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Electrochemical Activation of a Tetrathiafulvalene Halogen Bond Donor in Solution.

Raquel Oliveira, Sihem Groni, Claire Fave, Mathieu Branca, François Mavré, Dominique Lorcy, Marc Fourmigué and Bernd Schöllhorn.

Supplementary information

1) Experimental

1.1 General

All liquids substrates were filtered over activated neutral aluminum oxide. Cyclic voltammetry experiments were performed using a CHI 660D potentiostat (CH Instruments. Inc., USA). If not indicated otherwise the measurements were performed in a standard one-compartment three electrode cell containing 0.1 M solution of $TBAPF_6$ in anhydrous DMF or acetonitrile thermostated at 293 K. A mechanically polished glassy carbon disk electrode (carbon rod of 3 mm diameter embedded in an insoluble polymer matrix, CHI Instruments. Inc., USA) was used as working electrode and a platinum wire as auxiliary electrode. A salt bridge containing the electrolyte was used to connect the electrochemical cell with a saturated calomel reference electrode (SCE).

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.

1.2 Titration Experiments

The titrations experiments were performed by adding increasing concentrations of TBACl to a solution of I-TTF. The concentration of electrolyte and I-TTF was kept constant as well as the final volume.

A stock solution 10 mM of I-TTF was prepared in anhydrous DMF (without supporting electrolyte). Electrolyte (solvent + 0.1M $TBAPF_6$, v= 4875 µL) 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, 125 µL of XB donor stock solution was added (0.25 mM) and the cyclic voltammogram was recorded. During the titration small volumes of a second stock solution containing TBAX (eg X=Cl; 0.1 M) and I-TTF (0.25 mM) in solvent DMF (without supporting electrolyte).

The total volume of the electrochemical cell was kept constant (5 mL) during the entire titration (before each addition the same volume was taken from the cell keeping the final volume after each addition equal to 5 mL).

The titrations were repeated three times in order to estimate the standard deviation. In one of the three titrations the complex $Os(bipy)_2Cl_2$ (0.1mM) was added as an internal reference.

Only one scan rate (0.1 V/s) has been used for the fittings.

2) Electrochemical data of the $TTF^{0/1+}$ and $I\text{-}TTF^{0/1+}$.

Table S-01. CV data of **TTF** and **TTF-I** derivatives (0.25 mM) in the absence and the presence of 100 equiv. of TBACl in 0.1 M $TBAPF_6$/DMF on glassy carbon vs. SCE, scan rate: 100 mV/s, T=293K.

	E_p^a [a]	E_p^c [b]	$E^{\circ\prime}$ [c]	ΔE_p [d]	ΔE_p^a [e]	ΔE_p^c [f]	$\Delta E'$ [g]	I_p^c/I_p^a [h]
TTF	416	350	383	66	-	-	-	0.996
TTF + TBACl	408	343	376	65	-6	-8	-7	1.05
TTF + TBABr	414	349	382	65	-2	-1	-1	1.09
I-TTF	507	442	475	65	-	-	-	0.957
I-TTF + TBACl	456	388	422	68	-51	-54	-53	0.974
I-TTF + TBABr	470	403	437	67	-37	-39	-38	0.990

[a] anodic peak potential in mV; [b] cathodic peak potential in mV; [c]; $E^{\circ\prime}=(E_p^a+E_p^c)/2$ in mV; [d] $\Delta E_p = E_p^a - E_p^c$ in mV; [e] anodic and [f] cathodic and [g] formal standard potential shifts in mV after the addition of 100 equivalents of TBACl; [h] current ratio.

Table S-02. I_p^a/I_p^c of **TTF** and **I-TTF** (0.25 mM) in the absence and the presence of 100 equiv. of **TBAX** or **water** in 0.1 M $TBAPF_6$/DMF on glassy carbon, vs. SCE, scan rate: 100 mV/s, T=293K.

	TTF				I-TTF						
donor	-	TBACl	TBABr	H_20	-	TBACl	TBABr	$TBANO_3$	TBAOTf	$TBAClO_4$	H_20
I_p^a/I_p^c	0.996	1.05	1.09	0.989	0.957	0.974	0.990	1.04	1.02	??	0.986

