

# Room Temperature Defluorination of Poly(tetrafluoro)ethylene by a Magnesium Reagent

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## **Abstract**

Perfluoroalkyl substances (PFAS) are now pervasive in the environment. The largest single use material within the PFAS compound class is poly(tetrafluoro)ethylene (PTFE), a robust and chemically resistant polymer. Despite their widespread use and serious concerns about their role as pollutants, methods for repurposing PFAS are rare. Here we show that a nucleophilic magnesium reagent reacts with PTFE at room temperature, generating a molecular magnesium fluoride which is easily separated from the surface-modified polymer. The fluoride in turn can be used to transfer the fluorine atoms to a small array of compounds. This proof-of-concept study demonstrates that the atomic fluorine content of PTFE can be harvested and re-used in chemical synthesis.

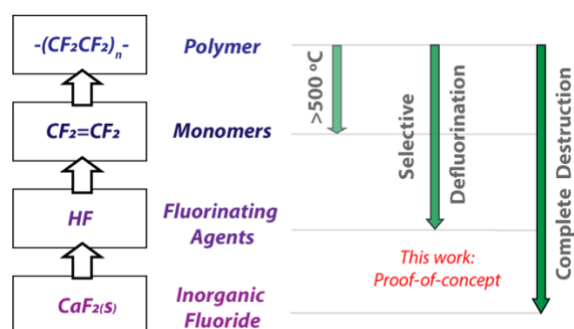
## **Introduction**

Poly(tetrafluoro)ethylene (PTFE) is produced on an estimated  $2 \times 10^8$  kg / year scale through a multistep process that converts fluorite ( $\text{CaF}_2$ ) to HF to  $\text{CHClF}_2$  to  $\text{C}_2\text{F}_4$ , which is then subject to a radical polymerisation.<sup>1</sup> PTFE is a high-molecular weight semi-crystalline polymer and is among the most chemically resistant materials in existence. PTFE finds applications as a wire coating and insulation, in non-stick cookware, in weather-resistant materials, alongside many others such as in carbon fibre composites, aerosol lubricants and in military grade pyrotechnics. Despite its widespread use, current methods for recycling or destruction of PTFE are limited and there is an urgent need to establish methods for its remediation.

Depolymerisation of PTFE to  $\text{C}_2\text{F}_4$  (and related low molecular weight fluorocarbons) by vacuum pyrolysis is an energy intensive process; at 510 °C the half-life of conversion of PTFE to monomers has been estimated as  $\sim 30$  min.<sup>2</sup> Although this provides a viable route for reprocessing of PTFE, it is not an effective approach to recycle this material in any other way. In this regard, defluorination holds

promise as means to harvest fluorine atoms from PTFE while also creating structurally modified materials. Such an approach could allow waste PTFE to be directly used as a fluorine source in chemical synthesis, providing an alternative (and more circular) approach to current synthetic methods that almost exclusively rely on mineral sources of  $\text{CaF}_2$  e.g. fluorite. Chemical approaches to the defluorination of PTFE include reactions with Mg in supercritical  $\text{CO}_2$  above  $510\text{ }^\circ\text{C}$ ,<sup>3</sup>  $\text{Ca}(\text{OH})_2$  in supercritical water above  $650\text{ }^\circ\text{C}$ ,<sup>4</sup> with zinc powder as a template at  $700\text{ }^\circ\text{C}$ ,<sup>5</sup> or with  $\text{Mg}_2\text{Si}$  at  $600\text{ }^\circ\text{C}$  to form silicon carbide nanoparticles.<sup>6</sup> Low temperature reactions ( $<100\text{ }^\circ\text{C}$ ) require strong reductants such as s-block metals in liquid ammonia, lithium-mercury amalgam, sodium naphthalide, benzoin dianion, or alkyl lithium reagents.<sup>7–16</sup> At the most extreme, destruction of PTFE occurs in military grade pyrotechnic materials such as Magnesium-Teflon-Viton pyrolants.<sup>17</sup> Common to these methods is the proposed formation of inorganic metal fluoride  $\text{MF}_{(s)}$  ( $\text{M} = \text{Li}, \text{Na}$  or  $\text{K}$ ) or  $\text{MF}_{2(s)}$  ( $\text{M} = \text{Mg}, \text{Ca}$ ) as a reaction by-product. Only in a limited number of cases, however, has the formation of metal fluorides been confirmed by spectroscopic methods (e.g. powder XRD, XPS, SS  $^7\text{Li}$  NMR).

