Supporting Information

In situ Raman and FTIR Spectroscopic Study of Al MOF Isomer MIL-68(Al) and MIL-53(Al) Formation

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Table of Contents

1. Simulated MIL-68(Al) and MIL-53(Al) XRD patterns

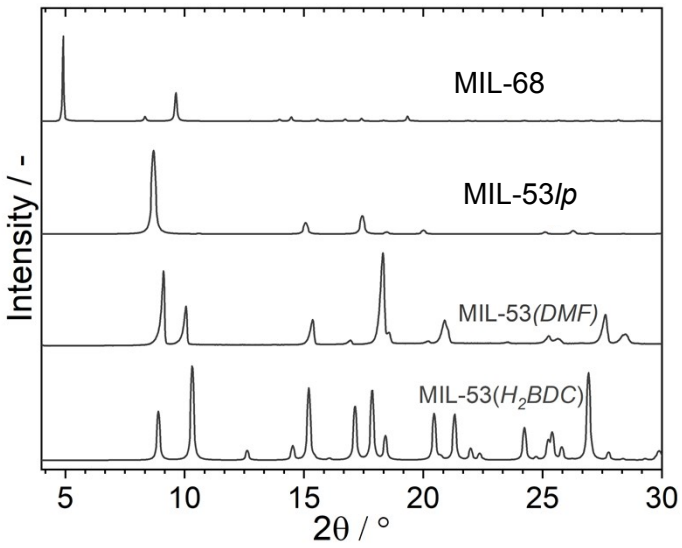

Figure S1. Simulated XRD patterns of MIL-68(Al), MIL-53*lp*, MIL-53(*DMF*), and MIL-53(*H*$_2$*BDC*) from the crystal unit structure.

2. MOF characterization

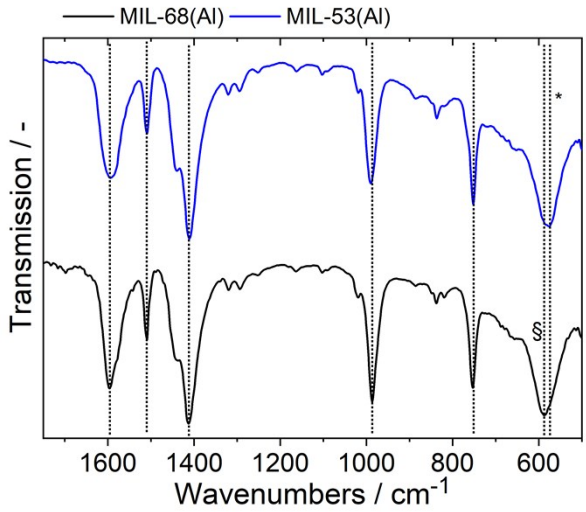

Figure S2. Comparison of the FTIR spectra of MIL-68(Al) and MIL-53(Al)

