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Dynamic Covalent Synthesis of Donor–Acceptor Interlocked Architectures in Solution and at the Solution:Surface Interface

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Abstract: Despite advances in the range of mechanically interlocked architectures that can be synthesized and operated as supramolecular machines, motors and sensors in solution, in many cases their synthesis is laborious and expensive requiring long multistep pathways with extensive purification at each stage. Dynamic covalent chemistry has been shown to overcome problems with traditional kinetically controlled synthetic approaches that often afford low yields of interlocked architectures due to irreversible formation of non-interlocked by-products. Herein, we describe the use of reversible disulfide exchange reactions as a means to assemble catenanes and rotaxanes in organic solutions. Moreover, the application of this thermodynamic approach to assemble interlocked architectures at the solution:surface interface, specifically polymer resins, is discussed.

Introduction

Significant developments in fundamental supramolecular concepts such as self-assembly,[1,2] self-organisation,[3] molecular recognition,[2,4] and template-directed synthesis,[5] have unlocked access to increasingly elaborate interlocked architectures including knots,[6,7] suitanes,[8] Borromean rings,[9] and ravels.[10] With increased topological complexity, however, comes synthetic challenges, and traditional kinetically controlled synthetic approaches prove problematic due to the potential formation of kinetic by-products that decrease the overall reaction efficiency. For example, in a clipping protocol for [2]rotaxane synthesis, the free macrocycle can form in addition to the desired rotaxane, thus reducing the yield of interlocked products.[11,12] If, however, reversible or dynamic bonds are used in the macrocycle formation, any non-interlocked macrocycle produced can reopen and reassemble around the dumbbell, thereby introducing a "proof-reading" mechanism.[13] As mechanically interlocked molecules are typically lower in free energy than their non-interlocked counterparts, increased yields of interlocked architectures are often observed.[11,13,14] The energetic bias towards interlocked architectures renders dynamic covalent chemistry—the chemistry of thermodynamically controlled bond formation—a powerful tool in the creation of mechanical bonds.[15] Numerous reversible covalent bond forming reactions, including imine, acetal, hydrazone, and ester formation as well as Aldol, Diels–Alder, Michael, nucleophilic substitution, and olefin metathesis reactions, have been used to prepare mechanically interlocked compounds in high yields;[12,14,16–20] however, the work described herein exploits disulfide exchange in the dynamic covalent assembly of catenanes and rotaxanes. Research undertaken by Sanders et al. have demonstrated the success of such an approach by synthesizing a range of electron-rich 1,5-dialkoxynaphthalene and electron-deficient 1,4,5,8-naphthalene tetracarboxylic diimide catenanes[16,18,21,22] and even a trefoil knot[7] via disulfide exchange from simple building blocks.

This work aims to extend previous research by investigating the use of disulfide exchange as a means of synthesizing not only donor–acceptor catenanes but also rotaxanes, with the ultimate view of implementing this approach at the solution:surface interface. The dithiol building blocks chosen for investigation in this work are the π-electron-rich 1,5-dialkoxynaphthalene **1** and the zinc-metallated porphyrin **2** as well as the π-electron-deficient naphthalene diimide **3** (Figure 1). The potential for the addition of dinaphtho-[38]-crown-10 ether macrocycles **4** or naphthalene diimide dumbbell **5** components to direct the dynamic covalent assembly of interlocked architectures will be discussed (Scheme 1).

Results and Discussion

Synthesis of Dithiol Building Blocks. The synthesis of the bis-thioacetate protected 1,5-dialkoxynaphthalene **SAc-1** and the bis-benzylthioacetate protected zinc porphyrin **SAc-2** were carried out according to literature procedures.[23,24] Thioacetate protected naphthalene diimide **SAc-3** was synthesised straightforwardly according to Scheme 2. A solution of 2-(2-aminoethoxy)ethanol and 1,4,5,8-napthalenetetracarboxylic dianhydride in DMF was refluxed overnight to afford the pure bis-alcohol **6**. This was subsequently reacted with tosyl chloride to

