

# Raman study of structural transformations in self-assembled diphenylalanine nanotubes at elevated temperatures

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Self-assembled peptide diphenylalanine (NH<sub>2</sub>-Phe-Phe-COOH, FF) is one of the most important emergent functional materials, demonstrating wide range of fascinating physical and chemical properties including biocompatibility, chemical variability, exceptional rigidity, outstanding piezoelectric, pyroelectric and ferroelectric responses. Up to now, the phase transitions in FF nanotubes were investigated by scanning and transmission electron microscopy, atomic force microscopy, differential scanning calorimetry, thermogravimetry and mass spectroscopy. The Raman spectroscopy was implemented at room temperature only, and the microscopic details of these transitions remained unknown. In this work, the structural transformations in FF nanotubes at elevated temperatures (up to tubes destruction at 160 °C) were studied by Raman spectroscopy. Two structural transformations were observed in this region: hexagonal to orthorhombic transition at about 100 °C and the cyclization of FF molecules at about 150 °C. For the first time, these transformations were considered in the context of reconstruction of the water subsystem in the nanotubes, thus demonstrating the strong relation between the peptide tube and the state of the water inside. Using an effective frequency of nanotubes' lattice vibrations, we found that many effects observed earlier by other methods are induced by the variation of the water subsystem. The analysis of certain lines in the middle part of the Raman spectrum allowed us to describe the microscopic details of FF molecule cyclization. These results improve the understanding of the role of water in the origin of outstanding properties of FF nanotubes and thus promote developing new functional devices on their basis. Copyright © 2017 John Wiley & Sons, Ltd.

**Keywords:** peptide nanotubes; diphenylalanine; phase transition; cyclization; water

## Introduction

Self-assembled short dipeptides are recognized as important building blocks in a novel generation of 'smart' nanomaterials combining biocompatibility, chemical variability, and outstanding physical properties.<sup>[1–3]</sup> Diversity of noncovalent intermolecular interactions<sup>[4]</sup> realized by the peptides allows them to assemble micro- and nanostructures of various morphologies: vesicles, micelles, monolayers, bilayers, fibers, tubes, ribbons and tapes,<sup>[5]</sup> thus expanding their possible applications in biocompatible micromechanical systems<sup>[6,7]</sup> as well as in biosensors and biochips.<sup>[8–11]</sup>

One of the most studied aromatic dipeptide is diphenylalanine (NH<sub>2</sub>-Phe-Phe-COOH, FF). Growth and morphology of FF nanostructures have been rigorously studied as a function of external conditions.<sup>[12,13]</sup> Nanotubes of FF demonstrate exceptionally high rigidity,<sup>[14]</sup> piezoelectric properties comparable with those of lithium niobate,<sup>[6,15]</sup> notable pyroelectric effect<sup>[6]</sup> and ferroelectric-like properties with high enough transition temperature.<sup>[17,18]</sup> Such tubes were used for fabrication of high-quality prototypes of biocompatible microresonators.<sup>[7,12]</sup>

Recently, the temperature transition from the polar to non-polar phase in FF nanotubes was detected.<sup>[19]</sup> An irreversible loss of piezoelectric response and second harmonic generation occurred at about 150 °C have been attributed to the phase transition from hexagonal P6<sub>1</sub> group to orthorhombic Pbc<sub>a</sub><sup>[19]</sup> and irreversible FF

cyclization.<sup>[20]</sup> Up to now, the phase transitions in FF nanotubes were investigated by scanning and transmission electron microscopy,<sup>[21,22]</sup> atomic force microscopy,<sup>[22]</sup> differential scanning calorimetry,<sup>[23]</sup> thermogravimetry,<sup>[22,23]</sup> mass spectroscopy<sup>[20,23]</sup> etc. However, the details of these transformations at the microscopic level can be revealed by the Raman spectroscopy, which is a powerful supplementary tool for indirect studying the structure and the conformation of molecular species,<sup>[24,25]</sup> and which was implemented before at room temperature only.<sup>[26–28]</sup> Recently, different behavior of several Raman lines at elevated temperatures was demonstrated,<sup>[29]</sup> but the details of the phase transformations were not discussed.<sup>†</sup>

