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Letter

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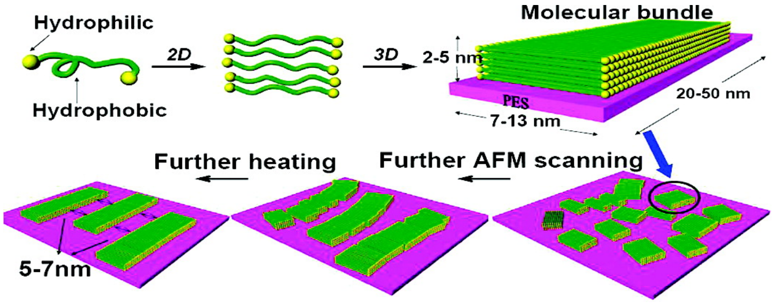

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Formation of Hierarchical Molecular Assemblies from Poly(oxypropylene)-Segmented Amido Acids under AFM Tapping

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Molecular self-aligning of amphiphilic molecules into bundles with a constant width of 7−13 nm was observed under tapping-mode atomic force microscopy (TM-AFM). The requisite amphiphile, a poly(oxypropylene)-trimellitic amido acid sodium salt, is constituted of a symmetric amido acid structure with potential noncovalent forces of ionic charges, hydrogen bonds, $\pi-\pi$ aromatic stacking, and hydrophobic interactions for intermolecular interaction. The amphiphiles are able to self-align into orderly hierarchical assemblies after simply being dissolved in water and dried under spin-coated evaporation. Under the TM-AFM tapping process, the bundles increased their length from an initial 20 to 600 nm. A sequential TM-AFM scanning and interval heating process was designed to probe the morphological transformations from the molecular bundles to lengthy strips (nearly micrometer scale) and to columns (with 5−7 nm spacing between the parallel strips). The formation of hierarchical arrays via molecular stretching, aligning, and connecting to each other was simultaneously observed and accelerated under the TM-AFM vibration energy. The molecular self-alignment caused by vibrations is envisioned to be a potential methodology for manipulating molecules into assembled templates, sensors, and optoelectronic devices.

Introduction

Recently, advances in nanotechnology have developed a number of techniques to detect and manipulate organic molecules into assembled nanostructures.[1] The molecular manipulations using scanning tunneling microscopy (STM) and atomic force microscopy (AFM) enables the observation, measurement, and manipulation of individual atoms or molecules.[2] Currently, STM may be used to extract or displace atoms from the surface, the self-assembly monolayer, or the Langmuir−Blodgett film.[3,4] Nanoscale fabrication techniques, including microcontact printing[5] and dip-pen nanolithography,[6] could produce patterned surfaces or guide molecular assemblies. However, only recently has the AFM technique been used to manipulate molecular rearrangement[7,8] and monitor crystal growth,[9] but few reports have described the oscillating tip−sample interaction energy.[10,11]

Molecular self-assembly is an important "bottom-up" method for fabricating highly ordered structures on the nanometer scale. The examples of nanostructure architectures are numerous, including colloids,[12] nanotubes,[13] nanorods,[14] nanowires,[15] and so forth. These self-assemblies may possess unique properties and may potentially be utilized in optics,[16] electronics,[17] and biosensors.[18] The formation of molecular assemblies is generally driven by weak noncovalent bonding forces. The intermolecular interaction commonly requires the molecules to have different kinds but complementary forces for the geometric arrangement.

Here, we wish to report a new way of manipulating the formation of nanoscale molecular bundles and their further morphological transformations into hierarchical arrays through molecular stretching, aligning, and aggregating under TM-AFM scanning energy.[10,11] The self-aligning molecule is amphiphilic in nature and composed of distinctly different functionalities including amides, sodium carboxylates, and a middle poly(oxypropylene) (POP) block. We prepared the requisite amphiphile by a one-step reaction of POP-diamine (2000 g/mol molecular weight) and trimellitic anhydride at a 1:2 molar ratio according to the previously reported procedures.[19] Upon exposure to the TM-AFM energy, the amphiphiles were found to have the ability to self-assemble and transform into highly ordered molecular arrays. The energy level of intermolecular noncovalent bonding interaction appears to be synchronized with the TM-AFM tapping process.

