Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2020

Supporting Information

Biologically Inspired Catalyst for Electrochemical Reduction of Hazardous Hexavalent Chromium

Shambhulinga Aralekallu[1‡], Manjunatha Palanna[1‡], Sowmyashree Hadimani[1], Keshavananda Prabhu C P[1], Veeresh A Sajjan[1], Musthafa Ottakam Thotiyl[2], Lokesh Koodlur Sannegowda[1]*

[1]*Department of Studies in Chemistry, Vijayanagara Sri Krishnadevaraya University, Cantonment, Vinayakanagara, Ballari-583105, India*

[2]*Department of Chemistry and Centre for Energy Science, Indian Institute of Science Education and Research (IISER) Pune, Dr. Homi Bhabha Road, Pashan, Pune 411008, India*

Author Information

Corresponding Author
*Address: Department of Studies in Chemistry,
Vijayanagara Sri Krishnadevaraya University, Cantonment, Ballari-583105
Tel: +91 9035500208.
Email: kslokesh@vskub.ac.in

Measurements

The elemental analysis of the synthesized compounds was carried out with CHN&S Elemental Analyzer (Elementar). The metal content of the synthesized compound was determined by using the acid decomposition method. The Lambda 35 spectrophotometer (Perkin-Elmer) was used to extract the UV-visible spectra of the sample in wavelength range of 280-950 nm. FT-IR spectra were collected from Spectrum two FT-IR spectrometer with a resolution of 1 cm^{-1}. The thermo-stability of the synthesized phthalocyanine was measured in varying temperature range 30-800°C using a STA 6000 simultaneous thermal analyzer (Perkin-Elmer) with a scan rate of $10°C·min^{–1}$ under air flow (30 $mL·min^{–1}$). Mass spectrometer (Agilent Technologies) was utilized to record the mass spectra of the synthesized compounds. The ^{1}H NMR spectrum was collected with a Bruker AMX-400 NMR instrument. All electrochemical experiments were carried out using a potentiostat CHI 800 electrochemical workstation (CH Instrument, USA). A standard 3-electrode system was used for the electrochemical experiments with glassy carbon electrode (GCE) modified with iridium phthalocyanine is used as the working electrode, platinum foil as the counter electrode and Ag/AgCl (3M KCl) as the reference electrode. The CVs were recorded from -0.2 to +1.0 V at scan rates of 5, 10, 20, 50, and 100 $mVs^{–1}$.

Fabrication of working electrode

Prior to modification, GCE (3 mm diameter) was polished on micro-cloth pad with 0.3 and 0.05 micron size alumina powder. Then the GCE was sonicated for about ten min for removing the possible adsorbed species. Further, the GCE was rinsed with ethanol, washed with distilled water and dried at room temperature. 5.0 mg of iridium phthalocyanine was dispersed uniformly and homogeneously in 0.5 mL 2-propanol with 50 µL 5 wt% Nafion by sonicating for 20 min. Then 10 µL of the suspension ink was casted onto the cleaned GCE and allowed to dry for 2 h in hot air oven.

Detection procedure

In electrochemical methods, the sensing of toxic Cr(VI) is based on the electrocatalytic reduction of Cr(VI). Therefore, the current response for analyte sample should get stabilized, for measuring the reduction current.. Hence, 5 µL of 1.0 mmol L^{-1} Cr(VI) solution was added into the electrochemical cell which contain 10 mL of 0.1 M HCl to obtain 10 µmol L^{-1} homogeneous solution of Cr(VI). The modified working electrode was used to detect the chromium species by the current-voltage experimental technique. Different volumes of stock solution of 1.0 mmol L^{-1} Cr(VI) were injected into the cell for further detection. Current response was noted down for each incremental addition of Cr(VI). Further, different volumes of diluted 0.01 mmol L^{-1} Cr(VI) solution was added to cell during amperometric measurements.

