A bifunctionalized [3]rotaxane and its incorporation into a mechanically interlocked polymer[†]

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A novel bifunctionalized [3]rotaxane based on a triptycenederived macrotricyclic host was conveniently synthesized. On the basis of the [3]rotaxane, a linear main-chain poly[3]rotaxane was further obtained by the highly efficient Huisgen 1,3-dipolar cycloaddition.

Rotaxanes,¹ mechanically linked molecules, have recently attracted great interest for not only their aesthetic structures but also their potential applications in nanotechnology and molecular machines.² Especially, rotaxane-based molecular machines, controlled by external stimuli, seem to be particularly important in the field of information storage and processing.³ During the past two decades, various rotaxanes have been synthesized in high efficiency approaches since transition metal templates⁴ or organic templates⁵ have been applied. However, the synthesis of high order [n]rotaxanes remains a considerable challenge for supramolecular chemists.

The mechanical (noncovalent) bond is the distinguishing characteristic of mechanically interlocked molecule-incorporated polymers. It could be deduced that the incorporation of flexible mechanical bonds would have repercussions for the polymer-chain behaviour, and subsequently produce new types of polymers with specific properties in both solution and the solid state.⁶ Despite significant attention paid to synthesize these types of macromolecules, few successful examples⁷ exist, on account of considerable challenges in the synthesis. Recently, Stoddart and Grubbs described an efficient strategy for the polymerization of a bifunctionalized [c2]daisy-chain monomer,⁸ which was obviously different from a template-directed self-assembly for the polymerization step.⁹

Triptycene,¹⁰ with its unique three-dimensional rigid structure and electron-rich property, has been found to be a useful building block for the construction of novel receptors.¹¹ As a result, we recently reported a triptycene-based macro-tricyclic host **1** (Fig. 1a), and found that the host could self-assemble with two dibenzylammonium salts to form [3]pseudorotaxanes (Fig. 1b).¹² On the basis of this work, we herein report the facile synthesis of a novel bifunctionalized [3]rotaxane and its further incorporation into a mechanically interlocked polymer (Fig. 1).



Fig. 1 Graphical representation of (a) macrotricyclic host **1**, (b) [3]pseudorotaxane, (c) [3]rotaxane, and (d) poly[3]rotaxane.

The synthesis of the functionalized dibenzylammonium salt **2-H·PF**₆ is outlined in Scheme 1. Reaction of 4-cyanophenol **5** with tosylated **6** in acetonitrile in the presence of K₂CO₃, and then reduction of the cyano group by LiAlH₄ in THF, gave the primary amine **4**. Condensation of amine **4** with aldehyde **3** gave the corresponding reversible dynamic imine, which was then reduced by NaBH₄ in MeOH to give the kinetically stable amine. Protonation of the free amine with an excess of HCl and subsequent counterion exchange with a saturated NH₄PF₆ solution afforded the unsymmetrical dibenzylammonium salt **2-H·PF**₆ in 62% total yield for the four steps. The salt **2-H·PF**₆ has good solubility in acetonitrile, but poor solubility in chloroform.

A mixture of the triptycene-based macrotricyclic host 1 (1 mM) and 2-H·PF₆ (2 mM, 2.0 equiv) in 1:1 CD₃CN:CDCl₃ at room temperature provided a complicated ¹H NMR spectrum after one day (see ESI†),¹³ with corresponding rates



Scheme 1 Synthesis of the dibenzylammonium salt 2-H PF₆.

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of association and/or dissociation slower than the NMR spectroscopic time scale under the tested conditions. However, the signals of protons H_5 and H_6 of the guest obviously shifted upfield, while a downfield shift of the aromatic proton H_1 of host 1 was also observed. These observations indicated that complexation between host 1 and the guest occurred, and that complex $1 \cdot (2-H \cdot PF_6)_2$ thus formed. The electrospray ionization mass spectrum (ESI-MS) provided more evidence for the formation of the 1:2 complex $1 \cdot (2-H \cdot PF_6)_2$ when a strong peak at m/z 1059.48 for $[1 \cdot (2-H)_2]^{2+}$ was observed.¹³ The formation of complex $1 \cdot (2-H \cdot PF_6)_2$ provides a chance to further synthesize a [3]rotaxane.

