

Supporting Information

Oxygen reduction reactivity of cobalt(II) hangman porphyrins

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General Methods

¹H NMR spectra (500 MHz) were recorded on samples in CDCl₃ at room temperature unless noted otherwise. All cobalt(II) hangman porphyrins (CoHPX) are paramagnetic compounds. Silica gel (60 μm average particle size) was used for column chromatography. Compounds (C₆F₅)₄,¹ free-base hangman porphyrins HPX-1, HPX-2, HPX-3, HPX-4, HPX-5, Co(C₆F₅)₄, and CoHPX-1 were prepared as described in the literature.² THF (anhydrous), methanol (anhydrous), CH₂Cl₂ (anhydrous), CHCl₃ and all other chemicals were reagent grade and were used as received. LD-MS data were collected in the absence of matrix. UV-vis spectra were recorded at room temperature in quartz cuvettes in anhydrous THF on a Varian Cary 5000 UV-vis-NIR spectrophotometer.

The microwave-assisted metallation of free-base hangman porphyrins were performed inside the cavity of a CEM Discover microwave synthesis system equipped with infrared, pressure, and temperature sensors for monitoring the synthesis. The reaction vessels were 10 mL crimp-sealed thick-wall glass tubes. The contents of each vessel were stirred with a magnetic stirrer.

Cyclic Voltammetry. All cyclic voltammograms (CV) were recorded in acetonitrile solutions containing 0.1 M NBu₄PF₆ (tetrabutylammonium hexafluorophosphate) and the porphyrin compound. A three compartment cell was employed possessing a 0.07 cm² glassy carbon button electrode as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl as a reference electrode. CVs were collected with scan rates of 10-100 mV/s with iR compensation.

Synthesis of Hangman Porphyrins

General Protocol for Metallation of Hangman Porphyrins under Microwave Irradiation. A microwave glass tube (10 mL) containing a magnetic stir bar was charged with CHCl₃ (5 mL) and HPX (0.038 mmol). The solution was stirred at room temperature for 10 min to obtain a homogenous mixture. Co(OAc)₂ (34 mg, 0.19 mmol, 5 mol equiv. versus corresponding hangman porphyrin) was added. The resulting mixture was stirred at room temperature for 10 min, the reaction vessel was sealed with a septum and subjected to microwave irradiation at 60 °C. The protocol was as follows: (1) the reaction vessel was heated from room temperature to 60 °C, (2) The temperature of the vessel was held at 60 °C and irradiate for 30 min (temperature overshoots of 65 °C - 70 °C were permitted; temperature was re-established at 60 °C by using open flow valve option), (3) the reaction mixture was then cooled to room temperature, and (4) the reaction mixture was analyzed by silica TLC analysis. Steps 1-4 were repeated until all of the starting material was consumed. Upon complete reaction, the crude reaction mixture was analyzed by MALDI-TOF. A sample of triethylamine (5 mol equiv to metal salt) was added to the solution, which was washed with water and brine, dried over Na₂SO₄, and concentrated to

¹ A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* 1967, **32**, 476.

² D. K. Dogutan, D. K. Bediako, T.S. Teets, M. Schwalbe, D. G. Nocera, *Org. Lett.* 2010, **12**, 1036.

dryness. The resulting crude product was chromatographed on silica to afford the corresponding cobalt hangman porphyrin (CoHPX).

5-[4-(2,7-Di-*tert*-butyl-5-hydroxycarbonyl-9,9-dimethylxanthene)]-10,15,20-tris(4-*tert*-butylphenyl)porphyrinatocobalt(II) (CoHPX-2). A sample of HPX-2 (40 mg, 0.037 mmol) in CHCl₃ (5 mL) was treated with Co(OAc)₂ (34 mg, 0.19 mmol). The reaction mixture was subject to microwave irradiation for 6 h. Standard workup was followed with column chromatography on silica (hexanes/CH₂Cl₂ (1:1) → CH₂Cl₂) to afford a brown-red solid (39 mg, 94%). ESI-MS obsd: 1127.5242, and dimer: 2255.0523, calcd: 1127.5244 [M⁺, M = C₇₄H₇₆CoN₄O₃], LD-MS obsd. 1127.93. Anal. Calcd. for C₇₄H₇₆CoN₄O₃: C, 78.77; H, 6.79; N, 4.97. Found: C, 78.73; H, 6.84; N, 4.94. λ_{max,abs}/nm (THF) = 428, 542.

5-[4-(2,7-Di-*tert*-butyl-5-hydroxycarbonyl-9,9-dimethylxanthene)]-10,15,20-tris(2,4,6-trimethylphenyl)porphyrinatocobalt(II) (CoHPX-3). A sample of HPX-3 (39 mg, 0.038 mmol) in CHCl₃ (5 mL) was treated with Co(OAc)₂ (34 mg, 0.19 mmol). The reaction mixture was subject to microwave irradiation for 5 h. Standard workup was followed with column chromatography on silica (hexanes/CH₂Cl₂ (1:1) → CH₂Cl₂) to afford a brown-red solid (31 mg, 75%). ESI-MS obsd. 1085.4748, Calcd. 1085.4774 [M⁺, M = C₇₁H₇₀CoN₄O₃], LD-MS obsd. 1085.51. Anal. Calcd. for C₇₁H₇₀CoN₄O₃: C, 78.50; H, 6.50; N, 5.16. Found: C, 78.52; H, 6.46; N, 5.19. λ_{max,abs}/nm (THF) = 431, 544.

5-[4-(2,7-Di-*tert*-butyl-5-hydroxycarbonyl-9,9-dimethylxanthene)]-10,15,20-tri(4-methoxyphenyl)porphyrinatocobalt(II) (CoHPX-4). Method 1 was followed. A sample of HPX-4 (37 mg, 0.037 mmol) in CHCl₃ (5 mL) was treated with Co(OAc)₂ (34 mg, 0.19 mmol). The reaction mixture was subject to microwave irradiation for 5 h. Standard workup was followed with column chromatography on silica (hexanes/CH₂Cl₂ (1:1) → CH₂Cl₂) to afford a brown-red solid (36 mg, 92%). ESI-MS obsd. 1049.3655 and the dimer 2098.7510, Calcd 1049.3688 [M⁺, M = C₆₆H₅₈CoN₄O₆], LD-MS obsd. 1049.24. Anal. Calcd. for C₆₆H₅₈CoN₄O₆: C, 74.34; H, 5.57; N, 5.34. Found: C, 74.30; H, 5.61; N, 5.37. λ_{max,abs}/nm (THF) = 427, 544.

5-[4-(2,7-di-*tert*-butyl-5-hydroxycarbonyl-9,9-dimethylxanthene)]-10,15,20-tripentylporphyrin porphyrinatocobalt(II) (CoHPX-5). Method 1 was followed. A sample of HPX-5 (34 mg, 0.039 mmol) in CHCl₃ (5 mL) was treated with Co(OAc)₂ (34 mg, 0.19 mmol). The reaction mixture was subject to microwave irradiation for 4 h. Standard workup was followed with column chromatography on silica (hexanes/CH₂Cl₂ (1:1) → CH₂Cl₂) to afford a brown-red solid (34 mg, 97%). ESI-MS obsd. 941.4746, Calcd. 941.4774 [M⁺, M = C₅₉H₇₀CoN₄O₃], LD-MS obsd. 941.79 Anal. Calcd. for C₅₉H₇₀CoN₄O₃: C, 75.21; H, 7.49; N, 5.95. Found: C, 75.28; H, 7.53; N, 5.92. λ_{max,abs}/nm (THF) = 433, 552.

X-Ray Crystallographic Details

The crystal of Co-HPX3 was mounted on a Bruker three circle goniometer platform equipped with an APEX 2 detector. A graphic monochromator was employed for wavelength selection of the Cu K α radiation ($\lambda = 1.54178\text{\AA}$). The data were processed and refined using the program SAINT supplied by Siemens Industrial Automation. The crystals were found to be non-merohedral twins. Two unit cell domains were located using the program cell_now, and the program TWINABS was used for the absorption correction. The structure was refined against the reflections for the major twin component. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms bound to carbon were placed in calculated positions using the standard riding model and refined isotropically. Hydrogen atoms bound to oxygen were located in the difference map and refined semi-freely; all non-hydrogen atoms were refined anisotropically. One of the *t*-butyl groups in the structure was modelled as a two-part disorder. The structure also contained an acetone solvate molecule refined at half-occupancy. The 1 – 2 and 1 – 3 distances of all disordered parts were restrained to be similar using the SADI command; the rigid-bond restraints SIMU and DELU were also used on disordered parts.

Table S1. Crystallographic Summary for Co-HPX3.

Co-HPX3·0.5Me₂CO	
Formula	C _{78.5} H ₇₉ CoN ₄ O _{3.5}
fw, g/mol	1193.39
temperature	100(2) K
cryst. syst.	Triclinic
space group	PT
colour	Purple
a (Å)	13.6816(8)
b (Å)	14.9382(8)
c (Å)	19.8125(12)
α (°)	100.854(4)
β (°)	103.727(4)
γ (°)	109.497(4)
V (Å ³)	3546.3(4)
Z	2
R1 ^a (all data)	0.1593
wR2 ^b (all data)	0.3578
R1 [(I>2σ)]	0.1232
wR2 [(I>2σ)]	0.3330
GOF ^c	1.218

^a $R1 = \frac{\sum ||F_o - |F_c||}{\sum |F_o|}$. ^b $wR2 = \frac{(\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}}$. ^c $GOF = \frac{(\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}}$ where n is the number of data and p is the number of parameters refined.

