Supporting Information

for

Dip In Colorimetric Fluoride Sensing by a Chemically Engineered Polymeric Cellulose/bPEI Conjugate in the Solid State

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Preparation of the TOCNF

TOCNF samples were obtained according to a published protocol,[1] and hereafter reported for convenience of the reader. 1.19 g of KBr (10.0 mmol) and 156 mg of TEMPO (2,2,6,6-Tetramethyl-1-piperidiniloxy radical, 1 mmol) were dissolved in 450 mL of deionized water using a three-necked round bottom flask. 8.1 g of cotton wool (50.0 mmol of anhydroglucose) were added to the solution and soaked for 1 h at room temperature, after which a variable volume of a sodium hypochlorite solution 12.5% (w/w) was added (namely 28 mL, 36 mL, 48 mL, 60 mL and 72 mL). The pH value was maintained in the range of 10.5–11 by using a 0.5 M sodium hydroxide solution in water. The obtained suspension was maintained under stirring for 6 h. The cellulose fibers were then collected by filtration onto a sintered glass funnel, washed with deionized water (250 mL, 3 times), and re-dispersed in water at pH 11.0 (200mL). The slurry thus obtained was sonicated at 0 °C using a Branson Sonifier 250 equipped with a 6.5 mm probe tip working at 20 kHz in continuous mode, with an output power 50% the nominal value (200 W) (approximately 1 h of sonication). After acidification (up to pH 1 – 2) with concentrated HCl (37 % w/w water solution), the white precipitate was recovered onto a sintered glass funnel and washed extensively with deionized water (6 times x 200mL). The final weight of **TOCNF** paste was measured in order to quantify the cellulose content. The amount of carboxylic groups was determined by conductimetric titration of the dried solid. The FT-IR spectra were obtained after preparing KBr pellets.

Use of FT-IR spectroscopy for the quantification of the content of carboxylic groups onto TOCNF.

Here it is described a simple and reliable procedure for the estimation of the carboxylic groups content of **TOCNF** using FT-IR spectroscopy. This is based on the fact that the peak associated to the C=O stretching of the carboxylic groups of **TOCNF** (at 1733 cm^{-1}) increases with the specific concentration of COOH (mmol/g). The TEMPO/NaClO oxidation of the cellulose leads essentially to the conversion of the primary hydroxyl groups of the anhydroglucose units to the corresponding carboxylic acid, with only a minor formation of aldehydes.[2] Therefore, the contribution of the C=O stretching associated to the aldehydes (generally found in the range 1740-1720 cm^{-1} for aliphatic aldehydes) it is expected to be negligible.

Weighted samples of cotton cellulose oxidized with different amounts of NaClO according to the above reported procedure, were titrated with a standardized 0.1 M NaOH (aq) solution in order to quantify the real content of COOH groups (mmol/g). The FT-IR spectra of the dried samples, powdered with infrared grade KBr, were recorded using a Varian 640-IR spectrometer. The data were analyzed with Origin Pro 8 software.

Figure S1 shows the FT-IR spectra of the samples at different degree of oxidation (indicated as mmol of COOH per gram of solid) in the 400 cm^{-1} to 1910 cm^{-1} range (baseline corrected). It is possible to observe that there are no significant differences between the different spectra, except for the peak at 1733 cm^{-1} associated to C=O

stretching whose intensity increases along with the oxidation level. This peak is partially overlapped with the one associated to the OH bending of the absorbed water (1638 cm^{-1}). After a non-linear fitting procedure using a Gaussian function, it is possible to integrate the area of the C=O stretching peak (area **A**, Figure S2). Then, after integrating the area of the absorption band comprised between 800 cm^{-1} and 1574 cm^{-1} (area **B**, Figure S2), the numerical ratio **A/B** was plotted against the content of COOH (mmol/g). As shown by the Figure S3, there is a fairly good linear correlation between these data. No physical meaning is attributed to the numerical ratio **A/B**. This approach is useful for a quick and reliable characterization of the TOCNF in order to quantify the specific content of COOH groups.
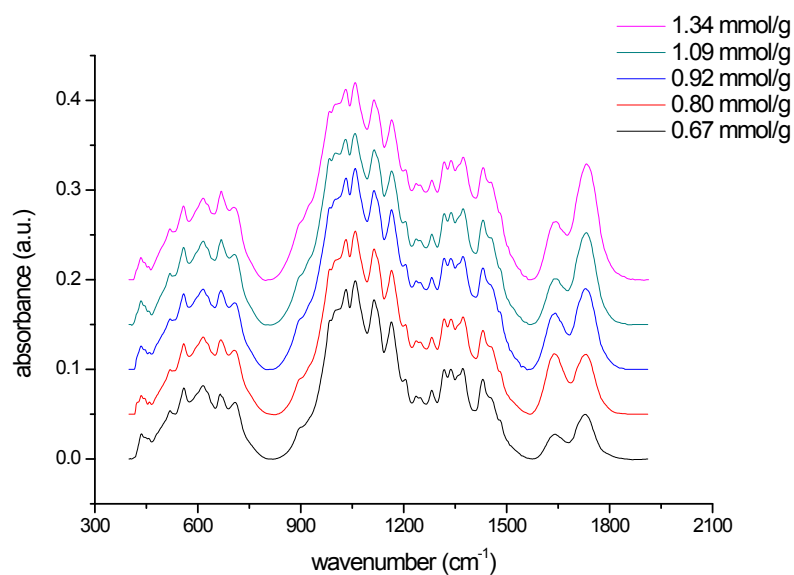