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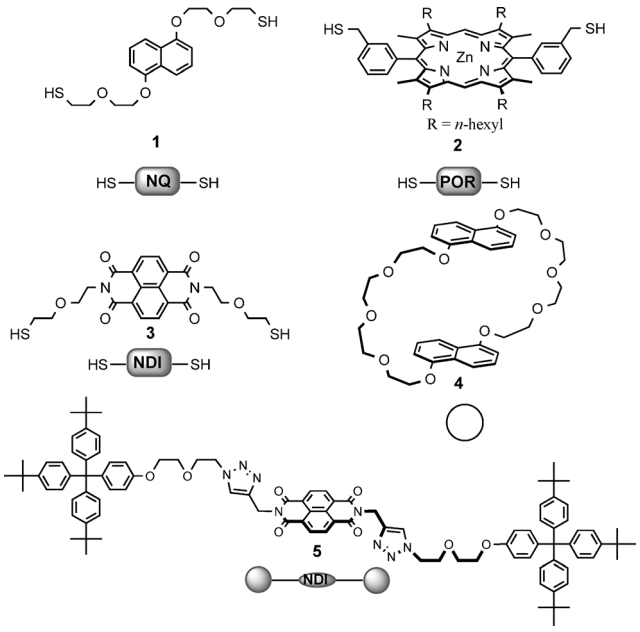
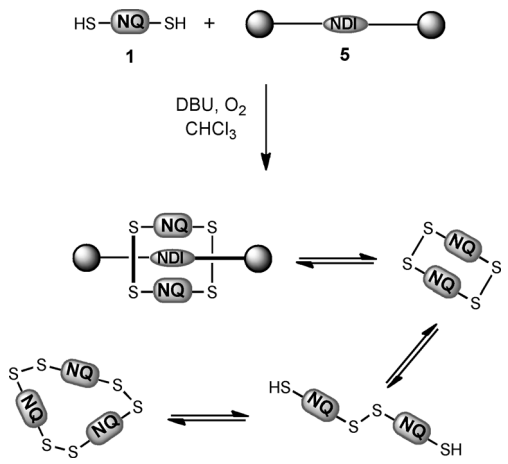


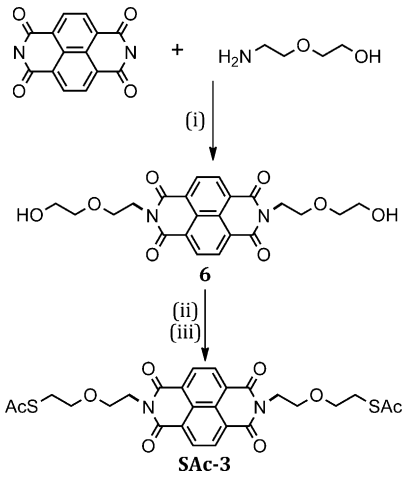
Figure 1. Building blocks chosen for investigation in dynamic covalent synthesis of mechanically interlocked architectures.



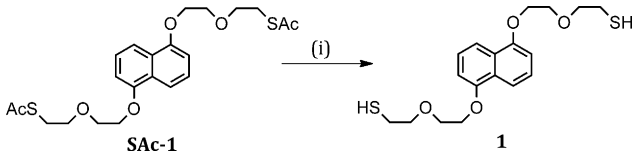
Scheme 1. Cartoon representation of dynamic covalent synthesis of interlocked architectures from dithiol building blocks and preformed dumbbell components.

afford the tosylate derivative **7** which was then reacted with potassium thioacetate to give the desired bis-thioacetate diimide **SAc-3** in 95% yield.

Initial attempts following literature reports[23,25] to deprotect the bis-thioacetate precursors **SAc-1**, **SAc-2** and **SAc-3** using hydrazine monohydrate were unsuccessful, with incomplete deprotection of the thioacetate being observed. A more efficient strategy using sodium methoxide and Zemplén deacetylation conditions was adopted.[20,26] In this approach, a solution of sodium methoxide in dry degassed methanol was added to the bis-thioacetate dissolved in dry, degassed CH_2Cl_2, and the reaction was stirred at room temperature (Scheme 3). Whilst this method proved to be far more efficient, with complete deprotection occurring within 5–15 min for each building block,



Scheme 2. Synthesis of bis-thioacetate naphthalene diimide **SAc-3**. Reagents and conditions: (i) DMF, 90 °C, argon, 18 h, 84%; (ii) TsCl, TEA, DMAP, CH_2Cl_2, RT, 3 days, 88%; (iii) KSAc, DMF, RT, 62 h, 95%.



Scheme 3. Synthesis of 1,5-dialkoxynaphthalene thiol building block **1** with sodium methoxide. Reagents and conditions: (i) NaOMe, CH_2Cl_2/MeOH (1:1), argon, RT.

the yields were compromised by concomitant decomposition. Consequently, the reaction conditions had to be optimized for each building block to ensure complete deprotection whilst minimizing monomer decomposition. A summary of the optimal reaction conditions determined for each building block by monitoring the deprotection reactions by ^{1}H NMR spectroscopy is outlined in Table 1.

Table 1. Optimized conditions for deprotection of thioacetate precursors to dithiols **1**–**3**.

Dithiol	NaOMe [equiv]	Reaction Time	Yield
1	8.0	5 min	89%
2	6.0	10 min	88%
3	8.0	10 min	57%

Control Studies. Having synthesized the dithiol building blocks **1**–**3**, our attention turned to optimization of disulfide exchange in organic solvents. In order to better understand the conditions required to promote disulfide exchange, and thus replicate literature reports, a series of disulfide-exchange experiments examining the effect of concentration of both building blocks and base were investigated. A balance between reaching equilibrium in reasonable time frames (ideally 3–4 days) by increasing the concentration of DBU, without resulting in the decomposition of the thiol building blocks, was needed. In general, the optimal balance was achieved by air

oxidation of a 5 mM solution of dithiol (**1**–**3**) in the presence of 1 equivalent of DBU (see Figure S1, Supporting Information).