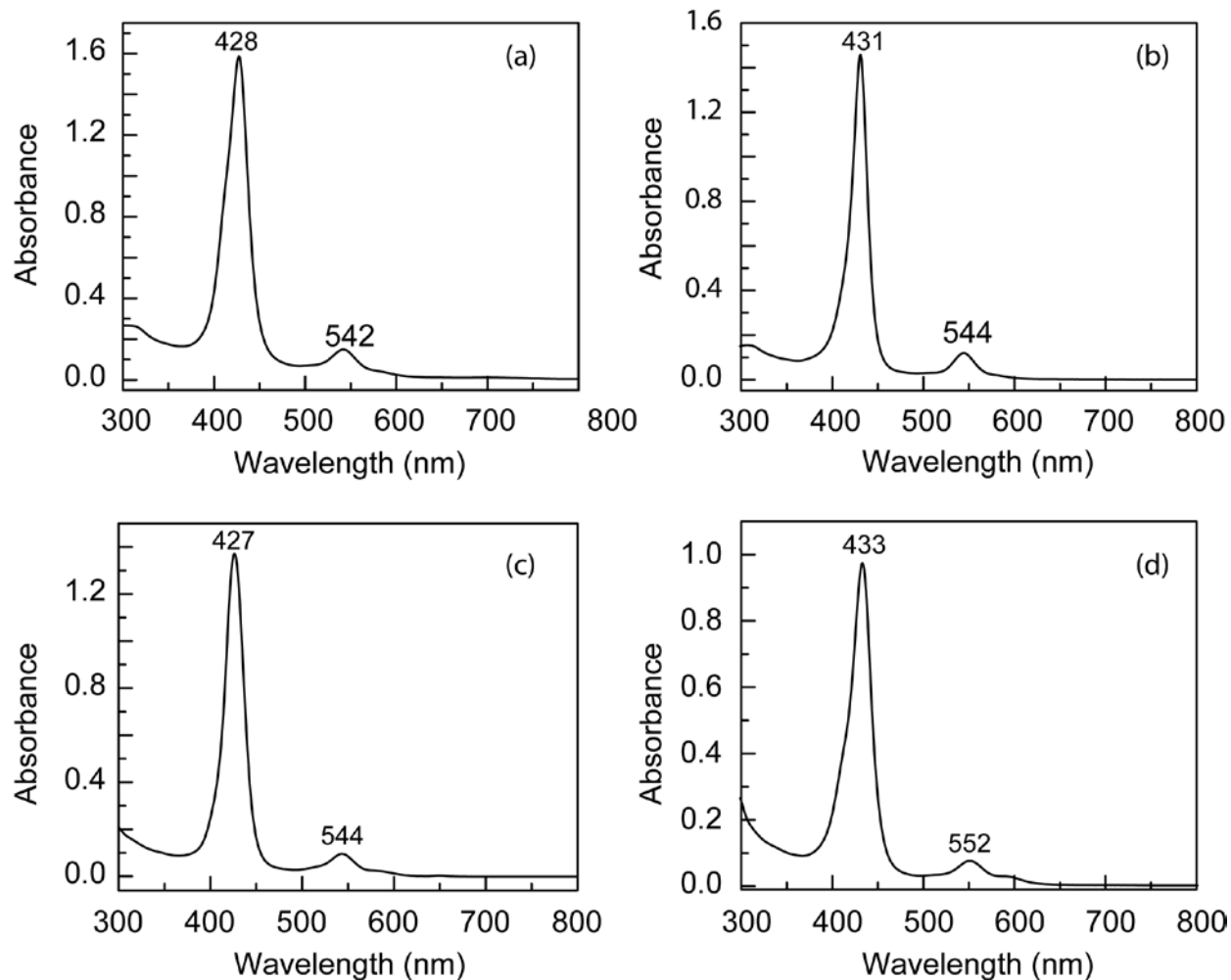
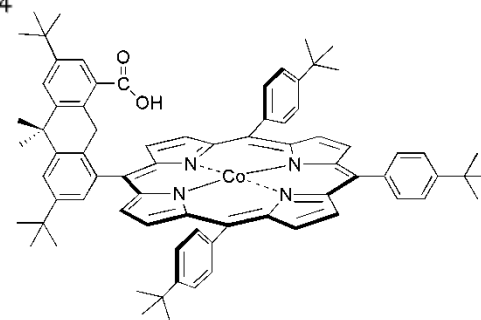


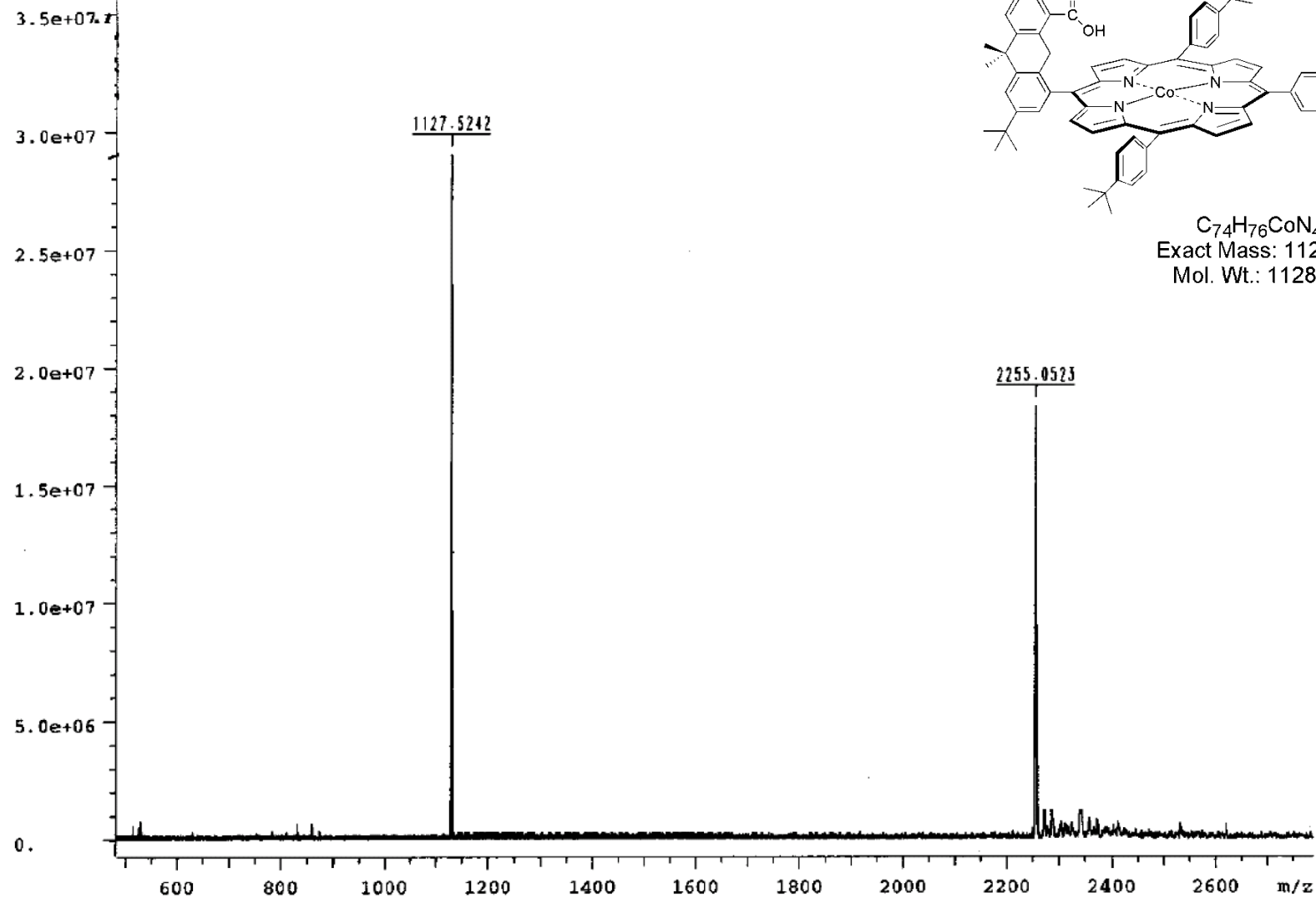
Figure S1. Electronic absorption spectra of (a) CoHPX-2, (b) CoHPX-3, (c) CoHPX-4 and (d) CoHPX-5 in THF at room temperature.

a. i.

Sample ID: **CoHPX-2**
C₇₄H₇₆CoN₄O₃, Theoretical Mass [M+]: 1127.5244



C₇₄H₇₆CoN₄O₃
Exact Mass: 1127.5249
Mol. Wt.: 1128.3534



/Bruker/data/2009/NC/NCdkip_ESI/CoHPX3-CO2H/pdata/1 FTMSuser Mon Dec 21 16:21:17 2009

Figure S2a. Full ESI-MS spectrum of CoHPX-2.

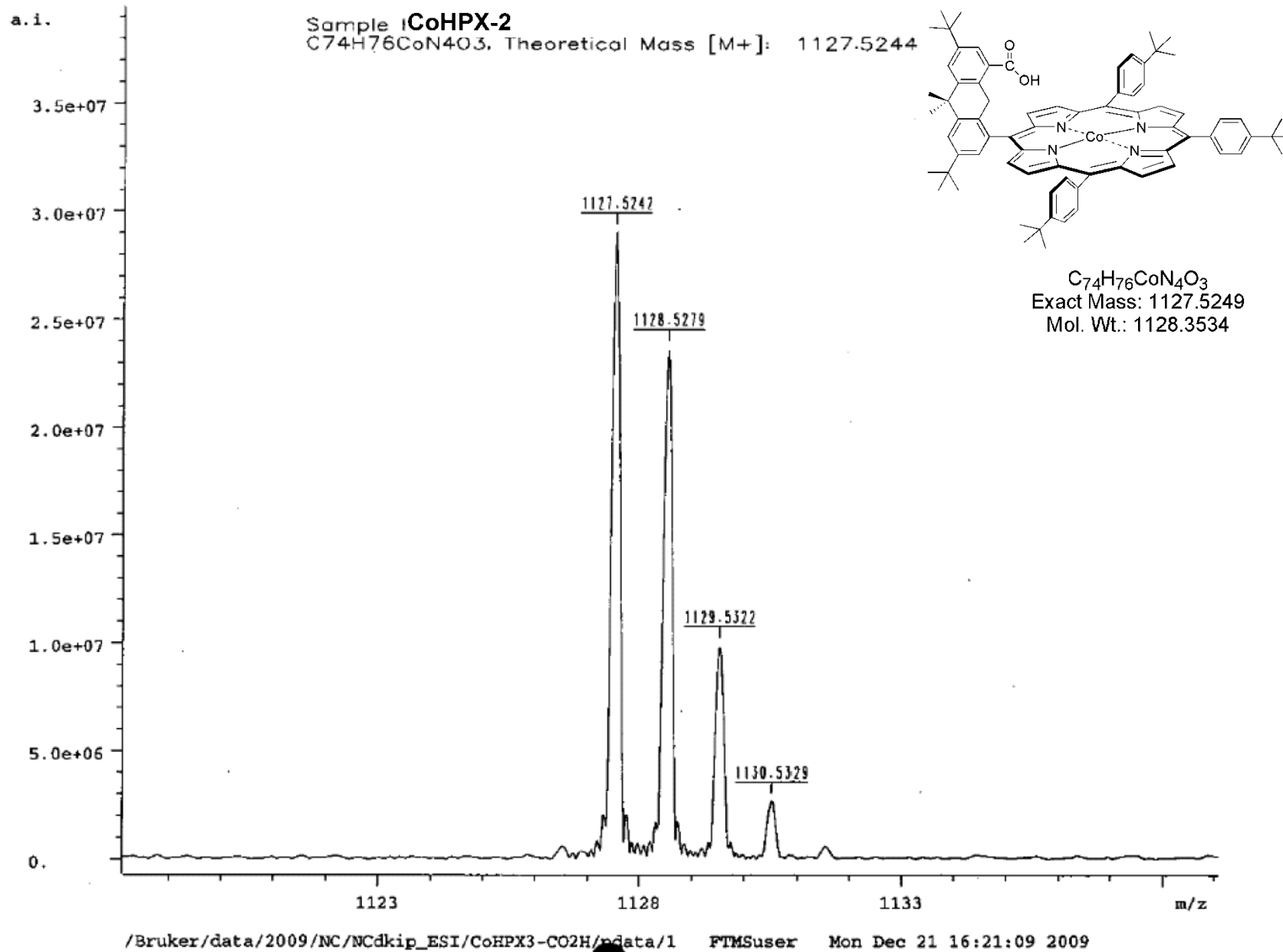


Figure S2b. ESI-MS spectrum of CoHPX-2.

