

Supporting Information

Graphyne-like Porous Carbon-rich Network Synthesized via Alkyne Metathesis

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Section S1. Materials and Methods

1,3,5-tribromobenzene, anhydrous zinc bromide, 1-propynyl-magnesium bromide (0.5 M, THF), Pd(PPh₃)₄, tris(t-butoxy)(2,2-dimethylpropylidyne)-tungsten(VI), tetrahydrofuran and toluene were purchased from J&K Scientific. Anhydrous and anaerobic solvents were obtained from a PureSolv™ MD-5 solvent system consisting of a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst. 1,3,5-tripropynylbenzene was synthesized according to the literature¹.

¹H NMR and ¹³C NMR spectra were measured on a Bruker AVANCE III Fourier 400 M spectrometer. ¹³C Solid-state NMR spectra was recorded on a VARIAN VNMRS-400WB spectrometer with a 7.5 mm T3HX probe at 100.54 MHz and a spinning rate of 9 kHz. Fourier transform infrared (FT-IR) spectra was recorded on a Nicolet Magna 550 Fourier transform infrared spectroscopy. Raman data was collected on Dilor Super LabRam II. Field-emission Scanning (FE-SEM) was performed on a HITACHI S4800 operating at an accelerating voltage ranging from 1.0 to 15 kV. The

sample was prepared by dispersing the material onto conductive adhesive tapes attached to a flat aluminum sample holder and then coated with Platinum. Transmission Electron Microscope (TEM) was measured on a FEI Tecnai G2 F20. Atomic Force Microscope (AFM) was examined on a Nanoscope IIIa Multimode through Tapping Mode in air at room temperature. Elemental analysis was conducted on a VARIO EL cube. Impedance measurement was performed on a BAS Epsilon Electrochemical Workstation. The X-ray diffraction pattern (XRD) of the material was characterized using X-ray diffraction (D/MAX-2000 with CuK α radiation). X-ray photoelectron spectra (XPS) was collected on Dilor Super LabRam II. Ultraviolet photoelectron spectra (UPS) was obtained on a Thermo Scientific Escalab 250Xi. UV-Vis Diffuse Reflection Spectroscopy (UV-Vis DRS) was recorded on a SHIMADZU UV-2600. Thermogravimetric analysis (TGA) from 20-800 °C was carried out on a Perkin-Elmer 7 Series in nitrogen atmosphere using a 10 °C/min ramp without equilibration delay.

Energy calculations were based on density functional theory (DFT) and were implemented in the CASTEP package². The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)³ for the exchange-correlation term was applied. Considering that the van der Waals interaction is significant for layered structures, the empirical correction method proposed by Grimme (DFT-D3)^{4, 5} was used. For our computation, 3 \times 3 \times 3 k-points were used, and 520 eV was chosen as the cutoff energy.

The nitrogen isotherms were measured at 77 K using a Quantachrome Nova 4000e surface area size analyzer. Before measurement, the samples were degassed in vacuum at 100 °C for 12 h. N₂ and CO₂ physisorption isotherms were measured up to 1 bar at 281 K and 298 K using a Micrometrics ASAP 2020 surface area analyzer. Prior to measurements, samples were degassed for over 12 h at 100 °C.

Section S2 Synthesis and Methods

Synthesis of 1,3,5-Tripropynylbenzene¹. To a solution of anhydrous zinc bromide (676 mg, 3 mmol) in 10 mL of THF was added dropwise 1-propynylmagnesium bromide (0.5 M, THF, 6 mL) at 0 °C followed by Pd(PPh₃)₄ (86 mg, 0.08 mmol) and 1,3,5-tribromobenzene (312 mg, 1.0 mmol). The cooling bath was removed, the

reaction mixture was heated at reflux for 8 h, and the solution was cooled to room temperature and quenched by a saturated aqueous solution of ammonium chloride. The organic layer was washed successively with water and brine and then dried over MgSO_4 . After evaporation of the solvent, column chromatography (silica gel, hexane/ether 50/1) afforded the product as white solid in yield 72%. ^1H NMR (CDCl_3 , Me_4Si): δ (ppm) 2.02 (s, 9H, CH_3), 7.28 (s, 3H, Ar-H). ^{13}C NMR (CDCl_3 , Me_4Si): δ (ppm) 4.31, 78.53, 86.60, 124.31, 133.51. HR-MS: m/z calcd. for $\text{C}_{15}\text{H}_{12}$ 192.0939, found 192.0941. Anal. Calcd. for $\text{C}_{15}\text{H}_{12}$: C 93.71; H 6.29. Found: C 93.67; H 6.39.

