Chapter 6

Stabilities of Cooperatively Formed Cyclic Pseudorotaxane Dimers

6.1. Introduction

In chapter 5 we described the preparation of supramolecular linear polymer **8b** (Figure 6.1) with up to 9.1 repeat units in which monomeric homoditopic molecules **1** and **5b** containing dibenzo-24-crown-8 (DB24C8) and dibenzylammonium hexafluorophosphate moieties (Figure 6.2), respectively, are linked non-covalently via pseudorotaxane geometries in equimolar concentrated solutions (>1.0 M in acetone-d_6/chloroform-*d*, 1/1, v/v at 22°C).[1]

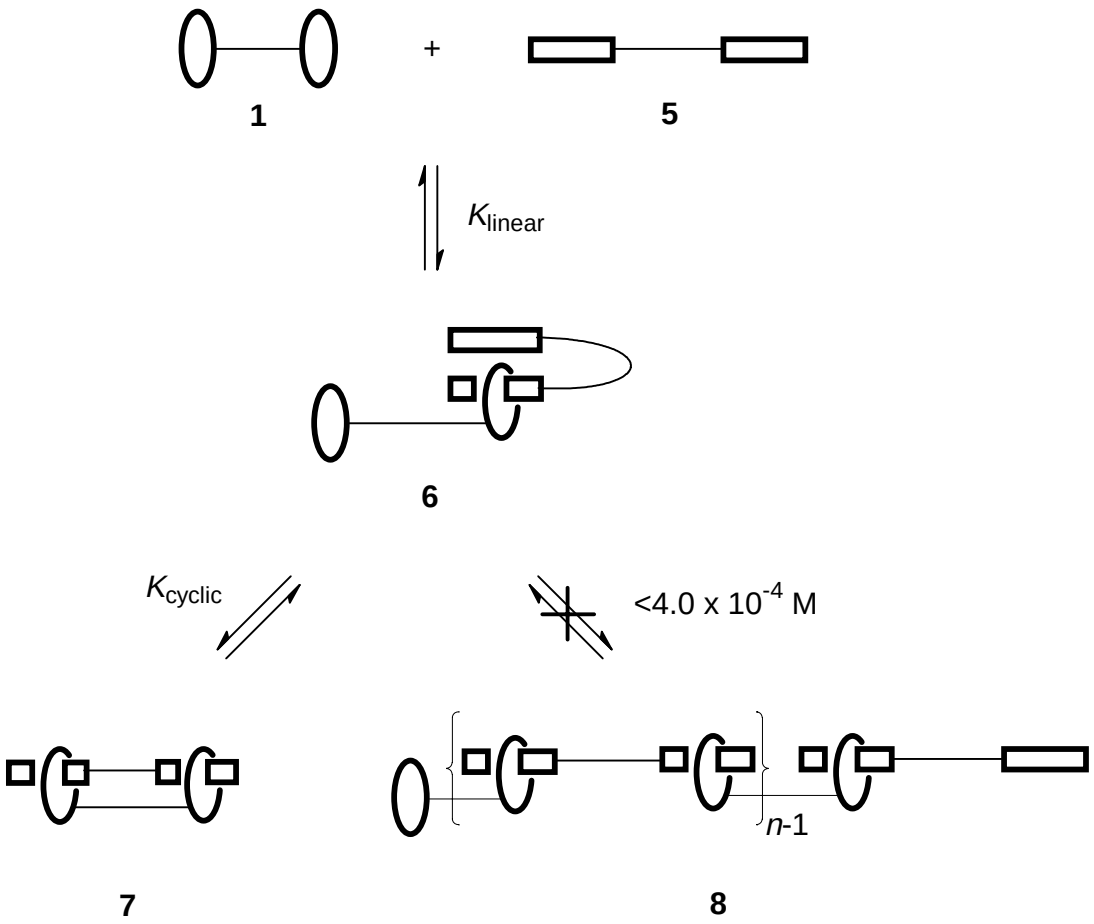

Figure 6.1. Cartoon illustrations of formation of the linear dimer complex **6** and cyclic dimer complex **7** from homoditopic molecules **1** and **5** in substantially dilute conditions.

