

Communication

Packing of Helices: Is Chirality the Highest Crystallographic Symmetry?

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Abstract: Chiral structures resulting from the packing of helices are common in biological and synthetic materials. Herein, we analyze the noncentrosymmetry (NCS) in such systems using crystallographic considerations. A comparison of the chiral structures built from helices shows that the chirality can be expected for specific building units such as $3_1/3_2$ or $6_1/6_5$ helices which, in hexagonal arrangement, will more likely lead to a chiral resolution. In these two systems, we show that the highest crystallographic symmetry (i.e., the symmetry which can describe the crystal structure from the smallest asymmetric unit) is chiral. As an illustration, we present the synthesis of two materials ($[\text{Zn}(2,2'\text{-bpy})_3](\text{NbF}_6)_2$ and $[\text{Zn}(2,2'\text{-bpy})_3](\text{TaF}_6)_2$) in which the 3_n helices pack into a chiral structure.

Keywords: Crystallography; Chirality; Helical System; Oxide-fluorides

1. Introduction

Acentric basic building units (BBUs) provide interesting blocks to target noncentrosymmetric (NCS) structures exhibiting potential physical properties, for example piezoelectricity, optical activity, or ferroelectricity. However, one must be able to predict the packing of these BBUs into the 3D acentric structure. Two packings are usually described in the literature: (i) the packing of chiral units of one-handedness into chiral materials and (ii) the alignment of polar units into polar materials [1–8]. As a next step towards the engineering of NCS, it is important to explore the general concepts which drive the BBUs to pack in one of these structural arrangements.

In the solid state, the components tend to crystallize in the highest possible crystallographic symmetry. Thus, about 92% of crystal structures contain only one crystallographically independent molecule or formula unit [9,10]. In most cases, the presence of an inversion center is required to describe the highest crystallographic symmetry. However, systems where the highest symmetry is reached only without an inversion center can also be investigated to understand and predict the noncentrosymmetric arrangements. In this context, the helical systems are of interest. Chiral structures built from helices are common in either biological or synthetic materials [11–13]. To describe the packing of helical proteins in biology, Chothia et al. proposed the “ridges and grooves” model in which the proteins tend to pack in the way that the ridges and grooves on the surface intercalate [14]. Using a similar model, Boncheva et al. described the self-assembly of millimeter-sized helical drill bits and bolts into 3D aggregates via capillary forces [15]. These authors showed that, in the case of a high degree of shape complementarity, the components tend to aggregate into chiral structures with enantiomerically pure helices. The shape compatibility depends on the periodicity, handedness and arrangement of the helices and is also a general concept which can be extended to analyze the

NCS in the solid state. In organic and inorganic solid state, the interactions between helices are also symmetry-dependent. Thus, Meille et al. previously reported that helical polymers with a hexagonal arrangement have a high probability to crystallize into a chiral space group [16]. They reported that it is not possible to pack two helices of opposite chirality in the hexagonal arrangement and keep them symmetrically equivalent. In parallel to this work, we reported a similar result in hybrid materials. We previously showed that 3_1 helices in the $P3_121$ space group (i.e., in hexagonal arrangement) tend to pack with helices of the same handedness because they share identical spatial and translational orientation. From the investigation of these compounds, we emphasized that the packing of helices with opposite handedness does not allow equivalent bridging of the helices. Thus, the packing of helices is also dependent on their symmetries but independent of the system (millimeter-sized helical drill bits, proteins, helical polymers, organic or inorganic structure) or the nature of interactions (capillary forces [15], close-packing of proteins [14,17], covalent [18], or entropic [16]).

2. Results and Discussion

In helical systems, one can determine the arrangements in which every helicate (the smallest repetitive unit of a helix) can crystallize with a similar environment and which are also symmetrically equivalent. In such conditions, the helices can share identical spatial and translational orientations. Symmetry patterns can be drawn by considering different configurations for 3_n helices in hexagonal arrangement (Figure 1a), 6_n helices in hexagonal arrangement (Figure 1b), and 4_n helices in tetragonal arrangement (Figure 1c,d).

