

Redox Controlled Chalcogen Bonding for Switchable Anion Recognition and Sensing

Robert Hein, Andrew Docker, Jason J. Davis,* Paul D. Beer*

Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, U. K.

*jason.davis@chem.ox.ac.uk, paul.beer@chem.ox.ac.uk

Abstract

Inspired by the success of its related sigma-hole congener halogen bonding (XB), chalcogen bonding (ChB) is emerging as a powerful non-covalent interaction with a plethora of applications in supramolecular chemistry and beyond. In spite of its increasing importance, the judicious modulation of ChB donor strength remains a formidable challenge. Herein, we present, for the first time, the reversible and large-scale modulation of ChB potency by electrochemical redox control. This is exemplified by both the switching-ON of anion recognition via ChB oxidative activation of a novel bis(ferrocenyltellurotriazole) anion host and switching-OFF reductive ChB deactivation of anion binding potency with a telluroviologen receptor. The direct linking of the redox-active centre and ChB receptor donor sites enables strong coupling, which is reflected by up to a remarkable 3 orders of magnitude modulation of anion binding strength. This is demonstrated through large voltammetric perturbations of the respective receptor ferrocene and viologen redox couples, enabling, for the first time, ChB-mediated electrochemical anion sensing. The sensors not only display significant anion-binding induced electrochemical responses in competitive aqueous-organic solvent systems but can compete with, or even outperform similar, highly potent XB and HB sensors. These observations serve to highlight a unique (redox) tuneability of ChB and pave the way for further exploration of the reversible (redox) modulation of ChB in a wide range of applications including anion sensors as well as molecular switches and machines.

Introduction

Sigma-hole interactions, in particular halogen bonding (XB) and more recently chalcogen bonding (ChB), defined as the attractive interaction between Lewis bases and an electron deficient region of a group 17 and group 16 atom respectively, have emerged as highly potent and versatile non-covalent interactions.¹ Their utility is becoming well-established across diverse fields including crystal engineering,²⁻³ materials chemistry,⁴⁻⁹ organocatalysis¹⁰⁻¹⁵ and anion supramolecular chemistry.¹⁶⁻²⁰ The latter includes anion recognition,²¹⁻²⁴ transport²⁵⁻²⁹ and sensing,^{28, 30-39} wherein a notably enhanced performance of sigma-hole based anion receptors, in particular XB hosts, in comparison to their traditional hydrogen bonding (HB) analogues is well-documented. This includes enhanced anion binding affinities, selectivities, transport efficacies and sensory performances, attributable to the more stringent linearity requirements of the electron deficient

XB/ChB donor atom—anion interactions as well as their unique electronic properties and tuneability.⁴⁰⁻⁴³

Indeed, recent reports have demonstrated that the ChB donor potency is highly sensitive to the local electronic environment, and can be modulated through either covalent substituent variation^{24, 26, 43-44} or heteroditopic ion-pair recognition.⁴⁵ In the context of anion recognition, this tuneable ChB donor potency provides an attractive strategy to generate stimuli responsive host systems. For example, Gabbai and co-workers have recently reported the notable increased potency of Te(IV) cations as ChB anion receptors and transporters in comparison to their parent, neutral Te(II) analogues (Figure 1).²⁶ This was achieved by the oxidative methylation of diaryltellurides, a powerful, but irreversible, means of tuning the ChB donor properties.

Conceivably, control of local ChB donor potency could also be achieved by coupling of a chalcogen centre to a redox-active moiety, wherein oxidation or reduction reversibly switches-ON or -OFF chalcogen centred electrophilicity.

While thus far unprecedented for ChB, the reversible (electrochemical) redox control over XB donor strength is already established, in particular with XB ferrocene and TTF receptor based systems.^{32-33, 46-50} This is saliently reflected in an associated cathodic perturbation of the redox potential of the electroactive XB receptor in the presence of Lewis bases, thereby presenting a simple, yet powerful, means of electrochemical anion detection, as increasingly exploited in advanced sensors.^{32, 36-37, 39}

Given the compelling evidence for the tuneable nature of ChB interactions, it was envisaged that the construction of redox responsive ChB receptor systems would facilitate a potentially powerful means to electrochemically modulate sigma-hole donor potency with high degrees of ON-OFF state fidelity. To explore this concept, we investigated two redox-active chalcogen-containing anion receptor motifs, namely chalcogenoviologens and a bis-ferrocenyltellurotriazole, wherein the ChB donor potency can, by redox-control, be reversibly switched-OFF or -ON, respectively (Figure 1). In the case of the natively dicationic chalcogenoviologens we demonstrate a complete deactivation of ChB sigma-hole donor strength and associated anion binding affinity upon electrochemical

reduction. Conversely an activation of anion binding potency of up to 3-orders of magnitude is achieved by oxidation of the neutral ChB bis(ferrocenyltellurotriazole) host system. Not only does this provide a powerful and unprecedented means of reversible control over ChB donor strength, but also enables highly sensitive voltammetric anion detection. This work thereby constitutes a very rare example of ChB-mediated sensing,^{28, 38} and the first exploitation of ChB in electrochemical sensing.

Results and Discussion

Synthesis of Redox-Active ChB Anion Receptors

The synthesis of the chalcogenoviologens **1.Te²⁺** and **1.Se²⁺** was achieved via reaction of the chalcogen functionalised bipyridine precursors⁵¹ with benzyl bromide, followed by salt metathesis with sodium (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) (NaBAR^F₄), to afford the target receptors **1.Te²⁺** and **1.Se²⁺**, in yields of 61% and 57% respectively (Scheme 1).

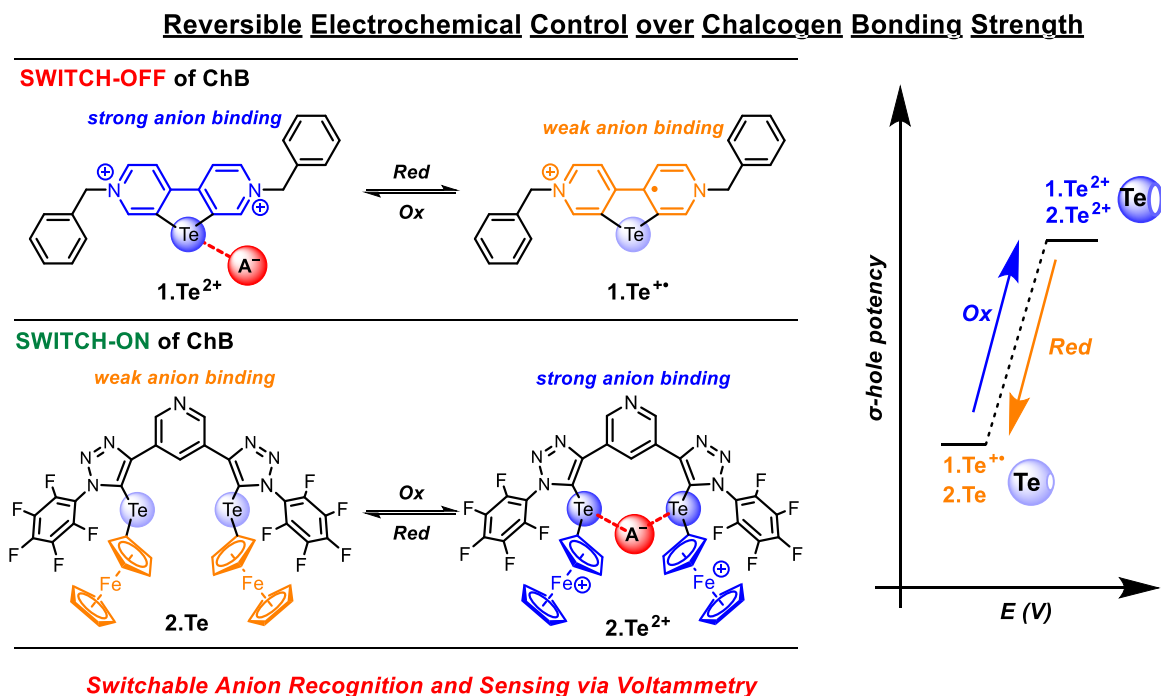
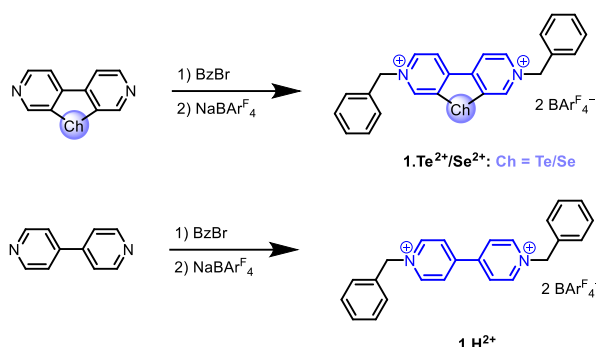


