Anion induced displacement studies in naphthalene diimide containing interpenetrated and interlocked structures†‡

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This article describes investigations into the development of supramolecular systems capable of sensing anions through either displacement type assays or molecular motion. An electron deficient naphthalene diimide thread and an electron rich isophthalamide naphthohydroquinone macrocycle were shown to form a coloured pseudorotaxane assembly. Investigations into the ability of such interpenetrated systems to sense anions colorimetrically were undertaken. Anion complexation at the isophthalamide group of the macrocycle causes displacement of the naphthodiimide thread resulting in the loss of colour. The enhanced mechanically bonded binding strength between the naphthodiimide axle and the naphthohydroquinone groups of the macrocycle wheel in the corresponding rotaxane structure, however, was found to negate the anion induced displacement process.

Introduction

The field of anion supramolecular chemistry is rapidly growing due to the realisation of the many important roles that anions play in various environmental, chemical and biological processes.[1–3] Of particular importance is the development of systems capable of selectively sensing anions. Anion receptors incorporating redox- or photo-active signalling components have been used successfully in the development of selective anion sensors.[4] This field has been extended recently to incorporate the use of interlocked host structures such as rotaxanes or catenanes to act as highly selective anion complexing reagents.[5–15]

One powerful method of sensing anions that has been used to advantage by the groups of Anslyn,[16–18] Sessler,[19] Martínez-Máñez,[20,21] and Gale[22] is the development of displacement assays, whereby anion binding results in the expulsion of a dye and hence an associated colour change. Such systems may be capable of acting as colorimetric sensors. In the case of interpenetrated and interlocked molecules the dynamic behaviour of such systems also enables molecular motion to be utilised as a potential means of sensing anions. Although cations have been frequently used to induce chemically driven molecular motion, anion induced switching is to date underexploited. The groups of Chiu,[23,24] Leigh,[25,26] Stoddart[27] and Prodi[28] have used anions to induce the translocation of macrocycles in rotaxane structures, and we have reported the first anion induced circumrotation in catenane structures.[11]

With this in mind, this paper reports attempts towards the synthesis of anion switchable rotaxanes incorporating neutral naphthodiimide threads. We have previously shown that isophthalamide based macrocycles such as **1** strongly bind a variety of anions.[9] Furthermore anion templation together with π–π interactions between electron deficient positively charged pyridinium guests and the electron rich hydroquinone units of the macrocycle can result in high yields of interlocked structures.[5–8,29] Thus it was hypothesised that the macrocycle's electron rich hydroquinone units may provide sufficient π–π stacking to stabilise the threading of a neutral electron deficient naphthalene diimide guest such as **2**. Previous studies by Sanders *et al*. and Gunter *et al*. have shown that naphthalene-diimide entities form stable complexes with crown ether macrocycles through a series of π–π and C–H···O interactions, which have been exploited to synthesise catenanes and rotaxanes.[30–36] Therefore it is feasible that naphthalene diimide guests may form stable interpenetrated assemblies with the isophthalamide-type macrocycles *via* analogous interactions. Subsequent addition of anions might trigger the displacement and dethreading of the diimide moiety as the anion coordinates to the isophthalamide macrocycle. Furthermore such displacement is likely to result in an observable colour change. The pseudorotaxane assembly is predicted to be coloured due to charge transfer interactions between the electron rich macrocycle and electron deficient naphthalenediimide thread. Anion induced dissociation would result in a colour change, thus the system has the potential to operate as a displacement type assay capable of colorimetrically sensing anions (see Scheme 1).

Results and discussion

Before anion displacement studies could be undertaken, it was first necessary to determine whether naphthalene diimide moieties would indeed thread through the cavity of isophthalamide based macrocycles such as **1**. Thus the simple hexyl substituted diimide thread **2** was synthesised according to literature procedures.[34]

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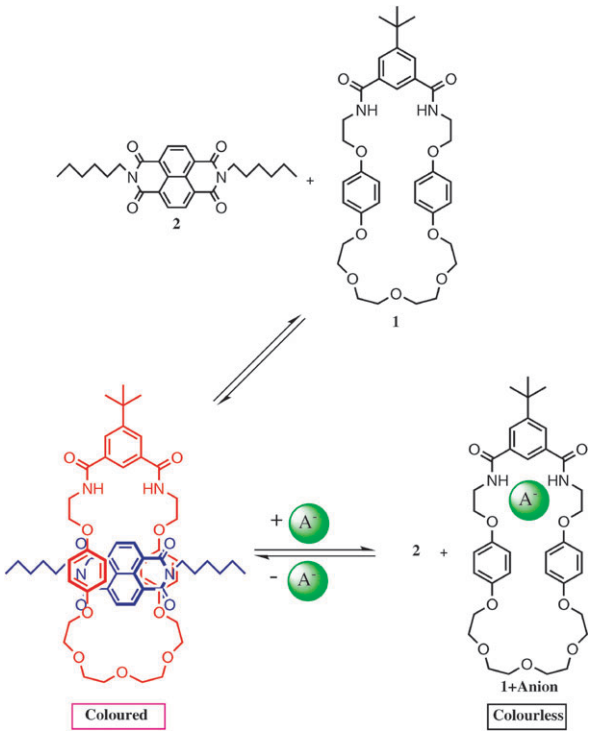
† Dedicated to Professor J. Rebek and Professor J. de Mendoza on the occasion of their 65th birthdays.

