Electronic Supplementary Material (ESI) for Dalton Transactions

Soft synthesis of isocyanate-functionalised Metal Organic Frameworks

(Electronic Supplementary Information)

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EXPERIMENTAL SECTION

For scrupulousness due to the reactive nature of azide and nitrene groups, all the samples were handled in a protected atmosphere (M Braun Lab Star Glove Box supplied with pure 5.5 grade Nitrogen, <0.01 ppm O_2, <0.01 ppm H_2O).

Post-Synthesis Functionalization of MIL-68(In)-NH_2 to MIL-68(In)-N_3. In a typical synthesis, the freshly dried MIL-68(In)-NH_2 (80 mg, 0.26 mmol equiv of -NH_2) was placed into a vial (10 mL capacity) with 3.0 mL of solvent (THF) and 1.48 mL (12.48 mmol, 48 eq) of tBuONO and 1.3 mL (9.88 mmol, 38 eq) of $TMSN_3$. The sample was left to react 6 hours at room temperature to produce the azide MOF. The reaction was quenched by decanting the solvent. Excess reactants were removed by washing three times in THF followed by three times in CH_2Cl_2. Drying at room temperature yielded a yellow powder of MIL-68(In)-N_3. The mass of dried MIL-68(In)-N_3 obtained was 70 mg.

Post-Synthesis Functionalization to MIXMOF-MIL-68(In)-NCO. The MIXMOF-MIL-68(In)-N_3 samples were activated on a glass vacuum line equipped with an ultra-high vacuum pump system by degassing at RT until a dynamic vacuum of $5 \cdot 10^{-4}$ mbar was reached and then the temperature was increased up to 90°C and maintained for at least 12 h. After this time, the sample was cooled down to RT and then CO was dosed in excess with respect to the stoichiometric amount (about 300 mbar). The sample was warmed up to 120°C and left at this temperature for 24 h. After this time, the sample was cooled down to RT, degassed and then contacted with a fresh dose of CO and let at 120°C for 12 h. This step was repeated a second time.

Fourier-Transformed Infrared spectroscopy. The FTIR spectra were collected in transmission mode (2 cm^{-1} resolution, average on 64 scans) on a Nicolet 6700 FT-IR Spectrometer (Thermo Fisher Scientific) equipped with a MCT detector. The samples were used in form of thin self-supporting wafers, having comparable weight and thickness. After the wafer preparation the samples were placed inside an IR cell, which also allowed gas dosage and low temperature IR measurements.

Gas adsorption measurements. The N_2 sorption isotherm measurements at 77 K were made using a Micromeritics ASAP 2020 sorption analyzer. All the samples, in powder form, were outgassed at 90°C for 24 h before the analysis and handled inside the glove box. The specific surface area of the materials was calculated using the Brunauer–Emmet–Teller[1] and the Langmuir methods,[2] while the pore diameter and the pore size distribution were evaluated using the Non-Local DFT (Density Functional Theory) method on the basis of the cylindrical pore model proposed by Tarazona[3] on DataMaster V5.00 Software (Micromeritics). This method has been successfully adopted for the determination of the pore size distribution in MOFs.[4, 5] It is important to stress as we are aware that the BET method, on the contrary of the Langmuir method, is not suitable to estimate the area of microporous MOFs as MIL-68 (negative BET constant values in the standard pressure range). However, this is the method most applied in the literature to calculate the MOF area and then the obtained BET surface areas have been then reported in this study in order to facilitate the comparison with other literature results. The micropore volume has been evaluated with the t-plot method adopting the Harkins and Jura equation of thickness in the $0.15 < p/p_0 < 0.50$ range.[6] All the reported quantities are affected by an error of 10%.

Powder XRD measurements. Powder X-Ray Diffraction measurements have been performed in the 2θ range 2° – 90° (step size of 0.001°) using a laboratory diffractometer (Panalytical X'Pert Pro Multipurpose Diffractometer) equipped with Ni filtered Cu source in Debye-Scherrer geometry. Samples of as-synthesized MOF and after reaction with CO were sealed into boron silica glass capillaries of internal diameter 1.0 mm in a protected atmosphere.

