

Chapter 12

Mechanically Interlocked Structures by the Slippage Approach

12.1. Introduction

In chapter 11, we discussed the self-organization of a heteroditopic molecule containing two complementary units, namely bis-*m*-phenylene-32-crown-10 (BMP32C10) and dipyridinium based paraquat, to spontaneously construct linear arrays in solution.¹ Similarly, Stoddart and his coworkers generated linear arrays from a series of heteroditopic molecules.² ¹H NMR spectroscopy, was an important tool for characterizing the self-organized supramolecular architectures. However, no large aggregates were observed by the mass spectra of the solid state samples (FABMS and MALDI-TOF) of the linear arrays. Presumably, the heteroditopic ionic molecules held together in linear arrays by noncovalent interactions (electrostatic, π - π stacking, and hydrogen bonding) either were not volatile or dissociated during the ionization. This observation led us to explore the possibility of generating mechanically interlocked linear arrays, which should ultimately be characterized by the standard techniques available in polymer chemistry. These novel polymeric structures may possess interesting properties because of the mechanically “locked-in” features of these materials.

Conceptually, there are two synthetic routes, *i.e.*, blocking and slipping, to achieve such mechanically “locked-in” structures as illustrated in Figure 12.1. In the blocking approach,^{3,4} a heteroditopic molecule is first self-organized to high aggregates and the reactive ends of the linear units are coupled with blocking units to generate a mechanically interlocked structure, which prevents the slip-off process of the trapped crown ether unit. Since the blocking approach has been problematic in the past in our laboratories, the slippage approach was pursued. In the slippage approach,⁵⁻⁸ a preformed heteroditopic molecule with blocking unit of proper size already attached undergoes the slip-on process under appropriate conditions to generate mechanically interlocked polymeric materials. In this chapter, we describe the synthesis of a

heteroditopic molecule capable of creating mechanically “locked-in” structure *via* the slippage approach.

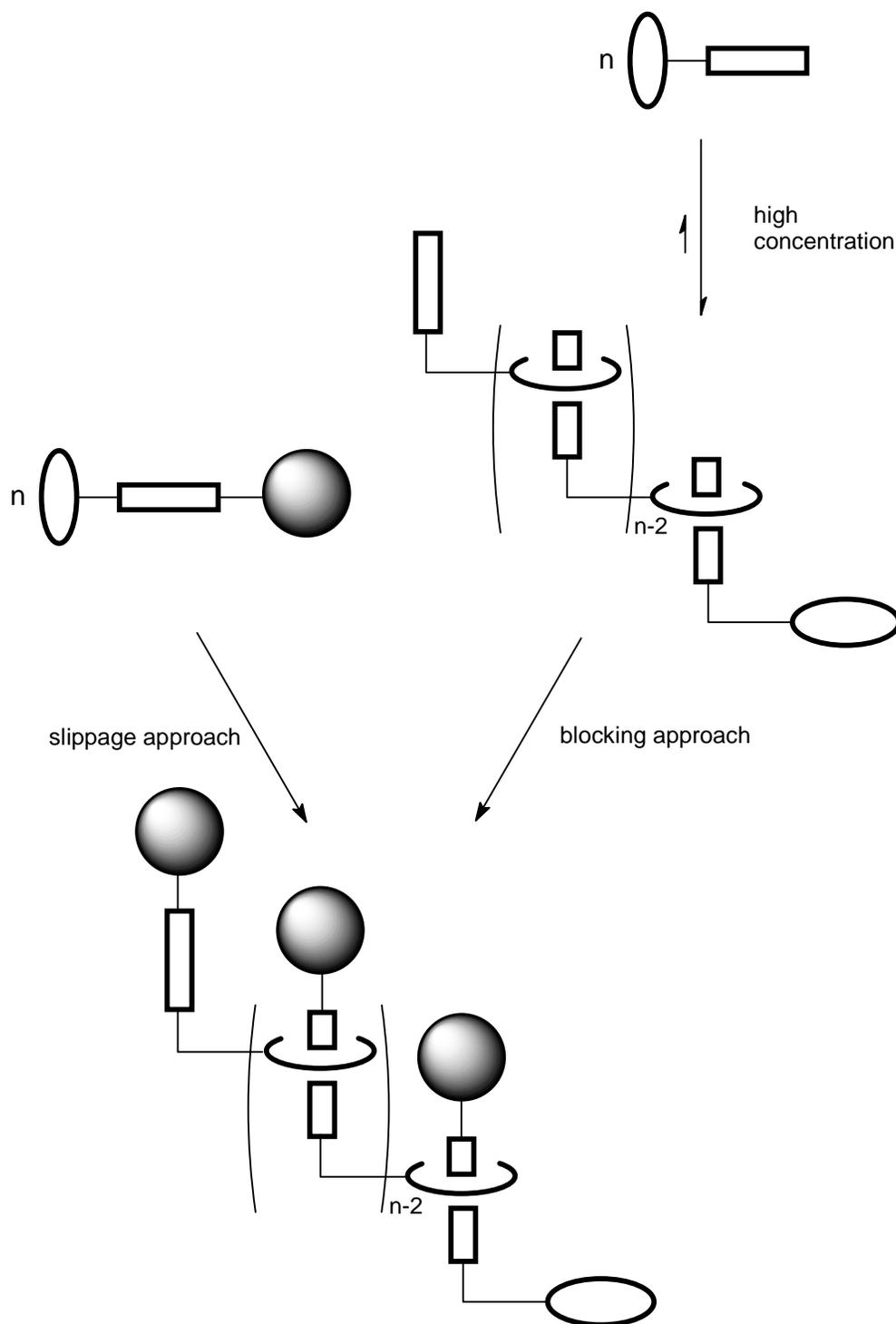


Figure 12.1. Cartoon representations of the blocking and slippage approach to mechanically interlocked polymeric materials.

