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Tricopper Cluster Complex Functionalized Carbon Electrode: A Strategy to Overcome the Overpotential and Production of Hydrogen Peroxide in the Oxygen Reduction Reaction

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Abstract: A study of the oxygen reduction reaction (ORR) on a electrode surface mediated screen printed carbon by the tricopper cluster complex Cu₃(7-N-Etppz(CH₂OH)) dispersed on electrochemically reduced carbon black, where 7-N-Etppz(CH₂OH) is the ligand 3,3'-(6-(hydroxymethyl)-1,4-diazepane-1,4-diyl)bis(1-(4ethyl piperazin-1-yl)propan-2-ol), is described. Onset oxygen reduction potentials of ~0.92 V and ~0.77 V are observed at pH 13 and pH 7 vs. the reversible hydrogen electrode, which are comparable to the best values reported for any synthetic copper complex. Based on half wave potentials (E_{1/2}), the corresponding overpotentials are ~0.42 V and ~0.68 V, respectively. Kinetic studies indicate that the trinuclear copper catalyst can accomplish the 4-e⁻ reduction of O2 efficiently and the ORR is accompanied by the production of only small amounts of H₂O₂. The involvement of the copper triad in the O₂ activation process is verified by comparing the performances between electrodes modified by a Cu₃ and Cu₂ catalyst, underscoring the significance of having three reducing equivalents readily available for ORR to alleviate the overpotential as well as production of H_2O_2 .

The 4-e⁻ reduction of dioxygen (O₂) to water (H₂O), *i.e.*, the oxygen reduction reaction (ORR), is biologically and technologically significant, especially in fuel cell applications.^[1] The cathodic process affects the efficiency of fuel cells. Though platinum has an onset reduction potential of ~1.0 V (vs. RHE), given its sluggish ORR kinetics and cost, large-scale usage of platinum is neither practical nor viable.^[2] On the other hand, the binding and cleavage of O2 in various processes is carried out by many copper-containing proteins.^[3] Multi-copper oxidases, such as laccase, catalyze the $4-e^{-1}$ reduction of O₂ to H₂O efficiently and show excellent electrochemical activity much closer to the reversible oxygen reduction potential of 1.23 V (vs. RHE).⁴ Laccase has 4 copper centers, including a type 1 Cu¹⁺ site for electron transfer, and a Cu triad composed of a type 2 (T2) Cu^{1+} site and a type 3 (T3) dinuclear Cu^{1+} center for the binding and cleavage of O_2 .^[4] Despite superior performance, enzymes are unstable, and have decreased current density due to larger molecular sizes.^[5] However, systematic studies of O₂binding copper proteins, have provided key insights into their

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structures and mechanisms, leading to development of many synthetic copper complexes mimicking the active sites of the enzymes as part of a strategy to overcome the overpotential (η) .^[6]

Mononuclear Cu¹⁺ complexes that largely use phenanthroline as ligand show that electron withdrawing substituents and bulky groups placed near the metal center decrease η in the ORR. Also, proximally placed mononuclear Cu¹⁺ phenanthroline complexes with polynuclear assembly further reduce η .^[7] Similarly, mono and binuclear complexes with pyridyl-based ligands have been developed to mimic the T₃ center of enzymes.^[8] O₂ activation of two mononuclear Cu¹⁺ tris(2-pyridylmethyl)amine in close juxtaposition shows the lowest ORR η (at pH 1).² Among binuclear complexes, Cu₂-3,5-diamino-1,2,4-triazole (Cu₂-Hdartz) exhibits an ORR onset reduction potential of 0.73 V and 0.86 V vs. RHE (at pH 7 and 13, respectively) making it the best performing catalyst of any synthetic complex at pH 7.^[9]

Aside from the Cu triad in laccase being the active and vital center for O_2 binding and O–O bond cleavage, the spatial arrangement of the Cu centers and the details of O_2 activation must be essential for ORR. Case in point, in synthetic models, the T_2 Cu mimic of the trinuclear Cu system often does not participate in the reduction process and the electrochemistry yields performances similar to the binuclear system.^[10] Moreover, many trinuclear copper systems have been synthesized and found to be ineffective towards O_2 activation.^[11] Thus, it is evident that ligand design is paramount for effective ORR.