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It is known that at ambient conditions the structure of FF nanotubes grown from aqueous solution includes water molecules localized in the hydrophilic nanochannels of about 1 nm in diameter.<sup>[30–35]</sup> This water plays a crucial role in the nanotube formation<sup>[36–38]</sup> and determines their structure,<sup>[39,40]</sup> electrical,<sup>[39]</sup> optical<sup>[33]</sup> and mechanical properties.<sup>[41]</sup> Therefore, the role of the water in the structural transformations in nanotubes cannot be overestimated. Unfortunately, up to now, these phase transitions were not associated with the water state.

In this work, we studied structural transformations in FF nanotubes by Raman spectroscopy in a temperature range from 25 up to 160 °C. We analyzed both low-frequency lattice vibrations and water content in the nanotubes and demonstrated that observed phase transitions are related to the reconstruction of the water subsystem and the cyclization of FF molecules. Analysis of specific lines in the middle part of the Raman spectrum allowed us to describe the microscopic details of FF molecules cyclization.

## Experimental details

FF microtubes were grown from the solution of FF powder (Bachem, Switzerland) in 1,1,1,3,3,3-hexafluoro-2-propanol (Sigma-Aldrich) at a concentration of 100 g/l. Then, 2  $\mu$ l of the obtained solution was put on acetone cleaned Pt/SiO/Si substrate, and 98  $\mu$ l of deionized water was immediately added in order to make the final concentration of FF equal to 2 g/l. The droplet was naturally dried at ambient conditions in open air (temperature is about 25 °C, relative humidity is about 50%), and finally sufficiently long microtubes were obtained.<sup>[12]</sup>

Raman spectra were measured by confocal Raman microscope Alpha 300AR (WiTec, GmbH, Germany). Excitation of Raman scattering has been performed by He–Ne laser with wavelength 632.8 nm and maximum power 35 mW. Scattered light was collected by 10 $\times$  objective (NA = 0.2) in backscattering geometry. The diffraction grating with 600 lines per mm provided the spectral resolution of about 1.9  $\text{cm}^{-1}$ . The spectrum has been detected by CCD camera with 1600  $\times$  200 pixels. Multimode optical fiber with diameter 50  $\mu$ m has been used as a confocal pinhole.

The sample was placed into hermetically closed thermal stage THMS600 (Linkam, UK) mounted onto the sample holder of the

microscope. No special ventilation of the stage was performed. Raman spectra have been measured in the temperature range from 25 to 160 °C with the cooling rate 10 °C/min. In order to reduce the temperature gradient in the nanotubes, the spectra were measured 10 min after the reaching the required temperature. The acquisition time for all the measurements was 10 s.

