



Influence of chloro substituent on photoisomerization, redox reactions and water oxidation catalysis of mononuclear ruthenium complexes



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ABSTRACT

distal-[Ru(Cl-tpy)(pynp)Cl]⁺ (*d-2Cl*) (Cl-tpy = 4'-chloro-2,2';6',2''-terpyridine, pynp = 2-(2-pyridyl)-1,8-naphthyridine), and *distal*- and *proximal*-[Ru(Cl-tpy)(pynp)OH₂]²⁺ (*d*- and *p-2H₂O*) complexes are newly synthesized and characterized to compare structures and physicochemical properties with a 2,2';6',2''-terpyridine (tpy) ligand derivatives of *distal*-[Ru(tpy)(pynp)Cl]⁺ (*d-1Cl*), *distal*- and *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ (*d*- and *p-1H₂O*). The equilibrium turned out to be involved in the aquation reaction of *d-2Cl* to *d-2H₂O* in contrast to observed irreversible aquation reaction of *d-1Cl* under the same conditions. The kinetic analysis showed that the aquation reaction of *d-2Cl* is slightly slower than that of *d-1Cl*. The stoichiometric photoisomerization of *d-2H₂O* to *p-2H₂O* occurs by visible light irradiation as it is for *d-1H₂O*, and Φ (2.1%) at 520 nm for photoisomerization of *d-2H₂O* was higher than that (1.5%) observed for *d-1H₂O*. *d-2H₂O* undergoes the two-step reaction involving the successive one-proton-coupled one-electron reactions of the Ru^{II}—OH₂/Ru^{III}—OH and Ru^{III}—OH/Ru^{IV}=O redox couples, whereas *p-2H₂O* undergoes the one-step reaction involving the two-proton-coupled two-electron reaction of the Ru^{II}—OH₂/Ru^{IV}=O redox couple. These redox potentials of *d*- and *p-2H₂O* are higher than those for *d*- and *p-1H₂O* at pH 7.0 by 10~50 mV due to the electron-withdrawing chloro substitution. The turnover frequency ($k_{O_2} = 6.3 \times 10^{-3} \text{ s}^{-1}$) of *d-2H₂O* for water oxidation was higher than that ($3.9 \times 10^{-4} \text{ s}^{-1}$) of *p-2H₂O* by a factor of 16. k_{O_2} for *d-2H₂O* was also 1.6 times higher than that ($3.8 \times 10^{-3} \text{ s}^{-1}$) for *d-1H₂O*, whereas k_{O_2} for *p-2H₂O* was 1.2 times lower than that ($4.8 \times 10^{-4} \text{ s}^{-1}$) for *p-1H₂O*.

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1. Introduction

The ruthenium(II) complexes with polypyridyl ligands have been extensively studied as promising functional molecules due to the unique photochemical [1–6] and photophysical [7–9] properties related to a photoexcited triplet metal-to-ligand charge transfer (³MLCT) state as well as redox properties including electrochromism [10,11], and the multi-electron transfer catalysis [12–15]. These properties are responsible for potential applications of the ruthenium(II) complexes to a large variety of devices including sensors [16,17], photovoltaic cells [18–20], displays [21,22], and photocatalysts [7,23]. Polypyridyl ruthenium(II) aquo complexes have recently been attracting much attention as active water oxidation catalysts that are essential for artificial photosynthesis [12–15,24–29]. Although water oxidation catalysts are

expected to be applied to photochemical systems (finally to artificial photosynthesis), there are only a few reports on any photochemical reaction of the ruthenium(II) aquo complexes as water oxidation catalysts [30–32]. We recently reported that the observed catalytic activity of *distal*-[Ru(tpy)(pynp)OH₂]²⁺ (*d-1H₂O*) (tpy = 2,2';6',2''-terpyridine, pynp = 2-(2-pyridyl)-1,8-naphthyridine; see Fig. 1) for water oxidation significantly changes by visible light irradiation due to photoisomerization to *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ (*p-1H₂O*) in water because the catalytic activity of *distal*-isomer is higher than that of the *proximal*-isomer by one order of magnitude [30,34]. This photoisomerization is an irreversible and stoichiometric reaction, being very rare with respect to polypyridyl ruthenium(II) aquo complexes, although a huge number of photochemical reactions [1–6,30–38] of the ruthenium(II) complexes have been reported.

