In order to determine the oxidation states of the vanadium ions within ImVOF, a bond-valence sum analysis (BVS) of the five unique vanadium sites was carried out. In this way, the oxidation state, v_i, of a central vanadium ion *i* is defined by,

$$v_i = \Sigma s_{ij} \quad (1)$$

where s_{ij} is the valence of the bond between the pair of ions V_i and F_j or O_j given by,

$$s_{ij} = \exp[(R_{ij} - d_{ij}) / b] \quad (2)$$

Here, d_{ij} is the experimentally observed bond length between *i* and *j*, R_{ij} is a tabulated value expressing the ideal bond length between *i* and *j* and *b* is an empirical constant, 0.37 Å. For the BVS calculations of ImVOF, shown in Table S1, the tabulated R_{ij} values were taken from reference [16]. The bond-valence sums for vanadium sites V1, V2, V3 in the kagome layers and V5 in the inter-layer are consistent with the V^{4+} S = ½ oxidation state. The BVS of ~ 3.5 for the V4 site in the inter-layer suggests a V^{3+}/V^{4+} mixed valency at this position.

Table S1. The bond-valence sum (BVS) analysis of the vanadium sites within the structure of ImVOF.

Site	Bonding Environment	Bond Length / Å	Assumed Oxidation State	s_{ij}	BVS	Assumed Oxidation State	s_{ij}	BVS
V1	V – O	1.586	IV	1.708	3.933	III	1.529	3.766
	V – F	2.254		0.224			0.225	
	V – F	1.963		0.491			0.494	
	V – F	1.974		0.477			0.479	
	V – F	1.948		0.512			0.514	
	V – F	1.941		0.521			0.524	
V2	V – O	1.585	IV	1.712	3.951	III	1.533	3.785
	V – F	2.177		0.275			0.277	
	V – F	1.973		0.478			0.481	
	V – F	1.956		0.501			0.503	
	V – F	1.941		0.521			0.524	
	V – F	1.984		0.464			0.467	
V3	V – O	1.597	IV	1.658	3.970	III	1.484	3.808
	V – F	2.203		0.257			0.258	
	V – F	1.957		0.500			0.502	
	V – F	1.939		0.524			0.527	
	V – F	1.963		0.491			0.494	
	V – F	1.928		0.540			0.543	
V4	V – OH_2	2.124	IV	0.399	3.465	III	0.357	3.439
	V – F	1.724		0.937			0.942	
	V – F	1.965		0.489			0.491	
	V – F	1.919		0.553			0.556	
	V – F	1.899		0.584			0.587	
	V – F	1.954		0.503			0.506	
V5	V – F × 2	1.825	IV	0.713	3.644	III	0.717	3.664
	V – F × 2	1.903		0.578			0.581	
	V – F × 2	1.934		0.531			0.534	

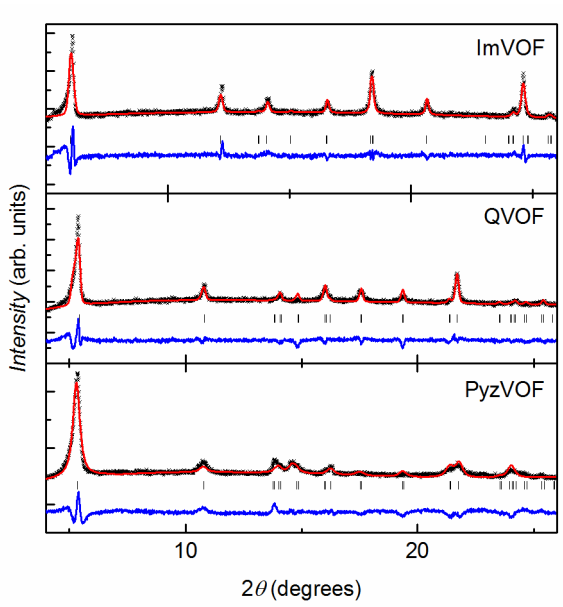
The overall charge on the inorganic slabs within ImVOF, according to the BVS analysis is $[V_9O_6F_{24}(H_2O)_2]^-$, implying that there is one imidazolium $[C_3H_5N_2]^+$ cation per formula unit. The calculated carbon, hydrogen and nitrogen contents based on this structural formula are given in Table S3, along with the experimentally observed values obtained from CHN elemental analysis. The calculated and observed CHN contents for the QVOF and PyzVOF analogues are also included in Table S3, with the assumption that the overall charge on the inorganic slabs is the same as in ImVOF.

Table S3. The calculated and observed percentage values of the CHN contents in ImVOF, QVOF and PyzVOF.

System	Calculated			Observed		
	C / %	H / %	N / %	C / %	H / %	N / %
ImVOF	3.23	0.81	2.51	4.49	1.00	3.39
QVOF	7.26	1.57	1.21	7.52	1.54	1.81
PyzVOF	4.26	0.81	2.48	4.48	1.25	4.42

The orthorhombic $C222_1$ structural model of ImVOF was refined against the data collected for samples of ImVOF, QVOF and PyzVOF, with cell constants, background and profile parameters allowed to vary to give wRp = 0.0623, 0.0728, 0.0634 and χ^2 = 3.61, 5.55, 4.71 for 12 variables, respectively. The refined values of the lattice constants are given by a = 7.355(1) Å, b = 12.757(2) Å and c = 28.737(2) Å for ImVOF, a = 7.403(1) Å, b = 12.798(3) Å and c = 32.739(4) Å for QVOF and a = 7.395(1) Å, b = 12.725(1) Å and c = 32.541(4) Å for PyzVOF, respectively. Rietveld plots of ImVOF, QVOF and PyzVOF are shown in Figure S1.

