

## Supporting information

# **Pyridyl-Containing Graphdiyne Stabilizes Sub-2-nm Ultrasmall Copper Nanoclusters for the Electrochemical Reduction of CO<sub>2</sub>**

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## Experimental details

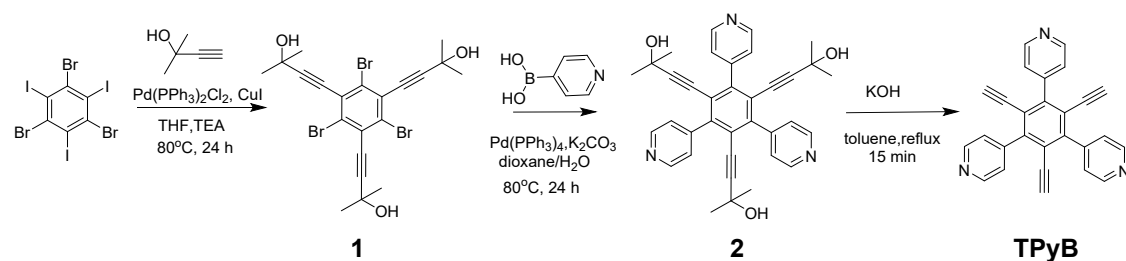
### Materials

All the chemical reagents were purchased commercially and used without further purification unless otherwise stated. Tetrahydrofuran (THF) and dioxane were pretreated under reflux with sodium to remove the small amount of water. Toluene and triethylamine (TEA) were super dry solvents stored with 3Å molecular sieve. All reactions are performed under an argon atmosphere.

### Characterization

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE NEO 400 instrument at room temperature. High-resolution mass spectra (HRMS) were performed on an Orbitrap Fusion Mass spectrometer. Infrared Spectra of solid samples were recorded on a Bruker Vertex 80. Raman spectra were collected at room temperature on a HORIBA LabRAM HR Evolution system with a He/Ne laser as an excitation source with a wavelength of 532 nm. Transmission electron microscopy (TEM) images and elemental analysis were performed by the FEI Talos F200X G2 transmission electron microscope operated at 200 kV. X-ray diffraction (XRD) patterns were obtained using a Rigaku SmartLab workstation with a Cu K $\alpha$  ( $\lambda = 0.15418$  nm) emitting source. The X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 5000 VersaProbe III with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV). The surface wettability was performed on a Kruss DSA 30 contact angle analyser equipped with commercial video-based software at room temperature. Inductively coupled plasma atomic emission spectroscopy tests were measured on the Agilent ICPMS 7850.

### Synthesis



Scheme S1 Synthesis route of 1,3,5-triethynyl-2,4,6-tris(4-pyridyl)benzene.

#### ■ Synthesis of compound 1

Compound **1** was synthesized by the reported methods.<sup>1</sup> 1,3,5-tribromo-2,4,6-triiodobenzene<sup>2</sup> (2000 mg, 2.88 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (303 mg, 0.43 mmol),  $\text{CuI}$  (27 mg, 0.14 mmol), 2-methylbut-3-yn-2-ol (872 mg, 10.37 mmol) were added in a 200 mL Schlenk tube under a nitrogen atmosphere, followed by the addition of 60 mL THF and 20 mL TEA. The mixture was stirred for 24 h under reflux conditions. After the reaction, the solvent was removed by evaporation under reduced pressure. Then the mixture was washed with water and extracted with dichloromethane (DCM). The organic layer was collected and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the solvent was evaporated, the product was further purified by column chromatography on silica gel using DCM: methanol (100:1, v:v) as the eluant to give the target product as a white

powder (840 mg, 52% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 5.64 (s, OH), 1.51 (s,  $\text{CH}_3$ ) ;  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  128.08, 126.78, 106.49, 79.09, 64.01, 40.15, 39.94, 39.73, 39.52, 39.10, 38.89, 31.14.

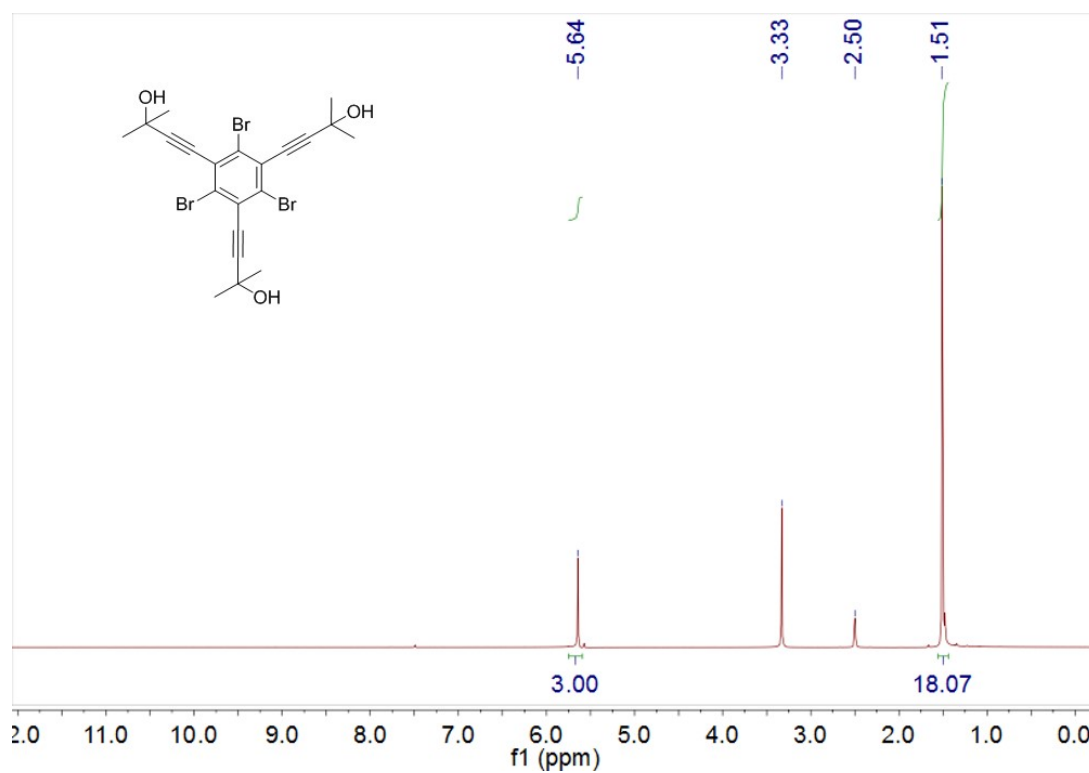


Figure S1.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **1**.

