Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Exquisite regulation of supramolecular polymers in water: Chain stoppers control length, polydispersity and viscoelasticity

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Abbreviations: **TAP**, 2,4,6-triaminopyrimidine; **CyCo6**, 1-(5-Carboxypentyl)-1,3,5-triazin-2,4,6-trion; **TMPyP**, 5,10,15,20-tetra(*N*-methyl-4-pyridyl)porphine; **EB**, Ethidium Bromide.

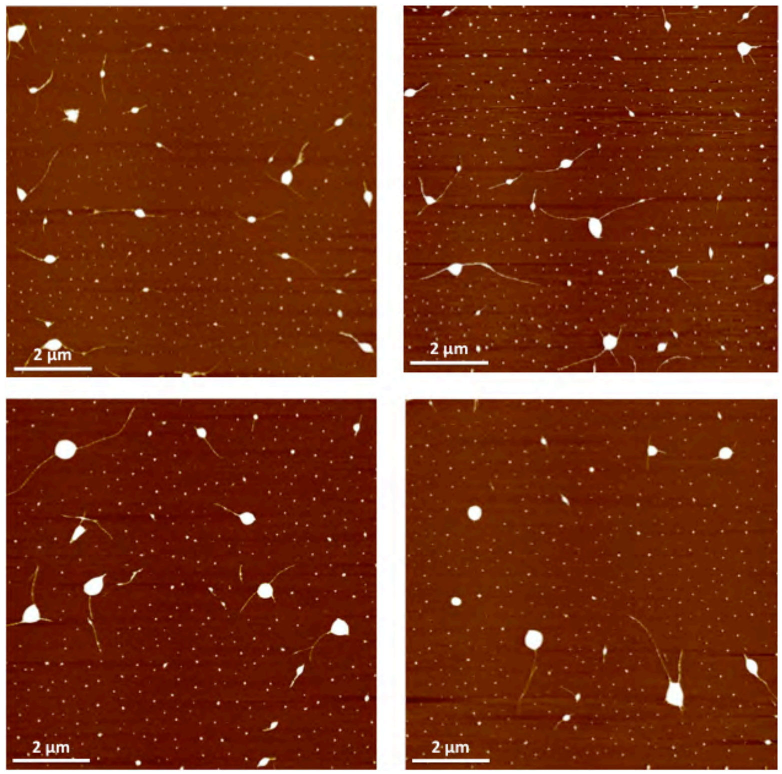

Fig. S1. Example AFM images of **TAP-CyCo6** supramolecular polymers in a sample containing 30 mM each monomer and 7.5 µM **TMPyP**.

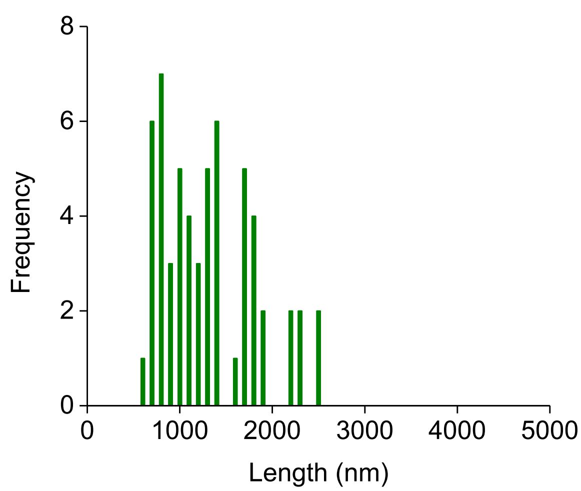

Fig. S2. Histogram of **TAP-CyCo6** supramolecular polymer lengths measured in AFM images of a sample containing 30 mM of each monomer 7.5 µM **TMPyP**.

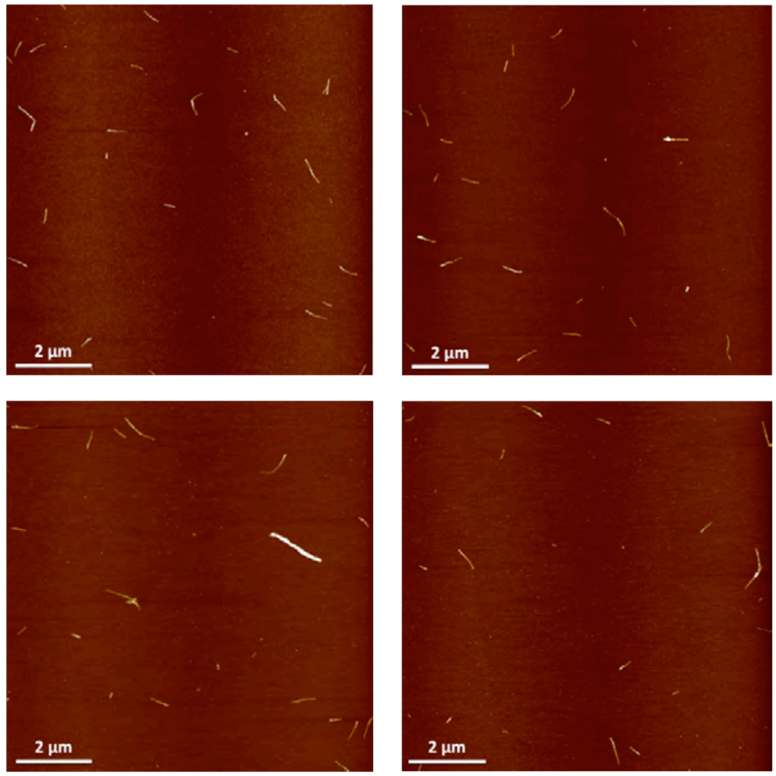

Fig. S3. Example AFM images of **TAP-CyCo6** supramolecular polymers in a sample containing 30 mM each monomer and 15 µM **TMPyP**.

