

Supporting information

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Synthesis of UiO-66-NH₂

ZrCl₄ (300 mg) was dissolved into 60 mL DMF in a 250 ml flask, following sonication with ca. 1 min. The organic ligands BDC-NH₂ (232 mg) was subsequently added into the pre-dissolved ZrCl₄ solution and adequately stirred for fully dissolve ligands. 4 mL concentrated HCl and 75 μL deionized water were chosen as modulators to assist in the solvothermal synthetic procedure of UiO-66-NH₂. The above precursor solution was poured into a 100 mL stainless steel autoclave, completely sealed, and then heated to 393 K lasts 24 h. After complete solvothermal reaction, the resulting solid production was collected by filtering using nylon filter membrane (0.22 μm). The obtained solid was rinsed with DMF and anhydrous ethanol three times for each and the production was immersed in ethanol over night for thorough solvent exchange. Ultimately, the as-synthesized UiO-66-NH₂ powders were dried under vacuum, and further activated at 353 K for 6 h then at 383 K for 12-18 h under vacuum.

Synthesis procedure of PAAO

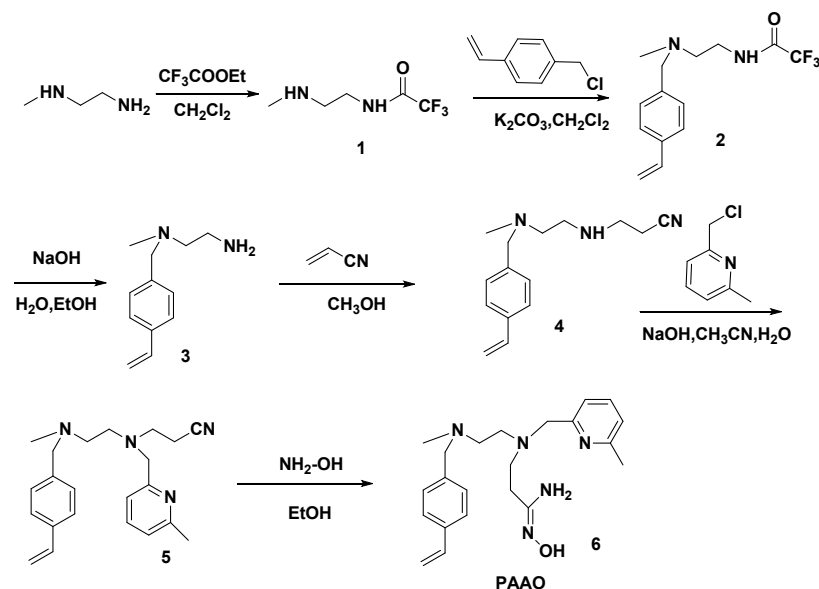


Fig. S1 Synthetic route of PAAO.

Synthesis of 2,2,2-trifluoro-N-(2-methylamino-ethyl)-acetamide (1)

Compound 1 was synthesized according to the literature[1]. Ethyl trifluoroacetate (4.8 g, 33.7 mmol) was added dropwise to a solution of N-methyl-ethylenediamine (2.5 g, 33.7 mmol) in CHCl_3 in an ice-water bath over 30 minutes. After being stirred for 2 days, the mixture was concentrated in vacuo to remove CHCl_3 , dissolved in CH_2Cl_2 and washed with saturated brine. The organic layer was dried over MgSO_4 , filtered, and evaporated to give the title compound 1 as a viscous oil (3.4 g, 60%). ^1H NMR (400 MHz, CDCl_3) δ = 3.45–3.40 (m, 2H, N- CH_2), 2.85–2.77 (m, 2H, N- CH_2), 2.44 (s, 3H, N- CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ = 157.64 (CF_3), 157.28 (CF_3), 117.40 (C=O), 114.54 (C=O), 49.51 (N-C), 38.80 (N-C), 35.71 (CH_3). HRMS (ESI) m/z calc'd for $\text{C}_5\text{H}_{10}\text{F}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$:171.0745, found 171.0743.

Synthesis of 2,2,2-trifluoro-N-(2-(methyl(4-vinylbenzyl)amino)ethyl)acetamide (2)

A mixture of the compound 1 (3.4 g, 20.1 mmol), N,N-diisopropylethylamine (1.2 g, 30 mmol) and 4-vinylbenzyl chloride (3.6 g, 23.6 mmol) and in 50 ml CHCl_3 was stirred at 40°C for 2 days. The mixture was evaporated, then purified with silica column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (100/1) to yield compound 2 as yellow oil (2.9 g, 52%). ^1H NMR (400 MHz, CDCl_3) δ = 7.37 (d, $J=7.9$, 2H, Ph), 7.22 (d, $J=7.9$, 2H, Ph), 6.70 (dd, $J=17.6$, 10.9, 1H, $\text{CH}=\text{CH}_2$), 5.74 (d, $J=17.6$, 1H, $\text{CH}=\text{CH}_2$), 5.24 (d, $J=10.9$, 1H, $\text{CH}=\text{CH}_2$), 3.52 (s, 2H, Ph- CH_2), 3.39 (dd, $J=10.1$, 4.9, 2H, N- CH_2), 2.54 (t, $J=5.8$, 2H, N- CH_2), 2.27 (s, 3H, N- CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ =157.21, 156.83 (C=O), 137.89 (Ph), 136.98 (Ph), 136.45 (Ph), 129.08 (Ph), 126.43 (C=C), 113.92 (CF_3), 62.02 (N-C), 53.94 (N-C), 41.84 (N-C), 36.85 (CH_3). HRMS (ESI) m/z calc'd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$:287.1371, found 287.1368.

Synthesis of N-methyl-N-(4-vinylbenzyl)ethane-1,2-diamine (3)

30 ml $\text{NaOH}/\text{H}_2\text{O}$ (500 mM) mixture was added dropwise to a ethanol solution of compound 2 (2.9 g, 10.1 mmol) in an ice-water bath. After stirred at room temperature overnight, the mixture was concentrated in vacuo to remove methanol, dissolved in CHCl_3 and washed with saturated brine. The organic layer was dried over MgSO_4 , filtered, and evaporated to give the compound 3 as a yellow oil (1.7 g, 90%). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 8.1$ Hz, 2H), 6.70 (dd, $J = 17.6$, 10.9 Hz, 1H), 5.72 (d, $J = 17.6$ Hz, 1H), 5.21 (d, $J = 10.9$ Hz, 1H), 2.77 (t, $J = 6.0$ Hz, 2H), 2.44 (t, $J = 6.0$ Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ = 138.91 (Ph), 136.67 (Ph), 136.42 (Ph), 129.17 (Ph), 126.14 (C=C), 113.45 (C=C), 62.36 (N-C), 60.02 (N-C), 42.16 (N-C), 39.50 (CH_3). HRMS (ESI) m/z calc'd for $\text{C}_{12}\text{H}_9\text{N}_2$ $[\text{M}+\text{H}]^+$:191.1548, found 191.1545.

