Supporting Information

Preparation of carbon-containing, compressible, microporous, polymeric monoliths that regulate macroscopic conductivity

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Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using Bruker 400 MHz NMR spectrometers at 25 ℃. Proton chemical shift are expressed in part per million (ppm, δ scale) and are referenced to tetramethylsilane ((CH_3)$_4$Si 0.00 ppm) or to residual protium in the solvent ($CDCl_3$, δ 7.26 ppm).

Nitrogen adsorption–desorption isotherms were measured at 77 K by using a Belsorp-Max (BEL Japan, Inc.) apparatus. Samples were degassed at 150 ℃ under vacuum for at least 12 h before measurements, and ultra-high purity grade nitrogen gas was used for all measurements. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method and the pore size distribution was estimated according to the nonlocal density function theory (NLDFT) with a slit model. Total pore volumes were calculated at a relative pressure of $P/P_0 = 0.990$.

Uniaxial compressive tests were performed using a universal testing machine (UTM) (MCT-2150, A&D, Japan) with a 500-N load cell at 25 ℃ in air. The cylindrical samples (diameter × height, 7.8 mm × 8.0 mm) were compressed at a rate of 10 mm min^{-1} and triplicated during the measurement. Then, stress-strain curves were recorded. Young's

modulus was obtained from the initial slope of the stress-strain curve in the strain range of 5–10%.

Micromorphology of dried hydrogels was observed using a Carl Zeiss SUPRA 55VP scanning electron microscope (SEM) at an accelerating voltage of 2 kV. Before the measurement, the sample was dried in vacuum and coated with a thin platinum layer.

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was performed using IFS66/S (Bruker) was used to observe absorption spectra of hydrogels.

Water Contact angle measurements were conducted using a SurfaceTech GSA-X goniometer at 25 ℃ in air. The contact angle measurement was performed on a flat surface. The angles were measured immediately after dripping a water droplet on the surface of sample.

Synthetic Procedures for Polymer Networks

Synthesis of 1,3,5-triethynylbenzene (TEB):
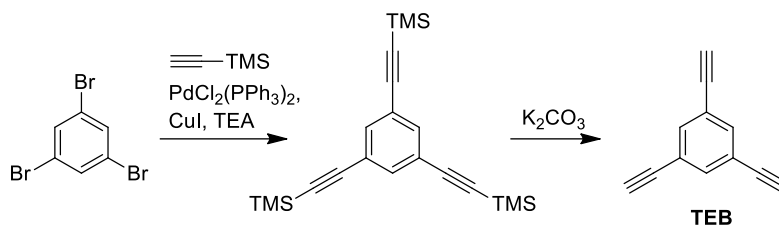
Scheme S1. Synthetic procedures for **TEB**.

1,3,5-Tris((trimethylsilyl)ethynyl)benzene: 1,3,5-Tribromobenzene (2.42 g, 7.69 mmol, 1.0 equiv), PdCl$_2$(PPh$_3$)$_2$ (97.1 mg, 0.14 mmol, 0.018 equiv) and CuI (13.2 mg, 0.07 mmol, 0.01 equiv) were transferred to a vacuum-dried 250 mL round bottom flask. Toluene (12 ml) and trimethylamine (6 mL) were added and stirred for 15 min under nitrogen atmosphere. Trimethylsilylacetylene (3.8 ml, 27.67 mmol, 3.6 equiv) was added and the reaction solution was heated to 80 °C and stirred for 24 h. After cooled to room temperature, the solid was filtered and washed with *n*-hexane. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with hexane to afford 1,3,5-tris((trimethylsilyl)ethynyl)benzene (2.58 g, 91.6 %) as pale yellow solid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.49 (s, 3H), 0.23 (s, 27H). The spectrum matched with the reported data in S1.

1,3,5-Triethynylbenzene (TEB): 1,3,5-Tris((trimethylsilyl)ethynyl)benzene (3.0 g, 8.18 mmol, 1.0 equiv) was dissolved in 75 mL of methanol, and potassium carbonate (5.97 g, 36.61 mmol, 4.5 equiv) was added to the solution. The mixture was stirred at room temperature for 5 hours. The residue was extracted with DCM, water, and brine. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with gradient elution with 10% ethyl acetate in hexanes to afford TEB (1.09 g, 89%).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.57 (s, 3H), 3.10 (s, 3H). The spectrum matched with the reported data in S1.

