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The role and analysis of molecular systems in electrocatalysis

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Appendix A

Supplementary information for Chapter 2:

The influence of the ligand in the iridium mediated
electrocatalytic water oxidation

A.1 Cyclic voltammetry of iridium picolinate series

To study the picolinate complexes with cyclic voltammetry (CV), a glassy carbon (GC) electrode (0.07 cm^2) was used. The electrode was in contact with the electrolyte via a hanging meniscus configuration. The electrolyte is a 0.1 M phosphate buffer of pH 7 that is strengthened to 0.5 M ionic strength with additional NaClO_4 . A 1 mM catalyst concentration was used. Figure A.1 shows the first scan of the CVs of the different catalysts. The more electron donating complexes **4-OH₁** and **6-OH₁** have an earlier onset for the irreversible anodic wave at 1.55 V . The other complexes have an anodic wave starting at 1.65 V . This onset was consistently found at the same potential over several measurements (Figure A.3) with freshly polished GC working electrodes in the same catalyst solution. The magnitude of the maximum current reached at 2.1 V differs slightly among the catalysts (Figure A.1). In contrast to the onset, the magnitude of the current fluctuates significantly as became evident from several separate measurements (Figure A.3). This discrepancy in CVs is observed for the entire range of the iridium (hydroxyl)picolinate complexes. Any difference in the CV of the complexes lies within the experimental error. The hanging meniscus configuration is not the reason for the discrepancy as two of the three measurements shown in Figure A.3 show identical capacitive double layer currents but distinct maximum currents. As became clear from the electrode-rinse-test (Figure A.2) and the EQCM experiments (Figure 2.2), the complexes deposit material on the electrode. Electrodeposition, catalyst degradation (Figure A.4), oxygen evolution (Figure 2.1) and GC oxidation (Figure A.7) simultaneously

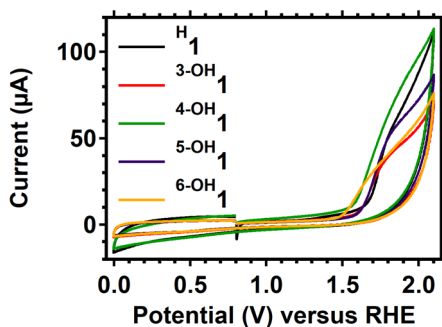


Figure A.1. Shown are the first scans of the cyclic voltammogram taken at 0.1 V/s with a glassy carbon working electrode. A 1 mM complex solution was used in combination with a 0.1 M phosphate buffer of pH 7 with an ionic strength of 0.5 M by adding NaClO_4 as supporting electrolyte.

contribute to the magnitude of the anodic current. This complexity results in large error margins for the magnitude of the current.

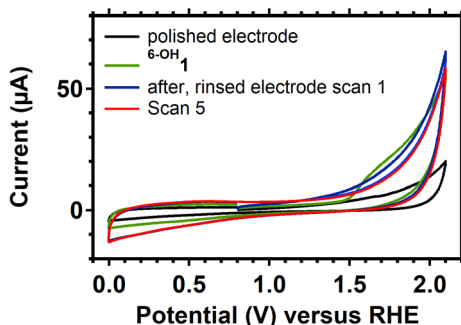


Figure A.2. The cyclic voltammograms of a GC electrode in a pH 7 phosphate buffer before (polished electrode, black line), during (green) and after (blue and red) it has been tested in electrolyte containing 1 mM of 6-OH₁. The CVs before and after were obtained in a catalyst free electrolyte. The electrode was rinsed copiously with Milli-Q grade water before the CVs in blue and red were obtained. All CVs were taken at a 0.1 V/s scan rate.

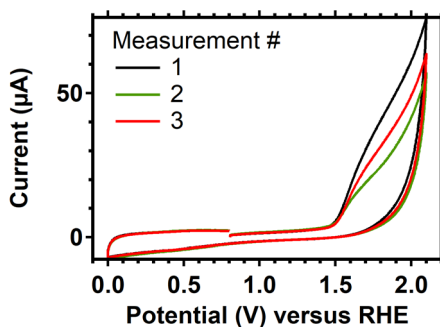


Figure A.3. The first scans are shown of three separate cyclic voltammetry measurements of a 1 mM 6-OH₁ solution in a pH 7 phosphate buffer taken at a 0.1 V/s scan rate. The glassy carbon working electrode was polished before each measurement and used in a hanging meniscus configuration. The same electrolyte containing 6-OH₁ was used for each measurement.

A.2 Post-electrolysis spectroscopy studies.

A.2.1 NMR

^1H NMR spectra were recorded of the D_2O based electrolyte used in the bulk electrolysis experiment of $4\text{-OH}\mathbf{1}$ (Figure A.4). For comparison, the spectrum of 4-hydroxypicolinate was recorded by adding NaOH to a mixture of 4-hydroxypicolinic acid and D_2O to be able to dissolve the ligand. The electrolyte spectrum before bulk electrochemistry shows three peaks corresponding to coordinated picolinate ligand as the spectrum has shifted with respect to metal-free ligand due to the electron withdrawing effect of iridium (III). Furthermore, two peaks can be linked to the Cp^* ligand indicating the presence of at least two iridium complexes in the solution. The iridium complex with the weakly coordinating nitrate might be in equilibrium with an iridium complex where the nitrate is exchanged for a water or phosphate in solution. After 6 hours of bulk electrolysis, the major peaks are still present. The picolinate ligand seems unaffected. However, new peaks have risen in the region of the Cp^* ligand. Two additional peaks can be observed. In a region slightly more downfield, three more peaks can be observed. Though close to

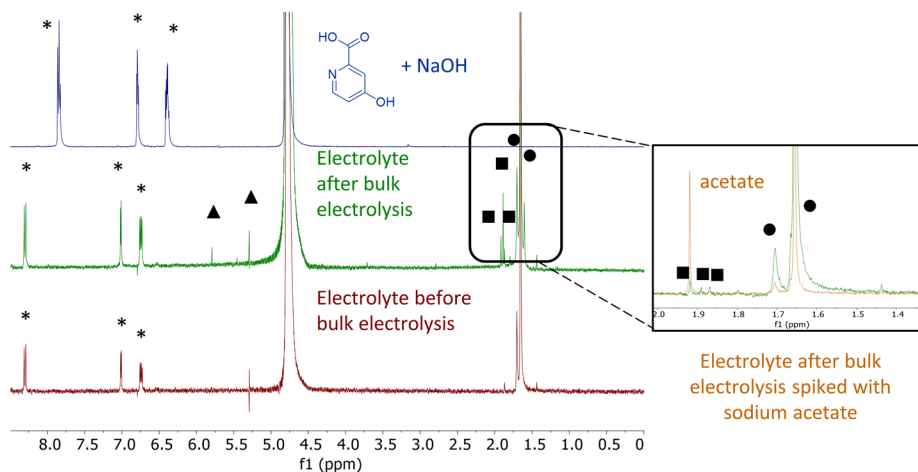


Figure A.4. ^1H NMR spectra of the deprotonated 4-hydroxypicolinic acid ligand (blue spectrum) and the electrolyte of the bulk electrolysis experiment before (red spectrum) and after (green spectrum) containing $4\text{-OH}\mathbf{1}$. All spectra are recorded in D_2O . The asterisks indicate the signals corresponding to the (coordinated) 4-hydroxypicolinate ligand. The circles correspond to Cp^* coordinated to iridium. The squares indicate possible degradation products of Cp^* . The triangles indicate unknown compounds. The inset shows a part of the ^1H NMR spectrum of the electrolyte after bulk electrolysis before (green) and after (orange) it has been spiked with sodium acetate.

the region of Cp^* , these latter peaks are usually associated with acetate and/or other decomposition products of Cp^* .¹⁻¹⁸ Specifically, the peak at 1.92 ppm corresponds to acetate as it increases in intensity after the solution has been spiked with sodium acetate (inset Figure A.4). Two more unknown peaks are observed at relatively high chemical shifts.

A.3 UV-vis

Minor changes are observed in the UV-vis spectrum of the electrolyte solution before and after bulk electrolysis was employed (Figure A.5). The overall spectrum of a 10 times diluted electrolyte solution seems to be lower in intensity after the bulk electrolysis experiment. This drop might be caused by a slight osmotic-driven dilution of the electrolyte solution during 6-hour experiment. The Luggin of the reference electrode was filled with catalyst-free solution and was in direct contact with the bulk solution. Thus, diffusion and dilution could have taken place over the course of the experiment of 6 hours. The fact that no spectral shifts were observed indicates that the majority of the solution is unaffected and still contains $4\text{-OH}\mathbf{1}$. Moreover, the lack of absorption above 450 nm indicates that there are no iridium oxide nanoparticles in solution which usually absorb around 580 nm.¹⁹⁻²¹

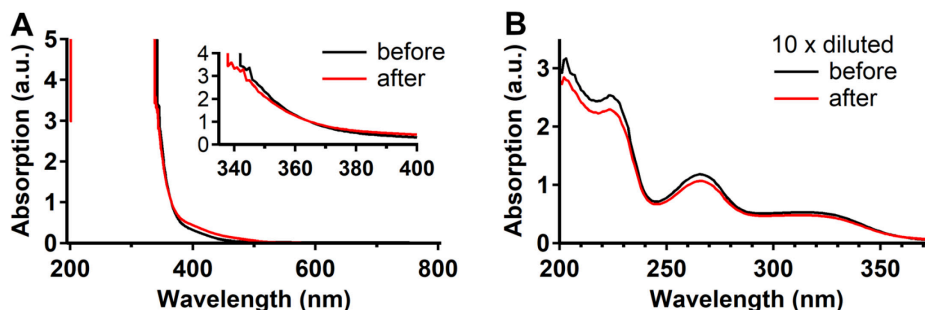


Figure A.5. UV-vis spectra of the electrolyte solution used for the bulk-electrolysis experiment containing 1 mM of $4\text{-OH}\mathbf{1}$ before and after the bulk electrolysis was performed. A) shows the full spectrum of the undiluted electrolyte. The inset is a zoom of the region between 330 and 400 nm. B) shows the UV-vis spectrum of electrolyte that was diluted 10 times with D_2O . The spectra are recorded in a quartz crystal cuvet with 10.0 mm path length.

A.4 CV of electrode

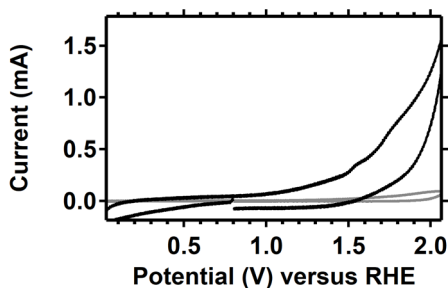


Figure A.6. CV of the large surface area GC electrode (0.79 cm^2) in 0.1 M phosphate buffer of pH 7. The CV at a scan rate of 0.1 V/s was taken before (grey line) and after (black line) the electrode was used for performing bulk electrolysis at 1.95 V for 6 hours in the presence of 4-OH1 .

A.5 Chronoamperometry experiments of **1** – **5**

Chronoamperometry allows for studying the current over time at a fixed potential. This way, any activation/deactivation process becomes more visible and better comparisons can be made. The amperograms at potentials of 1.8, 1.9, 2.0 and 2.1 V of complexes **1** – **5** which were recorded for 1 hour are shown in Figure A.7. These were taken with a freshly polished, but not pre-anodized GC electrode. The currents that are produced by the complexes are minimal and just barely above the current produced by GC alone (Figure A.7). Also, these amperograms showed clearly that the GC electrode is oxidized at these potentials which has a large influence on the shape of the amperogram of complexes **1** – **5** as well. Moreover, random artefacts are observed. For example, the current produced by 3-OH1 suddenly increases to a higher plateauing current halfway the measurement at 2.1 V (Figure A.7D and Figure A.8). This feature was not observed in a second measurement of a fresh solution of 3-OH1 with a freshly polished electrode (Figure A.8). Therefore, the electrode was pre-anodized for 25 minutes at 2.1 V before the amperometry measurements (Figure A.9) were taken to construct Figure 2.3. In these amperograms, artefacts such as in Figure A.8 were not observed anymore. In addition, it was found that the current would steadily increase over the period of 30 minutes in the potential window of 1.8 to 1.95 V as indicated by the green lines in Figure A.9. However, above potentials of 1.95 V, the potential either decreases immediately or decreases after an initial maximum was reached as indicated by the red lines in Figure A.9. These potential windows correlate with the potential windows of the kink in the plots of Figures 3A, B, C and E.

