

Supporting Information for

“Rational Synthesis and Characterization of Robust Microporous Metal-Organic Frameworks with Base-Functionality”

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Syntheses and characterization of organic ligands and MOFs.

General Remarks: L^1 and L^2 were prepared through reported procedure. The reactions for the synthesis of L^3 were carried out under nitrogen using standard Schlenk techniques. Distilled, dry, and oxygen-free THF was used throughout. Routine ^1H NMR spectra and ^{13}C NMR were recorded with a Bruker 300 spectrometer. Elemental analyses were performed at National Center for Inter-University Research Facilities, Seoul National University. The EA measurements were carried out after samples were dried *in vacuo* for a day. High-resolution mass spectra were carried out at the Korea Basic Science Institute (Daegu). Infrared spectra were recorded on a JASCO FT/IR-660 spectrometer.

Synthesis of 1-(4-pyridyl)-2-(3-methyl-4-pyridyl)ethene (L^3). To a solution of LDA {generated *in situ* by the reaction of diisopropylamine (1.8 mL, 12.8 mmol) in 30 mL of THF with *n*-BuLi (2.5 M, 5.5 mL, 13.8 mmol) at $-78\text{ }^\circ\text{C}$ } was added 3,4-lutidine (1.0 mL, 8.9 mmol) at $-78\text{ }^\circ\text{C}$. While the solution was stirred at room temperature for 30 min, the solution turned to reddish. To the reddish solution was added pyridine 4-carboxaldehyde (0.85 mL, 8.9 mmol) at room temperature. The resulting solution was stirred for 4 h and quenched by addition of water (30 mL) and dichloromethane (30 mL). The dichloromethane layer was collected, evaporated to dryness, and dissolved in 15

mL of pyridine. The pyridine solution was cooled to 0 °C. Excess POCl₃ (2 mL) was added dropwise to the pyridine solution. The resulting solution was heated up to 70 °C and stirred for 12 h. And then, it was quenched by addition of ice. After evaporation of pyridine, the residue was dissolved in water (30 mL) and basified by addition of aqueous 4 M NaOH. Extraction with dichloromethane (100 mL) followed by chromatography on a silica gel column eluting with Et₂O/MeOH (v/v, 10:1) gave 0.35 g of **L**¹ (18 %). ¹H NMR (CDCl₃, 25 °C, TMS): δ=8.61 (d, 4.3 Hz, 2 H), 8.44 (d, 4.2 Hz, 1 H), 8.43 (s, 1H), 7.47~7.41 (m, 4H), 7.11 (d, 16.3 Hz, 1 H), 2.42 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 25 °C, TMS) δ=151.66, 150.50, 147.92, 144.27, 142.96, 131.51, 131.30, 129.65, 121.67, 119.70, 16.92 ppm; HRMS M⁺ calc. 196.1000, obsd. 196.0998.

Complexation of *L*¹ with Co(NCS)₂ in DMF/H₂O. A 5 mL of DMF solution containing **L**¹ was layered onto a 5 mL H₂O solution of Co(NCS)₂ in a vial with 20 mm of diameter. The solution was stood at 90 °C oven for several days. When **L**¹ and Co(SCN)₂ in a ratio of 1 : 2 was used, orange long block-like crystals of **1**, red needle-like crystals of **2**, and red block-like crystals of **3** simultaneously appeared on the bottom of the reaction vial. When excess amount of **L**¹ was used, crystals of **2** were obtained as predominant product. Characterization of **2**: Elemental Analysis for **2**·2(DMF) (calc), H:4.19(4.69), C: 52.35(52.40), N: 20.09(20.37), S:9.50(9.32); IR (KBr pellet), 3415 (br w), 3059 (w),

2931 (w), ν_{CN} 2067 (vs) ν_{CO} 1647 (vs), 1585 (s), 1496 (w), 1468 (w), 1417 (m), 1382 (s), 1254 (m), 1221 (w), 1174 (m), 1111 (s), 1007 (s), 849 (s), 681 (s), 561(s), 480 (m) cm^{-1} . Characterization of **3**: Elemental Analysis (calc), H: 4.35(4.60), C: 45.61(45.24), N: 19.13(19.43), S:12.26(12.71); IR (KBr pellet), 3388 (br w), 3057 (w), ν_{CN} 2060 (vs) 1589 (vs), 1468 (m), 1419 (w), 1390 (s), 1221 (w), 1176 (w), 1012 (m), 972 (m), 849 (m), 814 (s), 557 (s), 480 (w) cm^{-1} .

