Electronic Supplementary Information

Bioactive transparent films based on polysaccharides and cholinium carboxylate ionic liquids

Liliana C. Tomé,[a,b] Nuno H. C. S. Silva,[a,b] Hugo R. Soares,[a,c] Ana S. Coroadinha,[a,c] Patrizia Sadocco,[d] Isabel M. Marrucho,[a] and Carmen S. R. Freire[b*]

[a]*Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. República, 2780-157 Oeiras, Portugal.*

[b]*CICECO, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.*

[c]*iBET, Instituto de Biologia Experimental e Tecnológica, Apartado 12, 2781-901 Oeiras, Portugal.*

[d]*INNOVHUB – Divisione Carta, Piazza Leonardo Da Vinci, 16, 20133 Milan, Italy.*

[*]*Corresponding author: cfreire@ua.pt*

Table S1- Minor Inhibition Concentration (MIC) values of a set of cholinium-based ILs against several microbial strains.

Ionic liquid	**MIC *S. aureus* (mg/ml)**	**MIC *K. pneumoniae* (mg/ml)**	**MIC *E. coli* (mg/ml)**	**MIC *C. albicans* (mg/ml)**	**MIC *B. subtilis* spores (mg/ml)**
[Ch][DHph]	> 15.82	> 15.82	n.d.	> 15.82	n.d.
[Ch][Lac]	> 12.72	> 12.72	n.d.	> 12.72	n.d.
[Ch][Gly]	5.8	5.8	5.8	> 11.5	5.8
[Ch][Sal]	2.65	10.58	10.52	> 13.4	5.26
[Ch][Hex]	> 12.45	> 12.45	n.d.	> 12.45	n.d.
[Ch][Cit]	> 14.46	> 14.46	n.d.	14.46	n.d.
[Ch][Aze]	> 10.0	10.0	10.0	5	10.0
[Ch][Non]	5.07	> 5.07	n.d.	0.1	n.d.
[Ch][Dod]	2.8 (*)	11 (*)	n.d.	2.8 (*)	n.d.

n.d.- not determined
" > " is higher than. So it means that to see the real MIC concentration we should further increase the analysed concentration of the sample.
* = some turbidity was visible in the sample at the beginning of the test, probably due to precipitation when the bacteria broth was added to the IL sample solution. Therefore, the determination of bacteria inhibition was carried out by plating the final suspension on agar growing media.

Table S2- Thermal properties of the cholinium carboxylate ionic liquids used in this study to prepare the bioactive transparent films: onset (T_{onset}), decomposition (T_{dec}), melting (T_m) and glass transition (T_g) temperatures.

Ionic liquid	T_{onset} (ºC) [a]	T_{dec} (ºC) [a]	T_m (ºC)	T_g (ºC)
[Ch][Cit] [b]	165	215	103	n.d.[d]
[Ch][Hex] [c]	106	169	52	n.d.[d]

[a] T_{onset} and T_{dec} defined as the temperatures at which the baseline slope changes during the heating, and at 50% weight loss, respectively. Please note that these are from scanning TGA, and do not represent isothermal stabilities.
[b] Values taken from Mourão *et al*.[1]
[c] Values taken from Petkovic *et al.*[2]
[d] n.d.: not detected.

