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A Novel Strategy To Assemble Achiral Ligands to Chiral Helical Polyrotaxane Structures

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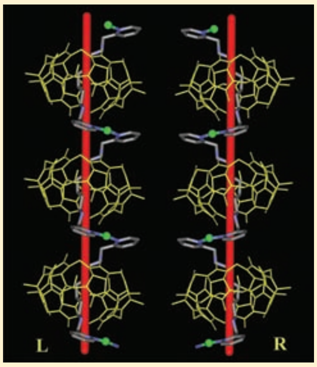
S *Supporting Information*

ABSTRACT: Using the achiral *N*,*N*′-bis(2-pyridylmethyl)-1,6-hexanediamine ligand bearing two end pyridyl groups as the source of conformational chirality, a novel type of TMeQ[6]-based helical polyrotaxane was prepared and characterized by X-ray crystallography and ^{1}H NMR spectroscopy. The chirality of the polyrotaxane was generated from twisting of the hexylidene of the *N*,*N*′-bis(2-pyridylmethyl)-1,6-hexanediamine "string" when bound within the hydrophobic cavity of TMeQ[6]. Two opposite chiral helical polyrotaxanes crystallize as a racemic compound.



INTRODUCTION

Over the past 2 decades, poly(pseudo)rotaxanes,[1] in which a number of cyclic molecular "beads" such as crown ethers, cyclodextrins, calix[*n*]arenes, and cyclophanes are threaded onto a linear "string", have received much attention because of their unique structures and their promising applications. One of the unique applications of these polyrotaxanes is electron transportation.[2] For example, Terao and co-workers synthesized a highly insulated molecular wire (IMW), in which the conductive π-conjugated polymer core is encapsulated by a protective sheath (permethylated α-cyclodextrin).[3] To date, different methods have been invented to construct polyrotaxanes and various polyrotaxanes have been prepared as new materials.

The cucurbit[*n*]urils[4,5] ($n = 5-8$ and 10; hereafter abbreviated as Q[*n*]; Figure 1), a family of pumpkin-shaped macrocycles derived from glycoluril and formaldehyde, have also been investigated to construct rotaxanes and poly(pseudo)rotaxanes.[6−8] Among these reports, Kim and co-workers reported two particularly interesting examples on Q[*n*]-based chiral helical polyrotaxanes.[8] Very recently, we discovered that the long alkyl chain of *N*,*N*′-bis-[4-(dimethylamino)benzyl]dodecane-1,12-diamine takes a different chiral helical conformation when bound within the hydrophobic cavity of Q[8].[9] Inspired by Kim et al.'s results, we hypothesized that the long alkyl chain could be assembled as a chiral helical coordination polymer by transition ions to construct Q[*n*]-based chiral helical polyrotaxanes. Thus, we set out to design and synthesize a series of *N*,*N*′-bis(*n*-pyridylmethyl)-1,6-hexanediamine ($n = 2-4$) organic ligands containing two typical functional pyridyl groups and one 1,6-hexanediamine chain. We also investigated interactions between the chains and the symmetrical α,α′,δ,δ′-tetramethylcucurbit[6]uril (hereafter abbreviated as TMeQ[6]).[10,11]

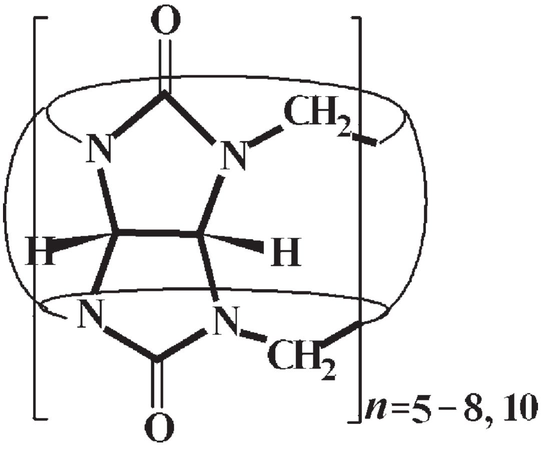


Figure 1. Molecular structure of Q[*n*] ($n = 5-8$ and 10).