Synthesis of 3-((2-(methyl(4-vinylbenzyl)amino)ethyl)amino)propanenitrile (4)

A solution of compound 3 (1.7 g, 8.9 mmol) and acrylonitrile (0.47 g, 8.9 mmol) in CH_3OH was stirred in an ice-water bath over 30 minutes, then the mixture was carried out overnight at ambient temperature. The solvent was evaporated under reduced pressure to obtain compound 4 (2.1 g, 96%) as a brown liquid. ^1H NMR (400 MHz, CDCl_3) δ = 7.36 (d, $J=8.1$, 2H, Ph), 7.26 (d, $J=8.1$, 2H, Ph), 6.70 (dd, $J=17.6$, 10.9, 1H, $\text{CH}=\text{CH}_2$), 5.73 (d, $J=17.6$, 1H, $\text{CH}=\text{CH}_2$), 5.22 (d, $J=10.9$, 1H, $\text{CH}=\text{CH}_2$), 3.50 (s, 2H, Ph- CH_2), 2.86 (t, $J=6.7$, 2H, N- CH_2), 2.72 (t, $J=5.8$, 2H, N- CH_2), 2.50 (dt, $J=13.4$, 6.4, 4H, N- CH_2 - CH_2 -CN), 2.21 (s, 3H, N- CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ = 138.71 (Ph), 136.60 (Ph), 129.19 (Ph), 126.21 (C=C), 118.81 (CN), 113.56 (C=C), 62.42 (N-C), 56.46 (N-C), 46.60 (N-C), 45.20 (N-C), 42.31 (N-C), 18.82 (C-CN). HRMS (ESI) m/z calc'd for $\text{C}_{15}\text{H}_{22}\text{N}_3$ $[\text{M}+\text{H}]^+$:244.1814, found 244.1812.

Synthesis of 3-((2-(methyl(4-vinylbenzyl)amino)ethyl)((6-methylpyridin-2-yl)methyl)amino)propanenitrile (5)

A mixture of the compound 4 (2.1 g, 8.7 mmol), 2-(chloromethyl)-6-methylpyridine (1.3 g, 9.2 mmol) and NaOH (0.7 g, 17.3 mmol) in 60 ml CH₃CN /water (5:1) was stirred at 40 °C for 2 days. The organic layer was separated and evaporated, purified with silica column chromatography eluting with CH₂Cl₂/MeOH (100/1) to yield compound 5 as yellow oil (0.95 g, 31%). ¹H NMR (400 MHz, CDCl₃) δ = 7.53 (t, J=7.7, 1H, Py-H), 7.34 (d, J=8.0, 2H, Py-H), 7.26 (dd, J=16.1, 7.8, 3H, Ph-H), 7.01 (d, J=7.6, 1H, Ph-H), 6.70 (dd, J=17.6, 10.9, 1H, CH=CH₂), 5.72 (d, J=17.6, 1H, CH=CH₂), 5.22 (d, J=10.9, 1H, CH=CH₂), 3.78 (s, 2H, Py-CH₂), 3.49 (s, 2H, Ph-CH₂), 2.89 (t, J=6.9, 2H, N-CH₂), 2.74 (t, J=6.7, 2H, N-CH₂), 2.59 – 2.53 (m, 2H, N-CH₂), 2.52 (s, 3H, Py-CH₃), 2.45 (t, J=6.9, 2H, CN-CH₂), 2.21 (s, 3H, N-CH₃). ¹³C NMR (101 MHz, CDCl₃) δ = 158.56, 157.64 (Py-N), 136.91 (Py), 136.648 (Py), 129.24 (Ph), 126.18 (Ph), 121.73 (C=C), 121.73 (CN), 113.55 (C=C), 62.49 (N-C), 60.59 (N-C), 55.46 (N-C), 52.14 (N-C), 50.20 (N-C), 42.65 (N-C), 24.48 (CH₃), 16.46 (C-CN). HRMS (ESI) m/z calc'd for C₂₂H₂₉N₄ [M+H]⁺:349.2392, found 349.2389.

Synthesis of N'-hydroxy-3-((2-(methyl(4-vinylbenzyl)amino)ethyl)(2-(6-methylpyridin-2-yl)ethyl)amino)propanimidamide (6)

A mixture of the compound 5 (0.95 g, 2.7 mmol), hydroxylamine (50% hydroxylamine by wt. in water, 2.0 ml, 32.4 mmol) in 30 ml EtOH was stirred at 60°C overnight. The mixture was evaporated, then purified with silica column chromatography eluting with dichloromethane/methanol/Et₃N (60/2/1) to yield the title compound 6 as brown oil. (0.9 g, 84%). ¹H NMR (400 MHz, CDCl₃) δ = 7.49 (t, J=7.7, 1H, Py-H), 7.34 (d, J=8.1, 2H, Py-H), 7.25 (d, J=11.3, 2H, Ph-H), 7.13 (d, J=7.6, 1H, Ph-H), 6.99 (d, J=7.6, 1H, Ph-H), 6.68 (dd, J=17.6, 10.9, 1H, CH=CH₂), 5.72 (d, J=17.6, 1H, CH=CH₂), 5.23 (d, J=10.9, 1H, CH=CH₂), 3.71 (s, 2H, Py-CH₂), 3.63 (s, 2H, Ph-CH₂), 2.75 (dt, J=12.7, 6.0, 4H, N-CH₂), 2.63 (t, J=6.2, 2H, N-CH₂), 2.48 (s, 3H, Py-CH₃), 2.34 (t, J=6.0, 2H, CN-CH₂), 2.26 (s, 3H, N-CH₃). ¹³C NMR (101 MHz, CDCl₃) δ = 158.09 (Py-N), 157.80 (Py-N), 155.52 (C=N), 136.93 (Py), 136.47 (Py), 136.17 (Ph), 129.85 (Ph), 126.28(Ph), 121.84 (Ph), 120.41(C=C), 113.97 (C=C), 61.59 (C-N), 60.19(C-N), 54.34 (C-N), 51.77 (C-N), 51.15 (C-N), 41.86 (C-N), 28.14 (CH₃), 24.32 (C-CN). HRMS (ESI) m/z calc'd for C₂₂H₃₂N₅O [M+H]⁺: 382.2607, found 382.2605.

