Electronic Supplementary Material (ESI) for Dalton Transactions.

Amino-substituted Cobalt(III)Corrole: Bifunctional Electrocatalyst for Oxygen and Hydrogen Evolution Reactions

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1. Electrocatalytic calculations:

The electrochemical potential was converted relative to the normal hydrogen electrode (NHE; all potentials reported in this work are referenced to the NHE) following a literature protocol.[S1] Current and peak potentials for the catalytic waves were compared without addition of H_2O or TFA (i_p) and with addition of H_2O or TFA (i_{cat}). Current ratios, i_{cat}/i_p, were plotted vs $[H_2O]^{1/2}$ and $[TFA]^{1/2}$ to determine first order rate constants (k) using the of eq. 1 for OER and eq. 2 for HER.

$$\frac{i_{cat}}{i_p} = \frac{(RT)^{1/2}}{0.446(nFv)^{1/2}} k_{cat}{}^{1/2} = \frac{(RT)^{1/2}}{0.446(nFv)^{1/2}} k^{1/2}(H_2O)^{1/2} \quad (1)$$

$$\frac{i_{cat}}{i_p} = \frac{(RT)^{1/2}}{0.446(nFv)^{1/2}} k_{cat}{}^{1/2} = \frac{(RT)^{1/2}}{0.446(nFv)^{1/2}} k^{1/2}(TFA)^{1/2} \quad (2)$$

Wherein, R, T, n, F, and v are the universal gas constant, temperature, number of electrons transferred, Faraday constant, and scan rate, respectively.

The chronoamperometry experiment has been performed in stirring electrolyte solution (1.0 M KOH), in order to make the solution free from in-situ generated oxygen bubbles. A potential of 0.95 V versus NHE has been chosen for the chronoamperometry experiment. The turnover number (TON) and turnover frequency (TOF) have been estimated by using the eq. 3 and 4, wherein charge was calculated by integrating chronoamperogram. The number of electron transfer for water oxidation is 4 and F represents the Faraday's constant.

$$TON = \frac{Charge}{4 \times F \times \, catalyst\ concentration\ in\ moles} \quad (3)$$

$$TOF = \frac{TON}{time\ for\ electrolysis\ (t)} \quad (4)$$

2. Figures.

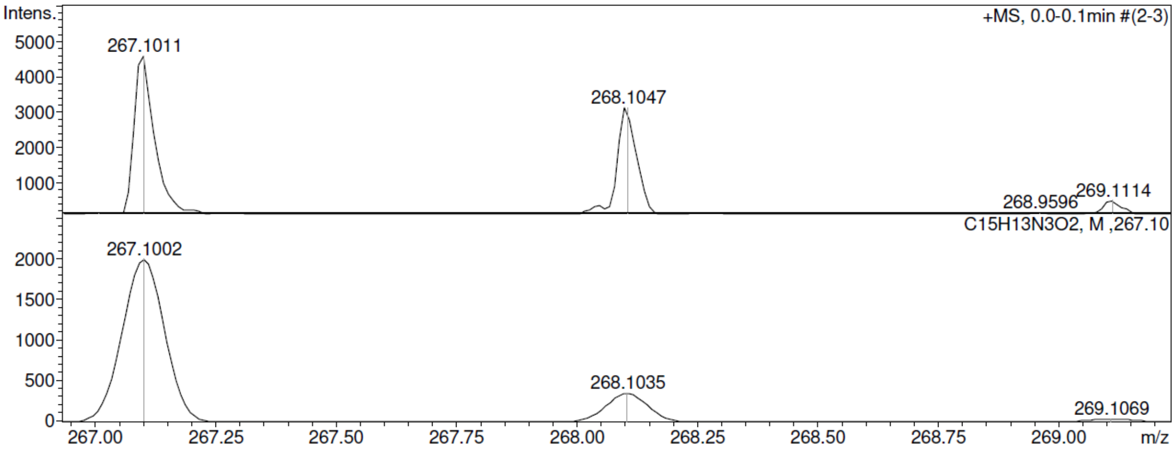

Fig. S1 ESI-HRMS of 5-(4-nitrophenyl)dipyrromethane $[M + H]^+$.

