Structural diversity in hybrid Vanadium (IV) Oxyfluorides based on a Common Building Block

Farida H. Aidoudi[a], Cameron Black[a], Kasun S. Athukorala Arachchige[a] , Alexandra M. Z. Slawin[a], Russell E. Morris[a] and Philip Lightfoot[a]

Supplementary materials

Synthesis of the ionic liquids

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 using the following procedure:[1] EMIM Br (25.33 g, 0.132 mol) was prepared according to the literature procedure,[1] then was dissolved in 40 ml of H_2O, after that lithium bis(trifluoromethylsulfonyl)imide (38.07 g, 0.132 mol, fisher) was added. The mixture was stirred at room temperature for 3 hrs. The aqueous phase was separated from the ionic liquid. After separation of the phases, the ionic liquid was washed several times with small amounts of water until no bromide was detected when testing with silver nitrate. The product was dried under vacuum at 60°C for 24 hrs. ^{1}H-NMR(400 MHz, $CDCl_3$): δ (ppm) 1.40 (t, 3H, CH3, J = 7.3 Hz), 3.80 (s, 3H, NCH3), 4.15 (q, 2H, NCH2, J = 7.3 Hz), 7.38 (d, 2H, NC(H)C(H)N, J = 21.0 Hz), 8.66 (s,1H, NC(H)N)

Synthesis of N-butylpyridinium bromide (BPB, mp = 105°C):

BPB was synthesised according to the literature procedure.[2] Under inert atmosphere conditions, degassed *N*-butyl bromide (68.43 g, 0.50 mol) was added to pyridine (40.06 g, 0.50 mol) with constant stirring. This was refluxed at 30 °C for 24 hrs. The product was then washed with ethyl acetate and dried under vacuum for 10 hrs yielding a white solid. The product was stored under an inert atmosphere. ^{1}H NMR (400 MHz, D_2O): δ (ppm) 8.74(d, 2H, J = 6.8 Hz)), 8.44 (t, 2H, J = 7.5 Hz), 7.96 (t, 1H, J = 6.6 Hz), 4.51 (t, 2H, J = 7.6 Hz, N-CH_2-$(CH_2)_2$-CH_3 , 1.85-1.93 (m, 2H, N-CH_2-CH_2-CH_2-CH_3), 1.19-1.3 (m, 2H, N-$(CH_2)_2$-CH_2-CH_3), 0.96 (t, 3H, J = 7.2 Hz, N-$(CH_2)_3$-CH_3).

1. Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* 1996, *35*, 1168.
2. Owens, G. S.; Abu-Omar, M. M. *J. Mol. Catal. A: Chem.* 2002, *187*, 215.

Synthesis of VOF-n

Synthesis of VOF-1 "$[HN_2C_7H_6][V_2O_2F_5]$": A Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.118 g, 1 mmol, Sigma aldrich) of benzimidazole. The stainless steel autoclave was then sealed and heated in an oven at 170°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material and CHN analysis confirmed phase purity (CHN: (Calc: %C : 24.15, % H : 2.02 , % N : 8.05; Found: %C: 24.23 ,%H : 1.95, % N : 8.05).

Synthesis of VOF-2 "$[HN_2C_4H_4][V_2O_2F_5]$": A Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.080 g, 1 mmol, Sigma aldrich) of pyrazine. The stainless steel autoclave was then sealed and heated in an oven at 170°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material and CHN analysis indicated the presence of a small impurity (CHN: : (Calc: %C : 15.50, % H : 1.62 , % N : 9.04; Found: %C: 12.01 ,%H : 1.25, % N : 7.36).

Synthesis of VOF-3 "$[HN_2C_3H_4][V_2O_2F_5]$ and VOF-5 "$[NH_4(HN_2C_3H_4)][V_2O_2F_6]$": A Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.068 g, 1 mmol, Sigma aldrich) of imidazole. The stainless steel autoclave was then sealed and heated in an oven at 170°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material and CHN analysis indicated the presence of a small impurity "**VOF-5**" (Calc: %C : 11.37, % H : 1.57 , % N : 8.84; Found: %C: 12.93 ,%H : 1.23, % N : 8.57).

Synthesis of VOF-4 $V_2(N_2C_4H_4)O_2F_4$: A Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.080 g, 1 mmol, Sigma aldrich) of pyrazine. The stainless steel autoclave was then sealed and heated in an oven at 140°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material and CHN analysis confirmed phase purity : (Calc: %C : 16.56, % H : 1.39 , % N : 9.66; Found: %C: 16.65 ,%H : 1.36, % N : 9.61).

Synthesis of VOF-6"$[K(HN_2C_3H_4][V_2O_2F_6]$": a Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.068 g, 1 mmol, Sigma aldrich) of imidazole and (0.101 g, 1 mmol, Fluka) of KNO_3. The stainless steel autoclave was then sealed and heated in an oven at 170°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered,

washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material confirmed phase purity.

Synthesis of VOF-7 "[$HNH_2CH_2CH_3$][VOF_3]": ATeflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.045 g, 1 mmol, Sigma aldrich) of ethylamine. The stainless steel autoclave was then sealed and heated in an oven at 170°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material and CHN analysis confirmed phase purity (Calc: %C : 14.12, % H : 4.74 , % N : 8.24; Found: %C: 12.82 ,%H : 4.54, % N : 8.06).

Synthesis of VOF-8 "[$HN_2C_7H_6$][VOF_3]": A Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.177 g, 1.5 mmol, Sigma aldrich) of benzimidazole. The stainless steel autoclave was then sealed and heated in an oven at 170°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material indicated the presence of **VOF-1** within the sample.

Synthesis of VOF-9 "[$H_2N_2C_4H_6$][$V_2O_2F_6$]": A Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.082 g, 1 mmol, Sigma aldrich) of 2-methylimidazole. The stainless steel autoclave was then sealed and heated in an oven at 170°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material indicated the presence of an unidentified impurity.

Synthesis of VOF-10 "β-$RbVOF_3$": V_2O_5 (0.182 g, 1 mmol, Sigma Aldrich) and RbF (0.2089 g, 2 mmol) were dissolved in HF (0.5 mL, 13.8 mmol, Sigma Aldrich). A solution of 3:1 H_2O/ DMSO was added. The resultant solution was sealed in a 40 mL Teflon lined steel autoclave and heated at 160°C for 24 hrs. After the autoclave had been cooled to room temperature, the product was washed with methanol and water yielding a mixture of dark powder and large green crystal chunks.

Synthesis of VOF-11"α-$KVOF_3$": V_2O_5 (0.182 g, 1 mmol, Sigma Aldrich) and K_2CO_3 (0.136 g, 1 mmol) were dissolved in HF (0.5 mL, 13.8 mmol, Sigma Aldrich). A solution of 4:5 H_2O/ ethylene glycol was added. The resultant solution was sealed in a 40 mL Teflon lined steel autoclave and heated at 160°C for 72 hrs. After the autoclave had been cooled to room temperature, the product was washed with methanol and water yielding a mixture of dark powder and large green prismatic crystals.

Synthesis of VOF-12"β-$KVOF_3$": V_2O_5 (0.182 g, 1 mmol, Sigma Aldrich) and K_2CO_3 (0.176 g, 1.3 mmol) were dissolved in HF (0.5 mL, 13.8 mmol, Sigma Aldrich). A solution of 7:1 H_2O/ ethylene glycol was added. The resultant solution was sealed in a 40 mL Teflon lined steel autoclave and heated at 160°C for 24 hrs. After the autoclave had been cooled to

room temperature, the product was washed with methanol and water yielding a mixture of dark and light blue crystals.

