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Claire Fave and Bernd Schöllhorn

Abstract

In the past, noncovalent interactions have been extensively studied by electrochemical methods. In this context, halogen bonding (XB) has been a long-time overlooked item in the toolbox of supramolecular chemistry. The article is treating electrochemical activation of XB in solution and at the solid–liquid interface. Key principles and recent work on the use of electrochemistry as a tool for detecting and controlling XB are reported. Different types of redox-switching XB are identified in the context of molecular recognition and detection. First evidence for XB promoted electron transfer reactions involving the activation of covalent bonds represents a completely new and emerging domain, ripe for exploration.

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Keywords

Halogen bonding, Noncovalent interactions, Redox switching, Molecular recognition, Molecular electrochemistry, Anion detection.

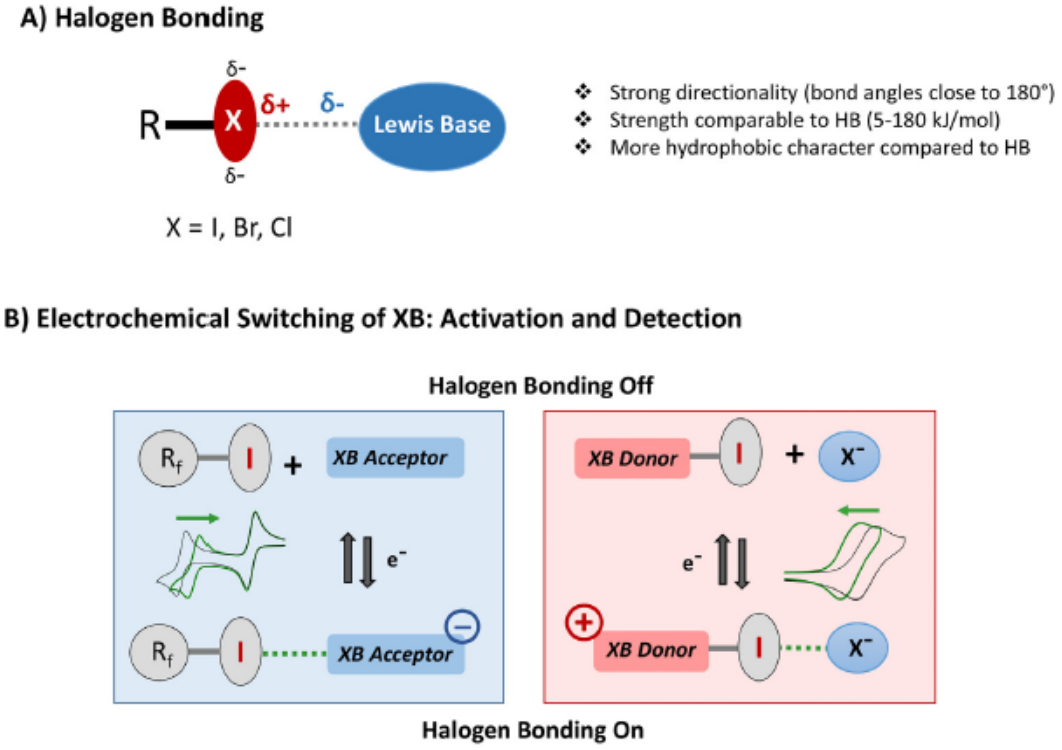
Introduction

Halogen bonding (XB), an attractive interaction between a halogen atom acting as an electrophilic species (called XB donor) and a Lewis base (called XB acceptor) (Figure 1), is nowadays fully recognized by the scientific community as an important noncovalent interaction and an interesting tool for applications either in crystal engineering or materials science but also for (bio)supramolecular chemistry in solution and at the liquid—solid interface. [1,2] In 2013, the term 'halogen bonding' was officially defined by International union of pure and applied chemistry (IUPAC) [3], stressing its complementarity with hydrogen bonding (HB), and is well documented in the solid state [4—9]. This is not the case for systems in homogeneous solution or at the electrode surface despite the interest of emerging applications in molecular recognition, anion sensing and transport, medicinal chemistry, and organocatalysis. [1,2], [10—12] Most published studies of XB in solution rely on spectroscopic techniques such as ultraviolet-visible (UV-vis), infrared (IR), Raman, and nuclear magnetic resonance (NMR) spectroscopy [10]. In the seventies, dielectric polarization measurements were conducted for the characterization of organohalides in organic solvents allowing for a distinction of the observed XB from other noncovalent interactions [13]. Surprisingly, and despite their low cost and relatively simple implementation, electrochemical methods remained absent until 2014 [14]. The challenge to explore the electrochemical activation of XB for molecular recognition in solution and in surface confined systems is, in our view, a new and attractive topic, and some questions have only recently been addressed. Tuning the strength of a redox active XB donor via a reversible electrochemical reaction should change its affinity toward XB acceptors and *vice versa* (Figures 1 and 3). Such type of redox switching is of great interest because the electrochemical probing and controlling of XB will help to better understand the corresponding supramolecular properties and reactivity in complex systems such as liquid electrolytes involving multiple competing noncovalent interactions. The present article reports on the most recent studies in this field.

