A Comparative Study of the Effect of Functional Groups on C_2H_2

Adsorption in NbO-Type Metal-Organic Frameworks

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Synthesis of 5,5'-(1-aminebenzene-2,5-diyl) diisophthalic aicd (H₄L1)

To a 250-mL single-neck round-bottom flask equipped with a condenser and a magnetic stirring bar was added 2,5-dibromobenzenamine (1.00 g, 3.98 mmol), dimethyl 5-(pinacolbory)isophthalate (2.81 g, 8.78 mmol), Cs_2CO_3 (3.89 g, 11.94 mmol) and Pd(PPh_3)_4 (0.23 g, 0.20 mmol). The flask was evacuated and then back-filled with nitrogen. After the process was repeated three times, dry dioxane (50 mL) was added *via* syringe. The resulting suspension was stirred under reflux for 72 h. After the reaction mixture was allowed to cool to room temperature, the solvents were removed, and CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The mixture was filtered. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous MgSO₄, filtered and evaporated under reduced pressure. Recrystallization of the residue from toluene afforded the tetramethyl ester intermediate in 23% yield (0.44 g, 0.92 mmol).

To a solution of the tetramethyl intermediate (0.44 g, 0.92 mmol) in THF (40 mL) and MeOH (40 mL) was added 6 M NaOH (40 mL, 240 mM). The resulting mixture was stirred at 60 °C for 12 h. After the removal of the solvents, the residue was dissolved in water, and acidified with conc. HCl under an ice-water bath. The precipitation was collected by filtration, and dried in a vacuum at 70 °C to afford the target compound in a quantitative yield.

Synthesis of 5,5'-(1-methylbenzene-2,5-diyl) diisophthalic aicd (H₄L2)

To a 250-mL single-neck round-bottom flask equipped with a condenser and a magnetic stirring bar was added 1,4-dibromo-2-methylbenzene (1.00 g, 4.00 mmol), dimethyl 5-(pinacolbory)isophthalate (2.82 g, 8.80 mmol), Cs_2CO_3 (3.91 g, 12.00 mmol) and Pd(PPh_3)_4 (0.23 g, 0.20 mmol). The flask was evacuated and back-filled back with nitrogen. After the process was repeated three times, dry dioxane (50 mL) was added *via* syringe. The resulting suspension was stirred under reflux for 72 h. After the reaction mixture was allowed to cool to room temperature, the solvents were removed under reduced pressure, and CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The mixture was filtered. The organic phase was separated and the aqueous

phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous MgSO₄ and filtered. Volatiles were removed by rota-evaporation under reduced pressure and recrystallization of the residue from toluene afforded the tetramethyl ester intermediate in 17% yield (0.32 g, 0.67 mmol).

To a suspension of the tetramethyl intermediate (0.32 g, 0.67 mmol) in THF (30 mL) and MeOH (30 mL) was added 6 M NaOH (30 mL, 180 mM). The resulting mixture was heated at 80 °C overnight with stirring. After the removal of the solvents, the residue was dissolved in water, and acidified with conc. HCl under an ice-water bath. The precipitation was collected by filtration, and dried in a vacuum at 70 °C to afford the target compound in a quantitative yield.

Synthesis of 5,5'-(1-nitrobenzene-2,5-diyl) diisophthalic aicd (H₄L3)

To a 250-mL single-neck round-bottom flask equipped with a condenser and a magnetic stirring bar was added 1,4-dibromo-2-nitrobenzene (1.00 g, 3.56 mmol), dimethyl 5-(pinacolbory)isophthalate (2.51 g, 7.84 mmol), Cs₂CO₃ (3.48 g, 10.68 mmol) and Pd(PPh₃)₄ (0.20 g, 0.17 mmol). The flask was evacuated and then back-filled with nitrogen. After the process was repeated three times, dry dioxane (50 mL) was added *via* syringe. The resulting suspension was stirred under reflux for 72 h. After the reaction mixture was allowed to cool to room temperature, the solvents were removed, and CH₂Cl₂ (100 mL) and H₂O (100 mL) were added. The mixture was filtered. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous MgSO₄ and filtered. Volatiles were removed by rota-evaporation under reduced pressure and the residue was purified by silica gel column chromatography with petroleum ether/dichloromethane/ethyl acetate (10/1/1, $\nu/\nu/\nu$) as eluent, affording the tetramethyl ester intermediate in 17% yield (0.31 g, 0.61 mmol).

To a suspension of the tetramethyl intermediate (0.31 g, 0.61 mmol) in THF (30 mL) and MeOH (30 mL) was added 6 M NaOH (30 mL, 180 mM). The resulting mixture was heated at 40 °C for 12 h. After the removal of the solvents, the residue was

dissolved in water, and acidified with conc. HCl under an ice-water bath. The precipitation was collected by filtration, and dried in a vacuum at 70 °C to afford the target compound in a quantitative yield.