## Results and discussion

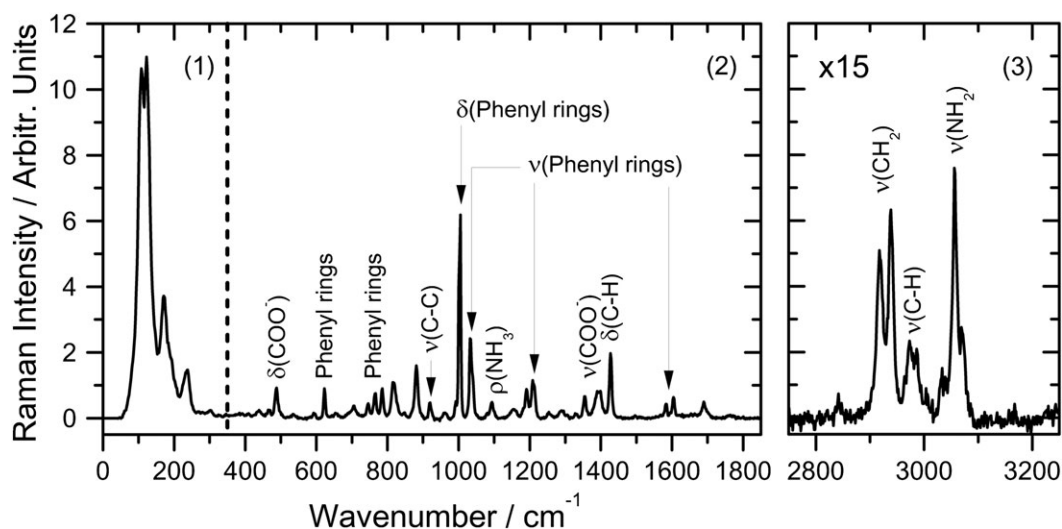
Typical Raman spectrum of FF microtubes consists of three main regions (Fig. 1). The low-wavenumber region propagates from 10 to 375  $\text{cm}^{-1}$  and corresponds to lattice vibrations of the tubes. Regions 2 (from 375 to 1850  $\text{cm}^{-1}$ ) and 3 (from 2750 to 3250  $\text{cm}^{-1}$ ) are due to vibrations of the molecular functional groups. Heating of FF tubes leads to changes in all three regions of the spectrum. In this work, we consider the temperature effects in low- and middle-wavenumber regions only. The assignment of middle- and high-wavenumber spectral lines (Fig. 1) can be based on the analysis of the published data,<sup>[42]</sup> whereas the assignment of several low-wavenumber lines<sup>[35,43]</sup> provides little information about the tube structure.

Raman spectra measured at different temperatures are presented in Fig. 2. At temperatures above 105 °C, a profound modification of the spectra takes place. Up to this temperature no essential changes can be observed; therefore, the structure of the tubes and FF molecules remains more or less the same.

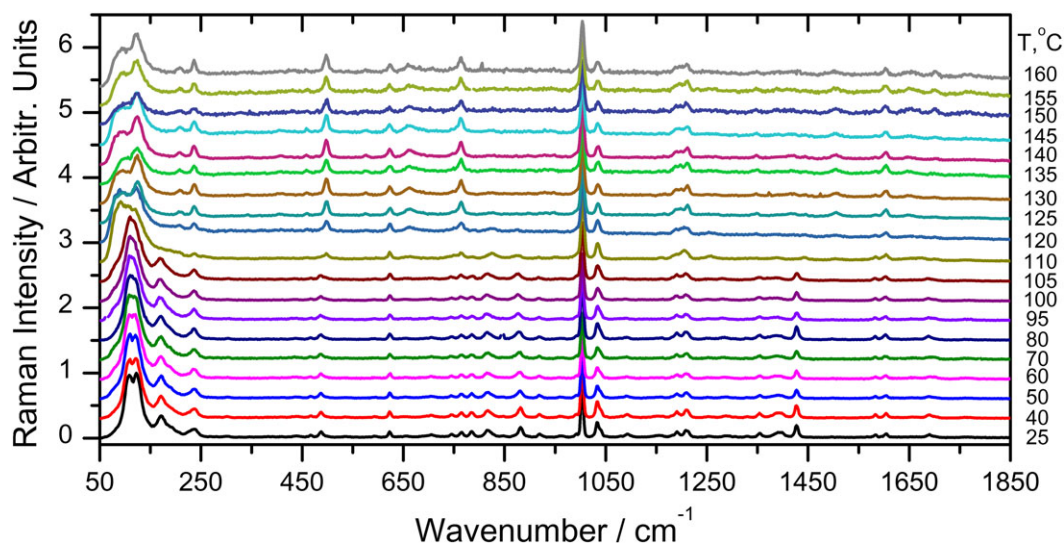
Noticeable variations of relative intensities of several lines in the middle-wavenumber region occur above 105 °C. This indicates the reconstruction of the tubes' crystal structure and changes in the form of the molecules or in their surroundings. Below, we present a detailed study of these effects.

