

Supporting Information

**Non-precious cobalt phthalocyanine embedded iron ore
electrocatalyst for hydrogen evolution reaction**

*Keshavananda Prabhu CP[‡],¹, Shambhulinga Aralekallu[‡],¹, Veeresh A Sajjan¹, Manjunatha
Palanna¹, Sharath Kumar², Lokesh Koodlur Sannegowda^{*,1}*

¹*Department of Studies in Chemistry, Vijayanagara Sri Krishnadevaraya University,
Vinayakanagara, Cantonment, Ballari-583105. Karnataka, INDIA.*

**Email: kslokesh@vskub.ac.in*

²*Department of Mineral Processing, Vijayanagara Sri Krishnadevaraya University, Nandihalli,
Sandur, Ballari, Karnataka, India*

Characterization methods

The Vario EL III CHNS elemental analyzer was used for the elemental analysis. Gravimetric procedure was used to determine the amount of metal content in the macrocyclic complex. Ocean optics spectrometer (serial number: FLMSO 4808 in the region of 300–800 nm) was used for UV-Vis spectral analysis using 0.1×10^{-3} M complex in DMSO. Perkin Elmer Spectrum-Two spectrometer was used for the Fourier transform infrared (FTIR) spectroscopic analysis of the materials using KBr-pellet press method ranging from 4000 - 500 cm^{-1} . The 500 MHz Varian instrument was used for NMR study. 6100 series GC/MS instrument from Agilent technologies was used for the mass analysis. Bruker D8 Advance X-ray diffraction instrument was used for PXRD analysis. STA-6000 machine was used to study the thermal stability from room temperature to 700 °C (heating rate of 10 °C min^{-1}). Electrical conductivity of the phthalocyanine complex and the composite hybrid was measured using the Keithley instrument (2450 source meter).

The electrochemical measurements were performed with a CHI6005E Electrochemical analyzer work station with three electrode setup. The working electrode was a pristine or modified glassy carbon electrode (GCE) with a surface area of 0.071 cm^2 (diameter of the electrode is 3 mm). A graphite rod was used as the counter electrode, Ag/AgCl electrode was employed as the reference electrode. Prior to each experiment, the GCE surface was cleaned by polishing with alumina 0.05 micron (Baikalox, Japan) using polishing pad (Buehler, Ltd.), washed with water and rinsed with the piranha solution (3:1 ratio of H_2SO_4 and H_2O_2) for 10 min. Finally GCE was rinsed sequentially with copious amount of double distilled water (DD water), acetone and ethanol. High purity N_2 was used to remove dissolved O_2 by purging for at least 20 min prior to each electrochemical experiment and the nitrogen atmosphere was maintained over the solution during the measurements. Electrocatalytic measurements were performed using LSV technique.

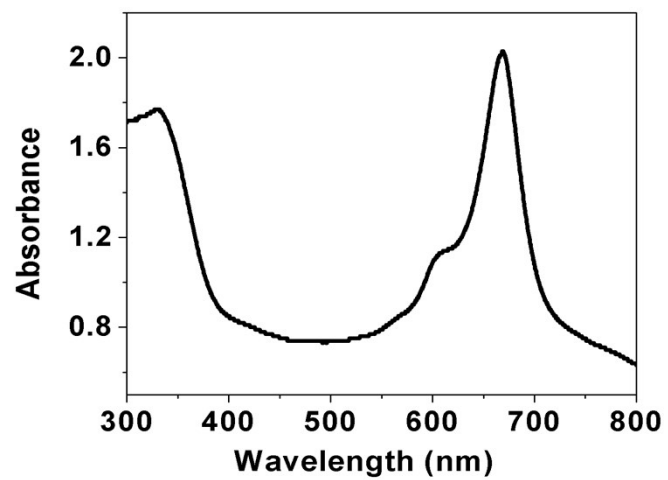


Fig S1. UV-Visible absorption spectrum for CoTBImpc complex.