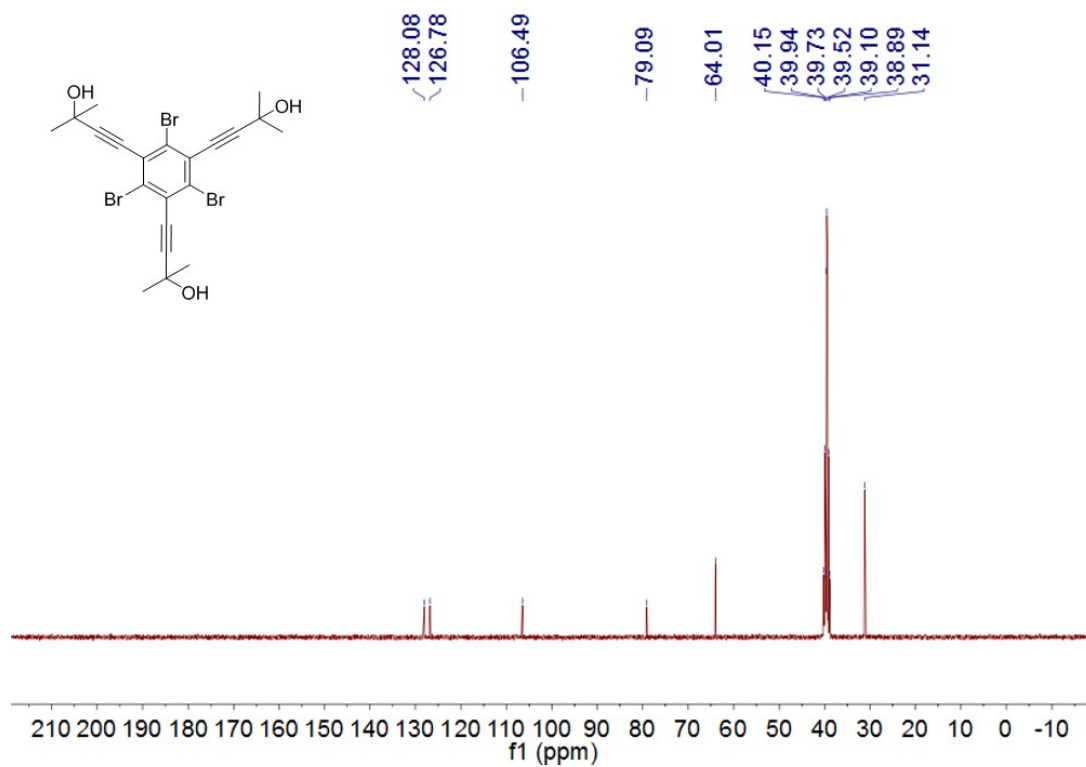


Figure S2.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound 1.

### ■ Synthesis of compound 2

In a 200 mL Schlenk tube, compound 1 (700 mg, 1.25 mmol), 4-Pyridinylboronic acid (920 mg, 7.48 mmol),  $\text{K}_2\text{CO}_3$  (1035 mg, 7.49 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (217 mg, 0.19 mmol) were added to the solution of dioxane (50 mL) and water (5 mL). The mixture was bubbled with  $\text{N}_2$  for 30 min, then heated for 24 h at 100 °C. Afterward, the system was cooled to room temperature. DCM was added to the mixture. After being washed with water three times, the organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (pre-neutralized with TEA) using DCM: methanol (15:1,v:v) as the eluent. The product was white powder (535 mg, 76% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.66 (d, 6H,CH), 7.47 (d, 6H,CH), 5.05 (s, 3H,CH), 0.96 (s, 18H, $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  149.03, 146.00, 143.50, 124.77, 121.41, 105.05, 77.19, 63.30, 30.36. HRMS:  $m/z$  calcd for  $\text{C}_{36}\text{H}_{34}\text{N}_3\text{O}_3$   $[\text{M}+\text{H}]^+$ : 556.2600. Found: 556.2594.

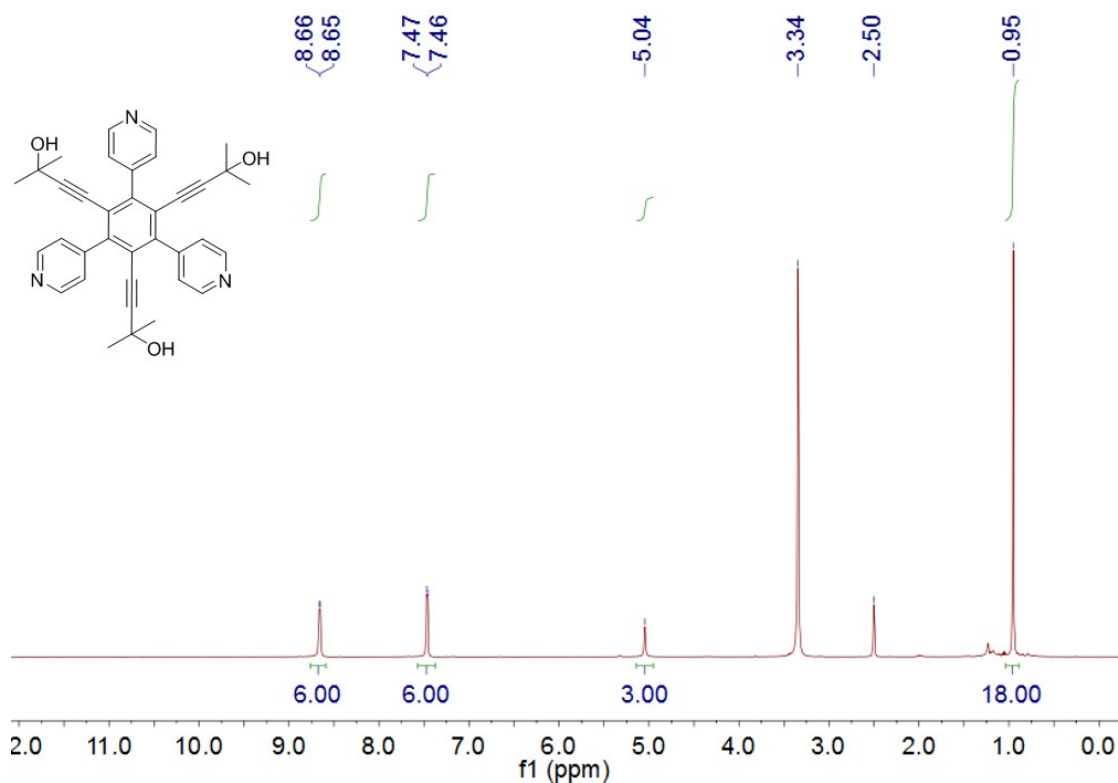


Figure S3.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound 2.