These conditions were then applied to more complex libraries involving two or three dithiol building blocks. It was envisioned that π-donor/acceptor interactions between these motifs would direct the assembly of donor–acceptor macrocycles and potentially catenanes, as has been reported in aqueous studies (see Scheme S2, Supporting Information).[16,17,21] Libraries were set up using the optimized conditions of equimolar solutions of **1** and **3** (5 mM) in $CHCl_3$ in the presence of 1 equivalent of DBU. A gradual color change from pale yellow to pink was observed in this library, indicative of donor–acceptor intermolecular interactions between the diimide and naphthyl motifs. Thermodynamic equilibrium was achieved after 21 days, and the HPLC analysis indicated that the major product of the library was the cyclic heterodimer **8** (90%), with proportions of the cyclic naphthyl dimer **9** (7%) also being observed (Figure 2). The presence of the molecular ion adduct at

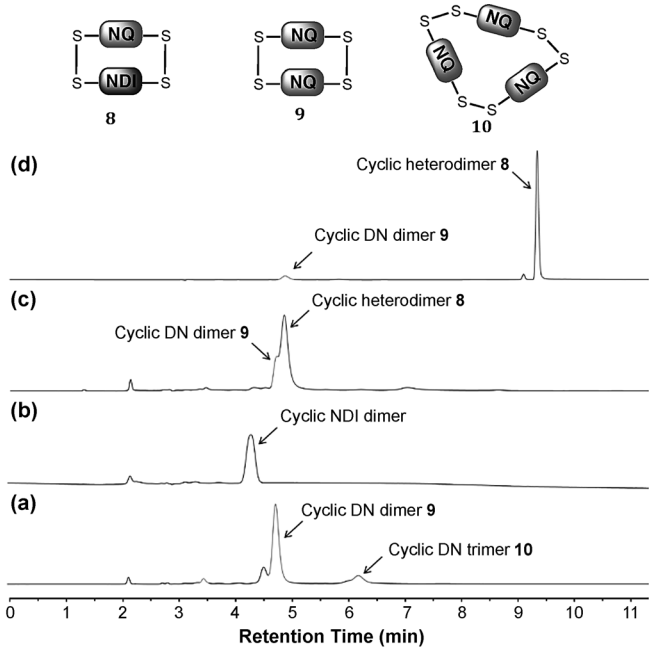
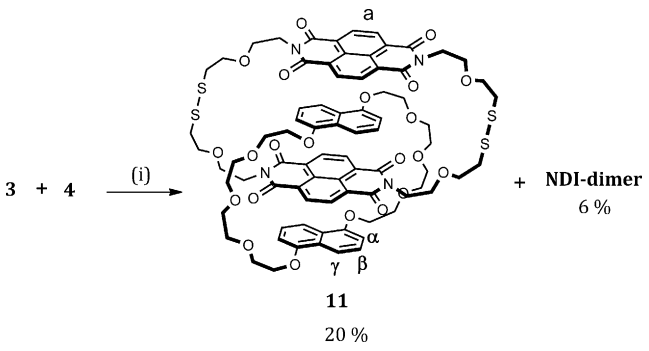


Figure 2. Comparison of HPLC traces of equilibrating mixtures of one or two dithiol building blocks: (a) RP-HPLC trace of 5 mM of **1** with 1 equiv DBU, (b) RP-HPLC trace of 5 mM of **3** with 1 equiv DBU, (c) RP-HPLC trace of 5 mM of **1** and **3** with 1 equiv DBU, and (d) NP-HPLC trace of 5 mM of **1** + **3** with 1 equiv DBU. Absorbance was recorded at 383 nm for (b) and at 292 nm for (a), (c) and (d).

$m/z = 861.1601$ $[M+Na]^+$ in the LC-MS confirmed the identity of heterodimer **8**. Smaller amounts of the cyclic naphthyl trimer (< 2%) were observed; however, no traces of donor–acceptor catenane species were detected in this library. Similarly, the mixed heterodimer was the dominant species in libraries containing porphyrin dithiol **2** and naphthoquinol thiol **1** (see Figure S2).

Dynamic Covalent Synthesis of Interlocked Architectures. Having investigated the assembly of simple donor–acceptor macrocycles via disulfide exchange, our attention turned to incorporating either π-rich crown ether macrocycle **4** or π-deficient naphthalene diimide dumbbell **5** in disulfide libraries in an effort to synthesize donor–acceptor interlocked architectures. Firstly, solutions containing the π-rich aromatic crown ether **4** with diimide **3** were examined as it was envisaged that π-donor/acceptor interactions between diimide **3** and crown **4** could direct the assembly of the [2]catenane **11** (Scheme 4).



Scheme 4. Dynamic covalent synthesis of [2]catenane **11**. Reagents and conditions: (i) 1 equiv DBU, $CHCl_3$, air, RT, 14 days.

