Supporting Information

Thermoplasmonic effect of silver nanoparticles modulates peptide amphiphile fiber into nanowreath like assembly

Narendra Kumar Mishra,[#, b] Vikas Kumar,[#, a] Khashti Ballabh Joshi*[a]
[a]*Dr. Harisingh Gour Central University Sagar (MP), 470003, India. E-mail(s): kbjoshi@dhsgsu.ac.in and kbjoshi77@gmail.com*
[b]Department of Chemistry Indian Institute of Technology Kanpur, Kanpur-208016,

Experimental section

General- Methanol, Water, $AgNO_3$ were purchased from Spectrochem, Mumbai, India, and used without further purification.

Atomic Force Microscopy (AFM) – Neat and co-incubated solution of sPA with AgNPs was imaged with an atomic force microscope. The samples were placed on freshly cleaved muscovite mica surfaces followed by imaging with an atomic force microscope (INNOVA, ICON analytical equipment, Bruker, Sophisticated Instrument Center(SIC)-Dr. Harisingh Gour Central University, Sagar-M.P.) operating under the acoustic AC mode (AAC or tapping mode), with the aid of a cantilever (NSC 12(c) from MikroMasch, Silicon Nitride Tip) by NanoDrive™ version 8 software. The force constant was 2.0 N/m, while the resonant frequency was ~290 kHz. The images were taken in air at room temperature, with the scan speed of 1.5-2.0 lines/sec. The data analysis was done using of nanoscope analysis software. The sample-coated substrates were dried at dust free space under 60W lamp for 6h followed by high vacuum drying and subsequently examined under AFM.

Transmission Electron Microscopy (TEM) **–** The samples were placed on a 400 mesh carbon coated copper grid. After 1 minute, excess fluid was removed and the grid was/wasn't negatively stained with 2% uranyl acetate solution. Excess stain was removed from the grid and the samples were viewed using a FEI Technai 20 U Twin Transmission Electron Microscope, operating at 80 kV. The microscope is a STEM and is also equipped with a EDS detector, HAADF detector and Gatan digital imaging system.

Fluorescence studies- Fluorescence spectra were recorded on varian luminescence cary eclipsed and CARY win 100 Bio UV-Vis spectrophotometer with a 10 mm quartz cell at 25 ± 0.1 ºC. The solutions of **sPA** and Ag(I) salt were prepared separately in CH_3OH/H_2O (50:50). Deionized water and methanol (HPLC grade) were used in these studies. The solution containing **sPA** (10^{-5} M) and different concentrations of silver salt in different ratios were prepared and recorded their fluorescence spectra in fresh as well as in aged conditions. All

fluorescence scans were saved as ACSII files and further processed in Excel™ to produce all graphs shown.

Circular Dichroism spectroscopy- All CD experimnt were carried out at room temperature. Spectra were collected at final concentration for each at 100 μM of sPA **1** and **2** alone and with in situ prepared silver nanoparticle, on JASCO J-815 CD SPECTROMETER by using quartz cuvette with a path length of 1mm. CD spectra were collected between 195 nm to 270 nm and each spectrum were the average of 5 scans. To avoid any instrumental baseline drift between any measurements, the background value was substracted for each individual sample measurement with 50% methanol-water.

Preparation of AgNPs: To the freshly prepared solution of compound **1** and **2** (1mM, 1mL) in methanol water (1: 1), 50μL, $AgNO_3$ added from the stock solution of $AgNO_3$ (10^{-3} M) was added separately and the mixture was kept in sunlight for 10-15 minute. A characteristics colour of silver nanoparticle was appeared with an appropriate SPR band at ~450 nm and confirmed the formation of AgNPs.

Purification of silver nanoparticle colloid: Purification of silver nanoparticle colloid done by using centrifugation method before using it for the imaging/analysis. After the formation of AgNPs-Peptide hybrids the solution was centrifuged at 12,000g for 30 minutes followed by removal of the supernatant and washing with methanol. The residue/pallets were re-dissolved in the 50% aqueous methanol in the appropriate volume of solvent. The colloid solution was stable for several days.

Rheometry: Rheological assays were performed on a 50 mm parallel plate Modular Compact Rheometer, MCR 502 by Anton Paar. Samples were dissolved in 50% methanol-water at a final concentration of 4 mM and sonicated for 15 minutes, one day before analysis. A volume of 3 mL of sample was loaded on the lower plate, and the upper plate was set to a gap size between 0.4 and 0.45 mm. Dynamic frequency sweep tests were performed in a range of frequencies from 100 to 0.1 rad/s. Solution of silver ions with optimum concentration was added to sPA followed by 15 min sunlight exposure. The characteristic color change of silver nanoparticles was appeared and this solution was used for the rheology.

