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Self-Assembled Monolayers of Mono-Tetrathiafulvalene Calix[4]pyrroles and Their Electrochemical Sensing of Chloride

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Since the first reports more than a half-century ago,^[1] interest in self-assembled monolayers (SAMs) on metal surfaces has increased almost exponentially. At present, such supported SAMs are used for numerous applications, ranging from metallurgy—wherein the surface properties, such as conductivity,^[2] wettability,^[3] corrosion resistance,^[4] and etching resistance,^[5] are modified—to the preparation of sensors^[6] and materials for use in separations.^[7] In fact, the use of SAMs is now recognized as offering a convenient, flexible, and simple way to tailor the interfacial properties of metals.^[8] This is because the spontaneous organization and absorption of molecules on metal, metal oxide, or semiconducting surfaces often creates highly ordered systems with well-defined dimensions on the nanoscale.^[9]

During the last decade,^[10,11] increasing attention has been dedicated to the design and elaboration of SAMs that integrate a molecular or ionic receptor unit with a transducer element so as to create sensing devices for environmental or biologic purposes. If a redox-active element is incorporated into the monolayer or the guest, the recognition event can be followed by cyclic voltammetry (CV). In other cases, the

monitoring can be completed by using impedance spectroscopic measurements. Although, cation (generally metallic ions) recognition using SAMs is well documented, and several systems that exhibit both excellent selectivity and sensitivity have been described in the literature,^[12,13] much less work on anion recognition by using SAMs has been reported, perhaps reflecting the fact that anions have variable sizes and shapes and exhibit strong solvation in most solvents. The first anion recognition SAM systems were reported by Astruc et al. and involved the use of ferrocene derivatives for dihydrogenophosphate anion detection.^[14] More recently, Echegoyen et al. described SAMs for use in acetate anion recognition.^[15] Although these systems are very selective, their sensitivity is relatively low and the limits of detection do not reach the sub-millimolar scale.

Calix[4]pyrrole and its derivatives have been extensively studied in the search for chemosensors capable of recognizing specific chemical species, with a number of optically active calix[4]pyrrole-based sensors having now been reported.^[16] Some of us have recently described^[17] the first fully successful examples of electrochemically active sensors^[18] based on calix[4]pyrroles; these were prepared by attaching one, two, or four redox-active tetrathiafulvalene^[19] (TTF) units directly to the calix[4]pyrrole platform so as to produce receptors with enhanced binding affinities toward anions as compared to the parent *meso*-octamethyl calix[4]-pyrrole.^[20] In the case of the mono-TTF calix[4]pyrrole, we observed^[17b] selectivity between the chloride anion ($K_a = 2900 \text{ M}^{-1}$) and the bromide anion ($K_a = 96 \text{ M}^{-1}$) in CH_2Cl_2 solution.

This success has led us to consider that TTF calix[4]pyrroles could be used to create anion-sensing SAMs. These kinds of receptors are attractive in this regard because they incorporate within one molecular framework both pyrrole-based anion recognition and TTF-derived transducer subunits. We wish to report here that such SAMs may be prepared and that they are effective for chloride anion recognition at the sub-millimolar level, thus providing a sensitivity that differs dramatically from previously reported systems.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200901394>.

To test whether TTF calix[4]pyrroles could be used to construct anion-selective SAMs (i.e., solid-supported devices for which the solution phase recognition properties would be transferred to the condensed phase provided by a metal surface), we synthesized the two mono-TTF calix[4]pyrroles **1** and **2** shown in Figure 1. Both derivatives are functional-

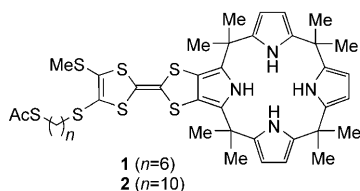


Figure 1. Structural formulas of mono-TTF calix[4]pyrroles **1** and **2**; as detailed in the text, these receptors bear an acetyl-protected alkanethiol anchoring group suitable for formation of SAMs.

ized with an alkanethiol anchor group (protected with an acetyl group) that was expected to allow for attachment to a gold substrate.^[21] As detailed below, the kinetics for the formation of the SAMs were then followed using quartz crystal microbalance (QCM) measurements; this allowed us to probe the effects of conformational changes in the mono-TTF calix[4]pyrrole skeleton and obtain insights into the molecular events associated with chloride anion complexation.

