Controlled morphological changes in self-assembled structures formed by Fmoc variants of Threonine and Serine

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Abstract

We report for the very first time the self-assembly of Fmoc variant 2-(9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(tert-butoxy)butanoic acid of threonine (**Fmoc-Thr(tbu)-OH**) and of serine (**Fmoc-Ser(tbu)-OH**. The self-assembled structure formation of Fmoc variants of threonine and serine were examined under varying concentration and temperature conditions..Our studies reveal that the self-assembled structures formed by **Fmoc-Thr(tbu)-OH** and **Fmoc-Ser(tbu)-OH** reveal morphological transitions at the supramolecular level as we alter its concentration and temperature. **Fmoc-Thr(tbu)-OH** self-assembles to sphere at lower concentration which changes to dumb-bell shapes at higher concentration under room temperature conditions. When the solution at lower concentration is heated the spheres changes to rods while the dumb bell shapes at higher concentrations change to elongated dumb-bell-rod like morphologies. **Fmoc-Ser(tbu)-OH** on the other hand give flower like morphologies at lower concentration which changes to long rods at higher concentration. On heating at higher temperature 70 ^{o}C flower-like structures change to small rods while the long rods obtained at higher concentration changes to big flower-like structures. The controlled morphological changes noted in the modified single amino acids is very interesting and pave

the way for the design of novel self-assembled architectures for applications in material science and technology.

Keyword

Self-assembly, Fmoc-variant, modified single amino acid; dumb-bell; flower.

Introduction

Self-assembly is a process through which molecules assemble to well-ordered structures through non-covalent interactions via bottom-up-approach.[1,2] The main driving force responsible for the formation of self-assembled structure are non-covalent interactions like hydrogen bonding,[3, 4] vander waals force,[5, 6] electrostatic interaction,[7, 8] pi-pi stacking,[9, 10] and hydrophobic interactions.[11, 12] The study of formation of supramolecular architectures through the process of self-assembly of biomolecules is particularly crucial due to its wide range of application in various fields such as material science,[13, 14] biology,[15, 16] chemistry,[17, 18]biomedical engineering,[5, 19] tissue engineering,[20, 21] sensor designing,[22, 23] and nanotechnology. Moreover, biomolecules possess excellent biocompatibility,[24, 25] and good stability due to which they can be efficiently used as drug delivery Herein this manuscript, we have reported the self-assembled structure formation by Fmoc variant of threonine (**Fmoc-Thr(tbu)-OH)** and Fmoc variant of serine (**Fmoc-Ser(tbu)-OH)** under varying concentration and temperature**.** Previous literature reports, suggest formation of gel like structures by the self-assembly of Fmoc-amino acids.[26] Banerjee et al reported gel-like morphologies of Fmoc-Phe[27]while Gazit et al reported the gel like structure formation by Fmoc-Phe-Phe[28] Fmoc variant of single amino acid has immense applicationd in the field of biomedical research, due to their diverse applications from biology to nanotechnology. Recently, our group reported the self-assembly of single amino acid cysteine and methionine[3] Wangoo et al also reported the self-assembly of various single amino acids and reported potential application of these supramolecular building blocks in material science,[29] In other

study Fmoc variant cysteine is used as anticancer drug delivery agent,[30] In another report self-assembly of fluorenyl-methoxy-carbonyl-β,β-diphenyl-Ala-OH (Fmoc-Dip-Ala) to opel gemstone like morphologies is reported,[31] Bai et al designed different Fmoc-dipeptide and examined its catalytic role as thermolysin.[32]In another study mechanical properties of Fmoc-diphenylalanine were studied[33] and also the self-assembly of Fmoc-peptides was used for the preparation of nanostructures and hydrogels,[34]

