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Supporting Information

WtF-Nano: One-Pot Dewatering and Water-Free Topochemical Modification of Nanocellulose in Ionic Liquids or γ-Valerolactone

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S1. Materials

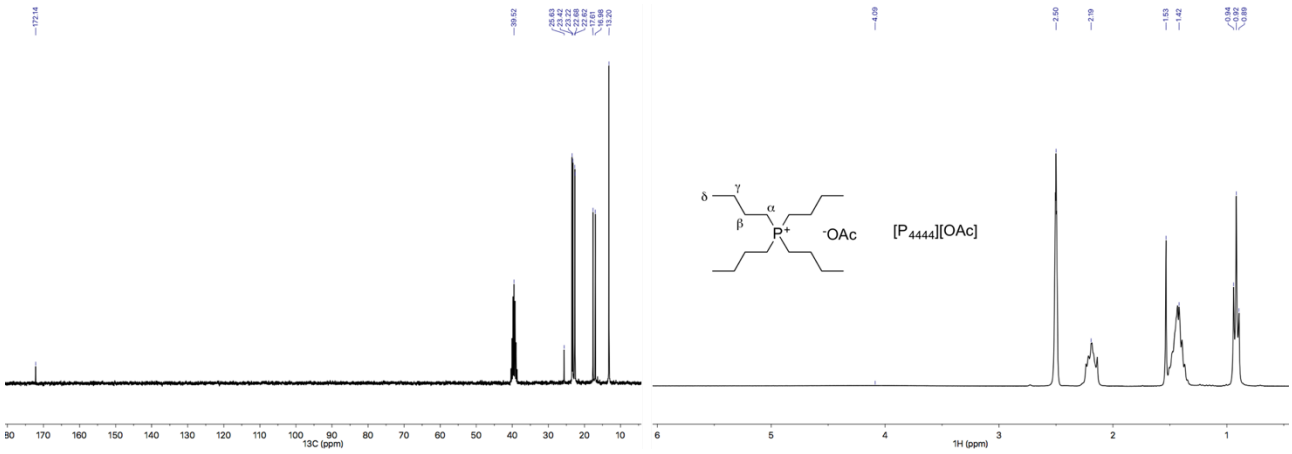
CNF solutions (1.20 wt% and 1.7 wt% dry pulp contents) were produced by six passes in a microfludiser, from birch kraft pulp (UPM Kymmene, Pietarsaari, Finland). This pulp still contained 24 wt% xylan (surface adsorbed) and was not pre- or post-oxidised to improve dispersibility. *N,N*-diethylnitroaniline was purchased from Fluorochem Ltd (Hadfield, UK). Ionic liquids IoLiLyte® 221PG, 1-ethyl-3-methylimidazolium triflate ([emim][OTf]), 1-ethyl-3-methylimidazolium mesylate ([emim][OMs]), 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]), were purchased from Iolitec GmbH (Heilbronn, Germany) and used without further purification. γ-Valerolactone (GVL), 4-nitroaniline, acetic anhydride (Ac_2O), potassium acetate, HPLC acetone, *N,N*-dimethylaminopyridine (DMAP), anhydrous *N,N*-dimethylformamide (DMF) and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye) were all purchased from Sigma-Aldrich Finland Oy (Helsinki, Finland) and used without further purification Acid impurities in these ionic liquids were assessed by diluting the ionic liquids to 10 wt % with deionised water and measuring the pH. Tetrabutylphosphonium chloride ($[P_{4444}]Cl$, 80 % aq) was purchased from Tokyo Chemical Industry – Europe (Product #: T1649) and was dried by high vacuum rotary evaporation at 90 °C for several hours. DMSO-d_6 was purchased from Euriso-Top. HPLC-grade methanol was purchased from Fischer Scientific (Loughborough, UK).

S2. General Procedure for Synthesis of $[P_{4444}][OAc]$

$[P_{4444}]Cl$ was dissolved in isopropanol, in a 1:5 mass ratio and heated to 80 °C with stirring. Potassium acetate, 1.01 molar equivalents, was added in small portions and stirred to ensure homogenization in the mixture. After stirring at 80 °C for one hour, the mixture was stirred at room temperature for a further 16 hours, and refrigerated for a further 16 hours to ensure complete precipitation of KCl. The KCl by-product was vacuum filtered over a glass sinter filter and celite and the isopropanol was removed under reduced pressure. Cold acetone was added to the crude product to precipitate any remaining salts. The mixture was again filtered with a glass sinter filter and celite. Acetone was evaporated under reduced pressure, and the product was dried under in a vaccuum rotary evaporator (90 °C fro several hours) to produce a highly viscous, amber liquid. This crystallised on standing at room temperature. The purity, by ^{1}H NMR (**SF1**), was practically the same as for our previous published method using silver acetate for the metathesis procedure.[10e] (see main text)

^{1}H NMR (300 MHz, DMSO-d_6) δ 0.92 (12H, t, J=6.9 Hz, $P(CH_2)_3CH_3$), 1.42 (16H, m, $PCH_2(CH_2)_2CH_3$), 1.53 (3H, s, CO_2CH_3), 2.19 (8H, m, $PCH_2(CH_2)_2CH_3$).

^{13}C NMR (75 MHz, DMSO-d_6) δ 13.20, 17.30 (d, J=47.3 Hz, $PCH_2(CH_2)_2CH_3$), 22.65 (d, J=4.42 Hz, $P(CH_2)_2CH_2CH_3$), 23.32 (d, J=15.56 Hz, $PCH_2CH_2CH_2CH_3$), 25.63, 172.14.



SF1. *^{1}H (right) & ^{13}C (left) NMR spectra for $[P_{4444}][OAc]$, in DMSO-d_6 at 27 ^{o}C.*

S3. Dewatering (Evaporation) Procedure

The ionic liquids were mixed with the aqueous CNF solutions (1:1 w/w). The mixtures were thoroughly mixed and then rotary evaporated in round bottom flasks, at 80 ^{o}C until a pressure of 15 mbar was reached. This was achieved in a Büchi R-210 rotary evaporator with a V-710 diaphragm pump and a V-855 vacuum controller. The evaporation was carried out without added ionic liquid and with added ionic liquid, or GVL. Typically, an equal volume of ionic liquid or GVL was added to the mixtures. Finally, the samples were put under vacuum for 30 min and the water contents were measured by Karl-Fischer titration, before and after the final vacuum step (**ST1**). The final drying step was necessary to avoid consumption of the acetylating reagent, to ensure a comparative procedure between different drying sequences.

