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Materials Chemistry B

†Electronic Supplementary Information (ESI)

Blend electrospinning of dye-functionalized chitosan and poly(ε-caprolactone): towards biocompatible pH-sensors†

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^{1}H-NMR spectra

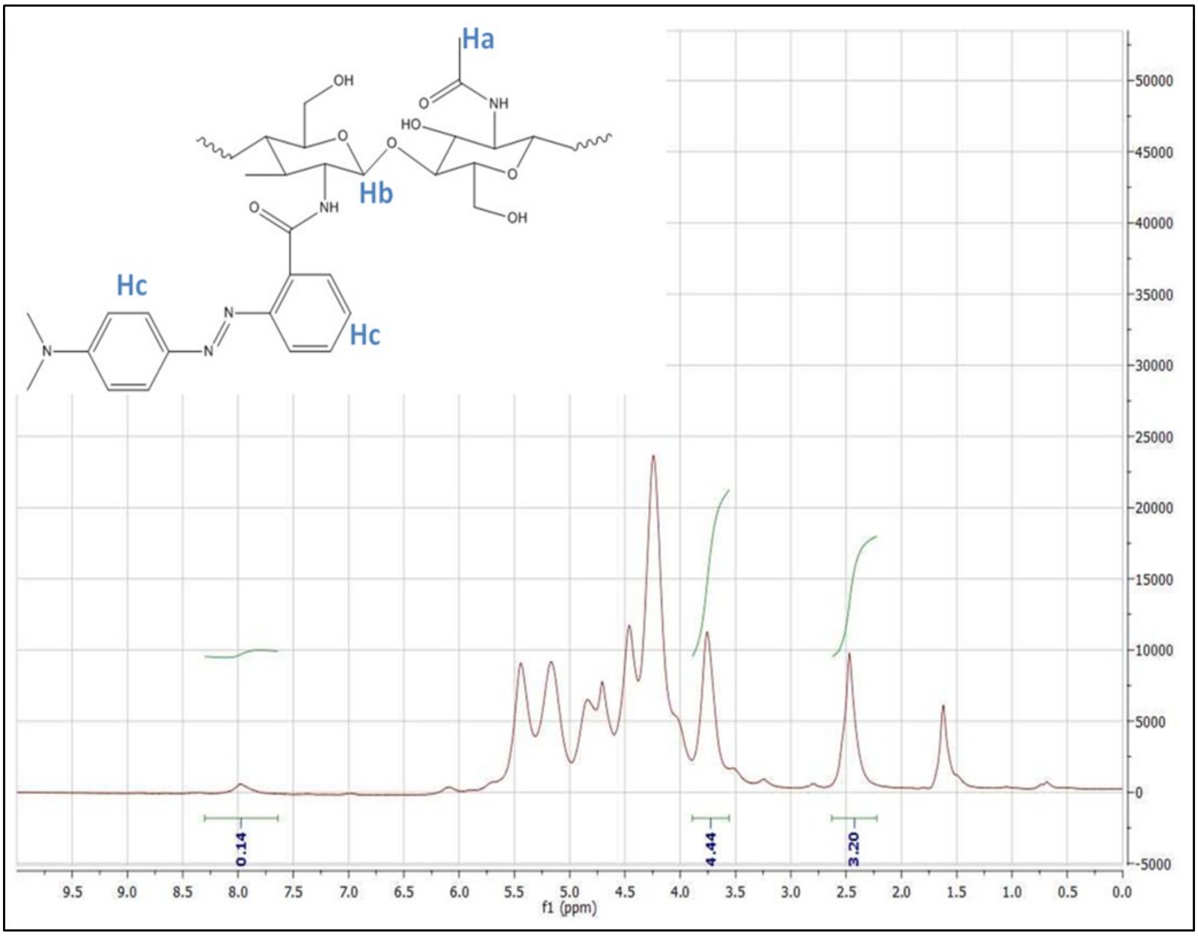

Figure a. ^{1}H-NMR spectrum of Cs-MR$_5$ (500 MHz, TFA-d): δ(ppm) 8.5 – 7.5 (8H, Hc), 3.6 (1H, Hb), 2.5 (3H, Ha)