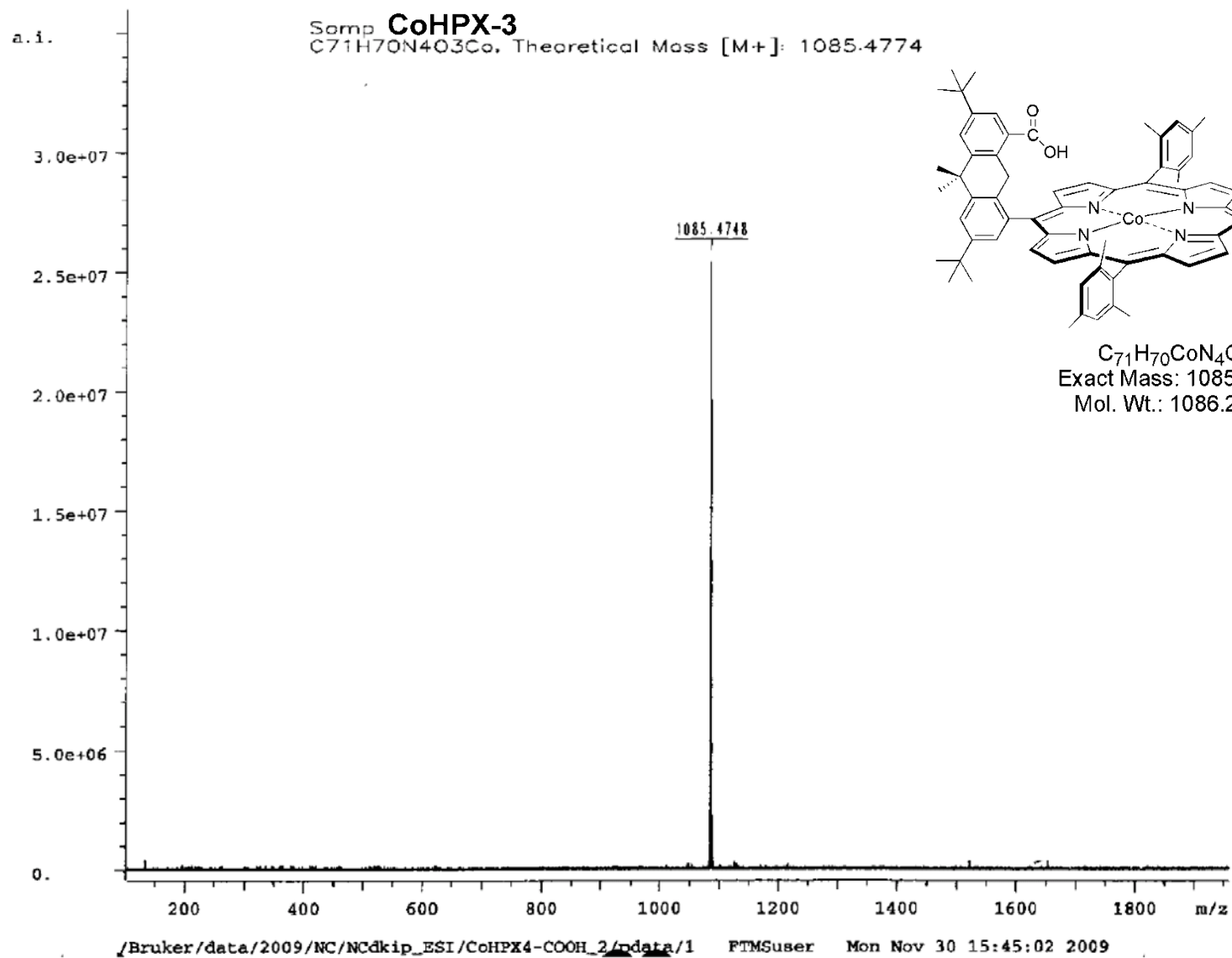


Figure S3a. Full ESI-MS spectrum of CoHPX-3.

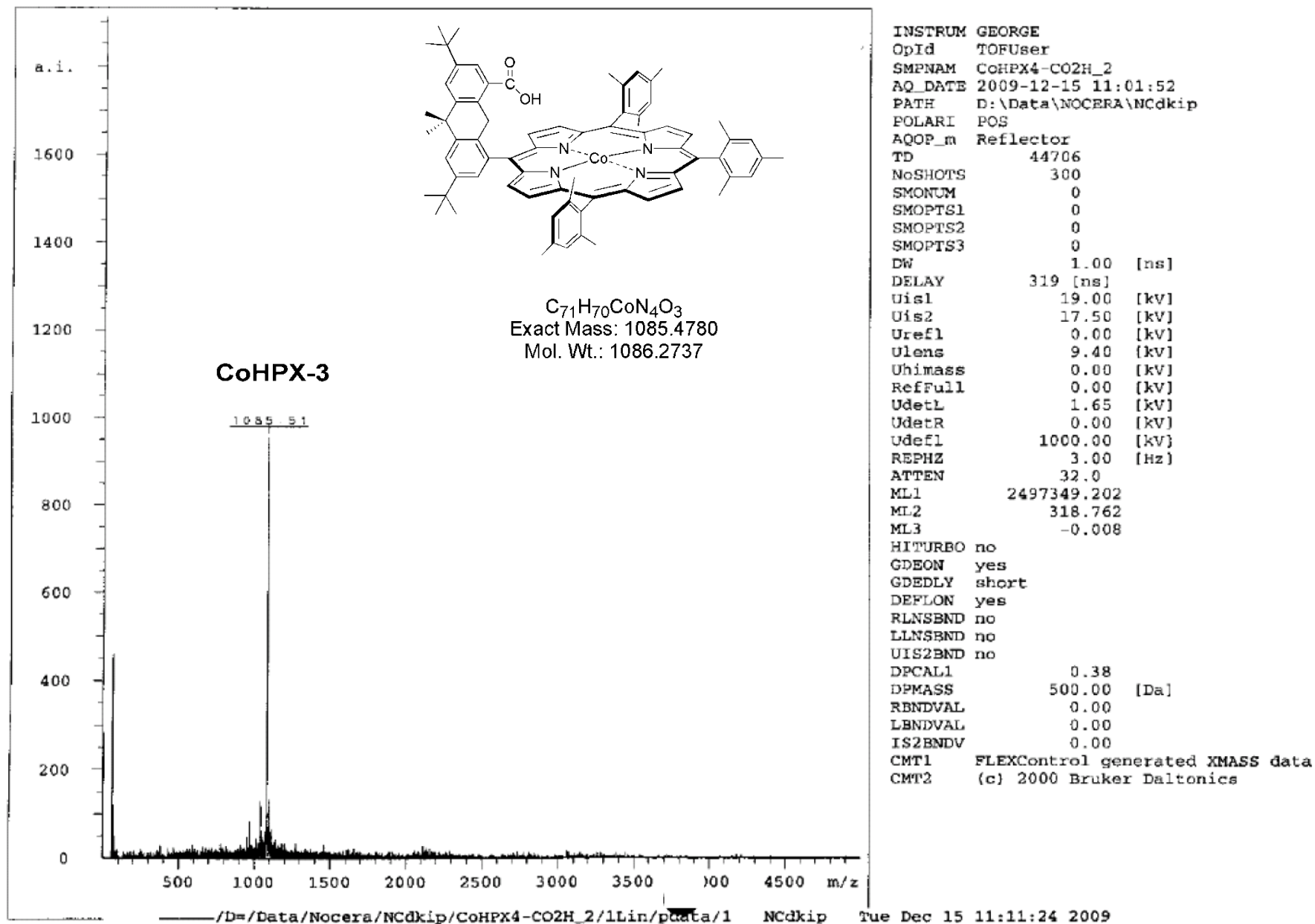


Figure S3c. LD-MS spectrum of CoHPX-3.

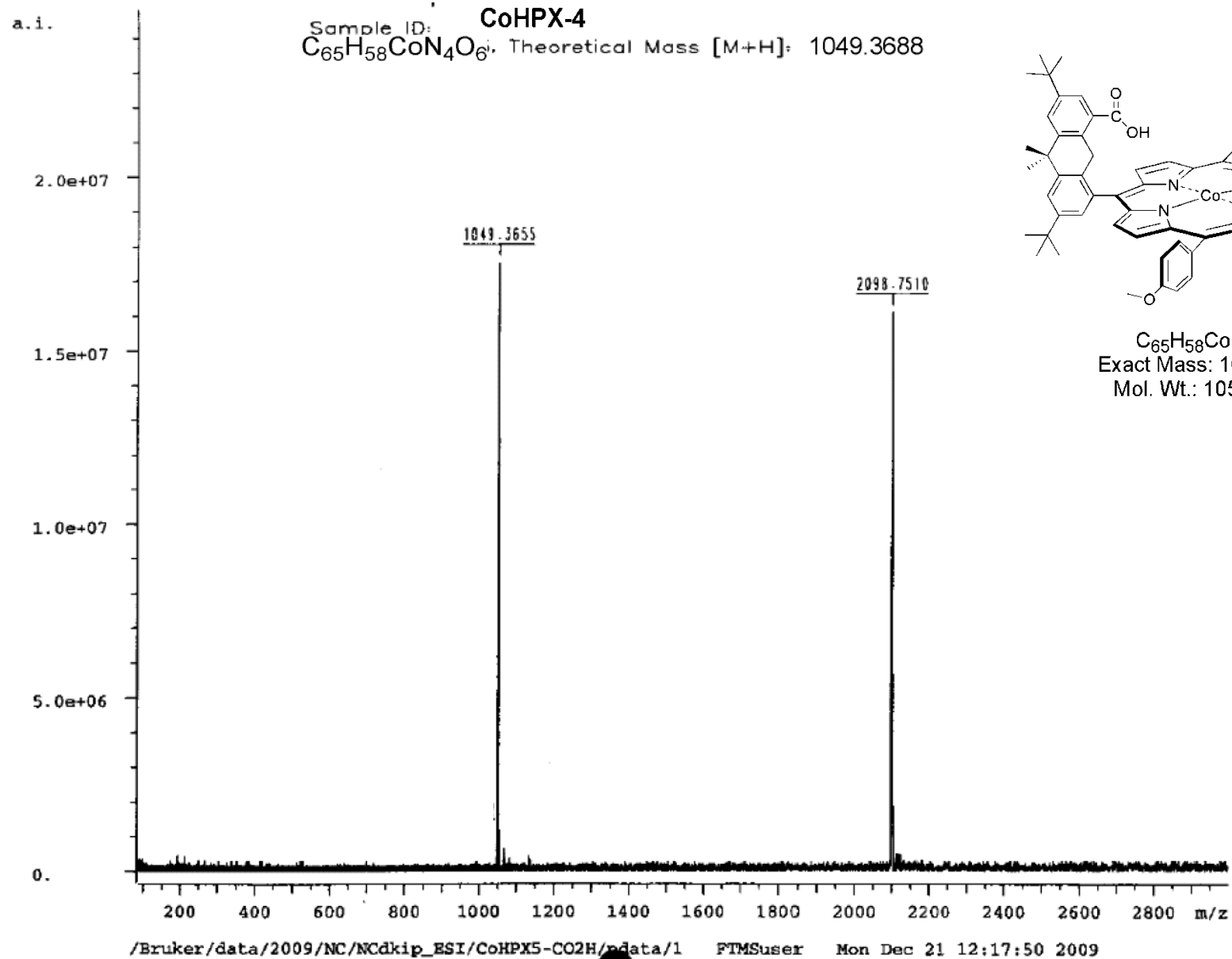
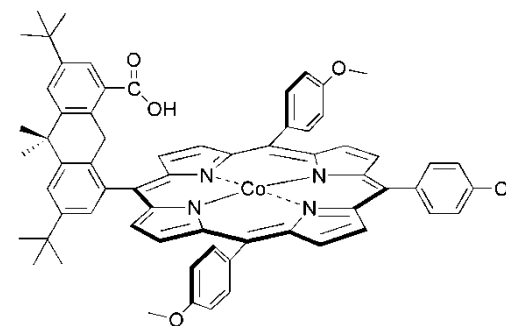


