

# Supporting Information

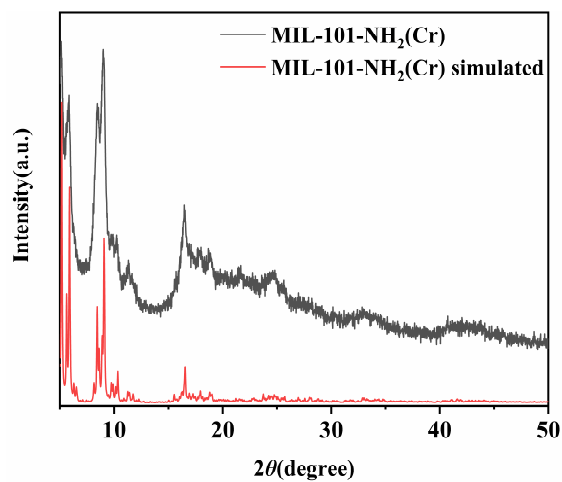
## **Metal-Organic Frameworks as the Efficient Pickering Interfacial Catalyst for Deacetalization-Knoevenagel Tandem Reaction**

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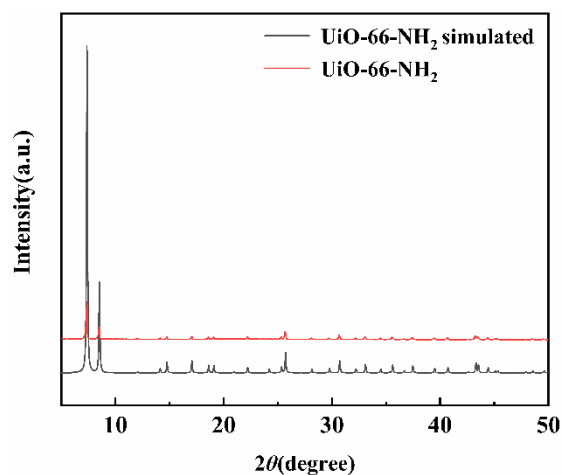
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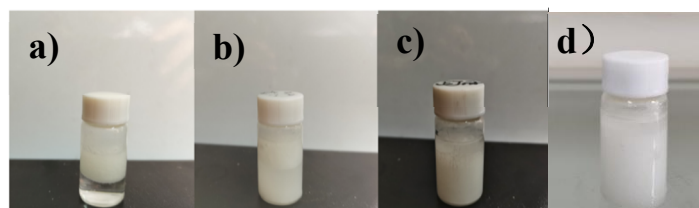
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**Figure S1.** PXRD patterns of MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Cr)-NH<sub>2</sub> simulated.



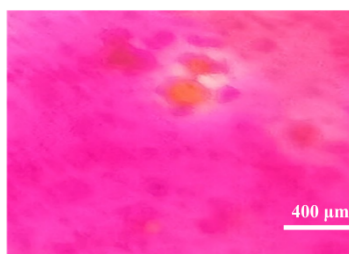
**Figure S2.** PXRD patterns of UiO-66(Zr)-NH<sub>2</sub>, UiO-66(Zr)-NH<sub>2</sub> simulated.



**Figure S3.** Photographs of Organic phase-water emulsions stabilized by 50mg ZIF-8: The vial contains (a) 2 mL of cyclohexane and 3 mL of water ; (b) 2 mL of n-hexane and 3 mL of water; (c) 2 mL n-butanol of and 3 mL of water. (d) 2 mL toluene of and 3 mL of water.



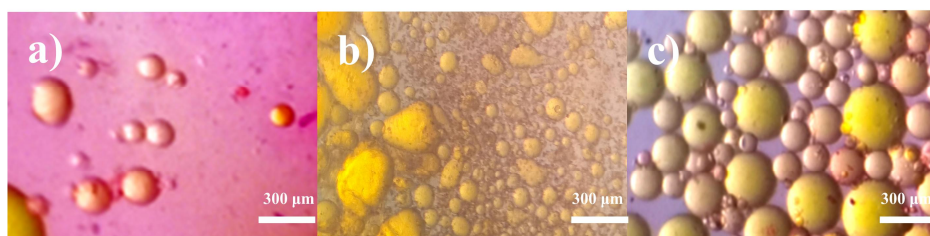
**Figure S4.** Optical microscope images of the 40 mg ZIF-8 stabilized Pickering emulsion with a water-to-toluene ratio of 3:2 and the emulsion stained with Rhodamine B and methyl red.