12.2. Results and Discussion

12.2.1. Inspiration

In Stoddart's work on the slippage approach to create kinetically stable rotaxanes, the crown ether, bis-*p*-phenylene-34-crown-10 (BPP34C10), and paraquat units with blocking groups attached on the both ends are preformed separately and then mixed in solution.⁵⁻⁸ The paraquat unit with the tris(-*p-t*-butylphenyl)(hydroxyphenyl)methane based blocking groups yielded virtually no corresponding rotaxanes when mixed with 4 equimolar of BPP34C10 in acetonitrile at 60°C after 10 days. Presumably, the blocking groups are too large to allow the slip-on process of the crown ether. However, the passage of the crown ether becomes possible when the size of the blocking units are adjusted slightly. The size control of the blocking groups was achieved by substituting one of the three *t*-butyl groups with a hydrogen. The paraquat unit sandwiched by the bis(-*p-t*-butylphenyl)(hydroxyphenyl)phenylmethane-based blocking groups captured BPP34C10 to form the corresponding rotaxane in 54% yield when mixed with an excess of the crown ether (4 equiv.) under the identical conditions as a result of hydrogen bonding, π - π stacking and electrostatic interactions. Once BPP34C10 manages to slip-on at the elevated temperature, it is trapped to form the thermodynamically stable superstructure due to the non-covalent interactions at lower temperatures. In other words, the energy required for the slip-off process is greater than the slip-on process because of the thermodynamic driving force of complexation. And also in this system without thermal energy the energy barriers for both slip-on and slip-off processes cannot be overcome.

These observations inspired us to construct mechanically interlocked linear arrays employing the slipping approach. A heteroditopic molecule, sandwiching a dipyrindinium site with BMP32C10 and the bis(-*p-t*-butylphenyl)(hydroxyphenyl)phenylmethane based blocking group, was prepared as depicted in Figure 12.2. In this case, the BMP32C10 moiety not only hosts the paraquat moiety but also serves as a blocking group at the other end of the molecule, providing a thermodynamical trap in the middle of the molecule. An acetonitrile solution of the heteroditopic compound was stirred at 60°C and the progress of the slippage process was periodically monitored by the use of ¹H NMR spectroscopy.

12.2.2. Synthesis

A standard Grignard reaction was employed to synthesize **1** in 83% yield (Figure 12.2). The Grignard reagent, prepared *in situ* by the reaction of *p*-bromo-*t*-butylbenzene and magnesium in dry THF, was treated with ethyl benzoate in anhydrous THF. The formation of **1** was confirmed by the ^1H NMR spectrum of **1**. **1** was then reacted with an excess of phenol in the presence of a catalytic amount of concentrated hydrochloric acid to afford **2** as a white solid in 65% yield. The reddish color of the reaction mixture after the addition of a few drops of the acid indicated the carbocation formation. The ^1H NMR spectrum of the aromatic region of **2** (Figure 12.3) reveals four sets of doublets corresponding to H_b , H_c , H_d , and H_e at 7.30, 7.08, 7.05 and 6.69 ppm, respectively, along with one multiplet signal for H_a at 7.16-7.21 ppm. H_b shows a coupling interaction with H_c ($J = 8.8$ Hz) and H_d and H_e are coupling to cause spin-spin splitting ($J = 8.8$ Hz).

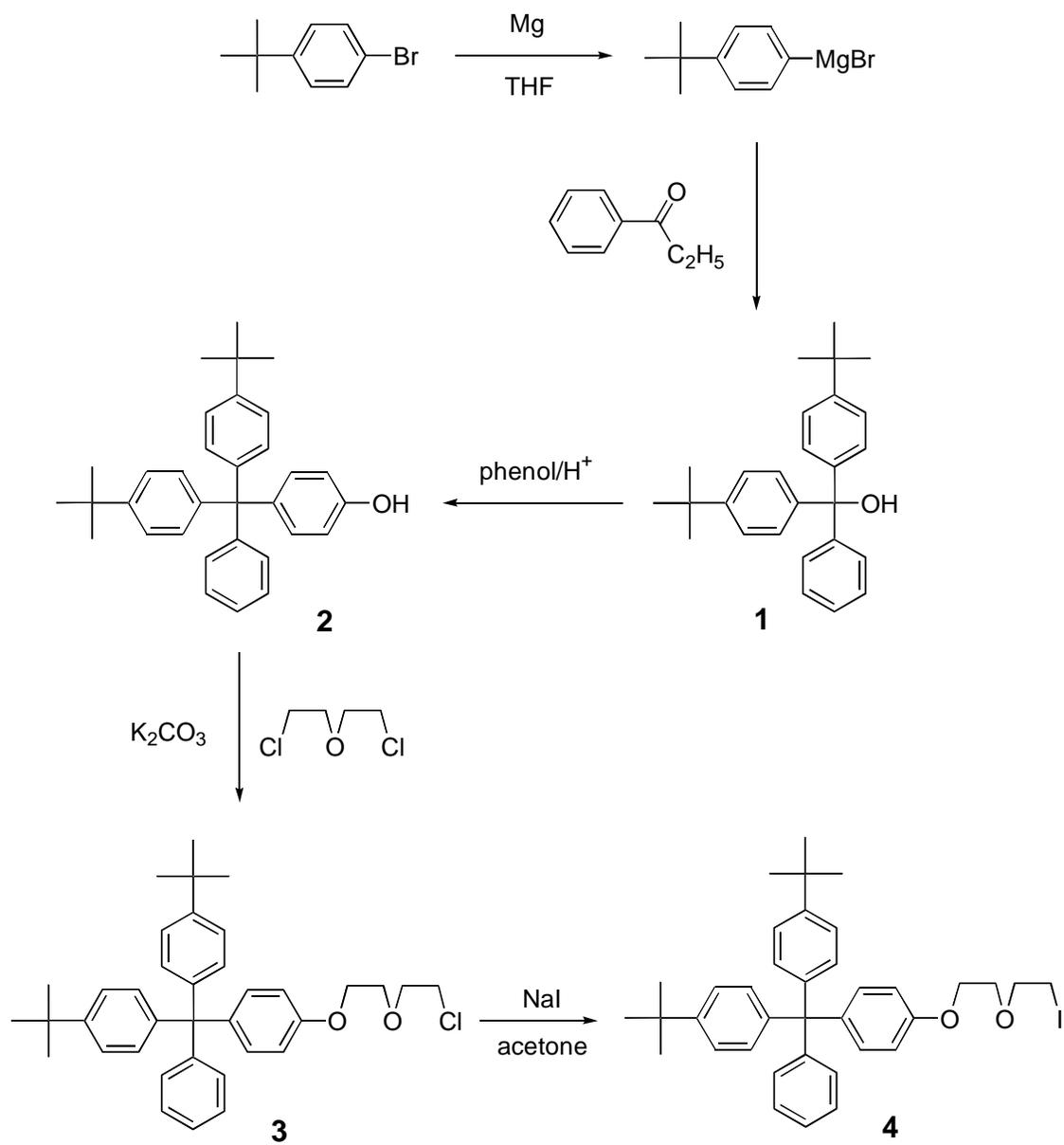


Figure 12.2. Synthesis of the blocking group.