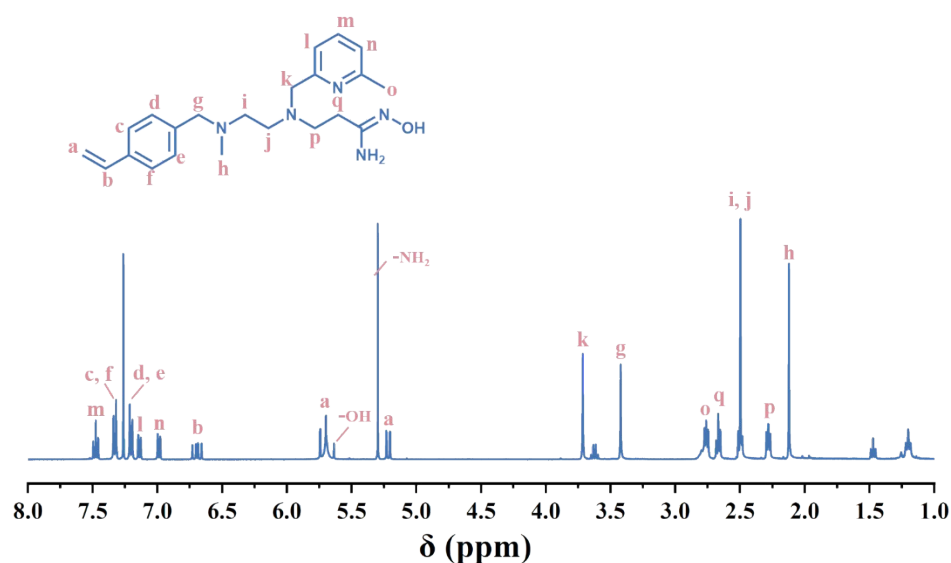


Fig. S2 ^1H NMR spectrum of PAAO monomer.

Preparation of MOFs_x@PHIPPs-n (x represents the weight ratio of MOFs to the whole system; n represents internal phase fractions)

Taking MOFs₁@PHIPPs-75 as an example, 0.2 g UiO-66-NH₂ were added to 15mL of water as aqueous phase, while the oil phase is composed of 1mL of MMA, 2mL of toluene, 0.6g of Span80, 2mL of DVB, and 0.3g of AIBN. The oil phase is placed in a round-bottom flask (50 mL) and the aqueous phase is slowly added dropwise at a rate of one drop per second under a rotation speed set at 400 rpm. Once all drops are added, the rotation speed is increased to 1000 rpm while introducing N₂ gas and stirring for ten minutes to form an emulsion paste MOFs₁@PHIPPs-75. Subsequently, the obtained MOFs₁@PHIPPs-75 undergoes polymerization at a temperature of 80°C under N₂ protection to yield solid polymer blocks. These blocks are subjected to three rounds (each lasting four hours) of methanol soaking for removal of Span80 followed by drying under atmospheric pressure in an oven set at 80°C for 24h and further activated at 383 K for 12 h under vacuum until obtaining the MOFs₁@PHIPPs-75. The other MOFs@PHIPPs with different MOF particle concentrations and internal phase fractions were synthesized using a same method. The detailed compositions of the Pickering emulsions are summarized in Table S1.

Table S1. A summary of various experimental conditions for synthesis of MOF@PHIPPs.

	Volume of water (ml)	Mass of UiO-66-NH ₂ (g)	Volume of MMA (ml)	Volume of DVB (ml)	Volume of toluene (ml)	Mass of Span 80 (g) ^a
MOFs ₁ @PHIP Ps-75	15	0.2	1	2	2	0.6
MOFs ₃ @PHIP Ps-75		0.6	1	2	2	0.6
MOFs ₅ @PHIP Ps-75		1.0	1	2	2	0.6
MOFs ₇ @PHIP Ps-75		1.4	1	2	2	0.6
MOFs ₉ @PHIP Ps-75		1.8	1	2	2	0.6
MOFs ₁₁ @PHIP Ps-75		2.2	1	2	2	0.6
MOFs ₁ @PHIP Ps-80	16	0.2	0.8	1.6	1.6	0.6
MOFs ₃ @PHIP Ps-80		0.6	0.8	1.6	1.6	0.6
MOFs ₅ @PHIP Ps-80		1.0	0.8	1.6	1.6	0.6
MOFs ₇ @PHIP Ps-80		1.4	0.8	1.6	1.6	0.6
MOFs ₉ @PHIP Ps-80		1.8	0.8	1.6	1.6	0.6
MOFs ₁₁ @PHIP Ps-80		2.2	0.8	1.6	1.6	0.6
MOFs ₁ @PHIP Ps-85	17	0.2	0.6	1.2	1.2	0.6
MOFs ₃ @PHIP Ps-85		0.6	0.6	1.2	1.2	0.6
MOFs ₅ @PHIP Ps-85		1.0	0.6	1.2	1.2	0.6
MOFs ₇ @PHIP Ps-85		1.4	0.6	1.2	1.2	0.6
MOFs ₉ @PHIP Ps-85		1.8	0.6	1.2	1.2	0.6
MOFs ₁₁ @PHIP Ps-85		2.2	0.6	1.2	1.2	0.6

Preparation of MOFs_x@PHIPMIPs_y-n (x represents the weight ratio of MOFs to the whole system; y represents the quality concentration of PAAO to the oil phase; n represents internal phase fractions)

Taking MOFs₇@PHIPMIPs₃₀-85 as an example. Firstly, equimolar functional monomers PAAO, Zn(NO₃)₂·6H₂O and template molecule DMNP were dissolved in methanol solution, then the mixture was evaporated under reduced pressure to obtain PAAO-Zn²⁺-DMNP complexes after stirring for 12 h at room temperature. A series of MOF₇@PHIPMIPs were further prepared using different amounts of functional complexes. Typically, taking MOFs₇@PHIPPs-75 as an example, 1.4g of UiO-66-NH₂ were dissolved in 17mL of water, while the oil phase is composed of 0.6mL of MMA, PAAO-Zn²⁺-DMNP containing 90mg of PAAO, 0.6mL of toluene, 0.6mL of acetonitrile, 0.6g of Span80, 1.2mL of DVB, and 0.3g of AIBN. The oil phase is placed in a round-bottom flask (50 mL) and the aqueous phase is slowly added dropwise at a rate of one drop per second under a rotation speed set at 400 rpm. Once all drops are added, the rotation speed is increased to 1000 rpm while introducing N₂ gas and stirring for ten minutes to form an emulsion paste MOFs₇@PHIPMIEs₃₀-85. Subsequently, the obtained MOFs₇@PHIPMIEs₃₀-85 undergoes polymerization at a temperature of 80°C under N₂ protection to yield solid polymer blocks. These blocks are subjected to three rounds (each lasting four hours) of methanol soaking for removal of Span80 followed by template elution procedure that cleaning with a mixture (v/v=1/2) of 100 mM NaOH aqueous solution and 4,4-bipyridyl methanol solution for 2h. The resulting solid blocks were washed with methanol and deionized water three times, and then reloaded zinc ions followed by drying under atmospheric pressure in an oven set at 80°C for 24h and further activated at 383 K for 12 h under vacuum until obtaining the MOFs₇@PHIPMIPs₃₀-85. The other MOF@PHIPMIPs were synthesized using a same method. The detailed experimental conditions for synthesis of MOF@PHIPMIPs are listed in Table S2 and S3, besides, it should be noted that we have identified that the MOF₇@PHIPPs series with an internal phase ratio of 85% exhibit superior performance after measuring the DMNP hydrolytic rates catalyzed by a series of MOFs_x@PHIPPs-n. Consequently, we maintained this proportion and further investigated the catalytic performance of MOFs₇@PHIPMIPs_y-85 by varying the proportion of functional monomers PAAO.

