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Induced-Fit Binding of π-Electron-Donor Substrates to Macrocyclic Aromatic Ether Imide Sulfones: A Versatile Approach to Molecular Assembly

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Abstract: Novel macrocyclic receptors that bind electron-donor aromatic substrates through π-stacking donor–acceptor interactions are obtained by cycloimidisation of an amine-functionalised aryl ether sulfone with pyromellitic and 1,4,5,8-naphthalenetetracarboxylic dianhydrides. These macrocycles can form complexes with a wide variety of π-donor substrates, including tetrathiafulvalene, naphthalene, anthracene, pyrene, perylene and functional derivatives of these polycyclic hydrocarbons. The resulting supramolecular assemblies range from simple 1:1 complexes to [2]- and [3]pseudorotaxanes and even (as a result of crystallographic disorder) an apparent polyrotaxane. Direct five-component self-assembly of a metal-centred [3]pseudorotaxane is also observed on complexation of a macrocyclic ether imide with 8-hydroxyquinoline in the presence of palladium(II) ions. Binding studies in solution were carried out by using ^{1}H NMR and UV/Vis spectroscopy, and the stoichiometries of binding were confirmed by Job plots based on the charge-transfer absorption bands. The highest association constants were found for strong π-donor guests with large surface areas, notably perylene and 1-hydroxypyrene, for which K_a values of 1.4×10^3 and $2.3\times10^3\,\text{M}^{-1}$, respectively, were found. Single-crystal X-ray analyses of the receptors and their derived complexes reveal large induced-fit distortions of the macrocyclic frameworks as a result of complexation. These structures provide compelling evidence for the existence of strong attractive forces between the electronically complementary aromatic π systems of host and guest.

Keywords: diimides · macrocycles · molecular recognition · pi interactions · pseudorotaxanes

Introduction

Among non-covalent interactions, aromatic–aromatic π-stacking interactions have played a very significant role in the development of supramolecular chemistry,[1,2] with π donor–π acceptor interactions being widely exploited for the construction of complex supramolecules[3,4] and novel types of co-crystal.[5,6] For example, the π-electron-accepting tetracationic cyclophanes discovered by Stoddart et al.[7] have led to the synthesis of entire families of charged catenanes and rotaxanes through templated self-assembly with π-electron-donor 1,5-dialkoxynaphthalene units and/or tetrathiafulvalenes.[8,9] This type of chemistry has also enabled the fabrication of nanoscale devices, including light- and redox-driven switches and, most recently, molecular logic gates.[10,11] A second important group of π-electron-accepting receptors, developed by Sanders et al.,[12] is based on aromatic diimides, especially pyromellitic and naphthalene-tetracarboxylic diimides. Neutral catenanes and rotaxanes were obtained by templated self-assembly of aromatic diimides with 1,5-dialkoxynaphthalene derivatives.[12] This type of donor–acceptor interaction has also recently been used to direct the supramolecular assembly of arenes with

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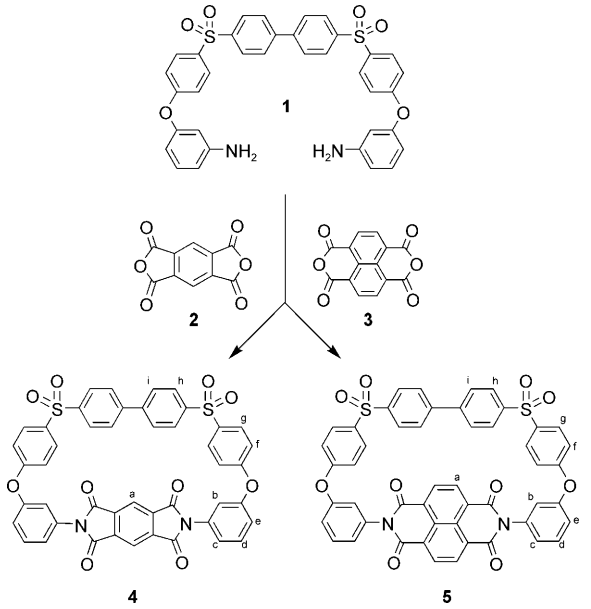
perfluoroarenes,[13,14] to promote the chain-folding of aliphatic poly(ether imides)[15] and to generate double-stranded "zipper-type" supramolecular complexes,[16] foldamers and duplexes.[17]

However, the long-term chemical stability of these, and related,[18] π-electron-acceptor units must be very limited because they contain labile aliphatic linkages, such as benzyl pyridinium, alkynylmethylene imide or N-alkylene imide units. Moreover, the range of reactions available for the elaboration of such systems is heavily constrained by this chemical lability. On noting the extreme thermochemical and oxidative stability of all-aromatic poly(ether imides) and poly(ether sulfones),[19] we sought to develop aromatic receptor molecules based on macrocyclic analogues of such polymers. In a preliminary communication we observed that all-aromatic macrocyclic diimides can be readily accessed by direct cyclo-condensation of bis(amine)-functionalised arylene ether sulfones with aromatic dianhydrides.[20] The resulting macrocycles have extremely high melting points (sharp DSC (differential scanning calorimetry) endotherms in the region of 500 °C under nitrogen), and show no evidence of thermo-oxidative decomposition in air at temperatures up to 400 °C. These relatively rigid receptors not only have π-electron-accepting aromatic diimide residues but also biphenylene units with strongly electron-withdrawing arenesulfonyl substituents. Indeed, we describe detailed investigations into the interactions of these novel π-electron-accepting macrocycles with aromatic π donors both in solution (using ^{1}H NMR and UV/Vis spectroscopy) and in the solid state (using single-crystal X-ray analysis).

Results and Discussion

Synthesis: An early study of macrocyclic aromatic ether imide synthesis was reported by Takekoshi et al.[21] They used the fluoro-desilylative route to aromatic ethers originally developed by Kricheldorf.[22] This approach was successful in generating mixtures of macrocycles, but was limited in scope by the insolubility of the difluoro-aromatic monomers and by the moisture sensitivity of silylated bis(phenols). Herein, pure macrocyclic ether sulfone diimides **4** and **5** were obtained by direct [1+1] cycloimidisation of aromatic diamine **1** with an aromatic dianhydride (**2** or **3**) in *N*,*N*-dimethylacetamide (DMAc) at reflux under pseudo high dilution conditions. These novel macrocycles were isolated by column chromatography in yields of 23 and 20%, respectively (Scheme 1), and the yield of **5** could be increased to 26% by using zinc acetate as a catalyst. Compounds **4** and **5** were fully characterised using ^{1}H, ^{13}C NMR and IR spectroscopy, DSC, MS (CI) and elemental analysis. They show only limited solubility in conventional chlorocarbon solvents, such as CD_2Cl_2 or $CDCl_3$, but their solubilities improve dramatically on adding a small proportion of a proton-donor solvent, such as hexafluoropropan-2-ol (6F-*i*PA) or trifluoroacetic acid (TFA) to these chlorocarbons.



Scheme 1. Synthesis of macrocyclic ether sulfone diimides **4** and **5**. The labels refers to ^{1}H NMR assignments used throughout the paper.

Single-crystal X-ray analyses revealed that the diimide and 4,4′-biphenylene disulfonyl residues in receptors **4** and **5** are oriented face-to-face across the centre of the macrocycle (Figure 1). The transannular (centroid–centroid) separations are 7.91 Å for **4** and 8.17 Å for **5**, which indicates that the cavities can comfortably accommodate planar aromatic substrates.

After the synthesis and characterisation of **4** and **5**, we explored their complexation behaviour with electron-rich π-donors **6–17**.