Synthesis of VOF-13 "$[H_2(NH_2)_2(CH_2)_2][V_2O_2F_6]$": a Teflon-lined autoclave (volume 30 mL) was charged with V_2O_5 (0.182 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (1 mL, 27.6 mmol, Sigma Aldrich) and then the IL EPB (2.16 g, ~10 mmol) was added along with (0.060 g, 1 mmol, Sigma aldrich) of ethylenediamine. The stainless steel autoclave was then sealed and heated in an oven at 140°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding blue crystals. Powder X-ray diffraction of the bulk material and CHN analysis confirmed phase purity (CHN: **VOF-13:** (Calc: %C: 8.25, % H : 3.43 , % N : 9.62; Found: %C: 8.14 ,%H : 3.34, % N : 9.66).

Synthesis of VOF-14 "$[H_2N_2C_6H_{12}][V_2O_2F_7]$": A Teflon-lined autoclave (volume 30 mL) was charged with VOF_3 (0.124 g, 1 mmol, Sigma Aldrich) and HF (48 wt% in H_2O) (0.1 mL, 2.76 mmol, Sigma Aldrich) and then the IL EMIM Tf_2N (4 g, ~10 mmol) was added along with (0.112 g, 1 mmol, Sigma aldrich) of 1,4-diazabicyclo[2.2.2]octane "DABCO", The stainless steel autoclave was then sealed and heated in an oven at 130°C for 24hrs. After the autoclave had been cooled to room temperature, the product was filtered, washed with methanol and dried in air for 24 hrs yielding a mixture of blue and green crystals.

Observed and Calculated powder XRD patterns

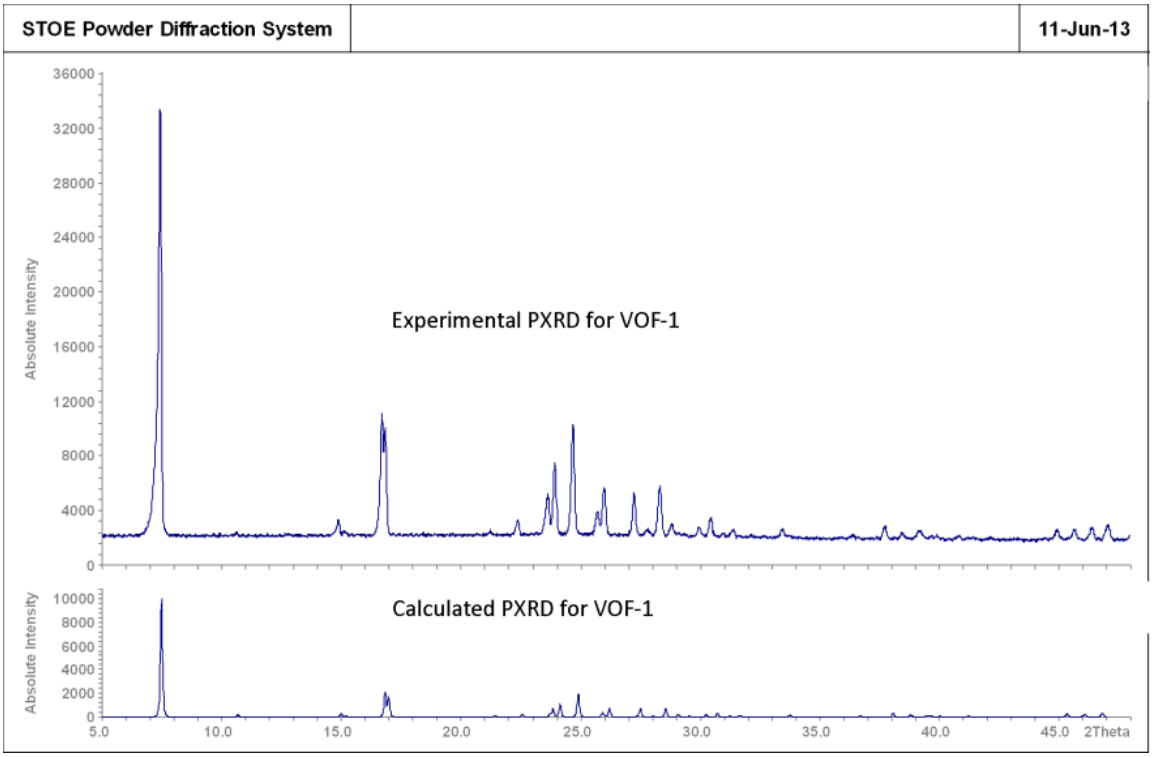

Fig.S1 Observed (above) and calculated (below) PXRD for **VOF-1.**

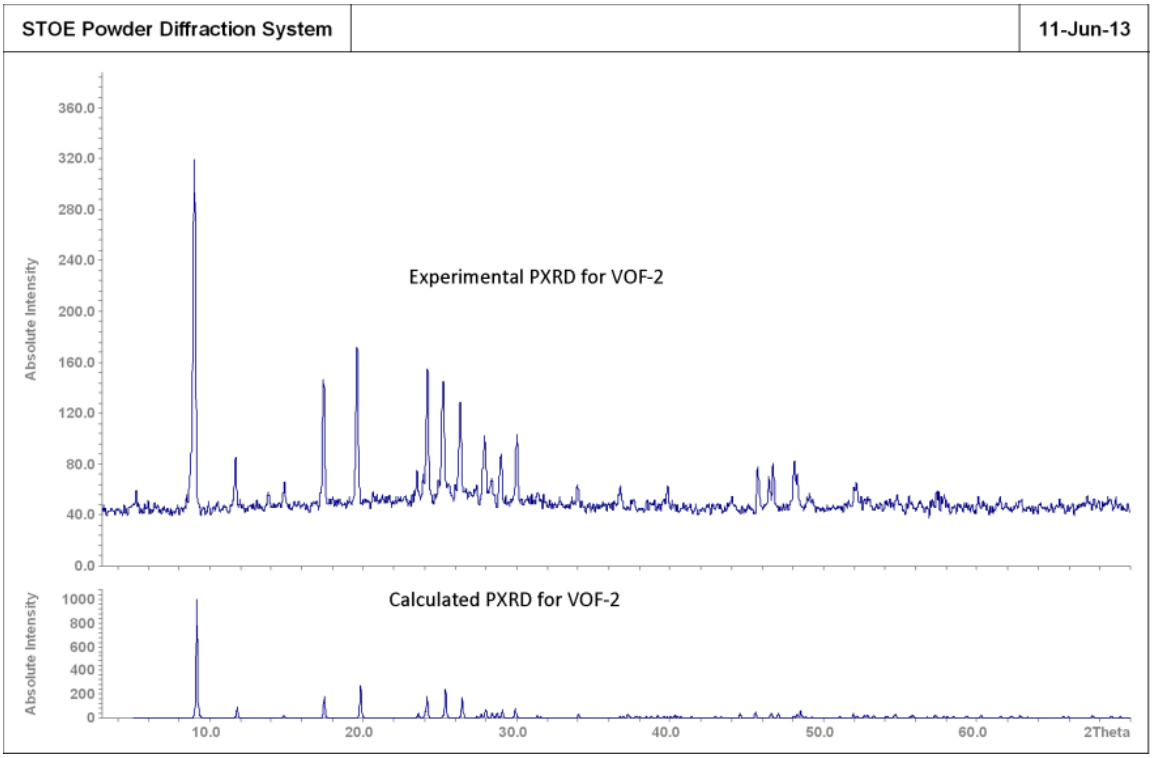

Fig. S2 Observed (above) and calculated (below) PXRD for **VOF-2**.

