

Supplementary Information

Competitive inhibition of metal-free porphyrin oxygen-reduction catalyst by water

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1. Experimental details

All chemicals were used as received. Bis(triphenylphosphoranylidene) ammonium chloride (BTPPACl, >98%), 5,10,15,20-*meso*-tetraphenylporphyrin (H₂TPP, >99%, lot no. 25996KH), bis(η^5 -cyclopentadienyl)iron(II) (Fc, 98%) were purchased from Sigma-Aldrich. DCE (puriss.p.a.) and Lithium tetrakis(pentafluorophenyl)borate ethyl etherate (LiTB) were obtained from Fluka. Tetrakis(pentafluorophenyl)boric acid (HTB) was synthesized in the crystalline form following a procedure similar to that employed for the synthesis of tetrakis[3,5-bis(trifluoromethyl)phenyl]boric acid.^{S1} BTPPATB, which was used to adjust the concentration of TB⁻ in DCE, was prepared by metathesis of LiTB and BTPPACl.

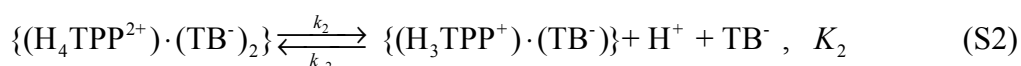
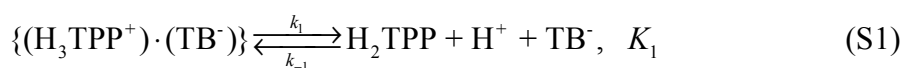
Water content (ppm, w/w) in the DCE solutions was determined by DL39 Karl Fischer Coulometer (Mettler Toledo). DCE in the freshly opened bottle received from Sigma-Aldrich contained 4.8 mM (70 ppm) of water. After three weeks of drying over 3Å molecular sieve the water content dropped to the level of 69 µM H₂O (1 ppm). Solutions for the stopped-flow measurements were prepared from a dried solvent with various amounts of highly purified water (Milli-Q Gradient, Millipore) added, e.g., 10 microlitres of water added to 100 ml of dry DCE made 79.6ppm solution of water). In spite of the fact that all respective chemicals were over a long period stored in the dissicator before use, the prepared solutions generally exhibited certain increase in the resulting water content compared to the pure solvent. That is why the water content was determined in all prepared solutions separately and the initial water content was considered as the average water content of the relevant injected solutions couple. Before the use the molecular sieve 3Å (Aldrich) was regenerated by heating in the oven at 300°C for 24 hours.

Stopped-flow kinetic measurements were performed at the ambient temperature 25 ± 2 °C on a USB2000+ UV/Vis fiber optic spectrometer (Ocean Optics, U.S.A.) with a sampling time of 1 ms. The air-saturated DCE solution of Fc was mixed with the air-saturated DCE solution of HTB and H₂TPP, or HTB, H₂TPP and BTPPATB in a quartz cuvette (path length 0.2 cm) using a single-mixing instrument SFA-20 (TgK Scientific, UK). Rate of the Fc to Fc⁺ conversion was monitored by a rise in absorbance at the wavelength $\lambda=300$ nm due to Fc⁺ ($\epsilon = 7938 \text{ M}^{-1}\text{cm}^{-1}$).

2. Numeric simulations of the Fc⁺ formation

Time profiles of the Fc⁺ concentrations were fitted with the help of the commercial simulation software (KinFitSim 3.0, BASi) for the mechanism comprising

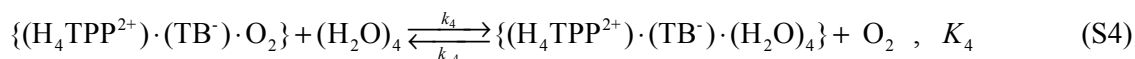
(a) monoacid and diacid dissociation equilibria:



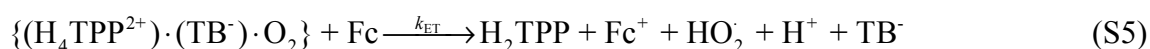
(b) exchange reaction describing the competitive inhibition of the catalyst by TB⁻:



(c) exchange reaction describing the competitive inhibition of the catalyst by (H₂O)₄:



(d) irreversible electron transfer from Fc to the O₂ complex:



(d) irreversible reduction of $\text{HO}_2^\bullet$ with Fc to H_2O_2 :



