

ELECTROCHEMICAL ACTIVATION OF A TETRATHIAFULVALENE BASED HALOGEN BOND DONOR FOR ANION RECOGNITION IN POLAR SOLVENTS.

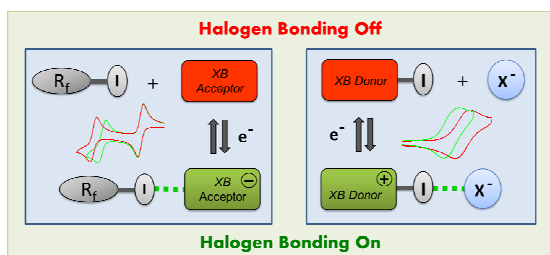


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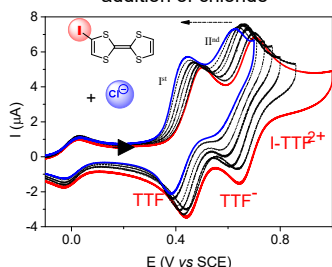
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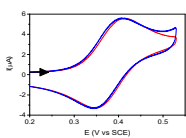
Abstract: The importance of halogen bonding (XB) for controlling self-assembly in the solid state has been demonstrated in many applications in crystal engineering and materials science.[1,2] Concerning XB in solution so far only few examples have been described in literature. A recent review [3] summarizes solution-phase thermodynamic data for XB interactions and highlights emerging applications in molecular recognition, medicinal chemistry and catalysis. Up to day there are almost no electrochemical techniques among the applied methods reported in literature.[4,5] In a recent paper we have demonstrated the electrochemical XB switching in homogeneous solution, validating that the XB acceptor strength of *p*-quinones can be controlled by the modulation of their redox state.[6] Here we extend the concept further to redox switchable XB donors (iodo-tetrathiafulvalene) for anion recognition with the aim of quantifying the influence of halogen bonding in polar systems.[7] The electrochemical probing and controlling of XB will help to better understand the supramolecular properties and reactivity of complex systems such as liquid electrolytes involving multiple competing interactions.

XB donor: I-TTF in DMF

Iodo-tetrathiafulvalene (I-TTF): addition of chloride

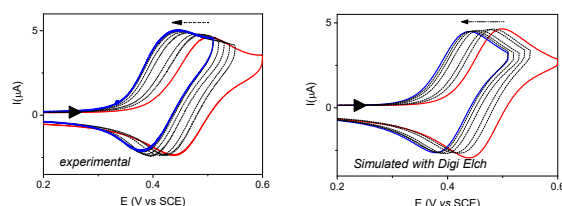


CVs of I-TTF (0.25 mM) and Os(bipy)₂Cl₂ (0.1 mM) on a glassy carbon electrode in a solution of TBAPF₆ (0.1 M) in DMF in the absence and in the presence of increasing concentrations of TBACl (from right to left: 0, 0.15, 1.5, 5, 10, 25 and 50 mM). Scan rate 0.1 V s⁻¹.



Blank experiment: CVs of TTF (0.25 mM) on a glassy carbon electrode in a solution of TBAPF₆ (0.1 M) in DMF in the absence (red) and in the presence of 25 mM TBACl (blue).

First wave (I-TTF/I-TTF⁺)

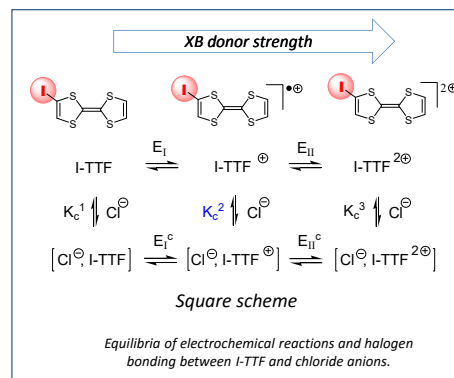


Anion recognition

	Cl ⁻	Br ⁻	OTf ⁻	ClO ₄ ⁻	H ₂ O
TTF	-7	-1	-	-	-1
I-TTF-I	-53	-38	-2	2	-2

Cyclic voltammetry data of TTF and I-TTF derivatives (0.25 mM) in the absence and in the presence of 100 equiv. of TBACl

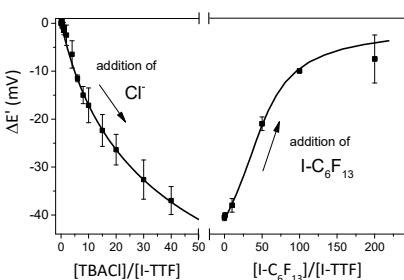
$$\Delta E' = E^{o'} - E^{o'}_{\text{free}} = -\frac{RT}{nF} \ln \left(\frac{1 + K_{\text{ox}}[LB]_0}{1 + K_{\text{red}}[LB]_0} \right)$$