Scheme 1. Structures of various di- and trinuclear copper complexes used in this work. Structures **1**, **2**, **3** are based on studies reported previously¹² and **4** is derived from HR-ESI-MS data acquired during this study (SI).

We recently prepared several rationally designed trinuclear Cu^{1+} complexes that, upon O_2 activation, efficiently oxidize methane and other light alkanes to their corresponding alcohols at

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ambient conditions.^[13] These complexes include Cu₃(7-N-Etppz) 1 and Cu₃(7-Dipy) 3, where 7-N-Etppz and 7-Dipy denote the ligands 3,3'-(1,4-diazepane-1,4-diyl)bis(1-(4-ethylpiperazin-1-yl) propan-2-ol) and 3,3'-(1,4-diazepane-1,4-diyl)bis(1-(bis(pyridin-2-yl)methyl)amino)propan-2-ol), respectively. These tricopper complexes are biomimics of the active site of the particulate methane monooxygenase (pMMO) in methanotrophic bacteria. Although the structural arrangements of the trinuclear Cu clusters and specifics of the O2 activation in pMMO and in these pMMO biomimetics differ from that of the T_2/T_3 Cu triad in laccases, the O-O bond is cleaved at the 3-e level of reduction in both incidences.^[6a,14] Accordingly, we can expect the designed trinuclear copper complexes to behave similar to laccase on the electrode surface during electrocatalytic reduction of O2. This is indeed the case. Here we demonstrate the ability of the tricopper cluster complex Cu₃(7-N-Etppz(CH₂OH)) 2, where 7-N-Etppz(CH₂OH) stands for the ligand 3.3'-(6-(hydroxymethyl)-1,4diazepane-1,4-divl)bis(1-(4-ethylpiperazin-1-vl)propan-2-ol), towards efficient reduction of O2 at pH 13 and 7 with onset reduction potentials of ~0.92 V (η = 0.42 at E_{1/2}) and ~0.77 V (η = 0.68 at $E_{1/2}$) vs. RHE, respectively, in the ORR. In experiments comparing the performance of the $Cu_3(7-Dipy)$ complex 3 under different pHs with that of the Cu₂(7-Dipy) complex 4. we find n to be significantly higher in the latter complex (by ca. 70 mV at pH 7), verifying the prominent role of the Cu triad in reducing n in ORR. Details of the synthetic procedures and characterization of various catalysts are provided in the Supporting Information (SI). The Cu triad and dicopper complexes are confirmed by highresolution ESI-MS. To study the ORR, 7 µL of the catalyst dissolved in acetonitrile (concentration ~20 mM) is drop casted on to an electrochemically reduced carbon black (CB) modified screen printed carbon electrode (SPCE) and allowed to dry.

The cyclic voltammogram (CV) of SPCE modified by catalyst 2, in N2 saturated Britton-Robinson (B-R) buffer (pH 7), exhibits a guasi-reversible peak with a half wave potential (E1/2) of ~0.55 V (vs. RHE) with additional small shoulder anodic and cathodic waves at 0.65 V and 0.45 V, respectively (Figure 1a). From the slope value of the plot of reduction peak current vs. scan rate, a surface coverage (m) of 1.1×10^{-12} mol/cm² is estimated for the active tricopper catalyst (Figure S1b; equation (1) in SI).^[15] The anodic and cathodic slope values in the plot of log (lp) vs. log (scan rate) obtained from the scan rate study (Figure S1c), indicate a surface-confined redox process with our tricopper catalyst. The heterogeneous electron transfer rate constant (ks) of 2.4 s⁻¹ is obtained by Laviron's method (equation (2) in SI for $n\Delta E_p$ >200 mV/s), indicating reasonably fast ET to the modified electrode (Figure S1).^[16] In this analysis, we assume n = 3 for the number of electrons transferred to the catalyst per cycle, as the redox potentials of the three copper ions are similar.

