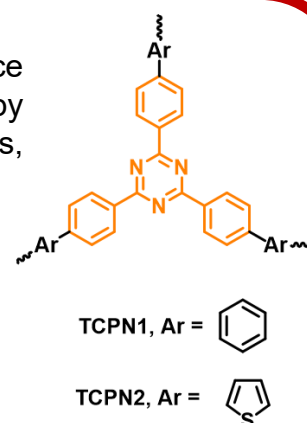


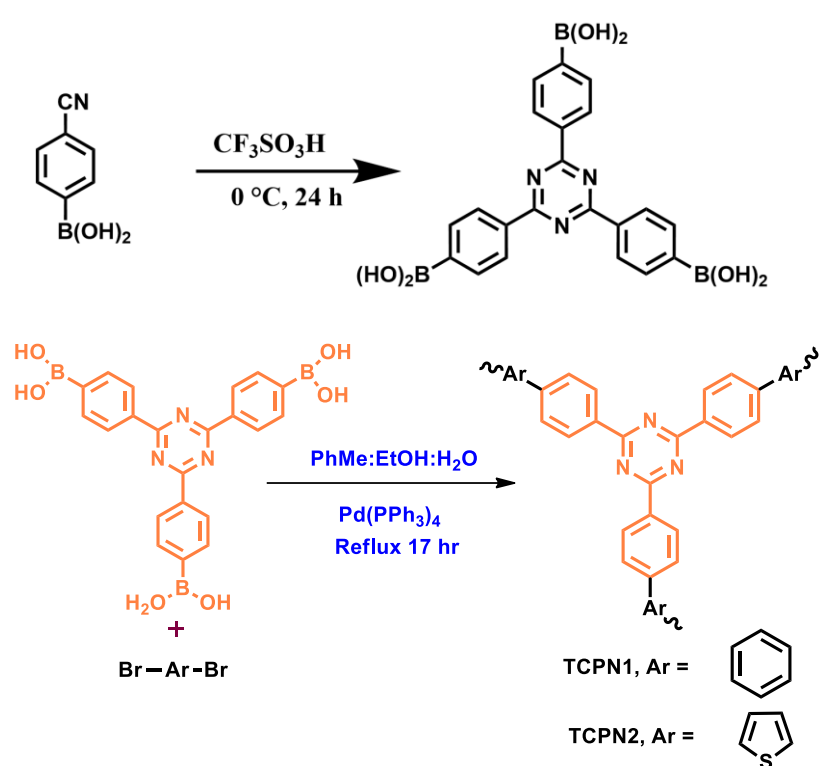
## Introduction

- Conjugated porous organic polymers (CPOPs), a family of lightweight semiconducting polymers with high surface areas, tunable pores, and designable components and structures, comprise organic building units connected by covalent bonds.<sup>1</sup> Due to all these advantages, CPOPs are particularly promising for numerous potential applications, including catalysis,<sup>2</sup> gas storage,<sup>3</sup> lithium batteries, sensing, light emission, energy storage, conversion etc.
- Conjugated polymer networks (CPNs), a subclass of CPOPs with amorphous and interconnected network structure are of particular interest. Nitrogen-rich, electron-deficient triazine-based conjugated polymer network (TCPN) with ultra-strong aromatic C=N linkage should be ideal as a versatile platform for heterogeneous catalysis for HER.
- Here, we have synthesized two simple and novel triazine-based CPNs - TCPN1 and TCPN2, by coupling a triazine acceptor core with phenyl (donor) or thiophene (donor) units, respectively, via a phenyl spacer. Their HER performance was systematically evaluated experimentally in acidic media.



## Synthesis of TCPNs

- TCPNs, they were synthesized from their respective monomer through a Pd-catalyzed cross-coupling reaction between aryl dibromide and ((1,3,5-Triazine-2,4,6-triyl)tris-(benzene-4,1-diyl))triboronic acid (TBBA)