In the present work, we report the construction and characterization of a novel type of chiral helical polyrotaxane in which the *N*,*N*′-bis(2-pyridylmethyl)-1,6-hexanediamine "string" adopts

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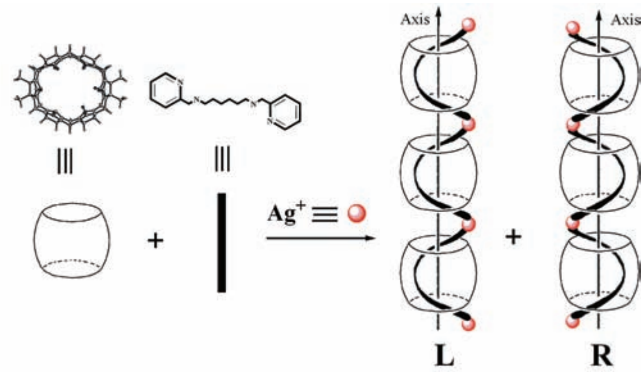
Scheme 1. Construction of Chiral Helical Polyrotaxanes



different chiral conformations when bound within TMeQ[6] "beads" and is linked with silver ions to form two opposite chiral helical coordination polymers (Scheme 1). From our previous work, we knew that the reaction of TMeQ[6] and *N*,*N*′-bis-(2-pyridylmethyl)-1,6-hexanediamine leads to the formation of a dumbbell-shaped inclusion complex both in the solid state and in aqueous solution. The pyridyl moieties, rather than the alkyl chains, are located in the cavity of TMeQ[6], which was characterized by X-ray crystallography and ^{1}H NMR spectroscopy.[11]

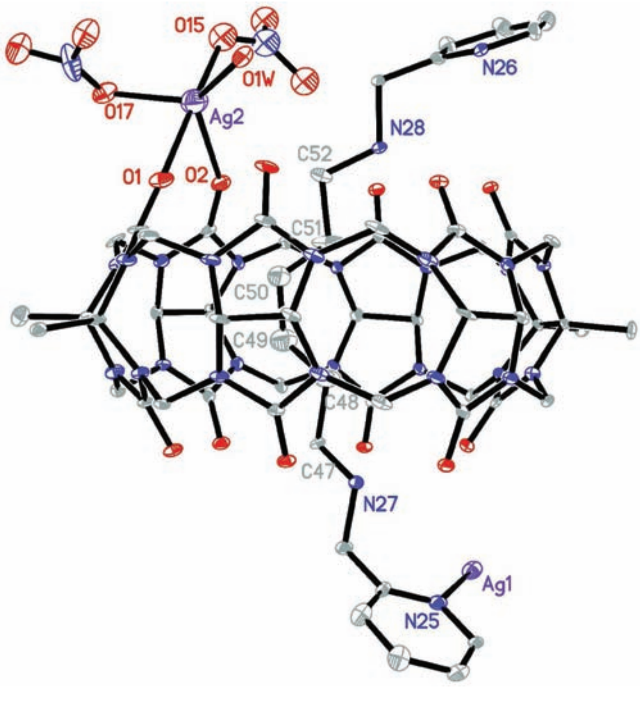


Figure 2. ORTEP diagram of complex **1** (asymmetric unit). Displacement ellipsoids are drawn at the 30% probability level. Solvate water molecules and anions are omitted for clarity.