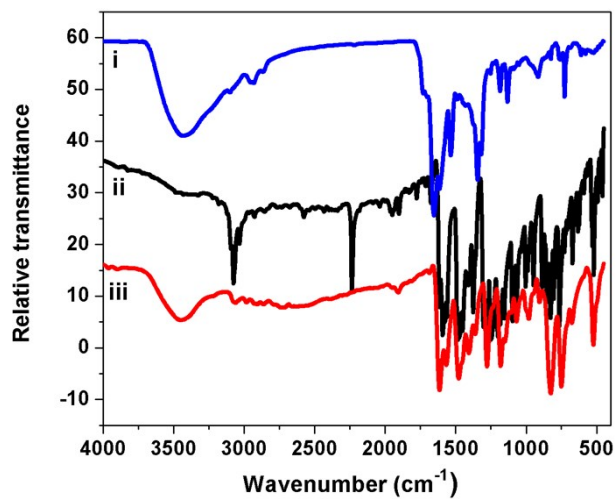


Fig S2. FT-IR spectra of i) precursor, ii) ligand and iii) phthalocyanine complex dispersed in KBr.

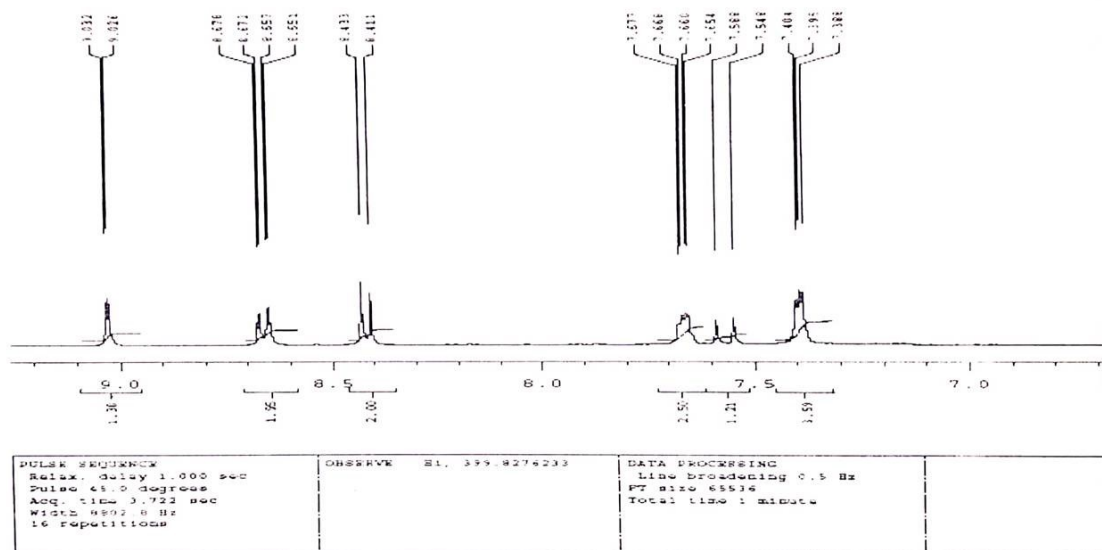


Fig S3. ^1H -NMR spectrum of the precursor ligand compound **ii**.

