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Multidimensional SuFEx Click Chemistry: Sequential Sulfur(VI) Fluoride Exchange Connections of Diverse Modules Launched From An SOF_4 Hub

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Abstract

Sulfur(VI) Fluoride Exchange (SuFEx) is a new family of click-chemistry based transformations that enables the synthesis of covalently linked modules via S(VI) hubs. Here we report on thionyl tetrafluoride (SOF_4) as the first multidimensional SuFEx connector. SOF_4 sits between the commercially mass-produced gases SF_6 and SO_2F_2 , and like them, is readily synthesized on scale. Under SuFEx catalysis conditions, SOF_4 reliably seeks out 1°-amino groups [R-NH_2] and becomes permanently anchored via a tetrahedral iminosulfur(VI)-link: $\text{R-N}=(\text{O})\text{S}(\text{F})_2$. The pendant, prochiral difluoride groups $\text{R-N}=(\text{O})\text{SF}_2$, in turn, offer two further SuFExable handles, which can be sequentially exchanged to create 3-dimensional covalent departure vectors from the tetrahedral sulfur-(VI)-hub.

Multidimensional Clicking

Sulfur(VI) Fluoride Exchange (SuFEx) is a metal free, multi-connective click chemistry technology, allowing the flawless synthesis of covalently linked modules via S(VI) hubs. We report SOF_4 (Thionyl tetrafluoride) as the first multidimensional connective gas for SuFEx click chemistry. Reliably seeking out “1°-amino groups [R-NH_2]”, SOF_4 becomes permanently anchored via a tetrahedral imino-sulfur-(VI)-link: $\text{R-N}=(\text{O})\text{S}(\text{F})_2$. The pendant difluoride groups $\text{R-N}=(\text{O})\text{SF}_2$, in turn, offer two further SuFExable and prochiral **S-F** bonds, which can be

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sequentially exchanged to create 3-dimensional covalent departure vectors from the tetrahedral sulfur-(VI)-hub.

Keywords

Click Chemistry; SuFEx reaction; SOF₄; Amines; Phenols

The foundation of click chemistry as a framework for creating functional molecular assemblies was inspired by the examination of the central metabolism of life—a process orchestrated by functional oligomers of a few dozen reactive modules, all stitched together via heteroatom links and reversible condensation processes.^[1] Seeking to match the efficiency of Nature's near perfect synthesis machinery, a stringent criterion was defined for a reaction to earn click chemistry status.^[1]

The discovery of the Cu(I) catalyzed azide–alkyne cycloaddition reaction (CuAAC) in 2002,^[2] had a profound influence on the evolution of click chemistry, demonstrating immense versatility and application in fields as diverse as materials science,^[3] bioconjugation^[4] and drug discovery.^[5,6] In 2014, we reported a new embodiment of ideal click chemistry: SuFEx (Sulfur(VI) Fluoride Exchange)—a technology for creating molecular connections with absolute reliability and unprecedented efficiency through a sulfur(VI)-hub.^[7] SuFEx reliably allows the flawless substitution of S^{VI}–F with aryl silyl ethers to give S^{VI}–O bonds, and with amines to give S^{VI}–N- bonds. While the mechanistic details are yet to be fully elucidated, these transactions are made possible by a special coaction between the hydrogen-bonding environment of fluoride ion, and the kinetic and thermodynamic properties of the bonds to sulfur(VI) and silicon centers. Key to SuFEx activation is the requirement for fluoride to transit from a strong covalent bond to a leaving group—a process mediated by 3° amine derived catalysts^[8] and thought to involve bifluoride ion and related species.^[7, 9–13]

Early in the development of SuFEx, we identified sulfuryl fluoride (SO₂F₂)^[7,14] as a sulfur(VI) hub for creating diaryl sulfate links between molecules. Under SuFEx conditions the latent reactivity of the otherwise stable S^{VI}–F bond is roused to react with SuFExable substrates.^[7,15]

While SuFEx is still an emerging technology it has already found diverse applications including, for example: the synthesis of tosylates^[9] and sulfonyl azides;^[10] application in polymer chemistry^[11] and post polymerization modification;^[12,13] Suzuki coupling of aryl-

and heteroaryl-fluorosulfates with boronic acids.^[15] Of particular significance, however, is the potential for SuFEx in biochemical applications—*we have growing evidence to believe that proteins provide molecular and dynamic electrostatic field environments that sulfur(VI) fluoride linkages are adept at reading and reacting to.*^[16]

In a recent study with the Kelly group, we demonstrated fluorosulfate based probes as remarkable substrates capable of selectively capturing protein side-chain groups; especially the hydroxyl on tyrosine, in live human cells.^[16a]

