Electronic Supplementary Information

On the solubility of wood in non-derivatising ionic liquids

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S1. Commercial Materials

1-Ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([emim][NTf₂], 99%) was provided by Solvent Innovation GmbH (now Merck KGaA). 4-Nitroaniline was purchased from Fluka AG. N,N-diethyl-4-nitroaniline was purchased from Fluorochem. Reichardt’s dye was purchased from Sigma-Aldrich. All other reagents used below were purchased from Sigma-Aldrich and all reagents were used without further purification.
S2. Synthesis of [amim]Cl

1-Methylimidazole (125 ml, 1.57 mol) was added slowly (over 1 h) to neat allyl chloride (160 ml, 1.97 mol) at room temperature, with stirring under argon. The mixture was then refluxed at 55 °C for 18 h under argon. Excess allyl chloride was removed by rotary evaporation, in a fume-hood. The mixture was then rotary evaporated at 70 °C under high vacuum (vacuum pump) for 6 h, to yield a clear orange liquid (15.80 g, 100%). It is critical to avoid the introduction of moisture into the mixture before all traces of allyl chloride are removed. $^1$H NMR (300 MHz; CDCl$_3$): δ 10.39 (1H, s), 7.94 (1H, s), 7.69 (1H, s), 6.07 (1H, ddt, $J$ = 16.9, 10.3, 6.5 Hz), 5.48 (2H, m), 5.09 (2H, d, $J$ = 6.4 Hz), 4.18 (3H, s). Water content was determined to be less than 0.4 % w/w by Karl-Fischer titration. The mixture was stored in a tightly sealed bottle to avoid moisture uptake.

$^1$H NMR Spectra:
S3. **Synthesis of [emim][OTf]**

1-Ethylimidazole (5.86 g, 0.0609 mol) was added dropwise (over 1 h) to neat methyl trifluoromethylsulphonate (10 g, 0.0609 mol) in an ice bath. The reaction was very exothermic and the solution was allowed to stir for a further 18 h at room temperature. The mixture was rotary evaporated at 65 °C under high vacuum for 18 h. Trace acid was removed by stirring the product in water (10 ml) with the addition of NaHCO3 (1 g). The salt was reprecipitated with acetonitrile and filtered through celite. Solvents were evaporated under high vacuum yielding the product, as a clear pale yellow oil. (15.80 g, 100%). 1H NMR (300 MHz, DMSO-d6): δ 1.41 (3H, t, J=7.2 Hz), 3.85 (3H, s), 4.18 (2H, q, J=7.3 Hz), 7.67 (1H, s), 7.76 (1H, s), 9.08 (1H, s); IR (ATR, cm⁻¹) 3159 (CH₃), 3120 (CH₂), 2982 (CH₃), 1578 (C=N, C=C), 1454 (CH₃), 1251 (CF₃), 1145 (CF₃), 640 (CF₃).

1H NMR Spectra:
**S4. Synthesis of \([\text{emim}]\)[\(\text{Me}_2\text{PO}_4\)]**

1-Ethylimidazole (48.0 g, 0.500 mol) was added dropwise (over 1 h) to neat trimethylphosphate (70.0 g, 0.500 mol) at 100 °C. The reaction was allowed to stir for a further 18 h at 80 °C. The mixture was rotary evaporated at 65 °C under high vacuum for 18 h, to yield a clear pale yellow oil (118.0 g, 100%). \(^1\)H NMR (300 MHz, DMSO-d6): δ 1.39 (3H, t, \(J=7.3\) Hz), 3.24 (6H, d, \(J=10.3\) Hz), 3.85 (3H, s), 4.19 (2H, q, \(J=7.3\) Hz), 7.74 (1H, s), 7.83 (1H, s), 9.50 (1H, s); IR (ATR, cm\(^{-1}\)) 3139 (CH\(_3\)), 3055 (CH\(_2\)), 2936 (CH\(_3\)), 1565 (C=N, C=C), 1460 (CH\(_3\)), 1231 (CH\(_3\)), 1034 (Me\(_2\)PO\(_4\)), 765 (Me\(_2\)PO\(_4\)).

