

Oligomeric Pseudorotaxanes Adopting Infinite-Chain Lattice Superstructures**

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Polyrotaxanes and polypseudorotaxanes^[1] are relatively new types of polymeric materials, comprising polymer chains threaded through cyclic components in the presence or absence, respectively, of bulky stoppers at both ends of their polymeric chains. They often demonstrate^[2] unusual macroscopic properties compared with their small-molecule counterparts^[3]—that is, rotaxanes and pseudorotaxanes, respectively—in relation to properties such as stability, solubility, and viscosity, as well as thermal, mechanical, and electronic performance. Crystallinity, if it occurs, is one of the key factors affecting the thermal, optical, mechanical, and chemical properties of polymers, but it is difficult for long polymer chains—typically those in excess of 10 monomer repeating units or those with molecular weights higher than 1000 Da—to form macroscopic single crystals, because of both 1) dif-

fusion limitations resulting from chain entanglements and 2) the heterogeneous length distributions of most synthetic polymers. Crystal structures of synthetic polymers are thus usually obtained^[4] by computational model-building and diffraction simulation of X-ray powder- or fiber-diffraction data by using structural information from single-crystal analyses of small oligomeric homologues.^[5] Although obtaining macroscopic single crystals of high-molecular-weight polyrotaxanes might seem to be even less realistic than it is for simple polymer chains, a small number of polypseudorotaxane crystal superstructures are known as a result of the end-to-end linking of small-molecule pseudorotaxanes by, for example, metal coordination^[6] or hydrogen bonding^[7] of the chain components. Cyclodextrins have also been found to crystallize with threaded chains, either of disordered surfactants^[8] or of low-molecular-weight polyethylene or polypropylene glycols, which are present in channels created by the stacked cyclodextrin tori running through the crystalline lattices.^[9]

Here, we report a series of single-crystal X-ray superstructures of donor–acceptor polypseudorotaxanes. Remarkably, although the oligomeric chains are undoubtedly discrete and monodisperse, they nevertheless appear to be infinite in the crystal. These polypseudorotaxanes lie on polymeric crystalline lattices with oligomer end-groups constituting crystallographically invisible defects in their superstructures. It follows that the solid-state superstructures of the corresponding high-molecular-weight “genuine” polypseudorotaxanes can be described in full atomic detail despite the fact that single crystals of these supramolecular polymers have not been, and may never be, obtained.

A series of donor–acceptor oligorotaxanes, currently under investigation^[10] for their foldamer-like properties, have been obtained from oligomeric chains containing electron-rich 1,5-dioxynaphthalene (NP) units, separated by tetraethylene glycol loops, and with cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) as the ring components. The secondary structures of these foldamers are stabilized by a combination of C–H...O hydrogen-bonding interactions and π – π stacking interactions between the π -electron-rich NP units in the polymer chains and the π -electron-deficient bipyridinium (BIPY²⁺) units in the CBPQT⁴⁺ rings. Single-crystal X-ray analyses of the complexes (Figure 1a) formed between CBPQT⁴⁺ and both 3NPP and 3NPE have revealed the anticipated formation of [2]- and [3]pseudorotaxanes, respectively, in which one CBPQT⁴⁺ ring encircles the central NP unit in the first case, while two such rings encircle the two outer NP rings in the second case. The crystal superstructure^[11] of the corresponding pseudorotaxane formed from the

