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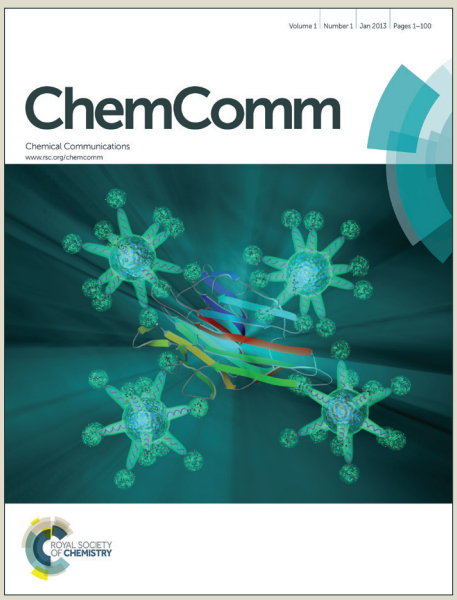

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ARTICLE TYPE

Formation of "pseudosuitane"-type complex between triptycene-derived bis(crown ether) host and 1,1'-(anthracene-9,10-diyl)bis(*N*-benzylmetha-naminium): a new method for the synthesis of linear polyrotaxanes

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"Pseudosuitane"-type complex between triptycene-derived bis(crown ether) host and 1,1'-(anthracene-9,10-diyl)bis(*N*-benzylmethanaminium) can be formed in solution and solid state, which provides us a new method for the synthesis of linear polyrotaxanes.

Polyrotaxanes,[1] a kind of interlocked supramolecules formed by threading many cyclic molecules onto the polymer chain, show not only the unique structural features but also wide potential applications in biology,[2] molecular machines,[3] and optoelectronic material.[4] During the past two decades, various macrocyclic molecules, such as cyclodextrins,[1b, 4b, 5] crown ethers,[6] and cucurbiturils,[7] have been employed to construct polyrotaxanes. Among them, crown ethers have attracted much attention for their diverse binding selectivities. Generally, linear polyrotaxanes based on crown ethers could be synthesized by the "threading-followed-by-stoppering"[3d] and the template-directed "clipping" method.[8] The former method is relatively simple, but has low efficiency since the threading of the rings does not complete for each available binding site. While the latter one was usually used to synthesize lower order rotaxanes. Although significant efforts have been made till now, new and efficient methods for the synthesis of polyrotaxanes are still important and attractive.

In 2006, Stoddart and coworkers[9] reported a kind of novel interlocked molecule called suit[2]ane, which consists of two linked crown ether rings and a linear rigid scaffold with a centrally located bulky core. Previously,[10] we reported a new triptycene-derived host **1** containing two DB24C8 cavities (Fig. 1a), and found that it could form a bis[2]pseudorotaxane complex with dibenzylammonium salts. Moreover, it was also known that anthracenyl group is too big to thread the cavity of DB24C8.[11] On the basis of these results, we deduced that if 1,1'-(anthracene-9,10-diyl)bis(*N*-benzylmethanaminium) **2** (Fig. 1b) could form a 1:1 "pseudosuitane"-type complex **1**·**2** (Fig. 1c) with host **1**, a new and convenient method for the synthesis of polyrotaxanes (Fig. 1d) could be developed by just connecting the "pseudosuitane" with an appropriate linker. Herein, we report the formation of a "pseudosuitane"-type complex between host **1** and guest **2** in both solution and solid state, which results in the synthesis of a linear polyrotaxane by an effective copper(I)-catalysed azide-alkyne cycloaddition (CuAAC 'click') reaction.

