

## Chapter 19

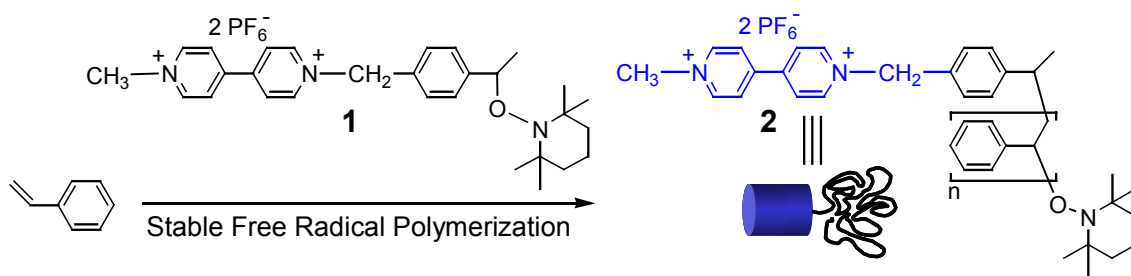
### **A Supramolecular Triarm Star Polymer from a Homotritopic Tris(Crown Ether) Host and a Complementary Monotopic Paraquat-Terminated Polystyrene Guest by a Supramolecular Coupling Method**

#### **19.1. INTRODUCTION**

The construction of analogs of traditional macromolecules by supramolecular methods is a topic of great current interest due to not only their topological importance but also their potential functions.<sup>1</sup> Recent examples include dendrimers from cooperative complexation of a homotritopic guest and complementary monotopic dendron hosts,<sup>2</sup> supramolecular modification of dendrimers,<sup>3</sup> a hyperbranched polymer from self-assembly of an AB<sub>2</sub> monomer,<sup>4</sup> and linear polymers from self-organization of well-defined building blocks.<sup>5</sup> Covalent star polymers have been widely studied.<sup>6,7</sup> General methods of preparing them are living polymerizations with multifunctional initiators, coupling reactions of macromolecular chains with multifunctional cores, and polymerizations of difunctional monomers with living polymer precursors as initiators.<sup>6b</sup> Here we report the preparation of the first supramolecular star polymer based on the pseudorotaxane complexation.<sup>8</sup> It is from self-assembly of a homotritopic tris(crown ether) host and a complementary monotopic paraquat-terminated polystyrene guest based on the bis(*m*-phenylene)-32-crown-10/paraquat recognition motif<sup>9</sup> by a supramolecular coupling method, a new method for fabrication of star polymers by using noncovalent interactions.

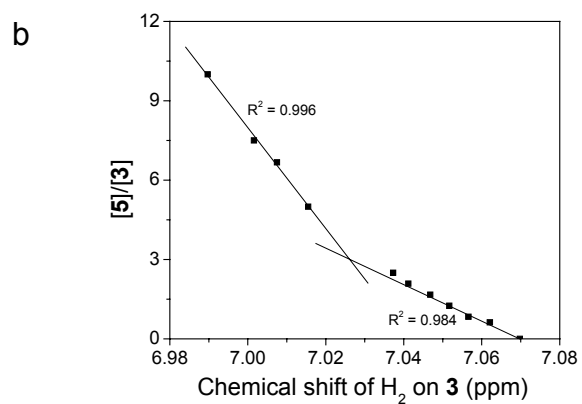
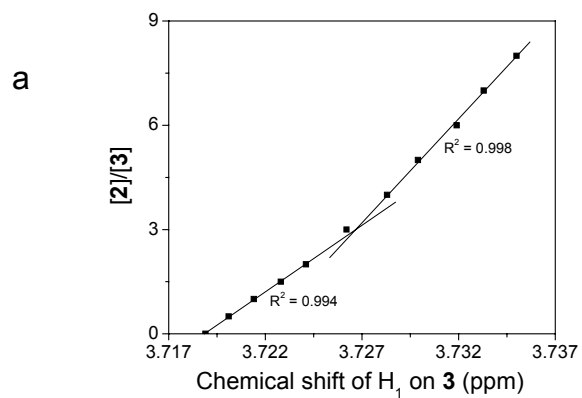
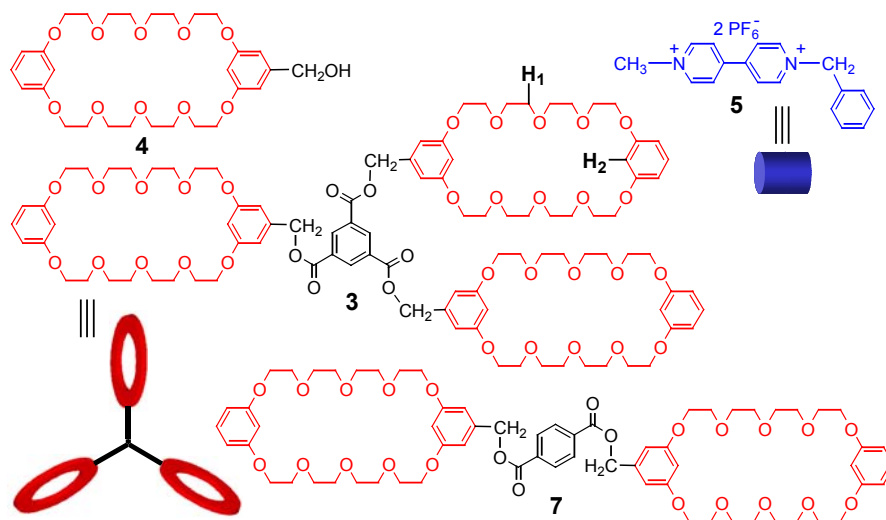
## 19.2. RESULTS AND DISCUSSION