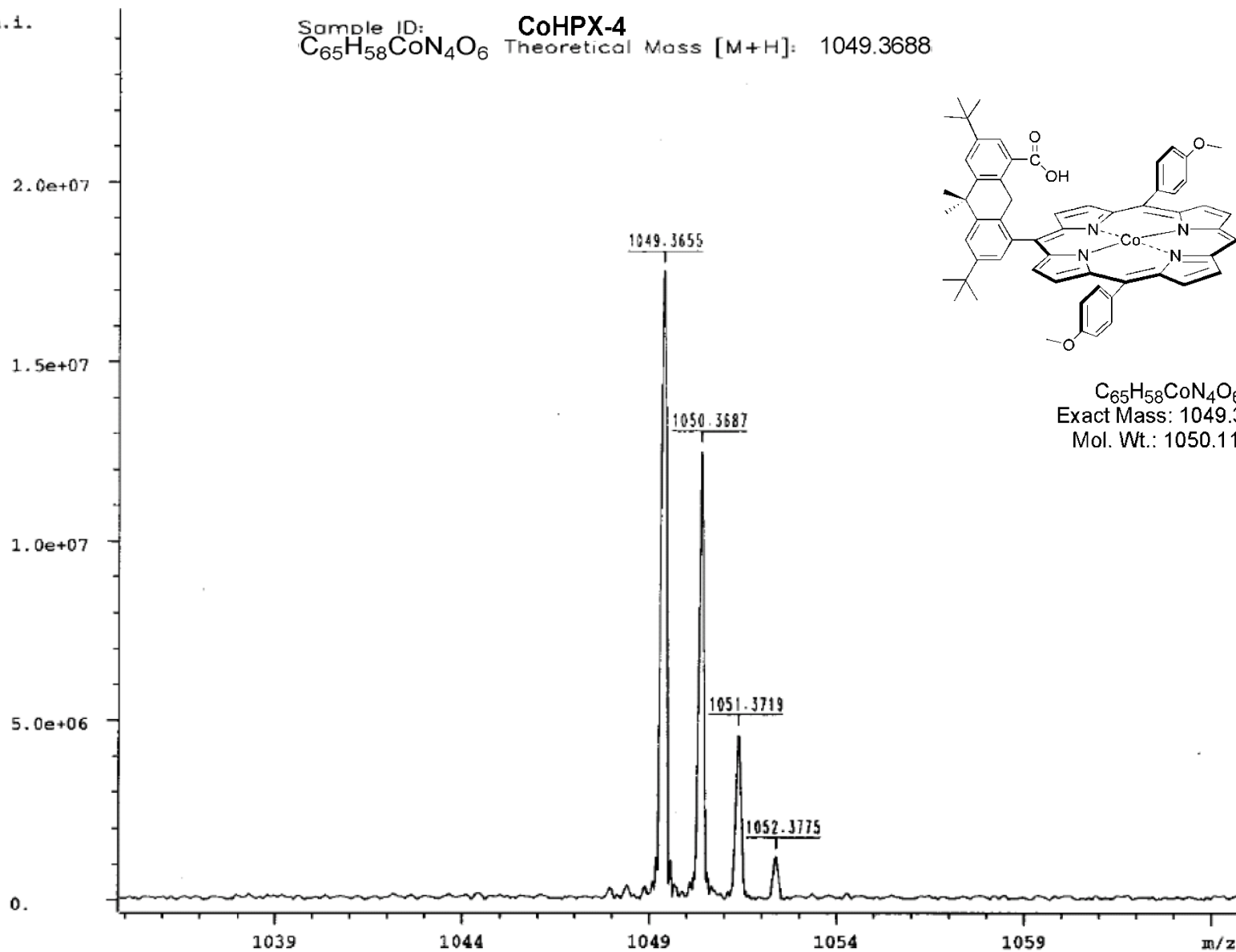
Figure S4a. Full ESI-MS spectrum of CoHPX-4.

a. i.

Sample ID: **CoHPX-4**
 $C_{65}H_{58}CoN_4O_6$ Theoretical Mass [M+H]: 1049.3688



$C_{65}H_{58}CoN_4O_6$
Exact Mass: 1049.3688
Mol. Wt.: 1050.1124



/Bruker/data/2009/NC/NCdkip_ESI/CoHPX5-CO2H/data/1 FTMSuser Mon Dec 21 12:18:02 2009

Figure S4b. ESI-MS spectrum of CoHPX-4.

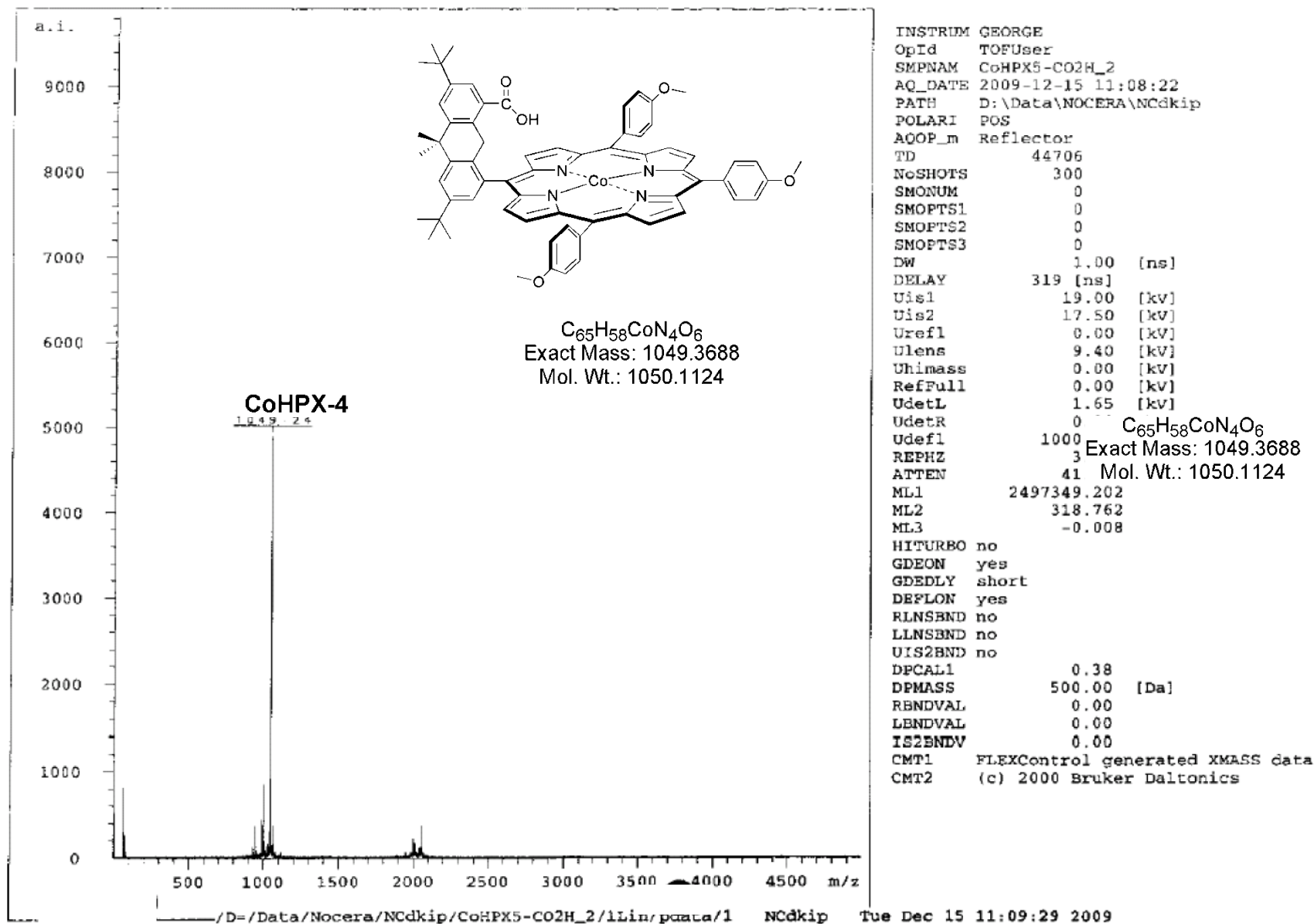
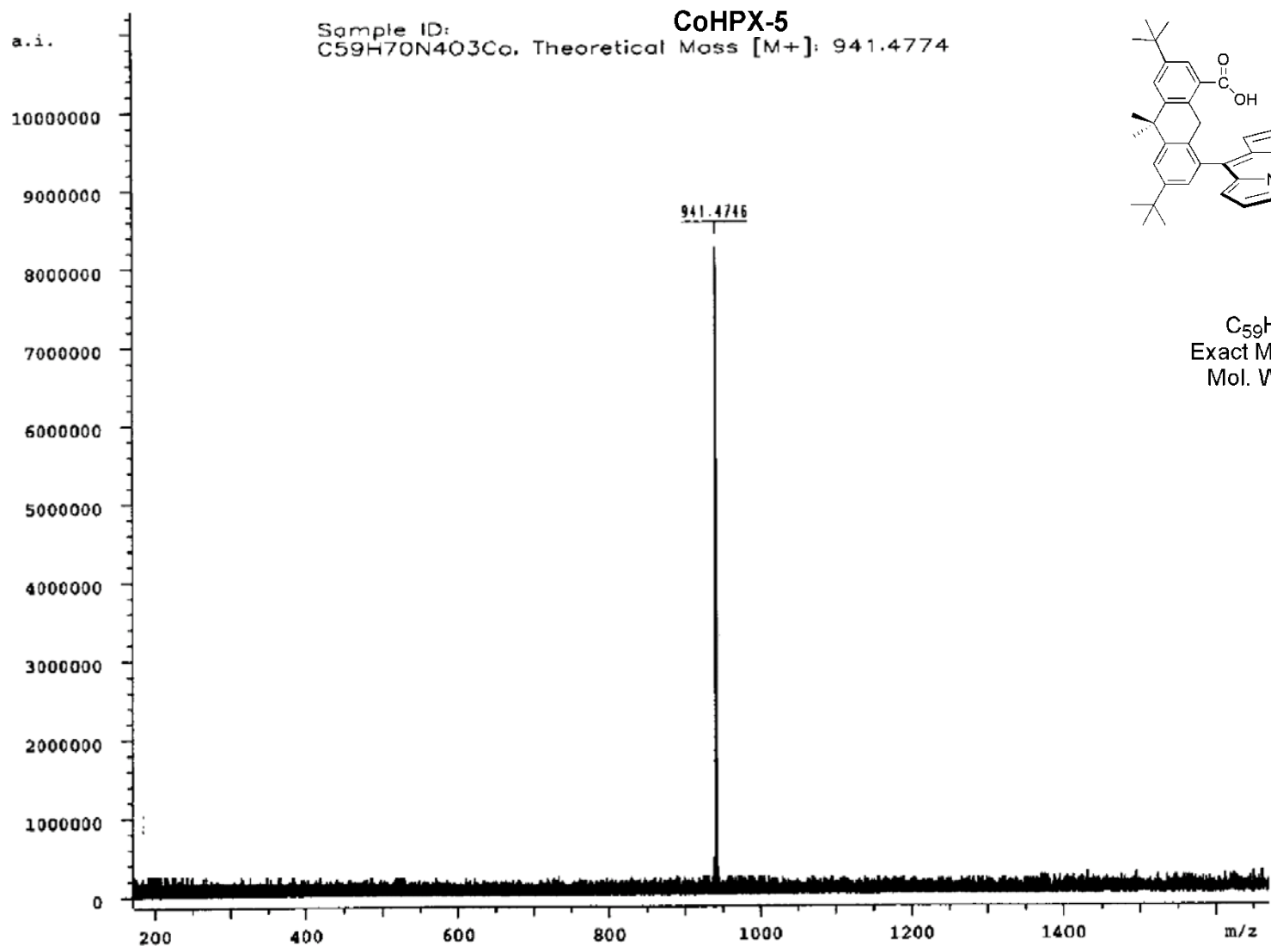


Figure S4c. LD-MS spectrum of CoHPX-4.