Figure S1. FT-IR spectra (KBr) of **TOCNF** at different degree of oxidation (mmol g^{-1} of COOH).
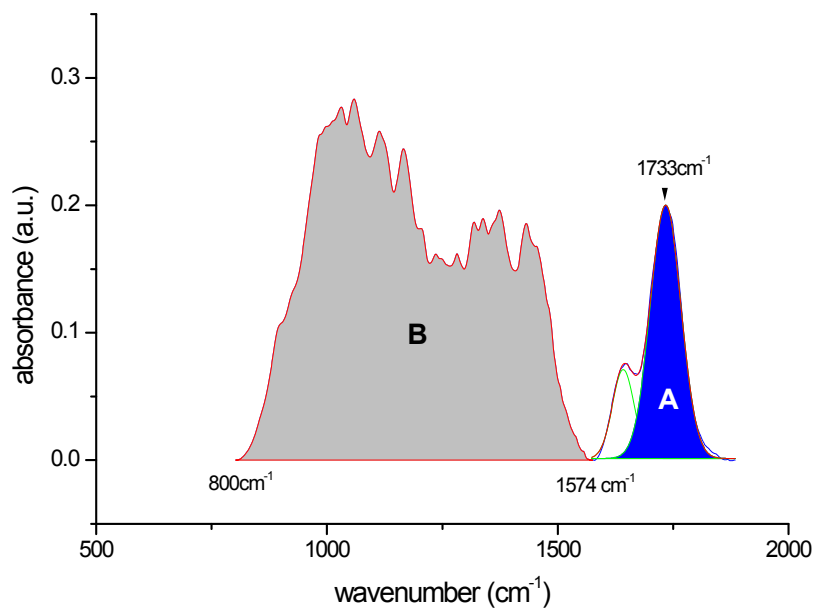
Figure S2. FT-IR bands which have been considered for the calculation of the **A/B** ratio.
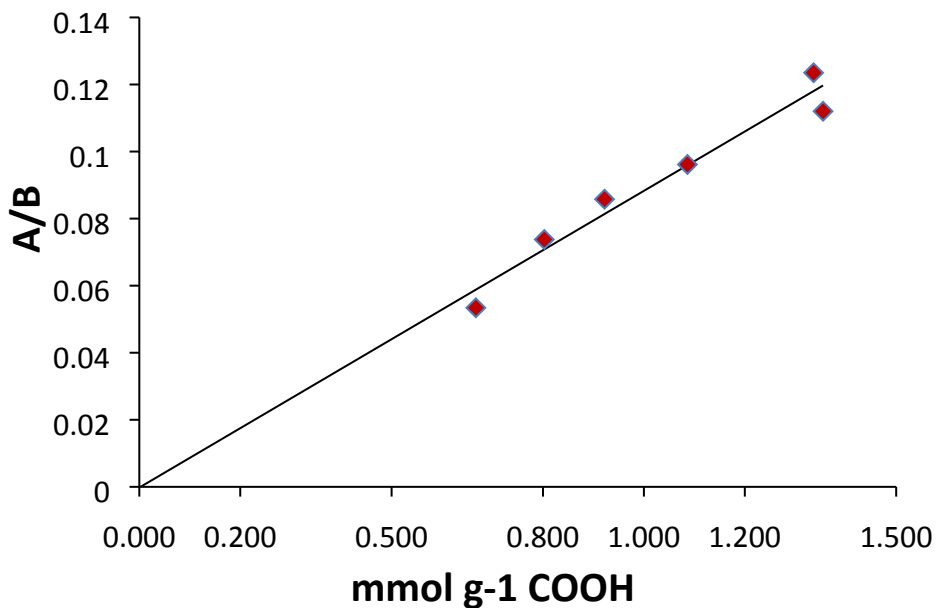