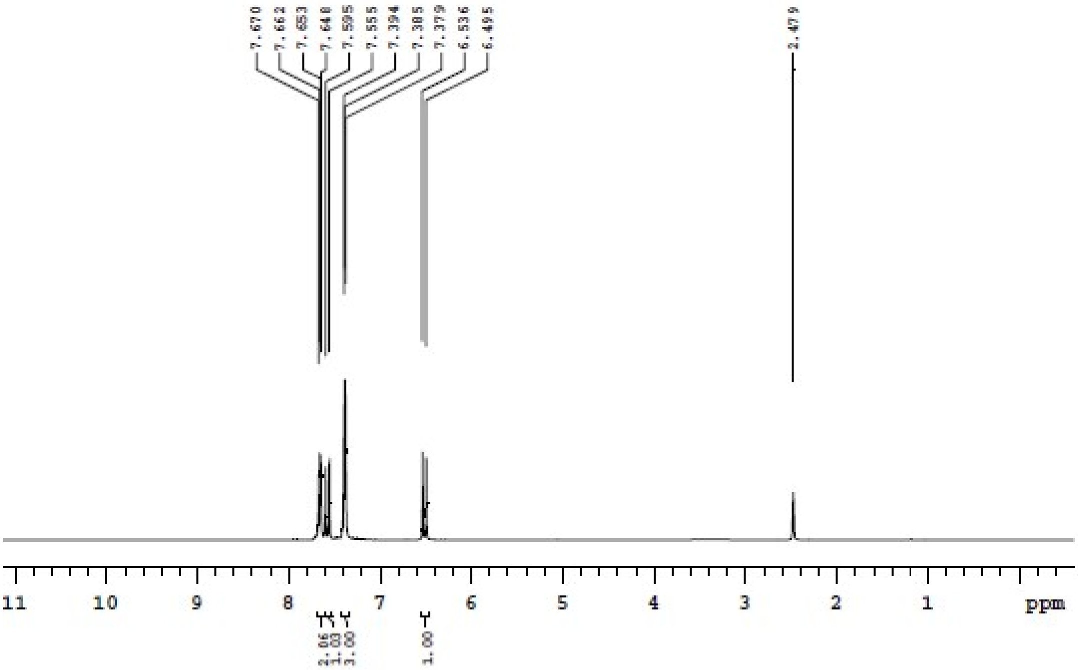

Fig S1. ^{1}H-NMR spectrum of the precursor ligand **i**

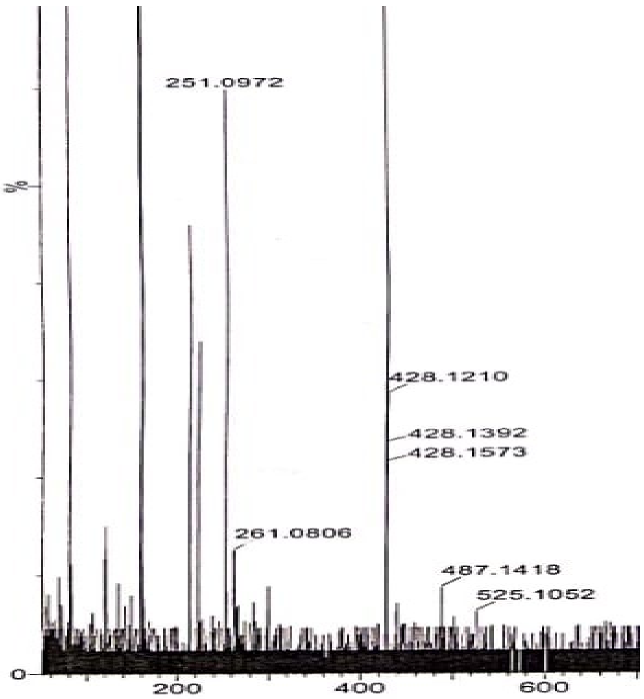

Fig S2. Mass spectrum of the compound (**i**) with mass fragment (M^{+1}) =251.

UV-Vis spectrum

The UV-Visible spectrum of PcIrCl is displayed in **Fig. S3**, which contain two absorption bands at 327 and 665 nm. The band at 665 nm is the characteristic Q-band absorption of PcIrCl and corresponds to the π–π* transition of the HOMO to LUMO of the Pc macrocycle. Further, the shoulder-like peak shown around 604 nm, could be responsible to the vibronic coupling of the excited state. The band at 327 nm belongs to B-band absorption of PcIrCl arising as a result of the transition from deeper levels to LUMO i.e. n- π* transition.

