

Electronic Supplementary Information

A Pillared Metal-organic Framework Incorporated with 1,2,3-Triazole Moiety Exhibiting Remarkable Enhancement of CO₂ Uptake

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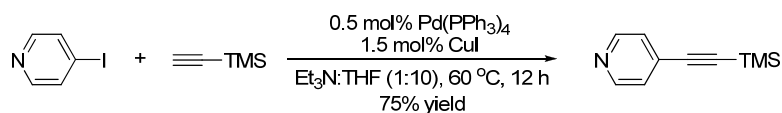
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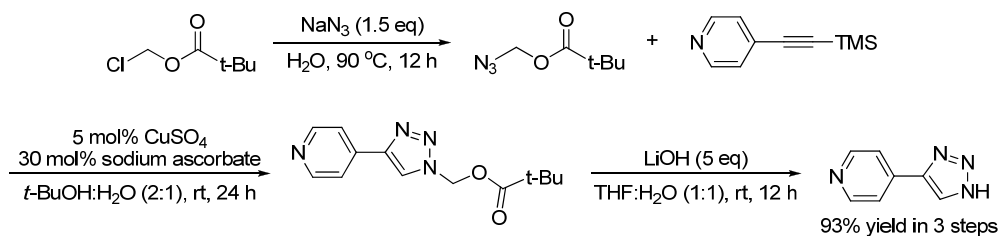
General methods

Commercially available reagents were purchased as high purity from Fisher Scientific or Frontier Scientific and used without further purification. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res from 30°C to 450 °C at the speed of 5 °C/min. X-ray powder diffraction (XPD) data were recorded on a Bruker D8 Advance X-ray diffractometer at 20 kV, 5 mA for CuK α ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of 0.5 s/step (6°/min) and a step size of 0.05° in 2 θ at room temperature. The simulated XPD patterns were produced using Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, 2000).

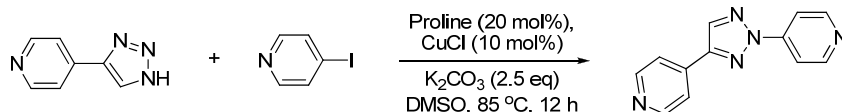
Synthesis of 4,4'-(2H-1,2,3-triazole-2,4-diyl)dipyridine



4-iodopyridine (1 mmol) and ethynyltrimethylsilane (2 mmol) were suspended in a solution of 50 mL dry THF and 5 mL Et₃N under N₂ atmosphere. Pd(PPh₃)₄ (0.005 mmol) and CuI (0.015 mmol) were added. The reaction mixture was stirred for 12 hours at 60°C and subsequently evaporated and chromatographed (silica gel, EtOAc/hexane = 1:10) to give the product as a yellow liquid (75% yield).



The detailed procedure for preparation of 4-(1H-1,2,3-triazol-4-yl)pyridine (yield: 93%) can be found in the reported reference.¹



Into a round-bottom bottle (25 mL) was successively added 4-(1H-1,2,3-triazol-4-yl)pyridine (1 mmol), potassium carbonate (345 mg, 2.5 mmol), L-proline (23 mg, 0.2 mmol), copper(I) chloride (10 mg, 0.1 mmol), and 4-iodopyridine (1.2 mmol) in DMSO (10 mL) under N₂ protection. The reaction mixture was stirred and heated up to 85°C for 12 h, and the reaction progress was monitored by TLC. After the reaction was completed, water (20 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed with brine (50 mL) and dried with anhydrous Na₂SO₄. The solvent was removed under reduced pressure to get a residue and the residue was purified by flash silica gel chromatography (hexane/ethyl acetate 1:1) to give the product 4,4'-(2H-1,2,3-triazole-2,4-diyl)dipyridine as the white solid (yield: 82%). m.p. 204-206 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.77 (d, *J* = 6.0 Hz, 2H), 8.75 (d, *J* = 6.0 Hz, 2H), 8.23 (s, 1H), 8.05 (d, *J* = 6.0 Hz, 2H), 7.79 (d, *J* = 6.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 151.3, 150.5, 147.7, 145.4, 136.8, 134.6, 120.5, 112.8; HRMS Calculated for [C₁₂H₉N₅+H]⁺: 223.0858, Found: 223.0864.