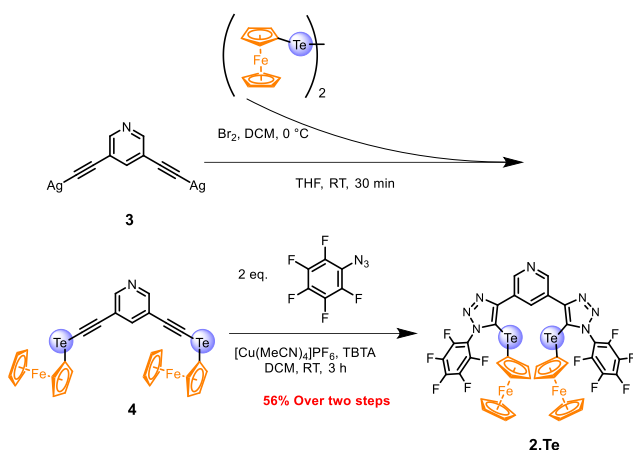
Figure 1. Illustrative overview of the redox control of chalcogen bonding (ChB) potency. We demonstrate both reversible electrochemical reductive deactivation of ChB in telluroviologens as well as oxidative activation of ChB in ferrocenyltellurotriazole receptors.

In addition, for the purposes of delineating the role of non-specific electrostatic interactions in the anion sensing behaviour of the viologen systems, an unfunctionalised derivative **1.H²⁺**, was also prepared.



Scheme 1. Synthetic route for dicationic redox-active chalcogenoviologen hosts **1.Te²⁺** and **1.Se²⁺** as well as the control proto-congener **1.H²⁺**.

The novel ChB bis(ferrocene-telluro-triazole) receptor **2.Te**, was constructed by *direct* appendage of ferrocene (Fc) redox reporters onto an established bis(tellurotriazole) anion receptive scaffold (Scheme 2).^{25, 43, 45}



Scheme 2. Synthetic route for neutral redox-active pyridine bis(ferrocenyltellurotriazole) receptor **2.Te**.

This was achieved by reaction of pyridine bis(silveracetylide)⁴³ **3** with *in situ* generated ferrocenyl tellurobromide, obtained from reaction of diferrocenyl ditelluride⁵² with bromine, affording 3,5-pyridine bis(ferrocenylalkyne) **4**. This compound was immediately subjected to copper(I)-catalysed azide-alkyne cycloaddition (CuAAC)²² with two equivalents of azido pentafluorobenzene⁵³ affording the title compound **2.Te** in 54% yield over two steps. Further details and full compound characterization of all receptors by ¹H and ¹³C NMR as well as ESI-MS can be found in the SI.

¹H NMR and UV-vis Anion Binding Studies

The ChB donor halide anion binding capabilities of the natively dicationic viologen receptors **1.Te²⁺** and **1.Se²⁺** in their switch-ON state were initially investigated via ¹H NMR titrations in CD₃CN/D₂O 9:1. This competitive aqueous solvent system was chosen to ensure solubility of the charged ChB hosts and their anion complexes. As representatively shown for the titration of **1.Te²⁺** with iodide, addition of all halide anions as their tetrabutylammonium (TBA) salts induced notable chemical shift perturbations of the proximal viologen proton *a* for both **1.Te²⁺/Se²⁺**, in excellent agreement with ChB-participation as schematically shown in Figure 2A.

Analysis of the corresponding binding isotherms (Figure 2C) revealed moderately strong 1:1 host-guest stoichiometric binding with association constants *K_a* of up to 1036 M⁻¹ for Br⁻ recognition with **1.Te²⁺** (Table 1).⁵⁴ Both Cl⁻ and I⁻ displayed similarly strong binding to **1.Te²⁺** of ≈880 M⁻¹. Notably, the affinity of all halides is, as expected, markedly lower for the lighter, less polarisable ChB analogue **1.Se²⁺** with *K_a* ≈180 M⁻¹. Furthermore, the proto viologen analogue **1.H²⁺** displays even weaker halide affinities of up to *K_a* = 139 M⁻¹ for Br⁻.

These observations importantly confirm ChB participation in anion binding, especially for **1.Te²⁺**, and to a lesser extent **1.Se²⁺**, and highlight that halide anion recognition by **1.Te²⁺/Se²⁺** is not driven by electrostatic or HB interactions alone. Of further note is the modest bromide selectivity observed for **1.Te²⁺**, while neither **1.Se²⁺** nor **1.H²⁺** exhibit any halide preference.

Table 1. Anion association constants *K* (M⁻¹) of **1.Te²⁺/Se²⁺/H²⁺** as determined by ¹H NMR titrations in CD₃CN/D₂O 9:1.

	1.Te²⁺	1.Se²⁺	1.H²⁺
Cl ⁻	877 ± 3	181 ± 1	127 ± 1
Br ⁻	1036 ± 3	182 ± 2	139 ± 1
I ⁻	888 ± 4	179 ± 3	130 ± 1

Having established the ChB potency of the dicationic **1.Te²⁺**, attention turned to the assessment of the anion binding capability of the natively neutral bis(ferrocenyltellurotriazole) **2.Te** receptor in the switch-OFF state.* Analogous ¹H NMR anion binding studies revealed, as expected with the neutral receptor, that the ChB potency was strongly diminished.

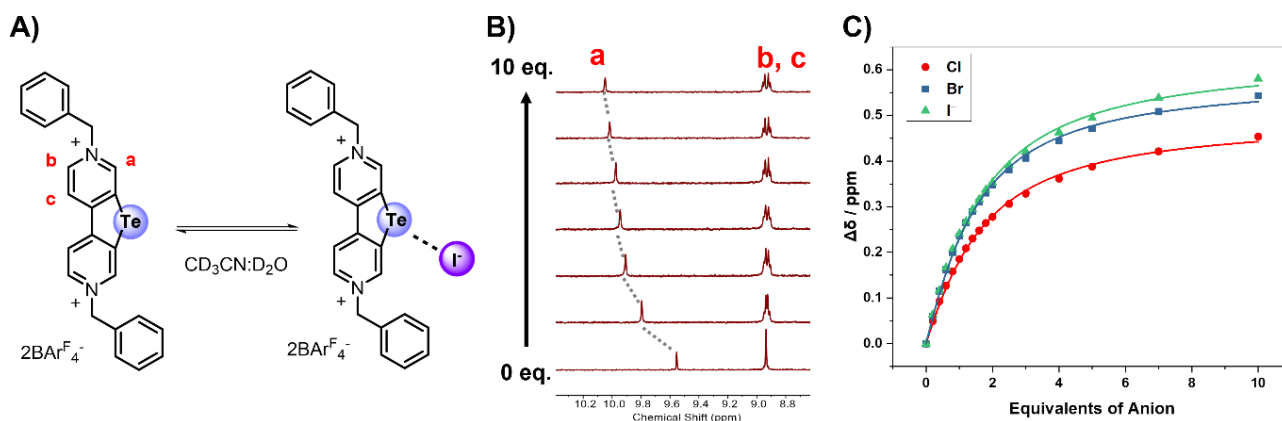


Figure 2. A) Proposed anion binding mode of **1.Te²⁺** with iodide as a representative halide anion. B) Representative ¹H NMR chemical shift perturbations of protons *a-c* of **1.Te²⁺** upon titration with TBA-iodide in CD₃CN/D₂O 9:1. C) The corresponding halide anion binding isotherms.

Indeed, no measurable ¹H NMR perturbations for a range of halide or oxoanion guests were observed in the much less competitive d₆-acetone. Only the addition of H₂PO₄⁻ induced significant chemical shift perturbations of the internal pyridine proton of **2.Te**, wherein analysis of the binding isotherm determined a weak 1:1 host-guest stoichiometric association constant of 111 M⁻¹ (Figure S12 and Table S1). Structurally related pyridine bis(tellurotriazole) ChB receptors typically display stronger anion binding in this solvent,⁴³ indicating a somewhat decreased neutral ChB potency of **2.Te**, presumably arising due to a combination of an increased electron density at the chalcogen centre as well as steric constraints from the large and comparably electron-rich ferrocene substituents.