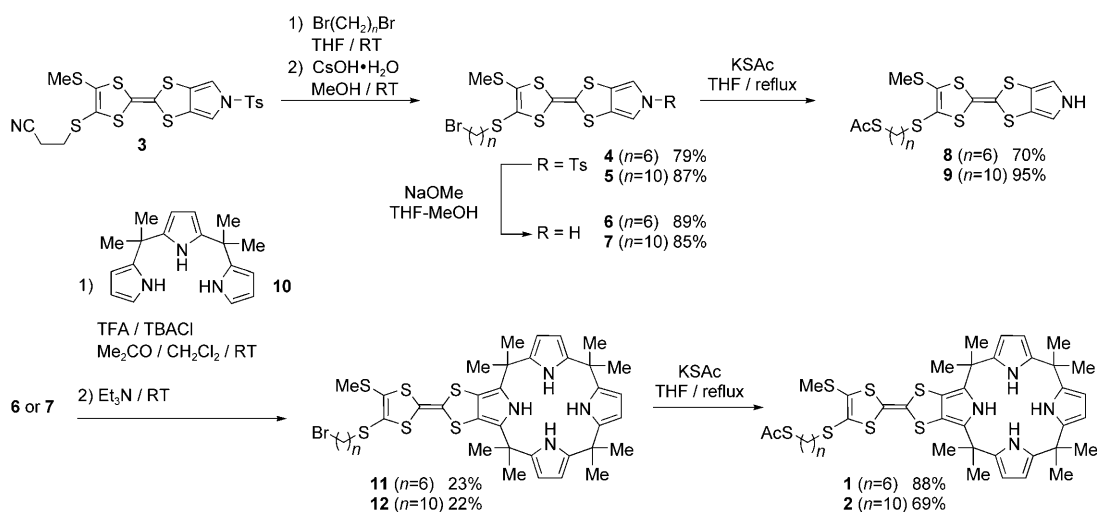
The syntheses of the mono-TTF calix[4]pyrroles **1** and **2**, as well as those of two mono-pyrroloTTF (MPTTF) model compounds **8** and **9**, were carried out as outlined in Scheme 1.

The routes employed are based on the use of two key precursors already reported in the literature, namely i) the MPTTF derivative^[22] **3** and ii) the tripyrrane^[23] **10**. A solution of the MPTTF building block^[22] **3** and an excess of either 1,6-dibromohexane or 1,10-dibromodecane was treat-

ed with 1 equivalent of CsOH·H₂O affording the MPTTF derivatives **4** or **5**, in 79 and 87% yield, respectively. Removal of the tosyl group was carried out by heating **4** or **5** carefully in a 3:1 solvent mixture of THF and MeOH, in the presence of an excess of NaOMe.^[24] This gave **6** and **7** in good yields. Mixing these latter MPTTF derivatives with approximately two equivalents of the tripyrrane^[23] **10** in a mixture of Me₂CO and CH₂Cl₂ in the presence of one equivalent of tetrabutylammonium chloride (TBACl) and excess trifluoroacetic acid (TFA) provided the mono-TTF calix[4]pyrroles **11** or **12** in 23 and 22% yield, respectively. Heating a solution of these latter precursors under reflux in the presence of excess potassium thioacetate (KSac) in anhydrous THF then afforded the corresponding thioesters **1** or **2** in 88 and 69% yield, respectively. The control thioesters **8** or **9** were obtained in 70 and 95% yield, respectively, by likewise heating a mixture of the MPTTF derivatives **6** or **7** with an excess KSac in an analogous fashion.

Both mono-TTF calix[4]pyrroles **1** and **2** were isolated as yellow solids and fully characterized (cf. Supporting Information) using traditional techniques. Electrochemical characterization of these species was carried out in a glovebox in CH₂Cl₂ solution at room temperature using cyclic voltammetry (CV). The electrochemical behavior of the MPTTF model compounds **8** and **9** was also monitored under similar conditions. As expected, compounds **1**, **2**, **8**, and **9** display two one-electron oxidation processes ($E_{1/2}^1 = 0.010\text{--}0.030\text{ V}$ and $E_{1/2}^2 = 0.450\text{--}0.465\text{ V}$ vs. Fc/Fc⁺), which are ascribed to a first and second one-electron TTF-centered oxidation event, respectively.

The mono-TTF calix[4]pyrroles **1** and **2** were designed to allow the complexation of anions to be detected via binding-induced changes in the electrochemical properties of the TTF units. CV was used to probe the putative chloride anion-induced changes in the redox potentials of compound **1** and **2**. Chloride anions were chosen for these initial studies since they are known to bind well to calix[4]pyrroles, at



Scheme 1. Synthesis of the two mono-TTF calix[4]pyrroles **1** and **2**. Also shown is the synthesis of the two mono-pyrroloTTF (MPTTF) model compounds **8** and **9**.

least under non-competitive conditions, and to induce a conformational flip between the limiting 1,3-alternate and cone conformations.^[16,25] The progressive addition of chloride anions to a solution of the mono-TTF calix[4]pyrroles **1** and **2** in CH₂Cl₂ at room temperature revealed features that are consistent with chloride anion binding. These studies also provided evidence for an exchange rate that is slow on the CV time scale. For instance, the addition of 0.4 equivalent of chloride anions (as the tetrabutylammonium salt) to a solution of the mono-TTF calix[4]pyrrole **2** in CH₂Cl₂ was observed (Figure 2) to give rise to a new peak in the region

