Supporting Information

New Approach towards Tetrahedral Imidazolate Frameworks for High and Selective CO$_2$ uptake

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Methods

Synthesis of [Zn(ad)(int)]·(DMF) (TIF-A1): The mixture of Zn(NO$_3$)$_2$·6H$_2$O (0.5 mmol, 0.150 g), Adenine (0.5 mmol, 0.070 g), isonicotinic acid (0.5 mmol, 0.06 g) and 3mL DMF in a 20 ml vial was heated to 120 °C for 3 days, and then cooled to room-temperature. The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 88 %). Anal. Calcd for C$_{14}$H$_{15}$N$_7$O$_3$Zn (394.7): C, 42.60; H, 3.83; N, 24.84. Found: C, 42.72; H, 3.91; N, 24.50. IR (KBr cm$^{-1}$): m = 3127 (s), 1608 (vs), 1572 (m), 1524 (s), 1371 (vs), 1304 (m), 1071 (s), 966 (w), 783 (m), 660 (w), 504 (w).

Synthesis of Zn$_2$(im)$_3$(int) (TIF-A2): The mixture of Zn(NO$_3$)$_2$·6H$_2$O (0.5 mmol, 0.150 g), imidazole (0.5mmol, 0.034 g), isonicotinic acid (0.5 mmol, 0.06 g), 1 mL H$_2$O and 3 mL DMF in a 20 mL vial was heated to 120 °C for 3 days, and then cooled to room-temperature. The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 80 %). Anal. Calcd for C$_{15}$H$_{13}$N$_7$O$_2$Zn$_2$ (454.06): C, 39.68; H, 2.89; N, 21.59. Found: C, 39.55; H, 2.95; N, 21.67. IR (KBr cm$^{-1}$): 3123(m), 1643(s), 1617(m), 1557(m), 1496(m), 1483(m), 1372(s), 1239(m), 1170(m), 1087(s), 951(m), 866(m), 827(m), 773(m), 755(m), 698(m).

Synthesis of Zn$_2$(im)(int)$_2$(OH) (TIF-A3): The mixture of ZnF$_2$ (0.5 mmol, 0.051 g), imidazole (0.5mmol, 0.034 g), isonicotinic acid (0.5 mmol, 0.06 g), 1 mL H$_2$O and 3 mL DMF in a 20 mL vial was heated to 120 °C for 3 days, and then cooled to room-temperature. The colorless crystals were obtained in pure phase, washed with water and ethanol, and dried at room temperature (Yield: 80 %). Anal. Calcd for C$_{15}$H$_{12}$N$_4$O$_5$Zn$_2$ (459.03): C, 39.25; H, 2.63; N, 12.21. Found: C, 39.09; H, 2.84; N, 12.26. IR (KBr cm$^{-1}$): 3313(w), 3106(s), 1618(s), 1557(m), 1400 (vs), 1085(w), 1055(m), 745(m), 726(m).

Crystallographic study. Diffraction data for TIF-A1 to A3 were collected on a Oxford Xcalibur diffractometer equipped with confocal-monochromated Mo-Ka radiation (λ = 0.71073 Å) at room temperature. The CrystalClear program was used for absorption correction. The structure was solved by direct methods and refined on $R^2$ by full-matrix, least-squares methods using the SHELXL-97 program package.
Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The adsorption experiments were performed on Micromeritics ASAP 2020 surface area and pore size analyzer.

Figure S1. The TGA plots of TIF-A1.

Figure S2. The Powder XRD patterns of TIF-A1.

Figure S3. The N₂ isotherm adsorption of TIF-A1 at 77K.
Figure S4. Part of the dia-type 3D framework of TIF-A2.

Figure S5. Single neb-type 3D framework of TIF-A3.