

Supporting Information for

Synthesis of Hydrogen-Substituted Graphdiyne via Dehalogenative Homocoupling Reaction

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Experimental Section:

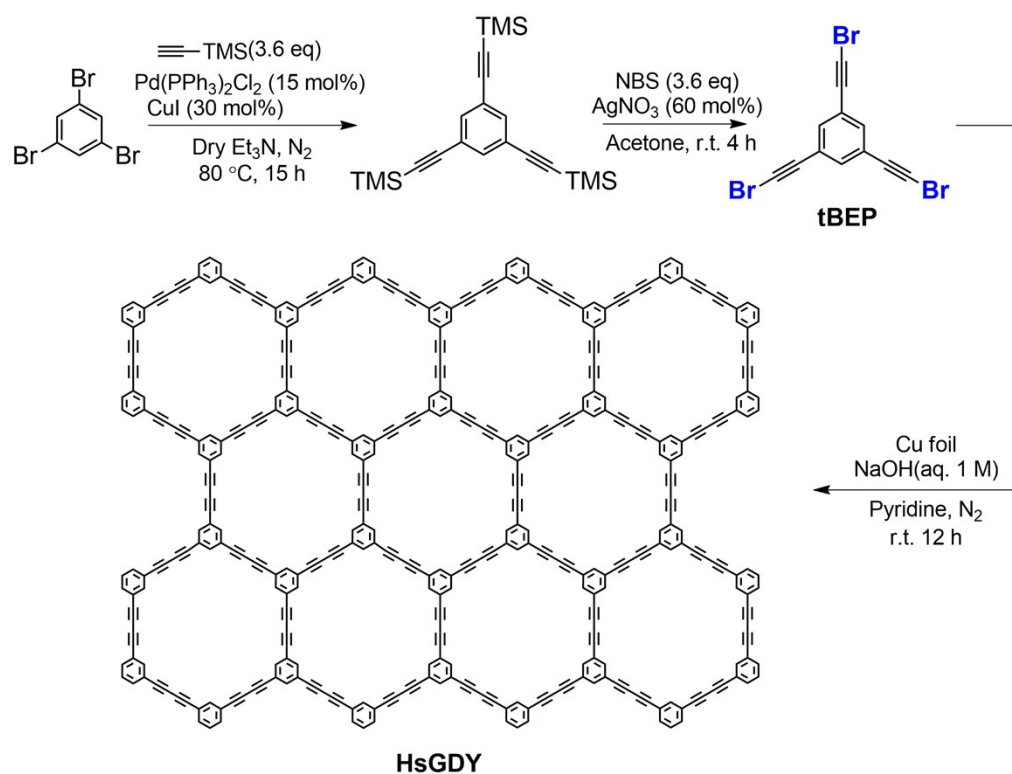
Materials and Methods

All commercially available chemicals were purchased from Adamas-beta, Aldrich and TCI, and used as received without further purification except triethylamine which was distilled over CaH_2 . Thin layer chromatography (TLC) was performed on glass plates coated with 0.20 mm thickness of silica gel. Column chromatography was performed using neutral silica gel PSQ100B.

The morphology details were examined with scanning electron microscopy (SEM, ZEISS Sigma 300/VP, acceleration voltage 3 kV). Fourier transform infrared spectroscopy (FT-IR, BRUKER EQUINOX55) and Raman spectroscopy (HORIBA HR800, 532 nm) was conducted to analysis the structure of the product. The X-Ray photoelectron spectrometer (XPS) was collected on Thermo Scientific ESCALAB 250Xi photoelectron spectrometer with Al $K\alpha$ radiation as the excitation sources. The XRD patterns were recorder on a Bruker ADVANCE D8 with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning speed of 6° min^{-1} . The solid-state ^{13}C NMR was examined with Varian 400M spectrometer. All electrochemical measurements were conducting with Bio-Logic potentiostat (VMP3) in a three-electrode setup at room temperature. For HER and OER, 1 M KOH aqueous solution was used as electrolyte saturated with H_2 and O_2 , respectively, platinum mesh (size: 15 mm \times 15 mm) and graphite rod (diameter: 6 mm) was used as counter electrodes, separately. An Hg/HgO electrode was used as the reference electrode. The as-prepared HsGDY film (with copper

foil) was directly used as the working electrode without any further treatment. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The chemical shifts are reported in δ ppm with reference to residual protons of CDCl_3 (7.26 ppm in ^1H NMR).