ST1. *Water contents of the dewatering ionic liquids after rotary evaporation (80 ^{o}C to 15 mbar) and then vacuum drying (30 min), as determined by Karl-Fischer titration.*

Dewatering Solvent	Water Content after Rotary Evaporation (wt %)	Water Content after Vacuum Drying (wt %)
[emim][OTf]	0.51	0.12
[emim][OMs]	0.61	0.26
[emim][DCA]	0.24	0.12
[emim][TCM]	0.11	0.04
GVL	0.40	0.11

S4. Acetylation Procedures

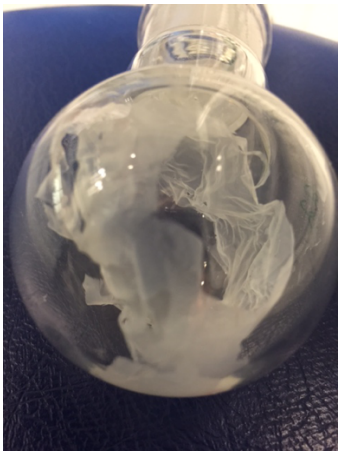
Procedure 1 (Initial Procedure in [emim][OTf]): CNF gel (13.69 g, 1.7 wt%) was dried with [emim][OTf] (9.50 g). The final amount of CNF was 2.4 wt % CNF (1.44 mmol, 233 mg, assuming 100 % cellulose). Acetic anhydride (8.64 mmol, 880 mg, 815 μL, 6.0 eq per AGU) and DMAP (10.0 mg, catalytic) were added to a round bottom flask containing the dewatered CNF. The reaction

mixture was thoroughly mixed and heated to 80 °C overnight. Reaction mixture was let to cool to rt. before addition of 30 mL of methanol. The ionic liquid-CNF mixture was thoroughly mixed with water in a vortexing homogeniser and poured to falcon tube. Flask was washed with additional 10 mL of methanol, which was then combined into the centrifugation tube. The mixture was then centrifuged for 10 min at 4000 rpm and at 15 °C. The pellet was recovered and the centrifugation procedure was repeated an additional 2 times (2*40 mL of methanol). Finally, AcCNF was transferred to a round bottom flask, using a small amount of methanol. The solvent was evaporated and the product dried under vacuum to form a clear film (**S5**). The residual solutions from centrifugation were combined and evaporated for analysis of the residual ionic liquid (**S16**).

Procedure 2 (Comparative Procedure): Dewatered CNF solutions were prepared by drying CNF (5.0 g)in each ionic liquid (5.0 g). Acetic anhydride (3.33 mmol, 340 mg, 315 μL, 9.0 eq per AGU) and DMAP (3.0 mg, catalytic) were added to a round bottom flask containing the dewatered CNF in selected solvent (60 mg CNF in 5 g total weight). The reaction mixture was thoroughly mixed and heated to 80 °C overnight. Reaction mixture was let to cool to rt. before addition of 10 mL of water. The ionic liquid-CNF mixture was thoroughly mixed with water in a vortexing homogeniser and poured to falcon tube. Flask was washed with additional 10 mL of water, which was then combined into the centrifugation tube. The mixture was then centrifuged for 10 min at 4000 rpm and at 15 °C. The pellet was recovered and the centrifugation procedure was repeated an additional 3 times (3*20 mL of water). Finally, the CNF was washed two times with 15 mL of MeOH. The AcCNF was transferred to a round bottom flask, using a small amount of methanol. The solvent was evaporated and the product dried under vacuum. The residual solutions from centrifugation were combined and evaporated for purity analysis.

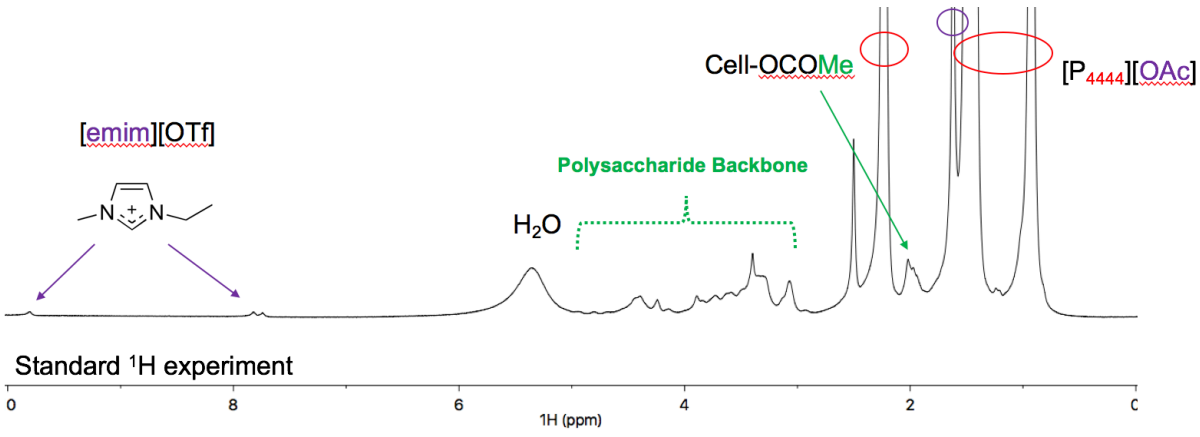
Procedure 3 (High Biomass Loading): A 10 wt% dewatered CNF solution were prepared by drying CNF (9.5 g) in [emim][OMs] (1.03 g); [emim][OMs] was added into the CNF (aq) gel and heated at 60 °C for 15 min, with mixing, before rotary evaporation down to 8 mbar at 80 °C. The sample was the dried by vacuum pump for 2 hr at 80 °C. Acetic anhydride (2.11 mmol, 215 mg, 200 μL, 3.0 eq per AGU) was added to a round bottom flask containing the dewatered CNF gel (114 mg CNF in 1.14 g total weight). The reaction mixture (clear paste) was thoroughly mixed and heated to 80 °C for 4 hr. Reaction mixture was let to cool to rt. before addition of 6 mL of water. The ionic liquid-CNF mixture was thoroughly mixed with water in a vortexing homogeniser and poured to falcon tube. Flask was washed with additional 10 mL of water, which was then combined into the centrifugation tube. The mixture was then centrifuged for 10 min at 4000 rpm and at 25 °C. The pellet was recovered and the centrifugation procedure was repeated an additional 3 times (3*20 mL of water). Finally, the CNF was washed two times with 15 mL of EtOH. The AcCNF was transferred to a round bottom flask, using a small amount of ethanol. The solvent was evaporated and the product dried under vacuum to yield a white foam (85.5 mg, 75 wt% yield). This was then subjected to ATR-IR analysis (S12).

