

Employing photoluminescence to rapidly follow aggregation and dispersion of cellulose nanofibrils SI

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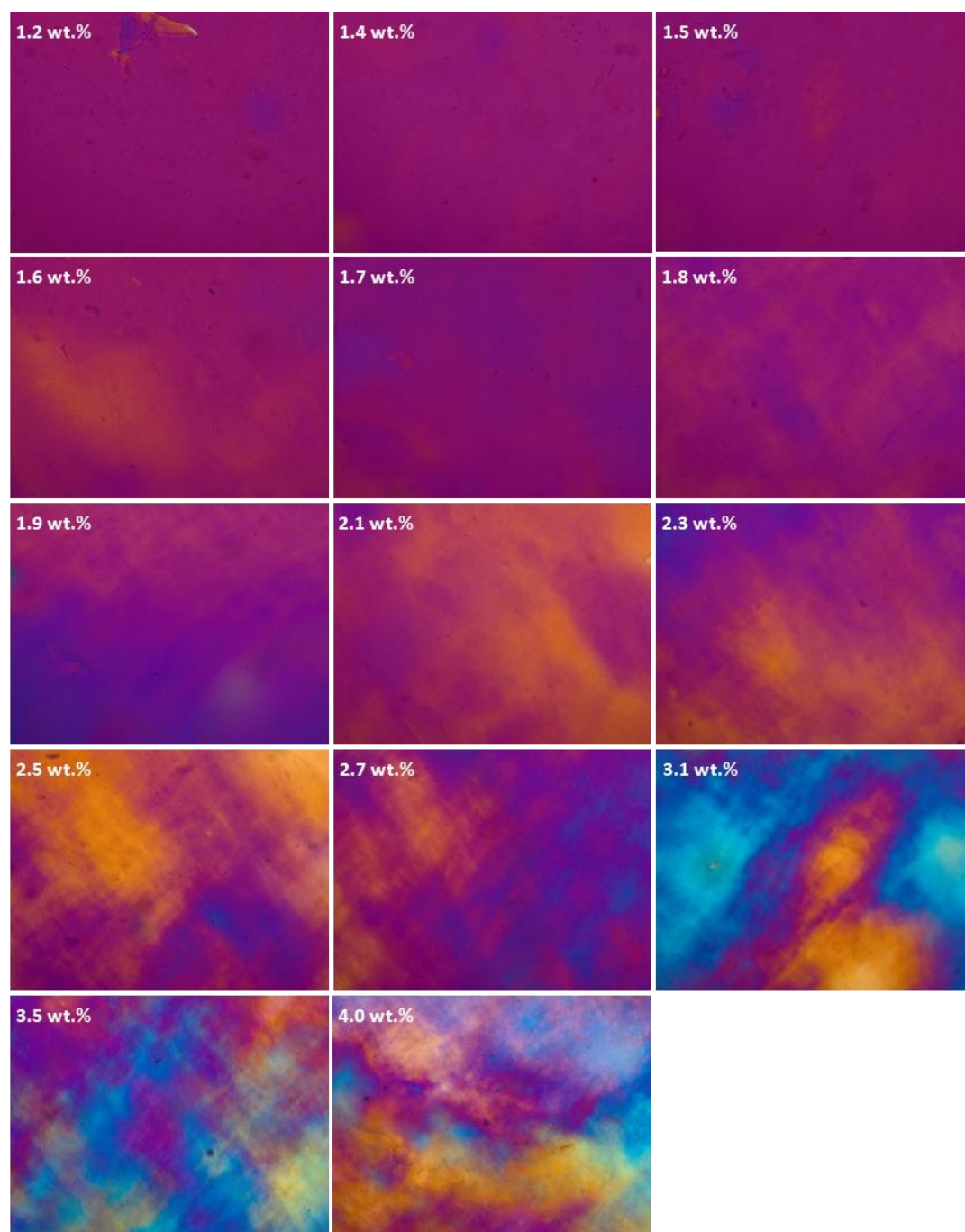


Figure S1. Typical cross-polarized light microscopy images of OCNF gels at varying concentrations.

Table S1. Data relating to OCNF MCLSS concentration experiments, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Values calculated from each data set equation, plus their average, are also included. These are the 468:504 nm intensity ratio at [OCNF] of 0 and 100 wt.%; the initial and final gradient equations, and their interception point; and the [OCNF] at which no change in the 468:504 nm ratio occurs (referred to as the plateau concentration). N = 3, n = 3. Error: \pm SE.

