Supporting Information

Homogeneously Mixing Different Metal–Organic Framework Structures in Single Nanocrystals through Forming Solid Solutions

Ming Xu,1 Sha-Sha Meng,1 Peiyu Cai,2 Yu-Hao Gu1, Tong-An Yan3, Tian-Hao Yan4, Qing-Hua Zhang4, Lin Gu4, Da-Huan Liu3, Hong-Cai Zhou3,5,*, and Zhi-Yuan Gu1,6

1Jiangsu Key Laboratory of Biofunctional Materials, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of New Power Batteries, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China, e-mail: guzhiyuan@njnu.edu.cn
2Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, United States, e-mail: zhou@chem.tamu.edu
3State Key Laboratory of Organic–Inorganic Composites, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
4Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
5Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77842, United States
6Ming Xu, Sha-Sha Meng and Peiyu Cai contribute equally.
Section S1: Chemicals and Instrumentation

All chemicals employed were of analytical grade and used as supplied without further purification. The ZrCl₄, acetic acid, trifluoroacetic acid (TFA), ZrOCl₂·8H₂O, xylene, ethyltoluene, chlorotoluene, dichlorobenzene, C₆H₁₄, C₈H₁₈, C₉H₂₀ and C₁₀H₂₂ were purchased from Aladdin Industrial Inc (Shanghai, China). Ethanol (EtOH), N,N-Dimethylformamide (DMF) and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H₄TBAPy) and [1,1',3',1"-terphenyl]-4,4"-dicarboxylic acid (L₈) were synthesized following the published procedures. Powder X-ray diffraction (PXRD) patterns were obtained from Bruker Powder Diffractometer ECO with a CuKα radiation (1.54056 Å). Transmission electron microscopy (TEM) images were performed on JEOL JEM-2100F transmission electron microscopy ope, rated at an accelerating voltage of 200 kV. Scanning electron microscope images (SEM) were taken by FEI Quanta 600 FE-SEM and Thermo Fisher Apreo 2S Scanning Electron Microscope X ray Energy Dispersive Spectroscop. Some of the high angle annular dark field images (HAADF) were recorded on an ARM-200CF TEM (JEOL, Tokyo, Japan) operated at 200 keV and equipped with double spherical aberration (Cs) correctors. The attainable resolution of the probe defined by the objective pre-field is 78 picometers. The others were recorded on a Titan Themis Cubed G2 60-300 transmission electron microscope (FEI, US) with a probe corrector operated at 300 keV. Thermogravimetric analysis (TGA) was collected on a Perkin-Elmer Pyris Diamond 1 TGA analyzer. Nitrogen adsorption isotherm was measured using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry system. Each sample was activated under high vaccum at 80 °C for 10 h prior to measurement. All of the separations were performed on an Agilent 7890B gas chromatographic system with a flame ionization detector (FID). Data acquisition and processing were controlled by ChemStation software. Nitrogen (99.999%, Air Liquide, France) was employed as the carrier gas. The inlet temperature of the GC was set to 250 °C, while the temperature of FID was set to 300 °C. A 2.5 μL analyte was introduced
to a 20 mL gastight sealed glass vial and homogenized at 120 °C before the injection for gas chromatographic separation.

**Caution!** The analytes (xylene, ethyltoluene, chlorotoluene, dichlorobenzene, C₆H₁₄, C₈H₁₈, C₉H₂₀ and C₁₀H₂₂) constitute safety hazards. Facemask and latex gloves are needed when using these analytes. Ventilation installation should be turned on.
Section S2: Synthesis of MOSS, Nano-NU-1000 and typical NU-1000

Synthesis of MOSS

These MOSS were synthesized with two steps. First, 10 mg ZrCl$_4$, different amount of L$_B$ (20, 40, 60, 80, 100 and 120 mg) and 120 μL acetic acid were dissolved in 2 mL N,N-Dimethylformamide (DMF) in a 20 mL vial. The vial was sealed and heated at 100 °C for 1 h. After cooling down to room temperature, 10 mg H$_4$TBApy ligand, 160 μL acetic acid, and 20 μL deionized water were added to the mixture. Then, the vial was sealed again and heated at 120 °C for 24 h. The yellow product was collected by centrifugation and washed with DMF and acetone three times, respectively. The obtained MOSS was named as MOSS-1 to MOSS-6 for the amount of L$_B$ from 20 to 120 mg. For instance, MOSS-3 represents the MOSS synthesized with the addition of 60 mg L$_B$. Notably, the nano-NU-901 was synthesized with the same method without the addition of L$_B$. This synthesis method is different from the published ones.$^{1-5}$