The effects of the Fc and H_2TPP concentrations indicated that the reduction of the complex $\{(\text{H}_4\text{TPP}^{2+})\cdot(\text{X}^-)\cdot\text{O}_2\}$ with Fc is the rate-determining step.^{S2} Therefore, the second-order rate constant k_{ET} characterizing the electron transfer between the oxygen complex and Fc, cf. eq. S5, was considered to be a variable of the numeric fit, while all other rate constants were fixed and assumed to have as high as possible values compatible with the known acid dissociation constants $K_1 = k_1 / k_{-1} = 8 \times 10^{-13} \text{ M}^2$ and $K_2 = k_2 / k_{-2} = 5 \times 10^{-9} \text{ M}^2$,^{S2} and with the equilibrium constants $K_3 = k_3 / k_{-3} = 3.3 \times 10^6$ and $K_4 = k_4 / k_{-4} = 3 \times 10^5$, as estimated from the DFT data. The highest value of the second-order rate constant was supposed to be represented by the diffusion-controlled limit of $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The highest value of the third-order rate constant, such as that characterizing the acid association reactions described by eq. S1 and S2, was supposed to be $2 \times 10^{13} \text{ M}^{-2} \text{ s}^{-1}$, as formally derived from the diffusion-controlled limit divided by the typical acid concentration (0.5 mM). Rate constants used as the fixed parameters were: $k_{-1} = 2 \times 10^{13} \text{ M}^{-2} \text{ s}^{-1}$, $k_1 = 16 \text{ s}^{-1}$, $k_{-2} = 2 \times 10^{13} \text{ M}^{-2} \text{ s}^{-1}$, $k_2 = 1 \times 10^5 \text{ s}^{-1}$, $k_{-3} = 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $k_3 = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{-4} = 1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $k_4 = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_6 = 2 \times 10^{13} \text{ M}^{-2} \text{ s}^{-1}$.

3. DFT calculations

DFT calculations were performed using Gaussian 09 software package.^{S3} Counteranions were included in the quantum mechanical region, and the solvent effect was modeled by the polarizable continuum model (PCM).^{S4} Density functional M05-2X^{S5} designed for the correct description of the non-covalent interactions was chosen and together with 6-31G* polarized double- ζ basis sets were used for geometry optimizations and calculations of free energies. Geometry optimizations were accomplished by means of the vibrational analysis in order to characterize the stationary points (for minima no imaginary frequencies were found). G09 uses vibrational frequencies for calculation of the zero-point energies, and the vibrational contributions to the partition functions needed for enumeration of Gibbs free energies. Stabilization energies were calculated at M05-2X/6-311++G** level for the M05-2X/6-31G*

optimized geometries following the procedure that has been recently used to evaluate weak interactions in the Lewis pairs.^{S7} Optimized structures of complexes of $\{(H_4TPP^{2+}) \cdot (TB^-)\}$ with H_2O , H_2O_2 , $(H_2O)_2$, $(H_2O)_3$ and O_2H are together with the averaged O-H distances depicted in figures S1 – S3.

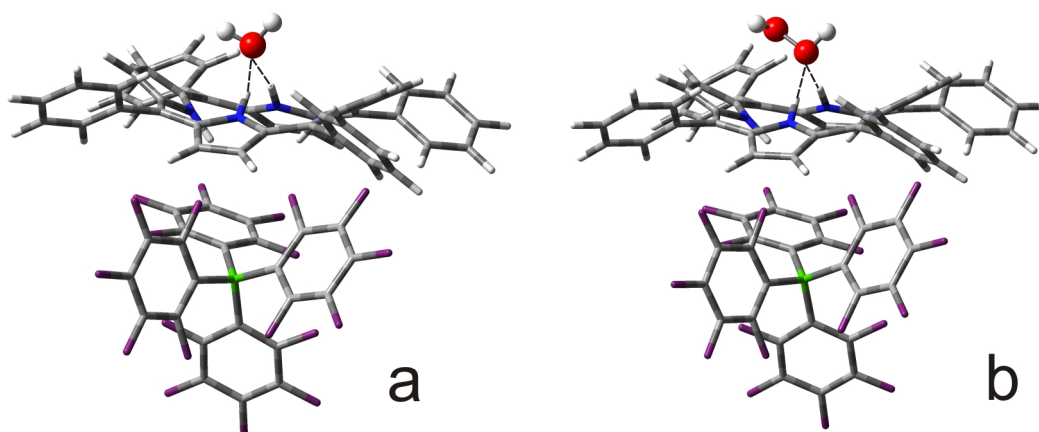


Fig. S1 DFT/M05-2x optimized structure of (a) $\{(H_4TPP^{2+}) \cdot (TB^-) \cdot (H_2O)\}$ and (b) $\{(H_4TPP^{2+}) \cdot (TB^-) \cdot (H_2O_2)\}$ systems; the averaged O-H(N) distances were calculated to be 1.860 Å and 1.944 Å for H_2O and H_2O_2 , respectively.

