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Towards Atomic-Scale Inorganic Double Helices via Carbon Nanotubes Matrices – Induction of Chirality to Carbon Nanotubes

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ABSTRACT

SnIP, an atomic-scale inorganic double helix compound is composed by a hexagonal rod-packing of double helices in the bulk phase. A racemic mixture of *P*- and *M*-SnIP double helices is energetically most-favored and present in the

solid. In order to evaluate if enantiomer-pure SnIP might be realizable three different stacking models of seven chiral double helices, an enantiomer pure, a 2:1 and a racemic 1:1 ratio were investigated according to their energies of formation. While a top down approach didn't lead to single isolated double helices the development of a bottom up approach might be beneficial. Motivated by templating strategies in confined geometries we performed first-principles density functional theory calculations (DFT) using Carbon nanotubes (CNT) featuring different electronic properties and suitable sizes as matrices to accommodate chiral SnIP double helices. With the aid of DFT, we determined the ideal diameter, stability and electronic properties of different SnIP@CNT systems. Appropriate molecular starting materials and a feasible formation mechanism are identified based on chemical considerations. An interaction between the CNTs and the SnIP units is evident, causing structure and property modifications of the hybrids. The intercalation of SnIP into a suitable CNT leads to a gain in total energy compared to the isolated systems. Based on our findings a straight forward way to introduce chirality in suitable CNTs via SnIP@CNT hybrids is feasible.

KEYWORDS *hybrid materials, carbon nanotubes, SnIP, inorganic semiconducting double helices, density functional theory, nanomaterials*

Helices and double helices of elements and multinary compounds are subject to intensive scientific research due to their exceptional structural features, intriguing physical properties and stereochemistry.^{1,2} Quantum chemistry has recently been used to initiate new ideas for the development of materials ranging from new element allotropes to intriguing composite materials.

Often predicted by first principle calculations like in the case of phosphorus³⁻⁵ or LiP,⁶ it became obvious that such materials are interesting but challenging candidates to be synthesized. Especially for solely inorganic materials the atomic scale double helix is extremely rare and only very few examples are known to date. The preparation of hybrids composed by multi-walled carbon nanotubes containing a phosphorus chain in a helical arrangement⁷ or a selenium double helix⁸ was successfully realized after the prediction by theory. In the past few years, the interaction of matter with nanotubes, i.e. by insertion or adsorption of materials⁹ were evaluated. Insertion of selenium or phosphorus into CNTs resulted in efficient battery materials¹⁰⁻¹² or nanotube-stabilized nanowires.¹³ Also the stabilization of metastable compounds consisting of non-helical structures like polymerized white phosphorus¹⁴ or yellow arsenic,¹⁵ the encapsulation of metals¹⁶ or simply the band gap change by the application of bending stress to the nanotubes¹⁷ were investigated.

Pfister et al.^{18, 19} synthesized SnIP, the first inorganic atomic-scale double helix, in 2016. It consists of an inner helix made up of a $[P]^-$ chain and an outer helix made up of $[SnI]^+$ units. Due to its double helical structure, either a left- or a right-handed helix results, which are called *M*- and *P*-helix, respectively. In two independent studies the existence of structure homologues of SnIP has been predicted^{20, 21} where the formation of group 15 element phosphide iodides and bromides are more favored than the lighter homologues. Fluorides are the less-probable candidates to exist adopting this structure. Even more complex double helical compounds with a hetero atomic inner helix are also mentioned in literature, but their formation might be even more challenging to realize.²²

In order to use the full potential of an inorganic double helical semiconductor, including the chirality of isolated single strands, either the separation after the double helix bundles synthesis of the racemic bulk phase or a bottom up synthesis of double helices is needed. By using a top down approach via mechanical delamination of the bulk phase, a particle size down to approximately 15 nm in diameter was realized (equivalent to 6-7 shells of double helix rods attached to each other).¹⁸ As all efforts to achieve further delamination were not successful so far, a bottom-up procedure might be more realistic.

SnIP itself, as a 1.8 eV semiconductor was successfully used to fabricate composites in inorganic matrices and 2D materials. TiO₂ was used as a matrix to create effective photochemical materials for various catalytic applications.²³⁻²⁹ Here, in some cases nano-sized arrays are formed by electrochemical etching, which are modified by semiconductors afterwards. The nanotube approach was first adopted by Üzer et al. to SnIP to form an effective photocatalytic hybrid^{30, 31} for water splitting. In this work TiO₂ channels of approximately 100 nm were used to accommodate SnIP. Layered and halide-doped C₃N₄ as a prominent 2D material has successfully been applied to create self-assembled SnIP@C₃N₄ heterostructures. Creating effective heterojunctions, this material can split water with an almost fourfold increase of performance compared to separate components. Motivated by this recent report on the self-assembly of SnIP@C₃N₄ heterostructures³² and their intriguing performance in water splitting, we therefore decided to evaluate if the formation of SnIP@CNT heterostructures might be possible. CNTs as such are ideal candidates to act as templates or nano containers due to their structural variety and adjustable physical properties (e.g. by functionalization, intercalation or bending).³³⁻³⁶ Also their usage as nano-reactors is subject to recent research where for instance interesting semiconductors like SnSe have been crystalized.³⁷⁻