Synthesis of Nano-NU-1000

The nano-NU-1000 was synthesized based on the reported method with a few changes.$^6$ Two solutions were prepared and heated at 100 °C for 1 h, respectively. In the first solution, 12.125 mg ZrOCl$_2$·8H$_2$O and 200 mg benzoic acid were dissolved in 1 mL DMF. In the second solution, 2.5 mg H$_4$TBApy ligand was dissolved in 1 mL DMF. After the heating procedure, the two solutions were mixed in a 4 mL vial. Then, 20 μL trifluoroacetic acid (TFA) was added to the mixture. The vial was sealed and heated at 100 °C for 1 h. The yellow product was collected by centrifugation and washed with DMF and acetone three times, respectively.

Synthesis of NU-1000/NU-901/NU-1000 heterostructure

The NU-1000/NU-901/NU-1000 heterostructure was synthesized based on the reported method with a few changes. Typically, 0.097 g ZrOCl$_2$·8H$_2$O and 2.7 g benzoic acid were dissolved in 8 mL DMF in a 20 mL vial. The mixture was heated at 80 °C for 1 h. After cooling down to the room temperature, 0.04 g H$_4$TBApy ligand was added into
the above mixture. The vial was sealed and heated at 100 °C for 24 h. The yellow product was collected by centrifugation and washed with DMF and ethanol three times, respectively.
Section S3: Characterization of MOF Solid Solutions, nano-NU-901, nano-NU-1000, NU-1000/NU-901/NU-1000 Heterostructure and Other Materials

Figure S1. SEM and TEM images of (a) nano-NU-901 and (b) nano-NU-1000.
Figure S1. (continued) PXRD patterns of (a) nano-NU-1000 and (b) nano-NU-901.
Figure S2. (a) SEM images and (b-c) TEM images of MOSS-1.
Figure S3. (a) HAADF images, (b) SEM images and (c-d) TEM images of MOSS-2.
Figure S4. (a-c) HAADF images, (d-f) SEM images and (g-h) TEM images of MOSS-3.
Figure S5. (a-f) HAADF images, (g) SEM images and (h-i) TEM images of MOSS-4.
Figure S6. (a-g) HAADF images and (g-i) TEM images of MOSS-5.
Figure S7. (a-f) HAADF images, (g-h) SEM images and (i) TEM images of MOSS-6.
Figure S8. SEM images of NU-1000/NU-901/NU-1000 heterostructure.
Figure S9. FFT images of different regions in a single particle MOSS-4.
Figure S9, (continued) FFT images of different regions in a single particle MOSS-5.
Figure S9. (continued) FFT images of different regions in a single particle MOSS-6.
Figure S10. N₂ adsorption-desorption isotherms and pore size distribution of MOSS-3 and nano-NU-1000 measured at 77 K.
**Figure S11.** PXRD patterns of material 1, material-2 and material-3. Here, a lightly shorter ligand 4,4'-sulfonyldibenzoic acid was chosen as the modulators, replacing L_B in the synthetic procedure. The obtained materials were named material-1, material-2 and material-3 with the addition of 20 mg, 40 mg and 60 mg of 4,4'-sulfonyldibenzoic acid, accordingly. The PXRD patterns show that there is no diffraction peak at 2.6° which belongs to csq topology.
Section S4: Cell Parameters of NU-901 and NU-1000

Figure S12. PXRD of MOSS-1, MOSS-2, MOSS-3, MOSS-4, MOSS-5 and MOSS-6 after Pawley refinement with Material Studio 7.0 software. Considering the structure of all MOSS, the PXRD patterns of MOSS-1 and MOSS-2 were refined with the CIF of NU-901 and the PXRD patterns of MOSS-3, MOSS-4, MOSS-5 and MOSS-6 were refined with the CIF of NU-1000.
Table S1. The $a$-axis length of all MOSS, simulated NU-1000 and simulated NU-901.

| Material               | $a$ axis length (Å) |
|------------------------|---------------------|
| simulated NU-901       | 19.146\textsuperscript{7} |
| MOSS-1                 | 19.014              |
| MOSS-2                 | 19.286              |
| MOSS-3                 | 39.363              |
| MOSS-4                 | 39.100              |
| MOSS-5                 | 38.779              |
| MOSS-6                 | 38.631              |
| simulated NU-1000      | 39.388\textsuperscript{8} |

The mixing of micropore and mesopore windows only exists on the ab-plane. Thus, the change of the values of unit cell parameter c was not considered here.
Section S5: Computational Simulation of the Energy of Two Ligands in the NU-1000 and NU-901

