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Synthesis of a polypseudorotaxane, polyrotaxane, and polycatenane using 'click' chemistry

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ABSTRACT

The synthesis of a polypseudorotaxane, polyrotaxane, and polycatenane containing the electron-deficient cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) subunit in the side chain is described. These interlocked supramolecular polymers have been prepared from an azide-functionalized polystyrene derivative and an acetylene-functionalized [2]rotaxane, [2]catenane and their parent tetracationic cyclophane via Cu(I)-catalyzed 1,3 dipolar cycloadditions ('click chemistry'). The synthesis and characterization of the polymers and intermediates has been described using IR, ^1H NMR, UV spectroscopies, and voltammetry. We have shown that the $CBPQT^{4+}$ unit of the side chain polystyrene derivative has the ability to reversibly undergo complexation with a complementary dialkoxynaphthalene derivative.

1. Introduction

The synthesis of interlocked[1] supramolecular polymers[2] (e.g., polyrotaxanes and polycatenanes) has received considerable attention in attempts to synthesize novel macromolecular architectures. Indeed the juxtaposition of covalent and mechanical bonds in systems of this type has led to the creation of macromolecules with interesting new topologies and function.[3] Although a number of synthetic methods exist for synthesizing main-chain and side-chain interlocked polymers, there still remains significant scope for developing new protocols with improved convenience, applicability, and effectiveness.

'Click' chemistry is a generic term describing a range of chemical transformations characterized by high efficiency, mild conditions, and convenient purification.[4,5] This methodology has led to the bespoke synthesis of a range of systems with applications encompassing biological[5] to materials chemistry.[6] Possibly the most versatile method is based upon the Huisgen Cu(I)-catalyzed 1,3-cycloaddition of appropriately functionalized azide and alkyne-functionalized building blocks.[7] Recently, this 'click' methodology has been extended to feature interlocked structures (e.g., rotaxanes and catenanes).[8] This methodology is particularly attractive for the synthesis of systems of this type, as it offers advantages over more traditional methods in terms of improved yields and increased sophistication of the resulting structures. Here, we extend this methodology to include polymeric structures by reporting the synthesis of new alkyne-functionalized cyclophane **1** and its corresponding [2]rotaxane **2** and [2]catenane **3**, and their ability to be conveniently 'clicked' onto an azide-functionalized polystyrene derivative. Moreover, the ability of the $CBPQT^{4+}$ pendant side chain polystyrene to reversibly undergo complexation with a complementary dialkoxynaphthalene derivative is reported.

2. Results and discussion

The synthesis of the alkyne-functionalized building blocks **1**–**3** is shown in Scheme 1. Derivative **5** is conveniently prepared from 1-pentynoic acid and alcohol **4**, and proved to be a versatile building block for the construction of cyclophane **1** and its corresponding interlocked structures **2** and **3**.[9] Cyclophane **1** was synthesized from compounds **5** and **6**[10] using a template-directed

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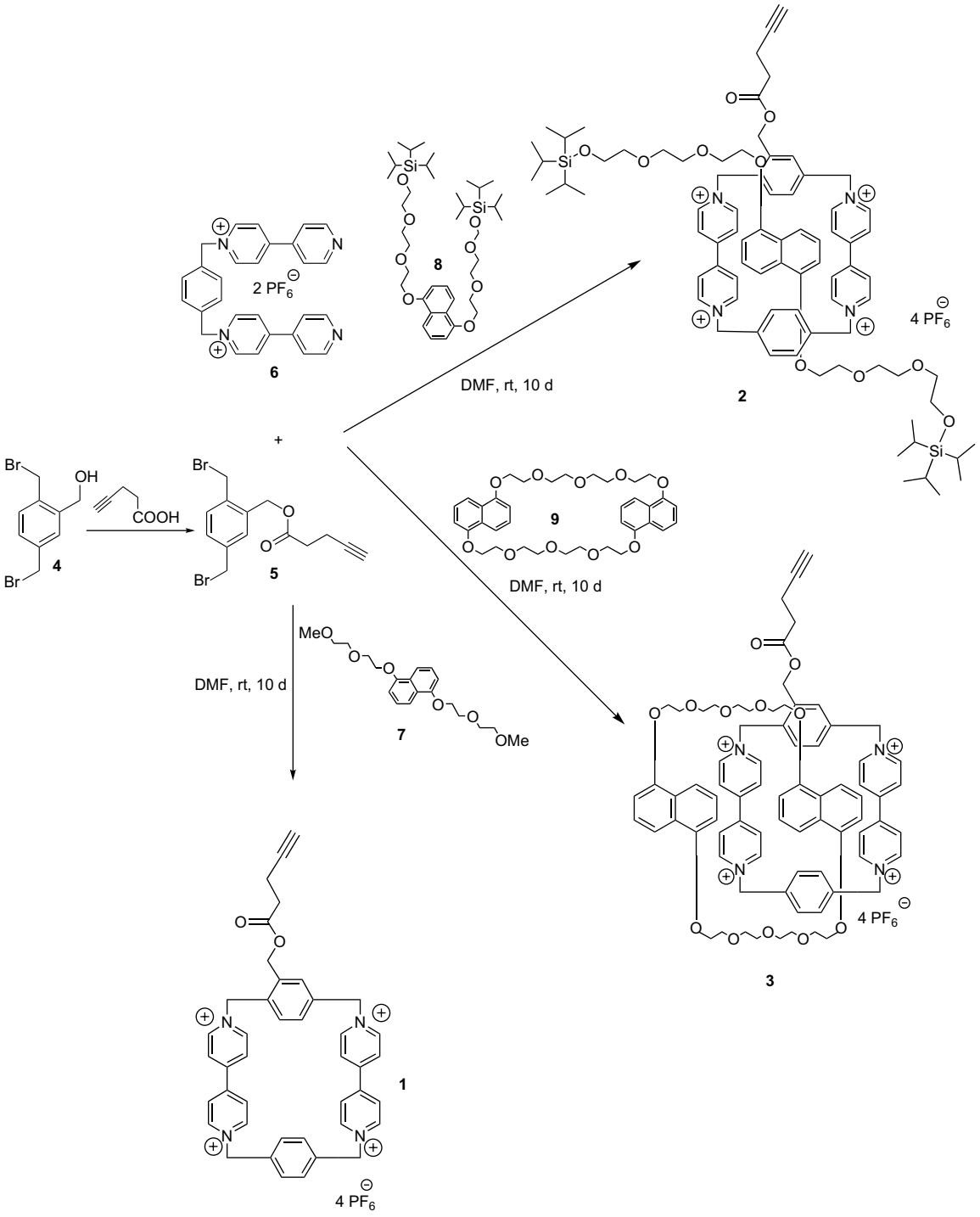


