Rapid Iron(III)–Fluoride-Mediated Hydrogen Atom Transfer

Chakadola Panda, Lorna M. Doyle, Robert Gericke, and Aidan R. McDonald*

Abstract: We anticipate high-valent metal–fluoride species will be highly effective hydrogen atom transfer (HAT) oxidants because of the magnitude of the H–F bond (in the product) that drives HAT oxidation. We prepared a dimeric Fe(III)(F)–Fe(III)(F) complex (1) by reacting [Fe(III)(NCCH3)3(TPA)][ClO4]2 (TPA = tris(2-pyridylmethyl)amine) with difluoro(phenyl)-2-fluoro-iodane (difluoroiodobenzene). 1 was a sluggish oxidant, however, it was readily activated by reaction with Lewis or Brønsted acids to yield a monomeric [Fe(F)(TPA)(F)(X)]+ complex (2) where X = F/OTf. 1 and 2 were characterized using NMR, EPR, UV/Vis, and FT-IR spectroscopies and mass spectrometry. 2 was a remarkably reactive Fe(III) reagent for oxidative C–H activation, demonstrating reaction rates for hydrocarbon HAT comparable to the most reactive Fe(III) and Fe(IV) oxidants.

Introduction

The functionalization of alkanes via C–H bond activation is critically important from industrial and environmental perspectives.[1] Owing to their relatively strong C(sp2)–H bonds, practical large-scale synthetic applications of oxidative C–H activation have been hindered.[2] Nature has evolved to perform such transformations by employing iron enzymes under ambient conditions. High-valent iron–hydroxide (Fe–OH) or iron–oxo (Fe=O) oxidants drive such reactions both in the reduced metal and the corresponding hydrohalic acid (H–X). The magnitude of H–X bond dissociation energy (BDEH–X) would thus provide the driving force for C–H activation. The BDEH–X values for H–F/Cl are considerably higher than those measured for Fe–OH species so far (BDEH–X = 135 kcal mol–1; BDEH–F = 103 kcal mol–1).[3] This discussion omits the role of the Fe–O/X bond in the oxidant, which will also affect the thermodynamic driving force for C–H activation. In the current manuscript we focus on the role of the magnitude of BDEH–X in the product. Metal–fluoride oxidants thus appear to be ideal candidates to activate strong C–H bonds at high rates. Indeed, we found that substituting F for Cl in Ni(II)–X increased the rate of reaction by three orders of magnitude.[6] Doyle and co-workers demonstrated Ni–Cl complexes were effective HAT oxidants under irradiation,[7] while Nocera and co-workers demonstrated Fe(III)–Cl species yielded a chlorine radical (Cl) that acted as an HAT oxidant.[8] High-valent metal–halides are thus effective oxidants that could activate the strongest of C–H bonds under the right conditions.

An abundance of synthetic Fe(IV)=O oxidants has now been accumulated,[3a,b,4,9] providing insight into their physical and reactivity properties.[1b,2,3b,5] Fe(III) oxidants that perform oxidative activation of C–H bonds are rare[13] with most studies limited to synthesis and electronic structure determination.[12] Several complexes of the formula [Fe(III)(OR)(L)] (L = ligand and R = H/alkyl) have been targeted as models of lipoygenase but were shown to be sluggish HAT oxidants.[13] A recent Fe(III)=O identified in the gas phase was incapable of activating C–H bonds.[14] Very few Fe(III) oxidants can match Fe(IV)=O species in terms of the rates of C–H activation and the strength of the C–H bond that they can activate. Herein, we present an Fe(III)=F complex that reacts at rates comparable to Fe(IV)=O oxidants and outperforms the majority of Fe(III) oxidants reported to date.

