Intermolecular interactions in self-assembled monolayers of tetrathiafulvalene derivatives

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The elaboration of mixed self-assembled monolayers (SAMs) of tetrathiafulvalene derivatives allows the modulation of intermolecular interactions and provides evidence of segregated distribution of redox centers.

During the last decade, increasing attention has been dedicated to the design and elaboration of redox-responsive SAMs.[1,2] Employing of redox SAM-modified electrodes for catalysis, recognition and sensing has resulted in some elegant examples that incorporate sophisticated receptors on the electrode surfaces.[2]
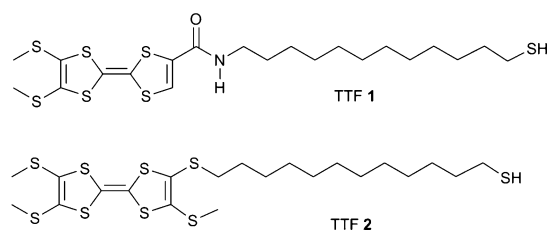
The reliable electrochemical response and synthetic accessibility of tetrathiafulvalenes (TTFs) have stimulated the development of electroactive molecular and supramolecular assemblies based on these versatile building blocks. Indeed, TTF can be oxidized reversibly and sequentially to the corresponding mono- and dicationic forms at moderate potentials. The redox character survives the formal substitution of one or more hydrogen atoms on the TTF core with a variety of functional groups.

Many authors have reported the electrochemical properties of TTF derivative SAMs. Such studies include the redox activity of TTF derivatives on gold,[3–6] metal ion recognition[7–10] and host–guest complexation.[11,12] The electrochemical processes of TTF terminated SAMs exhibit two successive one-electron redox waves. The peak widths of the redox waves were strongly dependent on the oxidation states of the TTF moieties, the packing arrangement of the SAMs, and the contacting medium.[13]

Because the structure of monolayer limits the accessibility of interfacial reactive sites,[14] the control of the structure–electroactivity relationship is decisive for enhancing interfacial reactions. Here, we report an approach to improve the problems arising from intermolecular interactions by diluting the electroactive species in the monolayer with alkanethiols.

Two different targets were designed to elaborate TTF derivative SAMs. TTF **1** consists of a trisubstituted TTF core containing an amide group supposed to enhance interactions in the SAM by formation of hydrogen bonds.[15] The SAMs obtained with this compound will be compared with the ones formed with TTF **2**, which is tetrasubstituted and does not contain an amide group (Scheme 1).

TTF **1** was synthesized in three steps. The first step involved a coupling[16] between 4,5-bis(thiomethyl)tetrathiafulvalene-4′-carbonyl chloride[17] and 1-bromododecylammonium

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Scheme 1 Structure of TTF **1** and TTF **2**.

bromide.[18] A substitution of the terminal bromide by potassium thioacetate followed by a deprotection step led to TTF **1**.[19] The first step of synthesis of TTF **2** involved the deprotection and alkylation of 2-(2-cyanoethylthio)-3,6,7-tris(methylthio)tetrathiafulvalene[20] with 1.5 eq. of caesium hydroxide and 10 eq. of 1,12-dibromododecane in DMF.[21] The two following steps leading to the thiol TTF **2** were similar to the ones employed for TTF **1**.

Only few examples of such TTF/alkanethiol mixed SAMs, obtained by insertion of TTF thiols in an n-alkanethiol SAM, and characterized by STM, are related in the literature.[22] In the present study, mixed SAMs A and B were prepared by successive adsorptions of TTF **1** or **2** and dodecanethiol (C12) immersing the Au/glass substrate for 15 min in a millimolar solution of TTF **1** or **2** in dichloromethane and then in a millimolar solution of C12 in dichloromethane. The immersion time in the C12 solution varied from 1 min to 48 h to obtain the expected TTF **1** or **2** surface coverages. We chose a 12-carbon chain for this study for two reasons. First, because 12 carbons is about the shortest chain length for which the high-quality packing is found in the n-alkanethiol; we expect it to be the chain length at which the disruptive effects of surface functional groups are most prominent.[23] Second, because a 12 carbon chain allows to obtain a complete surface covering range in our experimental conditions.

