

Supporting Information

Tricycloquinazoline-Containing 3D Conjugated Microporous Polymers and 2D Covalent Quinazoline Networks: Microstructure and Conductivity

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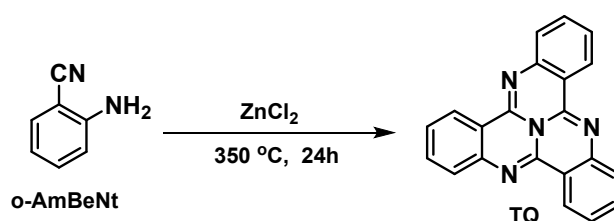
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S1. Experimental section

Materials: All the rest of the reagents and solvents, unless otherwise specified, were used as received without further purification. The main materials required for the reaction are 2-aminobenzonitrile (98%, Aladdin), 2,5-dichloroterephthalonitrile (97%, Bidepharm), benzophenone imine (97%, Macklin), sodium tert-butoxide (NaOtBu, 98%, Aladdin), tris(diphenylacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 97%, Macklin), 1,1'-Binaphthalene-2,2'-diylbis(diphenylphosphane) (rac-BINAP, 98%, Aladdin), and were used as received. Air and moisture sensitive reagents were stored in an argon-filled glove box. Anhydrous toluene, anhydrous tetrahydrofuran and anhydrous chloroform were distilled with sodium/benzophenone under nitrogen protection to use.

S1.1. Synthesis of TQ

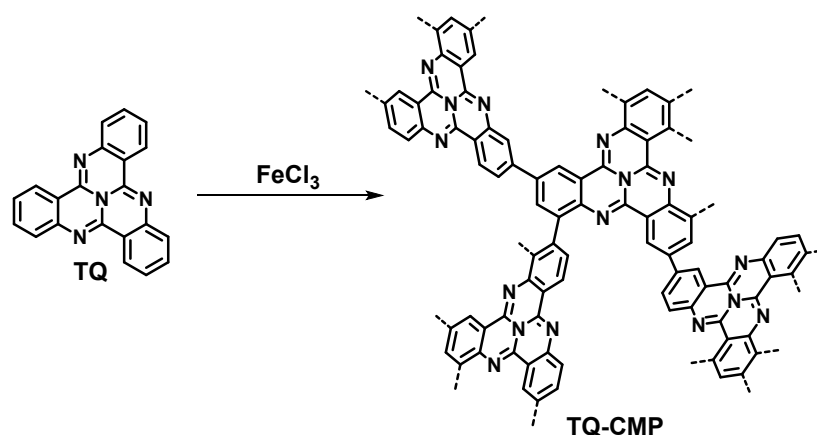
The TQ was prepared according to the previous literature.¹ 2-aminobenzonitrile (o-AmBeNt) (100 mg, 0.85 mmol) and anhydrous zinc chloride (116 mg, 0.85 mmol) were placed in a Pyrex ampoule under the protection of N_2 . The ampoule was evacuated, flame-sealed and then heated at 350 °C for 24 h in the tube furnace. After cooling to room temperature, the flame-sealed ampoule was opened to obtain yellow solid. The solid powders were ground and washed with dilute HCl (1M) and ultra-pure water, respectively, then dissolved in chloroform. NaSO_4 was added to remove water. After filtration, the TQ was obtained via distillation and heat-treatment at 80 °C for 12 h in vacuum as sequence.



S1.2. Synthesis of TQ-CMP

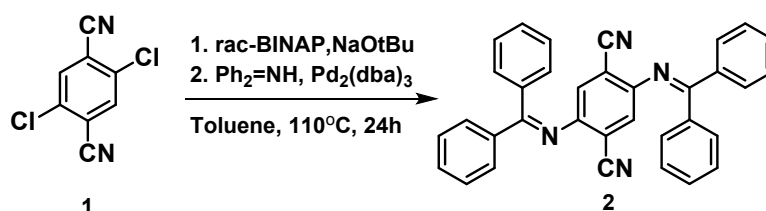
Under nitrogen protection, the monomer TQ (100 mg, 0.31 mmol) was dissolved in 30 mL of anhydrous chloroform. And then a suspension of ferric chloride (778 mg, 4.8 mmol) in 20 mL of anhydrous chloroform was dropped into above solution. After stirring for 72 hours at room temperature, the mixture was added 100 mL of methanol and continue stirred for 30 min. The resulting product was filtered and washed with methanol and ultra-pure water in

turn. After being purified with methanol in a soxhlet extractor for 48h, the TQ-CMP was obtained after vacuum drying at 80 °C overnight.



