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COMMUNICATION

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

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The catalytic effect of tetraphenylporphyrin on the oxygen reduction with ferrocene in 1,2-dichloroethane can be finely tuned by varying the molar ratio of the acid to the catalyst present in the solution. The mechanism involves binding of molecular oxygen to the protonated free porphyrin base, in competition with ion pairing between the protonated base and the acid anion present.

Metalloporphyrins have been used to activate molecular oxygen for the controlled oxygenation of hydrocarbons,[1] as well as for the reduction of O_2 to hydrogen peroxide and/or to water in solution,[2] at liquid/liquid interfaces,[3] or at solid electrodes.[4] The activation process involves binding of O_2 to the metal center and the electron delocalization from the metal to O_2, which can be considered to be a coordinated superoxide or peroxide anion, *i.e.*, a stronger Brønsted base.[5] Protonation of the coordinated O_2 could then make it more susceptible to reduction.[6] The Density Functional Theory (DFT) method was used to investigate the role of O_2 and proton binding in the activation process.[7]

Recently, we have demonstrated that the oxygen reduction at the polarized water/1,2-dichloroethane (DCE) interface is catalyzed by 5-(*p*-aminophenyl)-10,15,20-tris(pentafluoro-phenyl)-porphyrin (H_2FAP),[8] and 5,10,15,20-*meso*-tetraphenyl-porphyrin (H_2TPP).[9] The diprotonated forms of these metal-free porphyrins, H_4FAP^{2+} and H_4TPP^{2+}, were asssumed to bind oxygen in a complex, which is reduced in the organic phase by ferrocene (Fc),[8] and decamethylferrocene (DMFc).[9] The homogeneous O_2 reduction was found to be catalyzed by H_4FAP^{2+} only in the DCE solutions acidified with tetrakis-(pentafluorophenyl)boric acid (HTB), while the reaction was quite slow in the presence of trifluoroacetic acid (HTFA).[8] The homogeneous reaction was proposed to follow the overall scheme,[8]

$$O_2 + 2\,Fc + 2\,H^+ \rightarrow H_2O_2 + 2\,Fc^+ \qquad (1)$$

In this communication, we report a significant acceleration of the reduction of O_2 with Fc in DCE in the presence of H_2TPP and HTB which, however, occurs within a rather narrow range of the acid-to-H_2TPP molar ratio. This fine tuning of the catalytic effect represents a new phenomenon in the non-metal catalysis of the O_2 reduction, which we have studied in the present work using absorption spectroscopy, stopped-flow kinetic measurements and the DFT calculations.

Fig. 1 (panel a) depicts the absorption spectrum of H_2TPP in the absence of HTB (black line) and a red shift of the Soret band upon protonation of H_2TPP in the presence of HTB at ratios of 1:1 (red line) and 1 : 2.5 (blue line). Like in the presence of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($TFPB^-$),[10] the absorption spectrum of the base (Soret band centered at 418 nm) changes into that of the diprotonated form (Soret band centered at 438 nm) without any isosbestic point, which indicates the intermediate formation of the monoprotonated form. Ion pairing between the mono- and diprotonated forms of H_2TPP and the counteranion X^- was proposed to be the key factor influencing the relative values of

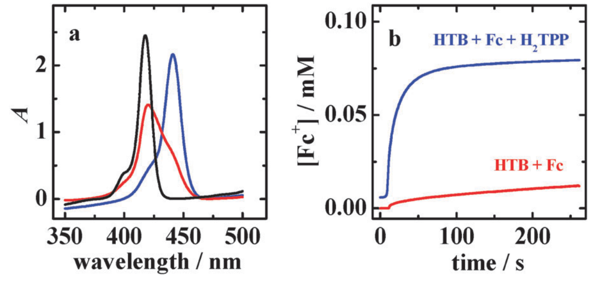

Fig. 1 (a) Absorption spectra of the air-saturated DCE solutions containing: 5×10^{-5} M H_2TPP (black line), 5×10^{-5} M H_2TPP and 5×10^{-5} M HTB (red line) or 1.25×10^{-4} M HTB (blue line). (b) Time profile of conversion of Fc to Fc^+ monitored at 300 nm (ε = 7938 M^{-1} cm^{-1}) in air-saturated DCE solutions containing 1 mM Fc and 1.25×10^{-4} M HTB (red line), or 1 mM Fc, 1.25×10^{-4} M HTB and 5×10^{-5} M H_2TPP (blue line). Cell path length 0.1 cm (a) or 0.2 cm (b).