Image Processing by MATLAB: Image background was estimated by using morphological operation function. This estimated background was subtracted from the main image. The image contrast was improved and then grayscale image was changed into binary image for further processing. The function “graythresh” was used to compute an appropriate threshold to use to convert the grayscale image to binary. Further, background noise was removed with function “bwareaopen” and obtained the final processed image.

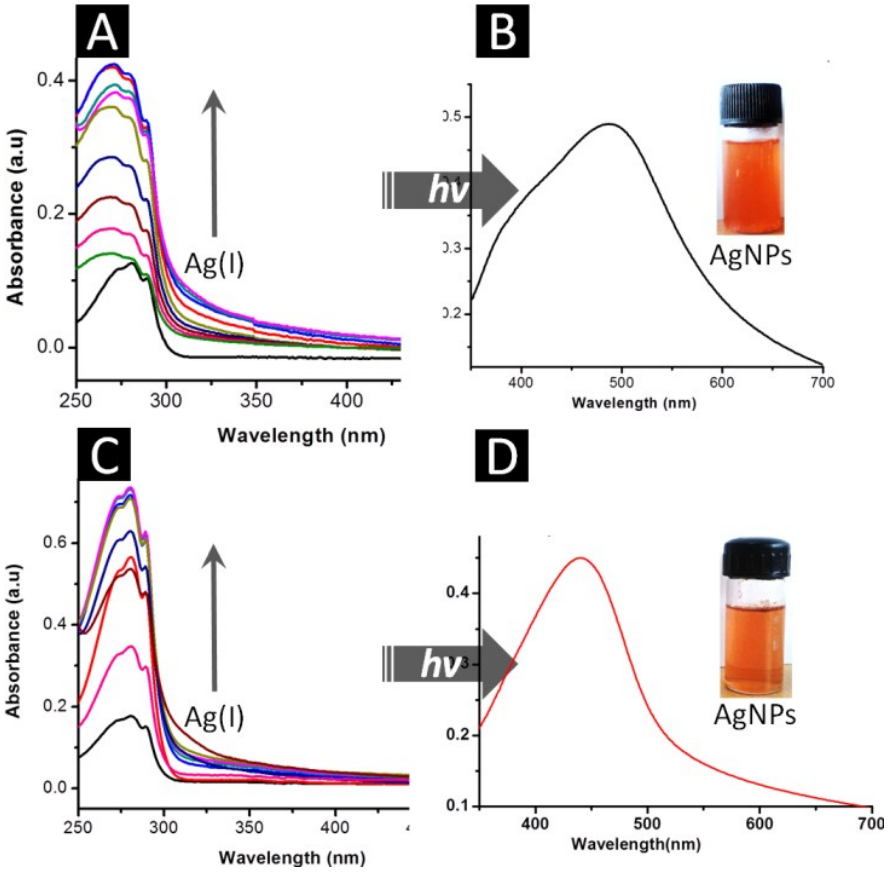

Figure S1. UV-Vis spectra of conjugate **1** (A) and **2** (C) in the presence of increasing Ag(I) ions depicts the interaction and complex formation mainly between Trp(λ_{abs} 280 nm) side chain and Ag(I). After the complex formation followed by brief exposure of sunlight formation of AgNPs were seen which were further confirmed by corresponding (B, D) SPR bands.