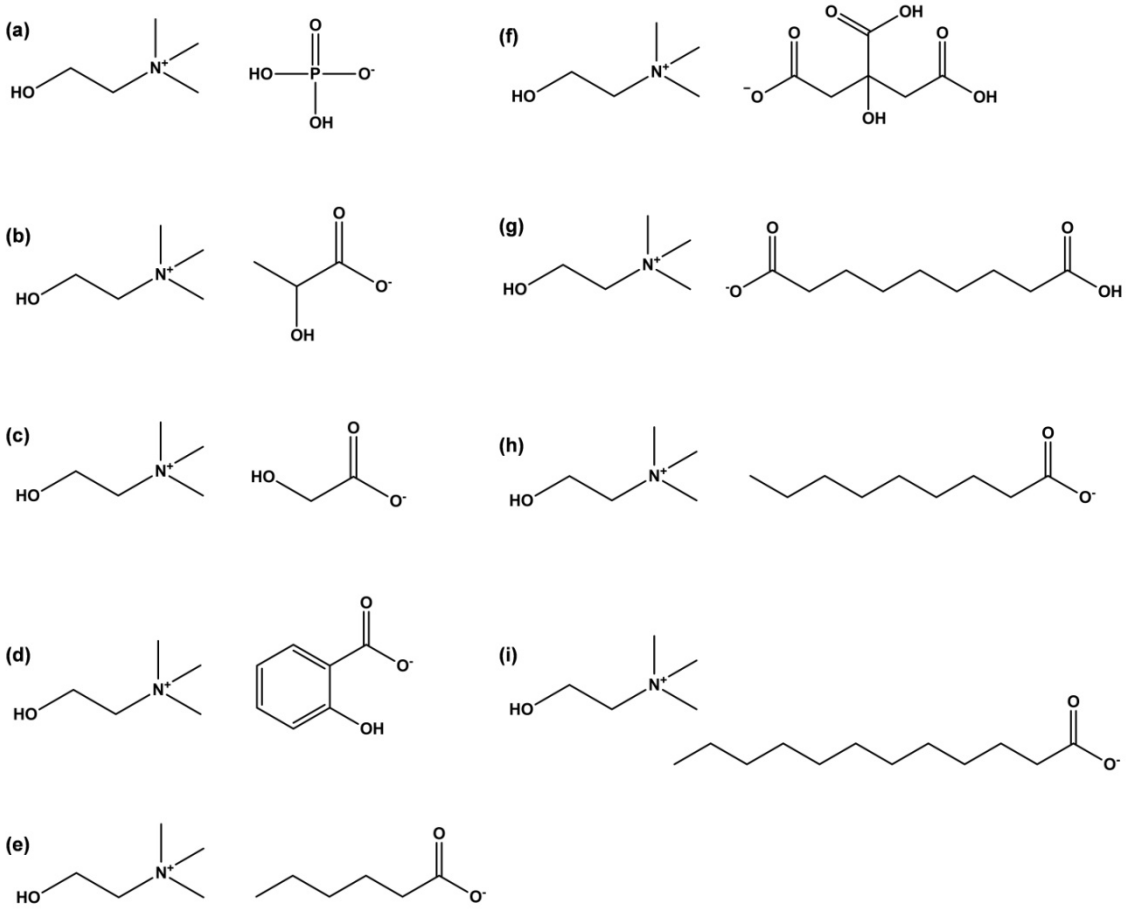


Figure S1 – Chemical structures of cholinium carboxylate ionic liquids used in the preliminary assessment of the MIC (Minor Inhibition Concentration) values: (a) cholinium dihydrogenphosphate ([Ch][DHph]), (b) cholinium lactate ([Ch][Lac]), (c) cholinium glycolate ([Ch][Gly]), (d) cholinium salicylate ([Ch][Sal]), (e) cholinium hexanoate ([Ch][Hex]), (f) cholinium citrate ([Ch][Cit]), (g) cholinium azelate ([Ch][Aze]), (h) cholinium nonanoate ([Ch][Non]), and (i) cholinium dodecanoate ([Ch][Dod]).