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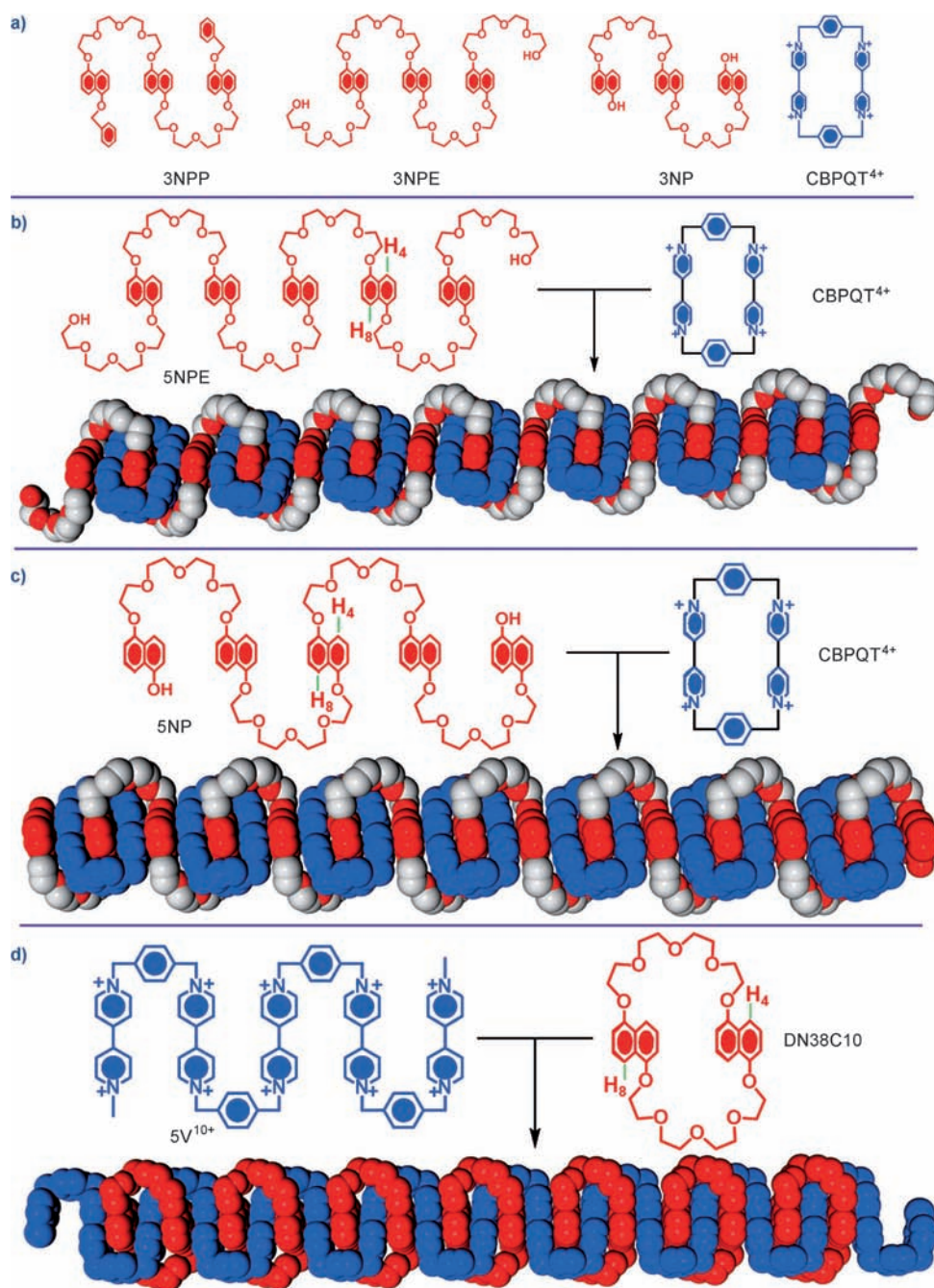


Figure 1. a) Structural formulas and space-filling representations of the X-ray single-crystal superstructures of the apparently infinite polypseudorotaxanes formed between CBPQT-4 PF₆ and b) 5NPE and c) 5NP, and d) between DN38C10 and 5V-10 PF₆.

pentameric 5NPE and CBPQT⁴⁺ reveals, however, an apparently infinite polypseudorotaxane with the NP-containing oligomers extending indefinitely throughout the superstructure (Figure 1b) and accommodating CBPQT⁴⁺ rings on every alternate NP unit. Furthermore, crystallization of CBPQT-4 PF₆ with a completely different NP-containing oligomer—namely 5NP (Figure 1c), where the terminal polyether chains present in 5NPE are now absent—results in the identical polypseudorotaxane superstructure^[12] being observed (Figure 1c) with the same space group and very

similar unit-cell parameters for the crystal. Although these pseudorotaxanes appear to crystallize as supramolecular polymers, detailed spectroscopic analyses confirm (see Figures S1–S4 in the Supporting Information) that the oligomeric chains are indeed the pure, monodisperse oligomers 5NPE and 5NP, respectively.

It is clear that the NP chains in these superstructures are not high-molecular-weight polymers: rather, one in every six NP units present in the superstructure must, in reality, be absent. It is not immediately apparent where the vacancies occur: either encircled NP units (Figure 2a) or those (Figure 2b) in between adjacent CBPQT⁴⁺ rings are missing. Moreover, because the solid-state superstructure appears to be polymeric, there is evidently no positional correlation between vacancies from chain to chain, since such a feature would result in an ordered, discrete-chain superstructure, which is not observed. The occupancies of the two crystallographically unique 5NPE superstructures (Figure 2a,b) are thus mingled so that they sum to a 1/6th vacancy. Site occupancy factors for the encircled and non-encircled NP units were determined to be 0.900 and 0.767, respectively, thus indicating a preference for the vacancies to occupy regions between the CBPQT⁴⁺ rings, rather than the cavities inside them.