Synthesis of graphyne-like porous carbon-rich network through Alkyne Metathesis⁶. 1,3,5-Tripropynylbenzene (192 mg, 1.0 mmol) and tris(*t*-butoxy)(2,2-dimethylpropylidene)tungsten(VI) (23.5 mg, 0.05 mmol) were dissolved in anhydrous toluene which were obtained from a PureSolv™ MD-5 solvent system consisting of a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (12 mL) and heated for 24 h to 90 °C under argon atmosphere without stirring. In order to form large flakes, the efficient removal of 2-butyne is necessary. The reaction mixture was then exposed to a vacuum for five times at 30 min intervals across 2.5 h period. The solvent evaporated during the vacuum exposure was compensated, and the reaction vessel was sealed. Acetone (~100 mL) was added, and the gel like network was broken into tiny pieces. The graphyne-like porous carbon-rich network was isolated as a brown powder from the solvent by filtration and was insoluble in common organic solvents.

Section S3 Characterization of precursors and model compounds

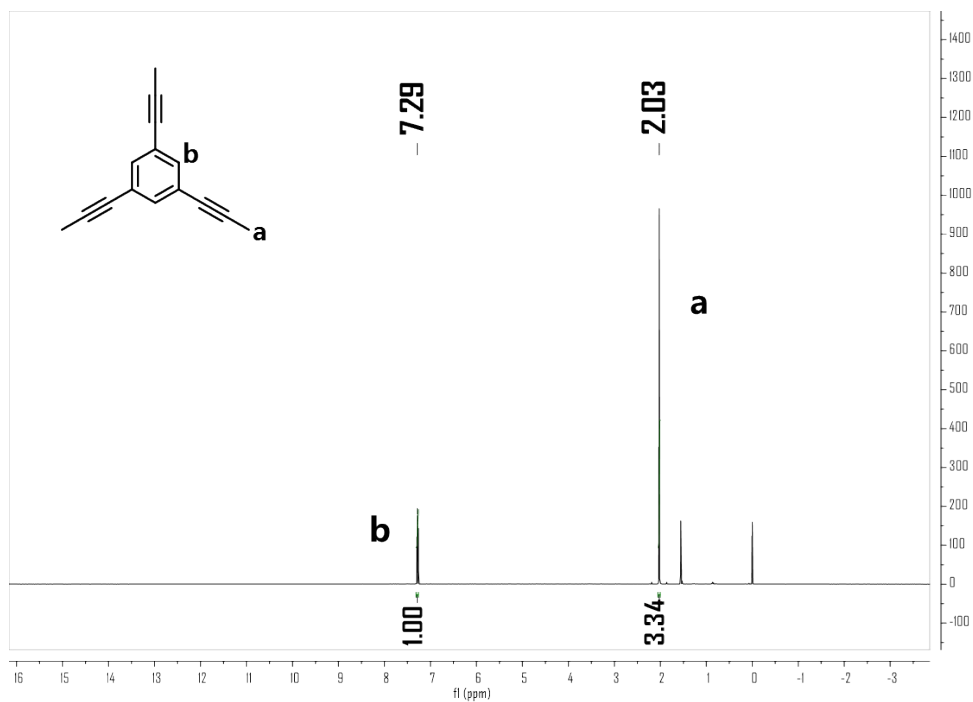


Figure S1. ¹H-NMR of 1,3,5-tripropynylbenzene (Chloroform-d).

