

## Supporting Information

### **Magnetic metal-organic framework composites: solvent-free synthesis and regeneration driven by localized magnetic induction heat**

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The supporting information has 11 pages in total and contains 8 Figures.

## Experimental

**Materials:** The following reagents were commercially obtained from Sigma-Aldrich and used as received: sodium acetate trihydrate (99%), iron(III) nitrate nonahydrate (99%), 2,5-Dihydroxyterephthalic acid (H<sub>4</sub>DOT, 98%), magnesium nitrate hexahydrate [Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], 1,3,5-benzenetricarboxylate (H<sub>3</sub>BTC, 98%), Copper (II) nitrate trihydrate [Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], Zirconium tetrachloride (ZrCl<sub>4</sub>, >99.5%) 1,4-benzenedicarboxylic acid (BDC, 98%), benzoic acid (98%), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%), 2-methylimidazole (2-mIm, 97%). 3,3',5,5'-azobenzene tetracarboxylic acid was obtained from (J&K, 97%) . All the solvents were HPLC grade and used as received.

**Synthesis of MFCs through sMIFS:** Citrate-passivated Fe<sub>3</sub>O<sub>4</sub> NPs with 21.5nm in average diameter were pre-synthesized according to the method described previously.<sup>[S1]</sup>

PCN-250 was synthesized through a previously established solvothermal approach.<sup>[S2]</sup> In a typical process to synthesize magnetic PCN-250 (mPCN-250) through a sMIFS, Fe<sub>2</sub>Co(μ<sub>3</sub>-O)(CH<sub>3</sub>COO)<sub>6</sub> metal clusters was firstly prepared according to reported procedures:<sup>[S3]</sup> a solution of sodium acetate trihydrate (42 g, 0.31 mol) in water (70 ml) was added to a filtered solution of iron(III) nitrate nonahydrate (8 g, 0.02 mol) and the cobalt(II) nitrate (0.1 mol) in 70 ml of water with stirring. After the reaction proceeded for 12 h, the resulting brown precipitate was filtered off, washed with water and with ethanol, and dried in air. To synthesize magnetic PCN-250 (mPCN-250) through a sMIFS, 50 mg of pre-synthesized Fe<sub>3</sub>O<sub>4</sub> MNPs, 250 mg of as-prepared Fe<sub>2</sub>Co(μ<sub>3</sub>-O)(CH<sub>3</sub>COO)<sub>6</sub> metal clusters and 250 mg of 3,3',5,5'-azobenzene tetracarboxylic acid organic linkers were placed in a 10 mL of glass vial and mixed with a Vortex Mixer. The powder reaction mixture was then exposed to a 39 mT of magnetic field generated with an EasyHeat frequency generator equipped with eight-turn coil (Ambrell, 350 kHz). After the reaction proceeded for 1.5 h, the reaction mixture was cooled down to

room temperature and thoroughly washed with dry DMF (5 mL) and then immersed in DMF (10 mL) for two days to remove un-reacted starting materials. Thereafter, solid sample was decanted from DMF and washed with dry methanol (5 mL) for three times and immersed in methanol (10 mL) at 65 °C for 6 h. This cycle was repeated three times to completely substitute the coordinating molecules. After that, the solid sample was decanted from methanol and thoroughly washed with dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and then soaked in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> at 60 °C for 3 days for solvent exchange. Followed by the removal of CH<sub>2</sub>Cl<sub>2</sub> solvent on a vacuum line, the resultant mPCN-250 was collected for the further use. Following the similar procedures, variation of the reaction times (2.0 h and 2.5 h), using amount of MNPs (100 mg and 150 mg), and the applied magnetic field strength (66.1 mT and 92.8 mT) resulted in a series of mPCN-250.