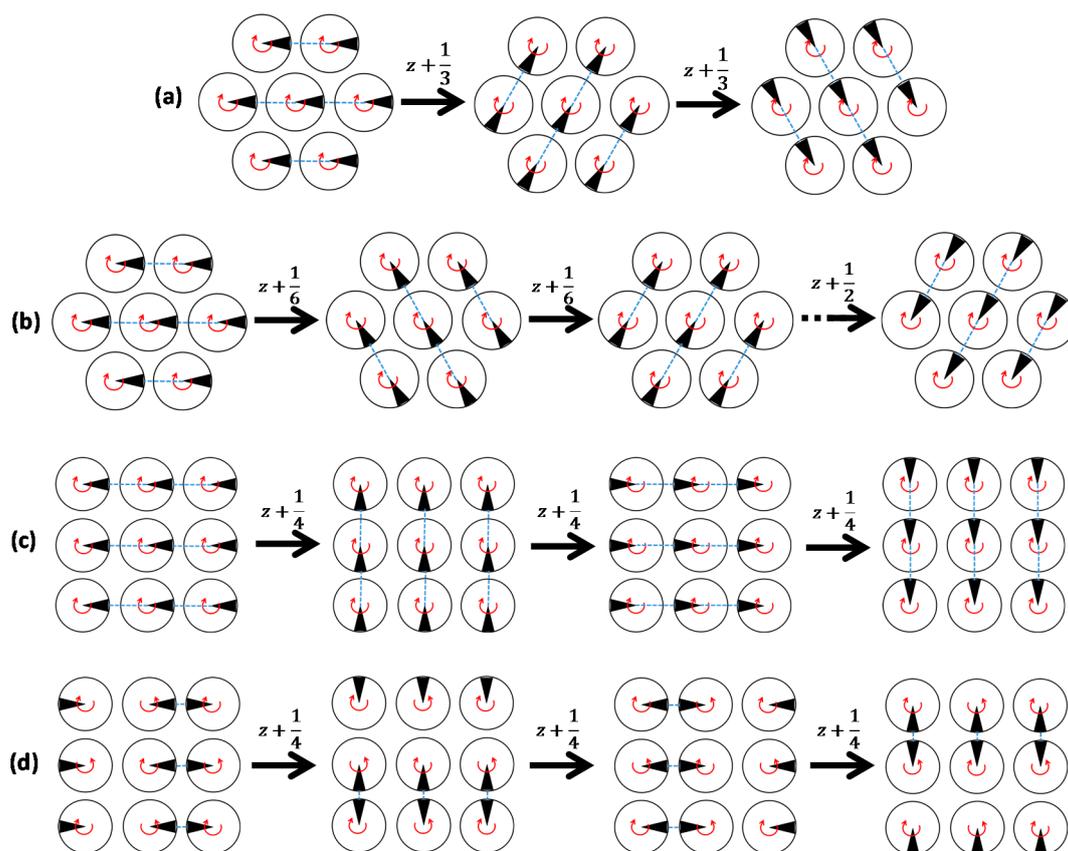


Figure 1. Representation of examples of packings for (a) a chiral assembly of 3_n helices in hexagonal arrangement, (b) a chiral assembly of 6_n helices in hexagonal arrangement, (c) a chiral assembly of 4_n helices in tetragonal arrangement, (d) a non-chiral assembly of 4_n helices in tetragonal arrangement. The red arrows and black triangles represent the handedness of helices and the helicates, respectively. In order to be symmetrically equivalent, the helicates must have the same environment.

In a hexagonal arrangement of 3_n or 6_n helices, the helicates can have the same environment only if the helices are of the same-handednesses (i.e., in a chiral structure) (Figure 1a,b). For every other case in which one would consider the packing of helices of both-handednesses, the helicates would have different environments. Conversely, 4_n helices in a tetragonal arrangement can either crystallize in chiral (Figure 1c) or non-chiral structure (Figure 1d) in order for the helicate to have the same environment.

This observation from the symmetry patterns could also be generalized from group theory. To reach the highest possible crystallographic symmetry in the solid state, the smallest repetitive unit of the helices should also be (if possible) the repetitive unit of the overall arrangement. In other words, the 3D arrangement should be described only from the helicates together with symmetry operations.

