Supporting Information

Acetylenic Bond-Driven Efficient Hydrogen Production of Graphdiyne based Catalyst

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Contents:

1. Experiment section

1.1 Reagent and experiment conditions

All reactions were carried out under Argon condition unless otherwise noted. Tetrahydrofuran (THF) and toluene were dried by distillation over sodium/benzophenone, respectively. Pyridine was pretreated under reflux with calcium hydride. BuLi (2.5 M solution in hexane), Tetra-(triphenyl-phosphine) Palladium were purchased from Aldrich and used without further purification. Trimethylsilylacetylene, Zinc chloride, tetrabutylamonium fluride (TBAF) were obtained from Acros Organics. Copper foil was purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC) and treated by sonicating in 3 M HCl, water, ethanol and acetone, sequentially, for 20 minutes, dried under vacuum at 60 °C and used immediately.

^{1}H NMR, ^{13}C NMR were recorded on Bruker AVANCE-III 600 (600 MHz for 1H, 150 MHz for ^{13}C) instrument in $CDCl_3$ with tetramethylsilane as an internal standard. The chemical structure of the products was characterized by Fourier transform infrared spectroscopy (FT-IR, Thermo-Fisher Nicolet iN10) and Raman spectroscopy (Thermo Scientific DXRxi, 532 nm). Morphology details were examined using field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, HITACHI H-7650). HRTEM and element mapping analysis were carried out using JEM-2100F electron microscope. XPS spectra were collected using a Thermo Scientific ESCALab 250Xi (Al Kα radiation as excitation source). Nitrogen adsorption/desorption measurements were performed at 77 K using a Quantachrome Autosorb gas−sorption system and calculated through the

Brunauer−Emmett−Teller (BET) method. The *I-V* curve was measured on Keithley-4200.

All electrochemical measurements were carried out using three-electrode system (CHI. 660D, Shanghai CH. Instruments, China). The as-prepared TPN-GDY and TPM-GDY film grown on carbon cloth (CC) was directly used as working electrode. A saturated calomel electrode (SCE) and a carbon plate were employed as the reference electrode and counter electrode, respectively. Polarization curves were recorded at room temperature in 0.5 M H_2SO_4 (pH=0).

1.2 Calculation conditions

All the calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) based on density functional theory (DFT) **[S1-S4]**. The Perdew−Burke−Ernzerhof (PBE) functional with generalized gradient approximation (GGA) was used for the electronic exchange and correlation effects **[S5]**. The core electrons were approximated with the projector-augmented wave (PAW) method using the periodic plane waves basis set **[S6]**. The energy cutoff was set as 450 eV, and the first Brillouin zone was sampled in the Monkhorst−Pack grid with Γ-point center k-points mesh **[S7]**. The energy was converged to 1.0×10^{-6} eV/atom and the force was converged to 0.01 eV/Å for the geometries optimization. To describe the vdw interaction, the DFT-D3 version of dispersion corrections was added. The geometries optimization for the TPN-GDY and TPM-GDY models are performed in a 35 Å × 35 Å × 35 Å box to avoid the periodic interaction. The molecule surface electrostatic potential were calculated using the Gaussian 16 program (Revision B01) **[S8]** with the popular B3LYP hybrid function **[S9-S11]**. Besides, the hydrogen evolution activities were evaluated using the descriptor of H adsorption free energy (i.e., ΔG_H), which is defined as follow:

$$\Delta G_H = E_{H+sub} - E_{sub} - 1/2G_{H2} + \Delta E_{ZPE} - T\Delta S$$

The references for the calculation method are listed as follows:

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K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT, 2016.

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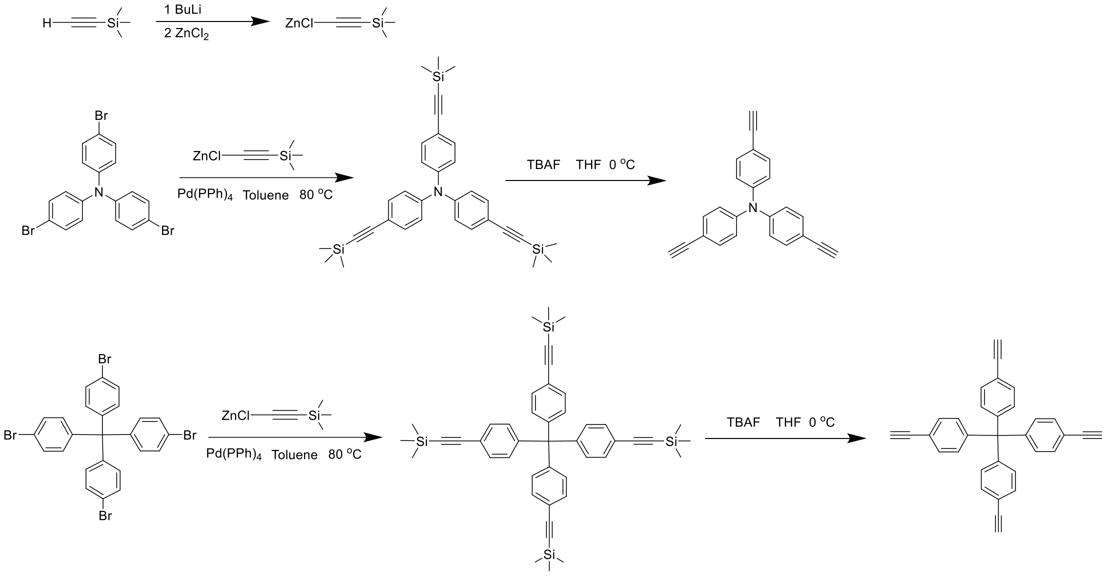
1.3 Synthesis



Scheme S1 The synthetic route for the precursors.