\(^1\)H NMR Spectra:
**S5. \(^{31}P\) NMR Analysis Procedure**

Milled wood samples were phosphitylated and analysed using the following procedure: Ionic liquid (∼0.40 ml, 475 mg) was added, by syringe, to pulverized wood (25 mg) in a 8 ml sample vial. The mixture was manually mixed with a needle, until homogeneous, flushed with argon and sealed. The sample was heated at 90 °C until clear (or a maximum time of 18 hr was reached). Pyridine (150 µl, 1.88 mmol) was added in one portion and the sample vortexed, at 2500 rpm, using an Janke & Kunkel Vibrofix VF1 Electronic orbital shaker, until visibly homogeneous (∼20 s). The sample was allowed to cool to room temperature, whereby 2-Cl-TMDP (200 µl, 1.26 mmol) was added in one portion and vortexed until visibly homogeneous (∼30 s), as a cream paste. A stock solution of Cr(acac)\(_3\)/CDCl\(_3\) (0.04 M, 500 µl) was added in 4*125 µl portions with vortexing (∼30 s) between each addition. \(e\)-HNDI solution (121.5 mM in 3:2 pyridine:CDCl\(_3\), 125 µl) was added in one portion and the solution vortexed (∼30 s). Further Cr(acac)\(_3\)/CDCl\(_3\) (0.04 M, 3.5 ml) was added in a 500 µl and 3*1 ml portions, with vortexing (∼30 s) between each addition. \(^{31}P\) NMR spectra (243 MHz) were recorded with 700 µl samples, in a 5 mm o.d. NMR tube. Spectral width was 20000 Hz. The transmitter offset was centered on 150 ppm. The pulse flip angle was 80 °. The pre-relaxation delay was 5 s and acquisition time was 1 s. The samples were measured using a Varian Inova 600 MHz spectrometer equipped with a direct detection probe for broadband nuclei such as \(^{31}P\). CDCl\(_3\) was used as locking solvent, and standard transients of 700 were collected. The experiment temperature was maintained at 27 °C for all experiments. This data was processed routinely, without baseline correction, using VNMRJ version 2.1b by Varian Inc. A 0 Hz (fourier transformed) exponential line-broadening factor was used in all cases. Drift correction was performed between 160 and 130 ppm. The anhydride peak, derived from reaction of 2-Cl-TMDP with water, was used as the calibration peak at 132.2 ppm. The ‘total hydroxyl’ integration region was 133 - 151.5 ppm. The guaiacyl hydroxyl integration region was defined as 138.75 - 140.5 ppm. The internal standard was at ∼152.3 ppm.
NMR Spectra for 98 hr planetary milled spruce, phosphitylated from [amim]Cl:
S6. **Kamlet-Taft Parameterisation Procedure**

All samples were prepared in similar fashion. The absorbance of the dye compounds was adjusted so that $\text{Abs}_{\text{max}} < 1.5$. This was achieved with following concentrations, nitroaniline 24 µl/ml, diethylnitroaniline 24 µl/ml and Reichardt’s dye 100 µl/ml.

Samples were recorded on Varian Cary 50 conc. UV Vis spectrometer with a Varian Cary Single Cell Peltier accessory. The UV spectrometer creates the spectra using 1000 data points, changing the wavelength as a function of absorbance. From a closer view the distance between adjacent data points is few nanometers and the $A_{\text{max}}$ value, given by the software, is the data point at the highest $A$ value. To improve accuracy, we transferred the data points to ORIGIN 7.5. We selected only the data representing the $A_{\text{max}}$ peak (~200 nm) from each measurement and fitted a polynomial function to these data points, to get more accurate view of the peak shape. The polynomial function that was used was as follows:

$$Y = A + B_1X + B_2X^2 + B_3X^3 + B_4X^4 + B_5X^5,$$

(eq.1)

where $Y$ and $X$ are the relative axes, $B$ is slope and $A$ is constant. The $A_{\text{max}}$ value was extracted from the plot data simply sorting the plot data points in decreasing order. From the extracted data KT parameters were calculated using equations from Hauru et al.\(^5\)