Supporting information

Graft-modified cellulose nanocrystals as CO_2-switchable Pickering emulsifiers

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Characterisation of unmodified and modified CNC by SEM

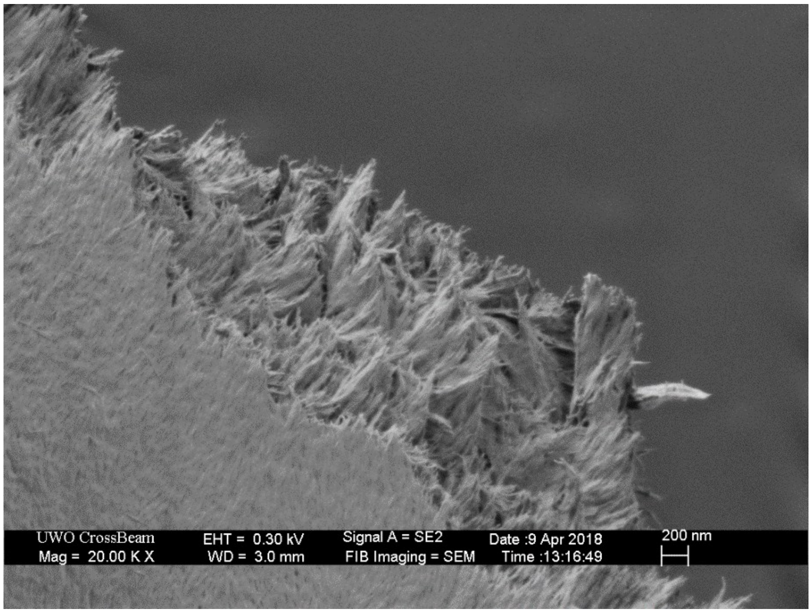

Figure S1 SEM image of unmodified CNC.

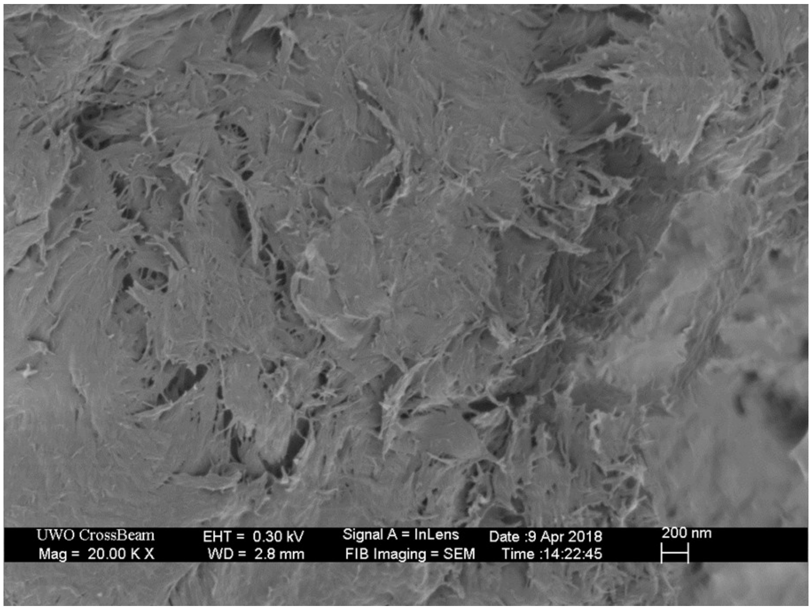

Figure S2 SEM image of CNC-*g*-P(DMAPMAm-*co*-S)-2

Synthesis of CNC-*g*-P(DMAPMAm-*co*-S) and CNC-*g*-P(DEAEMA-*co*-S)

The materials were obtained from previously reported work.[1] Detailed procures can be found below:

SG1-mediated copolymerisation of DMAPMAm and styrene in bulk

DMAPMAm (20.0 g, 0.117 mol), styrene (1.22 g, 11.7 mmol), NHS-BlocBuilder (0.62 g, 1.3 mmol), and SG1 (38 mg, 0.013 mmol) were added to a 50 mL three-neck round-bottom flask fitted with a reflux condenser, a nitrogen inlet and a thermometer. The flask was immersed in an ice-water bath and the mixture stirred and deoxygenated under nitrogen for 20 min. The flask was introduced into a preheated oil bath at 80 °C, representing time zero of the polymerisation. The reaction mixture was stirred at 300 rpm under N_2 for 1-3 h, depending on the targeted molecular weight, with samples withdrawn periodically for kinetic studies and raw polymer analysis. Samples were quenched by immersion in an ice-water bath, precipitated in cold hexane and dried under air flow until constant mass was attained. To stop the polymerisation, the flask was cooled in an ice-water bath. P(DMAPMAm-*co*-S)-SG1 was purified using dialysis in 20-fold volume of hexane and obtained as a transparent, glassy polymer. P(DMAPMAm-*co*-S)-SG1 was analyzed by ^{1}H NMR and inverse gated (IG) ^{13}C NMR spectroscopy.

SG1-mediated copolymerisation of DEAEMA and styrene in bulk

DEAEMA (20.0 g, 0.108 mol), styrene (1.12 g, 10.8 mmol), NHS-BlocBuilder (0.57 g, 1.2 mmol), and SG1 (35 mg, 0.12 mmol) were added to a 50 mL three-neck round-bottom flask fitted with a reflux condenser, a nitrogen inlet and a thermometer. The rest of the procedure follows the aforementioned for P(DMAPMAm-*co*-S)-SG1. The macroalkoxyamines were purified by precipitation and dialysis in 20-fold volume of diethyl ether and yielding a white paste. P(DEAEMA-*co*-S)-SG1 was analyzed by SEC and ^{1}H NMR spectroscopy.

Modifying CNC with glycidyl methacrylate (GMA)

In a three neck round bottom flask, CNC (1 g of solids, 6.2 mmol of total hydroxyls) was dissolved in 100 mL 0.4 M acetic acid and sonicated for 20 min until the CNCs were completely dispersed. Next, KOH (5 mL, 0.05 M) and hydroquinone (10 mL, 9.09×10^{-5} mol) were added to the flask. The reaction mixture was degassed with nitrogen for 30 min and subsequently immersed into an oil bath preheated to 65 °C. Glycidyl methacrylate (GMA) (3.53 g, 24.8 mmol) was added to the system dropwise using a 100 ml dropping funnel. The mixture was magnetically stirred for 2 h at 65 °C. The reaction system was cooled down with an ice bath and the product was separated from the acid medium by centrifugation. The supernatant was decanted and the GMA modified was redispersed into 60 ml of methanol and vigorously stirred for 1 h at room temperature to remove unreacted GMA. The purification was repeated three times. The particles were analyzed by FT-IR and ^{13}C CP-MAS NMR spectroscopy and TGA.

Grafting to reaction of P(DMAPMAm-*co*-S)-SG1 and P(DEAEMA-*co*-S)-SG1 to GMA modified CNC

In a 100 ml three neck flask, 3 g of GMA modified CNC (wet cake, about 0.21 g of solids) was suspended in 45 ml of DI water and subjected to sonication for 20 min. The flask was fitted with a reflux condenser, a nitrogen inlet and a dropping funnel and the dispersion stirred and purged with N_2 for 20 min. In a second 50 ml round bottom flask, 0.8 g of dried P(DMAPMAm-*co*-S)-SG1 was dissolved in 30 ml of deionized water (DIW), and the solution deoxygenated for 30 min. The solution was then transferred into the dropping funnel and degassed throughout the reaction. The reaction flask was transferred to an oil bath preheated to 85 °C and 10 ml of the macroalkoxyamine solution was added through the dropping funnel. After 30 and 60 min, another 10 ml was added and the system was allowed to react further for 2 h. The reaction was quenched in an ice bath and the modified CNC particles separated from the solvent by centrifugation. The precipitate was washed with 60 ml of THF by stirring in a beaker for 20 min and then subjected to ultrasound for another 30 min. The modified CNC particles were collected by centrifugation. To ensure the absence of free polymer, exhaustive product purification with repeated centrifugation/redispersion cycles was performed 4 times. The procedure for the synthesis of CNC-*g*-P(DEAEMA-*co*-S) followed the aforementioned for CNC-*g*-P(DMAPMAm-*co*-S), with the exception that P(DEAEMA-*co*-S)-SG1 was dissolved in 30 ml of 0.4 M acetic acid. CNC-*g*-P(DEAEMA-*co*-S) and CNC-*g*-P(DMAPMAm-*co*-S) particles were analyzed by ^{13}C CP-MAS NMR and FT-IR spectroscopy, TGA and EA.

