Electronic Supplementary Material (ESI) for CrystEngComm

Cu-Mediated Solid-State Reaction into Post-Functionalized Metal-Organic Framework

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1. General considerations

Chemicals

All chemicals were used as received without any further purification: N,N'-dimethylformamide, DMF, C_3H_7NO (Aldrich, 99.8%); dichloromethane, CH_2Cl_2 (Acros Organics, 99.99%); tetrahydrofuran, THF, C_4H_8O (Aldrich, 99%); acetonitrile, ACN, C_2H_3N (Aldrich, 99.9%), amino-terephthalic acid, bdc, $C_8H_5O_4$ (Aldrich, 98%); 2-aminoterephthalic acid, NH_2-bdc, $C_8H_7NO_4$ (Alfa Aesar, 99%); dimethylaminoterephthalate, $C_{10}H_{11}O_4$ (Aldrich, 97%); indium nitrate, $In(NO_3).4H_2O$ (Alfa Aesar, 99.99%); tert-butyl nitrite, tBuONO, $C_4H_9NO_2$ (Aldrich, 90%); trimethylsilyl azide, $TMSN_3$, $C_3H_9N_3Si$ (Aldrich, 99.5%); tetrakis(acetonitrile)copper(I) hexafluorophosphate, $Cu^I(CH_3CN)_4PF_6$ (Aldrich, n.c); propargylamine, C_3H_5N (Aldrich, 98%); propylamine, $C3H_7N$, (Aldrich, 98%), deuterium chloride, DCl (Aldrich, 99% D); deuterated dimethyl sulfoxide, DMSO-d_6, C_2D_6OS (Eurisotop, 99.8% D)

^{1}H NMR Analysis

NMR spectra were recorded on a Bruker Avance 250 spectrometer operating at 250 MHz for ^{1}H. The following abbreviations are used: s, singlet; d, doublet; t, triplet; and m, multiplet. **(1)** and **(2)** derivate samples were digested and dissolved in 0.45 mL of DMSO-d_6 and 0.05 mL of dilute DCl (35% DCl in D_2O).

PXRD Analysis

Powder X-ray diffraction patterns were recorded using a Bruker D8 ADVANCE diffractometer (Bragg–Brentano geometry, Cu Kα radiation, 50 kV, 35 mA, λ= 0.154184 nm).

Gas Sorption Analysis

N_2 isotherms were carried out at 77 K using an ASAP 2010 (Micromeritics) analyzer. **(1)** and **(2)** derivate samples were degassed for one night at 150°C under vacuum.

Infrared Spectroscopy. IR spectra were recorded on a Fourier Transform Vector 22 Bruker spectrometer in KBr pellets in the 400-4000 cm^{-1} region.

1. Post-synthetic modifications of (In) MIL-68-NH_2 (1)

(In) MIL-68-NH_2 (**1**) was prepared following the protocol presented in a recent patent.[1] It was obtained by precipitation in a 100 mL Pyrex® beaker. 0.325 g (1.08 mmol) of indium nitrate and 0.227 g (1.25 mmol) of 2-aminoterephthalic acid were dissolved in 20 ml of DMF. The reaction mixture was stirred for 5 min, then 1 mL (1.38 mmol) of 1.38 M DABCO solution (0.192 g DABCO in 1 mL DMF) was dropwise added. The reaction mixture was stirred for 20 h at room temperature. The precipitate obtained was washed with DMF at 160°C, then soaked in CH_2Cl_2 for 24 h.
^{1}H NMR 250 MHz, (DCl/D_2O/DMSO-d_6) δ: 7.52 (d, 1H, J = 8.2Hz), 7.78 (s, 1H), 7.92 (d, 1H, J = 8.2Hz). BET surface area: 1120 ± 17 $m^2.g^{-1}$.