To provide guidance for the interpretation of the experimental work, a density functional theory (DFT) study was performed to examine the relative stabilities of two ligands in the NU-1000 and NU-901. The computations were performed with the DMol3 programs of Materials Studio 7.0. The functional B3LYP and default settings embedded in Materials Studio 7.0 were employed for all calculations. The carboxylates of linkers were terminated by H to balance the charge. The distances between two C atoms from neighboring carboxylates were fixed to 11.64 and 11.25 Å respectively, corresponding to the C-C distances in the crystal structure of NU-1000 and NU-901. The equilibrium geometries and energy of model compounds were calculated with the C2h (NU-1000) and C2v (NU-901) symmetric constraints in the gas phase. For comparison, the energies of a linker in different frameworks were normalized by subtracting the lowest value.
Section S6: HNMR of the Destroyed MOF Solid Solutions

Typically, the ratio of L\textsubscript{B} and H\textsubscript{4}TBApy in MOSS were calculated from the HNMR patterns of the destroyed materials. About 5 mg material were added into a 1.5 mL plastic tube, mixed with about 1 mL DMSO-d\textsubscript{6} and 20 µL D\textsubscript{2}SO\textsubscript{4}. Then, the tube was heated until all the solid was dissolved. The solution was transferred to a NMR tube and analyzed on an Inova 500 MHz spectrometer.

![HNMR pattern of MOSS-1](image)

**Figure S13.** HNMR pattern of MOSS-1.
Figure S14. HNMR pattern of MOSS-2.
Figure S15. HNMR pattern of MOSS-3.
Figure S16. HNMR pattern of MOSS-4.
Table S2. The Ratio of H₄TBApy to L₂, and the Ratio of H₄TBApy to CH₃COOH.

| Material | H₄TBApy: L₂ | H₄TBApy: CH₃COOH |
|----------|-------------|------------------|
| MOSS-1   | 1.00:0.86   | 1.00:0.98        |
| MOSS-2   | 1.00:0.88   | 1.00:0.70        |
| MOSS-3   | 1.00:1.59   | 1.00:0.23        |
| MOSS-4   | 1.00:1.75   | 1.00:0.15        |
Section S7: BET Surface Area and the Volume Ratio of Mesopores to Micropores in All MOSS

Table S3. BET surface area and the volume ratio of mesopores to micropores in all MOSS.

| Material | BET surface area (m²/g) | The volume ratio of mesopores to micropores |
|----------|------------------------|---------------------------------------------|
| MOSS-1   | 488                    | 0.2:1                                       |
| MOSS-2   | 697                    | 0.33:1                                      |
| MOSS-3   | 1125                   | 1:1                                         |
| MOSS-4   | 1010                   | 0.72:1                                      |
| MOSS-5   | 1045                   | 0.68:1                                      |
| MOSS-6   | 845                    | 0.47:1                                      |
Section S8: SEM Images of MOF Solid Solutions, nano-NU-901, nano-NU-1000 and NU-1000/NU-901/NU-1000 heterostructure Coated Columns

Capillary pretreatment:

A fused silica capillary (15 m long × 0.25 mm i.d., Yongnian Optic Fiber Plant, Hebei, China) was pre-treated according to the following recipe before dynamic coating with the materials: the capillary was washed sequentially with 1 mol/L NaOH for 2 h, ultrapure water for 30 min, 0.1 mol/L HCl for 2 h, ultrapure water again until the outflow reached pH=7.0, and finally methanol for 30 min. After the above process, the capillary was modified with 3-aminopropyltriethoxysilane (APTES) to provide the amino groups to enhance the interactions with nanosheets on the inner wall of the capillary column. The pretreated capillary was filled with a methanol solution of APTES (50%, v/v), and incubated in a 40 °C water bath overnight with both ends of the capillary sealed. The APTES-modified capillary was rinsed with methanol to flush out the residuals and dried with a stream of nitrogen at 120 °C.