Polymer network (6–8):

The polymer networks from **6** to **8** were prepared by following the same procedure for **5** except for using different monomers without ethanol.

Quantities of monomers and reagents for **6**: 1,3,5-Triethynylbenzene (50 mg, 0.33 mmol, 1.0 equiv), 1,3-diiodobenzene (109.83 mg, 0.33 mmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) dichloride (7.0 mg, 0.01 mmol, 0.03 equiv), and copper(I) iodide (2.0 mg, 0.01 mmol, 0.03 equiv). The product was obtained as a sponge-like, yellow monolith.

Quantities of monomers and reagents for **7**: 1,3,5-Triethynylbenzene (50 mg, 0.33 mmol, 1.0 equiv), 2,5-diiodothiopene (111.84 mg, 0.33 mmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) dichloride (7.0 mg, 0.01 mmol, 0.03 equiv), and copper(I) iodide (2.0 mg, 0.01 mmol, 0.03 equiv). The product was obtained as a compressible, yellow monolith.

Quantities of monomers and reagents for **8**: 1,3,5-Triethynylbenzene (50 mg, 0.33 mmol, 1.0 equiv), 1,4-diiodobenzene (109.83 mg, 0.33 mmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) dichloride (7.0 mg, 0.01 mmol, 0.03 equiv), and copper(I) iodide (2.0 mg, 0.01 mmol, 0.03 equiv). The product was obtained as a compressible, yellow monolith.

Polymer network containing carbon black (6C–8C):

The carbon-containing networks from **6C** to **8C** were prepared by following the same procedure for **5C** except for using different monomers without ethanol.

Quantities of monomers and reagents for **6C**: 1,3,5-Triethynylbenzene (50 mg, 0.33 mmol, 1.0 equiv), 1,3-diiodobenzene (109.83 mg, 0.33 mmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) dichloride (7.0 mg, 0.01 mmol, 0.03 equiv), carbon black (15.98 mg, 10 wt%), and copper(I) iodide (2.0 mg, 0.01 mmol, 0.03 equiv). The product was obtained as a sponge-like, yellow monolith.

Quantities of monomers and reagents for **7C**: 1,3,5-Triethynylbenzene (50 mg, 0.33 mmol, 1.0 equiv), 2,5-diiodothiopene (111.84 mg, 0.33 mmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) dichloride (7.0 mg, 0.01 mmol, 0.03 equiv), carbon black (16.18 mg, 10 wt%), and copper(I) iodide (2.0 mg, 0.01 mmol, 0.03 equiv). The product was obtained as a compressible, yellow monolith.

Quantities of monomers and reagents for **8C**: 1,3,5-Triethynylbenzene (50 mg, 0.33 mmol, 1.0 equiv), 1,4-diiodobenzene (109.83 mg, 0.33 mmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) dichloride (7.0 mg, 0.01 mmol, 0.03 equiv), carbon black (15.98 mg, 10 wt%), and copper(I) iodide (2.0 mg, 0.01 mmol, 0.03 equiv). The product was obtained as a compressible, yellow monolith.
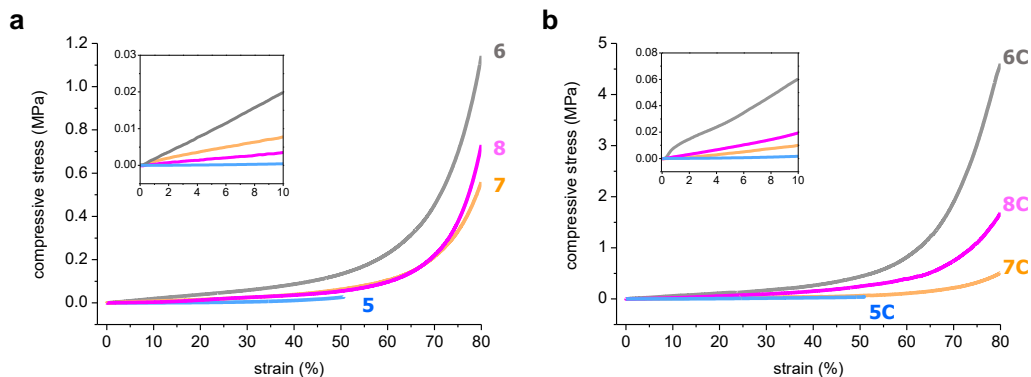
Mechanical Properties of Materials

