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Electrocatalytic O_2 Reduction by Covalently Immobilized Mononuclear Copper(I) Complexes: Evidence for a Binuclear Cu_2O_2 Intermediate

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Ⓢ *Supporting Information*

ABSTRACT: A Cu^I complex of 3-ethynyl-phenanthroline covalently immobilized onto an azide-modified glassy carbon surface is an active electrocatalyst for the four-electron (4-e) reduction of O_2 to H_2O. The rate of O_2 reduction is second-order in Cu coverage at moderate overpotential, suggesting that two Cu^I species are necessary for efficient 4-e reduction of O_2. Mechanisms for O_2 reduction are proposed that are consistent with the observations for this covalently immobilized system and previously reported results for a similar physisorbed Cu^I system.

Discrete copper complexes are potential catalysts for the 4-electron (4-e) reduction of O_2 to water in ambient-temperature fuel cells, as evidenced by Cu-containing fungal laccase enzymes that rapidly reduce O_2 directly to water at a trinuclear Cu active site at remarkably positive potentials.[1−5] Several groups have studied molecular Cu complexes immobilized onto electrode surfaces as an entry into the study of 4-e O_2 reduction.[6−19] In particular, physisorbed copper(I) 1,10-phenanthroline, $Cu(phen^P)$, reduces O_2 quantitatively by four electrons and four protons to water.[8−10] Anson et al. determined that this reaction was first-order in Cu coverage, suggestive of a mononuclear Cu site as the active catalyst.[8,10]

In the present study, similar Cu^I complexes are *covalently* attached to a modified glassy carbon electrode surface to form a species denoted $Cu(phen^C)$, and the effect of Cu coverage on the kinetics of electrocatalytic O_2 reduction is investigated. At low overpotentials, we observe a second-order dependence of the O_2-reduction rate on the coverage of $Cu(phen^C)$, from which we infer that two physically proximal $Cu(phen^C)$ species bind O_2 to form a binuclear Cu_2O_2 species required for 4-e reduction. We suggest that a similar binuclear species also forms in the case of $Cu(phen^P)$[8,10] but that rate-limiting binding of O_2 to the first $Cu(phen^P)$ followed by rapid surface diffusion of the second $Cu(phen^P)$ has, until now, obscured the binuclear nature of the reaction.

The covalent attachment of 3-ethynyl-1,10-phenanthroline to an azide-modified glassy carbon electrode to form $Cu(phen^C)$ relies on the Cu^I-catalyzed cycloaddition of azide and ethynyl groups to form a triazole linker, commonly referred to as the "click" reaction.[20,21] The electrode is azide-terminated by treating a roughly ground, heat-treated glassy carbon surface with a solution of IN_3 in hexanes, a procedure modified from that first described by Devadoss and Chidsey.[22] An XPS survey of the azide-modified surface shows two N 1s peaks at 399 and 403 eV in a 2:1 ratio attributable to the azide nitrogens.[22−24] Upon exposure to 3-ethynyl-1,10-phenanthroline under the click reaction conditions,[25] the 403-eV peak disappears and the 399-eV peak broadens, consistent with the formation of the 1,2,3-triazole linker.[22,24] XPS peaks at 934 and 953 eV corresponding to the Cu $2p^{3/2}$ and $2p^{1/2}$ transitions[26] and a N-to-Cu coverage ratio of 5.3 ± 0.3 are attributable to a covalently attached Cu(3-(4-triazolyl-1,10-phenanthroline) complex, $Cu(phen^C)$.