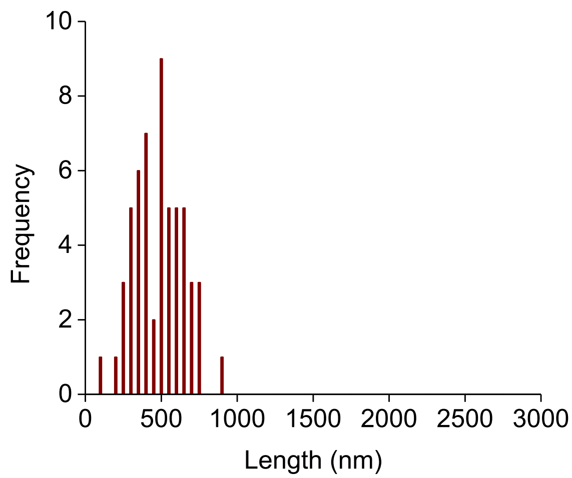

Fig. S4. Histogram of **TAP-CyCo6** supramolecular polymer lengths measured in AFM images of a sample containing 30 mM of each monomer 15 µM **TMPyP**.

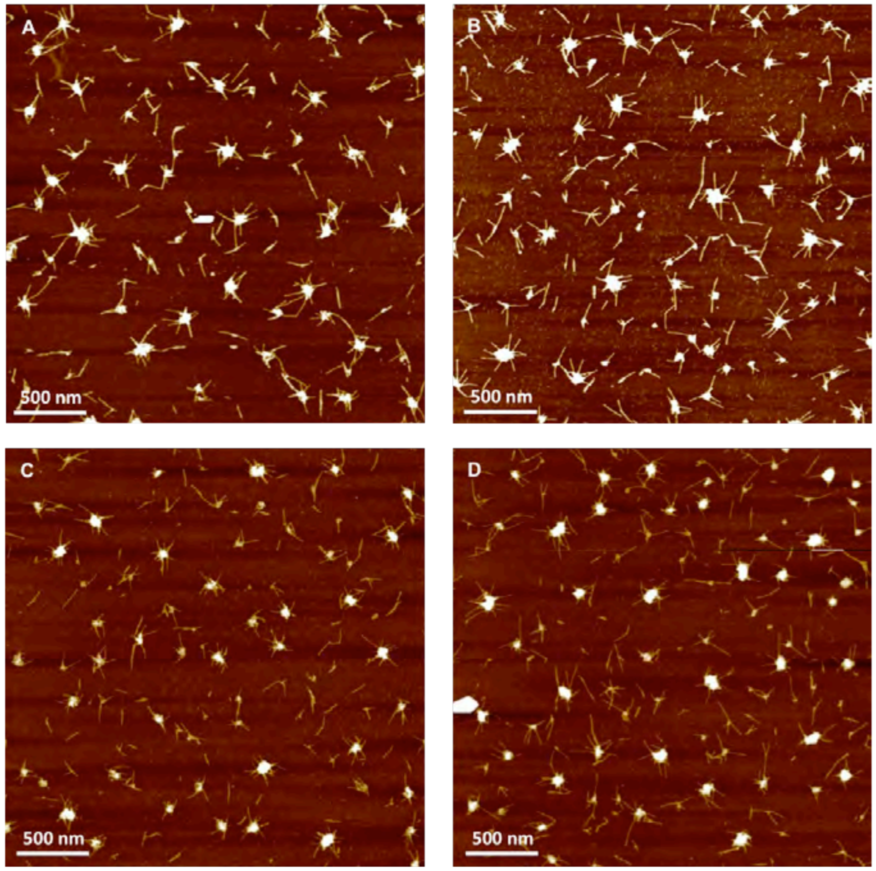

Fig. S5. Example AFM images of **TAP**-**CyCo6** supramolecular polymers in a sample containing 30 mM each monomer and 31 μM **TMPyP**.