(In) MIL-68-N_3 (2). In a typical synthesis, the freshly dried MIL-68-In-100-NH2 (1 g, 3.22 mmol equiv of -NH_2) was placed into a round-bottom flask (100 mL capacity) with 30 mL of solvent (THF) and 21 mL (177 mmol, 55 eq) of tBuONO and 18 mL (137 mmol, 42 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 CH2Cl2. Drying at room temperature yielded a yellow powder of (In) MIL-68-N_3.
^{1}H NMR 250 MHz, (DCl/D2O/DMSO-d6) δ: 7.73-7.83 (m, 3H) ppm.
BET surface area: 801 ± 11 $m^2.g^{-1}$

Functional MOF 3a. To a suspension of 80 mg of (In) MIL-68-N_3 (**2**), propargylamine (1.13 mL, 17.6 mmol, 74 eq) and $Cu(CH_3CN)_4PF_6$ (96 mg, 0.52 mmol, 2.2 eq) in 1.5 mL of THF were added and the mixture was stirred continuously for 24 h. After decantation, the supernatant was removed. The solid was washed three times by THF (x 8 ml) and three times by CH_2Cl_2 (x 8 ml) in order to remove unreactive substrates. Drying under vacuum at room temperature yielded 60 mg of a yellow powder of functionalized MIL-68 **3a**.
^{1}H NMR 250 MHz, (DCl/D2O/DMSO-d6) δ: 8.62 (s, 1H), 8.12 (d, 1H, J= 6.5Hz), 8.05 (s, 1H), 8.06 (d, 1H, J= 8Hz), 4.08 (s, 2H) ppm.
BET surface area: 548 ± 5 $m^2.g^{-1}$

Functional MOF 4a. To a suspension of 80 mg of (In) MIL-68-N_3 (**2**), phenylacetylene (1.92 mL, 17.6 mmol, 74 eq) and $Cu(CH_3CN)_4PF_6$ (96 mg, 0.52 mmol, 2.2 eq) in 1.5 mL of THF were added and the mixture was stirred continuously for 24 h. After decantation, the supernatant was removed. The solid was washed three times by THF (x 8 ml) and three times by CH_2Cl_2 (x 8 ml) in order to remove unreactive substrates. Drying under vacuum at room temperature yielded 60 mg of a yellow powder of functionalized MIL-68 **4a**.
^{1}H NMR 250 MHz, (DCl/D2O/DMSO-d6) δ: 9.13 (s, 1H), 8.20 (d, 1H, J= 6.5Hz), 8.14 (s, 1H), 8.04 (d, 1H, J= 8Hz), 7.92 (d, 2H, J= 6Hz), 7.42 (m, 3H) ppm.
IR data (KBr pellet), υ (cm-1): 3422(br), 3049 (w), 2980 (w), 2120 (w), 1570 (s), 1482 (m), 1405 (s), 1298 (m), 1143 (m), 1042 (m), 898 (w), 836 (w), 745 (m), 683 (m), 566 (w), 512 (w).
BET surface area: 471 ± 12 $m^2.g^{-1}$

Derivatives **3b** and **4b** are obtained by heating **3a** and **4a** respectively at 100°c under primary vacuum overnight.

