

Supplementary Information

Fine tuning of the catalytic effect of a metal-free porphyrin on the homogeneous oxygen reduction

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Experimental details: All chemicals were used as received. Fc (>98%), and H₂TPP (>99%) were purchased from Sigma-Aldrich. The same results were obtained with the commercial sample of H₂TPP (lot no. 25996KH) and with H₂TPP synthesized following the procedure described elsewhere.^{S1} DCE (puriss.p.a.) and LiTB ethyl etherate were obtained from Fluka. HTB was synthesized in the crystalline form following a procedure similar to that employed for the synthesis of HTFPB.^{S2} The UV/Vis spectra and stopped-flow kinetic measurements were performed with a single-mixing instrument SFA-20 (TgK Scientific, UK) using a Perkin-Elmer Lambda 25 spectrophotometer with a quartz cuvette (path length 0.2 cm) in the closed chamber of the spectrophotometer to prevent the photo-excitation of the porphyrin species. In the stopped-flow measurements, the air-saturated DCE solution of ferrocene was mixed with the air-saturated DCE solution of HTB, or HTB and H₂TPP. All measurements were carried out at the ambient temperature of 25±2 °C.

Monitoring of ferrocenium ion in DCE by UV/Vis spectroscopy: Formation of Fc⁺ in DCE can be monitored by a rise in absorbance at 250 -350 nm or at 500-700 nm (Figure S1). In the present study we used absorbance measured at $\lambda = 300$ nm ($\epsilon = 4529 \text{ M}^{-1}\text{cm}^{-1}$).

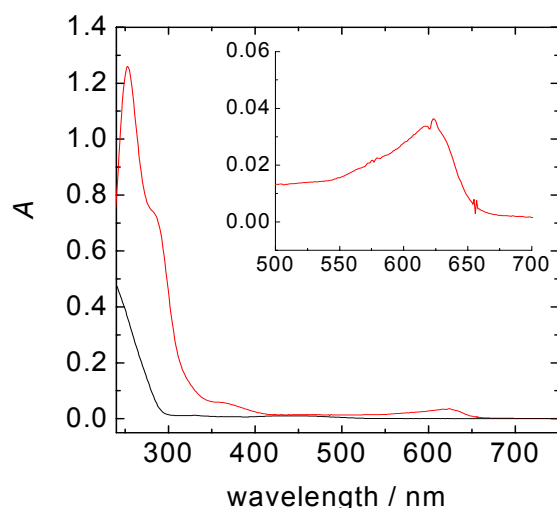
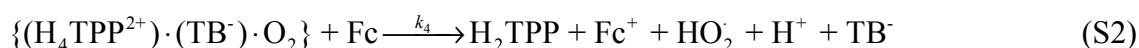
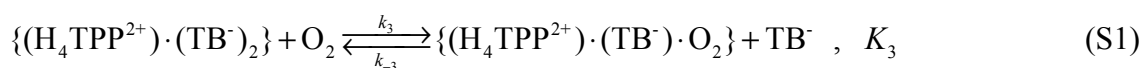


Figure S1. Absorption spectra of 1 mM Fc (black line), and 1 mM Fc fully oxidized with oxygen to Fc^+ in the presence of 0.02 M trifluoroacetic acid (red line). Inset: Absorption spectra of 1 mM Fc^+ in the range 500-700 nm showing the band centered at 620 nm ($\epsilon = 350 \text{ M}^{-1}\text{cm}^{-1}$). Cell path length 0.1 cm.

Equation for the initial rate: Let us consider the reaction mechanism



The equilibrium constant K_3 for the former reaction is given by

$$K_3 = \frac{k_3}{k_{-3}} = \frac{[\{(\text{H}_4\text{TPP}^{2+}) \cdot (\text{TB}^-) \cdot \text{O}_2\}][\text{TB}^-]}{[\{(\text{H}_4\text{TPP}^{2+}) \cdot (\text{TB}^-)_2\}][\text{O}_2]} \quad (\text{S3})$$

By applying the concept of the steady state to the concentration of the complex

$\{(\text{H}_4\text{TPP}^{2+}) \cdot (\text{TB}^-) \cdot \text{O}_2\}$, the initial rate v_0 can be described by the equation

$$v_0 = \frac{k_3 k_4 [\text{Fc}][\text{O}_2][\{(\text{H}_4\text{TPP}^{2+}) \cdot (\text{TB}^-)_2\}]}{k_{-3}[\text{TB}^-] + k_4[\text{Fc}]} \quad (\text{S4})$$

When $k_4 [\text{Fc}] \ll k_{-3} [\text{TB}^-]$, the initial rate v_0 can be expressed by the equation

$$v_0 = k_4[\text{Fc}][\{(H_4\text{TPP}^{2+}) \cdot (\text{TB}^-) \cdot \text{O}_2\}] \quad (\text{S5})$$

When $k_4 [\text{Fc}] \gg k_{-3} [\text{TB}^-]$, the rate v_0 reaches the limit, which is independent of the Fc concentration,

$$v_0 = k_3[\text{O}_2][\{(H_4\text{TPP}^{2+}) \cdot (\text{TB}^-)_2\}] \quad (\text{S6})$$

Since both Fc and O_2 are present at a large excess over H_2TPP , their concentrations are practically equal to the analytical ones, i.e. $[\text{Fc}] \approx [\text{Fc}]_0$ and $[\text{O}_2] \approx [\text{O}]_0$.

