

A pillar[5]arene-based anion responsive supramolecular polymer†

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An AB-type heteroditopic monomer was prepared by incorporating a dialkylammonium salt into a copillar[5]arene prepared from the co-oligomerization of 1-(10-bromodecyloxy)-4-methoxybenzene and 1,4-dimethoxybenzene. Based on the self-assembly of this new monomer in chloroform, a linear supramolecular polymer formed. The formation of the supramolecular polymer was characterized by various techniques including ¹H NMR, NOESY, DOSY, specific viscosity and SEM. This supramolecular polymer was anion responsive, since the self-assembly of the monomers could be destroyed by the addition of chloride anions. This study provides an efficient and convenient strategy to control the formation of supramolecular polymers.

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Introduction

Controlling the self-assembly and disassembly of monomers by external stimuli is of great importance in the study of supramolecular polymer chemistry and has attracted more and more attention in the past few years.¹ Supramolecular polymers,² the combination of supramolecular chemistry and traditional polymer chemistry, consist of the same or different kinds of monomers held together by reversible and directional noncovalent interactions. Based on the responsive and reversible nature of the noncovalent bonds, supramolecular polymers have shown unique and interesting properties, such as gelation and self-healing, and have become one of the most active fields in supramolecular chemistry and materials science.³ Hydrogen bonds, π - π stacking interactions, hydrophobic interactions and metal-ligand coordinations are the common noncovalent interactions used for the construction of supramolecular polymers.⁴ Now, as an important part of supramolecular chemistry, host-guest interactions have become more and more popular in the fabrication of supramolecular polymers.⁵

Pillararenes,^{6–13} a new kind of calixarene analogues, have become one of the hottest topics in macrocyclic chemistry since they were found in 2008.^{6a} Their syntheses,⁶ functionalizations,⁷ conformations,⁸ host-guest properties⁹ and applications in different areas¹⁰ have been actively investigated. Previously, Huang and coworkers found that a pillar[5]arene

could form a complex with a hexane molecule resulting in a [2]pseudorotaxane-type threaded structure with quadruple C–H \cdots π interactions as the main driving force.^{6c} With this important finding, a series of alkyl chain-based guests, such as alkanediamines,^{11a} bis(imidazole) derivatives,^{9b} alkanediacids^{7a} and alkanedinitriles,^{9c} were designed and applied to investigate their complexation with pillar[5]arenes.¹² Meanwhile, based on this new pillar[5]arene-linear alkyl chain molecular recognition motif, a supramolecular polymer driven by quadruple C–H \cdots π interactions was successfully prepared in solution and in the solid state.^{11b} Moreover, Wang and coworkers prepared supramolecular polymers including poly-pseudorotaxanes and polyrotaxanes based on the combination of quadruple hydrogen bonding interactions and pillar[5]arene-based host-guest interactions.^{11c–e} Interestingly, Huang and coworkers prepared an alkyl chain-based dialkylammonium salt, *n*-octylethyl ammonium hexafluorophosphate (**3**), and found that it formed a complex with 1,4-dimethoxypillar[5]arene (DMPillar[5]arene **4**) in chloroform and in the solid state resulting in a [2]pseudorotaxane with N–H \cdots π interactions and C–H \cdots π interactions as the main driving forces.^{13b} Based on this new molecular recognition motif, we herein synthesized a mono-functionalized pillar[5]arene with a dialkylammonium salt as an AB-type heteroditopic monomer to construct a novel anion responsive supramolecular polymer.

