Electronic Supplementary Information

Four-Electron Reduction of Dioxygen Catalysed by Dinuclear Cobalt Complexes Bridged by Bis(terpyridyl)anthracene

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General Experimental Details

The synthesis of 1,8-bis(2,2′:6′,2″-terpyrid-4′-ly)anthracene (btpyan) was carried out according to literature procedures.[1] Dicobalt complexes **1** and **2** were synthesised by using commercial-grade reagents and solvents without any further purification. CSI TOF-MS spectra were recorded on a JEOL JMS-T100LP AccuTOF. ^{1}H-NMR spectra were recorded on a JEOL JMN ECA300. Raman spectra were recorded on a JASCO NRS-5100 with a Nd:YVO$_4$ laser (λ = 532 nm, 100 mW). The chemical reduction of dioxygen with Fc was observed with an UNISOKU RSP-1000 rapid scan-stopped flow spectrometer. Cyclic voltammograms were recorded on an ALS electrochemical analyser model 7200. Linear-sweep voltammograms were measured on the electrochemical analyser with a BAS RRDE-3A rotating ring-disk electrode.

Synthesis Procedures

[Co$_2$(μ-O$_2$)(phen)$_2$(btpyan)](PF$_6$)$_4$·5H$_2$O (1·5H$_2$O)

To an ethanol suspension (70 mL) of btpyan (51 mg, 80 μmol) was added the distilled-water solution (10 mL) of CoSO$_4$·7H$_2$O (45 mg, 160 μmol). After the solution was refluxed for 18 h, 9,10-phenanthroline·H$_2$O (phen·H$_2$O, 36 mg, 180 mmol) was added to the solution. The solution was refluxed with bubbling of Air for further 24 h. Addition of saturated water solution (10 mL) of NH$_4$PF$_6$ was added to the resulting reddish brown solution, leading to the precipitation of a brown powder. The crude product was purified by the slow diffusion of ether in a CH$_3$CN solution. (yield: 121 mg, 87%). CSI–TOF–MS(in CH$_3$CN): *m/z* 288 (M^{4+} + 2H^{+}). UV–vis spectrum: $\lambda_{\max}$ (CH$_3$CN)/nm (ε /dm^3 mol^{-1} cm^{-1}) 273 (9.36 × 10^4) and 252 (1.34 × 10^5). ^{1}H NMR (300 MHz, Acetone-d$_6$, 233 K, under O$_2$): δ 9.75 (d, J = 6.2 Hz, 2H, bpy), 9.14 (dd, *J* = 8.5 Hz, 2H, bpy), 9.04 (s, 1H, anthracene), 8.98 (d, *J* = 8.9 Hz, 2H, bpy), 8.91 (s, 4H, trpy), 8.82 (d, *J* = 8.1 Hz, 2H, bpy), 8.64 (dd, *J* = 8.8 Hz, 2H, bpy), 8.61 (dd, *J* = 6.2 Hz, 2H, bpy), 8.53 (d, *J* = 7.2 Hz, 2H, bpy), 8.44 (d, *J* = 7.9 Hz, 4H, trpy), 8.23 (dd, *J* = 7.5 Hz, 2H, bpy), 8.13 (dd, *J* = 8.0 Hz, 4H, trpy), 7.91 (d, *J* = 4.1 Hz, 2H, anthracene), 7.68 (d, *J* = 5.2 Hz, 4H, trpy), 7.63 (s, 1H, anthracene), 7.51-7.46 (m, 8H, anthracene, anthracene, trpy). Elemental analysis: Found: C, 44.78; H, 3.03; N, 7.42. Calc. for C$_{68}$H$_{54}$N$_{10}$F$_{24}$O$_7$P$_4$Co$_2$: C, 44.85; H, 2.99; N, 7.69%.

