Supporting Information for

Water Oxidation Catalysis with Nonheme Iron Complexes under Acidic and Basic Conditions: Homogeneous or Heterogeneous?

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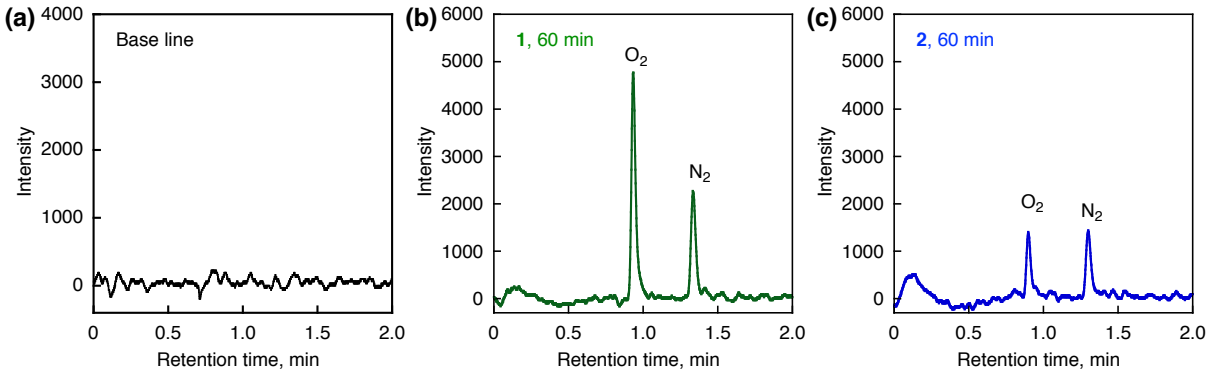

Figure S1. GC charts of (a) a base line and the gas evolved at 60 min in the catalytic water oxidation with (b) **1** (12.5 μM) and (c) **2** (12.5 μM) by CAN (125 mM) in a non-buffered aqueous solution (2.0 mL).

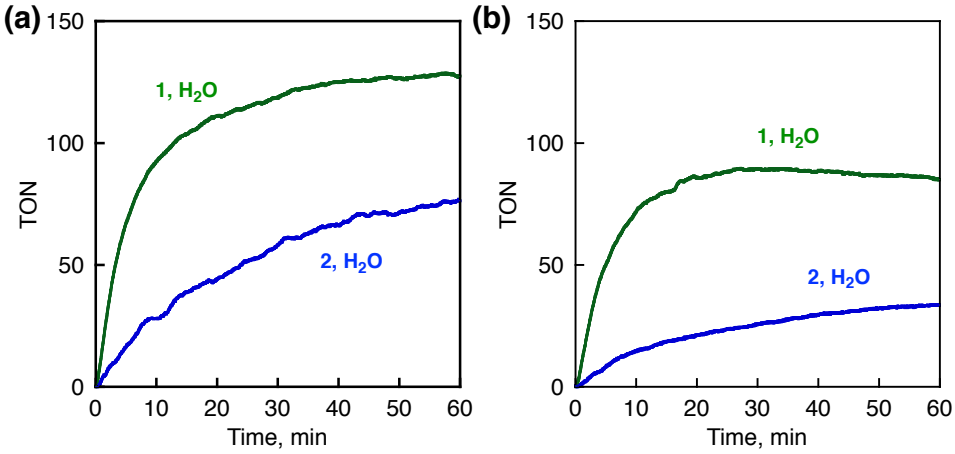

Figure S2. Time courses of O_2 evolution quantified by manometry in the catalytic water oxidation by CAN (125 mM) with **1** and **2** (12.5 μM) in a non-buffered aqueous solution (2.0 mL). (a) Addition of CAN into iron complexes; CAN (250 μmol) was dissolved in 0.20 mL water and added into 1.8 mL of iron complex solution (b) Addition of iron complexes into CAN; CAN (250 μmol) was dissolved in 1.95 mL water in the reaction vial. The reaction was started by adding 50 μL of iron complex solution into CAN solution.

