Electronic Supplementary Information （ESI）

Superhydrophobic MOF/Polymer Composite with Hierarchical Porosity for Boosting Catalytic Performance in Humid Environment

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1. Experimental Section/Methods

1.1 General Information

All chemicals were purchased from commercial sources and used without further purification. PXRD patterns were remeasured on a Japan Rigaku Miniflex 600 rotation anode X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation ($\lambda = 1.54$ Å) and setting the 0.03^o of step sizes in the 2θ range of 5 to 40°. Fourier transform infrared (FT-IR) spectra of samples were recorded at room temperature and performed on a PerkinElmer. The average spectra were scanned sixteen times in the range of 4000-400 cm^{-1}. Raman spectra were obtained using a Renishaw Confocal micro-Raman Spectrometer equipped with a HeNe (633 nm) laser operating at 10% power. The size and morphology details of the materials were determined by scanning electron microscope (SEM) Hitachi 3030 equipped with an energy dispersive X-ray detector (EDX). Transmission electron microscope (TEM) and selected-area electron diffraction (SAED) images of the typical samples were captured with Carl Zeiss Libra 200. Thermogravimetric (TG) analysis was performed on a PerkinElmer/Pyris1 machine in the temperature range of room temperature to 750 ^oC at 5 ^oC min^{-1} under N_2 atmosphere. Wetting properties of as-prepared samples were characterized by obtaining their contact angles with liquid water using Biolin Attension Theta. Nitrogen adsorption isotherm measurements were measured using 3H-2000PS1 analyzer (Beishide Instrument Co., China) at 77 K to determine the surface area of the samples and the pore size distribution was calculated using NLDFT models. The products of Friedel-Crafts alkylation reaction were monitored by ^1H NMR spectra recorded on a Varian-300 MHz NMR spectrometer.

1.2 Catalyst Preparation

1.2.1 Preparation of ZIF-8. The synthetic process of ZIF-8 was according to the previous literature with a little modification.[S1] Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol) of was dissolved in 350 mmol of MeOH to form A solution. 4 mmol of 2-Mim with another 350 mmol MeOH was mixed to form B solution. Later, B solution was added into the A solution and vigorously stirred for 24 h. The resulted ZIF-8 particles were separated by centrifugation at 14000 rpm for 10 min and washed with MeOH several times. The obtained ZIF-8 powder was dried in vacuum at 60 °C for 24 h.

1.2.2 Preparation of PDVB-vim. In a typical synthesis, 30 mmol of divinylbenzene (DVB) and 10 mmol of 1-vinylimidazole (vim) were added to a solution containing 0.85 mmol of

azodiisobutyronitrile (AIBN) and 30 mL of ethyl acetate. The formed clear solution was stirring at room temperature for 3 h, the mixture was hydrothermally treated at 100 °C for 24 h, followed by slow evaporation of the solvent at room temperature for 2 days. The obtained solid block material was washed with ethyl acetate and MeOH several times, respectively. The resulted PDVB-vim was dried overnight at 75 °C.[S2]

1.2.3 Preparation of ZIF-8/PDVB-vim composite. A certain amount of PDVB-vim was dispersed in 350 mmol MeOH and then 4 mmol of 2-Mim was added for ultrasonic treatment for 60 min. A solution consisting of 0.5 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ and 350 mmol of MeOH was added into the above solution and vigorously stirred for 24 h. The ZIF-8/PDVB-vim composite was separated from the milky dispersion by centrifugation and washing with fresh MeOH. This procedure was repeated twice and dried at 60 °C in air.

1.2.4 UV-Vis Spectroscopy Test. To investigate its adsorption properties, 10 mg of ZIF-8/PDVB-vim composite was well dispersed in MeCN (5 mL) and placed in a centrifuge tube by stirring for 30 minutes. To the stable suspension of samples, a freshly prepared trans-*β*-nitrostyrene or indole solution (1 mL, 1 mM in MeCN) was added.

1.3 Catalytic Performance Evaluation.

The liquid-phase Friedel-Crafts reaction between aromatic compounds and electron-deficient alkenes including indole and trans-*β*-nitrostyrene was performed in a 10 mL Synthware glass equipped a condenser-west tube. The reaction tests were carried out at room temperature under atmosphere for 24 h. Typically, indole (180 mg, 1.5 mmol), trans-*β*-nitrostyrene (150 mg, 1.0 mmol), and catalyst 5 mol% based on Zn(II) center were added to 5 mL of CH_3CN. Reaction mixtures solvent was evaporated under vacuum and the obtained dry product was monitored by ^{1}H NMR spectroscopy. After reaction, the catalyst was separated by centrifugation, washed with MeOH several times, dried under vacuum and then reused for the next run of the reaction as described above.

1.4 Oil-Water Separation and Recyclability Experiments.

The gravity-assisted oil–water separation method was used. After ZIF-8/PDVB-vim composite was fixed in a glass funnel, a blend of chloroform (100 mL) and dyed water (with methylene blue, 100 mL) was poured from the funnel top. Collecting the chloroform and dyed water that had been separated came from the top and bottom funnel, respectively.