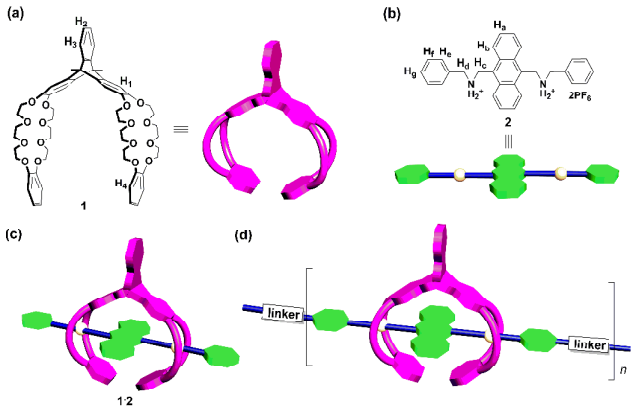


Fig. 1 Graphical representation of structures and the proton designations of (a) host **1**, (b) guest **2**, (c) "pseudosuitane"-type complex **1**·**2**, and (d) linear polyrotaxanes.

Host **1**[10] and guest **2**[11a] were synthesized according to the literature procedures. Initially, we used ^{1}H NMR spectroscopy to investigate the complexation between host **1** and guest **2**. As shown in Fig. 2, the ^{1}H NMR spectrum of an equimolar mixture of **1** and **2** in $CDCl_3/CD_3CN$ (1:1, v/v) solution showed a significantly difference from those of host **1** and guest **2**. The signals for protons H_a, H_b of **2** shifted upfield probably owing to the strong shielding effect of the aromatic rings of **1**. Meanwhile, the signals for methylene protons H_c and H_d of **2** showed considerable downfield shifts, which might be attributed to the hydrogen bonding interactions and its position in the deshielding region of the aromatic rings of **1**. It was also found that the signal corresponding to proton H_1 of host **1** showed downfield shift. Furthermore, the signal of phenyl proton H_4 was found to split into multiple peaks, indicating the asymmetry of the two phenyl rings. These observations suggested that a stable complex between host **1** and guest **2** could be formed, and the anthracenyl core of **2** was located in the cavity of host **1**. Fluorescence spectroscopy provided more evidence for formation of the complex between host **1** and guest **2** (see ESI). It was found that after **1** and **2** were mixed by an equimolar ratio in $CHCl_3/CH_3CN$ (1:1, v/v), the fluorescence of the mixed solution quenched nearly 80% compared with guest **2** with a strong fluorescence at room

temperature, suggesting that the anthracenyl core of **2** was located inside the cavity of **1**, which is consistent with the previous results. To further determine the stoichiometry of the complex, Job plot experiments were carried out, which revealed the formation of 1:1 complex between host **1** and guest **2** (see ESI). Moreover, the fluorescence titration experiments also afforded a quantitative estimate for the complexation between **1** and **2** by monitoring the fluorescence changes of **2** (see ESI). Consequently, the association constant K_a of complex **1·2** was calculated by the plot of F_0/F_{cal} (F_{cal}: the calibrated fluorescence intensity[12]) versus concentration of **1** to be 4.4 (±0.1) $\times 10^3$ M^{-1}.

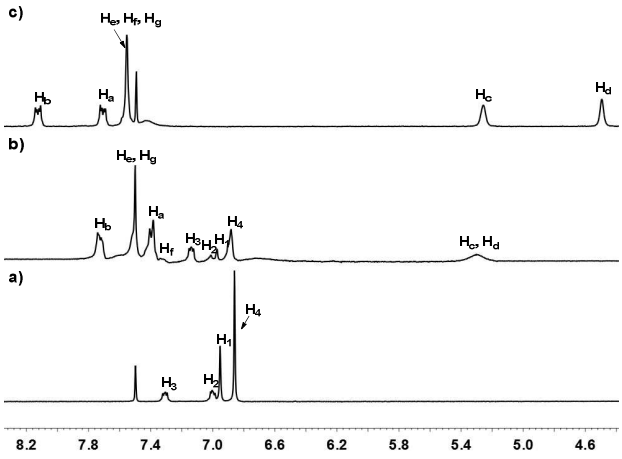


Fig. 2 Partial ^{1}H NMR spectra (300 MHz, CD_3CN: $CDCl_3$ = 1:1, 295 K) of (a) free host **1**, (b) **1** and 1.0 equiv of **2**, and (c) free **2**. $[\mathbf{1}]_0$ = 3.0 mM.