The strategy we used to introduce a paraquat moiety at the end of every polystyrene chain is to utilize paraquat-functionalized initiator **1** in the stable free radical polymerization<sup>9</sup> of styrene. The polydispersity from GPC analysis of polymer **2** in 1-methyl-2-pyrrolidinone, 1.37, indicated the living nature of this polymerization.  $M_n$  from GPC analysis, 32.3 kg/mol, is close to the value, 35.0 kg/mol, determined from proton NMR integrations of peaks corresponding to pyridinium and aromatic protons. These results demonstrated that every polystyrene chain has a paraquat moiety at one of its two ends.



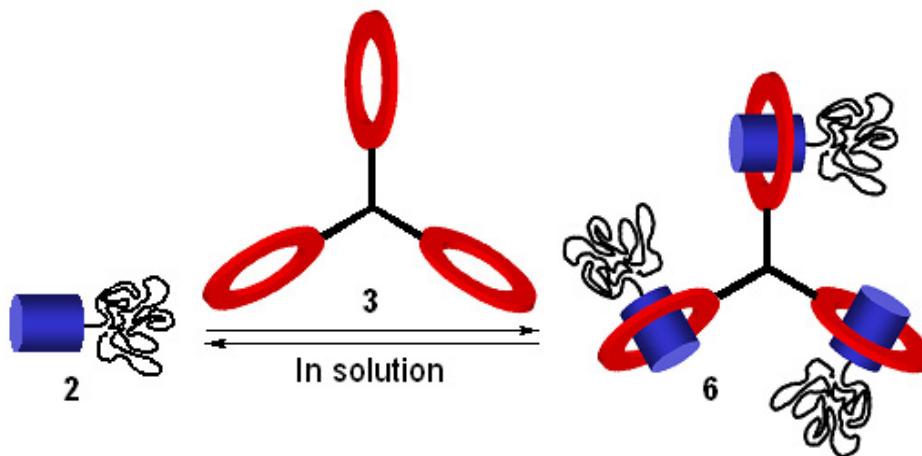
The homotritopic core molecule, **3**, was prepared by the reaction of monofunctional crown ether **4**<sup>10</sup> and 1,3,5-benzenetricarbonyl trichloride.

Chloroform solutions of host **3** and guest polymer **2** are yellow due to charge transfer interactions between electron-rich crown ether moieties on **3** and the electron-poor paraquat end unit on **2**. The complex between the homotritopic host **3** and monotopic paraquat-terminated polystyrene guest **2** has a 1:3 stoichiometry as demonstrated by a mole ratio plot (Figure 1a). The model system based on **3** and monotopic guest **5**<sup>5a</sup> also has a 1:3 stoichiometry (Figure 1b). Therefore, supramolecular triarm star polymer **6** forms from tritopic host **3** and monotopic polymeric guest **2** in solution (Scheme 1).

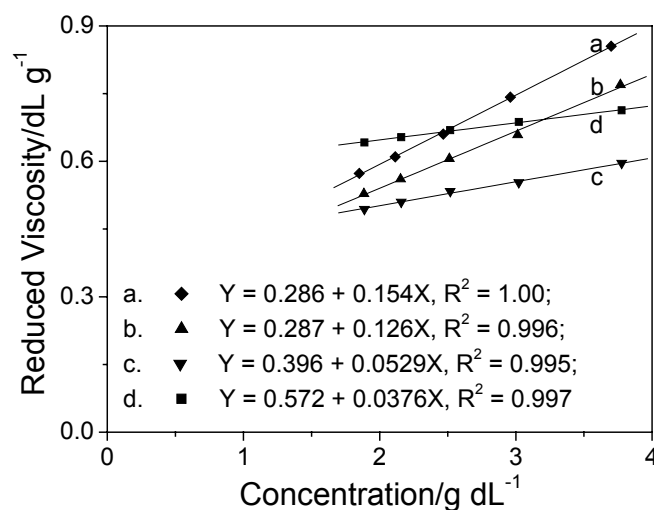


**Figure 1.** (a) Mole ratio plot for **3** and **2**, indicating 1:3 stoichiometry. The solvent is CDCl<sub>3</sub>. [3]<sub>0</sub> = 0.100 mM. (b) Mole ratio plot for **3** and **5**, indicating 1:3 stoichiometry. The solvent is 2:1 CD<sub>3</sub>COCD<sub>3</sub>:CDCl<sub>3</sub>. [3]<sub>0</sub> = 0.100 mM.

**Scheme 1.** Schematic illustration of the formation of a supramolecular triarm star polymer **6** from a homotritopic host **3** and monotopic polymeric guest **2**.

