Electronic Supporting Information (ESI) of the manuscript entitled

**Efficient nitrogen-doping and structural control of hierarchical carbons using unconventional precursors in form of deep eutectic solvents**

by N. Lopez-Salas et al.

Table S1 – Chemical shifts obtained by $^1$H NMR spectroscopy – at 90 °C and using deuterated DMSO as reference solvent – of resorcinol (Re), 4-Hexylresorcinol (4Re), $p$-nitrophenol (pNP) and choline chloride (ChCl), and the eutectic mixtures prepared with different molar ratios of the components.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Re</th>
<th>4Re</th>
<th>pNP</th>
<th>ChCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H$ at C5</td>
<td>$H$ at C4&amp;6</td>
<td>$H$ at C2</td>
<td>$H$ at C12</td>
</tr>
<tr>
<td>Re</td>
<td>6.9 (1H)</td>
<td>6.2 (2H)</td>
<td>6.2 (1H)</td>
<td></td>
</tr>
<tr>
<td>4Re</td>
<td></td>
<td>0.9 (3H)</td>
<td>1.3 (6H)</td>
<td>1.5 (2H)</td>
</tr>
<tr>
<td>pNP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ChCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$<em>{1</em>{des}}$</td>
<td>6.1 (1H)</td>
<td>6.2 (2H)</td>
<td>5.8 (1H)</td>
<td>0.0 (3H)</td>
</tr>
<tr>
<td>RC31</td>
<td>6.1 (3H)</td>
<td>5.7 (6H)</td>
<td>5.8 (3H)</td>
<td>-</td>
</tr>
<tr>
<td>AReC31</td>
<td></td>
<td>0.2 (3H)</td>
<td>0.6 (18H)</td>
<td>0.8 (6H)</td>
</tr>
<tr>
<td>pNPC31</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>

* These peaks are all included in the signal at 5.8 ppm.
** These peaks are all included in the signal at 6.2 ppm.
**Table S2** – Chemical shifts obtained by $^1$H NMR spectroscopy – at room temperature and using CDCl$_3$ as the external reference – of resorcinol (Re), 4-Hexylresorcinol (4Re), $p$-nitrophenol (pNP) and choline chloride (ChCl), and the D$_2$O diluted eutectic mixtures prepared with different compositions of them (N1$_{DES}$, N2$_{DES}$ and N3$_{DES}$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ (ppm)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re</td>
<td>4Re</td>
<td>pNP</td>
<td>ChCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H at C5</td>
<td>H at C4&amp;6</td>
<td>H at C12</td>
<td>H at C11-9</td>
<td>H at C8</td>
<td>H at C7</td>
<td>H at C6</td>
<td>H at C5</td>
<td>H at C2</td>
<td>H at C3&amp;S</td>
<td>H at C2 &amp;5</td>
</tr>
<tr>
<td>Re</td>
<td>7.0 (1H)</td>
<td>7.4 (2H)</td>
<td>6.3 (1H)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4Re</td>
<td></td>
<td>0.9 (3H)</td>
<td>1.3 (6H)</td>
<td>1.5 (2H)</td>
<td>2.5 (2H)</td>
<td>6.3 (1H)</td>
<td>6.9 (1H)</td>
<td>6.3 (1H)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pNP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.1 (2H)</td>
<td>6.9 (2H)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ChCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.1 (2H)</td>
<td>3.6 (2H)</td>
</tr>
<tr>
<td>Diluted N1$_{DES}$</td>
<td>6.6 (1H)</td>
<td>6.3 (2H)</td>
<td>*6.2 (1H)</td>
<td>0.6 (3H)</td>
<td>1.0 (6H)</td>
<td>1.2 (2H)</td>
<td>2.2 (2H)</td>
<td>*6.2 (1H)</td>
<td>6.4 (1H)</td>
<td>*6.2 (1H)</td>
<td>6.8 (2H)</td>
</tr>
<tr>
<td>Diluted N2$_{DES}$</td>
<td>6.8 (1H)</td>
<td>6.4 (2H)</td>
<td>*6.3 (1H)</td>
<td>0.6 (3H)</td>
<td>0.9 (6H)</td>
<td>1.2 (2H)</td>
<td>2.2 (2H)</td>
<td>*6.3 (1H)</td>
<td>6.6 (1H)</td>
<td>*6.3 (1H)</td>
<td>7.6 (4H)</td>
</tr>
<tr>
<td>Diluted N3$_{DES}$</td>
<td>6.8 (1H)</td>
<td>6.4 (2H)</td>
<td>*6.3 (1H)</td>
<td>0.5 (3H)</td>
<td>0.9 (6H)</td>
<td>1.2 (2H)</td>
<td>2.2 (2H)</td>
<td>*6.3 (1H)</td>
<td>6.6 (1H)</td>
<td>*6.3 (1H)</td>
<td>7.6 (6H)</td>
</tr>
</tbody>
</table>

