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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 06 Mar 2018

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SUPRAMOLECULAR PSEUDOROTAXANE POLYMERS FROM BISCRYPTANDS & BISPARAQUATS

Terry L. Price, Jr.,[§] and Harry W. Gibson*

Department of Chemistry
Virginia Tech
Blacksburg, VA 24060

ABSTRACT

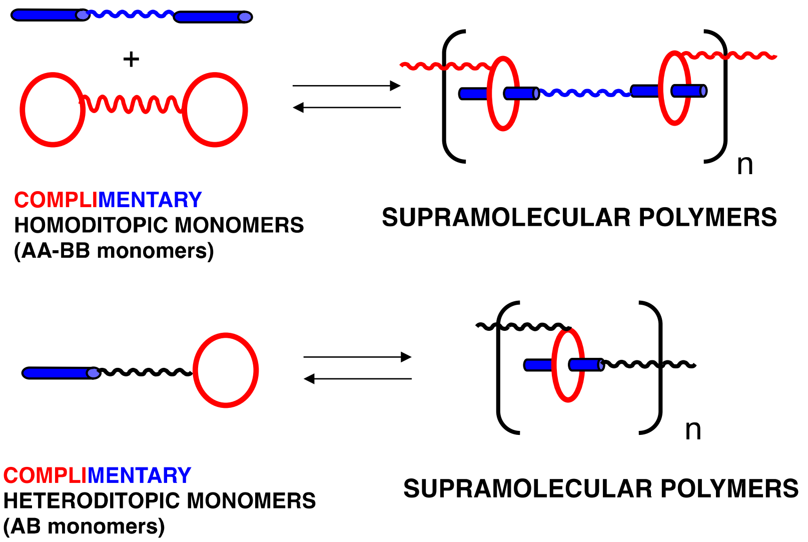
Five new bis(dibenzo-30-crown-10-based cryptand)s were synthesized, two of which (**16** and **17**) had long (12 atom), flexible spacers that led to cooperative complexation of dibenzyl paraquat TFSI ($K_{ave} = 4.36 \times 10^5\ M^{-1}$ for **17•2b).** Self-assembly of **16** and **17** with bisparaquats with similar spacers (**18**, **21** and **23**) led to high molecular weight supramolecular pseudorotaxane polymers in solution. Continuous, flexible fibers were drawn from concentrated solutions. **17** with C_{10}-linked bisparaquat **23** in dichloromethane (DCM) produced a log-log viscosity vs. concentration plot with limiting slope 3.55, confirming high molecular weight; at 37 mM the degree of polymerization was estimated to be 126 and M_n = 407 kDa. These are the first truly polymeric pseudorotaxane-type AA/BB supramolecular polymers.

[§] Present address: Zestron Corporation, 11285 Assett Loop, Manassas, VA 20109 USA

* Corresponding author; e-mail: hwgibson@vt.edu

INTRODUCTION

Supramolecular polymers are of particular interest because of their dynamic character, which allows for reversibility and stimuli responsiveness.[1] Polymers



The degree of polymerization (DP) is related to the association constant of the complex and the concentrations (**Eq. 1, Figure 1**; $[H]_o$ is the total concentration of an AB monomer).[2] When $4K_a[H_o] >> 1$ the equation simplifies to **Eq. 2, Figure 1**. In general the association constant can be controlled via stimuli such as temperature, solvent, pH, electrochemistry, counter ion or light.

Equation 1. Full equation.

$$DP = 2\ K_a\ [H]_o / \{(1 + 4\ K_a\ [H]_o)^{1/2} - 1\}$$

Equation 2. Simplified equation.

$$DP = (K_a\ [H]_o)^{1/2}$$

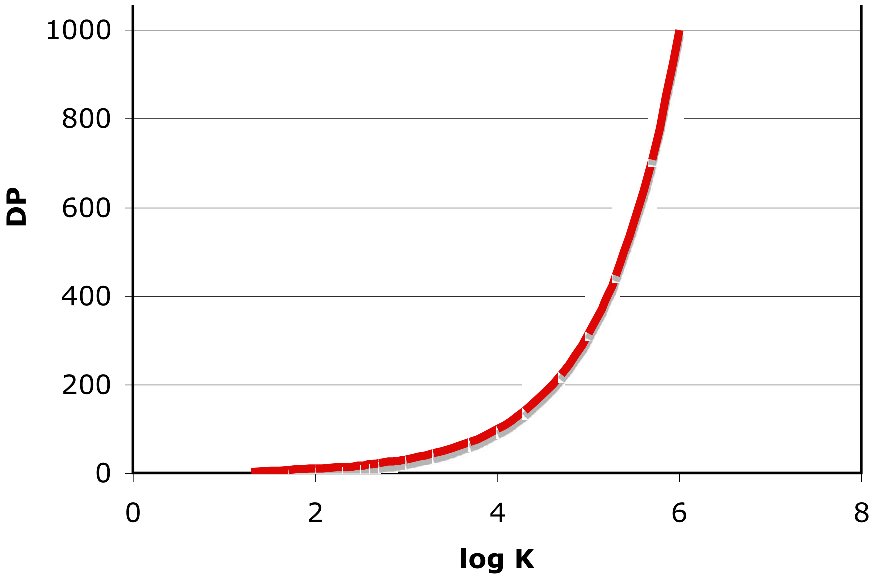
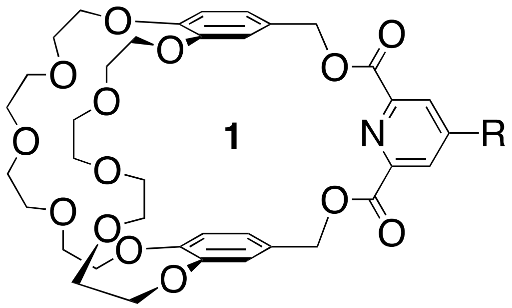
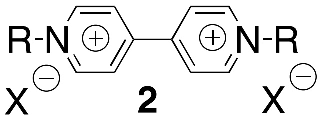


Figure 1. DP vs K_a at 1 M.

Among reported pseudorotaxane supramolecular polymers the crown ether host motif has been well studied.[2b,3] In the meantime crown ether host systems, however, have evolved into cryptands.[4] Specifically, pyridyl cryptands have exceptionally high binding constants with paraquat derivative guests (N,N'-dialkyl-4,4'-bipyridinium salts).[4c,4e,4g-4j] Recently supramolecular polymers have been reported using cryptand motifs of varying types,[5] including an extremely high binding pyridyl cryptand motif in an AB or heteroditopic monomer.[5a]



a. R = H
b. R = Br
c. R = $OCH_2C_6H_4Br$-*p*



a. R = CH_3, X = PF_6
b. R = $CH_2C_6H_5$, X = TFSI
c. R = CH_3, X = TFSI

TFSI = $(CF_3SO_2)_2N$

To illustrate the importance of strong complexation, consider that in **Figure 1** DP = 100 is not achieved until $K_a = 10^4$ M^{-1} at 1 M concentration. For step-growth polymers, which these are, the rule of thumb is that for good physical properties DP ≥ 100 is required. For most crown ether based complexes $K_a \leq 10^3$ M^{-1}, leading to maximum DP = 32 at 1 M concentration assuming that no cyclics form, i. e., only oligomers will form. The pyridyl dibenzo-30-crown-10 cryptand (**1a**) with dimethyl paraquat PF_6 (**2a**) in acetone has an association constant of 1 x 10^5 M^{-1},[4g] while the same cryptand with dibenzyl paraquat TFSI (**2b**) in DCM has an association constant of 1 x 10^6 M^{-1}.[6] Appropriate monomers with these association constants would afford DP = 316 and DP = 1,000 at 1 M concentration, respectively, i. e., truly high molecular weight polymers.

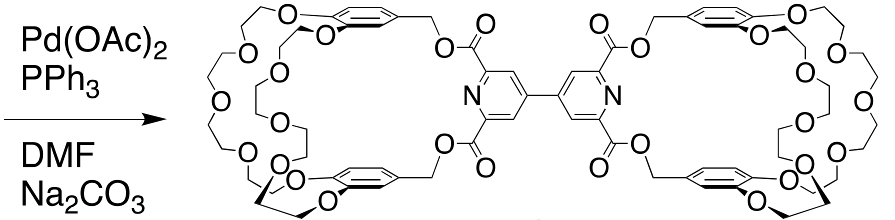
New templated synthetic pathways for cyclization of dibenzocrown ethers by the Wang-Peterson-Wessels protocol [4e,4g,4h,7] and cryptands [8] now allow more efficient development of ditopic cryptands. Here we report our efforts to prepare pyridyl cryptand AA monomers and bisparaquat BB monomers and their self-assembly to pseudorotaxane-type supramolecular polymers.

RESULTS AND DISCUSSION

A. Synthesis of Biscryptand Monomers

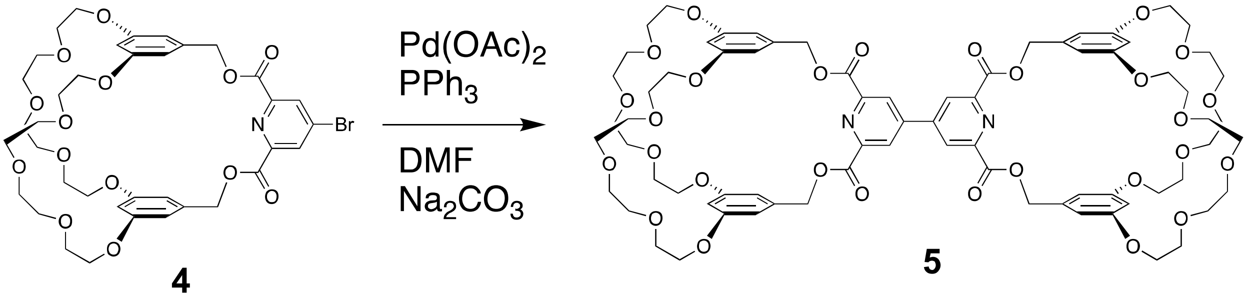
Our initial attempts to synthesize a biscryptand employed the dibenzo-30-crown-10-based pyridyl cryptand **1b** with the intent of Heck coupling with a diolefin. These attempts were unsuccessful; coupling with the olefin was not observed. Instead Ullmann coupling prevailed and biscryptand **3** was formed in 26% yield, with a large fraction of **1** left unreacted after 36 h. Without the diolefin the Ullmann coupled product was isolated in 25% yield with a large fraction of unreacted **1b**. These conditions are known to promote Ullmann couplings.[9]

1b



3

A similar reaction was carried out using the 32-crown-10 bromocryptand **4** to produce biscryptand **5** in 11% yield; the yield reduction vs. **3** is attributed to the small reaction scale (18 mg). Once again a large fraction of the aryl bromide was unreacted.



