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Porphyrin-Based Molecular Tweezers as a Receptor for Bipyridinium Guests

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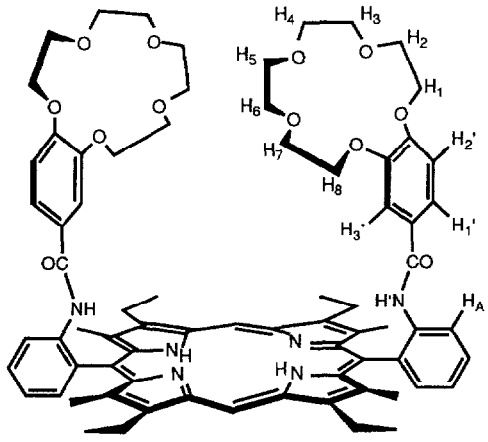
Abstract: *A porphyrin with two appended benzo-crown ethers in the form of a porphyrin-based molecular tweezer was synthesised and shown to bind the bipyridinium guests paraquat, diquat and $Pt(bpy)(NH_3)_2$ dications in several solvents. The conformations of the host molecule were shown to be solvent dependent. Lack of binding by a non-crown ether containing analogue demonstrated the necessity of the crown ether chains for the binding of guest molecules.*

The complexation of bipyridinium derivatives including paraquat (PQ^{2+}), diquat (DQ^{2+}), and $Pt(bpy)(NH_3)_2^{2+}$ by a wide range of benzo-crown ethers differing in size and complexity has been extensively studied by Stoddart and coworkers[1]. We have extended these concepts to the production of new receptor molecules which incorporate benzo-crown ethers in contiguity to porphyrins. Such molecules have a well defined binding site in close proximity to a potential reaction centre (*viz.* the porphyrin). Porphyrin macrocycles containing overlaid benzo-crown ethers have been shown by us previously to complex the paraquat dication[2]. Utilising "tweezers" to complex this and similar bipyridinium molecules represents a simplified and novel approach to the positioning of electron transfer agents to create new systems with the possibility of efficient photoactive interaction between a bound bipyridinium cation and the porphyrin macrocycle in the form of a potential *supramolecular photochemical device.*

Although relatively recent additions to the field of host-guest chemistry, the systems known as "molecular tweezers" were first synthesized by Chen and Whitlock[3]; these contained a *flexible* spacer unit and complexed aromatic molecules in a π-sandwich arrangement. Zimmerman and co-workers[4] have constructed numerous tweezers containing *rigid* spacers between complexing chromophores, and with varying degrees of "stickyness" in the form of hydrogen bonding to further enhance the receptor's affinity for specific guests. Use of porphyrins as the pincers of rigidly spaced "tweezers" has been the approach adopted by Chang[5] with a view to activation of a substrate anchored as a bridging ligand. Lehn's earlier work on crown ether-based multisite molecular complexes[6] has been developed by Stoddart[1] for crown ether receptors specifically designed for bipyridinium derivatives.

By incorporating these concepts we have designed and synthesized a molecular tweezer with a rigid porphyrin *spacer* and with two benzocrown-ethers as the *complexing unit*, indicated by (**1**). The synthesis of (**1**) was straightforward: 4'-formyl benzo-15-crown-5[7] was oxidised (CrO_3/H_2SO_4) to the acid, which was then converted to the acid chloride ($SOCl_2/CH_2Cl_2$) and condensed with α,α-5,15-*bis*(2'aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin[8].