EXPERIMENTAL SECTION

Materials and Methods. All commercially available chemicals were used as supplied without further purification. The TMeQ[6][10] and the HCl salt of *N*,*N*′-bis(2-pyridylmethyl)-1,6-hexanediamine[11] were synthesized according to literature methods. The ^{1}H NMR spectra were recorded at 20 °C on a Varian INOVA-400 spectrometer. The C, H, and N microanalyses were carried out with a PerkinElmer 240C elemental analyzer. Thermogravimetric analysis (TGA) data were recorded on a Netzsch STA 449 C instrument under an air atmosphere with a heating rate of 10 °C/min. Powder X-ray diffractometry was performed with a Panalytical X-Pert pro diffractometer using Cu Kα radiation at 25 °C.

Computational Methods. All calculations were performed using the *Gaussian 03W* (revision C.02) software package.[12] The initial geometries of all structures were constructed with the aid of the *Hyperchem*, release 7.52, package.[13] Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP)[14,15] was used for full geometry optimization and a basis set superposition error (BSSE) corrected[16,17] binding energy with a 3-21G* basis set.[18,19]

Preparation of Complex 1. TMeQ[6] (0.0640 g, 0.05 mmol) and the HCl salt of *N*,*N*′-bis(2-pyridylmethyl)-1,6-hexanediamine (0.0190 g, 0.05 mmol) were dissolved in 10.0 mL of water with stirring at room temperature. The mixture was heated to 100 °C and refluxed for 2.5 h. When the pH of the solution was adjusted to about 5−6 by 1.0 mol/L $NH_3 \cdot H_2O$, $AgNO_3$ (0.0430 g, 0.25 mmol) was added to the mixture. Undissolved AgCl was filtered. The filtrate was left to stand at room temperature in an open beaker. After 3 weeks, X-ray-quality colorless crystals of complex **1** were obtained and collected with a yield of 12.9%. Anal. Calcd for complex **1**: C, 37.14; H, 4.57; N, 23.15. Found: C, 37.01; H, 4.68; N, 22.93.

Single-Crystal X-ray Crystallography. Diffraction data for complex **1** were determined with a Bruker SMART Apex-II CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.710 73 Å) in a $\omega/2\theta$ scan mode at 173 K. The data were corrected for absorption by the *SADABS* program in the BrukerAXS program package. The structure of complex **1** was solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms for C−H were positioned at their calculated positions and were assigned common isotropic temperature factors. The program *PLATON* cannot offer higher symmetric space groups. No hydrogen atoms are given for all isolated water molecules because chloride anions and some water molecules in the lattice are disordered.

Crystal Data for Complex 1. Empirical formula $C_{116}H_{170}Ag_4Cl_2N_{62}O_{51}$, M_r = 3751.52, triclinic, space group $P\bar{1}$, a = 11.9276(9) Å, b = 12.5672(10) Å, c = 25.0317(19) Å, α = 100.238(3)°, β = 96.555(3)°, γ = 100.003(3)°, V = 3595.3(5) Å^3, Z = 1, D_c = 1.733 g/cm^3, $F(000)$ = 1930, GOF = 1.168, R1 = 0.1249 [$I > 2\sigma(I)$], wR2 = 0.3445 (all data).

CCDC 795200 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or by e-mailing data_request@ccdc.cam.ac.uk or contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44 1223 336033).

RESULTS AND DISCUSSION

Slow evaporation of the reaction solution of *N*,*N*′-bis-(2-pyridylmethyl)-1,6-hexanediamine, TMeQ[6], and silver nitrate at pH ca. 5−6 and room temperature resulted in the formation of crystals of complex **1**, $\{[Ag(C_{18}H_{28}N_4)\cdot(C_{40}H_{44}N_{24}O_{12})Ag(H_2O)(NO_3)_2]NO_3\cdot Cl\cdot 3.5H_2O\}_n$. X-ray analysis of complex **1** (Figure 2) revealed a chiral helical polyrotaxane, in which the TMeQ[6] "bead" is located over the hexylidene chain part of the *N*,*N*′-bis(2-pyridylmethyl)-1,6-hexanediamine "string". It should be noted that, in the unit cell, two different types of silver ions are present. One type of silver ion, Ag2, leans toward one side of the portal of the TMeQ[6] "bead", being coordinated to two carbonyl oxygen atoms at the portal with Ag2−O distances of 2.550(4) and 2.474(4) Å. One water molecule and two nitrate anions are also bound to Ag2 with distances of 2.368(5), 2.353(9),

