guest molecules. Such host–guest interaction can be controlled and detected electrochemically when organic, organometallic or inorganic redox-active centers are incorporated into calix[4]arene framework. For example, ferrocenium, cobaltocenium and tri(2,2′-bipyridyl)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) moieties were combined with calix[4]arene to recognize cations, anions and neutral species.[20] Calixquinone receptors have been found to enhance electrostatic affinity to cations when the quinone moiety is reduced to its dianion. Similarly, in the case of a quinone-bridged calix[6]arene, in which the quinone unit is quite rigid, it was found[21] that the reduction potential of the quinone moiety is negatively shifted in comparison with reference compounds without the calixarene macrocycle. The newly synthesized compounds **9**, **13** and **16**, with redox-active TCNAQ and NQ moieties, could potentially act as electrochemical sensors for cations when electrostatic interaction is switched on by reduction of the acceptor unit(s). As far as we know, so far, no NQ or TCNAQ unit has been chemically bound to any calixarene skeleton, as ionophore. Therefore, the electrochemical behavior of TCNA Q-calixarene diad **9** and triad **13**, which have stronger acceptor units than **16**, have been studied in the presence of various metallic cations by CV, UV–Vis and ^1H NMR spectroscopy. Surprisingly, CV experiments (1 mM substrate, in CH_2Cl_2–0.1 M But_4ClO_4) of the above compounds with metal ions of various ionic radii and charges, such as perchlorate salts of Li^+, Na^+, $Mg^{2+}$and Ba^{2+}, have shown little changes in the voltammograms, indicating that the electrostatic effects between the metal ions studied and the reduced TCNAQ moiety in **9** is very weak. Also, the ^1H NMR spectra did not change upon addition of alkali metal perchlorate to solutions of **9** and **13** in CD_3OD. This indicates that binding is probably not taking place in this case. Often the phenolic groups at the lower rim of calixarenes are hydrogen bonding to one another, thus reducing their ability for cations binding. In conclusion, we have found no evidence for cation binding or sensing using NMR or electrochemical methods. At present, it is not clear at which stage receptors **9** and **13** fail.

2.3. UV–Vis spectra

It is well known that calix[4]arene derivatives bearing nitriles on the upper rim and alkoxy groups on the lower rim present nonlinear optical (NLO) properties.[14b] Compared with other NLO-phores consisting of a single π-conjugated system, calix[4]arene can contain up to four D–π–A moieties in one molecule. When the four D–π–A units are symmetrically oriented in one direction (*cone* conformation), the molecular hyperpolarizability (β) value is about three times higher than the value of a derivative with one D–π–A unit. Compounds **9** and **13** could be regarded as D–σ–A systems, in which the TCNAQ moiety is the acceptor and the calix[4]arene unit is the donor. Similar to D–π–A systems, the number of D–σ–A units might be important for the expression of charge transfer (CT) prosperities. Indeed, as evidenced by its UV–Vis spectra, triad **13** which contains two D–σ–A units, exhibits a weak and broad absorption band in the 420–580 nm region, in dichloromethane, in addition to the usual TCNAQ and calix[4]arene absorption bands (Fig. 2), whereas diad **9**

