

Electronic Supplementary Information

Heterogeneous Catalysis with Coordination Modulation Synthesized MOF: Morphology-Dependent Catalytic Activity

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Experimental Section

Synthesis of the ligands: **bpta**, **bpfb** and **bpfn**

The simple route for the synthesis of amide-containing compounds is the coupling of an acid chloride with an amine group. Note here that the acid chloride-amine reaction is exothermic. Therefore, all organic reactions performed in this study were carried out at low temperature in the presence of triethylamine (TEA) to capture *in situ* the generated side product HCl.

*Synthesis of N,N'-di(pyridin-4-yl)terephthalamide (**bpta**):* 4-aminopyridine (1.882 g; 20 mmol) and 2.84 ml of TEA (20.4 mmol) were dissolved in 50 ml of dry THF. Then, terephthaloyl chloride (2.030 g; 10 mmol) was added into this solution and heated under reflux for 24 h. The resulting yellow suspension was filtered, dried under ambient conditions, and poured into an aqueous saturated solution of Na_2CO_3 (50 ml). The resulting white solid was finally filtered and dried, obtaining the pure ligand bpta in ca. 73 % yield.

*Synthesis of N,N'-bis-(4-pyridylformamide)-1,4-benzenediamine (**bpfb**) and N,N'-bis-(4-pyridylformamide)-1,5-naphthalenediamine (**bpfn**):* 1,4-phenylenediamine (1.081 g; 10 mmol; for bpfb) and 1,5-diaminonaphthalene (1.580 g; 10 mmol; for bpfn) were dissolved in 50 ml of dry THF containing 2.84 ml of TEA (20.4 mmol). Then, isonicotinoyl chloride hydrochloride (3.560 g, 20 mmol) was added into these solutions and heated under reflux for 24 h. Both reactions were then treated as above indicated for the synthesis of bpta. The yellowish powders were filtered and dried, obtaining the pure ligands in ca. 82% (bpfb) and 87 % (bpfn) yields.

