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Electronic Supplementary Information (ESI)

Fine-tuning metal-organic framework performances by spatially-differentiated postsynthetic modification

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Experimental section

Materials and Instruments

All reagents and solvents were purchased from commercial sources and used without further purification. ^1H NMR spectrum was recorded on Bruker DPX 400 spectrometer (400 MHz). Powder X-ray diffraction patterns (PXRD) of the samples were measured on Rigaku Ultima IV X-Ray diffractometer under room temperature. Infrared spectra were obtained as KBr disks on a Nicolet Avatar 360 FT-IR spectrometer. Low-pressure (up to 1 bar) gas adsorption isotherms (CO_2, N_2, and CH_4) were measured on a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. The water adsorption isotherms were measured on an Intelligent Gravimetric Sorption Analyzer (IGA100B). Scanning electron microscopy (SEM) analysis were carried out on a Gemini 300 Field Emission Scanning Electron Microscope at an accelerating voltage of 10.0 kV. The SEM specimens were prepared by placing dried samples on a conductive carbon adhesive, followed by gold coating in a sputter coater (Desk-II; Den-ton Vacuum).

Synthesis of ZIF-90 micron-sized particles

ZIF-90 micron-sized particles were synthesized according to a modified procedure from literature.[S1] $Zn(NO_3)_2{\cdot}6H_2O$ (5 mmol) and imidazole-2-carboxaldehyde (20 mmol) were added to 50 ml of DMF (N,N-dimethylformamide) in 500 mL round bottom flask. To obtain a clear solution, the mixture was stirred at 80 °C for 4 h. After the solution cooled down to room temperature, 50 ml of H_2O was quickly poured into the solution while applying vigorous stirring. After further stirring at room temperature for 30 min, the as-obtained products were collected by centrifugation (8000 rpm,15 min), washed with excess methanol (50 mL) 3 times, then kept at 60 °C in methanol overnight.

Synthesis of ZIF-90 nanoscale particles

[S1] T.-H. Bae, J. S. Lee, W. Qiu, W. J. Karos, C. W. Jones and S. Nair, *Angew. Chem. Int. Ed*. 2010, **49**, 9863.

ZIF-90 nanoscale particles were synthesized according to a modified procedure from literature.[S2] $Zn(NO_3)_2\cdot 6H_2O$ (0.75 mmol) were added to 50 ml of DMF. In a separate vial, imidazolate-2-carboxyaldehyde (2.10 mmol) was added to 100 mL of DMF and was heated at 80 °C for 2 h with stirring to fully dissolved. A third solution was prepared by adding triethylamine (2 mmol) to 50 mL of DMF. The metal salt, ligand, amine solutions and ethanol were placed in a freezer at -20 °C for 1 h. Once all solutions reached -20 °C, the metal salt, ligand and triethylamine solutions were sequentially and quickly poured into a 500 mL round bottom flask while stirring. After reacting for 1 min, the reacting solution was quenched with 100 mL of ethanol. The as-obtained products were collected by centrifugation (8000 rpm,15 min), washed with excess methanol (50 mL) 3 times, then kept at 60 °C in methanol overnight.

Post-synthetic modification of ZIF-90 with excess aliphatic amine

Micron-sized ZIF-90 samples were functionalized with octadecanamine to form C18_ duration time@ZIF-90. Approximately 150 mg of ZIF-90 (ca. 1.2 mmol equiv of -CHO) were placed in a 250 mL flask with 50 mL methanol at 60 °C. In a separate vial, 1.4 equiv. amount of octadecanamine relative to that of aldehyde groups in ZIF-90 was dissolved in 50 mL of methanol at 60 °C with stirring. When octadecanamine was totally dissolved, the solution was quickly poured into the 250 mL flask with ZIF-90 while applying gentle stirring. 15 mL of resulting suspensions were decanted at 15 min, 30 min, 1 h, 3 h, 6 h and 16 h. The products were collected by centrifugation (4500 rpm, 5 min), washed with methanol (15 mL) twice, and vacuum dried at room temperature for 3 h, then at 150 °C for 24 h.

C18_duration time@nanoZIF-90 samples were harvested by a procedure similar with that of C18_duration time@ZIF-90, only replacing micron-sized ZIF-90 particles with nanoscale ZIF-90 particles.

C2_duration time@ZIF-90 samples were harvested by a procedure similar with that of C18_duration time@ZIF-90, only replacing octadecanamine with ethylamine.

[S2] C. G. Jones, V. Stavila, M. A. Conroy, P. Feng, B. V. Slaughter, C. E. Ashley and M. D. Allendorf, *ACS Appl. Mater. Interfaces*, 2016, **8**, 7623.

Post-synthetic modification of ZIF-90 with quantitative aliphatic amine

Micron-sized ZIF-90 samples were functionalized with quantified octadecanamine to form C18_introduction percentage@ZIF-90 samples. Approximately 150 mg of ZIF-90 (ca. 1.2 mmol equiv of -CHO) were placed in a 250 mL flask with 50 mL methanol at 60 °C. In a separate vial, quantified (1%, 5%, 10% equiv. amount of amines relative to that of aldehyde groups of ZIF-90) octadecanamine was dissolved in 50 mL of methanol at 60 °C with stirring. When octadecanamine was totally dissolved, the solution was quickly poured into the 250 mL flask with ZIF-90 while applying gentle stirring. After 4 h, the products were collected by centrifugation (8000 rpm, 15 min), washed with methanol (50 mL) twice, and vacuum dried at room temperature for 3 h, then at 150 °C for 24 h.

Samples handing for NMR analysis

Methanol-d6 (0.6 mL) and DCl in D_2O (20 wt. %) (60 μL), were added to 4 mL vial containing the dried MOFs (*ca*. 3 mg, but for C18_1%@ZIF-90 sample, 20 mg). To obtain clear solution, the resulting suspensions were heated to 80 °C for 5 min and then sonicated for 1 min.

Characterization and physical measurement

Contact angle

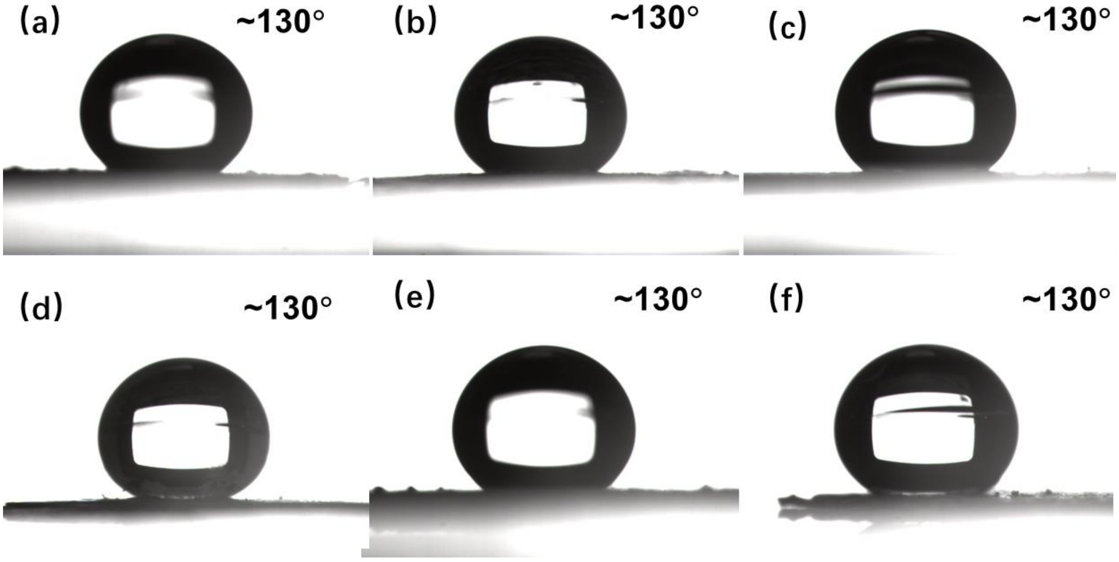
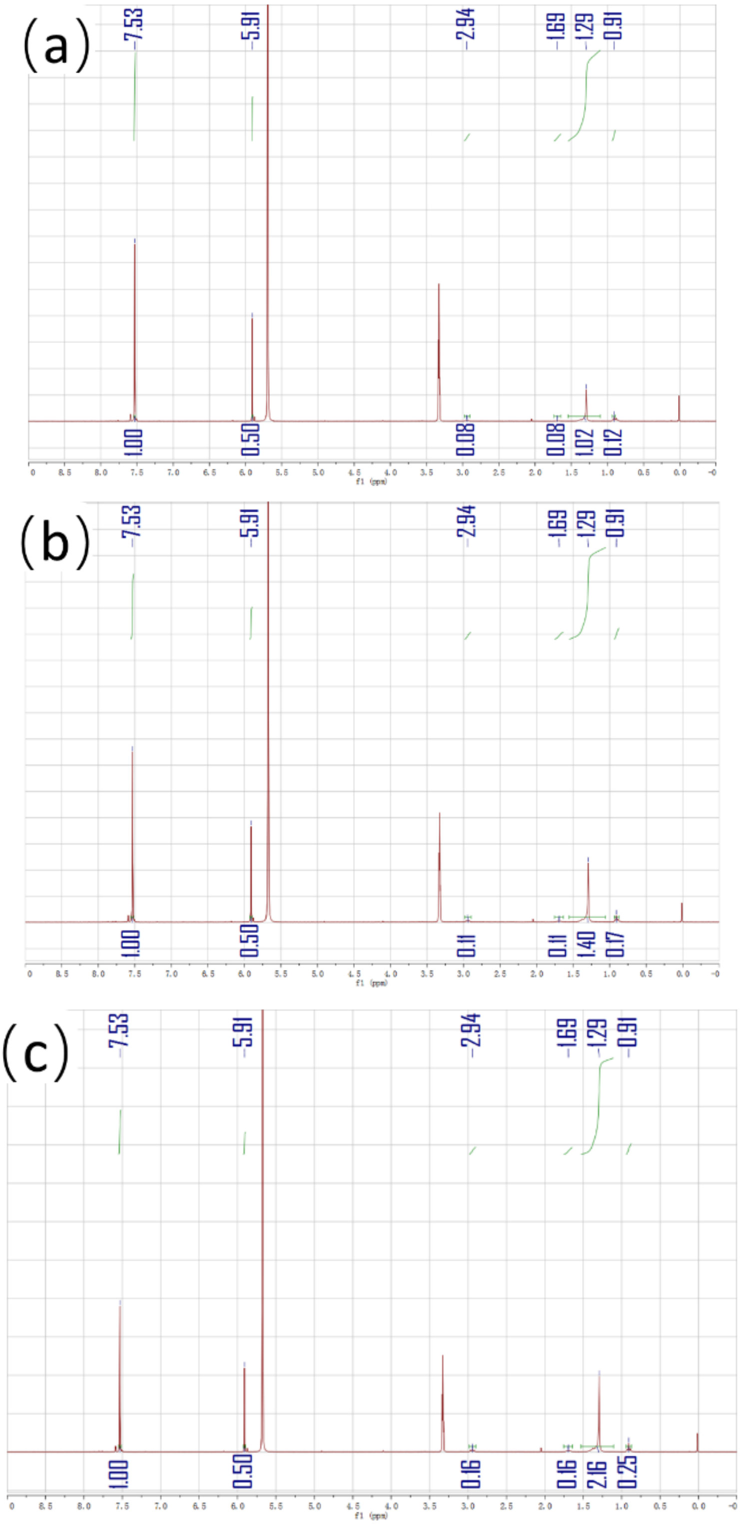
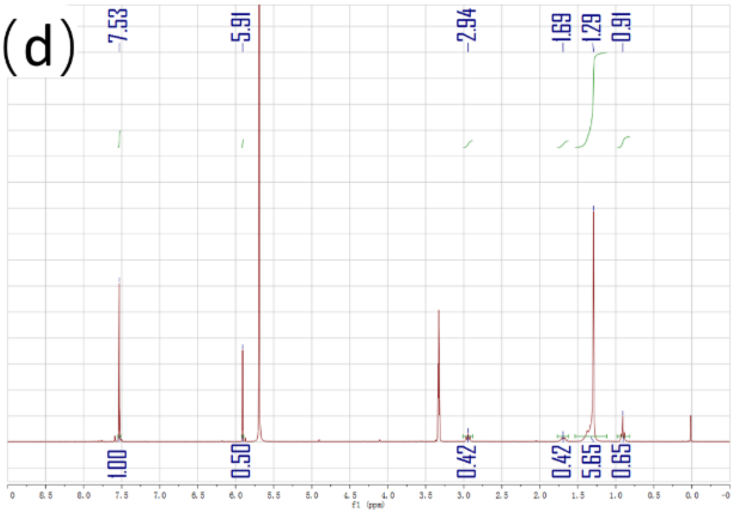