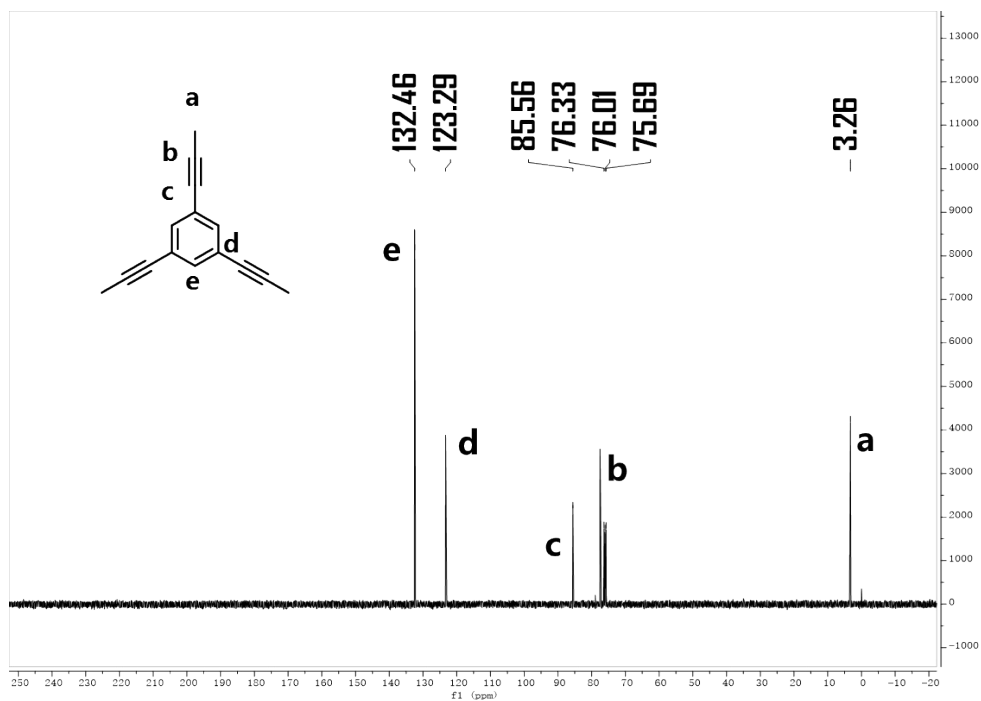


Figure S2. ¹³C-NMR of 1,3,5-tripropynylbenzene (Chloroform-d).

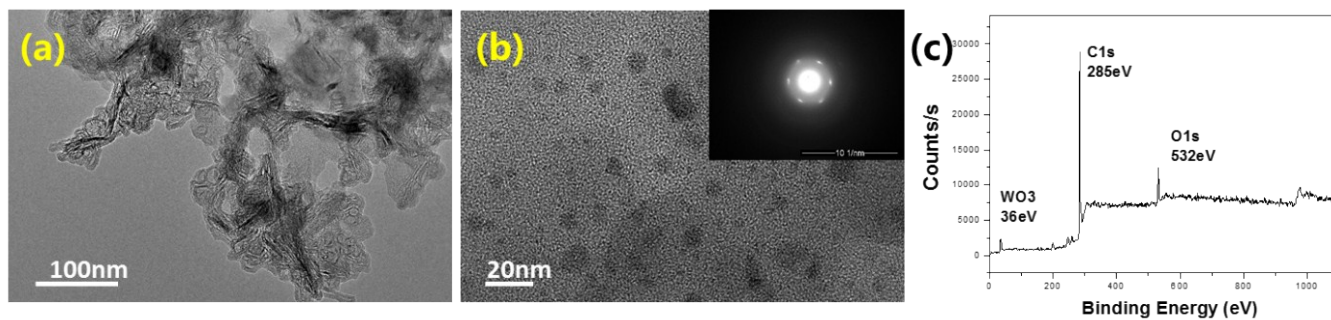


Figure S3. TEM images (a) magnification $\times 97000$; (b) magnification $\times 285000$ (inset: SAED pattern); (c) XPS spectra (survey scan) of graphyne-like porous carbon-rich network from samples prepared by reaction time of 72h).