4 **5**

Isothermal titration calorimetric (ITC) examination (**Figure 2**) of the complexation of biscryptand **3** with dimethyl paraquat (**2a**) revealed a reasonably high average binding constant, 2.33 x 10^5 M^{-1}. However, analysis of the isotherm revealed that K_{a1} =

4.50 x 10^5 M^{-1}, while K_{a2} = 1.78 x 10^4 M^{-1}. For statistical complexation K_{a2} = (1/4) K_{a1},[10] so the system is anti-cooperative [K_{a2} = (3.96 x 10^{-2}) K_{a1}]. The anti-cooperative behavior of **3•2a** is attributed to the close proximity of the two host cavities and the rigidity of the linker, causing the complexation of the second paraquat to suffer a repulsive electrostatic force from the first complexed paraquat. Thus, compounds **3** and **5** were abandoned for constructs that contain longer, more flexible linkers between the two cryptand units to avoid anticooperativity.

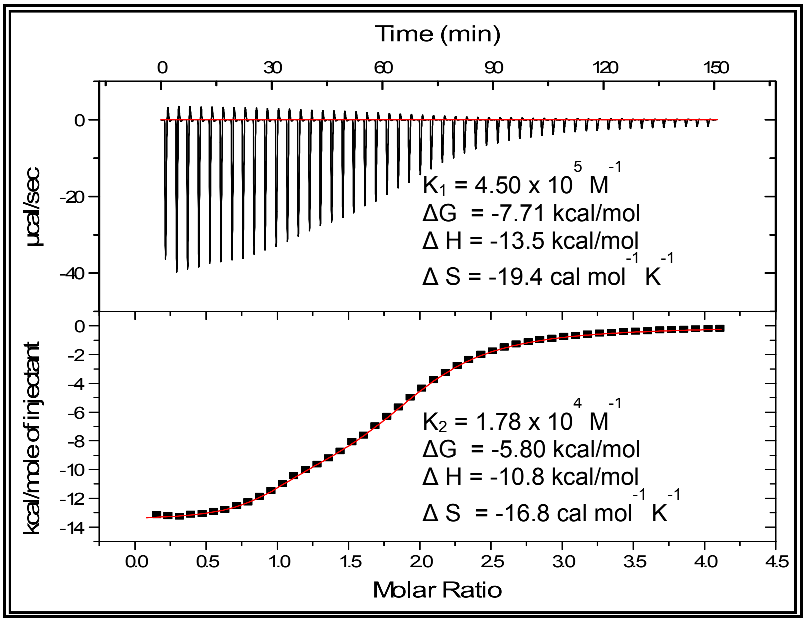
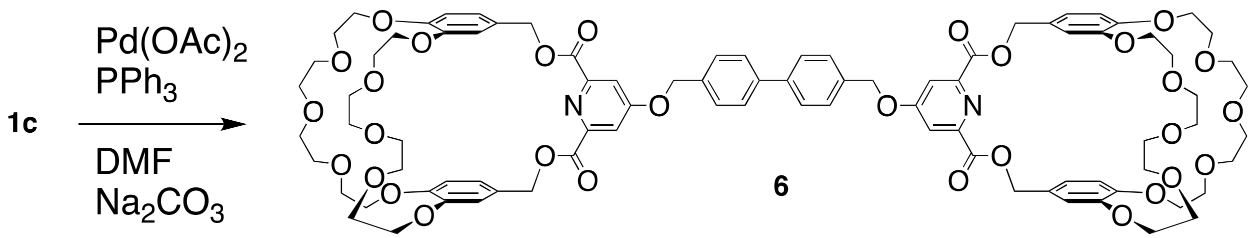
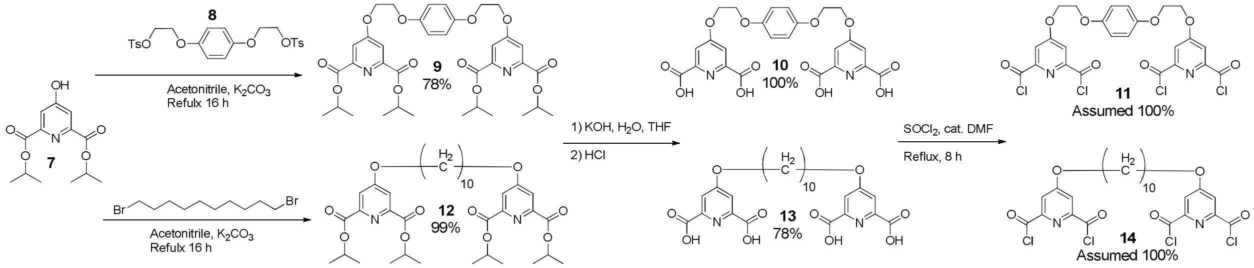


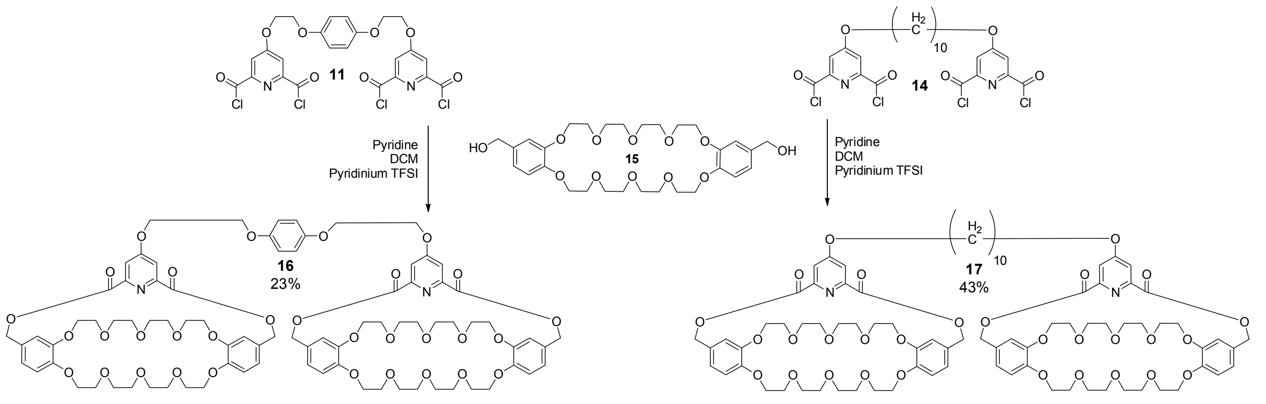
Figure 2. ITC titration of biscryptand **3** with dimethyl paraquat PF_6 (**2a**) in CH_3COCH_3 at 25 °C.

Since Ullmann coupling proved to be possible using aryl bromides **1b** and **4**, aryl bromide **1c** was prepared and subjected to those conditions to yield biscryptand **6**, whose longer linker would overcome the anticooperativity observed with **3**. Synthesis of **6** was achieved in a yield of 12% after 17 h. Chromatography allowed recovery of unreacted starting material. At the same time progress had been made on templation of the formation of cryptands [8] and it became evident that biscryptands could be prepared more readily by this method. Thus pursuit of **6** and analogs was abandoned.



Two biscryptands, **16** and **17**, were chosen (**Scheme 2**). Our previous work [3c,11] indicated that if the linker in the ditopic host is ≥ 10 atoms, the formation of cyclic species, a side reaction in the formation of supramolecular polymers, is minimized. The syntheses proceed from the known [12] diisopropyl chelidamate (**7**); the isopropyl ester groups essentially eliminate N-alkylation; this allowed formation of bischelidamates **9** and **12** in high yields. Their hydrolyses to tetra-acids **10** and **13** and thence conversion to tetra-acid chlorides **11** and **14** proceeded smoothly. Finally their dual templated cyclizations with dibenzo-30-crown-10 diol (**15**) afforded the biscryptands **16** and **17**. The ^{1}H NMR spectrum of new biscryptand **17** is shown in **Figure 3**.





Scheme 2. Synthesis of biscryptands **16** and **17.**

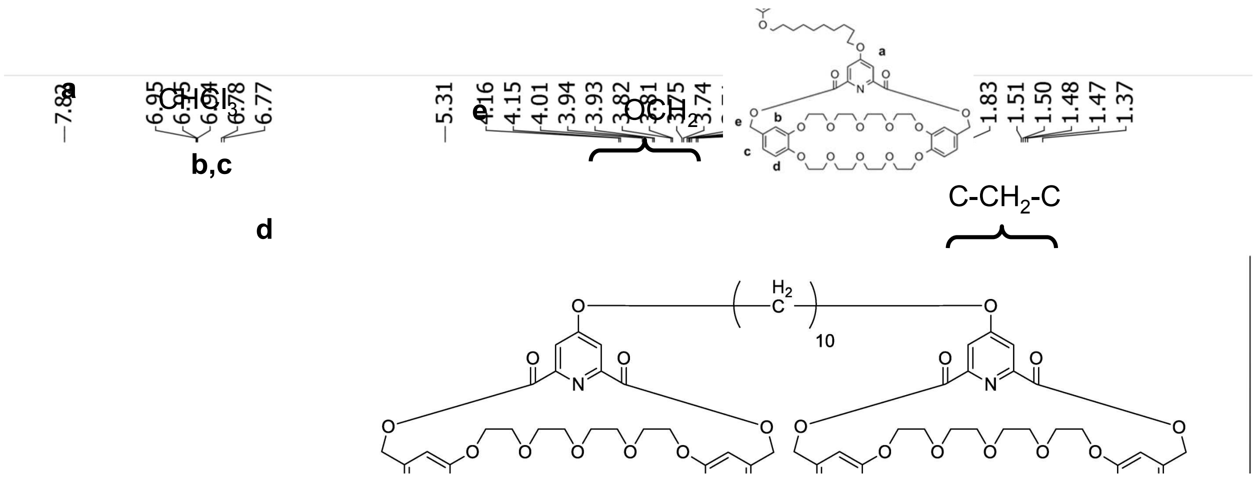


Figure 3. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ^{o}C) of biscryptand **17**.

