

Supporting Information for:

Tracking Fe^{IV}(O) intermediate and O-O bond formation of a nonheme iron catalyst for water oxidation

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Experimental Section

Materials

All experiments were carried out using standard Schlenk techniques under an Ar atmosphere unless otherwise indicated. All chemicals were purchased from Inno-Chem and were used without further purification unless noted otherwise.

NMR Spectroscopy

NMR spectra were recorded with a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard.

Mass Spectroscopy

HRMS (ESI) spectra were measured with an ThermoFisher Q-Exactive Mass Spectrometer.

UV-Vis Spectroscopy

UV-Vis data were obtained using Shimadzu UV-1601PC UV-Visible spectrophotometer.

Electrochemistry

Cyclic Voltammetry (CV) and controlled-potential electrolysis experiments were performed on a Potentiostat/Galvanostat Model 283. Glassy carbon disk electrodes (0.07 cm²) were used as working, platinum wire as auxiliary and a SCE as reference electrode. Glassy carbon disk electrodes were polished with 0.05 μm alumina paste and all electrodes were washed with water and acetone and dried before use.

Oxygen Evolution Experiments

The oxygen evolution was recorded with a Hansatech Clark Oxygen Electrode.

ESR Analysis

The ESR data were obtained using X Band Bruker E500 Electron Spin Resonance Spectrometer.

TEM Analysis

The TEM images were obtained using JEM 2100 and JEM 2100F Transmission Electron Microscope.

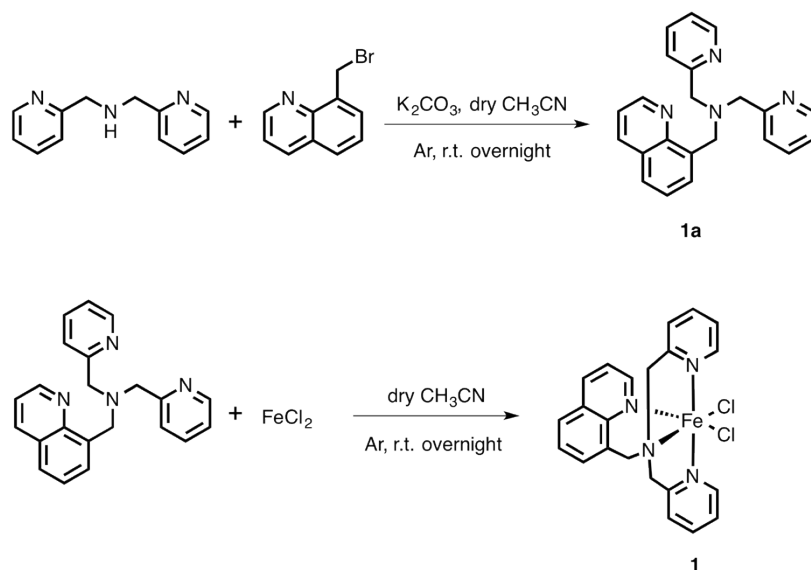
DLS Measurements

The DLS data were obtained using DynaPro NanoStar Dynamic Light Scattering.

XAS Experiments

The XAS data were collected at the Beijing Synchrotron Radiation Facility (BSRF) on beamline 1W1B.

Synthesis of Complex 1



Synthesis of ligand **1a**

Bis(2-pyridylmethyl)amine (0.4 mL, 2.25 mmol) was added dropwise to the mixture of 8-(Bromomethyl)quinoline (0.5 g, 2.25 mmol) and K_2CO_3 (0.93 g, 6.75 mmol) in dry acetonitrile (30 mL) and then the system was stirred at room temperature under Ar atmosphere overnight. The solvent was removed and DCM (100 mL) and 1 M Na_2CO_3 (50 mL) aqueous solution were added. The organic phase was dried over Na_2SO_4 and purified by column chromatography on silica gel using DCM-methanol (100/1 to 20/1, v/v) as eluents, **1a** was obtained as red oil (0.74 g, 97.4 % yield). 1H -NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, $J = 4.1, 1.5$ Hz, 1H), 8.51 (d, $J = 4.8$ Hz, 2H), 8.16 – 8.10 (m, 2H), 7.73 – 7.67 (m, 3H), 7.63 (td, $J = 7.6, 1.5$ Hz, 2H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.38 (dd, $J = 8.2, 4.2$ Hz, 1H), 7.14 – 7.07 (m, 2H), 4.52 (s, 2H), 4.00 (s, 4H). HRMS (ESI+) m/z calculated for $C_{22}H_{21}N_4$ $[M+H]^+$ 341.1766, found 341.1757.

