Dioxygen binding of water-soluble iron(II) porphyrins in phosphate buffer at room temperature†

Christian Ruzié, Pascale Even and Bernard Boitrel*

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Two water-soluble tris(2-aminoethylamine) (tren) capped iron porphyrins were synthesized. The stability of their dioxygen adducts was studied in phosphate buffer, leading to half-life times around 7 min for the oxygenated species.

Introduction

Dioxygen transport and storage have been studied at the fundamental level for over 35 years as hemoglobin (Hb) and myoglobin (Mb) synthetic models.[1] In most studies, the models were composed of more or less functionalized porphyrins soluble in organic solvents such as toluene or benzene.[2] However, although water-solubility at physiological pH is a prerequisite for any efficient dioxygen carrier, this type of water soluble carrier based on synthetic heme is rather scarce in the literature.[3] Actually, in organic solvents, the main decomposition mechanism of the oxygenated complex occurs *via* formation of the μ-peroxo complex and is now properly controlled by steric hindrance.[4] Conversely, in a protic medium, the superoxo complex resulting from the coordination of dioxygen to a five-coordinated heme can be protonated according to the mechanism described by Momenteau and Reed (Scheme 1).[5] This mechanism also explains why species that cannot form dimers for steric reasons, are able to decompose.[6]

$$LPFe^{II} + O_2 \longrightarrow LPFe(O_2)$$
$$LPFe(O_2) + H_2O \longrightarrow LPFe^{III}(OH) + HO_2$$
$$2\,HO_2 \longrightarrow H_2O_2 + O_2$$

Scheme 1 Water-driven decomposition of oxygen adducts.

Various strategies have been used to investigate the few attempts to obtain stable dioxygen species in aqueous media. Among them, the formation of an ensemble composed of a cationic iron porphyrin embedded in a cyclodextrin unit *via* the fifth ligand of the iron was studied.[7] The half-life time of this complex at 5 °C in a mixture of DMF–water was 40 min. Another approach consisted of the formation of phospholipidic bilayer vesicles reported by Tsuchida *et al.* and leading to the more advanced system.[8] Indeed, starting from a known dioxygen carrier, namely the picket-fence of Collman,[9] the authors have elongated the original pickets with zwitterionic phospholipid groups. In an aqueous medium, these "lipido-porphyrins" form vesicles of about 100 nm of diameter. In the presence of an excess of axial base, the reversible formation of an oxygenated complex was observed, as its decomposition was delayed by the lipidic environment. Later on, the incorporation of the iron picket-fence porphyrin bearing an intramolecular fifth ligand on human serum albumin led to a particularly interesting system in a physiological medium.[10] For instance, the authors have demonstrated the efficiency of their system in delivering dioxygen in the organism while the oxygenated complex exhibited an *in-vivo* half-life time of 4.1 h at 37 °C. An impressive result was also reported by Kano *et al.* in 2005.[11] Indeed, they prepared a very stable 1 : 1 complex (hemoCD) between iron(II) *meso*-tetrakis-(*p*-sulfonatophenyl)porphyrin and a per-*O*-methylated β-cyclodextrin dimer having a pyridine linker. This complex was found to bind reversibly dioxygen in aqueous solution. More recently, a water-soluble cobalt porphyrin was reported and its dioxygen binding studied by ESR spectroscopy, with an iron analogue too transient to analyze.[12]

We ourselves have reported a series of tren-capped iron porphyrins with specially high affinities for dioxygen in organic solvents.[13] Recently, we have also probed the influence of a nitrophenol residue attached at the periphery of the tren pocket and shown that electrostatic repulsion could significantly decrease the dioxygen affinity in toluene.[14,15] However, these molecules suffer from a poor water-solubility and it appears that dioxygen binding of a synthetic five-coordinate iron(II) porphyrin alone has not been studied in an aqueous medium, so far. This is the reason why, herein, we report the synthesis of various alkylated and acylated tren-capped iron porphyrins as well as the study of two water-soluble synthetic heme complexes towards dioxygen binding at room temperature.