Table S2. A summary of various experimental conditions for synthesis of MOF@PHIPMIPs.

	Volume of water (ml)	Mass of UiO-66-NH ₂ (g)	Volume of MMA (ml)	Volume of DVB (ml)	Volume of toluene (ml)	Volume of acetonitrile (ml)	Mass of Span 80 (g) ^a	Mass of PAAO (mg)
MOFs ₇ @PHIPMIPs ₃₀₋₈₅			0.6	1.2	0.6	0.6	0.6	90
MOFs ₇ @PHIPMIPs ₆₅₋₈₅			0.6	1.2	0.6	0.6	0.6	195
MOFs ₇ @PHIPMIPs ₁₀₀₋₈₅	17	1.4	0.6	1.2	0.6	0.6	0.6	300
MOFs ₇ @PHIPMIPs ₁₃₅₋₈₅			0.6	1.2	0.6	0.6	0.6	405

Table S3. A summary of various experimental conditions for synthesis of MOF_x@PHIPMIP_{S100-n}

	Volume of water (ml)	Mass of UiO-66-NH ₂ (g)	Volume of MMA (ml)	Volume of DVB (ml)	Volume of toluene (ml)	Volume of acetonitrile (ml)	Mass of Span 80 (g)	Mass of PAAO (mg)
MOFs ₁ @PHIPMIP _{S100-75}	15	0.2	1	2	1	1	0.6	500
MOFs ₃ @PHIPMIP _{S100-75}		0.6	1	2	1	1	0.6	500
MOFs ₅ @PHIPMIP _{S100-75}		1.0	1	2	1	1	0.6	500
MOFs ₇ @PHIPMIP _{S100-75}		1.4	1	2	1	1	0.6	500
MOFs ₉ @PHIPMIP _{S100-75}		1.8	1	2	1	1	0.6	500
MOFs ₁₁ @PHIPMIP _{S100-75}		2.2	1	2	1	1	0.6	500
MOFs ₁ @PHIPMIP _{S100-80}	16	0.2	0.8	1.6	0.8	0.8	0.6	400
MOFs ₃ @PHIPMIP _{S100-80}		0.6	0.8	1.6	0.8	0.8	0.6	400
MOFs ₅ @PHIPMIP _{S100-80}		1.0	0.8	1.6	0.8	0.8	0.6	400
MOFs ₇ @PHIPMIP _{S100-80}		1.4	0.8	1.6	0.8	0.8	0.6	400
MOFs ₉ @PHIPMIP _{S100-80}		1.8	0.8	1.6	0.8	0.8	0.6	400
MOFs ₁₁ @PHIPMIP _{S100-80}		2.2	0.8	1.6	0.8	0.8	0.6	400
MOFs ₁ @PHIPMIP _{S100-85}	17	0.2	0.6	1.2	0.6	0.6	0.6	300
MOFs ₃ @PHIPMIP _{S100-85}		0.6	0.6	1.2	0.6	0.6	0.6	300
MOFs ₅ @PHIPMIP _{S100-85}		1.0	0.6	1.2	0.6	0.6	0.6	300
MOFs ₇ @PHIPMIP _{S100-85}		1.4	0.6	1.2	0.6	0.6	0.6	300
MOFs ₉ @PHIPMIP _{S100-85}		1.8	0.6	1.2	0.6	0.6	0.6	300
MOFs ₁₁ @PHIPMIP _{S100-85}		2.2	0.6	1.2	0.6	0.6	0.6	300

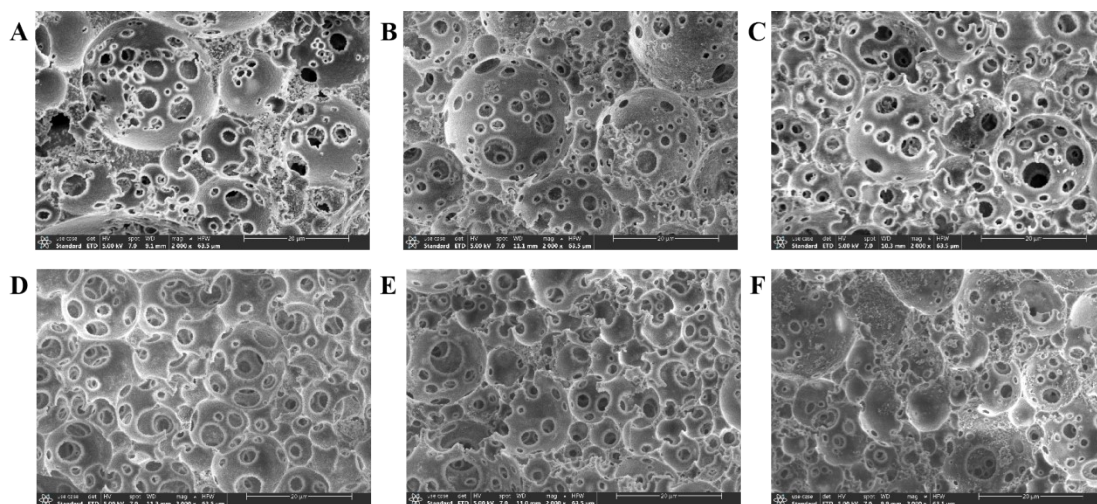


Fig. S3 The SEM of MOFs@PHIPMIPs in the internal ratio is 75% with different UiO-66-NH₂ contents: (A) 1wt%; (B) 3wt%; (C) 5wt%; (D) 7wt%; (E) 9wt%; (F) 11wt%.

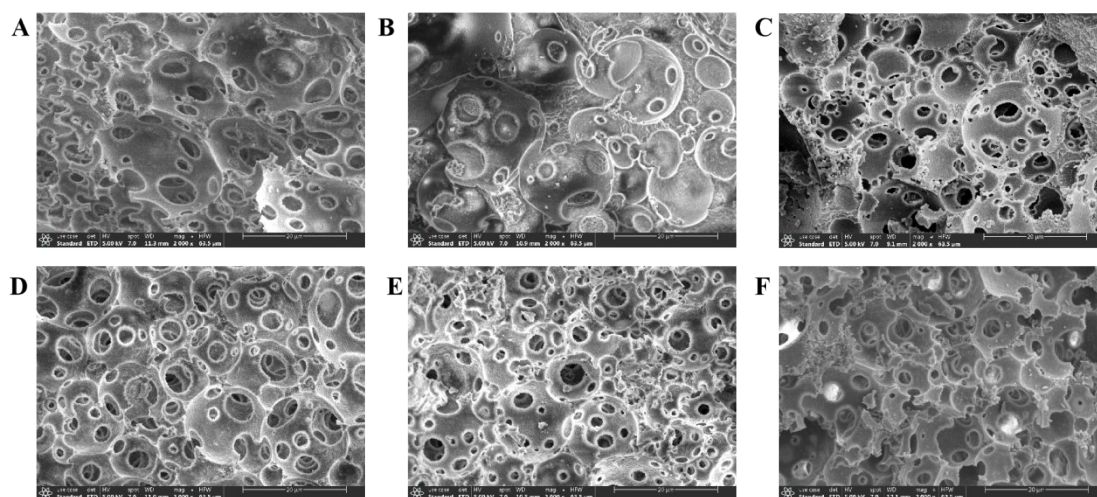


Fig. S4 The SEM of MOFs@PHIPMIPs in the internal ratio is 80% with different UiO-66-NH₂ contents: (A) 1wt%; (B) 3wt%; (C) 5wt%; (D) 7wt%; (E) 9wt%; (F) 11wt%.