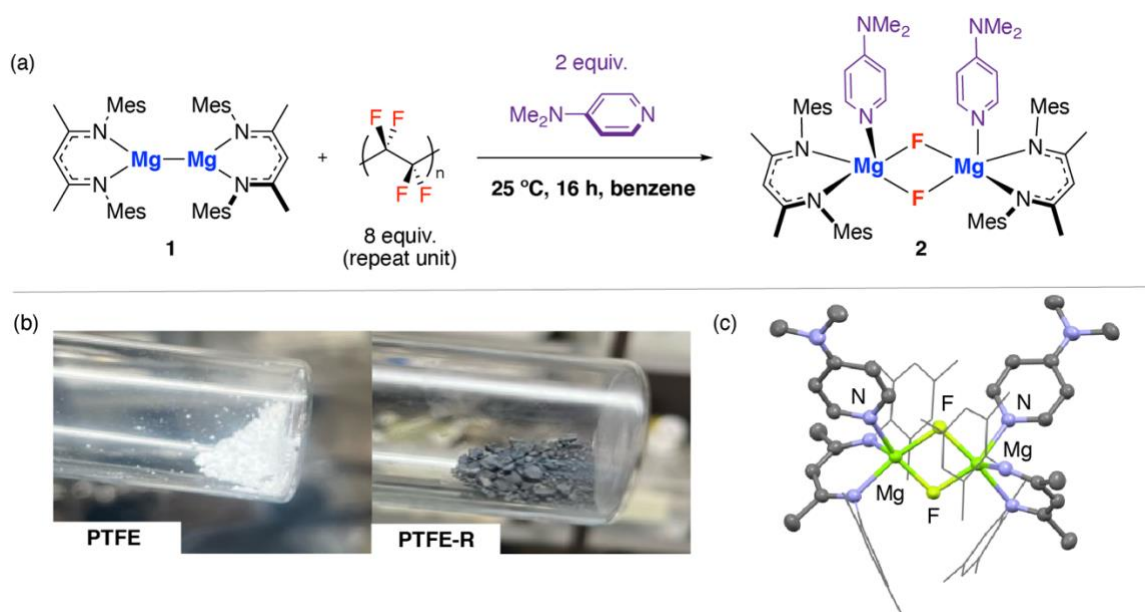
Here we report the controlled defluorination of PTFE powder with a molecular magnesium-based reducing agent under extremely mild conditions ( $25\text{ }^\circ\text{C}$ , 1 atm.). The approach allows the formation of a hydrocarbon-soluble magnesium fluoride coordination compound which is easily separable and recoverable from the modified PTFE. This kinetically stabilised species can be used as a fluoride carrier and is expected to be more reactive than inorganic metal fluorides,  $\text{MF}_{(s)}$  or  $\text{MF}_{2(s)}$ , which suffer from high lattice enthalpies and high stability. We show that PTFE derived molecular fluoride can be used as a fluorinating agent, establishing proof-of-concept for the direct re-use of the atomic fluorine content of PTFE in synthesis (Figure 1).



**Figure 1.** Product-chain for production of PTFE, along with potential routes for recycling including (a) thermal depolymerisation (above  $500\text{ }^\circ\text{C}$ ), selective defluorination (this work) to form fluorinating agents, and complete destruction back to inorganic metal fluoride.

## Results and Discussion

PTFE (250 mg powder, 1  $\mu\text{m}$  particle size, Sigma-Aldrich,  $M_n = 10^6 - 10^7$ ), **1** (250 mg, 0.35 mmol, 8 equiv. repeat units), 4-(dimethylamino)pyridine (DMAP 85 mg, 0.70 mmol) and benzene (10 mL) were combined under an inert atmosphere of argon. Jones and co-workers have shown that the magnesium nucleophile used in this reaction, **1**,<sup>18,19</sup> displays enhanced reactivity on the addition of a Lewis base.<sup>20,21</sup> The reaction mixture was agitated and left to proceed for 16 h at 25 °C. The red solution turns dark red-brown as the reaction progresses, PTFE remains undissolved throughout and it is assumed the process is heterogeneous. The reaction mixture was filtered to remove PTFE and the mother liquor was concentrated to a brown solid, which was identified by multinuclear NMR spectroscopy to be **2** (Figure 2). Recrystallisation of the crude product was achieved by slow evaporation of a concentrated benzene solution. **2** was isolated in 85 % yield based on **1** as the limiting agent. **2** demonstrates a characteristic resonance at  $\delta = -183.9$  ppm in the  $^{19}\text{F}$  NMR spectrum. In the solid-state, **2** demonstrates a dimeric structure in which a pair of 5-coordinate magnesium sites supported by terminal  $\beta$ -diketiminate and DMAP ligands are bridged by fluoride atoms derived from PTFE (Figure 2).<sup>22</sup>