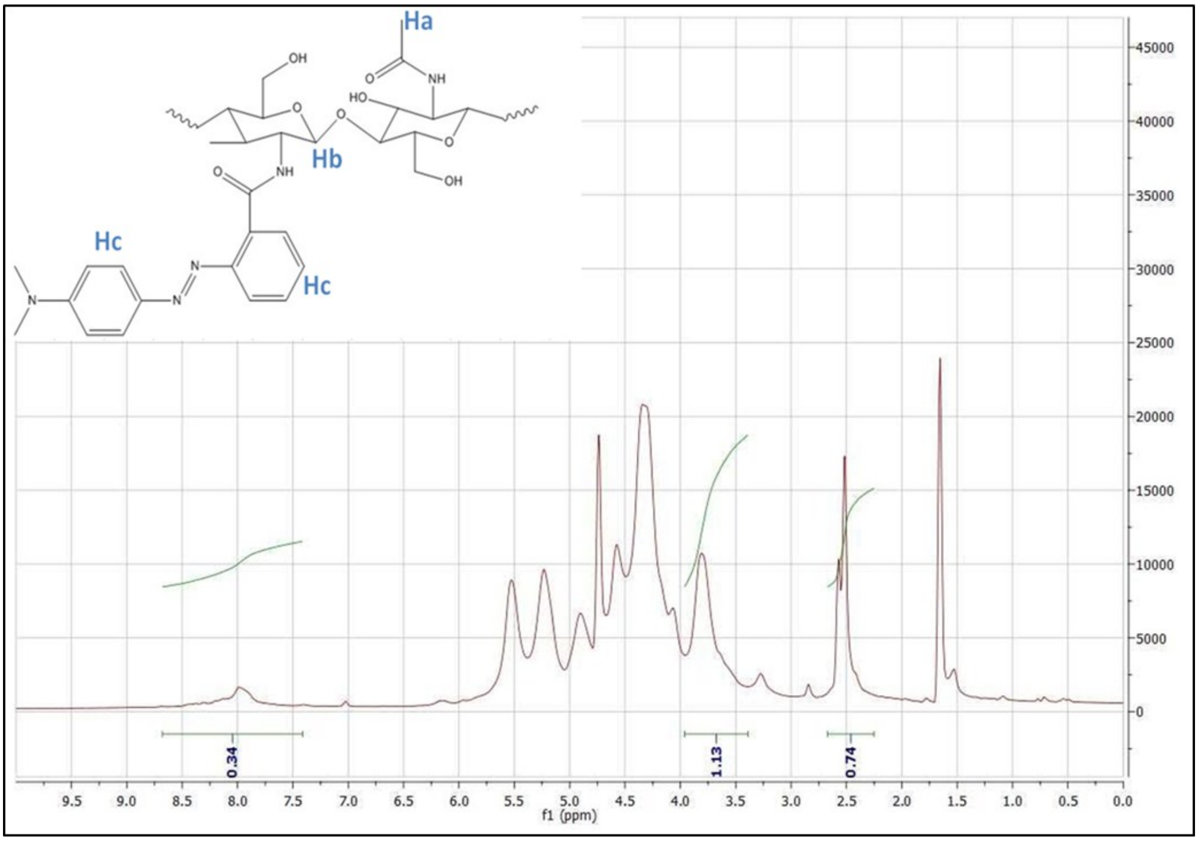

Figure b. 1H-NMR spectrum of Cs-MR10 (500 MHz, TFA-d): δ(ppm) 8.5 – 7.5 (8H, Hc), 3.6 (1H, Hb), 2.5 (3H, Ha)

