

## Research Article

# Self-Assembly of Diphenylalanine-Based Nanostructures in Water and Electrolyte Solutions

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Diphenylalanine (FF) is a peptide that can form different nanostructures; this makes it particularly attractive for both biological and technological applications. However, any application using this type of nanostructures requires controlling their size and shape. Information is provided about the various structures formed through the peptide FF self-assembly in different salt solutions (NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub>), concentrations (50 mM, 100 mM, and 200 mM), and pH (3 to 10). Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Fourier-transform infrared (FTIR) spectroscopy were used to characterize the nanotubes. Results show that FF nanotube formation through self-assembly is a delicate balance between electrostatic, hydrogen bonding, and hydrophobic interactions; any imbalance in these can impede nanotube formation. Our results demonstrate that salts, such as NaCl and CaCl<sub>2</sub>, along with the studied concentrations promote the formation of very long nanotube agglomerates. This would be due to a combined screening effect and the fact that cations are structure-forming and promote hydrophobic interactions; therefore, nanotube agglomeration occurs and also benefits electrostatic interactions, hydrogen bonds, and longer nanotubes. The presence of AlCl<sub>3</sub> produces an imbalance in the abovementioned interactions because of excess Cl<sup>-</sup>, a structure-breaking anion that impedes the nanostructure formation.

## 1. Introduction

Peptide self-assembly to form well-ordered hierarchical structures has drawn much attention because of its centrality in biological processes such as amyloid fibril formation associated with neurodegenerative diseases and also in the design of novel nanostructures with potential applications ranging from biotechnology to nanotechnology [1–13]. The great variety of structures formed is directly related to the forces and their synergies, manifested during the self-assembly process [14–19]. The simplest peptide building block is diphenylalanine (FF), the core recognition motif of Alzheimer's  $\beta$ -amyloid polypeptide, which has proven very interesting because it can self-assemble into different nanostructures depending on experimental conditions [1, 2, 15, 20–30]. Along with the fine tuning of the experimental procedures emerges the great challenge of using these nanostructures,

which requires quantitative control to obtain nanostructures free of defects [28, 30, 31]. Particularly interesting is the effect of the ionic strength of the solution. Concentrated salt solutions affect the structure and nature of proteins, including their solubility, denaturation, and dissociation [32–36]. Generally, the size and stiffness of nanostructures increase according to the Hofmeister series in which ions are arranged according to their ability to precipitate or “salt-out” proteins [36–41]. Self-assembled structures and their transformations in the presence of salts have been explained on the basis of charge screening mechanisms and peptide solubility [42, 43], although the increase in viscosity induced by water structure-maker cations appears not to have been considered. FF self-assembly has been studied extensively as the nanostructures that are formed. Remarkable is that almost always the FF is dissolved in organic solvent, for example, 1,1,1,3,3,3-hexafluoro-2-propanol, and some of them were

environmentally very unfriendly and then redissolved in water [1, 3, 27, 44, 45]. More recently, however, it has been shown that solvents other than water are not critical for self-assembly [24, 46].

Here, we study both the self-assembly of FF dissolved in water and the effect of electrolyte type and concentration and solution pH on the formed nanostructures. For characterization of the various structures, we use SEM and TEM.

## 2. Materials and Methods

**2.1. Preparation of FF Nanotubes in Water (Control Sample).** FF nanotubes were prepared by dissolving 4 mg of lyophilized peptide FF (H-D-Phe-D-Phe-OH, Bachem AG Switzerland) directly in 2 ml ultrapure water (Millipore) and placed in a thermo-regulated bath (Wise Bath, Wisd Laboratory Instruments, Korea) at 65°C for 30 min, pH 5.3. The solution was left to cool at room temperature and then placed in frozen storage at -18°C until characterization.

**2.2. Preparation of FF Nanotubes in Salt Solution.** To evaluate the effect of salt concentration and electrolyte valence on the formation of FF nanotubes, instead of diluting in water as in the control sample, we used 2 ml solution of either NaCl or CaCl<sub>2</sub> (Merck). Three different concentrations were used, 50 mM, 100 mM, and 200 mM.

**2.3. Effect of pH in the Preparation of FF Nanotubes.** A range of pH from 3 to 10 was used. Nanotubes were formed under the same conditions as for the control sample. Once FF was added, pH was adjusted to the desired value by using 0.1 M NaOH and 0.1 M HCl solutions (Merck). The pH was measured with a pH meter (Orion, model 410 A, USA).