Figure S1. Compressive stress–strain curves of polymer networks **5**–**8** (a) or carbon-containing composites **5C**–**8C** (b) respectively. Initial stress–strain curves of samples were used for the estimation of compressive Young's moduli as shown in the insets.

Table S1. Compressive Young's moduli obtained from polymer networks **5**–**8** and carbon-containing composites **5C**–**8C**.

Compound	**5**	**6**	**7**	**8**	**5C**	**6C**	**7C**	**8C**
Young's modulus (MPa)	0.006	0.21	0.07	0.03	0.02	0.64	0.22	0.12

Contact Angle Measurement

Table S2. Contact angles measured from polymer networks **5**–**8** and carbon-containing composites **5C**–**8C**.

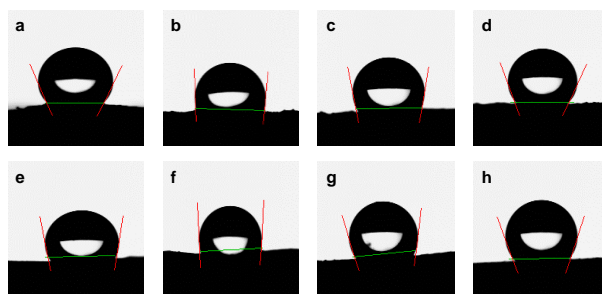| Compound	5	6	7	8	5C	6C	7C	8C
Trial 1	116.1	93.47	101.07	112.59	99.22	93.5	109.5	104.26
Trial 2	113.85	93.01	102.46	106.05	96.79	83.43	109.39	112.78
Trial 3	108.78	93.79	101.07	106.05	99.22	105.19	103.1	110.8
Avg.	112.91	93.42	101.53	108.23	98.41	94.04	107.33	109.28
Std.	3.75	0.39	0.8	3.78	1.4	10.89	3.66	4.46

Figure S2. Representative photographs of water droplets on polymer networks **5**–**8** (a–d) or carbon-containing composites **5C**–**8C** (e–h) respectively.
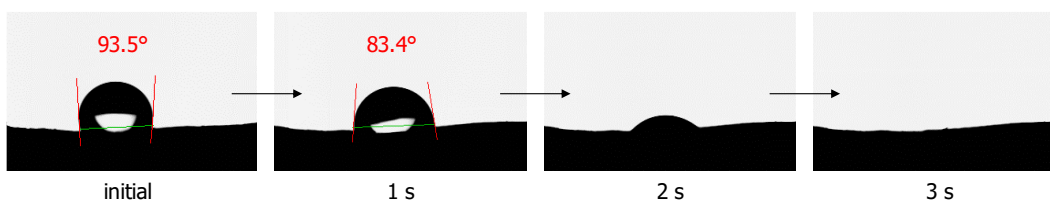