## Characterization of TCPNs

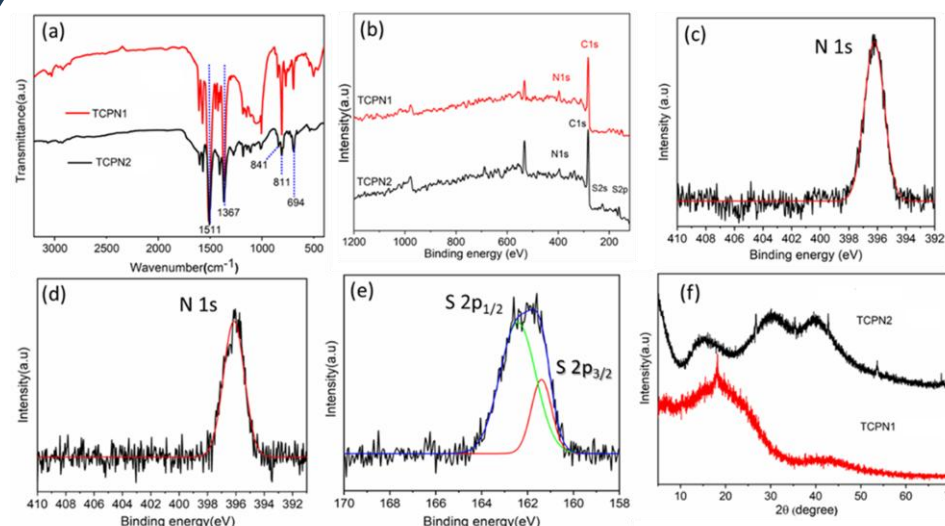


Figure1: (a) FTIR spectra of TCPN1 and TCPN2, (b) XPS survey spectra (c) N 1sXPS spectra of TCPN1 (d) N 1s XPS spectra of TCPN2 (e) S 2p XPS spectra of TCPN2 (f) PXRD pattern of TCPN1 and TCPN2.

- FTIR study:** Triazine ring incorporation into both polymers by high levels of polymerization is clearly demonstrated by the strong signals at 1511 cm<sup>-1</sup>, 1367 cm<sup>-1</sup>, and 811 cm<sup>-1</sup> that correspond to the triazine ring.
- XPS survey and high resolution spectra** reveal the inclusion of triazine ring in both TCPN and thiophene ring in TCPN2 through high degree of polymerization.
- The powder X-ray diffraction (PXRD) analysis revealed amorphous structure.

### Further characterization performed

- FESEM and TEM image show Interconnected porous nanostructure
- TCPN1 and TCPN2 exhibit BET surface area of 59.55 m<sup>2</sup>/gm and 92 m<sup>2</sup>/gm respectively with average pore of 2.44 and 2.40 nm respectively.

## Electrocatalytic activity toward hydrogen evolution (HER)

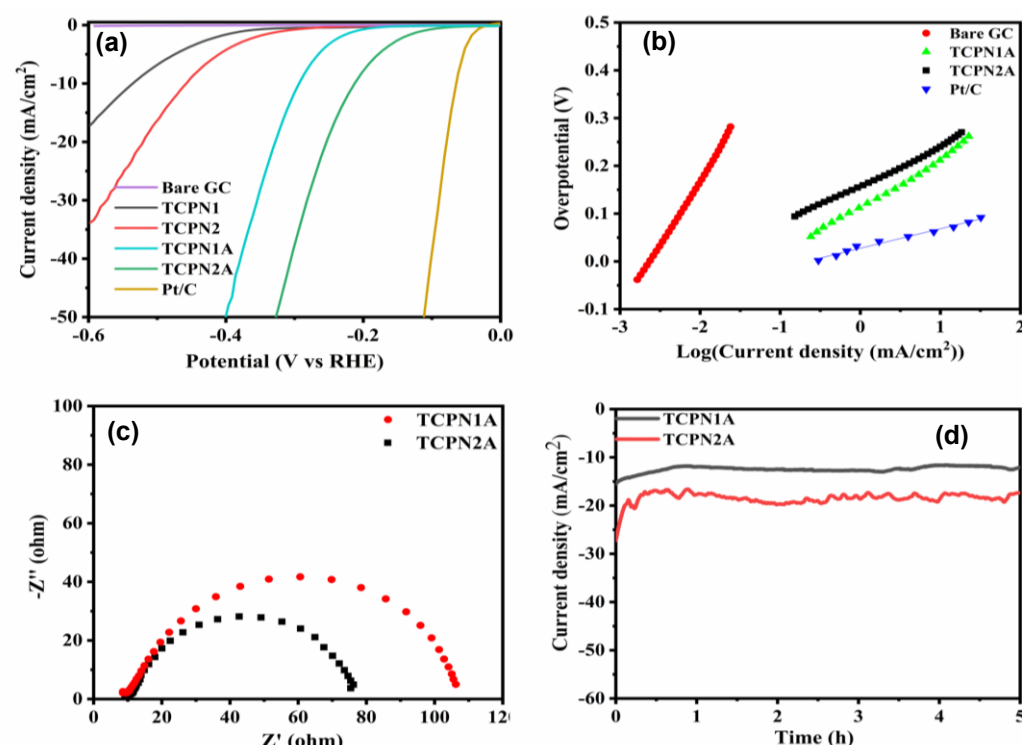


Figure 2: (a) LVS polarization plot for hydrogen evolution reaction of different samples at a scan rate of 5 mV/s in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. (b) Tafel plots. (c) Impedance spectra (Nyquist plot) of TCPN1A and TCPN2A catalyst. (d) Chronoamperometric plot of TCPN1A and TCPN2A catalyst.