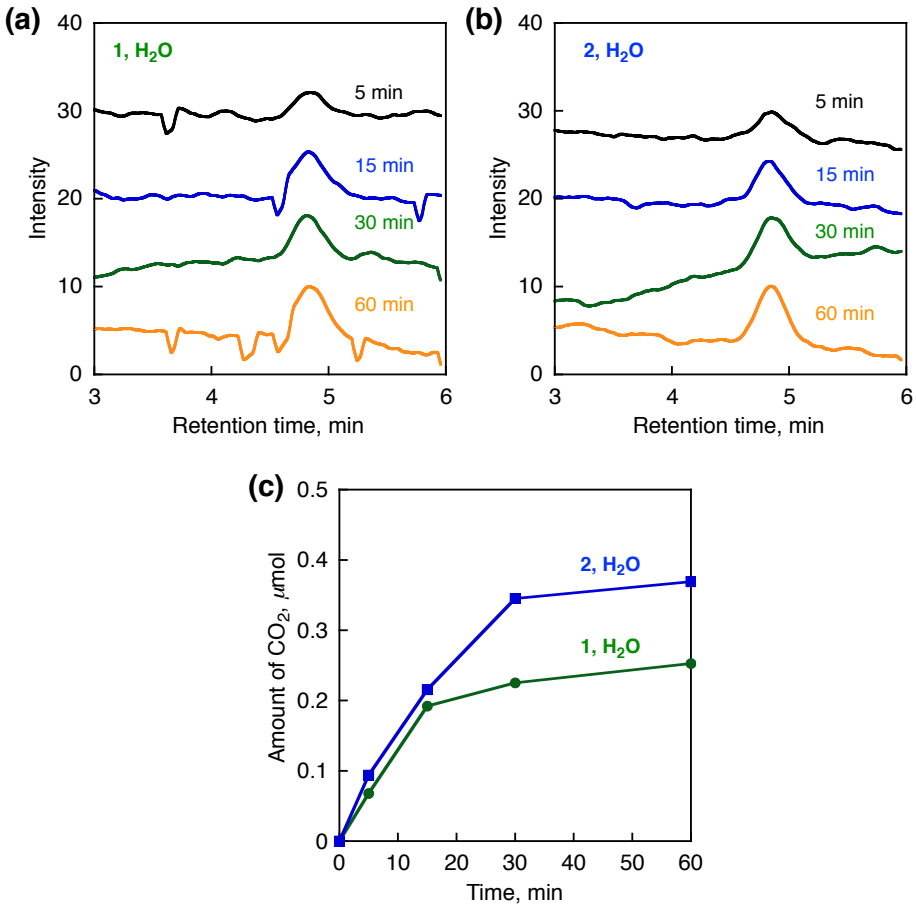

Figure S3. GC charts of CO_2 evolution in the catalytic water oxidation with (a) **1** (12.5 μM) and (b) **2** (12.5 μM) by CAN (125 mM) in a non-buffered aqueous solution (2.0 mL). (c) Time courses of CO_2 evolution with **1** (green cycles) and **2** (blue squares) in the reaction.