Results and Discussion

The prepared POP-segmented amido acid, structure shown in Figure 1, is amphiphilic and able to demonstrate the surface activity of lowering toluene/water interfacial tension from 22.8 to 2.5 mN/m (Supporting Information Figure S1). For performing molecular self-alignment, the sodium salt of the amphiphile was dissolved in water at dilute concentration and spin-coated on a polyethersulfone (PES) film. The hydrophobic PES was chosen in order to minimize the molecular interaction with the film substrate. The image of the molecular arrays was observed by using TM-AFM (phase and topographical images). Experimentally, the aqueous solution of the amphiphile (1.0 wt %) was

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[1] (a) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550−575. (b) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418−2421.

[2] Sheiko, S. S.; Möller, M. *Chem. Rev.* **2001**, *101*, 4099−4123.

[3] García, R.; Pérez, R. *Surf. Sci. Rep.* **2002**, *47*, 197−301.

[4] Smith, R. K.; Lewis, P. A.; Weiss, P. S. *Prog. Surf. Sci.* **2004**, *75*, 1−68.

[5] Xia, Y.; Whitesides, G. M. *Langmuir* **1997**, *13*, 2059−2076.

[6] Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661−663.

[7] Liu, G. Y.; Xu, S.; Qian, Y. *Acc. Chem. Res.* **2000**, *33*, 457−466.

[8] Wang, L.; Wang, E. *Langmuir* **2004**, *20*, 2677−2682.

[9] Liu, X.; Zhang, Yi.; Goswami, D. K.; Okasinski, J. S.; Salaita, K.; Sun, P.; Bedzyk, M. J.; Mirkin, C. A. *Science* **2005**, *307*, 1763−1766.

[10] Schmitz, I.; Schreiner, M.; Friedbacher, G.; Grasserbauer, M. *Anal. Chem.* **1997**, *69*, 1012−1018.

[11] Jalili, N.; Laxminarayana, K. *Mechatronics* **2004**, *14*, 907−945.

[12] Mezzenga, R.; Ruokolainen, J.; Fredrickson, G. H.; Kramer, E. J.; Moses, D.; Heeger, A. J.; Ikkala, O. *Science* **2003**, *299*, 1872−1874.

[13] Blau, W. J.; Fleming, A. J. *Science* **2004**, *304*, 1457−1458.

[14] Peng, G.; Qiu, F.; Ginzburg, V. V.; Jasnow, D.; Balazs, A. C. *Science* **2000**, *288*, 1802−1804.

[15] Yan, H.; Park, S. H.; Finkelstein, G.; Reif, J. H.; LaBean, T. H. *Science* **2003**, *301*, 1882−1884.

[16] Zhou, G. J.; Zhang, S.; Ye, C. *J. Phys. Chem. B* **2004**, *108*, 3985−3988.

[17] Fendler, J. H. *Chem. Mater.* **2001**, *13*, 3196−3210.

[18] Lin, V. S.-Y.; Motesharei, K.; Dancil, K.-P. S.; Sailor, M. J.; Ghadiri, M. R. *Science* **1997**, *278*, 840−843.

[19] Wang, C. H.; Tsai, W. C.; Wei, K. L.; Lin, J. J. *J. Phys. Chem. B* **2005**, *109*, 13510−13514.