S5. Picture of the AcCNF Film Obtained from [emim][OTf] Using Procedure 1



S6. ^{1}H NMR Analysis of AcCNF Film, in [P_{4444}][OAc]/DMSO-d_6

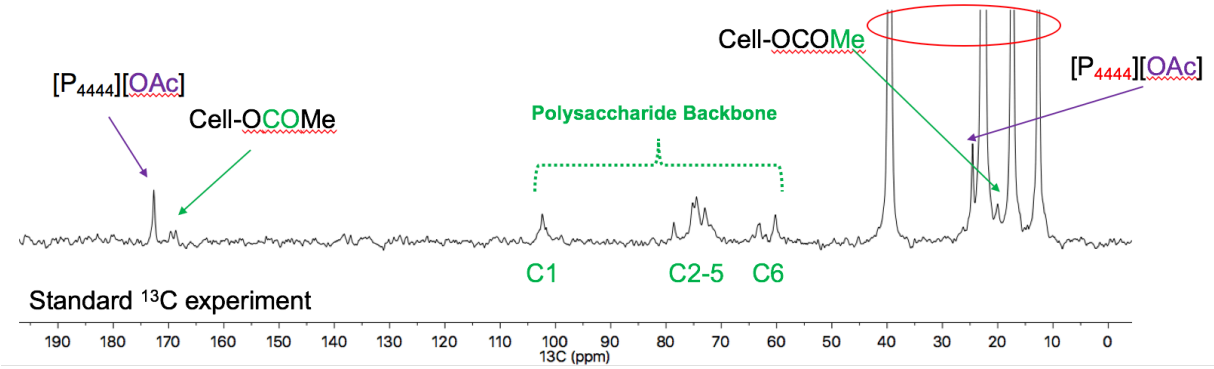
A ^{1}H-spectrum was measured using a Varian Inova 600 MHz spectrometer, equipped with a triple resonance probe head. Spectral width was 9595 Hz. The transmitter offset was 5.5 ppm. The pulse flip angle was 45 °. The relaxation delay was 1 s and acquisition time was 1.7 s. DMSO-d_6 in the sample was used as locking solvent, and 128 transients were collected. The experiment temperature was maintained at 65 °C. The processed spectrum is shown in **SF2**.



SF2. *^{1}H NMR spectra for AcNFC in [P_{4444}][OAc] and DMSO-d6 (1:4 w/w) at 65 °C.*

S7. ^{13}C NMR Analysis AcCNF Film, in [P_{4444}][OAc]/DMSO-d_6

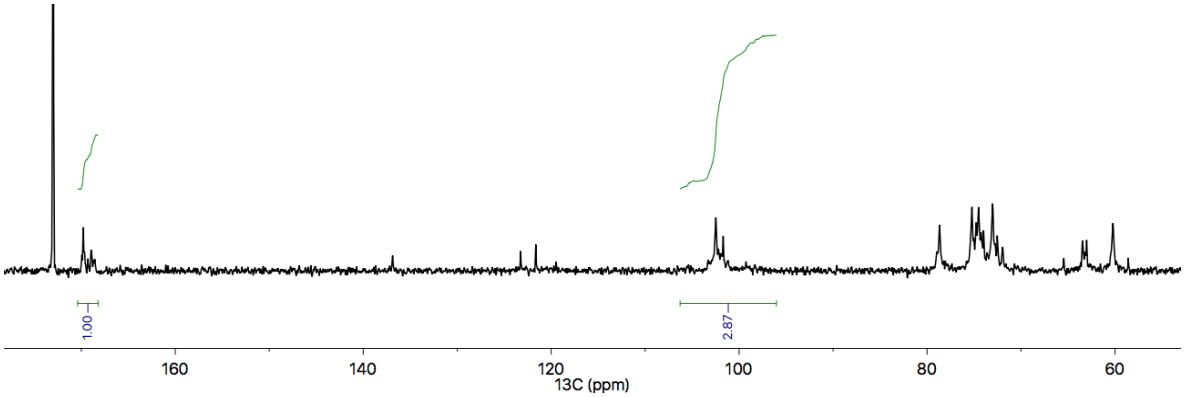
A broadband ^{1}H-decoupled ^{13}C-spectrum was measured using a Varian Unity Inova 600 MHz spectrometer equipped with a triple resonance probe head. Spectral width was 37700 Hz. The transmitter offset was 100 ppm. The pulse flip angle was 45 °. The relaxation delay was 1 s and acquisition time was 0.87 s. DMSO-d_6 in the sample was used as locking solvent, and 500 transients were collected with an initial 32 steady-state scans. The experiment temperature was maintained at 65 °C. The processed spectrum is shown in **SF3**.



***SF3**. ^{13}C NMR spectra for AcNFC in [P_{4444}][OAc] and DMSO-d6 (1:4 w/w) at 65 °C. **Note**: Trace [emim][OTf] is visible in the ^{1}H spectrum of the AcCNF film. Only further washing is required to remove this as there is no indication that the imidazolium ring is chemically bound to the biopolymers.*

S8. Quantitative ^{13}C NMR Analysis AcCNF Film, in [P_{4444}][OAc]/DMSO-d_6

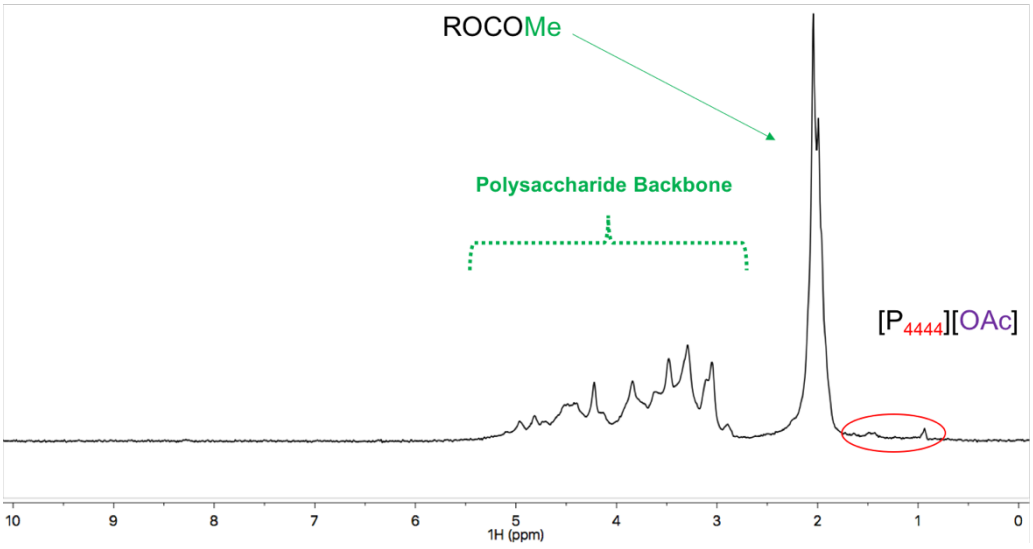
An inverse-gated ^{1}H-decoupling technique was used to measure quantitative ^{13}C-data. The experiment was performed using Varian Unity Inova 600 MHz spectrometer equipped with 5 mm broadband probe head. Spectral width was 37700 Hz. The transmitter offset was 100 ppm. The pulse flip angle was 45 °. The relaxation delay was 20 s and acquisition time was 0.87 s. DMSO-d_6 in the sample was used as locking solvent, and 10000 transients were collected with an initial 32 steady-state scans. The experiment temperature was maintained at 65 °C. The processed spectrum is shown in **SF4.**



