Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Hybrid supramolecular gels of Fmoc-F/halloysite nanotubes: systems for sustained release of camptothecin

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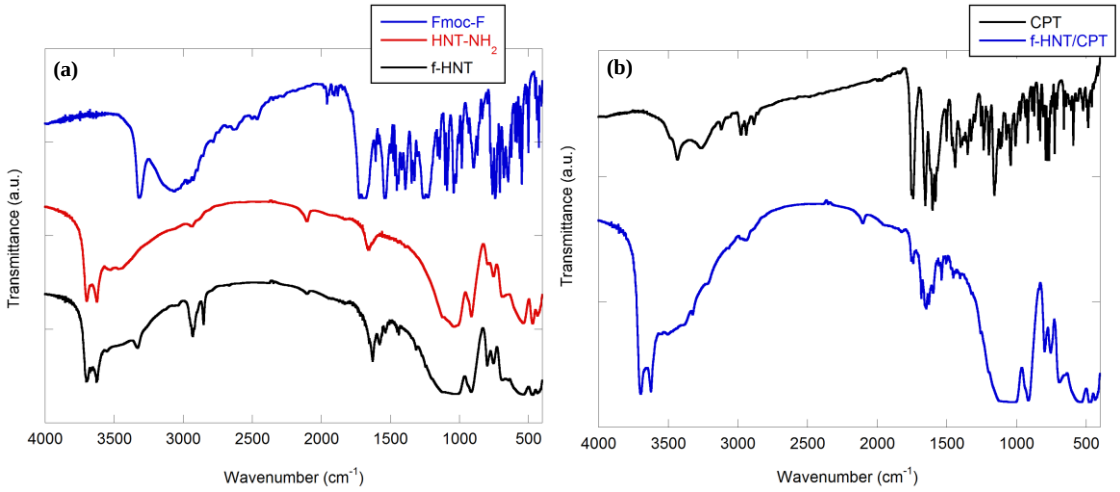


Figure S1. FTIR spectra of **(a)** HNT-NH_2, Fmoc-F and f-HNT and **(b)** CPT and f-HNT/CPT complex.

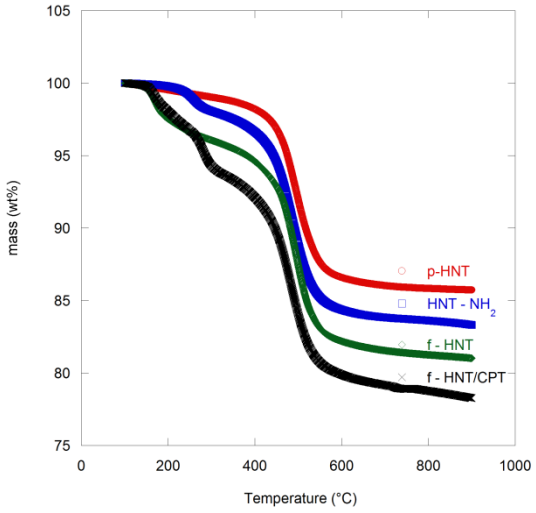


Figure S2. Thermogravimetric curves of pristine and modified Halloysite nanotubes.

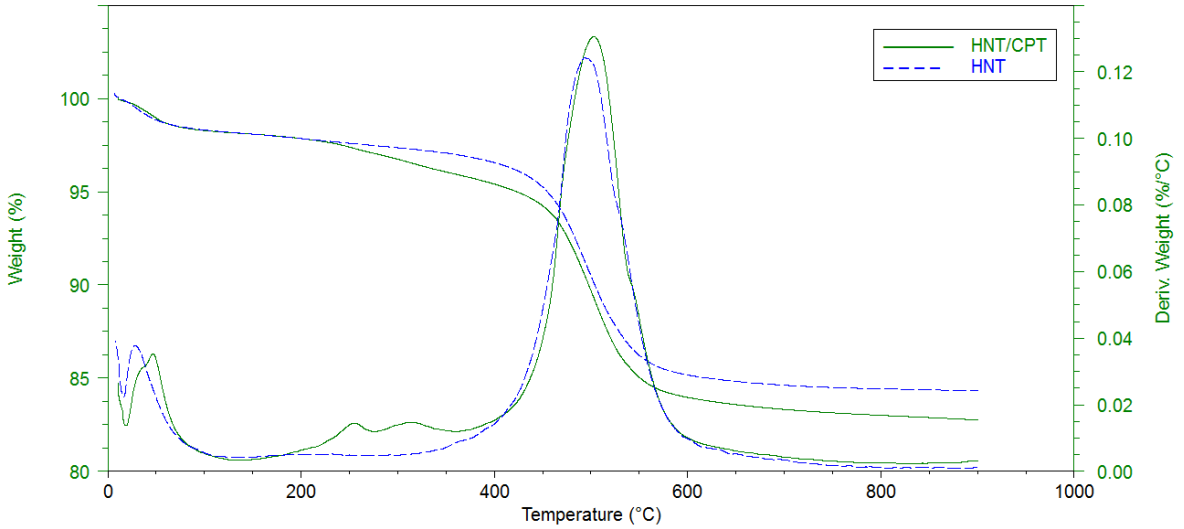


Figure S3. Thermogravimetric and derivative thermogravimetric curves of p-HNT and HNT/CPT hybrid.