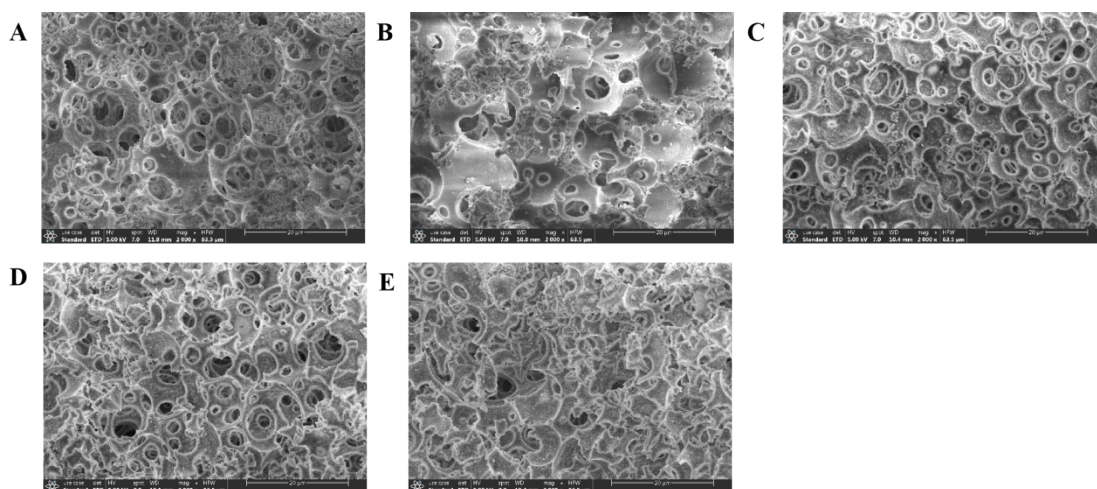
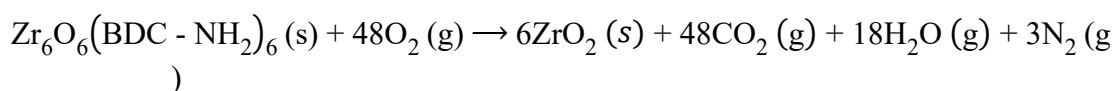


Fig. S5 The SEM of MOFs@PHIPMIPs in the internal ratio is 85% with different UiO-66-NH₂ contents: (A) 1wt%; (B) 3wt%; (C) 5wt%; (D) 7wt%; (E) 9wt%.

Calculation of the mass fraction of UiO-66-NH₂ in the MOF@ PHIPMIPs based on TGA

Thermogravimetric analysis (TGA) was carried out using NETZSCH TG209 apparatus under air atmosphere, the ramping temperature rate set as 10 °C min⁻¹ and the temperature range start from 298 K to 1073 K. The TGA data of MOFs_x@PHIPMs showed mass remaining when heated up to 800°C. In this stage, it is feasible to achieve complete elimination of organics, leaving behind a residue of zirconium oxide. The combustion reaction equation of dehydroxylated UiO-66-NH₂ illustrating the formation of zirconium oxide as follows:



Based on the crucial assumption: that the residue at 800°C in TGA experiment is ZrO₂, the mass fraction of UiO-66-NH₂ in MOFs_x@PHIPMIPs₁₀₀₋₈₅ could be calculated by the percentage content of residues obtained from the TGA curves according to the following formula:

$$\begin{aligned} & \text{Mass fraction}_{\text{UiO-66-NH}_2 \text{ in MOFs@PHIPMIPs}} \\ &= \frac{m_{\text{UiO-66-NH}_2 \text{ in MOFs@PHIPMIPs}}}{m_{\text{MOFs@PHIPMIPs}}} = \frac{m_{\text{ZrO}_2 \text{ remaining of MOFs@PHIPMIPs}}}{m_{\text{ZrO}_2 \text{ remaining of UiO-66-NH}_2}} \\ &= \frac{\text{Residue percentage of MOFs@PHIPMIPs at 800}^\circ\text{C}}{\text{Residue percentage of UiO-66-NH}_2 \text{ at 800}^\circ\text{C}} \end{aligned}$$

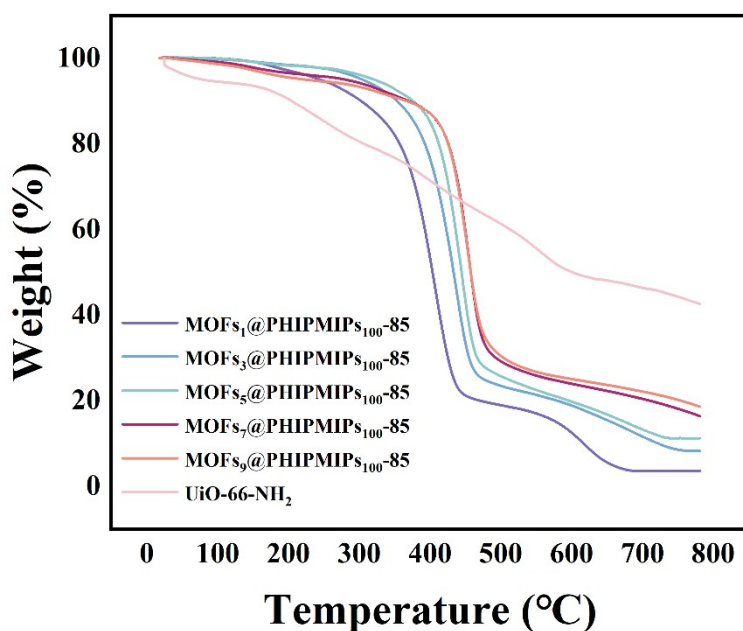


Fig. S6 TGA curves of MOFs_x@PHIPMIPs₁₀₀₋₈₅ (x=1, 3, 5, 7, 9) and UiO-66-NH₂.

