

Electronic Supplementary Information for

Chiroptical Luminescent Nanostructured Cellulose Films

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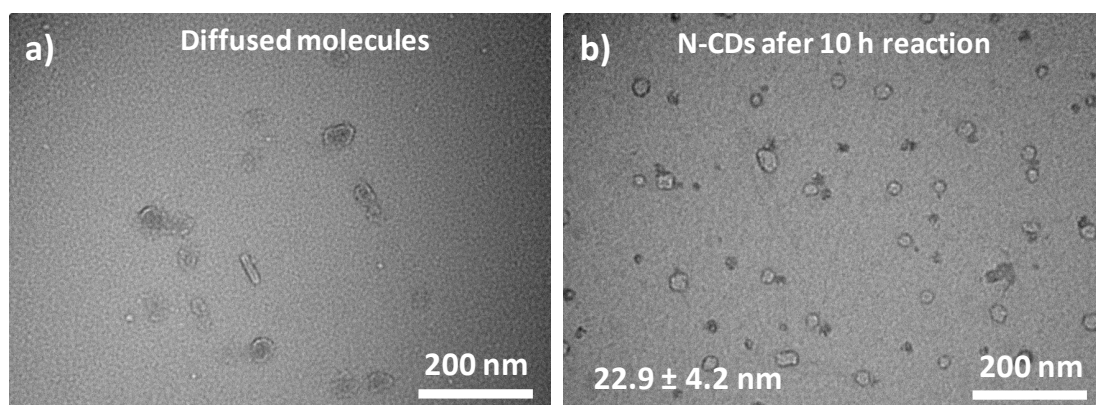


Fig. S1. TEM images of a) diffused molecules through dialysis membrane and b) N-CDs prepared after 10 h of hydrothermal reaction. The average and standard deviation diameter of N-CDs is based on a count of 50 nanoparticles.

N-CDs were obtained after hydrothermal synthesis of melamine with D-glucose at 160 °C for different times. All syntheses result in a brownish dispersion together with a deposition of black carbonaceous material. The amount of calcined material depends on the reaction time. Short reaction times yield almost transparent dispersions, while long reactions yield mainly carbonized materials. Since short times are not enough to build-up N-CDs and long reactions result in highly carbonaceous materials, a synthesis time of 4 h was selected as the most suitable for the development of N-CDs.

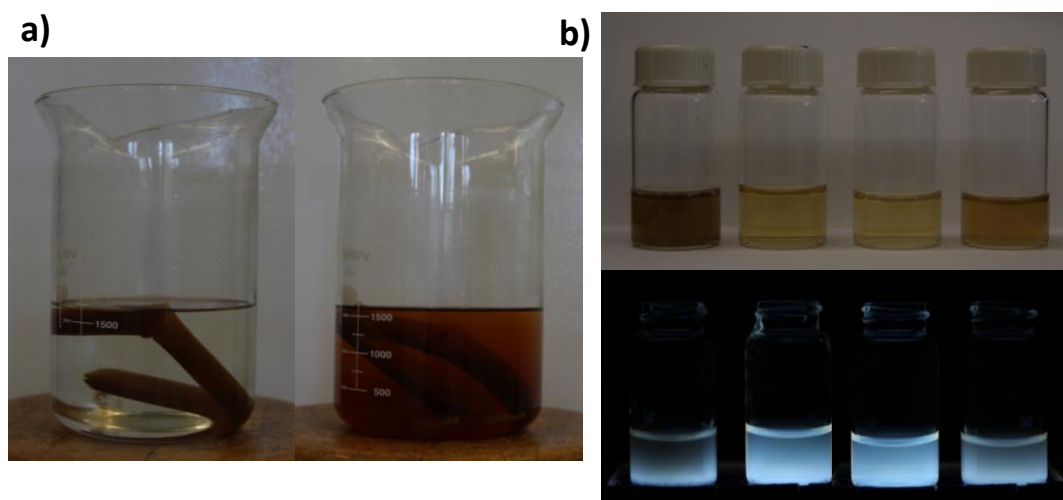


Fig. S2. N-CDs were obtained after filtration through a 0.45 µm pore-size PVDF filter membrane and further dialysis of the remaining fine brownish stable dispersion for 6 days. a) Photographs showing the fine brownish dispersion into the dialysis bag suspended in distilled water at the beginning (left) and at the end (right) of the dialysis process. Note the large amount of diffused molecules through the membrane. b) From left to right: photographs under natural (top) and 365 nm UV light (bottom) for the whole hydrothermal reaction, the fine brownish stable dispersion after removing the carbonaceous material, after filtration through 0.45 µm pore-size PVDF filter and after dialysis. Note that the luminescence intensity is slightly decreased after the removal of diffused organic fluorophores.