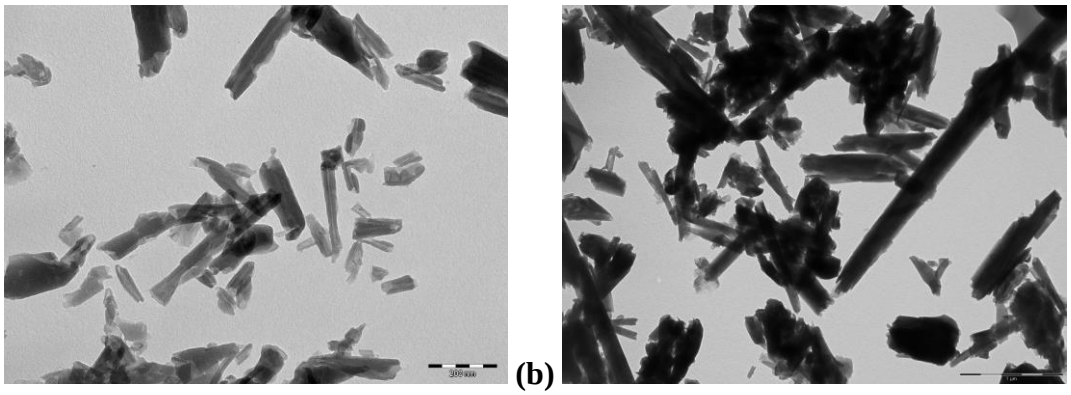


Figure S4. TEM images of (a) pristine HNT and (b) f-HNT.

