Supporting Information

Bio-inspired Electro Active Polymeric Benzimidazole Phthalocyanine: A Sustainable Electrocatalyst for Enhanced Hydrogen Evolution Reaction

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Experimental section

Materials: Ortho-phenylenediamine, OPDA ($C_6H_4(NH_2)_2$), salicylic acid ($C_7H_6O_3$), 4-nitrophthalonitrile (>98%), 4-bromophenol (C_6H_5BrO), cobaltous chloride hexahydrate ($Co(II)Cl_2.6H_2O$, 99.9%), hydrochloric acid (HCl), potassium carbonate (K_2CO_3), dimethyl formamide, DMF ($HCON(CH_3)_2$), 1-pentanol ($C_5H_{12}O$,>98%), 1,8-diazabicyclo[5,4,0] undec-7-ene DBU, dimethyl sulfoxide DMSO (C_2H_6OS), methanol (CH_3OH, 99.8%), acetone (C_3H_6O, 99.5%), hexane (C_6H_{14}, 98.5%), ethanol (C_2H_5OH, 99.5%), chloroform ($CHCl_3$, 99.5%), tetra-butylammonium perchlorate (TBAP), potassium hexacyanoferrate(II) [$K_4Fe(CN)_6$] were purchased from Sigma-Aldrich, India and SD Fine, India. Double-distilled water was used for all the reactions and experiments.

Characterization techniques:

The synthesized poly[Co(II)TBBImPc] complex was analyzed by UV-visible absorption spectroscopic technique using an Ocean Insight Spectrometer (FLAME-SUV-VIS-ES; Serial no. FLS 04808). The poly[Co(II)TBBImPc] complex in DMSO (5 mg/10 mL) was used for recording the electronic absorption spectrum in the region of 300-800 nm. The FT-IR spectra of the ligands (i)-(iii) and poly[Co(II)TBBImPc] compound were recorded on a PerkinElmer Spectrum in the wavenumber range of 400-4000 cm^{-1} using the KBr pellet method. The mass spectra (2.5 kV, electron impact mode) were measured with Mass spectrometer-MS model: Waters; Synapt G2 High detection Mass spectrometer The thermal stability of polymeric cobalt(II) benzimidazole-substituted phthalocyanine is studied in the temperature range of 50-950 °C with an STA 6000 simultaneous thermal analyzer (PerkinElmer) with a scan rate of 20 $°C.min^{-1}$ under air flow (20 $mL.min^{-1}$). The surface morphology was imaged using a field-

emission scanning electron microscope (FE-SEM, Carl Zeiss, Germany, Model: EVO LS 15) at 30 kV. The transmission electron microscope (HR-TEM) and HAADF-STEM images were recorded using TALOS 200FG2 at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a SPECSMXPS system. The deconvolution of the high-resolution XPS spectral peaks was obtained using XPS peak 4.1 and origin 8.5 software. The Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), and chronoamperometric experiments were performed using an Electrochemical workstation (Potentiostat CH16005E, CH-Instruments, Inc.) controlled by CH-Instruments Software in a standard three electrode system. Here, Ag/AgCl was used as the reference electrode, Pt-wire as a counter electrode, and bare GCE, or modified GCE was used as the current collector working electrode.

Mass and NMR spectroscopic analysis

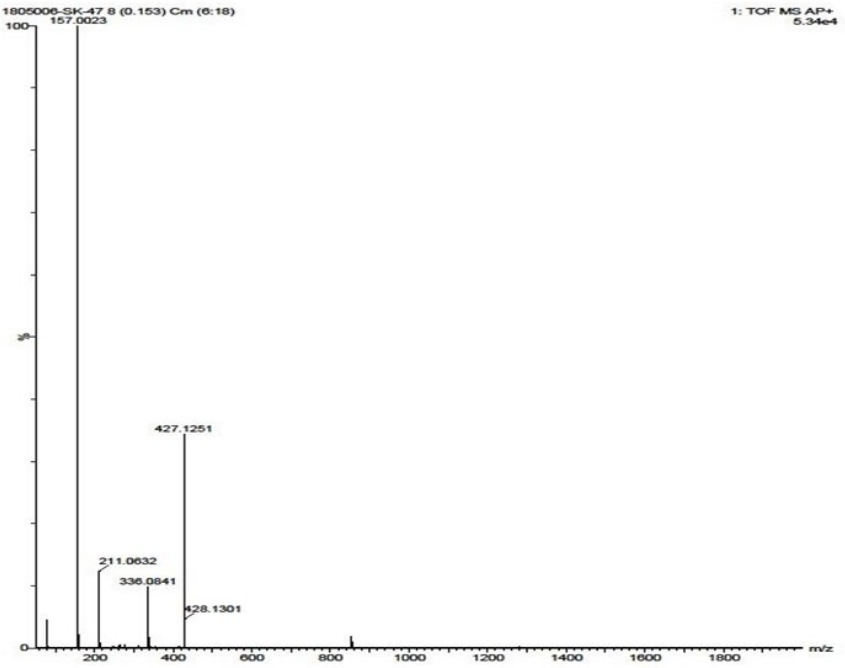

Fig. S1. Mass spectrum of 2-(1H-benzimidazole-2-yl)phenol ligand (*i*), Molecular ion peak at m/z =211 for [M+1H]

