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Halogen Bonding

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An All-Halogen Bonding Rotaxane for Selective Sensing of Halides in Aqueous Media**

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Abstract: *The synthesis and anion binding properties of the first rotaxane host system to bind and sense anions purely through halogen bonding, is described. Through a combination of polarized iodotriazole and iodotriazolium halogen bond donors, a three-dimensional cavity is created for anion binding. This rotaxane incorporates a luminescent rhenium(I) bipyridyl metal sensor motif within the macrocycle component, thus enabling optical study of the anion binding properties. The rotaxane topology was confirmed by single-crystal X-ray structural analysis, demonstrating halogen bonding between the electrophilic iodine atoms and chloride anions. In 50% H_2O/CH_3CN solvent mixtures the rotaxane host exhibits strong binding affinity and selectivity for chloride, bromide, and iodide over a range of oxoanions.*

Halogen bonding (XB) is the intermolecular interaction between a polarized, electron-deficient halogen atom, and a Lewis base.[1] As a highly directional analogue to hydrogen bonding,[2] XB has been used extensively in the solid-state crystal engineering[3] of liquid-crystalline, magnetic, and conducting materials,[4] and more recently in the design of catalysts[5] and potential pharmaceuticals.[6]

The undeniable importance of anions in a range of biological, environmental, medical, and chemical processes has provoked a considerable effort to develop synthetic anion receptors.[7] Many efficient anion receptors have been reported and exploit a variety of supramolecular synthons including electrostatic, hydrogen bonding, Lewis acid–base,[8] and anion–π interactions.[9] Nevertheless, the challenge of developing synthetic receptors that rival the recognition properties of biotic systems thus far remains unfulfilled. By virtue of their comparable strength to hydrogen bonds and more strict linear geometry preference,[10] a promising avenue to raise the bar of anion-binding affinity and selectivity of anion host systems is to integrate XB motifs into their structural frameworks.[11]

Taking inspiration from nature's selective anion-binding proteins, we have used anion templation to form interlocked architectures with unique three-dimensional anion-binding cavities.[12] Through electrostatics, convergent hydrogen bonding, and cavity size, these systems have demonstrated high degrees of selectivity between different anionic species. We recently reported the first XB rotaxane, containing an iodotriazolium axle, which selectively bound iodide in aqueous media through a combination of halogen and hydrogen bonding.[13] In addition, an XB catenane was shown to selectively bind chloride and bromide through cooperative halogen bond bromoimidazolium donor groups.[14]

Herein we describe the anion-templated synthesis of the first all-halogen bonding rotaxane, which cooperatively uses two iodotriazole and two iodotriazolium XB donors to selectively recognize chloride, bromide, and iodide. Through the incorporation of a photoactive rhenium(I) bipyridyl center within the rotaxane's macrocycle component, we demonstrate, by using luminescence spectroscopy, the rotaxane's ability to optically sense these halide anions in aqueous solvent mixtures containing up to 50% water.

Figure 1 illustrates schematically the synthetic strategy undertaken for the construction of the target XB rotaxane. Halogen bond donor iodotriazole and iodotriazolium motifs, integrated into the rhenium(I) bipyridyl macrocycle precursor and carbazole axle components, respectively, form an anion-templated orthogonal assembly which upon cyclization by ring-closing metathesis (RCM) affords an all-halogen bonding rotaxane.

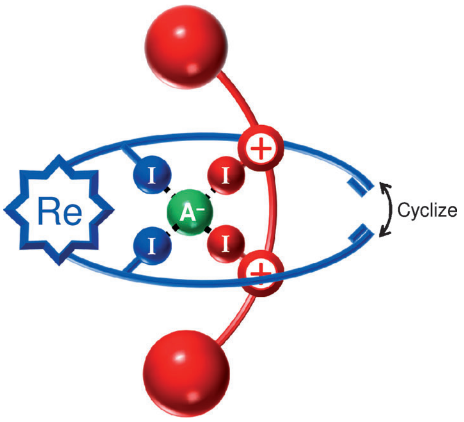

Figure 1. Anion-templated assembly to be used for the synthesis of the target all-halogen bonding rotaxane.