Fig. S1 Contact angle of micron-sized ZIF-90 samples functionalized with octadecanamine (C18 amine) after scheduled duration time. (a) 10 min, (b) 30 min, (c) 1 h, (d) 3 h, (e) 6 h, (f) 16 h.

^{1}H NMR spectra (over time)



(d)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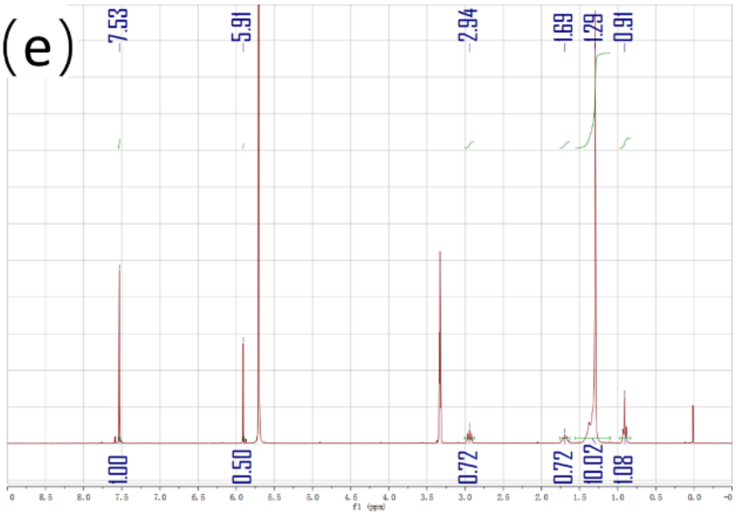
5.91
2.94
1.69
1.29
0.91
1.00
0.50
0.42
0.42
5.65
0.65
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(e)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10.02
1.08
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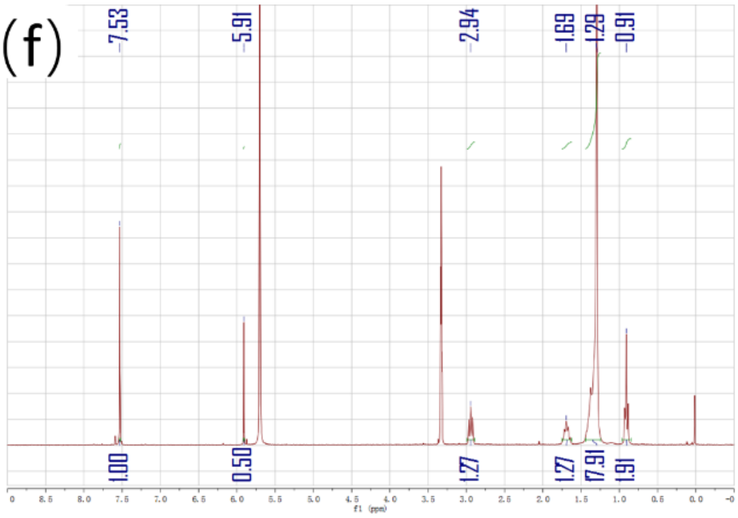
f1 (ppm)

(f)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f1 (ppm)

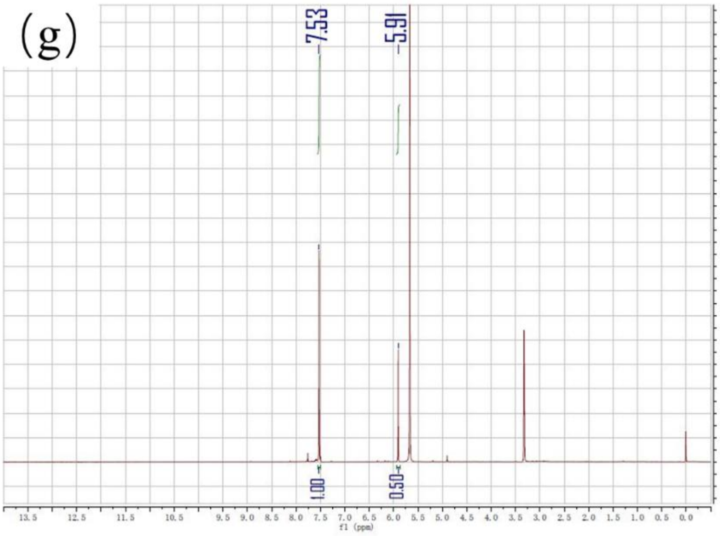
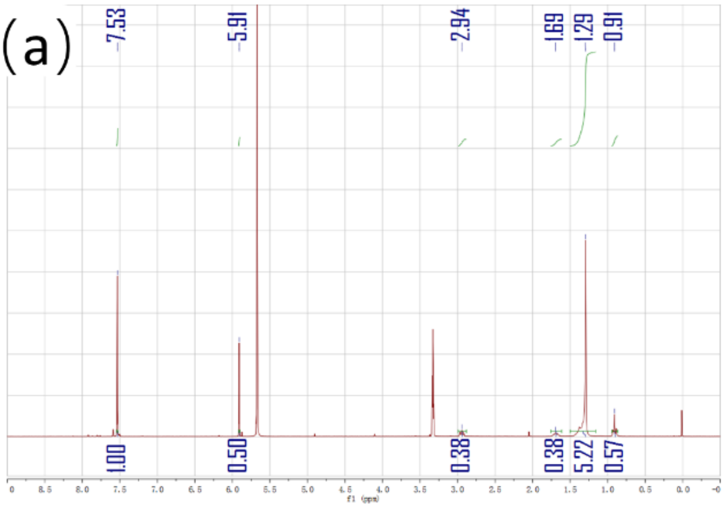


Fig. S2 ^{1}H NMR spectra of micron-sized ZIF-90 samples functionalized with octadecanamine (C18 amine) after scheduled duration time. (a) 10 min, (b) 30 min, (c) 1 h, (d) 3 h, (e) 6 h, (f) 16 h and (g) pristine ZIF-90. The ratio of the organic struts present in the modified MOF structures, was calculated by the integral ratio of the ^{1}H NMR signals corresponding to each strut in the digested MOF samples. The signals at 7.53 ppm (2H), was used to determine the relative amount of imidazole strut, and the signals at 2.94 ppm (2H, α-H in aliphatic chain), 1.69 ppm (2H, β-H in aliphatic chain) and 0.91 ppm (3H, terminal CH_3 in aliphatic chain) were utilized to quantify the relative amount of aliphatic amine strut in the modified MOF structures. The introducing ratios calculated over 100% are attributed to physisorption during PSM processes.

