Supporting Information

Hybrid Materials of Ni NP@MOF by a Simple Synthetic Method

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Experimental section

General information. 2, 5-Dihydroxyterephthalic acid was purchased from TCI. All other chemicals were purchased from Wako Pure Chemical Industries and used as received.

Synthesis of Ni-MOF-74. Ni_2(dhtp) (Ni-MOF-74, CPO-27-Ni) was synthesized using a slight modification to an established procedure. To a solid mixture of H_4dhtp (4.79 g, 24.2 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ (23.8 g, 81.8 mmol) was added a 1:1:1 (v/v/v) mixture of DMF–ethanol–water (2 L) in a 3 L eggplant flask. The suspension was mixed until homogeneous and then heated to 100 °C. After 5 days, the sample was cooled to RT. A yellow material was isolated and washed with methanol (1 L). The washing was repeated four times over 2 days. The material was then washed twice with deionised water (1 L). The solvent was removed under vacuum at RT over 1 day.

TG-DTA. The thermogravimetric analysis of Ni-MOF-74 was performed using a NETZSCH Japan TG-DTA 2,000SA with a heating rate of 2 K per min under a constant He flow.

XRD measurements. Powder X-ray diffraction (PXRD) patterns were measured using beamline BL02B2 of SPring-8 (λ = 0.998, 1.001 Å).

FT-IR spectra. Fourier-transform infrared (FT-IR) spectra were collected using a Perkin-Elmer Spectrum 100.

XPS spectra. The XPS spectra of samples on a carbon sheet were recorded using an ESCA-3400 (Shimadzu). The binding energies were corrected by referencing the C(1s) line at 284.3 eV.

TEM images. Transmission electron microscope (TEM) images were obtained using a HITACHI HT7700 at an accelerating voltage of 100 kV. High-resolution scanning transmission electron microscope (HRSTEM) images were obtained using a JEM-ARM200F at accelerating voltages of 80 kV and 120 kV, respectively. The JEM-ARM200F was also equipped with an energy dispersive X-ray spectrometer (EDX) system that allows for the elemental analysis of samples.

Nitrogen sorption. N_2 adsorption/desorption isotherms were measured using a BELSORP-max at 77 K up to 1 bar. Before starting the adsorption measurements, each sample was activated by heating under vacuum at 120 °C for 12 h.

Magnetic property measurements. Magnetization curves and magnetic susceptibility were measured using a QUANTUM DESIGN MPMS-XL, and AC susceptibility was measured using a QUANTUM DESIGN MPMS-5S.

Table S1. Synthesis conditions and sample names for Ni NP@MOF.

	6 h	12 h	24 h	3 days	7 days
250 °C	**250-6h**	**250-12h**	**250-24h**		**250-7d**
300 °C	**300-6h**	**300-12h**	**300-24h**	**300-3d**	
350 °C	**350-6h**	**350-12h**	**350-24h**		
400 °C	**400-6h**	**400-12h**	**400-24h**		