The structure and inner diameter of a CNT can be varied by the way how graphite layers are formally cut and reconnected. Such resulting nanotubes can be classified by a descriptor composed by two integer numbers. They are multiples of the graphitic hexagonal lattice vectors and define the translational area and thus the entire nano tube. There are known to be three classes of nanotubes called armchair, zigzag, or chiral nanotubes,⁴³ which is determined by the direction of their propagation vector. Their electronic structures are well-examined and can be drastically changed from metallic to semiconducting by slight modifications in their diameter and wrapping angle.^{44, 45} Three different kinds of nanotubes result: metallic, semi-metallic and semiconducting. The metallic ones all have the descriptor (n,m) with $n = m$ (e.g. (10,10)), while for semi-metallic systems the descriptor is (n,m) with $n - m$ equals an integer multiple of 3, e.g. (3,0), (4,1), (18,0) and lots of other possibilities. The rest of the nanotubes result in semiconducting systems, e.g. (4,0), (5,0), (19,0) and many more. All of those are promising for tuning band gaps^{17, 35} in a hybrid system. This scheme is graphically summarized by the company Quantum Wise on their “periodic table of carbon nanotubes”.⁴⁶ As SnIP is a chiral, inorganic and highly flexible material, the aim of this study is to evaluate the possibility to synthesize single inorganic SnIP double helix strands in suitable templates/containers. Ideally, such an approach will induce chirality to CNT hosts due to the given chirality of the guest and may lead to a non-racemic formation of SnIP or even an effective separation of the *M*- and *P*-helices.

RESULTS AND DISCUSSION

After SnIP's discovery and characterization by Pfister et al¹⁸ the question arose, if a single double helix strand can be realized by a top down approach. Efforts to delaminate SnIP down to a single double helix strand were not successful. The smallest systems we achieved by mechanical and soft-chemical delamination techniques in our lab still showed six to eight shells of double helices resulting in rod diameters between 10 and 20 nm.¹⁸ Each chiral SnIP double helical strand (see Figure 1a) has a diameter of 0.98 nm and shows either left- (*M*-helix) or right-handed (*P*-helix) chirality. Those two different enantiomeric rods appear as a racemic mixture arranged in a pseudo-hexagonal rod-packing along the *a*-axis. SnIP crystallizes monoclinically, in space group *P2/c* (No. 13). It contains *Z*=14 formula units in the unit cell, with lattice parameters of *a* = 7.934 Å, *b* = 9.802 Å, *c* = 18.439 Å and $\beta = 110.06^\circ$.¹⁸

Seven SnIP units and two chain windings are needed to form the repetition unit in each rod, building a right- and a left-handed helix pair. Every single rod consists of two separately winding helices, one made up of a phosphorus chain and the other of alternating Sn and I atoms. With the stoichiometry of 1:1:1 (Sn:I:P), the winding of the phosphorus chain has 7 atoms in the repetition unit, while the outer chain consists of 14 atoms for the same length. Following the Hermann-Mauguin notation, the symmetry of single *M*-helix is *p7₃2*, while the *P*-helix corresponds to *p7₄2*, as already described in detail using crystallographic approaches by Müller.⁴⁷ Due to the prominent structure, SnIP exhibits high flexibility and compressibility for an inorganic semiconductor and thus qualifies for electronic, optical and sensor applications.^{32, 48}

Formation and stereochemistry of SnIP. In a first set of calculations, the influence of the stacking order of SnIP double helices is explored by varying the neighboring shell, which surrounds a center strand.

Figure 1. a) Single strand of double helical *P*-SnIP (sticks representation). The translation unit of the double helix is marked with the orange arrow. On the right side the view along the *a*-axis is given (ball and sticks representation). b) Simulated 1D-models of SnIP rods with a center rod and one surrounding shell of additional double helices. The screwing direction of each double helix is marked red (*M*-SnIP enantiomeric form) or green (*P*-SnIP enantiomer). Model 1: center and shell consist of the same SnIP enantiomer; Model 2: the shell is built by only one enantiomer, while the central double helix is of the other enantiomer; Model 3: central double helix surrounding as realized in bulk-SnIP; At the right bottom of each representation a Scheme is given, where the double helices are symbolized by colored dots. Sn atoms: green spheres; I atoms: violet spheres; P atoms: blue spheres.