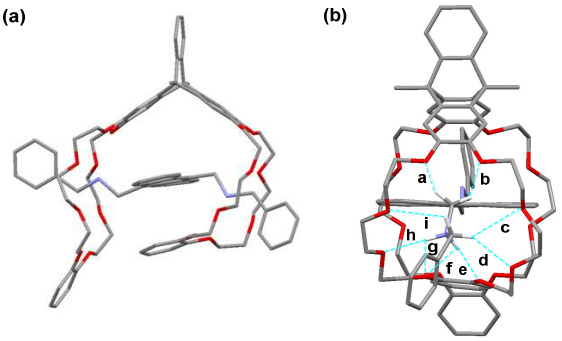
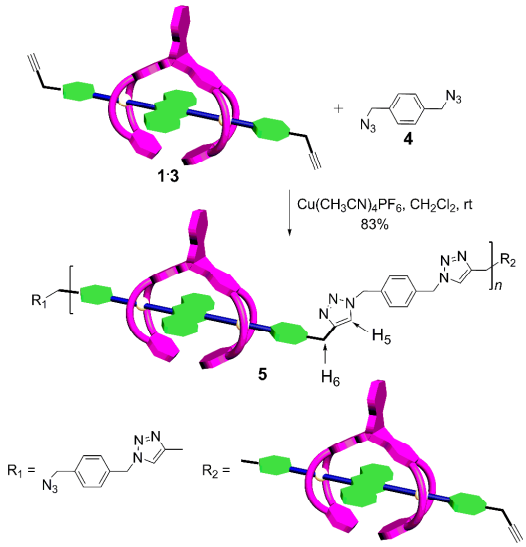


Fig. 3 Top view (a) and side view (b) of the crystal structure of complex **1·2**. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the hydrogen bonding interactions are omitted for clarity. Hydrogen-bond distances (Å): a = 2.60, b = 2.69, c = 2.68, d = 2.47, i = 2.69 for C-H···O; e = 2.15, f = 2.57, g = 2.56, h = 2.10 for N-H···O.

Formation of the 1:1 complex between host **1** and guest **2** was further confirmed by its X-ray crystal structure. Consequently, faint yellow single crystals of complex **1·2** were obtained by diffusion of ether into an equimolar mixture of **1** and **2** in $CH_3CN/CHCl_3$ (1:1, v/v) solution. As shown in Fig. 3, the benzylammonium ions of guest **2** threaded the two DB24C8 cavities of host **1**, and the bulky anthracenyl core of **2** was located in the central cavity of host **1**, which resulted in the formation of a "pseudosuitane"-type complex. It was found that there existed multiple hydrogen-bonding interactions between the polyether oxygen atoms and the hydrogen atoms of the ammonium ions with the distances of 2.15 (e), 2.57 (f), 2.56 (g) and 2.10 Å (h), respectively. The C-H···O interactions between the benzylic methylene hydrogen atoms and the crown oxygen atoms of the host, as well as those between the anthracenyl methylene hydrogen atoms and the oxygen atoms of the host were further found. Moreover, there also existed additional face-face π···π stacking interactions between the aromatic rings of anthracenyl group and the phenyl ring of one DB24C8 unit with the distance of 3.46 Å. Consequently, because of the multiple non-covalent interactions between host **1** and guest **2**, complex **1·2** showed a high stability, which was consistent with the result in solution.



Scheme 1. Synthesis of linear polyrotaxane **5**.