[Co$_2$(μ-O$_2$)(bpy)$_2$(btpyan)](PF$_6$)$_4$·5H$_2$O (2·5H$_2$O)

This complex was prepared using a procedure analogous to that described previously for **1.** Yield of **2**: 64 mg, 45%. CSI–TOF–MS(in CH$_3$CN): *m/z* 276 (M^{4+} + 2H^{+}). UV–vis spctrum: $\lambda_{\max}$ (CH$_3$CN)/nm (ε /dm^3 mol^{-1} cm^{-1}) 277 (5.47 × 104) and 252 (1.19 × 10^5). ^{1}H NMR (400 MHz, Acetone-d$_6$, 233 K, under O$_2$): δ 9.58 (m, J = 8.4 Hz, 2H, phen), 9.20-9.17 (m, 5H, phen, phen, anthracene), 9.02 (s, 4H, trpy), 8.80

(d, *J* = 7.9 Hz, 4H, trpy), 8.69 (d, *J* = 3.6 Hz, 2H, phen), 8.66 (d, *J* = 3.2 Hz, 2H, phen), 8.62 (dd, *J* = 7.1 Hz, 4H, trpy), 8.58 (d, *J* = 3.6 Hz, 2H, phen), 8.41 (d, *J* = 8.9 Hz, 2H, phen), 8.17 (dd, *J* = 7.5 Hz, 4H, trpy), 7.98-7.91 (m, 5H, anthracene, anthracene, phen), 7.70 (dd, *J* = 6.8 Hz, 2H, anthracene), 7.91 (d, *J* = 4.1 Hz, 2H, anthracene), 7.68 (d, *J* = 5.2 Hz, 4H, trpy), 7.63 (s, 1H, anthracene), 7.44 (d, *J* = 5.8 Hz, 2H, anthracene), 7.28 (d, *J* = 6.6 Hz, 4H, trpy). Elemental analysis: Found: C, 43.24; H, 2.81; N, 7.76. Calc. for $C_{64}H_{54}N_{10}F_{24}O_7P_4Co_2$: C, 43.36; H, 3.07; N, 7.90%.

Raman Spectra

The Raman spectra of CH_3CN solution of the complexes (5 mM) in test tubes with silicon caps were measured with irradiation at 532 nm. The Raman measurement of the $^{18}O_2$ substituted forms of the complexes was conducted after bubbling a stream of $^{18}O_2$ into the solution for ca. 5 min using a needle tube through the silicon cap. Then, the stirring of the solution for ca.10 min in the air resulted in the same spectrum as that obtained for solution prior to $^{18}O_2$ gas bubbling. Figure 1 and S1 display the Raman spectra of complex **1** and **2** before and after $^{18}O_2$ passing, respectively.

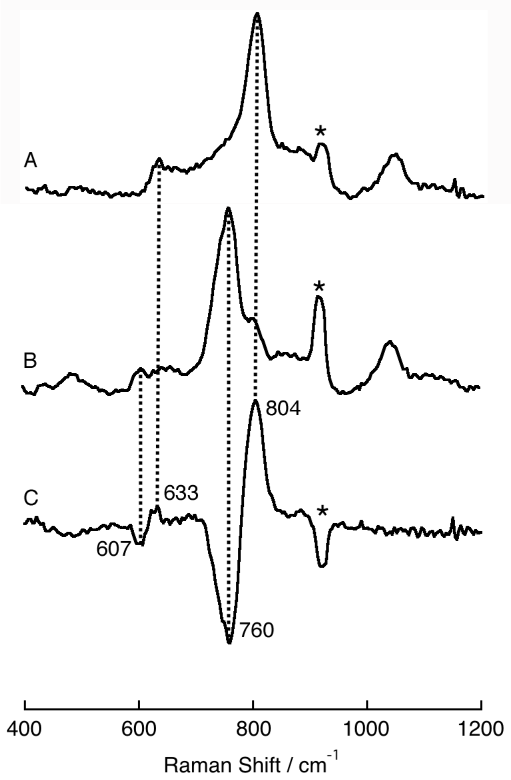

Fig. S1 Raman spectra of **2** in CH_3CN in the air (A) and after bubbling of $^{18}O_2$ through the solution (B), and their difference spectrum (C). Asterisks are Raman bands of CH_3CN.