**2.4. Characterization by TEM.** TEM images were obtained with a transmission electron microscope (JEOL/JEM 1200 EX II, Japan) operated at 120 kV. Samples were prepared by dispersing a droplet of the solution on a 200-mesh copper grid. Samples were individually introduced under the microscope for examination.

**2.5. Characterization by SEM.** SEM images were obtained with a scanning electron microscope (JEOL JSM-6610LV, Japan). Each solution sample was pretreated by placing a droplet in an aluminum sample holder covered with carbon paper and then heated in an oven (Tempra, model ZRD-5055) at 50°C for 10 min and immediately cooled in a desiccator with silica gel for 1 min. Then, each sample was covered with a carbon bath to improve conductivity, and a sputtering unit (Denton Vacuum, Desk V, USA) was used for 5 min at a pressure of 0.05 torr. Finally, all the sample holders were placed in a rack for microscope examination.

**2.6. Characterization by FTIR.** Sample solutions were analyzed using a FTIR spectrophotometer (IRPrestige-21; Shimadzu, Japan) equipped with an ATR unit. The samples were placed onto the face of the germanium (Ge) crystal of the ATR unit to obtain the corresponding spectra. Absorbance spectra were acquired by scanning the specimens 126 times over a 1000–4000 cm<sup>-1</sup> range at a resolution of

1 cm<sup>-1</sup>. Ultrapure water was used as background. After baseline correction, the spectra were analyzed with available software (IRsolution 1.21; Shimadzu, Japan). Between each measurement, the ATR was flushed with ultrapure water.

## 3. Results and Discussion

Figure 1 shows TEM and SEM micrographs of the structures formed. Self-assembly of FF is driven by a greater affinity of nanotubes among themselves than with water. Nanotubes, thin fibrils, and thick fibres coexist; they are 100 nm to 1 μm in diameter and several hundred microns in length. The TEM images in Figure 1 also show a few small globular structures [22], 100 nm in diameter, attached to nanotubes.

Figure 2 shows TEM images of nanotubes prepared independently with NaCl and CaCl<sub>2</sub> at 50 and 200 mM, for partial accounts on the effect of salts on the self-assembly and stability of the structures formed, see [43, 47–50]. The effect of NaCl on FF self-assembly is shown in Figure 2(a) for low salt and Figure 2(b) for high salt. At low salt, the main difference with the control sample is the proliferation of nanovesicles; however, at high salt, no nanovesicles are formed and nanotubes are thicker and longer. Figure 2(b) shows a nanotube that has grown a thin branch. Regarding the formed nanotubes, these are noticeably less agglomerated and shorter than in the control. The effect of a strong water structure maker such as Ca<sup>2+</sup> is shown in Figure 2(c) at low concentration and Figure 2(d) at high concentration. The almost total absence of nanovesicles and the larger dimensions of the nanotubes formed at any concentration of Ca<sup>2+</sup> were remarkable. Nanotubes are significantly wider and longer than those in the control sample and with NaCl solution, and these dimensions are even greater, particularly the length, at the higher concentration of Ca. In the presence of Al salt, there are no surprises; precipitated or undissolved aluminum salts block the active sites on the FF, inhibiting their self-assembly. At any concentration of Al, many small structures covered with aluminum salt (not shown) abound, which prevents further growth or further evolution. The pH remains between 5.2 and 5.4.

The intermolecular interactions driving the self-assembly of FF as shown in Figure 1 have been determined in the literature by using a variety of experimental techniques (FT-IR, CD and fluorescence spectroscopy, XRD, TGA, microscopy) (see for instance [1, 2, 23, 45]) and also molecular simulation (see for instance [22, 27]). A π-π stacking interaction between the aromatic chains of the FF monomers has been suggested to provide the energy and direction to initiate the growth of an extended sheet stabilized via electrostatic interaction and H bonding between N-termini (NH<sub>3</sub><sup>+</sup> or head) and neighbour C-termini (COO<sup>-</sup> or tail) and hydrophobic and van der Waals interactions between the nonpolar chains. It also seems to be agreed that the architecture of a nanotube begins with the closure of the sheet formed along one of its axes; the interactions acting on the closure are again stacking, hydrophobic, and van der Waals between nonpolar chains and electrostatic interaction and H bonding between neighbouring polar head and tail groups. Figure 2 clearly shows that FF self-assembly into nanotubes in water is aided by simple ions, particularly those of biological significance such as