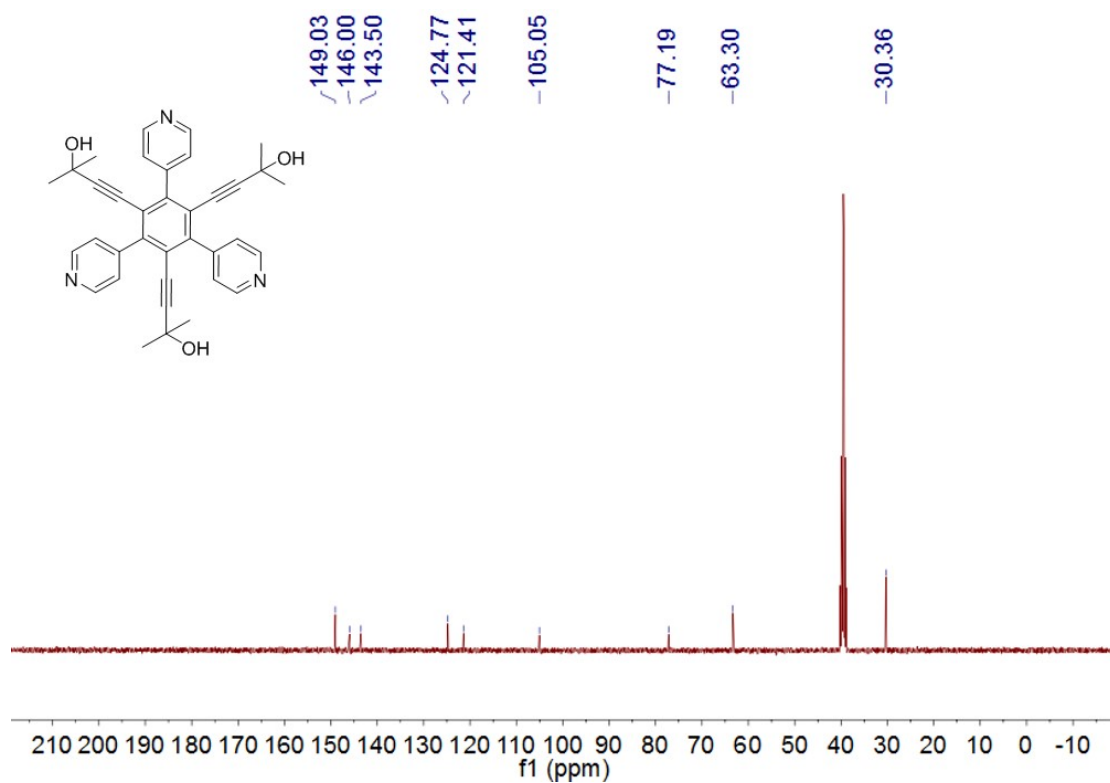


Figure S4. <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) spectrum of compound 2.

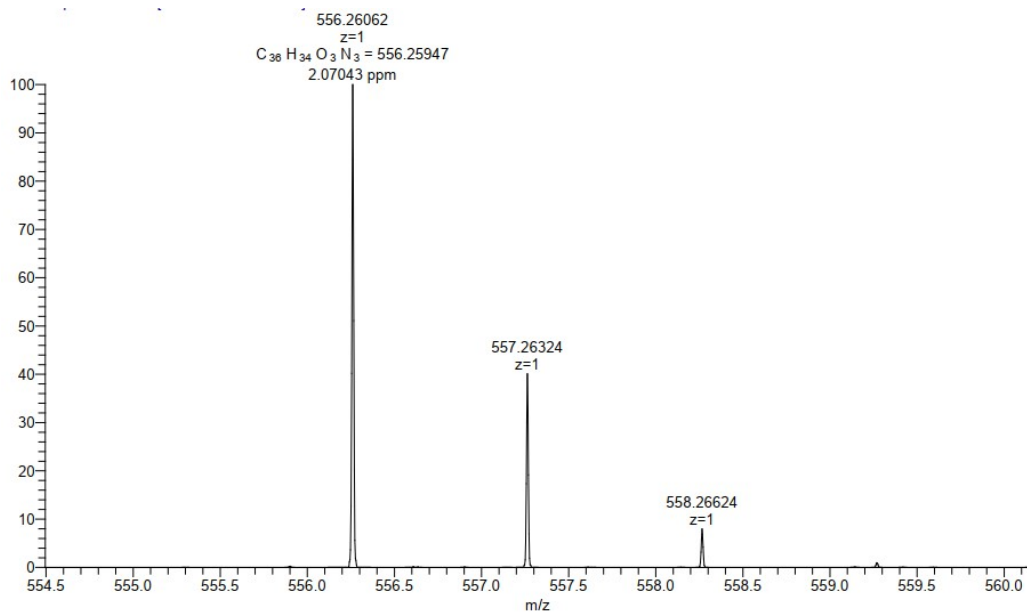


Figure S5. Mass spectrum of compound 2.

### ■ Synthesis of 1,3,5-triethynyl-2,4,6-tris(4-pyridyl)benzene (TPyB)

Under a nitrogen atmosphere, ground KOH (212 mg, 3.8 mmol) and Compound **2** (420 mg, 0.76 mmol) were added to a solution of toluene (10 mL). The mixture was heated at 120 °C for 30 min. After that, water (10 ml) was added to the reaction mixture. Due to the low solubility of the product in water and toluene, the product was filtrated first. And the organic layer was also separated and evaporated. The crude product was combined and purified by column chromatography on silica gel (pre-neutralized with TEA) using DCM: methanol (100:1,v:v) as the eluent. The pure product was white powder (175 mg, 60% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ (ppm): 3.56 (s, 3H, CH), 7.29-7.30(m, 6H, CH), 8.37-8.38 (m, 6H, CH); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ (ppm): 78.27 (3CH), 88.57 (3Quant.C), 121.14 (3Quant.C), 124.72 (6CH), 145.23 (3Quant.C), 147.32 (3Quant.C), 148.27 (6CH). HRMS: m/z calcd for C<sub>36</sub>H<sub>34</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 382.1338. Found: 382.1333