The effect of the oxygen concentration is less straightforward, because $[\text{O}]_0$ influences also the concentrations of the complexes $\{(H_4\text{TPP}^{2+}) \cdot (\text{TB}^-) \cdot \text{O}_2\}$ and $\{(H_4\text{TPP}^{2+}) \cdot (\text{TB}^-)_2\}$. The treatment above can be modified by assuming that the sum of the concentrations of the latter two complexes is constant that is approximately equal to the analytical concentration of H_2TPP ,

$$[\text{H}_2\text{TPP}]_0 \approx [\{(H_4\text{TPP}^{2+}) \cdot (\text{TB}^-) \cdot \text{O}_2\}] + [\{(H_4\text{TPP}^{2+}) \cdot (\text{TB}^-)_2\}] \quad (\text{S7})$$

Eq. S4 can be then replaced by

$$v_0 = k_4[\text{Fc}]_0[\{(H_4\text{TPP}^{2+}) \cdot (\text{TB}^-) \cdot \text{O}_2\}] \approx \frac{k_4[\text{Fc}]_0[\text{O}_2]_0[\text{H}_2\text{TPP}]_0}{[\text{O}_2]_0 + (k_{-3}[\text{TB}^-] + k_4[\text{Fc}]_0)/k_3} \quad (\text{S8})$$

which shows that the rate v_0 should be always proportional to the analytical concentration of H_2TPP .

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 after testing the performance of several density functionals (MPWB1K,^{S6} MPW1B95^{S6} M05-2X^{S5} and B3LYP) on the complex $\{(H_4\text{TPP}^{2+}) \cdot \text{O}_2\}$

without considering the counteranion. 6-31G* polarized double- ζ basis sets were used for geometry optimizations. Molecular structures were optimized without geometrical constraints. In order to characterize the stationary points, geometry optimizations were accomplished by means of the vibrational analysis. 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}

In addition to the optimized structures of complexes $\{(H_4TPP^{2+})\cdot(X^-)\cdot O_2\}$ ($X^- = Cl^-$, PF_6^- or TB^-), two stable forms **a** and **b** of the adduct $\{(H_4TPP^{2+})\cdot O_2\}$ were also found (Figure S2), of which the form **a** is more stable.

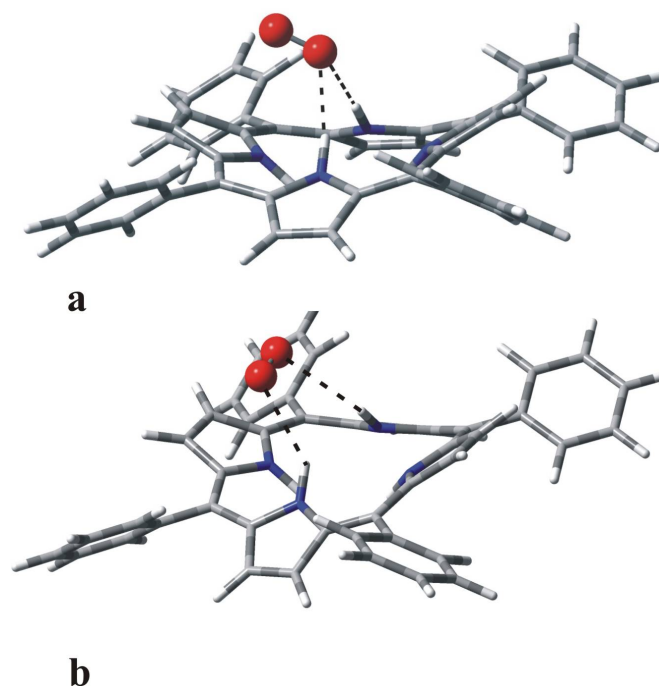


Figure S2. DFT/M05-2x/PCM optimized structures for the complex of H_4TPP^{2+} with O_2 , form **a** (top) and form **b** (bottom); the averaged O-H distances were calculated to be 2.279 Å and 2.702 Å, respectively. Their stabilization energies were found to be 0.201 eV and 0.191 eV, respectively. In vacuo DFT/M05-2x calculations gives the averaged O-H distances of 2.293 Å and 2.338 Å for **a** and **b** form, respectively. BSSE corrected M05-2x stabilization energies calculated in vacuo were 0.136 eV and 0.098 eV, respectively.

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