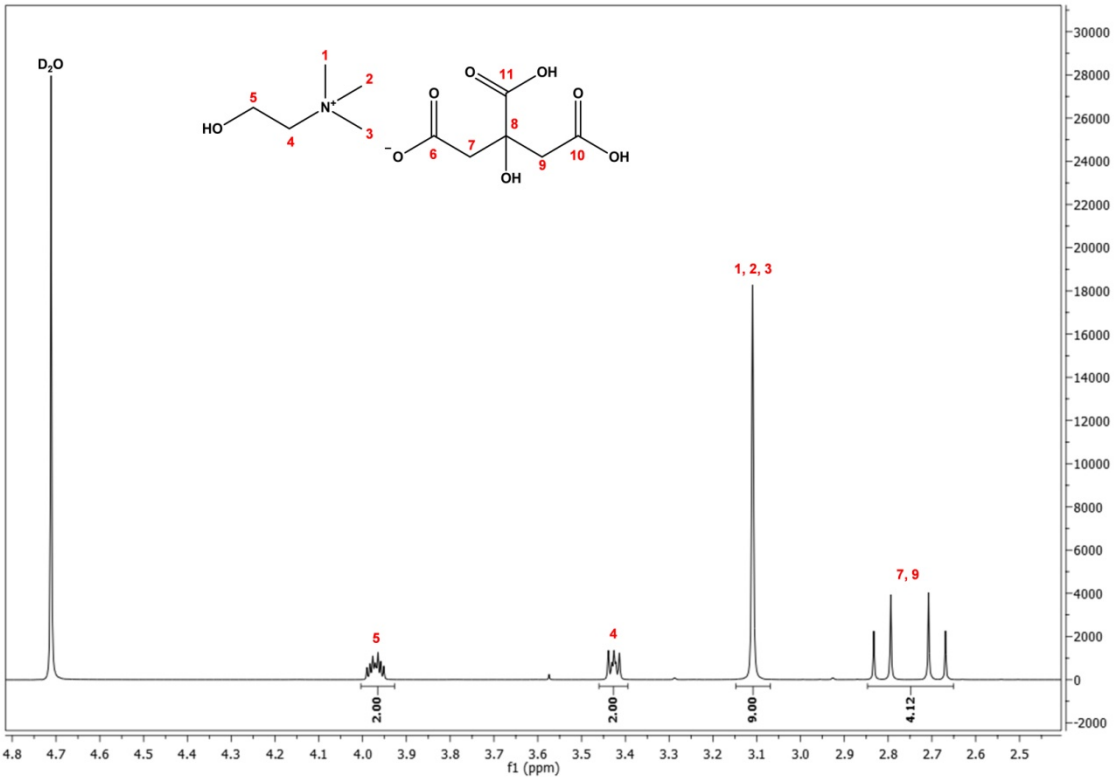


Figure S2- ^{1}H-NMR spectrum of [Ch][Cit] in D_2O.

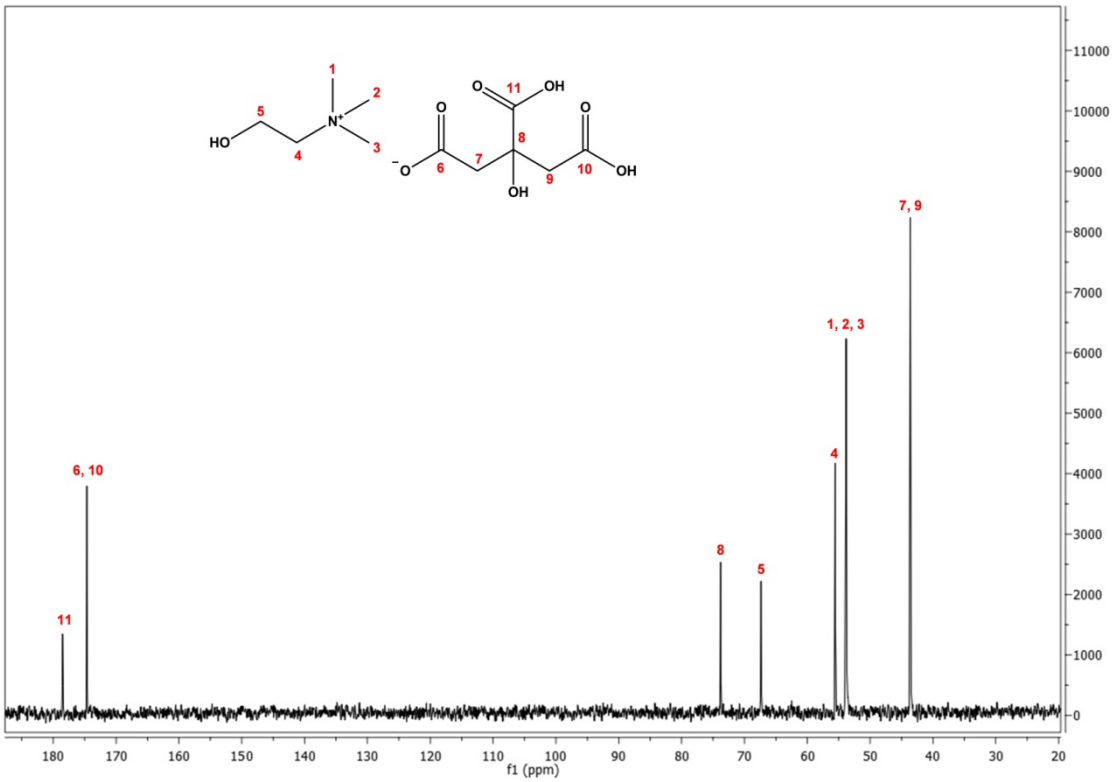


Figure S3- ^{13}C-NMR spectrum of [Ch][Cit] in D_2O.