NMR. All ^{1}H-NMR spectra were recorded with the same automated procedure for routine analysis on a Bruker Avance 250 spectrometer operating at 250 MHz for ^{1}H. Spectra are calibrated using the deuterium signals of DMSO. Following the procedure adopted by Volkringer and Cohen,[7] before measurements, MIL-68(In) derivate samples were digested in HF/ DMSO-d_6.In particular, in Ref. 7 this method has been successfully adopted to quantify the degree of conversion of MIL-53(Al)-NH_2 to MIL-53(Al)-NCO and MIL-53(Al)-NCS.

Theoretical Calculations. The theoretical surface area of MIL-68(In) was estimated on the XRD refined unit cell reported in Ref. [8] as the accessible solvent surface using a Monte Carlo algorithm as implemented in the Materials Studio 5.5 suite of programs[9] and then normalizing this value to the mass of the XRD cell. The surface was evaluated as the locus of the probe center as the probe rolls over the vdW surface of the material (r_{vdW_H} = 1.2 Å, r_{vdW_C} = 1.7 Å, r_{vdW_N} = 1.550 Å, r_{vdW_O} = 1.520 Å, r_{vdW_In} = 1.930 Å), in accessible regions only. The radius of the solvent was set to 1.82 Å, coincident with the kinetic radius of N_2.[10] The corresponding surface areas of MIXMOF-MIL-68(In)-N_3 and MIXMOF-MIL-68(In)-NCO have been obtained by weight-scaling the value obtained for MIL-68(In), hypothesizing that the effect of the different weight of the linker was the predominant on the final value of the surface area.

TGA. The stability of the materials was investigated by thermogravimetric analyses under N_2 flow (100 ml/min, ramp 1°C min^{-1}) by a TA instrument Q600 SDT Simultaneous DSC-TGA heat flow analyzer.

Nitrogen adsorption measurements

Surface area, pore volume and pore size distribution were obtained by N_2 adsorption measurements carried out at 77 K on a Micromeritics ASAP 2020 sorption analyzer. The results obtained are reported in Figure S1 and in Table S1. It is evident from Figure S1 as all the materials are characterized by an isotherm of Ib type, typical of perfect microporous materials. The absence of a hysteresis loop indicates the absence of mesopores, which could originate from defects, both in the pristine and in the CO reacted samples: this is an indication of the good quality of the starting material and a further proof of the softness of the method used for the isocyanate production. This qualitative analysis is confirmed by the pore size distributions (PSD) reported in part (b) of Figure S1.

Analyzing in more details the data reported in Table S1, an increase of the micropore area and volume is obtained after the reaction with CO. The activation temperature for the azide containing materials was limited to 90°C in order to avoid the decomposition of the azide group (see Figure S4). Although the change in the surface area is close to the experimental error, it could be explained by the higher activation temperature that can be adopted for the –NCO modified material.

Table S1. Textural properties of the MIL-68(In) MOFs materials.

	S_{MC} [a]	S_{BET} [b]	$S_{Langmuir}$ [b]	S_{micro} [c]	V_{micro} [c]
MIXMOF-MIL-68(In)-N_3	1128	920	1225	1094	0.37
MIXMOF-MIL-68(In)-NCO	1128	985	1305	1221	0.41

[a]Theoretical surface area obtained on the XRD refined structure reported in Ref. 8. [b]Total area evaluated following the BET and Langmuir models in the standard pressure ranges, respectively. [c]Micropore surface area and volume obtained from the t-plot.

