

Supporting Information

Carbon-conjugated Co complexes as model electrocatalysts for oxygen reduction reaction

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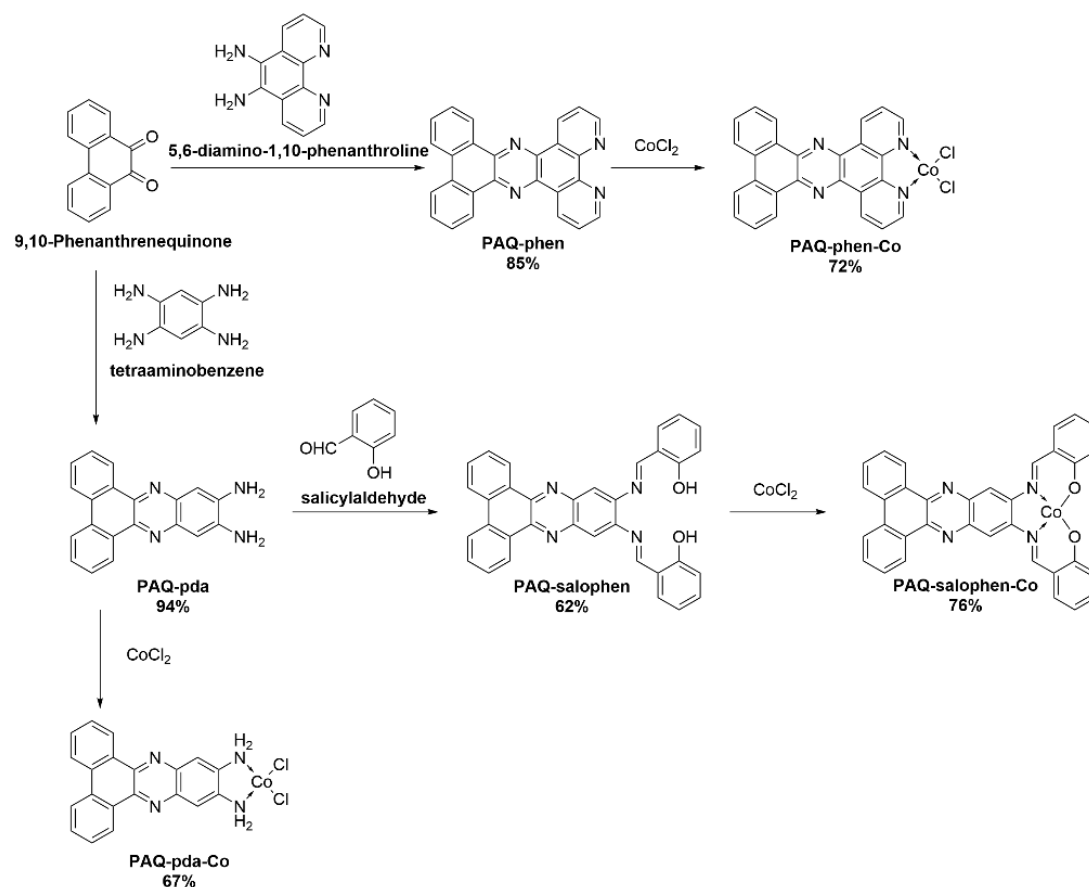
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Chemicals and materials. Benzene-1,2,4,5-tetraamine tetrahydrochloride ($\text{C}_6\text{H}_{14}\text{Cl}_4\text{N}_4$, 99.9%, Bidepharm), 5,6-diamino-1,10-phenanthroline ($\text{C}_{12}\text{H}_{10}\text{N}_4$, 96%, Bidepharm), *o*-phenylenediamine ($\text{C}_6\text{H}_8\text{N}_2$, 98%, Energy Chemical), salicylaldehyde ($\text{C}_7\text{H}_6\text{O}_2$, 99%, Adamas-beta), phenazine ($\text{C}_{12}\text{H}_8\text{N}_2$, 99.89%, Bidepharm), sodium bromate (NaBrO_3 , 99.5%, Macklin), sulfuric acid (H_2SO_4 , 98%, Dongjiang Reagent), cobalt chloride (CoCl_2 , 98%, Adamas-beta), potassium bicarbonate (KHCO_3 , 99.5%, Macklin), potassium hydroxide (KOH , 85%, Shanghai Lingfeng), perchloric acid (HClO_4) and Ketjen black (EC-300J, Canrd) were directly used as received without additional treatment. Deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used throughout all the experiments.