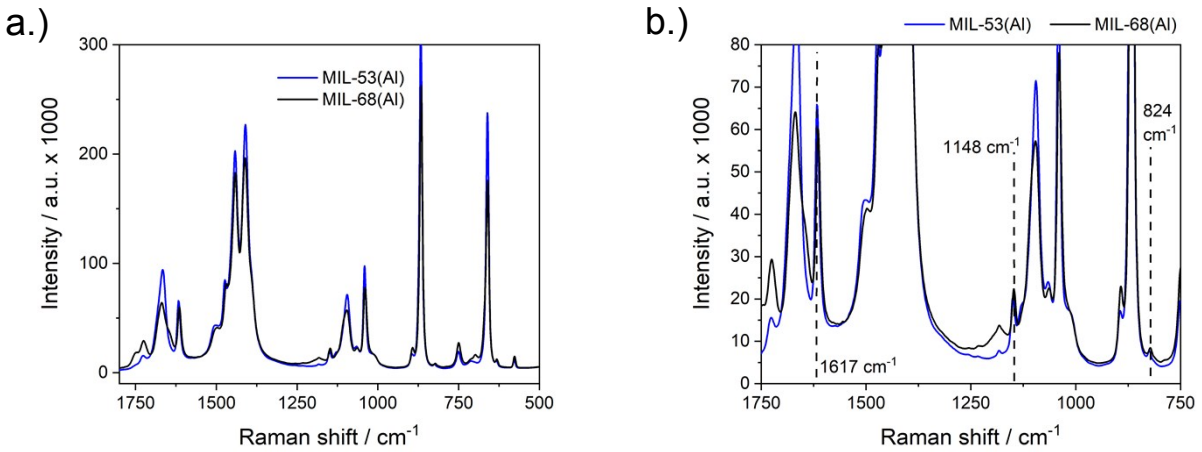

Figure S3. Comparison of the Raman spectra of MIL-68(Al) and MIL-53(Al) in DMF: (a) full intensity spectra and (b) close-up of the spectral range between 1750 and 750 cm^{-1}. The three MOF band vibrations at 1617, 1148 and 824 cm^{-1} are assigned to νCC, (νCC + δCH) and ωCC, respectively. Vibration bands have been assigned according to Hoffmann et al. reference 42 of the paper.

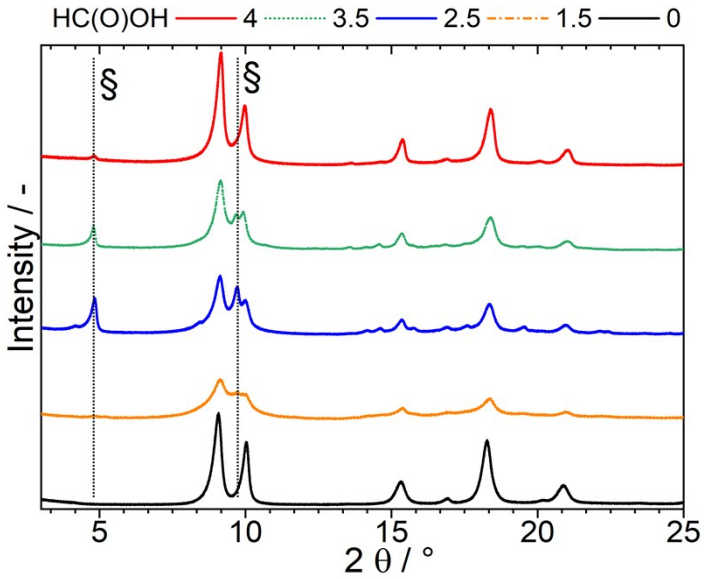

Figure S4. XRD patterns of MOF product synthesized with 0, 1.5, 2.5, 3.5, and 4 M formic acid modulation at 80 °C. § = MIL-68.