(a)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3.0
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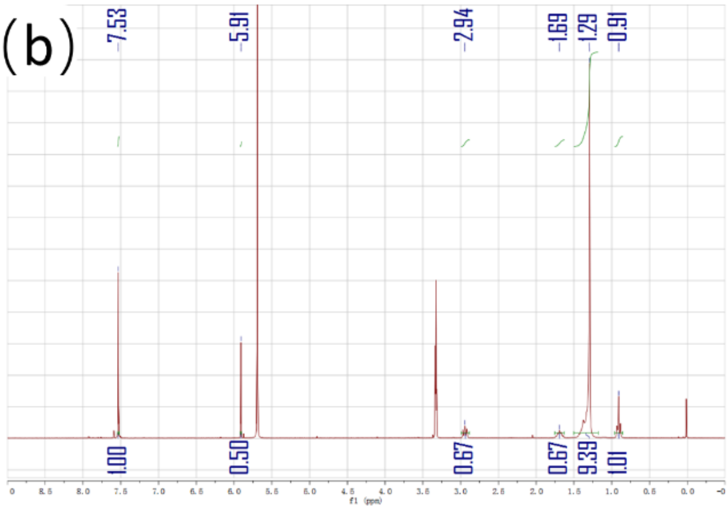
f1 (ppm)

(b)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6.5
6.0
5.5
5.0
4.5
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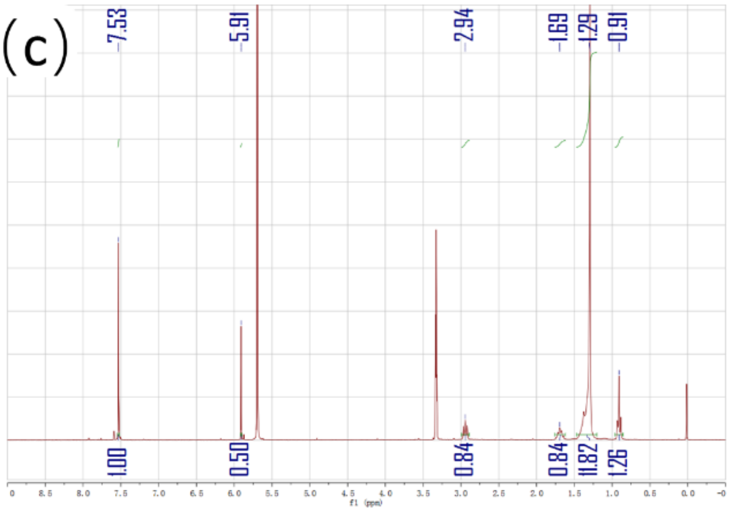
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(c)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6.0
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0.5
0.0
f1 (ppm)

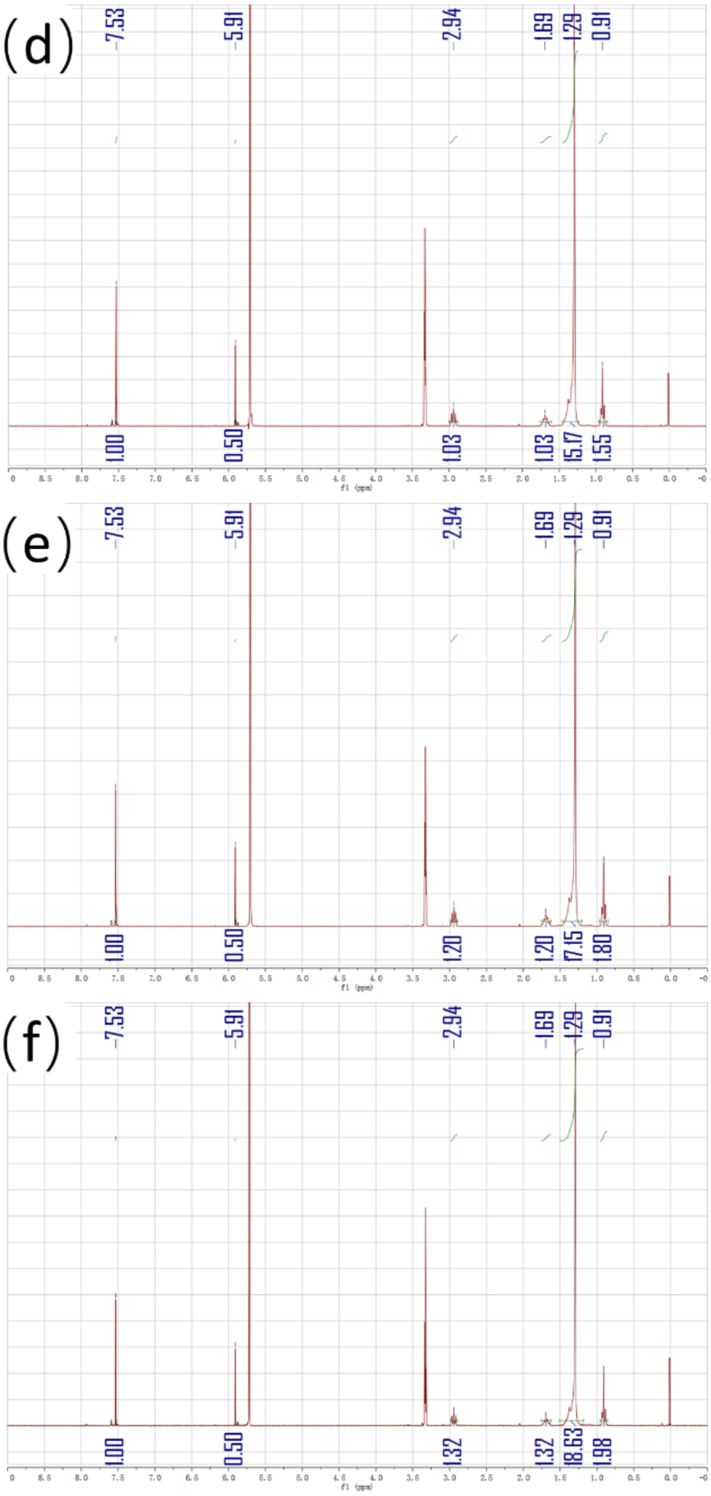
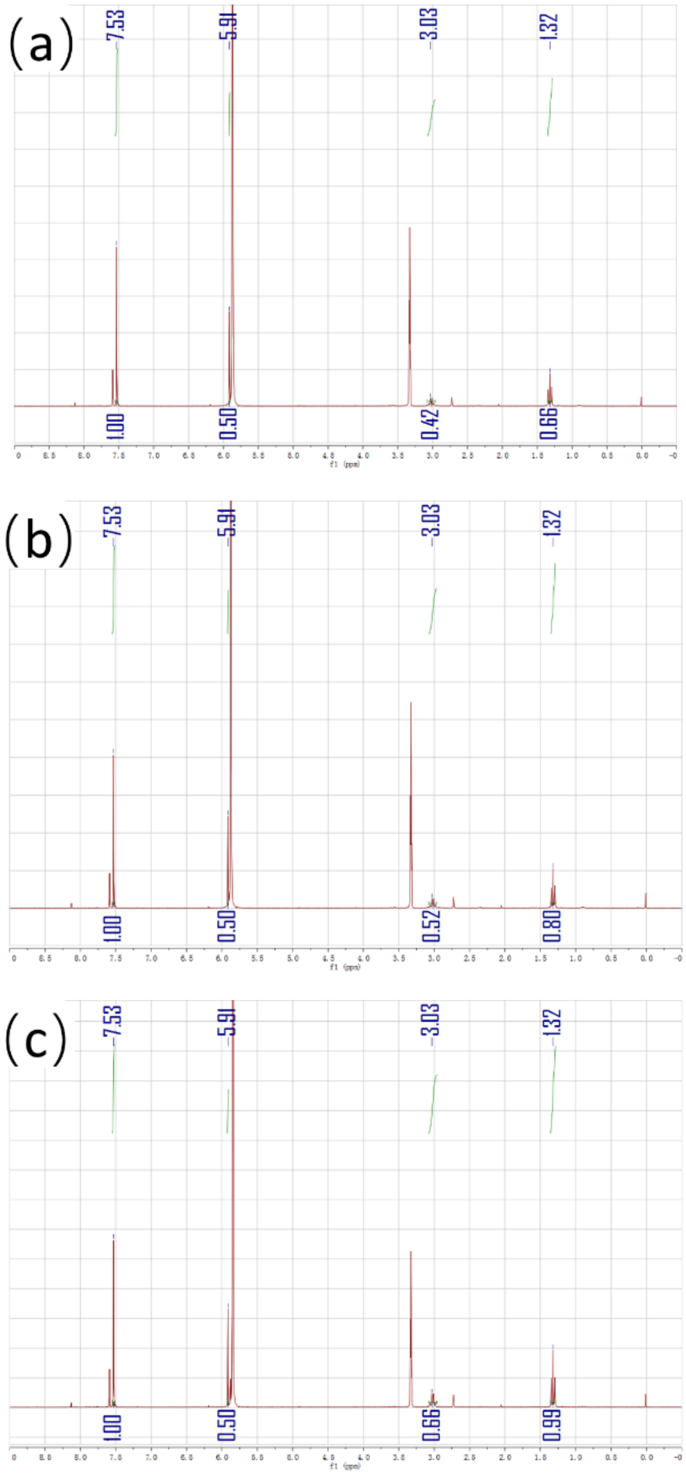


Fig. S3 ^{1}H NMR spectra of nanoscale ZIF-90 samples functionalized with octadecanamine (C18 amine) after scheduled duration time. (a) 10 min, (b) 30 min, (c) 1 h, (d) 3 h, (e) 6 h and (f) 16 h. The signals at 7.53 ppm (2H), was used to determine the relative amount of imidazole strut, and the signals at 2.94 ppm (2H, α -H in aliphatic chain), 1.69 ppm (2H, β -H in aliphatic chain) and 0.91 ppm (3H, terminal CH_3 in aliphatic chain) were utilized to quantify the relative amount of aliphatic amine strut in the modified MOF structures.