S1 Thermogravimetric analysis (TGA) for Ni-MOF-74

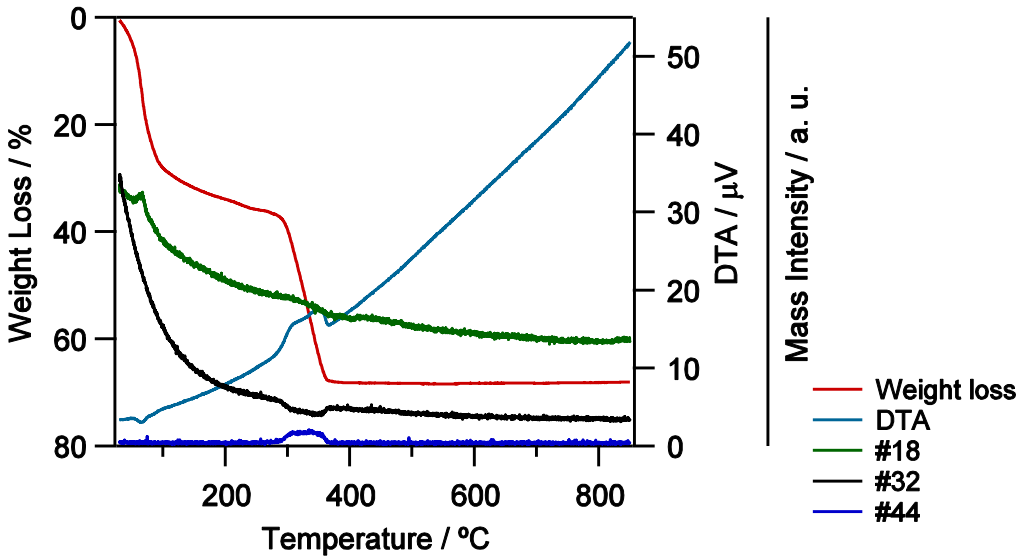


Figure S1. Thermogravimetric analysis (TGA) curves of Ni-MOF-74 (in He flow).