A cyclic voltammogram (CV) of $Cu(phen^C)$ on a static glassy carbon electrode shows quasi-reversible reduction and oxidation peaks under anaerobic conditions, which are assigned to the $Cu^{II/I}$ redox couple (Figure 1a). The standard redox potential of the complex is taken as the average of the cathodic and anodic peak potentials: $E^0_{Cu} = 275 \pm 15$ mV vs NHE.[27] The Cu coverage was varied by controlling the initial azide coverage of the glassy carbon electrode,[25] and the amount of immobilized Cu catalyst was determined by Faraday's law from the $Cu^{II/I}$ redox charge, Δq. This value was taken to be the average of the absolute values of the integrated current in the negative and positive scans of the CV, corrected by the same scans after the surface was stripped of all copper.[28] For the CV presented in Figure 1a, $\Delta q = 21.8\ \mu C$, which is equivalent to a coverage of 7.0×10^{14} molecules cm^{-2}. The relatively high surface coverage is consistent with significant roughness of the roughly ground surface.[29]

O_2 reduction by $Cu(phen^C)$ was measured at a rotating-disk electrode (RDE) at several rotation rates (Figure 1b).[30] The currents show an onset of O_2 reduction negative of E^0_{Cu}. The currents are independent of the scan rate at or below 25 mV/s (not shown) but increase with increasing rotation rate as shown. In the limit of high rotation rate, the current is expected to asymptotically approach a potential-dependent kinetic current, i_K, independent of the rate of mass transfer to the electrode surface and limited only by O_2-binding and reduction kinetics. A Koutecky−Levich plot of the inverse of the current as a function of the inverse square root of the rotation rate yields the inverse of the kinetic current, i_K^{-1}, as the intercept (Figure 1b, inset).[31] The slope of the Koutecky−Levich plot is inversely proportional to the number of electrons, n, by which O_2 is reduced.[31] The measured slope in Figure 1b yields n = 3.6,[32] suggesting

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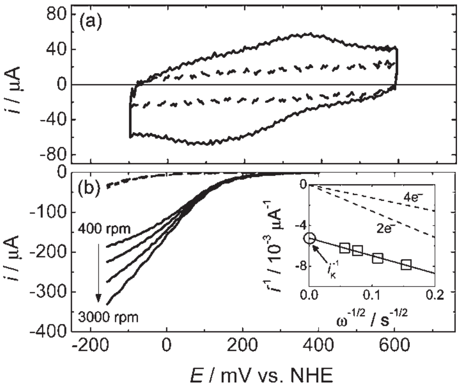

Figure 1. (a) Cyclic voltammogram of Cu(phen^C) on a static glassy carbon electrode in an Ar-purged aqueous solution (scan rate = 1000 mV/s). The dashed line is the same CV repeated after Cu was removed by exposing the surface to a Cu chelating agent for 20 min while rotating the electrode at 3000 rpm. (b) Rotating-disk voltammograms for the reduction of O_2 in an O_2-saturated aqueous solution by Cu(phen^C) (scan rate = 25 mV/s). The dashed lines are the same set of rotating-disk voltammograms repeated after Cu was removed by exposing the surface to a copper-chelating agent for 20 min while rotating the electrode at 3000 rpm. The inset is a Koutecky—Levich plot of the inverse of the disk current measured at 0 mV vs NHE as a function of the square root of the inverse of the rotation rate. The dashed lines are calculated diffusion-limited currents for the reduction of O_2 by two and four electrons. The fitted line yields n = 3.6 electrons. The intercept is the inverse of the kinetically limited current, $(i_K)^{-1}$. All solutions contained 0.05 M sodium acetate, 0.05 M acetic acid, and 1 M sodium perchlorate with measured pH = 4.8.

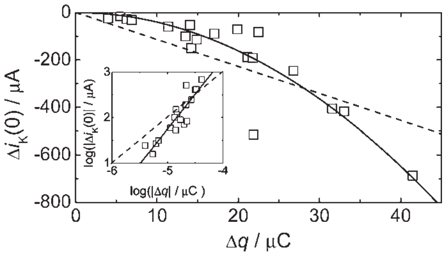

Figure 2. Difference in kinetic currents for O_2 reduction with and without Cu, Δi_K, at 0 mV vs NHE, for different Cu(phen^C) coverages as measured by the redox charge Δq. The solid line is the best fit of the form $y = ax^2$. The dashed line is the best fit of the form $y = ax$. The inset is a log/log plot of the same data. The solid line in the inset is a linear fit with slope = 1.98. The dashed line has slope = 1 for comparison.

preferential catalysis of 4-e, rather than two-electron (2-e), reduction of O_2.