The separation efficiency (%) was then calculated:

$$\text{Separation efficiency (\%)} = V_{terminative}/V_{original} \times 100\%$$

where the volumes of chloroform before and after separation experiments are denoted by $V_{original}$ and $V_{terminative}$, respectively. The cycling performance of super-hydrophobic filter paper fixed with ZIF-8/PDVB-vim composite was evaluated by performing 30 replicate experiments of chloroform and dyed water separation.
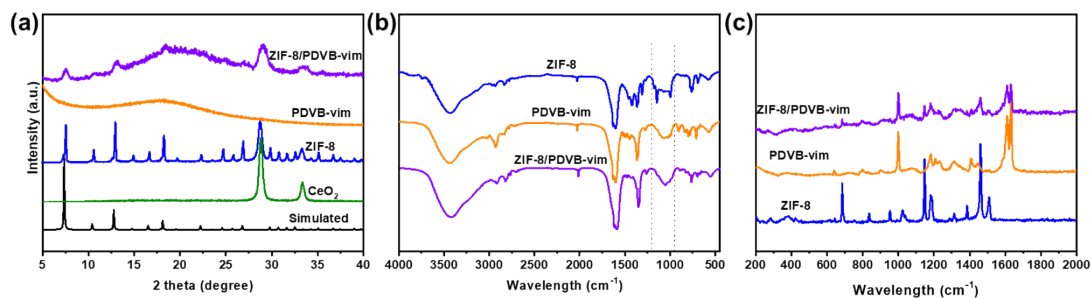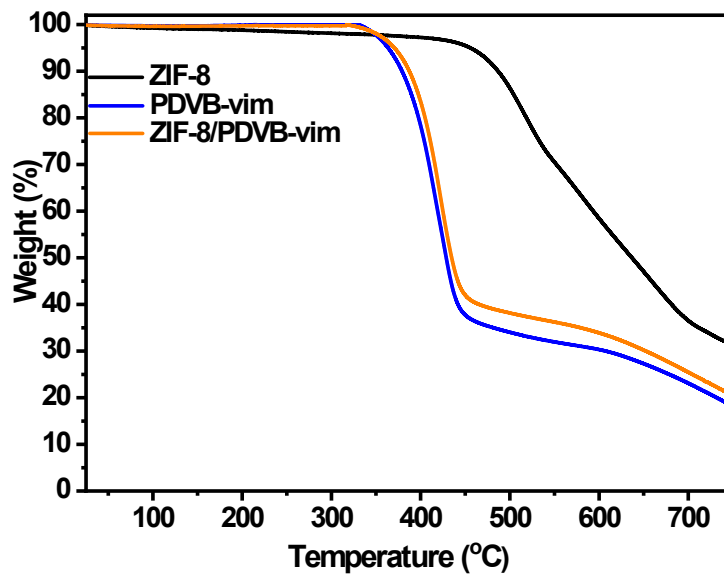

Fig. S1 (a) the PXRD patterns, (b) FT-IR spectra and (c) Raman spectra of ZIF-8, PDVB-vim and ZIF-8/PDVB-vim composite (nano CeO_2 as an internal standard).
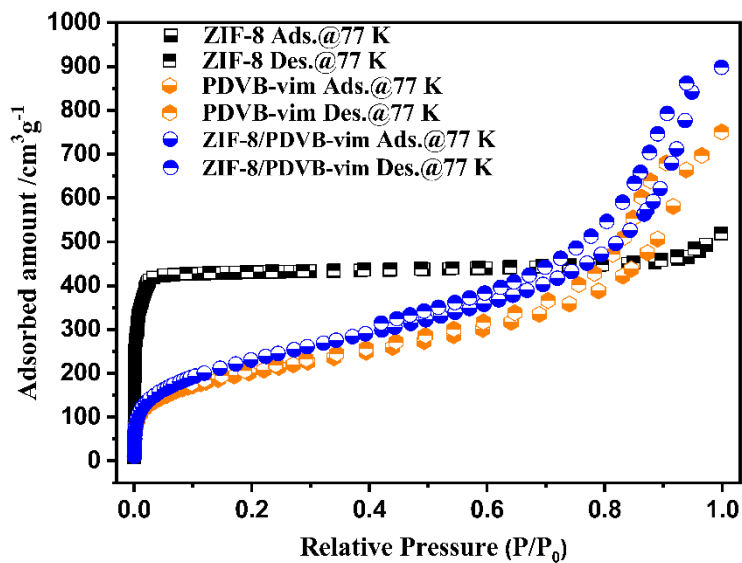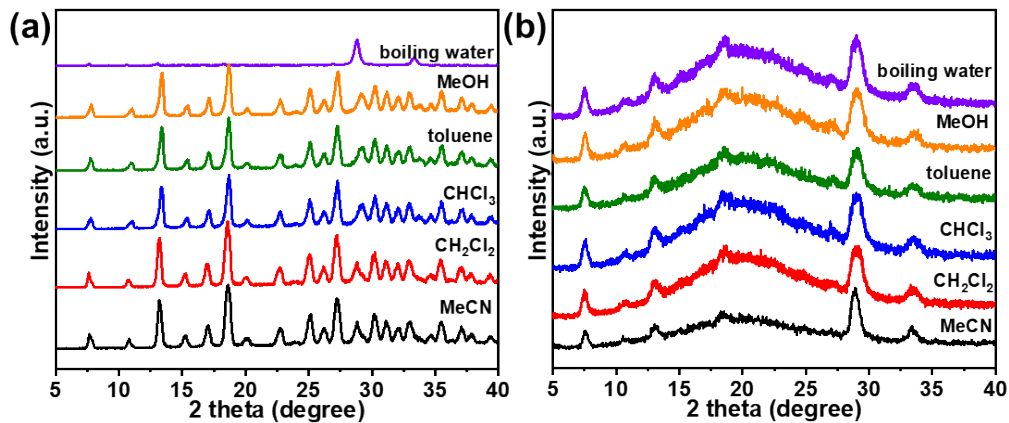