Complexation of 4 and 5 with naphthalene and its derivatives: Addition of naphthalene (**6**, equimolar quantity) to a solution of macrocycle **5** (8 mM) in $CDCl_3$/6F-*i*PA (6:1 v/v) produced a slight upfield shift ($\Delta\delta = 0.045$ ppm) of the singlet diimide resonance, which is consistent with aromatic ring-current shielding of these protons by a bound naphthalene molecule. However, the magnitude of the complexation shift indicated only very weak binding and, in keeping with this, no colour change attributable to a charge-transfer absorption was observed. However, it seemed possible that 2,6-dimethoxynaphthalene (**7**), with its π-electron-donating substituents, would interact more strongly with receptors **4** and **5**, especially as the formation of a donor–acceptor complex between *N*,*N*′-diethyl pyromellitic diimide and **7** has been demonstrated previously both in solution and in the solid state.[23] Herein, co-dissolving the pale yellow macrocycles **4** or **5** and colourless 2,6-dimethoxynaphthalene (1:1 mole ratio) in either $CHCl_3$/6F-*i*PA or $CHCl_3$/TFA produced intense pink colours that could be assigned to charge-transfer absorptions. In keeping with this observation, the ^{1}H NMR spectrum of an equimolar mixture of **7** and **4** (8 mM) in CD_2Cl_2/6F-*i*PA showed appreciable ring-current complexation shifts (Figure 2). Two resonances of receptor **4**

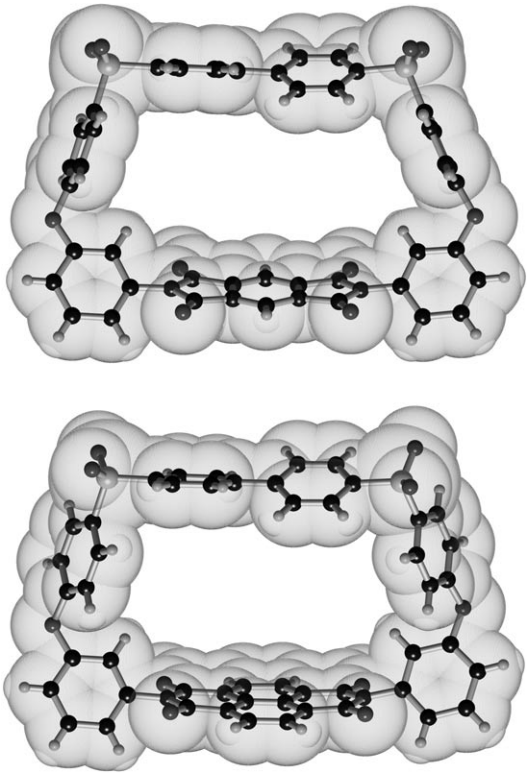
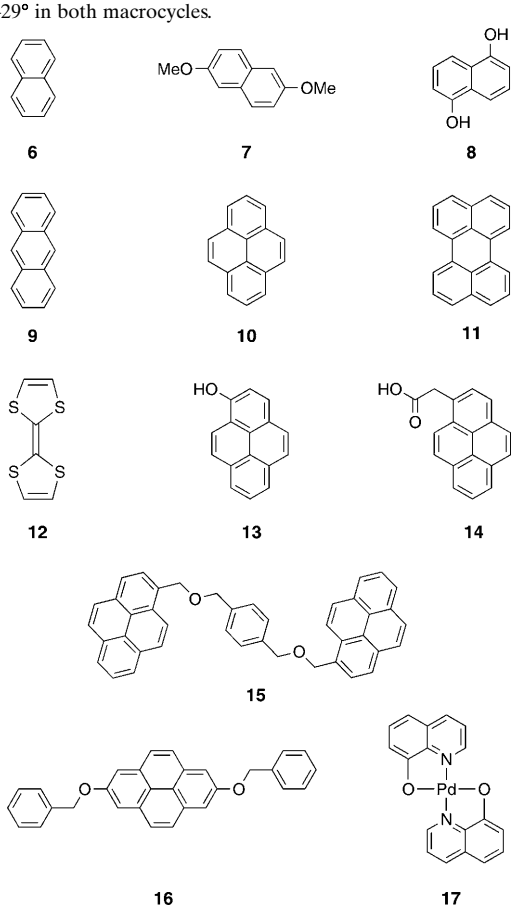


Figure 1. Single-crystal X-ray structures of macrocycles **4** (top) and **5** (bottom) showing their essentially identical cavity shapes and sizes as defined by van der Waals surfaces. Torsion angles at the biphenyl linkages are 28–29° in both macrocycles.



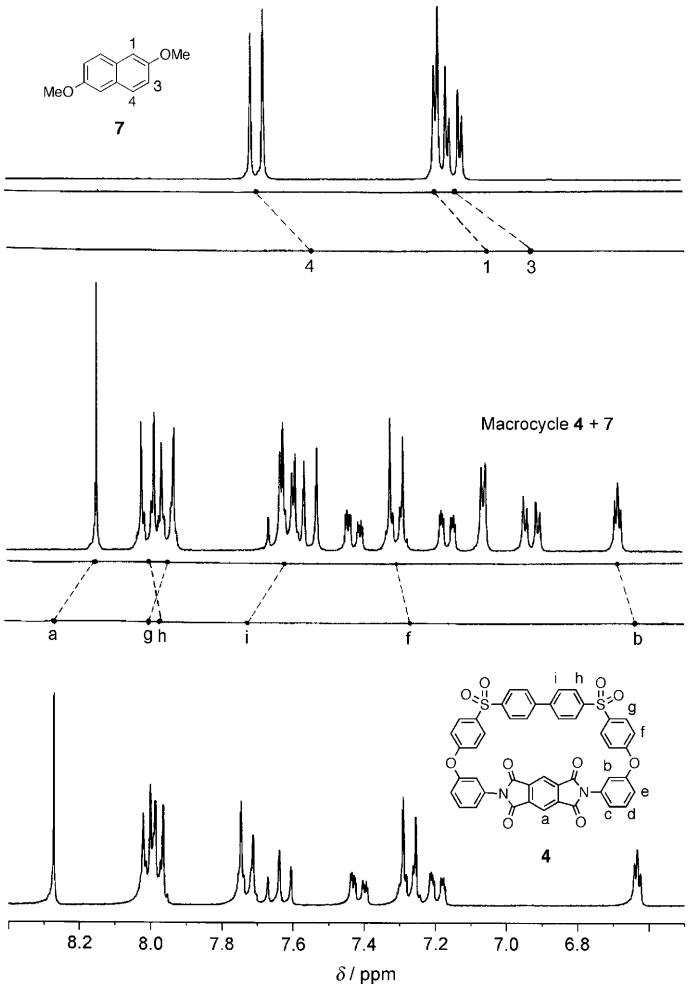


Figure 2. ^{1}H NMR spectra indicating complexation of **4** with **7** (1:1 mole ratio, 8 mM of each component) in CD_2Cl_2/6F-*i*PA (6:1 v/v).

(H^a and H^i) moved to higher field ($\Delta\delta = 0.12$ ppm for both protons) and corresponding upfield shifts occurred for the three different aromatic protons of **7** ($\Delta\delta = 0.13$, 0.22 and 0.15 ppm for H^1, H^3 and H^4, respectively). Formation of a donor–acceptor complex between **4** and **7** was confirmed by single-crystal X-ray analysis. Deep pink crystals of a 1:1 complex, **4·7**, were obtained from a solution of the two components in $CHCl_3$/TFA by vapour diffusion with diethyl ether. The structure of complex **4·7** (Figure 3) shows that the 2,6-dimethoxynaphthalene molecule is inserted almost symmetrically into the macrocyclic cavity, with distances between the centroid of the naphthalene unit and the centroids of the biphenyl linkage and the imide ring system of 3.77 and 3.69 Å, respectively. The vectors linking these centroids are essentially co-linear, subtending an angle of 178°. The transannular distance between the centroids of the biphenyl disulfonyl and pyromellitimide units is 7.46 Å, a very significant reduction from the value of 7.91 Å found for uncomplexed macrocycle **4**. The binding constant, K_a, for 1:1 complexation of **7** with macrocyle **4** in $CHCl_3$/6F-*i*PA (6:1) at 20 °C (determined from the charge-transfer band at $\lambda =$

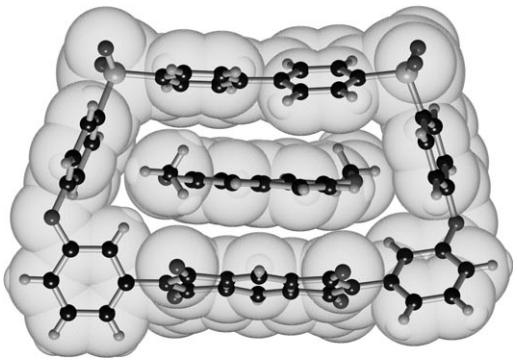


Figure 3. Single-crystal X-ray structure of 1:1 complex **4·7** formed between **4** and **7**; van der Waals surfaces are shown.

540 nm by the UV/Vis dilution method)[24] was found to be (33 ± 5) M^{-1}, which corresponds to a free energy of binding $(-\Delta G°)$ of (8.8 ± 1.3) kJ mol^{-1}.