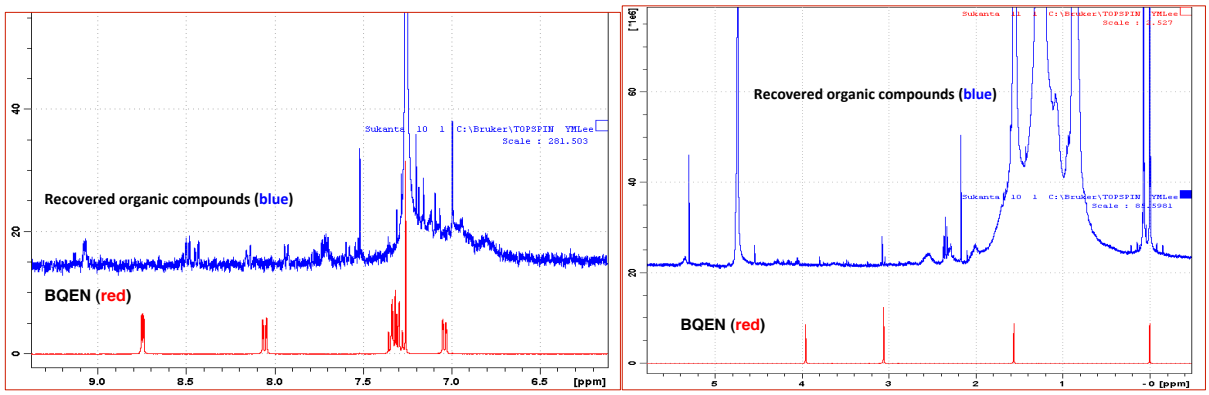

Figure S4. ^{1}H NMR spectra (in $CDCl_3$) of BQEN ligand (red line) and the organic material (blue line) obtained from the water oxidation reaction by CAN (0.10 M) with **1** (1.0 mM) in a non-buffered aqueous solution after 1 h. The organic compounds were collected as follows: H_2SO_4 was added to the resulting solution to remove the precipitates (cerium sulphate) formed in the solution by centrifugation, and a yellow-brown solution was obtained. Addition of excess KCN into the yellow-brown solution (to remove iron ions) generated brown precipitates along with a red solution. The precipitates were separated from the red solution by centrifugation. The precipitates and the red solution were washed separately with CH_2Cl_2. Then the combined CH_2Cl_2 solutions were washed with water and dried over Na_2SO_4. Finally, the yellow oily residue was obtained by removal of CH_2Cl_2.

