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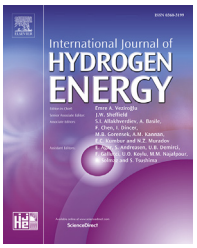

# Ligand modification to stabilize the cobalt complexes for water oxidation

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ABSTRACT

Ligand modifications with electron-withdrawing and electron-donating groups were applied to afford three novel mononuclear cobalt-based catalysts $[Co(TPA\text{-}R)]^{2+}$ (TPA = tris(2-pyridylmethyl) amine; R = tri-α F, **1**; R = tri-αOMe, **2**; R = mono-αF, **3**) for water oxidation. Characterization of the catalysts shows that steric and electronic factors play important roles in inhibiting spontaneous intermolecular dimerization of two cobalt centers, and influence the catalytic behavior. Complex **1** exhibits the best catalytic ability and stability, showing a good efficiency with TOF of 6.03 ± 0.02 mol $(O_2)$/(mol (cat)*s) in photo-induced water oxidation experiments using Ru $(bpy)_3^{2+}$ as photosensitizer and $Na_2S_2O_8$ as electron acceptor. The bulky electron donating groups in **2** led to degradation of the complex and formation of $CoO_x$ particles acting as the real catalyst. Electron-withdrawing substituents on the TPA ligand can stabilize the catalyst under both electrochemical and photo-induced conditions, with the enhancement increasing with the number of the electron-withdrawing groups.



## Introduction

Water oxidation catalysts based on earth-abundant first row transition metal represent an appealing strategy to broaden the scope of catalysts and make them more feasible and practical for future large scale applications [1]. Combined with photo-activated systems, these catalysts open up a possibility towards better functional artificial photosynthesis systems. Recently, as the field of artificial photosynthesis has progressed, the demand of molecular catalysts has increased due to their potential advantages for well-defined mechanistic characterization, facile structural tunability, and greater atom economy under homogeneous reaction conditions [2]. Ligand development and design has attracted a lot of interest due to its cooperative functionality for the catalyst. A robust multidentate ligand framework is essential to hinder demetalation by strong coordination to the metal center and at the same time allow for the redox properties of the metal complex to be readily tuned [3].

The base metal cobalt is often chosen to make molecular water oxidation catalysts. Cobalt has the advantage in

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pronounced mesoionic resonance that contributes to mechanistic account of the complicated reaction landscape [4]. However, it has been frequently observed that ligand dissociation occurs to generate $CoO_x$ nanoparticles that act as water oxidation catalysts [5]. Although heterogeneous systems with $CoO_x$ nanoparticles as real catalysts sometimes show much higher efficiency for water oxidation, it is still necessary to develop cobalt homogeneous systems. Homogeneous catalysts are advantageous for mechanistic study and the resulting understanding can be applied to the development of new catalysts. It is also important to find methods to improve catalyst activity and stability, among which ligand modification by systematically controlling structural and electronic groups provides accessible strategies. It is hoped to develop cobalt molecular catalyst based on ligand coordination. In 2014, tris-(2-pyridylmethyl) amine (TPA) was reported to coordinate with a cobalt (II) center (**RC**), giving a mononuclear complex that can act as a photo-induced homogeneous catalyst for water oxidation in the presence of a photosensitizer and an electron acceptor [6]. TPA is a well-known and multidentate ligand scaffold, which should be interesting to explore modified TPA ligands to make novel homogeneous catalysts. Recently we reported a tri-α F modified TPA ligand that was used to chelate with a copper center, providing a molecular catalyst which functions both in photo-induced and electrochemical water oxidation [7]. Following our initial discovery, we have carefully modified the TPA ligand in an attempt to improve catalyst performance and to establish structure activity and stability relationships, which is still something rare within the field of homogeneous water oxidation.

## Material and methods

**General**. The UV–vis absorption spectra were measured on a U-3900H Spectrophotometer. HPLC-MS data were obtained using anekspert ultraLC 100-XL. Solvents used for HPLC: 0.05% formic acid in $H_2O$ and 0.05% formic acid in $CH_3OH$. $^1H$ NMR spectra were recorded on a Bruker-400 MHz spectrometer at 293 K. Chemical shifts are given in ppm and referenced internally to the residual solvent signal.

**Materials.** All reactions and operations were carried out under a dry argon atmosphere with standard Schlenk technique. All solvents were dried and distilled prior to use. 2-fluoro-6-methyl pyridine, NBS, benzoyl peroxide, 2-methoxy-6-methyl pyridine, dimethyl pyridine-2,6-dicarboxylate, $NaBH_4$, and $CoCl_2{\cdot}6H_2O$ were purchased from HEOWNS and used as received.