The ORR activity of the catalyst **2** modified SPCE at pH 7 is shown in the *inset* of Figure 1a. The linear sweep voltammetry (LSV) curve of the modified electrode exhibits an onset reduction potential of ~0.77 V vs. RHE (Table S1). This value is *more positive* than the onset reduction potential reported for any Cu complex modified electrode at this pH.^[9] For a molecular catalyst that exhibits a redox peak, η at E_{1/2} is a better indicator of performance as it can be systematically measured from the E_{1/2}.^[17] Although it is more appropriate for a homogenous system, where the current density is constant at η beyond E_{1/2}, it would still be meaningful for comparison of different molecular catalysts. For the catalyst **2** modified SPCE at pH 7, $\eta_{Cu/ORR} = E_{O2/H2O} - E_{Cu(IM)} = ~0.68 V vs. RHE at pH 7 (E_{O2/H2O} = 1.23 V vs. RHE). The LSV curves of CB and the catalyst modified SPCE, and the Tafel plot (with a slope of 97 mV/decade at 300 RPM) for the catalyst$ **2**modified SPCE, are given in Figures S2a and S2b. From these data, we deduce a turn-over frequency (TOF) of 12 s⁻¹ at E_{1/2} of the active tricopper sites. (TOF =*JA/4Fm*, where*J*is current density,*A*is electrode geometric area,*F*is Faraday constant, and*m*is the active catalyst surface coverage mentioned earlier.^[18])

To estimate the fraction of H_2O_2 (*p*) generated during the ORR, we use a screen printed ring-disk electrode (SPRDE)-flow injection analysis (FIA) system following previous work (Figure S2c).^[19] The **2** modified disk and MnO₂ ring electrode potentials are fixed at 0.42 V and 1.2 V *vs.* RHE, respectively. With N₂ saturated B-R buffer (pH 7) as the mobile phase, 20 µL of O₂ saturated B-R buffer is injected at regular intervals. Currents measured at the ring (I_r) and disk (I_d) electrodes are 0.23 µA and 14.05 µA, respectively, corresponding to ~27% H₂O₂ (equation (6) in SI; Table S1). From I_r/I_d, the n value is 3.46 (equation (7) in SI). For comparison, the simple CB/SPCE generates 88% H₂O₂ (n = 2.24) at pH 7 (Figure S2d).



Figure 1. a) CV of the Cu₃(7-*N*-Etppz(CH₂OH)) CB/SPCE in N₂ saturated B-R buffer, pH 7. *Inset*: LSV curves obtained with **2**/SPCE, scan rate 10 mV/s, pH 7. b) CV of the Cu₃(7-*N*-Etppz(CH₂OH)) CB/SPCE in N₂ saturated 0.1 M NaOH. *Inset*: LSV curves obtained with CB/SPCE and **2**/ SPCE, scan rate 10 mV/s, pH 13.

Given the less corrosive nature and other advantages of an alkaline medium,^[20] we have also evaluated the ORR kinetics at pH 13. The **2** modified SPCE in N₂ saturated 0.1 M NaOH solution exhibits a quasi-reversible peak with E_{1/2} of 0.81 V vs. RHE (Figure 1b). The *inset* in Figure 1b shows an onset reduction potential of ~0.92 V vs. RHE, which is *more positive* than the value of 0.86 V reported for Cu₂-Hdartz at the same pH.^[9] The corrresponding $\eta_{Cu/ORR}$ and TOF at E_{1/2} are ~0.42 V vs. RHE and 12 s⁻¹, respectively. For comparison, the simple CB/SPCE has an onset reduction potential of 0.85 V vs. RHE at pH 13.

To elucidate the ORR kinetics at pH 13, we obtain LSV curves at different rotation rates with the **2** modified electrode in O_2 saturated 0.1 M NaOH solution using the rotating-disk electrode



Figure 2. a) LSV curves of the Cu₃(7-*N*-Etppz(CH₂OH)) modified CB/GCE in O₂ saturated 0.1 M NaOH (pH 13) obtained at different rotation rates, scan rate 10 mV/s. b) Koutecky-Levich plots of the LSV data. c) Tafel slope at 300 RPM. d) FIA performed with a MnO₂/Cu₃(7-*N*-Etppz(CH₂OH)) modified ring-disk electrode in 0.1 M NaOH at flow rate of 0.4 mL/min.