As expected, ITC results revealed that the complexation of biscryptand **17** with dibenzyl paraquat TFSI (**2b**) was actually cooperative (**Figure 4**); $K_{avg} = 4.36 \times 10^5\ M^{-1}$, $K_{a1} = 2.49 \times 10^5\ M^{-1}$ and $K_{a2} = 6.23 \times 10^5\ M^{-1}$; $K_{a2} = 2.5\ K_{a1}$! Cooperative behavior found in other cryptand/paraquat systems has been attributed to conformational restrictions promoting the complexation of a second site.[13] The crystal structure of the complex of 2,6-pyridyl cryptand **1a** with dimethyl paraquat PF$_6$ (**2a**) revealed the guest π–stacked within the host in such a way that the paraquat methyl groups interact with the oxygen atoms of the host.[4g] It is likely that the electron poor benzyl moieties of paraquat **2b** are capable of interacting via hydrogen bonding with the adjacent uncomplexed cryptand motif in **17**, causing the latter moiety to adopt a conformation favorable for complexation of the next paraquat guest. It is noteworthy that strong cooperativity was also demonstrated in a different solvent; in 1:1 $CHCl_3$:CH_3CN titration of biscryptand **17** with dimethyl paraquat TFSI (**2c**) yielded $K_{a1} = 2.2 \times 10^3\ M^{-1}$ and $K_{a2} = 1.3 \times 10^5\ M^{-1}$. $K_{a2} = 55\ K_{a1}$!

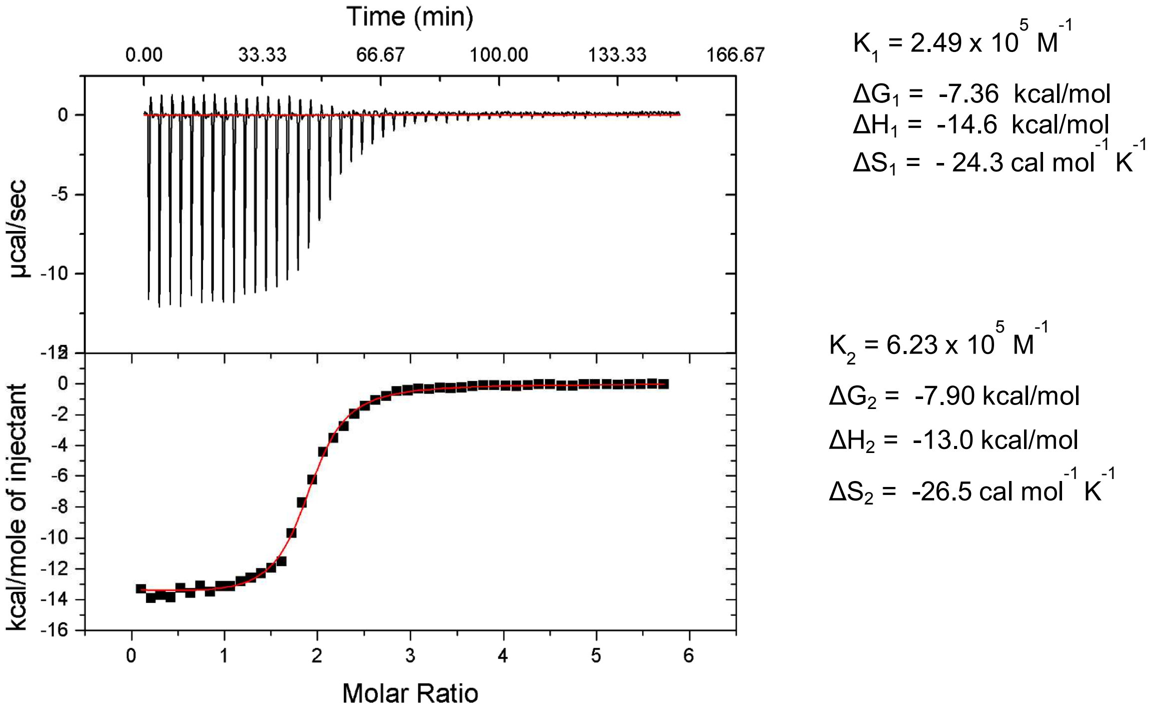
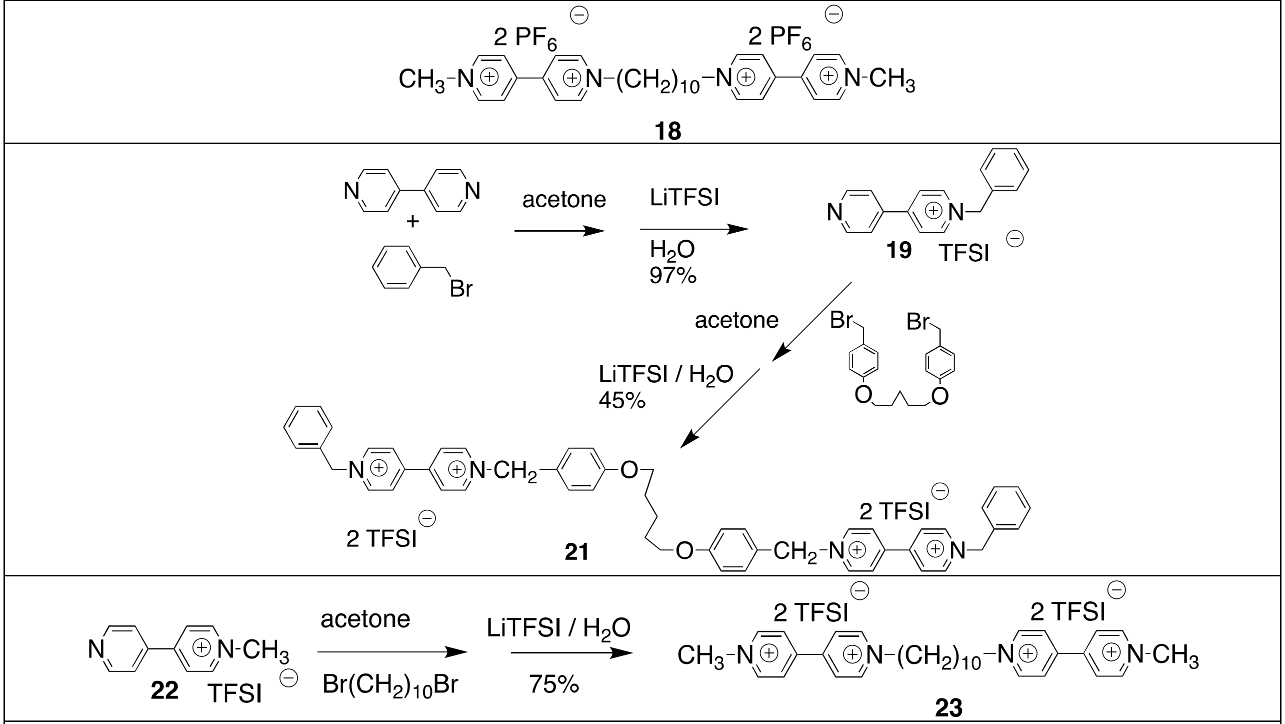


Figure 4. ITC titration of biscryptand **17** with dibenzyl paraquat TFSI (**2b**) in DCM at 25 °C.

B. Ditopic Guest Monomers

Bisparaquats used for this study, **18**,[5b] **21**, and **23**, were synthesized in acceptable yields by standard methods (**Scheme 3**).



Scheme 3. Bisparaquat guest monomers **18**, **21** and **23**.

C. Self-Assembly of Supramolecular Polymers

Using the AA host monomers **16** and **17** along with the BB guest monomers **18**, **21**, and **23**, five supramolecular polymers were self-assembled in solution (**Figure 5**): **17** + **18** → **P1**, **16** + **18** → **P2**, **17** + **23** → **P3**, **17** + **21** → **P4** and **16** + **21** → **P5**.

Figure 5. **Left**: Supramolecular polymers **P1** – **P5**. **Right:** Films were cast via slow solvent evaporation using the following solvents/substrates: **P1** ($CHCl_3$:CH_3CN, 1:1 v/v on Teflon); **P2** ($ClCH_2CH_2Cl$ on silicon); **P3** (*o*-$C_6H_4Cl_2$ on glass); **P4** ($ClCH_2CH_2Cl$ on Teflon); **P5** ($CHCl_3$:CH_3CN, 1:1 v/v on glass).

The polymers were self-assembled by dissolving the host monomer in chloroform and the guest monomer in acetone. The solutions of host and guest monomers independently were either colorless or slightly yellow. However, upon mixing the solutions instantly turned either a dark yellow or deep orange color, which persisted after solvent evaporation, indicative of charge transfer binding between electron rich cryptand hosts and electron poor paraquat guests.

