

# Supplementary Information

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

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# 1. Experimental

## 1.1 General

Cyclic voltammetry experiments were performed using a Potentiostat PGSTAT 128N equipped with a high speed module ADC10M (Metrohm Autolab) controlled by Nova 1.10.4 software.

Polycrystalline golden disc electrodes (1.6 mm diameter) were mechanically polished with a slurry of graded alumina (from 1 to 0.3  $\mu\text{m}$ ), then ultra-sonicated in acetone, water and absolute ethanol for 3 min each. The Au surfaces were then electrochemically restructured in 0.5 M aqueous  $\text{H}_2\text{SO}_4$  by applying three consecutive cyclic voltammetric scans from  $-0.1$  V to 1.5 V (vs. SCE) at a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ . The electrodes were finally rinsed with distilled water and acetonitrile before use.

If not indicated otherwise the measurements were performed in a conventional one-compartment three-electrode cell containing 0.1 M solution of TBAPF<sub>6</sub> in anhydrous DMF or acetonitrile at 293 K.

In case of functionalized electrodes, the gold electrode was used as working electrode (diameter 1.6 mm) and a platinum wire as counter electrode while in case of homogenous solution studies a mechanically polished glassy carbon disk electrode (diameter 0.3 cm) was employed. Electrolyte and solvent were put into the electrochemical cell equipped with the working, auxiliary and reference electrode under anhydrous argon atmosphere. The solvents were degassed for a few minutes prior to the experiment. After taking a background scan, a solution containing the XB donor was added and the cyclic voltammogram was recorded.

All reactions were performed using air free Schlenk techniques unless otherwise stated.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR were recorded on a 400 MHz Bruker Advance III and a Bruker AV300III spectrometers. NMR spectra were recorded on Chemical shifts are reported in ppm and  $^1\text{H}$  NMR spectra were referenced to residual  $\text{CHCl}_3$  (7.26 ppm),  $^{13}\text{C}$  NMR spectra were referenced to  $\text{CHCl}_3$  (77.2 ppm). High resolution mass spectrometry (HRMS) were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes.

For the electrochemical simulation and following a square scheme when all the reactants are adsorbed on the surface according to a Langmuir isotherm:  $E_1^0 = 0.685$  V,  $E_{*0} = +0.525$  V,  $\nu = 10 \text{ V}\cdot\text{s}^{-1}$ ,  $T = 293$  K and  $\Gamma = 0.66 \cdot 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ . Note that a constant double layer capacitance of  $0.2 \mu\text{F}$  was added in simulation. Note also that KISSA-1D© assumes chemical reactions between adsorbed species according to a Langmuir isotherm, excluding therefore a Frumkin isotherm with lateral interactions between species. Thus, the voltammetric wave widening/thinning, resulting from these interactions, are not taken into account.<sup>1</sup> KISSA Group web site address <http://www.kissagroup.com/>

## 1.2 Chemicals

Chemicals and materials from commercial sources were used without further purification. The solvents were purified and dried by standard methods. The TTF **3b** was synthesized according to literature procedures from TTF **2b**.<sup>2</sup>

Tetra-butylammonium salts (X = PF<sub>6</sub>, Cl, Br, OTf) were bought from Sigma-Aldrich and used without further purification. Thiocetic acid, DMAP (2-(Dimethylamino)pyridine), DCC (dicyclohexylcarbodiimide), EDC (1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride), CuSO<sub>4</sub> sodium ascorbate, ethynylbenzene and all solvents were purchased from Sigma-Aldrich, Acros, and Alfa Aesar and used as received without further purification.

## 1.3 SAM formation

SAMs were prepared according by simple immersion method in which clean and freshly polished and restructured electrodes were immersed in 1 mM acetonitrile solution of the adsorbate for duration of 16 – 24 hours. Consequently, electrodes were rinsed with pure acetonitrile before employing in electrochemical cell for CV experiments.

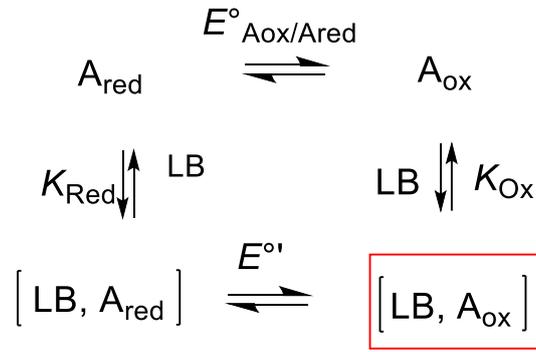
## 1.4 Titration Experiments

### 1.4.1 In solution

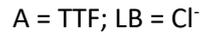
The titrations experiments were performed by adding increasing concentrations of TBACl to a solution of TTF derivative. The concentration of electrolyte and TTF derivative was kept constant throughout the titration procedure.

Electrolyte (solvent + 0.1 M TBAPF<sub>6</sub>) was added to electrochemical cell equipped with the working, auxiliary and reference electrode under anhydrous argon atmosphere. The solvents were degassed for a few minutes. After taking a background scan, appropriate volume of XB donor stock solution was added so that its final concentration was adjusted to be 0.25 mM and the cyclic voltammogram was recorded. During the titration small volumes of a second stock solution containing TBAX (eg X=Cl) and TTF derivative (0.25 mM) in solvent CH<sub>3</sub>CN (including the supporting electrolyte) were added stepwise. Only one scan rate (0.1 V/s) has been used for the fittings.

## **Equations for the determination of the affinity constants**



We present here a derivation of the classical equations allowing the extraction of affinity constants from the potential shifts observed during the titration.



