

Supporting Information

Serrated Single-wall metal-organic nanotubes (SWMONTs) for benzene adsorption

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Experimental Section

Materials and Physical Measurements

All commercially available chemicals and solvents were of reagent grade and used without further purification. The ligand 5-(3-methyl-5-phenyl-4*H*-1, 2, 4-triazol-4-yl) isophthalic acid (H_2L) was synthesized according to the method reported previously [1]. PXRD intensities were measured on a Rigaku D/max-III A diffractometer (Cu-K α , $\lambda = 1.54056 \text{ \AA}$). The single crystalline powder samples were prepared by crushing the crystals and scanned from 3 ° to 60 ° with a step of 0.1 °/s. TGA were performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C/min in the flowing air atmosphere. IR spectra were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer spectrometer with KBr pellets. Elemental analyses for C, H, and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. Fluorescence spectroscopy data were recorded on HORIBA Jobin Yvon HJY-FL3-221-TCSPC spectrophotometer.

Synthesis of H_2L

¹H-NMR (400 MHz, DMSO- d_6): $\delta = 2.24$ ppm (s, 3 H, CH_3); 7.32 (d, 3 H, arom. C-H); 8.10 (d, 2 H, arom. C-H); 8.37 (s, 2 H, arom. C-H); 8.50 (s, H, arom. C-H); 10.27 (br, 2 H, CO_2H).
IR (KBr): $\tilde{\nu}[\text{cm}^{-1}]$ 3351.20, 2597.09, 2360.23, 2024.71, 1902.88, 1694.67, 1551.39, 1482.99,

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1460.68, 1416.30, 1378.86, 1330.76, 1257.18, 948.66, 923.97, 902.34, 831.74, 779.43, 749.38, 716.69, 696.70, 675.09, 611.56.

Preparation of Compounds

Synthesis of $[\text{Zn}(\text{L})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (**1**).

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), H_2L (0.1 mmol), and trimesic acid (0.2 mmol) were dissolved in 14 mL water, reacted for 20 minutes under the 100 W of ultrasound, transferred to a 25 mL Teflon-lined pot. 6 mL water was added into the mixture. And the reaction mixture was heated within 2 hours up to 160 °C. The temperature was kept on a constant level for 72 hours, then the autoclave was cooled slowly to room temperature during a period of 72 hours. The block crystals of **1** were obtained by filtration and washed by water.

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0595 g), H_2L (0.2 mmol, 0.0648 g), and triethylamine (a drop) were dissolved in 6 mL methanol, reacted for 20 minutes under the 100 W of ultrasound, transferred to a 25 mL Teflon-lined pot. 6 mL water was added into the mixture. And the reaction mixture was heated within 2 hours up to 170 °C. The temperature was kept on a constant level for 72 hours, then the autoclave was cooled slowly to room temperature during a period of 29 hours. The powder of **1** were obtained by filtration and washed by water. Elemental analysis (%): Calcd for $\text{C}_{17}\text{H}_{15}\text{ZnN}_3\text{O}_6$: C, 48.30; H, 3.58; N, 9.94. Found: C, 48.32; H, 3.57; N, 9.92. IR (KBr, cm^{-1}): 3417.17, 2360.19, 2026.41, 1619.84, 1481.70, 1417.71, 1360.09, 1299.62, 1109.48, 1081.21, 924.27, 838.69, 775.44, 739.37, 694.07, 621.38, 479.97.

X-ray Structure Determination

Diffraction data for compound **1** was collected with a Bruker SMART APEX CCD instrument with graphite monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected at 293(2) K. The absorption corrections were made by multiscan methods. The structure was solved by charge flipping methods with the program Olex2 and refined by full-matrix leastsquares methods on all F^2 data with Olex2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were located in a different Fourier map and refined isotropically in the final

refinement cycles. Other hydrogen atoms were placed in calculated positions and refined by using a riding model. The final cycle of full matrix least-squares refinement was based on observed reflections and variable parameters. Crystallographic data for **1** is given in Table S2. Selected bond lengths and angles are given in Tables S3.

Benzene Adsorption

Activated **1a**, is formed by thermal activation of **1** at 140 °C under vacuum for 24 h. Compound **1** and Activated **1a** were exposed to air saturated with benzene vapor in a set of beakers for 1 h at room temperature. After taken out from the container, samples were kept at air atmosphere for different time (1h, 3days, 8days, 17days). The SWMONTs with adsorbed benzene - that is, benzene/SWMONTs (**1b**) - was measured by the thermogravimetric analysis (TGA) equipment under nitrogen atmosphere. Before starting the weight measurement, we kept the benzene/SWMONTs (**1b**) in this nitrogen gas flow for about 30 min. The weight decrease due to benzene desorption was measured as we increased the temperature from room temperature to 800 °C with a temperature-elevation rate of 10 °C/min in the nitrogen atmosphere [2].

