Supporting Information for

Autocatalytic radical chain pathway in formation of an iron(IV)-oxo complex by oxidation of an iron(II) complex with dioxygen and isopropanol

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Experimental section

Materials. Commercially available chemicals were used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under N_2 prior to use.[1] Iodosylbenzene (PhIO) was prepared by a literature method.[2] Isopropanol and isopropanol-d_8 were purchased from Aldrich Chemical Co. and Chembridge Isotope Laboratories, Inc., respectively. Hydrogen peroxide (H_2O_2), 35 wt. % in water and galvinoxyl radical were purchased from Kishida Chemical Co., Ltd. and Tokyo Chemical Industry Co., Ltd., respectively. TMC ligand was purchased from Aldrich Chemical, and Iron complexes, $[Fe^{II}(TMC)(CH_3CN)_2](CF_3SO_3)_2$, and $[Fe^{IV}(O)(TMC)]^{2+}$, were prepared by literature methods.[3]

Kinetic measurements. Kinetic measurements were performed on a Hewlett Packard 8453 photodiode-array spectrophotometer at 298 K. Typically, the formation reaction of $[Fe^{IV}(O)(TMC)]^{2+}$ was started by adding solution of $[Fe^{II}(TMC)]^{2+}$ (5.0 mM) into air-saturated MeCN in the presence of isopropanol with other additives such as $[Fe^{IV}(O)(TMC)]^{2+}$, H_2O_2, and galvinoxyl radical. The reaction between $[Fe^{IV}(O)(TMC)]^{2+}$ and isopropanol was started by adding solution of $[Fe^{IV}(O)(TMC)]^{2+}$ into deaerated MeCN solution of isopropanol.

NMR measurements. Nuclear magnetic resonance (NMR) detection of acetone and H_2O was performed as follows: an air-saturated MeCN-d_3 solution of $[Fe^{IV}(O)(TMC)]^{2+}$ (1.0×10^3 M) was added to an air-saturated MeCN-d_3 solution of isopropanol (18 mM). After 5 h, ^1H NMR spectra were recorded on a JEOL JMN-AL-300 NMR spectrometer at room temperature.

EPR measurements. Electron paramagnetic resonance (EPR) detection of iron(III) complexes was performed as follows: an MeCN solution of isopropanol (2.6 M) in an EPR cell (3.0 mm i.d.) purged with N_2 for 5 min. Then, a deaerated MeCN solution of $[Fe^{IV}(O)(TMC)]^{2+}$ (1.0×10^{-3} M) was added to the solution. The EPR spectra of the iron(III) complexes were recorded on a JEOL JES-RE1XE spectrometer at 85 K. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (S/N) ratio of the observed spectra under non-saturating microwave power conditions. The g value was calibrated using an Mn^{2+} marker (g = 2.034 and 1.981).

References

(S1) W. L. F. Armarego and D. D. Perrin, Ed.; *Purification of Laboratory Chemicals*, 6th ed.; Pergamon Press: Oxford, 2009.

(S2) H. Saltzman and J. G. Sharefkin Ed.; *Organic Syntheses*; Wiley: New York, 1973, Collect. Vol. V, pp. 658.

(S3) J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Münck, W. Nam and L. Que, Jr. *Science*, 2003, **299**, 1037.

