Porphyrin–Crown Ether Based Macrocyclic Receptors for Bipyridinium Cations

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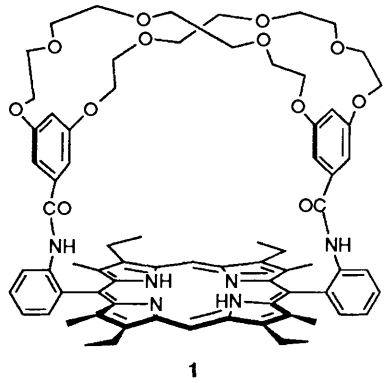
Design modifications to potential receptors for the bipyridinium cations paraquat, diquat and $[Pt(bpy)(NH_3)_2]^{2+}$, in which a porphyrin is appended by benzo crown ethers in two different configurations, are reported. A porphyrin strapped by a single dibenzo crown ether **4**, and a porphyrin-based *molecular tweezer* **7**, in which a porphyrin is surmounted by two benzo-15-crown-5 units, are described. The macrobicyclic receptor **4** failed to complex either the paraquat or diquat dications to any significant extent, yet formed an inclusion complex with $[Pt(bpy)(NH_3)_2]^{2+}$ (K_a 155 dm^{-3} mol^{-1}, $\Delta G°$ −2.9 kcal mol^{-1}) with an orthogonal orientation of the guest relative to the porphyrin plane. This lack of paraquat and diquat complexation may be due to either an incorrect number or geometry of ether oxygen atoms for electrostatic interactions, and/or unfavourable orientations of the crown aromatic rings due to their increased conformational mobility within **4** when compared to the macrotricyclic analogue **1** reported previously by us. The complexation of $[Pt(bpy)(NH_3)_2]_2(PF_6)_2$ by **4** was accompanied by a conformational change within the crown ether subunit, and a deformation of the porphyrin nucleus indicating that the ether strap is stretched to accommodate $[Pt(bpy)(NH_3)_2]^{2+}$. This suggests that (i) decreasing the number of ether chains from two to one only partially removes the steric effects from the ether chain on the crown aromatic rings, or (ii) the amide bond is still dominant in influencing the solution conformations of the crown aromatic rings. The crystal structure of an isomer **4** showed the ether chain twisted around the porphyrin, as a result of atropisomerisation during the crystallisation process.

The crown ether subunit of **9** was found to be conformationally solvent dependent. Two conformational extremes were identifiable; in acetone the crown aromatic rings are essentially co-planar with the *meso*-phenyl plane, whereas in chloroform the crown aromatic rings are nearly orthogonal to the *meso*-phenyl ring. The tweezer was observed to bind paraquat, diquat, and $[Pt(bpy)(NH_3]_2]^{2+}$ in acetone solution with association constants and free energies of complexation of 32, 20, 140 dm^3 mol^{-1}, and −2.1, −1.8, −2.9 kcal mol^{-1}, respectively. The stronger complexation of $[Pt(bpy)(NH_3)_2]^{2+}$ presumably reflects the additional stabilisation of the inclusion complex by hydrogen bonding between the ammine ligands of $[Pt(bpy)(NH_3)_2]^{2+}$ and the oxygen atoms of the crown tweezer. The inclusion geometry of these guests within the pincers of **7** is consistent with the aromatic rings of the guest sandwiched between the aromatic benzo-crown rings as predicted. An analogous tweezer molecule **8** lacking the crown ether chains did not bind any of the guests. Although **7** was observed to complex all three guests, the smaller association constants and free energies of complexation compared to **1** at 298 K reflect the lesser degree of *preorganisation* present in the crown-ethers of the complexing subunit of **7**. Thus, although the removal of the bridging ether chains allows an increase in the conformational mobility of the crown aromatic rings the nett result is a decrease in the level of pre-organisation, and a reduction in the receptor binding strength.

In a search for suitable components which might function in artificial photosynthetic or other photodynamic systems, we have focussed on supramolecular assemblies where a bipyridinium dication is reversibly bound in a porphyrin–crown ether receptor of appropriate design.[1-3] We have shown that macrotricyclic systems incorporating in each case a porphyrin with a dibenzo-crown ether of suitable dimension strapped across its face, exemplified by **1**, can act as hosts for certain bipyridinium salts.[1,2] Nevertheless, the binding ability of these receptors was found to be restricted by the extent of conformational *reorganisation* accompanying complexation due, in part, to the conjugational requirements of the amide bond linking the crown ether unit with the basal porphyrin, and the consequential restricted mobility of the crown ether chain. Reduction of the carbonyl group of the macrotricyclic receptor represented one partially successful approach to the solution of the problem of increasing the conformational mobility of the crown aromatic rings within these porphyrin hosts.[1] We saw that another possible approach to increasing conformational



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freedom was to alleviate any constraints imposed on the aromatic rings by the ether chains. Decreasing the number of ether chains connecting the aromatic rings from two to one

should reduce the steric congestion within the crown ether subunit, allowing the crown aromatic rings increased conformational freedom, and possibly lessening the reorganisation of the crown ether required for complexation, while not constraining the structure to over restrictive *preorganisation*.

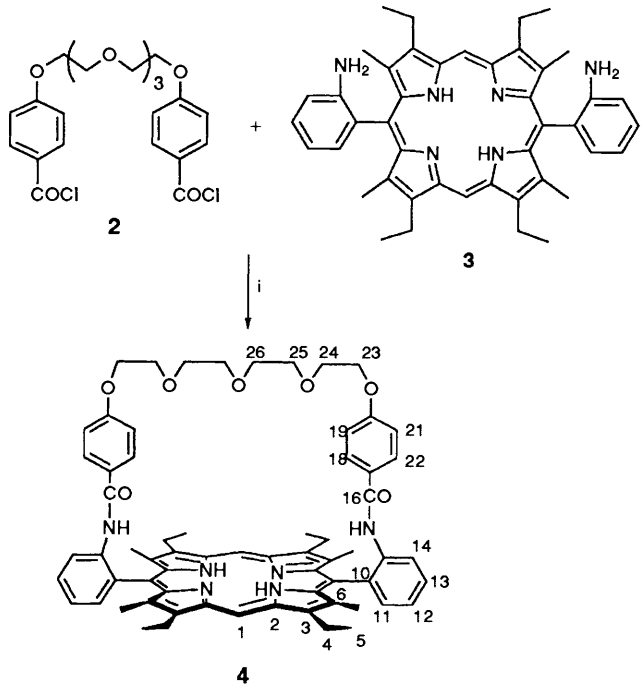
In what might be considered a two-pronged attack on the same problem, we reasoned that the total removal of the ether chains connecting the crown aromatic rings, allowing the rings essentially independent movement, would eliminate all constraints associated with the linking crown ether. The ether chains cannot be totally discarded, however, since they are necessary for stabilisation of the dication guests through electrostatic interactions with the phenolic oxygen atoms, and hydrogen bond formation with the remaining oxygen atoms. This suggested the use of two separate functionalised benzo-crown ethers, in which an ether chain is cyclised onto each aromatic ring, for attachment to a porphyrin to create a porphyrin-based *molecular tweezer*.[3] This paper describes the synthesis, conformational properties, and complexing behaviour of systems incorporating these concepts.

Macrobicyclic Crowned Porphyrin

Open-chain polyethers (non-cyclic ether systems) containing terminal aromatic functionalities have been shown to undergo ready reaction with a variety of metal ions forming crystalline complexes.[4] Although the complexation of bipyridinium dications has not yet been investigated with open-chain polyethers, it was reasoned that their incorporation within a porphyrin-based host may be regarded as a derivative of the efficient receptor to bipyridinium cations, *viz* BPP34C10,* in which one of the ether chains has been replaced by the porphyrin ring. The complexation of diquat by BPP34C10 is characterised by only one electrostatic interaction between opposing phenolic oxygens and a nitrogen cationic atom, charge-transfer interactions, and hydrogen bonding involving only one ether chain.[5,6] Thus, the incorporation of a porphyrin into the ether structure may, in fact, increase the rigidity and preorganisation of the host, possibly enhancing complexation, while being offset by reduced opportunities for dipolar and hydrogen bonding interactions in comparison to BPP34C10.[6,7]

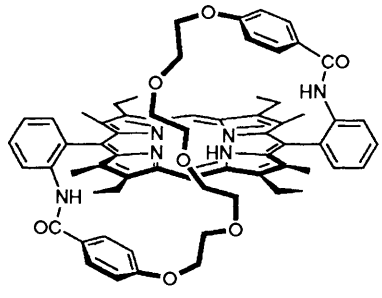
Thus, the target molecule described here is a macrocyclic receptor incorporating a porphyrin strapped by a single dibenzo-crown ether chain.