Thus, one can identify the space groups in which two conditions are satisfied: (i) the presence of screw axes along which the helix could be described in one direction from a unique repetitive unit, and (ii) the presence of symmetry operations to relate the screw axes to each other along the other two directions. If these conditions are satisfied, the helix can pack in this space group and reach the highest symmetry.

Figure 2 lists the different space groups which include the screw axes related by symmetry [19]. For example, 3_n screw axes are only included in chiral space groups (Figure 2a). It results that the 3_n helices in hexagonal arrangement reach the highest symmetry only when crystallizing in a chiral space group. In the case of the hexagonal arrangement of 6_n helices (Figure 2b), the highest symmetry can also be only reached when crystallizing in a chiral space group. However, for the tetragonal arrangement of 4_n helices (Figure 2c), the resulting structure can either be chiral or non-chiral to reach the highest crystallographic symmetry because 4_1 and 4_3 can be related by symmetry in this arrangement.

This analysis shows that the hexagonal arrangement of helices in the solid state differs from the tetragonal one. The highest symmetry of a hexagonal arrangement of either 3_n or 6_n helices is only reached when the structure is chiral (i.e., when a chiral resolution occurs), whereas the tetragonal arrangement of 4_n helices can reach the highest symmetry when the structure is either centrosymmetric or noncentrosymmetric.

(a)		
Space Groups with 3_1 screw axes in hexagonal arrangement	Space Groups with 3_2 screw axes in hexagonal arrangement	
<i>P 3₁</i> <i>P 3₁12</i> <i>P 3₁21</i>	<i>P 3₂</i> <i>P 3₂12</i> <i>P 3₂21</i>	
(b)		
Space Groups with 6_1 screw axes in hexagonal arrangement	Space Groups with 6_5 screw axes in hexagonal arrangement	
<i>P 6₁</i> <i>P 6₁22</i>	<i>P 6₅</i> <i>P 6₅22</i>	
(c)		
Space Groups with 4_1 screw axes in tetragonal arrangement	Space Groups with 4_3 screw axes in tetragonal arrangement	Space Groups with 4_1 and 4_3 screw axes in tetragonal arrangement
<i>P 4₁</i> <i>P 4₁22</i> <i>P 4₁2₁2</i>	<i>P 4₃</i> <i>P 4₃22</i> <i>P 4₃2₁2</i>	<i>I 4₁md</i> <i>I 4₁cd</i> <i>I 4₁/a</i> <i>I 4₁/amd</i> <i>I 4₁/acd</i>

Figure 2. List of space groups exhibiting (a) 3_n screw axes in hexagonal arrangement, (b) 6_n screw axes in hexagonal arrangement and, (c) 4_n screw axes in tetragonal arrangement. Space groups in red color are chiral. Space groups in bold are polar. No space groups combining 3_1 and 3_2 screw axes or 6_1 and 6_5 screw axes exist.

Two new compounds, $[\text{Zn}(2,2'\text{-bpy})_3](\text{MF}_6)_2$ ($\text{M} = \text{Nb}^{5+}$ (I) and Ta^{5+} (II)), isostructural to the previously reported $[\text{A}(2,2'\text{-bpy})_3](\text{PF}_6)_2$ ($\text{A} = \text{Mn}, \text{Ru}, \text{Ni}, \text{Cu}, \text{Zn}$ and Cd), allow us to validate this investigation (Experimental Details in Supplementary Information) [20–22]. Chiral metal trischelates $[\text{A}(2,2'\text{-bpy})_3]^{2+}$ are described as a pair of enantiomers Δ and Λ - $[\text{M}(\text{ligand})_3]^{n+}$ with the symmetry D_3 (Figure 3). In the structures of I–II and previously reported isostructural compounds, these units are the helicates of helices propagating along the c axis. Thus, π -stacking occurs between the 2,2'-bipyridyne ligands of the helicates. Such interactions are common in organometallic or DNA helices [23–25]. The handedness of the helices is induced by the intrinsic character of helicates: the Δ enantiomer leads to the 3_1 helices while the Λ enantiomer leads to the 3_2 helices. [26]. Thus, two enantiomorphous crystal forms ($P3_1$ and $P3_2$) are induced by the chiral resolution of Δ and Λ - $[\text{Zn}(2,2'\text{-bipy})_3]^{2+}$, respectively. Thus, in order to reach the highest symmetry, the $3_1/3_2$ helices in hexagonal arrangement crystallize in the chiral space group $P3_1/P3_2$. The structure determination carried out on several crystals showed the presence of both configurations in equal amount.