Parameters and calculated values	Data Set				
	Mean - SE	Mean	Mean + SE	Average	
Exponential equation parameters	A	0.208	0.321	0.469	-
	B	1.04	1.42	1.76	-
	C	1.02	1.04	1.06	-
468:504 nm ratio at 0 wt.%	1.59	1.91	2.33	1.94 \pm 0.22	
468:504 nm ratio at 100 wt.%	1.02	1.04	1.06	1.04 \pm 0.01	
Initial gradient equation	$-0.28x + 1.49$	$-0.45x + 1.68$	$-0.64x + 1.89$	-	
Final gradient equation	$0.0x + 1.02$	$0.00x + 1.04$	$0.00x + 1.03$	-	
Interception point	1.69	1.44	1.30	1.47 \pm 0.11	
Plateau concentration	26.6	13.8	13.8	18.1 \pm 4.3	

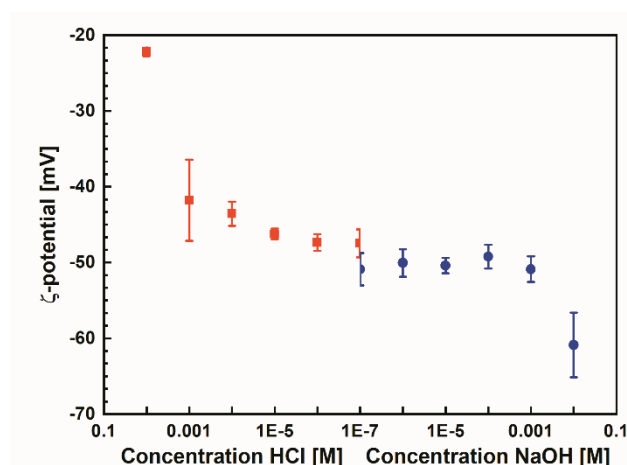


Figure S2. OCNF ζ -potential vs. concentration of HCl (red squares) and NaOH (blue circles). N = 1, n = 3. Error bars: \pm SE.

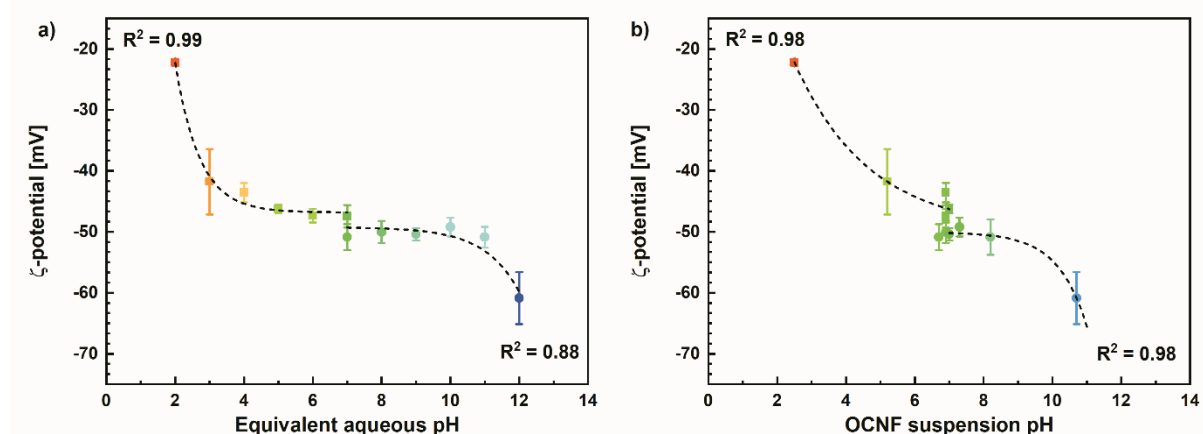


Figure S3. a) OCNF ζ -potential vs. the equivalent aqueous pH calculated from the concentration of HCl and NaOH present. **b)** OCNF ζ -potential vs. the experimentally measured pH. For both figures, Equation 4 used to generate lines of best fit. HCl modified suspensions denoted as squares, NaOH modified by circles. N = 1, n = 3. Error bars: \pm SE.

Table S2. Data relating to OCNF ζ -potential experiments assuming equivalent aqueous pH, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Interception points calculated from each data set equation, plus their average, are also included. N = 1, n = 3. Error: \pm SE.