(a)
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3.03
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(b)
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3.03
1.32
1.00
0.50
0.52
0.80
(c)
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5.91
3.03
1.32
1.00
0.50
0.66
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

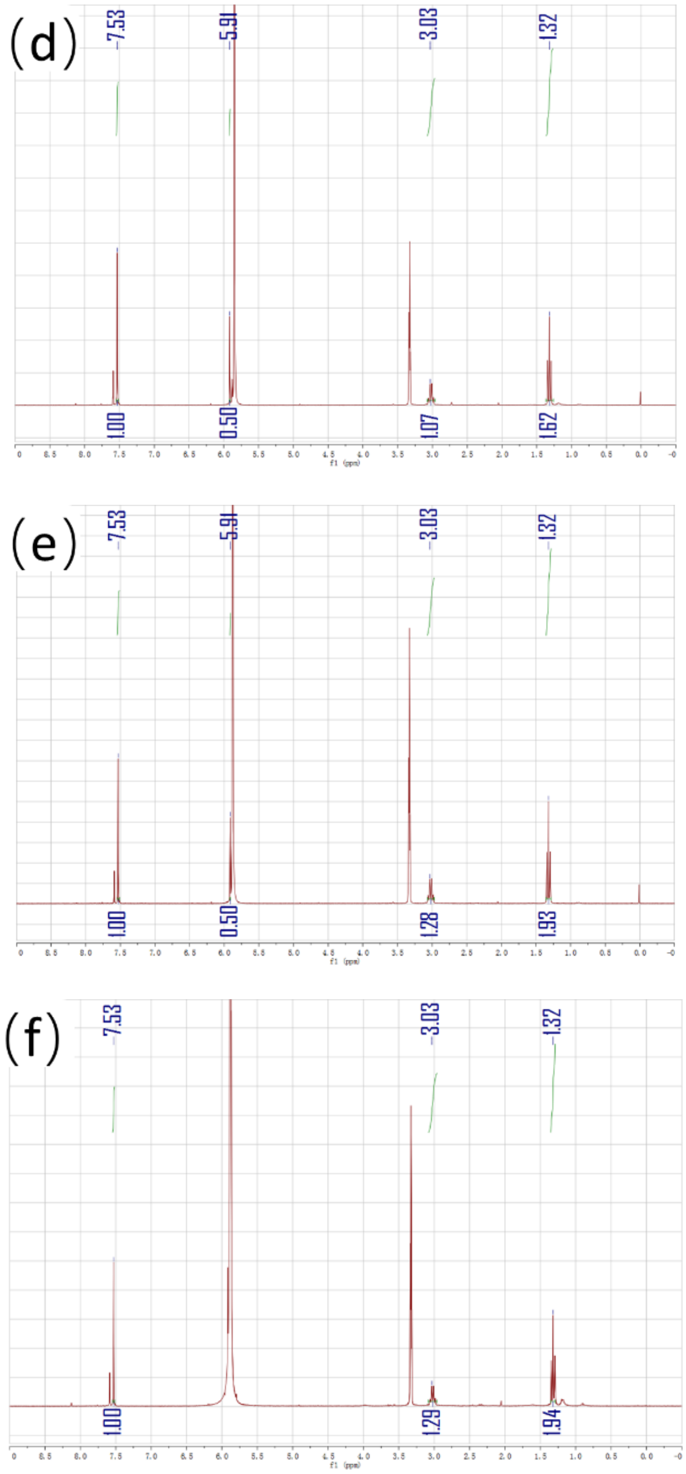

Fig. S4 ^{1}H NMR spectra of micron-sized ZIF-90 samples functionalized with ethylamine (C2 amine) after scheduled duration time. (a) 10 min, (b) 30 min, (c) 1 h, (d) 3 h, (e) 6 h, (f) 16 h. The signals at 7.53 ppm (2H), was used to determine the relative amount of imidazole strut, and the signals at 3.03 ppm (2H, α-H in aliphatic chain) and 1.32 ppm (3H, CH_3 in aliphatic chain) were utilized to quantify the relative amount of aliphatic amine strut in the modified MOF structures.

FT-IR spectra

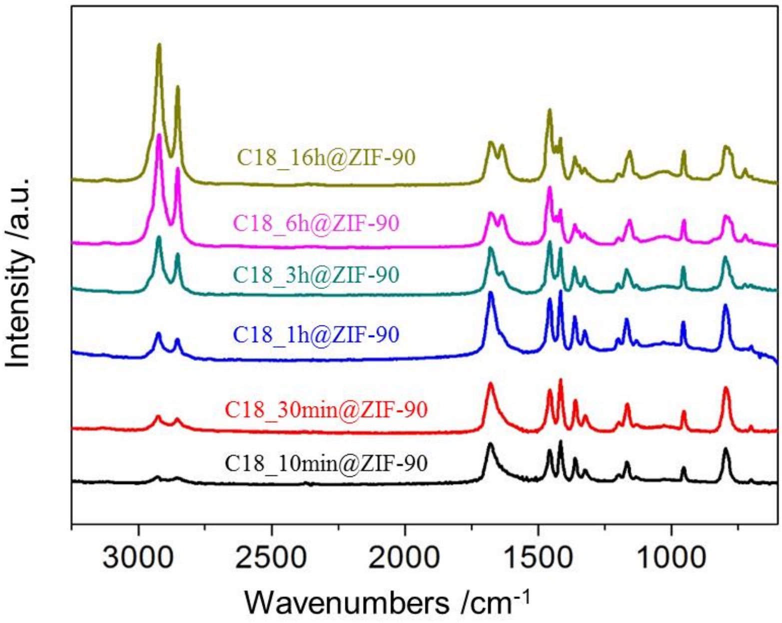

Fig. S5 FT-IR spectra of micron-sized ZIF-90 samples functionalized with octadecanamine (C18 amine) after scheduled duration time. Reduction of the aldehyde peak at a wavenumber of 1679 cm^{-1}, the appearance of the imine peak at 1635 cm^{-1} and aliphatic chains peaks at 2923 and 2852 cm^{-1}, indicated the introduction of octadecanamine into ZIF-90 via imine condensation.

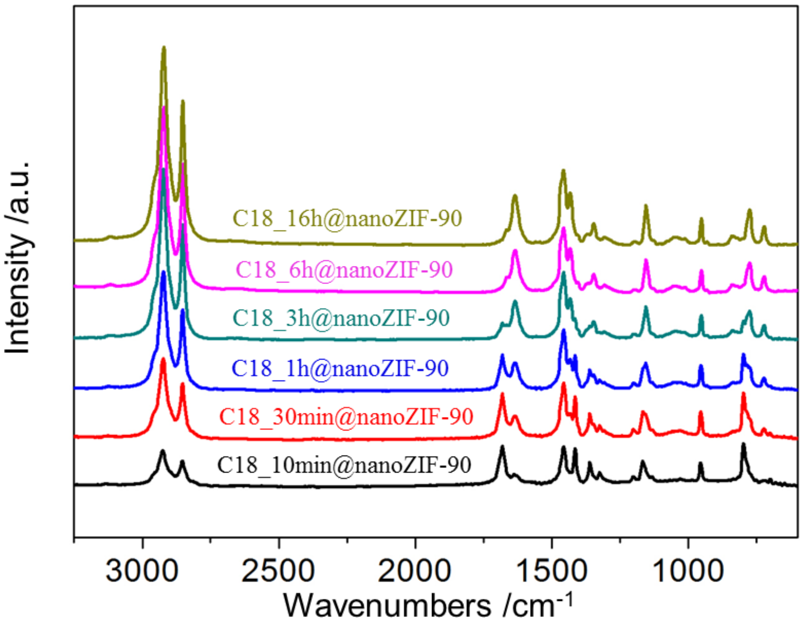

Fig. S6 FT-IR spectra of nanoscale ZIF-90 samples functionalized with octadecanamine (C18 amine) after scheduled duration time. Reduction of the aldehyde peak at a wavenumber of 1679 cm^{-1}, the appearance of the imine peak at 1635 cm^{-1} and aliphatic chains peaks at 2923 and 2852 cm^{-1}, indicated the introduction of octadecanamine into nanoscale ZIF-90 via imine condensation.