In these studies, 1 equivalent of DBU was added to a 2:1 mixture of diimide **3** and crown **4** (5 mM total concentration), and the library was then monitored daily by reverse-phase HPLC using 100% MeOH isocratic mobile phase. During its equilibration, the solution turned intense red, which is indicative of strong complexation between the electron-deficient diimide and electron-rich naphthalene motifs in mechanically interlocked assemblies. HPLC analysis indicated that while the [2]pseudorotaxane complex dominated, the [2]catenane **11** was produced in a 20% yield (Figure 3). The identity of [2]catenane **11** was confirmed by LC-MS analysis with peaks observed at $m/z = 1603.4288$ $[M+Na]^+$ and 1619.4034 $[M+K]^+$.

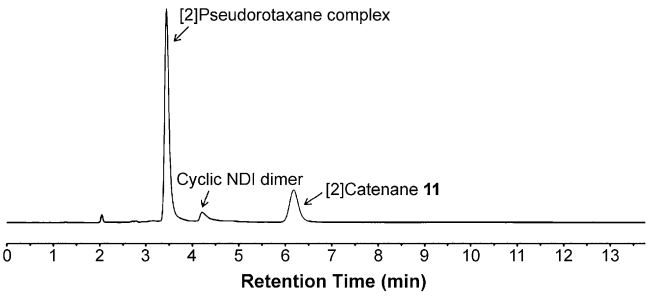
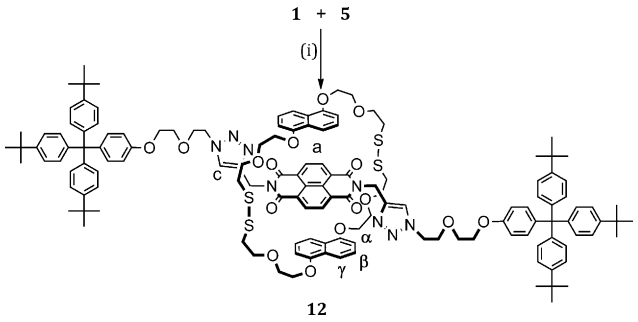


Figure 3. Reverse-phase HPLC trace of 5 mM library generated from **3** and **4**. Absorbance was monitored at 292 nm.

A second directed library incorporating the electron-deficient dumbbell **5** and the electron-rich 1,5-dialkoxynaphthalene **1** was investigated. It was anticipated that π–donor–acceptor interactions would direct the cyclization of dimer **9** around dumbbell **5** to afford [2]rotaxane **12** (Scheme 5). Identical conditions to those described in the [2]catenane synthesis mentioned above were used.



Scheme 5. Dynamic covalent synthesis of [2]rotaxane **12.** Reagents and conditions: (i) 1 equiv DBU, $CHCl_3$, air, RT, 14 days.

Pleasingly, over time a color change from pale yellow to dark pink was observed, suggesting donor–acceptor interaction between the diimide and naphthoquinone motifs. HPLC analysis revealed the gradual formation of [2]rotaxane **12**, which was confirmed by LC-MS analysis with a mass peak observed at $m/z = 2332.0458$ $[M+Na]^+$. The equilibrium composition of this mixture was reached after 14 days, and contained [2]rotaxane **12** (22%) as well as non-interlocked compounds, namely linear dimer (5%), cyclic dimer **9** (34%), cyclic trimer **10** (4%), and diimide dumbbell **5** (27%), in smaller proportions (Figure 4).

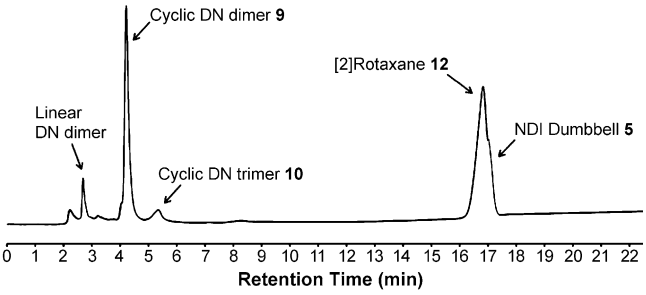
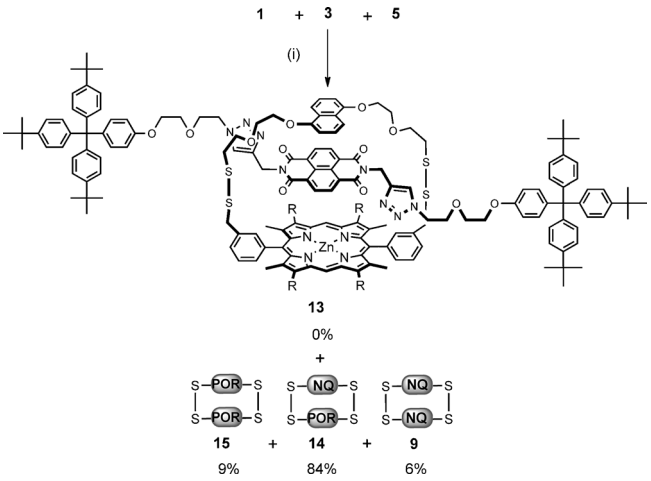


Figure 4. Reverse-phase HPLC trace of library produced by mixing **1** and **5**. Absorbance was monitored at 292 nm.