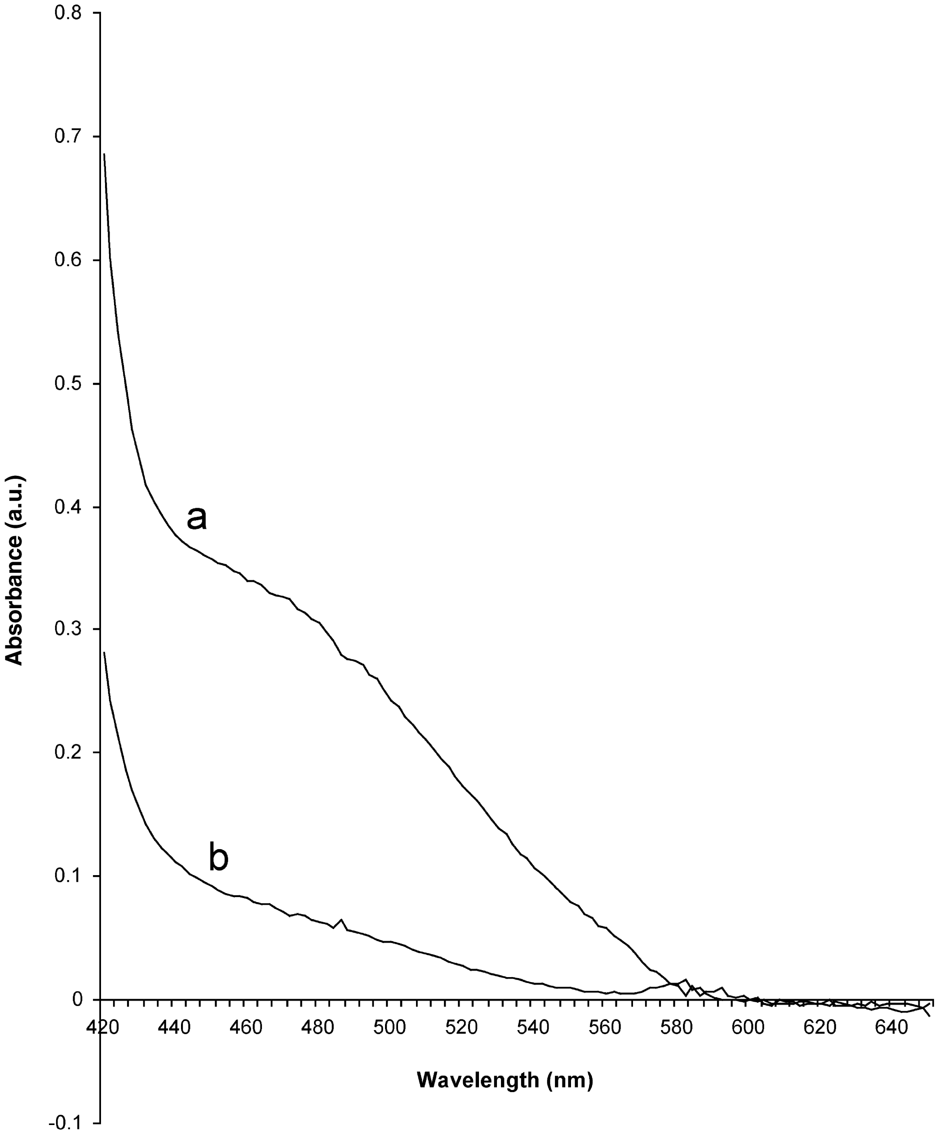

Figure 2. UV–VIS spectrum of compounds (1.4 mM) **13** (a) and **9** (b) in dichloromethane.

which contains only one TCNAQ moiety does not show a CT band under the same conditions. A mixture of 1:2 molar ratios of a TCNAQ derivative **14** and a calix[4]arene derivative **10** does not exhibit a similar absorption band under the same conditions. Also, the intensity of the absorption band of **13** shows a dependence on concentration that is expected for an intramolecular charge transfer process. It is noteworthy that to date, a similar phenomenon of intramolecular charge transfer property was reported[8] only for TCNAQ systems in which the two TCNAQ moieties are chemically linked through a conjugated vinylene bridge to the donor (see compound **3** in Scheme 1). However, there is an example[4e] of such a phenomenon in a *rigid* system involving TTF-σ-quinone diad in which the A and D units are spatially close to each other but lack a conjugation between them. Therefore, the CT phenomenon observed in **13**, which is not a rigid molecule and has two TCNAQ moieties connected by σ bonds to the calixarene framework, is unique. To try to explain the observation of intramolecular CT in this system seems to be a difficult task. Possibly, the two bulky TCNAQ substituents attached to the lower rim of the calix[4]arene scaffold impose a rigid *cone* conformation in **13**, so that the four benzene rings that are oriented in the same direction symmetrically, somehow leading to a spatial interaction between the phenols and the TCNAQ units (which could lie outside the calixarene cone), resulting in intramolecular charge-transfer band. Another possible reason (suggested by a referee) is that a single TCNAQ moiety is able to arrange itself underneath the calixarene ring, whereas in compound **13**, the presence of two TCNAQ moieties will not allow this. Consequently at least one of the TCNAQs must be outside the cone of the calixarene ring, and therefore be in a position to form a charge transfer interaction with the aryl rings.

Triad **16**, which also possesses two D–σ–A units like in **13**, and also has a cone conformation, does not show a charge transfer band. In this case it is not surprising because the electron accepting property of the NQ unit in **16** is quite weak relative to TCNAQ in **13**, as evidenced by their corresponding reduction potentials (Table 1).

Finally, it can be concluded that the relative strength of donor–acceptor affinity, the number of D–σ–A units and the specific orientation of the pending electron accepting group relative to the calixarene framework, maybe among other properties too, could play important roles in the intramolecular charge transfer process that takes place in molecules of type **13**.

3. Conclusion

Novel TCNAQ (diad **9** and triad **13**) and NQ (triad **16**) derivatives covalently linked to the lower rim of calix[4]-arenes have been synthesized. Of the three derivatives, only the UV–Vis spectrum of **13** shows an intramolecular charge transfer band. The redox properties of these derivatives have been investigated using CV measurements and all of them show a clear one irreversible oxidation wave corresponding to the phenolic groups. The TCNAQ derivatives exhibit one quasi-reversible reduction wave whereas the NQ derivative has two. Electrochemical cation recognition has also been studied for **9** and **13** but no binding or sensing was observed.