Scheme S1. The schematics of the synthesis of PAQ-conjugated complexes and the conversion yield of each step. PAQ and all the other reactants were added according to the stoichiometric ratios. In the preparation of CB-conjugated complexes, 5,6-diamino-1,10-phenanthroline, tetraaminobenzene, salicylaldehyde, and CoCl₂ were added in great excess relative to the reactive sites on CB. The actual conversion yields based on the quantity of the reactive sites on CB should be substantially higher than the values shown in this Scheme.

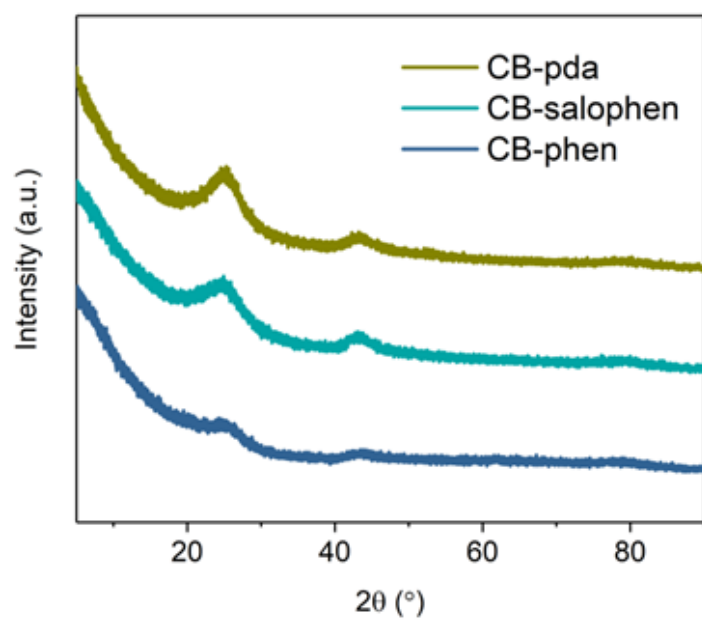


Figure S1. XRD patterns of CB-pda, CB-salophen and CB-phen.

