

Supplementary Information

Synergistic Reductive Catalytic Effect of Organic and Inorganic Hybrid Covalent Organic Framework for Hydrogen Fuel Production

Sonia Rani,^a Muhammad Nadeem,^b Mazen R. Alrahili,^c Marwan Shalash,^d Moazzam H. Bhatti,^b Khurram Shahzad Munawar,^{e, f} Muhammad Tariq,^{a*} Hafiz Muhammad Asif,^{a*} Zeinhom M. El-Bahy,^g

a. Inorganic Research Laboratory, Institute of Chemical Sciences, Bahauddin Zakariya University Multan, 60800, Pakistan.

b. Department of Chemistry, Allama Iqbal Open University, Islamabad, Pakistan.

c. Physics Department, School of Science, Taibah University, Janadah Bin Umayyah Road, 42353, Medina, Saudi Arabia.

d. Department of Chemistry, College of Science and Arts, Northern Border University, Arar 9280, Saudi Arabia.

e. Institute of Chemistry, University of Sargodha, 40100 Punjab, Pakistan.

f. Department of Chemistry, University of Mianwali, 42200 Punjab, Pakistan.

g. Department of Chemistry, Faculty of Science, Al-Azhar University, Nasar City 11884, Cairo, Egypt.

EXPERIMENTAL DETAILS

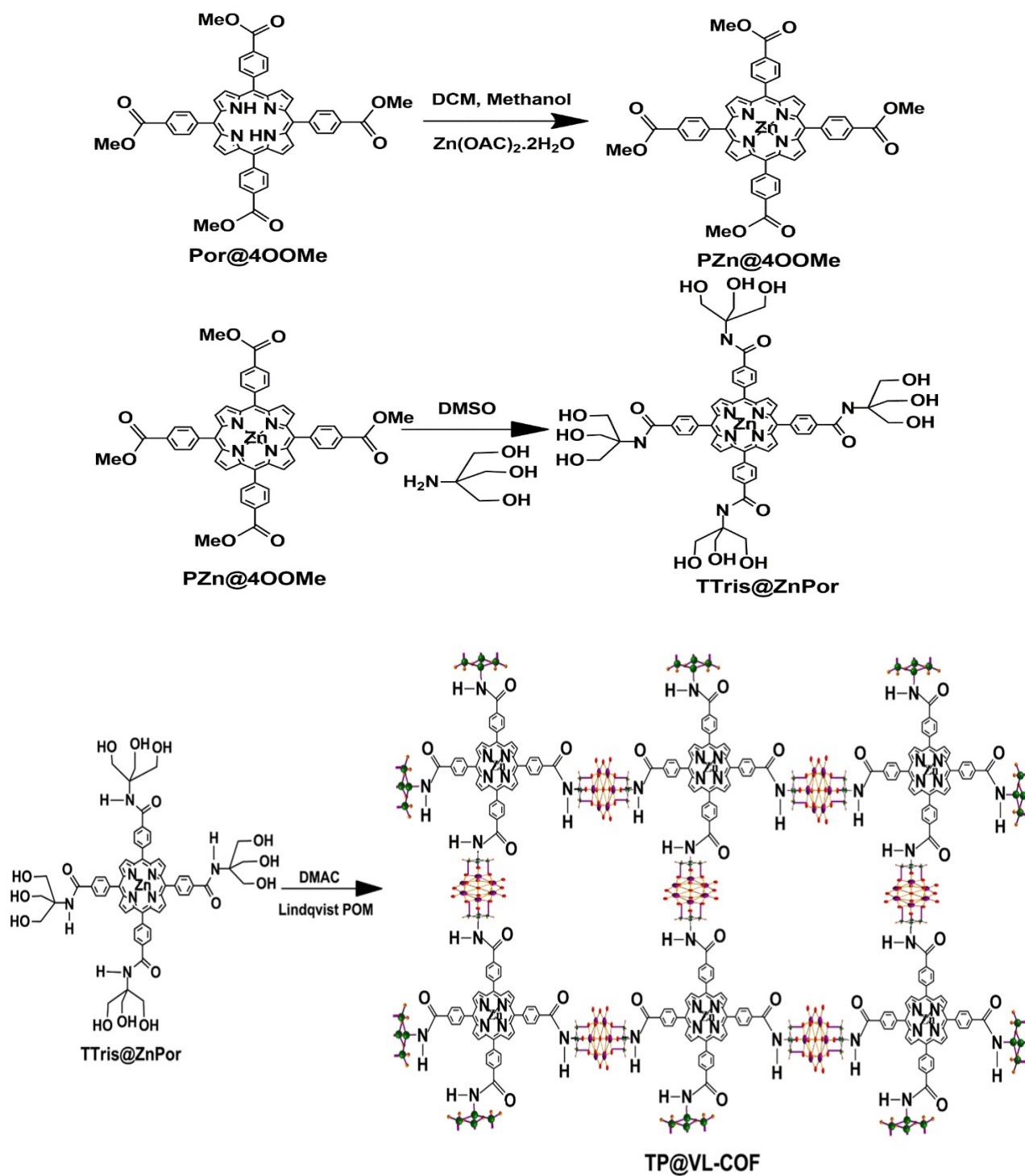
Synthesis of PZn@4OOME

A uniform mixture of 60ml dichloromethane and 70ml methanol was made with 0.036g (1 eq.) of P@4OOME¹ and 0.01g (1 eq.) of Zn(OAc)₂·2H₂O respectively. The solution was stirred constantly at room temperature for 3.5 hours. After the stirring period, the solvent was evaporated with a rotary evaporator and the residue was dried and redissolved in 100 mL of dichloromethane. The compound was then rinsed three times, once with 100ml distilled water and twice with 100ml of a concentrated aqueous KHCO₃ and NaCl solution and finally again with 100ml distilled water. This technique produced a purple powder containing zinc.

Synthesis of TTris@ZnPor