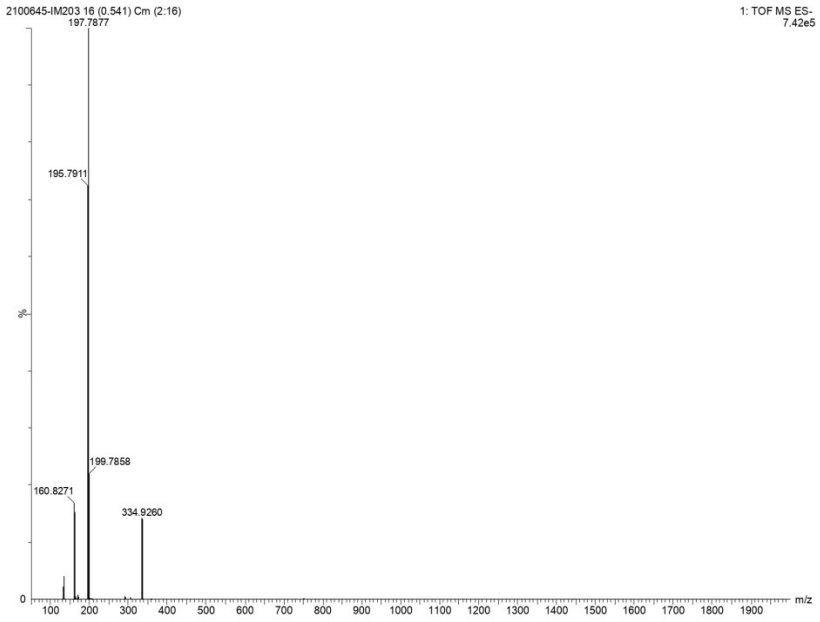

Fig. S2. Mass spectrum of 4-[2-(1H-benzimidazol-2-yl)benzene-1,2-dicarbonitrile] ligand (*ii*), Molecular ion peak at m/z= 334.92 for [M-2H]

NMR spectrum of 4-[2-(1H-benzimidazol-2-yl)benzene-1,2-dicarbonitrile] ligand (*ii*)

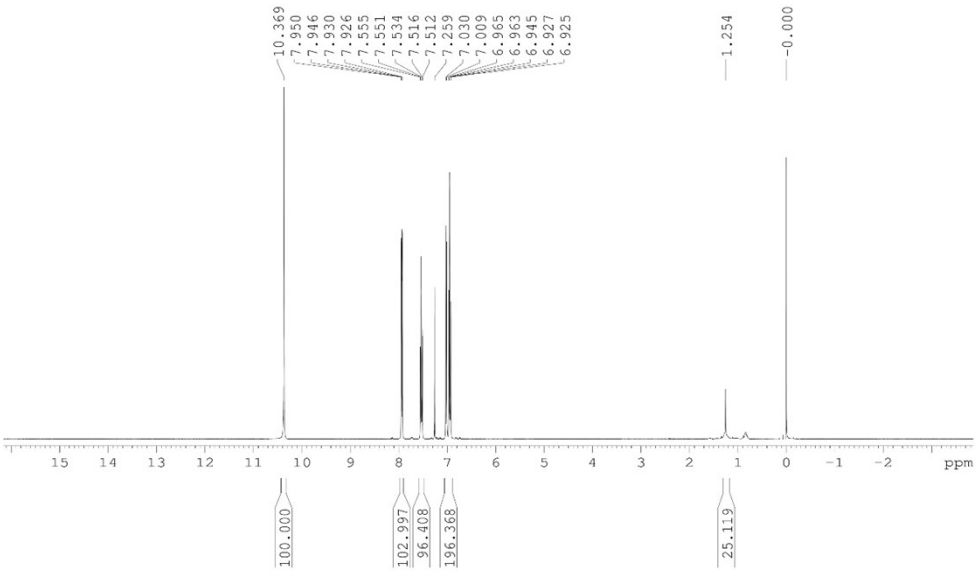

Fig. S3. NMR spectrum of ligand (*ii*)

Ligand (*ii*) Solvent: Chloroform-d

The peak at δ = 10.36 ppm (s, 1H) is due to proton of Ar –NH in the ligand (ii);

Here, the presence of benzimidazole Ar-NH group confirmed the attachment of benzene-1,2-dicarbonitrile at the hydroxyl group substitution and also the absence of peak at δ = 5.40 ppm which is assigned for the –OH group infers the formation of ligand (ii) at the reactive site of –OH functional group; and peaks at δ = 7.950 to 6.925 ppm assigned for Ar –H's of ligand.

