### Electronic Supplementary Information for

# Two-electron oxidation of water to form hydrogen peroxide catalysed by Silicon-porphyrins

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### ESI 1: Coordination of water molecules as the axial ligands of SiTPyP in acetonitrile.

Figure ESI 1 Absorption spectral change upon addition of water to acetonitrile solution of SiTPyP (left) and Benesi-Hildebrand type plot to deduce equilibrium constant K.

## ESI 2-1: Isosbetic points observed in the red shift region upon acid titration of SiTPyP (1.6 $\mu$ M) in CH<sub>3</sub>CN/H<sub>2</sub>O (8/2 v/v).



Figure ESI 2-1 Isosbetic points observed in the red shift region upon acid titration of SiTPyP (1.6  $\mu$ M) in CH<sub>3</sub>CN/H<sub>2</sub>O (8/2 v/v).

ESI 2-2: Blue shift of the absorption spectrum of SiTPyP (1.6  $\mu$ M) in CH<sub>3</sub>CN/H<sub>2</sub>O (8/2 v/v) upon acid titration from pH = 2.3 down to pH = 0.01.



ESI 3: Eight-step change of the absorption spectrum of SiTPyP under various pH conditions.



Figure ESI 3 Inflection points against pH values for the red shift processes (left) and the blue shift ones (right). The pKa value of each acid/base equilibrium relation was determined by the inflection point in the plot between the absorbance at fixed wavelength against the pH values. [SiTPyP] =  $1.6 \ \mu\text{M}$  in CH<sub>3</sub>CN/H<sub>2</sub>O (8/2 v/v) The pH was adjusted by the addition of H<sub>2</sub>SO<sub>4</sub>.

#### ESI 4: Saturation phenomena of the anodic current caused by SiTPyP

Saturation phenomena of the anodic current caused by SiTPyP (0.2mM) CH<sub>3</sub>CN/H<sub>2</sub>O (8/2 v/v) against scan rate of applied potential in CV measurement, indicating catalytic process. BDD as anode, Ag/AgNO<sub>3</sub> as reference electrode, Pt wire as the counter electrode, and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> (0.1M) as electrolyte.



Figure ESI 4 Saturation phenomena of the anodic current caused by SiTPyP (0.2mM) CH<sub>3</sub>CN/H<sub>2</sub>O (8/2 v/v) against scan rate of applied potential in CV measurement, indicating catalytic process. BDD as anode, Ag/AgNO3 as reference electrode, Pt wire as the counter electrode, and  $(C_4H_9)_4N^+PF_6^-$  (0.1M) as electrolyte. CV curves under various scan rate of applied potential (left) and the anodic current expressed as *I*c (catalytic current) against the scan rate of applied potential (v / Volt s<sup>-1</sup>) (right).

### ESI 5: Experimental procedure for quantitative estimation of free hydrogen peroxide.

The reagent, tetrapyridylporphyrinatetitanium (TiTPyP), was purchased from TCI Chemicals and the standard aqueous solution ( $3 \times 10^{-5}$ M) in 1 M sulphuric acid was prepared. The reaction mixture (pH = 12.5) after the electrolysis was acidified by aqueous sulfuric acid solution (H<sub>2</sub>SO<sub>4</sub>: 1 M) into acid solution (0.2 M of H<sub>2</sub>SO<sub>4</sub>) and was passed through a silica gel column. SiTPyP was effectively adsorbed on silica gel and was removed from the reaction mixture. The decolorized solution (2 mL) was mixed with standard solution of TiTPyP (1 mL,  $3 \times 10^{-5}$  M in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution) and stirred in the dark for 30 min. The amount of hydrogen peroxide was quantitatively estimated using a spectroscopic method to observe the increase of the absorbance at  $\lambda = 450$  nm in the difference spectrum between the two samples with and without the TiTPyP treatment in comparison with a calibration graph. The silica gel was found not to decompose hydrogen peroxide during the procedure, while simple distillation of the reaction mixture caused substantial decomposition of hydrogen peroxide.

