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For

Electrochemical reduction of dioxygen by copper complexes with pyridylalkylamine ligands dissolved in aqueous buffer solution: relationship between activity and redox potential

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Experimental

Materials

All chemicals used in this study, except the ligands and Cu^{II}-complexes, were commercial products, and were used without further purification. A 0.01 M Britton-Robinson buffer solution (pH 7.0) was prepared by combining CH₃COOH, H₃PO₄, and H₃BO₃ with 0.01 M Na₂SO₄ as a supporting electrolyte. Vulcan XC 72R was obtained from Cabot Co. Nafion was purchased from Sigma-Aldrich. All solutions used in electrochemical measurements were prepared with ultrapure water. Stock solutions of the Cu^{II}-complexes (0.03 M) were prepared in acetonitrile.

Synthesis of ligands

The ligands used in this study, tris(2-pyridylmethyl)amine (tmpa),¹ bis(2-pyridylmethyl)amine (bmpa)² and tris[2-(2-pyridyl)ethyl]amine (tepa),²⁻⁴ were prepared according to the reported methods and purified according to common procedures.

Synthesis of Cu^{II}-complexes

The Cu^{II}-complexes were also synthesised according to the reported procedures and their purity was confirmed by elemental analysis as follows.

 $[Cu^{II}(tmpa)(CH_3CN)](CIO_4)_2$ ($Cu^{II}-tmpa$):⁵ The tmpa ligand (29 mg, 0.1 mmol) was treated with $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ (37 mg, 0.1 mmol) in a minimal amount of acetonitrile (ca. 1 mL) at room temperature. The addition of Et₂O (10 mL) to the mixture gave a light blue solid material that was isolated by decantation and washed three times with Et₂O. This solution was recrystallised by vapor diffusion of Et₂O. ESI-MS (positive ion): m/z 451.9 [M⁺]; elemental analysis for [$Cu^{II}(tmpa)(CH_3CN)$](ClO_4)₂, calcd (%) for C₂₀H₂₁O₈N₅CuCl₂ : C 40.44, H 3.57, N 11.79; found: C 40.34, H 3.51, N 11.74.

 $[Cu^{II}(bmpa)(CH_3CN)_2](ClO_4)_2$ (Cu^{II} -bmpa):⁶ This compound was synthesised by the same procedure as described above (Cu^{II} -tmpa), except that the bmpa ligand was used instead of the tmpa ligand. ESI-MS (positive ion): m/z 451.0 [M⁺]; elemental analysis for [$Cu^{II}(bmpa)(CH_3CN)_2$](ClO_4)₂, calcd (%) for $C_{23}H_{25}O_8N_5CuCl_2$: C 43.57, H 3.98, N 11.05; found: C 43.37, H 3.94, N 10.89.

[Cu^{II}(tepa)(ClO₄)]ClO₄ (Cu^{II}-tepa):⁷ The tepa ligand (332.5 mg, 1.0 mmol) was

treated with Cu^{II}(ClO₄)₂·6H₂O (371 mg, 1.0 mmol) in acetonitrile (10 mL) for 30 min at room temperature. The addition of Et₂O (200 mL) to the mixture gave a blue oily material that was isolated by decantation and redissolved in methanol (10 mL). Addition of the methanol solution to Et₂O (200 mL) gave a blue solid that was isolated by decantation, and washed three times with Et₂O. This complex was recrystallised by the vapor diffusion of Et₂O into a methanol solution of the complex. ESI-MS (positive ion): m/z 494.0 [M⁺]; elemental analysis for [Cu^{II}(tepa)(ClO₄)](ClO₄), calcd (%) for C₂₁H₂₄O₈N₄CuCl₂ : C 42.39, H 4.07, N 9.42; found: C 42.52, H 4.03, N 9.35.

Caution! The perchlorate salts in this study are all potentially explosive and should be handled with care.

Preparation of Cu^{II}-complex-modified electrode

A Cu^{II}-complex-modified electrode was prepared as follows. Five milligrams of Vulcan XC 72R and 20 μ L of a 5 wt % solution of Nafion was mixed with 1.0 mL of mixed solvent (water : ethanol = 1:1). The suspension was homogenised by an ultrasonic generator for 1 minute to generate carbon slurry. A drop of the slurry (6.28 μ L) was applied to the surface of a GC disk electrode (BAS, geometric area = 0.1256 cm²) and dried in a drying oven at 50 °C for 3 min. A drop of the 0.03 M stock solution of a Cu^{II}-complex (6.28 μ L) was then applied to the carbon-modified GC electrode and dried at 50 °C for 1 min.

The Cu^{II}-complex-modified Vulcan XC 72R electrode was rinsed with ultrapure water and used for rotating disk electrode (RDE) or rotating ring disk electrode (RRDE) measurements.

Electrochemical measurements

The electrochemical properties and electrocatalytic activities of the Cu^{II}-complexes were investigated by cyclic voltammetry (CV) on an ALS electrochemical analyser (Model 700B).

CVs under quiescent conditions were measured as follows. Three mL of the buffer containing 30 μ L of the stock solution was added to an electrochemical cell. Before CV measurements, the solution was saturated with argon or oxygen for 15 min with stirring. During the measurements, the gases were passed above the solution so as not to disturb the mass transfer of the Cu^{II}-complexes by bubbling. CVs were measured in the 0.01 M buffer solution by a three-electrode system. A bare or modified glassy carbon (GC) electrode (BAS, geometric area = 0.07065 cm²) was used as a working electrode.