Synthesis of complex **1**

A 2.0 mL acetonitrile solution of **1a** (68 mg, 0.2 mmol) was added into the 2.0 mL $FeCl_2$ (25.4 mg, 0.2 mmol) acetonitrile solution and the mixture was stirred at room temperature under Ar atmosphere overnight. The precipitate was filtrated and washed with hexane (5.0 mL) and **1** was obtained as brick-red solid (37.8 mg, 40.5 % yield). HRMS (ESI+) m/z calculated for $C_{22}H_{20}ClFeN$ $[M-Cl]^+$ 431.0726, found 431.0711.

NMR Spectroscopy

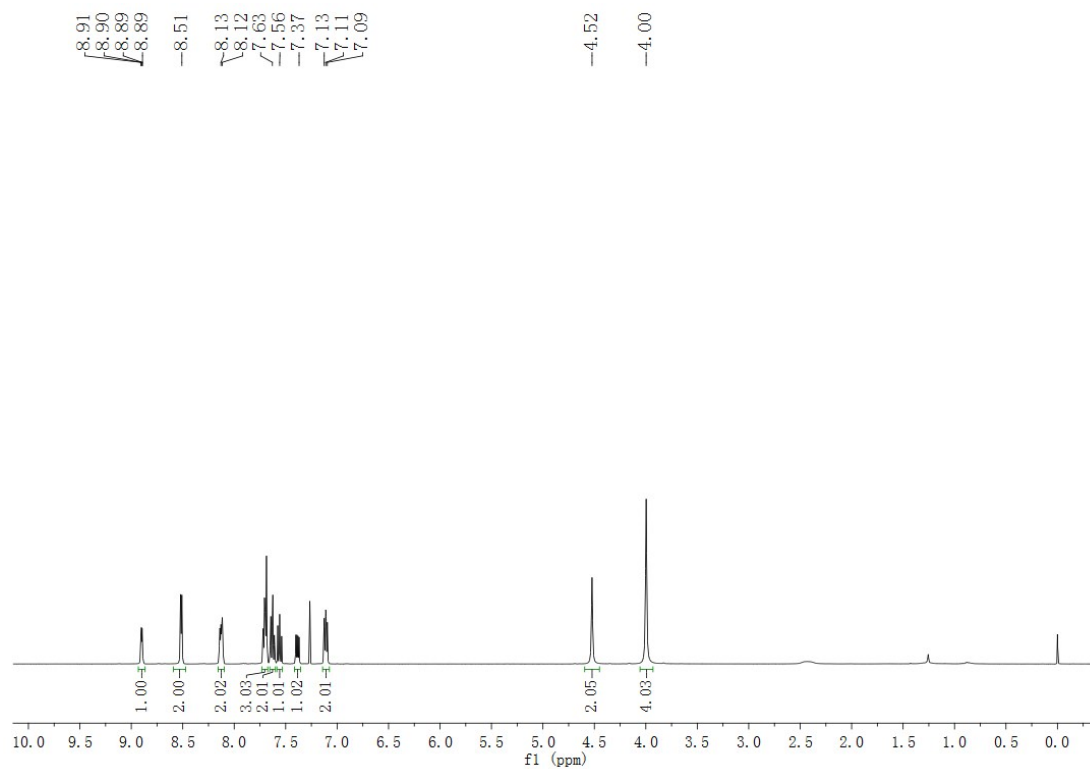


Fig. S1: ¹H-NMR spectrum of complex **1a** in CDCl₃ at 298 K.

