SUPPLEMENTARY MATERIAL

A hybrid vanadium fluoride with structurally isolated *S* = 1 kagome layers

Farida H. Aidoudi[1], Lewis J. Downie[1], Russell E. Morris[1], Mark de Vries[2] and Philip Lightfoot[1]*

1. EaStChem, School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK.
2. EaStChem, School of Chemistry, University of Edinburgh, EH9 3JZ, UK.

E-mail: pl@st-and.ac.uk

Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM Tf_2N, mp = -3°C):

EMIM Tf_2N was synthesised by an anion exchange between the IL 1-ethyl-3-methylimidazolium bromide "EMIM Br" and lithium bis(trifluoromethylsulfonyl)imide according to the literature procedure.[1]

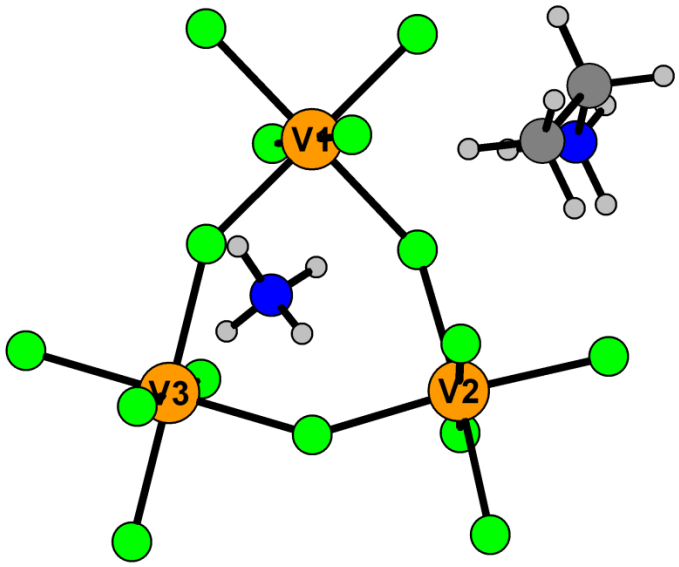

Figure S1. Building unit found in **1**.

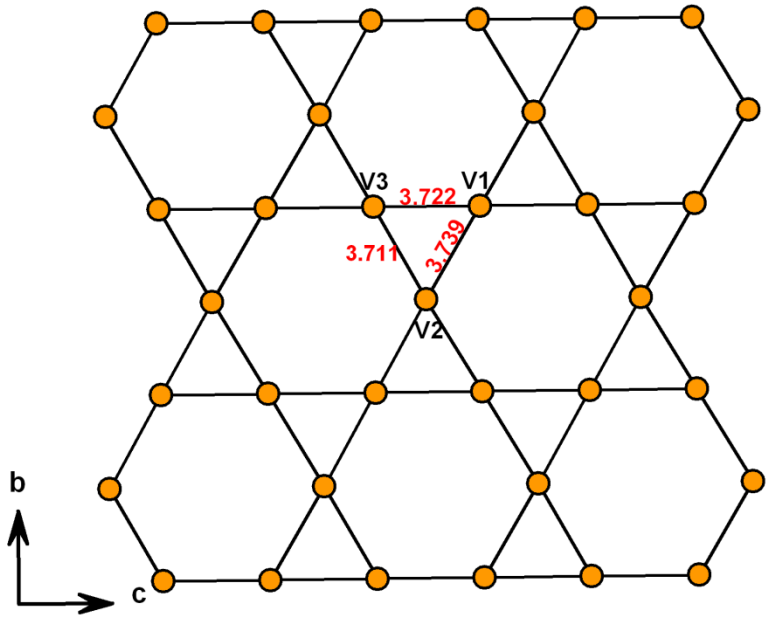

Figure S2. The kagome lattice found in **1**.