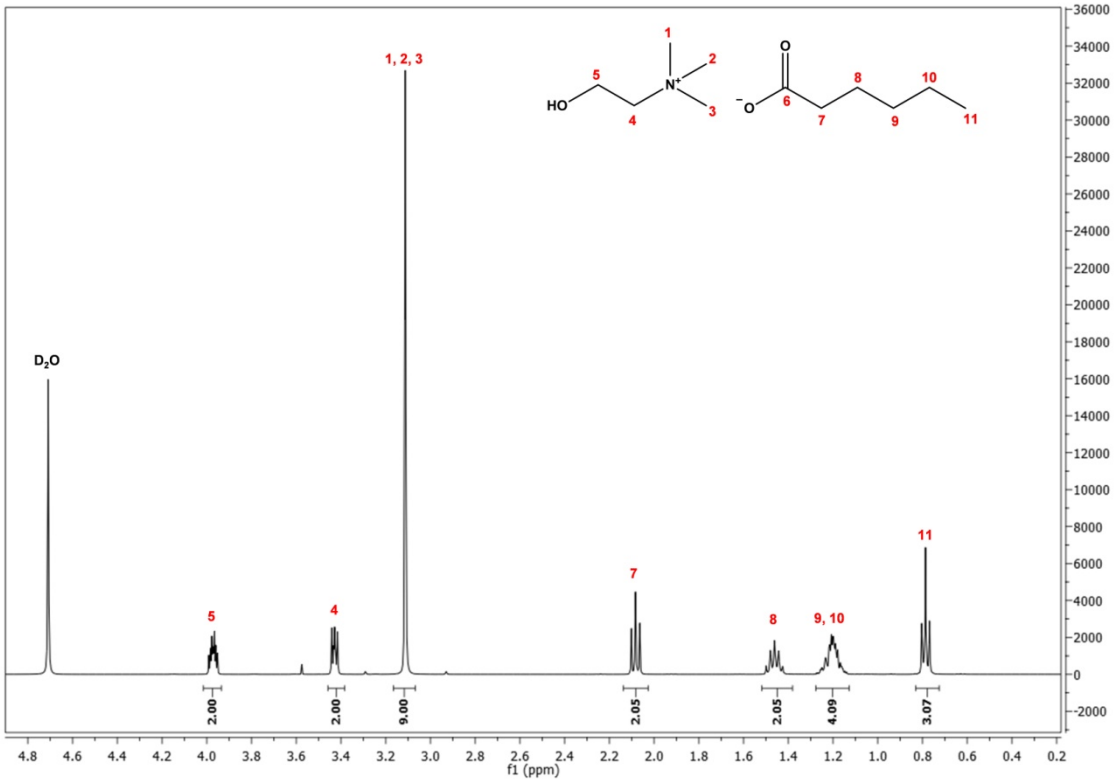


Figure S4- ^{1}H-NMR spectrum of [Ch][Hex] in D_2O.