Coating the materials:

Different materials were coated onto the pretreated capillary column by a simple dynamic coating method as follows: 1 mL (2 mg/mL) methanol suspension of each material was first filled into the capillary column and then pushed through the column at a velocity of 30 cm/min to leave a wet coating layer on the inner wall of the capillary column. After coating, the capillary column was settled for conditioning under nitrogen for 2 h to remove the solvent. Further conditioning of the capillary column was carried out using a temperature program: maintain 30 °C for 30 min, then ramp to 250 °C at a rate of 2 °C/min and keep 250 °C for 180 min. The temperature program was repeated 3 times.
**Figure S17.** SEM images of (a) capillary column, (b) NU-1000/NU-901/NU-1000 heterostructure, (c) nano-NU-901, (d) nano-NU-1000, (e) MOSS-1, (f) MOSS-2, (g) MOSS-3, and (h) MOSS-4 coated columns.
Figure S18. SEM images of the top-down view of the capillary column coated with MOSS-2.
**Figure S19.** SEM images of the top-down view of the capillary column coated with MOSS-3.
Section S9: Thermogravimetric Analysis of MOF Solid Solutions, Nano-NU-901 and Nano-NU-1000

Figure S20. Thermogravimetric analysis (TGA) of MOSS-1, MOSS-2, MOSS-3 and MOSS-4.
Section S10: Gas Chromatogram for the Separation of Different Analytes.

Figure S21. Gas chromatogram on the (a) nano-NU-901, (b) MOSS-1, (c) MOSS-2, (d) MOSS-3, (e) MOSS-4 and (f) nano-NU-1000 coated columns for the separation of linear alkanes from $\text{C}_6\text{H}_{14}$ to $\text{C}_{10}\text{H}_{22}$. The peaks marked with red “*” represent the impurities of the analytes. The different elution time of the first chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S22. Gas chromatogram on the (a) nano-NU-901, (b) MOSS-1, (c) MOSS-2, (d) MOSS-3, (e) MOSS-4 and (f) nano-NU-1000 coated columns for the separation of three C₆H₁₄ isomers (2-methylpentane, 3-methylpentane and n-hexane). The different elution time of the fist chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S23. Gas chromatogram on the (a) nano-NU-901, (b) MOSS-1, (c) MOSS-2, (d) MOSS-3, (e) MOSS-4 and (f) nano-NU-1000 coated columns for the separation of three C₈H₁₈ isomers (2,4-dimethylhexane, 3-methylheptane and n-octane). The different elution time of the first chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S24. Gas chromatogram on the (a) nano-NU-901, (b) MOSS-1, (c) MOSS-2, (d) MOSS-3, (e) MOSS-4 and (f) nano-NU-1000 coated columns for the separation of three C_{10}H_{22} isomers (4,4-dimethyloctane, 3,3-dimethyloctane and n-decane). The different elution time of the first chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S25. Gas chromatogram on the NU-1000/NU-901/NU-1000 heterostructure coated columns for the separation of (a) linear alkanes from C_6H_{14} to C_{10}H_{22}, (b) three C_8H_{18} isomers (2,4-dimethylhexane, 3-methylheptane and n-octane), (c) o,m,p-chlorotoluene isomers, and (d) o,m,p-xylene isomers. The different elution time of the first chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S26. Gas chromatogram on the MOSS-1 coated columns for the separation of (a) o,m,p-dichlorobenzene isomers, (b) o,m,p-xylene isomers, and (c) o,m,p-chlorotoluene isomers. The different elution time of the first chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S27. Gas chromatogram on the MOSS-2 coated columns for the separation of (a) o,m,p-dichlorobenzene isomers, (b) o,m,p-xylene isomers, and (c) o,m,p-chlorotoluene isomers. The different elution time of the fist chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S28. Gas chromatogram on the MOSS-3 coated columns for the separation of (a) o,m,p-dichlorobenzene isomers, (b) o,m,p-xylene isomers, and (c) o,m,p-chlorotoluene isomers. The different elution time of the first chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S29. Gas chromatogram on the MOSS-4 coated columns for the separation of (a) o,m,p-dichlorobenzene isomers, (b) o,m,p-xylene isomers, and (c) o,m,p-chlorotoluene isomers. The different elution time of the first chromatographic peak is resulted from the different temperature programming which does not represent the different separation performance.
Figure S30. Gas chromatogram on the MOSS-3 coated columns for the separation of o,m,p-dichlorobenzene isomers. The MOSS-3 was synthesized and kept at room temperature for about 8 months before the coating procedure. Each column aging cycle for MOSS-3 includes heating to 250 °C and cooling to 100 °C.
Table S4. Selectivity ($\alpha$) for different isomers on the MOSS, nano-NU-901 and nano-NU-1000-coated capillary columns.