Figure S3. Correlation between the real content of COOH groups (determined by titration) and the numerical ratio **A/B**.
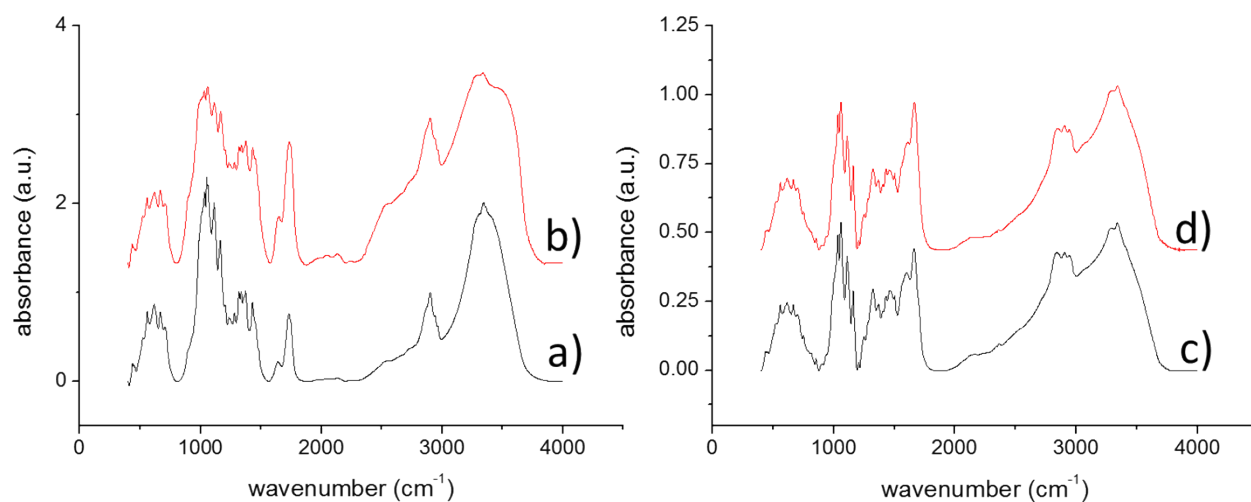
Figure S4. FT-IR (KBr) of: a) **TOCNF1** (0.83 mmol g^{-1} COOH); b) **TOCNF2** (1.54 mmol g^{-1} COOH); c) **TOCNF1-bPEI-Sens(10%)**; d) **TOCNF2-bPEI-Sens(10%),**
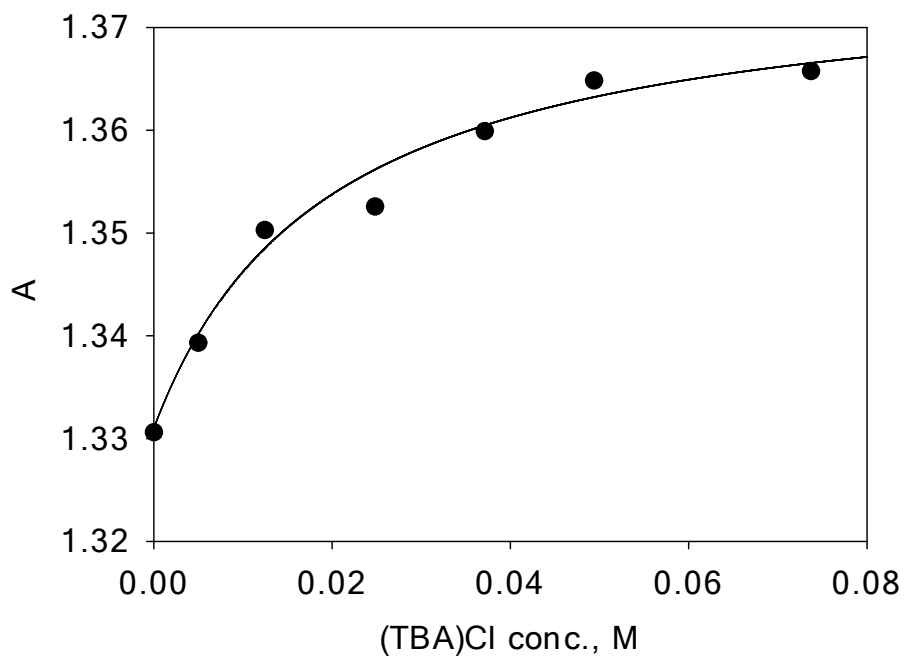
Figure S5. Absorbance vs. (TBA)Cl concentration titration plot at 349 nm, line corresponds to the calculated fit of the experimental data points (in DMSO).
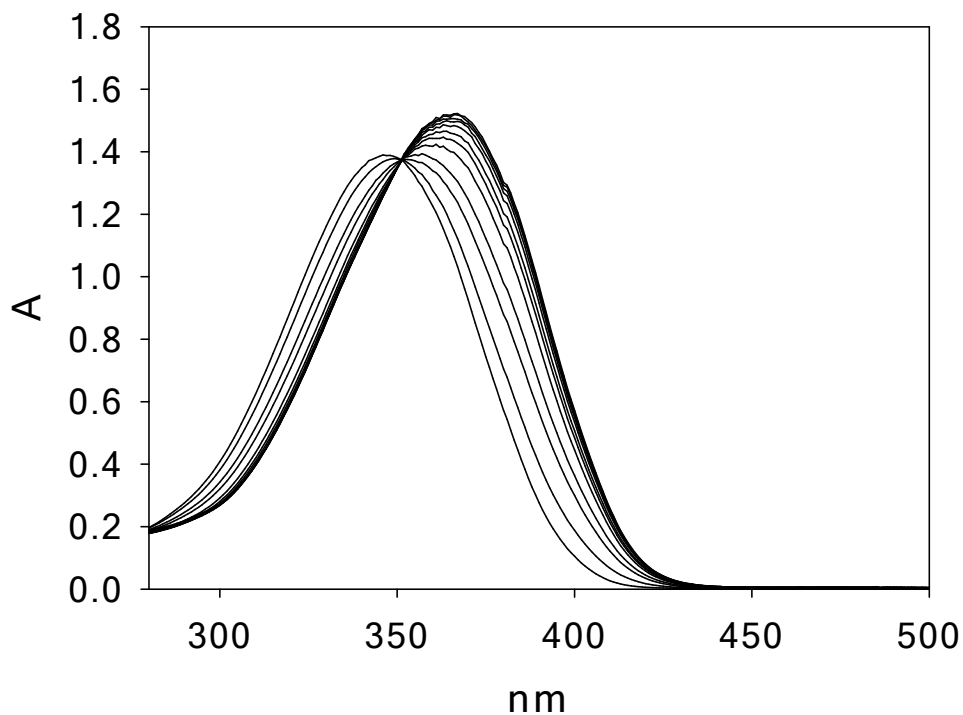
Figure S6. Family of spectra obtained upon addition of increasing amount of (TBA) H_2PO_4 to a 9.1 x 10^{-5} M solution of **1** in DMSO.
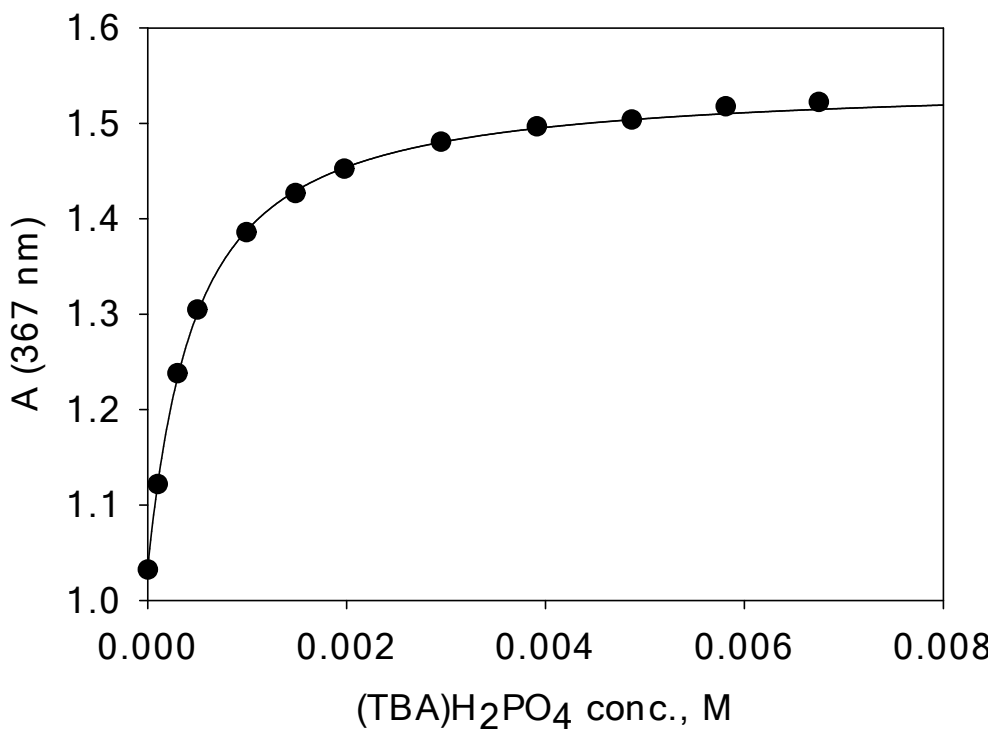