MS Analysis

Yangbing-48 #14 RT: 0.14 AV: 1 NL: 5.53E8
T: FTMS + p ESI Full ms [150.00-2000.00]

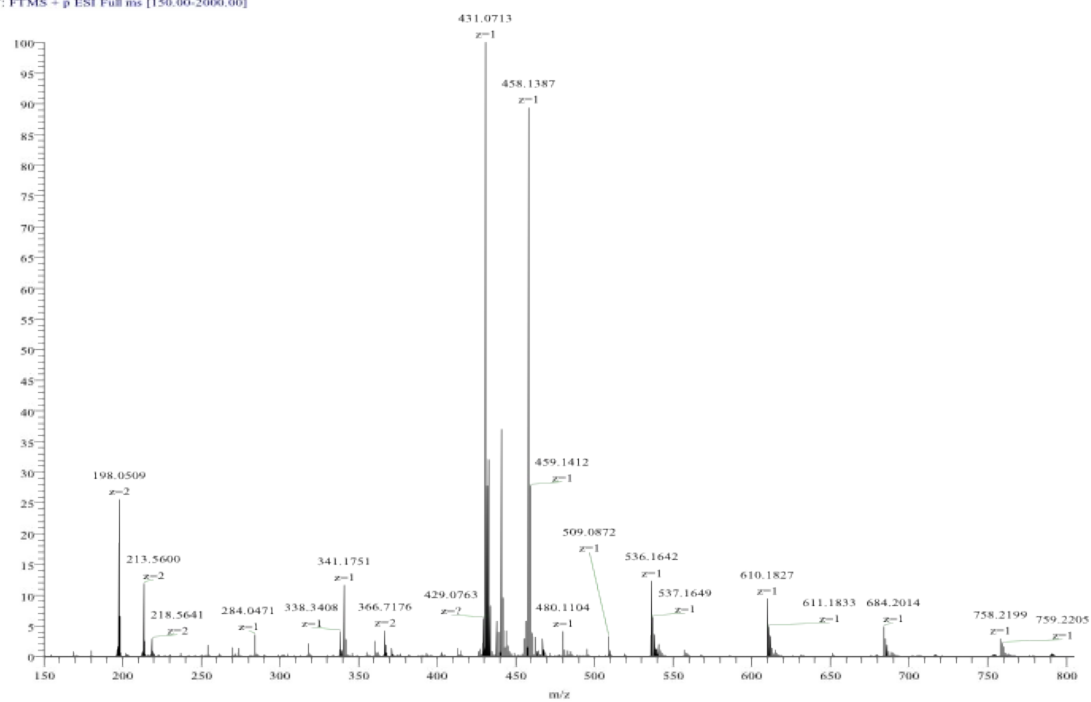


Fig. S2: HR-MS (ESI) of complex **1** in CH₃OH at 298 K.