(Figure 2a). The limiting current density increases with the rotation speed due to the higher O_2 flux available to the electrode surface. Using the Koutecky-Levich (K-L) equations (3)–(5) in SI, the kinetics of the catalyst **2** modified electrode is explored.^[21] From the plot of J^{-1} vs. $\omega^{-1/2}$ (Figure 2b), the n value of 3.3 at 0.6 V vs. RHE is obtained, which is close to the theoretical n value of 4 for O_2 reduction to H₂O. Based on equation (5) in SI, the *k* value for the catalyst **2** modified carbon black/glassy carbon electrode (CB/GCE) at 0.6 V is 7.94 x 10^{-3} cm s⁻¹. The Tafel slope of 77 mV/decade obtained from the LSV curve at 300 RPM (Figure 2c) indicates electron transfer as the rate determining step.²

The H₂O₂ (*p*) generated during the ORR at pH 13 is 21% (Table S1) from the SPRDE-FIA experiment (Figure 2d). The **2** modified disk and MnO₂ modified ring electrode potentials are fixed at 0.65 V and 1.1 V vs. RHE respectively. With N₂ saturated 0.1 M NaOH as the mobile phase, 20 μ L of O₂ saturated 0.1 M NaOH is injected at regular intervals (pH 13). Currents measured are 0.47 μ A and 38.72 μ A at I_r and I_d, respectively. The n value is 3.58, which is in close agreement with the result obtained by the K-L method and consistent with 4-e⁻ reduction pathway of O₂.

For comparison, the K-L plot obtained for the simple CB/GCE exhibits a 2-e⁻ reduction pathway with n value of 2.56. SPRDE-FIA study also indicates substantial production of H₂O₂ (71%) with n value of 2.58 (Figure S3a). The catalyst **1** modified CB/SPCE produced 12% H₂O₂ with n value of 3.76 but lower k_s = 1.6 s⁻¹ than **2** (Table S1). Stability of the **2** modified electrode tested under constant bubbling of O₂ at 0.67 V for 24 hr, retains ~80% of the initial current (Figure S4).

Finally, the involvement of all three copper sites in the O_2 reduction process is validated by comparing the performance of electrodes modified by the Cu₃-complex with that of the Cu₂-complex. For this study, we select Dipy as the ligand to assemble the complexes, since the Cu²⁺ ions have higher affinity toward dipicolylamine than Ag^{1+,[22]} a property that we exploit to replace the Cu²⁺ in the apical position of the tricopper triad with Ag¹⁺ to prepare the Cu₂Ag(Dipy) complex. Following a previous



Figure 3. CVs of the Cu₃(7-Dipy)- and Cu₂(7-Dipy)-CB/SPCEs in the presence of O₂ in B-R buffer, pH 7, at a scan rate of 10 mV/s. *denotes electrochemically pre-treated electrodes.

study, 10 we electrochemically pretreat the $\mbox{Cu}_2\mbox{Ag}(\mbox{Dipy})$ complex on a CB/SPCEs in N₂ saturated buffer, where upon continuous cycling (40 cycles) the Ag1+ ions are removed to form the dicopper system 4 (Figure S5). We compare the 3 and 4 modified SPCEs for their activity towards ORR using B-R buffer (pH 7). The CVs of catalyst 3 and 4 modified CB/SPCEs under N₂ atmosphere are shown in Figure S6. When these SPCEs are tested in an O₂ saturated buffer, the system with the dicopper center 4 shows a less positive onset reduction potential by ~70 mV compared to 3. The 3 and 4 modified SPCEs generate 25% and 58% of H₂O₂ at pH 7, respectively. The Tafel slope obtained at 300 rpm for the 4 modified SPCE is 165 mV/decade, which is higher than that of the catalyst 3 modified SPCE (117 mV/decade) at pH 7 (Figure S7). These observations underscore the key role played by the Cu center at the apical position in the Cu triad in reducing n. Transfer of the third electron (possibly proton-coupled)^[23] to the tricopper cluster complex to cleave the O-O bond, is the rate limiting step in ORR kinetics, and presumably the binding of O2 to the complex does not limit turnover of the catalyst. As control, electrochemically pretreating catalyst 3 shows no significant change in the onset potential of this electrode (Figure 3), indicating that the electrochemical treatment does not alter the complex notably. However, the pretreatment can lead to some disproportionation of the complex without migration of the copper ions. The catalyst 3 modified SPCE has an onset reduction potential of ~0.71 V vs. RHE at pH 7 (Table S1). Experiments performed under pH 5 and 10 exhibit similar behavior albeit slight differences in the onset reduction potentials between the catalysts 3 and 4 modified SPCE, with the catalyst 3 always exhibiting a more positive onset reduction potential (Figure S8).