### *Synthesis*

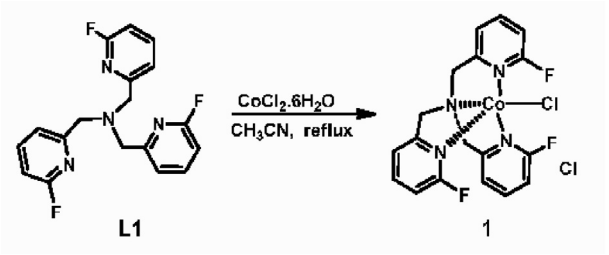
**[Co(TPA-tri-α F)Cl]Cl (1)**. An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and filled with nitrogen. In this flask, $CoCl_2{\cdot}6H_2O$ (80 mg, 0.23 mmol) was dissolved in $CH_3CN$ (5 mL), degassed with Ar, and heated to reflux. To the above refluxing mixture, **L1** (78 mg, 0.23 mmol) in 2 mL $CH_3CN$ was added dropwise to afford a green solution, which was kept refluxing overnight. When the solution was cooled down, the solvent was removed and $CH_3CN$/ether was used to recrystallize product to give **1** as blue solids 45.3 mg (41.5%). HR-ESI-MS: (*m*/*z*) 438.0201, [M-Cl], (calc: 438.7199). Elemental analysis of **1**, calcd (%) for $C_{18}H_{15}Cl_2CoF_3N_4{\cdot}1.8\ CH_2Cl_2$: C 37.93, H 2.99, N 8.93; found C 37.89, H 3.19, N 9.07 (Scheme 1).

**2-methoxyl-6-bromomethyl Pyridine**. A portion of the commercially available 2-fluoro-6-methyl pyridine (500 mg, 4.06 mmol) was dissolved in 25 mL of $CCl_4$. Then NBS (829 mg, 4.66 mmol) was added, and the medium was refluxed for 20 h in the presence of 30 mg benzoyl peroxide. The solvent was then evaporated and the solid extracted with $CH_2Cl_2$. The concentrated $CH_2Cl_2$ solution was chromatographed on silica gel using petroleum ether as eluent and the desired compound collected as the second fraction. Evaporation of the solvent yield 235 mg (28.6%) product as a pale yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ ppm):7.48 (t, $J = 7.2$, 3H), 7.12 (d, $J = 6.8$, 3H), 6.52 (d, $J = 7.6$, 3H), 3.84 (s, 15H).

**tris(6-methoxypyrid-2-ylmethyl)amine ($L_2$)**. In a Schlenk tube, acetonitrile (20 mL) was added to 2-(bromomethyl)-6-methoxypyridine (100 mg, 0.49 mmol) and ammonium carbonate (235 mg, 2.45 mmol) and then was sealed with a Teflon stopper. The mixture was heated to 75 °C with vigorous stirring for 18 h. The mixture was then allowed to cool to room temperature and carefully vented in a fume hood to release ammonia pressure. The solids were filtered, and washed with copious amounts of $CH_2Cl_2$. The combined filtrates were concentrated to a crude oily yellow residue. Addition of cold ethanol produced a white solid, which was washed with small amounts of cold ethanol, then hexanes and dried to give the title compound as a white powder. An additional crop of product was obtained by concentrating the combined ethanol/hexanes washes to minimal volume and cooling. Evaporation of the solvent yield 45 mg (71%) **L2** as light yellow solid. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ ppm): 7.48 (t, $J = 7.2$, 3H), 7.12 (d, $J = 6.8$, 3H), 6.52 (d, $J = 7.6$, 3H), 3.84 (s, 15H) (Scheme 2).

**[Co(TPA-tri-α OMe)Cl]Cl (2)**. The same method as the synthesis of **1** was carried out with **2** as blue solid with yield of 75%. HR-ESI-MS: (*m*/*z*) 474.0785, $[M\text{-}Cl]^+$, (calc: 474.8265). Elemental analysis of **2**, calcd (%) for $C_{21}H_{24}Cl_2CoN_4O_3{\cdot}5H_2O{\cdot}CH_2Cl_2$: C 39.96, H 5.14, N 8.40; found C 39.68, H 4.84, N 9.02.

**6-fluoro-2-(aminomethyl)pyridine**. Compound 2-fluoro-6-bromomethyl pyridine (100 mg, 0.41 mmol) in 25 mL of DMF was reacted with potassium phthalimide (163 mg, 0.88 mmol) and $NaHCO_3$ (85 mg, 1.01 mmol). The mixture was heated to reflux for 3 h and then cooled to room temperature. The white solid that formed was removed by suction filtration. The




**Scheme 1 – The synthesis of compound 1.**

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