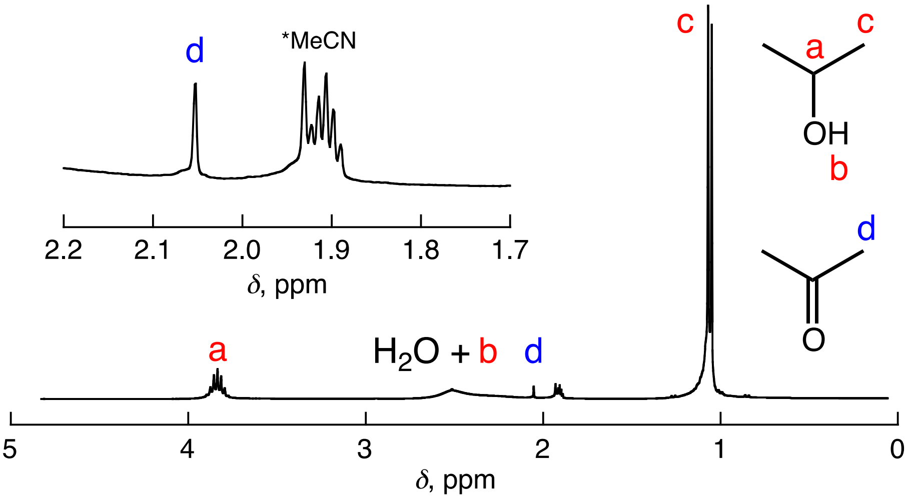

Fig. S1 ^{1}H NMR spectrum of a resulting solution obtained in the reaction of $[Fe^{II}(TMC)]^{2+}$ (1.0 mM) and isopropanol (18 mM) to produce $[Fe^{II}(TMC)]^{2+}$ (0.49 mM) and acetone (0.8 mM) in air-saturated MeCN at 298 K.

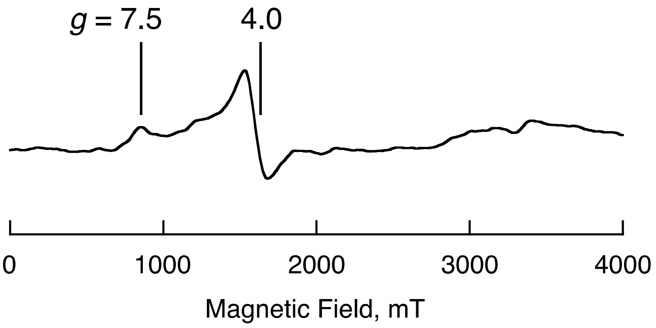

Fig. S2 EPR spectrum of a resulting solution obtained in the reaction of $[Fe^{IV}(O)(TMC)]^{2+}$ (1.2 mM) and isopropanol (2.6 M) in deaerated MeCN at 298 K. The spectrum was recorded at 85 K.