To summarize, the involvement of a trinuclear copper cluster in O_2 activation substantially reduces the overpotential and production of H_2O_2 . The results reveal a 4-e⁻ reduction of O_2 with the transfer of the third electron to the tricopper center as the rate-limiting step. The complex exhibits one of the lowest onset reduction potentials for any synthetic copper complex at pH 7. Improved oxygen reduction kinetics and further reduction of the overpotential are expected with an optimized ligand system.

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Keywords: alkaline oxygen reduction • copper triad • overpotential • screen printed carbon electrode • tricopper cluster complex

- C. Song, J. Zhang, Electrocatalytic Oxygen Reduction Reaction. PEM Fuel Cell Electrocatalysts and Catalyst Layers: Fundamentals and Applications; Springer: London 2008.
- [2] M. A. Thorseth, C. S. Letko, T. B. Rauchfuss, A.A. Gewirth, *Inorg. Chem.* 2011, 50, 6158-6162.
- [3] a) E. I. Solomon, P. Chen, M. Metz, S.-K. Lee, A. E. Palmer, Angew. Chem. Int. Ed. 2001, 40, 4570-4590; b) E. A. Lewis, W. B. Tolman, Chem. Rev. 2004, 104, 1047-1076; c) S.-K. Lee, S. D. George, W. E. Antholine, B. Hedman, K. O. Hodgson, E. I. Solomon, J. Am. Chem. Soc. 2002, 124, 6180-6193.
- [4] N. Mano, V. Soukharev, A. Heller, J. Phys. Chem. B 2006, 110, 11180-11187.
- [5] Y. C. Weng, F.-R. F. Fan, A. J. Bard, J. Am. Chem. Soc. 2005, 127, 17576-17577.
- [6] a) A. J. Augustine, C. Kjaergaard, M. Qayyum, L. Ziegler, D. J. Kosman, K. O. Hodgson, B. Hedman, E. I. Solomon, *J. Am. Chem. Soc.* 2010, 132, 6057-6067; b) M. A. Thorseth, C. E. Tornow, E. C. M. Tse, A. A. Gewirth, *Coord. Chem. Rev.* 2013, 257, 130-139; c) Y.-T. Xi, P.-J. Wei, R.-C. Wang, J.-G. Liu, *Chem. Commun.* 2015, 51, 7455-7458.
 d) F. He, L. Mi, F. Shen, X. Chen, Y. Yang, H. Mei, S. Liu, T. Mori, Y. Zhang, *J. Mater. Chem.* A 2017, 5, 17413-17420.
- a) C. C. L. McCrory, X. Ottenwaelder, T. D. P. Stack, C. E. D. Chidsey, J. *Phys. Chem. A* 2007, 111, 12641-12650; b) C. C. L. McCrory, A. Devadoss, X. Ottenwaelder, R. D. Lowe, T. D. P. Stack, C. E. D. Chidsey, J. Am. Chem. Soc. 2011, 133, 3696-3699.
- [8] a) L. Tahsini, H. Kotani, Y.-M. Lee, J. Cho, W. Nam, K. D. Karlin, S. Fukuzumi, *Chem. Eur. J.* **2012**, 18, 1084-1093; b) A. Gomila, N. L. Poul, J.-M. Kerbaol, N. Cosquer, S. Triki, B. Douziech, F. Conan, Y. L. Mest, *Dalton Trans.* **2013**, 42, 2238-2253; c) M. A. Thorseth, C. S. Letko, E. C. M. Tse, T. B. Rauchfuss, A. A. Gewirth, *Inorg. Chem.* **2013**, 52, 628-634.
- [9] M.S. Thorum, J. Yadav, A. A. Gewirth, Angew. Chem. Int. Ed. 2009, 48, 165-167.
- [10] Tse, E. C. M.; Schilter, D.; Gray, D. L.; Rauchfuss, T. B.; Gewirth, A. A. Inorg. Chem. 2014, 53, 8505-8516.
- [11] a) A. P. Cole, D. E. Root, P. Mukherjee, E. I. Solomon, T. D. P. Stack, Science 1996, 273, 1848-1850; b) M. Casarin, C. Corvaja, C. D. Nicola, D. Falcomer, L. Franco, M. Monari, L. Pandolfo, C. Pettinari, F. Piccinelli, *Inorg. Chem.* 2005, 44, 6265-6276; c) W. Ouellette, M. H. Yu, C. J. O. Connor, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* 2006, 45, 3497-3500; d) D. Maiti, J. S. Woertink, R. A. Ghiladi, E. I. Solomon, K. D. Karlin, *Inorg. Chem.* 2009, 48, 8342-8356; e) E. Y. Tsui, M. W. Day, T. Agapie, *Angew. Chem. Int. Ed.* 2011, 50, 1668-1672.
- [12] a) P. P.-Y. Chen, R. B.-G. Yang, J. C.-M. Lee, S. I. Chan, *PNAS* 2007, 104, 14570-14574; b) S. I. Chan, C. Y.-C. Chien, C. S.-C. Yu, P. Nagababu, S. Maji, P. P.-Y. Chen, *J. Catal.* 2012, 293, 186-194; c) S. Maji, J. C.-M. Lee, Y.-J. Lu, C.-L. Chen, M.-C. Hung, P. P.-Y. Chen, S. S.-F. Yu, S. I. Chan, *Chem. Eur. J.* 2012, 18, 3955-3968.