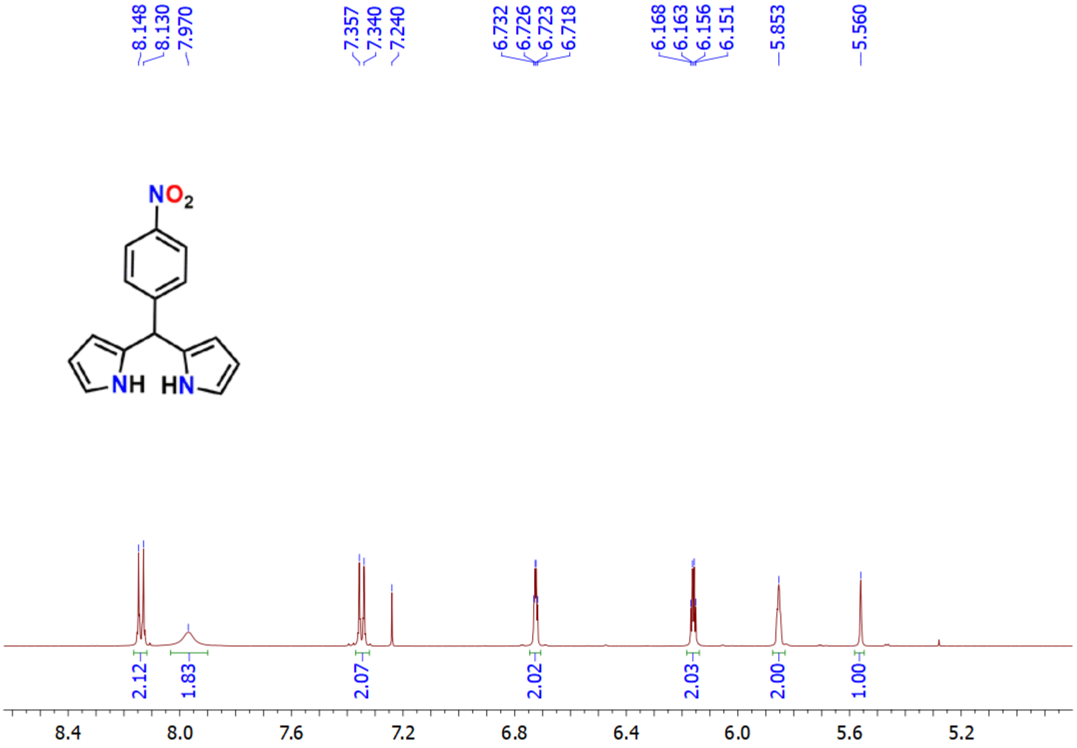

Fig. S2 ^{1}H NMR spectrum of 5-(4-nitrophenyl)dipyrromethane.

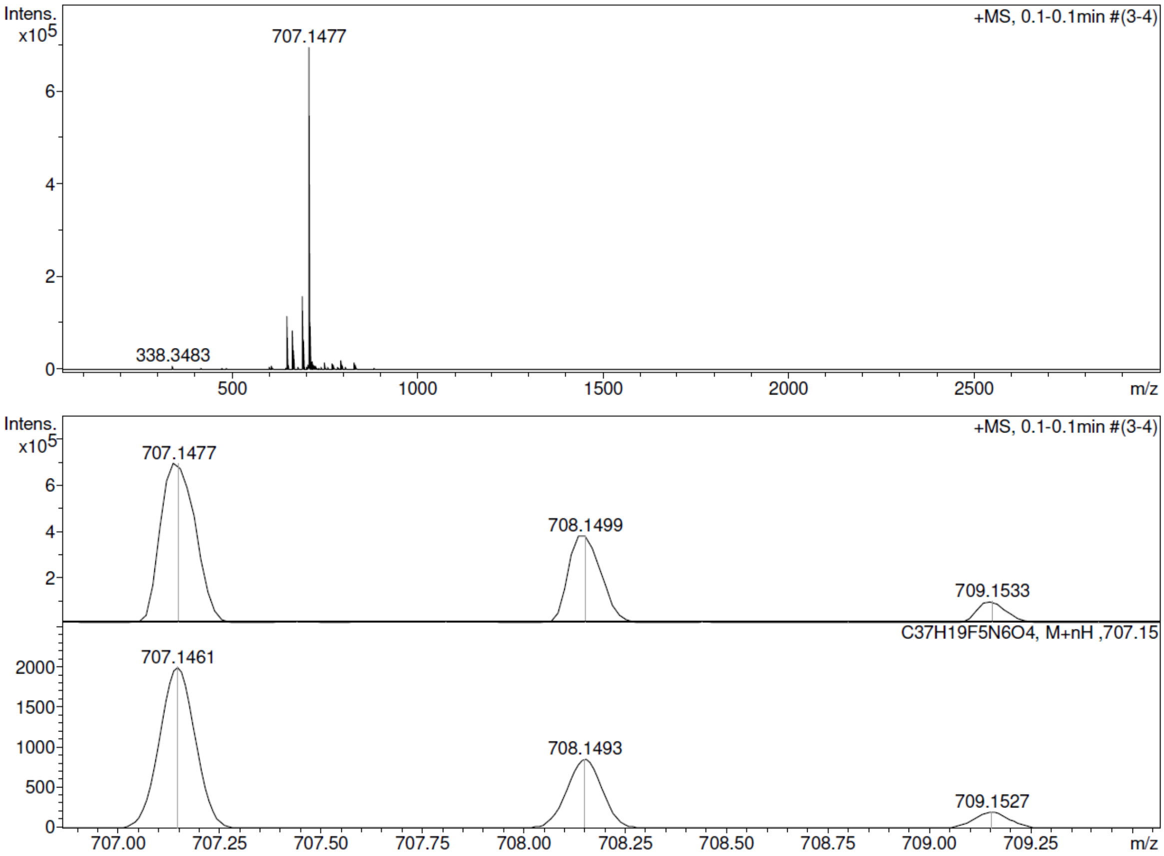

Fig. S3 ESI-HRMS of **H_3BNPC** $[M + H]^+$.

