Disruption of Diphenylalanine Assembly by a Boc-Modified Variant

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Supporting Information

AFM sample preparation:

When transferring liquid onto the substrate for AFM experiments, care was taken to include the visible precipitates in the solution and was still visible as white clusters on the substrate. Due to AFM Z limits, precipitates <1 µm were chosen for measurement. In all samples, fibrils exceeding these limits were observed in the optical image and avoided for AFM measurements.

Rigidity calculations:

End to end distance (R) and fibril length (L) were measured directly from AFM images using ImageJ in pixels, then converted into SI units using resolution (*e.g*. 512 pixels / 10 µm). Rigidity was calculated as follows:

$$Rigidity = \frac{R}{L}$$

Table S1: Rigidity detailed statistics

Ratio FF:Boc-FF	average	standard deviation	variance	kurtosis	skewness
FF solely	0.957	0.09	0.009	15.98	-3.88
40:1	0.973	0.04	0.002	6.32	-2.35
20:1	0.947	0.09	0.008	16.60	-3.67
10:1	0.930	0.09	0.008	2.56	-1.73
5:1	0.942	0.07	0.005	5.76	-2.15
Boc-FF solely	0.962	0.09	0.008	15.38	-3.80

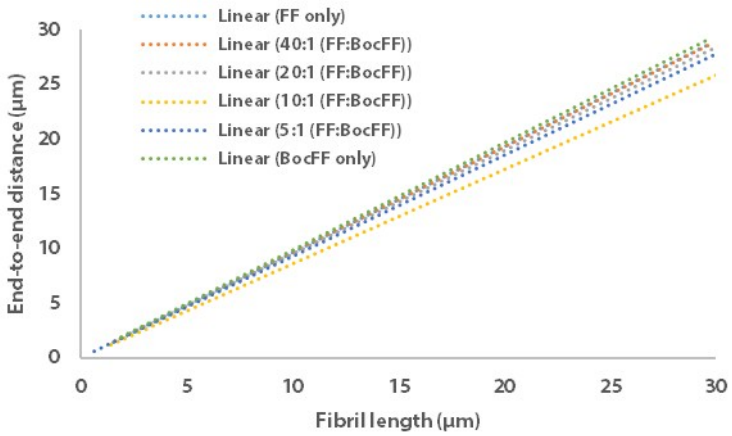

Figure S1: Linear trend lines fitted to show the relationship between end to end distance and fibril length as measured by AFM. Larger deviations from a 1:1 relationship reflect decreased rigidity (*e.g.,* 10:1 sample)

Persistence length (Lp) calculations were attempted by two models (results shown Table S2). The first attempt was using the following equation from Bortolini *et al.*[1]:

$$Lp = \frac{E\,I}{K_B\,T}$$

Where E is the average Young's Modulus obtained from table 1 (main text), I is the moment of inertia (using the fibril diameter measured from AFM height images, assuming a solid rod cross-section), K_B is the Boltzmann constant and T is room temperature.

The second attempt used a 2D worm-like chain model from Jordens *et al.*[2] and Bortolini *et al.*[1] as follows:

$$R^2 = 4LLp\left(1 - \frac{2Lp}{L}\left(1 - e^{\left(-\frac{L}{2Lp}\right)}\right)\right)$$

R^2 was plotted against L so that Lp could be fitted using a non-linear regression model in Graphpad Prism v7 (Figure S2). The results obtained were not meaningful in the context of the current datasets. Interaction between nanotube components, interactions between nanotubes, and uncertainty about the interior nature of the assemblies, all contribute to errors in using these models for calculating persistence length. As such, we have chosen to analyse the trends in the non-absolute term 'rigidity' when describing these co-assemblies.

Table S2: Persistence lengths calculated by two models

	calculated from Lp = EI/K_BT		*calculated from fit of WLC model*		
Sample	**Lp (m)**	**Standard Error (m)**	**Lp (m)**	**Standard Error (m)**	**R^2 of fit**
FF solely	48061.79	44049.8	9.85E+13	3.1E+13	0.99
40:1 (FF:BocFF)	26181.96	20718.3	2.80E+13	4.7E+12	0.97
20:1 (FF:BocFF)	130.22	39.7	3.41E+13	7.9E+12	0.96
10:1 (FF:BocFF)	199.56	116.8	8.69E+12	1.1E+12	0.89
5:1 (FF:BocFF)	288.77	276.0	1.72E+13	2.0E+12	0.96
BocFF solely	363.93	202.7	1.23E+14	8.2E+13	0.99