Scheme 1. Synthesis of cyclophane **1**, rotaxane **2**, and catenane **3**.

clipping methodology using **7**.[11] The interlocked structures **2** and **3** were synthesized by using the naphthalene-based axle **8**[12] and macrocycle **9**[13] as templates, respectively. The cyclophane **1** and interlocked structures **2** and **3** were purified by column chromatography ($MeOH/NH_4Cl$ (2 M)/$MeNO_2$, 4:4:2); and following counterion exchange with NH_4PF_6 were isolated either as a white solid (for **1**) or deep purple solids (for **2** and **3**).

Structures **1**–**3** were characterized by UV–vis, MS, ^1H NMR and ^{13}C NMR spectroscopies, which gave data that are consistent with the proposed structures **1**–**3**. For example, a notable feature in the ^1H NMR spectra is the significant upfield position of the resonances of the 1,5-dialkyloxynaphthalene protons of **2** and **3**, compared to the same protons of the corresponding free templates **8** and **9**, respectively (Fig. 1). This fact is particularly evident for the resonances of the protons attached to the 4- and 8- positions, which shift by $\Delta\delta \approx 5.3$ ppm for both interlocked structures.

We next investigated whether we could use standard Huisgen 'click' chemistry to graft the alkyne-functionalized building blocks **1**–**3** onto an azide-functionalized polystyrene derivative (Scheme 2).[14] Polymer **13** was readily synthesized from styrene **11** and

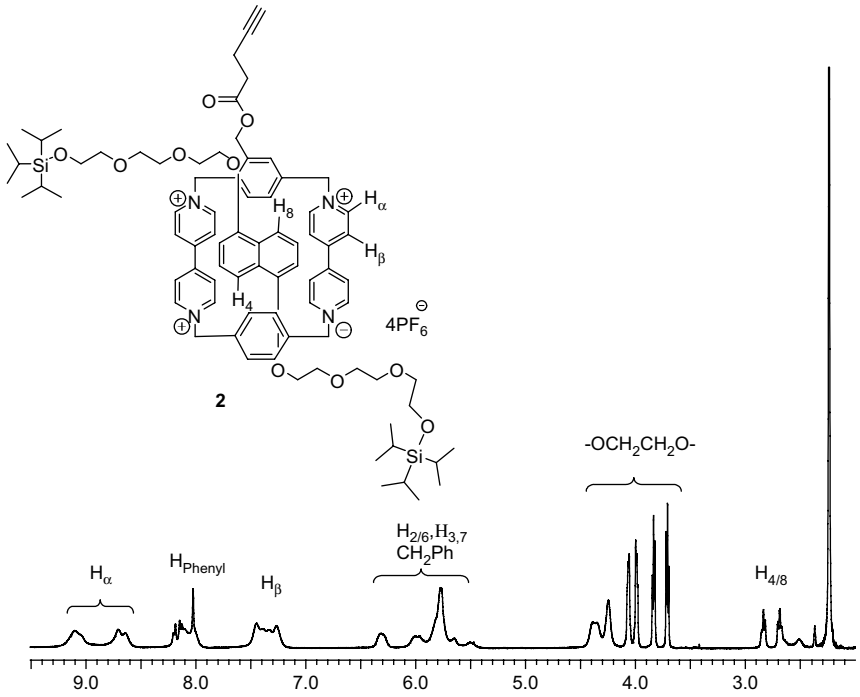


Figure 1. Partial ^{1}H NMR of **2** in CD_3CN.

p-chloromethyl styrene **12**. The chlorine was readily substituted by sodium azide to afford polymer **14**.[14a] This polymer underwent Cu(I)-catalyzed 1,3-cycloadditions with derivatives **2** and **3** to afford the pink-colored polymers **15** and **16**, respectively. We have investigated the use of either $CuSO_4$/ascorbic acid (Method 1) or CuI (Method 2) as catalyst. Moreover, we have also explored the application of catalytic amounts (e.g., 5 mol % $CuSO_4 \cdot 5H_2O$ and 10 mol % ascorbic acid; 10% CuI) or non-catalytic amounts of the copper catalyst.

