Supplementary Information of the manuscript

Resorcinol Based Deep Eutectic Solvents as Both Carbonaceous Precursors and Templating Agents in the Synthesis of Hierarchical Porous Carbon Monoliths

by

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Microporous specific surface area (S_{mic}) and external specific surface area (S_{ext}) were calculated by the t-plot (Figure S1),

$V_a\ (P/P°) = V_{a,mic} + k\ S_{ext}\ t\ (P/P°)$

where $V_{a,mic}$ is the adsorption in saturated micropores, S_{ext} the external surface area (surface area of pores larger than micropores) and t (P/P°) is the statistical thickness of the adsorbed layer calculated using the Halsey equation ($t = 0.354\ [-5/\ln(P/P°)]^{1/3}$, where t is given in nm) within the 0.354-0.5 nm range

Table S1

Sample	Slope (cm^3/g Å)	Y-intercept (cm^3/g)	Correlation Coefficient	S_{mic} (m^2/g)	S_{ext} (m^2/g)
C_{RUC1}	15.7	116.1	0.9837	333	243
C_{RUC2}	12.1	93.4	0.9824	267	188
C_{RC1}	17.1	85.5	0.9914	254	264
C_{RC2}	20.4	99.8	0.9910	296	316

Figure S1

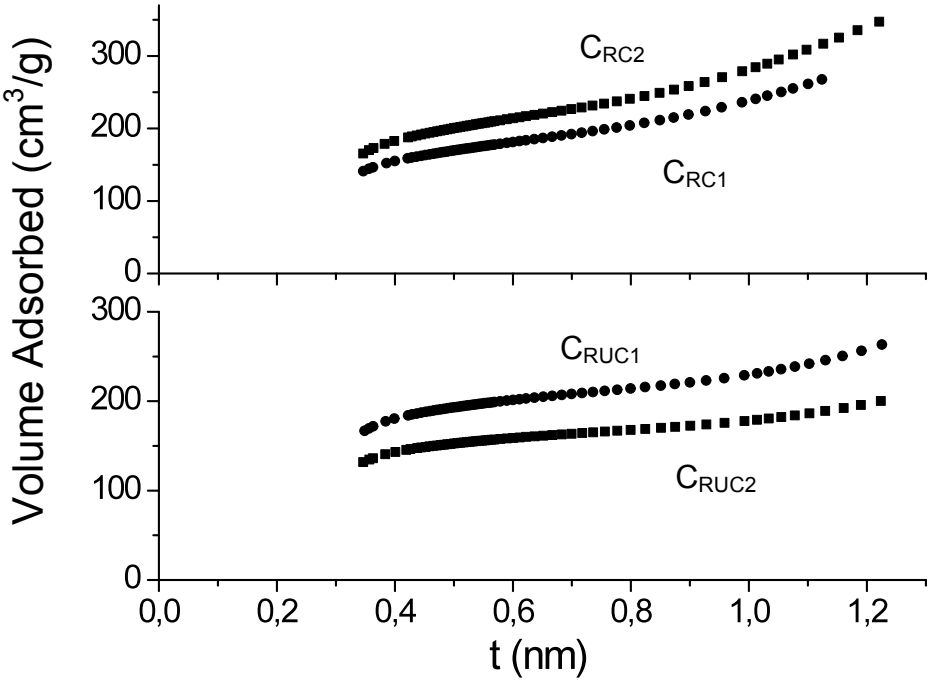


Table S2: ^{1}H-NMR spectroscopy data of non-diluted and diluted (in D_2O) RC1-DES and RC2-DES samples. DES content ranged from 85 to 56 up to 10 wt% in RC1-DES diluted samples and from 85 to 57 up to 10 wt% in RC2-DES diluted samples. Spectra were recorded using $CDCl_3$ as external reference. ^{1}H-NMR spectroscopy data of resorcinol (15 wt%) and choline chloride (12 wt%) in D_2O solution are also included for comparison.