The synthesis of the aromatic open chain polyether, and its subsequent strapping across a porphyrin, is outlined in Scheme 1 and is based on the procedure reported by Vögtle *et al.*[4] Thus, methyl *p*-hydroxybenzoate was allowed to react with tetraethylene glycol bistosylate (3,6,9-trioxaundecane-1,11-diyl ditosylate)[8] and the ester subsequently hydrolysed to give the acyclic polyether diacid,[9] which was subsequently converted into the corresponding acid chloride **2**. High-dilution conditions[10] and batchwise additions of components were employed in the condensation of the acid chloride **2** with the α,α-atropisomer of the diamino porphyrin **3**[11,12] to produce the single-strapped porphyrin **4**. Unlike the solvent dependent spectra of the porphyrin tweezer (*vide infra*), the NMR spectra of **4** show no solvent dependence, with similar spectra observed in both [$^2H_6$]acetone and deuteriochloroform, indicative of comparable solution conformations in both solvents. All the crown ether resonances are shifted upfield compared to their positions in precursor molecules in what has now become a predictable pattern for strapped porphyrins,[1-3,7] explicable in terms of relative proximity to the porphyrin ring current and consistent with the indicated structure.



Scheme 1 *Reagents and condition:* (i) CH_2Cl_2, pyridine, high dilution. The non-systematic numbering scheme is used in discussion of the NMR spectra.

Solid-state Structure of an Isomer of **4**.—During the slow recrystallisation of **4** in an attempt to obtain single crystals for an X-ray crystallographic structure determination, a minor component **4a** was isolated which was isomeric with **4**, but whose NMR spectra lacked the symmetrical nature of that of **4**. The crystal structure, shown in Fig. 1, revealed a molecule with



4a

pseudo-2 symmetry, with the ether chain wrapping itself *around* the porphyrin rather than strapping it, and accompanied by considerable deformation of the porphyrin ring from planarity. The deformation is characterised by the pyrrole rings attached to the *meso*-phenyl rings being forced downwards below the mean porphyrin plane, and the other two pyrrole rings distorted upwards from the mean plane in a saddle shape.†

The ^1H NMR spectrum of this isomer **4a**, while showing all of

* BPP34C10 is bis-*p*-phenylene-34-crown-10 or, systematically, 1,4,7,10,13,20,23,26,29,32-decaoxa[13.13]paracyclophane.[5]

† For the N_4 'plane', χ^2 = 134; deviations of the 4 nitrogens from the mean plane are δ_N −0.043(7), 0.042(7), −0.039(7) and 0.041(7) Å. Dihedral angles of the pyrrole planes are (1–4): 16.0(2), 11.0(3), 14.3(2), 10.6(2)°; interpyrrole dihedral angles are (1/2, 3, 4; 2/3, 4; 3/4): 19.3(3), 30.3(3), 17.3(3), 17.2(3), 21.5(3); 20.1(3)°.

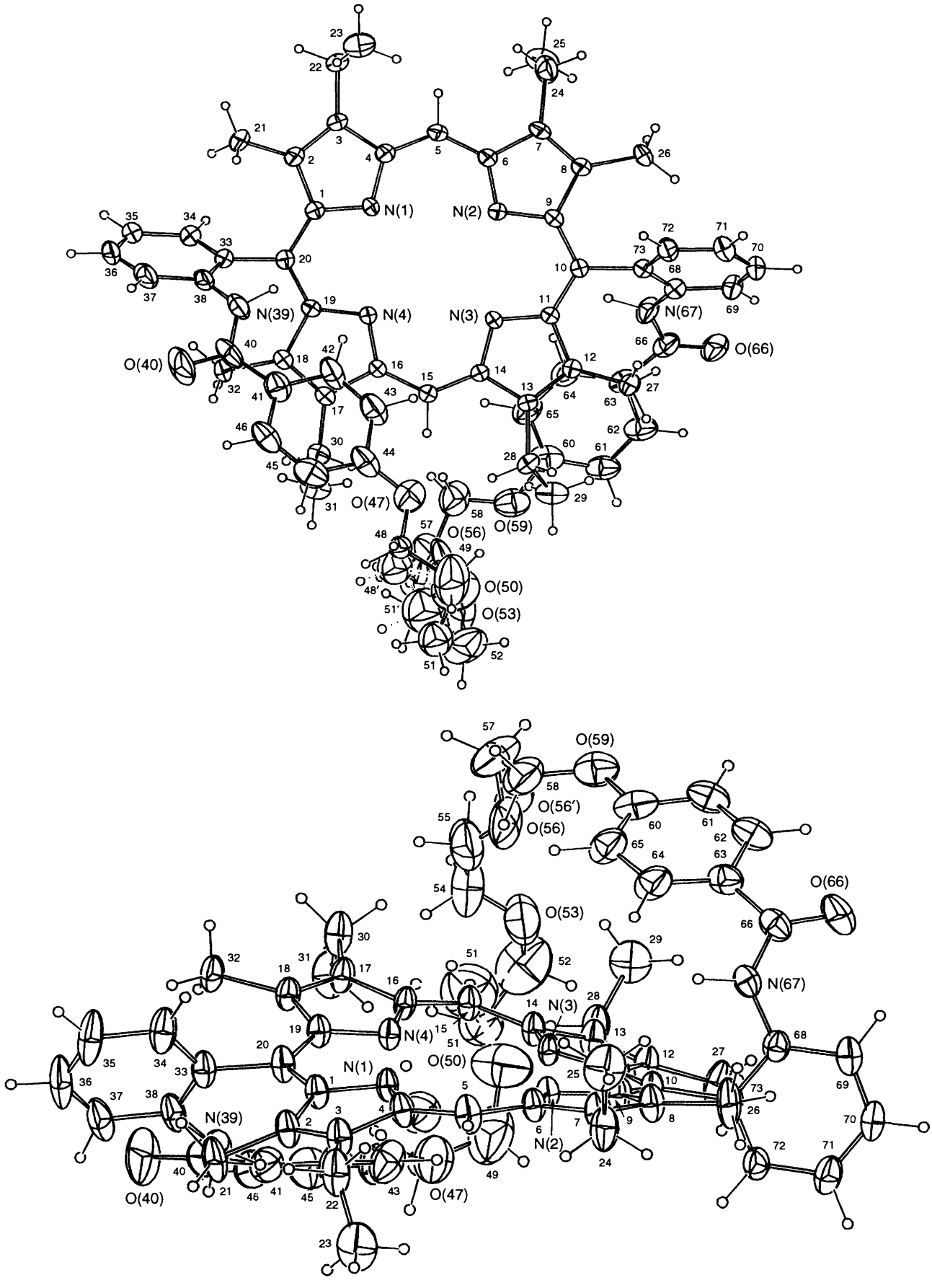


Fig. 1 Molecular projections normal to and through the porphyrin plane of **4a** revealing the ether chain wrapping around the porphyrin rather than strapping one face. 20% Thermal envelopes are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

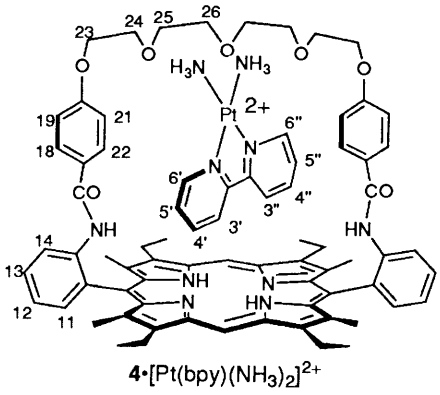
the peaks expected from a molecular formula identical with **4**, lacked the symmetry of that of **4** and was consistent with the conformation of the ether chain in the solid state. This indicated that the structure observed in the single crystals of **4a** had resulted from *meso*-phenyl ring rotation about the C(9)–(10) bond axis during the several weeks necessary for satisfactory crystal growth, and is not representative of the solution structure of **4** from the bulk of the sample and in samples not subject to slow recrystallisation. It was confirmed by the lack of signals characteristic of the isomeric **4a** that samples of **4** used in subsequent studies were free of any **4a**. In fact, it thus turned out that the characterisation of the isomeric **4a** provided reinforcing evidence for the integrity of **4**.