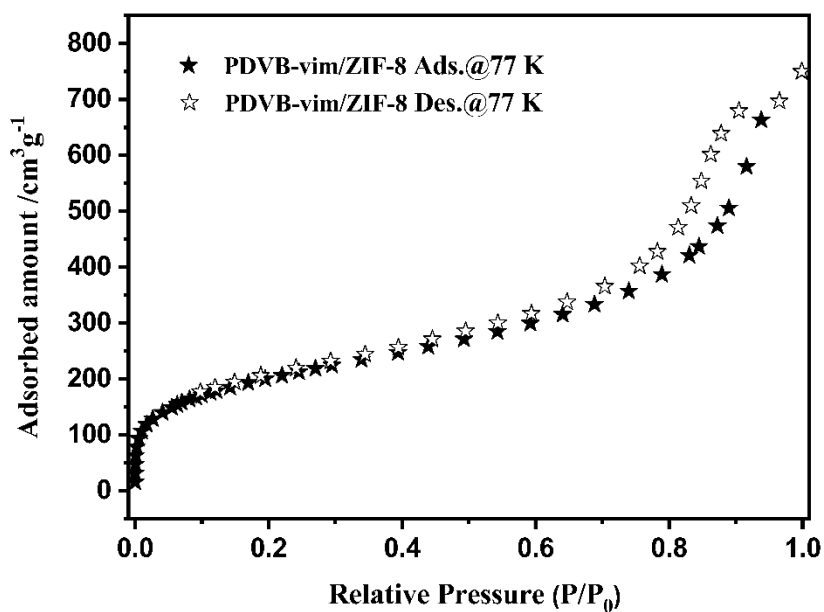**Fig. S2** N_2 adsorption isotherm of ZIF-8, PDVB-vim and ZIF-8/PDVB-vim composite.
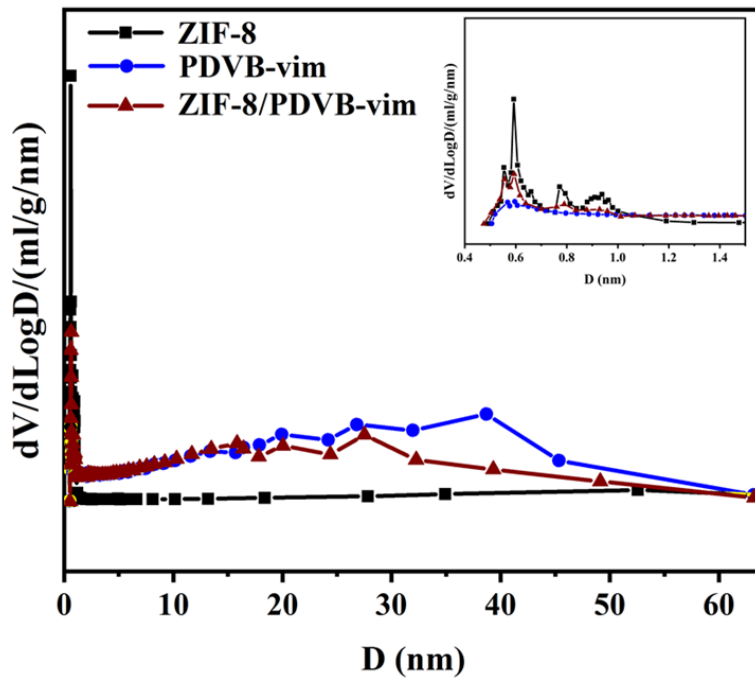
Fig. S3 The pore size distributions based on NLDFT models of ZIF-8, PDVB-vim and ZIF-8/PDVB-vim composite.
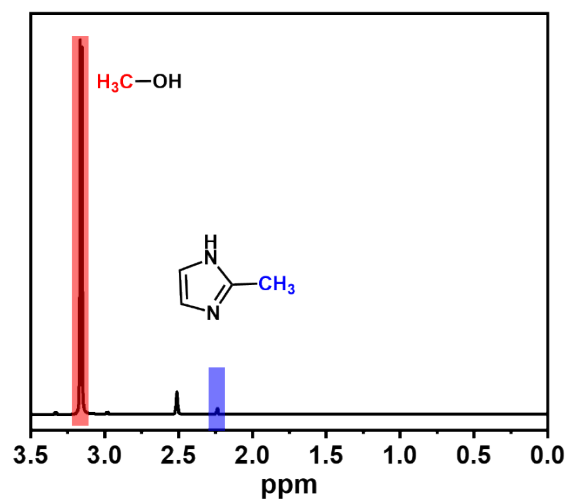

