Ligand Functionalization of Defect-Engineered Ni-MOF-74

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Experimental section

General procedure

The reagents were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D2 Phaser automated diffractometer at room temperature with a step size of \(2 \theta = 0.02^\circ\). Solution-state \(^1\)H nuclear magnetic resonance (NMR) spectra of acid digested samples in DMSO-d\(_6\), DCl (35\%), and D\(_2\)SO\(_4\) were recorded using a Bruker 400 MHz FT-NMR spectrometer at the UNIST Central Research Facilities. The \(^1\)H chemical shifts were referenced to the residual proton resonance of the DMSO-d\(_6\) solvent in ppm. Thermogravimetric analysis (TGA) was performed using an STD Q-600 series instrument (TA Instruments Inc.) at a heating rate of 10 °C min\(^{-1}\) under an N\(_2\) flow.

Gas adsorption measurements

Samples in amount of 20–40 mg were pretreated at 150 °C under vacuum for 24 h prior to gas adsorption measurements. N\(_2\) adsorption/desorption isotherms were measured at 77 K using a BELSORP-Max (BEL Japan, Inc.) low-pressure adsorption measuring system employing a standard volumetric technique up to saturation pressure. The adsorption data in the pressure range of \(< 0.1 \frac{P}{P_0}\) were fitted to the Brunauer–Emmett–Teller (BET) equation to determine the BET surface area using the BELMaster software (BEL Japan). CO\(_2\) adsorption/desorption isotherms were recorded using the BELSORP-Max adsorption measuring system equipped with a temperature control unit. For all defect-engineered Ni-MOF-74 derivatives, the CO\(_2\) adsorption isotherms were measured at 273 K up to 1 bar. For the defect-engineered derivatives selected for isosteric heat of adsorption (\(Q_{\text{st}}\)) calculations, CO\(_2\) adsorption isotherms were recorded at 273 K, 283 K, and 293 K, respectively. All adsorption data were manipulated with BEL-Master software provided by BEL Japan Inc.

Calculation of the Isosteric heat of adsorption

Virial equation (1) was employed to calculate the isosteric heat of adsorption (\(Q_{\text{st}}\)) for CO\(_2\) in the defect-engineered Ni-MOF-74.\(^{81}\)
In equation (1), $p$ is the pressure of the gas phase at equilibrium (kPa), $N$ is the adsorbed amount per mass of adsorbent (mmol g$^{-1}$), $T$ is the absolute temperature (K), $a_i$ and $b_j$ are virial coefficients, and $m$ and $n$ represent the number of coefficients required to adequately fit the isotherms. The coverage-dependent isosteric heat of adsorption $Q_{st}$ was evaluated using equation (2).