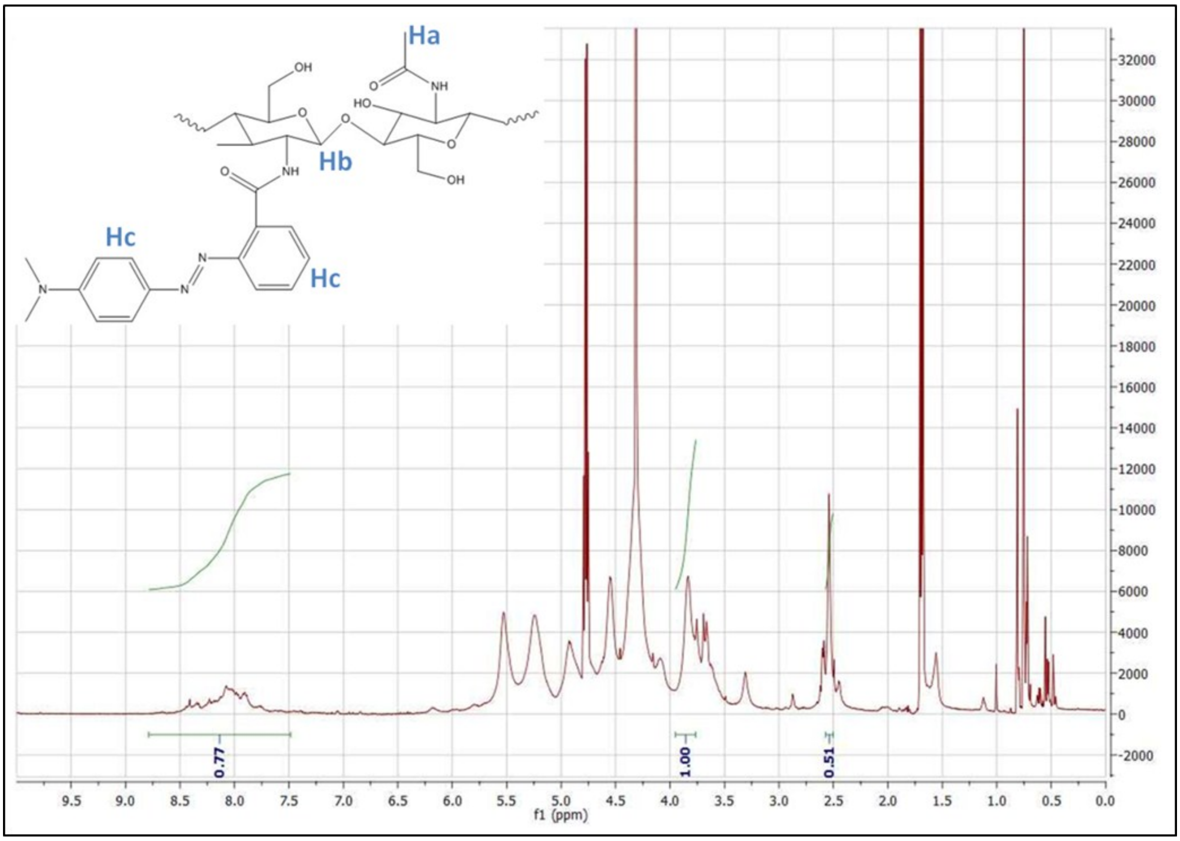

Figure c. 1H-NMR spectrum of Cs-MR20 (500 MHz, TFA-d): δ(ppm) 8.5 – 7.5 (8H, Hc), 3.6 (1H, Hb), 2.5 (3H, Ha). Sharp peaks correspond to the presence of remaining ethanol

