Supporting Information for article

pH−Dependent Electrochemically Catalyzed Oxygen Reduction Behaviors of *o*−Substituted Co(III)corroles

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pH−Зависимое электрохимически катализируемое окислительно−восстановительное поведение *o*−замещенных Co(III)корролов

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## Contents

1. Experimental Section

1.1. General

^{1}H NMR spectra were recorded on a Bruker AVANCE III 400M spectrometer. Infrared spectra (KBr) were measured on Nicolet 6700 spectrometer FT-IR spectrophotometer. UV-Visible absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer at ambient temperature with a 1 cm quartz cell. MCD spectra were measured on a JASCO-810 spectrometer with a permanent magnet (1.6 T). Elemental analyses for C, H and N were determined on a Perkin Elmer 240C elemental analyzer. MALDI-TOF MS data were measured using a Bruker mass spectrometer equipped with an electrospray. Cyclic voltammetry was performed with a three-electrode-compartment cell in o-dichlorobenzene (o-DCB) solutions with 0.1 M [n-Bu$_4$N](ClO$_4$) as the supporting electrolyte using a CHI-730D electrochemistry workstation. A glassy carbon electrode of 3 mm diameter was used as the working electrode, while platinum wire and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively.

### 1.2. Preparation of Modified Electrodes

1.0 mg of reduced graphene oxide (rGO) was mixed with 1 mL isopropyl alcohol containing 0.2 % nafion, and the mixture was sonicated in ultrasonic bath for 30 min to produce a homogeneous mixture of concentration 1.0 mg/mL. The surface of the glassy carbon electrode (GCE) was polished with 0.05 μm alumina and rinsed with doubly distilled water in an ultrasonic bath to remove any adhered Al$_2$O$_3$ particles. The electrodes were rinsed with ethanol and dried under room temperature for about 5 min. 3 μL of the TGO/isopropyl alcohol/nafion suspension was drop cast on the surface of the GC electrode three times and allowed to dry at room temperature. A 10 μL of 0.2 mM dichloromethane solutions of **1** and **3** were added dropwise to three different MWCNT/nafion-coated electrodes and dried at room temperature for 1 h. The modified electrodes were placed in CH$_3$CN for 5 min to remove any weakly adsorbed product. The samples are referred to as **1**/rGO and **3**/rGO and were stored in Milli-Q water in the dark.