Complexation of 1,5-dihydroxynaphthalene (**8**) by macrocycle **4** (8 mM in $CDCl_3$/TFA; 1:1 mole ratio) was also observed, with protons H^a and H^i now shifted upfield by $\Delta\delta=$ 0.29 and 0.27 ppm, respectively. The binding constant for **8** with macrocycle **4** (determined as above) was (37 ± 6) M^{-1}, but despite extensive efforts single crystals of complex **4·8** suitable for X-ray analysis could not be obtained from this system.

Complexation of 4 and 5 with anthracene: Anthracene (**9**) has a greater π-surface area than naphthalene and is known to be a good π-electron donor, forming a wide range of π-stacked complexes with electron-deficient aromatic molecules, such as 1,3,5-trinitrobenzene, 1,4,5,8-naphthalenetetracarboxylic dianhydride and dichloropyromellitic dianhydride.[25] Herein it was found that co-dissolving **5** and anthracene in $CDCl_3$/6F-*i*PA (6:1) gave a purple solution, clearly indicative of a charge-transfer absorption, and a 1:1 mixture of **5** (8 mM) and anthracene gave a $\Delta\delta=0.125$ ppm upfield complexation shift of the singlet naphthalene diimide resonance. The binding constant, K_a, measured from the charge-transfer band at $\lambda=570$ nm in $CHCl_3$/6F-*i*PA (6:1), was (29 ± 4) M^{-1}, which corresponds to a free energy of binding $(-\Delta G°)$ of (8.2 ± 1.2) kJ mol^{-1}.

Complexation of 4 and 5 with pyrene and derivatives: From the spectroscopic and crystallographic results described above, it can be seen that macrocycles **4** and **5** are clearly well-adapted, both geometrically and electronically, for encapsulation of electron-donor aromatic guests. However, the spacings between the diimide and biphenyl disulfone residues in the "free" macrocycles **4** and **5** are, at around 8 Å, significantly greater than the optimum value for π–π-stacking (≈6.8 Å; twice the van der Waals thickness of an aromatic ring).[26] Even though these macrocycles do contract markedly on complexation through an induced-fit mechanism, the complexes formed with molecules such as naphthalene (two fused rings) and anthracene (three fused rings) are still rather weakly bound ($K_a<40$ M^{-1}). Increasing the available π-surface area of the guest provides a possible method of enhancing the binding strength through increased numbers of atom–atom contacts; therefore, we next investigated pyrene (**10**, four fused rings) and its derivatives as potential substrates for complexation with macrocycles **4** and **5**.

Pyrene itself is known to form a crystalline donor–acceptor complex with pyromellitic dianhydride.[27] Computational modelling indicated that pyrene would fit comfortably within the cavities of **4** and **5**, and indeed, mixing solutions of the pale yellow macrocycles with (colourless) pyrene produced deep red solutions that arise from intense intermolecular charge-transfer absorptions. Moreover, the ^{1}H NMR spectrum of a mixture of **5** (9.85 mM) and pyrene (1:1 mole ratio in $CDCl_3$/6F-*i*PA (6:1 v/v)) showed very large $\Delta\delta$ values for both the macrocycle and the substrate, with resonances for H^a and H^i (Scheme 1) shifting upfield by $\Delta\delta=$ 0.632 and 0.934 ppm, respectively. A Job plot (Figure 4) confirmed the formation of a 1:1 complex between the two components in this solvent. The NMR spectroscopic data clearly suggest a relatively high association constant between the two components, and this was confirmed by a K_a value of $(8.1\pm1.2)\times10^2$ M^{-1}, obtained from the charge-transfer band at $\lambda=550$ nm by using the UV/Vis dilution method. Analogous results were obtained for the binding of pyrene by pyromellitimide-based macrocycle **4**, though now with a rather lower association constant ($(2.3\pm0.3)\times10^2$ M^{-1}).

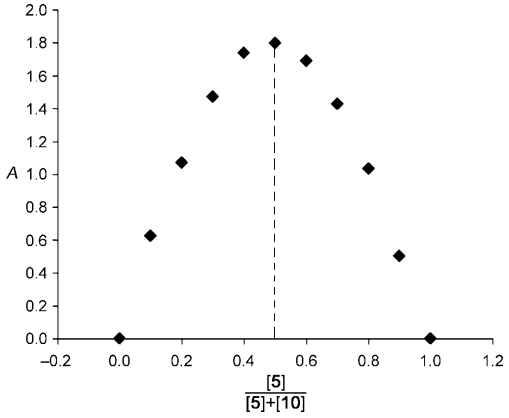


Figure 4. Job plot for complexation between macrocycle **5** and pyrene (**10**; total concentration 10 mM) based on the charge-transfer band at $\lambda=$ 550 nm ($A=$ absorbance). The peak at 0.5 confirms 1:1 complexation.

The interaction between macrocycle **5** and pyrene, but with TFA replacing 6F-*i*PA, showed that using TFA as a co-solvent resulted in even greater complexation shifts in receptor and substrate resonances. For example, at 8 mM in each component, protons H^a and H^i of macrocycle **5** are shifted upfield by $\Delta\delta=0.772$ and 0.633 ppm in the presence of TFA as the co-solvent (c.f. $\Delta\delta=0.681$ and 0.522 ppm, respectively, with 6F-*i*PA), and the resonances of pyrene are very much broadened. The broadening of pyrene resonances

must be associated with the interaction between macrocycle and substrate rather than, for example, proton exchange with the acid because sharp, well-resolved resonances are observed for pure pyrene in $CDCl_3$/TFA (6:1 v/v). These results suggest that the observed line-broadening arises from a close approach to slow-exchange kinetics on the NMR timescale. The increased strength of binding in the presence of TFA may simply be associated with the increased polarity of the solvent favouring desolvation of the non-polar pyrene and, therefore, shifting the equilibrium towards complexation with the macrocycle. However, an alternative explanation is that protonation of the diimide carbonyl groups by TFA enhances the electron-acceptor capacity of the diimide unit, which again leads to increased binding strength. Indeed, both effects could be operative. Although X-ray-quality single crystals of pyrene complexes with **4** or **5** could not be obtained, the magnitudes and directions of the observed complexation shifts are precisely those expected from the locations of the receptor protons relative to the ring-current shielding and deshielding zones of a pyrene molecule bound face-on to the pyromellitimide and biphenyl units. Thus, resonances for H^a and H^i (Scheme 1) should both be strongly shifted by insertion of a pyrene molecule into the macrocyclic cavity because these units would experience high levels of magnetic shielding by the polycyclic aromatic ring current. In contrast, external complexation of pyrene to the diimide residue would affect only the resonance arising from the diimide protons H^a. Although X-ray-quality single crystals of pyrene–macrocycle complexes could not be obtained, the NMR spectroscopic data clearly reflect insertion of pyrene into the macrocyclic cavity (as for **7** and **9**), with the pyrene molecule stacking face-to-face with the pyromellitimide and biphenylene disulfone subunits of the receptor.

Complexation of 4 and 5 with perylene (11): The pentacyclic fused-ring hydrocarbon perylene (**11**) has an even larger π surface available for complexation than pyrene, and is known to behave as a strong π-electron donor.[28] Computational modelling indicated that perylene could be readily accomodated within the macrocyclic cavitiy of **4** or **5** in much the same way as pyrene, and indeed intense dark green colours asssociated with charge-transfer absorptions (at $\lambda =$ 660 nm for **5**) were observed on adding perylene to solutions of the macrocycles. The binding constant between **5** and perylene is $(1.4 \pm 0.2) \times 10^3\,\text{M}^{-1}$, which corresponds to a free energy of complexation ($-\Delta G°$) of $(18 \pm 3)\,\text{kJ mol}^{-1}$. The value of K_a for complexation of perylene with **5** is thus significantly greater than that for pyrene ($(8.1 \pm 1.2) \times 10^2\,\text{M}^{-1}$) in the same solvent system. Formation of a discrete 1:1 donor–acceptor complex (**5·11**) with perylene was confirmed by single-crystal X-ray analysis of a dark green crystal grown by vapour diffusion of diethyl ether into a DMF (*N*,*N*-dimethylformamide) solution of the two components.

