†Supplementary Material: The effect of ionic liquid cation and anion combinations on the macromolecular structure of lignins, George *et al.* 2011

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S1. Discussion of SEC method validity

When using SEC the first point to note is that the information obtained is in no way comparable to a standard method, and can only be considered as relative information, or a best estimate. This is because SEC relies on an independent calibration to convert elution time to molecular mass, often referred to as a conventional calibration. The molecules used to calibrate the system need to be of known mass and be of similar structure to the unknown sample being investigated. There is a clear problem when applying this method to lignin due to a lack of suitable standard molecules from which to build a calibration and a lack of conclusive knowledge of its macromolecular structure. This point has been discussed at some length in both the lignin and coal/petroleum communities [1–4 and references therein]. To date no unequivocal solution has been found to this challenge; nevertheless, useful relative information can be obtained if the limitations of the method are understood and properly taken into consideration.

The primary metric in SEC is the hydrodynamic volume of the sample that is specific to the solvent used, rather than the samples mass, although the two terms are often used interchangeably. For polymers and some bio-polymers the relationship between hydrodynamic volume and mass is well defined hence SEC is routine in those fields. In complex samples such as lignin, where the macromolecular structure is inconclusively defined, larger errors can be introduced into mass estimations, due to the unknown relationship between lignins hydrodynamic volume and its mass. The eluent chosen for SEC is paramount to achieving a true size exclusion mechanism. For lignin THF is the most common organic SEC eluent[1]. It has been reported, however, that N-methylpyrrolidone (NMP) is a better SEC eluent than THF for materials that are not simple straight chain polymers, such as complex hydrocarbon mixtures from coal/petroleum/biomass and more branched/amorphous polymer like materials[2,3,5–7]. NMP is also known to provide identical calibration behaviour as that of THF for polymer standards. It is therefore considered a superior eluent. The SEC system used here, with NMP as eluent, is one of the most well calibrated and comprehensively understood of those reported[2,3,6,8–10]. The SEC system has been calibrated using polystyrene (PS), polymethylmethacrylate (PMMS), polyethylene oxide (PEO), polysaccharides, and polyaromatic hydrocarbon standards (PAH, including O- and N-PAHs) as well as fullerenes and spherical silica particles (with known diameters)[2,5,7]. In addition, the SEC calibration has been demonstrated to provide a near quantitative measure of mass that is independent of structure for coal and petroleum-derived samples (in the 15-25 minute retained region) by examining their SEC elution time fractions by laser desorption-MS[3,6].

With respect to sample aggregation in the SEC column, lignin is known to aggregate in many solvents and this is widely considered to influence SEC results. Aggregates are presumed to be present when a bi-modal distribution is obtained from SEC. However, it is not easy to determine at what concentration aggregation occurs or how it influences SEC. Salts such as LiCl or LiBr are often added to the SEC eluent to increase the solvent power and disrupt aggregation when examining lignin. It is presumed that dis-aggregation occurs if the SEC distribution changes from bi-modal to uni-modal on addition of salt. This would seem to be a logical conclusion; however, there are no methods available by which this can be unequivocally proven. On deeper investigation of coal and petroleum derived materials, it has been concluded that salts partially destroy the SEC mechanism and that the unimodal distribution was incorrect[11,12]. Many detailed studies have been undertaken to try and determine if there is evidence of sample aggregation in the SEC-NMP system; none has been found. In addition, for high mass samples, determined by mass spectrometric methods, there is a clear correlation between average mass and size of the excluded peak, where the higher the mass, the larger the excluded peak area. In summary there is no evidence that SEC with NMP as eluent suffers from sample aggregation.

The reason for the bi-modal distribution appears to be related to a change in structure for certain types of molecules with masses $\gtrsim$2000 u which means they elute much earlier than would be predicted from their mass (when compared to polystyrene) and these issues are discussed in detail elsewhere[2,3,5,7]. The only sample known to elute in the excluded region when it was expected to appear in the retained region from its mass is fullerene (mass 720 u, elution time $\sim$10 mins, polystyrene calibration predicts $>$1 million u), spherical silica standards also elute in the excluded region and a linear relationship was found for log diameter of these materials and fullerene[2,3]. A detailed review of these and other examinations of the SEC NMP system can also be found elsewhere[2,3,13,14]. The SEC system used here shows a bi-modal distribution for all high mass samples investigated that are not

simple straight chain polymers i.e. humic substances, coal, petroleum, and biomass derived materials and also for the lignin samples investigated here (cf. Figures 1A and B).

