Star-like supramolecular complexes of reducing-end functionalized cellulose nanocrystals

Ana Villares,[a]* *Céline Moreau,*[a] *Bernard Cathala*[a]

[a] INRA, UR1268 Biopolymères Interactions Assemblages, Rue de la Géraudière, 44316 Nantes, France

* Corresponding Author: Ana Villares

INRA, UR1268 Biopolymères Interactions Assemblages, Rue de la Géraudière, 44316 Nantes, France

Tel: 00 33 (0)2 40 67 50 18

Email: ana.villares@inra.fr

Experimental

FTIR

Infrared spectra were obtained from KBr pellets containing freeze-dried t-CNC samples placed directly in a Nicolet iS50 FTIR spectrometer (Thermo Scientific) in absorbance mode. All spectra were collected with a 4 cm^{-1} resolution after 200 continuous scans from 400 to 4000 cm^{-1}. Oxidized t-CNC were acidified to pH 2 by the addition of HCl in order to protonate carboxylic acids.

Preparation of poly(allylamine hydrochloride) (PAH)-coated surfaces

PAH films were deposited on QCM-D gold electrodes by spin-coating. 1 mL of a PAH solution (1 g L^{-1}, PolySciences, Mw 120-200 000 g mol^{-1}) was poured onto the substrate and, after 10 min of adsorption, the substrate was spun at 3600 rpm for 60 s. The film was than rinsed with 1 mL of deionized water and spun.

Results

T-CNC characterization

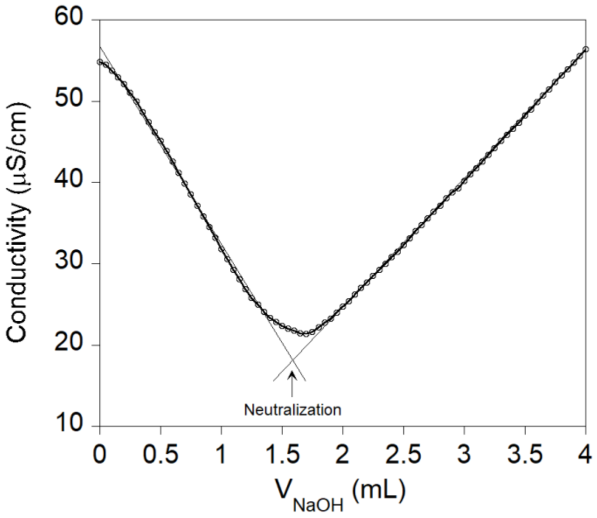

Figure S1. Conductometric titration curve of the unmodified t-CNC (10 mL, 6.9 g L^{-1}) titrated against NaOH (0.001 M) where the intersection of the two slopes (neutralization point) corresponds to the amount of strong acid (sulfate half ester groups) on the t-CNC surface.