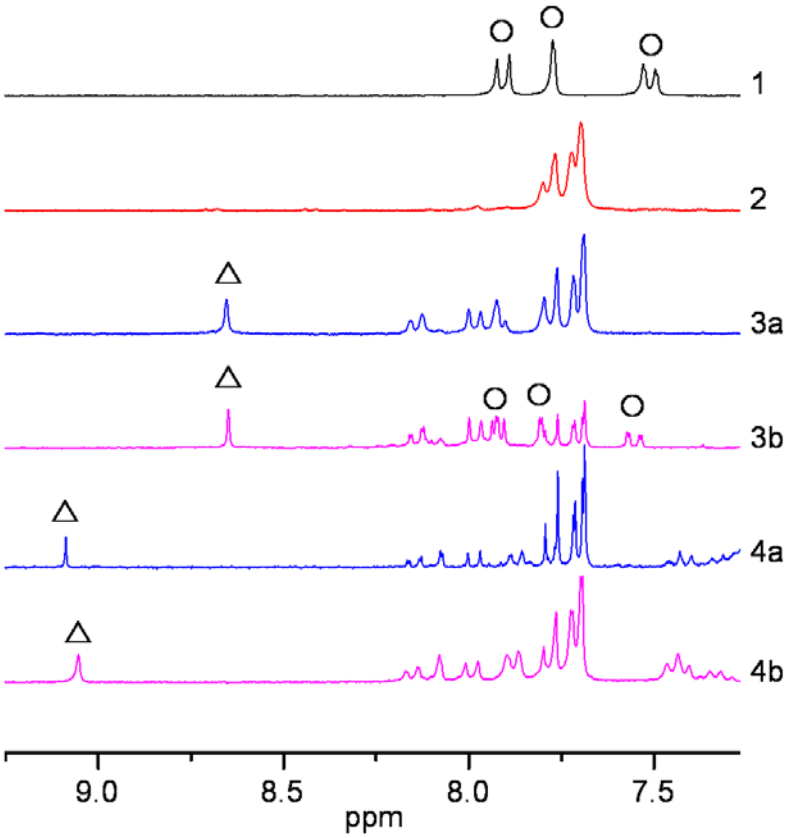
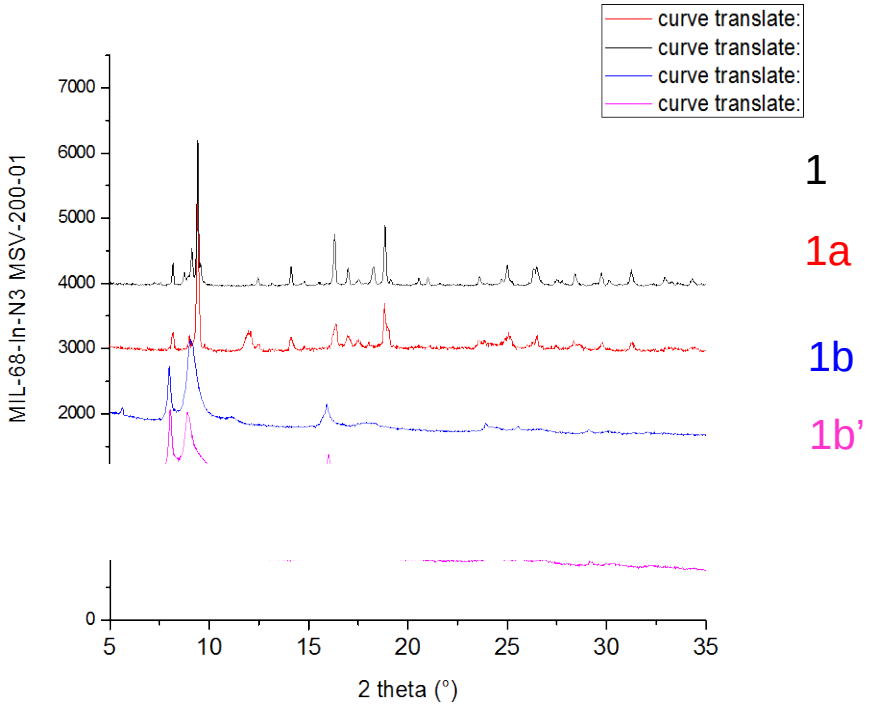


Figure S1. ^{1}H NMR of digested 1 to 4b.