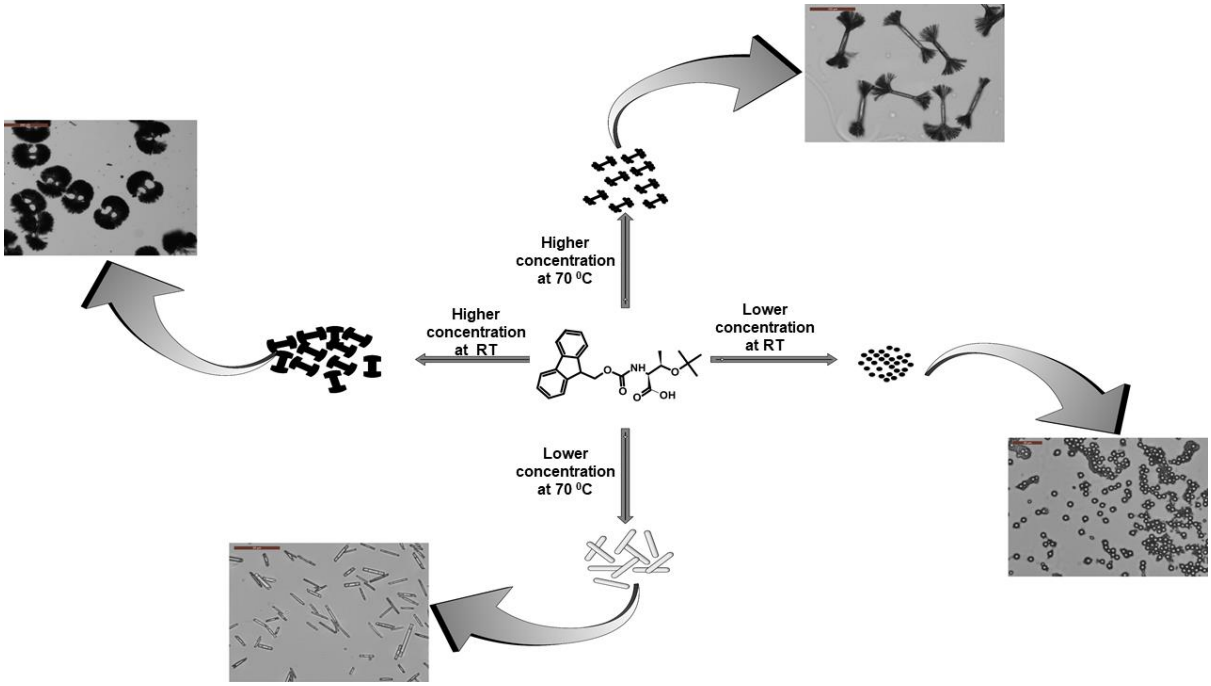


Figure 1. Controlled morphological changed in the self-assembled structures Fmoc variants of Threonine **Fmoc-Thr(tbu)-OH** under varying concentration and temperature.

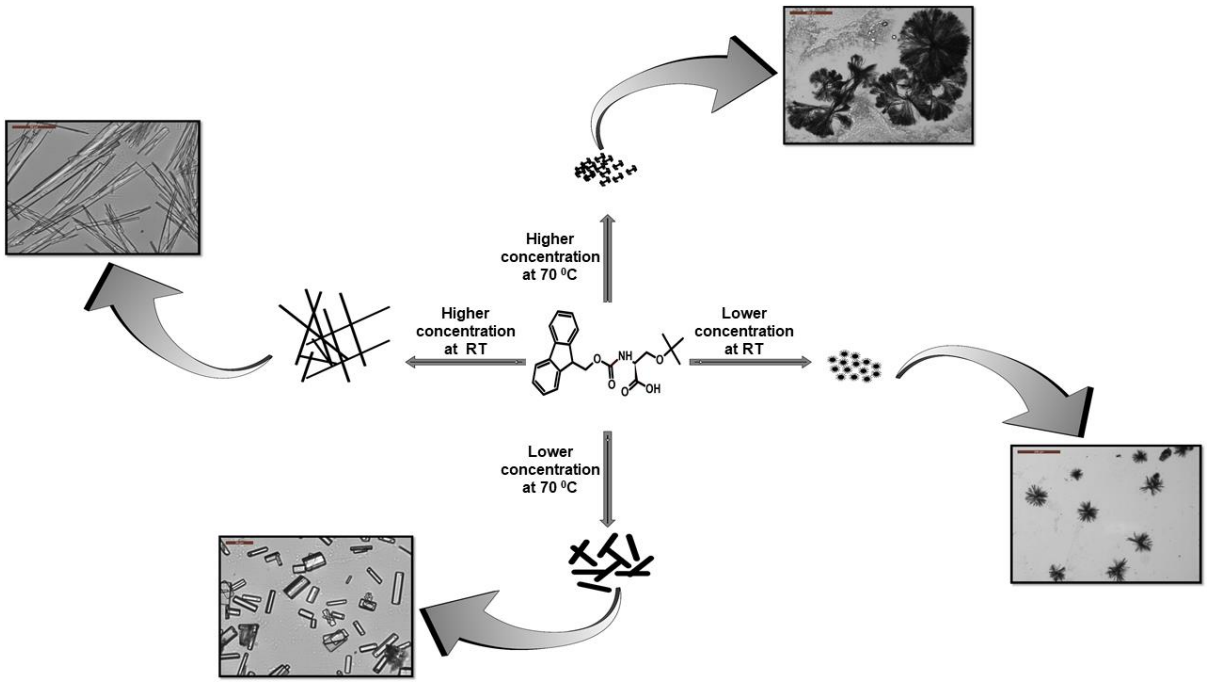


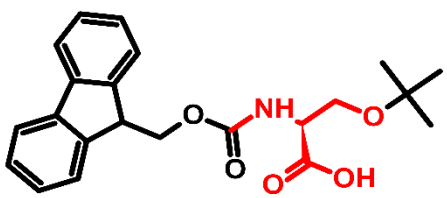
Figure 2> Controlled morphological changed in the self-assembled structures Fmoc variants of Threonine **Fmoc-Thr(tbu)-OH** under varying concentration and temperature..