The dependence of the rate of O_2 reduction on catalyst coverage was determined from the difference in the measured kinetic currents with and without Cu on the electrode surface, Δi_K. This procedure was chosen to compensate for variable redox charge and kinetic current baselines. A plot of Δi_K as a function of Δq measured at 0 mV vs NHE shows a second-order dependence (Figure 2), confirmed by a log/log plot slope of 1.98 (Figure 2, inset).[33]

This second-order dependence on coverage along with the onset of the O_2-reduction current negative of the Cu$^{II/I}$ redox potential suggests a potential-dependent rate of reduction of an O_2 species ligated by two proximal Cu^I(phen^C) sites, as presented in Figure 3 and eqs 1—3.[35] The proximal sites, {2 Cu^I},

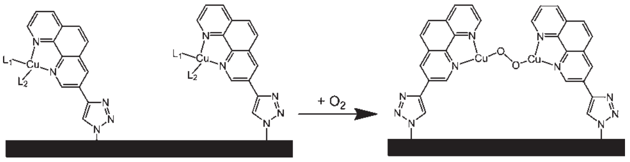

Figure 3. Proposed binding event between two proximal Cu centers and a single O_2 molecule to form a Cu_2O_2 intermediate species.[34]

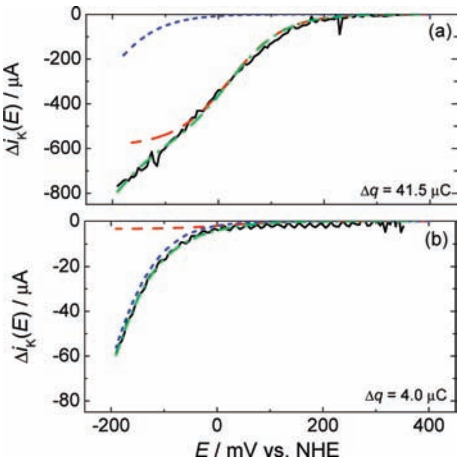

Figure 4. Difference in kinetic currents for O_2 reduction with and without Cu, Δi_K, at (a) high coverage (Δq = 41.5 μC) and (b) low coverage (Δq = 4.0 μC). The solid black line is the measured Δi_K. The dash-dotted green line is a proposed fit to the data comprised of the sum of the potential-dependent currents from two competing pathways (eq 8): a binuclear 4-e O_2-reduction pathway (red dashed) and a mononuclear 2-e O_2-reduction pathway (blue dotted).

reversibly bind O_2 to form {Cu_2O_2} (eq 1, Figure 3), followed by a potential-dependent reduction step (eq 2). Rapid protonation and further reduction regenerate the proximal Cu^I sites {2Cu^I} and release water (eq 3).[36]

$$\{2\mathrm{Cu^I}\} + \mathrm{O_2} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \{\mathrm{Cu_2O_2}\} \tag{1}$$

$$\{\mathrm{Cu_2O_2}\} + \mathrm{e^-} \xrightarrow{k_2(E)} \{\mathrm{Cu_2O_2}^-\} \tag{2}$$

$$\{\mathrm{Cu_2O_2}^-\} + 4\mathrm{H^+} + 3\mathrm{e^-} \xrightarrow{\text{fast}} \{2\mathrm{Cu^I}\} + 2\mathrm{H_2O} \tag{3}$$

The potential-dependent rate constant for the reduction of {Cu_2O_2}, $k_2(E)$, can be expanded using the Butler—Volmer parametrization (eq 4).

$$k_2(E) = k^0_{\{\mathrm{Cu_2O_2}\}} \exp\left(\frac{-\alpha F}{RT}(E - E^0_{\{\mathrm{Cu_2O_2}\}})\right) \tag{4}$$

where $k_{\{Cu_2O_2\}}^0$ is the standard rate constant of the electron-transfer reaction, F is Faraday's constant, α is the transfer coefficient typically taken to be 0.5, R is the ideal gas constant, T is the absolute temperature, and $E_{\{Cu_2O_2\}}^0$ is the standard reduction potential of {Cu_2O_2}.