Figure S3. Photographs of a water droplet on **6C** over the course of time. The water droplet gradually absorbed to the composite as time elapsed.
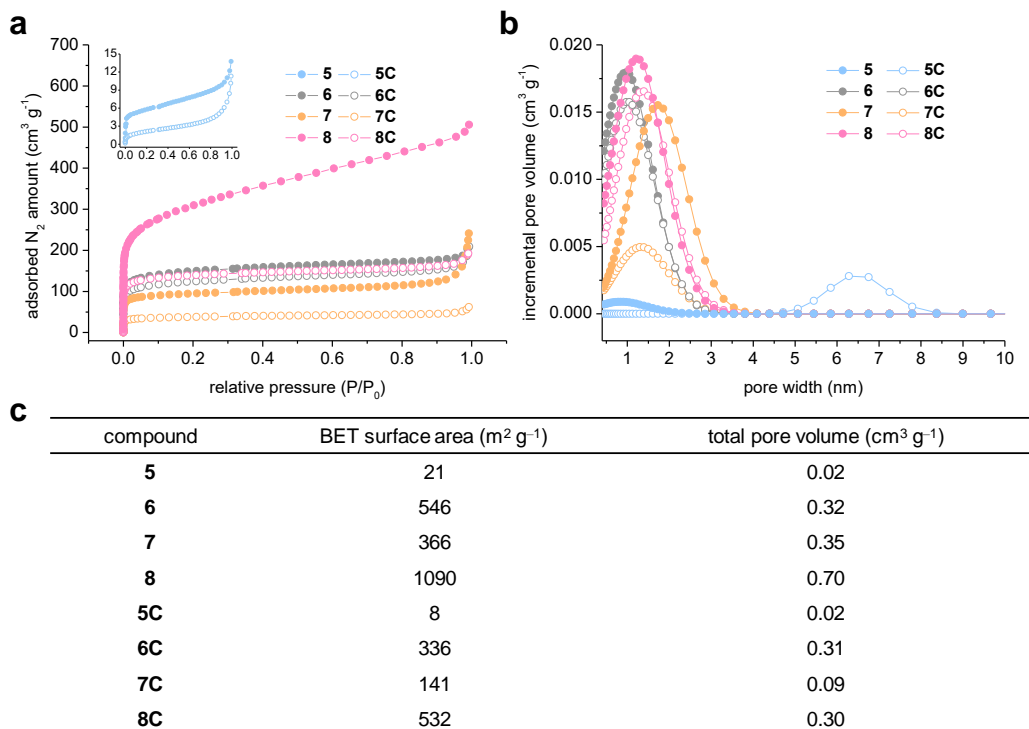
Measurement of Porosity of Materials

a

b

c

compound	BET surface area (m² g⁻¹)	total pore volume (cm³ g⁻¹)
5	21	0.02
6	546	0.32
7	366	0.35
8	1090	0.70
5C	8	0.02
6C	336	0.31
7C	141	0.09
8C	532	0.30

Figure S4. (a) Nitrogen adsorption isotherms of materials at 77 K. The adsorption curves of **5** and **5C** are shown in inset. (b) Pore size distributions calculated by nonlocal density function theory (NLDFT) with a slit model of polymer networks **5**–**8** and composites **5C**–**8C**. (c) Summary of gas sorption data.