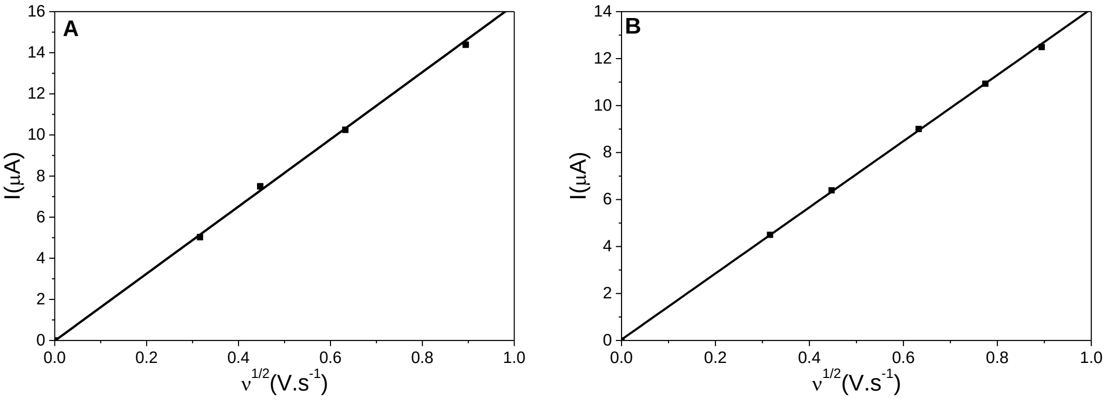

Figure S-01. Current intensity as function of the square roote of the scan rate. A) **TTF/TTF**$^{1+}$ and B) **I-TTF/I-TTF**$^{1+}$

3) **Variation of nature and concentration of the supporting electrolyte salt** (TTF and I-TTF with increasing chloride concentrations)

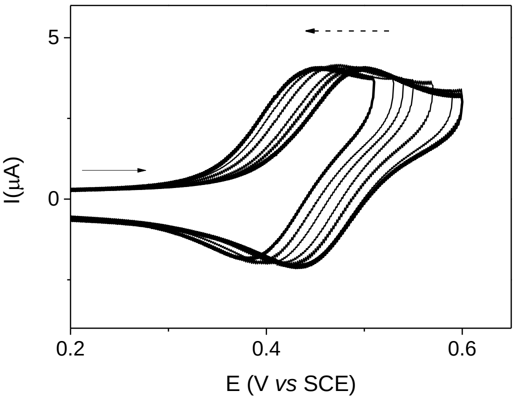

Figure S-02. CVs of **I-TTF** (0.25 mM) on a glassy carbon electrode in a solution **of tetra-*n*-hexyl-ammonium hexafluorophosphate** (0.1 M) in DMF in the absence and in the presence of increasing concentrations of TBACl. Scan rate 0.1 V/s.

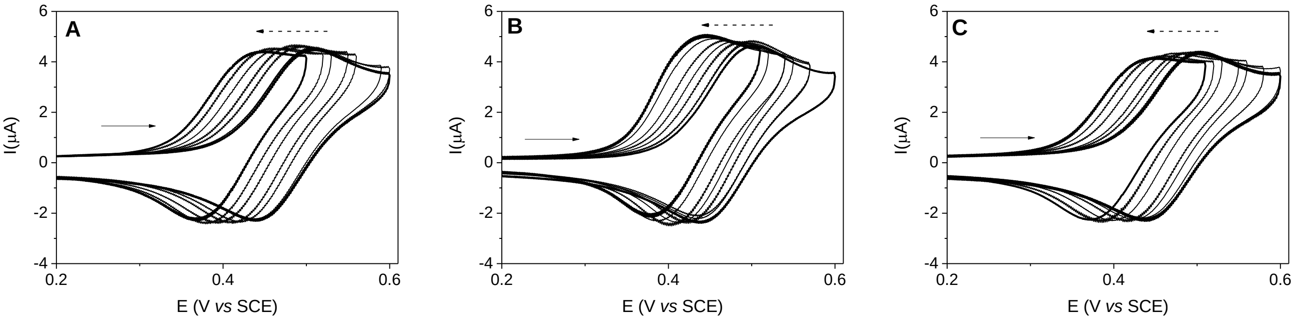

Figure S-03. CVs of **I-TTF** (0.25 mM) on a glassy carbon electrode in the absence and in the presence of increasing concentrations of **TBACl** in a solution of **TBAPF$_6$** (a) **0.05 M**, (b) **0.1 M** and (c) **0.2 M** in DMF. Scan rate 0.1 V/s.