/Bruker/data/2009/NC/NCdkip_ESI/CoHPX6-COOH_3/pdata/1 FIMSuser Mon Nov 30 15:48:12 2009

Figure S5a. Full ESI-MS spectrum of CoHPX-5.

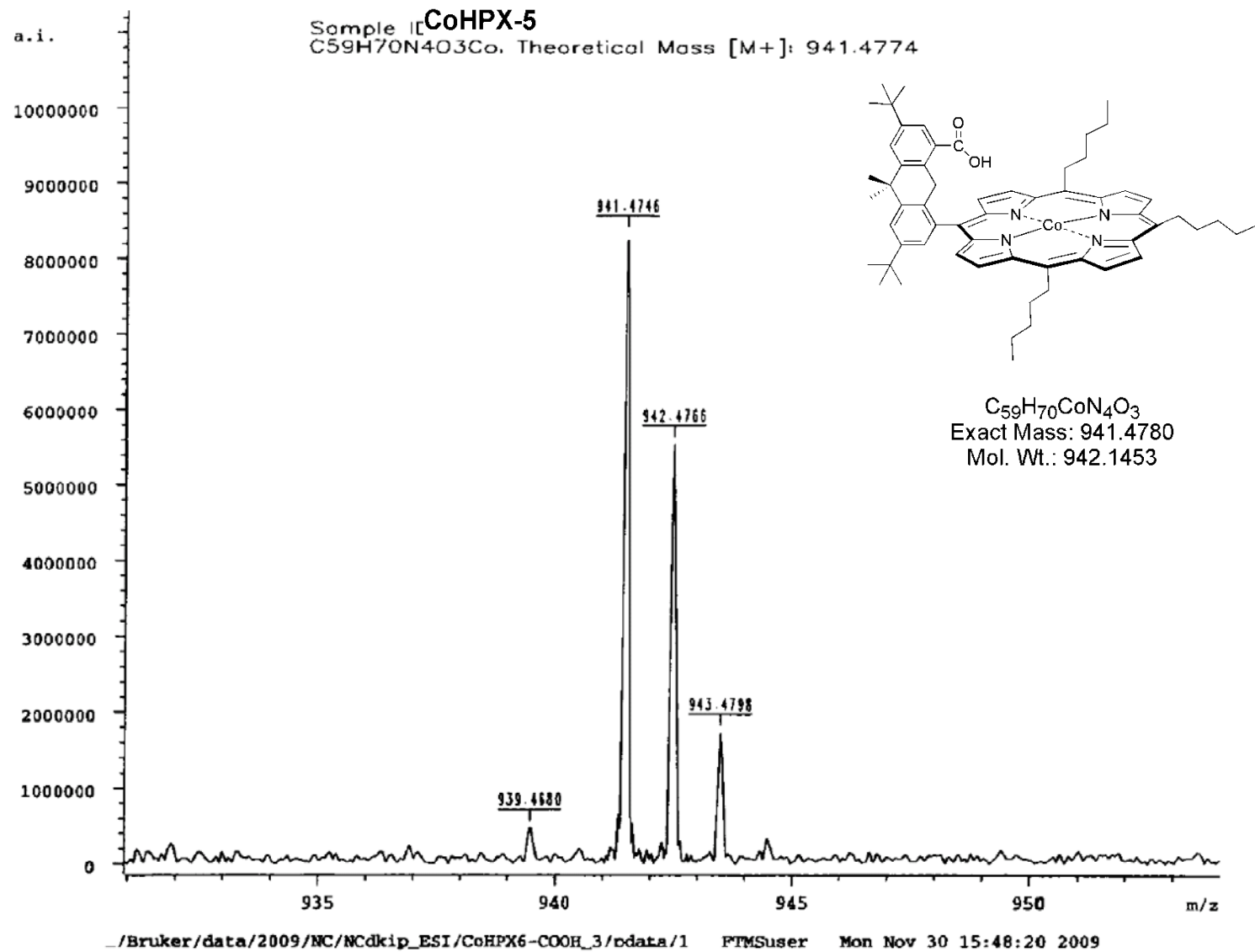


Figure S5b. ESI-MS spectrum of CoHPX-5.

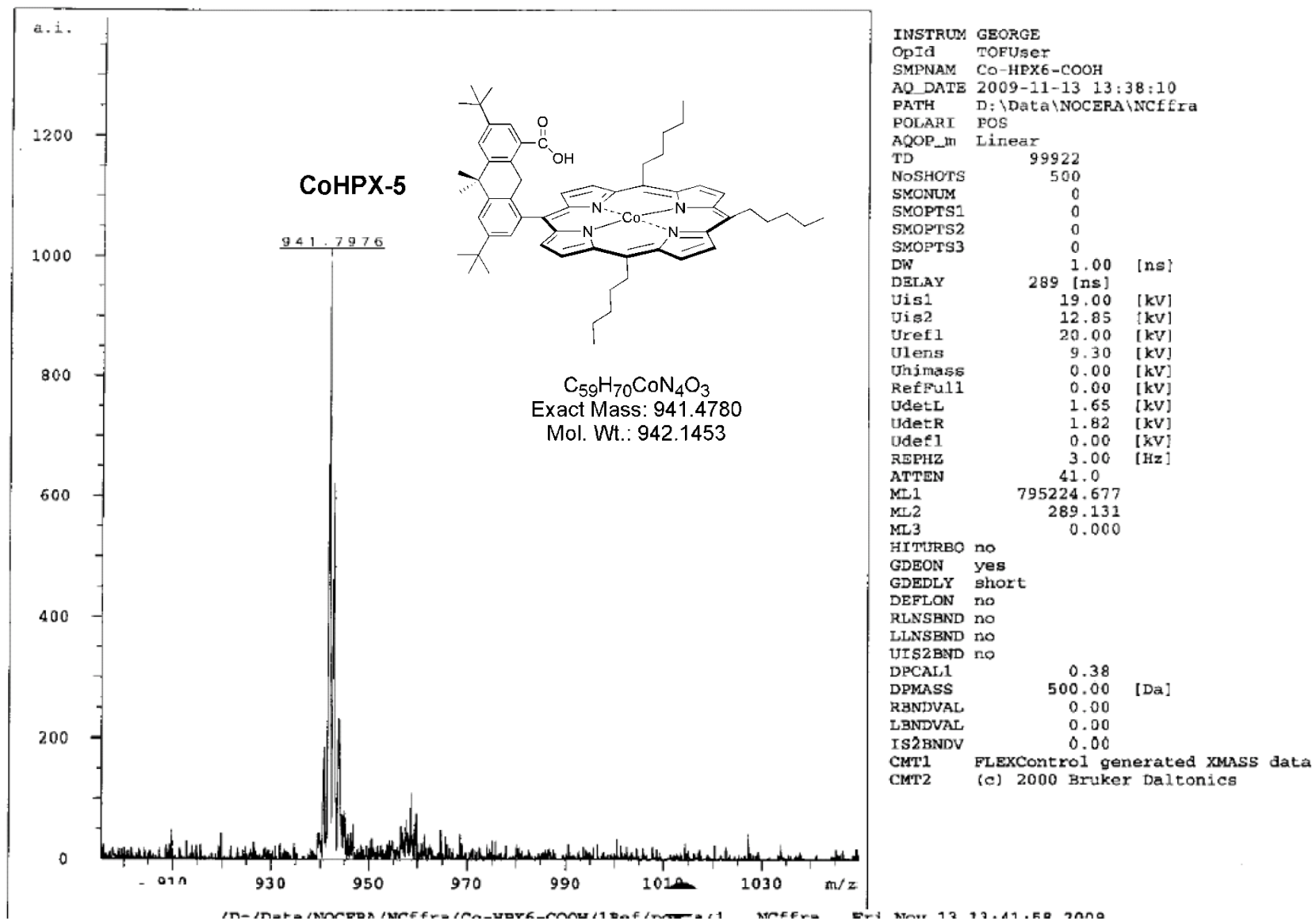


Figure S5c. Full LDI-MS spectrum of CoHPX-5.

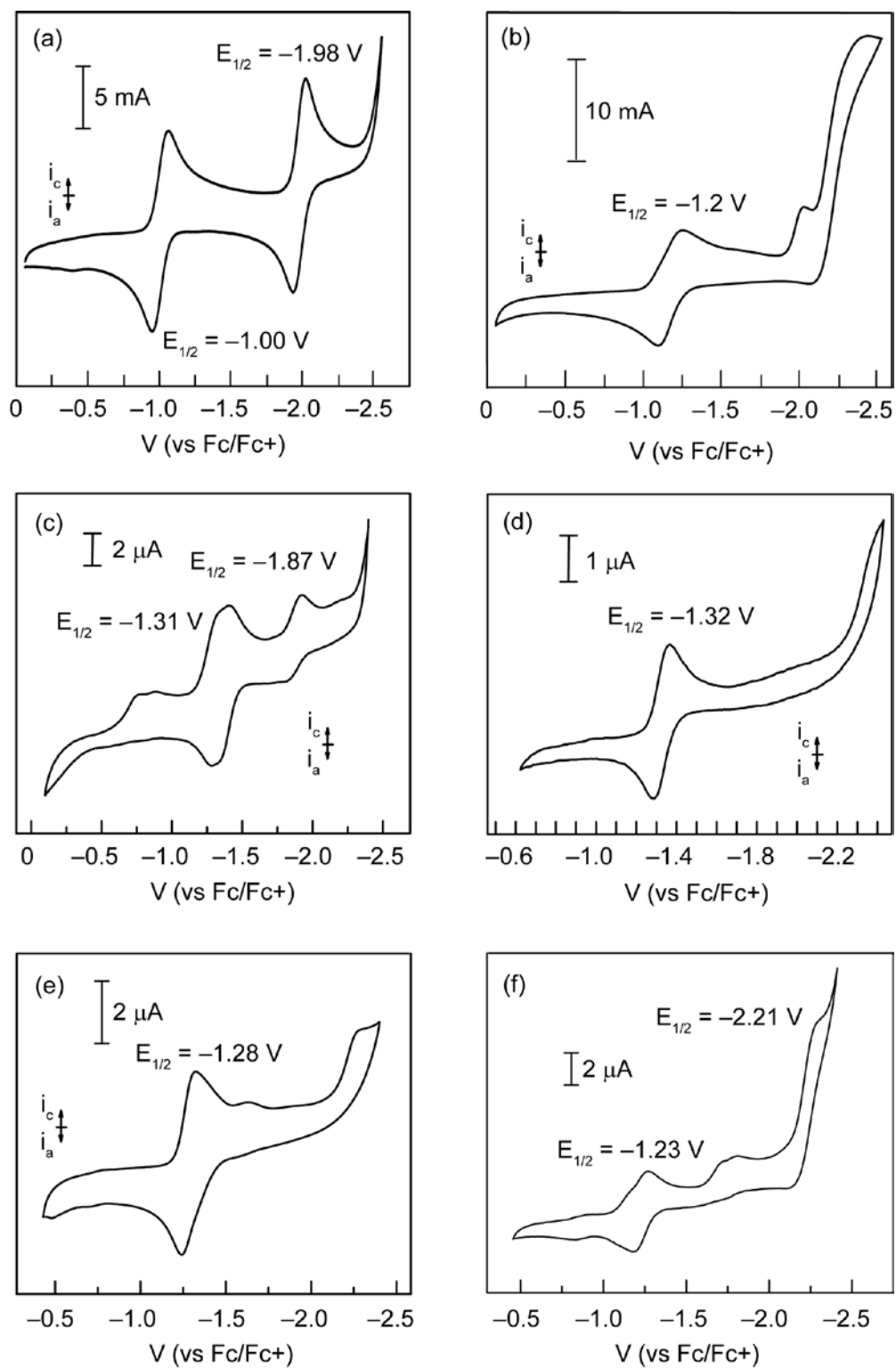


Figure S6. Cyclic voltammograms of (a) $\text{Co}(\text{C}_6\text{F}_5)_4$ (b) CoHPX-1 (c) CoHPX-2 (d) CoHPX-3 (e) CoHPX-4 and (f) CoHPX-5 in acetonitrile and 0.1 M NBu_4PF_6 electrolyte (scan rate = 25 mV/s).