Results and Discussion

µ-Fluorido-diiron(III) complex 1 was synthesized by treating [Fe(III)(NCCH3)3(TPA)][ClO4]2 (TPA = tris(2-pyridylmethyl)amine) with two molar equivalents of difluoro- (phenyl)-2-fluoro-iodane (difluoroiodobenzene) at room temperature in CH3CN (Scheme 1). Pale yellow crystals were
isolated by diffusing diethyl ether (Et₂O) into the reaction mixture giving 1 in 45% yield. 1 crystallized in the triclinic crystal system as a tricationic species with three ClO₄⁻ counter anions (Figure 1).[15] The μ-F-atom serves as the center of inversion and the Fe₁-F₂-Fe¹⁺ angle was 180°. The μ-F-Fe bonds (Fe₁-F₂ = 1.957(1) Å) were slightly longer than the terminal Fe-F bonds (Fe₁-F₁; 1.826(2) Å). This is consistent with previous observations distinguishing terminal- (1.834(2) Å[16]) and μ-F (1.944(3) Å) atoms.[17]

The ¹H NMR of 1 displayed seven paramagnetically shifted signals (Figure S3). Eleven resonances would be expected based on the crystallographically determined structure, however, given the paramagnetic ion effect, it is expected that some resonances are overlapping/not identifiable. Similar ¹H NMR spectra have been obtained for a structurally analogous Fe⁺(OH)-O–Fe⁺(OH) complex supported by the same ligand.[18] An Evans’ method magnetic moment measurement of 5.2 Bohr magnetons was obtained for 1 indicating the presence of four unpaired electrons in the ground state. The ¹³F NMR spectrum of 1 showed a broad single signal at δ = −179 ppm (Figure S4). The X-ray structure of 1 indicated two distinct F-atom environments, one would thus expect two resonances in the ¹³F NMR, although the paramagnetic ion may cause these signals to coalesce or not be visible at all. NMR spectroscopy confirms that 1 is pure in solution and indicates that the Fe–F interaction remains intact.

The perpendicular mode X-band EPR spectrum of 1 displayed no signal, suggesting a diamagnetic species where both the Fe⁴⁺ are antiferromagnetically coupled to each other (Figure S5). Therefore, we concluded that 1 remained as a dimer in solution. ESI-MS demonstrated two fragments at m/z = 182.54 and 384.08, which can be assigned to the dication [Fe⁴⁺(F)(TPA)]²⁺ and monocation [Fe⁴⁺(F)(TPA)]⁺, respectively (Figures S6–S8). We postulate that 1 was not stable under the ESI-MS instrumental conditions and underwent fragmentation into the mononuclear species. Similar ESI-MS-induced fragmentation of μ-oxo-diiron(IV) was previously reported.[19] The Fourier-transform infra-red (FT-IR) spectrum of 1 showed multiple signals including ʋ = 655, 410 cm⁻¹ that could be assigned to the bridging and terminal νₐ,F–F stretches (Figure S9). Terminal νₐ,F–F have been reported from ʋ = 400–500 cm⁻¹, while asymmetric νₐ,F–F,Fe are proposed to fall in the higher energy region ʋ = 650 cm⁻¹.[17b,20] We assign the peak at ʋ = 655 cm⁻¹ to the asymmetric νₐ,F–F,Fe stretch and the peak at ʋ = 410 cm⁻¹ to the terminal νₐ,F–F based on the above literature precedent and further experimentation below.

Previous work on Fe⁴⁺–F complexes has been limited to their electronic, structural, or magnetic properties.[17c,21] To the best of our knowledge, no such compounds have been explored for oxidation reactivity. We explored the reactivity of 1 as an oxidant towards C(sp³)–H bond activation. The reaction between 1 and 1,4-cyclohexadiene (CHD, 10 equiv., 25°C, Figure S10) was followed by electronic absorption spectroscopy using the shoulder at λ = 310 nm (Figure S2). This feature decreased slightly with a concomitant increase at λ = 400 nm (formation of Fe⁴⁺ precursor; Figure S11), indicating a reaction may have occurred. The product of this reaction was benzene, obtained in 6% yield with respect to 1 according to ¹H NMR (Figure S12). The observation of benzene indicated 1 was a capable PCET oxidant. The very slow rate of oxidation, incomplete reaction, and the low yields of product led us to explore methods to activate this promising oxidant further.