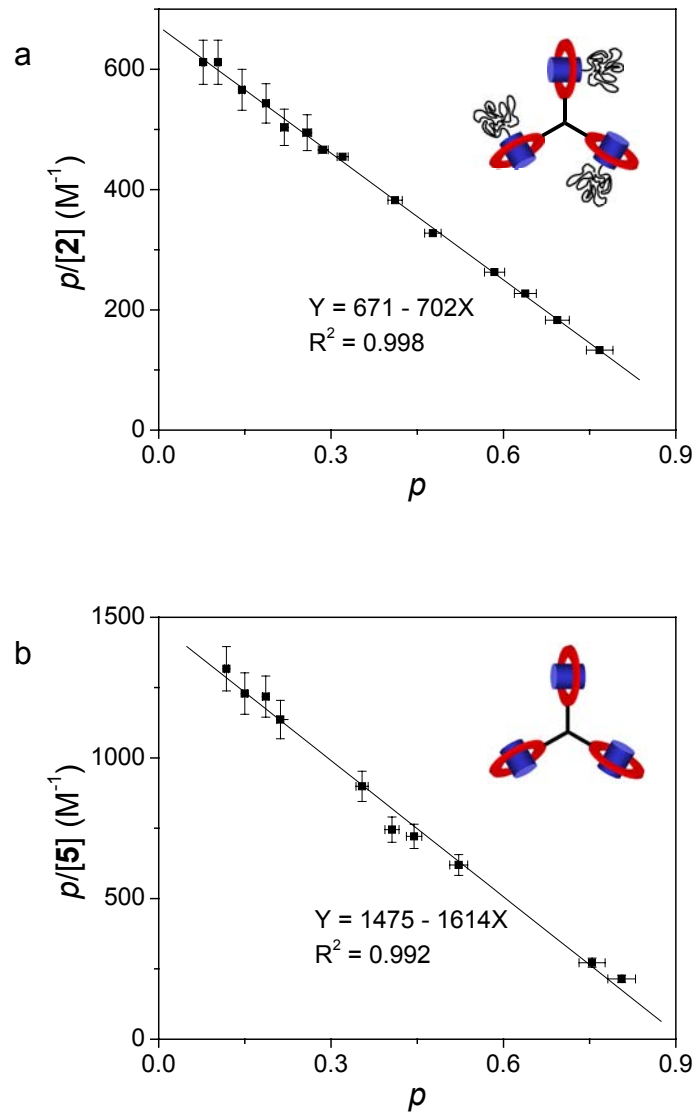


Viscosity studies (Figure 2) provided further evidence for the formation of supramolecular triarm star polymer **6**. As expected, the intrinsic viscosity,  $[\eta]$ , did not change from polymer **2** upon addition of monotopic host **4** (0.286 and 0.287 dL/g). However, it increased significantly (~33%) in the solution of ditopic host **7** and polymeric guest **2**,  $[\eta] = 0.396$  dL/g; this interaction corresponds to supramolecular chain extension. And finally, the solution of tritopic host **3** and polymeric guest **2** has an intrinsic viscosity (0.572 dL/g) nearly double that of **2** itself, consistent with formation of the supramolecular triarm star polymer **6**.



**Figure 2.** Reduced viscosity as a function of concentration (solutions in chloroform at RT): (a) polymeric guest **2**, (b) monotopic host **4** and polymeric guest **2** (molar ratio 1:1), (c) ditopic host **7** and polymeric guest **2** (molar ratio 1:2), and (d) tritopic host **3** and polymeric guest **2** (molar ratio 1:3).

In order to study the relationship among the three crown ether binding sites of **3** during the complexation with polymeric guest **2**, proton NMR characterizations were done on a series of chloroform solutions for which the initial concentration of host **3** was kept constant at 0.100 mM, while the initial concentration of guest **2** was systematically varied. Based on these data, the complexed fraction,  $p$ , of crown ether units was determined<sup>11</sup> and a Scatchard plot<sup>13</sup> was made (Figure 3a). The linear nature of this plot demonstrated that the complexation between host **3** and polymeric guest **2** is statistical, i. e., the three crown ether binding sites behave independently. From the intercept and the slope of the plot the average association constant<sup>14</sup> ( $K_{av}$ ) is  $687 (\pm 82) M^{-1}$ , which is much smaller than the value,  $1550 (\pm 186) M^{-1}$ , for the model system based on host **3** and model guest **5** in a more polar solvent (Figure 2b),<sup>15</sup> reflecting the steric effect of the polystyryl chains of **2** in host-guest complexation.



**Figure 3.** Scatchard plots for the complexations of homotrimeric host **3** with (a) monotopic paraquat-terminated polystyrene guest **2** in  $\text{CDCl}_3$  and (b) model monotopic paraquat guest **5** in 2:1  $\text{CD}_3\text{COCD}_3:\text{CDCl}_3$  at 22 °C.  $p$  = complexed fraction of crown ether units. Error bars in  $p$ :  $\pm 0.03$  absolute; error bars in  $p/[2]$  and  $p/[5]$ :  $\pm 0.06$  relative.

### 19.3. CONCLUSIONS

In summary, the first supramolecular star polymer based on the host-guest complexation was prepared by a supramolecular coupling method. The trapping of the paraquat moieties in this polymer by introducing appropriate blocking groups will produce a mechanically interlocked star polymer. We also provided a new method of preparing guest-terminated macromolecular building blocks, which are very valuable in fabrication of well-defined macromolecular architectures by self-assembly.

### 19.4. ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (DMR0097126) and the Petroleum Research Fund (40223-AC7). We thank Juan Yang for GPC analysis of **2**, Prof. James E. McGrath for use of his GPC instrument, and the National Science Foundation for funding the purchase of the Oxford Diffraction Xcalibur2 diffractometer (CHE-0131128). We are grateful indeed to the reviewer who pointed out Fraser et al.'s work (reference 8).

