Supplementary Information for

Tubular Metal Organic Frameworks from the Curvature of

2D-honeycombed Metal Coordination

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1. Materials

4'-iodoacetophenone, 4-pyridineboronic acid, tetrakis (triphenylphosphine) palladium (0) from TCI; silver nitrate, 2-methyl-3-butyn-2-ol (R1), 3-methyl-3-pentyn-3-ol (R2), 3-ethyl-1-pentyn-3-ol (R3), 3,4-dimethyl-1-pentyn-3-ol (R4), and 1-ethynycyclopentanol (R5) from J&K Scientific were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without purification. Tetrahydrofuran (THF) was dried by distillation from sodium-benzophenone immediately prior to use. Distilled water was polished by ion exchange and filtration. Flash chromatography was carried out with Silica Gel (200-300 mesh).

2. General

Fourier transform infrared spectroscopy (FTIR) spectra of the samples were obtained under ambient conditions at a resolution of 2 cm⁻¹ in the wave number range of 4000~400 cm⁻¹ by using an EQUINOX 55 spectrometer. ¹H NMR spectra were recorded from CDCl₃ solutions on a Bruker AVANCE III 400 MHz. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants are reported in Hz. The Uv/vis spectra were obtained from a Metash UV-8000S Spectrophotometer. MALDI TOF-MS spectroscopy (MALDI-TOF-MS) was performed on a Bruker ultrafleXtreme using trans-2-[3-(4-tert-Butylphenyl)-2methyl-2-propenylidene]malononitrile (DCTB) as a matrix. Scanning electron micrographs (SEM) were obtained by field emission scanning SU8010 instrument. The transmission electron microscopy (TEM) was performed at 200 kV using JEM-2010HR machine. The AFM measurements were performed using Bruker Multimode 8 in air at ambient temperature (ca. 25 $^{\circ}$ C) on mica with tapping mode. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALab250 Mark (VG) photoelectron spectrometer using a monochromatic Al Ka X-ray source. Elemental analysis was performed on an Elementar VARIO EL cube elemental analyzer. Thermal gravimetric analysis (TGA) measurements were performed on a TG209F1 under air flow, by heating to 900 $^{\circ}$ C at a rate of 10 $^{\circ}$ C min⁻¹. The N₂ adsorption and desorption measurements were performed on a Micromeritic ASAP2020Manalyzer at 77 K. Specific surface areas were calculated using the

Brunauer-Emmett-Teller (BET) methods and the pore size distributions were analyzed by using nonlocal density functional theory (NLDFT). All samples were degassed at 120 °C for 5 h under vacuum before analysis. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C X-ray beam line at Pohang Accelerator Laboratory, Korea, by depositing powder on glass substrate, from $2\theta = 2.0^{\circ}$ to 30° with 0.1° increment at 25 °C. Gas chromatographic (GC) analysis was performed on a GC2010 gas chromatograph (Shimadzu) equipped with a flame ionization detection and a capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 µm).



3. Synthesis of ligand, Ag-coordinated framework 1 and 2

Scheme S1 Synthesis of aromatic ligand 1,3,5-Tris[4-(4-pyridyl)phenyl]benzene (4).

Synthesis of compound 3

3 was prepared based on the literature.^{1,2}

Synthesis of ligand 4

Compound **3** (0.684 g, 1 mmol) and 4-pyridineboronic acid (0.492 g, 4 mmol) were dissolved in degassed THF (60 mL). Degassed K_2CO_3 aqueous solution (2M, 40 mL) was added to the above mixture and then Pd(PPh₃)₄ (0.06 g, 0.05 mmol) was added meticulously. The mixture was refluxed for 24 hours with vigorous stirring under argon atmosphere in a 90 °C oil bath. Subsequently, the reaction mixture was cooled down to room temperature before THF was removed by rotatory evaporation, and then the residual was extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous Na₂SO₄. The filtrate was condensed under

reduced pressure and purified by silica gel flash column using ethyl acetate/dichloromethane (4:1, v:v) and then ethyl acetate/ethanol (9:1, v:v) as eluent. Yield: 20%, white solid. ¹H NMR (400 MHz, Chloroform-d): δ 8.76 – 8.71 (m, 6H), 7.93 (s, 3H), 7.89 (d, J = 8.3 Hz, 6H), 7.83 (d, J = 8.3 Hz, 6H), 7.66 – 7.58 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*, δ): 151.75, 149.04, 143.16, 142.95, 138.88, 129.43, 128.95, 126.78, 122.87. MALDI-TOF mass: m/z calcd. for **4** [M+H]⁺, 538.23; found: [M+H]⁺, 538.23.

