

 Very Important Paper

# Streamlining Thionyl Tetrafluoride (SO<sub>F</sub><sub>4</sub>) and Pentafluoro-Oxosulfate [OSF<sub>5</sub>]<sup>−</sup> Anions Syntheses

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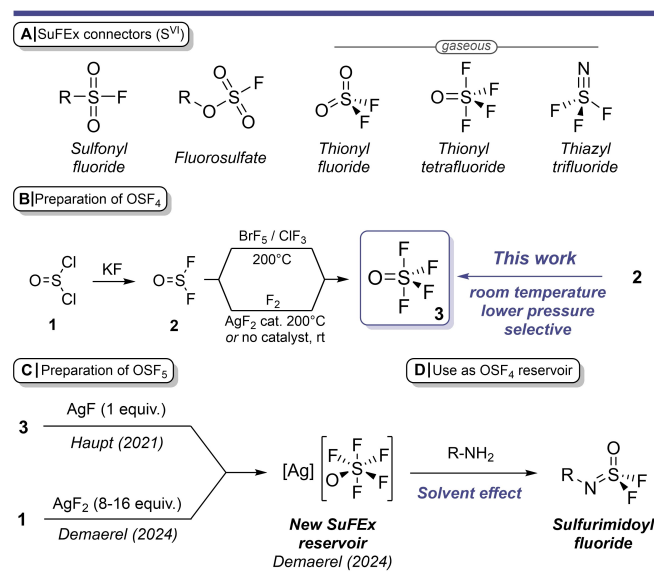
A one pot room temperature synthesis of thionyl tetrafluoride (SO<sub>F</sub><sub>4</sub>) from elemental fluorine (F<sub>2</sub>) and thionyl fluoride (SO<sub>F</sub><sub>2</sub>) is reported. The selective decagram scale process (100 mmol) allows a quantitative preparation of SO<sub>F</sub><sub>4</sub> with high purity. The solid-state structure has also been elucidated and compared with the reported gas phase one. The use of this reagent for the

formation of the emerging pentafluoro-oxosulfate [cat][OSF<sub>5</sub>] anions led to the preparation of multiple ion-pairs (cat=Ag, NEt<sub>3</sub>Me, PPN, PPh<sub>4</sub>) in different organic solvents. The SuFEX reservoir ability of this anion was studied and by tuning the solvent system, the reactivity of pure thionyl tetrafluoride was observed using Ag[OSF<sub>5</sub>] in THF and acetone.

## Introduction

The Sulfur<sup>VI</sup> fluoride exchange (SuFEX) is an efficient tool for the synthesis of sulfur containing molecules that uses the high S–F bond(s) reactivity.<sup>[1]</sup> Most SuFEX-related synthetic routes rely on the sequential formation of stable but reactive S(VI)-F intermediates acting as sulfuryl(VI) connectors (Figure 1.a).<sup>[2]</sup> Numerous examples were previously described from gaseous counterparts such as sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) that appeared as a promising reagent towards the formation of sulfonyl fluorides and fluorosulfates.<sup>[3]</sup> These monofluorinated connectors are easily isolated and able to undergo the addition of a supplementary organic moiety.

Accessing structural diversity required oxyfluoride intermediates obtained from versatile polyfluorinated connectors such as thionyl tetrafluoride<sup>[4,5]</sup> (SO<sub>F</sub><sub>4</sub>) or the poorly explored thiazyl trifluoride (NSF<sub>3</sub>).<sup>[6]</sup> The lack of modern methodology involving thionyl tetrafluoride (SO<sub>F</sub><sub>4</sub>) can be explained by the absence of suppliers, synthetic difficulty (Figure 1.b) combined with the fading away of gas handling in organic laboratory. However, recent examples showed the versatility of SO<sub>F</sub><sub>4</sub> as reagent for the preparation of valuable intermediates.<sup>[7]</sup> In addition, modern perfluoro-oxosulfate salts and complexes were recently brought up to date by Haupt from SO<sub>F</sub><sub>4</sub><sup>[8]</sup> as well as the gas free equivalent by Demaerel and co-workers (Figure 1.c).<sup>[9]</sup> Furthermore, these salts also found their place as SuFEX



**Figure 1.** a) Examples of sulfuryl connectors; b) Reported synthesis of thionyl halide; thionyl tetrafluoride and our work; c) Preparation of OSF<sub>5</sub>; d) SuFEX example from OSF<sub>5</sub>.

reagents acting as SO<sub>F</sub><sub>4</sub> reservoirs from an equilibrium displacement (Figure 1.d).