Determination of molecular weight and styrene content of P(DMAPMAm-*co*-S)-SG1 and P(DEAEMA-*co*-S)-SG1 by ^{1}H NMR spectroscopy

The molecular weight of the presynthesized P(DMAPMAm-*co*-S)-SG1 macroalkoxyamines was determined by ^{1}H NMR spectroscopy end-group analysis (previously reported)[1] as shown in Figure S3:

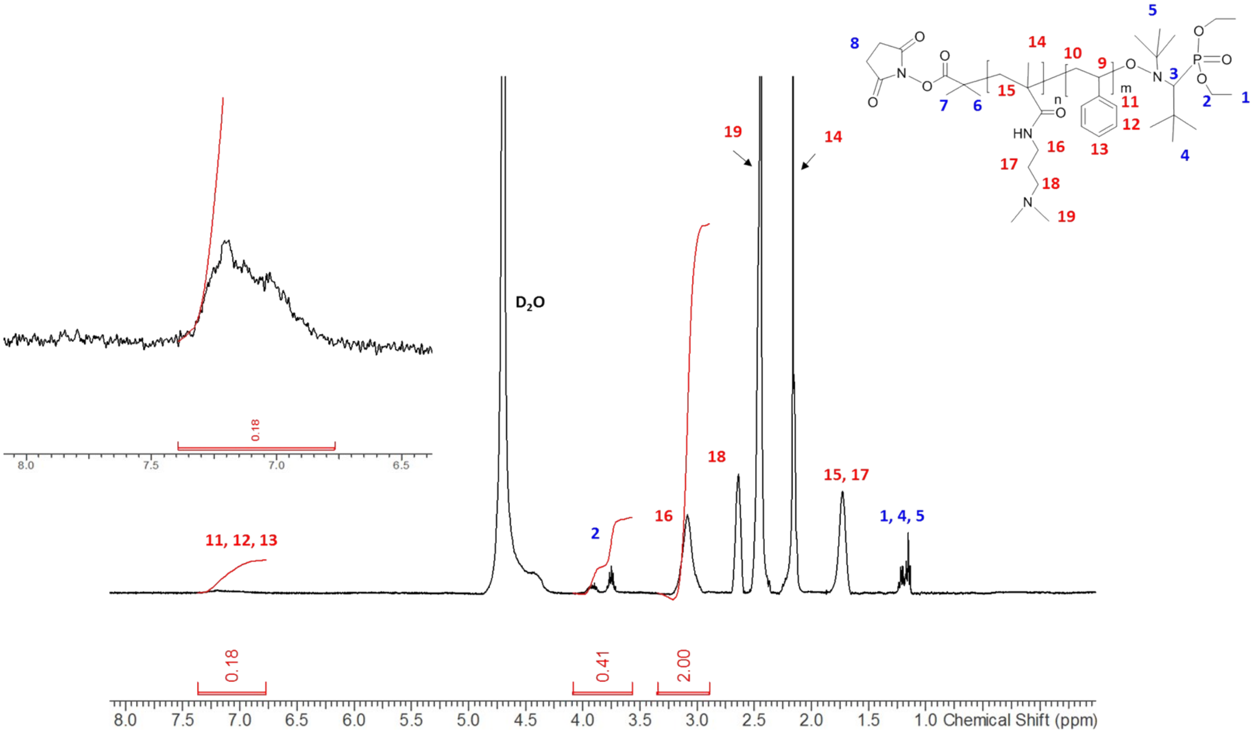

Figure S3 ^{1}H NMR (400.30 MHz, D$_2$O) of P(DMAPMAm-*co*-S)-SG1-1 with a calculated M_n ≈ 2200 g/mol, showing the SG1 terminated chain end.