Results and discussion

Starting from porphyrin **1** for which a high affinity for dioxygen has been measured in toluene, the basic idea of this study consists of tethering on the tren residue various groups that are expected to induce water-solubility. Therefore, it was logical to select groups such as aliphatic acids, polyethylene glycol derivatives (PEG) or methyl pyridinium as these three residues grafted at the periphery of a macrocycle lead usually to water soluble compounds.[16] Thus, porphyrin **1** was first alkylated with 2-bromoethyl acetate and the resulting porphyrin **2** was treated with potassium hydroxide in ethanol to saponify the two ester groups, leading to **3**. Unfortunately, the latter proved not to be water-soluble at all.

Therefore, we decided to acylate the two secondary amino functions of **1** with succinic anhydride. Indeed, with this synthetic

Université de Rennes1, Sciences Chimiques de Rennes, UMR CNRS 6226 (I.C.M.V.), 35042, Rennes Cedex, France. E-mail: Bernard.Boitrel@univ-rennes1.fr; Fax: (+33)2 2323 5637; Tel: (+33)2 2323 5856

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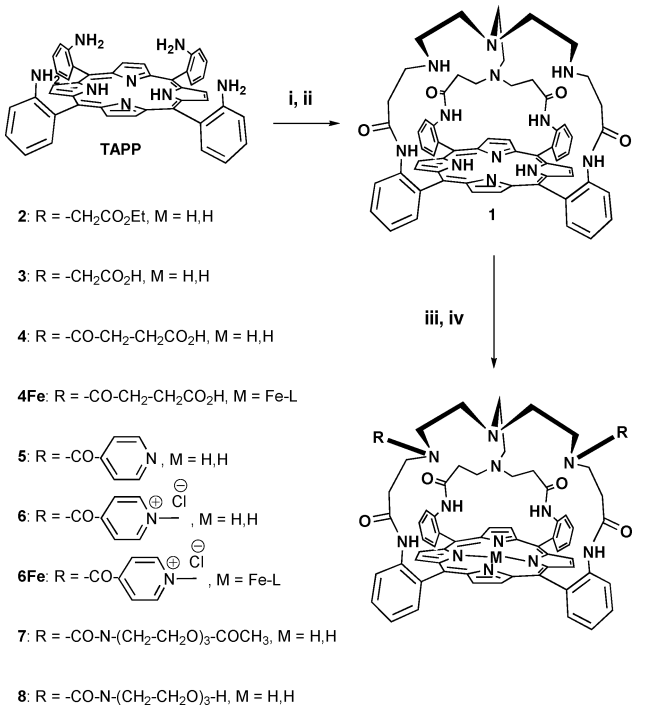
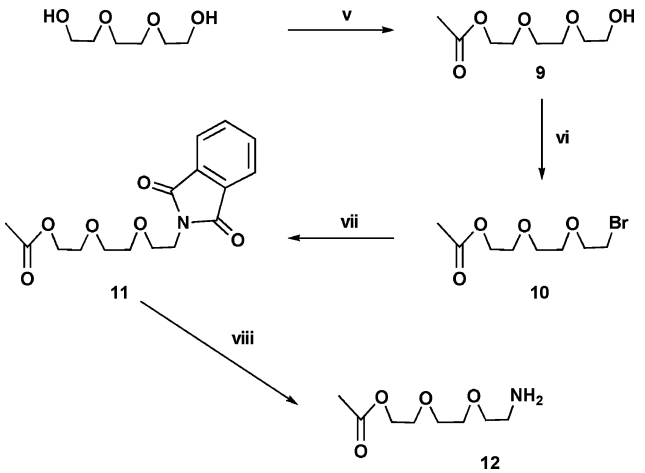
pathway, in one single step, we could elongate the alkyl chain bearing the acid group while avoiding the preliminary ester group which has to be hydrolyzed, and obtain compound **4** (Scheme 2). This compound, as expected was found to be water-soluble in phosphate buffer. Two other options were also considered to functionalize porphyrin **1**. The first consists of a typical acylation reaction with isonicotinoyl chloride to obtain porphyrin **5**, which was permethylated with methyl iodide affording water-soluble porphyrin **6**. We also experimented with the reaction of acetic acid 2-[2-(2-amino-ethoxy)-ethoxy]-ethyl ester **12** with **1**, *via* activation of **1** by diphosgene. Indeed, we chose to transform the bromo derivative **10** in the amino compound **12** *via* **11**, as we did not succeed in alkylating the amine groups of **1** directly with **10**. In contrast, the reaction of **1** with **12** and diphosgene proceeded easily under mild conditions. However, whether acetylated or not, the two resulting bis-PEG porphyrins, **7** and **8** respectively, did not exhibit the expected water-solubility. This result is really unpredictable in as much as it was known that tethering two PEG spacers on an expanded porphyrin clearly leads to a water-soluble compound.[17]