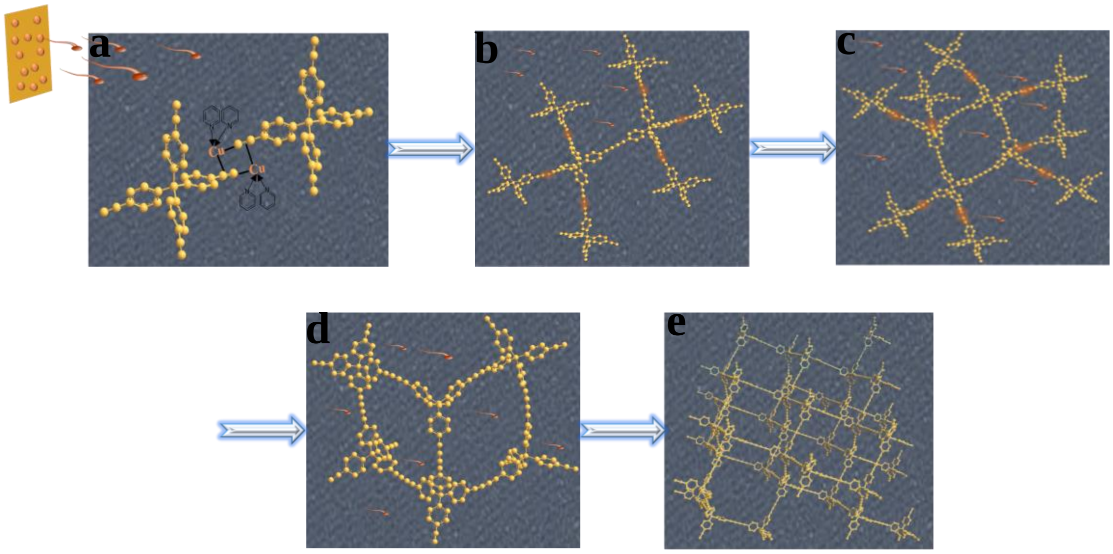


Figure S1. The synthetic routes for the precursors and a scheme for TPM of the 3D framework fabricated.

In the scheme, the precursors of TPM are catalyzed by copper ions in the presence of pyridine to form a dimer (a) and oligomer (b), the oligomer continues to grow in the three-dimensional direction (c), finally forming a 3D framework (d and e).

1.3.1 The synthetic procedure for tris(4-ethynylphenyl)amine.

50 mL of ethynyltrimethylsilane and 150 mL of n-Butyllithiu in hexane (2.5 M) were mixed in 220 ml THF. The solution was stirred at -78 °C for 30 min. Then 60 g of $ZnCl_2$ was added in the reaction solution, and the mixture was stirred for another 2 hours. After that 9.6 g of tris(4-bromophenyl)amine (20 mmol), 1.25 g of $Pd(TPP)_4$, and 220 mL of toluene were added in this order. The mixture was stirred under a nitrogen atmosphere at 80 °C for 3 days. The solvent was evaporated and the residue was then purified by column chromatography to yield tris(4-((trimethylsilyl)ethynyl)phenyl)amine as a pale yellow powder (9.0 g, 17.4 mmol, yield: 87%).

After that, to a solution of tris(4-((trimethylsilyl)ethynyl)phenyl)amine in 150 mL THF was added 25 mL TBAF (1 M in THF, 2.5 mmol) and stirred at 0 °C for 15 min. The solution was then diluted with ethyl acetate and washed with distilled water and dried with anhydrous Na_2SO_4. The solution was passed a flash column and then the solvent was removed in vacuum rotary evaporation to yield the precursor tris(4-ethynylphenyl)amine as pale yellow powder (5.5 g, 17.4 mmol, yield 100%).