Chemical Reduction of Dioxygen

The chemical reduction of dioxygen catalysed by the dicobalt complexes with ferrocene (Fc) was performed according to the literature procedures.[2] An air-saturated (1.7×10^{-3} M) PhCN solution containing $HClO_4$ (2.0×10^{-2} M) and Fc (2.0×10^{-1} M) was mixed with an air-saturated PhCN solution of $HClO_4$ (2.0×10^{-2} M) and the catalyst (4.0×10^{-5} M) at 295 K. The appearance of the absorption band due to ferricenium ions (Fc^+, λ_{max} = 620 nm, ε_{max} = 330 dm^3 mol^{-1} cm^{-1}) was monitored using a stopped-flow spectrophotometer. Spectral changes of reaction solutions of dioxygen reduction catalyzed by **1** and **2** as a catalyst are depicted in Figure 2S and 3S, respectively. Time profiles of formation of Fc^+ monitored at 620 nm are showed in Figure 2.

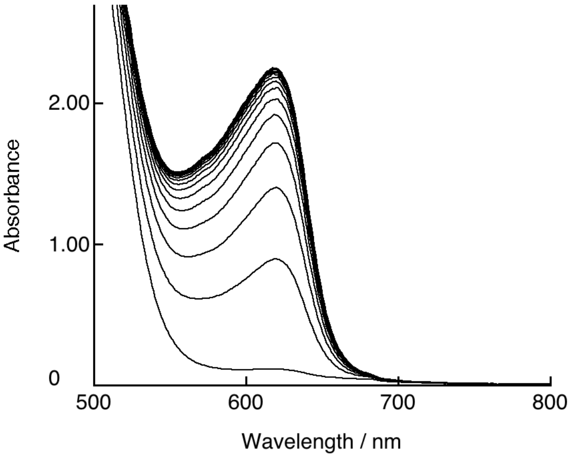

Fig. S2 Spectral change of the reaction solution of dioxygen reduction catalyzed by **1**.

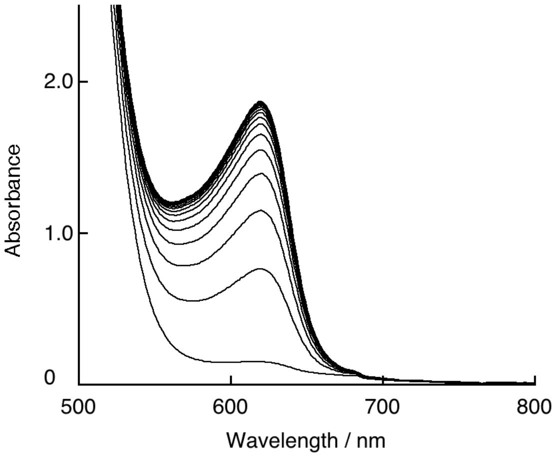

Fig. S3 Spectral change of the reaction solution of dioxygen reduction catalyzed by **2**.

Electrochemistry

Cyclic Voltammograms were measured in a PhCN solution of the complex (0.5 mM) containing 0.1 M of *n*Bu_4ClO_4 as an electrolyte at a scan rate of 50 mVs^{-1} at 298 K with a glassy carbon disk as the working electrode, a Pt wire as the counter electrode, and Ag/$AgNO_3$ as the reference electrodes. All the potentials were corrected against SCE ($E_{SCE} = E_{Ag/AgNO3}$ + 0.33 V). The solution was acidified via the addition of CH_3COOH (10 mM).

The cyclic voltammograms of complex **2** (Figure S4) under Ar shows three quasi-reversible redox waves at +0.14, +0.32, +0.50 and +0.61 V (vs. SEC). The +0.32 and +0.14 V waves are assignable to the redox reactions of $[Co(III), Co(III)]^{4+}/[Co(III), Co(II)]^{3+}$, and $[Co(III), Co(II)]^{3+}/[Co(II), Co(II)]^{2+}$, respectively, on the basis of the rest potentials of the complex at +0.42 V. The redox couples at +0.50 and +0.61 V probably result from O_2^{-}/O_2^{2-} and Co(III)/Co(IV). The CVs of **2** in PhCN acidified with $HClO_4$ (10 mM) under Ar (B) and in the air (C) are depicted in Figure S4. Furthermore, CVs of PhCN containing *n*Bu_4ClO_4 (0.10 M) and $HClO_4$ (10 mM) under Ar and in the air are showed in Figure S5 as the blank tests.