‡ Electronic supplementary information (ESI) available: NMR and UV pseudorotaxane binding studies of diimide **2** with macrocycles **1** and **8**. ROESY spectra of rotaxane **11**. See DOI: 10.1039/b819322c

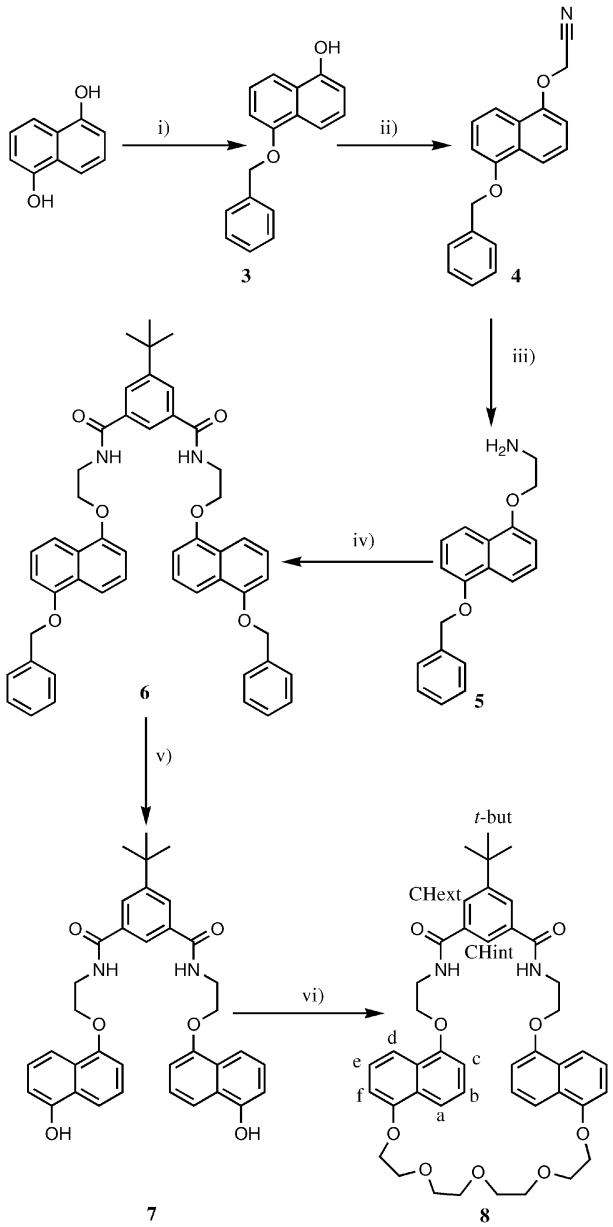


Scheme 1 Proposed anion induced displacement assay of interlocked structures incorporating naphthalene diimide threads.

^{1}H NMR was used initially to investigate the binding interactions between diimide **2** and hydroquinone macrocycle **1**. Addition of 1 equivalent of diimide thread **2** to a solution of macrocycle **1** in $CDCl_3$ resulted in only minor upfield shifts of the hydroquinone ($\Delta\delta$ 0.09 ppm) and diimide ($\Delta\delta$ 0.03 ppm) protons indicating weak binding (see ESI‡ Fig. S1).

This weak interaction could be attributed to insufficient π–π stacking with the hydroquinone units. It is known that naphthalene diimides display higher binding affinities for *dinaphtho*-crown ethers rather than their hydroquinone counter parts. It was hoped that modification of macrocycle **1** to incorporate two naphthohydroquinone units would be sufficient to stabilise diimides in future pseudorotaxane and rotaxane studies.

The new macrocycle **8** was thus synthesised according to Scheme 2. Reaction of 1,5-dihydroxynaphthalene with benzyl bromide in the presence of K_2CO_3 afforded the mono-protected naphthohydroquinone **3** in 23% yield. Reaction of this mono-protected naphthalene **3** with bromoacetonitrile followed by reduction with lithium aluminium hydride at room temperature gave the primary amine, **5** in good yields. Condensation of two equivalents of amine **5** with 5-*tert*-butylisophthaloyl dichloride in the presence of Et_3N afforded the benzyl protected precursor **6**. Deprotection was achieved using 10% Pd/C catalyst to give the macrocycle precursor diol **7**. The caesium cation mediated cyclisation reaction of **7** with tetraethylene glycol-bis-*para*-tosylate under high dilution conditions gave macrocycle **8** in 15% yield (which is comparable to the yields obtained in the synthesis of the analogous hydroquinone macrocycle **1**).



Scheme 2 Synthesis of macrocycle **8**; (i) benzyl bromide, K_2CO_3, DMF, 24 h, 23%; (ii) 2-bromoacetonitrile, K_2CO_3, acetone, Δ, 24 h, 99%; (iii) $LiAlH_4$, diethyl ether, 3 h, 82%; (iv) 5-*tert*-butylisophthaloyl dichloride, Et_3N, dry DCM, 24 h, 92%; (v) Pd/C (10%), DMF, EtOH, 24 h, 84%; (vi) bis-tosyltetraethylene glycol, Cs_2CO_3, DMF, Δ, 3 days, 15%.

Preliminary ^{1}H NMR binding studies were undertaken to determine the strength of binding between this naphtho-hydroquinone macrocycle **8** and the naphthalene diimide thread **2**. Addition of 1 equivalent of diimide thread **2** to a solution of macrocycle in $CDCl_3$ resulted in significant upfield shifts in the diimide proton a from 8.76 to 8.62 ppm which is indicative of a shielding effect from the macrocycle (see Fig. 1). The extent of this shift is comparable to other systems in which a naphthohydroquinone crown is bound around a diimide thread unit.[30,36–38] Similarly the naphthohydroquinone protons of the macrocycle have also been shifted upfield

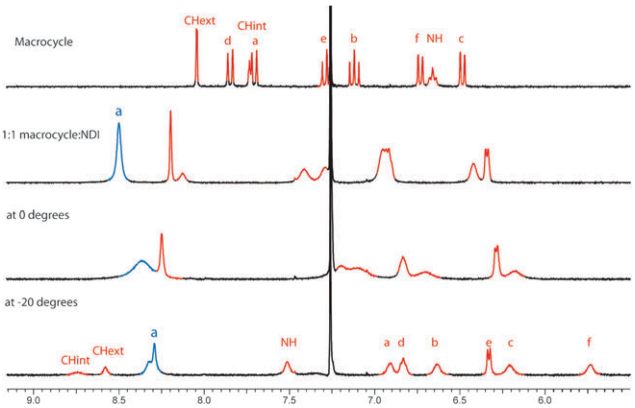


Fig. 1 ^{1}H NMR variable temperature binding study between macrocycle **8** and diimide **2** in $CDCl_3$.