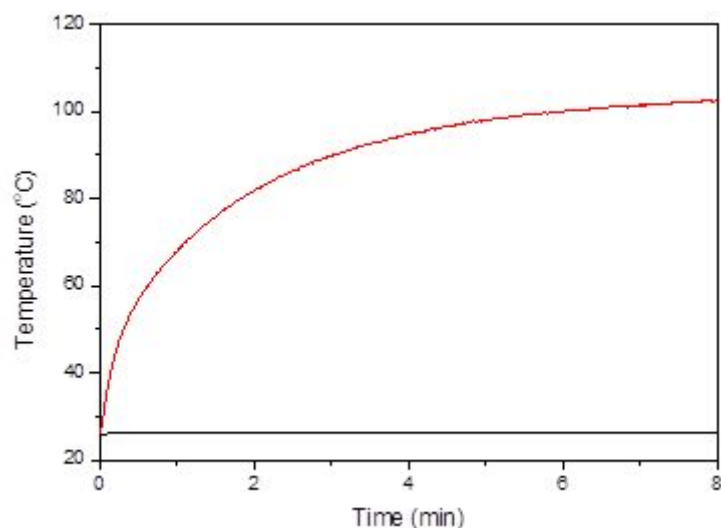
Following the similar synthetic protocol, magnetic Mg-MOF-74, magnetic HKUST-1, magnetic ZIF-8, and magnetic UiO-66 were also synthesized by exposing the corresponding powder reaction mixture consisting of 50 mg of MNPs and 500 mg of MOF precursors (Mg-MOF-74: 0.4 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.1 g of H<sub>4</sub>DOT; HKUST-1: 0.34 g of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.16 g of H<sub>3</sub>BTC; ZIF-8: 0.32 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.18 g of 2-mIm; UiO-66: 0.29 g of ZrCl<sub>4</sub>, 0.21 g of BDC) to a 39 mT of alternating magnetic field for 1.5 h. The corresponding activation procedures of the resulting MFCs were based on the well-established methods described in previous reports. [S4-S7]

**Characterisations:** The microstructures of MFCs were analysed using a Zeiss Merlin FESEM (3 kV). Dry samples were mounted on a silicon substrate followed by an Iridium coating. Powder X-ray diffraction of MOFs was measured at Bruker D8 Advanced X-ray Diffractometer operating under CuK $\alpha$  radiation (40 kV, 40 mA) equipped with a LynxEye detector. The diffraction pattern was collected in the 2 $\theta$  range of 3.5-80° with a step size of 0.02° and a count time of 3.2 s step<sup>-1</sup>.

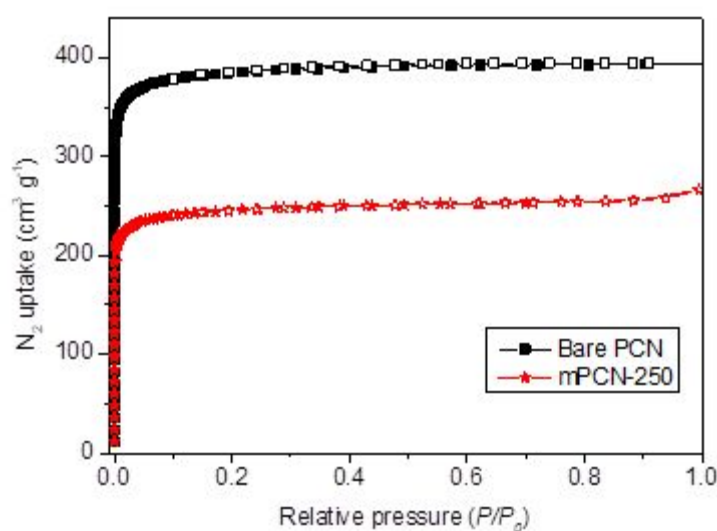
**Magnetic measurements:** Magnetic measurements were performed using a vibrating sample magnetometer by Quantum Design (Physical Property Measurement System with VSM option) at room temperature. The powdered samples were filled into gelatine capsules and sealed with two-component adhesive. The sealed 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 copper coil (Ambrell, 350 kHz). In brief, a glass vial containing 0.1 g of powder MFC was inserted into the copper coil. With switching on the magnetic field, the temperature change of the powder MFCs was monitored with an Opsens Pico M optic fiber temperature sensor.