Introduction of biotin functionality at reducing ends of t-CNC

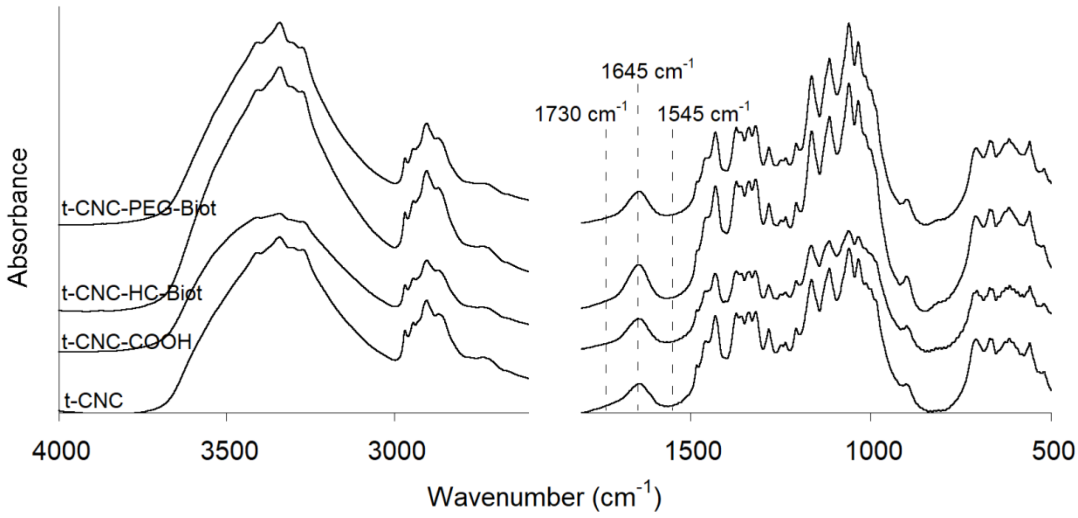

Figure S2. FTIR spectra in absorbance of the unmodified t-CNC, oxidized t-CNC (t-CNC-COOH) and both biotin-functionalized t-CNC (t-CNC-HC-Biot and t-CNC-PEG-Biot, respectively).

Table S1. FTIR relative peak intensities at 895, 1372, 1430 and 2900 cm^{-1} and total crystallinity index (TCI) and lateral order index (LOI) calculated from these FTIR data for the unmodified t-CNC, oxidized t-CNC (t-CNC-COOH) and both biotin-functionalized t-CNC (t-CNC-HC-Biot and t-CNC-PEG-Biot, respectively).

	895 cm^{-1}	1372 cm^{-1}	1430 cm^{-1}	2900 cm^{-1}	TCI	LOI
t-CNC	0.054	0.196	0.190	0.220	0.93±0.06	3.66±0.17
t-CNC-COOH	0.048	0.167	0.163	0.177	0.91±0.04	3.33±0.11
t-CNC-HC-Biot	0.065	0.256	0.246	0.275	0.98±0.07	3.82±0.02
t-CNC-PEG-Biot	0.048	0.191	0.182	0.199	0.99±0.00	3.82±0.02

Assembly of biotin-functionalized t-CNCs by streptavidin (SAV)

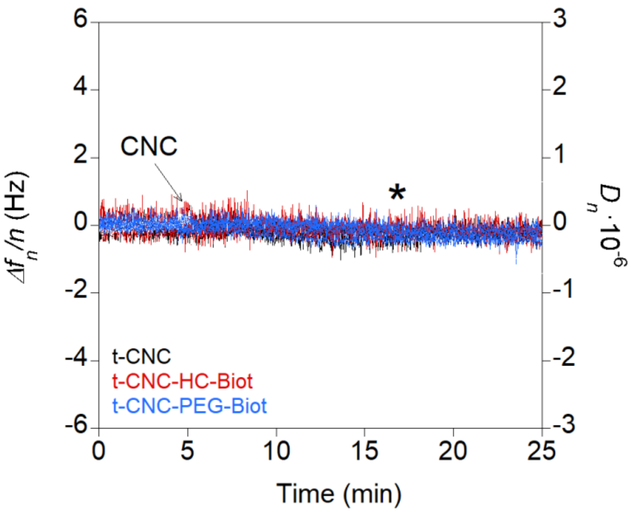

Figure S3. Frequency ($\Delta f_n/n$) and dissipation (ΔD_n) changes for the overtone n = 3 during adsorption of unmodified t-CNCs and biotin-functionalized t-CNCs (t-CNC-HC-Biot and t-CNC-PEG-Biot, respectively) at 0.5 g L^{-1} in water onto gold surfaces. The arrow indicates the injection of t-CNC, t-CNC-HC-Biot or t-CNC-PEG-Biot and asterisk the rinse step with water.