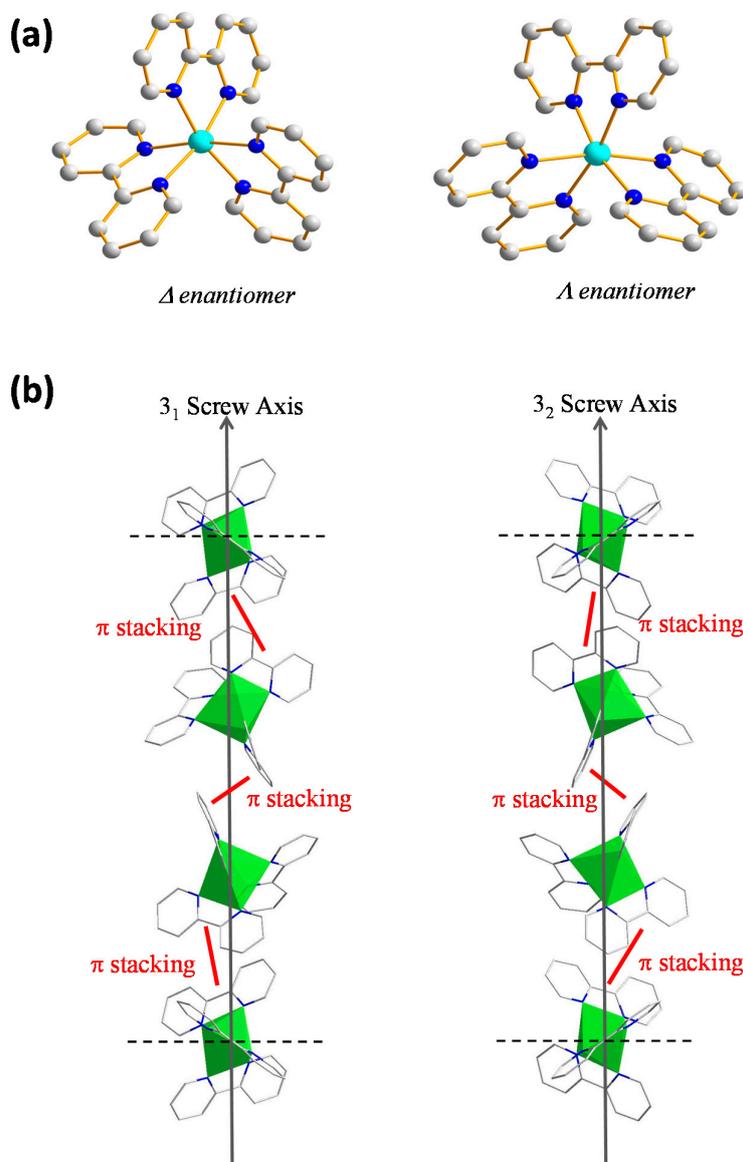


Figure 3. View of (a) the two enantiomers Δ and Λ - $[\text{Zn}(2,2'\text{-bipy})_3]^{2+}$, along the three-fold rotation axes, and (b) the two enantiomorphous 3_1 and 3_2 helices built from Δ and Λ - $[\text{Zn}(2,2'\text{-bipy})_3]^{2+}$, respectively; π -stacking occurs between $[\text{Zn}(2,2'\text{-bipy})_3]^{2+}$ helicates.