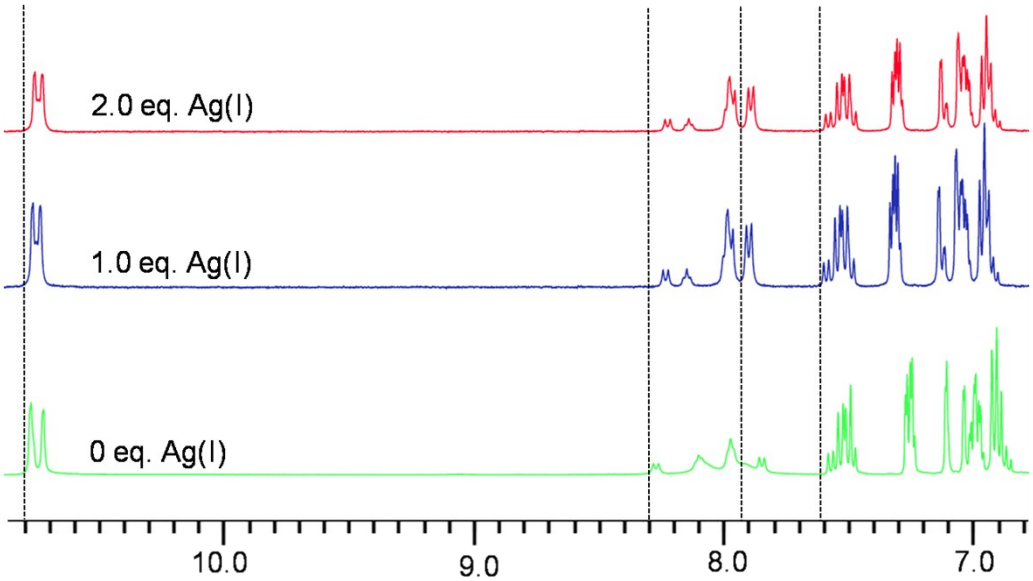

Figure S2: ^{1}H NMR titration spectra of sPA **1** in DMSO-d_6 in the presence of increasing amount of $AgNO_3$ solution.

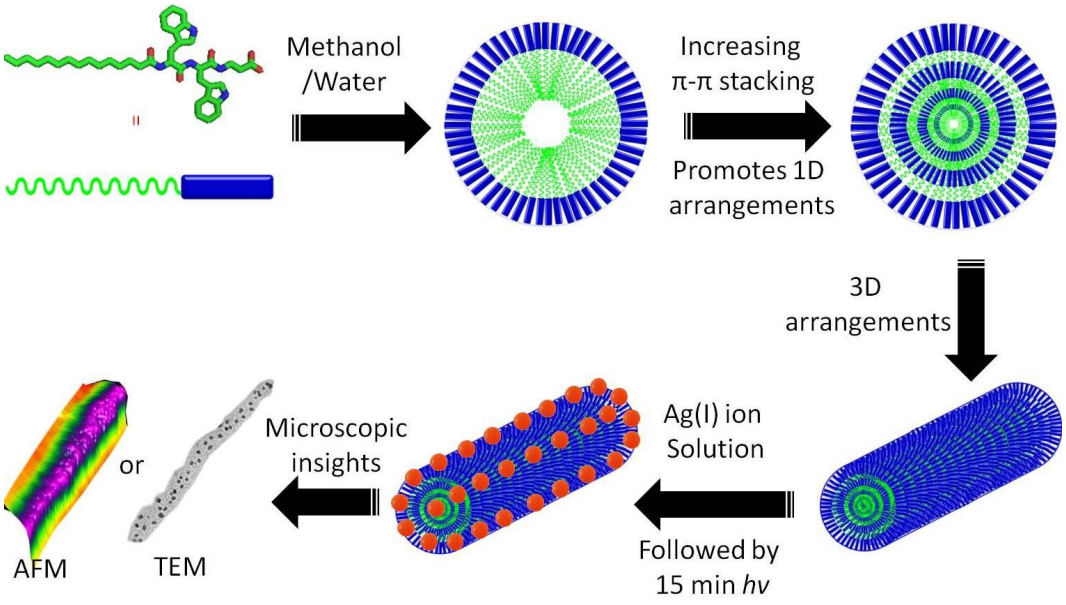

Figure S3: Proposed model for fiber formation in the presence of 50% methanol-water and AgNPs.