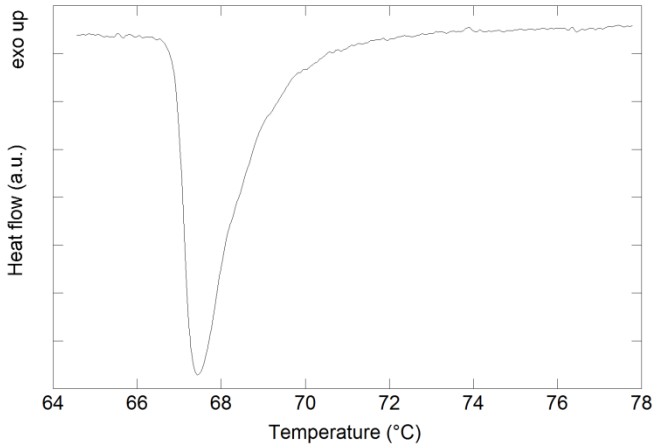
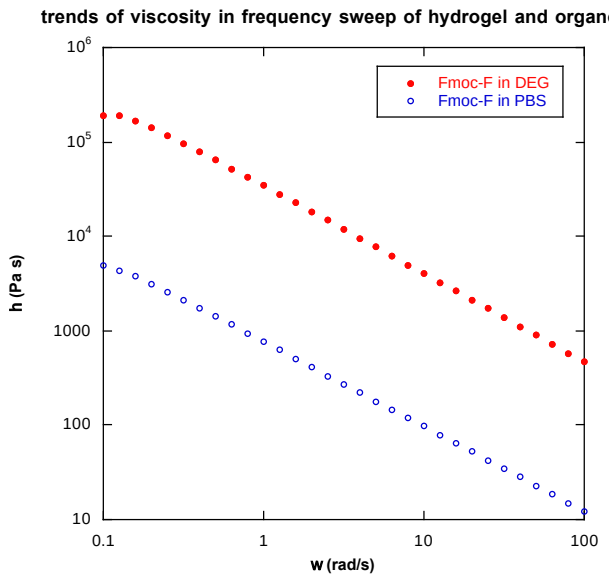
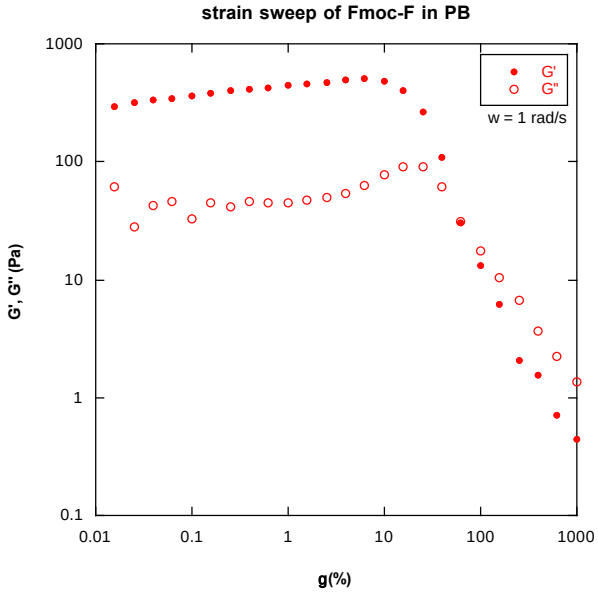
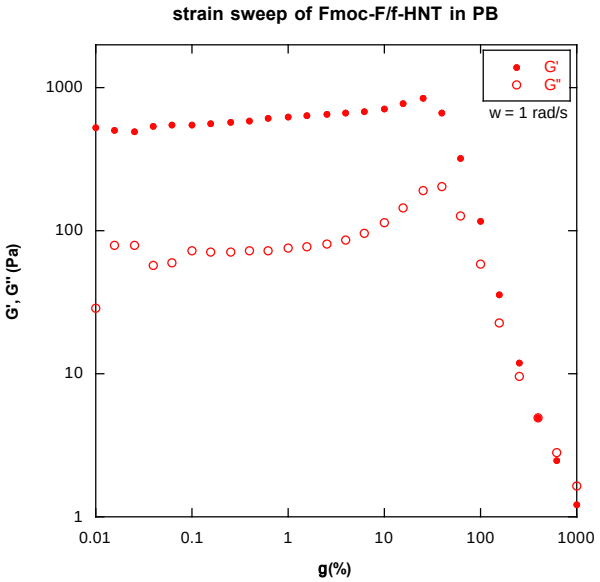
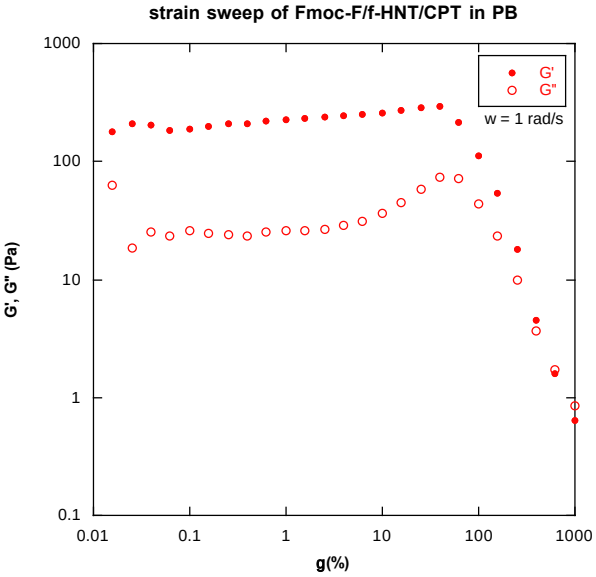


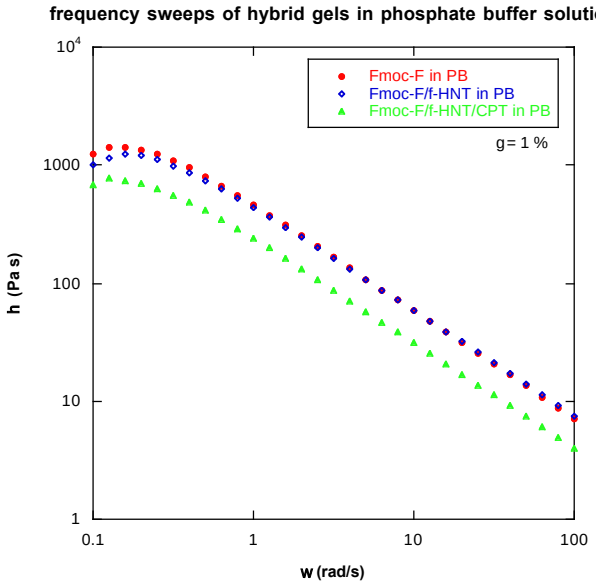
Figure S5. µ-DSC thermogram of Fmoc-F hydrogel in PB.