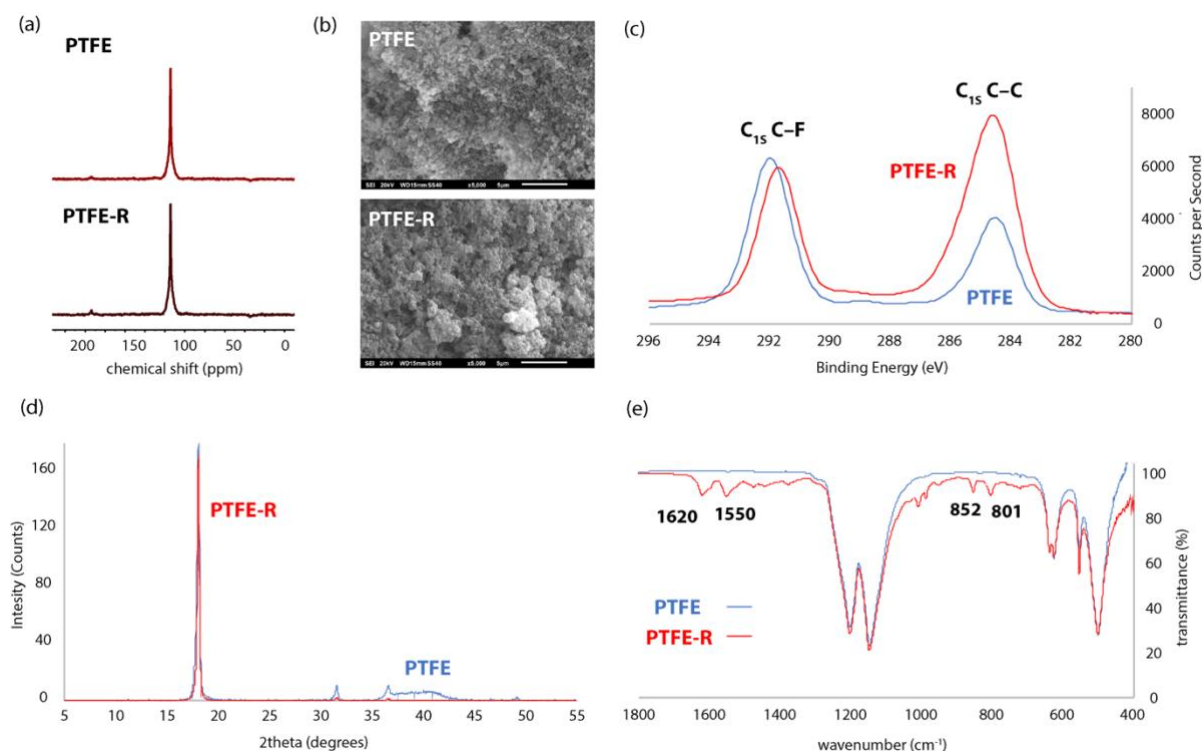
**Figure 2.** (a) Room temperature reaction of **1** with PTFE. (b) Samples of PTFE and PTFE-R before and after reaction respectively. (c) Single-crystal X-ray structure of **2** isolated in 80% yield from PTFE.

The tolerance of the reaction with **1** on the source and any pre-treatment of **PTFE** was investigated. **PTFE** (1  $\mu\text{m}$ ) from different commercial suppliers (Sigma Aldrich, Alfa Aesar), with or without a Soxhlet extraction (toluene or THF) prior to reduction behaved similarly, reacting with **1** to form **2** in > 70 % yield. Modification of the particle size however, impacted the recovery of **2** from the mixture. A series of particle sizes was investigated (1  $\mu\text{m}$ , 6-9  $\mu\text{m}$ , 15-25  $\mu\text{m}$ , 35  $\mu\text{m}$  and 200  $\mu\text{m}$ ), with larger particle sizes of **PTFE** generally leading to lower yields of **2** and longer reaction times. **2** could also be obtained from reaction of **1** + DMAP with poly(vinylidenedifluoride) (PVDF), albeit in a lower yield of 40%.

