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Carboxylic acid derivatives of tetrathiafulvalene: key intermediates for the synthesis of redox-active calixarene-based anion receptors

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Abstract—A series of calixarene–TTF (TTF=tetrathiafulvalene) receptors incorporating amide binding units for anion recognition have been synthesized and characterized. For this purpose, two synthetically versatile new TTF carboxylic acid derivatives were prepared and characterized by X-ray diffraction, these structures demonstrating the critical role of the carboxylic function in the solid-state organization. Some of the calixarene–amide–TTF assemblies exhibit strong binding of various anions, as shown by ^{1}H NMR titration studies, and one receptor is able to electrochemically respond in the presence of $H_2PO_4^-$, $C_6H_5CO_2^-$ or $CH_3CO_2^-$ anion.

1. Introduction

As a result of the importance of anions in a number of chemical and biochemical processes, the search for effective artificial molecular hosts is the subject of a strong interest.[1] Amide-based ligands designed for anion coordination are in the forefront of this research[1,2] and a special interest concerns receptors able to bind and to electrochemically detect anionic guests. Several examples of such amide-based electroactive ligands have been designed, most of them involving a metallocene moiety as the redox unit.[1,3] In particular, some have been built around a calixarene platform.[1,4]

In the course of our studies related to the chemistry and the use of the tetrathiafulvalene (TTF) unit in the electrochemical sensing or the binding control of guest cations,[5] we have examined various redox-responsive ligands built from the covalent association between a binding unit and the electroactive TTF framework. Such systems exploit the ability of the TTF unit to be reversibly oxidized in two successive one-electron steps to stable cation-radical and dicationic states.[6] In this regard, using the ability of the calix[4]arene platform to generate 3D binding sites, we have recently developed different series of redox-responsive calixarene–TTF assemblies designed to electrochemically recognize guest cations.[7] A similar strategy was used in the design of a related receptor designed to bind anions by incorporation of secondary amide units in the periphery of both the calixarene and the TTF subunits.[8] Some other examples of TTF-based anion receptors, devoid of calixarene unit, have also been published recently.[9] Here, we present the synthesis, detailed binding studies and anion electrochemical recognition properties of a complete series of redox-active calixarene-based receptors.

2. Results and discussion

2.1. Synthesis

Synthesis of the succinimidyl-activated TTF esters **4a**,**b** is outlined in Scheme 1. Key intermediates are the mono- and diacid derivatives **3a**,**b**. Treatment of known derivatives **1a** and **1b**[10] with caesium hydroxide monohydrate and subsequent nucleophilic attack on methylbromoacetate produced the new TTF ester derivatives **2a**,**b** in high yields. Compounds **2a** and **2b** were then saponified with lithium hydroxide to liberate the mono- and dicarboxylic acid derivatives **3a** and **3b** in high yields after acid treatment. Alternatively, the direct conversion of **1a** and **1b** to **3a** and **3b**, respectively, could be conducted advantageously without isolation of ester derivatives **2a** and **2b**. Yields then are as high as 90 and 96% for **3a** and **3b**, respectively. Reaction

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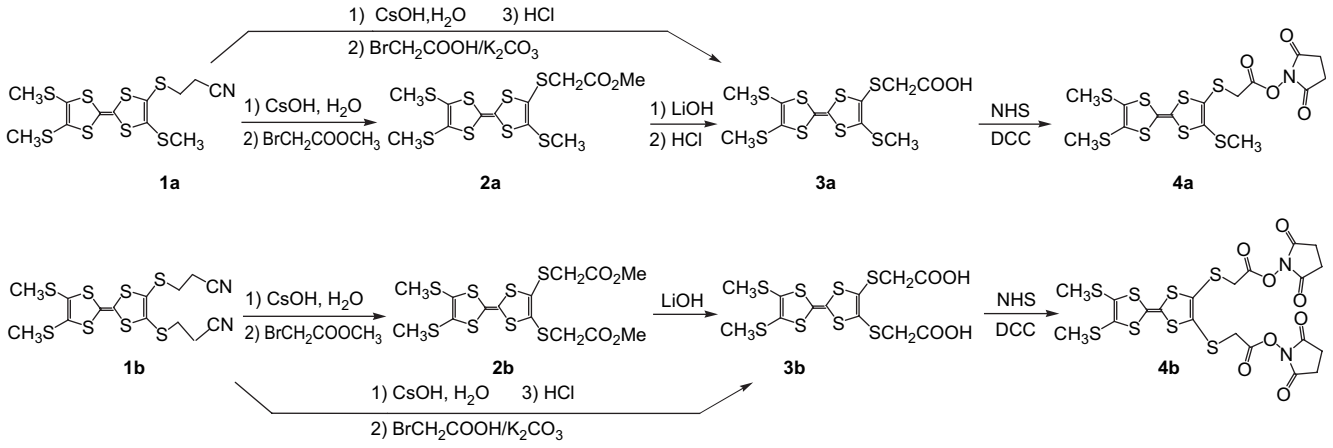


Scheme 1. Synthesis of tetrathiafulvalene acid derivatives **4a**,**b**.

of acids **3a** and **3b** with *N*-hydroxysuccinimide and DCC produced the activated mono- and diesters **4a** and **4b** in good yields (82–85%).[11]

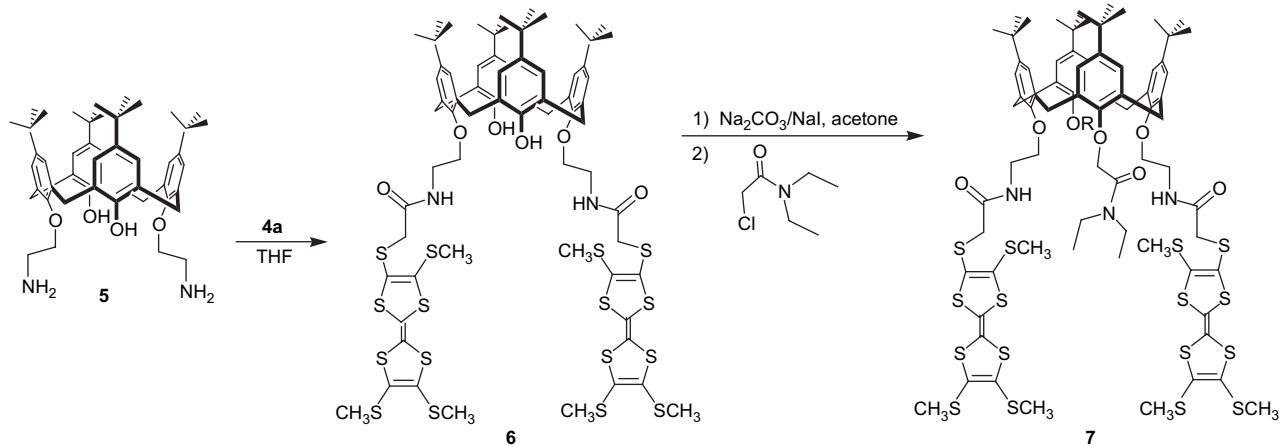
These versatile TTF derivatives were then attached to the *p-tert*-butylcalix[4]arene platform (Scheme 2). Synthesis of the 1,3-distally substituted calix[4]arene diamine **5** was carried out in two steps from the corresponding *p-tert*-butylcalix[4]arene.[12] The calix–diTTF amide **6** was obtained in 76% yield by reaction of **5** with the succinimidyl-activated TTF ester **4a** in dry THF at room temperature but could not be obtained by the direct reaction of **5** with **2a** in refluxing toluene/methanol.[13]

The two residual phenolic groups of **6** were then reacted with *N*,*N*-diethyl α-chloroacetamide in the presence of a Na_2CO_3/NaI mixture, to produce the target tetrasubstituted calix[4]arene **7** (55%) after silica gel chromatography (methylene chloride/acetone).