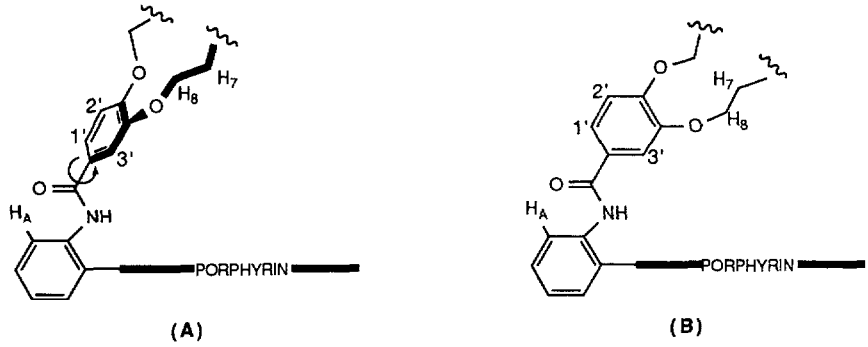


(1)

The solution conformations adopted by (**1**) are solvent dependent. These effects were studied by NMR methods, utilising COSY, NOESY, C-H correlated, selective INEPT and variable temperature methods; the results are consistent with the following (Figure):

- in $CDCl_3$, (**1**) adopts a conformation in which each of the two aromatic rings of the appended benzo-crowns is twisted out of complete conjugation with the amide and the *meso*-phenyl substituent; the two crown aromatics are then approximately cofacial and parallel (conformer **A**);
- in deuteroacetone, the crown aromatic rings essentially maintain conjugation with the amide and *meso* - phenyl substituent, and the two phenyl rings assume an approximate edge-on orientation to each other (conformer **B**)[9].

Thus in the solvent-induced change of conformation from (**A**) to (**B**) all the methylene protons of the crown ether ring are more shielded by the porphyrin aromatic ring current and are hence upfield of their position relative to those of (**B**), whereas $H_{1'}$ and $H_{2'}$ are moved downfield, with the most significant shifts being those of the protons H_7, H_8, and $H_{3'}$. The minimal shift of H_A is consistent with rotation about the bond indicated in (**A**) rather than the C_ϕ–N bond, since the shift of this proton has been shown to be particularly sensitive to any conformational change involving the relative orientation of the carbonyl group[2]. The remaining porphyrin and aromatic resonances also show minimal solvent dependent shifts.



(A) (B)

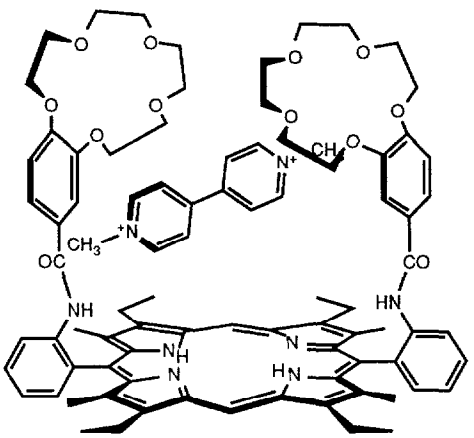
Figure. Limiting conformations[9] adopted by (**1**) in $CDCl_3$ (**A**), and acetone-d_6 (**B**).

Table: Selected ^{1}H NMR Chemical Shifts (δ, ppm) for (**1**) in $CDCl_3$ and Acetone-d_6, and with Paraquat Dication in Acetone-d_6

Solvent	$H_{1'}$	$H_{2'}$	$H_{3'}$	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	NH'
$CDCl_3$ (conformer **A**)	6.28	5.92	5.71	3.46	3.40	3.33	3.26	3.09	2.87	1.97	1.91	8.02
$(CD_3)_2CO$ (conformer **B**)[a]	6.58 (+0.30)	5.98 (+0.06)	4.76 (-0.95)	3.19 (-0.27)	3.11 (-0.29)	3.05 (-0.28)	2.95 (-0.31)	2.70 (-0.39)	2.45 (-0.42)	1.07 (-0.90)	0.78 (-1.13)	7.74 (-0.28)
$(CD_3)_2CO$ + PQ^{2+} [b]	6.53 (-0.05)	6.00 (+0.02)	4.75 (-0.01)	3.32 (+0.13)	3.19 (+0.08)	3.13 (+0.08)	3.02 (+0.07)	2.79 (+0.09)	2.52 (+0.07)	1.24 (+0.17)	0.86 (+0.08)	7.79 (+0.05)