### Analysis of lattice vibrations

Low-wavenumber Raman lines correspond to different vibrations of the tube's crystal lattice. Variation of this part of the spectrum during the heating is presented in Fig. 2 (for more details see Fig. S1). The detailed analysis of this region is hampered by the complicated tube's structure and overlapping spectral lines. Even the deconvolution of this region into separate lines provides little



**Figure 1.** Characteristic regions in the Raman spectrum of FF nanotube: (1) lattice vibrations, (2) and (3) vibrations of functional groups.

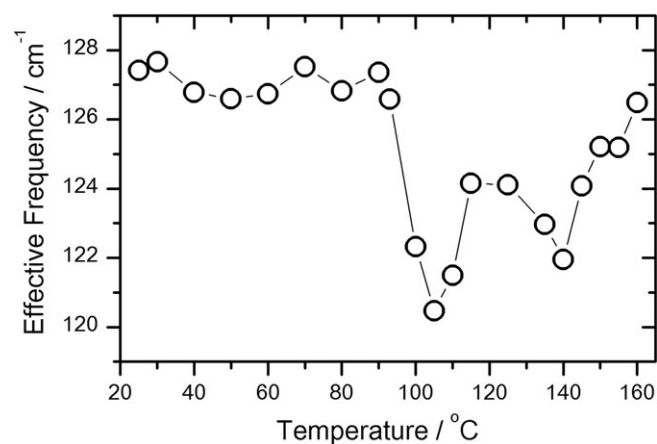


**Figure 2.** Raman spectra of FF nanotubes measured at different temperatures.

information about the tube's structure, in spite of the partial lines assignment was performed recently.<sup>[35,43]</sup>

Nevertheless, a lot of important information about the crystal structure and its behavior can be obtained from this region using an integrated approach based on the calculation of the effective frequency of the nanotubes' lattice vibrations.<sup>[41]</sup> Such frequency allows characterizing structural modifications and phase transitions in the tubes under the action of external forces. The accuracy of the calculation is comparable with that of classical first-principles calculations of phonons' frequencies in the solid state.<sup>[44]</sup> The details of the calculation are discussed in Ref. [41] and in Supporting Information.

Temperature dependence of the effective frequency calculated in the spectral range 50–375  $\text{cm}^{-1}$  demonstrates two pronounced features at  $T = 105$  and  $140$  °C (Fig. 3). The stability of the tube's structure at low temperatures (below 100 °C) is confirmed by the constant effective frequency. Abrupt decrease at 100–105 °C indicates a structural reconstruction and reorganization of the hydrogen bonds network between FF molecules and water. Further increasing of the effective frequency can be related to the stabilization of the new crystal structure.



**Figure 3.** Variation of the effective frequency of FF tubes lattice vibrations at elevated temperatures.

The temperature of the second dip in effective frequency, at 140 °C, is very close to that of cyclization of FF molecules.<sup>[20,23]</sup> The cyclization is accompanied by an extraction of a water molecule and formation of an additional cycle (2,5-diketopiperazine group) in FF molecule (Fig. 4).<sup>[20]</sup> At temperatures above 160 °C, the destruction of the tube started, and no Raman spectra could be recorded.

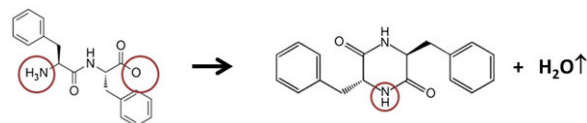
For better understanding the origin of the observed structural transformations in FF tubes under the heating, the analysis of middle-wavenumber range in Raman spectra was performed.

#### Analysis of water subsystem

The structure and the properties of FF nanotubes are strongly dependent on the state of the water subsystem.<sup>[39]</sup> Water molecules are weakly bound with peptides and can move along the nanochannel.<sup>[45–48]</sup> This movement can be initialized by sufficiently low external electric fields,<sup>[49]</sup> hydrostatic pressure,<sup>[48]</sup> light illumination<sup>[35]</sup> and changes of relative humidity.<sup>[50]</sup> Therefore, special attention in this work was directed to the variations of the water subsystem during the heating.