Redox switching of XB acceptors: reductive XB activation

In aprotic solvents, quinones can be reversibly reduced in two sequential one-electron transfer (ET) steps [15,16] generating the corresponding anion radical (semiquinone radical) and dianion, with a consequently significant increase of the respective Lewis base strength. The influence of HB donors and Lewis acids on the electrochemical behavior of quinones has been extensively studied in the past [17—21]. The observed shifts of the quinone reduction potentials were attributed to the stabilization of the corresponding anions because of their association with HB donors (in the absence of proton transfer reactions) and Lewis acids (eg. alkali and earth-alkali metal cations) [22,23]. An analogous behavior has been demonstrated recently for *p*-quinones such as tetrachloroquinone (TCQ, Figure 2) or dichlorodicyanoquinone (DDQ, Figure 2), validating for the first time the concept that the strength of XB can

Figure 1



a) Schematic representation of halogen bonding. **(b)** Electrochemical switching of redox-active XB acceptors and XB donors in the presence of iodo-perfluorocarbons and halide anions, respectively. XB, halogen bonding; HB, hydrogen bonding.

be controlled by the redox switching of the Lewis basic XB acceptor (Figures 2 and 3) [14]. Cyclic voltammetry (CV) was thus identified as an analytical technique well adapted to probe and control XB interactions in liquid electrolytes. Iodo-perfluorocarbons (I-R_f) induced high standard potential shifts exclusively of the second TCQ reduction wave (corresponding to the TCQ dianion formation) of up to 140 mV in polar electrolytes, such as acetonitrile containing 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte salt. A stoichiometry of 1:1 was deduced from Job plots, and binding enhancements (ratio of the equilibrium constants K_3/K_2 of the respective XB complexes, Figure 3) of up to 10^3 could be determined by simulation and fitting of the voltammograms to the experimental results. Competition experiments involving two different Lewis bases (dianionic quinone and chloride) were conducted evidencing reversible equilibra between the formed XB complexes and allowing for the indirect determination of affinity constants between the involved nonelectroactive species (halide anions and I-R_f).