(with upfield shifts ranging between $\Delta\delta$ 0.45 ppm for proton d and 0.14 ppm for proton c). Conversely, downfield shifts for the NH and CH_{int} and CH_{ext} protons for the macrocycle were observed ($\Delta\delta$ −0.31, −0.4, and −0.15 ppm, respectively) as the isophthalamide aromatic ring is in the deshielding region of the diimide aromatics. Variable temperature studies were also performed, and as expected, the extent of upfield shifts for the diimide and naphthohydroquinone protons increased upon decreasing temperature, confirming that pseudorotaxane formation is in fast exchange and that complexation is favoured at lower temperatures.

Further evidence of strong complexation between macrocycle **8** and diimide **2** arose from a UV-visible spectrum of the pseudorotaxane. Addition of one equivalent of macrocycle **8** to a solution of diimide **2** in $CHCl_3$ results in the appearance of a dark pink colour arising from a charge transfer interaction between the macrocycle and the diimide. A UV-visible titration of a solution of **2** into a solution of **8** in $CDCl_3$ was performed. Analysis of the data by SPECFIT[39] determined the binding constant to be 355 M^{-1} with a calculated extinction coefficient of 430 M^{-1} cm^{-1} (see ESI‡ Fig. S2). This is in a similar range to that observed in related crown-diimide supramolecular systems.[30,36–38]

Having established that the diimide thread **2** does form stable pseudorotaxanes with macrocycle **8**, investigations into the use of anions to induce dissociation were undertaken. It was anticipated that upon anion addition, the macrocycle would preferentially coordinate to the anion leading to displacement of the diimide thread component. Thus the intensity of the charged transfer interaction resulting from the diimide-macrocycle pseudorotaxane assembly would be expected to decrease and anion induced 'dethreading' could be monitored by UV-visible spectroscopy.

The addition of TBA sulfate to an equimolar solution of diimide **2** and macrocycle **8** in $CHCl_3$ resulted in a visible colour change of the solution from dark pink to colourless. The decrease in absorbance of the charged transfer band at 510 nm is indicative of the diimide being expelled from the cavity of the macrocycle (see Fig. 2). Systems that result in colour changes detectable by the naked eye in the presence of anions are rare.[18,19,22] Analogous titrations using TBA fluoride, TBA dihydrogen phosphate, TBA benzoate and

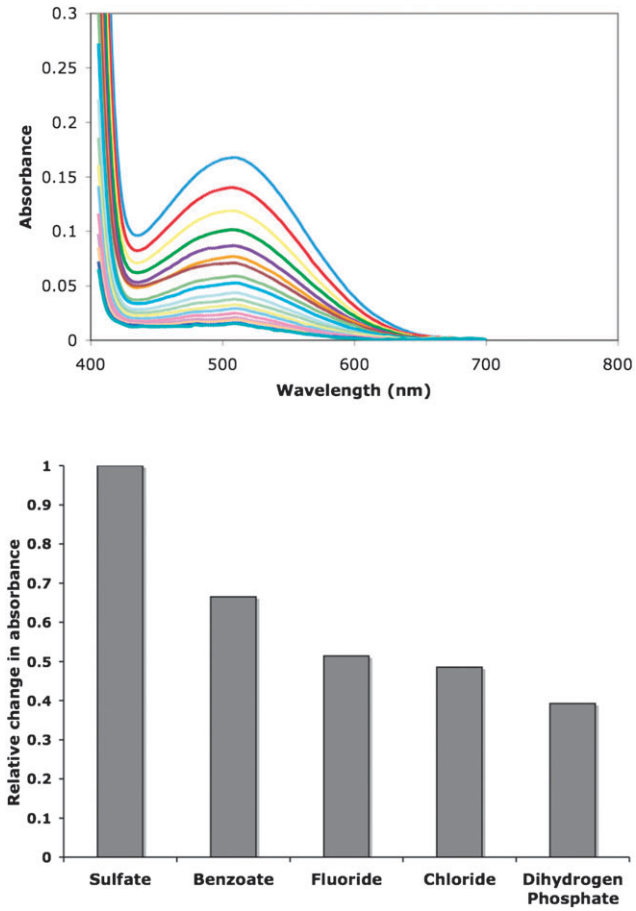


Fig. 2 *Top*: UV spectrum of the titration of sulfate into an equimolar solution of diimide **2** and macrocycle **8** in $CHCl_3$ (1.33×10^{-3} mol L^{-1}); *bottom*: relative changes in absorbance at 510 nm upon the addition of 10 equiv. of anion to an equimolar solution of diimide **2** and macrocycle **8** in $CHCl_3$ (1.33×10^{-3} mol L^{-1}).

TBA chloride were also undertaken in $CHCl_3$. In each case the colour of the solution decreased upon addition of anions and a comparison of the relative changes in absorbance upon the addition of 10 equivalents of various anions is shown in Fig. 2. The largest change in absorbance was observed upon the addition of $TBA_2(SO_4)$ indicating that the dethreading process was more effective with the dianion as compared to anions such as chloride or dihydrogen phosphate. Nevertheless it is clear that in a pseudorotaxane system anions are effective in displacing the diimide guest.

This anion induced dethreading behaviour was also monitored by ^{1}H NMR. To an equimolar mixture of macrocycle **8** and diimide **2** in $CDCl_3$ an excess of TBA sulfate was added. This resulted in the downfield shift in the diimide proton a to 8.76 ppm which is identical to the chemical shift of the diimide thread in the absence of any macrocycle. Furthermore the CH_{int} and CH_{ext} protons shifted downfield due to anion coordination, and these chemical shifts are the same as that observed in a solution of macrocycle containing the same number of equivalents TBA sulfate (see Fig. 3). Such observations confirm that the addition of anions is indeed resulting in the dethreading of this intermolecular system.