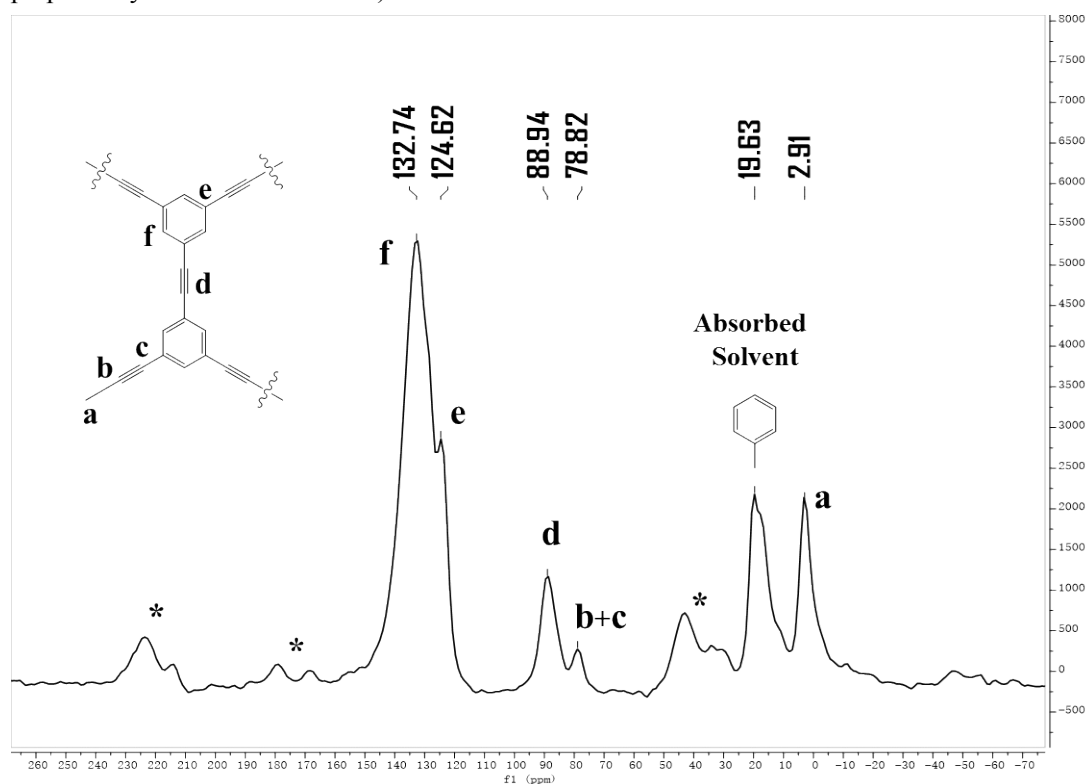


Figure S4. Solid state ^{13}C -NMR of graphyne-like porous carbon-rich network (9 kHz). Asterisks denote spinning sidebands.

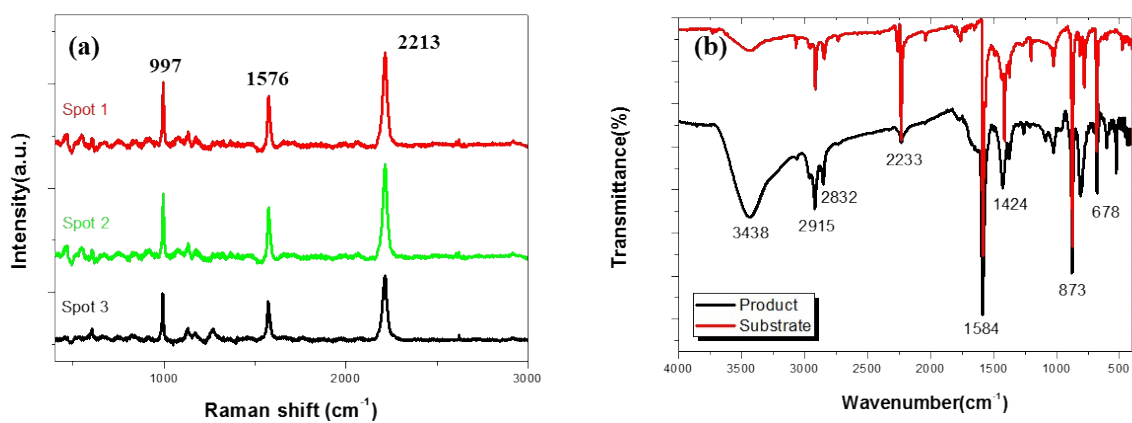


Figure S5. (a) FT-IR spectra and (b) Raman of graphyne-like porous carbon-rich network.