Due to our deep interest in the OSF<sub>x</sub> (x = 4, 5) chemistry, we herein report a safe and selective large-scale preparation of thionyl tetrafluoride to improve the reported procedure. Indeed, preparation of SO<sub>F</sub><sub>4</sub> was previously described from thionyl dihalide and involved the handling of highly reactive bromide pentafluoride (BrF<sub>5</sub>) or chlorine trifluoride (ClF<sub>3</sub>, Figure 1.b).<sup>[10]</sup> If the use of elemental fluorine (F<sub>2</sub>) appears as an excellent candidate, the direct reaction with thionyl fluoride (SO<sub>F</sub><sub>2</sub>) was previously highlighted only by means of catalyst such as silver(II) fluoride (AgF<sub>2</sub>) at high temperature and strong overpressure (Figure 1.b).<sup>[11]</sup> We also found a forgotten industrial synthesis by Ruff in 1964 with a moderate pressure but at room temperature that was not reproduced by their academic peer.<sup>[4]</sup> Finally, electrochemical fluorination of SO<sub>2</sub><sup>[12]</sup> and an interesting

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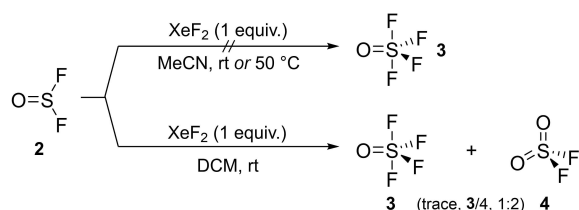
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fluorine free synthesis from sulfur tetrafluoride (SF<sub>4</sub>) and oxygen (O<sub>2</sub>) using nitrogen dioxide (NO<sub>2</sub>) as catalyst were also reported for the synthesis of SOF<sub>4</sub>.<sup>[13]</sup> Moreover, all these experimental conditions led to a mixture of gases that proved hard to separate.

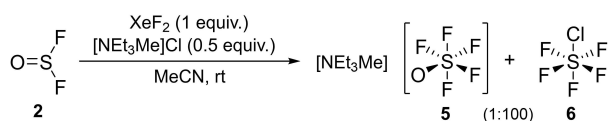
## Results and Discussion

We began our investigation by attempting a new fluorine (F<sub>2</sub>) free synthesis of thionyl tetrafluoride **3** from the commercially available thionyl fluoride (SOF<sub>2</sub>) and xenon difluoride (Scheme 1).

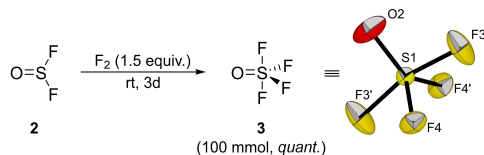
As the direct fluorination of SOF<sub>2</sub> in MeCN did not proceed, we then attempted to perform the direct oxidation of thionyl fluoride in DCM and observed dynamic processes by <sup>19</sup>F NMR but poor conversion in SOF<sub>4</sub> **3** and SO<sub>2</sub>F<sub>2</sub> **4**. Increasing the temperature for several days led to the full decomposition and observation of a mixture of chlorofluorocarbon species from DCM. Therefore, we examined a sequential strategy using chlorine (Cl<sub>2</sub>) generated from triethylmethylammonium chloride ([NEt<sub>3</sub>Me]Cl) decomposition with XeF<sub>2</sub> (Scheme 2). Indeed, the oxidative chlorination of S<sup>IV</sup> to S<sup>VI</sup> and subsequent Cl/F exchange with fluoride ions was already reported on sulfoxide and more recently with sulfynilamine.<sup>[14]</sup> Surprisingly, these experimental conditions led to a large amount of the interesting synthon sulfur chloride pentafluoride (**6**, SF<sub>5</sub>Cl) and a small amount of pentafluorooxosulfate ammonium salt (**5**, [NEt<sub>3</sub>Me][OSF<sub>5</sub>]). This salt was obtained from the reaction of [NEt<sub>3</sub>Me]F and generated SOF<sub>4</sub>. The experimental and simulated



Scheme 1. Attempted formation of SOF<sub>4</sub> using XeF<sub>2</sub>.



Scheme 2. Direct fluorination of SOF<sub>2</sub> in fluorine (F<sub>2</sub>) free manner.



