Supporting Information

A Porous Metal-Organic Framework with an Elongated Anthracene Derivative Exhibiting High Methane Working Capacity

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Synthesis of dimethyl 5-(10-bromoanthracen-9-yl)isophthalate (1).

9,10-Dibromoanthracene (3.3 g, 10 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) isophthalate (1.6 g, 5 mmol), K_3PO_4 (2.55g, 12 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.3 g, 0.26 mmol) were dissolved in dry 1,4-dioxane (60 mL) under N_2 atmosphere. The mixture was stirred at 80 ^oC for two days. After removal of the solvent under reduced pressure, the residue was extracted with dichloromethane, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/2, v/v) as eluent to give 1.35 g of the product. Yield: 60 %. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.91 (t, J = 1.6 Hz, 1H), 8.65 (d, J = 8.9 Hz, 2H), 8.30 (t, J = 1.5 Hz, 2H), 7.62 (dd, J_1 = 8.9 Hz, J_2= 3.2 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.41 (dd, J_1 = 9.3 Hz, J_2 = 3.3 Hz, 2H), 3.97 (s, 6H).

Synthesis of diethyl 5-((10-(3,5-bis(methoxycarbonyl)phenyl)anthracen-9-yl)ethynyl) isophthalate (2)

Compound **1** (1.3 g, 2.9 mmol) and 1,3-diethylcarboxylate-4-ethynylbenzene (0.73 g, 3.0 mmol) were dissolved in THF/diisopropylamine (v/v = 1/1, 120 mL) at room temperature under N_2 atmosphere. To the solution were added $Pd(PPh_3)_4$ (60 mg) and CuI (5 mg) . The reaction mixture was stirred for 24 h at room temperature. The reaction was monitored by TLC. Upon completion, the solution was first filtered and the filtrate was then concentrated under reduced pressure. The product was purified by silica gel column chromatography using dichloromethane-hexane (v/v = 1:1) as eluent. Yield: 55% (980 mg). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.92 (t, J = 1.6 Hz, 1H), 8.77 (d, J = 8.5 Hz, 2H), 8.73 (t, J = 2.0 Hz, 1H), 8.63 (d, J = 1.7 Hz, 2H), 8.33 (d, J = 1.5 Hz, 2H), 7.67 (dd, J_1 = 8.7 Hz, J_2 = 3.2 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.45 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 2H), 4.51 (q, J = 7.1 Hz, 4H), 3.98 (s, 6H), 1.50 (t, J = 7.1 Hz, 6H).