Synthesis of 5,5'-(1-fluorobenzene-2,5-diyl) diisophthalic aicd (H₄L4)

To a 250-mL single-neck round-bottom flask equipped with a condenser and a magnetic stirring bar was added 1,4-dibromo-2-fluorobenzene (1.00 g, 3.94 mmol), dimethyl 5-(pinacolbory)isophthalate (2.77 g, 8.65 mmol), Cs_2CO_3 (3.85 g, 11.82 mmol) and Pd(PPh_3)_4 (0.23 g, 0.20 mmol). The flask was evacuated and then back-filled back with nitrogen. After the process was repeated three times, dry dioxane (50 mL) was added *via* syringe. The resulting suspension was stirred under reflux for 72 h. After the reaction mixture was allowed to cool to room temperature, the solvents were removed, and CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The mixture was filtered. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous MgSO₄ and filtered. Volatiles were removed by rota-evaporation under reduced pressure and the recrystallization of the residue from toluene afforded the tetramethyl ester intermediate in 22% yield (0.41 g, 0.85 mmol).

To a suspension of the tetramethyl intermediate (0.41 g, 0.85 mmol) in THF (40 mL) and MeOH (40 mL) was added 6 M NaOH (40 mL, 240 mM). The resulting mixture was heated at 70 °C overnight. After the removal of the solvents, the residue was dissolved in water, and acidified with conc. HCl under an ice-water bath. The precipitation was collected by filtration, and dried in a vacuum at 70 °C to afford the target compound in a quantitative yield.

Synthesis of 5,5'-(1-trifluoromethylbenzene-2,5-diyl) diisophthalic aicd (H₄L5)

To a 250-mL single-neck round-bottom flask equipped with a condenser and a magnetic stirring bar was added 1,4-dibromo-2-(trifluoromethyl)benzene (1.00 g, 3.29 mmol), dimethyl 5-(pinacolbory)isophthalate (2.32 g, 7.25 mmol), Cs_2CO_3 (3.22 g, 9.88 mmol) and Pd(PPh₃)₄ (0.19 g, 0.16 mmol). The flask was evacuated and then

back-filled with nitrogen. After the process was repeated three times, dry dioxane (50 mL) was added *via* syringe. The resulting suspension was stirred under reflux for 72 h. After the reaction mixture was allowed to cool to room temperature, the solvents were reduced, and CH₂Cl₂ (100 mL) and H₂O (100 mL) were added. The mixture was filtered the organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous MgSO₄ and filtered. Volatiles were removed by rota-vaporation under reduced pressure, and the residue was purified by silica gel column chromatography with petroleum ether/dichloromethane/ethyl acetate (5:1:1, v/v/v) as eluent, affording the tetramethyl ester intermediate in 12% yield (0.21 g, 0.40 mmol).

To a suspension of the tetramethyl intermediate (0.21 g, 0.40 mmol) in THF (20 mL) and MeOH (20 mL) was added 6 M NaOH (20 mL, 120 mM). The resulting mixture was heated at 70 °C overnight. After the removal of the solvents, the residue was dissolved in water, and acidified with conc. HCl under an ice-water bath. The precipitation was collected by filtration, and dried in a vacuum at 70 °C to afford the target compound in a quantitative yield.



Fig. S1 Comparison of the as-synthesized and simulated PXRD patterns for **ZJNU-34** (a), **ZJNU-35** (b), **ZJNU-36** (c), **ZJNU-37** (d) and **ZJNU-38** (e).



Fig. S2 TGA curves of the as-synthesized ZJNU-34 (a), ZJNU-35 (b), ZJNU-36 (c), ZJNU-37 (d), ZJNU-38 (e) and NOTT-101 (f).



Fig. S3 Comparison of FTIR spectra of the organic ligands and the corresponding MOF compounds.



Fig. S4 Comparison of cage structures in five MOF compounds investigated.





Fig. S5 BET (a) and Langmuir (b) plots for ZJNU-34(NH₂)













Fig. S8 BET (a) and Langmuir (b) plots for ZJNU-37(F)







Fig. S10 BET (a) and Langmuir (b) plots for NOTT-101



Fig. S11 Low-pressure CH₄ isotherms at four different temperatures for **ZJNU-34** (a), **ZJNU-35** (b), **ZJNU-36** (c), **ZJNU-37** (d), **ZJNU-38** (e) and **NOTT-101** (f).



Fig. S12 Comparison of the pure-component isotherm data with the fitted isotherms (shown by continuous solid lines).