^{1}H NMR (400.30 MHz, D$_2$O, d, ppm) (Figure S3): 1.19 – 1.31 (m, 24H; H1, H4-5), 1.78 (s, 2H; H17), 2.22 (s, 3H; H14), 2.50 (s, 6H; H19), 2.69 (s, 2H, H18), 3.14 (s, 2H; H16), 3.76 – 4.07 (m, 4H; H2), 6.81 – 7.40 (m, 5H, H11-13).

The ratio of protons on the end-groups to protons on the polymer chain is determined by comparing the integral of the methylene protons H16 in DMAPMAm (2.0) and the aromatic protons H11-13 in styrene (0.18) to the integral of the methylene protons H2 in NHS-BlocBuilder (0.41). The integral per proton value is 2.0/2=1 for the H16 protons, 0.18/5=0.05 for the H11-13 protons, and 0.41/4=0.1 for the H2 protons, giving a ratio of 1:0.05:0.1. Taking into account the molecular weight of NHS-BB (478 g/mol), M_n is calculated as follows:

$$Mn = Mw\,(end\ groups + repeating\ unit) = 478.0\frac{g}{mol} + 10 \times 170.3\frac{g}{mol} + 0.5 \times 104.2\frac{g}{mol} \approx 2200\,\frac{g}{mol} \tag{1}$$

Similar calculations were performed for P(DMAPMAm-*co*-S)-2 and P(DEAEMA-*co*-S)-1 as shown in Table S1.

Table S1 Integral per proton values, degree of polymerisation DP_n, and final graft molecular weight M_n

	Integral per proton value			$DP_{DMAPMAm}$, DP_{DEAEMA}	$DP_{Styrene}$	Graft M_n [g/mol]
	H16	H11-13	H2			
P(DMAPMAm-*co*-S)-SG1-1	1	0.05	0.1	10	0.5	2200
P(DMAPMAm-*co*-S)-SG1-2	1	0.16	0.048	21	3	4400
P(DEAEMA-*co*-S)-SG1-1	1	0.11	-	19	2	4200

Elemental Analysis and Calculation of Amine Groups on the CNCs Surface

Table S2: Elemental Analysis data for the grafted products and the consequent graft weight percentage, moles of grafts, and moles of switchable amine groups per 1 g of CNC.

	Graft M_n [g/mol]	%C	%H	%N	%N[a]	Switch-able polymer %	Total polymer % [b]	Graft density $\times 10^{-2}$ [chains/ nm^2]	Amine groups [mmol] [c]
Native CNC	-	39.9	6.3	0.0	-	-	-	-	-
CNC-*g*-P(DMAPMAm-*co*-S)-1	2200	46.2	7.9	3.9	3.1	19	23	14.2	1.36
CNC-*g*-P(DMAPMAm-*co*-S)-2	4400	45.5	7.3	2.7	2.2	13	18	5.2	0.91
CNC-*g*-P(DEAEMA-*co*-S)-1	4200	45.3	7.3	1.4	1.3	17	20	6.2	1.12

[a] Corrected value subtracting the nitrogen content from NHS-BB. [b] Per one gram of grafted CNCs, accounting for the amount of styrene and NHS-BB in the copolymer. [c] Maximum theoretical amount of switchable groups per one gram of grafted CNC.

The weight percent of polymer grafted to the surface of CNCs was estimated following the reported procedure by Tang et al.[2] Assuming 1 g of CNC powders is obtained after the grafting reaction, the moles of DMAPMAm (M_w=170.3 g/mol) or DEAEMA (M_w=185.3 g/mol) grafted to the surface of CNC can be calculated by considering the increased nitrogen content (M_w=14.0 g/mol) after subtracting the nitrogen coming from NHS and SG1. Since only SG1-capped macroalkoxyamines can react with CNC-GMA, there are two nitrogen atoms per graft that account for NHS and SG1. The %N from NHS and SG1 (NHS-BB) can then be obtained by considering the ratio of the nitrogen in NHS-BB to the nitrogen in DEAEMA and DMAPMAm (Table S2):