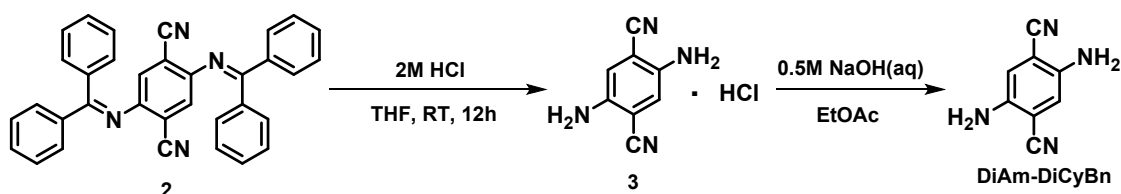
S1.3. Synthesis of monomer (DiAm-DiCyBn) of TQ-CQN

The DiAm-DiCyBn was prepared according to the previous literature.¹ Rac-BINAP (500 mg, 0.80 mmol) and $\text{Pd}_2(\text{dba})_3$ (tris(diphenylacetone)dipalladium(0)) (366 mg, 0.40 mmol) were placed in a 50 mL Schleck flask under the protection of N_2 atmosphere. The degassed anhydrous toluene (15 mL) was injected into the flask via a syringe and heated the black-rad solution to 110 °C for 2 h. Adding 2,5-dichloroterephthalonitrile (compound 1) (1.00 g, 5.07 mmol), benzophenone imine (2.28 g, 12.61 mmol) and sodium tert-butoxide (1.27 g, 13.24 mmol) into the solution when it was cooled down to room temperature. Continue to heat the mixture to 110 °C for 36 h in the N_2 atmosphere. The reaction solution was diluted using dichloromethane, filtered through a Buchner funnel and concentrated under vacuum. The final obtained solid product was purified using column chromatography with chloroform to get the yellow compound 2.



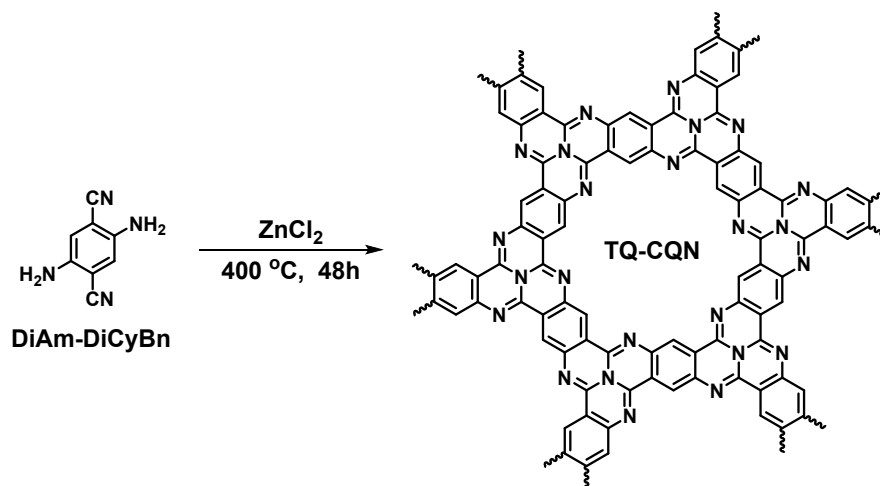
Dilute hydrochloric acid (2M) was dripped into the THF solution dissolved compound 2. The mixture solution was stirred at room temperature for 12 h. The excess solvent was steamed out in a vacuum, and then stirred with hexane for 10min. After filtration, the resulting

filtrate was washed with diethyl ether and dried under vacuum. The archived yellow product (Compound 3) was suspended in 0.5M NaOH solution stirred for 30 min. The ethyl acetate was added to the suspension to extract the product. After dried with anhydrous NaSO₄ and precipitates from the Ethyl acetate, the yellow solid product (DiAm-DiCyBn) was obtained under 80 °C for 12 h.



S1.4. Synthesis of TQ-CQN

The TQ-CQN was also prepared according to the previous literature.¹ DiAm-DiCyBn (60 mg, 0.38 mmol) and anhydrous zinc chloride (77.6 mg, 0.57mmol) were placed in a Pyrex ampoule under the protection of nitrogen. The ampoule was evacuated, flame-sealed and then heated at 400 °C for 48h in the tube furnace. After cooling to room temperature, the obtained black solid was ground into powder and washed with 1M HCl to remove zinc chloride. Then, the black powder was stirred and filtered in turn with ultra-pure water, THF and methanol. Finally, TQ-CQN was obtained after vacuum drying at 120 °C for 12h.