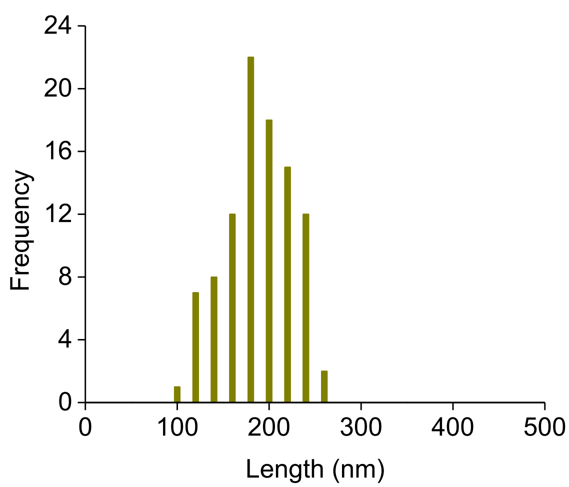

Fig. S6. Histogram of **TAP**-**CyCo6** supramolecular polymer lengths measured in AFM images of a sample containing 30 mM of each monomer 31 μM **TMPyP**.

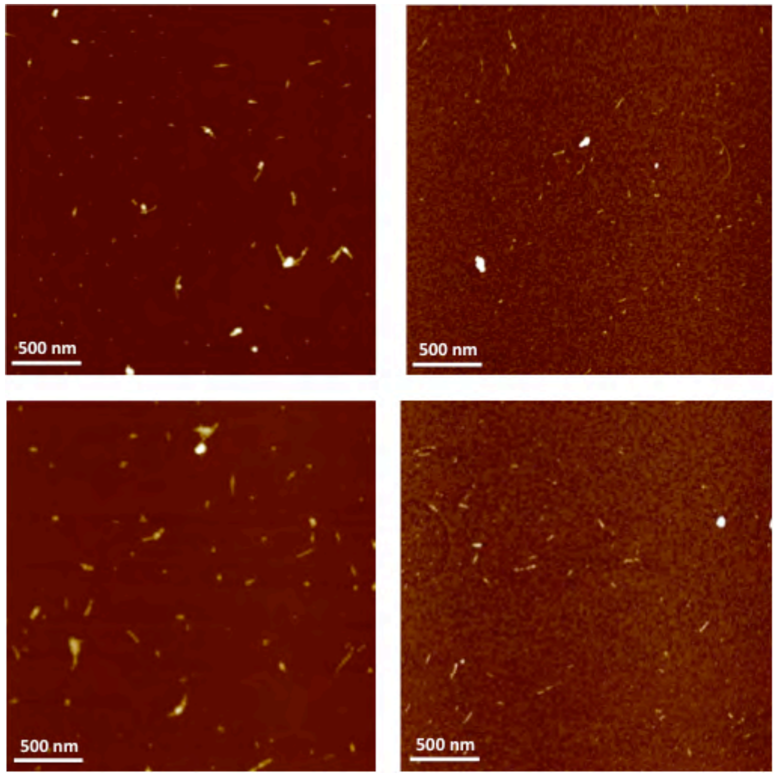

Fig. S7. Example AFM images of **TAP-CyCo6** supramolecular polymers in a sample containing 30 mM each monomer and 62 μM **TMPyP**.

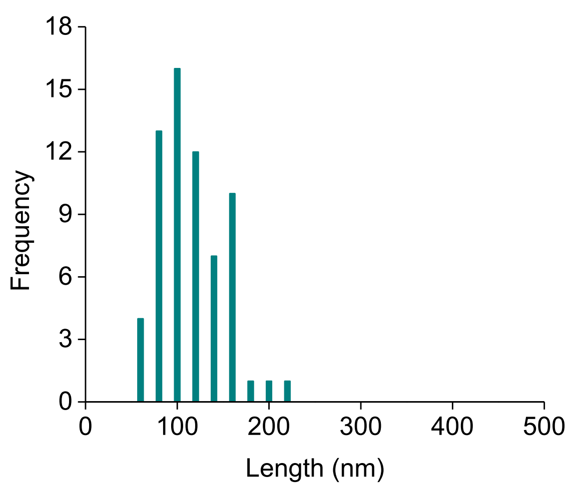

Fig. S8. Histogram of **TAP-CyCo6** supramolecular polymer lengths measured in AFM images of a sample containing 30 mM of each monomer 62 μM **TMPyP**.