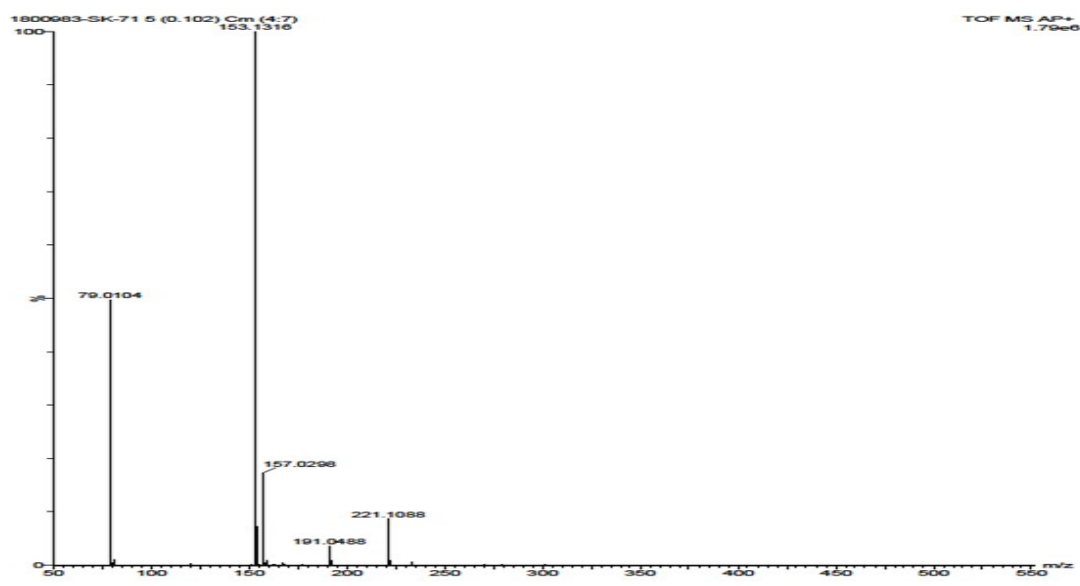


Fig S4. Mass spectrum of the precursor (**i**) with mass fragment (M^{+1}) =221.

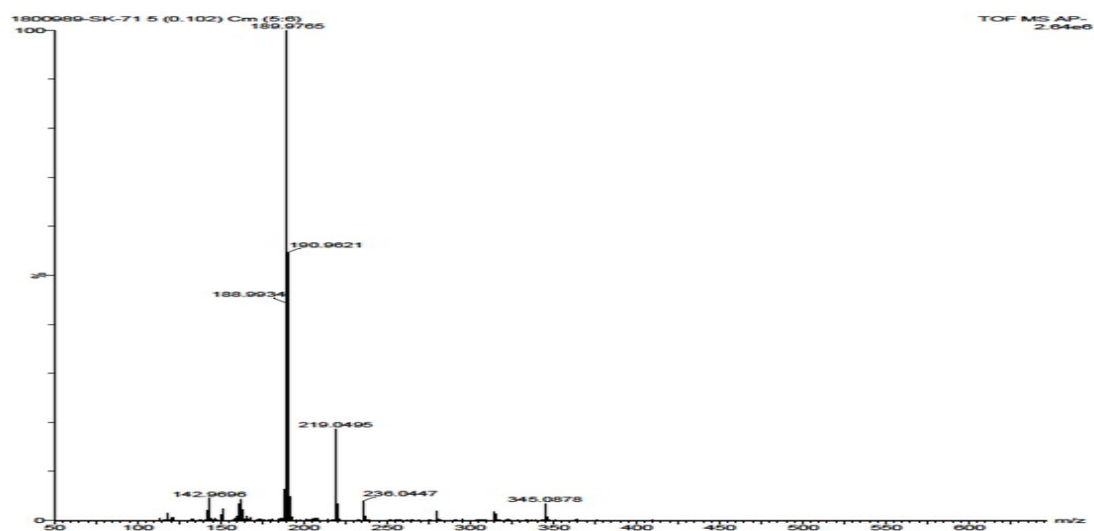


Fig S5. Mass spectrum of the compound (**ii**) with mass fragment (M^{-1}) =345.