The rhenium(I) bipyridyl macrocycle precursor **5** was prepared using the stepwise procedure shown in Scheme 1. The allyl-appended amine **1**[15] was converted into the azide

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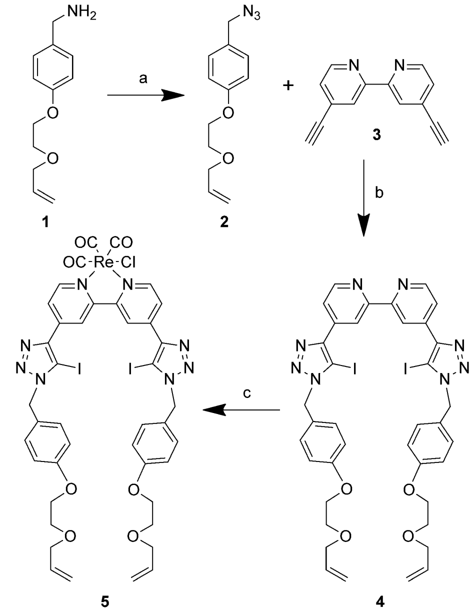
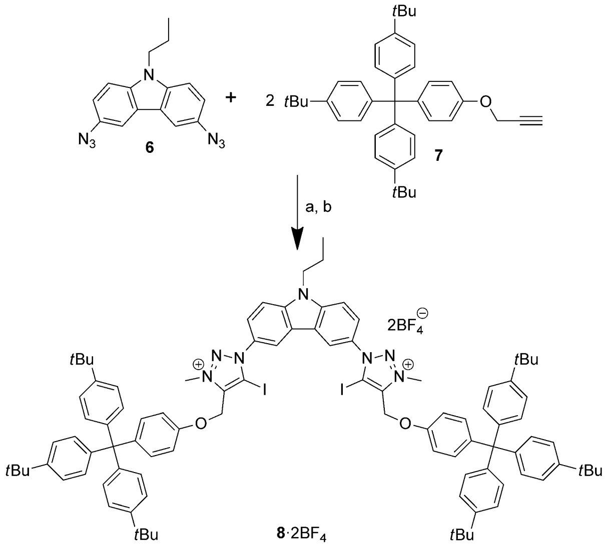
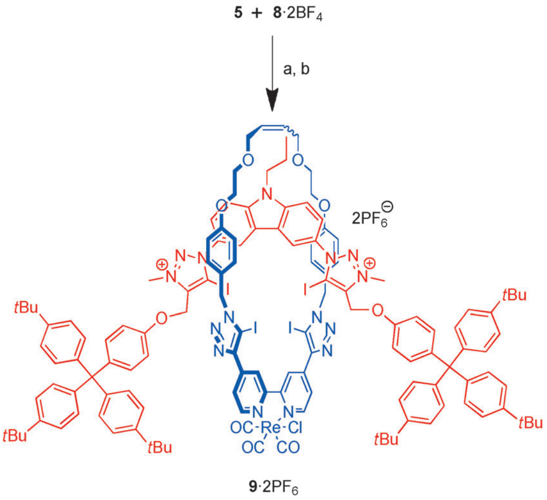


Scheme 1. Synthesis of the acyclic precursor **5**. Reagents and conditions: a) imidazole sulfonylazide hydrogensulfate, K_2CO_3, $CuSO_4{\cdot}5\,H_2O$, methanol, RT, 3 d (77%); b) NaI, $Cu(ClO_4)_2{\cdot}6\,H_2O$, TBTA, DBU, THF, RT, 16 h (80%); c) $[Re(CO)_5Cl]$, $CHCl_3$, reflux, 3 d (75%). DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TBTA = tris(benzyltriazolylmethyl)amine, THF = tetrahydrofuran.



Scheme 2. Synthesis of the axle component $\mathbf{8}{\cdot}2\,BF_4$. Reagents and conditions: a) NaI, $Cu(ClO_4)_2{\cdot}6\,H_2O$, TBTA, DBU, THF, RT, 16 h (76%); b) Me_3OBF_4, CH_2Cl_2, 16 h (82%).



