# Threading bromoplumbate nanochannels with polycationic chains

To obtain precise structural information of polymers in the solid state is of importance in chemistry, physics and materials science because such information not only provides fundamental understanding of the nature of polymers, but can also allow scientists to tune and control their synergistic properties. Unfortunately, in most cases, the chains of linear polymers are randomlyentangled with each other in the bulk and it becomes extremely difficult to precisely control the orientations of polymer chains to grow suitable single crystals for structural analysis. Therefore, the properties of polymers can only be regarded as the average contributions from a mass of disordered chains.

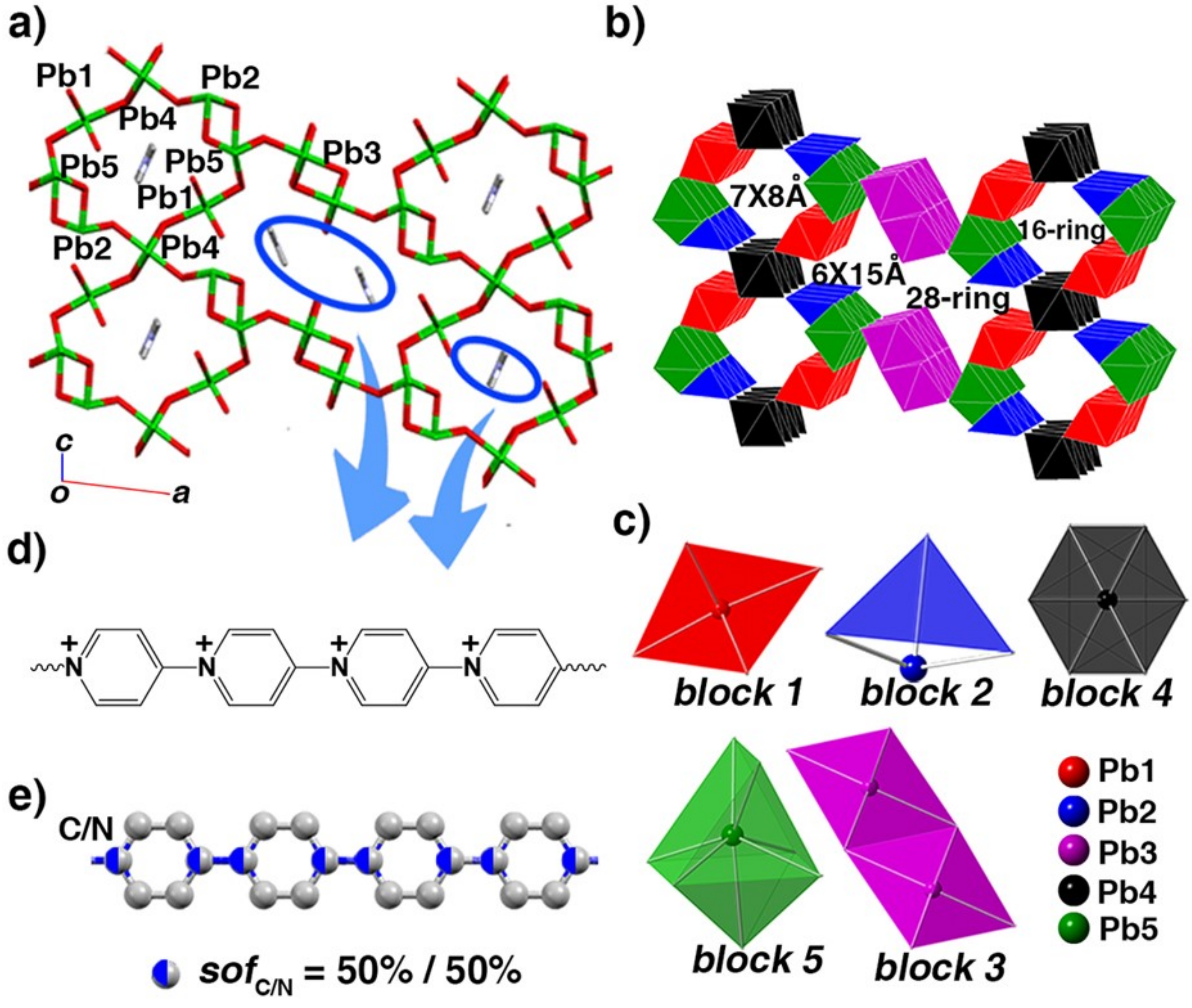

Fig. 1. (a) The encapsulated poly(1,4-pyridinium) polycationic chains in the nanochannels of [Pb9Br20]n2n 3D frameworks, viewed along the b axis. Color scheme: Pb(II), green; Br, red; C,

grey; N, blue. H atoms are omitted for clarity. (b) Two types of nano-channels in the hybrid crystal (formed from 16-ring and 28-ring). (c) The building blocks of the inorganic framework. (d) The schematic diagram of the molecular configuration of a poly(1,4-pyridinium) polycationic chain. (e) The conformation of one single poly(1,4-pyridinium) polycationic chain in the hybrid crystal.

To address this issue, researchers have already put in much effort towards developing several methods either to grow single crystals of linear polymers or to encapsulate linear polymers into inorganic materials. One well-known approach to prepare single crystals of polymers is the topochemical polymerization, where monomers are required to be pre-organized in confined crystal lattices and then a single-crystal-to-single-crystal polymerization could be triggered through ultraviolet light irradiation. However, only a few specific systems (diene and quinodimethane compounds) can meet such requirements to perform polymerization. On the other hand, recently, encapsulation of linear polymers into crystalline inorganic materials has received more and more attention because this approach not only allows insertion of self-assembled polymer chains into the interspaces of inorganic materials, but also brings potential novel properties that originate from the synergistic effect of polymers and inorganic materials. To date, three three-dimensional porous matrices