Supporting information for

# Impact of the functionalization onto structure transformation and gas adsorption of MIL-68(In)

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**Figure S1** Coordination environment of In3+ of (a) MIL-68(In) and MIL-53(In) ; (b) QMOF-2 (Color code: In, olive; C, French grey; O, red) .

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**Figure S2** PXRD patterns for (a) MIL-68(In) simulated from single–crystal structure analysis; (b) MIL-68(In)\_NH2; (c) MIL-68(In)\_Br; (d) MIL-68(In)\_NO2.

### *Infrared Spectroscopy*

The IR spectra of as-synthesized MIL-68(In)­\_X samples are investigated as shown in Figure S3. For comparison, the one of as-synthesized MIL-68(In)­ sample are investigated as well. All IR spectrum of as-synthesized samples exhibits the typical vibrational bands of the carboxylic acid function in the region of 1400-1700 cm-1. The adsorption band of the carboxyl groups of the ligand coordinated to the metal centers is visible at 1558 cm-1 whereas the one of pure ligand is observed at 1693 cm-1. Such difference proves the absence of free ligand in the as-synthesized samples. Moreover, the presence of occluded DMF molecules is also evidenced by its C=O band which appears at around 1660 cm-1. The broad peak between 3600 and 2500 cm-1 is mainly due to water molecules and the *μ*–OH of the network.

The peak at 1256 cm-1 corresponds to the stretching vibration of N-C and the two weak peaks at 3380 and 3472 cm-1 correspond to symmetric and asymmetric stretching vibrations of NH2 species of the ligand, respectively. The peak at 1039 cm-1 corresponds to the stretching vibration of Br-C and the two weak peaks at 1497 and 1304 cm-1 correspond to stretching vibrations of O-N and N-C for NO2 species, respectively. The appearance of these signals in the spectrum of MIL-68(In)\_X showing the incorporation of the ligand into the framework with the uncoordinated functionalization species.

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**Figure S3** The IR spectra for the activated samples of (a) MIL-68(In); (b) MIL-68(In)\_NH2; (c) MIL-68(In)\_Br; (d) MIL-68(In)\_NO2 (●, s(N–H) ; ●, as(N–H); ●, (C–N); \*, s(C–Br); ♦, (N–O); ♦, (C–N)).

### Stability Analysis of MIL-68(In)\_X

TGA and PXRD were performed to investigate the stability of MIL-68(In)\_X.

The TG curves of the as-synthesized MIL-68(In)\_X samples show three similar weight losses as the as-synthesized MIL-68(In) sample (Figure S4). The first two weight losses from room temperature to 200 °C indicated the existence of the trapped trapped water and occluded DMF molecules. The framework remains stable till around 400 °C, then collapses and transforms into In2O3. The TGA was also performed on the activated samples. The first two weight losses corresponding to the trapped solvent molecules in the crude samples are vanished in all the TG curves. This obvious difference indicates the efficient removal of all the guest molecules in the pores of the as-synthesized samples.

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**Figure S4** The TGA curves of (a) MIL-68(In); (b) MIL-68(In)\_NH2; (c) MIL-68(In)\_Br; (d) MIL-68(In)\_NO2 (as-synthsized samples, black; activatedsamples, red).

Simultaneously, seen from PXRD patterns of the as-synthsized samples, activated samples and the samples after N2 adsorption measurement, the good agreement indicates the perfect sustainment of the whole framework afterwards activation process and gas adsorption measurement (Figure S5).

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**Figure S5** The PXRD patterns for (a) MIL-68(In); (b) MIL-68(In)\_NH2; (c) MIL-68(In)\_Br; (d) MIL-68(In)\_NO2 (as-synthsized samples, black; activated samples, red; samples after N2 adsorption, blue).

### 1HNMR Spectroscopy Analysis of MIL-68(In)\_X

The 1H NMR spectra of pure ligands accompanied with corresponding as-synthesized and activated samples of MIL-68(In)\_X are depicted in Figure S6. All of the spectra display three distinct sets of signals assignable to the phenyl protons of each ligand (1HNMR (400 MHz, DCl/D2O/DMSO-d6) H2BDC-NH2: **7.87 (d, 1H, 3J= 8.31 Hz); 7.66 (s, 1H); 7.36 (d, 1H, 3J= 8.31 Hz); H2BDC-Br: **7.79 (d, 1H, 3J= 8.06 Hz), 7.95 (d, 1H, 3J= 8.06 Hz), 8.11 (s, 1H); H2BDC-NO2: **8.36 (s, 1H), 8.26 (d, 1H, 3J= 7.81 Hz), 7.92 (d, 1H, 3J= 7.81 Hz)). Three additional signals corresponding to DMF molecules are clearly evidenced on the as-synthesized MIL-68(In)\_X spectra. The disappearance of DMF signals in the 1H NMR spectrum of the activated MIL-68(In)\_X samples confirms the effectiveness of the activation method to remove trapped DMF molecules.

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**Figure S6** 1H NMR spectra of (a) (i) H2BDC-NH2 ligand; (ii) as-synthesized; (iii) activated MIL-68(In)\_NH2; (b) (i) H2BDC-Br ligand; (ii) as-synthesized; (iii) activatedMIL-68(In)\_Br; (c) (i) H2BDC-NO2 ligand; (ii) as-synthesized; (iii) activated MIL-68(In)\_NO2 (\* marks denote the signals belonging to DMF).

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**Figure S7** At 77 K, the N2 sorption isotherms of (a) MIL-68(In); (b) MIL-68(In)\_NH2; (c) MIL-68(In)\_Br; (d) MIL-68(In)\_NO2 (adsorption, solid; desorption, empty). The insets are the pore size distributions.

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**Figure S8** SEM photographs and the histograms of the size distribution of the samples: (a) MIL-68(In)\_NH2; (b) MIL-68(In)\_Br; (c) MIL-68(In)\_NO2.