Following the reaction with **1** + DMAP, **PTFE** is converted from a colourless solid to a grey powder which we label **PTFE-R**. The polymer remains completely insoluble over the course of the reaction and beyond **2** no further fluorinated products are observed in solution by  $^{19}\text{F}$  NMR spectroscopy. Solid-state magic angle spinning (SS-MAS) NMR spectroscopic data were collected on **PTFE** and **PTFE-R**, both samples show characteristic resonances at  $\delta = -124$  ppm and  $\delta = -110$  ppm in the  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectrum respectively consistent with little change to the bulk sample on reaction with **1** (Figure 3a). Powder X-ray diffraction (XRD) of **PTFE** shows a reflection at  $2\theta = 18^\circ$  assigned to a crystalline phase along with a diffuse scattering peak  $2\theta = 40^\circ$ , which has been assigned as an amorphous component. **PTFE-R** retains the reflection at  $2\theta = 18^\circ$ , however the intensity of the  $2\theta = 40^\circ$  peak is greatly reduced. Scanning electron microscopy (SEM) of **PTFE** and **PTFE-R** show changes to the surface of the polymer following reaction with **1** (Figure 3b). In combination, the SS-MAS NMR, powder XRD, and SEM data suggest that the most likely reactive sites of **PTFE** are in amorphous regions on the polymer surface.

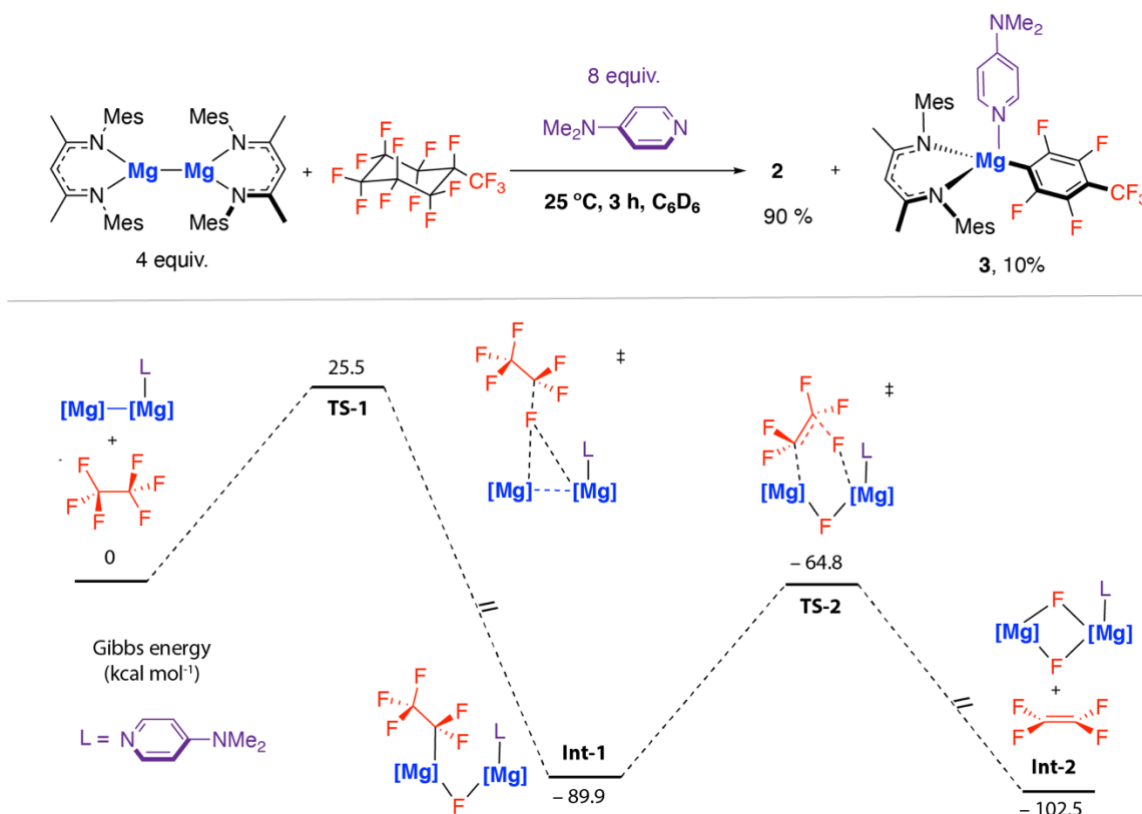
Surface sensitive techniques were used to further interrogate the changes to **PTFE** on reaction with **1**. X-ray Photoelectron Spectroscopy (XPS) measurements show the expected transitions characteristic of  $-\text{CF}_2-$  functional groups from the F(1s) orbitals (689.8 eV) and C(1s) orbitals (292.0 and 284.4 eV) of **PTFE** (Figure 3c).<sup>23,24</sup> The same transitions are also observed in **PTFE-R**, however integration of peaks in the C(1s) scan show that the C-F : C-C ratio has changed from 1 : 0.5 to 1 : 1.4 consistent with lower fluorine content near the surface of **PTFE-R** compared to **PTFE**. In addition, a new transition is observed at 684.7 eV assigned to a Mg bound F(1s) environment (Supplementary Information, Figure S9). Hence, while it is clear from the high recovery of **2** that most of the exercised fluorine content is transferred to the solution phase, we cannot discount the retention of small amounts of metal fluoride species at the surface of **PTFE-R**. Attenuated total reflectance IR spectroscopy also shows clear differences between **PTFE** and **PTFE-R**. **PTFE-R** shows vibrations 1620, 1550, 1006, 985, 852 and 801  $\text{cm}^{-1}$  not present in **PTFE**, which most likely derive from C=C stretching and bending modes of newly created alkene functional groups (Figure 3e).<sup>25</sup> To support this assignment, a sample of **PTFE-R** was