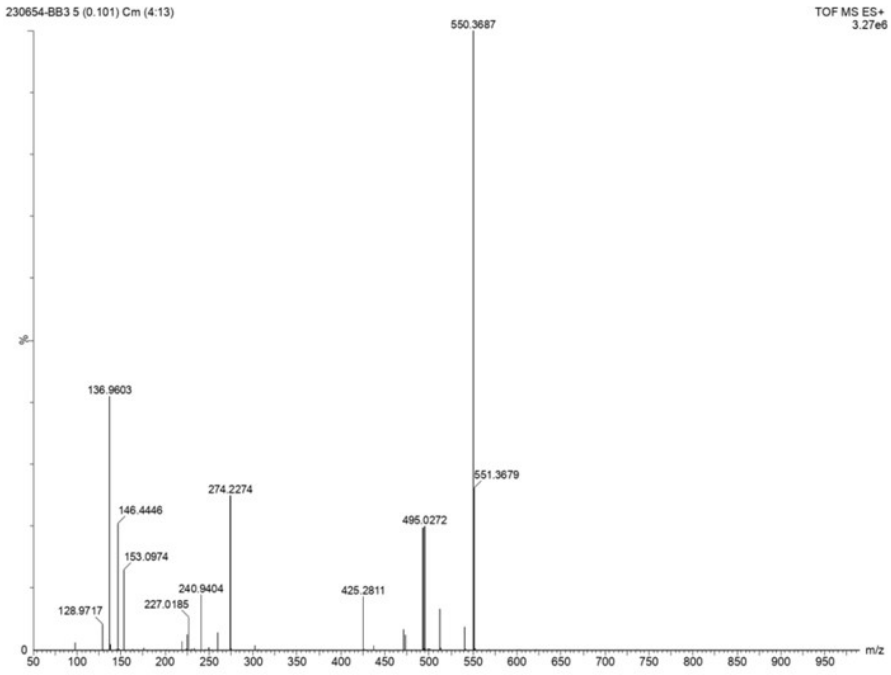

Fig. S4. Mass spectrum of ligand (*iii*) of poly[Co(II)TBBImPc]

Molecular ion peak at m/z= 550.368 for $[M-2H]^{-4}$ and 551.367 for $[M-2H]^{-3}$

NMR spectrum of 4-[2-(1H-benzimidazol-2-yl)benzene-1,2-dicarbonitrile substituted with 4-(4-bromophenoxy)benzene-1,2-dicarbonitrile) ligand (*iii*)

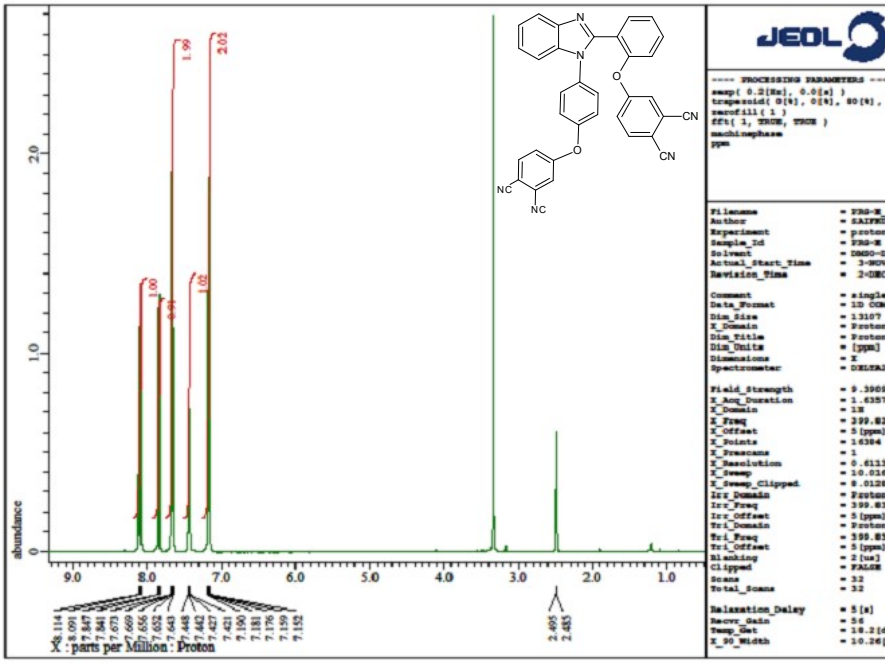

Fig. S5. NMR spectrum of ligand (*iii*)

Ligand (*iii*) Solvent: DMSO-d6

The peak at δ =7.152-8.114 ppm is due to Ar –H in the ligand (iii)

δ = 2.495 ppm assigned for solvent peak.