Figure S7. Abs vs. concentration titration profile obtained upon addition of (TBA)H_2PO_4 to **1** in DMSO; line corresponds to the calculated fit of the experimental data points.
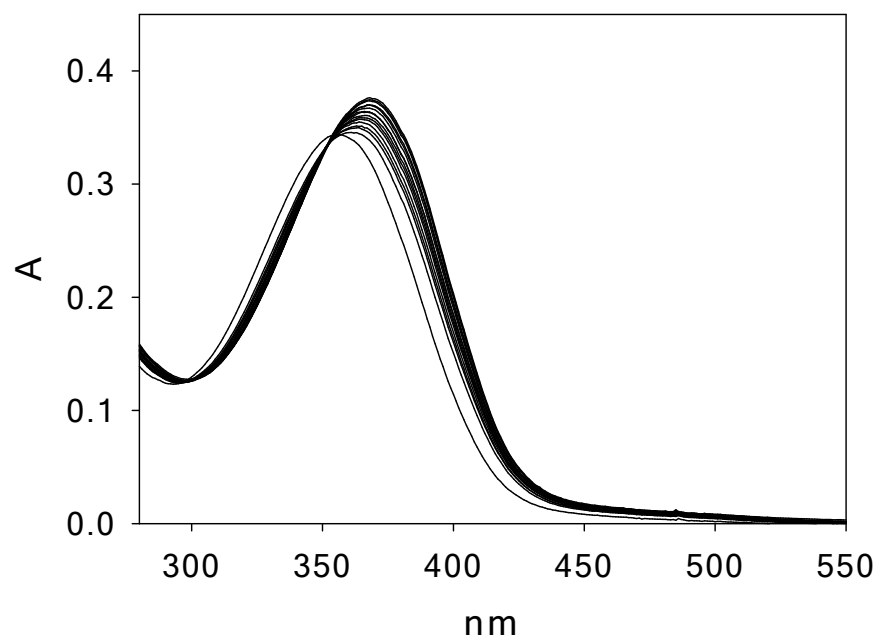
Figure S8. Family of spectra obtained upon addition of increasing amount of (TBA) H_2PO_4 to a 0.3 mg/mL solution of **bPEI-Sens(10%)** in DMSO.
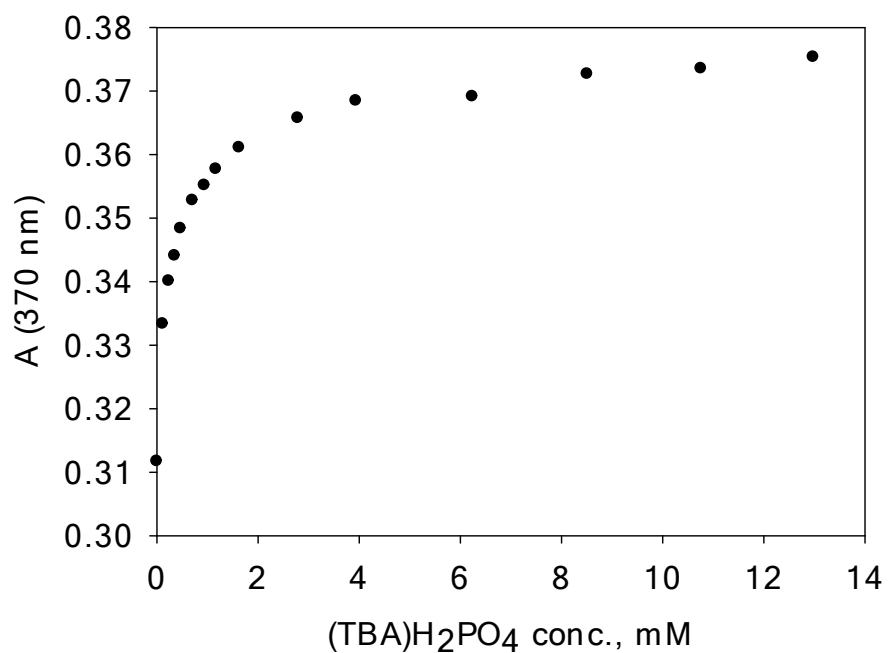