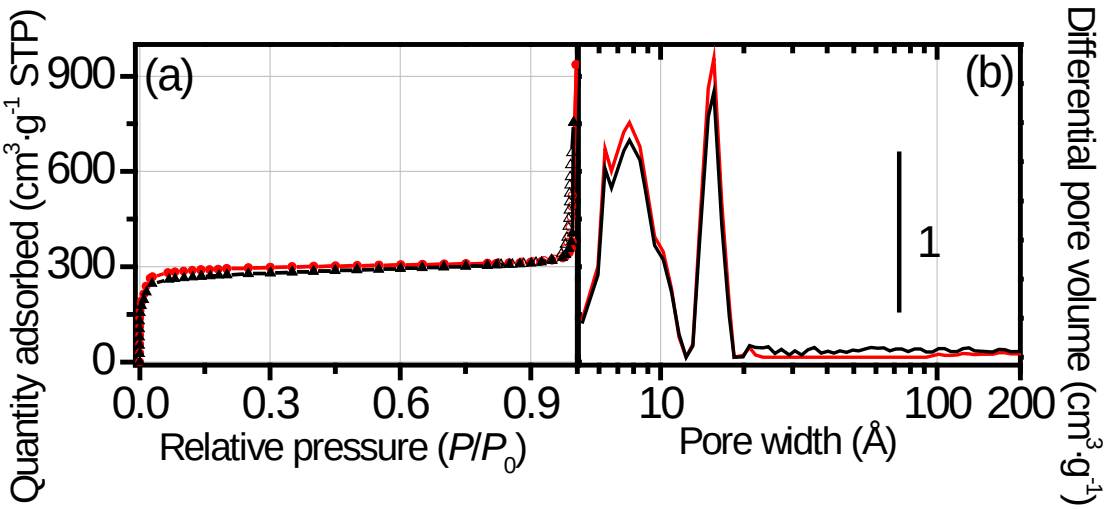

Figure S1. a) Volumetric N_2 adsorption/desorption isotherms obtained at 77 K and b) pore size distributions obtained by analyzing the data using NLDFT (Tarazona, cylinder model) for MIXMOF-MIL-68(In)-N_3 (degassed overnight at 90°C, black curve), MIXMOF-MIL-68(In)-NCO (obtained after reaction with 300 mbar of CO at 120°C for 48 hours, red curve). Filled and empty scatters of a) refer to adsorption and desorption branches, respectively.

XRPD

XRPD measurements indicate a good crystallinity of the starting material (MIXMOF-MIL-68(In)-N_3, black curve) and confirm as the reaction between CO and the $–N_3$ species in order to get the –NCO functional groups does not affect the MOF structure. These findings agree with the results obtained by the nitrogen adsorption measurements.