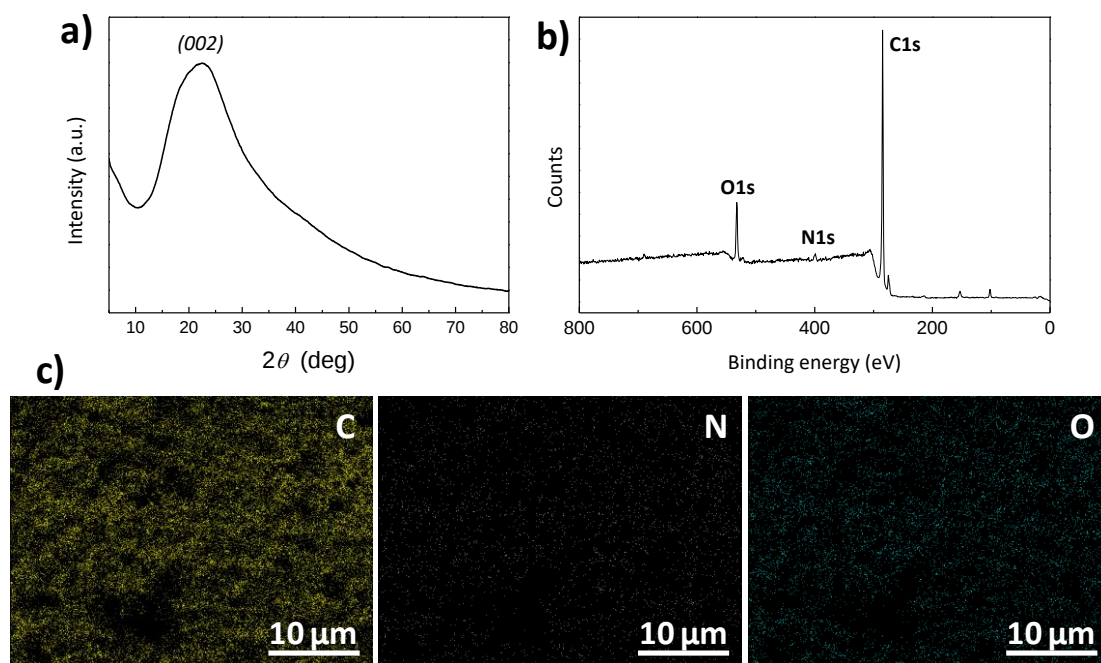


Fig. S3. a) PXRD pattern; b) XPS survey spectra and c) elemental mapping of synthesized N-CDs showing evenly distributed C, N and O atoms.