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the equilibrium constants K_1 and K_2 for the two dissociation steps,[10] respectively,

$$\{(H_3TPP^+)\cdot(X^-)\} \leftrightharpoons H_2TPP + H^+ + X^-,\ K_1 \qquad (2)$$

$$\{(H_4TPP^{2+})\cdot(X^-)_2\} \leftrightharpoons \{(H_3TPP^+)\cdot(X^-)\} + H^+ + X^-,\ K_2 \qquad (3)$$

The [1]H NMR and IR data actually suggest that the protonation of H_2TPP is induced by ion pairing with the counteranion.[11] Successive formation of both the protonated forms was followed by ion transfer voltammetry in the presence of an excess of TB^- (5×10^{-3} M).[12] The reported acid dissociation constants $K_{1a} = K_1/[TB^-]_0 = 1.6 \times 10^{-10}$ M and $K_{2a} = K_2/[TB^-]_0 = 10^{-6}$ M,[12] yield $K_1 = 8 \times 10^{-13}$ M^2 and $K_2 = 5 \times 10^{-9}$ M^2, respectively, $[TB^-]_0$ denoting the analytical molar concentration of TB^-. As expected,[10] K_2 is considerably larger than K_1, while in the presence of small and strongly coordinated anions, such as Cl^- or TFA^-, the order of K_1 and K_2 is reversed.[8,10]

An addition of Fc (10^{-3} M) to the air-saturated solution of HTB in DCE containing O_2 (1.39×10^{-3} M)[13] leads to the formation of the ferrocenium cation (Fc^+), which can be identified by UV/Vis spectroscopy at 250–350 nm or 500–700 nm (Fig. S1, ESI†). Fig. 1 (panel b) shows the time profile of the conversion of Fc to Fc^+, as monitored by absorption measurement at 300 nm. The formation of Fc^+ proceeds considerably faster in the presence of H_2TPP in catalytic amounts (blue line) than in its absence (red line). Fig. 2 (panel a) illustrates the gradual colour change of the reaction mixture from green to orange. The absorption spectrum (panel b) suggests that the diprotonated form of H_2TPP (Soret band centered at 438 nm) almost disappears within *ca.* 1.5 min, while approximately 20% of the H^+ present remains to be bound in the monoprotonated form $\{(H_3TPP^+)\cdot(TB^-)\}$ (Soret band centered at *ca.* 425 nm).[10a] The reaction then proceeds rather slowly, *cf.* also Fig. 1b (blue line), until all the H^+ is consumed and the free porphyrin base (Soret band centered at 418 nm) is recovered. The light pink colour of its solution is overlapped by the deep orange colour of the dissolved Fc.

Fig. 3 (panel a) demonstrates the effects of the acid concentration and the addition of H_2TPP on the initial rate v of the Fc^+ formation, as evaluated from the initial slope of the absorbance A *vs.* time plot, *cf.* Fig. 1 (panel b). In the presence of HTB, but the absence of H_2TPP, the oxidation of Fc proceeds at a low rate, which is practically independent of the acid concentration (solid circles). In the presence of both HTB and H_2TPP, a significant enhancement of the initial rate is observed, which has a sharp maximum at the HTB concentration, 1.25×10^{-4} M (empty circles). In contrast, when HTB is replaced by HTFA, the reaction rate decreases to almost zero (empty squares), like for H_2FAP.[8] The enhancement, Δv_0, of the initial rate relative to that measured in the absence of H_2TPP exhibits non-linear dependences on the analytical concentrations of H_2TPP and of Fc, *cf.* the solid and empty circles, respectively, in Fig. 3 (panel b).