Supplementary Figures

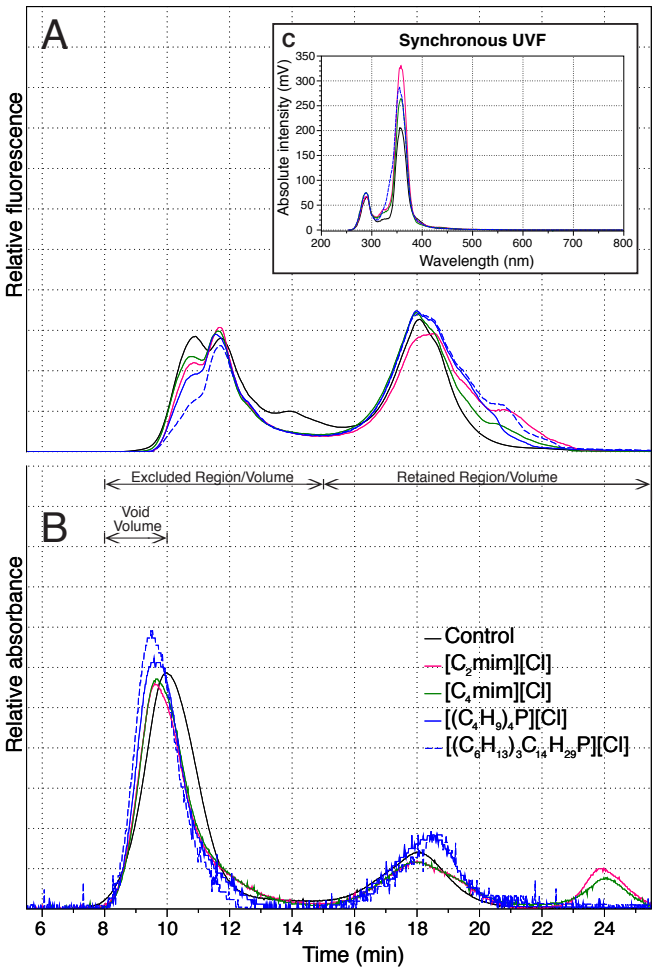

Fig. S 1 **A**: SEC UV-F$_{ex250/em450}$ chromatograms of alkali lignin dissolved in NMP and after treatment in Group-I (Cl^-) ILs . **B**: SEC-UVA$_{300}$ chromatogram of organosolv lignin dissolved in NMP, and after treatment. **C**: Synchronous UV-F spectra of organosolv lignin dissolved in NMP, and after treatment.

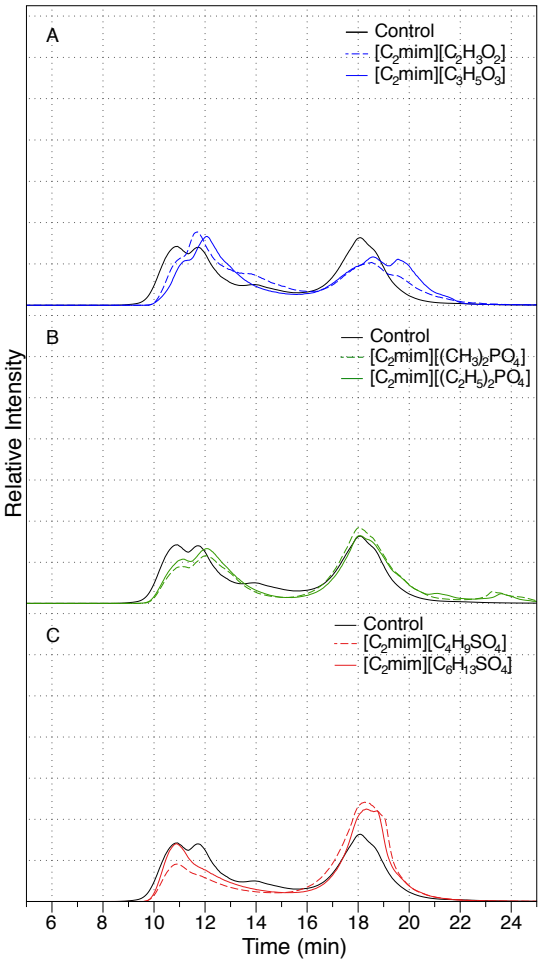

Fig. S 2 SEC UV-F$_{ex250/em450}$ chromatograms of alkali lignin dissolved in NMP and after treatment in Group-IIa (acetate and lactate) , IIb (dimethyl and diethyl phosphate), IIc (butyl and hexyl sulfate) ILs (see Table 1).

S2 Additional SEC Experimental Information

SEC with UV-A detection is commonly used to examine the polydispersity of lignin, and was conducted at 280, 300, 350 and 370 nm in this study. The chromophores observed when using UV-A (280-370 nm) are small-to-large polyaromatic hydrocarbons (naphthalene and bigger) or conjugated phenolic-like structures such as those in DHP[15,16], ferulic acid containing phenolic dimmers[15–18], phenylcoumarones, and stilbene[19]. Data are presented for absorption at 300 nm that was the most representative of the trends observed at all wavelengths and is a good all-purpose wavelength for small/medium sized chromophores, i.e. extents of conjugation. As an adjunct technique, SEC with UV-F detection was used which aids in the identification of the least conjugated systems thus enabling a larger proportion of the sample to be observed. SEC with UV-F detection was used to observe what are thought to be smaller, less conjugated, chromophores, and their associated fluorophores, than was possible with the UV-A conditions (most likely isolated phenolic rings). In this instance a 250 nm excitation wavelength was used and detection was conducted at 450 nm. This combination of wavelengths