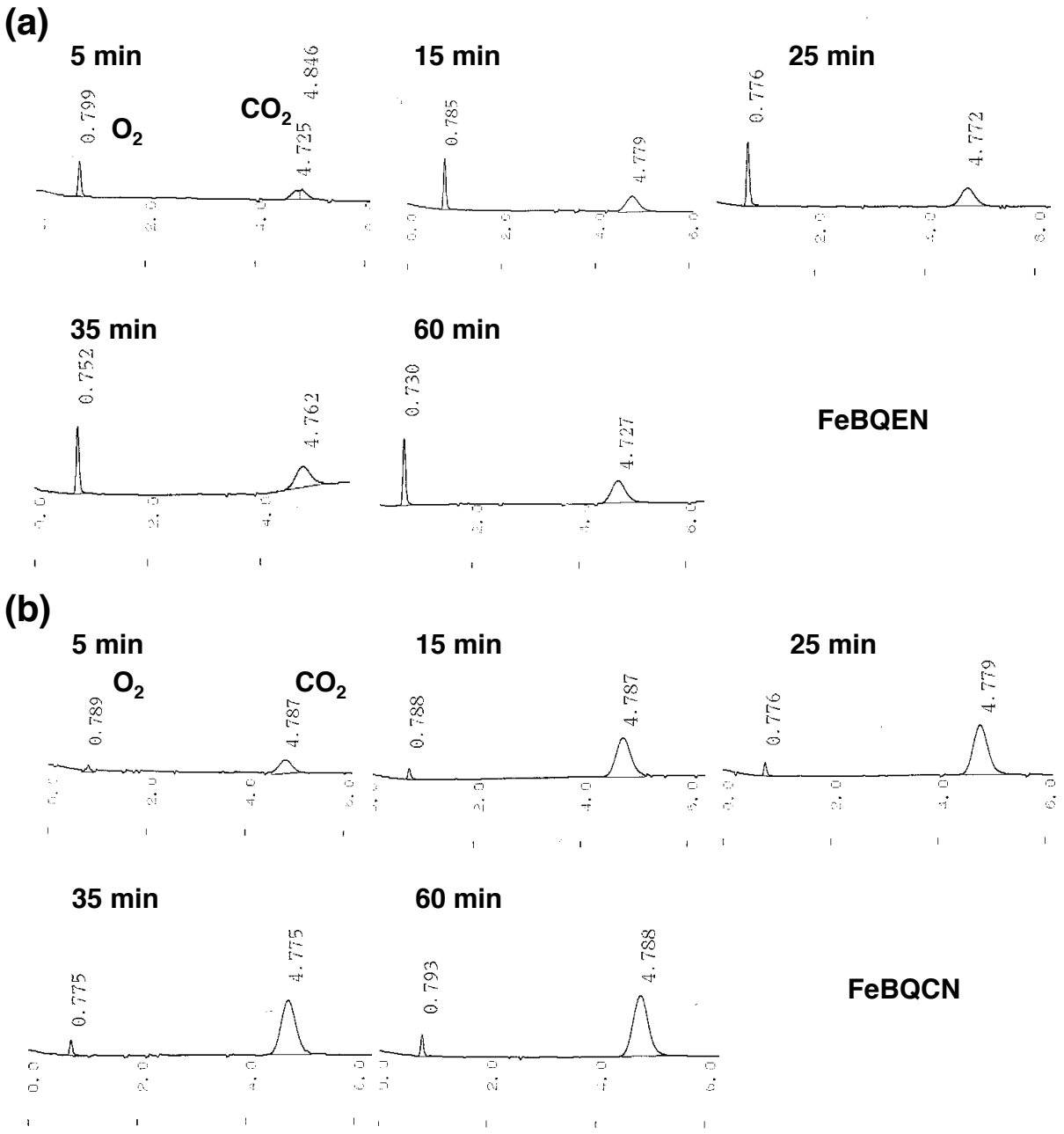

Figure S5. GC charts of CO_2 evolution observed with (a) **1** (1.0 mM) and (b) **2** (1.0 mM) in the catalytic reactions by CAN (0.10 M) in a non-buffered aqueous solution (2.0 mL).

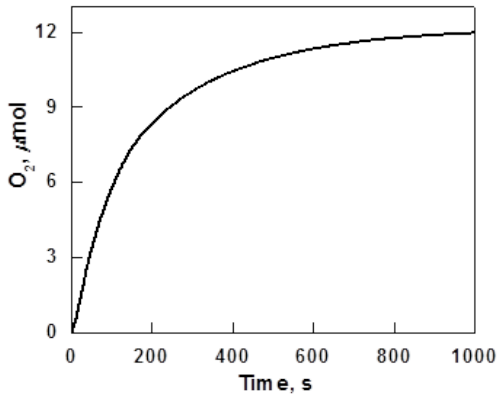

Figure S6. Time courses of O_2 evolution monitored by manometry in the catalytic water oxidation by CAN (0.10 M) with **1** (1.0 mM) in a non-buffered aqueous solution (2.0 mL).

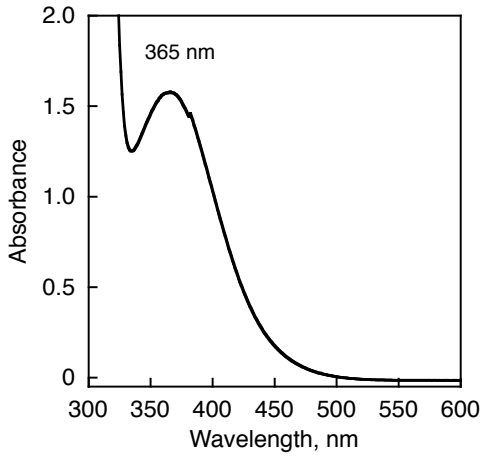

Figure S7. UV-vis spectra of an aqueous solution (2.0 mL) containing BQEN (1.0 mM) and HNO_3 (0.10 M).

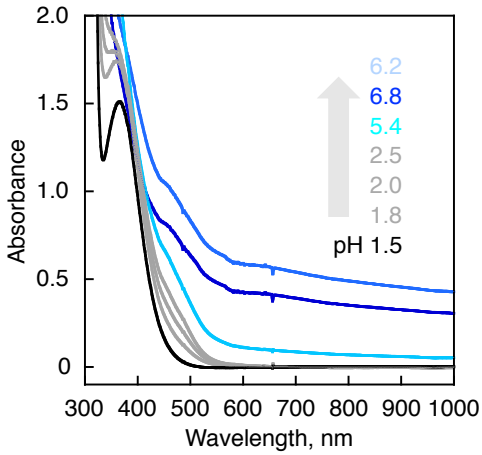

Figure S8. UV-vis spectral changes observed for the titration of an aqueous solution (2.0 mL) of **1** (1.0 mM) in HNO_3 (0.10 M) with NaOH.