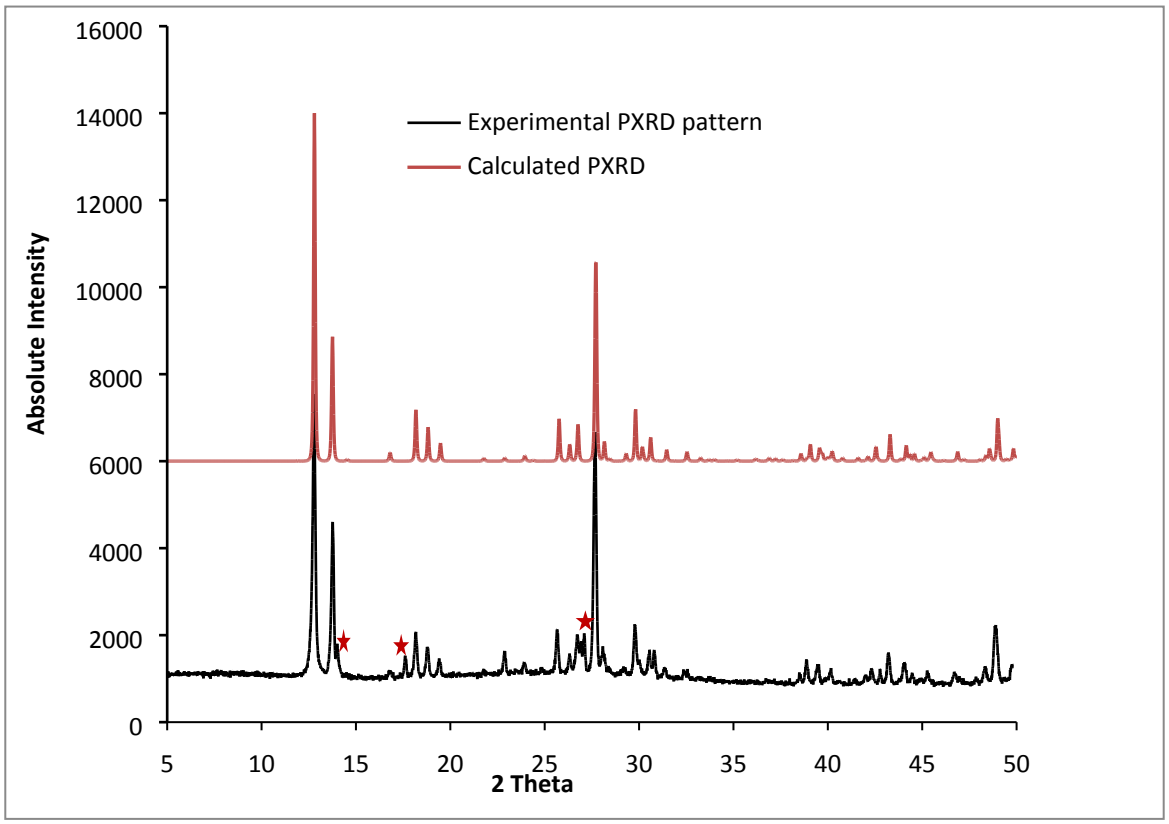

Figure S3. Calculated (above) and experimental (below) PXRDs for **1**. (red stars show small impurity of **2**.

Bond valence sums[2] were calculated using the program Valist.[3]

Table S1. Selected bond lengths (Å) and Bond Valence Sums S_i for **1**

Bond	**Bond length (Å)**	S_{ij}	**Bond**	**Bond length (Å)**	S_{ij}	**Bond**	**Bond length (Å)**	S_{ij}
V1—F1^{i}	1.941(2)	0.524	V2—F3	1.9714(19)	0.483	V3—F1	1.987(2)	0.463
V1—F1	1.941(2)	0.524	V2—F3^{ii}	1.9714(19)	0.483	V3—F1^{iii}	1.987(2)	0.463
V1—F2	1.892(2)	0.598	V2—F4	1.888(3)	0.605	V3—F5^{iii}	1.950(2)	0.512
V1—F2^{i}	1.892(2)	0.598	V2—F5	1.964(2)	0.493	V3—F5	1.950(2)	0.512
V1—F3	1.979(2)	0.473	V2—F5^{ii}	1.964(2)	0.493	V3—F7^{iii}	1.870(2)	0.635
V1—F3^{i}	1.979(2)	0.473	V2—F6	1.864(3)	0.645	V3—F7	1.870(2)	0.635
	∑ V1 = 3.19			**∑V2 = 3.20**			**∑V3 = 3.22**	

(i) -x, -y, 1-z; (ii) x, 0.5-y, z; (iii) -x, -y, -z.