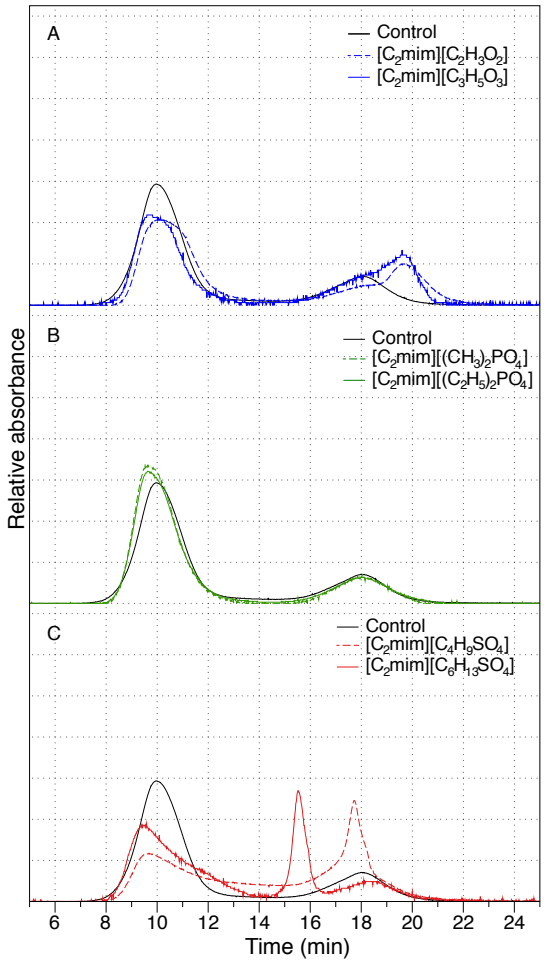

Fig. S 3 SEC UV-F$_{ex250/em450}$ chromatograms of organosolv lignin dissolved in NMP and after treatment in Group-IIa, IIb, IIc ionic liquids (see Table 1).

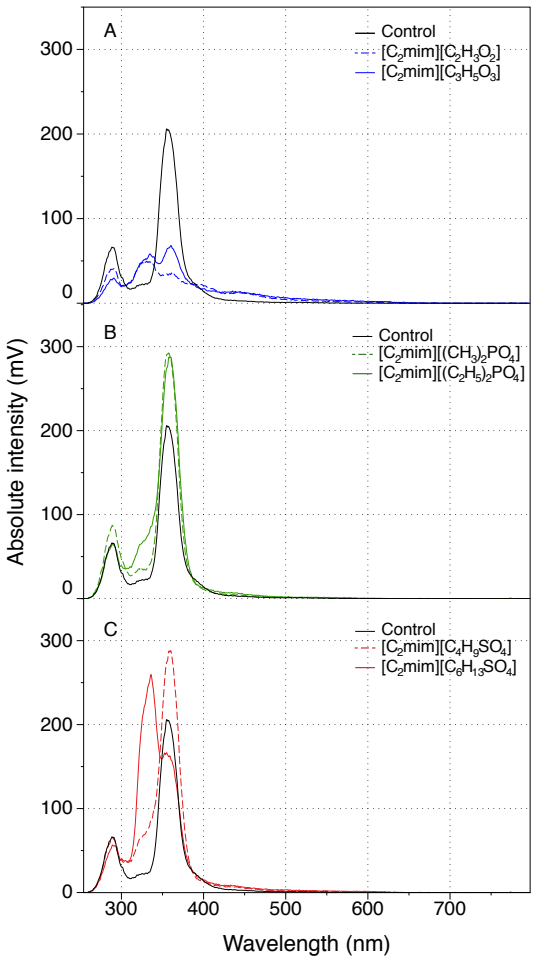

Fig. S 4 Synchronous UV-F spectra of alkali lignin dissolved in NMP and after treatment in [C$_2$mim] based ionic liquids with six different anions.

showed representative behaviour after a study of a variety of wavelengths pairs. The conditions used for this technique restrict the analysis to small chromophores; more highly conjugated ones are not observed. Analysing the data from both techniques in tandem would then, to the best of current knowledge, yield information on the sample in its entirety. More detailed information would be obtained by considering a larger variety of conditions; however, the methods presented here are to assess the relative differences between a large number of samples, rather than an exhaustive analysis of each sample.

The IL backgrounds were analysed by SEC and signal was observed eluting late in the retained region of the column. The signal observed from the ILs occurred at earlier elution times than would be expected for the pure IL. The purities of the ILs used were >90% so the background signal observed was possibly derived from impurities present. Where overlap was observed between the sample peak and the IL background peak, the IL background signal accounted for <10% of the sample peak area. This was taken into account when discussing the results; however, the numbers reported for percent changes (Table 3) have not been corrected to account for this. This complication is unavoidable at present as ILs are not readily available in the quantities required for this study at the purity levels of conventional analytical grade solvents.