Attempts to prepare porphyrin-containing [2]rotaxanes via disulfide exchange were also undertaken. It was anticipated that π–π interactions between diimide and porphyrin motifs and π-donor/acceptor recognition between naphthalene and diimide units could be simultaneously exploited to direct the assembly of heterodimer **14** around diimide dumbbell **5** to afford [2]rotaxane **13** (Scheme 6); however, no evidence of rotaxane was observed when employing the optimized disulfide exchange conditions. After 3 days, thermodynamic equilibrium was reached, and the heterodimer **14** (84%) was found to be the major constituent with smaller amounts of porphyrin homodimer **15** (9%) and naphthalene homodimer **9** (6%) also present.

Large-Scale Preparation and Characterization of Disulfide-Linked Interlocked Architectures. Preparative scale synthesis of [2]catenane **11** and [2]rotaxane **12** was then attempted



Scheme 6. Dynamic covalent synthesis of [2]rotaxane **13.** Reagents and conditions: (i) 1 equiv DBU, $CHCl_3$, air, RT, 14 days.

using the optimized conditions described above. In both cases the reaction mixtures were allowed to equilibrate for 14 days and, following purification by column chromatography, the desired [2]catenane **11** and [2] rotaxane **12** were isolated in 21% and 22% yields, respectively.

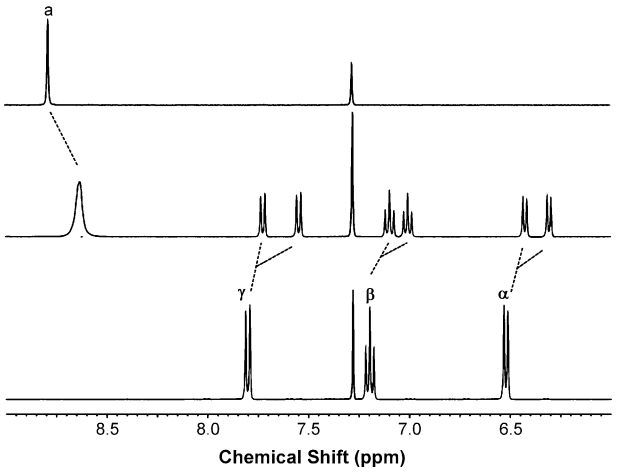


Figure 5. Aromatic region of the ^1H NMR spectra of naphthalene diimide **3** (top), [2]catenane **11** (middle), and dinaphth-[38]-crown-10 **4** (bottom) in $CDCl_3$ at 303 K.

The partial ^1H NMR spectra of [2]catenane **11** in $CDCl_3$ are displayed in Figure 5. In the ^1H NMR spectrum of the [2]catenane **11**, the aromatic naphthalene diimide proton a appears shifted upfield as a broad singlet at δ 8.63 ppm as compared to δ 8.78 ppm in the uncomplexed diimide **3**. Likewise, the aromatic protons α, β, and γ of crown **4** are also shifted upfield. Moreover, the doublet-triplet-doublet pattern that arises from coupling of aromatic protons in the 1,5-substituted naphthalene system is noticeably doubled in each case, thereby demonstrating that the symmetry of the crown ether ring is broken by catenation with the diimide ring, as has been previously reported in related systems.[27]

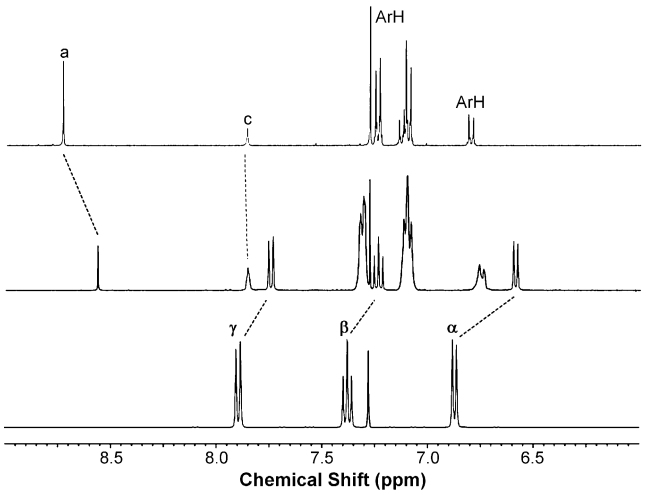
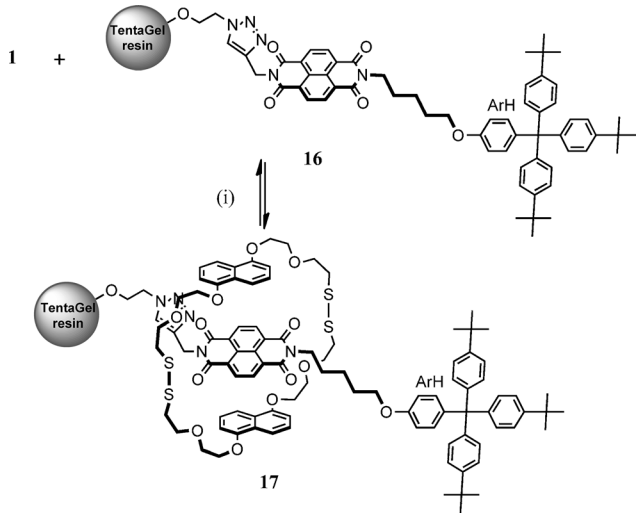