Raman line in the range of 1030–1040  $\text{cm}^{-1}$  corresponds to in-plane stretching–shrinking oscillations of the phenyl rings and its splitting is related to water molecules in the nanotubes.<sup>[34]</sup> In the case of empty nanotubes, the two components of this line have the same position, whereas increasing of the number of water molecules in the nanochannel increases the distance between them.<sup>[34]</sup> Therefore, this effect can be used for determination of the water content in the nanotubes at different temperatures.

It was found that at low temperatures the line consists of two components, whereas at higher temperatures it becomes one-component (Fig. S2a,b). Both components were fitted by Lorentzian curves, and their positions were plotted versus the



**Figure 4.** Scheme of the cyclization of FF molecule. Red circles denote the functional groups involved into the process.

temperature (Fig. S2c). At temperatures above 110 °C, the position of both components became equal.

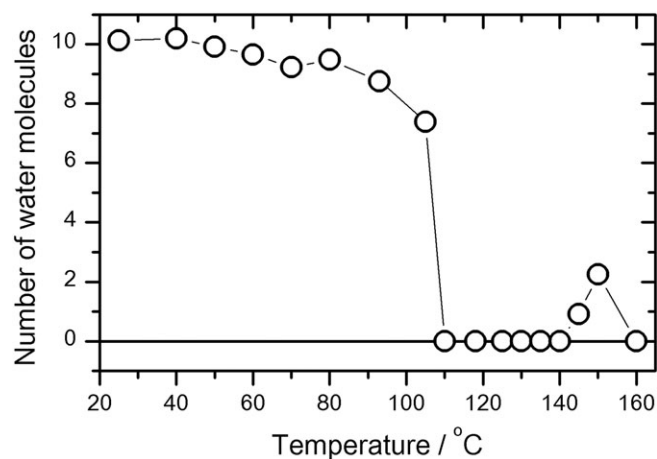
It is worth noting an additional line splitting observed at about 150 °C (Fig. S2c). The corresponding shape of the line is presented in Fig. S2b, and this confirms the effect, which is discussed in details below.

Using the data obtained in Ref. [34] and measured positions of the components of the line at 1030–1040  $\text{cm}^{-1}$ , the number of water molecules in a ring of the nanotube at different temperatures was calculated (Fig. 5). It is worth noting that the obtained number of molecules should be considered as an effective number, because the used method is only suitable for those water molecules, which directly interact with FF molecule. At the same time, additional water molecules can exist in the tubes' nanochannels, which are indirectly coupled to FF molecules and thus cannot be detected by this method.<sup>[40,46]</sup> Nevertheless, this method provides important information about the state of the water subsystem.

The number of water molecules in the ring gradually decreases with heating starting at about 50 °C and then abruptly goes to zero at about 110 °C, thus demonstrating fast water evaporation. This is in line with the simultaneous measurements by differential scanning calorimetry and mass spectrometry.<sup>[23]</sup> It is known that the symmetry of the nanotube changes from hexagonal to orthorhombic when water is completely removed from the nanochannel.<sup>[40]</sup> Such transition accompanied by the disappearance of piezoelectric and nonlinear optical properties in FF nanotubes was confirmed by X-ray powder diffraction.<sup>[19]</sup> Thus, the first jump of the effective frequency observed at 105 °C (Fig. 3) corresponds to hexagonal to orthorhombic phase transition.

At the temperature of about 150 °C, the number of water molecules unexpectedly increases (Fig. 5). This effect can be related to the cyclization of FF molecules. As it was shown above, the cyclization of FF molecule is accompanied by extracting the water molecule. These molecules can be extracted into the nanochannel or into the intertubes' space, but in any case their interaction with FF molecules should lead to the splitting of the line at 1030–1040  $\text{cm}^{-1}$ .

It was shown that X-ray diffraction pattern of FF nanotubes heated above 150 °C coincides with that of the structures made from the cyclic-FF dipeptides.<sup>[20]</sup> Therefore, no symmetry changes occur at 150 °C, and the nanotube remains in the orthorhombic phase. Thus, the jump of the effective frequency at 140 °C (Fig. 3) can be related to the beginning of the cyclization and formation



**Figure 5.** Temperature dependence of the number of water molecules in FF ring.

of 2,5-diketopiperazine group. This process can be directly observed in Raman spectra.