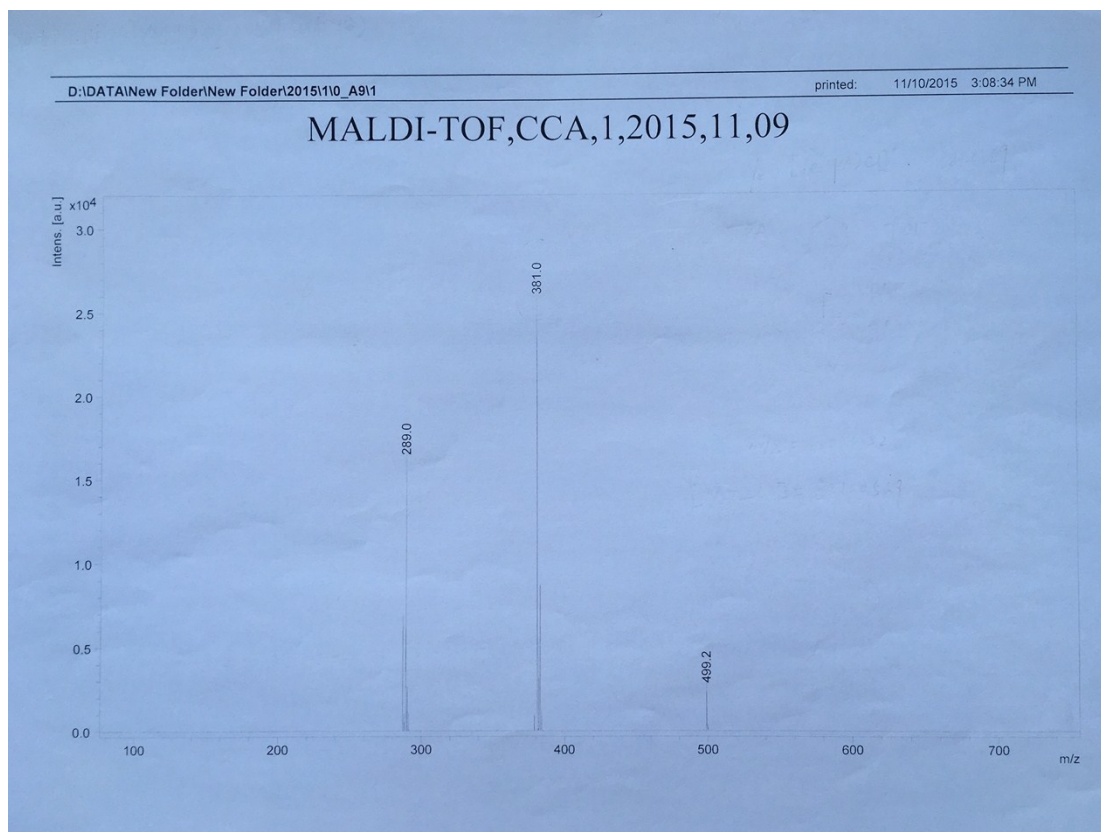


Fig. S3: MS (MALDI-TOF) of complex $\text{Fe}(\text{TPA})\text{Cl}_2$ in CH_3OH at 298 K.