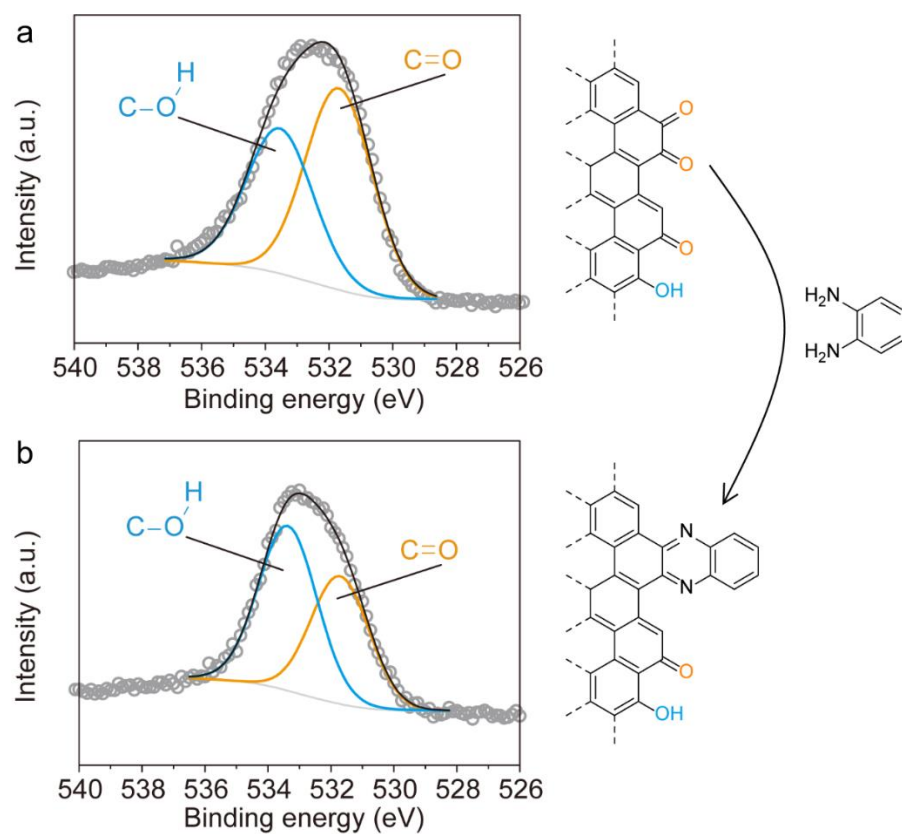


Figure S2. O 1s XPS spectra of (a) oxidized CB and (b) oxidized CB reacted with *o*-phenylenediamine. Each spectrum was deconvoluted into a peak corresponding to hydroxy group (C-OH) and a peak corresponding to carbonyl group (C=O).

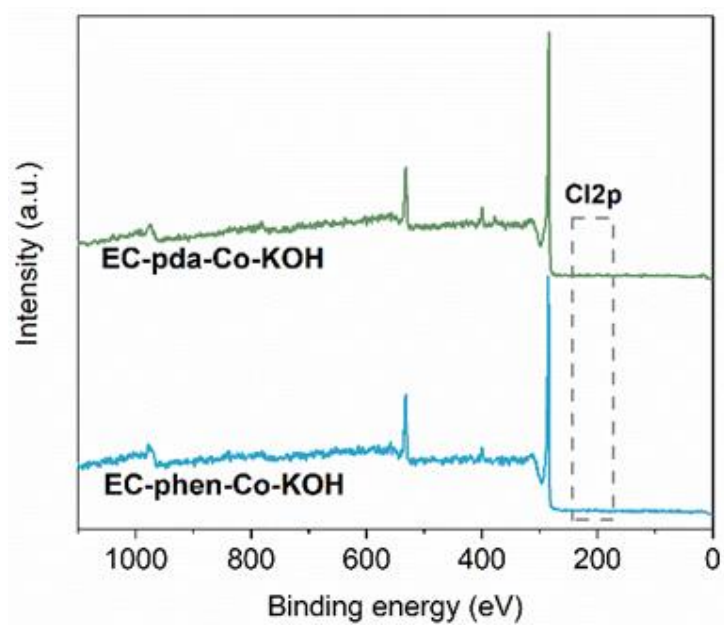


Figure S3. XPS surveys of BC-pda-Co (green) and BC-phen-Co (blue) after ORR measurements in 0.1 M KOH solution.