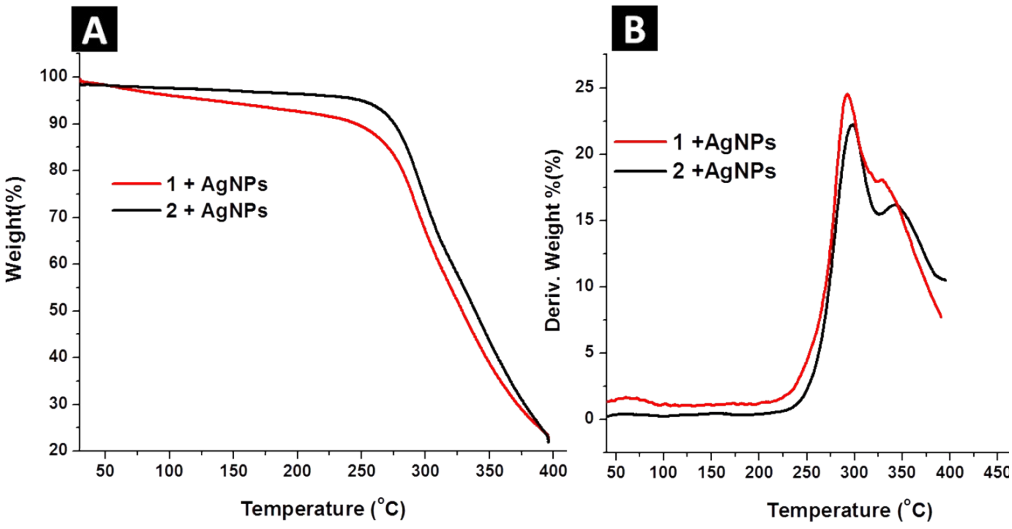

Figure S4: TGA of (A) sPA **1**-AgNPs and sPA **2**-AgNPs hybrids showing stability up to 345 °C, in the presence of AgNPs.

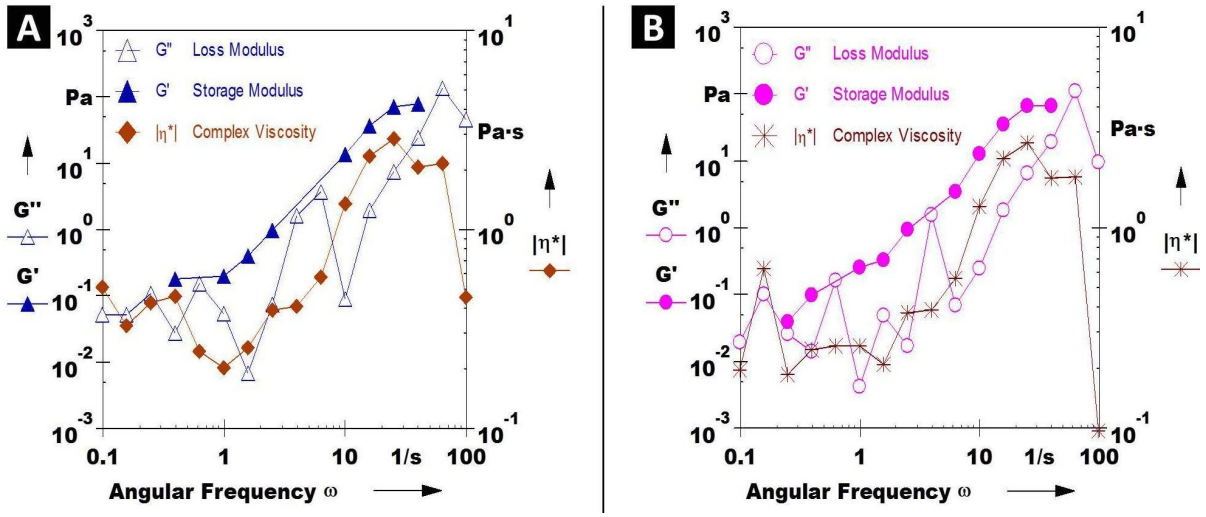

Figure S5: Depicts that the changes in storage modulus G′, loss modulus G″ and specific viscosity with angular frequency for sPA and sPA-AgNPs. (A) for sPA and (B) for sPA-AgNPs. The decreased value of storage modulus for the sPA-AgNPs hybrids compare to the sPA alone is perhaps due to the AgNPs are interfering and weakening the non covalent interactions between the units of sPA hence reduce the stability of sPA fibrous network.

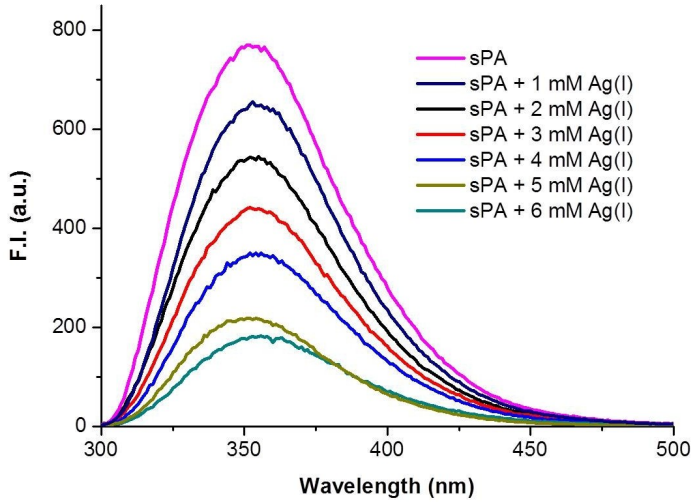

Figure S6: The figure depicts the fluorescence quenching of sPA **2** in the presence of increasing concentration of Ag(I) ion solution. Our observation reveals that upon addition of higher concentration of Ag(I) ions the fluorescence does not completely quench which is also supported by the NMR observation where we have mention that; *the sPA undergoes changes during the interaction and reduction of Ag(I) ion and perhaps few oxidized products were also formed during this process (page 3 first paragraph right).*

