

Electronic Supporting Information

for

**Postsynthetic modification of mixed-linker metal-organic
frameworks for ethylene oligomerization**

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1. General synthetic procedure

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen using standard Schlenk and glove-box techniques. Toluene (HPLC grade, Tedia Company) was refluxed over metallic potassium/sodium with benzophenone as an indicator and distilled under nitrogen prior to use. Diethylaluminum chloride (Et_2AlCl , 1.1 M in toluene) was purchased from Acros Chemicals. Terephthalic acid (H_2BDC), 2-aminoterephthalic acid (H_2ABDC), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NiBr_2 and 2-pyridine carboxaldehyde were obtained from J&K Scientific Ltd. and used as received. Polymerization-grade ethylene (TOPGRAND Petrification Industry Gas Ltd.) was purified by passing it through purification systems. All other chemical chemicals were obtained commercially and used without further purification unless otherwise stated.

Synthetic procedure of MixMOFs

The proportional H_2ABDC and H_2BDC (total amount of 0.27 mmol) were dissolved in 20 mL of DMF, and then $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.80 mmol) was added to the solution. The mixture was sonicated for 15 min and heated at 100 °C. After 48 h, the cubic-shape crystals formed were washed with DMF and then soaked in CHCl_3 .

Synthesis of MOFs-Ni

To a suspension solution of NiBr_2 (0.53 g, 2.43 mmol) in 19 mL of anhydrous methanol, 2-pyridine carboxaldehyde (0.26 g, 2.43 mmol) was added. The mixture was stirred at 50 °C for 6 h to give a clear green solution. After filtration, the solution was divided into seven different sections, which were separately added to outgassed MOFs (0.2 g). The mixtures were allowed to react at room temperature for the desired time. The resulting suspensions were centrifuged and washed with methanol and dichloromethane to give the yellowish-green solid.

2. Ethylene Oligomerization

Ethylene oligomerization was carried out in a 500 mL of stainless steel autoclave

with a mechanical stirrer and a temperature controller. After it was dried under vacuum, purged 3 times with nitrogen and replaced twice with ethylene, toluene (200 mL) and the required amount of co-catalyst were introduced to the reactor. Subsequently a prescribed amount of catalyst was added, and then filled ethylene to 20 bar to start the reaction. After the desired reaction time, the reaction was terminated by shutting in the ethylene feed, after which the autoclave was cooled rapidly to 0 °C with an ice bath and slowly depressurised. A sample of liquid reaction mixture was filtered and analysed by gas chromatography using a known amount of heptane as the internal standard.

3. Fourier transform-infrared (FT-IR) spectroscopy

The FT-IR spectra of samples were recorded on a Nicolet 5700 spectrometer using KBr disks at a 4 cm⁻¹ in the range of 4000–400 cm⁻¹.