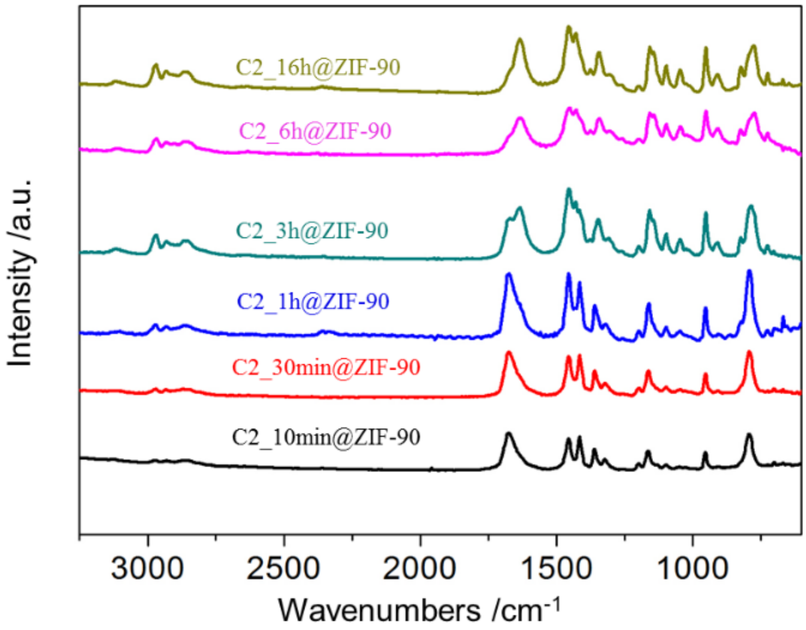

Fig. S7 FT-IR spectra of micron-sized ZIF-90 samples functionalized with ethylamine (C2 amine) after scheduled duration time. Reduction of the aldehyde peak at a wavenumber of 1679 cm^{-1}, the appearance of the imine peak at 1635 cm^{-1} and aliphatic chains peaks at 2852 and 2923 cm^{-1}, indicated the introduction of ethylamine (C2 amine) into ZIF-90 via imine condensation.

PXRD patterns

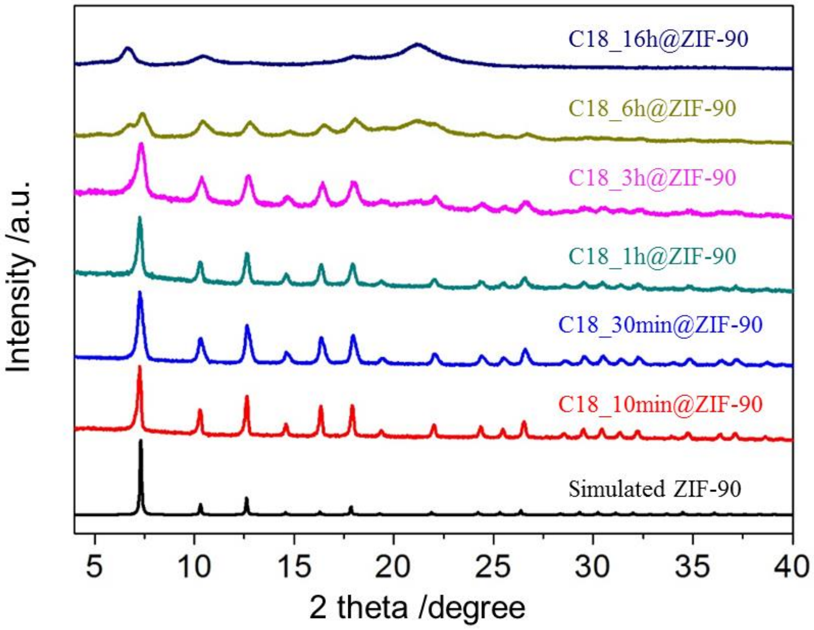

Fig. S8 PXRD patterns of micron-sized ZIF-90 samples functionalized with octadecanamine (C18 amine) after scheduled duration time. These results indicate the ZIF-90 sample maintained its crystalline SOD-type structure but experienced a chemical decomposition for long-term reaction.

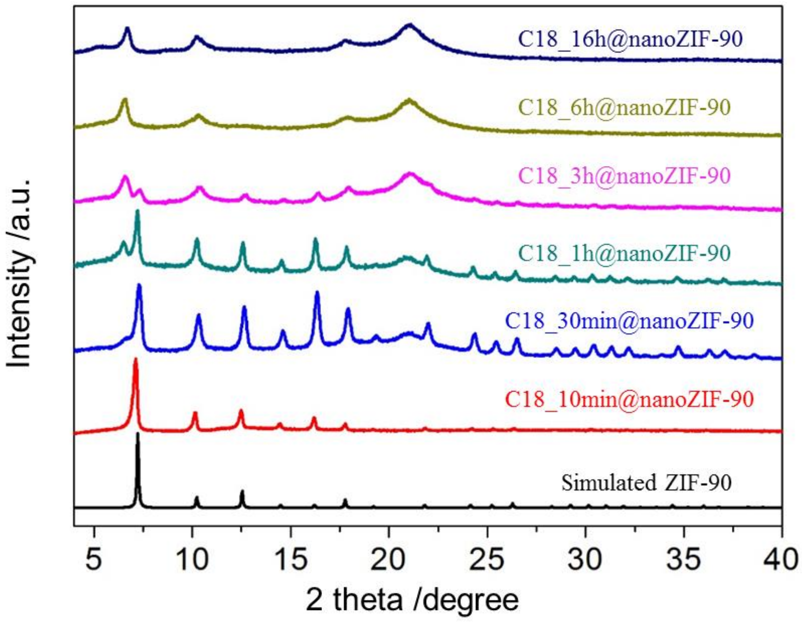

Fig. S9 PXRD patterns of nanoscale ZIF-90 samples functionalized with octadecanamine (C18 amine) after scheduled duration time. These results indicate the ZIF-90 sample maintained its crystalline SOD-type structure but experienced a chemical decomposition for long-term reaction.

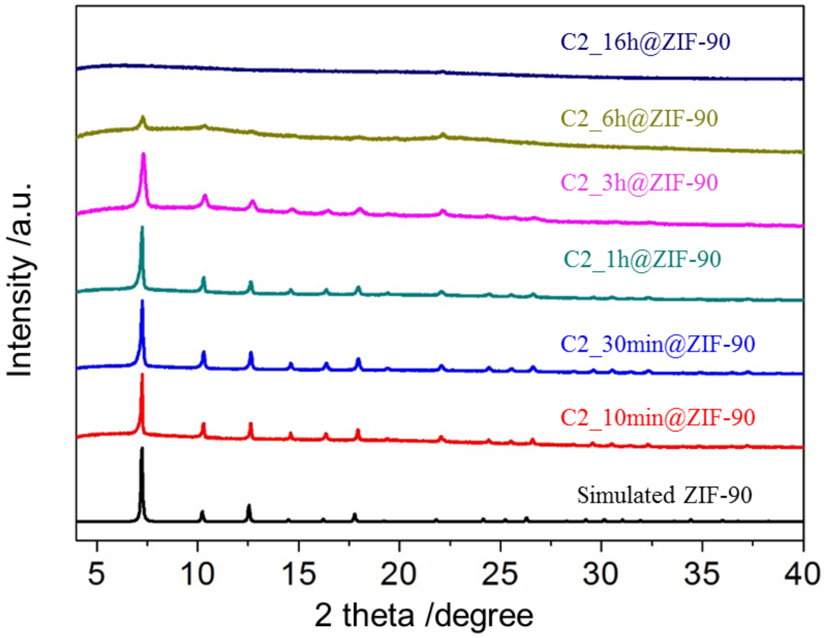

Fig. S10 PXRD patterns of micron-sized ZIF-90 samples functionalized with ethylamine (C2 amine) after scheduled duration time. These results indicate the ZIF-90 sample maintained its crystalline SOD-type structure but experienced a chemical decomposition for long-term reaction.

^{1}H NMR spectra (quantitatively modified)