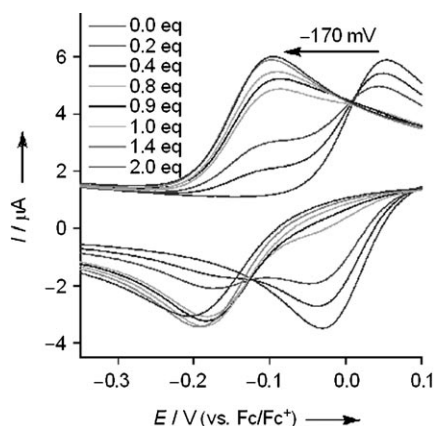


Figure 2. CVs of receptor **2** (CH₂Cl₂, 0.5 mM) obtained by adding increasing quantities of a concentrated CH₂Cl₂ solution of *n*Bu₄NCl containing 0.5 mM **2** so as to counter potential dilution effects (Reference electrode Fc/Fc⁺ with *n*Bu₄NPF₆ (0.1 M) as the supporting electrolyte; on Pt at 0.2 V s⁻¹).

corresponding to the first oxidation process.^[26] This new peak, at $E_{1/2}^1 = -0.13$ V (vs. Fc/Fc⁺), is ascribed to oxidation of the supramolecular complex formed from this receptor and chloride anions (i.e., 2·Cl⁻). Further addition of chloride anions caused the intensity of the peak at $E_{1/2}^1 = +0.03$ V (vs. Fc/Fc⁺), corresponding to oxidation of the uncomplexed mono-TTF calix[4]pyrrole **2**, to decrease along with a concurrent increase in the intensity of the peak at $E_{1/2}^1 = -0.13$ V (vs. Fc/Fc⁺) ascribed to 2·Cl⁻. After addition of ca. 1 equivalent of chloride anions to the mono-TTF calix[4]pyrrole **2**, the peak at $E_{1/2}^1 = +0.03$ V (vs. Fc/Fc⁺) could no longer be observed and only the peak at $E_{1/2}^1 = -0.13$ V (vs. Fc/Fc⁺) was seen in the voltammogram. From this point forward, further addition of chloride anions to compound **2** resulted in little observable change. This is taken as evidence that a strong binding interaction exists between the mono-TTF calix[4]pyrrole **2** and chloride anions under the conditions of the CV experiment. Similar results were obtained when the mono-TTF calix[4]pyrrole **1** was studied in the presence of chloride anions, with the maximum displacement of the first oxidation potentials being $\Delta E_{1/2}^1 = -0.16$ V and -0.17 V for compounds **1** and **2**, respectively. Control experiments, involving analogous titrations of the MPTTF model compounds **8** and **9** with chloride anions, did not

reveal any observable shifts in the waves ascribed to the first oxidation process.

The above background studies completed, SAMs derived from receptors **1** and **2** and model compounds **8** and **9** were prepared. Towards this end, the acetyl protecting groups present in compounds **1**, **2**, **8**, and **9** were removed to afford the corresponding thiols; this was done by treating with CsOH·H₂O in a mixture of THF and MeOH.^[27] The SAMs themselves were then obtained by immersing homemade gold substrates^[28] for 12 h into CH₂Cl₂ solutions (1 mM) containing the thiol in question under an anhydrous, oxygen-free (<1 ppm) argon atmosphere. The SAMs prepared from compounds **1**, **2**, **8**, and **9** were stable as confirmed by CV by scanning over repetitive cycles.^[29] The CVs of the SAMs did not show any shift between the oxidation and the reduction peaks. Moreover, linear dependencies between peak intensities and scan rates were observed for all four systems. Both observations are considered characteristic of an immobilized redox system.^[30]

A comparison of the surface coverage obtained for the SAMs prepared from the two MPTTF model compounds **8** and **9** with those obtained for the SAMs derived from the TTF calix[4]pyrroles **1** and **2** revealed that the MPTTF model compounds have a value which is almost three times higher (i.e., $(1.9 \pm 0.2 \times 10^{-10})$ mol cm⁻² and $(0.7 \pm 0.1 \times 10^{-10})$ mol cm⁻² for **8** and **1**, respectively^[31]). Based on Corey–Pauling–Koltun (CPK) models, the area per molecule for **8** and **1** were estimated to be (49 ± 7) and (79 ± 11) Å², respectively. On this basis, it was concluded that the TTF calix[4]pyrroles were not organized as close to the monolayer surface as were the control mono-pyrroles.

As true in case of the predicative solution phase analyses (vide supra), CV was used to probe the changes in the redox potentials of the SAMs prepared from compounds **1**, **2**, **8**, and **9** as a function of chloride anions. Although, it was expected that addition of chloride anions to the SAMs derived from the two MPTTF model compounds **8** and **9** would lead only to a minor negative shift of the first TTF-centered oxidation process, it was actually found that addition of a large amount of chloride anions to the SAMs induced a small, but significant positive shift ($\Delta E_{1/2}^1 = +15$ mV) to the corresponding waves. This observation, which remains somewhat recondite, stands in marked contrast to what is seen in the case of the SAMs derived from the TTF calix[4]pyrroles **1** and **2**. Here, the progressive addition of chloride anions between 0 and 0.5 μM^[32] induced (Figure 3) a significant negative shift ($\Delta E_{1/2}^1 \approx -30$ mV) in the first TTF-centered oxidation waves.

