Supporting Information

MaLISA – A Cooperative Method to Release Adsorbed Gases from Metal-Organic Frameworks

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Experimental

Synthesis of mPCNs: All reagents and solvents were commercially obtained from Sigma-Aldrich and used as received. Fe_3O_4 NPs with 28.5 nm in average diameter and $Fe_2Co(\mu_3\text{-}O)(CH_3COO)_6$ clusters were pre-synthesized according to the method described previously.[S1] PCN-250 was synthesized through a previously established solvothermal approach.[S2]

mPCNs were prepared by incorporating Fe_3O_4 NPs in PCN-250 by means of a one-pot solvothermal strategy. In a typical process, 50 mg of 3,3',5,5'-azobenzene tetracarboxylic acid (ABTC) ligand, 75 mg of $Fe_2Co(\mu_3\text{-}O)(CH_3COO)_6$ metal clusters, and a certain amount of Fe_3O_4 NPs were dissolved in a Pyrex vial containing 10 mL of dimethylformamide (DMF) and 5 mL of acetic acid. The resulting solution was then heated up at 140 °C for 12 h. After cooling down to room temperature, mPCN crystals were collected with a magnet and was subjected to a thorough rinse with dry DMF and then immersed in DMF for more than two days to remove un-reacted starting ligands, inorganic species and acetic acid. Thereafter, DMF was decanted and washed with dry methanol for several times and immersed in methanol at 65 °C. This cycle was repeated at least three times over two days to completely substitute the coordinating molecules. After that, methanol was decanted and sample was thoroughly washed with dry CH_2Cl_2 and then soaked in CH_2Cl_2 at 60 °C for 3 days for solvent exchange. Followed by the removal of CH_2Cl_2 solvent on a vacuum line, the sample was transported into a glove box to prevent the re-adsorption of moisture from the air. Following the same procedures, the use of various amount of Fe_3O_4 NPs resulted in a series of mPCNs with tunable content of Fe_3O_4 NPs.

Characterisation: The microstructures and elemental compositions of samples were analysed using a Zeiss Merlin FESEM equipped with an energy-dispersive X-ray spectrometer (EDX) unit. Dry samples were mounted on a silicon substrate followed by an Iridium coating. Transmission electron microscope (TEM) observation on MOF crystals was carried out on a

TEM (JEOL2010) equipped with an EDX unit. The MNP contents of mPCNs were measured on an Agilent 730 ICP-OES spectrometer after being wet-ashed in a mixture of hydrogen peroxide, sulphuric and nitric acids. Powder X-ray diffraction of MOFs was measured at Bruker D8 Advanced X-ray Diffractometer operating under CuKα radiation (40 kV, 40 mA) equipped with a LynxEyedetector. The diffraction pattern was collected in the 2θ range of 3.5-80° with a step size of 0.02° and a count time of 3.2 s $step^{-1}$. FTIR spectra of samples were recorded on a Thermo scientific Nicolet 6700 in powder form using the attenuated total reflectance method. The solid samples used were activated accordingly prior to measurements.

Magnetic measurements: Magnetic measurements were performed using a vibrating sample magnetometer by Quantum Design (Physical Property Measurement System with VSM option) at room temperature. The powdered samples were filled into gelatine capsules and sealed with two-component adhesive. The sealed capsules were fixed in a small plastic tube and mounted onto the instruments sample holder. Magnetic heating experiments were carried out on an EasyHeat frequency generator equipped with eight-turn coil (Ambrell, 350 kHz). An OpSens fiber optic sensor was used to online record temperature with resolution of 0.1 °C.

Low-pressure gas adsorption measurements: For gas adsorption isotherms, high-purity grade (99.999%) helium, nitrogen, and CO_2 were used throughout the adsorption experiments. Prior to the gas adsorption/desorption measurement, mPCNs were activated by using the 'outgas' function of the adsorption instrument at 190 ºC for 12 h. Low pressure volumetric nitrogen adsorption isotherms up to 1 Bar were measured using a micromeritics ASAP 2420 gas sorption analyzer. BET surface areas and pore size were determined by measuring N_2 adsorption isotherms at 77 K in a liquid nitrogen bath and calculated using the Micromeritics software. All volumetric CO_2 adsorption in our current work was collected in low pressure range and at 298 K using Micromeritics Tristar II instrument. Dynamic CO_2 adsorption profiles were obtained by intermittently exposing samples to 365 nm of UV-light or/and an alternating magnetic field during the CO_2 adsorption experiments at 298 K. 365 nm of UV light was produced with a UV/Vis spot cure system (Acticure 4000 containing a high pressure 100 W mercury vapour short arc lamp) equipped with a 365 nm light filter. The output light intensity was calibrated with an OmniCure R2000 radiometer. The alternating magnetic field was generated by an EasyHeat frequency generator equipped with eight-turn coil (Ambrell, 350 kHz).