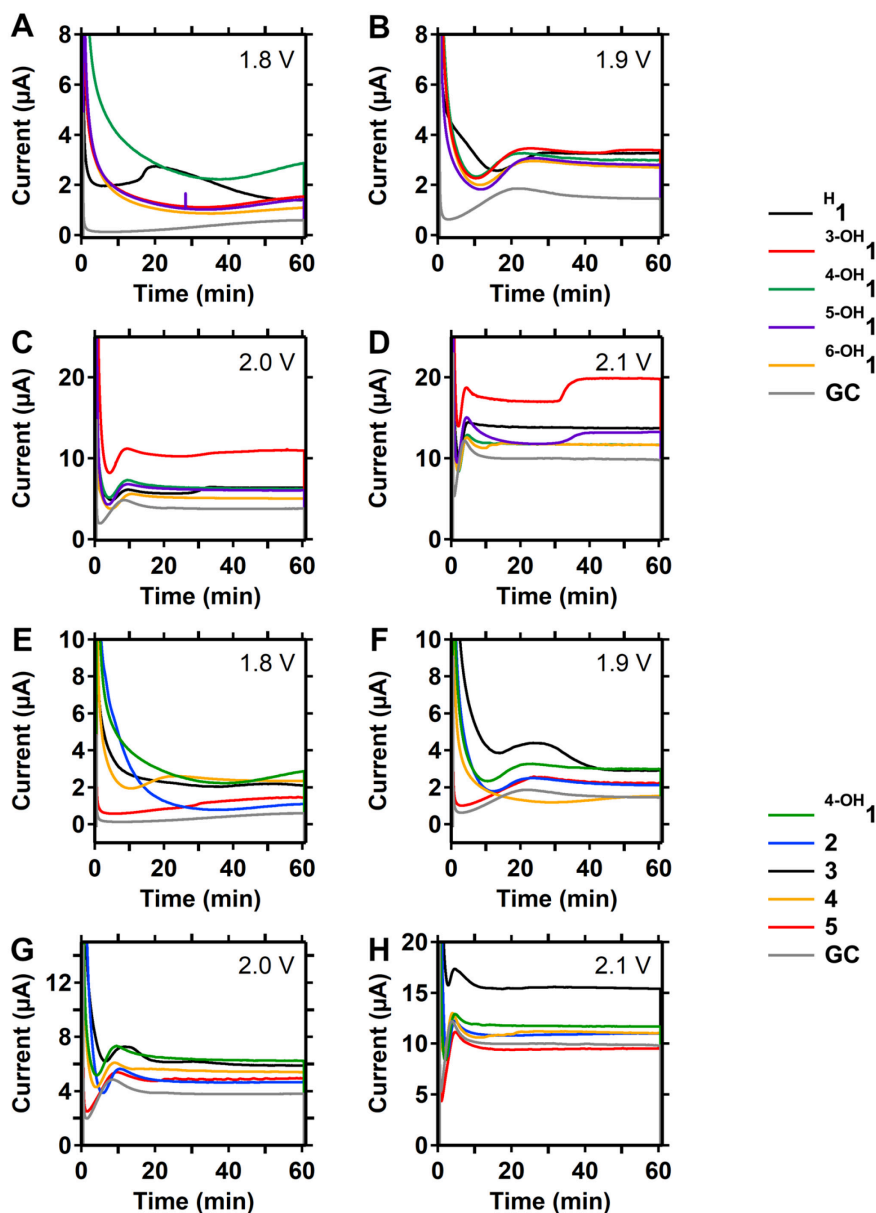


Figure A.7. The CA experiments of the iridium (hydroxy)picolinate complex series in a phosphate buffer electrolyte of pH 7 (A-D). The GC work electrode was fixed at a potential of 1.8, 1.9, 2.0 or 2.1 V versus RHE for 1 hour. E-H show the amperograms of **2** - **5** as well as that of 4-OH**1** for reference. The response of bare GC without any catalyst present in the electrolyte is indicated by the grey lines in all plots. For H_1 , a concentration of 0.4 mM was used whereas the other complexes were studied at 1 mM concentrations. The GC electrode was mechanically polished before each measurement.

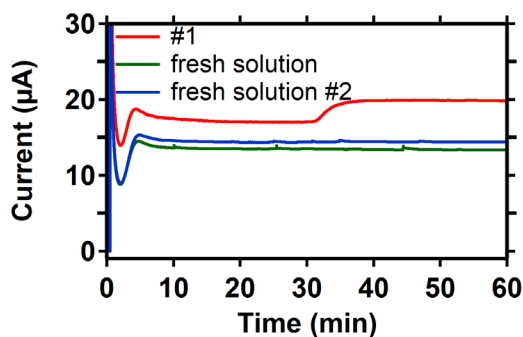


Figure A.8. Amperogram of 3-OH_1 with a 2.1 V applied potential and a GC as electrode. The red line depicts a measurement where a sudden increase in current is observed after 1800 seconds as is also displayed in Figure A.7D. The measurement was repeated with a fresh solution of 3-OH_1 that is depicted with the blue line. The green line depicts a second measurement of the fresh solution with a freshly polished electrode.

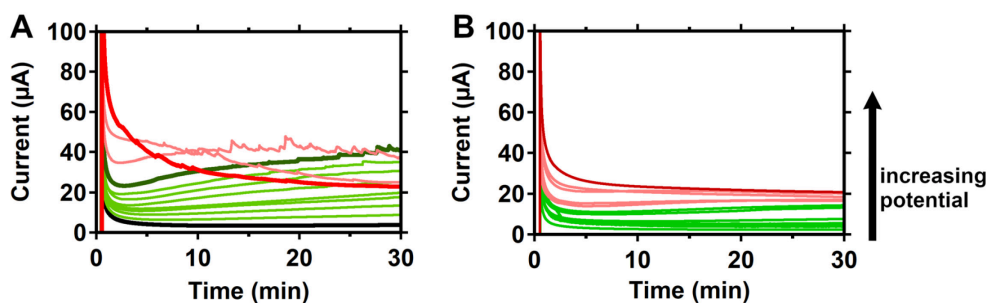


Figure A.9. The uncorrected amperograms of 3-OH_1 (A) and 4-OH_1 (B). The green lines depict the potential window where the current steadily increases over time (1.8 – 1.95 V) whereas the red lines indicate the potential window where the current steadily decreases after reaching a maximum (1.95 – 2.1 V). These regions correspond to the regions indicated in Figure 2.3.

A.6 X-Ray Photoelectron Spectroscopy characterization

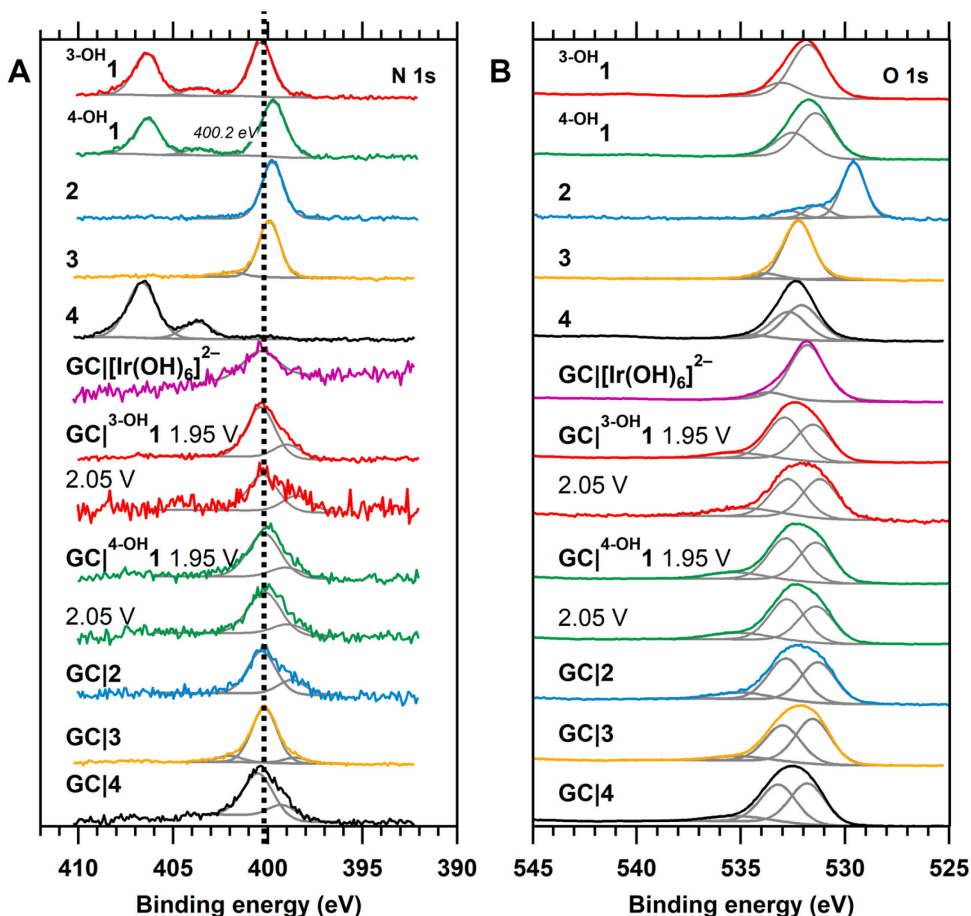


Figure A.10. N 1s (A) and O 1s (B) XPS spectra of GC|^{3-OH}1 (red) and GC|^{4-OH}1 (green) that were prepared at 1.95 V or 2.05 V and GC|**2** (blue), GC|**3** (orange) and GC|**4** (black) that were prepared at 1.95 V. Also included are the spectra of the parent complexes compounds **3-OH**₁ (red), **4-OH**₁ (green) **2** (blue), **3** (orange) and **4** (black). The deconvolution of the spectra is shown in grey.

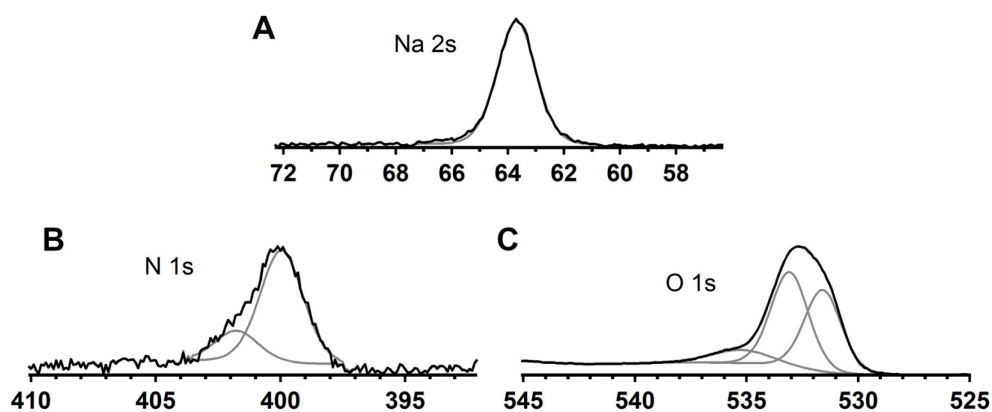


Figure A.11. XPS spectra of the Na 2s (A, same region as Ir 4f), N 1s (B) and O 1s (C) regions of the surface of a GC electrode that was anodized by performing chronoamperometry at 2.1 V in a 0.1 M phosphate buffer (pH 7) for 25 minutes.