Oxygen Evolution Experiments

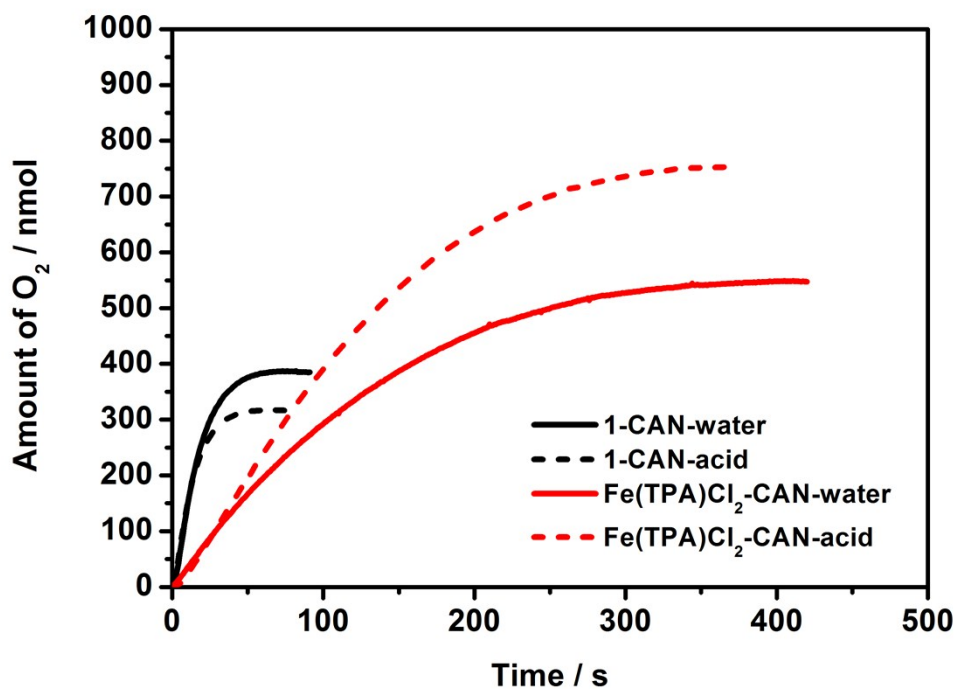


Fig. S4: O₂ evolution recorded by Clark oxygen electrode using CAN as the primary oxidant. Conditions: 2.0 mL aqueous solution (water) or 0.1 M HNO₃ aqueous solution (acid) containing **[1]** = [Fe(TPA)Cl₂] = 50 μM, [CAN] = 100 mM.

Electrochemistry

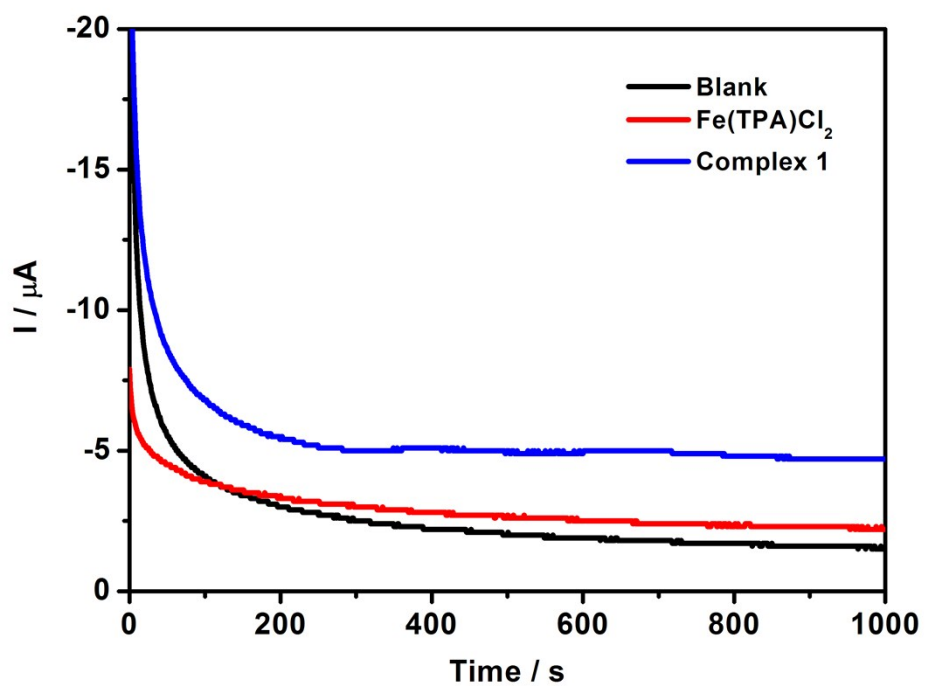


Fig. S5: Controlled-potential electrolysis of complex **1** and Fe(TPA)Cl₂ in 0.1 M HNO₃ aqueous solution at 1.3 V vs SCE on a glassy carbon disk working electrode (0.07 cm²) using Pt wire as an auxiliary and SCE as reference electrode, [**1**] = [Fe(TPA)Cl₂] = 1 mM.

HR-MS Characterization of Fe^{IV}(O)

Yangbing-54 #15 RT: 0.09 AV: 1 NL: 1.93E7
T: FTMS - p ESI Full ms [50.00-750.00]