Parameters and calculated values			Data Set			
			Mean - SE	Mean	Mean + SE	Average
Exponential equation parameters	HCl	A	58.5	154.9	55.2	-
		B	0.90	1.42	0.90	-
		C	-49.3	-46.8	-46.6	-
	NaOH	A	-1.5×10^{-8}	-2.4×10^{-5}	-1.8×10^{-5}	-
		B	-1.63	-1.00	-1.00	-
		C	-51.5	-49.3	-47.7	-
HCl	Initial gradient equation	$-15.5x + 7.2$	$-18.2x + 11.9$	$-14.6x + 6.6$	-	
	Final gradient equation	$-0.4x - 46.0$	$-0.1x - 46.4$	$-0.4x - 43.5$	-	
	Interception point	3.5	3.2	3.5	3.4 ± 0.1	
NaOH	Initial gradient equation	$-0.0x - 51.4$	$-0.1x - 48.5$	$-0.1x - 47.1$	-	
	Final gradient equation	$-10.5x + 62.5$	$-6.6x + 20.4$	$-4.9x + 3.9$	-	
	Interception point	10.9	10.6	10.6	10.7 ± 0.1	

Table S3. Data relating to OCNF ζ -potential experiments for the measured pH in presence of OCNF, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Interception points calculated from each data set equation, plus their average, are also included. N = 1, n = 3. Error: \pm SE.

Parameters and calculated values			Data Set			
			Mean - SE	Mean	Mean + SE	Average
Exponential equation parameters	HCl	A	304.2	31.9	50.3	-
		B	1.40	0.46	0.05	-
		C	-47.5	-49.8	-143.0	-
	NaOH	A	-1.6×10^{-7}	-1.1×10^{-5}	-4.1×10^{-8}	-
		B	-1.63	-1.20	-1.69	-
		C	-51.5	-50.1	-48.4	-
HCl	Initial gradient equation	$-36.8x + 71.8$	$-12.7x + 9.9$	$-5.8x - 7.1$	-	
	Final gradient equation	$-0.1x - 46.5$	$-2.0x - 32.1$	$-4.8x - 11.6$	-	
	Interception point	3.2	3.9	4.4	3.9 ± 0.4	
NaOH	Initial gradient equation	$-0.2x - 50.5$	$-0.3x - 48.1$	$-0.1x - 47.9$	-	
	Final gradient equation	$-106x + 1101$	$-35.3x + 326$	$-58.8x + 591$	-	
	Interception point	10.9	10.7	10.9	10.8 ± 0.1	

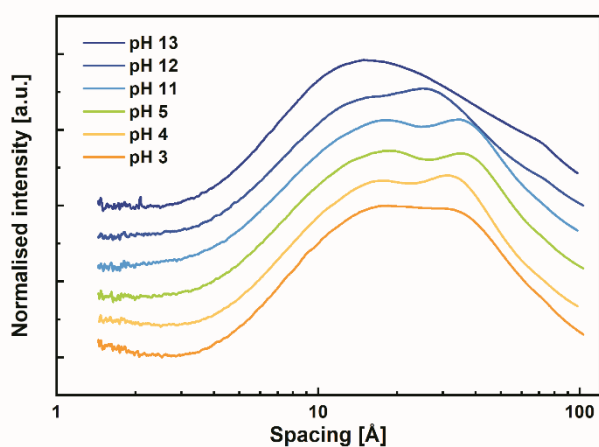


Figure S4. Offset selected Kratky plots for OCNF interfibrillar spacings as determined by SAXS.

Table S4. Change in average OCNF interfibrillar spacing lengths with pH determined by fitting Gaussian curves to the Kratky plots.

Peak no.	Interfibrillar spacing length [Å]				
	HCl		NaOH		
	pH 3,4	pH 5-7	pH 7-10	pH 11,12	pH 13
1	67.7 ± 0.9	70.6 ± 0.6	70.4 ± 0.8	66.8 ± 2.3	68.1
2	40.6 ± 2.8	40.6 ± 1.8	38.9 ± 0.6	36.7 ± 3.4	49.1
3	27.1 ± 1.5	25.6 ± 1.9	23.4 ± 0.5	22.2 ± 1.9	32.3
4	18.4 ± 0.5	17.0 ± 1.5	15.1 ± 0.5	15.0 ± 1.2	21.1
5	12.6 ± 0.1	11.5 ± 0.9	10.1 ± 0.4	10.3 ± 0.8	13.5
6	8.7 ± 0.0	7.8 ± 0.5	6.9 ± 0.4	7.1 ± 0.7	8.9
7	6.0 ± 0.2	5.4 ± 0.5	4.7 ± 0.4	5.0 ± 0.6	5.9
8	1.4 ± 0.0	-	-	-	-

Table S5. Change in average contribution of specific OCNF fibrillar spacings with pH calculated from the fitted Gaussian curve areas.