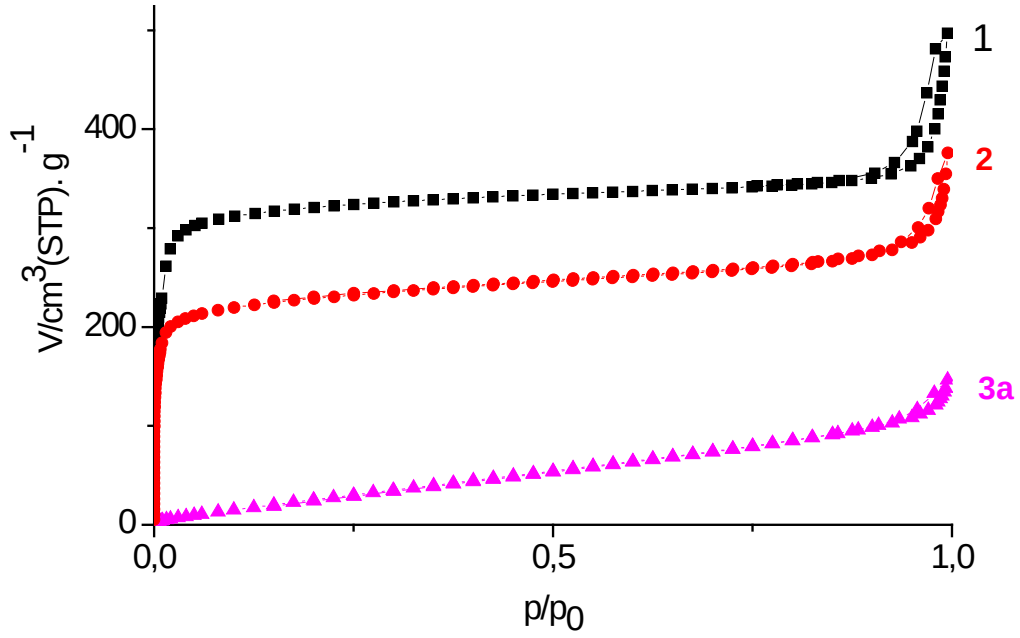


Figure S3. N_2 adsorption isotherms of 1 (■), 2 (●) and 3a (▲)

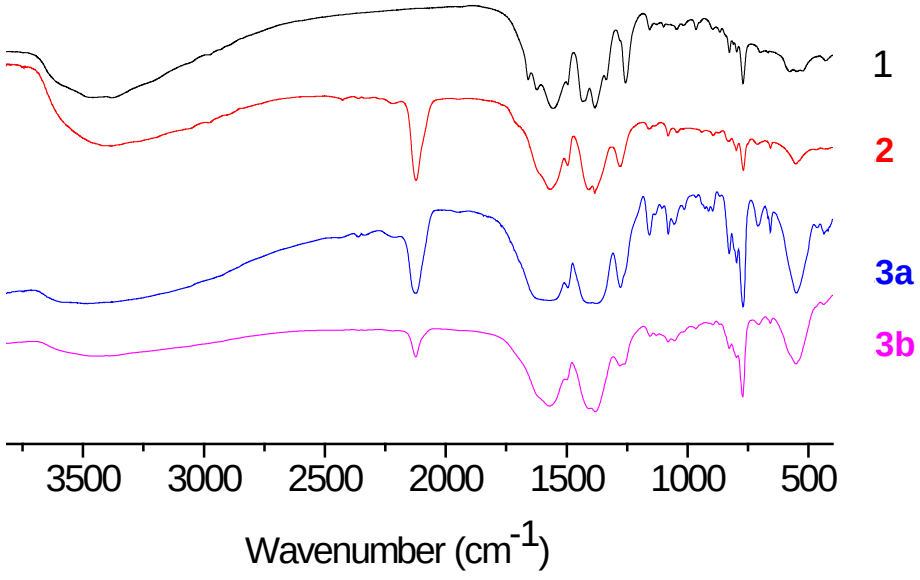


Figure S4. IR spectra of 1, 2, 3a and 3b

3. CW-EPR and HYSCORE experiments

X-band EPR spectra were recorded on a Bruker ESP-300 EPR spectrometer operating with a rectangular cavity and an Oxford Instruments ESR-9 flow cryostat. Spectra were recorded at room temperature with a microwave power of 1 mW and microwave frequency of 9.65 GHz

HYSCORE experiments were performed on a Bruker E-580 X band (frequency = 9.71 GHz) pulsed spectrometer with a Bruker ER4118X dielectric resonator and a continuous flow He cryostat (Oxford Instrument CF935) controlled by an Oxford Instrument temperature controller ITC 503. Experiments were performed at 10 K using the standard four-pulse sequence (p/2-t-p/2-t1-p-t2-p/2-echo) with a nominal pulse width of 16 ns for p/2 and p pulses, a t value of 132 ns and a pulse repetition rate of 2 kHz. Unwanted echoes were removed by four-step phase cycling. A 128*128 dataset was recorded with times t_1 and t_2 incremented in 24 ns steps from an initial value of 200 ns. The background decay in both dimensions was subtracted using a linear fit followed by apodization with a Hamming window and zero-filling to 2048 points in each dimension. The 2D Fourier Transform magnitude spectrum was then calculated. Spectra were acquired at a magnetic field of 3460 G, corresponding to the $g_\perp$ feature in CW EPR spectra.