Scheme 2 Synthesis of various tren-capped porphyrins (L = pyridine). *Reagents*: i, acryloyl chloride, NEt_3, THF, ii, tren, $CHCl_3$–MeOH, 50 °C; iii, 2-bromoethyl acetate, THF, NEt_3, → **2**; then KOH, EtOH, → **3**; succinic anhydride, acetic acid, 60 °C, → **4**; isonicotinoyl chloride, NEt_3, THF, → **5**; MeI, HCl (2 equiv.), DMF, → **6**; diphosgene + **12** (see Scheme 3), CH_2Cl_2, 0 °C, → **7**; **7** + K_2CO_3, MeOH, 60 °C, → **8**; iv, **4** + iron bromide, THF, 65 °C, then pyridine (L), → **4Fe**; **6** + iron bromide, DMF, 120 °C, then pyridine (L) → **6Fe**.

Finally, having in hand two water-soluble ligands **4** and **6**, after iron(II) insertion according to a well-described methodology,[18] the iron complexes were dissolved in a phosphate buffered solution to which a large excess of pyridine (5 drops for 10 mg of porphyrin) has previously been added to form the five-coordinate complex. It should be noted here that this method is only suitable with those capped porphyrins for which it has been unambiguously



Scheme 3 Synthesis of PEG-like substituents. *Reagents*: v, CH_3COCl, pyridine, 0 °C then rt overnight, vi, NBS, Ph_3P, CH_2Cl_2, −20 °C; vii, potassium phthalimide, Ph_3P, THF, 0 °C; viii, hydrazine, absolute ethanol, reflux overnight.

demonstrated that pyridine—or in general, the axial base—was not able to coordinate inside the pocket to occupy the sixth coordination site of iron(II). At this point, a first UV-vis. spectrum was recorded and then dioxygen added.

In the presence of dioxygen, both complexes **4Fe** and **6Fe** formed a six-coordinate complex with a typical blue-shifted (from 424 nm to 420 nm) Soret band as illustrated on Fig. 1 for **6Fe**. This blue shift was more pronounced in the case of **4Fe** (from 436 nm to 419 nm). Moreover, for the latter, if the UV-vis. absorbance at 436 nm is monitored, it is observed that the absorbance decreased rapidly ($t_{1/2}$ = 3.3 min, see page S6, supplementary information†) instead of being stable in equilibrium conditions which would allow an equilibrium rate measurement, an observation consistent with an oxidation of the complex in a few minutes. Indeed, the reversible decoordination of dioxygen was probed by argon bubbling but without any success.

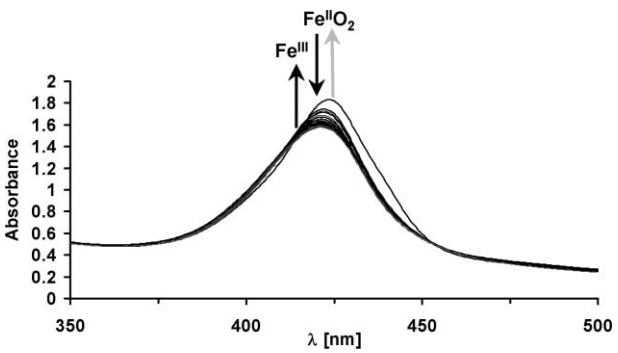


Fig. 1 UV-vis. monitoring of dioxygen binding on **6Fe** + pyridine (phosphate buffer, pH = 7.4, 25 °C).