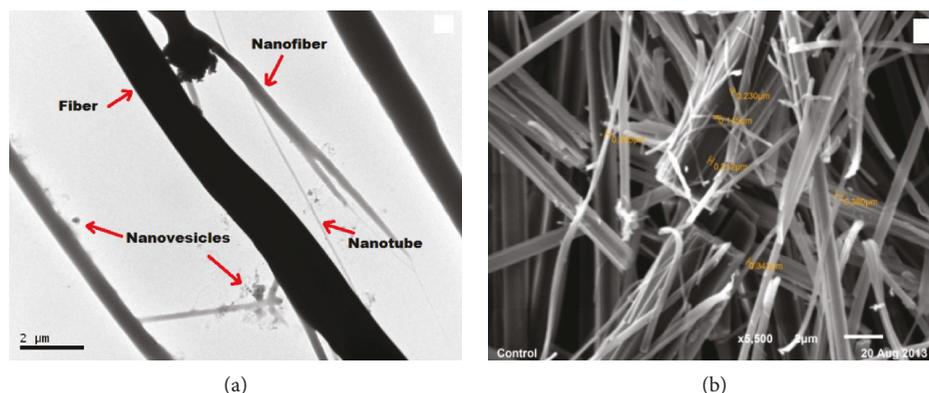


FIGURE 1: TEM (a) and SEM (b) micrographs of FF nanotubes in water (control sample).

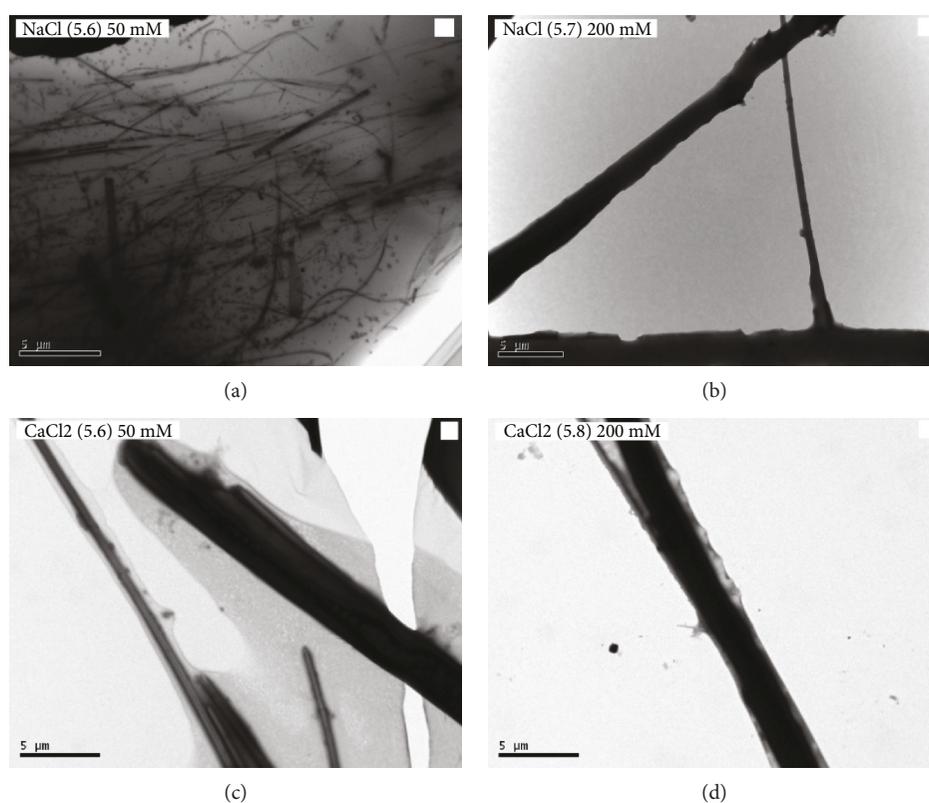


FIGURE 2: TEM images of FF nanostructures formed in NaCl (a, b) and CaCl<sub>2</sub> (c, d) at two concentration levels, 50 mM (left column) and 200 mM (right column). Resulting pH is indicated in parentheses.