S2 Sample Characterizations

Fourier transform infrared (FTIR) spectra were conducted on Thermo Scientific Nicolet iS10 spectrometer. Raman microscope spectrometer (Renishaw inVia Reflex, excitation at 532 nm) was used to obtain Raman spectra of materials. Scanning electron microscope (SEM, Hitachi S-4800) and Transmission electron microscope (TEM, JEOL, JEM-2100) recorded the morphologies of samples. The bonding state of samples was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Mg-K α radiation) spectra. N₂ sorption measurements at 77 K were collected using Autosorb iQ-Quantachrome Instrument. The electrochemical tests were examined in a three-electrode system by Zennium Pro workstation.

S2.1. Gas Adsorption Performance

The CO₂ and CH₄ adsorption-desorption isotherms were characterized by Quantachrome Autosorb apparatus at 273 K and 298 K. Before conducting the measurement, the samples were ground into powder and then degassed at 150 °C for 12 h. Then, isosteric heats of adsorption (Q_{st}) values for CO₂ and CH₄ were calculated using the Clausius-Clapeyron equation based on the CO₂ and CH₄ adsorption isotherms at 273 K and 298 K by fitting a plot of ln (P) vs 1/T.

S2.2. Electrochemical Measurements

Before carrying out the electrochemical analysis, the catalyst powder was mixed into 30 μ L of 5 wt% Nafion solution and 1 mL of water/ethanol (volume ratio = 3:1) solution. Next, it was sonicated for 30 min to form homogeneous solution. Finally, 5 μ L solution was dipped on the surface of glassy carbon electrode and the catalyst loading was 0.159 mg cm⁻².

The electrochemical tests were performed using a three-electrode system in 0.5 M H₂SO₄. The working electrode was prepared by coating synthetic sample on glassy carbon electrode (GCE, 4 mm in diameter). Besides, a platinum plate and saturated Ag/AgCl (sat. KCl) were used as counter electrode and reference electrode, respectively. All measurements were conducted with IR compensation. The potential was calibrated by reversible hydrogen electrode (RHE) using the equation of $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197\text{V} + 0.0591 \cdot \text{pH}$. Linear sweep voltammetry (LSV) was conducted at 5 mV s⁻¹. In the LSV curve, the overpotential was picked at the fixed current density of 10 mA cm⁻¹. The Tafel slope was calculated by LSV curve based

on the Tafel equation ($\eta = a + b \log J$, where η is the overpotential, a is a constant, b is the Tafel slope, J is the current density.) Exchange current density (j_0) was given by extrapolation of Tafel plots ($\eta = 0$, $j_0 = 10^{(-a/b)}$). Electrochemical impedance spectroscopy (EIS) measurements were conducted at a frequency range from 10^5 to 0.1 Hz with a 5 mV amplitude. According to the cyclic voltammetry (CV), long-term stability of electrocatalyst was performed between -0.4 to 0.1 V vs. RHE with a scan rate of 50 mV s^{-1} for 3000 cycles. Meanwhile, Double-layer capacitance (C_{dl}) was measured based on CV measurements between 0.1 and 0.35 V vs. RHE over scan rate ranges from 40 to 200 mV s^{-1} . Using the slope of the curves, which were made up capacitive currents of $\Delta j_{|j_a-j_c|}/2$ vs. RHE and corresponding scan rates, to represent the value of the C_{dl} .