It is a challenge to determine molecular weights for polyelectrolytes **P1** – **P5**. Due to the amount of material required to carry out viscosity experiments over a range of dilutions, only polymer **P3** was chosen for assessment. **Figure 6** shows a log-log plot of specific viscosity vs. concentration of precursors for **P3** in DCM; the critical concentration where supramolecular polymer begins to form is where the two trend lines cross (37 mM). This plot indicates that for equimolar concentrations of monomers **17** and **23** in DCM above 37 mM, a supramolecular polymer is present. Niu et al. reported a supramolecular polymer made from a biscryptand/bisparaquat pair that displayed a critical monomer concentration of 53 mM.[5b] The lower critical monomer concentration here is consistent with the ca. 100-fold higher K_a of the present biscryptand/bisparaquat system. Using the association constant of dibenzyl paraquat TFSI (**2b**) with **17** in DCM ($K_{a\ average} = 4.36 \times 10^5\ M^{-1}$) DP is estimated by **Eq. 2** to be 126 at 37 mM. With a repeat unit of 3,229 Da, this gives a molecular weight of 407 kDa. Our previous report of an AB self-assembly from an analogous 32-crown-10-based pyridyl cryptand and paraquat revealed a critical concentration of ca. 75 mM and a limiting slope of 3.54.[5a]

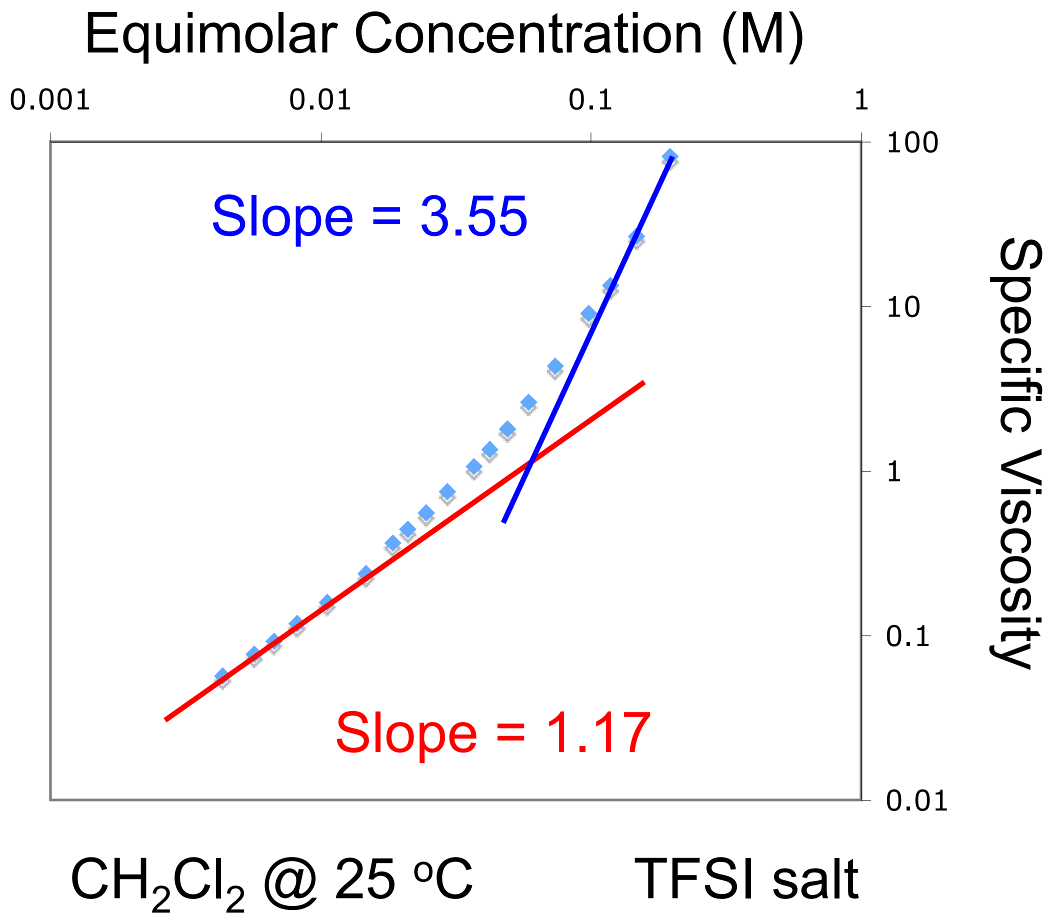


Figure 6. Log(specific viscosity) vs. Log(concentration) for equimolar solutions of **17** and **23** in DCM.

The slope of **Figure 6** at low concentrations is 1.17; this is attributed to the presence of cyclic dimeric species, acting as Einstein spheres. [2b,3b,3c,14] Interestingly, deviation from the line at low concentrations begins at 18 mM, indicating that large oligomers are already beginning to form. The slope at high concentrations, 3.55, is attributed to the formation of high molecular weight polymer and is the theoretical maximum, [15] observed here for only the second time with a pseudorotaxane system.[5a]

Films cast by slow solvent evaporation were brittle. Casting was attempted with all polymers using the following solvent systems (as well as specifically indicated solvents in **Figure 5**): DCM, $CHCl_3$:CH_3CN (1:1 v:v), and $ClCH_2CH_2Cl$.

P1 and **P2**, which employed PF_6^- counter ions, resulted in very brittle films that could not be peeled from substrates (glass, silicon, or Teflon) in their entirety or even pieces larger than small flakes. The picture of **P2** is shown before removal from the casting mold. Polymers with $TFSI^-$ counter ions (**P3** - **P5**) resulted in visually brittle polymers, but unlike their PF_6^- counter parts these polymers were removable from the surfaces of glass, silicon, and Teflon.

Castings of **P3** and **P4** were also carried out by redissolving the polymers in $CHCl_3$ and allowing slow solvent evaporation. The results for all attempts were the same: brittle materials. Casting of **P3** was carried out using *o*-$C_6H_5Cl_2$ (**Figure 5**), which resulted in a material that was bendable for approximately one day while the material was plasticized. After this point, once *o*-$C_6H_5Cl_2$ had time to evaporate, the film became brittle. For polymers containing the $TFSI^-$ counter ion and cast from $CHCl_3$:CH_3COCH_3 (50:50 v:v), it took 6 to 24 hours after casting for the film to reach its full brittleness. During this time slight deformations could be made to the material, again attributable to plasticization.

Polymers **P1** to **P4** resulted in the formation of optically clear films, indicating amorphous polymers. **P5** formed a monolith that seemed to be opaque as seen in **Figure 5**.

Fibers were pulled from high concentration solutions of all of the polymers. **Figure 7** shows images of a fiber (**P3**) pulled from a concentrated equimolar solution of **17** and **23.** Fibers of **P3** were flexible and strong enough to resist fracture while being bent, as seen in images A and B. Films of **P5** were brittle and fractured upon applying mild force, while the corresponding fibers were capable of withstanding stress from bending and pulling.

It is believed that as the films dry, one of the monomers precipitates. There is a large solubility difference between the neutral cryptands and the paraquat salts.[16] As the paraquat precipitates, the biscryptand stays in solution and the stoichiometry of this step-growth process is thrown away from 1:1 and DP is greatly reduced. However, as fibers are drawn, the solvent is more rapidly flashed off, negating precipitation. Fiber formation can only occur above the entanglement molecular weight. Thus, these results clearly demonstrate the self-assembly of truly polymeric materials.

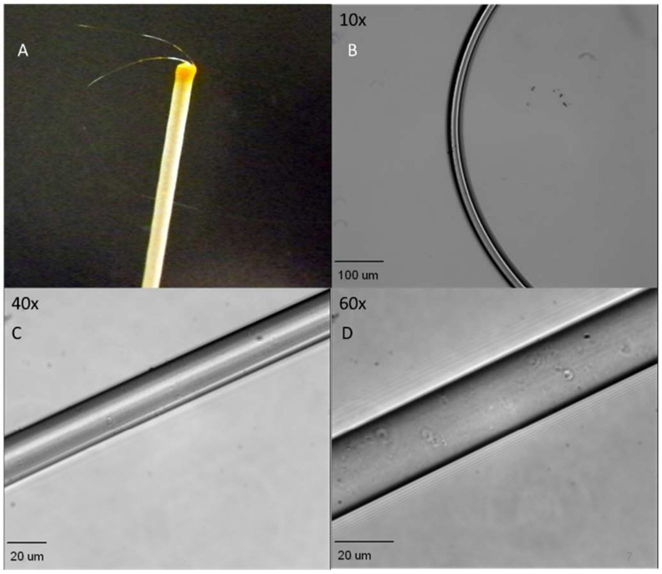


Figure 7. P3 fibers: A) color image taken on a black background, B) differential interference contrast image at 10x magnification, C**)** differential interference contrast image at 40x magnification, D) differential interference contrast image at 60x magnification.

Thermal measurements are summarized for **P1** – **P5** in **Table 1**. DSC traces show a clear loss of monomer crystallinity and the formation of amorphous polymers. For example, **Figure 8** shows an overlay of DSC traces for monomers **17** and **23** along with the resulting polymer **P3**. T_g values for polymers **P1** – **P5** vary in the range of 44 to 103 °C. By direct comparison of polymers **P1** and **P3**, changing from a PF_6^- to a $TFSI^-$ counter ion results in lowering the T_g by 59 °C; such plasticization effects have been observed in covalent polymers, particularly polymerized ionic liquids.[17] This decrease could be ascribed to the larger volume [17d] of the unsymmetrical, highly delocalized $TFSI^-$ anion and/or its lower ion pairing constant relative to the more symmetrical and compact PF_6^- anion. **P2** produced from guest monomer **18** (PF_6^- counter ion and C_{10} linker) and host monomer **16** (a hydroquinone linkage) provided the highest T_g (112 °C). By comparison of **P2** and **P1** there is no difference in thermal stability, but **P2** has a 9 °C higher T_g than **P1**. However, comparing **P5** and **P4**, both with the ditopic guest **21**, the T_g values are virtually identical for the hydroquinone linker vs. the C_{10} linker.

