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

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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.

Sample	δ (ppm)														
	Re			4Re							pNP		ChCl		
	H at C5	**H** at C4&6	**H** at C2	**H** at C12	**H** at C11-9	**H** at C8	**H** at C7	**H** at C6	**H** at C5	**H** at C2	**H** at C3&5	**H** at C2&5	**H** at C2	**H** at C1	**H** at NCH_3
Re	6.9 (1H)	6.2 (2H)	6.2 (1H)												
4Re				0.9 (3H)	1.3 (6H)	1.5 (2H)	2.5 (2H)	6.1 (1H)	8.5 (1H)	6.8 (1H)					
pNP											8.1 (2H)	6.9 (2H)			
ChCl													3.9 (2H)	3.5 (2H)	3.2 (9H)
$N1_{DES}$	6.1 (1H)	6.2 (2H)	*5.8 (1H)	0.0 (3H)	0.4 (6H)	0.7 (2H)	1.7 (2H)	*5.8 (1H)	6.2 (1H)	*5.8 (1H)	7.2 (2H)	6.0 (2H)	3.2 (2H)	2.5 (2H)	2.2 (9H)
RC31	6.1 (3H)	5.7 (6H)	5.8 (3H)	-	-	-	-	-	-	-	-	-	2.8 (2H)	2.0 (2H)	1.7 (9H)
AReC31				0.2 (3H)	0.6 (18H)	0.8 (6H)	1.8 (6H)	5.8 (3H)	6.1 (3H)	6.0 (3H)			3.1 (2H)	2.4 (2H)	2.0 (9H)
pNPC31	-	-	-	-	-	-	-	-	-	-	7.2 (6H)	6.3 (6H)	3.6 (2H)	3.1 (2H)	2.7 (9H)

* 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_2O diluted eutectic mixtures prepared with different compositions of them ($N1_{DES}$, $N2_{DES}$ and $N3_{DES}$).

Sample	δ (ppm)														
	Re			4Re							pNP		ChCl		
	H at C5	**H** at C4&6	**H** at C2	**H** at C12	**H** at C11-9	**H** at C8	**H** at C7	**H** at C6	**H** at C5	**H** at C2	**H** at C3&5	**H** at C2&5	**H** at C2	**H** at C1	**H** at NCH_3
Re	7.0 (1H)	7.4 (2H)	6.3 (1H)												
4Re				0.9 (3H)	1.3 (6H)	1.5 (2H)	2.5 (2H)	6.3 (1H)	6.9 (1H)	6.3 (1H)					
pNP											8.1 (2H)	6.9 (2H)			
ChCl													4.1 (2H)	3.6 (2H)	3.2 (9H)
Diluted $N1_{DES}$	6.6 (1H)	6.3 (2H)	*6.2 (1H)	0.6 (3H)	1.0 (6H)	1.2 (2H)	2.2 (2H)	*6.2 (1H)	6.4 (1H)	*6.2 (1H)	6.8 (2H)	6.4 (2H)	3.8 (2H)	3.1 (2H)	2.8 (9H)
Diluted $N2_{DES}$	6.8 (1H)	6.4 (2H)	*6.3 (1H)	0.6 (3H)	0.9 (6H)	1.2 (2H)	2.2 (2H)	*6.3 (1H)	6.6 (1H)	*6.3 (1H)	7.6 (4H)	6.6 (4H)	3.9 (2H)	3.2 (2H)	2.9 (9H)
Diluted $N3_{DES}$	6.8 (1H)	6.4 (2H)	*6.3 (1H)	0.5 (3H)	0.9 (6H)	1.2 (2H)	2.2 (2H)	*6.3 (1H)	6.6 (1H)	*6.3 (1H)	7.6 (6H)	6.6 (6H)	3.9 (2H)	3.3 (2H)	3.0 (9H)

* 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_2O 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_2O are similar to those of pNP and ChCl in $N1_{DES}$, $N2_{DES}$ and $N3_{DES}$ when they were also diluted in D_2O (see Table S2).

Sample	δ (ppm)				
	pNP		ChCl		
	H at C3&5	**H** at C2&5	**H** at C2	**H** at C1	**H** at NCH_3
pNP	8.1 (2H)	6.9 (2H)			
ChCl			4.1 (2H)	3.6 (2H)	3.2 (9H)
Diluted pNP:ChCl 0.15:1	7.5 (0.3 H)	6.3 (0.3 H)	3.5 (2H)	3.0 (2H)	2.6 (9H)

Table S4 - XPS binding energy values of carbon, nitrogen and oxygen - obtained after deconvolution of the XPS spectra - for $N3_{C@500}$ and $N3_{C@800}$.