Figure S1. Rietveld refinement of the ImVOF $C222_1$ structural model against powder X-ray diffraction data of ImVOF (top), QVOF (middle) and PyzVOF (bottom).



Magnetic susceptibility data were taken on a Quantum Design MPMS SQUID magnetometer in zero field cooled (ZFC) field cooled (FC) cycles over the temperature range 2 – 300 K in a 5 T field. The inverse magnetic susceptibilities were analysed in terms of the Curie-Weiss law, $\chi^{-1} = (T - \theta)/C$, where θ and C are the Weiss and Curie constants, respectively. Fitting the inverse susceptibility of ImVOF over the temperature range 50 – 300 K gave θ = –38.5(2) K and C = 3.757(3) emu mol^{-1} K, which corresponds to an effective magnetic moment of 5.482(4) μ_B per formula unit, and R^2 = 0.99989. Equivalent fits of the inverse susceptibility data of QVOF and PyzVOF yielded θ = –26.9(7) K, C = 3.98(1) emu mol^{-1} K, μ_{eff} = 5.63(1) μ_B and R^2 = 0.99864 and θ = –25.5(1) K, C = 3.643(2) emu mol^{-1} K, μ_{eff} = 5.400(3) μ_B and R^2 = 0.99995, respectively, shown in Figure S2. In order to confirm that the relatively strong applied magnetic field of 5 T does not affect the magnetic ground state of this family of

materials or obscure any weak ordering transition in the susceptibility data, χ vs. T measurements were repeated in a weaker field of 0.01 T. Figure S3(a) shows the magnetic and inverse susceptibility of ImVOF in 0.01 T over the temperature range 2 – 300 K. As with the 5 T data, the 0.01 T susceptibility shows Curie-Weiss dependence at high temperatures and the dominance of a Curie tail at low temperatures. Figure S3(b) shows that low temperature (2 – 20 K) region of the low field susceptibility data of ImVOF, QVOF and PyzVOF that were measured in finer temperature steps and confirm an absence of long range magnetic order to at least 2 K in 0.01 T.

Figure S2. Magnetic and inverse susceptibilities of (a) QVOF and (b) PyzVOF in a 5 T field in a zero field cooled (closed circles) field cooled (open circles) cycle. The solid white lines are fits to the data.

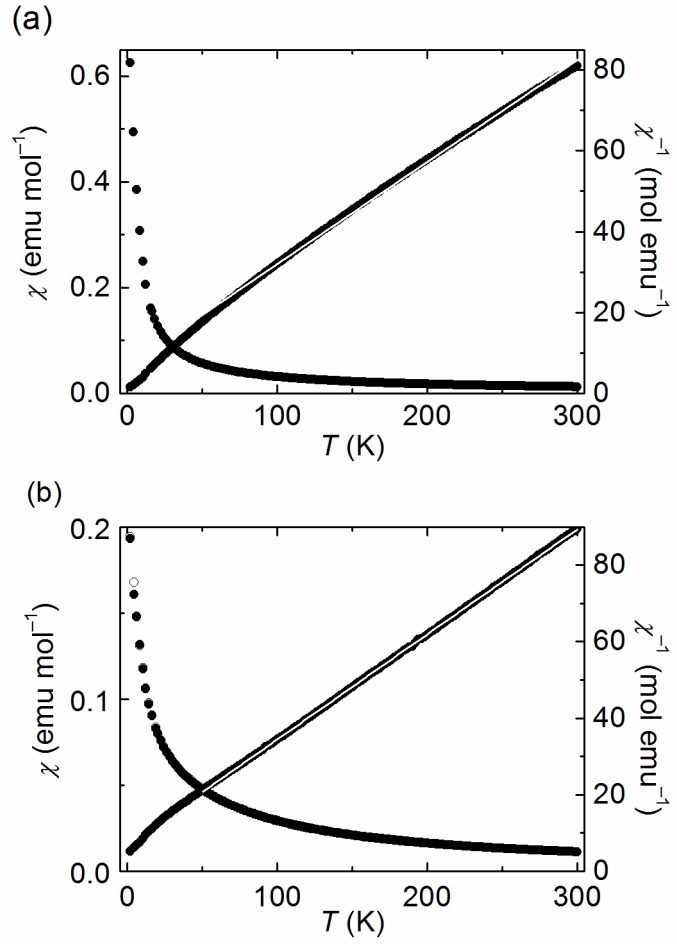


Figure S3. (a) The temperature dependence of the magnetic and inverse susceptibilities of ImVOF measured in an applied magnetic field of 0.01 T. (b) The low temperature region of the magnetic susceptibilities of ImVOF, QVOF and PyzVOF in a field of 0.01 T. Open and closed circles show zero field cooled and field cooled data, respectively.