3. Conclusions

In the solid state, most of the materials crystallize with the highest possible symmetry with a single chemical unit per asymmetric unit. The identification of systems in which the highest symmetry is polar or chiral could also be of great interest for the engineering of NCS materials. Thus, one could determine which characteristics a basic building unit must exhibit to target the NCS in the solid state. Our investigation of helical systems shows that 3_n or 6_n helices in hexagonal arrangement likely crystallize into a NCS agglomerate because the packing reaches the highest symmetry when the inversion center is excluded. Conversely, 4_n helices can reach the highest symmetry in either a centro- or noncentrosymmetric tetragonal packing. This new insight on the relationships between NCS and highest symmetry could be extended to other helical systems and could improve our understanding and control of the engineering of chirality in the solid state.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/6/9/106/s1>, X-Ray crystallographic file in CIF format for compounds I–II (CCDC 893952–893955), Experimental Details, and Table S1: Crystal data and summary of data collections, structure solutions and refinements for compounds $[\text{Zn}(2,2'\text{-bpy})_3](\text{NbF}_6)_2$ (space-group $P3_1$) (I) and $[\text{Zn}(2,2'\text{-bpy})_3](\text{TaF}_6)_2$ (space-group $P3_1$) (II); Figure S1: View along c and b of the structure with the relative orientation of the distortion represented by the shortest Nb-F bond. Along a and b axes, the individual dipole moments are canceled by the 3_n screw axis along c . The alignment of the individual polarizations is collinear to the polar axis of the structure.

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References

1. Pasteur, L. Sur les relations qui peuvent exister entre la forme cristalline, la composition chimique, et le sens de la polarisation rotatoire. *Ann. Chim. Phys.* **1848**, *24*, 442–459. (In French)
2. Pasteur, L. Recherches sur les propriétés spécifiques des deux acides qui composent l'acide racémique. impr. Bachelier. *Ann. Chim. Phys.* **1850**, *28*, 56–99. (In French)
3. Flack, H.D. Chiral and Achiral Crystal Structures. *Helv. Chim. Acta* **2003**, *86*, 905–921.
4. Donakowski, M.D.; Gautier, R.; Yeon, J.; Moore, D.T.; Nino, J.C.; Halasyamani, P.S.; Poeppelmeier, K.R. The Role of Polar, Lambda (Λ)-Shaped Building Units in Noncentrosymmetric Inorganic Structures. *J. Am. Chem. Soc.* **2012**, *134*, 7679–7689.
5. Gautier, R.; Poeppelmeier, K.R. Preservation of Chirality and Polarity between Chiral and Polar Building Units in the Solid State. *Inorg. Chem.* **2012**, *51*, 10613–10618.
6. Maggard, P.A.; Kopf, A.L.; Stern, C.L.; Poeppelmeier, K.R. Probing helix formation in chains of vertex-linked octahedra. *CrystEngComm* **2004**, *6*, 452–457. [[CrossRef](#)]
7. Gautier, R.; Norquist, A.J.; Poeppelmeier, K.R. From Racemic Units to Polar Materials. *Cryst. Growth Des.* **2012**, *12*, 6267–6271. [[CrossRef](#)]
8. Gautier, R.; Klingsporn, J.M.; Van Duyne, R.P.; Poeppelmeier, K.R. Optical activity from racemates. *Nat. Mater.* **2016**, *15*, 591–592. [[CrossRef](#)] [[PubMed](#)]
9. Padmaja, N.; Ramakumar, S.; Viswamitra, M.A. Space-group frequencies of proteins and of organic compounds with more than one formula unit in the asymmetric unit. *Acta Crystallogr. A* **1990**, *46*, 725–730. [[CrossRef](#)]
10. Steed, J.W. Should solid-state molecular packing have to obey the rules of crystallographic symmetry? *CrystEngComm* **2003**, *5*, 169–179. [[CrossRef](#)]
11. Sharma, V.; Crne, M.; Park, J.O.; Srinivasarao, M. Structural Origin of Circularly Polarized Iridescence in Jeweled Beetles. *Science* **2009**, *325*, 449–451. [[CrossRef](#)] [[PubMed](#)]
12. Chung, W.-J.; Oh, J.-W.; Kwak, K.; Lee, B.Y.; Meyer, J.; Wang, E.; Hexemer, A.; Lee, S.-W. Biomimetic self-templating supramolecular structures. *Nature* **2011**, *478*, 364–368. [[CrossRef](#)] [[PubMed](#)]