- [13] a) S. I. Chan, Y.-J. Lu, P. Nagababu, S. Maji, M.-C. Hung, M. M. Lee, I.-J. Hsu, P. D. Minh, J. C.-H. Lai, K. Y. Ng, S. Ramalingam, S. S.-F. Yu, M. K. Chan, *Angew. Chem. Int. Ed.* **2013**, 52, 3731-3735; b) P. P.-Y. Chen, P. Nagababu, S. S.-F. Yu, S. I. Chan, *ChemCatChem* **2014**, 6, 429-437; c) C.-C. Liu, C.-Y. Mou, S. S.-F. Yu, S. I. Chan, *Energy Environ. Sci.* **2016**, 9, 1361-1374.
- [14] a) S. I. Chan, K. H.-C. Chen, S. S.-F. Yu, C.-L C, S. S.-J. Kuo, *Biochemistry* **2004**, 43, 4421-4430. b) S. I. Chan, S. S.-F. Yu, *Acc. Chem. Res.*, **2008**, 41, 969-979.
- [15] S. Pintado, S. Goberna-Ferron, E. C. Escudero-Adan, J. R. Galan-Mascaros, J. Am. Chem. Soc., 2013, 135, 13270-13273.
- [16] E. Laviron, J. Electroanal. Chem. Interfacial Electrochem. 1979, 101, 19-28.
- [17] M. L. Pegis, B. A. McKeown, N. Kumar, K. Lang, D. J. Wasylenko, X. P. Zhang, S. Raugei, J. M. Mayer, ACS Cent. Sci. 2016, 2, 850-856.
- [18] M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, J. Am. Chem. Soc. 2013, 135, 8452-8455.
- [19] T.-H. Yang, C.-Y. Liao, J.-L. Chang, C.-H. Lien, J.-M. Zen, *Electroanalysis* 2009, 21, 2390-2394.
- [20] a) X. Ge, A. Sumboja, D. Wuu, T. An, B. Li, F. W. T. Goh, T. S. A. Hor, Y. Zong, Z. Liu, ACS Catal. 2015, 5, 4643-4667; b) N. Ramaswamy, S. Mukerjee, Adv. Phy. Chem. 2012, DOI: 10.1155/2012/491604.
- [21] F. H. B. Lima, J. Zhang, M. H. Shao, K. Sasaki, M. B. Vukmirovic, E. A. Ticianelli, R. R. Adzic, *J. Phys. Chem. C* 2007, 111, 404-410.
- [22] J. J. Zuckerman, A. P. Hagen, Inorganic Reactions and Methods, The Formation of Bonds to N, P, As, Sb, Bi; Wiley: New York, **2009**.
- [23] E. C. M. Tse, C. J. Barile, N. A. Kirchschlager, Y. Li, J. P. Gewargis, S. C. Zimmerman, A. Hosseini, A. A. Gewirth, *Nat. Mater.* 2016, 15, 754-759.

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Involvement of a synthetic copper triad in binding and reduction of O_2 is demonstrated. The presence of the third Cu ion is crucial to supplying the third reducing equivalent for O–O bond cleavage and reduces the overpotential.

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