reacted with an excess of  $\text{BH}_3\cdot\text{THF}$  in THF for 72 h. Following re-isolation of the polymer, the key vibrations assigned to C=C modes are no longer present (as would be expected from hydroboration of the C=C functional group) (Supplementary Information, Figure S7). The XPS and IR data suggest that defluorination occurs at the surface of PTFE, most likely with the creation of alkene functionality through a 1,2-defluorination of polymer chains.



**Figure 3.** Solid-state data on **PTFE** and **PTFE-R**. (a) SS-MAS NMR data, (b) SEM images, (c) powder XRD, (d) XPS data and (e) ATR-IR spectroscopic data.

To further probe the potential formation of unsaturated C=C bonds through 1,2-defluorination, **1** was reacted with a short-chain PFAS in the presence of DMAP. Hence, reaction with perfluoro(methylcyclohexane) produced **2** and gave clear evidence for the formation of unsaturated C=C bonds (Figure 4). Reaction of 4 equiv. of **1**, 8 equiv. of DMAP and 1 equiv. perfluoro(methylcyclohexane) after 3 h at 25 °C yielded **2** (90 % based on theoretical yield by NMR spectroscopy) alongside **3** (10 % based on theoretical yield by NMR spectroscopy). Despite being formed in small amounts, observation of **3** is most readily explained from a stepwise defluorination of perfluoro(methylcyclohexane) to form unsaturated intermediates, and ultimately octafluorotoluene. Octafluorotoluene is proposed to react further with **1** to effect metalation at the 4-position of the newly unsaturated ring system, allowing trapping of the organic fragment to form **3** (Figure 4). A control reaction between octafluorotoluene, **1** and DMAP also formed **3**.



**Figure 4.** (a) Reaction of **1** with perfluoromethylcyclohexane. (b) DFT calculated mechanism for the 1,2-defluorination of PFAS with **1**.