At high Cu coverage, the dependence of Δi_K on potential (Figure 4a, solid) approximates the sigmoidal curve expected for an electrocatalytic process that is limited at high overpotential by a nonelectrochemical step such as that in eq 1.[31] The deviation from sigmoidal behavior at more negative potentials suggests an additional O_2-reduction pathway at greater overpotential. More striking evidence of this pathway is observed at low Cu coverage (Figure 4b, solid), with an approximately exponential rise in O_2 reduction below 0 mV vs NHE.

We propose that the second O_2-reduction pathway is due to site-isolated mononuclear Cu complexes, $\{Cu^I\}$, which reduce O_2 by two electrons and two protons to H_2O_2 at more negative potentials (eqs 5−7). This model is supported by the increased H_2O_2 production detected in rotating ring-disk voltammetry experiments at high overpotentials.[37]

$$\{Cu^I\} + O_2 \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \{CuO_2\} \tag{5}$$

$$\{CuO_2\} + e^- \xrightarrow{k_2'(E)} \{CuO_2^-\} \tag{6}$$

$$\{CuO_2^-\} + 2H^+ + e^- \xrightarrow{\text{fast}} \{Cu^I\} + H_2O_2 \tag{7}$$

$k_2'(E)$ can be expanded using the Butler−Volmer model in a similar manner as shown in eq 4. The total kinetic current for 4- and 2-e reduction of O_2 expected by the two pathways is given in eq 8.[25]

$$i_K = \frac{4FAk_1\Gamma_{\{2Cu^I\}}[O_2]k^0_{\{Cu_2O_2\}} \exp\left(\frac{-\alpha F}{RT}\left(E - E^0_{\{Cu_2O_2\}}\right)\right)}{k_{-1} + k^0_{\{Cu_2O_2\}} \exp\left(\frac{-\alpha F}{RT}\left(E - E^0_{\{Cu_2O_2\}}\right)\right)} + \frac{2FAk_1'\Gamma_{\{Cu^I\}}[O_2]k^0_{\{CuO_2\}} \exp\left(\frac{-\alpha F}{RT}\left(E - E^0_{\{CuO_2\}}\right)\right)}{k_{-1}' + k^0_{\{CuO_2\}} \exp\left(\frac{-\alpha F}{RT}\left(E - E^0_{\{CuO_2\}}\right)\right)} \tag{8}$$

This model provides a good fit to the observed kinetic currents for O_2 reduction by Cu(phen^C) at both high and low coverage (Figure 4).

The second-order dependence of O_2 reduction on the coverage of Cu(phen^C), best observed at positive potentials, is distinct from the first-order dependence on Cu coverage determined by Anson et al. for Cu(phen^P) on edge-plane graphite.[10] We have confirmed the Anson result at 0 mV vs NHE[25] and have previously reported that there is no rate-limiting step for electrocatalytic O_2 reduction by Cu(phen^P) subsequent to O_2 binding.[19,38] In the physisorbed case, the expected high surface lateral mobility of Cu(phen^P)[39] will ensure that, once one Cu(phen^P) coordinates O_2, another Cu(phen^P) will be able to combine rapidly in an unconstrained manner to form a Cu_2O_2(phen^P)$_2$ complex. This would lead to the observed first-order dependence on the Cu coverage if all reduction and protonation steps beyond the peroxide level intermediate are fast.

In conclusion, controlling the coverage of a covalently attached electrocatalyst allows for detailed mechanistic study of electrocatalytic processes. Here, this method yields evidence that the electrocatalytic 4-e reduction of O_2 to water by adsorbed discrete Cu catalysts requires two proximal Cu^I sites to coordinate and efficiently reduce O_2. A general mechanism is proposed for electrocatalytic O_2 reduction by adsorbed Cu catalysts that is consistent with both the observed second-order rate dependence on Cu coverage for covalently immobilized Cu(phen) and the observed first-order rate dependence on Cu coverage for physisorbed Cu(phen). This study suggests that having a polynuclear assembly is the key to attain 4-e reduction of O_2 at low overpotentials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental preparation of Cu(phen^C) on glassy carbon, method of Cu removal, and study of the dependence of O_2 reduction on the coverage of Cu(phen^P) on edge-plane graphite. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563–2605.