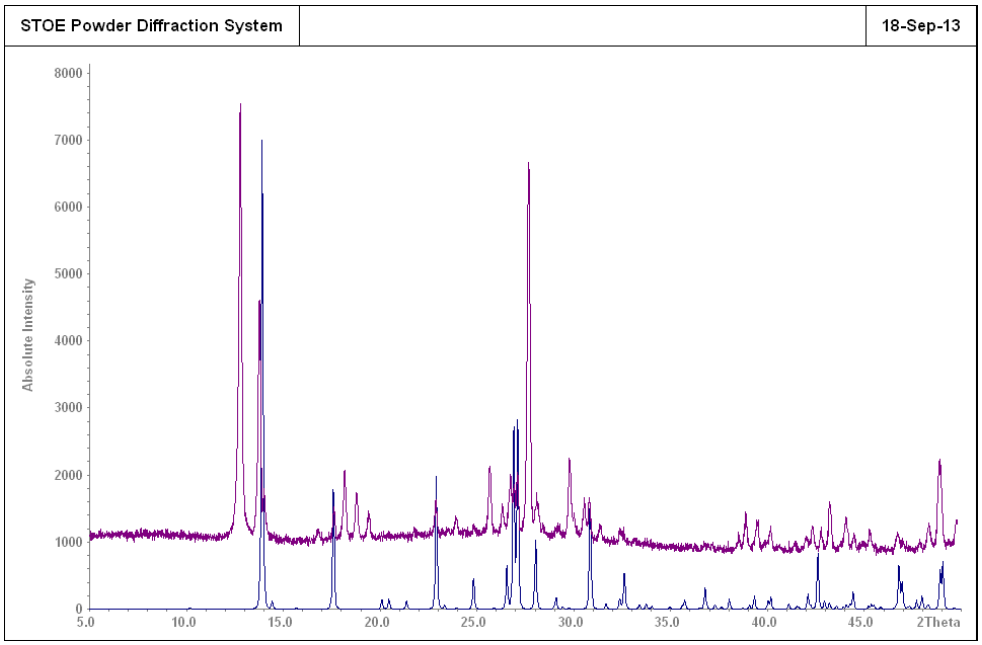

Figure S4. Calculated PXRD (below) for **2** and experimental PXRD (above) for **1** **(**Calculated PXRD of **2** fits well to the small impurity phase found in the experimental PXRD of **1**)

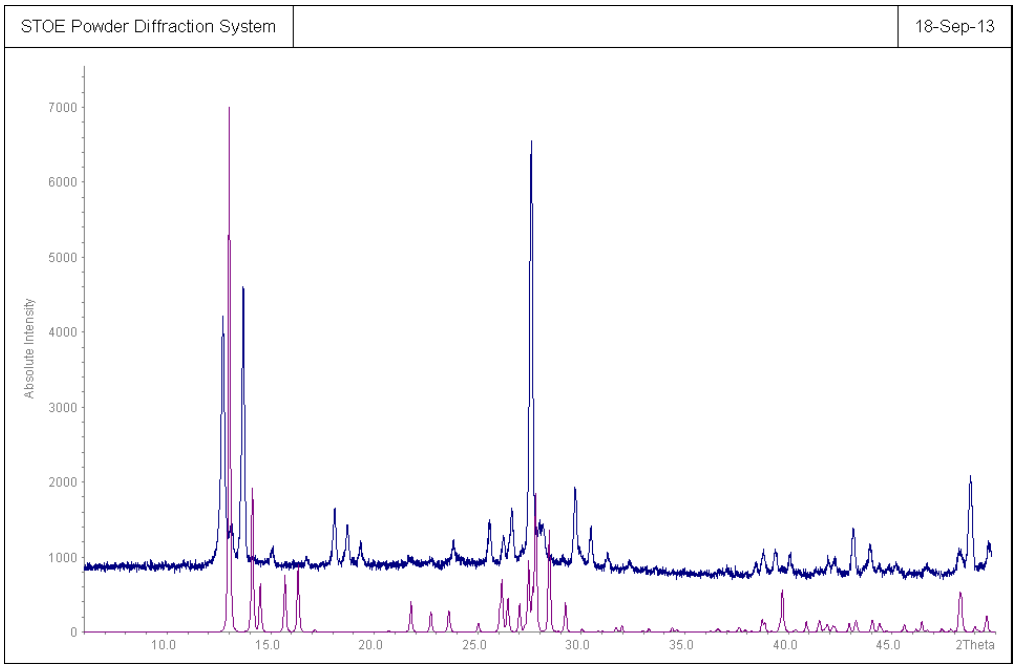

Figure S5. Calculated (below) PXRD for **3** and experimental (above) PXRD for **1**. **(**Calculated PXRD of **3** fits well to the small impurity phase found in the experimental PXRD of **1**)

Note that the experimental PXRDs for **1** in Figure S4 and Figure S5 are for samples obtained from two different reactions. Although the two reactions were carried out using the same conditions, very small amount (< 5%) of different impurity phase was present in each case.

Table S2 Crystallographic Data for **2** and **3**.