The square-scheme mechanism presented in Scheme 1 depicts the interplay between the binding reaction and the electrochemical reaction. We assume that the system is under dynamic equilibrium, that is, the chemical binding reactions are so fast that chemical binding steps in the square scheme can be considered always at equilibrium during the electrochemical perturbation. This implies that the system can be considered as a single redox couple with an apparent standard potential  $E^{0'}$  which is defined through the following Nernst equation:

$$E = E^{0'} + \frac{RT}{nF} \ln \left( \frac{[A_{\text{ox}}] + [A_{\text{ox}}, \text{LB}]}{[A_{\text{red}}] + [A_{\text{red}}, \text{LB}]} \right) \quad (\text{S1})$$

Another implication is that mass action laws for the two binding reactions are satisfied at any moment,

$$K_{\text{ox}} = \frac{[A_{\text{ox}}, \text{LB}]_{\text{eq}}}{[A_{\text{ox}}]_{\text{eq}} [\text{LB}]_{\text{eq}}} \quad \text{and} \quad K_{\text{red}} = \frac{[A_{\text{red}}, \text{LB}]_{\text{eq}}}{[A_{\text{red}}]_{\text{eq}} [\text{LB}]_{\text{eq}}}$$

Leading to

$$E = E^{0'} + \frac{RT}{nF} \ln \left( \frac{[A_{\text{ox}}]_{\text{eq}} (1 + K_{\text{ox}} [\text{LB}]_{\text{eq}})}{[A_{\text{red}}]_{\text{eq}} (1 + K_{\text{red}} [\text{LB}]_{\text{eq}})} \right) \quad (\text{S2})$$

The Nernst equation applied also for the couple  $A_{\text{ox}}/A_{\text{red}}$

$$E = E^0_{A_{\text{ox}}/A_{\text{red}}} + \frac{RT}{nF} \ln \left( \frac{[A_{\text{ox}}]}{[A_{\text{red}}]} \right) \quad (\text{S3})$$

Subtraction of S3 from S2 gives the following equation:

$$\Delta E^{\ast} = E^{0'} - E^0_{A_{\text{ox}}/A_{\text{red}}} = -\frac{RT}{nF} \ln \left( \frac{1 + K_{\text{ox}} [\text{LB}]_{\text{eq}}}{1 + K_{\text{red}} [\text{LB}]_{\text{eq}}} \right) \quad (\text{S4})$$

For initial conditions for which LB is introduced in large excess ( $[LB]_0 \gg [A]_0$ ), the amount of LB that is involved in the complex formation may be neglected, and therefore  $[LB]_{eq} \approx [LB]_0$ . It follows that:

$$\Delta E' = -\frac{RT}{nF} \ln \frac{(1 + K_{ox} [LB]_0)}{(1 + K_{red} [LB]_0)} \quad (S5)$$

It is worth noting that this equation is used to fit to the experimental titration in Figure 3 of the publication. Therefore, only the experimental points for which B is in excess should be considered for the fitting.

#### 1.4.2 At the interface (SAMs)

The titrations experiments were performed by adding increasing concentrations of TBAX (eg X=Cl) to a solution of TTF derivative. The concentration of electrolyte and TTF derivative was kept constant throughout the titration procedure.

Electrolyte (solvent + 0.1 M TBAPF<sub>6</sub>) was added to electrochemical cell equipped with the working, auxiliary and reference electrode under anhydrous argon atmosphere. The solvents were degassed for a few minutes.

After taking a background scan using a GC disk electrode as a working electrode, the functionalized disk gold electrode was employed and an initial CV was recorded before any anion addition. Afterwards, small volumes of a stock solution containing TBAX (eg X=Cl) in CH<sub>3</sub>CN (containing the supporting electrolyte) were added stepwise and a CV was recorded after each addition, at scan rate 10 V/s.

## 2. Synthesis

### 2.1. Synthesis of derivative **3a**

To a solution of 4,5-bis(cyanoethylthio)4',5'-di(iodo)-TTF **2a** (500 mg, 0.8 mmol) in 40 mL of DMF was slowly added under argon a solution of CsOH, H<sub>2</sub>O (138 mg, 0.8 mmol) in 10 mL of anhydrous MeOH. The mixture was allowed to stir for 30 min. at RT after which, iodomethane (0.05 mL, 0.8 mmol) was added. Stirring was continued for 1h. Solvents were rotary evaporated, and the resulting oil was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organic extract was purified by column chromatography over silica and CH<sub>2</sub>Cl<sub>2</sub>: ether petroleum (70:30) as eluent to afford an orange powder which was used directly into the next step without further purification.

<sup>1</sup>H NMR (CDCl<sub>3</sub>; 300MHz): δ= 2.50 (s, 3H), 2.71 (t, <sup>3</sup>J=7.2Hz, 2H), 3.04 (t, <sup>3</sup>J=7.2Hz, 2H).

To a solution of 4-cyanoethylthio-4',5'-di(iodo)-5methylthio-TTF (250 mg, 0.42 mmol) in 20 mL of DMF was slowly added under argon a solution of CsOH, H<sub>2</sub>O (80 mg, 0.48 mmol) in 5 mL of MeOH. The mixture was allowed to stir for 30 min. at RT after which, 2-bromoethan-1-ol (60 mg, 0.48mmol) was added. Stirring was continued for 1h. Solvents were rotary evaporated, and the resulting oil was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organic extract was purified by column chromatography over silica and CH<sub>2</sub>Cl<sub>2</sub>: ether petroleum (70:30) as eluent to afford **3a** as a dark red powder in 30 % overall yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>; 300MHz): δ= 2.32 (t, <sup>3</sup>J=6.7Hz, 1H), 2.48 (s, 3H), 2.96 (t, <sup>3</sup>J=5.7Hz, 2H), 3.75 (dt, <sup>3</sup>J=6.6, 5.6 Hz, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>; 125.77 MHz) : δ= 19.4 (s, SCH<sub>3</sub>), 39.2 (s, CH<sub>2</sub>), 60.1 (s, CH<sub>2</sub>-OH), 110.3 (s, C=C), 122.9 (s, C=C), 123.9 (s, C=C), 133.3 (s, C=C). HRMS calcd for [C<sub>9</sub>H<sub>8</sub>I<sub>2</sub>OS<sub>6</sub>]<sup>+</sup> : m/z<sub>experimental</sub> = 577.698 (m/z<sub>theoretical</sub> = 577.6983).

### 2.2. Synthesis of derivative **1a**

In a schlenk tube **3a** (20 mg, 0.034 mmol, 1 eq.) was added to 3.4 mL of dry distilled CH<sub>2</sub>Cl<sub>2</sub> and cooled to 0 °C. Thiocetic acid (8.25 mg, 0.04 mmol, 1.2 eq.) was then added and the mixture was kept to stir for 15 minutes at 0 °C. Then dicyclohexylcarbodiimide (DCC) (10.52 mg, 0.051 mmol, 1.5 eq.) and 2-(Dimethylamino)pyridine (DMAP) (1.25 mg, 0.0102 mmol, 0.3 eq.) dissolved in 3.4 mL dry distilled CH<sub>2</sub>Cl<sub>2</sub> were added and the mixture was stirred for 15 minutes. The cooling bath was then removed, and the solution allowed to warm to room temperature. After being stirred for 24 h under argon, the reaction mixture was washed with water (3 x 40 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure. The residue was subjected to column chromatography with CH<sub>2</sub>Cl<sub>2</sub>: cyclohexane (70:30) as eluent, and the product was collected and concentrated under reduced pressure with a yield 31% of reddish powder.