Synthesis of Monomer



Scheme S1. Synthetic routes of **tBEP** and **HsGDY**.

1,3,5-tris((trimethylsilyl)ethynyl)benzene: To a mixture of 1,3,5-tribromobenzene (0.63 g, 2 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.21 g, 0.30 mmol) and CuI (0.11 g, 0.60 mmol) in dry Et_3N (30 mL) was added trimethylsilylacetylene (1.0 mL, 7.2 mmol). The reaction mixture was

stirred at 80 °C for 15 h under N₂ and monitored by TLC. After solvent removal, the residue was purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.4) to afford **1** (0.4162 g, 1.14 mmol, 57% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (s, 3H), 0.22 (s, 27H).

1,3,5-tris(bromoethynyl)benzene (tBEP): To a solution of **1** (0.249 g, 0.68 mmol) in acetone (16 mL) was added NBS (0.436 g, 2.45 mmol) and AgNO₃ (0.069 g, 0.408 mmol, 60 mol %) at r.t.. After 4 h (monitored by TLC), the reaction mixture was diluted with hexane and filtered off the crystals formed. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.68) to afford **tBEP** (0.255 g, 0.66 mmol, 96% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.38, 123.69, 78.25, 52.21.

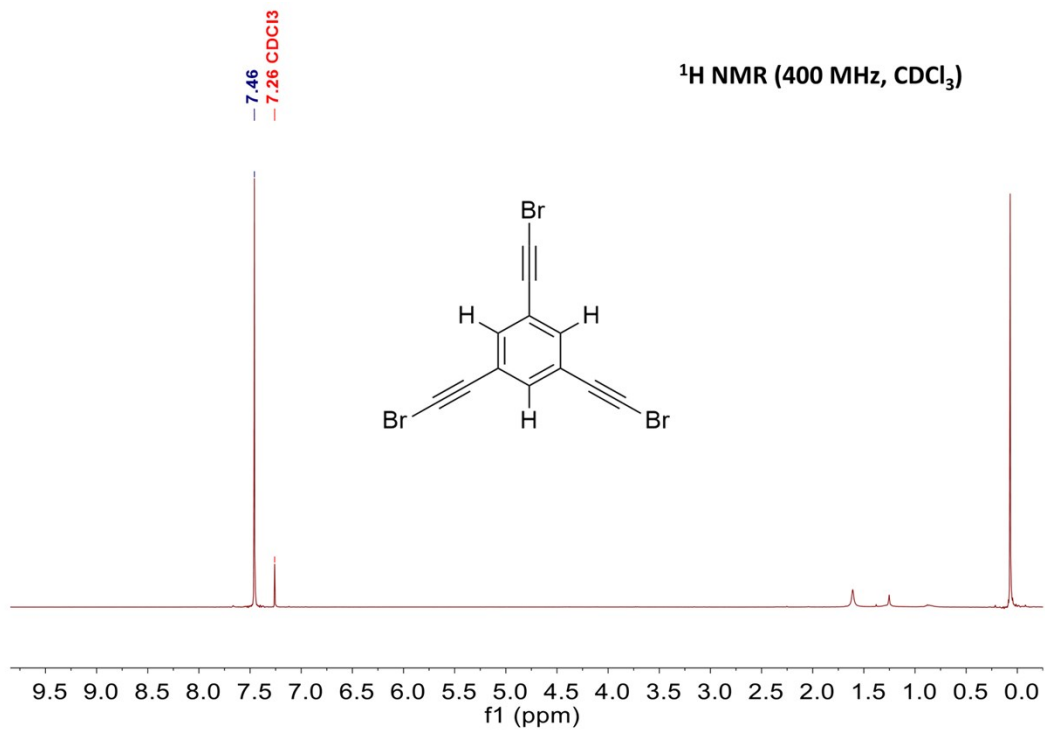


Fig. S1 ¹H NMR spectrum of **tBEP**.