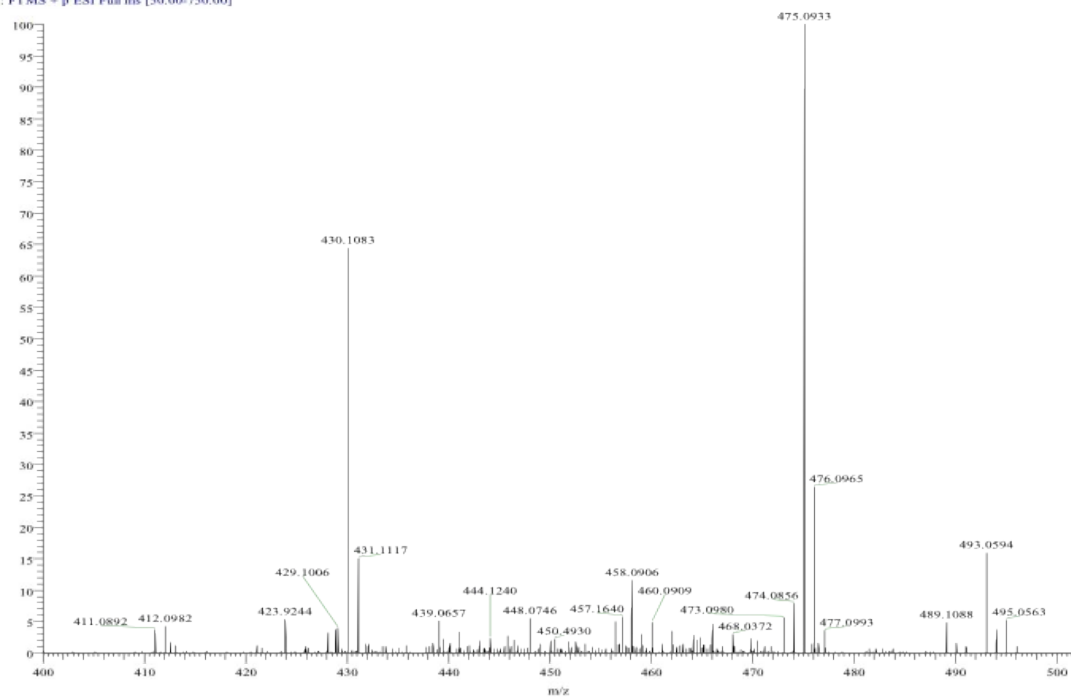


Fig. S6: HR-MS (ESI) of complex **1** in aqueous solution after adding 200 equiv. CAN at 298 K.