Table 1. Thermal Properties of Polymers **P1** - **P5**.

Host	Guest (linker X^-)	Polymer	T_g (°C)	TGA 5 % wt loss (°C)
17 (C_{10})	**18** (C_{10} PF_6)	**P1**	103	217
16 (HQ)*	**18** (C_{10} PF_6)	**P2**	112	216
17 (C_{10})	**23** (C_{10} TFSI)	**P3**	44	223
17 (C_{10})	**21** (Bn TFSI)**	**P4**	78	224
16 (HQ)	**21** (Bn TFSI)	**P5**	76	218

* HQ = hydroquinone linkage.
** Bn = benzylic linkage.

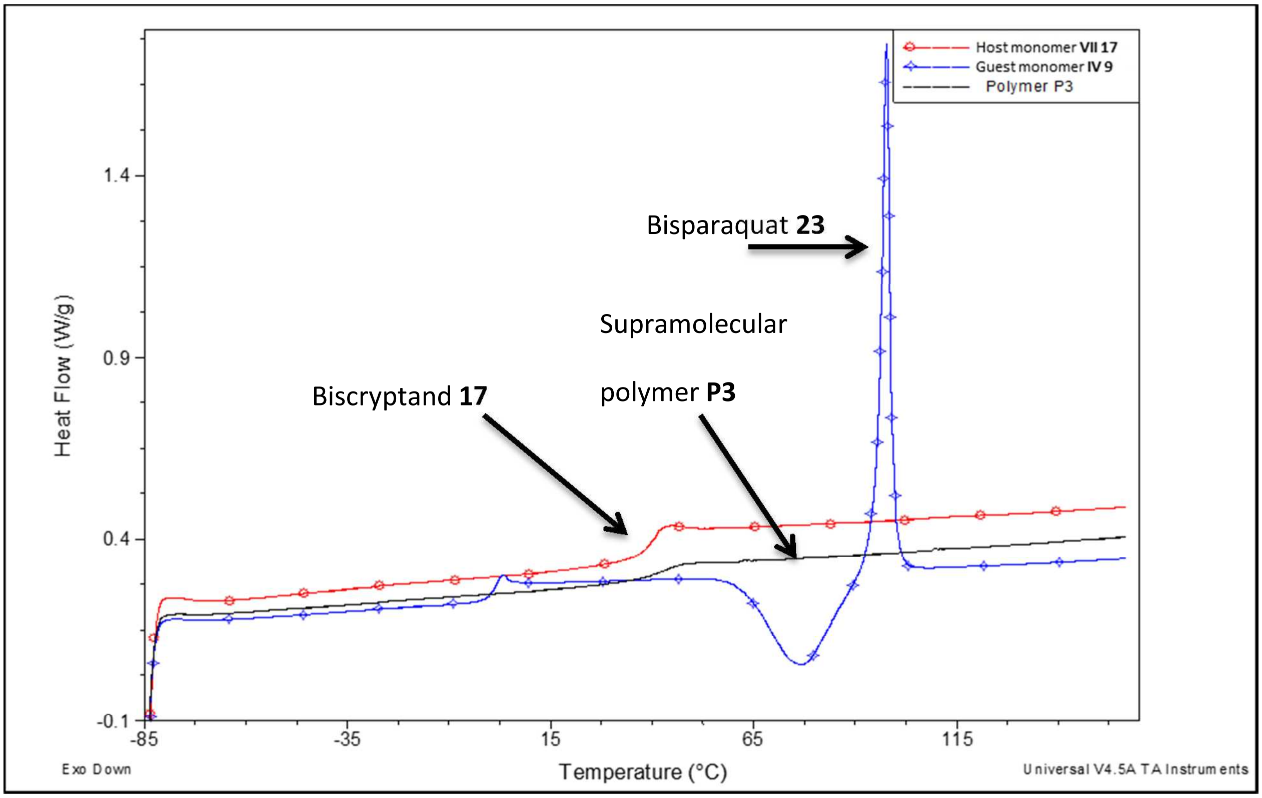


Figure 8. DSC curves of third heating scans of monomer **17,** monomer **23**, and polymer **P3** at 5 °C/min.

Analysis via TGA showed 5 % weight losses for polymers **P1** – **P5** closely grouped in the range of 216 to 224 °C (**Figure 9**). Degradation patterns varied, dependent upon the guest monomer and counterion; c. f. **P1** and **P2** with "less stable" PF_6^- counter ions vs. **P3** - **P5** with TFSI counter ions.

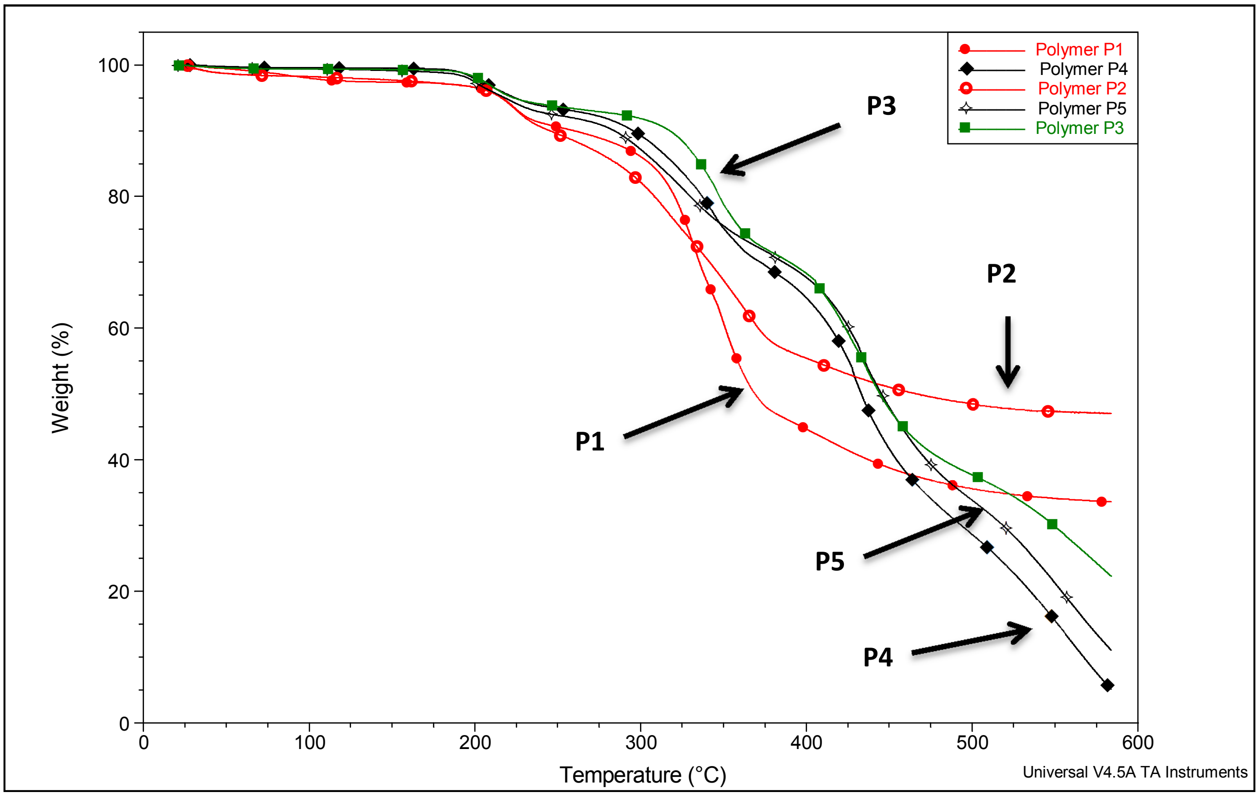


Figure 9. TGA overlay of polymers **P1** - **P5** using a heating rate of 20 °C/min under N_2.

CONCLUSIONS

Aryl bromide cryptands **1** and **3** produced the respective biscryptands **2** and **4** through Ullmann reactions. ITC results indicated that these ditopic hosts bind paraquats anti-cooperatively and we thus abandoned this approach to biscryptands. Biscryptand **6** was similarly synthesized to extend the linkage between the cryptand units, but was abandoned in favor of **16** and **17**, which were produced directly from reactions of tetra(acid chloride)s **11** and **14** with crown diol **15**. Importantly, the complexation of ditopic biscryptand **16** with monotopic paraquat derivative **2b** demonstrated highly positive cooperativity.

Five high molecular weight supramolecular polymers, **P1** – **P5**, were self-assembled in solution from biscryptands and bisparaquats as AA/BB monomer pairs. Fibers were drawn from concentrated solutions. Brittle films were cast from various solvents. The glass transition temperature was reduced by 59 □ by changing from PF_6^- to $TFSI^-$ counterions in **P1** vs. **P3**. T_gs ranged from 44 °C for **P3** to 112 °C for **P2**; all 5 % weight loss values were grouped in the range of 217 to 224 °C. **P3** was found to have a critical monomer concentration of 37 mM and the slope at high concentration, 3.55, was the theoretical maximum and the highest reported for an AA/BB pseudorotaxane supramolecular polymer. Development of films suitable for mechanical property evaluation will need to focus on processing techniques; one possible solution may be spin casting, since the solvent is removed quickly.

EXPERIMENTAL

Measurements: ^{1}H-NMR spectra were obtained on JEOL ECLIPSE-500, BRUKER-500, and AGILENT-NMR-vnmrs400 spectrometers at 23 ^{o}C. ^{13}C-NMR spectra were collected at 125 MHz and 101 MHz on these instruments at 23 ^{o}C. HR-MS were obtained using an Agilent LC-ESI-TOF system; CH_3CN was the solvent in all cases. Reagents were purchased and used as received without further purification. TGA data were obtained on a TA Instrument TGA Q500 under N_2. DSC data were obtained on a TA Instrument Q2000 differential scanning calorimeter under N_2. Viscosities were measured with a Cannon-Ubbelohde semi-micro dilution viscometer. Light microscopy was performed by Dr. Michelle B. Price using an Olympus IX81 Epifluorescene microscope. Fibers were H_2O-mounted between two coverslips and imaged using differential interference contrast (DIC) microscopy at 10X magnification (with a H_2O-immersion objective), 40X magnification (using an oil-immersion objective) and 60X magnification (using an oil-immersion objective). Images were captured with an EMCCD Rolera-MGI FAST 1394 monochromatic camera (Olympus) and processed using Slidebook 3I software.