Scheme 3. Synthesis of the rotaxane $\mathbf{9}{\cdot}2\,PF_6$. Reagents and conditions: a) Stewart–Grubbs' catalyst (10 wt%), TBACl, CH_2Cl_2, 3 d (7%); b) anion exchange for PF_6^- achieved by repeated washing with aqueous NH_4PF_6 (0.1 м). TBACl = tetra-*n*-butylammonium chloride.

derivative **2** using the hydrogensulfate salt of imidazole sulfonylazide in the presence of K_2CO_3 and a catalytic amount of $CuSO_4{\cdot}5\,H_2O$[16] in 77% yield. Reaction of two equivalents of **2** with 4,4′-diethynyl-2,2′-bipyridine (**3**) in the presence of $Cu(ClO_4)_2{\cdot}6\,H_2O$, NaI, DBU, and TBTA,[17] gave bis(iodotriazole) bipyridyl compound **4** in 80% yield. Complexation with $[Re(CO)_5Cl]$ afforded the macrocycle precursor **5** in a yield of 75%.

The axle **8** was synthesized as shown in Scheme 2. The bis(azido)carbazole **6** was reacted with two equivalents of the alkyne-appended stopper **7** in a one-pot reaction[17] to form the neutral bis(iodotriazole) axle precursor in 76% yield, which was methylated to form $\mathbf{8}{\cdot}2\,BF_4$ in a yield of 82%.

The rotaxane $\mathbf{9}{\cdot}Cl{\cdot}BF_4$ was synthesized by Stewart–Grubbs'-catalyzed RCM reaction of an equimolar mixture of **5** and $\mathbf{8}{\cdot}2\,BF_4$, in dry dichloromethane in the presence of one equivalent of the TBACl template (Scheme 3). After purification by preparative silica TLC, the rotaxane was anion exchanged with aqueous NH_4PF_6, to give the rotaxane $\mathbf{9}{\cdot}2\,PF_6$ in 7% overall yield upon isolation.[18] The rotaxane synthesis was undertaken in the absence of chloride and although evidence of rotaxane formation was observed by electrospray mass spectrometry, no interlocked product could be isolated, which suggests the rotaxane is only formed in negligible yield in the absence of a chloride anion template. The rotaxane $\mathbf{9}{\cdot}2\,PF_6$ was characterized by ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, and ^1H-^1H ROESY NMR spectroscopy (see the Supporting Information).

The interlocked nature of the rotaxane $\mathbf{9}^{2+}$ was confirmed by single-crystal X-ray diffraction analysis (Figure 2).[19] Single crystals of the chloride salt of $\mathbf{9}^{2+}$ were obtained by slow evaporation of a 45:45:10 $CDCl_3/CD_3OD/D_2O$ mixed solvent solution of the rotaxane with excess TBACl. The structure clearly shows convergent halogen bonding between the iodotriazoles and iodotriazoliums, and the two Cl^- counterions (Figure 3). One of the Cl^- anions is bound by three halogen bond donors within the rotaxane cavity, two from the macrocycle and one from the minor component of the disordered axle, while the other halide counterion forms a halogen bond to the remaining axle iodotriazolium [$d_{I\cdots Cl} = 2.98$–$3.13(6)$ Å]. The halogen bond distances are all significantly lower than the sum of the van der Waals radii,[20] with $\%\,vdW_{I,Cl} = 79$–85%, thus confirming the strength of these halogen bonding interactions.[21]

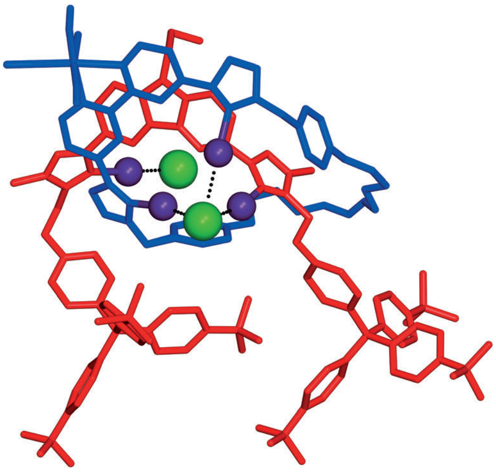


Figure 2. Single-crystal structure of rotaxane **9**·2 Cl, displaying the interlocked topology and halogen bonds. Green chloride, purple iodine. Solvent molecules, hydrogen atoms and disorder have been omitted for clarity.