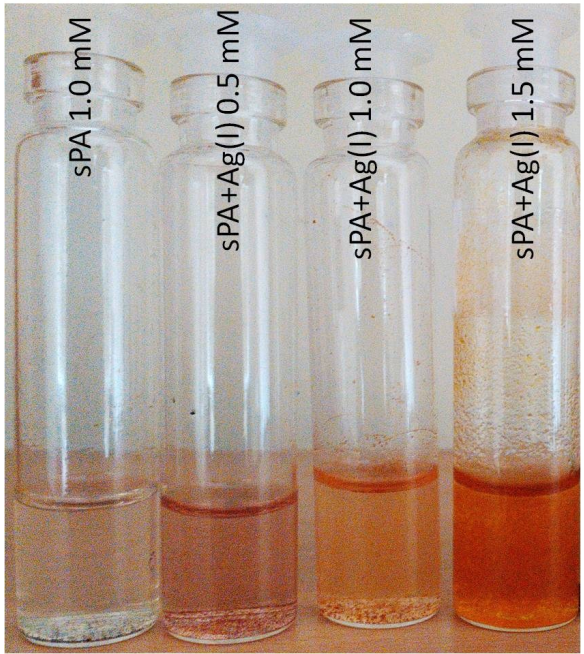

Figure S7: The figure depicts the formation of AgNPs and with increasing concentration of Ag(I) solutions. The formation of well defined hydrogel was not observed during this process however some sedimentation or aggregation of sPA with Ag(I) ion and sPA with AgNPs solution were observed on the wall or at the bottom of the glass vessels.

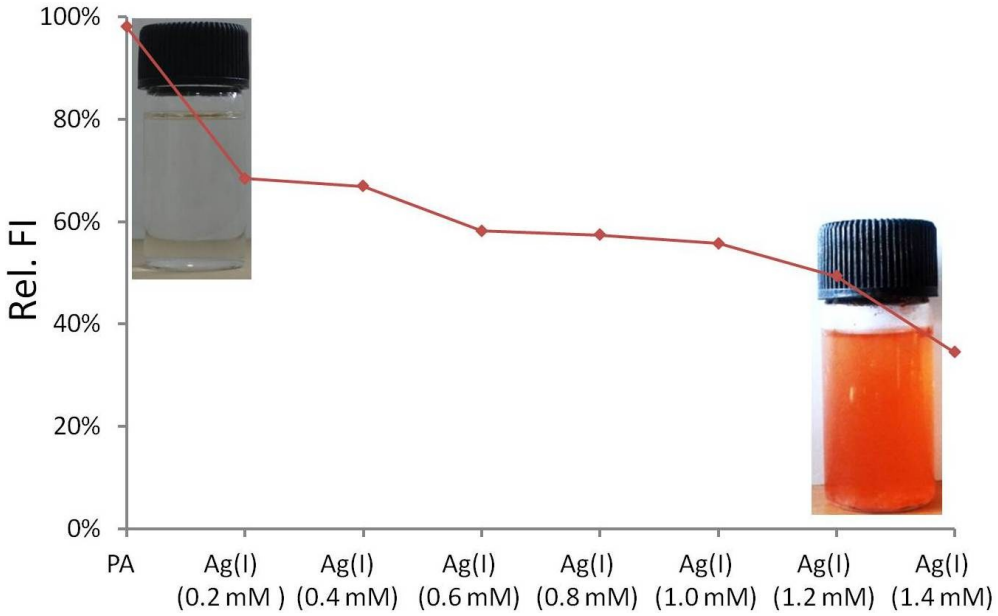

Figure S8: The figure depicts the formation of stable sPA-AgNPs colloid. With the help of florescence quenching experiments of Trp residue of sPA upon addition of certain amount of Ag(I) ion solution and the appropriate color change was observed. The optimum color change without any aggregation was found between 1.0 -1.4 mM concentration of Ag(I) ions solution and this solution was used for the studies.