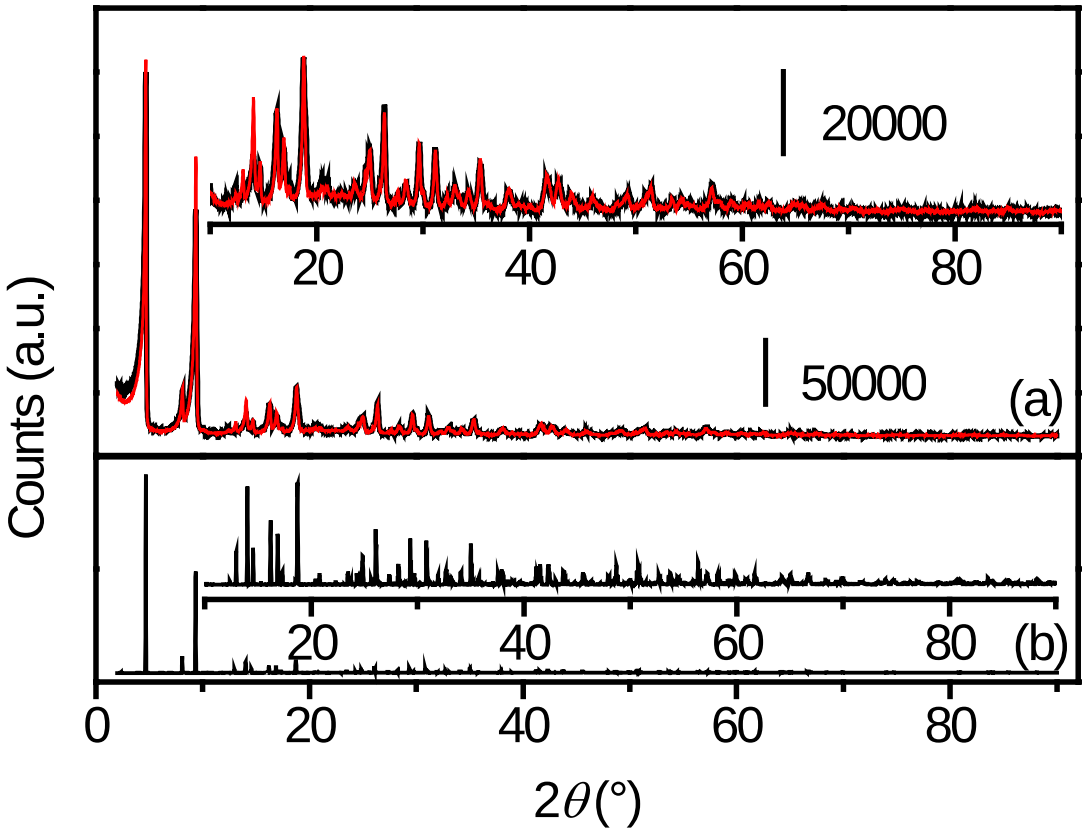

Figure S2. Part (a): Experimental XRPD patterns of MIXMOF-MIL-68(In)-N_3 (black curve) and MIXMOF-MIL-68(In)-NCO (red curve). All the patterns have been normalized with respect to the intensity of the peak at 18.7°. Part (b): theoretical XRPD pattern as obtained for the MIL-68(In) structure reported in Ref. 8 by using the Reflex module in the Materials Studio suite of program (default setting values).[9] In the inset, a magnification of the 10-90° range is reported.

MIL-68(In) structure

MIL-68 is a MOF constituted by wires of $InO_4(OH)_2$ octahedra linked between them by BDC-based linkers (BDC: 1,4-benzenedicarboxylate) giving rise to a Kagomé structure characterized by two families of 1D pores of hexagonal (17.8 Å, nucleus-nucleus distances) and triangular shape (7.8 Å).[8]