Seeking to expand the range of useful SuFEx connectors, we considered other sulfur(VI) fluoride gases, including: SF₆ (sulfur hexafluoride) and SOF₄ (thionyl tetrafluoride) (Figure 1, A). While SF₆ is loaded with the most SuFEx potential, it is also famously inert. SOF₄, on the other hand, is a S(VI)-hub with a functional balance between reactivity and available S-F functionality.^[17]

As with most of click chemistry, many of the essential features of SOF₄ were discovered long ago: first reported in 1902 by Moissan and Lebeau,^[18] SOF₄ is a trigonal bipyramidal colorless gas that boils at −49 °C, with a trigonal bipyramid structure (Figure 1, A).^[19,20] An improved synthesis of SOF₄ (for labs with no access to F₂) was reported in 1960 by Smith and Engelhardt at CRD DuPont. They found that in the presence of a catalytic amount of NO₂, the oxidation of SF₄ by O₂ gave enhanced yields of SOF₄ gas.^[21]

Despite being known for more than one hundred years, the reactions of SOF₄ have scarcely been studied, let alone exploited. Cramer and Coffman (also at CRD DuPont) reported the first detailed study of its chemistry in 1961. They found that SOF₄ reacts with primary amines and anilines to form the corresponding tetrahedral iminosulfur oxydifluorides (R-N=SOF₂) products in moderate yields (Figure 1B).^[22] Seppelt and Sundermeyer later reported (1971) an early manifestation of silicon mediated SuFEx: [(Me)₃Si]₃N upon reaction with SOF₄ gave the TMS-iminosulfur oxydifluoride ((Me₃Si)₃N + SOF₄ → Me₃Si-N=SOF₂) in 85% yield (Figure 1, B).^[23] In the 50 years following these seminal reports, we locate no practical applications of SOF₄—perhaps not surprising *before* SuFEx catalysis.

The opportunity for creating further connections through the two SuFExable S-F handles of the SOF₄ derived tetrahedral iminosulfur oxydifluoride products did not escape our attention. Until now, the Click '*linkages*' created *via* CuAAC-derived triazoles and the SuFEx connective gas SO₂F₂, are confined to trajectories in a plane. SOF₄ is different: it is the first polyvalent SuFEx connective gas that opens the door to another dimension and trajectory (Figure 1, C). This is important because from biology to synthetic materials applications, having access to the 3-dimensional world adds value to the existing toolbox of click connections.

Herein, we report our detailed studies on the SuFEx chemistry of SOF₄ and its iminosulfur oxydifluoride products. We found that both the rates and yields for SOF₄ transformations are much improved by the presence of 3° amine bases (e.g. Et₃N and DIPEA). The initial products have two SuFExable S-F handles, and we found that each fluoride can be substituted in a serial manner by 2° alkyl amines and/or phenols (as their aryl silyl ether under SuFEx catalysis^[7]). The final products, for up to three steps, arise in excellent over all

yields,^[24] thereby allowing controlled projections to be deliberately substituted along 3 of the 4 tetrahedral axes departing the S-(VI)-central hub.

Given the fidelity and scope of these three serial transformations, we identify thionyl tetrafluoride (SOF₄) as *another good connective hub for click chemistry*.

1st Dimension Connectivity: SOF₄ Reacts with Primary Amines and Anilines

Our experience with SO₂F₂, a sister gas to SOF₄ (Figure 1, A), taught us about the benefits that 3° amine additives (e.g. TEA, DIPEA, DBU) can have on the speed and yield of the desired reaction.^[7] Similarly for SOF₄, the presence of a 3° amine base significantly improved the outcome of these transformations: exposing a solution of primary amine, 1 to 2 mol equiv of Et₃N or DIPEA in CH₃CN, to SOF₄ gas, resulted in excellent yields of the tetrahedral iminosulfur oxydifluoride products (**2**) (Figure 2). The observed chemoselective preference for the primary amine over the other functional groups present in the substrates was notable (e.g. catechol **2-16** and the indole **2-17**).

The selective decoration of –NH₂ moieties in biologically significant building blocks was also readily accomplished, giving the SuFExable steroid-N=SOF₂ cases (**2-21** and **2-22**) and also the nucleotide-N=SOF₂ cases (**2-23** and **2-24**) in good yields. With the α-amino amide **1-25**, intramolecular displacement of the remaining fluoride, activated by amide hydrogen bonding, gave the cyclic sulfamide **2-25** in moderate yield (Figure 2). Generating the reactive amine *in situ*, from the corresponding azide under Staudinger conditions, did not adversely affect the yield of the iminosulfur oxydifluoride products (**2-9**, **2-22**, **2-23**).