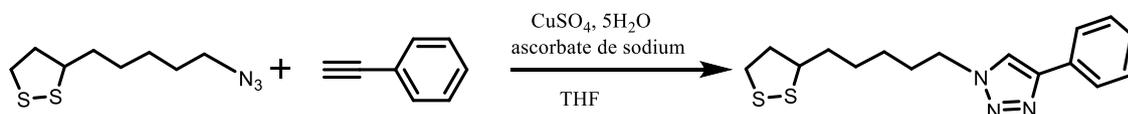
**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>; 400 MHz) : δ= 1.47 (m, 2H, SC-C-CH<sub>2</sub>) , 1.65-1.71 (m, 4H, C=OCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>), 1.92 (m, 1H, S-SCH<sub>2</sub>), 2.34 (t, <sup>3</sup>J=7.4 Hz, 2H, C=OCH<sub>2</sub>), 2.43 (s, 3H, CH<sub>3</sub>), 2.48 (m, 1H, S-SCH<sub>2</sub>), 3.03 (t, <sup>3</sup>J=6.4 Hz, 2H, C-O-CH<sub>2</sub>CH<sub>2</sub>), 3.10-3.18 (m, 2H, S-SCH-CH<sub>2</sub>), 3.57 (m, 1H, S-SCH), 4.26 (t, <sup>3</sup>J=6.3 Hz, 2H, C-O-CH<sub>2</sub>). **<sup>13</sup>C-NMR** (CDCl<sub>3</sub>; 100.6 MHz) : δ= 19.4 (s, CH<sub>3</sub>), 24.8 (s, C=O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 28.9 (s, S-C-C-CH<sub>2</sub>), 34.0 (s, C=O-CH<sub>2</sub>), 34.8 (d, C-O-CH<sub>2</sub>-CH<sub>2</sub> and C=O-CH<sub>2</sub>-CH<sub>2</sub>), 38.7 (S-S-CH-CH<sub>2</sub>), 40.4 (S-S-CH<sub>2</sub>), 56.5 (S-S-CH), 63.1 (C-O-CH<sub>2</sub>), 123.6 (C=C-S-CH<sub>2</sub>), 132.5 (C=C-S-CH<sub>3</sub>), 173.4 (C=O). **MS** [C<sub>17</sub>H<sub>20</sub>I<sub>2</sub>O<sub>2</sub>S<sub>8</sub>]<sup>+</sup> : m/z<sub>experimental</sub> = 765.54 (m/z<sub>theoretical</sub> = 766.63).

### 2.3. Synthesis of derivative **1b**

In a schlenk tube **3b** (30 mg, 0.07 mmol, 1 eq.) was dissolved into 5 mL of dry freshly distilled CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Thiocctic acid (21.66 mg, 0.105 mmol, 1.5 eq.) and DMAP (6.84 mg, 0.056 mmol, 0.8 eq.) were then added to the mixture. Finally, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (26.8 mg, 0.14 mmol, 2 eq.) was directly added and the mixture was kept to stir overnight at room temperature. Consequently, solvent was evaporated under reduced pressure and the crude product was purified through column chromatography on silica gel using EtOAc/petroleum ether (20:80) as the eluent in which the product R<sub>f</sub> = 0.43. The product was then collected and concentrated via reduced pressure with a yield 60% of reddish oil.

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>; 400 MHz) : δ= 1.47 (m, 2H, S-CH-CH<sub>2</sub>) , 1.65 and 1.71 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>CO), 1.92 (m, 1H, S-S-CH<sub>2</sub>), 2.35 (t, <sup>3</sup>J=7.4 Hz, 2H, CH<sub>2</sub>-CO), 2.43 (s, 6H, S-CH<sub>3</sub>), 2.44 (s, 3H, S-CH<sub>3</sub>), 2.49 (m, 1H, S-S-CH<sub>2</sub>), 3.04 (t, <sup>3</sup>J=6.4 Hz, 2H, CO-O-CH<sub>2</sub>-CH<sub>2</sub>), 3.15 (m, 2H, S-S-CH-CH<sub>2</sub>), 3.58 (m, 1H, S-S-CH), 4.26 (t, <sup>3</sup>J=6.3 Hz, 2H, CO-O-CH<sub>2</sub>). **<sup>13</sup>C-NMR** (CDCl<sub>3</sub>; 100.6 MHz) : δ= 19.3 (s, S-CH<sub>3</sub>), 24.8 (s, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO), 28.9 (s, S-CH-CH<sub>2</sub>), 34.1 (s, CH<sub>2</sub>-C=O), 34.2 (s, CH<sub>2</sub>-CH<sub>2</sub>-CO), 34.7 (s, CO-O-CH<sub>2</sub>-CH<sub>2</sub>), 38.6 (s, S-S-CH-CH<sub>2</sub>), 40.4 (s, S-S-CH<sub>2</sub>), 56.5 (s, S-S-CH), 63.0 (s, CO-O-CH<sub>2</sub>), 127.7 (s, C=C-S-CH<sub>2</sub>), 132.4 (C=C-S-CH<sub>3</sub>), 173.3 (s, C=O). **MS** [C<sub>19</sub>H<sub>26</sub>O<sub>2</sub>S<sub>10</sub>]<sup>+</sup> : m/z<sub>experimental</sub> = 605.9 (m/z<sub>theoretical</sub> = 607.8).