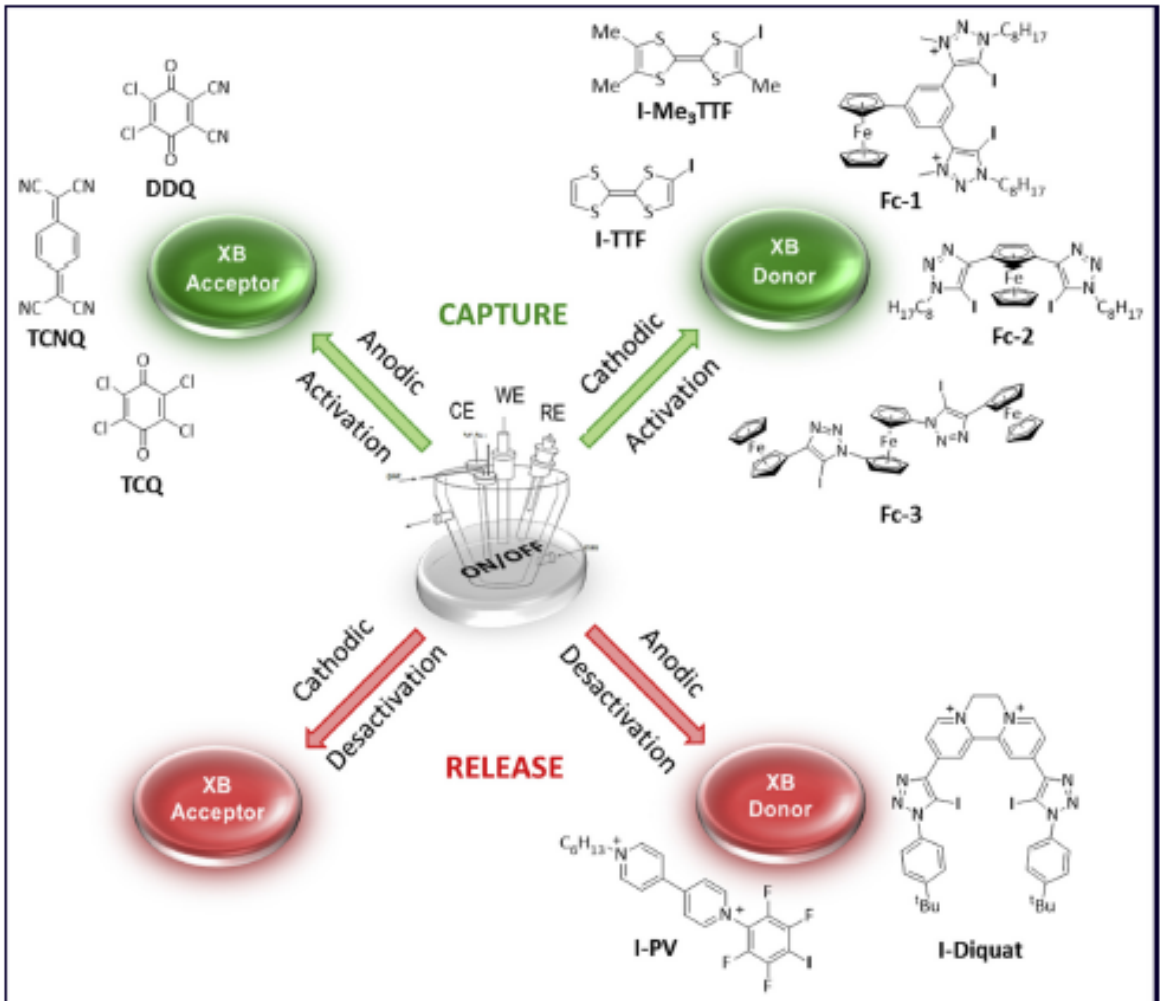
Redox switching of XB donors

Two different ways to electrochemically switch XB donors have been described in recent literature (Figure 2). In the first case, the donor strength is increased upon oxidation of a neutral or cationic redox center, thus activating XB. In a second case, cationic XB donors are reduced involving XB deactivation. Both switching modes have been applied to selective anion detection, an important issue in analytical chemistry [24,25].

Oxidative XB activation

Iodinated tetrathiafulvalene (TTF) and ferrocene (Fc) derivatives have been used as redox moieties for XB activation upon electrochemical oxidation. In general, the XB-donor strength of organohalides increases with the size and polarizability of the halogen atom (I > Br >> Cl >> F) and the presence of electron withdrawing groups. Iodo-alkynes and iodo-perfluorocarbons are known to be particularly strong XB donors. Besides these neutral compounds, more recently, it has been proven by NMR spectroscopy that cationic halogenated compounds (halo-imidazolium and triazolium derivatives) [26,27] also possess strong XB-donor properties. The use of positively charged receptors that benefit from a Coulombic attraction to anions is recognized as a promising general strategy for anion recognition. Electrochemical oxidation represents a well-adapted tool for conveniently generating positive charges in molecular systems under ambient conditions. Since 1995, electrocrystallization was used to prepare various solid-state donor-acceptor complexes based on