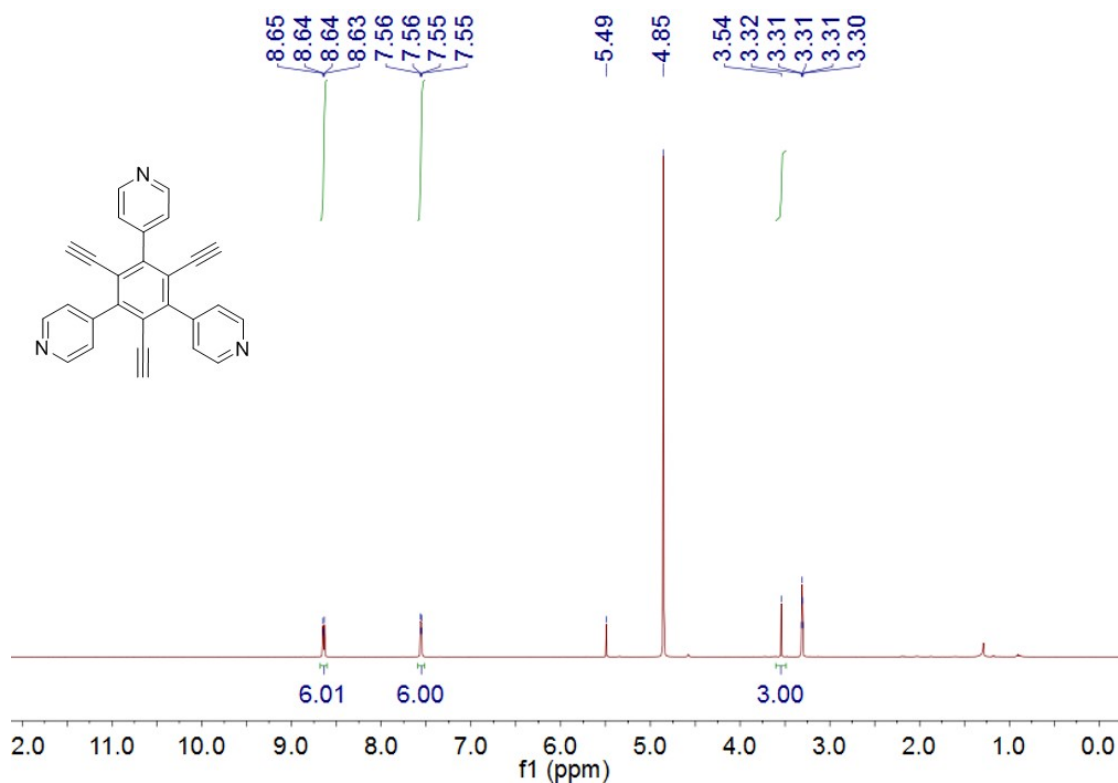


Figure S6. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) spectrum of TPyB.

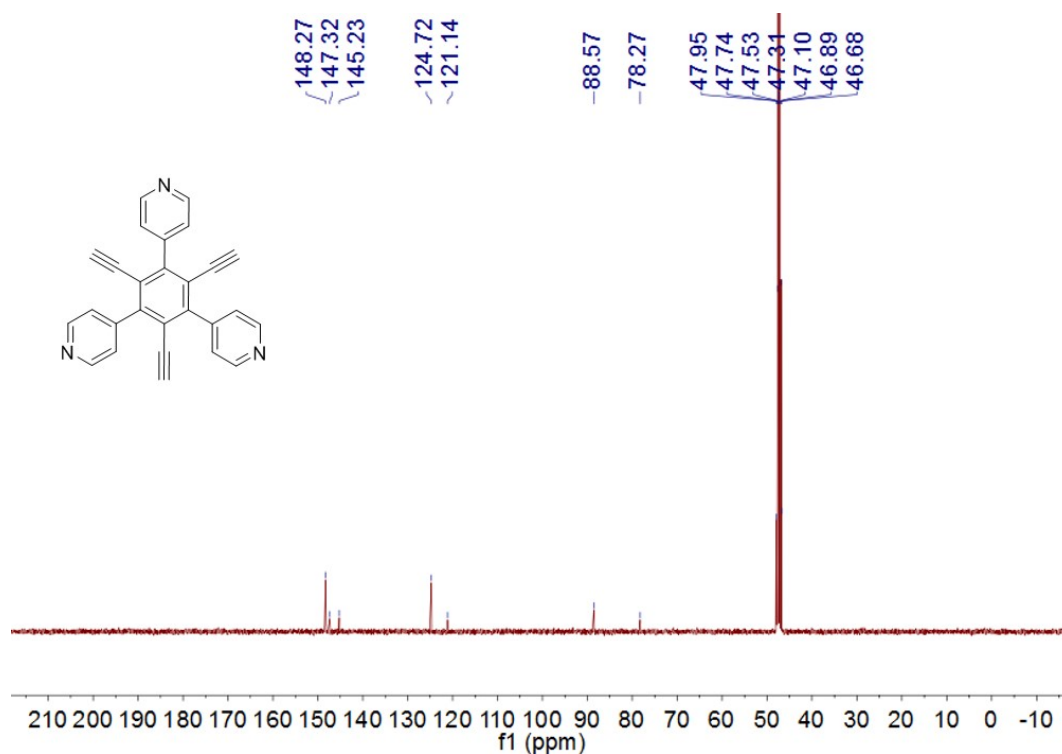


Figure S7.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of **TPyB**.

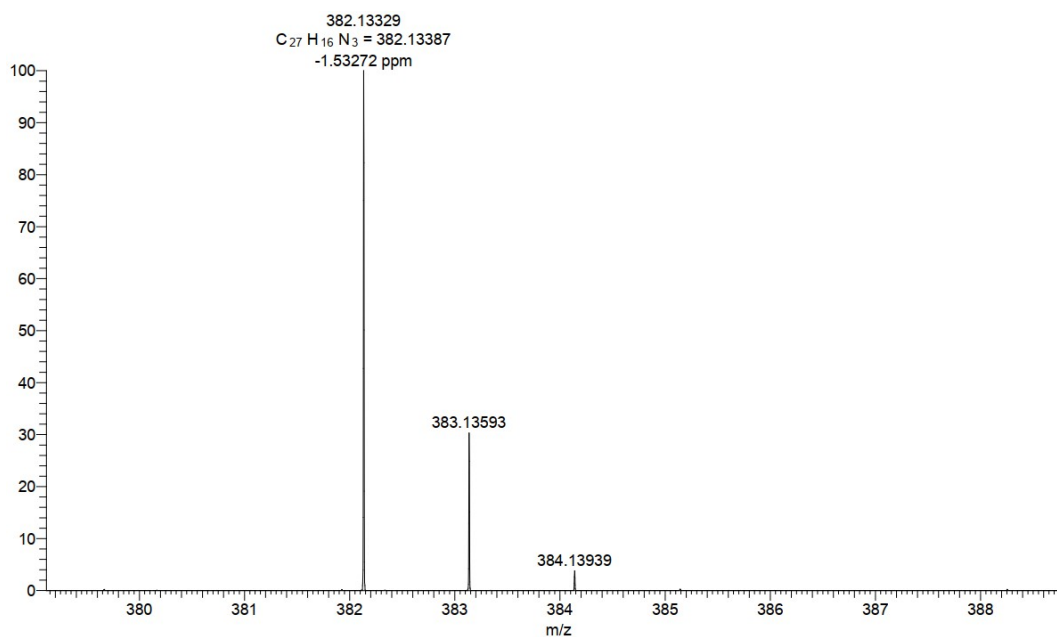


Figure S8. Mass spectrum of **TPyB**.