As shown in Figures 5 and 6, the perylene molecule inserts almost symmetrically into the macrocyclic cavity, with the distances between the centroid of the perylene molecule and the centroids of the biphenylene unit and diimide ring system of 3.57 and 3.51 Å, respectively, being very similar. The vectors linking these centres are essentially co-linear (179°). Most importantly, the transannular separation between the centres of the biphenyl disulfonyl and diimide units in the complex is now contracted to only 7.08 Å. This is the largest reduction (≈14%) from the "free macrocycle" value (8.19 Å) observed to date, and is thus consistent with the high association constant for perylene. Moreover, the normally twisted biphenylene unit in **5·11** is markedly flattened through its close contact with the perylene guest; the torsion angle at the biphenyl linkage is only 19° in **5·11** compared to 29° in **5** itself. These very large induced-fit distortions, by which the macrocyclic receptor flexes and twists to bring its diimide and biaryl disulfone acceptor centres into

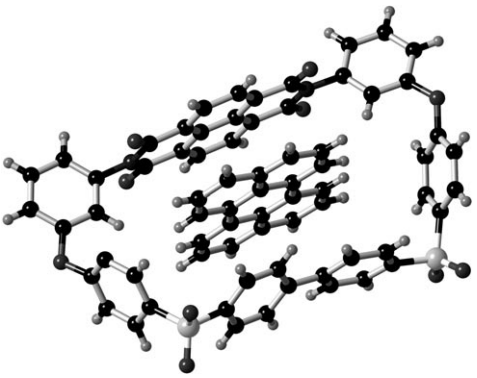


Figure 5. X-ray structure of complex **5·11** between macrocycle **5** and perylene (**11**).

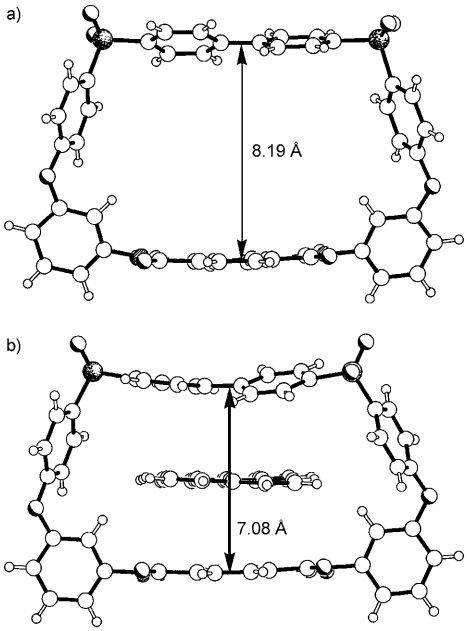


Figure 6. X-ray structures viewed parallel to the plane of the diimide unit a) in macrocycle **5** (CH_2Cl_2 solvate) and b) in complex **5·11**, which indicates the large induced-fit distortions of the macrocycle that occur on binding to the guest.

closer contact with the perylene donor substrate, provide compelling evidence for existence of strong, attractive forces between the electronically complementary aromatic ring systems. The fact that relatively rigid macrocycles **4** and **5** can undergo a facile "breathing" distortion of this type (Figure 6) immediately explains their surprisingly powerful complexation properties for aromatic molecules. Without this distortion, the guest molecule would be unable to contact both binding surfaces of the macrocycle (biphenyl and diimide) simultaneously and would render it only a simple monovalent rather than a divalent receptor.

Complexation of 4 and 5 with tetrathiafulvalene (TTF, 12): Tetrathiafulvalene and its derivatives are generally regarded as a strong π-electron donors, and their π–π-stacking interactions with electron-accepting 4,4′-bipyridinium-based macrocycles have been widely exploited in the construction of mechanically interlocked systems, such as catenanes and rotaxanes.[10a,c,29] Herein, NMR spectroscopy studies of TTF complexation were found to be feasible only at low concentrations (2 mM) in pure $CDCl_3$ because using 6F-*i*PA or TFA as co-solvents broadened the TTF resonance to the point of invisibility. At these low concentrations, however, only slight complexation shifts were observed for the resonances of both TTF ($\Delta\delta = 0.021$ ppm) and macrocycle **4**, ($\Delta\delta =$ 0.03 ppm, pyromellitimide resonance) at a mole ratio of 1:1 of the two components.

Dark green needle-like crystals of a 1:1 complex were obtained by vapour diffusion of diethyl ether into a $CHCl_3$/TFA solution of **4** and **12**, and single-crystal X-ray analysis of this complex, **4·12**, showed the TTF molecule to be bound almost symmetrically between the pyromellitimide and biphenyl disulfonyl residues of macrocycle **4** (Figure 7).

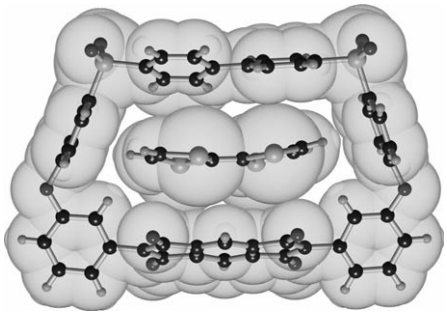


Figure 7. Crystal structure of 1:1 complex **4·12** between macrocycle **4** and TTF (**12**). Van der Waals surface contacts clearly indicate a close association between the two components, but the site-occupancy of **12** in the crystal is only ≈70%, which suggests a relatively weak free energy of binding.

The centroid–centroid distances between TTF and the diimide and biphenyl units are, however, much longer than in other complexes of this type, at 4.0 and 3.93 Å respectively, which perhaps reflects the greater van der Waals radius of sulfur (1.85 Å) relative to that of an aromatic ring (1.70 Å). In agreement with this, the spacing between the centroids of the biphenylene disulfone and pyromellitimide units in **4·12** is unchanged from the value (7.91 Å) observed in free macrocycle **4**.

Complexation of 4 and 5 with substituted pyrenes: Because X-ray-quality single crystals of complexes with pyrene itself could not be obtained, we next turned to a series of its substituted derivatives to obtain more detailed information on pyrene-macrocycle systems. For example, for 1-hydroxypyrene (**13**), computational modelling suggested that the hydroxy substituent might form hydrogen bonds to a carbonyl group of macrocycle **4** or **5**. Moreover, the mesomeric effect of a hydroxyl group directly attached to the aromatic nucleus of pyrene should enhance its π-donor capabilities. Indeed, interaction of (colourless) 1-hydroxypyrene with macrocycle **5** gave an intensely green solution, and ^{1}H NMR spectroscopy experiments (8 mM in each component) involving 1:1 complexation in $CDCl_3$/TFA (6:1) and in $CDCl_3$/6F-*i*PA (6:1) revealed very large complexation shifts for both components. Macrocycle **5** resonances for H^a and H^i in macrocycle **5** were thus shifted upfield by $\Delta\delta = 0.937$ and 1.402 ppm, respectively, in $CDCl_3$/TFA (6:1) and by $\Delta\delta =$ 0.882 and 1.341 ppm, respectively, in $CDCl_3$/6F-*i*PA (6:1). The resonances associated with 1-hydroxypyrene are strongly broadened on macrocycle complexation in $CDCl_3$/6F-*i*PA (6:1) and are barely discernable in $CDCl_3$/TFA (6:1), which indicates that the kinetics of complexation have now essentially reached the slow-exchange limit. The binding constant for complexation of **5** with 1-hydroxypyrene (measured by using the charge-transfer band at $\lambda = 630$ nm) was $(2.3 \pm 0.3) \times 10^3\ M^{-1}$, which corresponds to a free energy of complexation ($-\Delta G°$) of (19 ± 3) kJ mol^{-1}. This is the highest binding constant so far observed for complexation of a single aromatic π system with macrocycle **5**, in keeping with the proposal that 1-hydroxypyrene should be a very strong π donor. Hydrogen bonding to the macrocycle may, as noted above, also be implicated in this system, but extensive efforts to obtain X-ray-quality single crystals to test for this were unsuccessful.

Computational modelling suggested that 1-pyreneacetic acid (**14**) might also form hydrogen bonds to a carbonyl oxygen atom of **4** or **5** and so provide additional binding energy to that resulting from complementary π–π stacking. Formation of a donor–acceptor complex between macrocycle **5** and 1-pyreneacetic acid was indeed obvious from UV/Vis and NMR spectroscopic measurements in solution, and this was confirmed in the solid state by X-ray analysis of the dark red crystals grown by vapour diffusion of diethyl ether into a DCM/6F-*i*PA solution of the two components (Figure 8).