The same experiment was carried out with iron complex **6Fe**. A similar evolution of the UV-vis. spectra (Fig. 1) was observed with first, the formation of the oxygen adduct and then, a slow oxidation of the latter leading to an irreversible reaction. It should be noted that the half-life time of pyridine-**6Fe**–O_2 is twice longer than that of pyridine-**4Fe**–O_2 ($t_{1/2}$ = 7 min, Fig. 2). Even if this difference is not marked, it remains nevertheless significant as the

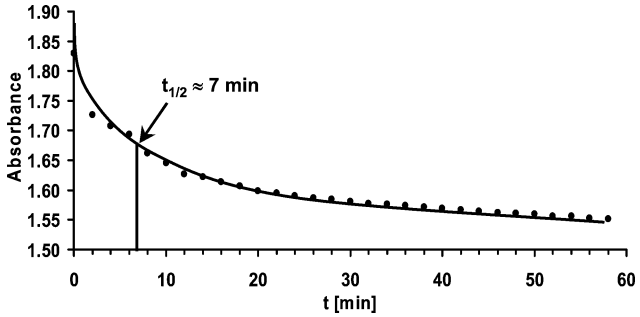


Fig. 2 Decrease of the absorbance at 424 nm upon dioxygen binding on **6Fe** + pyridine (phosphate buffer, pH = 7.4, 25 °C).

structure of the capped molecule is exactly the same. The only structural difference between **4** and **6** consists of the flexible arms in **4** bearing a terminal carboxylic group. The lower dioxygen affinity of **4Fe** appears inconsistent with the fact that a carboxylic group around the dioxygen binding site is in favour of a more stable oxygenated complex. Indeed, it has already been reported in the case of a Co^{II}–O_2 "C-clamp" porphyrin, that the presence of a carboxylic acid around the porphyrin can induce a high O_2 binding in DMF solution.[19] In this instance, the carboxylic group was brought by a Kemp triacid residue and therefore was located in a "lateral hanged" position. Incidentally, this location was unambiguously established by an X-ray structure of the free-base porphyrin. In our case, although we do not have this structural evidence for porphyrin **4**, in light of the crystallographic data of the basic scaffold of **1**,[15] it is quite possible that the succinic motif is long enough to allow the terminal group to fold back towards the center of the pocket built by the tren and to interact with the bound dioxygen. But in phosphate buffer at pH = 7.4, the equilibrium between the carboxylic and the carboxylate forms is slightly in favour of the deprotonated species and the latter is expected to destabilize the superoxo complex. In the case of **6Fe** bearing a shorter arm, this type of interaction can be ruled out for steric reasons.

Conclusions

In this work, we have shown that water-soluble tren-capped iron porphyrins exhibit a relative stability in the presence of dioxygen, without the need of any additional component but a nitrogen base as pyridine. The dioxygen affinity of the complex depends on the nature of the peripheral groups attached to the cap. We propose that the possible interaction of a carboxylate flexible arm with the bound superoxo complex may result in a smaller stability of the dioxygen adduct in phosphate buffer.

Experimental

Compounds **1** and **2** were synthesized according to published procedures.[20]

α-5,10,15,20-{2-[3,3′,3″,3‴-(*N*,*N*,*N*′,*N*″-Tris(2-aminoethyl)-amine)(*N*′,*N*″-bis(4-(succinate)propionamido)-tetrapropionamido]-tetraphenyl}porphyrin 4