SEC UV-A and SEC UV-F data interpretation: Due to the intricate nature of UV-absorbance and fluorescence in large and inconclusively defined molecules, the data will be discussed using the following simplified terminology: the parts of the molecules that are detected only by SEC UV-F will be referred to as small chromophores this should be understood to mean chromophores that absorb at 250 nm (conditions used for SEC UV-F), but not at 280-370 nm (used for SEC UV-

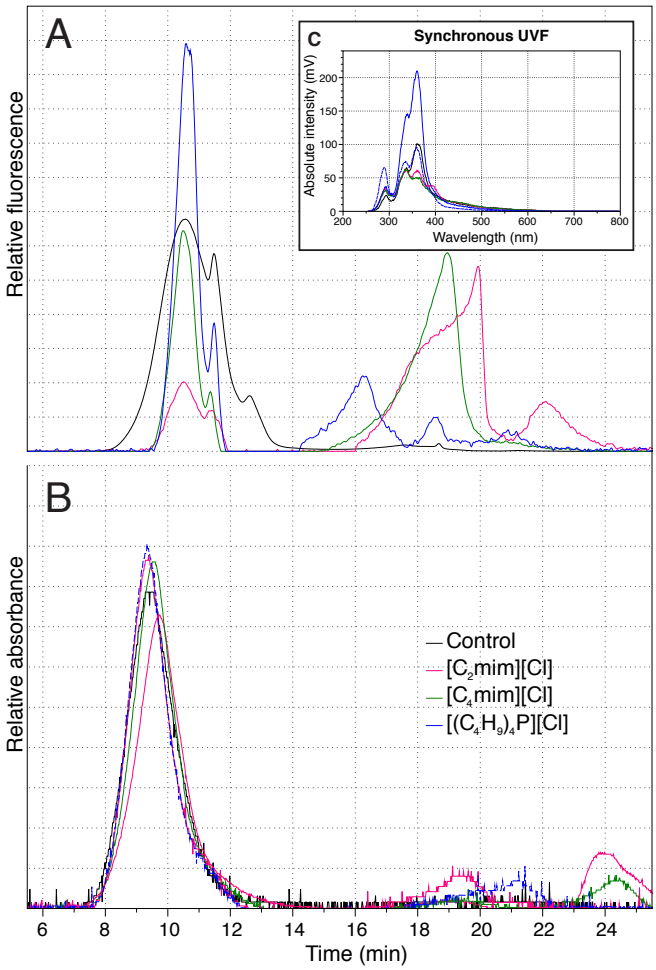

Fig. S 5 A: SEC UV-F$_{ex250/em450}$ chromatograms of ALS lignin dissolved in NMP and after treatment in Group-I (Cl^-) ILs . **B**: SEC-UVA$_{300}$ chromatogram of organosolv lignin dissolved in NMP, and after treatment. **C**: Synchronous UV-F spectra of organosolv lignin dissolved in NMP, and after treatment.

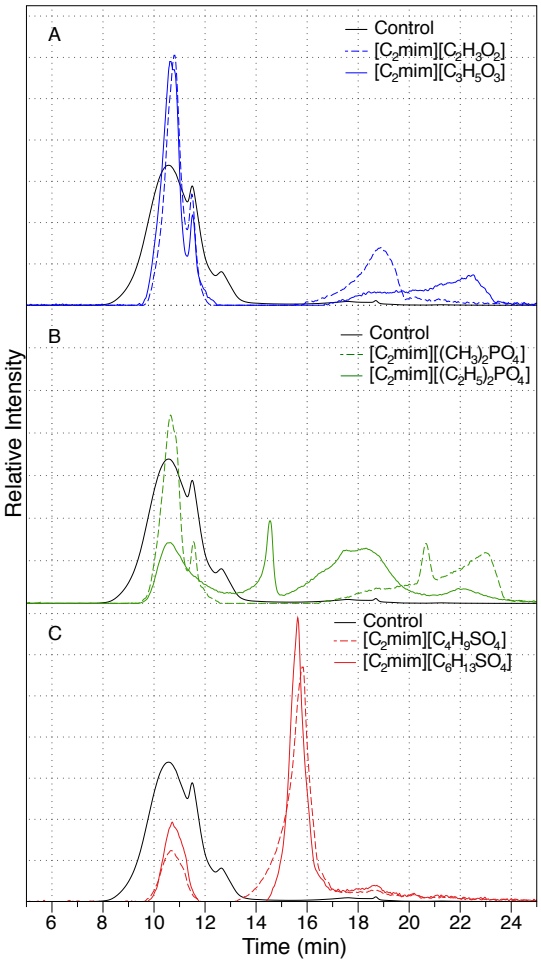

Fig. S 6 SEC UV-F$_{ex250/em450}$ chromatograms of ALSlignin dissolved in NMP and after treatment in Group-IIa, IIb, IIc ionic liquids (see Table 1).

