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Preliminary communication

REVERSIBLE OXYGENATION OF A "TAIL-BASE" FERROPORPHYRIN COVALENTLY BOUND TO HIGHLY CROSS-LINKED POLYSTYRENE

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Summary

A modified iron deuteroporphyrin, with an attached imidazole axial base was covalently bound to a highly cross-linked aminopolystyrene. After reduction of the iron, the effect of exposure to oxygen in the solid state was monitored by UV-visible diffuse reflectance spectroscopy. Several oxygenation—deoxygenation cycles were performed without any noticeable irreversible oxidation to iron(III). Reversible binding of carbon monoxide was similarly observed.

A major challenge in the design of oxygen-binding hemoprotein models is to mimic in a simple way the environment of the porphyrin provided by the protein chain [1—6], i.e.: (i) a hydrophobic pocket surrounding the active site, and (ii) site isolation to protect the iron(II) from irreversible oxidation by bimolecular reaction between the dioxygen complex and the deoxy form [7]:

$$Fe(P)O_2 + Fe^{II}(P) \rightarrow Fe^{III}(P)—O—O—Fe^{III}(P) \rightarrow \rightarrow Fe^{III}(P)—O—Fe^{III}(P),$$

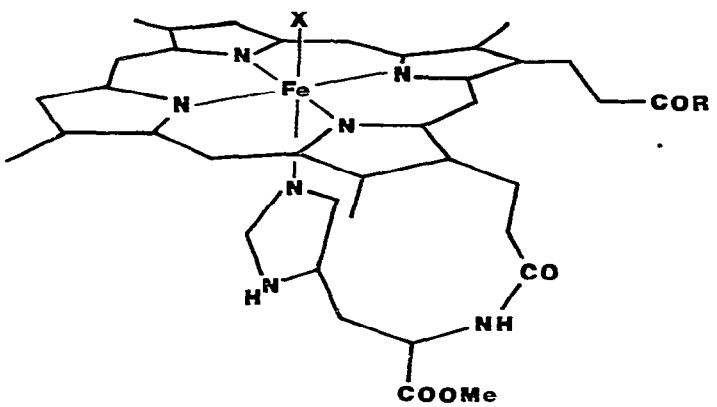
and (iii) control of the axial coordination.

During the last decade numerous examples of reversible dioxygenation of iron porphyrins have been reported [8], but only in one case were these three features present in the same complex [9]. However, the synthesis of that complex, which has facial steric hindrance to protect the coordination site of dioxygen and an attached imidazole base to control the axial coordination, involves many steps, including two atropisomer separations, and thus is extremely lengthy.

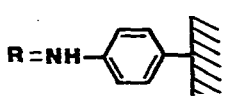
Our recent work on site separation on polymers demonstrated that the use of iron(II) porphyrins covalently bound to highly cross-linked polystyrene resulted in a hydrophobic environment and an efficient separation of the macrocycles [10]. In this communication we report a simple synthesis of a polystyrene supported "tail-base" iron(II)-porphyrin which coordinates reversibly molecular oxygen and carbon monoxide.

Macroporous amino-polystyrene was prepared by copolymerisation of a water suspension of a mixture of styrene, 4-aminostyrene, and divinylbenzene (65/5/30 weight%) at 80°C, in the presence of azobisisobutyronitrile [11]. The beads of polymer were filtered off and extracted with methanol, in a Soxhlet apparatus, over a period of 24 h and then dried under vacuo. The concentration of the amino groups into the polymer was estimated from nitrogen elemental analysis to be 4×10^{-4} mol/g, corresponding to 3.8% of phenyl substitution.

Chloroiron(III) deutero[mono(histidyl methyl ester)amide]porphyrin (I, X = Cl) [12] (60 mg, 8×10^{-5} mol) was dissolved at 50°C in anhydrous dimethylformamide (40 ml) under argon and the aminopolystyrene (2 g) and dicyclohexylcarbodiimide (100 mg, 4.8×10^{-4} mol) were added. This mixture was kept at 50°C with occasional gentle hand-shaking. After 10 days the solid was filtered off and washed five times with dimethylformamide (10 ml), then with a 1/1 mixture of methanol and dichloromethane (150 ml), and was finally dried under vacuo. Analysis for iron revealed that covalent linking of the metalloporphyrin to the polymer had occurred to the extent of about 5.5% of the available amino groups present in the starting polystyrene, which corresponds to 0.2% of phenyl substitution.