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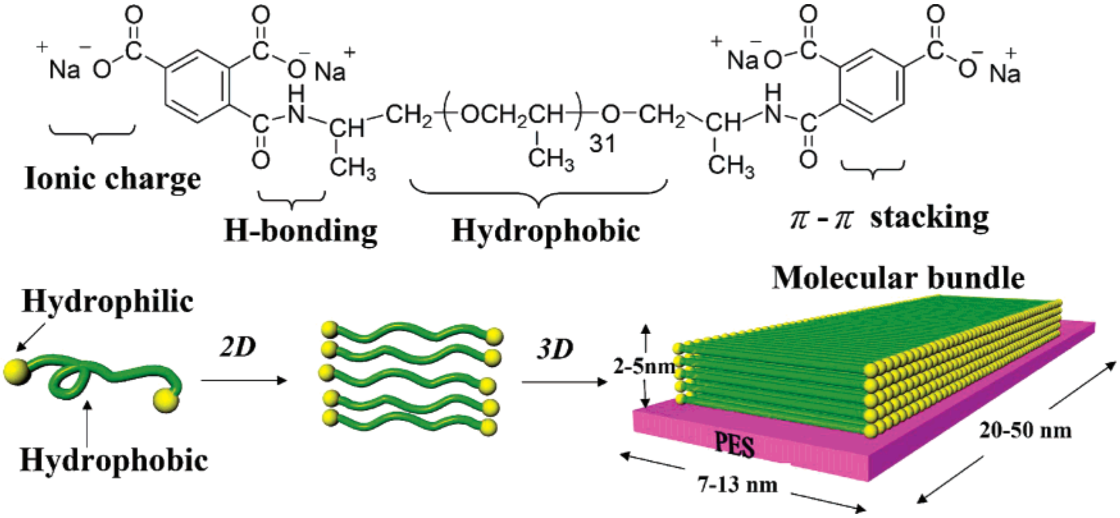

Figure 1. Chemical structure of the amphiphile and its noncovalent bonding (top) and schematic diagram (bottom) of a molecular bundle formed on PES film, through molecular stretching and intermolecular end-to-end alignment.