***SF4**. Quantitative ^{13}C NMR spectra for AcNFC in [P_{4444}][OAc] and DMSO-d6 (1:4 w/w) at 65 °C.*

S9. BPPSTE DOSY NMR Analysis of AcCNF, in $[P_{4444}][OAc]$/DMSO-d_6

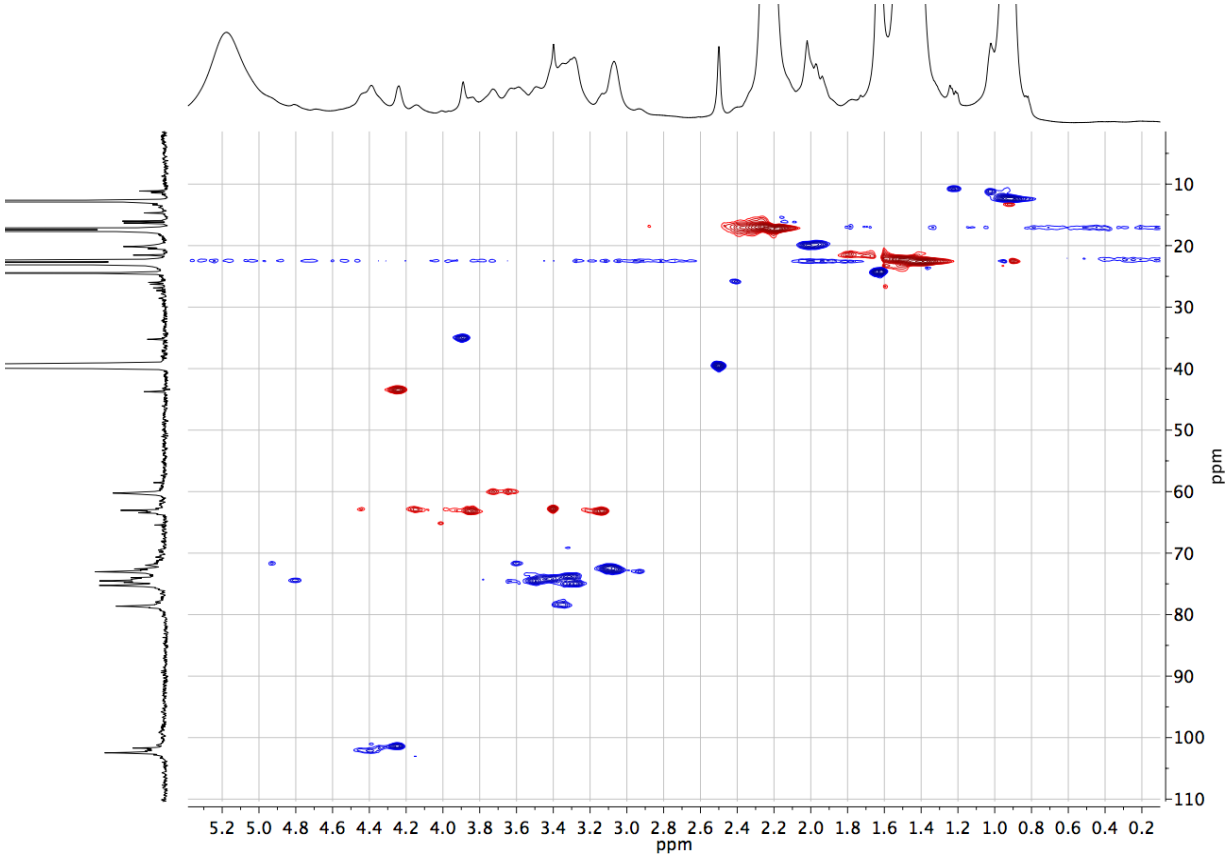
A ^{1}H DOSY array was measured using a Varian Unity Inova 600 MHz spectrometer equipped with a triple resonance probe head. The BPPSTE pulse sequence was used.[16a,b] (see main text) Spectral width was 10000 Hz. The transmitter offset was 6 ppm. The relaxation delay was 9 s and acquisition time was 1 s. DMSO-d_6 in the sample was used as locking solvent, and 16 transients were collected per pulsed gradient strength, with an initial 16 steady-state scans. The diffusion delay was 0.2 s, the total diffusion-encoding pulse width was 3.4 ms and there were 15 exponentially spaced diffusion gradients, starting at gzlvl1 = 100 (0.17 G cm^{-1}) and finishing at gzlvl1 = 32000 (53 G cm^{-1}). The experiment temperature was maintained at 27 °C. The final gradient strength increment, where the low molecular weight species are almost no longer visible, is shown in **SF5**.



***SF5**. Final DOSY (BPPSTE) array increment showing complete dissappearance of the low molecular weight species and retention of the polymeric AcCNF signals.*

S10. Multiplicity-Edited HSQC NMR Analysis of AcCNF, in $[P_{4444}][OAc]$/DMSO-d_6