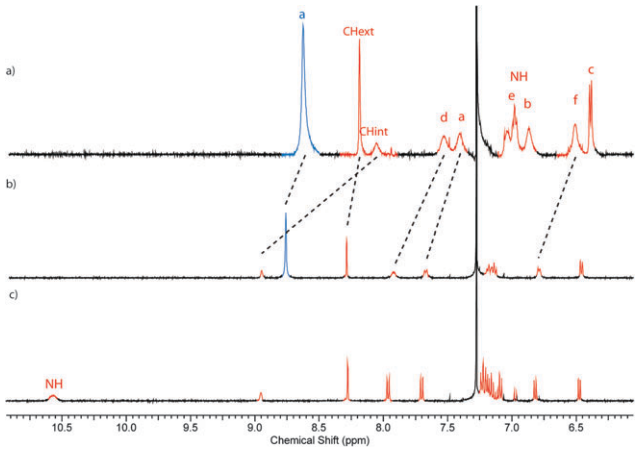
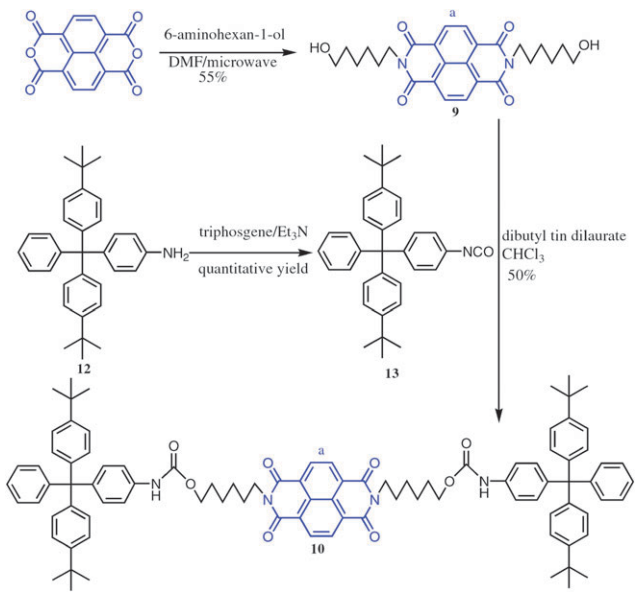


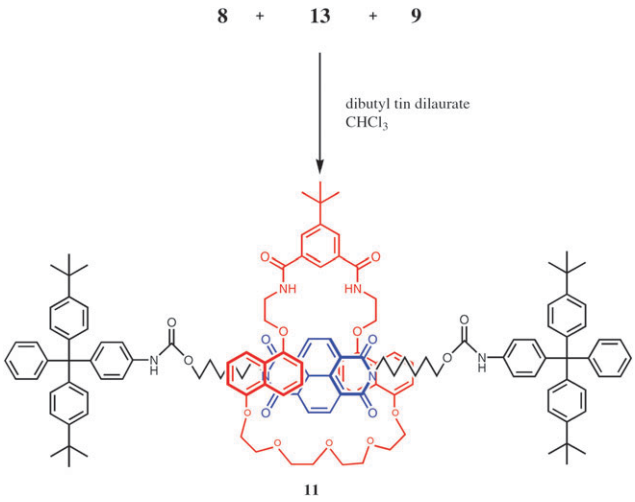
Fig. 3 (a) ^{1}H NMR spectrum of an equimolar solution of macrocycle **8** and diimide **2**; (b) ^{1}H NMR spectrum of an equimolar solution of macrocycle **8** and diimide **2** plus 10 equiv. of TBA sulfate; (c) ^{1}H NMR spectrum of macrocycle **8** and 10 equiv. of TBA sulfate. All spectra are in $CDCl_3$.

Having established that anion triggered 'dethreading' was possible in a pseudorotaxane system incorporating the naphthohydroquinone macrocycle **8** and diimide thread **2**, it was of interest to see whether molecular motion would be possible in a permanently interlocked rotaxane system. Thus a modified diimide thread **9** with hydroxy functionalised tethers was synthesised. It was envisioned that a urethane stoppering reaction with isocyanate stopper groups in the presence of macrocycle could be used to synthesise a rotaxane. This stoppering method has been used to advantage in the synthesis of interlocked structures due to the mild reaction conditions it employs.[23,40,41] Thus control experiments were performed on the synthesis of dumbbell **10** by reacting diimide thread **9** with the isocyanate stopper **13** in the presence of a tin catalyst (see Scheme 3).

Dumbbell **10** was synthesised in reasonable yields (50%) and characteristic ^{1}H NMR chemical shifts of the dumbbell



Scheme 3 Synthesis of diimide **9** and dumbbell **10**.



Scheme 4 Synthesis of naphthalenediimide rotaxane **11**.

(particularly diimide proton a at 8.65 ppm, and urethane proton at 6.73 ppm) were noted for comparison with such entities in the planned rotaxanes.

Having successfully isolated the dumbbell **10**, the reaction was again repeated in the presence of 1 equivalent of macrocycle **8** in order to synthesise the new rotaxane **11** (see Scheme 4). After three days at room temperature the reaction was complete producing both dumbbell **10** (42%) and the diimide rotaxane **11** (4%). The ES-MS analysis of the diimide rotaxane **11** gave the expected mass peak at m/z 2186.9528 $[M + Na]^+$.