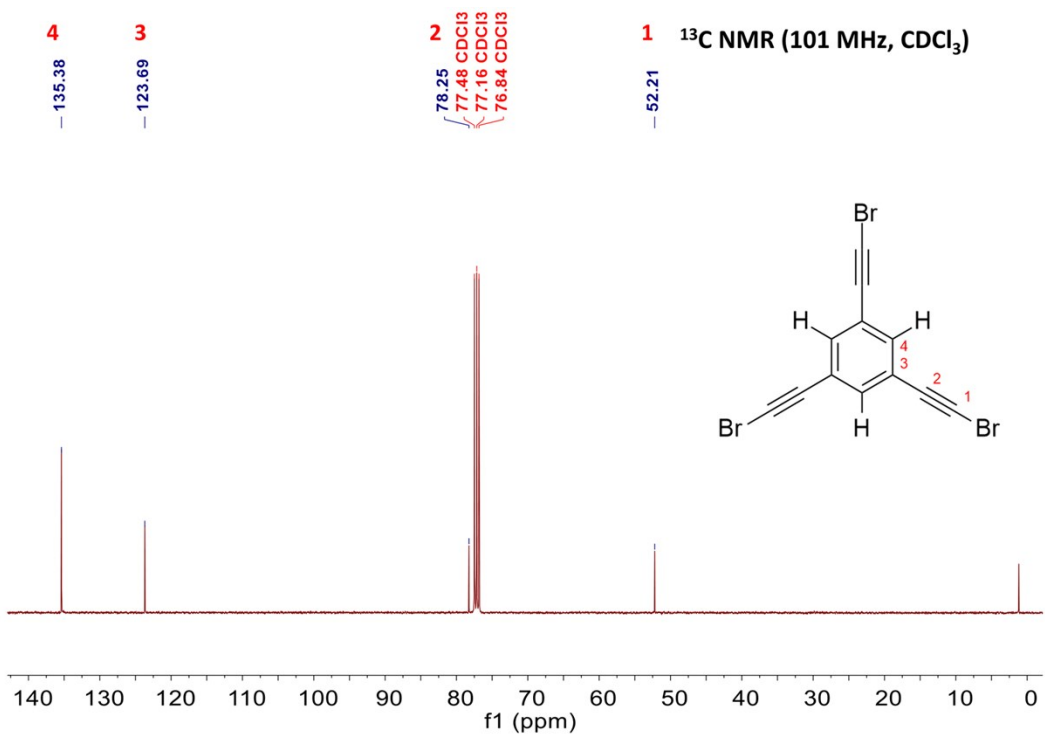
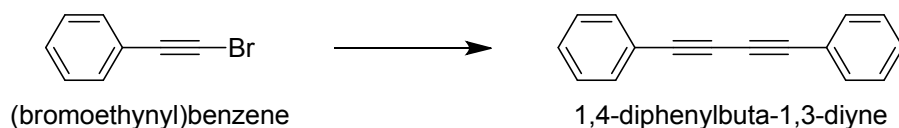


Fig. S2 ¹³C NMR spectrum of **tBEP**.

Synthesis of 1,4-diphenylbuta-1,3-diyne:



To a three-necked flask, pretreated copper foil and (bromoethynyl)benzene (28 mg) were added. Then the flask was sealed and filled with nitrogen. 20 mL pyridine was added into the flask and stirred for 2 minutes. After that, 6 ml NaOH aqueous solution (0.1 M) was added into the system and the mixture was stirred under nitrogen at r.t. for 24-48 h. The mixture was filtered, and the residue was washed by 0.1 M HCl and extracted with ethyl acetate. The organic phases dried with NaSO_4 and was concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate=99:1, $R_f = 0.7$) to afford 1,4-diphenylbuta-1,3-diyne (14.5 mg, 93% yield) as a white solid. ^1H NMR (400 MHz, DMSO): $\delta=7.64-7.59(\text{m}, 4\text{H}), 7.51-7.43(\text{m}, 6\text{H})$. ^{13}C NMR (101MHz, DMSO): $\delta=132.39, 129.98, 128.90, 120.41, 81.81, 73.50$.