In complex **5·14**, the 1-pyreneacetic acid molecule is bound symmetrically within the macrocyclic cavity, with centroid–centroid distances from the pyrene unit to both the diimide and biphenyl ring systems of 3.71 Å. The transannular distance across the macrocycle, between the centroids of the biphenyl and diimide units, is 7.33 Å, again a very substantial (≈11%) reduction from the value of 8.19 Å found

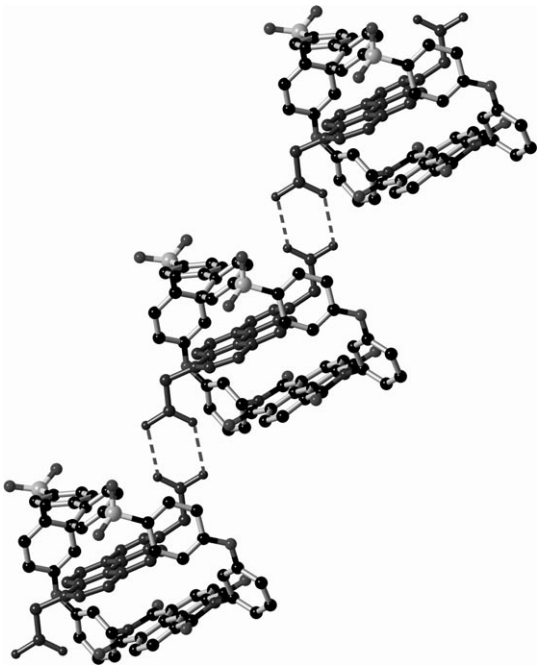


Figure 8. Apparent polyrotaxane-type "infinite chain" assembly produced by orientational disordering and hydrogen bonding of 1-pyreneacetic acid (**14**) in the crystal of complex **5·14**. Hydrogen atoms are omitted for clarity.

for the uncomplexed macrocycle. The carboxylic acid group of 1-pyreneacetic acid does not in fact interact with macrocycle **5**, but instead forms a pair of intermolecular hydrogen bonds with a second centrosymmetrically-related molecule. This results in non-covalent dimerisation of complex **5·14**, with formation of a 4-component supramolecular assembly that resembles a [3]pseudorotaxane. Moreover, orientational disorder about the centre of the pyrene ring system creates a crystallographic inversion centre, which means that the crystal appears to contain continuous chains of 1,6-pyrenediacetic acid molecules linked by pairs of hydrogen bonds in an apparent polyrotaxane-type assembly (Figure 8).[30] The existence of this structure clearly predicts that 1,6-pyrenediacetic acid should assemble with macrocycle **5** to form an infinite, hydrogen-bonded, psuedo-polyrotaxane-type chain.

The strong interactions found between macrocycles **4** and **5** and derivatives of pyrene suggests that more complex supramolecular assemblies might be achieved through the interactions of these macrocycles with bis(pyrenyl) substrates. For example, α,α′-bis(1-pyrenylmethoxy)-1,4-xylene (**15**), was synthesised by *O*-alkylation of 1-pyrenemethanol with α,α′-dibromo-1,4-xylene in the presence of sodium hydride in DMF and gave, after recrystallisation from toluene, diether **15** in 60% yield. There is clearly a stronger interaction between **15** and macrocycle **5** than between pyrene itself and **5**, as indicated by larger complexation shifts ($\Delta\delta \approx 1$ ppm) at a 1:1 mole ratio of **15** to **5** (8.7 mM) in $CDCl_3$/6F-*i*PA (6:1). These were initially ascribed to a possible tweezer-type interaction[31] between **15** and macrocycle **5**, which would require **15** to adopt an overall *syn* conformation. However, X-ray analysis of the deep red single crystals obtained by vapour diffusion of diethyl ether into a $CHCl_3$/6F-*i*PA solution that contained equimolar amounts of the two components revealed that, at least in the crystal, **15** adopts the *anti* conformation and gives a 2:1 complex with the macrocycle, that is, it forms a [3]pseudorotaxane (**5_2·15**, Figure 9). The structure has a crystallographic centre of symmetry, but unlike the situation in 1-pyreneacetic acid complex **5·14**, in which the guest is symmetrically located within the macrocycle, the structure of the **5_2·15** complex places the substrate closer to the diimide unit than to the biphenylene fragment (centroid–centroid separations are now 3.66 and 3.91 Å, respectively).

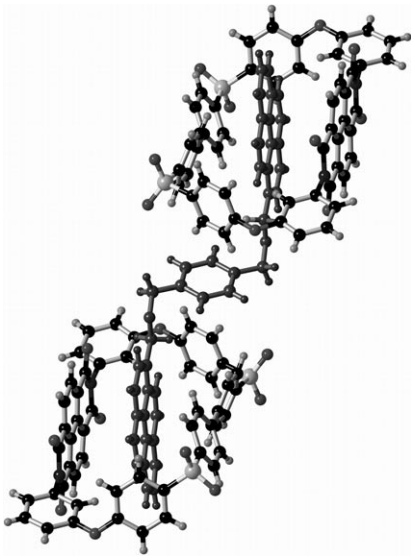


Figure 9. X-ray structure of the 2:1 complex between **5** and **15**.

Complexation of 5 with 2,7-bis(benzyloxy)pyrene: Iridium-catalysed borylation of pyrene has recently been shown to proceed selectively at the least hindered 2 and 7 positions,[32] and subsequent oxidative cleavage of the diborylated product affords 2,7-dihydroxypyrene in very good yield.[33] Herein, the generally low solubility of 2,7-dihydroxypyrene made complexation studies of this aromatic diol difficult, but the corresponding dibenzyl ether (**16**) proved very much more soluble. Large complexation shifts ($\Delta\delta > 1$ ppm) were observed in the ^{1}H NMR spectrum of **16** in the presence of macrocycle **5**, and strong binding between **5** and **16** in solution was confirmed by a association constant of $(1.2 \pm 0.2) \times 10^3\ M^{-1}$ in $CDCl_3$/6F-*i*PA (6:1), which was measured by using the charge-transfer absorption at $\lambda = 526$ nm. Formation of a 1:1 complex between **5** and **16** in solution was indicated by the linear plot obtained in the binding constant analysis, but single crystals obtained by vapour diffusion of methanol into a 1:1 solution of the two components in CD_2Cl_2/6F-*i*PA surprisingly proved to be of a [3]pseudorotaxane-type complex, with 2:1 (macrocycle/guest) stoichiometry **(5_2·16)**.

The X-ray structure of this complex is shown in Figure 10. The two macrocycles bind quite differently, one encircling the pyrene core of the guest and the second packing in close

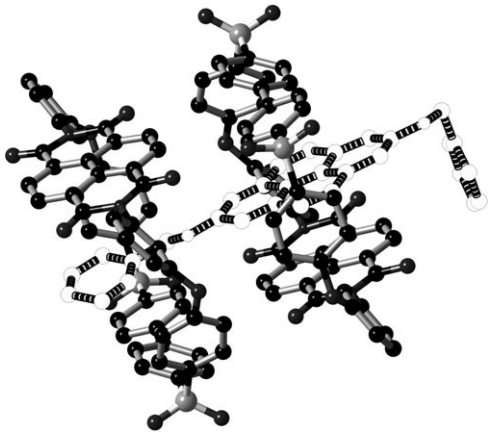


Figure 10. X-ray structure of 2:1 complex **5_2·16** formed between macrocycle **5** and 2,7-bis(benzyloxy)pyrene (**16**). Hydrogen atoms are omitted for clarity.

contact with the first so as to form a π-stacked complex with one of the two benzyl residues. The remote benzyl group lies essentially orthogonal to the pyrene unit, forming a close C–H···π contact with a macrocyclic diimide unit. Given the probable weakness of binding between the macrocycle and the benzyl group, and the 1:1 stoichiometry of binding in solution, it seems likely that formation of a 2:1 complex in the solid state is driven mainly by crystal packing forces, especially the van der Waals contacts between the two closely-packed macrocycles threaded onto a molecule of **16**.