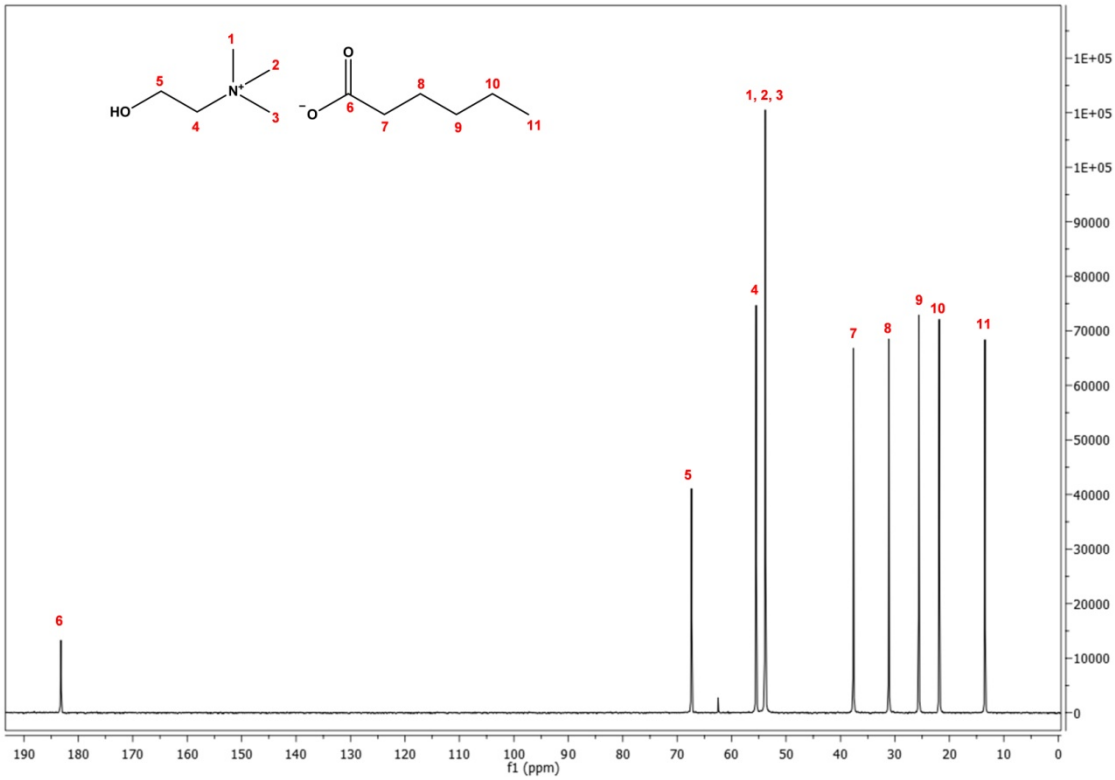
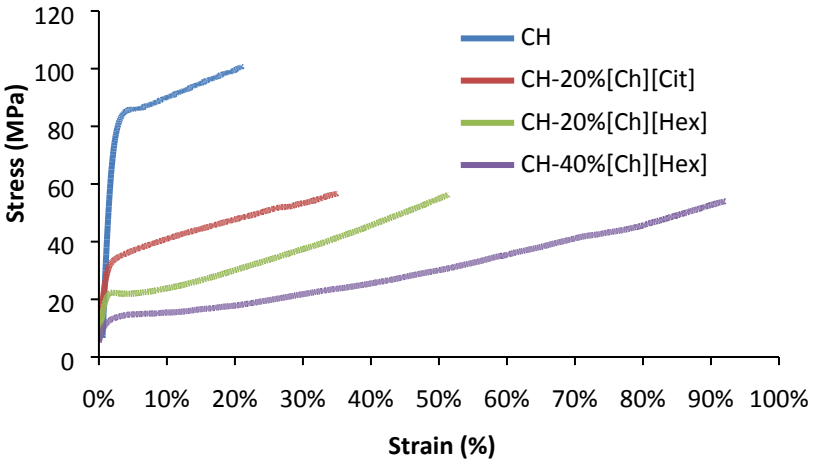
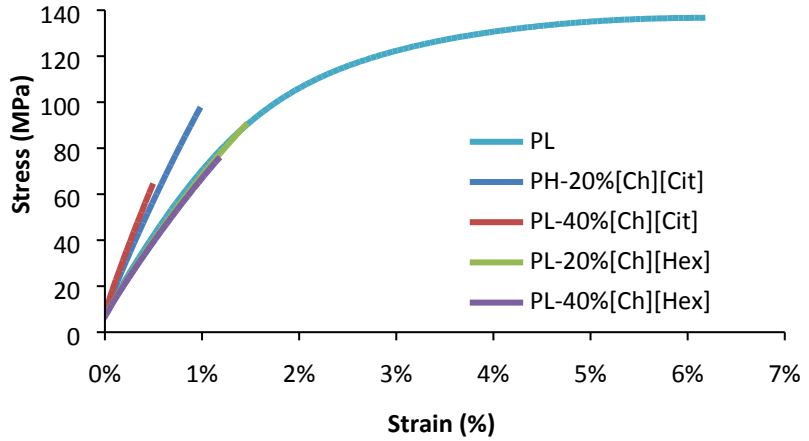


Figure S5- ^{13}C-NMR spectrum of [Ch][Hex] in D_2O.