We postulated that the addition of Sc⁴⁺(OTf)₃ (OTf = trifluoromethanesulfonate, triflate) might activate 1 to be a more effective PCET oxidant. It has been shown that the use of a Lewis acid can promote PCET reactivity.[22] Furthermore, the Lewis acid cleavage of a bis-μ-O-Mn⁴⁺Mn⁴⁺ complex to form a mononuclear Mn⁴⁺=O resulted in fast epoxidation of olefins.[23] Addition of Sc⁴⁺(OTf)₃ (2 equiv.) to a solution of 1 (0.1 mM, CH₂CN, 0°C) generated a new species (2) with a band at λ = 375 nm (Scheme 1 and Figure 2). A titration of Sc⁴⁺(OTf)₃ with 1 suggested that two equivalents were necessary to obtain 2 in maximum yield. This equates to an Fe:Sc ratio of 1:1 in 2, indicating that Sc⁴⁺(OTf)₃ may have broken the dimer to yield a monomer. 2 was stable at 0°C (Figure S13), however, attempts to isolate single crystals of 2 for X-ray diffraction measurements were unsuccessful.

Brønsted acids are also known to activate M=O oxidants in an analogous fashion to Lewis acids.[22] We reacted 1 (0.1 mM, CH₂CN, 0°C; Figure S14) with a strong Brønsted acid, HClO₄ (2 equiv.), and observed very similar UV/Vis spectral changes as observed when Sc⁴⁺ was added (i.e. the formation of 2) but in lower yield. Additionally, 2 generated
from HClO, decayed relatively rapidly with respect to 2 generated from Sc\textsuperscript{III} (Figure S14). We conclude that both Lewis acids and Brønsted acids cause the break-up of dimer \textbf{1} to yield a monomeric species 2. Lewis acids can react with adventitious water present in a reaction media thereby releasing strong Brønsted acids (HOTf for Sc\textsuperscript{III}(OTf)) which may be responsible for the formation of 2.\textsuperscript{[23]} Hence, we performed the reaction of 1 with Sc\textsuperscript{III}(OTf), in the presence of 2\% v/v water. Firstly, \textbf{1} did not react with water (a weak Brønsted acid). Secondly, we did not observe the formation of 2 (Figure S15), and therefore, we rule out the involvement of any adventitious water in the reaction media.

The X-band EPR spectrum of 2 exhibited a rhombic signal with $g = 2.70, 2.40, \text{ and } 1.53$ (Figure 3). The average $g$-value $g_a = 2.21$ is indicative of a metal-based radical and such $g$-values have previously been ascribed to mononuclear $S = 1/2$ Fe\textsuperscript{III} species.\textsuperscript{[24]} For example, several heme and non-heme ligand supported $S = 1/2$ Fe\textsuperscript{III} compounds with similar $g$-values to that of 2 have also been reported (Table S1).\textsuperscript{[25]} Spin quantification was performed using 2,2,6,6-tetramethyl-1-piperidinylxoyl (TEMPO) as a reference (see Supporting Information for details), showing the yield of 2 was close to quantitative ($75\% \pm 10\%$ with respect to \textbf{1}). EPR thus indicated the conversion of \textbf{1} to 2 represented the formation of a mononuclear $S = 1/2$ Fe\textsuperscript{III} species in high yields.

$^1$H NMR analysis of 2 displayed eight paramagnetically shifted signals (Figure S16). For a mononuclear [Fe(TPA)] complex, eleven resonances would again be expected. In comparison with \textbf{1}, the resonances for 2 were shifted to higher field, while they are also remarkably similar to other mononuclear $S = 1/2$ Fe\textsuperscript{III} complexes supported by polypyridine ligands.\textsuperscript{[26]} The spectrum was consistent with 2 being a pure mononuclear Fe\textsuperscript{III} complex supported by TPA and did not contain a mixture of paramagnetic species. $^{39}$Fe NMR analysis showed only one signal at $\delta = -79$ ppm which can be assigned to the OTf counterion (derived from Sc\textsuperscript{III}(OTf), Figure S17) and no signals that could be associated with the Fe\textsuperscript{III}–F moiety, presumably because of the paramagnetic ion effect.