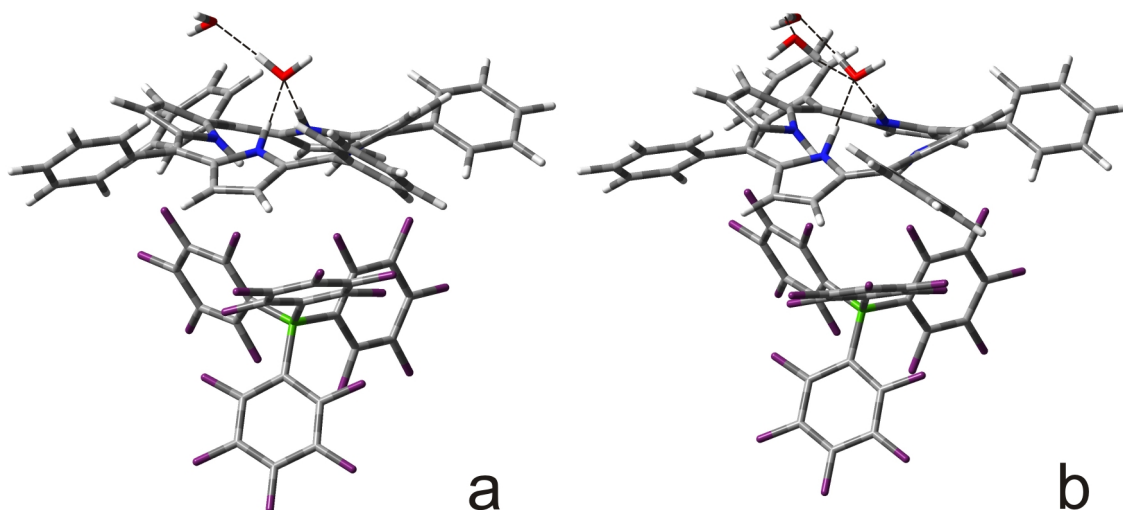


Fig. S2 DFT/M05-2x optimized structure of (a) $\{(H_4TPP^{2+}) \cdot (TB^-) \cdot (H_2O)_2\}$ and (b) $\{(H_4TPP^{2+}) \cdot (TB^-) \cdot (H_2O)_3\}$ systems; the averaged O-H(N) distances were calculated to be 1.805 Å and 1.861 Å for $(H_2O)_2$ and $(H_2O)_3$, respectively.

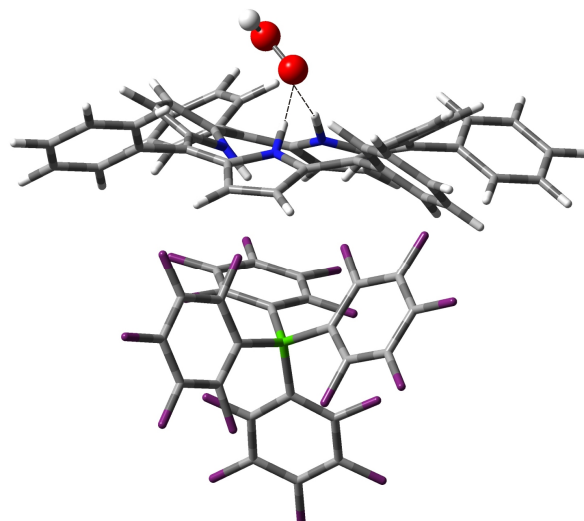


Fig. S3 DFT/M05-2x optimized structure of (a) $\{(H_4TPP^{2+}) \cdot (TB^-) \cdot (HO_2^\bullet)\}$ system; the averaged O-H(N) distance was calculated to be 1.985 Å. Stabilization energy of $HO_2^\bullet$ is 0.386 eV, free energy $\Delta G(L)$ for the extraction of the ligand $HO_2^\bullet$ is -0.049 eV.

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