A comparison of the maximum negative shifts induced by the addition of chloride anions to a solution of the TTF calix[4]pyrrole **2** ($\Delta E_{1/2}^1 = -170$ mV) and to the SAM derived from it ($\Delta E_{1/2}^1 = -30$ mV) reveals that the chloride anion induced shift is much smaller in the case of the supported system than in solution. This observation is rationalized by the fact that immobilization of the TTF calix[4]pyrrole receptor renders more difficult the conformational change from a 1,3-alternate conformation to the cone conformation

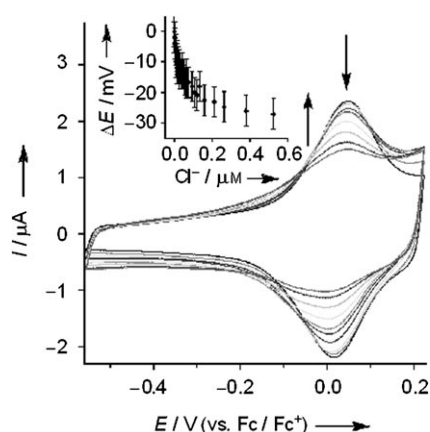


Figure 3. CVs in CH_2Cl_2 of the SAM prepared from the TTF calix[4]pyrrole **2** (the surface coverage of **2** is $(0.7 \pm 0.1 \times 10^{-10}) \text{ mol cm}^{-2}$) recorded after additions of successive aliquots of $n\text{Bu}_4\text{NCl}$ (Reference electrode Fc/Fc^+ with $n\text{Bu}_4\text{NPF}_6$ (0.1 M) as the supporting electrolyte; at 0.2 V s^{-1}). Insert: CV titration curves showing the negative shift of the first oxidation potential (measured at the maximum intensity) of **2** seen upon addition of Cl^- ions.

known to favor anion binding.^[33,34] In fact, it is possible that only a fraction of the immobilized TTF calix[4]pyrroles have enough free space to undergo this crucial conformational change. Support for this latter notion came from a close inspection of the CVs recorded in the presence of chloride anions. The CVs show (Figure 3) that the oxidation and reduction peaks become broader upon addition of chloride anions. Such an observation is consistent with a system that results from the superposition of two different redox processes, one corresponding to the first redox process associated with the uncomplexed TTF calix[4]pyrrole **2** and one corresponding to the complex (i.e., $\mathbf{2}\cdot\text{Cl}^-$) formed between the TTF calix[4]pyrrole **2** and chloride anions. Unfortunately, however, the separation between these two presumed oxidation processes proved too small to resolve under the conditions of the experiment.

To test further whether conformational restrictions involving the appended TTF calix[4]pyrroles were influencing their binding ability when contained in SAMs, we performed measurements by using a quartz crystal microbalance (QCM). For these experiments, a vertical cell setup^[35] with a 20 mL cell containing CH_2Cl_2 was used. The thiol derivatives (vide supra) were initially dissolved in CH_2Cl_2 (500 μL) and subsequently added in one portion to the cell under stirring. This resulted in a final concentration of 1 mM (in thiols) in the cell. Both the MPTTF model compound **8** and the TTF calix[4]pyrrole **1** showed very fast adsorption kinetics with a maximum coverage being reached within 100 seconds. The surface coverage calculated from the deposited mass ($(1.8 \pm 0.2 \times 10^{-10})$ and $(0.8 \pm 0.1 \times 10^{-10}) \text{ mol cm}^{-2}$, respectively, for **8** and **1**) are in good agreement with those values determined from the CV experiments described above.

Considering that the mass difference between complexed (i.e., $\mathbf{1}\cdot\text{Cl}^-$) and uncomplexed TTF calix[4]pyrrole (i.e., **1**) is too small to be measured using our QCM set-up, we decided

to investigate how the use of a TTF calix[4]pyrrole bearing a pre-coordinated chloride anion (i.e., $\mathbf{1}\cdot\text{Cl}^-$) would affect SAM formation. Consequently, the deposition kinetics of **1** in the absence and presence of chloride anion were compared. Because the binding constant ($K_a = 2.9 \times 10^3 \text{ M}^{-1}$ in CH_2Cl_2 at 298 K)^[36] for the interaction between **1** and Cl^- is not large enough to preclude the presence of substantial amounts of uncomplexed material when mixed at a 1:1 stoichiometry at initial concentrations of 1.0 mM, these studies were carried out using 20 equivalents of chloride anions (tetrabutylammonium counter cation; CH_2Cl_2 solution; $[\mathbf{1}] = 1.0 \text{ mM}$). Under these conditions, the fraction of $\mathbf{1}\cdot\text{Cl}^-$ is expected to be very large ($\geq 98\%$) compared with the small amount of residual free receptor **1**. By employing the Langmuir adsorption isotherm model,^[37] it proved possible to establish (Figure 4) that the deposition kinetics are almost six-