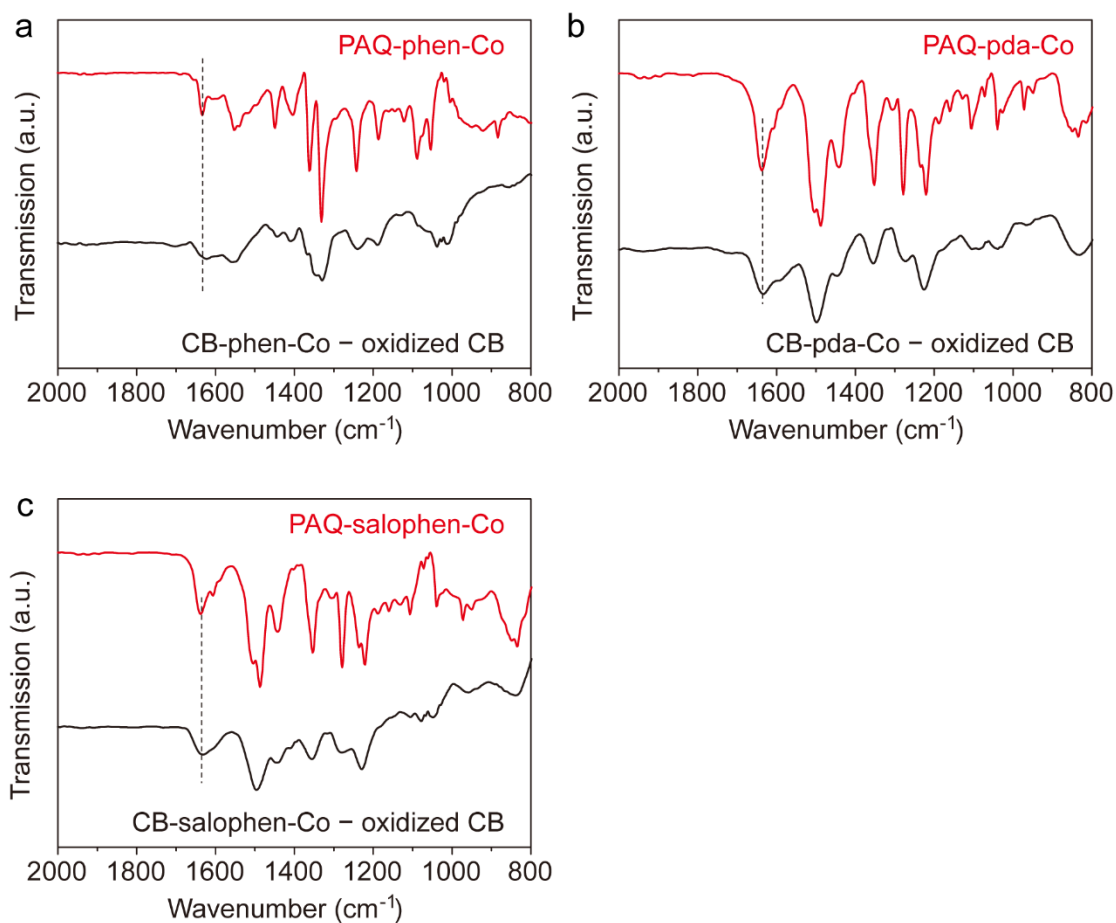


Figure S4. Difference IR spectra of CB-conjugated complexes and oxidized CB (black) and IR spectra of the corresponding PAQ-conjugated complexes (red). (a) CB-phen-Co and PAQ-phen Co; (b) CB-pda-Co and PAQ-pda-Co; (c) CB-salophen-Co and PAQ-salophen-Co. The dashed horizontal lines at 1635 cm^{-1} indicate the stretching of C=N bonds in pyrazine moieties.