These findings support a very weak ChB sigma-hole donor capability of the neutral **2.Te** receptor (ChB OFF) in acetone, while the dicationic **1.Te²⁺/Se²⁺** receptor systems expectedly display much improved native anion binding capabilities even in competitive aqueous media (CD₃CN/D₂O 9:1; ChB ON), providing a first indication of the strong dependence of ChB sigma-hole donor strength on the respective receptor's redox state.

The significant ChB anion recognition potency of **1.Te²⁺** was further supported by UV-vis anion binding studies in the same solvent system as employed for ¹H NMR studies. In CH₃CN/H₂O 9:1 **1.Te²⁺** displays significant absorbance changes upon titration with halide anions, whereby, in the presence of iodide, the absorbance band at λ_{max} = 481 nm shifts bathochromically with appearance of an isosbestic point at 505 nm (Figure 3 and Figures S13-S15). These perturbations are large enough to be detectable by the

naked eye (change from yellow to red) and present a rare example of ChB-mediated optical anion sensing.^{7, 24, 28, 55-56} Pleasingly, the 1:1 host-guest stoichiometric binding constants obtained by global fitting of the UV-vis titration data are in good agreement with those obtained by ¹H NMR titrations; Br⁻ is bound strongest with K = 873 M⁻¹, while binding of Cl⁻ and I⁻ is slightly weaker with 690 and 627 M⁻¹, respectively (Figures S13-S15).

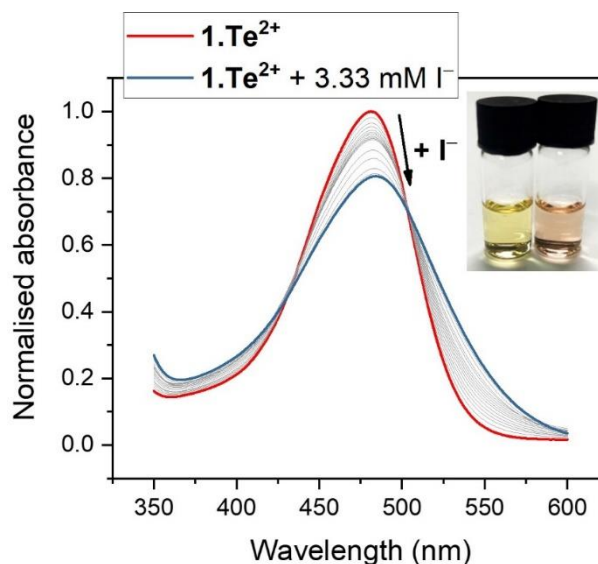


Figure 3. Normalized UV-vis spectra of **1.Te²⁺** upon titration with up to 3.33 mM iodide in ACN/H₂O 9:1. The inset shows the colour of the receptor in the absence (left, yellow) and presence of 3.33 mM I⁻ (right, red).

Furthermore, **1.Se²⁺** displays only minor UV-vis perturbations towards halide anions (Figure S16), which are too small to accurately quantify. Similarly, and again in good agreement with ¹H NMR studies, the proto analogue

$1.H^{2+}$ is neither coloured nor optically responsive to anions (Figure S17).

Electrochemical Characterization of Receptors

The electrochemical characterization of all the ChB redox-active receptors was carried out by cyclic voltammetry (CV) and square-wave voltammetry (SWV) in the presence of 100 mM TBAPF₆ as supporting electrolyte. For solubility reasons $1.Te^{2+}/Se^{2+}/H^{2+}$ were only studied in the same solvent system of ACN/H₂O 9:1 as employed for ¹H NMR and UV-vis studies. As shown in Figure 4A, all the viologen receptors displayed two well-defined, one-electron reductive couples ($V^{2+}/V^{•+}$ and $V^{•+}/V$) at similar, moderately cathodic potentials (Table S2), in good agreement with related previous studies.^{51, 57} Both couples display a high degree of reversibility as evidenced by a close to unity ratio of anodic and cathodic peak currents (i_{pa}/i_{pc}) and excellent linearity of peak currents on the square-root of the scan rate (Figures S18-S20), confirming a diffusion-controlled process. These observations highlight that introduction of the chalcogen donor atom into the viologen scaffold does not significantly affect its electrochemical properties. For example, the half-wave potentials $E_{1/2}$ of all three viologens are very similar and lie between -0.720 and -0.770 V for the first reductive couple ($V^{2+}/V^{•+}$) and between -1.160 and -1.210 V for the second reductive couple ($V^{•+}/V$) (Table S2).

The improved solubility of neutral **2.Te** in comparison to dicationic $1.Te^{2+}$ enabled electrochemical studies across a wider range of solvent systems. In all tested solvents DCM, acetone, ACN (Figure 4B) and MeOH containing 100 mM TBAPF₆ supporting electrolyte, **2.Te** displayed a single, well-defined, reversible, diffusion-controlled redox couple (see also Figures S21-24). This suggests both Fc motifs undergo one-electron oxidation simultaneously and independently of one another, thereby generating the dicationic $2.Te^{2+}$. Only in the presence of the much larger, less-coordinating BARF₄⁻ anion as electrolyte in DCM, was electronic communication between the Fc motifs observed, as evidenced by appearance of two separate redox couples with a peak separation of ≈ 90 mV (Figure S25-S26).⁵⁸

As a result of the strongly electron-withdrawing perfluorobenzene appendages, the receptor's half-wave potential $E_{1/2} = 0.218$ V in ACN, is significantly more positive than that of parent Fc (0 V) (Table S3).

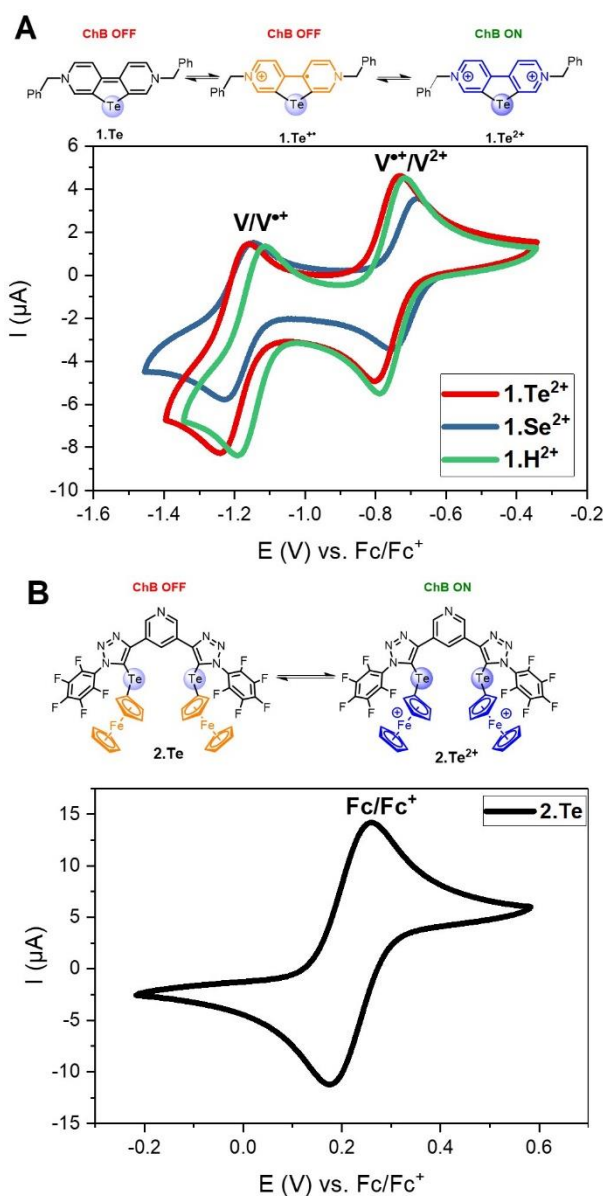


Figure 4. A) CVs of $1.Te^{2+}/Se^{2+}/H^{2+}$ in degassed ACN/H₂O 9:1. B) CVs of **2.Te** in ACN. All CVs were recorded at a scan rate of 100 mV/s in the presence of 0.25 mM receptor and 100 mM TBAPF₆ supporting electrolyte. Shown are also the different receptor oxidation states.

