Supporting Information

Nanostructure-templated control of drug release from peptide amphiphile nanofiber gels

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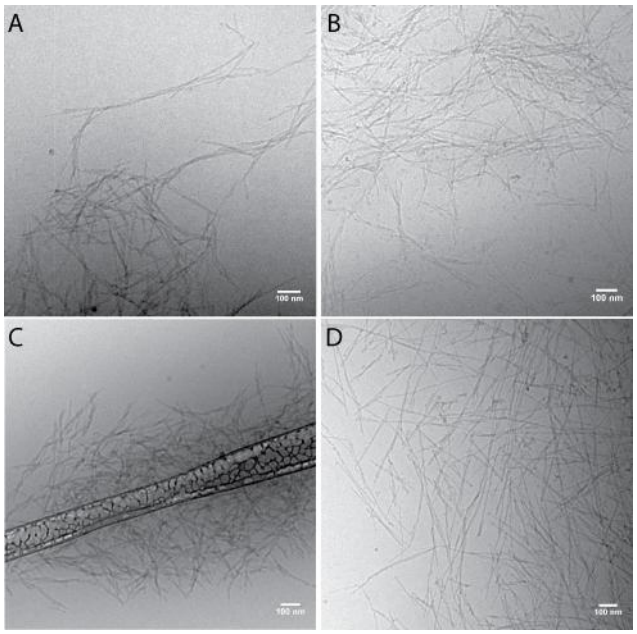

Figure S1. CryoTEM micrographs of PAs **5** (A), **6** (B), **7** (C) and **8** (D) at 0.1% total PA concentration from 2 mM with 1 mM $CaCl_2$.

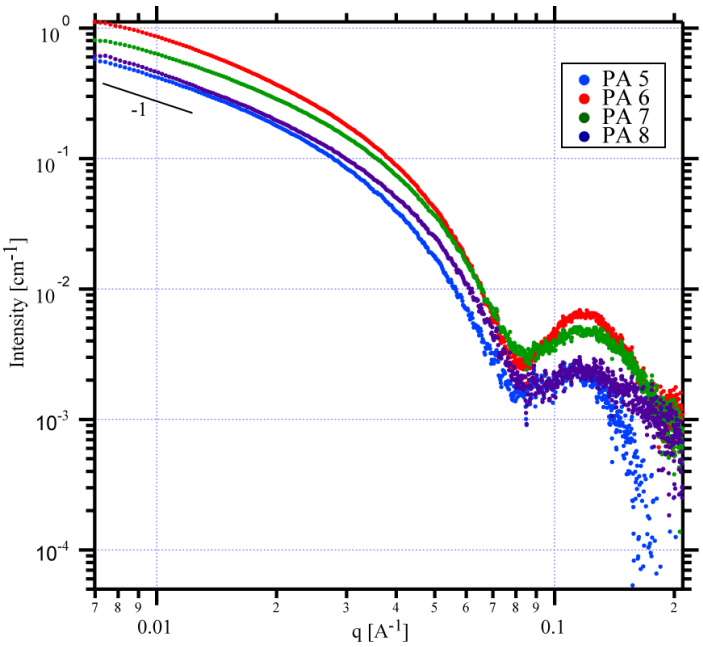

Figure S2. Solvent-subtracted SAXS curves of PAs **5**-**8** at 0.25 wt. % in 4 mM NaOH. Black line shows -1 slope.