Complexation Properties.—The complexation between the various bipyridinium salts and the host molecules described here were carried out by ^{1}H NMR titrations as previously described.[1]

Diquat hexafluorosphosphate and paraquat hexafluorophosphate. Minimal changes in the chemical shifts observed in the host (δ_{av} +0.04 ppm) and guest (δ_{av} 0.01 ppm) proton resonances in equimolar solutions of **4** and either paraquat or diquat hexafluorophosphate, were interpreted as a lack of significant inclusion complex formation between the single chain porphyrin **4** and these guests.*

$[Pt(bpy)(NH_3)_2](PF_6)_2$. Although the single-strap porphyrin **4** was not observed to form inclusion complexes with either of the diquat or paraquat dications, it was reasoned that the complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ should still be possible, given that the *cis*-ammine ligands within the complex have been observed to bind, *via* hydrogen bonding, to only *one* of the ether chains within bicyclic crown ether systems.[13] Thus **4** may still complex $[Pt(bpy)(NH_3)_2](PF_6)_2$ in an analogous manner to the previously reported porphyrin host **1**.[1] Indeed, the formation of an inclusion complex between **4** and $[Pt(bpy)(NH_3)_2]^{2+}$ was confirmed by the ^{1}H NMR spectrum of a [$^2H_6$]acetone solution containing equimolar quantities of each.†

The protons of $[Pt(bpy)(NH_3)_2]^{2+}$ all experience significant shielding upon complexation consistent with the inclusion geometry indicated in Fig. 2. The resonance for the 3′,3″ protons



4•$[Pt(bpy)(NH_3)_2]^{2+}$

Fig. 2 Inclusion geometry of $[Pt(bpy)(NH_3)_2]^{2+}$ within the single-strap porphyrin **4**, deduced from ^{1}H NMR data

undergoes the largest shift ($\Delta\delta$ −1.62 ppm) on complexation, with the ammine ligands resonance exhibiting the smallest change ($\Delta\delta$ −0.24 ppm); the remaining proton resonances within the bipyridyl ligand experience intermediate shifts consistent with their assigned positions relative to the porphyrin nucleus. The shifts observed are larger than those reported for the complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ with dibenzo-30-crown-10[14] due to the large porphyrin ring-current present in the host **4**.

The changes in proton resonances of the porphyrin host upon complexation may be explained in terms of the effects of: (i) guest inclusion in the case of the ether chain, amide NH, and groups on the porphyrin periphery, (ii) a combination of guest inclusion and a conformational change in the case of the crown aromatic protons and (iii) a deformation in the porphyrin nucleus for the *meso*-phenyl protons, 11-H and 12-H.

The ether chain protons, and groups on the porphyrin periphery both experience deshielding from the complexed bipyridyl's ring current, moving downfield upon complexation. In particular, the pyrrole NH resonance moves by $\Delta\delta$ +0.05 ppm indicative of an orthogonal mode of binding.[15] Contrasting this, the amide NH proton experiences shielding ($\Delta\delta$ −0.11 ppm) resulting from its position close to the face of the bound bipyridyl ligand.

In the case of the crown aromatic protons, complex formation enforces a more orthogonal arrangement of the aryl rings with respect to the *meso*-phenol ring compared to the more parallel arrangement assumed for the uncomplexed host **4**. This conformational change must occur *via* a rotation in the C(16)–Ar bond [rather than the alternative C(15)–NH bond rotation] since the resonance of 14-H is virtually unchanged ($\Delta\delta$ −0.03 ppm), indicating no change in orientation of the carbonyl group, and associated shielding effects.‡ The conformational change results in a deshielding of the crown aryl protons, and allows stabilisation of the guest by electrostatic and π-π interactions similar to those observed in previous hosts. The small shifts then observed for these protons result from deshielding due to the conformation change, counteracted by the shielding effect of the bound bipyridyl ligand.

Additionally, the *meso*-phenyl ring protons 11-H and 12-H experience significant downfield movements upon complexation, $\Delta\delta$ +0.12 and +0.11 ppm respectively, suggesting the presence of strain on the porphyrin ring. The *ortho*-proton of the *meso*-phenyl ring along with the pyrrole NH have been used as indicators§ for porphyrin skeletal deformations within short-

* Small complexation-induced changes in porphyrin host resonances were, in previous porphyrin hosts,[1] accounted for by the combination of a conformational rearrangement of the host upon complexation, along with the effect of the aromatic ring current of the guest within the inclusion complex. However, in the case of the single-strap porphyrin **4** and paraquat in solution, there is no evidence to suggest a conformational alteration due to complex formation and, furthermore, the shifts observed cannot be explained solely in terms of the effects of the guest ring current. In other porphyrin host systems, a complexation-induced conformational change was especially evidenced by changes to the chemical shifts of 14-H, and the amide NH resonances. However, in the case of **4** no significant changes were observed to the resonances of either proton. For these reasons the results have been interpreted as indicating a lack of significant paraquat complexation by **4**, with the shifts of the paraquat resonances due to an undefined overall effect of porphyrin-induced changes in the overall solvent properties, or very weak complex formation.

† Selected ^{1}H NMR shifts for the complexation of **4** and $[Pt(bpy)(NH_3)_2](PF_6)_2$ in [$^2H_6$]acetone at 298 K are collected below. Spectra were recorded at 300 MHz using CD_2HCOCD_2H as reference (δ 2.05 ppm). Values in parentheses ($\Delta\delta$) indicate differences in chemical shifts between bound and unbound resonances. Porphyrin and $[Pt(bpy)(NH_3)_2](PF_6)_2$ concentrations were 8 mmol dm^{-3}: pyrrole NH, −2.26 (+0.05); 1-H, 10.42 (+0.09); 4-H, 4.10 (+0.07); 5-H, 1.76 (+0.04); 7-H, 2.68 (+0.06); amide NH, 8.35 (−0.11); 18–22-H, 6.64 (−0.09); 19–21-H, 6.05 (−0.01); 23-H, 3.66 (+0.20); 24-H, 3.50 (+0.19); 25-H, 3.38 (+0.17); 26-H, 3.38 (+0.17); $[Pt(bpy)(NH_3)_2](PF_6)_2$ 3′,3″, 7.11 (−1.62); 4′,4″, 7.64 (−0.95); 5′,5″, 7.64 (−0.34); 6′,6″, 8.61 (−0.34); NH_3, 5.11 (−0.24).

‡ This contrasts the complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ by hosts **1** and its shorter chain analogue in which the 14-H resonance undergoes shifts of −0.35 and −0.85 ppm respectively.[1]

§ In this case the pyrrole NH shifts cannot be used as an indicator since they are also affected by the bipyridyl ring current.

chain basket-handle porphyrins.[15-17] The deshielding of 11-H and 12-H (although smaller than that observed for tightly strapped porphyrins[16]) implies a puckering of the porphyrin ring, and the movement of the *meso*-phenyl rings into a position where both these protons experience increased deshielding from the porphyrin ring current. In this case, such strain suggests a tight fit of the $[Pt(bpy)(NH_3)_2]^{2+}$ guest within the cavity of **4** stretching the bridging ether chain and resulting in a deformation of the porphyrin nucleus into a saddle or shallow U-shape, similar to the effect previously observed in the analogous macrotricyclic system **1**.[1]