* These peaks are all included in the signal at ca. 6.2-6.3 ppm.
Table S3 – Chemical shifts obtained from the $^1$H NMR spectrum – at room temperature and using deuterated DMSO as the external reference – of a D$_2$O dilution of pNP-ChCl (25 wt%) with a molar ratio of 0.15:1. It is worth noting that the chemical shifts of the pNP-ChCl mixture in D$_2$O are similar to those of pNP and ChCl in N$_1$$_{DES}$, N$_2$$_{DES}$ and N$_3$$_{DES}$ when they were also diluted in D$_2$O (see Table S2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pNP</td>
</tr>
<tr>
<td></td>
<td>$H$ at C3&amp;5</td>
</tr>
<tr>
<td>pNP</td>
<td>8.1 (2H)</td>
</tr>
<tr>
<td>ChCl</td>
<td></td>
</tr>
<tr>
<td>Diluted pNP:ChCl 0.15:1</td>
<td>7.5 (0.3 H)</td>
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</tbody>
</table>

Table S4 - XPS binding energy values of carbon, nitrogen and oxygen - obtained after deconvolution of the XPS spectra - for N$_3$_C@500 and N$_3$_C@800.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s</th>
<th>N1s</th>
<th>O1s</th>
<th>O/C at</th>
<th>N/C at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_3$C@500</td>
<td>284.8 (67)</td>
<td>398.6 (39)</td>
<td>532.4 (47)</td>
<td>0.118</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>286.2 (27)</td>
<td>400.0 (40)</td>
<td>533.8 (53)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>288.2 (6)</td>
<td>401.6 (13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>405.0 (8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_3$C@800</td>
<td>284.8 (70)</td>
<td>398.6 (31)</td>
<td>532.4 (58)</td>
<td>0.099</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>286.2 (15)</td>
<td>400.0 (52)</td>
<td>533.8 (42)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>287.5 (10)</td>
<td>401.4 (17)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>289.4 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure S1** – From top to bottom, $^1$H NMR spectra – at 90 °C and using deuterated DMSO as the external reference – of N1$_{\text{DES}}$, and of the binary DESs formed between Re:ChCl, pNP:ChCl, and 4Re:ChCl with a 3:1 molar ratio.
**Figure S2** – $^1$H NMR spectra – at 90 °C and using deuterated DMSO as reference solvent – of (from top to bottom) of Re, 4Re, pNP, and ChCl.
Figure S3 – $^1$H NMR spectra – at room temperature and using deuterated CDCl$_3$ as the external reference – of diluted DES (from top to bottom) N$_{1\text{DES}}$, N$_{2\text{DES}}$ and N$_{3\text{DES}}$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure_s3.png}
\end{figure}
Figure S4 – $^1$H NMR spectra – at room temperature and using deuterated CDCl$_3$ as the external reference – of the freeze-dried extracts obtained after thorough full washing of N1$_{GEL}$, N2$_{GEL}$ and N3$_{GEL}$. 
Figure S5 - $^1$H NMR spectrum – at room temperature and using deuterated DMSO as the external reference – of a D$_2$O dilution of pNP-ChCl (25 wt%) with a molar ratio of 0.15:1.

Figure S6 – XRD pattern of the residue – e.g. pNP-ChCl with a molar ratio of 0.15:1 as revealed by NMR – obtained from the thorough full washing of the resin resulting from co-condensation. Crystals were formed upon the evaporation of the water – 90 ºC overnight – used for washing.
Figure S7 – SEM micrographs of (from left to right) N1C@400, N1C@500 and N1C@600.
**Figure S8** – SEM micrographs of (from left to right) \( \text{N}_2\text{C}@400 \), \( \text{N}_2\text{C}@500 \) and \( \text{N}_2\text{C}@600 \).
**Figure S9** – SEM micrographs of (from left to right) N3\textsubscript{C@400}, N3\textsubscript{C@500} and N3\textsubscript{C@600}.