Supplemental Information

Supramolecular templating of hydroxyapatite mineral across length scales

Christina J. Newcomb, Ronit Bitton, Yuri Velichko, Malcolm L. Snead, Samuel I. Stupp

Supplemental Figures

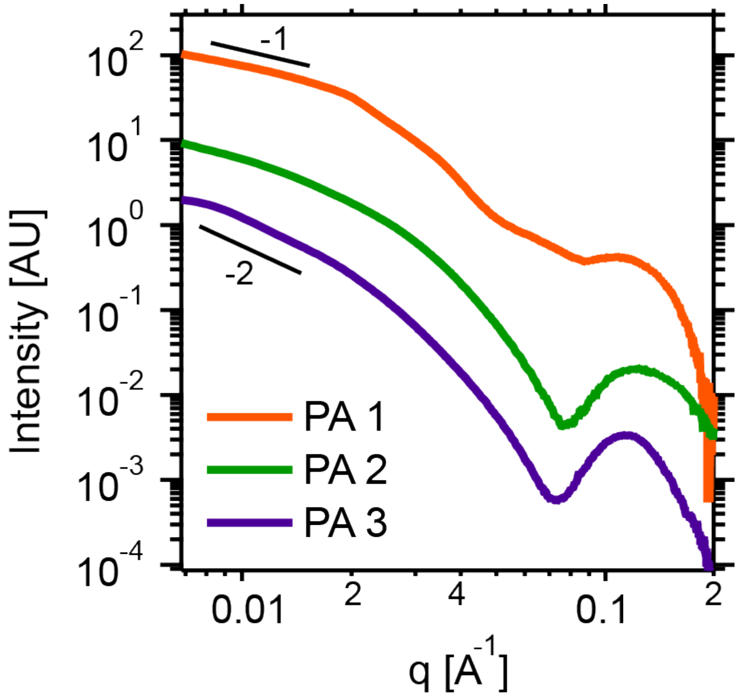

Figure S1: Small angle X-ray scattering of PA 1, PA 2, and PA 3 at 1%(w/v) in water after heating to 80°C for 30 minutes and cooling to room temperature. PA 1 shows a q^{-1} dependence indicative of rods, PA 3 shows a q^{-2} dependence indicative of flat structures, and PA 2 shows an intermediate slope.

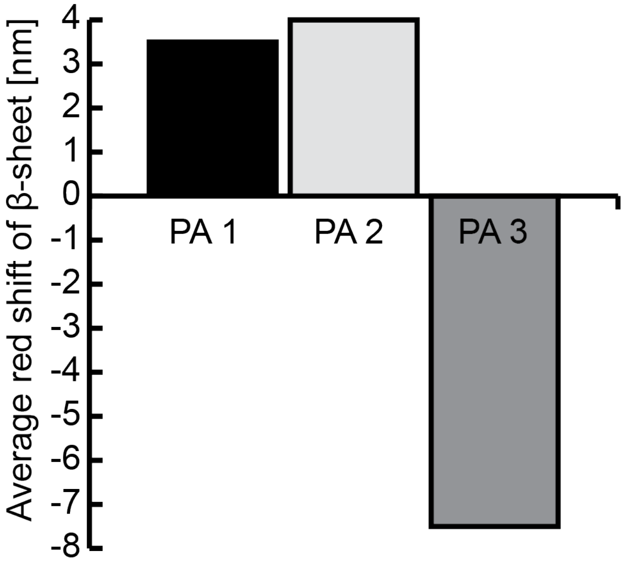

Figure S2: Average red shift of the circular dichroism signal of each PA molecule as compared to a standard protein β-sheet spectrum. PA 1 and PA 2 both show a red shift, indicative of twist in the β-sheet as compared to a standard protein, while PA 3 shows a blue shift, indicative of planar and possible stacking of β-sheets.