Figure 2

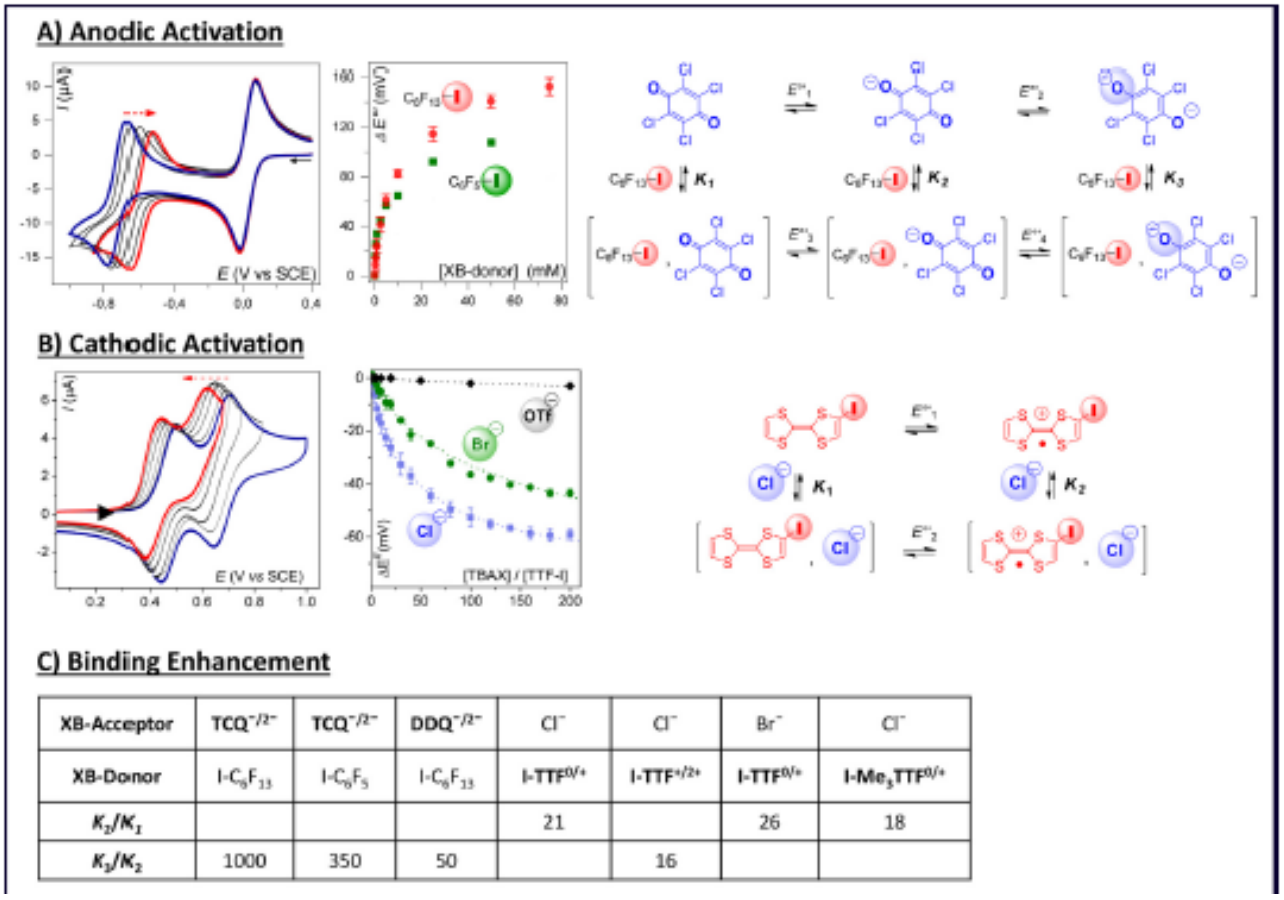


Classification of the redox probes used for electrochemical XB activation/deactivation. XB, halogen bonding; TCQ, tetrachloroquinone; TTF, tetrathiafulvalene; Fc, ferrocene; DDQ, dichlorodicyanoquinone CE, counter electrode; WE, working electrode; RE, reference electrode; TCNQ, tetracyanoquinone; PV, phenylviologen.