Figure S9. Abs vs. concentration titration profile obtained upon addition of (TBA)H_2PO_4 to a 0.3mg/mL solution of **bPEI-Sens(10%)** in DMSO.
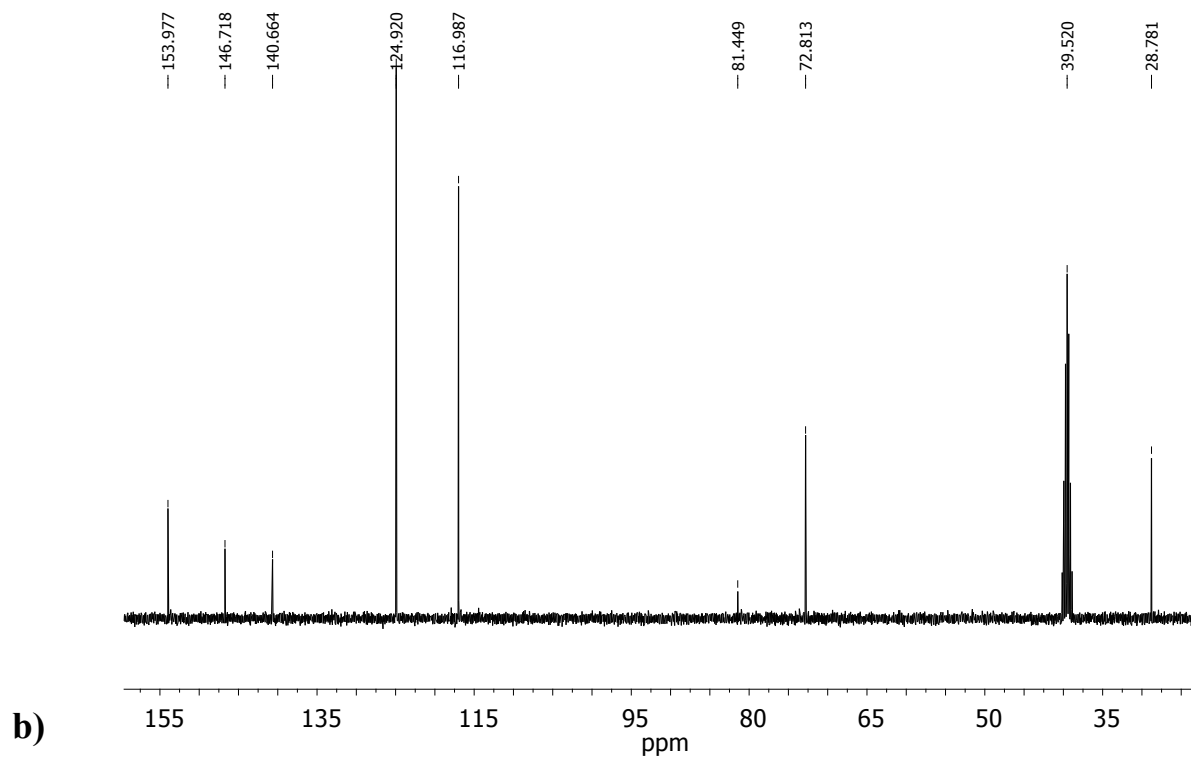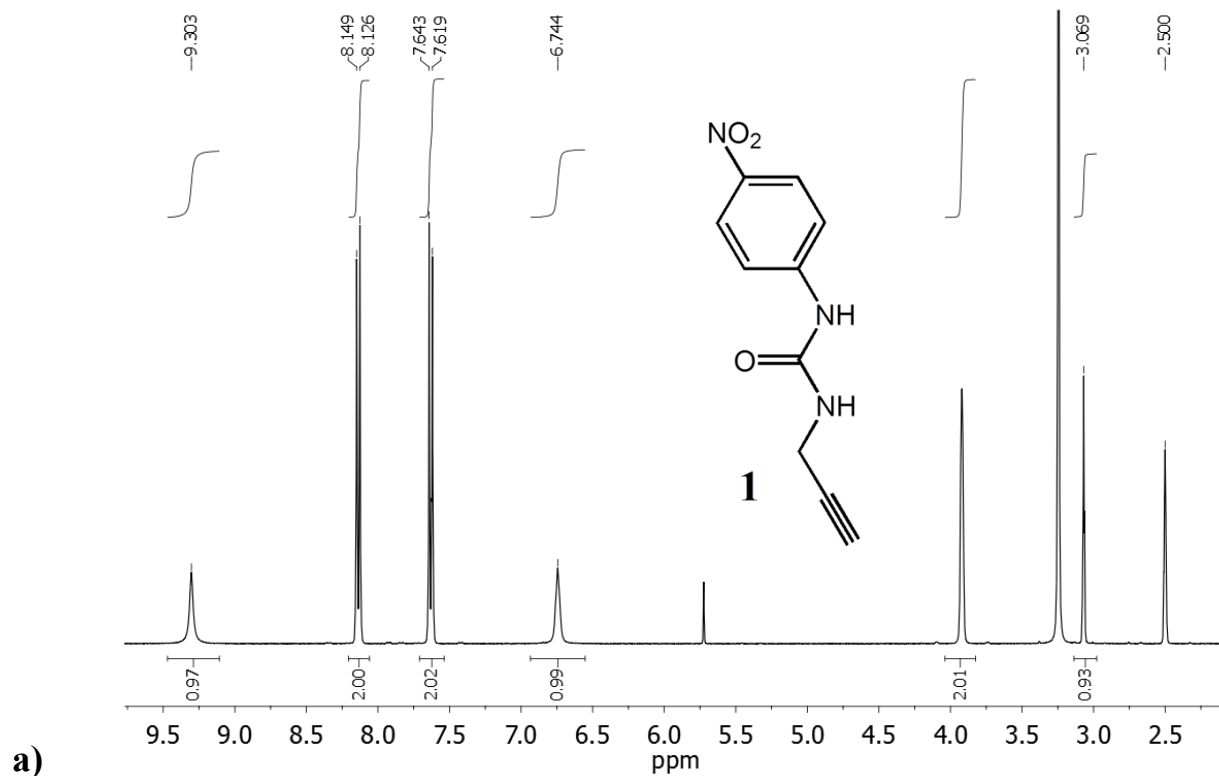
a)