1.3. Theoretical Calculations

Geometry calculations were carried out for **3a-c** by using the B3LYP functional of the Gaussian software package[1] with 6-31G(d) basis sets. The CAM-B3LYP functional was used for the TD-DFT calculations, since it contains a long-range correction.
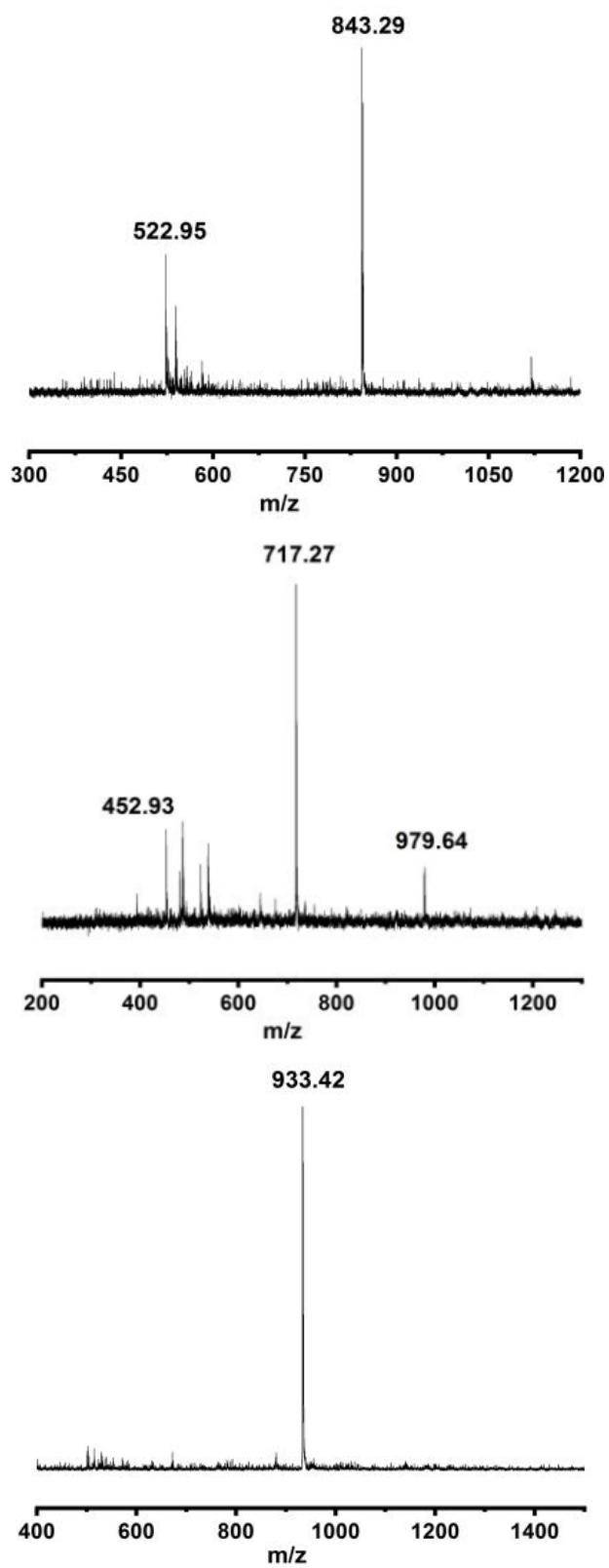
Figure S1. MALDI-TOF-mass spectra of Co(III)PPh$_3$ corrole **3a-c**.
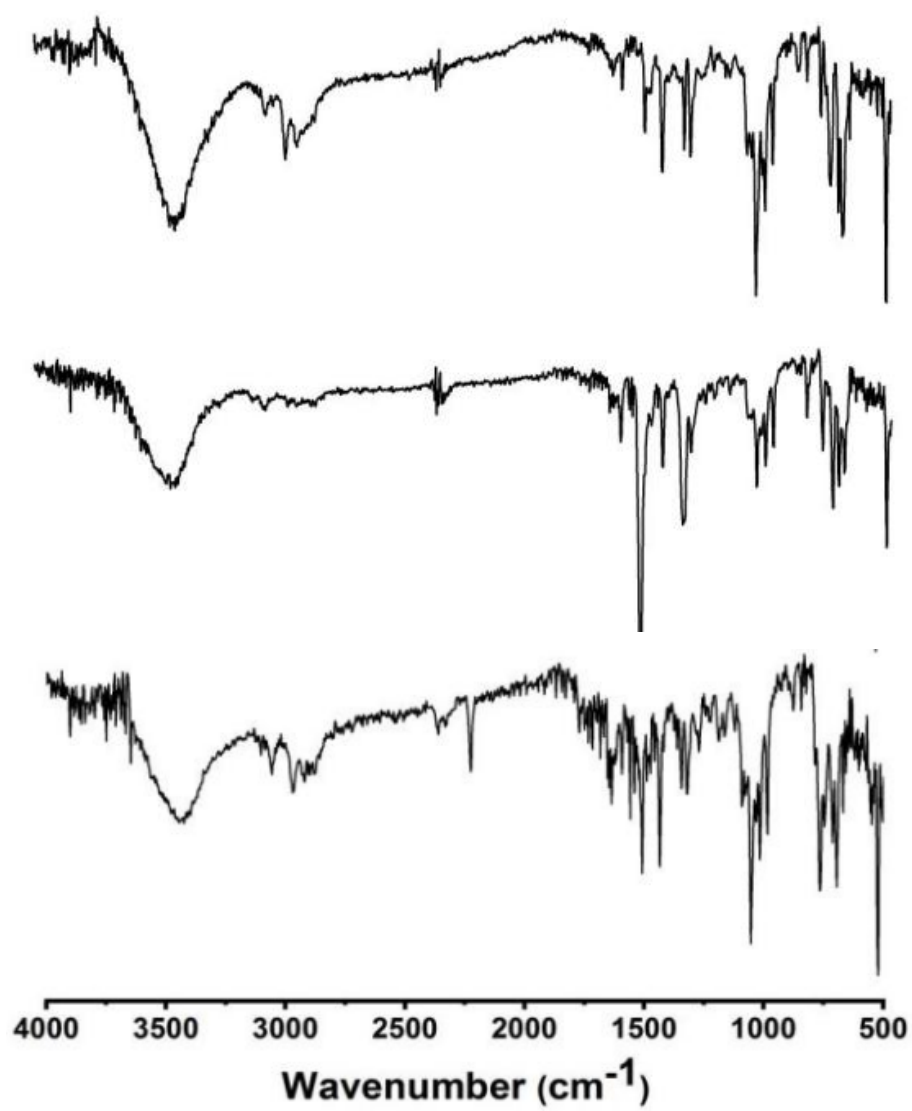
Figure S2. IR spectra of Co(III)PPh$_3$-corrole **3a-c**.
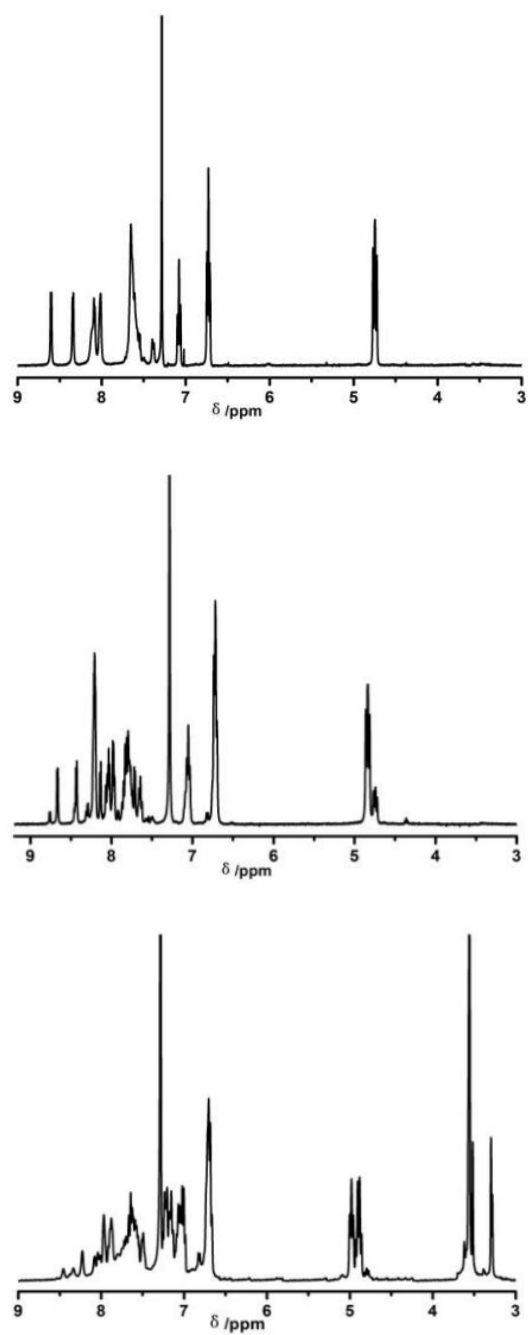
Figure S3. ^{1}H NMR spectra of Co(III)PPh₃-corrole **3a-c**.