Our group has been interested in assessing the self-assembling properties of single amino acids, [3,35] peptides,[36-38] and heterocyclic compounds.[10, 38-42] Recently, we reported self-assembled structure formation of cysteine and methionine and its amyloid like characteristic.[3] In other study our group has also reported the self-assembled structure formed by proline, hydroxyproline[35] and lysine.HCl.[43] Further in our another research we study the self-assembly of acyl thiourea based organic molecules and its application for the sequential detection of copper and lactic acid and it has been used for the cell imaging applications[43] Hence, from our previous studies we were motivated to synthesizea modified version of single amino acid which can be effectively used forvarious biomedical applications.

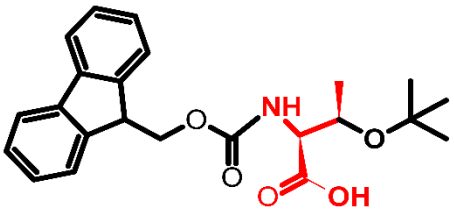
In this manuscript we reported the self-assembly of L-Threonine and its Fmoc variant 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(tert-butoxy)butanoic acid (**Fmoc-Thr(tbu)-OH**). Threonine shows the fibre like morphology while the self-assembled structure of **Fmoc-Thr(tbu)-OH** shows different morphological transition as spheres, dumb-bells, rods as

and dumb-bell rosa under varying concentration and temperature. Similary, serine alone also assemble to fiber like structures while the **Fmoc-Ser(tbu)-OH** reveal morphological transitions from flower-like morphologies to rod structures based on the concentration and temperature conditions.

Result and Discussion



Fmoc-O-tert-butyl-L-serine



Fmoc-O-tert-butyl-L-threonine

Scheme 1: Chemical structure of Fmoc-O-tert-butyl-L-serine and Fmoc-O-tert-buty-L-threonine.

The chemical structure of of Fmoc-O-tert-butyl-L-serine and Fmoc-O-tert-buty-L-threonine is shown in Scheme 1. Both the compounds were purchased from commercial suppliers and had purity greater than 99%. The compounds were used as such without further purification for the self-assembly studies. The self-assembled structures formed by Threonine and **Fmoc-Thr(tbu)-OH** were studied by optical microscopy at various concentration. Figure 1 shows the graphical representation of self assembled structure formation by Thr and **Fmoc-Thr(tbu)-OH** under varying conditions**.** Indeep very interesting controlled morphological changes could be observed and it may be noted that **Fmoc-Thr(tbu)-OH** at lower concentration assembles to spheres while at higher concentration they assemble to dumbbell like self-assembled structures. When we heated **Fmoc-Thr(tbu)-OH** at lower concentration, their was a morphological transition from sphere to rod-like structure while at higher concentrations, the dumb-bell shapes became. dumb-bell-rod like structures.

Figure 2 reveal optical microscopy image of self-assembly of single amino acid threonine alone. Figure 3a and 3b reveal self-assembled structures formed by **Fmoc-Thr(tbu)-OH**

under low concentration of 3mM showing spherical structures. These structures changes to dunb-bell shapes at higher concentration of 8mM as can be in Figure 3cand 3d. When these self-assembled structures are heated at 70 ^{0}C an interesting morphological transition from spheres to rods (3mM) and from dumb-bell to dumb-bell-rod like structures could be observed as seen in Figure 4.

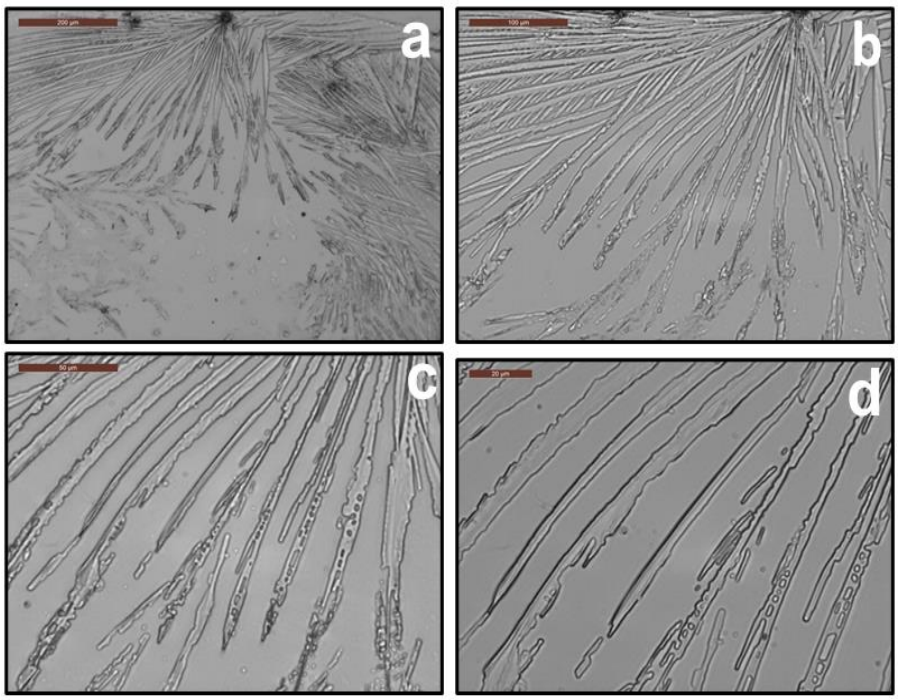


Figure 2. Self-assembled structure formed by Thr at 1 mM concentration a) Optical microscopic image under 10X; b) Optical microscopic image under20X; c) Optical microscopic image under40X; d) Optical microscopic image under63X