charge-assisted XB involving iodo-tetrathiafulvalene (I-TTF) derivatives [28]. Recently, the XB-donor strength of iodinated TTF derivatives (I-TTF and IMe_3-TTF, Figures 2 and 3) has been electrochemically modulated and controlled in DMF solution [29,30]. A significant binding enhancement to Cl^- upon oxidation of I-TTF *('XB OFF')* to $I\text{-}TTF^+$ *('XB ON')* was observed and attributed to the strong inductive effect of the generated positive charge polarizing the C-I bond. The significant contribution of XB to the observed stabilization of $I\text{-}TTF^+$ was proven, and other noncovalent interactions such as HB or π-anion interactions could be excluded. First spectroelectrochemical measurements in the Uv-vis range along with Time-dependent density functional theory (TD-DFT) calculations confirmed XB formation upon generation of the cation radical. Depending on the nature of the anion (Cl^-, Br^-, TfO^-), oxidation potential shift values in the range of 0−50 mV have been observed and affinity constants of up to 425 M^{-1} could be determined for the XB adducts, corresponding to a binding force of around −12 to −15 kJ mol^{-1}. Moreover, competition between $I\text{-}TTF^{1+}$ and other XB donors (iodo-perfluorocarbons) as well as HB donors (alcohols, water) for the recognition of Cl^- allowed for the quantitative comparison of the relative donor strength. This competitive approach is an interesting electroanalytical tool for probing noncovalent XB and HB interactions in solution. Thanks to the second oxidation step affording, the more electrophilic dication $I\text{-}TTF^{2+}$, it was possible to detect XB even in protic media (water/DMF and ethanol/DMF mixtures).

The redox properties of Fc have been exploited in a similar way for the electrochemical detection of anions

Figure 3



XB-Acceptor	$TCQ^{-/2-}$	$TCQ^{-/2-}$	$DDQ^{-/2-}$	Cl^-	Cl^-	Br^-	Cl^-
XB-Donor	$I\text{-}C_6F_{13}$	$I\text{-}C_6F_5$	$I\text{-}C_6F_{13}$	$I\text{-}TTF^{0/+}$	$I\text{-}TTF^{+/2+}$	$I\text{-}TTF^{0/+}$	$I\text{-}Me_3TTF^{0/+}$
K_2/K_1				21		26	18
K_3/K_2	1000	350	50		16		

CVs were recorded on a glassy carbon electrode in a solution of 0.1 M $TBAPF_6$ in acetonitrile at a scan rate 0.1 V s^{-1}. **(a)** CVs of TCQ (0.5 mM) in the presence of IC_6F_{13} (0, 0.5, 5, 25 and 50 mM); titration curves; corresponding Square Scheme. **(b)** CVs of I-TTF (0.25 mM) in the presence of chloride (0, 0.25, 1, 2.5, 5, 10, 25, and 50 mM); titration curves; corresponding Square Scheme. **(c)** Table of affinity constant ratios (K_{i+1}/K_i) for XB-donor/XB-acceptor couples. XB, halogen bonding; CV, cyclic voltammetry; TCQ, tetrachloroquinone; TTF, tetrathiafulvalene; $TBAPF_6$, tetrabutylammonium hexafluorophosphate; DDQ, dichlorodicyanoquinone; SCE, saturated calomel electrode; TBAX, tetrabutylammonium X (X= anion).

in solution. Beer and colleagues have prepared several Fc derivatives bearing two iodo-triazoles or cationic iodo-triazolium units (Figure 2). Some of these bidentate XB donors showed interesting anion receptor properties, suggesting a significant contribution of XB. In CV and square wave voltammetry (SWV) measurements, standard potential shifts of the ferrocenyl probes were observed in the presence of various anions, in particular halides (Fc-1, Figure 2) [31] and azide (Fc-2, Figure 2) [32]. In all cases, the respective affinity constants (K_a) of the iron (II) (Fc) containing XB donors could be determined by ^1H NMR which was not possible for the activated paramagnetic iron (III) complexes (ferricinium). Thus, electrochemical techniques have not been used yet to quantify, via titration experiments and fitting to an appropriate model, the affinity constants for the activated receptors. However, when comparing the potential shift values of analogs XB (iodinated triazoliums) and HB receptors, XB proved to be equivalent or even stronger in the investigated liquid electrolytes. A tri-ferrocenyl-bis(iodotriazole) (Fc-3, Figure 2), conceived by the group of Molina, showed two reversible oxidation steps involving a two-electron and a one-electron transfer and proved to be remarkably selective toward oxo-anions, affecting either the oxidation potential of the second ET (sulfate, acetate) or of both (dihydrogenophosphate and hydrogenopyrophosphate), whereas halides and nitrate showed no effect [33]. Electrochemical activation of Fc-based XB donors could also be performed in up to 10% of water-containing solvent mixtures [31]. Recently, a tetraiodinated monocationic [2]-Rotaxane bearing a ferrocenyl moiety as an interlocked host molecule showed weak perturbation of the voltammetric signal (in a acetone/acetonitrile/water mixture) but still selective recognition of bromide versus chloride or linear thiocyanate [34].