Two successive one-electron redox waves were observed for both full covered TTF SAMs by cyclic voltammetry† (Fig. 1). The peak widths of the redox waves were strongly dependent on the oxidation states of the TTF moieties. The pronounced dissymmetry of the first peak in the case of SAM A associated to a very large full width at half-maximum (FWHM) ~ 190 mV in 0.1 M Bu_4NPF_6/CH_2Cl_2, may suggest the presence of a distribution of redox potentials (a distribution of local environments around the redox centers), although the contribution of other factors might be possible (i.e., repulsive interaction[24,25] and double-layer effects).[13,26,27]

Despite drastic controlled conditions, only SAM B prepared from TTF **2** led to really reproducible electrochemical
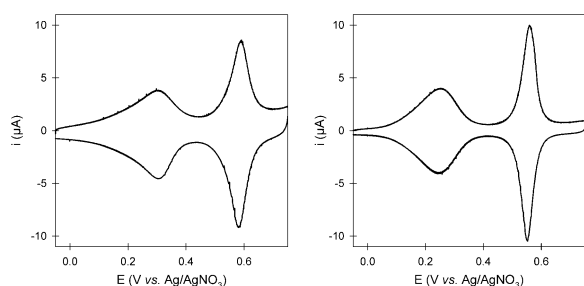
Fig. 1 (Left) CV of SAM A in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$ at 0.1 V s^{-1}, prepared from TTF **1**, leading to 2.5×10^{-10} mol cm^{-2}. (Right) CV of SAM B in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$ at 0.1 V s^{-1}, prepared from TTF **2**, leading to 3.0×10^{-10} mol cm^{-2}. The surface coverages are deduced by integration of the voltammetric peaks, without taking into account of background charge.

characteristics, so we have focussed our attention on SAMs B. As expected, immersion of SAMs B in an alkanethiol solution (C12) led to decrease of the surface coverage (θ) by partial replacement of the TTF derivative by C12. Moreover, the charges under the two redox peaks were identical and independent of scan rate or protocol elaboration.

At low surface coverage, the FWHM values of the two redox peaks move to 90 mV (expected value of an ideal system based on the Langmuir model without interaction between electroactive centers) (Fig. 2, left) and the ratio of the peak currents ($i_{Peak\ 1}/i_{Peak\ 2}$) tends to reach the unit (Fig. 2, right). Variations of these two parameters (*i.e.* FWHM and $i_{Peak\ 1}/i_{Peak\ 2}$) as a function of surface coverage provide results (when redox centers present two successive redox waves) supporting the presence of lateral interactions between the electroactive species, the overall effect decreasing with surface coverage.[25]

To go further into the establishment of structure–electroactivity relationship for TTF SAMs, the evolution of FWHM, which was found to be the most sensitive parameter to highlight intermolecular interactions,[19,28] was studied. Indeed, the linear dependence of FWHM *vs.* θ (Laviron's model)[25] provides evidence of a random distribution of redox sites on SAM and a peculiar nonlinear dependence can suggest a phase segregation (CNT (CoNsTraint) distribution coupled with the generalized Laviron's model).[28c,d] Electrochemical behaviours of mixed SAMs, prepared from TTF **2**/C12 mixtures, can only be fitted with the CNT distribution: the full
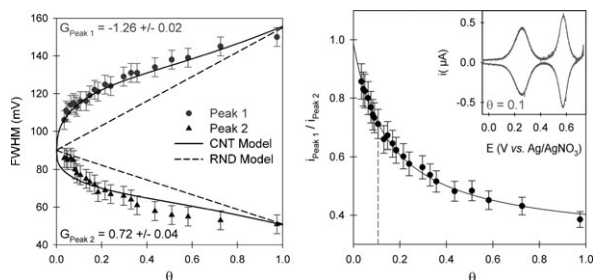
width at half maximum (Fig. 2, left) is non-linear dependent of the surface coverage. From the generalized Laviron's model, interaction parameters of the first and second redox processes were estimated by non-linear regression with a CNT distribution.[28d] At 293 K, the first redox process is characterized by a strong attractive interaction between TTF and TTF$^{\bullet+}$ centers ($a_{OR} = 0.65 \pm 0.03$, extracted from G and S parameters),[19,28] and the second one by a strong attractive interaction between TTF^{2+} centers ($a_{OO} = 0.72 \pm 0.05$, extracted from G and S parameters).[19,28] The first estimated interaction parameters support the well-known attractive interaction between adjacent TTF molecules in oxidation states occurring during the first redox process. The suggested attractive interaction during the second process could be correlated to the adsorption already observed in solution at this oxidation state.[29]

The non-linearity of FWHM *vs.* θ, supported by a qualitative (*i.e.* shape) and quantitative (*i.e.* intensities) agreement between simulated and experimental CVs (Fig. 3), provides evidence of a phase segregation of TTF centers on gold.