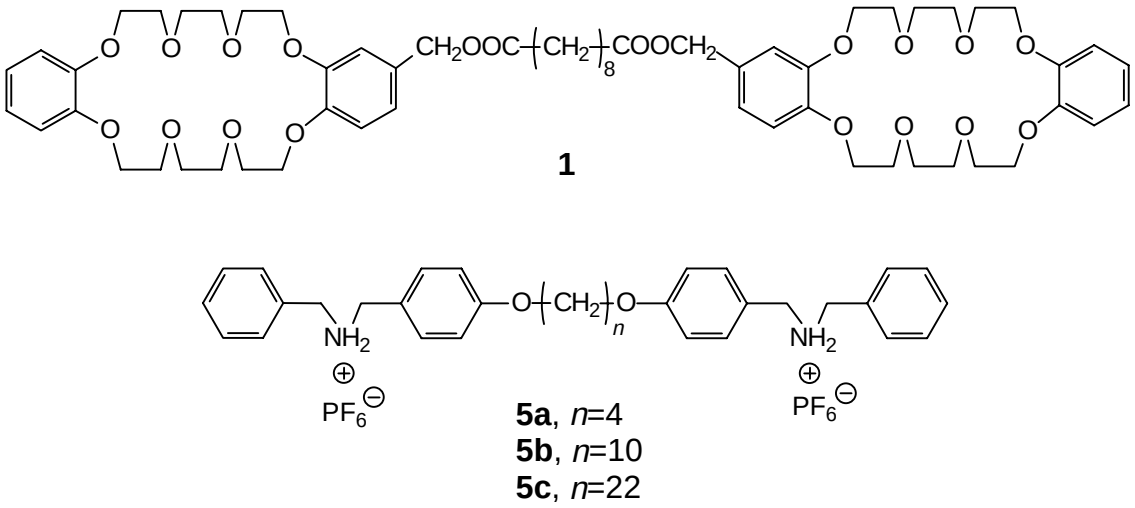

Figure 6.2. Complementary homoditopic molecules.

Unsurprisingly, cyclic dimer **7b** (Figure 6.1) was preferentially formed in equimolar dilute solutions (<1.0 x 10^{-3} M in acetone-d_6/chloroform-*d*, 1/1, v/v at 22°C) as observed in other cases.[2-8] In pursuit of more efficient construction of supramolecular polymers **8**, we speculated that by mismatching the lengths of the aliphatic spacer units in the homoditopic molecules (*e.g.,* **1** and **5**), the equilibrium process may be reversed to favor linear extension (*e.g.,* **6** and then to **8**) even in dilute conditions largely due to a greater steric penalty associated with the corresponding cyclic dimer complex (*e.g.*, **7**).[8] In this chapter we investigate the stabilities of cyclic and linear dimer complexes based on complementary homoditopic molecules whose spacer segments were varied systematically.

6.2.Results and Discussion

6.2.1. Synthesis

The synthetic strategies to prepare **5a-c** are depicted in Figure 6.3. The dialdehydes **2**[9] were reacted with benzyl amine with simultaneous removal of water to obtain bisimines **3**. Reduction of the bisimines with sodium borohydride gave the corresponding secondary amines **4**, which were subsequently acidified with 2M HCl and

followed by ion exchange reaction with aqueous ammonium hexafluorophosphate to afford the bisammonium salts **5**.