### 19.5. SUPPORTING INFORMATION

#### *Viscosity Measurements*

Reduced viscosities were measured with acetonitrile/chloroform (1:1) as the solvent on a Cannon-Ubbelohde semi-micro dilution viscometer with 200 centipoise inner diameter capillary.

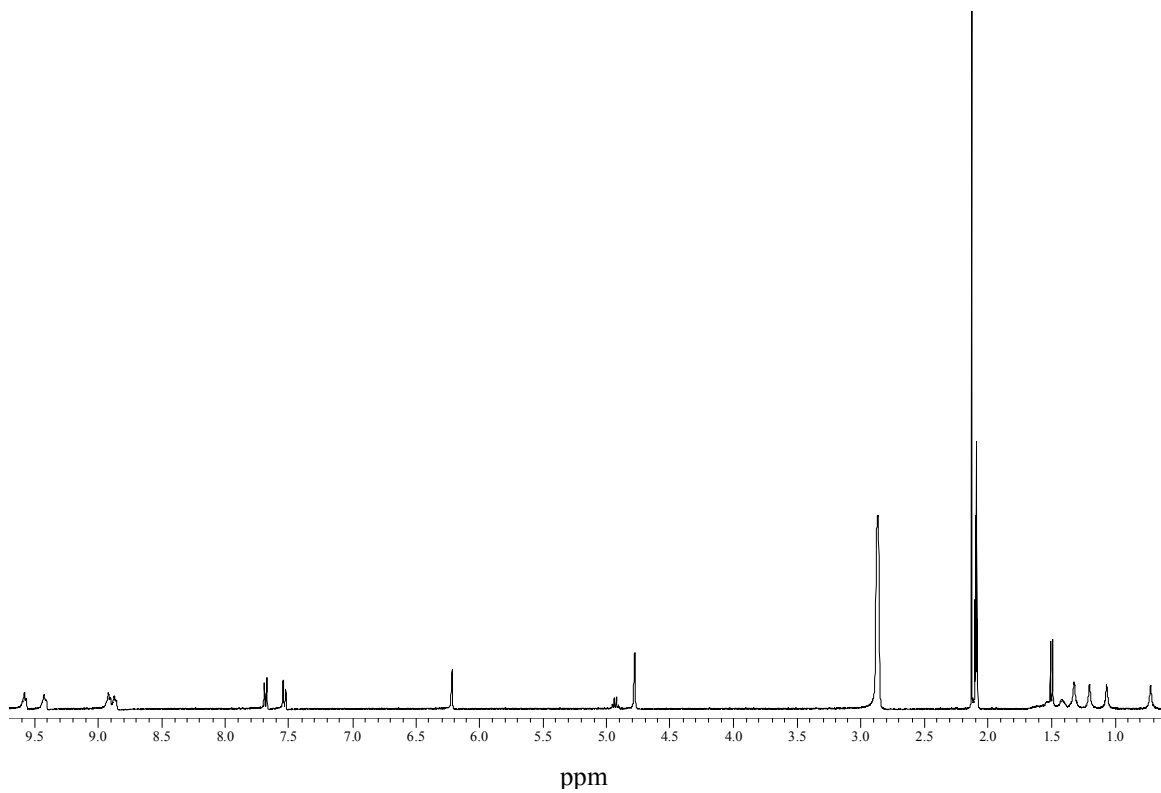
*Synthesis of 1-{p-[ $\alpha$ -Methyl- $\alpha$ -(2'',2'',6'',6'')-tetramethyl-N-piperidinyloxy)methyl]benzyl}-1'-methyl-4,4'-bipyridinium Bis(hexafluorophosphate) (1)*

A mixture of 1-methyl-4,4'-bipyridinium hexafluorophosphate<sup>S1</sup> (632 mg, 2.00 mmol) N-[p-(chloromethyl)- $\alpha$ -methylbenzyloxy]-2,2,6,6-tetramethylpiperidine<sup>S2</sup> (650 mg, 2.10 mmol), and sodium iodide (600 mg, 4.00 mmol) in acetone (100 mL) were refluxed for 48 hours. The precipitate was filtered off, dissolved in 100 mL deionized water, and extracted with chloroform (3  $\times$  20 mL). Solid NH<sub>4</sub>PF<sub>6</sub> was added into aqueous layer until no further precipitation was observed. The new precipitate was filtered off and recrystallized from deionized water three times to afford **1** as a white solid, 1.23 g (84%), mp 201.8-202.9 °C. The proton NMR spectrum of the product is shown in Figure S1. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 22 °C)  $\delta$ (ppm): 9.57 (2H, d,  $J$  = 5.8 Hz), 9.41 (2H, d,  $J$  = 5.8 Hz), 8.91 (2H, d,  $J$  = 5.8 Hz), 8.86 (2H, d,  $J$  = 5.8 Hz), 7.68 (2H, d,  $J$  = 8.2 Hz), 7.53 (2H, d,  $J$  = 5.8 Hz), 6.21 (2H, s), 4.93 (1H, q,  $J$  = 6.6 Hz), 4.78 (3H, s), 1.50 (3H, d,  $J$  = 6.6 Hz), and 0.68~1.64 (18H, m). LRFABMS (NBA)  $m/z$  736.2 [M + H]<sup>+</sup>, 591.2 [M - PF<sub>6</sub>]<sup>+</sup>, 446.1 [M - 2PF<sub>6</sub>]<sup>+</sup>; HRFABMS (NBA/PEG)  $m/z$  calcd for [M + H]<sup>+</sup> C<sub>29</sub>H<sub>40</sub>N<sub>3</sub>O<sub>1</sub>P<sub>2</sub>F<sub>12</sub>, 736.2455, found 736.2464, error 1.2 ppm. Anal. calcd for C<sub>29</sub>H<sub>39</sub>N<sub>3</sub>O<sub>1</sub>P<sub>2</sub>F<sub>12</sub>•0.5H<sub>2</sub>O: C, 46.76; H, 5.42; N, 5.64. Found: C, 46.58; H, 5.32; N, 5.67.