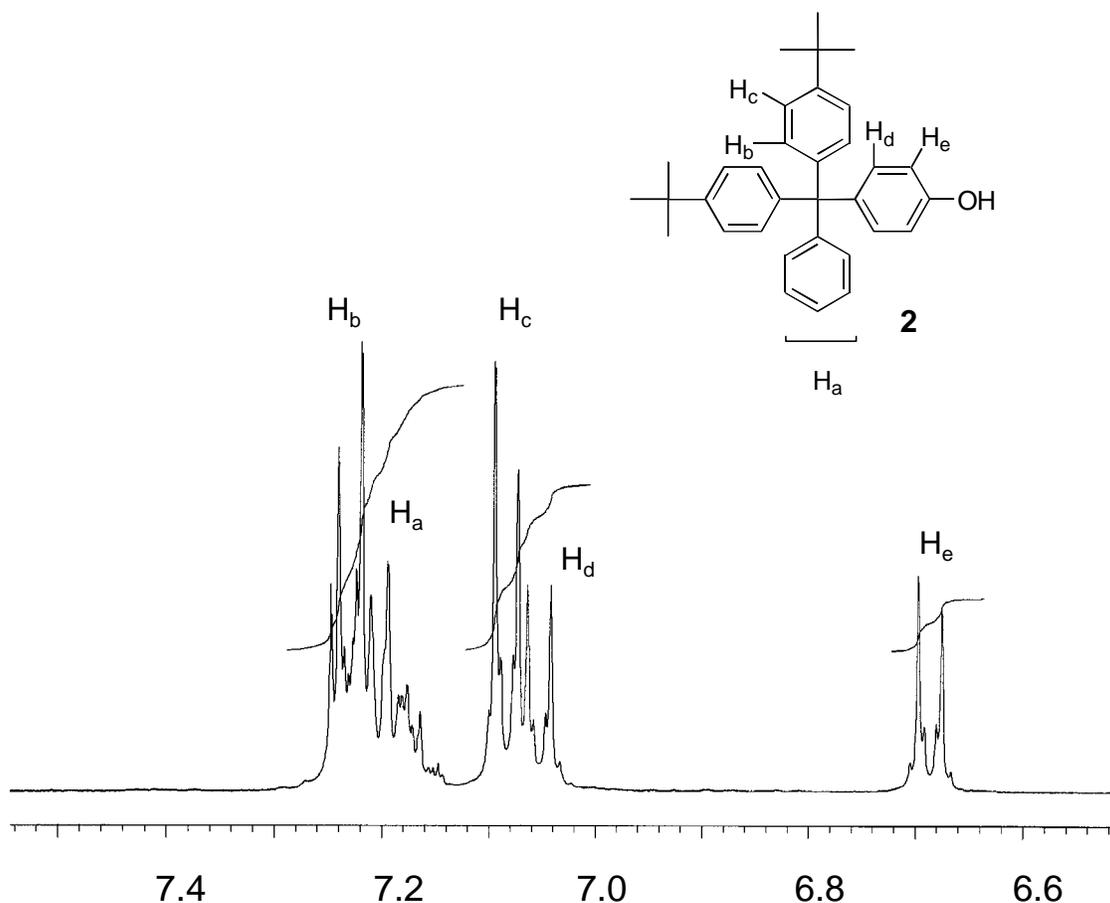


Figure 12.3. The ^1H NMR spectrum of **2** (400 MHz, chloroform-*d*, 22°C).

Figure 12.2 also shows the next two steps, involving the introduction of the aliphatic ethyleneoxy units to the phenolic blocking group **2** and the exchange of the leaving groups from chloride to iodide. The ethyleneoxy units were incorporated to serve as a spacer between the blocking group and the paraquat unit. An excess of 2-chloroethyl ether was used to drive the reaction equilibrium forward to favor the formation of **3**. Since **3** shows a low reactivity toward 4,4'-dipyridyl, the chloride was replaced with iodide in the subsequent step to afford **4** in order to enhance the leaving ability of the halide. **4** was contaminated mainly with the starting material based on the TLC analysis which displayed two spots with similar R_f values. The ^1H NMR spectrum of the isolated product revealed **4** is contaminated with **3** (approximately 5 mol %). Any combination of the mobile phase and stationary phase (silica gel and neutral alumina) in column

chromatography did not allow the separation of the two molecules. Thus, we decided to proceed without further purification of this product.

As outlined in Figure 12.4, in the following step **4** was reacted with 5-fold excess of 4,4'-dipyridyl. The crude product was subject to a short column of silica gel first using ethyl acetate to elute unreacted 4,4'-dipyridyl and then using methanol to elute the desired product. The ion exchange reaction on this product afforded **5** as a brownish solid, which was readily soluble in the most common organic solvents including ethereal solvents. The first indication of the formation of **5** came from the ^1H NMR spectrum, which revealed a significant downfield chemical signal shift for the methylene protons adjacent to the monoquat unit due to the cationic site. In addition, four sets of doublets in the region of 7.98-9.15 ppm corresponding to the aromatic protons of the monoquat unit are in good agreement with the structure of **5**. **5** was reacted with 5-bromomethyl-bis(1,3-phenylene)-32-crown-10 in boiling acetonitrile over 5 days to afford **6** as a purple solid in 83% yield. As for **5**, **6** demonstrated excellent solubility in common organic solvents. The first evidence for the formation of **6** came from ^1H NMR spectroscopy. The spectrum was recorded in $\text{DMSO-}d_6$ in order to obtain the chemical signals of uncomplexed **6**. The ^1H NMR spectrum of **6** (Figure 12.5) revealed the signal for the benzylic proton was shifted downfield due to the adjacent cationic site. The chemical shifts of the signals for the protons on the paraquat unit are consistent with the dication formation. The signals furthest downfield at 9.26 and 9.44 ppm correspond to H_j and H_m , respectively. The signal for H_m jumped from 7.98 to 9.44 ppm due to the newly formed cationic site.