We intend to evaluate why SnIP crystallizes as a racemic mixture of *M*- and *P*-double helices and how much this is energetically favored compared to an enantiomeric pure SnIP. In Figure 1b, the three different model systems analyzed in this study are shown, where the colored arrows indicate the rotation symmetry relative to the helix axis perpendicular to the paper layer and a vector pointing into the paper. Every model system consists of a central rod surrounded by one complete shell of six other helices in a hexagonal rod array. Exactly the hexagonal rod array of Model 3 can be found in SnIP and can therefore be regarded as a direct cut-out of the bulk material.¹⁸ Three different model systems, which differ in the surrounding shell of the central double helix are analyzed. Model 1 represents the enantiomeric pure systems, where the shell and the central double helices are of the same kind. In Model 2 we investigate a *P*- and *M*-central double helix with an entire shell of the other enantiomer. This results in a 2:1 ratio of the different *P*- and *M*-double helices for the bulk material. It is important to emphasize the non-racemic nature of the first two Models. In Model 3 the shell for the central double helix corresponds to the surrounding in the racemic bulk resulting in a 1:1 ratio of double helices.

The comparison of the total energy values derived from DFT calculations after geometry optimization are shown in Figure 2a. The racemic mixture of SnIP is already known since its discovery in 2016,¹⁸ but now we can show the differences in energy for other stacking orders. For a single double helix with only one shell (diameter of the entire system approximately 2.8 nm), the gain in total energy compared to a single double helix is already 126 kJ/mol for each double helix, if the realized Model 3 is applied. Meaning for the whole system there is a gain of total energy of 879 kJ/mol when seven double helices are attached to each other. In the case of Model 2 (2:1 ratio of double helix strands) the energy gain per SnIP strand (117.0 kJ/mol) is smaller than for the racemic Model 3 resulting in an energy difference of 8.5 kJ/mol.

Figure 2. a) Total Energy differences for three different SnIP models varying the central and neighboring double helix strands. Model 1 is an enantiomer pure one of either *M* (red) or *P* (green) helices, Model 2 represents a 2:1 ratio of double helix strands and Model 3 represents the realized situation in bulk SnIP (1:1 ratio of double helices). All values are normalized to the number of single SnIP double helices in the repetition unit (NSnIP). b) Energy difference (dE) for SnIP@CNT hybrid systems in relation to separate components, referenced to a SnIP repetition unit (NSnIP).

The less-favored Models are the enantiomeric pure ones with a difference of 13.2 kJ/mol compared to the realized racemic one. It is evident, that both non-racemic Models 1 & 2 are slightly disfavored, however the entropy of mixing is not included.

Nonetheless it is obvious, that SnIP greatly prefers to aggregate in larger systems with several shells rather than to form single double helices. Thus the stabilization of single strands is an essential step to atomic-scale “nano-rods”. Therefore, a matrix, which should also be versatile concerning its size and electronic structure, is needed. Carbon nanotubes are chosen to support the stabilization of single strand SnIP and to enable electronic properties tuning.

DFT evaluation on formation and stability of SnIP@CNT hybrids. In order realize single SnIP double helices we followed the idea of a template assisted route and selected CNTs as possible

reaction containers or matrices for a bottom up process. Due to our experience with short way transport reactions of polypnictides and polychalcogenides⁴⁹⁻⁵², our successful incorporation of phosphorus and SnIP inside TiO₂ nanotube arrays^{30, 31} and the self-assembly of SnIP and the 2D material C₃N₄³² we are confident that such a procedure will most probable lead to success. At the moment, we are working on a gas phase transport or CVD process adapted from the original SnIP synthesis.

In the first step, we identified and selected suitable CNTs from all existing classes considering their electronic structure (metallic, semimetallic, or semiconducting) and the inner CNT diameter which is supposed to be capable of hosting a single double helix strand. Based on structure considerations we identified a metallic CNT(10,10), a semiconducting, chiral CNT(15,5), a semimetallic CNT(18,0) and a semiconducting CNT(19,0) as matrices for SnIP and therefore suitable candidates for our DFT calculations (see Table 1). The inner diameters between 13.8 and 15.1 Å fit well to the SnIP double helix space demand of 9.8 Å in the bulk¹⁸ taking also the required distance to the CNTs into account. In Figure 3, the SnIP@CNT hybrid materials are denoted. Each set of structure section used in the DFT calculations is given in Figure 3b and c. Dependent on the CNT structure, a symmetry-optimized structure section was chosen for the model calculations. In the case of the (10,10), (18,0) and (19,0) CNTs a single repetition unit of the SnIP double helix was sufficient while for the (15,5) one, a doubled representation was necessary due to the symmetry constrains of the CNT matrix.

For each CNT, we implemented a *M*- and *P*-SnIP double helix and performed a DFT structure optimization with full relaxation. Initial 1D geometries are provided with the length of the respective symmetry-optimized CNT section and an assimilated SnIP substructure, because of the flexibility of SnIP.³²

Figure 3. Geometry optimized structure models of SnIP@CNT hybrids viewing along a), d) and perpendicular b), c) the CNT propagation axis, featuring a *M*-SnIP helix (a, b) and a *P*-SnIP helix (c, d), respectively. Furthermore, in d) a space filling model with van der Waals radii (Sn: 2.17 Å; I: 2.15 Å; P: 2.08 Å) for SnIP is given. Sn: green spheres; I: violet spheres; P: blue spheres.