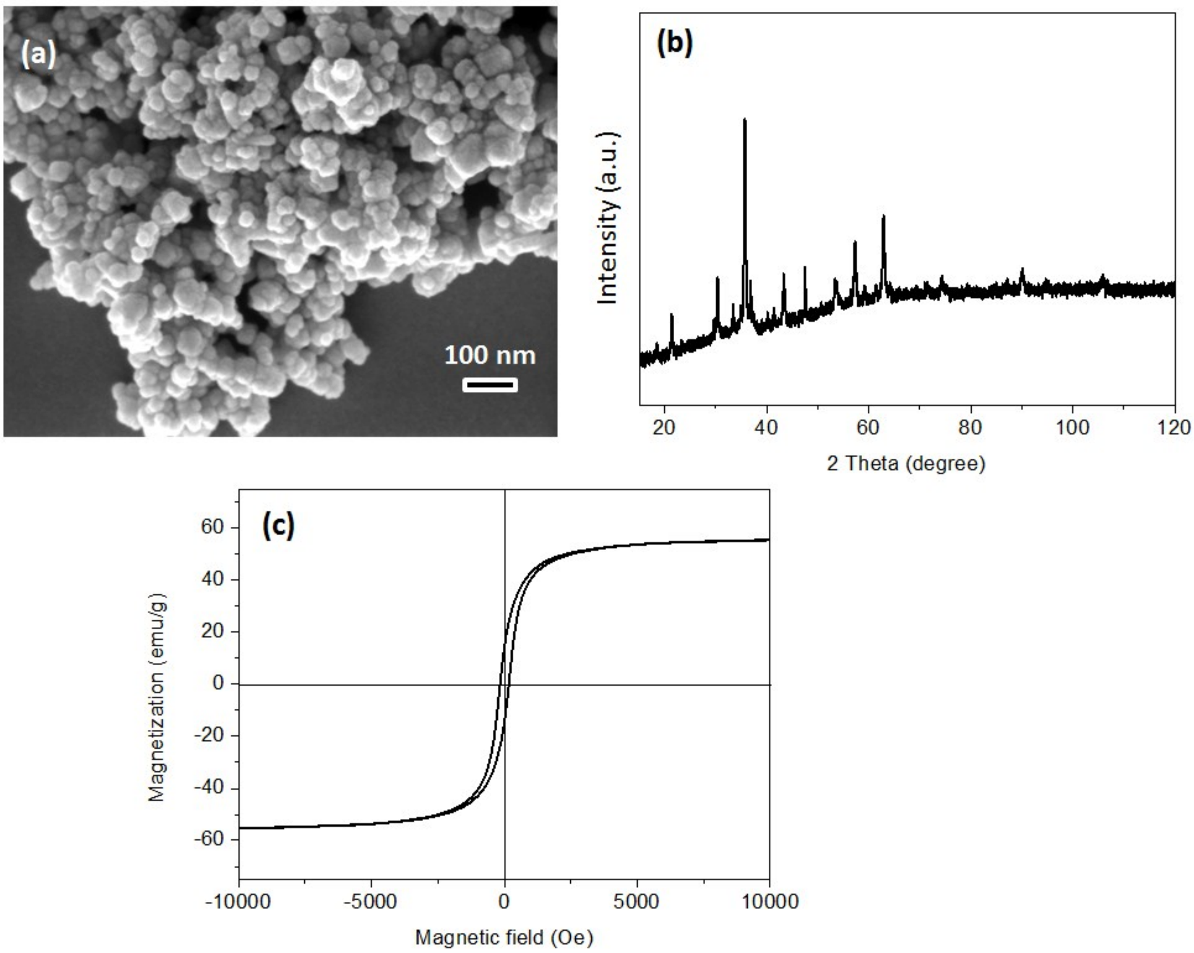

Figure S1. SEM image (a), powder X-ray diffraction pattern (b), and magnetic hysteresis loop of HP-passivated Fe_3O_4 nanoparticles.