| Analytes                              | Nano-NU-901 | Nano-NU-1000 | MOSS-1 | MOSS-2 | MOSS-3 | MOSS-4 |
|---------------------------------------|-------------|--------------|--------|--------|--------|--------|
| 2-methylpentane/3-methylpentane       | 1.00        | 1.05         | 1.06   | **1.08** | 1.03   | 1.07   |
| 3-methylpentane/hexane                | **1.28**    | 1.12         | 1.04   | 1.10   | 1.01   | 1.05   |
| 2-methylpentane/hexane                | **1.28**    | 1.18         | 1.10   | 1.03   | 1.04   | 1.12   |
| 2,4-dimethylhexane/3-methylheptane    | **1.21**    | 1.14         | 1.10   | 1.07   | 1.04   | 1.12   |
| 3-methylheptane/octane                | **1.24**    | 1.08         | 1.09   | 1.11   | 1.03   | 1.11   |
| 2,4-dimethylhexane/octane             | **1.50**    | 1.23         | 1.20   | 1.18   | 1.07   | 1.24   |
| 4,4-dimethyloctane/3,3-dimethyloctane | **1.17**    | 1.07         | 1.11   | 1.09   | 1.07   | 1.11   |
| 3,3-dimethyloctane/decane             | **1.69**    | 1.20         | 1.23   | 1.16   | 1.14   | 1.20   |
| 4,4-dimethyloctane/decane             | **1.98**    | 1.28         | 1.36   | 1.27   | 1.22   | 1.33   |
| o-xylene/m-xylene                     | 1.07        | 1.05         | **1.12** | **1.12** | **1.12** | **1.12** |
| m-xylene/p-xylene                     | **1.15**    | 1.08         | 1.07   | 1.05   | 1.06   | 1.07   |
| o-xylene/p-xylene                     | 1.08        | **1.13**     | 1.05   | 1.07   | 1.06   | 1.04   |
| o-dichlorobenzene/m-dichlorobenzene   | **1.18**    | 1.11         | 1.10   | 1.10   | 1.06   | 1.10   |
| m-dichlorobenzene/p-dichlorobenzene   | 1.12        | 1.03         | 1.23   | 1.19   | 1.14   | **1.24** |
| o-dichlorobenzene/p-dichlorobenzene   | 1.06        | 1.06         | **1.11** | 1.08   | 1.07   | 1.04   |
| o-chlorotoluene/m-chlorotoluene       | **1.06**    | **1.06**     | 1.04   | 1.04   | 1.04   | **1.06** |
| m-chlorotoluene/p-chlorotoluene       | **1.18**    | 1.00         | 1.13   | 1.12   | 1.10   | 1.14   |
| o-chlorotoluene/p-chlorotoluene       | **1.25**    | 1.06         | 1.18   | 1.16   | 1.15   | 1.21   |

The highest value for each pair is marked as bold.
Table S5. Separation resolution ($R_s$) for different isomers on the MOSS, nano-NU-901 and nano-NU-1000-coated capillary columns.

| Analytes                        | Nano-NU-901 | Nano-NU-1000 | MOSS-1 | MOSS-2 | MOSS-3 | MOSS-4 |
|---------------------------------|-------------|--------------|--------|--------|--------|--------|
| 2-methylpentane/3-methylpentane | 0           | 0.31         | 1.27   | 1.10   | 1.55   | 0.98   |
| 3-methylpentane/hexane          | 0.75        | 0.94         | 0.93   | 0.34   | 0.95   | 0.46   |
| 2-methylpentane/hexane          | 0.79        | 1.14         | 2.20   | 1.23   | 2.40   | 1.08   |
| 2,4-dimethylhexane/3-methylheptane | 0.69    | 1.32         | 1.56   | 1.51   | 2.80   | 0.97   |
| 3-methylheptane/octane          | 0.90        | 0.97         | 1.53   | 1.45   | 2.07   | 0.91   |
| 2,4-dimethylhexane/octane       | 1.67        | 1.93         | 3.25   | 2.92   | 4.79   | 1.80   |
| 4,4-dimethyloctane/3,3-dimethyloctane | 0.48   | 0.73         | 1.75   | 2.24   | 2.63   | 1.40   |
| 3,3-dimethyloctane/decane       | 1.92        | 1.31         | 3.81   | 4.18   | 5.22   | 2.86   |
| 4,4-dimethyloctane/decane       | 2.10        | 2.02         | 5.80   | 6.39   | 8.18   | 4.03   |
| o-xylene/m-xylene               | 0.16        | 0.92         | 1.79   | 2.01   | 2.28   | 1.00   |
| m-xylene/p-xylene               | 0.47        | 1.14         | 1.08   | 0.86   | 1.17   | 0.87   |
| o-xylene/p-xylene               | 0.27        | 0.35         | 0.88   | 1.13   | 1.12   | 0.45   |
| o-dichlorobenzene/m-dichlorobenzene | 0.31    | 0.31         | 1.72   | 1.96   | 2.06   | 0.9    |
| m-dichlorobenzene/p-dichlorobenzene | 0.60   | 1.05         | 3.86   | 4.05   | 4.48   | 2.15   |
| o-dichlorobenzene/p-dichlorobenzene | 0.23   | 0.72         | 2.06   | 1.73   | 2.35   | 1.10   |
| o-chlorotolune/m-chlorotoluene  | 0.10        | 0.37         | 0.80   | 0.59   | 1.03   | 0.68   |
| m-chlorotoluene/p-chlorotoluene | 0.36        | 0.00         | 2.80   | 1.96   | 2.87   | 1.41   |
| o-chlorotoluene/p-chlorotoluene | 0.22        | 0.40         | 3.66   | 2.7    | 4.43   | 2.45   |