S3. Supplementary Figures and Tables

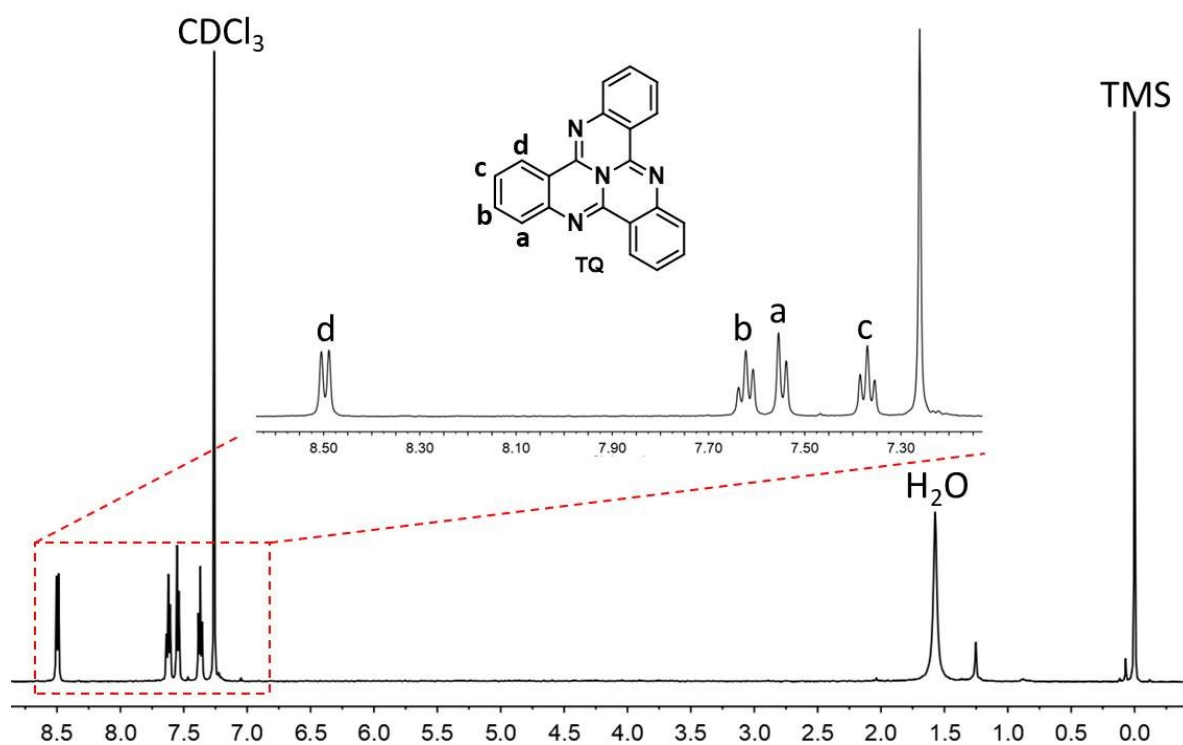


Fig. S1. ^1H NMR spectrum of TQ. ^1H NMR (600 MHz, CDCl_3): δ (ppm) = 8.50 (d, 3H); 7.62 (t, 3H); 7.55 (d, 3H); 7.37 (t, 3H).

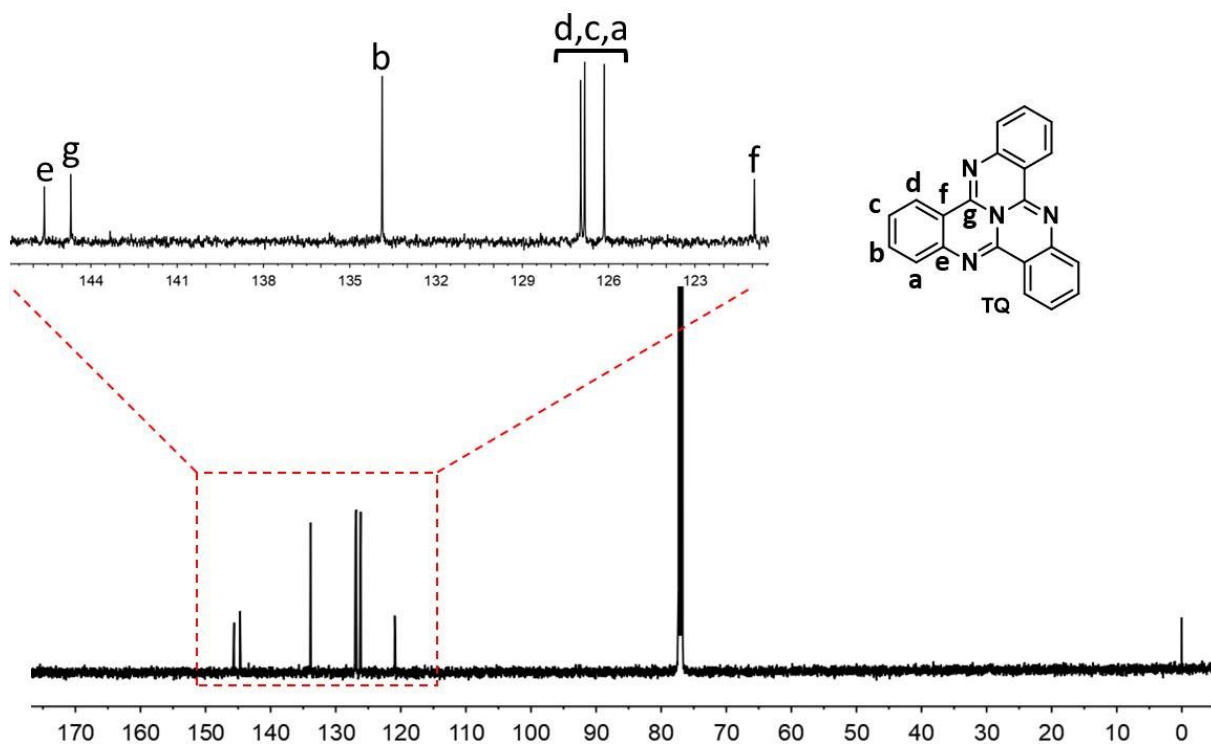


Fig. S2. ^{13}C NMR spectrum of TQ. ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) = 145.62, 144.69, 133.87, 126.97, 126.83, 126.16, 120.93.