Na<sup>+</sup>, Ca<sup>2+</sup>, and Cl<sup>-</sup>. We argue that salt bridges between tails and between heads, mediated, respectively, by cations and anions, are alternatives to peptide bonds, the preferred bond in pure water, thus favouring radial and longitudinal nanotube growth. The nanostructures formed in salt solutions are also aided by ion- $\pi$  interactions, particularly with cations of high charge density such as calcium. The reinforced structure of water by structure-maker cations, such as Na<sup>+</sup> and Ca<sup>2+</sup>, restricts the mobility of FF monomers, and thus salt bridges of type tail-cation-tail and head-anion-head save the energy required to align head and tail groups to form peptide bonds. The additional energy expenditure for self-assembly in water that is more structured due to maker ions

is rarely considered in the analysis of underlying aggregation mechanisms.

FF-based nanostructures at different pH in the absence of salt are shown in Figure 3. At pH 3, nanotubes are very clean and clearly isolated, most remain short and thin, and aggregation is definitely not favoured. At pH 5, nanotubes were slightly less than the isoelectric point (ip) of FF [51], thicker and longer nanotubes abound, growth is not always longitudinal as branches seem to intricate, and few nanovesicles exist. At pH 10, only amorphous structures are formed, with no preferential direction for the growth. The results show that in acid solutions, neutralization of the C-terminus is no impediment to interaction via H bond with a neighbour

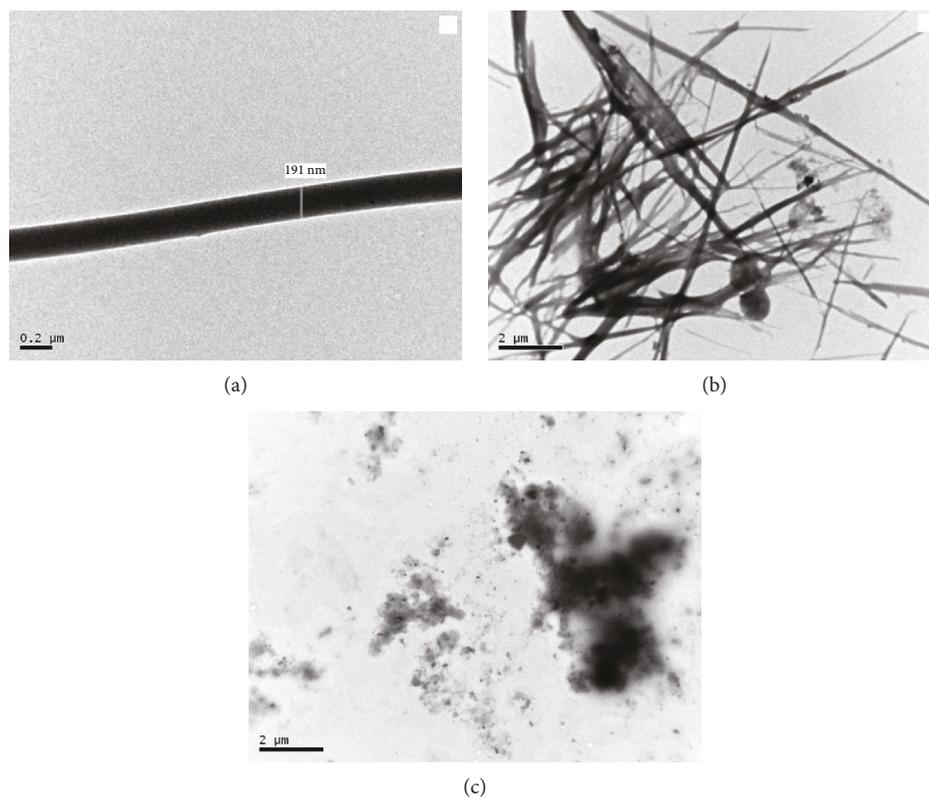


FIGURE 3: TEM images of FF nanostructures formed at pH = 3 (a), pH = 5 (b), and pH = 10 (c).

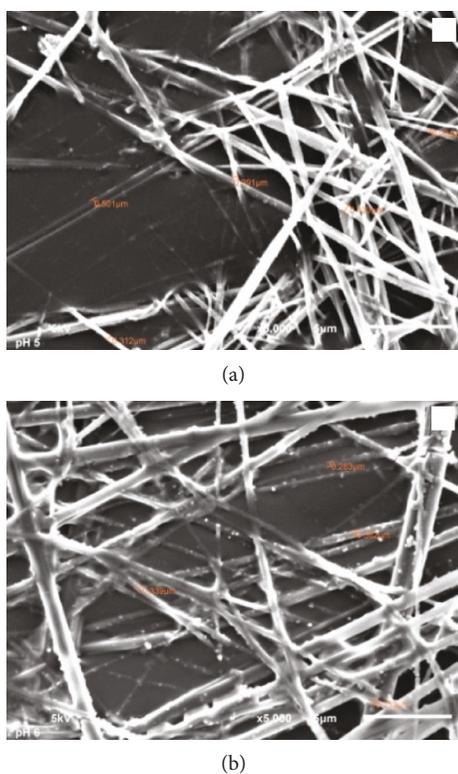


FIGURE 4: SEM images of FF-based nanotubes prepared at pH 5 (a) and pH 6 (b).