The correlation between structure and reactivity is of fundamental importance for understanding and predicting the outcome and mechanism of chemical reactions. The investigation of substitution effects on chemical reactions is a useful method

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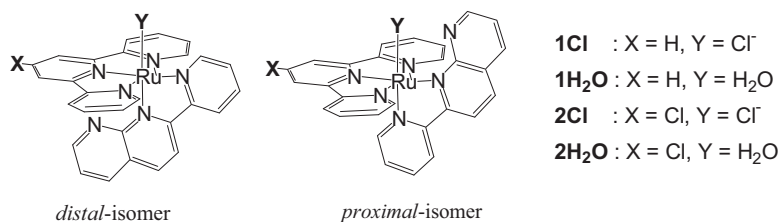


Fig. 1. Structures of *distal*- and *proximal*-isomers of **1** and **2** derivatives.

due to their simplicity and predictability in gaining insight into the dependence on electronic factors. Although molecular catalysts for water oxidation have prospered during the last decade, the catalysts which offer simple systematic tuning of the ligand environment are still relatively scarce [26,39–41]. Likewise, there are no reports of the substitution effect on photoisomerization of polypyridyl ruthenium(II) aquo complexes. In the present paper, *distal*-[Ru(Cl-tpy)(pynp)Cl]⁺ (**d-2Cl**) (Cl-tpy = 4'-chloro-2,2':6',2''-terpyridine), *distal*- and *proximal*-[Ru(Cl-tpy)(pynp)OH₂]²⁺ (*d*- and *p*-**2H₂O**) complexes are newly synthesized and characterized to compare structures and physicochemical properties with **1** derivatives with a tpy ligand (*distal*-[Ru(tpy)(pynp)Cl]⁺ (*d*-**1Cl**) and *d*- and *p*-**1H₂O**) (see Fig. 1). The unique reactions of the aquation reaction, photoisomerization, proton-coupled electron transfer and water oxidation catalyses of **2** derivatives are investigated to gain insight into influence of electronic factors on these reactions.

2. Experimental

2.1. Materials

2-(2-Pyridyl)-1,8-naphthyridine (pynp) [42] and Ru(Cl-tpy)Cl₃ [43] were synthesized according to literatures. All the chemicals of analytical grade were used as received.

2.2. Synthesis of complexes

2.2.1. *distal*-[Ru(Cl-tpy)(pynp)Cl]Cl ([*d*-**2Cl**]Cl)

distal-[Ru(Cl-tpy)(pynp)Cl]Cl was prepared referring to the previous report [30], as follows. 108.8 mg (0.229 mmol) of Ru(Cl-tpy)Cl₃ and 45.8 mg (0.221 mmol) of pynp were refluxed in 20 mL of 75 (v/v)% ethanol/water containing 52 mg (1.23 mmol) of LiCl and 1.45 mL (10.4 mmol) of triethylamine as a reductant for 4 h in the dark. The reaction mixture was filtered remaining hot, and the filtrate was concentrated to 4 mL with a rotary evaporator. The solution was then chilled in a refrigerator for 24 h. The solid was collected on a frit and washed with chilled 3 M HCl, acetone, and ether, and then dried *in vacuo* at room temperature to give *distal*-[Ru(Cl-tpy)(pynp)Cl]Cl (101.8 mg, 0.157 mmol, 71% yield). It was characterized by UV–vis absorption and NMR spectroscopic measurements and elemental analysis. UV–vis absorption spectrum (EtOH): λ_{max} (ε) = 559 nm (9200 M⁻¹ cm⁻¹). ¹H NMR (399.937 MHz, CDCl₃) δ ppm 10.43 (dd, *J* = 5.50, 0.99 Hz, 1H), 9.63 (d, *J* = 8.68 Hz, 1H), 9.38 (d, *J* = 8.26 Hz, 1H), 8.49 (d, *J* = 8.31 Hz, 1H), 8.36 (t, *J* = 7.35, 7.35 Hz, 1H), 8.15 (dd, *J* = 8.04, 1.67 Hz, 1H), 8.08 (dd, *J* = 4.09, 1.61 Hz, 1H), 8.04 (d, *J* = 7.97 Hz, 2H), 7.84 (dd, *J* = 7.20, 5.99 Hz, 1H), 7.68 (t, *J* = 7.42, 7.42 Hz, 2H), 7.52 (d, *J* = 5.16 Hz, 2H), 7.26 (dd, *J* = 7.99, 4.14 Hz, 1H), 8.22 (s, 2H), 7.14 (t, *J* = 3.62 Hz, 2H). ¹³C NMR (175.993 MHz, CDCl₃) δ ppm 165.99, 160.12, 158.76, 158.57, 156.97, 153.09, 151.53, 151.21, 137.91, 137.07, 135.34, 131.79, 131.10, 129.39, 128.37, 127.14, 126.09, 125.11, 123.84, 118.75, 110.23. Anal. calcd. for C₂₈H₁₉Cl₃N₆Ru: C, 51.98; H, 2.96; N, 12.99; Found: C, 51.61; H, 2.73; N, 12.66.