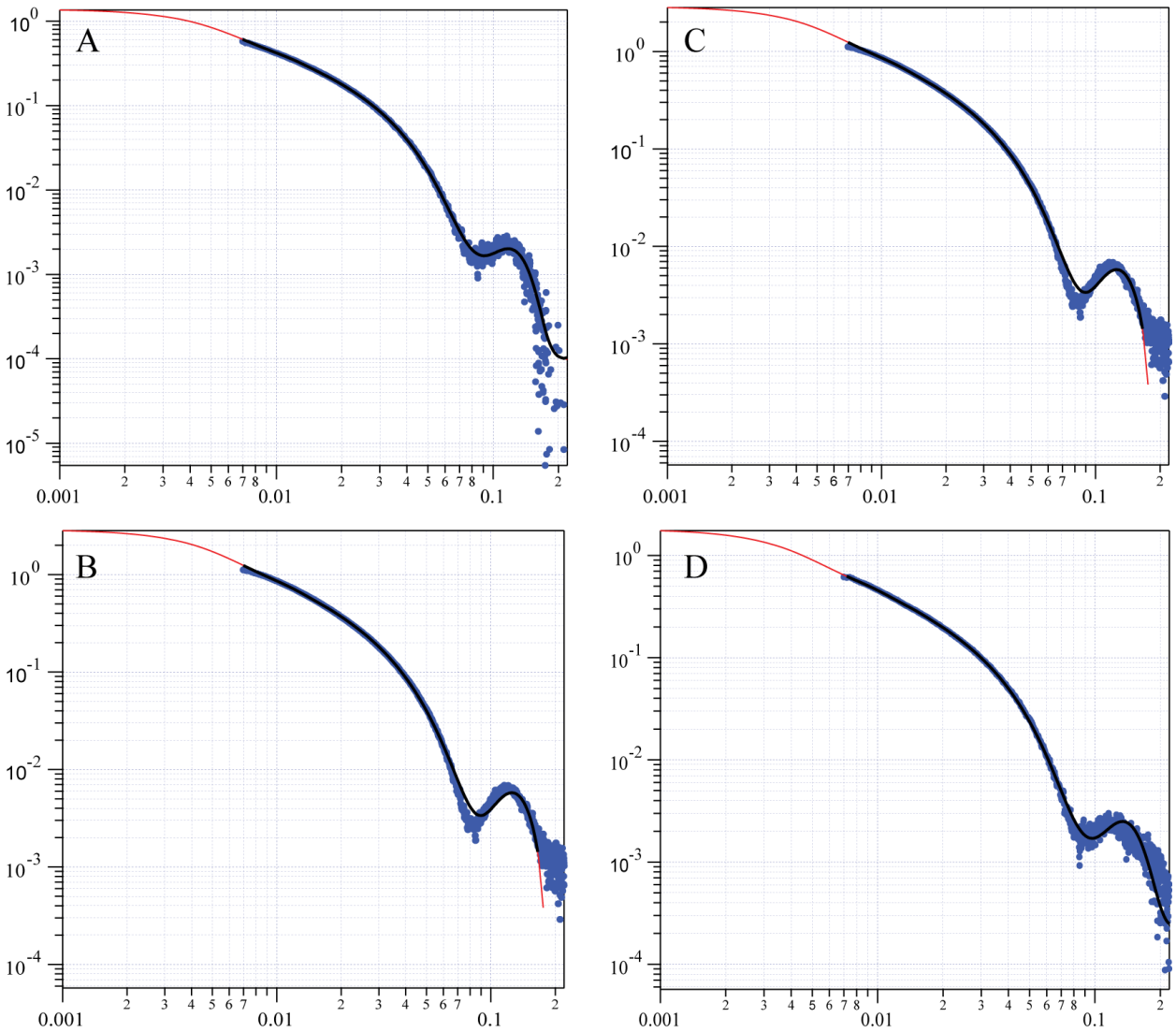

Figure S3. Individual solvent-subtracted SAXS traces of PAs **5-8** (A-D) fitted to a polydisperse core-shell cylinder model. The solid red line represents the best fit to a core-shell cylinder form factor given by the equations below, where the core was allowed to be polydisperse according to a log-normal distribution. The solid black line represents the portion of the curves where fits were performed.

PA	**5**	**6**	**7**	**8**
Mean core radius (A)	12	12	12	12
Radial shell thickness (A)	29	27	25	25
Total diameter (nm)	8.2	7.8	7.4	7.4
Radial polydispersity (σ)	0.3	0.27	0.3	0.28

Table S1. Selected SAXS data from PAs **5-8** at 0.25% in 4 mM NaOH without $CaCl_2$.

SAXS modeling. Data analysis was based on fitting the scattering curve to an appropriate model by a least-squares method using software provided by NIST (NIST SANS analysis version 7.0 on IGOR). The scattering intensity of a monodisperse system of particles of identical shape can be described as:

$$I(q) = NP(q)S(q)$$

where N is the number of particles per unit volume, P(q) is the form factor revealing the specific size and shape of the scatterers and S(q) is the structure factor that accounts for the interparticle interactions. In dilute solutions, where the interactions between the objects can be neglected, S(q) equals one. In a polydisperse system of particles having identical shape, the total intensity scattered from a can be described by:

$$I(q) = N\int_0^\infty D_n(R)P(q,R)dR$$

where $D_n(R)$ is a distribution function and $D_n(R)dR$ is the number of particles, the size of which is between R and R + dR, per unit volume of sample.

A form factor for a simple polydisperse core-shell cylinder, where the core and the shell have a uniform electron density, is given by:

$$P(q) = \int_0^{\pi/2} \sin\theta \cdot d\theta \cdot \left[V_l(\rho_l - \rho_{solv}) \frac{\sin\left(\frac{qH_l\cos\theta}{2}\right)}{\frac{qH_l\cos\theta}{2}} \frac{2J_1(qR_l\sin\theta)}{qR_l\sin\theta} + V_p(\rho_p - \rho_l) \frac{\sin\left(\frac{qH_p\cos\theta}{2}\right)}{\frac{qH_p\cos\theta}{2}} \frac{2J_1(qR_p\sin\theta)}{qR_p\sin\theta} \right]^2$$

$$V_x = \pi R_x^2 H_x$$

where J1(x) is the first order Bessel function. Theta is defined as the angle between the cylinder axis and the scattering vector, q. R_p and R_l are the core and shell radii respectively. H_p and H_l are the core and shell lengths and ρ is electron density.