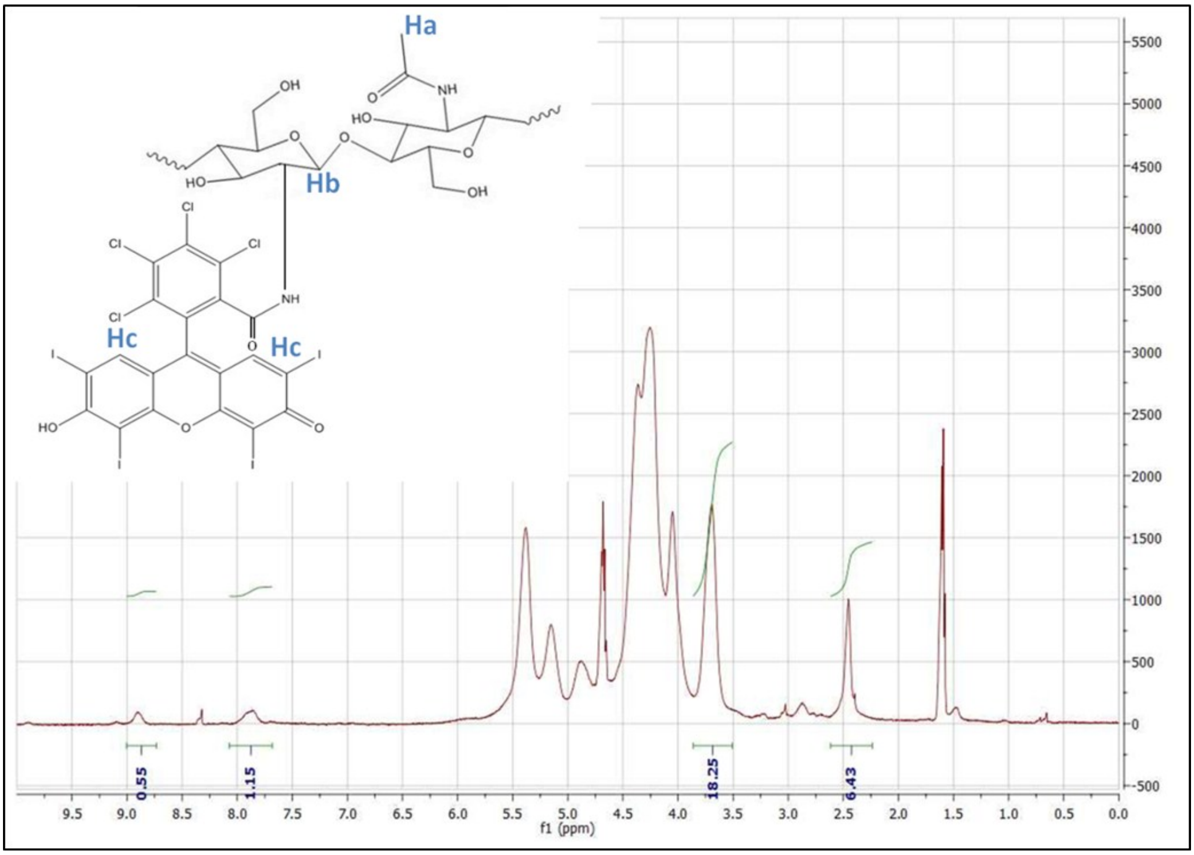

Figure d.1H-NMR spectrum of Cs-RB (500 MHz, TFA-d): δ(ppm) 8.9 and 7.85 (1H, Hc), 3.6 (1H, Hb), 2.5 (3H, Ha)

