Modulation of the mechanical energy storage performance of the MIL-47(V\textsuperscript{IV}) Metal Organic Framework by ligand functionalization

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1. Mercury intrusion

Figure S1 and S2 show the compression/decompression Hg curves obtained for MIL-47(V\textsuperscript{IV})-BDC\textsubscript{Br} and MIL-47(V\textsuperscript{IV})-BDC\textsubscript{CF\textsubscript{3}}.

**Figure S1**: *Cumulative volume of intruded mercury in two intrusion-extrusion cycles as a function of the applied pressure obtained for the dehydrated MIL-47(V\textsuperscript{IV})-BDC\textsubscript{Br} solid (V\textsubscript{initial} and V\textsubscript{final} are the volumes of mercury intruded before and after the contraction of the solid respectively).*
Figure S2: Cumulative volume of intruded mercury in two intrusion-extrusion cycles as a function of the applied pressure obtained for the dehydrated MIL-47(V)-BDC$_3$ showing no contraction of the solid in the pressure range.
2. Synchrotron X-ray powder diffraction

Figure S3: Structure-independent refinements of the unit-cell of the X-ray powder diffraction pattern of MIL-47(V\textsuperscript{IV})-BDC-Br at atmospheric pressure Large pore form (LP) S.G. Pmcn, \(a=17.008(4)\) Å; \(b=12.795(2)\) Å; \(c=6.806(6)\) Å, \(V=1481.2(1)\) Å\(^3\) and Narrow pore form with solvent inside the porous framework (NP+DMF) S.G. C2/c, \(a=18.883(5)\) Å; \(b=10.533(2)\) Å; \(c=6.7556(3)\) Å, \(\beta=108.02(5)^\circ\), \(V=1277.5(1)\) Å\(^3\) (Rp=0.63, wRp=1.29).
Figure S4: Structure-independent refinements of the unit-cell of the X-ray powder diffraction pattern of MIL-47(V\textsuperscript{IV})-BDC \_Br at 990 MPa S.G. C2/c, a=19.480(1) Å; b=8.900(3) Å; c=6.746(2) Å; β=105.69(5)°, V=1126.2 Å\textsuperscript{3} (Rp=0.93, wRp=1.84).
Figure S5: Structure-independent refinements of the unit-cell of the X-ray powder diffraction pattern of MIL-47(V)\textsuperscript{IV} -BDC\_CF\textsubscript{3} at atmospheric pressure S.G. Pmcn, a=16.864(6) Å; b=13.641(3) Å; c=6.954(2) Å, V=1599.7(1) Å\textsuperscript{3} (Rp=0.51, wRp=0.86).
Figure S6: Structure-independent refinements of the unit-cell of the X-ray powder pattern of MIL-47(V IV)-BDC_CF3 at 910 MPa: S.G. C2/c a=19.321(4) Å; b=9.083(3) Å; c=6.685(2) Å; beta=105.06(3)°, V=1145.3 Å³ (Rp=0.47, wRp=0.74).
3. Comparison between the theoretical XRPD patterns calculated from the plausible structural models and the corresponding experimental data.

**Figure S7:** XRPD pattern calculated from the predicted structure model and obtained from the experiment for MIL-47(V$^{	ext{IV}}$)-BDC$_2$Br open pore form under atmospheric pressure ($\lambda=0.5100$ Å). Peaks marked by stars are attributed to a phase that incorporates remaining traces of solvent.

**Figure S8:** XRPD pattern calculated from the predicted structure model and obtained from the experiment for MIL-47(V$^{	ext{IV}}$)-BDC$_2$Br closed pore form under 990 MPa ($\lambda=0.5100$ Å).
Figure S9: XRPD pattern calculated from the predicted structure model and obtained from the experiment for MIL-47(VIV)-BDC_CF₃ open pore form under atmospheric pressure ($\lambda=0.5100$ Å).

Figure S10: XRPD pattern calculated from the predicted structure model and obtained from the experiment for MIL-47(VIV)-BDC_CF₃ closed pore form under 910 MPa ($\lambda=0.5100$ Å).