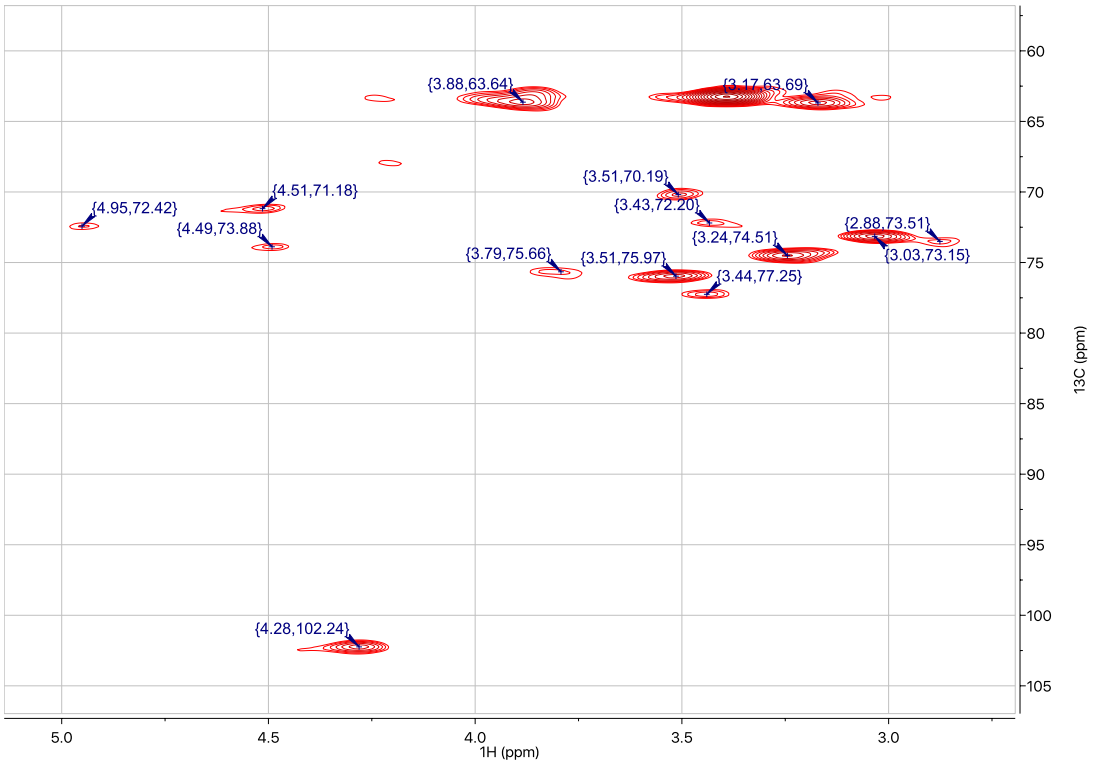
The sample was measured using a Varian Unity Inova 600 MHz spectrometer equipped with a triple resonance probe head. The HSQC pulse sequence with multiplicity editing was used.[16c-f] (see main text) Spectral width in the ^{13}C dimension was 20000 Hz. The ^{13}C transmitter offset was 70 ppm. Spectral width in the ^{1}H dimension was 7000 Hz. The ^{1}H transmitter offset was 4.5 ppm. The relaxation delay was 1 s and acquisition time was 0.2 s. There were 128 transients were collected per increment with an initial 16 steady-state scans. There were 256 increments in the ^{13}C dimension. DMSO-d_6 was used as locking solvent. The experiment temperature was maintained at 40 °C. The processed spectra, including the ionic liquid and acetate region, is shown in **SF6.**



***SF6**. Full multiplicity-edited HSQC spectra for AcNFC in [P_{4444}][OAc] and DMSO-d6 (1:4 w/w), recorded at 40 ^{o}C.*

S11. Multiplicity-Edited HSQC NMR Analysis of AcCNF Extracted with DMSO-d_6

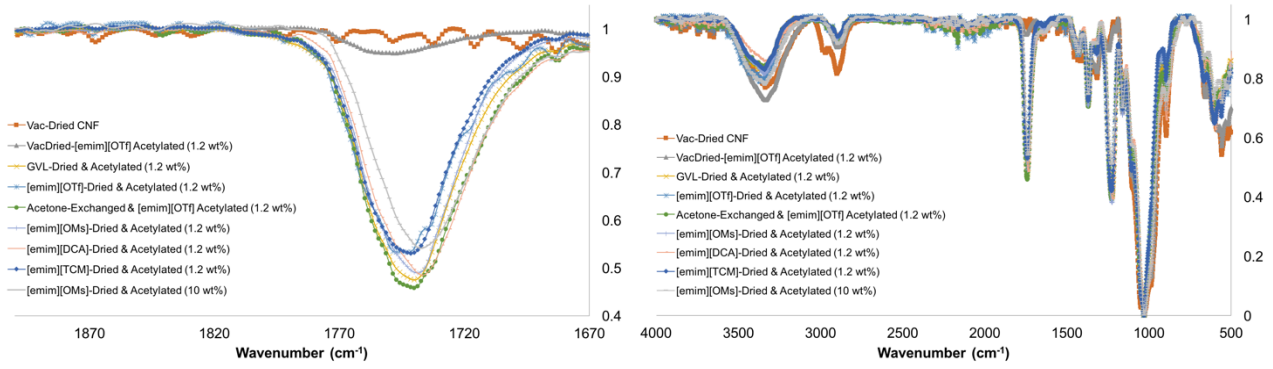
AcCNF (~ 50 mg) was added to an NMR tube with DMSO-d_6 and heated at 100 ^{o}C for 2 hr. The sample was measured using a Varian Unity Inova 600 MHz spectrometer equipped with a triple resonance probe head. The HSQC pulse sequence with multiplicity editing was used. **[16c-f] (see main text)** Spectral width in the ^{13}C dimension was 20000 Hz. The ^{13}C transmitter offset was 70 ppm. Spectral width in the ^{1}H dimension was 7000 Hz. The ^{1}H transmitter offset was 4.5 ppm. The relaxation delay was 1 s and acquisition time was 0.2 s. There were 128 transients were collected per increment with an initial 16 steady-state scans. There were 256 increments in the ^{13}C dimension. DMSO-d_6 was used as locking solvent. The experiment temperature was maintained at 40 ^{o}C. The processed spectra, including the ionic liquid and acetate region, is shown in **SF7.**



***SF7**. Multiplicity-edited HSQC spectra for AcNFC extracted with DMSO-d_6, recorded at 40 ^{o}C.*

S12. ATR-IR Analysis of the Regenerated AcCNFs

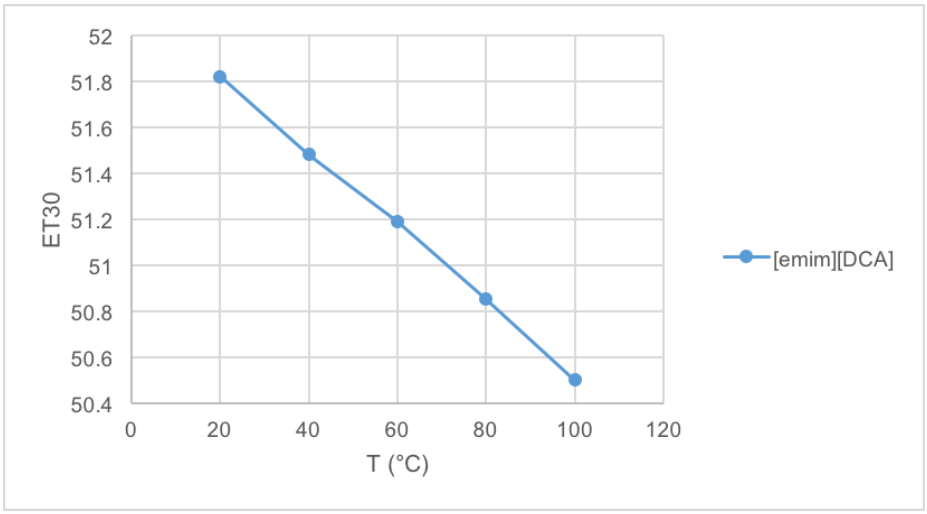
The regenerated AcCNFs were analysed by ATR-IR as a relative measure of the degree of acetylation. The spectra were all baseline corrected and normalised against the largest peak before measuring peak height of the carbonyl signal (~1745 cm^{-1}) *vs* the pyranose backbone signal (~1035 cm^{-1}). This ratio was used to give the absolute degrees of acetylation by comparison with a quantitative ^{13}C spectra obtained for AcCNF, acetylated in [emim][OTf] using procedure 1. The IR spectra are given in **SF8**.

