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Largest perfluorometallate $[Ti_{10}F_{45}]^{5-}$ oligomer and polymeric $([Ti_3F_{13}]^-)_\infty$ and $([TiF_5]^-)_\infty$ anions prepared as $[XeF_5]^+$ salts

Zoran Mazej,* and Evgeny A. Goreshnik

Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, Tel: +386 1 477 3301;

E-mail: zoran.mazej@ijs.si

Table S1 Stoichiometries used to synthesize and crystallize $[XeF_5]^+$ poly[perfluorotitanates(IV)] and phases detected in the isolated solids after reactions or crystallizations of various $n$$XeF_2$/$TiF_4$/UV-irradiated F_2/aHF mixtures.

Starting n(XeF_2) : n(TiF_4) molar ratio	Phases detected after syntheses and/or crystallizations[a]
4 : 1	XeF_4, XeF_5TiF_5
3 : 1	XeF_4, XeF_5TiF_5, $[XeF_5]_3[Ti_4F_{19}]$
2 : 1	XeF_4, XeF_5TiF_5, $[XeF_5]_3[Ti_4F_{19}]$
1.5 : 1 (3:2)	XeF_5TiF_5, $[XeF_5]_3[Ti_4F_{19}]$
1 : 1	XeF_5TiF_5, $[XeF_5]_3[Ti_4F_{19}]$
1 : 1.33 (3:4)	$[XeF_5]_3[Ti_4F_{19}]$[b]
1 : 2	$[XeF_5]_3[Ti_4F_{19}]$, $[XeF_5]_5[Ti_{10}F_{45}]$, $[XeF_5][Ti_3F_{13}]$, TiF_4
1 : 3	$[XeF_5][Ti_3F_{13}]$, TiF_4
1 : 4	$[XeF_5][Ti_3F_{13}]$, TiF_4, $(O_2)_2Ti_7F_{30}$

[a]List of phases detected using Raman spectroscopy or by determining the unit cells of grown crystals on a diffractometer. There is always a possibility that traces of some phases weren't detected. However, general trend about formation of various phases is obvious.

[b]Z. Mazej, E. Goreshnik, *Eur. J. Inorg. Chem.*, 2009, 4503–4506.

Table S2 Raman frequencies of XeF_5TiF_5, $[XeF_5]_5[Ti_{10}F_{45}]$ and $[XeF_5][Ti_3F_{13}]$[a]

XeF_5TiF_5	$[XeF_5]_5[Ti_{10}F_{45}]$	$[XeF_5][Ti_3F_{13}]$
752	780	784
733	673	774
675	664	755
671	652	680
656	620	665
636	425	657
629	416	620
623	317	603
612	302	405
593	289	393
590	275	304
576	227	230
419	213	217
413		195
213		
287		
230		
212		

[a]Spectra were recorded on the randomly oriented single crystals sealed in a quartz glass capillaries at 23 °C using 632.81 nm excitation.

