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A PORPHYRIN-BASED CROWN ETHER CO-RECEPTOR FOR THE COMPLEXATION OF PARAQUAT

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Abstract:

A porphyrin strapped by a dibenzo- crown ether was synthesized and shown by ^1H nmr spectroscopy to bind paraquat in acetone solution.

Host / guest complexes that mimic the first intermediates in enzyme-model processes represent a bourgeoning area of current chemical interest in such areas as enzymatic catalysis, ion transport, and photosynthesis[1]. The goal of the next generation of model compounds is to position in purposeful proximity both the host cavity and a reaction centre[2].

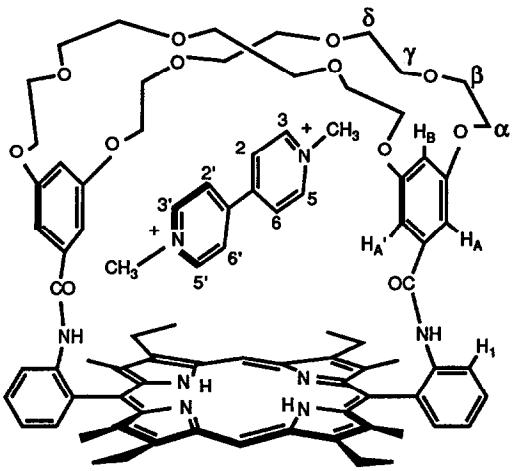
In addition to the well known ability of crown ethers to bind certain cations[1,3] more recently bipyridinium derivatives such as paraquat (PQ^{2+}) and diquat (DQ^{2+})[4] have also been found to form stable complexes with aromatic crown ether derivatives. A wide range of these derivatives differing in both the types of aromatic moieties and sizes of ether chains have been well characterized both in the solid state and in solution by Stoddart and co-workers[5]. Wide variations of crown ether chains, aromatic ring size and substitution have been studied systematically and illustrate the versatility of these complexations. Nevertheless, a significant increase in the complexation strength was obtained when the aromatic ethers were incorporated into a macrobicyclic receptor molecule by a suitable bridging sub-unit, thus increasing the rigidity and pre-organisation of the crown ether molecule[6].

As an extension to this concept, we have designed and synthesized a molecule (**1**) in which a similar dibenzo-crown ether is strapped across the face of a porphyrin. Such a molecule now has a well defined binding site in close proximity to a reaction centre (*viz.* the porphyrin). The potential for efficient photoactive interaction between a bound bipyridinium cation and the porphyrin macrocycle is thus created in the form of a supramolecular photochemical device.

Although it has been shown that diquat is more strongly complexed by various other crown ethers[5a], the ether chosen for the initial synthesis was of the BMP32C10[7,5c] type containing meta- substituted aromatic groups. The advantages of this derivative are (i) symmetry which aids in structural elucidation, and (ii) similar crown structures have been shown to complex both paraquat and diquat dications. This is in contrast to receptor molecules based on o-substituted aromatic groups, which tend to show preferential binding of only one class of bipyridinium cation[5a].

Macrocycle (**1**) was synthesized using standard strategies for the stepwise construction of dibenzo-crown ethers and difunctional porphyrins[5,8]. The methyl ester of α-resorcylic acid was mono-benzylated; subsequent reaction with tetraethylene glycol bistosylate[9] yielded the protected asymmetrical ether. Catalytic hydrogenolysis produced the diphenol acyclic ether which upon further reaction with bistosylate gave the carbomethoxy BMP32C10 derivative. Hydrolysis of the ester functionality followed by reaction with thionyl chloride yielded the acid chloride. High dilution conditions[10] were then used in coupling the acid chloride with the appropriate α,α-

diaminoporphyrin[11] to give (1)[12]. All of the above reaction products, with the exception of the diphenol acyclic ether, were purified by extensive flash column chromatography.



[(1).PQ] $(PF_6)_2$

The ^1H NMR spectrum of (1) (Table) shows the crown ether resonances moved considerably upfield compared with BMP32C10[5c] consistent with a structure in which the crown ether is strapped across the face of the porphyrin[13].

Table : Partial ^1H NMR data for the binding of paraquat by various hosts in acetone[14].