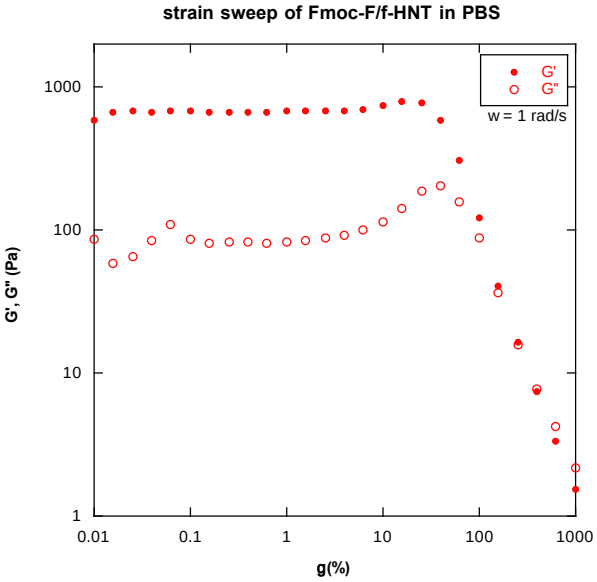

trends of viscosity in frequency sweep of hydrogel and organogel
Fmoc-F in DEG
Fmoc-F in PBS
h (Pa s)
w (rad/s)


strain sweep of Fmoc-F in PB
G'
G"
w = 1 rad/s
G', G" (Pa)
g(%)


strain sweep of Fmoc-F/f-HNT in PB
G'
G"
w = 1 rad/s
G', G" (Pa)
g(%)


strain sweep of Fmoc-F/f-HNT/CPT in PB
G'
G"
w = 1 rad/s
G', G" (Pa)
g(%)


frequency sweeps of hybrid gels in phosphate buffer solution
Fmoc-F in PB
Fmoc-F/f-HNT in PB
Fmoc-F/f-HNT/CPT in PB
g= 1 %
h (Pa s)
w (rad/s)


strain sweep of Fmoc-F/f-HNT in PBS
G'
G"
w = 1 rad/s
G', G" (Pa)
g(%)