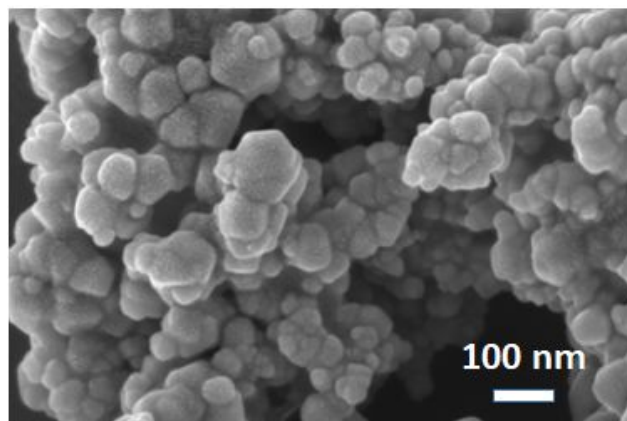
**Low-pressure gas adsorption measurements.** For gas-adsorption isotherms, high-purity grade (99.999%) helium, nitrogen, and CO<sub>2</sub> were used throughout the adsorption experiments. Prior to the BET measurement, magnetic PCN-250, Mg-MOF-74, HKUST-1, ZIF-8, and UiO-66 were activated under vacuum at 120 °C for 12 h, 250 °C for 5 h, 120 °C for 6 h, 100 °C for 8 h, and 120 °C for 12 h, respectively. Low-pressure volumetric nitrogen isotherms up to 1 bar were measured using a Micromeritics ASAP 2420 gas sorption analyzer. BET and Langmuir surface areas and pore size were determined by measuring N<sub>2</sub> adsorption isotherms at 77 K in a liquid-nitrogen bath and calculated using Micromeritics software. Static and dynamic CO<sub>2</sub> adsorption isotherms up to 1 bar were measured using a Micromeritics Tristar II instrument. Static CO<sub>2</sub> adsorption isotherms were collected at 298 K. Dynamic CO<sub>2</sub> adsorption experiments were performed on Micromeritics Tristar II instrument equipped with EasyHeat frequency generator (Ambrell). Dynamic CO<sub>2</sub> adsorption profiles were obtained by intermittently exposing MFCs to a magnetic field during the adsorption experiments at 298 K.



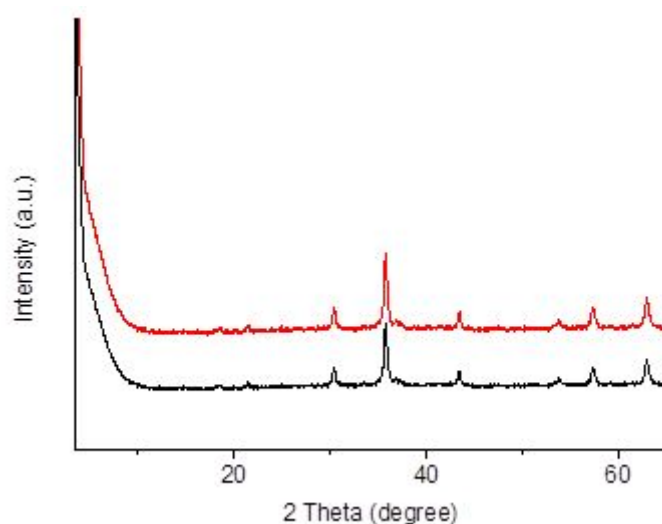
**Figure S1.** Magnetic induction heating profiles of powder reaction mixture consisting of 50 mg of MNPs, 250 mg of  $\text{Fe}_2\text{Co}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6$  metal clusters, and 250 mg of 3,3',5,5'-azobenzene tetracarboxylic acid organic linkers after exposing it to an alternating magnetic field of 39 mT.



