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Electrochemically Driven Interfacial Halogen Bonding on Self-Assembled Monolayers for Anion Detection

Hussein Hijazi,^a Antoine Vacher,^b Sihem Groni,^a Dominique Lorcy,^b Eric Levillain,^c Claire Fave*^a and Bernd Schöllhorn*^a

Electrochemically driven interfacial halogen bonding between redox-active SAMs and halide anions was quantitatively studied for the first time. The halogen bond donor properties were switched on by electrochemically controlling the oxidation state of the adsorbates. Experimental data and simulation show high binding enhancement towards halide anions compared to homogeneous systems.

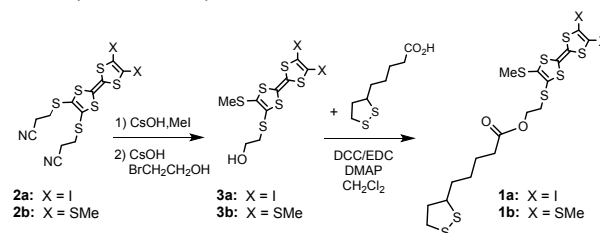
Without doubt, self-assembled monolayers (SAMs) are one of the best systems for studying the structure-reactivity relationship of surface confined molecules at the solid/liquid interface.¹ Over the past decade a plethora of SAMs applications have been extensively explored in fields such as wettability, recognition, sensing and catalysis.¹⁻⁴ While numerous results have been obtained for ion recognition in homogeneous solution,⁴ the combination of molecular receptors and SAMs should generate an amplification of the recognition process (faster response, easier reproducibility...) at the monolayer/solution interface⁵ due to the pre-organization of receptors on the surfaces.^{2,6} Non-covalent interactions are key parameters for recognition with a stronger effect at the interface than in solution.⁷ Among weak interactions, Halogen bonding (XB)⁸ is becoming more and more popular to control supramolecular recognition in solution.⁹ XB is a net attractive interaction occurring between the electrophilic site (σ -hole)¹⁰ of a bound halogen atom and a nucleophilic Lewis base. Due to strong directionality, XB interactions are excellent candidates for molecular receptors and their use may lead to numerous potential applications for

interfacial systems. However up to date XB remains scarcely explored at the interface and only few systems have been described so far using either STM, AFM,¹¹ SPR,^{12,13} TEM¹⁴ or even Transient absorption spectroscopy.¹⁵ Recently, we have demonstrated the potential of electrochemistry as a powerful technique to detect and to control XB in solution. Cyclic voltammetry is an economical, simple but precisely controllable tool well adapted for the investigation of such weak interactions in solution. Electrochemical activation of either redox-active XB acceptors¹⁶ or XB donors^{17,18,19} showed significant and reversible XB binding enhancement upon electrochemical manipulation.

Our study aims at transferring this concept from homogeneous solution to the interface of a conductive material. Tetrathiafulvalene (TTF) derivatives display many advantages and are therefore a suitable choice for transferring the concept onto the surface. In literature TTF based SAMs with cation recognition²⁰ have been described but to the best of our knowledge never for anion detection.

Here we describe for the first time electrochemically driven interfacial XB formation between redox-active SAMs and halide anions in solution with a high binding enhancement. The ability to detect halides such as chloride and bromide is crucial in many aspects of medicine, industrial processes and environmental analyses. Chloride is a key indicator of fecal contamination in the environment, while bromide is used in medicine.²¹ Recently we demonstrated the decisive role of the anchoring group on the formation and the stability of SAMs²² and thus chose thioctic acid derivatives bearing TTF groups for the

Scheme 1. Synthesis of compounds **1a** and **1b**



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*Electronic Supplementary Information (ESI) available: General procedures as well as data and data plots, such as the corresponding CVs and absorption spectra. See DOI: 10.1039/x0xx00000x

chemisorption onto gold electrodes. Two TTF containing adsorbates **1a** and **1b** have been studied (Scheme 1). **1a** was synthesized from the dissymmetrical TTF derivative **2a**.²³ We also prepared a reference TTF derivative, **1b**, in which the two iodine atoms were replaced by methylthio substituents, starting from the precursor **2b**.²⁴ Compounds **2a-b** are substituted on one side by two cyanoethylthio groups which can lead under basic conditions to the corresponding dithiolates.²⁵ When employing one equivalent of cesium hydroxide followed sequentially by the addition of iodomethane, a second equivalent of base and then 2-bromo-ethanol, TTF **3a** was obtained. According to the same sequential procedure, **3b**²⁴ was synthesized from **2b**. Adsorbates **1a-b** were prepared by esterification of the respective parent alcohols **3a-b** with commercially available thioctic acid.