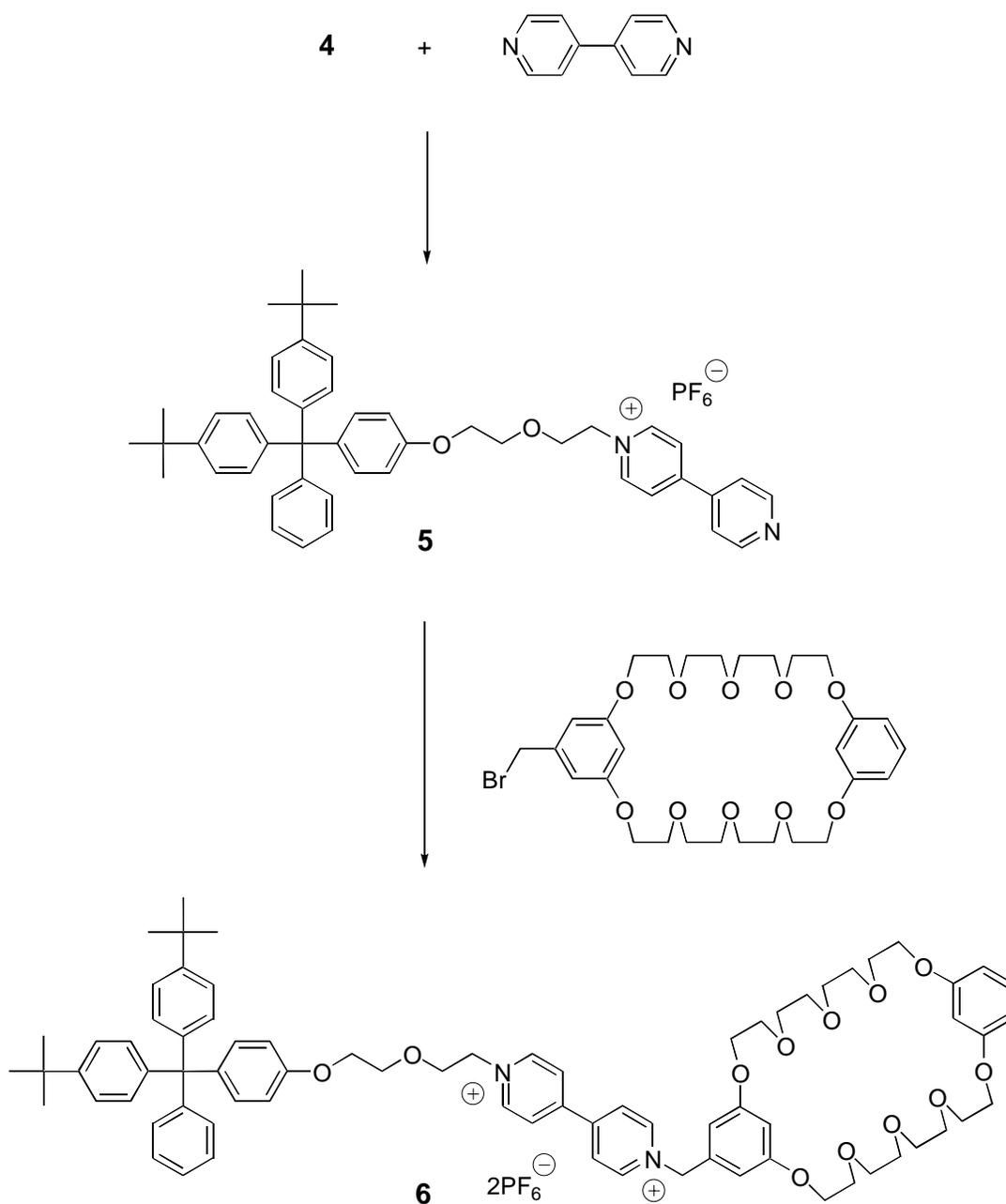


Figure 12.4. Synthesis of heteroditopic molecule **6**.

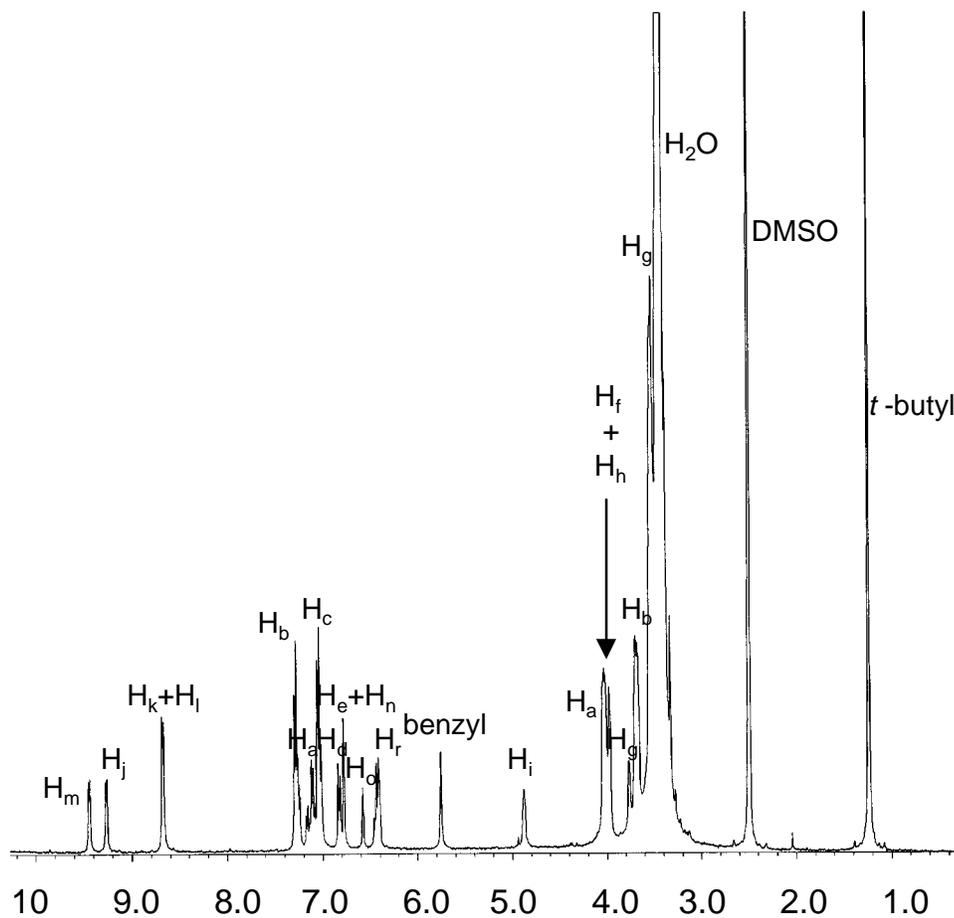
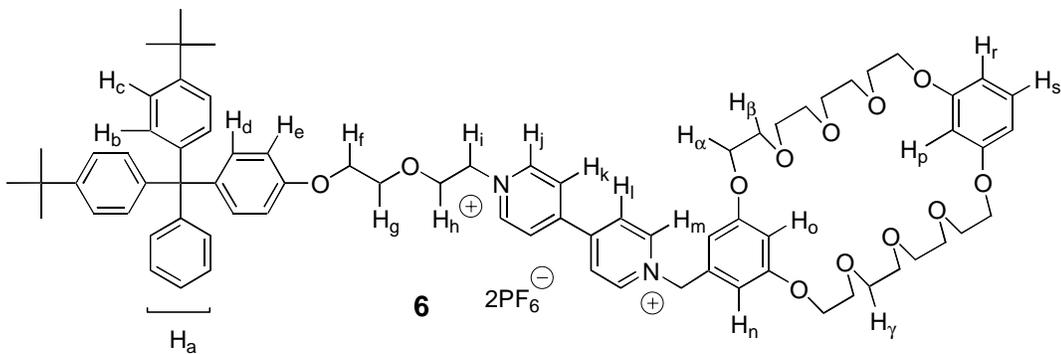