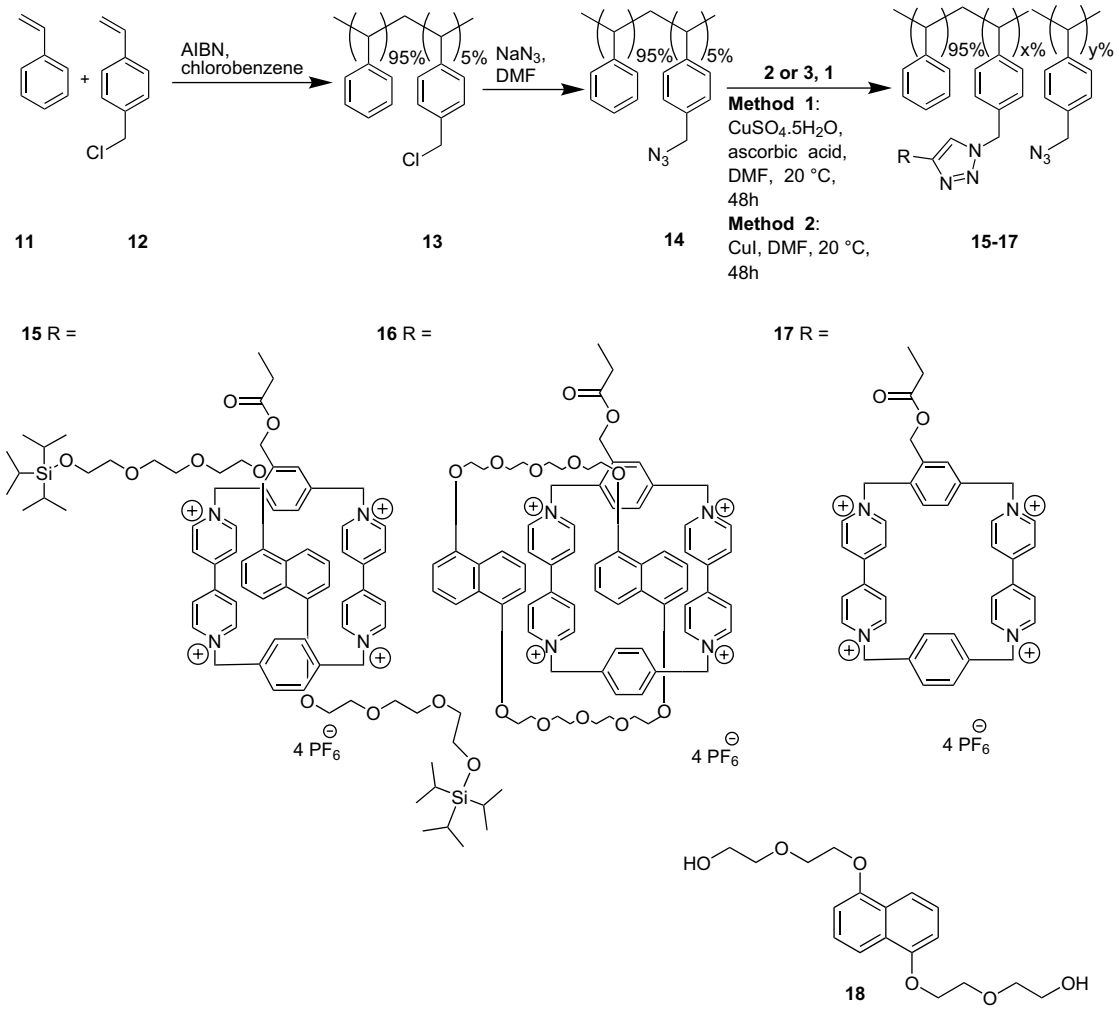
^{1}H NMR spectroscopy of the products from these reactions clearly revealed that an excess of the copper catalyst was required for Method 1 to achieve effective functionalization of the azide groups of the polymer, whereas when excess copper catalyst was used in Method 2, a noticeable change in color of both the reaction solution and the resulting polymers was observed (purple to brown) indicating possible decomposition of the interlocked structures. Overall, the most effective method for synthesizing polymers **15** and **16**, with regard to proportion of grafted interlocked structure and convenient purification, proved to be Method 1 using an excess of $CuSO_4 \cdot 5H_2O$ and ascorbic acid.

The differing solubility characteristics of derivatives **2** and **3** (compared to the 'clicked' polymers) in THF conveniently allowed preliminary separation of unreacted reagents from polymers **15** and **16**. Subsequent precipitation of these polymers into methanol provided macromolecules free from their parent interlocked structures **2** and **3** as judged by thin layer chromatography experiments (silica gel: MeOH/NH_4Cl(2 M)/$MeNO_2$, 4:4:2). Although in both cases resonances for the interlocked structures could be seen in the ^{1}H NMR spectra of the polymers, the broad nature of the signals for the polymer backbone and the grafted interlocked moieties prevented accurate determination of the ratio of interlocked structures 'clicked' onto the polymer versus unreacted azido groups to be determined (Fig. 2). However, we estimate that around 40–50% of available azido groups were functionalized.