### Cyclization of FF

As follows from Fig. 4, two main functional groups of FF molecules are involved in the cyclization process: carboxyl group ( $\text{COO}^-$ ) and ammonium group ( $\text{NH}_3^+$ ). The carboxyl group possesses two lines in the spectrum corresponding to stretching (1390  $\text{cm}^{-1}$ ) and bending (535  $\text{cm}^{-1}$ ) vibrations. Both lines completely disappear at about 150 °C (Fig. S3a,b), whereas the spectral line, previously absent in the spectra, appears at 1655  $\text{cm}^{-1}$ , that corresponds to stretching vibrations of the carbonyl group ( $\text{C}=\text{O}$ ) (Fig. S3c).

The ammonium group is represented in the spectrum by a line at 1094  $\text{cm}^{-1}$  corresponding to rocking vibrations, which disappears at about 150 °C (Fig. S3d). This process is accompanied by an appearance of two lines at 1134  $\text{cm}^{-1}$  and 1505  $\text{cm}^{-1}$  corresponding to rocking vibration of N—H group and a superposition of bending vibrations of N—H and stretching vibrations of C—N groups (Amide II line), respectively (Fig. S3e,f).

All the described effects in the Raman spectra are in line with the cyclization process described above. The disappearance of the carboxyl group is a result of the oxygen atom detaching, so that the carbonyl group forms. Simultaneously, ammonium group loses two hydrogen atoms thus leading to the formation of N—H group involved into several vibrations. Formation of new functional groups, in particular 2,5-diketopiperazine group, leads to re-orientation of the cycled FF molecules and thus to variations in effective frequency of lattice vibrations, while the general symmetry of the tube remains the same.

### Conclusions

Structural transformations in FF nanotubes were studied by Raman spectroscopy in a temperature range from 25 up to 160 °C. For the first time, these transformations were considered in the context of reconstruction of the water subsystem in the nanotubes. We demonstrated that the effective frequency implemented for analysis of tubes' lattice vibrations is sensitive to the structural transformations of the nanotubes and to the cyclization of FF molecules. Joint analysis of the temperature dependence of the effective frequency and water content in the nanotubes allowed us to reveal the hexagonal to orthorhombic phase transition at about 105 °C and to describe in details the process of FF molecules cyclization at about 150 °C. These results improve the understanding of the role of water in the origin of outstanding properties of FF nanotubes and thus promote developing new functional devices on their basis.