^{1}H, COSY and ROESY NMR studies were used to characterise the diimide rotaxane **11** (see Fig. 4). The position of the diimide resonance a in the diimide rotaxane was significantly upfield relative to its position in the uncomplexed dumbbell component, shifting from 8.65 to 8.03 ppm. This is attributed to substantial shielding from the naphthohydroquinone moieties in the macrocycle. Similarly the naphthohydroquinone protons of the macrocycle have also been shifted upfield (with upfield shifts of $\Delta\delta$ 0.96 ppm for proton d, 0.98 for proton a, 0.52 for proton e, 0.74 for proton b, 0.51 for proton f, and 0.56 ppm for proton c), which again is due to shielding by the diimide moiety, and is indicative of a co-facial

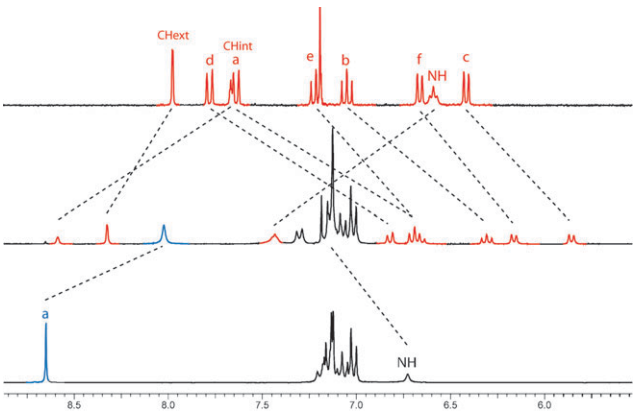


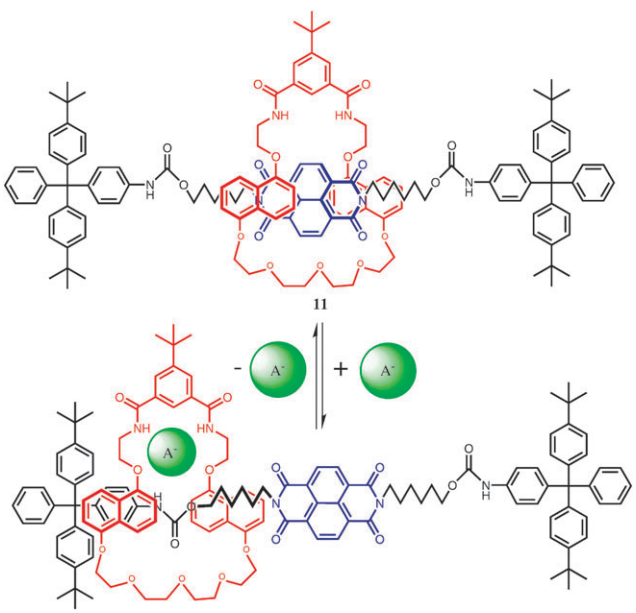
Fig. 4 ^{1}H NMR spectrum of macrocycle **8** (top), compared to the diimide rotaxane **11** (middle) and the dumbbell **10** (bottom) in $CDCl_3$.

arrangement between the macrocycle and thread. Conversely, the NH, CH_{int} and the CH_{ext} protons are all shifted downfield ($\Delta\delta$ −0.84, −0.92 and −0.35 ppm, respectively) due to the orientation of the isophthalamide aromatic ring in the deshielding region of the diimide aromatics.

Further evidence for the interlocked nature of this system was provided by ROESY experiments. Clear through space interactions between the diimide proton peak a and the macrocycle naphthohydroquinone protons a–f were observed (see ESI‡ Fig. S3). Furthermore interactions between the diimide proton and the ethoxy and NH amide protons of the macrocycle were also evident which is indicative of an interlocked structure in which the diimide is threaded through the cavity of the macrocycle.

Having isolated the diimide rotaxane **11**, as in the case for the pseudorotaxane counterparts, it was hypothesised that the addition of anions to this system may result in the displacement of the diimide as the macrocycle bound the anion in its cavity (see Scheme 5). Furthermore the inclusion of the urethane linkers may give the macrocycle an ideal second station to bind in the presence of anions.

UV titration experiments with the diimide rotaxane **11** were undertaken to determine if the addition of anions would indeed disrupt the π–π interaction between the macrocycle and diimide moiety. A solution of $(TBA)_2SO_4$ was titrated into a solution of diimide rotaxane in $CHCl_3$. Unfortunately little change in the charge transfer absorbance band was observed which could be attributed to changes in concentration due to dilution rather than anion binding (see Fig. 5). Similar titrations were performed using TBACl and TBAF, however again only minor changes in the charge transfer absorbance band were observed. The titration was again repeated but in this case in the more competitive solvents acetonitrile and DMSO. It should be noted that in acetonitrile and DMSO pseudorotaxane formation between macrocycle **8** and diimide



Scheme 5 Anion induced shuttling anticipated in the naphthalene diimide rotaxane **11**.

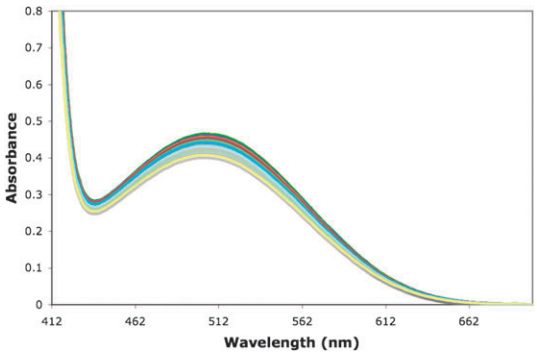


Fig. 5 UV titration of $(TBA)_2SO_4$ into a solution of diimide rotaxane **11** in $CHCl_3$ (1.43×10^{-4} mol L^{-1}).

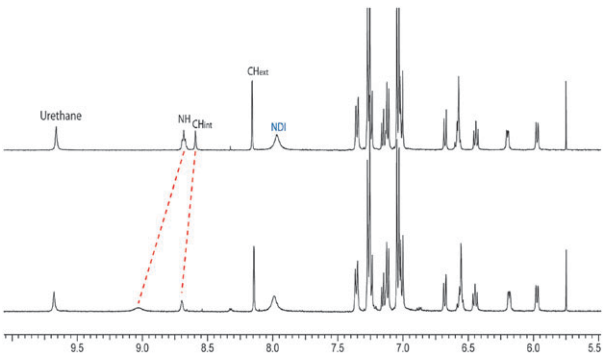


Fig. 6 ^{1}H NMR spectrum in d_6-DMSO of (top) diimide rotaxane **11** and (bottom) diimide rotaxane **11** plus 1 equiv. of $(TBA)_2SO_4$.

2 does not occur as π–π is not favoured in more polar solvents. Again however, minimal changes in the UV absorbance of the charge transfer band were observed indicating that the diimide remained inside the cavity of the macrocycle.