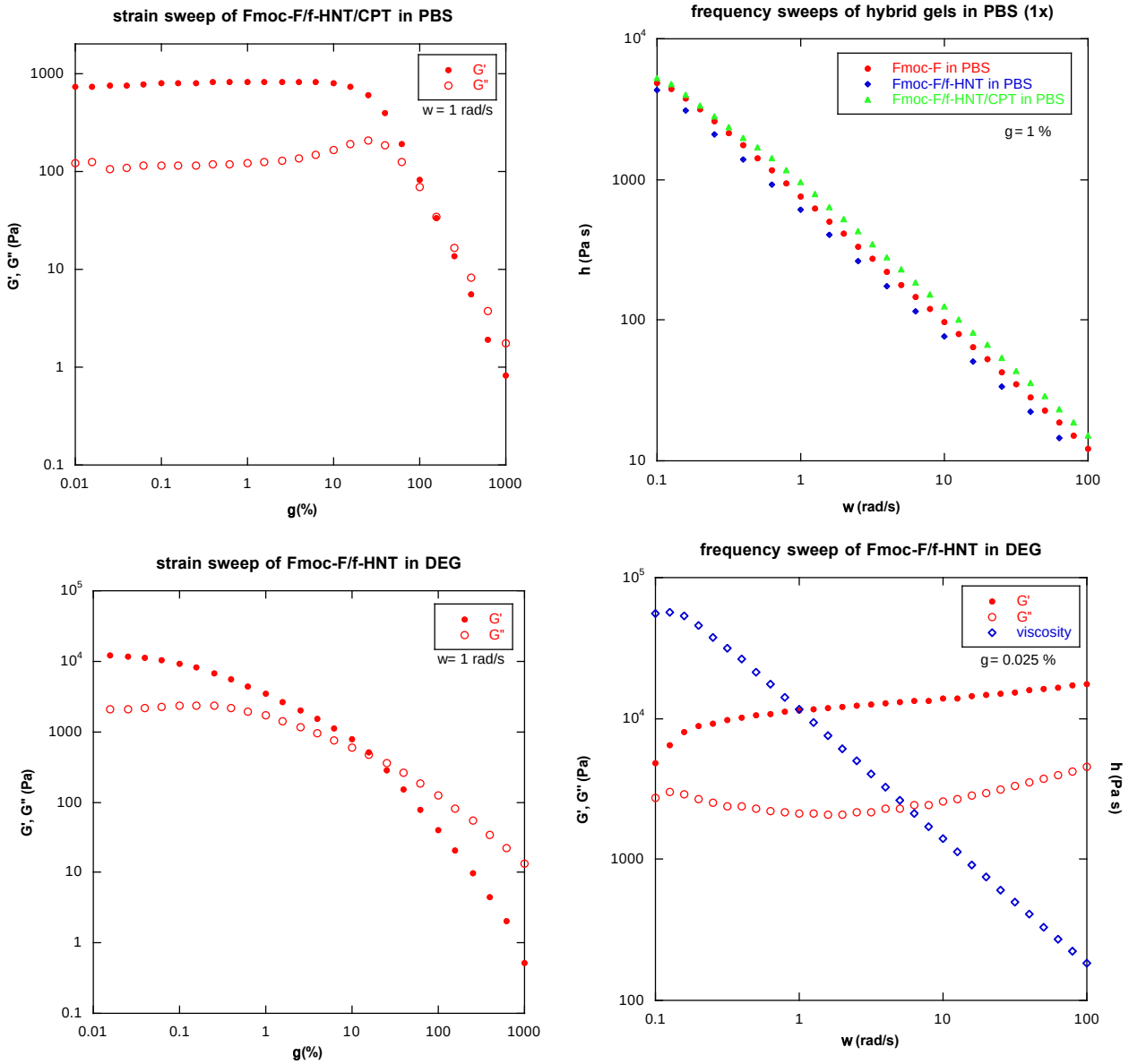


Figure S6. Variation of G′, G″ and viscosity of pure and hybrid gels in strain sweeps and frequency sweeps experiments.

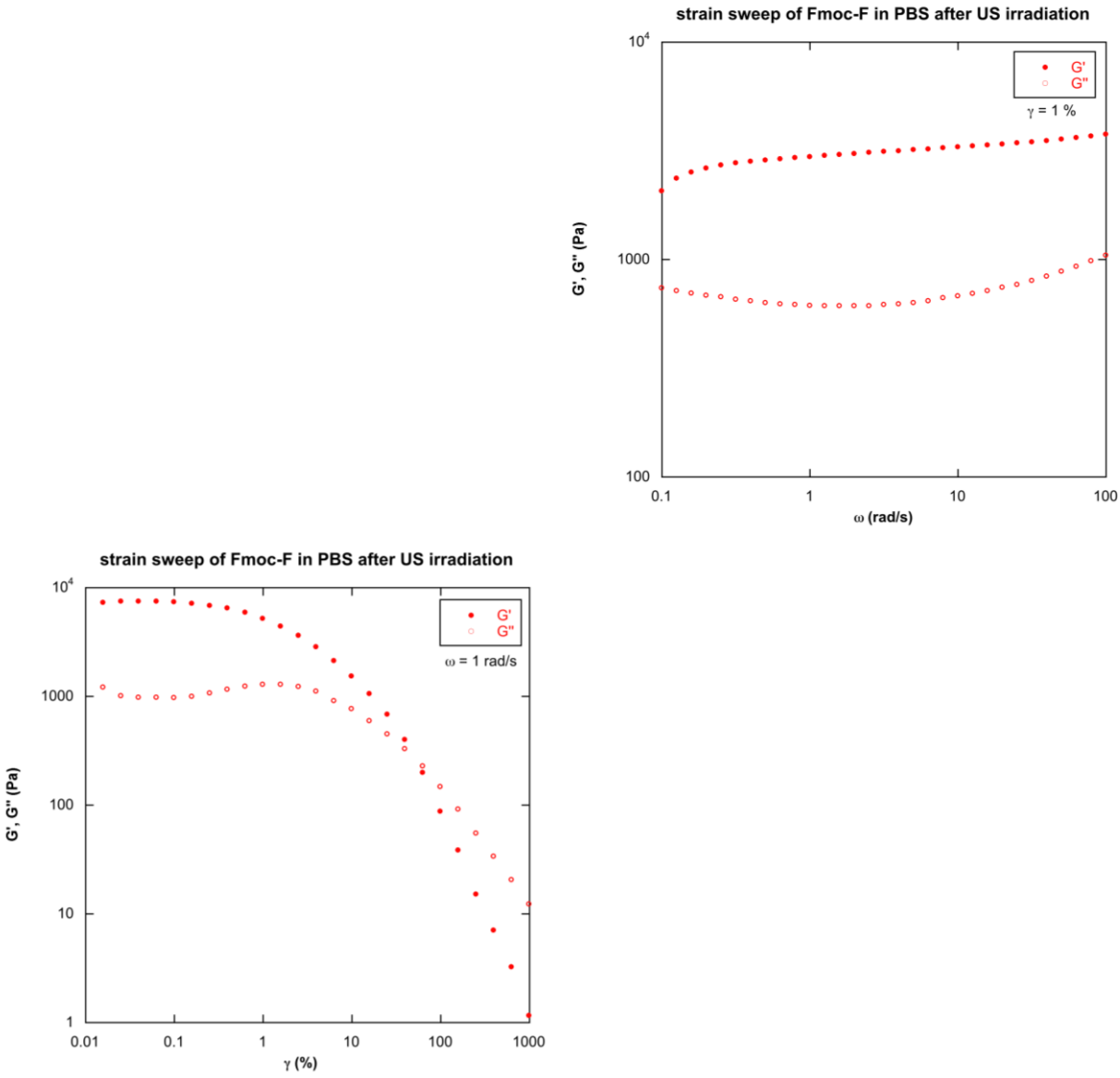
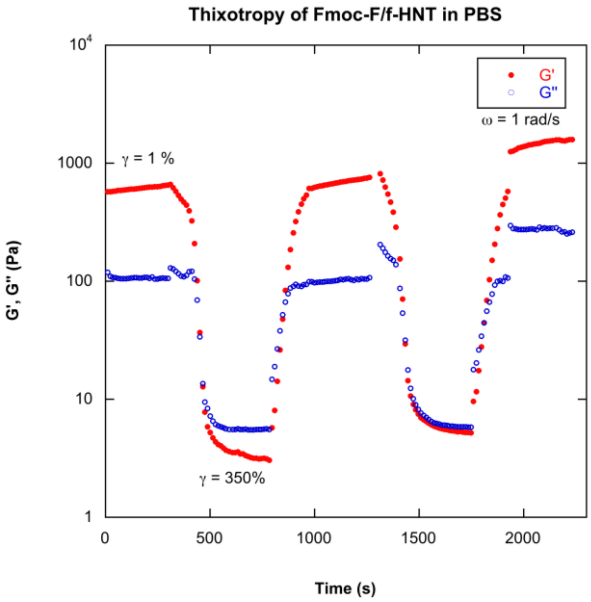
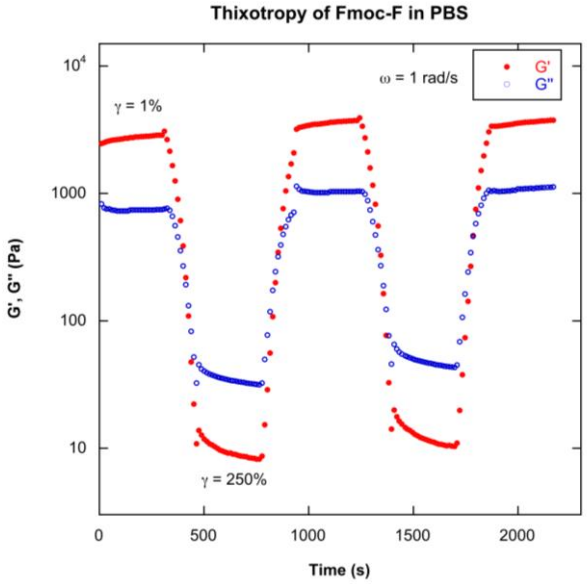