And no aromatic –NH peak appeared which confirmed the attachment of benzoxy-substituted ligand.

NMR spectrum of 4-(4-bromophenoxy)benzene-1,2-dicarbonitrile) ligand

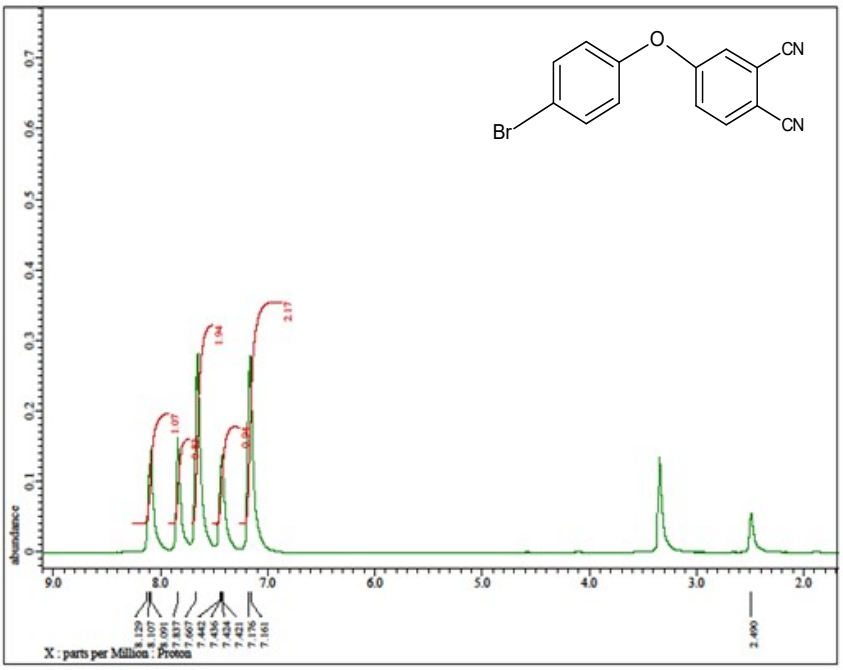

Fig. S6. NMR spectrum of 4-(4-bromophenoxy)benzene-1,2-dicarbonitrile) ligand

Solvent: Deuterated DMSO (DMSO-d6)

Peak at δ = 7.161-8.129 ppm (with different coupling constant values) assigned for Ar-H of the ligand

Peak at δ = 2.490 ppm refers to the DMSO-d6 solvent peak.

The spectrum did not show the –OH peak at 5.13 ppm and it confirmed the formation of phthalonitrile ligand from the bromo-phenol precursor.

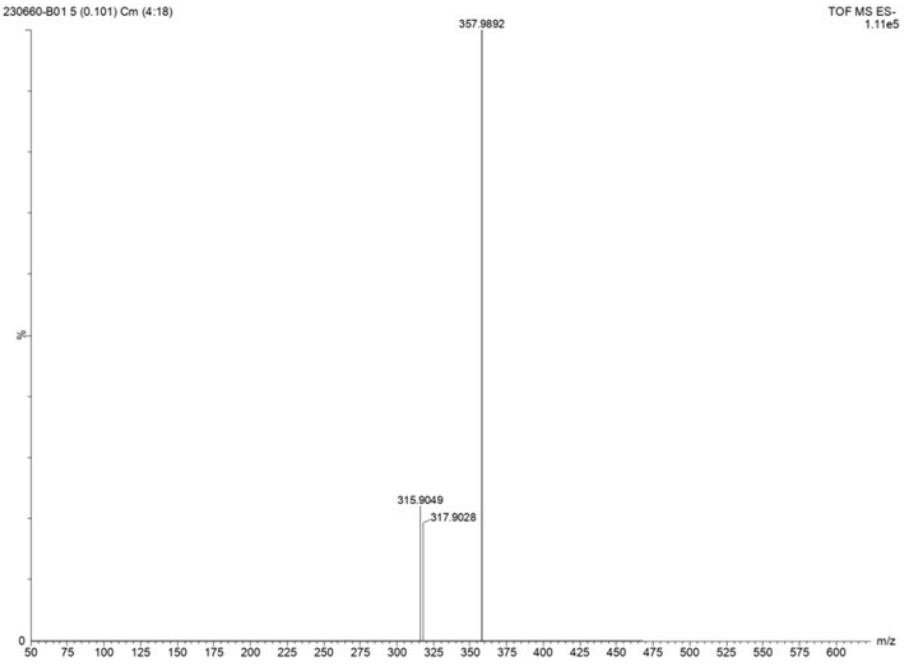

Fig. S7. Mass spectrum of 4-(4-bromophenoxy)benzene-1,2-dicarbonitrile

Molecular weight [M]= 301.13 amu

Molecular ion peak m/z of 317.903 for $[M+H_2O]^{-2}$, 315.90 for $[M+H_2O]^{-4}$ and