Fig. S13. Comparison of C_2H_2/CH_4 adsorption selectivity







Fig. S14 ¹H NMR spectra

| MOFs | ZJNU-34(NH ₂) | ZJNU-35(CH ₃) | ZJNU-36(NO ₂) | ZJNU-37(F) | ZJNU-38(CF ₃) |
|--|--|------------------------------|---------------------------|--|------------------------------|
| Empirical formula | C ₂₂ H ₁₅ Cu ₂ NO ₁₀ | $C_{23}H_{16}Cu_2O_{10}$ | $C_{22}H_{13}Cu_2NO_{12}$ | C ₂₂ H ₁₃ Cu ₂ FO ₁₀ | C23 H13 Cu2 F3 O10 |
| Formula weight | 580.43 | 579.44 | 610.43 | 583.40 | 633.41 |
| Temperature (K) | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) |
| Wavelength (Å) | 1.54184 | 0.71073 | 0.71069 | 0.71073 | 0.71073 |
| Crystal system | Trigonal | Trigonal | Trigonal | Trigonal | Trigonal |
| Space group | <i>R</i> -3m | <i>R</i> -3m | <i>R</i> -3m | <i>R</i> -3m | <i>R</i> -3m |
| | a = 18.6153(7) Å | a = 18.6166(7) Å | <i>a</i> = 18.555(3) Å | a = 18.7065(19) Å | <i>a</i> = 18.5503(6) Å |
| | b = 18.6153(7) Å | b = 18.6166(7) Å | <i>b</i> = 18.555(3) A | b = 18.7065(19) Å | <i>b</i> = 18.5503(6) A |
| | c = 38.3750(13) Å | c = 38.6451(14) Å | c = 38.688(6) A | c = 38.488(3) Å | c = 38.8068(12) A |
| Unit cell dimensions | $\alpha = 90^{\circ}$ | $\alpha = 90^{\circ}$ | $\alpha = 90^{\circ}$ | $\alpha = 90^{\circ}$ | $\alpha = 90^{\circ}$ |
| | $\beta = 90^{\circ}$. | $\beta = 90^{\circ}$ | $\beta = 90^{\circ}$ | $\beta = 90^{\circ}$ | $\beta = 90^{\circ}$ |
| | $\gamma = 120^{\circ}$ | $\gamma = 120^{\circ}$ | $\gamma = 120^{\circ}$ | $\gamma = 120^{\circ}$ | $\gamma = 120^{\circ}$ |
| Volume (Å ³) | 11516.5(7) | 11599.1(7) | 11535(3) | 11663.8(19) | 11564.9(6) |
| Ζ | 9 | 9 | 9 | 9 | 9 |
| $D_{\rm c} ({\rm g}{\rm cm}^{-3})$ | 0.753 | 0.747 | 0.791 | 0.748 | 0.819 |
| $\mu (\mathrm{mm}^{-1})$ | 1.261 | 0.850 | 0.861 | 0.849 | 0.865 |
| F(000) | 2628 | 2628 | 2753 | 2628 | 2844 |
| Crystal size (mm) | 0.25 ×0.18 ×0.13 | $0.20\times 0.18\times 0.16$ | 0.22 ×0.14 ×0.10 | 0.26 ×0.21 ×0.12 | $0.22\times 0.18\times 0.12$ |
| θ range for data collection (°) | 3.46 to 73.91 | 1.37 to 25.01 | 1.37 to 27.58 deg. | 1.36 to 25.02 | 1.37 to 25.02 |
| | $-23 \le h \le 20$ | $-22 \le h \le 22$ | $-24 \le h \le 24,$ | $-22 \le h \le 22$ | $-22 \le h \le 22$ |
| Limiting indices | $-22 \le k \le 19$ | $-22 \le k \le 22$ | $-24 \le k \le 24,$ | $-22 \le k \le 22$ | $-22 \le k \le 22$ |
| | $-46 \le l \le 32$ | $-45 \le l \le 45$ | $-50 \le l \le 47$ | $-45 \le l \le 45$ | $-46 \le l \le 46$ |
| Reflections collected / unique | 14559 / 2816 | 65985 / 2512 | 77586 / 3259 | 66423 / 2523 | 66045 / 2506 |
| R _{int} | 0.0277 | 0.1541 | 0.1629 | 0.2139 | 0.1244 |
| Completeness | 98.6 % | 100.0 % | 100.0% | 100.0 % | 100.0 % |
| Max. and min. transmission | 0.8532 and 0.7433 | 0.8759 and 0.8483 | 0.9189 and 0.8332 | 0.9050 and 0.8095 | 0.9033 and 0.8325 |
| Data/restraints/parameters | 2816 / 1 / 103 | 2512 / 18 / 92 | 3259 / 0 / 121 | 2523 / 0 / 103 | 2506 / 25 / 116 |
| Goodness-of-fit on F^2 | 1.130 | 1.090 | 1.073 | 1.152 | 1.204 |
| | $R_1 = 0.0501,$ | $R_1 = 0.0577$ | $R_I = 0.0631$ | $R_1 = 0.0528$ | $R_{I} = 0.0557$ |
| Final R indices $[I > 2\sigma(I)]$ | $wR_2 = 0.1762$ | $wR_2 = 0.1814$ | $wR_2 = 0.1580$ | $wR_2 = 0.1506$ | $wR_2 = 0.1476$ |
| | $R_1 = 0.0538,$ | $R_1 = 0.0832$ | $R_1 = 0.0997$ | $R_1 = 0.0814$ | $R_1 = 0.0720$ |
| <i>R</i> indices (all data) | $wR_2 = 0.1806$ | $wR_2 = 0.1926$ | $wR_2 = 0.1759$ | $wR_2 = 0.1564$ | $wR_2 = 0.1604$ |
| Largest diff. peak and hole (e.Å-3) | 1.086 and -0.378 | 0.727 and -0.525 | 0.424 and -0.798 | 0.722 and -0.564 | 0.719 and -0.547 |
| CCDC | 1529129 | 1529132 | 1529130 | 1529131 | 1529128 |