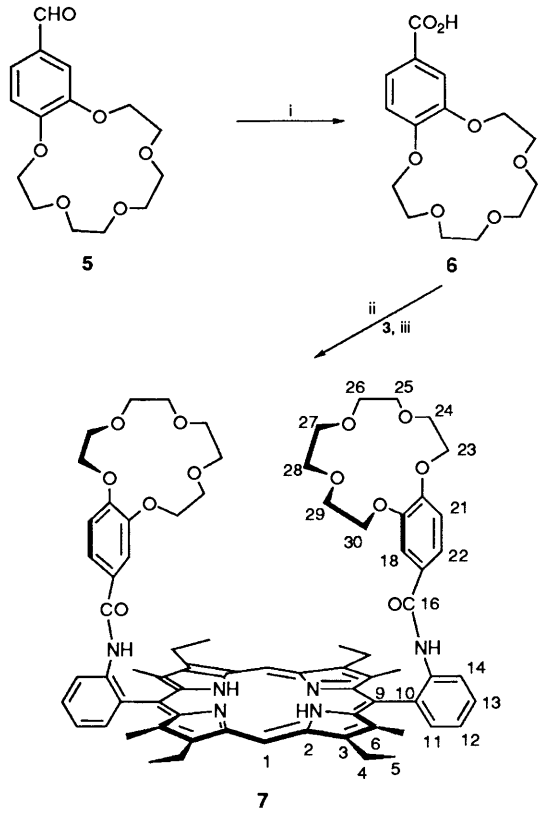
The association constant for the complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ by **4** was determined using non-linear least-squares curve-fitting of ^1H NMR titration data, and was found to be K_a 155 $dm^3\ mol^{-1}$ with -2.9 kcal mol^{-1}. Such a $\Delta G°$ is considerably smaller in comparison to $[Pt(bpy)(NH_3)_2](PF_6)_2$ complexation by **1** ($\Delta G°$ -4.3 kcal mol^{-1}) or by dibenzo-30-crown-10 ($\Delta G°$ -7.2 kcal mol^{-1}), reflecting the tight fit of $[Pt(bpy)(NH_3)_2](PF_6)_2$ within the cavity of **4**.

Porphyrin-based Molecular Tweezers

A recently recognised class of host molecules described as *molecular tweezers*,[18,19] can complex various guests by a pincering action, reminiscent of everyday tweezers. The pincers have usually been aromatic in nature, providing π-π electron interactions for aromatic guests, although other modes of substrate binding have also been utilised. Linking the two pincer groups is the pivot moiety, which positions the pincers at a specific interplanar distance for optimum guest interaction and, in some cases, provides an additional point for guest binding. Zimmerman and co-workers have synthesised tweezers which contain a *rigid* pivot enabling *preorganisation* of the cavity before complexation.[20] Although the complexity of these hosts has increased with the addition of binding features to increase their 'stickiness', a common feature is an inter-chromophore distance of 7 Å in these molecules which is crucial for π-π stabilisation of bound aromatic guests.[20-25]

Within our design requirements, to provide a true tweezering action it would be necessary to incorporate the complexing aryl rings within *separate* ether rings, positioned at an optimum separation for complexation using a porphyrin pivot group, while retaining most of the desirable features that characterise complexation between dibenzo-crowns and bipyridinium derivatives.* Furthermore, the non-flexibility of the porphyrin should enhance complexation.† The use of non-linked crown aromatic rings would also represent a considerable synthetic simplification since a high dilution cyclisation would not be required to produce the porphyrin host.

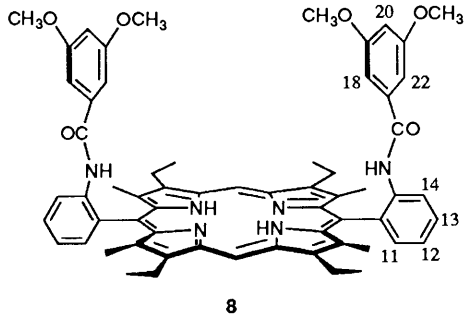
The design of the ether pincer groups was based on a 3,4-dihydroxybenzene ring; this allows the incorporation of phenolic oxygens into the ether chains, since these oxygen atoms have been identified as being crucial to guest stabilisation. Benzo-crown ethers incorporating the more



Scheme 2 *Reagents:* (i) CrO_3, H_2SO_4; (ii) $SOCl_2$; (iii) CH_2Cl_2, pyridine. The non-systematic numbering scheme is used in discussion of the NMR spectra.

symmetrical 3,5-dihydroxy aryl groups have not been reported previously.[29]

The construction of the benzo-crown ether pincers was straightforward, utilising methods previously reported for the synthesis of *ortho*-substituted benzo crowns[30] (Scheme 2). Condensation with the diamino porphyrin **3** produced the porphyrin tweezer **7**. As a control, an analogous porphyrin **8** lacking the ether chains was synthesised in parallel fashion from 3,5-dimethoxybenzoic acid.‡



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The NMR resonances of **7** were assigned using a combination of COSY-45 and NOESY experiments. Of particular significance is the relative chemical shifts of the crown aromatic protons 18-, 21-and 22-H. The orientation of the crown moiety with 18-H, rather than 21- or 22-H over the porphyrin (Scheme 2) was deduced by the further upfield position of the resonance for 18-H (δ 5.71) compared to those of 21-H (δ 5.92) and 22-H

* The complexation of bipyridinium dications by the porphyrin hosts discussed previously[1] may be essentially regarded as a tweezer-like action of the crown aromatic rings acting as pincer groups, since they also sandwich the guest molecules. However a molecular tweezer, by definition, contains no linking groups between the pincer groups other than the pivot moiety.

† The inclusion of either porphyrins or crown ethers into molecular tweezers is not new. Porphyrins were first incorporated by Chang[26] using tetraethyltetramethylporphyrins connected by either anthracene or biphenylene rigid pivot units. Crown ethers, on the other hand, have been used as pincers as discussed by Beer in a review of responsive macrocycles,[27] as well as in macrocycles providing recognition sites for alkali- and transition-metal cations.[28]

‡ Although the *meta*-substitution pattern of the crown aromatic ring differs from that of the *ortho*-substituted porphyrin tweezer **7**, this was not considered to detract from the ability of **8** to act as a control for binding.

Table 1 Selected ^{1}H NMR chemical shifts for **7** in various solvents[a,b]

Solvent	21-H	22-H	18-H	23-H	24-H	25-H	26-H	27-H	28-H	29-H	30-H	NH[d]
$CDCl_3$ (conformer **A**)	5.92	6.28	5.71	3.46	3.40	3.33	3.26	3.09	2.87	1.97	1.91	8.02
CD_2Cl_2	5.95 (+0.03)	6.38 (+0.10)	5.32 (−0.39)	3.33 (−0.13)	3.26 (−0.14)	3.21 (−0.12)	3.12 (−0.14)	2.92 (−0.17)	2.73 (−0.14)	1.54 (−0.43)	1.43 (−0.48)	7.87 (−0.15)
CD_3CN/ $CDCl_3$ (1:1)[c]	6.01[e] (+0.09)	6.56 (+0.28)	4.81 (−0.90)	3.29 (−0.17)	3.18 (−0.22)	3.12 (−0.21)	3.00 (−0.26)	2.74 (−0.35)	2.46 (−0.41)	1.08 (−0.89)	0.83 (−1.08)	7.69 (−0.33)
$(CD_3)_2CO$ (conformer **B**)	5.97 (+0.05)	6.58 (+0.30)	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)

[a] Chemical shifts are in ppm relative to TMS, with values in parentheses indicating shifts ($\Delta\delta$ ppm) relative to the $CDCl_3$ solution. [b] Labelling as per Scheme 2. [c] Referenced using CD_2HCN residual peak (δ 1.95). [d] Amide NH. [e] Broad peak.

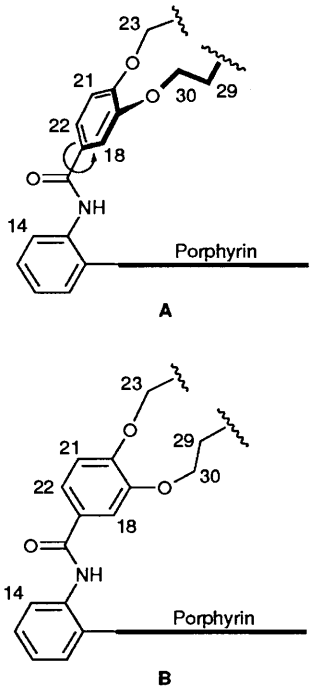

Fig. 3 Limiting conformations adopted by **7** in [^{2}H]chloroform (**A**), and [$^2H_6$]acetone (**B**), deduced from the ^{1}H NMR data

(δ 6.28). The ether chain proton resonance assignments are also consistent with this conformation, since the resonance for the methylene protons 30-H (δ 1.91) is shifted furthest upfield implying a closer proximity to the porphyrin compared to the resonance for 23-H (δ 3.46) which is least affected. The intermediate methylene protons (29 to 24) have resonances which are consistent with an increasing distance from the porphyrin nucleus on progression along the ether chain.