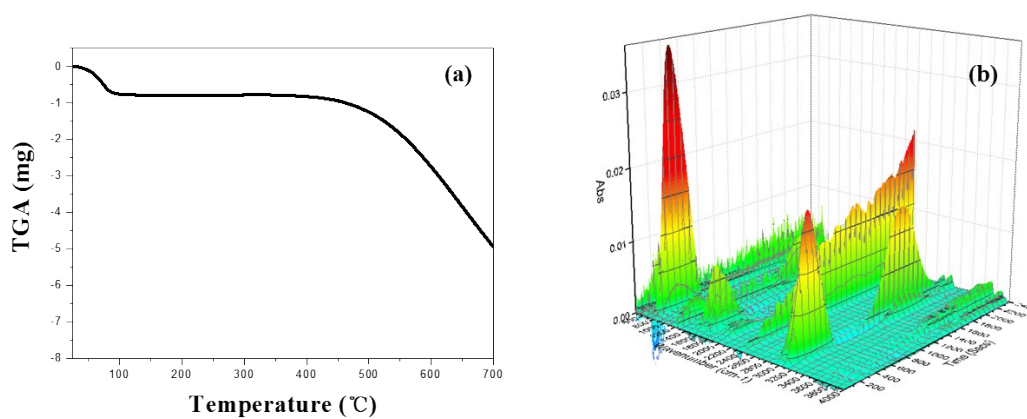
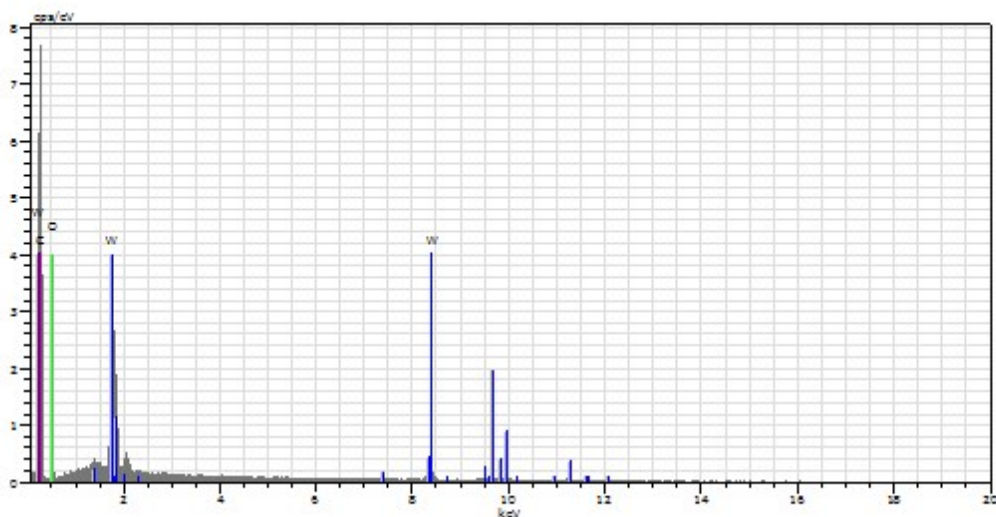


Figure S6. (a) TG and (b) TG-IR of graphyne-like porous carbon-rich network.



El	AN	Series	unn. C norm. C Atom. C Error			
			[wt.%]	[wt.%]	[at.%]	[wt.%]
C	6	K-series	80.36	83.47	95.59	9.9
O	8	K-series	3.89	4.04	3.48	0.9
W	74	L-series	12.02	12.49	0.93	0.4
Total:			96.28	100.00	100.00	

Figure S7. EDS of graphyne-like porous carbon-rich network (detailed information).