S2 X-ray diffraction measurements

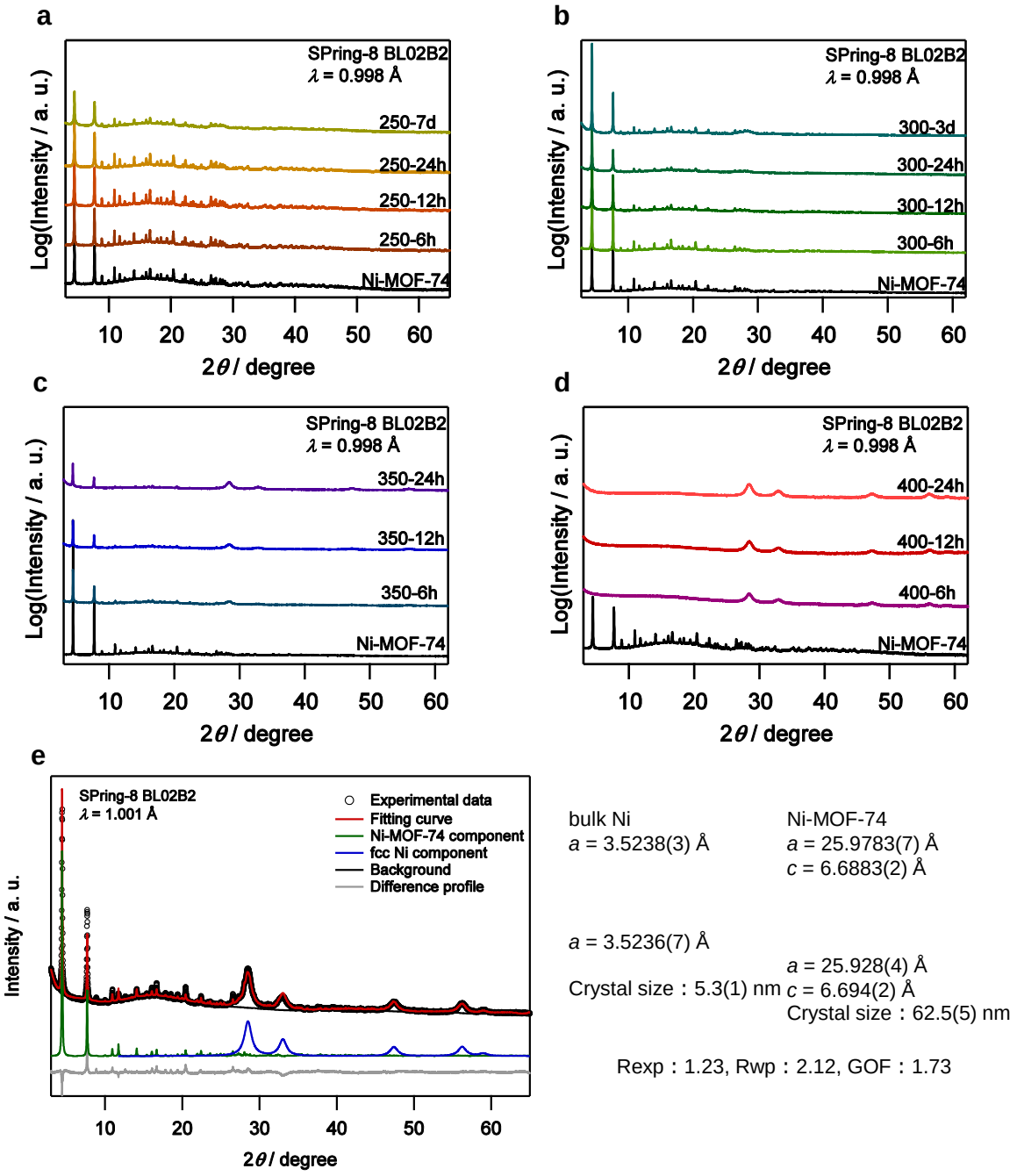


Figure S2. Powder X-ray diffraction (PXRD) patterns of **250-6h**, **250-12h**, **250-24h**, and **250-7d** (a), **300-6h**, **300-12h**, **300-24h**, and **300-3d** (b), **350-6h**, **350-12h**, and **350-24h** (c), **400-6h**, **400-12h**, and **400-24h** (d), and the result of Rietveld analysis for **350-12h** (e).

S3 FT-IR

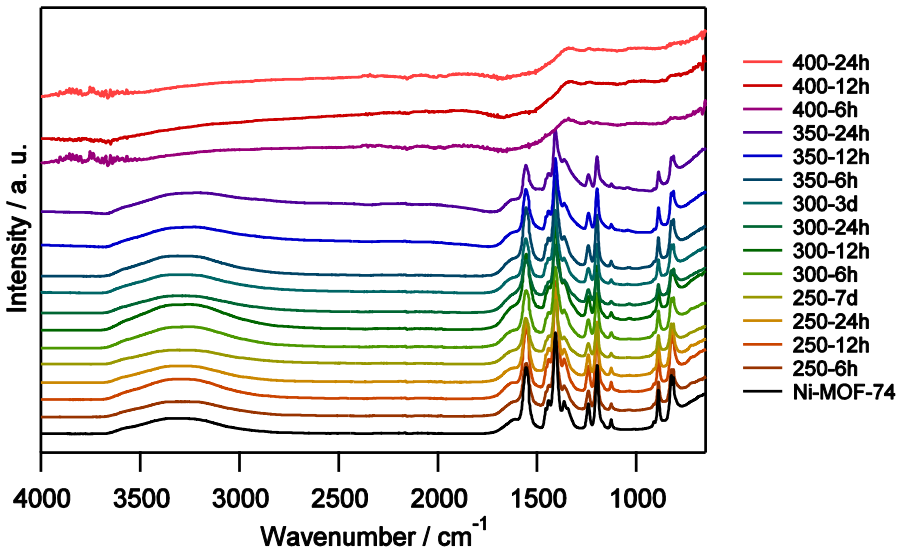


Figure S3. Fourier-transform infrared (FT-IR) spectra of Ni-MOF-74 and composites.