A.7 Chronoamperometry and CV experiments of $[\text{Ir}(\text{OH})_6]^{2-}$ and colloidal IrO_x solutions

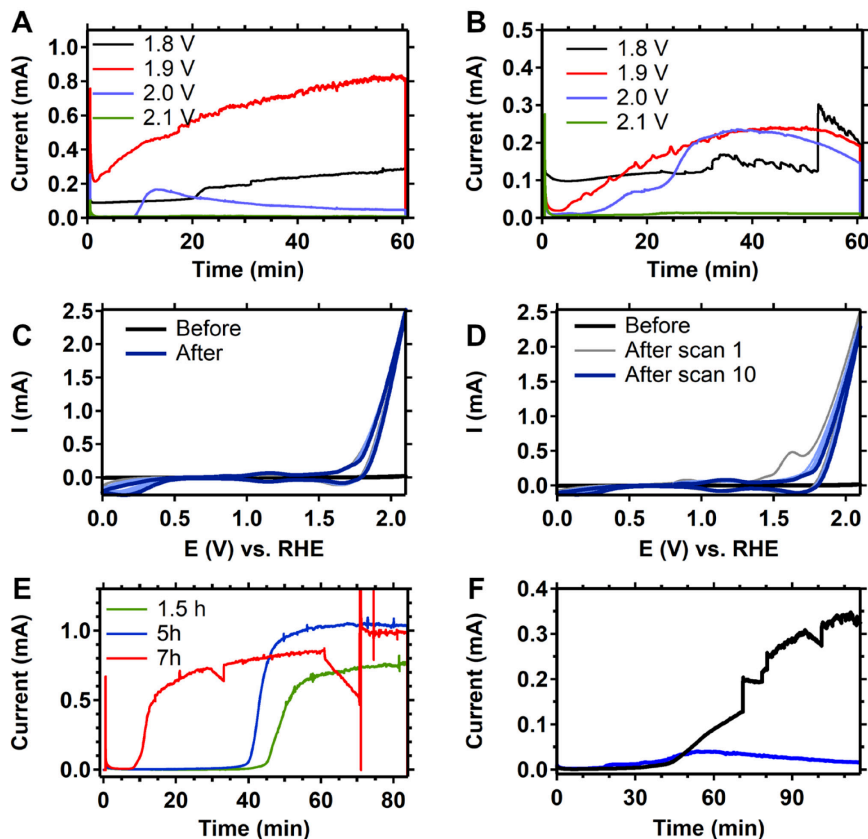


Figure A.12. Amperograms of the current generated when a glassy carbon electrode was held at 1.8 V (black), 1.9 V (red), 2.0 V (blue) or 2.1 V (green) versus RHE for 1 hour in a solution containing 1 mM $[\text{Ir}(\text{OH})_6]^{2-}$ (A, one day old solution) or a colloidal solution of IrO_x nanoparticles (B) with a 1 mM iridium concentration. Also displayed are the CVs of the glassy carbon work electrode in a iridium-free 0.1 M phosphate buffer solution before and after amperometry was performed for $[\text{Ir}(\text{OH})_6]^{2-}$ (C) and IrO_x nanoparticles in solution (D). Measurements taken at 1.95 V with an anodized GC electrode with a fresh solution of $[\text{Ir}(\text{OH})_6]^{2-}$ show the lag time between the start of the measurement and the increase in current (E). These measurements were taken 1.5 hours (green), 5 hours (blue) and 7 hours (red) after the preparation of the $[\text{Ir}(\text{OH})_6]^{2-}$ solution. The spikes are due to bubble formation on the electrode. (F) The influence of 1 mM 4-hydroxypicolinic acid (blue) present in a 1 mM $[\text{Ir}(\text{OH})_6]^{2-}$ solution as ligand at 1.95 V with a pre-anodized glassy carbon electrode. In black, the amperogram for the same batch of $[\text{Ir}(\text{OH})_6]^{2-}$ solution without ligand is shown. Both solutions were measured simultaneously 2 hours after preparation. The ligand was added 30 minutes before measurement to allow for deoxygenation of the solution by purging with argon.

A

A.8 NMR of 3-,4-,5-,6-OH₁

These ¹H NMR spectra in DMSO-d₆ are from the iridium complexes 3-OH₁, 4-OH₁, and 6-OH₁ that have been prepared by a different synthetic route than previously reported.²² This new synthetic route allowed for easy removal of silver contamination. The ¹H NMR spectra all correspond to the previously published spectra that were reported for the synthetic route using [Cp*IrCl₂]₂ as precursor instead of **4**.

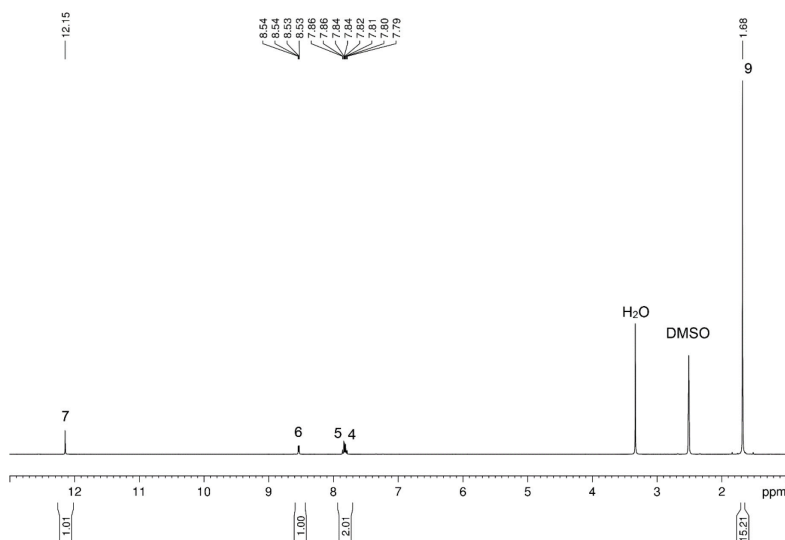


Figure A.13. ¹H NMR of 3-OH₁ in DMSO-d₆ prepared via the alternative synthetic route using **4** as precursor.

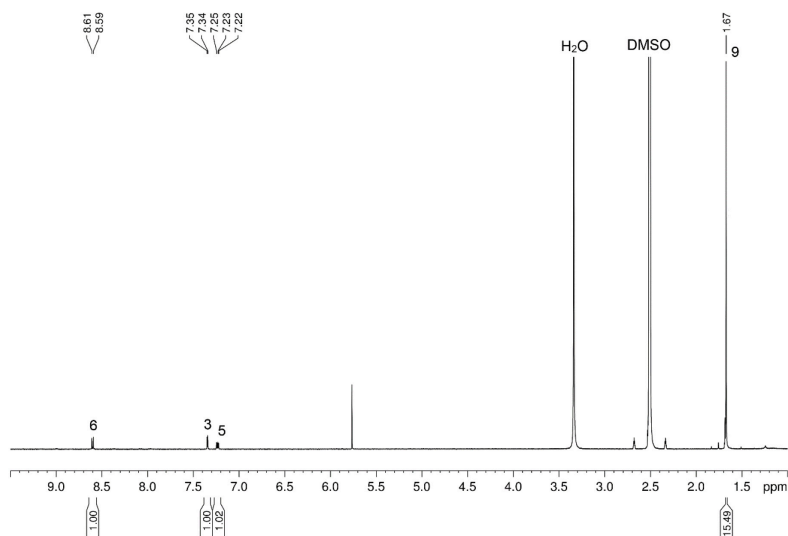


Figure A.14. ^1H NMR of 4-OH1 in DMSO-d_6 prepared via the alternative synthetic route using **4** as precursor.

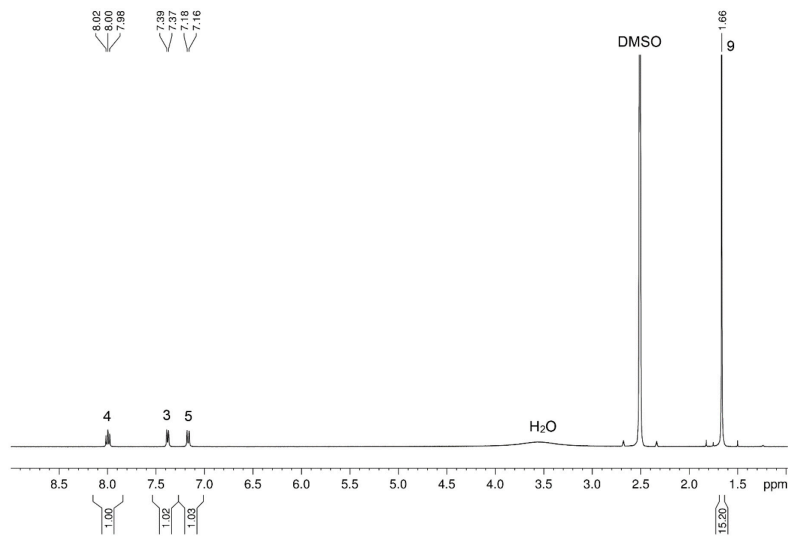


Figure A.15. ^1H NMR of 6-OH1 in DMSO-d_6 prepared via the alternative synthetic route using **4** as precursor.

A.9 References

1. Savini, A.; Belanzoni, P.; Bellachioma, G.; Zuccaccia, C.; Zuccaccia, D.; Macchioni, A., *Green Chem.* **2011**, *13*, 3360–3374.
2. Wang, C.; Wang, J.-L.; Lin, W., *J. Am. Chem. Soc.* **2012**, *134*, 19895–19908.
3. Zuccaccia, C.; Bellachioma, G.; Bortolini, O.; Bucci, A.; Savini, A.; Macchioni, A., *Chem. - Eur. J.* **2014**, *20*, 3446–3456.
4. Blakemore, J. D.; Schley, N. D.; Olack, G. W.; Incarvito, C. D.; Brudvig, G. W.; Crabtree, R. H., *Chem. Sci.* **2011**, *2*, 94–98.
5. Grotjahn, D. B.; Brown, D. B.; Martin, J. K.; Marelius, D. C.; Abadjian, M.-C.; Tran, H. N.; Kalyuzhny, G.; Vecchio, K. S.; Specht, Z. G.; Cortes-Llamas, S. A.; Miranda-Soto, V.; van Niekerk, C.; Moore, C. E.; Rheingold, A. L., *J. Am. Chem. Soc.* **2011**, *133*, 19024–19027.
6. Zuccaccia, C.; Bellachioma, G.; Bolaño, S.; Rocchigiani, L.; Savini, A.; Macchioni, A., *Eur. J. Inorg. Chem.* **2012**, *2012*, 1462–1468.
7. Hong, D.; Murakami, M.; Yamada, Y.; Fukuzumi, S., *Energy Environ. Sci.* **2012**, *5*, 5708–5716.
8. Blakemore, J. D.; Mara, M. W.; Kushner-Lenhoff, M. N.; Schley, N. D.; Konezny, S. J.; Rivalta, I.; Negre, C. F. A.; Snoeberger, R. C.; Kokhan, O.; Huang, J.; Stickrath, A.; Tran, L. A.; Parr, M. L.; Chen, L. X.; Tiede, D. M.; Batista, V. S.; Crabtree, R. H.; Brudvig, G. W., *Inorg. Chem.* **2013**, *52*, 1860–1871.
9. Hintermair, U.; Sheehan, S. W.; Parent, A. R.; Ess, D. H.; Richens, D. T.; Vaccaro, P. H.; Brudvig, G. W.; Crabtree, R. H., *J. Am. Chem. Soc.* **2013**, *135*, 10837–10851.
10. Codolà, Z.; M. S. Cardoso, J.; Royo, B.; Costas, M.; Lloret-Fillol, J., *Chem. - Eur. J.* **2013**, *19*, 7203–7213.
11. Savini, A.; Bucci, A.; Bellachioma, G.; Rocchigiani, L.; Zuccaccia, C.; Llobet, A.; Macchioni, A., *Eur. J. Inorg. Chem.* **2014**, *2014*, 690–697.
12. Ingram, A. J.; Wolk, A. B.; Flender, C.; Zhang, J.; Johnson, C. J.; Hintermair, U.; Crabtree, R. H.; Johnson, M. A.; Zare, R. N., *Inorg. Chem.* **2014**, *53*, 423–433.
13. Thomsen, J. M.; Sheehan, S. W.; Hashmi, S. M.; Campos, J.; Hintermair, U.; Crabtree, R. H.; Brudvig, G. W., *J. Am. Chem. Soc.* **2014**, *136*, 13826–13834.
14. Zhang, T.; deKrafft, K. E.; Wang, J.-L.; Wang, C.; Lin, W., *Eur. J. Inorg. Chem.* **2014**, *2014*, 698–707.
15. Lewandowska-Andralojc, A.; Polyansky, D. E.; Wang, C.-H.; Wang, W.-H.; Himeda, Y.; Fujita, E., *Phys. Chem. Chem. Phys.* **2014**, *16*, 11976–11987.
16. Corbucci, I.; Ellingwood, K.; Fagioli, L.; Zuccaccia, C.; Elisei, F.; Gentili, P. L.; Macchioni, A., *Catal. Today* **2017**, *290*, 10–18.
17. Wan, X.; Wang, L.; Dong, C.-L.; Menendez Rodriguez, G.; Huang, Y.-C.; Macchioni, A.; Shen, S., *ACS Energy Lett.* **2018**, *3*, 1613–1619.
18. Graeupner, J.; Hintermair, U.; Huang, D. L.; Thomsen, J. M.; Takase, M.; Campos, J.; Hashmi, S. M.; Elimelech, M.; Brudvig, G. W.; Crabtree, R. H., *Organometallics* **2013**, *32*, 5384–5390.
19. Zhao, Y.; Hernandez-Pagan, E. A.; Vargas-Barbosa, N. M.; Dysart, J. L.; Mallouk, T. E., *J. Phys. Chem. Lett.* **2011**, *2*, 402–406.
20. Zhao, Y.; Vargas-Barbosa, N. M.; Hernandez-Pagan, E. A.; Mallouk, T. E., *Small* **2011**, *7*, 2087–2093.
21. Hintermair, U.; Hashmi, S. M.; Elimelech, M.; Crabtree, R. H., *J. Am. Chem. Soc.* **2012**, *134*, 9785–9795.
22. Menendez Rodriguez, G.; Bucci, A.; Hutchinson, R.; Bellachioma, G.; Zuccaccia, C.; Giovagnoli, S.; Idriss, H.; Macchioni, A., *ACS Energy Lett.* **2017**, *2*, 105–110.