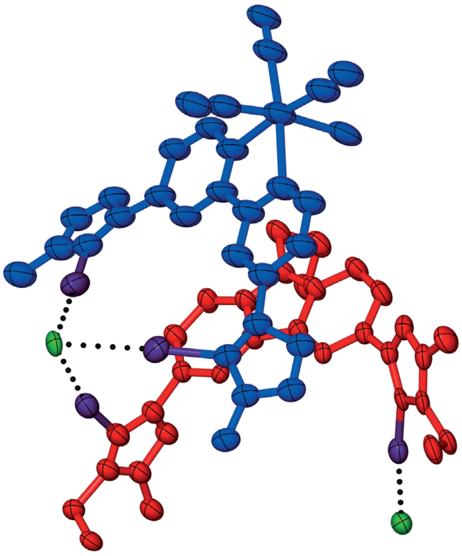


Figure 3. Close-up of the receptor portions of the single-crystal structure of **9**·2 Cl. Thermal ellipsoids are displayed at 30 % probability.

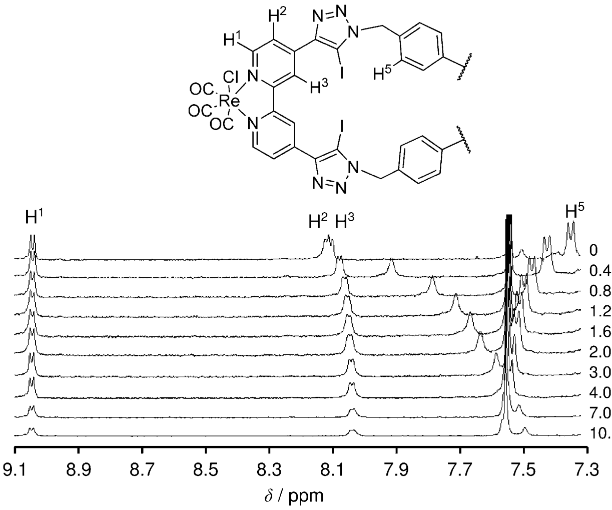


Figure 4. ^{1}H NMR spectral changes observed in **9**·2 PF_6 in 45:45:10 $CDCl_3/CD_3OD/D_2O$ after addition of up to 10 equivalents of chloride ions. Only macrocycle peaks are visible in the spectral range shown.

Preliminary ^{1}H NMR anion-binding studies of **9**·2 PF_6 were first undertaken with TBACl in 45:45:10 $CDCl_3/CD_3OD/D_2O$ (Figure 4). Importantly, significant perturbations were observed in the chemical shifts of the rotaxane's macrocycle component protons H^3 and H^5, which are proximal to the XB donor iodotriazole groups, which suggests the halide anion is being bound within the interlocked cavity. Downfield shifts in the external carbazole protons of the axle were also noted (see the Supporting Information). The changes in the chemical shift of the proton H^5 were monitored, and a 1:1 stoichiometric association constant of 1030(30) M^{-1} was determined using the WinEQNMR2 software.[22] An analogous ^{1}H NMR titration experiment with TBAI determined an association constant for iodide of $K_a > 10^4\,\text{M}^{-1}$, thus indicating strong selective binding of the larger halide anion.[23]