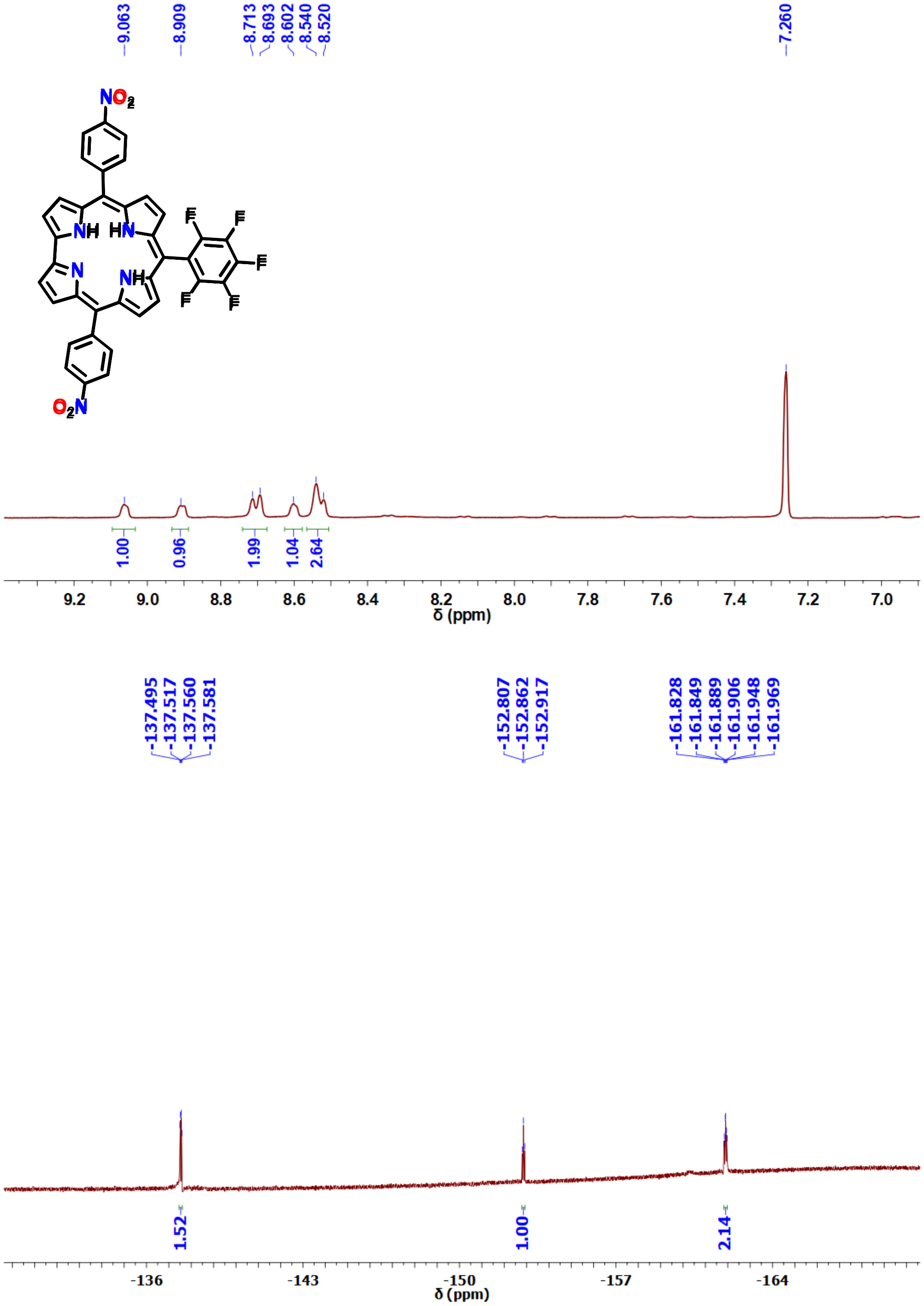

Fig. S4 ^{1}H and ^{19}F NMR spectra of **H_3BNPC**.