#### ESI 6: Oxidative titration of electrolysis solution with KMnO<sub>4</sub> solution.

The solution after electrolysis were used to estimate the total peroxide produced during electrolysis. The solution were acidified with 1M sulphuric acid and aqueous solution of KMnO<sub>4</sub> with known concentration was added. The KMnO<sub>4</sub> band at 470 nm found to be raised after consuming the peroxides in the solution. The titration end point was determined by plotting  $\Delta$ O.D.470 nm vs. concentration of KMnO<sub>4</sub> added as shown below for Run 1 as the typical example. The amount of

peroxide in the total solution were calculated based on the dilution factors and stoichiometry of reaction between hydrogen peroxide and  $KMnO_4$ .



 $2KMnO_4+5H_2O_2+3H_2SO_4 \rightarrow 2MnSO_4+K_2SO_4+5O_2+8H_2O$ 

Figure ESI 6 KMnO<sub>4</sub> titration curve for Run 1 End point concentration of KMnO4 = 56.6  $\mu$ M Peroxide equivalent to 25micrM KMnO4 = 37.4 x 5/2 = 93.5  $\mu$ M Concentration of peroxide in electrolysis solution = 93.5 x 6/4(dilution factor) = 140.25  $\mu$ M = 1.82  $\mu$ moles

ESI 7: Absorption spectra of the reaction mixture before and after the controlled potential electrolysis at 0.92 Volt vs Ag/AgNO<sub>3</sub>.



Figure ESI 7 Absorption spectra before and after the controlled potential electrolysis of water catalysed by SiTPyP(O<sup>-</sup>)<sub>2</sub> (0.15 mM) in CH<sub>3</sub>CN/H<sub>2</sub>O (7/3 v/v) at the applied potential 0.92 Volt vs Ag/AgNO<sub>3</sub> with [(Bu)4NPF6]= 0.1 M as electrolyte in the presence of Na<sub>2</sub>CO<sub>3</sub> (0.1M). (Run 2 in Table 1)

#### ESI 8. Calculation procedures for the incorporation of O-18.



On the basis of the observed total number of electrons in the <sup>18</sup>O study (see above), the turnover number of the catalyst in the system was calculated by the following procedures.

Number of electrons at 360 min = 19.5  $\mu$ moles, which compares with the sum of the amount of products (= 16.76  $\mu$ moles electron) of oxygen detected (= 10.72 (2.68 x 4)  $\mu$ moles electron) and the amount of hydrogen peroxide plus peroxide complex (= 6.04 (3.02 x 2)  $\mu$ moles electron).

The total number of electrons (19.5  $\mu$ moles) = (number of reaction cycle in the unit of  $\mu$ moles) x (4(number of electron for O<sub>2</sub> formation) x fraction of O<sub>2</sub> formation (0.54) + 2(number of electron for H<sub>2</sub>O<sub>2</sub> formation) x fraction of H<sub>2</sub>O<sub>2</sub> formation (0.31).

The number of reaction cycle in the unit of  $\mu$ moles is thus calculated to be 19.5/2.78 = 7.01  $\mu$ moles. Based on the relation, catalyst turnover number in the system = (number of reaction cycles in the unit of  $\mu$ moles) / (total number of catalyst in the unit of  $\mu$ moles) = (7.01  $\mu$ moles / (2.25  $\mu$ moles) = 3.1 cycles per catalyst.

The isotope incorporation in the reaction with 10%  $H_2^{18}O$  was thus calculated to be  ${}^{32}O_2 - 83\%$ ,  ${}^{34}O_2 - 15.7\%$ ,  ${}^{36}O_2 - 0.7\%$ , for the three cycles of the catalytic reaction as shown below.

Isotope distribution among $O_2$ formed.	<sup>16</sup> O- <sup>16</sup> O	<sup>16</sup> O- <sup>18</sup> O	<sup>18</sup> O- <sup>18</sup> O
Accumulated ratio in the 1 <sup>st</sup> cycle	1.0 x 0.9	1.0 × 0.1	0.0 x 0.0
in the 2 <sup>nd</sup> cycle	0.9 x 0.9	(0.1 x 0.9) + (0.9x0.1)	0.1 x 0.1
in the 3 <sup>rd</sup> cycle	0.9 x 0.9	(0.1 x 0.9) + (0.9x0.1)	0.1 x 0.1
in the 3.1 <sup>th</sup> cycle	(0.9x0.9) x 0.1	[(0.1 x 0.9) + (0.9x0.1)]x0.1	(0.1 x 0.1)x0.1
Total uptake expected			
(averaged over 3.1 cycles)	0.84	0.154	0.0067