Gas Adsorption Experiments

Gas adsorption isotherms of MTAF-3 were collected using the surface area analyzer ASAP-2020. Before the measurements, the freshly prepared samples were exchanged with methanol for 3 days. N₂ gas adsorption isotherm was measured at 77K using a

liquid N₂ bath. CO₂ isotherms were measured at 273K using a water-ice bath and at 298K with a water bath. MOF-508 sample were prepared by the literature.²

Preparation of MTAF-3

A mixture of terephthalic acid (H₂BDC) (30mg), Zn(NO₃)₂·6H₂O (90mg), 4,4'-(2H-1,2,3-triazole-2,4-diyl)dipyridine (TDD) (15mg) and N,N'-diethylformamide (DEF) (10.0mL) was put into 20 mL vial and heat to 85 °C for 48 hours. The resulting cubic yellow crystals, as [Zn₄(BDC)₄(TADP)₂](DEF)₂(H₂O), were obtained. (yielding: 75% based on TDD) Anal. Calc. for MTAF-3: C, 50.28; H, 3.20; N, 10.66; Found: C, 50.10; H, 3.21; N, 10.64.

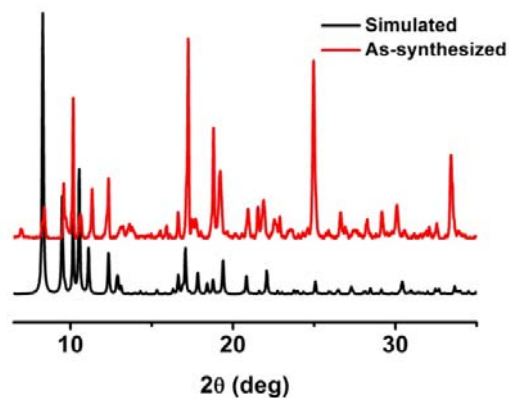


Figure S1. Powder X-ray patterns of MTAF-3

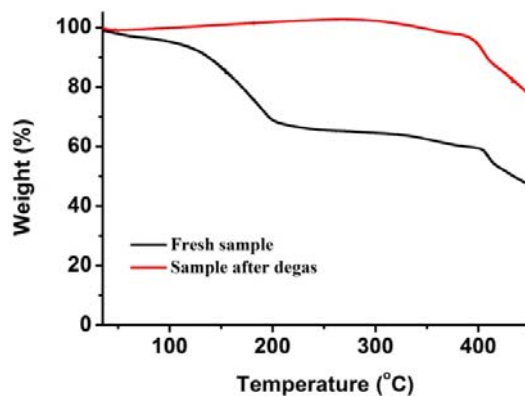


Figure S2. TGA plots of MTAF-3

Single-Crystal X-Ray Diffraction for MTAF-3

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer using CuK α ($\lambda = 1.54178 \text{ \AA}$). Indexing was performed using *APEX2* (Difference Vectors method).³ Data integration and reduction were performed using *SaintPlus 6.01*.⁴ Absorption correction was performed by multi-scan method implemented in *SADABS*.⁵ Space groups were determined using *XPREP* implemented in *APEX2*.³ MTAF-3 was solved using *SHELXS-97* (direct methods) and refined using *SHELXL-97* (full-matrix least-squares on F^2) contained in *APEX2* [2] and *WinGX*.^{6,7,8,9} All non-H atoms were found in the difference Fourier map and refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: $U_{iso}(H) = 1.2U_{eq}(-CH)$, $U_{iso}(H) = 1.5U_{eq}(-CH_3)$. The occupancy of O10 water molecule has been established through the refinement to be ~ 0.5 . The contribution of disordered DEF molecules was treated as diffuse using Squeeze procedure implemented in *Platon* program.^{10,11} Crystal data and refinement conditions are shown in Table S1.

Table S1. Crystal data and structure refinement for MTAF-3

Identification code	MTAF-3
Empirical formula	C ₆₆ H ₅₆ N ₁₂ O ₁₉ Zn ₄
Formula weight	1582.71
Temperature	228(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	$a = 34.6925(7)$ Å $\alpha = 90$ deg. $b = 16.6027(4)$ Å $\beta = 105.3030(10)$ deg. $c = 13.7633(3)$ Å $\gamma = 90$ deg.
Volume	7646.4(3) Å ³
Z, Calculated density	4, 1.375 Mg/m ³
Absorption coefficient	2.039 mm ⁻¹
F(000)	3232
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	2.64 to 68.40 deg.
Limiting indices	-41 ≤ h ≤ 40, -19 ≤ k ≤ 20, -16 ≤ l ≤ 16
Reflections collected / unique	47412 / 6948 [R(int) = 0.0544]
Completeness to theta = 68.40	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6859 and 0.6859
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6948 / 0 / 462
Goodness-of-fit on F ²	1.021
Final R indices [I > 2σ(I)]	R1 = 0.0416, wR2 = 0.1129
R indices (all data)	R1 = 0.0487, wR2 = 0.1176
Largest diff. peak and hole	0.722 and -0.524 e.Å ⁻³

References:

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