General procedure 1. 4-Bromopyridine-2,6-dicarbonyl dichloride. 4-Bromopyridine-2,6-dicarboxylic acid [18] (0.724 g, 2.94 mmol) and $SOCl_2$ (5 mL, 0.07 mol) and DMF (1 drop) were held at reflux under N_2 4 h with magnetic stirring. Excess $SOCl_2$ was removed by distillation and the off-white material, 0.832 g (100 %), was used without purification.

General procedure 2. Dibenzo-30-crown-10-based 4-bromopyridyl cryptand (1b). Crown ether diol **15** [4g] (0.257 g, 0.430 mmol) and freshly prepared 4-bromopyridine-2,6-dicarbonyl dichloride (0.122 g, 0.430 mmol) were each dissolved in 50.0 mL of freshly distilled DCM. The two solutions were loaded into plastic syringes whose metal needles were replaced with HPLC tubing and added via syringe pump at 1 mL/h to pyridine (2.4 mL) in freshly distilled DCM (1.5 L). After additions were complete, the reaction mixture was stirred for 3 days, after which time solvent was removed by rotary evaporation and the resulting solid was dissolved in $CHCl_3$, washed with 1M HCl (x 1), H_2O (x 3), followed by drying over Na_2SO_4. The mixture was filtered and solvent was removed by rotary evaporation. The resulting residue was passed through a neutral Al_2O_3 column, eluting with $CHCl_3$:CH_3OH (97:3 v:v); the first eluting band contained the product: 81.1 mg (43%), mp 144.1 – 148.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 2H), 6.94 (m, 2H), 6.93 (s, 2H), 6.78 (d, *J* = 9 Hz, 2H), 5.33 (s, 4H), 4.21 – 4.12 (m, 4H), 4.04 – 3.97 (m, 4H), 3.95 – 3.90 (m, 4H), 3.86 – 3.79 (m, 4H), 3.70 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.80, 148.99, 148.89, 148.40, 138.14, 128.17, 127.98, 121.60, 114.21, 113.94, 70.98, 70.75, 70.72, 70.61, 69.68, 69.46, 68.97, 68.79, 67.60 (19 signals expected and 19 signals found). High res MS: calc. for $C_{37}H_{48}N_2O_{14}Br$ $[M + NH_4]^{+1}$ *m/z* 823.2283, found *m/z* 823.2300 (error -2.1 ppm).

Biscryptand 3 (dibenzo-30-crown-10-based pyridyl cryptand linked directly at the 4-pyridyl position). Bromocryptand **1b** (34.7 mg, 0.0430 mmol), $Pd(OAc)_2$ (2.1 mg, 0.0094 mmol), PPh_3 (18.9 mg, 0.072 mmol), and Na_2CO_3 (21.8 mg, 0.206 mmol) in DMF (20 mL) were stirred in an oil bath at 90 °C under N_2 for 36 h. A portion of solvent was removed by rotary evaporation and the remaining mixture was dissolved in $CHCl_3$ and washed with 1M HCl (2x), H_2O (3x), and dried over Na_2SO_4. After filtration and evaporation of the solvent, chromatography on neutral Al_2O_3 was used to isolate the coupled biscryptand product [EtOAc:DCM:CH_3OH (30:30:2 v:v:v)]: 15.8 mg (25%), mp 107.8-114.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (s, 2H), 6.98 (d, *J* = 8 Hz, 4H), 6.80 (d, *J* = 8 Hz, 2H), 5.40 (s, 4H), 4.18 (t, *J* = 4, 4H), 4.03 (t, *J* = 4, 4H), 3.93 (t, *J* = 4, 4H), 3.84 (t, *J* = 4, 4H), 3.70 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.47, 150.02, 149.20, 149.04, 146.54, 128.06, 125.60, 121.94, 114.41, 114.01, 71.08, 70.80 (overlap of two signals), 69.75, 69.56, 69.09, 68.89, 68.15 (18 peaks expected and 18 peaks found). High res MS: calc. for $C_{74}H_{92}N_3O_{28}$ $[M+NH_4]^+$ *m/z* 1470.5862, found *m/z* 1470.5845 (error -1.2 ppm).

Bis(*m*-phenylene)-32-crown-10-based 4-bromopyridyl cryptand (4). General procedure 2 was used with the diacid chloride (0.153 g, 0.541 mmol), bis(5-

hydroxymethyl-1,3-phenylene)-32-crown-10 [19] (0.323 g, 0.542 mmol) and pyridine (4.0 mL, 50 mmol) to produce a white solid that was purified by passing over neutral Al_2O_3, eluting with $CHCl_3$:CH_3OH (98:2 v:v) to give the desired product: 0.106 g (24%), mp 137.9 – 143.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 2H), 6.52 (m, 4H), 6.45 (m, 2H), 5.30 (s, 4H), 3.93 (m, 8H), 3.76 – 3.72 (m, 8H), 3.65 (m, 8H), 3.61 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.92, 160.11, 149.25, 137.07, 134.97, 131.42, 106.49, 102.27, 71.03, 70.84, 69.69, 67.94, 67.71 (13 signals expected and 13 signals found). High res MS: calc. for $C_{37}H_{48}N_2O_{14}{}^{79}Br$ $[M + NH_4]^+$ *m/z* 823.2283, found *m/z* 823.2278 (error 0.6 ppm); calc. for $C_{37}H_{48}N_2O_{14}{}^{81}Br$ $[M + NH_4]^+$ *m/z* 825.2263, found *m/z* 825.2269 (error 0.7 ppm).

Biscryptand 5 [bis(*m*-phenylene)-32-crown-10-based pyridyl cryptand linked directly at the 4-pyridyl position]. Bromocryptand **4** (18.0 mg, 0.0223 mmol), $Pd(OAc)_2$ (2.2 mg, 9.8 μmol), PPh_3 (5.2 mg, 20 μmol), DMF (4 mL), and Na_2CO_3 (22 mg, 0.21 mmol) were stirred in an oil bath at 90 °C under N_2 for 42 h, after which the mixture was diluted with $CHCl_3$ and washed with 1 M HCl (2x), H_2O (3x), and dried over Na_2SO_4. The solution was filtered, followed by solvent removal. Product isolation was achieved using preparative scale TLC [neutral Al_2O_3 eluting with EtOAc:DCM:CH_3OH (30:30:1.5 v:v:v)]: 1.8 mg (11 %), mp: 96.1-105.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 3H), 6.58 (m, 6H), 6.50 – 6.47 (m, 7H), 5.39 (s, 8H), 4.05 – 4.00 (m, 9H), 3.82 (s, 11H), 3.79 – 3.74 (m, 18H), 3.72 – 3.61 (m, 70H). Integration was poor and indicated impurities, but further purification was not possible due to the small amount of material; also no 13C NMR spectrum was acquired.. High res MS: calc. for $C_{74}H_{88}N_2O_{28}$ $[M]^+$ *m/z*

1452.5524, found *m/z* 1452.5546 (error 1.6 ppm); calc. for $C_{74}H_{92}N_3O_{28}$ $[M + NH_4]^+$ *m/z* 1470.5862, found *m/z* 1470.5848 (error 0.95 ppm).

Biscryptand 6 (dibenzo-30-crown-10-based pyridyl cryptand employing a biphenyl linkage). A mixture of DMF (5 mL), bromobenzyl 30-crown-10 cryptand **1c**[6] (37.0 mg, 40.5 μmol), $Pd(OAc)_2$ (1.0 mg, 4.5 μmol) and K_2CO_3 (31.7 mg, 229 μmol) under N_2 was held at reflux for 17 h and the solvent was removed by rotary evaporation. The crude material was dissolved in DCM, washed with 1 M HCl (7x), H_2O (5x), and dried over Na_2SO_4. The solution was filtered and rotary evaporation gave a material which was passed over neutral Al_2O_3, eluting with $CHCl_3$:CH_3OH (97:3 v:v): 4.2 mg (12%), mp 113.4-120.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 4H), 7.66 (d, *J* = 8 Hz, 4H), 7.54 (d, *J* = 8 Hz, 4H), 6.94 (d, *J* = 8 Hz, 8H), 6. 77 (d, *J* = 8 Hz, 4H), 5.31 (s, 8H), 5.29 (s, 4H), 4.18 – 4.14 (m, 8H), 4.02 – 3.97 (m, 8H), 3.95 – 3.90 (m, 8H), 3.83 – 3.79 (m, 8H), 3.74 (m, 8H), 3.71 – 3.68 (m, 16H), 3.64 (m, 8H). ^{13}C NMR spectrum not obtained due to the small amount of material. High res MS: calc. for $C_{88}H_{104}N_3O_{30}$ $[M + NH_4]^+$ *m/z* 1683.6733, found *m/z* 1683.6582 (error -8.97 ppm).