CNC-*g*-P(DMAPMAm-*co*-S)-1 with a graft M_n of 2.2 kDa:

Total %N − %N from NHS-BB $= 3.9\ \% - \left(\frac{2}{10} \cdot 3.9\ \%\right) = 3.1\ \%$ (%N from DMAPMAm only)

CNC-*g*-P(DEAEMA-*co*-S)-1 with a graft M_n 4.2 kDa:

Total %N − %N from NHS-BB $= 1.4\ \% - \left(\frac{2}{19} \cdot 1.4\ \%\right) = 1.3\ \%$ (%N from DEAEMA only)

As DEAEMA bears one nitrogen atom and DMAPMAm bears two nitrogen atoms, the final moles of DEAEMA and DMAPMAm in the grafted products (i.e. the maximum theoretical amount of switchable amine groups) can be derived as:

CNC-*g*-P(DMAPMAm-*co*-S)-1 with a graft M_n of 2.2 kDa:

$$\frac{n \cdot 2 \cdot 14.0}{1 + n \cdot 170.3} = 3.1\ \%$$

Solving for n we obtain:

n = **1.36** mmol DMAPMAm / g CNC.

Thus, the weight percentage of PDMAPMAm in CNC-*g*-P(DMAPMAm-*co*-S)-1 is:

$$\frac{1.36 \cdot 170.3 \cdot 10^{-3}}{1 + 1.36 \cdot 170.3 \cdot 10^{-3}} = 19\ \%$$

Accounting for 5 % styrene and 10 % NHS-BB in P(DMAPMAm-*co*-S)-SG1-1 (Table S2), we obtain 0.05 * 1.36 mmol styrene (M_w=104.2 g/mol) and 0.1 * 1.36 mmol NHS-BB (M_w=462.5 g/mol) per 1 g of CNC. Hence, the total weight percentage of P(DMAPMAm-*co*-S)-1-SG1 in CNC-*g*-P(DMAPMAm-*co*-S)-1 is:

$$\frac{1.36 \cdot (170.3 + 0.05 \cdot 104.2 + 0.1 \cdot 462.5) \cdot 10^{-3}}{1 + 1.36 \cdot (170.3 + 0.05 \cdot 104.2 + 0.1 \cdot 462.5) \cdot 10^{-3}} = 23\ \%$$

CNC-*g*-P(DEAEMA-*co*-S)-1 with a graft M_n 4.2 kDa:

$$\frac{n \cdot 1 \cdot 14.0}{1 + n \cdot 185.3} = 1.3\ \%$$

Solving for n we obtain:

$$n = \mathbf{1.12} \text{ mmol DEAEMA / g CNC}$$

Therefore, the weight percentage of PDEAEMA in CNC-*g*-P(DEAEMA-*co*-S)-1 is:

$$\frac{1.12 \cdot 185.3 \cdot 10^{-3}}{1 + 1.33 \cdot 185.3 \cdot 10^{-3}} = 17\ \%$$

Taking into account the styrene (11 %) and NHS-BB content (2/19) in the copolymer in CNC-*g*-P(DEAEMA-*co*-S)-1, we obtain the total weight percentage of P(DEAEMA-*co*-S)-1-SG1 in CNC-*g*-P(DEAEMA-*co*-S)-1:

$$\frac{1.33 \cdot (185.3 + 0.11 \cdot 104.2 + 0.05 \cdot 462.5) \cdot 10^{-3}}{1 + 1.33 \cdot (185.3 + 0.11 \cdot 104.2 + 0.05 \cdot 462.5) \cdot 10^{-3}} = 20\ \%$$

Similar calculations as above were performed for CNC-*g*-P(DMAPMAm-*co*-S)-2 with data presented in Table S2.

Calculation of Graft Densities

Atomic force microscopy (AFM) was performed on a Veeco Dimension 5000 multimode atomic force microscope with a Nanoscope IV controller (Digital Instruments) by scanning in contact mode. After preparation of a dilute solution of water, one drop was deposited onto freshly cleaved mica. Tips of µmash NSC 15 type were used with a resonance frequency of 200 - 400 kHz, spring constants of 13-77 N/m, and a tip radius <10 nm. Micrographs were captured at a scan rate of 1 Hz and resolution of 256 number of samples/line. All images were treated with Nanoscope 1.50 software.