$C_{70}H_{68}N_{12}O_{10}$. In a round bottom flask equipped with a stir bar, porphyrin **1** (0.09 mmol, 100 mg) was charged with acetic acid (10 mL). The reaction mixture was heated to 60 °C then succinic anhydride (0.38 mmol, 38.6 mg) was added. The solution was stirred overnight then diethyl ether was added. The precipitate was filtrated, dissolved in THF and precipitated again with diethyl ether. The crude product was dried for several hours and the expected compound was obtained in 88% yield (105 mg). δ_H (500.13 MHz, DMSO-d_6, 343 K) −2.86 (2H, broad s), −2.74 (2H, s, -NH_{pyr}), −1.29 (2H, broad s), −1.15 (2H, broad s), 0.48 (2H, t, $J = 8.3$), 1.50 (6H, m), 1.65 (4H, broad s), 2.11 (2H, m), 2.28 (2H, m), 2.39 (6H, m), 2.61 (4H, m), 3.23 (4H, broad s), 7.49 (2H, t, $J = 7.3$, H_{aro}), 7.59 (4H, m, H_{aro}), 7.75 (1H, d, $J = 7.3$, H_{aro}), 7.85 (5H, m, H_{aro}), 8.13 (2H, d, $J = 7.1$, H_{aro}), 8.31 (2H, broad s, H_{aro}), 8.50 (2H, s, $H_{\beta pyr}$), 8.53 (2H, s, $H_{\beta pyr}$), 8.63 (2H, d, $J = 4.4$, $H_{\beta pyr}$), 8.79 (2H, d, $J = 4.4$, $H_{\beta pyr}$), 8.83 (2H, s, -N*H*CO), 9.70 (2H, s, -N*H*CO) and 12.83 (2H, broad s, -COO*H*); *m*/*z* (ESI HRMS) 1259.5075 ([M + Na]$^+$ $C_{70}H_{68}N_{12}O_{10}Na$ requires 1259.5079).

4Fe

In a dry-box, a solution of porphyrin **4** (0.008 mmol, 10 mg) in THF (6 mL) was added iron(II) bromide (0.1 mmol, 20 mg). The mixture was stirred overnight at 65 °C, then pentane was added. The precipitate was filtrated, washed with a benzene–methanol (10 : 1) mixture and dried for several hours. *m*/*z* (ESI HRMS) 1290.4380 ([M]$^+$ $C_{70}H_{66}N_{12}O_{10}{}^{56}Fe$ requires 1290.4374); Soret (λ_{max}, phosphate buffer pH 7.4): **4Fe** + pyridine: 436 nm, + O_2: 419 nm.

α-5,10,15,20-{2-[3,3′,3″,3‴-(*N*,*N*,*N*′,*N*″-Tris(2-aminoethyl)-amine)(*N*′,*N*″-bis(4-carbamoyl-pyridine)tetra-propionamido]-tetraphenyl}porphyrin 5

$C_{74}H_{66}N_{14}O_6$. In a 100 mL round bottom flask, isonicotinic acid (0.48 mmol, 59 mg) was added with thionyl chloride (10 mL). The reaction was stirred at 80 °C overnight then evaporated under vacuum and dried with benzene. The resulting powder was dissolved in THF (60 mL) then Et_3N (2 mL), pyridine (1 mL) and porphyrin **1** (0.19 mmol, 200 mg) were added. The reaction mixture was stirred for 1.5 h at room temperature then solvents were removed under vacuum. The resulting powder was dissolved in $CHCl_3$ and directly loaded on a silica gel chromatography column. The expected compound eluted with $CHCl_3$–NH_{3g} was obtained in 99% yield (239 mg). δ_H (500.13 MHz, DMSO-d_6, 323 K) −2.71 (4H, broad s, -NH_{pyr} + CH_{2tren}), −0.67 (4H, broad s), 0.59 (3H, broad t, $J = 7,8$), 1.39 (2H, broad s), 1.51 (6H, broad s), 1.61 (3H, m), 2.11 (2H, m), 2.21 (2H, m), 3.01 (4H, m), 7.31 (4H, d, $J = 4.1$, $H_{3pyridine}$), 7.53 (4H, q, $J = 7.3$, H_{aro}), 7.65 (2H, d, $J = 7.2$, H_{aro}), 7.78 (6H, m, H_{aro}), 8.06 (2H, d, $J = 7.2$, H_{aro}), 8.20 (2H, broad s, H_{aro}), 8.46 (2H, s, $H_{\beta pyr}$), 8.53 (2H, d, $J = 4.3$, $H_{\beta pyr}$), 8.65 (4H, d, $J = 4.1$, $H_{2pyridine}$), 8.70 (2H, s, $H_{\beta pyr}$), 8.76 (2H, d, $J = 4.3$, $H_{\beta pyr}$), 8.78 (2H, s, -N*H*CO) and 9.67 (2H, s, -N*H*CO); *m*/*z* (ESI HRMS) 1269.5203 ([M + Na]$^+$ $C_{74}H_{66}N_{14}O_6Na$ requires 1269.5187); $\lambda_{max}(CH_2Cl_2)$/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1}) 420.0 (370.0), 513.0 (19.5), 546.0 (3.9), 586.5 (6.1), 642.0 (1.6).