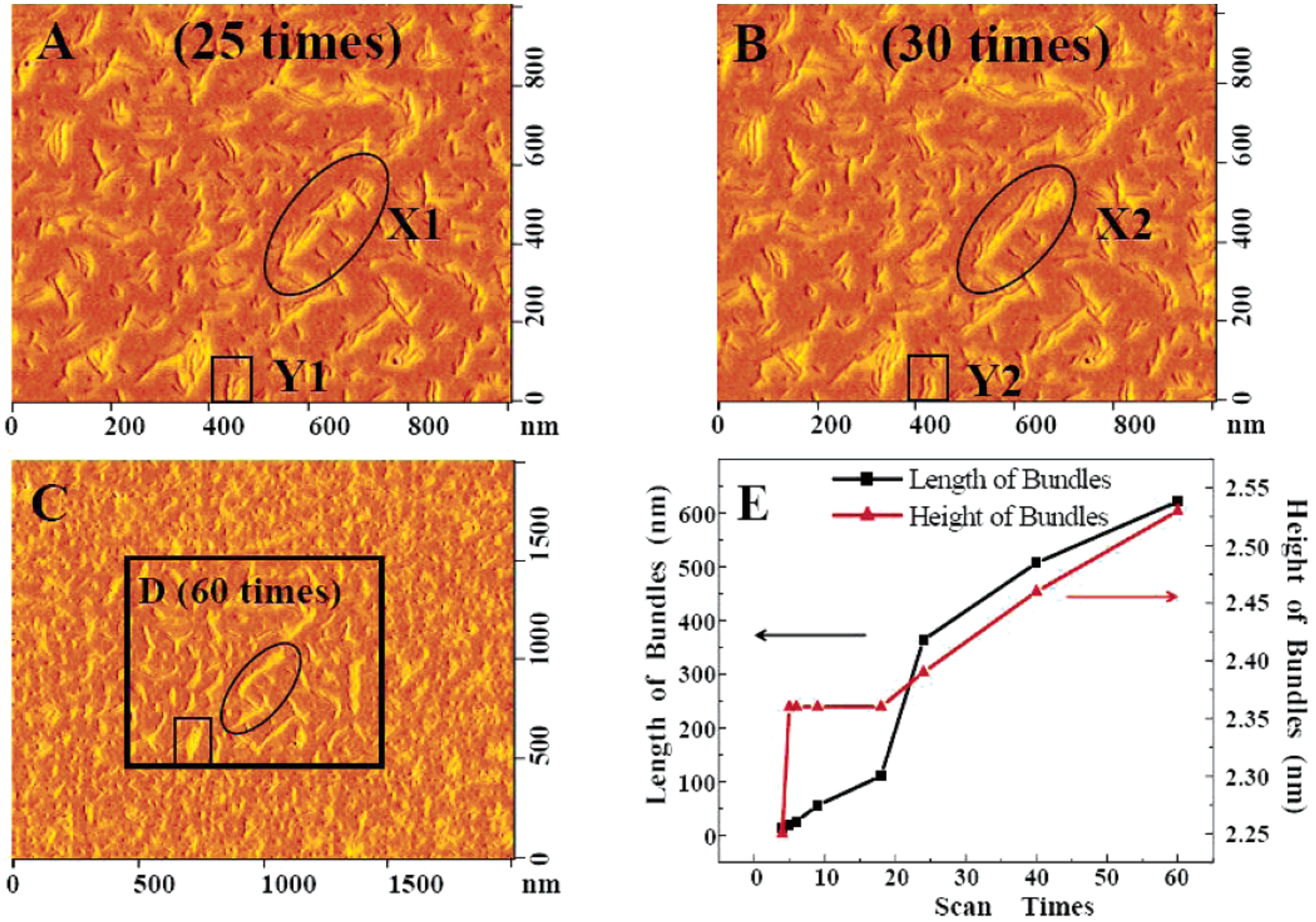

Figure 2. TM-AFM (phase images) showing the morphological changes of the molecular bundles under continuous TM-AFM tapping; (A) (25 times) vs (B) (30 times); the difference in the bundle strips lining up in length (X1 into X2 and Y1 into Y2). The difference can be further seen in (C,D), where the middle square zone represents concentrated scanning 60 times more than the outer square, and in (E), the graph summarizing the bundle height and length increases (from the circle area in D) during TM-AFM scanning.

spin-coated on a PES film, evaporated at ambient temperature, and examined by TM-AFM at 20 °C. The phase image has an orderly array of 7−13 nm in width and an initial bundle length of 20−50 nm. This molecular self-alignment into such a bundle array was first reported by us.[19] It was noticed that the bundle strips occurred only on a hydrophobic PES surface but not on glass or on a mica substrate where the hydrophilic surface may interfere with the amphiphilic molecules. It appears that the amphiphiles have a strong tendency to self-aggregate through intermolecular interactions. These molecules tend to stretch out from random coils into rodlike shapes and aggregate into bundles (Figure 1). The theoretical length of a fully stretched molecule for a POP-2000 backbone was calculated to be 10.9 nm (or 109 Å), on the basis of a 33 oxypropylene unit backbone [-OCH_2-$CH(CH_3)$-]$_{33}$ with the proper bond lengths (1.54 Å for C−C and 1.43 Å for C−O) and bond angles (109.6° and 112°, respec-