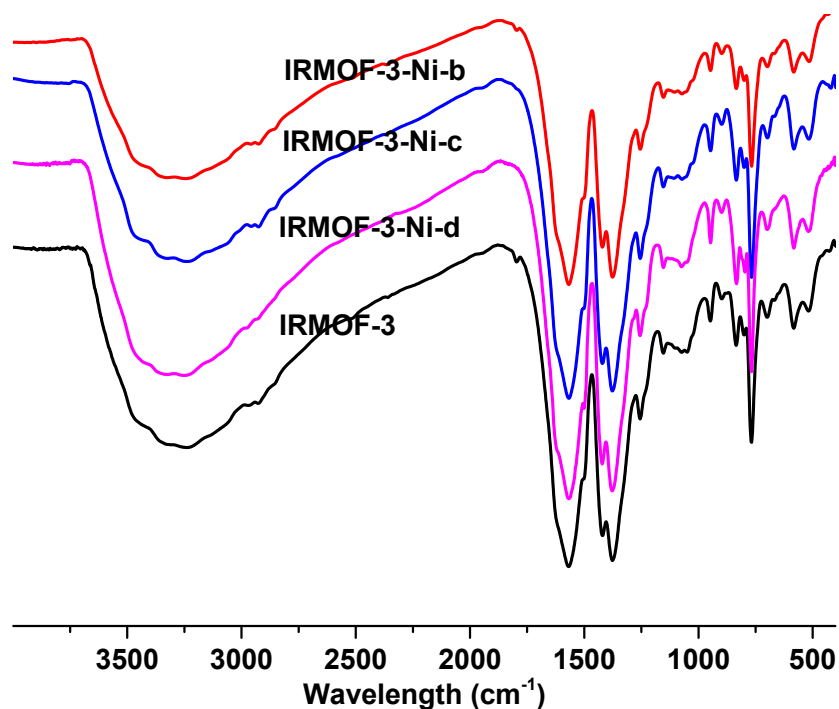


Fig. S1 FT-IR spectra of IRMOF-3-Ni-b, IRMOF-3-Ni-c, IRMOF-3-Ni-d and IRMOF-3.