**Figure S2.** Nitrogen gas adsorption isotherms of bare PCN-250 synthesized with traditional solvothermal reaction and mPCN-250 synthesized through sMIFS by using 50 mg of MNPs, 250 mg of  $\text{Fe}_2\text{Co}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6$  metal clusters, and 250 mg of 3,3',5,5'-azobenzene tetracarboxylic acid organic linkers upon their exposure to a 39 mT of alternating magnetic field for 1.5 h. The isotherms were recorded at 77 K.

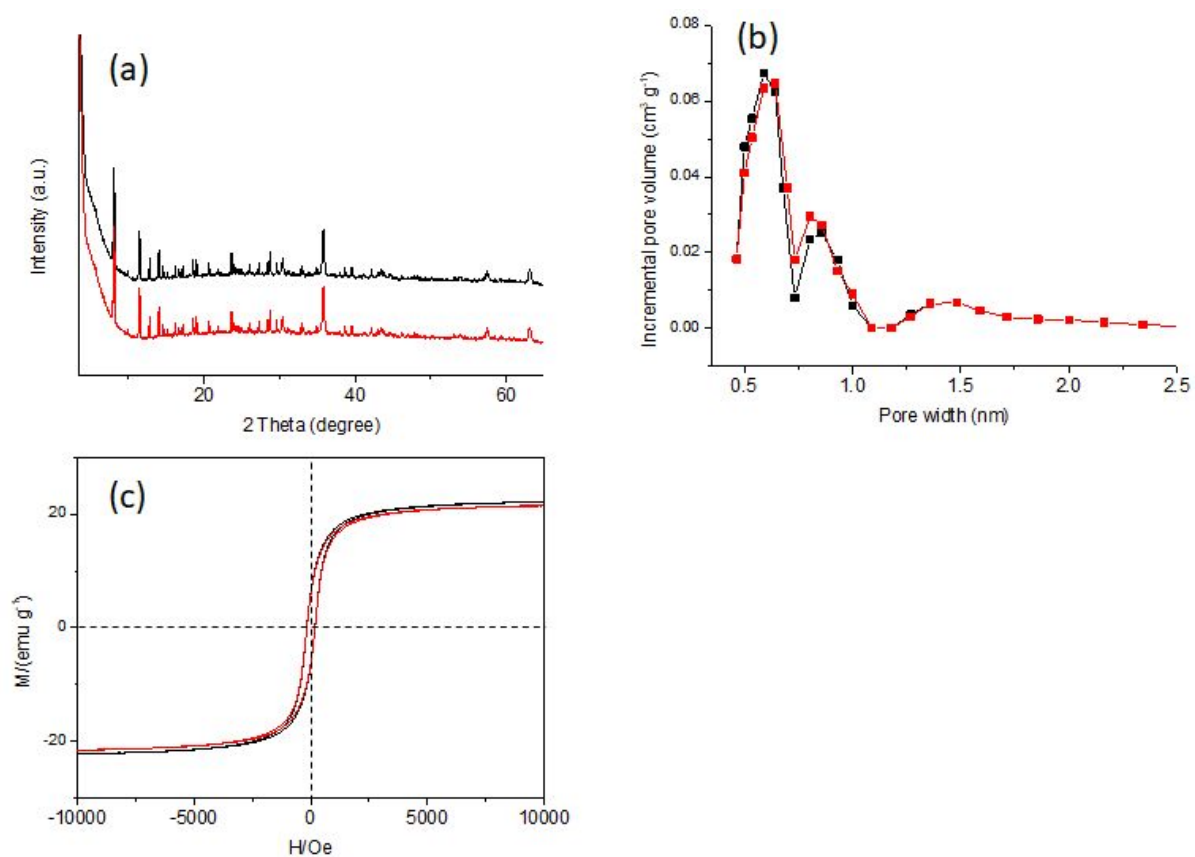


**Figure S3.** SEM image of mPCN-250 prepared by dissolving 50 mg of MNPs, 250 mg of  $\text{Fe}_2\text{Co}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6$  metal clusters, and 250 mg of 3,3',5,5'-azobenzene tetracarboxylic acid organic linkers in 33 mL of DMF solvent, following by an exposure to 93 mT of magnetic field for 1.5 h.