Sample	δ (ppm)						
	HDO	Resorcinol = Benzene-1,3-diol			Choline chloride = 2-hydroxy-*N*,*N*,*N*-trimethylamonium chloride		
		C<u>H</u> in position 5	C<u>H</u>s in positions 4,6	C<u>H</u> in position 2	C<u>H</u>$_2$ in position 2	C<u>H</u>$_2$ in position 1	3×C<u>H</u>$_3$ in N
R	4.85	6.99 (1H)	6.34 (2H)	6.31 (1H)			
C	4.76				4.10 (2H)	3.56 (2H)	3.24 (9H)
RC1-DES		6.58 (4H)[a]	6.17 (8H)[a]	6.30 (4H)[a]	3.27 (2H)[a]	2.36 (2H)[a]	2.04 (9H)[a]
RC1-DES85		6.65 (4H)[a]	6.18 (8H)[a]	6.29 (4H)[a]	3.31 (2H)[a]	2.40 (2H)[a]	2.10 (9H)[a]
RC1-DES56	5.17	6.75 (4H)[a]	6.20 (8H)[a]	6.26 (4H)[a]	3.44 (2H)[a]	2.63 (2H)[a]	2.34 (9H)[a]
RC1-DES10	4.83	7.09 (4H)[a]	6.43 (8H)[a]	6.37 (4H)[a]	3.92 (2H)[a]	3.30 (2H)[a]	3.00 (9H)[a]
RC2-DES		6.59 (3.75H)[a]	6.17 (7.5H)[a]	6.31 (3.75H)[a]	3.29 (2H)[a]	2.42 (2H)[a]	2.10 (9H)[a]
RC2-DES85		6.66 (3.75H)[a]	6.20 (7.5H)[a]	6.32 (3.75H)[a]	3.33 (2H)[a]	2.43 (2H)[a]	2.12 (9H)[a]
RC2-DES57	5.13	6.77 (3.75H)[a]	6.22 (7.5H)[a]	6.26 (3.75H)[a]	3.46 (2H)[a]	2.66 (2H)[a]	2.37 (9H)[a]
RC2-DES10	4.83	7.10 (3.75H)[a]	6.44 (7.5H)[a]	6.38 (3.75H)[a]	3.93 (2H)[a]	3.31 (2H)[a]	3.01 (9H)[a]

[a] The molar ratio of resorcinol to choline chloride was 4:1 in RC1-DES and 3.75:1 in RC2-DES.

Table S3: ^{1}H-NMR spectroscopy data of non-diluted and diluted (in D_2O) RUC1-DES and RUC2-DES samples. DES content ranged from 85 to 62 up to 10 wt% in RUC1-DES diluted samples and from 85 to 63 up to 10 wt% in RUC2-DES diluted samples. Spectra were recorded using $CDCl_3$ as external reference. ^{1}H-NMR spectroscopy data of resorcinol (15 wt%) and choline chloride (12 wt%) in D_2O solution are also included for comparison.

Sample	δ (ppm)						
	HDO	Resorcinol = Benzene-1,3-diol			Choline chloride = 2-hydroxy-*N*,*N*,*N*-trimethylamonium chloride		
		C<u>H</u> in position 5	C<u>H</u>s in positions 4,6	C<u>H</u> in position 2	C<u>H</u>$_2$ in position 2	C<u>H</u>$_2$ in position 1	3×C<u>H</u>$_3$ in N
R	4.85	6.99 (1H)	6.34 (2H)	6.31 (1H)			
C	4.76				4.10 (2H)	3.56 (2H)	3.24 (9H)
RUC1-DES		6.68 (3.5H)[a]	6.20 (7H)[a]	6.33 (3.5H)[a]	3.37 (2H)[a]	2.51 (2H)[a]	2.21 (9H)[a]
RUC1-DES85	6.05	6.70 (3.5H)[a]	6.19 (7H)[a]	6.29 (3.5H)[a]	3.47 (2H)[a]	2.66 (2H)[a]	2.37 (9H)[a]
RUC1-DES62	5.19	6.82 (3.5H)[a]	6.24 (7H)[a]	6.29 (3.5H)[a]	3.53 (2H)[a]	2.75 (2H)[a]	2.47 (9H)[a]
RUC1-DES10	4.82	7.12 (3.5H)[a]	6.44 (7H)[a]	6.40 (3.5H)[a]	3.96 (2H)[a]	3.36 (2H)[a]	3.06 (9H)[a]
RUC2-DES		6.72 (3H)[a]	6.23 (6H)[a]	6.36 (3H)[a]	3.42 (2H)[a]	2.59 (2H)[a]	2.28 (9H)[a]
RUC2-DES85	6.12	6.73 (3H)[a]	6.21 (6H)[a]	6.31 (3H)[a]	3.45 (2H)[a]	2.64 (2H)[a]	2.34 (9H)[a]
RUC2-DES63	5.17	6.83 (3H)[a]	6.26 (6H)[a]	6.29 (3H)[a]	3.56 (2H)[a]	2.80 (2H)[a]	2.50 (9H)[a]
RUC2-DES10	4.82	7.12 (3H)[a]	6.45 (6H)[a]	6.40 (3H)[a]	3.95 (2H)[a]	3.36 (2H)[a]	3.06 (9H)[a]

[a] The molar ratio of resorcinol to choline chloride was 3.5:1 in RUC1-DES and 3:1 in RUC2-DES.