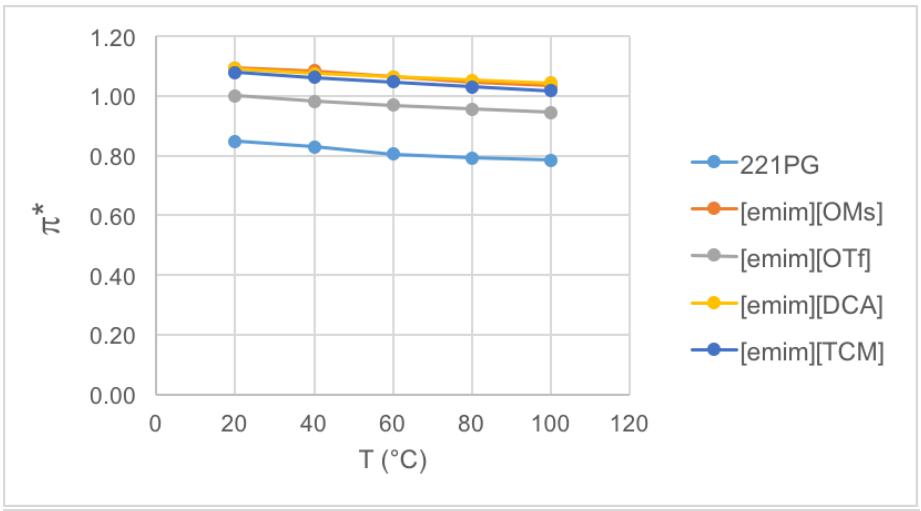


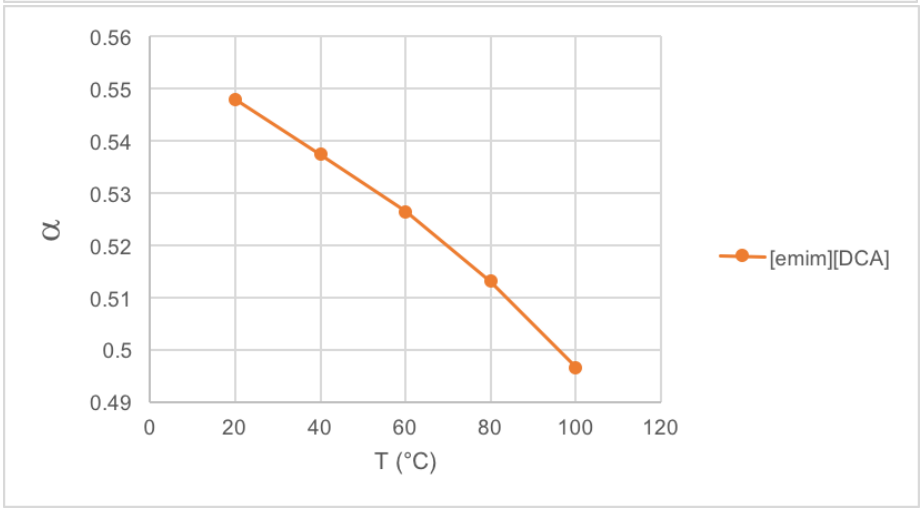
***SF8**. ATR-IRs for all dried or acetylatd CNFs showing the carbonyl region (left) and full spectra (right), normalised against the pyranose ring peak.*

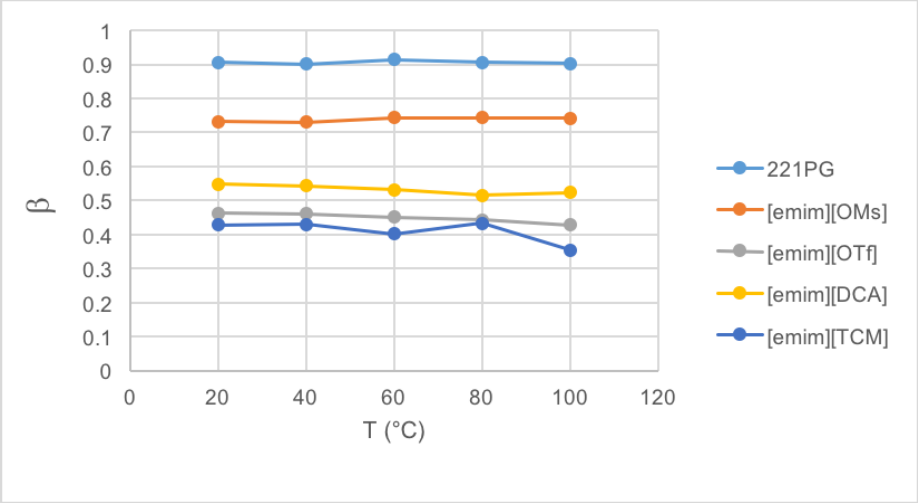
S13. Kamlet-Taft Data

Kamlet-Taft parameters were measured for all ionic liquids in the temperature range of 20-100 ºC using a UV spectrometer equipment with a Peltier cell (**SF9**).









SF9. *Kamlet-Taft Parameters for all Ionic LIquids, in the temperature range* of 20-100 ºC.