S4 EDX maps

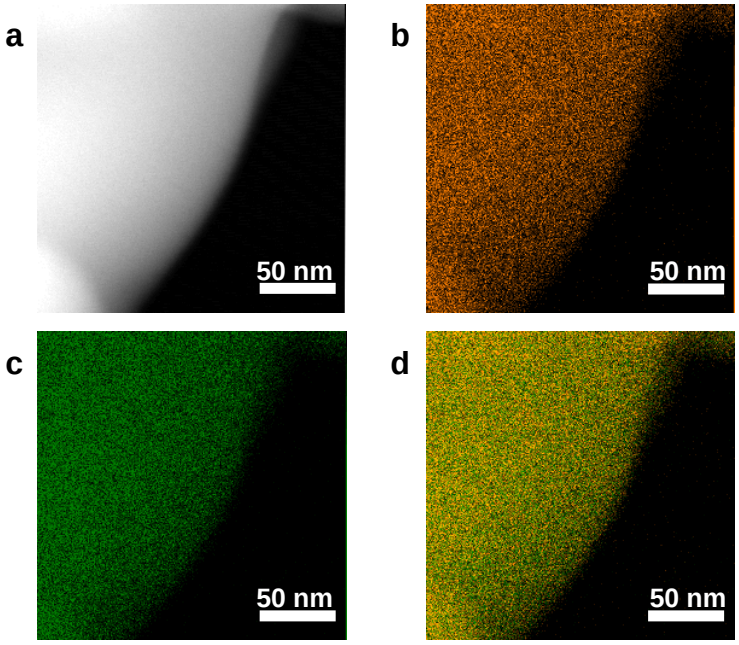
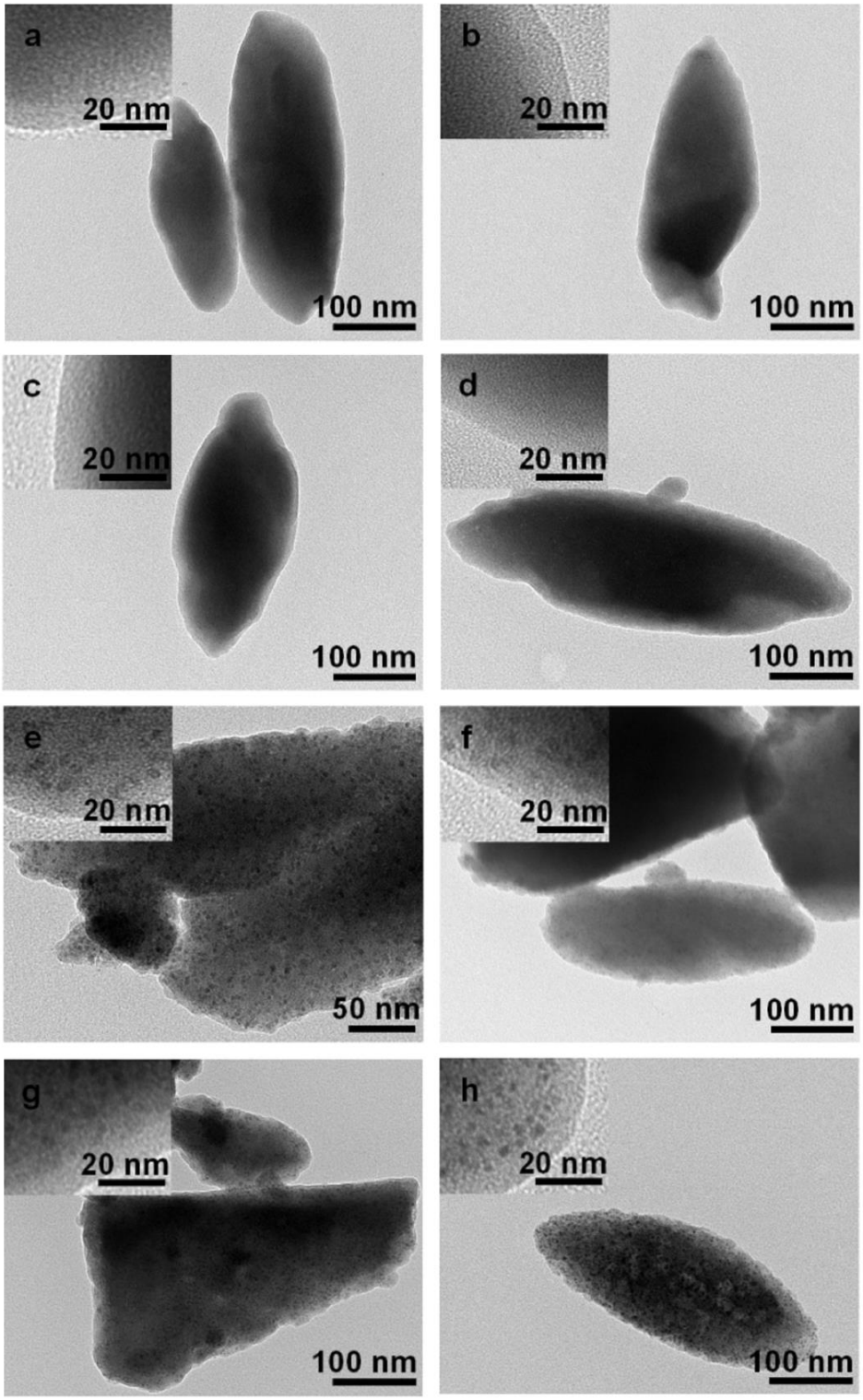


Figure S4. HAADF-STEM image (a), C-K STEM-EDX map (b) and Ni-K STEM-EDX map (c) of Ni-MOF-74. (d) The reconstructed overlay image of the maps shown in (b) and (c).