The uncomplicated nature of the NMR spectrum of **7** indicates a fast conformational equilibrium in solution; however the NMR spectrum is considerably solvent dependent. The majority of resonances that exhibit solvent dependence originate from the crown moiety, with resonances on the porphyrin periphery remaining essentially constant. Outlined in Table 1 are selected proton shifts in various solvents. The changes in chemical shifts are a reflection of a solvent-induced conformational change within **7**, as depicted in Fig. 3.

In chloroform the conformation is such that the two crown aromatic rings are twisted out of conjugation with the amide group and *meso*-phenyl ring, resulting in an approximately co-facial and parallel arrangement of the crown aromatics (conformer **A**, Fig. 3). By contrast, in [$^2H_6$]acetone, all the ether ring resonances are more shielded by the porphyrin ring current, moving upfield (Table 1). The most significant shifts are observed for protons 18, 29 and 30 which move upfield by −0.95, −0.90, −1.13 ppm respectively. In comparison, the resonances of 21-, 22-H move downfield ($\Delta\delta$ +0.05, +0.30 ppm). These downfield shifts combined with the minimal shift of 14-H are consistent with rotation of the crown aromatic ring about the C(16)–Ar bond (Fig. 3) to yield conformation **B**. This allows the crown aromatic ring to maintain conjugation with the amide and *meso*-phenyl ring, resulting in the crown aromatic rings assuming an *edge-on* orientation.*

Between the extremes of chloroform and acetone, are the conformations of **7** observed in the solvents [$^2H_2$]dichloromethane and [$^2H_3$]acetonitrile/[^{2}H]chloroform (1:1). Examination of the changes in chemical shift (Table 1) reveals that the solvents may be ordered approximately in their expected polarity order *viz.*, chloroform ≈ dichloromethane, acetonitrile–chloroform (1:1), and acetone reflecting their transition from conformation **A** to conformation **B**.

Complexation Properties.—The conformational solvent-dependence suggests that in chloroform compound **7** (conformer **A**) is more preorganised for complexation since it contains the crown aromatic rings at an increased orthogonal position to the *meso*-phenyl plane compared to that adopted in acetone (conformer **B**). However, the insolubility of the bipyridinium dications in chloroform precluded complexation studies in this solvent, and the usual solvent employed for dibenzo-crown ether complexations with bipyridinium cations[5,31,32] *viz*, acetone, was thus used.

In rationalising the complexation of **7** with bipyridinium dications it was necessary to compare complexation-induced changes in chemical shifts to the non-crown ether-containing porphyrin tweezer **8** analogue employed as a control host.

Paraquat Hexafluorophosphate and Diquat Hexafluorophosphate.—Equimolar solutions of **7** and both paraquat and diquat in [$^2H_6$]acetone showed considerable complexation-induced shifts for the guest proton resonances, yet only minimal changes in the host resonances (Table 2). The shifts are consistent with an inclusion geometry shown in Fig. 4. The marginal shifts for the resonances of **7** may be rationalised by a combination of a complexation-induced conformational change within **7**, offset by the inclusion of the bipyridinium cations and the effects of their magnetic anisotropy. By comparison, little change is observed in the resonances of either the porphyrin **8** or paraquat or diquat in an analogous experiment, indicating that no complexation has occurred.

The numerous studies of dibenzo-crown ether/bipyridinium dication complexations by Stoddart[31,32] has revealed the propensity of host and guest aromatic rings to align in a co-

* The conformations shown in Fig. 3 do not imply *absolute orthogonality* (chloroform) or *co-planarity* (acetone) of the crown aromatic and *meso*-phenyl rings. The NMR data imply inter-phenyl dihedral angles approaching 90 and 0°, respectively.

parallel arrangement in order to maximise both electrostatic and charge-transfer contributions toward complex stability.[5] If such a geometry is maintained in the complexation of the dications by **7**, then the conformation of the complexed tweezer molecule would approach that maintained by free **7** in chloroform, *viz*, conformer **A** (Fig. 3). The chemical shift of the crown protons in **7** would thus undergo downfield movements on complexation compared to their unbound positions in acetone (Table 1). Inclusion of the dications in the orientation depicted in Fig. 4 implies a shielding of the aromatic crown protons by the guests' magnetic anisotropy, counteracting the shifts from the conformational change and resulting in the small shifts observed in Table 2 for the host protons. Similar compromising shifts in the host **4** and for other porphyrin-based receptors including **1** have been observed.[1]

Table 2 Selected ^{1}H NMR chemical shifts for the complexation of paraquat, diquat, and $[Pt(bpy)(NH_3)_2]^{2+}$ by **7**[a]

	7·PQ^{2+} (1:1)	**7**·DQ^{2+} (1:1)	**7**·$[Ptbpy(NH_3)_2]^{2+}$ (1:1)
18-H	4.75 (−0.01)	4.76 (0.00)	5.17 (+0.36)
21-H	6.00 (+0.02)	5.98 (0.00)	5.93 (−0.32)
22-H	6.60 (+0.02)	6.59 (+0.01)	6.25 (−0.45)
23-H	3.32 (+0.12)	—	3.47 (+0.03)
24-H	3.19 (+0.07)	—	3.38 (+0.09)
25-H	3.13 (+0.08)	3.06 (+0.01)	3.32 (+0.15)
26-H	3.02 (+0.07)	2.98 (+0.03)	3.19 (+0.14)
27-H	2.79 (+0.09)	2.76 (+0.05)	2.97 (−0.20)
28-H	2.52 (+0.07)	2.45 (+0.01)	—[b]
29-H	1.24 (+0.17)	1.20 (+0.13)	1.78 (−0.70)
30-H	0.86 (+0.07)	0.86 (+0.07)	1.55 (−0.74)
NH[c]	7.83 (+0.10)	7.80 (+0.07)	7.73 (−0.10)
2′,6′	9.15 (−0.20)	—	—
3′,5′	8.55 (−0.27)	—	—
^+N–CH_3 3′3″	4.60 (−0.13)	—	—
(DQ^{2+}) or Pt complex 4′,4″	—	8.98 (−0.28)	5.62 (−3.11)
(DQ^{2+}) or Pt complex 5′,5″	—	8.87 (−0.23)	6.90 (−1.70)
(DQ^{2+}) or Pt complex 6′,6″	—	8.39 (−0.21)	7.36 (−0.62)
(DQ^{2+}) or Pt complex N-$(CH_2)_2$ or NH_3	—	9.25 (−0.25)	8.28 (−0.67)
(DQ^{2+}) or Pt complex	—	5.49 (−0.20)	4.80 (−0.55)

[a] Spectra were recorded at 300 MHz and 298 K in [$^2H_6$]acetone using CD_2HCOCD_2H as reference (δ 2.05). Porphyrin concentrations were 59, 70 and 7 mmol dm^{-3}, respectively for the three guests PQ^{2+}, DQ^{2+} and Pt complex. Values in parentheses indicate differences between host and guest solutions and their 1:1 mixture. Paraquat and diquat were used as their hexafluorophosphate salts. [b] Peak was not visible in the equimolar solution. [c] Amide NH.

The resonances of the paraquat and diquat protons all experience upfield shifts upon complexation consistent with inclusion within **7** in the manner indicated (Fig. 4). A lack of observable inequivalence between the protons within the paraquat molecule indicates a fast complexation/decomplexation equilibrium and fast rotation within the cavity of **7**.

The stability constant for the complexation of **7** and paraquat at 298 K was determined by non-linear least-squares fitting of ^{1}H NMR titration data to be 32 dm^3 mol^{-1} with a $\Delta G°$ of −2.1 kcal mol^{-1}. This is approximately equal in strength to the macrotricyclic host **1** (K_a 50 dm^3 mol^{-1}, $\Delta G°$ −2.3 kcal mol^{-1}) indicating that in the complexation of paraquat, removal of the bridging ether chains from **1** has little effect, and a crown aromatic ring conformational change is observed in both cases. In the case of diquat an association constant of 20 dm^3 mol^{-1} and $\Delta G°$ −1.8 kcal mol^{-1} was determined. This complexation, although small in comparison to the reduced macrotricyclic host reported previously (K_a 80 dm^3 mol^{-1}, $\Delta G°$ −2.6 kcal mol^{-1})[1], represents an improvement on the lack of complexation observed between the corresponding amide-linked macrotricyclic host **1** and diquat.[1] Thus, for the diquat dication, the increased conformational mobility of the crown aromatic rings resulting from removal of the bridging ether chains enhances complexation.