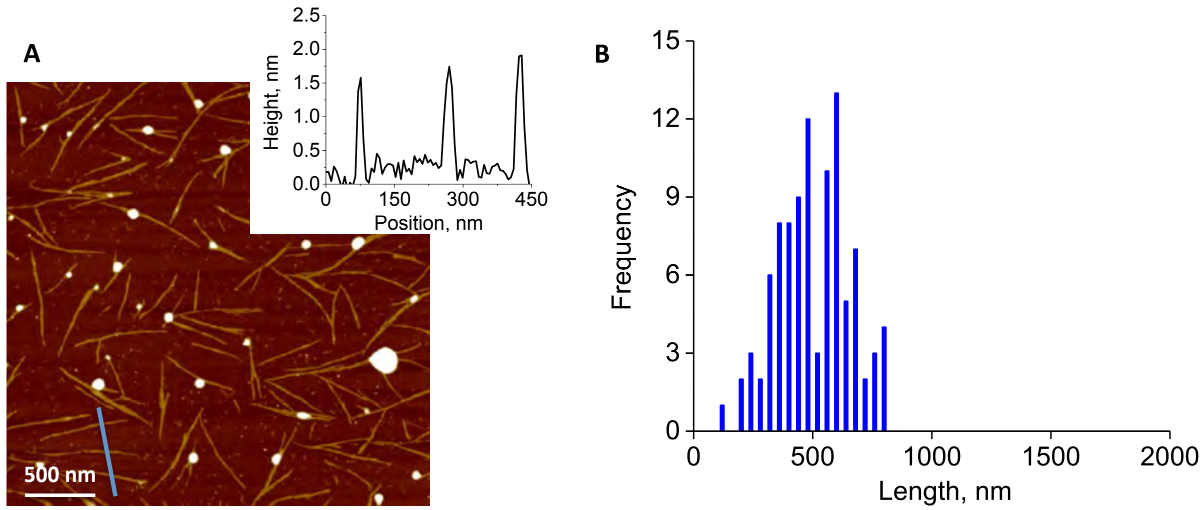

Fig. S9. Example AFM images and histogram of measured lengths of **TAP-CyCo6** supramolecular polymers in a sample containing 30 mM each monomer and 1 mM **EB**. Inset shows heights measured along blue line indicated in main panel.

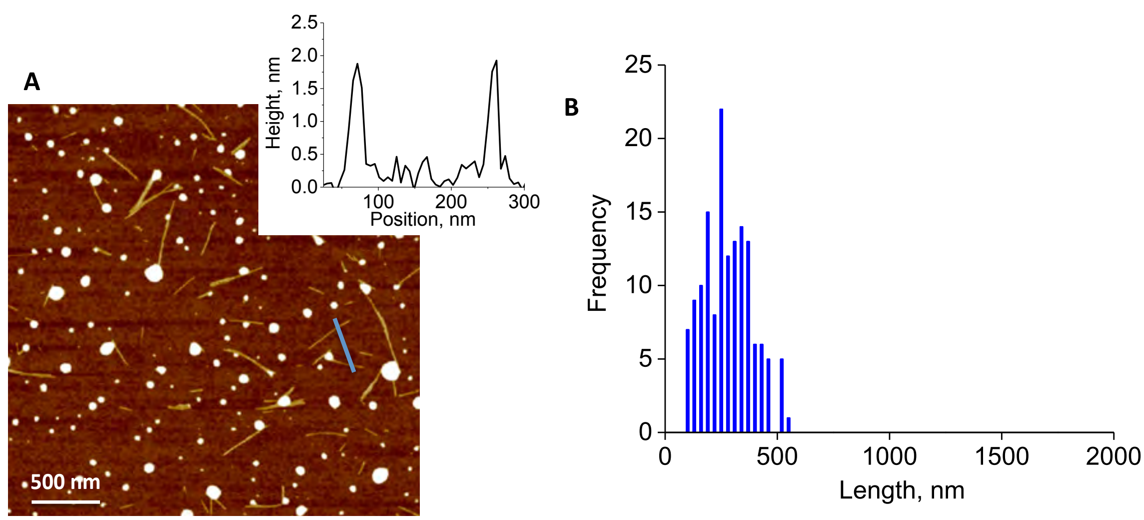

Fig. S10. Example AFM images and histogram of measured lengths of **TAP-CyCo6** supramolecular polymers in a sample containing 30 mM each monomer and 2.5 mM **EB**. Inset shows heights measured along blue line indicated in main panel.