b)

Figure S10 a) ^{1}H-NMR (400 MHz, DMSO-d6): δ 9.32 (s, 1H), 8.17 – 8.05 (m, 2H), 7.70 – 7.53 (m, 2H), 6.75 (t, J = 5.6 Hz, 1H), 3.92 (dd, J = 5.6, 2.4 Hz, 2H), 3.08 (q, J = 2.4 Hz, 1H); b) ^{13}C NMR (101 MHz, DMSO-d6): δ 153.97, 146.70, 140.65, 124.91, 116.97, 81.44, 72.80, 28.77.

Hill Plots: Hill plots[3] were generated from raw titration data by calculating θ and by plotting it versus the concentration of the anion, **[anion]** (M) in double logarithmic scale:

$$\theta = \frac{Y}{(1-Y)} \; ; \qquad \text{eq. 1a}$$

$$Y = \frac{(A - A_o)}{(A_{max} - A_o)} \qquad \text{eq. 1b}$$

$$log\,\theta = - m\,logK + m\,log[anion] \qquad \text{eq. 2[3b]}$$

where **A** is the absorbance recorded during the titration experiment, **A_o** is the absorbance recorded in the absence of anion and **A_{max}** is the absorbance recorded at the plateau (at the end of the titration in excess of anion).

In Equation 2, the Hill equation, **K** is the average microscopic association constant and **m** represents the cooperativity factor (Hill Coefficient).
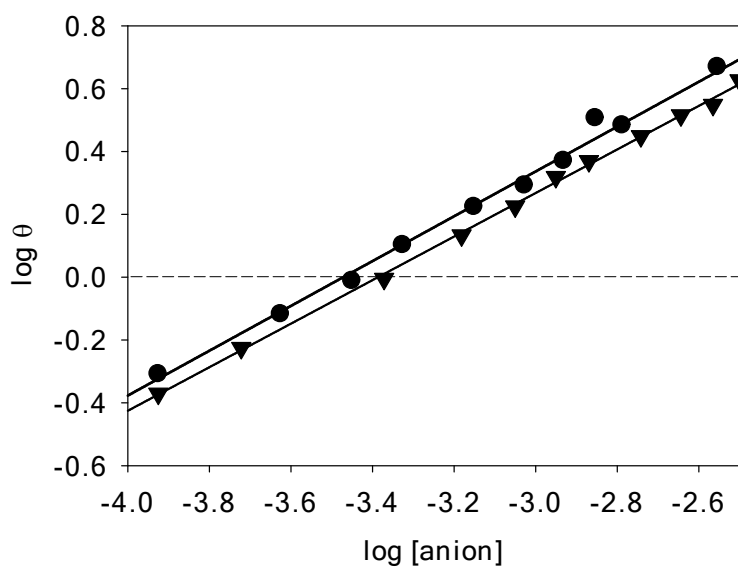

Figure S11. Reproduction of Figure 6b in the manuscript which represent the Hill Plots relative to the interaction of acetate (●) and phosphate (▼) with **bPEI-Sens(10%).**

Method for the determination of the degree of functionalization of bPEI with pNO$_2$-phelyl urea units:

In addition to the validity of Lamber&Beer law, the method is based on two assumptions: 1) the molar absorptivity of **1** at 476 nm, ε_{476}, (wavelength of maximum absorbance of **1** in its deprotonated form) and that of the chromophore when embedded in **bPEI** are equal; 2) all chromophores in **bPEI** are in their deprotonated form in conditions of excess fluoride anion.