(2) Farver, O.; Pecht, I. In *Multi-Copper Oxidases*; Messerschmidt, A., Ed.; World Scientific: Singapore, 1997.

(3) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013–1046.

(4) Schweiger, H.; Vayner, E.; Anderson, A. B. *Electrochem. Solid-State Lett.* **2005**, *8*, A585–A587.

(5) Vayner, E.; Schweiger, H.; Anderson, A. B. *J. Electroanal. Chem.* **2007**, *607*, 90–100.

(6) Zhang, J.; Anson, F. C. *J. Electroanal. Chem.* **1992**, *341*, 323–341.

(7) Zagal, J. H.; Paez, C.; Aguirre, M. J.; Garcia, A. M.; Zamudio, W. *Bol. Soc. Chil. Quim.* **1993**, *38*, 191–199.

(8) Zhang, J.; Anson, F. C. *Electrochim. Acta* **1993**, *38*, 2423–2429.

(9) Zhang, J.; Anson, F. C. *J. Electroanal. Chem.* **1993**, *348*, 81–97.

(10) Lei, Y.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 5003–5009.

(11) Marques, A. L. B.; Zhang, J.; Lever, A. B. P.; Pietro, W. J. *J. Electroanal. Chem.* **1995**, *392*, 43–53.

(12) Losada, J.; del Peso, I.; Beyer, L. *Inorg. Chim. Acta* **2001**, *321*, 107–115.

(13) Dias, V. L. N.; Fernandes, E. N.; da Silva, L. M. S.; Marques, E. P.; Zhang, J.; Marques, A. L. B. *J. Power Sources* **2005**, *142*, 10–17.

(14) Weng, Y. C.; Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 17576–17577.

(15) Wang, M.; Xu, X.; Gao, J.; Jia, N.; Cheng, Y. *Russ. J. Electrochem.* **2006**, *42*, 878–881.

(16) Pichon, C.; Mialane, P.; Dolbecq, A.; Marrot, J.; Riviere, E.; Keita, B.; Nadjo, L.; Secheresse, F. *Inorg. Chem.* **2007**, *46*, 5292–5301.

(17) Hermann, A.; Silva, L. S.; Peixoto, C. R. M.; Oliveira, A. B. d.; Bordinhão, J.; Hörner, M. *Eclet. Quim.* **2008**, *33*, 43–46.

(18) Thorum, M. S.; Yadav, J.; Gewirth, A. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 165–167.

(19) McCrory, C. C. L.; Ottenwaelder, X.; Stack, T. D. P.; Chidsey, C. E. D. *J. Phys. Chem. A* **2007**, *111*, 12641–12650.

(20) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.

(21) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064.

(22) Devadoss, A.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2007**, *129*, 5370–5371.

(23) Wollman, E. W.; Kang, D.; Frisbie, C. D.; Lorkovic, I. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 4395–4404.

(24) Collman, J. P.; Devaraj, N. K.; Eberspacher, T. P. A.; Chidsey, C. E. D. *Langmuir* **2006**, *22*, 2457–2464.

(25) See Supporting Information

(26) Fuggle, J. C.; Martensson, N. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 275–281.

(27) This redox potential is ca. 250 mV positive of that reported for Cu(phen^{P}) on edge-plane graphite electrodes under similar solution conditions.[19] Although the addition of the electron-withdrawing triazole partially accounts for this potential shift, other factors are likely operative. We suspect secondary ligation by a surface-bonded species such as surface oxides may contribute to this shift. Unfortunately, 1:1 Cu-to-phen complexes are not isolable in aqueous solutions, precluding a direct comparison of the redox potentials of discrete homogeneous and heterogenized species.

(28) Cu was removed with 1 M sodium diethyldithiocarbamate in MeOH.[25]

(29) Similar coverages were determined for covalently immobilized ethynylferrocene on identically prepared glassy carbon electrodes[37] and edge-plane graphite surfaces.[22]

(30) Rotating the electrode sweeps dissolved O_2 past the disk at a fixed rate, providing for steady-state O_2 reduction.