4. Experimental

All melting points were measured with a melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded with a 200 MHz spectrometer (200 MHz ^{1}H frequency, 50 MHz ^{13}C frequency) or 500 MHz spectrometer (500 MHz ^{1}H frequency, 125 MHz ^{13}C frequency). Chemical shifts are given as values (internal standard: TMS). Cyclic voltammograms were measured by Princeton Applied Research Potentiostat/Galvanostat Model 273A equipped with electrochemical analysis software. A one-compartment cylindrical cell, containing 0.1 M Bu_4NClO_4 in dichloromethane (or acetonitrile), and a glassy carbon (GC) working electrode, Pt wire counter electrode and Ag/AgCl (in 2 M NaCl) reference electrode, were employed. Solvents were chemically pure and purified by standard procedures.

Compounds **4**,[22] **5**,[23] **8**,[8a] **10**[24] **11**,[25] **14**[8b] and **15**[26] were synthesized according to literature procedures. Compound **6** was prepared similar to a known procedure,[25] by refluxing a suspension of **5** (2 moles) in ethanol (30 mL)–water (20 mL), containing NaOH (50 moles), for 24 h. The cooled solution was acidified to pH=1 by 50% sulphuric acid. The resulting precipitate was isolated, washed with water, dried under vacuum and recrystallized from ethanol–water to give a white powder, in 55% yield.

4.1. General procedure for the synthesis of compound 9 and 13

A mixture of monoacid **6** (710 mg, 1 mmol) or diacid **11** (764 mg, 1 mmol) and an excess of $SOCl_2$ (40 mmol, 2.9 mL) was stirred under reflux for 3 h. The solvent was distilled off, the residue was dissolved in anhydrous CH_2Cl_2 (5 mL) and the solvent was again evaporated under reduced pressure. This procedure was repeated twice to remove all traces of thionyl chloride. The resulting solid (acyl chloride **7** or **12**) was then dried in a high vacuum for 1 h. The solid was dissolved in 15 mL of dry dichloromethane and was added dropwise a solution of 2-hydroxy-TCNAQ (38.4 mg, 1.1 mmol for **7** or 77 mg, 2.2 mmol for **12**) at room temperature and followed by pyridine (1.1 mmol for **7** or 2.2 mmol for **12**) in 5 mL of dry dichloromethane. The reaction mixture was stirred for 12 h and the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ (20 mL) and washed with water (20 mL). The separated organic layer was dried over $MgSO_4$. After the evaporation of solvent, the crude product was purified by column chromatography on silica gel eluting with a mixture of petroleum ether and ethyl acetate with a gradient increase of ethyl acetate to give products **9** and **13** as a yellow powders.

4.1.1. Monoacid 6. Yield: 55% (white powder). Mp: > 270 °C (decomposed); ^{1}H NMR (DMSO-d_6): 1.11 (s, 9H, *t*-Bu), 1.14 (s, 18H, *t*-Bu), 1.16 (s, 9H, *t*-Bu), 3.45 (d, 4H, J=13.6 Hz, ArCH_2Ar), 4.06 (d, 2H, J=14.3 Hz, ArCH_2Ar), 4.34 (d, 2H, J=12.9 Hz, ArCH_2Ar), 4.74 (s, 4H, CH_2O), 7.03 (s, 2H, Ar-*H*), 7.12 (s, 2H, Ar-*H*), 7.19 (s, 2H, Ar-*H*), 7.24 (s, 2H, Ar-*H*), ^{13}C NMR ($CDCl_3$): 30.96, 31.20, 31.70, 33.79, 33.90, 34.03 (C(CH_3)$_3$ and (ArCH_2Ar), 71.84 (OCH_2), 125.11, 125.55, 126.04, 127.55, 127.84, 128.56, 133.76, 142.72, 143.05, 147.66, 150.60, 171.22 (C=O). IR (KBr): ν=3300–2500 (br), 1765, 1480 cm^{-1}. HRMS for $C_{46}H_{58}O_6$: found, (M+1)=707.4290 (calc. 707.4312).