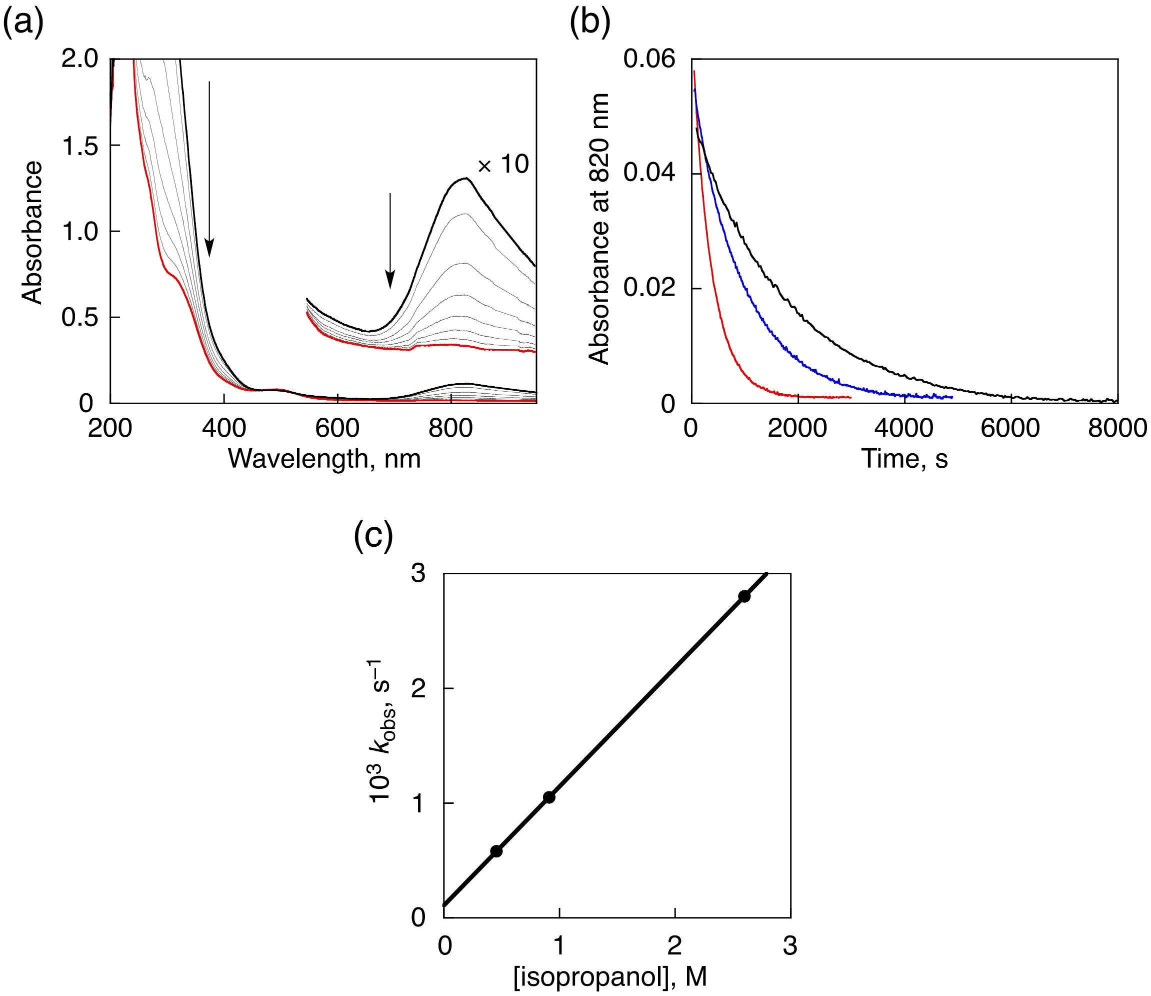

Fig. S3 (a) UV-vis-NIR spectral changes observed in the oxidation of isopropanol (0.91 M) by $[Fe^{IV}(O)(TMC)]^{2+}$ (0.15 mM) in deaerated MeCN at 298 K. (b) Time courses of absorbance at 820 nm due to $[Fe^{IV}(O)(TMC)]^{2+}$ in the reaction of $[Fe^{IV}(O)(TMC)]^{2+}$ (0.15 mM) with isopropanol (red, 2.6 M; blue, 0.91 M; black, 0.46 M) in deaerated MeCN at 298 K. (c) Plot of pseudo-first-order rate constant vs. concentration of isopropanol.

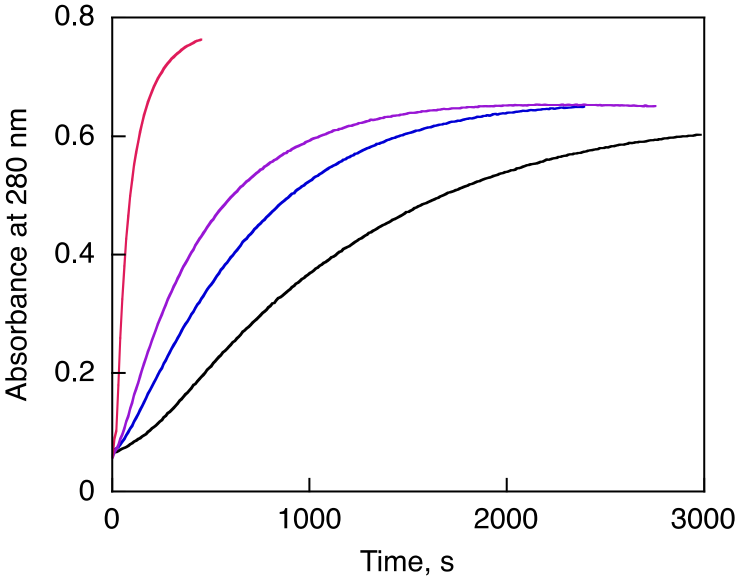

Fig. S4 Time traces of the absorption change monitored at 280 nm during formation of [Fe^{IV}(O)(TMC)]$^{2+}$ in the reaction of [Fe^{II}(TMC)]$^{2+}$ (0.10 mM) with isopropanol (0.26 M) in the absence and presence of a catalytic amount of H_2O_2 (black, 0.0 M; blue 0.020 mM; purple 0.20 mM; red, 2.0 mM) in air-saturated MeCN at 298 K.