Synthesis of coordinated framework 1 and 2



Scheme S2 Schematic representations of coordinated frameworks. The strategy for creation of porous crystalline framework 1 and curled tubules 2 from 2D infinite honeycombed frameworks.

The coordinated framework **1** and **2** for the creation of both catalysts were derived from titration between AgNO₃ acetonitrile (ACN) solution (12 mM) and tetrahydrofuran (THF) solution (3.3 mM) of ligand with a coordinative pyridine at the termination. The framework **1** that stacked into porous crystal was prepared by the dropwise addition of 60 mL THF of ligand into 25 mL Ag(I) acetonitrile solution, while framework **2** curling into tubular catalyst was prepared by the dropwise addition of 25 mL ACN of Ag(I) into ligand THF solution (Scheme S2). After completion of addition, white solid product was obtained by centrifugation(5000 r/min \times 20 min) and washed with acetonitrile for three times.

4. Methods

Scanning electron microscopy (SEM) experiments: The solid samples were dispersed in acetonitrile, and the corresponding solution (0.1 wt%, respectively) was dropped onto aluminum foil which coated on a slice of conductive adhesive adhered to a flat copper platform sample holder. After evaporation of the solvent under ambient conditions, samples were submitted to SEM characterization.

Transmission electron microscopy (TEM) experiments: A drop of well-dispersed samples in acetonitrile (0.1 wt%) was placed on a carbon-coated copper grids and then evaporated under ambient conditions. The dried specimen was observed by using a JEM-2010HR machine operated at 200 kV.

Atomic force microscope (AFM) experiments: In order to determine vertical and lateral growth of both frameworks, concentration dependent AFM experiments were performed. To observe vertically stacked porous crystal **1**, 20 μ L of AgNO₃ in ACN solution (12 mM) with 0.2 mmol ligand, 0.4 mmol ligand, 0.6 mmol ligand and 2.0 mmol ligand were casted on mica. After slow evaporation under air at room temperature, the excessive AgNO₃ was dissolved by dropping ACN. Then, the solution was absorbed using filter paper. As for observing laterally connected framework **2**, 20 μ L of ligand in THF solution (3.3 mM) with 0.3 mmol AgNO₃, 0.6 mmol AgNO₃, 0.9 mmol AgNO₃ and 1.5 mmol AgNO₃ were casted on mica. After slow evaporation under air at room temperature, the excessive ligand was dissolved by dropping THF. Then, the solution was absorbed using filter paper. All dried specimen were performed with tapping model. The typical settings of the AFM for the high-magnification observations were as follows: a free amplitude of the oscillation frequency of ca. 1.0-1.5 V, a set-point amplitude of 0.9-1.4 V, and a scan rate of 1.0 Hz.

Typical procedures for the cycloaddition reaction of propargylic alcohols with CO₂

The reaction was performed in a stainless steel autoclave with a Teflon tube. Firstly, propargyl alcohol (1 mmol), DBU (0.2 mmol), acetonitrile (2 mL), naphthalene (0.5 mmol) and catalyst were added into the autoclave. After sealing and purging with CO₂ for 3 times, the autoclave was pressurized with CO_2 to the requested pressure for 5 min, followed by stirring at a speed of 400 r/min in a 40 °C water bath for 1 h. After reaction, the autoclave was cooled down to 0 $\,^{\circ}$ C in an ice bath and the excess of CO₂ was released slowly. Subsequently, the reaction mixture was transferred to a 2 mL vial after centrifugation at a speed of 5000 r/min (5 min), and the product yield and selectivity were determined by GC analysis through the internal standard method. The purity and structure of products were also confirmed by ¹H NMR, ¹³C NMR spectra, and GC-MS analysis. For catalytic evaluation under low CO2 concentration, balloon with CO₂ was loaded onto a single-neck round bottom flask. When the gram-scale experiment was conducted, 15 mmol substrate (2-methyl-3-butyn-2-ol), 20 mol% DBU, 1 mg catalyst 2 was added to a stainless autoclave without solvent under 0.6 MPa in a 40 °C water bath. During the process, pressure decreased to 0.4 MPa as the pressure gauge indicated, and the system was then pressurized to 0.6 MPa again for about three times within 15 hours, using the ¹H NMR to determine yield.