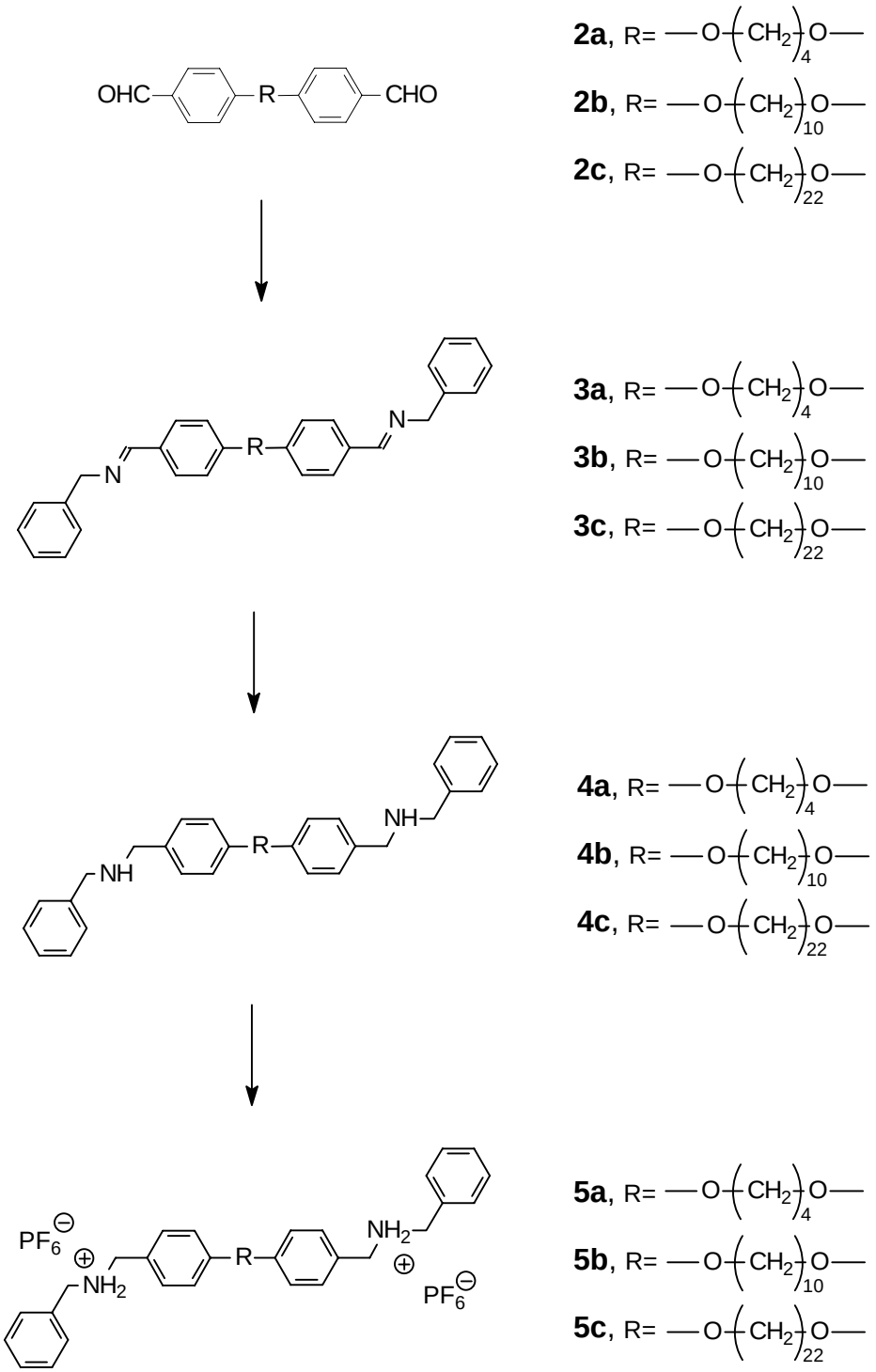

Figure 6.3. Synthetic approach to a series of homoditopic molecules.

6.2.2. Complexation studies in dilute solution

The ^{1}H NMR spectra of dilute equimolar solutions of **1** and **5** (Figures 6.4a-c) revealed four sets of N-CH_2 signals corresponding to 1) uncomplexed moieties of the ditopic guest molecule (H(**5**)$_u$), 2) complexed moieties in cyclic dimer (H(**7**)), and 3) complexed and 4) uncomplexed moieties in the linear dimer (H(**6**)$_c$ and H(**6**)$_u$, respectively) on the basis of slow exchange on the NMR time scale. The four sets of signals are assigned for the benzylic protons of the ammonium salt units in **5** (uncomplexed, u), **6** (complexed end, c, and uncomplexed end, u), and **7**. In Figure 6.4d the three sets of signals are assigned for the benzylic protons of the ammonium salt units in **5b** (uncomplexed, u) and **9b** (complexed end, c, and uncomplexed end, u). A vertically enlarged version of the spectrum in the region of 4.45-4.75 ppm in Figure 6.4a is shown in Figure 6.4a'. Integration of H(**6**)$_c$ and H(**6**)$_u$ gave a ratio of 1:1 for each solution, indicating that the signals assigned to H(**6**)$_c$ and H(**6**)$_u$ arise from the same species. It is noteworthy that the ^{1}H NMR spectra of three sets of each solution were recorded with at least 50 min of acquisition time for determination of ratios of the H(**6**)$_c$ and H(**6**)$_u$ signals. Each spectrum was enlarged vertically (thus the signals of interest were detectable from the baselines and the signals were integrated by using a deconvolution technique. Ratios of the H(**6**)$_c$ and H(**6**)$_u$ signals were determined within experimental errors (*ca*. 5%).