A). It is implicit that these small chromophores interact with a related fluorophore. The chromophores excited by the SEC UV-A conditions are probably more conjugated than those targeted by SEC UV-F; hence they will be referred to as large chromophores. From the information available it is not possible to elucidate the actual nature of the chromophores and fluorophores, work is ongoing to address this issue.

During alkali delignification of biomass, and therefore during the extraction of the alkali and low sulphonate lignins used in this study, it is known that both chromophores and leucochromophores, which are reportedly converted to chromophores during air oxidation, are formed[20]. This is evinced by the light absorption coefficient during the alkali lignin extraction process increasing from 5-10 m^2kg^{-1} to 500 m^2kg^{-1}. Mechanisms for this are the formation of aryl coumarones and stilbene quinines from stilbene and butadiene quinines from hydroxarylbutadienes[20]. It is possible that reactions of this nature are occurring during lignin pretreatment. In addition to this increasing extent of conjugation, the reverse is also possible. This has implications on the interpretations of the results whereby material only observed by UV-A before pretreatment could be reduced in conjugation, to be detected only by UV-F after pretreatment or that chromophores are destroyed during pretreatment and that the fragments are observed neither by UV-A nor UV-F. These processes are not straight forward to determine and work is ongoing to clarify if they occur. To account for these uncertainties the SEC results are presented area normalised; this was considered the most robust method by which to make comparisons.

It is important to note that, depending on the sample, only

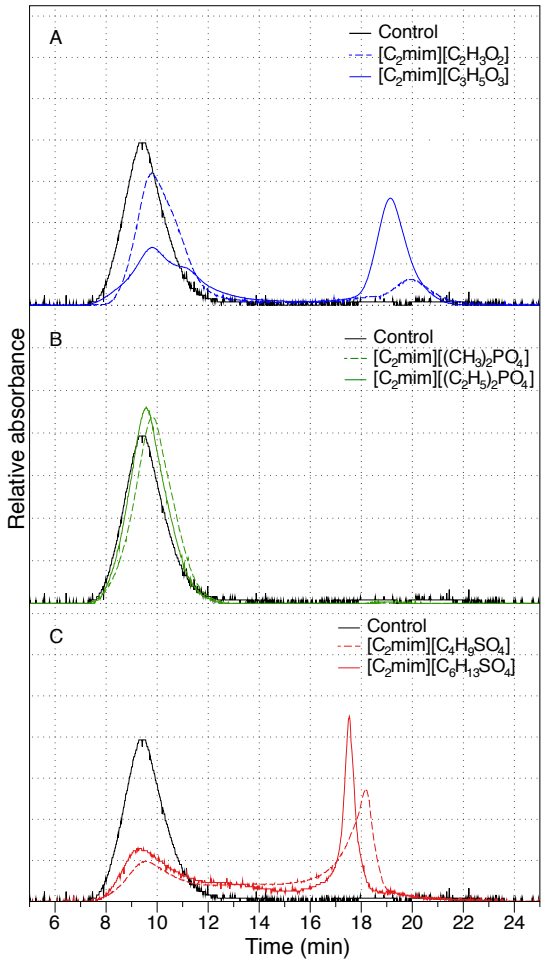

Fig. S 7 SEC UV-F$_{ex250/em450}$ chromatograms of organosolv lignin dissolved in NMP and after treatment in Group-IIa, IIb, IIc ionic liquids (see Table 1).

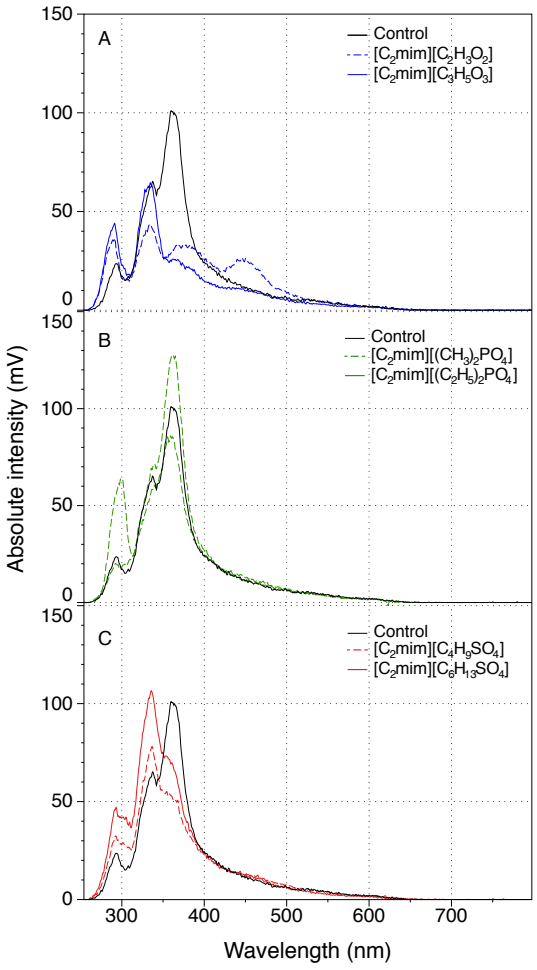

Fig. S 8 Synchronous UV-F spectra of ALS lignin dissolved in NMP and after treatment in [C$_2$mim] based ionic liquids with six different anions.