Reductive Switch-OFF Deactivation of ChB in Telluroviologen

In order to assess the ChB donor strength of the redox-active receptors we conducted voltammetric anion sensing studies. This provides a particularly convenient and straight-forward means of assessing the ChB potency as the magnitude of voltammetric perturbation in the presence of the analyte is directly dependent on its binding strength to the different receptor oxidation states, as discussed in more detail below. As shown in Figure 5, the first reductive couple ($V^{•+}/V^{2+}$) of $1.Te^{2+}$ displayed significant, continuous

cathodic voltammetric shifts towards all tested anions in CH₃CN/H₂O 9:1, with a notable preference for the halides according to the following response selectivity, defined by the maximum cathodic voltammetric perturbation ΔE_{max} : Br⁻ > Cl⁻ > I⁻ > HSO₄⁻ > NO₃⁻. Bromide induced the largest cathodic shifts of up to -61 mV in the presence of 50 mM anion (Table 2), with an almost identical shift observed for Cl⁻ of up to -57 mV while the response towards I⁻ was smaller (-49 mV). Both oxoanions hydrogen sulfate and nitrate displayed an attenuated response of -36 and -22 mV, respectively. The initial equivalent additions of H₂PO₄⁻ also induced significant cathodic perturbations (≥ 50 mV), however precipitation problems precluded quantitative binding data being determined. In contrast, the second reductive couple did not display significant perturbations in the presence of any anion.

Selected comparative halide sensing studies were also carried out with **1.Se²⁺** and **1.H²⁺**. Both responded weakly with the largest cathodic perturbation observed for **1.Se²⁺** in the presence of Cl⁻ (-22 mV), while the response of **1.H²⁺** towards Cl⁻ and Br⁻ was even smaller (-17 and -13 mV, respectively, see Table 2 and Figure S27). These observations are in excellent agreement with the ¹H NMR and UV-vis binding studies and crucially confirm that the anion binding and sensing performance of **1.Te²⁺** is mediated by ChB interactions *via* the Te-donor atoms.

The significant cathodic response magnitudes observed for **1.Te²⁺** arise as a result of anion recognition-induced stabilization of the native, oxidized redox state. The response magnitude ΔE is hereby dependent on the ratio of the anion binding constants to the native, oxidized

1.Te²⁺/Se²⁺ ($K_{\text{Ox}} = K_{1.\text{Te}^{2+}/\text{Se}^{2+}}$) and the mono-reduced **1.Te⁺/Se⁺** ($K_{\text{Red}} = K_{1.\text{Te}^{+}/\text{Se}^{+}}$) receptor states, and is, according to eqn. 1, directly proportional to their ratio ($K_{\text{Ox}}/K_{\text{Red}}$), called the binding-enhancement factor (BEF).³⁹

The absolute values of both K_{Ox} and K_{Red} were obtained by fitting of the voltammetric response isotherms (Figure 5C) according to the established 1:1 host-guest stoichiometric Nernst model (eqn. 1).^{33, 39, 47, 50}

$$\Delta E = -\frac{RT}{nF} \ln \left(\frac{1+K_{\text{Ox}}[A^-]}{1+K_{\text{Red}}[A^-]} \right) \text{eqn. 1}$$

As shown in Table 2, $K_{1.\text{Te}^{2+}}$ towards the halides and bisulfate is moderate, but significant (77 – 205 M⁻¹) and largest for Br⁻. Pleasingly, this is in good agreement with ¹H NMR binding studies where strongest Br⁻ binding was observed (Table 1).[†] In all cases $K_{1.\text{Te}^{+}/\text{Se}^{+}}$, that is binding to the monocationic **1.Te⁺/Se⁺**, is negligible ($K_{1.\text{Te}^{+}/\text{Se}^{+}} \approx 0$ M⁻¹), indicative of complete ChB switch-OFF and anion decomplexation from the **1.Te²⁺** host upon mono-reduction to **1.Te⁺**. This is in excellent agreement with negligible voltammetric perturbations observed for the second reductive couple, i.e. in this solvent system mono-reduction is sufficient to completely deactivate ChB-mediated anion binding, such that a further reduction to **1.Te** has no additional impact on anion binding strength.[#]

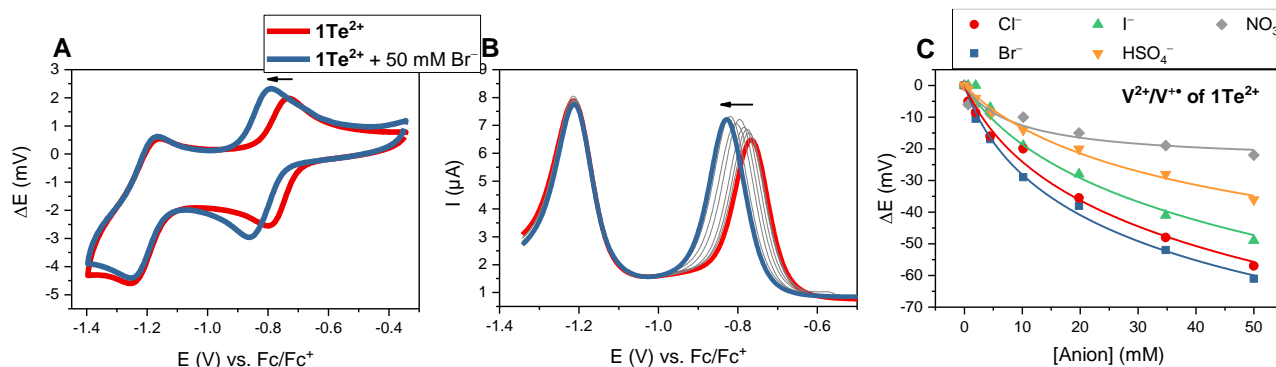


Figure 5. A) CVs and B) SWVs of 0.1 mM **1.Te²⁺** in degassed ACN/H₂O 9:1, 100 mM TBAPF₆ upon titration with up to 50 mM bromide. C) Voltammetric binding responses of first reductive couple (V^{2+}/V^{+}) of 0.1 mM **1.Te²⁺** in the same solvent upon titration with various anions. Solid lines represent fits according to the 1:1 host-guest Nernst model (eqn. 1). All titrations were carried out at constant host concentration and ionic strength.

Table 2. Maximum cathodic voltammetric shifts ΔE_{\max} of $1.\text{Te}^{2+}/\text{Se}^{2+}/\text{H}^{2+}$, in the presence of 50 mM anion, and $K_{\text{Ox}} = K_{1.\text{Te}^{2+}/\text{Se}^{2+}}$ as determined by fitting of the voltammetric binding isotherms according to eqn. 1, for first reductive couple of viologen hosts towards various anions in degassed ACN/H₂O 9:1, 100 mM TBAPF₆.

Anion	1.Te ²⁺			1.Se ²⁺		1.H ²⁺	
	ΔE_{\max} (mV) ^a	$K_{1.\text{Te}^{2+}}$ (M ⁻¹) ^b	BEF ^c	ΔE_{\max} (mV) ^a	$K_{1.\text{Se}^{2+}}$ (M ⁻¹) ^b	ΔE_{\max} (mV) ^a	$K_{1.\text{H}^{2+}}$ (M ⁻¹) ^b
Cl ⁻	-57	156	9.3	-22	26	-17	n/a
Br ⁻	-61	205	10.8	-15	n/a	-13	n/a
I ⁻	-49	107	6.8	-16	n/a	/	/
HSO ₄ ⁻	-36	77	4.1	/	/	/	/
NO ₃ ⁻	-22	n/a	n/a	/	/	/	/

a – estimated error ± 3 mV. b – $K_{\text{Red}} = K_{1.\text{Te}^{2+}/\text{Se}^{2+}}$ is ≈ 0 in all cases. c – Binding enhancement factor ($\text{BEF} = K_{1.\text{Te}^{2+}/\text{Se}^{2+}}/K_{1.\text{Te}^{2+}/\text{Se}^{2+}}$), calculated from ΔE_{\max} according to eqn. S2, see SI for further details. / – not conducted. n/a – not meaningful due to small response.