#### ■ Synthesis of 1,3,5-triethynyl-2,4,6-triphenyl-benzene (TPB)

This compound was synthesized according to the reported method.<sup>3</sup> The procedures were similar to the synthesis of **TPyB**, except that phenylboronic acid was used instead of 4-pyridinylboronic acid in the second step.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.52 (m, 6H), 7.36-7.46 (m, 9H), 2.79 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.76, 139.17, 129.85, 128.01, 127.79, 121.57, 85.57, 80.75.

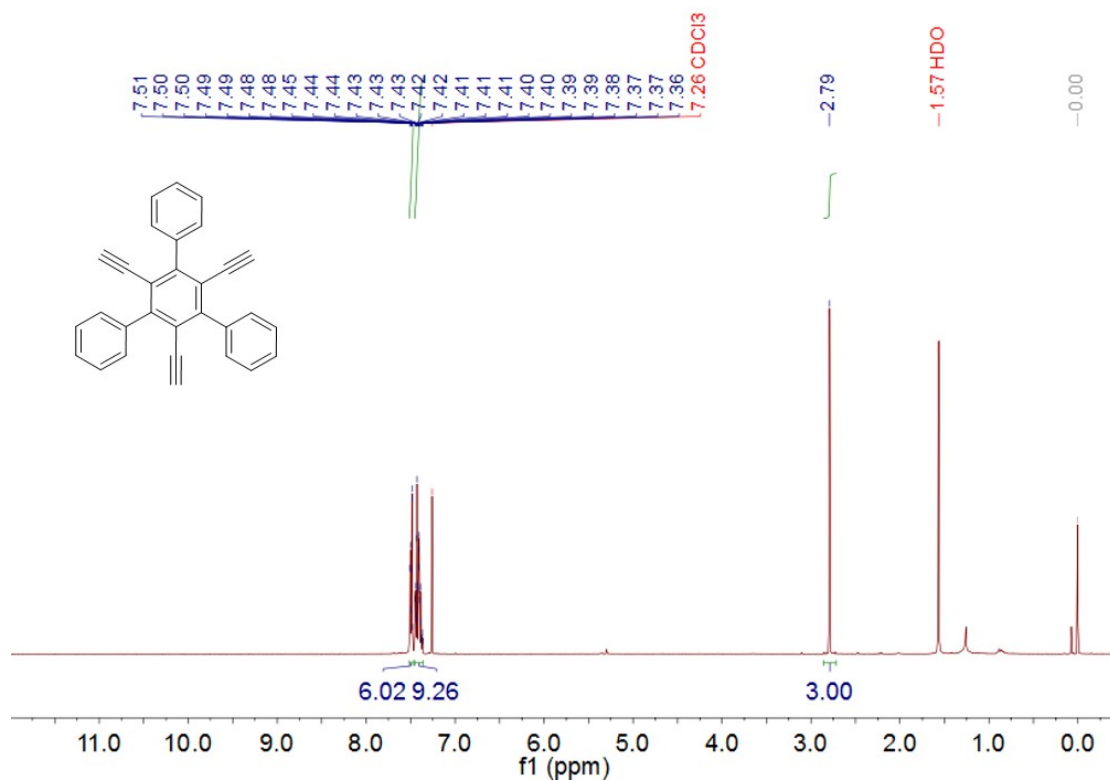


Figure S9. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectrum of TPB.

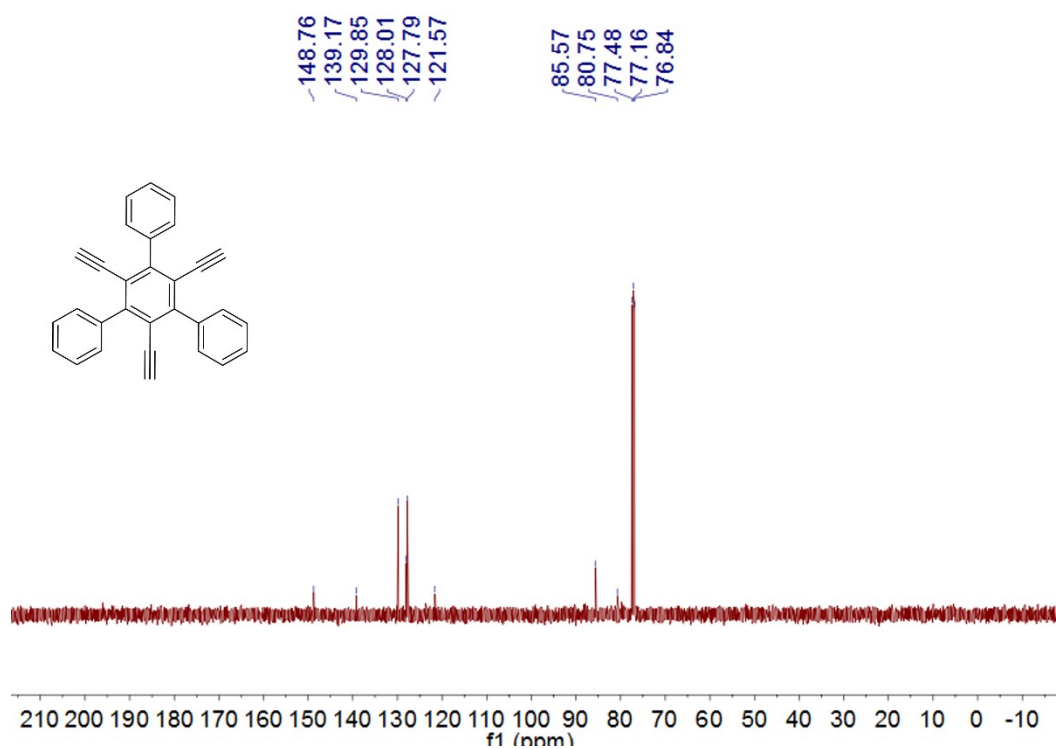


Figure S10. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of TPB.



### ■ Synthesis of Py-GDY, Py-Ph-GDY, Ph-GDY

**Py-GDY:** Di- $\mu$ -hydroxy-bis(N,N,N',N'-tetramethylethylenediamine) copper(II) chloride ( $[\text{Cu}(\text{OH})\text{TMEDA}]_2\text{Cl}_2$ ) (580 mg, 1.25 mmol) and **TPyB** (80 mg, 0.21 mmol) were dissolved in 20 mL pyridine. The mixture was stirred under an argon atmosphere at 100°C for 3 days. After cooling to room temperature, the mixture was centrifuged. The precipitate was washed with ethanol, 3 M HCl, 3M NaOH, and water, then dried in a vacuum to give a brown powder (70 mg, 87%).

**Py-Ph-GDY:** **TPyB** (25 mg, 0.066 mmol), **TPB** (25 mg, 0.066 mmol), and  $[\text{Cu}(\text{OH})\text{TMEDA}]_2\text{Cl}_2$  (350 mg, 0.75 mmol) were dissolved in 20 mL pyridine. The mixture was stirred under an argon atmosphere at 100°C for 3 days. After cooling to room temperature, the mixture was centrifuged. The precipitate was washed with ethanol, 3 M HCl, 3M NaOH, and water, then dried in a vacuum to give a brown powder.

