Homogenous electrochemical water oxidation by a nickel(II) complex based on a macrocyclic N-heterocyclic carbene/pyridine hybrid ligand

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Electronic Supplementary Information

Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2019

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Caution! Dibromomethane is skin sensitive flammable liquid, while the 2-(Chloromethyl)pyridine hydrochloride is harmful by ingestion, inhalation and skin absorption. It should be handled carefully during chemical reaction.

UV–Vis absorption spectra. The cells for UV–vis spectrometer (Shimadzu UV–1800) were cleaned by acetone, ethanol and ultrapure water, respectively.

3 Electrodes. Prior to experiments, the GC electrode (0.07 cm²) was polished with 0.3, 0.1 and 0.05 µm Al₂O₃ slurry for 60 s each to obtain a mirror surface, followed by sonication in distilled water for ~60 seconds to remove debris, and was thoroughly rinsed with ultrapure water (Millipore MilliQ® A10 gradient, 18.25 MΩ cm, 2–4 ppb total organic content). The platinum counter electrode was flame annealed and washed with ultrapure water before placing it into the cell. Calomel electrode (3.50 M KCl, 0.25 V vs. NHE) was washed by ultrapure water before every measurement.

ITO electrode. Prior to the experiments, the ITO (0.8 cm², 6–7 Ω resistivity) slides were cleaned by sonication in acetone, ethanol and ultrapure water for ~10 min, respectively.

Cyclic voltammetry (CV). CV measurements were conducted under an air atmosphere without deaeration. All experiments were performed at room temperature (25 °C).

Controlled potential electrolysis (CPE). Long-term CPE (11 h) made in water was performed in a three-compartment electrochemical cell except for the measurement of Faradaic efficiency. An ITO was used as the working electrode for electrolysis conducted in aqueous media. The auxiliary electrode was a Pt wire and the reference electrode was a calomel electrode. The sample was bubbled with Ar for 20 min before measurement and the CPE experiment was carried out under Ar (purity 99.999%) with constantly stirring.

Determination of Faradaic Efficiency. Bulk electrolysis was performed in an air-tight electrochemical cell containing 1.0 mM 2 in 0.1 M NaPi buffer (pH = 9.0, 20 mL) at an applied potential of 1.50 V vs. NHE for 2 h with an ITO electrode under Ar atmosphere. The cell was sealed with a parafilm and deaerated for 30 min with Ar. The O₂ content in the headspace of the cell was determined by gas chromatogram with thermal-conductivity detector (GC-TCD) during the electrolysis at 20 min interval and the background O₂ from cell leakage was deducted from the total content of O₂. Faradaic efficiency (FE) was determined (93%, Fig. S15) by comparing the detected oxygen (DO) amount by GC-TCD with the theoretical oxygen (TO) amount calculated from the total consumed charge during electrolysis (FE = DO/TO × 100%).
Synthetic procedures of a tetradeinate NHC/pyridine hybrid ligand (1) and its corresponding nickel complex (2):

Scheme S1. Synthetic procedure to a tetradeinate NHC/pyridine hybrid ligand, [H₂L](PF₆)₂ (1). i) 1H–imidazole, KOH, THF, reflux; ii) CH₂Br₂, reflux; iii) NH₄PF₆ as reaction steps.

Scheme S2. Synthetic procedure to Ni(II) complex based on a tetradeinate NHC/pyridine hybrid ligand, [NiL](PF₆)₂ (2) with the help of previously reported procedures with little modification.
Figure S1. $^1$H‒NMR spectrum of a tetradebate NHC/pyridine hybrid ligand (1) in DMSO–$d_6$.

Figure S2. $^{13}$C‒NMR spectrum of a tetradebate NHC/pyridine hybrid ligand (1) in DMSO–$d_6$. 
Figure S3. $^1$H–NMR spectrum of complex 2 in DMSO–$d_6$.

Figure S4. $^{13}$C–NMR spectrum of complex 2 in DMSO–$d_6$. 
**Figure S5.** H–H COSY NMR spectrum of complex 2 in DMSO–d$_6$.

**Figure S6.** FTIR spectrum of complex 2 ranging from 400 to 4000 cm$^{-1}$ at 25 °C.
Figure S7. Experimental ESI‒MS of complex 2 in positive mode with acetonitrile as a solvent (calcd: m/z^{2+} = 194.05; [M–2PF_6^{2–}]^{2+}).

Figure S8. UV–vis spectra of a tetradeutate NHC-type ligand 1, complex 2 and Ni^{2+} salt in acetonitrile and 0.1 M aqueous buffer solutions (NaOAc and NaPi) at pHs 7.0 and 9.0.
Figure S9. CVs of 1.0 mM 2 in 0.1 M aqueous buffers (NaOAc and NaPi) at pH 7.0 with a GC (0.07 cm²) as working electrode at a scan rate 100 mV/s. Background at pH 7.0 NaPi (black; dotted) is shown for comparison.

Figure S10. LSVs (a) and DPVs (b) of 1.0 mM 2 in 0.1 M aqueous buffers (NaOAc and NaPi) at pHs 7.0 and 9.0 with a GC electrode (0.07 cm²) as working electrode. Background at pH 7.0 NaPi (black; dotted) is shown for comparison.
Figure S11. DPV traces in the pH range $4.0 < \text{pH} < 11.0$ of $2$ (1.0 mM) in 0.1 M NaPi buffers at scan rate, 100 mV/s for the construction of Pourbaix diagram.