Scheme 3. Synthesis of thionyl tetrafluoride SOF<sub>4</sub> (**3**, CCDC 2380907) and molecular structure. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angle [°]: S1–O2 1.390(3), S1–F3 1.583(2), S1–F4 1.5204(19); O2–S1–F3 97.02(9), O2–S1–F4 122.96(7), F4–S1–F3 86.19(5).

<sup>19</sup>F NMR spectrum of **5** can be found in the SI (Figure S5). Further attempts for OSF<sub>5</sub> preparation from ClSF<sub>5</sub> or oxidation/fluorination of thionyl chloride **1** are also reported in the SI.

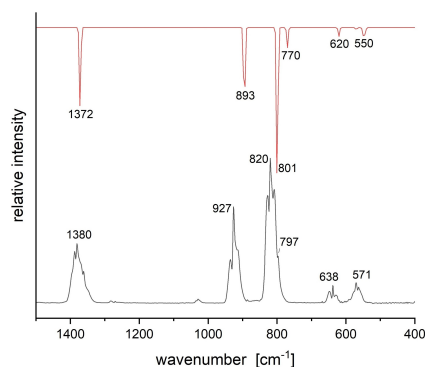
As a fluorine free synthesis of SOF<sub>4</sub> using XeF<sub>2</sub> appears delicate to setup, due to the over oxidation or fluorination (formation of [OSF<sub>5</sub>]<sup>−</sup> and ClSF<sub>5</sub>) we decided to re-investigate the direct room temperature fluorination of thionyl fluoride at even lower pressure.<sup>[4]</sup>

Our designed reaction for the synthesis of thionyl tetrafluoride **3** (Scheme 3) was conducted in a passivated 3 L stainless steel reactor at 100 mmol scale. This allowed us the handling of thionyl fluoride **2** and a slight excess of fluorine (F<sub>2</sub>) with a relative pressure of 1 bar (corresponding to an absolute pressure of 2 bar).

After shaking the reaction vessel for 3 days at room temperature, the absolute pressure decreased to 1.25 bar. The excess of fluorine was removed and thionyl tetrafluoride **3** was obtained quantitatively as a colourless gas. These unique synthetic conditions being in great contrast with the previously harsh reported methodology, we questioned the influence of the metal wall or perhaps the passivation layer of our stainless-steel reactor. A control experiment (30 mmol, V = 1260 mL) using a quartz reaction vessel was performed and we concluded that the passivated layer does not catalyse this reaction.<sup>[15]</sup> Therefore, a practical and direct synthesis of thionyl tetrafluoride in larger amounts is now available. Indeed, the previous complex gas separation is finally avoided.

The molecular structure of **3** is depicted in Scheme 3 and a suitable crystal of **3** was obtained by *in-situ* crystallization on the diffractometer in a capillary tube at 100 K. The SOF<sub>4</sub> structure is now fully elucidated and agrees with the determined gas phase structure (gas phase electron-diffraction with distances (GED, reported as *d*<sub>gas</sub>)<sup>[16]</sup> as it was recently achieved for SF<sub>4</sub>.<sup>[17]</sup> Here, for **3** the S1–F3 (*apical or axial*) distance is similar to the gas phase structure (1.583(2); *d*<sub>gas</sub> 1.583 Å) when the equatorial distance S1–F4 is shorter (1.5204(19); *d*<sub>gas</sub> 1.550 Å) similarly for S=O bond (1.390(3); *d*<sub>gas</sub> 1.413 Å). In the solid-state structure, angles are different from the reported gas phase one. Indeed, the F4–S1–F4' angle is 114.08(15)°, the F3–S1–F3' angle is 165.95(18)° and the O2–S1–F3 97.02(9)° in solid-state versus respectively 110, 178 and 90° in the gas phase. As expected, we herein observed a significant distortion from the ideal trigonal bipyramidal structure (TBP) suggesting a stronger repulsion from the S=O bond in solid-state than in the gas phase. Our quantum-chemical calculations at the DFT level (B3LYP/def2-TZVP) support this distorted trigonal bipyramidal arrangement, where the corresponding angles (F4–S1–F4', F3–S1–F3', O2–S1–F3) have been computed to be 112.9, 164.2 and 97.9° respectively. More information can be found in the supplementary Table S4.