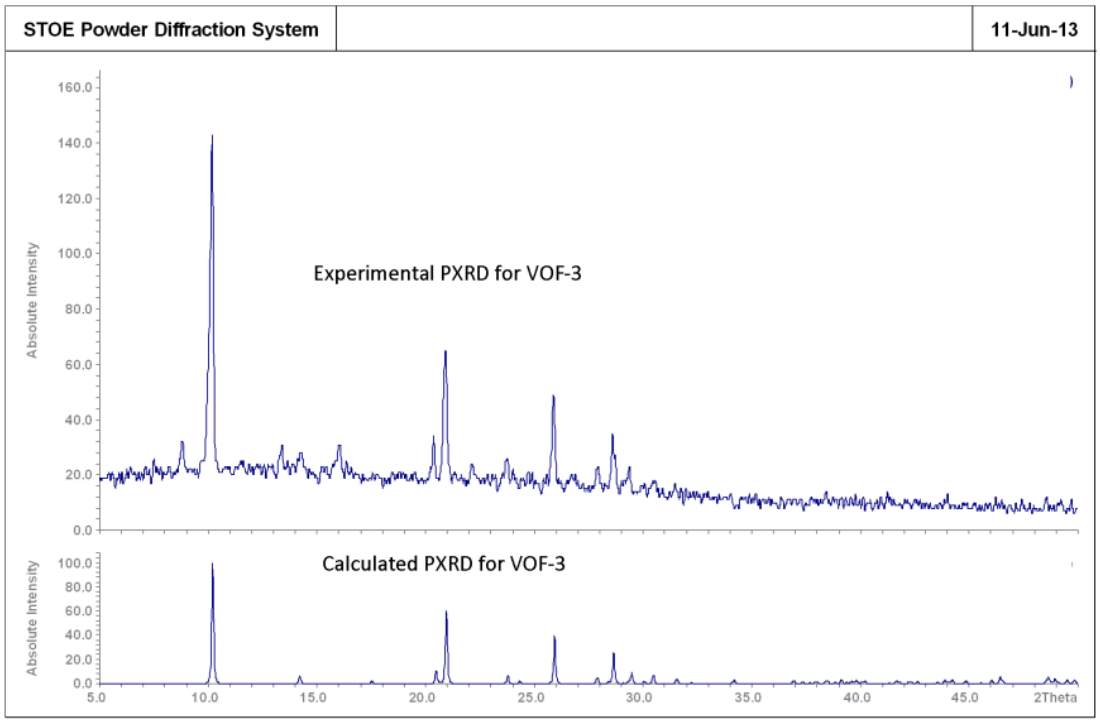

Fig. S3 Observed (above) and calculated (below) PXRD for **VOF-3**.

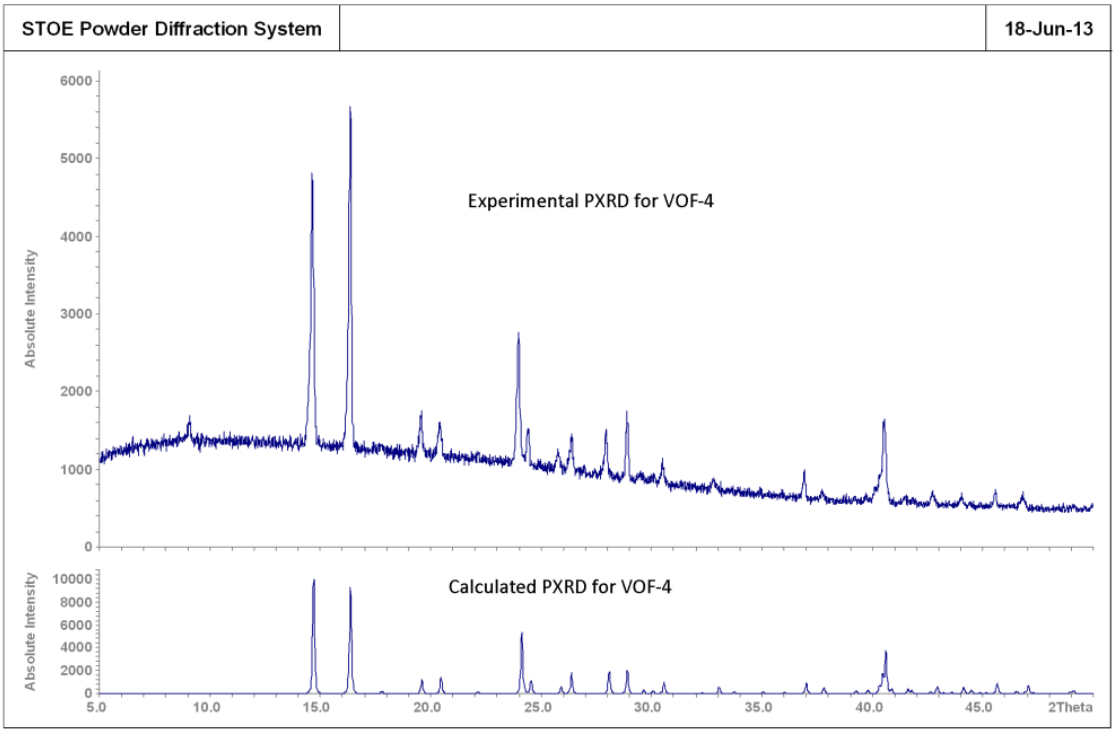

Fig. S4 Observed (above) and calculated (below) PXRD for **VOF-4**.

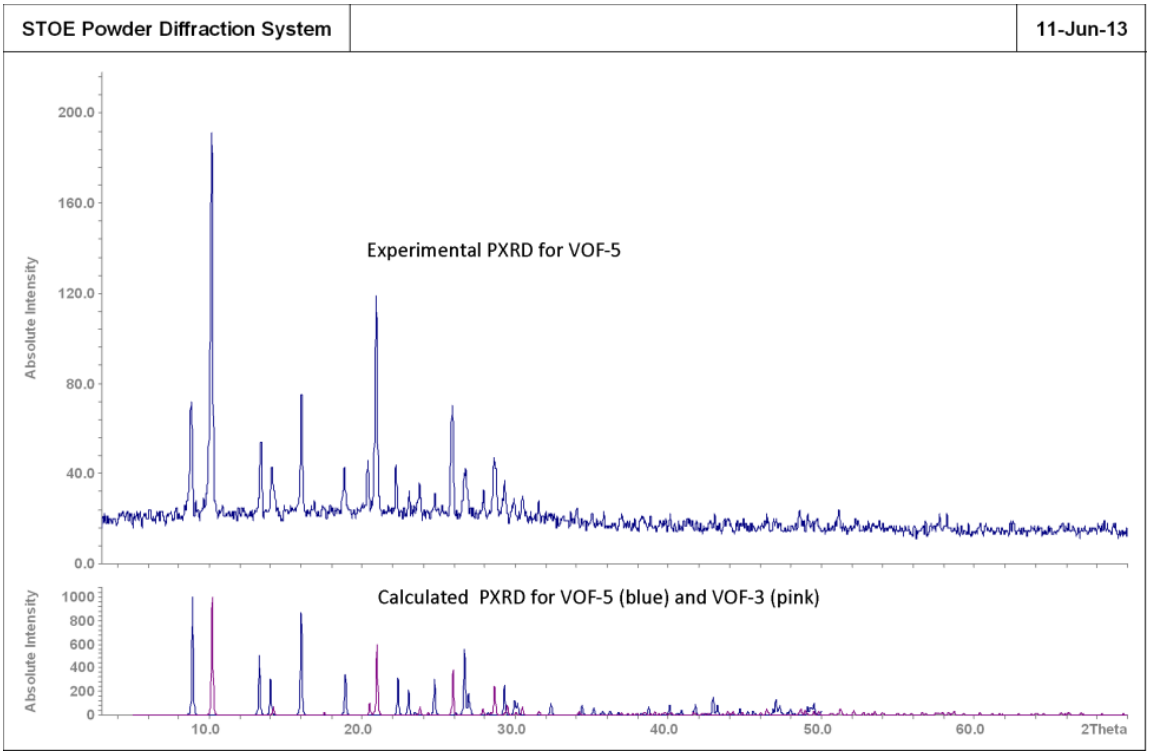

Fig. S5 Observed (above) and calculated (below) PXRD for **VOF-5** and **VOF-3**.