Base peak of 357.98 for $[M+3H_2O]^{+2}$

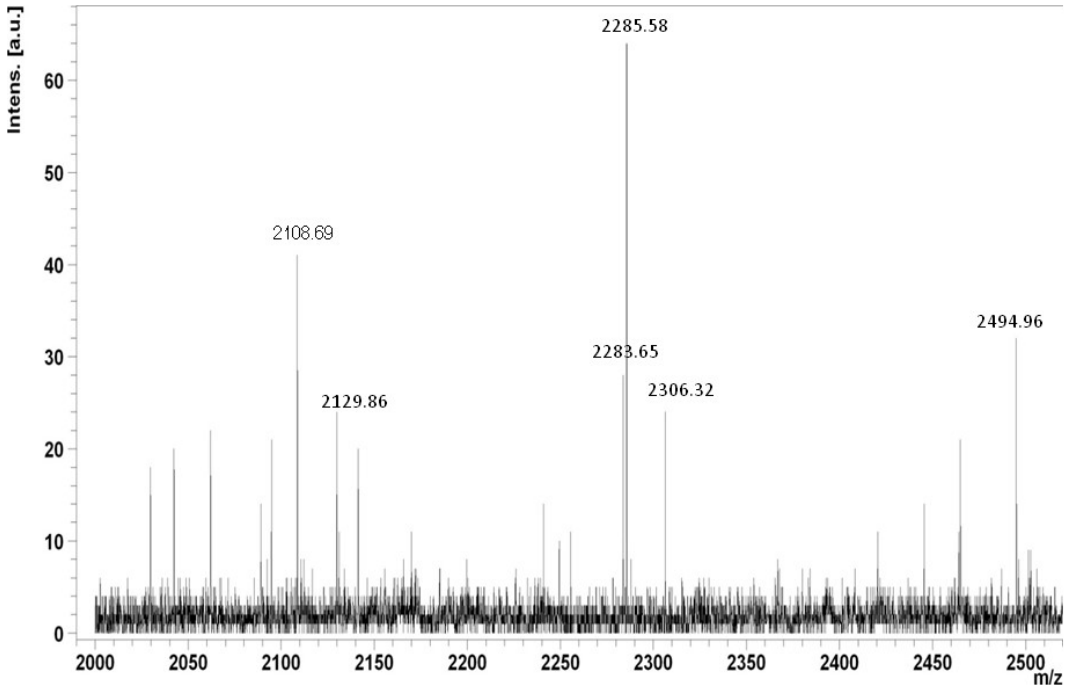

Fig. S8. Mass spectrum of poly[Co(II)TBBImPc]

Molecular weight of monomeric [Co(II)TBBImPc], = 2280.21 amu and Molecular ion peak= 2283.65 for $[M^{+3}]$, and 2285.58 for $[M^{+5}]$