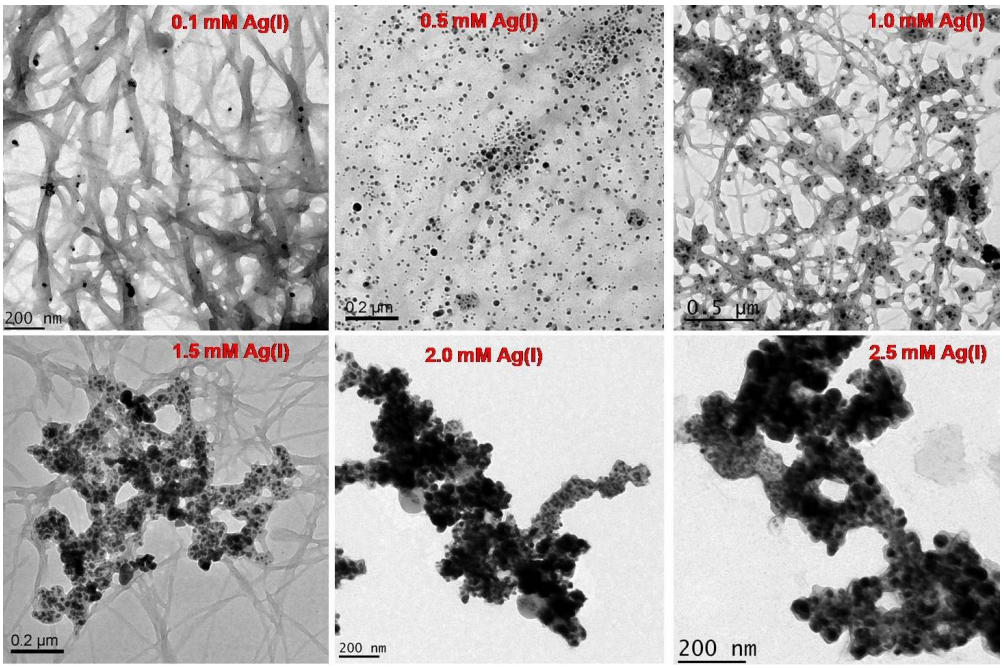

Figure S9: Depicts the Ag(I) concentration dependent destruction of fiber network of sPA-AgNPs hybrids. These observation reveal that the Ag(I) concentration and AgNP quantity having impacts on the sPA/AgNPs hybrid morphology, and the observed optimal Ag(I) concentration range is 0.5-1.5 mM which is crucial to obtain the sPA/AgNPs hybrid. This observation is further supported the spectroscopic observations of figure 3 experiments.