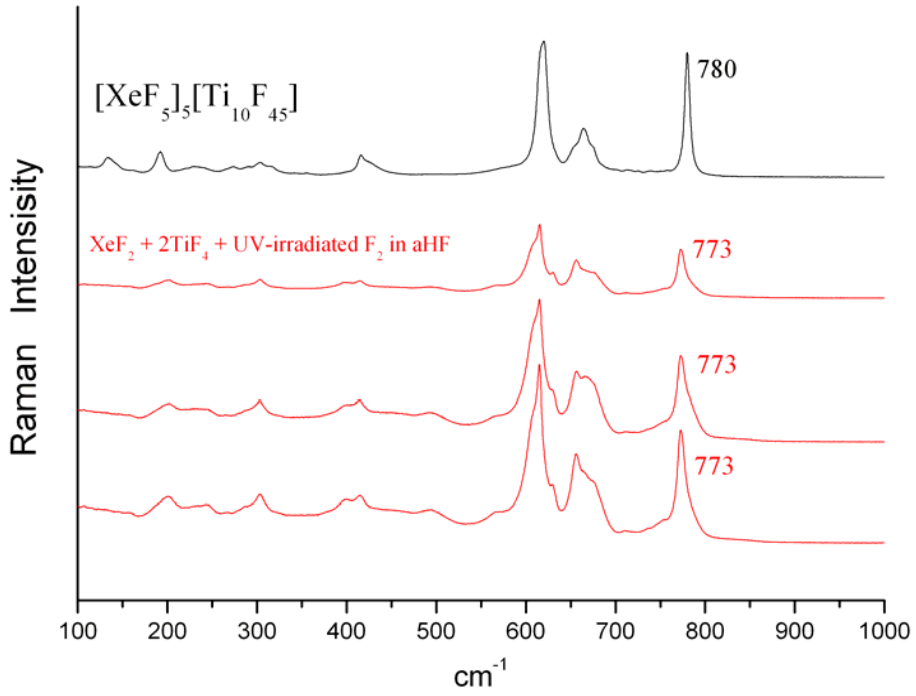

Fig. S1 Raman spectrum of $[XeF_5]_5[Ti_{10}F_{45}]$ and Raman spectra of solid (measured on different spots) isolated after the **reaction** between XeF_2, $2TiF_4$ and UV-irradiated F_2 in aHF.

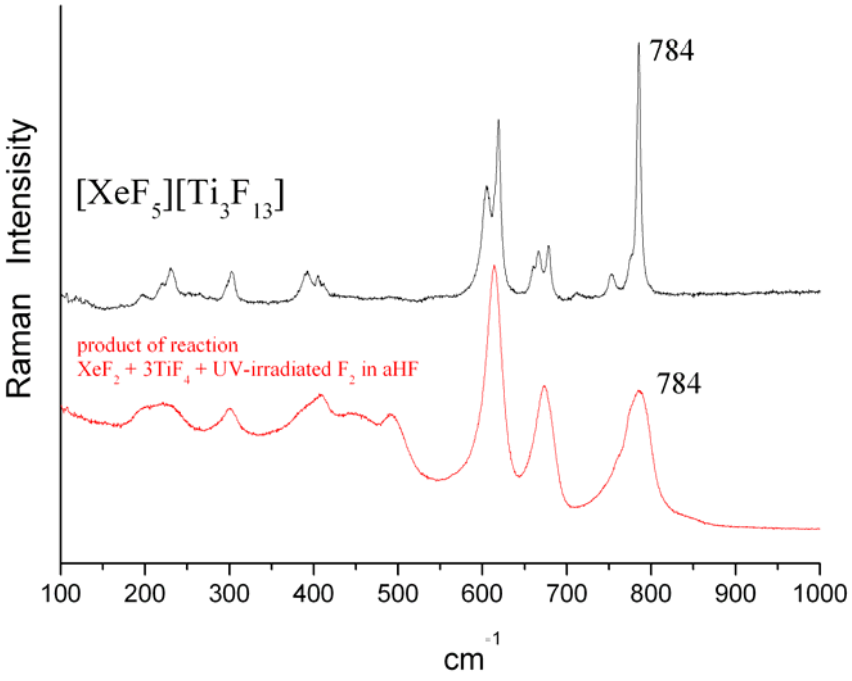

Fig. S2 Raman spectrum of $[XeF_5][Ti_3F_{13}]$ and Raman spectrum of solid isolated after **reaction** between XeF_2, $3TiF_4$ and UV-irradiated F_2 in aHF.