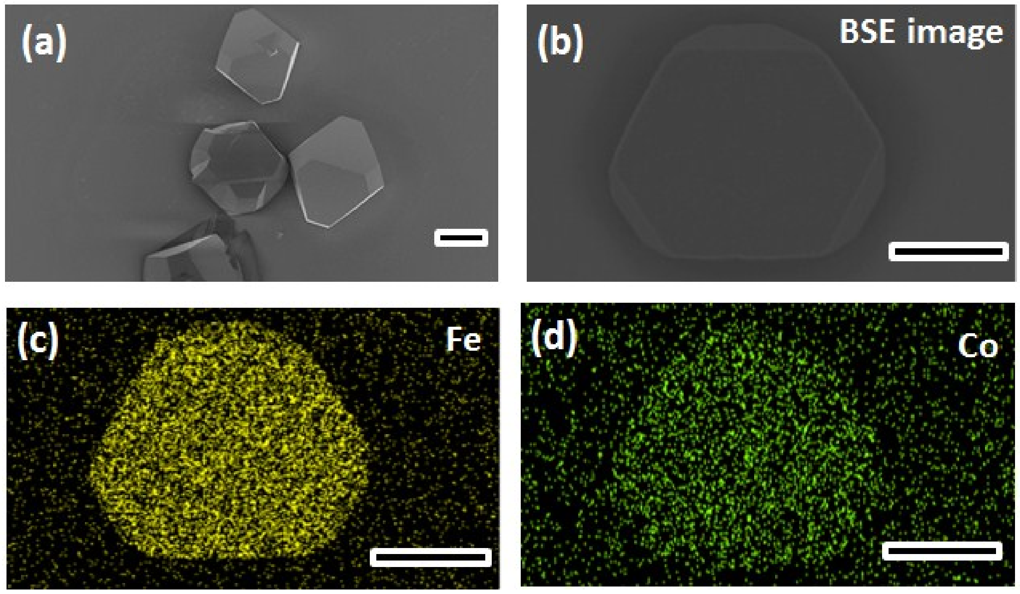

Figure S2. SEM images of bare PCN-250 crystals (a); BSE image (b), Fe (b) and Co (c) elemental mapping of a selective PCN-250 crystal. The scale bars are 100 µm.

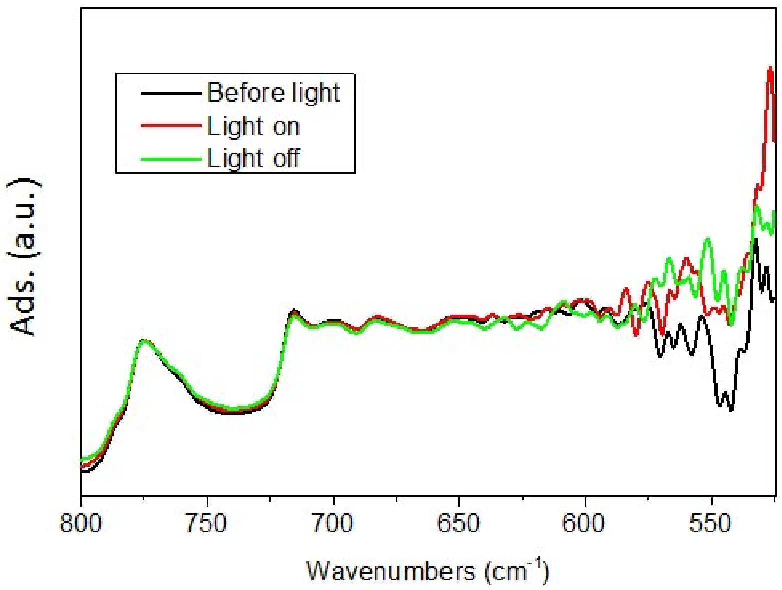

Figure S3. Time resolved FT-IR spectra of mPCN-M before and after irradiation with 365 nm of UV light.

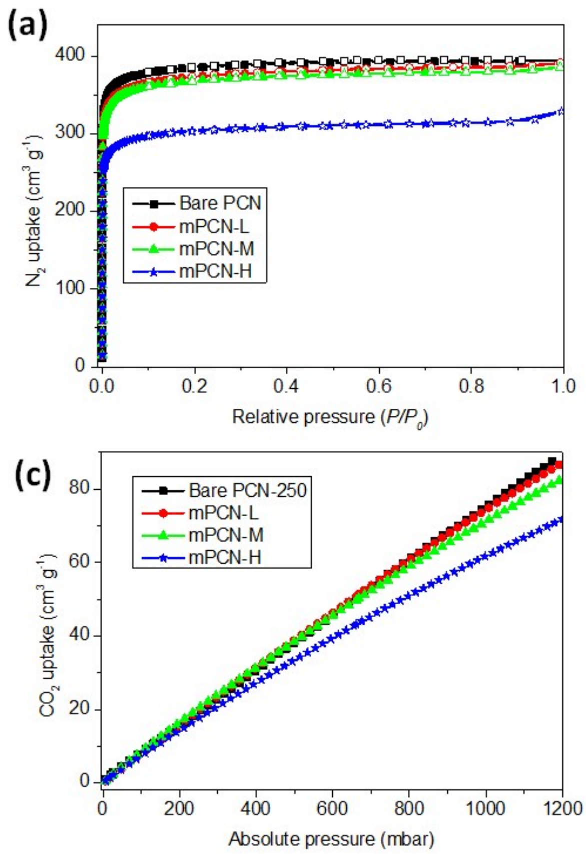

Figure S4. N_2 adsorption isotherms at 77.3 K (a), pore size distributions (b), and CO_2 adsorption isotherms at 298 K of bare PCN-250 and mPCNs with different magnetic nanoparticle content (c).