We further quantified the redox switching magnitude of $1.\text{Te}^{2+}$ by calculating the $\text{BEF} = K_{1.\text{Te}^{2+}}/K_{1.\text{Te}^{2+}}$ according to a simplified model ($\text{BEF} = 10^{\frac{\Delta E_{\max}}{-0.059 \text{ V}}}$ (eqn. S2), see Table 2, and SI for further details). This confirmed significant ChB binding modulation (i.e. deactivation) by a factor of up to ≈ 11 -fold in the case of bromide.

Importantly, the redox reversibility of both redox couples of the telluroviologen host is generally maintained in the presence of anions, highlighting that ChB potency and anion binding can be judiciously reversibly switched OFF by redox control. As discussed in more detail in a later section, the sensory performance of this simple ChB voltammetric anion sensing system and redox-switch compares very favourably with a range of more elaborate XB or HB redox active systems (see Figure S34).

Oxidative Switch-ON Activation of ChB in Ferrocenyltellurotriazole 2.Te

Having established the general utility of (reductive) redox-controlled ChB in simple telluroviologens, our attention

focused on a further elaboration of this concept in the more advanced anion receptor scaffold $2.\text{Te}$. The ChB potency of this natively neutral receptor can be reversibly switched-ON by redox control of the ferrocene/ferrocenium (Fc/Fc⁺) couple, a more common, and arguably more useful approach for anion recognition and sensing, circumventing the isolation of charged compounds.^{36, 39, 48, 59-60}

To assess this capability, voltammetric sensing studies with halides and oxoanions were undertaken. Due to the improved solubility of neutral $2.\text{Te}$, these were conducted in a range of solvent systems. In ACN $2.\text{Te}$ voltammetrically responded to all tested anions (H₂PO₄⁻, HSO₄⁻, NO₃⁻, Cl⁻ and Br⁻) via significant, continuous cathodic shifts, as shown in Figure 6A.† In all cases a well-defined, monotonic and reproducible response (Figures S28-S30) of the sensor was observed with the following response magnitude selectivity, defined by the maximum cathodic voltammetric shift ΔE_{\max} : H₂PO₄⁻ > Cl⁻ > Br⁻ > HSO₄⁻ > NO₃⁻, with an impressively large perturbation magnitude towards H₂PO₄⁻ of -217 mV (Table 3).§

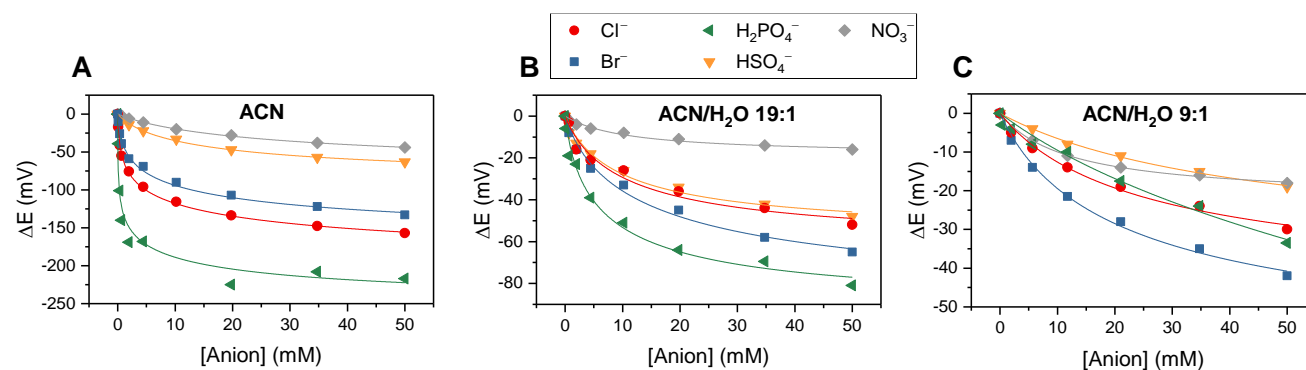


Figure 6. Voltammetric binding responses of $2.\text{Te}$ in A) ACN, B) ACN/H₂O 19:1 and C) ACN/H₂O 9:1 upon titration with various anions. $[2.\text{Te}] = 0.1$ mM with 100 mM TBAPF₆ supporting electrolyte. The overall ionic strength was kept constant at 100 mM throughout. Solid lines represent fits to a 1:1 host-guest Nernst model eqn. 1). Note the different y-axis scaling for the graphs.

Table 3. Maximum cathodic voltammetric shift ΔE_{\max} (mV), binding constants to the oxidized receptor $K_{Ox} = K_{2,Te2+}$ (M^{-1}) and BEF of **2.Te** in the presence of various anions in ACN, ACN/H₂O 19:1 and ACN/H₂O 9:1. K_{Ox} was obtained by fitting of the voltammetric binding isotherms according to eqn. 1.

Anion	ACN			ACN/H ₂ O 19:1			ACN/H ₂ O 9:1		
	ΔE_{\max}^a	$K_{2,Te2+}^b$	BEF ^c	ΔE_{\max}^a	$K_{2,Te2+}^b$	BEF ^c	ΔE_{\max}^a	$K_{2,Te2+}^b$	BEF ^c
Cl ⁻	-157	10200	458	-52	300	7.6	-30	88	3.2
Br ⁻	-133	4050	180	-65	348	12.6	-42	141	5.2
H ₂ PO ₄ ⁻	-217	174000	4760	-81	902	23.6	-34	41	3.8
HSO ₄ ⁻	-63	333	11.7	-48	300	6.5	-19	n/a	n/a
NO ₃ ⁻	-44	127	5.6	-16	n/a	n/a	-18	n/a	n/a

a – estimated error ± 3 mV. b – $K_{Red} = K_{2,Te}$ is ≈ 0 in all cases. c – Binding enhancement factor ($BEF = K_{2,Te2+} / K_{2,Te}$), calculated from ΔE_{\max} according to eqn. S2, see SI for further details. n/a – not meaningful due to small response.

Notably, as discussed above, ¹H NMR anion titration investigations demonstrated the neutral receptor **2.Te** displayed no detectable binding of most of these anions in acetone.

This confirms, as expected, receptor oxidation to **2.Te**²⁺ significantly enhances ChB potency and enables voltammetric anion sensing. Quantified analysis of the voltammetric response isotherms determined impressively large binding constants in the oxidized state of $K_{2,Te2+}$ of up to 174,000 M^{-1} for H₂PO₄⁻ and for the halides with binding of 4050 and 10,200 M^{-1} for Br⁻ and Cl⁻, respectively (Table 3). The H₂PO₄⁻ preference in this non-aqueous solvent is again in good agreement with the aforementioned ¹H NMR studies in which only this anion induced measurable, but weak binding to **2.Te** in d₆-acetone.

The large-magnitude anion recognition-induced voltammetric perturbations of **2.Te** towards Cl⁻, Br⁻ and H₂PO₄⁻ correspond to an impressively substantial binding switch-ON upon oxidation with BEFs of 458, 180 and 4760, respectively (Table 3). This reversible ChB donor modulation, by up to over 3-orders of magnitude, is notably greater than that attainable by cooperative ion-pair recognition in related heteroditopic ChB receptors.⁴⁵

Unsurprisingly, the introduction of 5 or 10% water into the ACN solvent system is associated with moderately diminished response magnitudes, K_{Ox} binding constants and BEFs (Figure 6B-C, Figure 7 and Table 3).⁵⁰ Nevertheless, significant shift responses and switching magnitudes are retained in these competitive, aqueous solvent systems, a particularly impressive accomplishment when considering that the native neutral **2.Te** receptor exhibits no significant anion affinity in less competitive

pure organic solvent media. For example, even in ACN/H₂O 9:1 significant cathodic shifts of up to -41 mV towards Br⁻ are observed, corresponding to a BEF = 5.2.

Of further note is the sensor's response selectivity is altered in the presence of water (Figure 7). The response towards the halides and dihydrogen phosphate in particular is attenuated upon introduction of 5% water, most likely a reflection of their respective large hydration enthalpies. This also results in a somewhat altered selectivity pattern in ACN/H₂O 19:1 of ΔE_{\max} : H₂PO₄⁻ > Br⁻ > Cl⁻ \approx HSO₄⁻ > NO₃⁻.