In a round-bottom flask, dissolve 0.05g (4 eq.) of tris(hydroxymethyl) aminomethane, 0.1g (1 eq.) of PZn@4OOME and 0.05g (4 eq.) of K₂CO₃ in 3ml of dried DMSO. The mixture was then heated to 85°C and agitated constantly for 17 hours in a nitrogen environment, covered from

light by Al-foil. After heating, the mixture was let to cool to room temperature. It was then gradually added dropwise to 100mL of cooled distilled water. The resultant purple substance was centrifuged and vacuum-dried.



Scheme S1: The step-by-step pictorial illustration for the synthetic process for TP@VL-COF

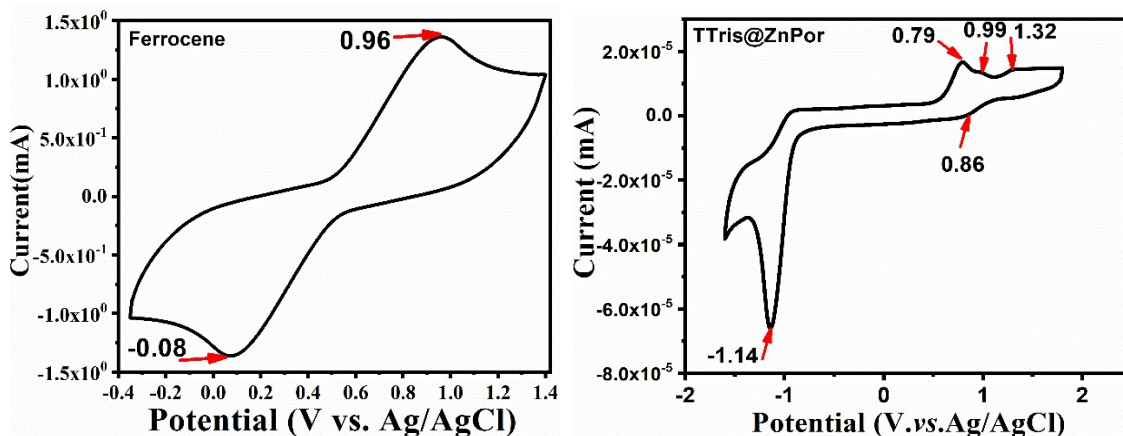
Table S1: Fourier Transform Infrared Spectroscopic (FT-IR) spectrum data of lindqvist POM, TTris@ZnPor, and TP@VL-COF with required assignments.

Lindqvist POM	TTris@ZnPor	TP@VL-COF	Assignments	Abbreviations
---	3600-2800	---	$\nu(\text{O-H})$	ν =stretching vibration
3649, 3586, 3473	3628, 3549	3649, 3511	$\nu(\text{N-H})$	dep=deprotonated form of pyrrole
2966, 2933, 2874	2922, 2885, 2852	2964, 2935, 2874	$\nu(\text{C-H})$ Phenyl, TBA ⁺ [Bu ₄ N] ⁺	δ =bending vibration(in plane)
----	1635	1637	$\nu(-\text{HN-C=O})$	Py=pyrrole
----	995	998	$\nu(\text{N-Zn})$	asy=asymmetric
----	1541-1464	1577-1458	Phenyl	sy=symmetric
----	1402	1396	$\nu(\text{Py half ring})_{asy}^{pro}$	bre=breath
----	1053	1072	$\nu(\text{C-O})$	def=deformation
----	1000	1001	$\delta(\text{Py half ring})_{asy}^{dep}$	[Bu ₄ N] ⁺ = tetra-butyl ammonium cation
954	---	970, 890, 875	$\nu(\text{V=O})$	pro=protonated form of pyrrole
742	---	721, 751, 798	$\nu(\text{V-O-V})$	

Table S2: TP@VL-COF, TTris@ZnPor, and lindqvist POM UV-vis spectral data in DMSO solvent with 1.0x10⁻⁵M concentration and 1cm optical path length, showing wavelength, molar absorptivity and electronic transitions.