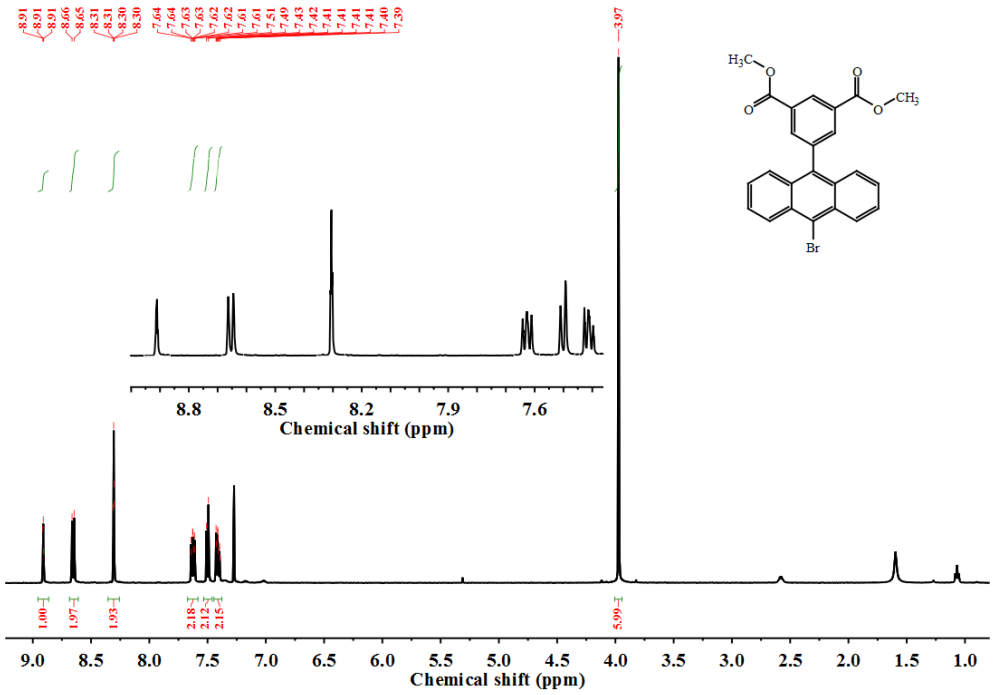

Figure S1. ^{1}H ($CDCl_3$, 500MHz) spectra of compound **1**.

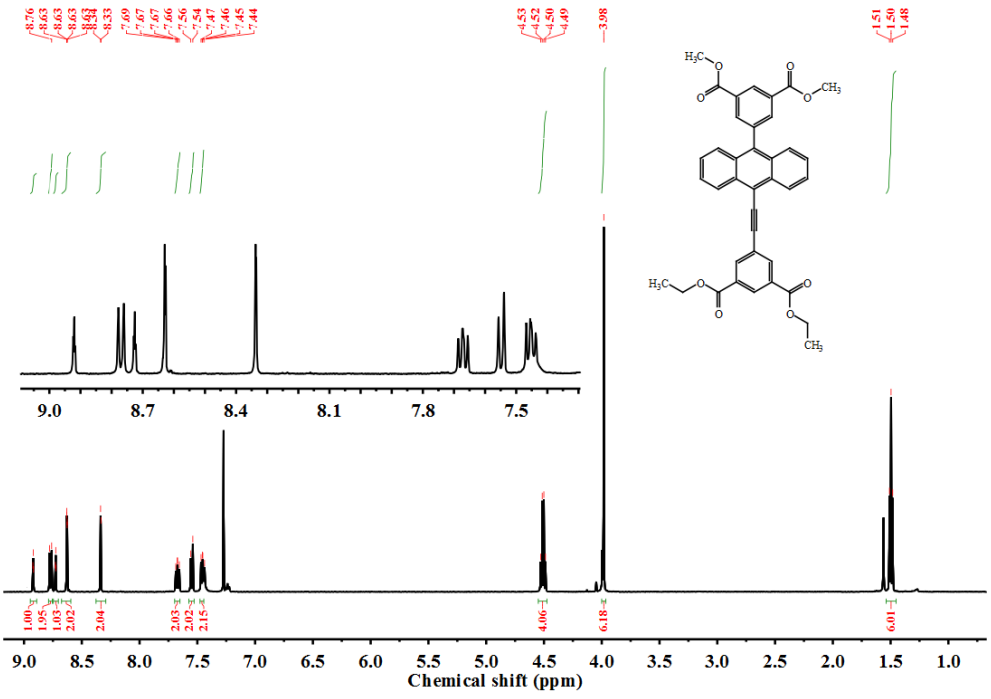

Figure S2. ^{1}H ($CDCl_3$, 500MHz) spectra of compound **2**.