Magnetization experiments were performed on a Quantum Design MPMS XL5.0 SQUID. A home made suprasil silica glass was used . its main feature consists in a small silica glass container which can be conveniently heated under vacuum. Compound **3a** was placed in this device and its magnetic properties were recorded. The silica glass container with **3a** were then heated at 100 °C under vacuum for 12 hours and new magnetic measurements were performed. Magnetic measurements were analysed with standard procedures (diamagnetic contribution determination and subtraction, fit with Brilloin function) to determine the total amount of S=1/2 electronic spins present in the sample.

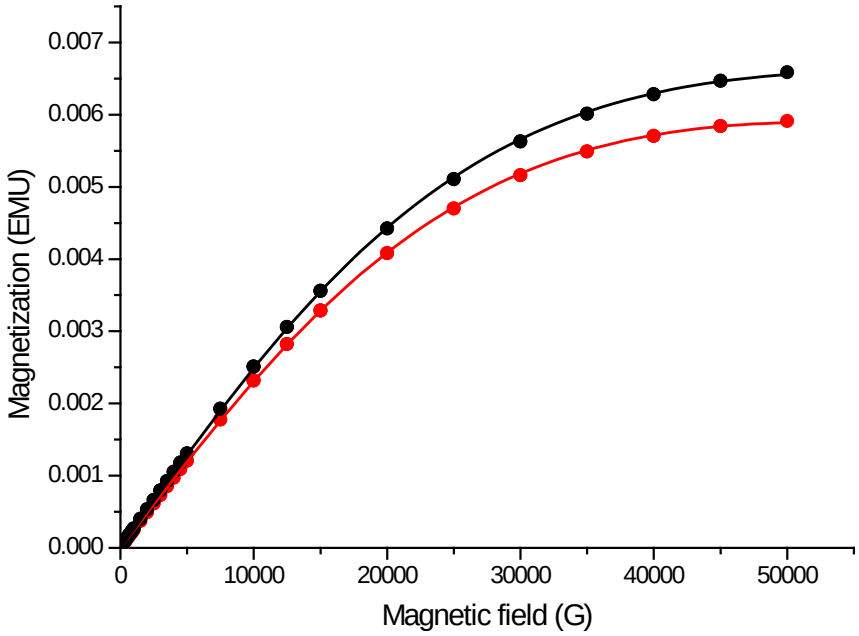


Figure S5. Brilloin curves at 1.8 K of 13.6 mg of **3a** before heating (red) and after heating (black). Solid circles represent experimental points and solid line the best fit with an S=1/2 brilloin function. The increase of magnetization correspond to oxidation of Cu(I) to Cu(II) (see text).

3. Homogeneous azide reduction

*Synthesis of dimethylazidoterephthalate (**B**) as reduction susbtrate:*
Dimethyl-2-aminoterephthalate **A** (1g, 4.78 mmol) was dissolved in THF (20 mL) in a 50 mL round-bottomed flask and cooled to 0°C in an ice bath. To this stirred mixture was added tBuONO (0.81 mL, 6.85 mmol, 1.4 eq), followed by a dropwise addition of $TMSN_3$ (0.72 mL, 5.49 mmol, 1.1 eq). The resulting solution was stirred at room temperature for one night. The mixture was concentrated under vacuum to give pur dimethylazidoterephthalate (**B**).
^{1}H NMR 250 MHz, (DMSO-d_6) δ: 3.86 (d, 6H, J = 12.2 Hz), 7.8-7.9 (m, 3H)

For a typical run under homogeneous conditions, dimethylazidoterephthalate (**B**) (20 mg, 0.09mmol) was dissolved in 3 mL of THF in a 10 mL vial. Propylamine (0.04 mL, 0.4 mmol, 4.5 eq) and an amount of $Cu^I(CH_3CN)_4PF_6$ (20 mg, 0.11 mmol, 0.5 eq) were added and the mixture was stirred continuously for 12 h at 37°C. The mixture was concentrated under vacuum to give **C**, which correspond to the dimethyl-2-aminoterephthalate **A**.
^{1}H NMR 250 MHz, (DMSO-d_6) δ: 3.8 (d, 6H, J = 5.5 Hz), 6.8 (s, 2H, -NH_2), 7 (dd, 1H, J = 1.5 Hz, J = 8.4 Hz), 7.4 (s, 1H), 7.8 (dd, 1H, J = 1.5 Hz, J = 8.4 Hz)

