

Supporting information

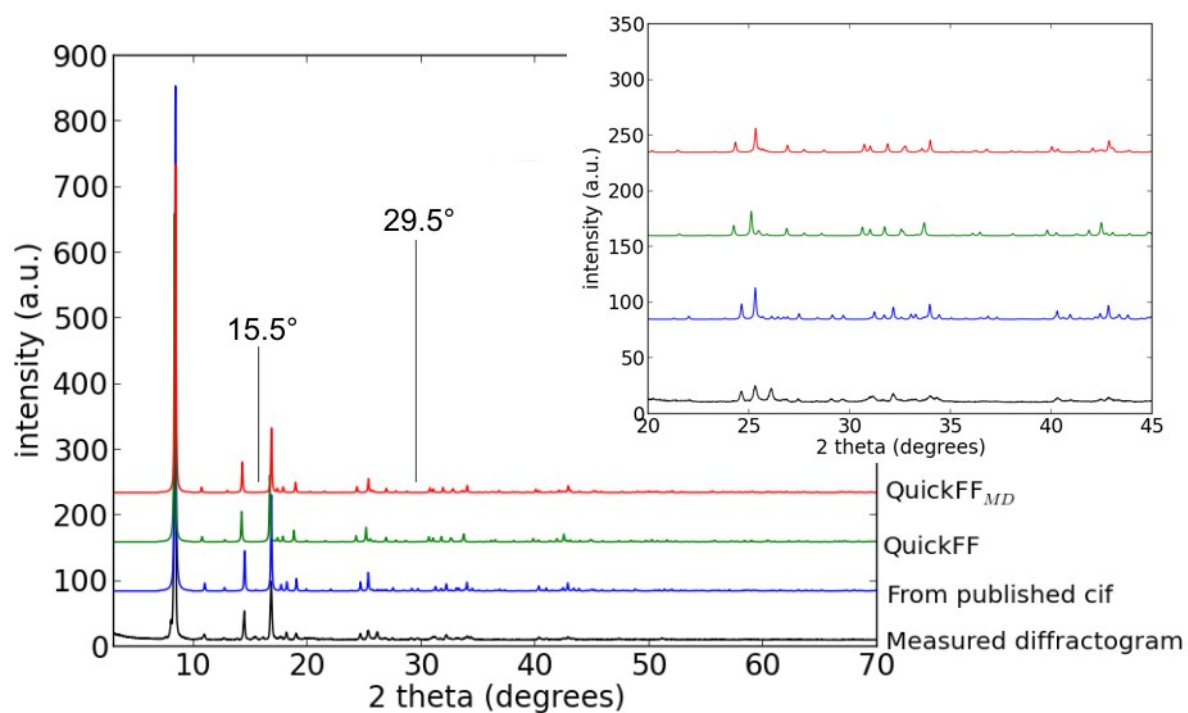


Figure S1. Overview of the comparison between the force field models, published structure and the experimental diffractogram.

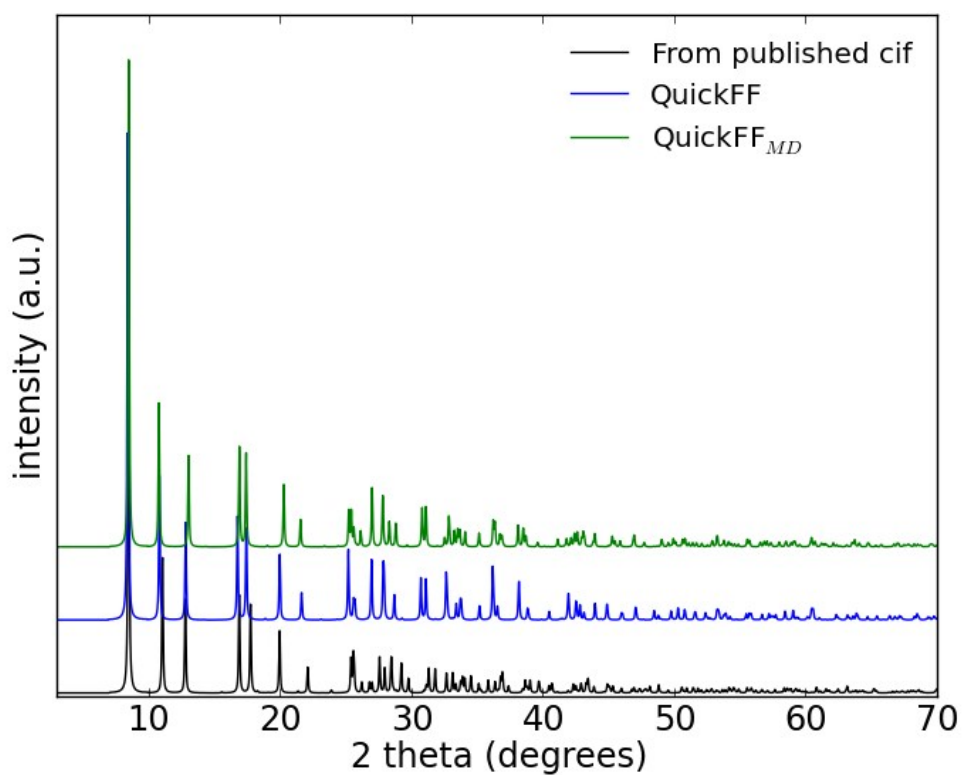


Figure S2. Comparison with the QuickFF geometry when only considering the vanadium chains.