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## References

- [1] L. Adler-Abramovich, E. Gazit, *Chem. Soc. Rev.* **2014**, *43*, 6881.
- [2] M. B. Avinash, T. Govindaraju, *Nanoscale* **2014**, *6*, 13348.
- [3] U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Nat. Mater.* **2014**, *14*, 23.
- [4] S. Cavalli, F. Albericio, A. Kros, *Chem. Soc. Rev.* **2010**, *39*, 241.
- [5] E. Kokkoli, A. Mardilovich, A. Wedekind, E. L. Rexeisen, A. Garg, J. A. Craig, *Soft Matter* **2006**, *2*, 1015.
- [6] A. Kholkin, N. Amdursky, I. Bdikin, E. Gazit, G. Rosenman, *ACS Nano* **2010**, *4*, 610.
- [7] E. D. Bosne, A. Heredia, S. Kopyl, D. V. Karpinsky, A. G. Pinto, A. L. Kholkin, *Appl. Phys. Lett.* **2013**, *102*, 73504.
- [8] A. B. Seabra, N. Durán, *Peptides* **2013**, *39*, 47.
- [9] R. de la Rica, C. Pejoux, C. Fernandez-Sanchez, A. Baldi, H. Matsui, *Small* **2010**, *6*, 1092.
- [10] J. Yuan, J. Chena, X. Wua, K. Fanga, L. Niub, *J. Electroanal. Chem.* **2011**, *656*, 120.
- [11] M. Yemini, M. Reches, E. Gazit, J. Rishpon, *Anal. Chem.* **2005**, *77*, 5155.
- [12] A. Nuraeva, S. Vasilev, D. Vasileva, P. Zelenovskiy, D. Chezganov, A. Esin, S. Kopyl, K. Romanyuk, V. Y. Shur, A. L. Kholkin, *Cryst. Growth Des.* **2016**, *16*, 1472.
- [13] H. Nezammahalleh, G. Amoabediny, *Fluid Phase Equilib.* **2013**, *347*, 28.
- [14] I. Azuri, L. Adler-Abramovich, E. Gazit, O. Hod, L. Kronik, *J. Am. Chem. Soc.* **2014**, *136*, 963.
- [15] S. Vasilev, P. Zelenovskiy, D. Vasileva, A. Nuraeva, V. Y. Shur, A. L. Kholkin, *J. Phys. Chem. Solid* **2016**, *93*, 68.
- [16] A. Esin, I. Baturin, T. Nikitin, S. Vasilev, F. Salehli, V. Y. Shur, A. L. Kholkin, *Appl. Phys. Lett.* **2016**, *109*, 142902.
- [17] I. Bdikin, V. Bystrov, I. Delgadillo, J. Gracio, S. Kopyl, M. Wojtas, E. Mishina, A. Sigov, A. L. Kholkin, *J. Appl. Phys.* **2012**, *111*, 74104.
- [18] I. Bdikin, V. Bystrov, S. Kopyl, R. P. G. Lopes, I. Delgadillo, J. Gracio, E. Mishina, A. Sigov, A. L. Kholkin, *Appl. Phys. Lett.* **2012**, *100*, 43702.
- [19] A. Heredia, I. Bdikin, S. Kopyl, E. Mishina, S. Semin, A. Sigov, K. German, V. Bystrov, J. Gracio, A. L. Kholkin, *J. Phys. D Appl. Phys.* **2010**, *43*, 462001.
- [20] N. Amdursky, P. Beker, I. Koren, B. Bank-Srouer, E. Mishina, S. Semin, T. Rasing, Y. Rosenberg, Z. Barkay, E. Gazit, G. Rosenman, *Biomacromolecules* **2011**, *12*, 1349.
- [21] A. Handelman, P. Beker, E. Mishina, S. Semin, N. Amdursky, G. Rosenman, *Ferroelectrics* **2012**, *430*, 84.
- [22] L. Adler-Abramovich, M. Reches, V. L. Sedman, S. Allen, S. J. B. Tendler, E. Gazit, *Langmuir* **2006**, *22*, 1313.
- [23] M. A. Ziganshin, A. V. Gerasimov, S. A. Ziganshina, N. S. Gubina, G. R. Abdullina, A. E. Klimovitskii, V. V. Gorbachuk, A. A. Bukharaev, *J. Therm. Anal. Calorim.* **2016**, *125*, 905.
- [24] K. J. R. da Silva, W. Paschoal Jr., E. A. Belo, S. G. C. Moreira, *J. Phys. Chem. A* **2015**, *119*, 9778.
- [25] E. A. Kapustin, V. S. Minkov, J. Stare, E. V. Boldyreva, *Cryst. Growth Des.* **2014**, *14*, 1851.