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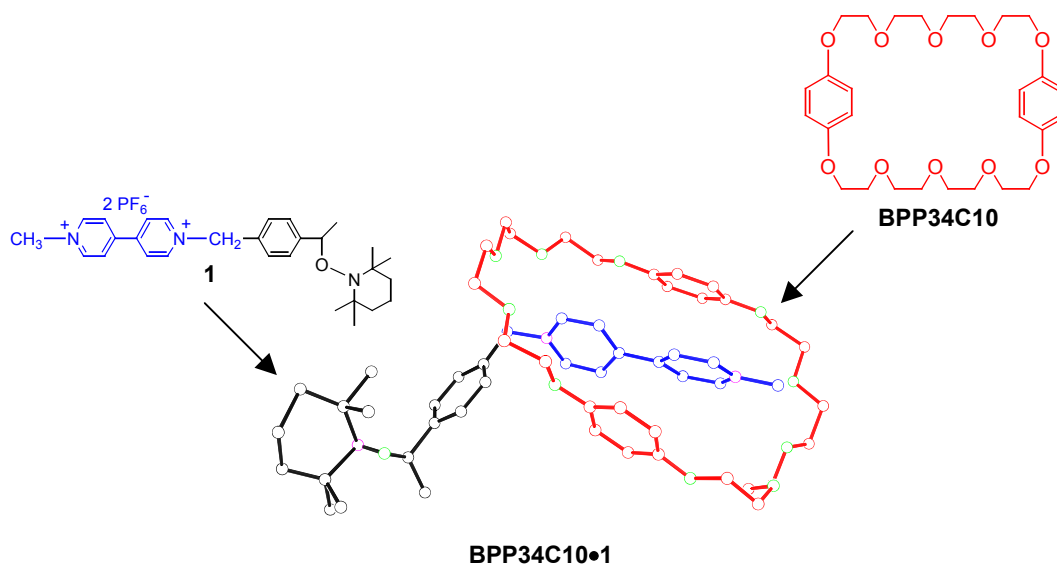
(S2) Dao, J.; Benoit, D.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2161-2167.





**Figure S1.**  $^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CD}_3\text{COCD}_3$ , 22 °C) of **1**.

*Confirmation of the structure of 1 by X-ray analysis of a pseudorotaxane **BPP34C10•1***



Red needles ( $0.09 \times 0.12 \times 0.47 \text{ mm}^3$ ) were crystallized from acetone/pentane by vapor diffusion at room temperature. The chosen crystal was mounted on a nylon CryoLoop™ (Hampton Research) with Krytox® Oil (DuPont) and centered on the goniometer of an Oxford Diffraction Xcalibur2™ diffractometer equipped with a Sapphire 2™ CCD detector. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis.<sup>S3</sup> The unit cell parameters were consistent with the triclinic space group  $P\bar{1}$ . The structure was solved by direct methods and refined using the SHELXTL NT program package.<sup>S4</sup> The asymmetric unit of the structure comprises one crystallographically independent host:guest complex and a variety mostly evaporated and thus unidentified solvent. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. After locating the main residues, additional residual electron density that was presumably evaporated/disordered solvent could not be modeled successfully. Consequently, the SQUEEZE<sup>S5</sup> subroutine of the program package PLATON<sup>S6</sup> was used to identify potential solvent/void regions and subtract any electron density contribution in this region from the structure factors. A total of  $660 \text{ \AA}^3$  void space was identified (18.6% of total cell volume), but electron density totaling only  $18.3 e^-$  was subtracted. Presumably the strong non-bonding interactions between the host and guest allowed the solvent to evaporate without the sample losing crystallinity. The TEMPO fragment of the guest molecule borders the void region and exhibits substantial disorder in the form of very large anisotropic displacement parameters and unreasonable metrical parameters. Attempts to model this disorder were unsuccessful. Presumably, the close proximity to the void region allows for substantial motion and/or multiple orientations of the TEMPO fragment. The program packages SHELXTL NT and PLATON were used to generate crystallographic tables.<sup>S4,S6</sup> The program package SHELXTL NT was used for molecular graphics generation.<sup>S4</sup>

(S3) CrysAlis v1.171, Oxford Diffraction: Wroclaw, Poland, 2004.