Fig. S4 Thermogravimetric analyses (TGA) of ZIF-8, PDVB-vim and ZIF-8/PDVB-vim composite.
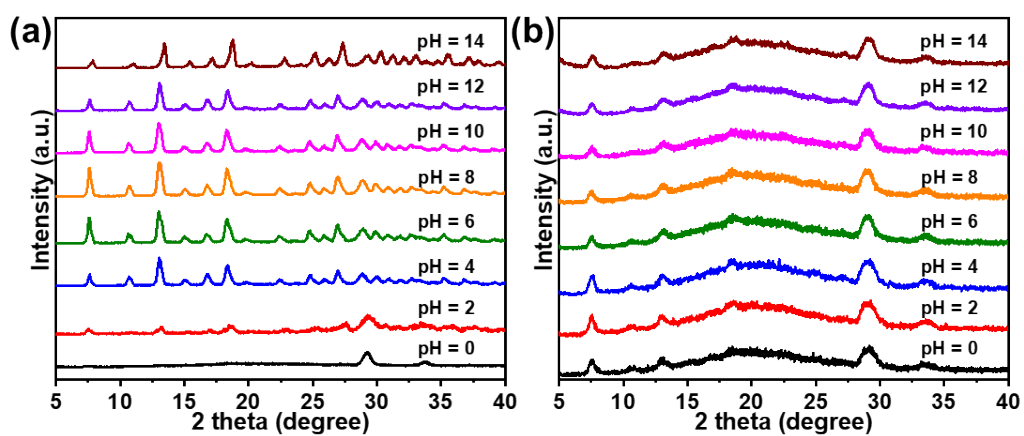
Fig. S5 The chemical stability of ZIF-8 and ZIF-8/PDVB-vim composite immersed in MeOH, CH_2Cl_2, $CHCl_3$, Toluene, MeCN, even in boiling water for 20 day (nano CeO_2 as an internal standard).
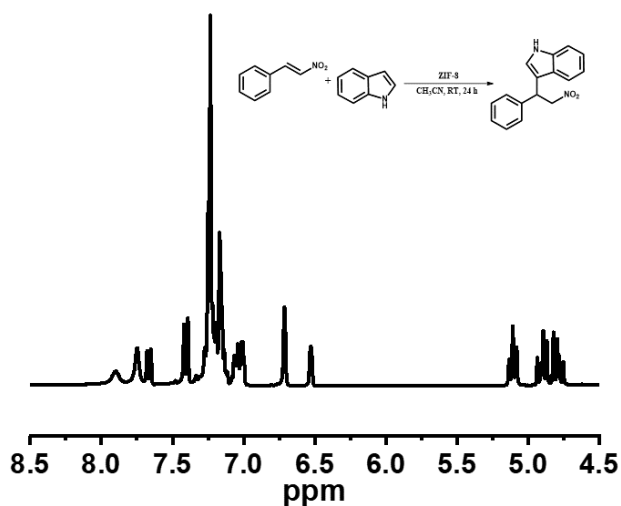

Fig. S6 N_2 adsorption isotherm of ZIF-8/PDVB-vim composite after boiling water treatment.

Fig. S7 The ^{1}H NMR of ZIF-8/PDVB-vim composite after immersed in boiling water for 24 h.

Fig. S8 The pH durability of ZIF-8 and ZIF-8/PDVB-vim composite in a range of pH 0-14 (nano CeO_2 as an internal standard).

Fig. S9 Example of integration in the ^{1}H NMR spectrum for the determination of % conversion of the reaction product catalyzed by ZIF-8 (Table 1, Entry 1).

## Calculation of the % conversion in the Friedel-Crafts reaction

The α-vinyl and *β*-vinyl proton of trans-*β*-nitrostyrene (reactant) appears at δ 8.01-8.06 ppm and the aliphatic proton of the product 3-(2-nitro-1-phenylethyl)-1H-indole appears at δ 4.5-5.3 ppm. Total amount of complex: unreacted trans-*β*-nitrostyrene + 3-(2-nitro-1-phenylethyl)-1H-indole = 1+ 3.24= 4.24