1.3.2 The synthetic procedure for tetrakis(4-ethynylphenyl)methane.

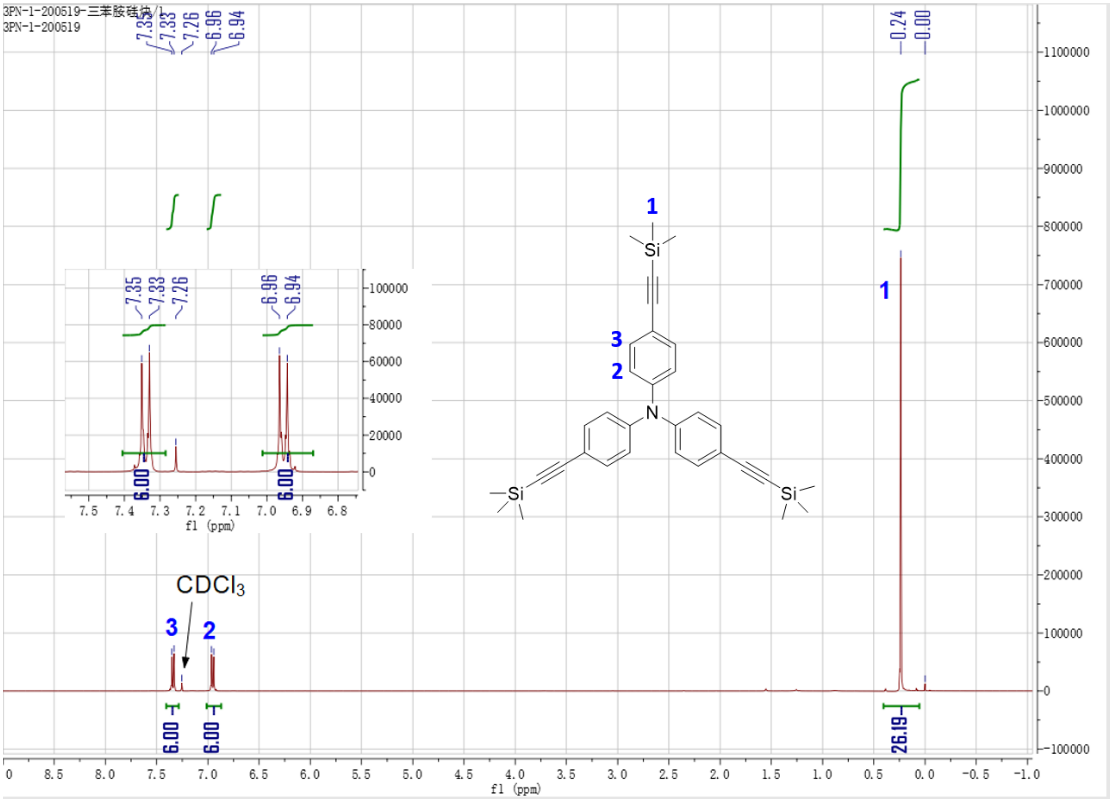
50 mL of ethynyltrimethylsilane and 150 mL of n-Butyllithiu in hexane (2.5 M) were mixed in 220 ml of THF. The solution was stirred at -78 °C for 30 min. Then 60 g of $ZnCl_2$ was added in the reaction solution, and the mixture was stirred for another 2 hours. After that 12.7 g of tetrakis(4-bromophenyl)methane (20 mmol), 1.25 g of $Pd(TPP)_4$, and 220 mL of toluene were added in this order. The mixture was stirred under a nitrogen atmosphere at 80 °C for 3 days. The solvent was evaporated and the residue was then purified by column chromatography to yield tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane as white powder (10.2 g, 14.8 mmol, yield: 74.0%).

After that, to a solution of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane in 150 mL THF was added 25 mL TBAF (1 M in THF, 25 mmol) and stirred at 0 °C for 15 min. The solution was then diluted with ethyl acetate and washed with distilled water and dried with anhydrous Na_2SO_4. The solution was pass a flash column and then the solvent was removed in vacuum rotary evaporation to yield the precursor tetrakis(4-ethynylphenyl)methane as white powder (6.1 g, 14.8 mmol, yield 100%).

1.3.3. The synthetic procedure for TPM-GDY and TPN-GDY on carbon cloth.

GDY was synthesized as previously reported. Several pieces of copper foils and commercial carbon cloth were kept at 60 °C for 2 hours in a three-necked flask containing pyridine. Subsequently, 50 mL pyridinic solution of the monomer was added in a very slow speed into the above reactor. After the 1-day reaction at 110 °C in dark, the surface of carbon cloth turned black, suggesting the successful loading of GDY. Then the fresh-prepared GDY was washed with hot acetone and DMF, KOH (4 M), HCl (6 M), KOH (4 M) and water sequentially, and followed by drying in 40 °C vacuum oven for 12 hours.