FTIR spectroscopy clearly revealed the presence of azide groups in polymers **15** and **16**, thereby further indicating that complete functionalization of all of the available azide groups did not occur (Fig. 3). This fairly low grafting density is likely to be due to a combination of Coulombic repulsion of the cyclophane units and steric congestion between the reactive groups in the side-chains and the polymeric backbone.[14g] ^{1}H NMR spectra of 1**5** and **16** displayed new resonances consistent with methylene group adjacent to the triazole moiety at ~5.7–5.8 ppm and the triazole hydrogen at ~8.7–8.8 ppm, further providing evidence for the proposed structures.

We have exploited the electrochemical signature of the electroactive cyclophane moiety to further confirm the attachment of the catenane unit to polymer **13** (Fig. 4). The cyclic voltammogram of parent catenane **3** recorded in DMF indicated that the catenation process provided similar electrochemical data to that obtained for related [2]catenanes.[15] In particular, two one-electron reduction waves were obtained for the formation of the diradical dication species, whereas the subsequent loss of two electrons resulting in the formation of the fully reduced macrocycle occurred at a more negative potential. Similar redox waves were observed for polymer **16**, however, two notable differences were observed. Firstly, the redox waves were broader and less well resolved for the macromolecule and secondly the reduction waves for the polymer became significantly more reversible as the scan rate was lowered, in accordance with the slower electron transfer rate of **16** compared to **3**.[16] The shape of the voltammograms when recorded using a scan rate of 100 mV s^{-1} did not change significantly with repeated cycling (five cycles), suggesting that decomposition did not occur to any significant extent under the conditions examined. Thus, the electrochemical data are in accordance with the aforementioned spectroscopic data and are consistent with the catenane being covalently bound to the polystyrene backbone.

We next investigated whether the parent cyclophane **1** could also be grafted onto polymer **13** using click chemistry. We have explored Method 1 and Method 2 (Scheme 2), however, the best methodology proved to be the use of CuI (10 mol %) to achieve effective grafting. Polymer **17** was purified in the same manner as that described for polymers **15** and **16**. ^{1}H NMR spectroscopy indicated that approximately ~50% of the available azide units were



Scheme 2. Attachment of **1**, **2**, or **3** onto a polystyrene derivative using the 'click' reaction.

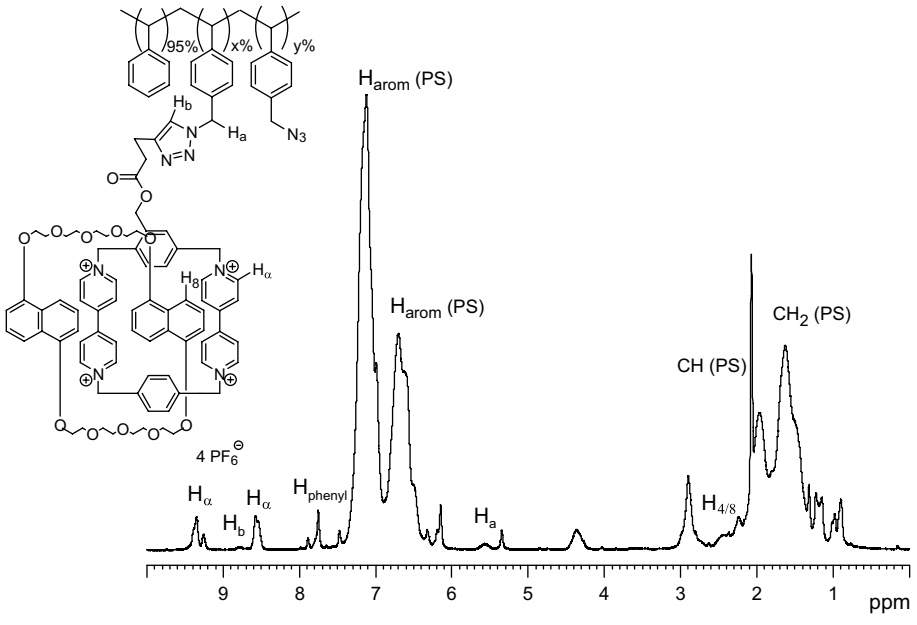


Figure 2. ^{1}H NMR of polymer **16** (acetone-d_6).

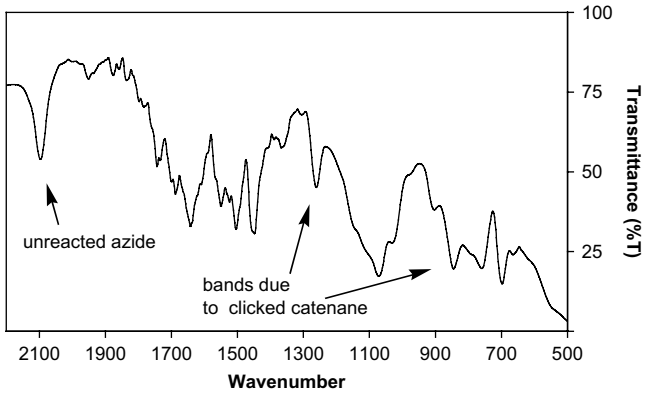


Figure 3. FTIR spectrum of a thin film polymer **16**.

