Title
An Inorganic Twist in Nanomaterials: Making an Atomically Precise Double Helix.

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Authors
Saleh, Liban MA
Dziedzic, Rafal
Spokoyny, Alexander M

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Molecular helical structures are prevalent in biomolecules such as proteins and polynucleotides (e.g., DNA, RNA). This structural arrangement imparts additional stability to biomolecules necessary for many important biological functions including replication, signal transduction, and catalysis. Since the revolutionary discovery in 1953 that DNA structure exists as a double helix (Figure 1A), numerous discoveries pertaining to this quintessential molecular shape have emerged. The central dogma in biology is intricately connected with the double helical structure of DNA and its importance in key processes such as transcription and translation, which are ultimately responsible for life.

Chemists’ fascination with the double helix motif has inspired a significant effort targeting semi- and fully abiotic structures mimicking natural systems. Tweaking the original structure of DNA by either synthetically modifying the base pairs or the phosphate backbone resulted in many new classes of helical biomaterials with promising applications such as therapeutics, diagnostics, and even building artificial life forms. Likewise, supramolecular chemists recognized that fully abiotic organic molecules can mimic the recognition properties of DNA base pairs and are capable of forming helices and double helices. Finally, inorganic coordination strategies, using various metal ions capable of directing and positioning molecules in a helical chain fashion, brought double helix structures into the realm of inorganic materials. However, many of these mimics rely on carbon-based building blocks that can constrain the thermal stability and electronic properties which make inorganic materials the workhorse of modern electronics and countless industrial processes.

Writing in Advanced Materials, Nilges and co-workers now report the first atomically precise carbon-free structure containing an unprecedented configuration of inorganic elements arranged in a double helical fashion. The surprisingly simple synthesis of SnIP (named after its constituent elements), with its chiral double helical rods, highlights the convergence of nanoscale materials design with atomically precise building blocks, all while impressively producing the material on a gram scale. The synthesis of SnIP is elegant in its simplicity and efficiency. A pellet comprised of Sn, SnI₄, and P₄S₇ is transformed into SnIP via a two-step synthesis involving SnI₄ vapor and SnI₂ crystals.

**Figure 1.** (A) Molecular structure of the DNA double helix. (B) Crystallographically derived X-ray structure representations of [SnI] and [P] helices forming (C) SnIP double helix comprising the bulk material reported by Nilges et al.
and P₄ precursors is pressed, sealed inside a silica glass ampule, and crystallized by slow cooling from 923 K. The bulk material can be regarded as a bundle of individual double helices (Figure 1B,C), with each double helix containing a negatively charged molecular phosphorus helix, [[P⁻]], surrounded by a positively charged Sn⁺ helix, [[Sn⁺]]. This bundle structure is believed to impart high flexibility in the bulk material. Particularly impressive is that the double helices can be formed without the use of a template, allowing for the uninhibited, yet controlled, layering of double helices.⁸⁸

Likewise, the SnIP bundles can be exfoliated by sonication in organic solvents to provide smaller bundles. The time-honored tradition of mechanically peeling layers using Scotch-tape also works. This is important because it makes SnIP an excellent system for studying quantum confinement effects. The atomically precise double helix layers mean that one can isolate SnIP bundles with “quantized” diameters. This effect may be further exploited in a similar fashion to provide layered two-dimensional (2D) materials analogous to graphene, MoS₂, WS₂, h-BN which exhibit different properties based on the number of layers.⁹ The band gap energy for a single SnIP double helix (2.28 eV) differs from bulk SnIP bundles (1.79 eV) by 0.49 eV, suggesting that the band gap of SnIP double helix bundles can be discretely controlled by the number of layers. Its amenability to processing makes SnIP an excellent system for creating new nanostructured electronics. Such nanoscale precision can be exploited in potential photovoltaic applications through band gap engineering to match the energy levels of metallic and semiconductor contacts with SnIP bundles.

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Most noteworthy is the material’s chirality. Without any templating agents the SnIP bundles contain equal amounts of left and right-handed double helices. This structural property, coupled with the high conductivity and visible-light absorption, makes SnIP a promising material for optoelectronics and nonlinear optics. If single-chirality SnIP bundles can be fabricated selectively, they may find potential applications in chiroptical materials as circularly polarized light sources or chiral molecule sensors.

Looking forward, the facile exfoliation of SnIP could lead to isolation of single-chirality SnIP double helices or bundles. Such single-chirality SnIP compounds could potentially serve themselves as templates for additional surface modification, leading to an increasingly diverse set of chiral, core–shell nanorod architectures. It remains to be seen how general this helicity is in the context of other inorganic materials and whether the Sn, I, or P atoms can be substituted for other elements.¹⁰ It is also unclear whether this material is an isolated example or a member of a broader class of similar inorganic materials. Regardless of these limitations, one thing is clear: Nilges and co-workers have opened a new and exciting chapter in inorganic and materials chemistry by providing the first synthesis and new insights into the first carbon-free structure featuring an atomically precise double helix.

**Author Information**

E-mail: spokorny@chem.ucla.edu.

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