Complex $[Pt(bpy)(NH_3)_2](PF_6)_2$. The apparently stronger complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ by **7** provided an opportunity to gain a fuller understanding of the conformational changes within **7** upon complexation of paraquat and diquat. The data in Table 2 are consistent with an inclusion geometry of $[Pt(bpy)(NH_3)_2]^{2+}$ within **7** as depicted in Fig. 4.

The protons in the coordination complex all experience shielding from the tweezer **7** resulting in upfield shifts. The relative sizes of the shifts within the guest reflect the position of the protons relative to the porphyrin, with the 3′,3″ resonance undergoing the largest change ($\Delta\delta$ −3.11 ppm), and the ammine ligands the smallest ($\Delta\delta$ −0.55 ppm) supporting the inclusion geometry of Fig. 4.

The resonances for groups on the porphyrin periphery, along with the pyrrole NH resonance move downfield upon complexation, experiencing deshielding ($\Delta\delta_{av}$ +0.02 ppm) from the bound bipyridyl ligand. The direction of shift of these resonances further supports the inclusion geometry of Fig. 4.[15]

The complexation-induced changes to resonances within the crown-ether moiety of **7** are again complicated by the combined effects of a conformational change upon complexation, and the magnetic anisotropy of the bipyridyl ligand. Upon complexation in acetone (conformer **B**) the crown aromatic rings are

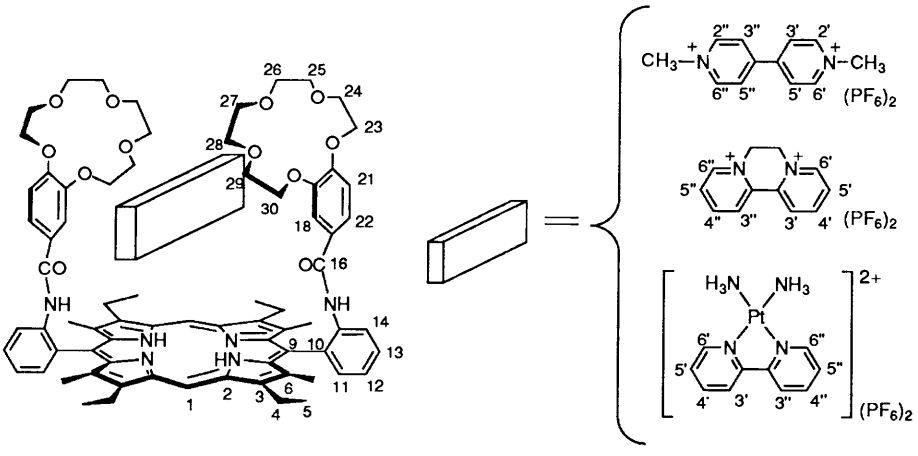

Fig. 4 Inclusion geometry of various guests with the porphyrin tweezer **7**, consistent with the ^{1}H NMR data

forced more orthogonal to the *meso*-phenyl plane (toward conformer **A**) in an attempt to increase electrostatic and π-π interactions with the guest. This conformational change is evidenced by the movement of the 14-H resonance upon complexation* ($\Delta\delta$ −0.12 ppm), along with the complicated shifts for crown aromatic ring proton resonances. The movement of the 14-H resonance suggests that the conformation change occurs not only by way of rotation in the C(16)–Ar bond (as was observed with the solvent-dependent spectra of **7**), but also in the C(15)–NH and N–C(16) bonds. Nevertheless, the apparently conflicting directions of the shifts observed for the crown aromatic ring proton resonances (Table 2) may still be explained by the different shifts undergone by these proton resonances upon a conformation change, with 21-, 22-H moving upfield and 18-H moving downfield. The subsequent inclusion of the shielding effects of the bipyridyl ring current then produces the shifts observed.

The amide NH, and the ether chain protons' complexation-induced shifts also reflect the combination of a conformational change within **7** from conformer **B** toward conformer **A**, and the complexed bipyridyl's ring current. For the ether chains, the largest shifts upon complexation are observed for 29-, 30-H ($\Delta\delta$ −0.70, −0.74 ppm), which were also observed to undergo the largest shift as a result of the conformation change.

The association constant for the complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ by **7** was determined by titration to be 140 dm^3 mol^{-1}, with a $\Delta G°$ of −2.9 kcal mol^{-1}. Such a free energy of complexation is appreciably smaller than that observed for $[Pt(bpy)(NH_3)_2](PF_6)_2$ with **1** (−4.3 kcal mol^{-1}), and dibenzo-30-crown-10 (−7.2 kcal mol^{-1}), presumably reflecting the lack of bridging ether chains within **7** for hydrogen bonding with the ammine ligands.

Conclusion

The inclusion geometry of the three bipyridinium guests studied with the singly strapped host **4**, and within the pincers of **7**, is consistent with the aromatic rings of the guest sandwiched between the aromatic benzo-crown rings in the manner predicted. These complexes are presumably stabilised by a combination of π-π electron charge transfer, electrostatic, and hydrogen bonding interactions. The lack of paraquat and diquat complexation by the singly strapped porphyrin host **4** may be taken as an indicator of the minimal requirements for efficient binding in these types of host molecules. Either an incorrect number or geometry of ether oxygen atoms for electrostatic interactions, and/or unfavourable orientations of the crown aromatic rings due to their increased conformational mobility within **4** could account for poor substrate recognition in this case. On the other hand, the complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ suggest that hydrogen bonding between the ammine ligands and the ether oxygens is an important stabilising force for the complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$, together with π-π charge transfer and electrostatic interactions. Since there is only one ether chain available for hydrogen bonding in the host **4**, the *cis*-ammine ligands can adopt the same straddling disposition observed in bicyclic systems (*i.e.* with the single ether chain passing between the two ammines rather than both chains in the bicyclic system encircling them). The fact that complexation of $[Pt(bpy)(NH_3)_2](PF_6)_2$ by **4** is accompanied by a conformational change and a stretching of the ether chains, along with a deformation of the porphyrin nucleus to accommodate the dication, is an indication of the reorganisation that is required for effective binding. These results suggest that (i) decreasing the number of ether chains from two to one only partially removes the steric effects from the ether chain on the crown aromatic rings, or (ii) the amide bond is still dominant in influencing the solution conformations of the crown aromatic rings.

When any constraints that might be imposed by a strap across the face of the porphyrin were removed, exemplified by the porphyrin tweezer **7**, there was indeed some improvement in complexation of paraquat and diquat.† Although the porphyrin tweezer **7** was observed to complex all three guests, the smaller association constants and free energies of complexation compared to **1** at 298 K (**1**·PQ^{2+} K_a 50 dm^3 mol^{-1} with $\Delta G°$ −2.3 kcal mol^{-1}, and **1**·$[Pt(bpy)(NH_3)_2]^{2+}$ K_a 1350 dm^3 mol^{-1} and $\Delta G°$ −4.3 kcal mol^{-1}) reflects the lesser degree of preorganisation present in the crown-ether complexing subunit of **7**. Within the three guests, the stronger complexation of $[Pt(bpy)(NH_3)_2]^{2+}$ can be attributed to the additional stabilisation of the inclusion complex by hydrogen bonding between the ammine ligands of $[Pt(bpy)(NH_3)_2]^{2+}$ and the oxygen atoms of the crown tweezer. Thus, although the removal of the bridging ether chains, compared to **1**, allows an increase in the conformational mobility of the crown aromatic rings the nett result is a decrease in the level of preorganisation, reducing the strength and stability of complexation.

Thus, overall, these molecules are particularly instructive in determining the factors that must be kept in fine balance, between the necessity for a certain degree of preorganisation and minimal but necessary reorganisation, for efficient complexation of bipyridinium cations in these porphyrin hosts. These results now allow for the next obvious steps in fine-tuning the design for the desired receptor selectivity and binding strength. The stage is now set for the introduction of another variable into the conceptual design—the relationship between receptor binding strength and the desired photochemical reactivity that is required if these supramolecules are to be used in artificial photosynthetic or related devices.