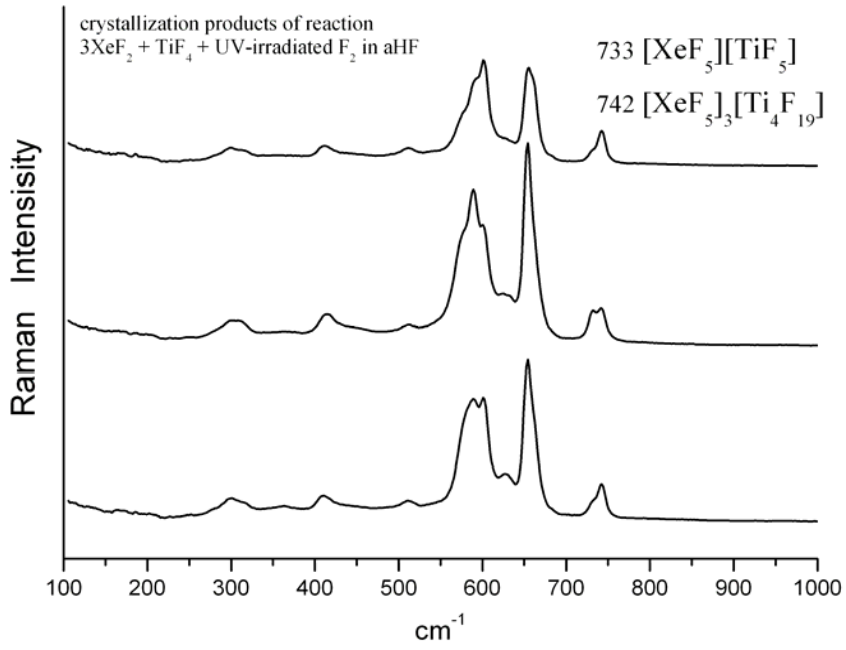

Fig. S3 Raman spectra (measured on different spots) of solid obtained after the **crystallization** from the solution prepared by the reaction between $3XeF_2$, TiF_4 and UV-irradiated F_2 in aHF.

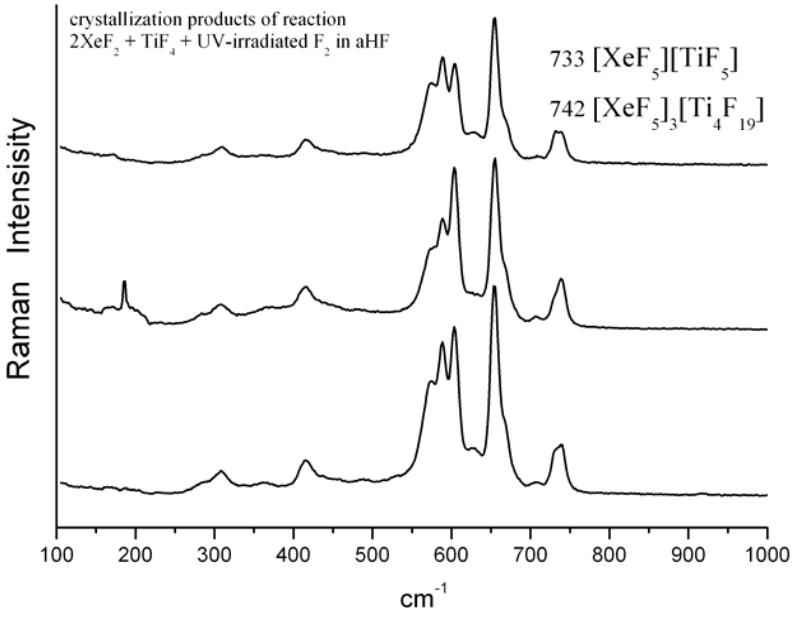

Fig. S4 Raman spectra (measured on different spots) of solid obtained after the **crystallization** from the solution prepared by the reaction between $2XeF_2$, TiF_4 and UV-irradiated F_2 in aHF.

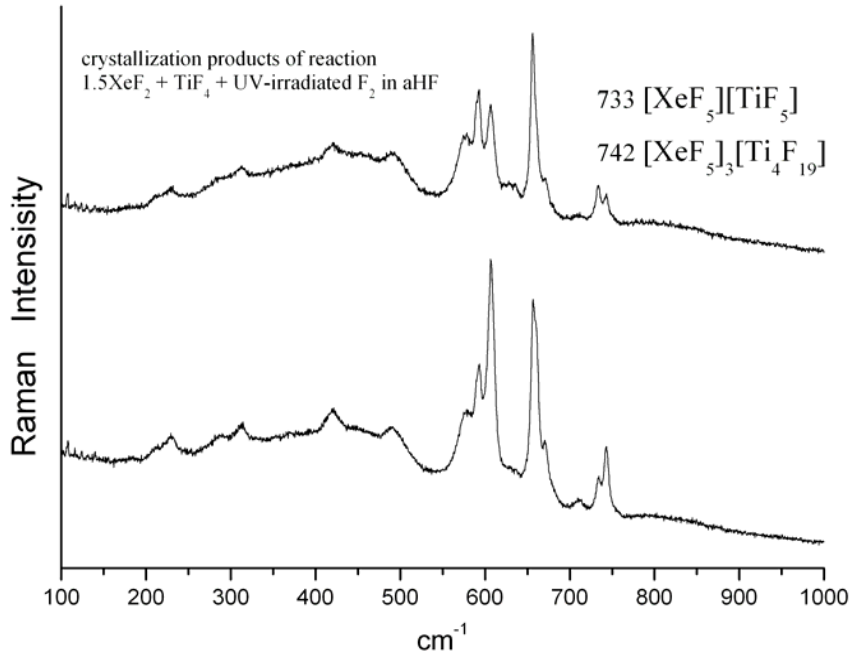

Fig. S5 Raman spectra (measured on different spots) of solid obtained after the **crystallization** from the solution prepared by the reaction between $1.5XeF_2$, TiF_4 and UV-irradiated F_2 in aHF.