Appendix B

Supplementary information for Chapter 3:
Pinpointing the active species of the Cu(DAT)
catalyzed oxygen reduction reaction

B.1 EPR and SQUID of Cu(DAT) powder

A **Cu(DAT)** powder was obtained by removing water under reduced pressure of a 6.6 mM aqueous solution of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT. Electron paramagnetic resonance (EPR) spectroscopy (Figure B.2) was employed to check whether the powder agrees upon the structure of **Cu(DAT)** in solution. A broad peak at $g = 2.16$ was observed as well as the weak signal for the forbidden $M_s = \pm 2$ transition both indicating the presence of the dinuclear $\text{Cu}_2(\mu\text{-DAT})_2$ core. Moreover, SQUID data (Superconducting Quantum Interference Device) of the same **Cu(DAT)** powder was obtained (Figure B.2). The χ_m versus T plot with χ_m being the magnetic susceptibility per two Cu^{II} ions. A maximum at 102.5 K can be found which is characteristic of two antiferromagnetically coupled Cu^{II} sites that are closely spaced and have a diamagnetic $S = 0$ state. Some paramagnetic impurity was found (estimated at 2.4% when a pure spin center with $g = 2.0$ is assumed) which was most likely corresponding to a mononuclear $[\text{Cu}^{\text{II}}(\text{DAT})]^{2+}$ species. By correcting the data for this small impurity, the data for **Cu(DAT)** could be obtained and fitted to find the J -coupling constant, isotropic g -factor, and temperature independent (orbital) paramagnetism value of -115.8 cm^{-1} , 2.11, and $5.2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ respectively which fall in the range of other triazole-bridged copper complexes. The small intermolecular J -coupling of $1.0 \times 10^{-4} \text{ cm}^{-1}$ could exclude the presence of polymeric chain structures in the solid state. These results confirm that the **Cu(DAT)** powder that was used for XPS analysis has the same electronic structure as the **Cu(DAT)** complex in solution.

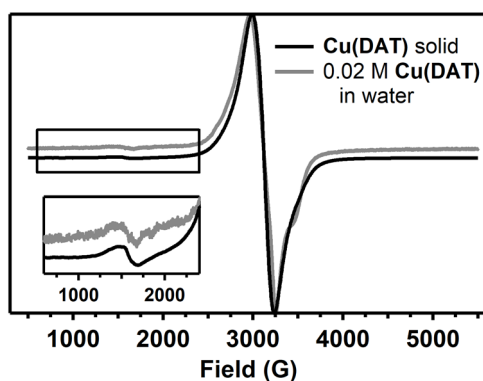


Figure B.1. In black, the normalized EPR spectrum of the **Cu(DAT)** powder depicted. The spectrum was obtained at 9.35 GHz at 77 K. For comparison, the normalized EPR spectrum of **Cu(DAT)** in water (Figure 3.2) is depicted in grey. The inset depicts a zoom of the spectrum between 600 and 2400 Gauss.

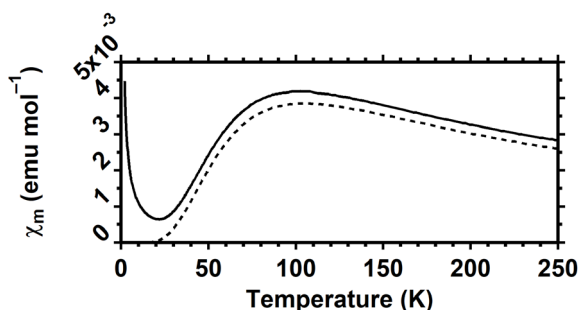


Figure B.2. SQUID data of the **Cu(DAT)** powder (solid) and the extracted spectrum where the influence of paramagnetic impurity was excluded (dashed).

B.2 Long-term stability of Cu(DAT) solutions

The stability of a **Cu(DAT)** solution was monitored by UV-vis over time (Figure B.3). Before the first spectrum was taken, two solutions were prepared: a 5 ml 0.1 M NaClO_4 solution containing 13.2 mM $\text{Cu}(\text{OTf})_2$ and 5 ml of a 0.1 M NaClO_4 solution containing 13.2 mM 3,5-diamino-1,2,4-triazole (DAT). These solutions were mixed and within a minute, the first UV-Vis spectrum was taken. Slowly, the absorption at 380 nm was observed to increase. After 10.75 hours, the absorption at 380 nm reached a maximum and the absorption between 600 and 1000 nm had shifted. In addition, precipitation had formed in the solution. In the following hours, the absorption at 380 nm was found to decrease. Clearly, the **Cu(DAT)** solution is

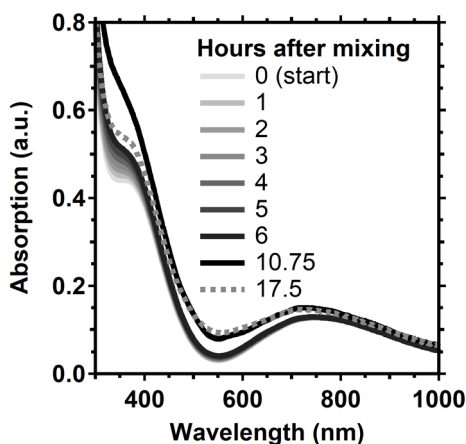


Figure B.3. UV-vis spectra recorded over the course of 17.5 hours of a 0.1 M NaClO_4 solution containing 6.6 mM of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT. The evolution in time is illustrated with the color change from light grey to black. The grey dotted line represents the spectrum after 17.5 hours.

not stable over long periods of time. Therefore, all experiments were performed within 0-4 hours after preparation of the **Cu(DAT)** solution when only minor changes are observed in the UV-vis spectrum.

B.3 pH titrations on Cu(DAT)

pH titrations were performed to study the influence of the pH on the complex as the triazole ligand might be protonated (pK_a of H DAT^+ is 4.4) or deprotonated (pK_a of DAT is 12.1).¹⁻³ An acidic titration on a 0.1 M NaClO_4 solution containing 30 mM of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT was performed with 1.0 M HClO_4 (Figure B.4A). A perchlorate solution was used in order to resemble the conditions of electrochemical measurements. At the inflection point, 2.1 equivalents of acid with respect to $\text{Cu}_2(\mu\text{-DAT})_2$ are transferred. This equals 1.05 equivalents with respect to the ligand DAT. At the inflection point, both of the coordinated DAT ligands of the $\text{Cu}_2(\mu\text{-DAT})_2$ core are protonated simultaneously with an estimated pK_a value of 3.5. The drop in pH is accompanied by a color change from green to light blue. The UV-vis spectrum of **Cu(DAT)** at pH 4.8 has two distinct absorptions at 380 nm and circa 740 nm (Figure B.4B). This latter signal has shifted to circa 800 nm in the UV-vis spectrum upon acidification of the **Cu(DAT)** solution to pH 1 using HClO_4 . Simultaneously, the distinctive absorption at 380 nm almost completely

B

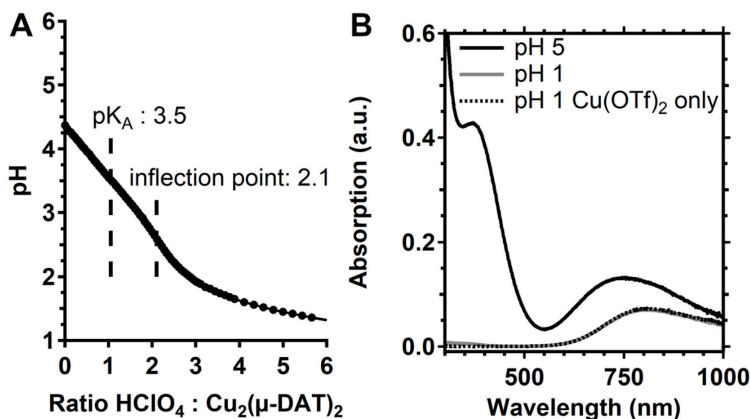


Figure B.4. (a) shows the pH titration with 1.0 M HClO_4 of a 0.1 M NaClO_4 solution containing 30 mM of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT with 1.0 M HClO_4 . The ratio is given with respect to the dinuclear $\text{Cu}_2(\mu\text{-DAT})_2$ core. (b) shows the UV-Vis spectrum of a 0.1 M NaClO_4 solution containing 6.6 mM of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT (pH 5, black solid line). Also depicted are the spectra of a 0.1 M HClO_4 solution (pH 1) containing either 6.6 mM of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT (grey solid line) or only 6.6 mM $\text{Cu}(\text{OTf})_2$ (black dotted line).

disappeared. The UV-vis spectrum of **Cu(DAT)** at pH 1 was found to be qualitatively identical to the UV-vis spectrum of $\text{Cu}(\text{OTf})_2$ in absence of DAT.

Starting from a 15 mM solution of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT a titration with 1.1 M NaOH was performed under continuous stirring (Figure B.5). Small amounts of green precipitation were observed to form above pH 5.5 and increased in quantity as the pH further increased. At circa pH 12 a turbid solution was obtained. The titration with NaOH was stopped and immediately followed by a back titration with 1.0 M HClO_4 . The back titration showed hysteresis around the inflection point. Moreover, the precipitation slowly disappeared while the pH was lowered and eventually a clear solution was obtained below pH 5. The observed hysteresis around the inflection point indicates that an additional process coupled to a deprotonation takes place. A coordinating H_2O is most likely deprotonated as one equivalent of NaOH is required to reach the inflection point. As a result, the anionic hydroxyl is now able to form an intermolecular bridge between complexes. Ultimately, this can lead to the formation of insoluble coordination polymers, which are frequently observed in case of aqueous copper complexes.⁴⁻⁶

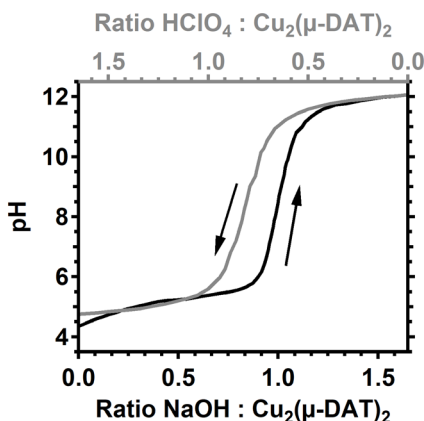


Figure B.5. pH titration of an aqueous 15 mM solution of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT with 1.1 M NaOH (black line, bottom axis) and the back-titration with 1.0 M HClO_4 (grey line, top axis). The ratio is given with respect to the dinuclear $\text{Cu}_2(\mu\text{-DAT})_2$ core.

B.4 Copper and DAT titrations followed by UV-vis spectroscopy

In order to investigate the influence of different ligand to copper ratios, two titrations were performed in 0.1 M NaClO_4 . First, 10 μL aliquots of a solution containing 0.42 M $\text{Cu}(\text{OTf})_2$, 6.6 mM DAT, and 0.1 M NaClO_4 were added to a 2.5 ml solution of 6.6 mM DAT in 0.1 M NaClO_4 . UV-vis spectra were recorded after every

addition (Figure B.6). As soon as $\text{Cu}(\text{OTf})_2$ was added, the characteristic absorption at 380 nm as well as a broad absorption with a maximum at 720 nm corresponding to the d-d transition of Cu^{II} started to appear. While the $\text{Cu}(\text{OTf})_2$ concentration was increased, the absorption at 380 nm increased and sharpened. Moreover, the d-d absorption not only increases but also shifts to 780 nm. The latter event is an indication for a change in ligand environment as this affects the d-d transition. An opposite shift is observed when a 0.42 M DAT solution containing 6.6 mM $\text{Cu}(\text{OTf})_2$ and 0.1 M NaClO_4 is titrated to a 6.6 mM $\text{Cu}(\text{OTf})_2$ solution in 0.1 M NaClO_4 (Figure B.7). In this case, the d-d band shifts to lower wavelengths most likely due to a larger ratio of coordinated DAT with respect to copper. The absorption at 380 nm quickly increases in intensity but is eventually overlapped by a large absorption in the UV area.