Experimental section

General methods

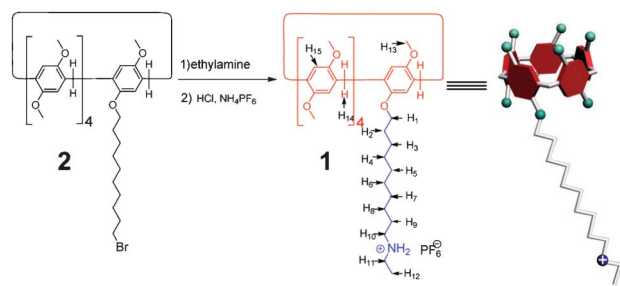
All reagents were commercially available and used as supplied without further purification. Compound **2** (Scheme 1) was prepared according to a published procedure.^{13a} ¹H NMR

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Scheme 1 Synthesis and cartoon representation of monomer 1.

spectra and ^{13}C NMR spectra were collected on a Bruker 400 MHz spectrometer. Low-resolution electrospray ionization (LRESI) mass spectra were obtained with chloroform solutions on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained with chloroform solutions on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument operating at an energy of 3 keV. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer (0.53 mm inner diameter) at 25 °C in CHCl_3 .

Design of AB-type monomer 1

Recently, Huang and coworkers reported that DMpillar[5]arene (**4**) could bind *n*-octylethyl ammonium hexafluorophosphate (**3**) to form a [2]pseudorotaxane both in chloroform and in the solid state.^{13b} Interestingly, this complexation process could be inhibited by adding chloride anions since they formed intimate ion pairs with the *n*-octylethyl ammonium cations in chloroform which interferes with the complexation between the pillar[5]arene and the cation,^{13b} an effect also observed in other pseudorotaxane systems.¹⁴ In consideration of the anion-responsiveness of this host-guest system, we designed an anion responsive supramolecular polymer based on this new pillar[5]arene-dialkylammonium cation recognition motif (Fig. 1).

Synthesis of monomer 1

Our strategy to synthesize the corresponding heteroditopic monomer is shown in Scheme 1. First, we prepared the monofunctional pillar[5]arene **2** by a reported procedure.^{13a} Then, this monobromo pillar[5]arene was reacted with ethylamine, acidified by adding HCl, and ion exchange was performed with NH_4PF_6 to give **1**.

A mixture of **2** (0.770 g, 0.805 mmol) and ethylamine (68–72% in an aqueous solution, 20.0 mL) in THF (50.0 mL) was stirred at room temperature overnight. The organic solvent was removed under vacuum and the residue was neutralized with 1.00 M HCl solution. After THF (50.0 mL) and NH_4PF_6 (0.650 g, 4.00 mM) were added, the mixture was stirred for 4 h at room temperature. When the organic solvent was removed, the residue was extracted with CH_2Cl_2 (50.0 mL) 3 times. The

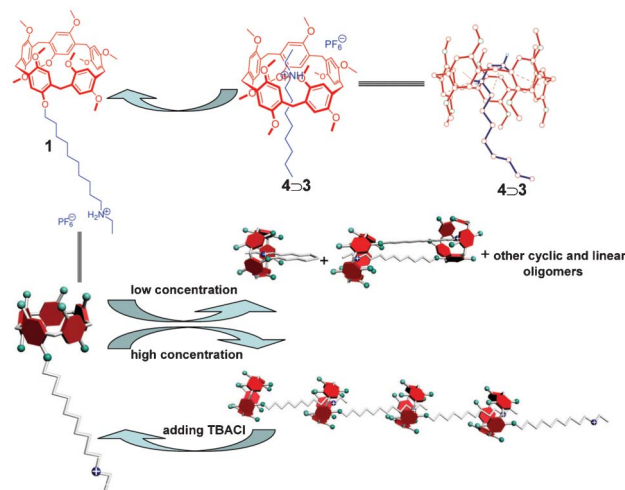


Fig. 1 The design of monomer 1, cartoon representation of the self-assembly of the monomer 1 and the disassembly of the supramolecular polymer. The crystal structure of $4 \supset 3$ was previously reported by Huang and coworkers.^{13b}