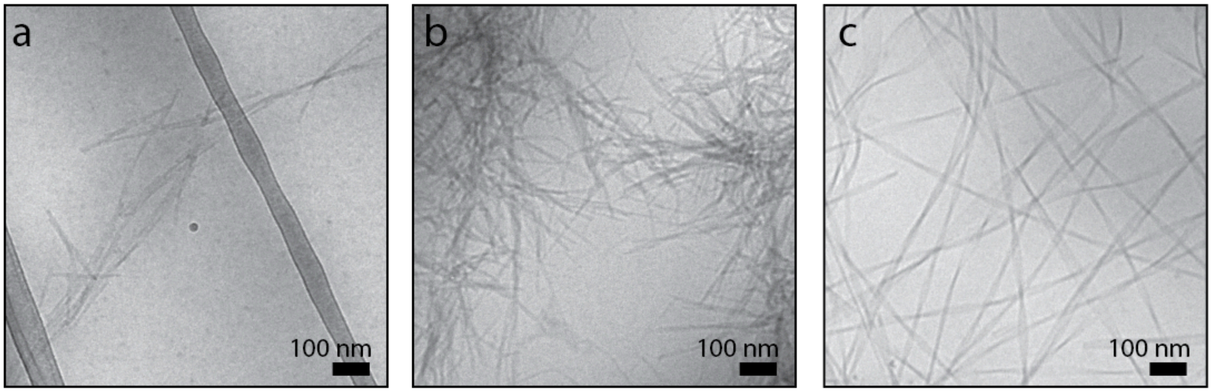

Figure S3: Cryogenic transmission electron micrographs of (a) PA 1, (b) PA 2, and (c) PA 3 in mineralization solution containing $CaCl_2$, Tris HCl, and beta-glycerophosphate to demonstrate the morphology in the presence of salts used for mineralization.

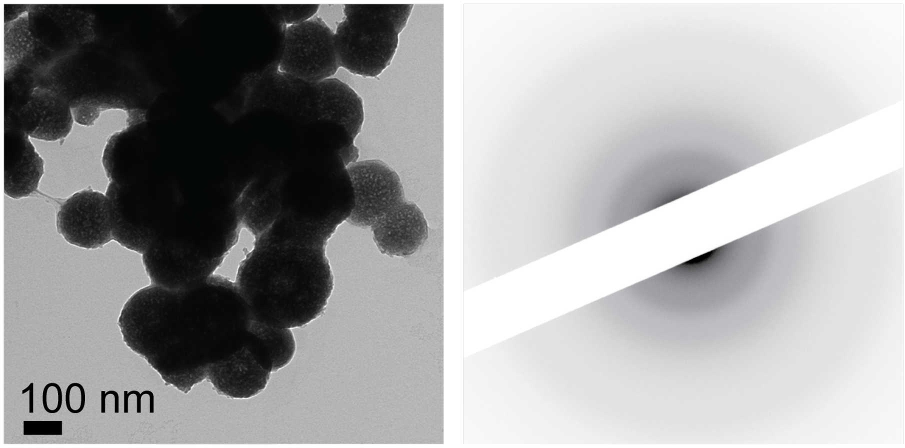

Figure S4: Conventional TEM of a dried, cast film of mineralization solution without PA after 1 hour of incubation at 37°C. Amorphous calcium phosphate spheres are present (left), and no crystalline calcium phosphate was observed. The corresponding electron diffraction pattern (right) only exhibits diffuse rings that are observed from the supporting carbon film.