There are two possible scenarios for the adoption of a “polymeric” crystal superstructure by the complexes formed between 5NP and CBPQT⁴⁺. One (Figure 3a) has only the polyether end-loops missing, so that the encircled “polymer chain” alternates between three and two CBPQT⁴⁺ rings per oligomer. The other scenario (Figure 3b) comprises only three CBPQT⁴⁺ rings per oligomer, thus leaving the terminal polyether loops and terminal NP units vacant from between every clutch of three CBPQT⁴⁺ rings. In the first case, the atoms of the polyether loops are absent in only 1/5th of their

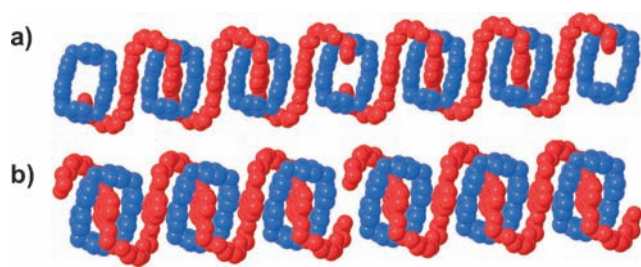


Figure 2. Space-filling representations of the infinite-chain lattice superstructures of the complexes formed between 5NPE and CBPQT⁴⁺ in which the vacancies occur a) within the cavities of the rings and b) between the rings.

sites, whereas, in the second case, the polyether loops and NP units are absent in 1/3rd of their sites. Both models were tested and a better refinement was achieved for the first one. Since other spectroscopic data suggest that the supramolecular species can exist in multiple states,^[13] it is possible that this crystal comprises a mixture of two and three CBPQT⁴⁺ rings on the 5NP units. In any event, the single-stranded polypseudorotaxanes^[14] are organized into densely packed parallel-layered superstructures (see Figures S5 and S6 in the Supporting Information), with the spaces between the layers being filled with solvent molecules and counterions.

The adoption of polymeric lattices by oligomers in previous work can be ascribed^[15] to the heterogeneous nature of the oligomeric chains and consequent disorder in the crystal,^[16] whereas in the present study we show that polymeric lattices can be preferred even for rigorously pure, homogeneous oligomers. It would appear that the critical chain length for the formation of the polymer lattice in the crystal occurs between 3NPE and 5NPE. The fact that there must be a minimum critical chain length for the formation of the polymer lattice was confirmed by crystallizing the shorter 3NP oligomer with CBPQT·4PF₆ to afford a [2]pseudorotaxane in which the ring encircles only the NP unit so as to maximize donor–acceptor interactions. This superstructure (see Figure S7 in the Supporting Information) is completely distinct from that found for the polypseudorotaxanes based on 5NPE and 5NP. Crystals of complexes incorporating longer, but still monodisperse, NP oligomers such as the 7-, 9- and 11-mers, grown in the presence of CBPQT·4PF₆, had

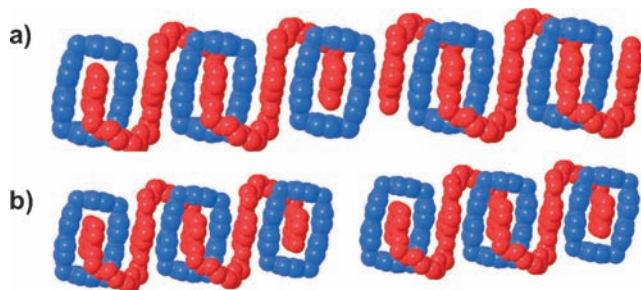


Figure 3. Space-filling representations of the infinite-chain lattice superstructures of the complexes formed between 5NP and CBPQT⁴⁺, showing the presence of a) vacant polyether end loops and b) vacancies between CBPQT⁴⁺ rings.

unit-cell dimensions identical to those of the complex formed between 5NP and CBPQT⁴⁺. This finding indicates that these higher homologues also crystallize to form the same polymer lattice.

To test the generality of the principle of polypseudorotaxane formation in donor–acceptor complexes, the electronic properties of the oligomeric and ring components were reversed. Even though the electron-deficient oligomer^[17] 5V¹⁰⁺ is much more compact and rigid than its 5NPE counterpart,^[18] single-crystal X-ray analysis^[19] of the complex formed between 5V·10PF₆ and 1,5-dioxynaphtho[38]crown-10 (DN38C10)^[20] once again reveals (Figure 1d) a polypseudorotaxane in which the DN38C10 ring encircles every other BIPY²⁺ unit in the oligomer, which once again adopts a zigzag conformation. This solid-state superstructure is analogous to that observed for the complex formed between 5NP and CBPQT·4PF₆. To produce discrete 5V¹⁰⁺ chains, one in every five paraphenylene linkers has to be absent. The atoms in the paraphenylene rings were thus refined with a site occupancy factor of 0.80. In this case, the oligomeric chains contain five BIPY²⁺ units and are either encircled by two or three DN38C10 rings in a crystal, comprising a mixture of both pseudorotaxanes (Figure 4). Once again, there are no long-range, longitudinal correlations