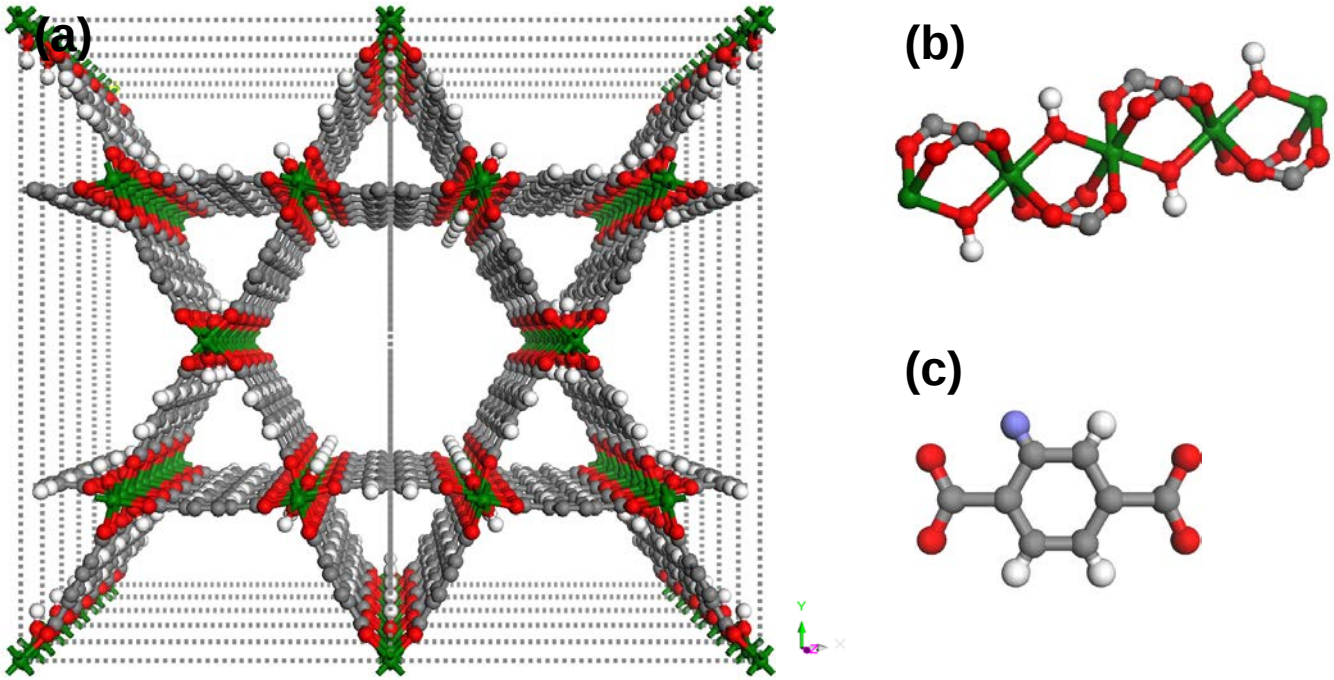

Figure S3. Pictorial representation, at different magnification grades, of a dehydrated MIL-68(In) sample: (a) 3D view of the structure; (b) inorganic nodes involving In^{4+} and running along *c* axis; (c) organic linker. The atoms are represented as spheres with the color code: red (oxygen), gray (carbon), white (hydrogen), blue (nitrogen) and green (indium). As violet sphere is represented a generic nitrene or isocyanate group.

Thermal gravimetric analysis

Thermal gravimetric analysis has been conducted on MIXMOF-MIL-68(In)-N_3 (dotted line in Figure S4), evidencing three temperature regions:

25 < *T* <200°C, where the weight loss is associable to the desorption of solvent molecules and the decomposition of the $–N_3$ groups,

200 < *T* < 360°C where the weight loss is very small (4%).

T > 360°C, where the complete collapse of the structure is observed with the loss of the organic moieties.

In order to better appreciate the different components of the weight loss in the first region, a second ramp has been conducted (solid line in Figure S4) by imposing three isothermal steps of 3 h each, at: (a) 90°C (the activation temperature adopted for all the samples because the highest temperature at which the $–N_3$ species have been demonstrated to be stable for long time in the IR characterization: see below), (b) 120°C (decomposition temperature of the $–N_3$ species adopted in the study) and (c) 150°C (the temperature corresponding to the maximum of the transformation of azide species into nitrene ones in the first run and also to the max temperature at which the MIL-68 framework has been reported to be stable).[8, 11]

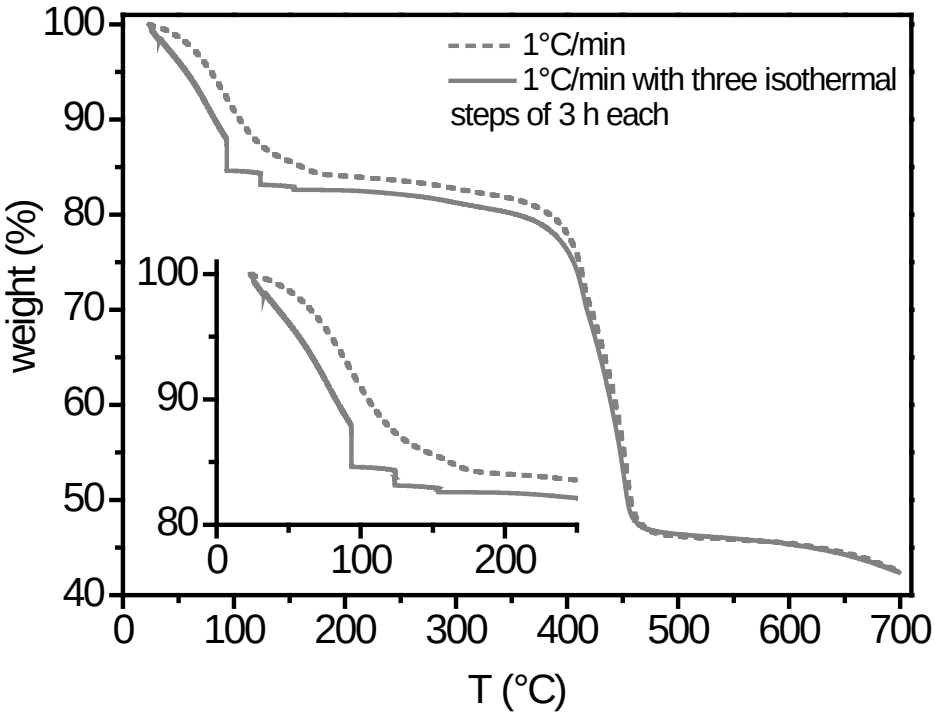

Figure S4. TGA curves of MIXMOF-MIL-68(In)-N_3 collected in N_2 flow (100 ml/min). Dashed line obtained using a ramp rate of 1°C/min, solid line by adopting the same ramp rate but imposing three isothermal steps of 3 hours each at 90, 120 and 150°C.