Tetraisopropyl 4,4'-(((*p*-phenylenebis(oxy))bis(ethane-2",1"-diyl))bis(oxy))bis(pyridine-2"',6"'-dicarboxylate) (9). A mixture of CH_3CN (100 mL), ditosylate **8**[20] (5.78 g, 11.4 mmol), hydroxypyridine diester **7**[12] (6.79 g, 25.4 mmol), and K_2CO_3 (5.85 g, 42.3 mmol) was held at reflux for 24 h with magnetic stirring under N_2. After cooling to room temperature the mixture was filtered through Celite® p545 and solvent was removed by rotary evaporation. The crude material was dissolved in DCM and washed with aq. Na_2CO_3 (x2), saturated NaCl (x3), and dried over Na_2SO_4. The product was obtained after filtration and removal of solvent: 6.21 g (78%) of colorless solid, mp 193.1-195.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 4H), 6.89 (s, 4H), 5.30 (hept, *J* = 6 Hz, 4H), 4.52 – 4.46 (m, 4H), 4.37 – 4.32 (m, 4H), 1.43 (d, *J* = 6 Hz, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.53, 164.10, 153.00, 150.64, 115.82, 114.18, 70.21, 67.32, 66.73, 21.81 (10 peaks expected and 10 peaks found). High res MS: calc. for $C_{36}H_{45}N_2O_{12}$ $[M+H]^+$ *m/z* 697.2967, found *m/z* 697.3000 (error 4.7 ppm)

4,4'-(((*p*-Phenylenebis(oxy))bis(ethane-2”,1”-diyl))bis(oxy))bis(pyridine-2’”,6’”-dicarboxylic acid) (10). A mixture of tetraester **9** (0.379 g, 0.544 mmol) in THF (50 mL) and 10% aqueous KOH (50 mL) was stirred at reflux for 27 h. THF was removed by rotary evaporation and conc. HCl was added until pH=1. The precipitate was collected and washed with cool H_2O and dried: 0.287 g (100%) of a colorless solid, mp 260.0-265.0 □ (dec). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 (s, 4H), 6.93 (s, 4H), 4.57 (s, 4H), 4.30 (s, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.53, 165.26, 152.42, 149.76, 115.49, 113.69, 67.61, 66.43 (8 peaks expected and 8 peaks found). HR MS: calc. for $C_{24}H_{21}O_{12}N_2$ $[M + H]^+$ *m/z* 529.1089, found *m/z* 529.1084 (error 0.9 ppm); calc. for $C_{48}H_{40}O_{24}N_4Na$ $[2M + Na]^+$ *m/z* 1079.1925, found *m/z* 1079.1926 (error 0.1 ppm).

4,4'-(((*p*-Phenylenebis(oxy))bis(ethane-2”,1”-diyl))bis(oxy))bis(pyridine-2’”,6’”-dicarbonyl dichloride) (11). Tetra-acid **10** (0.112 g, 0.212 mmol), $SOCl_2$ (3 mL, 0.04 mol) and DMF (1 drop) were held at reflux under N_2 for 12 h and the solvent was removed under vacuum. The material was used directly without further purification; the yield was assumed to be quantitative.

Tetraisopropyl 4,4'-(decane-1”,10”-diylbis(oxy))bis(pyridine-2,6-dicarboxylate) (12). A mixture of CH_3CN (200 mL), $Br(CH_2)_{10}Br$ (7.04 g, 23.5 mmol), 4-hydroxypyridine diester **7** [12] (12.78 g, 47.82 mmol) and K_2CO_3 (8.50 g, 61.5 mmol) under N_2 was held at reflux for 4 days, after which it was filtered through Celite® p545 and the solvent was removed by rotary evaporation. The crude material was dissolved in DCM and washed with Na_2CO_3 (2x), saturated NaCl (4x), and dried over Na_2SO_4. Filtration and removal of the solvent provided the desired product as a colorless solid: 15.63 g (99%), mp 76.8-78.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 4H), 5.29 (hept, *J* = 6 Hz, 4H), 4.12 (t, *J* = 6 Hz, 4H), 1.89 – 1.80 (m, 4H), 1.76 – 1.27 (m, 36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.92, 164.29, 150.52, 114.08, 70.13, 68.91, 29.44, 29.27, 28.80, 25.88, 21.81 (11peaks expected and 11 peaks found). High res MS: calc. for $C_{36}H_{53}N_2O_{10}$ $[M+H]^+$ *m/z* 673.3695, found *m/z* 673.3707 (error 1.8 ppm)

4,4'-(Decane-1”,10”-diylbis(oxy))bis(pyridine-2,6-dicarboxylic acid) (13). Tetraester **12** (1.86 g, 2.76 mmol), THF (50 mL) and 10 wt. % KOH (50 mL) were held at reflux for 24 h, followed by the removal of THF by rotary evaporation. The solution was acidified to pH 1 using conc. HCl and the precipitate was collected via filtration: 1.08 g (78 %) of a colorless solid, mp 192.8-196.1 □. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.69 (s, 4H), 4.21 (t, *J* = 6 Hz, 4H), 1.85 – 1.68 (m, 4H), 1.35 (m, 12H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 166.71, 165.27, 149.65, 113.51, 68.69, 28.83, 28.59, 28.12, 25.21 (9 peaks expected and 9 peaks found). HR MS: calc. for $C_{24}H_{29}O_{10}N_2$ $[M + H]^+$ *m/z* 505.1817, found *m/z* 505.1840 (error -4.6 ppm).

4,4'-(Decane-1”,10”-diylbis(oxy))bis(pyridine-2,6-dicarboxylic acid chloride) (14). Tetra-acid **13** (0.202 g, 0.401 mmol), $SOCl_2$ (2.0 mL, 28 mmol) and DMF (1 drop) under N_2 were held at reflux for 12 h and the solvent was removed under vacuum. The material was used directly without further purification, assuming the yield was quantitative.

Biscryptand 16 (dibenzo-30-crown-10-based pyridyl cryptand containing a hydroquinone linkage). A mixture of dry DCM (700 mL), crown ether diol **15** [4g] (0.5291 g, 0.8868 mmol), pyridine (2 mL) and acidic Al_2O_3 (1.00 g) was stirred for 1 h. Tetra-acid chloride **11** (0.2670 g, 0.4434 mmol) dissolved in 20 mL of DCM was added. Stirring was continued for 32 h; the mixture was filtered through a small plug of neutral Al_2O_3. The solvent was removed by rotary evaporation and the crude material was taken up in DCM and washed with 1 M HCl (3x), H_2O (3x) and dried over Na_2SO_4. After filtration the solvent was removed by rotary evaporation and the material was purified using flash column chromatography, eluting with DCM to MeOH over neutral Al_2O_3: 0.1697 g (23%) of a colorless solid, mp 197.6-200.5 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 4H), 6.99 – 6.93 (m, 8H), 6.90 (m, 4H), 6.79 - 6.77 (m, 4H), 5.31 (s, 8H), 4.53 – 4.48 (m, 4H), 4.36 (m, 4H), 4.20 – 4.14 (m, 8H), 4.03 – 3.99 (m, 8H), 3.96 – 3.92 (m, 8H), 3.85 – 3.80 (m, 8H), 3.75 (m, 8H), 3.73 – 3.68 (m, 16H), 3.65 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.66, 164.84, 153.04, 150.10, 149.05, 148.94, 128.16, 121.73, 115.89, 114.61, 114.32, 114.00, 71.02, 70.79, 70.76, 70.65, 69.72, 69.49, 69.03, 68.84, 67.74, 67.46, 66.74 (23 signals expected and 23 signals found). High res MS: calc. for $C_{84}H_{102}N_2O_{32}$ $[M + 2H]^{+2}$ m/z 825.3203, found m/z 825.3223 (error 2.4 ppm); calc. for $C_{84}H_{100}N_2O_{32}•2NH_4$ $[M+2NH_4]^{+2}$ m/z 842.8484, found m/z 842.8493 (error 1 ppm); calc. for $C_{84}H_{100}N_2O_{32}$ $[M]^+$ *m/z* 1648.6259, found *m/z* 1648.6256 (error -0.19 ppm).

Biscryptand 17 (dibenzo-30-crown-10-based pyridyl cryptand containing a C_{10} linkage). A mixture of dry DCM (700 mL), crown ether diol **15** [4g] (0.4789, 0.8026 mmol), pyridine (2 mL) and acidic Al_2O_3 (1.0 g) was stirred for 1 h. Tetra-acid chloride **14** (0.2025 g, 0.4014 mmol) dissolved in 20 mL of DCM was added. Stirring was continued for 32 h; the mixture was filtered and the solvent was removed by rotary evaporation. The crude material was taken up in DCM and washed with 1 M HCl (3x), H_2O (3x) and dried over Na_2SO_4. After filtration the solvent was removed by rotary evaporation and the material was purified using flash column chromatography, eluting with DCM to MeOH over neutral Al_2O_3: 0.2828 g (43%) of a colorless solid, mp 103.9-106.2 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 4H), 6.97 – 6.92 (m, 8H), 6.77 (d, *J* = 9 Hz, 4H), 5.31 (s, 8H), 4.16 (m, 12H), 4.01 (m, 8H), 3.93 (m, 8H), 3.81 (m, 8H), 3.75 (m, 8H), 3.71 – 3.68 (m, 16H), 3.64 (m, 8H), 1.86 (m, 4H), 1.49 (m, 4H), 1.41 – 1.32 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.03, 165.00, 149.95, 149.04, 148.94, 128.19, 121.70, 114.52, 114.32, 114.02, 71.04, 70.81, 70.76, 70.66, 69.73, 69.49, 69.05, 68.86, 67.67, 29.43, 29.25, 28.76, 25.86 (24 peaks expected and 23 peaks found; it is believed that one peak overlaps another in the 71.04 to 70.66 region). HR MS: calc. for $C_{84}H_{108}N_2O_{30}$•H $[M+H]^+$ *m/z* 1625.7060, found *m/z* 1625.6921 (error -8.55 ppm); calc. for $C_{84}H_{108}N_2O_{30}$•NH_4 $[M+NH_4]^+$ 1642.7325, found *m/z* 1642.7185 (error 2.4 ppm); calc. for $C_{84}H_{108}N_2O_{30}$•Na $[M+Na]^+$ *m/z* 1647.6879, found *m/z* 1647.6753 (error 1.6 ppm).