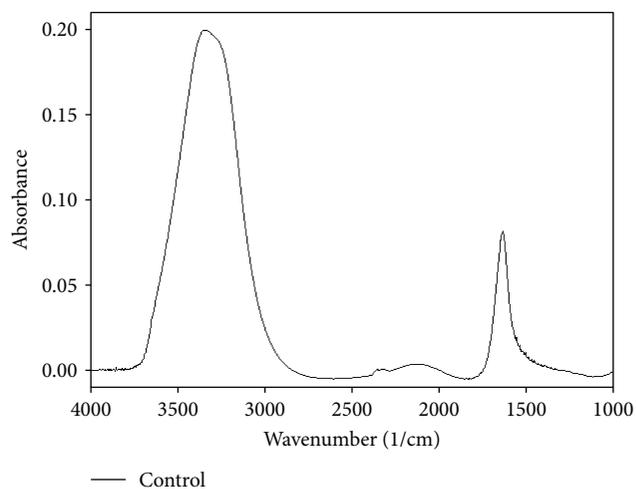


FIGURE 5: FTIR spectrum of FF nanotubes in pure water for the control sample.

N-terminus, yet few nanotubes are formed. Growth is preferentially longitudinal. Near the ip, the interaction between C- and N-termini via H bond is maximized and nanotubes abound, forming intricate networks perceived as gels. In basic solutions, the complete neutralization of the N-terminus critically inhibits the interaction via H bond with the neighbour C-terminus.

Figure 4 depicts SEM images of FF-based nanostructures at pH values of 5 and 6, embracing the ip of FF (pH = 5.68