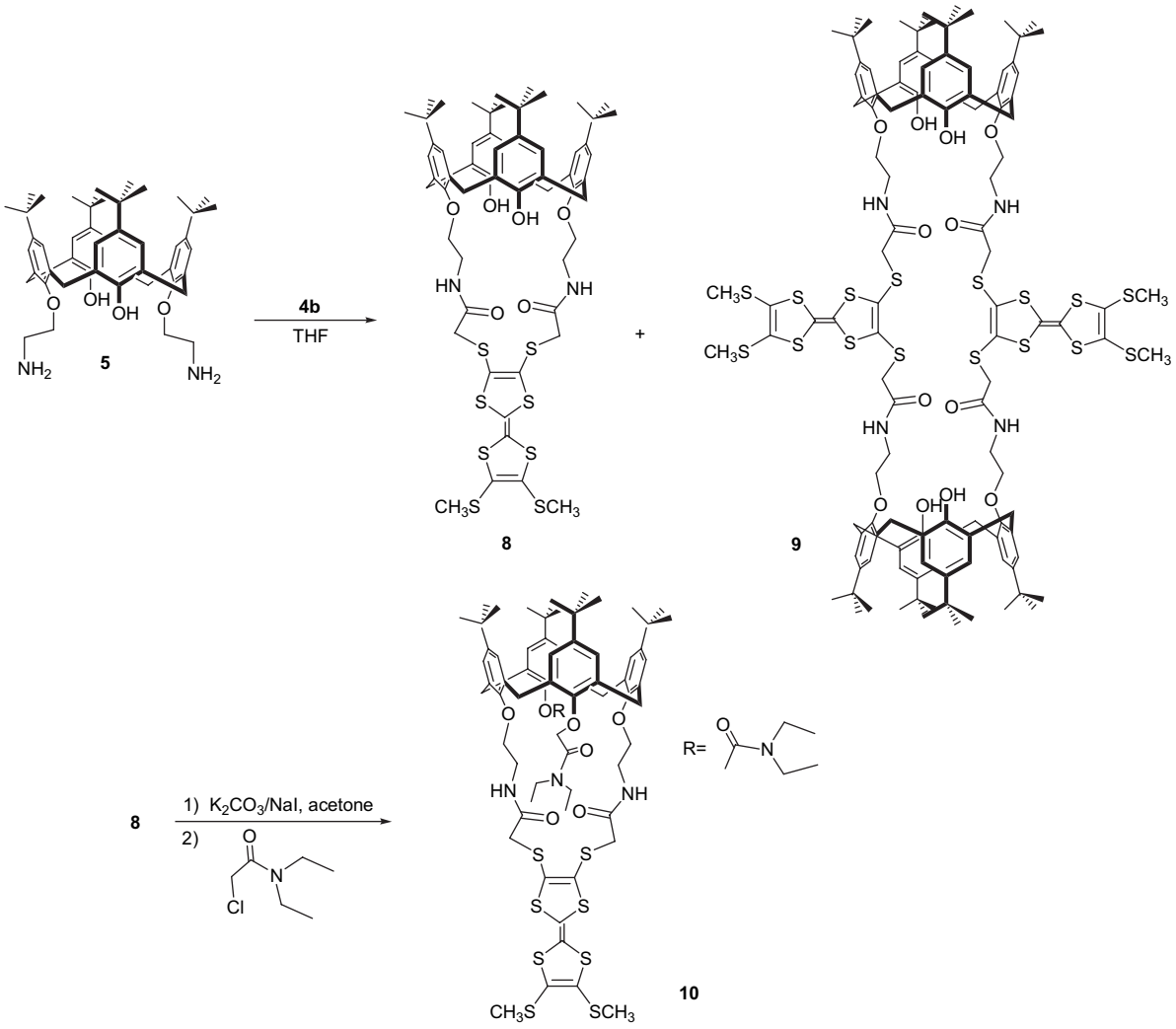
A similar strategy was used starting from the activated TTF diester analogue **4b** (Scheme 3). In this case, the reaction between **4b** and **5** afforded capped-calixarene **8** ([1+1] cyclocondensation) as well as the [2+2] product **9**, which could be separated and isolated in yields of 31 and 17%, respectively. The di-O-alkylation of **8** with chloroacetamide was then carried out in the presence of K_2CO_3/NaI to produce the target macrocyclic calix–TTF assembly **10** (35% yield). Structures of the calix–tetrathiafulvalene assemblies **6–10** were established by spectroscopic measurements.

2.2. X-ray crystallographic studies on mono- and diacid TTF 3a and 3b

Slow evaporation of tetrathiafulvalene acids **3a** and **3b** in $CHCl_3$ in both cases provided single crystals, which were then used for structure determinations by X-ray diffraction. Aspects of the molecular and crystal structures of **3a** and **3b** are presented in Figure 1. The donor molecules are quasi-planar and associated within hydrogen-bonded pairs in robust dimers. The geometric features of the C═O···H–O bonds are as expected for carboxylic acid derivatives,[14] with all intermolecular O···O distances of 2.66–2.70 Å within the TTF-dimers. In the case of compound **3b**, the four carboxylic acid functions in interaction within the dimer result in a double bridge between two TTF units, leading to the construction of a supramolecular cage (Fig. 1b). As observed in a different TTF carboxylic acid derivative,[15] the lattices of **3a** and **3b** are characterized by the formation of a layered architecture where the hydrophilic part, governed by electrostatic interactions involving the carboxylic function, is separated from the hydrophobic residue (Fig. 1c,d), and for which several intermolecular S···S distances in the range of 3.6–3.7 Å are found.



Scheme 2. Synthesis of calix–tetrathiafulvalene assemblies **6**,**7**.



Scheme 3. Synthesis of calix–tetrathiafulvalene assemblies **8**–**10**.

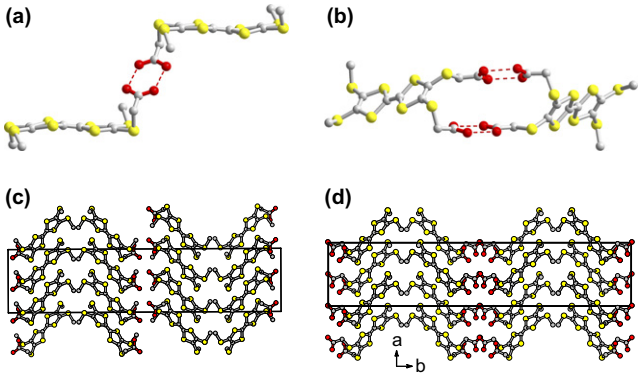


Figure 1. X-ray diffraction molecular structure of (a) **3a** and (b) diacid **3b** showing hydrogen-bonds. Packing diagram of (c) **3a** and (d) **3b**; (H atoms omitted for clarity).