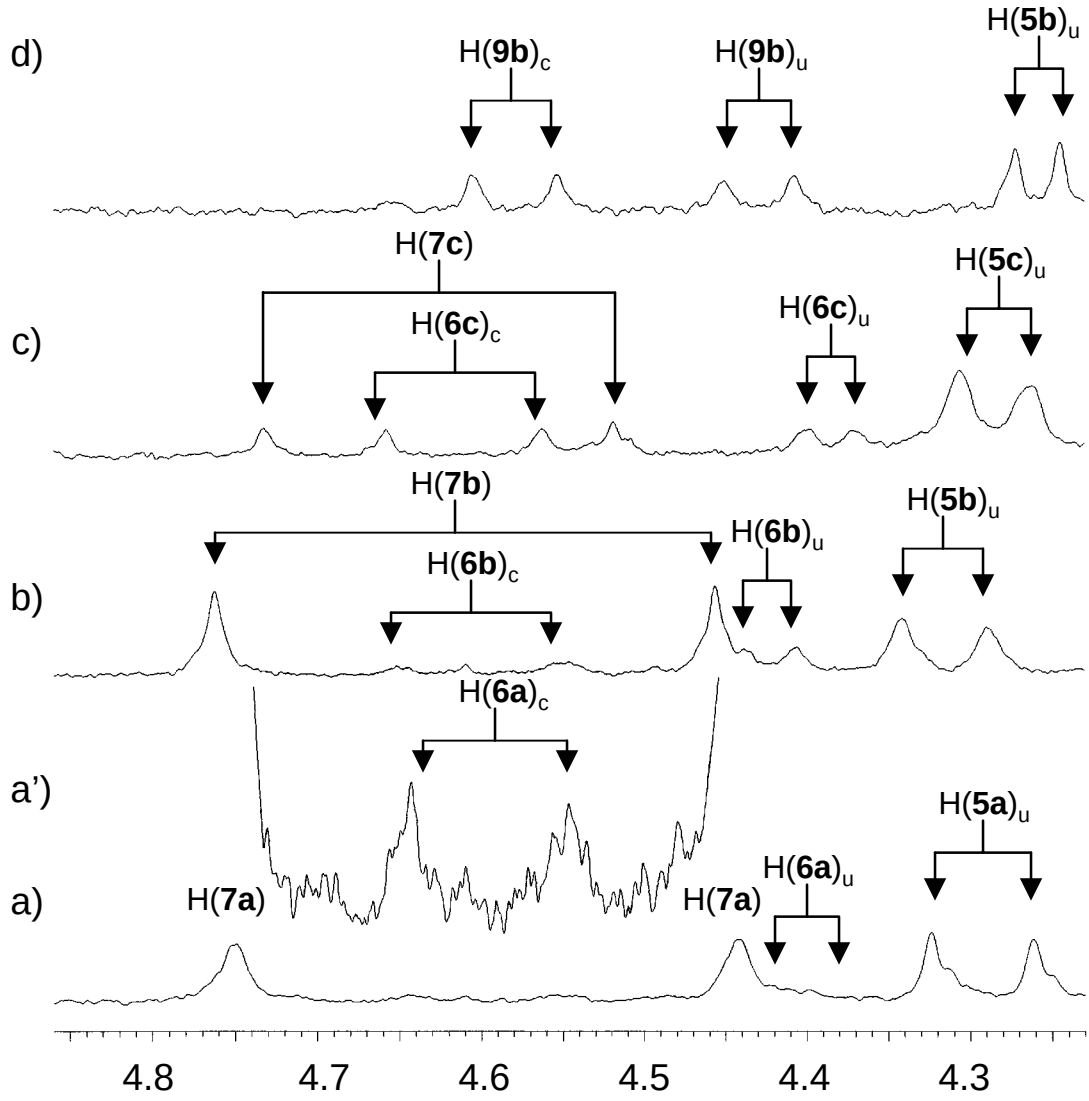

Figure 6.4. The stacked ^{1}H NMR spectra of equimolar solutions of a) **1** and **5a**, b) **1** and **5b**, and c) **1** and **5c** (4.0 x 10^{-4} M each) and d) a solution of DB24C8 and **5b** (8.0 x 10^{-4}/4.0x 10^{-4} M) at 22^{o}C (400 MHz, acetone-d_6/chloroform-*d*, 1/1, v/v).

The signal assignments were properly made based on our previous investigation in chapter 5 and the ^{1}H NMR spectrum (Figure 6.4d) of a dilute solution of DB24C8 and **5b** which exhibited three sets of N-CH_2 signals corresponding to uncomplexed ammonium salt moieties of **5b** (H(**5b**)$_u$) and complexed and uncomplexed ammonium salt moieties of **9b** (H(**9b**)$_c$ and H(**9b**)$_u$, respectively). The signals for H(**9b**)$_c$ and H(**9b**)$_u$ were integrated to be 1:1; thus complex **9b** was exclusively formed, confirming that the two signals assigned to **9b** (and to **6**) arise from the same species. The considerable