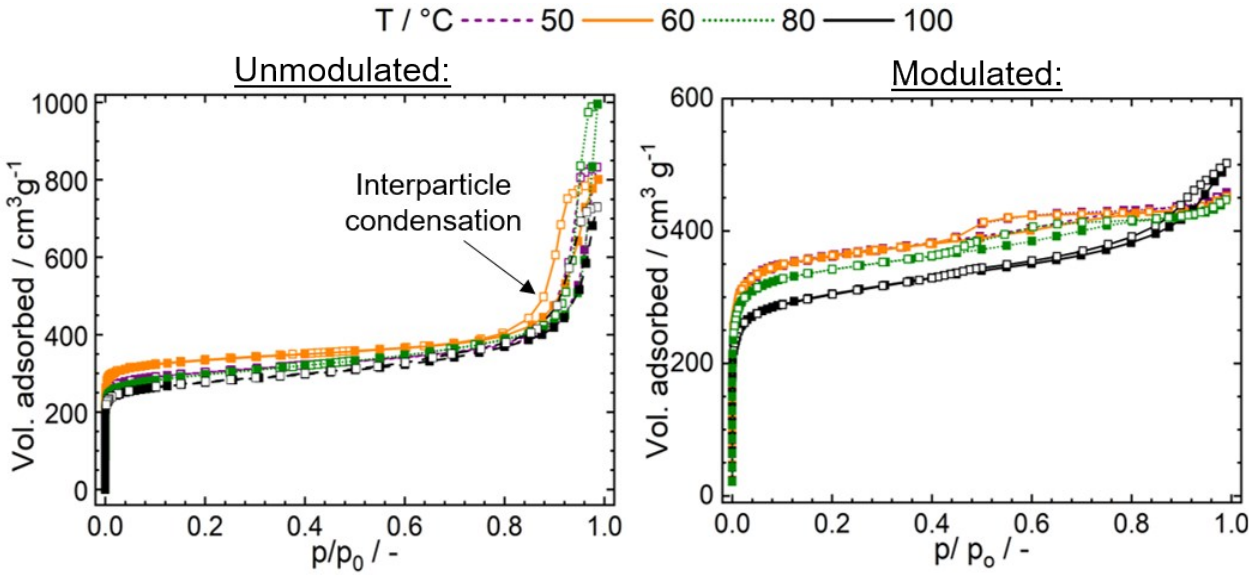

Figure S5. N_2 sorption isotherms of MOF product synthesized in DMF at various temperatures both without and with 2.5 M formic acid modulation.

Table S1. BET area in $m^2\ g^{-1}$ of MOF products synthesized at various temperatures in DMF with and without 2.5 M formic acid modulation.

	55 °C	60 °C	80 °C	100 °C
unmodulated		1294	1132	1062
modulated	1468	1411	1323	1161

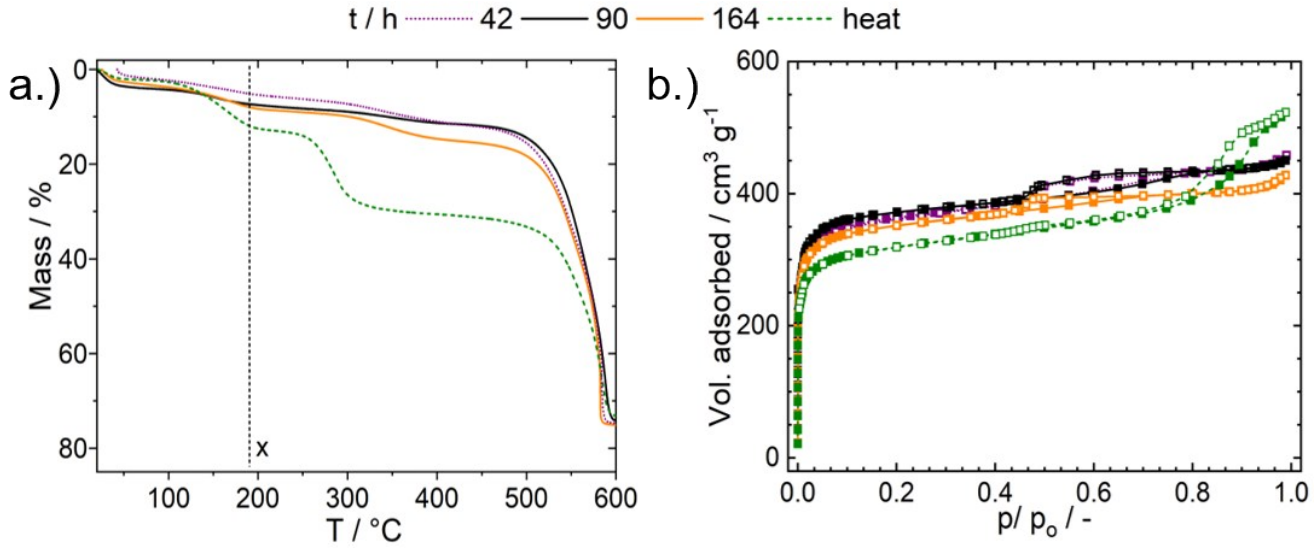

Figure S6. (a) TGA profiles, and (b) N_2 sorption isotherms of products of 2.5 M formic acid modulated synthesis in DMF at 55 °C after 42, 90 and 164 h heating and after an additional 48 h heating at 120 °C. x = MIL*(DMF)*.