### 2.3. Synthesis of derivative **4**



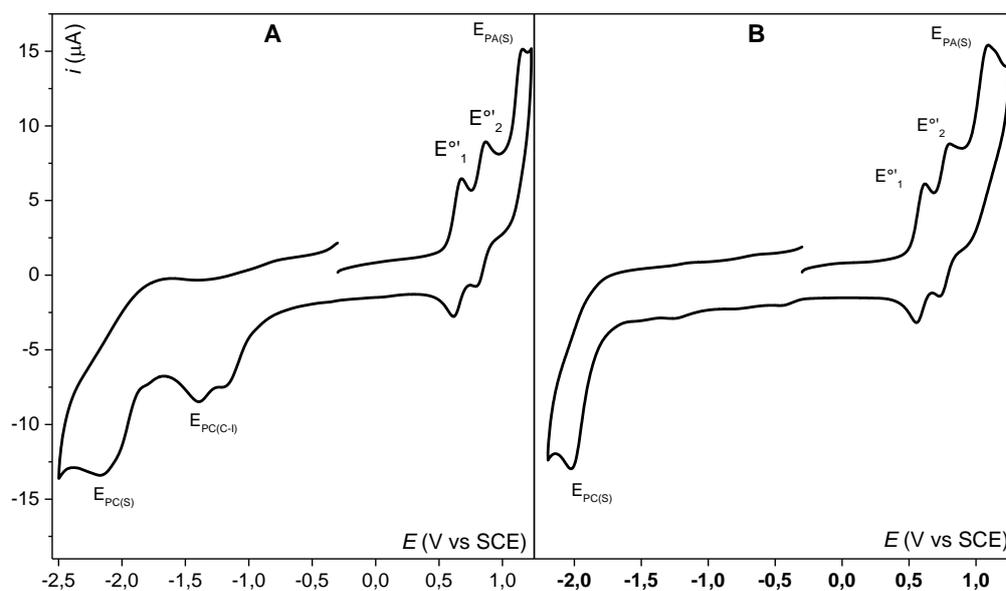
To an aqueous solution (12 mL) containing CuSO<sub>4</sub> (24.7 mg, 0.155 mmol) and sodium ascorbate (92.3 mg, 0.466 mmol) was added ethynylbenzene (105.7 mg, 1.04 mmol) previously dissolved in 9 mL of THF. This solution was then added dropwise to a solution of 3-(5-azidopentyl)-1,2-dithiolane<sup>3</sup> (225 mg, 1.04 mmol) in 9 mL in THF and the reaction mixture was allowed to stir during 3 days under argon at room temperature. The mixture was extracted with 3 x 10 mL of Et<sub>2</sub>O and the organic phase was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and crude

compound was purified by column chromatography on silicagel ( $\text{CHCl}_3$ ) giving compound **4** as a yellow oil in a 47% of yield (155.1 mg).

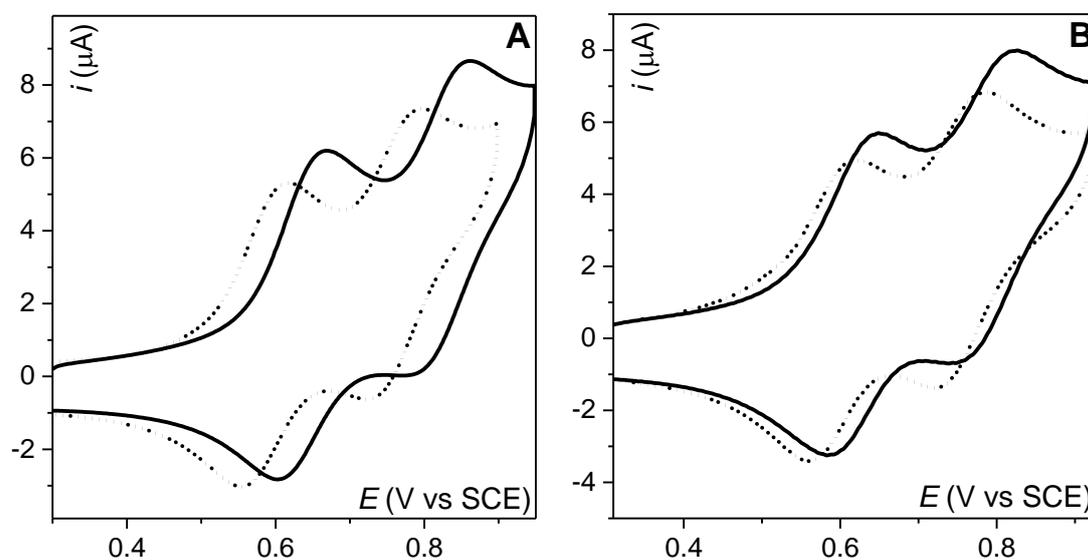
**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ; 400 MHz):  $\delta$  = 1.41 (m, 2H,  $\text{N}(\text{CH}_2)_2\text{CH}_2$ ); 1.50 (m, 2H,  $\text{N}(\text{CH}_2)_3\text{CH}_2$ ); 1.68 (m, 2H,  $\text{N}(\text{CH}_2)_4\text{CH}_2$ ); 1.90 (m, 1H,  $\text{SCH}_2\text{CH}_2$ ); 1.97 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ); 2.44 (m, 1H,  $\text{SCH}_2\text{CH}_2$ ); 3.16 (m, 2H,  $\text{SCH}_2$ ); 3.55 (m, 1H,  $\text{CHS}$ ); 4.41 (t,  $^3\text{J}(\text{H,H}) = 7.2\text{Hz}$ , 2H,  $\text{NCH}_2$ ); 7.34 (d,  $^3\text{J}(\text{H,H}) = 7.1\text{Hz}$ , 1H,  $\text{CH}_{\text{para}}$ ); 7.43 (t,  $^3\text{J}(\text{H,H}) = 7.5\text{Hz}$ , 2H,  $\text{CH}_{\text{meta}}$ ); 7.74 (s, 1H, triazole  $\text{CCHN}$ ); 7.83 (d,  $^3\text{J}(\text{H,H}) = 7.3\text{Hz}$ , 2H,  $\text{CH}_{\text{ortho}}$ ).  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ; 100.6 MHz):  $\delta$  = 26.4 (s,  $\text{SCH}(\text{CH}_2)_2\text{CH}_2$ ); 28.8 (s,  $\text{SCHCH}_2\text{CH}_2\text{CH}_2$ ); 30.3 (s,  $\text{NCH}_2\text{CH}_2$ ); 34.8 (s,  $\text{SCHCH}_2(\text{CH}_2)_2$ ); 38.6 (s,  $\text{SCH}_2$ ); 40.4 (s,  $\text{SCH}_2\text{CH}_2$ ); 50.4 (s,  $\text{NCH}_2$ ); 56.5 (s,  $\text{CHS}$ ); 119.5 (s,  $\text{NCH}_{\text{triazole}}$ ); 125.9 (s,  $\text{CH}_{\text{para}}$ ); 128.3 (s,  $\text{CH}_{\text{ortho}}$ ); 129.0 ( $\text{CH}_{\text{meta}}$ ); 130.8 (s,  $\text{C}_{\text{Ar}}$ ); 148.0 ( $\text{C}_{\text{triazole}}$ ).