Peak no.	Contribution of peak to total area [%]				
	HCl		NaOH		
	pH 3,4	pH 5-7	pH 7-10	pH 11,12	pH 13
1	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.1	0.3
2	6.1 ± 1.4	7.0 ± 0.8	6.9 ± 0.5	10.2 ± 1.8	1.2
3	6.0 ± 0.1	10.1 ± 2.4	11.8 ± 1.3	12.0 ± 0.1	3.9
4	11.8 ± 0.1	16.3 ± 1.4	17.4 ± 1.9	17.4 ± 0.9	10.0
5	17.5 ± 0.4	23.3 ± 1.6	22.7 ± 1.8	22.9 ± 1.7	23.1
6	21.5 ± 0.0	24.7 ± 2.2	23.2 ± 0.8	23.8 ± 0.7	32.4
7	18.3 ± 1.9	18.6 ± 4.1	17.9 ± 5.2	13.7 ± 5.0	29.1
8	18.7 ± 3.7	-	-	-	-

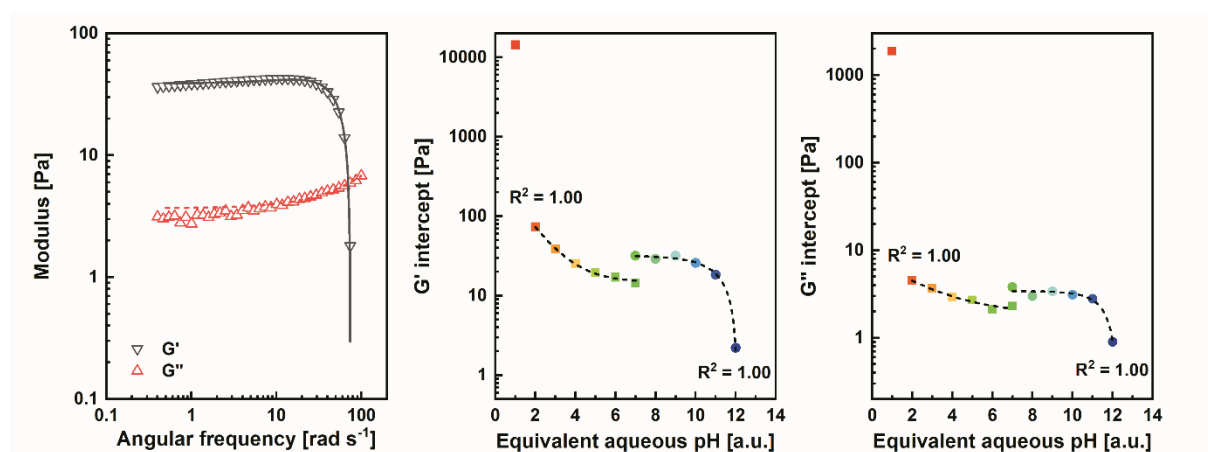


Figure S5. a) Representative rheological data of 2.5 wt.% OCNF gel providing data on storage (G') and loss (G'') moduli (inverted grey triangles and red triangles respectively) with increasing angular frequency. b) Change in calculated gel storage modulus at an angular frequency of 0 rad s⁻¹ with pH. c) Change in calculated gel loss modulus at an angular frequency of 0 rad s⁻¹ with pH. N = 1, n = 1.

Table S6. Data relating to OCNF gel intrinsic storage and loss moduli assuming equivalent aqueous pH, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Interception points calculated from each data set equation, plus their average, are also included. N = 1, n = 1.

