## SUPPORTING INFORMATION

## **Experimental and computational Studies of Pyridine-assisted Post**synthesis Modified Air Stable Covalent Organic Frameworks

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COF-10 or COF 5 sample was degassed to get rid of any contaminants adsorbed on the surface by evacuating it to  $10^{-5}$  torr dynamic vacuum and simultaneously heating to  $120^{\circ}$ C for 16 hours in Autosorb-1-C Analyzer of Quantachrome Instruments. A 77 K nitrogen isotherm was then performed on this sample from 0 to 1 atm (1 atm = P<sub>0</sub>). The Brunauer, Emmett and Teller (BET) model was applied to 5 points of the isotherm for P/P0 between 0.01 to 0.1. This yielded a surface area of 999 m<sup>2</sup>/g.





**Figure 1S.** Nitrogen adsorption (filled symbol) and desorption (open symbol) isotherm for as synthesis COF 5 (red), pyridine modified COF 5 (blue), partially decomposed COF 5 (black), measured at 77 K (a) and its log plot at low P/P0 (b). <sup>1</sup>



**Figure2S.** Pore size distribution of the pyridine modified COF10 calculated from nitrogen adsorption isotherm at 77K using Nonlocal Density Functional Theory (NLDFT) model for cylindrical pores  $4^{4}$  and interaction parameters for carbonaceous materials.  $5^{5}$ 

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro instrument in reflection mode with Cu KR radiation ( $\lambda$ ) 1.54178 Å). The accelerating voltage was set at 45 kV with 40 mA current. The diffractometer was equipped with X'Celerator detector. Scan rates were typically 0.03° s-1 (continuous scan, step size 0.0167°, time per step 70 s). 20 is ranged from 0.5° to 35°. Antiscatter slit, receiving slit, and divergent slit were all fixed to be 1/32'' for small angle measurement.



Figure 3S. PXRD patterns for pyridine modified COF 5 – fresh (blue), and exposed to air for 1 day (red)

## Solid-state nuclear magnetic resonance (SSNMR) measurement

All SSNMR measurements were carried out at 499.3 MHz for <sup>1</sup>H, 125.5 MHz for <sup>13</sup>C, and 50.6 MHz for <sup>15</sup>N, using a Varian 500 MHz *InfinityPlus*<sup>®</sup> spectrometer (11.7 T) equipped with a 1.6-mm FastMAS<sup>TM</sup> triple resonance probe. Samples were exposed in air for two weeks and packed in rotors at ambient conditions. All spectra were taken at room temperature. Due to the low natural abundance of <sup>15</sup>N, 98% <sup>15</sup>N labeled pyridine was utilized during sample preparation. All <sup>1</sup>H and <sup>13</sup>C chemical shifts are referenced to tetramethylsilane as zero ppm, and <sup>15</sup>N chemical shifts are given relative to solid NH<sub>4</sub>Cl as zero ppm.

One-dimensional (1D) and two-dimensional (2D) NMR spectroscopy were implemented at fast magic angle spinning. Tangentially ramped cross-polarization (CP) and low power two-pulse phase modulation (TPPM) was applied to improve sensitivity and resolution. For sensitivity enhancement, 2D <sup>1</sup>H-<sup>15</sup>N through-space heteronuclear correlation (HETCOR) spectrum was acquired via indirect detection, which has been described earlier<sup>2,3</sup>.

Listed below are experimental parameters performed in SSNMR measurements,  $v_{\rm R}$  indicates the magic angle spinning (MAS) rate,  $v_{RF}^{X}$  the magnitude of the RF magnetic field applied to X spins,  $\tau_{\rm CP}$  the CP contact time,  $\tau_{\rm RR}$  the rotary resonance recoupling time,  $\Delta t_1$  the  $t_1$  increment during 2D acquisition,  $\tau_{\rm RD}$  the recycle delay, NS the number of scans, and AT the total acquisition time.

Typically spectra were acquired using,  $v_{R} = 40$  kHz,  $v_{RF}^{H} = 125$  kHz during short pulses and 60 kHz during CP,  $v_{RF}^{X} = 100$  during short pulses and CP,  $v_{RF}^{H}$  and  $v_{RF}^{H} = 10$  kHz during TPPM decoupling.

<sup>13</sup>C CPMAS for p-COF 10 (Figure 4a):  $\tau_{CP} = 5$  ms,  $\tau_{RD} = 2$  s, NS = 1200, and AT = 40 min.

<sup>13</sup>C CPMAS for decomposed COF 10 (Figure 4b):  $\tau_{CP} = 2 \text{ ms}$ ,  $\tau_{RD} = 12 \text{ s}$ , NS = 540, and AT = 1.8 hr.

<sup>13</sup>C CPMAS for p-COF 5 (Figure 3s):  $\tau_{CP} = 2$  ms,  $\tau_{RD} = 1.5$  s, NS = 4000, and AT = 1.7 hr.

<sup>15</sup>N CPMAS for p-COF 10 (Figure 5a):  $\tau_{CP} = 3$  ms,  $\tau_{RD} = 2$  s, NS = 60000, and AT = 34 hr.

2D <sup>1</sup>H-<sup>15</sup>N HETCOR for p-COF 10 (Figure 5b):  $\tau_{CP} = 3 \text{ ms}$ ,  $\tau_{RR} = 30 \text{ ms}$ ,  $\tau_{RD} = 2 \text{ s}$ , 80 rows with  $\Delta t_1 = 25 \text{ µs}$ , 320 scans per row, and AT = 29 hr.



Figure 4S. <sup>13</sup>C CPMAS spectrum of P-COF 5.

All SEM images were conducted on cold field emission SEM Hitachi 4500, with operating voltage 5 KV and emission current 1 mA. Samples were mounted onto carbon film, without further coating before SEM measurements.



Figure 5S. SEM images of COF 10 and COF 5: pyridine modified vs. partially decomposed materials.

## Reference:

- (1) A. Côte, A. Benin, N. Ockwig, M. O'Keeffe, A. Matzger, O. Yaghi, Science, 2005, 310, 1166
- (2) J. W. Wiench, C. E. Bronnimann, V. S. Y. Lin, M. Pruski, J. Am. Chem. Soc. 2007, 129, 12076.
- (3) Y. Ishii, R. Tycko, J. Magn. Reson. 2000, 142, 199.
- (4) A.V. Neimark, P.I. Ravikovitch, Microporous and Mesoporous Materials 2001, 44-45, 697.
- (5) P. I. Ravikovitch, A. Vishnyakov, R. Russo, A.V. Neimark, Langmuir 2000, 16, 2311.