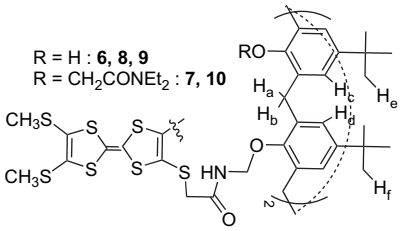
2.3. Conformational study of the calixarene–TTF receptors

Conformations were deduced from NMR measurements (Table 1). Based on the characteristic AB splitting pattern of the diastereotopic bridging methylene protons ($ArCH_aH_bAr$; J_{AB}=13 Hz, $\Delta\delta(H_b-H_a)$=0.87 for both), the TTF assemblies **6** and **7** were assigned a cone conformation.[13a,16] This was confirmed by the ^{13}C spectra, where the methylene carbon resonances appear at δ 32.17 and 31.37 for **6** and **7**, respectively.[16c]

Furthermore, the cone appears essentially symmetrical in both cases, as indicated by the low $\Delta\delta(H_d-H_c)$ value observed between the two different types of aromatic protons (0.08 and 0.21 for **6** and **7**), as well as for both *t*-Bu signals ($\Delta\delta(H_f-H_e)$=0.16 and 0.18 ppm). This indicates that the introduction of two additional amide substituents in **7** only slightly alters the cavity shape. As in the solid state,[8] the NH group in **6** is engaged in strong intramolecular hydrogen-bonds, as shown by the δ value of NH (8.50), which is significantly deshielded relative to the same signal in the tetrasubstituted compound **7** (7.97 ppm).

Receptors **8** and **9** also adopt cone conformations, as shown by the AB system for the bridging $ArCH_2Ar$ methylene protons, with similar standard $\Delta\delta(H_b-H_a)$ values [0.85 ppm]. As expected from its more constrained structure, the capped-calixarene system **8** related to the bis-calixarene assembly **9** has a more distorted cone form. This is seen from

Table 1. Selected ^{1}H NMR chemical shifts (δ, ppm, $CDCl_3$) of calix–TTF systems **6–10** and effect of anions X^- (n-Bu_4NX) on compound **7**



	δH_a	δH_b	$\Delta\delta(H_b-H_a)$	δH_c	δH_d	$\Delta\delta(H_d-H_c)$	δH_e	δH_f	$\Delta\delta(H_f-H_e)$	δOH	δNH
6	3.39	4.26	0.87	6.97	7.05	0.08	1.09	1.25	0.16	8.37	8.50
7	3.42	4.29	0.87	6.97	7.18	0.21	1.03	1.21	0.18	—	7.97
8	3.34	4.19	0.85	6.72	7.10	0.38	0.88	1.32	0.44	6.90	8.00
9	3.40	4.25	0.85	6.95	7.04	0.09	1.10	1.25	0.15	8.36	8.55
10	3.12	4.40	1.28	6.48	7.05	0.57	0.85	1.28	0.43	—	8.31
7+$H_2PO_4^-$ [a]	3.16	4.45	1.26	6.50	7.06	0.56	0.83	1.30	0.47	—	8.44
7+$PhCO_2^-$ [a]	3.16	4.45	1.29	6.50	7.05	0.55	0.83	1.30	0.47	—	8.47
7+AcO^- [a]	3.11	4.41	1.29	6.46	7.01	0.55	0.78	1.26	0.47	—	8.43
7+Br^- [a]	3.37	4.25	0.88	6.93	7.13	0.20	1.00	1.16	0.16	—	8.22

[a] Three equivalents.

the significantly higher $\Delta\delta$ values of the ArH and the *t*-Bu chemical shifts in **8** compared to **9** (0.38 and 0.44 vs 0.09 and 0.15 ppm, respectively). Thus, the shape of the cones seems similar for both the more flexible compounds **9** and **6**, whereas capped-calixarene **8** is strongly distorted. This is also confirmed by the chemical shift of the NH signals which indicate strong intramolecular H-bonds in the case of **9** and **6** (δ 8.55 and 8.50, respectively) unlike the case of **8** (8.00). Finally, the cone in the target bridged calix–TTF system **10** has an even greater distortion, as expected upon tetrasubstitution of the four phenolic positions. The steric constraint in this case leads to a strongly distorted structure with $\Delta\delta$ values of 0.57 and 0.43, respectively, for the ArH and the *t*-Bu signals. Note that in the case of **10** the N–H groups are engaged in intramolecular H-bonds (δ 8.31), whereas it is not the case with **7** (7.97), though it is also *O*-tetrasubstituted. On this basis, we anticipate that this interaction could have a negative effect on the binding properties of this calix–TTF assembly.

2.4. Binding studies

2.4.1. ^{1}H NMR titrations. The binding of receptors **6–10** by various anions introduced as tetrabutylammonium salts (n-Bu_4NX; X=$H_2PO_4^-$, CH_3COO^-, $C_6H_5COO^-$, Br^-) was monitored by ^{1}H NMR (Table 1).

No clear evidence of anion binding was found for the free phenolic compounds **6**, **8** and **9**. A possible explanation in the case of **6** and **9** lies on the presence of intramolecular hydrogen-bonds indicated by the NH and OH shifts (Table 1), which could prevent any interaction with the anion. In the case of **8**, the absence of anion binding may result from the highly constrained structure of the molecule, which therefore cannot accommodate a guest anion. This may also explain the lack of any anion binding with compound **10**. In contrast, compound **7** shows a good affinity for dihydrogenophosphate, benzoate and acetate (X^-) anions.

The ^{1}H NMR titration of **7** by these anions is characterized by the progressive disappearance of the signals corresponding to **7** and the parallel appearance of a new set of signals corresponding to the complex in slow equilibrium with the free ligand on the NMR time scale. As an illustrative example, the case of the titration of compound **7** by AcO^- is presented in Figure 2 (see also Figs. S1 and S2, Supplementary data for titrations with $PhCO_2^-$ and $H_2PO_4^-$ anions). In the presence of excess Bu_4NX, no signals of free **7** are detectable. The NMR spectra in the presence of X^- strongly suggest several structural changes of the calixarene platform in **7** upon anion binding. In particular, analysis of the $\Delta\delta$ values (Table 1) corresponding to the $ArCH_2Ar$, ArH and $C(CH_3)_3$ groups, indicates very significant changes upon introduction of X^-. The new set of $\Delta\delta$ values ($\Delta\delta(H_b-H_a)$=1.26, $\Delta\delta(H_d-H_c)$=0.55 and $\Delta\delta(H_f-H_e)$=0.47) observed for each of the different anions (X^-=$H_2PO_4^-$, CH_3COO^-, $C_6H_5COO^-$), is characteristic of a distorted, pinched cone conformation very close to the one observed for the constrained and rigid system **10** (Table 1). The conformational rigidity conferred upon anion binding is also illustrated by the better resolution of the signals observed for the ^{1}H NMR spectra of the complexes compared to the free ligand **7**. Finally, it is also noted that the N–H signal appears at lower fields in the complex (δ 8.44 vs 7.97 in **7**), as expected from its participation in the binding process of the anion. Very similar behaviour was observed when acetate and benzoate were used as anions (see Table 1). It is worth noting that very different behaviour is observed in the case of the spherical anion Br^-. Here, the binding process is manifested by a progressive downfield shift of the amide proton ($\Delta\delta$(N–H)=+0.25), but all other signals (H_{a-f}) are not significantly affected compared to those of free **7**, in marked contrast to the observations made with other anions (Table 1). Such data may probably be explained by a mismatched structure of the calix–TTF receptor **7** for spherical anions.