Percentage of the unreacted trans-*β*-nitrostyrene: (100/4.24)% ≈ 23.6%

Conversion of trans-*β*-nitrostyrene = yield of 3-(2-nitro-1-phenylethyl)-1H-indole = (100-23.6)% = 76.4%.
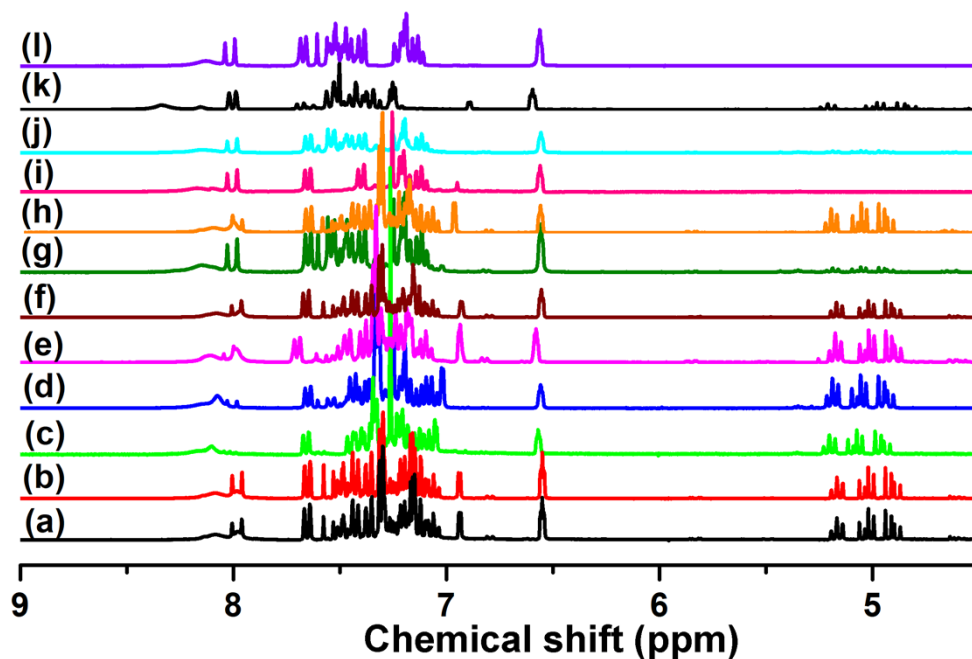
Fig. S10 ^{1}H NMR spectra monitoring the reaction between indole and trans-β-nitrostyrene using different solvent or condition at 25 $^\circ$C: (a)ZIF-8, MeCN, N$_2$; (b) ZIF-8, MeCN, Air; (c) ZIF-8/PDVB-vim, MeCN, N$_2$; (d) ZIF-8/PDVB-vim, MeCN, Air; (e) ZIF-8/PDVB-vim, CH$_2$Cl$_2$, air; (f) ZIF-8/PDVB-vim, THF, Air; (g) ZIF-8/PDVB-vim, MeOH, Air; (h) ZIF-8/PDVB-vim, toluene, Air; (i) no catalyst, MeCN, Air; (j) PDVB-vim, MeCN, Air; (k) Zn(COO)$_2$·2H$_2$O, MeCN, Air; (l) 2-Mim, MeCN, air.
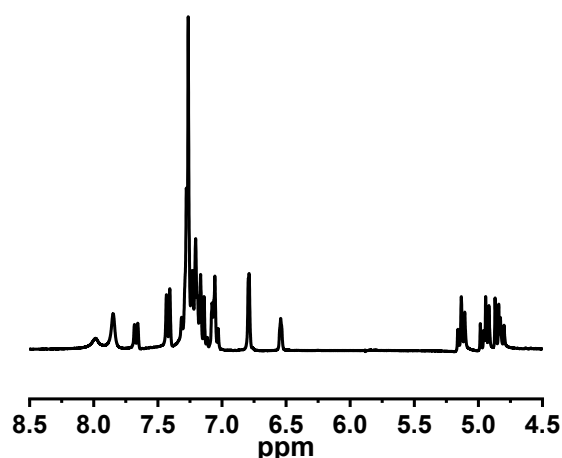