Formation of the "pseudosuitane" complex **1·2** encouraged us to further construct a linear polyrotaxane. Consequently, we first designed and synthesized a functionalized bis secondary dialkylammonium salt containing an anthracenyl core **3** by the condensation of anthracene-9, 10-dicarboxaldehyde with 2 equiv of 4-(prop-2-yn-1-yloxy)benzylamine,[13] and followed by the reduction of the resulting diimine, and then protonation and counterion exchange (see ESI). With **3** in hand, we then tested its complexation with host **1**, and found that similar to complex **1·2**, host **1** and guest **2** could also form a "pseudosuitane"-type complex **1·3** in solution (see ESI). Since complex **1·3** contains two terminal propargyl groups, we then tried to synthesize the linear polyrotaxane by the high efficient CuAAC 'click' reaction. As shown in Scheme 1, the mixture of equimolar host **1** and guest **3** in dry CH_2Cl_2 was stirred at room temperature overnight under nitrogen atmosphere to form complex **1·3**. Then, to the above solution was added one equivalent diazide **4** and catalytic amount of $Cu(CH_3CN)_4PF_6$, and the mixture was stirred for another 24h. During the reaction process, the precipitation was formed, which was filtered, washed with CH_2Cl_2, CH_3OH, H_2O, and Et_2O, respectively, and then dried in vacuo to give the linear polyrotaxane **5** in 83%. The polyrotaxane was characterized by FT-IR, ^{1}H NMR and gel permeation chromatography (GPC). In the FT-IR spectrum of **5**, the peaks at 1057, 2101 and 3502 cm^{-1} corresponding to the triazole and azido and unreacted alkynyl groups, respectively, could be observed. The ^{1}H NMR spectrum

of **5**[14] showed wide proton signals for not only the monomers and the 1,2,3-triazole subunit (H_5 at 8.27 ppm, H_6 at 5.08 ppm), but also the triptycene-derived bis(crown ether) host **1**. These observations indicated that polyrotaxane **5** could be successfully obtained by the effective CuAAC 'click' reaction of the "pseudosuitane"-type complex **1**·**3** and diazide **4**. Moreover, the number-average molecular weight (M_n) and the polydispersity index of polyrotaxane **5** were also determined by gel permeation chromatography using polystyrene (PS) as standard and dimethylformamide (DMF) as eluent. Consequently, it was found that the M_n value of the polyrotaxane is 11.9 kDa with the polydispersity index of 1.27 (see ESI), which indicates that each polymer chain of polyrotaxane **5** is composed of ca. seven "pseudosuitane" repeating units. Furthermore, the glass transition temperature of the polyrotaxane was determined by the differential scanning calorimetry (DSC) analysis, which was found to be 122 °C.

In conclusion, we have demonstrated that host **1** and guest **2** could form 1:1 stable "pseudosuitane"-type complex in both solution and solid state. On the basis of this result, we further developed a new method for the synthesis of linear polyrotaxanes. Consequently, a functionalized bis secondary dialkylammonium salt **3** containing an anthracenyl group as core was synthesized, and a linear main–chain polyrotaxane **5** could be conveniently synthesized in high yield by the highly efficient CuAAC reaction of "pseudosuitane"-type complex **1**·**3** with diazide **4**. By changing the structures and properties of the linkers, it can be expected that various polyrotaxanes would be conveniently obtained. Thus, the results presented here will provide us new opportunities for the construction of high order interlocked molecules, especially, for the synthesis of supramolecular polymers with specific structures and properties.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis of guest **3** and polyrotaxane **5**. Fluorescence titrations of host **1** and guest **2**. FT-IR and GPC spectra of polyrotaxane **5**. CCDC 998225 for crystal structure of complex **1**·**3**. For the ESI, see DOI: 10.1039/b000000x/

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14. As a comparison, polymer **6** was also prepared by the CuAAC 'click' reaction of compound **3** and diazide **4** in the absence of host **1** (see ESI). The ^{1}H NMR spectrum of polymer **6** showed proton signals for only the monomers and the triazole moiety, but no the triptycene-derived bis(crown ether) moiety, which are obvious different from those of polyrotaxane **5**. We also performed the ^{1}H NMR experiments of polyrotaxane **5** and polymer **6** in CD_3CN (see ESI). The results showed that obvious proton signals for triptycene-derived bis(crown ether) moiety were observed in polyrotaxane **5**, but no relative proton signals were found in **6** as well, which further confirmed the formation of polyrotaxane **5**.