Figure 6. Aromatic region of the ^{1}H NMR spectra of naphthalene diimide dumbbell **5** (top), [2]rotaxane **12** (middle), and 1,5-dialkoxynaphthalene **1** (bottom) in $CDCl_3$ at 303 K.

Similarly, in the ^{1}H NMR spectrum of the naphthalene diimide [2]rotaxane **12**, the diimide proton a was shifted upfield from δ 8.74 ppm to δ 8.54 ppm as a result of the shielding effect from the aromatic naphthalene protons (Figure 6). Upfield shifts of 0.15 ppm, 0.14 ppm, and 0.29 ppm were also observed for the naphthalene aromatic protons α, β, and γ, respectively, in comparison to the spectrum of 1,5-dialkoxynaphthalene **1**. These substantial changes in chemical shifts are characteristic of the interlocked nature of this architecture, and correlate with analogous [2]rotaxanes reported in the literature.[28]

In contrast to the non-interlocked counterparts which are all pale yellow or cream in color, both [2]catenane **11** and [2]rotaxane **12** possess a vibrant red color. This intense coloration is evidenced by broad absorption bands in the UV/Vis spectra at 506 nm ($\varepsilon = 1100\ M^{-1}\,cm^{-1}$) for **11** and at 525 nm for **12** ($\varepsilon = 1030\ M^{-1}\,cm^{-1}$), thereby reflecting strong complexation in the interlocked architectures (Figure S3). Similar charge-transfer bands have been observed in related crown-diimide catenane and rotaxane systems.[28,29]

Dynamic Covalent Synthesis of a Resin-Tethered Naphthalene Diimide [2]Rotaxane. Given the successful synthesis of a rotaxane and a catenane using disulfide exchange in solution, investigations into whether disulfide exchange could be used to assemble interlocked architectures at the solution–surface interface were carried out. We have previously reported the controlled self-assembly of rotaxane and pseudorotaxane systems on polystyrene TentaGel resins.[30,31] This work highlighted two important issues; firstly, surface functionalization using kinetically controlled bond formation can result in mixtures of the desired interlocked and undesired non-interlocked products on the surface, and secondly, the dynamic behavior of supramolecular architectures deposited on surfaces is not always directly comparable to that observed in solution, highlighting the importance of using characterization tools such as ^{1}H HR-MAS NMR spectroscopy. Despite the success of dynamic covalent chemistry in the construction of interlocked architectures in solution, the effectiveness of such an approach at the solution:surface interface remains unexplored. It was hoped that addition of naphthalene diimide thread functionalized beads **16** to a solution of 1,5-dialkoxynaphthalene **1** under the conditions of disulfide exchange would result in the self-assembly of disulfide-linked bead-tethered [2]rotaxane **17** (Scheme 7).



Scheme 7. Dynamic synthesis of disulfide-linked naphthalene diimide [2]rotaxane **17**. Reagents and conditions: (i) 1 equiv DBU, $CHCl_3$, air, RT, 14 days.

Naphthalene diimide functionalized beads **16** (1 equiv) were added to a solution of 1,5-dialkoxynaphthalene dithiol **2.1** (2 equiv) in $CHCl_3$, and disulfide exchange was initiated by the addition of DBU (1 equiv). The reaction was left to stir at ambient conditions for 14 days to ensure that thermodynamic equilibrium was reached. After this time the beads were washed extensively to remove any untethered library components. Pleasingly, visual inspections of beads **17** showed that, in contrast to the yellow thread functionalized resins **16**, the rotaxane functionalized beads **17** had a distinct red color (Figure S4, Supporting Information). This red coloration is indicative of a charge-transfer phenomenon between the π-rich dialkoxynaphthalene motifs of the macrocycle and the π-deficient naphthalene diimide motif in the thread, and has been seen in related solution and surface-bound rotaxanes.[28,30,31] This qualitatively suggests at least some rotaxane assembly at the bead–solvent interface.

^{1}H HR-MAS NMR analysis indicated that rotaxane formation had occurred on the surface as evidenced by the diimide peak at 8.03 ppm; however, peaks for the macrocycle napthoquinone protons were obscured under the bead and stopper aromatic protons (see Figure 7). The bound diimide proton chemical shift is consistent with that seen in related surface-bound diimide-containing rotaxanes.[30,31] Nevertheless, it is clear that significant amounts of uncomplexed diimide thread remain on the surface, and future work will look at optimizing reaction conditions to favor the formation of interlocked architectures at the solution:surface interface.