An NMR titration in d_6-DMSO was performed to determine whether the diimide binding was weakened to any extent in the presence of sulfate (see Fig. 6). Of particular importance was the fact that the pink coloration arising from the charge transfer interaction was present throughout the entire titration. This indicates that again the diimide remained bound inside the cavity of the macrocycle.

Closer inspection of the proton resonances for both the diimide proton and the naphthohydroquinone macrocycle protons confirmed this assumption by the fact that no changes in their chemical shift were observed upon addition of sulfate. Despite this, downfield shifts in both the NH and CH_{int} protons of the macrocycle were observed ($\Delta\delta$ −1.83 and −0.51 ppm, respectively). WinEQNMR[39] analysis of the titration data enabled an association constant of 75 M^{-1} to be determined for a 1 : 1 binding equilibrium. It is thought that the macrocycle in rotaxane **11** is capable of binding both the anion and diimide moiety simultaneously and the dianion is probably perched above the macrocycle.

Conclusion

This article describes efforts towards the development of supramolecular assemblies capable of sensing anions either

via use of pseudorotaxanes as displacement assays or through the anion induced molecular motion in the case of rotaxanes. We have shown that electron deficient naphthalene diimide threads form stable pseudorotaxane assemblies with an isophthalamide macrocycle incorporating naphthohydroquinone arms. Furthermore, anion complexation at the isophthalamide motif of the macrocycle causes dissociation of the diimide thread from the cavity of the macrocycle, which in turn results in an associated colour change. Thus this system has the potential to act as a colorimetric anion sensor *via* an analyte triggered dethreading mechanism.

In an attempt to extend this principle to permanently interlocked structures a new rotaxane **11** was successfully synthesised. In spite of control experiments demonstrating that the relatively weak π–π stacking interactions between a diimide derivative and the naphthohydroquinone macrocycle could be disrupted by anion binding, in the rotaxane the enhanced effective mechanically bonded binding strength between such components negates the anion induced displacement process. Similar enhancement of the effective binding strength in interlocked systems, as compared to pseudorotaxane analogues, has been recently reported for metal–ligand interactions.[42] Leigh *et al*. have also shown that although strong non-covalent interactions may be necessary to maximise the yield of rotaxanes and catenanes, the strength of such interactions provides significant energetic barriers that must be overcome in order to achieve molecular motion.[43,44] Thus in the future design of systems capable of molecular motion, either these templating interactions need to be significantly weakened in the final product (through the removal of a template, pH-dependent control, or photo- or electro-chemical induced changes), and/or the preference for complexation to a second station needs to be increased dramatically.

Experimental

General considerations

Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H_2O was de-ionised and microfiltered using a Milli-Q® Millipore machine. Tetrabutylammonium sulfate was purchased from Sigma-Aldrich as a 50% aqueous solution, which was concentrated on a rotary evaporator and subsequently dehydrated by azeotroping with tetrahydrofuran and then dried over phosphorus pentoxide in a vacuum desiccator. All tetrabutylammonium salts were stored in a vacuum desiccator over phosphorus pentoxide prior to use. All other solvents and commercial grade reagents were used without further purification.

Mass spectra were obtained using a Micromass GCT (EI) instrument or a Micromass LCT (ESMS) instrument. Microwave reactions were carried out using a Biotage Initiator 2.0 microwave. Melting points were recorded on a Gallenkamp capillary melting point apparatus and are uncorrected. Isophthalamide macrocycle **1**,[9] 2,7-dihexylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone **2**[34] and 1-benzyloxy-1-hydroxynaphthalene **3**[45] were prepared as described previously.

2-(5-(Benzyloxy)naphthalene-1-yloxy)acetonitrile (4)

A solution of 1-benzyloxy-1-hydroxynaphthalene **3** (5.32 g, 21.3 mmol), bromoacetonitrile (2.80 g, 23.3 mmol) and K_2CO_3 (3.26 g, 23.3 mmol) in dry acetone (200 mL) was refluxed under N_2 for 24 hours. After this time the reaction mixture was cooled to room temperature and filtered. The solvent was then evaporated to give a brown oil which was redissolved in DCM and filtered through a plug of silica. The solvent was then removed *in vacuo* to give the pure product as a pale yellow solid (6.07 g, 99%); mp 96–98 °C; *m*/*z* (ESI-MS) $[M + H]^+$ 290.1233 $C_{19}H_{16}NO_2$ (calc. 290.1181); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (1H, d, ^3J 8.5 Hz, Ar–H), 7.78 (1H, d, ^3J 8.5 Hz, Ar–H), 7.51–7.54 (2H, m Ar–H), 7.33–7.45 (5H, m, Ar–H), 6.96 (2H, d, ^3J 7.5 Hz, Ar–H), 5.25 (2H, s, $CNCH_2$), 4.96 (2H, s, OCH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 152.2, 137.3, 137.0, 128.7, 128.0, 127.5, 126.2, 125.3, 124.8, 117.2, 114.8, 114.0, 106.6, 106.1, 70.2, 53.8.

2-(5-(Benzyloxy)naphthalene-1-yloxy)ethylamine (5)

2-(5-(Benzyloxy)naphthalene-1-yloxy)acetonitrile **4** (6.07 g, 21.0 mmol) was dissolved in dry diethyl ether (200 mL) and added dropwise to a suspension of $LiAlH_4$ (1.75 g, 46 mmol) in dry diethyl ether (400 mL) and the mixture was then stirred at room temperature under N_2 for 3 hours. Aqueous 10% NaOH was added slowly until no further effervescence was observed. $NaCl_{(aq)}$ (200 mL) was then added and the organic layer separated. Diethyl ether (100 mL) was added to the aqueous layer and stirred for 20 minutes. The organic layer was then decanted. This procedure was repeated once more. The organic layers were combined, dried over $MgSO_4$ and the solvent removed to give the product as a white solid (5.02 g, 82%); mp 76–78 °C; *m*/*z* (ESI-MS) $[M + H]^+$ 294.1489 $C_{19}H_{20}NO_2$ (calc. 294.1489); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (1H, d, ^3J 8.5 Hz, Ar–H), 7.89 (1H, d, ^3J 8.5 Hz, Ar–H), 7.52–55 (2H, m Ar–H), 7.34–7.44 (5H, m, Ar–H), 6.94 (1H, d, ^3J 7.5 Hz, Ar–H), 6.88 (1H, d, ^{31}J 7.5 Hz, Ar–H), 5.25 (2H, s, OCH_2Ph), 4.17 (2H, m, CH_2) 3.23 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 137.2, 128.6, 127.9, 127.3, 126.8, 126.7, 125.2, 125.1, 114.6, 114.3, 106.0, 105.6, 70.5, 70.1, 41.7.