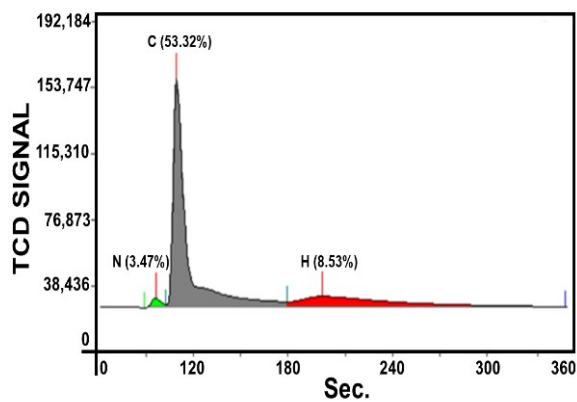
Compounds	Wavelength (λ_{max} , nm), Absorptivity (ϵ , M ⁻¹ cm ⁻¹)	Electronic Transitions
Lindqvist POM	294 (2.95×10 ⁵)	LMCT(O →V)

TTris@ZnPor	430.5 (1.66×10^5), 560.5 (0.87×10^6), 601 (0.47×10^6)	$S_0 \rightarrow S_2$, $S_0 \rightarrow S_1$
TP@VL-COF	430 (1.02×10^7), 563 (0.62×10^6), 604 (0.43×10^6)	LMCT, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_1$



(a)

(b)



(c)

Figure S1: Cyclic voltammograms of Ferrocene(a) and TTris@ZnPor(b) in DMF/CH₃CN(v/v = 1:1). (c) Elemental analysis chromatogram of TP@VL-COF for carbon, hydrogen and nitrogen.

Table S3: HOMO and LUMO energy levels data, band gap energy (E_g) attained from Tauc's plot of TTris@ZnPor, TP@VL-COF, and lindqvist POM.

Compound name	Band gap E_g ^(a) (eV)	HOMO ^(b) (eV)	LUMO ^(c) (eV)	E_{red} (onset) ^(d)
TTris@ZnPor	2.82	-6.12	-3.3	-1.14
TP@VL-COF	2.832	-6.32	-3.49	-0.87
LindqvistPOM	3.09	-7.02	-3.93	-0.43

Data was estimated (a) obtained direct bandgap energy from Tauc plot, (b) calculated from $HOMO = LUMO - E_g$ (eV), (c) examined from equation (2), and (d) obtained from CV results.

Table S4: Powder X-ray diffraction (PXRD) spectrum calculated data of TP@VL-COF using W-H Plot Method (Cu-K α , $\lambda = 1.54056\text{\AA}$).

Peak Position (2θ) ^o	FWHL(β) ^o	$\beta\cos\theta$	$4\sin\theta$	Strain(ϵ)	Crystal Size (D)(nm)
20.0237	0.984	0.016904	0.695058		
24.355	0.492	0.00839	0.843343		
27.1949	0.1968	0.003337	0.939928		
28.7836	0.5904	0.009976	0.993712		
30.010	0.3444	0.005803	1.035104	0.00177	14.45
33.0199	0.246	0.004115	1.136167		
36.448	0.1968	0.003261	1.250319		
48.4671	0.2952	0.004696	1.641046		
54.3839	0.492	0.007635	1.827036		

56.0406	0.5904	0.009093	1.878262
58.2445	0.492	0.007499	1.945798
62.5641	0.1968	0.002934	2.076059
73.1688	0.5904	0.008272	2.382985
75.9565	0.36	0.004951	2.46039

Table S5: Powder X-ray diffraction (PXRD) crystallinity percentage of TP@VL-COF attained via W-H Plot Method.