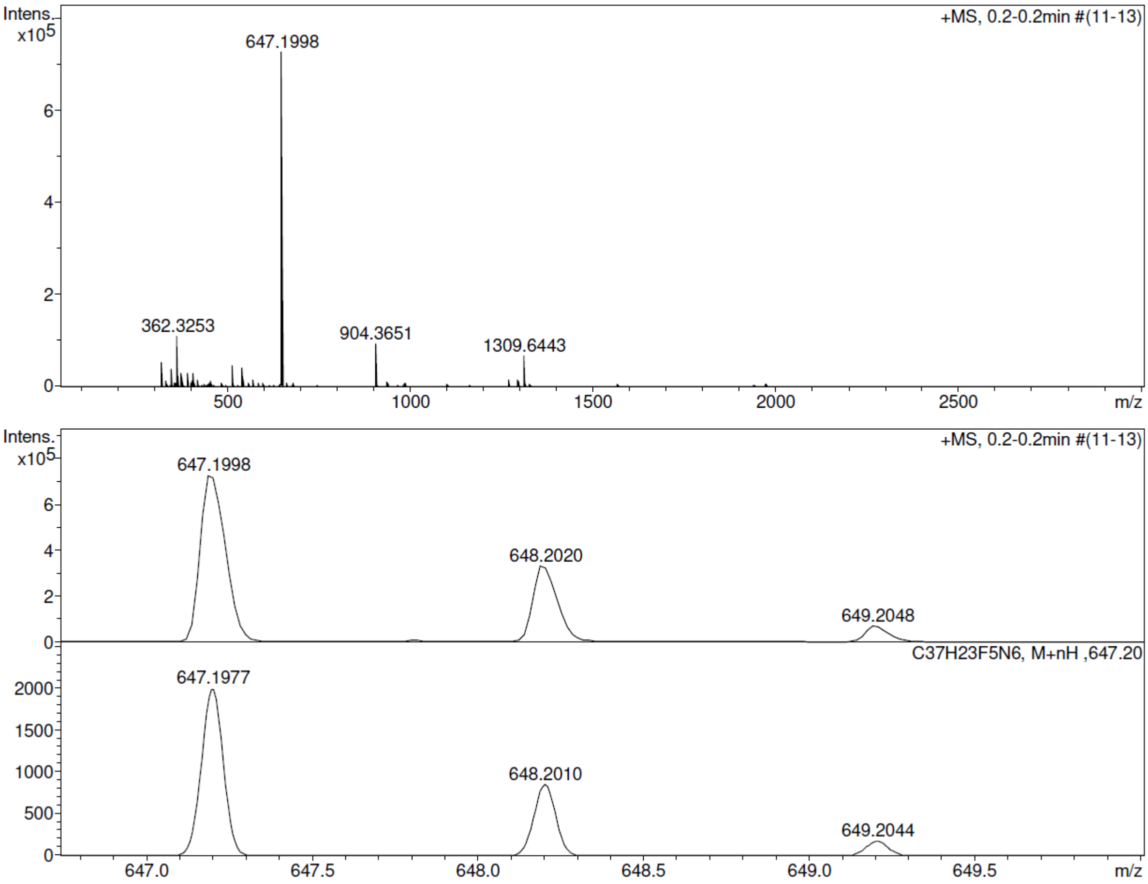

Fig. S5 ESI-HRMS of **H_3BAPC** $[M + H]^+$.