R = OH (I)



(II)

R = OMe (III)

These polymer-bound porphyrins (II) have been characterized in the solid state by UV-visible diffuse reflectance spectroscopy performed on the whole beads. As shown on Fig. 1, the iron(III) complex (λ_{max} 590 and 408 nm) was reduced by gaseous piperidine (λ_{max} 542, 515 and 411 nm) and kept overnight under vacuo to remove any traces of base. Careful control experiments revealed that no piperidine was released when the polymer was heated at 95°C under 0.01 Torr. Upon exposure to oxygen (650 Torr) new absorbances were observed (λ_{max} 544, 515 and 411 nm) but the previous spectrum was fully restored after

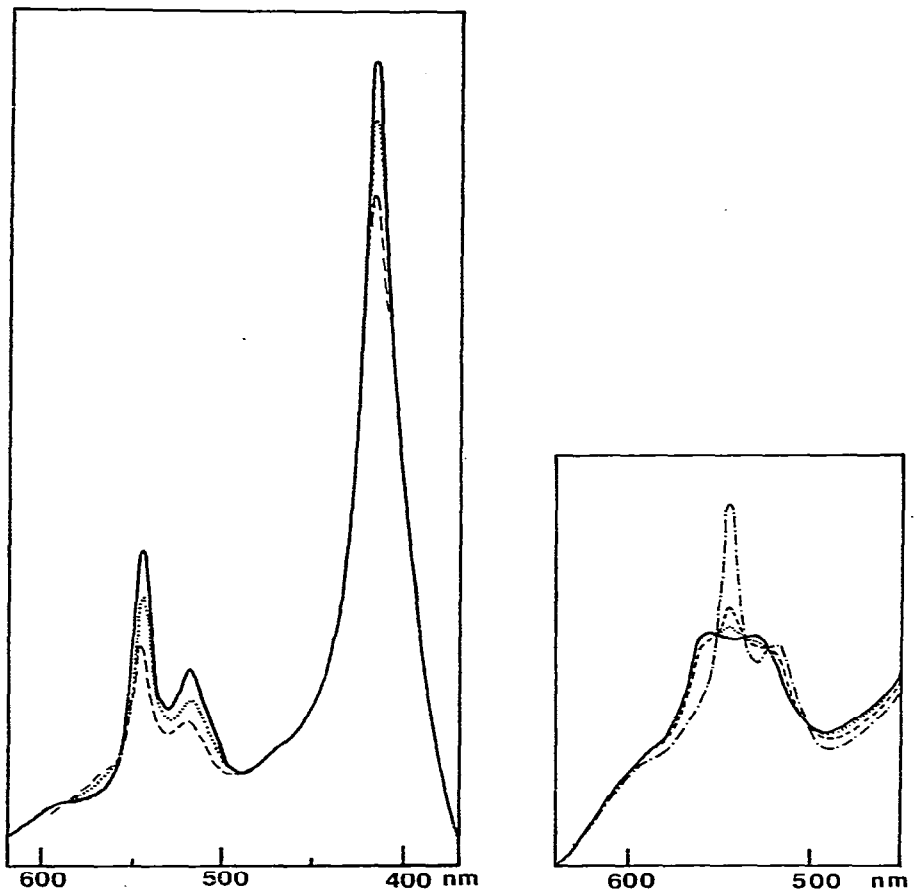


Fig. 1. Diffuse reflectance UV-visible spectra of the polymer-bound iron porphyrin II. (a) —— after reduction by piperidine. (b) - - - - under oxygen at room temperature; (c) . . . . after evacuation, 5 min under 0.1 Torr; after 20 min the spectrum is identical with (a).

Fig. 2. Diffuse reflectance visible spectra of the polymer-bound iron porphyrin II. (a) —— dioxygen complex flushed under carbon monoxide; (b) . . . . and (c) - - - - under evacuation; (d) –.–.– after 30 min under 0.1 Torr.

evacuation (20 min under 0.01 Torr). More than 10 oxygenation—deoxygenation cycles have been performed without any noticeable irreversible alteration of the spectra. However, when a sample was kept 24 h under pure oxygen (650 Torr), the intensity of the absorbances associated with the dioxygen complex were reduced to about half of their initial values and a new band appeared at 590 nm, as expected for an iron(III) complex.

When a freshly prepared dioxygen complex was flushed with carbon monoxide, a new spectrum was observed (λ_{max} 555, 528 and 411 nm) which compared well with that reported [12] for the parent iron(II) porphyrin carbonyl complex III (X = CO). Evacuation under vacuo restored the deoxy spectrum with isobestic points at 550, 535, 520 and 500 nm as shown in Fig. 2. The pressure of half-saturation by carbon monoxide has been roughly estimated from these spectral data to be ca. 20 Torr at room temperature. This high value [12]

suggests that free amino groups present in the polymer backbone may be competing with carbon monoxide for the sixth coordination site of the iron porphyrin, in agreement with the UV-visible spectrum which indicates that the deoxy form is more likely to be hexacoordinated [13]. Probably for the same reason, only a partial oxygenation of the macrocycle is obtained, as evidenced by the rather small red-shift of the β band in the visible spectrum: $\Delta\lambda$ ca. 2 nm for II vs. $\Delta\lambda$ 16 nm for the parent complex III, toluene solution; –60°C [12]. Similarly, an unusually low dioxygen affinity has been reported in the case of silica-gel modified imidazole-attached iron(II) porphyrin where a large excess of base was available as a sixth ligand [14].

In conclusion, the efficiency of the site separation observed in highly cross-linked polystyrene could provide an easy access to oxygen-binding hemoprotein models. Several synthetic variations of these polystyrene-supported "tail-base" porphyrins with different local environment and axial ligands are currently under investigation.

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