Further characterization of **3** was performed by gas phase IR and by <sup>19</sup>F NMR spectroscopy and are in agreement with the literature.<sup>[18]</sup> Furthermore, DFT calculations have been performed to simulate and examine the resulting IR spectrum (Figure 2).<sup>[19]</sup> Based on this the experimental bands are assigned to  $\nu_s(\text{SF}_{\text{ap}})$  571 cm<sup>−1</sup>,  $\nu_s(\text{SF}_{\text{ap}})$  820 cm<sup>−1</sup> and  $\nu_s(\text{SF}_{\text{eq}})$  797 cm<sup>−1</sup>,  $\nu_s(\text{SF}_{\text{eq}})$  927 cm<sup>−1</sup>. The S=O stretching mode is found at 1380 cm<sup>−1</sup> and the wagging ( $\omega$ ) probably overlaps with the



**Figure 2.** Experimental IR spectrum of  $\text{SOF}_4$  (**3**, black) in comparison to the calculated spectrum (B3LYP/def2-TZVP, red).

band at  $571\text{ cm}^{-1}$ . In the  $^{19}\text{F}$  NMR spectrum, the fluorine atoms appear equivalent displaying a singlet at  $\delta = 79.5$  ppm, this being explained by the Berry-pseudorotation in a TBP system.

We then prepared the silver pentafluorooxosulfate (**7**,  $\text{Ag}[\text{OSF}_5]$ ) salt by condensing 1 equivalent of  $\text{SOF}_4$  **3** into silver fluoride ( $\text{AgF}$ ) in acetonitrile (Scheme 4a). We also conducted this experiment in propionitrile and were able to isolate the resulting silver salt (Scheme 4.b). From the solution containing the silver salt **4**, we then performed several cation exchange reactions. Firstly, the solution was added on triethylmethylammonium chloride ( $[\text{NET}_3\text{Me}]\text{Cl}$ ) leading to the precipitation silver chloride ( $\text{AgCl}$ ). After filtration, the desired ammonium salt (**5**,  $[\text{NET}_3\text{Me}][\text{OSF}_5]$ ) was obtained quantitatively and is in accordance with the observed ion-pair obtained in the  $\text{XeF}_2$  experiment (Scheme 2).

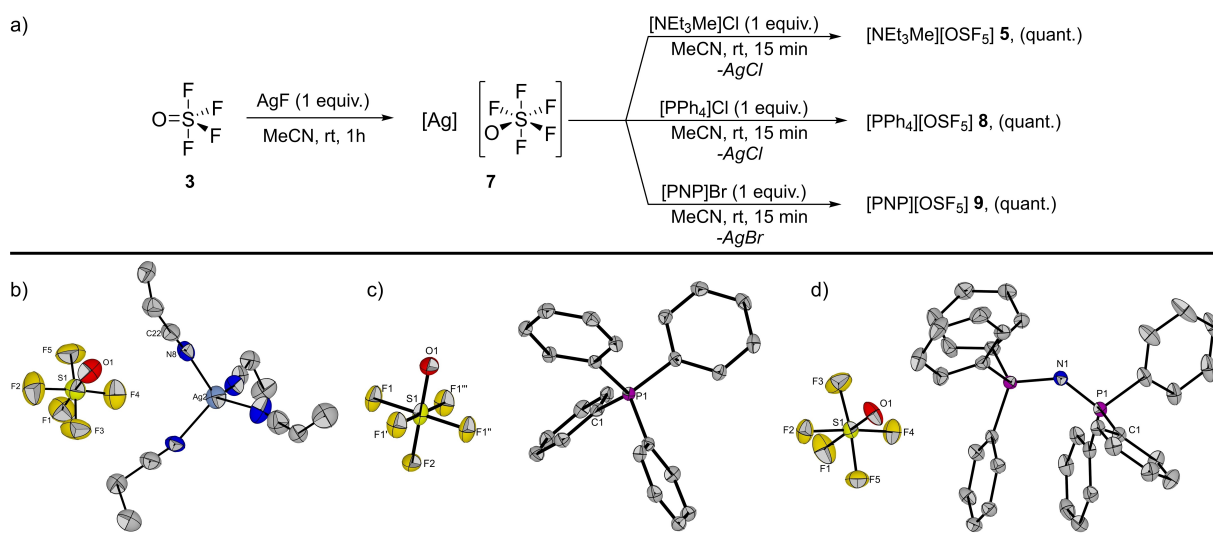
In the same manner, we investigated the formation of the phosphonium derivatives respectively from tetraphenylphosphonium chloride ( $[\text{PPh}_4]\text{Cl}$ ) and

bis(triphenylphosphine)iminium bromide ( $[\text{PNP}]\text{Br}$ ) with precipitation of the corresponding silver halide (Scheme 4).