13. Meister, R.; Hallé, M.A.; Dumoulin, H.; Pieranski, P. Structure of the cholesteric focal conic domains at the free surface. *Phys. Rev. E* **1996**, *54*, 3771–3782. [[CrossRef](#)]
14. Chothia, C.; Levitt, M.; Richardson, D. Helix to helix packing in proteins. *J. Mol. Biol.* **1981**, *145*, 215–250. [[CrossRef](#)]
15. Boncheva, M.; Bruzewicz, D.A.; Whitesides, G.M. Formation of chiral, three-dimensional aggregates by self-assembly of helical components. *Langmuir* **2003**, *19*, 6066–6071. [[CrossRef](#)]
16. Meille, S.V.; Allegra, G. Chiral crystallization of helical polymers. *Macromolecules* **1995**, *28*, 7764–7769. [[CrossRef](#)]
17. Yin, P.; Zhang, Z.; Lv, H.; Li, T.; Haso, F.; Hu, L.; Zhang, B.; Bacsá, J.; Wei, Y.; Gao, Y.; et al. Chiral recognition and selection during the self-assembly process of protein-mimic macroanions. *Nat. Commun.* **2015**, *6*. [[CrossRef](#)] [[PubMed](#)]
18. Maggard, P.A.; Stern, C.L.; Poepelmeier, K.R. Understanding the Role of Helical Chains in the Formation of Noncentrosymmetric Solids. *J. Am. Chem. Soc.* **2001**, *123*, 7742–7743. [[CrossRef](#)] [[PubMed](#)]
19. Hahn, T. *Int. Tables Crystallogr.*; D. Reidel: Dordrecht, The Netherlands, 1983.
20. Breu, J.; Domel, H.; Stoll, A. Racemic Compound Formation versus Conglomerate Formation with [M (bpy) 3](PF6) 2 (M = Ni, Zn, Ru); Molecular and Crystal Structures. *Eur. J. Inorg. Chem.* **2000**, *2000*, 2401–2408. [[CrossRef](#)]
21. Wang, L.; Yang, X.-Y.; Huang, W. Tris (2, 2'-bipyridyl-κ2N, N') copper (II) hexafluoridophosphate. *Acta Crystallogr. Sect. E* **2007**, *63*, m835–m836. [[CrossRef](#)]
22. Kundu, N.; Mandal, D.; Chaudhury, M.; Tiekink, E.R.T. Luminescence characteristics and X-ray crystal structure of [Cd (bipy) 3][PF6] 2 (bipy = 2, 2'-bipyridine). *Appl. Organomet. Chem.* **2005**, *19*, 1268–1270. [[CrossRef](#)]
23. He, C.; Zhao, Y.; Guo, D.; Lin, Z.; Duan, C. Chirality transfer through helical motifs in coordination compounds. *Eur. J. Inorg. Chem.* **2007**, *2007*, 3451–3463. [[CrossRef](#)]
24. Ghazzali, M.; Langer, V.; Öhrström, L. The role of intermolecular interactions in the assemblies of Fe^{II} and Co^{II} tetrakis-isothiocyanatometalates with tris(1,10-phenanthroline)-Ru^{II}: Crystal structures of two dual-metal assemblies featuring octahedral cationic and tetrahedral anionic modules. *J. Solid State Chem.* **2008**, *181*, 2191–2198. [[CrossRef](#)]
25. Matta, C.F.; Castillo, N.; Boyd, R.J. Extended Weak Bonding Interactions in DNA: π-Stacking (Base–Base), Base–Backbone, and Backbone–Backbone Interactions. *J. Phys. Chem. B* **2005**, *110*, 563–578. [[CrossRef](#)] [[PubMed](#)]
26. Zheng, X.-D.; Jiang, L.; Feng, X.-L.; Lu, T.-B. Constructions of 1D helical chains with left-handed/right-handed helicity: A correlation between the helicity of 1D chains and the chirality of building blocks. *Dalton Trans.* **2009**, 6802–6808. [[CrossRef](#)] [[PubMed](#)]

