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## **Supporting Information**

## CO<sub>2</sub>-Switchable amidine-modified ZIF-90 stabilized Pickering emulsions for controllable Knoevenagel condensation reaction

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Number of pages: 12 Number of figures: 26



**Figure S1** General procedure for the preparation of the amidine-modified ZIF-90.



Figure S2 XPS spectra (a), high-resolution XPS spectra of N 1s (b) and O 1s (c) for DMIAB-ZIF-90.



Figure S3 SEM image of the original ZIF-90.



**Figure S4** Photographs of the appearance of emulsion droplets in water and cyclohexane: (a) the DMIAB-ZIF-90-stabilized Pickering emulsion droplet dispersed in water, and (b) the emulsion droplet dispersed in cyclohexane.



**Figure S5** Photographs of the reversible switching between emulsification (a) and demulsification (b) of DMIAB-ZIF-90-stabilized Pickering emulsions ( $V_{\text{benzene}}/V_{\text{water}} = 3: 2$ ) driven by CO<sub>2</sub>.



**Figure S6** Photographs of the reversible switching between emulsification (a) and demulsification (b) of DMIAB-ZIF-90-stabilized Pickering emulsions ( $V_{\text{toluene}}/V_{\text{water}} = 3: 2$ ) driven by CO<sub>2</sub>.



**Figure S7** Photographs of the reversible switching between emulsification (a) and demulsification (b) of DMIAB-ZIF-90-stabilized Pickering emulsions ( $V_{n-hexane}/V_{water} = 3: 2$ ) driven by CO<sub>2</sub>.



**Figure S8** Photographs of the reversible switching between emulsification (a) and demulsification (b) of DMIAB-ZIF-90-stabilized Pickering emulsions ( $V_{n-heptane}/V_{water} = 3: 2$ ) driven by CO<sub>2</sub>.



Figure S9 Conductivity of 1 wt% DMIAB-ZIF-90 dispersed in water as a function of time by alternating treatment with  $CO_2$  and  $N_2$ .



**Figure S10** The variation of 2-benzylidenemalononitrile yield with reaction time in DMIAB-ZIF-90-based Pickering emulsion at 25 °C.



Figure S11 <sup>1</sup>H NMR spectra of 2-benzylidenemalononitrile.



Figure S12 XRD patterns of DMIAB-ZIF-90 before and after each catalytic run.



Figure S13  $N_2$  adsorption-desorption isotherms of DMIAB-ZIF-90 after three cycles of catalysis.



Figure S14 Proposed mechanism for the Knoevenagel condensation catalyzed by DMIAB-ZIF-90.



Figure S15 <sup>1</sup>H NMR spectra of 2-(2-nitrobenzylidene)malononitrile.



Figure S16 <sup>1</sup>H NMR spectra of 2-(4-methylbenzylidene)malononitrile.





Figure S17 <sup>1</sup>H NMR spectra of 2-(4-nitrobenzylidene)malononitrile.



Figure S18 <sup>1</sup>H NMR spectra of 2-(4-chlorobenzylidene)malononitrile.



Figure S19 <sup>1</sup>H NMR spectra of 2-(4-bromobenzylidene)malononitrile.



Figure S20 <sup>1</sup>H NMR spectra of 2-(3-nitrobenzylidene)malononitrile.



Figure S21 <sup>1</sup>H NMR spectra of 2-(3-chlorobenzylidene)malononitrile.



Figure S22 <sup>1</sup>H NMR spectra of 2-(furan-2-ylmethylene)malononitrile.



Figure S23 <sup>1</sup>H NMR spectra of 2-(4-methoxybenzylidene)malononitrile.



Figure S24 <sup>1</sup>H NMR spectra of 2-cyclohexylidenemalononitrile.



methoxyphenyl)methylidene]propanedinitrile.