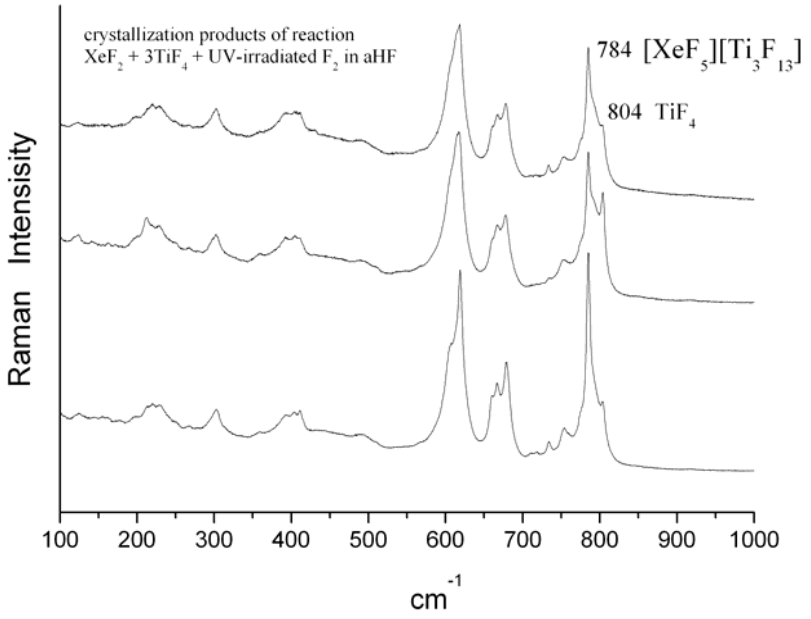

Fig. S6 Raman spectra (measured on different spots) of solid obtained after the **crystallization** from the solution prepared by reaction between XeF_2, $3TiF_4$ and UV-irradiated F_2 in aHF.