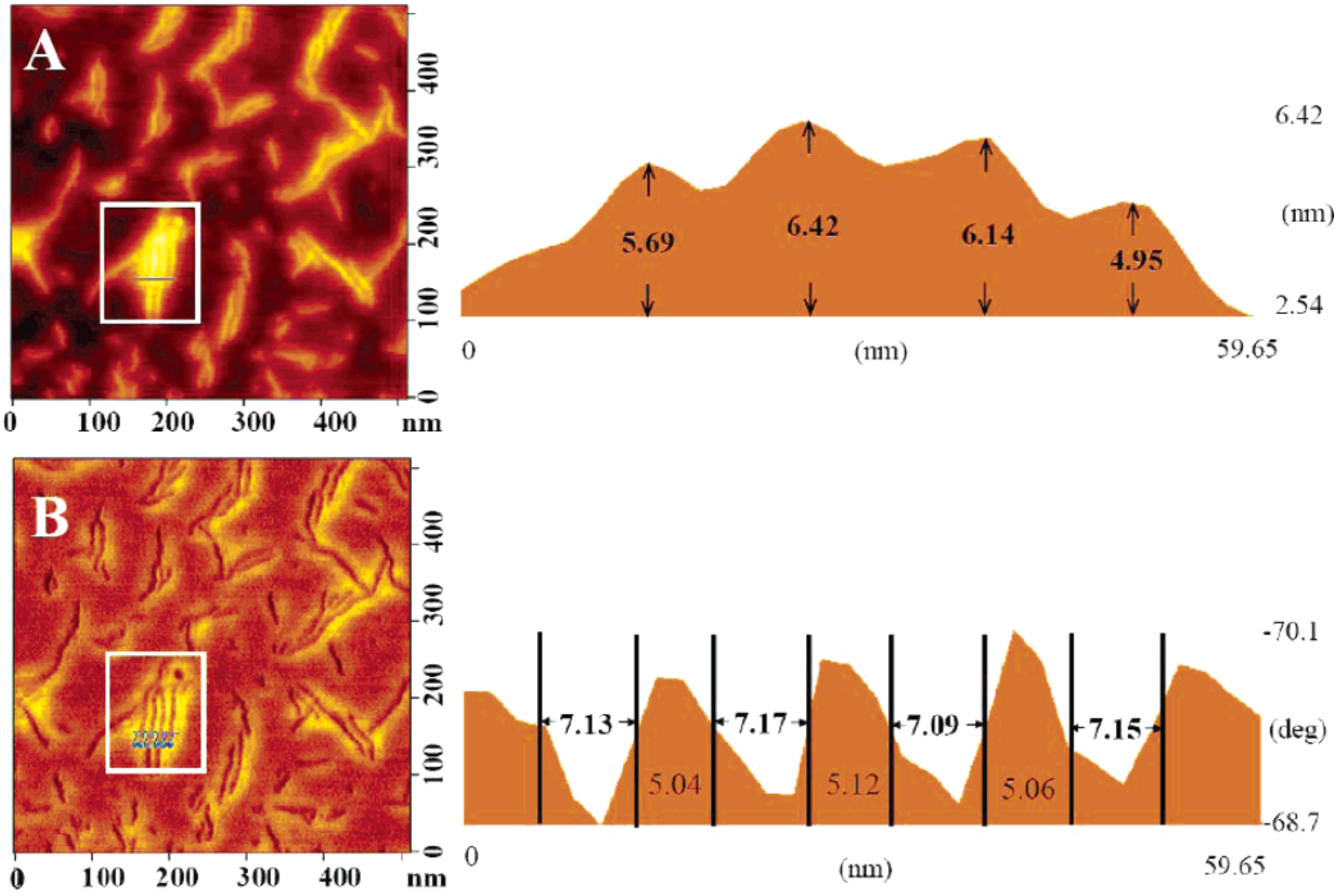

Figure 3. TM-AFM of the enlarged area in Figure 2D (or 61 times tapping): (A) topographical image with the analyses of bundle height (4.95−6.42 nm) and (B) phase image with the bundle width (7.09−7.17 nm) and spacing distance (5.04−5.12 nm) between the neighboring bundles (the measurements are from the same square area as in Figure 2D).

tively).[20] The observed bundle width in the range 7−13 nm is consistent with the calculated molecular length when fully stretched and remains constant throughout the further transformation into higher orders of hierarchical array.

During the TM-AFM examination, initially we found that the length of the bundle strips could be altered in the AFM tapping mode (TM-AFM). The normal mode of TM-AFM detection may provide the vibration energy for molecular movement, that is, molecular stretching and aligning into bundles. The added TM-AFM energy[10,11] seems to play a critical role in assisting the movement of the molecular blocks. Accordingly, we are able to design a series of experiments to investigate the phenomenon of simultaneous bundle detection and morphological shaping. Experimentally, when we repetitively scanned the same area of the AFM sample (3 min and 43 s for each scan to take one phase image), the bundle strips were observed to have increased their lengths. As exhibited in Figure 2A,B, the strips were observed to be increasing in length and connecting between the 25th and 30th scans. In order to further demonstrate the character of morphology change under the TM-AFM detection, a sample was directly compared by scanning on different areas in a sequential manner. The sample was first scanned 60 times in a small area (1 μm^2 in the central square, Figure 2D), and then one time in a larger area surrounding the center square (2 μm^2, Figure 2C). As a result, the middle square micrometer had been exposed to the tapping energy 60 times more than the outer area. The difference in bundle strip lengths is significant. During the additional 60 times scanning process, the individual bundles had lengthened (up to 600 nm) and connected from the scattered bundles in the outer area. This demonstrates that, during the scanning process, the bundles transformed into lengthy strips under the influence of the TM-AFM tapping energy.