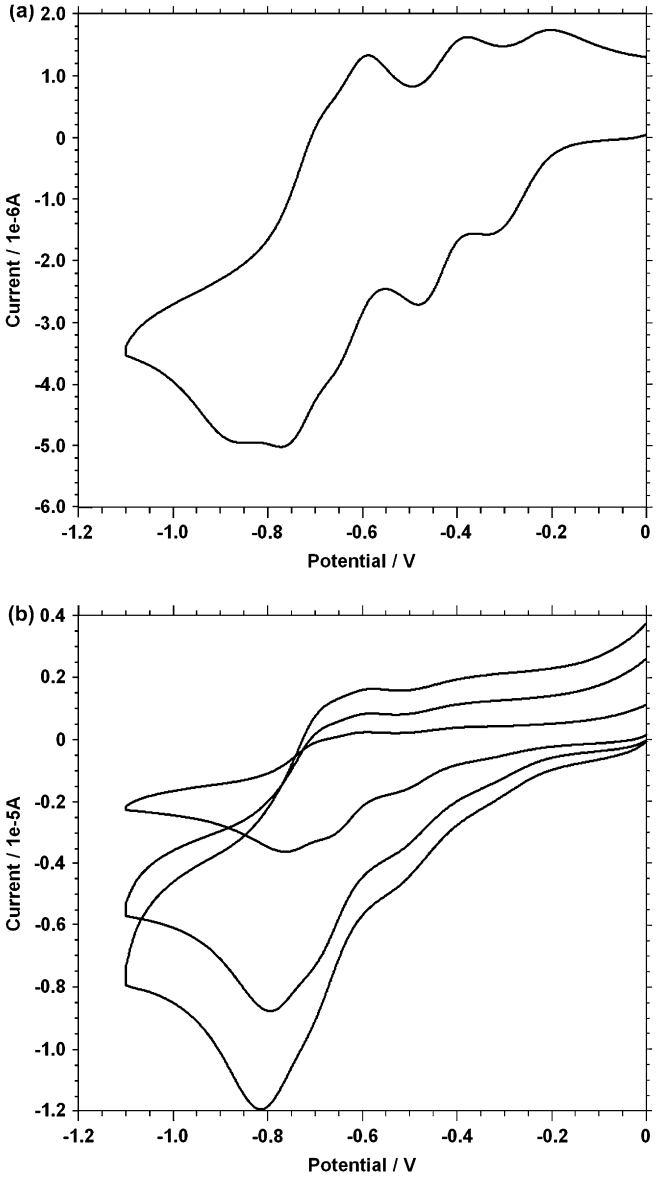


Figure 4. Cyclic voltammograms of (a) **3** recorded in DMF at scan rate 0.1 V s^{-1} and (b) polymer **16** recorded in DMF at different scan rates (scan rate=1 V s^{-1} (largest peak current), 0.5 V s^{-1}, and 0.1 V s^{-1} (smallest peak current)).

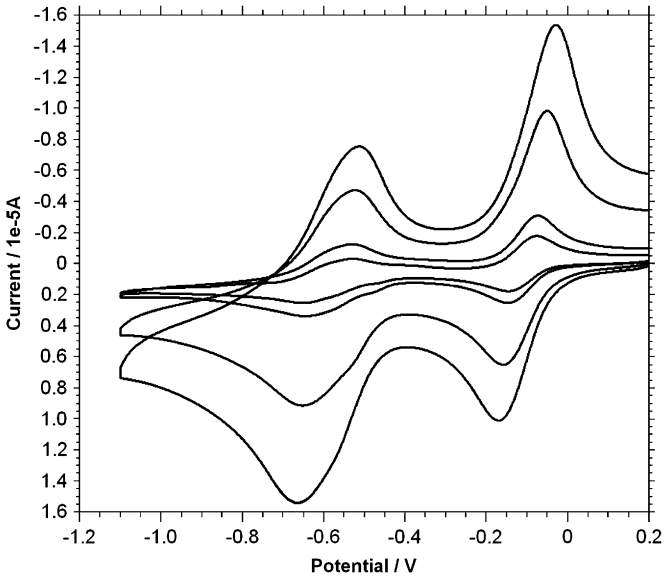


Figure 5. Cyclic voltammetry of polymer **17** (20 mg). Recorded in acetone at 298 K at different scan rates (scan rate=1 V s^{-1} (largest peak current), 0.5 V s^{-1}, 0.1 V s^{-1}, and 0.05 V s^{-1} (smallest peak current)).

functionalized. We have exploited the redox active nature of the cyclophane to further prove the structure of polymer **17** (Fig. 5). Cyclic and square wave voltammetry clearly shows the formation of two redox waves, presumably corresponding to the sequential formation of the diradical dication and fully reduced states of the cyclophane, respectively.[10] Cyclic voltammetry indicated that the reversibility of the redox waves increased as the scan rate was lowered, which is consistent with its polymeric nature.