Table S1. Desorption temperature and loss for Benzene

	Dehydration temperature in theory(°C)	Desorption temperature(°C)	Water loss(%)	Benzene loss(%)
B1h	140-220	74-220	4.26	5.77
B3d	140-220	97-220	4.26	5.31
B8d	140-220	99-220	4.26	4.07
B17d	140-220	123-220	4.26	2.91

Table S2. Crystallographic Data and Structure Refinement Summary for Compound **1**

Identification	compd 1
Empirical formula	C ₁₇ H ₁₅ N ₃ O ₆ Zn
Formula weight	422.71
<i>T</i> (K)	293(2)
Crystal system	Rhombohedral
Space group	<i>R</i> -3
<i>a</i> (Å)	29.935(4)
<i>b</i> (Å)	29.935(4)
<i>c</i> (Å)	11.194(2)
α (deg)	90
β (deg)	90
γ (deg)	120
<i>Z</i>	18
ρ_{calc} (g·cm ⁻³)	1.454
μ (mm ⁻¹)	1.309
<i>F</i> (000)	3887
2 θ scan range	3.96 to 55.66°
Reflections collected	27432
<i>R</i> _{int}	0.0693
Independent reflections	4570
parameters	257
Goodness-of-fit on <i>F</i> ²	1.101
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.0700, 0.1907
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0790, 0.1981

Table S3. Selected bond lengths [Å] and angles [°] for **1**

Selected bonds (Å) and angles (°)			
Zn(1)-O(3)#1	1.949(2)	O(3)#1-Zn(1)-O(1)	104.41(11)
Zn(1)-O(1)	1.977(3)	O(3)#1-Zn(1)-O(5)	116.59(11)
Zn(1)-O(5)	1.991(3)	O(1)-Zn(1)-O(5)	112.38(12)
Zn(1)-N(3)#2	2.037(3)	O(3)#1-Zn(1)-N(3)#2	104.89(12)
O(3)-Zn(1)#3	1.949(2)	O(1)-Zn(1)-N(3)#2	119.26(12)
N(3)-Zn(1)#4	2.037(3)	O(5)-Zn(1)-N(3)#2	99.73(13)
		N(2)-N(3)-Zn(1)#4	117.4(2)

Symmetry transformations used to generate equivalent atoms: #1 *x*-*y*, *x*, -*z*+2; #2 *x*-*y*, *x*, -*z*+1; #3 *y*, -*x*+*y*, -*z*+2; #4 *y*, -*x*+*y*, -*z*+1.

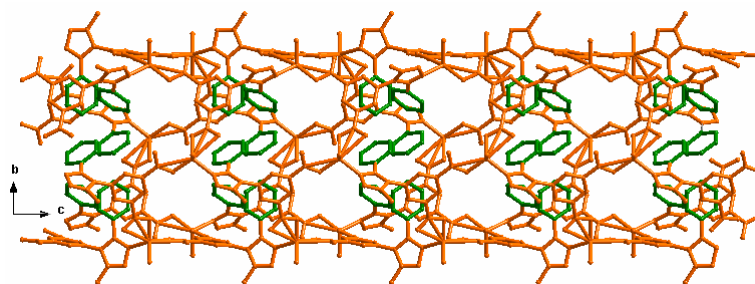


Figure S1. Structure of 1D tube for **1** along the bc-plane (All solvent molecules are omitted for clarity).

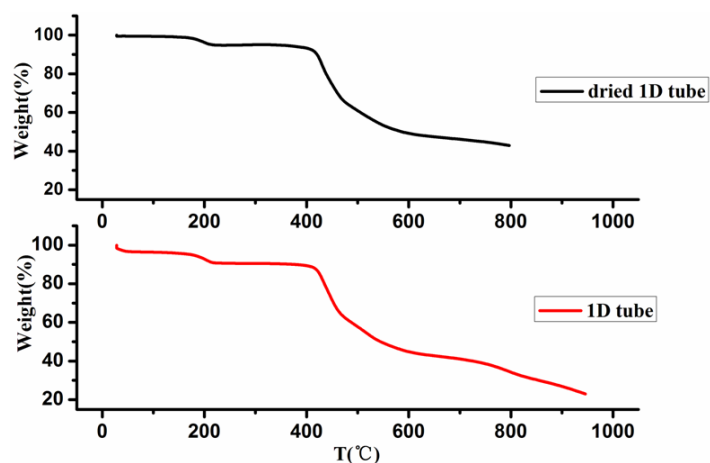


Figure S2. TG curve of compound **1**.

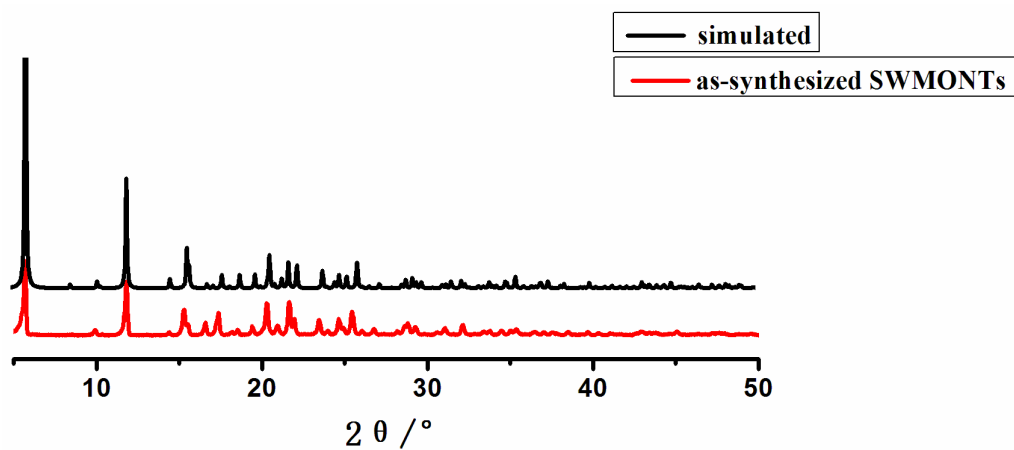


Figure S3. PXRD patterns of compound **1**.

[1] D. Lässig, J. Lincke, H. Krautscheid, *Tetrahedron Letters* 51 (2010) 653.

[2] J. Fan, M. Yudasaka, Y. Kasuya, D. Kasuya, S. Iijima, Influence of water on desorption rates of benzene adsorbed within single-wall carbon nanohorns, *Chemical Physics Letters* 397 (2004) 5-10.