2.4.2. Cyclic voltammetry. The electrochemical behaviour of the redox-active calix–TTF systems **6–10** was studied by cyclic voltammetry using Bu_4NPF_6 as supporting electrolyte in a 1:1 acetonitrile/dichloromethane mixture. Oxidation peak potentials are gathered in Table 2.

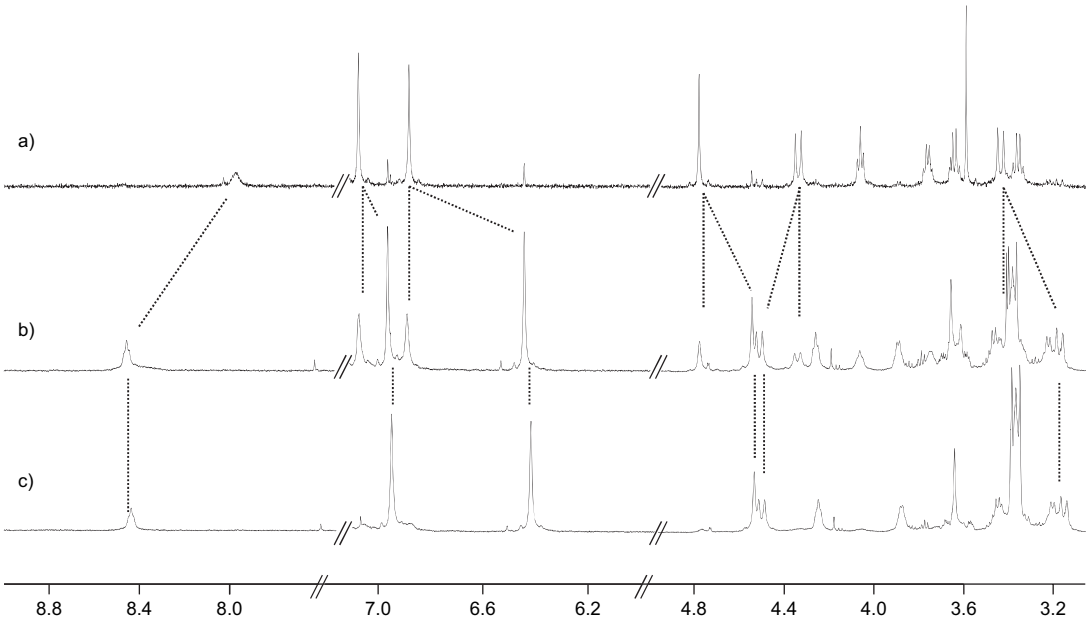


Figure 2. ^{1}H NMR spectra of calix–TTF assembly **7** ($CDCl_3$), in the presence of TBAOAc: (a) ([AcO^-]/[**7**])=0; (b) ([AcO^-]/[**7**])=1; (c) ([AcO^-]/[**7**])=2.

Table 2. Oxidation peak potentials (E_i^{ox}) of calix–TTF systems **6–10** (10^{-4} M in CH_3CN/CH_2Cl_2 1:1 (v/v); Bu_4NPF_6 0.1 M; Pt, Fc^+/Fec; 100 mV s^{-1})

	6	**7**	**8**	**9**	**10**
E^1_{ox} (V)	0.123	0.117	0.128	0.131	0.159
E^2_{ox} (V)	0.401	0.382	0.442	0.424	0.443

The voltammograms of all these calix–TTF assemblies show the usual two redox waves of TTF derivatives, which correspond to the two successive one-electron reversible oxidations (E_i^{ox}) of each TTF unit into radical cation and dication states (Fig. 3).

Evolution of the electrochemical behaviour of the TTF probe upon anion binding by the receptor was studied with various anions. Whereas no clear effect was observed in the case of **6**, **8**, **9** and **10**, significant variations of the redox behaviour occurred in the case of receptor **7** in the presence of the different anions ($X^-=H_2PO_4^-$, CH_3COO^-, $C_6H_5COO^-$, Br^-). Figure 3 presents the electrochemical behaviour of **7** in the presence of acetate and dihydrogenophosphate anions (see also Figs. S3, S4 for the cases of benzoate and bromide anions). In the cases of the carboxylate anions ($X^-=CH_3COO^-$, $C_6H_5COO^-$), as often observed with other redox-active receptors upon titration of anions,[1e,3,4] the electrochemical signature of the binding is a flattening of the reduction waves, typical of an EC mechanistic response (Fig. 3a and Fig. S4). This indicates that the anion strongly interacts with the oxidized TTF moiety, therefore inhibiting the electron-transfer back to the TTF. Nevertheless, the binding process is clearly accompanied on the positive scan by a diminution of the first redox wave of **7** to the benefit of a new one, located at a more negative potential ($\Delta E^1_{ox}=-80$ mV), corresponding to the oxidation of the complex (Fig. 3a). As previously noted with several amide–ferrocene receptors,[1e,3,4] the bound anion stabilizes the positively charged TTF moiety, facilitating the oxidation process (lowering of E^1_{ox}). Thus, compound **7** constitutes a new example of a TTF-based ligand capable of electrochemical recognition upon anion titration. In the case of $X^-=H_2PO_4^-$, the host–guest interaction is even more clearly manifested by two-wave behaviour with the appearance of a distinct voltammetric curve growing at more negative potential

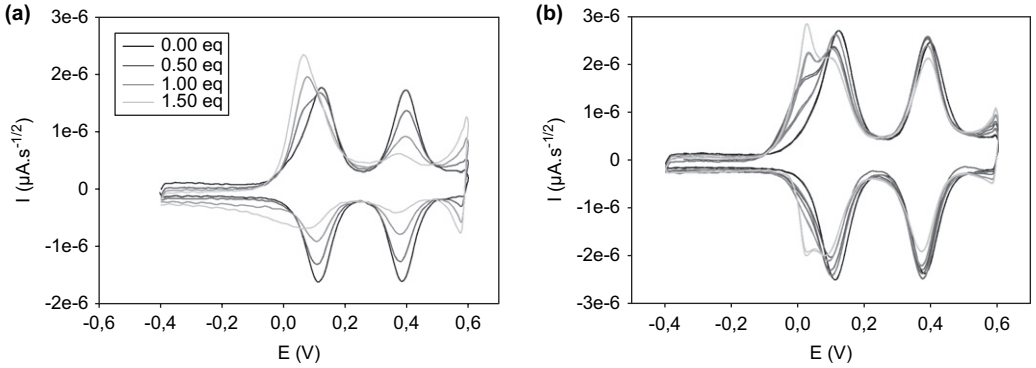


Figure 3. Deconvoluted cyclic voltammetry of (a) **7** ($C=2.79\times10^{-4}$ M) in CH_3CN/CH_2Cl_2, $TBAPF_6$ (0.1 M) in the presence of increasing amounts of TBAOAc; Pt, diam=1.6 mm; $v=100$ mV s^{-1}, versus Fc^+/Fec and (b) **7** (2.79×10^{-4} M) in the presence of increasing amounts of $TBAH_2PO_4$.