5. Supplementary Tables

Name	Weight	С	Ν	Н	C/N	C/H
	[mg]	[wt%]	[wt%]	[wt%]		
1	2.281	56.90	7.02	3.83	8.10	14.86
2	2.211	56.89	6.98	3.93	8.14	14.47
Ideal		59.1	7.95	3.4	7.43	17.38

Table S1 Elemental analysis of framework 1 and 2.

Catalyst	Additive	T/⁰C	P/MPa	TOF/ h ⁻¹	TON	Products
Cu ₄ I ₄ -In-MOF ³	TEA(0.14 equiv.)	50	1.5	14	14400	
		50	0.5	9.7	97	
AgOAc ⁴	$(n-C_7H_{15})_4NBr$	60	4.5	33	6024	
Cat. 1 (0.74 mol%)	DBU(0.2 equiv.) /			124	124 ^a	
Cat. 2 (0.56 mol%)	ACN	40	0.6	173	173 ^a	
Cat. 2 (0.01 mol%)				153	2300 ^b	O //
AgI ⁵	[EMIM]OAc as	45	0.1	31	93	o-K
	solvent	45	0.1	24	1920 ^c	
AgI^{6}	KOAc/DMF	45	0.1	165	1980	
		50	0.5	15.5	1860 ^c	
$AgWO_4^7$	PPh ₃	25	0.1	4	48	
AgI@C ⁸	DBU(0.2 equiv.) /	rt	0.1	8.3	33	
	ACN					
Cu ₄ I ₄ -Dy- MOF ⁹	DBU(1 equiv.) /	rt	0.1	7.6	38	
	ACN					
Cat. 1 (0.9 mol%)	DBU(0.2 equiv.) /	40	1	101	101 ^d	0 //
Cat. 2 (0.5 mol%)	ACN			188	188 ^d	ol
Cat. 1 (1.3 mol%)	DBU(0.2 equiv.) /	40	1	71	71 ^d	0
Cat. 2 (0.7 mol%)	ACN			138	138 ^d	Ă
						\int
						Et Et
						
Cat. 1 (2.5 mol%)	DBU(0.2 equiv.) /	40	1	36	36 ^d	0
Cat. 2 (1.5 mol%)	ACN			66	66 ^d	0-4
Cat. 1 (3.0 mol%)	DBU(0.2 equiv.) /	40	1	31	31 ^d	O //
Cat. 2 (1.5 mol%)	ACN			65	65 ^d	o-K
						$(\langle \rangle)$

Table S2 Substrates test for evaluating the catalytic activity of framework 1, 2 andcomparison with other systems.

^a 0.6 MPa CO₂, 1 h, GC yield.

^b 15 mmol substrate, 20 mol% DBU, neat, 0.6 MPa CO₂, 40 °C, 15 h, ¹H-NMR yield.

^c control experiment by reported in Supplementary Reference 3.

^d Reaction conditions: 1 mmol substrate, 0.5 mmol naphthalene, 20 mol% DBU, related catalyst loading, 2 mL ACN, 1.0 MPa CO₂, 1 h, 40 °C. Yields were determined by GC using naphthalene as an internal standard as shown

in Fig. S9.