Experimental

Structure Determination.—A unique room-temperature diffractometer data set (T ~ 295 K; $2\theta_{max}$ 50°, $2\theta/\theta$ scan mode; monochromatic Mo-Kα radiation, λ 0.7107_3 Å) was measured yielding 10 277 independent reflections, 3611 with $I > 3\theta(I)$ being considered 'observed' and used in the large block least-squares refinement without absorption correction after the solution of the structure by direct methods. Anisotropic thermal parameters were refined for C, N, O; (x, y, z, $U_{iso})_H$ were included constrained at estimated values. Final conventional residuals on $|F|$ at convergence, R, R_w [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4 - (I_{diff})$] were 0.080, 0.074. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system[33] implemented by S. R. Hall. Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.‡

Crystal data. $C_{66}H_{70}N_6O_7$·$0.5(CH_3)_2CO$, M = 1088.3. Triclinic, space group $P\bar{1}$ (C_1^1, No. 2), a = 15.775(4), b = 15.091(2), c = 15.068(6) Å, α = 68.70(2), β = 62.24(2), γ = 87.42(1), V = 2924(2) $Å^3$; D_c(Z = 2) 1.24 g cm^{-3}; F(000) 1160, μ_{Mo} 0.8 cm^{-1}; specimen: 0.47 × 0.10 × 0.24 mm.

Abnormal features/variations in procedure. The precision of

* In the complexation of **1** by $[Pt(bpy)(NH_3)_2](PF_6)_2$ the resonance of 14-H was shifted by $\Delta\delta$ −0.35 ppm, and indicated a similar rotation of the crown aromatic ring.[1]

† This trend in binding strengths differs from that previously reported by us,[3] and which was based on qualitative observations.

‡ For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

the study and accessible data are limited by the high thermal motion and disorder. Within the 'strap' of the molecule, C(48), C(51), O(56) were each modelled as disordered over pairs of sites, occupancies being set at 0.5 after initial refinement; isotropic thermal parameter forms were used for C(48,51). Lattice difference map residues were modelled as 0.5 acetone. Central NH hydrogen atoms were not unambiguously evident in difference maps and were omitted from the refinement.

Synthetic Procedures.—General experimental conditions, and procedures for the determination of the stability constants have been described previously.[1]

1,11-*Bis*(4′-*chloroformylphenoxy*)-3,6,9-*trioxaundecane* **3**. The carboxylic acid precursor[9] obtained from tetraethylene glycol bistosylate and methyl 4-hydroxybenzoate acid was suspended in CH_2Cl_2 (dry) and refluxed for 2 h with an excess of oxalyl chloride. Upon cooling, the solution was pumped dry, washed (CH_2Cl_2, dry, × 2), and pumped further to give **3** as a yellow oil; ν(CO)/cm^{-1} 1770. The compound was used without further purification.

Single strapped porphyrin **4**. The acid chloride **3** in CH_2Cl_2 (dry; 50 cm^3) was added dropwise to a solution of the α,α-diaminoporphyrin **4** (0.14 g, 0.21 mmol) in CH_2Cl_2 (dry; 750 cm^3) and pyridine (dry; 2 cm^3) under a blanket of N_2. The solution was refluxed for 48 h, after which time additional **4** (0.13 g), and acid chloride **3** (0.24 g) were added and refluxing continued for a further 48 h. The solution was then cooled, partially concentrated by rotary evaporation, washed (0.05 dm^3 mol^{-1} HCl solution, water, aq. Na_2CO_3, H_2O) and dried (Na_2SO_4). Purification was carried out using column chromatography with CH_2Cl_2–Et_2O (4:1) + EtOH (2%) as eluent to yield the strapped porphyrin **4** (0.18 g, 42%), m.p. 284 °C (from acetone) (Found: C, 72.6; H, 6.7; N, 7.6. $C_{66}H_{70}N_6O_7$·$2H_2O$ requires C, 72.37; H, 6.81; N, 7.67%); δ_H(300 MHz; $CDCl_3$) 10.44 (2 H, s, *meso*-H), 9.23 (2 H, d, *J* 9, ArH), 8.44 (2 H, s, NH), 8.02 (2 H, t, *J* 9, ArH), 7.71 (2 H, d, *J* 9, ArH), 7.60 (2 H, t, *J* 9, ArH), 6.92 (4 H, d, *J* 9, ArH), 6.24 (4 H, d, *J* 9, ArH, 4.16 (8 H, q, *J* 6, CH_2CH_3), 3.69 (4 H, t, *J* 3, α-OCH_2), 3.58 (4 H, t, *J* 3, β-OCH_2), 3.50 (8 H, s, γ-, δ-OCH_2), 2.76 (12 H, s, CH_3), 1.90 (12 H, t, *J* 6, CH_3CH_2) and −2.19 (2 H, br s, NH); δ_C($CDCl_3$) 164.94, 161.07, 145.67, 145.35, 141.70, 138.99, 135.94, 133.79, 130.74, 130.15, 128.26, 126.56, 124.03, 120.21, 113.94, 111.46, 97.13, 70.61, 69.09, 67.26, 19.91, 17.63 and 13.52.

Isomeric **4a**. This compound was obtained as a minor component by slow recrystallisation of **4** from acetone over several weeks. δ_H(300 MHz; $CDCl_3$) 9.98 (2 H, s, *meso*-H), 8.92 (2 H, d, *J* 8, ArH), 8.20 (2 H, d, *J* 8, ArH), 8.15 (2 H, s, NH), 7.89 (2 H, t, *J* 8, ArH), 7.62 (2 H, t, *J* 8, ArH), 6.34 (4 H, d, *J* 8, ArH), 6.09 (4 H, d, *J* 8, ArH), 4.04 (4 H, m, OCH_2), 3.97–3.75 [19 H, m, OCH_2 (12 H), $CHCH_3$ (7 H)], 3.46 (1 H, m, $CHCH_3$), 2.40 (6 H, s, CH_3), 2.39 (6 H, s, CH_3), 1.60 (6 H, t, *J* 7, CH_2CH_3), 1.29 (6 H, t, *J* 7, CH_2CH_3) and −2.12 (2 H, br s, pyrrole NH).

(4′-*Carboxybenzo*)-15-*crown*-5 **6**. 4′-Formylbenzo-15-crown-5 **5**[30] (2.0 g, 6.75 mmol) dissolved in acetone (50 cm^3) was treated with an excess of Jones reagent (CrO_3/H_2SO_4/H_2O) with stirring until the orange colour persisted for at least 25 min. The solution was filtered, and the residual chromium salts were washed well with acetone. The filtrate was taken to dryness and water added to it; the insoluble ether compound was then filtered off and washed well (H_2O) to give **6** (1.6 g, 76%), m.p. 185–187 °C (lit.,[34,35] 184–186 °C) (Found: C, 57.6; H, 6.4. $C_{15}H_{20}O_7$ requires C, 57.68; H, 6.46%); δ_H(300 MHz; $CDCl_3$, CD_3OD) 7.47 (1 H, d, *J* 8, ArH), 7.34 (1 H, s, ArH), 6.69 (1 H, d, *J* 8, ArH), 4.18 (1 H, br s, OH), 3.97 (4 H, m, α-OCH_2), 3.71 (4 H, m, β-OCH_2) and 3.55 (8 H, m, γ-, δ-OCH_2).

4′-*Chloroformylbenzo*-15-*crown*-5.[35,36] Carboxybenzo-15-crown-5 **6** was suspended in dry $CHCl_3$ and an excess of thionyl chloride was added dropwise to it; the solution was then refluxed for 3 h. After cooling, the solvent was removed under high vacuum, and the residue washed with dry benzene (× 2), and pumped further. The resulting clear oil was used without further purification; ν(CO)/cm^{-1} 1747.