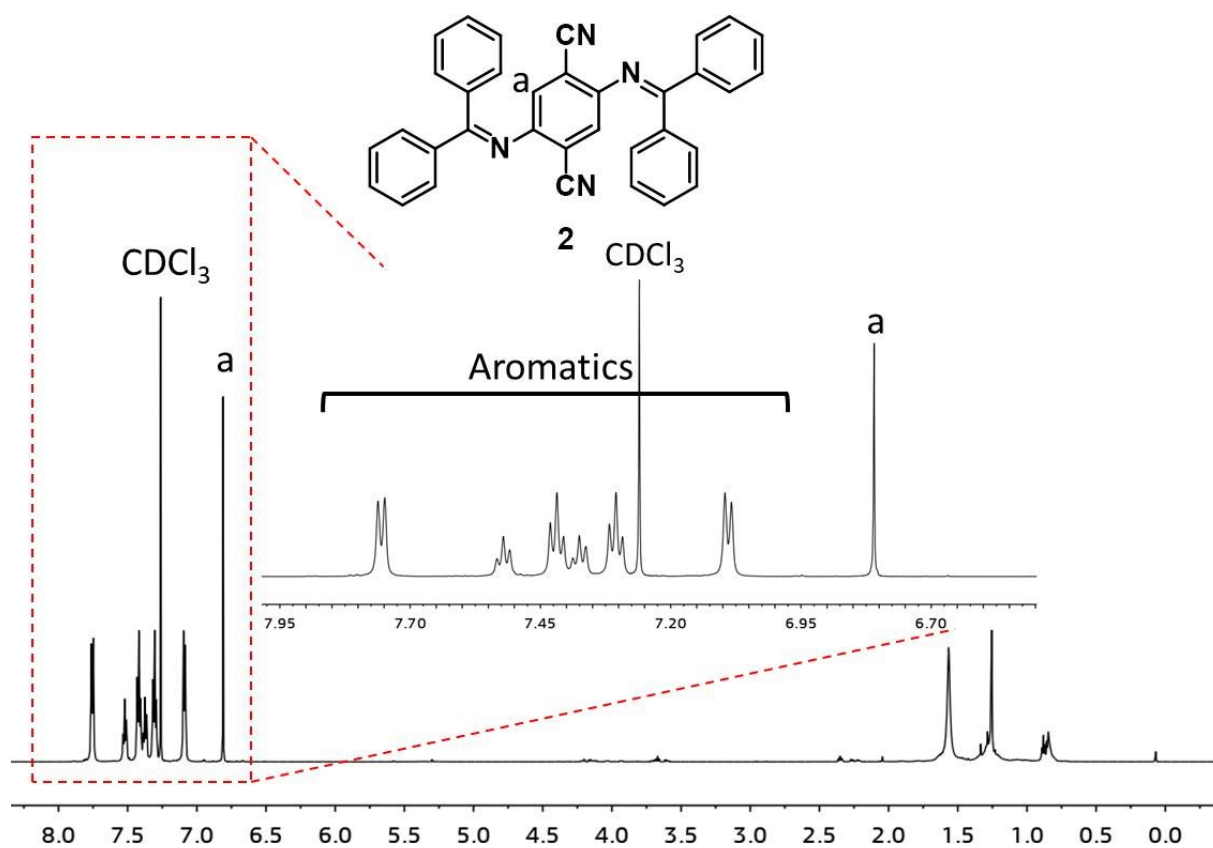


Fig. S3. ^1H NMR spectrum of Compound 2. ^1H NMR (600 MHz, CDCl_3): δ (ppm) = 7.76 (d, 4H); 7.52 (t, 2H); 7.48 - 7.35 (m, 6H); 7.30 (t, 4H); 7.09 (d, 4H); 6.81 (s, 2H).