S5 TEM images



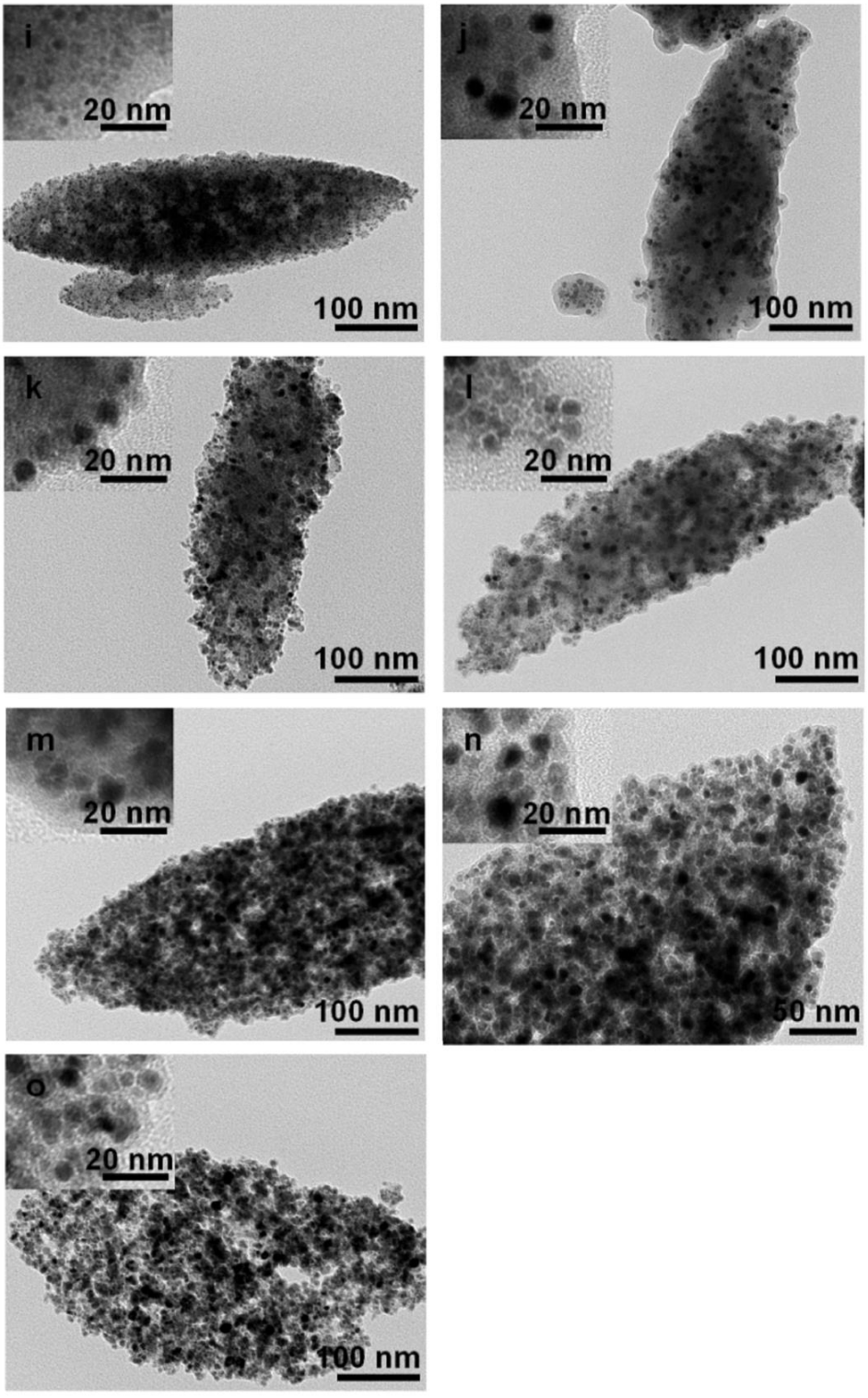


Figure S5. TEM images of Ni-MOF-74 (a), **250-6h** (b), **250-12h** (c), **250-24h** (d), **250-7d** (e), **300-6h** (f), **300-12h** (g), **300-24h** (h), **300-3d** (i), **350-6h** (j), **350-12h** (k), **350-24h** (l), **400-6h** (m), **400-12h** (n), and **400-24h** (o).