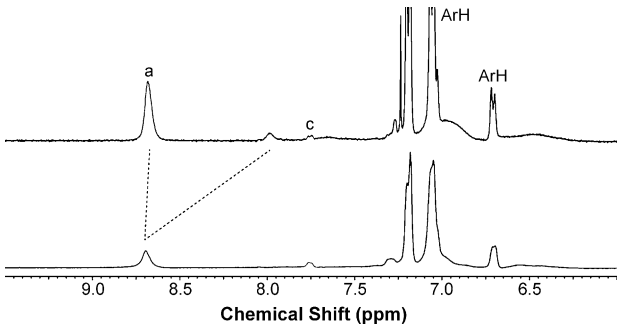


Figure 7. Aromatic region of the ^{1}H HR-MAS NMR spectra of the rotaxane-functionalized beads **17** (top) and naphthalene diimide tether beads **16** (bottom) in $CDCl_3$ at 303 K.

Conclusions

Disulfide exchange has been shown to be an effective synthetic route for the synthesis of interlocked architectures both in solution and at the solution:surface interface. Starting with relatively simple dialkoxynaphthalene, diimide, and porphyrin thiol building blocks, their disulfide exchange reactions were explored in organic solutions. Reaction conditions were optimized to find the balance between reaching thermodynamic equilibrium in reasonable timeframes (up to 21 days) without concomitant decomposition. As the intermolecular interactions between naphthalene diimide and dialkoxynaphthalene building blocks are weaker in organic solvents, due to the absence of any favorable hydrophobic effects, no interlocked architectures were isolated when using only mixtures of **1**, **2** or **3**. Addition of dinaphthocrown ether **4** or diimide stoppered thread **5** provided sufficient pre-organization to overcome these issues allowing the [2]catenane **11** and [2]rotaxane **12** to be isolated in 21 and 22% yields, respectively. The use of reversible disulfide exchange as a means to assemble interlocked architectures on surfaces was then examined. In this case disulfide exchange was initiated using dialkoxynaphthalene thiol **1** in the presence of polymer resins that had been functionalized with a stoppered diimide thread **16**. The concentration of thiol and base were identical to those that had been successful in synthesizing the [2]rotaxane **12**. Pleasingly, evidence of rotaxane formation on the polymer resin was observed both qualitatively by the red coloration of the bead and by the presence of peaks for the bound diimide resonance in the ^{1}H HR-MAS NMR spectrum. Clear evidence of the naphthoquinone aromatic protons was obscured by the bead and stopper aromatic proton signals. Future work needs to look at optimizing reaction conditions to increase the proportion of rotaxane on the surface, which will facilitate characterization. Nevertheless, these are promising results indicating that dynamic covalent chemistry can be used to assemble interlocked architectures at the solution:surface interface.

Experimental Section

General Considerations. Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. All solvents were dried before use over type 3 Å or 4 Å molecular sieves according to standard procedures. Silica gel column chromatography was carried out using Merck Silica Gel 60 (grade 9385, 230–400 mesh). Analytical TLC was carried out on Merck silica gel 60 F_{254} pre-coated aluminium sheets. Reverse-phase chromatography was carried out using an Agilent Super-Flash C18n (SF 25–55 g) column.

Solution NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to the relevant solvent peak. TentaGel-HL-OH resins were purchased from Peptides International with a quoted loading of 0.43 mmol g^{-1} and a particle size of approximately 90 μm. HR MAS-NMR spectra were acquired on a Bruker DRX400 spectrometer at room temperature using a Bruker HR-MAS probe. Rotors containing a suspension of the beads in $CDCl_3$ were spun at 4 kHz. One-dimensional HR-MAS spectra were obtained with 64 scans. Unless otherwise stated, the CPMG pulse sequence contained 0, 8, 32 or 64 π-pulses with a repetition time of 30 ms.

ESI high-resolution mass spectra were obtained using a QTOF LC mass spectrometer which utilized electrospray ionization. Melting points were measured on a variable-temperature apparatus by the capillary method and are uncorrected. IR spectra were obtained using a Thermo Nicolet Nexus 870 esp spectrometer equipped with a 45° Ge ATR accessory at 4 cm^{-1} resolution using 64 scan averaging.

Colored bead images were taken using a Leica MZ6 modular stereomicroscope with a Leica CLS 150 light source and Leica camera mounted at 4x magnification.

Synthetic Procedures. The synthesis of the bis-thioacetate protected 1,5-dialkoxynaphthalene **SAc-1** and the bis-benzylthioacetate protected zinc porphyrin **SAc-2** were carried out according to literature procedures.[23,24] Likewise, the synthesis of the dinapthocrown **4**, diimide stoppered thread **5**, and diimide-functionalized TentaGel resins **16** have all been previously reported.[28,31] The synthesis of the thiol building blocks can be found in the Supporting Information.