Ion Chromatography Analysis

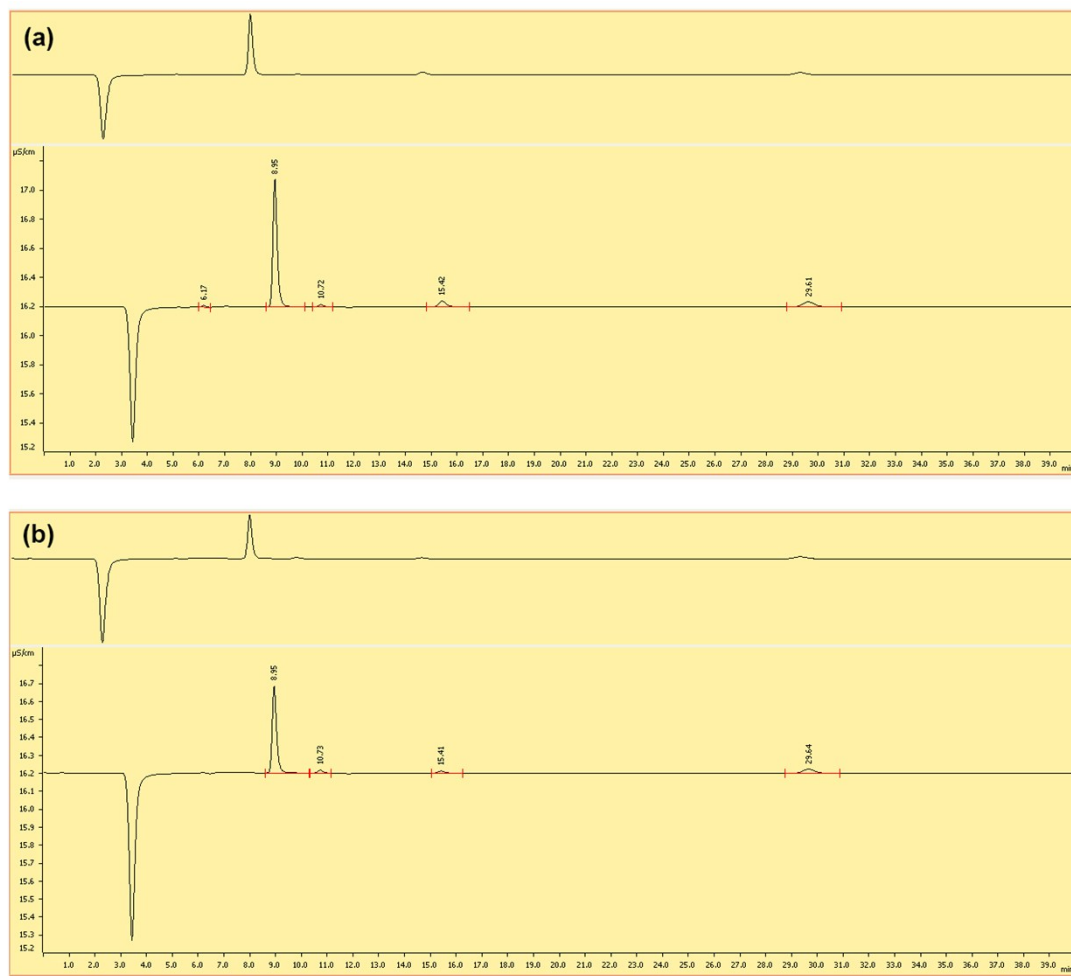


Fig. S7: Ion chromatography analysis of Cl⁻ (retention time = 8.95 min) for the aqueous solution of complex **1** (a) and NaCl aqueous solution (b), [1] = [NaCl] = 10 µM, the peak area for **1** and NaCl were 0.174 and 0.096 [(µS/cm) × min], respectively.

UV-Vis Absorption Spectroscopy

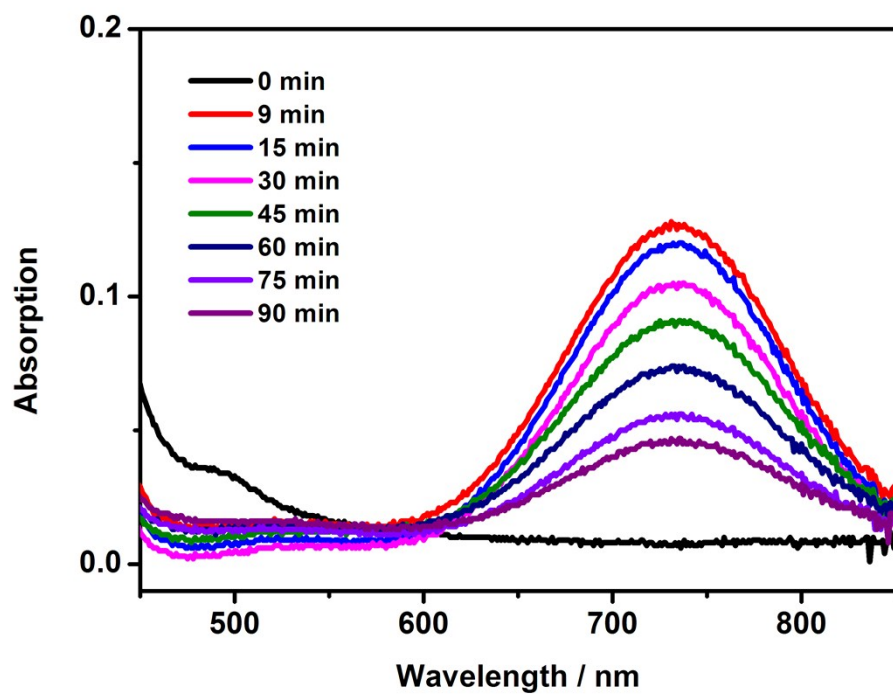


Fig. S8: UV-Vis absorption spectra changes for the reaction of Fe(TPA)Cl₂ with 6 equiv. CAN in aqueous solution at room temperature, [Fe(TPA)Cl₂] = 1 mM.