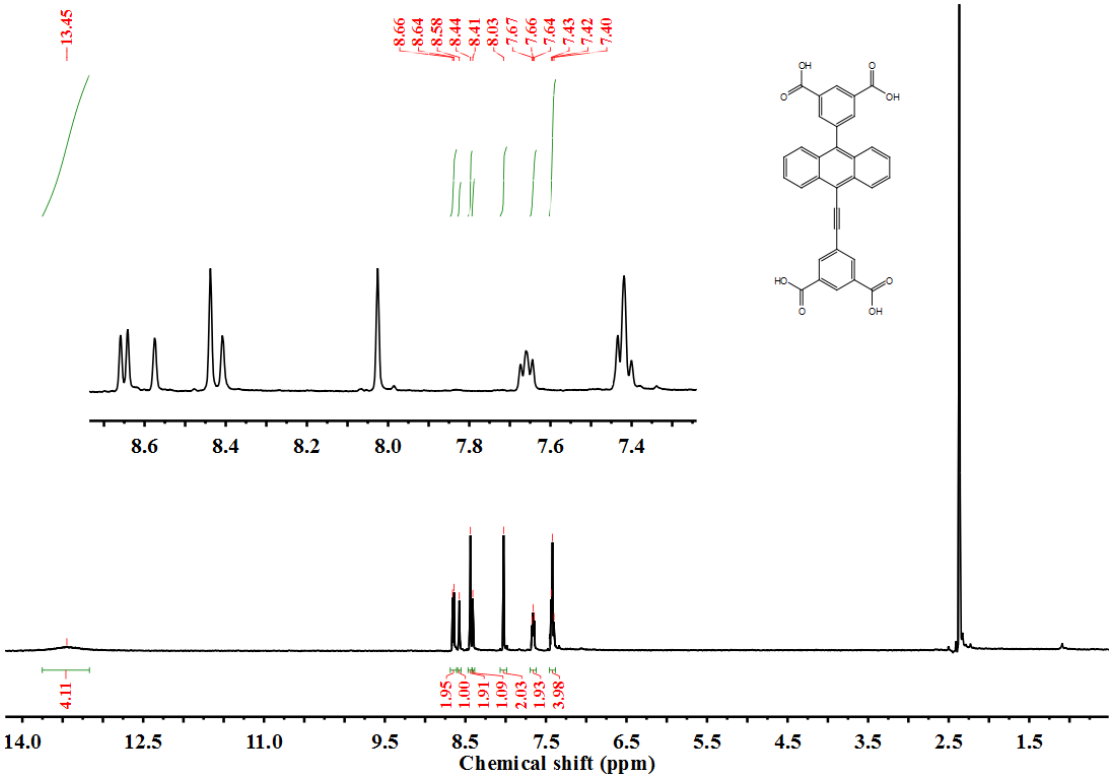

Figure S3. ^{1}H (DMSO-d_6, 500MHz) spectra of the ligand H_4L.

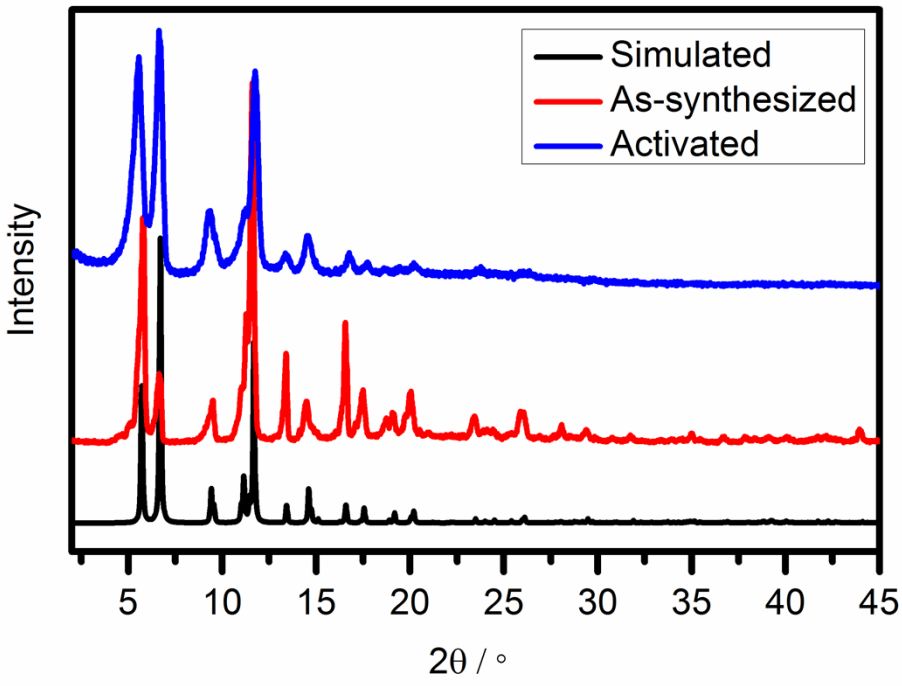

Figure S4. PXRD patterns of as-synthesized UTSA-80 (red) and activated UTSA-80a (blue) along with the simulated XRD pattern from the single-crystal X-ray structure (black).