Figure S7. Variation of G′, G″ and viscosity of pure and hybrid gels in strain sweeps and frequency sweeps experiments after disruption of gel with US irradiation.


Thixotropy of Fmoc-F/f-HNT in PBS
G'
G"
ω = 1 rad/s
γ = 1 %
γ = 350%
G', G" (Pa)
Time (s)
10^4
1000
100
10
1
0
500
1000
1500
2000


Thixotropy of Fmoc-F in PBS
G'
G"
ω = 1 rad/s
γ = 1%
γ = 250%
G', G" (Pa)
Time (s)
10^4
1000
100
10
0
500
1000
1500
2000

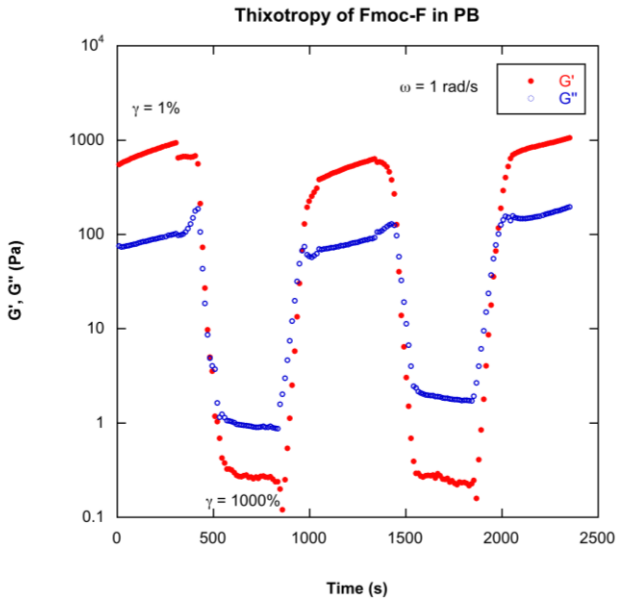


Figure S8. G′ and G″ as a function of time at low (G′>G″ regimes) and destructive strain (G″>G′ regimes).