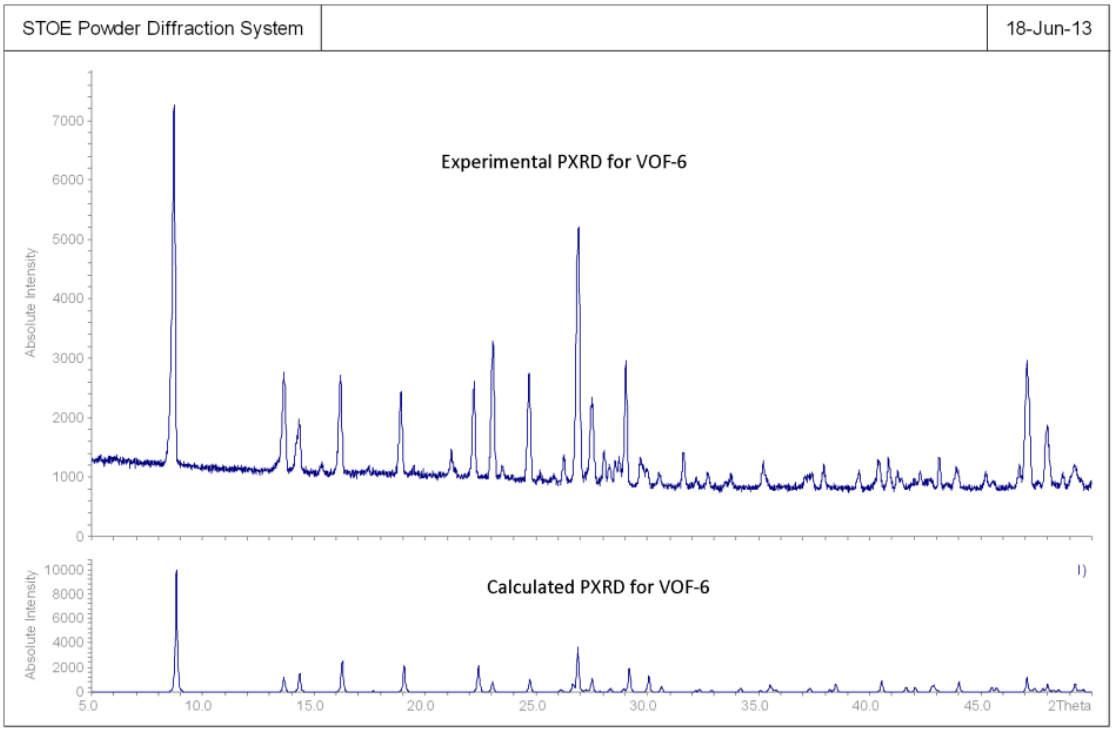

Fig.S6 Observed (above) and calculated (below) PXRD for **VOF-6**.

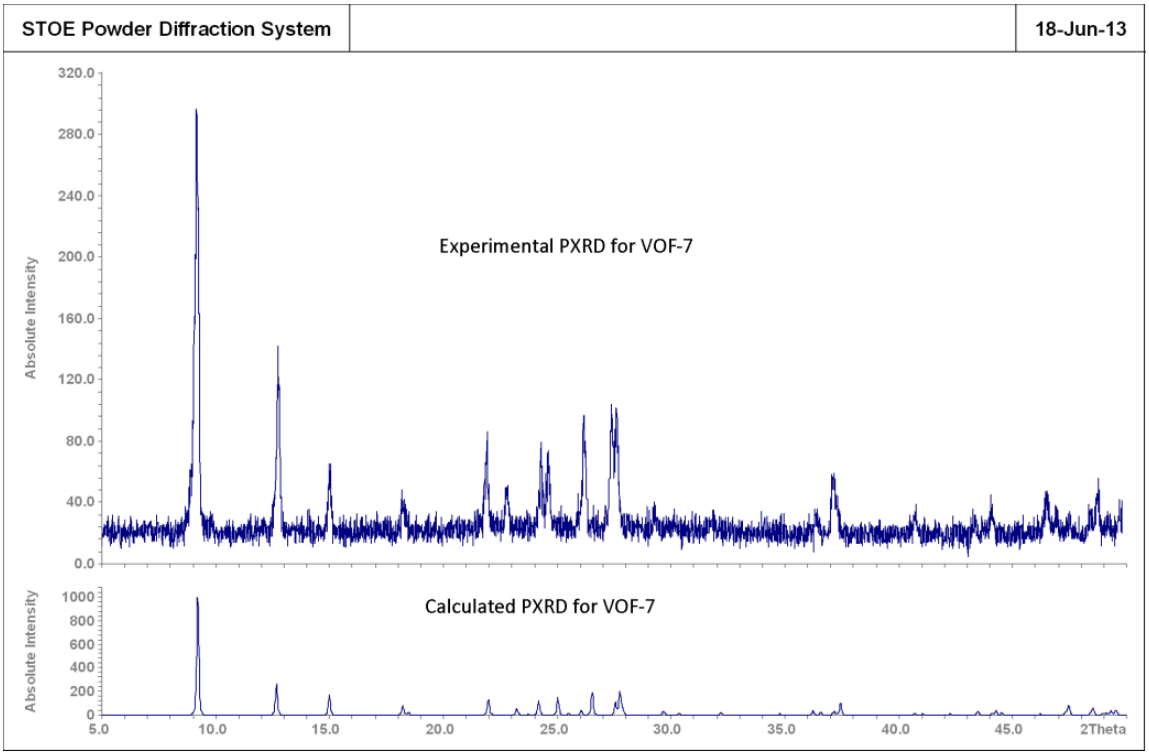

Fig.S7 Observed (above) and calculated (below) PXRD for **VOF-7**

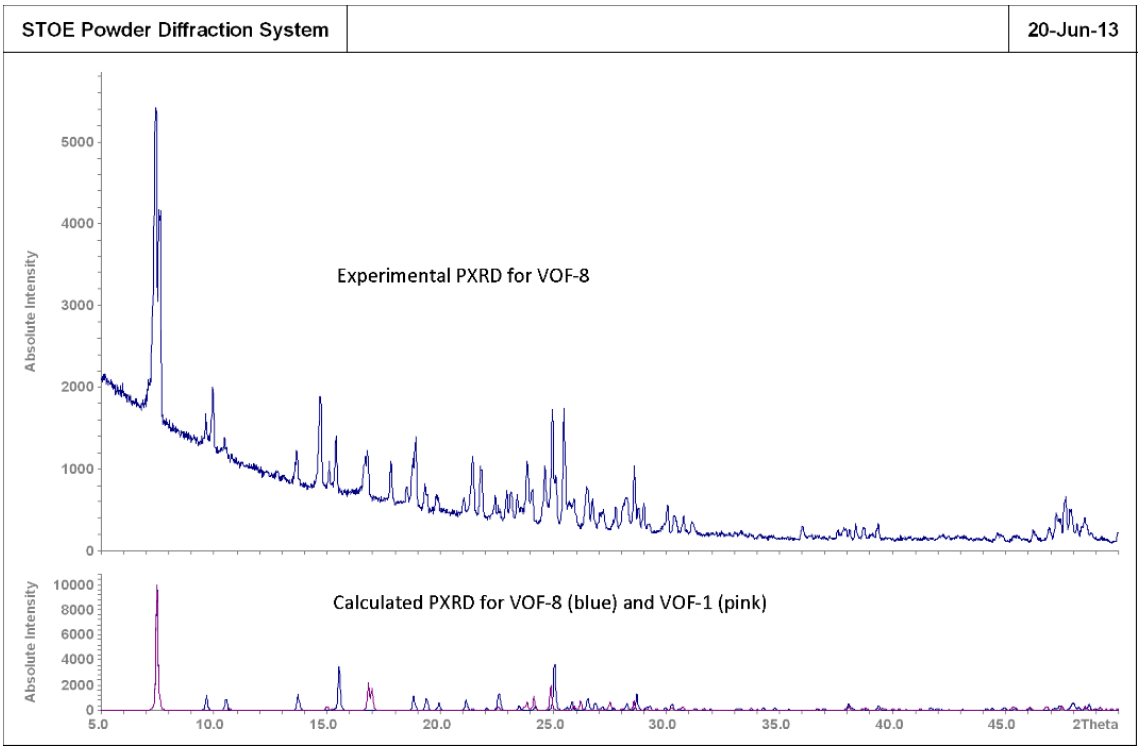

Fig.S8 Observed (above) and calculated (below) PXRD for **VOF-1** and **VOF-8**.