Binding of 4 and 5 to a palladium complex: Bis(8-quinolinolato)palladium(II) (**17**) is known to form π–π-stacked complexes with π-electron-acceptors, such as 1,3,5-trinitrobenzene.[34] It has also recently been shown to give molecular-tweezer-type complexes (stabilised by π-stacking interactions) with bis(terpyridyl) palladium derivatives.[35] Therefore, it seemed possible that analogous interactions might lead to complexation between **17** and macrocycles **4** and **5**, and computational modelling indicated that the planar palladium complex would fit comfortably within the cavities of these receptors. Brown palladium complex **17** gave deep green solutions in the presence of both **4** and **5**, although a 1:1 mixture of **5** (2 mM) and **17** in $CDCl_3$/6F-*i*PA (6:1) resulted in only a $\Delta\delta = 0.07$ ppm upfield shift for the diimide protons H^a, which is indicative of rather weak complexation. Dark green crystals of a complex of **5** and **17** were isolated by slow evaporation of a $CHCl_3$/6F-*i*PA solution that contained equimolar amounts of the two components, but as with 2,7-bis(benzyloxy)pyrene, the crystals were found by X-ray analysis to be a 2:1 [3]pseudorotaxane, **5_2·17**, rather than the anticipated 1:1 complex. In the crystal, a macrocycle is bound to each of the quinolinolato(1−) ligands of the palladium complex, and the two macrocycles are again in close van der Waals contact with one another, so that the palladium complex is almost completely encapsulated (Figure 11). It is significant that the two macrocycles have a

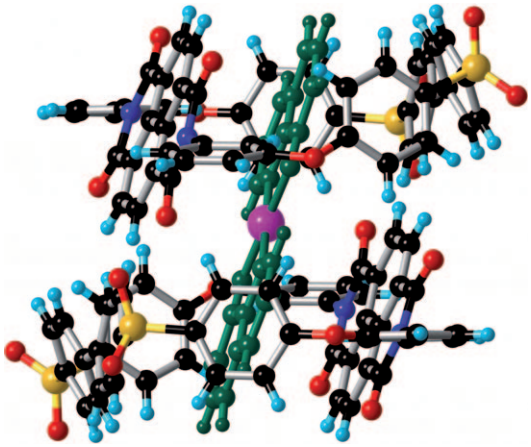


Figure 11. X-ray structure of 2:1 complex **5_2·17** formed between macrocycle **5** and bis(8-quinolinolato)palladium(II) (**17**; ligands in green, Pd in magenta).

very similar spatial relationship to one another in pseudorotaxanes **5_2·17** and **5_2·16**, in which they are related by crystallographic and approximate centres of symmetry, respectively. Inspection of the structures shows that this arrangement permits a very close shape-complementary fit between the edges of the macrocycles when they are brought into contact by threading onto their respective guests.

The geometries of the intercomponent interactions in **5_2·17** are consistent with the relatively weak binding suggested by NMR spectroscopy measurements in solution. In particular, the transannular (imide biphenylene) distance in the bound macrocycle (8.01 Å) is only very slightly contracted from its value in the free compound (8.17 Å). Nevertheless, it proved possible to assemble all five components present in the metal-centred [3]pseudorotaxane (two ligands, two macrocycles and a palladium(II) ion) in a one-step reaction between macrocycle **5**, 8-hydroxyquinoline, palladium acetate and triethylamine (2:2:1:4 mole ratio) in $CHCl_3$/6F-*i*PA (6:1) at room temperature. The reaction was rapid, as observed by the characteristic colour change of the solution from brown to olive-green, and on partial evaporation of the solvent, dark green [3]pseudorotaxane **19** crystallised directly from the reaction mixture in high purity and essentially quantitative yield.

Factors affecting the strength of arene binding to 4 and 5: In these systems, the most important driving force for complexation is clearly the donor–acceptor π–π-stacking interaction. This interaction represents the net coulombic attraction resulting from inter-atomic polar and dispersion forces, together with a contribution from charge transfer between the electron-donating and electron-accepting π systems.[1b,12j] These effects are evident in the complexation of receptors **4**

and **5** with pyrene in $CDCl_3$/6F-*i*PA (6:1), for which binding constants of $(2.3\pm0.3)\times10^2$ and $(8.1\pm1.2)\times10^2\,M^{-1}$, respectively, are observed. The increase in the binding constant between **4** and **5** is entirely in keeping with the greater π-surface area of this receptor and also with its substantially greater electron affinity (which results from replacement of the pyromellitimide unit by the naphthalene tetracarboximide residue). Together these lead to a considerably stronger overall π–π interaction between the two components. Correspondingly, the 1:1 complexes between macrocycle **5** and aromatic π-donors naphthalene, anthracene, pyrene and perylene show progressively increasing NMR spectroscopic complexation shifts and binding constants. This trend correlates with both the increasing π-surface area (i.e., increasing numbers of atom–atom contacts) and the diminishing ionisation potential of the aromatic donors (Table 1).[36]

Table 1. Complexation between macrocycle **5** and different aromatic substrates in $CDCl_3$/6F-*i*PA (6:1 v/v).

	Naphthalene	Anthracene	Pyrene	Perylene
$\Delta\delta_{H_a}$[a] [ppm]	0.045	0.125	0.681	n/d[b]
K_a[c] [M^{-1}]	n/d[d]	(29±4)	$(8.1\pm1.2)\times10^2$	$(1.4\pm0.2)\times10^3$
N_C[e]	10	14	16	20
I.P [eV][f]	8.15	7.43	7.41	6.97

[a] Solutions 8 mM in each component were used in the ^{1}H NMR spectroscopic experiments. [b] Not determined due to peak-broadening effects. [c] Determined by using the UV/Vis dilution method. [d] Not determined due the absence of a charge-transfer band. [e] Number of carbon atoms in the aromatic π-system. [f] See ref. [33].

Macrocycles **4** and **5** have only limited solubility in simple chlorohydrocarbons, such as CD_2Cl_2 or $CDCl_3$, but show good solubility in dipolar aprotic solvents, such as DMF and dimethylsulfoxide. However, these dipolar solvents were found to strongly inhibit complexation with arene substrates, probably by solvation of the dipolar regions associated with the macrocyclic cavity. In contrast, proton-donor co-solvents, such as 6F-*i*PA and especially TFA in $CDCl_3$ or CD_2Cl_2, were found to enhance complexation relative to the situation in pure chlorocarbons. This effect may well result from hydrogen bonding to (or even, with TFA, protonation of) the macrocyclic imidocarbonyl groups and/or sulfone oxygen atoms. Such interactions should enhance the electron-acceptor capabilities of the macrocycle π systems and thus could in principle increase the binding constant for complexation. Thus, for example, complexation of **5** (2 mM) and pyrene (equimolar ratio) in pure $CDCl_3$ produces an upfield shift of $\Delta\delta=0.227$ ppm for diimide proton H^a, whereas in $CDCl_3$/6F-*i*PA (6:1) at the same solute concentration, a complexation shift of twice this value ($\Delta\delta=$ 0.466 ppm) is observed.

Using TFA as a co-solvent leads to even stronger complexation than 6F-*i*PA. For example, 1:1 complexation of **5** (8 mM) with pyrene in $CDCl_3$/6F-iPA (6:1) produces upfield complexation shifts for protons H^a and H^i of $\Delta\delta=0.681$ and 0.552 ppm respectively, compared with values of $\Delta\delta=0.772$ and 0.633 ppm in $CDCl_3$/TFA (6:1) at the same solute concentration. More quantitatively, the binding constant for 1:1 complexation of **5** with pyrene is $(8.1\pm1.2)\times10^2\,M^{-1}$ in $CHCl_3$/6F-*i*PA (6:1) but $(1.4\pm0.3)\times10^3\,M^{-1}$ in $CHCl_3$/TFA (6:1). The imide carbonyl groups are undoubtedly protonated by TFA, and the resulting positive charge can be delocalised throughout the imide π system of the macrocycle, which makes it a stronger π-electron acceptor than its neutral or (in the presence of 6F-*i*PA) hydrogen-bonded counterpart.

Conclusions

Extremely stable macrocyclic ether sulfone diimide receptors, synthesised by direct cycloimidisation chemistry, are found to be well-adapted conformationally and electronically for supramolecular complexation with electron-donor aromatic molecules. The complexation behaviour of these receptors was studied by ^{1}H NMR spectroscopy in solution and by X-ray crystallography in the solid state, which enabled supramolecular assemblies ranging from simple 1:1 complexes to [3]pseudorotaxanes to be identified and in many cases isolated and characterised. Binding constants of up to $(2.3\pm0.3)\times10^3\,M^{-1}$ were measured by analysing the charge-transfer bands observed by using UV/Vis spectroscopy. The relationships between molecular structure and strength of binding can be rationalised in terms of 1) the available π-surface areas of the substrate and receptor, 2) their ionisation potentials (π donors) and electron affinities (π acceptors), 3) the nature of the substituents on the π donor and 4) the nature of the solvent, with strongly polar *n*-donor solvents leading to inhibition and strongly acidic solvents leading to enhancement of binding. A wide range of supramolecular assemblies, including [2]- and [3]pseudorotaxanes, were identified, and direct self-assembly of a five-component metal-centred [3]pseudorotaxane achieved through complexation of a macrocyclic receptor with the anion of 8-hydroxyquinoline in the presence of palladium(II) ions.

