

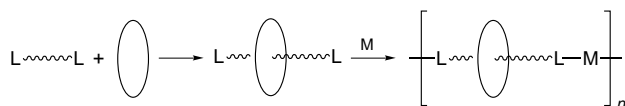
Helical polyrotaxane: cucurbituril 'beads' threaded onto a helical one-dimensional coordination polymer

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Formation of a pseudorotaxane by threading a cucurbituril 'bead' with a *N,N'*-bis(3-pyridylmethyl)-1,4-diaminopentane 'string' followed by reaction of the pseudorotaxane with AgNO₃ yields a polyrotaxane, the X-ray crystal structure of which reveals the 'beads' threaded onto a helical one-dimensional coordination polymer.

Polyrotaxanes¹ in which a number of cyclic molecular 'beads' are threaded onto a linear 'string' have received considerable attention in recent years due not only to their structures and properties but also to their potential applications as new materials.^{1c} We have recently reported² a simple one-step approach to construct 1D and 2D polyrotaxane coordination polymers in the solid state. It involves formation of a pseudorotaxane first by threading a molecular 'bead' with a 'string' which has suitable functional groups at both ends and then formation of a polyrotaxane coordination polymer by allowing the end functional groups of the pseudorotaxane to coordinate to metal centers (Scheme 1). In this approach a

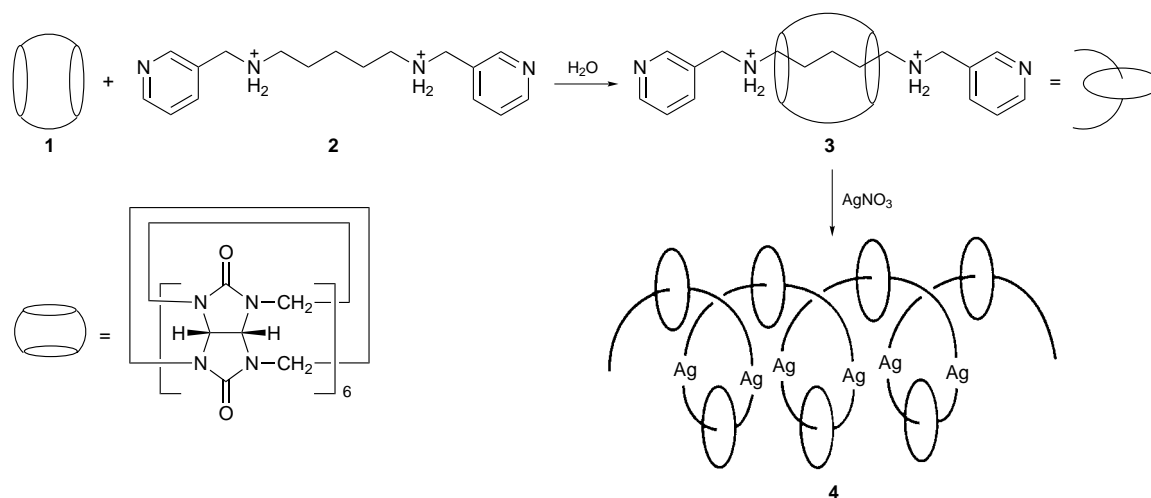


Scheme 1

judicious choice of metal ion is important to achieve the desired solid state structure. Under the same or similar conditions, for instance, Mn²⁺, Cu²⁺ and Ag⁺ result in totally different structures; they are a simple rotaxane, a 1D polyrotaxane and a 2D polyrotaxane, respectively.² Counter-anions also play an important role in determining the solid state structure: for example, silver nitrate leads to a 2D polyrotaxane whereas silver tosylate yields a 1D polyrotaxane.^{2b} A unique and interesting twist in this approach to construction of poly-

rotaxanes results from changing the 'string' from *N,N'*-bis(4-pyridylmethyl)-1,4-diaminobutane, used previously in this procedure,² to *N,N'*-bis(3-pyridylmethyl)-1,5-diaminopentane. Herein we report the first example of helical polyrotaxanes in which cyclic beads are threaded on helical one-dimensional coordination polymers.

The formation of the pseudorotaxane **3**, by threading cucurbituril **1**³ with *N,N'*-bis(3-pyridylmethyl)-1,5-diaminopentane dihydronitrate **2**, followed by the reaction of **3** with AgNO₃ yielded **4** (Scheme 2).[†] The X-ray crystal structure[‡] of **4** reveals a 1D polyrotaxane in which cucurbituril 'beads' are threaded on a 1D coordination polymer with a formula of [Ag-pyCH₂NH₂(CH₂)₅NH₂CH₂py-]_n³ⁿ⁺. The asymmetric unit consists of a Ag ion, a pseudorotaxane **3**, one of the pyridine units of which is coordinated to the silver ion, and three nitrate ions to balance the charge (Fig. 1). Most interestingly, the coordination polymer has a helical structure extended along the *b* axis with a pitch of 17.9 Å which is the same as the *b* axis length (Fig. 2). There are equal amounts of right- and left-handed helices in the crystal (it is a racemic mixture). In each helix, two 'supermolecules' of **3** and two silver ions constitute one turn. Each silver ion is coordinated by two 'supermolecule' **3** in a linear fashion: Ag-N(25) 2.133(8), Ag-N(28) 2.138(7) Å, N(25)-Ag-N(28) 177.9(3)°. A cucurbituril 'bead' is held tightly at the middle of each repeating unit by strong hydrogen bonds between the protonated amine nitrogen atoms of the 'string' **2** and the oxygen atoms of cucurbituril: N(26)⋯O(1) 2.914(10) Å, N(26)⋯O(2) 3.082(10) Å, N(26)⋯O(6) 2.893(10) Å, N(27)⋯O(8) 2.793(9) Å, N(27)⋯O(9) 2.754(9) Å, N(27)⋯O(10) 3.089(9) Å. It is interesting to note that N(26) is displaced from the six-oxygen plane of the portal by only 0.037(7) Å, but from the other amine nitrogen N(27) by 0.721(8) Å. Moreover, the 3-pyridyl unit attached to N(26) make a dihedral angle of 61° with the six-oxygen plane whereas that connected to N(27) is nearly parallel to the portal plane



Scheme 2