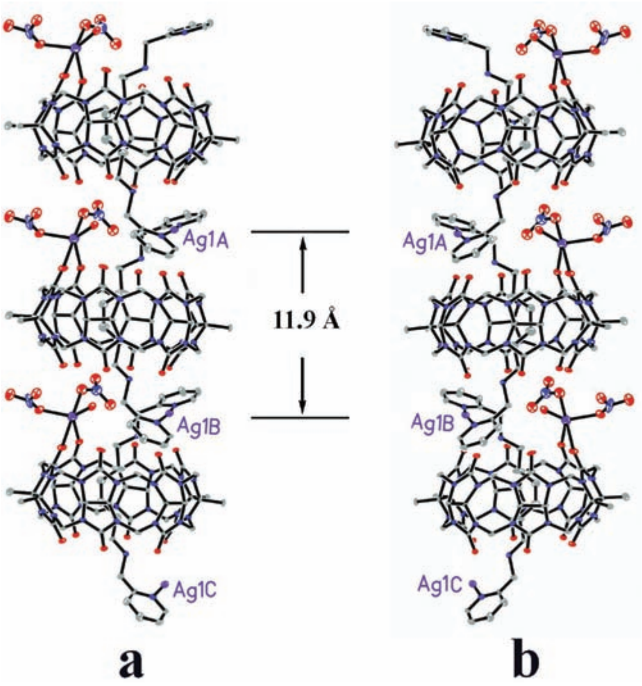


Figure 3. X-ray crystal structure of complex **1** showing TMeQ[6] "beads" threaded onto a helical 1D coordination polymer: (a) left-handed helix; (b) right-handed helix. Solvate water molecules and anions are omitted for clarity.

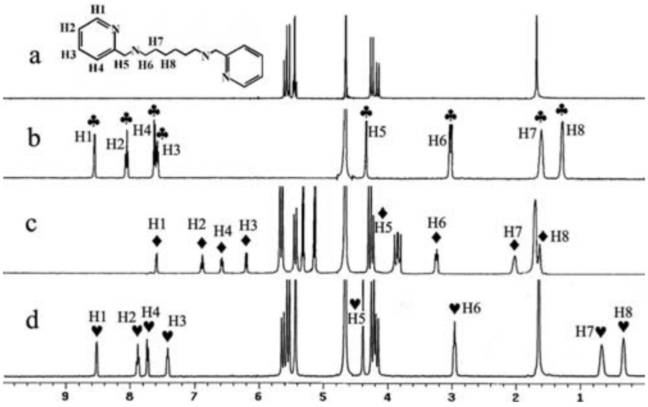


Figure 4. ^{1}H NMR spectra of (a) the host TMeQ[6] in D_2O, the *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine in the (b) absence of TMeQ[6] and (c) presence of 2.0 equiv of the host TMeQ[6] in D_2O, and (d) complex **1** in D_2O.

and 2.383(5) Å. The other type of silver ion, Ag1, behaves as a node binding two *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine "strings": Ag1−N26 2.205(5) Å, Ag1−N25 2.218(5) Å, N26−Ag1−N25 167.81(16)°. The *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine "string" is twisted, yielding a spiral-like conformation with a C48−C49−C50−C51 torsion angle of 66.03°. The spiral-like "string" behaves as a ligand bridging two silver ions with its two end pyridyl groups. Consequently, a 1D helical polyrotaxane extended along the *a* axis is formed. Examples of a silver-containing 1D helical chain also appear in other literatures.[20] Interestingly, there are two types of helical polyrotaxane chains in complex **1**, one exhibiting right-handedness (Figure 3a) and the other exhibiting left-handedness (Figure 3b). Neighboring opposite chiral helical polyrotaxanes were parallel to each other and were interlinked by hydrogen bonds, generating a racemic mixture.