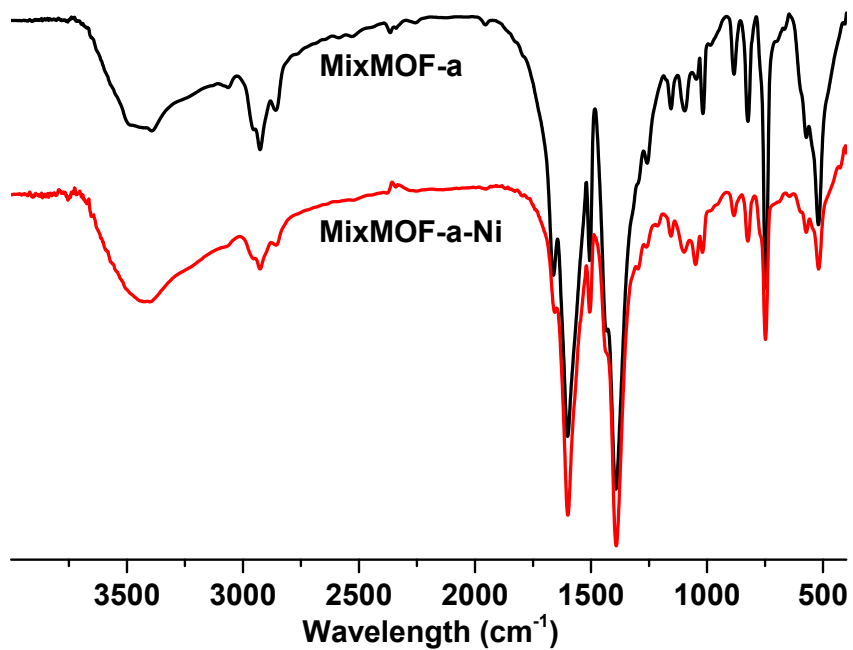


Fig. S2 FT-IR spectra of the MixMOFs-a and MixMOFs-a-Ni

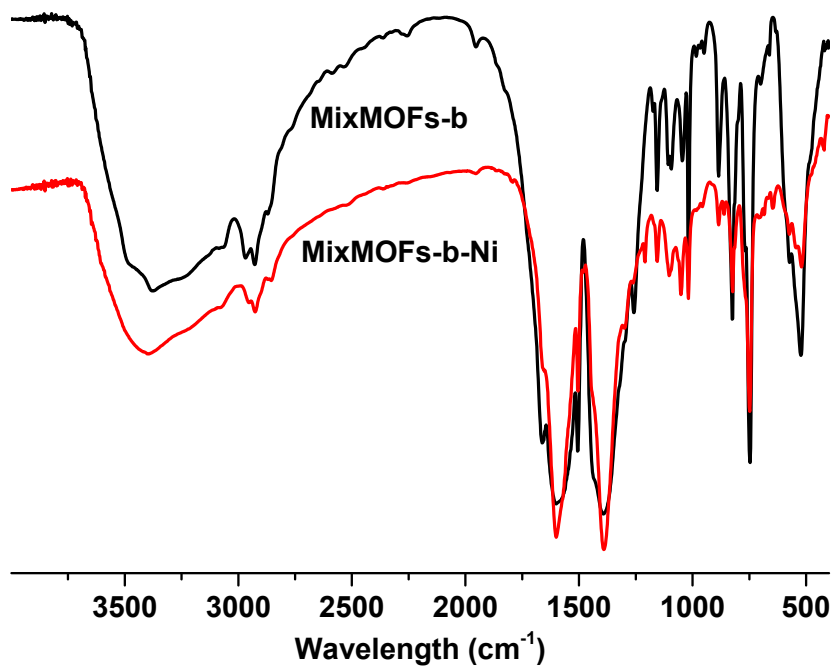


Fig. S3 FT-IR spectra of the MixMOFs-b and MixMOFs-b-Ni

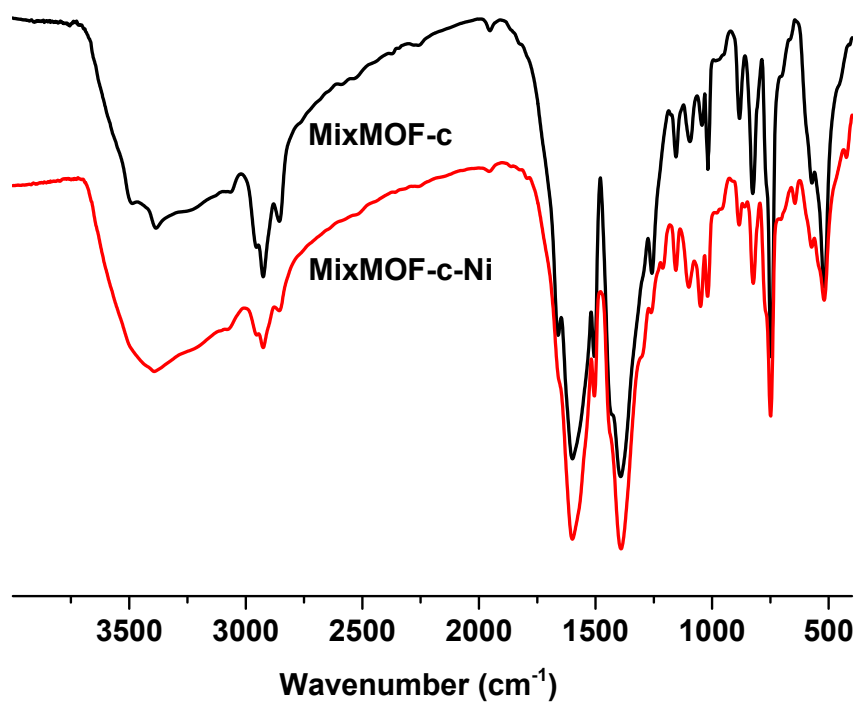


Fig. S4 FT-IR spectra of MixMOFs-c and MixMOFs-c-Ni

4. Power X-Ray Diffraction

The crystallinity of the materials was characterized by powder X-ray diffraction (XRD) on a PANalytical B.V.-Empyrean diffractometer using Cu-K α radiation source.