Bis(*benzo*-15-*crown*-5)*porphyrin* **7**. 4′-Carboxybenzo-15-crown-5 **6** (0.17 g, 0.5 mmol) was converted into its acid chloride derivative as outlined above. This acid chloride was then dissolved in dry CH_2Cl_2 (20 cm^3) and added dropwise through the condenser to a refluxing solution of the α,α-diaminoporphyrin **3** (0.14 g, 0.2 mmol) in dry CH_2Cl_2 (50 cm^3) and dry pyridine (1 cm^3). Refluxing was continued for 4.5 h when the reaction was essentially complete (TLC). The solution was cooled, washed (0.05 mol dm^{-3} HCl × 2, H_2O, aq. Na_2CO_3, H_2O) and dried (Na_2SO_4). The crude material was then loaded onto a flash chromatography column and eluted with CH_3COCH_3/Et_2O (1:1) followed by $CHCl_3$ + 10% EtOH to give **7** (0.16 g, 61%) (Found: C, 69.9; H, 6.6; N, 6.4. $C_{74}H_{84}N_6O_{12}$·H_2O requires C, 70.12; H, 6.84, N, 6.63%); δ_H(300 MHz; $CDCl_3$) 10.28 (2 H, s, *meso*-H), 9.05 (2 H, d, *J* 9, ArH), 8.02 (2 H, s, NH), 7.91 (2 H, t, *J* 9, ArH), 7.84 (2 H, d, *J* 9, ArH), 7.55 (2 H, t, *J* 9, ArH), 6.28 (2 H, d, *J* 9, ArH), 5.92 (2 H, d, *J* 9, ArH), 5.71 (2 H, s, ArH), 4.01 (8 H, q, *J* 9, CH_2CH_3), 3.46 (4 H, d, *J* 3, OCH_2), 3.40 (4 H, d, *J* 3, OCH_2), 3.33 (4 H, d, *J* 3, OCH_2), 3.26 (4 H, d, *J* 3, OCH_2), 3.09 (4 H, d, *J* 6, OCH_2), 2.87 (4 H, d, *J* 3, OCH_2), 2.61 (12 H, s, CH_3), 1.97 (4 H, d, *J* 6, OCH_2), 1.91 (4 H, d, *J* 3, OCH_2), 1.77 (12 H, t, *J* 6, CH_2CH_3) and −2.35 (2 H, br s, NH); δ_C-($CDCl_3$) 164.46, 151.32, 147.84, 145.72, 145.26, 141.75, 139.03, 135.99, 133.43, 130.64, 130.31, 126.54, 124.08, 120.08, 119.97, 112.12, 111.52, 110.05, 97.09, 70.52, 70.09, 69.70, 69.41, 68.68, 68.15, 67.39, 66.40, 19.83, 17.57 and 13.57.

5,15-*Bis*[o-(3′,5′-*dimethoxybenzamido*)*phenyl*]-2,8,12,18-*tetraethyl*-3,7,13,17-*tetramethylporphyrin* **8**. 3,5-Dimethoxybenzoyl chloride (150 mg, 0.7 mmol) dissolved in CH_2Cl_2 (dry; 20 cm^3) was added dropwise with stirring to a solution of CH_2Cl_2 (20 cm^3) containing the α,α-diaminoporphyrin **3** (50 mg, 0.07 mmol) and dry pyridine (1 cm^3) under a N_2 blanket. The solution was then refluxed for 4 h. Upon cooling, the solution was washed (0.05 mol dm^{-3} HCl, H_2O, aq. Na_2CO_3, H_2O) and dried (Na_2SO_4). Purification was carried out using column chromatography (alumina) using CH_2Cl_2 followed by CH_2Cl_2–Et_2O (10%) as eluents to give **8** (53 mg, 77%), m.p. > 230 °C (from CH_2Cl_2–MeOH) (Found: C, 74.5; H, 6.75; N, 8.3. $C_{62}H_{64}N_6O_6$·0.5 H_2O requires C, 74.60; H, 6.56; N, 8.42%); δ_H(300 MHz; $CDCl_3$) 10.25 (2 H, s, *meso*-H), 8.98 (2 H, d, *J* 9, ArH), 8.02 (2 H, d, *J* 9, ArH), 7.92 (2 H, t, *J* 6, ArH), 7.65 (2 H, s, NH), 7.60 (2 H, t, *J* 6, ArH), 5.57 (2 H, t, *J* 3, ArH), 5.36 (4 H, t, *J* 3, ArH), 4.01 (8 H, q, *J* 6, CH_2CH_3), 2.60 (12 H, s, CH_3), 1.99 (12 H, s, CH_3O), 1.77 (12 H, t, *J* 6, CH_2CH_3) and −2.39 (2 H, S, NH); δ_C($CDCl_3$) 164.78, 159.88, 145.77, 145.19, 141.61, 139.06, 136.20, 135.92, 133.20, 130.97, 130.43, 124.24, 120.15, 116.24, 111.30, 104.11, 102.93, 97.14, 53.74, 19.91, 17.60 and 13.72.

Acknowledgements

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References

1 M. J. Gunter and M. R. Johnston, *J. Chem. Soc., Perkin Trans. 1*, 1994, preceding paper.
2 M. J. Gunter and M. R. Johnston, *Tetrahedron Lett.*, 1990, **31**, 4801.
3 M. J. Gunter and M. R. Johnston, *Tetrahedron Lett.*, 1992, **33**, 1771.
4 B. Tümmler, G. Maass, F. Vögtle, H. Sieger, U. Heimann and E. Weber, *J. Am. Chem. Soc.*, 1979, **101**, 2588.
5 B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1061.

6 P. R. Ashton, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1066.
7 B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1064.
8 J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, 1972, **26**, 1471.
9 P. Nieri, C. Ramireddy, C. N. Wu, P. Munk and R. W. Lenz, *Macromolecules*, 1992, **25**, 1796.
10 J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval and F. C. Anson, *J. Am. Chem. Soc.*, 1980, **102**, 6027.
11 M. J. Gunter and L. N. Mander, *J. Org. Chem.*, 1981, **46**, 4792.
12 R. Young and C. K. Chang, *J. Am. Chem. Soc.*, 1985, **107**, 898.
13 H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 487.
14 H. M. Colquhoun, S. M. Doughty, J. M. Maud, J. F. Stoddart, D. J. Williams and J. B. Wolstenholme, *Isr. J. Chem.*, 1985, **25**, 15.
15 M. Momenteau, J. Mispelter, B. Loock and E. Bisagni, *J. Chem. Soc., Perkin Trans. 1*, 1983, 189.
16 U. Simonis, F. A. Walker, P. Lani Lee, B. J. Hanquet, D. J. Meyerhoff and R. W. Scheidt, *J. Am. Chem. Soc.*, 1987, **109**, 2659.
17 D. Reddy and T. K. Chandrashekar, *J. Chem. Soc., Dalton Trans.*, 1992, 619.
18 J. Rebek (Jr.), *Top. Curr. Chem.*, 1988, **149**, 190.
19 M. Harmata and C. L. Barnes, *J. Am. Chem. Soc.*, 1990, **112**, 5655.
20 S. C. Zimmerman and C. M. VanZyl, *J. Am. Chem. Soc.*, 1987, **109**, 7894.
21 S. C. Zimmerman, M. Mrksich and M. Baloga, *J. Am. Chem. Soc.*, 1989, **111**, 8528.
22 S. C. Zimmerman, C. M. VanZyl and G. S. Hamilton, *J. Am. Chem. Soc.*, 1989, **111**, 1371.
23 S. C. Zimmerman and W. Wu, *J. Am. Chem. Soc.*, 1989, **111**, 8054.
24 S. C. Zimmerman, Z. Zeng, W. Wu and D. E. Reichert, *J. Am. Chem. Soc.*, 1991, **113**, 183.
25 S. C. Zimmerman, W. Wu and Z. Zeng, *J. Am. Chem. Soc.*, 1991, **113**, 196.
26 J. P. Fillers, K. G. Ravichandran, I. Abdalmuhdi, A. Tulinsky and C. K. Chang, *J. Am. Chem. Soc.*, 1986, **108**, 417.
27 P. D. Beer, *Chem. Soc. Rev.*, 1989, **18**, 409.
28 P. D. Beer, C. G. Crane and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1991, 3235.
29 J. S. Bradshaw and P. E. Stott, *Tetrahedron*, 1980, **36**, 461.
30 R. Ungaro, B. E. Haj and J. Smid, *J. Am. Chem. Soc.*, 1976, **98**, 5198.
31 B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1058.
32 B. L. Allwood, F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, 311.
33 S. R. Hall, H. D. Flack and J. M. Stewart (eds), *The XTAL 3.2 Reference Manual*, Universities of Western Australia, Geneva and Maryland, 1992.
34 A. H. Haines, I. Hodgkisson and C. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1983, 311.
35 M. Bourgoin, K. H. Wong, J. Y. Hui and J. Smid, *J. Am. Chem. Soc.*, 1975, **97**, 3462.
36 V. Percec, G. Johansson, J. Heck, G. Ungar and S. V. Batty, *J. Chem. Soc. Perkin Trans. 1*, 1993, 1411.

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