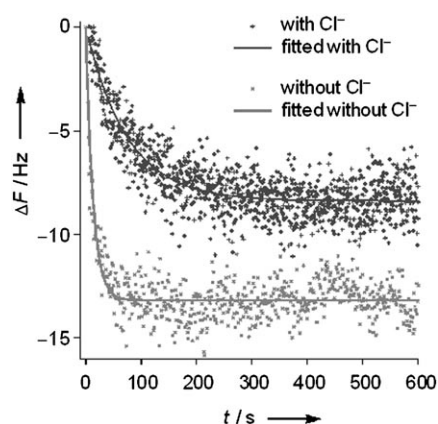


Figure 4. Frequency variations as a function of time for the gold-coated quartz crystal observed during the addition of a 1 mM CH_2Cl_2 solution of **1** into the QCM cell in the presence of 20 mM of Cl^- (top) and without Cl^- (bottom). The data points have been fitted according to the Langmuir adsorption isotherm model.^[37]

fold slower in the presence of chloride anions than in their absence ($k_{\text{obs}} = (0.077 \pm 0.004) \text{ s}^{-1}$ for uncomplexed **1** and $(0.0134 \pm 0.008) \text{ s}^{-1}$ for complexed $\mathbf{1}\cdot\text{Cl}^-$). On the other hand, the deposition kinetics for the MPTTF model compound **8** do not change (see the Supporting Information) when chloride anions are added into a CH_2Cl_2 solution of **8** prior to adsorption to a metal surface ($k_{\text{obs}} = (0.035 \pm 0.001) \text{ s}^{-1}$ with and without chloride anions).

The fact that the kinetics for the formation of SAMs derived from the TTF calix[4]pyrrole **1** are dramatically affected by the presence of chloride anions, whereas no effect is observed in the case of the MPTTF model compound **8**, serves to highlight the negative effects that electrostatic repulsion and/or steric obstruction can have on the self-assembly process when the complexed TTF calix[4]pyrrole $\mathbf{1}\cdot\text{Cl}^-$ is present. Furthermore, in accord with what was seen in the absence of chloride anion (vide supra), it should be noted that a clear difference in surface coverage was seen for $\mathbf{1}\cdot\text{Cl}^-$ ($(0.5 \pm 0.1 \times 10^{-10}) \text{ mol cm}^{-2}$; calculated from the QCM

data) vs. **1** ($(0.8 \pm 0.1 \times 10^{-10}) \text{ mol cm}^{-2}$). Taken in concert, these results provide further support for the claim that the conformational change from the initial 1,3-alternate conformation (as in **1**) to the corresponding cone conformation (as in **1-Cl⁻**) is restricted in the case of the surface bound TTF calix[4]pyrroles, and that this has a profound influence on both the kinetics of chloride recognition by the resulting SAM, as well as the extent of the surface coverage. In particular, it is suggested that the cone conformation, **1-Cl⁻**, is not able to arrange as close to the supporting surface monolayer as the corresponding anion-free, 1,3-alternate conformer (i.e., **1**). This decrease in coverage density and reduced conformational flexibility presumably serves to mask the potential chloride-induced response of the SAMs derived from **1** and **2**. Nevertheless, it is important to appreciate that a clear anion dependence on the electrochemical signature of these SAMs is seen upon exposure to chloride anions, and that, in contrast with earlier systems, this response is produced at sub-micromolar anion concentrations.

In summary, we have prepared two different mono-TTF calix[4]pyrroles **1** and **2** bearing protected alkanethiol anchoring groups and demonstrated that, after deprotection, they may be used to form SAMs on gold surfaces. The resulting systems are chemically stable under conditions of electrochemical analysis. As such, the effect of immobilizing redox-active mono-TTF calix[4]pyrroles on a surface could be analyzed directly using electrochemical methods. It was found that addition of chloride anions gave rise to a maximal shift in the first TTF-centered oxidation wave of ($\Delta E_{1/2}^1 = -30 \text{ mV}$). Although this shift is smaller than that seen in solution ($\Delta E_{1/2}^1 = -170 \text{ mV}$), SAMs built up from the present mono-TTF calix[4]pyrrole receptors respond to added chloride anion at a submicromolar sensitivity level. Further work is aimed at developing mixed SAMs designed to decrease the problems associated with the lack of conformational freedom inferred from the QCM experiments and to develop systems that are optimized for other substrates of interest.