Figure 12.5. The ^1H NMR spectrum of **6** (400 MHz, $\text{DMSO-}d_6$, 22°C).

12.2.3. Slippage in solution

As illustrated in Figure 12.6, *N*-benzyl-*N'*-methyl-4,4'-dipyridinium hexafluorophosphate (**7**) and BMP32C10 were chosen as model systems to emulate the binding geometry of **3** by forming the pseudorotaxane **8**. The ^1H NMR spectra of

equimolar solutions of BMP32C10 and **7** were directly compared to those of **6**. The signals of our interest were the inner protons on the paraquat system (H_b and H_c of **7** and H_k and H_l of **6**), the benzylic protons and the protons adjacent to the cationic site (methyl protons of the model paraquat and H_i of **6**). Figure 12.7 shows the stacked ^1H NMR spectra of a) **7** (2.0×10^{-2} M in acetonitrile- d_3) and b) equimolar solutions of BMP32C10 and **6** (2.0×10^{-2} M each in acetonitrile- d_3). In this model system the most noticeable chemical shifts are observed for the signals for H_b and H_c ($\Delta\delta=0.33$ and 0.34 ppm, respectively). In addition, the signals for the benzylic and $-\text{CH}_3$ protons slightly shift downfield by 0.01 and 0.02 ppm, respectively. Therefore, once the crown ether moiety of the heteroditopic molecule **6** slips-on and becomes trapped on the paraquat moiety to maintain the threaded geometry, similar chemical shifts of the signals for the above mentioned protons are expected.

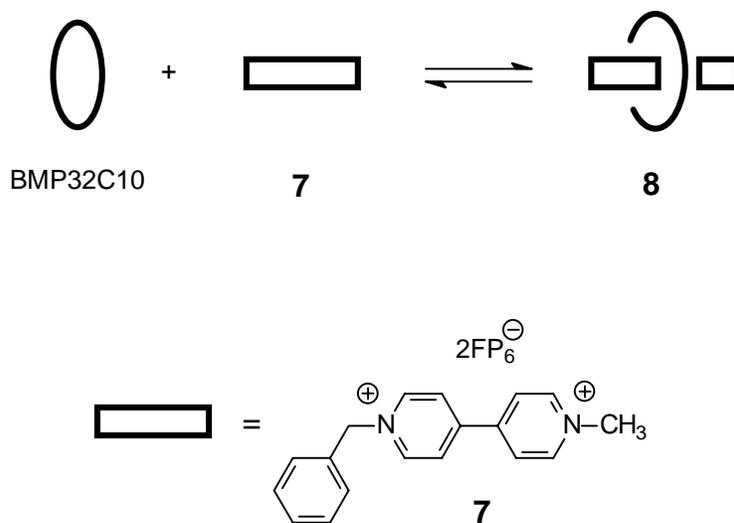


Figure 12.6. Illustration of the model system between **7** and BMP32C10 to form **8**.