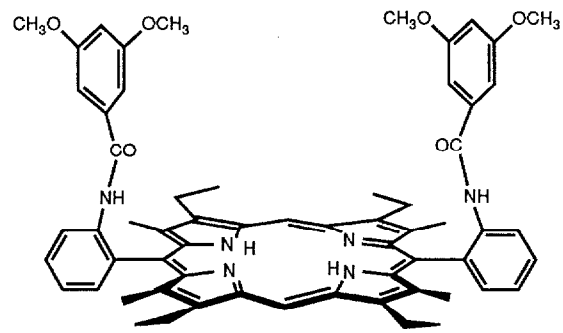
[a] Numbers in parentheses indicate shifts (Δδ, ppm) relative to $CDCl_3$ solution. [b] Chemical shifts for a solution containing equimolar amounts of (**1**) and $PQ^+.PF_6$; numbers in parentheses indicate shifts (Δδ, ppm) relative to acetone-d_6 solution.

Stoddart and co-workers have shown that for efficient binding of bipyridinium derivatives by benzo-crowns, the optimum interfacial distance between parallel aromatic rings is ~7 Å. In the molecule (**1**), molecular modelling indicates that this is maintained, and that for effective binding the conformation must approach that indicated by (**A**) above. Indeed solution studies indicate that (**1**) binds PQ^{2+} in acetone-d_6 solution, and the spectral evidence is consistent with a shift in conformation on binding towards that maintained by the free molecule in $CDCl_3$ *viz,* conformer (**A**)[10]. However, the NMR shifts (Table) on complexation are complicated by a change in conformation of the host, as well as shielding and deshielding effects of the host and guest on each other. Nevertheless, the shifts can be rationalised in terms of a binding geometry as indicated. More obvious are the significant upfield shifts of the paraquat resonances, being strongly shielded by the porphyrin (Δδ -0.31 and -0.23 ppm for the aromatic protons, and -0.15 ppm for the $^+$NMe protons)[11].



Substrate binding was also investigated in other solvent systems, including CD_3CN, $CD_3CN/CDCl_3$, and CD_2Cl_2. In those cases where binding was observed, the spectral changes were qualitatively similar to those for paraquat in acetone, but actual shift values were dependent on the strength of binding and on the solvent. The qualitative trend in binding ability is paraquat dication < diquat dication < $Pt(bpy)(NH_3)_2^{2+}$, although measurement of binding constants was not possible due to the complication of the conformational changes accompanying complexation.

The necessity of the crown ether chains for substrate binding was demonstrated by the synthesis of the simpler analogue (**2**). This *did not* bind any of the above substrates in the solvent systems studied.



(2)

In these models, the presence of the amide bonds linking the receptor moieties to the porphyrins add additional constraints to the preorganisation towards substrate binding; both π-conjugative effects and the geometric demands of this linkage induce a flexing or distortion of the molecular framework to accommodate the ideal cofacial parallel orientation of the crown aromatics which is required for strong binding. This may be overcome to some extent by reduction to the amine. Further work is continuing on these aspects.

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9. These conformations do not imply *absolute* orthogonality (in **A**) or coplanarity (in **B**) of the two phenyl rings; the NMR shifts are consistent with inter-phenyl dihedral angles approaching, but not necessarily reaching, 90° and 0°, respectively. Complete co-planarity would perhaps be unlikely because of trans-porphyrin steric interactions of the crown ethers, although their conformational flexibility could accommodate such an arrangement.
10. Inspection of molecular models indicate that approximate parallelity of the host and guest aromatic rings can be achieved with dihedral angles between the host crown aromatic rings and the *meso*-phenyl rings of between about 45 and 90°. We have observed similar substrate binding-induced conformational changes in a related crown-capped porphyrin.[2]
11. Variable temperature NMR studies were not able to distinguish resonances of the bound and unbound substrate, or any inequivalence within the paraquat or porphyrin protons, indicating rapid exchange and/or rotation of the guest. As previously noted[2], the porphyrin ring proton resonances are little affected on complexation (av. $\Delta\delta \leq 0.04$ ppm).

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