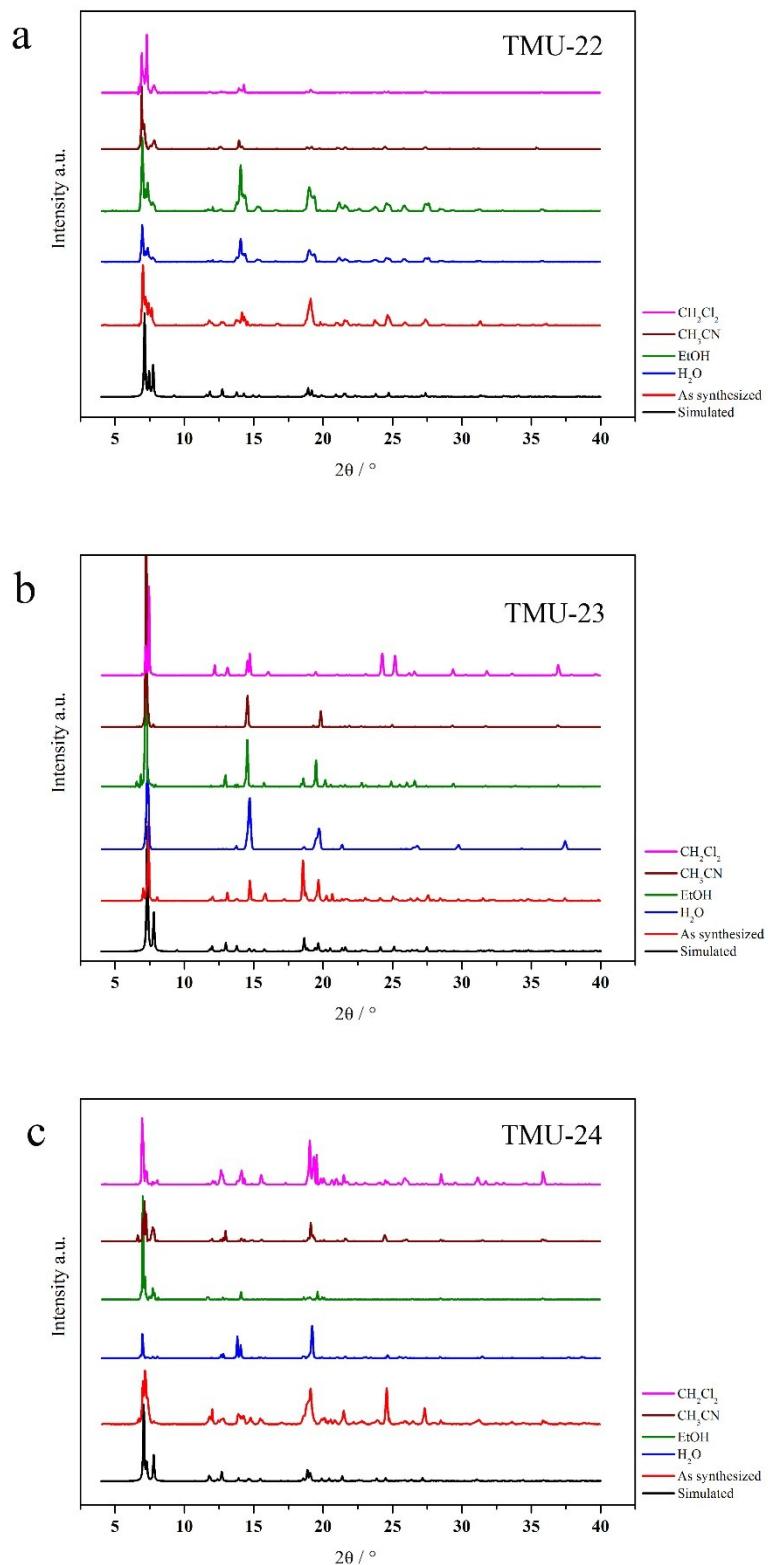


Fig. S1 PXRD patterns of (a) **TMU-22**, (b) **TMU-23** and (c) **TMU-24** in different solvents for 24 h. Simulated (black), as-synthesized (red), water (blue), ethanol (green), acetonitrile (brown) and dichloromethane (purple). Note that, due to their interdigitated nature, some of the materials seems to exhibit small structural changes; characteristic from swelling of “soft” materials when immersed in solvents.