A weighted sample of each **bPEI-Sens(n%)** (μg_{PEI}) is introduced in a vessel containing 1mL of DMSO and an excess of (TBA)F. Known volumes of dissolved polymer (μL) are then added to a DMSO solution and the absorption spectra are recorded (A).

$$A = \varepsilon \cdot [c] \cdot d = \varepsilon \cdot \frac{\mu mol}{\mu L} \cdot d$$

$$\frac{A_{476}}{\varepsilon_{476}} \cdot \mu L = \mu mol\ chromophore\ unit$$

$$(\frac{mmol}{g}) \cdot mg_{PEI} \cdot \frac{\mu L}{1\ mL} = \mu mol\ of\ available\ NH_2\ unit$$

ε_{476} of **1** is 34100 M^{-1}cm^{-1}

$d = 1$

Ratio of mmol of primary amine units per gram of bPEI (mmol/g) = 7.43

Plot of $\mu mol\ of\ chromophore\ unit\ versus\ \mu mol\ of\ available\ NH_2\ unit$ gives straight lines (as reported in Figure S12) whose slopes corresponds to the % of functionalization.
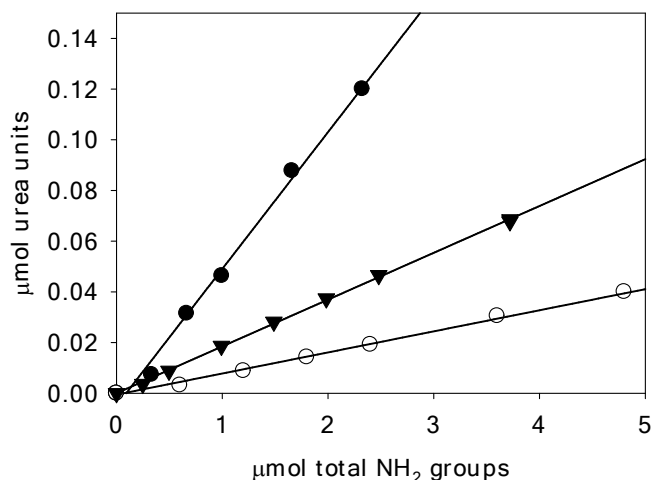
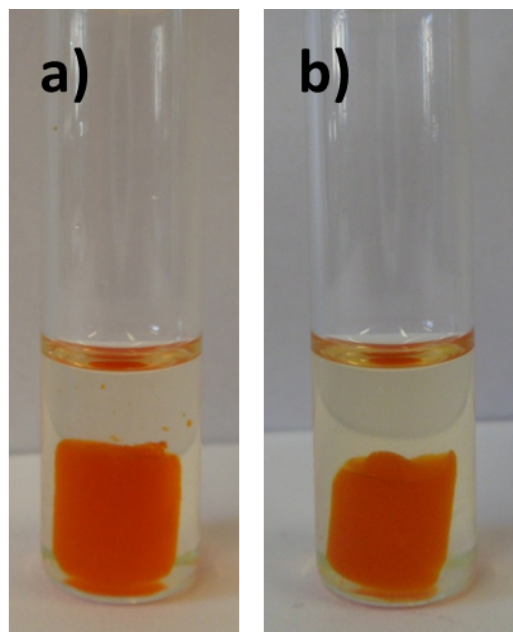**Figure S12**: Reproduction of Figure 6d in the manuscript.

Figure S13. Comparison between **TOCNF1-bPEI-Sens(10%)** (a) and **TOCNF2-bPEI-Sens(10%)** (b) in the presence of (TBA)F (1 mL, 0.5 M, DMSO). T= 55 °C. Contact time: 30 min.
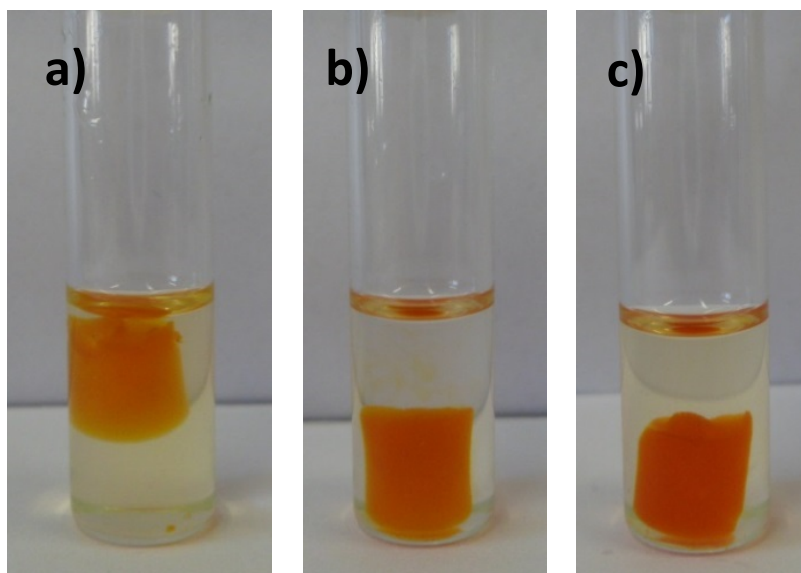