- Pristine TCPN1 and TCPN2 exhibited large over potential of 535 mV and 457 mV towards HER indicating poor electrocatalytic activity
- Electrochemical activation of both TCPNs was done by performing chronoamperometry at -0.40 V vs RHE for 5 hr.
- The activated catalyst shows dramatic improvement in catalytic activity through reduction of overpotential from 535 and 457 mV to 293 and 211 mV for TCPN1 and TCPN2 respectively.

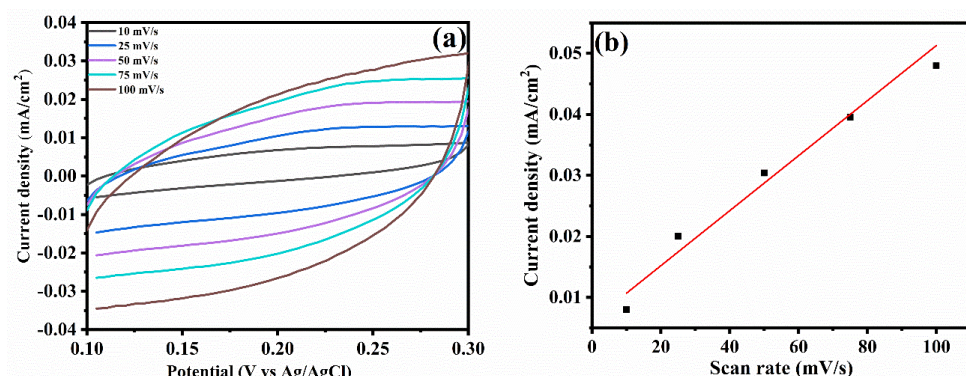


Figure 3: Cyclic Voltammogram of (a) TCPN2A at different scan rate of 10 mV/S-100 mV/s (b) Current densities at different scan rate of TCPN2A catalyst materials.

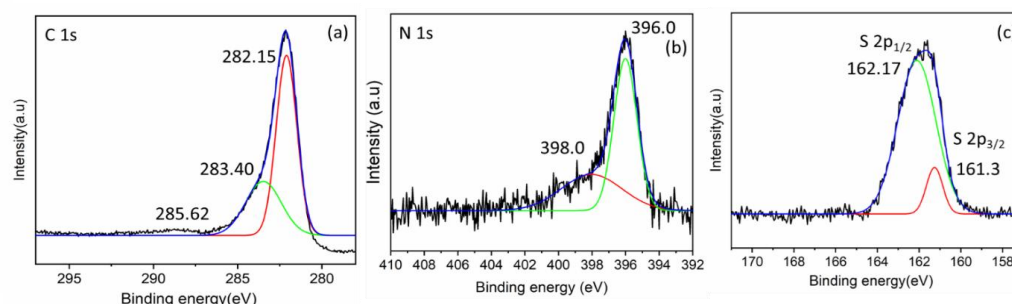


Figure 4: High-resolution XPS spectra of TCPN2A (a) C 1s XPS spectra of TCPN2A (b) N 1s XPS spectra of TCPN2A (c) S 2p XPS spectra of TCPN2A.

- The deconvoluted N 1s peak for TCPN2A was observed around 396.0 eV with an additional significant peak at 398.0 eV compared to pristine TCPN2. The peak at 398.0 eV corresponds to -NH- group clearly indicate the hydrogenation of the triazine ring during electrochemical activation.
- We have performed Density functional theory (DFT) calculations which indicate enhancement of HER activity in both the TCPNs after hydrogenation of the triazine ring.

## SUMMARY

- We have designed two triazine-based conjugated polymer networks TCPN1 and TCPN2 for HER electrocatalyst.
- The electrochemical activation of TCPNs were performed by applying cathodic polarization which effectively results hydrogenation of the TCPN as confirmed by XPS and FTIR study.
- The activated catalyst shows dramatic improvement in catalytic activity through reduction of overpotential from 535 and 457 mV to 293 and 211 mV for TCPN1 and TCPN2 respectively with improvement of other electrochemical parameters like Tafel slope and electrochemical active surface area.

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