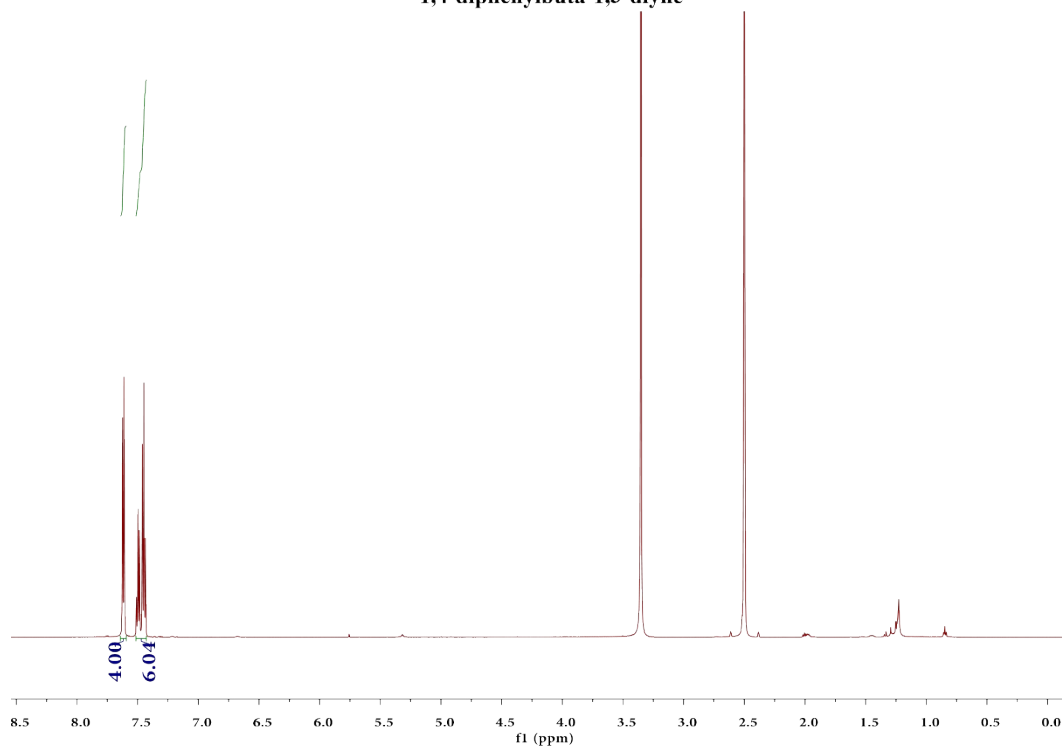
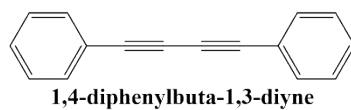


Fig. S3 ¹H NMR spectrum of 1,4-diphenylbuta-1,3-diyne

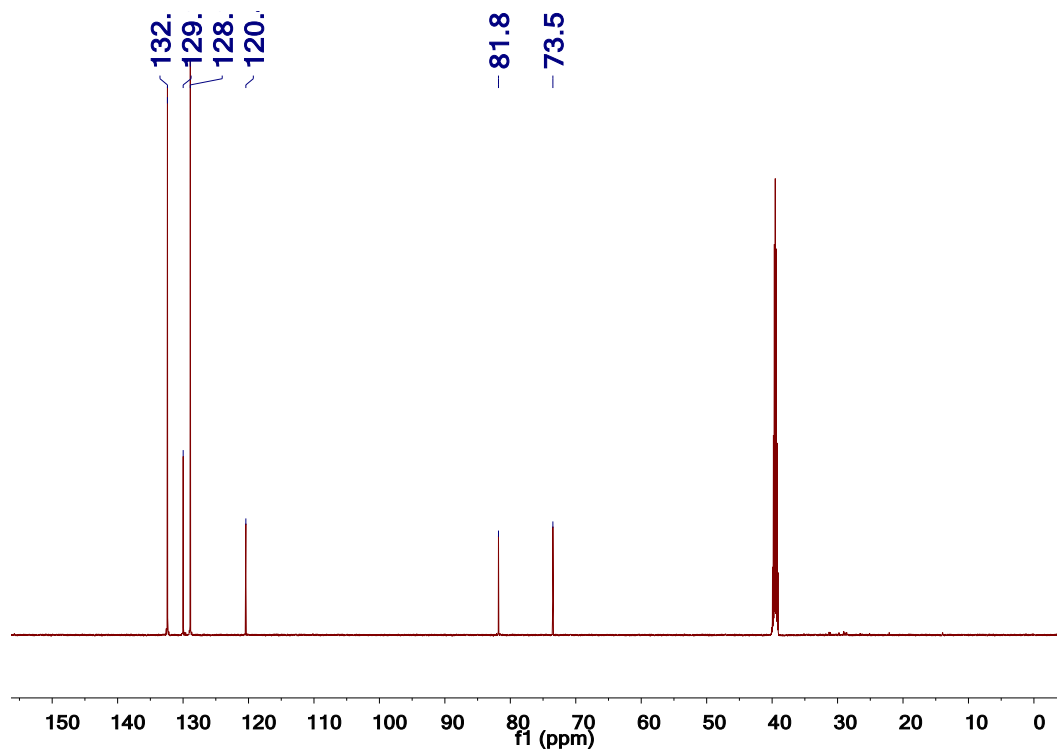
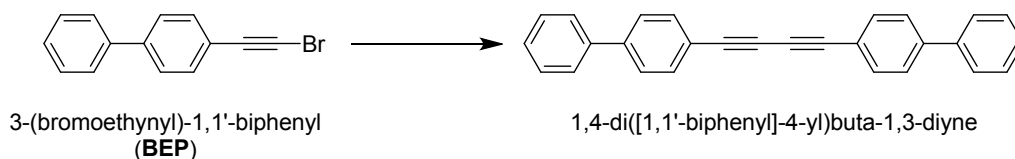