Parameters and calculated values			Data Set	
			G'	G''
Exponential equation parameters	HCl	A	123	2.33
		B	0.87	0.43
		C	14.7	1.84
	NaOH	A	-5.8×10^{-4}	-2.1×10^{-7}
		B	-0.82	-1.27
		C	32.0	3.41
HCl	Initial gradient equation	$-33.8x + 139$	$-0.93x + 6.37$	
	Final gradient equation	$-1.05x + 22.7$	$-0.17x + 3.34$	
	Interception point	3.5	4.0	
NaOH	Initial gradient equation	$-0.62x + 35.9$	$-0.01x + 3.49$	
	Final gradient equation	$-16.6x + 203$	$-1.77x + 22.3$	
	Interception point	10.4	10.7	

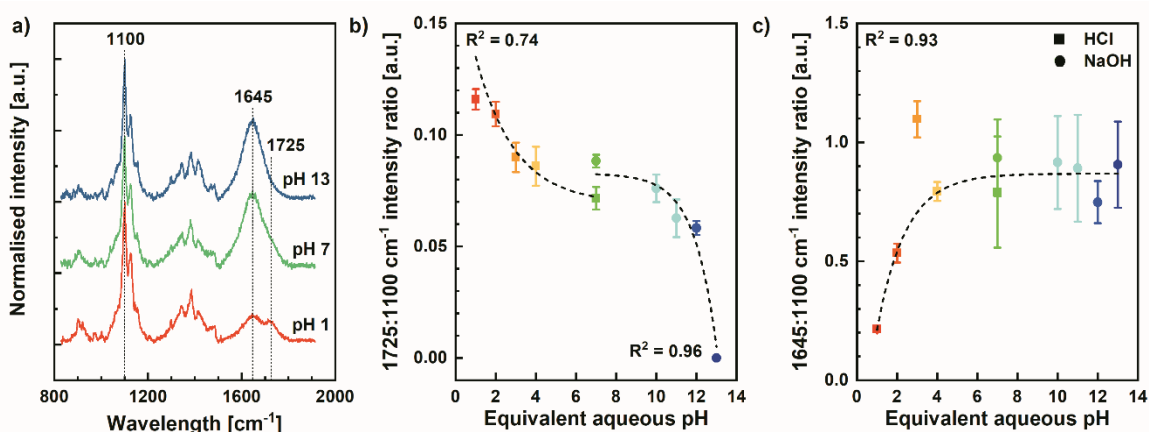


Figure S6. a) Representative Raman spectra of 2.5 wt.% OCNF gels at pH 1, 7, and 13. b) Change in ratio between 1725 and 1100 band intensities with pH. c) Change in ratio between 1645 and 1100 band intensities with pH. N = 1, n = 3. Error bars: \pm SE.

Table S7. Data relating to the OCNF 1725:1100 band intensity ratio, acquired via Raman spectroscopy, assuming equivalent aqueous pH, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Interception points calculated from each data set equation, plus their average, are also included. N = 1, n = 3. Error: \pm SE.

Parameters and calculated values			Data Set			
			Mean - SE	Mean	Mean + SE	Average
Exponential equation parameters	HCl	A	0.05	0.04	0.03	-
		B	0.68	0.51	0.36	-
		C	0.07	0.07	0.07	-
	NaOH	A	-1.5×10^{-4}	-2.5×10^{-7}	-8.6×10^{-7}	-
		B	-0.41	-0.90	-0.81	-
		C	0.10	0.08	0.09	-
HCl	Initial gradient equation	$-0.02x + 0.14$	$-0.02x + 0.14$	$-0.01x + 0.14$	-	
	Final gradient equation	$-0.00x + 0.08$	$-0.00x + 0.09$	$-0.00x + 0.10$	-	
	Interception point	3.7	3.8	4.1	3.9 ± 0.1	
NaOH	Initial gradient equation	$-0.00x + 0.11$	$-0.00x + 0.09$	$-0.00x + 0.10$	-	
	Final gradient equation	$-0.02x + 0.27$	$-0.02x + 0.28$	$-0.02x + 0.32$	-	
	Interception point	10.0	10.5	10.4	10.3 ± 0.2	

Table S8. Data relating to the OCNF 1645:1100 band intensity ratio, acquired via Raman spectroscopy, assuming equivalent aqueous pH, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Interception points calculated from each data set equation, plus their average, are also included. N = 1, n = 3. Error: \pm SE.