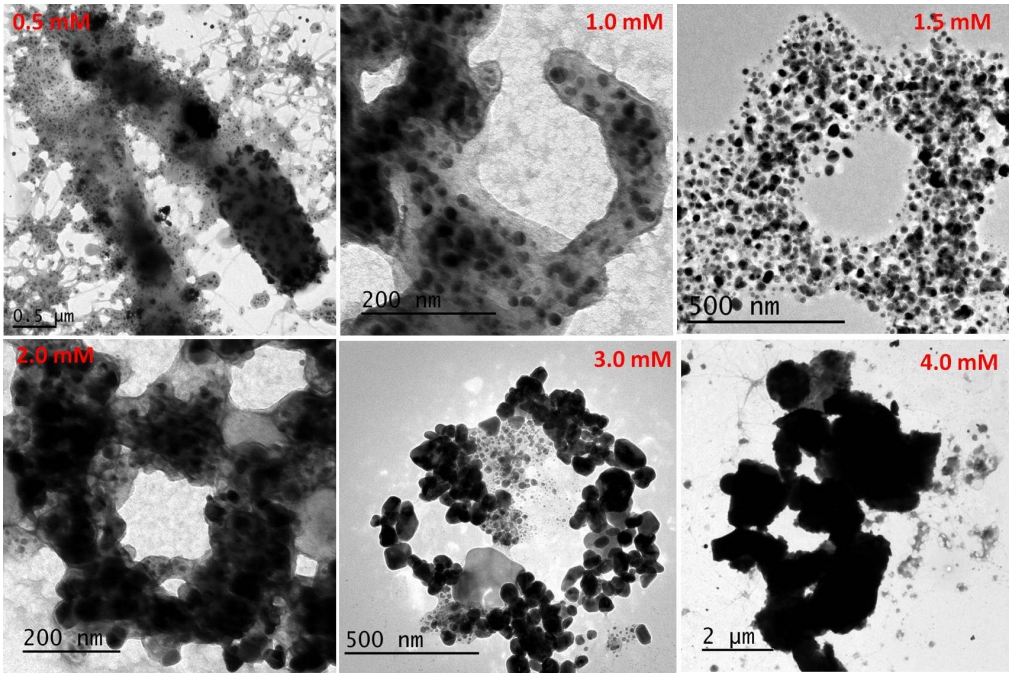

Figure S10: Depicts the Ag(I) concentration dependent nanowreath-like architecture formation. Sedimentation was not observed during the nanowreath formations at optimum concentration and reveal that the Ag(I) concentration and AgNP quantity having impacts on the sPA/AgNPs hybrid morphology. The observed optimal AgNPs concentration range is 1.0-1.5 mM which is crucial to obtain the sPA/AgNPs hybrid.

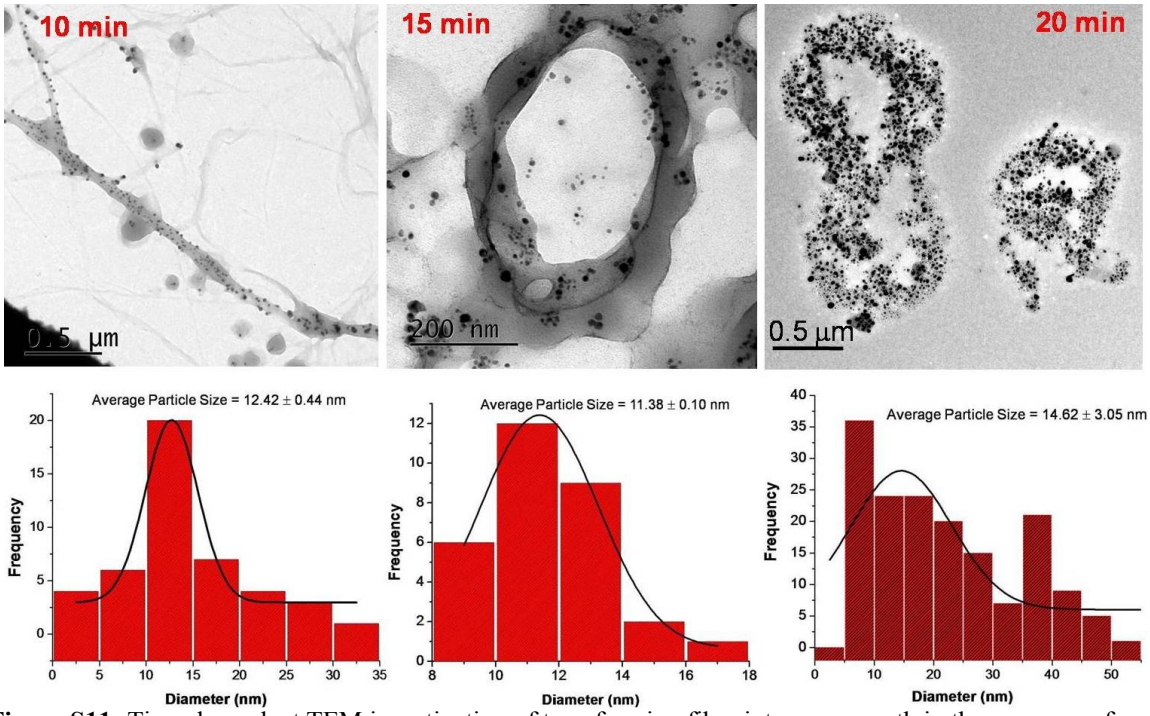

Figure S11: Time dependent TEM investigation of transforming fiber into nanowreath in the presence of sunlight at different time interval and corresponding particle size distribution (PSD) analysis depicted that the AgNPs sizes at different time interval are ranging from 11-15 nm.

Figure S12: The effect of pH in nanohybrid formation. The figure depicts that the optimum pH for the nanohybrid formation is pH 7.0.