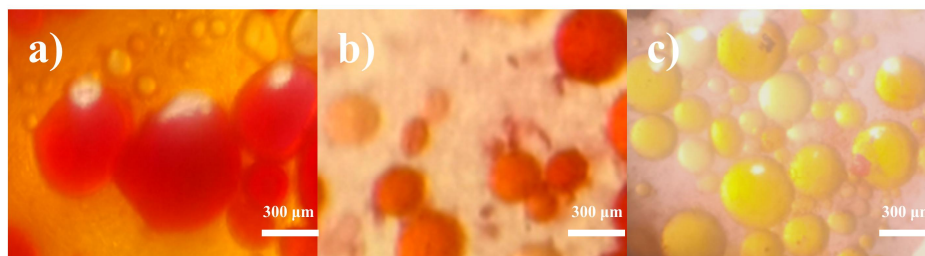
**Figure S5.** Optical microscope images of the 60 mg ZIF-8 stabilized Pickering emulsion with a water-to-toluene ratio of 3:2 and the emulsion stained with Rhodamine B and methyl red.



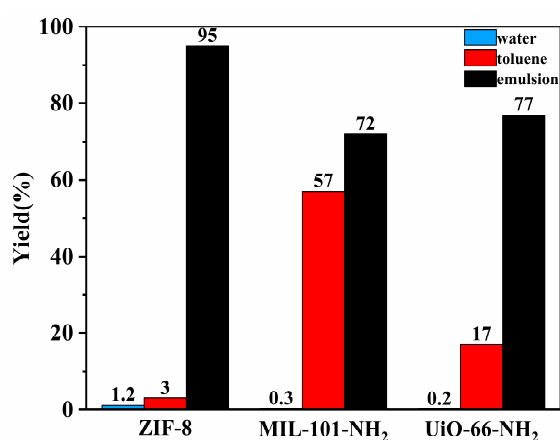
**Figure S6.** Photographs of the toluene-water emulsion stabilized by 50 mg ZIF-8( photograph was taken after standing for 3 weeks).



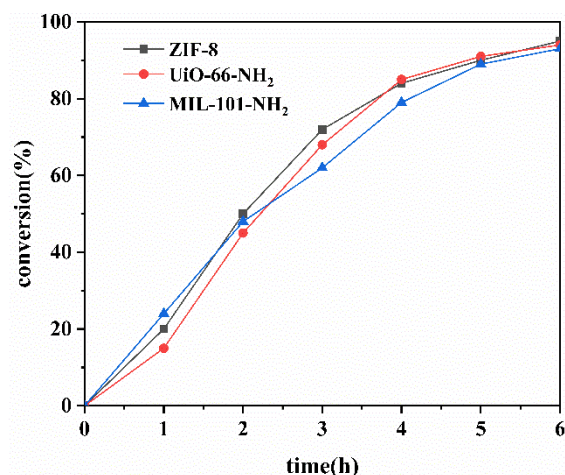
**Figure S7.** Optical microscope images of 50 mg MIL-101(Cr)-NH<sub>2</sub> stabilized Pickering emulsions stained with Rhodamine B and methyl red with different water-to-toluene ratios of (a) 3:2 (b) 1:1 and (c) 2:3.



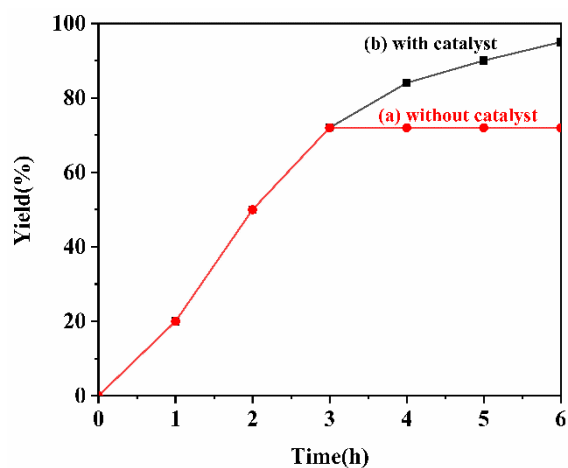
**Figure S8.** Optical microscope images of 50 mg UiO-66(Zr)-NH<sub>2</sub> stabilized Pickering emulsions stained with Rhodamine B and methyl red with different water-to-toluene ratios of (a) 3:2 (b) 1:1 and (c) 2:3.



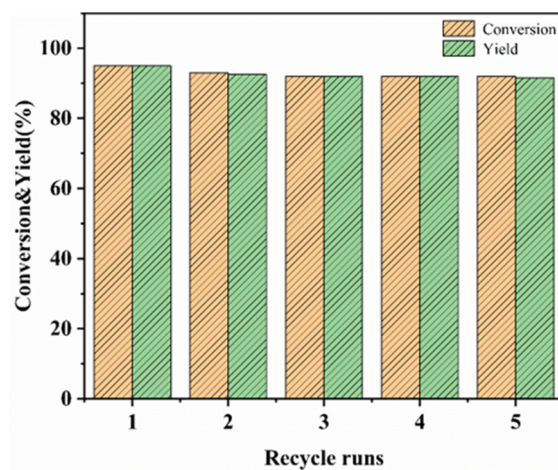
**Figure S9.** The yield of deacetalization-Knoevenagel reaction by ZIF-8, UiO-66(Zr)-NH<sub>2</sub>, and MIL-101(Cr)-NH<sub>2</sub> in water, toluene, and emulsion respectively. Reaction conditions: benzaldehyde dimethyl acetal (1 mmol) and malononitrile (1.5 mmol), 5.0 mL Pickering emulsion (3 mL water, 2 mL toluene), reaction time (6 h), reaction temperature: 353 K, catalyst (50 mg). The yield was determined by GC.