Table S1. TD-DFT UV-Visible spectra of B3LYP optimized geometry of **3a-c** using CAM-B3LYP functional with 6-31G(d) basis set of Gaussian 09 software package.

Band[a]	#[b]	Calc[c]			Exp[d]		Wave Function[e] =
							3a
----	1	----	----	----	----	----	Ground State
Q	7	20.4	492	(0.11)	17.1	584	72 % **s** → **-a**; 24 % **a** → **-s**; ...
	8	21.2	477	(0.04)	17.8	561	67 % **a** → **-a**; 27 % **s** → **-s**; ...
B	11	27.7	361	(0.51)	25.9	386	57 % **s** → **-s**; 20 % **a** → **-a**; ...
	12	27.7	361	(0.26)			27 % **a** → **-s**; 20 % d_{yz} → $d_{x^2-y^2}$; ...
							3b
----	1	----	----	----	----	----	Ground State
Q	7	20.3	489	(0.07)	17.1	584	61 % **s** → **-a**; 19 % **a** → **-s**; ...
	8	20.9	472	(0.04)	17.8	561	62 % **a** → **-a**; 20 % **s** → **-s**; ...
B	17	27.7	361	(0.43)	25.9	386	58 % **s** → **-s**; 14 % **a** → **-a**; ...
	18	27.8	360	(0.39)			55 % **a** → **-s**; 13 % **s** → **-a**; ...
							3c
----	1	----	----	----	----	----	Ground State
Q	7	20.5	488	(0.08)	17.1	584	66 % **s** → **-a**; 26 % **a** → **-s**; ...
	8	21.1	475	(0.04)	17.8	561	66 % **a** → **-a**; 25 % **s** → **-s**; ...
B	11	27.6	362	(0.48)	25.9	386	33 % **a** → **-s**; 20 % **s** → **-s**; 12 % **s** → **-a**; ...
	12	27.6	362	(0.49)			40 % **s** → **-s**; 19 % **a** → **-s**; 13 % **a** → **-a**; ...

a − Band assignment described in the text; b − The number of the state assigned in terms of ascending energy within the TD-DFT calculation; c − Calculated band energies ($10^3 \cdot cm^{-1}$), wavelengths (nm) and oscillator strengths in parentheses (f); d − Observed energies ($10^3 \cdot cm^{-1}$) and wavelengths (nm); e − The wave functions based on the eigenvectors predicted by TD-DFT. One-electron transitions associated with the **a**, **s**, **-a** and **-s** MOs are highlighted in bold.

References

1. Gaussian 09, Revision D.01, Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Jr, Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas Ö., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J. Gaussian, Inc., Wallingford CT, **2009**.