(ΔE^1_{ox}=−100 mV) (Fig. 3b). The CV of the parent TTF(SMe)$_4$ also remains unchanged under the same conditions in the presence of these different anions, which illustrates the critical contribution of the X···H–N hydrogen bonding promoted by the amide functionalities of **7**, in synergy with electrostatic ion-pairing interaction. The selectivity of this process is also illustrated by the fact that these experiments were performed in the presence of a [PF_6^-]/[X^-] ratio~3600 (for X^-=$H_2PO_4^-$, CH_3COO^-, $C_6H_5COO^-$). No redox potential shift is observed for the second redox system of the TTF probe (E^2_{ox}), which could indicate a lack of anion binding for the fully oxidized $\mathbf{7}^{4+}$ state. This may be due to conformational changes which certainly arise upon oxidation to $\mathbf{7}^{4+}$, and which result from repulsive interactions between the dicationic TTF units, leading to the disappearance of any synergy between amide functions in the binding of an anion. Such conformational modifications upon oxidation of TTF units were recently described by us in alternative calixarene–TTF assemblies.[7a] In the case of Br^-, oxidation of the anion in the same redox potential window as for **7** prevents any informative CV titration experiments (Fig. S4).

3. Conclusion

We have established synthetic access to a series of new calixarene–TTF assemblies incorporating secondary amide binding units. Their synthesis involves the preparation of new TTF carboxylic acid synthons, whose solid-state X-ray structures are governed by strong intermolecular C═O···H–O interactions. ^{1}H NMR titration studies show that depending on their capped or open structure, some of these calixarene–amide–TTF receptors exhibit a good binding ability for $H_2PO_4^-$, CH_3COO^- and $C_6H_5COO^-$ but not for Br^-. Most importantly, an electrochemical recognition process is observed for one of these assemblies in the presence of the above-mentioned anions. The potential of the calixarene scaffold to preorganize a 3-D environment for multifunctional systems appears very promising and extension of this strategy to other types of calixarene–TTF-based receptors is underway.

4. Experimental

4.1. General

Where necessary, solvents were purified prior to use and stored under nitrogen. Unless stated otherwise, commercial grade chemicals were used without further purification.

Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 500 instrument (500.13 MHz for ^{1}H NMR and 125.75 MHz for ^{13}C NMR). The mass spectra were either recorded on a Bruker Biflex-IIITM (MALDI-TOF), or on a Jeol JMS 700 (high resolution mass spectra (HRMS)) by electronic impact (EI). The infrared spectra were recorded on an FTIR BIORAD FTS 155. The cyclic voltammetry (CV) studies used EGG PAR 273 or 273A potentiostats.

X-ray data collection was performed at 293 K on an STOE-IPDS diffractometer for **3a** and on a BRUKER KappaCCD diffractometer for **3b**, both equipped with a graphite monochromator utilizing Mo Kα radiation (λ=0.71073 Å). The structures were solved by direct methods (SIR92)[17] and refined on F^2 by full matrix least-squares techniques using the SHELX97 package.[18] All non-H atoms were refined anisotropically and the H atoms were included in the calculation without refinement. Absorption was corrected by an empirical multiscan method for **3a** and by the Gaussian technique for **3b**.

4.2. Anion binding studies

The binding ability of receptors **6–10** was evaluated by ^{1}H NMR titrations and cyclic voltammetry. A solution of the receptor (3 mM in $CDCl_3$) was prepared and ^{1}H NMR titration experiments with solutions of tetrabutylammonium dihydrogenphosphate, benzoate, acetate or bromide dissolved in deuterated chloroform were undertaken. Stepwise additions of the salt were made until no additional change in chemical shift was observed. All measurements were carried out at 298 K.

The electrochemical properties of receptors **6–10** were studied by cyclic voltammetry (CV) in CH_2Cl_2/CH_3CN with $TBAPF_6$ (0.1 M) as supporting electrolyte. The working electrode was a Pt disc and the counter electrode consisted of a Pt wire; potentials were calibrated with the ferrocene/ferrocenium couple. The potential window was 0.40–0.80 V and the scan rate 100 mV s^{-1}. Electrochemical titrations were carried out for receptors **6** and **7** by recording cyclic voltammograms after a progressive addition (0.00–5.00 equiv) of a given tetrabutylammoniun salt TBAX (X^-=dihydrogenophosphate, acetate, benzoate or bromide) dissolved in an acetonitrile solution containing the supporting electrolyte.

4.3. Synthesis

4.3.1. Methyl 2-(3,6,7-trimethylsulfanyl tetrathiafulvalen-2-ylthio)acetate (2a). TTF derivative **1a**[10] (0.427 g, 1.0 mmol) was dissolved in dry DMF (25 mL) and degassed with N_2 for 15 min. A solution of $CsOH·H_2O$ (0.185 g, 1.1 mmol, 1.1 equiv) in dry methanol (5 mL) was added over a period of 10 min under N_2. Afterwards, a solution of methylbromoacetate (0.305 g, 2.0 mmol, 2.0 equiv) in dry degassed DMF was added. The reaction mixture was stirred for 4 h at room temperature and then concentrated in vacuo. The crude product was dissolved in methylene chloride, washed with water three times and then dried over $MgSO_4$. The organic solvent was evaporated in vacuo and the resulting solid was purified by silica column chromatography (CH_2Cl_2/petroleum ether (2:3)). Evaporation of the solvent produced **2a** as a red oil (92% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 3.76 (s, 3H, OCH_3), 3.53 (s, 2H, SCH_2), 2.45 (s, 3H, SCH_3), 2.42 (s, 6H, SCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 169.03 (C═O), 134.10, 127.76, 127.46, 122.36 (lateral C═C), 111.44, 110.37 (central C═C), 52.76 (OCH_3), 37.28 (SCH_2), 19.22, 19.18 (SCH_3). FTIR (KBr, cm^{-1}): 1738.2 (vs, C═O). MS (MALDI-TOF): m/z=445.80 [$M^{+\bullet}$].