Experimental Section

General methods: All synthetic procedures were performed under an atmosphere of dry nitrogen unless otherwise specified. Commercial solvents and reagents were used without purification unless otherwise stated. DMAc was distilled over calcium hydride before use. Diamine **1** was prepared according to a literature procedure.[16] ^{1}H and ^{13}C NMR spectra were recorded by using Bruker DPX 250 MHz and Bruker AMX 400 MHz spectrometers. Chemical shifts are reported in ppm relative to TMS and multiplicities as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Mass spectra (EI/CI) were performed by using a VG Autospec spectrometer. IR spectra were recorded by using a Perkin–Elmer 1700 FTIR spectrometer. UV/Vis spectra were recorded by using a Cary 50 Scan UV/Vis spectrophotometer. Elemental analyses were provided by Medac (UK). Melting points were measured under nitrogen on a Mettler DSC 20 system at a heating rate of 10 °C min^{-1}; peak values are given. Computational modelling by using molecular mechanics with

charge equilibration, (Cerius2, Accelrys, San Diego) was carried out by using an SGI-O2 workstation with a custom-modified Dreiding-II force field. Single-crystal X-ray data for complexes **5·9** and **5_2·16** were measured at Reading by using an Oxford Diffraction X-Calibur CCD diffractometer with $Mo_{K\alpha}$ radiation for **5·9** and $Cu_{K\alpha}$ radiation for **5_2·16**. X-ray data for macrocycles **4** and **5** and for complexes **4·7**, **5·11**, **4·12**, **5·14**, **5_2·15** and **5_2·17** were determined at Imperial College by using a Siemens P4/RA diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation. Binding constants were determined by using the UV/Vis dilution method[24] and have an uncertainty of around ±15%.

Synthesis of macrocyclic ether imide 4: A solution of **1** (0.501 g, 0.772 mmol) and pyromellitic dianhydride (0.168 g, 0.772 mmol) in dry DMAc (45 mL) was added by syringe pump over 18 h to DMAc (32 mL) heated at reflux under nitrogen. After a further 2 h, the reaction mixture was cooled to RT, poured into water (300 mL) and the precipitate was filtered off. After washing with water and then with methanol, the solid was dried and purified by column chromatography (eluent: 2% ethyl acetate in CH_2Cl_2) to give **4** as a very pale yellow crystalline solid (0.150 g, 23%). M.p. 493°C; ^{1}H NMR ($CDCl_3$/CF_3COOH, 6:1, 250 MHz): δ=8.35 (s, 2H), 8.07 (d, J=8.6 Hz, 4H), 8.03 (d, J=8.9 Hz, 4H), 7.77 (d, J=8.6 Hz, 4H), 7.63 (t, J=8.2 Hz, 2H), 7.40 (dm, 2H), 7.27 (d, J=8.9 Hz, 4H), 7.20 (dm, 2H), 6.65 ppm (t, J=2.1 Hz, 2H); ^{13}C NMR ($CDCl_3$/TFA, 6:1, 62.5 MHz): δ=166.0, 161.4, 157.8, 144.6, 141.1, 137.3, 135.4, 131.8, 131.3, 130.8, 128.9, 128.8, 122.6, 121.4, 120.2, 115.7 ppm; MS (CI): m/z: 830 (100) $[M]^+$; elemental analysis calcd (%) for $C_{46}H_{26}O_{10}N_2S_2$: C 66.49, H 3.15, N 3.37; found: C 66.40, H 3.10, N 3.35.

Synthesis of macrocyclic ether imide 5: A solution of **1** (1.622 g, 2.5 mmol) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.671 g, 2.5 mmol) in dry DMAc (150 mL) was added by syringe pump over 24 h to DMAc (100 mL) heated at reflux under nitrogen. After a further 2 h, the reaction mixture was cooled to RT, poured into water (600 mL) and the precipitate was filtered off. After washing with water and then with methanol, the solid was dried and purified by column chromatography (eluent: 4% ethyl acetate in CH_2Cl_2) to give **5** as a pale yellow crystalline solid (0.438 g, 20%). M.p. 547°C; ^{1}H NMR ($CDCl_3$/TFA, 6:1, 250 MHz): δ=8.82 (s, 4H), 8.05 (d, J=8.6 Hz, 4H), 8.04 (d, J=8.9 Hz, 4H), 7.68 (d, J=8.6 Hz, 4H), 7.68 (t, J=8.2 Hz, 2H), 7.47 (dm, 2H), 7.32 (d, J=8.9 Hz, 4H), 7.16 (dm, 2H), 6.53 ppm (t, J=2.1 Hz, 2H); ^{13}C NMR ($CDCl_3$/TFA, 6:1, 62.5 MHz): δ=164.2, 160.8, 158.8, 144.4, 141.3, 135.7, 134.5, 132.8, 132.3, 130.9, 128.9, 128.7, 127.3, 126.9, 123.8, 122.0, 121.3, 115.9 ppm; MS (CI): m/z: 880 (100) $[M]^+$; elemental analysis calcd (%) for $C_{50}H_{28}O_{10}N_2S_2$: C 68.17, H 3.20, N 3.18; found: C 67.89, H 3.11, N 2.97.

Synthesis of α,α′-bis(1-pyrenylmethoxy)-1,4-xylene (15): A mixture of 1-pyrenemethanol (0.499 g, 2.15 mmol) and α,α′-dibromo-*p*-xylene (0.264 g, 1 mmol) in DMF (5 mL) was stirred at RT for 10 min and then cooled to 0°C. Sodium hydride (60% dispension in mineral oil) (0.0912 g, 2.28 mmol) was added to the mixture. After stirring at RT for 0.5 h, a yellow precipitate had formed. The mixture was stirred at RT for 24 h, and the excess NaH was then carefully decomposed by the addition of water (100 mL). The precipitate was filtered and washed extensively with water and methanol. The crude mixture was recrystallised from toluene with charcoal treatment to give **15** as a white crystalline solid (0.34 g, 60%). M.p. 166°C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ=8.39 (d, J=9.3 Hz, 2H), 8.21 (d, J=7.7 Hz, 4H), 8.18 (d, J=7.7 Hz, 2H), 8.15 (d, J=8.2 Hz, 2H), 8.08 (s, 4H), 8.03 (m, 4H), 7.44 (s, 4H), 5.29 (s, 4H), 4.70 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ=138.2, 131.7, 131.7, 131.2, 129.9, 128.5, 128.1, 127.8, 127.6, 126.3, 125.6, 125.4, 125.1, 124.9, 124.0, 72.4, 71.0 ppm; MS (CI): m/z: 350 (100) [M−pyrenylmethyl]$^+$; elemental analysis calcd (%) for $C_{42}H_{32}O_2$: C 88.70, H 5.67; found: C 88.93, H 5.40.

Synthesis of 2,7-bis(benzyloxy)pyrene (16): A mixture of 2,7-dihydroxypyrene (30.0 mg, 0.13 mmol), and K_2CO_3 (35.34 mg, 0.256 mmol) in DMF (5 mL) was stirred at RT for 10 min. A solution of benzyl bromide (65.68 mg, 0.05 mL, 0.384 mmol) in DMF (5 mL) was added dropwise to the mixture, which was stirred at RT for 3 h, then at 60°C for 14 h and finally at 80°C for 2 h. The mixture was precipitated in water (50 mL), then the solid was washed with water and methanol and dried to give a crude product, which was purified by column chromatography (eluent: CH_2Cl_2) to afford **16** as a white crystalline solid, (43.5 mg, 82%). M.p. 189°C; ^{1}H NMR (CD_2Cl_2, 250 MHz): δ=7.89 (s, 4H), 7.69 (s, 4H), 7.48 (d, J=8.8 Hz, 4H), 7.38–7.24 (m, 6H), 5.26 ppm (s, 4H); ^{13}C NMR (CD_2Cl_2, 62.5 MHz): δ=156.9, 137.7, 132.0, 129.0, 128.4, 128.1, 127.9, 120.5, 111.9, 70.9 ppm; MS (CI): m/z: 414 (100) $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{22}O_2$: C 86.93, H 5.35; found C 86.13, H 5.40.