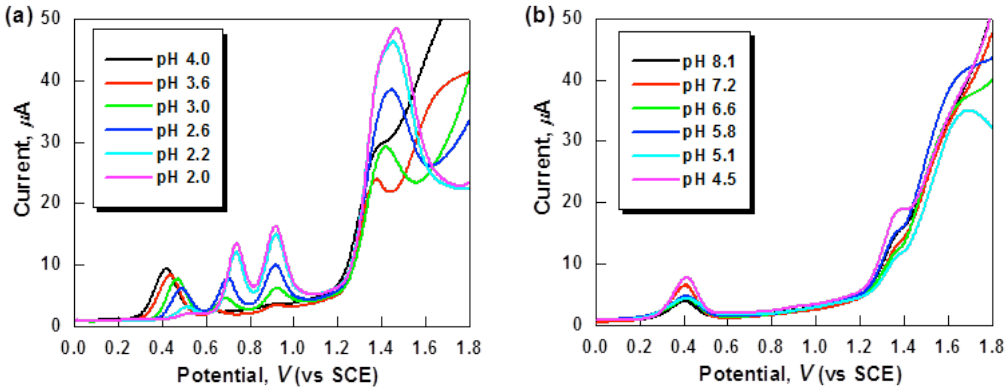

Figure S9. Differential pulse voltammetry (DPV) of an aqueous solution containing **1** (0.50 mM) and $NaNO_3$ (0.10 M) in different pH ranges: (a) from 2.0 to 4.0 and (b) from 4.5 to 8.1 (conditions: amplitude = 50 mV; pulse period = 0.2 s).

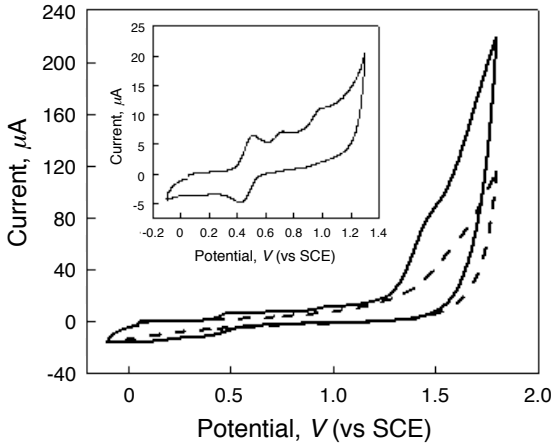

Figure S10. CVs of glassy carbon background (black dashed) and complex **1** (0.50 mM, black solid) in an aqueous solution (pH 3.4, 0.10 M $NaNO_3$) with scan rate of 100 mV s^{-1}. Inset shows the CV of **1** up to potential 1.3 V with a reversible $Fe^{III/II}$ couple at $E_{1/2}$ = 0.47 V followed by two dissociated BQEN ligand centered irreversible oxidation waves.

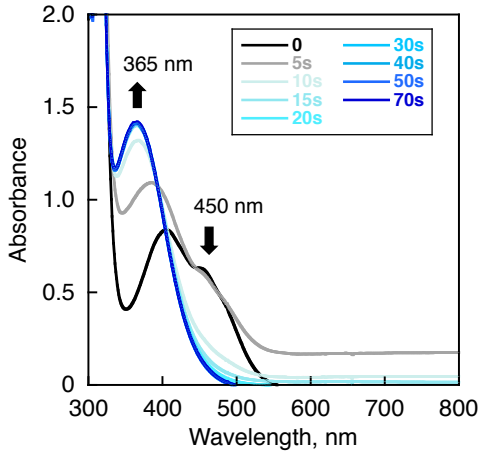

Figure S11. UV-vis spectral changes observed by adding HNO_3 (70 wt%, 20 μL) to **1** (1.0 mM) in a non-buffered aqueous solution (2.0 mL).