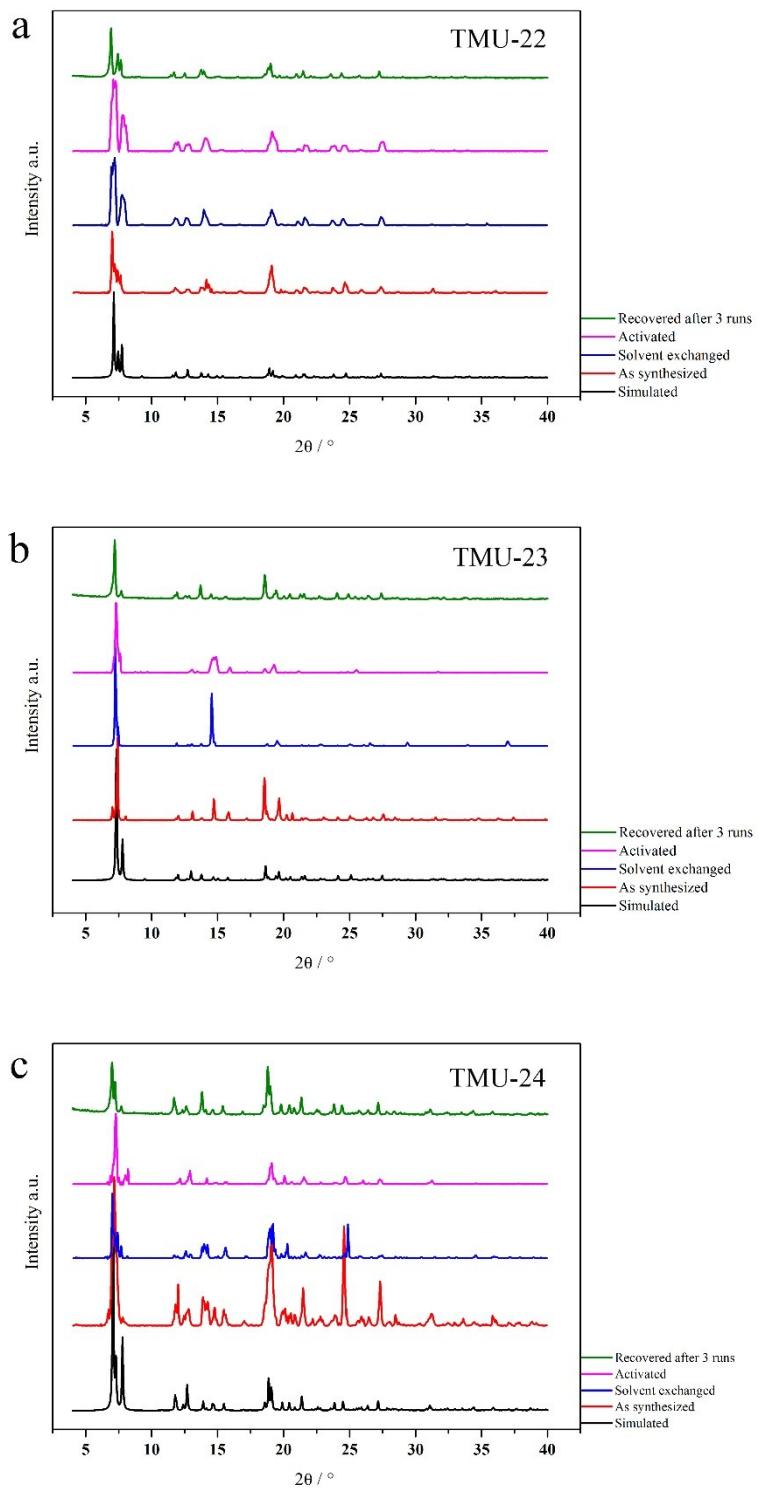


Fig. S2 The comparison of the PXRD patterns reveals that structural backbones of (a) **TMU-22**, (b) **TMU-23** and (c) **TMU-24** are retained after the activation processes and three runs catalytic processes, confirming that all the frameworks are robust. Simulated (black), as-synthesized (red), solvent exchanged (blue) and full activated (purple).

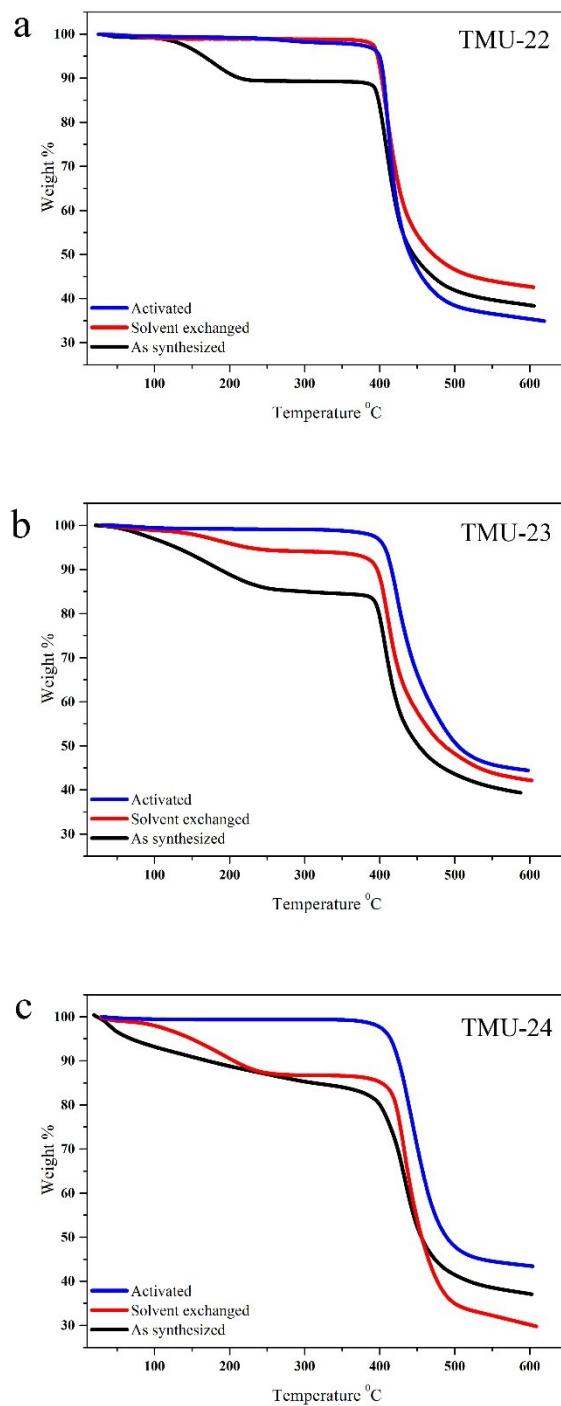


Fig. S3 Thermogravimetric profiles of (a) TMU-22, (b) TMU-23 and (c) TMU-24 isolated by conventional heating.

Table S1. Catalytic activity of **TMU-23** on condensation reaction ^a

Entry	Time (h)	Conversion (%) ^b
1	1	91.5
2	2	98.3
3	3	99.6
4	3	40 ^c

^a *Reaction conditions:* catalyst (**TMU-23**) 4 mol %, reaction temperature 25 ±1 °C, Benzaldehyde 1 mmol, EtOH 3 mL,

Time 3 h.^b Conversions are based on Benzaldehyde, ^c without catalyst

Table S2. Effect of solvents on condensation reaction ^a

Entry	Solvent	Conversion (%) ^b
1	EtOH	99.5
2	CH ₂ Cl ₂	12
3	THF	26
4	Toluene	7

^a *Reaction conditions:* catalyst (**TMU-23**) 4 mol %, temperature 25 ±1 °C, Benzaldehyde 1 mmol, solvent 3 mL.,

Reaction time 3 h, ^b Conversions are based on Benzaldehyde