Figure S2: ^{1}H NMR spectra of D_2O dilutions of (from top to bottom) RC1-DES, RC2-DES, RUC1-DES and RUC2-DES. D_2O dilutions were prepared by adding 56 mg of RC1-DES to 44 mg of D_2O, 57 mg of RC2-DES to 43 mg of D_2O, 62 mg of RUC1-DES to 38 mg of D_2O and 63 mg of RUC2-DES to 37 mg of D_2O dilution.

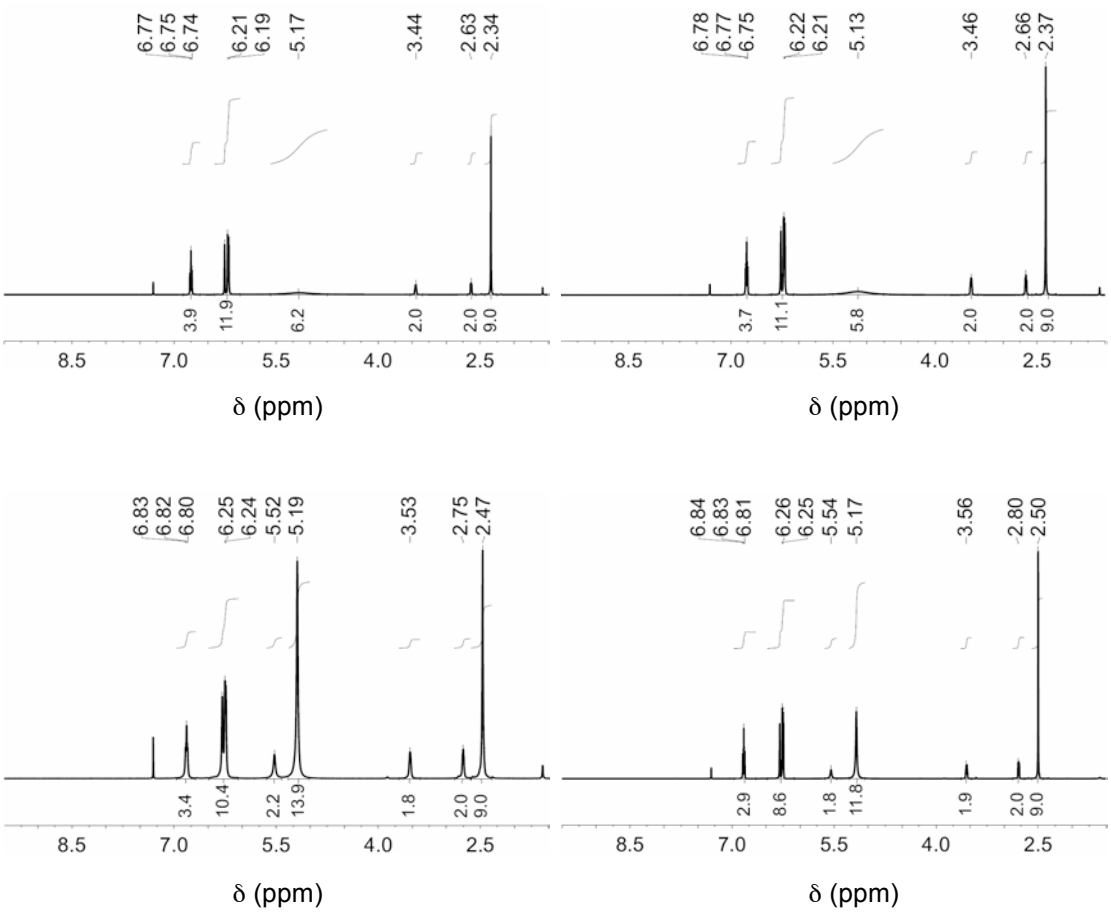


Figure S3: Adsorption (solid symbols) and desorption (open symbols) nitrogen isotherms of $RF_{RC1\text{-}DES}$ (squares), $RF_{RC2\text{-}DES}$ (circles), $RF_{RUC1\text{-}DES}$ (inverted triangles) and $RF_{RUC2\text{-}DES}$ (triangles) gels.