Regeneration Energy ($Q_{thermal}$) calculations.

$Q_{thermal}$ is an important parameter that estimates the thermal energy requirement per unit mass of CO_2 captured in a typical post combustion capture and storage (CCS) process. $Q_{thermal}$ is the sum of the energy required to heat the adsorbent to the desorption temperature and the energy required to undo the adsorption.[S3,S4] For a process that involves the removal of CO_2 from a two component gas stream (CO_2 and N_2), the adsorption condition is fixed while the desorption conditions are varied to allow the calculation of CO_2 and N_2 loading differential between the adsorption and desorption conditions.[S5] The amount of CO_2 captured can then be estimated. The regeneration energy ($Q_{thermal}$) per kilogram of CO_2 captured can be expressed mathematically as:

$$Q_{thermal} = \frac{C_p m_{sorbent} \Delta T + (\Delta h_{CO_2} \Delta\sigma_{CO_2} + \Delta h_{N_2} \Delta\sigma_{N_2})}{m_{CO_2}}$$

Where,

C_p = specific heat capacity of adsorbent (jg^{-1}K^{-1})

$m_{sorbent}$ = mass of adsorbent (g)

ΔT = Temperature difference between adsorption and desorption conditions (K)

Δh = heat of adsorption (kJmol^{-1})

$\Delta\sigma$ = working capacity (mol)

m_{CO2} = mass of captured CO_2

For the purpose of this work, regeneration energy calculations were estimated from single component dynamic CO_2 adsorption isotherms at 393 K with desorption conditions corresponding to the maximum temperature rise of the mPCN-M at 17.6 mT of magnetic field strength. Hence the regeneration energy was computed by equating the N_2 component of equation 1 to zero.

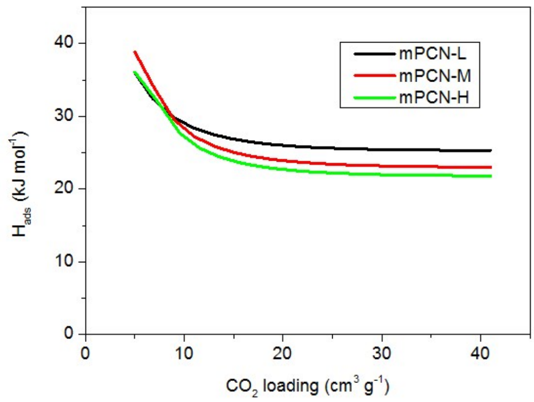

Figure S5: Isosteric heat of adsorption as a function of CO_2 uptake of mPCN.

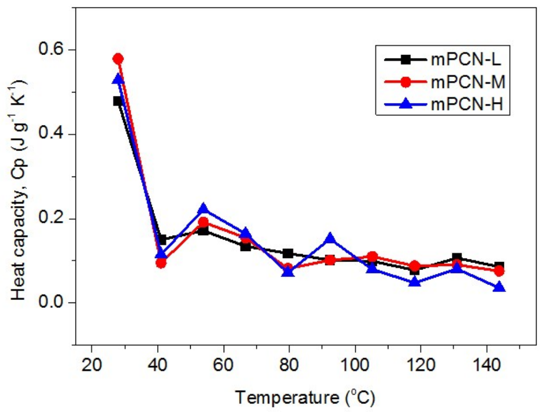

Figure S6: Heat capacity of mPCN-M as a function of temperature measured under He.

References:

[S1] H. Li, M. M. Sadiq, K. Suzuki, R. Ricco, C. Doblin, A. J. Hill, S. Lim, P. Falcaro and M. R. Hill, Adv. Mater., 2016, 28, 1839.

[S2] H. Li, M. R. Martinez, Z. Perry, H.-C. Zhou, P. Falcaro, C. Doblin, S. Lim, A. Hill, B. Halstead and M. R. Hill, Chem. Eur. J., 2016, 22, 11176

[S3] G. E. Cmarik, M. Kim, S. M. Cohen, K. S. Walton, *Langmuir* **2012**, *28*, 15606.

[S4] L.-C. Lin, A. H. Berger, R. L. Martin, J. Kim, J. A. Swisher, K. Jariwala, C. H. Rycroft, A. S. Bhown, M. W. Deem, M. Haranczyk, B. Smit, *Nat. Mater.* **2012**, *11*, 633.

[S5] J. M. Huck, L.-C. Lin, A. H. Berger, M. N. Shahrak, R. L. Martin, A. S. Bhown, M. Haranczyk, K. Reuter, B. Smit, *Energy Environ. Sci.* **2014**, *7*, 4132.