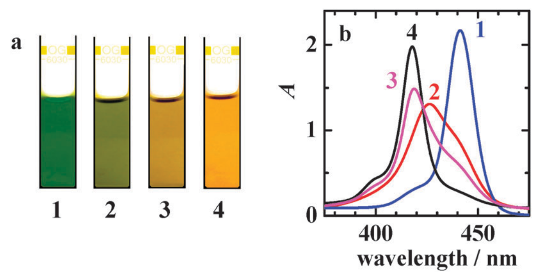

Fig. 2 Colour change (a) and absorption spectrum (b) of the reaction mixture containing 5×10^{-5} M H_2TPP and 1.5×10^{-4} M HTB in the air-saturated DCE solution prior (1), and 1.5 min (2), 60 min (3) and 200 min (4) after the addition of 10 mM Fc.

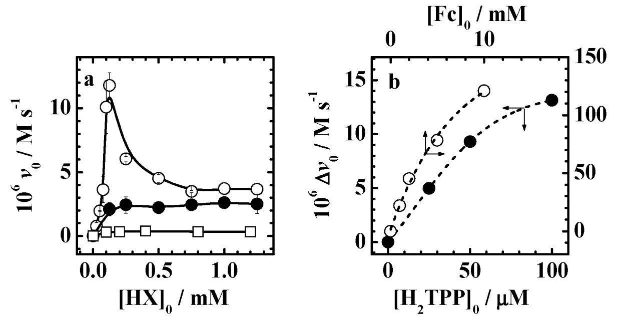

Fig. 3 (a) Initial rate v_0 of the formation of Fc^+ from Fc (1 mM) in the air-saturated DCE solution *vs.* the analytical concentration of HTB (○,●) or HTFA (□) in the presence (○, □) and absence (●) of 5×10^{-5} M H_2TPP. (b) Enhancement of the initial rate Δv_0 of the formation of Fc^+ *vs.* the analytical concentration $[H_2TPP]_0$ of H_2TPP (●) at the fixed ratio $[HTB]_0/[H_2TPP]_0 = 2.5$ and $[Fc]_0 = 10^{-3}$ M, and *vs.* the analytical concentration $[Fc]_0$ of Fc in the presence of 5×10^{-5} M H_2TPP and 1.25×10^{-4} M HTB (○).

These observations could be understood on the basis of the kinetic model, which involves the O_2 binding to the mono- or diprotonated forms of H_2TPP *via* the $NH^+\cdots O_2$ hydrogen bond.[8,9] An increased concentration of HTB results in an increased number of the NH^+ binding sites for O_2 which, however, are simultaneously being blocked with TB^-. As a result, the concentration of the O_2 complex, and thereby the O_2 reduction rate, should pass through a maximum. Since the maximum rate is observed at the HTB to H_2TPP molar ratio that is much larger than unity, the O_2 reduction is likely to be assisted by the diprotonated rather than monoprotonated H_2TPP form. The appropriate catalytic cycle consists of the reversible exchange of TB^- bound to H_4TPP^{2+} for O_2,

$$\{(H_4TPP^{2+})\cdot(TB^-)_2\} + O_2 \leftrightharpoons \{(H_4TPP^{2+})\cdot(TB^-)\cdot O_2\} + TB^-,\ K_3 \qquad (4)$$

that is followed by the irreversible reduction of the bound O_2,

$$\{(H_4TPP^{2+})\cdot(TB^-)\cdot O_2\} + Fc \rightarrow \{(H_3TPP^+)\cdot(TB^-)\} + Fc^+ + HO_2^\bullet \qquad (5)$$

and the regeneration of $\{(H_4TPP^{2+})\cdot(TB^-)_2\}$ through the acid association, eqn (3). The spontaneous reduction of the highly reactive $HO_2^\bullet$ with Fc is expected to yield H_2O_2 as the first stable reduction product.[8,10] The kinetic model predicts a non-linear dependence of the reduction rate, v_0, on the analytical concentration of Fc (eqn (S5) and eqn (S6), ESI†) and a linear dependence of v_0 on the analytical concentration of H_2TPP (eqn (S8), ESI†).