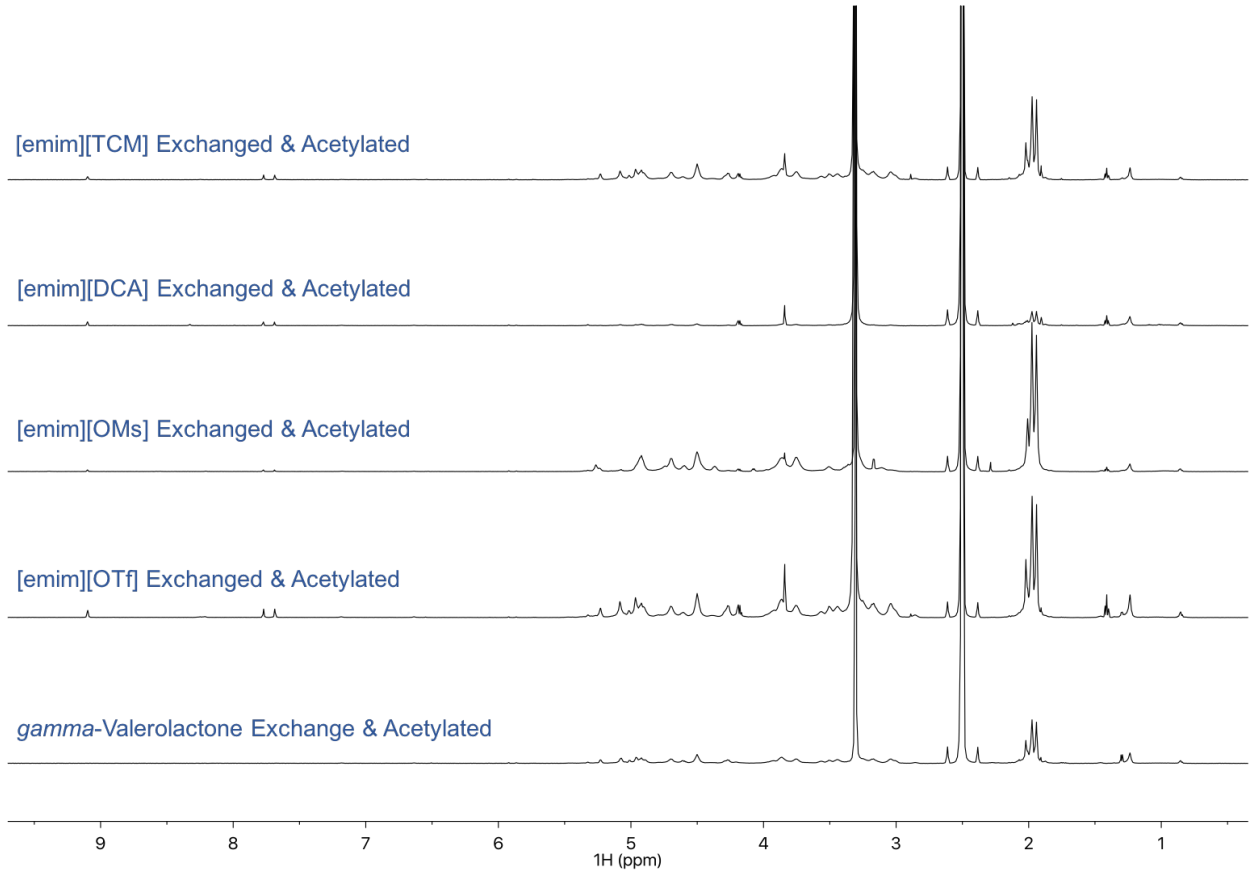
S14. Rheology Procedure

Shear rheology of the neat ionic liquids and dewatered NFC gels were measured on an Anton Paar MCR 300 rheometer with a plate and plate geometry (25 mm plate diameter, 1 mm gap size). The neat ionic liquids were measured in steady shear mode. First, a flow curve was recorded at 20 °C, over the shear rate range of 0.1–100 s^{-1}. Due to the low viscosity of some ILs, approaching the sensitivity limit of the device, the data at low shear rates showed fluctuation. Thus, the following steady shear temperature sweep was performed at a constant shear rate of 50 s^{-1} where all ILs showed stable and reproducible results. The temperature profile was recorded at a linear heating rate of 3.6 K/min.

Oscillatory shear rheology of dewatered gels was measured with the same set up (25 mm plate diameter, 1 mm gap distance). The viscoelastic domain was determined by performing a dynamic strain sweep test and a strain of 0.1%, which fell well within the linear viscoelastic regime, was chosen for the frequency sweep measurements. Each sample was subjected to a dynamic frequency sweep at 20 °C, over an angular frequency range of 100–0.01 s^{-1}.

S15. ^{1}H NMR Spectra of the Extracted AcCNFs for All Ionic Liquids and GVL

The ^{1}H NMR spectra of the DMSO-d_6 extracts for all the AcCNF films, prepared from the different ionic liquids, were collected (**SF10**). Extraction temperature in this case was ~120 ^{o}C and extraction for 5 mins.



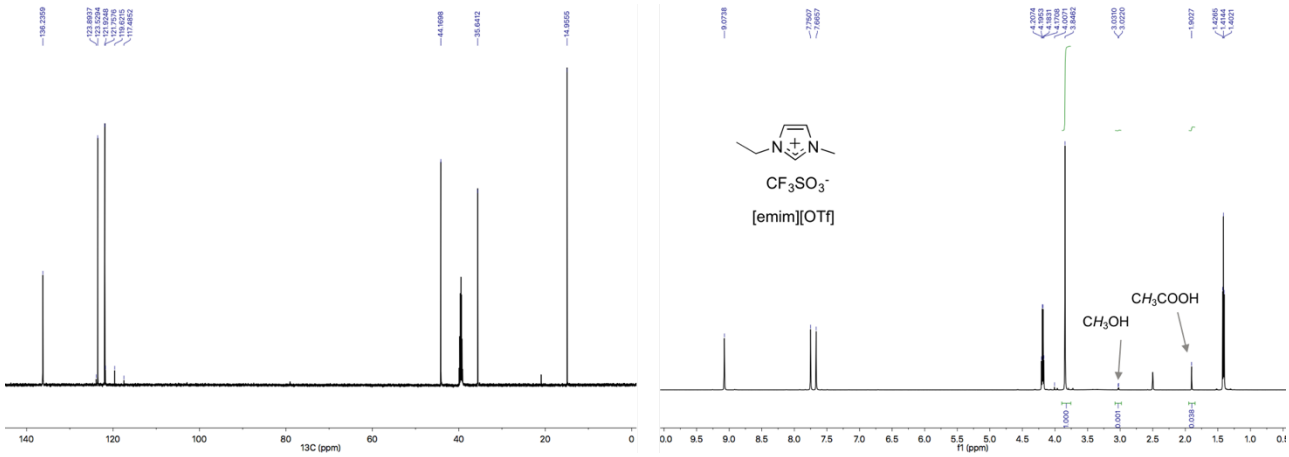
***SF10**. ^{1}H NMR spectra for DMSO-d6 extracted AcNFCs, from the different ionic liquids.*

S16. ^{1}H & ^{13}C NMR Spectra of the recycled ionic liquids after acetylation

After the initial acetylation in [emim][OTf] to give AcCNF, the residual ionic liquid in methanol solution was evaporated down to dryness (80 ^{o}C down to 30 mbar) in a rotary evaporator. This yielded a clear pale brown liquid. ^{1}H and ^{13}C NMR analysis was performed in DMSO-d_6 to show that there was no decomposition of of the ionic liquid. The sample contained residual methanol and acetic acid, from the hydrolysis of acetic anhydride, which amounted to less than 1 wt% of volatile impurities, with no other visible contamination (**SF11**).

