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Crystal structure and growth kinetics of self-assembled microtubes with different chirality

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Chirality is an intrinsic universal property of matter inherent to many organic molecules as amino acids, sugars, etc. Chirality has a major influence in engineering of new nonlinear optical materials [1] and recently became a central concept in spintronics [2]. Detailed study of chirality-dependent material properties needed for practical applications. The simplest objects for this investigation are peptides due to their wide range of self-assembled structures such as thin films, nanobelts, vesicles, nanospheres, fibers, nano- and microtubes etc. [3]. These structures possess chirality at different hierarchical levels of organization and are considered as advanced functional materials for nanotechnological and biomedical applications since they possess many attractive properties, such as inherent biocompatibility, structural and functional flexibility, biodegradability, availability and cost-effectiveness.

Diphenylalanine (H-Phe-Phe-OH, FF) is the simplest aromatic dipeptide and the most studied self-assembled peptide for now [4]. Intensive research of FF-based nanotubes (NTs) and microtubes (MTs) in last years showed their unique assembly characteristics and remarkable physical properties such as high rigidity [5] notable thermal stability [6] interesting electronic [7] nonlinear optical [8] and photoluminescent [9] properties as well as exceptional piezoelectric effect [10] and pyroelectricity [11]. However, despite of the numerous studies on the FF self-assembly, physical properties and applications, the role of chirality in its structure and properties is still poorly studied and understood.

Since FF is a chiral molecule it can exist in two enantiomeric forms: H-L-Phe-L-Phe-OH (L-FF) and H-D-Phe-D-Phe-OH (D-FF). Recent study by molecular modeling had shown that α-helix NTs of L-FF and D- FF possess different total energies and dipole moments [12]. In this way, here could be the differences in structure and properties of L-FF and D-FF NTs and MTs.

Therefore, this work is aimed to perform an experimental and theoretical study of the structure and growth kinetics of L-FF and D-FF microtubes. Better understanding the role of chirality in the growth process will allow improving the methods for NTs and MTs fabrication, their better implementation in various functional devices, and may assist in developing new drugs and biomaterials. It was shown that L-FF and D-FF MTs simultaneously grown under identical ambient conditions have quite different morphology. L-FF MTs have a tendency to branching and their length is almost twice comparison to D-FF MTs. Along with this fact, the diameter of L-FF MTs is 20% lower than that of D-FF MTs (Table 1). The *in-situ* study of MTs growth showed that both L-FF and D-FF MTs have similar growth kinetics with small difference. The average growth rate of L-FF MTs, taken from the linear regression slope considering all experimental points, is significantly lower than that of D-FF (0.5 μm/s for L-FF vs. ~ 2 μm/s for D-FF). At the same time, step-like growth behaviour in case of L-FF MTs is not that pronounced as in case of D- FF MTs, which means that in nonregular plateaus the length of D-FF MTs almost does not change.

Table 1. Comparison of morphologies of L-FF and D-FF MTs.

Enantiomer configuration	Mode length, μm	Median length, μm	Diameter, μm
L-FF	860 ± 230	1089	1.9 ± 0.6
D-FF	490 ± 120	610	2.3 ± 1.0

The X-ray diffraction study showed L-FF tubes belong to $P6_1$ space group which leads to right-handed helix for L-FF NTs, while D-FF MTs belong to $P6_5$ space group which leads to left-handed helix for D-FF NTs. Obviously, this symmetry difference is attributed to FF monomer chirality.

In order to understand the differences in morphology and growth kinetics, the total energy of six-molecule FF rings – structural units of the nanotubes, and the interaction energy between two FF rings for both forms were calculated using experimentally determined data. The obtained total energy for L-FF ring appears to be higher than that for D-FF ring, however this difference does not depend on the distance and the direction of removal of one FF monomer. The interaction energy between two FF rings was calculated along either *c*-axis or *a*-axis, thus simulating the interaction at growing and side facets of the MT, respectively. For arrangement of the rings along *c*-axis the values of interaction energy are almost the same for both L-FF and D-FF rings. At the same time, for arrangement of the rings along *a*-axis the value of interaction energy for D-FF rings is about 25% higher than that for L-FF rings. Thus, this difference could shed light on the origin of different morphology and growth kinetics of L-FF and D-FF MTs.

It was found for the first time that L-FF and D-FF microtubes have different crystal structure and demonstrate their different growth kinetics, regardless of the chemically identical composition of these L- and D- enantiomers. L-FF microtubes demonstrate gradual continuous growth leading to almost doubling their lengths with respect to D-FF, showing a step-like growth. The essential difference in interaction energies of the rings at side facets of the growing L-FF and D-FF microtubes was found which satisfactorily explains the observed effects. These effects can be considered in the design of biocompatible electronic components and biosensors, where the enantiospecific interaction between the sensor and the analyte can take place.

The measurements of microtubes growth kinetics and morphology analysis were done in Ural Federal University (UrFU) and made possible by Russian Science Foundation (Grant No. 18-72-00052). The equipment of the Ural Center for Shared Use “Modern nanotechnology” UrFU was used. Computer simulation was performed under the support of Russian Foundation for Basic Research (Grant No. 19-01-00519 A). X-ray diffraction data were collected under the experiment SC-4587 at the European Synchrotron Radiation Source (ESRF, Grenoble, France). S.K., P.Z., L.M. and A.K. are grateful to FCT project PTDC/CTM-CTM/31679/2017. P.Z. and L.M. are grateful to FCT project PTDC/QEQ-QAN/6373/2014. S.K and A.K were also supported by the joint Portugal-Turkey project (TUBITAK/0006/2014). Part of this work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES.

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