### 3. Electrochemical experiments in solution

#### 3.1. CV in solution

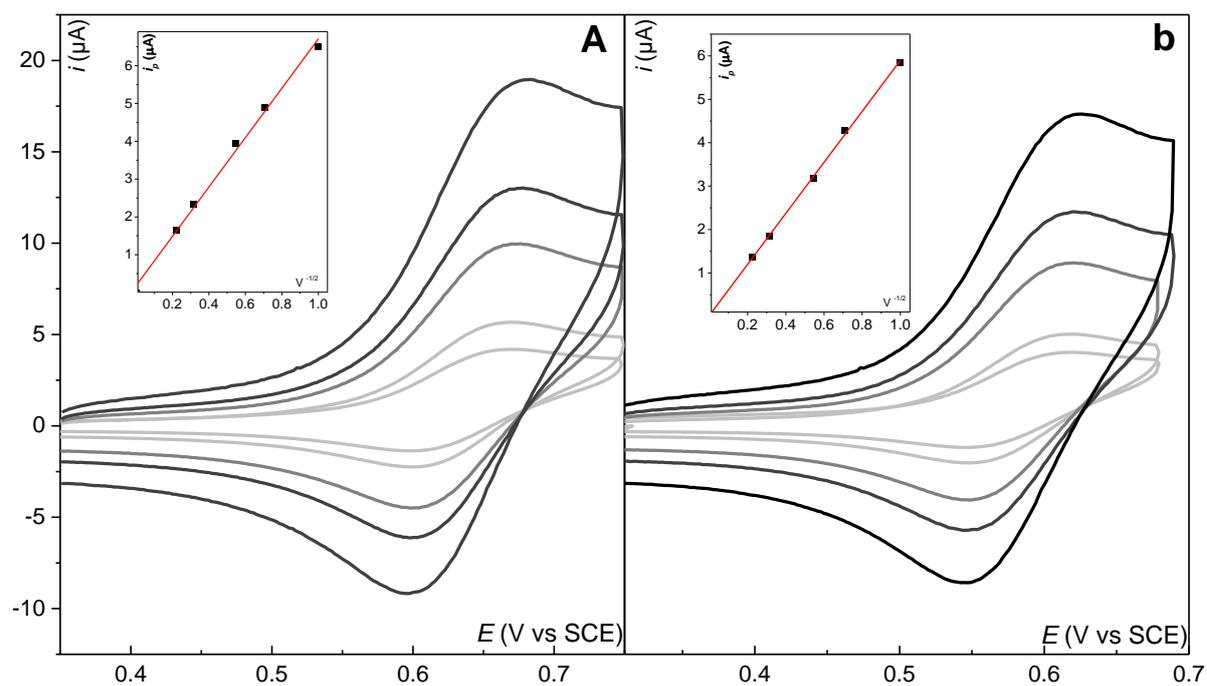


**Figure S1.** CVs recorded in a solution of 0.1 M TBAPF<sub>6</sub> in 30% ACN/70% DMF on a GC electrode of A) **1a** (0.25 mM) and B) **1b** (0.25 mM). Scan rate 0.1 V/s.



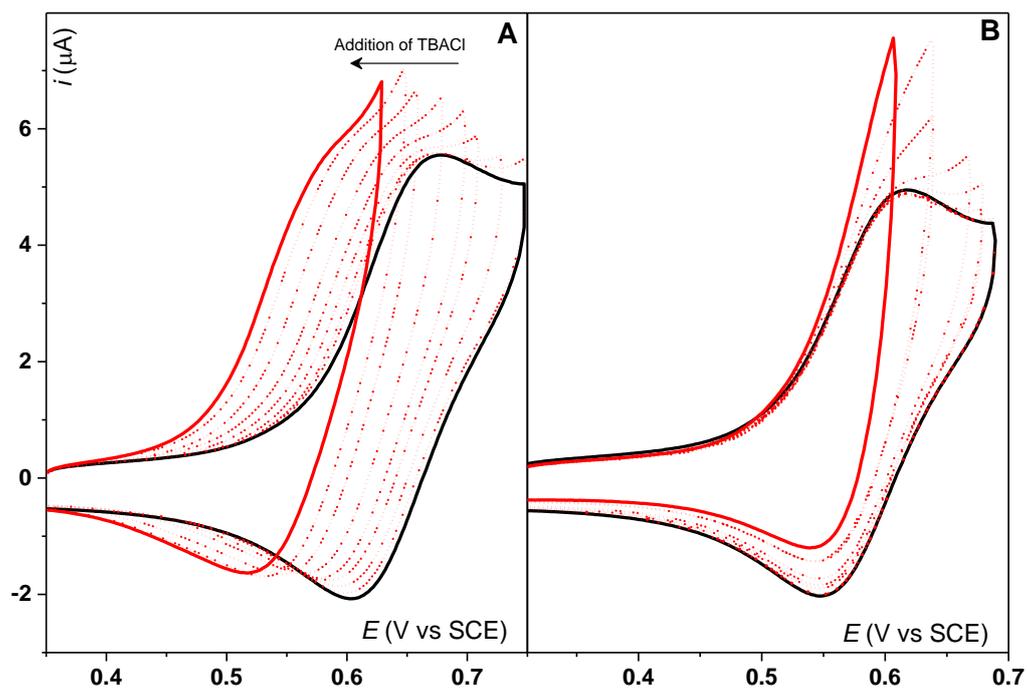
**Figure S2.** A) CVs recorded in a solution of 0.1 M TBAPF<sub>6</sub> in 30% ACN/70% DMF on a GC electrode of **1a** (black plain trace) and **1b** (black dotted trace). C = 0.25 mM. Scan rate 0.1 V/s. B) CVs recorded in a solution of 0.1 M TBAPF<sub>6</sub> in 30% ACN/70% DMF on a GC electrode of **3a** (black plain trace) and **3b** (black dotted trace). C = 0.25 mM. Scan rate 0.1 V/s.