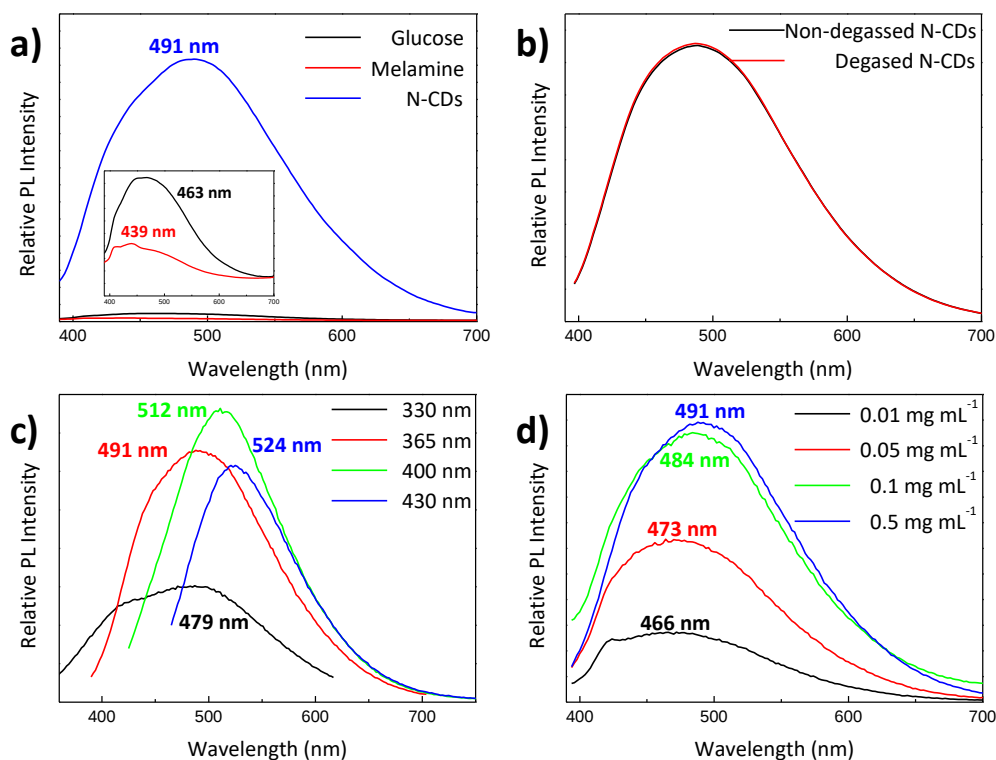


Fig. S4. Photoluminescence emission spectra of a) glucose, melamine, and glucose+melamine (N-CDs) suspensions after hydrothermal treatment at 160 °C for 4 h; b) water-dispersed N-CDs before and after degassing to elucidate fluorescence/phosphorescence contribution; c) aqueous N-CDs suspensions for different excitation wavelengths and d) emission spectra of aqueous N-CDs suspensions having different concentration when excited at 365 nm. Note that if not stated, a N-CD concentration of 0.5 mg mL⁻¹ has been excited under 365 nm UV light.

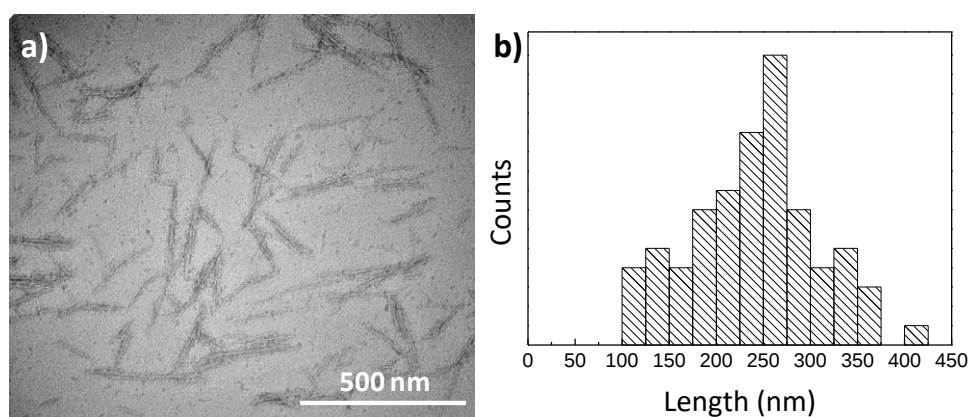


Fig. S5. a) Representative transmission electron microscopy (TEM) and b) length-distribution of CNTs (based on count of 80 particles).