Sample	C1s	N1s	O1s	O/C at	N/C at
$N3_{C@500}$	284.8 (67) 286.2 (27) 288.2 (6)	398.6 (39) 400.0 (40) 401.6 (13) 405.0 (8)	532.4 (47) 533.8 (53)	0.118	0.039
$N3_{C@800}$	284.8 (70) 286.2 (15) 287.5 (10) 289.4 (5)	398.6 (31) 400.0 (52) 401.4 (17)	532.4 (58) 533.8 (42)	0.099	0.016

Figure S1 – From top to bottom, ^{1}H NMR spectra – at 90 °C and using deuterated DMSO as the external reference – of $N1_{DES}$, and of the binary DESs formed between Re:ChCl, pNP:ChCl, and 4Re:ChCl with a 3:1 molar ratio.

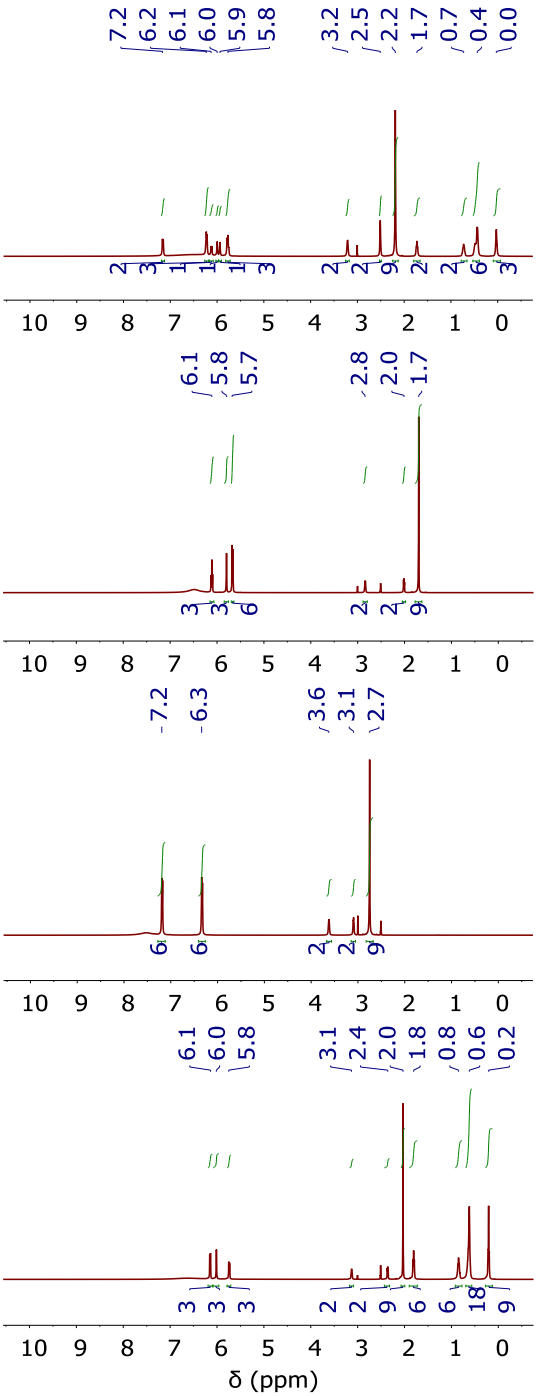

Figure S2 – ^{1}H NMR spectra – at 90 °C and using deuterated DMSO as reference solvent – of (from top to bottom) of Re, 4Re, pNP, and ChCl.