ESI-MS analysis of 2 showed peaks at $m/z = 182.54$ and 514.03 which were assigned to [Fe(TPA)(F)]$^+$ and [Fe(TPA)-(F)(OTf)]$^+$ (Figure S18). Given the nature of the anions in solution, either F$^-$ or OTf could be the counterions for these ions in 2. An ESI-MS of 2 generated from HClO displayed two major peaks at $m/z = 464.03$ and 543.98 corresponding to the ions [Fe(TPA)(F)(OClO$^-$)]$^+$ and [Fe(TPA)(OClO$^-$)]$^+$, respectively (Figures S19–S21). These results lead us to conclude that 2 contains an $\text{Fe}^{III}$(TPA)(X)$^+$ core structure where X is either F or OTf. The X anions could be bound to the Fe or could act as non-coordinating anions. Finally, the ESI-MS of 2 generated from Sc\textsuperscript{III}(OTf)$^+$ showed a dicaticonic peak at $m/z = 438.05$ which can be assigned to a scandium adduct with the formulation [Fe(TPA)(F)$_2$Sc(OTf)]$^{2+}$ (Figures S18, S22). Rational formal metal oxidation states for this ion would be $\text{Fe}^{IV/IV}$Sc$^{III}$ or $\text{Fe}^{III/IV}$Sc$^{IV}$ which are not in agreement with our EPR analysis of 2. We therefore assume this species is derived from $[\text{Fe}^{III}(\text{TPA})(\text{F})_2\text{Sc}(\text{OTf})]^{2+}$ and is formed in the mass spectrometer. ESI-MS analysis indicates that the elemental formulation of 2 is best defined as $[\text{Fe}^{III}(\text{TPA})(\text{F})_2\text{OTf}]^+$. A comparison of the FT-IR of 1, 2, and Sc\textsuperscript{III}(OTf)$^+$, revealed a prominent peak at $\tilde{\nu} = 655$ cm$^{-1}$ (putative asymmetric ν(Fe–F–Fe)) for 1 was absent in 2 (Figures S23, S24). This indicates the cleavage of a μ-Fe–F–Fe moiety leading to a mononuclear species. Additionally, the putative terminal ν(Fe–F) peak at $\tilde{\nu} = 410$ cm$^{-1}$ for 1 was shifted to $\tilde{\nu} = 417$ cm$^{-1}$ for 2. This may be associated with a Sc$^{III}$ interaction with the F-atom in the newly formed terminal Fe–F bonds in 2 or simply a break-up of the dimer causing a modest shift in Fe–F stretch. We conclude that Sc\textsuperscript{III}(OTf)$^+$ cleaved the dimeric structure of 1, yielding 2 with the formula $[\text{Fe}^{III}(\text{TPA})(\text{F})_2\text{OTf}]^+$. X = F/OTf, this structure is supported by EPR, NMR, FT-IR, and ESI-MS analyses.

**Hydrogen atom transfer reactivity by 2**: In comparison to \textbf{1}, \textbf{2} reacted readily with CHD. We explored the reactivity of \textbf{2} generated from Sc\textsuperscript{III}(OTf), because when \textbf{2} was generated with HClO, it displayed short lifetimes making reactivity/kinetic studies unreliable (Figure S25). Upon addition of CHD (10 equiv.), the chromophore at $\lambda = 375$ nm converted to a broader absorption feature with $\lambda = 380$, 400 nm (Figure 4).

![Figure 2](image1) UV/Vis spectra for the addition of Sc\textsuperscript{III}(OTf) to a solution of 1 (black trace, 0.1 mM, CH$_3$CN, 0°C) to yield 2 (blue trace). Inset: Time trace of absorbance change at $\lambda = 375$ nm during the sequential titration of Sc\textsuperscript{III}(OTf) (1 equiv. per tier). $*$ = the point when each tier of Sc\textsuperscript{III}(OTf) was added.

![Figure 3](image2) X-band EPR spectrum of 2 (black trace) obtained from the reaction of 1 (20 mM) and Sc\textsuperscript{III}(OTf), in CH$_3$CN. Measured at 77 K, 9.2 GHz microwave frequency, 1.99 mW microwave power, and 0.3 mT modulation amplitude. Simulated spectrum for 2 (red trace; $g = 2.70, g_\perp = 2.40, g_\parallel = 1.53$).