downfield shift observed for H(**9b**)$_u$ with respect to H(**5b**)$_u$ ($\Delta\delta$ =0.17 ppm) is presumably a consequence of interaction(s) between the pseudorotaxane and free ammonium salt moiety in **9b** (and by analogy in **6**); *e.g.*, "intramolecular" π–stacking between a benzo ring of complexed DB24C8 and the terminal phenyl ring of the free ammonium salt moiety achieved by folding of the flexible aliphatic spacer as illustrated in Figure 6.5. Indeed, in the crystal structure of the pseudorotaxane from DB24C8 and dibenzylammnoium hexafluorophosphate one of the benzo rings π-stacks with one of the phenyl rings.[10,11] The other electron rich benzo ring is uncomplexed. In the present systems **6a**, **6b**, **6c**, and **9b** we propose that the "vacant" benzo ring π-stacks "intramolecularly" with the somewhat electron poor terminal phenyl ring of the free ammonium salt moiety. These spectroscopic observations allowed us to conclude that the signals in the region of 4.35 to 4.45 ppm in Figures 6.4a-c correspond to H(**6**)$_u$ and that only **6** and **7** exist and cyclic or linear oligomers **8** are not present in detectable amounts in these dilute solutions.

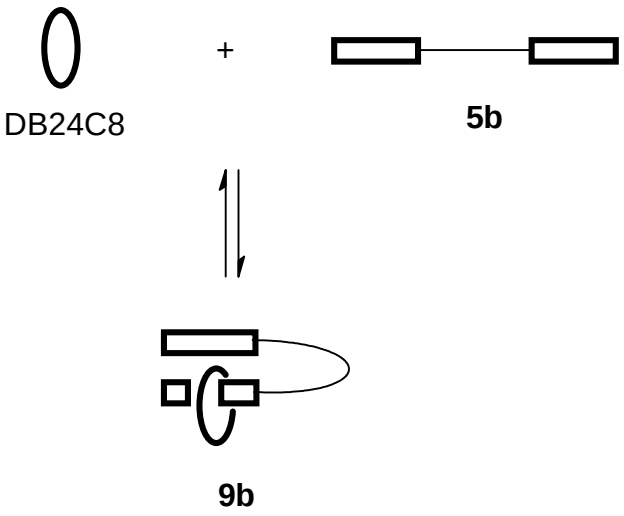

Figure 6.5. Cartoon illustrations of the formation of the 1:1 dimer complex **9b** from DB24C8 and homoditopic molecule **5b** in substantially dilute conditions.

To prove the "proposed folding effects" experimentally we have carried out an additional ^{1}H NMR investigation. The ^{1}H NMR spectrum of a dilute solution of DB24C8 with a methyl ester substituent on one of the benzo rings (the chemical structure shown in Figure 6.6) and **5b** (8.0×10^{-4}/4.0×10^{-4} M) in the same solvent system revealed only two

sets of N-CH_2 signals for complexed and uncomplexed ammonium salt moieties. This observation shows that the unoccupied ammonium salt moiety in the 1:1 complex is magnetically in the same environment as those in **5b**, indicating that there is no "folding effect" in this case. Hydrogen bonding and π–π stacking interactions between one of the phenyl rings of the ammonium salt moiety in **5b** and the unsubstituted benzo ring of DB24C8 shift the equilibrium toward the 1:1 complex. However, the "vacant" benzo ring, which is somewhat electron poor due to the electron withdrawing substituent is not capable of π–π stacking with the somewhat electron poor terminal phenyl ring of uncomplexed ammonium salt moiety in the 1:1 complex. Thus, the ^{1}H NMR experiment, using DB24C8 having an electron withdrawing substituent on one of the benzo rings, supports the "proposed folding effects".

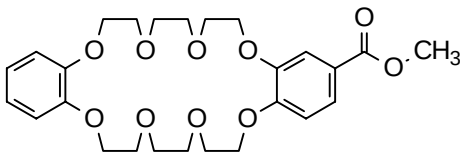

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Figure 6.6. Structure of DB24C8 derivative **10**.

Since the concentrations of each species (**1**, **5**, **6**, and **7**) at equilibrium are readily known, one can estimate the association constants (K_{linear} and K_{cyclic}); the results at 22^{o}C are summarized in Tables 1 and 2 with ΔH and ΔS values.

K_{linear} (Table 1) varies systematically, increasing as the length of the aliphatic spacer increases (from **6a** to **6c**). Note that ΔH_l and ΔS_l become more negative from **6a** to **6b**, but the values for **6b** and **6c** are essentially identical. This observation is consistent with more effective stabilization of **6b** and **6c** relative to **6a** by "intracomplex" interaction between the threaded crown ether and the non-threaded ammonium salt moiety; as shown by CPK models the longer spacers in the latter two species allow more effective interaction.