4.3.2. Dimethyl 2,2′-(6,7-dimethylsulfanyl tetrathiafulvalene-2,3-diyl)bis(sulfanediyl)diacetate (2b). TTF derivative **1b**[10] (0.932 g, 2 mmol) was dissolved in dry DMF (50 mL) and degassed with N_2 for 15 min. A solution of

$CsOH \cdot H_2O$ (0.370 g, 2.2 mmol, 2.2 equiv) in dry methanol (4 mL) was added over a period of 10 min under N_2. Afterwards, a solution of methylbromoacetate (0.305 g, 2 mmol, 2 equiv) in dry degassed DMF was added. The reaction mixture was stirred for 16 h at room temperature and then concentrated in vacuo. The crude product was dissolved in methylene chloride, washed with water three times and then dried with $MgSO_4$. The organic solvent was evaporated in vacuo and the resulting solid was purified by silica gel column chromatography (CH_2Cl_2). Evaporation of the solvent produced **2a** as a red oil (80% yield). ^1H NMR ($CDCl_3$, ppm): δ 3.77 (s, 6H, OCH_3), 3.59 (s, 4H, SCH_2), 2.42 (s, 6H, SCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 168.80, 128.96, 127.54, 111.96, 109.61, 52.76, 37.42, 19.12. FTIR (KBr, cm^{-1}): 1738.2 (vs, C=O). MS (MALDI-TOF): m/z=504.50 [$M^{+\bullet}$].

4.3.3. 2-(3,6,7-Trimethylsulfanyl tetrathiafulvalen-2-ylthio) acetic acid (3a). *Procedure A* (from ester **2a**). A solution of LiOH (0.924 g, 39.0 mmol) in H_2O (25 mL) is added to a suspension of ester **2a** (1.0 g, 2.2 mmol) in 60 mL THF. The mixture was stirred for 20 h at room temperature. The solvents were removed in vacuum, and the residue was treated with HCl 1 M (80 mL) and CH_2Cl_2 (100 mL). The resulting mixture was stirred overnight. The organic phase was then washed with water to neutral pH, dried over $MgSO_4$ and concentrated in vacuum. Analytically pure **3a** was obtained as an orange solid after silica gel column chromatography (CH_2Cl_2/AcOEt (1:1)) (75% yield). *Procedure B* (direct conversion from **1a**). Compound **1a** (1.00 g, 2.34 mmol) was dissolved in dry DMF (50 mL) and degassed with N_2 for 15 min. A solution of caesium hydroxide monohydrate (0.43 g, 2.58 mmol, 1.1 equiv) in dry methanol (5 mL) was added under N_2 over a period of 10 min. A solution of bromoacetic acid (0.36 g, 2.58 mmol, 1.1 equiv) with potassium carbonate (1.80 g, 13 mmol) in dry degassed DMF was then added. The reaction mixture was stirred for 2 h at room temperature. The solvents were removed in vacuum, and the residue was treated with HCl (100 mL, 1 mol L^{-1}). A large amount of orange solid appeared, which was filtered off and washed to afford analytically pure **3a** (90% yield). Mp=114 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 3.59 (s, 2H, SCH_2), 2.50 (s, 9H, SCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 173.36 (C=O), 128.39, 127.45, 127.37, 126.53 (lateral C=C), 112.70, 109.30 (central C=C), 41.48 (SCH_2), 19.25, 19.22, 19.21 (SCH_3). FTIR (KBr, cm^{-1}): 1730.2 (vs, C=O). MS (MALDI-TOF): m/z=431.70 [$M^{+\bullet}$].

4.3.4. 2,2′-(6,7-Dimethylsulfanyl tetrathiafulvalene-2,3-diyl)bis(sulfanediyl)diacetic acid (3b). *Procedure A* (from ester **2b**). We applied a similar strategy as for the synthesis of **3a**, using a solution (25 mL) of LiOH (1.85 g, 77 mmol) in H_2O and a suspension of diester **2b** (1.1 g, 2.2 mmol) in 60 mL THF. The mixture was stirred for 10 h at room temperature. The solvents were removed in vacuum, and the residue was treated with an aqueous solution of HCl 1 M (100 mL) and CH_2Cl_2 (125 mL). The resulting mixture was stirred for 12 h. The organic phase was then washed with water to neutral pH, dried over $MgSO_4$ and concentrated in vacuum. Analytically pure **3b** was obtained as an orange-brown solid (96% yield). *Procedure B* (direct conversion from **1b**). Compound **1b** (300 mg, 0.64 mmol) was dissolved in dry DMF (10 mL) and degassed with N_2 for 15 min. A solution of caesium hydroxide monohydrate (322 mg, 1.92 mmol, 3 equiv) in dry methanol (3 mL) was added under N_2 over a period of 10 min. During this period, a solution of bromoacetic acid (889 mg, 6.4 mmol, 10 equiv) with potassium carbonate (2.67 g, 19.2 mmol, 30 equiv) in a degassed MeOH/DMF (1:1) solution (20 mL) was prepared, and then added. The resulting reaction mixture was stirred for 2 h at room temperature. The solvents were removed in vacuum, and the residue was treated with HCl (100 mL, 1 mol L^{-1}). A large amount of orange solid appeared, which was filtered off and washed to afford analytically pure **3b** as an orange-brown solid (85% yield). Mp=172–174 °C; ^1H NMR ($CDCl_3$, ppm): δ 3.59 (s, 4H, SCH_2), 2.49 (s, 6H, SCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 173.4 (C=O), 128.4, 127.3 (C=C lateral), 112.7, 109.3 (C=C central), 41.6 (SCH_2), 19.3 (SCH_3). FTIR (KBr, cm^{-1}): 3112, 1730.2. MS (MALDI-TOF): $C_{12}H_{12}O_4S_8$, m/z=476.22 [$M^{+\bullet}$].

4.3.5. 2,5-Dioxopyrrolidin-1-yl 2-(3,6,7-trimethylsulfanyl tetrathiafulvalen-2-ylthio)acetate (4a). A solution of acid derivative **3a** (0.540 g, 1.25 mmol) and *N*-hydroxysuccinimide (NHS) (0.150 g, 1.25 mmol) in 30 mL of dry THF was stirred at room temperature for 15 min. Then, *N*,*N*′-dicyclohexylcarbodiimide (0.25 g, 1.25 mmol) in 20 mL dry THF was slowly added to the above suspension. A white precipitate appeared and the reaction mixture was stirred for 2 h. The precipitate (DCU) was filtered off and the solvent was removed in vacuum. The resulting material was dissolved in CH_2Cl_2 (50 mL) and the remaining solid (DCU) was filtered off. The organic phase was washed with water (×3) and dried over $MgSO_4$. The solvent was evaporated in vacuum, and the crude product was purified by silica gel column chromatography (CH_2Cl_2/petroleum ether (1:2)) to afford activated ester **4a** as an orange powder (82% yield). Mp=134 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 3.80 (s, 2H, SCH_2), 2.84 (s, 4H, CH_2CH_2), 2.45 (s, 3H, SCH_3), 2.42 (s, 6H, SCH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 168.42 (NCO), 164.41 (COO), 135.99, 127.95, 127.25, 120.62 (lateral C=C), 112.26, 109.83 (central C=C), 53.39, 34.19 (SCH_2), 25.61 (CH_2CH_2), 19.31, 19.19 (SCH_3). FTIR (KBr, cm^{-1}): 1784.6, 1743.9 (vs, C=O). MS-ESI$^+$ $C_{15}H_{15}NO_4S_8$: calcd 528.877, found 528.879.