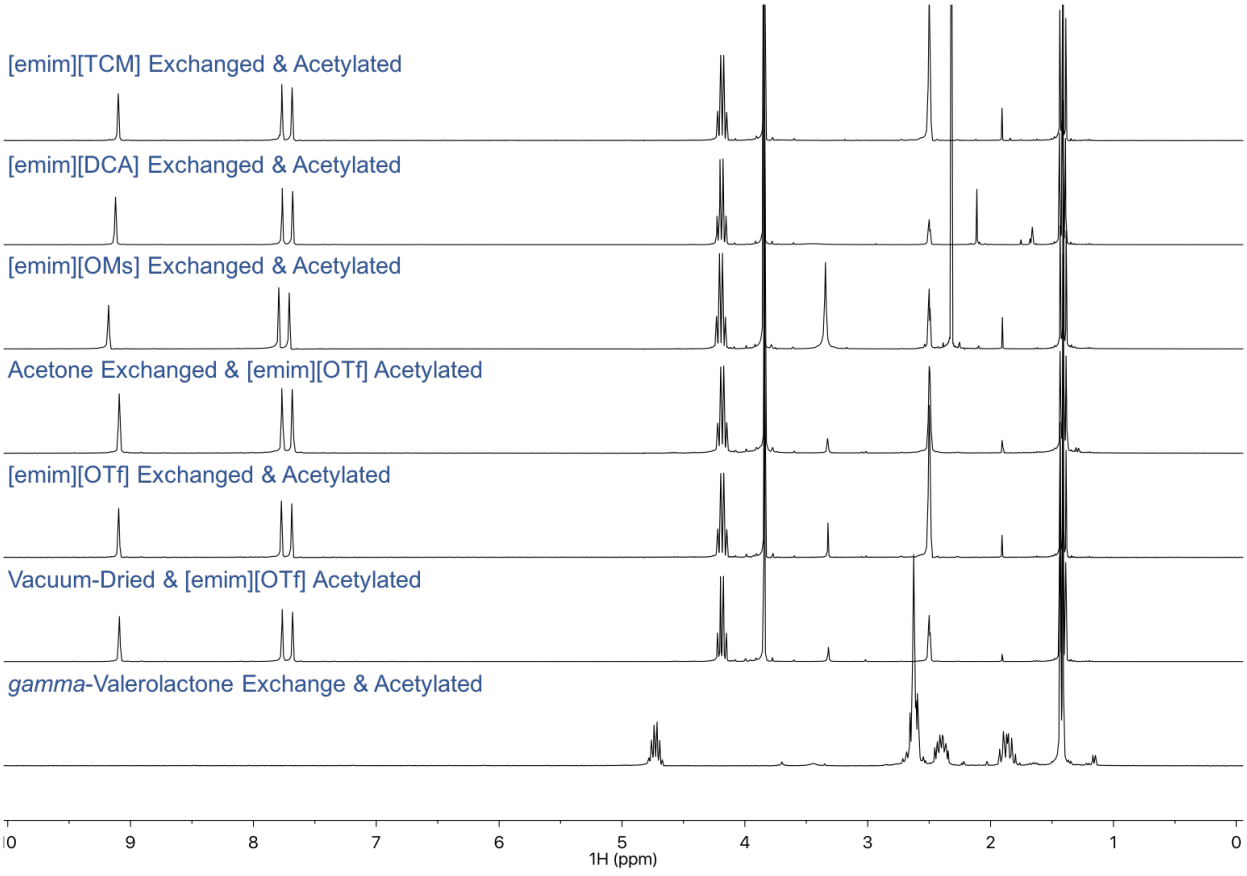
^{1}H NMR (600 MHz, DMSO-d_6) δ 1.41 (3H, t, J=7.3 Hz, NCH_2CH_3), 3.85 (3H, s, NCH_3), 4.19 (3H, q, J=7.3 Hz, NCH_2CH_3), 7.67 (3H, s, CH), 7.75 (3H, s, CH), 9.07 (3H, s, CH).

^{13}C NMR (150 MHz, DMSO-d_6) δ 14.96, 35.64, 44.17, 120.69 (q, J=320.5 Hz, SO_3CF_3), 121.93, 123.53, 136.24.



SF11. *^{1}H (right) & ^{13}C (left) NMR spectra of the recycled [emim][OTf], from the acetylation of CNF, in DMSO-d_6 at 27 ^{o}C.*

When Procedure 2 (see main text & S4) was applied for all ionic liquids and GVL, a similar recycling was performed to obtain samples for ^{1}H NMR analysis (**SF12**). These spectra are consistent with no degradation of the imidazolium cation portion. Trace solvent peaks are observable.



SF12. *^{1}H NMR spectra for the recycled ionic liquids and GVL, after acetylation of CNF, in DMSO-d_6 at 27 ^{o}C.*

S17. GPC Analysis of the Comparative Solvent Exchanges and Acetylations

Molar mass determination was performed using Agilent Infinity 1260 LC-system including degasser, pump, auto sampler, and refractive index detector (RID) from 1200 -series. The gel permeation columns were Agilent PLgel guard column (50*7.5 mm) with three PLgel MIXED 10µm (300*7.5 mm) columns connected in series. The mobile phase 0.5 % LiCl/DMA was used at a flow rate of 1 ml/min. Agilent pullulan polysaccharide standard kit was used for calibration with 10 standards in the range of 180 - 708000 Da. The Agilent Open Lab CDS ChemStation Edition (Rev. C.01.03) with Agilent GPC-Addon data analysis software (Rev. B.01.02) was used to calculate the molar mass distributions. The correction factors according to (Berggren et al. 2003)[18a] (see main text) for the pullulan standards were used: MMcellulose = q × MMP pullulan, with q = 12.19 and p = 0.78.

The sample preparation for GPC analysis was done according to (Timpa 1991)[18b] (see main text) with the modifications of (Kakko et al. 2017)[18c] (see main text). The tabulated data is given in ST2.

***ST2**. Molecular weight distribution data for the comparative dried and acetylated samples*.

	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	PDI
Vacuum-Dried CNF	48860	221500	578600	4.53
GVL Exchanged & Acetylated	26950	251100	3369000	9.32
Acetone Exchanged & [emim][OTf] Acetylated	32900	257500	1833000	7.83
[emim][TCM] Exchanged & Acetylated	30070	145600	357600	4.84
[emim][OTf] Exchanged & Acetylated	54150	226300	807800	4.18
[emim][DCA] Exchanged & Acetylated	51310	283400	1724000	5.52
[emim][OMs] Exchanged & Acetylated	60220	248400	570400	4.12
Vacuum-Dried & [emim][OTf] Acetylated	50070	229700	547000	4.59