Fig. S11 ^{1}H NMR spectra monitoring the reaction between indole and trans-β-nitrostyrene over mechanical-mixing composition of ZIF-8 crystals and PDVB-vim as catalyst.
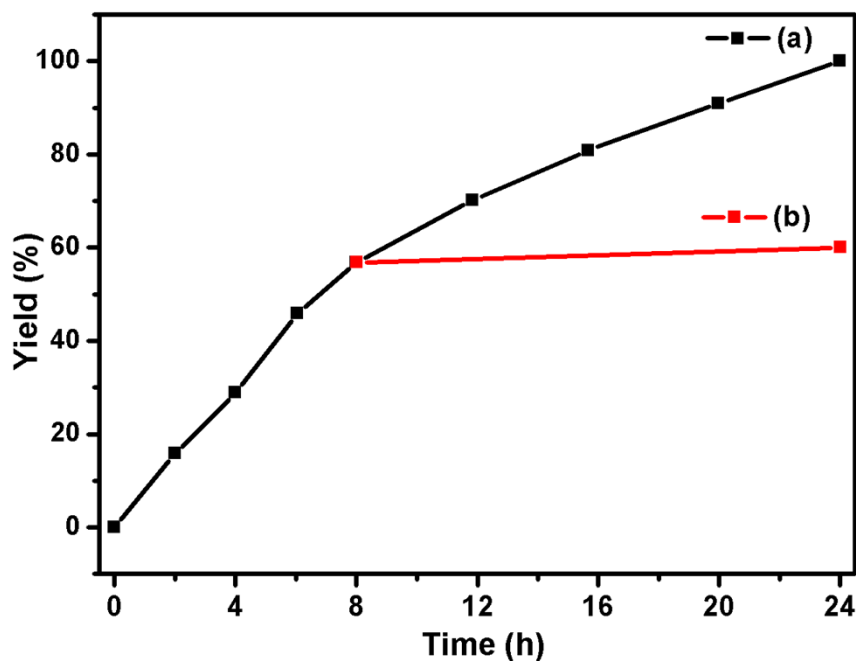
Fig. S12 Time versus yield plot for the Friedel-Crafts alkylation reaction between indole and trans-β-nitrostyrene (a) in the presence of ZIF-8/PDVB-vim composite and (b) upon filtration of ZIF-8/PDVB-vim solid after 8 h and the reaction mixture stirred without catalyst under identical conditions. Reaction conditions: trans-β-nitrostyrene (1 mmol), indole (1.5 mmol), ZIF-8/PDVB-vim composite, room temperature.
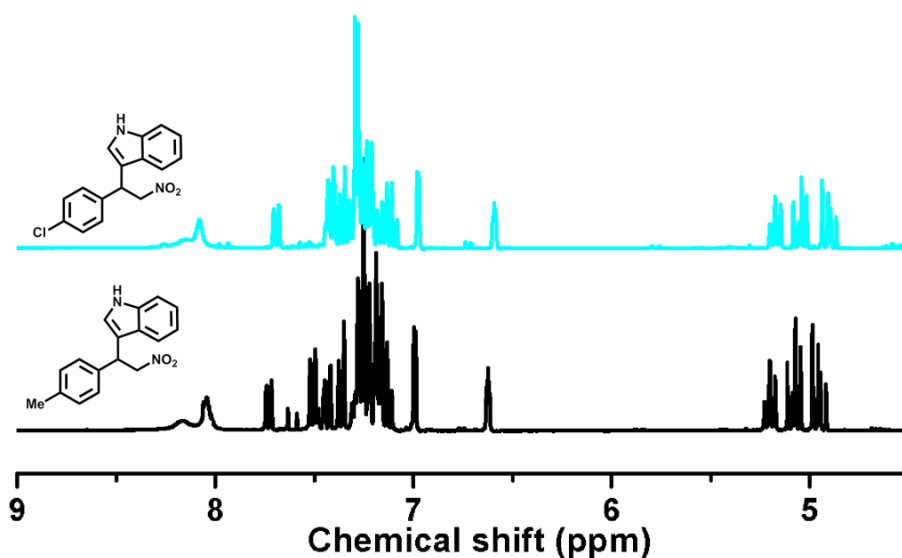
Fig. S13 ^{1}H NMR spectrums for the substrate scope of trans-β-nitrostyrene in Friedel-Crafts alkylation reaction catalysed by ZIF-8/PDVB-vim (Table 2, entries 1-2).
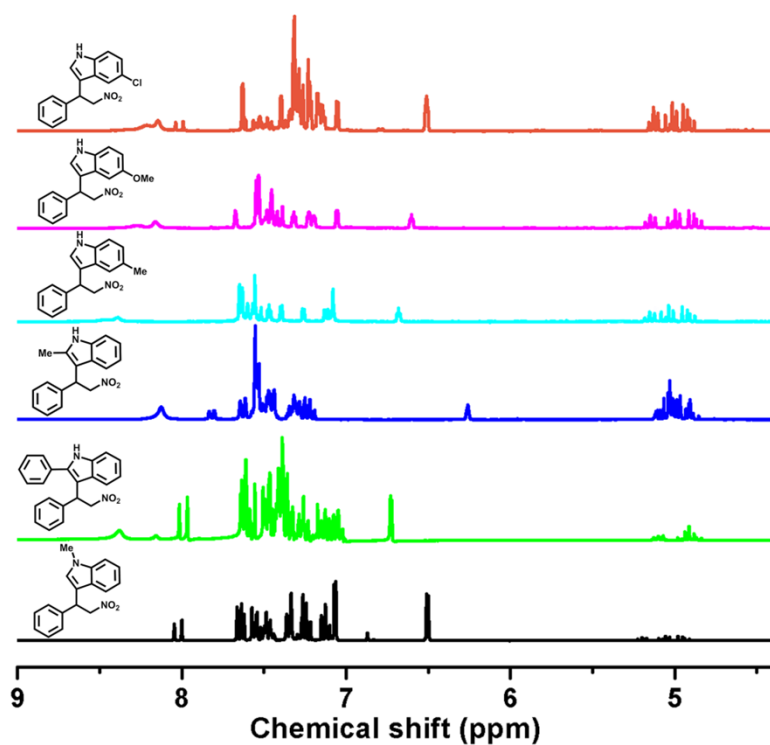
Fig. S14 ¹H NMR spectrums for the substrate scope of indole in the Friedel-Crafts alkylation reaction catalysed by ZIF-8/PDVB-vim (Table 2, entries 3-8).
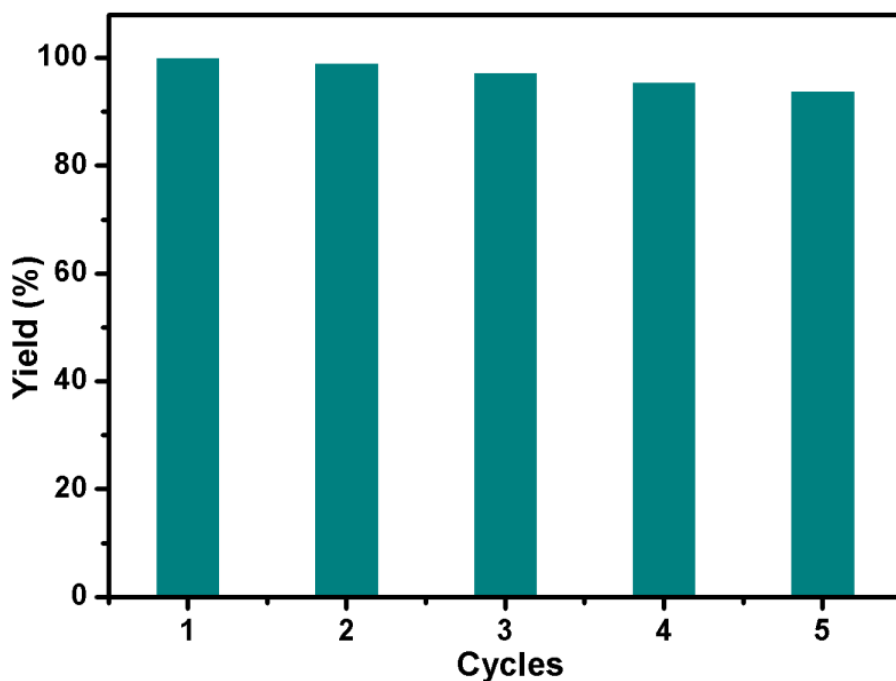
Fig. S15 Reusability data for the Friedel-Crafts alkylation reaction between indole and trans-β-nitrostyrene using ZIF-8/PDVB-vim composite as a heterogeneous solid catalyst.
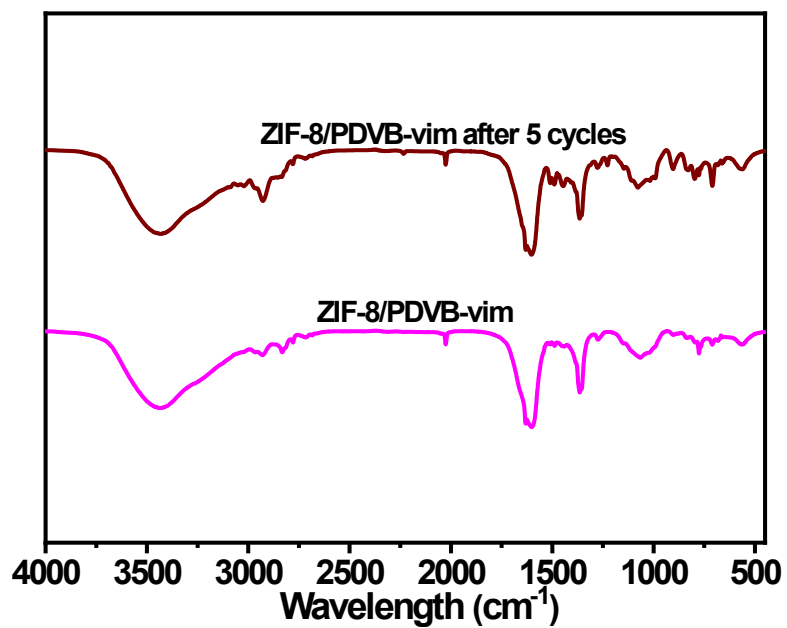
Fig. S16 FT-IR spectrums of ZIF-8/PDVB-vim before and after 5 cycles of catalytic experiments.
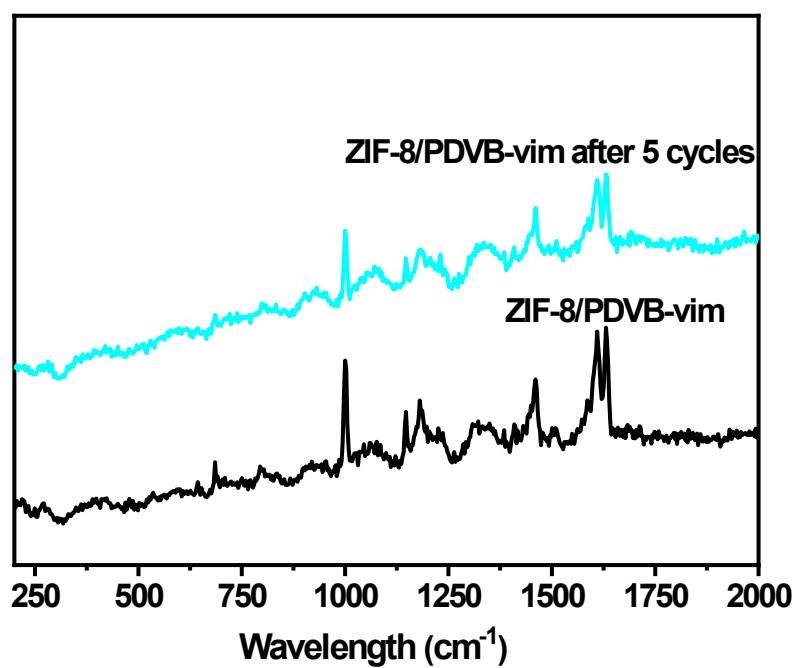
Fig. S17 Raman spectrums of ZIF-8/PDVB-vim before after 5 cycles of catalytic experiments.