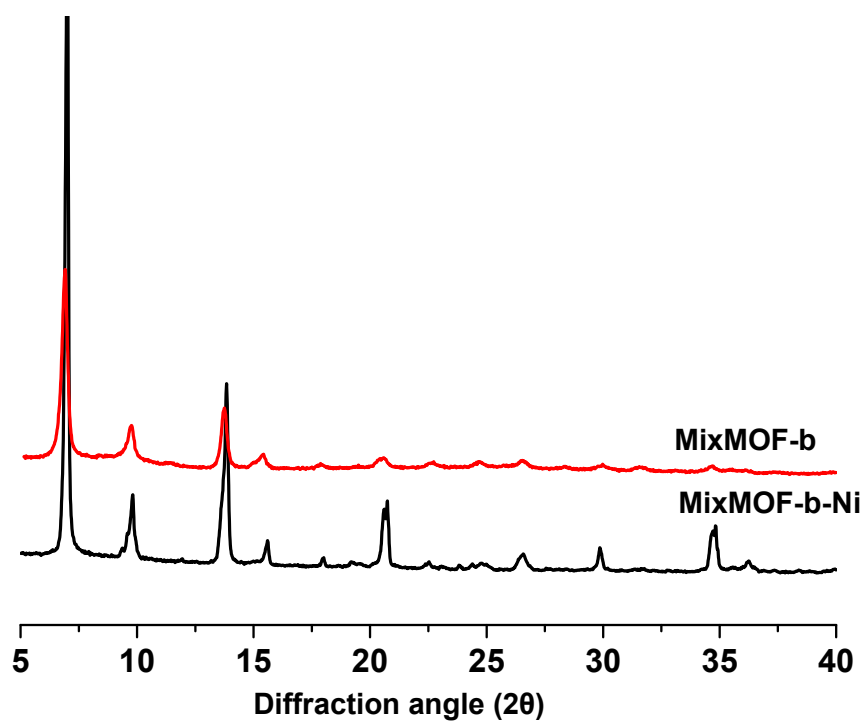


Fig. S5 PXRD patterns of MixMOFs-b and MixMOFs-b-Ni

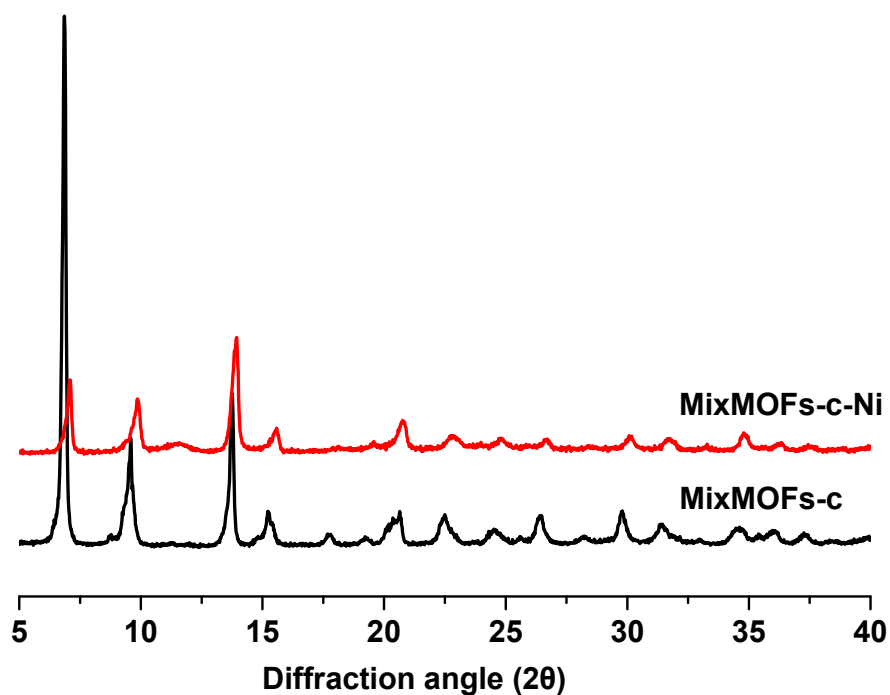


Fig. S6 PXRD patterns of MixMOFs-c and MixMOFs-c-Ni

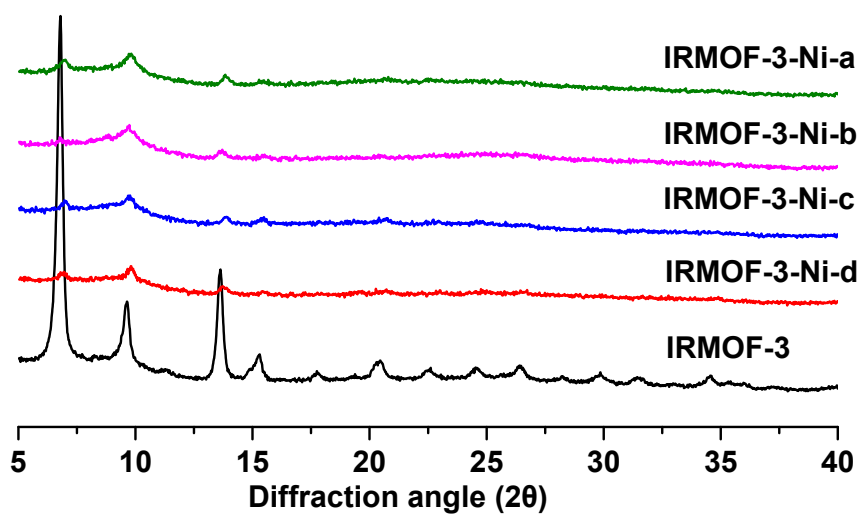


Fig. S7 PXRD patterns of IRMOF-3-Ni-a, IRMOF-3-Ni-b, IRMOF-3-Ni-c, IRMOF-3-Ni-d and IRMOF-3.

5. Thermogravimetric analysis (TGA)

Thermogravimetric experiments were carried out using Pyris 1 TGA analyser in

flowing air from 50 to 800 °C with a heating rate of 10 °C·min⁻¹.