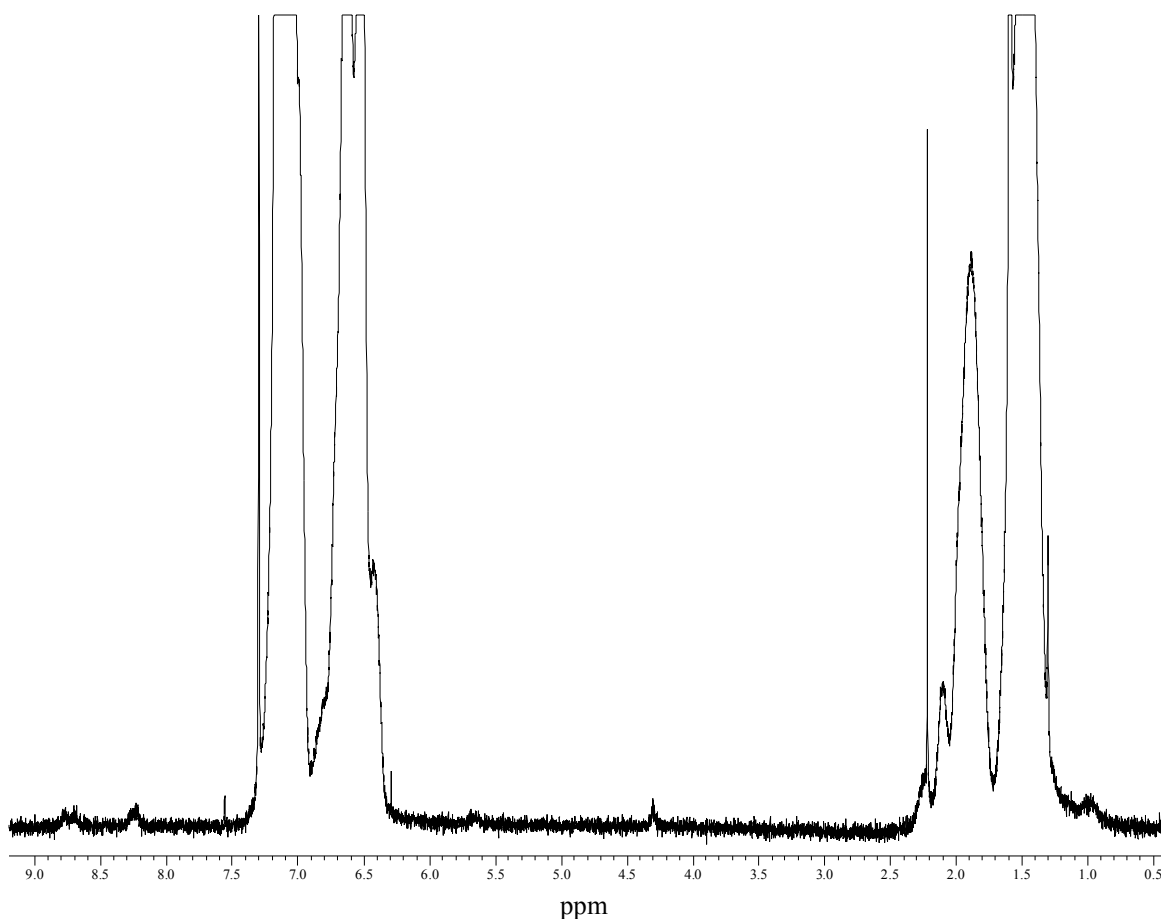
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### *Synthesis of Paraquat-terminated Polystyrene (2)*

A stirred mixture of the initiator **1** (0.184 g, 0.250 mmol) and styrene (5.21 g, 50.0 mmol) under N<sub>2</sub> was maintained at 125°C in an oil bath for 1 h. The reaction mixture became viscous and the magnetic stirrer stopped. The reaction mixture was dissolved in chloroform and precipitated into methanol; the solid was reprecipitated several times and vacuum dried to afford **2** as a white solid (2.51 g, 47%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 22 °C) δ(ppm): 8.66-8.80 (4H, m), 8.20-8.30 (4H, m), 5.65 (2H, s), and 4.30 (3H, s). GPC Results (polystyrene as the standard and 1-methyl-2-pyrrolidinone as the solvent):  $M_w = 44.3$  kg/mol,  $M_n = 32.3$  kg/mol, PDI = 1.37. <sup>1</sup>H NMR end group analysis by referencing α- and β-pyridinium proton signals of the paraquat moiety (8.66-8.80 and 8.20-8.30 ppm) to the aromatic signals (6.3-7.3 ppm) indicated  $M_n = 35.0$  kg/mol, including the paraquat and TEMPO end groups.