4.3.6. Bis(2,5-dioxopyrrolidin-1-yl) 2,2′-(6,7-dimethylsulfanyl tetrathiafulvalene-2,3-diyl)bis(sulfanediyl)diacetate (4b). A solution of diacid derivative **3b** (0.620 g, 1.31 mmol) and *N*-hydroxysuccinimide (NHS) (0.430 g, 3.75 mmol, 1.4 equiv) in 30 mL of dry THF was stirred at room temperature (15 min). Then, *N*,*N*′-dicyclohexylcarbodiimide (0.773 g, 3.75 mmol, 1.4 equiv) was dissolved in dry THF (20 mL) and added slowly to the above suspension. A white precipitate appeared and the reaction mixture was stirred for 2 h. The precipitate (DCU) was filtered off and the solvent was removed in vacuum. The resulting material was dissolved in CH_2Cl_2 (50 mL) and the remaining solid (DCU) was filtered off. The solvent was evaporated in vacuum, and the crude product was purified by silica gel column chromatography (CH_2Cl_2/AcOEt (10:1)) to afford **4b** as an orange powder (85% yield). Mp=202 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 3.85 (s, 2H, SCH_2CO), 2.9–2.8 (s, 4H, $OCCH_2CH_2CO$), 2.45 (s, 3H, SCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 168.4 (NCO), 164.4 (COO), 135.9,

127.3 (C═C lateral), 113.1, 109.8 (C═C central), 52.9 (SCH_2), 25.6 (CH_2CH_2), 19.2 (SCH_3). FTIR (KBr, cm^{-1}): 1784.6, 1743.9. HRMS-ESI$^+$ $C_{20}H_{18}N_2O_8S_8$: calcd 669.8829, found 669.8840.

4.3.7. Calixarene–TTF assembly 6.[8] Tetrathiafulvalene derivative **4a** (0.5 g, 0.95 mmol) was dissolved in dry THF (20 mL) and degassed with N_2 for 10 min. A solution of the calix[4]arene diamine **5** (0.28 g, 0.38 mmol) in dry THF (10 mL) was then added. The reaction mixture was stirred overnight. The solvent was removed in vacuum. The resulting solid was dissolved in CH_2Cl_2, washed with water, dried with $MgSO_4$ and purified by silica column using CH_2Cl_2/ethyl acetate (9:1) to give **6** as an orange powder in 76% yield. Mp=100–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 8.50 (t, 2H, CONH), 8.37 (s, 2H, OH), 7.05 (s, 4H, ArH), 6.97 (s, 4H, ArH), 4.26 (d, J=13.5 Hz, 4H, $ArCH_2Ar$), 4.14 (t, J=5 Hz, 4H, OCH_2), 3.96 (m, 4H, NCH_2), 3.58 (s, 4H, SCH_2), 3.39 (d, J=13.5 Hz, 4H, $ArCH_2Ar$), 2.42 (s, 6H, SCH_3), 2.35 (s, 6H, SCH_3), 2.33 (s, 6H, SCH_3), 1.25 (s, 18H, $C(CH_3)_3$), 1.09 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 171.12, 167.75 (CONH), 149.32, 148.58 (Ar-*ipso*), 148.16, 142.95 (Ar-*para*), 133.10, 133.02 (Ar-*ortho*), 127.75, 127.62 (Ar-*meta*), 127.44, 126.08, 125.72, 123.01, 110.96, 75.45, 60.38, 39.97, 39.71, 39.55, 34.18, 33.90 ($C(CH_3)_3$), 32.17, 31.59 ($C(CH_3)_3$), 31.58, 31.07 ($ArCH_2Ar$), 19.24 (SCH_3), 19.21 (SCH_3). FTIR (KBr, cm^{-1}): 3317.9 (OH), 1656.9 (C═O). ESI-MS: *m/z* 1587.2 [M+Na$^+$, 100], 1562 [M$^+$, 87]. HRMS-ESI$^+$: $C_{70}H_{86}N_2O_6S_{16}$: calcd 1562.2017, found 1562.2018.

4.3.8. Calixarene–TTF assembly 7.[8] A solution of calix[4]-arene **6** (0.125 g, 0.08 mmol) in dry acetone (10 mL) was stirred under N_2 in the presence of Na_2CO_3 (0.170 g, 1.60 mmol) and NaI (0.240 g, 1.60 mmol). The solution was refluxed for 30 min. Then *N*,*N*-diethyl-α-chloro-acetamide (0.024 g, 0.022 mL, 0.16 mmol) was added. After six days, the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was dissolved in 20 mL of CH_2Cl_2 and washed with 10% HCl (10 mL×3). The organic layer was separated and dried over $MgSO_4$. The solution was concentrated in vacuum. Purification was carried out by column chromatography on silica gel (CH_2Cl_2/acetone (4:1)) to give 79 mg of **7** as an orange powder in 55% yield. Mp=74–84 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 7.97 (br s, 2H, CONH), 7.18 (s, 4H, ArH), 6.97 (s, 4H, ArH), 4.71 (s, 4H, OCH_2CO), 4.29 (d, J=12.5 Hz, 4H, $ArCH_2Ar$), 4.02 (t, J=6.5 Hz, 4H, OCH_2), 3.73 (m, 4H, CH_2N), 3.62 (q, J=7.0 Hz, 4H, NCH_2CH_3), 3.57 (s, 4H, SCH_2CO), 3.42 (d, J=12.5 Hz, 4H, $ArCH_2Ar$), 3.35 (q, J=7.0 Hz, 4H, NCH_2CH_3), 2.42 (s, 6H, SCH_3), 2.40 (s, 6H, SCH_3), 2.39 (s, 6H, SCH_3), 1.33 (t, J=7.0 Hz, 6H, CH_3CH_2N), 1.27 (t, J=7.0 Hz, 6H, CH_3CH_2N), 1.21 (s, 18H, $C(CH_3)_3$), 1.03 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 167.99 (CON), 167.51 (CONH), 149.01, 148.81 (Ar-*ipso*), 148.56, 147.52 (Ar-*para*), 134.56, 133.82 (Ar-*ortho*), 131.59, 127.53 (Ar-*meta*), 125.98, 123.45 (C═C), 111.60, 110.69 (C═C), 75.51, 73.93 (OCH_2CON), 41.89, 41.46 (NCH_2CH_3), 39.60, 39.16 ($NHCH_2$), 34.24, 34.01 ($C(CH_3)_3$), 31.37, 31.11 ($C(CH_3)_3$), 31.42, 31.07 ($ArCH_2Ar$), 19.28 (SCH_3), 14.39, 13.22 (NCH_2CH_3). FTIR (KBr, cm^{-1}): 1656, 1648. MS (MALDI-TOF): *m/z*=1812.88 [M$^{+\bullet}$+Na]. HRMS-ESI$^+$ $C_{82}H_{108}O_8N_4S_{16}Na$: calcd 1813.3599, found 1813.3499.