Preparation of 1. A 5 mL of DMF solution containing 0.30 g (1.6 mmol) of **L**¹ was layered onto a 5 mL H₂O solution of 0.29 g (1.6 mmol) of Co(NCS)₂ in a vial with 20 mm of diameter. The solution was stood at room temperature for one day to give 0.51 g (1.0 mmol) of powdery **1** (63 % yield). Elemental Analysis (calc), H: 4.46(4.60), C: 45.50(45.24), N: 19.57(19.43), S: 12.54(12.71); IR (KBr pellet), 3057 (w), 2931 (w), ν_{CN} 2069 (vs) ν_{CO} 1647 (vs), 1585 (s), 1468 (w), 1417 (m), 1377 (s), 1254 (w), 1219 (w), 1173 (w), 1111 (m), 1007 (s), 849 (m), 814 (s), 681 (m), 561(m), 480 (w) cm^{-1} .

Preparation of 4. 26 mg of **1** (0.05 mmol) and 12 mg of **L**³ (0.063 mmol) were dissolved in 5 mL of DMF and stood at 90 °C for several days to give 27 mg of **4** (94 % yield) at the bottom of the vial. Elemental Analysis (calc), H: 3.68(3.82), C: 55.98(56.31), N: 17.81(17.68), S:11.27(11.56); IR (KBr pellet), 3388 (br s), ν_{CN} 2063 (vs) ν_{CO} 1606 (vs), 1552 (w), 1419 (w), 1387 (w), 1120 (s), 972 (w), 835 (m), 619(m),

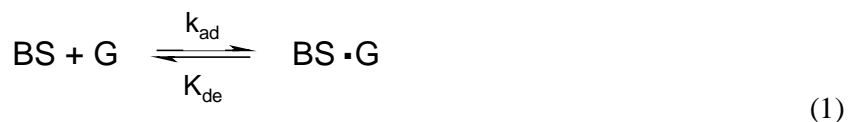
557(m) cm⁻¹.

Crystal structure determination.

All diffraction data for single crystallography were measured by an Enraf-Nonius CCD single-crystal X-ray diffractometer at room temperature using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically. And all hydrogen atoms not involving the hydrogen bonding were treated as idealized contributions. The calculated XRPD patterns (in figure 4 and figure 5) were produced using the Powder Cell 2.4 program based on the single-crystal structure. X-ray powder diffraction data (XRPD) were recorded on a Mac Science Co. M18XHF22-SRA diffractometer at 20 kV, 400 mA for CuK α ($\lambda = 1.5406$ Å), with a scan speed of 10 deg/min.

Guest binding experiment.

Crystals of **2**, **4**, and $[\text{Co}(\text{L}^2)_2(\text{NCS})_2]_\infty$ were kept in vacuum oven at 80 °C for 2 days to evacuate any included solvents. The exactly weighed solids (20 mg) were immersed in 2 ml of toluene solutions containing 2.0-100 mM of methanol, ethanol and phenol for 6 hr at 25 °C. The concentration changes of the organic guests were measured with GC using decane as the internal standard. The GC system was fitted with a 30 m x 0.25 mm x 0.25 μm cross-linked polydimethylsiloxane capillary column. Injection and detection temperatures were set at 250 °C and 280 °C, respectively, and the oven temperatures were 65 °C for methanol and ethanol, and 110 °C for phenol. Formation constant K_f for the complexes formed between Binding site (BS) of insoluble host and guest molecules (G) was defined as k_{ad}/k_{de} by analogy with Langmuir isotherm for adsorption of gas molecules on solid surfaces.



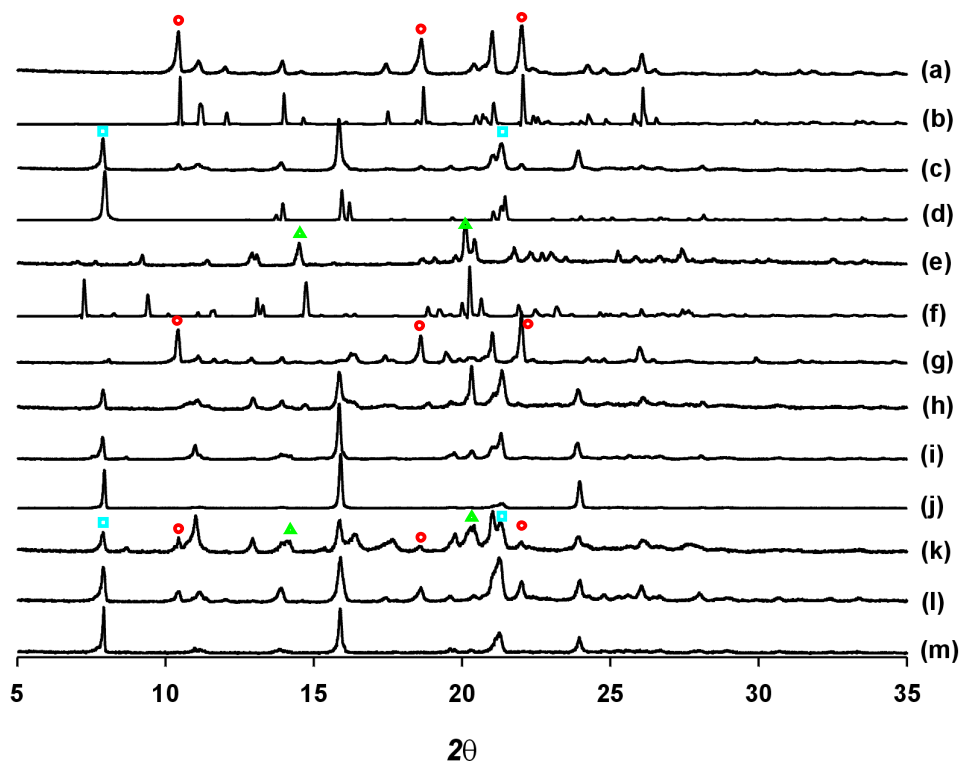
$$K_f = \frac{k_{ad}}{k_{de}} = \frac{[\text{BS} \cdot \text{G}]}{[\text{BS}][\text{G}]} \quad (2)$$