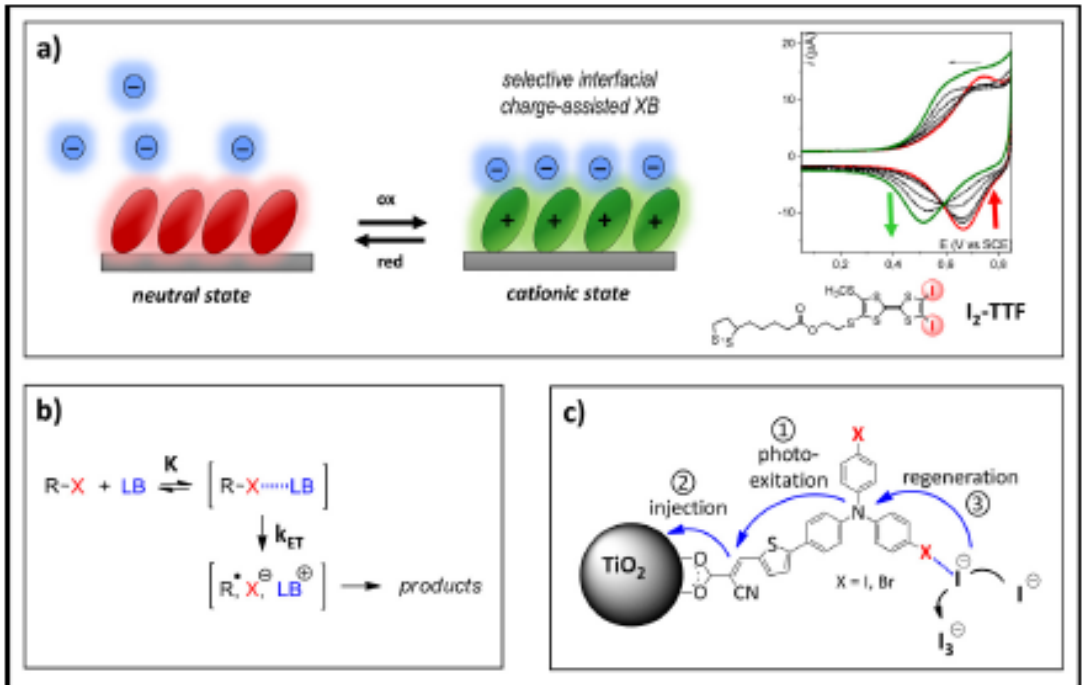
Reductive XB deactivation

N,N′-disubstituted viologens constitute an important class of redox mediators widely applied in catalysis and the elaboration of supramolecular complexes [24]. Iodinated dicationic viologen derivatives were used as potent XB donors in the thermodynamically stable redox state. Reduction to the cation radical or the neutral state proved to significantly decrease the respective XB-donor strength. Based on this principle, reversible reduction of a diquat bis-iodotriazole derivative (I-Diquat, Figure 2) was used for the electrochemical sensing of halide anions [35]. A comparative study of different noncovalent interactions between cationic N-phenylviologens and halides was performed (I-PV, Figure 2) [36]. XB contributed to a stabilization of the initially dicationic redox state of the iodo-tetrafluorophenyl viologen derivative in the presence of chloride and bromide, although the role of other competing noncovalent interactions (HB, ion pairing and π—anion interactions) is not fully understood. CV allowed the quantification of the overall affinity of halide anions toward N-phenylviologens depending on their redox state. Local probing of the various interactions was possible, thanks to NMR spectroscopy of the diamagnetic phenyl viologen dications.

Interfacial redox switching of halogen bonding

Noncovalent interactions play an important role in interfacial supramolecular electrochemistry [37]. Recently, the concept of electrochemical XB activation has been transferred onto the electrode surface via the immobilization of diiodinated TTF dithiolane derivatives in form of self-assembled monolayers (SAMs) on gold surface. Thus electrochemically driven interfacial charge-assisted halogen bonding between redox-active SAMs and halide anions has been explored for the first time [38]. The XB-donor properties of the surface adsorbates (I_2-TTF, Figure 4A) were activated by electrochemical switching their oxidation state. A particularly high and selective binding enhancement of 565 (ratio of affinity constants for the two TTF oxidation states) upon oxidation of the SAM toward chloride anions was estimated from electrochemical simulation, suggesting a significant surface chelate effect of the assembled 2D material. Strong evidence is provided for a significant contribution of XB as the dominant noncovalent interaction in the investigated system. A high sensitivity (limit of detection = $6 \cdot 10^{-6}$ M) was determined for chloride detection which is a promising finding considering a potential application of the