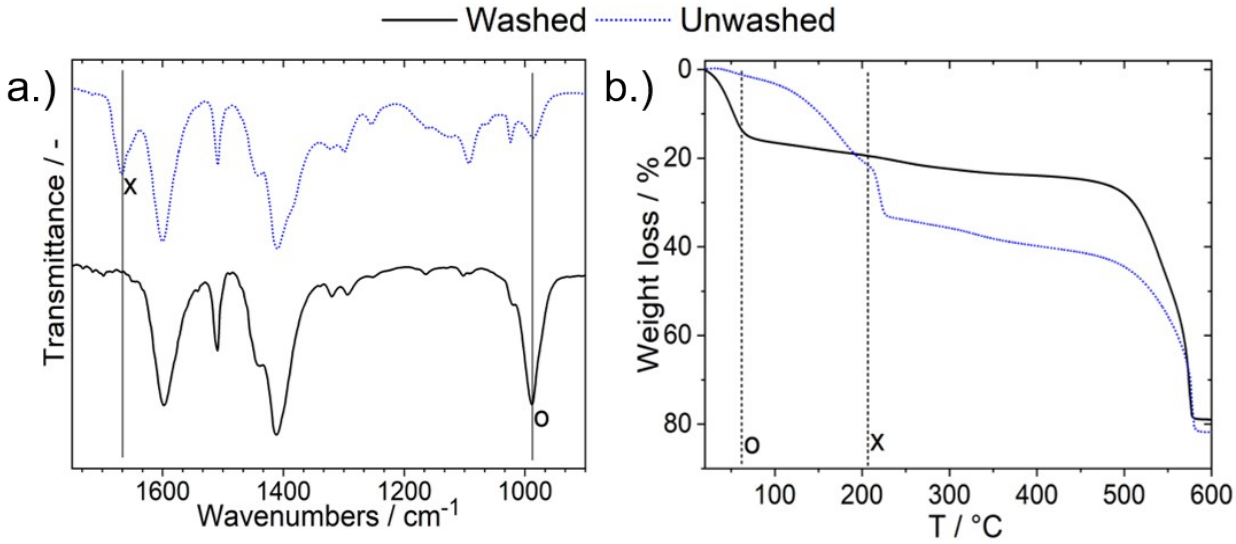

Figure S7. (a) FTIR, and (b) TGA profiles of MIL-68(Al) isolated after 42 h synthesis at 55 °C modulated with 2.5 M formic acid directly after synthesis (unwashed) and after three centrifugation rounds in ethanol (washed). x = MIL*(DMF)*. o = MIL*(H_2O)*.

Table S2. BET area of MOF products synthesized in DMF with 2.5 M formic acid modulation at 55 °C after 42, 90, and 164 h and after an additional 48 h heating at 120 °C.

	42 h	90 h	164 h	+ heating

BET area / $m^2\ g^{-1}$	1422	1468	1372	1238

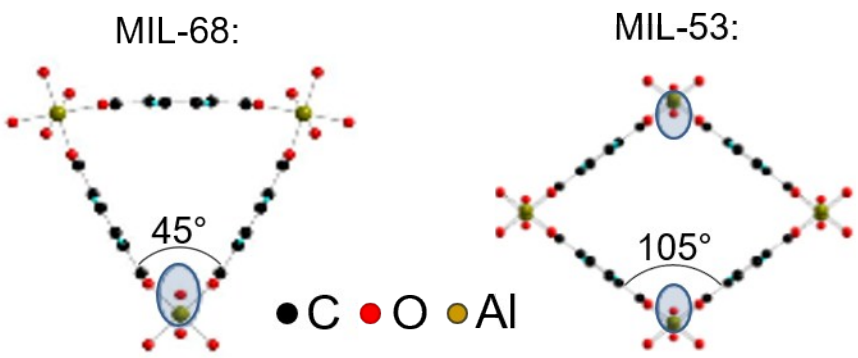

Figure S8. Pore geometry around the Al μ-OH group in MIL-68(Al) compared to that in MIL-53(Al).