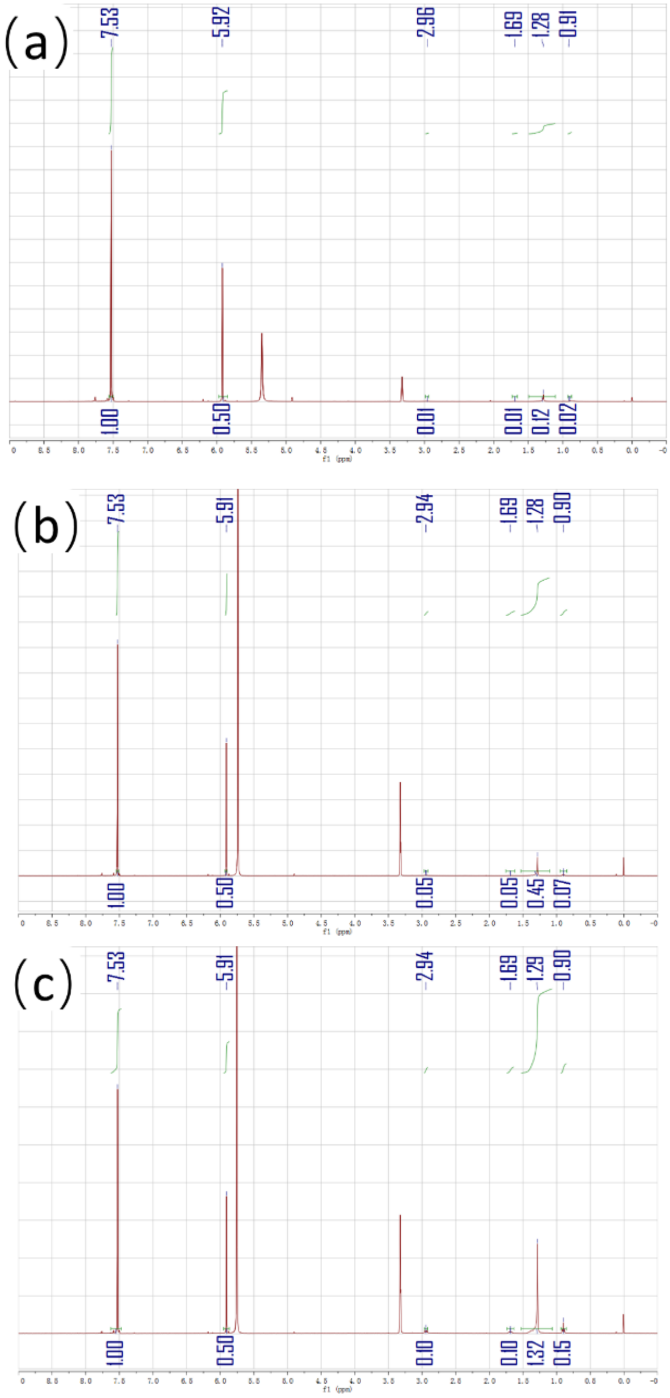

Fig. S11 ^{1}H NMR spectra of micron-sized ZIF-90 samples functionalized with quantitative amount octadecanamine (C18 amine). (a) 1%, (b) 5%, (c) 10%. The signals at 7.53 ppm (2H), was used to determine the relative amount of imidazole strut, and the signals at 2.94 ppm (2H, α-H in aliphatic chain), 1.69 ppm (2H, β-H in aliphatic chain) and 0.91 ppm (3H, terminal CH_3 in aliphatic chain) were utilized to quantify the relative amount of aliphatic amine strut in the modified MOF structures.

Calculated Pore size distribution

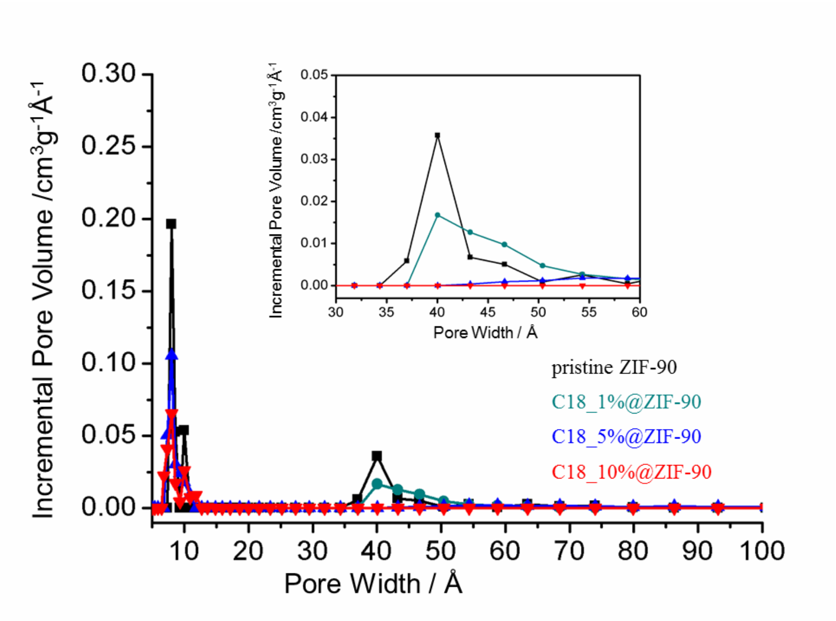

Fig. S12 Pore size distribution of pristine and quantitatively modified ZIF-90 samples calculated using density functional theory (DFT) based on N_2 sorption data at 77 K. Calculated percentages of pore volume of mseopores: 17.21% (pristine ZIF-90), 16.22% (C18_1%@ZIF-90), negligible (C18_5%@ZIF-90 and C18_10%@ZIF-90).
Inset: a magnified figure of mesopore region for clarity.

Gas adsorption isotherms

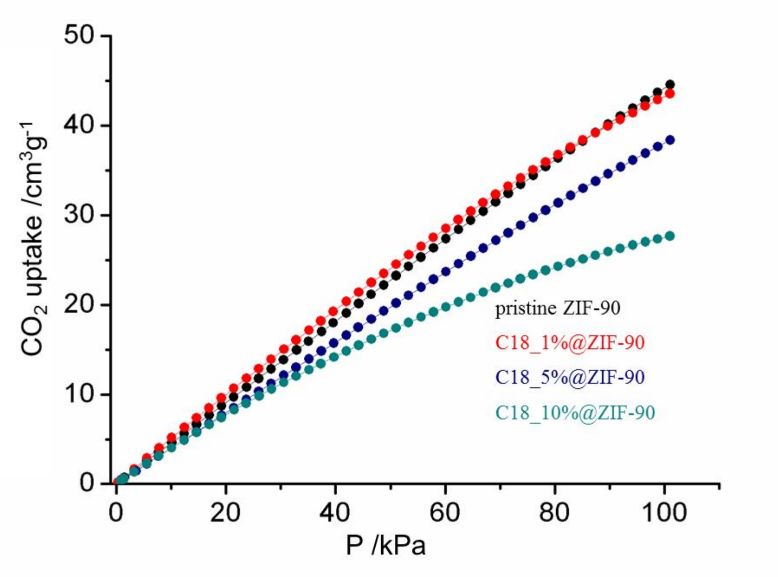

Fig. S13 Gravimetric CO_2 adsorption isotherms measured at 298 K for pristine and quantitatively modified ZIF-90 samples.

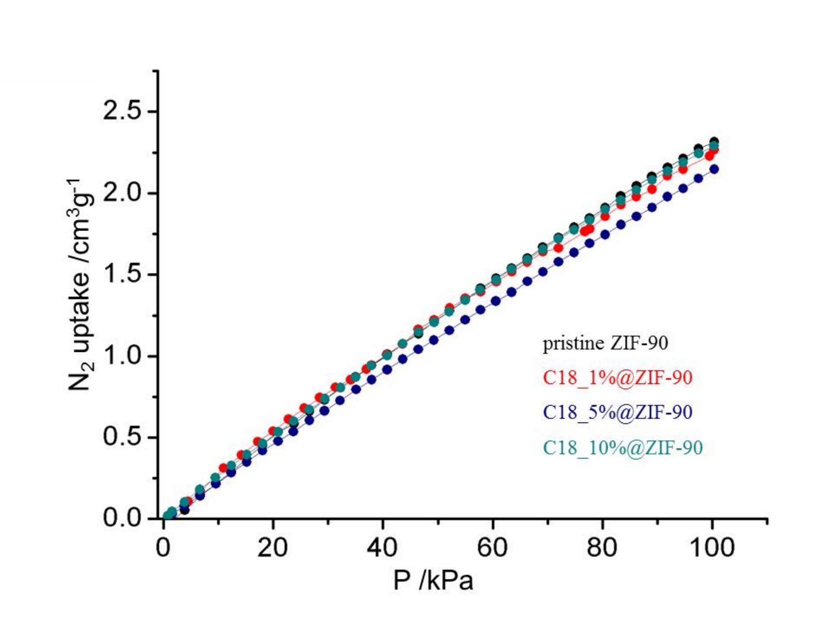

Fig. S14 Gravimetric N_2 adsorption isotherms measured at 298 K for pristine and quantitatively modified ZIF-90 samples..

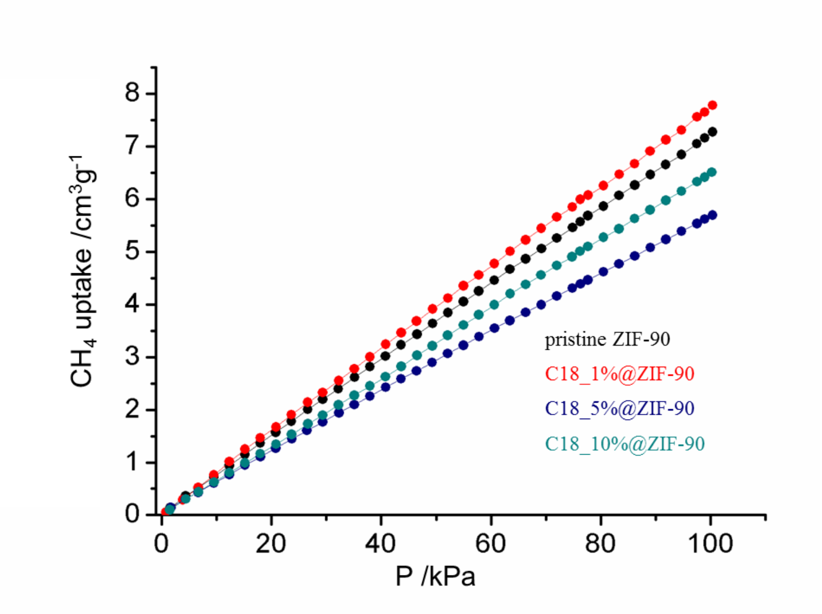

Fig. S15 Gravimetric CH_4 adsorption isotherms measured at 298 K for pristine and quantitatively modified ZIF-90 samples.