**Ph-GDY:** **TPB** (25 mg, 0.066 mmol) and  $[\text{Cu}(\text{OH})\text{TMEDA}]_2\text{Cl}_2$  (350 mg, 0.75 mmol) were dissolved in 20 mL pyridine. The mixture was stirred under an argon atmosphere at 100°C for 3 days. After cooling to room temperature, the mixture was centrifuged. The precipitate was washed with ethanol, 3 M HCl, 3M NaOH, and water, then dried in a vacuum to give a brown powder.

### ■ Synthesis of Py-GDY-Cu, Py-Ph-GDY-Cu, Ph-GDY-Cu

**Py-GDY-Cu:** **Py-GDY** (10 mg) was dispersed in a mixture of 3 ml ethanol and 3 ml water. The mixture was sonicated for 1 h, followed by the addition of 100  $\mu\text{L}$  0.1 M  $\text{CuCl}_2$  solution. After sonicated for another half hour, the mixture was bubbled with  $\text{N}_2$  for 15 min, and ascorbic acid (50 mg, 0.28 mmol) was added. Under the  $\text{N}_2$  atmosphere, the mixture was heated at 85°C for 12 h. After cooling to room temperature, the mixture was centrifuged, and the precipitate was washed with ethanol and water each for three times. The product was dried in a vacuum to give a brown powder.

**Py-Ph-GDY-Cu** and **Ph-GDY-Cu** were prepared following the same procedure.

### Electrochemical test

The  $\text{CO}_2$  electroreduction measurements were performed on a CHI760E electrochemical workstation using a flow cell (Gaossunion). The Ag/AgCl electrode and  $\text{IrO}_2$ -coating titanium sheet were used as the reference electrode and counter electrode. To prepare the working electrode, 5 mg of the catalyst was dispersed by sonication in 300  $\mu\text{L}$  of water, 150  $\mu\text{L}$  of ethanol, and 50  $\mu\text{L}$  of 5 wt % of Nafion for 30 min. The ink was dropped onto the gas diffusion layer (GDL, YLS-30T) with a coating area (0.5\*2  $\text{cm}^2$ ). The loading amount was about 0.5  $\text{mg cm}^{-2}$ . During the electrochemical test, the flow rate of  $\text{CO}_2$  was set to 20 sccm using a mass flow controller (Alicat). 1M KOH was used as the catholyte and the anolyte. The cathode chamber and anode chamber were separated by an anion-exchange membrane (Fumasep FAB-PK-130). The applied potential was converted to the reversible hydrogen electrode (RHE) scale without iR compensation:  $E$  (vs. RHE) =  $E$  (vs. Ag/AgCl) + 0.0592\*pH + 0.197 V. The electrodes were pre-scanned from -0.5 V to -1.5V versus the Ag/AgCl electrode at 200 mV/s for 60 cycles to reach a steady state. During the electroreduction of  $\text{CO}_2$ , the gaseous products were quantified by a gas

chromatography instrument (Fuli GC9790P) equipped with a thermal conductivity detector and a flame ionization detector. The Faradaic efficiency (FE) of the gaseous products was calculated by the following equation:

$$FE(\%) = \frac{n \times V \times F \times x}{j} \times 100\%$$

Where n is the number of transferred electrons to generate the product, F is Faraday's constant, x is the volume fraction of the gaseous product, V is the total molar flow rate of gas and j is the recorded current. The FE of the gaseous product was the average value of three measurements.

Liquid products were analyzed by <sup>1</sup>H-NMR spectroscopy. 400 μL of the catholyte was mixed with 50 μL of D<sub>2</sub>O and 50 μL of H<sub>2</sub>O containing 80 ppm of DMSO as the internal standard. The FE of liquid products was calculated by the following equation:

$$FE(\%) = \frac{n \times F}{Q} \times 100\%$$

### **Contact angle measurement**

The powder was compressed into a tablet, and then the water contact angle is measured using the sessile drop method at room temperature.

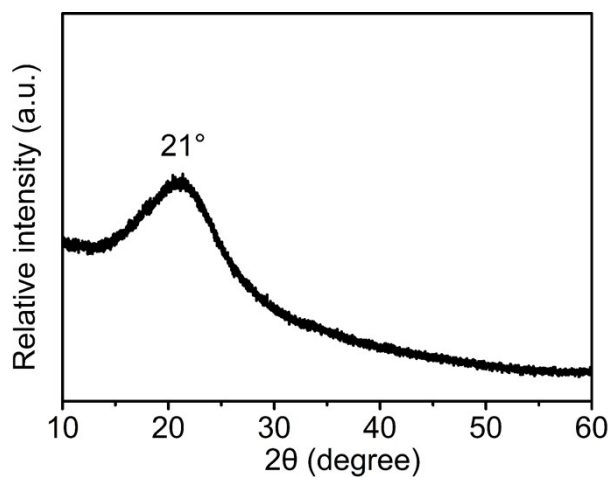


Figure S11. XRD pattern of **Py-GDY**.

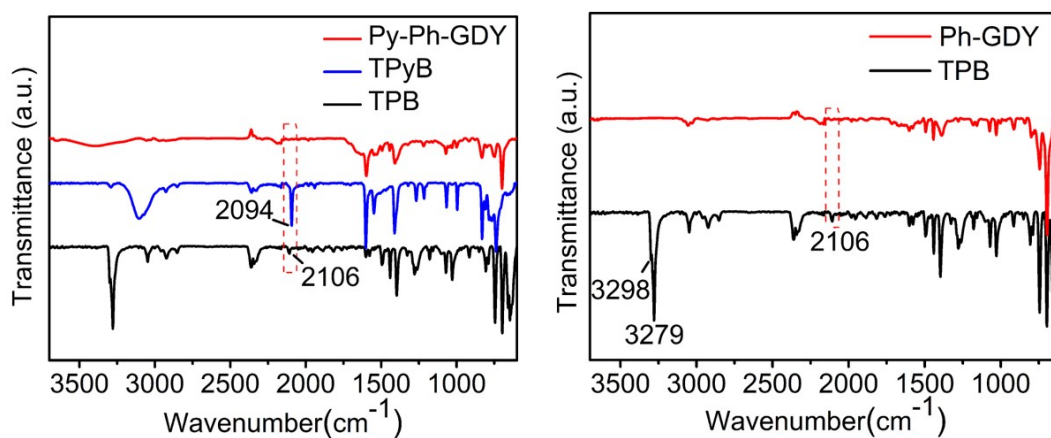


Figure S12. FTIR spectra of **Py-Ph-GDY** (left) and **Ph-GDY** (right).