2.2.2. *distal*-[Ru(Cl-tpy)(pynp)OH₂](NO₃)₂ ([*d*-**2H₂O**](NO₃)₂)

30 mg (0.0435 mmol) of [*d*-**2Cl**]Cl and 14.78 mg (0.087 mmol) of AgNO₃ were refluxed in 10 mL of 75 (v/v)% acetone/water for 1 h. After cooling at room temperature, the mixture was filtered, and then concentrated to 2 mL with a rotary evaporator. To the solution was added a saturated NaNO₃ aqueous solution by drops, and then it was chilled in a refrigerator for 24 h. The solid was collected on a frit and washed with chilled water, and then dried *in vacuo* at 50 °C for 5 h to give *distal*-[Ru(Cl-tpy)(pynp)OH₂](NO₃)₂ (27.5 mg, 0.0361 mmol, 83% yield). The product was characterized by UV–vis absorption and NMR spectroscopic measurement and elemental analysis. UV–vis absorption spectrum (H₂O): λ_{max} (ε) = 524 nm (8600 M⁻¹ cm⁻¹). ¹H NMR (400 MHz, D₂O): ¹H NMR (399.937 MHz, D₂O): δ ppm 9.70(d, *J* = 5.68 Hz, 1H), 8.94(d, *J* = 8.24 Hz, 1H), 8.67(s, 1H), 8.49(d, *J* = 8.64 Hz, 1H), 8.42(d, *J* = 8.20 Hz, 1H), 8.33(d, *J* = 8.16 Hz, 1H), 8.26(dd, *J* = 1.52 and 2.4 Hz, 1H), 8.23(d, *J* = 8.64 Hz, 1H), 8.12(dd, *J* = 1.72 and 6.52 Hz, 2H), 8.10(t, *J* = 6.72 Hz, 1H), 7.88(t, *J* = 8.04, 2H), 7.71(d, *J* = 5.48 Hz, 2H), 7.35(dd, *J* = 4.24 and 3.88 Hz, 1H), 7.24(t, *J* = 6.48 Hz, 2H). Anal. calcd. for C₂₈H₂₁ClN₈O₇Ru·H₂O: C, 46.84; H, 2.95; N, 15.61; Found: C, 46.58; H, 2.73; N, 15.46.

2.2.3. *proximal*-[Ru(Cl-tpy)(pynp)OH₂](NO₃)₂ ([*p*-**2H₂O**](NO₃)₂)

p-**2H₂O** was formed by visible-light (λ > 420 nm) irradiation to an aqueous *d*-**2H₂O** solution over 30 min from a filtered halogen lamp. The *in situ* stoichiometric formation *p*-**2H₂O** in water was corroborated by UV–vis absorption and NMR spectroscopic measurement of the completed reaction solution. ([*p*-**2H₂O**](NO₃)₂) λ_{max} (ε) = 518 nm (9120 M⁻¹ cm⁻¹). ¹H NMR (699.841 MHz, D₂O): δ ppm 9.09 (dd, *J* = 4.37 and 1.86 Hz, 1H), 8.86 (d, *J* = 8.90 Hz, 1H), 8.71(s, 2H), 8.61(d, *J* = 7.96 Hz, 1H), 8.41(d, *J* = 7.87 Hz, 2H), 8.01(dd, *J* = 8.33, 4.37 Hz, 1H), 7.93(dt, *J* = 7.96, 7.91, and 1.49 Hz, 2H), 7.80–7.72 (m, 1H), 7.66 (dd, *J* = 5.59 and 0.77 Hz, 2H), 7.58(dd, *J* = 5.87 and 0.69 Hz, 1H), 7.20 (ddd, *J* = 7.46, 5.62 and 1.25, 2H), 7.07(ddd, *J* = 7.34, 5.90 and 1.30 Hz, 1H), 8.95–8.93 (m, 1H), 8.93–8.92 (m, 1H).

3. Experimental details

¹H NMR spectra were recorded with 400 and 700 MHz NMR spectrometers (Varian). ¹H NMR spectra were referenced using tetramethylsilane in organic solvents or sodium trimethylsilyl propanesulfonate in D₂O as an internal standard. X-ray diffraction data were recorded on a diffractometer (Rigaku, XtaLAB mini) using the ω scan technique to a maximum 2θ value of 55.0° with graphite-monochromated MoKα (λ = 0.71075 Å) radiation at 25 °C. Crystals for X-ray diffraction measurements were mounted on a glass fiber. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on the observed reflections (*I* > 2.00 σ(*I*)) and variable parameters and converged with unweighted and weighted agreement factor *R* and *R*_w. The cyclic voltammogram (CV) were measured in 0.5 mM Ru complex solutions (pH 0.5–13.0) using a conventional single-compartment

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