Compound	TP@VL-COF
Area of Crystalline Peaks	20.96463
Area of all Peaks	28.03379
Crystallinity %	75%

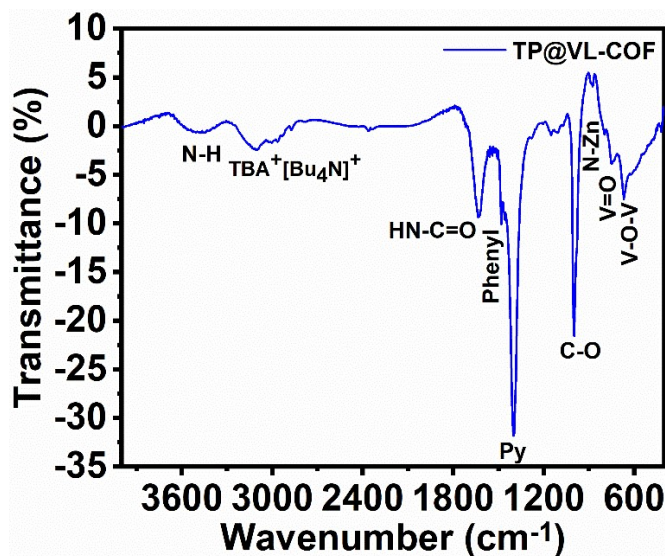


Figure S2: Fourier Transform Infrared Spectroscopic(FT-IR) spectrum of TP@VL-COF.

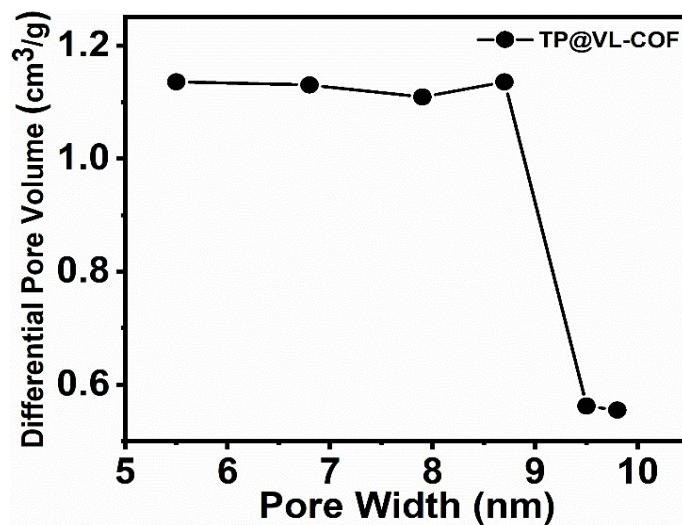


Figure S3: Pore size distribution(PSD) curve for TP@VL-COF calculated from Non-Local Density Functional Theory (NLDFT).

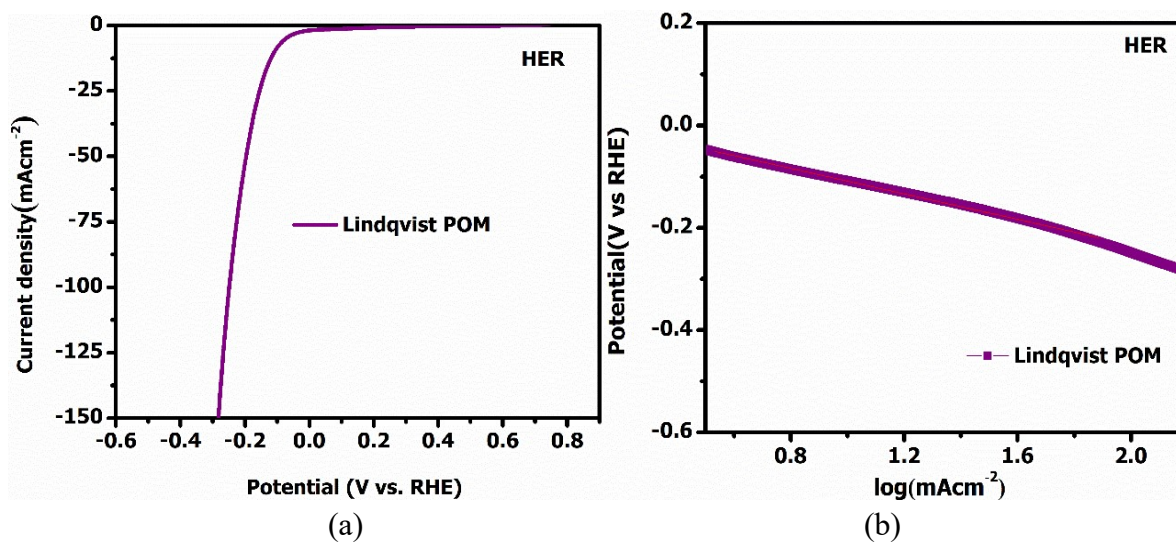


Figure S4: Electrocatalysis observations for Lindqvist POM in alkaline medium(1M KOH) at 10mVs⁻¹ scan rate. (a) LSV curve or HER (b) Tafel plot for HER.

REFERENCES

1. H. M. Asif, A. Iqbal, Y. Zhou, L. Zhang, T. Wang, M. I. U. Farooqi, R. Sun, *Dyes and Pigments* **2021**, *184*, 108758.