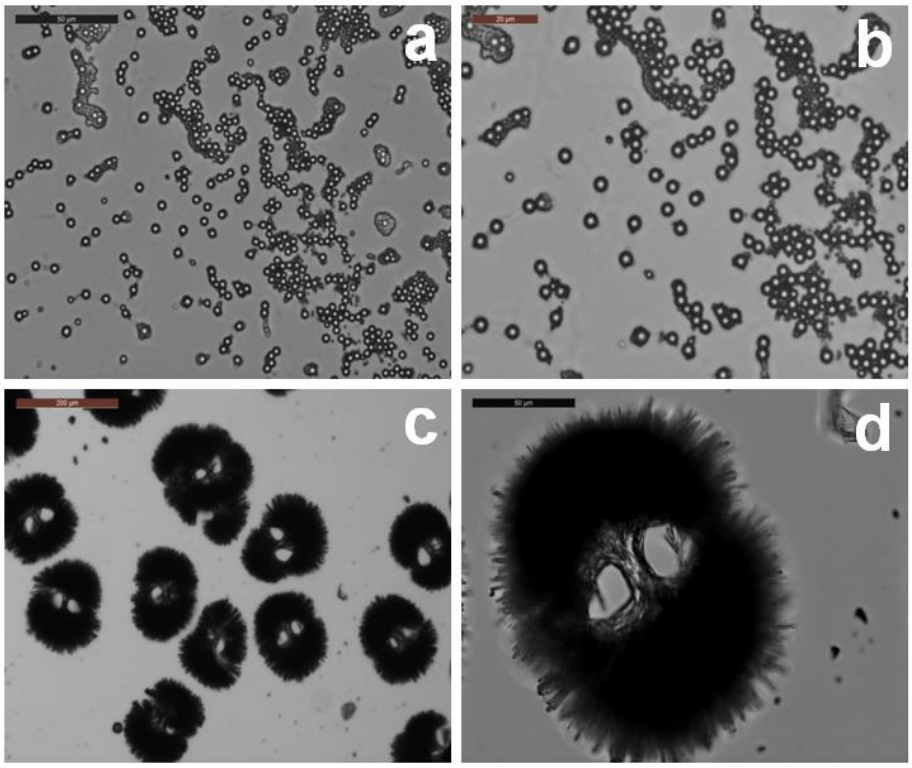


Figure 3.Self-assembled structures formed by **Fmoc-Thr(tbu)-OH** (a) Optical microscopy image at 3 mM under 40X (b) Optical microscopy image at 3 mM under 63X (c) Optical microscopy image at 8 mM under 10X (d) Optical microscopy image at 8 mM under 40X.

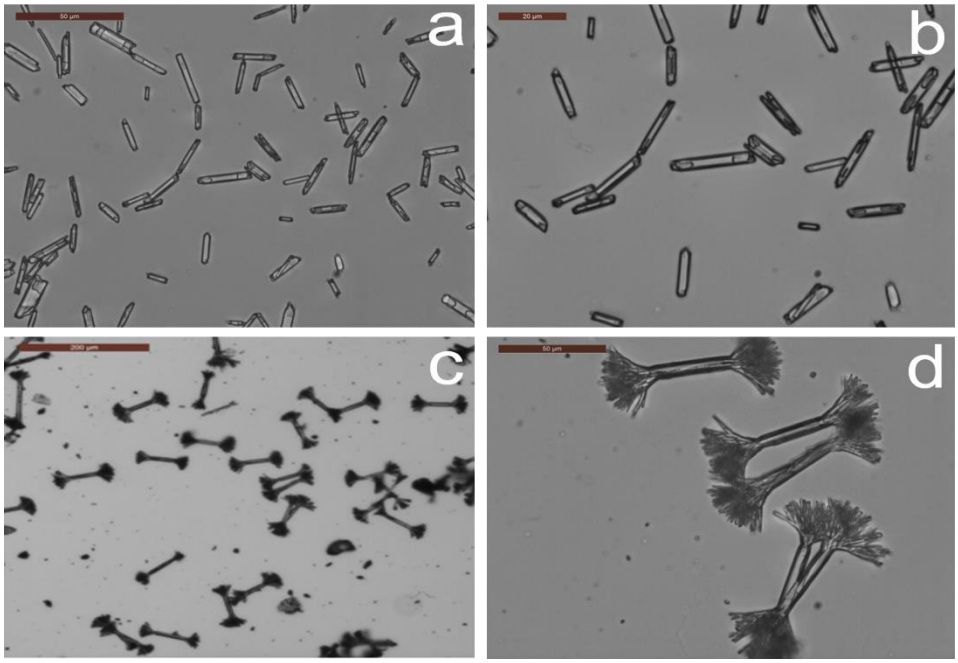


Figure 4.Self-assembled structure formed by **Fmoc-Thr(tbu)-OH** when heated at 70 ^{0}C (a) Optical microscopy image at 3 mM under 40X (b) Optical microscopy image at 3 mM under 63X (c) Optical microscopy image at 8 mM under 10X (d) Optical microscopy image at 8 mM under 40X.