The polydispersity of the core radius is modeled using a log-normal distribution

$$D_n(R_p) = \frac{\exp\left(-\frac{1}{2}\left[\frac{\ln\left((R_p/R_0\right)}{\sigma_p}\right]^2\right)}{\sqrt{(2\pi)}\sigma_p R_p}$$

where Ro is the mean core radius and σ is equivalent to the standard deviation of the log-normal distribution.

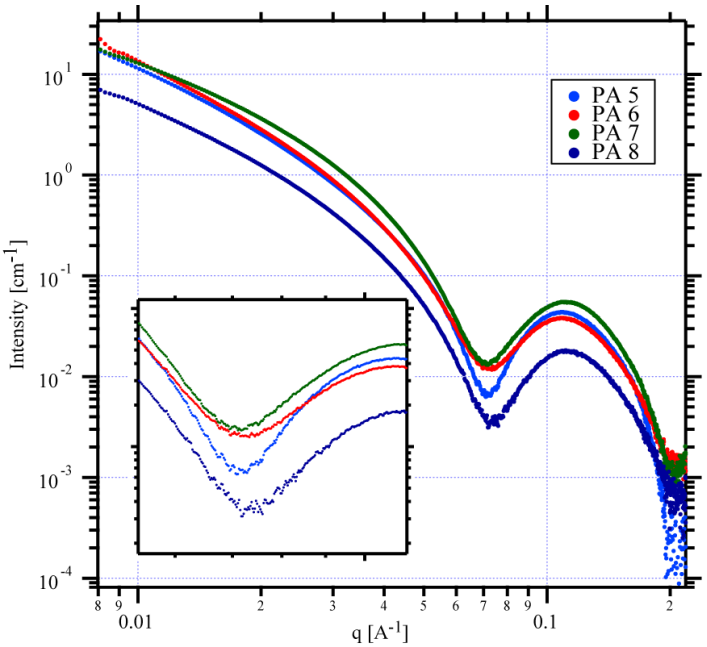

Figure S4. Solvent-subtracted SAXS data of PA gels. Gels were prepared at 3:1 (w/w) PA **E2** to Prodan PA **5**, **6**, **7** or **8** and crosslinked with 10 mM $CaCl_2$. Inset: magnified view of minima.

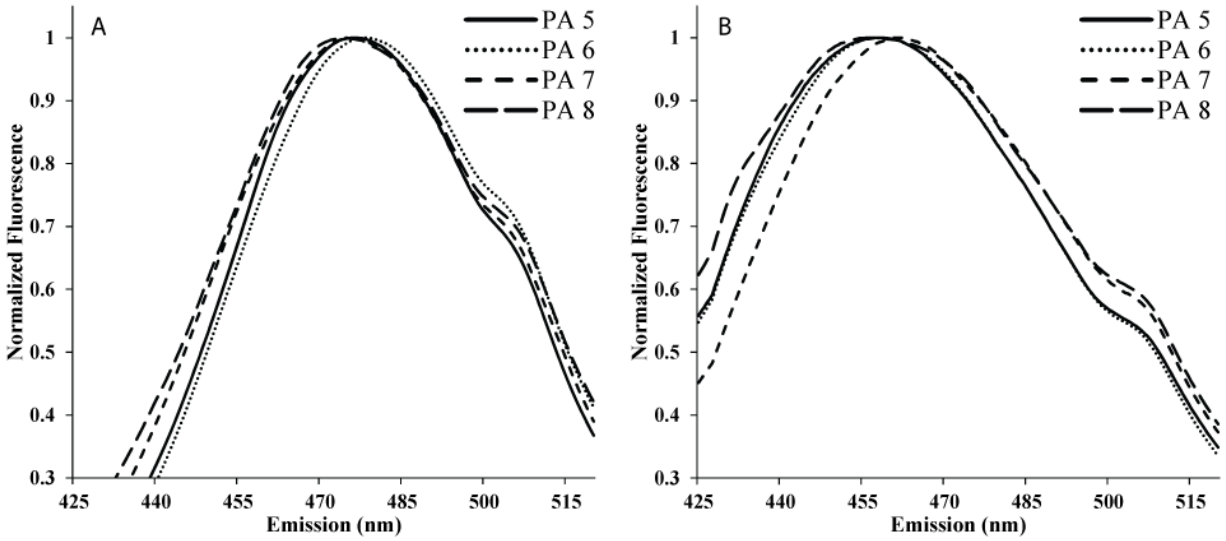

Figure S5. Fluorescence spectroscopy (λ_{ex}=350 nm) of (A) Prodan PAs **5-8** at 0.005 wt. % + 0.05 mM $CaCl_2$ and (B) Prodan PAs **5-8** + diluent PA **9** (1:3) at 0.1 wt. % + 1 mM $CaCl_2$. The shoulder at 506 nm is due to free Prodan as an artifact of sample preparation.