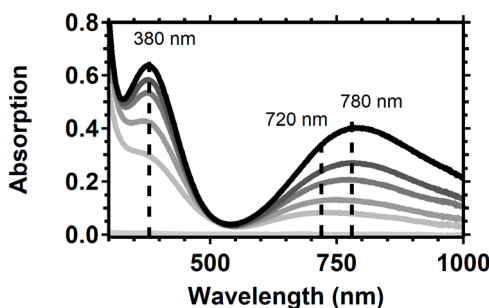


Figure B.6. UV-vis spectra of the titration of $\text{Cu}(\text{OTf})_2$ to a 6.6 mM DAT solution in 0.1 M NaClO_4 . In the order of increasing darkness are depicted the spectra of 0, 0.5, 1, 2, 3 and 4 equivalents of $\text{Cu}(\text{OTf})_2$ with respect to DAT.

Titration experiments were also performed at pH 1 to see the effect of protonated DAT (Figures B.8 and B.9). When $\text{Cu}(\text{OTf})_2$ was titrated to a DAT solution in 0.1 M HClO_4 , the absorption corresponding to the d-d absorption increased in intensity but did not shift (Figure B.8). The maximum was found at 800 nm which corresponds to a $\text{Cu}(\text{OTf})_2$ only solution at pH 1 (Figure B.4). A slight absorption can be observed at 355 nm but only becomes significant when the amount of DAT was increased up to 11 equivalents with respect to $\text{Cu}(\text{OTf})_2$ (Figure B.9). This indicates that an infinite small amount of HDAT^+ still coordinates but hardly has a change on the ligand environment of copper, as the d-d transition at 800 nm does not shift nor changes in intensity.

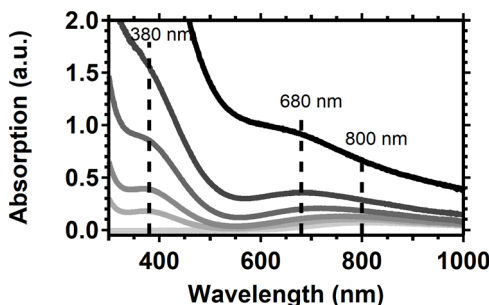


Figure B.7. UV-vis spectra of the titration of DAT to a 6.6 mM $\text{Cu}(\text{OTf})_2$ solution in 0.1 M NaClO_4 . In the order of increasing darkness are depicted the spectra of 0, 0.5, 1, 2, 3 and 4 equivalents of DAT with respect to $\text{Cu}(\text{OTf})_2$.

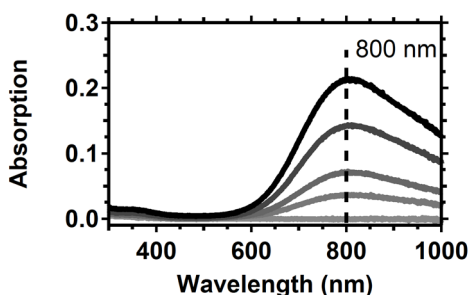


Figure B.8. UV-vis spectra of the titration of $\text{Cu}(\text{OTf})_2$ to a 6.6 mM DAT solution in 0.1 M HClO_4 . In the order of increasing darkness are depicted the spectra of 0, 0.5, 1, 2, and 3 equivalents of $\text{Cu}(\text{OTf})_2$ with respect to DAT.

B.5 Influence of MES buffer on $\text{Cu}(\text{DAT})$

It was found that the combination of **Cu(DAT)** and a phosphate or Britton-Robinson buffer led to precipitation of **Cu(DAT)**. Hence, 0.03 M of 2-(*N*-morpholino)ethanesulfonic acid (MES) was investigated as a buffer, since it has a $\text{p}K_a$ of 6.15 and thus a useful buffering range close to pH 4.8.^{7, 8} Moreover, no immediate precipitation was observed in combination with **Cu(DAT)**. Although it has been reported that MES is not likely to coordinate to Cu^{II} ,⁹ a deviation in the UV-vis spectrum was observed implying that some coordination of MES does take place (Figure B.10). The absorption belonging to the d-d transition shifts while the absorption at 380 nm increases significantly. Coordination can be expected for a complex such as **Cu(DAT)** with labile ligands in the coordination sphere but the $\text{Cu}_2(\mu\text{-DAT})_2$ core remains intact as illustrated by the 380 nm absorption and the identical EPR spectra of **Cu(DAT)** in the presence and absence of MES (Figure B.11).

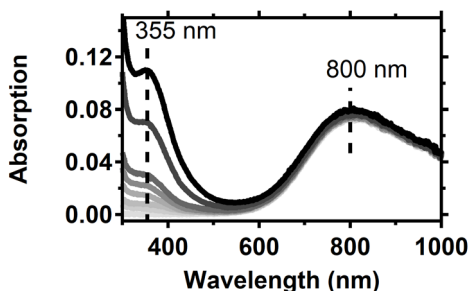


Figure B.9. UV-vis spectra of the titration of DAT to a 6.6 mM $\text{Cu}(\text{OTf})_2$ solution in 0.1 M HClO_4 . In the order of increasing darkness are depicted the spectra of 0, 0.5, 1, 2, 3, 4, 8 and 11 equivalents of DAT with respect to $\text{Cu}(\text{OTf})_2$.

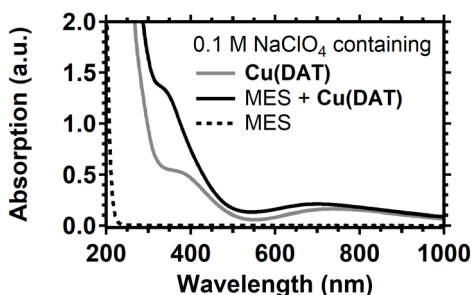


Figure B.10. The UV-vis spectra of a 0.1 M NaClO_4 solution with 6.6 mM of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT (**Cu(DAT)**, grey solid line), 0.03 M MES buffer (dotted black line) and a mixture of both (solid black line).

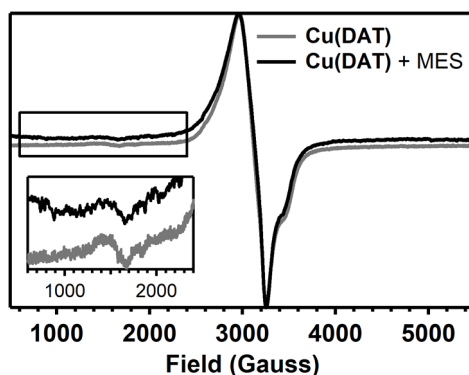


Figure B.11. In grey, the normalized EPR spectrum of a 6.6 mM **Cu(DAT)** solution (Figure 3.2, taken at 9.36 GHz) is shown. The black lines show the normalized EPR spectrum of 6.6 mM **Cu(DAT)** + 0.03 M MES (taken at 9.34 GHz). The inset shows a zoom of the spectrum between 600 and 2400 Gauss. Both spectra were taken at 77 K.

B.6 Electrochemical Quartz Crystal Microbalance experiments

For the sensitive microbalance experiments a sensitivity coefficient relating the frequency to mass can be determined by the electrodeposition of Pb^0 as is described elsewhere.¹⁰ However, frequency changes might not solely depend on mass changes as for example the viscoelasticity and surface roughness of the deposition also have an effect on the frequency.¹¹

A separate electrochemical quartz crystal microbalance (EQCM) measurement was performed for a solution containing 6.6 mM of only DAT. In the potential window of 0.0 to 1.0 V an anodic peak is during cyclic voltammetry (CV) observed accompanied by a negligible frequency change. When the potential window is broadened to 1.2 V it becomes clear that the oxidation that has an onset at 0.9 V *versus* the reversible hydrogen electrode (RHE) is part of an oxidation that produces significant currents above 1.0 V (Figure B.12). The initial positive sweep is followed by a negative sweep where a broad reductive peak between 0.9 and 0.4 V *versus* RHE can be observed. Accordingly, the oxidation starting at 0.9 V is linked to the oxidation of DAT but does not lead to significant deposition.

The electrochemical deposition of material by **Cu(DAT)** can also be induced by chronoamperometry. Applying a fixed potential of 0.2 V on a gold electrode induces a steady decrease of frequency, thus increase of mass, of the electrode (Figure B.13). Figure B.14 shows that the ORR activity of the electrodeposition induced by chronoamperometry ($^{\text{CA}}\text{Au}|\text{Cu(DAT)}$) shows the same current profile on gold as the deposition generated by cyclic voltammetry ($^{\text{CV}}\text{Au}|\text{Cu(DAT)}$, 30 cycles between 0 and 1 V at 100 mV/s). Also, for both $^{\text{CV}}\text{Au}|\text{Cu(DAT)}$ and $^{\text{CA}}\text{Au}|\text{Cu(DAT)}$ the activity increases by circa 30% in the course of 40 scans. The difference in absolute current might be caused by the difference in the amount of deposited material. During modification with cyclic voltammetry, part of the deposition is stripped above 0.8 V whereas during chronoamperometry the potential is held at 0.2 V.

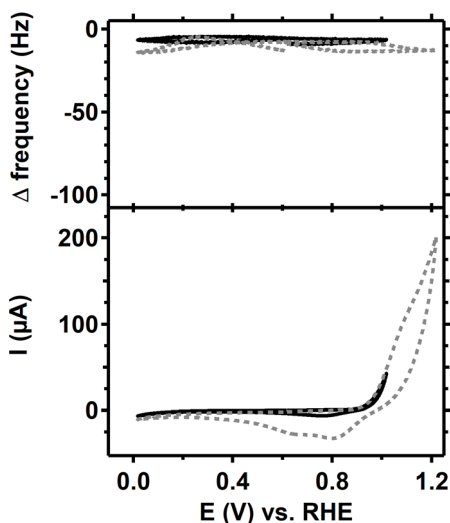


Figure B.12. A cyclic voltammogram combined with a quartz crystal microbalance experiment of a 0.1 M NaClO_4 solution (pH 4.4) containing 6.6 mM DAT measured at a 10 mV/s scan rate. The voltammograms were recorded between 0 and 1 V (solid black line) or 1.3 V (dotted grey line).

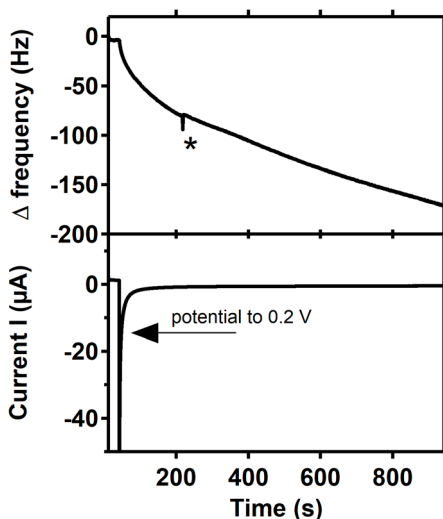


Figure B.13. A quartz crystal microbalance experiment combined with chronoamperometry. A gold electrode in a 0.1 M NaClO_4 (pH 4.8) solution containing 6.6 mM of a 1:1 mixture of $\text{Cu}(\text{OTf})_2$ and DAT was modified by chronoamperometry. For the first 30 seconds, the potential was held at 0.8 V. Next, the potential was set at 0.2 V for 15 minutes. The current response is displayed in the bottom panel while the corresponding frequency change is displayed in the top panel. The asterisk (*) depicts an artifact.

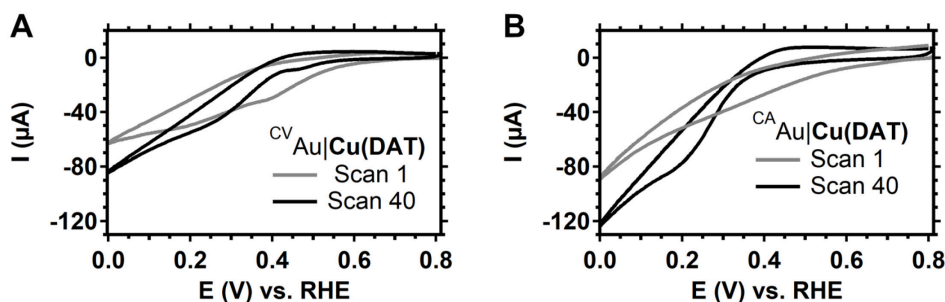


Figure B.14. Cyclic voltammograms at a scan rate of 100 mV/s of modified gold electrodes in an oxygen-purged 0.03 M MES buffer in a 0.1 M NaClO₄ solution (pH 5.2). The electrodes were either pre-modified by cyclic voltammetry (a) or chronoamperometry (b) in a **Cu(DAT)** solution. For clarity, only the first (light grey) and last (40th, black) scans are shown.

