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Short communication

New trinuclear dendritic complexes with $[Ru(tpy)(bpy)X]^{n+}$ ($X = Cl, H_2O$; $n = 1, 2$) for enhanced water oxidation and light-driven alcohol oxidation

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ABSTRACT

A symmetric trinuclear ruthenium complex with $[Ru(tpy)(bpy)(Cl)]^{+}$ (tpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine) connected by 2,4,5-trimethylbenzene was easily prepared. The complex showed effective chemical water oxidation and light-driven oxidation activity of alcohols to corresponding aldehydes in water. When Cl^{-} is replaced by H_2O, the resulting complex exhibited over a twofold increase in O_2 evolution activity compared with its parent complex. Moreover, compared with equimolar ruthenium amounts of the mononuclear complex with the H_2O ligand, the trinuclear ruthenium complex with the conjugated ligand motif also displayed a two time increase in water oxidation activity.

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1. Introduction

Developing effective catalysts for performing water splitting into hydrogen and oxygen is at the forefront of research trends in artificial photosynthesis [1,2]. However, water oxidation is generally considered the bottleneck of the water-splitting process because it requires mediation of four electrons and four protons through proton-coupled electron transfer (PCET) [3,4]. During the last decades, numerous single-site water oxidation catalysts based on different metals were developed to perform effective water oxidation activities [5–12]. Among these, $[Ru(tpy)(bpy)X]^{n+}$ ($X = $ halogen, H_2O; $n = 1, 2$) catalysts based on polypyridyl ligands have been extensively investigated by Meyer's group and others, with detailed and clear mechanistic insights presented in a series of influential works [5,9,10]. Plausible water nucleophilic attack (WNA) mechanisms of single-site ruthenium polypyridyl-mediated water oxidation have been elucidated using spectrochemical techniques [5]. Moreover, single-site ruthenium polypyridyl-based complexes were utilized in a series of photochemical and electrochemical generating oxidation reactions [13,14]. Assembly of ruthenium polypyridyl chromophores with $[Ru(tpy)(bpy)X]^{n+}$ catalysts have been demonstrated to drive efficient O_2 evolution under visible light irradiation [14]. Grafting the complex onto a TiO_2 film which has been deposited onto a fluorine-doped tin oxide substrate was also demonstrated to be a viable approach for the preparation of effective photoanodes for achieving water splitting [13,15]. On the other hand, optimization of the water oxidation activity of $[Ru(tpy)(bpy)X]^{n+}$ catalysts by modulating the electronic and steric effects through modification of the ligand scaffold have been extensively investigated [16–18], and the effects of a redox mediator on the water oxidation rate was reported [19]. In addition, many $[Ru(tpy)(bpy)(H_2O)]^{2+}$-based complexes have been applied as catalysts for light-driven alcohol oxidation reactions with the Ru(IV) = O species possessing excellent reactivity for the oxidation of organic substrates [20,21]. Previously, our group reported on the facile preparation of two chromophore-catalyst assemblies based on $[Ru(tpy)(bpy)X]^{n+}$ catalysts for visible-light driven photooxidation of alcohols [22,23]. In the present work, we have devoted our efforts to the preparation of conjugated dendritic complexes (Scheme 1) and investigations into their chemical water oxidation and visible-light driven alcohol oxidation activities.

2. Experimental

2.1. Synthesis of ligand and complexes

All of the compounds were synthesized in a stepwise manner [24–26] (ESI).

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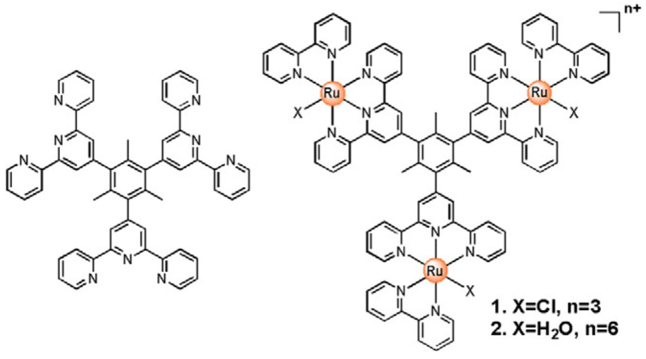

Scheme 1. Simplified molecular structures of ligand and complexes.