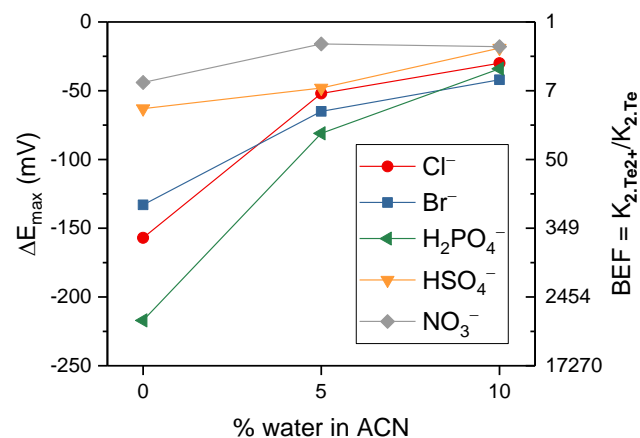


Figure 7. Maximum cathodic perturbations of **2.Te** towards 50 mM of various anions in ACN, ACN/H₂O 19:1 and ACN/H₂O 9:1, highlighting a change in selectivity and a significantly retained sensing capability in highly competitive aqueous solvents, in particular towards bromide. Displayed is also the magnitude of redox-induced binding switch-ON as quantified by the BEF according to eqn. S2. Connecting lines are to guide the eye only.

Upon further increasing the water content to 10%, the response and binding magnitudes further decrease, however not as sharply. Again, the most strongly affected anion is H₂PO₄⁻, which now induces a similar response as Cl⁻, both of which are lower than that of Br⁻ (Br⁻ > H₂PO₄⁻ \approx Cl⁻ > HSO₄⁻ \approx NO₃⁻). The observation that the halide

response is more significantly retained than that of the oxoanions hints at a unique halide selectivity associated with ChB recognition, akin to that observed in XB systems.⁵⁰

Chalcogen Bonding 1.Te²⁺ and 2.Te Receptors as Potent Redox Controlled ON/OFF Switches and Sensors

In spite of their weak ChB anion binding strength in their reduced states and comparable structural simplicity, both **1.Te²⁺** and **2.Te** are among the most potent voltammetric anion sensors reported to date, as measured by their response magnitudes.³⁹

In fact, to the best of our knowledge, **2.Te** significantly outcompetes every reported solution-phase XB voltammetric anion sensor, as well as the vast majority of redox-active HB anion sensors, for the sensing of most anions in ACN, in particular chloride and bromide.^{33, 39, 49-50, 61-62}¶ This is particularly noteworthy considering the generally weaker sigma-hole donor-ability of ChB receptors in comparison to analogous XB systems.^{18, 40, 45} As shown in a direct comparison with structurally similar XB and HB sensors (Figures S31-S34),⁵⁰ Br⁻ especially elicits an up to 2.4-fold larger response than its structurally closest XB congener, in both ACN and ACN/H₂O 19:1. Due to its enhanced response magnitudes, **1.Te²⁺** even outcompetes these XB and HB sensors (recently reported as some of the most potent voltammetric sensors), for the sensing of Cl⁻ and Br⁻ at high concentrations in ACN/H₂O 9:1.⁵⁰ These observations support a developing picture that supports a ChB preference for the “softer” halides in comparison to oxoanions (akin to XB), in spite of their lower basicity.

As discussed above, the large response magnitudes of **1.Te²⁺** and **2.Te** are a direct reflection of their large anion binding enhancement factors ($BEF = K_{Ox}/K_{Red}$), that is the *relative* change in anion binding constants upon reduction/oxidation.^{33, 39} The impressive sensing performance of both **1.Te²⁺** and **2.Te** can thus be attributed to a uniquely potent switching-OFF or -ON of anion binding, respectively, as previously observed in a range of XB voltammetric anion sensors. We ascribe this to the high sensitivity of the ChB donor strength to electronic inductive substituent effects⁴³ as well as the most intimate spatial and electronic coupling of the sigma-hole donor binding site to the redox transducer, afforded by the *direct* appendage of the Te sigma-hole donor to Fc or viologen. As a result, the redox modulation of the electroactive transducer more strongly influences the ChB sigma-hole

depth and thereby anion binding strength, which in turn translates to a large voltammetric response.

The direct appendage of Te ChB donor atoms with optical or redox transducer groups remains a largely unexplored, but promisingly highly potent, design feature of ChB receptors that not only enables sensing with improved sensitivity but can, in the case of the **2.Te** scaffold, also “free up” a substituent, such that other functional groups can easily be incorporated into the receptor (here via the azide component). This is notably not easily achievable in XB or HB systems, in which the XB/HB bond donor atom typically carries only one substituent.

As a result of this structural adaptability, combined with the high-fidelity redox-control of ChB potency, as demonstrated with **1.Te²⁺** and **2.Te**, we envision these electroactive ChB centres as ideal motifs for further exploration in ion sensors as well as molecular redox switches and machines.

Conclusions

We report, for the first time, ChB-mediated electrochemical anion sensing and reversible redox-controlled switch-ON and switch-OFF of ChB donor potency exemplified by 3,5-bis-ferrocenetellurotriazole pyridine and telluroviologen anion receptors. In spite of their structural simplicity and comparably weak anion binding strength in the reduced receptor states, both systems displayed large scale anion binding enhancements, of up to 3 orders of magnitude, in the oxidized state. This is directly reflected in large cathodic voltammetric shifts in the presence of anions, which persist even in the competitive ACN/H₂O 9:1 solvent system, with a noteworthy selectivity towards the halides, in particular bromide. Impressively, the high sensitivity of these sensors compares very favorably with related XB and HB sensors, in some cases outcompeting the best XB sensors reported to date.⁵⁰ This high sensitivity can be attributed to a unique, most intimate electronic coupling of redox-active centre and ChB donor sites and the sensitivity of sigma hole donors to inductive effects. These observations lend further support to recent findings that ChB interactions are highly electronically tuneable⁴³ and not only pave the way towards the further exploitation of ChB in anion sensor design and redox switches, but also present fundamental insights into the nature of ChB interactions.

Acknowledgements

A.D. thanks the EPSRC (Grant reference number EP/N509711/1) for a studentship. R.H. thanks Somerville College, University of Oxford for support through a Fulford Junior Research Fellowship. We thank Sophie Patrick and Andrew Taylor, University of Oxford, for helpful comments. We further thank Prof. Gang He and co-workers (Frontier Institute of Science and Technology) for helpful suggestions for the synthesis of the chalcoviologens.

References

* We did not attempt to conduct ^1H NMR anion binding studied on the oxidized $2.\text{Te}^{2+}$ because even if isolable it is paramagnetic.

† The slightly smaller magnitude of K_{ox} determined voltammetrically in comparison to the analogous ^1H NMR binding constants most likely arises from electrolyte effects as detailed elsewhere.⁶³

Note that in less competitive media $1.\text{Te}^{2+}$ could, as a result of possessing three redox-addressable states, display multistate switching with intermediate binding strength in the mono-reduced $1.\text{Te}^{+}$ and full OFF switching only in the fully reduced $1.\text{Te}$ state, thereby changing its switching pattern from the observed ON-OFF-OFF to ON-ON-OFF.

‡ Iodide could not be studied due to overlapping redox activity with the Fc transducers.

§ The response of $2.\text{Te}$ towards the halides in ACN is somewhat more complex and accompanied by the emergence of an additional anodic shoulder peak. In the presence of water this behaviour is not observed. We hypothesize that the non-idealities observed in pure ACN may arise from receptor degradation by reaction with the anions, e.g. by oxidative addition of halides to the Te centres.⁶⁴⁻⁶⁶

¶ $2.\text{Te}$ also outcompetes a range of XB receptors studied in different solvents, most notably various sensors studied in DMF by the groups of Schöllhorn and Fave.^{47, 63, 67}

- Gilday, L. C.; Robinson, S. W.; Barendt, T. A.; Langton, M. J.; Mullaney, B. R.; Beer, P. D., Halogen bonding in supramolecular chemistry. *Chem. Rev.* **2015**, *115* (15), 7118-7195.
- Metrangolo, P.; Resnati, G.; Pilati, T.; Biella, S., Halogen bonding in crystal engineering. *Halogen Bonding* **2007**, 105-136.
- Teyssandier, J.; Mali, K. S.; De Feyter, S., Halogen Bonding in Two-Dimensional Crystal Engineering. *ChemistryOpen* **2020**, *9* (2), 225-241.