Fig. S18 The PXRD patterns of ZIF-8/PDVB-vim before after 5 cycles of catalytic experiments (nano CeO$_2$ as an internal standard).
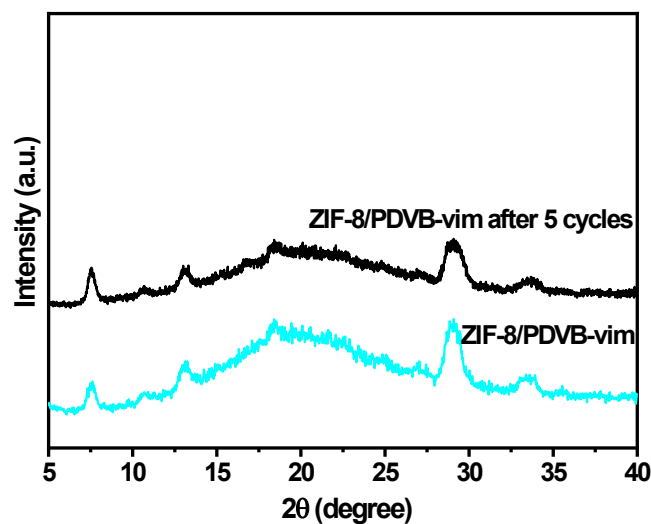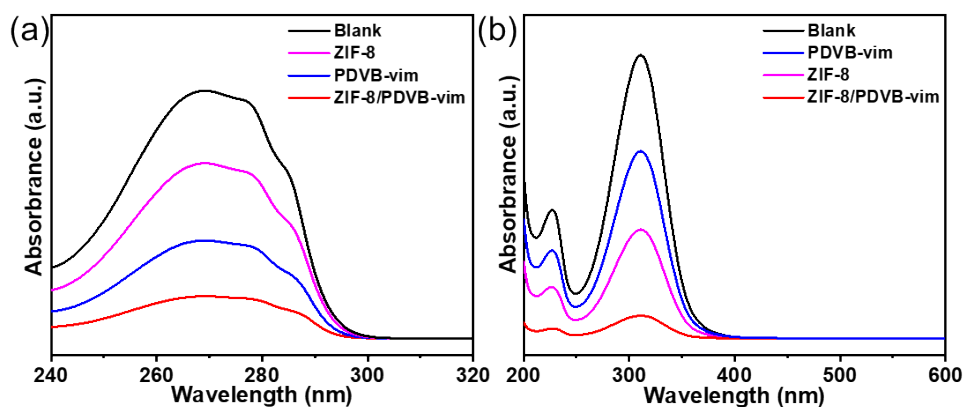