Fitting of adsorption isotherms

Before further calculation and analysis of the adsorption and separation properties, the adsorption isotherms must be fitted properly to adsorption models of physical meanings. Here the measured experimental data on pure component isotherms for CO_2, N_2 and CH_4 at 298 K are fitted using single-site Langmuir (SSL):

$$\text{SSL:}\quad q = \frac{q_{\text{sat}}\text{b}p}{1+\text{b}p} \qquad \text{(E1)}$$

where q is the adsorption quantity, q_{sat} is the saturate adsorption quantity, b is the coefficients of Langmuir equation.

The fitting results and parameters are given in Fig. S15-S18, and Table S1–S4.

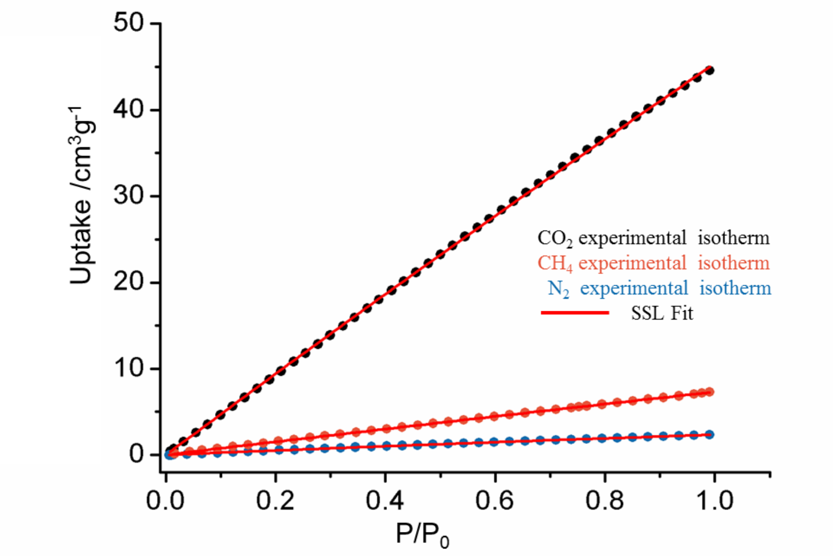

Fig. S16 Single site Langmuir model fitting CO_2, CH_4 and N_2 adsorption isotherms of pristine ZIF-90 at 298 K.

Table S1 Single site Langmuir fitting parameters of CO_2, CH_4 and N_2 adsorption isotherms for pristine ZIF-90 at 298 K.

	CO_2	CH_4	N_2
q_{sat}	1034.3852	162.87054	24.68158
b	0.04591	0.04705	0.10572
R^2	0.99987	0.99997	0.99935

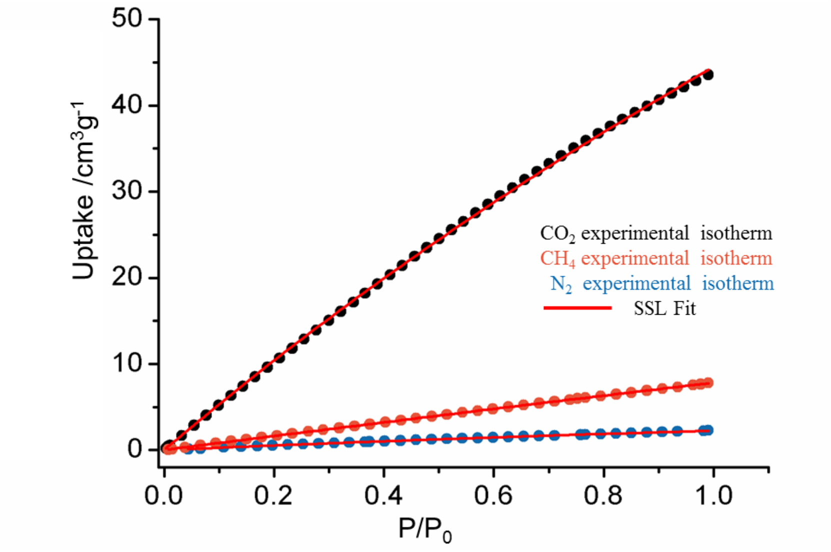

Fig. S17 Single site Langmuir model fitting CO_2, CH_4 and N_2 adsorption isotherms of C18_1%@ZIF-90 at 298 K.

Table S2 Single site Langmuir fitting parameters of CO_2, CH_4 and N_2 adsorption isotherms for C18_1%@ZIF-90 at 298 K.

	CO_2	CH_4	N_2
q_{sat}	247.06818	166.08731	12.25384
b	0.21958	0.04947	0.22609
R^2	0.99976	0.99995	0.99938

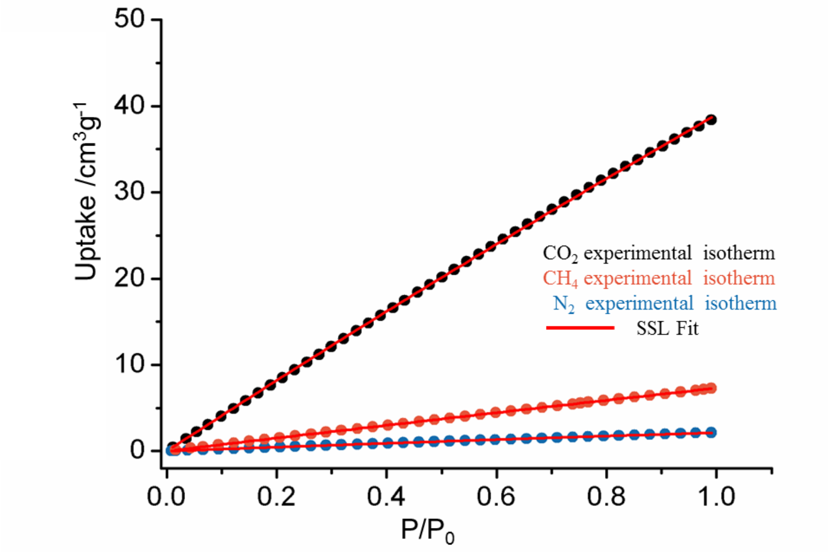

Fig. S18 Single site Langmuir model fitting CO_2, CH_4 and N_2 adsorption isotherms of C18_5%@ZIF-90 at 298 K.

Table S3 Single site Langmuir fitting parameters of CO_2, CH_4 and N_2 adsorption isotherms for C18_5%@ZIF-90 at 298 K.

	CO_2	CH_4	N_2
q_{sat}	621.79832	68.9255	25.90299
b	0.06697	0.09057	0.09109
R^2	0.99991	0.99992	0.99996

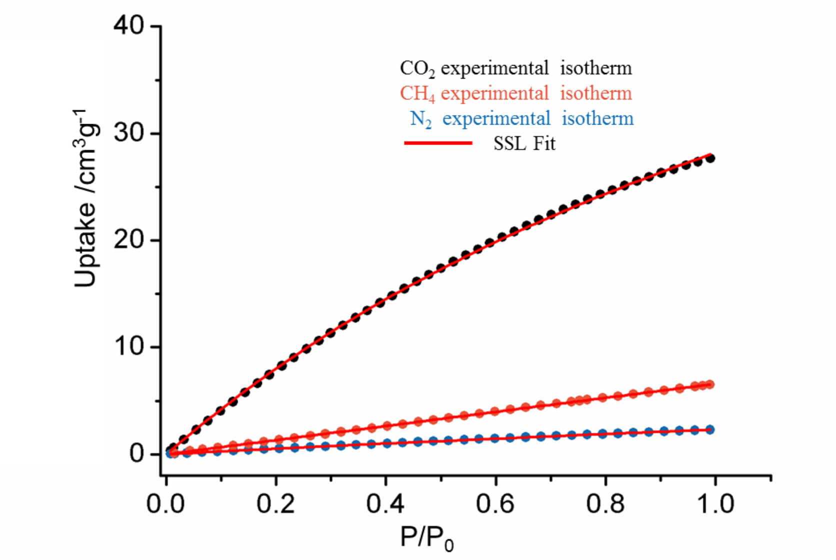

Fig. S19 Single site Langmuir model fitting CO_2, CH_4 and N_2 adsorption isotherms of C18_10%@ZIF-90 at 298 K.

Table S4 Single site Langmuir fitting parameters of CO_2, CH_4 and N_2 adsorption isotherms for C18_10%@ZIF-90 at 298 K.

	CO_2	CH_4	N_2
q_{sat}	76.12145	739.83601	18.00077
b	0.5887	0.009	0.14818
R^2	0.99972	0.99982	0.99995

Calculation of IAST selectivity

The Ideal Adsorbed Solution Theory (IAST)[S3] is used to estimate the composition of the adsorbed phase from pure component isotherm data and predict the selectivity of the binary mixture CO_2/N_2 and CO_2/CH_4. For the IAST, the following equation is proposed:

$$\int_0^{p_\mathrm{a}} \frac{q_\mathrm{a}}{p}\mathrm{d}p = \int_0^{p_\mathrm{b}} \frac{q_\mathrm{b}}{p}\mathrm{d}p \quad \text{(E2)}$$

where p_a and p_b are the pressure of component a and b at the same spreading pressure and the same temperature as that of the mixture respectively. And for the ideal binary gas mixture, according to the Raoult's law, there are the following two equations:

$$\mathrm{y}\ p_\mathrm{t} = \mathrm{x}\ p_\mathrm{a} \qquad \text{(E3)}$$

$$(1-\mathrm{y})\ p_\mathrm{t} = (1-\mathrm{x})\ p_\mathrm{b} \qquad \text{(E4)}$$

where p_t is the total gas pressure, y and x are the molar fraction of a in bulk phase and molar fraction of a in the adsorbed phase respectively. Combining equations (E1), (E2), (E3) and (E4), the molar fraction of a in the adsorbed phase can be obtained from the following equation:

$$\int_0^{\frac{\mathrm{y}p_\mathrm{t}}{\mathrm{x}}} \frac{q_\mathrm{a}}{p}\mathrm{d}p = \int_0^{\frac{(1-\mathrm{y})p_\mathrm{t}}{1-\mathrm{x}}} \frac{q_\mathrm{b}}{p}\mathrm{d}p \qquad \text{(E5)}$$

Before using equation (E5), the adsorption isotherms of the pure components must be fitted properly by the Langmuir adsorption models or others. Then one can get the Langmuir fitting parameters of adsorption equilibrium of pure a and pure b. Given the total pressure p_t and the molar fraction of a in bulk phase y, there is only one unknown variable quantity x (absorbed phase) in equation (E5), which is solvable.