Table S2. Mean diameter of Ni nanoparticles.

	6 h	12 h	24 h	3 days	7 days
250 °C					2.5 ± 0.6
300 °C	2.2 ± 0.4	2.3 ± 0.6	2.4 ± 0.5	3.0 ± 0.6	
350 °C	4.0 ± 1.4	4.3 ± 1.4	4.6 ± 1.3		
400 °C	4.3 ± 1.1	4.5 ± 1.2	5.0 ± 1.2		

S6 Nitrogen sorption

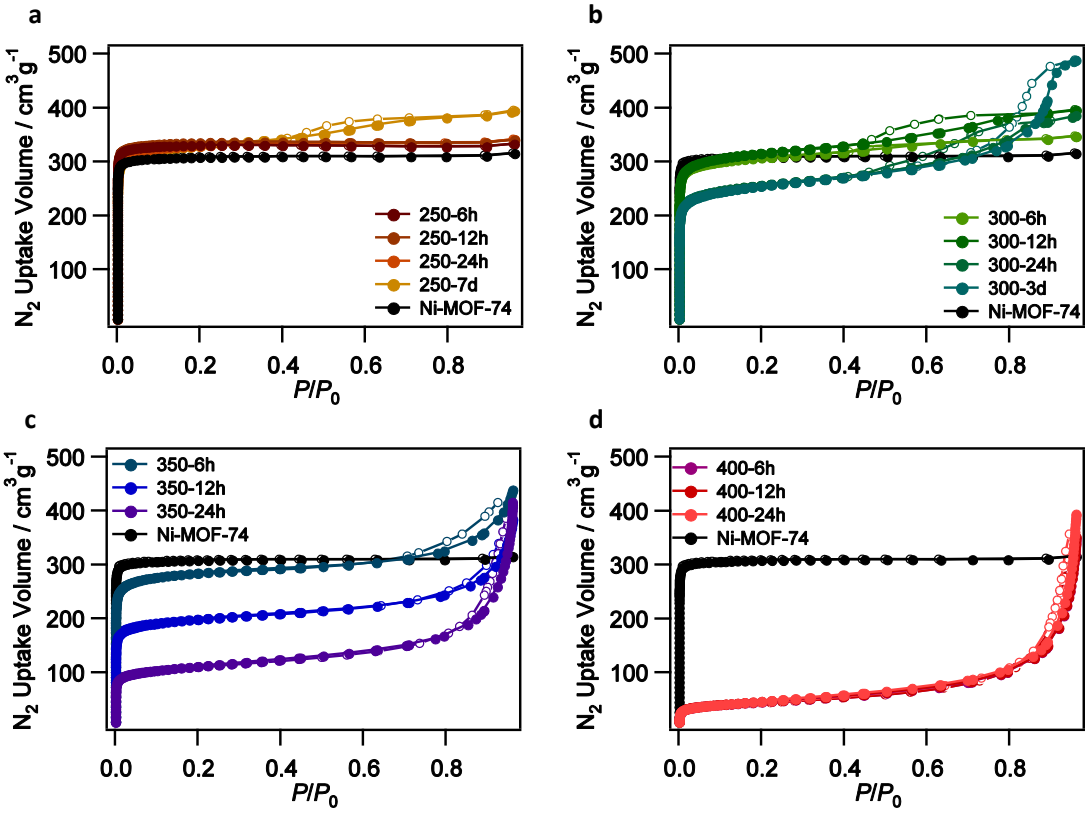


Figure S6. Nitrogen sorption isotherms for **250-6h**, **250-12h**, **250-24h**, and **250-7d** (a), **300-6h**, **300-12h**, **300-24h**, and **300-3d** (b), **350-6h**, **350-12h**, and **350-24h** (c), **400-6h**, **400-12h**, and **400-24h** (d) at 77 K up to 1 bar. The solid and open symbols represent adsorption and desorption, respectively.