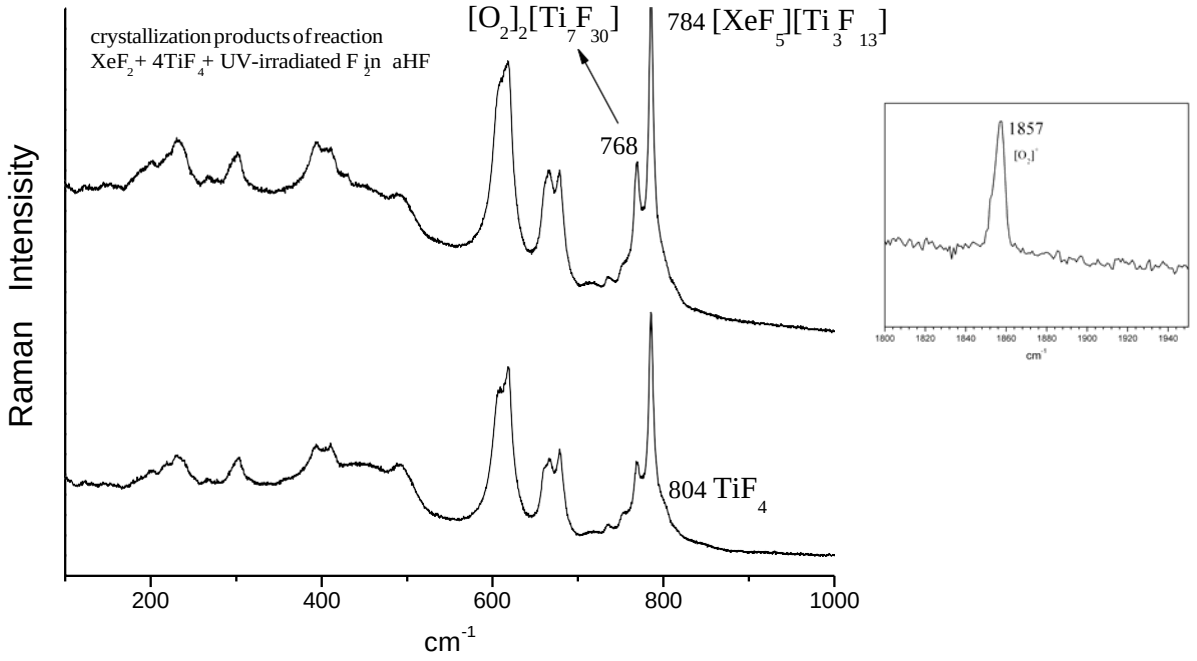

Fig. S7 Raman spectra (measured on different spots) of solid obtained after the **crystallization** from the solution prepared by reaction between XeF_2, $4TiF_4$ and UV-irradiated F_2 in aHF.

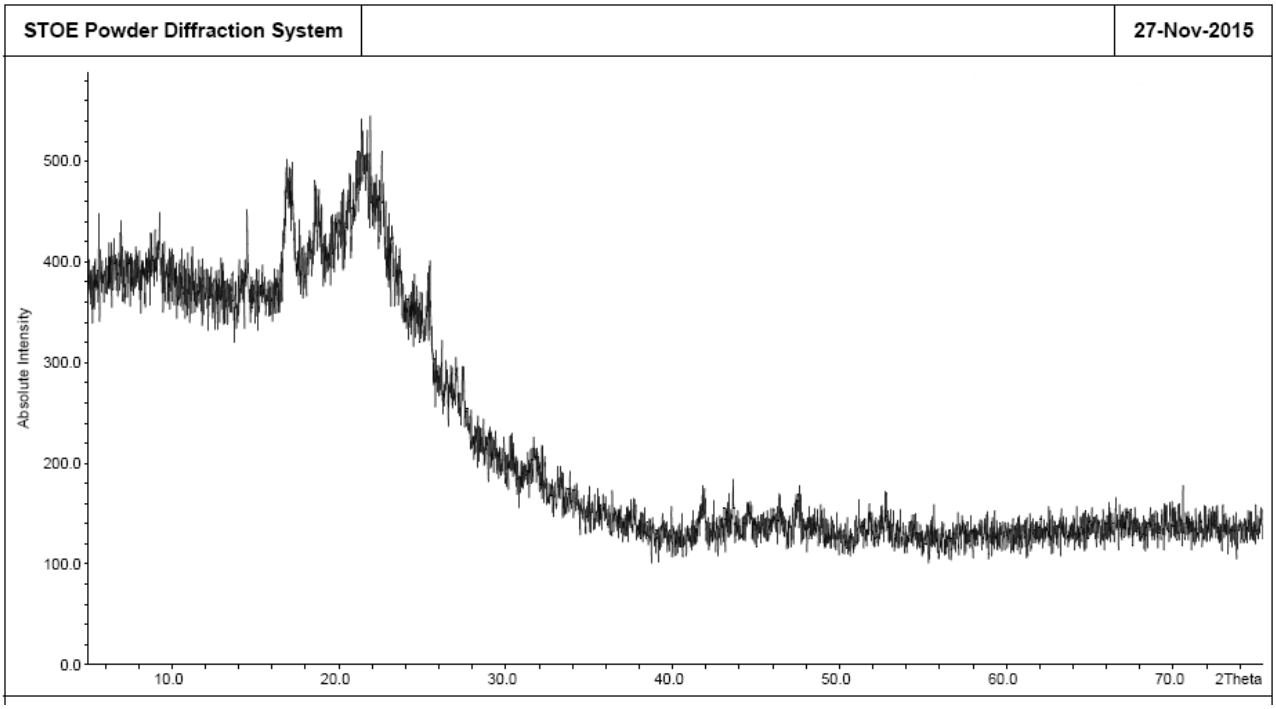

Fig. S8 X-ray powder diffraction pattern of the product of **reaction** between XeF_2 and $2TiF_4$ in the presence of UV-irradiated F_2 in aHF.

