## 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 AgNO<sub>3</sub> yields a polyrotaxane, the X-ray crystal structure of which reveals the 'beads' threaded onto a helical onedimensional coordination polymer.

Polyrotaxanes<sup>1</sup> 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.<sup>1c</sup> We have recently reported<sup>2</sup> 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



judicious choice of metal ion is important to achieve the desired solid state structure. Under the same or similar conditions, for instance,  $Mn^{2+}$ ,  $Cu^{2+}$  and  $Ag^+$  result in totally different structures; they are a simple rotaxane, a 1D polyrotaxane and a 2D polyrotaxane, respectively.<sup>2</sup> 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.<sup>2b</sup> 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,<sup>2</sup> 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 AgNO<sub>3</sub> yielded 4 (Scheme 2).<sup>†</sup> The X-ray crystal structure<sup>‡</sup> of 4 reveals a 1D polyrotaxane in which cucurbituril 'beads' are threaded on a 1D coordination polymer with a formula of -[AgpyCH<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>CH<sub>2</sub>py-]<sub>n</sub><sup>3n+</sup>. 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:  $N(26)\cdots O(1)$ 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



Fig. 1 Asymmetric unit of the crystal structure of 4. Counter-ions ( $NO_3^-$ ) and water molecules in the lattice are omitted for clarity.



Fig. 2 Structure of 4 showing cucurbituril 'beads' threaded onto a helical 1D coordination polymer

(angle  $9^{\circ}$ ). The parallel conformation of the 3-pyridyl unit makes the polymer chain change its direction sharply, which eventually leads to a helical structure (Fig. 3).

In conclusion, we present here an unprecedented helical 1D polyrotaxane in which cyclic 'beads' are threaded onto a helical



**Fig. 3** The helical 1D coordination polymer threading cucurbituril 'beads' (omitted) in **4**. The pitch of the helix is 17.9 Å. Bond distances (Å) and angle (°) around the silver ion: Ag–N(25) 2.133(8), Ag–N(28) 2.138(7), N(25)–Ag–N(28) 177.9(3).

coordination polymer. It still remains to be determined how one enantiomer, either right- or left-handed polyrotaxane helices can be enantioselectively constructed. Such chiral helical polyrotaxanes may have interesting applications.

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## **Footnotes and References**

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<sup>†</sup> Cucurbituril (1) decahydrate (1.00 g, 0.85 mmol) and *N,N'*-bis(3-pyridylmethyl)-1,5-diminopentane dihydronitrate 2 (0.246 g, 0.60 mmol) were added to water (20 ml). After overnight stirring, undissolved cucurbituril was filtered. The <sup>1</sup>H NMR spectrum of the filtrate (using D<sub>2</sub>O) reveals the formation of a 1 : 1 complex (pseudorotaxane 3) of 1 and 2. A 0.2 M solution of AgNO<sub>3</sub> in methanol was layered over the filtrate in a diffusion tube to produce colorless X-ray quality crystals of 4 in one week (21%). Satisfactory elemental analysis was obtained.

‡ Crystal data for 4: AgC<sub>53</sub>H<sub>86</sub>N<sub>31</sub>O<sub>33</sub>, M = 1793.40, monoclinic, space group  $P2_1/n$ , a = 16.680(4), b = 17.889(2), c = 24.335(4) Å,  $\beta = 101.355(8)^\circ$ , U = 7119(2) Å<sup>3</sup>, Z = 4,  $D_c = 1.673$  g cm<sup>-3</sup>,  $\mu$ (Mo-K\alpha) = 3.99 cm<sup>-1</sup>, T = 293 K; 7126 unique reflections measured;  $R_1$  [ $I > 2\sigma(I)$ ] = 0.063,  $wR_2$  (all data) = 0.1693, GOF = 1.06. The intensity data were collected with an Enraf-Nonius CAD4 diffractometer using monochromated Mo-K\alpha radiation [ $\lambda$ (K $\alpha$ ) = 0.71073 Å]. The structures were solved by direct methods (SHELXL-86) and refined by full-matrix leastsquares methods (SHELXL-93). All non-hydrogen atoms were refined anisotropically. CCDC 182/674.

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