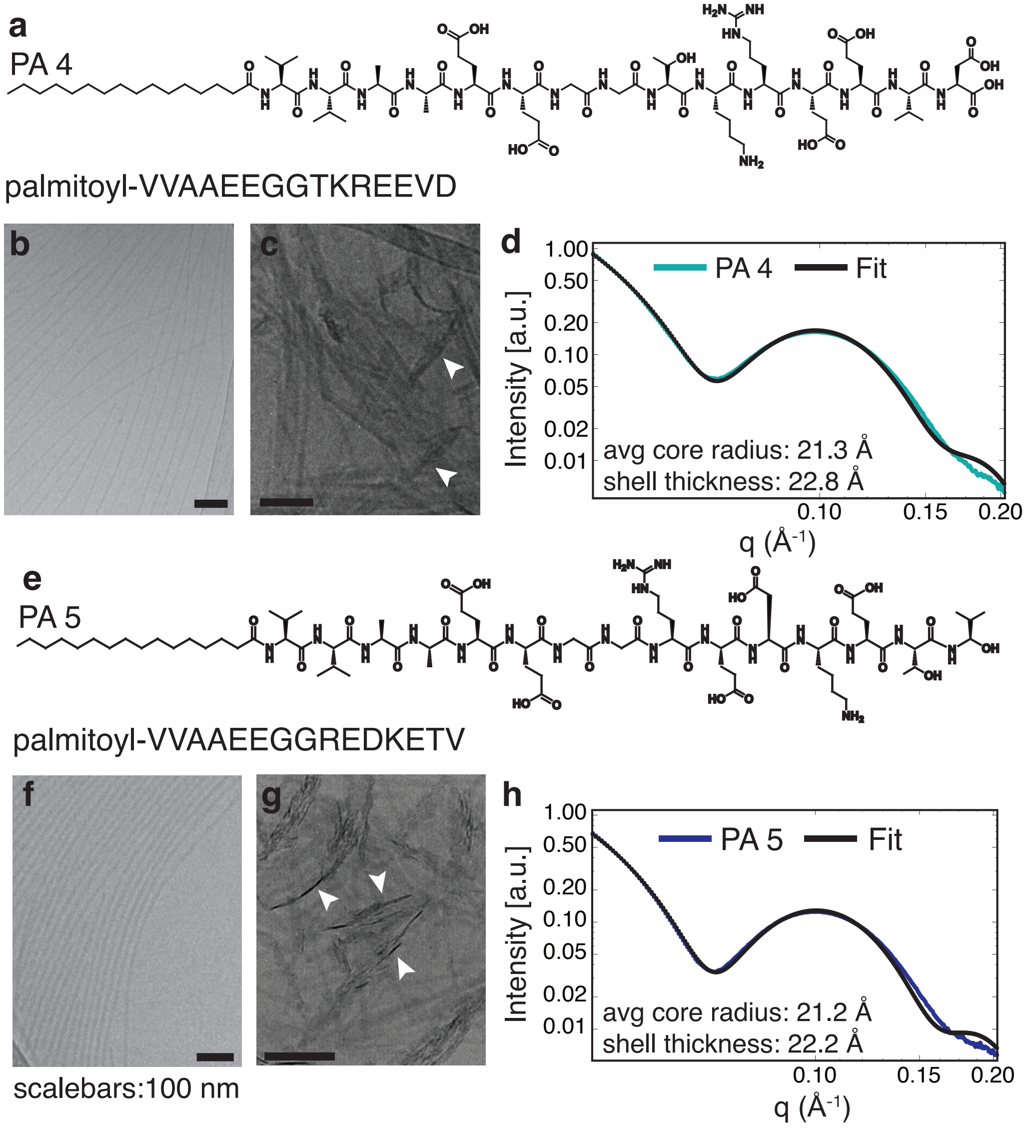

Figure S5: Two acidic PA molecules that form cylindrical micelles demonstrate alignment of mineral crystallites along the long axis of the nanostructure. The chemical structure of (a) PA 4 and (e) PA 5 are shown. (b, f) Cryogenic TEM reveals that the PAs form cylindrical micelles (no heating and cooling) and (d, h) SAXS supports this observation. The SAXS scattering curve was fitted to a cylindrical core-shell form factor where the core was allowed to be polydisperse according to a Gaussian distribution. The best fit to this model, represented by the black lines, yielded core radius and shell thickness values that correspond to a fiber diameter of approximately 8 -11 nm, agreeing with cryogenic TEM. Following mineralization for 2 hours (c, g) cryogenic TEM revealed the orientation of crystallites (arrows) with the inorganic aligned along the long axis of the nanostructure.

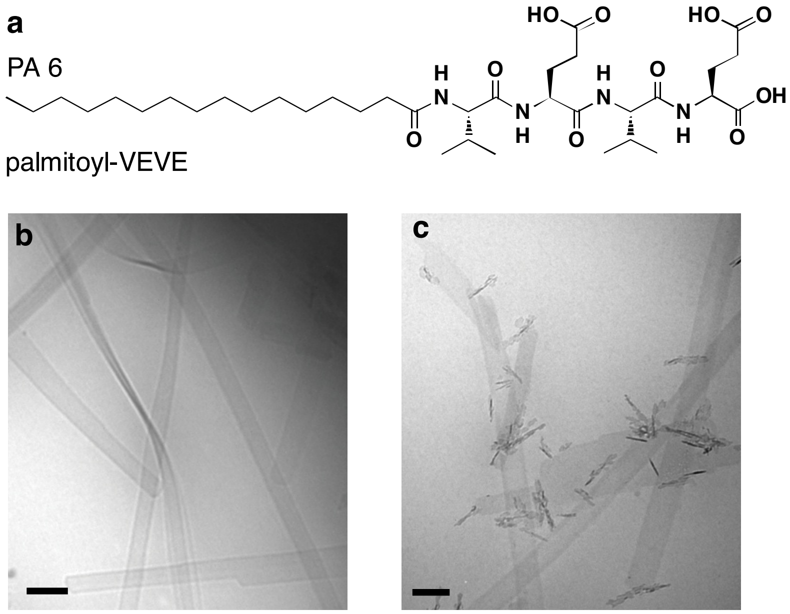

Figure S6: An example of mineralization of a flat PA nanostructure. (a) PA 6, a peptide amphiphile that has previously been shown to form flat nanobelt structures[1]. (b) Cryogenic TEM of PA 6 without mineralization and (c) cryogenic TEM of mineralized structures reveals no alignment of the crystallites with the long axis of the nanostructures. Scalebars: 100 nm.

References

1. Cui, H.; Muraoka, T.; Cheetham, A.; Stupp, S., Self-Assembly of Giant Peptide Nanobelts. *Nano Lett* **2009**.