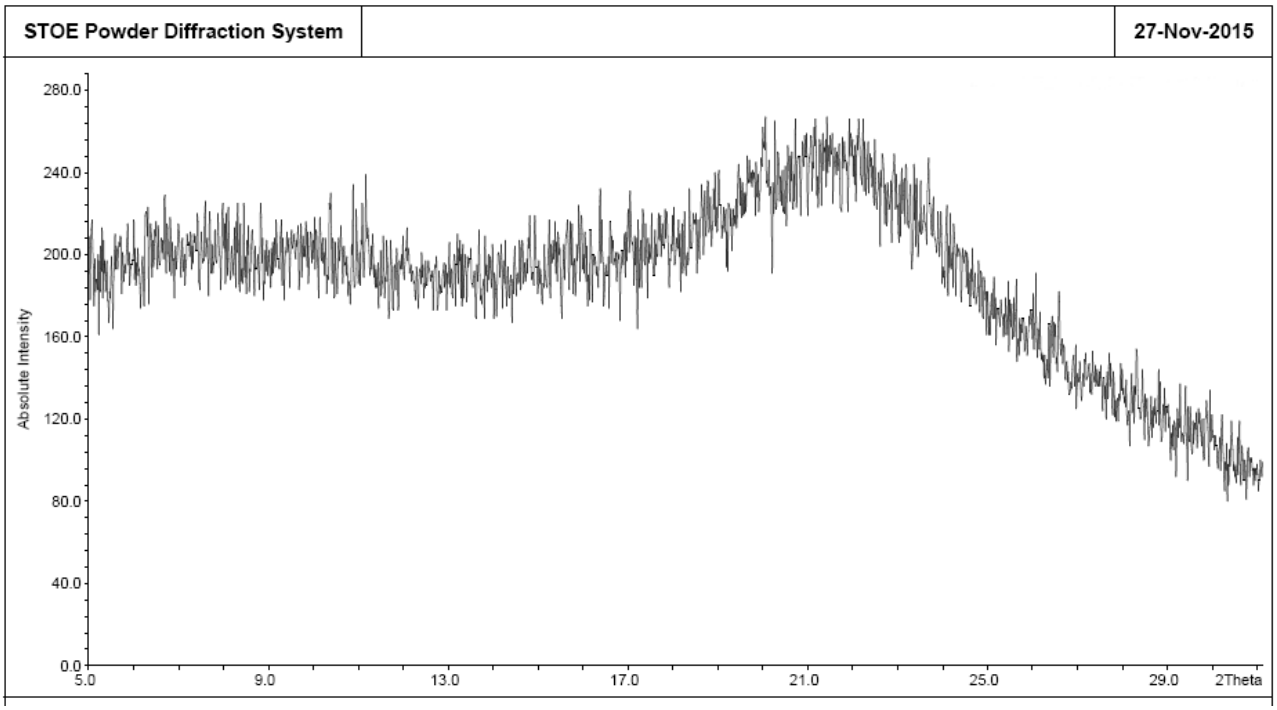

Fig. S9 X-ray powder diffraction pattern of the product of **reaction** between XeF_2 and $3TiF_4$ in the presence of UV-irradiated F_2 in aHF (1^{st} batch)