In Figure S12, the two IR bands at 2106 and 2094 cm<sup>-1</sup> are assigned to the C≡C stretching vibration in **TPB** and **TPyB**, respectively. After the Glaser coupling reaction, **Py-Ph-GDY** and **Ph-GDY** exhibit no peaks in the regions, indicating the conversion of terminal acetylenic groups during the Glaser coupling reaction.

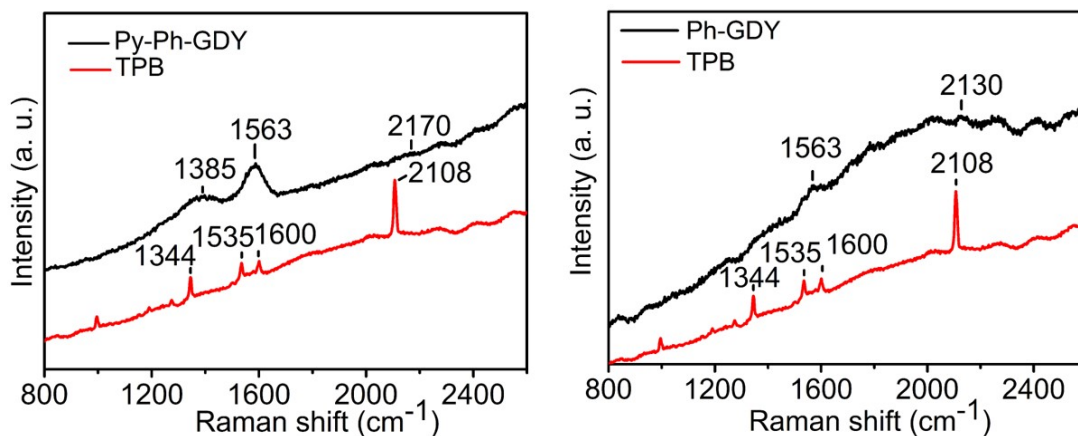


Figure S13. Raman spectra of **Py-Ph-GDY** (left) and **Ph-GDY** (right).

As depicted in Figure S13, the emerging bands at 2170 and 2130  $\text{cm}^{-1}$  are attributed to the stretching vibration of conjugated diyne links ( $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ ) in **Py-Ph-GDY** and **Ph-GDY**,<sup>4</sup> which further verify the cross-coupling of the terminal acetylenic groups in the corresponding **TPyB** and **TPB**.

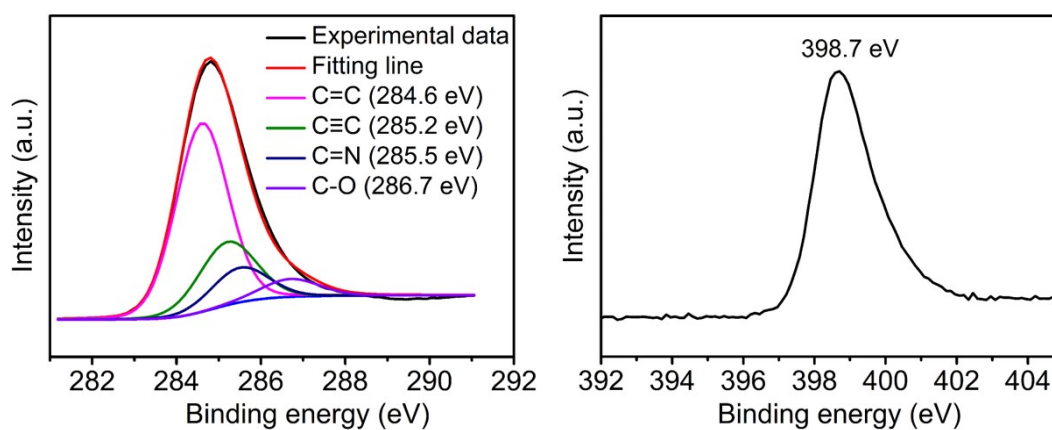


Figure S14. XPS spectrum of **Py-Ph-GDY**, C 1s region (left) and N 1s (right).

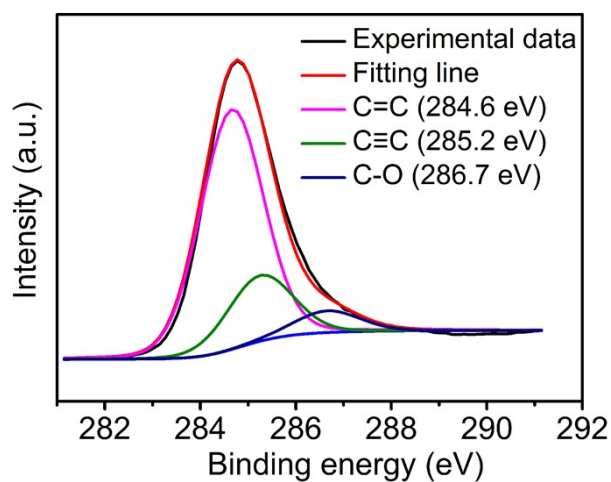


Figure S15. XPS spectrum of **Ph-GDY**, C 1s region.