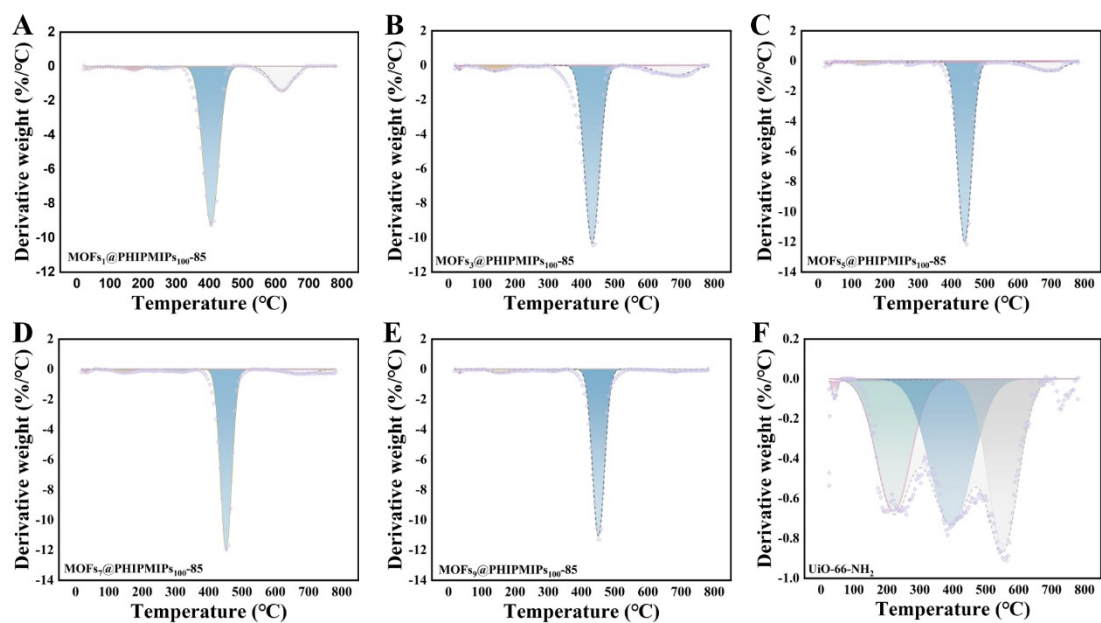


Fig. S7 DTG curves of $\text{MOFs}_x@PHIPMIPs_{100-85}$ ($x=1, 3, 5, 7, 9$) and UiO-66-NH_2 .

Table S4. The mass fraction of UiO-66-NH_2 in $\text{MOFs}_x@PHIPMIPs_{100-85}$.

Samples	Mass fraction of UiO-66-NH_2 in $\text{MOFs}_x@PHIPMIPs_{100-85}$ (wt%)
$\text{MOFs}_1@PHIPMIPs_{100-85}$	8.31
$\text{MOFs}_3@PHIPMIPs_{100-85}$	19.2
$\text{MOFs}_5@PHIPMIPs_{100-85}$	26.3
$\text{MOFs}_7@PHIPMIPs_{100-85}$	38.3
$\text{MOFs}_9@PHIPMIPs_{100-85}$	43.5

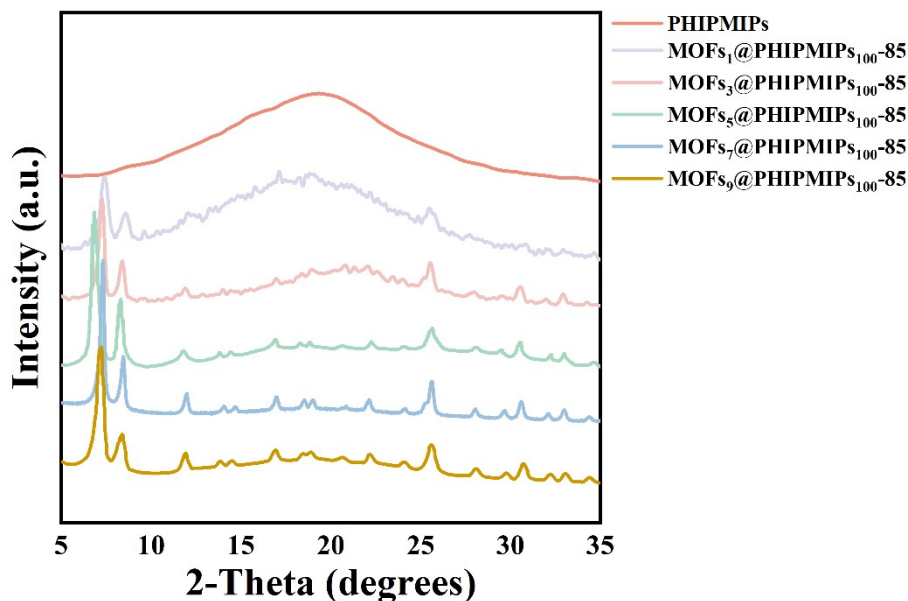


Fig. S8 XRD patterns of PHIPMIPs and a series of MOF_x@PHIPMIPs₁₀₀₋₈₅ with varying MOF loadings.

The construction method of standard curves for 4-nitrophenoxide

The calculation of conversion rate in our work was based on the monitoring of concentration of hydrolysis product 4-nitrophenoxide. In order to detect the variation of 4-nitrophenoxide, calibration curves for 4-nitrophenoxide were constructed by calibration standard solutions with a series of concentration gradients. Specifically, stock solutions of 0.3 M 4-nitrophenoxide were prepared in 10 ml ethanol solvent, and the stock solution were diluted by 0.45 M *N-ethyl-morpholine* buffer to give testing sample solutions with concentration ranges of 0.01-0.06 mM. Standard curves were constructed by plotting the UV-vis absorbance at 407 nm against analyte concentration and fitted by least-squares linear regression analysis, as shown in Figure S9.

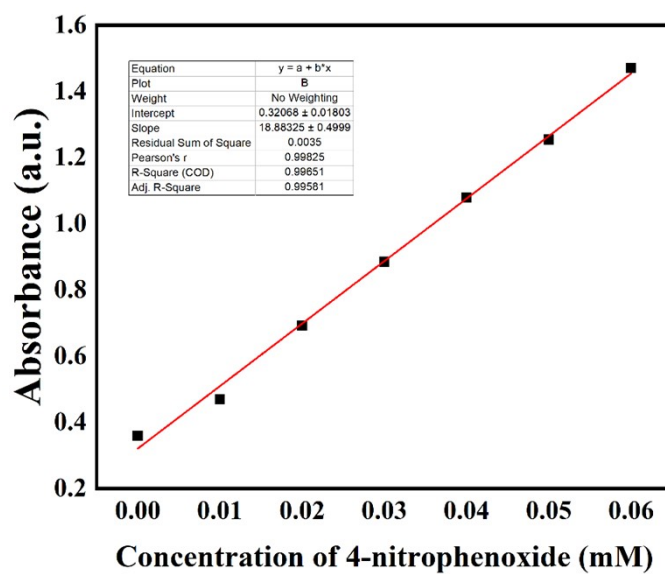


Fig. S9 Standard curve of UV-vis absorbance versus concentration of 4-nitrophenoxide.