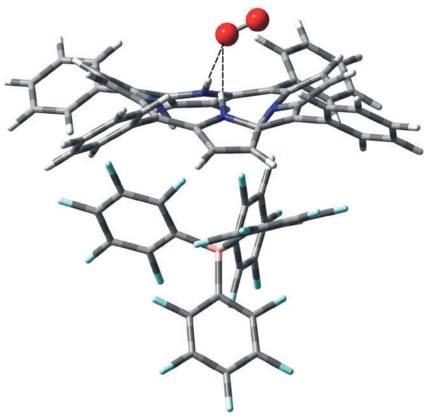

Fig. 4 DFT/M05-2x optimized structure of $\{(H_4TPP^{2+})\cdot(TB^-)\cdot O_2\}$ system; the averaged O–H distances were calculated to be 2.338 Å.

Table 1 DFT stabilization energies (eV) of X^- or O_2 in the complexes $\{(H_4TPP^{2+})\cdot(X^-)_2\}$ or $\{(H_4TPP^{2+})\cdot(X^-)\cdot O_2\}$, respectively, with PCM solvent correction. BSSE corrected values in vacuum are given in parentheses

Complex/X^-	Cl^-	PF_6^-	TB^-
$\{(H_4TPP^{2+})\cdot(X^-)_2\}$	0.971	0.914	0.759
	(4.222)	(3.489)	(2.514)
$\{(H_4TPP^{2+})\cdot(X^-)\cdot O_2\}$	0.112	0.101	0.118
	(0.099)	(0.096)	(0.110)

The binding and activation of O_2 in the complex $\{(H_4TPP^{2+})\cdot(X^-)\cdot O_2\}$, and the effects of ion pairing with the counteranion $X^- = Cl^-$, PF_6^- or TB^-, as well as the solvent effect on the stabilization energy of O_2 and of X^- were treated by the quantum chemical DFT method (ESI†). The optimized structure of $\{(H_4TPP^{2+})\cdot(TB^-)\cdot O_2\}$ is depicted in Fig. 4; analogous structures were found for Cl^- and PF_6^-. The stabilization energies were calculated at the M05-2X/6-311++G** level for the M05-2X/6-31G* optimized geometries, following the procedure that has recently been used to evaluate weak interactions in the Lewis pairs.[14] Table 1 demonstrates that the stabilization energies of O_2 (*i.e.*, the work required to extract O_2 from $\{(H_4TPP^{2+})\cdot(X^-)\cdot O_2\}$) are somewhat lower than those calculated for the end-on O_2 adduct with Co porphyrin (0.28 eV),[7] which is known to catalyze the oxygen reduction to H_2O_2 and/or H_2O.[2] It is worth noticing that the binding of O_2 in $\{(H_4TPP^{2+})\cdot(TB^-)\cdot O_2\}$ polarizes the O–O bond; the Mulliken charge at the O atom attached to H is −0.091, the remote O atom carries the charge of +0.251. The electron delocalization should facilitate the activation of O_2, similar to the complex with a metal porphyrin.[5] As expected, the stabilization energy of X^- (*i.e.*, the work required to extract X^- from $\{(H_4TPP^{2+})\cdot(X^-)_2\}$) decreases considerably with increasing size of the counteranion. The data in Table 1 also show that the inclusion of the solvent effect substantially diminishes the stabilization energies of the counteranions, while the stabilization energy for O_2 varies only slightly. The difference between the stabilization energies of X^- and O_2 points to a much stronger bond of the counteranion, which follows the order, $TB^- \ll PF_6^- < Cl^-$, indicating that small anions are likely to block the reaction site for dioxygen.

To summarize the results, we have shown that the catalytic effect of tetraphenylporphyrin on the reduction of molecular oxygen can be finely tuned by the acid-to-catalyst molar ratio. The catalytic mechanism involves the binding of O_2 to the diprotonated form of tetraphenylporphyrin, in competition with the counteranion present. We conclude that TB^- cannot be classified as a non-coordinating anion, on the contrary to the previous assumption.[8,10] The activation of O_2 by coordination to the acidic moiety of a metal-free porphyrin or the imidazolium ring[15] appears to be an alternative catalytic route to the redox catalysis of the O_2 reduction by metal porphyrins. This investigation is relevant to studies of the non-metal sites binding O_2 in biological enzyme-catalyzed oxidations.[16,17] Mechanistic considerations are supported by the DFT calculations.