Dendritic tris-terpyridine ligand: ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.72 (d, 6H, $J = 4.0$ Hz; H_a), 8.681 (d, 6H, $J = 7.6$ Hz; H_d), 8.414 (s, 6H; H_e), 7.89–7.82 (m, 6H; H_c), 7.36–7.29 (m, 6H; H_b), 1.91 (s, 9H; H_l).

Complex 1: ESI-MS: 564.0554 $[M\text{-}3(PF_6)]^{3+}$. ^1H NMR (400 MHz, acetone-d_6): $\delta =$ 10.25 (d, 3H, $J = 5.0$ Hz), 8.76–8.55 (m, 15H), 8.49 (t, 3H, $J = 6.8$ Hz), 8.277 (t, 3H, $J = 8$ Hz), 8.00–7.82 (m, 9H), 7.77–7.64 (m, 9H), 7.51 (d, 3H, $J = 5.2$, 37.6 Hz), 7.31 (t, 6H, $J = 6.0$ Hz), 6.99 (t, 3H, $J = 6.0$ Hz), 2.50 (s, 9H).

Complex 2: ^1H NMR (400 MHz, acetone-d_6): $\delta =$ 9.87 (d, 3H, $J =$ 10.2 Hz), 9.07–8.80 (m, 15H), 8.67 (t, 3H, $J = 6.8$ Hz), 8.53 (t, 3H, $J =$ 6.4 Hz), 8.29–8.03 (m, 15H), 7.88 (t, 3H, $J = 7.6$ Hz), 7.72 (d, 3H, $J =$ 4.0 Hz), 7.59 (t, 6H, $J = 4.0$ Hz), 7.17 (t, 3H, $J = 3.6$ Hz), 5.90 (m, 6H), 2.52 (s, 9H).

2.2. Chemical water oxidation

In a typical experiment, 100 μL 1.0 mM catalyst solution of **1** or **2** was injected into 10 mL pH = 1.0 HNO_3 aqueous solution containing 548 mg of $(NH_4)_2Ce(NO_3)_6$ (CAN) in a degassed cell with 21 mL volume, the oxygen evolution curve over time was reflected using an ocean optics FOXY-OR125G probe. The turnover numbers (TON) were calculated by TON = $n(O_2)$/n(catalyst) and the turnover frequency (TOF) was calculated by TOF = TON/t(s).

2.3. Photocatalytic oxidation of alcohols

A quartz tube (15 mL) containing 1.0 mM of $Ru(bpy)_3Cl_2$, 0.01 mM of catalyst, 10 mM of substrate, 20 mM of $[Co(NH_3)_5Cl]Cl_2$ and 0.1 M phosphate buffer was irradiated ($\lambda > 420$ nm) using light-emitting diodes (LEDs) (30 × 1 W) for 8 h in degassed aqueous solution (5 mL) at pH 6.8 and room temperature. The resulting solution was extracted with CH_2Cl_2 (3 × 20 mL). The organic fraction was dried over anhydrous Na_2SO_4 and then evaporated to give the crude product. The results were obtained by ^1H NMR spectroscopy with quantitative analyses via the ratio of integrated peak intensities of products to that of corresponding substrates.

3. Results and discussion

Structures of the compounds were characterized by nuclear magnetic resonance (NMR) and electrospray ionization mass spectrometry (EI-MS) (Fig. S1–4). The ^1H NMR spectrum of **1** showed fair characteristic resonances of one stereoselective polypyridyl complex with only one double peak observed at 10.25 ppm (Fig. S2), and the high-resolution mass spectral peaks at m/z = 564.0554 are ascribed to the $[M - 3(PF_6)]^{3+}$ species (Fig. S3). Formation of **2** was performed by adopting an established procedure in which complex **1** was refluxed with $AgClO_4$ in acetone/water solution for over 3 days and then precipitated by NH_4PF_6 [25]. The ^1H NMR spectrum showed the appearance of a new peak at 5.90 ppm with an area in a 2:3 ratio to that of the methyl group on the dendritic structure motif. This peak is attributed to the coordinated H_2O on the complex (Fig. S4).