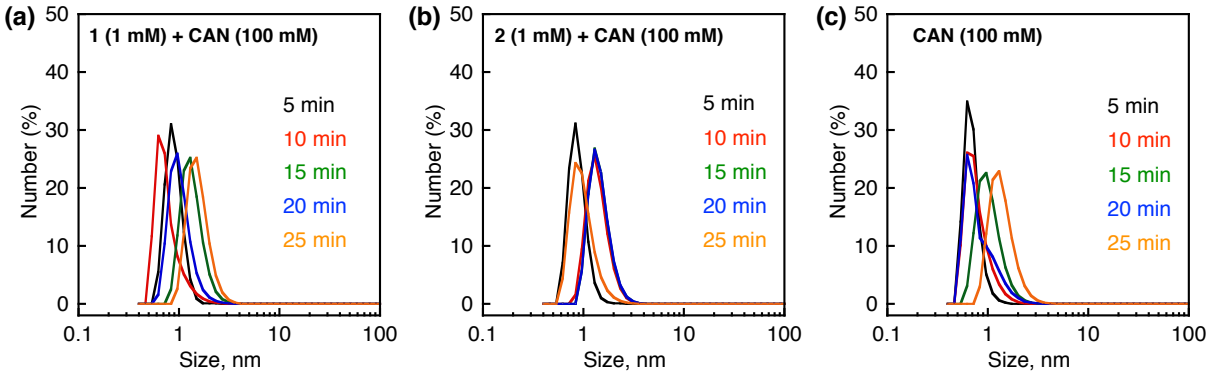

Figure S12. Particle size distribution determined by dynamic light scattering (DLS) measurements of non-buffered aqueous solutions of (a) **1** (1.0 mM) plus CAN (0.10 M), (b) **2** (1.0 mM) plus CAN (0.10 M), and (c) only CAN (0.10 M) at reaction times of 5.0 min (black line), 10 min (red line), 15 min (green line), 20 min (blue line), and 25 min (orange line).

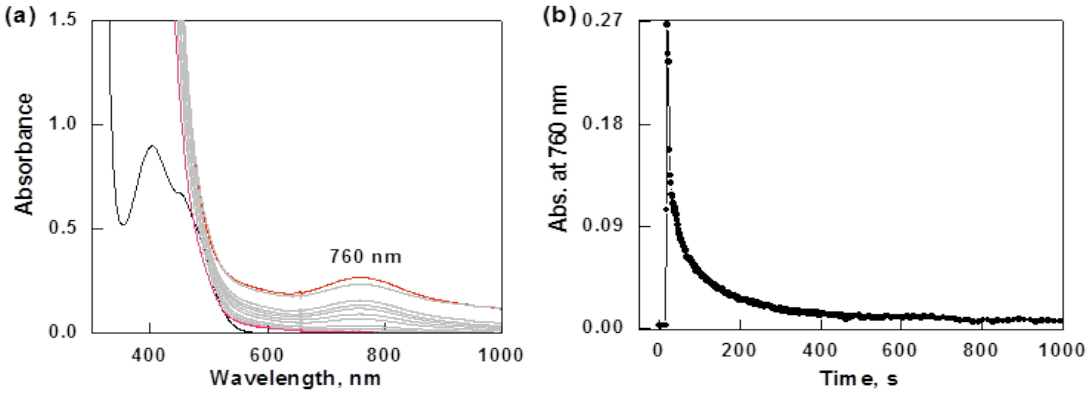

Figure S13. (a) UV-vis spectral changes observed in the water oxidation by CAN (0.10 M) in the presence of **1** (1.0 mM) in a non-buffered aqueous solution. (b) Time courses of the decay of absorption band at 760 nm due to $[Fe^{IV}(BQEN)(O)]^{2+}$ in the water oxidation by CAN (0.10 M) in the presence of **1** (1.0 mM).

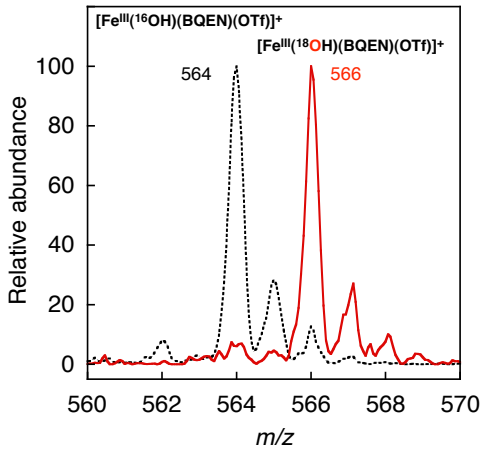

Figure S14. ESI-MS spectra of the solutions obtained in the reaction of **1** (1.0 mM) with CAN (2.0 mM) in $H_2{}^{16}O$/MeCN [1:4 (v/v), black dots] and $H_2{}^{18}O$/MeCN [1:4 (v/v), red line]. The peaks at m/z 564.0 and 566.0 correspond to $[Fe^{III}(BQEN)(^{16}OH)(OTf)]^+$ and $[Fe^{III}(BQEN)(^{18}OH)(OTf)]^+$ (calcd *m/z* = 564.1 and 566.1, respectively).