	2	**3**
Formula	$[NH_4][VF_4]$	$[NH_4][CH_6N]_2[V_3F_{12}]$
Fw/g/mol	144.98	463
Space group	$P4_2/ncm$ (4)	$P\bar{1}$
a /Å	12.270(4)	7.5410(10)
b /Å	12.270(4)	7.5380(10)
c /Å	12.723(4)	14.1890(10)
α /°	90	74.590(10)
β /°	90	87.180(10)
γ /°	90	59.940(10)
V / Å^3	1915.5(14)	669.57(13)
Z	20	2
Crystal size /mm	0.03×0.03×0.03	0.05×0.04×0.01
Crystal shape and colour	Brown prism	Brown Plate
F(000)	1400	
R_{int}	0.0422	
Obsd data [I>2σ(I)]	931	
Data/restraints/parameters	937/0/103	
GOOF on F^2	1.195	
R1, *w*R2 (I >2 σ(I))	0.0194, 0.0508	
R1, *w*R2 (all data)	0.0195, 0.0509	
Largest diff. peak / hole	0.346/-0.519	

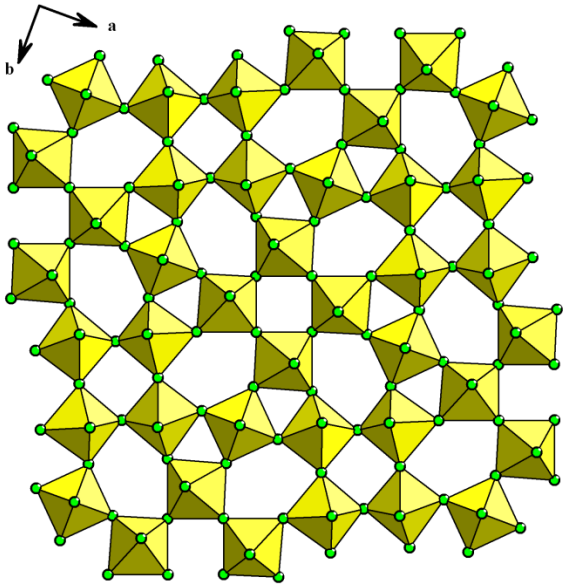

Figure S6. TTB layer type found in **2**.

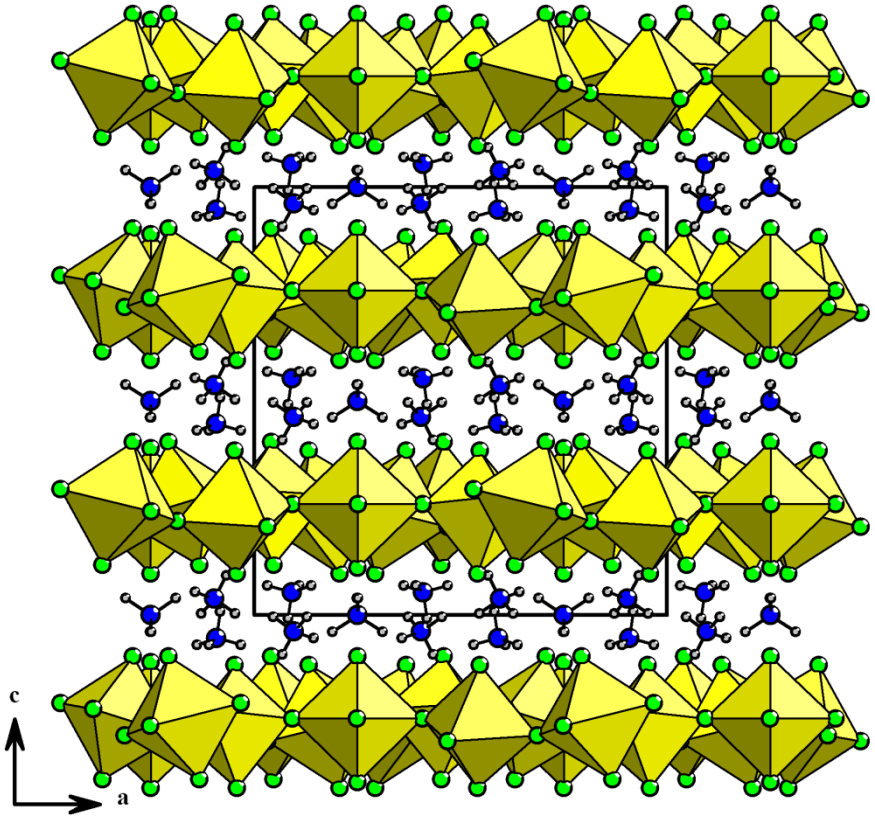

Figure S7. Structure of **2**, showing the TTB-type layers separated by ammonium cations.