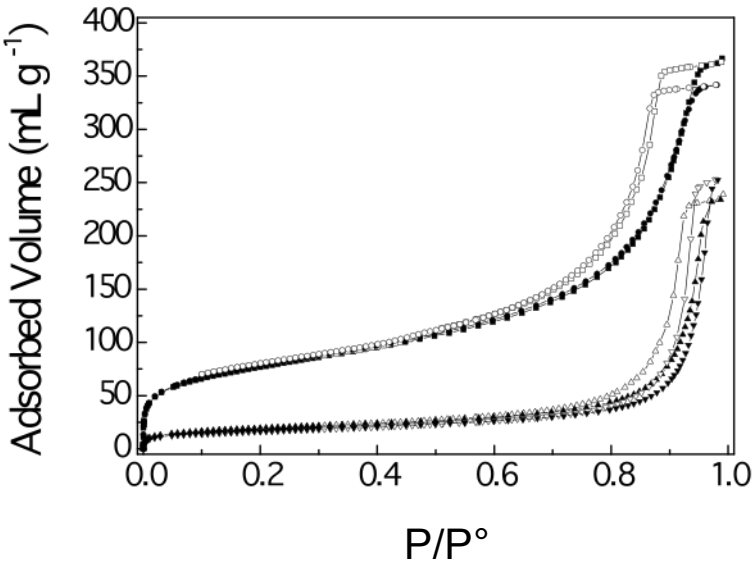


Figure S4: ^{1}H NMR spectra of the residue recovered after washing $RF_{RC1\text{-}DES}$ and $RF_{RC2\text{-}DES}$ (left and right in top panel, respectively), and $RF_{RUC1\text{-}DES}$ and $RF_{RUC2\text{-}DES}$ (left and right in bottom panel, respectively) gels and freeze-drying. Spectra were recorded using D_2O as solvent and $CDCl_3$ as external reference. ^{1}H NMR spectra did not allow to determine the urea recovered because the protons were exchangeable with D_2O and convoluted together with residual water.