The deposition formed by **Cu(DAT)** can readily be stripped off by performing CV in a potential window up to 1.3 V (Figure B.15). A gold electrode was modified by repeated CV scans in an 0.1 M NaClO₄ electrolyte containing **Cu(DAT)**. The EQCM measurement shows that the intensity of the oxidative peak at 0.8 *versus* RHE drastically increases above 1.0 V and is accompanied by a severe decrease in mass indicating loss of material. Subsequent scanning in this broader potential window shows that deposition formed in the cathodic region is readily stripped above 1.0 V so build-up of material on the electrode does not take place anymore.

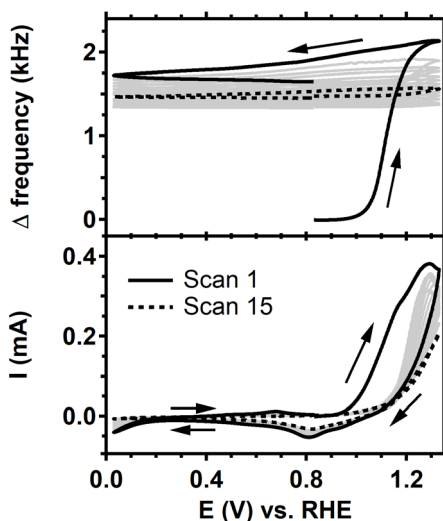


Figure B.15. Stripping of the deposition of a modified gold electrode in a 0.1 M NaClO₄ (pH 4.8) solution containing 6.6 mM of a 1:1 mixture of Cu(OTf)₂ and DAT by EQCM combined with cyclic voltammetry at a 10 mV/s scan rate. The material was deposited on the electrode by performing CV for 15 scans between 0 and 1 V at a 10 mV/s scan rate in the same electrolyte prior to stripping.

B.7 Cyclic voltammetry in the presence of Cu(DAT) with gold and pyrolytic graphite electrodes

A gold disk electrode was modified using the same procedure as the EQCM experiments were performed: a CV was taken in a 6.6 mM solution of a 1:1 ratio of $\text{Cu}(\text{OTf})_2$ and DAT in a 0.1 M NaClO_4 electrolyte solution. 30 cycles at a 100 mV/s scan rate were performed to obtain the modified electrode $^{\text{CV}}\text{Au}|\text{Cu}(\text{DAT})$. Compared to unmodified gold, the onset is at slightly higher potentials and larger currents are acquired. Also, the ring shows less current implying better selectivity. However, the activity drops over repetitive scanning. Most likely, the deposition cannot bind strong enough on gold to perform rotating ring disk electrode (RRDE) experiments with high rotation rates. In contrast, when a stationary gold electrode is used, the activity increases upon repetitive potential cycling (Figure B.14 and B.19) similar to the behavior of $\text{PG}|\text{Cu}(\text{DAT})$ (Figure 3.4). As gold is active in the same potential window for the ORR (Figure B.16), any attributions to active species cannot be made unambiguously when gold is used. Therefore, pyrolytic graphite (PG) was

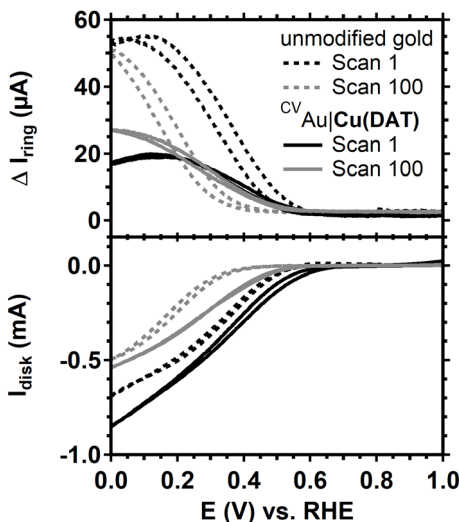


Figure B.16. RRDE experiment with a gold disk electrode (0.196 cm^2) in an oxygen-purged 0.1 M NaClO_4 solution containing 0.03 M MES buffer (pH 5.2). The cyclic voltammogram of the gold disk which was rotated at 2000 rpm (bottom panel) and the current response of the platinum ring that was set at a potential of 1.2 V (top panel) are depicted. The dotted lines correspond to an unmodified gold disk while the solid lines correspond to the modified electrode $^{\text{CV}}\text{Au}|\text{Cu}(\text{DAT})$. In black, the first scan is shown while the grey lines show the last (100th) scan. The CV was taken at a 100 mV/s scan rate.

used as electrode as it shows qualitatively the same electrochemistry for **Cu(DAT)** as with gold (Figure B.17).

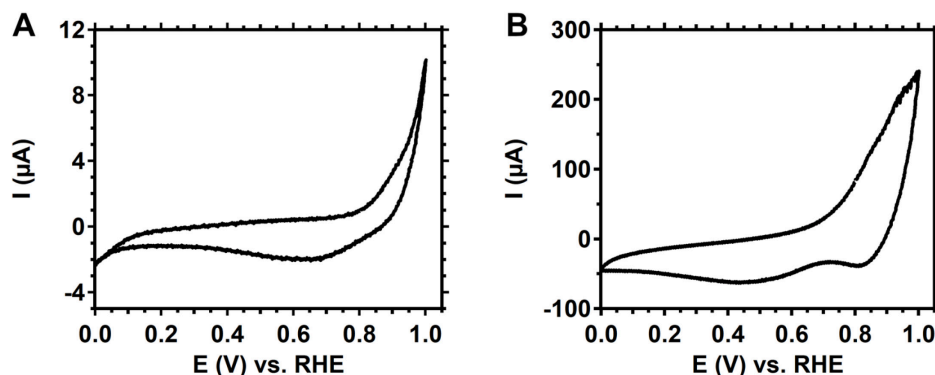


Figure B.17. Cyclic voltammograms that are recorded at a 25 mV/s scan rate in a 0.1 M NaClO_4 (pH 4.8) solution with 6.6 mM of a 1:1 ratio of $\text{Cu}(\text{OTf})_2$ and DAT with (a) gold and (b) pyrolytic graphite (PG) working electrodes.

B.8 Koutecky-Levich analysis

The linear fits in Figure B.18A show that the limiting current for dioxygen reduction at different rotation rates behaves according to the Koutecky-Levich equation (see Chapter 1).¹² The Levich equation (Eqn. 1.7) can be simplified to Equation B.1 with B being the Levich constant. This constant was determined by performing rotating ring disk electrode (RRDE) experiments with a platinum disk electrode, as platinum is known to be a 4-electron dioxygen reduction catalyst. B can be calculated using the slope of the Koutecky-Levich plot as the following equation holds (Equation B.2):¹³

$$I_L = 0.62nFAD_o^{2/3}C_o\nu^{-1/6}\omega^{1/2} = BnA\omega^{1/2} \quad \text{Eqn. B.1}$$

$$\text{slope} = \frac{1}{BnA} \quad \text{Eqn. B.2}$$

For the platinum electrode the slope, n (4) and A (0.196 cm^2) are known, so B could be determined and used to calculate n for the modified PG electrode for which A (0.12 cm^2) and the slope are known as well. n was calculated to be 1.2 indicating that dioxygen is reduced to mainly superoxide and partly peroxide species.

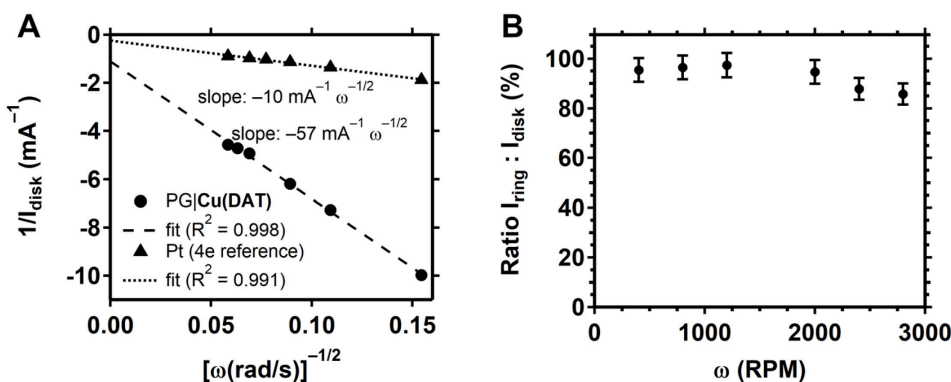


Figure B.18. (a) shows the Koutecky-Levich plot of the inverse of the average limiting current between 0.40–0.42 V of PG|Cu(DAT) (rounds, Figure 3.4B) versus the inverse square root of the rotation rate and the result of a linear fit. Also shown is the inverse of the average limiting current between 0.30 and 0.35 V for a Pt disk electrode (triangles) used as calibration for the Levich equation in oxygen-saturated 0.1 M NaOH. (b) shows the ratio of the average limiting current of the ring to the average limiting current of PG|Cu(DAT) between 0.40 and 0.42 V versus the rotation speed in 0.1 M NaOH. The ratio was corrected for the collection efficiency (22%) of the ring that was determined with the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ redox couple.

B.9 XPS analysis of C 1s and N 1s regions of modified gold and pyrolytic graphite electrodes

For X-ray photoelectron spectroscopy (XPS) analysis (Figure B.19, B.20 and Table B.1), the following procedures were followed to obtain $^{\text{CV}}\text{Au}|\text{Cu}(\text{DAT})$ and $^{\text{CA}}\text{Au}|\text{Cu}(\text{DAT})$. EQCM gold electrodes were used in a similar set-up as the EQCM experiments. Sample $^{\text{CV}}\text{Au}|\text{Cu}(\text{DAT})$ was prepared with cyclic voltammetry by performing 30 CV scans between 0 and 1 V at a 100 mV/s scan rate in a 0.1 M NaClO_4 solution containing 6.6 mM of a 1:1 ratio of $\text{Cu}(\text{OTf})_2$ and DAT at pH 4.8. Sample

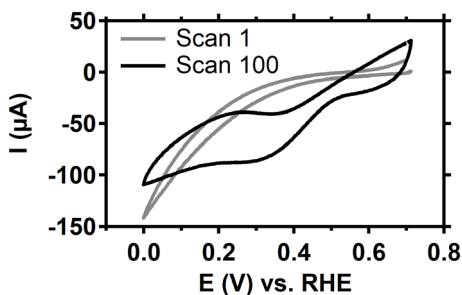


Figure B.19. Cyclic voltammogram of $^{\text{Cat}}\text{Au}|\text{Cu}(\text{DAT})$ directly after the modification in an oxygen purged 0.1 M NaClO_4 solution containing 0.03 M MES buffer at a pH of 5.2. 100 cycles at a 100 mV/s scan rate were performed.

$^{CA}Au|Cu(DAT)$ was prepared potentiostatically by applying 0.2 V for 15 minutes. The whole set-up was stationed in a glove bag under an N_2 atmosphere to prevent contact with air upon removal of the electrode from the EQCM cell. The electrodes were rinsed with Ar purged water and dried under high vacuum before XPS analysis.

$^{Cat}Au|Cu(DAT)$ was prepared with cyclic voltammetry by performing 30 CV scans between 0 and 1 V at a 100 mV/s scan rate in a 0.1 M $NaClO_4$ solution containing 6.6 mM of a 1:1 ratio of $Cu(OTf)_2$ and DAT at pH 4.8. Next, the electrode was put in an oxygen-saturated 0.03 M MES buffer (pH 5.2) in 0.1 M $NaClO_4$. 100 CV cycles between 0 and 1 V at a 100 mV/s scan rate were performed. The ORR onset was observed to increase after repetitive scanning up to 100 scans (Figure B.19) as was also observed with RRDE experiments on $PG|Cu(DAT)$.

$PG|Cu(DAT)$ was prepared in a regular electrochemical set-up by performing 90 CV scans between 0 and 1 V at a 100 mV/s scan rate in a 0.1 M $NaClO_4$ solution containing 6.6 mM of a 1:1 ratio of $Cu(OTf)_2$ and DAT at pH 4.8. 90 instead of 30 CV scans were used to increase the intensity of the XPS signal. The electrode was rinsed with N_2 purged water and dried under high vacuum. Care was taken to prevent contact with air during handling and transferring the electrode into the XPS apparatus.