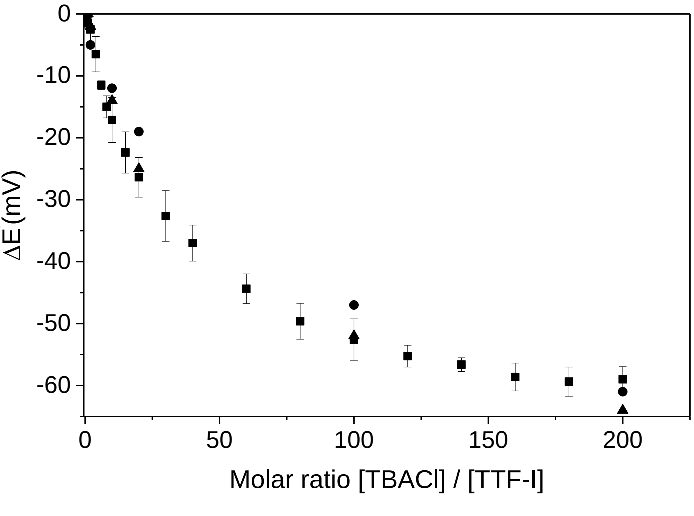

Figure S-04. Dependence of the potential shift, ΔE', corresponding to the first oxidation step of **I-TTF** (0.25 mM) on the concentration of **TBACl** in DMF at 293 K for different concentration of supporting electrolyte: 0.05M (●) 0.1M (■) and 0.2M (▲).

4) TTF and I-TTF in the presence of increasing halide and water concentrations

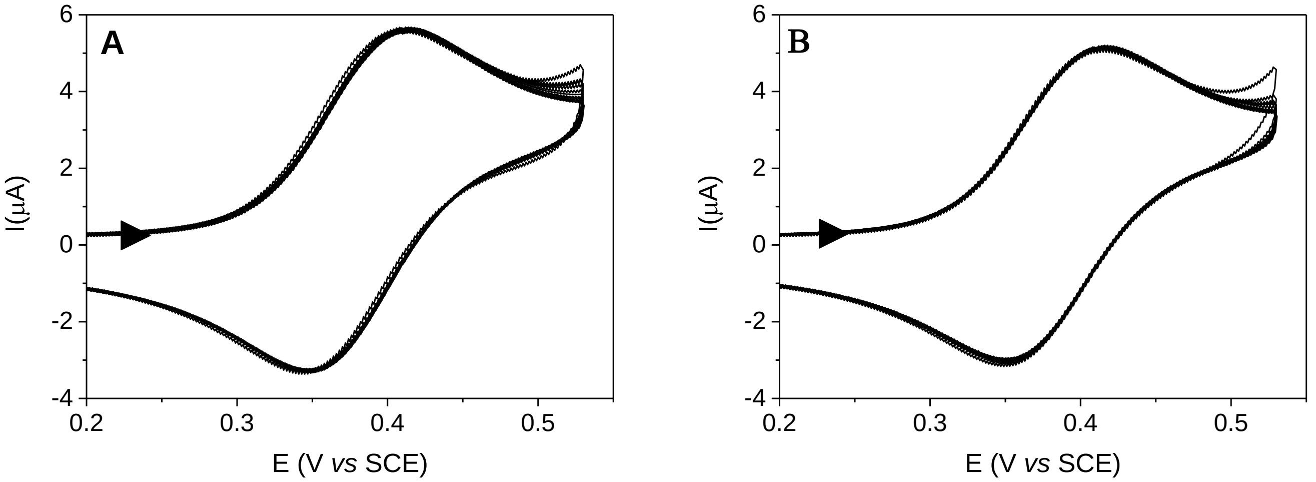

Figure S-05. CVs of **TTF** (0.25 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of increasing concentrations (0, 0.25, 1.25, 2.5, 5, 7.5, 10, 12.5 and 25 mM) of (A) **TBACl** and (B) **TBABr**. Scan rate 0.1 V s^{-1}.

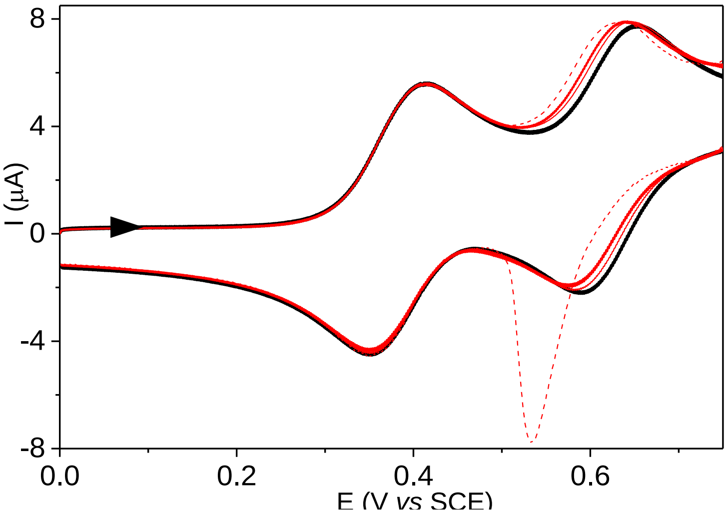

Figure S-06. CVs of **TTF** (0.25 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of increasing concentrations of **TBACl**: 0 mM (black), 2.5 mM (red thin line), 5 mM (red bold line) and 12.5 mM (red dashed thin line). Scan rate 0.1 V s^{-1}.