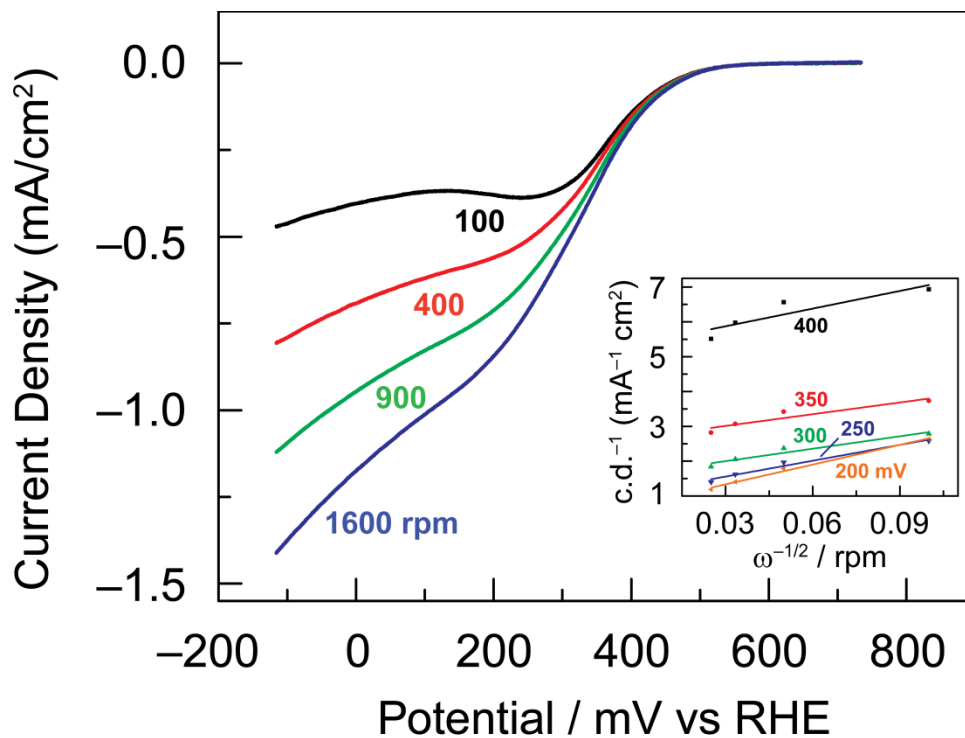


Figure S7a. RDE of CoHPX-2 in O₂ saturated 0.5 M H₂SO₄ (scan rate 20 mV/s). Inset: Koutecky-Levich analysis at various potentials.

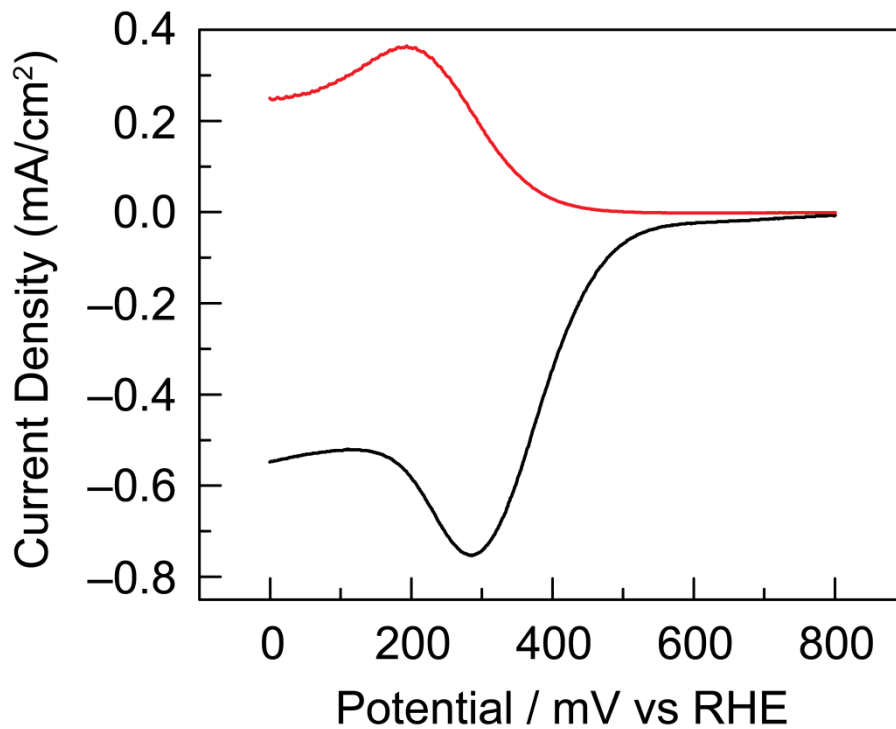


Figure S7b. RRDE (100 rpm) of CoHPX-2 in O₂ saturated 0.5 M H₂SO₄ (scan rate 20 mV/s), disc (black), ring (red). Platinum ring held at 1.2 V vs SCE.

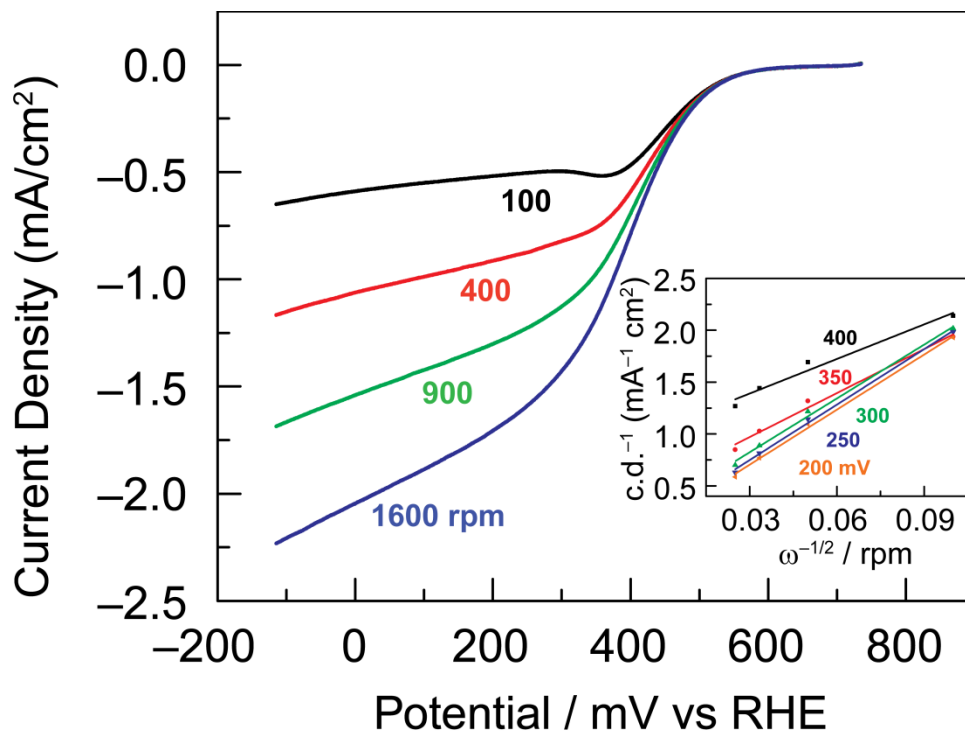


Figure S8a. RDE of CoHPX-3 in O₂ saturated 0.5 M H₂SO₄ (scan rate 20 mV/s). Inset: Koutecky-Levich analysis at various potentials.

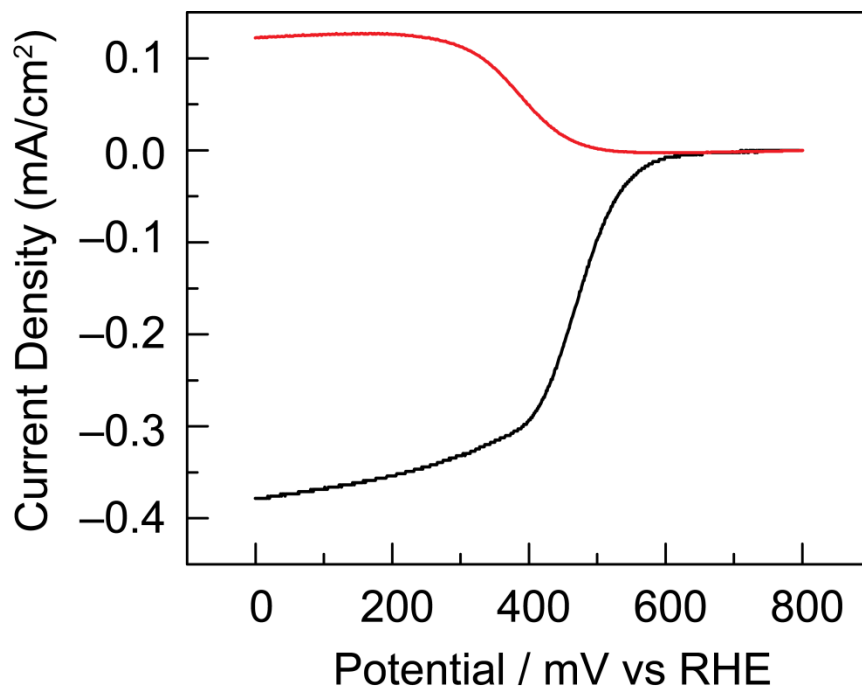


Figure S8b. RRDE (100 rpm) of CoHPX-3 in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s, disc (black), ring (red). Platinum ring held at 1.2 V vs SCE.