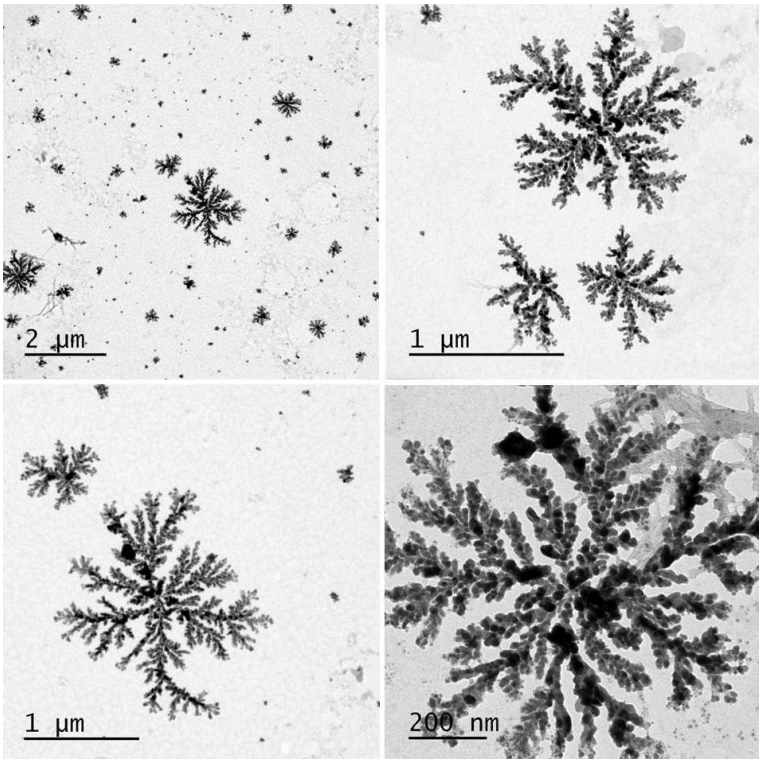

Figure S13: TEM images depict the fractal formation of AgNPs embedded sPA fiber. The presynthesized AgNPs were incubated with the solution of sPA and the aliquots were deposited over 400 mesh carbon coated TEM grids followed by imaging. This observation reveals the role of AgNPs for the morphological transitions.

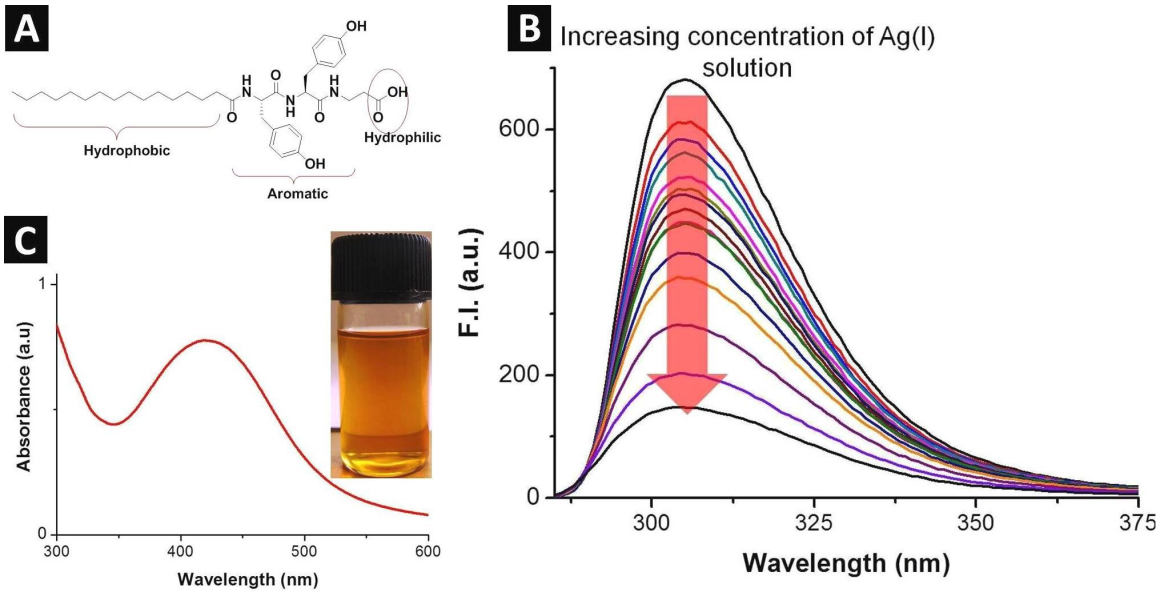

Figure S14. Control experiments: (A) Depicts the molecular structure of Pal-Try-Try-β-Ala, (B) Fluorescence quenching of Try based sPA (10^{-5} M) by increasing concentration of $AgNO_3$ solution in 20% methanol/water. The quenching experiment reveal that the interaction of Ag(I) ions to Pal- Try-Try-β-Ala. This was further confirmed by the (C) characteristic color of AgNPs colloid and corresponding SPR band obtained from the brief exposure of sunlight. Florescence intensity measured at E_{em} = 304 nm, after excitation at E_{ex} = 274 nm.