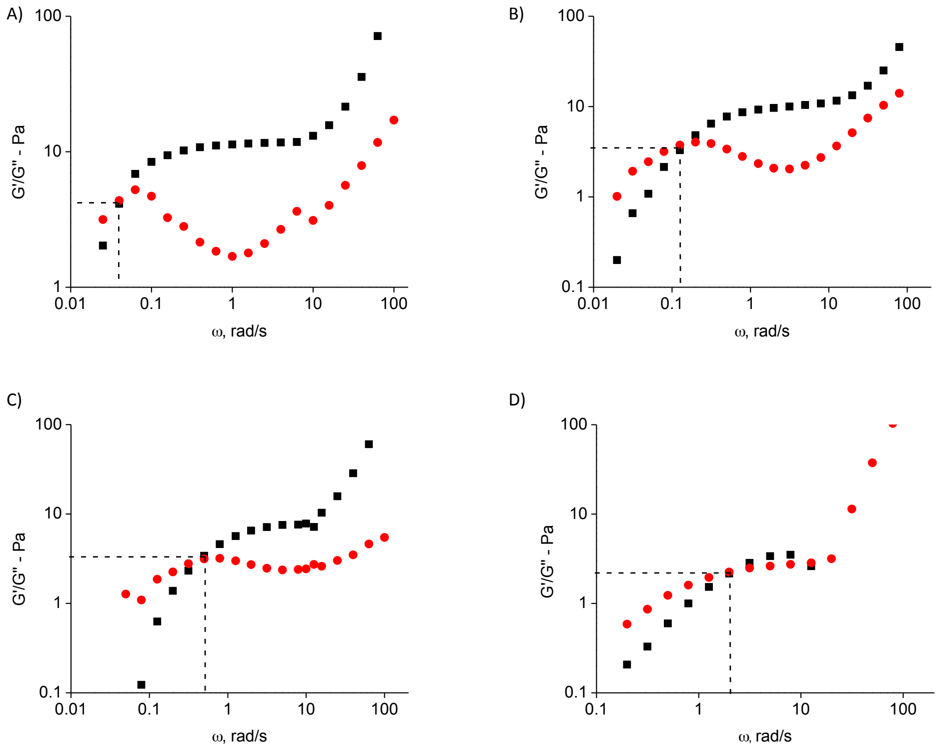

Fig. S11. Frequency dependent dynamic shear storage modulus (G', squares) and loss modulus (G", circles) of the **TAP-CyCo6** supramolecular assembly (30 mM each monomer) in the presence of (A) 0.062, (B) 0.125, (C) 0.25 and (D) 0.5 mM **EB**.

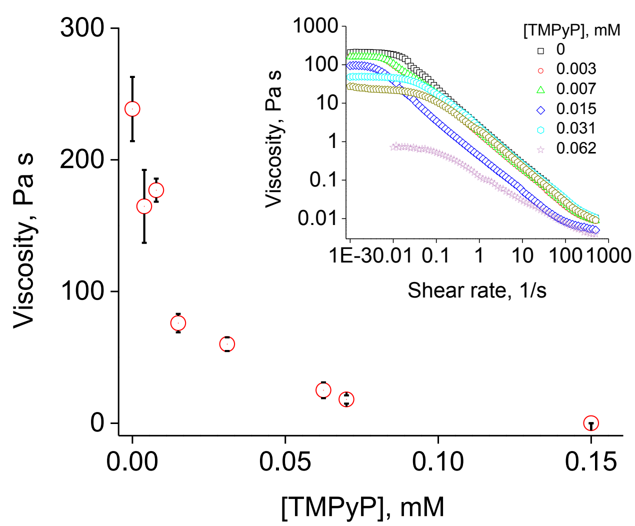

Fig. S12. Measured values of low shear viscosity of **TAP-CyCo6** hydrogels for a sample containing 30 mM in each monomer and various concentrations of **TMPyP** concentrations. These results corroborate the decrease in length of fibers observe by AFM. The dependence of shear rate on viscosity is shown as inset.

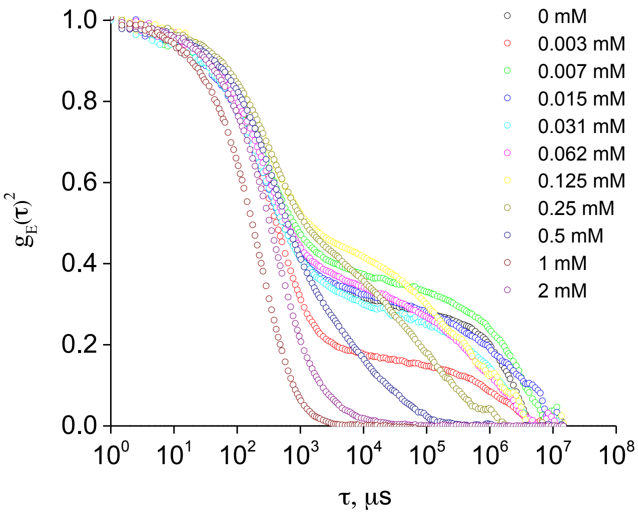

Fig. S13. Electric field autocorrelation functions for a **TAP-CyCo6** sample 30 mM in each monomer, in the absence and presence of various concentrations of ethidium bromide (**EB**) (0.003 to 2 mM).

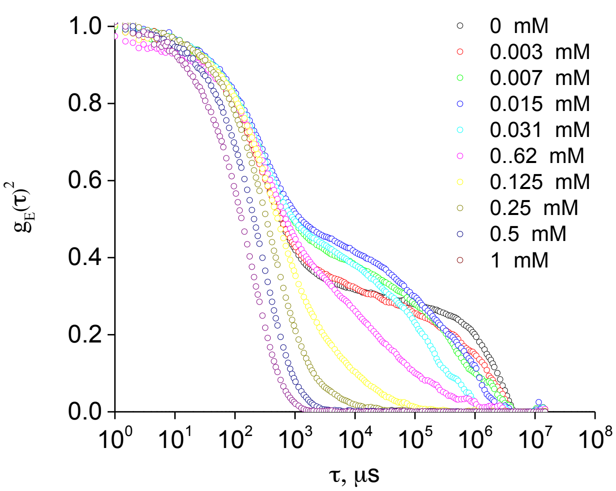

Fig. S14. Electric field autocorrelation functions for a **TAP-CyCo6** sample 30 mM in each monomer, in the absence and presence of various concentrations of **TMPyP** (0.003 to 1 mM).