2. Characterization of precursors and GDY framework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7.26
6.96
6.94
0.24
0.00
1
Si
3
2
N
Si
Si
1
CDCl$_3$
3
2
6.00
6.00
26.19
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
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7.33
7.26
6.96
6.94
100000
80000
60000
40000
20000
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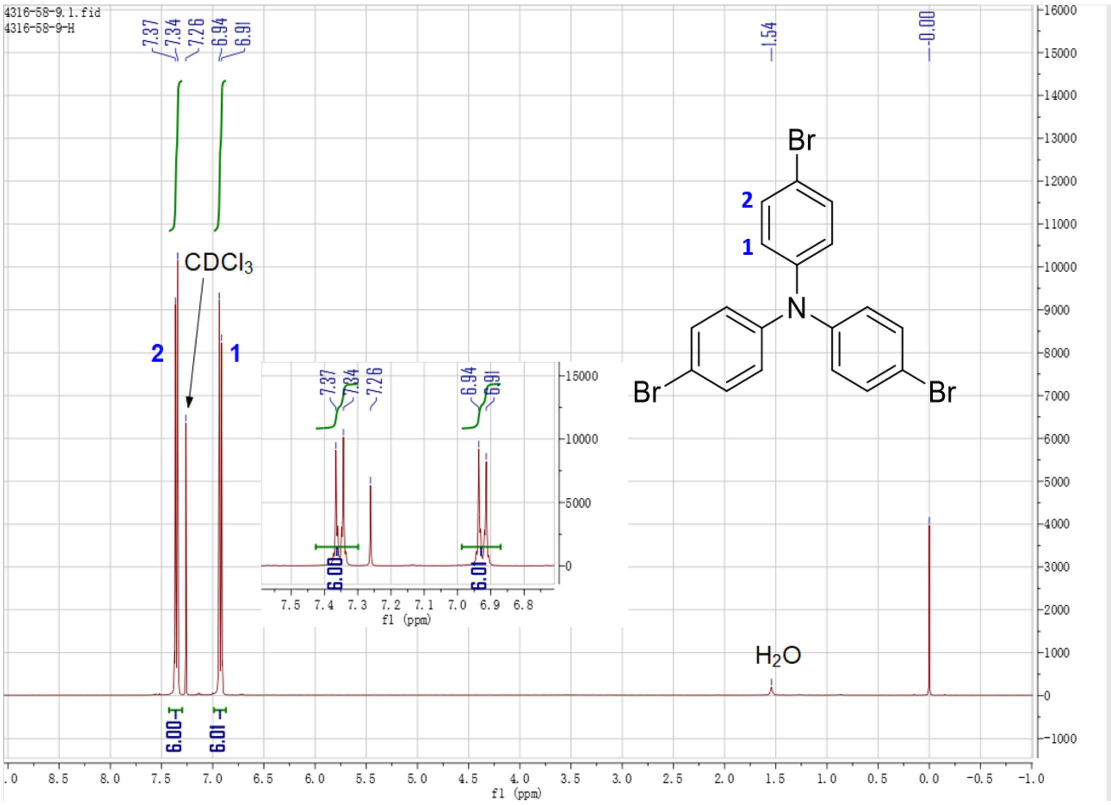
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)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1
N
Br
Br
CDCl$_3$
2
1
H$_2$O
6.00
6.01