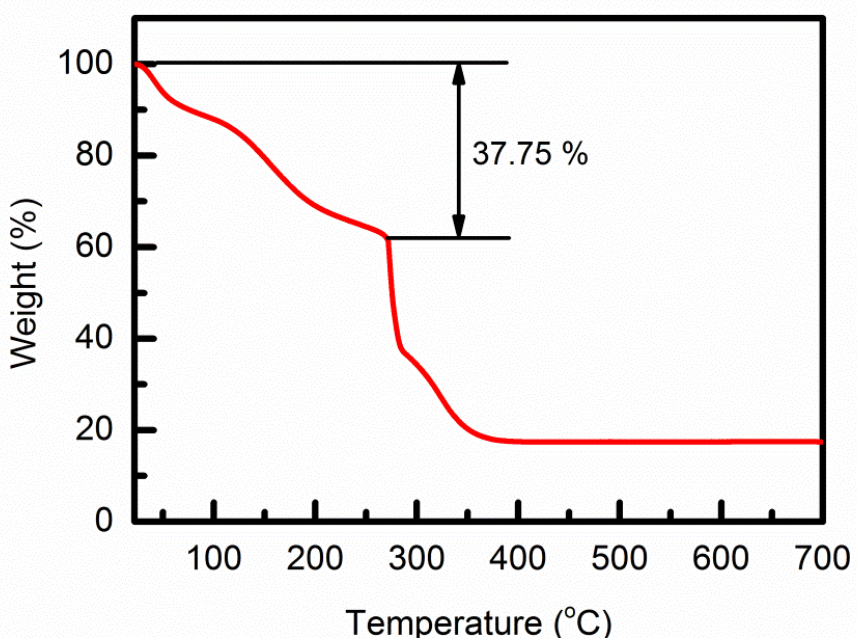

Figure S5. TGA curves of as–synthesized UTSA-80.

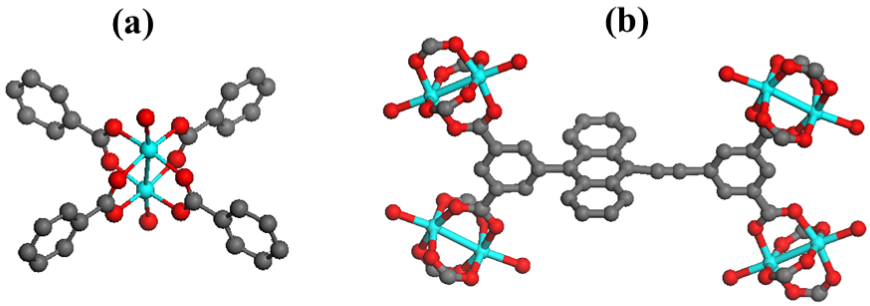

Figure S6. X-ray single crystal structure of UTSA-80: (a) the 4-connected $Cu_2(O_2CR)_4$ paddle-wheel unit; (b) one tetracarboxylate ligand connects with four $Cu_2(O_2CR)_4$ clusters. Turquoise, red, and gray spheres represent Cu, O, and C atoms, respectively.