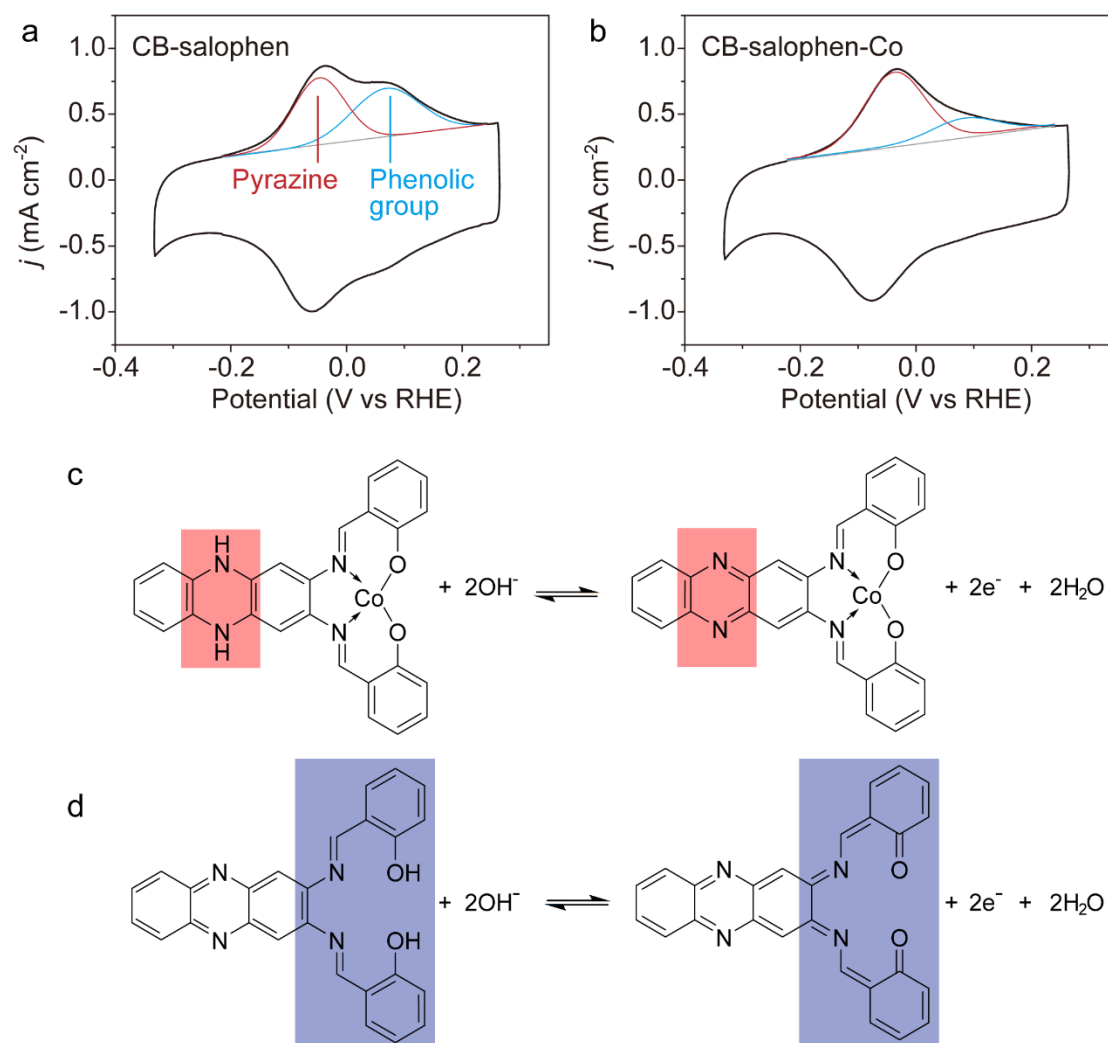


Figure S5. CV curves of (a) CB-salophen and (b) CB-salophen-Co. The oxidation peaks were deconvoluted into two features at -0.04 V (red) and $+0.07$ V (blue) vs RHE, assigned to the oxidation of pyrazine moieties and phenolic groups, respectively. Schematics of the oxidation of (c) pyrazine moieties and (d) phenolic groups in salophen ligand.