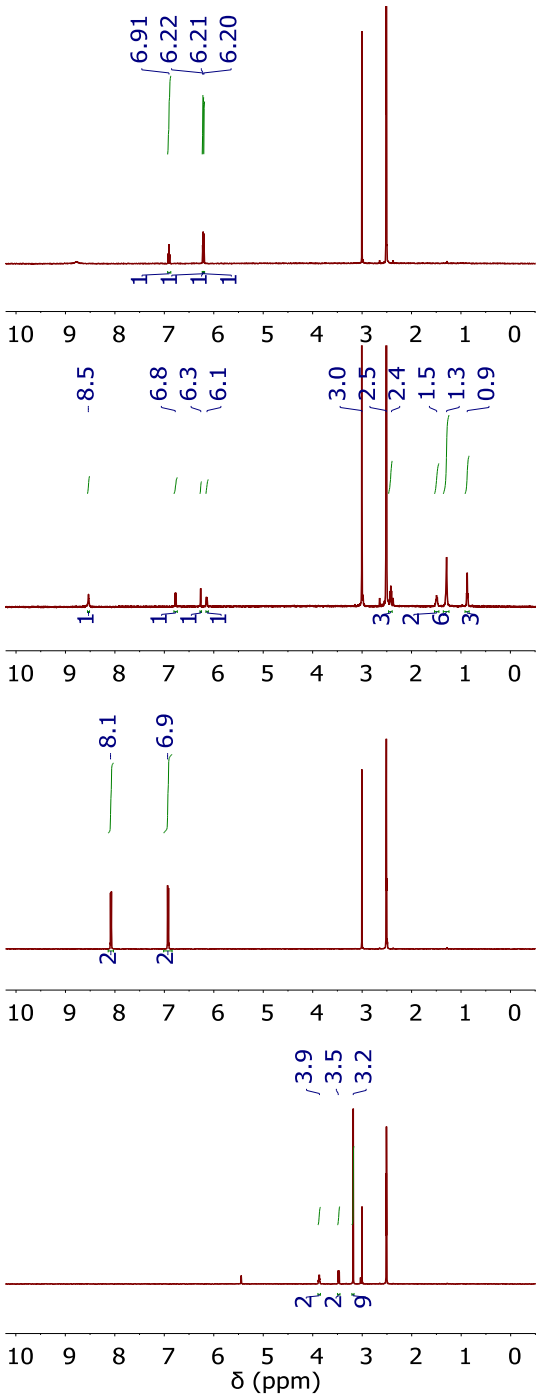

Figure S3 – ^{1}H NMR spectra – at room temperature and using deuterated $CDCl_3$ as the external reference – of diluted DES (from top to bottom) $N1_{DES}$, $N2_{DES}$ and $N3_{DES}$.

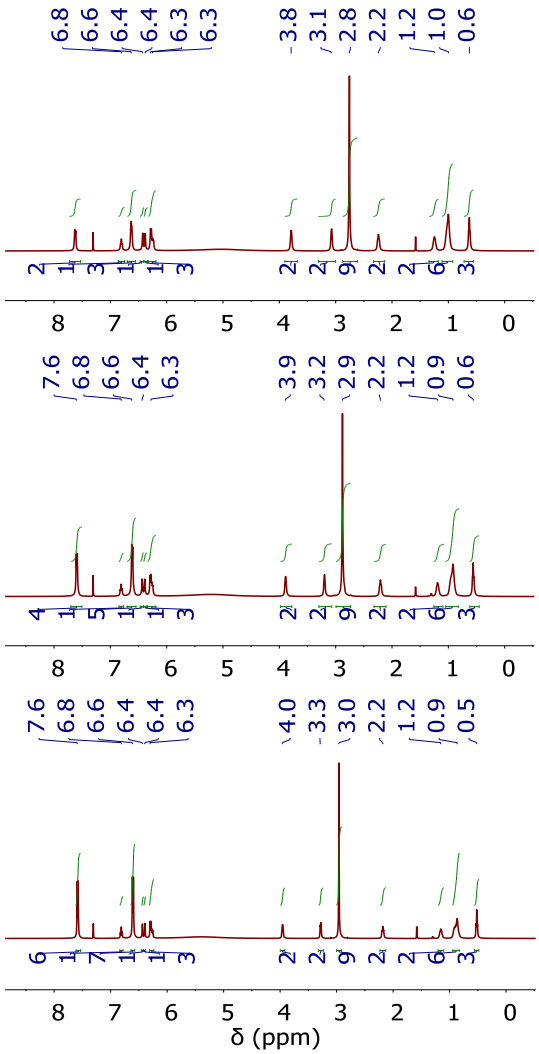

Figure S4 – ^{1}H NMR spectra – at room temperature and using deuterated $CDCl_3$ as the external reference – of the freeze-dried extracts obtained after thorough full washing of $N1_{GEL}$, $N2_{GEL}$ and $N3_{GEL}$.