4.3.9. Calixarene–TTF assemblies 8 and 9. Tetrathiafulvalene **4b** (0.650 g, 0.97 mmol) was dissolved in dry THF (40 mL) and degassed with N_2 for 10 min. Then, a solution of calix[4]arene diamine **5** (0.730 g, 0.97 mmol) in 10 mL dry THF was added. The reaction mixture was stirred overnight. The solvent was removed in vacuum. The resulting solid was dissolved in CH_2Cl_2, washed with water, dried with $MgSO_4$ and purified by silica column using CH_2Cl_2/ethyl acetate (9:1 and then 4:1) as eluent to produce successively **8** as a yellow powder (31% yield) and **9** as an orange powder (17% yield). *Calixarene–TTF assembly* ***8***: mp=120 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 8.00 (t, 2H, CONH), 7.10 (s, 4H, ArH), 6.90 (s, 2H, OH), 6.72 (s, 4H, ArH), 4.19 (d, J=13.0 Hz, 4H, $ArCH_2Ar$), 4.13 (t, J=4.9 Hz, 4H, OCH_2), 3.84 (m, 4H, J=4.9 Hz, NCH_2), 3.58 (s, 4H, SCH_2), 3.34 (d, J=13.0 Hz, 4H, $ArCH_2Ar$), 2.43 (s, 6H, SCH_3), 1.32 (s, 18H, $C(CH_3)_3$), 0.88 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 166.89, 149.96, 149.12, 147.52, 142.43, 131.85, 130.49, 127.84, 127.64, 125.60, 125.34, 112.02, 109.25, 74.45, 39.76, 39.32, 33.86, 31.63, 31.35, 30.86, 19.33, 12.87. FTIR (KBr, cm^{-1}): 3316, 2961, 2869, 1653, 1485. MS (MALDI-TOF): *m/z*=1174.36 [M$^{+\bullet}$]; HRMS [M$^{+\bullet}$+Na$^+$] $C_{60}H_{74}O_6N_2S_8Na$: *m/z* (%) observed 1197.3208, theo 1197.3210. *Calixarene–TTF assembly* ***9***: mp >260 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 8.55 (t, 4H, CONH), 8.36 (s, 4H, OH), 7.04 (s, 8H, ArH), 6.95 (s, 8H, ArH), 4.25 (d, J=13.0 Hz, 8H, $ArCH_2Ar$), 4.10 (t, 8H, CH_2O), 4.00 (m, 8H, CH_2NH), 3.52 (s, 8H, SCH_2CO), 3.41 (d, J=13.0 Hz, 8H, $ArCH_2Ar$), 2.34 (s, 12H, SCH_3), 1.25 (s, 36H, $C(CH_3)_3$), 1.10 (s, 36H, $C(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 167.87, 156.74, 149.33, 148.69, 147.96, 142.92, 132.91, 132.86, 128.93, 127.78, 127.55, 126.01, 125.66, 111.00, 110.32, 75.08, 49.09, 40.03, 39.41, 34.12, 34.08, 33.92, 33.88, 32.13, 31.69, 31.57, 31.43, 31.16, 31.05, 30.97, 30.96, 25.59, 24.92, 19.16 (34C). FTIR (KBr, cm^{-1}): 3327, 2957, 1653, 1485. MS (MALDI-TOF): *m/z*=2352.07.

4.3.10. Calixarene–TTF assembly 10. A sample of calix[4]arene **8** (0.150 g, 0.13 mmol) was dissolved in dry acetone (5 mL). To this stirred solution, K_2CO_3 (0.034 g, 0.32 mmol), NaI (0.048 g, 0.32 mmol) and *N*,*N*-diethyl-α-chloro-acetamide (0.038 g, 0.035 mL, 0.26 mmol) were added and the reaction mixture heated to reflux for 50 h. The solvent was removed under pressure and the residue was treated with 1 M HCl (75 mL) and dried over $MgSO_4$. The solvent was distilled off to afford the crude product, which was purified by silica chromatography, CH_2Cl_2/CH_3COOEt (3:1). Compound **10** was obtained as an orange powder in 35% yield. Mp=118 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 8.31 (t, 2H, CONH), 7.05 (s, 4H, ArH), 6.48 (s, 4H, ArH), 4.51 (s, 4H, OCH_2CO), 4.40 (d, J=12.5 Hz, 4H, $ArCH_2Ar$), 4.05 (t, 4H, OCH_2), 4.02 (t, 4H, CH_2N), 3.66 (s, 4H, SCH_2CO), 3.45 (q, 4H, CH_2N), 3.24 (q, 4H, CH_2N), 3.12 (d, J=12.5 Hz, 4H, Ar–CH_2–Ar), 2.40 (s, 6H, SCH_3), 1.28 (s, 18H, $C(CH_3)_3$), 1.20 (t, 6H, CH_3CH_2N), 1.09 (t, 6H, CH_3CH_2N), 0.85 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): δ 168.14, 167.56, 153.89,

152.39, 145.32, 144.32, 144.96, 135.10, 131.91, 128.06, 127.11, 125.50, 124.88, 72.63, 72.47, 59.63, 41.71, 40.63, 40.42, 40.13, 39.91, 39.30, 34.02, 33.58, 31.62, 31.00, 19.03, 14.36, 13.83, 13.12, 12.86. FTIR (KBr, cm^{-1}): 1649, 1637. MS (MALDI-TOF): m/z=1400. HRMS m/z (%): calcd 1401.5072, found 1401.5116.

4.4. Crystal data

Compound ***3a***: orange plate ($0.46\times0.17\times0.02\ mm^3$), $C_{11}H_{12}O_2S_8$, Mr=432.69, orthorhombic, space group *Pbcn*, a=44.786(4) Å, b=7.6473(5) Å, c=10.3894(7) Å, V=3558.3(5) $Å^3$, Z=8, ρ_{calcd}=1.615 $g\,cm^{-3}$, μ (Mo Kα)=1.002 mm^{-1}, $F(000)$=1776, θ_{min}=2.70°, θ_{max}=22.38°, 10,733 reflections collected, 2248 unique (R_{int}=0.056), restraints/parameters=0/190, $R1$=0.0439 and $wR2$=0.1043 using 1531 reflections with $I>2\sigma(I)$, $R1$=0.0698 and $wR2$=0.1110 using all data, GOF=0.991, $-0.400<\Delta\rho<0.509\ eÅ^{-3}$.

Compound ***3b***: orange plate ($0.31\times0.29\times0.07\ mm^3$), $C_{12}H_{12}O_4S_8$, Mr=476.70, orthorhombic, space group *C*2*cb*, a=10.274(2) Å, b=48.829(5) Å, c=7.695(2) Å, V=3860(1) $Å^3$, Z=8, ρ_{calcd}=1.640 $g\,cm^{-3}$, μ (Mo Kα)=0.939 mm^{-1}, $F(000)$=1952, θ_{min}=2.50°, θ_{max}=28.08°, 22,047 reflections collected, 4058 unique (R_{int}=0.059), restraints/parameters=1/219, $R1$=0.0425 and $wR2$=0.0890 using 3143 reflections with $I>2\sigma(I)$, $R1$=0.0655 and $wR2$=0.0961 using all data, GOF=1.033, $-0.423<\Delta\rho<0.547\ eÅ^{-3}$.

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Supplementary data

NMR titrations ($C_6H_5COO^-$ and $H_2PO_4^-$) as well as CV titrations ($C_6H_5COO^-$ and Br^-) are available in supplementary data. Crystallographic data, tables of bond distances and angles, positional parameters and general displacement parameters for **3a** and **3b** (eight pages). Supplementary data in the form of a CIF have been deposited with the Cambridge Crystallographic Data Centre (CCDC 638732 for **3a** and CCDC 638733 for **3b**). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.119.

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