Turnover number (TON) was defined as the mole number of product per mole number of catalyst, and turnover frequency (TOF) was defined as the mole number of product per mole number of catalyst per hour, where TOF=TON/time.

h	k	l	$q_{ m obsd}/ m nm^{-1}$		$q_{ m calcd}/ m nm^{-1}$
			1	2	
1	0	0	1.87	1.83	1.79
2	0	0	3.54	3.50	3.58
4	-2	0	6.27	6.24	6.23
6	-2	0	9.60	9.61	9.52
8	-2	0	12.5		12.46
0	0	1	17.9	17.9	17.95

Table S3 X-ray diffraction data for framework 1 and framework 2.^a

 a q_{obsd} and q_{calcd} are the scattering vectors of the observed reflections, and calculated for the hexagonal structure with lattice parameters a = 4.0 nm, b = 4.0 nm, and c = 0.35 nm.

6. Supplementary Figures



Fig. S1 X-ray photoelectron spectra (XPS) of N1s (a) and Ag3d (b) spectra of ligand, framework **1** and **2**.



Fig. S2 TGA curves of framework **1**, **2**, and ligand **4** heating at a rate of 10 °C min⁻¹ under air flow.



Fig. S3 Plots of ICP-OES analysis for Ag(I) in 5% HNO₃ aqueous solution and leaching experiments of 1 and 2.



Fig. S4 XRD of coordinated framework 2 (a), corresponding 1D small-angle xray diffraction of coordinated framework 1, 2 and simulated XRD result of hexagonal perforated layer (b), and representation of infinite honeycombed framework based on the hexameric coordinated polymer (c). N₂ sorption isotherms of framework 1 (d) and 2 (e) at 77 K and insets of (d) and (e) are corresponding pore size distribution.



Fig. S5 IR spectra of framework 1, 2, and ligand 4.



Fig. S6 AFM images from 12 mM of AgNO₃ in ACN solution with 0.2 mmol ligand (a, height: 0.8 nm), 0.4 mmol ligand (b, height: 6 nm), 0.6 mmol ligand (c, height: 15 nm) and 2.0 mmol ligand (d, height: 400 nm), (all scale bars are 500 nm). AFM images from 3.3 mM of ligand in THF solution with 0.3 mmol AgNO₃ (e, height: 1 nm), 0.6 mmol AgNO₃ (f, height: 1 nm), 0.9 mmol AgNO₃ (g, height: 1 nm), and 1.5 mmol AgNO₃ (h, height: 1 nm), (all scale bars are 500 nm).



Fig. S7 Energy minimization for the disc-like model with z-type coordination and boat-like model with w-type coordination.



Fig. S8 Conversion of reactions catalyzed by framework 1 (a) and 2 (b) with respect to time elapse at different temperatures (30 °C, 34 °C, 38 °C, 42 °C), and corresponding fitting for first-order reaction of 1 (c) and 2 (d).

According to the Arrhenius equation $lnk = lnk_0 - Ea/RT$, *Ea* was calculated as 60.0 kJ mol⁻¹ and logarithm of pre-exponential factor lnk_0 is 17.1 and 17.8 for catalyst 1 and 2, respectively.



Fig. S9 Catalyst loading dependent catalysis by framework 1 and 2 (under 0.6 MPa CO₂).



Fig. S10 Catalytic cycle test for framework 1 and 2 (2-methyl-3-butyn-2-ol as the substrate, under 0.6 MPa CO_2).



Fig. S11 Plots of internal standard method for quantifying reactants.

For R1: y = 2.3834x + 0.0498, R = 0.9987.

For R2: y = 1.8248x + 0.0402, R = 1.

For R3: y = 1.5861x + 0.0375, R = 0.9999.

For R4: y = 1.8617x + 0.0257, R = 1.

For R5: y = 1.6256x + 0.0466, R = 0.9999.

The linear relationship between molar ratio (substrate to naphthalene) to GC area ratio

is rational for determining yields of different reactions.

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Author Contributions

J.B. and S.W. performed most of the experiments and data analysis. J. K. and X.X. performed TEM and XRD experiment. L.Z. and L.H. performed AFM experiment. X.Z., Y.C., and H.J. provided the CO_2 catalysis instruments and did the GC analysis. J.B., S.W., and Z.H. wrote the paper. Z.H. designed all experiments.