The formation of molecular bundles and their transformation into higher orders of structure is explainable by the intermolecular interactions of different noncovalent bonding forces in a complementary manner. Shown in Figure 1 is the chemical structure of the amphiphile comprising a hydrophobic POP middle block and two symmetrical end groups of phenyl amido acid salts, which are capable of forming hydrogen bonds, aromatic $\pi-\pi$ stacks, and ionic bridges, as well as POP-backbone hydrophobic interactions. Through these intermolecular bonding forces in a symmetric manner, the energy drives the molecule coils to stretch and further align into bundles. The initially formed bundles may attract the surrounding molecules to align together and consequently grow in length on the flat PES surface. It was also noticed that the height of the molecular bundles could vary widely in different bundles (usually in the range 2−5 nm). In an area of representative bundles, the height increased gradually from an average of 2.25 to 2.55 nm (Figure 2E, graphical representation from the specified area of Figure 2D), while the strip length increased from 13 to 600 nm during the 60 repetitive scans. Another measurement of bundle height (5−6 nm) is exemplified in Figure 3A (topographical image), and bundle width (approximately 7 nm) is shown from the phase image in Figure 3B. Furthermore, it is noticed that the bundles grow into a pattern of parallel strips which maintain a spacing distance of 5−7 nm, also shown in Figure 3 phase images. The constant spacing between the parallel strips implies the presence of a

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[20] Lin, J. J.; Cheng, I. J.; Wang, R.; Lee, R. J. *Macromolecules* **2001**, *34*, 8832−8834.