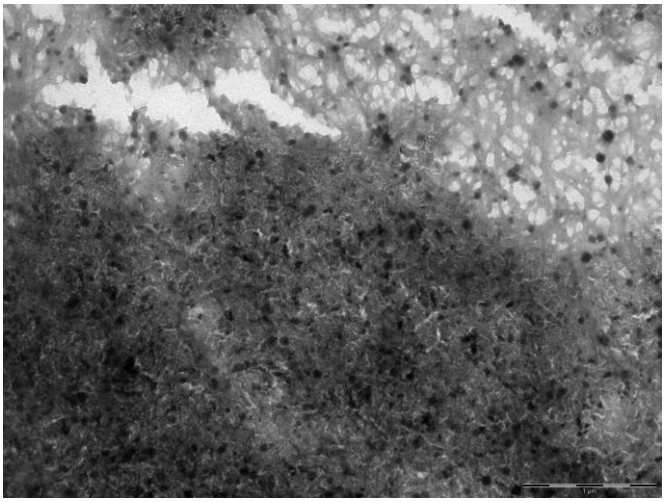


Figure S9. TEM images of hybrid gels in PBS at 0.3 wt % of Fmoc-F and 0.1 wt % of f-HNT/CPT.

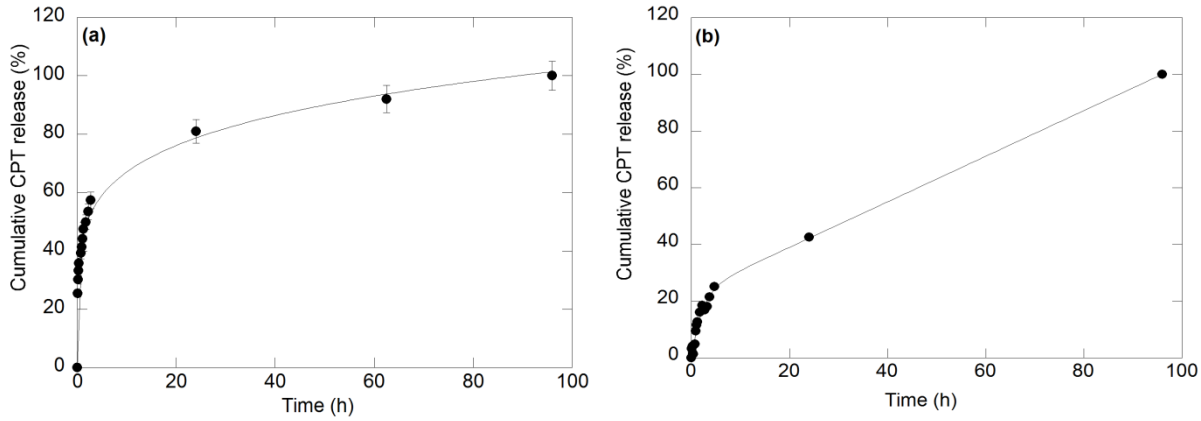


Figure S10. Kinetic release of camptothecin from **(a)** p-HNT; **(b)** f-HNT**.**

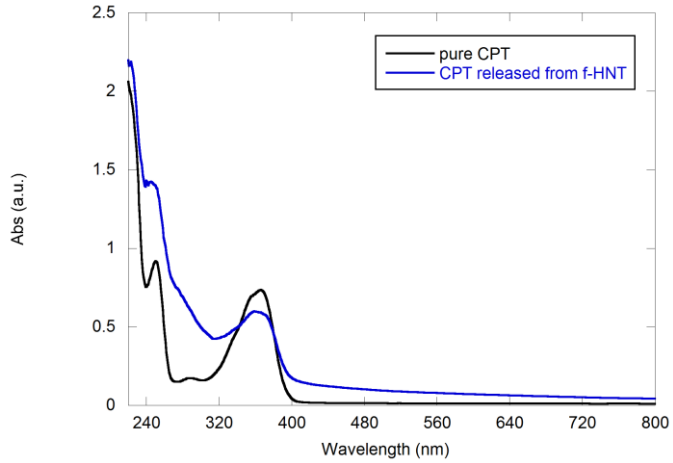


Figure S11. UV-vis spectra of pure CPT (black line) and CPT released from HNT lumen after 96 h (blue line).