Further, to understand the role of solvent in the process of self-assembly, various solvent dependent studies were performed which revealed that as the solvent was changed the morphologies were also affected.Our study revealed that both Thr and **Fmoc-Thr(tbu)-OH** do not form any assemblies in non polar aprotic solvents like Tetrahydrofuran (THF) and Dichloromethane (DCM) clearly revealing crucial role of hydrogen bonding and electrostatic interactions in the formation of these self-assembled structure. However, as we increased the percentage of water in THF weak interaction such as hydrogen bonding, electrostatic interaction, and hydrophobic attractions are facilitated resulting in sphere like self assembled structure formation again.

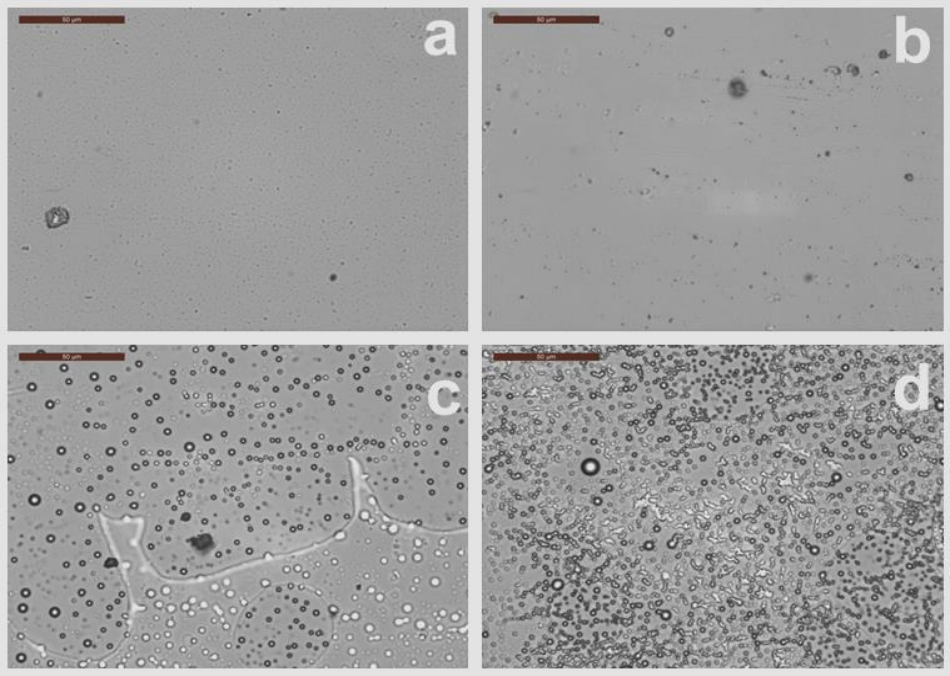


Figure 5.Optical microscopic images of **Fmoc-Thr(tbu)-OH** a) at 3 mM in THF under 40X; b) at 3 mM in DCM under 40X; c) at 3 mM with 20 % water in THF; d) at 8 mM with20 % water in THF