	H_A	H_B	α	β	γ	δ	$^+$N-Me	2,6H	3,5H
BMP32C10	6.48	6.48	4.06	3.78	3.61	3.61	-	-	-
(1)	5.51 (-0.97)	5.82 (-0.66)	2.99 (-1.07)	2.79 (-0.99)	2.28 (-1.33)	2.48 (-1.13)	-	-	-
(1):PQ^{2+}	5.47 (-0.04)	5.75 (-0.07)	2.59 (-0.40)	2.51 (-0.20)	2.91 (+0.63)	3.04 (+0.56)	4.63 (-0.10)	9.07 (-0.28)	8.30 (-0.52)
PQ^{2+}	-	-	-	-	-	-	4.73	9.35	8.82
BMP32C10:PQ^{2+}	(-0.37)	(-0.37)	(-0.34)	(-0.06)	(+0.11)	(+0.11)	(-0.08)	(-0.23)	(-0.49)

The ability of (1) to complex bipyridinium cations[15] was examined by ^1H NMR in d_6-acetone. In the case of paraquat, both the host and guest protons undergo shifts upon complexation (Table). The data shown may be interpreted in terms of a 1:1 complex between paraquat and macrocycle (1) in which the bipyridinium rings are sandwiched between the crown aromatics. On complexation, the protons of the polyether chains undergo significantly larger shifts than those previously observed for diaryl crown ethers[5b,c,d]. In (1) the flexible ether chains are folded symmetrically inwards so that the γ and δ protons experience the largest shielding by the porphyrin ring. On binding PQ^{2+}, the rings must fold outwards to assume an orientation as depicted. The γ and δ protons are now removed from the shielding region of the porphyrin, and into the deshielding region of the guest, accounting for the large shifts observed for these protons.

The crown aromatic protons (H_A, H_B) experience only small negative shifts upon complexation (Δδ - 0.04 and −0.07 ppm respectively). This may be explained as being due to a combined effect of both a complexation-induced conformational change in the ether and the shielding effects of paraquat: on complexation,

the crown aromatic rings are enforced towards orthogonality with the porphyrin *meso*-aromatic substituent, which decreases the degree of delocalisation that is possible through the more coplanar aromatic-amide-aromatic system assumed for the uncomplexed (**1**). Further evidence for such a conformational change on binding is the change in the chemical shift of H_1 ($\Delta\delta$ -0.18 ppm). Such a shift is consistent with reduced shielding by the carbonyl group as the crown aromatic ring is rotated with respect to the *meso*-amidophenyl plane[16].

Other significant shifts in the porphyrin resonances are those of the CH_3 resonances of the pyrrole ethyls which are shielded by $\Delta\delta$ -0.18 ppm, and the pyrrolic NH protons which are deshielded by $\Delta\delta$ +0.19 ppm. Such shifts are in accord with a structure as indicated with the PQ^{2+} aligned perpendicular to the porphyrin plane[17]. The remaining porphyrin resonances are little affected by PQ^{2+} binding (av.$\Delta\delta$ 0.02 ppm).

The resonances of paraquat move in an analogous fashion to that previously observed for the non-porphyrin based crown derivatives[5b,c,e] with 2,6–H, 3,5–H and N-Me protons all experiencing negative shifts of a similiar magnitude on complexation. The fact that these shifts are perhaps less than might be expected may be explained by weaker binding in (**1**):PQ^{2+} compared to BMP32C10:PQ^{2+} [18].

Indeed, the binding of paraquat by (**1**) was found to be both dilution and temperature dependent. Thus since the complex is kinetically unstable[19] a detailed conformational analysis was not possible. A decrease in temperature of the 1:1 complex solution to 228K failed to separate resonances of bound and unbound paraquat, or any inequivalence within the paraquat or porphyrin protons, indicating rapid exchange and/or rotation of the guest.

In the case of diquat (DQ^{2+}), little change was observed in the proton resonances of (**1**) on the addition of guest (av.$\Delta\delta$ 0.02ppm). The protons of diquat were shifted slightly upfield (av. $\Delta\delta$ –0.07ppm) by the presence of (**1**), which may be interpreted as a bulk effect in solution of (**1**) on the bipyridinium cation rather than host / guest binding.

Any evidence of a charge-transfer band expected around 400 nm ($\varepsilon\approx400$)[5a] in the UV-visible spectrum of (**1**):PQ^{2+} is obscured by the porphyrin Soret band at 405 nm ($\varepsilon\approx3\times10^5$), although a slight broadening on the high energy side of the band is evident. The luminescent properties of (**1**):PQ^{2+} and related derivatives are currently under investigation.

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