crude product was purified after removal of the solvent of the combined organic phases by recrystallization in methanol to yield **1** as a white solid (0.510 g, 59%), mp 118.4–119.0 °C. ^1H NMR (400 MHz, CDCl_3 , room temperature, 4.00 mM) δ (ppm): 6.88–7.01 (m, 10H), 3.97 (t, $J = 4.8$ Hz, 2H), 3.76–3.82 (m, 37H), 1.89 (br, 2H), 1.63 (br, 4H), 1.44 (br, 2H), 1.35 (br, 2H), 1.06 (br, 2H), 0.59 (br, 2H), 0.45 (br, 3H), 0.14 (br, 2H), -0.25 (br, 2H), -0.62 (br, 2H). ^{13}C NMR (100 MHz, CDCl_3 , room temperature, 100 mM) δ (ppm): 150.58, 150.53, 150.48, 150.42, 150.06, 129.57, 129.42, 129.26, 129.18, 129.10, 128.96, 128.92, 128.89, 115.58, 114.40, 114.11, 114.06, 113.99, 113.81, 113.71, 77.48, 77.16, 76.84, 69.17, 56.68, 56.57, 56.49, 56.11, 56.00, 46.69, 43.68, 29.82, 29.30, 29.17, 28.58, 25.29, 10.15. LRESIM: m/z 920.5 $[\text{M} - \text{PF}_6]^+$ (100%). HRESIMS: m/z calcd for $[\text{M} + \text{Na}]^+$ $\text{C}_{54}\text{H}_{72}\text{NaO}_{20}^+$, 1063.4509, found 1063.4521, error 1.1 ppm.

Results and discussion

Proton NMR experiments

According to the ^1H NMR spectrum of **1** at 1.00 mM (Fig. 2a), the signals of the long alkyl chain containing a dialkylammonium salt were well dispersed and could be clearly identified because they shifted upfield significantly, especially below 0 ppm for H_8 and H_9 , indicating the existence of intramolecular or intermolecular cyclic species at low concentrations. ^1H NMR spectra of monomer **1** at concentrations ranging from 1.00 to 500 mM were obtained at room temperature (Fig. 2). As expected, the ^1H NMR spectra of **1** (Fig. 2) were concentration-dependent, reflecting the involvement of fast-exchanging noncovalent interactions in chloroform on the NMR time scale. The protons H_{8-10} showed great upfield chemical shift changes as the concentration of monomer **1** increased from 1.00 to 500 mM. These phenomena were in accordance with the previously reported crystal structure of $4 \supset 3$ (Fig. 1);^{13b} these protons were located in the electron-rich cavity of the

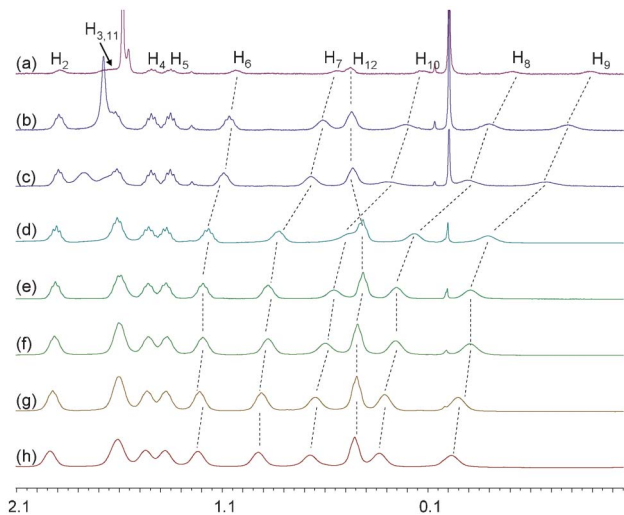


Fig. 2 Partial ^1H NMR spectra (400 MHz, CDCl_3 , room temperature) of **1** at different concentrations: (a) 1.00; (b) 7.50; (c) 15.0; (d) 31.3; (e) 62.5; (f) 125; (g) 250; (h) 500 mM.