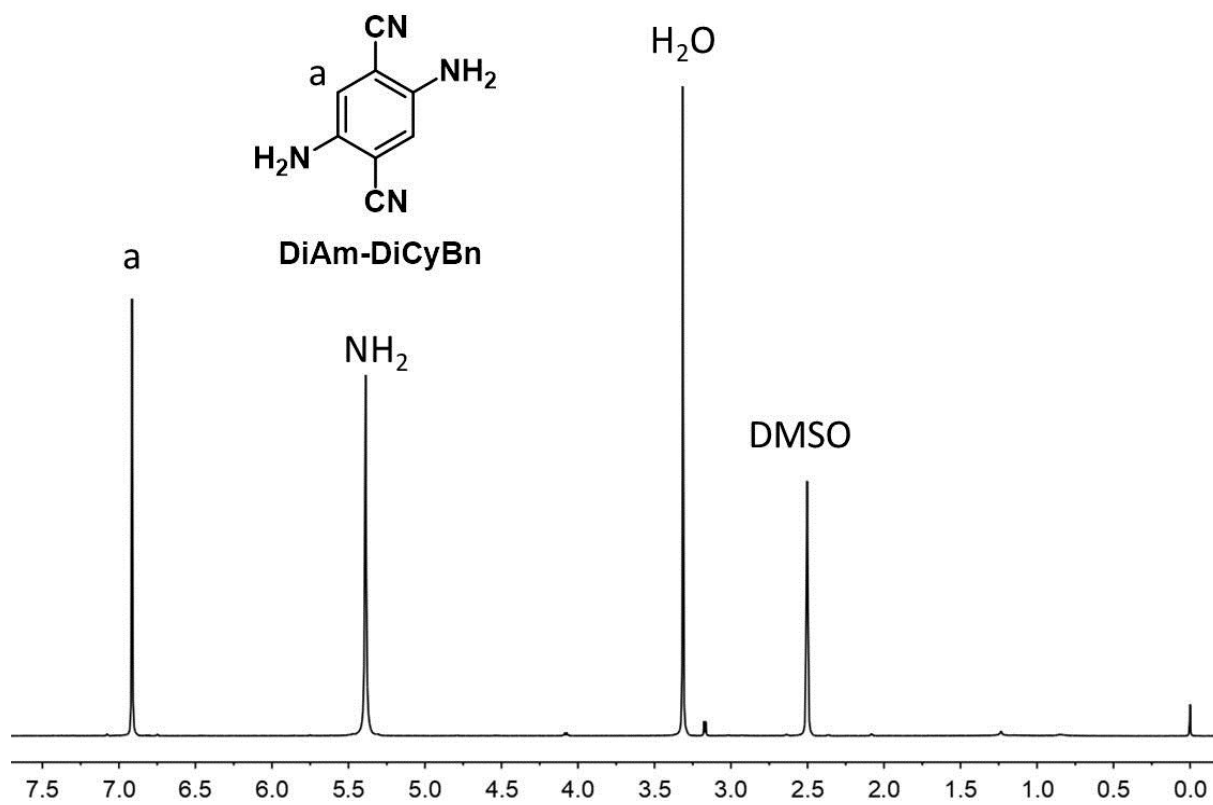


Fig. S4. ¹H NMR spectrum of DiAm-DiCyBn. ¹H NMR (600 MHz, DMSO): δ (ppm) = 6.91 (s, 1H); 5.39 (s, 2H).

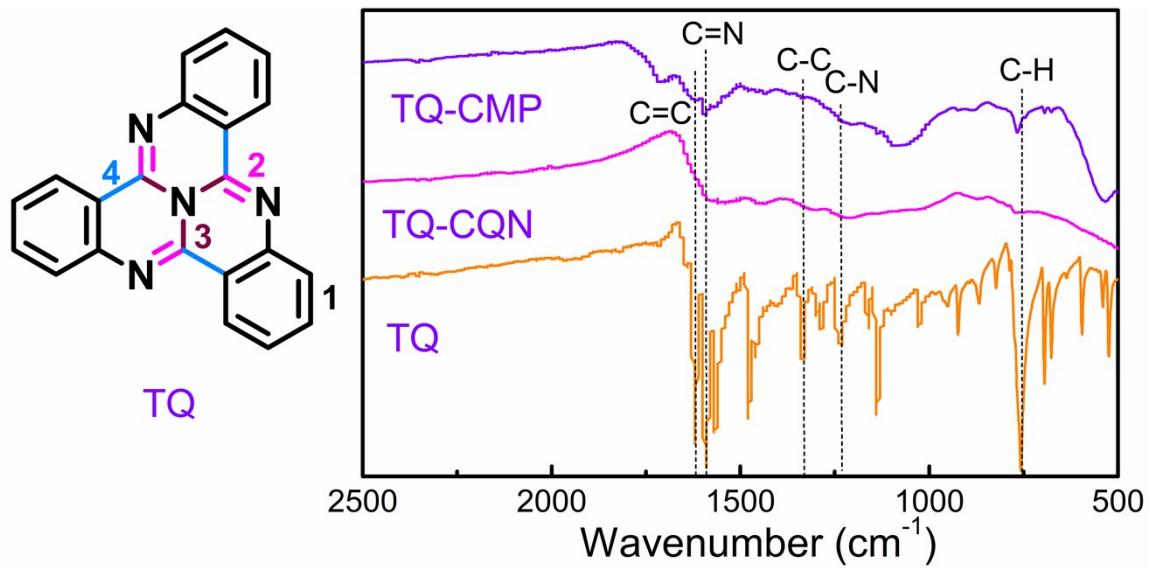


Fig. S5. FTIR spectra of TQ-CMP, TQ-CQN and TQ.