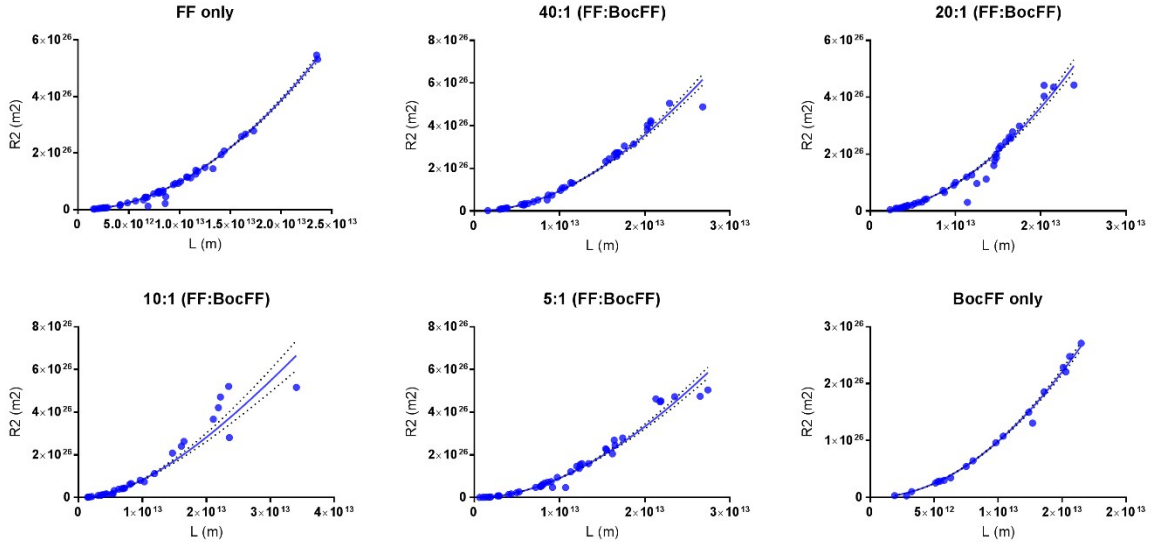

Figure S2: Plots of R^2 versus L and fits thereof using a 2D WLC model to find Lp.

AFM mechanical data; Young's Modulus Calculation:

Force data was analyzed using the Asylum Research Elastic Fitting module (found in the master force panel). The model used was the JKR model (Johnson, Kendall and Roberts), fitted to the retract curves to obtain the reduced Young's Modulus as output by the Asylum software. Tip radius was estimated using a PS:LDPE calibration standard. Lever sensitivity and spring constant were initially estimated using the Asylum "GetReal" feature, then calibrated after the experiments (and prior to analysis) on clean Silicon using the InVOLS and thermal method, respectively. Tip and sample poisson were kept as per the default values in the software; 0.17 and 0.33, respectively.