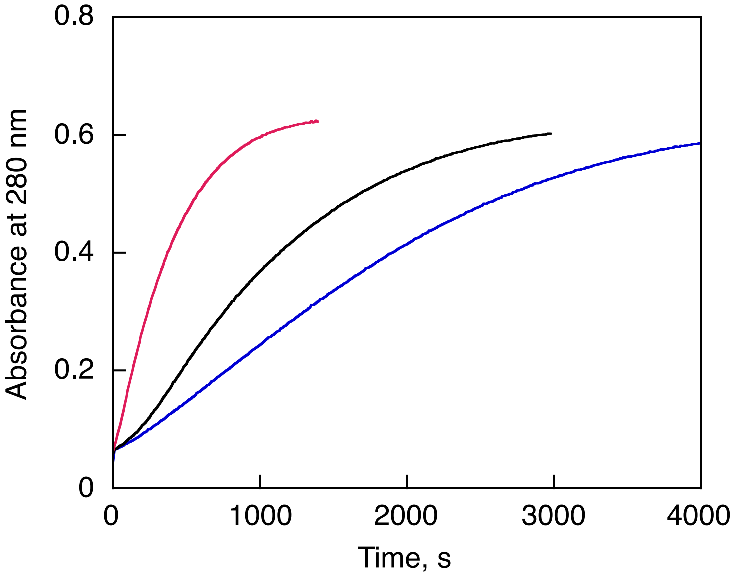

Fig. S5 Time courses of the absorbance at 280 nm due to [Fe^{IV}(O)(TMC)]$^{2+}$ in the reaction of [Fe^{II}(TMC)]$^{2+}$ (0.10 mM) with various concentrations of isopropanol (blue, 0.13 M; black, 0.26 M; red 0.52 M) in air-saturated MeCN at 298 K.

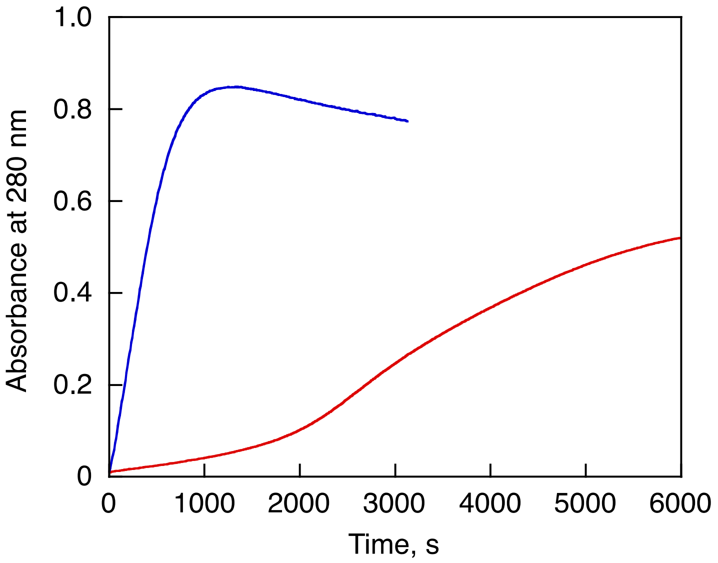

Fig. S6 Time courses of the absorbance at 280 nm due to $[Fe^{IV}(O)(TMC)]^{2+}$ in the reaction of $[Fe^{II}(TMC)]^{2+}$ (0.10 mM) with isopropanol (0.26 M) in air-saturated (red) and O_2-saturated (blue) MeCN at 298 K.