Electronic Supplementary Information

Surfactant controlled zwitterionic cellulose nanofibril dispersions

Vincenzo Calabrese, [a] Marcelo A. da Silva, [a] Julien Schmitt, [a] Juan C. Muñoz-Garcia, [b] Valeria Gabrielli,[b] Janet L. Scott, [a,c] Jesus Angulo, [b] Yaroslav Z. Khimyak, [b] Karen J. Edler [a*]

[a] Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK. E-mail: k.edler@bath.ac.uk; Tel: 01225 384192
[b] School of Pharmacy, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, UK
[c] Centre for Sustainable Chemical Technology, University of Bath, Claverton Down, Bath, BA2 7AY, UK. E-mail: j.l.scott@bath.ac.uk University of Bath Tel: 01225 386307
* Corresponding author: E-mail: k.edler@bath.ac.uk; Tel: 01225 384192

Conductimetric titration (Fig. S1) of the oxidised cellulose nanofibril (OCNF) and the zwitterionic cellulose nanofibril (ZCNF) were performed in according to the protocol of da Silva Perez *et. al* using the following equation:[1]

$$DO = \frac{162\ C\ (V_2 - V_1)}{w - 37\ C\ (V_2 - V_1)}$$

where C is NaOH concentration (mol/l), V_1 and V_2 the volume of NaOH (l) based on the plateau of the curves, *w* the dry weight of OCNF (g). The value of 162 is the molecular weight of the anydroglucose unit (AGU, 162 (g/mol)) whilst 36 corresponds to the difference in molecular weight between the AGU and that of the sodium salt of the glucuronic acid (162-199=37 (g/mol)).

The ZCNF did not show a well defined region where conductivity is weakly dependent on NaOH addition, hence, the DO of oxidation was not evaluated using conductimetric titration.

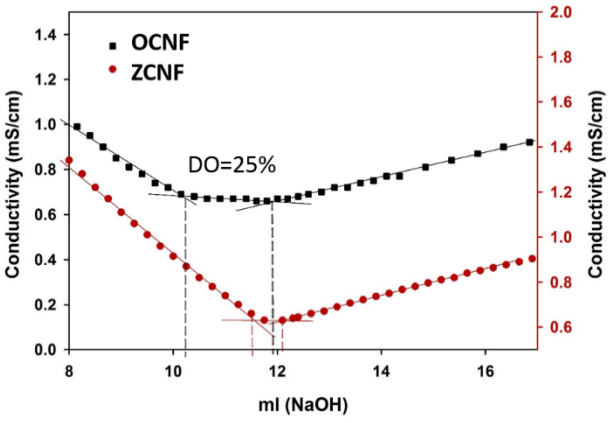

Fig. S1 Conductimetric titration of OCNF and ZCNF.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Perkin Elmer Frontier. The samples were freeze dried in order to remove all the water and the spectra collected in the range 600 to 4000 cm^{-1}. The spectra of OCNF and ZCNF are similar except

for a small difference at 1479 cm^{-1} in the ZCNF spectra (Fig. S2). Zaman *et. al* associated this peak with the CH_2 band arising from the cationic substituent.[2]

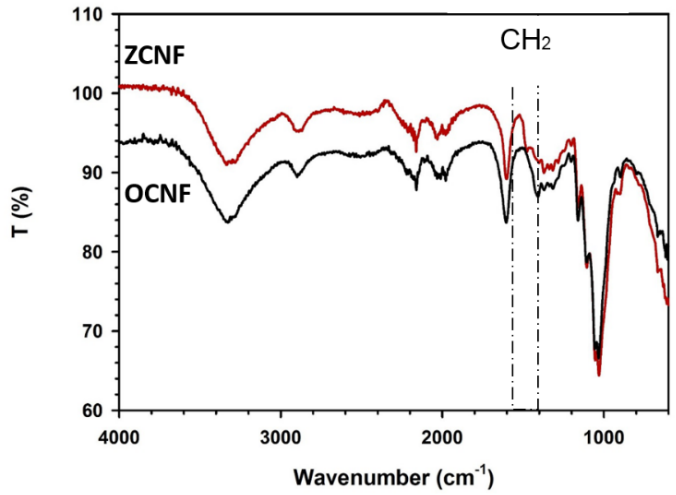

Fig. S2. FTIR spectra of OCNF and ZCNF.

The degree of oxidation (DO) derived from $^{13}C\{^1H\}$ DP NMR, calculated as the ratio between the peak areas of the carboxyl group (indicated by an arrow) and the anomeric carbon (peak at 105 ppm), kept constant (*ca.* 25 %) between OCNF and ZCNF samples using 200 s relaxation delay (†ESI Fig. S3). The assessment of DO using the spectra acquired with 800 s relaxation delay is hampered due to poor S/N for the carboxylate peak after 512 scans (Figure 1, †ESI Fig. S4), in spite of 5 days of experimental time. The DO obtained from the experiments with 200 s relaxation delay demonstrates the absence of impact of GTMAC coupling on the degree of oxidation.