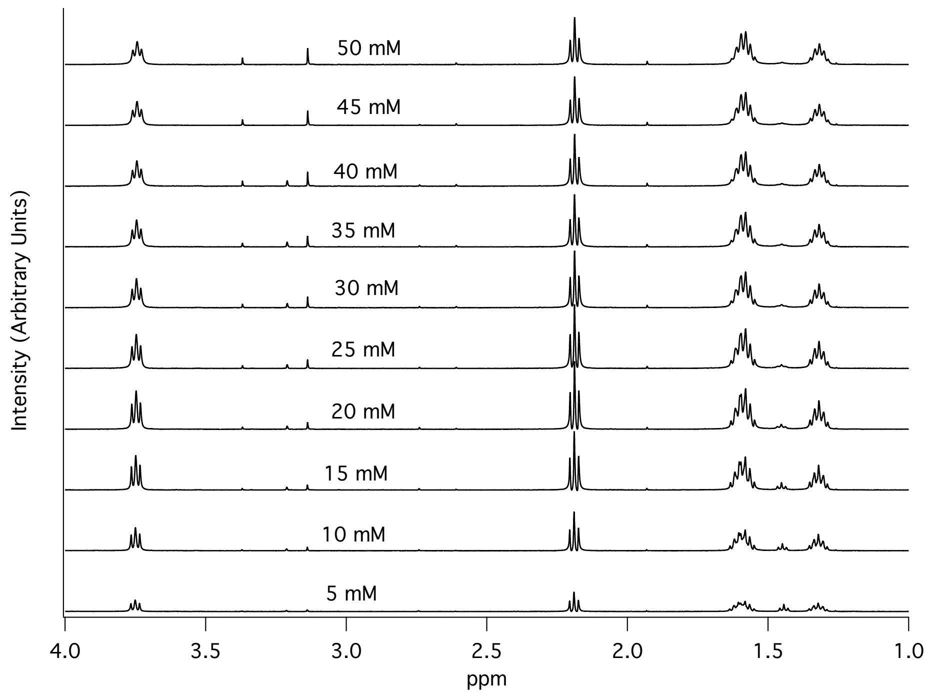

Fig. S15. ^{1}H NMR spectra of a **TAP-CyCo6** sample as a function of monomer concentration. Both monomers were present at concentrations shown.

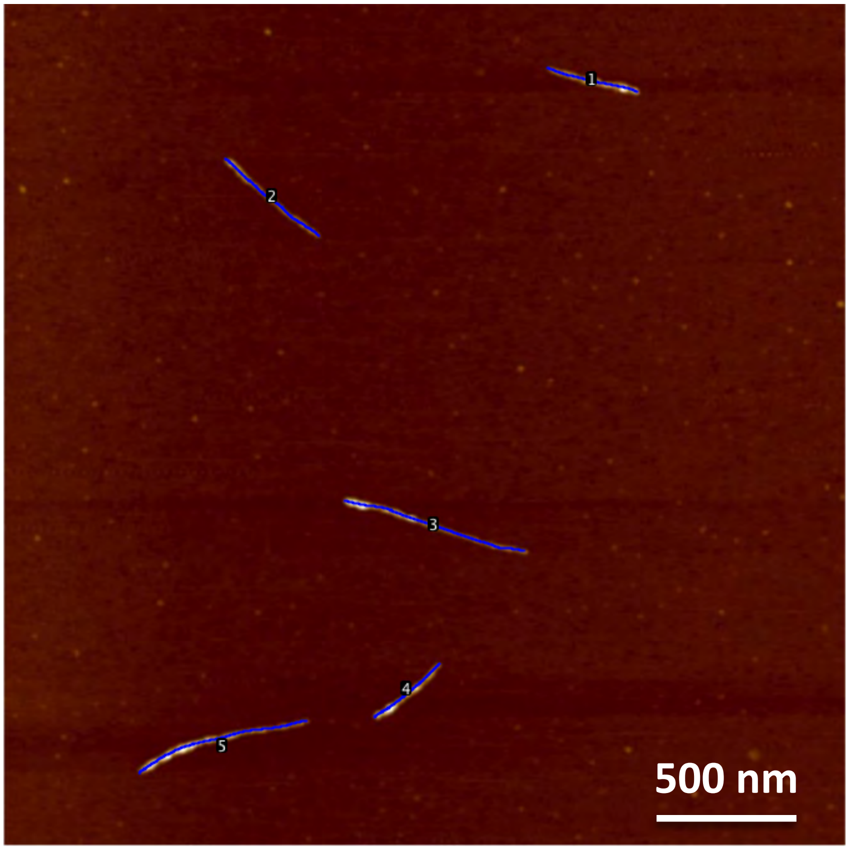

Fig. S16. Representative atomic force microscopic (AFM) images of self-assembled **TAP-CyCo6** supramolecular polymers in the presence of **TMPyP** (A, 0.008; B, 0.015; C, 0.031; D, 0.062 mM) showing the traces of contour length measuring using image J software.

