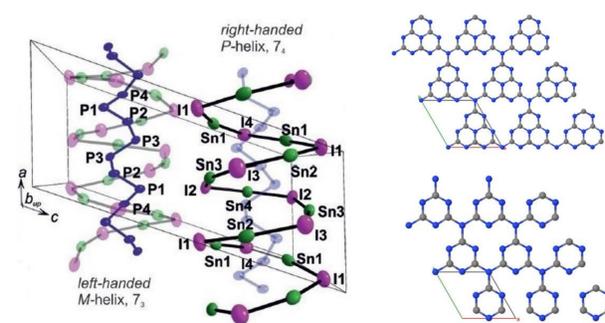


SnIP Hybrids: Stabilization of Single SnIP Rods in Nanotubes

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Introduction

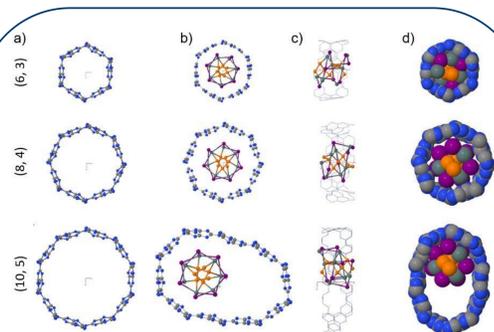
Inorganic helices have gained interest over the last decade, as their electronic, optical and mechanic properties make them promising catalysts among other things.^[1] In 2016, SnIP, the first inorganic double helix fabricated without a template, was reported. SnIP contains a [P]⁻ inner helix and a [Sn]⁺ outer helix with a dative ionic bond between P and Sn. Highly polarized lone pairs of Sn point away from the center of the helices and cause van der Waals forces between adjacent double helices. Therefore, SnIP is thought to be cleavable into single rods, but dissection methods have so far not led to the desired result.^[2] Consequently, a bottom up rather than a top down approach might be more successful. By DFT, SnIP has already been inserted into single wall carbon nanotubes, but due to the stiff π -electron network of the nanotubes, no adjustment to SnIP was observed.^[3] In this poster, we present the insertion of SnIP by DFT into nanotubes made from two different graphitic carbon nitride structures based on tri-*s*-triazine, C₆N₈v₄ (v being the number of vacancies), and *s*-triazine, C₃N₄v₁, with more flexible π -electron networks.



Left: Structure of *M*- and *P*-SnIP along the *b*-axis. Graphic adapted from Lit. [2]. Right: Slabs of C₆N₈v₄ (top) and C₃N₄v₁ (bottom), 3x3 unit cells.

Optimized geometry of SnIP@C₆N₈v₄ hybrids

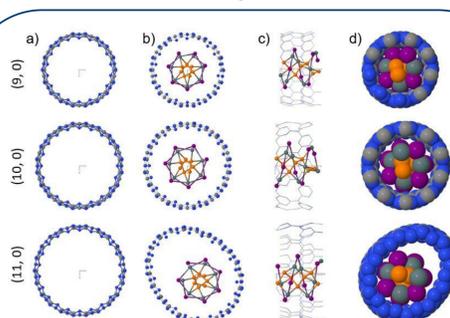
All geometries were optimized by using the PBE-functional, a *Generalized Gradient Approximation* (GGA) functional that accounts for inhomogeneities in the electron density, with an additional Grimme-*D3*-correction for van der Waals forces.



Optimized geometries of a) bare C₆N₈v₄ NTs, b, c) *M*-SnIP@C₆N₈v₄ hybrids along the *a*- and *b*-axis, 15% v.d.W. radii, d) space filling model of *P*-SnIP@C₆N₈v₄ hybrids along the *a*-axis.

→ Oval deformation of largest hybrid, shift of SnIP towards one side

Optimized geometry of SnIP@C₃N₄v₁ hybrids



Optimized geometries of a) bare C₃N₄v₁ NTs, b, c) *M*-SnIP@C₃N₄v₁ hybrids along the *a*- and *b*-axis, 15% v.d.W. radii, d) space filling model of *P*-SnIP@C₃N₄v₁ hybrids along the *a*-axis.

C ₃ N ₄ v ₁ Hybrid	<i>d</i> (I-C) / Å	<i>d</i> (Sn-N) / Å
(9, 0)	3.27–3.53	3.34–4.08
(10, 0)	3.67–3.95	3.93–5.37
(11, 0)	3.56–6.08	3.74–6.08

Oval deformation of largest NT:
Optimal distance of approx. 3.6–4.0 Å for interaction between SnIP and NT

Enantiomeric Effect

C ₆ N ₈ v ₄ Hybrid	ΔE_{tot} (<i>M</i> -SnIP hybrid) / kJ·mol ⁻¹	ΔE_{tot} (<i>P</i> -SnIP hybrid) / kJ·mol ⁻¹
(6, 3)	+970.0	+970.0
(8, 4)	-236.0	-209.9
(10, 5)	-119.2	-112.3

Insertion of chiral SnIP into chiral NT:
→ enantiomeric effect

Largest energy gain for (8, 4) *M*-SnIP hybrid (*d* = 15.2 Å)

C ₃ N ₄ v ₁ Hybrid	ΔE_{tot} (<i>M</i> -SnIP hybrid) / kJ·mol ⁻¹	ΔE_{tot} (<i>P</i> -SnIP hybrid) / kJ·mol ⁻¹
(9, 0)	-230.1	-230.0
(10, 0)	-339.1	-339.4
(11, 0)	-253.4	-253.2

Insertion of chiral SnIP into achiral NT:
→ no enantiomeric effect

Largest energy gain for (10, 0) hybrids (*d* = 15.2 Å)

Conclusion

By DFT calculations, SnIP was inserted into nanotubes made from two different graphitic carbon nitride structures. An enantiomeric effect was observed for the hybrids based on chiral (2*n*, *n*) C₆N₈v₄ NTs, but not for achiral (*n*, 0) C₃N₄v₁ NTs. In both cases, CNNTs with a diameter of approximately 15 Å ((8, 4) C₆N₈v₄ NT and (10, 0) C₃N₄v₁ NT) gave the highest energy gain upon hybrid formation. In larger CNNTs, an oval deformation with a shift of SnIP towards one side of the oval was observed, indicating the importance of attractive interactions for the formation of hybrids.

Also, in future studies hybrid based on other 2D materials such as MoS₂, black phosphorus or hexanoal BN, should be calculated. By the exchange of the host NT, the interaction with SnIP can be investigated further.

* This work has been performed under the supervision of M. Pielmeier in the group of Prof. T. Nilges.

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