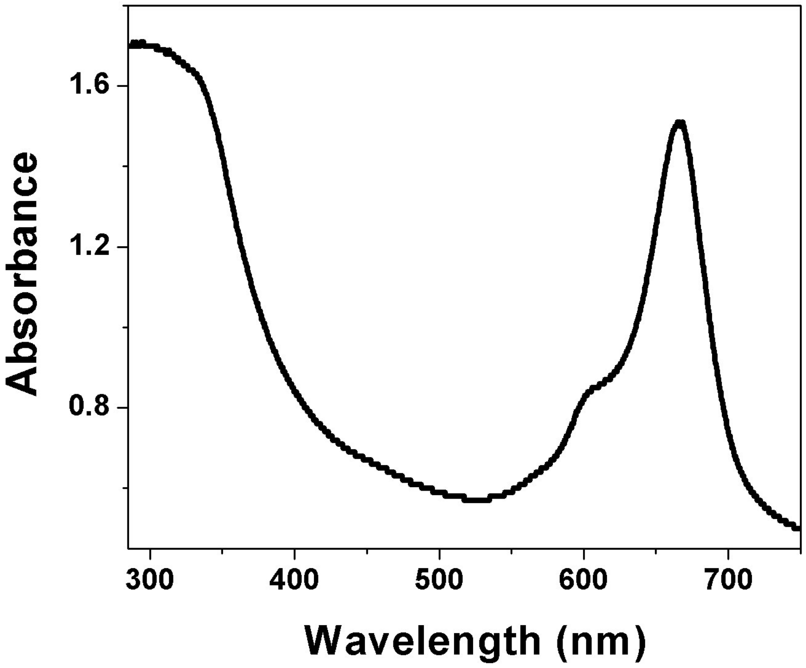

Fig S3. UV-Visible absorption spectrum of PcIrCl complex.

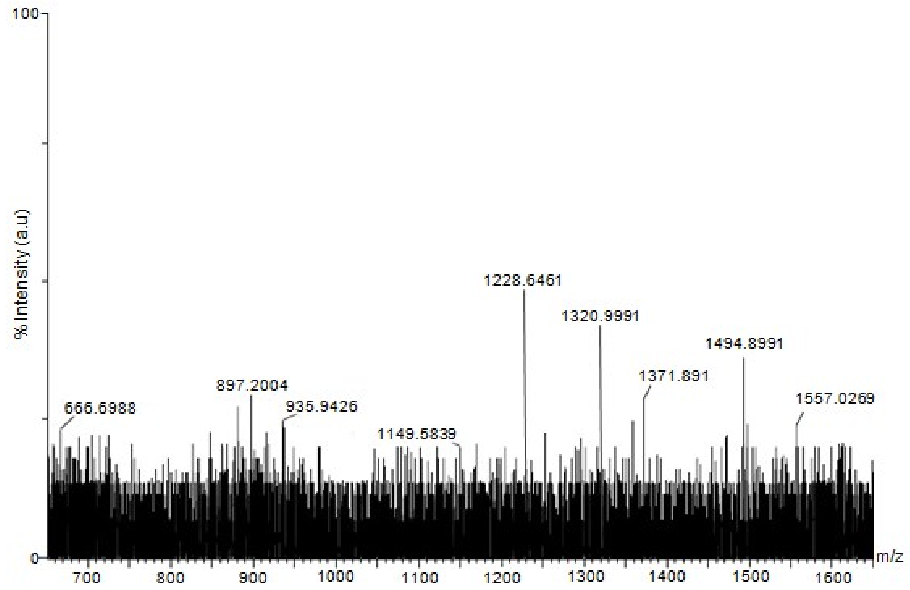

Fig S4. Mass spectrum of iridium phthalocyanine (**ii**) with mass fragment (M·) = 1228

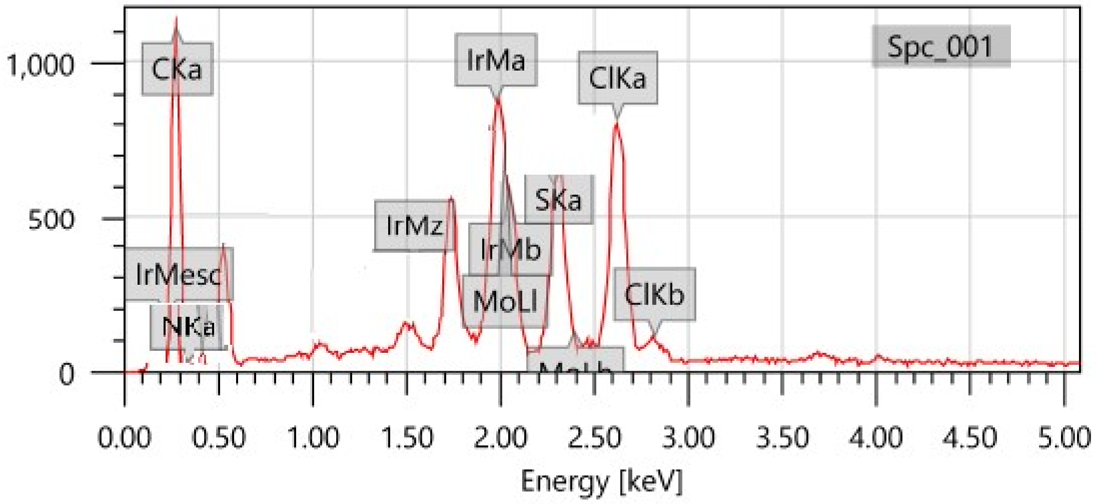

Fig. S5. The EDX spectrum of the synthesized iridium phthalocyanine (**ii**)