The highest value for each pair is marked as bold.
Section S11: Calculation of Thermodynamic Parameters

The adsorption enthalpy (ΔH) was calculated via the van’t Hoff equation:

\[ \ln k' = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \phi \]

Where \( k' \) is the retention factor, \( R \) is the gas constant, \( T \) is the absolute temperature, and \( \phi \) is the phase ratio (the ratio of the volume of the stationary phase (V_s) to that of the mobile phase (V_m)). To obtain \( \phi \), \( V_s \) was calculated from the film thickness of nanosheets coated capillary column, while \( V_m \) was calculated from the column internal volume subtract the \( V_s \).

The \( k' \) was calculated according to the next equation:

\[ k' = \frac{t - t_0}{t_0} \]

Where \( t \) is the retention time of the analyte, and \( t_0 \) is the retention time of an unretained compound on the column.

**Figure S31.** The van’t Hoff plots for xylene isomers on the (a) nano-NU-901, (b) nano-NU-1000 and (c) MOSS-3 coated column.
Table S6. $\Delta H$ of xylene isomers on the MOSS-3 detected from 433.15 K to 473.15 K

| Stationary Phase | $\Delta H$ (kJ/mol) |  |
|------------------|---------------------|--|
|                  | p-xylene            | o-xylene | m-xylene |
| MOSS-3           | $-74.77\pm0.03$     | $-73.26\pm0.11$ | $-73.18\pm0.18$ |

Table S7. $\Delta H$ of xylene isomers on the nano-NU-901 detected from 453.15 K to 493.15 K

| Stationary Phase | $\Delta H$ (kJ/mol) |  |
|------------------|---------------------|--|
|                  | p-xylene            | o-xylene | m-xylene |
| nano-NU-901      | $-71.18\pm1.53$     | $-68.77\pm0.82$ | $-68.32\pm0.68$ |

Table S8. $\Delta H$ of xylene isomers on the nano-NU-1000 detected from 353.15 K to 393.15 K

| Stationary Phase | $\Delta H$ (kJ/mol) |  |
|------------------|---------------------|--|
|                  | p-xylene            | o-xylene | m-xylene |
| nano-NU-1000     | $-58.31\pm1.12$     | $-62.34\pm2.19$ | $-61.48\pm0.47$ |
Section S12: Calculation of Diffusion Constant

The diffusion constant ($D_s$) was calculated via the Golay equation:

$$H = \frac{2D_g}{u} + \frac{1 + 6k + 11k^2}{24(1 + k)^2} \times \frac{r^2}{D_g} \times u + \frac{2}{3} \times \frac{k}{(1 + k)^2} \times \frac{d_f^2}{D_s} \times u$$

Where $D_g$ is the diffusion constant of analyte in the gaseous phase, $D_s$ is the diffusion constant of analyte in the stationary phase, $r$ is the radius of the capillary column, $d$ is the thickness of the stationary phase, $u$ is the linear velocity of the carrier gas, $H$ is the height equivalent of theoretical plate and $N$ is the number of theoretical plates. The elution temperature of the first isomer among all three isomers using temperature programming process was chosen here.

Figure S32. The Golay equation for xylene isomers on the (a) NU-901, (b) NU-1000 and (c) MOSS-3 coated column.
Table S9. $D_s$ of xylene isomers on the MOSS-3 at 453.15 K

| Stationary Phase | $D_s$ (m$^2$/s) |
|------------------|------------------|
|                  | p-xylene         | o-xylene         | m-xylene         |
| MOSS-3           | 8.70×10^{-11}    | 5.65×10^{-11}    | 8.38×10^{-11}    |