Acetonitrile (ACN) has been identified as a well-adapted solvent for the characterization of the SAMs while compounds **1a** and **1b** showed a better solubility in 30% ACN/DMF containing 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as supporting electrolyte. CVs of both compounds showed two reversible single-electron oxidation waves with standard potentials (vs. SCE) of + 0.64 V and + 0.83 V for compound **1a** and + 0.59 V and +0.77 V for **1b** (Table 1 and Fig.S1, see ESI[†]). Furthermore both compounds show two irreversible peaks at relatively high anodic and cathodic potentials of +1.17 V / +1.09 V ($E_{PA(S-S)}$) and -2.17 V / -2.03 V ($E_{PC(S-S)}$) respectively for **1a** and **1b**, characteristic of the reductive and oxidative cleavage of the disulphide bond. For **1a**, two supplementary cathodic irreversible waves at - 1.19 and - 1.39 V were recorded and can be attributed to the dissociative reduction of the C-I bonds.

Halide anions (Lewis Bases) proved to be strong XB acceptors in the presence of iodo-TTF⁺ cation radicals.¹⁷ Upon the addition of Cl⁻ as tetrabutylammonium chloride (NBu₄Cl) the first oxidation wave shifted significantly to lower potentials ($\Delta E_{ox} = 55$ mV for 50 equiv. of Cl⁻) indicating the formation of a XB complex with the radical cation of **1a** (Fig.S4A, see ESI[†]).

Such behaviour can be attributed to a substantial stabilization of the cation through XB interaction with the anion and has recently been proven in the case of iodo- and (Me)₃-iodo-TTF.¹⁷ In contrast, reference compound **1b** did not show any potential shift (Fig.S4, see ESI[†]). In order to validate the predominant XB interaction with Cl⁻, we also studied the electrochemical behaviour of the precursor alcohols (Scheme 1) **3a** and **3b**. As expected, in contrast to **3b**, **3a** showed a similar potential shift behaviour as compound **1a** (Fig.S5, see ESI[†]). After addition of 100 equivalents of NBu₄Cl in solution, comparable shifts for the first wave have been obtained (84 mV for **3a** and 78 mV for **1a**, Fig.S6, see ESI[†]). The corresponding affinity constants K_{red} (between the anion and the neutral state of the TTF) and K_{ox} (between the anion and the radical cation state of the TTF) were determined by fitting the experimental titration curves (see ESI[†]). Both compounds present similar affinity constant leading to $K_{ox} = 800$ M⁻¹ for **1a**, and to $K_{ox} = 1200$ M⁻¹ for **3a** illustrating the importance of the XB donor strength. In fact we have previously reported two to three times lower K_{ox} for mono iodo-TTF derivatives toward Cl⁻.

Table 1. Electrochemical data for compounds **1a** and **1b**.

	Solution [a]		SAMs [b]	
	1a	1b	SAM-1a	SAM-1b
E'_{1} [c]	+ 0.64	+ 0.59	+ 0.72	+ 0.58
E'_{2} [c]	+ 0.83	+ 0.77	+ 0.98	+ 0.89
$E_{PA(S-S)}$ [c]	+ 1.17	+ 1.09		
$E_{PC(S-S)}$ [c]	- 2.17	- 2.03		
$E_{PC(C-I)}$ [c]	- 1.19 / - 1.39			
D [d]	1.56	1.93		
Γ [e]			1.45 ± 0.07	1.94 ± 0.15

[a] in 30 % ACN / 70% DMF. [b] in ACN. [c] in V, vs. SCE. [d] Diffusion coefficient in 10⁻⁶ mol.cm⁻² [e] Surface coverage in 10⁻¹⁰ mol.cm⁻².

The presence of two iodine substituents in **1a** and **3a** is likely responsible for the increase of the XB donor strength. As expected, K_{red} values are negligible and cannot be determined precisely. The K_{ox}/K_{red} ratios represent the most reliable values for an estimation of the relative binding enhancement upon oxidation and are indicated in **Table 2**. After rinsing of the resulting modified electrodes (see ESI[†] for details), **SAM-1a** and **SAM-1b**, CVs were conducted in pure 0.1 M n-Bu₄PF₆ / ACN (Fig.1). **SAM-1a** and **SAM-1b** display two distinct oxidation peaks having the characteristic features of surface confined redox centres: decreased capacitive current (Fig.1); linear dependence of peak currents with the scan rate (Fig.S7, see ESI[†]). These results provide evidence of a non-diffusional system with the redox moieties attached to the surface. Assuming that the two oxidation peaks are corresponding to two successive one-electron processes as for homogeneous solution, the integration of the signals allowed estimating the surface coverage of the electrode, leading to 1.5·10⁻¹⁰ mol.cm⁻² for **SAM-1a** and 1.9·10⁻¹⁰ mol.cm⁻² for **SAM-1b**, values matching with relatively dense TTF mono-layers.²⁶ It is notable that the peak shapes were significantly sharper and much more symmetrical for **SAM-1b** as a results of the beneficial effect of the thiomethyl group.