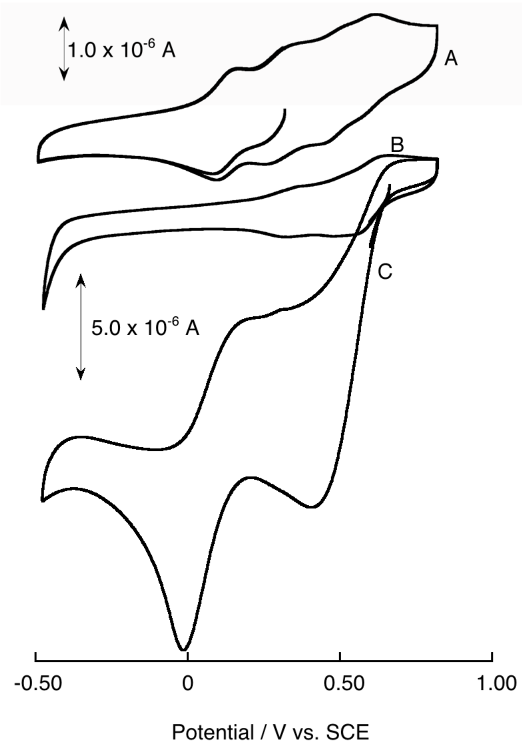

Fig. S4 Cyclic voltammograms of PhCN solutions of **2** (0.5 mM) containing of *n*Bu_4ClO_4 (0.10 M) under Ar (A) and $HClO_4$ (10 mM) under Ar (B), and in the Air (C). A is an enlarged compared with B and C.

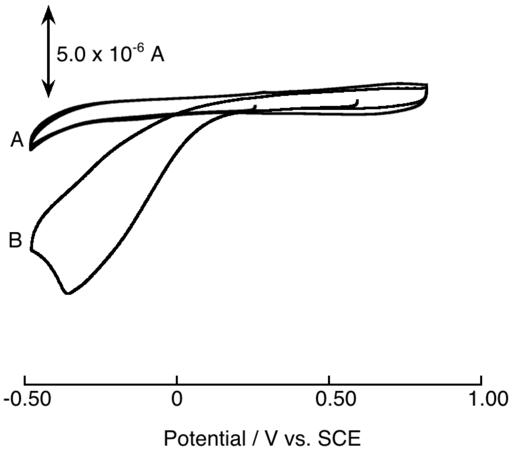

Fig. S5 CVs of PhCN containing $n\mathrm{Bu_4NClO_4}$ (0.10 M) and $HClO_4$ (10 mM) under Ar (A) and in the air (B).

Linear Sweep Voltammetry using a Rotating Ring-Disk Electrode (RRED)

A commercial rotating graphite disk-platinum ring electrode (BAS) with a glassy carbon disk (GC) and a platinum ring (diameter of the GC disk: 4 mm, Pt ring: 7 mm (outside) / 5 mm (inside)) was polished with 0.3 μm alumina on a microcloth. The collection efficiency of the RRDE employed was 0.34 at 1000 rpm, as established by measurements with an $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ couple. An acetone solution (20 µl) of of the complex (0.5 mM) was dropped on the dried GC disk using a microsyringe, and the complex-modified electrode was dried at room temperature. Linear sweep voltammetric experiments were performed in a one compartment cell containing of the RRDE modified with the complex, a Pt wire as the counter electrode, and an SCE reference electrode. An H_3PO_4/NaH_2PO_3 buffer solution (0.1 M) was used as the solvent and pH was adjusted to 1.0 via the addition of $HClO_4$.

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References

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2. S. Fukuzumi, K. Okamoto, C. P. Gros and R. Guilard, *J. Am. Chem. Soc.* 2004, **126**, 10441-10449.