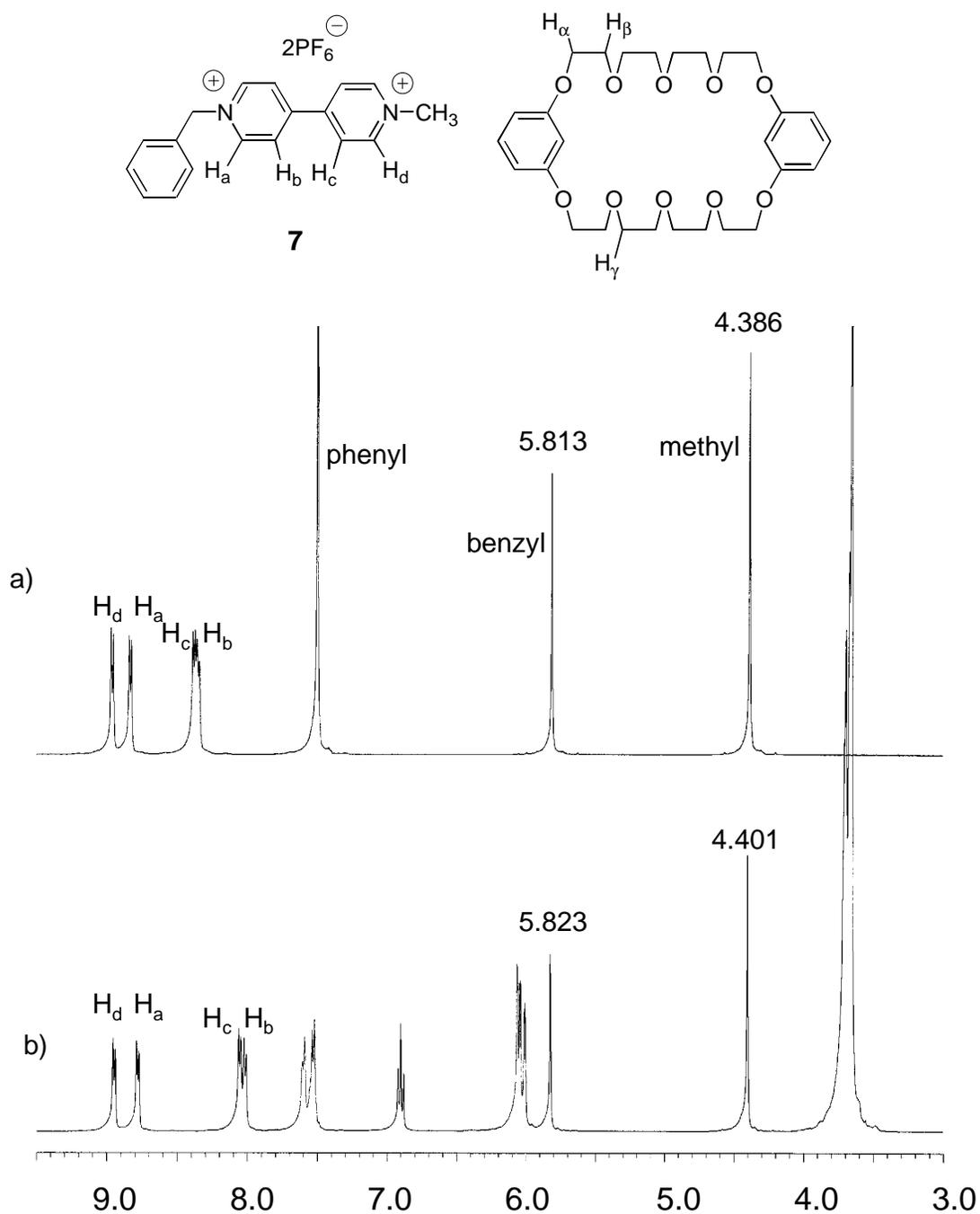


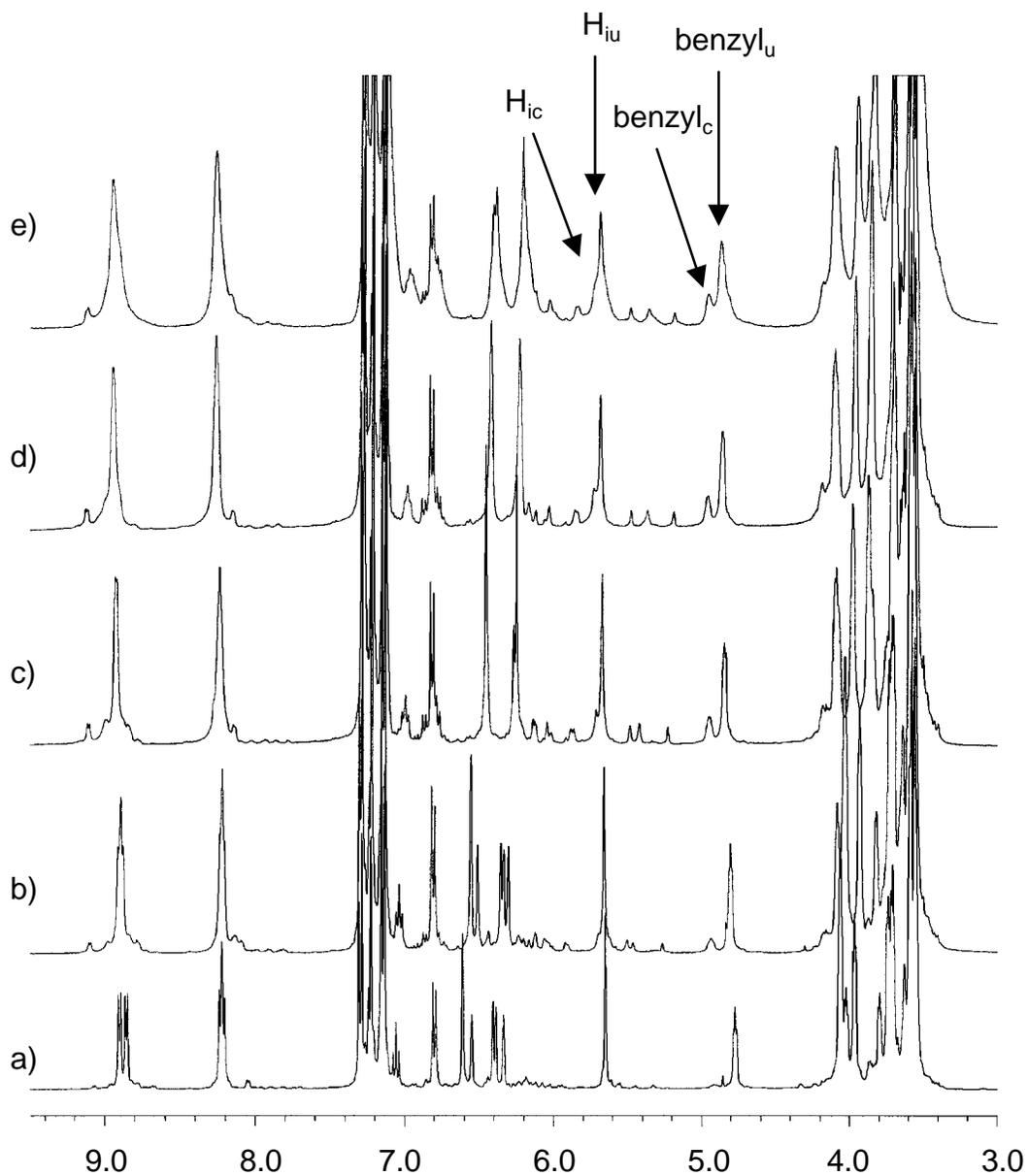
Figure 12.7. The stacked ^1H NMR of a) **7** (2.0×10^{-2} M) and b) equimolar solutions of BMP32C10 and **7** (2.0×10^{-2} M each) (400 MHz, acetonitrile- d_3 , 22°C).

A 3.2×10^{-2} M solution of **6** in acetonitrile- d_3 was warmed at 60°C and stirred for 37 days in a 5 mm NMR tube to investigate the slip-on process in solution. The progress was monitored regularly by ^1H NMR spectroscopy. Figure 12.8 shows the stacked ^1H NMR spectra of **6** as a function of time. The signals corresponding to the protons of our

interest, the benzyl and H_i proton, are assigned on the spectra. A new signal slightly downfield from the signal for uncomplexed benzylic protons corresponds to complexed benzylic protons. A new signal for complexed H_i also appears to be overlapped with the left shoulder of the signal for uncomplexed H_i. The intensities of the both peaks increase as a function of time. The signals for complexed and uncomplexed benzylic protons were integrated in each spectrum using a deconvolution technique to gain more information on the slippage approach to mechanically interlocked structures. The results are summarized in Table 12.1. After a day of mixing 15% of the crown ether moieties actually have slipped-on to form the thermodynamically stabilized mechanically “locked-in” structures. After 17 days the fraction of the crown ether moiety slipped-on was increased by more than 2-fold. A steady increase of the fraction slipped-on was observed up to 17 days but eventually the slippage process slowed down after the first 1/3 of the crown ether moiety has slipped-on. 35% for the fraction of crown ether complexed corresponds to the formation of some dimer of **6** (n=1.5). The association constant (K_a) of the slippage process was determined to be 17 M⁻¹ in acetonitrile-*d*₃ at 60°C. The TLC analysis on the reaction mixture after 37 days gave a streak using methanol as the eluent.