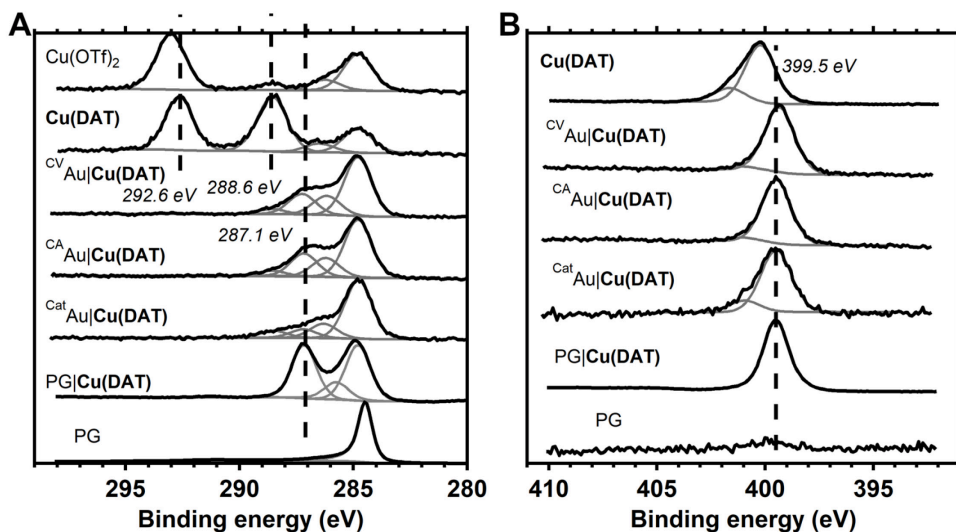


Figure B.20. C 1s (A) and N 1s (B) XPS spectra (black lines) of the modified electrodes $^{CV}Au|Cu(DAT)$, $^{CA}Au|Cu(DAT)$, $^{Cat}Au|Cu(DAT)$, $PG|Cu(DAT)$ and the reference compounds $Cu(DAT)$, $Cu(OTf)_2$ and PG electrode. In grey, the deconvolution is depicted.

Table B.1. The C : Cu ratio of several carbon species with respect to the total amount of copper of the modified electrodes ^{CV}Au|**Cu(DAT)**, ^{CA}Au|**Cu(DAT)**, ^{Cat}Au|**Cu(DAT)** and the reference compounds **Cu(DAT)** and Cu(OTf)₂ as determined by XPS.

Corresponding					
carbon species	Cu(OTf) ₂	Cu(DAT)	^{CV} Au Cu(DAT)	^{CA} Au Cu(DAT)	^{Cat} Au Cu(DAT)
(eV) ^a					
293.0 (OTf ⁻)	1.6				
292.6 (OTf ⁻)		2.0			
288.6 (DAT)		2.2			
286.2			1.1	1.2	
287.2			1.4	1.2	
288.5			0.3	0.3	
286.4					1.9
287.7					1.1
289.1					0.7

^aThe ratio of the carbon species at 284.8 eV is omitted as this mostly corresponds to adventitious carbon for these samples.

B.10 Influence of DAT on the ORR activity of copper electrodes

To study the electrochemical effect of DAT on a copper surface, a copper disk was modified by cyclic voltammetry similar to the modification of PG to obtain PG|**Cu(DAT)**. A copper disk electrode was modified by cyclic voltammetry between 0 and 1 V *versus* RHE in a 0.1 M NaClO₄ solution containing 6.6 mM DAT to obtain Cu|DAT. Notably, oxidation of copper occurs above 0.5 V thus the scan rate was adjusted to 250 mV/s to reduce the corrosion time of the copper disk per cycle. The amount of scans was increased to 75 to maintain the same total modification time of 10 minutes. Figure B.21 shows the ORR activity studied with RRDE experiments of Cu|DAT compared to PG|**Cu(DAT)**. Cu|DAT was studied at both pH 5.2 and pH 13. In both cases, the CV of the disk differs significantly from PG|**Cu(DAT)**. Also, the shape of the CV of Cu|DAT stabilized after repetitive CV cycling. Figure B.22 shows a comparison of the ORR activity of Cu|DAT as compared to an unmodified copper disk electrode. At pH 5.2, the shape of the CV of Cu|DAT is more similar to copper than to PG|**Cu(DAT)** (Figure B.21). However, the surface modification did lead to some differences in the CV of the disk. Furthermore, some ring current can be

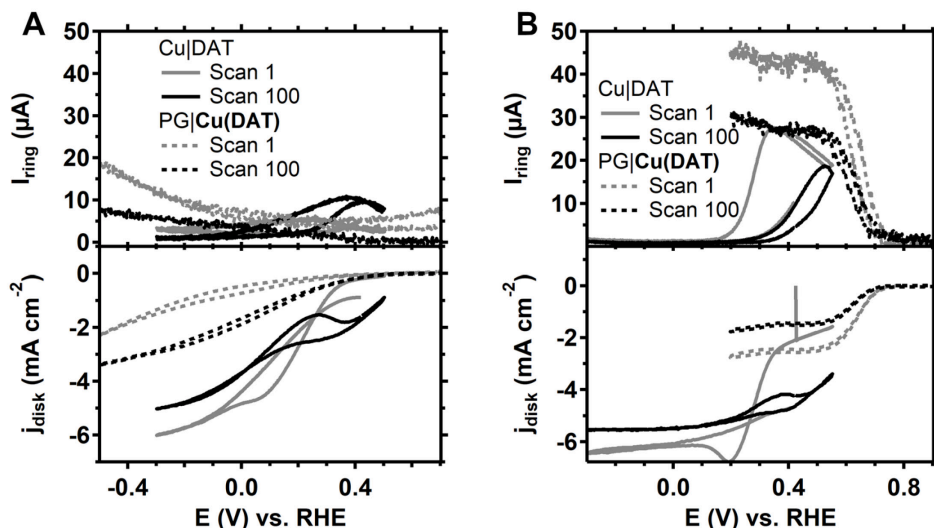


Figure B.21. RRDE experiment of Cu|DAT in an oxygen-saturated electrolyte (solid line). Cu|DAT was studied in both 0.03 M MES in 0.1 M NaClO₄ at pH 5.2 (A) and 0.1 M NaOH at pH 13 (B). For comparison, the results of PG|Cu(DAT) (Figure 3.4) are depicted as well (dotted lines). Current densities are given for the disk as the surface from Cu|DAT (0.196 cm²) is different from PG|Cu(DAT) (0.12 cm²). The CV was taken at a 100 mV/s scan rate while the disk was rotated at 2000 RPM.

observed for Cu|DAT whereas unmodified copper does not show any ring current. At pH 13 the shape of the last CV of Cu|DAT and unmodified copper are more comparable than at pH 5.2.

Possibly, the modified layer of Cu|DAT is quickly stripped off during the ORR experiments, because the shape of the CV of Cu|DAT resembles the CV of unmodified copper. Therefore, the ORR activity of unmodified copper was also studied in electrolytes containing 6.6 mM DAT at pH 5.2 and pH 13 (Figure B.23) with RRDE. At both pH 5.2 and pH 13, the CV of the copper electrode did not change after repetitive potential cycling in contrast to the PG|Cu(DAT) electrode. Also, larger currents are observed in the case of the copper electrode. Experiments in combination with a ring could not be performed because DAT is oxidized above 0.9 V (Figure B.12). Moreover, the copper electrode is oxidized above 0.5 V thus limiting the potential window wherein CV was performed. Notably, the solution slowly developed a yellow color in the course of the ORR experiments that were performed at pH 13. Most likely, DAT is slowly disintegrated due to the combination of electrochemistry and high pH. A pH 13 solution containing DAT not subjected to electrochemical measurements remained colorless.

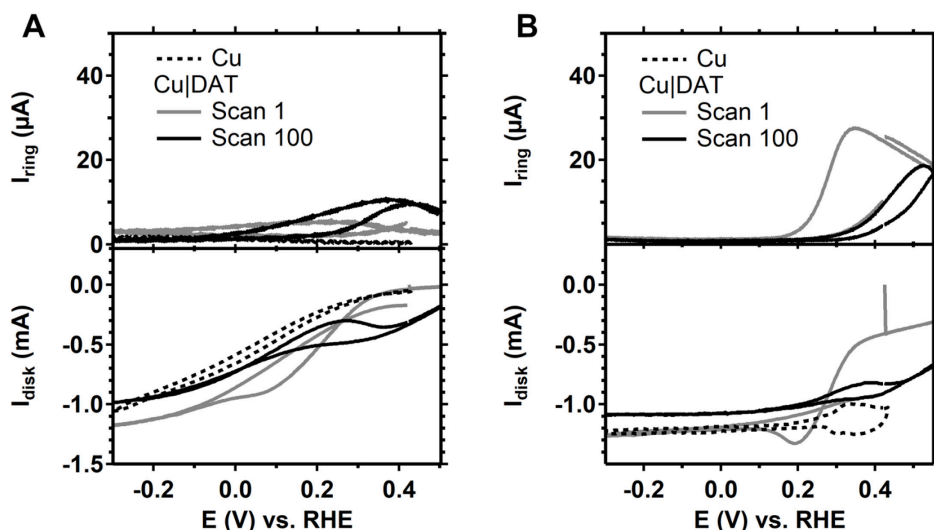


Figure B.22. RRDE experiment with unmodified Cu (black dotted lines) and modified Cu|DAT disk electrodes (solid lines) in an oxygen-saturated electrolyte. Both the electrodes were studied in a 0.03 M MES in 0.1 M NaClO_4 at pH 5.2 (A) and 0.1 M NaOH at pH 13 (B). The CV was taken at a 100 mV/s scan rate while the disk was rotated at 2000 RPM. In B the ring current during the CV of the unmodified Cu disk was not monitored.

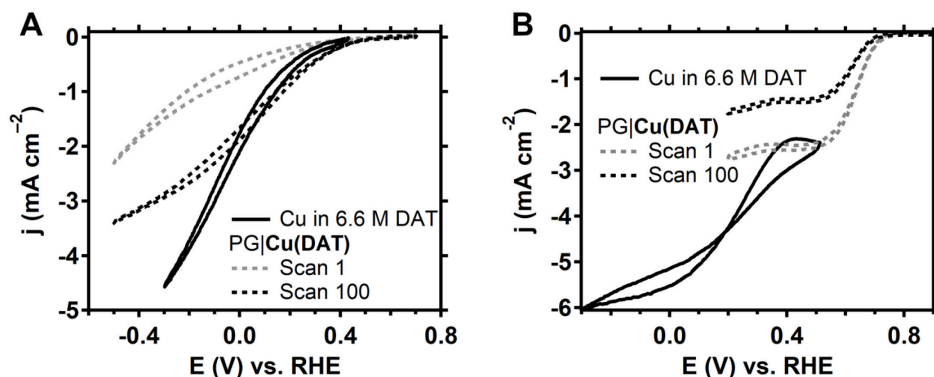


Figure B.23. Rotating disk electrode experiments of a copper electrode (0.196 cm^2) in an oxygen-saturated electrolyte containing 6.6 mM DAT (black solid line). The copper electrode was studied in both 0.03 M MES in 0.1 M NaClO_4 at pH 5.2 (A) and 0.1 M NaOH at pH 13 (B). For comparison, the results obtained with PG|Cu(DAT) (Figure 3.4) are depicted as well (dotted lines). Current densities are given as the surface from PG|Cu(DAT) (0.12 cm^2) is different from the copper electrode (0.196 cm^2). The CV was taken at a 100 mV/s scan rate while the disk was rotated at 2000 RPM.

B.11 RRDE and XPS experiments of Vulcan|Cu(DAT)

Vulcan|**Cu(DAT)** was prepared according to the reported procedure¹⁴ from DAT and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($\geq 99.995\%$ trace metal basis, Sigma Aldrich) by mixing 1.00 g Vulcan XC-72R (Cabot) with 0.200 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.995%, Sigma Aldrich) in 20 ml water and sonicating the mixture for 2 hours to obtain a viscous suspension. Next, a solution of 0.159 g DAT in 10 ml water was added dropwise to the stirred suspension. After addition of DAT, the mixture was left stirring for an additional 20 hours. Subsequently, the black solids were collected through filtration. The remaining black paste was further dried in a vacuum oven at 90 °C for 3.5 hours. Following, the brittle solid was pulverized with pestle and mortar to obtain Vulcan|**Cu(DAT)** which was further analyzed by XPS (Figure B.24 and B.25).