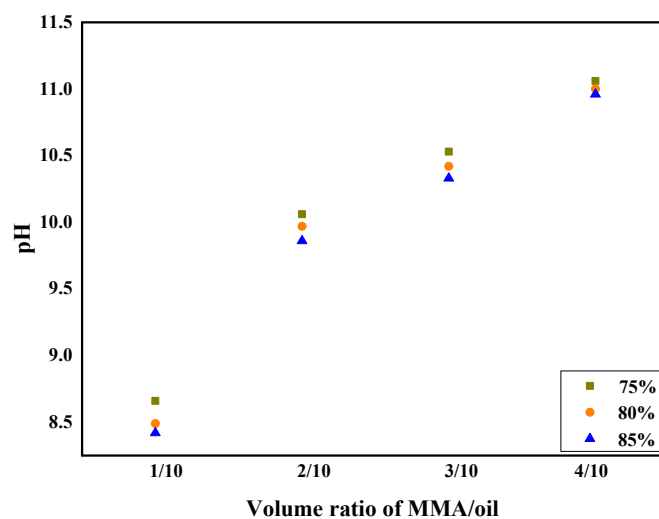


Fig. S10 The influence of MMA introduction quantity on MOF@PHIPMIPs pH.

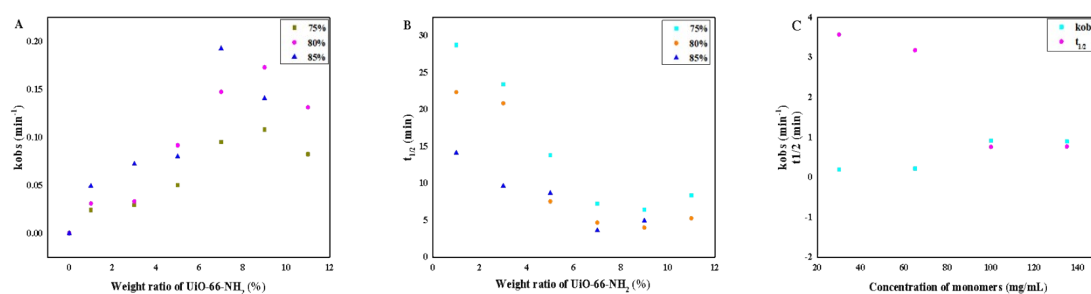


Fig. S11 k_{obs} and $t_{1/2}$ variation of MOF@PHIPPs (A, B) with different component allocation ratios of internal phase and UiO-66-NH₂; k_{obs} and $t_{1/2}$ variation of MOF@PHIPMIPs (C) with different component allocation ratios of functional monomers PAAO.

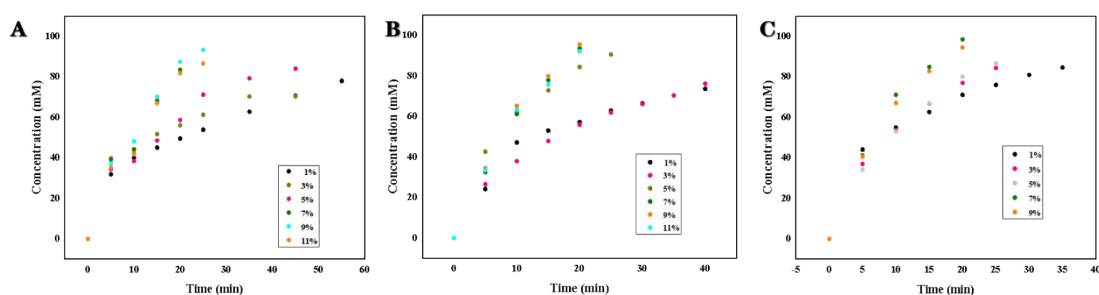


Fig. S12 Catalytic hydrolysis profiles of DMNP by MOF@PHIPPs with different internal phase ratio: (A) 75% internal phase ratio; (B) 80% internal phase ratio; (C) 85% internal phase ratio.

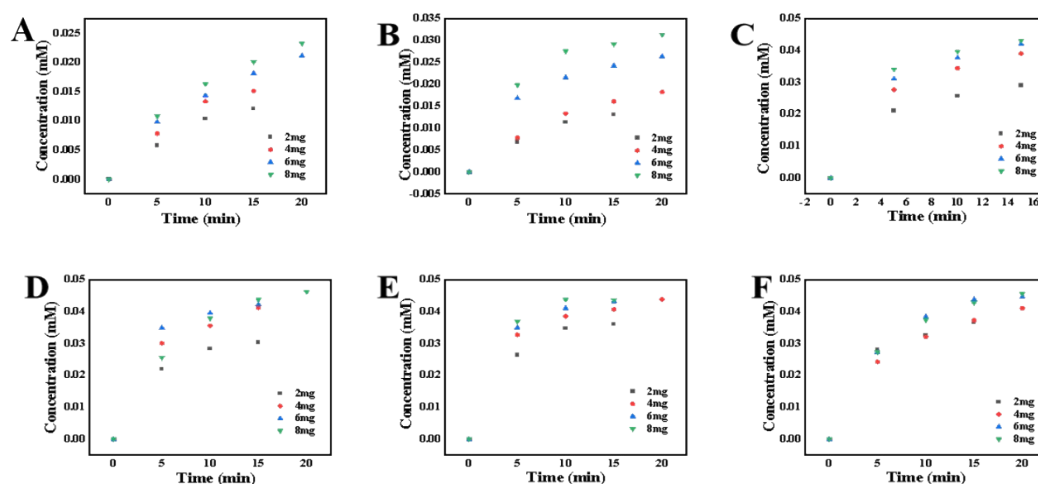


Fig. S13 Catalytic degradation kinetics of DMNP with different dosage of MOFs₁@PHIPPs-85 catalysts (A), MOFs₃@PHIPPs-85 catalysts (B), MOFs₅@PHIPPs-85 catalysts (C), MOFs₇@PHIPPs-85 catalysts (D), MOFs₉@PHIPPs-85 catalysts (E), MOFs₁₁@PHIPPs-85 catalysts (F).

Table S5. Catalysts dosage, catalytic reaction rates and half-lives for MOFs_x@PHIPPs-85 in DMNP degradation.