### 3.2 Characterization in solution

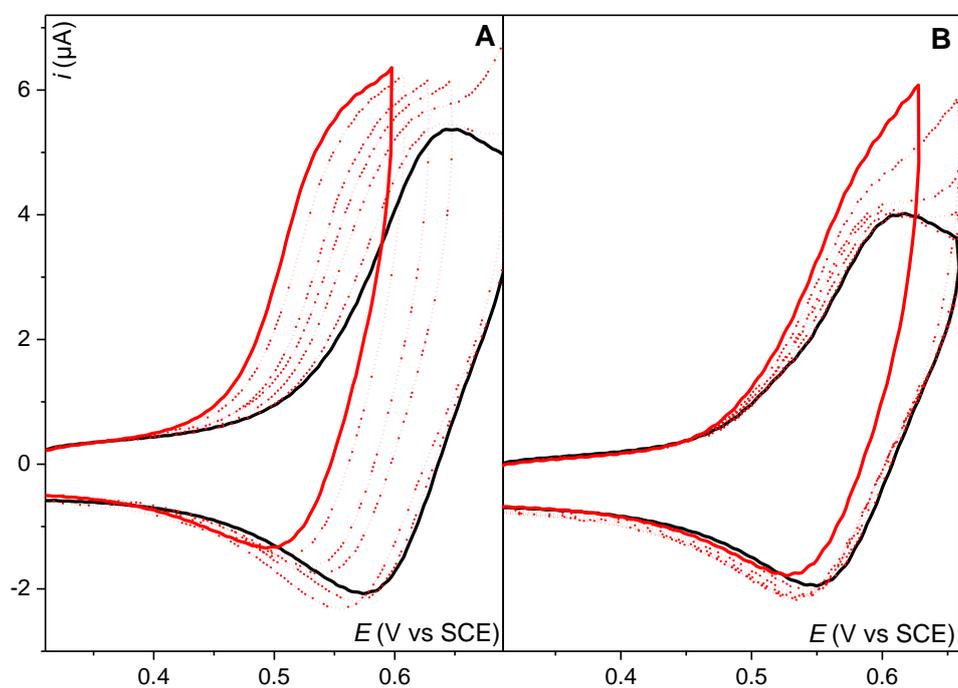


**Figure S3.** CVs recorded at various scan rates (from bottom: 50, 100, 300, 5000 and 100 $\text{mV}\cdot\text{s}^{-1}$ ) and the plot of the peak currents versus the square root of the scan rates for **1a** (A) and **1b** (B).

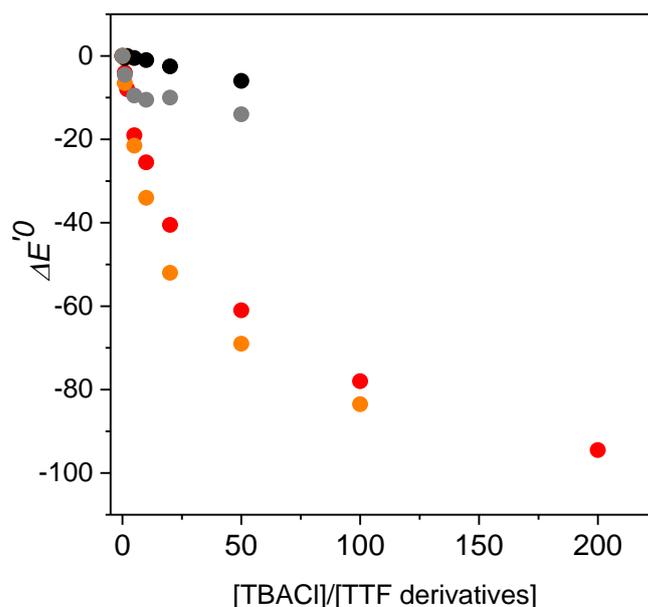
### 3.3. Titration in solution



**Figure S4.** CVs of 0.25mM of **1a** (A) and **1b** (B) on GC electrode for the first oxidation wave in of 0.1 M TBAPF<sub>6</sub> in 30% ACN/70% DMF in the absence (black) and in the presence (red) of increasing concentrations of TBACl (0.25, 0.5, 1.25, 2.5, 5, 12.5, 25 and 50 mM). Scan rate 0.1 V/s.



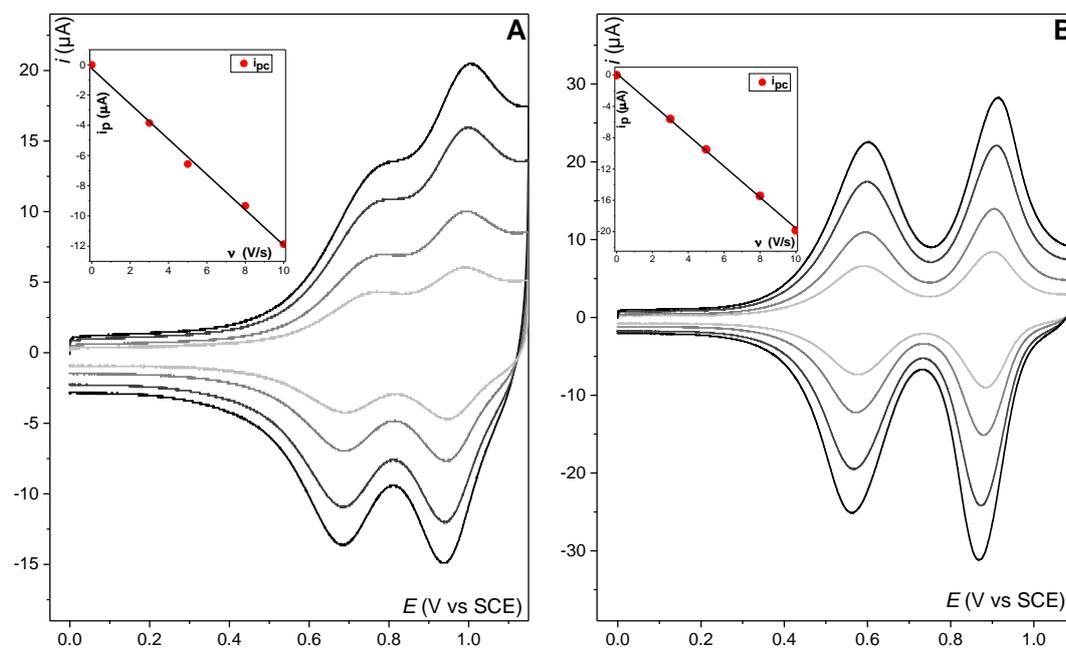
**Figure S5.** s of 0.25mM of **3a** (A) and **3b** (B) on GC electrode for the first oxidation wave in of 0.1 M TBAPF<sub>6</sub> in 30% ACN/70% DMF in the absence (black) and in the presence (red) of increasing concentrations of TBACl (0.25, 0.5, 1.25, 2.5, 5, 12.5, 25 and 50 mM). Scan rate 0.1 V/s.