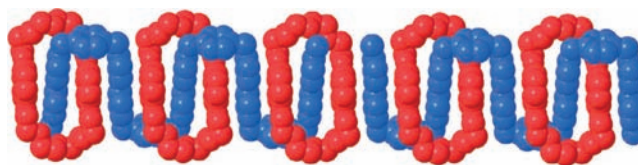


Figure 4. Space-filling representations of the infinite-chain lattice superstructures of the complexes formed between 5V·10PF₆ and DN38C10, showing a vacant paraphenylene linker.

between chains, leading to a pseudopolymeric superstructure. The single-strand polypseudorotaxane is organized into a densely packed parallel-layered superstructure (see Figure S10 in the Supporting Information), with the space between the layers being filled with solvent molecules and counterions. The requirement for a minimum critical chain length for polypseudorotaxane formation in the crystal is also evident here, from a comparison with the discrete [2]pseudorotaxane observed^[21] previously in the solid-state superstructure of 3V·6PF₆·DN38C10 comprising three BIPY²⁺ units and a DN38C10 ring.

Thus, above a certain chain length, the superstructures derived from mixed pseudorotaxane components adopt the same crystal lattices as those based on authentic high-molecular-weight polypseudorotaxanes. The crystal superstructures of these polypseudorotaxanes can be employed to predict the corresponding crystal structures of related polyrotaxanes, even when the latter cannot be obtained in a single-crystalline form.

Experimental Section

Complex between 5NPE and CBPQT-4PF₆: Colorless solutions of 5NPE in MeCN (4 mM, 0.2 mL) and CBPQT-4PF₆ in MeCN (4 mM, 0.6 mL) were mixed together to produce a deep-red solution, which was passed through a Pall syringe filter (pore size 0.45 µm) into VWR culture tubes (6 × 50 mm). The tubes were allowed to stand at room temperature in a closed scintillation vial containing iPr₂O (5 mL). After 1 week, red crystals appeared in the tubes, from which a red tabular crystal, with dimensions of about 0.16 × 0.08 × 0.05 mm³, was selected and mounted using oil (Infineum V8512) on a glass fiber and transferred to the cold gas stream cooled by liquid N₂ on a Bruker APEX-II CCD with graphite monochromated MoK_α radiation. The structure was solved by direct methods and refined subsequently using OLEX2 software.^[22]

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- [12] Crystal data for the complex formed between 5NP and CBPQT-4PF₆: C_{153.6}H_{163.2}F₄₈N₁₆O_{17.6}P₈, *M_r* = 3674.76, monoclinic, space group *P*₂₁/*c*, *a* = 14.0020(5), *b* = 13.7439(4), *c* = 21.1562(7) Å, β = 97.422(2)°, *V* = 4037.2(2) Å³, *T* = 100(2) K, *Z* = 1, ρ_{calc} = 1.500 g cm^{−3}, μ(CuK_α) = 1.907, *F*(000) = 1890. Independent measured reflections 17230. *R*1 = 0.167, *wR*2 = 0.425 for 3957 independent observed reflections [2θ ≤ 117.8°, *I* > 2σ(*I*)]. CCDC 872023 contains the supplementary crystallographic data for this paper.
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- [14] In both pseudopolymeric superstructures, whereas the NP units are essentially planar and strain-free in the oligomers, the BIPY²⁺ units in the cyclophanes are distorted by the strain imposed by the CBPQT⁴⁺ ring itself. Thus, the CH₂–N⁺ bonds in the cyclophanes subtend angles of about 156° and 159°, respectively, in the complexes involving 5NPE and 5NP units, that is, deviations of 24° and 21°, respectively, from the colinearity associated with the conventional planar geometries of BIPY²⁺ units. The mean planes of the NP and BIPY²⁺ units are oriented parallel to another. The supramolecular assemblies in both cases are stabilized by a) C–H⋯O interactions (F. M. Raymo, M. D. Bartberger, K. N. Houk, J. F. Stoddart, *J. Am. Chem. Soc.* **2001**, 123, 9264–9267) between the protons α to nitrogen atoms in the BIPY²⁺ units and some of the oxygen atoms in the polyether loops and b) C–H⋯π interactions between the *peri*-hydrogen atoms of the encircled NP units and the planes of the paraphenylene linkers in the CBPQT⁴⁺ rings, as well as donor–acceptor interactions between the electron-rich NP units and the electron-deficient BIPY²⁺ units. While the separations between the encircled NP units and their interacting BIPY²⁺ units are 3.41 Å for the complex involving 5NPE, and 3.40 Å for the one involving 5NP, the separations between the alongside NP units and the two BIPY²⁺ units on neighboring CBPQT⁴⁺ rings are 3.41 Å and 3.34 Å, respectively, for the first and second complexes.
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