### ESI 9: Isotope labeled experiment for hydrogen peroxide detection using catalase enzyme.

The reaction mixture (3 mL) after the controlled potential electrolysis of water catalyzed by SiTPyP was neutralized with 40  $\mu$ l of 1 M aqueous H<sub>2</sub>SO<sub>4</sub> and phosphate buffer (60  $\mu$ l, pH 6.8) was added. The mixture was degassed by repeated freeze-thaw-vacuum cycles (3×) and was stored under nitrogen atmosphere. Catalase solution (10 mL, 1 g/L) was also degassed in the same manner. The oxygen-free catalase solution (1 mL, 1 g/L) was carefully injected into the SiTPyP solution and stirred well to allow the conversion of hydrogen peroxide into molecular oxygen, as indicated by the equation below. The isotope distribution of molecular oxygen in the gas phase sample was analyzed by GC-MS.

 $2H_2O_2 \xrightarrow{Catalase} O_2 + 2H_2O$ 

### ESI 10: Spectrophotometric studies for the complex formation between SiTPyP with hydrogen peroxide under different pH conditions.

The formation of peroxide complex of SiTPyP with hydrogen peroxide as the axial ligand was confirmed by mixing an aqueous solution of hydrogen peroxide with SiTPyP solution under different conditions. Basic condition with sodium hydroxide (pH = 12.5) in the presence of sodium sulphate (0.1 M) was examined.

Estimation of equilibrium constants K1

SiTPyP was found to be form complex with hydrogen peroxide efficiently under neutral or slightly acidified condition. The first process occurs under very low concentration of hydrogen peroxide. So simple Benesi-Hildebrand treatment should be modified for the equilibrium process.

К  $[SiTPyP] + [H_2O_2]$  $\rightleftharpoons$  [SiTPyP(OOH)] Initial 0 C<sub>0</sub>  $C_1$  $C_1 - C_0 X$ C<sub>0</sub>(1-X)  $C_0 X$ After COX (CO(1 - X))(C1 - COX) $KC0^{2}X^{2} - x[KC0(C1 + C0) + C0) + KC0C1 = 0$  $(\text{KC1} + \text{KC0} + 1) - \sqrt{(\text{KC1} + \text{KC0} + 1)^2 - 4K^2C0C1}$ X = 2KC0Ax<sup>2</sup>+Bx+C=0 form (solution with + term is invalid due to at C1=0 the equation is not giving zero result)  $\Delta OD = CO \Delta E X$  $CO = [SiTPyP], C1 = [H_2O_2]$ The equation could be expanded as follow  $\Delta OD + \frac{\Delta \mathcal{E}^2 [SiTPyP][H2O2]}{\Delta OD} = \Delta \mathcal{E}[H2O2] + \Delta \mathcal{E} \left( [SiTPyP] + \frac{1}{K} \right)$ Y = mX + C form, where plot between  $\Delta OD + \frac{\Delta \mathcal{E}^2 [SiTPyP][H2O2]}{\Delta OD}$  vs. [H2O2] will fit to ΔOD straight line and from the intercept of the plot K were estimated



Slope =  $\Delta \mathcal{E} = 4.79 \times 10^4$  Intercept =  $\Delta \mathcal{E} \left( [SiTPyP] + \frac{1}{K} \right) = 3.69 \times 10^2$ [SiTPyP] = 0.12 x 10<sup>-6</sup> M K = 1.2 x 10<sup>2</sup> M<sup>-1</sup>

### ESI 11: Experimental set-up for the controlled potential electrolysis in separated cell.

The salt-bridge was prepared by a conventional method using potassium nitrate (1 M) with agar (Kanto Chem., 2 g in 100 mL of water) made into solution at  $90^{\circ}$ C for 30 min under stirring. The uniformity of the slurry was checked, and it was filled carefully in a specially made U-tube without any gas bubble inclusion. The U-tube was thoroughly filled and maintained at room temperature overnight. Both terminals of the prepared salt-bridge were immersed in 30% aqueous acetonitrile containing 0.1M TBAPF<sub>6</sub>. The electrical conductance was confirmed by checking the cyclic voltammetry with and without salt bridge.