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
7.37
7.34
7.26
6.94
6.91
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10000
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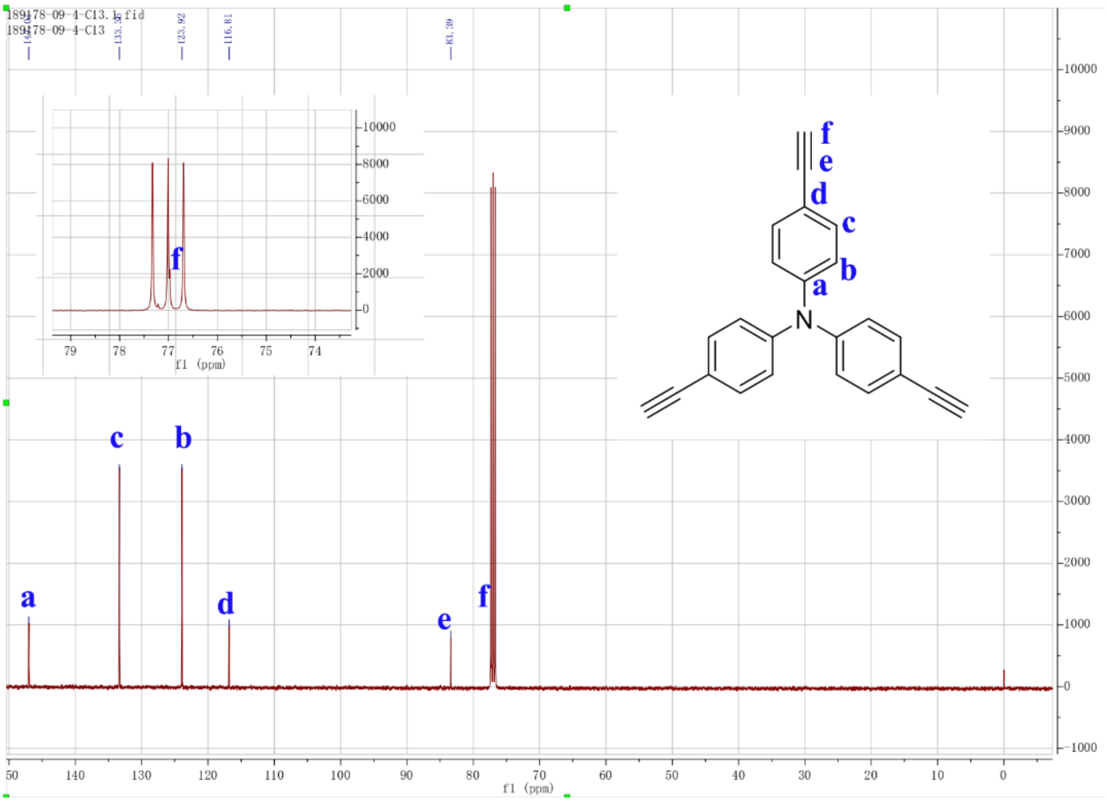
6.9
6.8
f1 (ppm)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d
e
f
N
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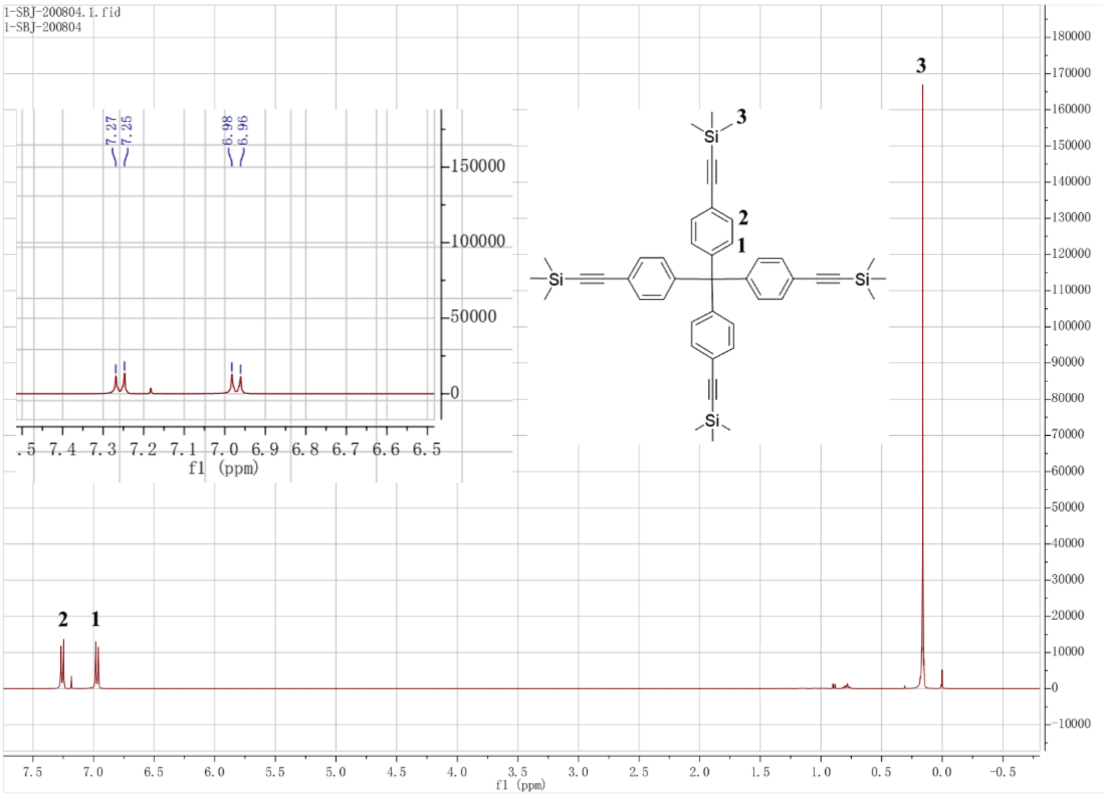
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3
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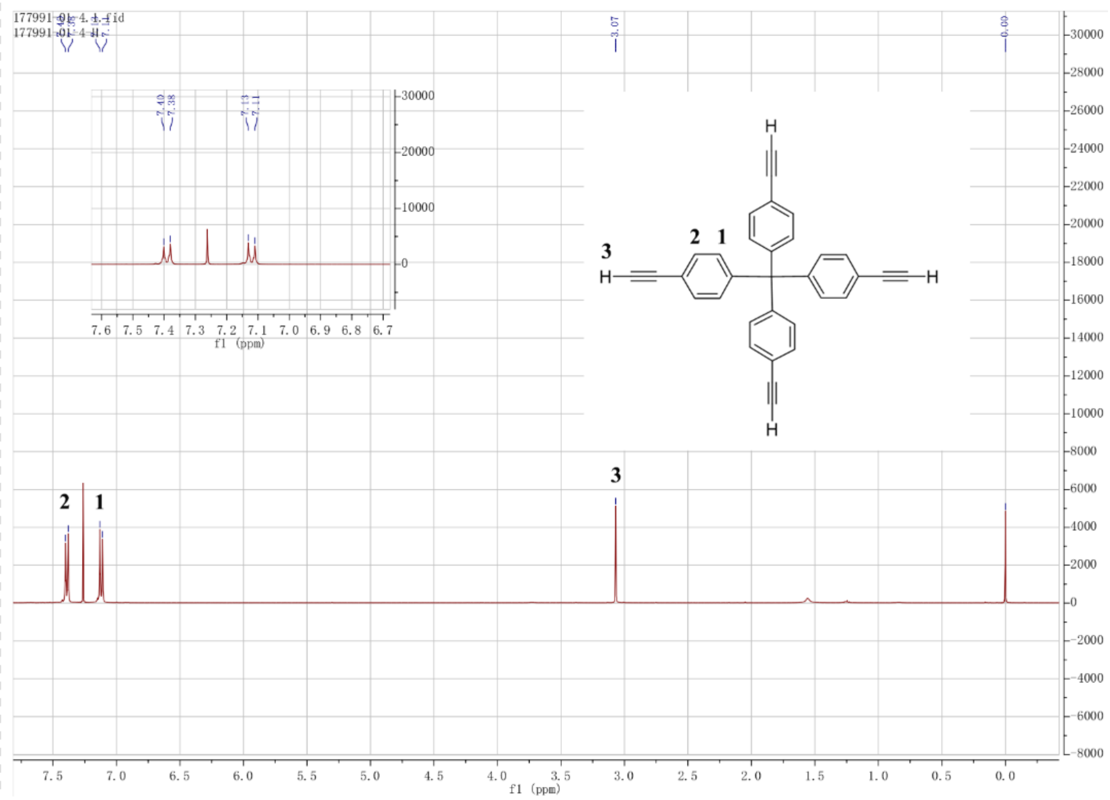