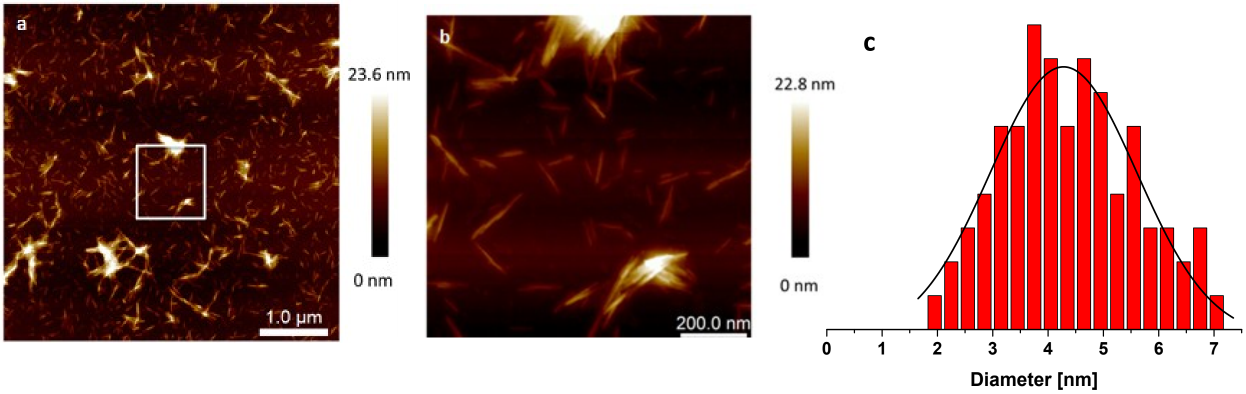

Figure S4 Characterization of CNC. (a) AFM height image with a height-range of 23.6 nm. (b) Zoom-in height image of CNC particles highlighted in part (a) by the white box with a height range of 22.8 nm. (c) Statistical analysis of the height of about 200 CNC particles illustrating the average diameter of ca. 4.4 nm.

The average center diameter of CNC determined by statistical analysis from the AFM images in Figure S4 is $d \approx 4.4$ nm. For simplicity an infinitely long cylinder was assumed resembling the shape of CNC rods with a radius of $r \approx 2.2$ nm. From this, a cylindrical volume segment with a height of h=1 nm is considered and the volume calculated according to (2):

$$V = \frac{1}{2}\pi r^2(2h) \approx 1.52 \times 10^{-26}\, m^3 \tag{2}$$

The surface area is given by:

$$S = r\,\pi\,(2h) \approx 13.8\, nm^2 \tag{3}$$

Using the M_w of anhydroglucose (162 g/mol) and the density of crystalline cellulose (ca. 1.58 g/mL)[3] the molar amount of anhydroglucose within one volume segment is $n(C_6H_{10}O_5) = 1.48 \times 10^{-22}$ mol and the mass $m(C_6H_{10}O_5) = 2.4 \times 10^{-20}$ g.

The specific surface area of CNC equals:

$$A_{spec} = \frac{13.8\, nm^2}{2.4 \times 10^{-20}\, g} = 5.75 \times 10^{20}\, \frac{nm^2}{g} \tag{4}$$

And finally, the grafting density ρ of the graft can be calculated by:

$$\rho = \frac{w}{M_n} A_v \;/\; ((1-w) \cdot A_{spec}) \tag{5}$$

Whereby w is the weight fraction of P(DEAEMA-*co*-S) and P(DMAPMAm-*co*-S) as determined by EA, M_n is the number-average graft molecular weight and A_v is Avogadro's number.