S7, S8 Magnetic property measurements

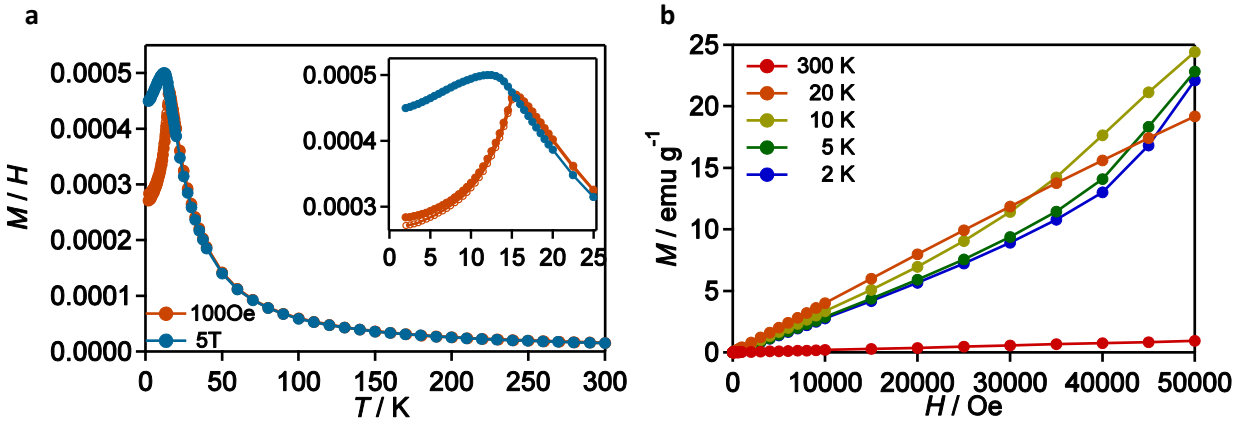


Figure S7. (a) The magnetic susceptibility as a function of temperature for Ni-MOF-74 (the open and solid symbols represent zero-field-cooled (ZFC) and field-cooled (FC), respectively). (b) Magnetization as a function of magnetic field for Ni-MOF-74. The kink structure around 4T indicates spin flop.

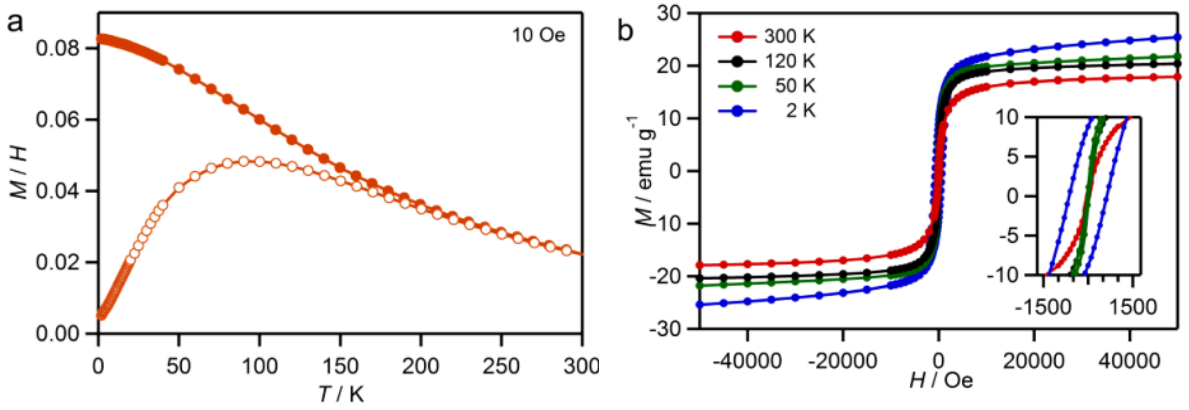


Figure S8. (a) The magnetic susceptibility as a function of temperature for **400-12h** at 10 Oe. The open and solid symbols represent zero-field-cooled (ZFC) and field-cooled (FC), respectively). (b) Magnetization as a magnetic field for **400-12h** at 2 K (blue circle), 50 K (green circle), 120 K (black circle) and 300 K (red circle).