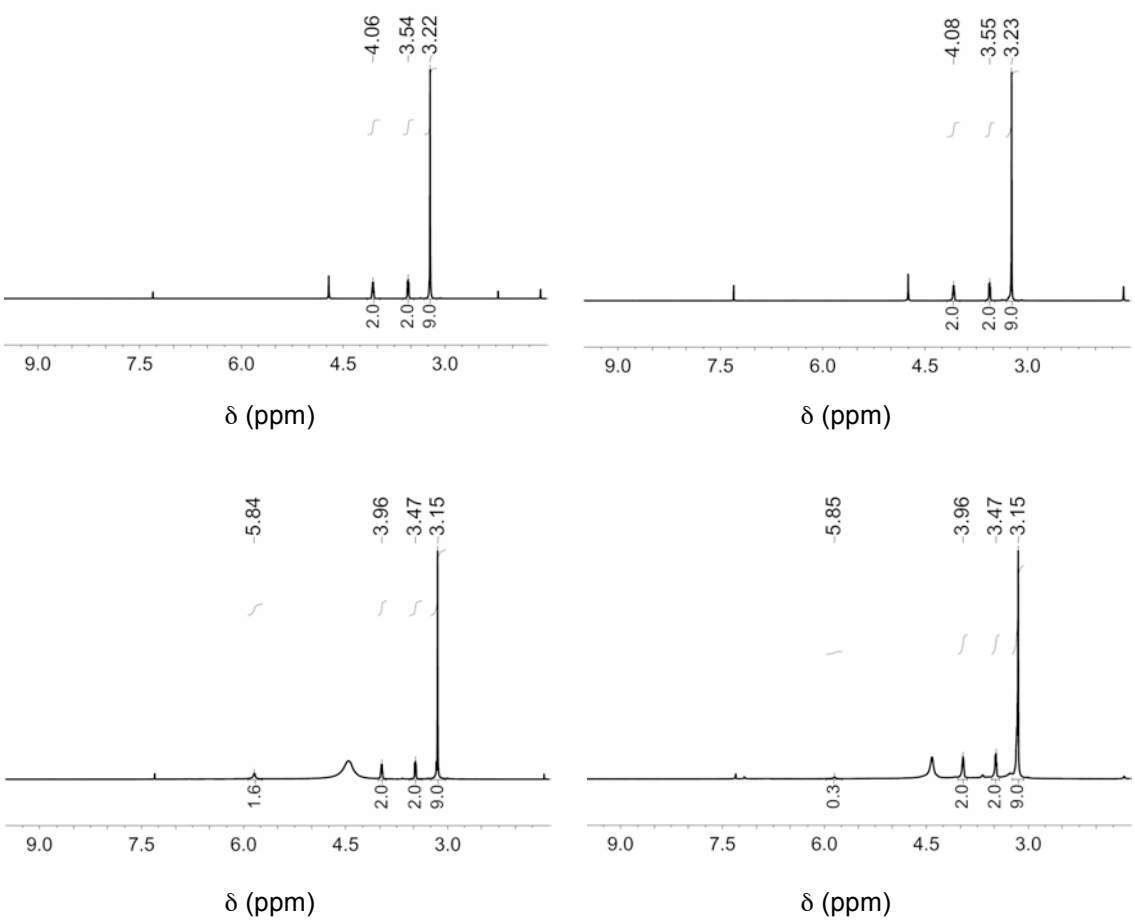
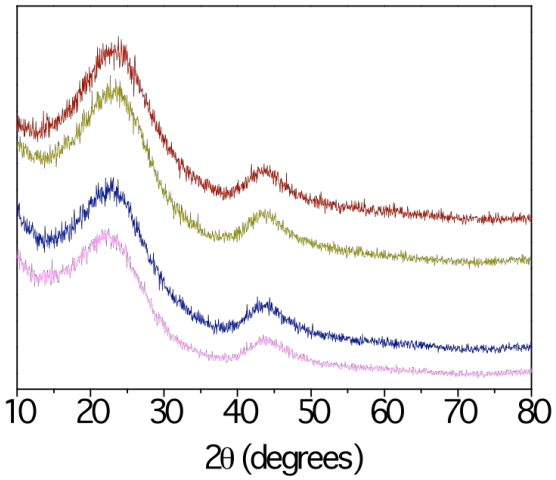


Figure S5: XRD (top) and Raman spectra (bottom) of $C_{RC1\text{-}DES}$ (blue line), $C_{RC2\text{-}DES}$ (magenta line), $C_{RUC1\text{-}DES}$ (red line) and $C_{RUC2\text{-}DES}$ (dark yellow line).



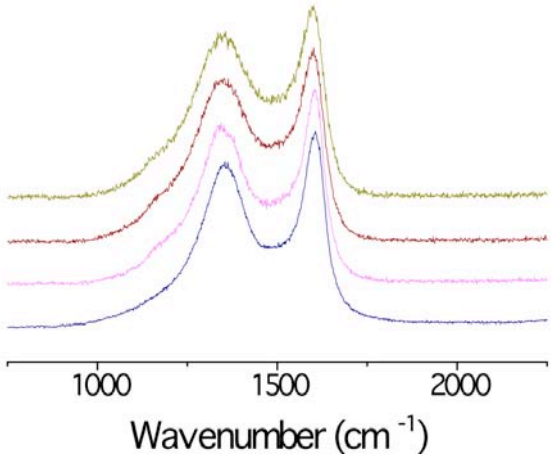


Figure S6: EDX analysis of of $C_{RC1\text{-}DES}$. EDX analyses of $C_{RC2\text{-}DES}$, $C_{RUC1\text{-}DES}$ and $C_{RUC2\text{-}DES}$ are not shown but they did not exhibit significant differences.