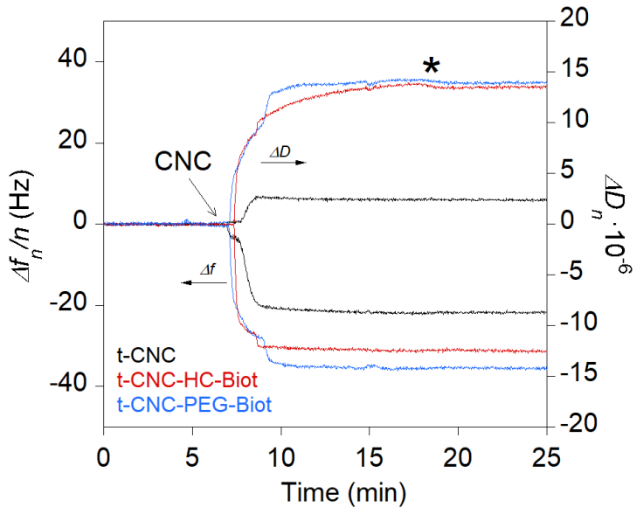

Figure S4. Frequency ($\Delta f_n/n$) and dissipation (ΔD_n) changes for the overtone n = 3 during adsorption of unmodified t-CNCs and biotin-functionalized t-CNCs (t-CNC-HC-Biot and t-CNC-PEG-Biot, respectively) at 0.5 g L^{-1} onto SAV-coated surfaces at pH 5. The arrow indicates the injection of t-CNC, t-CNC-HC-Biot or t-CNC-PEG-Biot and asterisk the rinse step with water.

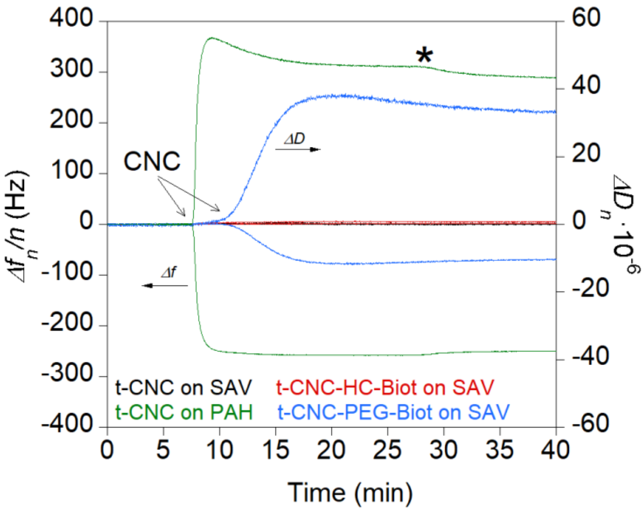

Figure S5. Frequency ($\Delta f_n/n$) and dissipation (ΔD_n) changes for the overtone n = 3 during adsorption of unmodified t-CNCs at 0.5 g L^{-1} onto PAH-coated surfaces (green line); and unmodified t-CNCs and biotin-functionalized t-CNCs (t-CNC-HC-Biot and t-CNC-PEG-Biot, respectively) at 0.5 g L^{-1} onto SAV-coated surfaces at pH 7. The arrow indicates the injection of t-CNCs and the asterisk the rinse step with water.

Table S2. Frequency ($\Delta f_n/n$), dissipation (ΔD_n) values at the end of the adsorption process, and dissipation-to-frequency ratios obtained from the ΔD_n - $\Delta f_n/n$ plots for the overtone n = 3 corresponding to the adsorption of t-CNC-PEG-Biot onto SAV layers and unmodified t-CNCs onto PAH layers.

	$\Delta f_n/n$ (Hz)	$\Delta D_n \cdot 10^{-6}$	$\lvert \Delta D_n/ \Delta f_n/n \rvert \cdot 10^{-6}$ Hz^{-1}
t-CNC-PEG-Biot on SAV	-75.8±97.0	36.6±44.2	0.57±0.20
t-CNC on PAH	-262.4±5.6	43.4±4.8	0.20±0.04

Table S3. Z-average diameter (Z-d) values and polydispersity indexes (PDI) determined by dynamic light scattering for the biotin-functionalized t-CNCs (t-CNC-HC-Biot and t-CNC-PEG-Biot, respectively), before and after the addition of streptavidin. Results are expressed as the mean of 6 measurements ± standard deviation.

	Before SAV addition		After SAV addition	
	Z-d (nm)	PDI	Z-d (nm)	PDI
t-CNC-HC-Biot	226.2±8.2	0.214±0.009	229.9±18.4	0.236±0.027
t-CNC-PEG-Biot	243.9±10.0	0.255±0.031	241.6±29.8	0.276±0.065