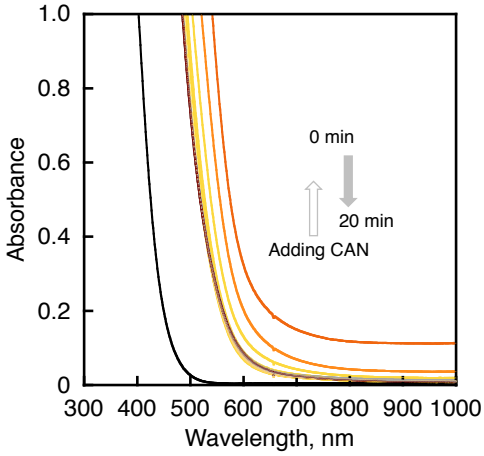

Figure S15. UV-vis spectral changes of an aqueous solution containing CAN (0.10 M), **1** (1.0 mM) and HNO_3 (0.10 M).

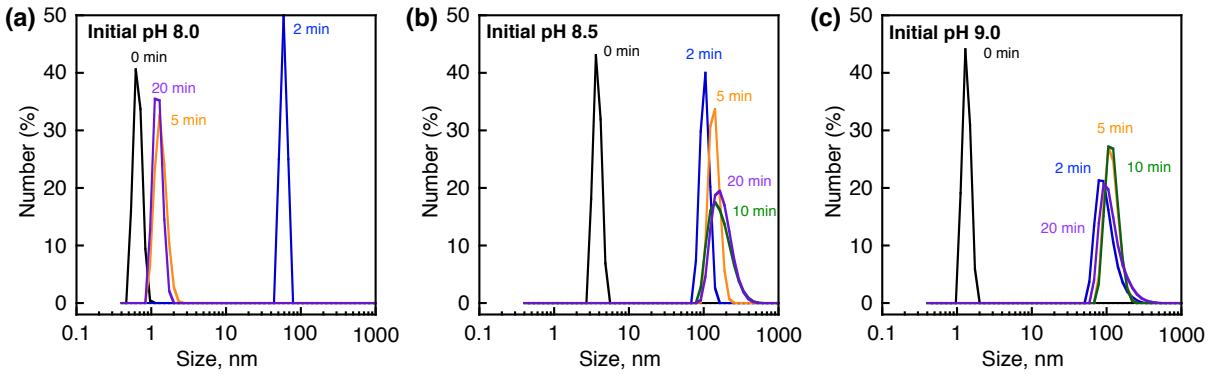

Figure S16. Particle size distribution determined by DLS measurements at initial pH (a) 8.0, (b) 8.5, and (c) 9.0 in borate buffer solutions containing **1** (5.0 μM), $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (0.25mM) at the irradiation times of 2.0 min (blue line), 5.0 min (orange line), 10 min (green line), and 20 min (purple line). The black line shows the particle size distribution in the absence of **1** at 0 min.

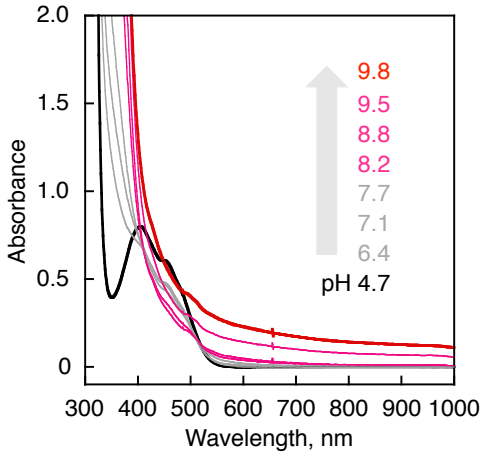

Figure S17. UV-vis spectral changes observed for the titration of a non-buffered aqueous solution (2.0 mL) containing **1** (1.0 mM) with NaOH.

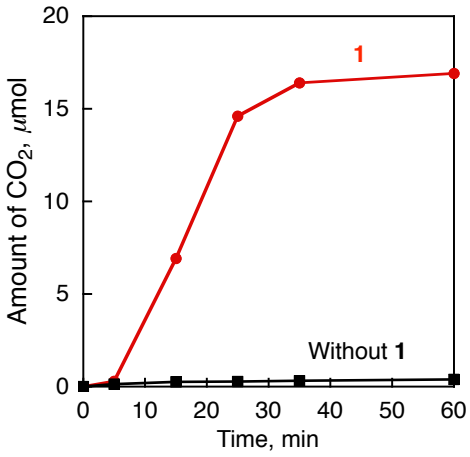

Figure S18. Time courses of CO_2 evolution under photoirradiation ($\lambda > 420$ nm) of a borate buffer solution (0.10 M, 2.0 mL) containing $Na_2S_2O_8$ (25 mM) and $[Ru(bpy)_3]SO_4$ (0.25 mM) in the absence (black squares) and presence of **1** (1.0 mM, red cycles). The CO_2 evolution was quantified by GC.