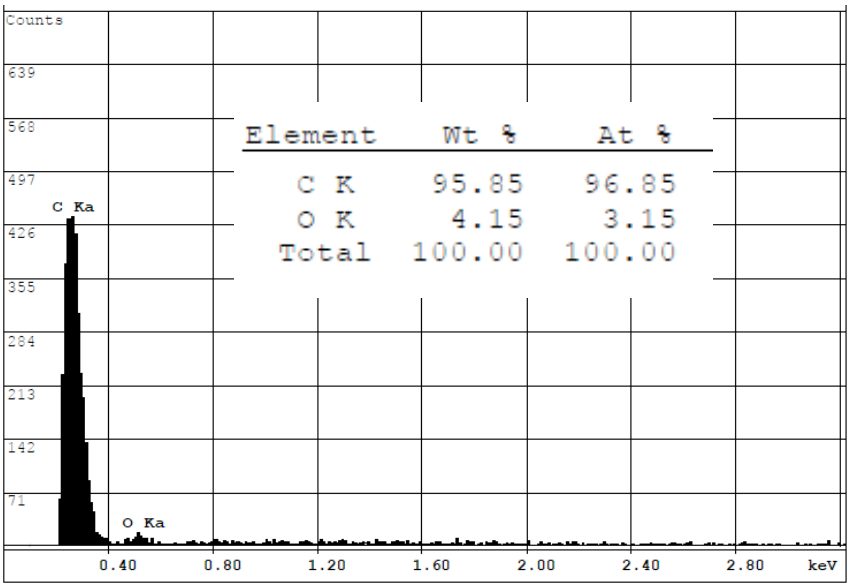


Figure S7: Top panel: Adsorption (solid symbols) and desorption (open symbols) branches of nitrogen isotherms of $C_{RC1\text{-}DES}$ (squares) and $C_{RUC2\text{-}DES}$ (triangles). **Bottom panel:** Pore size distributions of $C_{RC1\text{-}DES}$ (squares) and $C_{RUC2\text{-}DES}$ (triangles).

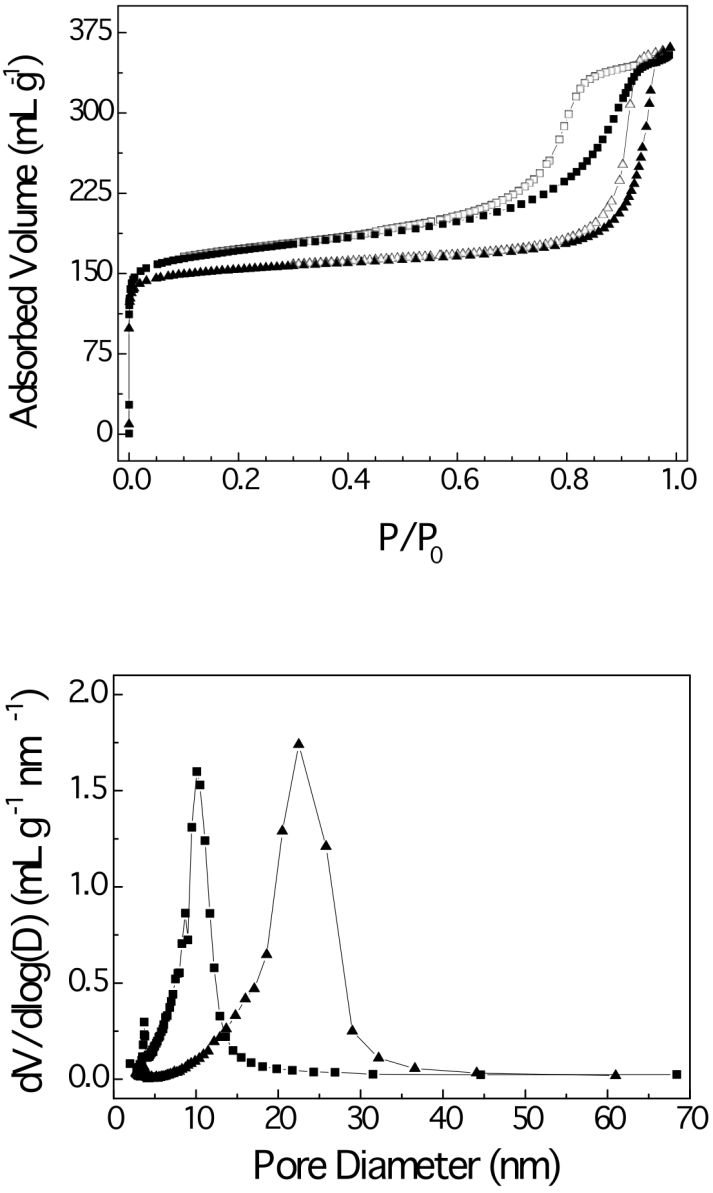


Figure S8: SEM micrographs of RF gels (prepared by resorcinol-formaldehyde polycondensation in presence of sodium carbonate) in absence of choline chloride without (left, bar is 2 μm) and with (right, bar is 4 μm) urea.