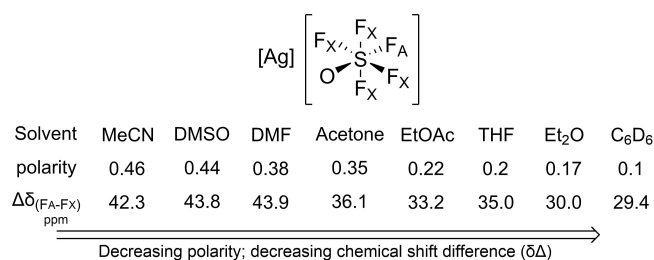
Both phosphonium salt **8** and iminophosphonium salt **9** were obtained quantitatively and isolated. Suitable crystals of **7**, **8** and **9** for X-ray diffraction analysis were obtained by cooling down a propionitrile or acetonitrile solution to  $-20^\circ\text{C}$  (Scheme 4, b–d). Data of these crystals are reported in the SI. As expected for coordinating solvent, each structure displays a dissociated ion-pair which is in contrast with its reported pentafluorooxothellurate ( $\text{OTeF}_5$ , teflate) counterpart obtained from non-coordinating solvent (i.e. DCM or Toluene).<sup>[20]</sup> For each structure, the  $[\text{OSF}_5]^-$  anion appears as a slightly distorted octahedron with the oxygen occupying the apical position. For most structures (**7**<sub>MeCN</sub> & EtCN; **9**), the bond distances can be described as  $d(\text{S}-\text{O}) < d(\text{S}-\text{F}_{\text{eq}}) < d(\text{S}-\text{F}_{\text{ap}})$  and is explained by the  $\text{O}\rightarrow\text{S}$  backbonding. In the case of **8**, the O1 and F2 atom are disordered due a symmetry element, therefore we did not include it in the structural discussion. The salts **8** and **9** display hydrogen bond interaction in the solid-state structure between the aromatic ring, two equatorial fluorine atoms and the negatively charged oxygen.

The strong ion-pair dissociation of these compounds (**4**–**7**) was also observed in solution by  $^{19}\text{F}$  NMR as minor chemical shift variations were observed independently from the solvent or cation. (Table S1, entry 1–2). To further investigate the coordination behaviour of the  $[\text{OSF}_5]^-$  salts, we then decided to prepare several stock solutions from **3** in different organic solvents with a wide range of polarity and different binding properties of the  $\text{Ag}^+$  cation (Figure 3 and Table S1, entry 3–8).

Surprisingly, the preparation of the desired stock solutions can be achieved in various coordinating organic solvents (Figure 3). This allowed us the first observation of an overall correlation between the chemical shift difference  $\delta\Delta$  and the polarity of the solvent for such  $[\text{OYF}_5]^-$  ( $\text{Y}=\text{S}, \text{Se}, \text{Te}$ ) species. To begin, with decreased polarity and decreased  $\delta\Delta$ , the reaction



**Scheme 4.** a) Preparation of  $[\text{cat}][\text{OSF}_5]$  ( $\text{cat} = \text{NET}_3\text{Me}$  (**5**);  $\text{PPh}_4$  (**8**);  $\text{PNP}$  (**9**)) ion-pairs from the silver salt **7**; For molecular structure of **7**–**9**, the disorder of the  $[\text{OSF}_5]^-$  anion and hydrogen have been omitted for clarity. b) X-ray crystallographic structure (CCDC 2380906) of **7**, thermal ellipsoids are drawn at 50% probability level, 35% for N and C atoms of EtCN; c,d) X-ray crystallographic structure **8** (CCDC 2380904) and (CCDC 2380905) of **9**, thermal ellipsoids are drawn at 50% probability.



**Figure 3.** Solvent influence toward  $\text{Ag}[\text{OSF}_5]$  the shift difference  $\delta\Delta(\text{F}_A-\text{F}_X)$  in ppm.