3. Activation energy calculations

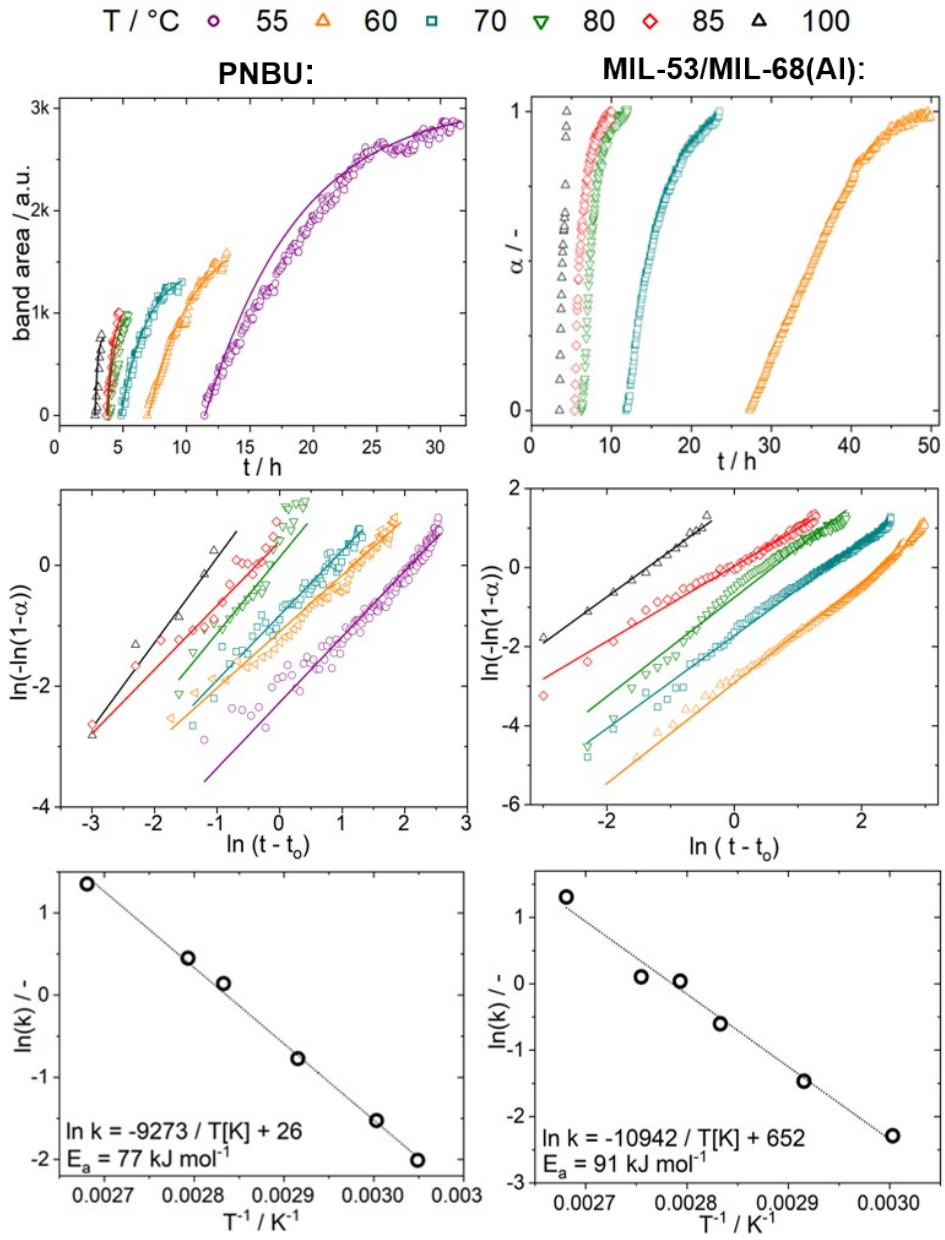

Figure S9. Sharp Hancock plots of the normalized Raman (νCC + δCH) MOF and $\delta(COO^-)$ PNBU band areas for 2.5 M formic acid modulated synthesis in DMF at various temperatures and the corresponding Arrhenius plots with slopes equal to – E_a (activation energy) / R.