At first glance, complex **1** is structurally very similar to its counterpart $\{[Ag(C_{17}H_{26}N_4)\cdot C_{36}H_{36}N_{24}O_{12}](NO_3)_3\cdot 12(H_2O)\}_n$, previously reported as the Q[6]-based helical polyrotaxane by Kim et al.[8a] They are both generated from achiral ligands, and both are racemic mixtures. However, upon closer examination, we realized that the two polyrotaxanes have different helicity origins. In the case of complex **1**, the twist of the "string" plays a crucial role in generating of spiral-like conformation. In the latter case, the coordinated silver ions changed the direction of the polymer chain and led to the helical structure. In addition, the two complexes have different screw axis structures. In complex **1**, one pseudorotaxane and one silver ion constitute one turn with a helical pitch of 11.9 Å, which is the same as the *a* axis length, while in the latter case, two pseudorotaxanes and two silver ions constitute one turn with the 2_1 screw axis along the *b* axis, in which the helical pitch is 17.9 Å. Finally, all TMeQ[6] beads in complex **1** are parallel to each other, while in the latter case, neighboring Q[6] beads spread toward different directions.

To better understand the interaction between the TMeQ[6] "bead" and the *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine "string" in solution, we studied the ^{1}H NMR spectra of complex **1**. By comparing with the dumbbell-shaped inclusion complex (Figure 4c), we noticed significant changes in the ^{1}H NMR spectra of complex **1**. As shown in Figure 4d, all of the protons of the long alkyl chain exhibited a considerable upfield shift, indicating that the TMeQ[6] "bead" is located over the middle position of the *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine "string". Meanwhile, the protons of the end pyridyl groups of the "string" exhibited a slightly upfield shift too. Because the cavity of TMeQ[6] is not large enough to accommodate one hexylidene chain and two pyridyl groups simultaneously, we believe that the hexylidene and the pyridyl groups are undergoing a fast exchange process on the NMR time scale. In other words, the TMeQ[6] "bead" can slip back and forth on the *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine "string" in aqueous solution.

To understand how the host−guest interactions can occur, quantum chemistry calculations based on density functional theory (DFT; B3LYP/3-21G* basis set) for the optimized geometries of inclusion complexes in the designed reaction route (Scheme 2) were performed and the calculation results have been collected in Table 1. A very negative ΔE_1 value of the interaction of the guest *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine with the host TMeQ[6] has been found, and the dumbbell-shaped inclusion was therefore stable in thermodynamics. The calculation results unambiguously demonstrate consistent models with analysis of the ^{1}H NMR experiments. A route of host−guest model transformation from dumbbell-shaped to pseudorotaxane has been designed. The negative values of ΔE_2 suggest that the reaction should occur. The designed dissociation of inclusion complexes gave very high energies (ΔE_3 or ΔE_{B3}), so the pseudorotaxanes were hardly to be dissociated. The above calculation results revealed that the host TMeQ[6] can remain on each moiety of the guest *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine.

When 1 equiv of KI was added to the solution containing complex **1**, a mass of white precipitate was formed immediately and all of the ^{1}H NMR signals of complex **1** disappeared, indicating that the polyrotaxane structure was destroyed thoroughly.