The UV–vis absorption profiles of the complexes were investigated in 0.1 M HNO_3 aqueous solution or in acetonitrile (Figs. 1a, S5 and S6). Both complexes exhibited characteristic broad and intense long-wavelength absorptions, which are attributed to the metal-to-ligand charge transfer (MLCT) in nature. Compared with **1**, complex **2** displayed blue-shifted MLCT absorption due to an increase in the $d\pi–\pi^*$ energy gap caused by the Cl^- to H_2O ligand exchange process [22,23]. Cyclic voltammetry (CV) measurements of **1** in pH 1.0 displayed one redox event at $E_{1/2} = 0.97$ V *vs* normal hydrogen electrode (NHE) was observed in a 0–1.7 V potential sweep window and this redox process is assigned to $Ru^{III/II}$ (Fig. S7). For complex **2**, three oxidation peaks were observed by CV and DPV at 0.93, 1.21 and 1.68 and are attributed to the $Ru^{III/II}$, $Ru^{IV/III}$ and $Ru^{V/IV}$ processes, respectively (Figs. 1b and S8). These values are lower than those determined for $[Ru(bpy)(tpy)(H_2O)]^{2+}$ in literature (1.04, 1.23 and 1.80) [10]. Previous insights into the electron withdrawing and donating effects of functional groups on the $[Ru(bpy)(tpy)(H_2O)]^{2+}$ motif have revealed that electron-donating groups can cause an increase in the π-back bonding of the tpy ligand to the bpy ligand and lower the oxidation potentials of the resulting complexes. This behavior eventually leads to an increase in catalytic activity but at a compromise to the catalytic stability [17]. It is therefore expected from the electrochemical data obtained that enhanced catalytic activity can be achieved, and are ascribed to the increase in the π-back bonding to the bpy ligand by the conjugated tris-terpyridine ligand. Additionally, the onset potential of the catalytic curve for complex **2** in pH 1.0 HNO_3 is almost 1.55 V *vs* NHE, 200 mV lower than the reduction potential of CAN (~1.75 V *vs* NHE), which meant the possibility of the utility of CAN as oxidant to drive complex **2** for chemical water oxidation.

Ce(IV)-driven water oxidation for complex **1** and **2** was investigated and showed in Fig. 2. Firstly, water oxidation catalyzed by complex **1** was performed at various concentrations (Fig. 2a). Oxygen evolution steadily increased over the time period of 12 h in the presence of excess amounts of CAN, over 63 μmol of O_2 was achieved at a catalyst concentration of 0.05 mM. In addition, by linear fitting of the oxygen evolved in the first 10,000 s, we found that the initial rate of oxygen evolution and the concentration of the catalyst can be fitted into a single exponential function with an order of 0.75 ($R^2 = 0.998$). The obtained value deviates from first order linear relationship (1.0, $R^2 = 0.991$) which is commonly known for mononuclear catalysts, and the catalytic behavior may be tentatively regarded as pseudo-first-order. The reason for the deviation can be explained on that the substitution of all three Cl ligands by H_2O on catalyst **1** is a gradual process, which may vary at different **1** concentrations, thereby leading various moiety ratios of $[Ru(bpy)(tpy)(H_2O)]^{2+}/[Ru(bpy)(tpy)(Cl)]^{+}$ (Fig. 2b). Complex **2** showed a great deal of enhanced catalytic activity but decreased stability; at a catalyst concentration of 0.01 mM, oxygen evolution reached a plateau at around 4 h, producing 30 μmol of O_2 (Fig. 2c). Finally, when systematically comparing the catalytic activities of complexes **1** and **2** with that of mononuclear $[Ru(tpy)(bpy)(OH_2)]^{2+}$, we found that the catalytic activity of **2** was more than two fold **1** or $[Ru(tpy)(bpy)(OH_2)]^{2+}$ for equimolar ruthenium amounts (Fig. 2d). Over 17.2 μmol of O_2 was produced by **2** in the first 5000 s while only 8.2 μmol and 7.9 μmol of O_2 were obtained by **1** and $[Ru(tpy)(bpy)(OH_2)]^{2+}$, respectively. Under the present experimental conditions, a TOF value of $3.44 \times 10^{-2}\ s^{-1}$ was obtained for **2** for the first 5000 s of reaction. In addition, 30.47 μmol of O_2 evolved over 5 h which gives a calculated turnover number (TON) value of 305 at a concentration of 0.01 mM of complex **2**. At equimolar ruthenium amounts, complex **1** and the mononuclear $[Ru(bpy)(tpy)(H_2O)]^{2+}$ exhibited similar catalytic water oxidation trends, the latter showing slightly better performance after 10,000 s. These results demonstrate the possibility of enhancing the catalytic efficiency of classical $[Ru(tpy)(bpy)(OH_2)]^{2+}$ catalysts by introducing a

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