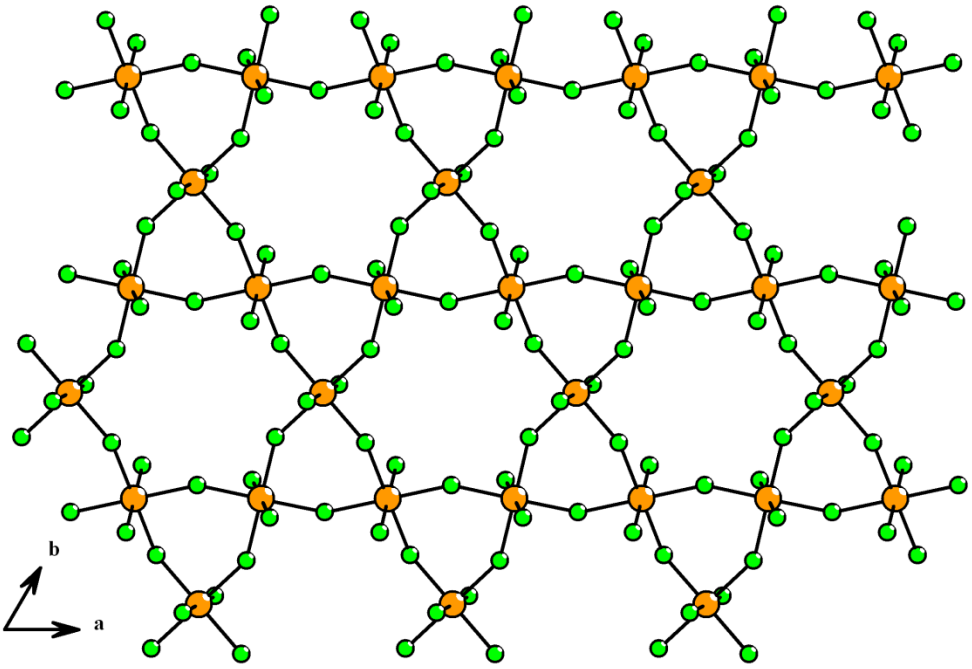

Figure S8. Kagome layer found in **3**.

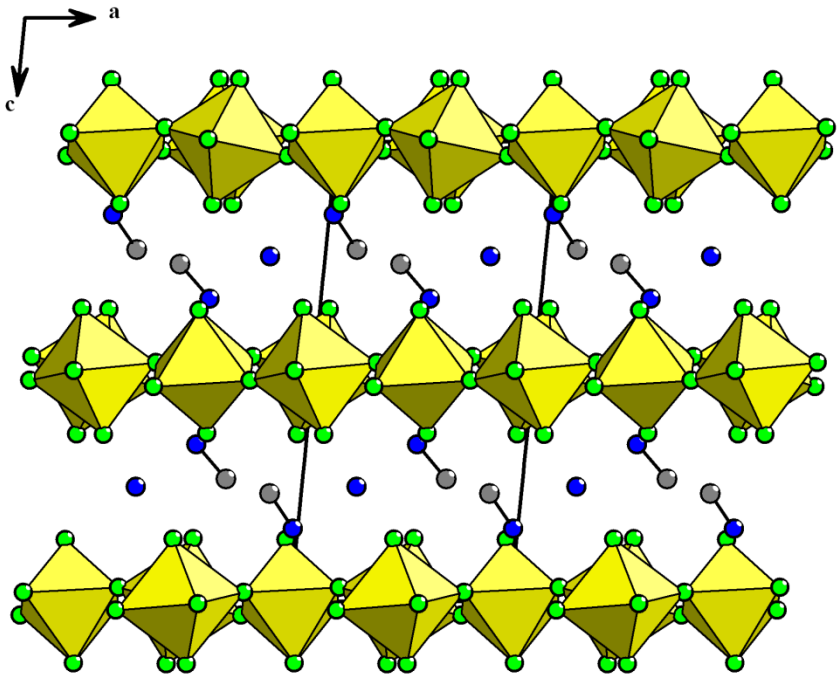

Figure S9. Structure of **3**, showing the kagome-type layers separated by methyl ammonium and ammonium cations.

Colour scheme used in all pictures: Vanadium (Orange), Fluorine (green), Nitrogen (dark blue), Carbon (dark grey), Hydrogen (light grey).

1. Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* 1996, *35*, 1168.
2. N. E. Brese, M. O'keeffe. *Acta Crystallogr. Sect. B,* 1991, **47**, 192.
3. Wills, A. S. Valist, 2010. (Program available from www.ccp14.ac.uk.)