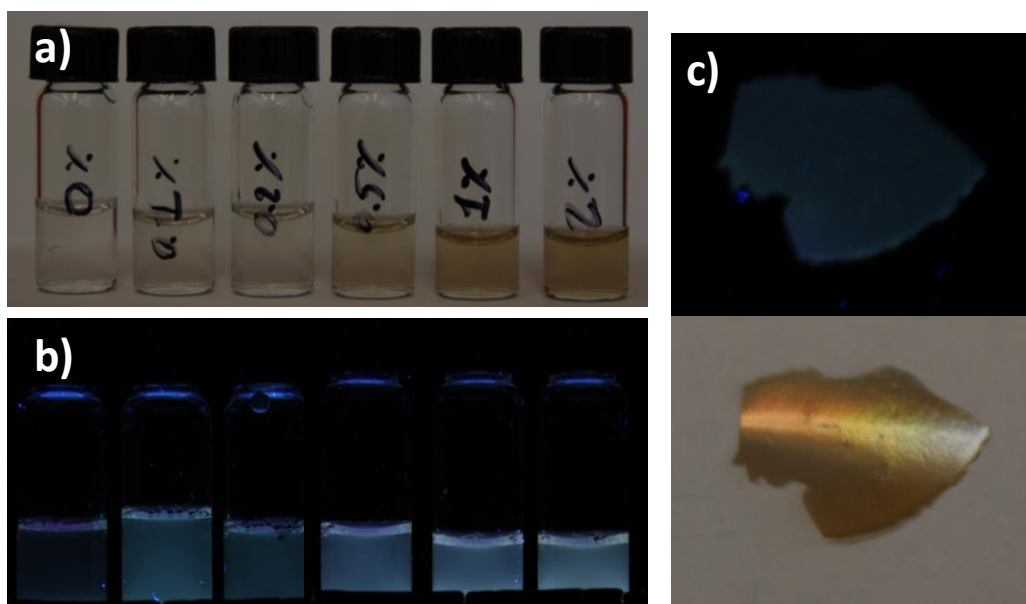


Fig. S6. Photographs of aqueous C-dot dispersions under a) natural and b) 365 nm UV light for aqueous N-CD/CNC dispersions having a N-CDs concentration of 0, 0.1, 0.2, 0.5, 1 and 2 wt% from left to right; c) photographs of chiral nematic films showing their luminescent properties when exposed to 365 nm UV light (up) and their iridescence under natural light (bottom).

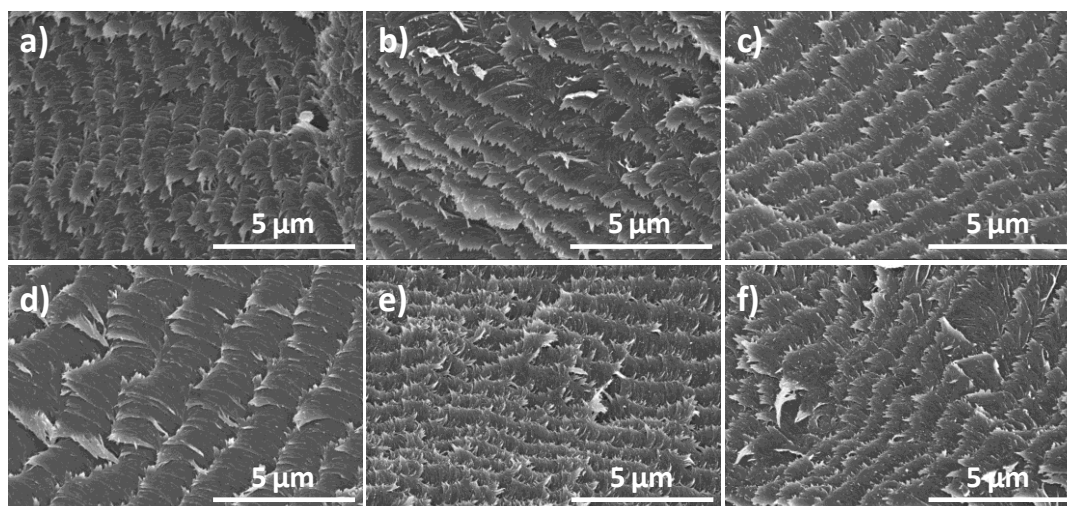


Fig. S7. FE-SEM micrographs viewed along fracture cross-sections of the N-CD/CNC composite films showing small differences on their twisted layers upon N-CD addition: a) 0; b) 0.1; c) 0.2; d) 0.5; e) 1 and f) 2 wt%. Note that chiral nematic order is maintained for all the compositions.