4. Effect of HNO_3 addition in DMF

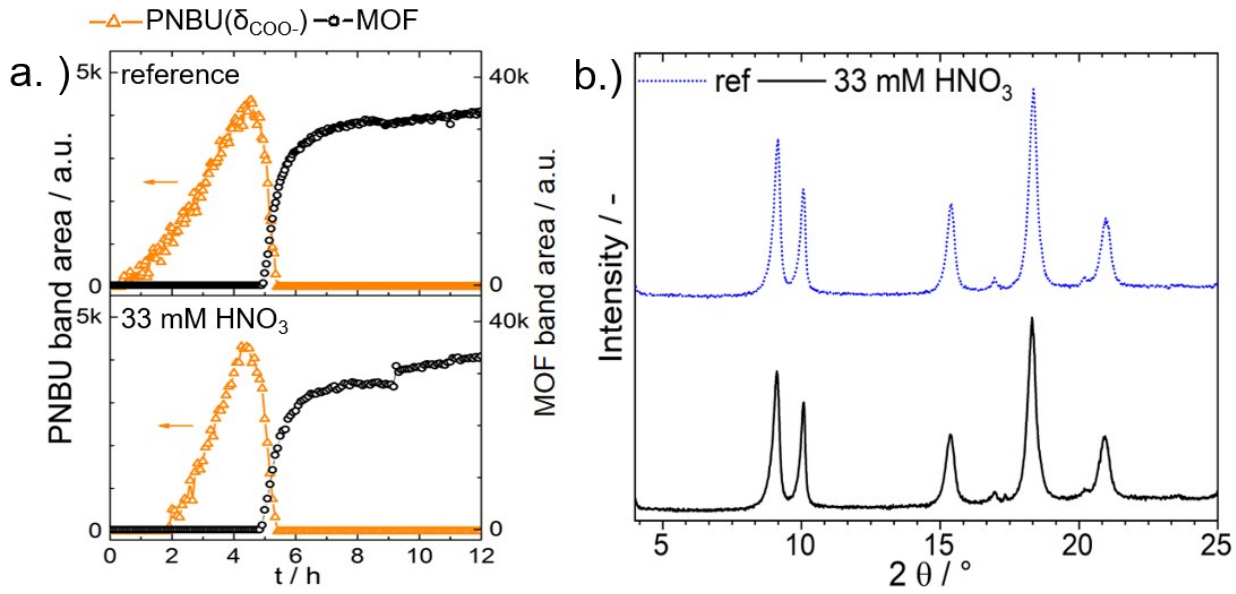

Figure S10. (a) Evolution of the characteristic PNBU and MOF band areas during MOF synthesis at 80 °C in DMF with and without 33 mM added HNO_3 (acid equivalent to 2.5 M formic acid). (b) XRD patterns of MIL-53(*DMF*) product synthesized at 80 °C for 17 h in DMF with and without 33 mM added HNO_3.

5. Reference ^{13}C-NMR measurements

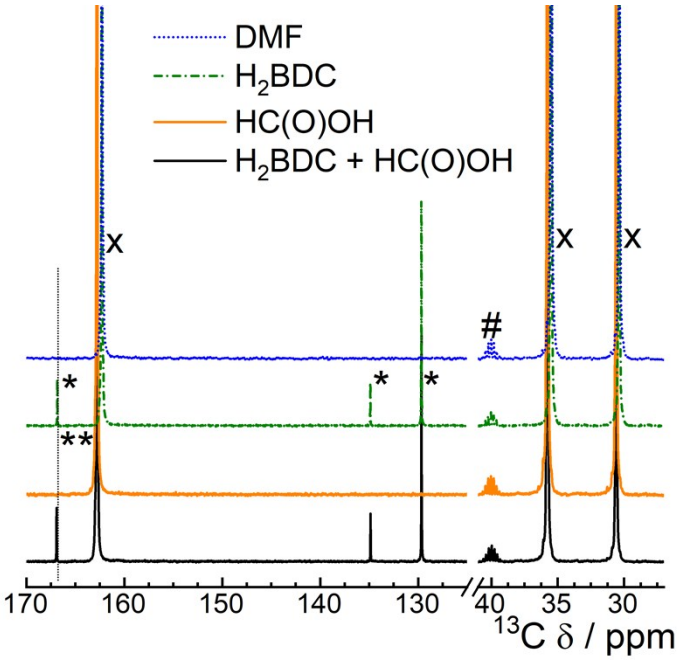

Figure S11. ^{13}C-NMR spectra of DMF, 0.33 M H_2BDC in DMF, 2.5 M HC(O)OH in DMF, and both 0.33 M H_2BDC and 2.5 M HC(O)OH in DMF. x = DMF, # = septet from DMSO, * = H_2BDC, ** = HC(O)OH.