(A)


120
100
80
60
40
20
0
Stress (MPa)
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Strain (%)
CH
CH-20%[Ch][Cit]
CH-20%[Ch][Hex]
CH-40%[Ch][Hex]


140
120
100
80
60
40
20
0
Stress (MPa)
0%
1%
2%
3%
4%
5%
6%
7%
Strain (%)
PL
PH-20%[Ch][Cit]
PL-40%[Ch][Cit]
PL-20%[Ch][Hex]
PL-40%[Ch][Hex]

(B)

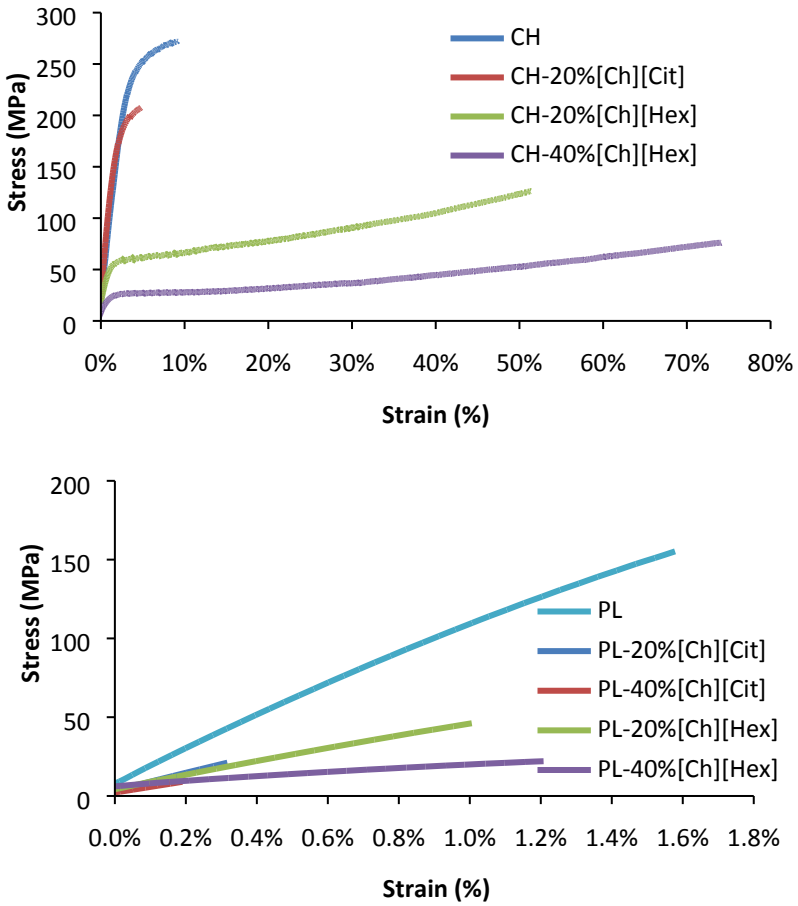
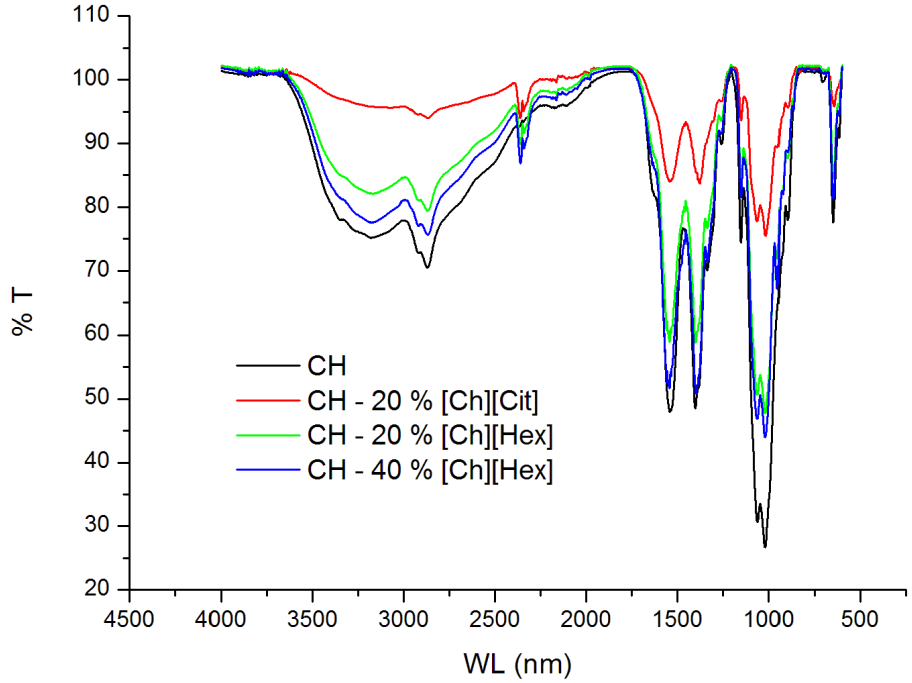