Acknowledgements

We gratefully acknowledge the Lundbeckfonden for a Post doc scholarship to KAN and financial support provided by the COST D31 Programme of the European Science Foundation to LGJ, the Danish Natural Science Research Council (FNU, projects no. 272-08-0047 to KAN and no. 272-08-0578 to JOJ), and the Danish Strategic Research Council in Denmark through the Young Researchers Programme (no. 2117-05-0115 to JOJ) for financial support. The work in Angers was supported by the Centre National de la Recherche Scientifique (CNRS—France), the “Agence Nationale de la Recherche” (ANR—France), and the “Région des Pays de la Loire” (France). Support from the U.S. National Science Foundation (CHE-0749571 to JLS) and Robert A. Welch Foundation (F-1018 to JLS) is also gratefully acknowledged.

Keywords: calix[4]pyrroles • cyclic voltammetry • self-assembled monolayers • sensors • tetrathiafulvalenes

- [1] W. C. Bigelow, D. L. Pickett, W. A. Zisman, *J. Colloid Interface Sci.* **1946**, *1*, 513–538.
- [2] F.-R. F. Fan, J. Yang, L. Cai, D. W. Price, S. M. Dirk, D. V. Kosynkin, Y. Yao, A. M. Rawlett, J. M. Tour, A. J. Bard, *J. Am. Chem. Soc.* **2002**, *124*, 5550–5560.
- [3] Y. Xiaa, D. Qinb, Y. Yinc, *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 54–64.
- [4] G. K. Jennings, J. C. Munro, T.-H. Yong, P. E. Laibinis, *Langmuir* **1998**, *14*, 6130–6139.
- [5] a) J. C. Love, D. B. Wolfe, M. L. Chabinyc, K. E. Paul, G. M. Whitesides, *J. Am. Chem. Soc.* **2002**, *124*, 1576–1577; b) N. Abbott, A. Kumar, G. M. Whitesides, *Chem. Mater.* **1994**, *6*, 596–602; c) A. Kumar, N. A. Abbott, E. Kim, H. A. Biebuyck, G. M. Whitesides, *Acc. Chem. Res.* **1995**, *28*, 219–226.
- [6] K. Ariga, J. P. Hill, H. Endo, *Int. J. Mol. Sci.* **2007**, *8*, 864–883.
- [7] M. Schaeferling, S. Schiller, H. Paul, M. Kruschina, P. Pavlickova, M. Meerkamp, C. Giammasi, D. Kambhampati, *Electrophoresis* **2002**, *23*, 3097–3105.
- [8] A. Ulman, *An Introduction to Ultrathin Organic Films From Langmuir-Blodgett to Self-Assembly*, Academic Press, Boston, **1991**.
- [9] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1169.
- [10] S. Flink, F. C. J. M. Van Veggel, D. N. Reinhoudt, *Adv. Mater.* **2000**, *12*, 1315–1328.
- [11] S. Zhang, C. M. Cardona, L. Echegoyen, *Chem. Commun.* **2006**, 4461–4473.
- [12] a) I. Rubinstein, S. Steinberg, Y. Tor, A. Shanzer, J. Sagiv, *Nature* **1988**, *332*, 426–429; b) I. Turyan, D. Mandler, *Anal. Chem.* **1994**, *66*, 58–63; c) A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Monkman, C. Marengo, J. Yarwood, M. J. Joyce, S. N. Port, *Adv. Mater.* **1998**, *10*, 395–398.
- [13] W.-R. Yang, D. Jaramillo, J. J. Gooding, D. B. Hibbert, R. Zhang, G. D. Willett, K. Fisher, *Chem. Commun.* **2001**, 1982–1983.
- [14] E. Alonso, A. Labande, L. Raehm, J. M. Kern, D. Astruc, *C. R. Acad. Sci. Ser. II* **1999**, 209–213.
- [15] S. Zhang, L. Echegoyen, *J. Am. Chem. Soc.* **2005**, *127*, 2006–2011.
- [16] a) H. Miyaji, P. Anzenbacher, Jr., J. L. Sessler, E. R. Bleasdale, P. A. Gale, *Chem. Commun.* **1999**, 1723–1724; b) P. Anzenbacher, Jr., K. Jursíková, J. L. Sessler, *J. Am. Chem. Soc.* **2000**, *122*, 9350–9351; c) H. Miyaji, W. Sato, J. L. Sessler, *Angew. Chem.* **2000**, *112*, 1847–1850; *Angew. Chem. Int. Ed.* **2000**, *39*, 1777–1780; d) H. Miyaji, W. Sato, J. L. Sessler, V. M. Lynch, *Tetrahedron Lett.* **2000**, *41*, 1369–1373; e) H. Miyaji, W. Sato, D. An, J. L. Sessler, *Collect. Czech. Chem. Commun.* **2004**, *69*, 1027–1049; f) K. A. Nielsen, W.-S. Cho, G. H. Sarova, B. M. Petersen, A. D. Bond, J. Becher, F. Jensen, D. M. Guldi, J. L. Sessler, J. O. Jeppesen, *Angew. Chem.* **2006**, *118*, 7002–7007; *Angew. Chem. Int. Ed.* **2006**, *45*, 6848–6853; g) K. A. Nielsen, G. H. Sarova, L. Martín-Gomis, F. Fernández-Lázaro, P. C. Stein, L. Sanguinet, E. Levillain, J. L. Sessler, D. M. Guldi, Á. Sastre-Santos, J. O. Jeppesen, *J. Am. Chem. Soc.* **2008**, *130*, 460–462; h) K. A. Nielsen, L. Martín-Gomis, G. H. Sarova, L. Sanguinet, D. E. Gross, F. Fernández-Lázaro, P. C. Stein, E. Levillain, J. L. Sessler, D. M. Guldi, Á. Sastre-Santos, J. O. Jeppesen, *Tetrahedron* **2008**, *64*, 8449–8463.
- [17] a) K. A. Nielsen, J. O. Jeppesen, E. Levillain, J. Becher, *Angew. Chem.* **2003**, *115*, 197–201; *Angew. Chem. Int. Ed.* **2003**, *42*, 187–191; b) K. A. Nielsen, W.-S. Cho, J. Lyskawa, E. Levillain, V. M. Lynch, J. L. Sessler, J. O. Jeppesen, *J. Am. Chem. Soc.* **2006**, *128*, 2444–2451.
- [18] For other examples of redox-active chemosensors, See: a) P. D. Beer, P. A. Gale, G. Z. Chen, *Coord. Chem. Rev.* **1999**, *185–186*, 3–36; b) P. D. Beer, J. Cadman, *Coord. Chem. Rev.* **2000**, *205*, 131–155; c) P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502–532; *Angew. Chem. Int. Ed.* **2001**, *40*, 486–516.
- [19] a) M. R. Bryce, *J. Mater. Chem.* **2000**, *10*, 589–598; b) J. L. Segura, N. Martín, *Angew. Chem.* **2001**, *113*, 1416–1455; *Angew. Chem. Int. Ed.* **2001**, *40*, 1372–1409; c) G. Schukat, E. Fanghänel, *Sulfur Rep.* **2003**, *24*, 1–282; d) J. Becher, J. O. Jeppesen, K. Nielsen, *Synth. Met.*