In order to obtain different surface distributions of the TTF units in the SAM, two other elaboration protocols were tested to dilute the TTF moieties on the surface. The first one consists in the partial desorption of the TTF units by ultrasonication of a SAM B: the surface coverage was tuned by varying the immersion time in the ultrasonic bath. The second one is based on the coadsorption of a mixture of TTF **2**/C12, the surface coverage was tuned by varying the proportion of the two components of the binary SAM. The electrochemical behaviours recorded using both methods were strictly identical to the one observed by successive adsorptions, demonstrating that the dilution method does not influence the surface distribution. These results are in agreement with elegant works reported by Enoki *et al.*[22] They have shown by STM investigations on other mixed TTF derivative SAMs, prepared by successive adsorption of *n*-alkanethiols and TTF thiols, the coexistence of segregated domains. These notable results contrast with the ones reported for aminoxylalkanethiolate SAMs.[28] Indeed, the ultrasonication of a compact TEMPO
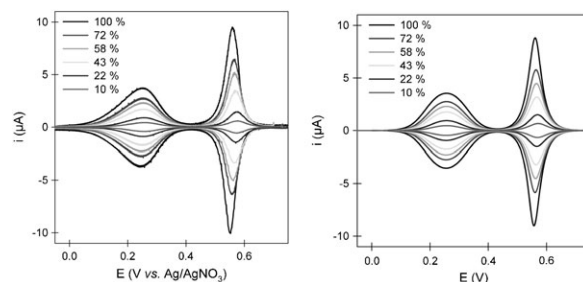

Fig. 2 (Left) Anodic full width at half maximum (FWHM) of SAM B as a function of the surface coverage. (Right) $i_{Peak\ 1}/i_{Peak\ 2}$ as a function of the surface coverage. Inset: experimental CV of SAM B at $\theta = 10\%$ (0.3×10^{-10} mol cm^{-2}) showing the two waves becoming similar at low surface coverage.

Fig. 3 (Left) CVs of SAM B in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$ at 0.1 V s^{-1}, prepared from different **2** : C12 ratios, leading to 3.0, 2.2, 1.7, 1.3, 0.7 and 0.4×10^{-10} mol cm^{-2}. The baselines were subtracted. The maximal surface coverage of SAMs B was estimated to be 3.0×10^{-10} mol cm^{-2}. (Right) CVs calculated from theoretical models based on a CNT model. In addition to the usual electrochemical parameters ($E_1 = 0.260$ and $E_2 = 0.580$ V), calculations were performed with $a_{OR} = 0.65$ for the first redox process and $a_{OO} = 0.72$ for the second redox process. Only one variable changes at a time, the surface coverage ($\theta = 1.00, 0.72, 0.58, 0.43, 22$ and 0.10).

derivative SAM led to the formation of aggregates on the surface whereas the successive adsorptions of the two components of the binary "TEMPO derivative/C12" led to randomly mixed SAMs.[28]

In the case of TTF **2** SAMs, it seems to be difficult to easily generate randomly distributed redox centers. This fact could be explained by the existence of attractive interaction between the immobilized TTF moieties as sulfur–sulfur interaction already described for similar TTF structures.[17]

Conclusions

This study provides evidence of intermolecular interactions between immobilized TTF sites and provides the first evidence of the versatility of the electrochemical approach to estimate interaction parameters in these systems.

This study also shows that mixed TTF derivative SAMs form aggregates independently of the elaboration protocols and the chain length ($n < 15$) of the diluents.

Accordingly to the enhancing of the redox activity observed in the case of mixed aminoxylalkanethiolate SAMs, this study recommends to prepare redox mixed TTF SAM-modified electrodes for recognition and sensing in order to reduce steric hindrance induced and intermolecular interactions.[19]

Notes and references

† Experimental conditions: electrochemical experiments were carried out with a Biologic SP-150 potentiostat in a glove box containing dry, oxygen-free (<1 ppm) argon, at 293 K. Cyclic voltammetry (CV) was performed in a three-electrode cell equipped with a platinum-plate counter electrode. Reference electrodes were Ag/AgNO$_3$ (0.01 M CH$_3$CN). CVs were recorded in dry HPLC-grade dichloromethane (CH$_2$Cl$_2$). The supporting electrolyte was tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$). Based on repetitive measurements, absolute errors on potentials were found to be approximately 5 mV. Au substrates were prepared by deposition of *ca.* 5 nm of chromium followed by *ca.* 50 nm of gold onto a glass substrate using a physical vapour deposition technique and were made immediately before use.

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