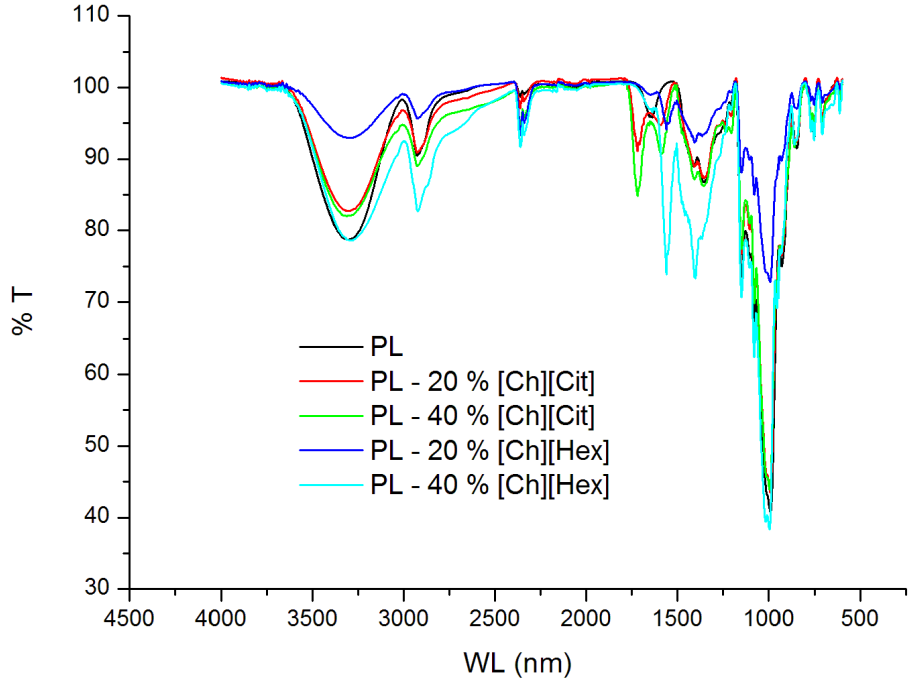


Figure S6- Tensile stress-strain plots of the obtained film (A) conditioned at 50% relative humidity and (B) vacuum dried and stored in a desiccator with phosphorous pentoxide.

(A)


% T
WL (nm)
CH
CH - 20 % [Ch][Cit]
CH - 20 % [Ch][Hex]
CH - 40 % [Ch][Hex]


% T
WL (nm)
PL
PL - 20 % [Ch][Cit]
PL - 40 % [Ch][Cit]
PL - 20 % [Ch][Hex]
PL - 40 % [Ch][Hex]

(B)