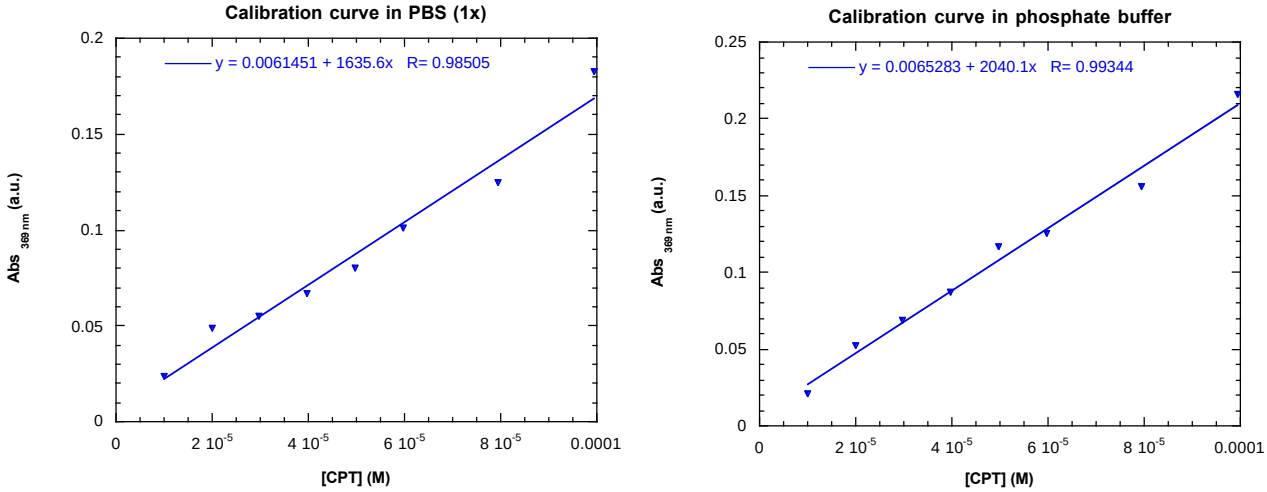


Figure S12. Calibration curves of camptothecin in PBS (1x) and phosphate buffer used to determine CPT concentration released from gel matrix.

Figure S13. Experimental systems used to determine kinetic of CPT release from gel matrix: **a)** hybrid gel**; b)** pure gel.

Table S1. Gelation tests of Fmoc-F alone and in presence of materials.

	Gelator			**Gelator/materials**				
solvents	Fmoc-F			Fmoc-F/f-HNT			Fmoc-F/HNT	
	conc.[a]	*appear.*[b]	T_{gel}[c]	*conc.*[d]	*appear.*[b]	T_{gel}[c]	*conc.*[d]	*appear.*[b]
PBS (1x)	0.06%	S		1%	I			
	0.065%	PG						
	0.1%*	TG	46.3	0.1%	OG	43.8	0.1%	NOG
				0.2%	OG	31.8		
				0.5%	OG	32.6		
PB pH=7.4	0.1%	S		0.1%	I			
				0.2%	I			
				0.5%	I			
	0.13%	PG		0.1%	OG	21.0		
	0.2%*	TG	57.7	0.1%	OG	44.9	0.1%	NOG
				0.2%	OG	43.9		
				0.5%	OG	41.4		
				1%	OG	37.0		

				2%	OG	49.3		
DEG	0.2%	S						
	1%*	OG	53.3	0.1%	OG	54.4	0.1%	I
				0.2%	OG	51.8		
				0.5%	I			
ethyl-lactate	0.2-1%	S						
glycerol	0.2%	I						
H_2O/DMSO 90/10	0.2%	I						
R-limonene	0.2-1%	I						
triethylene glycol	0.2-1%	S						

[a] concentration of Fmoc-F (%, w/w); *(%, w/w), critical gelation concentration (CGC); Fmoc-F at 0.1 wt %; [b] appearances: S = soluble; PG = gelling like precipitate; TG = transparent gel; OG = opaque gel; NOG = non homogeneous gel; I= insoluble; [f](°C), [c]T_{gel} determined by the lead-ball method and reproducible in 1 °C; [d] concentration of material in the gel, (%, w/w), the concentration of Fmoc-F is the one indicated in the same row.

Table S2. Intervals of time and % of CPT release for release in pure gel in PB.

Time (h)	(%) of CPT release
0.25	0.00
0.50	0.00
1.50	0.00
3.00	0.00
4.00	7.39
5.00	8.23
6.00	8.80
7.50	12.97
8.50	11.95
24.00	21.92
48.00	45.14
72.00	61.46
96.00	93.32

Table S3. Intervals of time and % of CPT release for release in hybrid gel in PBS.

Time (h)	(%) of CPT release
0.25	0.00
0.50	2.83
0.80	4.38
1.00	6.12
1.25	8.04
1.50	11.88
1.70	9.67
2.00	14.67
2.50	14.67
3.00	17.21
4.00	27.54
5.00	29.64
6.00	34.06

7.00	34.96
8.00	40.94
24.00	78.26
48.00	94.20
72.00	96.74
96.00	100.0

Table S4. Intervals of time and % of CPT release for release in hybrid gel in PB.

Time (h)	**(%) of CPT release**
0.25	0.00
0.50	2.30
0.80	9.30
1.00	11.34
1.25	13.05
1.50	19.55
1.70	22.51
2.00	24.22
2.50	23.94
3.00	27.06
4.00	33.79
5.00	40.50
6.00	44.97
7.00	47.48
8.00	47.76
24.00	81.84
32.00	95.39
48.00	94.13
72.00	100.00
96.00	93.57