- 2003, 133–134, 309–315; e) J. O. Jeppesen, J. Becher, *Eur. J. Org. Chem.* **2003**, 3245–3266; f) *TTF Chemistry* (Eds.: J.-i. Yamada, T. Sugimoto), Kodansha, Tokyo, **2004**; g) “Special issue on molecular conductors”: *Chem. Rev.* **2004**, *104*, 4887–5782; h) T. Otsubo, K. Takimiya, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 43–58.
- [20] Recently, the use of octafluorocalix[4]pyrrole for the creation of microelectrodes capable of sensing halide anions was reported. See: a) R. Cui, R. Q. Li, D. E. Gross, X. Meng, B. Li, M. Marquez, R. Yang, J. L. Sessler, Y. Shao, *J. Am. Chem. Soc.* **2008**, *130*, 14364–14365; b) Calixpyrrole derivatives have also been used to prepare ion-selective electrodes. See for instance: T. V. Shishkanova, R. Volf, V. Král, J. L. Sessler, S. Camiolo, P. A. Gale, *Anal. Chim. Acta* **2007**, *587*, 247–253, and references therein.
- [21] It is well-known that alkanethiols and gold substrates are able to form well-defined SAMs, see: A. Ulman, *Chem. Rev.* **1996**, *96*, 1533–1554.
- [22] a) J. O. Jeppesen, K. Takimiya, F. Jensen, T. Brimert, K. Nielsen, N. Thorup, J. Becher, *J. Org. Chem.* **2000**, *65*, 5794–5805; b) J. O. Jeppesen, J. Becher, J. F. Stoddart, *Org. Lett.* **2002**, *4*, 557–560; c) J. O. Jeppesen, K. A. Nielsen, J. Perkins, S. A. Vignon, A. Di Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani, J. Becher, J. F. Stoddart, *Chem. Eur. J.* **2003**, *9*, 2982–3007.
- [23] C. Bucher, R. S. Zimmerman, V. M. Lynch, C. Král, J. L. Sessler, *J. Am. Chem. Soc.* **2001**, *123*, 2099–2100.
- [24] Prolonged reaction time and high temperature should be avoided, in order to suppress the competing elimination reaction leading to the formation a terminal alkene.
- [25] J. L. Sessler, D. E. Gross, W.-S. Cho, W. M. Lynch, F. P. Schmidtchen, G. W. Bates, M. E. Light, P. A. Gale, *J. Am. Chem. Soc.* **2006**, *128*, 12281–12288.
- [26] As previously observed (See: Ref. [17b]), the oxidation of chloride anion to chlorine occurs close to the second oxidation process associated with the TTF unit. As a consequence of the overlapping nature of these two oxidation processes, it is not possible to obtain any information as to whether complexation of chloride anions to compounds **1** or **2** also affects the second oxidation process associated with the TTF unit in these two compounds.
- [27] The acetyl protecting group in compounds **1**, **2**, **8**, and **9** was cleaved using the following general procedure: A solution of CsOH·H₂O (2 equiv) was slowly added to a solution of the appropriate compound in anhydrous degassed THF. The reaction mixture was stirred for at least 3 h, where upon H₂O was added. The resulting mixture was extracted with CH₂Cl₂ and subsequently filtered through silica gel. Evaporation of the solvent afforded the corresponding thiol; these unprotected species were used directly without further purification.
- [28] The substrates were prepared by deposition of ≈5 nm of chrome followed by ≈50 nm of gold onto a glass substrate using physical vapor deposition techniques and were made immediately before use. See: a) L. Sanguinet, O. Alévêque, P. Blanchard, M. Dias, E. Levillain, D. Rondeau, *J. Mass Spectro.* **2006**, *41*, 830–833; b) M. Bounichou, L. Sanguinet, K. Elouarzaki, O. Alévêque, M. Dias, E. Levillain, D. Rondeau, *J. Mass Spectro.* **2008**, *43*, 1618–1626.