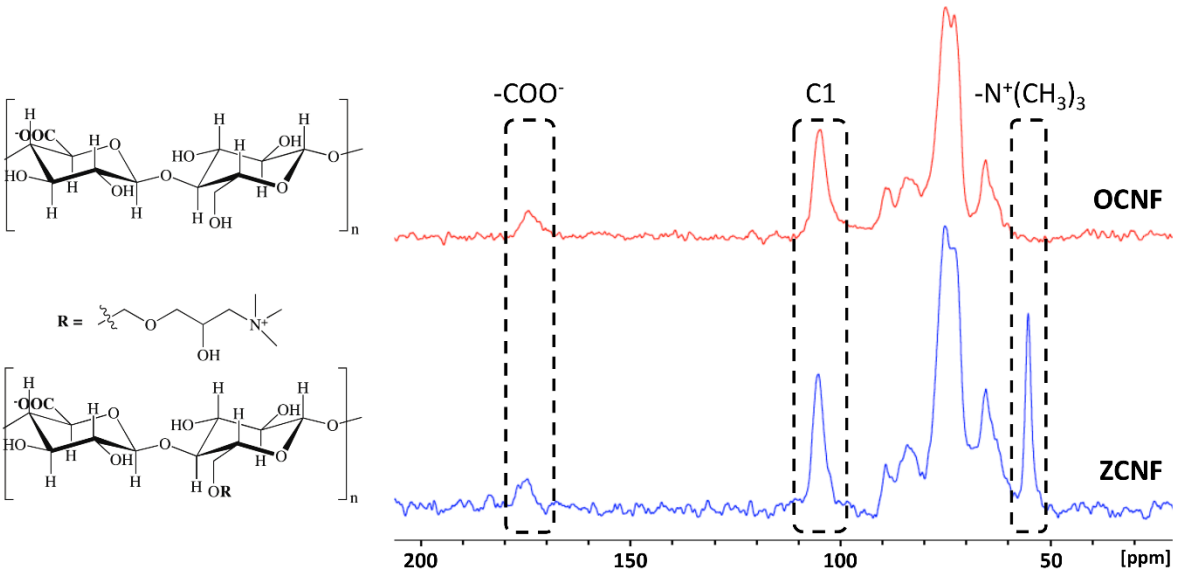

Fig. S3. ^{13}C DP MAS NMR spectra for non-washed ZCNF (blue line) and washed OCNF (red line), after 4k and 8k scans, respectively, acquired at 10 kHz MAS rate and 200 s relaxation delay. The

peaks corresponding to the anomeric carbon and the functionalisation groups are highlighted within dashed rectangles. A degree of oxidation (DO = ratio between the peak area of the carboxyl group and the anomeric carbon) of *ca.* 25 % was obtained for both powders.

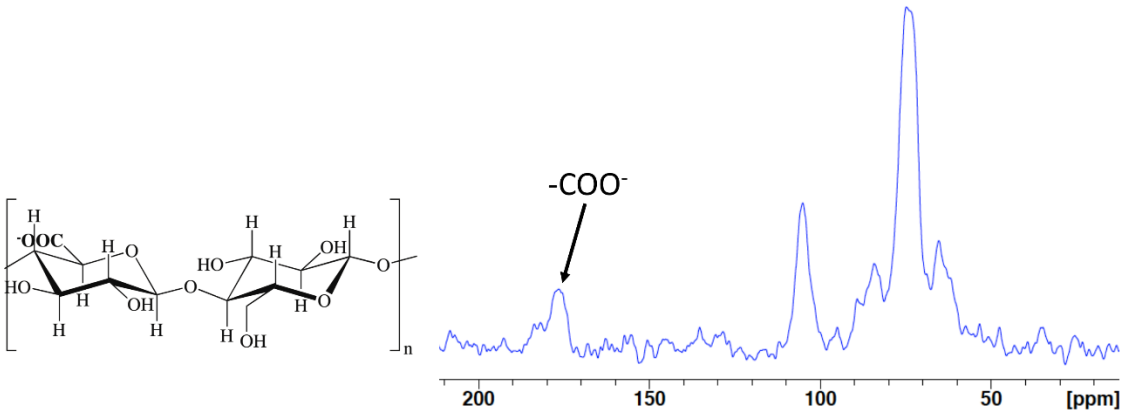

Fig. S4. $^{13}C\{^{1}H\}$ DP MAS NMR spectra for washed OCNF powder after 512 scans, acquired on a 300 MHz spectrometer at 10 kHz MAS rate and 800 s relaxation delay to allow for complete ^{13}C relaxation.[3] A line broadening of 80 Hz was used.

References

1 D. da Silva Perez, S. Montanari and M. R. Vignon, *Biomacromolecules*, 2003, **4**, 1417–1425.
2 M. Zaman, H. Xiao, F. Chibante and Y. Ni, *Carbohydr. Polym.*, 2012, **89**, 163–170.
3 K. Wickholm, P. T. Larsson and T. Iversen, *Carbohydr. Res.*, 1998, **312**, 123–129.