N,*N*-Bis(2-(5-(benzyloxy)naphthalen-1-yloxy)ethyl)-5-*tert*-butylisophthalamide (6)

2-(5-(Benzyloxy)naphthalene-1-yloxy)ethylamine **5** (5.02 g, 17.4 mmol) and Et_3N (5 mL, excess) were dissolved in dry DCM (100 mL) and the mixture was cooled in an ice bath to 0 °C. 5-*tert*-Butylisophthaloyl dichloride (2.14 g, 8.3 mmol) was dissolved in dry DCM (50 mL) and added dropwise to the reaction mixture. The reaction was stirred at 0 °C for 1 hour, and then at room temperature for a further 2 hours, during which time a precipitate was observed to have formed. This precipitate was filtered to yield the product as a white solid (5.9 g, 92%); mp 134–136 °C; *m*/*z* (ESI-MS) $[M + Na]^+$ 795.3408 $C_{50}H_{48}N_2O_6Na$ (calc. 795.3405); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94–7.97 (4H, m, Ar–H), 7.89 (1H, m, Ar–H), 7.85 (1H, s, Ar–H), 7.82 (1H, s, Ar–H), 7.50–7.53 (4H, m Ar–H), 7.31–7.43 (10H, m, Ar–H), 6.86–6.90 (4H, m, Ar–H), 6.68 (2H, t, ^2J 6 Hz, NH), 5.22 (4H, s, OCH_2Ph),

4.33 (4H, m, CH_2), 3.99 (4H, m, CH_2), 1.32 (9H, s, *tert*-butyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 154.4, 154.0, 151.5, 137.5, 134.9, 128.9, 128.3, 127.9, 127.1, 126.5, 126.0, 125.7, 124.2, 114.7, 114.3, 110.0, 106.8, 106.4, 69.9, 67.0, 35.2, 31.4.

5-*tert*-Butyl-*N*,*N*-bis(2-(5-hydroxynaphthalen-1-yloxy)ethyl)-isophthalamide (7)

N,*N*-bis(2-(5-(benzyloxy)naphthalen-1-yloxy)ethyl)-5-*tert*-butyl-isophthalamide **6** (5.9 g, 7.6 mmol) and 10% Pd on carbon (0.60 g, 10% by weight) were suspended in 4 : 1 DMF–EtOH (200 mL). The mixture was thoroughly degassed and then purged with H_2 and then stirred vigorously under H_2 overnight. After this time the reaction mixture was filtered through celite and the solvent removed *in vacuo*. The crude material was recrystallised from MeOH–DCM–hexane to give the pure product as a white solid (3.4 g, 84%); mp 138–141 °C; *m*/*z* (ESI-MS) $[M + Na]^+$ 615.2458 $C_{36}H_{36}N_2O_6Na$ (calc. 615.2466); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (2H, s, Ar–H), 8.36 (2H, t, ^2J 5 Hz, NH), 8.27 (1H, s, Ar–H), 8.11 (2H, s, Ar–H), 7.82 (4H, d, ^3J 8 Hz, Ar–H), 7.34 (2H, t, ^3J 8 Hz, Ar–H), 7.23 (2H, t, ^3J 8 Hz, Ar–H), 6.98 (2H, d, ^3J 8 Hz, Ar–H), 6.93 (2H, d, ^3J 8 Hz, Ar–H), 4.36 (4H, m, CH_2), 3.97 (4H, m, CH_2), 1.32 (9H, s, *tert*-butyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 167.1, 154.3, 152.9, 151.6, 134.9, 127.0, 125.3, 124.6, 123.5, 114.5, 113.2, 108.7, 108.6, 105.2, 66.6, 39.5, 34.7, 30.6.

Naphthohydroquinone macrocycle (8)

A solution containing the macrocycle precursor (1.37, 2.6 mmol) and bis-tosyltetraethylene glycol (1.27 g, 2.6 mmol) in dry degassed DMF (500 mL) was added dropwise over 6 hours to a solution of Cs_2CO_3 in dry degassed DMF (200 mL) at 80 °C. The reaction mixture was then heated at 80 °C under nitrogen for a further 3 days. After this time the solvent was removed *in vacuo* and the crude material was purified *via* column chromatography using a 30% EtOAc–hexane to EtOAc eluent gradient. The pure product was recrystallised from toluene to yield a white solid (290 mg, 15%); mp 130–132 °C; *m*/*z* (ESI-MS) $[M + Na]^+$ 773.3410 $C_{44}H_{50}N_2O_9Na$ (calc. 773.3409); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (2H, s, Ar–H), 7.79 (2H, d, ^3J 8.5 Hz, Ar–H), 7.63–7.67 (3H, m, Ar–H), 7.21 (2H, t, ^3J 8 Hz, Ar–H), 7.05 (4H, t, ^3J 8 Hz, Ar–H), 6.68 (2H, ^{3}d, *J* 8 Hz, Ar–H), 6.59 (2H, t, ^2J 5 Hz, NH), 6.43 (2H, d, ^3J 8 Hz, Ar–H), 4.16 (4H, m, OCH_2), 3.98 (4H, m, OCH_2), 3.90 (4H, m, OCH_2), 3.84 (4H, m, OCH_2), 3.65 (8H, m, OCH_2), 1.28 (9H, s, *tert*-butyl); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 154.1, 153.6, 151.0, 134.7, 126.5, 126.0, 125.7, 125.2, 123.6, 114.1, 113.7, 105.9, 105.4, 19.0, 70.1, 69.9, 68.9, 67.6, 67.1, 54.9, 34.7, 31.0.