FTIR spectra: Azide grafting

In Figure S5 the spectra of MIL-68(In)-NH_2 (green curve),and MIXMOF-MIL-68(In)-N_3 (black curve) are compared. The negligible presence of $–NH_2$ groups in MIXMOF-MIL-68(In)-N_3 can be appreciated by the absence in these materials of the 3506 and 3393 cm^{-1} bands that are out of scale in the amino-materials.

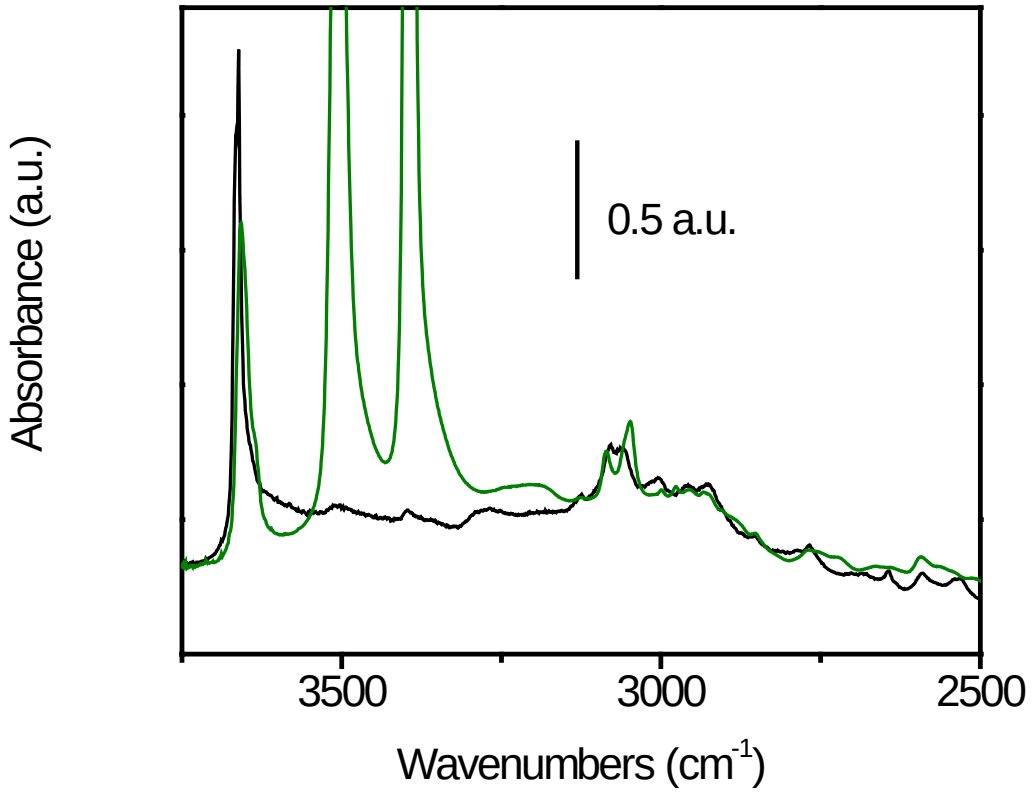

Figure S5. FTIR spectra for the dehydrated MIL-68(In)-NH_2 (green curve) and MIXMOF-MIL-68(In)-N_3 (black curve).

FTIR spectra: Effect of the reaction time

In Figure S6, the spectra obtained for intermediate reaction time for the reaction of CO with MIXMOF-MIL-68(In)-N_3 at 120°C are reported.