Figure S14. Comparison between **TOCNF1-bPEI-Sens(2%)** (a), **TOCNF1-bPEI-Sens(5%)** (b), and **TOCNF1-bPEI-Sens(10%)** (c) in the presence of (TBA)F (1 mL, 0.5 M, DMSO). T= 55 °C. Contact time: 30 min.
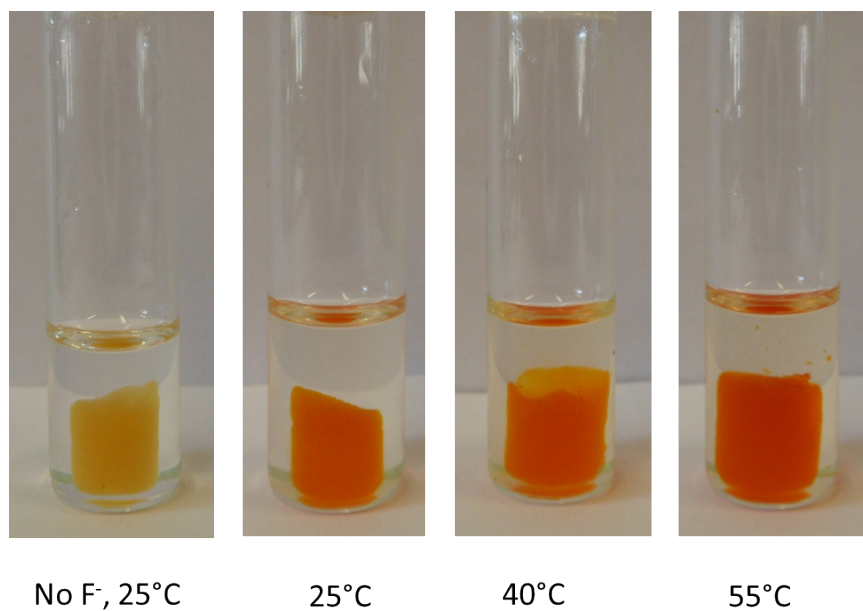
No F⁻, 25°C   25°C   40°C   55°C

Figure S15. Comparison between **TOCNF2-bPEI-Sens(10%)** in the presence of (TBA)F (1 mL, 0.5 M, DMSO) at different temperatures. Contact time: 30 min.
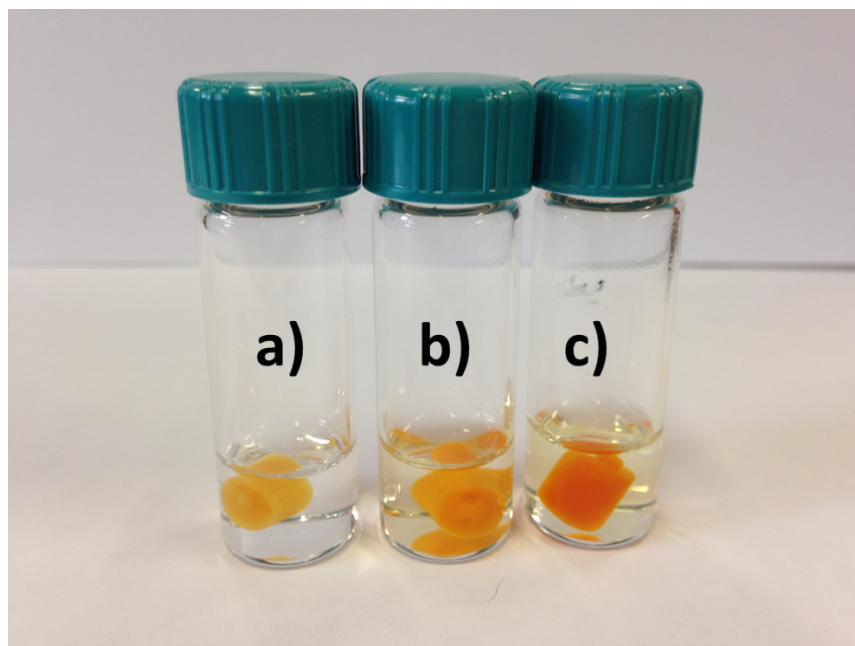

Figure S16. TOCNF2-bPEI-Sens(10%) in MeCN, alone (a), with (TBA)F 0.05M (b), with (TBA)F 0.5 M (c). T=55 °C. Contact time: 30 min.

References SI

[1] L. Melone, B. Rossi, N. Pastori, W. Panzeri, A. Mele, C. Punta, *ChemPlusChem 2015*, doi: 10.1002/cplu.201500145.

[2] A. Isogai, T. Saito, H. Fukuzumi, TEMPO-oxidized cellulose nanofibers, *Nanoscale*, 2011, **3**, 71-85.

[3] a) R. Sakai, S. Okade, E. B. Barasa, R. Kakuchi, M. Ziabka, S. Umeda, K. Tsuda, T. Satoh, T. Kakuchi*, Macromolecules,* **2010**, *43*, 7406–7411; b) see supporting info of T.-M. Ketola, M. Hanzlíková, L. Leppänen , M. Raviña, C. J. Bishop, J. J. Green, A. Urtti, H. Lemmetyinen , M. Yliperttula and E. Vuorimaa-Laukkanen, *J. Phys. Chem.* B, **2013**, *117*, 10405–10413.