pillar[5]arene host and were shielded. All protons became broad when the concentration was increased to 500 mM (Fig. 2h), indicating the formation of large size supramolecular polymer aggregates. As the concentration increased, the signals of protons H_{8-10} shifted downfield quickly at first and then slowly tended to a constant value, illustrating that the percentage of the cyclic species decreased while the percentage of the linear species increased. The above observations were also confirmed by a NOESY spectrum of **1** (Fig. 3). The phenyl protons H_{15} showed strong correlations with protons H_{8-9} and protons H_{11-12} (Fig. 3) at the end of the alkyl chain, suggesting that these protons threaded through the cavity of the pillar[5]arene. The values of the fraction p of the complexed dialkylammonium salts and the maximum possible polymerization degree n at different concentrations were calculated using the Carothers equation with the hypotheses that the association constant K_a remained unchanged in the

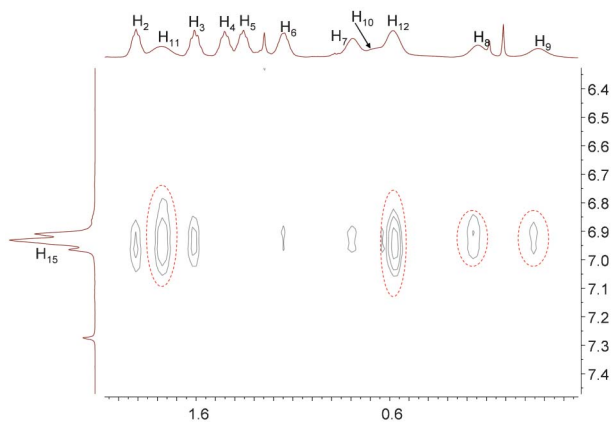


Fig. 3 Partial NOESY NMR spectrum (400 MHz, CDCl_3 , room temperature) of **1** at a concentration of 100 mM.

supramolecular polymerization process and the cyclic species could be ignored (Table S1, ESI†). As a reference, K_a was estimated to be 1090 M^{-1} for the complexation between DMpillar[5]arene **4** and *n*-octylethyl ammonium hexafluorophosphate (**3**) in chloroform.^{13b} As the concentration increased, the calculated polymerization degree increased quickly, and linear supramolecular polymers formed. For example, at 500 mM, p was 95.8%, and thus, according to the Carothers equation,¹⁵ n_{max} was 23.8, corresponding to a polymer with a molar mass of 25.4 kDa. Using an equation derived from this for supramolecular polymerization^{3a,d} and the K_a value of the model system, n_{max} was estimated to be 23.3 at 500 mM, providing good agreement between experiment and theory.

Specific viscosity

To further investigate the supramolecular polymer, a double logarithmic plot of specific viscosity *versus* the concentration of monomer **1** in CHCl_3 was produced from data obtained with a Cannon Ubbelohde semi-microdilution viscometer (Fig. 4), as viscometry is a convenient method to test the propensity of monomers to self-assemble into large aggregates. As presented in Fig. 4, the curve had a slope of 1.07 in the low concentration range, which meant that monomer **1** mainly formed low-molecular-weight cyclic oligomers at low concentrations. As the concentration of monomer **1** increased above the critical supramolecular polymerization concentration (CPC), a sharp increase in the viscosity (slope = 1.99) was observed, indicating the presence of a supramolecular polymerization process, in which the length of the resulting polymer increased with increasing monomer concentration. The CPC for monomer **1** in CHCl_3 was about 210 mM as evidenced by the change of slope occurring at this concentration, indicating a ring-chain transition from the formation of cyclic or linear oligomers to highly ordered linear supramolecular polymers.

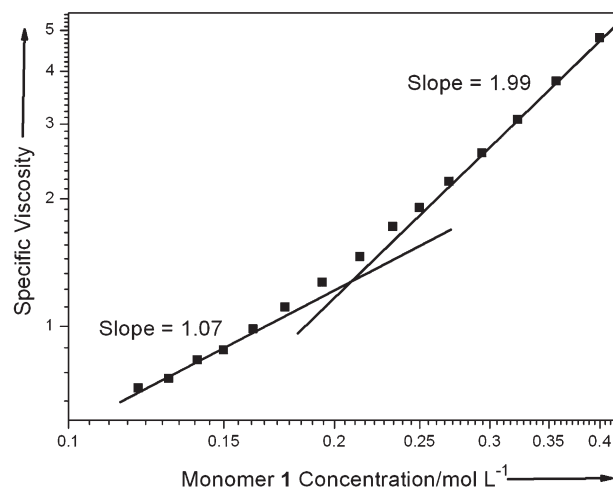


Fig. 4 Specific viscosity of the supramolecular polymer *versus* the concentration of monomer **1** in CHCl_3 at 25 °C.