f1 (ppm)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6.8
6.7
f1 (ppm)
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20000
10000
0
H
H
H
H
1
2
3
3
2
1
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7.0
6.5
6.0
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4.5
4.0
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2.0
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f1 (ppm)
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26000
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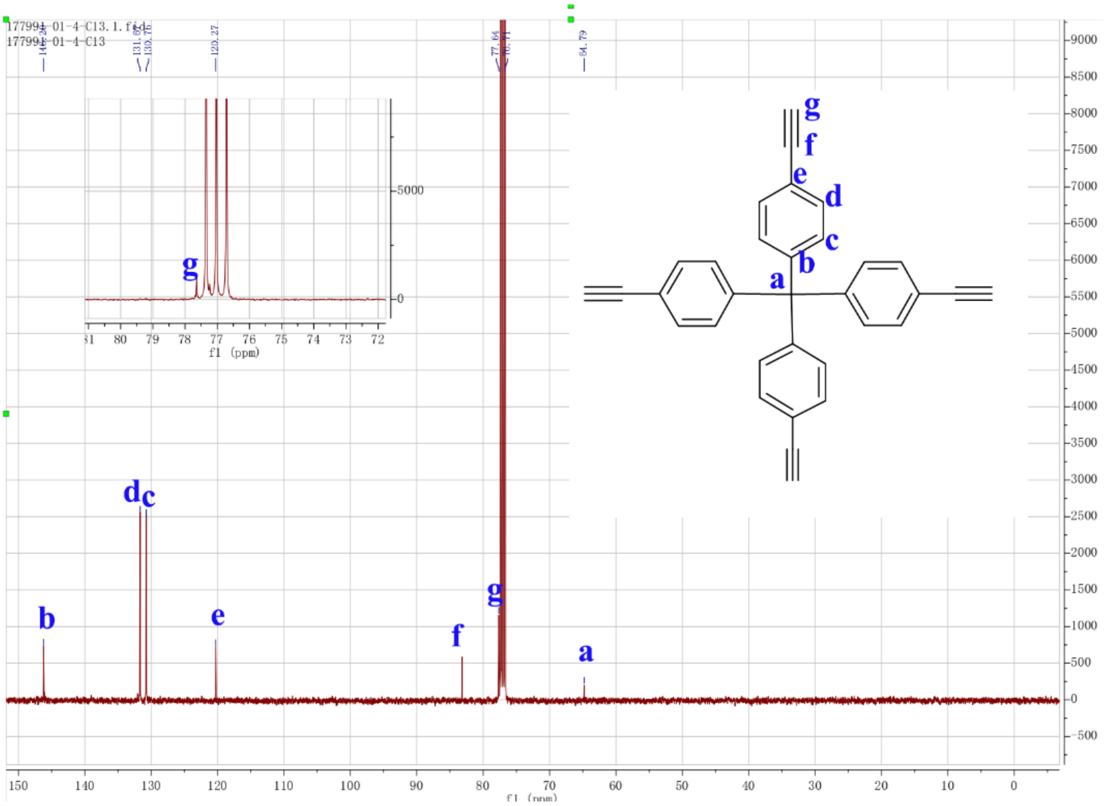
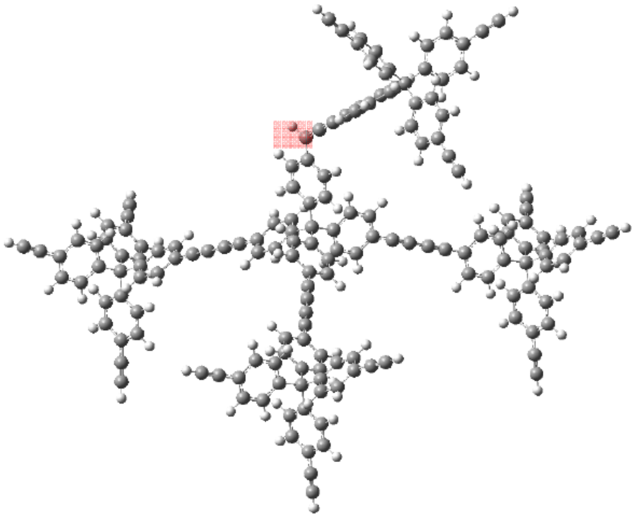