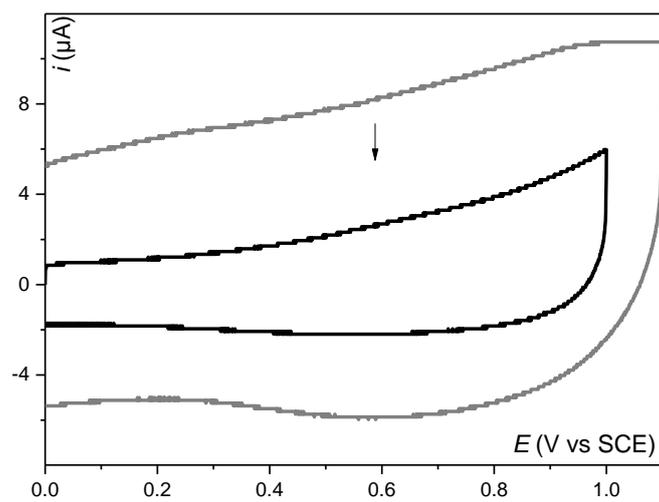
**Figure S6.** Dependence of the potential shift of ( $\Delta E^{\circ'}$ ) corresponding to the first oxidation step of TTF derivatives (0.25 mM) on the concentration of the TBACl (0, 0.25, 0.5, 2.5, 5, 12.5, 25 and 50 mM) wave in of 0.1 M TBAPF<sub>6</sub> in 30% ACN/70% DMF at 293 K, for **1a** (red), **1b** (black), **3a** (orange) and **3b** (gray).

## 4. Electrochemical experiments at the interface

### 4.1. Characterization of the SAMs



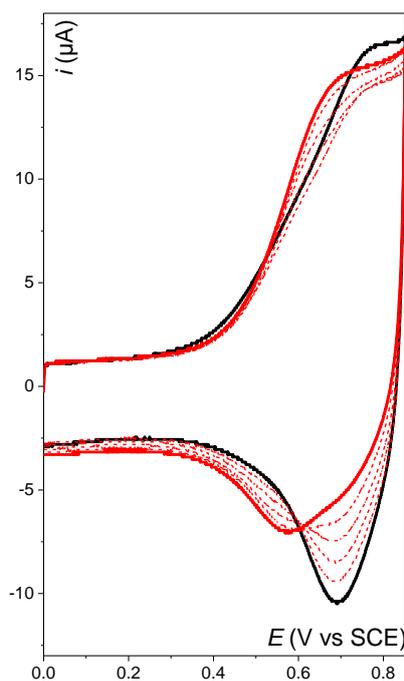
**Figure S7.** CV at different scan rate (3, 5, 8 and 10 V.s<sup>-1</sup>) the SAMs on Au electrodes of A) **SAM-1a** and B) **SAM-1b** with insert the corresponding trace of peak current versus scan rate .



**Figure S8.** CV at  $10 \text{ V}\cdot\text{s}^{-1}$  of bare gold electrode (grey trace) and of **SAM-4** (black trace)

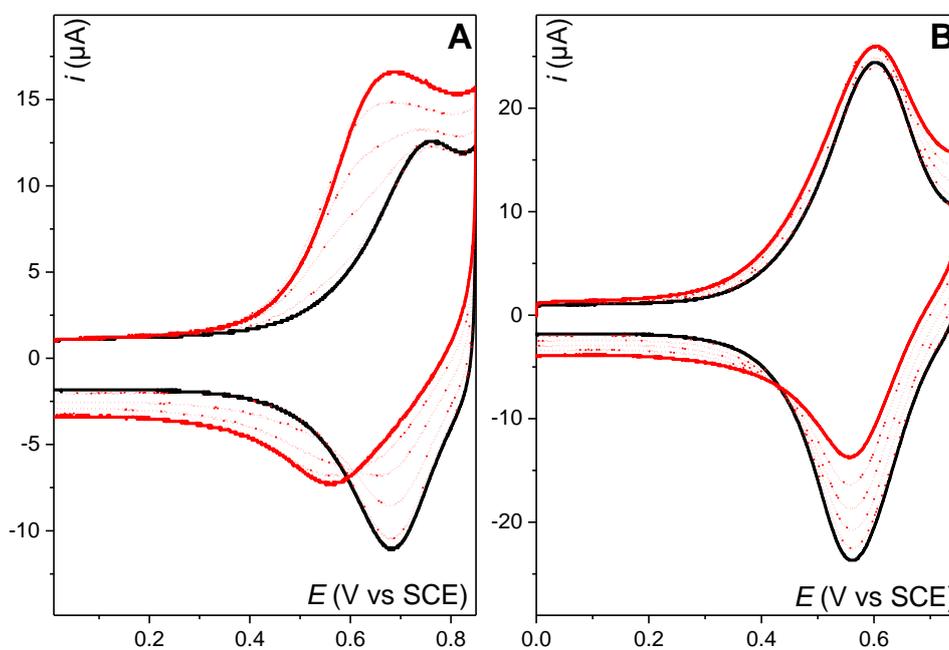
## 4.2. Titration with various Lewis bases

### 4.2.1 with Cl<sup>-</sup> in DMF



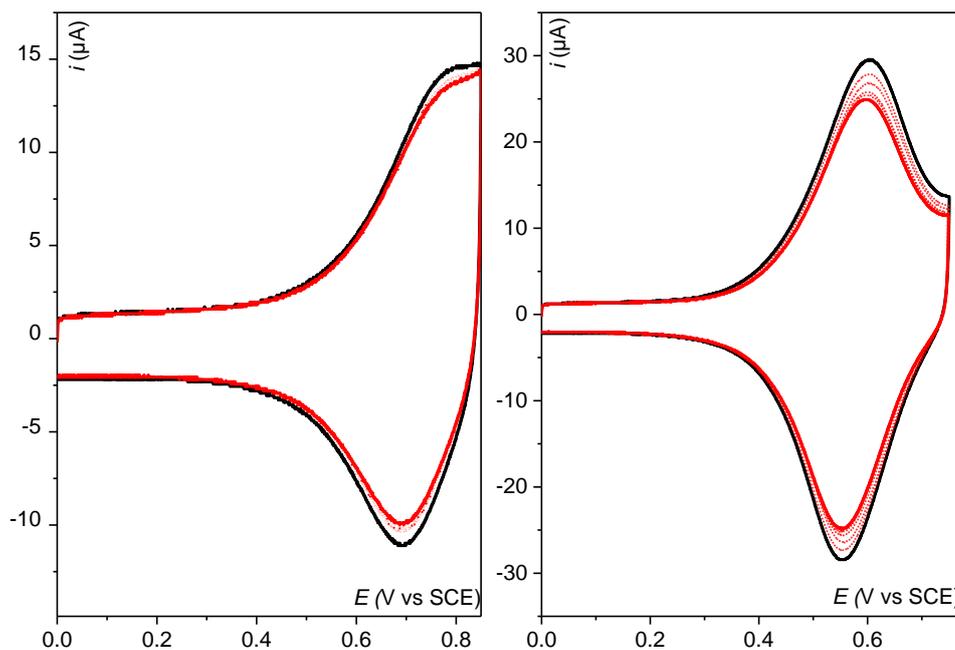
**Figure S9.** CVs of **SAM-1a** obtained in 0.1 M TBAPF<sub>6</sub>/DMF, in absence (black) and in presence (red) of increasing amounts of TBABr (0.01, 0.05, 0.1, 0.15 and 0.2 mM). Scan rate 10 V/s.