4.1.2. Compound 9. Yield: 48% (yellow powder). Mp: 272–274 °C. ^{1}H NMR ($CDCl_3$): 0.95 (s, 9H, *t*-Bu), 1.10 (s, 9H, *t*-Bu), 1.28 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 3.28 (d, 1H, J=13.4 Hz, ArCH_2Ar), 3.38 (d, 1H, J=13.5 Hz, ArCH_2Ar), 3.44 (d, 1H, J=14.3 Hz, ArCH_2Ar), 3.53 (d, 1H, J=13.5 Hz, ArCH_2Ar), 4.11–4.71 (br, m, 6H, ArCH_2Ar and ArOCH$_2$CO), 5.51 (s, 2H, Ar$_{TCAQ}$-CH_2O), 6.65 (s, br, 1H, Ar-O*H*), 6.83 (d, 1H, J=2.43 Hz, Ar-*H*), 6.84 (d, 1H, J=1.84 Hz, Ar-*H*), 6.85 (d, 1H, J=2.38 Hz, Ar-*H*), 7.04 (d, 2H, J=2.44 Hz, Ar-*H*), 7.06 (d, 1H, J=2.40 Hz, Ar-*H*), 7.10 (d, 2H, J=2.0 Hz, Ar-*H*), 7.17 (s, br, 1H, Ar-O*H*), 7.22 (s, br, 1H, Ar-O*H*), 7.62–7.77 (m, 3H, Ar$_{TCAQ}$-H), 8.11–8.35 (m, 3H, Ar$_{TCAQ}$-H), 8.44(s, 1H, Ar$_{TCAQ}$-H), ^{13}C NMR ($CDCl_3$): 30.89, 31.15, 31.40, 31.59 (C(CH_3)$_3$), 32.78, 32.99, 33.99, 33.98 (ArCH_2Ar), 34.08, 34.24, 34.36, 34.53, (C(CH_3)$_3$), 65.46 (ArOCH_2), 71.98 (Ar$_{TCAQ}$-CH_2O), 112.87 (CN), 113.12 (CN), 160.10 (C(CN)$_2$), 168.40 (C=O). IR (KBr): ν=3437, 2965, 2230(CN), 1750, 1480 cm^{-1}. MALDI-TOF MS: *m*/*z* 1045.38(M+Na$^+$) for $C_{67}H_{66}N_4O_6Na$. HRMS MS: *m*/*z*=1023.970: found, for (M+1) for $C_{67}H_{67}N_4O_6$ (calc. 1024.257).

4.1.3. Compound 13. Yield: 36% (orange powder). Mp: 206–208 °C; ^{1}H NMR ($CDCl_3$): 0.95 (s, 18H, *t*-Bu), 1.31 (s, 18H, *t*-Bu), 3.30 (d, 4H, J=13.26 Hz, ArCH_2Ar), 4.33 (d, 4H, J=13.4 Hz, ArCH_2Ar), 4.74 (s, 4H, CH_2OAr), 5.42 (s, 4H, Ar$_{TCAQ}$CH_2OCO), 6.80 (s, 4H, Ar-*H*), 7.07 (s, 4H, Ar-*H*), 7.15 (s, 2H, Ar-O*H*), 7.68–8.25 (m, 12H, Ar$_{TCAQ}$-*H*), 8.42 (d, 2H, Ar$_{TCAQ}$-*H*), ^{13}C NMR ($CDCl_3$): 31.08 (C(CH_3)$_3$), 31.82 (ArCH_2Ar), 34.05 (C(CH_3)$_3$), 65.69 (OCH_2), 72.28 (OCH_2), 112.98 (CN), 113.22 (CN), 125.50, 125.96, 127.17, 127.73, 127.94, 129.87, 130.21, 130.85, 131.77, 132.38, 132.55, 140.83, 142.16, 147.56, 149.45, 150.54, 160.00 (C(CN)$_2$), 160.27 (C(CN)$_2$), 168.37 (C=O). IR (KBr): ν=2950, 2230 (CN), 1757, 1487 cm^{-1}.

MALDI-TOF MS: m/z=1420.37 ($M+Na^+$) for $C_{90}H_{76}N_8O_8Na$. HRMS MS: m/z=1397.542: found, for (M+1) for $C_{90}H_{76}N_8O_8$ (calc. 1397.596).

4.1.4. Compound 16. Yield: 48% (dark brown powder). Mp: 130 °C (decomposed); ^1H NMR ($CDCl_3$): 0.93 (s, 18H, *t*-Bu), 1.27 (s, 18H, *t*-Bu), 3.30 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 4.34 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 4.83 (s, 4H, CH_2OAr), 5.36 (s, 4H, $Ar_{Quinone}CH_2O$), 6.75 (s, 4H, Ar-*H*), 6.95 (s, 4H, $Ar_{Quinone}$-*H*), 7.02 (s, 4H, Ar-*H*), 7.81–8.06 (m, 6H, $Ar_{Quinone}$-*H*); ^{13}C NMR ($CDCl_3$): 30.87($C(CH_3)_3$), 31.57($ArCH_2Ar$), 33.74($C(CH_3)_3$), 65.59(OCH_2CO), 72.24($COOCH_2$), 168.55($COOCH_2$), 184.47(Naphthoquinone). IR (KBr): ν=1757, 1675, 1485 cm^{-1}; MALDI-TOF MS: m/z 1127.39 ($M+Na^+$) for $C_{70}H_{72}O_{12}Na$, 1143.37($M+K^+$) for $C_{70}H_{72}O_{12}K$.

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