It is well established that naphthalene derivatives based upon structure **18** are effective guests for cyclobis(paraquat-*p*-phenylene)-based cyclophanes.[11] The addition of complementary guest **18** to a solution of polymer **17** resulted in the following observations. Firstly, the solution changed from colorless to purple resulting from an absorption around 520 nm characteristic of pseudorotaxane formation (Fig. 6). Secondly, the addition of **18** to a solution of **17** in an electrochemical cell immediately resulted in the first redox wave being shifted by ~60 mV to a more negative potential, consistent with donor–acceptor interactions between **18** and the cyclophane destabilizing the diradical dication state of the latter (Fig. 7). The

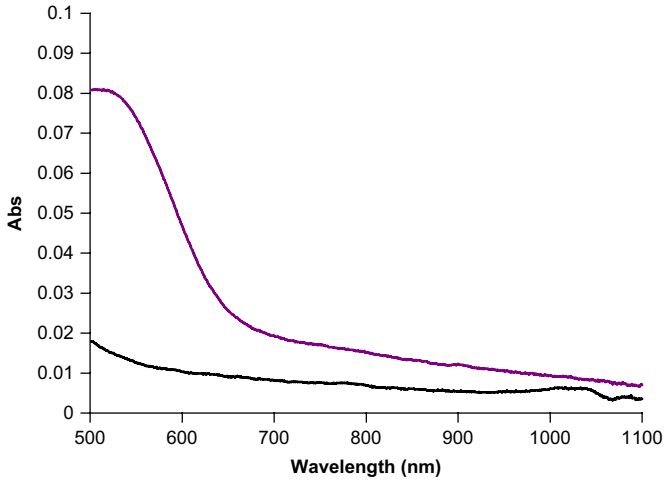


Figure 6. UV–vis spectrum of polymer **17** (10 mg in 10 mL of acetone) (—), and in the presence of **18** (~8×10^{-4} M) (—).

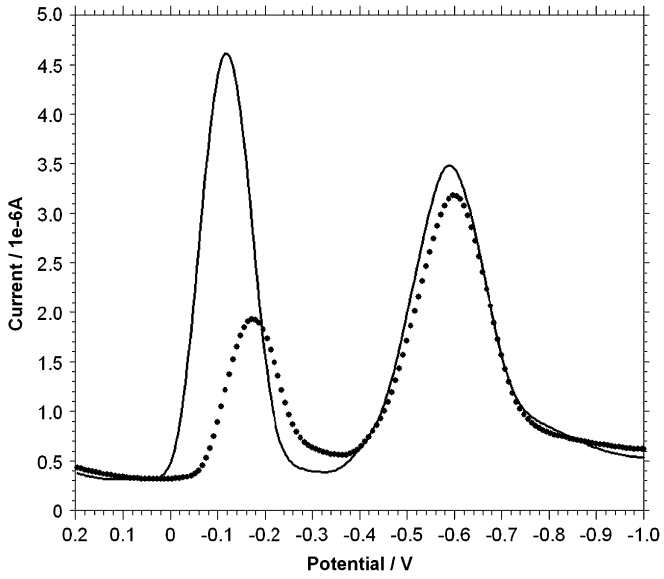


Figure 7. Square wave voltammetry of polymer **17** (13 mg in 6 mL) recorded in acetone (—) at 298 K and upon the addition of **18** ($\sim 9\times10^{-3}$ M) (···).

second redox wave is largely unaffected by this process, indicating that **18** decomplexes from the cyclophane upon the formation of the diradical dicationic state of the polymer-immobilized cyclophane.[10]

3. Conclusion

In conclusion, we have shown that we can readily synthesize alkyne-functionalized systems **1**–**3**, and that these building blocks can undergo Huisgen 'click' chemistry to conveniently attach these units onto a pre-formed azide-functionalized polystyrene derivative. We have shown that polymer **17** has the propensity to undergo electrochemically tunable interactions with compound **18**. We are currently further exploiting the synthetic versatility of 'click' chemistry as a means of attaching building blocks **1**–**3** onto other macromolecules and biomacromolecules. Our results from these investigations will be disclosed in due course.

4. Experimental section

4.1. Instrumentation

Infrared spectra were obtained on a Perkin–Elmer Lambda 25 instrument. Optically matched 1 cm cuvettes were used in the experiments. Spectra were recorded at 23 °C. The relative molecular weight of polymer **13** was determined using a Polymer Labs GPC50 (RI detector) gel permeation chromatography (GPC) equipment using tetrahydrofuran and polystyrene standards. All electrochemical experiments were performed using a CH Instruments 440 electrochemical workstation. The electrolyte solution (0.1 M) was prepared from recrystallized Bu_4NPF_6 and dry DMF or dry acetone. A three-electrode configuration was used with a platinum disc (2 mm diameter) working electrode, an Ag/AgCl reference electrode and a platinum wire as the counter electrode. The solution was purged with nitrogen prior to recording the electrochemical data, and all measurements were recorded under a nitrogen atmosphere.

4.2. Materials

Alcohol **4**,[9] component **8**,[12] macrocyclic polyether **9**,[13] bipyridium salt **6**,[10] and **7**[11] were obtained following the procedures described in the literature. Solvents were purified and dried by the literature methods. The stabilizers present in styrene and chloromethylstyrene were removed by elution over a basic Al_2O_3.