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Notes and references

1 J. T. Groves, K. Shalyaev and J. Lee, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, CA, 2000, vol. 4, pp. 17–40.

2 (*a*) S. Fukuzumi, S. Mochizuki and T. Tanaka, *Inorg. Chem.*, 1989, **28**, 2459; (*b*) S. Fukuzumi, K. Okamoto, C. P. Gros and R. Guilard, *J. Am. Chem. Soc.*, 2004, **126**, 10441.

3 (*a*) I. Hatay, B. Su, F. Li, M. Mendez, T. Khoury, C. P. Gros, J. M. Barbe, M. Ersoz, Z. Samec and H. H. Girault, *J. Am. Chem. Soc.*, 2009, **131**, 13453; (*b*) B. Su, I. Hatay, A. Trojanek, Z. Samec, T. Khoury, C. P. Gros, J. M. Barbe, A. Daina, P.-A. Carrupt and H. H. Girault, *J. Am. Chem. Soc.*, 2010, **132**, 2655; (*c*) R. Partovi-Nia, B. Su, F. Li, C. P. Gros, J. M. Barbe, Z. Samec and H. H. Girault, *Chem.–Eur. J.*, 2009, **15**, 2335.

4 (*a*) E. Song, C. Shi and F. C. Anson, *Langmuir*, 1998, **14**, 4315; (*b*) C. Shi and F. C. Anson, *Inorg. Chem.*, 1998, **37**, 1037.

5 (*a*) R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139; (*b*) J. P. Collman, R. Boulatov, C. J. Sunderland and L. Fu, *Chem. Rev.*, 2004, **104**, 561.

6 J. P. Collman, P. S. Wagenknecht and J. E. Hutchison, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1537; J. Rosenthal and D. G. Nocera, *Acc. Chem. Res.*, 2007, **40**, 543.

7 D. Rutkowska-Zbik, R. Tokarz-Sobieraj and M. Witko, *J. Chem. Theory Comput.*, 2007, **3**, 914.

8 I. Hatay, B. Su, M. A. Mendez, C. Corminboeuf, T. Khoury, C. P. Gros, M. Bourdillon, M. Meyer, J. M. Barbe, M. Ersoz, S. Zalis, Z. Samec and H. H. Girault, *J. Am. Chem. Soc.*, 2010, **132**, 13733.

9 A. Trojánek, J. Langmaier, B. Su, H. H. Girault and Z. Samec, *Electrochem. Commun.*, 2009, **11**, 1940.

10 (*a*) G. De Luca, A. Romeo, L. M. Scolaro, G. Ricciardi and A. Rosa, *Inorg. Chem.*, 2007, **46**, 5979; (*b*) R. Karaman and T. C. Bruice, *Inorg. Chem.*, 1992, **31**, 2455.

11 Y. Zhang, M. X. Li, M. Y. Lü, R. H. Yang, F. Liu and K. A. Li, *J. Phys. Chem. A*, 2005, **109**, 7442.

12 B. Su, F. Li, R. Partovi-Nia, C. Gros, J.-M. Barbe, Z. Samec and H. H. Girault, *Chem. Commun.*, 2008, 5037.

13 P. Luhring and A. Schumpe, *J. Chem. Eng.*, 1989, **34**, 250.

14 G. Erős, H. Mehdi, I. Pápai, T. A. Rokob, P. Király, G. Tárkányi and T. Soós, *Angew. Chem., Int. Ed.*, 2010, **49**, 6559.

15 D. S. Choi, D. H. Kim, U. S. Shin, R. R. Deshmukh, S. Lee and C. E. Song, *Chem. Commun.*, 2007, 3467.

16 P. F. Widboom, E. N. Fielding, Y. Liu and S. D. Bruner, *Nature*, 2007, **447**, 342.

17 Y. Goto and J. P. Klinman, *Biochemistry*, 2002, **41**, 13637.