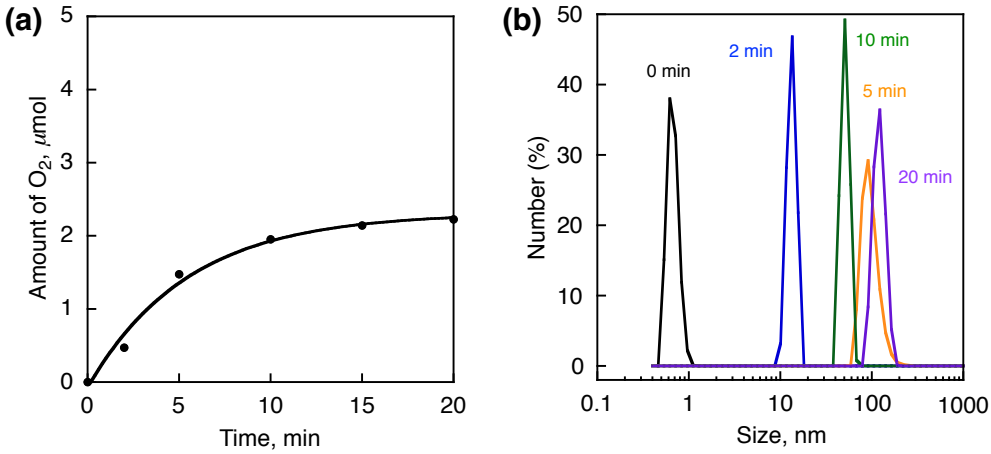

Figure S19. (a) Time course of O_2 evolution under photoirradiation ($\lambda > 420$ nm) of a borate buffer solution (0.10 M, 2.0 mL, initial pH 9.0) containing $Na_2S_2O_8$ (5.0 mM), $[Ru(bpy)_3]SO_4$ (0.25 mM), and **2** (5.0 μM). (b) Particle size distribution determined by DLS measurements at initial pH 9.0 in a borate buffer solution containing **2** (5.0 μM), $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (0.25mM) at the irradiation times of 2.0 min (blue line), 5.0 min (orange line), 10 min (green line), and 20 min (purple line). The black line shows the particle size distribution in the absence of **2** at 0 min.

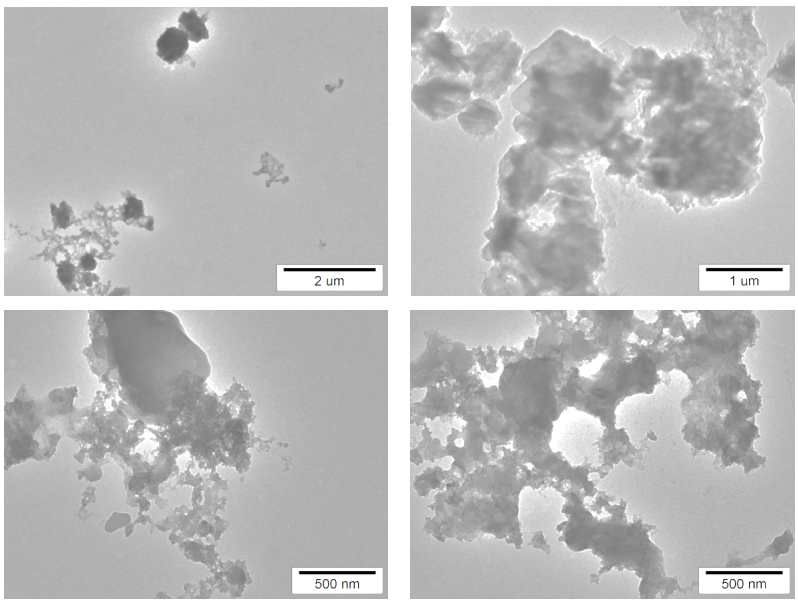

Figure S20. TEM images of the isolated particles formed in a borate buffer solution (0.10 M, 2.0 mL) containing $Na_2S_2O_8$ (5.0 mM), $[Ru(bpy)_3]SO_4$ (0.25 mM) and **1** (1.0 mM).