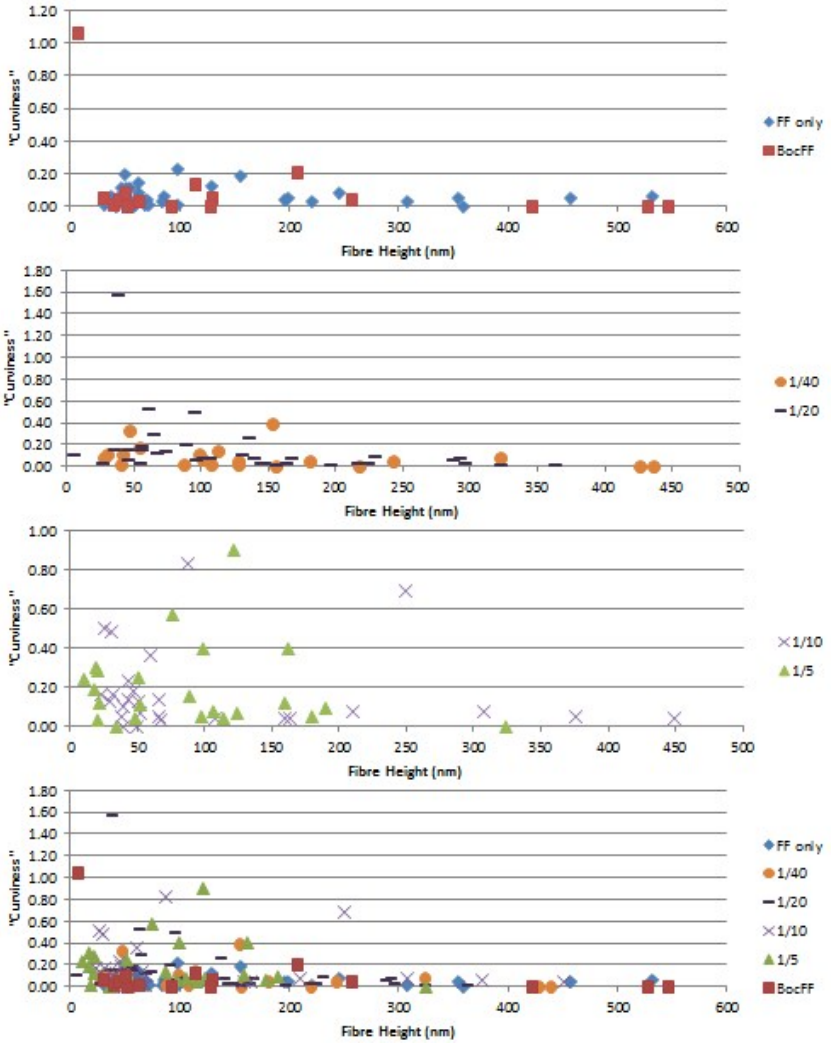

Figure S3: Curviness versus fiber diameter measured by AFM

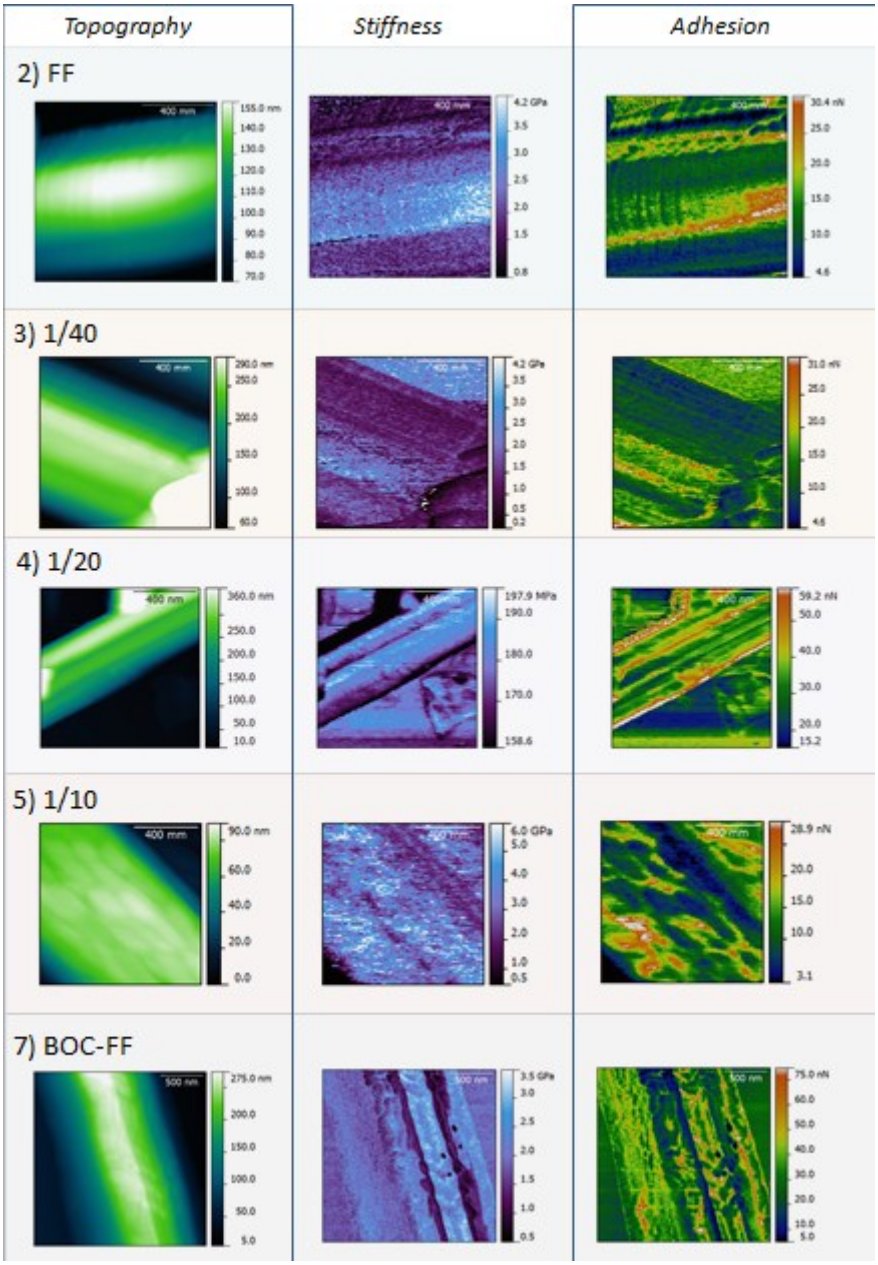

Figure S4: QNM mode AFM images on fiber assemblies

References

1 C. Bortolini, N. C. Jones, S. V. Hoffmann, C. Wang, F. Besenbacher and M. Dong, *Nanoscale*, 2015, **7**, 7745–7752.
2 S. Jordens, L. Isa, I. Usov and R. Mezzenga, *Nat. Commun.*, 2013, **4**, 1917.