2. Calculation of association constant from fluorescence

The fluorescence intensity of **TMPyP** was quenched by the addition of **TAP**-**CyCo6** assemblies (inset to Fig. 7 of main text). The fluorescence intensity at 718 nm was plotted against the hexad concentration and fit with the following the equation (Fig. 7 of main text):

$$\mathcal{F}_{obs} = \mathcal{F}_{\mathbf{TMPyP-CyCo6}} * [\mathbf{TMPyP - CyCo6}] + \mathcal{F}_{\mathrm{TMPyP-Hex}} * [\mathbf{TMPyP} - \mathrm{Hex}]$$

Where [**TMPyP**-**CyCo6**] and [**TMPyP**-Hex] were governed by the equilibrium equation:

[**TMPyP**-**CyCo6**] + [Hexad] <-> [**TMPyP**-Hex] + [**CyCo6**]

Explicitly,

$$\mathcal{F}_{obs} = \mathcal{F}_{\mathbf{TMPyP-CyCo6}} \left(\mathrm{t}\mathbf{TMPyP} - \left(\frac{\mathrm{t}\mathbf{TMPyP}}{1 + \frac{\mathrm{CyCo6}_{sol}}{K\mathrm{a} * \mathrm{Hexad}}} \right) \right) + \mathcal{F}_{\mathrm{Pro-Hex}} * \left(\frac{\mathrm{t}\mathbf{TMPyP}}{1 + \frac{\mathbf{CyCo6}_{sol}}{K\mathrm{a} * \mathrm{Hexad}}} \right)$$

Where $\mathcal{F}_{\mathrm{TMPyP-CyCo6}}$ is the fluorescence intensity at 718 nm when all **TMPyP** is bound to **CyCo6** in solution, $\mathcal{F}_{\mathbf{TMPyP}-\mathrm{Hex}}$ is the fluorescence intensity at 718 nm when all **TMPyP** is bound to hexad assemblies, tT**MPyP** is the total concentration of **TMPyP** in the sample, $\mathbf{CyCo6}_{sol}$ is the concentration of **CyCo6** in solution (not in assemblies), K_a is the equilibrium constant, and Hexad is the concentration of **TAP**-**CyCo6** hexad assemblies in the sample. For the spectra shown in Fig. 7 of the main text, $\mathcal{F}_{\mathrm{TMPyP-CyCo6}}$ was taken directly from the 10 mM **TAP**/**CyCo6** spectra, which does not have assembled hexads. t**TMPyP** was 31 μM for all samples. $\mathbf{CyCo6}_{sol}$ was 15 mM (the **TAP**/**CyCo6** minimal assembly concentration, MAC). Hexad was calculated for each spectra based on the MAC and the fact that each hexad contains three **TAP**/**CyCo6** monomers. With these values, an RMS-best-fit of the equation given above was obtained data points in Fig. 7 of the main text by allowing $\mathcal{F}_{\mathbf{TMPyP}-\mathrm{Hex}}$ and Keq to vary during RMS minimization. A best fit was obtained with K_a = 130 M^{-1} .

3. Considerations on the K_a of EB binding to TAP-CyCo6 polymers

The calculated amount of **EB** bound to the **TAP**-**CyCo6** polymers corresponds to an apparent K_a of **EB** for **TAP**-**CyCo6** hexads in the range of 0.7 to 2 M^{-1}, a range of values that is substantially less than the apparent K_a of 130 M^{-1} that we determined for the association of **TMPyP** for **TAP**-**CyCo6** hexads. Unlike **TMPyP**, we did not observe a unique spectroscopic signal with which to determine the association constant of **EB** with **TAP**-**CyCo6** hexads. The lack of observable change in the fluorescence of 1 mM **EB** in the presence of 5 mM **TAP**-**CyCo6** hexads is understandable given that only 0.07 to 0.2% of total **EB** in the sample is bound to the polymers. Nevertheless, our observation that increasing the concentration of **EB** decreases the length of the supramolecular polymers is qualitatively consistent with this equilibrium model. For example, we have measured an average length of **TAP**-**CyCo6** polymers in the presence of 2.5 mM **EB** to be 270 nm (Fig. S12). Based on our measurements of average **TAP**-**CyCo6** polymer lengths in the presence of 1 mM **EB**, our equilibrium model predicts an average polymer length of 192 nm when 2.5 mM **EB** is added. This value, being within 30% of the measured value, is again considered to represent good agreement between the model and experiment considering the errors intrinsic to measuring the length of supramolecular polymers that have a strong propensity to form lateral contacts.

4. Prediction of hexad assembly polydispersity in the presence of NCAs.

The equation for polymer dispersity based on this model can be easily derived as,

$$\text{Dispersity} \equiv Đ_M = \frac{M_w}{M_n}$$

$$M_w = \frac{\sum_{i=1} N_i M_i^2}{\sum_{i=1} N_i M_i}$$

$$M_n = \frac{\sum_{i=1} N_i M_i}{\sum_{i=1} N_i}$$

$$Đ_M = \frac{(\sum_{i=1} N_i)(\sum_{i=1} N_i M_i^2)}{(\sum_{i=1} N_i M_i)^2}$$

$$\sum_{i=1} N_i = N_t \; (total\ monomers\ in\ system)$$

$$N_i = \frac{N_t}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2\sigma^2}(i-\mu)^2}$$

$i\ is\ in\ units\ of\ monomer\ molecular\ weight. \mu\ is\ molecular\ weight\ of\ polymer\ with\ mean\ (most\ common) length.$