Naphthalene diimide disulfide [2]catenane (11). Naphthalene diimide dithiol **3** (35 mg, 0.074 mmol) and dinaphtho-38-crown-10 ether **4** (23 mg, 0.036 mmol) were dissolved in $CHCl_3$ (20 mL). DBU (11 μL, 0.074 mmol) was added to the red solution which was stirred at room temperature under air for 14 days. The solution was then washed with H_2O (20 mL), dried over Na_2SO_4, and the solvent was evaporated to yield a crude red solid. Purification of this crude material by column chromatography (EtOAc/CH_2Cl_2 3:7) afforded the desired [2]catenane as a red solid (13 mg, 21%); m.p. > 280 °C (decomp.); *m/z* (ESI-MS) $[M+Na]^+$ 1603.4288 $C_{80}H_{84}N_4NaO_{22}S_4^+$ (calc. 1603.4352); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.63 (8H, bs, a-H), 7.73 (2H, d, $J_{HH} = 8.2$ Hz, α-H), 7.53 (2H, d, $J_{HH} =$ 8.2 Hz, α-H), 7.12 (2H, t, $J_{HH} = 7.9$ Hz, β-H), 7.01 (2H, t, $J_{HH} = 7.9$ Hz, β-H), 6.44 (2H, d, $J_{HH} = 8.1$ Hz, γ-H), 4.48–4.35 (8H, m, CH_2), 4.06–3.96 (8H, m, OCH_2), 3.95–3.71 (40H, m, OCH_2), 2.91–2.78 ppm (8H, m, SCH_2).

Naphthalene diimide disulfide [2]rotaxane (12). 1,5-Dialkoxynaphthalene dithiol **1** (50 mg, 0.14 mmol) and naphthalene diimide dumbbell **5** (107 mg, 0.068 mmol) were dissolved in $CHCl_3$ (41 mL). DBU (20 μL, 0.14 mmol) was added to the orange solution which was stirred at room temperature under air for 14 days. During this time the solution became dark pink. The solution was then washed with H_2O (40 mL), dried over Na_2SO_4, and the solvent was evaporated to yield a crude dark pink solid. Purification of this crude material by column chromatography using (EtOAc/CH_2Cl_2 1:3) as the eluent afforded the desired rotaxane as a pale red solid (33 mg, 22%); m.p. 178–181 °C; *m/z* (ESI-MS) $[M+Na]^+$ 2332.0458

$C_{138}H_{156}N_8NaO_{16}S_4^+$ (calc. 2332.04198); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (4H, s, a-H), 7.86 (2H, s, c-H), 7.75 (4H, d, J_{HH} = 8.2 Hz, γ-H), 7.39–7.31 (12H, d, J_{HH} = 8.0 Hz, Ar-H), 7.24 (4H, t, J_{HH} = 7.9 Hz, β-H), 7.12–7.03 (16H, m, Ar-H), 6.76 (4H, d, J_{HH} = 8.0 Hz, Ar-H), 6.59 (4H, d, J_{HH} = 8.1 Hz, α-H), 4.95 (4H, s, CH_2), 4.54–4.52 (4H, m, CH_2), 4.32 (8H, t, J_{HH} = 4.8 Hz, OCH_2), 4.09–3.99 (12H, m, OCH_2), 3.93–3.89 (4H, m, OCH_2), 3.81–3.77 (12H, m, OCH_2), 3.21–3.16 (8H, m, SCH_2), 1.31 ppm (54H, s, CH_3).

Bead-tethered naphthalene diimide disulfiide [2]rotaxane (17). A solution of 1,5-dialkoxynaphthalene dithiol **1** (20 mg, 0.054 mmol) dissolved in $CHCl_3$ (16 mL) was added to a round bottom flask containing naphthalene diimide functionalised Teta-Gel resin beads **16** (26 mg, 0.027 mmol). DBU (8.1 μL, 0.054 mmol) was then added and the reaction mixture was kept under air at room temperature for 14 days. The beads were collected by filtration and washed with $CHCl_3$ (10 mL), acetone (10 mL), water (10 mL), CH_2Cl_2 (10 mL), and hexane (10 mL). The resulting red beads were dried under vacuum.

Keywords: catenanes · dynamic covalent chemistry · HR-MAS NMR spectroscopy · rotaxanes · supramolecular chemistry

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FULL PAPER

Supramolecular Chemistry

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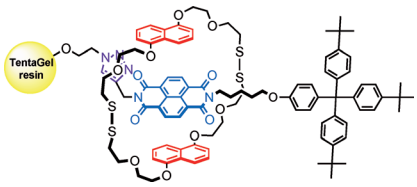
Dynamic Covalent Synthesis of Donor–Acceptor Interlocked Architectures in Solution and at the Solution:Surface Interface



Exchange program: The use of disulfide exchange to reversibly assemble interlocked architectures both in solution and on polymer resins is described.