DFT calculations were conducted to establish a feasible mechanistic model for the 1,2-defluorination of PFAS using **1** + DMAP.  $C_2F_6$  was used as a model for PTFE and perfluoro(methylcyclohexane), where both site selectivity ( $1^\circ$  vs  $2^\circ$ ) and conformational flexibility are complicating factors. Binding of DMAP to **1** was assumed to be fast and reversible under the reaction conditions. Fluxionality in  $^1H$  NMR spectroscopic data for **1**·DMAP suggests the DMAP can move rapidly between Mg centres.<sup>20,21</sup> Both **1**·DMAP and **1**·DMAP<sub>2</sub> could be prepared from **1** and DMAP,<sup>26</sup> and their structures were confirmed by single crystal X-ray diffraction (Supplementary Information, Figure S2). The calculations suggest an initial defluorination of  $C_2F_6$  by **1** + DMAP occurs by attack of **1**·DMAP at the fluorine atom of  $C_2F_6$  via **TS-1** ( $\Delta G^\ddagger_{298K} = 25.5$  kcal mol<sup>-1</sup>) to form **Int-1**. This mode of reactivity has been established for **1** in the absence of DMAP but appears to be accelerated by the presence of this additive.<sup>27</sup> The transition state for C–F bond breaking is asymmetric and the 3-coordinate Mg centre of **1**·DMAP acts as a nucleophilic site, while the 4-coordinate Mg centre acts as a fluoride acceptor. **Int-1** can undergo a second fluoride elimination via **TS-2** ( $\Delta G^\ddagger_{298K} = 25.1$  kcal mol<sup>-1</sup>) to create a C=C bond and form  $C_2F_4$ , and reaction of the magnesium fluoride by-product with a second equivalent of DMAP forms **2**. The overall reaction is highly exergonic ( $\Delta G^\circ_{298K} = -102.5$  kcal mol<sup>-1</sup>). **TS-1** was further analysed by natural bond orbital (NBO). Consideration of the charges on C and F atoms of the breaking C–F bond shows there is charge accumulation on both these sites as the transition state is approached, at the same time positive

charge accumulates at the three coordinate Mg atom. The analysis is consistent with a flow of electrons from the main group reagent to C<sub>2</sub>F<sub>6</sub>.

The reaction of C<sub>2</sub>F<sub>6</sub> with either **1** ( $\Delta G^{\ddagger}_{298\text{K}} = 30.2 \text{ kcal mol}^{-1}$ ) or **1**·(DMAP)<sub>2</sub> ( $\Delta G^{\ddagger}_{298\text{K}} = 38.2 \text{ kcal mol}^{-1}$ ) was calculated to proceed with a higher activation energy barrier than **1**·DMAP (Supplementary Information, Figure S16). It is likely that polarisation and stretching of the Mg–Mg bond in **1**·DMAP compared to the symmetric species leads to enhanced reactivity of this species.<sup>21</sup> NPA charges in **1**·DMAP reveal the 3-coordinate Mg atom has a more negative charge (0.84) compared to the 4-coordinate Mg atom (1.07), and hence nucleophilic attack originates from the 3 coordinate Mg atom. Alternative mechanisms including electron-transfer were found to be less accessible by DFT calculations and are less likely to be operating under the reaction conditions (Supplementary Information, Figure S18, Scheme S12).

Compound **2** is soluble in hydrocarbon solvents and is a viable fluorinating agent. **2** is potentially more reactive than inorganic metal fluorides such as MgF<sub>2(s)</sub> or CaF<sub>2(s)</sub> as there is no need to overcome the high lattice-enthalpies for an onwards reaction. To demonstrate proof-of-concept, **2** was used to transfer PTFE-derived fluorine atoms to a series of silicon-, boron-, aluminium-, and carbon-based electrophiles. These reactions allow the creation of Si–F, B–F, Al–F and C–F bonds from **2**. For example, **2** reacts with Me<sub>3</sub>SiCl to cleanly form Me<sub>3</sub>SiF (99 %). **2** can also be used to prepare tetrafluoroborate anions (e.g. [n-Bu<sub>4</sub>N][BF<sub>4</sub>]) from reaction with BF<sub>3</sub> and [n-Bu<sub>4</sub>NCl] (95 %). **2** can be used to generate a molecular aluminium difluoride (99%) previously used in the synthesis of acyl fluorides (e.g benzoyl fluoride).<sup>28</sup> Tetrafluoroborate anions find myriad uses in inorganic and organic synthesis, while acyl fluorides are versatile fluorine carriers which can act as a point of synthetic diversification to create numerous organofluorine products.<sup>29–31</sup>

## Conclusions

In summary, we report a method for the room temperature defluorination of PTFE (and short chain PFAS compounds) that produces a molecular magnesium fluoride reagent. Analysis of the PTFE post modification suggests that the reaction occurs primarily at the surface of the polymer, likely to create unsaturated carbon–carbon bonds within the polymer chain. The magnesium fluoride reagent is readily separated and was shown to be capable of transferring the fluorine atom to a small range of electrophiles. Our study provides proof-of-concept results that show fluoride can be harvested from PTFE and re-used in chemical synthesis.