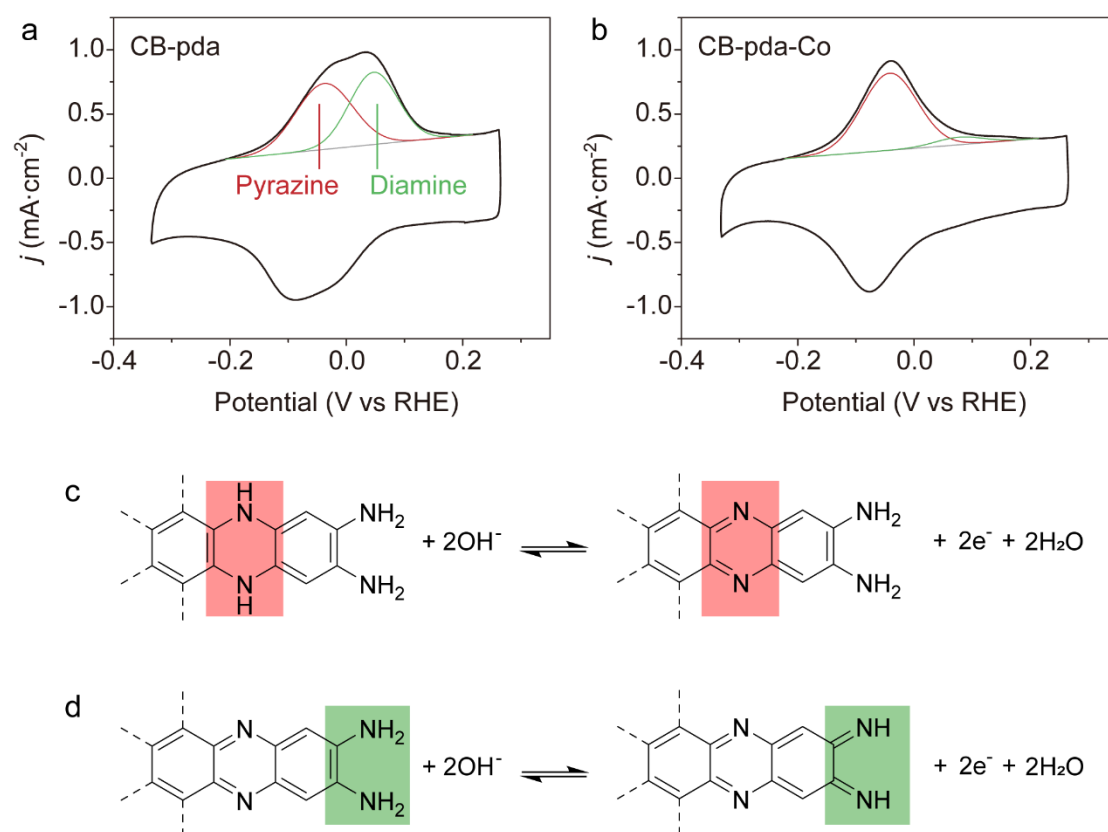


Figure S6. CV curves of (a) CB-pda and (b) CB-pda-Co. The oxidation peaks were deconvoluted into two features at -0.04 V (red) and +0.03 V (green) vs RHE, assigned to the oxidation of pyrazine moieties and diamine moieties, respectively. Schematics of the oxidation of (c) pyrazine moieties and (d) diamine moieties.

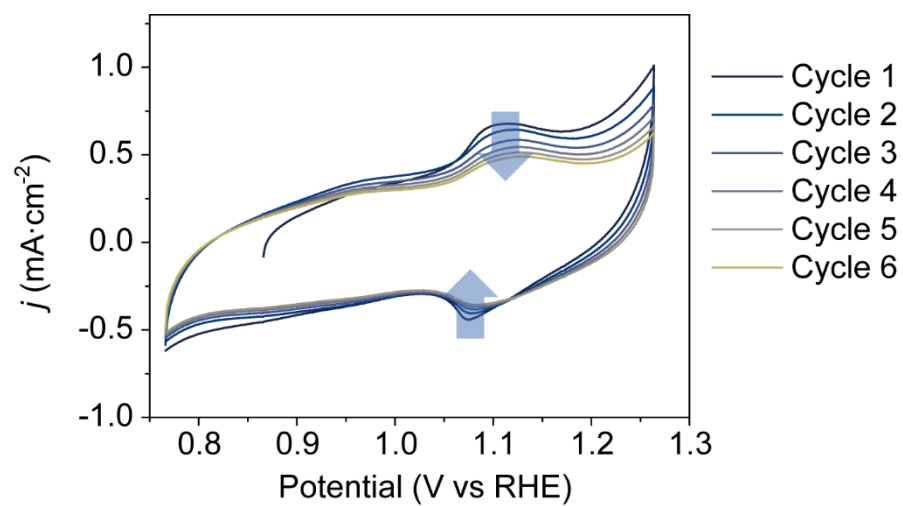


Figure S7. CV curves of CB-phen-Co in 0.1 M KOH. The blue arrows indicate the peak areas of $\text{Co}^{3+}/\text{Co}^{2+}$ decrease as the cycle number increases.