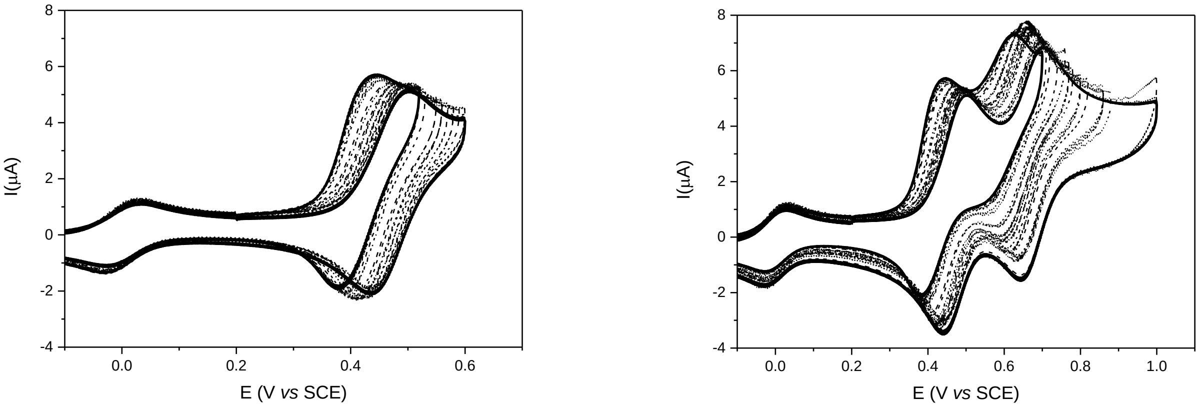

Figure S-07. CVs of **I-TTF** (0.25 mM) and the internal reference **Os(bipy)$_2$Cl$_2$** (0.1 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of increasing concentrations of **TBACl** (from right to left: 0, 0.025, 0.05, 0.1, 0.15, 0.25, 0.50, 1, 1.5, 2, 2.5, 3.75, 5, 7.5, 10, 20, 25, 30, 35, 40, 45 and 50 mM). Scan rate 0.1 V s^{-1}.

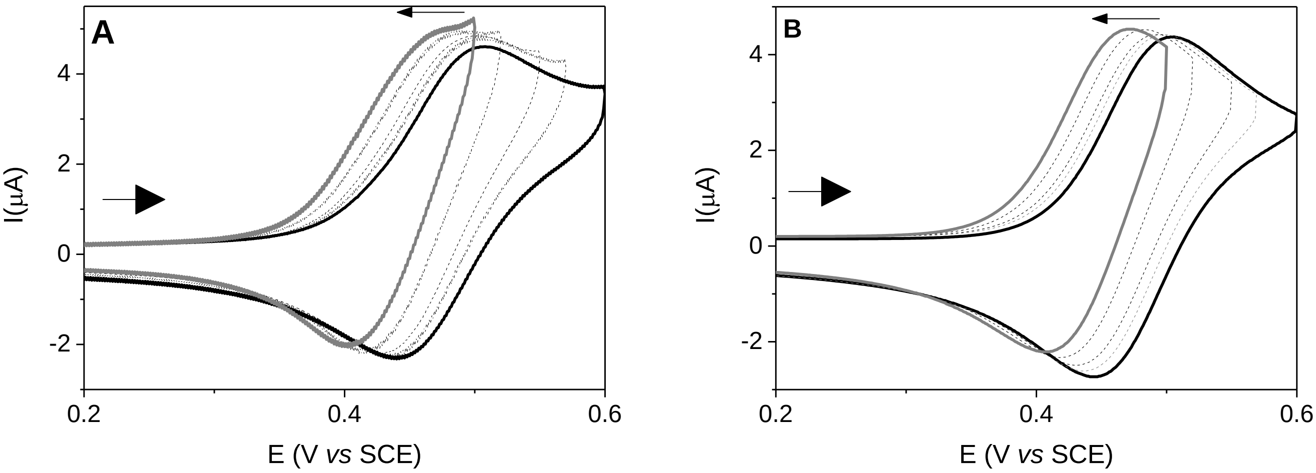

Figure S-08. CVs of **I-TTF** (0.25 mM): on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of increasing concentrations of **TBABr** (from right to left: 0, 2.5, 5, 12.5 and 25 mM) (A) experimental and (B) simulated (DigiElch). Scan rate 0.1 V s^{-1}.