Table S1 Crystal data and structure refinement for ZJNU-34-38.

Table S2 Langmuir-Freundich parameters for adsorption of C_2H_2 and CH_4 in ZJNU-34(NH₂)

| | $q_{\rm sat}$ (mmol g ⁻¹) | b_0 (kPa) ^{-ν} | E (kJ mol ⁻¹) | v |
|-----------------|---------------------------------------|---|---------------------------|--------|
| C_2H_2 | 27.75156 | 1.17624×10 ⁻⁵ | 18.208 | 0.6891 |
| CH ₄ | 12.92465 | 1.42418×10 ⁻⁶ | 15.577 | 1 |

Table S3. Langmuir-Freundich parameters for adsorption of C_2H_2 and CH_4 in ZJNU-35(CH₃)

| | $q_{\rm sat}$ (mmol g ⁻¹) | b_0 (kPa) ^{-ν} | E (kJ mol ⁻¹) | v |
|-----------------|---------------------------------------|---|---------------------------|--------|
| C_2H_2 | 40.53896 | 1.52868×10 ⁻⁵ | 16.663 | 0.6345 |
| CH ₄ | 12.23696 | 1.21437×10 ⁻⁶ | 15.920 | 1 |

| | $q_{\rm sat} \pmod{{\rm g}^{-1}}$ | b_0 (kPa) ^{-v} | $\frac{E}{(\text{kJ mol}^{-1})}$ | v |
|-----------------|-----------------------------------|------------------------------|----------------------------------|---------|
| C_2H_2 | 51.75956 | 1.78909×10 ⁻⁵ | 16.151 | 0.57666 |
| CH ₄ | 15.92367 | 1.32598×10 ⁻⁶ | 15.053 | 1 |

Table S4 Langmuir-Freundich parameters for adsorption of C_2H_2 and CH_4 in ZJNU-36(NO₂)

 Table S5 Langmuir-Freundich parameters for adsorption of C2H2 and CH4 in

 ZJNU-37(F)

| | $q_{\rm sat}$ (mmol g ⁻¹) | b_0 (kPa) ^{-v} | E (kJ mol ⁻¹) | v |
|-----------------|---------------------------------------|------------------------------|---------------------------|--------|
| C_2H_2 | 82.26879 | 1.43447×10 ⁻⁵ | 15.182 | 0.5883 |
| CH ₄ | 13.31489 | 1.07866×10 ⁻⁶ | 15.814 | 1 |

| | $q_{\rm sat}$ (mmol g ⁻¹) | b_0 (kPa) ^{-v} | E (kJ mol ⁻¹) | V |
|-----------------|---------------------------------------|------------------------------|------------------------------|---------|
| C_2H_2 | 63.28469 | 3.17191×10 ⁻⁵ | 14.048 | 0.55378 |
| CH ₄ | 17.62945 | 9.99285×10 ⁻⁷ | 15.017 | 1 |

Table S6 Langmuir-Freundich parameters for adsorption of C_2H_2 and CH_4 in ZJNU-38(CF₃)

 Table S7 Langmuir-Freundich parameters for adsorption of C2H2 and CH4 in

 NOTT-101

| | $q_{\rm sat}$ (mmol g ⁻¹) | b_0 (kPa) ^{-ν} | E (kJ mol ⁻¹) | v |
|-----------------|---------------------------------------|---|---------------------------|---------|
| C_2H_2 | 59.19957 | 1.48802×10 ⁻⁵ | 15.787 | 0.61397 |
| CH ₄ | 13.39522 | 3.93239×10 ⁻⁶ | 12.785 | 1 |