$\sigma = \sqrt{\mu}\ according\ to\ statistical\ mechanics, standard\ deviation\ is\ square\ root\ of\ mean\ value.$

$M_i = i, because\ M\ and\ i\ have\ units\ of\ monomer\ molecular\ weight, so\ that\ the\ ith\ polymer\ is\ of\ mw\ i.$

$$Đ_M = \frac{N_t(\sum_{i=1} \frac{N_t}{\sqrt{2\pi\mu}} e^{-\frac{1}{2\mu}(i-\mu)^2} i^2)}{(\sum_{i=1} \frac{N_t}{\sqrt{2\pi\mu}} e^{-\frac{1}{2\mu}(i-\mu)^2} i)^2}$$

$$Đ_M = \frac{\sqrt{2\pi\mu} \sum_{i=1} e^{-\frac{1}{2\mu}(i-\mu)^2} i^2}{(\sum_{i=1} e^{-\frac{1}{2\mu}(i-\mu)^2} i)^2}$$

By integrating top and bottom summations from *i* = 1 to 5*μ

$$Đ_M\ (\mu) = \frac{\sqrt{2\pi\mu}((\mu-\mu^2)e^{\frac{(\mu-1)^2}{2\mu}} - 6\mu^2 e^{-8\mu} + \sqrt{\frac{\pi}{2}}\left(\mu^{\frac{3}{2}} + \mu^{\frac{5}{2}}\right)(Erf\left(\frac{\mu-1}{\sqrt{2\mu}}\right) + Erf(2\sqrt{2\mu}))}{(\mu e^{-8\mu}\left(e^{\frac{15\mu}{2}} - 1\right) + \mu^{\frac{3}{2}}\sqrt{\frac{\pi}{2}}(Erf\left(\sqrt{\frac{\mu}{2}}\right) + Erf(2\sqrt{2\mu})))^2}$$

For polymers centered at μ = 500 monomers, $Đ_M$= 1.002.

Table S1. Polymer contour length values measured from AFM images						
	Measured Length, nm					
Chain stopper	**TMPyP**				**EtBr**	
Concentration, mM	0.008	0.015	0.031	0.062	1	2.5
	1888	260	163	104	113	363
	926	597	128	76	191	372
	1208	286	213	92	194	218
	1377	298	206	74	214	344
	1353	333	236	61	231	147
	605	479	114	77	239	193
	1609	481	142	52	267	179
	735	619	211	83	272	195
	2218	495	109	85	287	173
	1249	337	136	54	300	244
	1648	364	182	61	301	383
	1219	626	184	153	307	226
	591	585	144	86	310	243
	1387	559	151	72	310	326
	2438	508	181	113	327	318
	1156	886	226	72	332	365
	1748	668	160	96	336	444
	1051	633	200	65	340	121
	1326	401	170	69	343	270
	1741	384	192	112	347	88
	1006	458	172	151	352	87
	1842	571	125	104	353	277
	1153	466	149	85	362	97
	1572	399	176	71	364	268
	1262	684	198	67	367	158
	931	330	177	116	372	324
	602	453	210	142	375	111
	637	342	175	120	379	201
	609	386	211	113	390	270
	626	313	194	141	394	357
	830	396	141	125	407	355
	770	554	102	93	417	327
	601	702	233	71	417	379
	729	520	227	91	421	231
	720	615	168	115	425	359
	1070	460	161	140	428	105
	1373	267	186	86	431	179
	1771	615	189	159	434	239
	2235	259	154	115	438	234
	1741	545	145	160	442	167
	1152	377	207	152	454	399
	859	716	183	215	454	433
	1230	363	197	179	455	395
	781	683	202	127	458	415
	700	710	145	96	460	340
	768	486	180	92	465	334
	1017	231	100	105	467	75
	870	540	86	193	473	412
	999	231	111	132	473	165
	2122	185	141	125	476	199
	1644	340	135	89	479	427

	1668	77	171	111	489	165
	2476	432	223	148	493	288
	1255	548	171	120	518	155
	1640	245	104	90	522	345
	1375	463	182	79	524	340
	2162	544	184	58	524	158
	995	407	205	98	531	303
	1260	413	255	111	534	187
	923	496	234	154	534	310
			177		541	156
			235		546	242
			188		550	421
			255		551	308
			232		562	224
			145		563	97
			185		566	272
			133		569	353
			166		577	281
			232		581	136
			166		583	79
			181		586	293
			165		592	127
			179		596	235
			174		596	129
			206		597	454
			206		599	273
			200		601	177
			219		605	505
			137		612	245
			141		624	520
			179		626	547
			234		649	160
			180		650	324
			189		650	270
			126		652	348
			136		654	333
			210		658	253
			225		667	228
			165		692	225
			196		708	125
			171		721	291
			165		733	495
			116		745	351
			163		762	361
			205		772	172
			231		776	145
			149		797	150
Avg. Length, nm*	1257	460	177	107	484	266
Std. dev., nm	503	157	37	36	149	111
Calculated polydispersity	1.15	1.11	1.04	1.11	1.09	1.17
*Average length values reported in main text and SI are rounded to nearest 10 nm.						