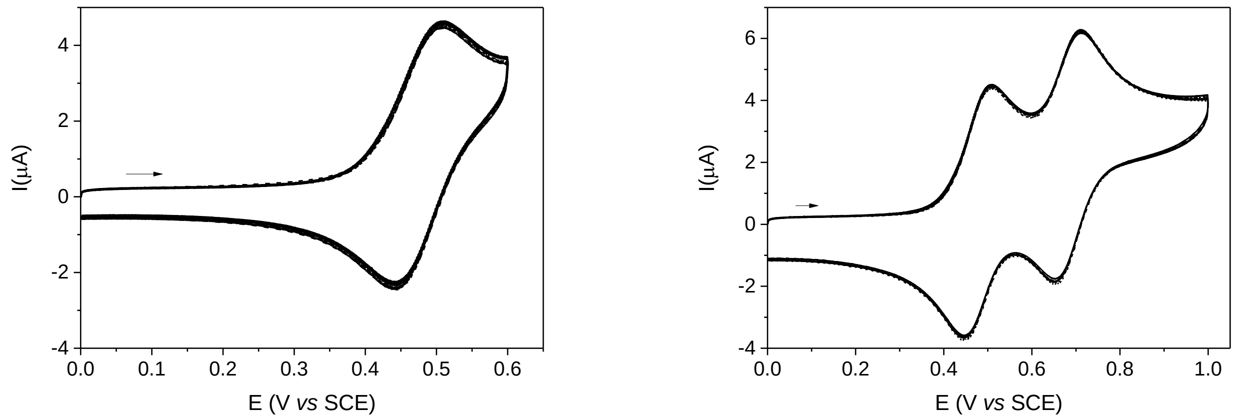

Figure S-09. CVs of **I-TTF** (0.25 mM): on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of increasing concentrations of **H$_2$O** (0.25, 0.5, 1.25, 2.5, 5, 25 and 50 mM). Scan rate 0.1 V/s.

5) **XB-donor competition:** CVs of I-TTF and 50 equivalents of chloride in the presence of increasing concentrations of halogenated alcanes and arenes.

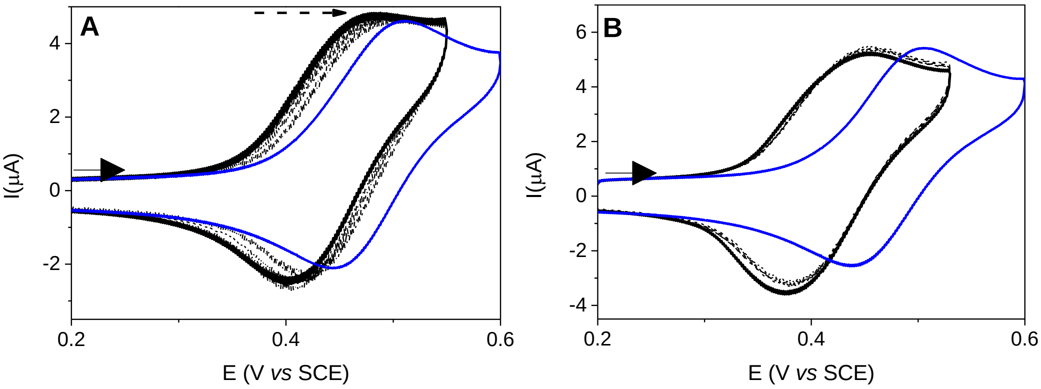

Figure S-10. CVs of **I-TTF** (0.25 mM) and 50 equiv. of **TBACl** on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of different concentrations of A) **iodoperfluoro-benzene** and B) **perfluoro-*n*-hexane** (black curves from left to right: 0, 0.25, 2.5, 5, 12.5, 12.5, 25 and 50 mM). CVs of **I-TTF** (0.25 mM) alone (blue curves). Scan rate 0.1 V s^{-1}.