Concentration Dependent NMR study

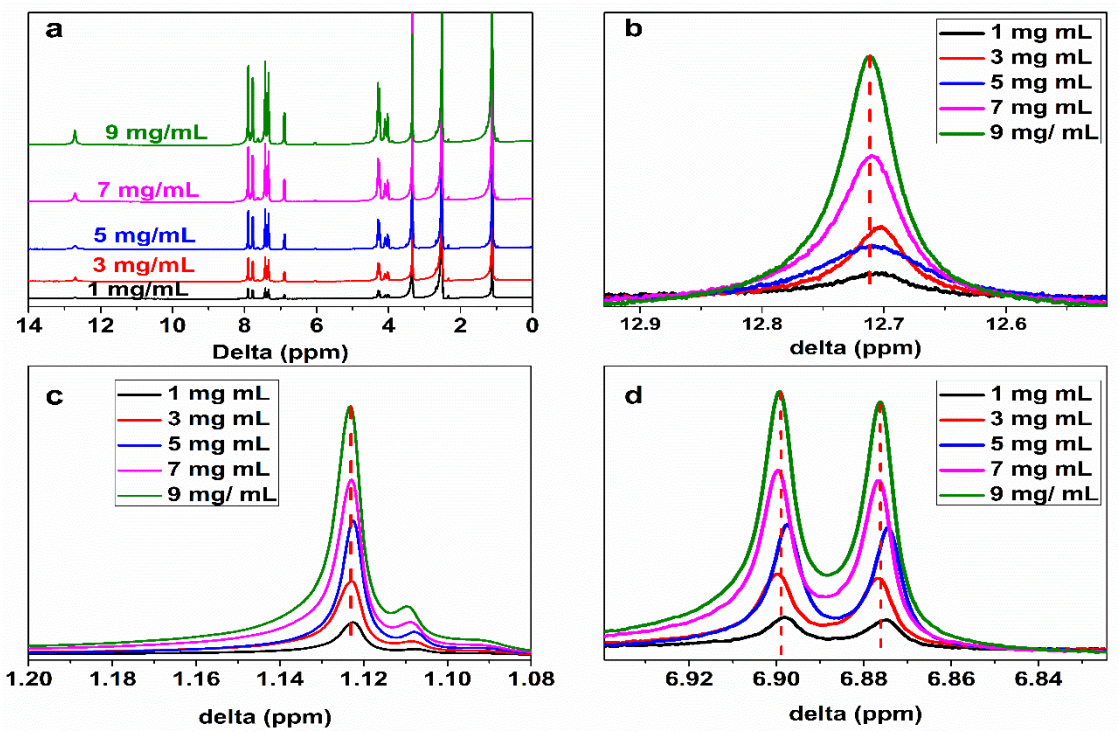


Figure 6. Concentration dependent NMR study of **Fmoc-Thr(tbu)-OH** at 1 mg/mL, 3 mg/mL, 5 mg/mL, 7 mg/mL and 9 mg/mLin dmso-d6.

The concentration dependent nuclear magnetic resonance (NMR) study was also performed to confirm the role of pi-pi stacking in the formation of self-assembled structures. NMR is a very useful spectroscopic technique which is used to prove a hydrogen bonding. NMR study of **Fmoc-Thr(tbu)-OH** demonstrated that as the concentration of **Fmoc-Thr(tbu)-OH** were increased the aromatic proton became slightly deshielded indicating pi-pi stacking interactions play a important role in the formation of self-assembly and the main cause for the deshilding of the aromatic protons is due to the close proximity of nuclei being stacked together resulting in enhanced electron density ans shielding causing the up-field shifts.[46-50]

Next, we assessed the self-assembly **Fmoc-Ser(tbu)-OH** at 1M concentration. The self-assembled structures formed by **Fmoc-Ser(tbu)-OH** were studied by optical microscopy. Figure 2 shows the graphical representation morphological transitions in the self assembled structure formed by **Fmoc-Ser(tbu)-OH** under varying conditions**.** As can be observed for **Fmoc-Thr(tbu)-OH,** controlled morphological changes could also be observed for **Fmoc-Ser(tbu)-OH** under varying concentration and temperature. **Fmoc-Ser(tbu)-OH** assembles to flower like assemblies at lower concentration while at higher concentration they cahnge to ling rod like structures. When we heated **Fmoc-Ser(tbu)-OH** at lower concentration, they

formed small rods while at higher concentrations, they again changed to big flower like structures probably due to less aggregation on heating.

Figure 2 reveal optical microscopy image of self-assembly of single amino acid threonine alone. Figure 3a and 3b reveal self-assembled structures formed by **Fmoc-Ser(tbu)-OH** under low concentration of 3mM showing spherical structures. These structures changes to dunb-bell shapes at higher concentration of 8mM as can be in Figure 3cand 3d. When these self-assembled structures are heated at 70 ^{0}C an interesting morphological transition from spheres to rods (3mM) and from dumb-bell to dumb-bell-rod like structures could be observed as seen in Figure 4.

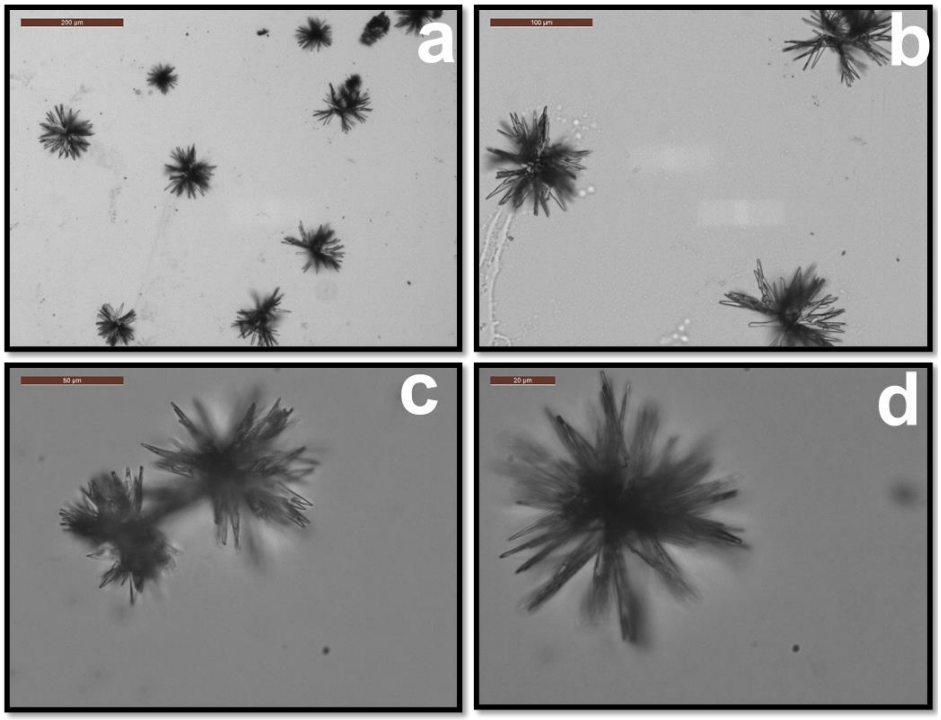


Figure 7: Optical microscopic images of **Fmoc-O-tert-butyl-L-serineat 1 mM** concentration under different magnifications: at room temperature a) 200 µm; b) 100 µm; c) 50 µm; d) 20 µm.