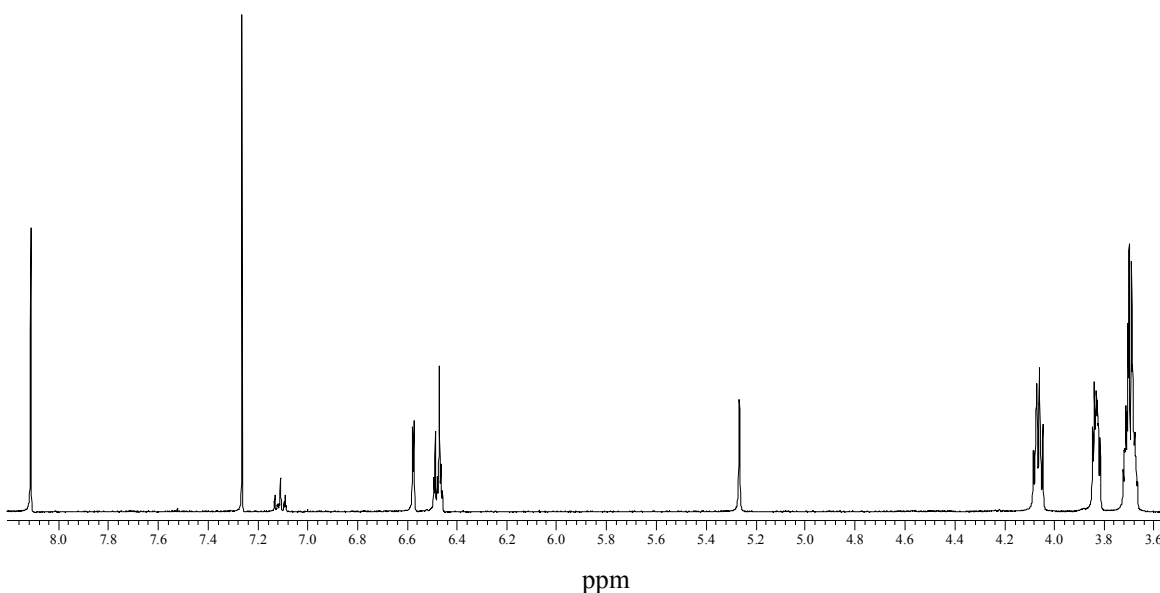


**Figure S2.**  $^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CDCl}_3$ , 22  $^\circ\text{C}$ ) of **2**.

*Synthesis of Bis(5-methylene-1,3-phenylene-1',3'-phenylene-32-crown-10) Terephthalate (7).*

Terephthaloyl chloride (1.01 g, 4.93 mmol) was added to a solution of 5-hydroxymethylene-1,3-phenylene-1',3'-phenylene-32-crown-10 (**4**, 5.6415 g, 9.963 mmol) in anhydrous THF (125 mL) containing pyridine (0.900 mL, 11.1 mmol) and the mixture was refluxed for 48 h. After cooling, the precipitated pyridinium hydrochloride salt was filtered and the organic layer was washed with water and 10% hydrochloric acid (25 ml) solution. The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness. The crude product was purified by silica gel column chromatography with ethyl acetate as the eluent. Evaporation of the solvent gave **7** (5.30 g, 85%) as an oil. Recrystallization from 2:8 dichloromethane / hexane gave a white solid, mp 75.7-77.9 $^\circ\text{C}$ . IR (neat): 2924 (-CH), 1722 (C=O), 1596, 1489, 1456 (C=C)

and 1264 [C-C(=O)-C] and 1124 (C-O-C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 22 °C)  $\delta$ (ppm): 8.11 (4H, s), 7.11 (2H, m,  $J = 8.5$  Hz), 6.57 (4H, d,  $J = 2.2$  Hz), 6.48 (8H, m), 5.26 (4H, s), 4.07 (16H, m), 3.83 (16H, m), and 3.69 (32H, m).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 22 °C)  $\delta$ (ppm): 66.945, 67.453, 67.582, 69.592, 69.645, 70.829, 70.851, 101.164, 101.612, 106.907, 107.028, 129.672, 129.740, 133.882, 137.675, 159.916, 160.075, 165.492 (18 peaks; theoretical 19). LRFABMS (NBA)  $m/z$  1260.7  $[\text{M}]^+$  and 1097.5  $[\text{M} - \text{C}_{10}\text{H}_{11}\text{O}_2]^+$ ; HRFABMS (NBA/PEG)  $m/z$  calcd for  $[\text{M}]^+$   $\text{C}_{66}\text{H}_{86}\text{O}_{24}$ , 1262.5509, found 1262.5461, error 3.8 ppm. Anal. calcd for  $\text{C}_{66}\text{H}_{86}\text{O}_{24}$ : C, 62.73; H, 6.86. Found: C, 62.65; H, 6.86.

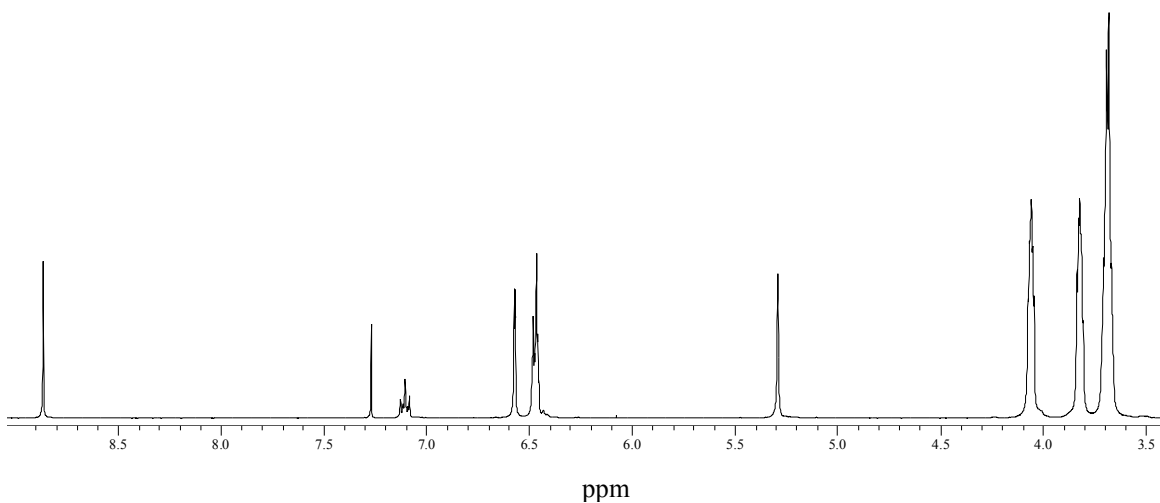


**Figure S3.**  $^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CDCl}_3$ , 22 °C) of **7**.

*Synthesis of 1,3,5-Benzenetricarbonyl Tris(5-methylene-1,3-phenylene-1',3'-phenylene-32-crown-10 (3)).*