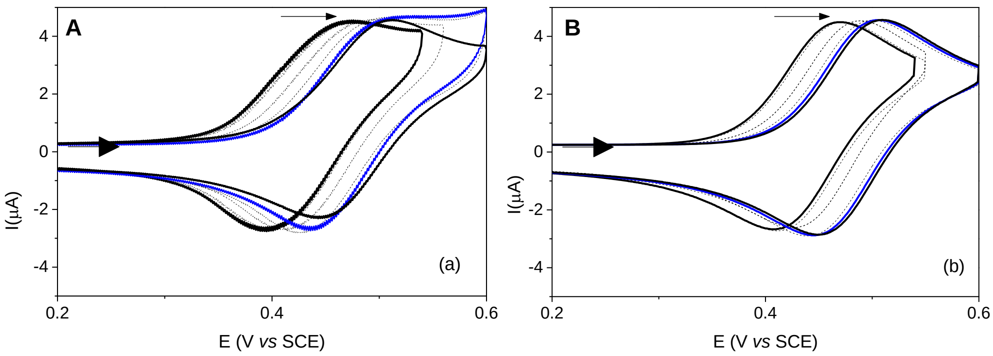

Figure S-11. Experimental (A) and simulated (B) CVs of **I-TTF** (0.25 mM) and **TBACl** (12.5 mM) on a glassy carbon electrode in a solution of 0.1 M TBAPF$_6$ in DMF in in the presence of increasing **iodoperfluoro-*n*-hexane** concentration (from left to right: c = 0, 0.25, 2.5, 12.5, 25 and 50 mM) at 293 K. CVs of **I-TTF** (0.25 mM) alone (blue curves). Scan rate 0.1 V s^{-1}.

6) **XB vs HB:** CVs of I-TTF and 50 equivalents of chloride in the presence of increasing concentrations of alcohols and water.

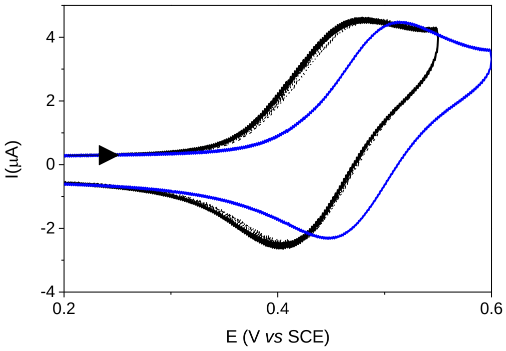

Figure S-12. CVs of **I-TTF** (0.25 mM) and **TBACl** (12.5 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of **ethanol** (from left to right: c = 0, 0.25, 2.5, 12.5, 25 and 50 mM). CVs of **I-TTF** (0.25 mM) alone (blue curve). Scan rate 0.1 V s^{-1}.

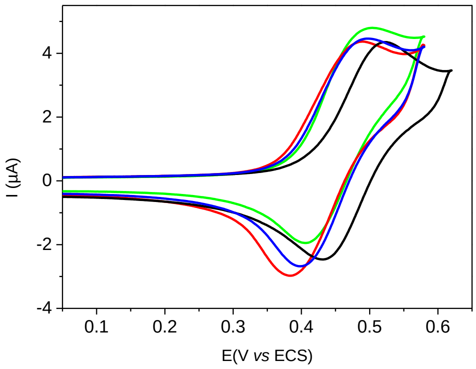

Figure S-13. CVs of **I-TTF** (0.25 mM, black curve) and **TBACl** (12.5 mM, red curve) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of **trifluoro-ethanol** (25 mM blue curve and 50 mM green curve). Scan rate 0.1 V s^{-1}.

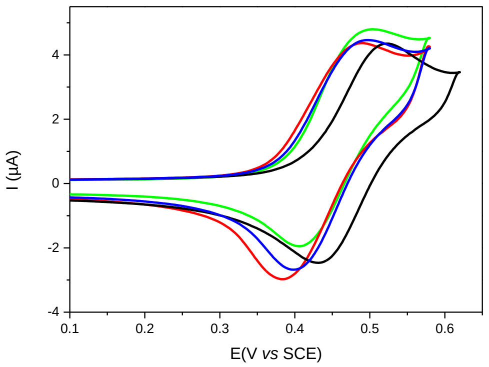

Figure S-14. CVs of **I-TTF** (0.25 mM, black curve) and **TBACl** (12.5 mM, red curve) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in DMF in the absence and in the presence of **water** 25 mM blue curve and 50 mM green curve). Scan rate 0.1 V s^{-1}.

7) CVs of TTF and I-TTF in the presence of increasing chloride concentrations in protic media.