Luminescence spectroscopy was used to investigate the anion sensing potential and to determine anion binding affinities of **9**·2 PF_6 in H_2O/CH_3CN solvent mixtures[23] by monitoring the intensity of MLCT emission band of the rotaxane's rhenium(I) bipyridyl macrocycle upon the addition of a variety of anions. Upon excitation at $\lambda_{ex} = 400$ nm the emission spectrum of the rotaxane exhibited the expected MLCT emission band of the rhenium(I) bipyridyl center at $\lambda_{em} = 583$ nm ($c = 1 \times 10^{-5}$ M in 10 % H_2O/CH_3CN). In 10 % H_2O/CH_3CN, the addition of up to 20 equivalents of Cl^- resulted in an initial increase in the intensity of the rotaxane's MLCT emission band, followed by a subsequent decrease in the intensity (see Figure S7 in the Supporting Information). Analogous behavior was observed upon addition of Br^-. Addition of I^- gave the most notable optical response, producing significant fluorescence quenching of the rotaxane.[24] In contrast, the oxoanions AcO^- and $H_2PO_4^-$ did not noticeably affect the emission properties of $\mathbf{9}^{2+}$, suggesting no binding. The data were modelled using Specfit[25] to determine 1:1 and 1:2 stoichiometric association constants (Table 1) which reveal strong binding of the halides with a selectivity preference of $I^- > Br^- \gg Cl^-$.

Considering the strong halide anion binding affinities exhibited by **9**·2 PF_6 in the 10 % water/solvent mixture, analogous titrations were undertaken with a wider range of anions in aqueous media containing a higher water content (20 % and 50 %). Similar luminescence sensing behavior was observed upon addition of the halides (Figure 5). Importantly, Table 1 shows that despite the increased water content, the association constants for Cl^-, Br^-, and I^- remain substantial in magnitude, especially for the heavier halides. Furthermore, it is noteworthy that the halides are bound preferentially over all the oxoanions and fluoride. Indeed, only HCO_3^- and SO_4^{2-} demonstrated any evidence of binding, which was much weaker than the aforementioned halides. These data indicate

Table 1: Anion association constants for **9**·2 PF_6 in H_2O/CH_3CN solvent mixtures at 298 K.

Anion[b]	10% H_2O[a] $\log(K_{11})$[c]	$\log(K_{12})$[c]	20% H_2O $\log(K_{11})$[c]	$\log(K_{12})$[c]	50% H_2O $\log(K_{11})$[c,d]
F^-	–		n.b.		–
Cl^-	4.04	2.81	3.49	2.63	2.71
Br^-	5.02	3.42	4.49	2.87	3.76
I^-	5.14	3.74	4.95	3.61	4.38
AcO^-	n.b.		n.b.		–
$H_2PO_4^-$	n.b.		n.b.		–
HCO_3^-	–		< 2.0[e]		–
NO_3^-	–		n.b.		–
ClO_4^-	–		n.b.		–
SO_4^{2-}	–		< 1.0[e]		–

[a] Excitation wavelength: $\lambda_{ex} = 400$ nm for 10% and 20% H_2O; $\lambda_{ex} = 390$ nm for 50% H_2O. [b] Anions were added as their tetrabutylammonium salts, except HCO_3^-, which was added as the tetraethylammonium salt. [c] Errors < 10%. [d] No evidence of 1:2 binding for Cl^- or Br^-. K_{12} values were not calculated for I^- because of precipitation problems at greater than 16 equivalents of I^-. [e] The binding strength was too low to accurately determine an association constant. n.b. = no evidence of binding.

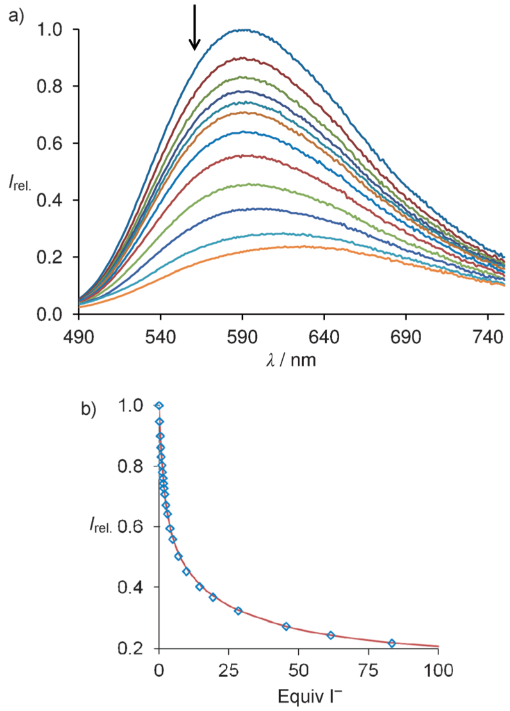


Figure 5. a) Changes in the emission spectra of **9**·2 PF_6 (1×10^{-5} M in 20% H_2O/CH_3CN) upon addition of iodide. b) Change in the emission intensity at $\lambda = 590$ nm upon addition of iodide. Points denote data and the line corresponds to the binding model.