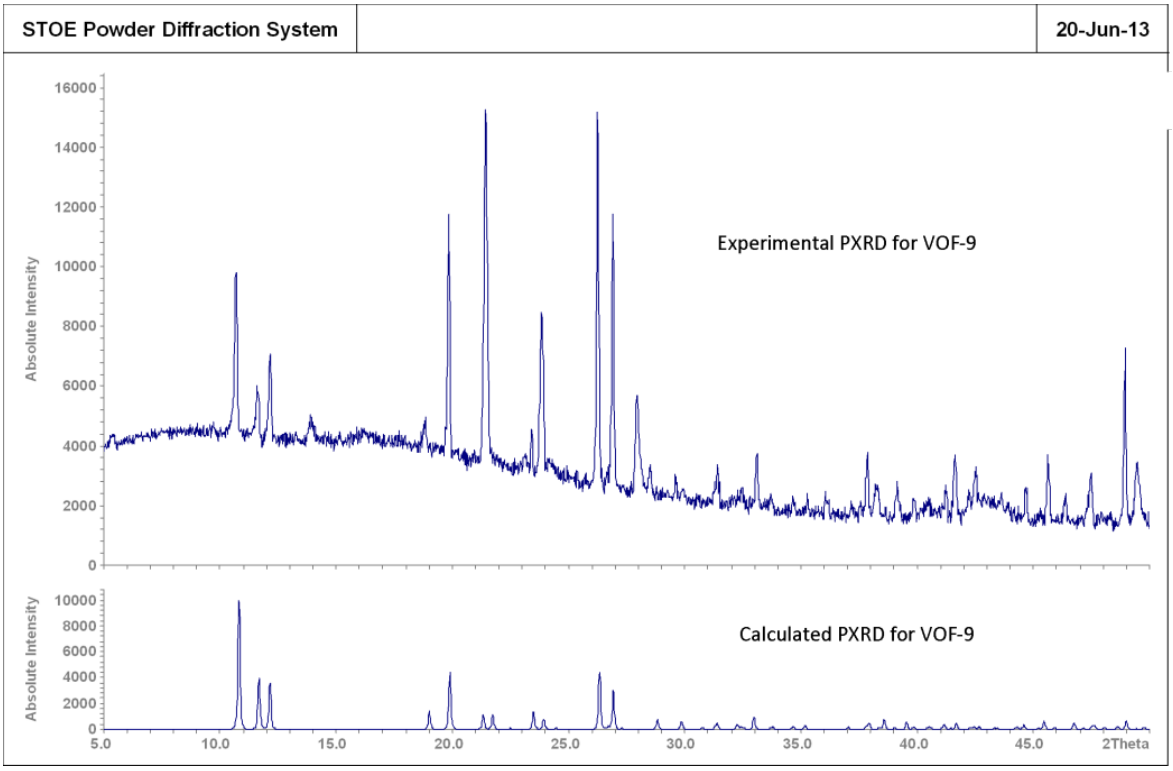

Fig.S9 Observed (above) and calculated (below) PXRD for **VOF-9**.