- [26] V. Sereda, N. M. Ralbovsky, M. C. Vasudev, R. R. Naik, I. K. Lednev, *J. Raman Spectrosc.* **2016**, *47*, 1056.
- [27] B. Lekprasert, V. Korolkov, A. Falamas, V. Chis, C. J. Roberts, S. J. B. Tendler, I. Notingham, *Biomacromolecules* **2012**, *13*, 2181.
- [28] B. Lekprasert, V. Sedman, C. J. Roberts, S. J. B. Tendler, I. Notingham, *Opt. Lett.* **2010**, *35*, 4193.
- [29] A. Handelman, S. Lavrov, A. Kudryavtsev, A. Khatchatourians, Y. Rosenberg, E. Mishina, G. Rosenman, *Adv. Opt. Mater.* **2013**, *1*, 875.<sup>‡</sup>
- [30] J. Kim, T. H. Han, Y.-I. Kim, J. S. Park, J. Choi, D. G. Churchill, S. O. Kim, H. Ihee, *Adv. Mater.* **2010**, *22*, 583.
- [31] N. Kol, L. Adler-Abramovich, D. Barlam, R. Z. Shneck, E. Gazit, I. Rousso, *Nano Lett.* **2005**, *5*, 1343.
- [32] J. F. Smith, T. P. J. Knowles, C. M. Dobson, C. E. MacPhee, M. E. Welland, *Proc. Natl. Acad. Sci.* **2006**, *103*, 15806.
- [33] M. Wang, S. Xiong, X. Wu, P. K. Chu, *Small* **2011**, *7*, 2801.
- [34] X. Wu, S. Xiong, M. Wang, J. Shen, P. K. Chu, *J. Phys. Chem. C* **2012**, *116*, 9793.
- [35] X. Wu, S. Xiong, M. Wang, J. Shen, P. K. Chu, *Opt. Express* **2012**, *20*, 5119.
- [36] P. S. Zelenovskiy, V. Y. Shur, A. S. Nuraeva, S. G. Vasilev, D. S. Vasileva, D. O. Alikin, D. S. Chezganov, V. P. Krasnov, A. L. Kholkin, *Ferroelectrics* **2015**, *475*, 127.
- [37] M. I. Souza, E. R. Silva, Y. M. Jaques, F. F. Ferreira, E. E. Fileti, W. A. Alves, *J. Pept. Sci.* **2014**, *20*, 554.
- [38] T. D. Do, M. T. Bowers, *Anal. Chem.* **2015**, *87*, 4245.
- [39] T. Andrade-Filho, F. F. Ferreira, W. A. Alves, A. R. Rocha, *Phys. Chem. Chem. Phys.* **2013**, *15*, 7555.
- [40] T. Andrade-Filho, T. C. Martins, F. F. Ferreira, W. A. Alves, A. R. Rocha, *Theor. Chem. Acc.* **2016**, *135*, 185.
- [41] P. Zelenovskiy, I. Kornev, S. Vasilev, A. Kholkin, *Phys. Chem. Chem. Phys.* **2016**, *18*, 29681.
- [42] B. Hernández, F. Pflüger, S. G. Kruglik, M. Ghomi, *J. Raman Spectrosc.* **2013**, *44*, 827.
- [43] P. M. G. L. Ferreira, M. S. Ishikawa, S. Kogikoski, W. A. Alves, H. Martinho, *Phys. Chem. Chem. Phys.* **2015**, *17*, 32126.
- [44] R. O. Jones, O. Gunnarsson, *Rev. Mod. Phys.* **1989**, *61*, 689.
- [45] M. Engels, D. Bashford, M. R. Ghadiri, *J. Am. Chem. Soc.* **1995**, *117*, 9151.
- [46] C. H. Görbitz, *Chem. A Eur. J.* **2001**, *7*, 5153.
- [47] J. Comer, F. Dehez, W. Cai, C. Chipot, *J. Phys. Chem. C* **2013**, *117*, 26797.
- [48] L. Ruiz, Y. Wu, S. Keten, *Nanoscale* **2015**, *7*, 121.
- [49] J. Su, H. Guo, *ACS Nano* **2011**, *5*, 351.
- [50] S. K. Nune, D. B. Lao, D. J. Heldebrant, J. Liu, M. J. Olszta, R. K. Kukkadapu, L. M. Gordon, M. I. Nandasiri, G. Whyatt, C. Clayton, D. W. Gotthold, M. H. Engelhard, H. T. Schaefer, *Nat. Nanotechnol.* **2016**, *11*, 791.

## Supporting information

Additional Supporting Information may be found online in the supporting information tab for this article.

<sup>‡</sup>Correction added on 20 February 2017, after first online publication: due to the addition of reference [29], the numbering of references [29] to [50] has changed.