Chemoselectivity of SOF₄: Anilines vs. Phenols

Noteworthy is the observed chemoselective preference of SOF₄ for aniline vs. phenol ((**1-16** → **2-16**; Figure 2), which contrasts with the SO₂F₂ sister gas.^[7,10] We were curious about the outcomes of reacting aminophenols with both gases (SOF₄ and SO₂F₂) simultaneously. When acetonitrile solutions of the aminophenols **1-26** – **1-28** were exposed to a 1:1 ratio of SOF₄: SO₂F₂ in the presence of Et₃N (3 equiv), the corresponding SuFEx products **2-26** – **2-28** were formed in excellent yields, respectively. This outcome is explained by the preferential reaction pairing of SO₂F₂ with phenol and SOF₄ with amine, together with the decreasing opportunities for cross-over reaction for each gas as the reaction proceeds and, at least in the case of the F₂OS=N–Ar–OH, the enhanced acidity of the phenol group (Figure 3).

This observation (*vide supra*), is taken to emphasize one of the most important principles of click chemistry - *it should not matter which permutation of the multi-reaction enabled core modules pays off in a given search, for the subsequent linking reactions are near perfect*. Benzene, being planar and highly symmetrical [hexagonal, (D_{6h})] has six identical C–H bonds to switch out for substituents, and best known is the family of disubstituted isomers of which there are three, i.e. *ortho*, *meta* and *para*. In the case at hand, one of the groups is an –OH and the other is an –NH₂, or precisely the three aminophenol isomers **1-26**, **1-27**, and **1-28**. All three permutations of the hexagonally determined departure vectors are opened up

nicely here by the ‘two gases’ at once,—between the three ‘gassed’ products, **2-26**, **2-27**, and **2-28**, we have one of each of the two new SuFExable groups, departing at either 60°, 120°, or 180° in plane vectors from the benzene core (Figure 3).

2nd Dimension Connectivity: Iminosulfur Oxydifluorides with Amines or Amino Acids

Cramer and Coffman surveyed the reactivity of Ph-N=SOF₂ with a selection of amines and found that weakly basic *N*-methylaniline gave no reaction. On the other hand, *tert*-butylamine could substitute both fluorines, while piperidine could substitute only one of them. The difluoride could also react with sodium ethoxide to form the ethyl phenylsulfamate.^[22]

With our extensive range of iminosulfur oxydifluorides [F₂SO(=NR)], we revisited Cramer and Coffman’s early work with a wider selection of amine nucleophiles (Figure 4). The reaction with secondary amines proceeded smoothly: when 2 mol equiv of the given amine were added to a solution of the iminosulfur oxydifluorides (**2**) in acetonitrile at room temperature, the mono-substituted products (**3**) were formed in excellent yields, leaving a single unreacted fluoride in place. These impressively clean transformations required no further purification.^[25] The reaction of the iminosulfur oxydifluorides (**2-4**) with a selection of amino acids proceeded equally well, albeit with concomitant hydrolytic loss of the second fluoride, giving the unsymmetrical sulfamide products (**4-1** – **4-3**) in excellent yields (Figure 5).

Iminosulfur Oxydifluorides with Aryl Silyl Ethers

In the spirit of click chemistry (i.e. the goal of creating stable and useful intermolecular linkages), we next investigated the reaction of the iminosulfur oxydifluorides (**2**) with aryl silyl ethers (**5**) under DBU/BEMP activation. With DBU (10 mol%) and 1 mol equiv of the respective aryl silyl ether (**5**), the SuFEx reactions of the iminosulfur oxydifluorides (**2**) reached completion within just 5 minutes, giving the corresponding sulfurofluoridoimides (**6**) in excellent yields (Figure 6). Reducing the catalyst loading to 2 mol% proved equally effective, resulting in similar yields of products on gram scale. Even the complex reactants: AZT derivative (**2-23**) and estrone (**5-3**) were readily connected.

The exchange of just one S–F bond under typical SuFEx conditions revealed that the reactivity of the remaining S–F bond of the sulfurofluoridoimide is significantly attenuated relative to the S–F bonds of the iminosulfur oxydifluoride. This is a welcome feature, particularly for instances when sequential SuFEx based modification are desirable. To further calibrate the relative reactivity profiles of the various S–F environments, we performed a series of competition experiments on substrates presenting two or more types of S–F functionality (Figure 7). When the *para*-disubstituted benzene derivative **2-3**, comprising both aryl sulfonyl fluoride (Ar–SO₂F) and aryl iminosulfur oxydifluoride groups (Ar–N=SOF₂), was treated with one equivalent of the aryl silyl ether **5-1** and DBU 10 mol% in acetonitrile, the SuFEx reaction occurred exclusively at the iminosulfur oxydifluoride center to give the corresponding product **6-5** in 95% yield—the sulfonyl fluoride (–SO₂F)