Fig. S4 ^{13}C NMR spectrum of 1,4-diphenylbuta-1,3-diyne

Synthesis of 1,4-di([1,1'-biphenyl]-4-yl)buta-1,3-diyne:



To a three-necked flask, pretreated copper foil and 3-(bromoethynyl)-1,1'-biphenyl (**BEP**) (40 mg) were added. Then the flask was sealed and filled with nitrogen. 20 mL pyridine was added into the flask and stirred for 2 minutes. After that, 6 ml NaOH aqueous solution (0.1 M) was added into the system and the mixture was stirred under nitrogen at r.t. for 24 h. The mixture was filtered, and the residue was washed by 0.1 M HCl and extracted with ethyl acetate. The organic phases dried with NaSO_4 and was concentrated under reduced

pressure and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate=9:1, $R_f = 0.68$) to afford 1,4-di([1,1'-biphenyl]-4-yl)buta-1,3-diyne (25.1 mg, 91% yield) as a white solid. ^1H NMR (400 MHz, DMSO): $\delta=7.82-7.70$ (m, 12H), 7.53-7.49 (t, 4H), 7.44-7.40 (t, 2H).

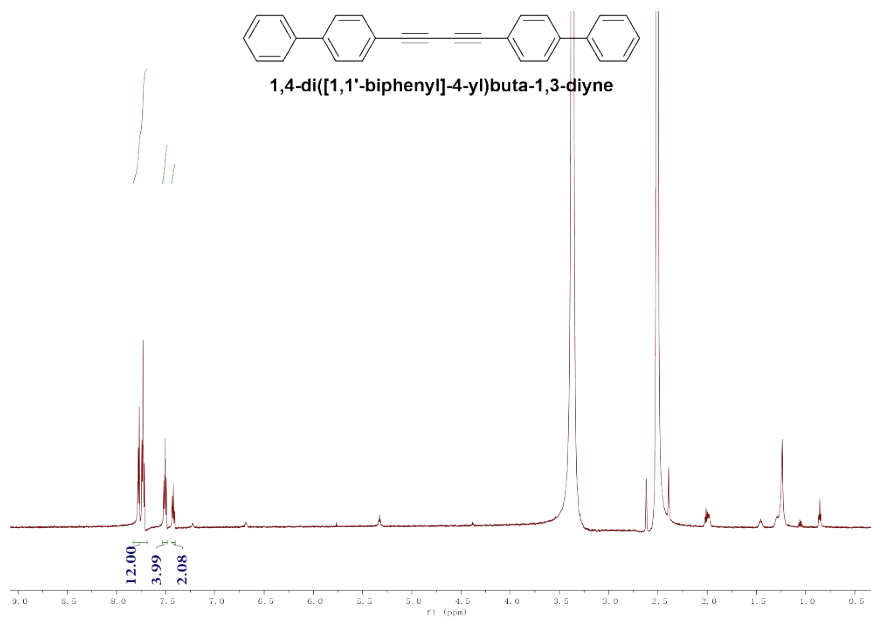


Fig. S5 ^1H NMR spectrum of 1,4-di([1,1'-biphenyl]-4-yl)buta-1,3-diyne

Characterization

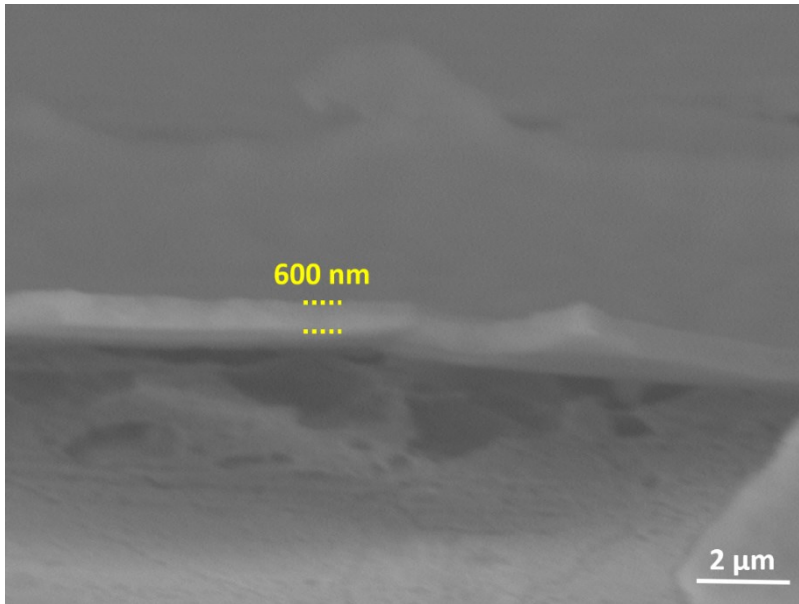


Fig. S6 The cross-section SEM image of HsGDY on copper foil (mode: BSE).

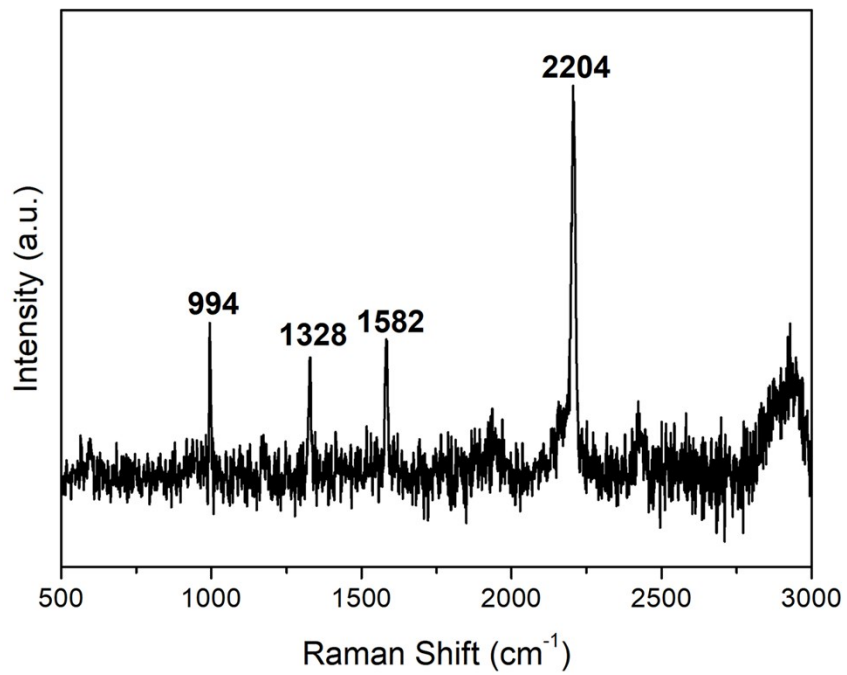


Fig. S7 Raman spectrum of **tBEP** monomer.