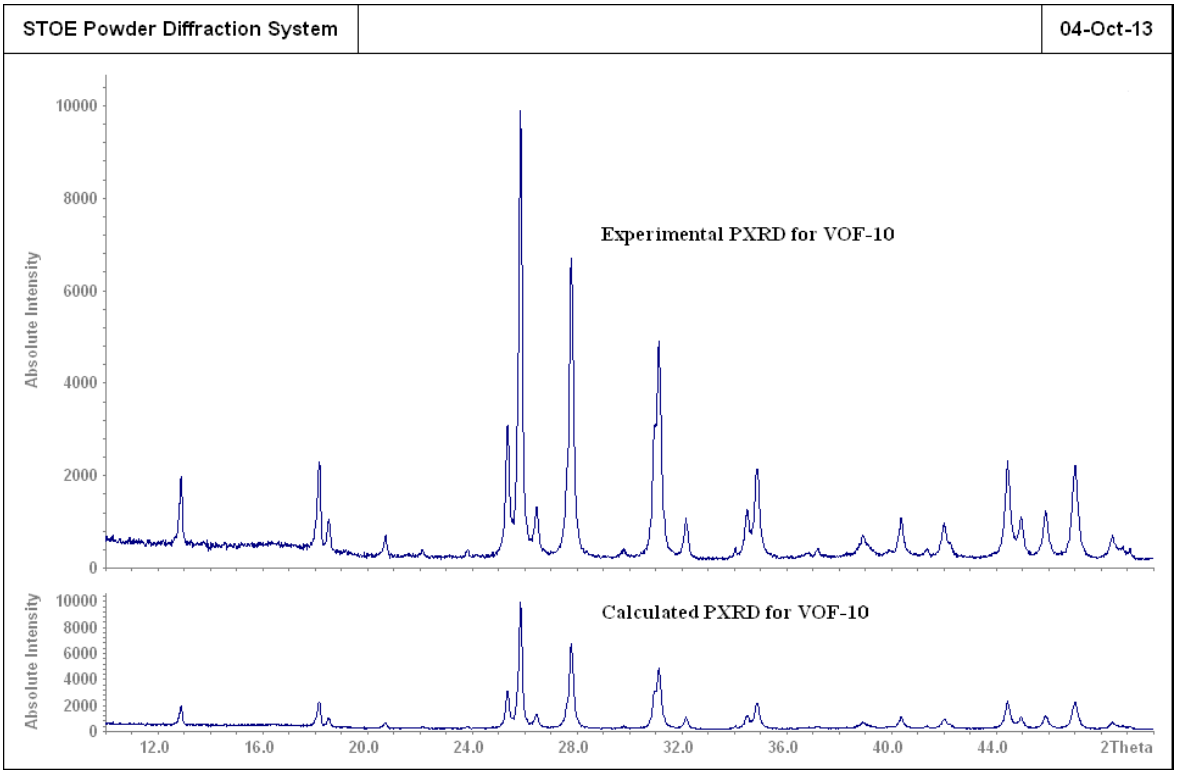

Fig.S10 Observed (above) and calculated (below) PXRD for **VOF-10**

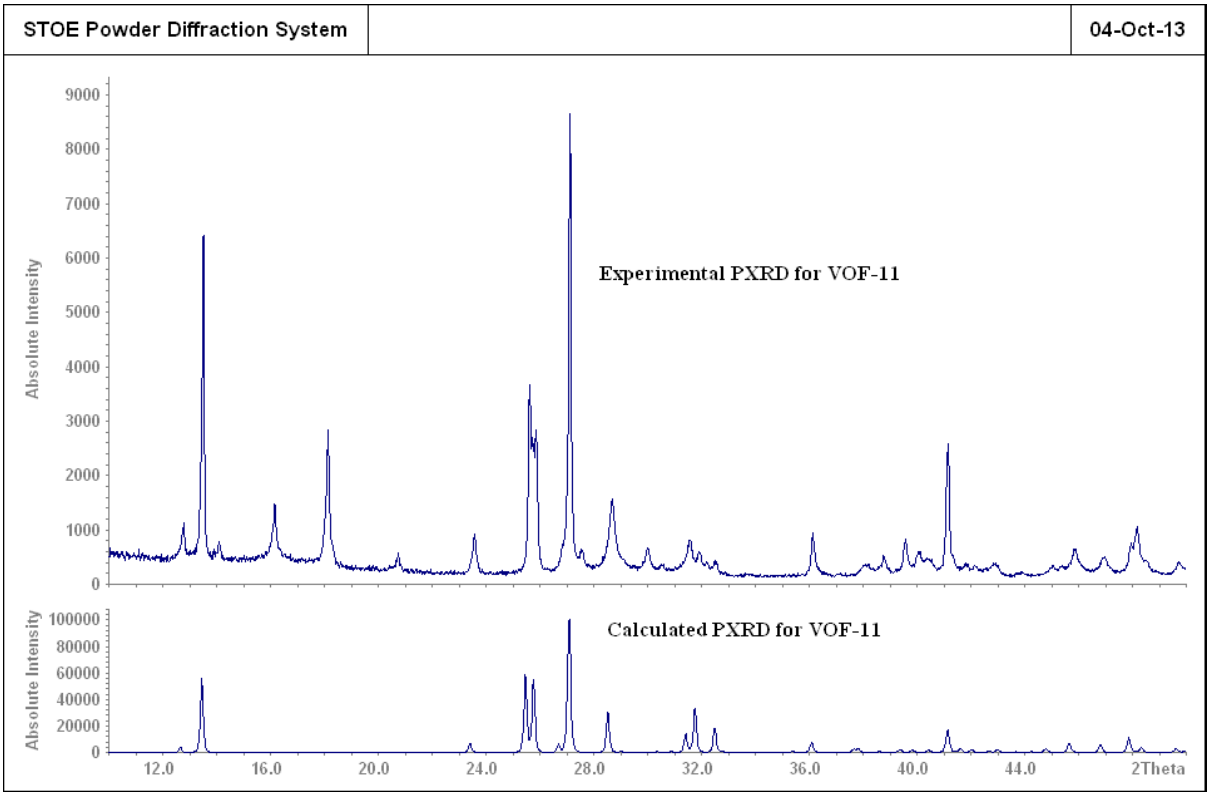

Fig.S11 Observed (above) and calculated (below) PXRD for **VOF-11**

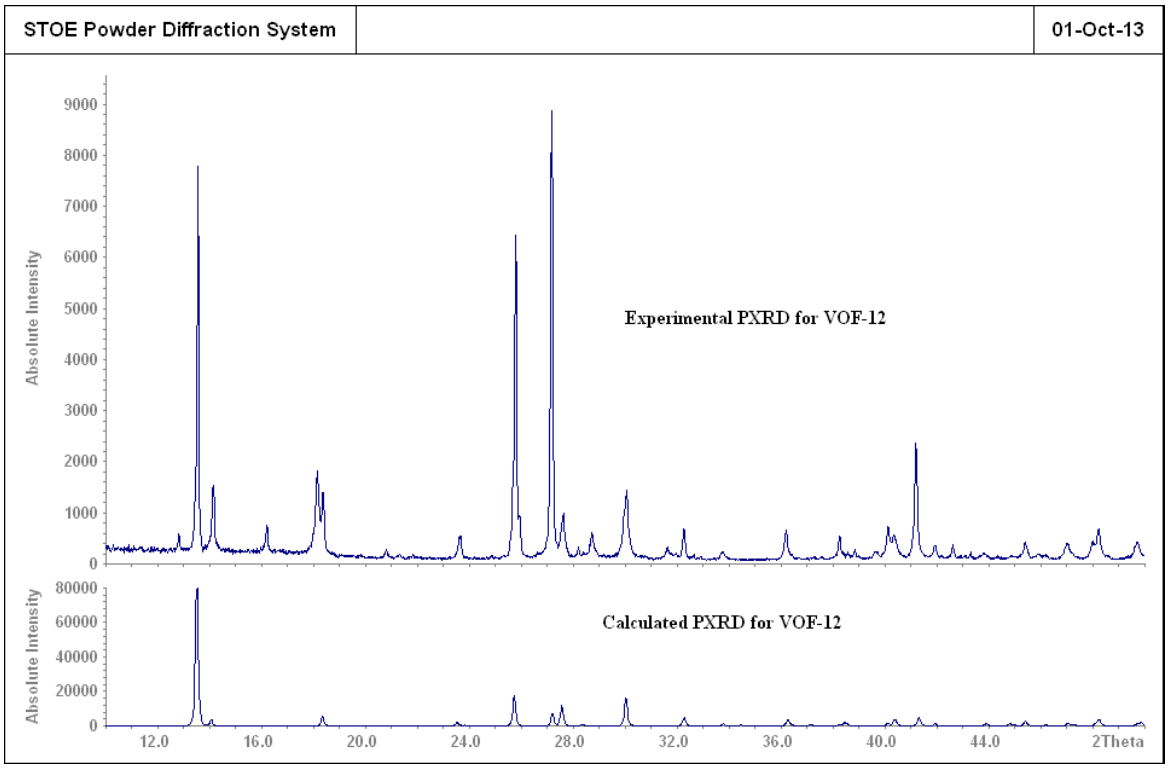

Fig.S12 Observed (above) and calculated (below) PXRD for **VOF-12** .

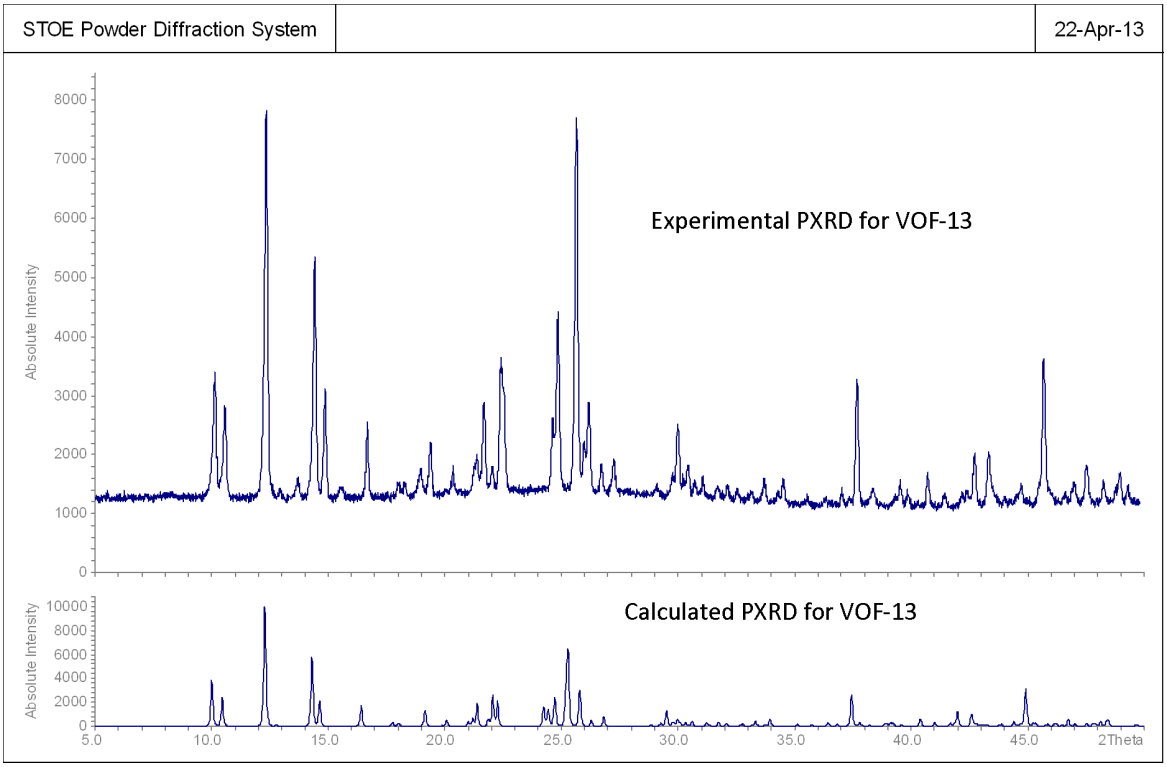

Fig. S13 Observed (above) and calculated (below) PXRD for **VOF-13**.