group remained untouched (Figure 7). Similarly, when the SuFEx reaction was performed with the analogous fluorosulfate ($-\text{OSO}_2\text{F}$) substrate **2-26** under modified conditions [DBU (5 mol%), the exchange occurred exclusively at the iminosulfur oxydifluoride center to give the corresponding product **6-6** in 94% yield. When the sulfurofluoridoimide **6-6** itself was exposed to the aryl silyl ether (**5-5**) in the presence of DBU (10 mol%) over 16 h, SuFEx catalysis achieved linkage exchange at the fluorosulfate group, yielding the mixed sulfate-sulfurofluoridoimide linked product **6-7** (Figure 7). From these few experiments, and related work,^[7,15] we tentatively suggest the order of reactivity of SO_2F_2 and SOF_4 derived S-F bonds towards SuFEx reactions with aryl silyl ethers: $-\text{N}=\text{SOF}_2 > -\text{SO}_2\text{F} > -\text{OSO}_2\text{F} > -\text{N}=\text{S}(\text{O})(\text{OAr})\text{F}$.

3rd Dimension Connectivity: with Amines and Aryl Silyl Ethers

From our earlier SuFEx studies with fluorosulfates ($-\text{OSO}_2\text{F}$), we found that 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) was the superior base for activating challenging substrates for exchange.^[7] BEMP was therefore the logical choice for activating the remaining $\text{S}^{\text{VI}}-\text{F}$ bond of the corresponding sulfurofluoridoimides (**6**). Indeed, the treatment of **6-2** with the aryl silyl ether **5-1** in the presence of 10 mol% BEMP (CH_3CN , r.t., 1 h), gave the corresponding sulfurimide **7-1** in almost quantitative yield. BEMP proved equally efficient at lower concentrations (5 mol%), and even two phenol linkages could be installed in one pot without compromising yield (**7-2**). Interestingly, secondary amines alone react directly with **6-2**, producing **7-3**, **7-4** in excellent yields (Figure 8).

Another manifestation of the 3rd dimension of SuFEx plugin-reactions from SOF_4 derived hubs is the direct reaction of phenyliminosulfur oxydifluorides (**2-4**) with TMS-protected catechols (Figure 9). The entrained inter- and intramolecular SuFEx reactions proceeded smoothly with DBU (5 mol%) to form the four (**9-1** – **9-4**) iminoxy cyclic catechol sulfuryl derivatives in excellent yields (Figure 9). Of particular significance: the imino cyclic catecholate **9-1** is readily ring opened by piperidine and Boc-piperazine to give the corresponding amino sulfonimide products **10-1** and **10-2** in excellent yields.

In summary, SOF_4 gas is the first multidimensional connector that reacts efficiently with primary amines to form reactive iminosulfur oxydifluoride derivatives. Tuning the SuFEx catalyst conditions allows the sequential activation and exchange of these SuFExable S-F bonds, which project outward along roughly tetrahedral vectors from the central S^{VI} -hub. This study complements our earlier work with SO_2F_2 , by expanding the SuFEx universe of available connectors. The benefit of a 2nd SuFExable $\text{S}^{\text{VI}}-\text{F}$ bond enriches the scope of this valuable click chemistry linker by allowing the extra departure links into the 3-dimensional tetrahedral world.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

A) Structure and boiling point of SF_6 , SOF_4 and SO_2F_2 ; B) Early examples of fluoride substitution reactions of SOF_4 ; C) Comparing the trajectories of the Click connections derived from: CuAAC-triazole, SO_2F_2 and SOF_4 .

Figure 2.

The reactions of primary amines with SO_2F_2 in the presence of Et_3N . [a] The yield in parenthesis is for the reaction without Et_3N . [b] The amine was generated *in situ* by reducing the azide under Staudinger conditions with PMe_3 and 1 to 3 equiv of H_2O , see supporting information.

Figure 3.
The selectivity of SO_2F_2 and SOF_4 towards aromatic hydroxyl and amino groups.

Figure 4.

The reaction of iminosulfur oxydifluorides with secondary amines. [a] 1.2 equiv of proline methyl ester and 2 equiv of Et₃N in MeCN. [b] 1 equiv of amoxapine and 2 equiv of Et₃N in DMSO.

Figure 5.
The reaction of iminosulfur oxydifluorides with amino acids.

Figure 7.
Comparison of the reactivity of iminosulfur oxydifluoride with sulfonyl fluoride and fluorosulfate.

Figure 8.
The connections of primary amines with two phenols or one phenol and one secondary amine.

Figure 9.

The reaction of iminosulfur oxydifluorides with catechols and the activity of the product towards amines.