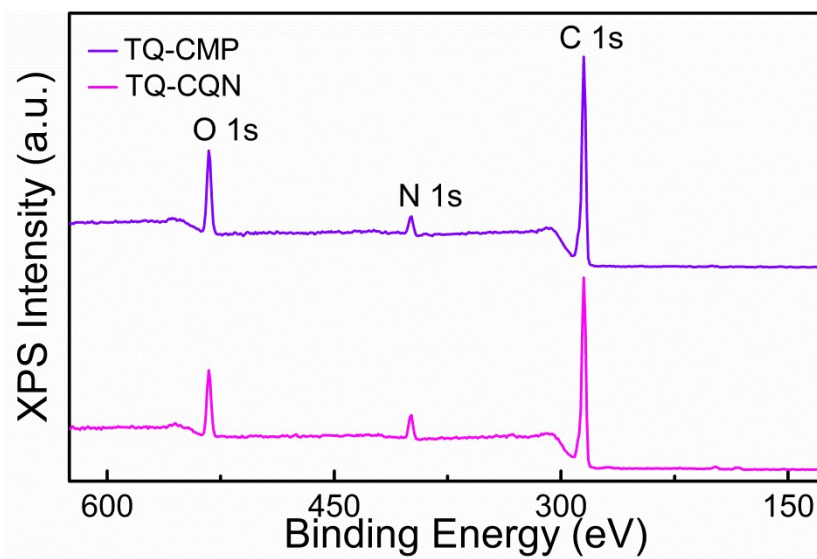


Fig. S6. TQ-CMP and TQ-CQN XPS results of O1s, C1s and N1s spectra.

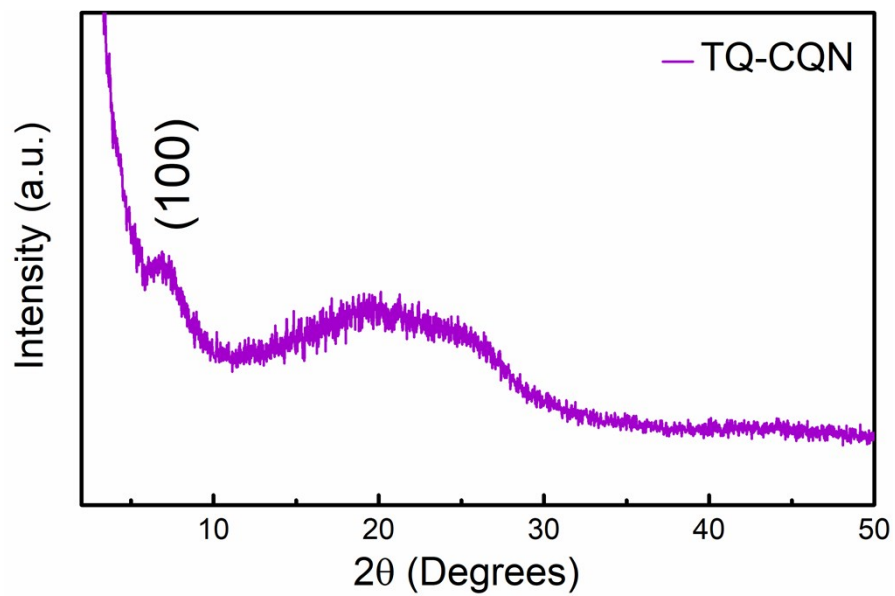


Fig. S7. Powder X-ray diffraction (XRD) patterns of TQ-CQN.