very small amounts of the total material is being detected by SEC UV-F, due to the high sensitivity of the instrument and its high selectivity. Therefore, UV-F can be greatly misleading on its own. The UV-F conditions used here for SEC detection were to provide additional information on parts of the lignin samples that were not amenable to UV-A detection with the instrumentation available. From the present data it is not possible to quantify how much of the total sample was being observed by each technique individually but it is deemed that the sample is observed in its entirety when both techniques are used in tandem.

S3 Calibrations equations determined for the SEC column

Application of the calibrations to lignin molecular mass interpretation: To obtain information on mass distribution from SEC it is necessary to convert the elution time into mass and this is typically achieved by comparison to polymer standards. As already described this SEC system has been extensively calibrated. Of the polymer standards studied the biggest difference in calibration was between polystyrene and polysaccharides, which can elute up to 2 min later than polystyrene of the same mass[2,5]. Thus for this system using straight chain polymers, polystyrene and polysaccharide mass distributions can be thought of as the high and low limits of mass respectively for a given elution time. It was also found that all the polymer calibrations underestimate the smallest material elut-

ing at the latest times. For example, signal from samples is often observed up to a 25-minute retention limit. However polysaccharide standards predict masses of less than 100 u at times longer than 21.2 min and polystyrene at times longer than 18.0 min, which is clearly incorrect for the samples in question. Therefore, a calibration based on polyaromatic hydrocarbon (PAH) standards, which provide more representative standards is used for that region. Details of the calibration equations are shown in Table S3.1 [3,14].

Table 1 Calibration equations used for each section of the mixed-D SEC column; void limit is 8.0 min (nothing should elute before this time); exclusion limit is 10.0 min (signal eluting before this time is too large to enter the porosity of the column and instead passes through the void volumes between the packing material); retention limit is 25.0 min and is the time taken by the solvent to pass through the column (if a true SEC mechanism is in place no sample should elute after this time)

	Elution time range (min)	Equation to convert elution time	Calibration method
	8.0-15.0	>2500 u	LD-MS (M_n)
Eq. 1	15.0 - 19.2	y = -0.353x + 9.598	Pullulan
Eq. 2	15.0 - 18.0	y = -0.356x + 9.301	Polystyrene
Eq. 3	19.2 - 23.5	y = -0.168x + 5.987	PAHs
	23.5 - 25.0	assumed to be 100 u	PAH

A common feature of SEC chromatograms of real high mass samples obtained using NMP as eluent is a bi-modal distribution with a near zero-intensity valley between the two peaks (cf. Figures 1-2) which is not observed when examining polymer standards. These two bands of material generally elute between 8-15 min (excluded region) and 15-25 min (retained region). It has been demonstrated by independent LD-MS analysis that the material eluting in the excluded region of this SEC system is of higher average mass than material recovered from the retained for coal and petroleum derived materials [3]. However, those studies also found that the high masses predicted from the excluded SEC region by polymer calibration were not detected by LD-MS. At present, there is only truly independent evidence for average mass (Mn) up to 3500 u (whereas SEC suggests $\gg$100,000 u) for materials recovered from the excluded region. Therefore, if the SEC calibration is based on mass values that can be independently verified the excluded region can only be said to contain molecules with average masses (Mn) greater than 2500 u. The polymer calibration was able to be independently verified by LD-MS for materials eluting between 15-25 min (retained region), for coal, petroleum and bitumen derived materials [3,13,21,22].

Lignin is more likely to have a structure closer to the macrostructure of coal and petroleum than straight chain polymers such as polystyrene or polysaccharides; therefore evidence dictates that great caution is required when applying the polystyrene or polysaccharide calibrations to material eluting before 15 min. Correspondingly, the molecular weight of material eluting before 15 min will only be estimated as being >2500 u (in terms of Mn), rather than using the numbers from the polysaccharide calibration (Table S3.1). Depending on the nature of the discussion, sometimes it is more insightful to refer to the time range over which material elutes and not simply the peak maximum elution time or the equivalent mass estimate. Hence for a peak maximum at 18 mins ($\sim$1750 u, M_n) it is entirely possible for this to be composed of molecules ranging from, e.g. 17-19 mins ($\sim$4000 800 u according to the polysaccharide calibration). Hence, in the main text all references to masses higher than 2500 u are solely for mass range estimates, not average masses.