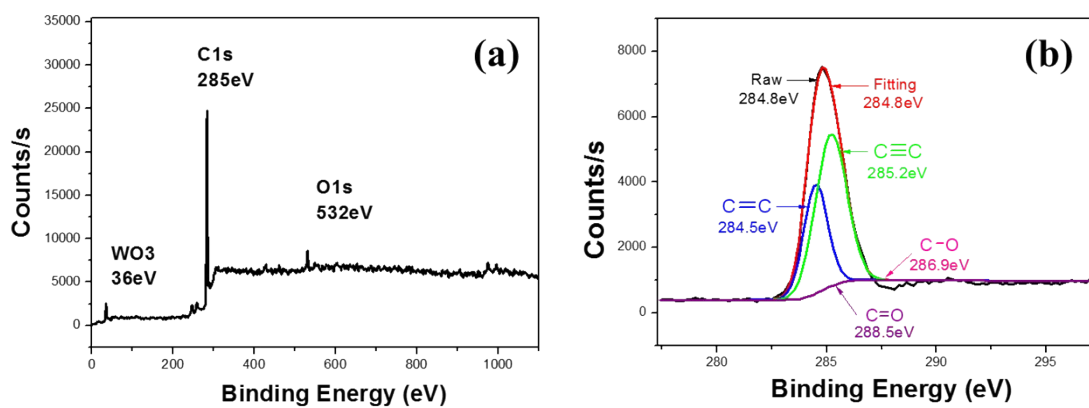


Figure S8. XPS spectra of graphyne-like porous carbon-rich network (a) survey scan (b) narrow scan for element C.

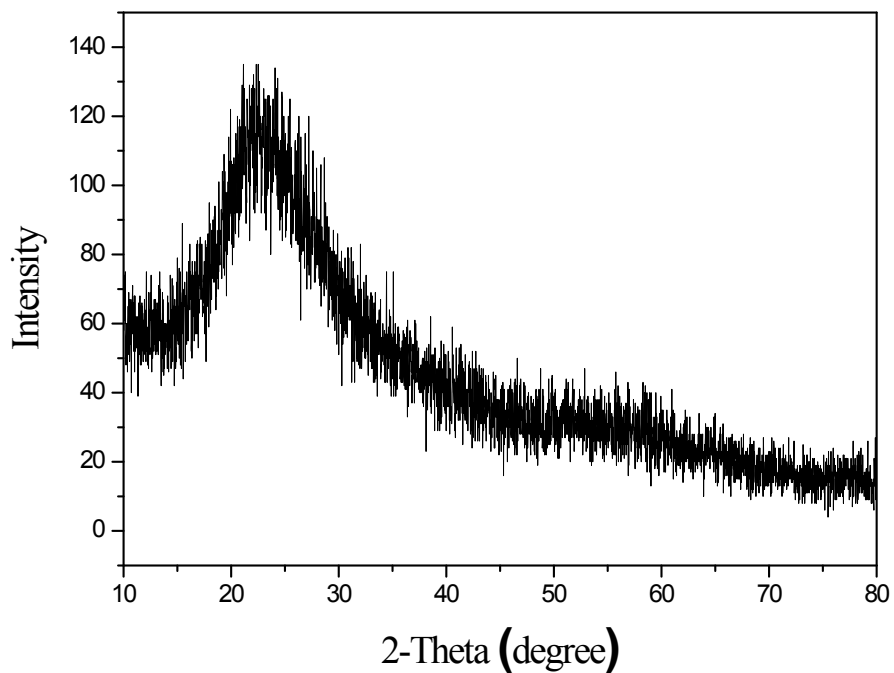


Figure S9. XRD spectra of graphyne-like porous carbon-rich network.