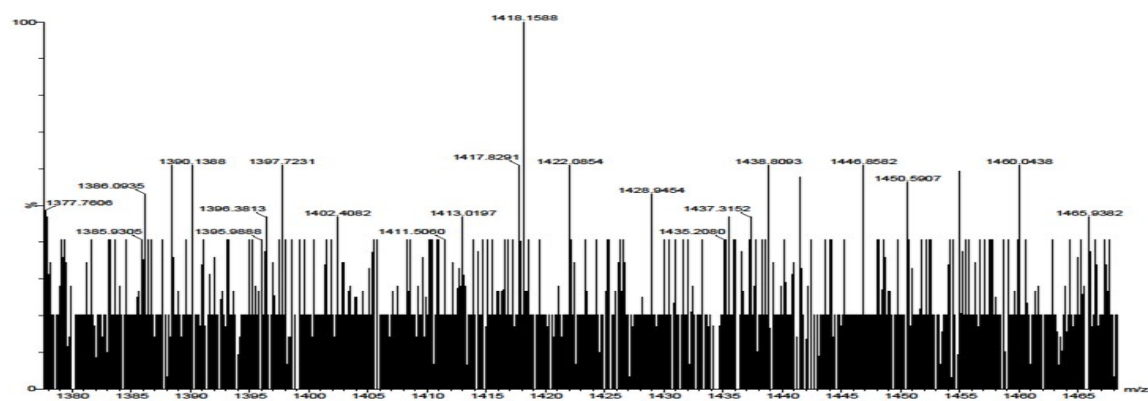


Fig S6. Mass spectrum of the cobalt benzimidazolephthalocyanine complex (**iii**) with mass fragment (M^{+2}) = 1446

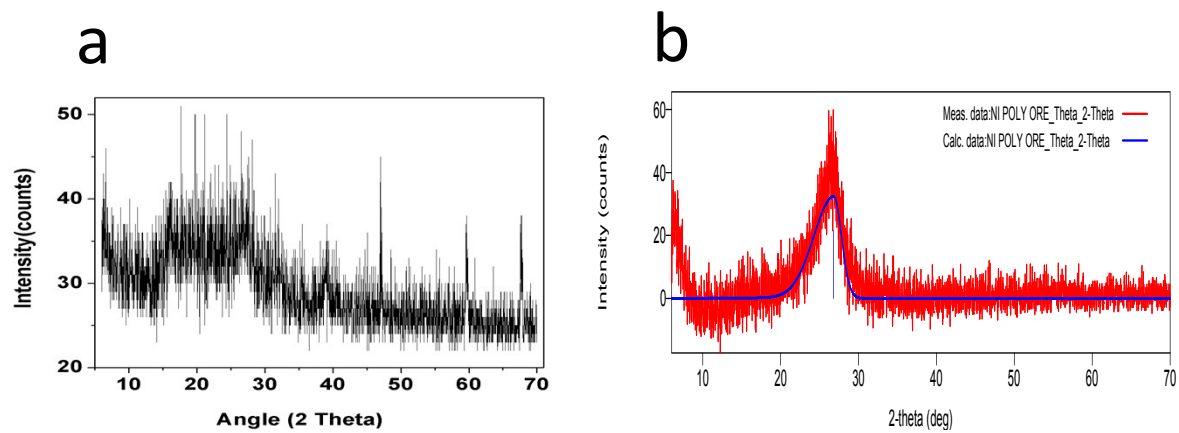


Fig.S7. PXRD pattern for the a) CoTBImPc complex and b) GCE/Fe₃O₄-CoTBImPc composite electrode.

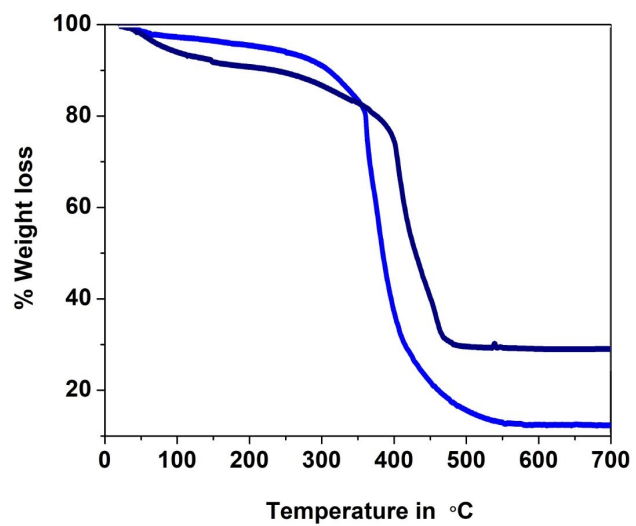


Fig S8. TGA analytical curves for a) CoTBImpc (blue color) and b) Fe₃O₄-CoTBImpc (navy color) composite.