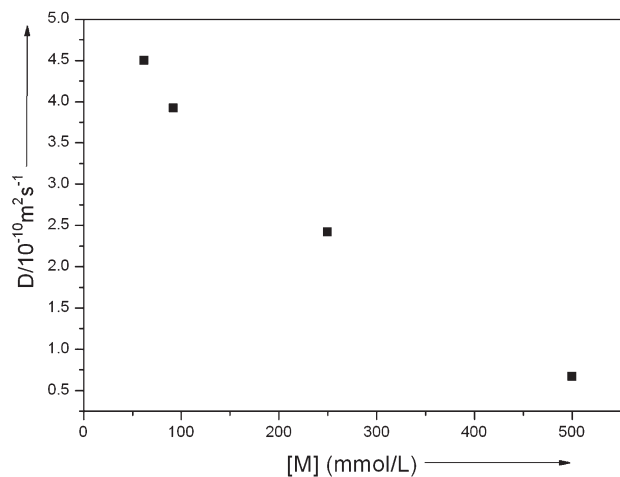


Fig. 5 Concentration dependence of diffusion coefficient D (from ^1H NMR spectroscopy; 500 MHz, CDCl_3 , 293 K) of **1**.

Two-dimensional diffusion-ordered NMR (DOSY)

We also used two-dimensional diffusion-ordered NMR (DOSY) to investigate the self-assembly process during linear supramolecular polymerization at different concentrations of monomer **1**. We found that different aggregates were in fast exchange both on the ^1H NMR and on the DOSY time scale, and the DOSY data were consistent with the above ^1H NMR results and specific viscosity experiments (Fig. 5). As the monomer concentration increased from 62.5 to 500 mM, the measured weight-average diffusion coefficients decreased considerably from 4.50×10^{-10} to $6.70 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (Fig. 5), indicating an increase in the average aggregation size due to the transition from the supramolecular oligomer species to supramolecular polymers. Based on previous reports,^{1h,5h,11b} it is known that a high degree of polymerization for the repeating units is necessary to observe a sharp decrease in the diffusion coefficient. Thus, the current measurements clearly indicate the formation of an extended, high-molecular-weight supramolecular polymeric structure.

SEM of the supramolecular polymer

Furthermore, rod-like fibers with a regular diameter of 80 μm were drawn from a highly concentrated solution and observed by scanning electron microscopy (Fig. 6), providing direct

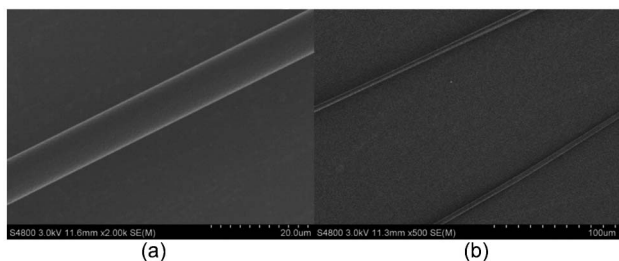


Fig. 6 SEM images of rod-like fibers drawn from a highly concentrated solution of **1** in chloroform.