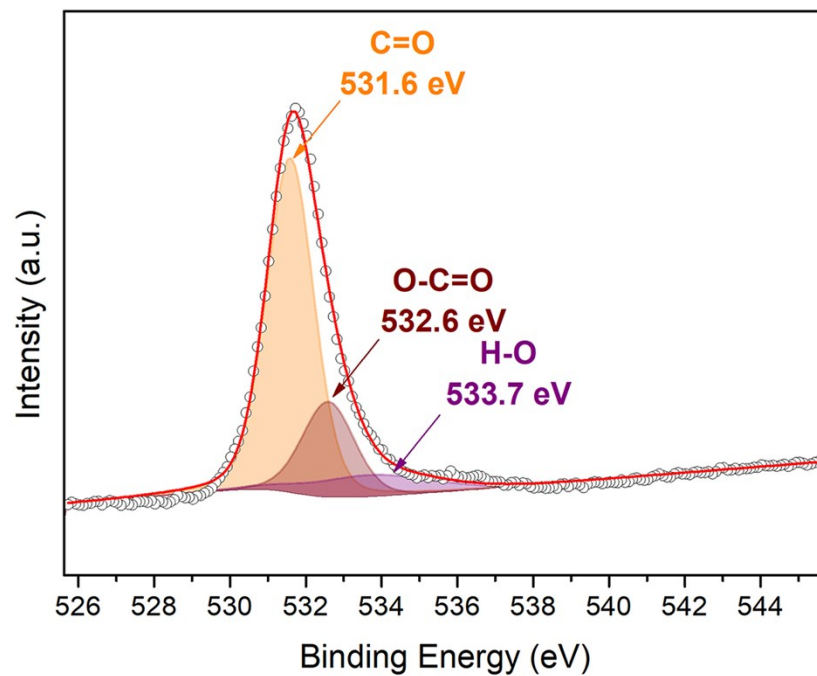


Fig. S8 XPS data of O1s spectrum of HsGDY.

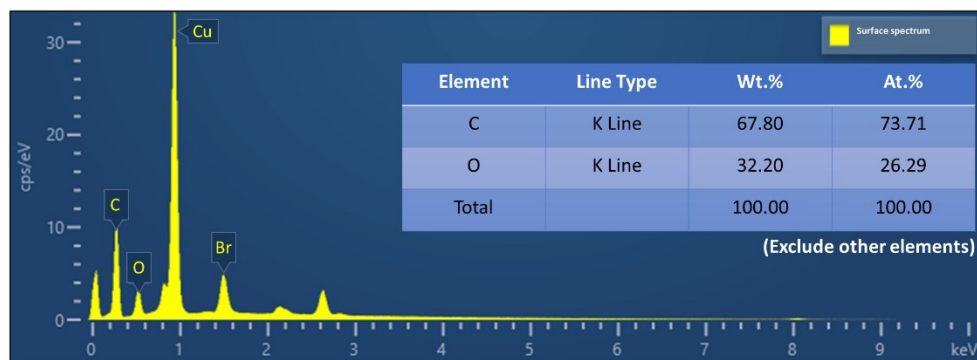


Fig. S9 EDS analysis for HsGDY film on Cu foil.

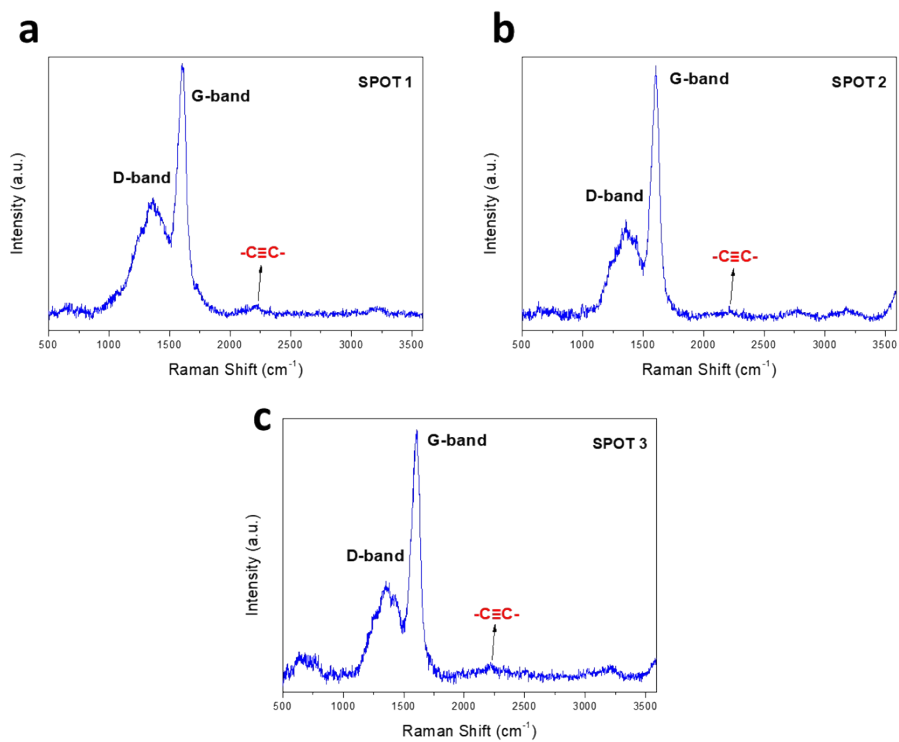


Fig. S10 The corresponding Raman spectra of the three spots in Fig. 3c