The detection of the XB formation on TTF-SAMs has been performed on the first peak corresponding to the formation of the radical cation due to better stability in this potential window.^{20a,22a} The first oxidation wave of **SAM-1a** was strongly affected in the presence of chloride contrary to **SAM-1b**. With **SAM-1a** the oxidation peak progressively decreases to negative potential upon raising the chloride concentration (Fig.2A). Simultaneously a new wave emerged at lower potential (+ 0.57 V, Fig.2A) suggesting strong adsorption of the chloride upon oxidation of the I₂-TTF moieties.

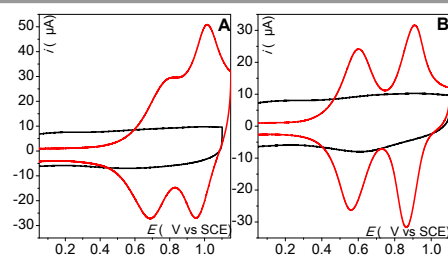


Fig. 1. CVs of unmodified (black) and modified (red) gold electrodes **SAM-1a** (A) and **SAM-1b** (B) in 0.1 M NBu₄PF₆/ACN. $v = 10$ V/s.

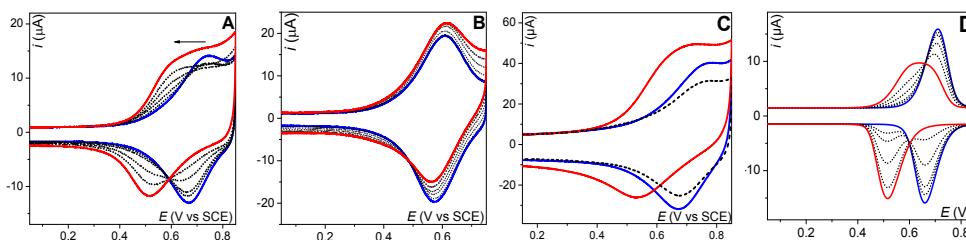


Fig.2. CVs of SAMs **1b** (B) in 0.1 M

presence of increasing amounts of NBu₄Cl (concentration: 0.01, 0.05, 0.1, 0.15 and 0.2 mM). $v = 10$ V/s. (C) CVs of **SAM-1a** in 0.1 M NBu₄PF₆/ACN, in absence (blue) and presence of 0.2 mM of NBu₄Cl (red) and after rinsing off the chloride salt (black dashed). $v = 10$ V/. (D) Simulated CVs for **SAM-1a**. (Details for the electrochemical simulation are given in ESI[†]).

of **SAM-1a** (A) and **SAM-**
NBu₄PF₆/ACN, in

The fact that **SAM-1b** did not at all respond to chloride, even at high concentration (Fig.2B), provides evidence for predominant XB interaction with **SAM-1a**. CVs in Figure 2A show an isobestic point at + 0.59 V, evidencing the co-existence of two different species. The oxidation peaks are less well defined which could be due either to the simultaneous and independent Cl⁻ oxidation at increasing concentrations or to a purely kinetic effect.

In order to verify the first hypothesis we prepared **SAM-4** containing the non-electroactive derivative **4** where TTF is replaced by a phenyl group. CVs of the electrochemically inactive **SAM-4** showed a significantly decreased capacitive current and no faradic current was obtained (Fig.S8, see ESI[†]). In the presence of chloride anions an irreversible anodic wave appeared at + 0.64 V (Fig.S12, see ESI[†]) and can be attributed to the direct oxidation of Cl⁻ at the modified electrode. This current is however low and can be neglected. The influence of the nature of the Lewis base was further investigated.

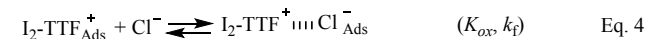
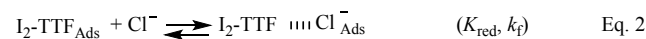
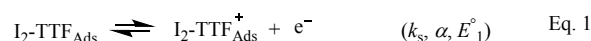
Addition of bromide in the solution afforded a similar response of **SAM-1a** with apparition of an isobestic point at + 0.59 V and a new oxidation peak centred at + 0.62 V (Fig.S10, see ESI[†]). These results are in accordance with the reported relative XB acceptor strength of halides (Fig.S11, see ESI[†]). No significant shift was observed in the presence of triflate and **SAM-1a** and similarly no shift was evidenced for **SAM-1b** in the presence of any of the investigated anions (Fig.S10-S11, see ESI[†]).