- Kampes, R.; Zechel, S.; Hager, M. D.; Schubert, U. S., Halogen bonding in polymer science: towards new smart materials. *Chem. Sci.* **2021**, *12* (27), 9275-9286.
- Ball, M. L.; Milić, J. V.; Loo, Y.-L., The Emerging Role of Halogen Bonding in Hybrid Perovskite Photovoltaics. *Chem. Mater.* **2022**, 10.1021/acs.chemmater.1c03117.
- Biot, N.; Bonifazi, D., Concurring Chalcogen- and Halogen-Bonding Interactions in Supramolecular Polymers for Crystal Engineering Applications. *Chem. Eur. J.* **2020**, *26* (13), 2904-2913.
- Zeng, R.; Gong, Z.; Chen, L.; Yan, Q., Solution Self-Assembly of Chalcogen-Bonding Polymer Partners. *ACS Macro Letters* **2020**, *9* (8), 1102-1107.
- Ho, P. C.; Wang, J. Z.; Meloni, F.; Vargas-Baca, I., Chalcogen bonding in materials chemistry. *Coord. Chem. Rev.* **2020**, *422*, 213464.
- Zeng, R.; Gong, Z.; Yan, Q., Chalcogen-Bonding Supramolecular Polymers. *J. Org. Chem.* **2020**, *85* (13), 8397-8404.
- Breugst, M.; von der Heiden, D.; Schmauck, J., Novel noncovalent interactions in catalysis: a focus on halogen, chalcogen, and anion- π bonding. *Synthesis* **2017**, *49* (15), 3224-3236.
- Sutar, R. L.; Huber, S. M., Catalysis of Organic Reactions through Halogen Bonding. *ACS Catalysis* **2019**, *9* (10), 9622-9639.
- Benz, S.; López-Andarias, J.; Mareda, J.; Sakai, N.; Matile, S., Catalysis with chalcogen bonds. *Angew. Chem.* **2017**, *129* (3), 830-833.
- Wang, W.; Zhu, H.; Liu, S.; Zhao, Z.; Zhang, L.; Hao, J.; Wang, Y., Chalcogen-chalcogen bonding catalysis enables assembly of discrete molecules. *J. Am. Chem. Soc.* **2019**, *141* (23), 9175-9179.
- Wang, W.; Zhu, H.; Feng, L.; Yu, Q.; Hao, J.; Zhu, R.; Wang, Y., Dual Chalcogen-Chalcogen Bonding Catalysis. *J. Am. Chem. Soc.* **2020**, *142* (6), 3117-3124.
- Wonner, P.; Dreger, A.; Vogel, L.; Engelage, E.; Huber, S. M., Chalcogen Bonding Catalysis of a Nitro-Michael Reaction. *Angew. Chem. Int. Ed.* **2019**, *58* (47), 16923-16927.
- Tepper, R.; Schubert, U. S., Halogen Bonding in Solution: Anion Recognition, Templated Self-Assembly, and Organocatalysis. *Angew. Chem. Int. Ed.* **2018**, *57* (21), 6004-6016.
- Erdelyi, M., Halogen bonding in solution. *Chem. Soc. Rev.* **2012**, *41* (9), 3547-3557.
- Taylor, M. S., Anion recognition based on halogen, chalcogen, pnictogen and tetrel bonding. *Coord. Chem. Rev.* **2020**, *413*, 213270.
- Lim, J. Y. C.; Beer, P. D., Sigma-Hole Interactions in Anion Recognition. *Chem* **2018**, *4* (4), 731-783.
- Pancholi, J.; Beer, P. D., Halogen bonding motifs for anion recognition. *Coord. Chem. Rev.* **2020**, *416*, 213281.
- Langton, M. J.; Robinson, S. W.; Marques, I.; Félix, V.; Beer, P. D., Halogen bonding in water results in enhanced anion recognition in acyclic and rotaxane hosts. *Nat. Chem.* **2014**, *6* (12), 1039-1043.
- Borissov, A.; Marques, I.; Lim, J. Y. C.; Félix, V.; Smith, M. D.; Beer, P. D., Anion Recognition in Water by Charge-Neutral Halogen and Chalcogen Bonding Foldamer Receptors. *J. Am. Chem. Soc.* **2019**, *141* (9), 4119-4129.
- Lim, J. Y.; Marques, I.; Thompson, A. L.; Christensen, K. E.; Félix, V.; Beer, P. D., Chalcogen bonding macrocycles and [2] rotaxanes for anion recognition. *J. Am. Chem. Soc.* **2017**, *139* (8), 3122-3133.