pH and IFT Measurements vs Concentration

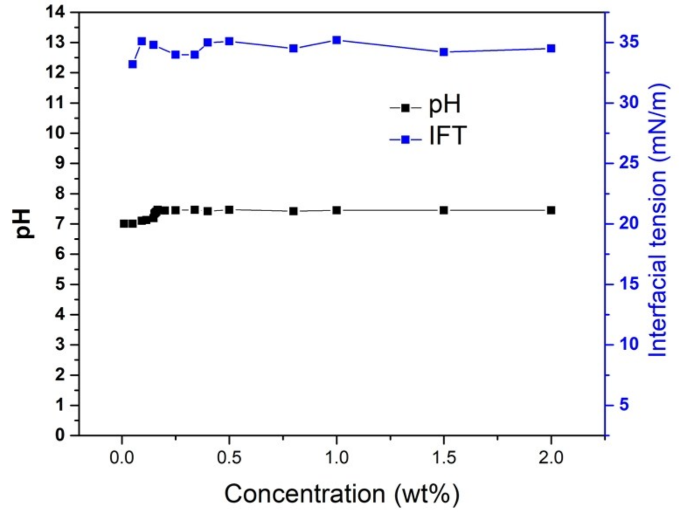

Figure S5 IFT of toluene/water and pH vs concentration of native CNC dispersed in the aqueous phase at ambient conditions.

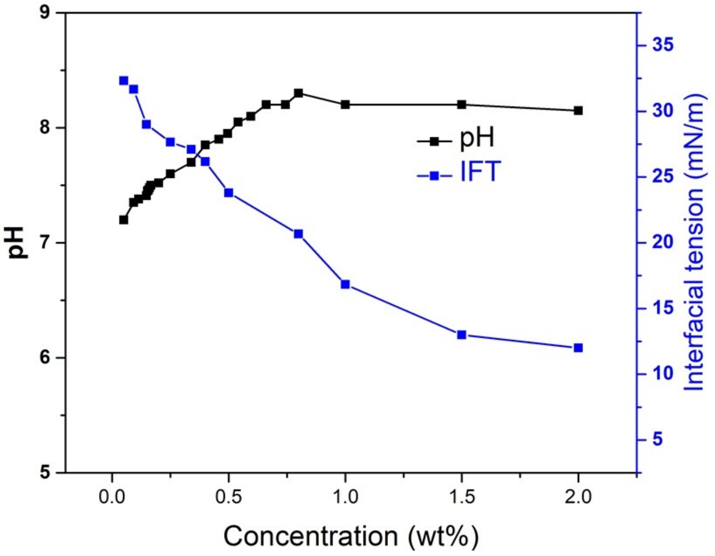

Figure S6 IFT of toluene/water and pH vs concentration of CNC-*g*-P(DEAEMA-*co*-S)-1 dispersed in the aqueous phase at ambient conditions.

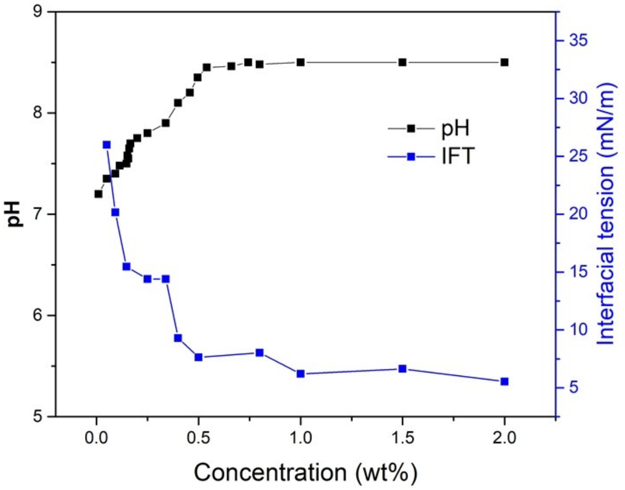

Figure S7 IFT of toluene/water and pH vs concentration of CNC-*g*-P(DMAPMAm-*co*-S)-1 dispersed in the aqueous phase at ambient conditions.

References

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3 J. Majoinen, A. Walther, J. R. McKee, E. Kontturi, V. Aseyev, J. M. Malho, J. Ruokolainen and O. Ikkala, *Biomacromolecules*, 2011, **12**, 2997–3006.