that the halogen bond donor cavity of the rotaxane is of complementary shape and size for the spherical halide guests, whereas oxoanions are too large and are of the wrong geometry to penetrate the interlocked host's binding domain.[26]

In summary, the first anion-templated all-halogen bonding rotaxane has been prepared. A photoactive rhenium(I) bipyridyl bis(iodotriazole) macrocycle is combined with a bis(iodotriazolium)-functionalized carbazole axle component to produce a rotaxane host system, which is capable of selectively sensing the halide anions Cl^-, Br^-, and I^- over a range of oxoanions in up to 50% H_2O/CH_3CN solvent mixtures, as determined by luminescence spectroscopy. These observations together with solid-state structural evidence imply that the rotaxane's unique preorganized halogen bond donor host binding cavity complements spherical halide guest species. Indeed, this halogen bonding rotaxane is the most potent interlocked host system for halide recognition reported to date.[12a] The integration of various halogen bond donor groups into interlocked host structural frameworks for sensing is ongoing in our laboratories.

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[18] Significant quantities of the ring-closed macrocycle product were also isolated. No significant improvement in the yield of isolated rotaxane was observed using iodide (added as TBAI) instead of chloride.

[19] Single-crystal diffraction data for were collected at low temperature with synchrotron radiation ($\lambda = 0.68890$ Å) using beamline I19 (EH1) at the Diamond Light Source (H. Nowell et al., *J. Synch. Rad.* **2012**, *19*, 435–441). The data were collected using CrystalClear (Rigaku) and reduced using CrysAlisPro (Oxford Diffraction/Agilent Technologies). The structure was solved with SuperFlip [L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786–790] and refined using full-matrix least-squares within CRYSTALS. (P. W. Betteridge et al., *J. Appl. Crystallogr.* **2003**, *36*, 1487; R. I. Cooper, A. L. Thompson, D. J. Watkin, *J. Appl. Crystallogr.* **2010**, *43*, 1100–1107; P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194–201; A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13) as per the Supporting Information (CIF). The macrocycle was modelled as being disordered over two positions with near-equal occupancy. Furthermore, one of the axle triazolium units is disordered over two positions antiparallel to one another, pointing either toward, or away from the cavity-bound Cl$^-$ (see Supporting Information for further details). CCDC 993328 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

[21] It is noteworthy that the solid-state structure also provides evidence of a weak C–H···Cl interaction from the methyl group of the disordered axle iodotriazolium group, with a C···Cl distance of 3.7638(2) Å, and an angle of 166.52°.

[22] M. J. Hynes, *J. Chem. Soc. Dalton Trans.* **1993**, 311–312.

[23] Unfortunately it was not possible to conduct further ^{1}H NMR titration experiments in the same water/acetonitrile solvent mixtures as used for the luminescence titration experiments because of solubility limitations of the rotaxane at the concentrations required for ^{1}H NMR analysis.

[24] A qualitative study was conducted on a neutral XB 4,4′-bis(iodotriazole)-2,2′-bipyridyl rhenium(I) acyclic model receptor in 10% water/acetonitrile, which demonstrated no change in the MLCT emission behavior upon addition of iodide, thus implying that there was no binding. This confirms that the quenching behavior observed with the rotaxane is a consequence of iodide binding within the interlocked host's cavity.

[25] Specfit v. 2.02 ed., Spectrum Software Associates Chapel Hill, NC, USA, **1997**.

[26] The anion association constants obtained for the rotaxane are significantly higher than those determined for acyclic systems based on the bis(iodotriazolium)carbazole axle motif, which displayed the selectivity trend Cl$^-$ > Br$^-$ > I$^-$. These results will be published as part of a future manuscript.