Affinity constants

	[I-TTF ⁺ , Cl ⁻]	[I-TTF ²⁺ , Cl ⁻]	[I-TTF ⁺ , Br ⁻]
K _{ox}	425±14	6730±900	131±9

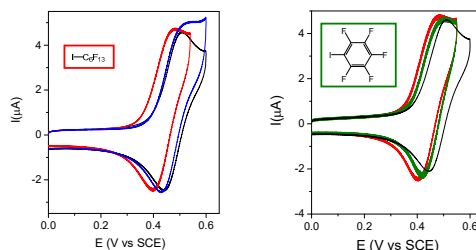
XB donor: Competition



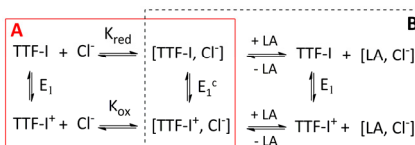
Dependence of the potential shift ($\Delta E'$) of I-TTF^{o1+} on the increasing concentrations of TBACl (left) and then of I-C₆F₁₃ (right) to a I-TTF (0.25 mM) solution of TBAPF₆ (0.1 M) in DMF at 293 K. The error bars indicated are standard deviations and each point is the average of four measurements.

$\Delta E'_{\text{comp}}$	I-C ₆ F ₁₃	I-C ₆ F ₅	C ₆ F ₁₄	EtOH	CF ₃ CH ₂ OH	H ₂ O
	-53	-38	-2	2	-2	7

XB and HB donor competition: Measured potential back shifts $\Delta E'_{\text{comp}}$ (in mV) of I-TTF^{o1+} upon the addition of various XB and HB donors (25 mM, 100 equiv.) to an electrolyte solution containing I-TTF (0.25 mM, 1 equiv.) and TBACl (12.5 mM, 50 equiv.) with $\Delta E'_{\text{comp}} = E^{o'} - E^{o'}_{\text{free}}$.

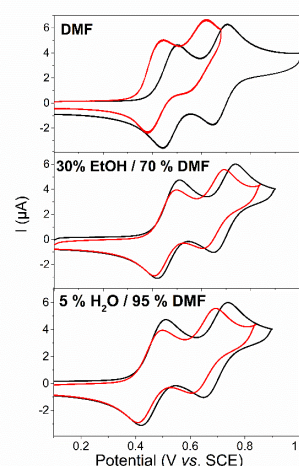


CVs of I-TTF (0.25 mM) on a glassy carbon electrode in a solution of TBAPF₆ (0.1 M) in DMF in the absence (black curve) and in the presence of 50 equiv of TBACl (red curve) and in the presence of 200 equiv of perfluorohexyl iodide (blue curve) or in the presence of 200 equiv of Iodopentafluorobenzene (green curve). Scan rate 0.1 V s⁻¹.



Square scheme: A) electrochemical oxidation of I-TTF in the presence of chloride ions; B) competition between the electrophilic I-TTF species and other electrochemically inactive XB- or HB-donors (LA).

XB vs HB



CV of 0.25 mM solutions containing I-TTF on a glassy carbon electrode in a solution in the absence (black curve) and in the presence (red curve) of TBACl (50 mM). Electrolyte: TBAPF₆ (0.1 M) in 1) DMF, 2) 30% EtOH / 70% DMF and 3) 5% H₂O / 95% DMF. Scan rate 0.1 V s⁻¹.

Conclusions

Proof of Principle: Concept of electrochemical XB switching in homogeneous solution

- Electrochemical techniques can monitor the dynamic XB interactions in solution
- Operable electrochemically active XB donors and XB acceptors
- XB prevailed among the numerous competing interactions
- Reversible XB acceptor competition was demonstrated

Beyond potential applications in molecular recognition (sensing devices, molecular redox switches), these results strongly encourage the use of electrochemistry as an economical and precisely controllable tool for the investigation of the impact of XB on chemical reactivity in solution.

Experimental conditions:

- Electrolyte: 0.1M TBAPF₆ in acetonitrile or DMF
- Glassy carbon working electrode, Pt counter electrode
- Calomel reference electrode (sat. KCl)
- Thermostated at 293K and 298 K
- Anhydrous conditions under argon atm.
- Scan speed: 0.1 V/s

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 [2] *Teir. Lett.* **2006**, 47, 1249-1252; *Chem. Commun.* **2008**, 5981-5983; *CrystEngComm* **2014**, 16, 10380-1084.
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