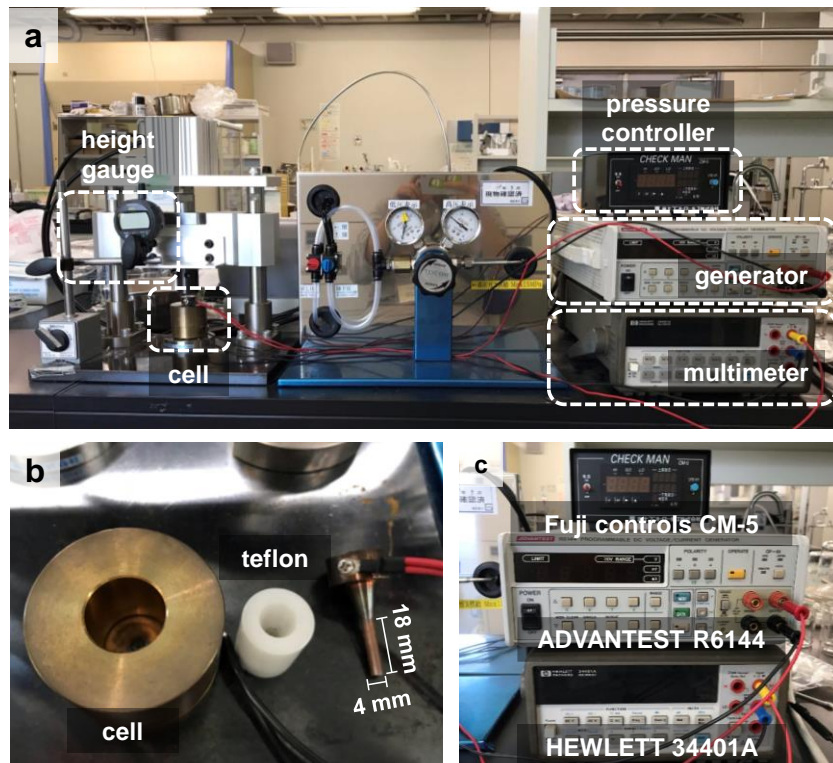# Change in the Resistivity of Materials

Figure S5. Photographs of the instrument set-up used for measuring change in resistivity with respect to density. (a) Overall appearance. Expanded views of (b) a hollow, cylindrical cell, and (c) electronics.
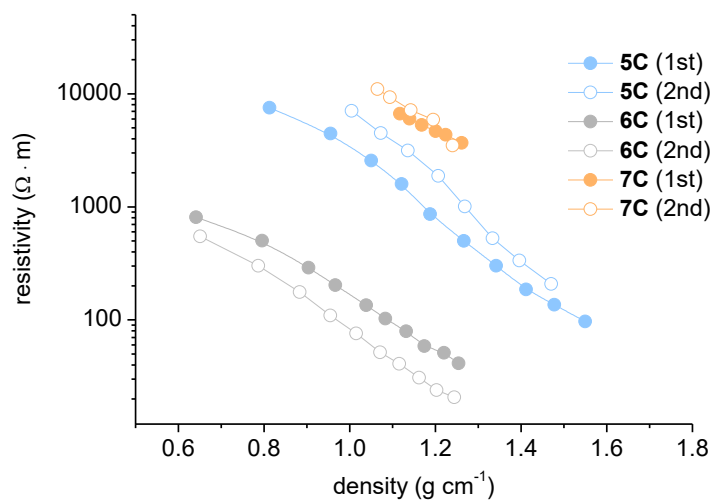

Figure S6. Change in resistivity of materials under repeating compressive force. Closed circles indicate the data obtained during the first compression; open circles, obtained during the second consecutive compression.

Theoretical Study for Binding Energy

For the calculation, we used the modelling tool, Hyperchem ver. 7.0 (Hypercube Inc.) for windows (2002) which is available from the website (http://www.hyper.com/), and optimized the model structures using open source package for Material eXplorer (Openmx) ver. 3.6. (OpenMX ver. 3.6, T. Ozaki group in the University of Tokyo (2000). Available from http://www.openmx-square.org/) within the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional.[S2,S3]

Table S3. Calculated binding energies and interlayer distance between model structures and single layer graphene.

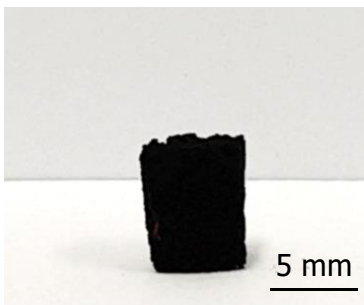| Model Structure	Interlayer Distance (Å)	Binding Energy; E_B (eV)
*m*DEB-graphene	3.699–3.572	–0.154
*p*DEB-graphene	3.638–3.558	–0.007
DET-graphene	3.859–3.468	0.521
TEP-graphene	3.694–3.468	0.750

Long-Term Stability Test

Figure S7. Photograph of **5C** after exposure to 1:1 EtOH–H_2O for 120 h at 70 °C.

References

S1.   Z. Chen, M. Chen, Y. Yu and L. Wu, *Chem. Commun.*, 2017, **53**, 1989.

S2.   J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.