**Figure S10.** Time conversion diagrams for the catalytic deacetalisation-Knoevenagel tandem reactions of ZIF-8, UiO-66-NH<sub>2</sub> and MIL-101-NH<sub>2</sub> in their respective optimum water-to-oil ratio emulsions.



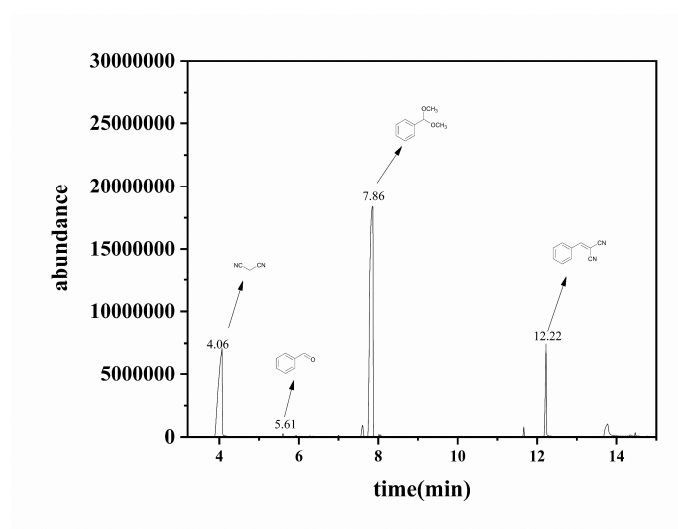
**Figure S11.** Hot filtration tests of the ZIF-8 catalyst for deacetalization-Knoevenagel tandem reaction: (a) catalyst was filtered out after the reaction lasted for 3 hours. (b) Normal reaction process.

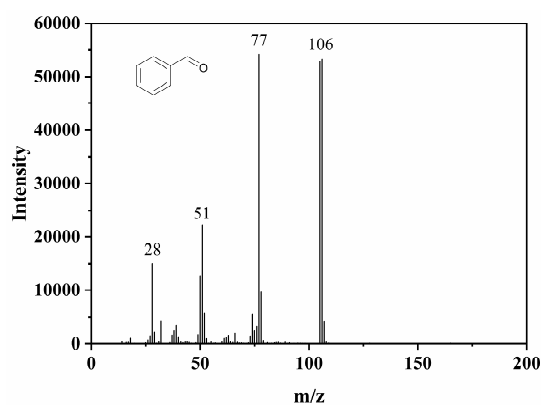
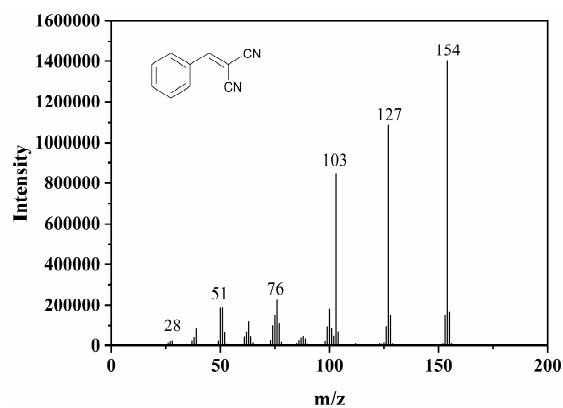


**Figure S12.** Recycle tests of ZIF-8 for deacetalization-Knoevenagel tandem reaction.



**Figure S13.** Optical microscope images of water (3 mL)-toluene (2 mL) emulsion stabilized by 50 mg ZIF-8 after the fifth catalytic run.





**Figure S14.** GC-MS spectrum of products after 2 hours of deacetalization-Knoevenagel tandem reaction by ZIF-8 in the emulsion.

**Table S1.** The surface areas, pore volumes, and pore sizes of the as-prepared catalysts.

Catalyst	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) <sup>a</sup>	$V_{\text{pore}}$ ( $\text{cm}^3/\text{g}$ ) <sup>b</sup>	Pore size (nm) <sup>c</sup>
MIL-101(Cr)-NH <sub>2</sub>	1990	1.61	3.24
UiO-66(Zr)-NH <sub>2</sub>	1044	0.72	2.76
ZIF-8	1211	0.65	2.14

<sup>a</sup>Specific surface area was measured by the BET method.

<sup>b</sup>Total pore volume

<sup>c</sup>Pore size determined by the BET method