For demonstrating the reversibility of the binding **SAM-1a** was thoroughly rinsed with many solvents and immersed into a new chloride free electrolyte. CVs in Figure 2C show that the initial oxidation peak is recovered. The small decrease of the current intensity is attributed to partial desorption during the experiment, a common drawback of SAMs.

For chloride a limit of detection (LOD) of 6×10^{-6} M was estimated, based on the fitting of the calibration curve with the Langmuir model (Fig S13). The observed CVs' features and the low LOD point towards a very high affinity constant between Cl⁻ and the one electron oxidized **SAM-1a**.

Scheme 2 illustrates our mechanism proposal involving the positively charged I₂-TTF⁺ layer stabilized by Cl⁻ anions arranged in positions close to the polarized iodine atoms, thus favouring XB formation. The supporting electrolyte anions (PF₆⁻) counter-balance the created TTF cations on the surface. When adding Cl⁻ a supplementary stabilization via localized XB likely contributes to the formation of a complex series with a lower oxidative potential.

The evidence of predominant XB interaction for **SAM-1a** (Fig.2D) is also supported by electrochemical simulation with Kissa-1D²⁷ from the previous square scheme¹⁷ dedicated to electrochemical oxidation of I-TTF in the presence of Cl⁻:

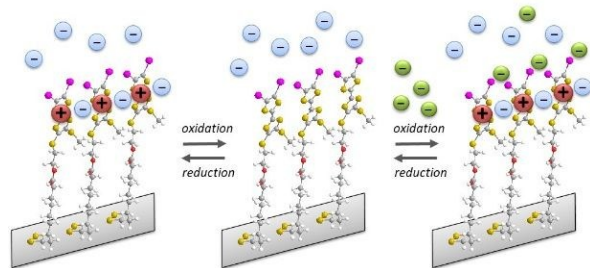


$$\text{With } \Delta E = E_1^{\circ} - E_2^{\circ} + \frac{RT}{F} \ln \left(\frac{K_{\text{red}}}{K_{\text{ox}}} \right)$$

Where E_1° and E_2° are redox standard potentials, k_s standard electron transfer rates, α the transfer coefficient, k_f forward rate constants and $K_{\text{ox(red)}}$ equilibrium constants.

According to our previous work,¹⁷ k_f for Eq (2) and (4) are equal to 10^{+6} s^{-1} , a sufficiently high value for the system to be under dynamic equilibrium. α and k_s are equal to 0.5 and 250 s^{-1} respectively, in accordance with a reversible and fast electron transfer system. Electrochemical simulations with a - 160 mV potential shift (ΔE) and $K_{\text{red}} = 1000 \text{ M}^{-1}$ (Table 2) are consistent with the experimental data for **SAM-1a** (Fig.2A) and lead to an isobestic point (Fig.2D), as found experimentally. Importantly, using such a square scheme while having one experimental observable (ΔE) and two unknown parameters leads only to the determination of the $K_{\text{ox}}/K_{\text{red}}$ affinity constants ratio. The K_{red} values used for the simulation were those giving the best fits and allowing a satisfactory description of the XB interactions obtained with **SAM-1a**.

It should however be noted that such values are in accordance with the organization of multiple XB-donors on a well-defined



Scheme 2. Principle of electrochemically driven XB formation in the presence of PF₆⁻ (blue) and halides (green).

Table 2. Affinity constants (in M⁻¹) toward Cl⁻ for compounds in solution and on surface.

	K_{red}	K_{ox}	$K_{\text{ox}}/K_{\text{red}}$
1a [a]	3	800	267 ± 40
3a [a]	10	1200	120 ± 25
SAM-1a [b]	1000 [c]	565065	565

[a] in 30% ACN / 70% DMF; [b] ACN; [c] estimated from electrochemical simulation.

surface, leading to a polytopic receptor able to strongly bind anions (surface chelate effect).²⁸

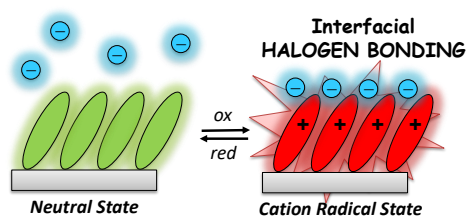
In conclusion we have designed and quantified electrochemically driven charge-assisted XB at a surface confined system. There is strong evidence for XB being the dominant non-covalent interaction in the investigated system. The particular high and selective binding enhancement towards halide anions association with the oxidized SAM points to a strong surface chelate effect of the assembled 2D material. Such effect could be used for the future conception and development of supramolecular assemblies for selective anion capture/release, sensors and organic electronics devices.

Conflicts of interest

There are no conflicts to declare.

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The concept of anion detection via a reversible electrochemically driven charge-assisted Halogen Bonding in solution was transferred on the surface.