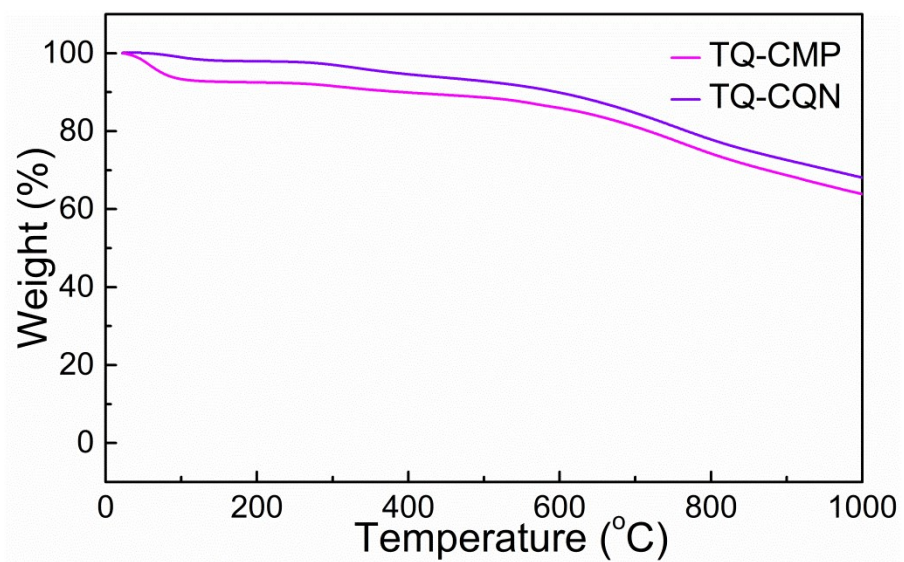
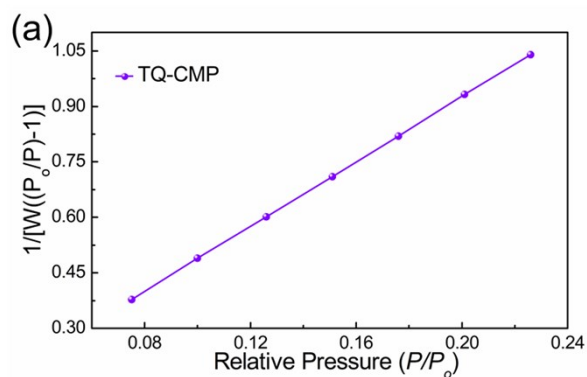
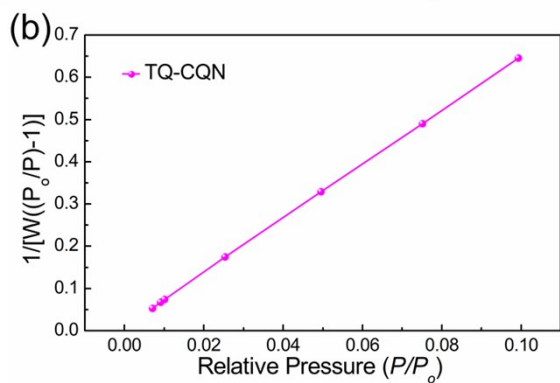


Fig. S8. Thermogravimetric analysis (TGA) of TQ-CMP and TQ-CQN under nitrogen atmosphere at in the range 25 °C to 1000 °C at a rate of 10 °C min⁻¹.



Surface Area = 781.0 m² g⁻¹
 Slope = 4.412 g⁻¹
 Intercept = 4.681e-02 g⁻¹
 Correlation coefficient, r = 0.999991
 C constant= 95.261



Surface Area = 542.8 m² g⁻¹
 Slope = 6.406 g⁻¹
 Intercept = 9.644e-03 g⁻¹
 Correlation coefficient, r = 0.999978
 C constant= 665.301

Fig. S9. BET plots of TQ-CMP (a) and TQ-CQN (b) calculated using N₂ adsorption–desorption isotherms.

Step-1 $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$ Volmer reaction

Step-2 $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$ Heyrovsky reaction

Step-3 $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$ Tafel reaction

Fig. S10. Three primary processes for HER in acidic media.

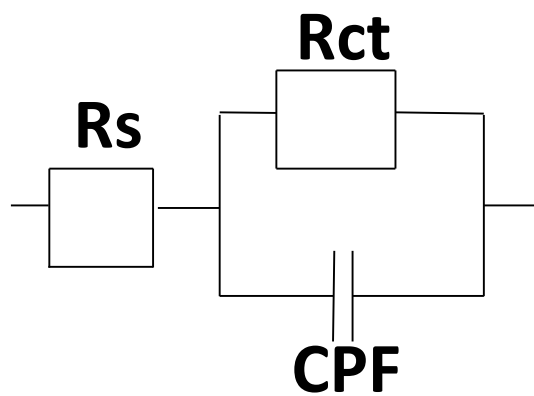


Fig. S11. The equivalent circuits of EIS data for all the catalysts

S4. Supplementary References

- 1 O. Buyukcakil, R. Yuksel, Y. Jiang, S. H. Lee, W. K. Seong, X. Chen and R. S. Ruoff, Synthesis of Porous Covalent Quinazoline Networks (CQNs) and Their Gas Sorption Properties, *Angew. Chem., Int. Ed.*, 2019, **58**, 872–876.