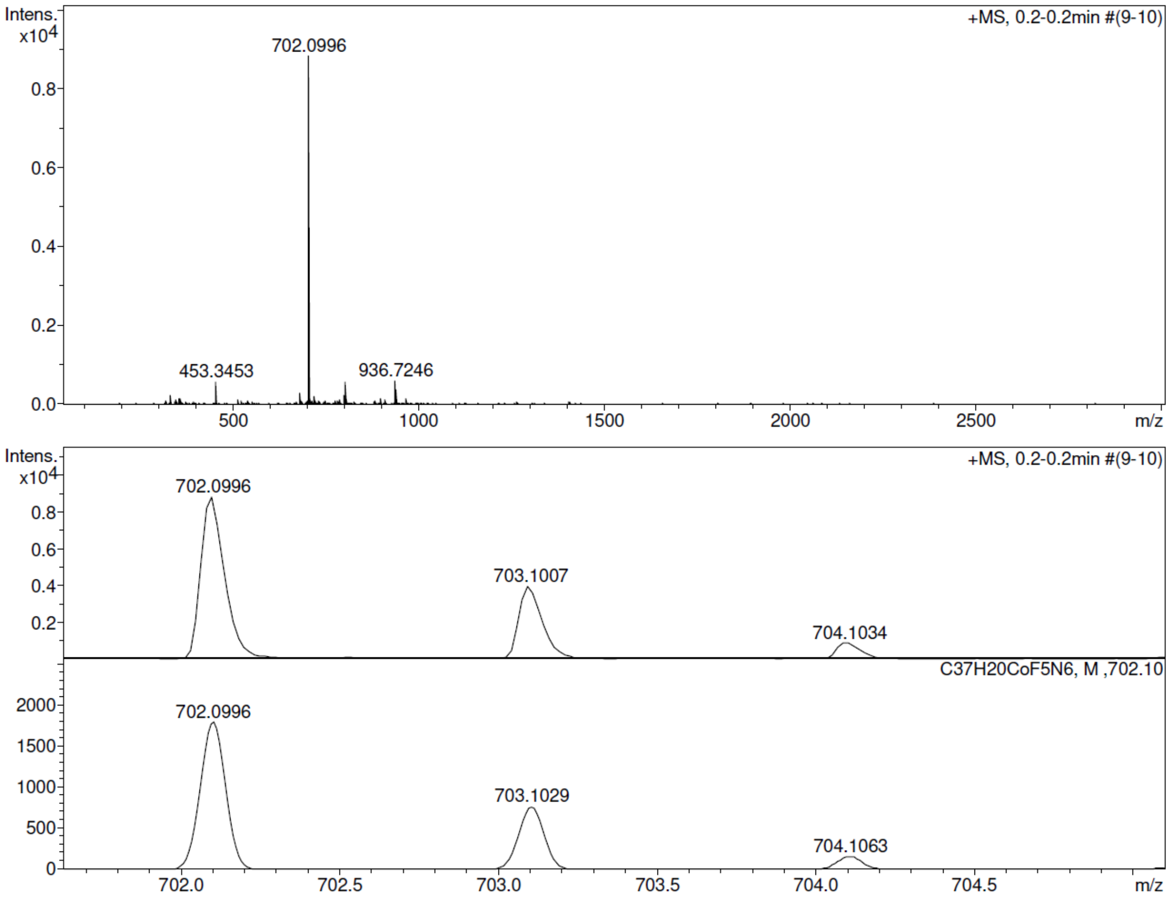

Fig. S6 ESI-HRMS of **Co(BAPC)Py$_2$** [M - 2Py]$^+$.

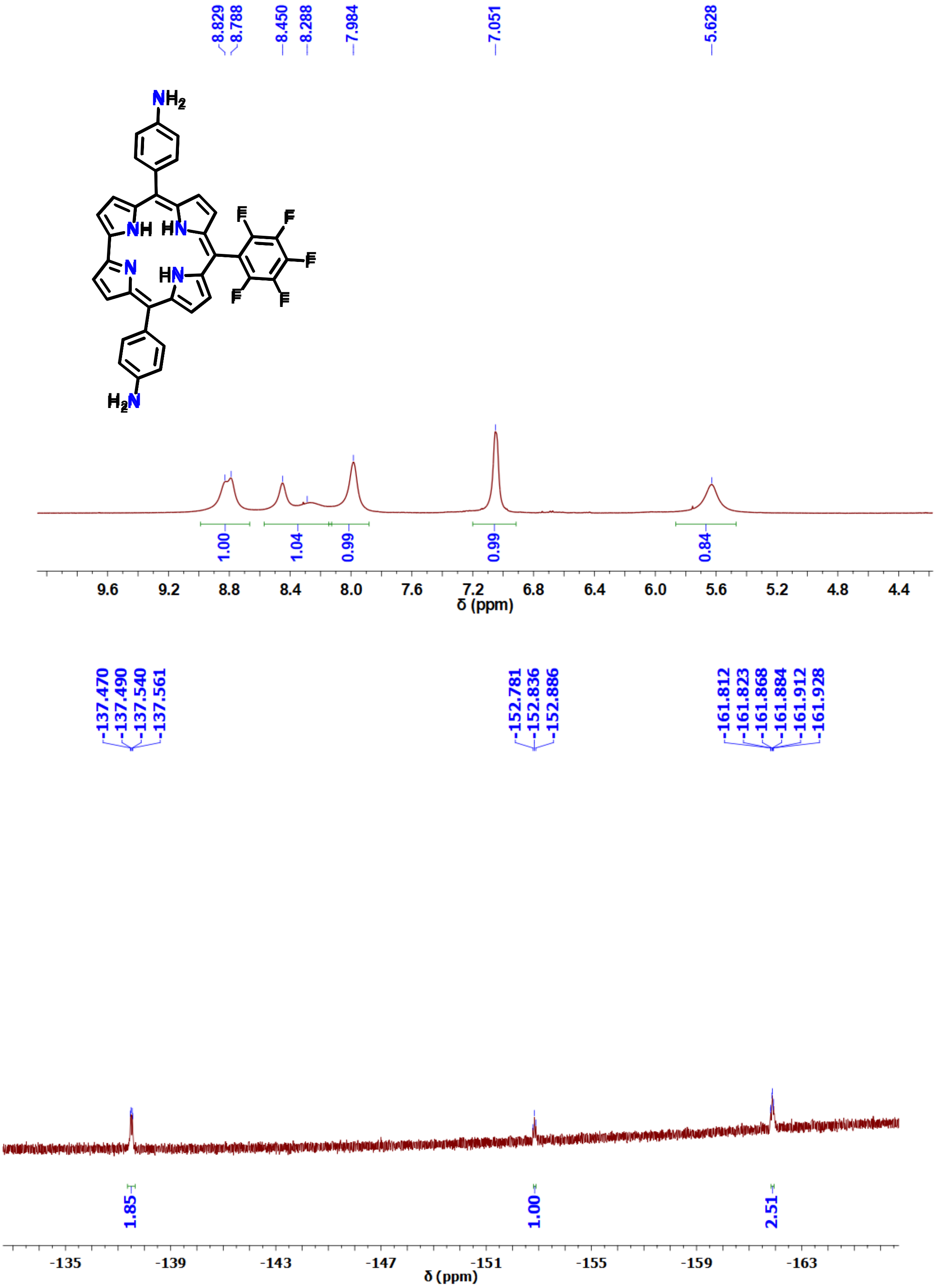

Fig. S7 ^{1}H and ^{19}F NMR spectra of **H$_3$BAPC**.