Table S10. $D_s$ of xylene isomers on the nano-NU-901 at 473.15 K

| Stationary Phase | $D_s$ (m$^2$/s) |
|------------------|------------------|
|                  | p-xylene         | o-xylene         | m-xylene         |
| nano-NU-901      | 6.76×10^{-12}    | 3.99×10^{-12}    | 9.46×10^{-12}    |

Table S11. $D_s$ of xylene isomers on the nano-NU-1000 at 373.15 K

| Stationary Phase | $D_s$ (m$^2$/s) |
|------------------|------------------|
|                  | p-xylene         | o-xylene         | m-xylene         |
| nano-NU-1000     | 7.97×10^{-12}    | 3.87×10^{-12}    | 4.16×10^{-12}    |
Section S13: Computational Simulation of Thermodynamic Parameters and Diffusion Constant

Density functional theory (DFT) simulation. To provide guidance for the interpretation of the experimental work, a DFT study was performed to examine the relative stabilities of two ligands in NU-1000 and NU-901. The computations were performed with the DMol3 programs of Materials Studio 7.0. The functional B3LYP and default settings embedded in Materials Studio 7.0 were employed for all calculations. The carboxylates of linkers were terminated by H to balance the charge. The distances between two C atoms from neighboring carboxylates were fixed to 11.64 Å and 11.25 Å, respectively, corresponding to the C-C distances in the crystal structure of NU-1000 and NU-901. The equilibrium geometries and energy of model compounds were calculated with the C2h (NU-1000) and C2v (NU-901) symmetric constraints in the gas phase. For comparison, the energies of a linker in different frameworks were normalized by subtracting the lowest value. The energy of H4TBApy ligand in NU-1000 is -1635.512525 Hartree, in NU-901 is -1635.519933 Hartree. The energy of L4 ligand in NU-1000 is -737.2981338 Hartree, in NU-901 is -737.2962046 Hartree.

Force Fields. In the simulations, the atoms on the materials were assumed to be frozen in their crystallographic positions and the partial point charges of the framework were distributed by QEq method. The interactions between the xylene-xylene isomers and xylene-framework are Lennard-Jones and electrostatic interactions. For the framework, the LJ parameters were taken from the UFF force field. Simulation parameters for xylenes were taken from the OPLS force field. The xylene isomers were treated as rigid planar molecules consisting of carbon atoms, hydrogen atoms and methyl groups. The bond distances of C−C, C−H and C−CH3 were fixed to 1.40, 1.08 and 1.51 Å, respectively. The angles of C−C−C, C−C−H, and C−C−CH3 were set to 120°. Except the atoms on the CH3 groups, the atoms on xylene molecules were defined one by one. The atoms on the CH3 groups were regarded as unified atoms centered on carbon atoms.

Simulation Details. GCMC and MD simulations were performed by RASPA package according to the experimental temperatures. In the GCMC simulations, translation, rotation, regrowth and swap of a molecule were considered. To ensure the simulation unit was extended to at least 28.0 Å along
each dimension, 1×1×2 of the MOF units was utilized. Meanwhile, the periodic boundary condition was applied. The adsorption was simulated with at least 50,000 cycles including 25,000 initialization cycles and at least 25,000 cycles to obtain the average values. The Peng-Robinson equation of state was used to convert the pressure into the corresponding fugacity. In the zero-coverage limit (infinite dilution), the $Q_{st}$ of each xylene isomer was calculated using the Widom\textsuperscript{13} particle insertion method.

Diffusion behavior of each xylene isomer was investigated by inserting one molecule into the unit cell in each material using a canonical (NVT) ensemble. The MD simulations were performed according to experimental conditions. The fixed temperatures were maintained by a Nosé–Hoover chain (NHC)\textsuperscript{14} thermostat. The velocity Verlet algorithm was used to integrate Newton's equation of motion. The simulation steps and a time step of each MD simulation were 6 ns cycles and 1 fs, respectively, and then preceeded by 3 ns of equilibration. Finally, 5 independent trajectories were output to calculate the self-diffusion coefficients on average. The self-diffusion coefficient of each xylene isomer was calculated from the slope of the mean square displacement (MSD) of the xylenes.

**Table S12. The simulated isotropic heat of adsorption ($Q_{st}$) of xylene isomers on the MOSS, nano-NU-901 and nano-NU-1000.**

| Stationary Phase | $Q_{st}$ (kJ/mol) |
|------------------|-------------------|
|                  | p-xylene | o-xylene | m-xylene |
| nano-NU-901      | -70.47    | -65.51   | -64.94   |
| nano-NU-1000     | -55.11    | -61.26   | -56.87   |
| MOSS-3           | -60.20    | -59.08   | -58.72   |

The highest value for each pair is marked as bold.
Figure S33. The self-diffusion coefficients for xylene isomers on the (a) NU-901, (b) NU-1000 and (c) MOSS-3 coated column.