Parameters and calculated values		Data Set		
		$\overline{\text{HCl}} - \text{SE}$	$\overline{\text{HCl}} - \text{SE}$	$\overline{\text{HCl}}$
		$\overline{\text{NaOH}} - \text{SE}$	$\overline{\text{NaOH}} + \text{SE}$	$\overline{\text{NaOH}}$
Exponential equation parameters	A	-0.52	-0.40	-0.49
	B	1.06	0.28	0.70
	C	0.69	1.05	0.87
Initial gradient equation		$0.11x + 0.31$	$0.15x + 0.15$	$0.16x + 0.22$
Final gradient equation		$0.00x + 0.69$	$0.01x + 0.88$	$0.00x + 0.86$
Interception point		3.5	4.3	3.9
Parameters and calculated values		Data Set		
		$\overline{\text{HCl}} + \text{SE}$	$\overline{\text{HCl}} + \text{SE}$	Average
		$\overline{\text{NaOH}} - \text{SE}$	$\overline{\text{NaOH}} + \text{SE}$	
Exponential equation parameters	A	-0.66	-0.52	-
	B	1.18	0.53	-
	C	0.77	1.05	-
Initial gradient equation		$0.12x + 0.38$	$0.20x + 0.17$	-
Final gradient equation		$0.00x + 0.77$	$0.00x + 1.03$	-
Interception point		3.3	4.6	3.9 ± 0.2

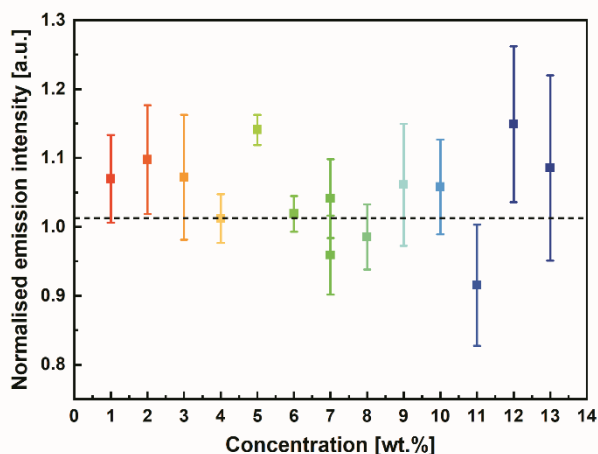


Figure S7. Change in normalized total emission intensity with pH. Intensity normalized to average intensity value at pH 7 for each reproduced sample. No significant change is observed across the pH range. N = 3, n = 3. Error: \pm SE.