4.3. Synthesis of 5

A solution of the alcohol **4** (1 g, 3.40 mmol), 4-pentynoic acid (0.33 g, 3.40 mmol), 1,3-dicyclohexylcarbodiimide (0.70 g, 3.40 mmol), and 4-dimethylaminopyridine (catalytic amount) in CH_2Cl_2 (40 mL) was stirred under N_2 for 6 h at room temperature. The resulting suspension was filtered, and the filtrate was evaporated and subjected to column chromatography (SiO_2: petroleum ether/EtAc, 2:18) to furnish **5** as a white solid. Yield: 68%. Mp=68–69 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ=7.43 (s, 1H), 7.37 (s, 2H), 5.29 (s, 2H), 4.56 (s, 2H), 4.47 (s, 2H), 2.67–2.62 (m, 2H), 2.57–2.51 (m, 2H), 1.99 (t, J=2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ=29.9, 32.4, 33.3, 63.3, 69.3, 82.3, 100.0, 129.7, 130.7, 131.2, 134.9, 136.5, 138.7, 171.4. MS (ES): $C_{14}H_{14}Br_2O_2$ m/z=397 [M+Na]. Elemental analysis: calcd (%) for $C_{14}H_{14}Br_2O_2$: C 44.95, H 3.77; found: C 45.11, H 3.99.

4.4. Synthesis of 1

A solution of **6** (0.76 g, 1.1 mmol), **5** (0.4 g, 1.1 mmol), and **7** (1.17 g, 3.2 mmol) in dry DMF (30 mL) was stirred under N_2 at room temperature for 10 days. The solvent was removed under vacuum and the residue was subjected to a liquid–liquid extraction ($CHCl_3/H_2O$). The aqueous layer was concentrated and the residue was purified using column chromatography (SiO_2: MeOH/NH_4Cl (2 M)/$MeNO_2$, 4:4:2). The fractions containing the product were combined and concentrated under vacuum. The residue was dissolved in hot water and an aqueous NH_4PF_6 solution was added. The precipitate was collected by filtration, washed with water and Et_2O, and finally dried under vacuum, yielding a white solid. Yield: 24%. Mp>300 °C; ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ=9.47 (d, J=6.6 Hz, 4H), 9.40 (d, J=6.9 Hz, 2H), 9.28 (d, J=6.6 Hz, 2H), 8.68–8.57 (m, 8H), 7.75–7.72 (m, 5H), 7.55–7.45 (m, 2H), 5.99 (s, 2H), 5.86 (s, 2H), 5.83 (s, 2H), 5.82 (s, 2H), 5.34 (s, 2H), 2.42 (t, J=6.6 Hz, 2H), 2.26 (t, J=2.4 Hz, 1H), 2.22–2.16 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ=13.4, 32.5, 62.8, 63.2, 70.9, 82.2, 123.3, 126.6, 127.0, 129.1, 129.8, 131.2, 134.6, 135.6, 136.3, 136.5, 144.9, 145.1, 145.6, 147.9, 148.2, 148.3, 170.9. Elemental analysis: calcd (%) for $C_{42}H_{38}F_{24}N_4O_2P_4$: C 41.66, H 3.16, N 4.63; found: C 41.89, H 3.22, N 4.85.

4.5. Synthesis of 2

A solution of component **8** (2.36 g, 3.2 mmol), **5** (0.40 g, 1.1 mmol), and **6** (0.76 g, 1.1 mmol) in dry DMF (30 mL) was stirred under N_2 at room temperature for 10 days. The solvent was removed under vacuum and the residue was purified using column chromatography (SiO_2: MeOH/NH_4Cl(2 M)/$MeNO_2$, 4:4:2). The fractions containing the product were combined together and concentrated under reduced pressure. The residue was dissolved in hot water and an aqueous NH_4PF_6 solution was added. The precipitate was collected by filtration, washed with water and Et_2O, and finally dried under vacuum, yielding **2** as a purple solid. Yield: 42%. Mp>300 °C; ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ=9.08 (br s, 4H), 8.80–8.51 (br m, 4H), 8.24–7.92 (br s, 7H), 7.51–7.16 (br m, 8H), 6.31 (br s, 2H), 6.09–5.40 (br m, 12H), 4.49–4.14 (br m, 8H), 4.13–4.02 (br m, 4H), 4.01–3.93 (br m, 4H), 3.88 (t, J=5.3 Hz, 4H), 3.71 (t, J=5.3 Hz, 4H), 2.93–2.76 (br m, 2H), 2.75–2.61(br m, 2H), 2.51 (br s, 2H), 2.41–2.33(br m, 1H), 1.05–0.94 (m, 42H); ^{13}C NMR (CD_3CN, 100 MHz, 298 K): δ=12.8, 15.0, 18.4, 34.2, 62.9, 63.7, 65.9, 66.1, 69.5, 70.7, 71.9, 72.3, 73.7, 83.9, 105.4, 109.4, 125.5, 125.8, 127.3, 128.7, 129.2, 132.4, 133.4, 134.3, 137.6, 137.9, 145.3, 146.2, 146.8, 152.2,