Table S13. The simulated self-diffusion coefficient of xylene isomers on the MOSS, nano-NU-901 and nano-NU-1000.

| Stationary Phase (Temperature) | p-xylene | o-xylene | m-xylene |
|-------------------------------|----------|----------|----------|
| NU-901 (473.15 K)             | 8.75×10⁻¹⁰ | 4.41×10⁻¹⁰ | **2.06×10⁻⁹** |
| NU-1000 (373.15 K)            | **1.99×10⁹** | 5.06×10⁻¹⁰ | 8.37×10⁻¹⁰ |
| MOSS-3 (453.15 K)             | 2.36×10⁹   | 7.80×10⁻¹⁰ | 9.41×10⁻¹⁰ |

The highest value for each pair is marked as bold.
Reference

1. Kung, C.-W., Wang, T. C., Mondloch, J. E., Fairen-Jimenez, D., Gardner, D. M., Bury, W., et al. Metal–Organic Framework Thin Films Composed of Free-Standing Acicular Nanorods Exhibiting Reversible Electrochromism. Chem. Mater. 2013, 25(24): 5012-5017.

2. Xu, M., Meng, S.-S., Cai, P., Tang, W.-Q., Yin, Y.-D., Powell, J. A., et al. Modulating the stacking modes of nanosized metal–organic frameworks by morphology engineering for isomer separation. Chem. Sci. 2021.

3. Garibay, S. J., Iordanov, I., Islamoglu, T., DeCoste, J. B., Farha, O. K. Synthesis and functionalization of phase-pure NU-901 for enhanced CO2 adsorption: the influence of a zirconium salt and modulator on the topology and phase purity. CrystEngComm 2018, 20(44): 7066-7070.

4. Deria, P., Yu, J., Smith, T., Balaraman, R. P. Ground-State versus Excited-State Interchromophoric Interaction: Topology Dependent Excimer Contribution in Metal–Organic Framework Photophysics. J. Am. Chem. Soc. 2017, 139(16): 5973-5983.

5. Verma, P. K., Huelsenbeck, L., Nichols, A. W., Islamoglu, T., Heinrich, H., Machan, C. W., et al. Controlling Polymorphism and Orientation of NU-901/NU-1000 Metal–Organic Framework Thin Films. Chem. Mater. 2020, 32(24): 10556-10565.

6. Li, P., Klet, R. C., Moon, S.-Y., Wang, T. C., Deria, P., Peters, A. W., et al. Synthesis of nanocrystals of Zr-based metal–organic frameworks with csq-net: significant enhancement in the degradation of a nerve agent simulant. Chem. Commun. 2015, 51(54): 10925-10928.

7. Ray, D., Goswami, S., Duan, J., Hupp, J. T., Cramer, C. J., Gagliardi, L. Tuning the Conductivity of Hexa-Zirconium(IV) Metal–Organic Frameworks by Encapsulating Heterofullerenes. Chem. Mater. 2021, 33(4): 1182-1189.

8. Mondloch, J. E., Bury, W., Fairen-Jimenez, D., Kwon, S., DeMarco, E. J., Weston, M. H., et al. Vapor-Phase Metalation by Atomic Layer Deposition in a Metal–Organic Framework. J. Am. Chem. Soc. 2013, 135(28): 10294-10297.

9. Wells, B. A., De Bruin-Dickason, C., Chaffee, A. L. Charge Equilibration Based on Atomic Ionization in Metal–Organic Frameworks. J. Phys. Chem. C 2015, 119(1): 456-466.

10. Rappe, A. K., Casewit, C. J., Colwell, K. S., Goddard, W. A., Skiff, W. M. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. J. Am. Chem. Soc. 1992, 114(25): 10024-10035.
11. Stacchiola, D., Tysoe, W. T. The Kinetics of Ethylidyne Formation from Ethylene on Pd(111). *J. Phys. Chem. C* 2009, **113**(19): 8000-8001.

12. Dubbeldam, D., Calero, S., Ellis, D. E., Snurr, R. Q. RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials. *Mol. Simulat.* 2016, **42**(2): 81-101.

13. Frenkel, D. & Smit, B. Understanding Molecular Simulation: From Algorithms to Applications (Academic Press, 2001).

14. Martyna, G. J., Tuckerman, M. E., Tobias, D. J., Klein, M. L. Explicit reversible integrators for extended systems dynamics. *Mol. Phys.* 1996, **87**(5): 1117-1157.