## Methods

Defluorination of PTFE with **1** and DMAP: In an N<sub>2</sub> filled glovebox, 500 mg (0.7 mmol) of **1** and 171 mg (1.4 mmol) of DMAP were added to a Schlenk flask (with no stirrer bar) and dissolved in 10 mL of C<sub>6</sub>H<sub>6</sub>. PTFE (500 mg) was then added. The flask was manually swirled for 15 seconds and left overnight. After 16 hours, the solution had gone from red to dark brown/red. The C<sub>6</sub>H<sub>6</sub> solution was separated from the solid by cannula filtration. The product **2** could be isolated by removal of the solvent *in vacuo*, in an 85 % yield (591 mg, 0.6 mmol). Single-crystals suitable for X-ray crystallography were grown by slow evaporation of a concentrated C<sub>6</sub>H<sub>6</sub> solution of **2**. The dark grey solid polymer product is isolated after cannula filtration, and washed with toluene (3x 5 mL) and hexane (3 x 15 mL), and dried under vacuum.

**<sup>1</sup>H NMR** (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 298K): 1.77 (s, 12H, NCCH<sub>3</sub>), 2.01 (s, 24H, ortho-CH<sub>3</sub>), 2.20 (s, 12H, DMAP N(CH<sub>3</sub>)<sub>2</sub>), 2.33 (s, 12H, para-CH<sub>3</sub>), 5.02 (s, 2H, CH<sub>3</sub>C(CH)<sub>2</sub>CCH<sub>3</sub>), 6.04 (d, 4H, <sup>3</sup>J<sub>H-H</sub> = 4.9 Hz, DMAP Ar-H), 6.95 (s, 8H, Ar-CH), 8.16 (d, 4H, DMAP Ar-H). **<sup>13</sup>C NMR** (C<sub>6</sub>D<sub>6</sub>, 125 MHz, 298 K): δ 19.15 (ortho-CCH<sub>3</sub>), 21.31 (para-CCH<sub>3</sub>), 23.76 (NCCH<sub>3</sub>), 38.19 (DMAP N(CH<sub>3</sub>)<sub>2</sub>), 93.36 (CH<sub>3</sub>C(CH)<sub>2</sub>CCH<sub>3</sub>), 106.28 (DMAP Ar-C), 129.01 (Ar-CH), 131.20 (C<sup>IV</sup>), 132.65 (C<sup>IV</sup>), 148.77 (C<sup>IV</sup>), 150.28 (DMAP Ar-C), 166.17 (NCCH<sub>3</sub>). **<sup>19</sup>F NMR** (C<sub>6</sub>D<sub>6</sub>, 100 MHz, 298 K): δ -183.9 (s, Mg-F).

*Crystal Data for 2.* C<sub>60</sub>H<sub>78</sub>F<sub>2</sub>Mg<sub>2</sub>N<sub>8</sub>, *M* = 997.92, orthorhombic, space group Pbcn (no. 60), *a* = 21.16360(10) Å, *b* = 22.10400(10) Å, *c* = 27.3220(2) Å, *V* = 12781.24(13) Å<sup>3</sup>, *Z* = 8, ρ<sub>calc</sub>/cm<sup>3</sup> = 1.037, μ(Cu Kα) = 0.691 mm<sup>-1</sup>, *T* = 173.05(10), F<sup>2</sup> refinement, R<sub>1</sub>(obs) = 0.0426, wR<sub>2</sub>(all) = 0.1369, 12814 independent observed reflections (*R*<sub>int</sub> = 0.0332), 10202 independent measured reflections [|*F*<sub>o</sub>| > 4σ(|*F*<sub>o</sub>|)], 2θ<sub>full</sub> = 147.516°, 669 parameters. CCDC 2243949.

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**Author contributions**

DJS contributed to all aspects of experimental and computational work. JP helped investigate the onwards reactions of **2** as a fluorinating agent. MRC conceived and managed the project. All authors contributed to writing of the manuscript.

**Competing Interests**

The authors declare no competing interests.

**Additional information**

Supplementary information is available online.