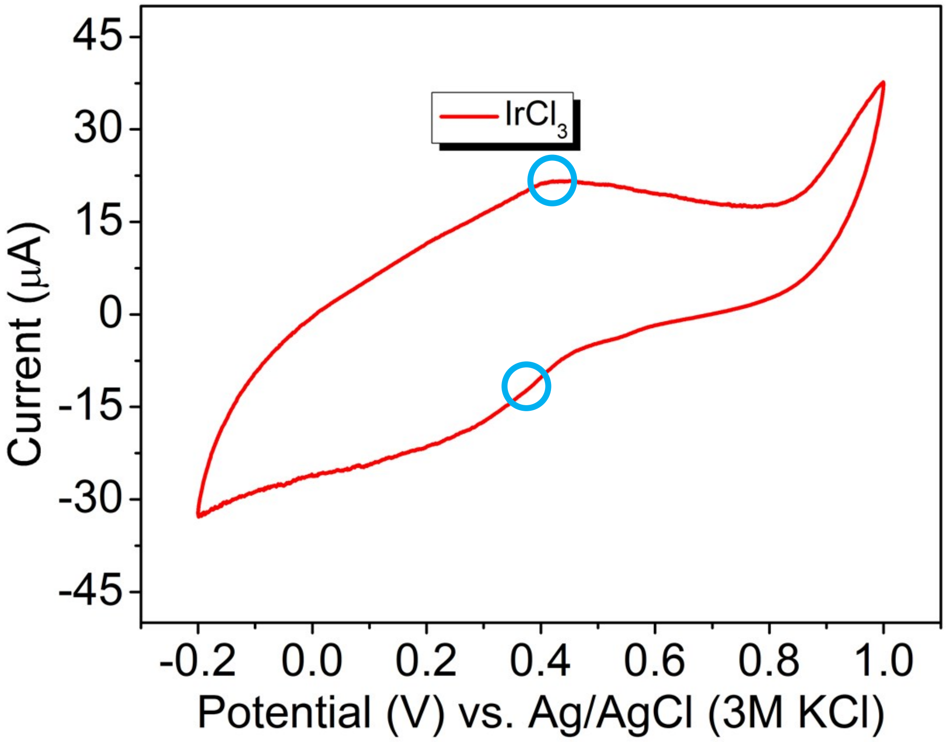

Fig. S6. Cyclic voltammogram of $IrCl_3$ in 0.1 M HCl at a scan rate of 10 mV/s.

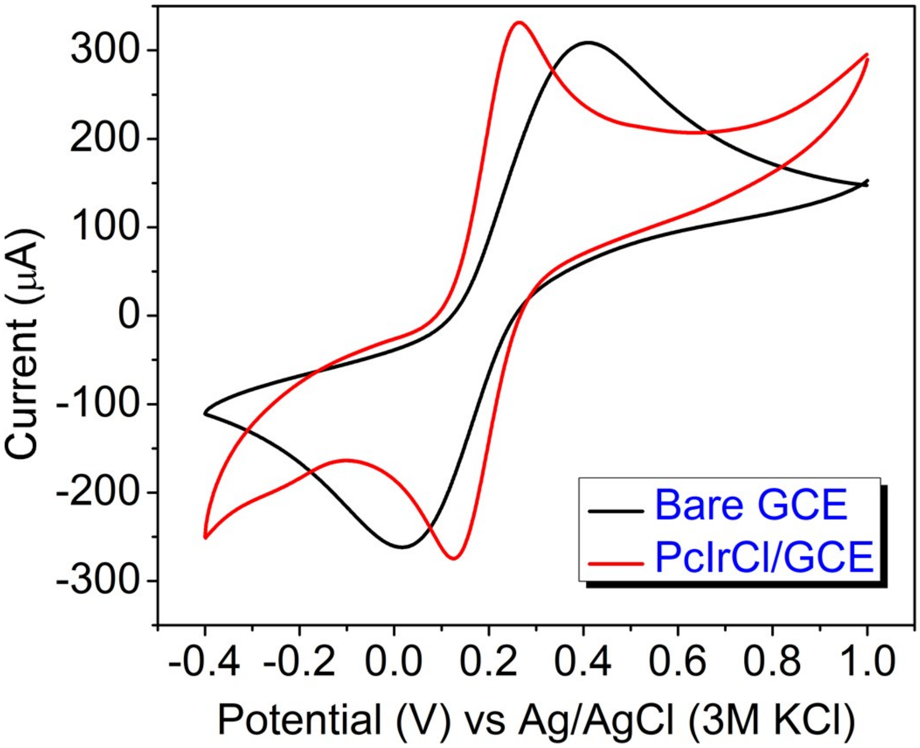

Fig. S7. Cyclic voltammograms of (i) bare GCE, (ii) PcIrCl/GCE in presence of 1 mM ferri/ferrocyanide system in 0.1 M HCl at a scan rate of 10 mV/s.