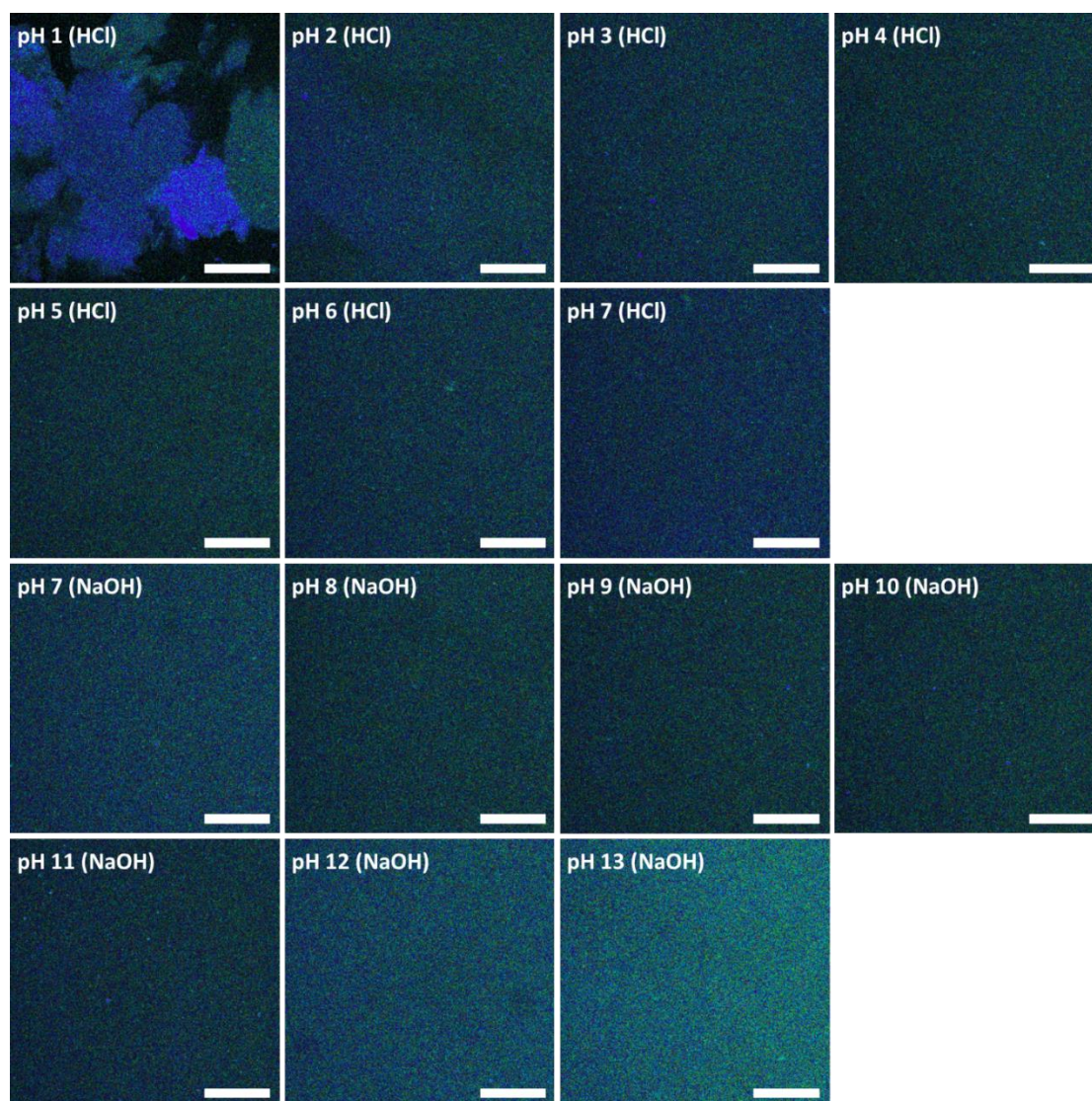


Figure S8. Typical MCLSS images of 2.5 wt.% OCNF gel at various equivalent aqueous pH values demonstrating aggregation of the fibrils at low pH. Scale bar: 200 μ m

Table S9. Data relating to OCNF MCLSS pH experiments for 468:504 nm emission intensity ratio, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Values calculated from each data set equation, plus their average, are also included. N = 4, n = 3. Error: \pm SE.

Parameters and calculated values			Data Set			
			Mean - SE	Mean	Mean + SE	Average
Exponential equation parameters	HCl	A	0.02	0.09	0.20	-
		B	0.19	0.70	0.73	-
		C	1.00	1.03	1.04	-
	NaOH	A	-4.4×10^{-6}	-2.3×10^{-7}	-1.2×10^{-6}	-
		B	-0.70	-0.92	-0.78	-
		C	1.04	1.05	1.06	-
HCl	Initial gradient equation	$-0.01x + 1.04$	$-0.03x + 1.15$	$-0.07x + 1.30$	-	
	Final gradient equation	$-0.00x + 1.03$	$-0.00x + 1.04$	$-0.00x + 1.07$	-	
	Interception point	4.2	3.7	3.1	3.7 ± 0.3	
NaOH	Initial gradient equation	$-0.00x + 1.05$	$-0.00x + 1.05$	$-0.00x + 1.07$	-	
	Final gradient equation	$-0.03x + 1.31$	$-0.02x + 1.28$	$-0.02x + 1.26$	-	
	Interception point	10.3	10.5	10.4	10.4 ± 0.1	

Table S10. Data relating to OCNF MCLSS pH experiments for 504:513 nm emission intensity ratio, including parameter values (A, B, and C) for the fitted exponential equation (Equation 4) for each data set. Values calculated from each data set equation, plus their average, are also included. N = 4, n = 3. Error: \pm SE.

Parameters and calculated values		Data Set			
		Mean - SE	Mean	Mean + SE	Average
Exponential equation parameters	A	-5.5×10^{-6}	-5.7×10^{-6}	-6.4×10^{-5}	-
	B	-0.57	-0.57	-0.39	-
	C	1.01	1.01	1.02	-
Initial gradient equation		$-0.00x + 1.01$	$-0.00x + 1.01$	$-0.00x + 1.02$	-
Final gradient equation		$-0.01x + 1.12$	$-0.01x + 1.14$	$-0.01x + 1.11$	-
Interception point		10.8	10.8	10.1	10.5 ± 0.3

Data access statement

Underlying data are openly available from data.bris.ac.uk/data under the DOI: