Improved Access to Organo-Soluble Di- and Tetrafluoridochlorate-(I)/(III) Salts

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SUPPORTING INFORMATION

Supporting Information

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Caution!

Fluorine, even under dilute conditions, is extraordinarily reactive and can react violently with organic materials under the formation of HF. Similarly, tetrafluoridochlorate(III) and difluoridochlorate(I) are strongly oxidizing compounds, which can decompose violently under certain conditions when exposed to organic materials. Exposure to acidic compounds (e.g. water or boron trifluoride) greatly enhances the reactivity due to the in-situ formation of ClF₃. Additionally, precipitation also greatly enhances the reactivity of tetrafluoridochlorate(III) and difluoridochlorate(I) compounds, leading to explosions at temperatures above −40 °C. Usage of PFA, FEP or PTFE may lower the risk of injury.

General Information

All experiments were performed under rigorous exclusion of moisture and oxygen using standard Schlenk techniques. Solids were handled in a dry box under argon atmosphere (O₂ < 0.5 ppm, H₂O < 0.5 ppm). HF addition experiments were performed in 3.8 mm PFA tubes with a stainless steel vacuum line. Acetonitrile and propionitrile were dried over Sicapent® prior to use. [NEt₄]Cl and [NEt₃Me]Cl were dried overnight at 120 °C under dynamic vacuum. All other chemicals were used as purchased. ClF was synthesized according to literature.[1] Raman spectra were recorded on a Bruker MultiRAM II equipped with a low-temperature Ge detector (1064 nm, 30-80 mW, resolution, 4 cm⁻¹). NMR spectra were recorded on a JEOL 400 MHz ECS or ECZ spectrometer. All reported chemical shifts are referenced to the values given in IUPAC recommendations of 2008 using the ²H signal of the deuterated solvent as internal reference. For external locking acetone-d₆ was flame sealed in a glass capillary and the lock oscillator frequency was adjusted to give δ(¹H) = 7.26 ppm for a CHCl₃ sample locked on the capillary. Crystal data were collected on a Bruker D8 Venture diffractometer with a Photon 100 CMOS area detector with MoKα radiation. Single crystal were picked at −80 °C under nitrogen atmosphere and mounted on a 0.15 mm Mitegen micromount using perfluoroether oil diluted with perfluorohexane. The structures were solved with the ShelXT[3] structure solution program using intrinsic phasing and refined with the ShelXL[4] refinement package using least squares minimizations by using OLEX2.[5] For visualization the Diamond V3.0 program was used.[6]

Structure optimizations and nonrelativistic shielding calculations for the [XF₆]⁻ (X = Cl, Br, I; n=2, 4, 6) anions and the CFCl₃ reference standard were performed using a developers’ version of the TURBOMOLE program, release 7.4.[7] Overall four sets of structures were optimized using def2-TZVPPD[8] basis sets (including an effective core potential, ECP, for iodine[8]) and TURBOMOLE standard grid setting 3. Two sets of structures were obtained at the BP86-D3(BJ)[10] level, either in the gas phase or using the Conductor-like Screening Model (COSMO)[11] with rₑₒᵣᵥ = 2.76 Å and ε = 35.94 (parameters for the solvent radius and finite permittivity of acetonitrile).
The other two sets were obtained at the B3LYP\textsuperscript{16}-D3(BJ)\textsuperscript{15} level of theory, also without and with COSMO solvent model. D3(BJ) stands for D3 atom-pairwise dispersion corrections with Becke-Johnson damping.\textsuperscript{10}

Subsequent nonrelativistic nuclear-shielding calculations at these structures used a recent improved DFT-GIAO\textsuperscript{33} implementation in Turbomole.\textsuperscript{14} extended to allow the use of local hybrid functionals.\textsuperscript{15} We used two functionals, which had previously been demonstrated to provide accurate $^{19}$F shielding.\textsuperscript{15,16} the global hybrid BHLYP,\textsuperscript{11b,17} and the LH12ct-SsifPW92\textsuperscript{18} local hybrid functional with position-dependent exact-exchange admixture.\textsuperscript{19} These computations used pcSeg-4 basis sets\textsuperscript{20s} for F, Cl, and Br and ANO-RCC-unc\textsuperscript{21} basis sets for I. For each of the abovementioned sets of structures, shielding calculations with these two functionals were performed without or with COSMO. This allows the evaluation of the role of solvent effects acting either indirectly via the structure or directly. The nonrelativistic shielding/shift results are given in Tables S3, S4.

To evaluate the role of spin-orbit and scalar relativistic effects, we also carried out four-component relativistic computations (at the BP86-D3(BJ)(COSMO,CH\textsubscript{3}CN)/def2-TZVPPD optimized structures) using the matrix Dirac-Kohn-Sham (mDKS) method\textsuperscript{22} implemented in the ReSpect program, version 5.1.0.\textsuperscript{23} As neither local hybrids nor BHLYP are currently available for shielding computations in ReSpect, we used a modified B3LYP functional with 50% admixture of exact Hartree-Fock exchange (B3LYP50), which should give results that are close to BHLYP data. Uncontracted Dyall valence quadruple-\(\zeta\) (Dyall-VQZ)\textsuperscript{24} basis sets were used for all atoms. Relativistic shielding/shift results are shown in Table S5.

**Experimental Section**

**Synthesis of [NEt\textsubscript{3}Me][ClF\textsubscript{4}] in solution (low concentration)**

[NEt\textsubscript{3}Me]Cl (100 mg, 0.659 mmol, 1 eq.) was dissolved in dried acetonitrile or propionitrile or CHFCl\textsubscript{2} (1 ml) and cooled to −35 °C (MeCN) or −55 °C (EtCN, CHFCl\textsubscript{2}). Dilute F\textsubscript{2} (10 % in Ar) was bubbled through the solution (16 min, 20 ml·min\textsuperscript{−1}, 2 eq.). Pure Ar (20 ml·min\textsuperscript{−1}) was bubbled through the solution for 15 min in order to remove residual amounts of reactive gases. A colorless solution was obtained.

$^{1}$H NMR (400 MHz, EtCN, ext. acetone-d\textsubscript{6}, 20 °C) \(\delta_{\text{ppm}}\) = 3.87 (q, \(3J^\text{1H,1H}\) = 7.30 Hz, 6H, CH\textsubscript{3}), 3.48 (s, 3H N-CH\textsubscript{3}), 1.85 (t, \(3J^\text{1H,1H}\) = 7.30 Hz, \(3J^\text{1N,1H}\) = 1.84 Hz, CH\textsubscript{3}). $^{19}$F NMR (377 MHz, EtCN, ext. acetone-d\textsubscript{6}, 20 °C) \(\delta_{\text{ppm}}\) = 67 (ClF\textsubscript{4}\textsuperscript{−}); FT-Raman (EtCN, −196 °C): \(\tilde{\nu}\) = [ClF\textsubscript{4}]: 500 (a\textsubscript{1g}), 407(b\textsubscript{1g}), 278 cm\textsuperscript{−1} (b\textsubscript{2g}).

**Synthesis of [NEt\textsubscript{3}Me][ClF\textsubscript{4}] in solution (high concentration)**

[NEt\textsubscript{3}Me][Cl\textsubscript{4}] was prepared by the addition of 1 eq. of Cl\textsubscript{2} to [NEt\textsubscript{3}Me]Cl. [NEt\textsubscript{3}Me][Cl\textsubscript{4}] (0.621 g, 2.79 mmol, 1 eq.) was diluted with acetonitrile (0.3 ml) and cooled to −30 °C. Dilute F\textsubscript{2} (10 % in Ar) was bubbled through the solution (68 min, 20 ml·min\textsuperscript{−1}, 2 eq.). To remove residual amounts of reactive gases, Ar was bubbled through the solution for (15 min, 20 ml·min\textsuperscript{−1}) . A colorless solution was obtained. Analytics was identical to samples with low concentration.

**Crystal growth of [NEt\textsubscript{3}][ClF\textsubscript{4}]**

The synthetic procedure is similar to [NEt\textsubscript{3}Me][ClF\textsubscript{4}]. Single crystals were obtained by slowly cooling a propionitrile solution to −80 °C over 1 week in a freezer. An ethanol bath in a Dewar was used to reduce the cooling rate.

**Synthesis of [NEt\textsubscript{3}][ClF\textsubscript{3}][ClF\textsubscript{2}] in solution**

[NEt\textsubscript{3}]Cl (300 mg, 1.81 mmol, 1 eq.) was dissolved in acetonitrile (3 ml) and cooled to −30 °C. Dilute F\textsubscript{2} (10 % in Ar) was bubbled through the solution (20 min, 20 ml·min\textsuperscript{−1}, 1.2 eq.) To remove residual amounts of reactive gases, Ar was bubbled through the solution for 15 min. A colorless solution was obtained.

$^{1}$H NMR (400 MHz, MeCN, ext. acetone-d\textsubscript{6}, −40 °C) \(\delta_{\text{ppm}}\) = 3.11 (q, \(3J^\text{1H,1H}\) = 7.18 Hz, 8H, CH\textsubscript{2}), 1.12 (t, \(3J^\text{1H,1H}\) = 7.18 Hz, \(3J^\text{1N,1H}\) = 1.84 Hz, CH\textsubscript{3}). $^{19}$F NMR (377 MHz, MeCN, ext. acetone-d\textsubscript{6}, −40 °C) \(\delta_{\text{ppm}}\) = 67 (s, [ClF\textsubscript{3}]), −125 (s, [ClF\textsubscript{2}]). FT-Raman (MeCN, −196 °C): \(\tilde{\nu}\) = [ClF\textsubscript{3}]: 500 (a\textsubscript{1g}), 407(b\textsubscript{1g}), 278 (b\textsubscript{2g}), [ClF\textsubscript{2}]: 455 cm\textsuperscript{−1} (a\textsubscript{1g}).

**Crystal growth of [NEt\textsubscript{3}][ClF\textsubscript{3}][ClF\textsubscript{2}]**

The synthetic procedure is similar to [NEt\textsubscript{3}][ClF\textsubscript{2}][ClF\textsubscript{3}]. Single crystals were obtained by slowly cooling a propionitrile solution to −35 °C over 2 days in a freezer. An ethanol bath in a Dewar was used to reduce the cooling rate.
Synthesis of [NEt$_3$Me][ClF$_2$] in solution

[Ne3Me]Cl (50 mg, 0.330 mmol, 1 eq) was dissolved in propionitrile (0.5 ml) and cooled to −50 °C. Dilute ClF (10 % in Ar) was bubbled through the solution (8.5 min, 20 ml min$^{-1}$, 2 eq). To remove residual amounts of reactive gases, Ar was bubbled through the solution for 15 min. A colorless solution was obtained. The reaction mixture was allowed to warm to −10 °C and subsequently slowly cooled to −80 °C in an ethanol bath Dewar to reduce the cooling rate. Single crystals were obtained after 4 days.

Raman (crystal, −196 °C): $\nu = [\text{ClF}_2^+]$: 457 cm$^{-1}$ (a$_{1g}$).

Figure S1. $^1$H NMR spectrum (400 MHz, EtCN, ext. acetone-d$_6$, 21 °C) of a solution of [NEt$_3$Me][ClF$_2$] in propionitrile.

Figure S2. $^{19}$F NMR spectrum (377 MHz, EtCN, ext. acetone-d$_6$, 21 °C) of a solution of [NEt$_3$Me][ClF$_2$] in acetonitrile. Asterisk (*) denotes CFCl$_3$. Unknown impurity at −91 ppm (t).
We realized that the $^{19}$F NMR signal of $[\text{NEt}_3\text{Me}][\text{ClF}_4]$ shows different line broadening under certain conditions. Therefore, we studied the influence of temperature and HF impurities on the line width. Figure S4 shows the $^{19}$F NMR spectra at $-20$ °C and $-40$ °C prior and after addition of 1 eq of HF. Raising the temperature from $-40$ °C to $-20$ °C leads to a significant line broadening ($-40$ °C: FWHM = 164.8 Hz, $-20$ °C: 414.8 Hz). Addition of HF also leads to line broadening at $-20$ °C and $-40$ °C ($-40$ °C + HF addition: FWHM = 251.6 Hz, $-20$ °C + HF addition: FWHM = 637.7 Hz).

**Figure S4.** $^{19}$F NMR spectra (377 MHz, EtCN, ext. acetone-d6) of a solution of $[\text{NEt}_3\text{Me}][\text{ClF}_4]$ in propionitrile at $-20$ °C and $-40$ °C prior and after addition of 1 eq HF.
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Figure S5. Raman spectra (−196 °C) of [NEt$_3$Me][ClF$_4$] in different solvents: CHFCl$_2$ (top), EtCN (middle), MeCN (bottom). Left: full spectrum, right: Extract from 200–600 cm$^{-1}$. [ClF$_4$]$^-$ bands are highlighted in red.

[NEt$_3$Me][ClF$_4$] in different solvents, CHFCl$_2$ (top), propionitrile (middle) and acetonitrile (bottom). The three characteristic bands for [ClF$_4$]$^-$ (500 cm$^{-1}$ ($a_{1g}$), 407 cm$^{-1}$ ($b_{1g}$), 278 cm$^{-1}$ ($b_{2g}$)) are highlighted in red. The different intensities are due to different concentrations. In case of propionitrile the concentration is too low (0.32 mol·l$^{-1}$) to observe the $b_{2g}$ vibration. In case of CHFCl$_2$ the band of the $b_{2g}$ vibration is superimposed by a solvent band.
Reactivity Studies

Disulfide activation

\[
5 \text{[NEt}_3\text{Me]}\text{[ClF}_4\text{]} \rightarrow \text{[NEt}_3\text{Me]}\text{[ClF}_2\text{]} + 2 \text{Ph}_2\text{S} \rightarrow \text{Ph}_2\text{SF}_5 + 2 \text{Ph}_2\text{SFCl}_4
\]

To a cooled (−55 °C) solution of [NEt₃][ClF₄] in propionitrile (1 ml, 0.659 mol·l⁻¹, 1 eq.) a solution of phenyl disulphide (28.8 mg, 0.132 mmol, 0.2 eq) in propionitrile (2 ml) was added dropwise. The solution was stirred for 15 min at −55 °C, then allowed to warm to r.t. and stirred over night. A 1 : 4 : 2 mixture of Ph₂SF₅ : cis-Ph₂SF₂Cl : trans-Ph₂SF₂Cl was obtained. After addition of H₂O (0.5 ml) trans-Ph₂SF₂Cl was selectively hydrolysed to PhSO₂F. Addition of dilute potassium hydroxide solution (1 ml) and heating to 90 °C over night led to the hydrolysis of cis-Ph₂SF₂Cl and PhSO₂F. Products were identified by ¹⁹F NMR spectroscopy. NMR yield PhSF₅: 17 %

¹⁹F NMR (377 MHz, EtCN, ext. acetone-d₆, 21 °C) δ= 85 (quin. 2J(¹⁹F,¹⁹F)=148Hz, 1F, PhSF₅ trans-F), 63 (d, 4F, PhSF₅ cis-F), 165 (td 2J(¹⁹F,¹⁹F)=164Hz, 3J(¹⁹F,¹⁹F)=149 Hz, 1F, cis-PhSF₂ trans-F), 100 (dd, 2J(¹⁹F,¹⁹F)=81 Hz, 2F, cis-PhSF₂ cis-F), 67 (dt, 2F, cis-PhSF₄ cis-F), 137 (s, 4F, trans-PhSF₂Cl), 64 ppm (s, 1F PhSO₂F).
Figure S7. $^{19}$F NMR spectra (377 MHz, EtCN, ext. acetone-d6, 21 °C) of the reaction mixture after the reaction of [NEt$_3$Me][ClF$_4$] with Ph$_2$S$_2$ showing three products: PhSF$_5$, cis-PhSF$_4$Cl and trans-PhSF$_4$Cl. Experimental spectra shown with positive intensities, simulated spectra shown with negative intensities.

Figure S8. $^{19}$F NMR spectrum (377 MHz, EtCN, ext. acetone-d6, 21 °C) of the hydrolysed reaction mixture (H$_2$O, r.t., 15 min) after the reaction of [NEt$_3$Me][ClF$_4$] with Ph$_2$S$_2$ showing three products: PhSF$_5$, cis-PhSF$_4$Cl and PhSO$_2$F.
Nitrile activation

\[
2 \text{[NEt}_3\text{Me][ClF}_4] + 2 \text{MeCN} \cdot \text{BF}_3 \xrightarrow{-55^\circ\text{C}} \text{CHFCI}_2 -2 \text{[NEt}_3\text{Me][BF}_4] -\text{N}_2 -\text{Cl}_2 \rightarrow 2 \text{CH}_3\text{CF}_3
\]

The acetonitrile boron trifluoride complex was synthesized by the addition of BF₃ to acetonitrile at r.t. followed by removal of residual acetonitrile under reduced pressure. To solid acetonitrile boron trifluoride complex (35.9 mg, 0.330 mmol, 0.5 eq) a solution of [NEt₃Me][ClF₄] (150 mg, 0.659 mmol, 1 eq) in dichlorofluoromethane (1 ml) was added at −60 °C. The reaction mixture was analyzed by ¹⁹F NMR spectroscopy (Figure S9). The reaction equation suggests the equimolar formation of CH₃CF₃ and [BF₄]⁻. The ¹⁹F NMR spectrum shows a ratio of 1:230 in favour of [BF₄]⁻ this can be rationalised due to several reasons: First, CH₃CF₃ has a boiling point of −50 °C. During the reaction and the transfer of the reaction mixture probably significant amounts of the product evaporated. Secondly, during the reaction highly reactive ClF₃ is formed leading to side products which are evident in the ¹⁹F NMR spectrum. The signal at −129 ppm can be identified as [SiF₄]²⁻ from a reaction with the glass vessel.

Figure S9. ¹⁹F NMR spectrum (377 MHz, EtCN, ext. acetone-d₆, 21 °C) of the hydrolysed reaction mixture (KOH aq, 90 °C, 8 h) after the reaction of [NEt₃Me][ClF₄] with Ph₂S₂ showing only PhSF₅.
**Figure S10.** $^{19}$F NMR spectrum (377 MHz, EtCN, ext. acetone-d6, 21 °C) of the reaction mixture. Symbols denote solvent impurities (*), side products generated during the reaction (#).
A solution of [NEt₃Me][ClF₄] (150 mg, 0.659 mmol, 1 eq) was stirred under a CO atmosphere for 30 min at r.t. Then the gas-phase was analyzed via FT-IR spectroscopy. The FT-IR spectrum (Figure S7) only shows the presence of starting material (CO) solvent (EtCN) and product (COF₂). The formation of COCl₂ or COClF was not observed.

Gold metal (16 mg) was dissolved over 2 days in a solution of [NEt₃Me][ClF₄] in acetonitrile (0.5 ml, 8 mol·l⁻¹) at r.t. The solution was analyzed with ¹⁹F NMR spectroscopy. The major product is [AuF₄]⁻ (95%) but traces of [AuF₃Cl]⁻ (3%) and cis-[AuF₂Cl₂]⁻ (2%) were also present in the reaction mixture.

**Equation:**

\[ 2 \text{[NEt}_3\text{Me][ClF}_4] + 2 \text{Au} \rightarrow \frac{\text{MeCN}}{\text{Cl}_2} \rightarrow 2 \text{[NEt}_3\text{Me][AuF}_4] \]
Figure S12. $^{19}$F NMR spectrum (377 MHz, MeCN, ext. acetone-d6, 21 °C) of the reaction mixture after the reaction of $[\text{NEt}_3\text{Me}]\text{[ClF}_4]$ with Au. Symbols denote fluorinated impurities: # fluorinated solvent (FCH$_2$CN), * halogenated cations.
Tetracyanoborate activation

\[
\text{[NET}_3\text{Me][ClF}_4] + \text{[NET}_3\text{Me][B(CN)}_4\text{]} \rightarrow \text{[NET}_3\text{Me][B(CF}_3\text{)}_x\text{CN)}_{4-x}\text{]} \quad \text{CHFCI}_2 \quad -55 \degree \text{C} \quad \text{BF}_3
\]

Potassium tetracyanoborate (500 mg, 3.25 mmol, 1 eq) was dissolved in acetonitrile (10 ml). A solution of triethylmethyldiammonium chloride (0.493 mg, 3.25 mmol, 1 eq) in acetonitrile (5 ml) was added. The colourless precipitate was filtrated and the solvent was removed under reduced pressure to yield tetramethylammonium tetracyanoborate.

Triethylmethyldiammonium tetracyanoborate (76.0 mg, 0.330 mmol, 0.5 eq) was dissolved in CHFCI 2 (1 ml) and boron trifluoride (67.0 mg, 0.989 mmol, 1.5 eq) was added. The solution was cooled to −60 °C. A cooled solution of Triethylmethyldiammonium tetrafluoridochlorate(III) (1 ml, 0.659 mol*l −1, 1 eq) was added at −60 °C, stirred for 5 min at −60 °C and let allowed to warm to r.t. Volatiles were removed and the residue was dissolved in CD 3 CN and analyzed via 19F and 11B NMR spectroscopy. [B(CF}_3\text{)}_x\text{CN)}_{4-x}\text{]}^{-} \text{anions were identified according to literature.}

Figure S13. 19F NMR spectrum (377 MHz, CD 3 CN, 21 °C) of the reaction mixture after the reaction of [NET}_3\text{Me][ClF}_4\text{]} with [NET}_3\text{Me][B(CN)}_4\text{].
**Figure S14.** $^{11}$B$^{[19]}$F NMR spectrum (129 MHz, CD$_2$CN, 21 °C) of the reaction mixture after the reaction of [NEt$_3$Me][ClF$_4$] with [NEt$_3$Me][B(CN)$_4$].
Difluoroaurate activation

\[ \text{[NEt}_3\text{Me][ClF}_4] + \text{[NEt}_3\text{Me}[\text{Au(CN)}_2] \xrightarrow{-55 \degree \text{C}} \text{[NEt}_3\text{Me}[\text{AuF}_2(\text{CF}_3)(\text{CN})] } \]

Cation metathesis was achieved in a similar procedure to triethylmethylammonium tetracyanoborate. Triethylmethylammonium dicyanoaurate (43 mg, 0.118 mmol, 0.18 eq) was dissolved in CHFCl$_2$ (1 ml). Boron trifluoride (19 mg, 0.280 mmol, 0.42 eq) was added. The solution was cooled to −60 °C. A cooled solution of triethylmethyammonium tetrafluoridochlorate(III) (1 ml, 0.659 mol*l$^{-1}$, 1 eq) was added at −60 °C, stirred for 5 min at −60 °C and let allowed to warm to r.t and analyzed via $^{19}$F NMR spectroscopy.

Cis-cyanodifluoro(trifluoromethyl)aurate(III) was identified using $^{19}$F NMR spectroscopy in comparison with literature values.$^{[25]}$ Due to the low concentration of cis-cyanodifluoro(trifluoromethyl)aurate(III) the region between −80 and −170 ppm in the NMR spectrum is not shown. It contains solvent signal CHFCl$_2$ at −81 ppm, [SiF$_6$]$_2^-$ at −129 ppm and [BF$_4$]$^-$ at −152 ppm δ[ppm]= −58.29 (dd, $^3$J($^{19}$F, $^{19}$F) = 5.8 Hz, $^3$J($^{19}$F, $^{19}$F) = 2.5 Hz, 3F), −196.66 (dq, $^2$J($^{19}$F, $^{19}$F) = 2.5 Hz, 1F), −254.31 (dq, $^2$J($^{19}$F, $^{19}$F) = 65.3 Hz, $^3$J($^{19}$F, $^{19}$F) = 5.8, 1F)

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**Figure S15.** $^{19}$F NMR spectrum (377 MHz, CHFCl$_2$, ext. acetone-d$_6$, 21 °C) of the reaction mixture after the reaction of [NEt$_3$Me][ClF$_4$] with [NEt$_3$Me][Au(CN)$_2$]. Omitted spectral area between −80 and −170 ppm contains solvent CHFCl$_2$ (−81 ppm), [SiF$_6$]$_2^-$ (−129 ppm) and [BF$_4$]$^-$ (−152 ppm).
### Crystallographic section

**Table S1.** Crystallographic details of [NEt₃][ClF₄][ClF₆] and [NEt₃][ClF₄].

| Compound | [NEt₃][ClF₄][ClF₆] | [NEt₃][ClF₄] | [Net₂][ClF₄] |
|----------|---------------------|-------------|-------------|
| Empirical formula | C₃H₆Cl₂F₁₂N₂ | C₃H₆Cl₂F₁₁N | C₃H₇Cl₂F₁₁N |
| Formula weight | 607.02 | 241.70 | 189.67 |
| Temperature/K | 100.0 | 99.92 | 100.0 |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | P1 | C2/c | P2₁/c |
| a[Å] | 6.9802(8) | 11.4818(9) | 11.2608(4) |
| b[Å] | 14.6749(16) | 7.5474(5) | 6.9954(2) |
| c[Å] | 15.3580(16) | 14.3613(11) | 12.6412(4) |
| α[°] | 97.19(4) | 90 | 90 |
| β[°] | 92.01(4) | 110.877(3) | 102.6650(10) |
| γ[°] | 92.68(4) | 90 | 90 |
| Volume/A³ | 1520.0(3) | 1162.81(15) | 971.57(5) |
| Z | 2 | 4 | 4 |
| μ/mm⁻¹ | 1.326 | 1.381 | 1.297 |
| F(000) | 648.0 | 512.0 | 408.0 |
| Crystal size/mm³ | 0.34 × 0.23 × 0.18 | 0.32 × 0.16 × 0.04 | 0.293 × 0.216 × 0.154 |
| Crystal size/mm³ | 0.34 × 0.23 × 0.18 | 0.32 × 0.16 × 0.04 | 0.293 × 0.216 × 0.154 |
| Crystal size/mm³ | 0.34 × 0.23 × 0.18 | 0.32 × 0.16 × 0.04 | 0.293 × 0.216 × 0.154 |
| Refinement collected | 85154 | 25147 | 24557 |
| Independent reflections | 7678 [R(int) = 0.0626, R_exp = 0.0322] | 1453 [R(int) = 0.0452, R_exp = 0.0173] | 2961 [R(int) = 0.0275, R_exp = 0.0157] |
| Data/restraints/parameters | 7678/0/331 | 1453/0/68 | 2961/0/117 |
| Goodness-of-fit on F² | 1.095 | 1.772 | 1.065 |
| Final R indexes [I>2σ(I)] | R₁ = 0.0372, wR₂ = 0.0910 | R₁ = 0.0300, wR₂ = 0.0752 | R₁ = 0.0268, wR₂ = 0.0751 |
| Final R indexes [all data] | R₁ = 0.0517, wR₂ = 0.0878 | R₁ = 0.0334, wR₂ = 0.0766 | R₁ = 0.0316, wR₂ = 0.0804 |
| Largest diff. peak/hole / e Å⁻³ | 0.34/−0.44 | 0.32/−0.38 | 0.34/−0.34 |
| CCDC deposition number | 1948997 | 1948998 | 2004243 |

**Table S2.** Bond lengths and angles of [ClF₄]⁻ anions in [NEt₃][ClF₄] and [NEt₃][ClF₄][ClF₆]. In comparison with the literature known compounds [ppy][ClF₄], [NO][ClF₄], Cs[ClF₄], Rb[ClF₄] and K[ClF₄].

| Bond/Angle | [NEt₃][ClF₄] | [NEt₃][ClF₄][ClF₆] | [ppy][ClF₄] | [NO][ClF₄] | Cs[ClF₄] | Rb[ClF₄] | K[ClF₄] |
|------------|--------------|---------------------|-------------|-------------|---------|--------|--------|
| C1–Cl1-F1 | 179.3(1) | 178.8(1) | 175.9(2) | 187.4(1) | 179.4(4) | 179.3(9) | - |
| C1–Cl1-F2 | 180.6(1) | 179.4(1) | 181.4(1) | 172.7(1) | 179.2(4) | 179.3(9) | - |
| C1–Cl1-F3 | - | 180.0(1) | 177.1(1) | - | - | - | - |
| C1–Cl1-F4 | - | 180.8(1) | 181.3(1) | - | - | - | - |
| C1–Cl2-F1 | 90.01(5) | 89.78(5) | 89.1(2) | 89.3(3) | 89.7(4) | - | - |
| C2–Cl1-F1 | 89.99(5) | 89.3(3) | 90.0(2) | 90.6(7) | 90.2(4) | - | - |
| F2–Cl1-F3 | - | 88.6(5) | - | - | - | - | - |
| F3–Cl1-F4 | - | 90.2(1) | - | - | - | - | - |
| F4–Cl1-F1 | - | 90.3(5) | - | - | - | - | - |

Figure S16. Hirshfeld surface of the [ClF₄]⁻ anion in [NEt₃][ClF₄]. Color code: blue = N, grey = C, white H, green dashed line displays hydrogen bond. [27]
By slowly cooling a reaction mixture of [NEtMe]Cl with 1.2 eq. fluorine in acetonitrile, single crystals of [NEtMe][ClF₄][ClF₂]₂ were obtained (Figure S16). This compound crystallizes in the space group $P\overline{1}$. In the asymmetric unit are four anionic moieties. One is a [ClF₄]⁻ anion, the second is an asymmetric [ClF₂]⁻ (F7Cl4F8) anion. Furthermore, there are two [ClF₂]⁻ units with the chlorine atom on centers of inversion (F6Cl3F6' and F5Cl2F5') (Figure 4). The bond lengths and angles in the [ClF₂]⁻ anion (F7Cl4F7) are very similar to the ones found in [NEt₄][ClF₂]. The Cl–F bond lengths of the [ClF₂]⁻ anions vary between 184.1(2) pm and 185.4(1) pm. The bond angle of the [ClF₂]⁻ anion (F7Cl4F7) is 179.66(5) °.

Figure S17. Crystal structure of [NEtMe][ClF₄][ClF₂]₂. Color code: yellow = F, green = Cl, blue = N, grey = C. Displacement ellipsoids are shown at 50 % probability at 100 K. Selected bond lengths [pm] and bond angles [°]: F1–Cl1 178.8(1), F2–Cl1 179.4(1), F3–Cl1 180.0(1), F4–Cl1 180.8(2), F5–Cl2 185.4(1), F6–Cl3 184.1(2), F7–Cl4 184.9(1), F8–Cl4 185.4(1), F7–Cl4–F8 179.66(5). Hydrogen atoms omitted for clarity.
SUPPORTING INFORMATION

Computational section

Table S3. Calculated $^1$H NMR chemical shifts relative to CFCI$_3$ (in ppm) of [XF$_n$]$_{-}$ (X = Cl, Br, I; n=2, 4, 6) in comparison with experimental values, at BP86-D3 structures.*

|          | BLYP | LH12ct-SsifPW92 |
|----------|------|-----------------|
| opt. NMR | gas  | gas            | gas  | gas    | gas    | gas    | gas    | gas    | $\delta_{exp}$ |
| [CI]$_{-}$ | -193.2 | -208.2       | -196.3 | -204.4 | -1663 | -178.2       | -171.3 | -174.4 | -125 |
| [ClF$_n$]$_{-}$ | 80.6 | 76.1 | 72.9 | 68.5 | 69.1 | 68.6 | 63.3 | 60.5 | 67 |
| [ClF$_n$]$_{-}$ | 284.3 | 286.8 | 278.6 | 277.6 | 255.1 | 257.6 | 246.6 | 248.9 | 0 |
| [BrF$_n$]$_{-}$ | -284.4 | -294.8 | -286.2 | -295.5 | -262.6 | -270.7 | -265.4 | -272.7 | -210 |
| [BrF$_n$]$_{-}$ | -32.2 | -38.3 | -36.3 | -42.0 | -36.6 | -41.6 | -40.7 | -45.4 | -37 |
| [BrF$_n$]$_{-}$ | 131.9 | 135.0 | 126.0 | 129.2 | 114.6 | 117.4 | 109.0 | 111.9 | 94 |
| [IF$_n$]$_{-}$ | -350.1 | -359.3 | -351.4 | -360.1 | -338.1 | -346.7 | -339.5 | -347.8 | -282 |
| [IF$_n$]$_{-}$ | -103.1 | -109.5 | -105.1 | -111.1 | -109.8 | -115.5 | -111.8 | -117.3 | -106 |
| [IF$_n$]$_{-}$ | 31.1 | 33.3 | 28.1 | 30.5 | 14.8 | 16.9 | 11.9 | 14.1 | 13 |

*$^*$ At BP86-D3(BJ)/def2-TZVPPD optimized structures. CFCI$_3$ reference shieldings at the same level have been used to obtain the relative shifts. Nonrelativistic results with pcSeg4-4 basis sets for F, Cl, Br, and ANO-RCC-unc for I.

Table S4. Calculated $^1$F NMR chemical shifts relative to CFCI$_3$ (in ppm) of [XF$_n$]$_{-}$ (X = Cl, Br, I; n=2, 4, 6) in comparison with experimental values, at B3LYP-D3 structures.*

|          | BLYP | LH12ct-SsifPW92 |
|----------|------|-----------------|
| opt. NMR | gas  | gas            | gas  | gas    | gas    | gas    | gas    | gas    | $\delta_{exp}$ |
| [CI]$_{-}$ | -190.6 | -196.4 | -193.4 | -198.4 | -169.8 | -171.0 | -173.3 | -169.8 | -125 |
| [ClF$_n$]$_{-}$ | 55.3 | 61.3 | 58.5 | 54.9 | 56.5 | 53.8 | 49.9 | 47.5 | 67 |
| [ClF$_n$]$_{-}$ | 250.8 | 252.9 | 243.0 | 245.3 | 224.7 | 226.7 | 217.5 | 219.7 | 0 |
| [BrF$_n$]$_{-}$ | -279.4 | -288.5 | -281.1 | -289.5 | -260.0 | -267.1 | -263.3 | -268.9 | -210 |
| [BrF$_n$]$_{-}$ | -38.2 | -43.7 | -41.5 | -46.7 | -43.3 | -47.8 | -46.6 | -50.8 | -37 |
| [BrF$_n$]$_{-}$ | 113.8 | 116.4 | 108.5 | 114.4 | 97.6 | 100.0 | 92.7 | 95.3 | 94 |
| [IF$_n$]$_{-}$ | -343.0 | -351.5 | -344.6 | -352.9 | -332.4 | -340.3 | -333.9 | -341.8 | -282 |
| [IF$_n$]$_{-}$ | -99.5 | -105.5 | -101.3 | -107.1 | -107.0 | -112.5 | -108.8 | -114.1 | -106 |
| [IF$_n$]$_{-}$ | 29.3 | 31.4 | 26.5 | 28.4 | 12.7 | 14.4 | 9.9 | 11.7 | 13 |

*$^*$ At B3LYP-D3(BJ)/def2-TZVPPD optimized structures. CFCI$_3$ reference shieldings at the same level have been used to obtain the relative shifts. Nonrelativistic results with pcSeg4-4 basis sets for F, Cl, Br, and ANO-RCC-unc for I.

Table S5. Fully relativistic 4c-mDKS/B3LYP50/Dyall-VQZ results for $^1$F NMR nuclear shieldings and chemical shifts of [XF$_n$]$_{-}$ (X = Cl, Br, I; n=2, 4, 6).*$^*$

|          | [CI]$_{-}$ | [ClF$_n$]$_{-}$ | [BrF$_n$]$_{-}$ | [BrF$_n$]$_{-}$ | [IF$_n$]$_{-}$ | [IF$_n$]$_{-}$ | CFCI$_3$ |
|----------|----------|----------------|----------------|----------------|----------------|----------------|-----------|
| $\sigma^{\cd}$ | 389.0     | 126.2 | -78.8 | 471.3 | 246.1 | 75.0 | 539.6 | 321.5 | 192.1 | 192.4 |
| $\delta$   | -196.5    | 66.2 | 271.2 | -276.9 | -43.7 | 117.4 | -347.2 | -129.2 | 0.3 | 0 |

*$^*$ Gas-phase results relative to CFCI$_3$ at the same level, at BP86-D3(BJ)(COSMO,CH4CN)/def2-TZVPPD structures.
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