$$Q_{st} = - R \sum_{i=0}^{m} a_i N^i$$  \hspace{1cm} (2)$$

In equation (2), $R$ is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). The virial coefficients were derived by fitting the experimental adsorption isotherms ($\ln p$ versus $N$) measured at 273 K, 283 K, and 293 K. The fitted parameter values are presented in Electronic Supplementary Information (ESI).
Figure S1. $^1$H NMR spectra of acid digested 5-fSA$_x$(a/b). (a) 5-fSA$_{0.08}$(9/1), (b) 5-fSA$_{0.21}$(7/3), and (c) 5-fSA$_{0.39}$(5/5). In 5-fSA$_x$(a/b), $x$ is the estimated molar fraction of the fragmented ligand, H$_2$-5-fSA, in the framework from the $^1$H NMR spectrum, and a/b is the molar ratio of H$_2$DOBDC and H$_2$-5-fSA used to prepare the defect-engineered Ni-MOF-74.
Figure S2. $^1$H NMR spectra of acid digested 3-hSA$_x$. (a) 3-hSA$_{0.06}$(9/1), (b) 3-hSA$_{0.21}$(7/3), and (c) 3-hSA$_{0.41}$(5/5).
Figure S3. $^1$H NMR spectra of acid digested 2-hNA$_x$. (a) 2-hNA$_{0.06}(9/1)$, (b) 2-hNA$_{0.17}(7/3)$, and (c) 2-hNA$_{0.29}(5/5)$. 
Figure S4. $^1$H NMR spectra of acid digested 5-hBImCA$_x$. (a) 5-hBImCA$_{0.04}(9/1)$, (b) 5-hBImCA$_{0.12}(7/3)$, and (c) 5-hBImCA$_{0.20}(5/5)$. 
Figure S5. Thermogravimetric analysis of defect-engineered Ni-MOF-74. (a) 5-fSA₅, (b) 3-hSA₅, (c) 2-hNA₅, and (d) 5-hBImCA₅.
Figure S6. Comparison of PXRD patterns for defect-engineered Ni-MOF-74 before and after exposure to boiling water for 3 days. (a) 5-fSA_{x}, (b) 3-hSA_{x}, (c) 2-hNA_{x}, and (d) 5-hBImCA_{x}. 
Figure S7. Nonlocal density functional theory (NLDFT) pore-size distribution of (a) 5-fSA<sub>x</sub>,
(b) 3-hSA<sub>x</sub>, (c) 2-hNA<sub>x</sub>, and (d) 5-hBImCA<sub>x</sub>.
Figure S8. Nonlocal density functional theory (NLDFT) pore-size distribution and cumulative pore volume of 3-hSA$_{0.41}$. The black line and squares represent the cumulative pore volume, and the red line and squares represent the pore-size distribution.
Figure S9. The overall correlation of CO₂ uptakes with (a) surface areas and (b) pore volumes of defect-engineered Ni-MOF-74 derivatives.
Figure S10. (a) CO$_2$ sorption isotherms of 5-fSA$_{0.08}$ recorded at 273 K, 283 K, and 293 K. (b) virial analysis of isotherms.
Figure S11. (a) CO₂ sorption isotherms of 5-hSA₀.₀₆ recorded at 273 K, 283 K, and 293 K. (b) Virial analysis of isotherms.
Figure S12. (a) CO$_2$ sorption isotherms of 2-hNA$_{0.06}$ recorded at 273 K, 283 K, and 293 K. (b) virial analysis of isotherms.
Figure S13. (a) CO$_2$ sorption isotherms of 5-hBImCA$_{0.12}$ recorded at 273 K, 283 K, and 293 K. (b) virial analysis of isotherms.
Figure S14. (a) CO$_2$ sorption isotherms of defect-free Ni-MOF-74 recorded at 273 K, 283 K, and 293 K. (b) Virial analysis of isotherms.
Table S1. Doping ratios of fragmented ligands in the defect-engineered Ni-MOF-74.

| Sample  | Doping Linker | Feeding ratio/% | Doped ratio/% |
|---------|---------------|-----------------|--------------|
| 5-fSA<sub>0.08</sub> | H<sub>2</sub>-5-fSA | 10 | 8 |
| 5-fSA<sub>0.21</sub> | H<sub>2</sub>-5-fSA | 30 | 21 |
| 5-fSA<sub>0.39</sub> | H<sub>2</sub>-5-fSA | 50 | 39 |
| 3-hSA<sub>0.06</sub> | H<sub>2</sub>-3-hSA | 10 | 6 |
| 3-hSA<sub>0.21</sub> | H<sub>2</sub>-3-hSA | 30 | 21 |
| 3-hSA<sub>0.41</sub> | H<sub>2</sub>-3-hSA | 50 | 41 |
| 2-hNA<sub>0.06</sub> | H<sub>2</sub>-2-hNA | 10 | 6 |
| 2-hNA<sub>0.17</sub> | H<sub>2</sub>-2-hNA | 30 | 17 |
| 2-hNA<sub>0.29</sub> | H<sub>2</sub>-2-hNA | 50 | 29 |
| 5-hBImCA<sub>0.04</sub> | H<sub>2</sub>-5-hBImCA | 10 | 4 |
| 5-hBImCA<sub>0.12</sub> | H<sub>2</sub>-5-hBImCA | 30 | 12 |
| 5-hBImCA<sub>0.20</sub> | H<sub>2</sub>-5-hBImCA | 50 | 20 |
Table S2. BET surface areas and pore volumes of defect-engineered Ni-MOF-74.

| Sample       | BET/m² g⁻¹ | Pore volume/cm³ g⁻¹ |
|--------------|------------|---------------------|
| 5-fSA₀.₀₈    | 1325       | 0.586               |
| 5-fSA₀.₂₁    | 1209       | 0.670               |
| 5-fSA₀.₃₉    | 894        | 0.517               |
| 3-hSA₀.₀₆    | 1323       | 0.608               |
| 3-hSA₀.₂₁    | 1042       | 0.607               |
| 3-hSA₀.₄₁    | 640        | 0.456               |
| 2-hNA₀.₀₆    | 1325       | 0.575               |
| 2-hNA₀.₁₇    | 1156       | 0.550               |
| 2-hNA₀.₂₉    | 934        | 0.570               |
| 5-hBImCA₀.₀₄ | 1196       | 0.539               |
| 5-hBImCA₀.₁₂ | 1189       | 0.514               |
| 5-hBImCA₀.₂₀ | 1038       | 0.486               |
Supplementary Reference

S1. A. Nuhnen and C. Janiak, *Dalton Trans.*, 2020, 49, 10295–10307.