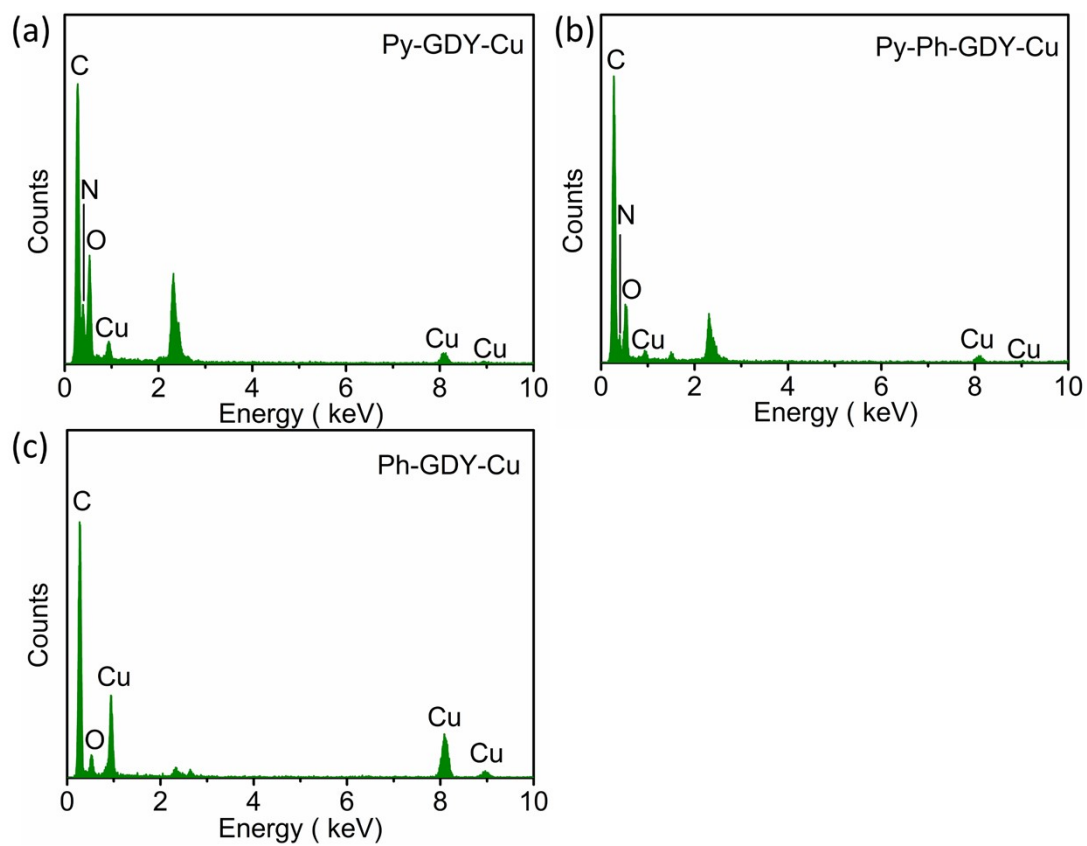


Figure S16. The energy-dispersive X-ray spectrum of (a) **Py-GDY-Cu**, (b) **Py-Ph-GDY-Cu**, (c) **Ph-GDY-Cu**.

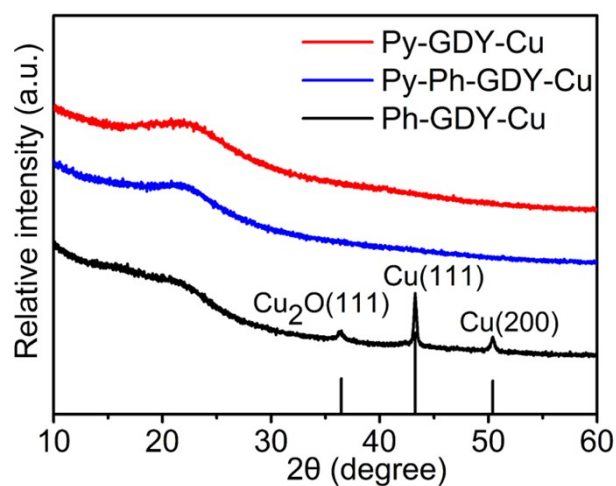


Figure S17. XRD pattern of **Py-GDY-Cu**, **Py-Ph-GDY-Cu**, **Ph-GDY-Cu**.

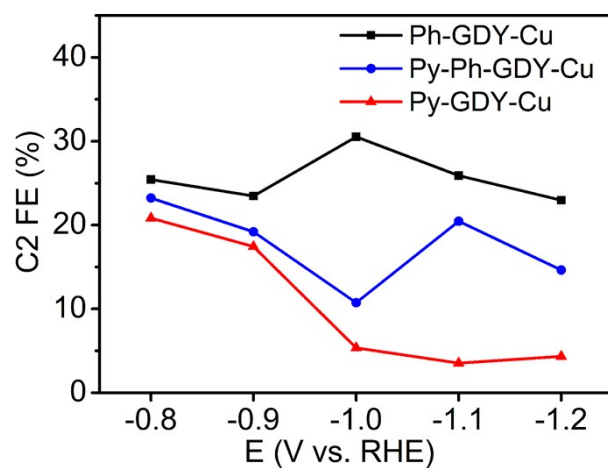


Figure S18. C2 FE of **Py-GDY-Cu**, **Py-Ph-GDY-Cu**, **Ph-GDY-Cu**.

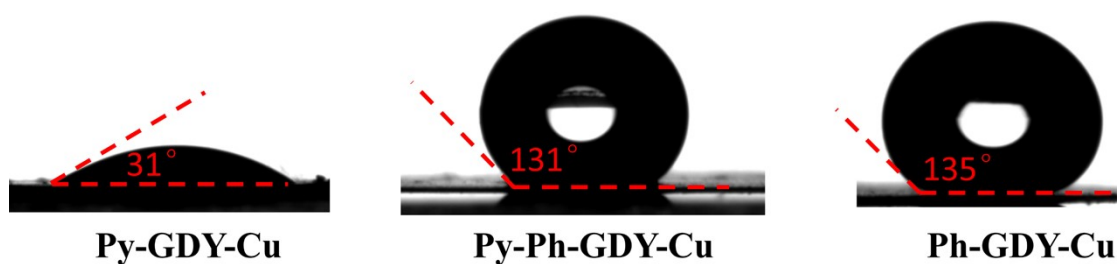


Figure S19. Water contact angle of **Py-GDY-Cu**, **Py-Ph-GDY-Cu**, **Ph-GDY-Cu**.

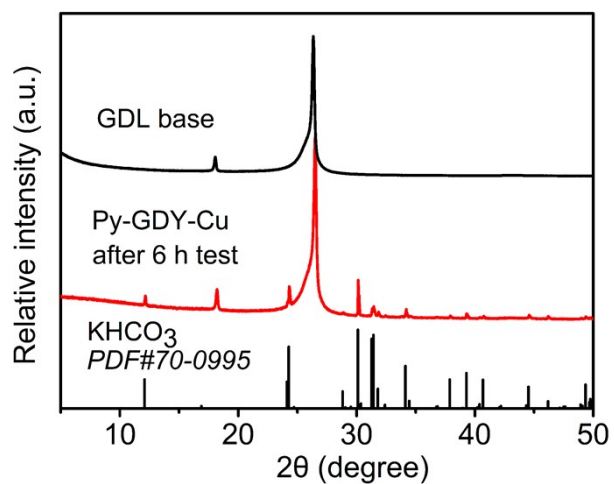


Figure S20. XRD patterns of **Py-GDY-Cu** after 6h electrocatalytic test (red line), GDL (black line), and KHCO<sub>3</sub> (PDF#70-0995).

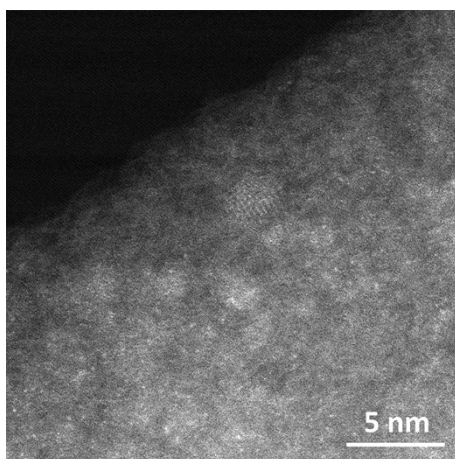


Figure S21. Aberration-corrected HAADF-STEM image of **Py-GDY-Cu** after 6h electrocatalytic test.

## References

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