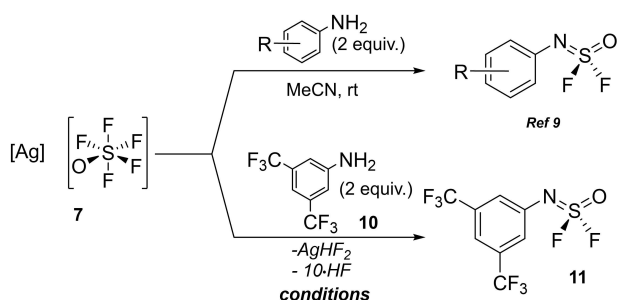
time to reach full conversion increases. With these results, we hypothesize that the shift difference  $\delta\Delta(\text{F}_A-\text{F}_X)$  between the two fluorine signals could act as a fluorine probe, strongly suggesting the electronic or charge contributions for such species. Here, the solvent and possible coordination reduces the signal differences by more than 10 ppm from the acetonitrile solution versus the benzene one (Figure 3). This shift could be attributed for our  $\text{S}^{\text{VI}}$  ion-pairs as correlated to the resulting interactions between the silver cation and  $[\text{OSF}_5]^-$ .

With these data in hand, we decided to further assess the stability of these ion-pairs based on the reported methodology published by Demaerel, De Borggraeve and Ismalaj (Scheme 5).<sup>[9]</sup> From their seminal observation, the  $[\text{OSF}_5]^-$  anion could react as a reservoir of  $\text{SOF}_4$  SuFEx reagent in presence of aniline (Equation (1)).



We decided to apply our  $\text{Ag}[\text{OSF}_5]$  stock solutions to compare the influence of the solvent on  $\text{Ag}[\text{OSF}_5]$  stability for the formation of reactive  $\text{SOF}_4$  resulting in a sulfurimidoyl fluoride compound **11** (Scheme 5).

We hypothesize that the use of less polar solvents such as acetone and THF could enhance the reaction rate as it should favor the precipitation of  $\text{AgHF}_2$  by the immediate reaction of the fluoroaniline **10** with  $\text{SOF}_4$ . We prepared several stock solutions (0.5 M, 0.1 M) of **7** in THF-d<sub>8</sub>, acetone-d<sub>6</sub> and MeCN-d<sub>3</sub>. In comparison with the reported reaction (0.05–0.1 M), the reaction rate was considerably increased using a higher concentration of **7** in MeCN (50% conversion in 1 h, <sup>19</sup>F NMR). To our delight, using acetone and THF at 0.5 M led immediately



**Scheme 5.** Synthesis of sulfurimidoyl fluoride **11** from  $\text{Ag}[\text{OSF}_5]$  (**7**).

to a large amount of precipitation attributed to  $\text{AgHF}_2$ , **10**•**HF** salts and **11** was obtained (by <sup>19</sup>F NMR) in solution. Both side-products undergo glass etching and two decomposition products  $[\text{Ag}]_2[\text{SiF}_6]$  and **10**•**HBF**<sub>4</sub> were also observed on standing. This observed reaction rate appears similar with the direct reaction between pure  $\text{SOF}_4$  **3** and **10**. The higher reaction rate in THF and acetone was confirmed as full conversion was also obtained almost immediately at 0.1 M.

## Conclusions

In summary, we report a selective synthesis of  $\text{SOF}_4$  at low pressure (maximum 1 BarG), low temperature (rt) and large scale (100 mmol). A control experiment in a quartz vessel suggests a non-catalyzed process: That allows to re-investigate a convenient synthesis of thionyl tetrafluoride. Furthermore, the structure of  $\text{SOF}_4$  was elucidated for the first time by SC-XRD and compared to the previous gas phase analysis (GED). Currently, we are actively working on the design of a small-scale chemical plant to optimize this reaction and to be able to efficiently provide  $\text{SOF}_4$  to the community. We then studied the transformation of the reagent with silver fluoride into the silver perfluorooxosulfate ion-pair  $\text{Ag}[\text{OSF}_5]$ . Cation exchanges were conducted allowing the formation of phosphonium and ammonium salts. The binding properties of these salts were studied in solid-state by SC-XRD and in solution by <sup>19</sup>F NMR. We successfully prepared and assessed the stability and binding properties of different salts in multiple solvents. This being observed by <sup>19</sup>F NMR and by its decomposition into sulfurimidoyl using perfluorinated aniline. Using THF and acetone, we were able to mimic the reactivity of pure  $\text{SOF}_4$  with the stability brought by these soluble salts that nowadays can be obtained in a gas free manner. We believe that the combination of both studies could greatly expand the  $\text{OSF}_5$  chemistry and perhaps allows further developments as a potential alternative to PFAS.

Further research involving the preparation of organic scaffolds bearing the perfluorooxosulfate moiety are actively ongoing in the laboratory.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Thionyl fluoride · Thionyl tetrafluoride · Pentafluorooxosulfate Salts (OSF<sub>5</sub>) · Sufex · Fluorination

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