172.4 HRMS (ESI): *m*/*z* calcd $C_{82}H_{110}F_{18}N_4O_{10}P_3Si_2$ [M−PF_6]: 1802.8351; found: 1802.8360.

4.6. Synthesis of 3

A solution of the macrocyclic polyether **9** (0.26 g, 0.48 mmol), **6** (0.14 g, 0.19 mmol), and **5** (0.07 g, 0.19 mmol) in dry DMF (15 mL) was stirred at room temperature for 10 days. The solvent was removed under reduced pressure and chloroform was added (40 mL). The precipitate was isolated by filtration and was purified using column chromatography (SiO_2: MeOH/NH_4Cl (2 M)/$MeNO_2$, 4:4:2). The fractions containing the product were combined together and concentrated under reduced pressure. The residue was dissolved in hot water and an aqueous NH_4PF_6 solution was added. The precipitate was collected by filtration, washed with water and Et_2O, and finally dried under vacuum, yielding **3** as a purple solid. Yield: 63%. Mp>300 °C; ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ=8.95–8.70 (br m, 4H), 8.43–8.17 (br s, 4H), 8.14–8.02 (br m, 1H), 8.01–7.92 (br s, 3H), 7.87–7.78 (br m, 3H), 7.12–6.98 (m, 5H), 6.84 (br s, 5H), 6.31–6.23 (m, 2H), 6.04–5.92 (m, 2H), 5.86–5.68 (m, 5H), 5.62–5.46 (m, 6H), 5.36 (d, *J*=17.6 Hz, 1H), 4.23–3.58 (m, 34H), 2.79–2.70 (br m, 2H), 2.65–2.56 (br m, 2H), 2.41 (d, *J*=11.6 Hz, 1H), 2.31 (br s, 1H), 2.20 (d, *J*=11.6 Hz, 1H); ^{13}C NMR (CD_3CN, 100 MHz, 298 K): δ=15.0, 34.2, 62.7 63.9, 65.8, 66.1, 68.8, 69.1, 70.7, 71.0, 71.1, 71.8, 72.0, 72.2, 72.4, 74.4, 104.8, 105.0, 106.6, 106.7, 109.3, 114.9, 124.5, 124.9, 125.3, 126.2, 126.6, 126.9, 128.6, 129.2, 132.0, 132.1, 132.5, 133.4, 137.7, 144.8, 145.3, 152.1, 154.4, 154.5, 172.4. HRMS (ESI): *m*/*z* calcd $C_{78}H_{82}F_{18}N_4O_{12}P_3$ [M−PF_6]: 1702.3978; found: 1702.3985.

4.7. Synthesis of polymer 13

AIBN (2 g, 12 mmol) was added to a solution of styrene (25.0 g, 240 mmol) and *p*-(chloromethyl)styrene (1.9 g, 12 mmol) in chlorobenzene (100 mL). The reaction mixture was stirred at 78 °C for 20 h. The reaction mixture was then cooled to room temperature and then added drop-wise to vigorously stirred methanol (700 mL). The precipitate was filtered and washed with copious amounts of methanol. The product was dried under high vacuum to afford **13** as a white solid. Yield: 64%; M_n=3578, M_w=6270 g mol^{-1}, PD=1.75.

4.8. Synthesis of polymer 14

To a solution of **13** (5 g) in DMSO (15 mL) was added NaN_3 (1.35 g, 20 mmol). The reaction was stirred at 60 °C for 3 days. The reaction mixture was cooled to room temperature and then added drop-wise to vigorously stirred water (600 mL). The precipitate was then filtered and washed with copious amounts of water and finally methanol. The polymer was dried under high vacuum to yield **14** as a white powder (4.2 g).

4.9. Synthesis of polymer 15

To a stirred solution of polymer **14** (0.1 g), **2** (0.05 g, 0.03 mmol) in DMF (20 mL) at 20 °C were added $CuSO_4\cdot5H_2O$ (0.05 g, 0.2 mmol) dissolved in DMF (1 mL) and ascorbic acid (0.07 g, 0.4 mmol) dissolved in DMF (1 mL). The solution was stirred for 48 h in the dark, and the solvent was carefully removed under high vacuum. THF (100 mL) was added and the mixture was filtered to remove unreacted starting materials. The filtrate was concentrated under reduced pressure and precipitated into a vigorously stirred solution of methanol (200 mL). The solid was collected by filtration and dried under high vacuum to yield **15** (0.09 g) as a pink powder.

4.10. Synthesis of polymer 16

To a stirred solution of polymer **14** (0.1 g), **3** (0.03 mmol) in DMF (20 mL) at 20 °C were added $CuSO_4\cdot5H_2O$ (0.05 g, 0.2 mmol) dissolved in DMF (1 mL) and ascorbic acid (0.07 g, 0.4 mmol) dissolved in DMF (1 mL). The solution was stirred for 48 h in the dark, and the solvent was carefully removed under high vacuum. THF (100 mL) was added and the mixture was filtered to remove unreacted starting materials. The filtrate was concentrated under reduced pressure and precipitated into a vigorously stirred solution of methanol (200 mL). The solid was collected by filtration and dried under high vacuum to yield **16** (0.9 g) as a pink powder.

4.11. Synthesis of polymer 17

To a stirred solution of **1** (0.05 g, 0.04 mmol) in DMF (10 mL) at 20 °C was added polymer **14** (0.1 g). Then, CuI (0.8 mg, 0.004 mmol, 10 mol %) was added. The solution was stirred for 48 h in the dark, and the solvent was carefully removed under high vacuum. THF (100 mL) was added and the mixture was filtered to remove unreacted starting materials. The filtrate was concentrated under reduced pressure and precipitated into a vigorously stirred solution of methanol (200 mL). The solid was collected by filtration and dried under high vacuum to yield **17** (0.9 g) as a white powder.

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References and notes

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