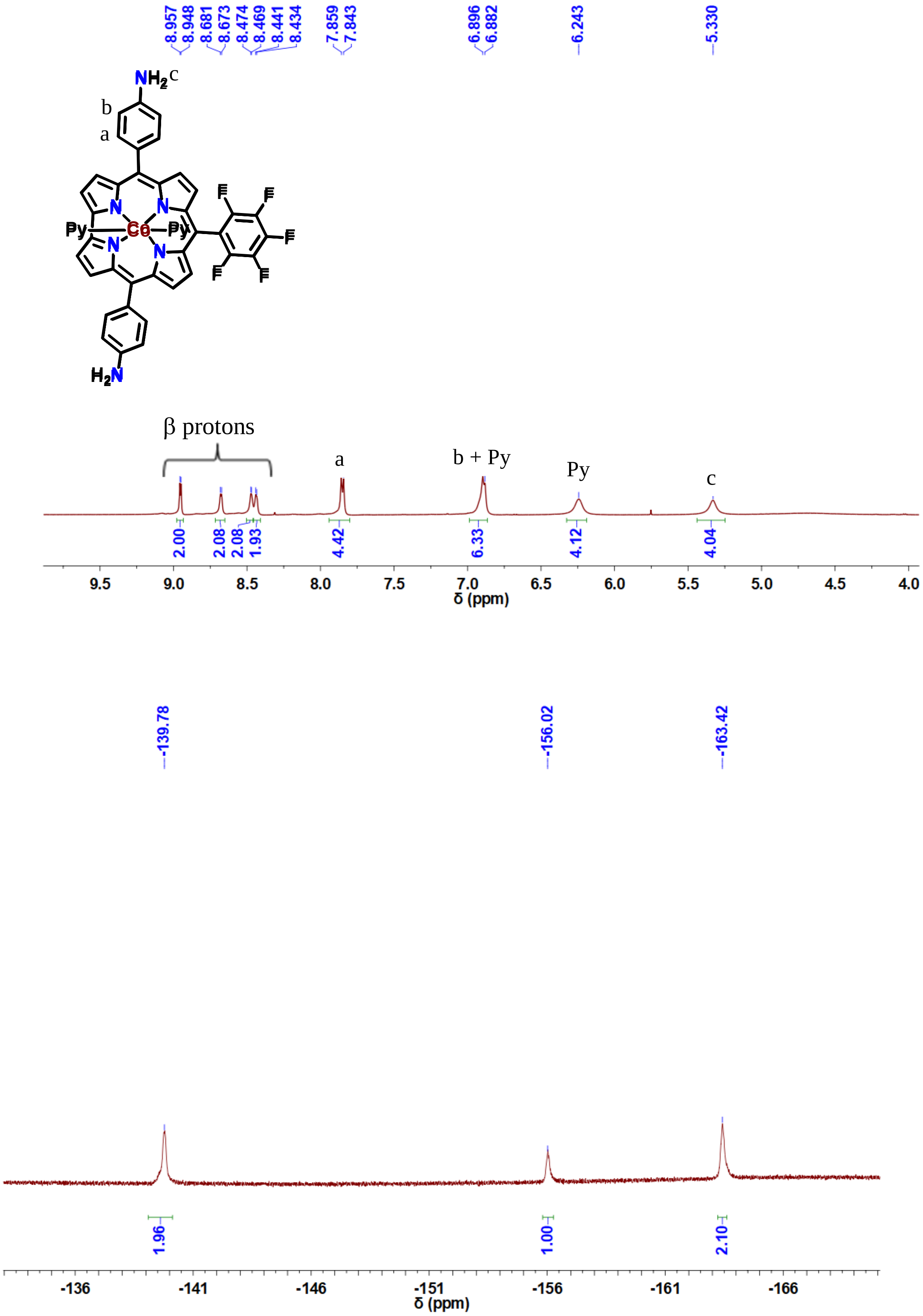

Fig. S8 ^{1}H and ^{19}F NMR spectra of Co(BAPC)Py_2.