It was known that the 3,5-dimethyl phenyl group could be used as an efficient stopper for 24-crown-8.14 Thus, we tried to prepare the [3]rotaxane, 3-2H-2PF₆, using two 3,5-dimethyl phenyl groups as the stoppers. As shown in Scheme 2, after the macrotricyclic host 1 and 2-H PF₆ were mixed and stirred at room temperature in a 1:1 CH₃CN-CHCl₃ solution for 24 h, the mixture was treated with 3,5-dimethylbenzoic anhydride in the presence of a catalytic amount of tri(n-butyl)phosphine to afford $3-2H \cdot 2PF_6$ in 37% yield. The partial proton NMR spectrum of the [3]rotaxane 3-2H-2PF6 in 1:1 CD3CN:CDCl3 is shown in Fig. 2b. The aromatic proton H_1 of 1 and proton H₄ of 2-H·PF₆ in 3-2H·2PF₆ moved downfield, while the aromatic protons H_5 and H_6 shifted upfield greatly $(\Delta \delta = 1.65 \text{ and } 1.58 \text{ ppm}, \text{ respectively})$, which might be due to the strong shielding effect of the aromatic rings in host 1. The ESI-HRMS of 3-2H-2PF₆ revealed a high-intensity signal at m/z = 1191.1187 corresponding to the ion mass of $[3-2H]^{2+}$ (see ESI[†]),¹³ that is, the loss of $2PF_6^-$ from the [3]rotaxane.

There are two terminal propargyl groups in the [3]rotaxane, which could provide an alternative means to further synthesize mechanically interlocked polymers. The highly efficient Cu-catalyzed, Huisgen 1,3-dipolar cycloaddition¹⁵ was chosen

Scheme 2 Synthesis of the [3]rotaxane $3-2H \cdot 2PF_6$.



Fig. 2 Partial ¹H NMR spectra (300 MHz, 1:1 CD₃CN:CDCl₃, 298 K) of (a) **2-H·PF₆** (2 mM), (b) the [3]rotaxane **3-2H·2PF₆** (1 mM), and (c) host **1** (1 mM). Resonance protons are labeled in Scheme 2.



Scheme 3 Synthesis of the poly[3]rotaxane 4-2mH·2mPF₆.

for the polymerization reaction on account of its mild nature and high conversion. The synthesis of the linear main-chain poly[3]rotaxane 4-2mH 2mPF₆ is outlined in Scheme 3. When the terminally bifunctionalized [3]rotaxane $3-2H \cdot 2PF_6$ was subjected to a step-growth polymerization with 1 equiv of the diazide 2 in DMF in the presence of a stoichiometric amount of CuI, the linear main-chain poly[3]rotaxane 4-2mH \cdot 2mPF₆ could be conveniently obtained. The structure of the poly[3]rotaxane was confirmed by FT-IR, ¹H NMR, MALDI-TOF MS and size exclusion chromatography (SEC).¹³ In the FT-IR spectrum of 4-2mH·2mPF₆, an absorption peak at 1062 cm⁻¹, corresponding to a triazole group,¹⁶ was observed, while the signals at 3303 cm^{-1} $(\equiv C-H)$ and 2091 cm⁻¹ ($-N_3$) were also found, which were caused by the remaining terminal unreacted alkyne and azide groups. The MALDI-TOF MS spectrum revealed signals at m/z = 2740 corresponding to the ion mass of $[4-H]^+$ (m = 1), and 5918 corresponding to the ion mass of $[4-4H\cdot 3PF_6]^+$ $(\mathbf{m} = 2)$. In the ¹H NMR of **4-2mH 2mPF₆**, the signals for H_a, corresponding to 1,2,3-triazole, and H_b emerged at 7.82 and 5.11 ppm, respectively. All the above results indicated the

occurrence of the polymerization reaction and the formation of the poly[3]rotaxane. Size exclusion chromatography (SEC) analysis of **4-2mH·2mPF**₆ was also performed using pure DMF as the eluent, which showed a major peak in the chromatograph. The calculated average molecular weight (M_m) is *ca.* 43 kDa with a polydispersity index (PDI) of 1.42. The M_m indicates that each polymer chain is composed of *ca.* 14 repeating units. Moreover, differential scanning calorimetry (DSC) analysis of **4-2mH·2mPF**₆ showed a characteristic glass transition process at 108 °C.

In conclusion, we have shown the facile synthesis of a novel bifunctionalized [3]rotaxane based on a triptycene-derived macrotricyclic host. On the basis of the [3]rotaxane, we have also synthesized a linear main-chain poly[3]rotaxane by the highly efficient Cu-catalyzed, Huisgen 1,3-dipolar cyclo-addition. Our further work will focus on the construction of the stimuli-responsive [3]rotaxanes and the corresponding poly[3]rotaxanes.

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