Ag|AgCl|KCl(sat.) was used as a reference electrode. A platinum coil was used as a counter electrode. All experiments were carried out at 25 ± 1 °C.

For hydrodynamic voltammetry, a rotating disk electrode (RDE) or rotating ring disk electrode (RRDE) was used as the modified working electrode (see the foregoing section). An ALS electrochemical analyser (Model 700B) equipped with a rotation controller (BAS, RRDE-3A) was used. The other conditions were the same as those in the quiescent measurements.

The ratio of generated H_2O_2 (X_{H2O2}) can be evaluated as follow:⁸

$$X_{H_2O_2} = \frac{2I_R/N}{I_D + I_R/N}$$

where $I_{\rm R}$, $I_{\rm D}$, and N represents ring current, disk current, and collection efficiency, respectively. N is defined as follow:

$$N = -\frac{I_R}{I_D}$$

N was evaluated as 0.43, where I_D and I_R are reduction/reoxidation currents of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ at 1600 rpm.



Fig. S1 (A) Cyclic voltammograms of Cu^{II}-tmpa at various scan rates: 0.005, 0.01, 0.02, 0.05, and 0.1 ($v / V s^{-1}$). Experimental conditions were the same as in Fig. 1, except for the scan rates. **(B)** Plots of the anodic (closed circle) and cathodic (open circle) peak currents (I) vs. square roots of the scan rates ($v^{1/2}$). Solid lines represent a linear approximation. **(C)** Plots of the peak potential separation (ΔE_p) vs. scan rate (v).



Fig. S2 (A) Cyclic voltammograms of Cu^{II}-bmpa at various scan rates: 0.005, 0.01, 0.02, 0.05, and 0.1 ($v / V s^{-1}$). Experimental conditions were the same as in Fig. 1, except for the scan rates. **(B)** Plots of the anodic (closed circle) and cathodic (open circle) peak currents (I) vs. square roots of the scan rates ($v^{1/2}$). Solid lines represent a linear approximation. **(C)** Plots of the peak potential separation (ΔE_p) vs. scan rate (v).



Fig. S3 (A) Cyclic voltammograms of Cu^{II}-tepa at various scan rates: 0.005, 0.01, 0.02, 0.05, and 0.1 ($v / V s^{-1}$). Experimental conditions were the same as in Fig. 1, except for the scan rates. **(B)** Plots of the anodic (closed circle) and cathodic (open circle) peak currents (I) vs. square roots of the scan rates ($v^{1/2}$). Solid lines represent a linear approximation. **(C)** Plots of the peak potential separation (ΔE_p) vs. scan rate (v).



Fig. S4 (A) Cyclic voltammograms of Cu^{II}-tmpa-adsorbed Vulcan XC 72R at various scan rates: 0.01, 0.02, 0.05, 0.1, and 0.2 ($v / V s^{-1}$) in 10 mM Britton-Robinson buffer containing 10 mM Na₂SO₄ (pH 7.0, 25 °C) under argon-saturated conditions. **(B)** Plots of the anodic (closed circle) and cathodic (open circle) peak currents (*I*) vs. scan rate (v). Solid line represents a linear approximation. **(C)** Plots of the peak potential separation (ΔE_p) vs. scan rate (v).



Fig. S5 RRDE voltammograms of Cu^{II}-tmpa-adsorbed Vulcan XC 72R (blue lines) and Vulcan alone (black lines). Lines (a) and (b) show disk currents of Cu^{II}-tmpa-adsorbed Vulcan XC 72R and Vulcan XC 72R, respectively. Lines (a') and (b') indicate the corresponding ring currents. The voltammograms were recorded in 10 mM Britton-Robinson buffer containing 10 mM Na₂SO₄ (pH 7.0, 25 °C) under O₂-saturated conditions. The rate of electrode rotation was fixed at 1600 rpm. All data were obtained at a scan rate of 10 mV s⁻¹.



Fig. S6 RDE voltammograms of Cu^{II}-tmpa-adsorbed Vulcan XC 72R and Koutecky-Levich analysis at -0.6 V. CVs were recorded at electrode-rotation rates of (a) 100 rpm (top curve), (b) 200, (c) 400, (d) 800 and (e) 1600 rpm (bottom curve). The inset shows a plot of reciprocals of disk current (I^{-1}) as a function of reciprocals of the square root of the angular velocity ($\omega^{-1/2}$) (ω defined as $2\pi \times$ rotation rate (r.p.s.)) (Koutecky-Levich plot). The straight dashed line in the inset shows a theoretical Koutecky-Levich plot for a two- or fourelectron transfer process with the following parameters: Faraday constant 96500 C mol⁻¹, O₂ concentration 1.2 mM, diffusion coefficient of O₂ 1.7 × 10⁻⁵ cm² s⁻¹ and kinematic viscosity of water 0.01 cm² s^{-1.9} All data were obtained at a scan rate of 10 mV s⁻¹.



Fig. S7 Electrocatalytic peroxide reduction by pyridylalkylamine Cu^{II} complexes. Lines (a-c) show voltammograms of (a) Cu^{II} -tmpa, (b) Cu^{II} bmpa, and (c) Cu^{II} -tepa under Ar-saturated conditions. The black dotted line shows the background current of GC. The concentration of hydrogen peroxide is 1.2×10^{-3} M. The other conditions are the same as those in Fig. 1.

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