24. Garrett, G. E.; Gibson, G. L.; Straus, R. N.; Seferos, D. S.; Taylor, M. S., Chalcogen Bonding in Solution: Interactions of Benzotelluradiazoles with Anionic and Uncharged Lewis Bases. *J. Am. Chem. Soc.* **2015**, *137* (12), 4126-4133.
25. Bickerton, L. E.; Docker, A.; Sterling, A. J.; Kuhn, H.; Duarte, F.; Beer, P. D.; Langton, M. J., Highly Active Halogen Bonding and Chalcogen Bonding Chloride Transporters with Non-Protonophoric Activity. *Chem. Eur. J.* **2021**, *27* (45), 11738-11745.
26. Zhou, B.; Gabbai, F. P., Redox-controlled chalcogen-bonding at tellurium: impact on Lewis acidity and chloride anion transport properties. *Chem. Sci.* **2020**, *11* (28), 7495-7500.
27. Bickerton, L. E.; Sterling, A. J.; Beer, P. D.; Duarte, F.; Langton, M. J., Transmembrane anion transport mediated by halogen bonding and hydrogen bonding triazole anionophores. *Chem. Sci.* **2020**, *11* (18), 4722-4729.
28. Benz, S.; Macchione, M.; Verolet, Q.; Mareda, J.; Sakai, N.; Matile, S., Anion Transport with Chalcogen Bonds. *J. Am. Chem. Soc.* **2016**, *138* (29), 9093-9096.
29. Vargas Jentzsch, A.; Matile, S., Transmembrane Halogen-Bonding Cascades. *J. Am. Chem. Soc.* **2013**, *135* (14), 5302-5303.
30. Zapata, F.; Caballero, A.; Molina, P., Ferrocene-Triazole Combination as a Benchmark for the Electrochemical Detection of Noncovalent Halogen-Bonding Interactions. *Eur. J. Inorg. Chem.* **2017**, *2017* (2), 237-241.
31. Hein, R.; Borissov, A.; Smith, M. D.; Beer, P. D.; Davis, J. J., A halogen-bonding foldamer molecular film for selective reagentless anion sensing in water. *Chem. Commun.* **2019**, *55* (33), 4849-4852.
32. Hijazi, H.; Vacher, A.; Groni, S.; Lorcy, D.; Levillain, E.; Fave, C.; Schöllhorn, B., Electrochemically driven interfacial halogen bonding on self-assembled monolayers for anion detection. *Chem. Commun.* **2019**, *55* (13), 1983-1986.
33. Hein, R.; Li, X.; Beer, P. D.; Davis, J. J., Enhanced voltammetric anion sensing at halogen and hydrogen bonding ferrocenyl SAMs. *Chem. Sci.* **2021**, *12* (7), 2433-2440.
34. Cheong Tse, Y.; Hein, R.; Mitchell, E. J.; Zhang, Z.; Beer, P. D., Halogen-Bonding Strapped Porphyrin BODIPY Rotaxanes for Dual Optical and Electrochemical Anion Sensing. *Chemistry* **2021**, *27* (58), 14550-14559.
35. Docker, A.; Shang, X.; Yuan, D.; Kuhn, H.; Zhang, Z.; Davis, J. J.; Beer, P. D.; Langton, M. J., Halogen Bonding Tetraphenylethene Anion Receptors: Anion-Induced Emissive Aggregates and Photoswitchable Recognition. *Angew. Chem. Int. Ed.* **2021**, *60* (35), 19442-19450.
36. Patrick, S. C.; Hein, R.; Beer, P. D.; Davis, J. J., Continuous and Polarization-Tuned Redox Capacitive Anion Sensing at Electroactive Interfaces. *J. Am. Chem. Soc.* **2021**, *143* (45), 19199-19206.
37. Patrick, S. C.; Hein, R.; Sharafeldin, M.; Li, X.; Beer, P. D.; Davis, J. J., Real-time Voltammetric Anion Sensing Under Flow**. *Chem. Eur. J.* **2021**, *27* (70), 17700-17706.
38. Lim, J. Y. C.; Marques, I.; Félix, V.; Beer, P. D., Chiral halogen and chalcogen bonding receptors for discrimination of stereo- and geometric dicarboxylate isomers in aqueous media. *Chem. Commun.* **2018**, *54* (77), 10851-10854.
39. Hein, R.; Beer, P. D.; Davis, J. J., Electrochemical Anion Sensing: Supramolecular Approaches. *Chem. Rev.* **2020**, *120* (3), 1888-1935.
40. Lim, J. Y.; Beer, P. D., Sigma-hole interactions in anion recognition. *Chem* **2018**, *4* (4), 731-783.
41. Robinson, S. W.; Mustoe, C. L.; White, N. G.; Brown, A.; Thompson, A. L.; Kennepohl, P.; Beer, P. D., Evidence for Halogen Bond Covalency in Acyclic and Interlocked Halogen-Bonding Receptor Anion Recognition. *J. Am. Chem. Soc.* **2015**, *137* (1), 499-507.
42. Pascoe, D. J.; Ling, K. B.; Cockroft, S. L., The origin of chalcogen-bonding interactions. *J. Am. Chem. Soc.* **2017**, *139* (42), 15160-15167.
43. Docker, A.; Guthrie, C. H.; Kuhn, H.; Beer, P. D., Modulating Chalcogen Bonding and Halogen Bonding Sigma-Hole Donor Atom Potency and Selectivity for Halide Anion Recognition. *Angew. Chem. Int. Ed. Engl.* **2021**, *60* (40), 21973-21978.
44. Park, G.; Gabbai, F. P., Redox-controlled chalcogen and pnictogen bonding: the case of a sulfonium/stibonium dication as a preanionophore for chloride anion transport. *Chem. Sci.* **2020**, *11* (37), 10107-10112.
45. Bunchuay, T.; Docker, A.; Eiamprasert, U.; Surawatanawong, P.; Brown, A.; Beer, P. D., Chalcogen Bond Mediated Enhancement of Cooperative Ion-Pair Recognition. *Angew. Chem. Int. Ed.* **2020**, *59* (29), 12007-12012.
46. Groni, S.; Maby-Raud, T.; Fave, C.; Branca, M.; Schöllhorn, B., Electrochemical controlling and monitoring of halogen bond formation in solution. *Chem. Commun.* **2014**, *50* (93), 14616-14619.
47. Oliveira, R.; Groni, S.; Fave, C.; Branca, M.; Mavre, F.; Lorcy, D.; Fourmigue, M.; Schöllhorn, B., Electrochemical activation of a tetrathiafulvalene halogen bond donor in solution. *Phys. Chem. Chem. Phys.* **2016**, *18* (23), 15867-15873.
48. Fave, C.; Schöllhorn, B., Electrochemical activation of halogen bonding. *Current Opinion in Electrochemistry* **2019**, *15*, 89-96.
49. Lim, J. Y. C.; Cunningham, M. J.; Davis, J. J.; Beer, P. D., Halogen bonding-enhanced electrochemical halide anion sensing by redox-active ferrocene receptors. *Chem. Commun.* **2015**, *51* (78), 14640-14643.
50. Patrick, S. C.; Hein, R.; Docker, A.; Beer, P. D.; Davis, J. J., Solvent Effects in Halogen and Hydrogen Bonding Mediated Electrochemical Anion Sensing in Aqueous Solution and at Interfaces. *Chem. Eur. J.* **2021**, *27* (39), 10201-10209.
51. Li, G.; Xu, L.; Zhang, W.; Zhou, K.; Ding, Y.; Liu, F.; He, X.; He, G., Narrow-Bandgap Chalcogenoviologens for Electrochromism and Visible-Light-Driven Hydrogen Evolution. *Angew. Chem. Int. Ed.* **2018**, *57* (18), 4897-4901.
52. Mathur, P.; Tauqeer, M.; Torubaev, Y. V.; Shaikh, M. M.; Lahiri, G. K.; Pasynskii, A. A.; Pavlova, A. V., Step-by-step transformations of ferrocenyltellurium complexes of Group VIB metal carbonyls. *J. Organomet. Chem.* **2014**, *758*, 55-59.
53. Jin, L.-M.; Xu, X.; Lu, H.; Cui, X.; Wojtas, L.; Zhang, X. P., Effective Synthesis of Chiral N-Fluoroaryl Aziridines through Enantioselective Aziridination of Alkenes with Fluoroaryl Azides. *Angew. Chem. Int. Ed.* **2013**, *52* (20), 5309-5313.
54. Thordarson, P., Determining association constants from titration experiments in supramolecular chemistry. *Chem. Soc. Rev.* **2011**, *40* (3), 1305-1323.
55. Garrett, G. E.; Carrera, E. I.; Seferos, D. S.; Taylor, M. S., Anion recognition by a bidentate chalcogen bond donor. *Chem. Commun.* **2016**, *52* (64), 9881-9884.
56. Zhao, H.; Gabbai, F. P., A bidentate Lewis acid with a telluronium ion as an anion-binding site. *Nat. Chem.* **2010**, *2* (11), 984-990.
57. Li, G.; Zhang, B.; Wang, J.; Zhao, H.; Ma, W.; Xu, L.; Zhang, W.; Zhou, K.; Du, Y.; He, G., Electrochromic Poly(chalcogenoviologen)s as Anode Materials for High-Performance Organic Radical Lithium-Ion Batteries. *Angew. Chem.* **2019**, *131* (25), 8556-8561.

58. Diallo, A. K.; Absalon, C.; Ruiz, J.; Astruc, D., Ferrocenyl-Terminated Redox Stars: Synthesis and Electrostatic Effects in Mixed-Valence Stabilization. *J. Am. Chem. Soc.* **2011**, *133* (3), 629-641.
59. Astruc, D., Why is Ferrocene so Exceptional? *Eur. J. Inorg. Chem.* **2017**, *2017* (1), 6-29.
60. Hein, R.; Beer, P. D., COMC IV: Organometallic Receptors for Charged and Neutral Guest Species. In *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier: 2021.
61. Mullaney, B. R.; Cunningham, M. J.; Davis, J. J.; Beer, P. D., Acyclic halogen and hydrogen bonding diquat-containing receptors for the electrochemical sensing of anions. *Polyhedron* **2016**, *116*, 20-25.
62. Lim, J. Y. C.; Beer, P. D., A Halogen Bonding 1,3-Disubstituted Ferrocene Receptor for Recognition and Redox Sensing of Azide. *Eur. J. Inorg. Chem.* **2017**, *2017* (2), 220-224.
63. Engelage, E.; Hijazi, H.; Gartmann, M.; Chamoreau, L. M.; Schöllhorn, B.; Huber, S. M.; Fave, C., Towards redox-switchable organocatalysts based on bidentate halogen bond donors. *Phys. Chem. Chem. Phys.* **2021**, *23* (7), 4344-4352.
64. Burgess, M. R.; Morley, C. P., Electrochemical and NMR spectroscopic studies of selenium-and tellurium-substituted ferrocenes I: ferrocenyl alkyl chalcogenides [Fe (η -C₅H₅)(η -C₅H₄ER)]. *J. Organomet. Chem.* **2001**, *623* (1-2), 101-108.
65. Shida, N.; Nishiyama, H.; Zheng, F.; Ye, S.; Seferos, D. S.; Tomita, I.; Inagi, S., Redox chemistry of π -extended tellurophenes. *Communications Chemistry* **2019**, *2* (1), 124.
66. Torubaev, Y.; Mathur, P.; Tauqeer, M.; Shaikh, M. M.; Lahiri, G. K.; Pasynskii, A.; Pavlova, A.; Grinberg, V., Mixed-valent ferrocenyltellurenyl halides. Synthesis, electrochemistry and unusual molecular structure. *J. Organomet. Chem.* **2014**, *749*, 115-119.
67. Creste, G.; Groni, S.; Fave, C.; Branca, M.; Schöllhorn, B., Comparative study of non-covalent interactions between cationic N-phenylviologens and halides by electrochemistry and NMR: the halogen bonding effect. *Faraday Discuss.* **2017**, *203* (0), 301-313.