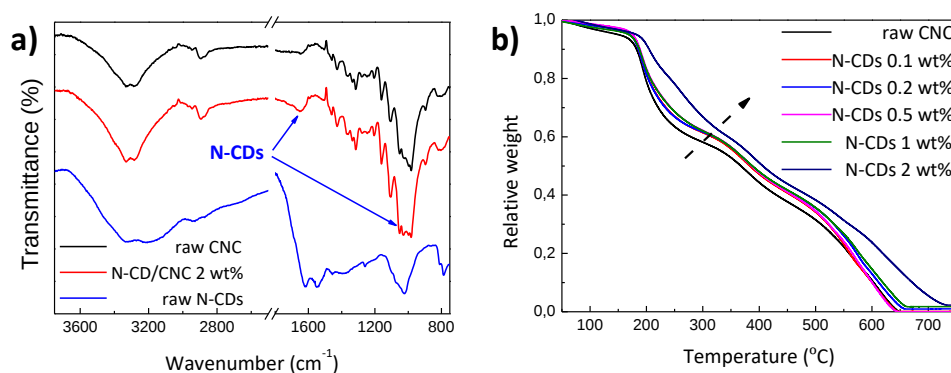


Fig. S8. a) FTIR spectra and d) thermogravimetric analysis of N-CD/CNCs films heated at 10 °C min⁻¹ under N₂ atmosphere. Note that upon N-CD loading the thermal stability of films is notably increased.

FTIR technique has been conducted to confirm the presence of N-CDs within the CNC matrix. Pure CNCs show (Fig. S7a) the characteristic spectrum of cellulose, having a broad band in the 3650–3200 cm⁻¹ region and another band centered at 2902 cm⁻¹, corresponding to the O–H stretching vibration and the asymmetric and symmetric stretching of methyl and methylene C–H groups, respectively. Moreover, the 1160 cm⁻¹ band is assigned as C–O–C bending and 897 cm⁻¹ band is due to the C–O–C asymmetric stretching at the β glycosidic linkage. On the other hand, N-CD/CNC 2 wt% film displays the characteristic cellulose bands together with the 1618 and 1030 cm⁻¹ bands arising from N-CDs, confirming their presence within the composite films.

TGA results (Fig. S7b) show that the thermal stability of composite films improves upon N-CD addition. Indeed, the onset of the thermodegradation process (taken as the temperature in which the first 10% of the mass is lost) takes place 22.3 °C higher with the addition of 2 wt% N-CDs. The depolymerization, dehydration and decomposition of cellulose glycosyl units may be delayed due to nitrogen release from the N-CDs upon heating, inhibiting the overall thermodegradation process.

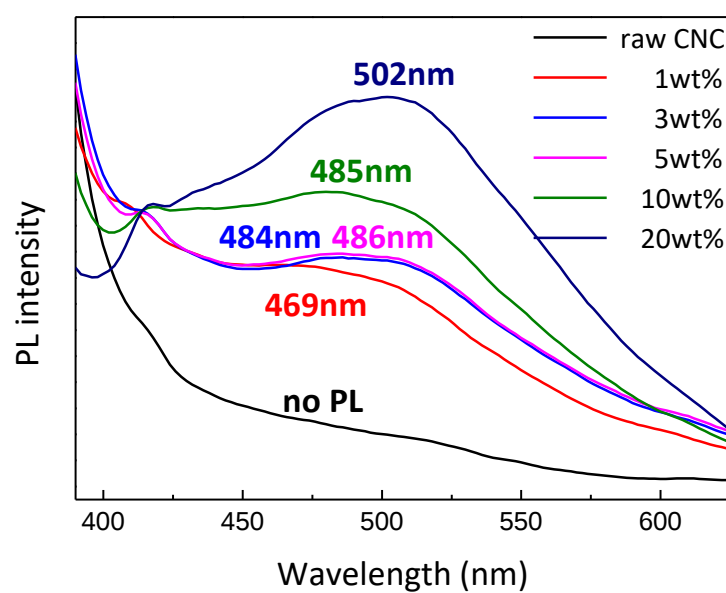


Fig. S9. PL spectra of CNC composite films having up to 20 wt% of unpurified N-CDs+fluorophores. A continuous increase in luminescence is observed.