Scheme 2. Designed Reaction Route

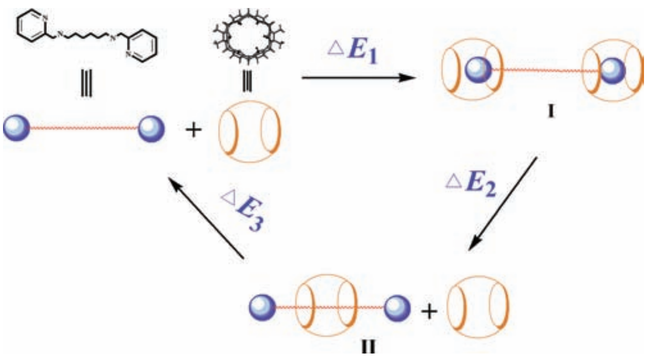


Table 1. Binding Energies Δ*E* (BSSE-Corrected Binding Energies, ΔE_B)[a] in the Interactions of TMeQ[6] with *N*,*N′*-Bis(2-pyridylmethyl)-1,6-hexanediamine (kJ/mol)

ΔE_1 (ΔE_{B1})	ΔE_2 (ΔE_{B2})	ΔE_3 (ΔE_{B3})
−870.8 (−501.7)	−265.8 (−126.4)	605.0 (375.2)

[a] $\Delta E_B = \Delta E$ + BSSE-corrected binding energy of the corresponding host−guest inclusion.

Figure 5. Pictorial representation of the reaction of complex **1** with (a) KI and (b) BaS.

Interestingly, when 1 equiv of BaS instead of KI was added, although a lot of dark-brown precipitate was observed (Figure 5), the ^{1}H NMR signals of complex **1** were unaffected. In comparison with the white precipitate, the quantity of the dark-brown precipitate was much less, and the quantity of the dark-brown precipitate remained unchanged when excess BaS was added. These observations suggest that the coordination polymers in complex **1** could remain untouched even when the silver ions coordinated to the portal of TMeQ[6] (Ag2) were removed.

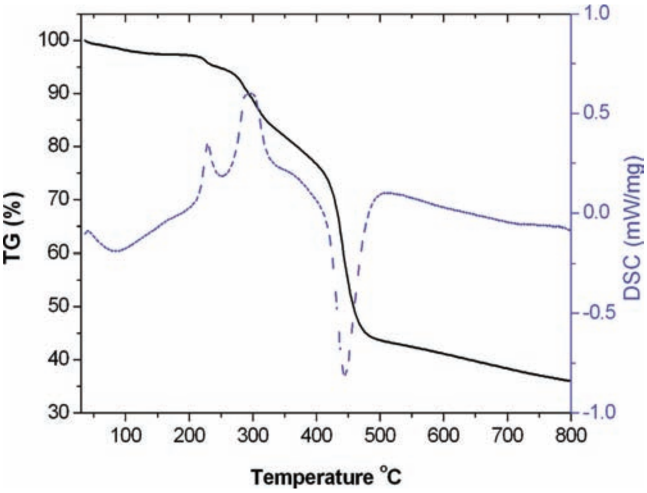


Figure 6. TGA diagram of complex **1**.

TGA curves have been obtained in air for crystalline samples of complex **1** in the temperature range 35−800 °C. It is seen from the TGA curve of complex **1** (Figure 6) that the first weight loss of 3.13% from 35 to 215 °C corresponds to the removal of seven free water molecules in each formula unit (calcd: 3.36%). The total weight loss of 3.13% is slightly smaller than the calculated value of 3.36%. The following weight loss (in the range from 215 to 800 °C) is attributable to the loss of the coordinating water molecules and decomposition of the organic component. The simulated and experimental PXRD spectra for complex **1** are presented in Figure S1 in the Supporting Information, which clearly shows that they are almost identical.

■ CONCLUSION

In conclusion, we present here a novel strategy to synthesizing chiral helical polyrotaxanes by utilizing the twist of the long alkyl chain when bound within the hydrophobic cavity of Q[*n*]. Such a synthetic strategy may be suitable for the construction of other chiral helical polyrotaxanes. We are actively investigating methods to induce the spontaneous resolution of the racemic mixtures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data in CIF format and powder X-ray diffractograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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