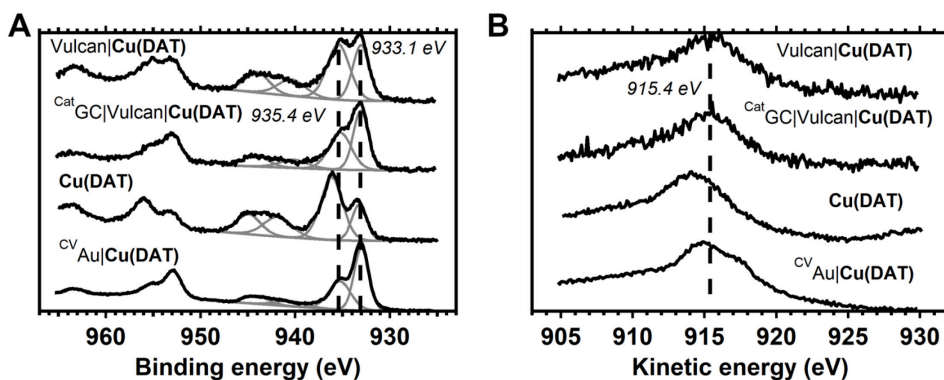


Figure B.24. XPS spectra (black lines) of the modified electrodes CVAu|Cu(DAT) and $\text{CatGC|Vulcan|Cu(DAT)}$ and the reference compounds Vulcan|**Cu(DAT)** and **Cu(DAT)**. In grey, the deconvolution of the $\text{Cu}2\text{p}_{3/2}$ region is depicted. A shows the Cu 2p region of the spectra and B shows the $\text{Cu L}_3\text{M}_{4,5}\text{M}_{4,5}$ Auger spectra.

A GC disk electrode (0.196 cm²) was modified by dropcasting Vulcan|**Cu(DAT)** on the electrode as previously reported.¹⁴ The onset for oxygen reduction with GC|Vulcan|**Cu(DAT)** was found to correspond to the reported onset (Figure B.26).¹⁴ In addition, GC|Vulcan|**Cu(DAT)** was tested under the same conditions as PG|**Cu(DAT)** in a pH 5 MES buffer (Figure B.27). GC|Vulcan|**Cu(DAT)** is clearly more active and seems to achieve limiting currents within the potential window. The 100th scan is displayed for both modified electrodes. For PG|**Cu(DAT)**, the 100th scan corresponds to the most active scan. For GC|Vulcan|**Cu(DAT)**, a minimal decrease in activity is observed over the course of 100 scans. These results indicate that the substrate plays an a very important role in the oxygen reduction activity.

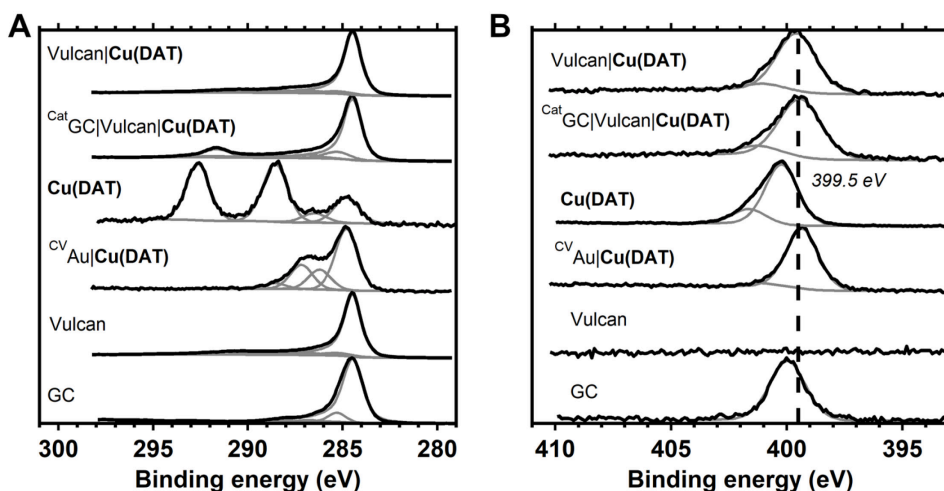


Figure B.25. C 1s (A) and N 1s (B) XPS spectra (black lines) of the modified electrodes $^{CV}Au|Cu(DAT)$ and $^{Cat}GC|Vulcan|Cu(DAT)$ and the reference compounds **Cu(DAT)** and **Vulcan|Cu(DAT)** as well as bare GC and Vulcan. In grey, the deconvolution is depicted.

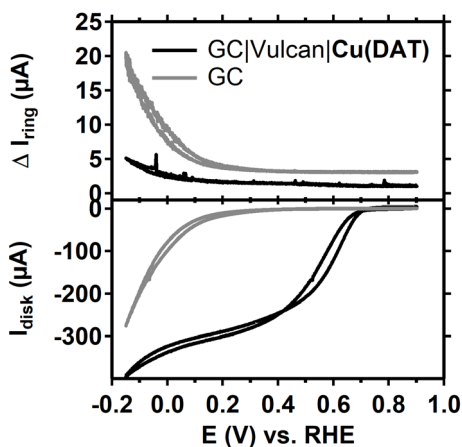


Figure B.26. RRDE experiment of $GC|Vulcan|Cu(DAT)$ disk in an oxygen-saturated pH 7 Britton-Robinson buffer in 0.1 M $NaClO_4$. The solid black lines depict the disk (bottom graph) and ring (top graph) current responses. The grey solid lines depict the current response when a freshly polished GC disk was used. The CV was performed at a 5 mV/s scan rate while the ring was set to 1.2 V and the disk rotated at 1600 rpm.

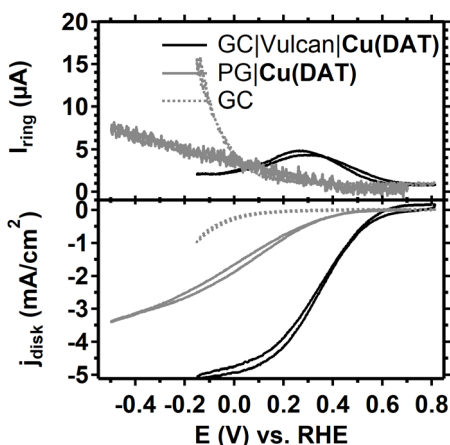


Figure B.27. RRDE experiment of GC|Vulcan|Cu(DAT) disk (0.196 cm^2) in an oxygen-saturated pH 5.2 MES buffer in 0.1 M NaClO_4 . The solid black lines depict the disk (bottom graph) and ring (top graph) current responses of the 100th scan. The grey dotted lines correspond to a freshly polished GC disk. The grey solid lines belong to the 100th scan of a PG|Cu(DAT) disk (0.12 cm^2). The CV was performed at a 100 mV/s scan rate while the ring was set to 1.2 V and the disk rotated at 2000 rpm .

Another GC electrode (0.07 cm^2) was modified by dropcasting Vulcan|Cu(DAT). With this electrode (^{Cat}GC|Vulcan|Cu(DAT)), 103 CV cycles between 0.9 and 0 V at a 100 mV/s scan rate were performed in an oxygen purged pH 7 Britton-Robinson buffer in 0.1 M NaClO_4 . After performing oxygen reduction, the electrode was rinsed with water and dried under a soft stream of air. XPS measurements were performed to analyze the composition of ^{Cat}GC|Vulcan|Cu(DAT) after catalysis (Figures B.24 and B.25). Within the Cu 2p region both ^{Cat}GC|Vulcan|Cu(DAT) and Vulcan|Cu(DAT) show similarities with ^{CV}Au|Cu(DAT) and ^{CA}Au|Cu(DAT). Copper species with Cu $2p_{3/2}$ binding energies of 933.1 and 935 eV are observed for all samples (Figure B.24A). Also, the Auger parameter in the Cu $L_{3}M_{4.5}M_{4.5}$ spectrum has a kinetic energy of 915.4 eV for all species (Figure B.24B). Two species are observed in the N 1s region for both Vulcan|Cu(DAT) and ^{Cat}GC|Vulcan|Cu(DAT) with BEs of 399.5 eV and 401.2 eV (Figure B.25B). The (unpolished) GC electrode also contains a N 1s species, but this is different from Vulcan|Cu(DAT) species. Most importantly, the reference Cu(DAT) powder was found to differ from Vulcan|Cu(DAT) implying that the complex Cu(DAT) is not present in Vulcan|Cu(DAT) when it is prepared according to the literature procedure.¹⁴ This is further supported by the (too) low nitrogen to copper ratio (Table 3.1). Moreover, the C 1s region is very different from Cu(DAT) and ^{CV}Au|Cu(DAT) (Figure B.25A). This is due to the use of Vulcan and GC which

are both carbon based materials and thus their strong signals overlap all other signals. Here, the most important species for both Vulcan|**Cu(DAT)** and ^{CatGC}|Vulcan|**Cu(DAT)** is the graphitic sp² carbon with a BE of 284.5 eV. The carbon species with a BE of 291.6 eV in ^{CatGC}|Vulcan|**Cu(DAT)** might correspond to the π - π^* transition shake-up of graphite and does not correspond to **Cu(DAT)**. Also, the carbon composition is different compared to ^{CV}Au|**Cu(DAT)**.

The negligible change of the copper composition between Vulcan|**Cu(DAT)** and ^{CatGC}|Vulcan|**Cu(DAT)** and the large resemblance with ^{CV}Au|**Cu(DAT)** indicate that most of the catalytic active sites of Vulcan|**Cu(DAT)** have not performed ORR due the diffusion limitation of oxygen. Figure B.28 shows the corresponding CV response. Clearly, most of the oxygen near the catalytic surface has been reduced in only the first scan as the following scans show a far lower current response. Purging the electrolyte after scan 3 with O₂ for a brief moment did lead to a slight increase of ORR current in the first following scan.

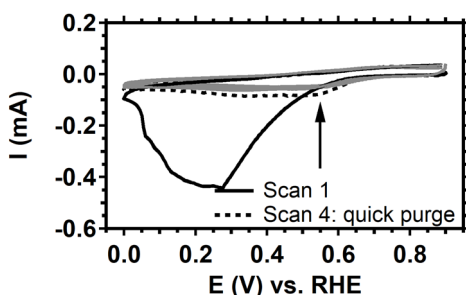


Figure B.28. ORR response of ^{CatGC}|Vulcan|**Cu(DAT)** that was analyzed by XPS hereafter. CV was performed between 0.9 and 0 V for 103 cycles with a scan rate of 100 mV/s in a pH 7 Britton-Robinson buffer in 0.1 M NaClO₄. After scan 3, the potential cycling was halted to re-purge the electrolyte with O₂ before continuing the potential cycling.

B.12 References

1. Antolini, L.; Fabretti, A. C.; Gatteschi, D.; Giusti, A.; Sessoli, R., *Inorg. Chem.* **1991**, *30*, 4858–4860.
2. Fabretti, A. C., *J. Crystallogr. Spectrosc. Res.* **1992**, *22*, 523–526.
3. Kröger, G. F.; Freiberg, W., *Z. Chem.* **1965**, *5*, 381–382.
4. Zhang, T.; Wang, C.; Liu, S.; Wang, J.-L.; Lin, W., *J. Am. Chem. Soc.* **2014**, *136*, 273–281.
5. Gomez, V.; Benet-Buchholz, J.; Martin, E.; Galan-Mascaros, J. R., *Eur. J. Inorg. Chem.* **2014**, *2014*, 3125–3132.
6. Boland, Y.; Tinant, B.; Safin, D. A.; Marchand-Brynaert, J.; Clerac, R.; Garcia, Y., *CrystEngComm* **2012**, *14*, 8153–8155.
7. Good, N. E.; Winget, G. D.; Winter, W.; Connolly, T. N.; Izawa, S.; Singh, R. M. M., *Biochemistry* **1966**, *5*, 467–477.
8. Kandegedara, A.; Rorabacher, D. B., *Anal. Chem.* **1999**, *71*, 3140–3144.
9. Mash, H. E.; Chin, Y.-P.; Sigg, L.; Hari, R.; Xue, H., *Anal. Chem.* **2003**, *75*, 671–677.
10. van der Ham, C. J. M.; Işık, F.; Verhoeven, T. W. G. M.; Niemantsverdriet, J. W.; Hetterscheid, D. G. H., *Catal. Today* **2017**, *290*, 33–38.

11. Buttry, D. A.; Ward, M. D., *Chem. Rev.* **1992**, 92, 1355–1379.
12. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*. Wiley: New York, 2000.
13. Boulatov, R.; Collman, J. P.; Shiryayeva, I. M.; Sunderland, C. J., *J. Am. Chem. Soc.* **2002**, 124, 11923–11935.
14. Thorum, M. S.; Yadav, J.; Gewirth, A. A., *Angew. Chem. Int. Ed.* **2009**, 48, 165–167.