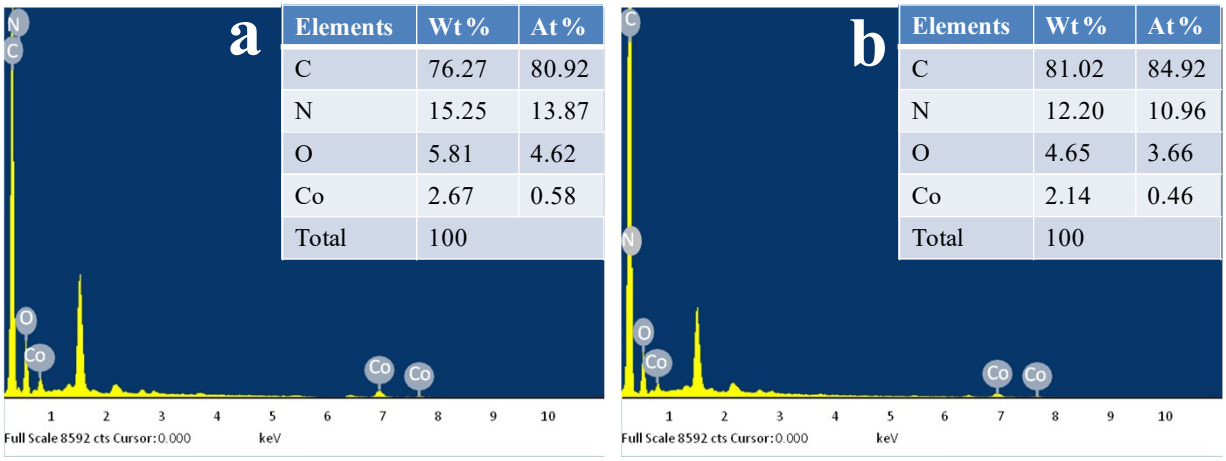

Fig. S9. EDX- spectra of (a) poly[Co(II)TBBImPc] and (b) poly[Co(II)TBBImPc]+KB (4:1 ratio) on Toray carbon

Cyclic voltammetric analysis

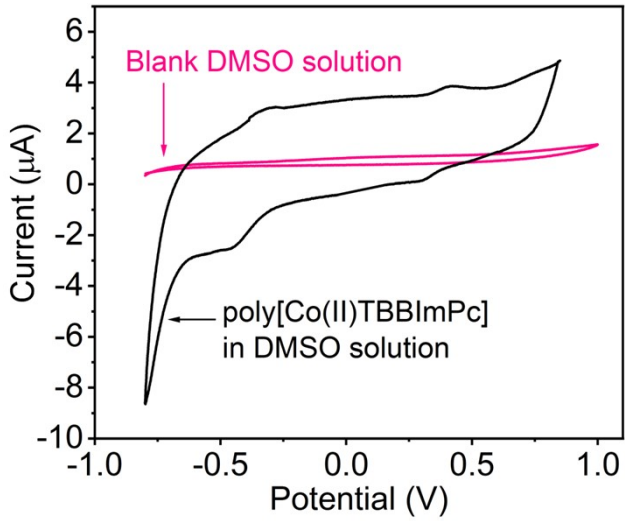

Fig. S10. Cyclic voltammograms of (i) bare GCE and (ii) poly[Co(II)TBBImPc] complex in DMSO with 0.1 M TBAP under the N_2 atmosphere at 50 $mV.s^{-1}$ scan rate.