![Figure 4](image3) Time trace of absorbance change at 375 nm during the sequential titration of Sc\textsuperscript{III}(OTf) (10 equiv.), the chromophore at 375 nm converted to a broader absorption feature with 380, 400 nm (Figure 4).
The species that formed was postulated to be the precursor complex \( \text{Fe}^{II}([\text{NCH}_{3}]_{3})(\text{TPA}) \) by a comparison of their absorption spectra (\( \lambda = 380, 400 \text{ nm} \); Figure S11). This would indicate reduction of the \( \text{Fe}^{III} \) in 2 and loss of fluoride ligand, presumably as \( \text{H–F} \). Pseudo-first order rate fitting for the decay of 2 was applied by monitoring the changes in \( \lambda = 400 \text{ nm} \) over time, to obtain the rate of the reaction (\( k_{\text{obs}} = 9.7 \times 10^{-3} \text{ s}^{-1} \)). A linear dependence of the \( k_{\text{obs}} \) with respect to [CHD] was observed yielding a plot with a slope of 0.15 M\(^{-1}\)s\(^{-1}\) (Figure S26). This value corresponds to the reaction second-order rate constant \( k_2 \). The product of CHD oxidation was determined by \( ^1H \) NMR to be benzene (42% yield; Figure S27). Yields of products were calculated based on one electron oxidation per iron atom (two iron atoms are consumed per molecule of benzene formation). The observed product is typical of PCET-mediated oxidation of CHD, where the removal of two formal hydrogen atoms yields benzene. 2 was thus a capable PCET oxidant of hydrocarbons.

We expanded the substrate scope by reacting 2 with xanthene, 9,10-dihydroanthracene (DHA), triphenylmethane, and cyclohexene. The formation of \( \text{Fe}^{II}([\text{NCH}_{3}]_{3})(\text{TPA}) \) was observed in all cases according to UV/Vis (Figures S28–S31). For all substrates we measured \( k_{\text{obs}} \) and \( k_2 \) values (Figures S22–S31). Product analyses for each substrate were performed using gas chromatography (GC), NMR, or ESI-MS (see Supporting Information for details; Figures S32–S35). In no case did we observe fluorinated products, indicating that while 2 is a capable PCET oxidant, fluoride rebound did not occur. Product analysis indicated initial PCET oxidation of all substrates prior to conversion to other products.

A kinetic isotope effect (KIE) value of 2.1 was measured for 2 using DHA and DHA-D\(_8\), (\( k_2 = 1.45 \) and 0.71 M\(^{-1}\)s\(^{-1} \), respectively, Figure S36). This is within the classical range (2–7) and indicates that either a hydrogen atom or a proton was involved in the rate-limiting step.\(^{[26,28]} \) This further supports the mechanism that the rate-determining step is a PCET process. Similarly low KIE values were recently observed for high-valent metal oxidants, when there is no terminal oxo ligand.\(^{[26,28]} \)

We obtained the activation parameters (\( \Delta H^* = 14 \pm 1 \text{ kcal mol}^{-1} \), \( \Delta S^* = -17 \pm 4 \text{ cal mol}^{-1} \text{K}^{-1} \)) for C–H activation by 2 by performing an Arrhenius plot (\( 10^0 \text{ to } 10^3 \text{℃} \)) for the reaction between 2 and CHD (Figure S37). These values are within the range for high-valent oxidants that perform PCET oxidation, in particular other high-valent metal–halides.\(^{[30]} \)

Such large and negative \( \Delta S^* \) values indicate that the HAT entity is the Fe–F complex rather than an F radical. Mayer and co-workers have demonstrated that HAT reactions involving transition metal complexes typically display large reorganizational energy resulting in significant entropic (\( \Delta S^* \approx 0 \)) contributions.\(^{[29]} \) In contrast, HAT reactivity by simple radicals (X\(^* \)) involves minimum reorganisation energy and hence \( \Delta S^* \) would be close to zero.\(^{[30]} \)