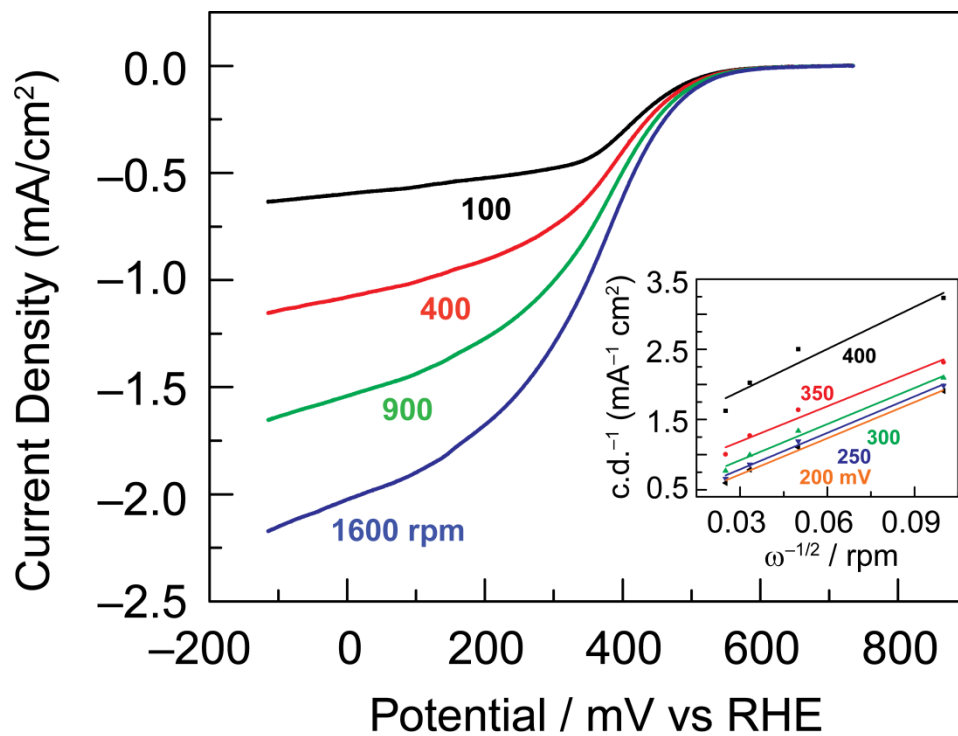


Figure S9a. RDE of CoHPX-4 in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s. Inset: Koutecky-Levich analysis at various potentials.

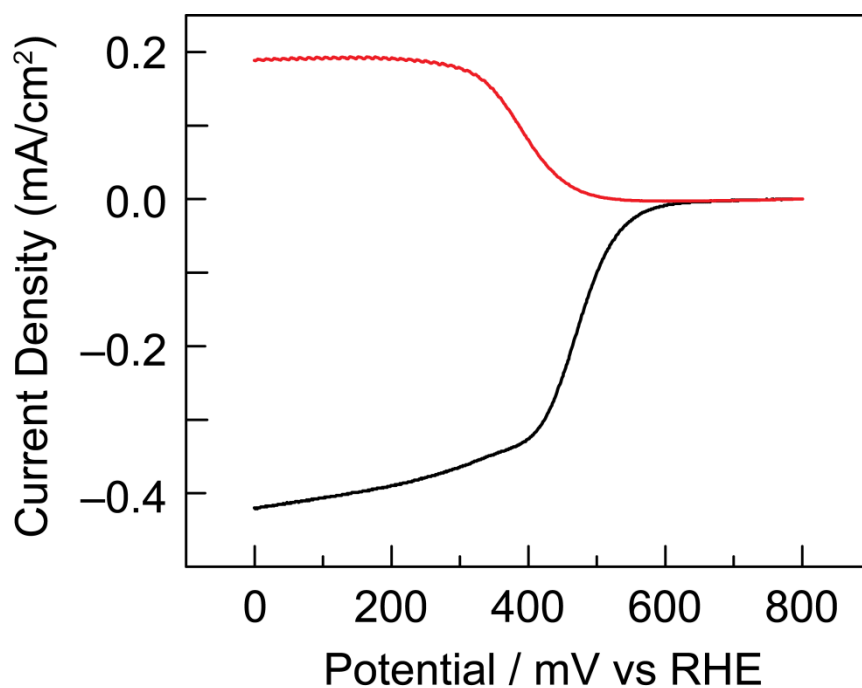


Figure S9b. RRDE (100 rpm) of CoHPX-4 in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s, disc (black), ring (red). Platinum ring held at 1.2 V vs SCE.

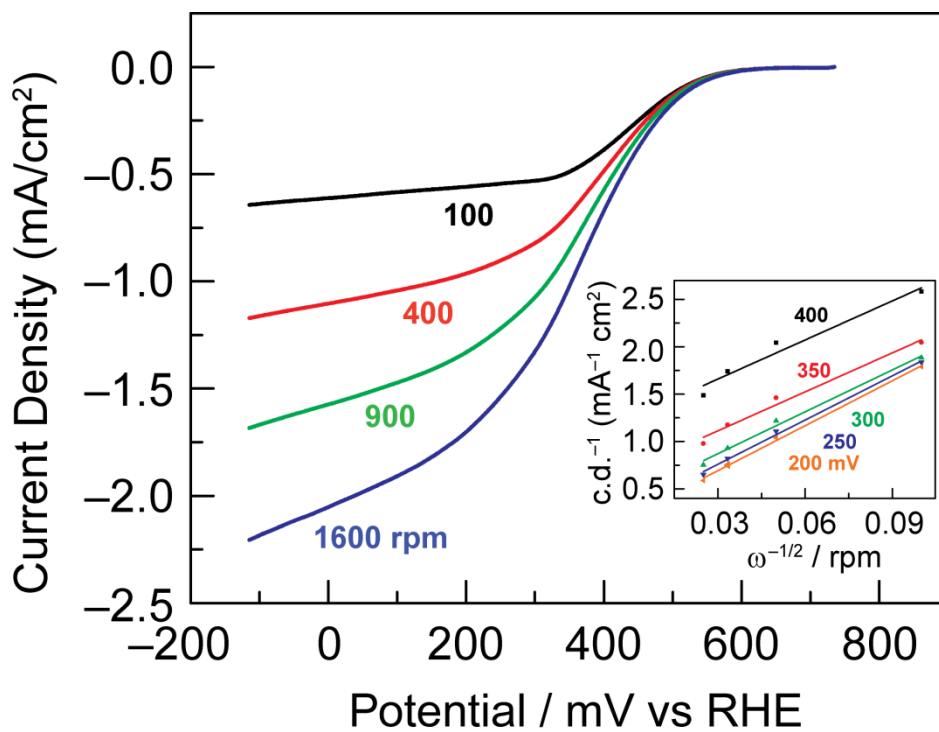


Figure S10a. RDE of CoHPX-5 in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s. Inset: Koutecky-Levich analysis at various potentials.

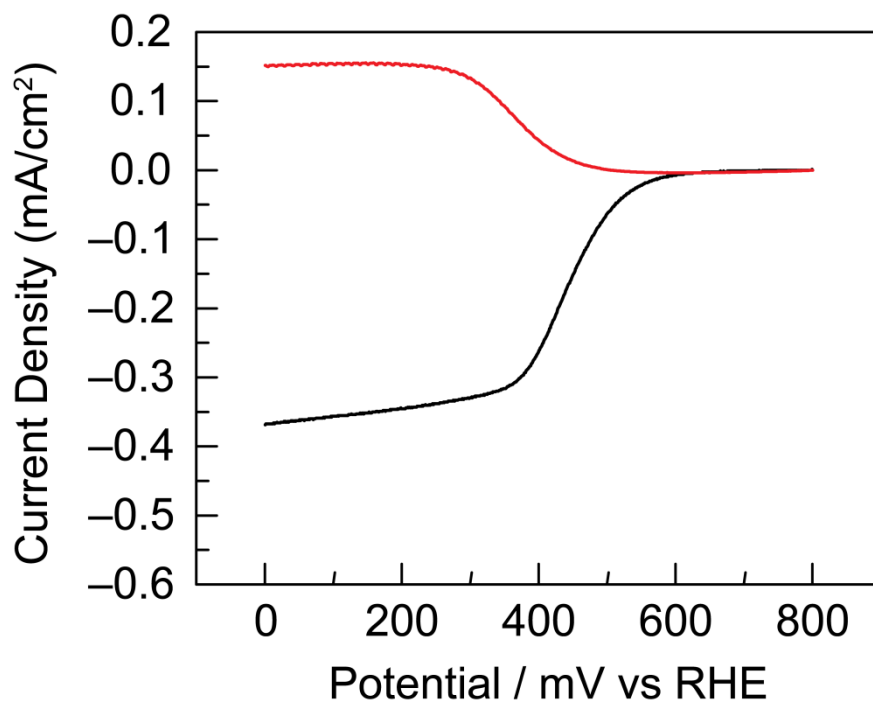


Figure S10b. RRDE (100 rpm) of CoHPX-5 in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s, disc (black), ring (red). Platinum ring held at 1.2 V vs SCE.

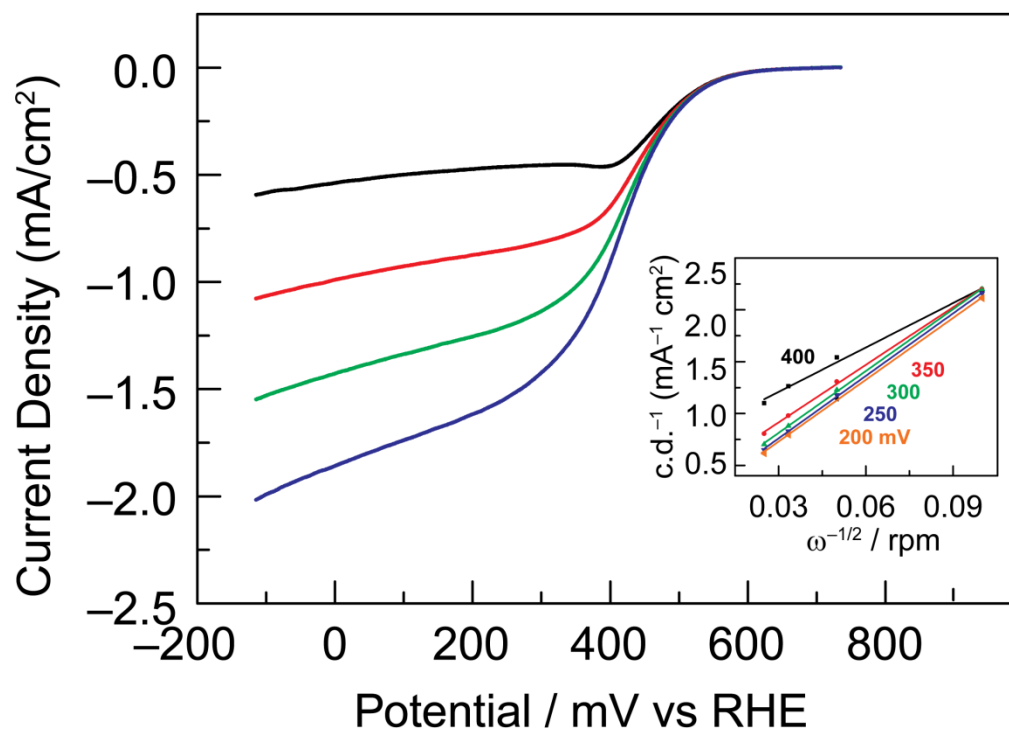


Figure S11. RDE of $\text{Co}(\text{C}_6\text{F}_5)_4$ in O_2 saturated $0.5 \text{ M H}_2\text{SO}_4$ scan rate 20 mV/s . Inset: Koutecky-Levich analysis at various potentials