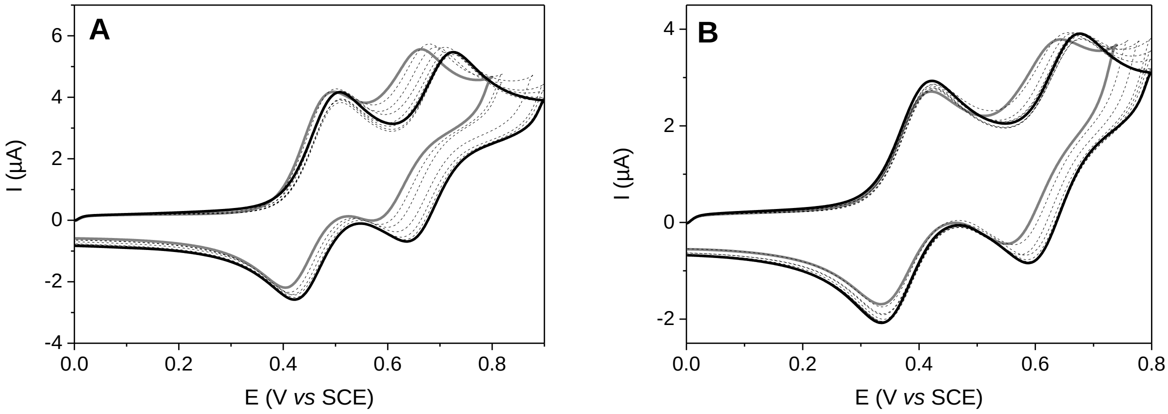

Figure S-15. CVs of 0.25 mM solutions containing **I-TTF** (A) and **TTF** (B) on a glassy carbon electrode in the absence and in the presence of increasing concentrations of **TBACl** (from right to left: 0, 2.5, 5, 12.5, 25 and 50 mM). Electrolyte: TBAPF$_6$ (0.1 M) in 5% H_2O/DMF. Scan rate 0.1 V s^{-1}.

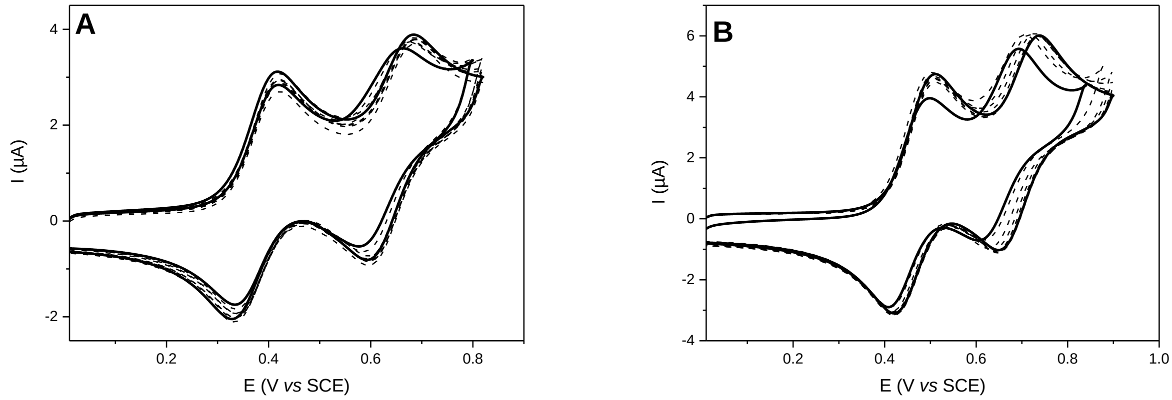

Figure S-16. CVs of 0.25 mM solutions containing **TTF** (a) and **I-TTF** (b) on a glassy carbon electrode in a solution in the absence and in the presence of increasing concentrations of **TBACl** (from right to left: 0, 0.25, 0.5, 1.25, 2.5, 5, 12.5, 25 and 50 mM). Electrolyte: TBAPF$_6$ (0.1 M) in **30% EtOH/DMF**. Scan rate 0.1 V s^{-1}.

8) 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.

A = I-TTF; LB = Cl$^-$

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:

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

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

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

Leading to

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

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

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

Subtraction of S3 from S2 gives the following equation:

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

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

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

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.

XB donor competition

A = I-TTF; LB = Cl^-; LA = I-C_6F_{13}

In the case of the XB donor competition, LB is involved either in the binding with A or with LA, and mass conservation writes as follows: $\left[LB\right]_0 = \left[LB\right]_{eq} + \left[A_{red}, LB\right]_{eq} + \left[A_{ox}, LB\right]_{eq} + \left[LA, LB\right]_{eq}$

Equation S4 still applies but the concentration of free B must also satisfy the mass action law corresponding to the equilibrium with LA, *i.e.*:

$$K_{LA,LB} = \frac{\left[LA, LB\right]_{eq}}{\left[LB\right]_{eq}\left[LA\right]_{eq}} \quad \text{(S6)}$$

Under initial conditions for which B is introduced in large excess ($\left[LB\right]_0 >> \left[A\right]_0$), the concentration $\left[LB\right]_{eq}$ is mainly set by its equilibrium with C (mass conservation becomes $\left[LB\right]_0 \approx \left[LB\right]_{eq} + \left[LA, LB\right]_{eq}$)

Equation S6 is therefore transformed into the following second order equation, in which $\left[CB\right]_{eq}$ is to be determined:

$$K_{LA,LB} = \frac{\left[LA, LB\right]_{eq}}{\left(\left[LB\right]_0 - \left[LA, LB\right]_{eq}\right)\left(\left[LA\right]_0 - \left[LA, LB\right]_{eq}\right)}$$