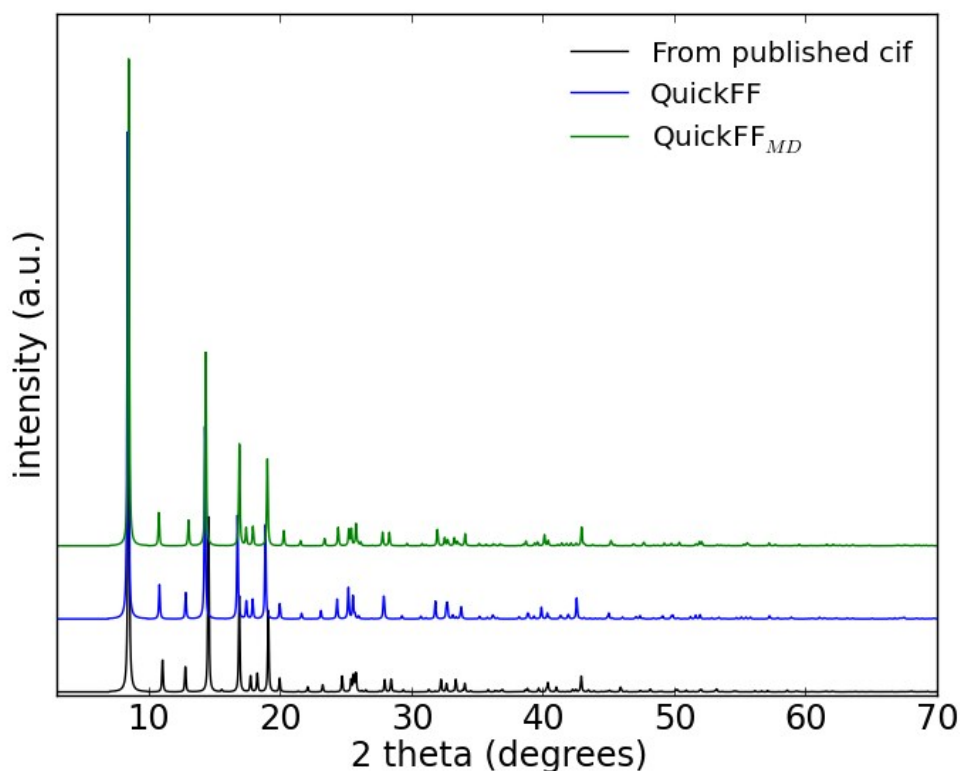


Figure S3. Comparison with the QuickFF geometry when only considering the linkers.

Table S1. Some key bond lengths and bending angles of the equilibrium structure of Mil-47 according to different sources. The symbol * indicates that these distances are taken from the linker cluster.

	Exp. periodic ¹	DFT (PBE) periodic ²	DFT (B3LYP) cluster	FF periodic
Bond lengths [Å]				
V - O (short)	1.672	1.654	1.588	1.593
V - O (long)	2.108	2.097	2.311	2.346
V - O ₁	1.970	1.990	1.977	1.980
V - O ₂	1.976	1.976	2.033	2.040
V - V	3.422	3.440	3.531	3.550
O ₁ - C _{ca}	1.277	1.281	1.275	1.273
O ₂ - C _{ca}	1.252	1.278	1.255	1.255
C _{ca} - C _{pc}	1.501	1.487	1.494*	1.496
C _{pc} - C _{ph}	1.372	1.404	1.399*	1.400
Bending angles [°]				
V - O - V	129.4	132.7	128.8	127.7
O ₁ - V - O ₁	91.5		91.3	90.3
O ₂ - V - O ₂	90.4		87.7	88.9
O ₁ - C _{ca} - O ₂	126.0	125.2	125.3	126.7

In Table S1, the force field values of some key bond lengths and bending angles in equilibrium are compared with several other sources, both ab initio and experimental. In first instance, the force field values (last column) need to be compared with the DFT cluster values (third column) that were used as input for the force field fitting. It is clear from the table that the force field reproduces these DFT cluster values very accurately, which illustrates the accuracy of the fitting methodology. However, when comparing the experimental values (first column) with the DFT cluster values (third

column) there is a clear discrepancy, especially in the vanadium oxygen bonds. These errors are mainly due to the lack of periodic constraints. Indeed, the periodic DFT computations (second column) do reproduce the experimental values well. As such, we can conclude that most of the errors that are found by using the force field are not due to the force field approximation itself. Instead, they can be traced back to the DFT cluster data and its inability to accurately represent the periodic constraints of the experimental structure.

1. K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angewandte Chemie International Edition*, 2002, **41**, 281-284.
2. D. E. P. Vanpoucke, J. W. Jaeken, S. De Baerdemacker, K. Lejaeghere and V. Van Speybroeck, *Beilstein Journal of Nanotechnology*, 2014, **5**, 1738-1748.