B (20 mg, 0.09mmol) was dissolved in 3 mL of THF in a 10 mL vial. An amount of $Cu^I(CH_3CN)_4PF_6$ (20 mg, 0.11 mmol, 0.5 eq) was added and the mixture was stirred continuously for 12 h at 37°C. The mixture was concentrated under vacuum to give **D.**

B (20 mg, 0.09mmol) was dissolved in 3 mL of THF in a 10 mL vial. Propylamine (0.04 mL, 0.4 mmol, 4.5 eq) was added and the mixture was stirred continuously for 12 h at 37°C. The mixture was concentrated under vacuum to give **E.**

Both **D** and **E** correspond to the azido derivative **B**.

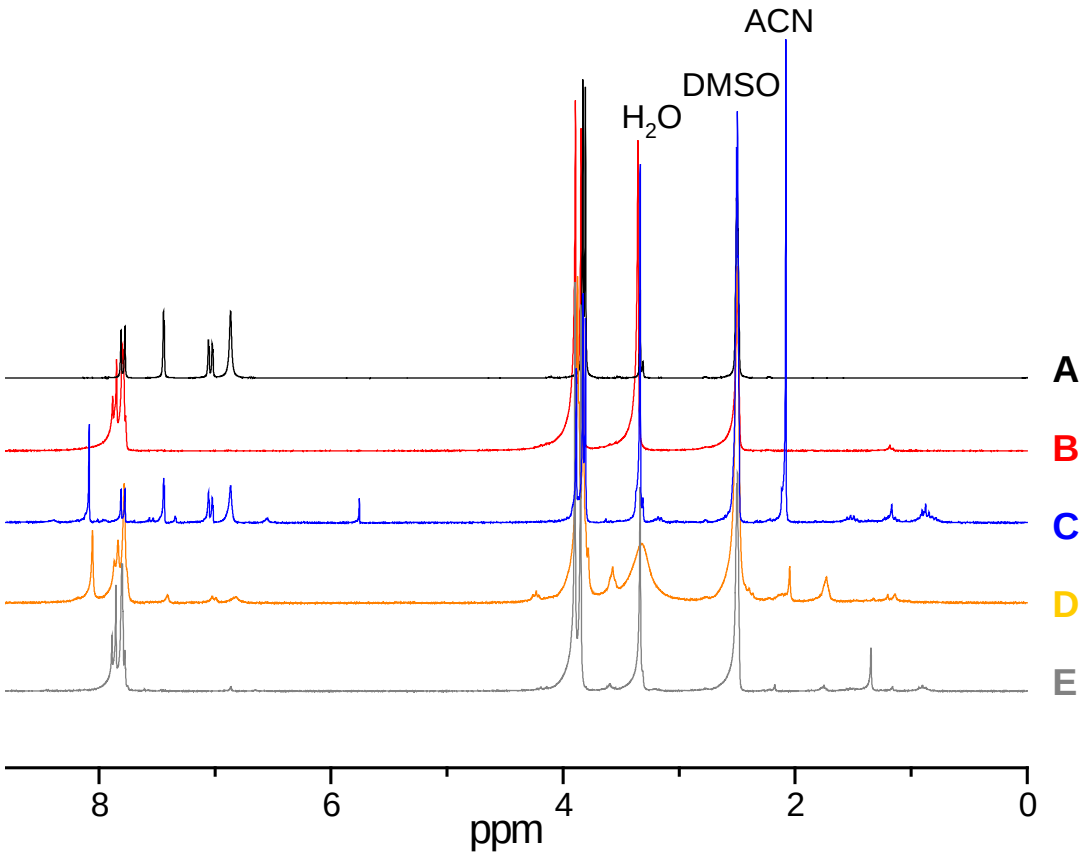


Figure 7: ^{1}H NMR of compounds A to E under acidic conditions.

References

[1] M. Savonnet, D. Bazer-Bachi, C. Pinel, V. Lecocq, N. Bats, D. Farrusseng, FR Patent 09/05.102, **2009**.