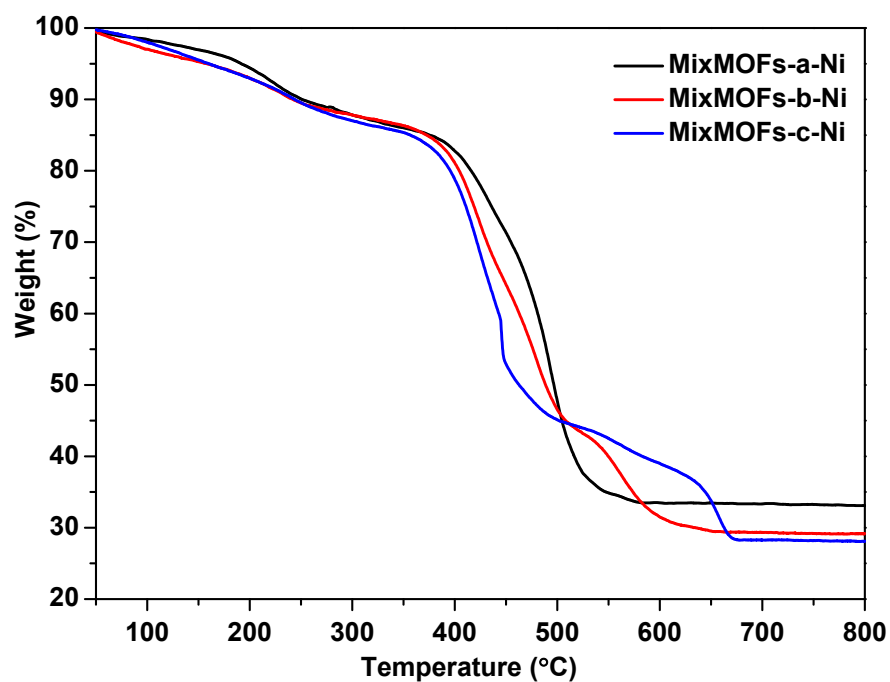


Fig. S8 TGA curves of MixMOFs-a-Ni, MixMOFs-b-Ni and MixMOFs-c-Ni

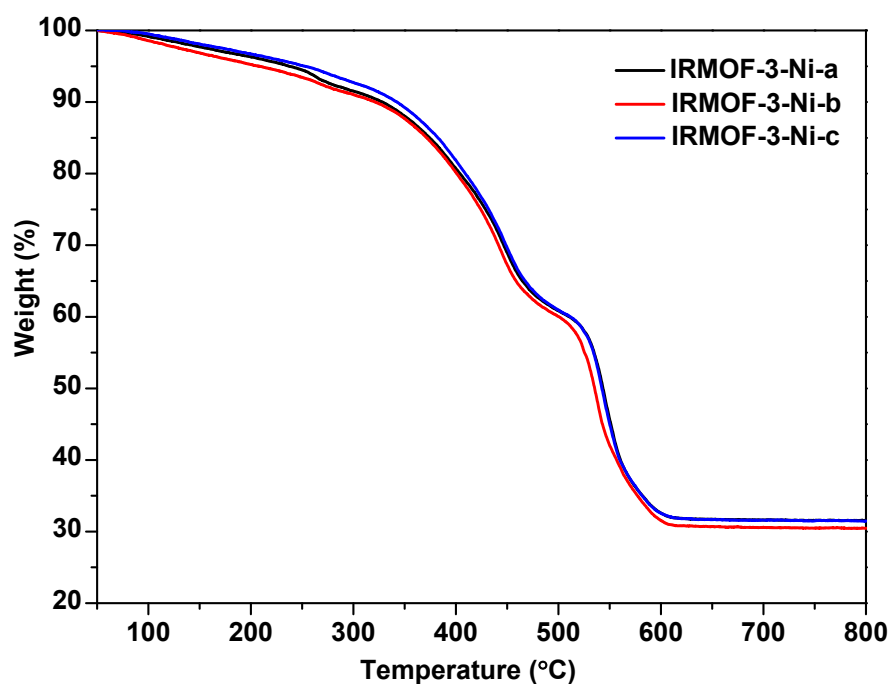


Fig. S9 TGA curves of IRMOF-3-Ni-a, IRMOF-3-Ni-b and IRMOF-3-Ni-c

6. N₂ adsorption-desorption isotherms

Nitrogen adsorption-desorption isotherms were measured at 77 K using a

Quantachrome Autosorb-1-C instrument. Prior to the BET analysis, the samples were degassed at 100 °C for 24 h.

Table S1 BET surface area of MOFs and MOFs-Ni

	MixMOFs-a	MixMOFs-a-Ni	MixMOFs-b	MixMOFs-b-Ni	MixMOFs-c	MixMOFs-c-Ni
surface area (m ² ·g ⁻¹)	1080	262	1213	176	1671	127
	IRMOF-3	IRMOF-3-Ni-a	IRMOF-3-Ni-b	IRMOF-3-Ni-c	IRMOF-3-Ni-d	
surface area (m ² ·g ⁻¹)	1086	8	11	6	-	