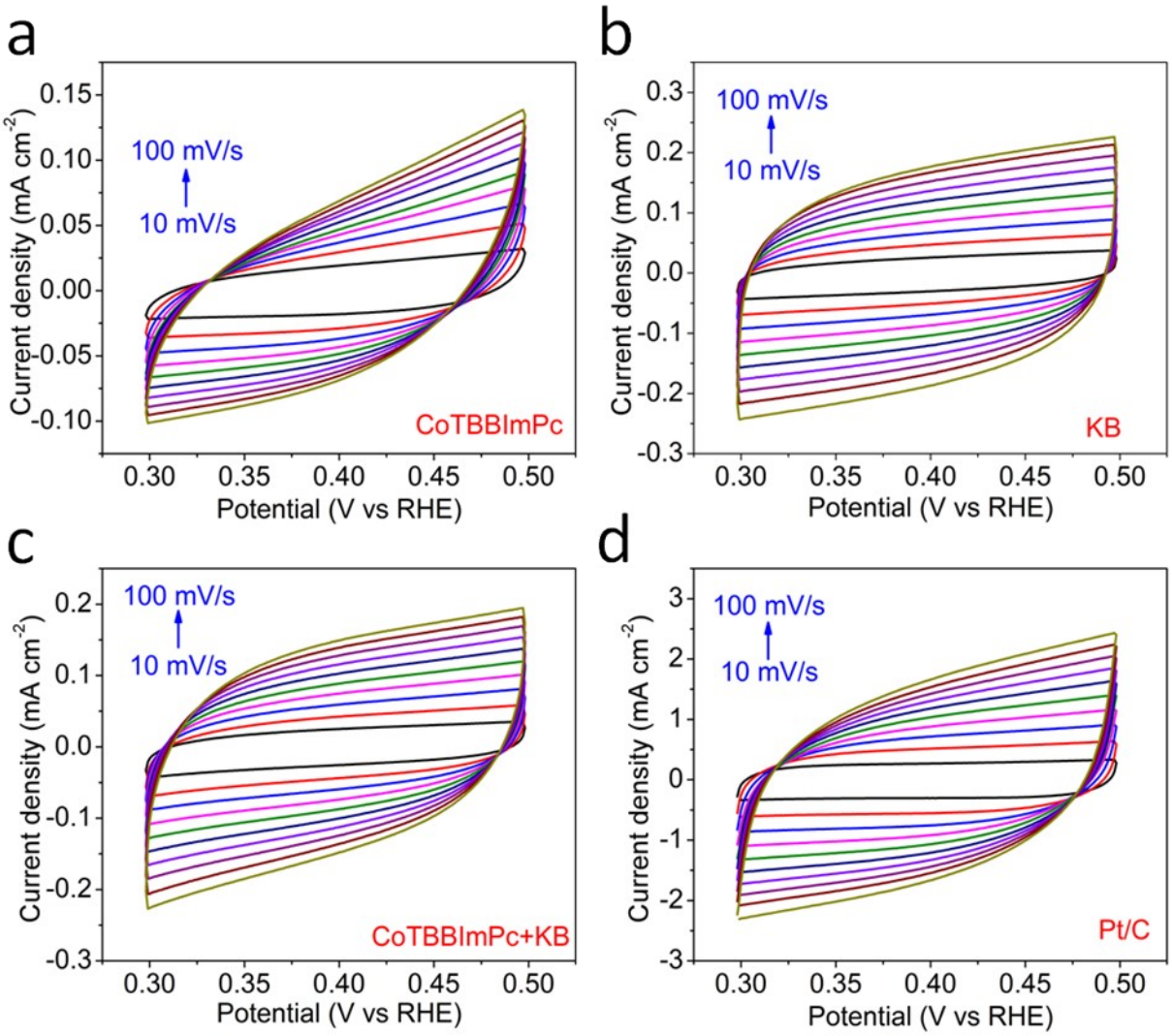

Fig. S11. (a-d) CVs (non-faradic region +0.30 to +0.50 V (vs RHE) for GCE/poly[Co(II)TBBImPc], GCE/KB, GCE/poly[Co(II)TBBImPc]+KB, and GCE/Pt/C electrodes.

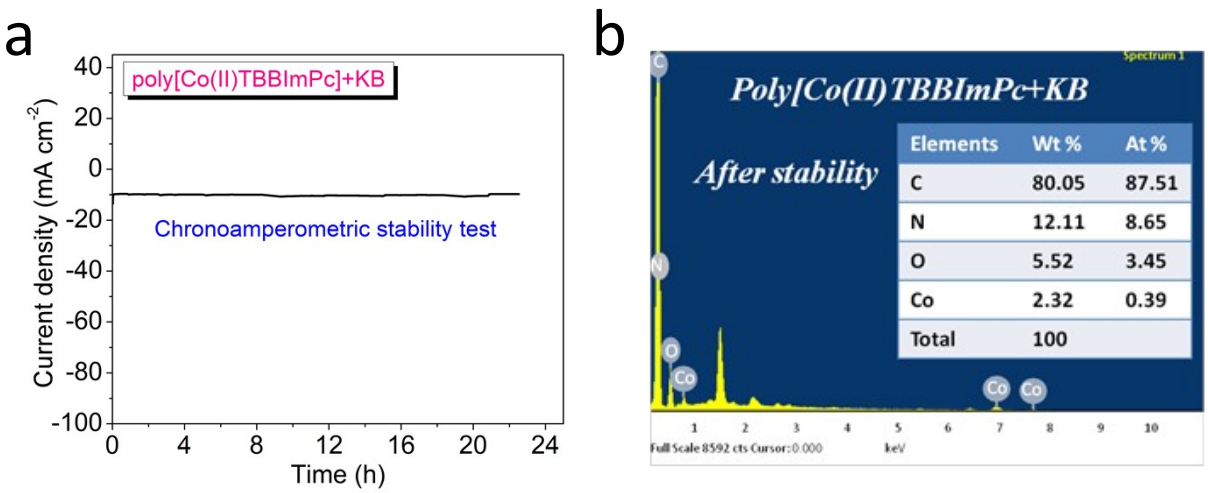

Fig. S12. (a) Stability study for the poly[Co(II)TBBImPc]+KB hybrid electrode at 10 mA cm^{-2} and (b) EDX spectrum of hybrid composite electrode poly[Co(II)TBBImPc]+KB (4:1) after long term stability study test (more than 20 hour) on Toray carbon towards HER in 0.5 M H_2SO_4.

