Electronic Supporting Information

Magnetically Induced Localized Heating Enabling Rapid and Efficient

Synthesis of Metal-Organic Frameworks

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Experimental

Materials and Methods

All reagents and solvents were purchased from commercial sources and used as received.

Characterization: Powder X-ray diffraction (PXRD) data was collected at room temperature using a Rigaku SmartLab diffractometer with copper radiation (Cu K α , λ = 1.5406 Å) and a secondary monochromator operating at 40 kV and 30 mA; whereby samples were measured between 5° and 50° at a scan speed of 4 s/min and step size of 0.01°. Infrared spectra measurements from 4000-400 cm⁻¹ were taken on a Thermo Scientific Nicolet i550 ATR-IR with 4 cm⁻¹ resolution. BET surface area measurements were performed on a Micromeritics ASAP2020Plus analyzer using N₂ sorption isotherms at 77 K. Scanning electron microscope (SEM) images were collected using JEOL JSM-IT200 benchtop electron microscope at a 15kV accelerating voltage whereby dry samples of HKUST-1, MOF-235 and MOF-5 were put on carbon tape. Dynamic light scattering (DLS) measurements were carried out using a Zetasizer Nano ZSP (Malvern Instruments) and disposable low volume cuvette. PEG-1000@IONPs dispersion in water (1 mg/mL) was measured at 25°C. The resulting data was averaged to get a mean size distribution profile. The change in mass magnetization (M) in response to the applied magnetic field (H) for PEG-1000@IONPs powders was measured using Lakeshore 8600 series Vibrating sample magnetometer (VSM). The magnetic properties were measured with an applied field range of ±3 Tesla at a rate of 50 Oe/sec. Magnetic heating experiments were carried using a 4.2 kW Ambrell Easy heat instrument under different magnetic field strength (H) values and constant frequency of 224 kHz. A 8 turn coil (dimensions of 8 turn coil: internal diameter of 25 mm and length of 43mm) was used to perform the heating experiments.

Synthesis of PEG -1000@IONPs: PEG-1000 coated nanoparticles were synthesized by co-precipitation method using a reported procedure¹ with slight modifications. Initially 1.054 g (0.00039 mmol) of FeCl₃.6H₂O and 0.387 g (0.000195 mmol) of FeCl₂.4H₂O (Fe⁺³: Fe⁺² in ratio 2:1) were dissolved in 75 mL Millipore water and then mechanically stirred for 1 h constantly at temperature of 70 °C. Black colored precipitate formed on addition of 45 mL 25% NH₄OH to above solution. Simultaneously, 3 g PEG -1000 already dissolved in 7.5mL Millipore water was also added to the black precipitate solution of iron oxide followed by constant stirring for another 1 h at 90 °C. The entire reaction was carried out under an inert atmosphere. Finally, the precipitates of the PEG-1000@IONPs obtained were separated using magnetic separation and washed using Millipore water to remove any excess salts or surfactant.

Magnetic Induction Heating (MIH) Synthesis of HKUST-1: HKUST-1 was synthesized using Magnetic induction heating based on a solvothermal synthesis procedure reported in literature.² Firstly, 0.2082 mmol of 1,3,5-benzenetricarboxylic acid and 0.3125 mmol of Cu (NO₃)₂.2.5H₂O were dissolved in 5 mL

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ethanol:H₂O (1:1) mixture. The metal salt and ligand were allowed to dissolve completely to make a homogenous solution, and then 5 mg/mL PEG 1000@IONPs were added to the former solution. The solution was then sonicated for 20 min and transferred into a 10 mL glass vial. Finally, the solution was exposed to an alternating magnetic field of 35.32 kA/m magnetic field strength and 224kHz frequency for different time periods (10 min, 20 min, 30 min, 1 h, 1.5 h, 2 h and 2.5 h). The resultant MOF was separated from PEG 1000@IONPs using magnetic separation and washed using ethanol 3-4 times over a period of 2 days. The obtained material was then collected and dried. For the BET surface area measurements, the material was activated at 120 °C under dynamic vacuum for 12 h.

Conventional solvothermal synthesis of HKUST-1 MOF: HKUST-1 was synthesized using conventional solvothermal heating from the procedure same as above except that no magnetic PEG-1000@IONPS were used. The solution containing the precursors was transferred into a Teflon lined autoclave (20 mL) and put into a preheated oven at 65 °C for 2.5 h. The resultant MOF was separated from PEG 1000@IONPs using magnetic separation and washed using ethanol 3-4 times over a period of 2 days. The obtained material was then collected and dried.