Figure S2. The ^{1}H NMR and ^{13}C NMR spectra for the precursors.



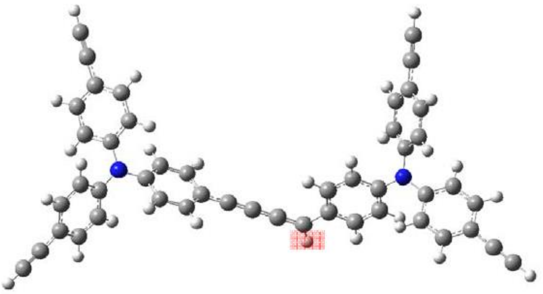


Figure S3. The optimized configuration of TPM-GDY and TPN-GDY adsorbed H.

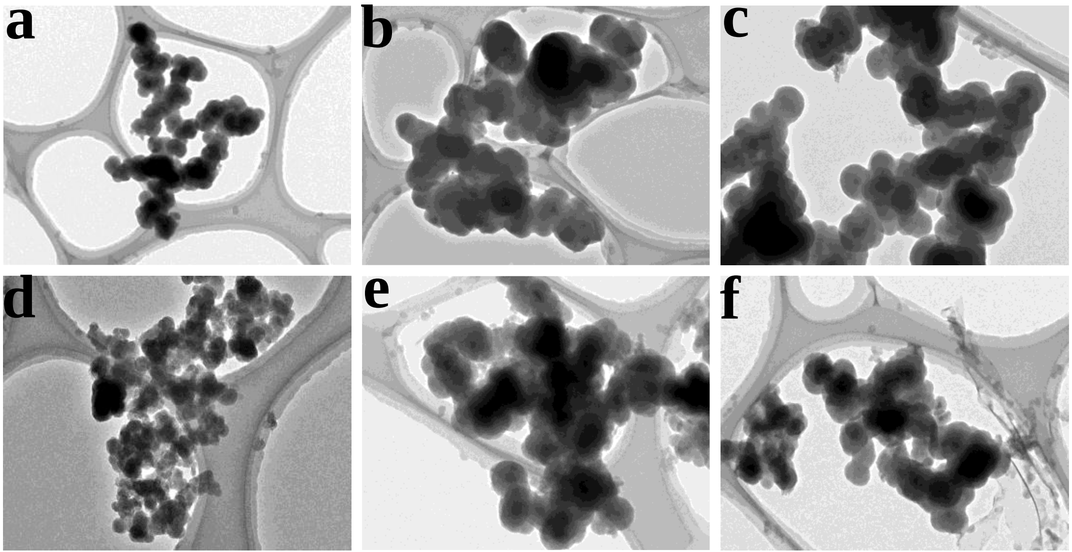


Figure S4. TEM images of TPM-GDY film exfoliated from CC. The images were obtained from different area of micro-grid to evaluate the size distribution of the aggregation structure.

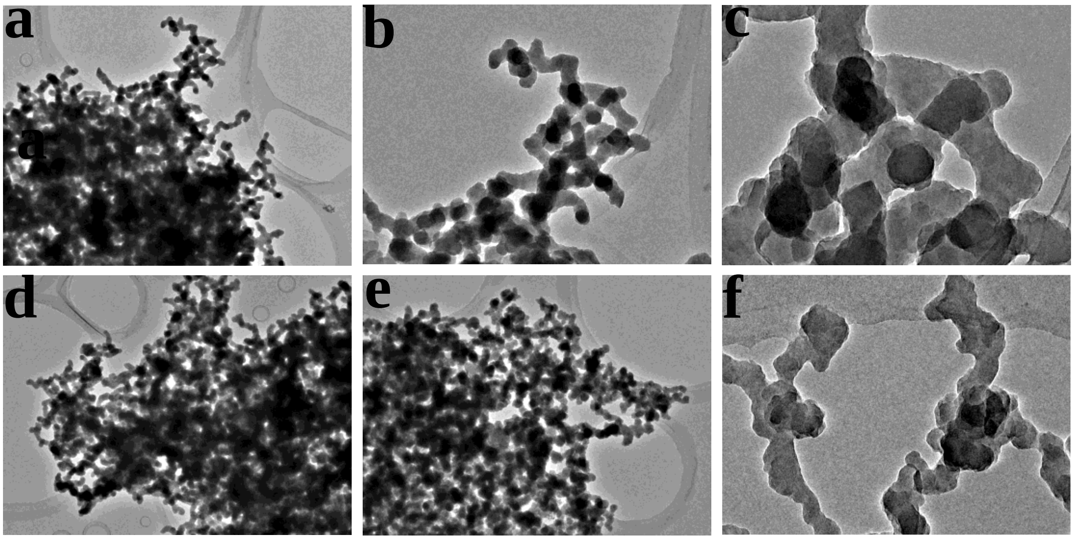


Figure S5 TEM images of TPN-GDY film exfoliated from CC. The images were obtained from different area of micro-grid to evaluate the size distribution of the aggregation structure.

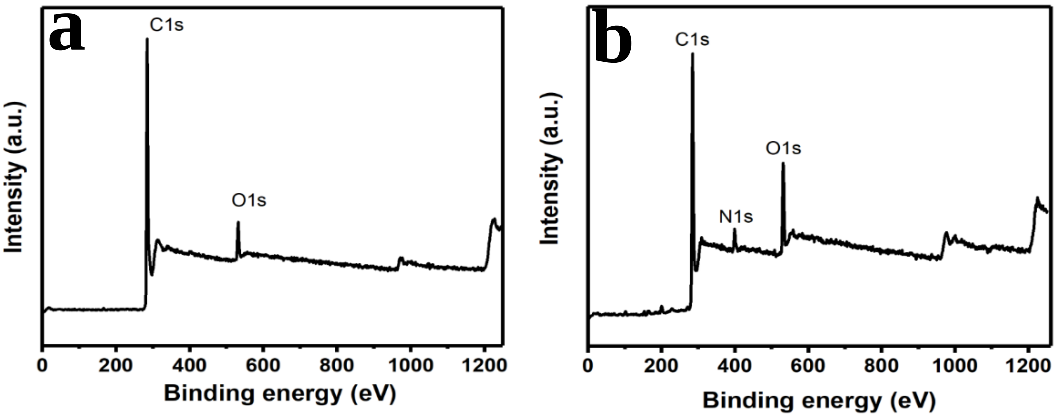
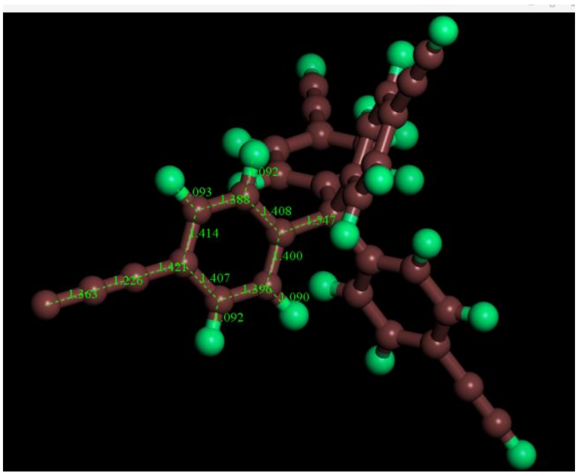
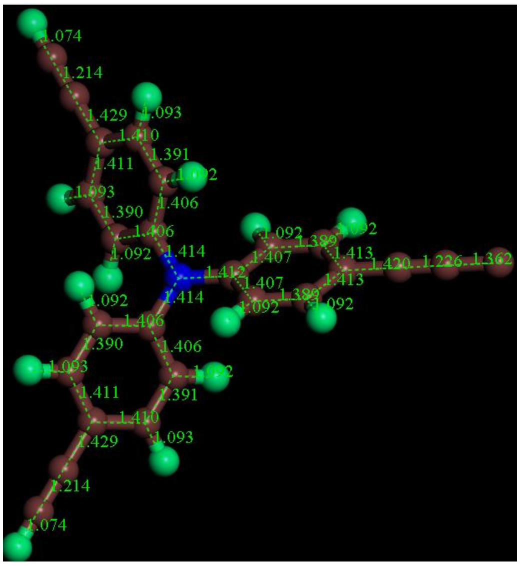