Figure 4



Interfacial redox switching and XB promoted electron transfer. **(a)** Scheme of selective interfacial anion detection on a SAM (left) and cyclic voltammograms of the electroactive I_2-TTF containing SAM in the presence of increasing chloride concentrations (right). **(b)** Proposed mechanism for XB assisted EC between halocarbons (R–X) and a redox-active Lewis Base (LB). **(c)** Postulated mechanism of XB promoted regeneration of a photo-oxidized halogenated dye in a solar cell. SAM, self-assembled monolayer; XB, halogen bonding; TTF, tetrathiafulvalene; EC, electrochemical-chemical.

concept for future development of novel selective anion sensors, capture/release systems, or molecular electronics.

XB promoted ET reactions

The group of Rosokha described halogen bond-assisted ET reactions of aliphatic bromo-substituted electrophiles [39,40]. The isolation of halogen-bonded prereactive complexes between aliphatic organobromides and Lewis bases (phenylene diamine and iodide) at low temperature and the kinetics of a subsequent ET are consistent with an inner-sphere mechanism involving strongly coupled redox centers (Figure 4B). Electronic coupling of XB donor and XB acceptor within the prereactive complex was suggested. Up to date, we are aware of only one example exploiting this potentiality for the regeneration of a photo-oxidized halogenated dye via iodide oxidation, thus impacting the open-circuit voltage of a solar cell (Figure 4C) [41]. Parlane et al [42] used X-ray absorption spectroscopy to directly detect interfacial XB between a homologous soluble halide species (Cl^-) and the activated dye cation demonstrating that these interactions occur after electron injection into TiO_2.

Conclusions and perspectives

Most of the work on the electrochemical investigation of XB has been published during the past 5 years, and many potentialities in this domain are still to be explored. However, the fundamental concept of electrochemical XB activation/deactivation for molecular recognition and detection is now well established. Several reversible redox probes have been used, covering the activation of XB donors (TTF, Fc) and XB acceptors (quinones) as well as the deactivation of XB donors (viologen cations). Examples of electrochemical deactivation of XB acceptors for XB are not described yet. The possibility of reversible switching between three different redox states ($0/\pm1/\pm2$) represents a decisive advantage for detecting a wide panel of analytes. It is noteworthy that besides some first conclusive results, there is still an important lack of spectroelectrochemical measurements.

Recognition of neutral Lewis bases [43], instead of anions, involving redox-active XB donors would also be an important and challenging issue. It is likely that the design of tailored oligo-dentate receptors will be required eventually benefitting from the cooperative interplay of multiple complementary noncovalent interactions. Another issue, already approached in some of the above cited examples, is the attempt to promote the high potential of XB to complement HB in the selective recognition and sensing of biologically and industrially relevant anions under aqueous conditions. Besides selective detection, also the specific capture/release of anions should be considered for biomedical applications in particular. The principle of redox switching of XB has been successfully transferred from solution onto an electrode surface. This approach opens the way for the development of new electrochemical sensors or sponge captors for depollution applications.

Finally, we believe that XB promoted ET reactions involving the activation of covalent bonds represents a completely new domain for exploration. Evidence for prereactive XB complexes in the dissociative reduction of C-X bonds involving an inner-sphere ET step provides a new perspective on electrochemical reduction of organic halides in general [44]. At the same time, it seems to be a pivotal question paving the way, not only to a better mechanistic understanding of other halogen involving electrochemical-chemical (EC) or electrochemical-chemical-electrochemical (ECE) [45] mechanisms but also helping to identify new electrochemically assisted catalytic reactions. In the first encouraging example concerning solar cells, it has been shown challenging but possible to experimentally prove how weak XB interactions can affect interfacial ET reactions.

In conclusion, we strongly believe that XB should be considered as a powerful tool in molecular electrochemistry at a similar level as complementary HB. The stronger directionality of XB should be an important advantage for the conception of supramolecular systems and property prediction. Furthermore, future work in this domain should be accompanied more often by molecular modeling as a computational tool for confirming, optimizing and predicting structure/property relationships.

Conflict of interest

Nothing declared.

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