Magnetic induction heating synthesis of MOF-235: MOF-235 was synthesized using magnetic induction heating based on solvothermal synthesis method reported in literature.³ Terephthalic acid (0.615 mmol) and FeCl₃.6H₂O (0.820 mmol) were dissolved in a 5mL solvent mixture of DMF:ethanol (3:1). Thereafter, PEG 1000@IONPs (5 mg/mL) were added to the former solution. The resultant mixture was then sonicated for 20 min and transferred into a 10 mL glass vial. Finally, the solution was exposed to an alternating magnetic field of 31.23 kA/m magnetic field strength and 224kHz frequency for 2.5 h. The resultant MOF was separated from PEG 1000@IONPs using magnetic separation and washed using first with DMF for 1-2 times followed by ethanol washing for 3-4 times over a period of 2 days. It was then collected and dried under vacuum to yield pure MOF-235 in 47.3% yield (based on ligand).

Magnetic induction heating synthesis of MOF-5: MOF-5 was synthesized using magnetic induction heating based on solvothermal synthesis method reported in the literature with slight modifications.⁴ Terephthalic acid (0.270 mmol) and Zn(NO)₃.6H₂O (1.512 mmol) were dissolved in 5mL DMF followed by the addition of 270 μ L of Millipore water. Finally, 7.5 mg/mL PEG 1000@IONPs were added to the former solution which was then sonicated for 20 min and transferred into a 10 mL glass vial. This solution was then exposed to an alternating magnetic field of 60.92kA/m magnetic field strength and 224kHz frequency for 2.5 h. The resultant MOF was separated from PEG 1000@IONPs using magnetic separation and washed using first with DMF for 1-2 times followed by chloroform washing for 3-4 times over a period of 2 days.

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The obtained material was then vacuum dried to yield MOF-5 (based on ligand) in 52.1% yield and stored in an inert atmosphere.

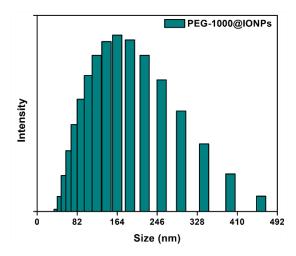


Fig. S1. The hydrodynamic size distribution of PEG-1000@IONPs measured using DLS.

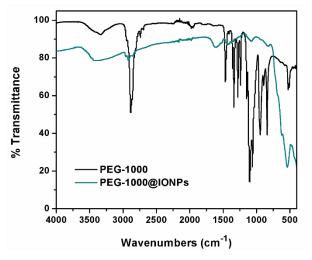


Fig. S2. Comparison of the FTIR spectra of PEG-1000 (black) and PEG-1000@IONPs (dark cyan).



Fig. S3. The experimental setup for carrying out the MIH synthesis of MOFs using the Ambrell EasyHeat magnetotherm instrument under varying magnetic field strength (H) and a constant frequency of 224 kHz.

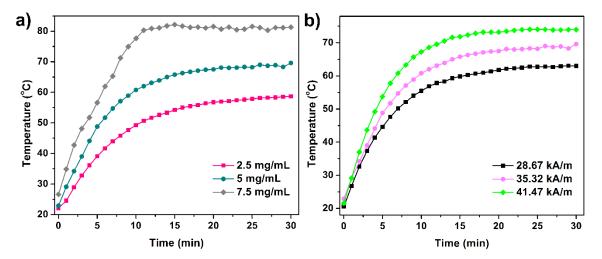


Fig. S4. The effect of (a) concentration, and (b) magnetic field strength on the heating properties of the PEG-1000@IONPs in the EtOH:water (1:1) solvent system.

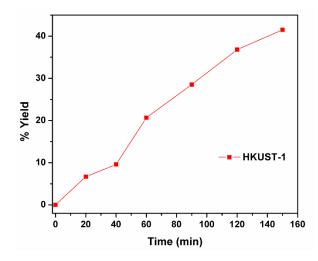


Fig. S5. The increase in yield over time for the MIH synthesis of HKUST-1.

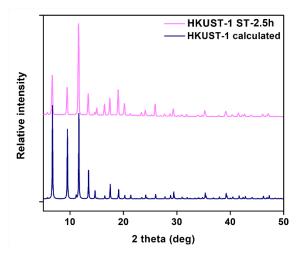


Fig. S6. The PXRD pattern of the product obtained from the conventional solvothermal synthesis carried out at 65 °C for 2.5 h (HKUST-1 ST-2.5h).