Figure S6 XPS spectra of TPM-GDY(a) and TPN-GDY(b).





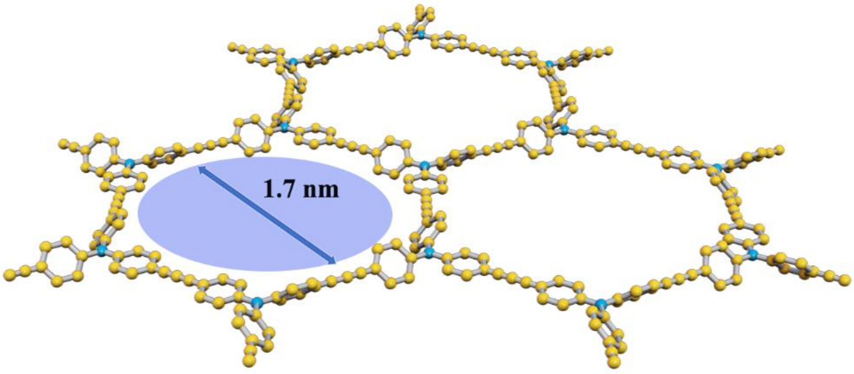


Figure S7 Calculated lengths of chemical bonds in a repeat unit of TPM and TPN.

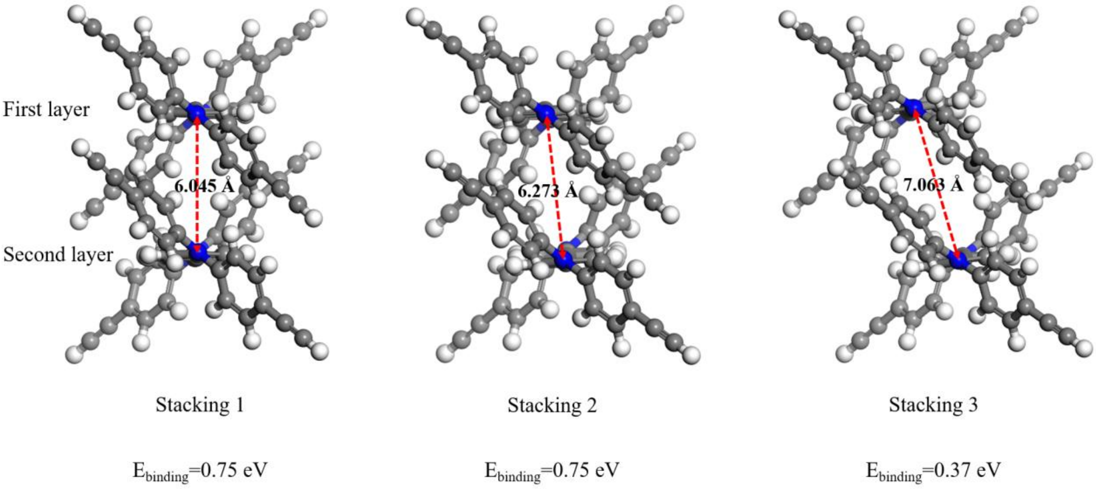


Figure S8 Three kinds of theoretical stacking mode of TPN with stable binding energy. The length data in the graph represents the distance between the two nitrogen atoms in the adjacent layers.

Table S1. Comparison of the HER performances of TPM-GDY/CC and TPN-GDY/CC reported metal-free catalysts.

Sample	Overpotentiala (mV)	Tafel slope ($mVdec^{-1}$)	Reference
TPM-GDY	105	45.1	This work
TPN-GDY	211	161.4	This work
p-FGDY	92	157	[1]
N-doped graphene	336	87	[2]
g-C3N4@S–Se-pGr	92	86	[3]
SCN–MPC	145	51	[4]
CNQDs@G	110	53	[5]
S-C3N4–CNT–CF	236	81.6	[6]
BCNs	70	100	[7]
3DNG-P	128	66	[8]
N-TCNT@NGS	62	50	[9]
Fep/CN	140	63.5	[10]

[a] Measured in an aqueous solution of 0.5 M H_2SO_4 at a current density of 10 mA cm^{-2}.

The references for Table S1

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