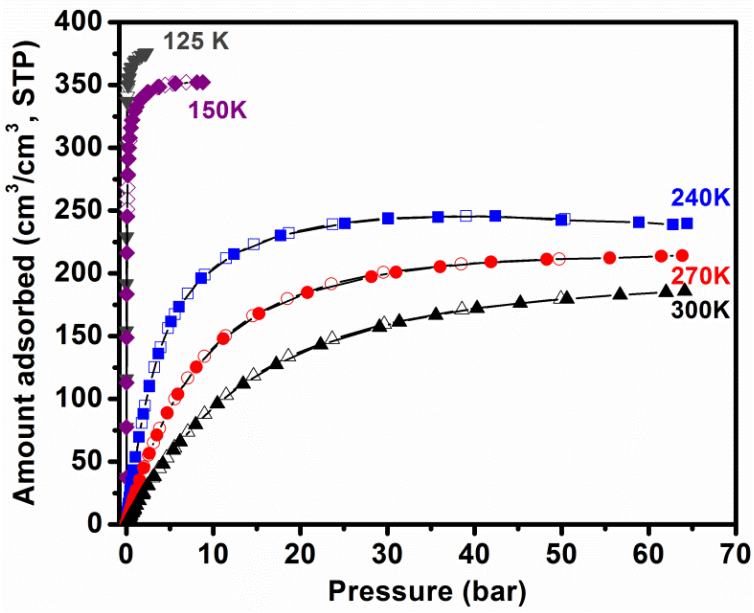

Figure S7. Excess volumetric high-pressure methane sorption isotherms of UTSA-80a at different temperatures. Filled and open symbols represent adsorption and desorption data, respectively.

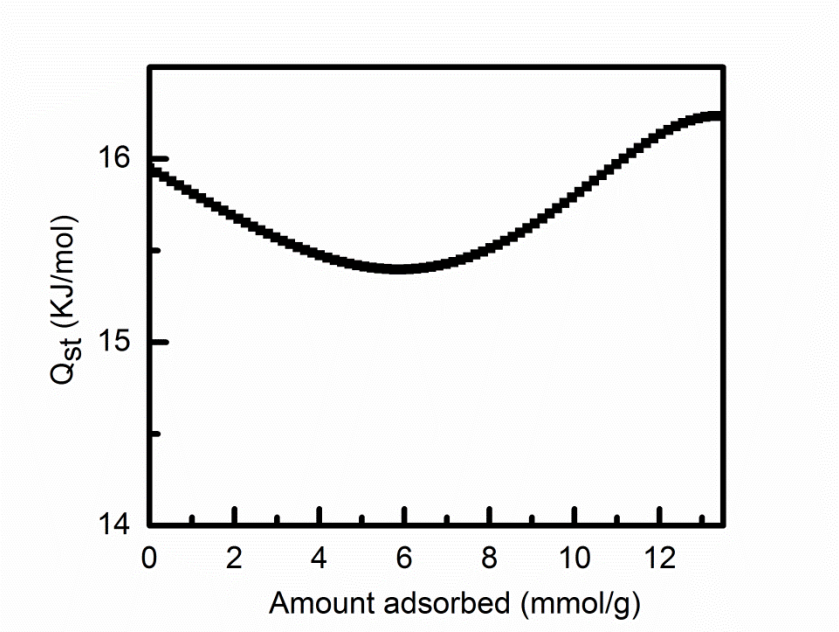

Figure S8. Isosteric heats of adsorption (Q_{st}) for CH_4 as a function of gas loading in mmol(gas) g^{-1}(UTSA-80a), calculated using the virial method.

Table S1. Crystallographic data and structure refinement results for UTSA-80 (from single-crystal X-ray diffraction analysis on the as-synthesized sample).

	UTSA-80
Formula	$C_{48}H_{24}Cu_3O_{15}$
Formula weight	1031.29
Temperature/K	100.00(19)
Crystal system	Trigonal
Space group	R-3m
a, b (Å)	18.4951(7)
c (Å)	46.337(3)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	13726.8(13)
Z	6
D_{calcd} (g cm^{-3})	0.749
μ (mm^{-1})	1.106
F(000)	3114
Crystal size/mm^3	0.2 × 0.16 × 0.10
GOF	1.202
R_{int}	0.0257
R_1, wR_2 [I>=2σ (I)]	0.1073, 0.2991
R_1, wR_2 [all data]	0.1290, 0.3276
Largest diff. peak and hole (e Å^{-3})	0.946 and -0.766

Disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.