This equation admits two solutions, only one making physical sense, i.e. :

$$\left[LA, LB\right]_{eq} = \frac{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right) - \sqrt{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right)^2 - 4\left[LB\right]_0\left[LA\right]_0}}{2} \quad \text{(S7)}$$

It follows that:

$$\left[LB\right]_{eq} = \left[LB\right]_0 - \frac{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right) - \sqrt{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right)^2 - 4\left[LB\right]_0\left[LA\right]_0}}{2} \quad \text{(S8)}$$

Considering equation S8, equation S4 change into equation S9:

$$\Delta E' = E^{0'} - E^0_{A_{ox}/A_{red}} = -\frac{RT}{nF}\ln\frac{\left(1 + K_{ox}\left(\left[LB\right]_0 - \frac{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right) - \sqrt{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right)^2 - 4\left[LB\right]_0\left[LA\right]_0}}{2}\right)\right)}{\left(1 + K_{red}\left(\left[LB\right]_0 - \frac{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right) - \sqrt{\left(K_{LA,LB} + \left[LB\right]_0 + \left[LA\right]_0\right)^2 - 4\left[LB\right]_0\left[LA\right]_0}}{2}\right)\right)}$$

(S9)

It is worth noting that this equation is used to fit to the experimental titration in Figure 4 of the publication. In that case, for all experimental points LB is in excess when compared to A, all points may thus be considered for the fitting.

9) Simulation parameters for DigiElch

As stated earlier we assume that the system is under dynamic equilibrium. It means that only standard potential and equilibrium constants may be extracted from our results. DigiElch program imposes the definition of both forward and backward kinetic constants of a reversible chemical reaction. We postulate here that all forward constants are equal to 10e6, which is a sufficiently high value for the system to be under dynamic equilibrium. Real values could be higher but they are not determined here. Imposing k_f and K_{eq} leads to values of k_b by simple calculation. In the same vein, values of alpha and k_s needed to define the electrochemical reaction cannot be carefully extracted from our set of experiments. The ones reported here and used in the simulation are however sufficient to describe a reversible and fast electron transfer system.

a) I-TTF + TBACl:

Charge-Transfer Reaction	**E° [mV] vs SCE**	**α**	**k_s [cm/s]**
A_{ox} + e = A_{red}	0.470	0.5	0.31
A_{ox};Cl + e = A_{red},Cl	0.393 (calc.)	0.5	0.31
Chemical Reaction	**K_{eq}**	**k_f**	**k_b**
A_{red} + Cl = A_{red},Cl	K_{red} = 20	10^6	5×10^4
A_{ox} + Cl = A_{ox},Cl	K_{ox} = 400	10^6	2500

A_{red} = I-TTF; A_{ox} = I-TTF^{+1}

The experimental CV's shown in Figure 2A (same experiment as in Figure 1) have been used for the fit displayed in Fig. 2 B. The CV's of four experimental series (including the one derived from the experiment of Fig. 1 and 2A) have been used to establish the titration curve in Figure 3 and the corresponding error bars.

b) I-TTF + TBABr:

Charge-Transfer Reaction	**E° [mV] vs SCE**	**α**	**k_s [cm/s]**
A_{ox} + e = A_{red}	0.476	0.5	0.31
A_{ox},Br + e = A_{red},Br	0.394 (calc.)	0.5	0.31
Chemical Reaction	**K_{eq}**	**k_f**	**k_b**
A_{red} + Br = A_{red},Br	K_{red} = 5	10^6	2×10^5
A_{ox} + Br = A_{ox},Br	K_{ox} = 120	10^6	8333

A_{red} = I-TTF; A_{ox} = I-TTF^{+1}

Cf Fig. S-08 and CV's of four experimental series.

c) I-TTF + 50eq TBACl + iodoperfluoro-*n*-hexane:

Charge-Transfer Reaction	**E° [mV] vs SCE**	**α**	**k_s [cm/s]**
A_{ox} + e = A_{red}	0.479	0.5	0.31
A_{ox};Cl + e = A_{red},Cl	0.402 (calc.)	0.5	0.31
Chemical Reaction	**K_{eq}**	**k_f**	**k_b**
A_{red} + Cl = A_{red},Cl	K_{red} = 20	10^6	5×10^4
A_{ox} + Cl = A_{ox},Cl	K_{ox} = 400	10^6	2500
Cl + I-R_f = Cl,I-R_f	K_a = 650	10^6	1539

A_{red} = I-TTF; A_{ox} = I-TTF^{+1}; I-R_f = I-C_6F_{13}

Cf Fig. S-11 and CV’s of four experimental series.