To simplify the discussion of the results only numbers from the polysaccharide and PAH calibrations (Eq 1 and 3, Table S3.1) will be quoted in relation to the SEC results; if the polystyrene calibration had been used lower numbers would have been obtained, cf. Table S3.2. The reason the polysaccharides calibration was favoured is because experience of this SEC system suggests that oxygen groups have a larger influence on elution time than aromatics [5,7]

Table 2 Mass estimates for the untreated lignin when compared to polysaccharides and polystyrene SEC calibration curves (peak maximum was used cf. Figure 1 and Figure 2)

Sample	Peak max SEC UV-A		Peak max SEC UV-F	
	P-Sac / u	PS / u	P-Sac / u	PS / u
ALS	1,800,000	850,000	700,000	330,000
Organosolv	1,300,000	600,000	300,000	150,000
Alkali	1,200,000	550,000	300,000	150,000

S4 Additional information regarding UV-F methodology and interpretation

By using a small δ between excitation and emission frequencies during synchronous UV-fluorescence analysis, data is obtained that is relatively straight forward to interpret [23]. As the extent of conjugation increases in a sample, a bathochromic shift is observed in the fluorescence [23,24]. Most of the available data from standard compounds is for poly-aromatic compounds, where a single ring gives signal at 270 nm, two rings (naphthalene) at 300 nm, and for every extra fused ring the signal, in general, the signal bathochromically shifts by 30 nm. Recent work supports these conclusions. A qualitative relationship has been noted between the wavelength of maximum fluorescence and number of conjugated aromatic rings in a polynuclear aromatic (PNA) system, as determined by synchronous mode UV-F and NMR spectroscopy respectively, cf. Table S4.1. This was for a number of coal, petroleum and bi-

tumen derived oils, tars, pitches and asphaltenes and their solubility sub-fractions[21,22,25]. This correlation was drawn from a comprehensive review into this and related analytical techniques; that work is under preparation for separate publication[26]. Little information is readily available for polyphenolics under these conditions; however confieryl alcohol is known to give a peak maximum at 315 nm (equivalent to 2.5 aromatic rings). To ease the discussion of the synchronous UV-F results they are reported in units of aromatic-ring equivalents (AR_{eq}).

Table 3 Correlations between the average numbers of rings in polynuclear aromatic ring systems (determined by NMR) and the wavelengths of maximum fluorescence intensity in the UV-fluorescence spectra[26].

Wavelength of peak with maximum intensity	Aromatic-ring equivalent (AR_{eq})
270 nm	1 ring
300 nm	2 rings
330 nm	3 rings
360 nm	4 rings
390 nm	5 rings
420 nm	6 rings
450 nm	7 rings
480 nm	8 rings

Some general points about fluorescence are worth considering in relation to lignin-like material: isolated benzene rings are weakly fluorescent, addition of an OH or electrophilic groups in general increases sample fluorescence, as does addition of conjugated C=C bonds. However, fluorescence of benzene is dramatically reduced when substituted by unsaturated functional groups (COOH, C=O, C=S, or N or S in heterocyclic rings). In addition, for aromatic carbonyls the reduction in fluorescence is strongly solvent dependent, highly polar and H-bonding solvents can cause them to fluorescence more intensely. Sulphonation of aromatics, generally, reduces fluorescence by up to 20%[26]. There is little known about the influence of ILs on the fluorescence of lignins; therefore refined interpretation of the UV-F data is unwise without further information. To simplify the discussion of the synchronous UV-F results they will be explained in terms of aromatic ring equivalents. However, it should be understood that increased conjugation of any type of chromophore would result in a bathochromic shift, i.e. phenolics, coniferyl alcohol-like units, not only aromatics. There are also many possible exceptions to these trends due to the number of substituents and the large size of the molecules in lignin.

The low fluorescence in the lignin samples implies that the chromophores / fluorophores observed by this technique are in low abundance, or that fluorescence intensity is reduced due to the large size of the molecules, as a result of heat losses through bond vibrations as well as stearic interactions and the influence of substituents (C=O, OH, OCH_3, SH, etc.). It should be clear that this technique is not quantitative; however it can provide rapid and insightful relative information on the parts of the sample that can be observed.

S5 Fragmentation pattern interpretation

Both lignin-control solvent mixtures showed exactly the same chromatograms and polydispersity in the unheated and heated scenarios. It may therefore be deduced that the control solvent is not reacting or acting as a catalyst at the pretreatment temperatures considered here and the IL polydispersity profiles may thus be compared to a control that is a true solvent system. Complete dissolution occurred with all the samples. Had the sample not dissolved entirely this could mean that the different ILs were preferentially dissolving differing components of the original lignin. As total dissolution did occur in all ILs, any reduction in mass observed in the chromatograms is caused by a reduction in lignin molecular weight. The data revealed fragmentation of the lignin molecule into smaller sized molecules. SEC with UV-F and UV-A detection highlighted four different lignin fragmentation schemes as a function of IL, when compared with the simply solvated control sample. The data will therefore be discussed in terms of these four fragmentation patterns observed from the experimental results, as defined below:

1. Primary A-fragments (1°A): These fragments contain small chromophores that before fragmentation appear in the same region of both SEC UV-F and SEC UV-A (10-14 min) chromatograms. After being cleaved from the original lignin molecule, these fragments contain only small isolated chromophores (and a related fluorophore), and so are only observed by SEC UV-F (but not by UV-A) at the conditions used. These fragments are represented in the SEC UV-F chromatograms by a diminution in the excluded region and a corresponding increase in the retained, whilst little change is observed in the corresponding SEC UV-A curves. From this, two possibilities may be deduced. In the first (i), before pretreatment it is the same molecules that are being observed by both SEC-UVA and SEC-UVF at a particular elution time. Here, the 1°A-fragments (small chromophores) are connected to large molecules that also contain sections with more conjugated chromophores (as observed by UV-A). During pretreatment these linkages are cleaved, releasing the 1°A-fragments, although the sections of the lignin molecules that contain the large chromophores are mostly unaffected. In the second scenario (ii), it is a different lignin molecule that is being observed at a particular elution time by each of SEC UV-

A and SEC UV-F techniques. Here, there are molecules that contain only the small chromophores (observed by SEC UV-F) and others that only contain the larger ones (observed by SEC UV-A); both elute at the same time as each other before pretreatment. During pretreatment only the molecules that contain the small chromophores are broken down, whilst the molecules that only contain the large chromophores are unaffected. Given the current knowledge of lignin structure it is unlikely that there are two completely distinct types of molecules that are each only detected by either SEC-UVA or SEC-UVF. Therefore it is likely that the mechanism occurring in 1°A fragmentation is the former scenario, (i). Additionally, the linkages hewn in 1°A-fragmentation appear to be common to many of the samples indicating bonds that are relatively easily cleaved by the ILs investigated.

2. Secondary A fragments (2°A): this is where a second set of linkages are broken within the 1°A-fragments. This is thought to be a second distinct process as no additional change in the excluded region is detected but different sizes of small/medium sized molecules (>200 u) are generated in the retained region of the column (observed only by SEC UV-F).

3. Primary B fragments (1°B): like 2°A-fragments, 1°B-fragments are also derived from the molecules that were observed by both SEC UV-A and SEC UV-F (mainly in the 10-12 min region). The fragments appear to contain both types of chromophores (small and large) in large/medium sized molecules (>500 u), and are therefore observed by both SEC UV-A and SEC UV-F. The ILs that cause the formation of1°B-fragments produce completely different sized-fragments to those in 1°A-fragmentation suggesting different linkages are cleaved. In this mode of fragmentation the larger material in the excluded peak is generally converted into a narrower product distribution then the other fragmentation mechanisms, which implies a repeating lignin linkage is being cleaved. As in 1°A-fragmentation, it is also possible that there are molecules that contain only the small chromophores and others that only contain the larger ones. Both of these types of molecules could elute at the same time as each other before pretreatment, and after pretreatment the fragments generated also elute at the same time as one another but this is considered a less likely scenario.

4. Primary C fragments (1°C): these fragments are formed solely from the largest material that is observed only by SEC UV-A and which before pretreatment elutes between 8-10 min. These fragments themselves are detected only by SEC UV-A and are represented by portions of the excluded peak in the UV-A chromatogram being converted to small material in the retained region. This implies that no small chromophores were originally present in these molecules before pretreatment and that none have been formed during the fragmentation process. The ILs capable of inducing this type of cleavage produce different sized fragments to those produced by the other ILs, suggesting different linkages are being hewn (or one common, then different secondary C fragmentation). Additionally Primary C fragments can be formed from 1°B fragments; if the 1°B contains a small and large chromophore it is possible that during pretreatment the linkage between these chromophores is cleaved which results in a 1°A- and C fragment being observed.

The results imply that 1°A-fragmentation is mainly the cleavage of linkages between a lignin back-bone and side-chains and/or end-groups. B-fragmentation could be cleavage of a side-chain or end-group that contains both a small and large chromophore from the back-bone or cleavage of linkages in the back-bone itself. C-fragmentation is the cleavage of side-chains/end groups that only contains large chromophores and/or linkages in the main back-bone. This is however, somewhat of an over simplification of the structure of lignin as it probably has multiply back-bones with linkages between them which could be considered as side-chains or as part of the back-bone itself, as well as side-chains that could also be extensively branched. Cleavage of a linkage in the back-bone is unlikely to break the molecule into two fragments as there may be other linkages still intact which hold the molecule together. This would result in new end groups/side-chain like sections in the molecules which could then undergo further attack resulting in release of sections that were initially embedded within the original lignin back-bone. Fragments released in this way could contain solely small chromophores or only large chromophores or both. For the complex high mass molecules found in lignin there are many types of chromophores and linkages present that could result in any number of possible processes. To simplify the discussion lignin will be considered to contain a main back-bone structure that is made up of units that contain mostly large chromophores with side-chain and end groups that contain mainly small chromophores. However, this is not meant to state that there is a fundamental reason why only small chromophores are found in side-chains and only large chromophores in the back-bone other than that this was loosely implied by the results.

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