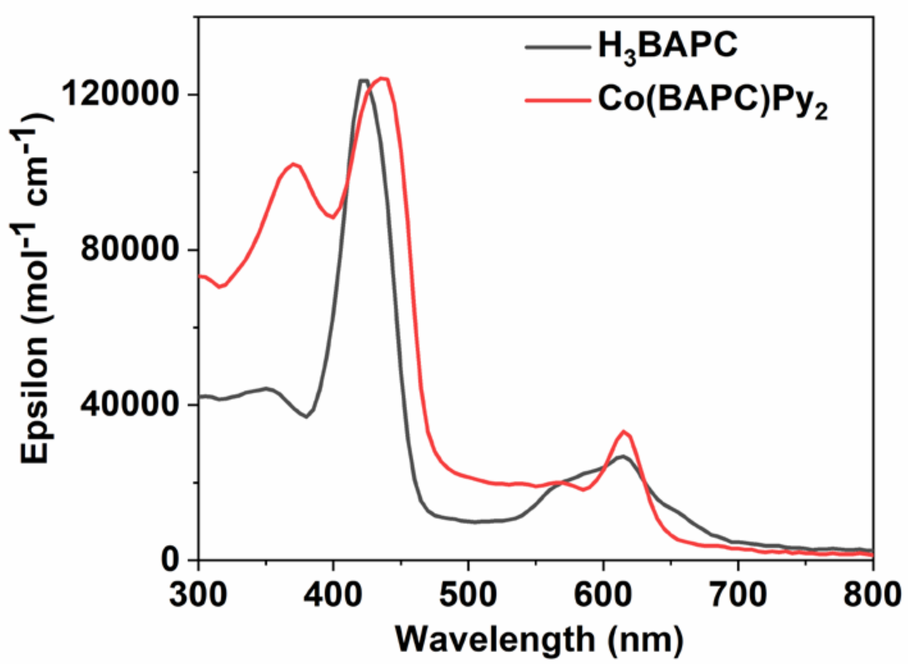

Fig. S9 UV-Vis spectra of H_3BAPC (CH_2Cl_2, c; 0.62 × 10^{-6} M) and Co(BAPC)Py_2 (CH_2Cl_2/Pyridine; 99/01, c; 0.43 × 10^{-6} M).

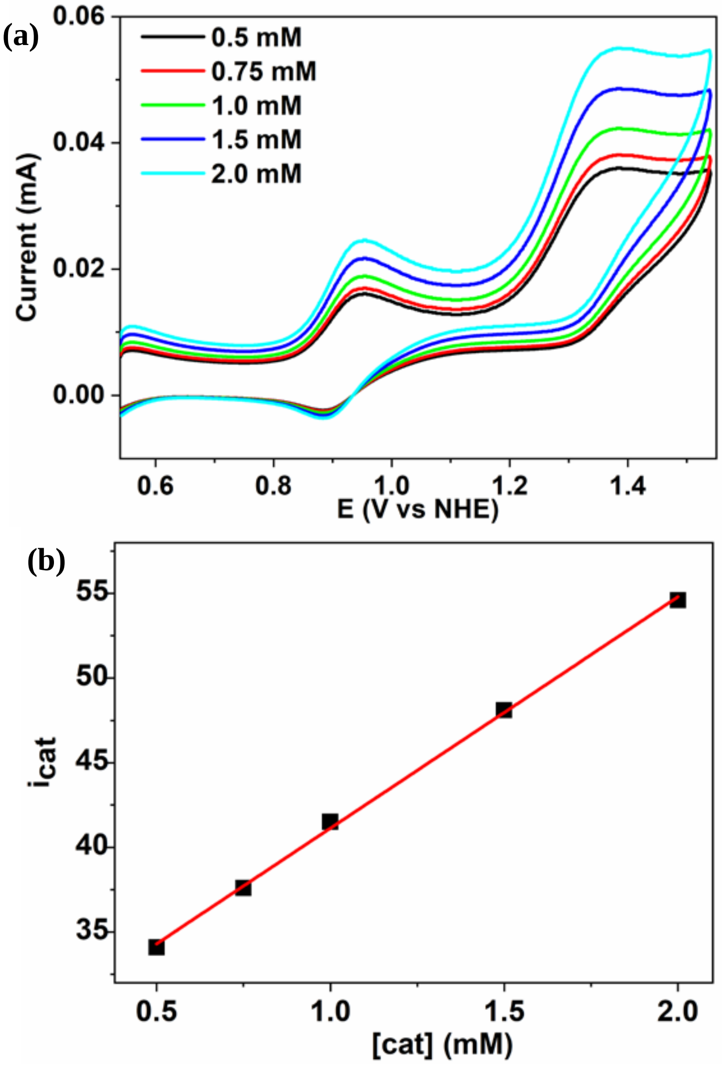

Fig. S10 (a) Cyclic voltammograms of Co(BAPC)Py$_2$ in acetonitrile solutions with varying concentration of Co(BAPC)Py$_2$ (0.5 mM - 2.0 mM) with 3% of water and (b) corresponding linear plot for i_{cat} *vs* [cat], using 0.1 M *n*Bu$_4$NPF$_6$ as supporting electrolyte with scan rate (ν) of 50 mV s^{-1}.