Sample	Dosage (mg)	k _{obs} (min ⁻¹)	t _{1/2} (min)
MOFs ₁ @PHIPPs-85	2	0.01508	45.96
	4	0.01901	36.46
	6	0.02208	31.39
	8	0.02531	27.39
MOFs ₃ @PHIPPs-85	2	0.01577	43.95
	4	0.01864	37.19
	6	0.02233	31.04
	8	0.03048	22.74
MOFs ₅ @PHIPPs-85	2	0.02229	31.10
	4	0.03571	19.41
	6	0.05373	12.90
	8	0.07192	9.63
MOFs ₇ @PHIPPs-85	2	0.03558	19.48
	4	0.06631	10.45
	6	0.08582	8.08
	8	0.10071	6.92
MOFs ₉ @PHIPPs-85	2	0.05338	12.96
	4	0.06872	10.08
	6	0.1328	5.22
	8	0.1414	4.90
MOFs ₁₁ @PHIPPs-85	2	0.05046	12.59
	4	0.07033	9.86
	6	0.09956	6.96
	8	0.11067	6.2

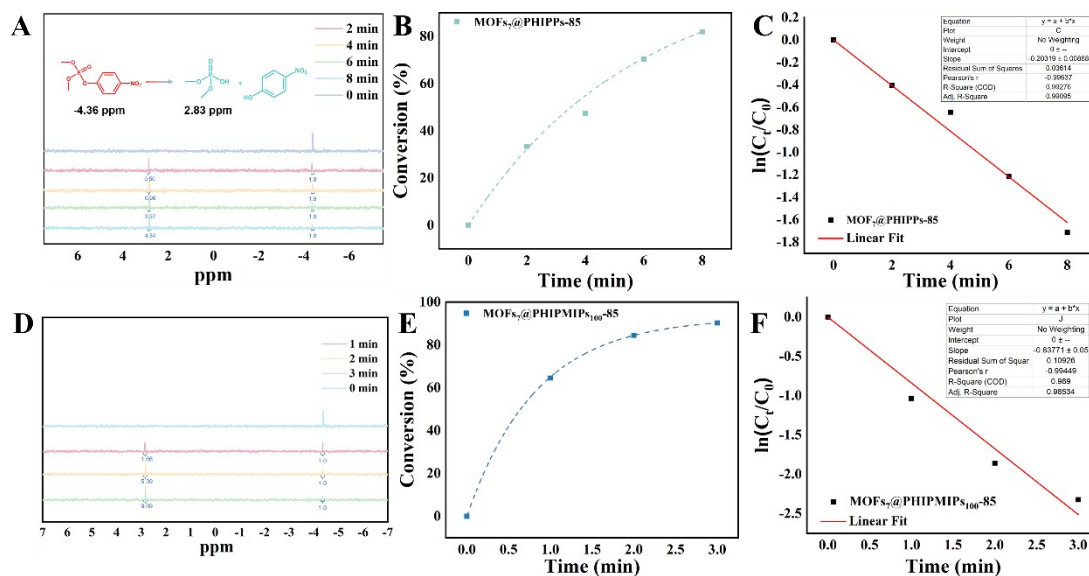


Fig. S14 ^{31}P NMR monitoring of catalytic degradation of (A-C) MOFs₇@PHIPPs-85; (D-F) MOFs₇@PHIPMIPs₁₀₀-85.

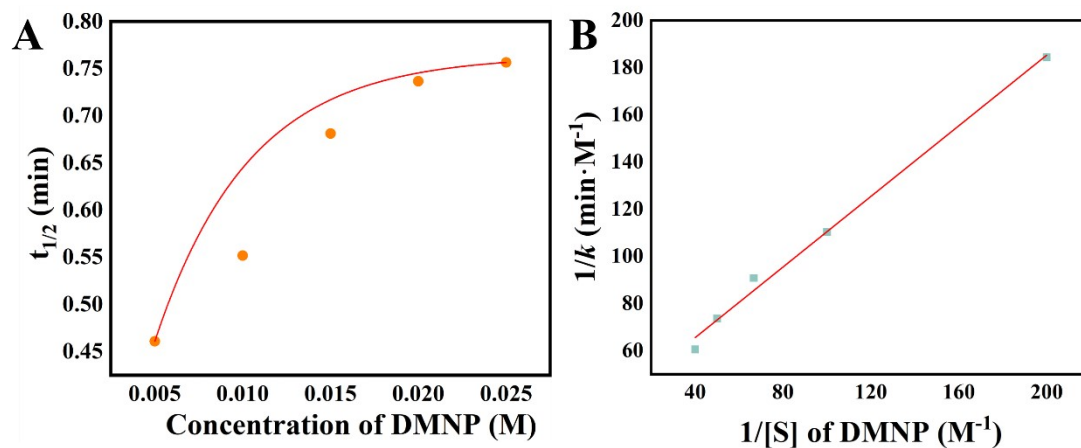


Fig. S15 Catalytic kinetics curves by plotting the half-lives versus concentration of DMNP; Lineweaver-Burk plot of hydrolysis kinetics data for DMNP catalyzed by MOFs₇@PHIPMIPs₁₀₀-85.

Table S6. Catalytic reaction rates of DMNP with different concentrations catalyzed by MOFs₇@PHIPMIPs₁₀₀₋₈₅.

c_{DMNP} (M)	$t_{1/2}$ (min)	k_{obs} (min^{-1})	k_{cat} ($\text{M}\cdot\text{min}^{-1}$)
0.005	0.4608	1.5041	0.00543
0.010	0.5517	1.2563	0.00906
0.015	0.6810	1.0178	0.01101
0.020	0.7365	0.9412	0.01358
0.025	0.7565	0.9162	0.01652

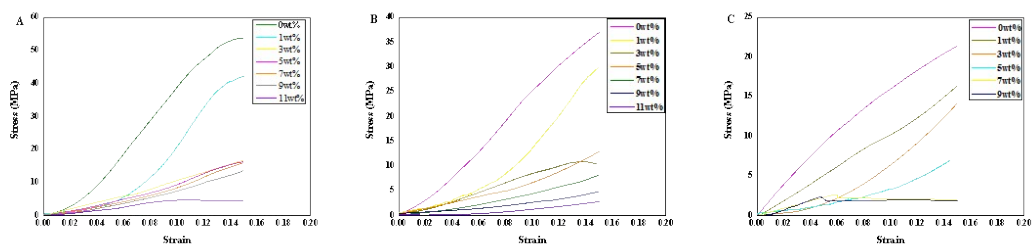


Fig. S16 Stress-strain curve of MOF@PHIPMIPs with different internal phase ratio and UiO-66-NH₂ content: (A) 75% internal phase ratio; (B) 80% internal phase ratio; (C) 85% internal phase ratio;

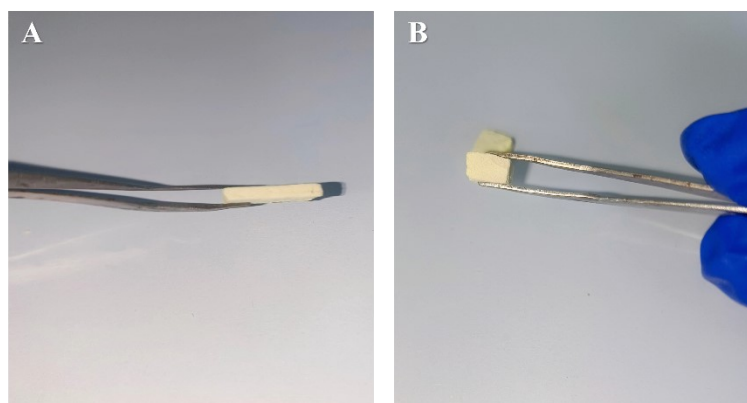


Fig. S17 Mchinability of MOFs₇@PHIPMIPs₁₀₀₋₈₅ examined by cutting manufacture.