Table 12.1. Fraction of crown ether moiety complexed and n as a function time

Time (days)	fraction complexed (%)	n
1	15	1.2
3	17	1.2
5	19	1.2
12	24	1.3
17	34	1.5
31	35	1.5
37	35	1.5



c=complexed, u=uncomplexed

Figure 12.8. The stacked ¹H NMR spectra of **6** (3.2×10^{-2} M) recorded after a) 1 day, b) 5 days, c) 17 days, d) 31 days, and e) 37 days (400 MHz, acetonitrile-*d*₃, 22°C).

12.2.4. Slippage in the melt

The feasibility of the slippage approach in the melt to construct mechanically interlocked structures was also investigated with **6**. To test this experimentally, small samples of **6** were held at 110, 120, 130, and 140°C for 24 hours. It should be noted that the melting point of **6** is at 125-128°C. After the samples were cooled to room

temperature, they were analyzed with GPC (solvent: CHCl₃, PS standards). The GPC results showed no evidence for the formation of higher aggregates. We attribute these results to the fact that the noncovalent forces for the slippage approach are not effective at such high temperatures, *i.e.*, K_a is too low.

12.3. Conclusion

We described the synthesis of a heteroditopic molecule containing BMP32C10, paraquat, and a blocking group. The slippage process of the heteroditopic molecule to form mechanically “locked-in” materials was investigated both in solution and melt. The ¹H NMR studies indicated that the slip-on process is time dependent and the dimeric species were formed. In contrast, there was no indication of high aggregate formation in melt.

12.4. Experimental

Tetrahydrofuran (THF) was distilled from Na and benzophenone. All other solvents were used as received. Melting points were taken on a Mel-Temp II apparatus and are uncorrected. The 400 MHz ¹H NMR spectra were recorded on a Varian Unity with tetramethylsilane (TMS) as an internal standard. The following abbreviations are used to denote splitting patterns: s (singlet), d (doublet), t (triplet), and m (multiplet). The IR spectra were taken on a Nicolet Impact 400 infrared spectrometer using pulverized KBr as the medium. Gel permeation chromatography (GPC) was performed with an ISCO model 2300, coupled with an ISCO UV detector, using PLgel 5 mm MIXED-D (300 x 7.5 mm) columns and chloroform as solvent and calibrated with PS standards. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Series-4 calorimeter under a nitrogen purge using indium as the calibration standard. Elemental analyses were obtained from Atlantic Microlab, Norcross, GA. Mass spectra were provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954).

Bis(*p-t*-butylphenyl)(phenyl)methanol (1). To a 500 mL three-necked round bottom flask equipped with a magnetic stirrer, a condenser, an addition funnel and a nitrogen

inlet were added magnesium (4.85 g, 195 mmol) and dry THF (150 mL). To this was added a solution of *t*-butylbromobenzene in dry THF (50 mL) through the addition funnel. The rate of the addition was adjusted to maintain a gentle reflux and the mixture was vigorously stirred for 3 h. After the reaction mixture was cooled to room temperature, a solution of ethyl benzoate (14.7 g, 97.8 mmol) in THF (50 mL) was added slowly and the mixture was reheated to reflux and stirred for 18 h. Upon completion of the reaction the reaction mixture was cooled to 0°C and neutralized with 10% HCl. The organic layer was extracted and concentrated on a rotary evaporator to give a yellow viscous liquid, which was subsequently recrystallized from a mixture of MeOH and acetone (1/1) to afford a white solid (30.2 g, 83% yield), mp 115-117°C (lit.^{7,9} mp 111-112°C). ¹H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.30 (s, 18H), 3.04 (s, 1H), 7.19 - 7.32 (m, 5H), 7.33 (d, 4H, *J* = 8.0 Hz), and 7.51 (d, 4H, *J* = 8.0 Hz).

Bis(*p*-*t*-butylphenyl)(*p*''-hydroxyphenyl)phenylmethane (2). To a 250 mL round bottom flask equipped with a magnetic stirrer and a condenser were added phenol (51.0 g, 542 mmol) and **1** and the mixture was heated to obtain homogeneity. To this were added three drops of concentrated HCl and the reaction mixture was vigorously stirred for 2 h at reflux. At the end of the reaction the mixture was diluted with toluene (200 mL) and the excess of phenol was washed away with H₂O (500 mL x 4). The organic layer was concentrated on a rotary evaporator to give a yellow viscous liquid, which was subsequently recrystallized from a mixture of MeOH and acetone to afford a white solid (7.93 g, 65% yield), mp 217-220°C (lit.^{7,9} mp 210.0-210.9°C). ¹H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.29 (s, 18H), 4.60 (s, 1H), 6.69 (d, 2H, *J* = 8.8 Hz), 7.05 (d, 4H, *J* = 8.8 Hz), 7.08 (d, 4H, *J* = 8.8 Hz), 7.16 - 7.21 (m, 5H), and 7.30 (d, 4H, *J* = 8.8 Hz).

2-[*p*-[Bis(*p*-*t*-butylphenyl)phenylmethyl]phenoxy]ethyl 2'-chloroethyl ether (3). To a 25 mL round bottom flask equipped with a magnetic stirrer, a condenser and a nitrogen inlet were added **2** (2.14 g, 4.77 mmol), K₂CO₃ (3.30 g, 5 equiv.) and DMF (10 mL) and the mixture was stirred for 1 h at 100°C. After the solution was cooled to room temperature, 2-chloroethyl ether (13.6 g, 95.4 mmol) was added at once and the reaction mixture was further stirred for 12 h at 100°C. Upon completion of the reaction the excess

of 2-chloroethyl ether was removed *via* vacuum distillation to give a brown viscous liquid, which was subsequently recrystallized from a mixture of MeOH and acetone (10v/1v) to afford a white solid (2.32 g, 86% yield), mp 113-115°C. ¹H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.30 (s, 18H), 3.65 (t, 2H, *J* = 5.6 Hz), 3.82 (t, 2H, *J* = 5.6 Hz), 3.87 (t, 2H, *J* = 5.6 Hz), 4.12 (t, 2H, *J* = 5.6 Hz), 6.79 (d, 2H, *J* = 8.8 Hz), 7.08 (d, 4H, *J* = 8.0 Hz), 7.09 (d, 2H, *J* = 8.8 Hz), 7.18 - 7.24 (m, 5H), and 7.23 (d, 4H, *J* = 8.0 Hz). LRESI: *m/z*=555 [*M*+H]⁺; HRMALDI: calcd for [*M*+Na]⁺ C₃₇H₄₃O₂ClNa 577.2849, found 577.2876.