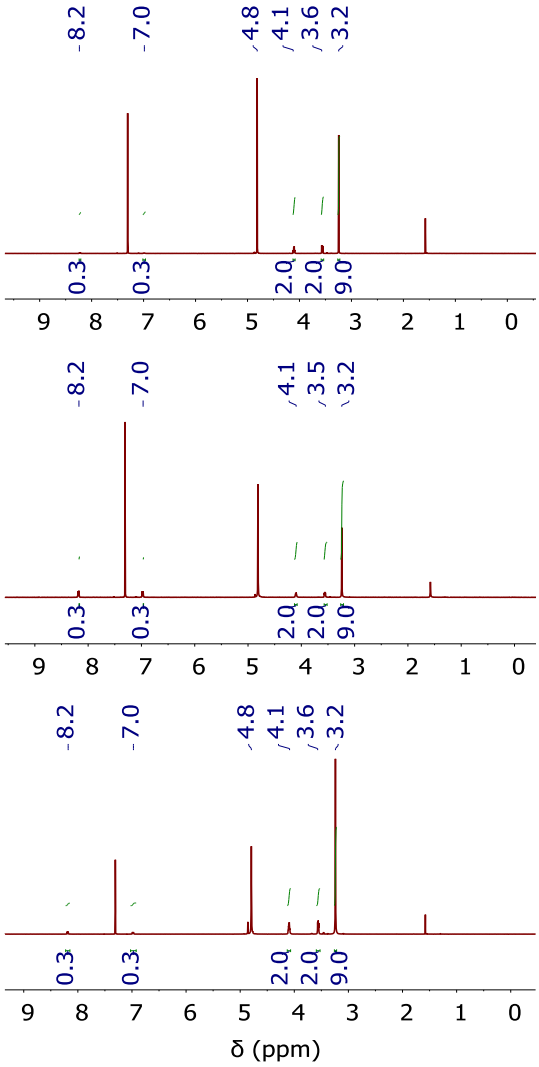

Figure S5 - ^{1}H NMR spectrum – at room temperature and using deuterated DMSO as the external reference – of a D_2O dilution of pNP-ChCl (25 wt%) with a molar ratio of 0.15:1.

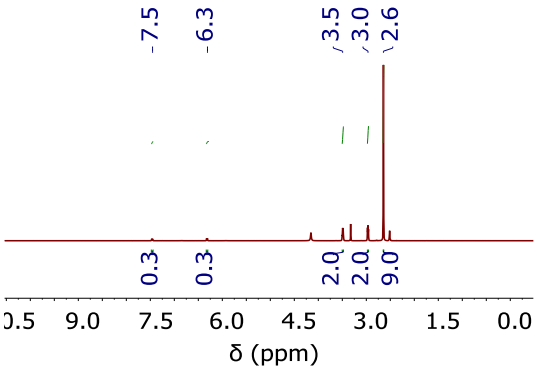

Figure S6 – XRD pattern of the residue – e.g. pNP-ChCl with a molar ratio of 0.15:1 as revealed by NMR – obtained from the thorough full washing of the resin resulting from co-condensation. Crystals were formed upon the evaporation of the water – 90 ºC overnight – used for washing.

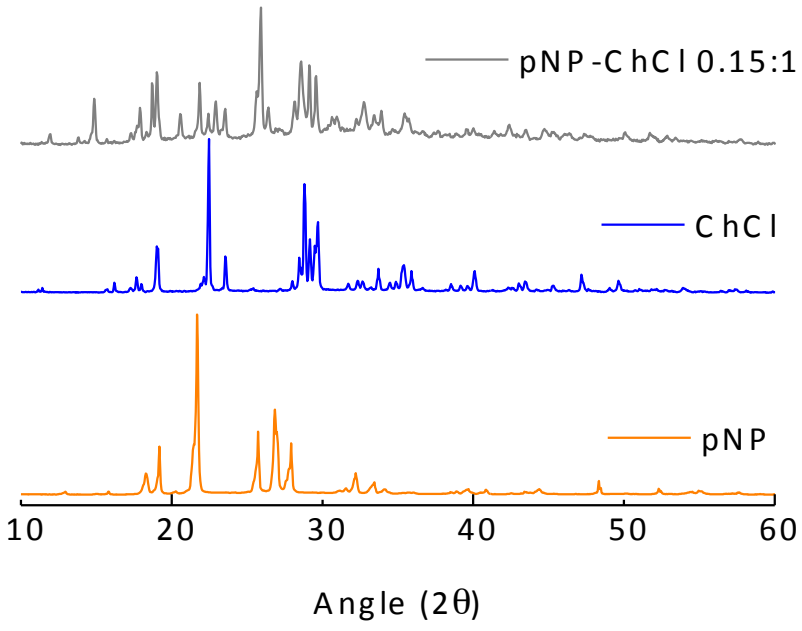

Figure S7 – SEM micrographs of (from left to right) $N1_{C@400}$, $N1_{C@500}$ and $N1_{C@600}$.