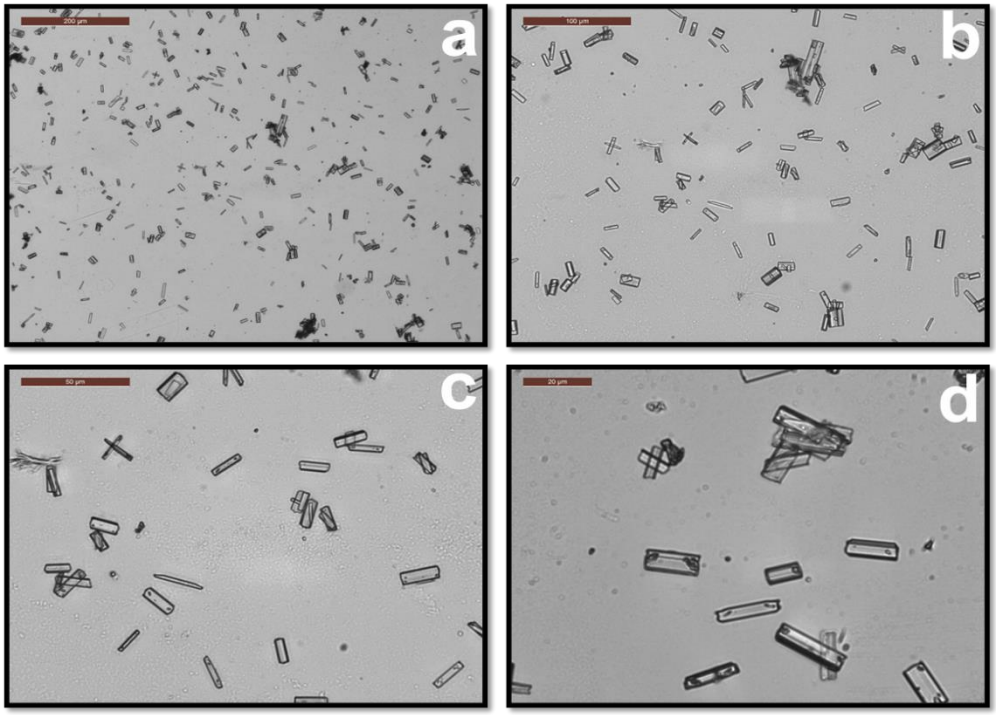


Figure 8: Optical microscopic images of **Fmoc-O-tert-butyl-L-serine** at 1 mM after heating at 70 ^{0}C under different magnifications: a) 200 µm; b) 100 µm; c) 50 µm; d) 20 µm.