Table 6.1. Association constants (K_{linear}) at 22°C and enthalpy and entropy for linear dimerization in acetone-d_6/chloroform-*d* (1/1, v/v).[a]

complex	K_{linear} (M^{-1})	ΔH_l (kcal mol^{-1})	ΔS_l (cal mol^{-1} K^{-1})
6a	$1.3\pm0.3x10^3$	-8.0±0.6	-13±1
6b	$3.7\pm0.7x10^3$	-11±2	-20±3
6c	$5.2\pm0.6x10^3$	-10±3	-23±7

a)± values represent standard deviations.

Similarly, K_{cyclic} (Table 2) varies systematically, decreasing as the length of the aliphatic spacer increases (from **7a** to **7c**). And ΔH_c and ΔS_c also become less negative as the spacer length increases, the most dramatic change taking place from **7a** to **7b**. These observations are consistent with two factors: 1) limited stabilization of precursor **6a** by intracomplex stacking interactions and 2) the increasing end-to-end distance of the linear precursors **6**.

Table 6.2. Association constants (K_{cyclic}) at 22°C and enthalpy and entropy for cyclic dimerization in acetone-d_6/chloroform-*d* (1/1, v/v).[a]

complex	K_{cyclic}	ΔH_c (kcal mol^{-1})	ΔS_c (cal mol^{-1} K^{-1})
7a	2.5±0.4	-8.6±1.0	-27±2
7b	1.7±0.3	-3.7±0.1	-12±1
7c	0.62±0.03	-2.1±0.6	-8.1±0.4

a)± values represent standard deviations.

As we anticipated, K_{cyclic} for **7c** was reduced, almost three-fold, compared to that for **7b**. Most importantly, the K_{linear}/K_{cyclic} value, which should be regarded as a critical parameter for the efficiency of linear extension to **8**, obtained for **6c**/**7c** (8.4×10^3 M^{-1}) clearly stands out, showing nearly a 16-fold improvement with respect to that of **6a**/**7a** (5.2×10^2 M^{-1}).

6.3. Conclusions

Our present results, contrary to our initial speculation, indicate that the steric penalty associated with **7** may not be as important as the end-to-end distance of **6** in terms

of shifting the equilibrium over to the linear dimer complex. Nevertheless, purposely increasing the length of the spacer in one component successfully reversed the equilibrium between **6** and **7** toward **6**. Our preliminary investigation of construction of a supramolecular polymer using **1** and **5c** as building components has revealed an improved linear extension in **8c** at lower concentrations relative to using **1** and **5b**. These results are described in the following chapter.

6.4. Experimental

Pyridine was stirred with CaH_2 overnight and distilled prior to the polymerization reactions. THF was distilled from Na and benzophenone. All other solvents were used as received. Melting points were taken on a Mel-Temp II melting point apparatus and are uncorrected. The 400 MHz ^{1}H 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). Variable-temperature ^{1}H NMR spectroscopy was performed in the range of 285-313 K. Plots of $R\ln K_{linear}$ and $R\ln K_{cyclic}$ versus $1/T$ yielded straight lines (R>0.97) from which ΔH and ΔS values for linear and cyclic dimerization were obtained. 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). The synthetic procedures for **1** and **5b** are described in the experimental part in chapter 5 (section 5.6). **2a** was prepared by using the literature protocol.[9,12]

2c. To 50 mL one necked round bottom flask equipped with a condenser and magnetic stirrer were added docasanedioic acid (5.00 g, 13.5 mmol), MeOH (30 mL), and H_2SO_4 and the heterogeneous reaction mixture was vigorously stirred at reflux for 12 h. The solvent and the catalyst were rotary evaporated to give a brown solid, which was redissolved in acetone and precipitated in H_2O to afford dimethyl docosanedicarboxylate as an off-white solid (5.30 g, 99% yield), mp 72-73^{o}C (lit.[13] mp 68-70^{o}C). ^{1}H NMR (400 MHz, chloroform-*d*, 22^{o}C): δ=1.25-1.28 (32H, br s), 1.61 (4H, q, J = 7.2 Hz), 2.30 (4H, t, J = 7.6 Hz), and 3.66 (6H, s). To a 500 mL three necked round bottom flask