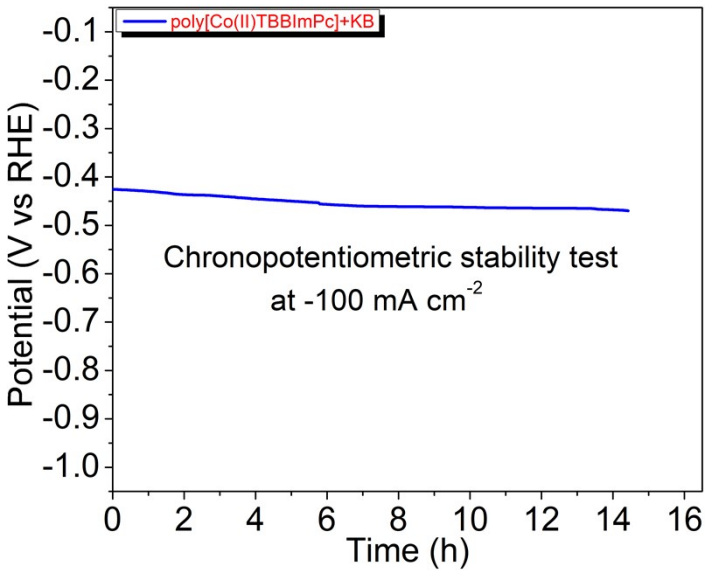

Fig. S13. Stability study for the poly[Co(II)TBBImPc]+KB hybrid electrode at higher current density.

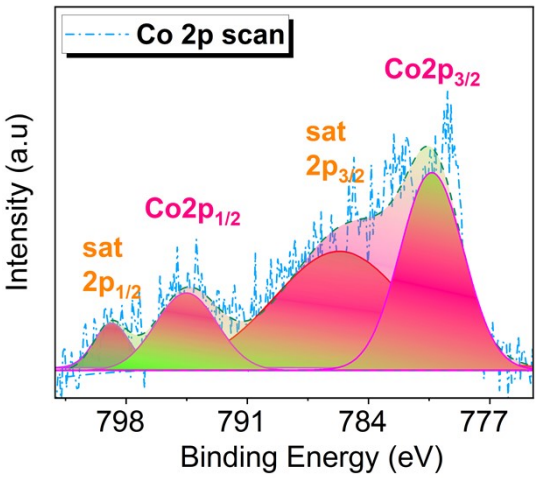

Fig. S14. Post-Chronoamperometry stability study by XPS analysis: XPS Co2p spectrum of poly[Co(II)TBBImPc]+KB (4:1 ratio)

The XPS analysis of poly[Co(II)TBBImPc]+KB after the CA studies (Fig 13) was performed in the region of Co2p which exhibited an area under the curve of 3433.35 with area % of 99.939%. and the corresponding Co $2p_{3/2}$, sat $2p_{3/2}$, $2p_{1/2}$, and sat $2p_{1/2}$ peak areas were 1054.23, 1269.89, 472.23, and 637 whereas no Co^{3+} peak appeared.

Hence, Total Co area = Sum of (Area of all fitted Co2p peaks)

= (Area % Co^{2+} + Area % Co^{3+})

= (Area under the curve of Co $2p_{3/2}$ + sat $2p_{3/2}$ + $2p_{1/2}$ + sat $2p_{1/2}$ in %)

Therefore, % Co^{2+} = [Total Area of Co^{2+} / Total Area of Co] *100

The $Co2p_{3/2}$ peak showed a slight positive shift from 780 to 780.34 eV, while the $Co2p_{1/2}$ peak exhibited a negligible shift from 794.69 to 794.49 eV. Importantly, the characteristic shake-up satellite peaks remain prominent in both cases ($Co2p_{3/2}$ satellite: 785.07 → 785.64 eV; $Co2p_{1/2}$ satellite: 799.67 → 798.85 eV), which is a well-established fingerprint of Co^{2+} species. These results confirm that cobalt retains its +2 oxidation state even after stability testing.

Table S1:

Comparison of HER performance of hybrid composite poly[Co(II)TBBImPc]+KB with various electrocatalysts (in same electrolytic medium) reported in the literature.

Electrocatalyst	**HER electrocatalytic activity**		**Electrolyte**	**Stability**	**Ref**
	Overpotential (mV) at j_{10} (mA cm^{-2}) V vs RHE	**Tafel slope (mV/dec)**			
Co@NG-800	286	118	0.5 M H_2SO_4	3000 cycles	[1]
GO-ZnPc	474	216	0.5 M H_2SO_4	7200 sec	[2]
WS_2-CuPc	285	207	0.5 M H_2SO_4	-	[3]
WS2-ZnPc	233	186	0.5 M H_2SO_4	24 h	[3]
Co-NHPC-900	230	95	0.5 M H_2SO_4	10 h	[4]
FeCo@N–C/KB	240	92	0.5 M H_2SO_4		[5]
CoPc-BCA-D-A-COF	65.9	75.4	0.5 M H_2SO_4	-	[6]
PyCoPc/GO	253	96	1.0 M KOH	-	[7]
FePc-MoS_2	123	32	0.5 M H_2SO_4	20 h	[8]
Pt/C	23.5	29	0.1 M $HClO_4$	29.7% loss in mass activity	[9]

				after 2000 cycles	
poly[Co(II)TBBImPc]+KB	190	32	0.5 M H_2SO_4	23 h	**This work**

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