- [29] Electrochemical experiments were carried out using an EGG PAR 273A potentiostat with positive feedback compensation in a glove box containing anhydrous, oxygen-free (<1 ppm) argon, at room temperature. Cyclic voltammetry (CV) was performed in a three-electrode cell equipped with a platinum-plate counter electrode and a silver wire served as the quasi-reference electrode; its potential was calibrated against the ferrocene/ferricinium couple (Fc/Fc⁺) before and after each experiment. The potentials were then recalculated and given against Fc/Fc⁺. CVs were recorded in anhydrous HPLC-grade CH₂Cl₂ using tetrabutylammonium hexafluorophosphate (nBu₄NPF₆) as the supporting electrolyte. Based on repetitive measurements, absolute errors in the stated potentials are considered to be ≤5 mV.
- [30] A. J. Bard, L. R. Faulkner *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, New York, **2001**.
- [31] Deduced from an integration of the voltammetric signal carried out in the absence of chloride anions.
- [32] 0.5 μm corresponds to ~10 equivalents of the amount of “immobilized” TTF calix[4]pyrrole **2** on gold ((0.7 ± 0.1 × 10⁻¹⁰) mol cm⁻²), added in 10 mL of 0.1 M nBu₄NPF₆/CH₂Cl₂ solution. This value depends on the area of the gold substrates. For this reason, the use of ultra-microelectrode could reach a subpicomolar sensitivity level. See for instance: C. Amatore, D. Genovese, E. Maisonhaute, N. Raouafi, B. Schöllhorn, *Angew. Chem.* **2008**, *120*, 5289–5292; *Angew. Chem. Int. Ed.* **2008**, *47*, 5211–5214.
- [33] M. P. Wintergerst, T. G. Levitskaia, B. A. Moyer, J. L. Sessler, L. H. Delmau, *J. Am. Chem. Soc.* **2008**, *130*, 4129–4139.
- [34] It is known that TTF calix[4]pyrroles, exists predominantly in the 1,3-alternate conformation in the absence of anions. However, in halogenated solvents TTF calix[4]pyrroles binds anions very tightly, with a binding constant (*K_a*) of 2.9 × 10³ M⁻¹ (CH₂Cl₂, 298 K) having been reported (see ref. [17b]) for the interaction between a mono-TTF calix[4]pyrrole (which is structural similar to the TTF calix[4]pyrrole **2** of this study) and chloride anion; it is known that this binding favors formation of the cone conformation. See ref. [16f,g,h].
- [35] G. Jerkiewicz, G. Vatankhah, A. Zolfaghari, J. Lessard, *Electrochem. Commun.* **1999**, *1*, 419–424.
- [36] The binding constant corresponding to the interaction between chloride anions and a mono-TTF calix[4]pyrrole—which is structural similar to **1**, but without an alkanethiol anchor group—has been reported (See: Ref. [17b]) to be 2.9 × 10³ M⁻¹ (CH₂Cl₂, 298 K).
- [37] a) D. S. Karpovich, G. J. Blanchard, *Langmuir* **1994**, *10*, 3315–3322; b) It is possible to extract the deposition rate constant (*k_{obs}*) from the following integrated equation:
- $$\theta(t) = K' [1 - \exp(-k_{\text{obs}} t)] \quad \text{where} \quad \begin{cases} k_{\text{obs}} = k_a C + k_d \\ K' = \frac{C}{C + \frac{k_d}{k_a}} \end{cases}$$
- θ* is the fraction of surface covered, (1–*θ*) represents the available sites for adsorption and *C* is the analytical concentration. The values of both *k_a* and *k_d* corresponding to adsorption/desorption rate constants enable the kinetic parameters to be calculated. The values of *K'* and *k_{obs}* are obtained by fitting the experimental data to the equation.

Received: May 25, 2009
Published online: July 11, 2009