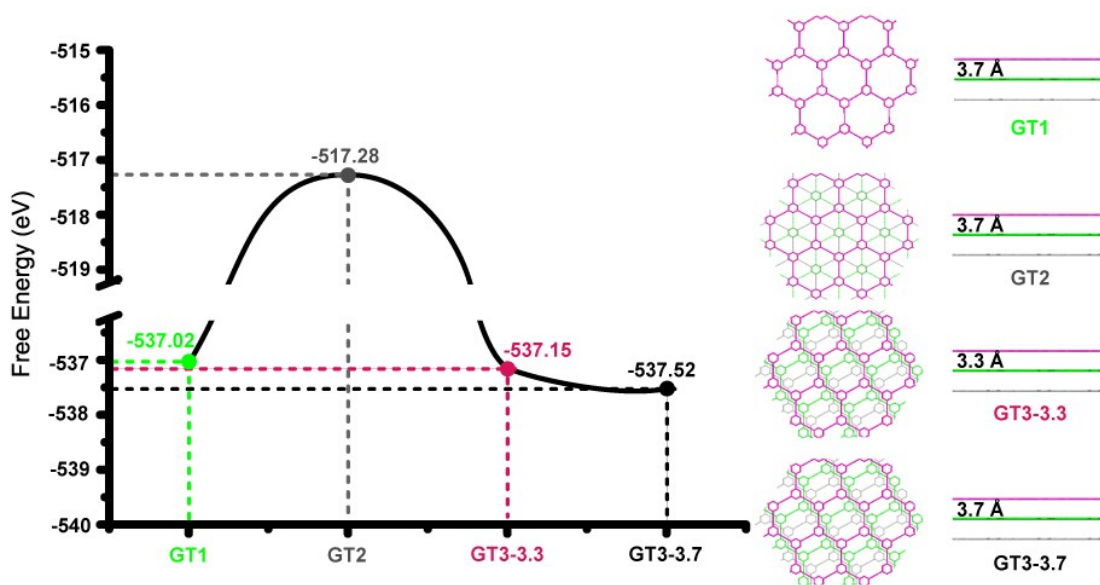


Figure S10. Energy diagram and structure representations of tilted layered structures of graphyne-like porous carbon-rich network GT1, GT2, GT3-3.3 and GT3-3.7.

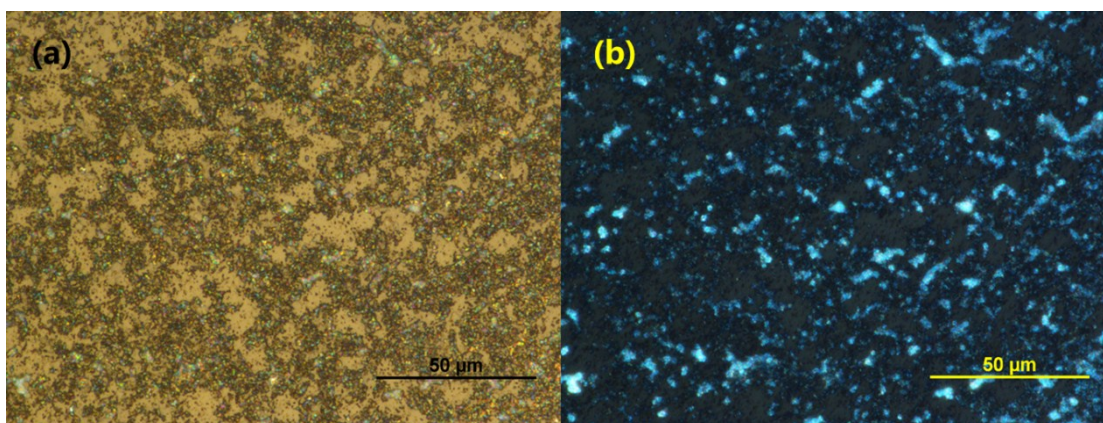


Figure S11. Polarizing Microscope images of graphyne-like porous carbon-rich network (a) bright field and (b) dark field.

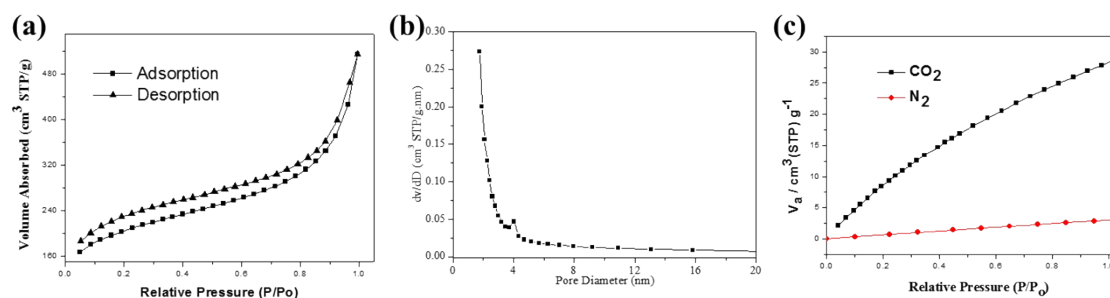


Figure S12. Gas sorption measurements for graphyne-like porous carbon-rich network. (a) N_2 adsorption and desorption isotherms at 77 K; (b) Pore size distribution; (c) CO_2 and N_2 isotherms at 281 K.

References:

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