Direct assembly of metallo–[3]pseudorotaxane 5·17: A (yellow) solution of palladium acetate (5.62 mg, 0.025 mmol) in $CHCl_3$ (0.2 mL) was added to an (orange) solution of macrocycle **5** (44 mg, 0.05 mmol) and 8-hydroxyquinoline (7.26 mg, 0.05 mmol) in $CHCl_3$/6F-*i*PA (6:1 v/v, 0.7 mL). After stirring at RT for 40 min., triethylamine (9.0 μL, 0.26 mmol) was added to give a dark olive-brown solution. After a further 40 min, the solvent was evaporated to half-volume in a stream of nitrogen and the resulting greenish-black crystals were filtered off, washed with methanol and diethyl ether and dried at 40°C (52.6 mg, 97.6%). Integration of the ^{1}H NMR spectrum and single-crystal X-ray analysis showed that product **19** contained macrocycle **5** and bis(8-quinolinolato)palladium(II) in a 2:1 mole ratio.

Crystallographic data

Compound ***4***: Empirical formula $2(C_{46}H_{26}N_2O_{10}S_2)\cdot1.5\,CHCl_3\cdot1.25\,CH_2Cl_2\cdot1.5\,CF_3COOH\cdot0.5\,CH_3OH\cdot1.5\,H_2O$; M_r=2160.91; triclinic; space group P-1; a=12.722(2), b=15.168(2), c=25.883 (4) Å; α=79.49(1), β=86.20(1), γ=69.80(1)°; V=4608.4(11) Å^3; T=183 K; Z=2, ρ_{calcd}=1.557 g cm^{-3}; $\mu(Cu_{K\alpha})$=3.60 mm^{-1}; $F(000)$=2207; indep. reflns 13619, R_1=0.0864, wR_2=0.1930 for 8273 indep. obsd reflns [$2\theta\leq120°$, $I>2\sigma(I)$].

Compound ***5***: Empirical formula $C_{50}H_{28}N_2O_{10}S_2\cdot4.3\,CH_2Cl_2$; M_r=1281.50; space group P-1; a=11.037(2), b=12.434(2), c=21.401(2) Å; α=100.79(1), β=91.49(1), γ=111.46(1)°; V=2670.7(8) Å^3; T=183 K; Z=2; ρ_{calcd}=1.594 g cm^{-3}; $\mu(Cu_{K\alpha})$=5.85 mm^{-1}; $F(000)$=1303; indep. reflns 7874, R_1=0.0869, wR_2=0.221 for 5189 indep. obsd reflns [$2\theta\leq120°$, $I>2\sigma(I)$].

Compound ***4·7***: Empirical formula $C_{46}H_{26}N_2O_{10}S_2\cdot C_{12}H_{12}O_2\cdot1.5\,CHCl_3$; M_r=1198.08; triclinic; space group P-1; a=11.829(2), b=12.651(2), c=19.500 (5) Å; α=91.05(2), β=96.37(2), γ=110.15(2)°; V=2717.6(10) Å^3; T=183 K; Z=2; ρ_{calcd}=1.464 g cm^{-3}; $\mu(Cu_{K\alpha})$=3.49 mm^{-1}; $F(000)$=1230; indep. reflns 7931, R_1=0.0914, wR_2=0.1976 for 4694 indep. obsd reflns [$2\theta\leq120°$, $I>2\sigma(I)$].

Compound ***4·12***: Empirical formula $C_{46}H_{26}N_2O_{10}S_2\cdot0.7\,C_6H_4S_4\cdot0.6\,CH_2Cl_2$; M_r=1024.80; orthorhombic; space group $P2_12_12_1$; a=7.052(2), b=18.274(3), c=32.508(6) Å; V=4457(2) Å^3; T=293(2) K; Z=4; ρ_{calcd}=1.527 g cm^{-3}; $\mu(Cu_{K\alpha})$=3.53 mm^{-1}; $F(000)$=2104; indep. reflns 3879, R_1=0.0598, wR_2=0.1290 for 2516 indep. obsd reflns [$2\theta\leq120°$, $I>2\sigma(I)$].

Compound ***5·9***: Empirical formula $C_{50}H_{28}N_2O_{10}S_2\cdot C_{14}H_{10}\cdot0.5\,CH_3OH\cdot0.5\,H_2O$; M_r=1083.61; space group P-1; a=8.923(4), b=14.013(6), c=22.011(9); α=77.671(10), β=79.586(10), γ=72.710(10)°; V=2546.9(19) Å^3; T=150 K; Z=2; ρ_{calcd}=1.413 g cm^{-3}; $\mu(Mo_{K\alpha})$=0.175 mm^{-1}; $F(000)$=1123; indep. reflns 10523, R_1=0.1164, wR_2=0.2964 for 4683 indep. obsd reflns [$2\theta\leq56°$, $I>2\sigma(I)$].

Compound ***5·11***: Empirical formula $C_{50}H_{28}N_2O_{10}S_2\cdot C_{20}H_{12}\cdot2\,C_3H_7NO$; M_r=1279.35; monoclinic; space group $P2_1/n$; a=9.8199(6), b=36.2332(12), c=17.4128 (7) Å; β=106.171(4)°; V=5950.5(5) Å^3; T=183 K; Z=4; ρ_{calcd}=1.428 g cm^{-3}; $\mu(Cu_{K\alpha})$=1.42 mm^{-1}; $F(000)$=2664; indep. reflns 9334, R_1=0.0423, wR_2=0.1014 for 7375 indep. obsd reflns [$2\theta\leq124°$, $I>2\sigma(I)$].

Compound ***5·14***: Empirical formula $C_{50}H_{28}N_2O_{10}S_2\cdot C_{18}H_{12}O_2\cdot0.25\,CH_2Cl_2$; M_r=1162.37; triclinic; space group $P1$; a=12.0148(8), b=12.7661(11), c=19.4123(15) Å; α=74.959(7), β=78.422(6), γ=71.353(7)°; V=2701.9(4) Å^3; T=183 K; Z=2; ρ_{calcd}=1.429 g cm^{-3}; $\mu(Cu_{K\alpha})$=1.72 mm^{-1}, $F(000)$=1201; indep. reflns 7833, R_1=0.0658, wR_2=0.1769 for 6280 indep. obsd reflns [$2\theta\leq124°$, $I>2\sigma(I)$].

Compound ***5_2·15***: Empirical formula $2(C_{50}H_{28}N_2O_{10}S_2)\cdot C_{42}H_{30}O_2\cdot4\,CHCl_3$; M_r=2805.86; monoclinic; space group $P2_1/c$; a=9.6206(7), b=43.267(3), c=15.1111 (11) Å; β=95.257(6)°; V=6263.7(8) Å^3; T=203 K; Z=2; ρ_{calcd}=1.488 g cm^{-3}; $\mu(Cu_{K\alpha})$=3.68 mm^{-1}, $F(000)$=2876; indep

reflns 9025, $R_1 = 0.0883$, $wR_2 = 0.2118$ for 4520 indep. obsd reflns [$2\theta \leq 120°$, $I > 2\sigma(I)$].

Compound ***5₂·16***: Empirical formula $2(C_{50}H_{28}N_2O_{10}S_2)\cdot C_{30}H_{39}N_2O_{11}S_2$; $M_r = 2176.24$; triclinic; space group *P*-1; $a = 11.9424(7)$, $b = 18.1706(8)$, $c = 28.4190(13)$ Å; $\alpha = 76.78(4)$, $\beta = 82.84(4)$, $\gamma = 80.88(4)°$; $V = 5902.6(5)$ Å^3; $T = 150$ K; $Z = 2$; $\rho_{calcd} = 1.224$ g cm^{-3}; $\mu(Mo_{K\alpha}) = 0.151$ mm^{-1}; $F(000) = 2252$; indep. reflns 11690, $R_1 = 0.0779$, $wR_2 = 0.2625$ for 7497 indep. obsd reflns [$2\theta \leq 42.46°$, $I > 4\sigma(I)$].

Compound ***5₂·17***: Empirical formula $2(C_{50}H_{28}N_2O_{10}S_2)\cdot C_{18}H_{12}N_2O_2Pd$; $M_r = 2496.13$; orthorhombic; space group *Pbca*; $a = 21.651(3)$, $b = 16.699(2)$, $c = 30.468$ (2) Å; $V = 11016.0(18)$ Å^3; $T = 293$ K; $Z = 4$; $\rho_{calcd} = 1.505$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 4.49$ mm^{-1}; $F(000) = 5088$; indep. reflns 7457, $R_1 = 0.0998$, $wR_2 = 0.1953$ for 2959 indep. obsd reflns [$2\theta \leq 120°$, $I > 2\sigma(I)$].

CCDC-174775 (**4**), -174776 (**5**), -174777 (**4·7**), -182918 (**4·12**), -182919 (**5·9**), -182920 (**5·11**), -198569 (**5·14**), -198570 (**5₂·15**), -734442 (**5₂·16**) and -734443 (**5₂·17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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