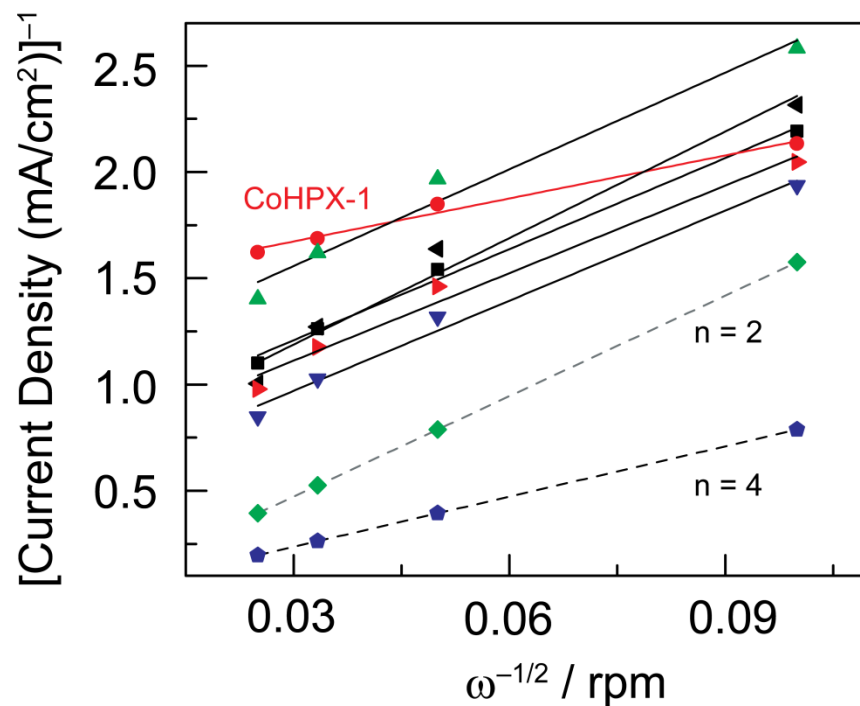


Figure S12. Koutecky Levich analysis at 400 mV for CoHPX-1 (red circles), CoHPX-2 (green triangle, up), CoHPX-3 (blue triangle, down), CoHPX-4 (black triangle, left), CoHPX-5 (red triangle, right) and $\text{Co}(\text{C}_6\text{F}_5)_4$ (black square). Theoretical plots for 2 (green diamond) and 4 (blue pentagon) electron transfers are shown. Comparison of CoHPX-1 and $n = 4$ is shown in red.

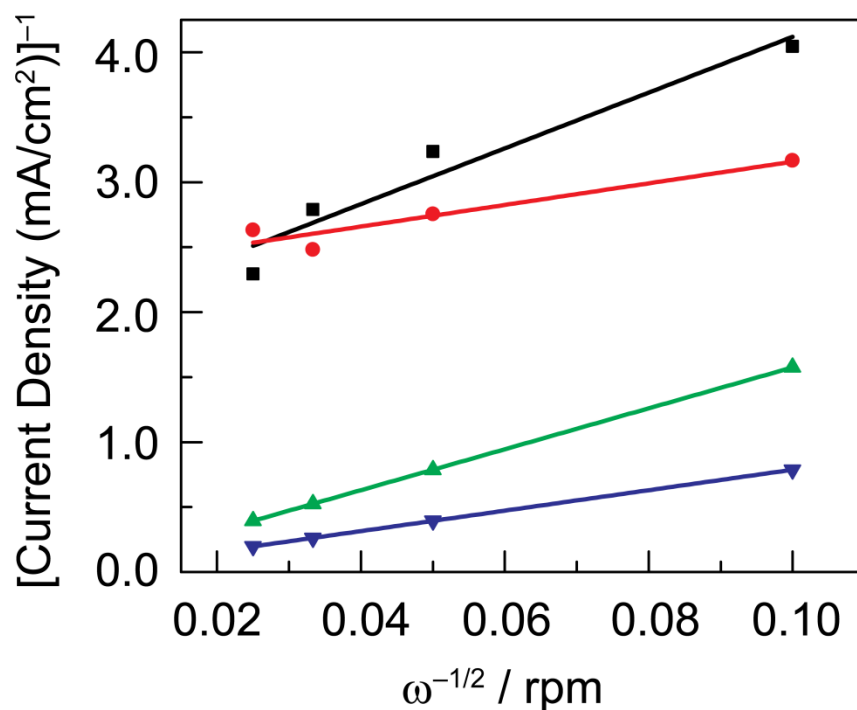


Figure S13. Koutecky-Levich analysis for Co₂(DPX) (red circles) and Co(OEP) (black squares). Theoretical plots for 2 (green triangles) and 4 (blue triangles) electron transfer are shown. Theoretical plots were calculated from the following values for O₂ saturated 0.5 M H₂SO₄.

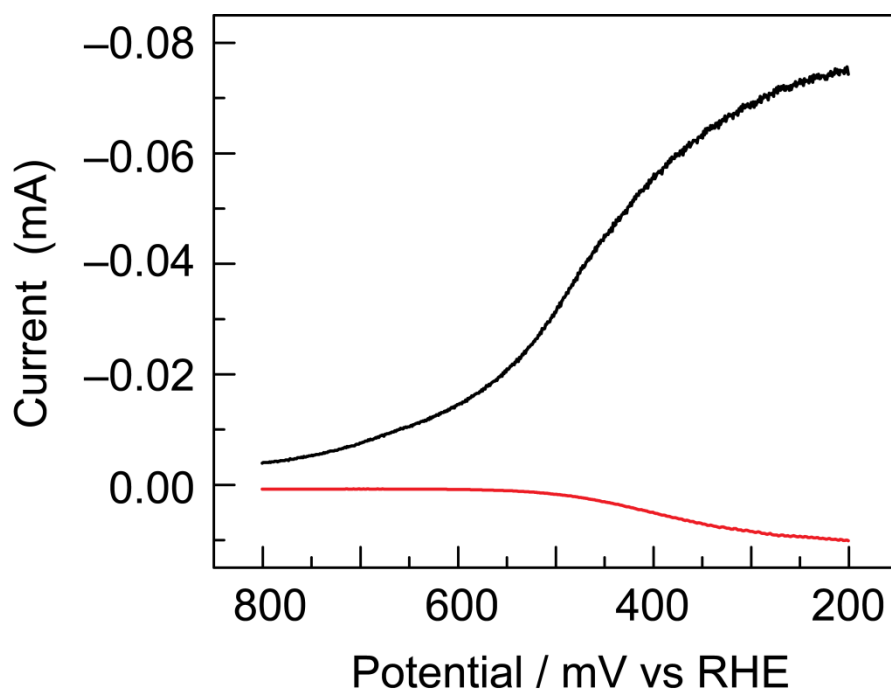


Figure S14. RRDE at 100 rpm of Co₂(DPX) in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s, disc (black), ring (red). Platinum ring held at 1.2 V vs SCE.

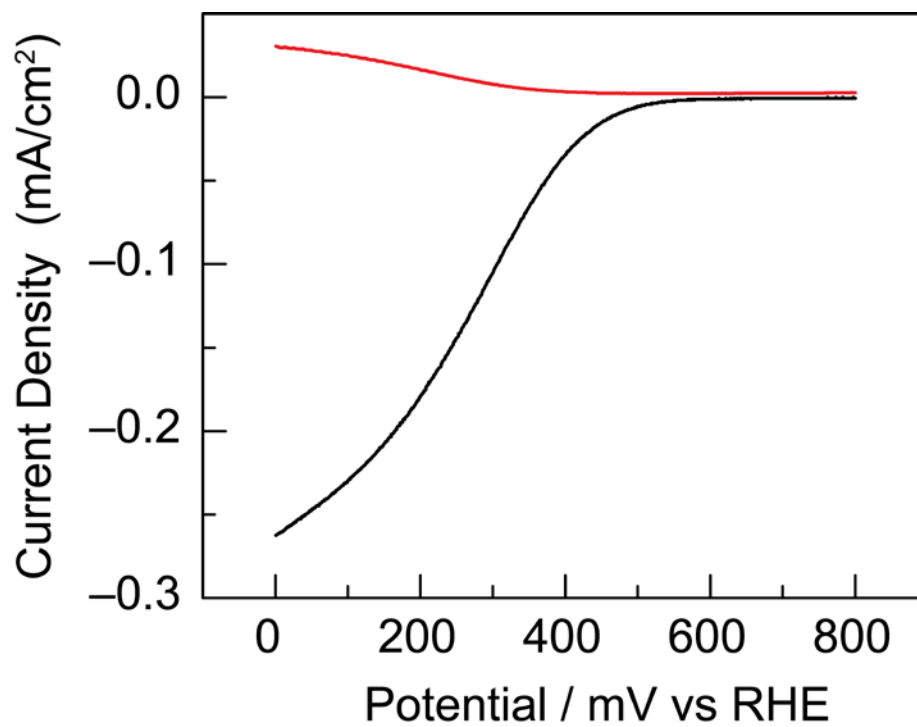


Figure S15. RRDE at 100 rpm of CoHPX-3 in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s, disc (black), ring (red). Platinum ring held at 1.2 V vs SCE.

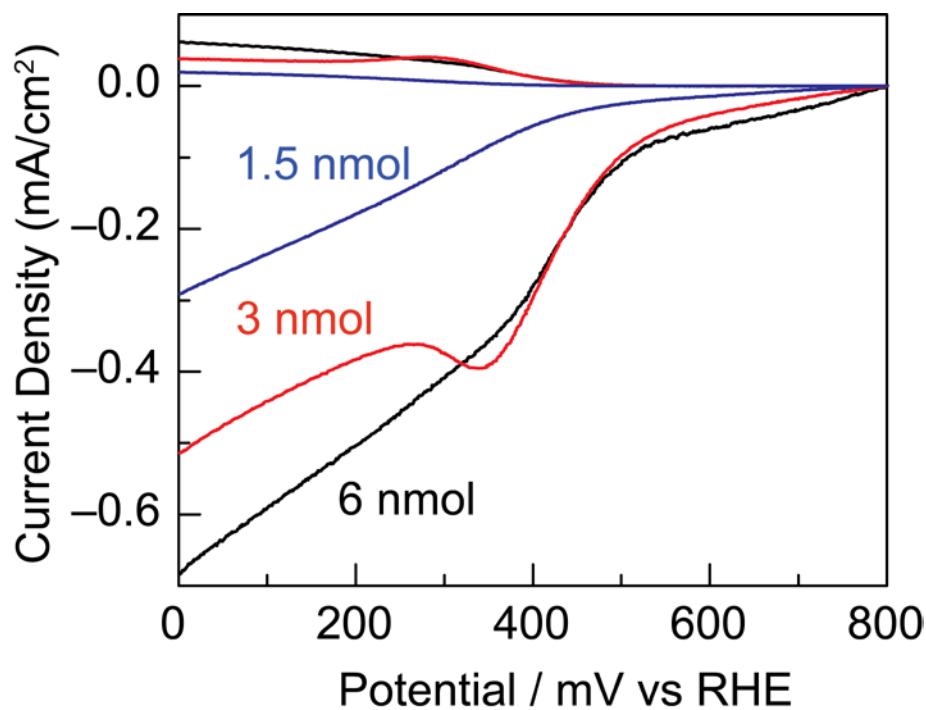


Figure S16. RRDE of CoHPX-3 at different loading concentration on MWCNT films at 100 rpm in O₂ saturated 0.5 M H₂SO₄ scan rate 20 mV/s. Platinum ring held at 1.2 V vs SCE.