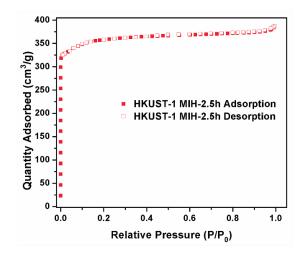


Fig. S7. The N_2 adsorption-desorption isotherms at 77K for HKUST-1 MIH-2.5h obtained from magnetothermal synthesis at 65 °C for 2.5 h.

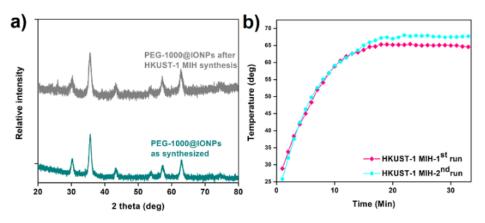


Fig. S8. The a) PXRD of the PEG-1000@IONPs before and after the HKUST-1 MIH synthesis, and b) heating profile of the PEG-1000@IONPs during reusability tests.

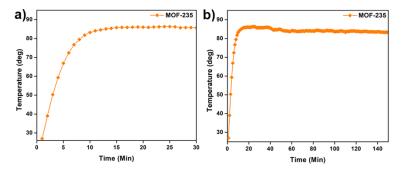


Fig. S9. The heating profile of PEG-1000@IONPs for (a) 30 min, and (b) 2.5 h synthesis of MOF-235.

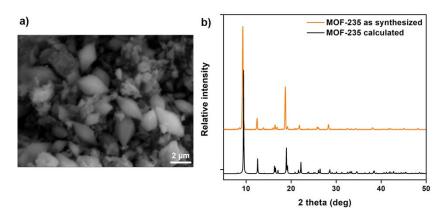


Fig. S10. The a) SEM image, and b) PXRD pattern for MOF-235 obtained from MIH synthesis indicating high crystallinity.

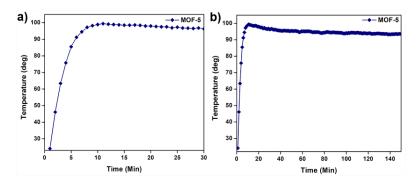


Fig. S11. The heating profile of PEG-1000@IONPs for (a) 30 min, and (b) 2.5 h synthesis of MOF-5.

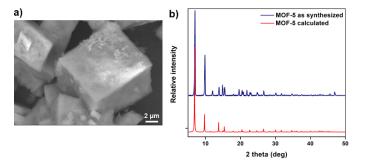


Fig. S12. The a) SEM image, and b) PXRD pattern for MOF-5 obtained from MIH synthesis.

Table S1. A comparison of the efficiency of magnetic induction heating and the conventional

	Convection Oven	Magnetic Induction Heating ²
Power rating	1680 W	191 W (at 65 °C)
Heat-up time ¹	25 min (for set temperature of	15 min (for set temperature of
	150 °C)	65 °C)
Heat dissipation to the	261 W (at set temperature of	Negligible
environment ¹	150 °C)	
Temperature deviation from set	<u>+</u> 4.5 °C	<u>+</u> 1 °C
value ¹		

solvothermal convection ovens for MOF synthesis.

¹Typical values for a set temperature of 150 °C. Source: <u>https://us.vwr.com/assetsvc/asset/en_US/id/12244825/contents/at-</u><u>vwr-collection-oven-operation-manual.pdf</u>

² Values for synthesis of HKUST-1 using MIH.

References

- 1. A. Domán, O. Czakkel, L. Porcar, J. Madarász, E. Geissler, K.László, *Appl.Surf.Sci.*, 2019, **480**, 138-147.
- 2. A. Rajan, M. Sharma, N. K. Sahu, Sci. Rep., 2020, **10**, 15045.
- 3. I. Simonsson, P. Gärdhagen, M. Andrén, P. L. Tam, Z. Abbas, *Dalton Trans.*, 2021, **50**, 4976-4985.
- 4. B. Chen, X. Wang, Q. Zhang, X. Xi, J. Cai, H. Qi, S. Shi, J. Wang, D. Yuan and M. Fang, *J. Mater. Chem.*, 2010, **20**, 3758-3767.