PA #	**5**	**6**	**7**	**8**
λ_{em} for pure PA (0.005%)	458	458	462	458
λ_{em} for PA + **E2** (0.02%)[a]	466	472	470	470
λ_{em} for PA + **E2** (0.1%)	476	478	476	474

Table S2. Fluorescence maxima (nm) of pure PAs **5-8** and PAs **5-8** mixed with diluent PA **E2** (1:3) at 0.1% from Figure S1. [a]From Table 4 in the main text.

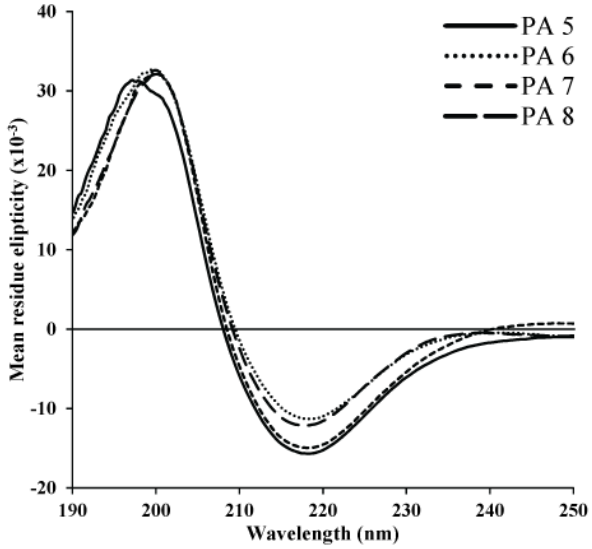

Figure S6. CD traces of PAs **5-8** at 0.05 wt. % and 0.5 mM $CaCl_2$ in 1 mm cell.

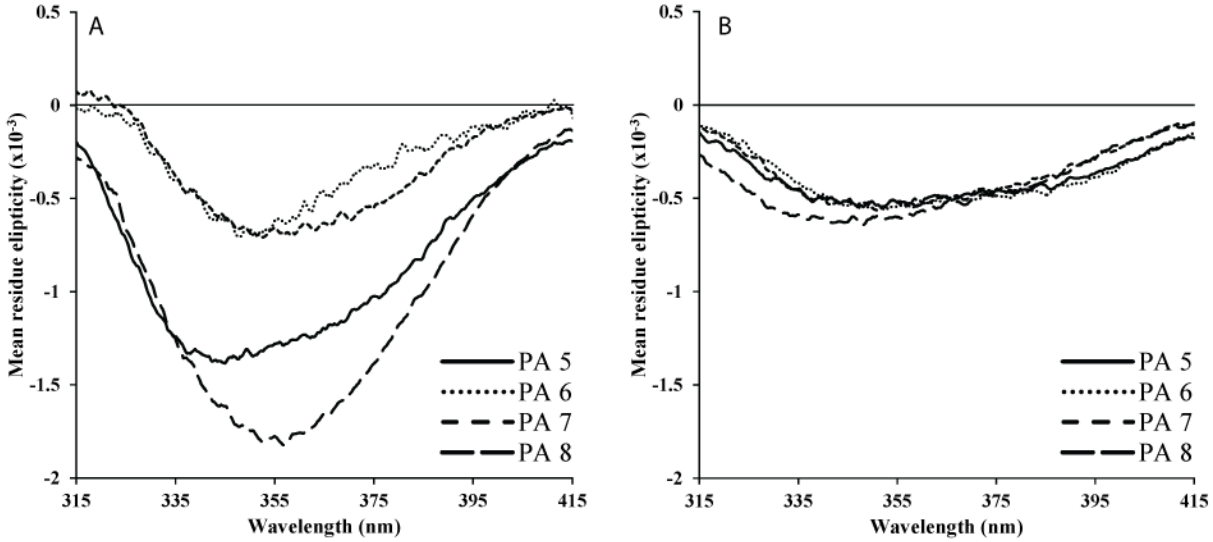

Figure S7. CD traces of (A) PAs **5-8** at 0.025 wt. % and 0.25 mM $CaCl_2$ and (B) PAs **5-8** mixed with diluent PA E2 at 0.1 wt. % and 1 mM $CaCl_2$. Spectra were taken in region of Prodan absorbance in a 10 mm cell. Negative Cotton effects indicate that the PAs reside in a chiral space.[1]

[1] Brunsveld, L.; Lohmeijer, B. G. G.; Vekemans, J.; Meijer, E. W. *Chem. Commun*. 2000, **23**, 2305-2306.