The concentration of G bound to BS ($[\text{BS} \cdot \text{G}]$) was plotted against $[\text{G}]$, and K_f and $[\text{BS}]_0/\omega$ were estimated by analysis of the data according to equations (3) and (4). In the experiment, the total concentration of guest ($[\text{G}]_0$) was varied to keep the θ values in the range of 20 – 80 %.

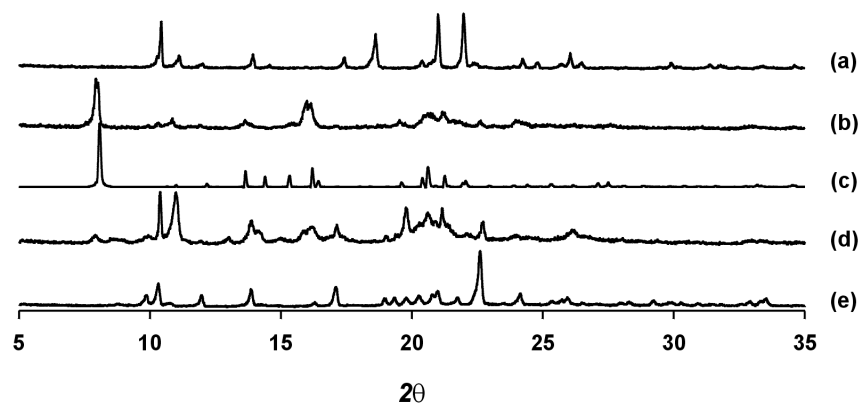
$$\theta = \frac{[\text{BS} \cdot \text{G}]}{[\text{BS}]_0} = \frac{[\text{G}]}{\left([\text{G}] + \frac{1}{K_f}\right)} \quad (3)$$

$$\frac{[\text{BS} \cdot \text{G}]}{\omega} = \frac{\left(\frac{[\text{BS}]_0}{\omega}\right)[\text{G}]}{\left([\text{G}] + \frac{1}{K_f}\right)} \quad (4)$$

ω is the amount of host solid per unit volume of the solution (mg mL^{-1})

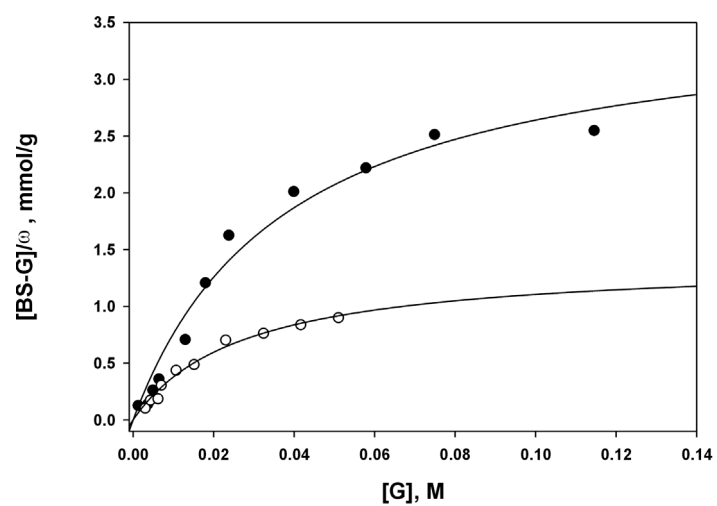


SI. XRPD patterns of a) pure solids of **1**, b) simulated pattern for **1**, c) pure solids of **2**, d) simulated pattern for **2**, e) pure solids of **3**, f) simulated pattern of **3**, g)-f) ensuing solids from reaction of $\text{Co}(\text{SCN})_2$ and **L**¹ with the reagent ratio of 1 : 1.5 (g), 1 : 2 (h), 1 : 2.5 (i), and 1 : 3.0 (j), and k)-m) ensuing solids from reaction of **1** and **L**¹ with the reagent ratio of 1 : 0.5 (k), 1 : 0.75 (l), and 1 : 1 (m).