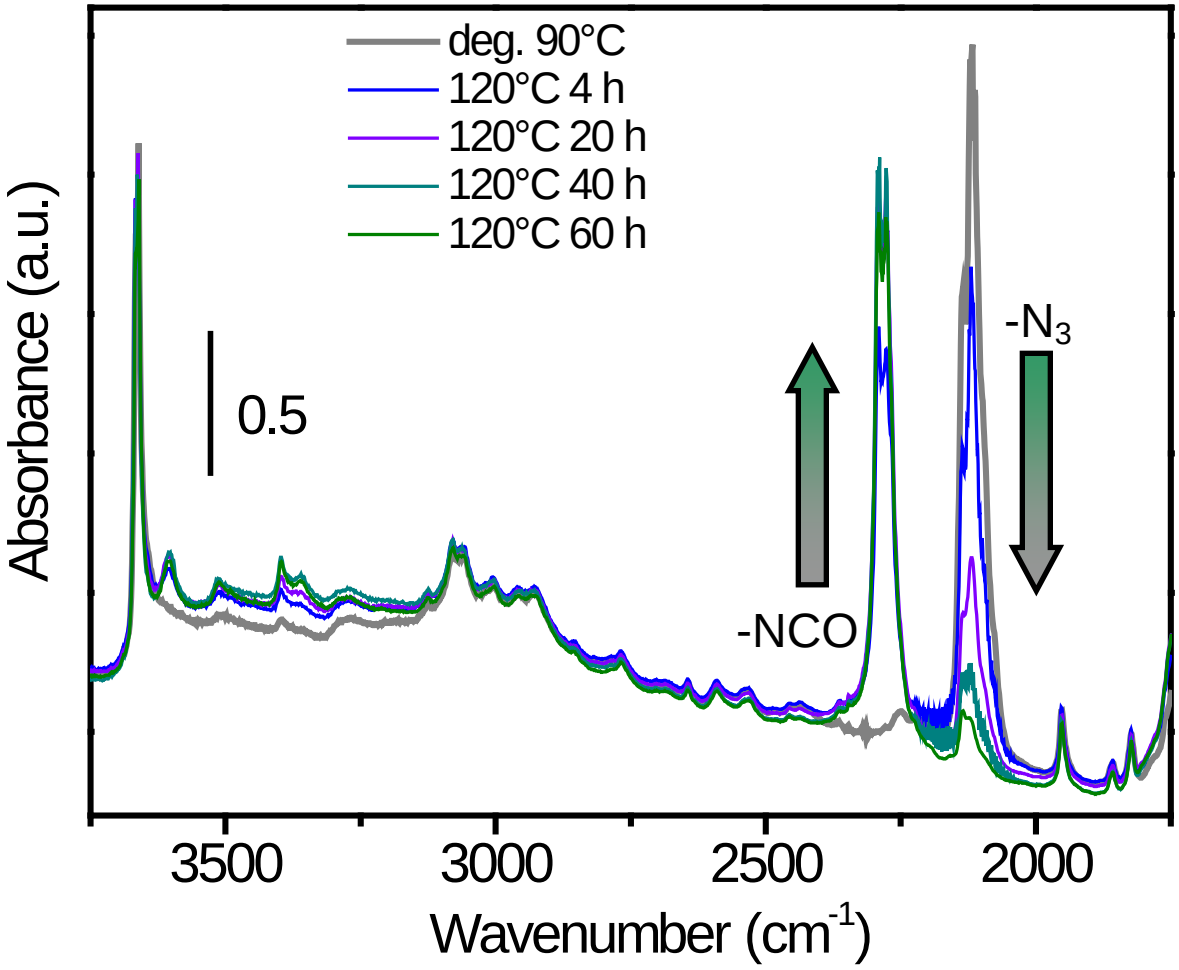

Figure S6. FTIR spectra recorded for MIXMOF-MIL-68(In)-N_3 after contact with 300 mbar of CO at 120°C for increasing contact time. The sample was recovered at RT, degassed and then 300 mbar of CO were dosed again. The spectrum recorded for MIXMOF-MIL-68(In)-N_3 after degassing overnight at 90°C is also reported as gray curve.

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