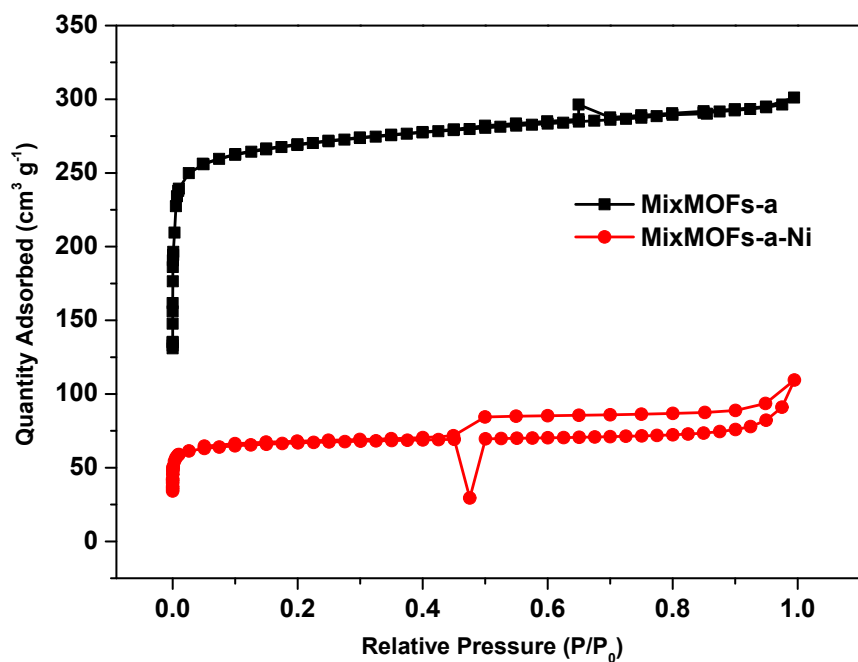


Fig. S10 N₂ adsorption isotherms (at 77 K) of MixMOFs-a and MixMOFs-a-Ni

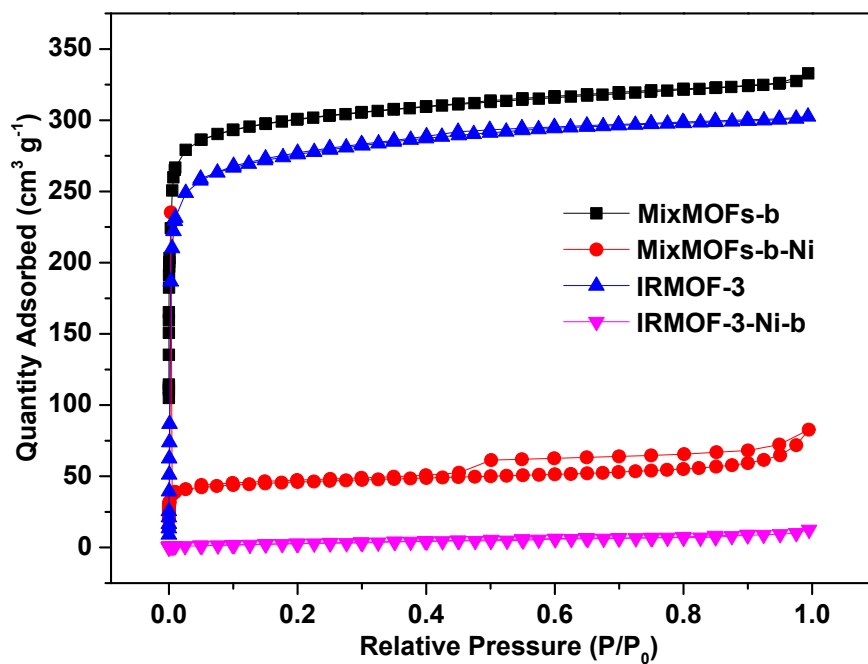


Fig. S11 N₂ adsorption isotherms (at 77 K) of MixMOFs-b, MixMOFs-b-Ni, IRMOF-3 and IRMOF-3-Ni-b.

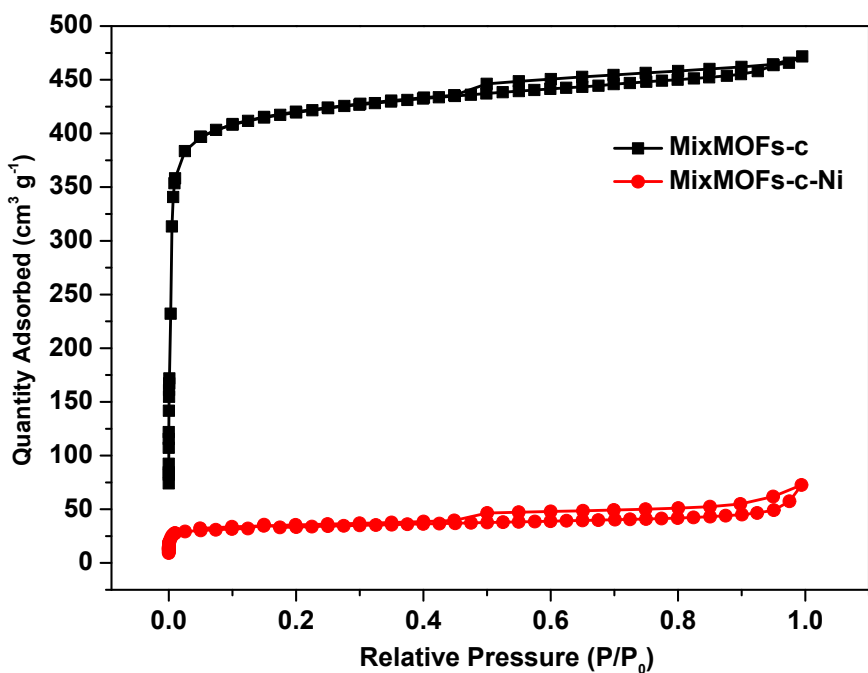


Fig. S12 N₂ adsorption isotherms (at 77 K) of MixMOFs-c and MixMOFs-c-Ni