(31) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, 2001; pp 332−357.

(32) For this determination, $D_{O_2} = 1.8 \times 10^{-5}$ cm^2 s^{-1} is the diffusion constant of O_2 in aqueous solutions (Chang, P.; Wilke, C. R. *J. Phys. Chem.* **1955**, *59*, 592–600.), $[O_2] = 1.1$ mM is the concentration of O_2 in O_2-saturated 1 M $NaClO_4$ solutions (Battion, R.; Rettich, T. R.; Tominga, T. *J. Phys. Chem. Ref. Data* **1983**, *12*, 163–178.), and $\nu = 0.009$ cm^2 s^{-1} is the kinematic viscosity of the solution.[31]

(33) These measurements were made at 0 mV vs NHE because it is the most positive potential at which a significant kinetic current exists due to O_2 reduction at all coverages.

(34) Although these electrochemical experiments give no information about the nature of the intermediate Cu_2O_2 species, reactions of other mononuclear Cu^{I} complexes with O_2 in solution tend to yield side-on or *trans*-1,2-peroxodicopper(II) complexes.[3] We will depict the structure of the proposed Cu_2O_2 intermediate with the sterically more-permissive *trans*-1,2-bonded dioxygen moiety.

(35) For immobilized Cu sites, second-order dependence suggests that 4-e O_2 reduction requires two Cu sites in sufficiently close proximity to both coordinate O_2. The number of Cu sites with another proximate Cu site is proportional to the product of the total Cu coverage and the fractional occupancy of sites.

(36) No dependence of the kinetic current on buffer concentration or pH is observed at 0 mV vs NHE.[25] This is evidence that the protonation steps are fast compared to the potential-dependent reduction steps. We arbitrarily assign the slow electron-transfer step to the first reduction of $\{Cu_2O_2\}$, but it could be a later reduction step.

(37) McCrory, C. C. L.; Devadoss, A.; Ottenwaelder, X.; Nakazawa, J.; Pearson, D. M.; Pellow, M. A.; Lowe, R. D.; Smith, B. J.; Williams, V. O.; Waymouth, R. M.; Stack, T. D. P.; Chidsey, C. E. D. Unpublished results.

(38) Lei and Anson determined O_2 binding to be the rate-limiting step for Cu(phen^{P}) on edge-plane graphite surfaces at high overpotentials.[10] O_2 reduction by Cu complexes of other substituted 1,10-phenanthroline ligands exhibit first-order behavior in Cu coverage at high overpotential as well,[19] but the order with respect to Cu has not been investigated at 0 mV vs NHE. Some data suggest that O_2 binding may not be rate-limiting at low overpotentials for more easily reduced Cu complexes with substituted 1,10-phenanthroline ligands.[19]

(39) For example, the translational diffusion coefficients of benzene and hexane on basal-plane graphite surfaces are $(1.99 \pm 0.06) \times 10^{-5}$ and $(3.69 \pm 0.11) \times 10^{-5}$ cm^2 s^{-1}, respectively (Fodi, B.; Hentschke, R. *Langmuir* **1998**, *14*, 429–437.), and the translational diffusion coefficients of anthracene and pyrene on small graphitic grains are 3.05×10^{-4} and 1.0×10^{-4} cm^2 s^{-1}, respectively (Neue, G. *Lecture Notes Phys.* **1989**, *331*, 378–380.). Even at a very low coverage of 1×10^{12} molecules cm^{-2} ($\Delta q = 1.95 \times 10^{-8}$ C, 2 orders of magnitude lower than the lowest coverage reported in this study), the average distance between a given Cu(phen) and its closest neighbor is only 1×10^{-6} cm. Assuming a translational diffusion constant of 2×10^{-5} cm^2 s^{-1}, the complexes would migrate together on the time scale of 3×10^{-8} s, which is 8 orders of magnitude faster than the measured time scale of a complete O_2-reduction event.[10,19]