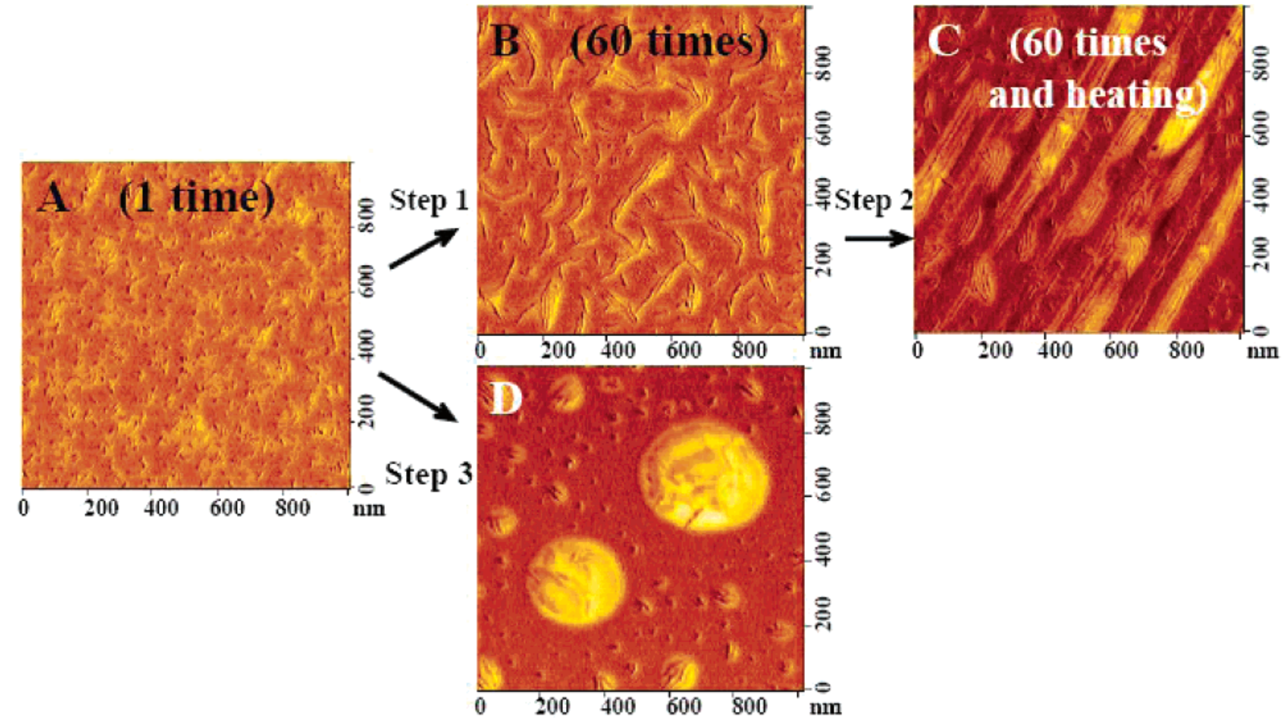

Figure 4. TM-AFM (phase images) showing the morphological differences between the sequential TM-AFM/heating (step 1 + 2) and direct heating (step 3). The short bundle strips (A, scanned once) were transformed into long strips after 60 times tapping (B), and further into parallel strips in columns after heating at 60 °C for 10 h (C), while (D) was formed by direct heating without TM-AFM tapping.

repulsive force between the molecular bundles. Since each single molecule consists of four $-\mathrm{COO^-Na^+}$ terminal functionalities, the same charge attraction that allows the formation of molecular bundles may in turn act as an expulsive force for distancing the bundle strips. Hence, by manipulating the bundle formation and strip repulsion, ordered arrays could be manufactured on a large scale.

For comparison, the same amphiphiles but with only 2 equiv of NaOH added (two $-\mathrm{COO^-Na^+}$ terminal functionalities) could only produce less orderly bundle strips (Supporting Information Figure S2). In another comparison, instead of the 2000 g/mol POP-2000 segment, the shorter POP-400 (400 g/mol Mw) analogs (POP-400/4COONa) failed to form orderly bundles, but formed irregular arrays (Supporting Information Figure S3). Apparently, the relatively hydrophilic POP-400 (averaging only 5−6 oxypropylene repeating units), unlike the hydrophobic POP-2000, could not provide sufficient bonding force for the intermolecular interactions. The proper balance between the POP hydrophobic and ionic charge polar interaction in the amphiphile structure is essential for the self-assemblies.

The effect of TM-AFM tapping on the transformation of molecular coils into stretched bundles is probably due to the similar energy level between the tapping and the molecular noncovalent bonding. Hence, proper heating may also affect the molecular alignment. In Figure 4 (step 1 and 2), it is demonstrated that the self-alignment is actually accelerated by applying heat energy. In a sequential procedure of AFM tapping (60 times) and heating (at 60 °C in an oven for 10 h), the sample demonstrated the formation of more orderly strips in the micrometer-scale regime. Further assemblies with 3−5 bundle strips in a large column and approximately 6 columns occupying an area of 1 $\mu\mathrm{m}^2$ were observed. Within each column, the constant 7−13 nm molecular bundle width is still maintained. However, in the direct heating route (step 3, in Figure 4), the short bundles were transformed into round-shaped aggregates (Figure 4D) rather than forming a column array. Perhaps the transformation of the directional strips requires an appropriate energy level to form the bundle templates as the first step. Excess heating probably destroys the bundle formation. The result indicates that the appropriate combination of TM-AFM scanning and controlled heating can be optimized for generating the molecular arrays.

Conclusion

The structurally tailored amphiphilic molecules with a hydrophobic POP middle block and symmetrically tethered aromatic amido acid functionalities could dictate the intermolecular interaction forces and consequently the molecular self-alignment and transformations into different orderly arrays. For the molecular bundles with an average 7−13 nm width, the process of aligning into higher orders of structure such as lengthy strips and parallel columns is controllable by TM-AFM energy. Furthermore, the molecular transformations are substantially accelerated by the combination of TM-AFM tapping energy and consequential heating. The intermolecular self-alignment generates orderly aggregates which are transformable under TM-AFM energy and may be useful for fabricating novel nanoarrays.

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Supporting Information Available: Synthesis, analysis, and interfacial tension for POP-2000/4COONa, and TM-AFM analyses of comparative POP-2000/2COONa and POP-400/4COONa. This material is available free of charge via the Internet at http://pubs.acs.org.

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