Table 1. Single-walled CNTs (SWCNT) ordered by an increasing diameter (Dt). The propagation vector T of the SnIP@CNT hybrid, T/a ratio (with a = translational period of the bare CNT), total number of atoms (N) per structure model (CNT + SnIP), and the electronic type of the CNT is summarized.

CNT (n,m)	Dt [Å]	T [Å]	ratio T/a	N /unit cell	Type of CNT
(10,10)	13.8	7.48	3	141	metallic
(15,5)	14.3	15.4	0.5	302	semiconducting
(18,0)	14.3	8.64	2	165	semimetallic
(19,0)	15.1	8.64	2	173	semiconducting

As shown in Figure 3d for structure optimized data, each SnIP double helix attaches well to the surrounding CNT matrix. In the space filling representations (Figure 3d), the fit between the two substructures are illustrated. Due to the achiral nature of the (10,10), (18,0) and (19,0) CNTs no differences in structure parameters are expected for an inserted M or P -SnIP double helix while in the case of a chiral (15,5) CNT differences may occur for the enantiomeric forms.

In general, each successfully realized SnIP@CNT system, independent of the CNT nature, will become chiral, because chirality will be induced by the implemented SnIP double helix. This feature might be of interest for the stereochemistry of the hybrids, its usage in light-driven applications and the separation of the chiral SnIP enantiomers.

In Table 2, a selection of structural parameters, which derived from DFT calculations, are summarized. Data is given for a M -SnIP and a P -SnIP helix separately. The structure of the CNTs are literally unaffected by the SnIP double helix as illustrated by comparable bond lengths and angles for the hybrid materials (see Table 2). In each case, C-C bond lengths are in the range of 1.42 to 1.43 Å, in accordance with the ones found in empty CNTs. Incorporation of a SnIP double helix into CNTs only affects the less rigid, highly compressible and flexible SnIP substructure.

Within the covalently-bonded [SnI] and [P] helices the Sn-I and P-P bond lengths are only slightly affected by the CNT matrix.

Table 2. Geometrical parameters of SnIP@CNT hybrids derived from DFT data after geometry optimization compared with a 1D SnIP double helical strand (1D) and experimental values derived from single crystal structure determination. All distances and angles are given in Angstrom (Å) and degrees (°), respectively. For experimental data the standard deviations are smaller than the last given digit.

	<i>M</i> -SnIP				
	@ CNT (10,10)	@ CNT (15,5)	@ CNT (18,0)	@ CNT (19,0)	experimental
P-P	2.21	2.22	2.25	2.25	2.17-2.21
P-P-P	93.3-93.4	94.4-94.5	97.7-97.8	97.8	94.8-96.3
Sn-I	3.07-3.08	3.12-3.13	3.09-3.10	3.15-3.16	3.06-3.28
I-Sn-I	147.8-148.0	151.0-151.1	153.1-153.7	155.7-155.8	152.6-153.8
Sn-I-Sn	110.9-111.1	107.9-108.0	106.0-106.1	103.6	104.8-106.3
Sn-P	2.65	2.68	2.74	2.75	2.66-2.71
I-C	3.22-3.26	3.35-3.41	3.39-3.53	3.62-3.69	-
C-C	1.43-1.44	1.42-1.43	1.42-1.43	1.42	-
C-C-C	119.3-120.1	119.3-120.1	119.4-120.0	119.3-120.1	-

	<i>P</i> -SnIP				
	@ CNT (10,10)	@ CNT (15,5)	@ CNT (18,0)	@ CNT (19,0)	1D
P-P	2.21	2.22	2.26	2.25-2.26	2.22
P-P-P	93.3	94.4-94.5	97.8	97.8	95.1
Sn-I	3.08	3.12-3.13	3.09-3.10	3.14-3.15	3.18-3.19
I-Sn-I	147.8-148.0	151.0-151.1	153.2-153.4	155.7-155.8	154.8-154.9
Sn-I-Sn	110.9-111.1	107.9	106.1-106.2	103.6-103.7	104.1
Sn-P	2.65	2.68	2.74	2.75	2.69
I-C	3.20-3.26	3.39-3.42	3.38-3.49	3.63-3.72	-
C-C	1.42-1.43	1.42-1.43	1.42-1.43	1.42	-
C-C-C	119.3-120.2	119.4-120.1	119.4-120.1	119.3-120.0	-

All Sn-I bond lengths are found in the same range that we determined for bulk SnIP. The P-P bond lengths are enlarged to 2.21-2.25 Å as compared with bulk SnIP where 2.17-2.21 Å are found.

In the dative ionic regime between the two helices, represented by the Sn-P interactions, only a little effect is present. In the case of the (10,10) and (15,5) CNT, we found Sn-P bond lengths in the same range as for bulk SnIP while for the (18,0) and (19,0) CNT the bond lengths are slightly enlarged to 2.74 and 2.75 Å.

The most prominent and obvious effect is present in the bond angles. Especially the I-Sn-I bond angles of the outer [SnI]⁺ helix are continuously increased from the (10,10) towards the (19,0) CNT, which directly correlates with the increasing inner CNT diameter. Due to the fact that the shortest distance between the CNT matrix and the SnIP double helix is the C-I contact, the structural ‘pressure’ affects the outer [SnI]⁺ chain significantly. According to Mulliken Population analysis data¹⁸ Sn shows a charge from +0.47 to +0.51, I from -0.31 to -0.33 and P between -0.16 and -0.17. An electrostatic repulsive interaction between negatively charged I and the electron cloud of the CNTs may cause the flattening of the I-Sn-I angle. On the other side, the Sn-I-Sn angle is significantly reduced which is equivalent to a shift of positively charged Sn towards the CNT electron cloud.

The question arises quickly if there are attractive interactions or driving forces present to allow the preparation of such SnIP@CNT systems, so we further investigate the hybrids. The hybrid systems are sorted by diameter of the CNTs starting with CNT (10,10) featuring a diameter of 13.8 Å. CNT (18,0), CNT (15,5) and CNT (5,15) have a diameter of 14.3 Å, while CNT (19,0) shows the largest diameter with 15.1 Å. A stabilization can be identified in the total energy plot in Figure 2b, which is referenced to the number of SnIP repetitions per unit cell (NSnIP in Figure 2b). Here it is evident that the two enantiomers of SnIP yield energetically equivalent systems (dE < 0.1%, see Supporting Information, chapter 1, Figure S1 and Tables S1 and S2), even with a chiral nanotube (15,5). In the same moment the energy gain in comparison to the non-chiral CNTs

becomes obvious. This might be explained by the better match of the CNT diameter to the SnIP strand, but (15,5) with a diameter of 14.31 Å is very close to (18,0) with 14.29 Å and the difference of approximately 44 kJ/mol seems too large to be explained by the slight change in diameter.

The comparison of the band structures of pure CNT to the filled hybrids (see Figure 4) indicates almost no changes for bands in the vicinity of the Fermi level. At a closer look, the band gaps stay practically the same as in pure CNTs, but the slope of some bands decreases significantly. The steepness of the bands in these materials correlates directly with the Fermi velocity, as the CNTs are Dirac materials.⁵³ Here, the decreasing slopes can be interpreted as less dispersion in the bands, which imply less strain in our SnIP@CNT hybrids. This effect is the most prominent in the cases of the metallic CNT(10,10) and the semiconducting CNT(19,0) hybrids, that feature the minimum and the maximum diameter of the considered CNTs.

All examined hybrids have no bands inside the range of 1 eV above the Fermi energy provided by SnIP except SnIP@CNT(15,5) at ~0.75 eV (red arrow, Figure 4). Though it is known that the PBE functional underestimates the band gap of SnIP a little^{18,20} the lowering of the states compared to other hybrids and the separated components is apparent. This hints to a better interaction in the case of the chiral nanotube compared to the achiral ones, which must be further investigated.

Crystal Orbital Overlap Population analysis (COOP⁵⁴) is a powerful tool, which differentiates bonding (positive) and antibonding (negative) states of selected kinds of atoms with each other. The most important part of CNT-SnIP interactions is localized between the outer SnI helix and the CNT.

Figure 4. Band structures of pure carbon nanotubes (left) and with SnIP filled nanotubes (right).

Therefore, C-I and C-Sn interactions might occur. COHP analysis is useful to identify which kind of interactions are present between the chosen atom species (see Supporting Information, Figure S 3a). To check the bonding situation, the final geometries are restarted as single point (sp)

calculations without the D3-correction. This yields the respective differences in total energies between 295 and 470 kJ/mol per SnIP repetition unit compared to the D3 corrected ones. The result can be interpreted as a mixture of dispersion and covalency, but the form of the graphs suggest, that dispersion gets more important for the chiral hybrid SnIP@CNT(15,5) (see Supporting Information, S 1 on the right.). By comparing the integrated densities of the COHPs in the same manner (see Supporting Information Figure S 3b), it becomes apparent that the Sn-P interactions are mainly dispersive in nature, which is in good agreement with the experimental data¹⁸. For further details and results, please refer to chapters 1 to 3 in the Supporting Information.

Identification and characterization of SnIP@CNT hybrids via Vibrational Spectroscopy.

Bulk SnIP is already well characterized and Raman spectroscopy has proven to be a powerful and quick tool to identify and investigate SnIP after formation. Calculated and measured Raman modes can therefore be used to identify synthesized SnIP@CNT hybrids and to monitor the bonding situation in the double helices. Vibrational modes were derived from DFT data using our hybrid models (see Methods). These modes are all situated in the fingerprint area of the spectra ($\sim 50 - 500 \text{ cm}^{-1}$). All selected modes for the bonding analysis are shown as an indicative illustration in Figure 5 (1-4) and provided as movies in the supporting information. The selection was made according to the investigations of Baumgartner²⁰, where characteristic breathing modes of Sn (green), I (magenta) and P (blue; $> 400 \text{ cm}^{-1}$) as well as a stretching mode of P (blue, $< 400 \text{ cm}^{-1}$) were chosen in the bulk material. Those vibrations were compared to a 1D *P*-SnIP strand as referenced at the bottom in Figure 5. The iodine vibrations show the expected behavior of consistently rising wavenumbers with declining diameter of the CNTs (from the bottom upwards), equivalent to rising pressure applied to bulk-SnIP, as reported in the work of Ott et al.³² The other selected modes show an equivalent behavior, meaning that first all of them lower the vibrational frequency compared to pure SnIP. By the looks of it, “pressuring” the iodine atoms just a little on

the outer perimeter first releases some strain from the rest of the SnIP helices in the CNT (19,0). The Sn-I-Sn angle (see Table 2) of 103.6° in SnIP@CNT(19,0) is the only one smaller than the experimental 104.8° , which equals a slight shift of the Iodine towards the CNT. This is confirmed by the longest Sn-I bond ($3.16 \text{ \AA}$) in the SnIP@CNT(19,0) for all hybrids. This also impacts the total energy landscape and leads to the minimum-like distribution of the total energies in Figure 2b.

Figure 5. Vibrational analysis of hybrids with respective CNT and a 1D *P*-SnIP strand. 1: I-breathing mode; 2: Sn-breathing mode; 3: P-stretching ($< 400 \text{ cm}^{-1}$) and 4: P-breathing ($> 400 \text{ cm}^{-1}$) modes. Movies of the modes are given in the supporting information (chapter 4).

Realization and routes to SnIP@CNT hybrids. Several semiconductors have been successfully incorporated into CNTs that are selenium as an atomic-scale double helix⁸, phosphorus as coil-like helical chain³, SnSe as chains or rods³⁷, and columnar or black phosphorus sheets.⁴⁰ For the latter it has been shown via calculations and experiments that the diameter of the

CNT plays a certain role for allotrope formation and that unusual and unexpected structures can be stabilized in such matrices. Obviously, the combination of helical arrangements and CNTs as matrices or reaction containers is beneficial and leads to a formation of hybrid materials. For a helical coil allotrope of phosphorus, as reported by the Tománek group recently, the interaction between the phosphorus allotrope and a neighboring graphene layer is in the same order than the inter layer interaction between two phosphorene sheets in the black phosphorus allotrope.³ They observed lone-pair electron states in the isolated phosphorus chain that contributes significantly to the electronic inter-chain coupling, which modified the band structure for the hybrid material in relation to the pure chain. Consequently, this allotrope has been synthesized and characterized one year later in a CNT.⁷ It has also been shown in this nice work that DFT as a method can only approximate the bonding situation for such weak interactions. As shown herein, PBE will underestimate and LDA will overestimate these interactions independent of the fact, if Grimme corrections are applied or not. Due to our own experiences with the description of weak interactions in phosphorus allotropes by quantum chemical calculations^{55, 56} and despite the weaknesses of DFT, we decided to use PBE and Grimme-D3 corrections in our investigations to get a first impression of the probability to realize the title compounds.

In all cases like Se@CNT or Phosphorus@CNT, the shortest contacts between the guests and the host matrix is defined by an extensive lone pair system of the guest pointing towards the surrounding host matrix. Interactions therefore occur between the lone pairs and the π -system of the sp^2 -hybridized carbon skeleton of the CNT. If SnIP is considered as a guest, we find a rather comparable situation where lone-pairs of tin and strongly polarized electron clouds of iodide define the surface of the SnIP double helices. The bonding situation between the double helix strands in SnIP, as well as the covalent interactions within the single helices, were reported elsewhere.¹⁸

According to our DFT calculations, exactly such weak but important interactions occur for SnIP incorporated in a CNT of suitable size.

For the Se@CNT hybrid also attractive but very weak electronic interactions between the guest and the host were found,⁸ nevertheless the hybrid was successfully synthesized. An interesting formation mechanism was postulated for the Se double helix inside the CNT, where the authors could show, that the realized Se double helix is compressed inside the matrix compared to their calculations. The incorporated Se double helix showed a much smaller diameter than a free-standing one after structure optimization and without significant compression caused by an external force. Therefore, the authors concluded that the formation of the double helix occurred within the CNT by reorganization of Se fragments or even atoms after encapsulation. The formation of the double helices can be regarded as an energetic compromise between minimizing the Se-CNT repulsion and the radial compression energy of the double-helix. Coming back to the title compounds the question now arises, if the formation of SnIP double helices might also be realized via short fragments and might be accelerated by compression of the surrounding matrix. If we now go back to SnIP as a potential host, the synthesis of bulk-SnIP is realized by a vapor transport mechanism, which might be very beneficial for a formation within the confined space of a suitable CNT. All components needed for the synthesis, that are SnI₂ and P₄, are highly volatile and available under suitable synthesis conditions with reasonable partial pressures.^{18,19} We predict, that SnIP double helices will form in a comparable mechanism than observed for the selenium case, when suitable CNTs are applied for the reaction. At least the transport of molecular components into the CNT is likely. In our calculations we also verified the effect of compression (and excess space) of the CNT matrix to SnIP as a driving force for the double helix formation within the CNT by using much smaller (and larger) diameters of the CNTs during our investigations. For instance, a (8,8) CNT with a diameter of 11.0 Å or a (25,0) CNT with 19.8 Å were also investigated. It was

not possible to compress a SnIP double helix (diameter of a free-standing SnIP double helix is 9.8 Å) to fit them into a CNT with significantly smaller diameters than the ones we reported in Table 1. If more space is available like in the case of a (25,0) CNT, a non-distorted SnIP double helix is attached to a certain area of the CNT without significant differences compared to a free standing one. Therefore, we believe that compression of the host matrix will not play a significant role and deformation of the SnIP double helix will not occur during the formation of SnIP inside CNTs.

As stated before the best possible synthesis route to incorporate SnIP into CNTs might be via the gas phase using highly volatile starting materials like phosphorus and tin iodide at elevated temperatures. Now the question arises quickly, if such starting materials can be supplied effectively into CNTs to allow the formation of SnIP. At least 50 % of 100 nm wide and several micrometer long channels in a TiO₂ membrane were successfully filled by this approach³¹ and nano-sized SnIP (diameter of SnIP rods approximately 30-50 nm) were successfully formed inside the channels. Red phosphorus was also effectively incorporated into multi-walled CNTs via the gas phase at 550° to 600 °C leading to a significant loading of red phosphorus inside the CNT.⁵⁷ During a conversion reaction with Na to Na₃P coming along with a volume increase of several hundred percent it became evident that incorporated red phosphorus is transformed to white phosphorus during this reaction. Such a highly reactive phosphorus allotrope is also needed to form SnIP with SnI₂ as the second gaseous component.

In a detailed ab initio DFT study it was shown that volatile niobium chlorides are suitable candidates to be incorporated as molecular species into CNTs via the gas phase. Species like NbCl₃ can be physisorbed to the walls with a gain in physisorption energy approaching the surface and they can fulfil a reasonable electron transfer to the carbon matrix upon adsorption.⁵⁸ A charge transfer of approximately 0.5 electrons per molecule was predicted in this case. The final postulated products after heat treatment and disproportionation at elevated temperatures were Nb metal

nanotubes and NbCl_5 . It has been shown herein that CNTs can be catalytically active for such a transformation and that they can act as electron acceptors for donating species. Therefore, SnI_2 can be a suitable candidate to be incorporated via the open ends of CNTs as a necessary second starting material beside afore mentioned phosphorus.

In recent studies it has been reported, that doping of the CNT with cations like platinum or phosphorus and phosphorus containing species under mild conditions (in contrast to the harsh conditions for a direct doping of CNTs with nitrogen or boron during the synthesis process⁵⁹) may increase the Lewis acidity of a given CNT.^{60, 61} Due to the temperature treatment of CNT with possible starting compounds like Sn/SnI_4 (which comproportionate to SnI_2 at elevated temperatures) and phosphorus during hybrid formation via the gas phase at temperatures $< 600\text{ }^\circ\text{C}$, a certain modification by doping of the CNT cannot be fully ruled-out. Any doping by cations to the CNT would be beneficial to enhance the interaction to the Lewis basic core of SnIP double helices. SnIP with its Sn lone pairs and the polarized iodide electron cloud pointing outwards the SnIP double helix tends to be Lewis-basic in nature.

Chirality in SnIP@CNT hybrids. Finally, a successful stabilization of a single chiral SnIP double helix (either a *M*- or *P*-SnIP double helix) in a CNT will directly lead to a chiral product. This is independent of the nature of the SnIP helix and the surrounding CNT and includes achiral CNTs. A chiral CNT like for instance the (15,5) one used in our calculations is not mandatory to create chirality but it will directly create enantiomer pairs. Unfortunately, we could not detect any significant energetic differences when the two different SnIP enantiomers are embedded in the same enantiomeric form of a (15,5) CNT. Nevertheless, once modifying CNTs by incorporating chiral and semiconducting entities is realized it will have a huge impact on the (stereo)chemistry of the CNT backbone in terms of functionalization⁶²⁻⁶⁴ and doping⁵⁹. Such hybrids may have a

certain potential in energy conversion applications due to the combination of different semiconductors or concerning the efficiency and the selectivity in catalysis.

CONCLUSION

DFT-based quantum chemical calculations were successfully used to evaluate early nucleation steps with different stereochemistry during SnIP formation and the occurrence of SnIP@CNT hybrids. For pure SnIP, the stability differences concerning the vicinity of a single rod are determined in terms of total energy. Three different models, each consisting of a center double helix strand neighbored by 6 additional ones in a hexagonal rod array, were compared featuring a racemic mixture of right and left-handed double helices, a 2:1 excess and finally the enantiomeric pure models with the same rotation direction for all double helices. It turned out that the realized racemic mixture (Model 1) is energetically favored by 8.5 kJ/mol compared with the excess Model 2 (2:1 ratio of double helices) and the enantiomeric pure SnIP seems to be the least favored one by another 4.7 kJ/mol relative to the previous case. Single SnIP double helices need to be stabilized either by themselves via agglomeration or by a surrounding matrix. The energy gain of 879 kJ/mol if one shell consisting of six double helix strands is coordinated to a single SnIP double helix substantiates this aspect, explains the difficulty to generate single double helices and renders a matrix approach necessary.

The simulation of a stable SnIP single double helical rod in a SWCNT was successful in different types of suitable CNTs. Four different CNTs, (10,10), (15,5), (18,0) and (19,0) were identified as suitable candidates to accommodate single SnIP double helix strands due to geometric constraints. In all cases we found no significant energy differences for the two incorporated enantiomeric forms of SnIP double helices, the *M*- and *P*-SnIP double helix, in the respective CNT's. There is no computational evidence, that an incorporation of a given enantiomeric form of a SnIP double helix is favored when a chiral CNT is present. The geometrical adjustments and structural changes after incorporation are fully performed within the SnIP substructure, as expected for the less ridged and flexible counterpart. The CNT host matrix remains almost unchanged. Compared to independently

calculated SWCNT and SnIP double helix strands only the very soft and flexible SnIP part is adjusted and reorganized slightly.

All three types of CNT's according to its electronic properties (metallic, semimetallic and semiconducting) are capable to host a single SnIP double helix strand without significant changes in their electronic properties. In each case, the electronic structure of the CNT is decisive for the resulting electronic structure of the hybrid SnIP@CNT system. The best candidate for a successful synthesis should be the SnIP@CNT (15,5) system, because it is energetically favored compared to the other hybrids, though its diameter is very close to the SnIP@CNT(18,0) structure.

The comparison of the stabilization energy ΔE of a seven SnIP double helix arrangement with a free-standing one in a CNT matrix (SnIP@CNT) gives a hint to the reason for the problematic delamination down to a single SnIP double helix by a top down approach. Though the hybrids show no mentionable amount of bonding states, the energy gain is in the same order of magnitude like in the pure SnIP needle for a single shell which renders a successful synthesis possible. A shielding of electrons and electron pairs pointing outward from the helix and the dispersion interactions between SnIP and the CNT are plausible features and very important in these hybrids.

METHODS

Ab initio calculations are carried out using the Crystal17 code⁶⁵ and its default settings unless noted otherwise. Due to the size of the studied periodic one-dimensional systems and the low symmetry ($P1$), all optimizations and frequency calculations are performed on the DFT-GGA-level with the functional from Perdew, Burke and Ernzerhof (PBE).^{66, 67} All-electron LCAO basis sets were applied for C and P, while effective core potential (ECP) and LCAO valence basis set were used for Sn and I (used basis sets are listed in Supporting Information in CRYSTAL format). Eight Monkhorst-Pack-type k -points were used for sampling the reciprocal space (a double-density Gilat net of 16 points was used in the calculation of the Fermi energy).⁶⁸ The structures were optimized using Grimme's DFT-D3 dispersion correction scheme as implemented in the Crystal17.^{69, 70} A Fermi smearing of 0.001 Hartree was applied, whenever carbon nanotubes were involved. This yields sufficient accuracy for the identification of crucial changes in the electronic structures of the hybrids, though we are aware the PBE functional might underestimate the bandgaps.⁷¹ The convergence threshold for the maximum gradient is 0.00045 and for the maximum displacement it is 0.0018. For the visualization of the structures, JMOL package^{72, 73} was used. The properties (band structure, DOS, COOP and vibrational analysis) were calculated with the Crystal17 properties code⁶⁵ and the number of k -points increased to 32 and 64 (for the Fermi energy). The plotted densities of states were expanded with 15 Legendre polynomials as implemented in the CRYSTAL software. The graphs were generated with the program Origin.

ASSOCIATED CONTENT

Supporting Information: The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

Details concerning the Total Energies, Density of States, Crystal Orbital Hamilton Population, Vibrational Modes of SnIP@CNT hybrids (PDF), and Quantum chemical basis sets and data (txt).

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M. Pielmeier conducted the DFT investigations with the aid of A. Karttunen under the supervision of T. Nilges. The manuscript was written by contributions from all authors.

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