1-Benzyl-[4,4'-bipyridin]-1-ium TFSI (19). A solution of CH_3COC for H_3 (200 mL), 4,4’-dipyridyl (5.02 g, 32.1 mmol) and $C_6H_5CH_2Br$ (3.2 mL, 27 mmol) was held at reflux for 45 min and cooled to room temperature. Half of the CH_3COCH_3 was removed by rotary evaporation and the solution was diluted with Et_2O and filtered. The solid was washed with Et_2O, air dried and 3.01 g of the precipitate was dissolved in 30 mL of H_2O and combined with a solution of LiTFSI (4.25 g, 14.0 mmol) in 10 mL of H_2O. The resultant mixture was stirred and extracted with DCM twice. The organic layers were combined and washed with H_2O (x3). Removal of solvent provided the desired product as a colorless solid: 4.71 g (97%), mp 90.8–92.5 □. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 7 Hz, 2H), 8.83 (d, *J* = 6 Hz, 2H), 8.22 (d, *J* = 7 Hz, 2H), 7.63 (d, *J* = 6 Hz, 2H), 7.51–7.39 (m, 5H), 5.75 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.89, 151.48, 144.80, 140.83, 131.52, 130.59, 130.01, 129.45, 126.16, 121.46, 119.80 (q, *J* = 321 Hz), 65.00 (12 peaks expected and 12 peaks found). High res MS: calc. for $C_{19}H_{15}N_2$ [M-TFSI]$^+$ *m/z* 247.1230, found *m/z* 247.1223 (error -3 ppm).

1',1'''-(((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(methylene))bis(1-benzyl-[4,4'-bipyridine]-1,1'-diium) TFSI (21). A solution of 1,5-bis[*p*-(bromomethyl)phenoxy]pentane,[21] (0.745 g, 1.68 mmol), CH_3CN (100 mL) and 1-benzyl-[4,4'-bipyridin]-1-ium TFSI (**19**, 1.86 g, 3.52 mmol) was held at reflux under N_2 for 24 h. After it had cooled to room temperature, the mixture was filtered and the solid was washed with CH_3CN, DCM, and dried on the filter. The precipitate was dissolved in 30 mL of boiling H_2O and mixed with a solution of LiTFSI (1.1 g, 4.2 mmol) in 10 mL of H_2O. The mixture was cooled, the H_2O was decanted and the semi-solid material was triturated with H_2O (x3), filtered and dried in vacuum: a yellow solid, 2.90 g (91%), which was purified by recrystallization from H_2O-CH_3COCH_3 three times: 1.43 g (45%), mp 116.4–118.8 □. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 9.49 (m, 8H), 8.73 (m, 8H), 7.61 (m, 8H), 7.54–7.41 (m, 6H), 7.03 (d, *J* = 9 Hz, 4H), 5.96 (s, 4H), 5.86 (s, 4H), 4.00 (t, *J* = 6 Hz, 4H), 1.85–1.72 (m, 4H), 1.61–1.51 (m, 2H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 160.11, 149.85, 149.66, 146.13, 145.85, 134.51, 131.26, 129.98, 129.73, 129.36, 127.70, 127.63, 126.19, 119.94 (q, *J* = 323 Hz), 115.52, 68.01, 64.03, 63.73, 28.77, 22.60 (20 signals expected and 19 signals found, two peaks are believed to overlap at 126.19). High res MS: calc. for $C_{61}H_{52}O_{18}F_{24}N_8NaS_8$ [M+Na]$^+$ *m/z* 1919.0674, found *m/z* 1919.0505 (error –8.81 ppm); calc. for $C_{61}H_{52}O_{18}F_{24}N_8NaS_8$ [M-TFSI]$^+$ *m/z* 1616.1604, found *m/z* 1616.1531 (error 4.5 ppm).

1',1'''-(Decane-1,10-diyl)bis(1-methyl-[4,4'-bipyridine]-1,1'-diium) TFSI (23). 1-Methyl-[4,4'-bipyridin]-1-ium TFSI [22] (**22**, 6.10 g, 13.5 mmol) and $Br(CH_2)_{10}Br$ (1.64 g, 5.47 mmol) in CH_3CN (75 mL) were held at reflux under N_2 for 12 h. The mixture was allowed to cool and the solid was collected on a glass frit and washed with cold CH_3CN followed by DCM. The solid was dissolved in H_2O and mixed with a solution of LiTFSI (4.01 g, 14.0 mmol) in H_2O (10 mL). The precipitate was collected and recrystallized from H_2O to yield an off-white product: 6.53 g (75 %), which was recrystallized from H_2O -CH_3COCH_3, mp 93.2–94.4 □. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.32 (d, *J* = 7 Hz, 4H), 9.24 (d, *J* = 7 Hz, 4H), 8.74 – 8.69 (m, 8H), 4.63 (t, *J* = 8 Hz, 4H), 4.40 (s, 6H), 1.94 (s, 4H), 1.40–1.18 (m, 12H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 149.03, 148.62, 147.04, 146.15, 126.95, 126.49, 119.89 (q, *J* = 323 Hz), 61.37, 48.46, 31.24, 29.28, 28.90, 25.98 (13 signals expected and 13 signals found). High res MS: calc. for $C_{40}H_{42}N_7O_{12}S_6F_{18}$ [M - TFSI]$^+$ *m/z* 1322.0923, found *m/z* 1322.0839 (error 6.4 ppm); calc. for $C_{36}H_{42}N_6O_8S_4F_{12}$ [M - 2TFSI]$^+$ *m/z* 521.0872, found *m/z* 521.0843 (error 5.6 ppm).

Example of an Isothermal Titration Microcalorimetry Experiment: Biscryptand 3 with Praquat 2a: The titration was run in CH_3COCH_3 at 25 ºC using a Microcal MCS ITC. The cryptand was in the cell and the paraquat was in the syringe. The concentrations were 26.58 mM for the paraquat and 0.5002 mM for the cryptand. Titration parameters were 50 injections of 2 µl each. The time per injection was 3 min. The primary filter period was 1 sec and lasted for 60 sec. The secondary filter period was 3 sec and lasted 120 sec. The titration was run on the high gain system using a 90 % reference offset. The system was fit with a two sets of sites model. The first datum point was not used.

Supramolecular Polymer P1. **17** (200.4 mg, 0.1233 mmol) in 2 mL of $CHCl_3$ and **18** (131.0 mg, 0.1233 mmol) in 2 mL of CH_3COCH_3 were mixed and a film was cast by slow evaporation (331.4 mg). After mixing the solution was yellow, but as the solvent evaporated, the film became more orange.

Supramolecular Polymer P2. **16** (199.7 mg, 0.1211 mmol) in 2 mL of $CHCl_3$ and **18** (128.7 mg, 0.1211 mmol) in 2 mL of CH_3COCH_3 were mixed and a film was cast by slow evaporation (328.4 mg). After mixing the solution was yellow, but as the solvent evaporated, the film became more orange.

Supramolecular Polymer P3. **17** (1.4052 g, 0.8643 mmol) in 2 mL of $CHCl_3$ and **23** (1.3857 g, 0.8643 mmol) in 2 mL of CH_3COCH_3 were mixed and a film was cast by slow evaporation (2.7909 g). After mixing the solution was yellow, but as the solvent evaporated, the film became more orange.

Supramolecular Polymer P4. **17** (203.1 mg, 0.1249 mmol in 2 mL of $CHCl_3$ and **21** (237.1 mg, 0.1249 mmol) in 2 mL of CH_3COCH_3 were mixed and a film was cast by slow evaporation (440.2 mg). After mixing the solution was yellow, but as the solvent evaporated, the film became more orange.

Supramolecular Polymer P5. **16** (203.9 mg, 0.1236 mmol) in 2 mL of $CHCl_3$ and **21** (234.5 mg, 0.1236 mmol) in 2 mL of CH_3COCH_3 were mixed and a film was cast by slow evaporation (438.4 mg). After mixing the solution was yellow, but as the solvent evaporated, the film became more orange.

SUPPORTING INFORMATION: Supporting Information is available free of charge on the ACS Publications website at DOI: ????.

^{1}H and ^{13}C NMR spectra, DSC and TGA traces, ITC titrations.

ACKNOWLEDGEMENT

We acknowledge and are thankful for support from the National Science Foundation (CHE-1106899, CHE-1507553). We thank Dr. Michelle B. Price for carrying out the optical microscopy.

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16. A reviewer suggested an alternative explanation. He or she states: “The brittleness of the P3 film is its intrinsic property. After the formation of host-guest complex, the solubility of the monomers should be “neutralized” and the monomer cannot easily precipitate out upon the film formation. If the film can be made thin enough, it will be flexible and bendable. For example, highly crystalline silicon wafer is also flexible and bendable when it is cut into very thin piece. In other words, the flexibility and bendability of the film or fiber from **P3** have no correlation with the precipitation of the monomer during fiber or film formation”.

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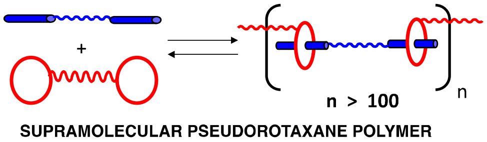
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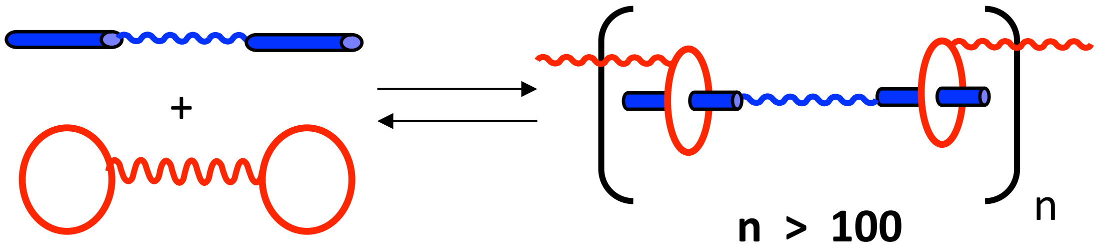

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