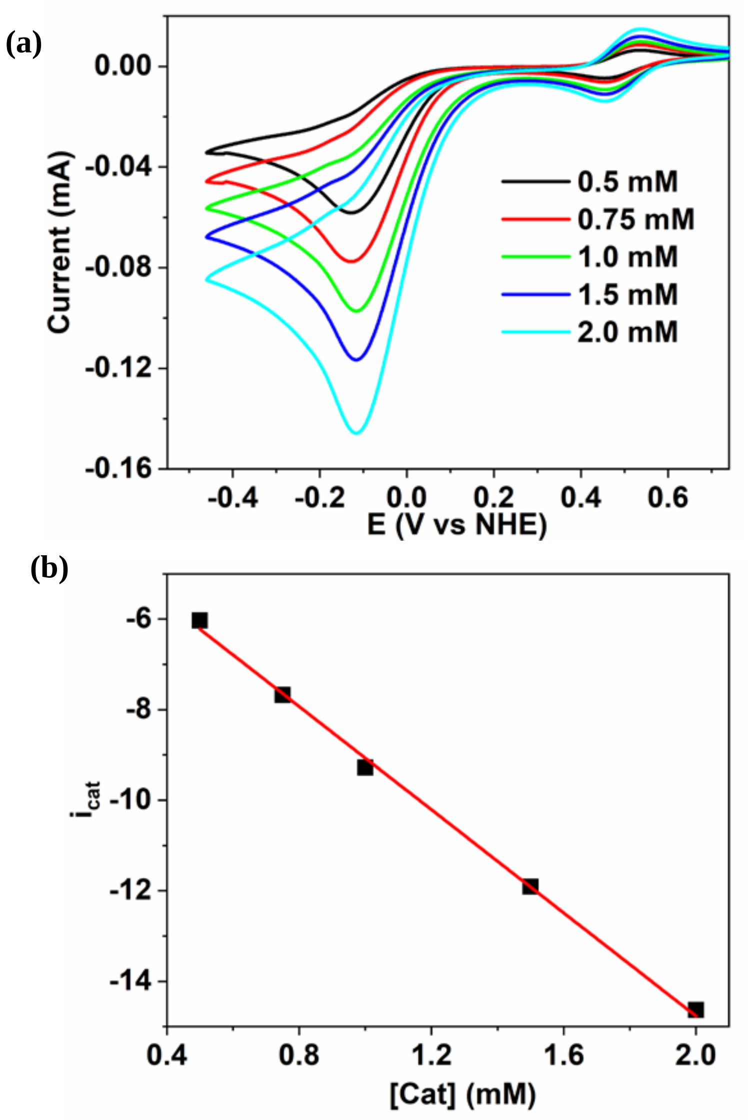

Fig. S11 (a) Cyclic voltammograms of Co(BAPC)Py$_2$ in acetonitrile solutions with varying concentration of Co(BAPC)Py$_2$ (0.5 mM - 2.0 mM) and fixed amount of TFA (10 equiv.) and (b) corresponding linear plot for i_{cat} *vs* [cat], using 0.1 M *n*Bu$_4$NPF$_6$ as supporting electrolyte with scan rate (ν) of 50 mV s^{-1}.

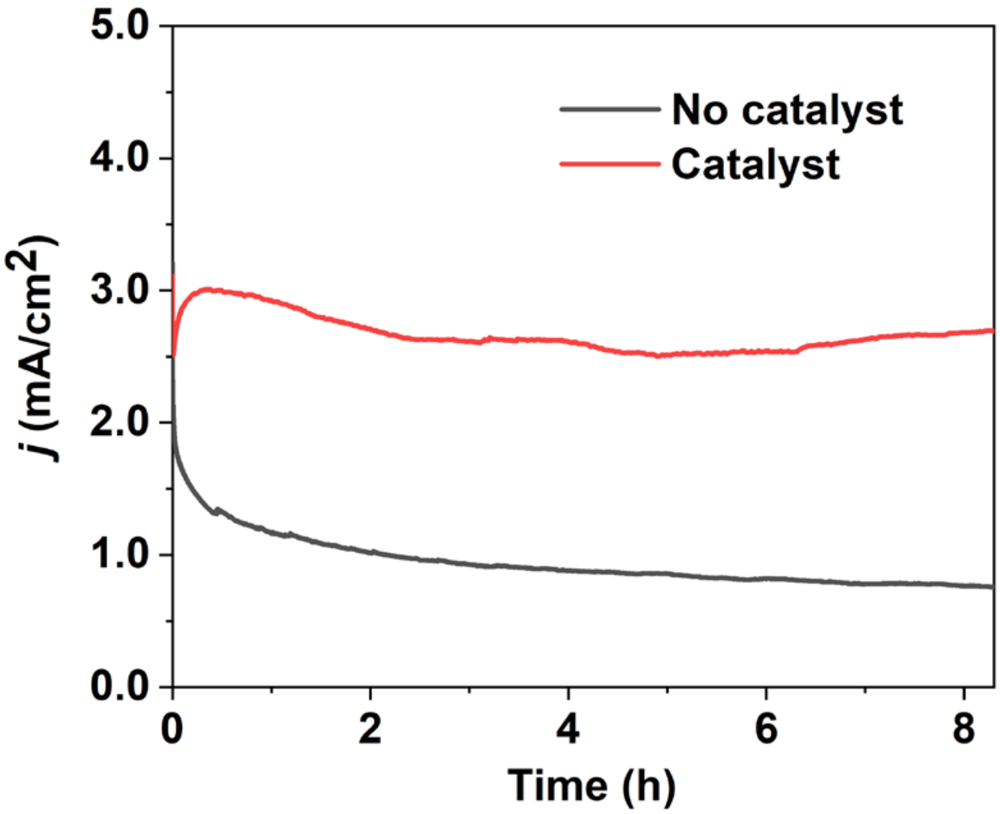

Fig. S12 Chronoamperogram showing the stability up to 8.3 h at a constant potential of 0.95 V (vs. NHE) in 1.0 M KOH during water oxidation for Co(BAPC)Py_2 catalyst. The redline shows chronoamperogram in presence of catalyst while the black line represents chronoamperogram without catalyst.

3. References

S1. V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97.