equipped with a N_2 inlet and magnetic stirrer were added the dimethyl carboxylate (5.19 g, 13.0 mmol) and anhydrous THF (250 mL). To this solution was added a solution of LAH (1.0 M, 26 mL) via syringe and the reaction mixture was vigorously stirred at room temperature for 12 h. After a small amount of EtOAc was added to quench the reaction, the solvent was rotary evaporated to give a white solid, which was suspended in H_2O and neutralized with 2M HCl and extracted with $CHCl_3$. The organic layers were combined and dried with $MgSO_4$ and concentrated to afford 1,22-docosanediol as a white solid (4.21 g, 94% yield), mp 103-105°C (lit.[14] mp 105.7-105.9°C). ^{1}H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.25-1.31 (28H, br s), 1.44 (4H, m), 1.56 (4H, m), and 3.64 (4H, t, J = 6.8 Hz). Anal. calcd for $C_{22}H_{46}O_2$: C, 77.13; H, 13.53, found: C 77.08; H, 13.46. To a 100 mL one necked round bottom flask equipped with a condenser, magnetic stirrer, and N_2 inlet were added the diol (2.25g, 6.57 mmol), thionyl chloride (3.13 g, 26.3 mmol), pyridine (2.08 g, 26.3 mmol), and toluene (50 mL) and the reaction mixture was vigorously stirred at reflux for 12 h. After a small amount of H_2O was added to quench the reaction the solvent was removed *in vacuo* to give a brown solid, which was thoroughly washed with H_2O. This solid was redissolved in chloroform and precipitated in H_2O to afford 1,22-dichlorodocosane as a brown solid (2.39 g, 96% yield), mp 62-63°C (lit.[15] mp 61-62°C). ^{1}H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.25-1.27 (28H, br s), 1.42 (4H, m), 1.77 (4H, m), and 3.53 (4H, t, J = 6.8 Hz). Anal. calcd for $C_{22}H_{44}Cl_2$: C, 69.63; H, 11.69, found: C 69.54; H, 11.63. To a 500 mL one necked round bottom flask equipped with a condenser and magnetic stirrer were added the dichloride (2.34 g, 6.17 mmol), 4-hydroxybenzaldehyde (3.01 g, 24.6 mmol), K_2CO_3 (8.52 g, 61.6 mmol), and DMF (200 mL) and the reaction mixture was stirred at 110°C for 5 days. The salts were filtered with Celite and the filtrate was precipitated into MeOH to afford 1,22-bis(4-formylphenoxy)docosane as a brown solid (2.76 g, 81% yield), mp 76-77°C. ^{1}H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.25-1.32 (28H, br s), 1.46 (4H, m), 1.83 (4H, m), 4.03 (4H, t, J = 6.8 Hz), 6.99 (4H, d, J = 8.8 Hz), 7.83 (4H, d, J = 8.8 Hz), and 9.88 (2H, s). Anal. calcd for $C_{36}H_{54}O_4 \cdot 1/3H_2O$: C, 77.65; H, 9.99, found: C 77.60; H, 9.92.

3. To a two necked round bottom flask equipped with a Dean-Stark trap, a condenser, and a N_2 inlet were added corresponding **2** (1.00 equiv.) and toluene. To this solution

was added benzylamine (2.20 equiv.) and the mixture was refluxed for 12h. The solvent was removed to give a yellow viscous liquid, which was precipitated into anhydrous hexanes to afford an off-white solid.

3a. 94% yield, mp 102-104°C. ^{1}H NMR (400 MHz, chloroform-*d*, 22°C): δ=2.00 (4H, t, *J* = 6.4 Hz), 4.08 (4H, t, *J* = 6.4 Hz), 4.80 (4H, s), 6.93 (4H, d, *J* = 8.8 Hz), 7.24-7.35 (10H, m), 7.75 (4H, d, *J* = 8.8 Hz), and 8.31 (2H, s). LRFAB: *m/z*=477.3 $[M+H]^+$. HRFAB: calcd for $[M+H]^+$ $C_{32}H_{33}O_2N_2$ 477.2542, found 477.2541. Anal. calcd for $C_{32}H_{32}O_2N_2$: C, 80.64; H, 6.77, N 5.88, found: C 80.22; H, 6.81, N 5.71.

3c. 92% yield, mp 99-101°C. ^{1}H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.25 (32H, s), 1.43 (4H, m), 1.79 (4H, m), 4.80 (4H, s), 6.92 (4H, d, *J* = 8.8 Hz), 7.33-7.35 (10H, m), 7.74 (4H, d, *J* = 8.8 Hz), and 8.29 (2H, s). LRFAB: m/z=729.5 $[M+H]^+$. HRFAB: calcd for $[M+H]^+$ $C_{50}H_{69}N_2O_2$ 729.5359, found 729.5361. Anal. calcd for $C_{50}H_{68}N_2O_2 \cdot 1.5H_2O$: C, 79.42; H, 9.47, N 3.70, found: C 79.67; H, 9.44, N 3.39.