Having established that 2 was a capable PCET oxidant, we attempted to understand the mechanism of PCET oxidation by 2. A plot of the free energy of activation (\( \Delta G^* \)), calculated from the respective \( k_2 \) values using the Eyring equation, against the substrate BDE\(_{\text{C–H}}\) can provide mechanistic insight (Figure 5). A slope of 0.27 was obtained which points towards a HAT or concerted proton and electron transfer (CPET) mechanism as per Marcus theory.\(^{[31]} \) For an ideal HAT or CPET, a slope of 0.5 would be expected and for a non-concerted PCET mechanism a slope close to one is expected.\(^{[32,33]} \) Although the measured slope here is slightly less than the expected 0.5, there have been several reports of similar deviations for a HAT mechanism, and the value is comparable for those obtained for other high-valent metal–halides.\(^{[34–36]} \)

\( \text{Fe}^{III}–\text{F} \) is thus a mononuclear \( \text{Fe}^{III}–\text{F} \) oxidant that readily breaks C–H bonds through a HAT mechanism. \( \text{Fe}^{II}([\text{NCH}_{3}]_{3})(\text{TPA}) \) was identified as the metal-based product of these reactions, leading us to conclude that H–F was the other product. We postulate that the strength of the H–F bond provides the driving force for oxidative C–H activation. As stated above, \( \text{Fe}^{III} \) oxidants that perform oxidative activation of C–H bonds are rare. 2 is a remarkably efficient oxidant when compared to well-established \( \text{Fe}^{III} \)-OR (R = H, alkyl) and \( \text{Fe}^{IV}–\text{O} \) oxidants (Table 1). In the oxidation of DHA, 2 displayed enhanced or comparable reactivity with the most reactive \( \text{Fe}^{III} \) oxidants reported to date, and compares well with both \( S = 1 \) and \( S = 2 \).
Table 1: Comparison of rate constants for the oxidation of DHA by Fe oxidants.

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<th>Complexes</th>
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<th>$T$ [°C]</th>
<th>Ref.</th>
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<td>$[Fe^{III}(OCH_3)(py)]^{II}$</td>
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<td>25</td>
<td>[11]</td>
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<td>[13a]</td>
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<tr>
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<td>50</td>
<td>[13b]</td>
</tr>
<tr>
<td>$[Fe^{III}(OH)(OH_2)(py)(Pz)]^{IV}$</td>
<td>73</td>
<td>20</td>
<td>[13c]</td>
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<td>18</td>
<td>25</td>
<td>[33a]</td>
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<td>[34]</td>
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<td>$[Fe^{II}(O)(TMG)(tren)]^{II}$</td>
<td>0.09</td>
<td>$-$</td>
<td>[35]</td>
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</table>

[a] $py = 2,6$-bis(2-pyridyl)methoxymethane; pyridine; $Hbct = N,N,N'$-tetakis(2-benzimidazolyl-methyl)orthodiamine-trans-cyclohexane; $Pz =$ tetramethyl-2,3-pyridino porphyrin; $N_{py} = N,N'$-bis(2-pyridyl)-N-bis(2-pyridyl)methylamine; $TMP =$ tetramethylporphinato; $TMG_{tren} = 1,1,1$-tris[2-[N2-1(1,1,3,3-tetramethylguanidino)]ethyl]-amine.

PCET oxidation. That it reacts at such high rates is an indicator that the strong H–F bond in the product is providing a high driving force for C–H activation.

**Conclusion**

We have presented the synthesis of an Fe$^{III}$(F)–F–Fe$^{II}$(F) complex (1) by reacting $[Fe^{II}(NCCCH_3)_3(TPA)]^{II}$ with difluoroiodobenzene. 1 presented sluggish reactivity in oxidative C–H activation. When Lewis or Brønsted acids were added to 1, a mononuclear Fe$^{III}$–F complex was obtained (2). 2 was a remarkably reactive Fe$^{III}$ reagent for oxidative C–H activation, demonstrating reaction rates for hydrocarbon oxidation comparable to the most reactive Fe$^{III}$ and Fe$^{IV}$ oxidants. A kinetic analysis suggested HAT was the mechanism of C–H activation. We postulate that the strength of the H–F bond in the product engenders the high reactivity observed in 2. Further development of high-valent metal-fluorides is underway in our laboratory with the anticipation that the strong H–F bond could yield exceptionally reactive oxidants.

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**Conflict of Interest**

The authors declare no conflict of interest.


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