have been extensively studied to realize this purpose because these materials possess regulated and tunable nanochannels. Besides, two-dimensional (2D) materials have also been demonstrated as excellent hosts to intercalate polymers. Unfortunately, none of the above mentioned systems generate highly-qualified single crystals for SCXRD studies because these methods are extremely challenging to maintain the long-range ordering of polymer–inorganic components through these multistep synthetic approaches. Thus, it is highly desirable to develop new methods to grow highly-qualified polymer–inorganic single crystals for structural analysis.

Previously, our group has, for the first time, demonstrated single-crystal growth of polymer/chalcogenide hybrids $[DBNH]_2[Sn_3Se_7]$-PEG (DBN = 1,5-diazabicyclo-[4.3.0]non-5-ene; PEG = polyethyleneglycol) by simultaneous crystallization of chalcogenides and PEG polymers through a surfactant-thermal method. Our method clearly indicates that the in situ formed inorganic framework is flexible enough to accommodate polymer guests. In this work, we believe that 3D bromoplumbate frameworks could be another class of promising hosts to encapsulate polymers because Pb(II) has a mild coordination ability to construct flexible dative bonds to protect/deprotect polymer guests. Thus, in this study, for the first time, we successfully encapsulated conjugated polymer chains into an inorganic matrix to form single crystals through synchronous in situ polymerization and crystallization of bromoplumbate under solvothermal conditions. This as-prepared poly(1,4-pyridinium)-bromoplumbate hybrid ($\{(C_{15}N_3H_{12})(Pb_9Br_{20})(OH)\}_n$)represents a novel 3D open-framework architecture with two types of nanochannels, where conjugated poly(1,4-pyridinium) polycationic chains are encapsulated within these nanochannels (Fig. 1). To our best knowledge, the hybrid crystal is the first example that encapsulates conjugated polymers into a crystalline inorganic material for single-crystal structural analysis. Further photoelectrochemical studies indicate that the hybrid crystal displays a p-type semiconductor behavior under visible-light illumination.

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## Publication

Simultaneous crystallization of an in situ formed conjugated polymer and inorganic matrix for structure solving.
Liu G, Gu P, Nie L, Zhang Q
*Chem Commun (Camb). 2017 Nov 14*