2-[*p*-[Bis(*p*-*t*-butylphenyl)phenylmethyl]phenoxy]ethyl 2'-iodoethyl ether (4). To a 50 mL round bottom flask equipped with a magnetic stirrer, a condenser and a nitrogen inlet were added compound **3** (0.81 g, 1.5 mmol), sodium iodide (0.26 g, 1.8 mmol) and acetone (30 mL) and the reaction mixture was vigorously stirred at reflux for 3 days. Upon completion of the reaction the salts were removed with an aid of Celite and the filtrate was concentrated on a rotary evaporator. The resulting white solid was diluted with CHCl₃ and washed with H₂O (100 mL x 2) and the organic layer was concentrated to give a white solid, which was subsequently recrystallized from MeOH to afford a white solid. The ¹H NMR spectrum of this product showed two signals corresponding to the desired product (95 mol %) and the starting material **3** (5 mol %) and the TLC analysis also indicated two spots with similar R_f values in various solvent systems. Since product purification was not achieved even by column chromatography, the mixture was used in the following step without further purification. ¹H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.30 (s, 18H), 3.76 (t, 2H, *J* = 4.8 Hz), 3.85 (t, 2H, *J* = 4.8 Hz), 4.10 (t, 2H, *J* = 4.8 Hz), 4.22 (t, 2H, *J* = 4.8 Hz), 6.77 (d, 2H, *J* = 8.8 Hz), 7.08 (d, 4H, *J* = 8.0 Hz), 7.09 (d, 2H, *J* = 8.8 Hz), 7.17 - 7.24 (m, 5H), and 7.22 (d, 4H, *J* = 8.0 Hz). LRESI: *m/z*=647 [*M*+H]⁺.

***N*-[*p*-[Bis(*p*-*t*-butylphenyl)phenylmethyl]phenoxyethoxyethyl]-4-(4'-pyridyl)**

hexafluorophosphate (5). To a 25 mL round bottom flask equipped with a magnetic stirrer, a condenser and a nitrogen inlet were added compound **4** (0.37 g, 0.57 mmol), 4,4'-dipyridyl (0.45 g, 5 equiv.) and CH₃CN (5 mL) and the reaction mixture was

vigorously stirred at reflux for 2 days. Upon completion of the reaction the solvent was evaporated to give a yellow viscous liquid, which was diluted with a small amount of ethyl acetate and applied on a short column of silica gel. First, the unreacted material was removed with ethyl acetate and the product was then eluted with MeOH. The second fraction was concentrated to give a green viscous liquid, which was diluted with H₂O. To this solution was added aq. NH₄PF₆ until no further precipitation was observed. The precipitate were filtered to give a brownish gray solid (0.25 g, 52% yield), mp 157-160°C. ¹H NMR (400 MHz, DMSO-*d*₆, 22°C): δ=1.24 (s, 18H), 3.75 (t, 2H, *J* = 4.0 Hz), 3.96 (t, 2H, *J* = 4.0 Hz), 4.00 (t, 2H, *J* = 4.0 Hz), 4.83 (t, 2H, *J* = 4.0 Hz), 6.75 (d, 2H, *J* = 8.8 Hz), 6.96 (d, 2H, *J* = 8.8 Hz), 7.00 (d, 2H, *J* = 8.8 Hz), 7.06 - 7.26 (m, 5H), 7.80 (d, 4H, *J* = 8.4 Hz), 7.98 (d, 2H, *J* = 5.6 Hz), 8.57 (d, 2H, *J* = 5.6 Hz), 8.81 (d, 2H, *J* = 5.6 Hz), and 9.15 (d, 2H, *J* = 5.6 Hz). LRESI: *m/z*=675 [*M*-PF₆]⁺; HRMALDI: calcd for [*M*-PF₆]⁺ C₄₇H₅₁O₂N₂ 675.3950, found 675.3921.

***N*-[*p*-[Bis(*p*-*t*-butylphenyl)phenylmethyl]phenoxyethoxyethyl]-*N'*-[5-methylene bis(1,3-phenylene)-32-crown-10]-4,4'-bipyridyl bis(hexafluorophosphate) (6).** To a 10 mL round bottom flask equipped with a magnetic stirrer, a condenser and a nitrogen inlet were added **5** (52 mg, 0.063 mmol), 5-bromomethylene bis(1,3-phenylene)-32-crown-10 (40 mg, 0.064 mmol) and CH₃CN (3 mL) and the mixture was vigorously stirred at reflux for 5 days. Upon completion of the reaction the solvent was evaporated to give a brown solid, which was dissolved in H₂O. To this solution was added aq. NH₄PF₆ until no further precipitation was observed. The precipitate was filtered to afford a purple solid (80 mg, 83% yield), mp 125-128°C. ¹H NMR (400 MHz, DMSO-*d*₆, 22°C): δ=1.23 (s, 18H), 3.51 (m, 16H), 3.68 (m, 8H), 3.76 (t, 2H, *J* = 4.0 Hz), 3.97 (t, 4H, *J* = 4.0 Hz), 4.03 (m, 8H), 4.87 (t, 2H, *J* = 4.0 Hz), 5.75 (s, 2H), 6.42 (d, 2H, *J* = 8.4 Hz), 6.58 (s, 1H), 6.78 (s, 2H), 6.78 (s, 2H), 6.83 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 2H, *J* = 8.4 Hz), 7.04 (d, 4H, *J* = 8.0 Hz), 7.05 (m, 5H), 7.28 (d, 4H, *J* = 8.0 Hz), 8.67 (d, 4H, *J* = 6.0 Hz), 9.26 (d, 2H, *J* = 6.0 Hz), and 9.44 (d, 2H, *J* = 6.0 Hz). LRESI: *m/z*=1370 [*M*-PF₆]⁺; HRMALDI: calcd for [*M*-2PF₆]⁺ C₇₆H₉₂O₁₂N₂ 1225.6729, found 1255.6734.

12.5. References

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