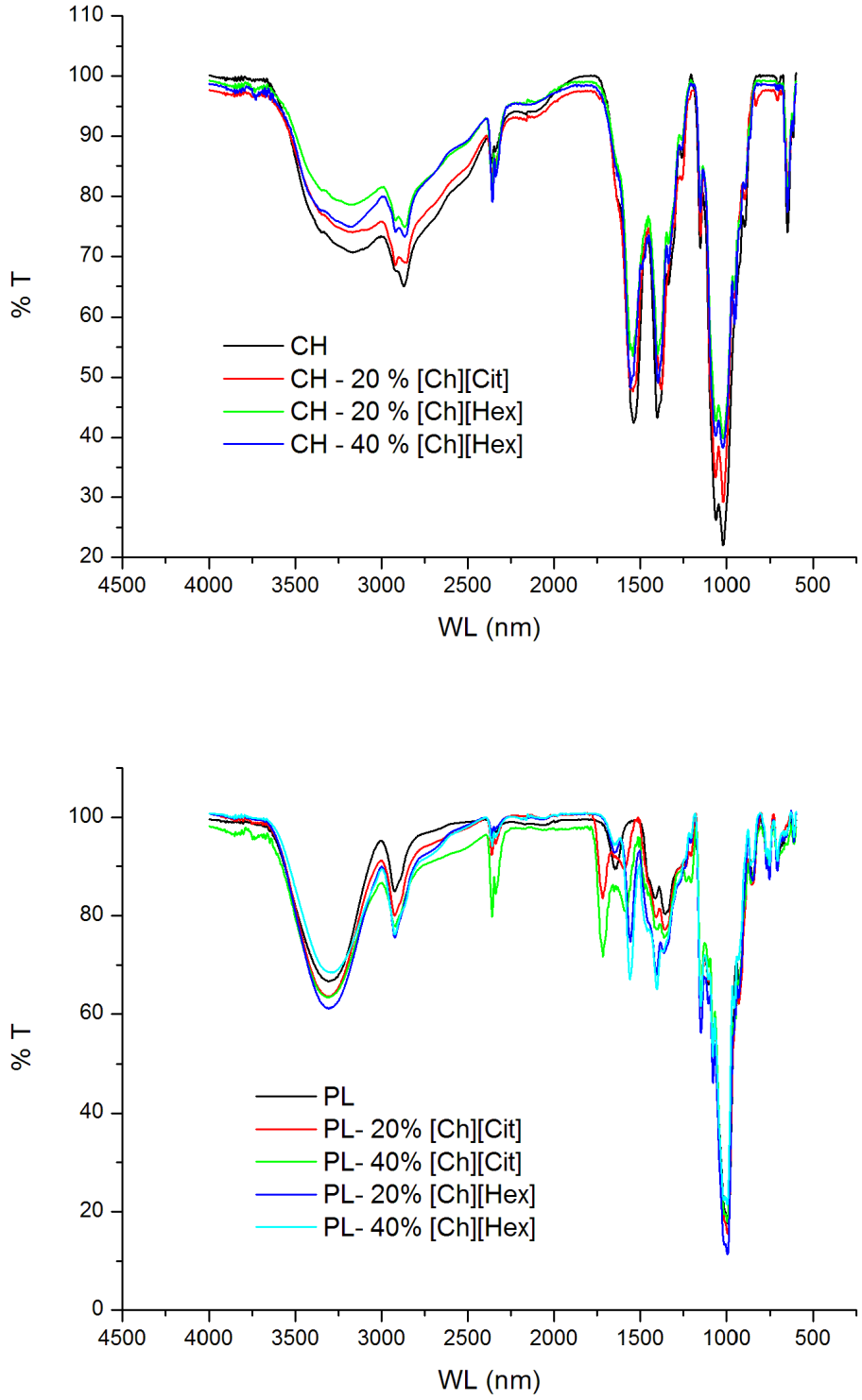


Figure S7-. FTIR spectra of the obtained films (A) conditioned at 50% relative humidity and (B) vacuum dried and stored in a desiccator with phosphorous pentoxide.

References:

1. T. Mourão, L. C. Tomé, C. Florindo, L. P. N. Rebelo and I. M. Marrucho, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2426-2434.
2. M. Petkovic, J. L. Ferguson, H. Q. N. Gunaratne, R. Ferreira, M. C. Leitao, K. R. Seddon, L. P. N. Rebelo and C. S. Pereira, *Green Chem.*, 2010, **12**, 643-649.