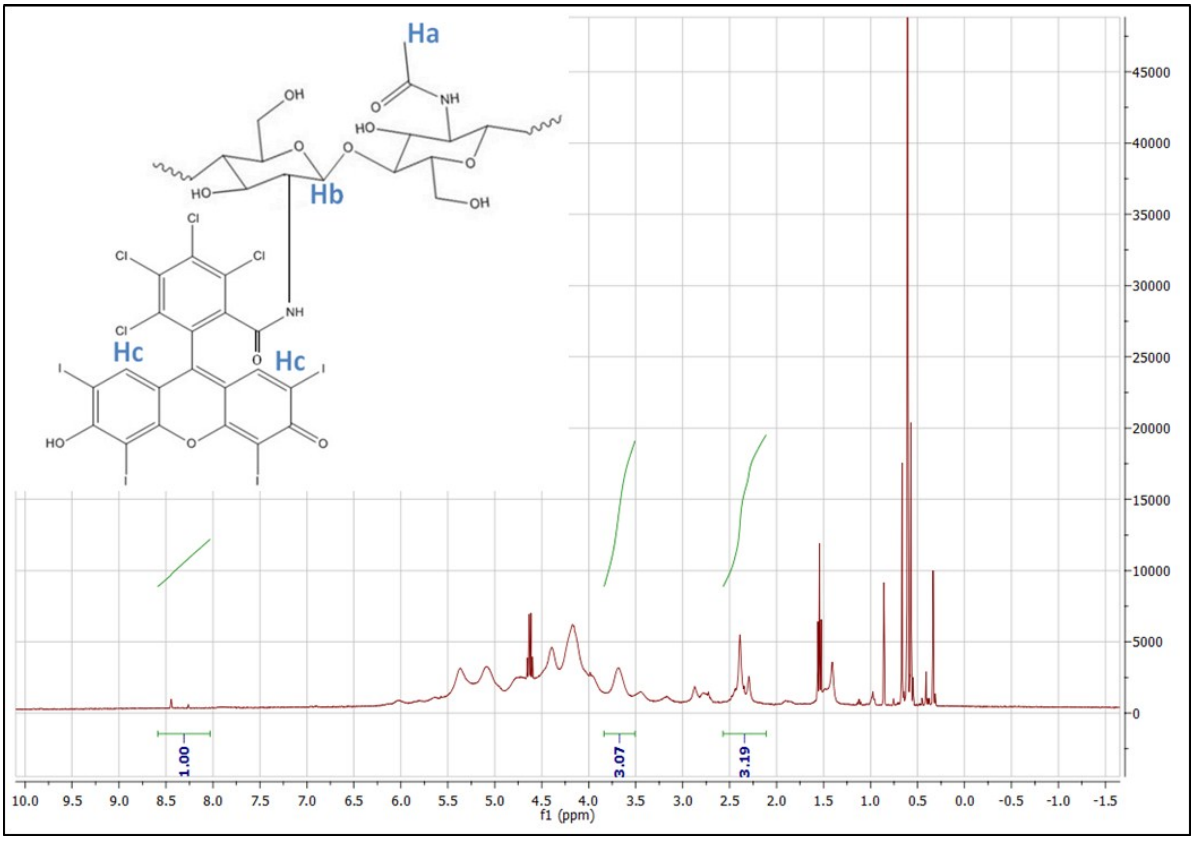

Figure e. 1H-NMR spectrum of CS-RB (500 MHz, TFA-d): δ(ppm) 8-8.5 (1H, Hc), 3.6 (1H, Hb), 2.5 (3H, Ha). Sharp peaks correspond to the presence of remaining ethanol

Dye-modification of chitosan

The produced dye-modified chitosan powders are brightly colored. Chitosan modified with less dye results into lightly colored powders, whereas chitosan modified with more dye results into darker colored powders.

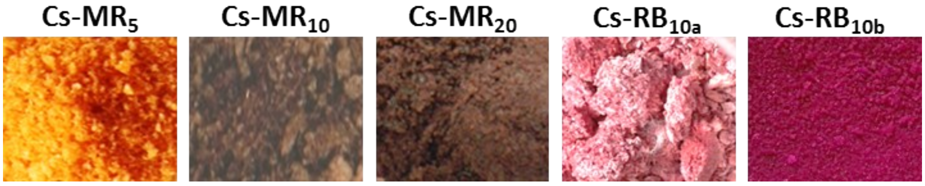

Figure f. Photos of the produced dye-modified chitosan powders

Electrospinning of dye-containing nanofibers

SEM-images show no significant influence of MR-doping or RB-doping on nanofiber morphology. MR-modification has no significant effect on fiber morphology at low dye-concentrations (first row). However, at high MR-concentrations, the insolubility of the MR-modified chitosan results in a lot of beads, *i.e.* poor electrospinnability (second row). For the nanofibers modified with a low RB-concentration, the fiber diameter is much smaller compared to RB-doped or RB-free nanofibers, due to the higher solubility and, thus, lower viscosity in the applied solvent system (third row). The electrospinning solutions containing chitosan modified with a higher RB-concentration remain well electrospinnable albeit with a PCL/Cs ratio of 95/5. This also explains the lower nanofiber diameter of both RB-doped and RB-modified nanofibers, since the addition of less chitosan is characterized by a drop in viscosity (fourth row).