S3.   J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
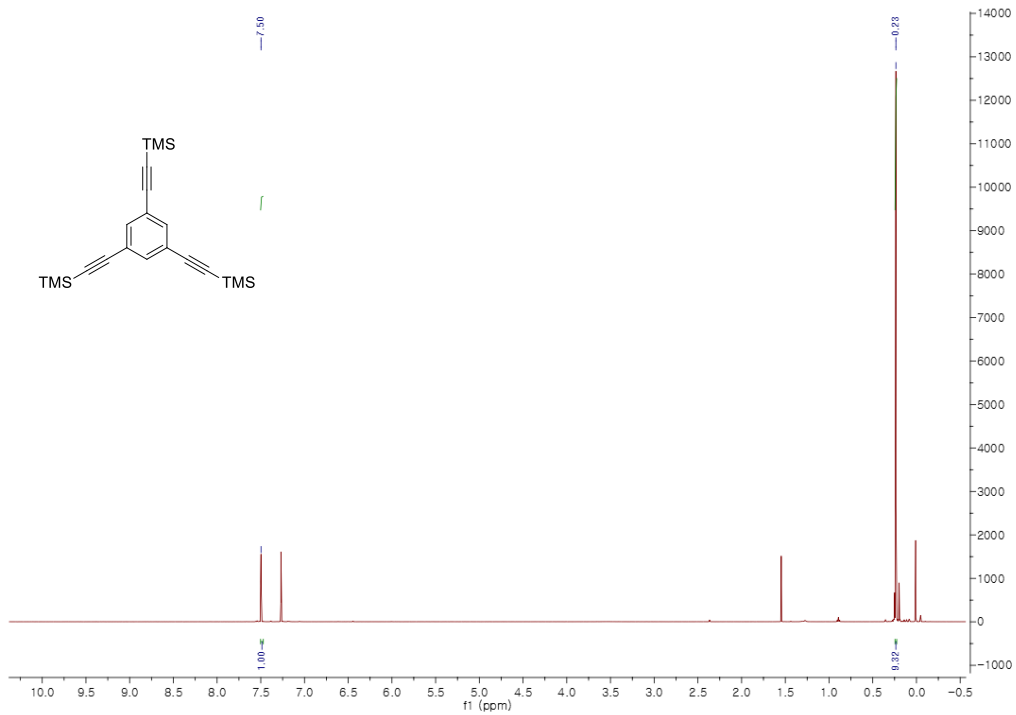
NMR Spectra

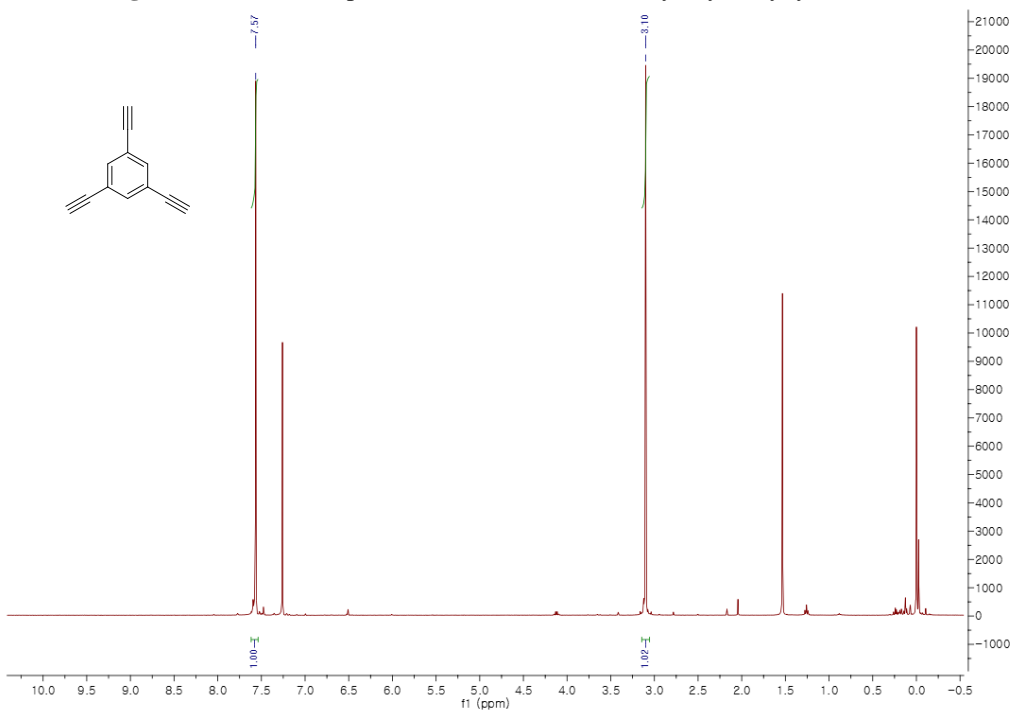**Figure S8.** ¹H NMR spectrum of 1,3,5-tris((trimethylsilyl)ethynyl)benzene.

Figure S9. ¹H NMR spectrum of TEB.