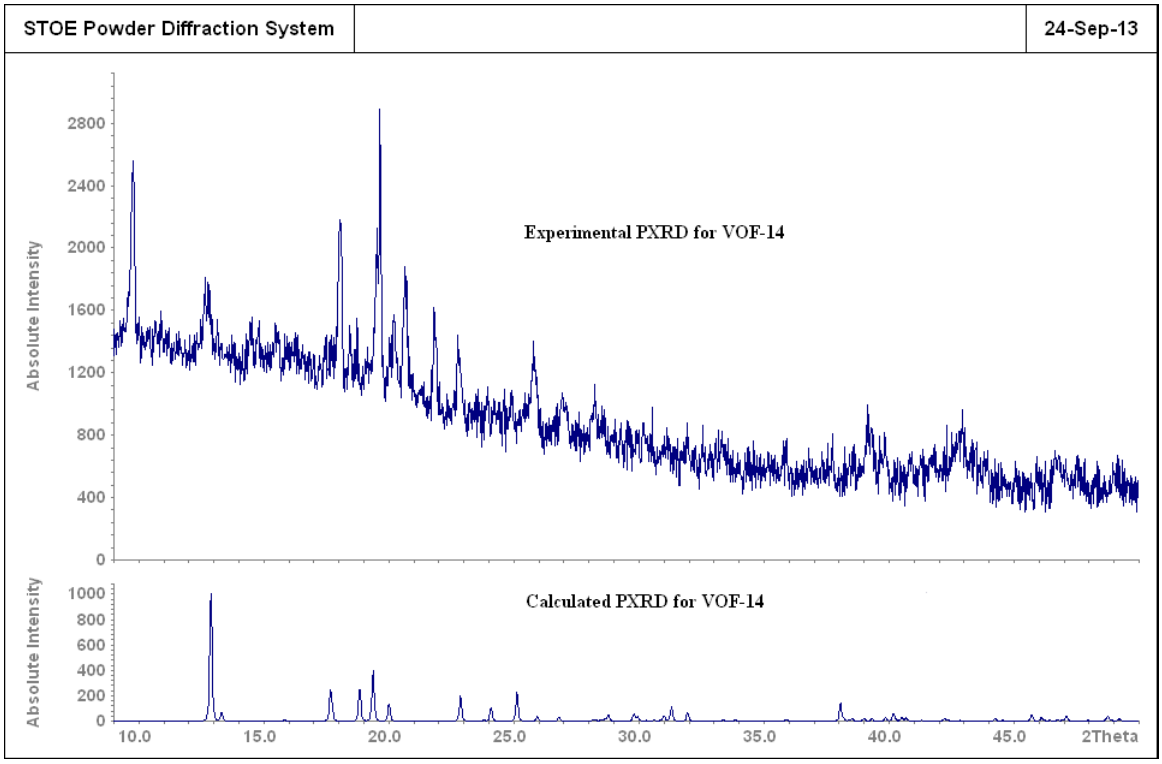

Fig.S14 Observed (above) and calculated (below) PXRD for **VOF-14**.

Electronic Supplementary Material (ESI) for Dalton Transactions

Crystallographic Data for VOF-1, VOF-2, VOF-5, VOF-6, VOF-7, VOF-8, VOF-9, VOF-10, VOF-11 and VOF-12

Table S1 Crystallographic Data for **VOF-1**, **VOF-2**, **VOF-5** and **VOF-6**

	VOF-1	**VOF-2**	**VOF-5**	**VOF-6**
Formula	$[HC_7N_2H_6][V_2O_2F_5]$	$[HN_2C_4H_4][V_2O_2F_5]$	$[NH_4][HC_3N_2H_4][V_2O_2F_6]$	$K[HC_3N_2H_4][V_2O_2F_6]$
Fw/g/mol	348.03	309.94	335.01	356.07
Space group	*P n* (7)	*P c m n*(62)	*P* 2 2 2_1(17)	*P* 2 2 2_1(17)
a /Å	7.5005(15)	7.551(3)	3.861(3)	3.8572(13)
b /Å	11.811(2)	11.904(5	6.664(4)	6.4795(2)
c /Å	11.636(2)	19.349(10)	19.840(13)	20.0510(6)
α /°	90	90	90	90
β /°	91.154(3)	90	90	90
γ /°	90	90	90	90
V / Å^3	1030.6(3)	1739.2(12)	510.5(5)	501.13(17)
Z	4	8	2	2
Crystal size /nm	0.25×0.03×0.03	0.12×0.09×0.02	0.20×0.08×0.02	0.20×0.02×0.02
Crystal shape and colour	Blue prism	Blue platelet	Blue platelet	Blue needle
F(000)	680	1200	364	344
R_{int}	0.0693	0.1207	0.0665	0.0370
Obsd data [*I*>2σ(*I*)]	3623	1102	892	868
Data/restraints/parameters	6092/2/326	1657/1/145	940/1/92	906/0/74
GOOF on F^2	0.939	1.109	1.165	1.263
R1, *w*R2 (I >2 σ(I))	0.0492, 0.0857	0.0931, 0.2793	0.0389, 0.0825	0.0528, 0.1421
R1, *w*R2 (all data)	0.1104, 0.1029	0.1414, 0.3293	0.0436, 0.0836	0.0583, 0.1746
Largest diff. peak / hole	0.489/-0.739	1.219/-1.746	0.722/-0.757	1.071/-1.058

Table S2 Crystallographic Data for **VOF-7**, **VOF-8**, **VOF-9** and **VOF-10**

	VOF-7	**VOF-8**	**VOF-9**	**VOF-10**
Formula	$[HNH_2CH_2CH_3][VOF_3]$	$[HN_2C_7H_6][VOF_3]$	$[H_2N_2C_4H_6][V_2O_2F_6]$	β-$RbVOF_3$
Fw/g/mol	170.03	243.09	329.99	209.41
Space group	*Pmcb*(55)	*C*2/*c*(15)	$P2_1/m$(11)	*Pbam*(55)
a /Å	3.828(2)	24.5014(10)	8.334(7)	6.7398(5)
b /Å	7.496(4)	3.8344(13)	7.430(6)	14.7495(13)
c /Å	19.2021(10)	18.979(7)	8.998(8)	3.8621(4)
α /°	90	90	90	90
β /°	90	105.454(7)	114.750(2)	90
γ /°	90	90	90	90
V / $Å^3$	551.0(4)	1718.6(9)	506.0(7)	383.93(6)
Z	4	8	2	4
Crystal size /nm	0.18×0.09×0.03	0.18×0.06×0.03	0.24×0.09×0.03	0.52×0.04×0.02
Crystal shape and colour	Blue platelet	Blue platelet	Blue platelet	Blue block
F(000)	340	968	320	380
R_{int}	0.0571	0.0628	0.0639	0.1105
Obsd data [*I*>2σ(*I*)]	462	1529	1005	367
Data/restraints/parameters	598/0/52	1745/0/155	1102/0/73	416/0/37
GOOF on F^2	1.150	1.276	1.180	0.992
R1, *w*R2 (I >2 σ(I))	0.0839, 0.1612	0.0618, 0.2080	0.0803, 0.1937	0.0509, 0.1318
R1, *w*R2 (all data)	0.1114, 0.1737	0.0874, 0.2644	0.0884, 0.2078	0.0593, 0.1407
Largest diff. peak / hole	2.404/-0.734	1.261,/-1.225	1.469/-1.150	1.589/-1.283