2,7-Bis(6-hydroxyhexyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (9)

1,4,5,8-Naphthalenetetracarboxylic dianhydride (0.35 g, 1.3 mmol), 6-aminohexanol (0.34 g, 2.87 mmol) and dry Et_3N (0.2 mL) were suspended in dry, degassed DMF (15 mL) and then subjected to microwave irradiation at 140 °C for 10 minutes. Upon cooling the product precipitated from solution, was filtered and washed with cold DMF to yield the product as fine pink crystals (0.33 g, 55%); mp 199–200 °C; *m*/*z* (ESI-MS) $[M]^+$ 489.1995 $C_{26}H_{30}N_2O_6Na$ (calc. 489.1996); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (4H, s, NDI), 4.11–4.16 (4H, m, N–CH_2), 3.56–3.61 (4H, m, O–CH_2), 1.67–1.73 (4H, m, CH_2), 1.49–1.55 (4H, m, CH_2), 1.37–1.42 (8H, m, CH_2), 1.25 (2H, s, OH); ^{13}C NMR (75 MHz, DMSO) δ 162.9, 130.8, 126.5, 61.0, 32.8, 27.9, 26.9, 25.7.

6,6′-(1,3,6,8-Tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7(1*H*,3*H*,6*H*,8*H*)-diyl) bis(hexane-6,1-diyl) bis(4-(bis(4-*tert*-butylphenyl)(phenyl)methyl) phenyl carbamate) (10)

The amine stopper **12**[8] (85 mg, 0.19 mmol) and triphosgene (28 mg, 0.094 mmol) were dissolved in dry, degassed toluene (50 mL). Et_3N (20 mg, 0.20 mmol) was then added and the mixture was heated to 70 °C for 4 hours. After this time the reaction mixture was filtered and the solvent removed *in vacuo* to give the isocyanate intermediate **13** in quantitative yield. This was then dissolved in $CHCl_3$ (10 mL) and added to a solution of diimide **9** (40 mg, 0.086 mmol) and dibutyl tin dilaurate (16 mg, 0.025 mmol) in $CHCl_3$ (10 mL). The reaction mixture was then stirred at room temperature, under N_2 for 5 days. After this time the solvent was evaporated and the residue purified by preparative TLC (eluent: CD_2Cl_2–3% MeOH) to give the product as a white solid (61 mg, 50%); mp 164–166 °C; *m*/*z* (ESI-MS) $[M + H]^+$ 1413.77 $C_{94}H_{100}N_4O_8$ (calc. 1413.76); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (4H, s, NDI), 7.00–7.21 (36H, m, Ar–H), 6.73 (2H, s, NH), 4.04–4.13 (8H, m, CH_2), 1.55–1.69 (8H, m, CH_2), 1.40 (8H, m, CH_2), 1.21 (36H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 153.8, 148.4, 147.2, 143.7, 142.2, 135.7, 131.8, 131.1, 131.0, 130.7, 127.3, 126.7, 126.6, 125.7, 124.2, 117.4, 65.2, 40.9, 34.3, 31.4, 28.5, 27.7, 26.5, 25.7.

Diimide rotaxane (11)

The amine stopper **12**[8] (293 mg, 0.65 mmol) and triphosgene (91 mg, 0.31 mmol) were dissolved in dry, degassed toluene (100 mL). Et_3N (52 mg, 0.51 mmol) was then added and the mixture was heated to 70 °C for 4 hours. After this time the reaction mixture was filtered and the solvent removed *in vacuo* to give the isocyanate intermediate in quantitative yield. This was then dissolved in $CHCl_3$ (10 mL) and added to a solution of diimide **9** (100 mg, 0.21 mmol), macrocycle **8** (160 mg, 0.21 mmol) and dibutyl tin dilaurate (40 mg, 0.063 mmol) in $CHCl_3$ (20 mL). The reaction mixture was then stirred at room temperature, under N_2 for 5 days. After this time the solvent was evaporated and the residue purified by preparative TLC (eluent: CD_2Cl_2–3% MeOH) to give the product both dumbbell **10** (128 mg, 42%) and the diimide rotaxane as a pink solid (18 mg, 4%); mp 172–174 °C; *m*/*z* (ESI-MS) $[M + Na]^+$ 2186.9528 $C_{138}H_{150}N_6O_{17}Na$ (calc. 2187.0983); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (1H, s, CH_{int}), 8.33 (2H, s, CH_{ext}), 8.03 (4H, s, a-NDI), 7.43 (2H, s, NH_{amide}), 7.30 (4H, d, ^3J 8.5 Hz, Ar–H), 7.00–7.19 (36H, m, Ar–H), 6.82 (2H, d, ^3J 8.0 Hz, d), 6.69 (4H, m, a e), 6.31 (2H, t, ^3J 7.0 Hz, b), 6.16 (2H, d, ^3J 8.0 Hz, f), 5.86 (2H, d, ^3J 7.0 Hz, c), 4.08–4.12 (4H, m, CH_2), 3.79–3.95 (28H, m, OCH_2), 1.56–1.74 (12H, m, CH_2), 1.37 (13H, m, CH_2, CH_{3macro}), 1.21 (36H, s, $CH_{3dumbbell}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 153.9, 153.3, 153.0, 152.8,

148.4, 147.2, 143.8, 142.0, 136.0, 133.5, 131.8, 131.1, 130.7, 129.5, 127.3, 125.7, 125.1, 125.0, 124.8, 124.2, 123.3, 121.4, 117.4, 114.1, 113.1, 105.6, 104.4, 71.1, 70.7, 69.5, 67.6, 67.0, 64.9, 63.7, 41.0, 40.9, 35.3, 34.3, 31.4, 31.2, 28.5, 28.0, 26.6, 25.9.

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