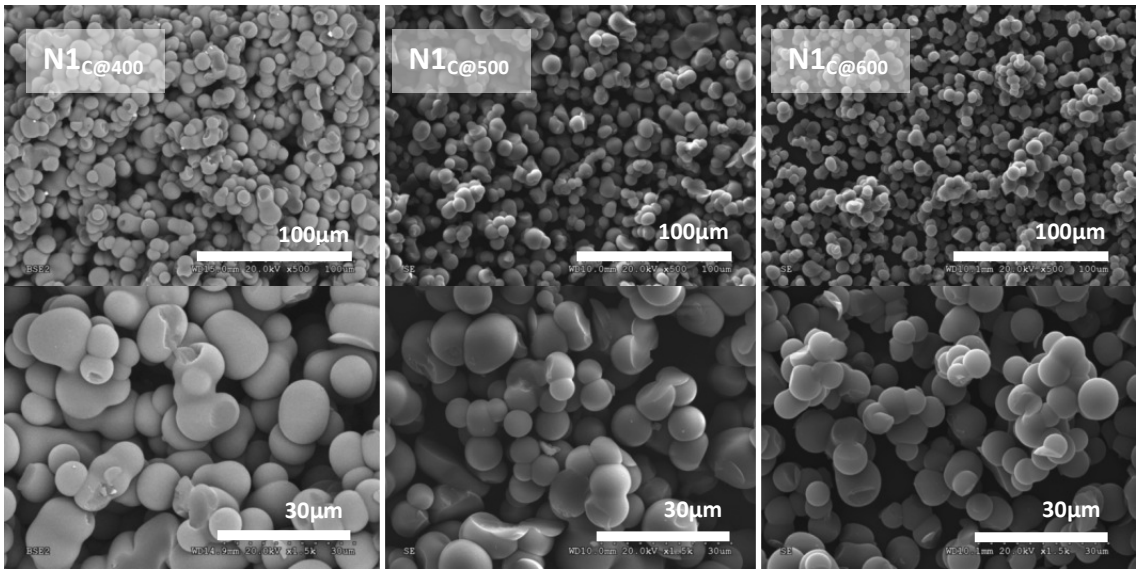

Figure S8 – SEM micrographs of (from left to right) $N2_{C@400}$, $N2_{C@500}$ and $N2_{C@600}$.

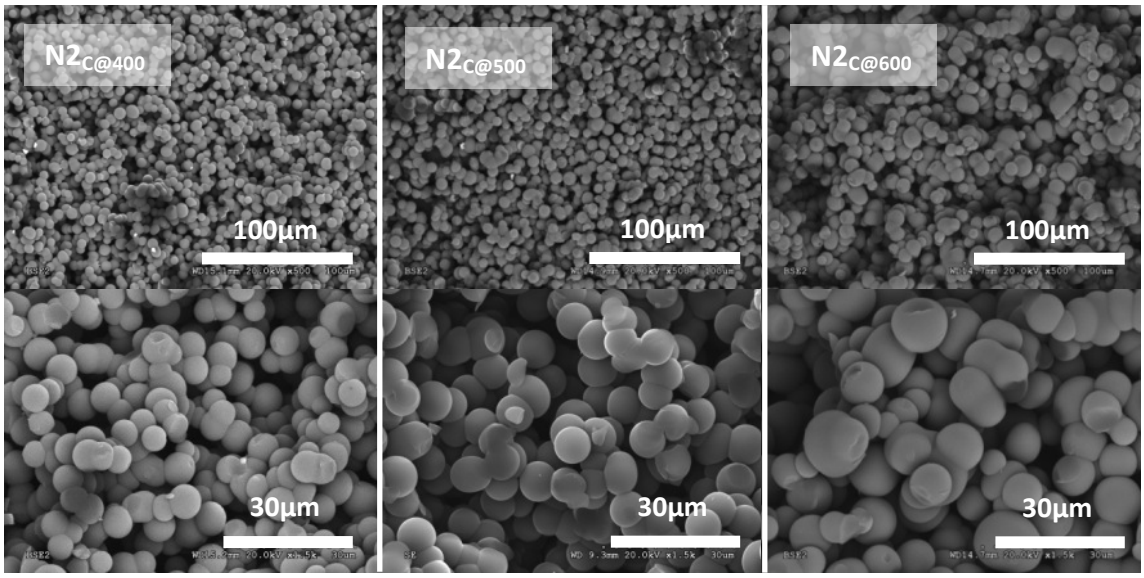

Figure S9 – SEM micrographs of (from left to right) $N3_{C@400}$, $N3_{C@500}$ and $N3_{C@600}$.