4. To a two necked round bottom flask equipped with a magnetic stirrer, condenser, and N_2 inlet were added corresponding **3** (1.00 equiv.) and MeOH. To this solution were added small portions of $NaBH_4$ (2.00 equiv.) and the mixture was brought to a gentle reflux and stirred for 12h. The solvent was removed to afford a white solid, which was suspended in H_2O and neutralized with 2M HCl. The product was extracted with $CHCl_3$, the organic layers were combined, dried over $MgSO_4$, and concentrated to give an off-white solid.

4a. 86% yield, mp 60-61°C. ^{1}H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.97 (4H, t, *J* = 6.4 Hz), 3.74 (4H, S), 3.80 (4H, S), 4.03 (4H, t, *J* = 6.4 Hz), 6.86 (4H, d, *J* = 8.8 Hz), 7.24 (4H, d, *J* = 8.8 Hz), and 7.25-7.37 (10H, m). LRFAB: m/z=481.3 $[M+H]^+$. HRFAB: calcd for $[M+H]^+$ $C_{32}H_{37}N_2O_2$ 481.2855, found 481.2861. Anal. calcd for $C_{32}H_{36}N_2O_2$: C, 79.97; H, 7.55, N 5.83, found: C, 79.22; H, 7.35, 5.80.

4c. 85% yield, mp 77-78°C. ^{1}H NMR (400 MHz, chloroform-*d*, 22°C): δ=1.25 (32H, s), 1.44 (4H, m), 1.77 (4H, m), 3.74 (4H, s), 3.79 (4H, s), 3.94 (4H, t, *J* = 6.4 Hz), 6.85 (4H,

d, J = 8.8 Hz), 7.24 (4H, d, J = 8.8 Hz), and 7.25-7.34 (10H, m). LRFAB: m/z=733.5 $[M+H]^+$. HRFAB: calcd for $[M+H]^+$ $C_{50}H_{73}N_2O_2$ 733.5672, found 733.5669. Anal. calcd for $C_{50}H_{72}N_2O_2 \cdot 1/2H_2O$: C, 80.81; H, 10.04, N 3.77, found: C 80.91; H, 9.86, N 3.75.

5a. To a one neck round bottom flask equipped with a magnetic stirrer were added **4a** (1.80 g, 3.74 mmol) and MeOH (150 mL). To this solution was added 2M HCl (5 mL) and the mixture was stirred for 1 h. The solvent was removed to give an off-white solid, which was then suspended in acetone and aq. NH_4PF_6 was added until complete dissolution occurred. The solvent was evaporated and the resulting solid was washed thoroughly with H_2O to afford an off-white solid (2.61 g, 90% yield), mp decomp. 220°C. ^{1}H NMR (400 MHz, acetone-d_6, 22°C): δ=1.92 (4H, t, J = 6.4 Hz), 4.03 (4H, t, J = 6.4 Hz), 4.39 (4H, s), 4.42 (4H, s), 6.88 (4H, d, J = 8.4 Hz), 7.37-7.47 (10H, m), 7.39 (4H, d, J = 8.4 Hz), and 8.45 (4H, s). LRFAB: m/z=627.3 $[M\text{-}PF_6]^+$. HRFAB: calcd for $[M\text{-}PF_6]^+$ $C_{32}H_{38}N_2O_2PF_6$ 627.2527, found 627.2551. Anal. calcd for $C_{32}H_{38}N_2O_2P_2F_{12} \cdot 1.5H_2O$: C, 48.06; H, 5.17, N 3.50, found: C, 47.91; H, 4.81, N 3.88.

5c. To a 250 mL one necked round bottom flask equipped with a magnetic stirrer were added **4c** (1.31 g, 1.79 mmol) and a mixture of MeOH/$CHCl_3$ (50 mL/100 mL). The solution was bubbled with HCl gas for 10 min. The solvent was removed to give a white solid, which was suspended in actone and aq. NH_4PF_6 was added and the mixture was stirred for 1 h. The insoluble particles were filtered and the filtrate was concentrated and precipitated into H_2O to afford a white solid (1.42 g, 76% yield), mp decomp. 150°C. ^{1}H NMR (400 MHz, acetone-d_6/chloroform-d (1/1, v/v), 22°C): δ=1.22 (32H, s), 1.41 (4H, m), 1.72 (4H, m), 3.93 (4H, t, J = 6.4 Hz), 4.43-4.46 (4H, m), 6.88 (4H, d, J = 8.4 Hz), 7.37-7.47 (12H, m), and 8.34 (4H, s). LRFAB: m/z=733.5 $[M\text{-}HPF_6\text{-}2HPF_6]^+$. HRFAB: calcd for $[M\text{-}HPF_6\text{-}2PF_6]^+$ $C_{50}H_{73}N_2O_2$ 733.5672, found 733.5671.

6.4. References

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