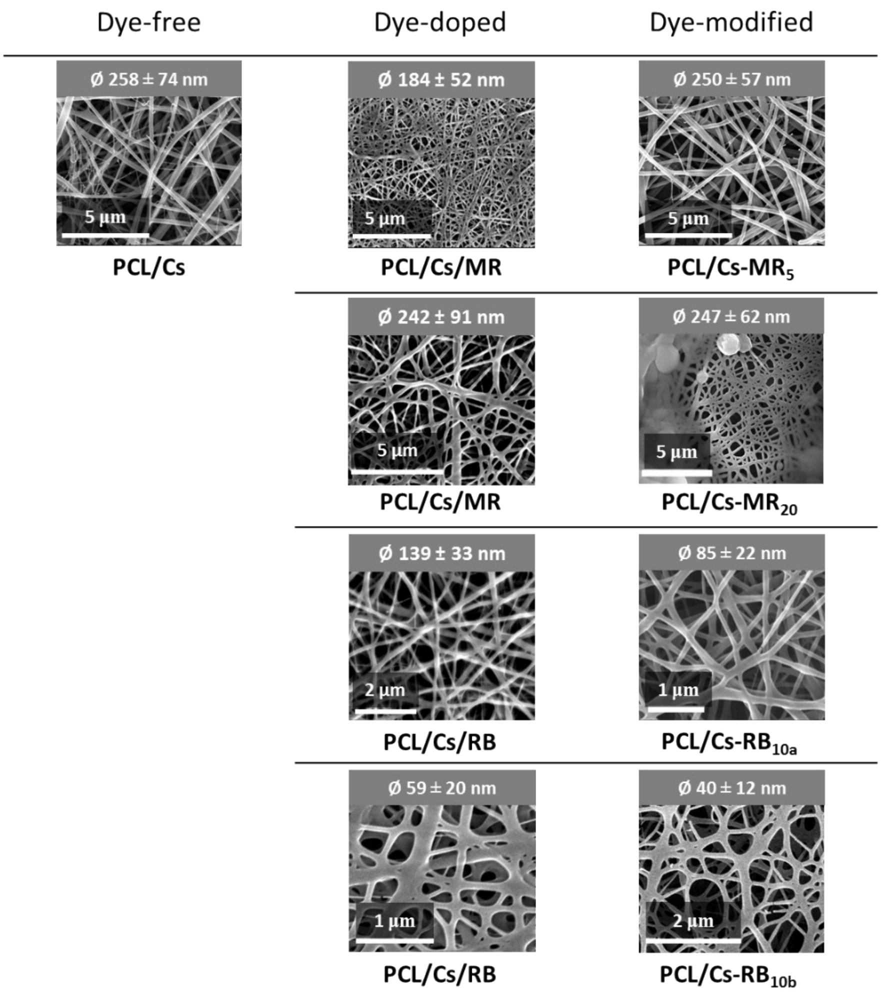

Figure g. Overview of the electrospun nanofibers

Halochromic properties

For clarity, the uncropped version of Figure 4 of the article is given below. Both the MR-containing nanofibers (Figure ha) and the RB-containing nanofibers (Figure hb) show a color change similar to the pure dyes in aqueous solutions. Therefore, it can be stated that the halochromic behavior of the dyes remains majorly intact.

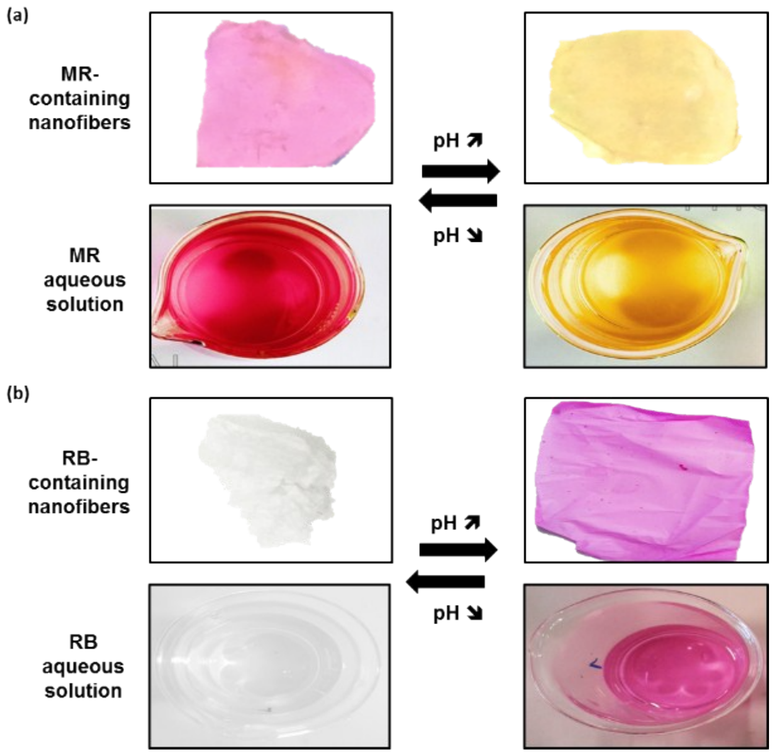

Figure h. Comparison of the halochromic behavior of MR and RB in aqueous solutions and inside the nanofibrous membranes (uncropped version).