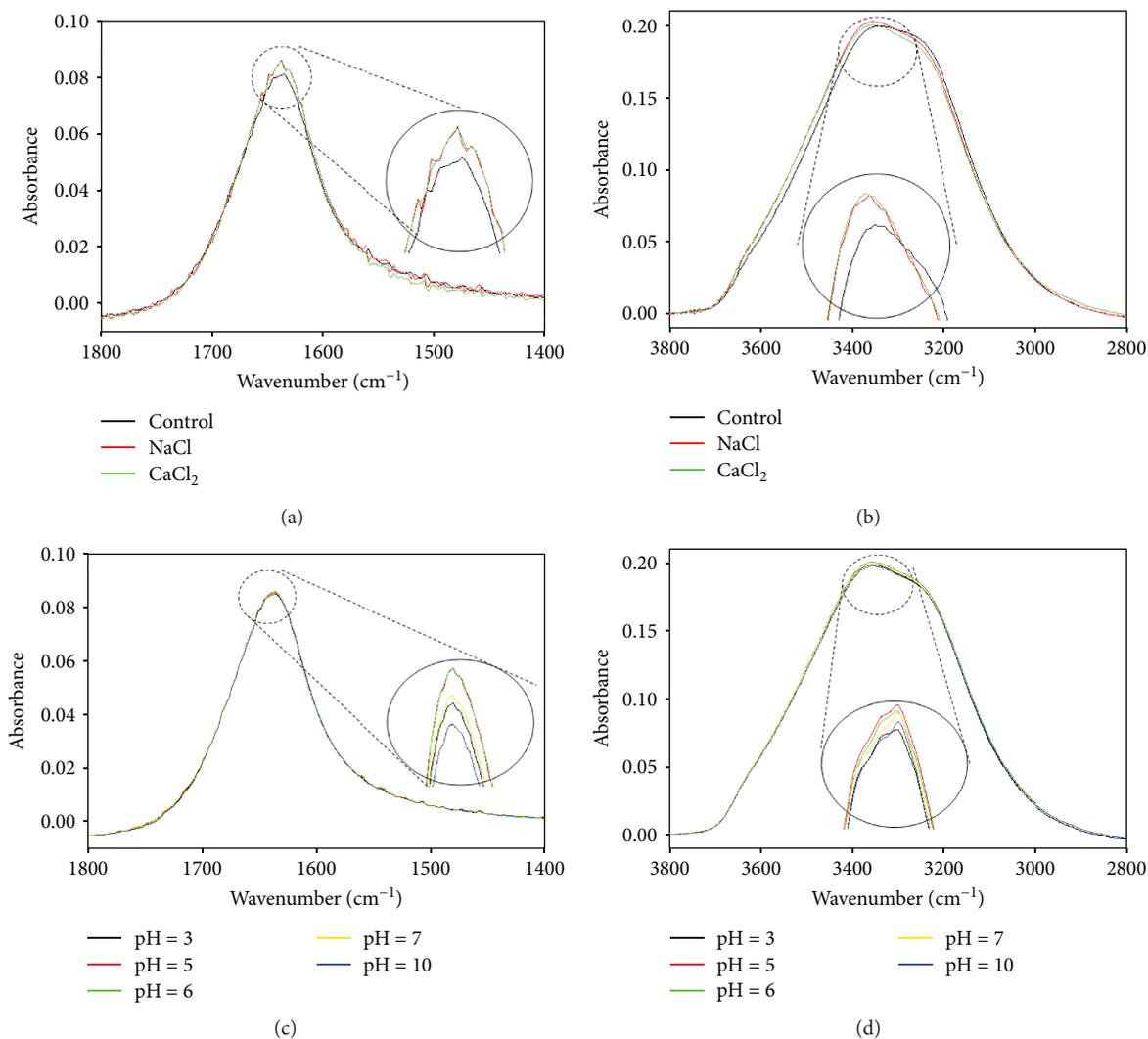


FIGURE 6: FTIR spectra of FF nanotubes in 50 mM NaCl and CaCl<sub>2</sub> solutions (a, b) and in water at pH from 3 to 10 (c, d) with zooming in regions with strong IR absorbance. Regions corresponding to amides I and II (a, c) and to amides A and B (b, d).

[51]). Thick and long nanotubes with extensive branching form dense and intricate networks at both pH. Nanotubes have diameters ranging from 200 nm to 500 nm and lengths of several microns.

There are nine characteristic IR bands of peptide bonds, amides A and B and I–VII [52–54]. The two most distinctive of the protein backbone are amides I and II. The amide I band (1700–1600 cm<sup>-1</sup>) is due almost entirely to C=O stretch vibrations and the amide II band (1480–1575 cm<sup>-1</sup>) to in-plane N–H bending and C–N stretching vibrations. Other important bands correspond to amide A (3300 cm<sup>-1</sup>) and amide B (3100 cm<sup>-1</sup>), both due to N–H stretching. Figure 5 shows the IR spectrum of FF in water (control in Figure 1). Without resolution enhancement, the IR bands of amides I and II appear overlapped in a single peak in the region 1700–1500 cm<sup>-1</sup>. The spectrum also shows that bands corresponding to amides A and B also overlap in a single broad peak in the region 3500–3000 cm<sup>-1</sup>. Figures 6(a) and 6(b) show IR spectra of FF in salt solutions; it is very interesting that the characteristic bands of amides I, II, and A–B are

stronger than those in pure water. Charge screening of the C-terminus either by Na or Ca ions and N-terminus by Cl ions, respectively, increases radiation adsorption of C=O and N–H, implying a molecular geometry more prone to H bond interactions that would be consistent with the larger size of the nanotubes in the presence of these salts. Figures 6(c) and 6(d) show IR spectra of FF in water at different pH. It is significant that the radiation adsorption of both C=O and N–H is the highest at a pH close to the ip of FF, meaning that they are better disposed to H bond interaction, thus benefiting nanotube growth.

#### 4. Conclusions

The presence of salts of the kind NaCl and CaCl<sub>2</sub> contributes to the self-assembly of FF nanotubes in water. Salt bridges between C-termini and between N-termini, mediated, respectively, by cations and anions, appear as alternatives to peptide bonds, the preferred bond in pure water, thus favoring radial and longitudinal nanotube growth. The reinforced

structure of water by structure-maker cations restricts the mobility of FF monomers, and thus salt bridges of the type tail-cation-tail and head-anion-head save the energy required for some configurations to align head and tail groups to form head-tail peptide bonds.

## Data Availability

Data is stored in a cloud, if required, they are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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