Table S3 Crystallographic Data for **VOF-11** and **VOF-12**

	VOF-11	**VOF-12**
Formula	α-$KVOF_3$	β-$KVOF_3$
Fw/g/mol	163.04	163.04
Space group	*C*2/*m*(12)	*Pnma*(62)
a /Å	13.564(6)	7.176(7)
b /Å	7.595(3)	7.540(7)
c /Å	7.207(3)	13.106(13)
α /°	90	90
β /°	104.102(11)	90
γ /°	90	90
V / $Å^3$	720.1(5)	709.1(12)
Z	8	8
Crystal size /nm	0.30×0.09×0.07	0.17×0.03×0.03
Crystal shape and colour	Green prism	Blue block
F(000)	616	616
R_{int}	0.0665	0.0449
Obsd data [*I*>2σ(*I*)]	811	659
Data/restraints/parameters	881/0/61	700/0/61
GOOF on F^2	1.881	1.067
R1, *w*R2 (I >2 σ(I))	0.0980, 0.2566	0.0268, 0.0976
R1, *w*R2 (all data)	0.1053, 0.2604	0.0334, 0.1221
Largest diff. peak / hole	4.028/-1.384	1.224/-1.270

Bond valence sum calculations:

Bond valence sums were calculated using the program Valist (Wills, A. S. Valist, 2010. (Program available from www.ccp14.ac.uk.)). Bond distances can be found in the CIF files provided with this publication.

VOF-1: ∑V1 = 3.90, ∑V2 = 3.99, ∑V3 = 3.94, ∑V4 = 3.95

VOF-2: ∑V1 = 3.95, ∑V2 = 3.93

VOF-3: ∑V1 = 3.97, ∑V2 = 3.84, ∑V3 = 3.80, ∑V4 = 3.79

VOF-4: ∑V1 = 3.77

VOF-5: ∑V1 = 3.86

VOF-6: ∑V1 = 3.90

VOF-7: ∑V1 = 4.03

VOF-8: ∑V1 = 4.08

VOF-9: ∑V1 = 3.80

VOF-10: ∑V1 = 4.03

VOF-11: ∑V1 = 3.77

VOF-12: ∑V1 = 3.92

VOF-13: ∑V1 = 3.68, ∑V2 = 3.86

VOF-14: ∑V1 = 4.77

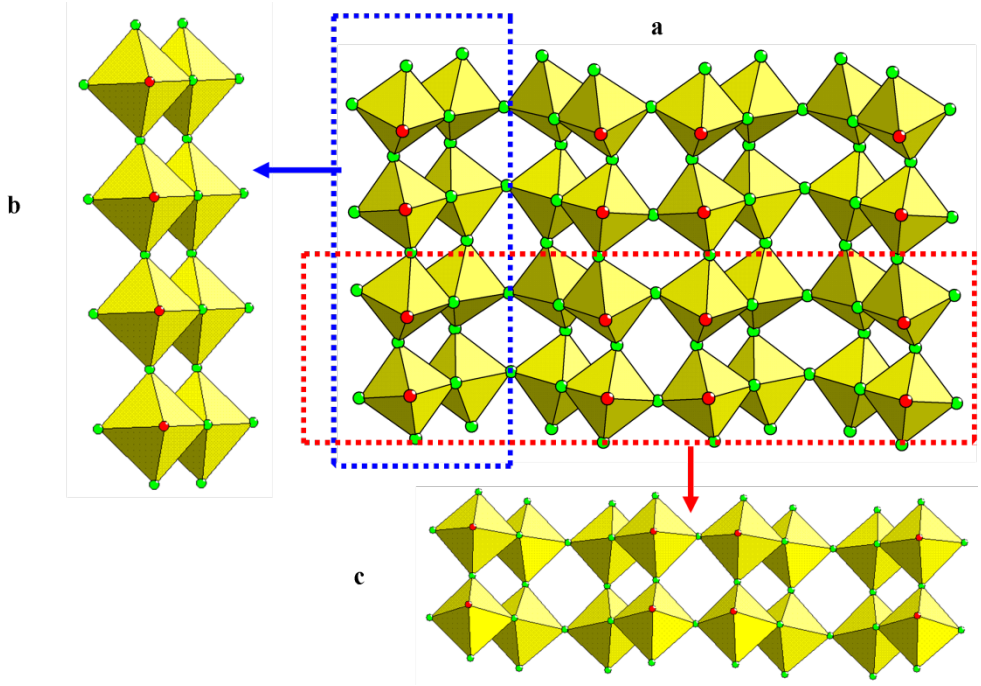

Fig. S15 A view of: the $[V_2O_2F_5]^-$ layer (a), the $[VOF_3]^-$ "standard "ladder (b) and the $[VOF_3]^-$"alternating "ladder (c)

Magnetic data fitting

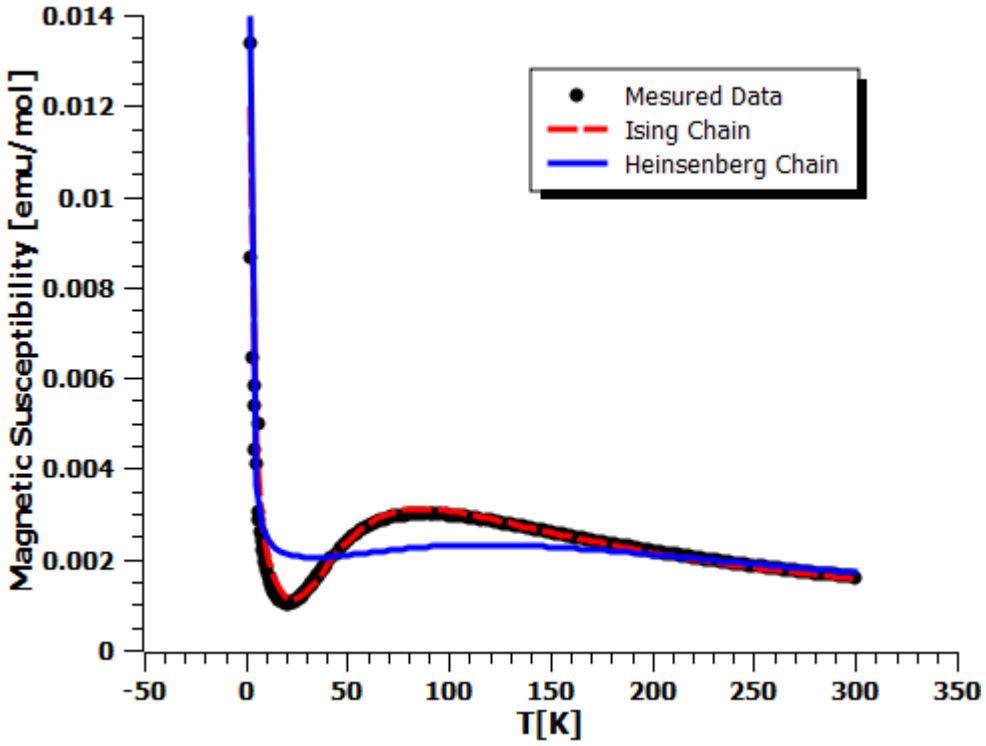

Fig. S16 Fit of the Ising chain and Heisenberg chain models to χ(T)

The difference between Ising and Heisenberg spins is related to their anisotropy; Heisenberg spins[1] *are isotropic whereas Ising spins*[2] *give a differing response to a magnetic field parallel and perpendicular to direction to their magnetic spin.*

1. Kaul, E. E.; Rosner, H.; Yushankhai, V.; Sichelschmidt, J.; Shpanchenko, R. V.; Geibel, C. *Phys. Rev. B* **2003**, *67*, 174417.
2. Fisher, M. E. *J.Math. Phys.* **1963**, *4*, 124.

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