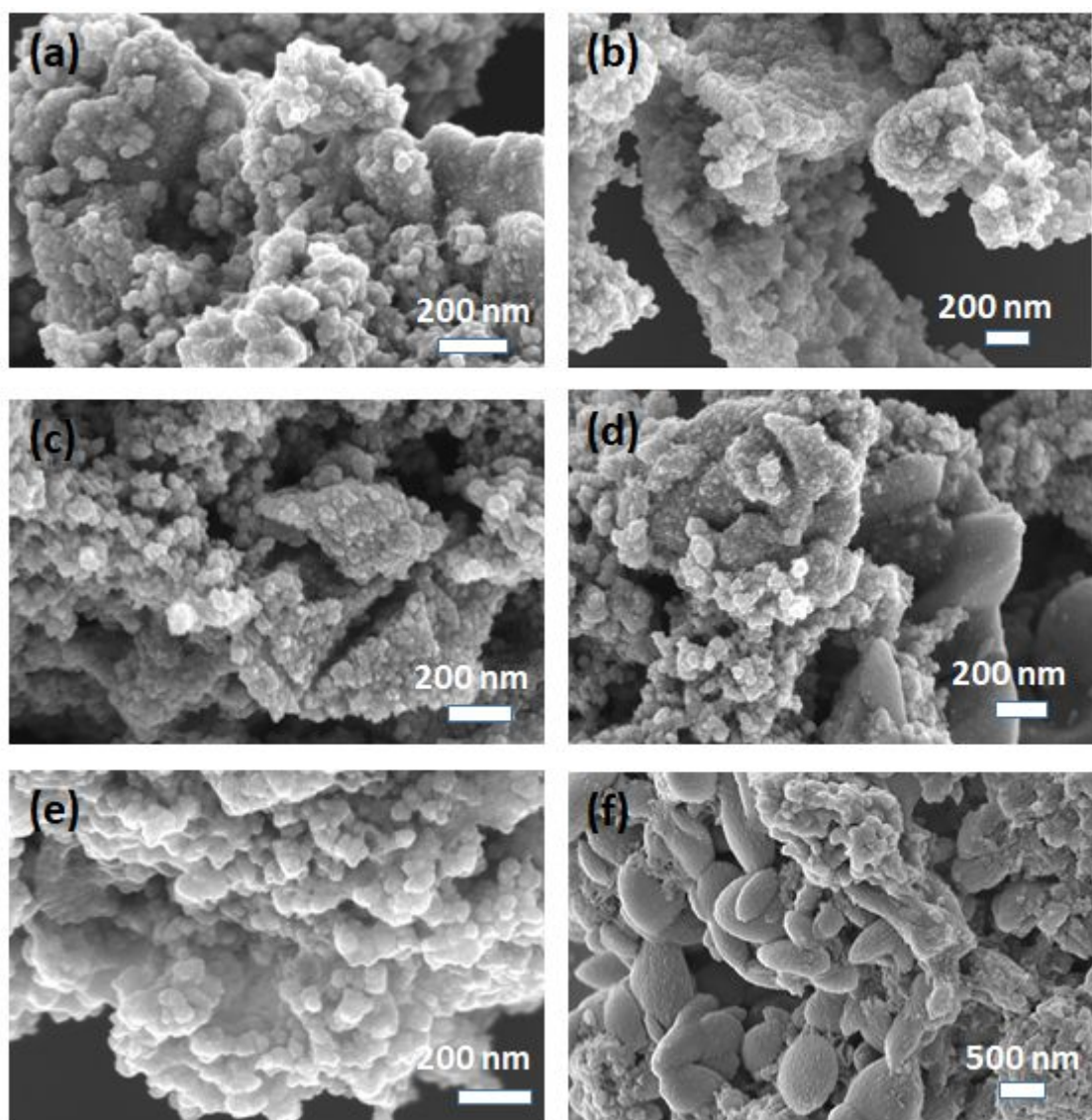


**Figure S4.** XRD patterns of MNPs (black line) and the solid product obtained by traditional oil bath heating the reaction mixture (50 mg of MNPs, 250 mg of  $\text{Fe}_2\text{Co}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6$

metal clusters, 250 mg of 3,3',5,5'-azobenzene tetracarboxylic acid organic linkers, 33 mL of DMF) at 96 °C for 1.5 h, followed by a thorough washing with DMF and methanol (red line).