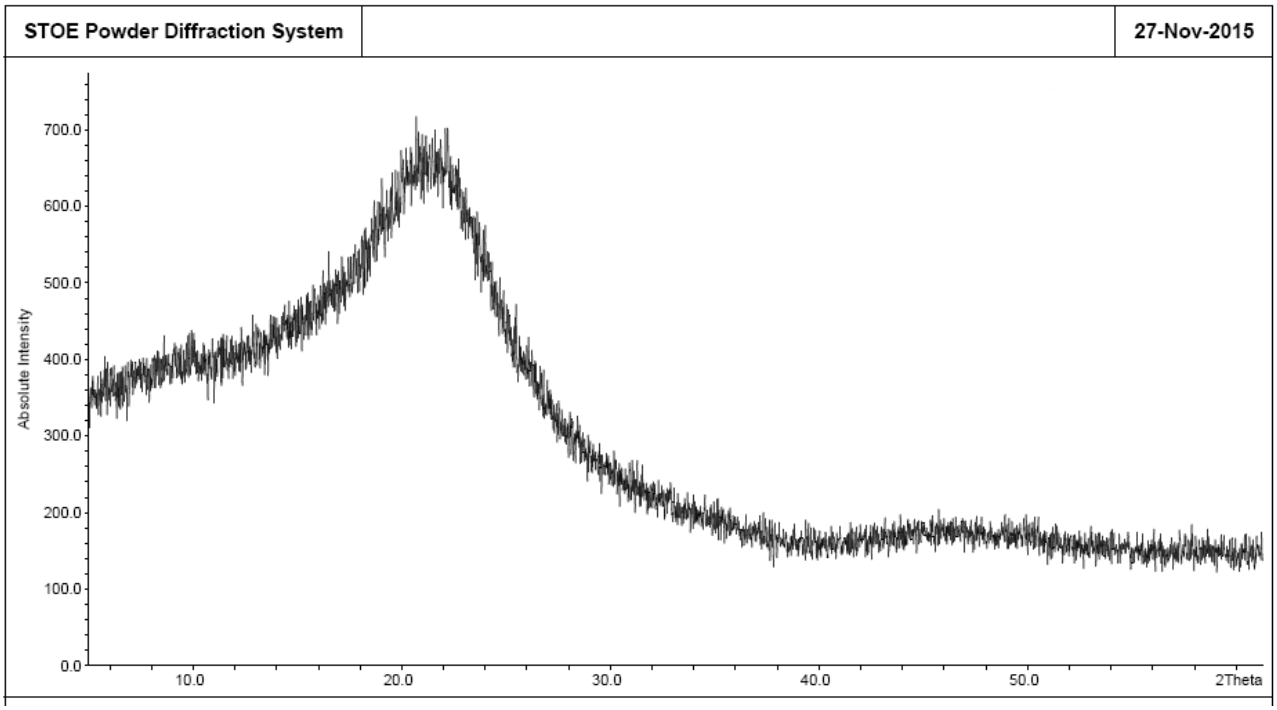

Fig. S10 X-ray powder diffraction pattern of the product of **reaction** between XeF_2 and $3TiF_4$ in the presence of UV-irradiated F_2 in aHF (2^{nd} batch).

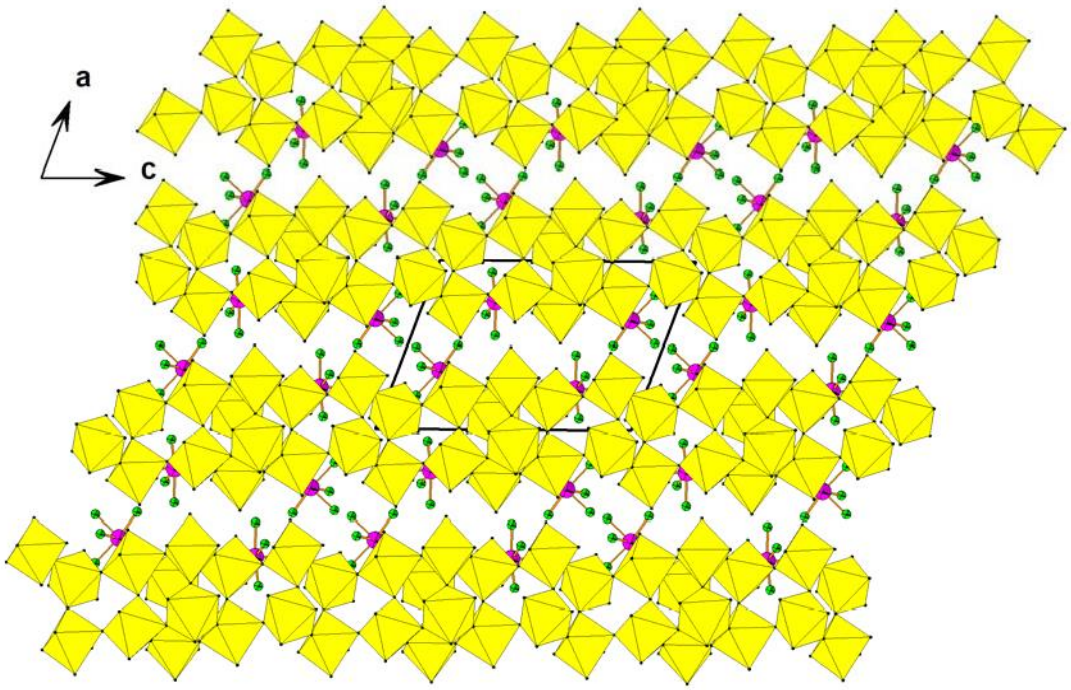

Fig. S11 Packing of $([Ti_3F_{13}]^-)_\infty$ columns and $[XeF_5]^+$ cations in the crystal structure of $[XeF_5][Ti_3F_{13}]$.