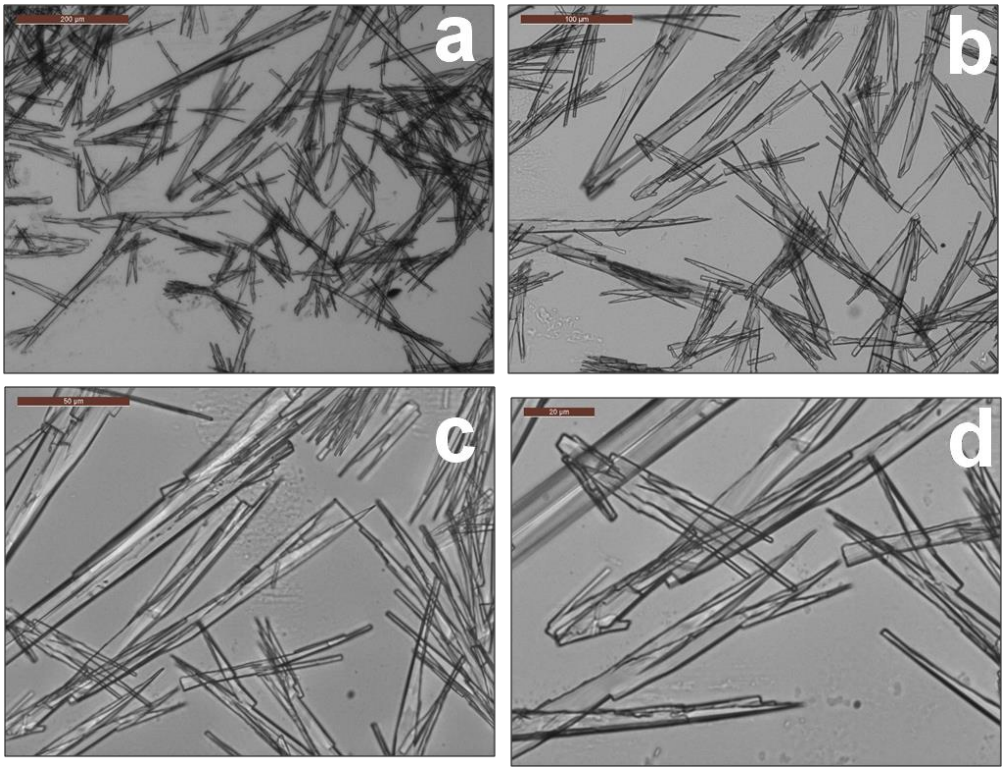


Figure 9: Optical microscopic images of **Fmoc-O-tert-butyl-L-serineat** at 9mM concentration under different magnifications: at room temperature a) 200 µm; b) 100 µm; c) 50 µm; d) 20 µm.

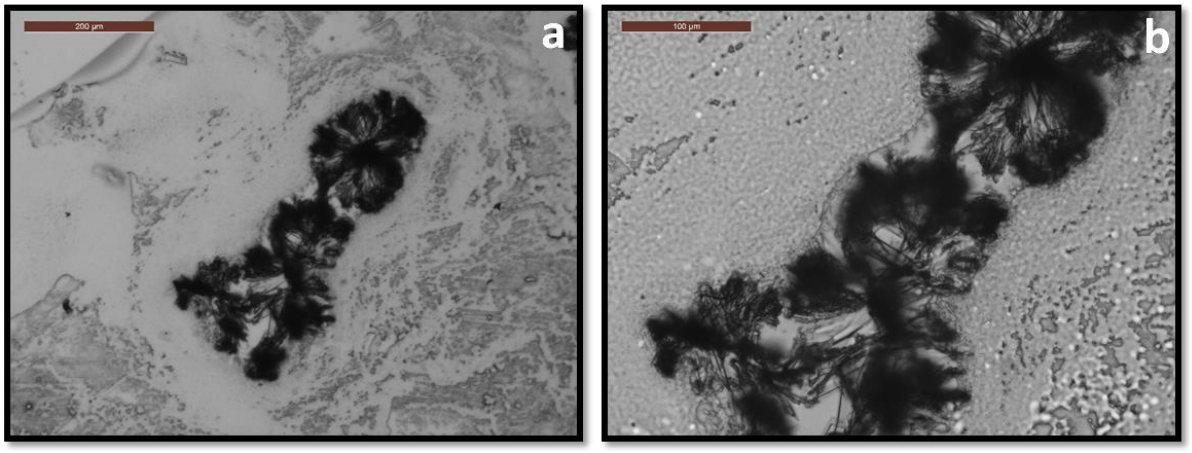


Figure 9: Optical microscopy images of **Fmoc-O-tert-butyl-L-serine** at 9 mM concentration after heating at 70 ^{0}C

Conclusion

In conclusion, we have reported interesting morphological transitions in modified single amino acids serine and threonine under varying concentration and temperature. The controlled morphological changes noted in **Fmoc-Thr(tbu)-OH** and **Fmoc-Ser(tbu)-OH** were very interesting and provide a facile technique for the manipulation of novel supramolecular architectures. It is envisaged the the results presented in this manuscript will be of crucial significances for the design of novel structures via bottom –up-approach and will create a lot of interest in the study of modified single amino acid self-assembly research in future dur to its simple and facile application as building blocks for the design of materials with immense applications.

Materials and method

Optical Microscopy

A 20 mM stock solution of **Fmoc-Thr(tbu)-OH and Fmoc-Ser(tbu)-OH,** were prepared in 50 % aqueous solution of methanol to get a clear solution, while a 10 mM stock solution of Thr were prepared in Milli Q water. The further dilutions were done using Milli Q water and in the case of **Fmoc-Thr(tbu)-OH** a turbid solutions has been observed on dilution. The self-assembling properties of this solution were studied via optical microscopy by drop casting a 20 μL solution on a clean glass slide. Also, the same solutions were heated at 70 ^{O}C and then drop casting 20 μL solution of this on a glass slide. For the self-assembly study

always a fresh solution has been prepared. All optical microscopic images were visualized using a Leica DM2500 upright fluorescent microscope at various magnifications.

Preparation of stock solution of for solvent dependent study.

A 20mM stock solution of **Fmoc-Thr(tbu)-OH**were prepared in the tetrahydrofuran (THF) and dichloromethane (DCM), aclear solution was observed. Further dilution was carried out in THF and DCM at 1 to 10 mM concentration. Self-assembly study of **Fmoc-Thr(tbu)-OH** at different fraction of water in THFA 20 mM stock solution of **Fmoc-Thr(tbu)-OH** were preparedin Tetrahydrofuran(THF).Further dilution was done in THF by adding different fraction of water.

Associated Content

The supporting information of this manuscript is available and contains additional figures and methods.

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