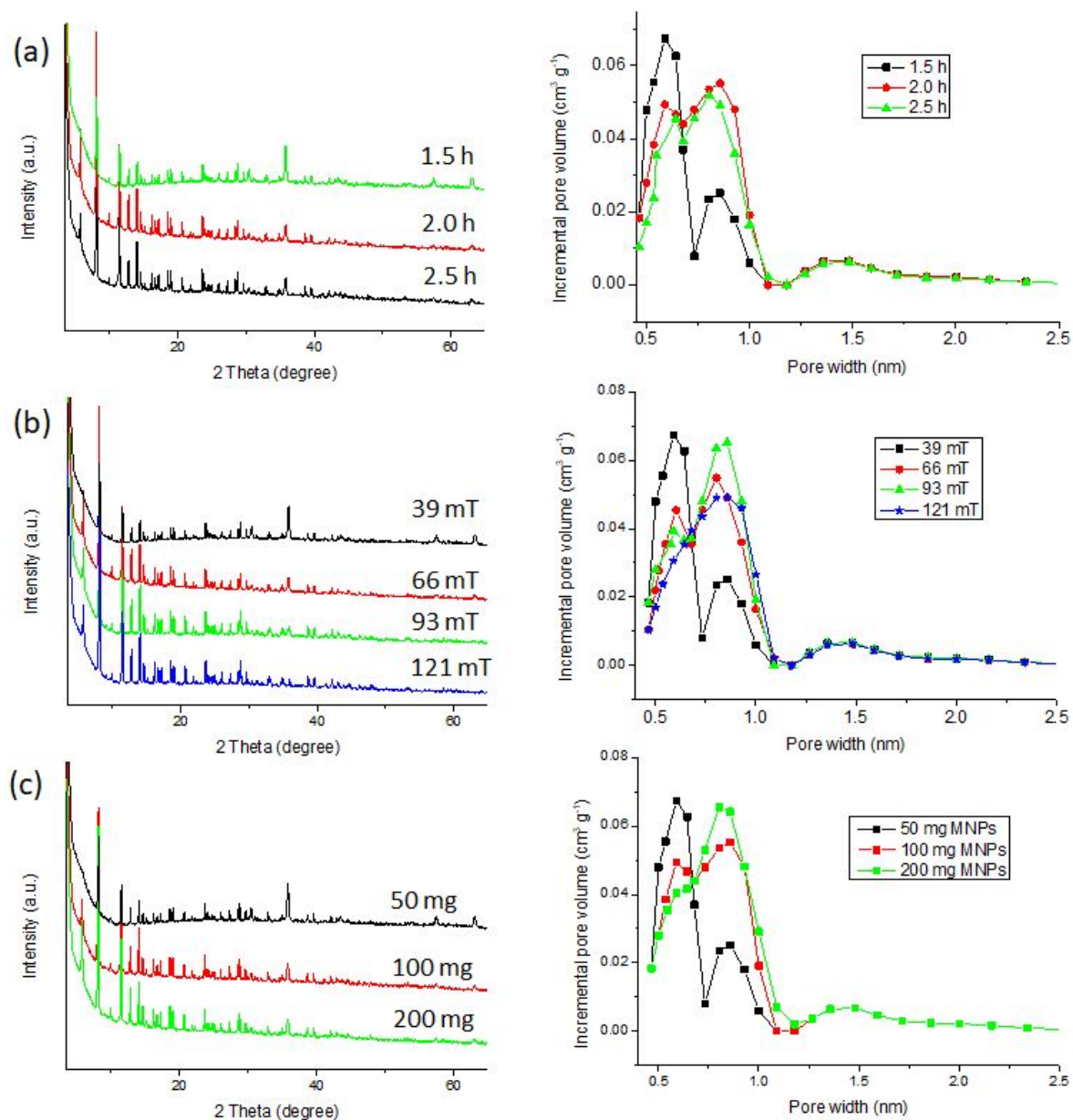


**Figure S5.** XRD patterns (a), pore size distributions (b), and Magnetic hysteresis loops (c) of mPCN-250 obtained in two separate sMIFS reactions under the same reaction conditions (50 mg of MNPs, 250 mg of  $\text{Fe}_2\text{Co}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6$  metal clusters, 250 mg of 3,3',5,5'-azobenzene tetracarboxylic acid organic linkers, 39 mT of magnetic field strength, 1.5 h of reaction time).

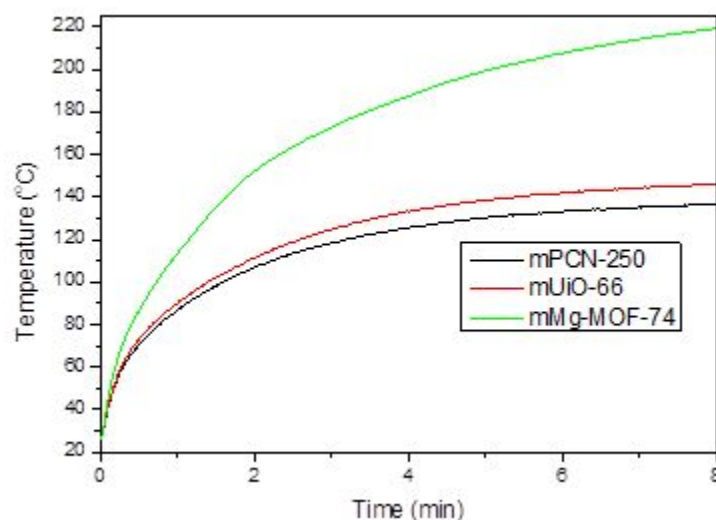


**Figure S6.** SEM images of mPCN-250 synthesized by exposing powder reaction mixture consisting of 50 mg of MNPs, 250 mg of  $\text{Fe}_2\text{Co}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6$  metal clusters, and 250 mg of 3,3',5,5'-azobenzene tetracarboxylic acid organic linkers to 93 mT of magnetic field for 2.0 h (a) and 2.5 h (b); mPCN-250 synthesized under the same reaction conditions with increased MNP using amount to 100 mg (c) and 150 mg (d); mPCN-250 synthesized under the same reaction conditions with increased magnetic field strength to 66 mT (e) and 93 mT (f).





**Figure S7.** XRD patterns and pore size distributions of mPCN-250 prepared depending on the reaction conditions: reaction time (a), the applied magnetic field strength (b), and MNP content in the powder reaction mixture (c).



**Figure S8.** Magnetic induction heating profiles of mPCN-250, mUiO-66, and mMg-MOF-74 upon the application of a 39 mT of alternating magnetic field.

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