### 4.2.2 with Br<sup>-</sup>



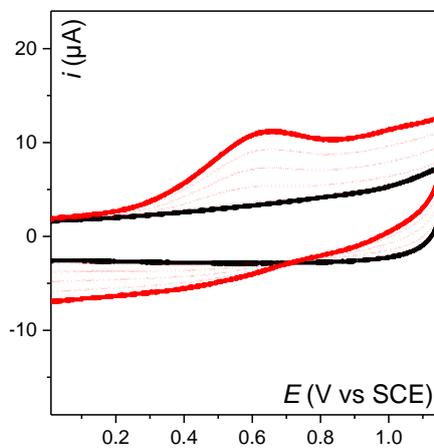
**Figure S10.** CVs of **SAM-1a** (A) and **SAM-1b** (B), obtained in 0.1 M TBAPF<sub>6</sub>/ACN, in absence (black) and in presence (red) of increasing amounts of TBABr (0.01, 0.05, 0.1, 0.15 and 0.2 mM). Scan rate 10 V/s.

#### 4.2.3 with OTf



**Figure S11.** CVs of **SAM-1a** (A) and **SAM-1b** (B), obtained in 0.1 M TBAPF<sub>6</sub>/ACN, in absence (black) and in presence (red) of increasing amounts of TBAOTf (0.01, 0.05, 0.1, 0.15 and 0.2 mM). Scan rate 10 V/s.

#### 4.3 Titration with TBACl on SAM-4



**Figure S12.** CVs of **SAM-4** obtained in 0.1 M TBAPF<sub>6</sub>/ACN, in absence (black) and in presence (red) of increasing amounts of TBACl (0.01, 0.05, 0.1, 0.15 and 0.2 mM). Scan rate 10 V/s.

#### 4.4. Limit of detection (LOD)

The LOD highly depends on the number of objects (TTF molecules) present on the surface of the electrode. This number is different for each prepared SAM. Furthermore the absolute electrode surface is also important. For instant, when using ultra-microelectrodes even lower LODs could be attained (because of signal-to-noise ratio). A precise determination of the LOD in the present system cannot be calculated based on a linear regression line.<sup>4</sup> Instead we got reasonable fits of our data with the Langmuir model. At a logarithmic scale of the chloride concentration the plot is in agreement with a sigmoid calibration curve with a linear part over approximately 2 decades, which is reasonable, although we cannot attain the data for the higher concentrations. Based on this model we can roughly estimate a value of  $6 \times 10^{-6}$  M for the LOD value (intercept of the tangent of the linear part of the calibration curve with the x axis).

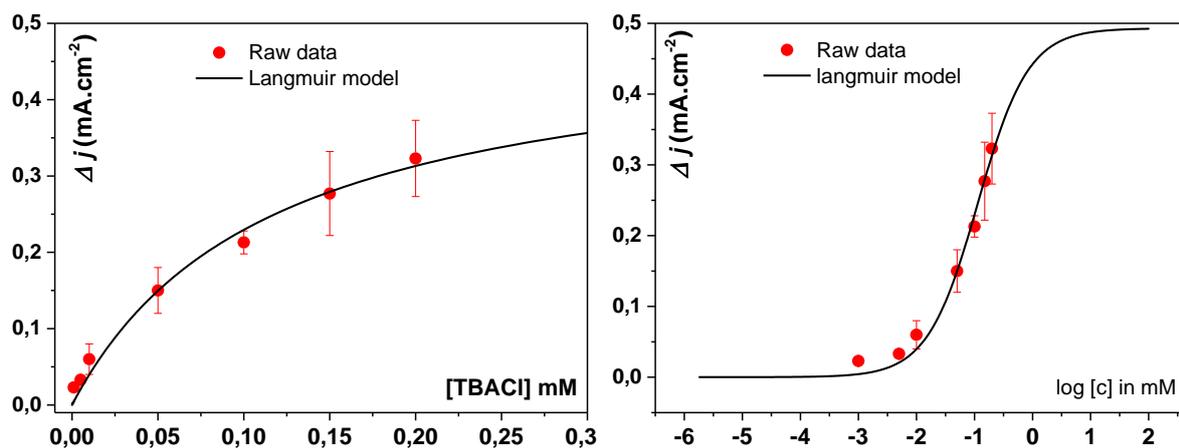


Figure S13. Calibration curves with the Langmuir model.

<sup>1</sup> P. Y. Blanchard, O. Alévêque, S. Boisard, C. Gautier, A. El-Ghayoury, F. Le Derf, T. Breton, E. Levillain, *Phys.Chem.Chem.Phys.* **2011**, *13*, 2118-2120.

<sup>2</sup> S. Matsumoto, W. Matsuda, H. Fueno, Y. Misaki, K. Tanaka, *Synthetic Metals*, **2005**, *153*, 429-432

<sup>3</sup> A) W. Russ Algar, U. J. Krull, *Langmuir*, **2008**, *24*, 5514-5520; b) M. Koufaki, C. Kiziridi, F. Nikoloudaki, M. N. Alexis, *Biorganic and Medicinal chemistry Letters*, **2007**, *17*, 4223-4227.

<sup>4</sup> J. Mocak, A. M. Bond, S. Mitchell, G. Scollary, *Pure and Applied Chemistry* **1997**, *69/2*, 297-328