

Mimicking the active site of cytochrome *c* oxidase

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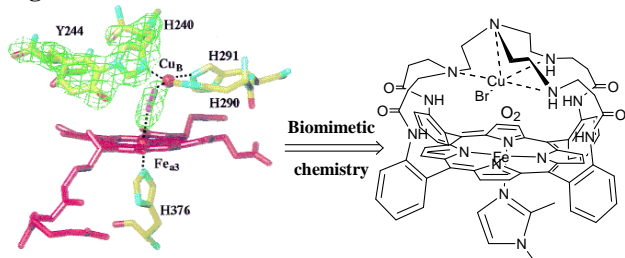
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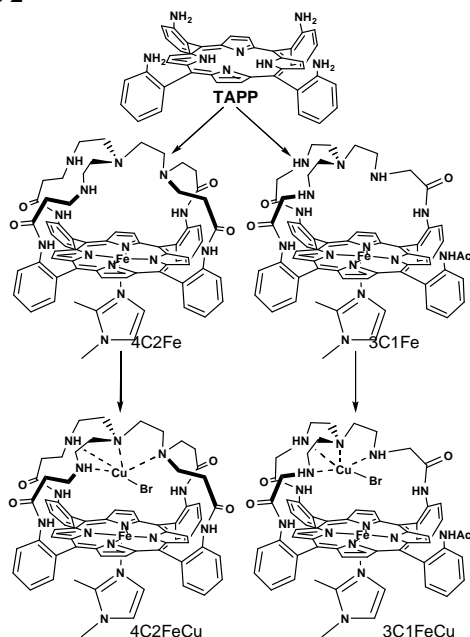
Through a biomimetic approach, our group has recently developed the synthesis of a series of tren (tris(2-aminoethyl)amine) capped porphyrins named “Arbor Porphyrins” to mimic the active site Fe_{a3}-Cu_B of a crucial membrane-bound protein complex : cytochrome *c* oxidase (fig. 1) which catalyses the electroreduction of dioxygen to water via a 4 electron pathway, without leakage of toxic reduced intermediates such as hydrogen peroxide.

Figure 1



Our models consist in iron porphyrins fitted on the distal side with either a tren moiety (possibly substituted) (fig. 2) or three quinolinoyl pickets (fig. 3), coordinated to a copper centre. In the case of the first series, the iron atom is coordinated to a non-covalently attached imidazole since we have demonstrated that an intramolecular imidazole does not provide supplementary stabilization; this was achieved in the case of the second series (fig. 3). The nature of O₂ interaction between the two metals centres has always been of interest, however many issues remain unresolved such as the role of Cu_B and the type of O₂-bound intermediate. More precisely, is the peroxide stage a hydroperoxo or μ -peroxo complex? We tried to give an answer by using rotating ring-disk voltammetry.

Figure 2

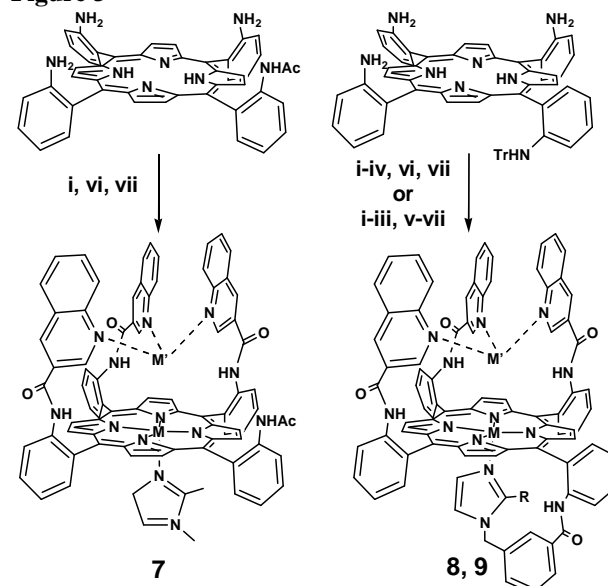


Surprisingly, it was shown that iron/copper catalysts are efficient but not selective catalysts for the dioxygen reduction at physiological pH whereas monometallic iron-only models are both efficient and selective catalysts for the 4 e⁻ reduction. This result excludes the postulated formation of a μ -peroxo intermediate as a prerequisite mediating O₂-activation.

We will discuss the similar behaviour of different series, the possible influence of the N-substitution of tren with electronic active ligands...

Different aspects of this research will be presented ranging from the design, to the rotating disk voltammetry through the synthesis and proton NMR study.

Figure 3



	M	M'
7a	2H	-
7b	Fe	-
7c	Fe	CuBr

	M	M'	R
8a	2H	-	H
8b	Fe	-	H
9a	2H	-	Me
9b	Fe	-	Me
9c	Fe	CuBr	Me
9d	Cu	-	Me

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