α-5,10,15,20-{2-[3,3′,3″,3‴-(*N*,*N*,*N*′,*N*″-Tris(2-aminoethyl)-amine)(*N*′, *N*″-bis(4-carbamoyl-1-methyl-pyridinium)-tetrapropionamido]tetraphenyl}porphyrin 6

$C_{76}H_{72}N_{14}O_6$. In a 100 mL round bottom flask, porphyrin **5** (0.08 mmol, 100 mg) was charged with DMF (20 mL) then HCl 1 M (0.16 mmol, 160 μL) in diethyl ether was added.

The reaction was stirred at room temperature 30 min then MeI (4.0 mmol, 250 μL) was added dropwise. The reaction was stirred at room temperature overnight then evaporated under vacuum. The resulting powder was dissolved in DMF (6 mL) then Et_3N (0.16 mmol, 23 μL) was added and the mixture stirred at room temperature for 1 h. Isopropanol (8 mL) and diethyl ether were added. The precipitate was filtrated, dissolved in MeOH and precipitated again with diethyl ether. Iodide anions were exchanged by chloride ions over an Amberlite IRA-900 resin in MeOH solution, and finally precipitated after filtration by addition of diethyl ether. The crude product was dried for several hours and the expected compound was obtained in 77% yield (83 mg). δ_H (500.13 MHz, DMSO-d_6, 343 K) −2.66 (2H, s, -NH_{pyr}), −2.55 (2H, broad s), −0.71 (2H, broad s), −0.41 (2H, broad s), 0.66 (2H, broad t, $J = 7,5$), 0.76 (2H, broad s), 1.30 (2H, broad s), 1.38 (2H, broad s), 1.58 (4H, broad s), 1.70 (2H, m), 2.10 (2H, m), 2.38 (2H, broad t, $J = 10.6$), 2.88 (2H, broad s), 3.01 (2H, broad d, $J = 8.5$), 4.41 (6H, s, -Pyr^+-CH_3), 7.54 (2H, t, $J = 7.8$, H_{aro}), 7.57 (2H, t, $J = 7.8$, H_{aro}), 7.74 (2H, d, $J = 8.0$, H_{aro}), 7.79 (4H, t, $J = 7.7$, H_{aro}), 7.84 (2H, t, $J = 7.4$, H_{aro}), 7.99 (4H, d, $J = 6.0$, $H_{3pyridine}$), 8.03 (d, 2H, $J = 7.4$ Hz, H_{aro}), 8.23 (2H, d, $J = 7.7$, H_{aro}), 8.48 (2H, s, $H_{βpyr}$), 8.50 (2H, s, -N*H*CO), 8.63 (2H, d, $J = 4.6$, $H_{βpyr}$), 8.74 (2H, s, $H_{βpyr}$), 8.77 (2H, d, $J = 4.6$, $H_{βpyr}$), 9.08 (4H, d, $J = 6.01$, $H_{2pyridine}$), 9.55 (2H, s, -N*H*CO); *m/z* (ESI HRMS) 638.2887 ([M]$^{++}$ $C_{76}H_{72}N_{14}O_6$ requires 638.2879); λ_{max}(phosphate buffer, pH 7.4)/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1}) 417.0 (333.1), 514.0 (15.8), 547.5 (3.4), 587.5 (4.6), 643.5 (1.4).

6Fe

In a dry-box, a solution of porphyrin **6** (0.007 mmol, 10 mg) in DMF (6 mL) was added iron(II) bromide (0.1 mmol, 20 mg). The mixture was stirred for one day at 120 °C, then solvent was evaporated. The resulting powder was dissolved in a methanol–THF mixture, then pentane was added. The precipitate was filtrated, washed with THF and dried for several hours. *m/z* (ESI HRMS) 665.2480 ([M]$^{++}$ $C_{76}H_{70}N_{14}O_6{}^{56}$Fe requires 665.2476); Soret (λ_{max}, phosphate buffer pH 7.4): 6Fe + pyridine: 424 nm, + O_2: 420 nm.

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