Figure S12. CVs of different concentrations of $2$ (0 \sim 2.0 \text{ mM}) in 0.1 M NaPi buffers at pHs 7.0 (a) and 9.0 (b). Electrode, GC (0.07 cm$^2$); scan rate, 100 mV/s.$^7$
Figure S13. CVs with 1.0 mM 2 in 0.1 M NaPi buffers at pHs 7.0 (a) and 9.0 (b) with GC electrode (0.07 cm²) at different scan rates of 10, 25, 50, 100, and 150 mV/s.\(^7\)

Figure S14. (a) CVs of 1.0 mM 2 with different concentrations of NaPi buffer ([NaPi] = 0~1.0 M; pH was kept constant at 9.0). (b) Current densities for 1.0 mM 2 with respect to [NaPi] at same condition for representing the linear relationship of current densities and [NaPi] at least up to 0.1 M.\(^8\)
Figure 15. (a) Catalytic current obtained over 2 h in CPE without (blank) and with 2 (1.0 mM) by an ITO (0.8 cm², 6–7 Ω resistivity) electrode at 1.50 V vs. NHE in 0.1 M NaPi buffer (pH = 9.0). (b) Faradaic efficiency of O₂ evolution for 2 over 2 h of bulk electrolysis at same condition in air-tight cell. The red lines represent the amount of detected O₂ quantified by GC-TCD analysis of the gas phase of the system, and the blue lines show the amount of O₂ expected for a 100% Faraday efficiency according to the passed charge during CPE experiment.²,³

Figure S16. UV–vis spectra of complex 2 in acetonitrile as a solvent over 72 h.
Figure S17. Time–dependent UV–vis absorption spectra of 1.0 mM 2 over 72 h and after long–term CPE (11 h) in 0.1 M buffer of the type NaOAc (a) and NaPi (b) at pH 7.0.\textsuperscript{9,10}

Figure S18. Time–dependent UV–vis absorption spectra of 1.0 mM 2 over 72 h and after long–term CPE (11 h) in 0.1 M buffer of the type NaOAc (a) and NaPi (b) at pH 9.0.\textsuperscript{9,10}
Figure S19. ESI–MS of 1.0 mM 2 in aqueous 0.1 M NaPi buffer (pH 7.0) for before (a) and after long–term CPE (b). Calcd. $m/z^{2+} = 194.05$ ([M–2PF$_6$–]$^{2+}$) is shown for comparison.

Figure S20. ESI–MS of 1.0 mM 2 in aqueous 0.1 M NaPi buffer (pH 9.0) for before (a) and after long–term CPE (b). Calcd. $m/z^{2+} = 194.05$ ([M–2PF$_6$–]$^{2+}$) is shown for comparison.
**Figure S21.** CVs of 1.0 mM 2 for before (red) and after (blue) 11 h CPE in 0.1 M NaPi buffer (pH 7.0) with ITO electrode (0.8 cm$^2$) at a scan rate = 100 mV/s. Blank (black) is shown for comparison.$^7$

**Figure S22.** 10 continuous CV cycles of 1.0 mM 2 in 0.1 M NaPi buffers at pHs 7.0 (a) and 9.0 (b) with GC electrode (0.07 cm$^2$) at a scan rate of 100 mV/s.$^7$
Figure S23. (a) The GC electrode (0.07 cm$^2$) was cycled 50 times in 1.0 mM 2 in 0.1 M NaPi buffer (pH 7.0) (red). It was rinsed off, but not polished, then cycled in catalyst–free electrolyte (blue). (b) The ITO electrode (0.8 cm$^2$) was cycled in 1.0 mM 2 at pH 7.0 of 0.1 M NaPi buffer (red). After 11 h CPE at 1.50 V vs. NHE, the ITO electrode was rinsed off and then cycled in a catalyst–free NaPi buffer (blue). CV was compared to one collected in the same catalyst–free buffer with a polished GC/ITO electrode (black).$^{7,11}$

Figure S24. (a) The GC electrode (0.07 cm$^2$) was cycled 50 times in 1.0 mM 2 in 0.1 M NaPi buffer (pH 9.0) (red). It was rinsed off, but not polished, then cycled in catalyst–free electrolyte (blue). (b) The ITO electrode (0.8 cm$^2$) was cycled in 1.0 mM 2 at pH 9.0 of 0.1 M NaPi buffer (red). After 11 h CPE at 1.50 V vs. NHE, the ITO electrode was rinsed off and then cycled in a catalyst–free NaPi buffer (blue). CV was compared to one collected in the same catalyst–free buffer with a polished GC/ITO electrode (black).$^{7,11}$
Figure S25. SEM images of the ITO (0.8 cm$^2$) electrodes in NaPi buffer (pH = 7.0) before (a) and after (b) 11 h CPE with 2.\textsuperscript{7,11}

Figure S26. SEM images of the ITO (0.8 cm$^2$) electrodes in NaPi buffer (pH = 9.0) before (a) and after (b) 11 h CPE with 2.\textsuperscript{7,11}
Figure S27. EDX spectrum of the ITO (0.8 cm$^2$) electrode after 11 h CPE with 2 in a 0.1 M NaPi buffer at pH 7.0. (Ca, Na, Mg, Si, In, and O are from the substrate, and Pt is from the coating).$^{7,11}$

Figure S28. EDX spectrum of the ITO (0.8 cm$^2$) electrode after 11 h CPE with 2 in a 0.1 M NaPi buffer at pH 9.0. (Ca, Na, Mg, Si, In, and O are from the substrate, and Pt is from the coating).$^{7,11}$
References