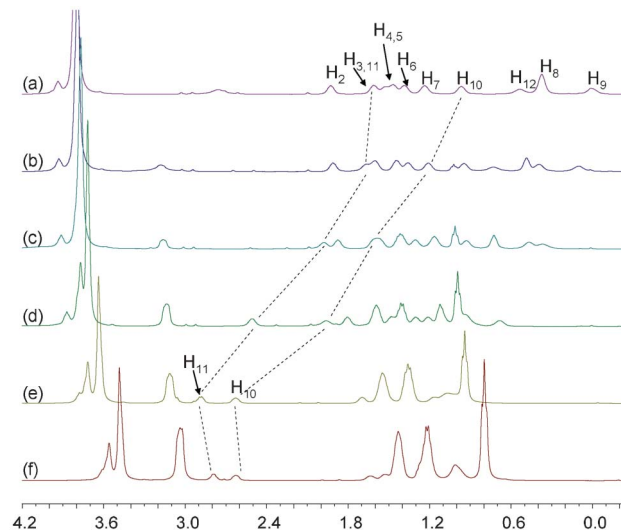


Fig. 7 ^1H NMR spectra (400 MHz, CDCl_3 , room temperature) of: (a) 240 mM **1**; with (b) 0.300 equiv. of TBACl; (c) 0.800 equiv. of TBACl; (d) 1.80 equiv. of TBACl; (e) 3.00 equiv. of TBACl; (f) 4.00 equiv. of TBACl.

evidence for the formation of a supramolecular polymer with high molecular weight.

Anion controlled disassembly

We then studied the anion responsive properties of the supramolecular polymer. Previously, Huang and coworkers reported that the chloride anion could disassemble the complex between DMpillar[5]arene **4** and *n*-octylethyl ammonium hexafluorophosphate **3**.^{13b} Based on this important finding, we successfully disassembled this pillar[5]arene-dialkyl ammonium-based supramolecular polymer by adding tetrabutylammonium chloride (TBACl) to destroy the host-guest complexation. As shown in Fig. 7, the protons of **1** that shifted upfield when the supramolecular polymer formed shifted downfield as tetrabutylammonium chloride was added. Especially protons H_{10} and H_{11} neighboring the nitrogen atom of the long alkyl chain in the supramolecular polymers shifted upfield because of the shielding effect caused by the complexation with the electron-rich cyclic ring of the pillar[5]arene. When TBACl was added, obvious downfield chemical shifts were observed, indicating the disassembly of the complex. As the concentration of TBACl increased to 3.00 equiv., the supramolecular polymer was fully destroyed (Fig. 7e). The chemical shifts of the protons of **1** changed back a little after adding 4.00 equiv. of TBACl. This is probably due to the change in ionic strength of the solution after the addition of excess tetrabutylammonium chloride¹⁴ (Fig. 7f). As mentioned before,^{13b} compared with the hexafluorophosphate anion, the chloride anion is smaller and charge-convergent and forms an intimate ion pair with the ammonium cation in chloroform. This ion pair is too large to fit into the cavity of the DMpillar[5]arene, so that the host-guest complex disassembles and the supramolecular polymer is destroyed. These studies confirm that the supramolecular polymer prepared from monomer **1** can be destroyed by adding chloride anions. In further studies, we are exploring whether other anions such

as F^- , Br^- , and I^- have the ability to disassemble the supramolecular polymer.

Conclusions

In conclusion, we designed and successfully prepared a novel supramolecular polymer based on the pillar[5]arene–dialkylammonium salt recognition motif with $N-H\cdots\pi$ interactions and $C-H\cdots\pi$ interactions as the main driving forces. By the combination of various techniques including 1D NMR, 2D NMR, DOSY, viscosity experiments at different concentrations and SEM, we found that the formation of the supramolecular polymer was highly dependent on the monomer concentration. In addition, rod-like fibers were drawn from a highly concentrated chloroform solution and observed by SEM, which provided direct evidence for the formation of the supramolecular polymer with a high molecular weight. We used the chloride anion to successfully destroy the supramolecular polymer and this proved that the supramolecular polymer had anion responsiveness. Considering the easy availability and good host–guest properties of pillararene derivatives and the anion-responsiveness of the resultant supramolecular polymers, the present study provides a new and simple way to fabricate stimuli-responsive supramolecular polymeric materials.

Acknowledgements

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