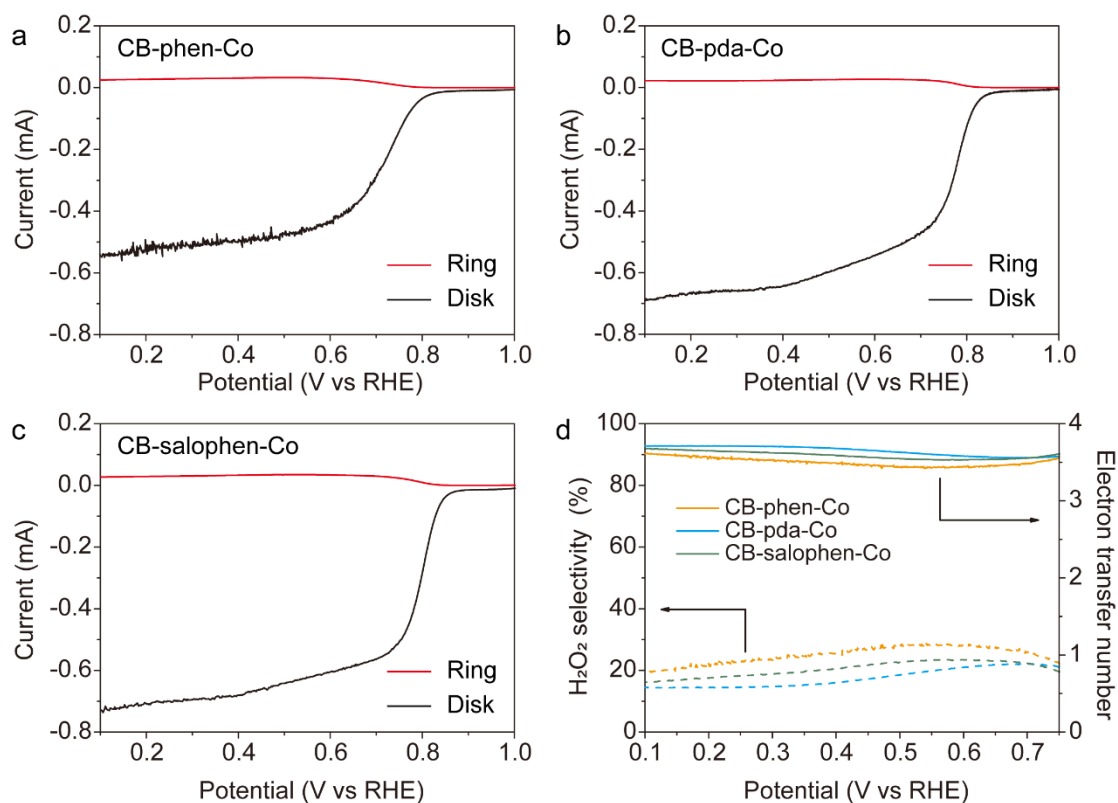


Figure S8. RRDE tests of CB-conjugated complexes. Disk current (black curves) and ring current (red curves) of (a) CB-phen-Co, (b) CB-pda-Co and (c) CB-salophen-Co in O₂ saturated 0.1 M KOH solution. (d) Selectivity of H₂O₂ (dashed curves) and the number of electron transfer of ORR (solid curves) of the three CB-conjugated complexes.

Table S1. Comparison of weight fractions of Co (in percentage) in CB-conjugated complexes detected by XPS and ICP-MS.

	XPS	ICP-MS
CB-phen-Co	2.84	2.31
CB-pda-Co	4.51	2.56
CB-salophen-Co	4.06	2.45