1,3,5-Benzenetricarbonyl trichloride (0.181 g, 0.683 mmol) was added to a solution of 5-hydroxymethylene-1,3-phenylene-1',3'-phenylene-32-crown-10 (**4**, 1.17 g, 2.05 mmol) in anhydrous THF (75 mL) containing pyridine (0.17 mL, 2.10 mmol). After refluxing for 72 h, the salt was filtered and the organic layer was washed with water and 10% hydrochloric acid (25 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness. The crude product was purified by silica gel column

chromatography by elution with ethyl acetate followed by absolute ethanol. Evaporation of the solvent gave **3** (1.12 g, 88.4%), an oil. IR (neat) 2924 (-CH), 1722 (C=O), 1602, 1489 (C=C) 1237 [C-C(=O)-O], and 1131 (C-O-C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 22 °C)  $\delta$ (ppm): 8.86 (3H, s), 7.10 (3H, m), 6.57 (6H, d,  $J = 2.2$  Hz), 6.47 (12H, m), 5.29 (6H, s), 4.06 (24H, m), 3.82 (24H, m), and 3.69 (48H, m).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 22 °C)  $\delta$ (ppm): 67.156, 67.452, 67.566, 69.576, 69.645, 70.813, 70.851, 101.353, 101.611, 107.035, 129.739, 131.165, 134.852, 137.538, 159.908, 160.067, and 164.634 (17 peaks; theoretical 19). LRFABMS (NBA)  $m/z$  2028.5  $[\text{M} + \text{Na}]^+$ , 1893.7  $[\text{M} + \text{K}]^+$ , and 1877.6  $[\text{M} + \text{Na}]^+$ ; HRFABMS (NBA/PEG)  $m/z$  calcd for  $[\text{M} + \text{Na}]^+ \text{C}_{96}\text{H}_{126}\text{O}_{36}\text{Na}$ , 1877.7927, found 1877.7974, error 2.5 ppm.



**Figure S4.**  $^1\text{H}$  NMR Spectrum (400 MHz,  $\text{CDCl}_3$ , 22 °C) of **3**.

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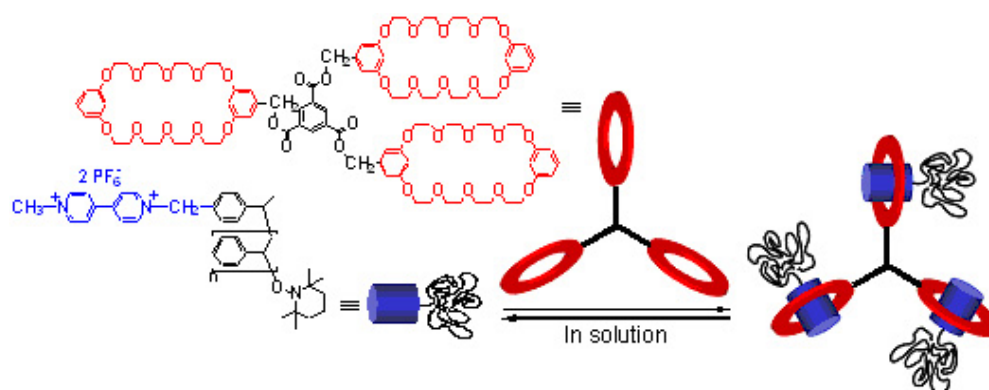
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12. Based on these NMR data,  $\Delta_0$ , the difference in  $\delta$  values for H<sub>1</sub> of **3** in the uncomplexed and fully complexed species under fast exchange, was calculated by extrapolation of a plot of  $\Delta = \delta - \delta_u$  vs  $1/[2]_0$ . Then  $p = \Delta/\Delta_0$ .
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14.  $K_1 = [3 \cdot 2]/\{[3][2]\}$ ,  $K_2 = [3 \cdot 2_2]/\{[3 \cdot 2][2]\}$ , and  $K_3 = [3 \cdot 2_3]/\{[3 \cdot 2_2][2]\}$ .  $K_{av} = (K_1 + K_2 + K_3)/3$ . The value of  $K_{av}$  is equal to the intercept and the absolute slope of the best fit line in Figure 3. Because  $K_1:K_2:K_3 = 9:3:1$ ,<sup>13</sup>  $K_1$ ,  $K_2$ , and  $K_3$  were calculated to be 1430, 476, and 159 M<sup>-1</sup>.
15. The three association constants corresponding to this model system in 2:1 CD<sub>3</sub>COCD<sub>3</sub>:CDCl<sub>3</sub> were calculated to be 3220, 1070, and 358 M<sup>-1</sup>.



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**TOC Graphic:**

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**Abstract:** The first supramolecular star polymer based on the host-guest complexation was prepared from statistical complexation of a homotriplic tris(crown ether) host and monotopic paraquat-terminated polystyrene guest in solution by a supramolecular coupling method. The formation of this supramolecular star polymer was confirmed by proton NMR characterization and viscosity studies.

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