After calculating the molar faction of a in adsorbed phase x, one can calculate the adsorption selectivity, which is defined as:

[S3] A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.

$$S = \frac{x_a / y_a}{x_b / y_b} \qquad (E6)$$

where x_a, y_a are the molar fraction of a in the adsorbed phase and molar fraction of a in bulk phase respectively, x_b, y_b are the molar fraction of b in the adsorbed phase and molar fraction of b in bulk phase respectively.

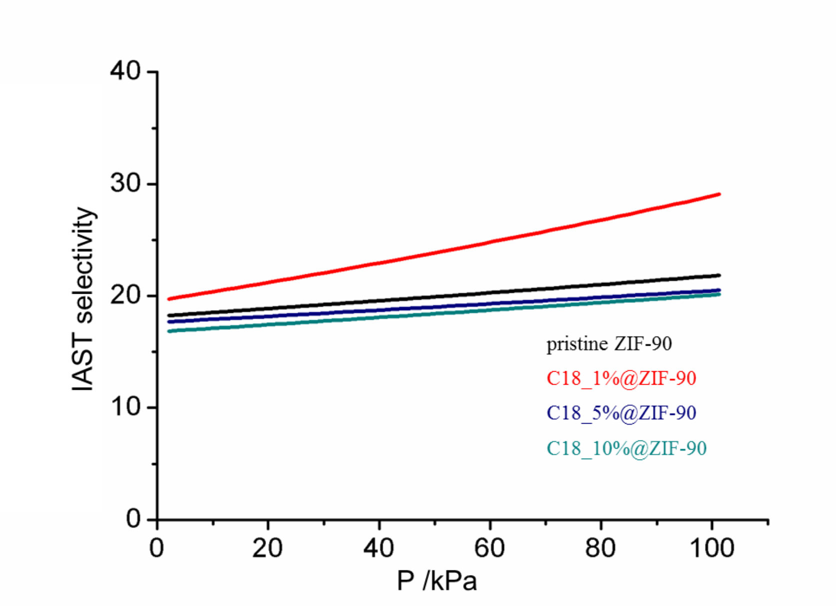

Fig. S20 Adsorption selectivity plots for 15/85 of CO_2/N_2 at 298 K predicted by IAST.

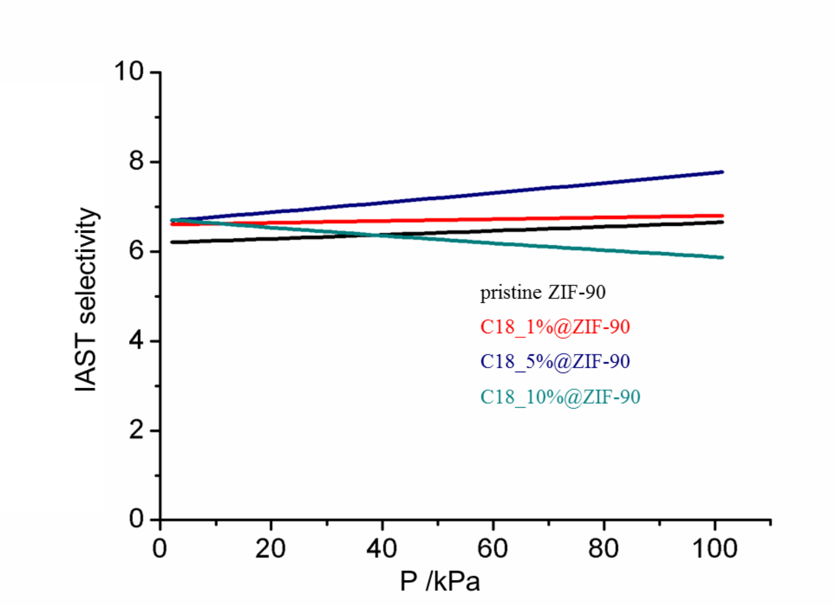

Fig. S21 Adsorption selectivity plots for 50/50 of CO_2/CH_4 at 298 K predicted by IAST.

Indexing of PXRD patterns

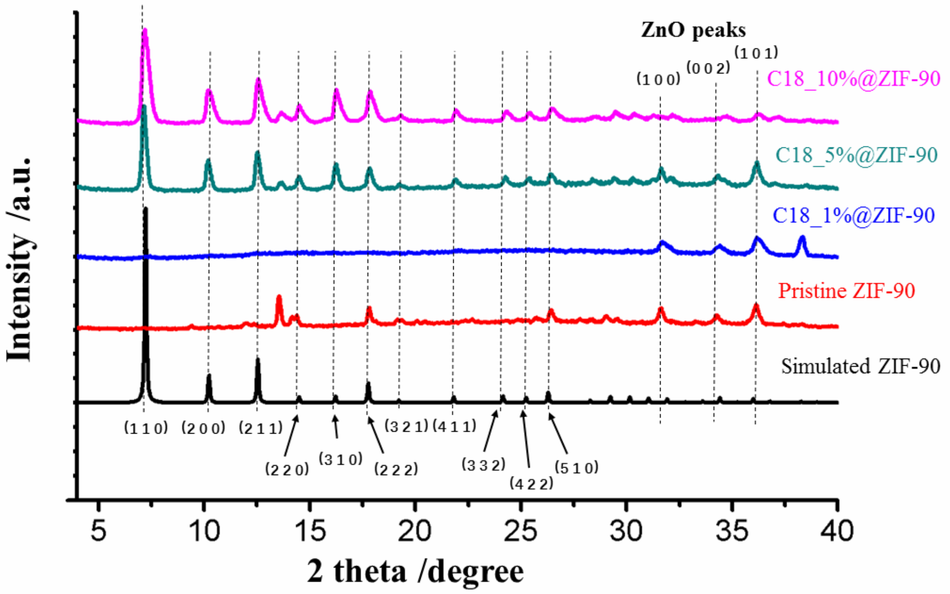

Fig. S22 Indexed PXRD patterns of pristine and quantitatively modified ZIF-90 samples after treatment of boiled water for 24 h. The additional PXRD peaks in the experimental patterns compared with that of the simulated one are attributed to partial decomposition of samples in hydrothermal conditions. The peaks located at ~31, 34, 36 are attributed to ZnO (simulated peaks at 31.776, 34.431, 36.263) generated from the hydrolysis of Zn-containing ZIF-90, while the peak at ~13-14 is from unknown residual (perhaps organic components) in the hydrolysis. The 10% sample showed better hydrothermal stability than the 5% sample, as evidenced by the diminished ZnO peaks for the former case, while the 1% sample showed mainly ZnO patterns, indicating complete decomposition.

Introducing ratios after further washing procedure

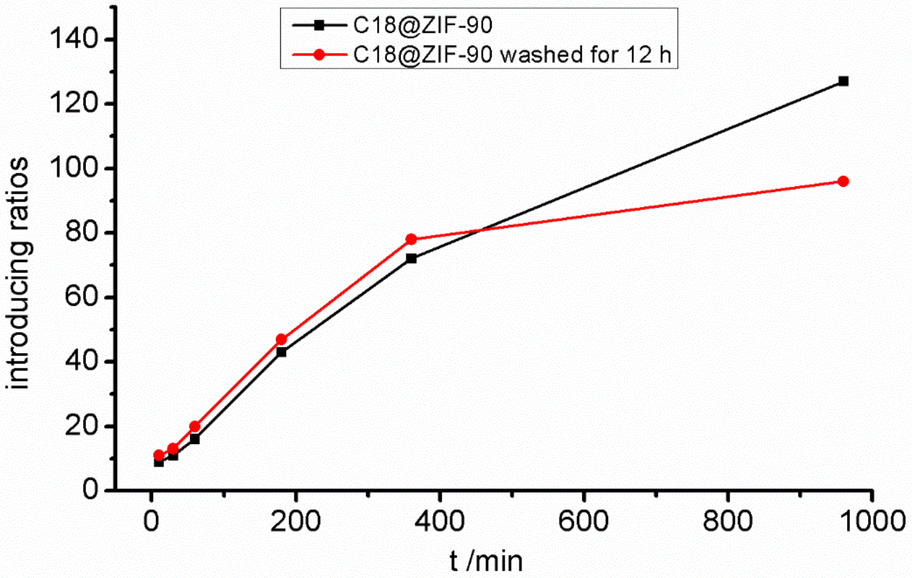

Fig. S23 Plots comparing the introducing ratios before and after a further wash by flash methanol for 12 h determined by ^{1}H-NMR. The ratios of C18_16h@ZIF-90 indicate a minor physisorption during later part of PSM process.