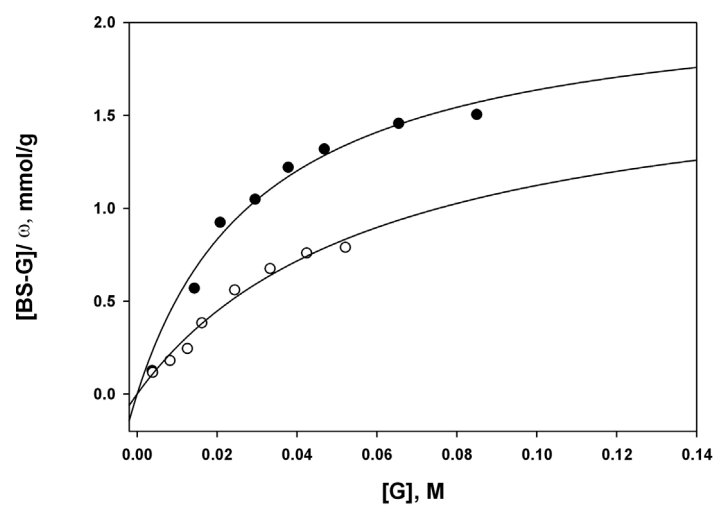


S2. XRPD patterns of a) pure solids of **1**, b) ensuing solids from reaction of **1** and **L**³, c) simulated pattern for **4**, d) ensuing solids from reaction of **L**¹, **L**³ and Co(SCN)₂, and e) ensuing solids from the reaction of Co(SCN)₂ and **L**³ with 1 : 2 reagent ratio.

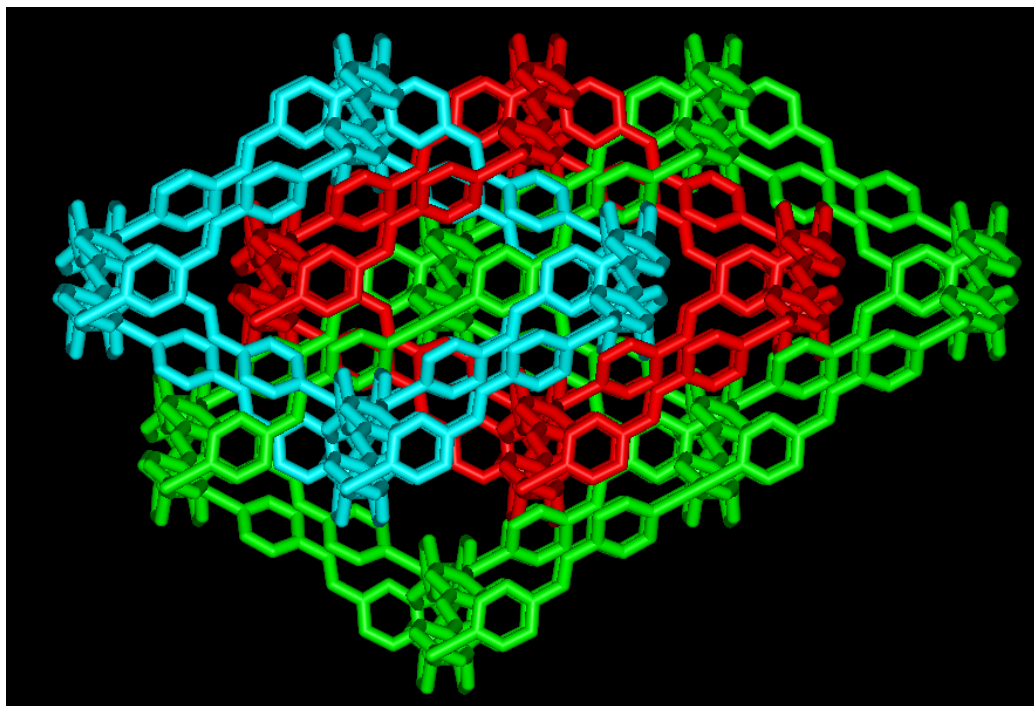
a)



b)



S3. Binding of desolvated solid of **2** (a) and **4** (b) with MeOH (solid circle) and EtOH (open circle).



S4. Top view of **3** showing the three-fold interpenetration mode.