Fig. S19 The adsorption experiments of ZIF-8, PDVB-vim and ZIF-8/PDVB-vim for indole/trans-β-nitrostyrene in MeCN solution.

Table S1 The amount of Zn species loaded into ZIF-8/PDVB-vim based on ICP-AES results.

Entry	Catalyst	wt %
1[a]	ZIF-8/PDVB-vim	4.579
2[b]	ZIF-8/PDVB-vim	4.576
3[c]	ZIF-8/PDVB-vim	4.571

[a] the as- prepared ZIF-8/PDVB-vim sample; [b] the ZIF-8/PDVB-vim after boling water treatment; [c] the ZIF-8/PDVB-vim after reaction.

Table S2 The lower catalyst loading for catalyzing trans-β-nitrostyrene and indoles in the Friedel-Crafts Reaction.

Entry	Catalyst	Atmosphere	Yield (%)
1	ZIF-8/PDVB-vim	N_2	52.6
2	ZIF-8/PDVB-vim	Air	51.0

Trans-β-nitrostyrene (150 mg, 1.0 mmol), Indoles (180 mg, 1.5 mmol), catalyst 2 mol% based on Zn(II) center, MeCN 5 mL, under N_2 or Air atmosphere at 25 °C for 24 h.
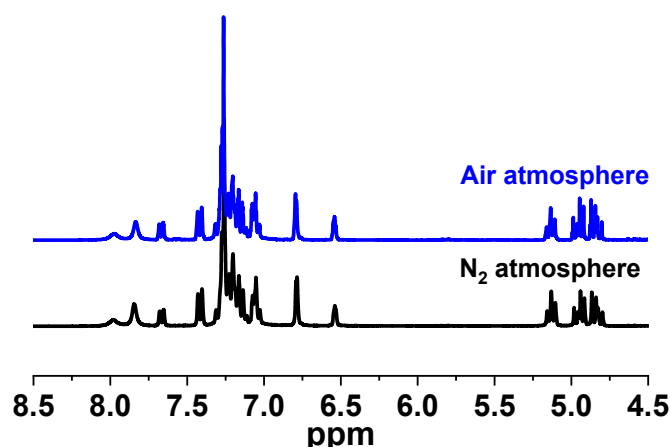
Due to all the yield of the product is >99% in humid air and dry N_2 over ZIF-8/PDVB-vim catalyst, the catalyst might reach the full conversion in both instances. So, the lower catalyst loading was used to distinguish the effect of water. The yields of product in ZIF-8/PDVB-vim were similar no matter whether in humid air and dry N_2. Yet, the results of ZIF-8 were distinguishing (Table 1, entry 1 and 2 in text). These results imply the superiority of the material design strategy.

Table S3 Comparison of Various MOF Catalysts in the Friedel-Crafts Reaction of Indole and trans-β-nitrostyrene.

Entry	Catalyst	Mol (%)	Time (h)	Solvent	Temp (°C)	Yield (%)	Ref.
1	Zr-UiO-67	10	24	CH_2Cl_2	25	22	S3
2	Zr-UiO-67-Urea	3.8	24	toluene	70	97	S4
3	Uio-67-Squar/bpdc	10	24	CD_2Cl_2	RT	78	S4
4	Cr-MIL-101	15	48	CH_3CN	60	22	S5
5	Cr-MIL-101-UR3	15	24	CH_3CN	60	93	S5
6	$[CuL_1 \cdot H_2O].2DMF$	1.5	18	CH_3CN	60	98	S6
7	$Zn_4O(L_2)(DMF)_2$	22	24	Toluene	60	90	S7
8	$Cu_4(dbda)_2 \cdot (CH_3OH)_4$	5	24	$CHCl_3$	50	99	S4
9	$Zn_2(2\text{-BQBG})(BDC)_2$	3	24	CH_2Cl_2	27	83	S8
10	$Cu_3(BTC)_2$	16.5	24	toluene	50	98	S9

| 11 | ZIF-8/PDVB-vim | 5 | 24 | CH$_3$CN | 25 | >99 | This work |

References

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