Supplementary Materials

Lignosulfonate-Based Conducting Flexible Polymeric Membranes for Liquid Sensing Applications

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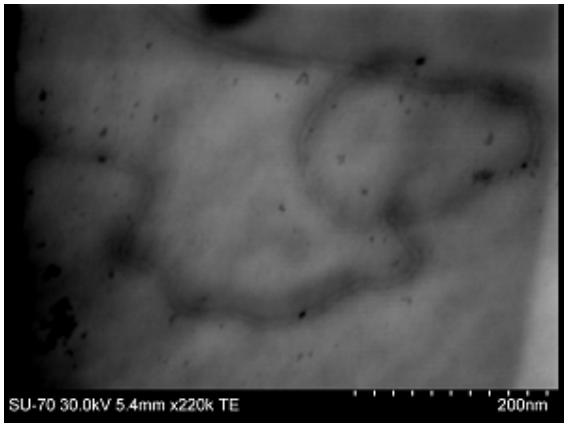


Figure S1. TEM image of the LS-based PU film doped with 1% w/w MWCNTs.

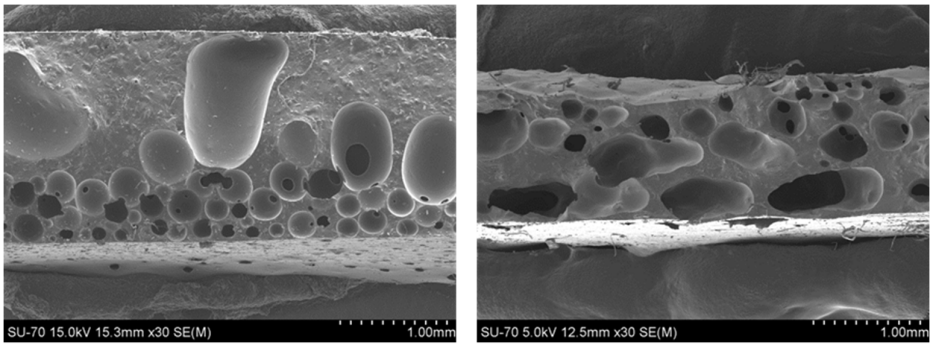


Figure S2. SEM images of the cross-section of LS-based PU films (a) undoped and (b) doped with 1% w/w of MWCNTs.

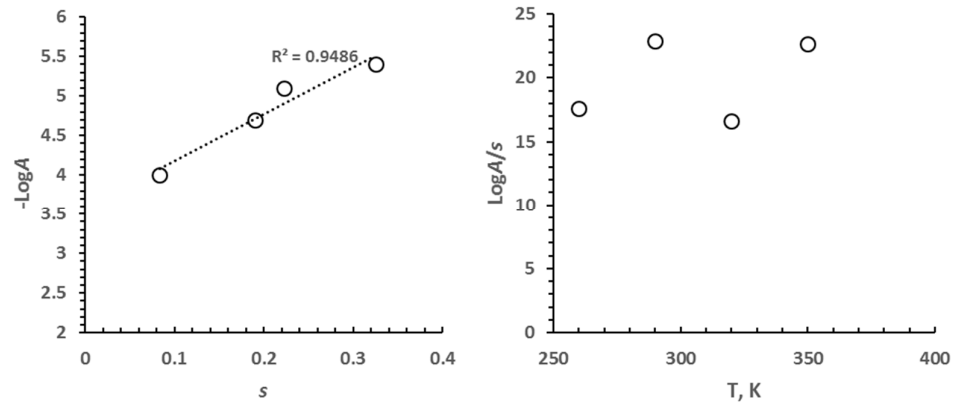


Figure S3. -Log*A* versus *s* and Log*A*/*s* versus *T* plots of LS-based PU film doped with 1% w/w of MWCNTs.

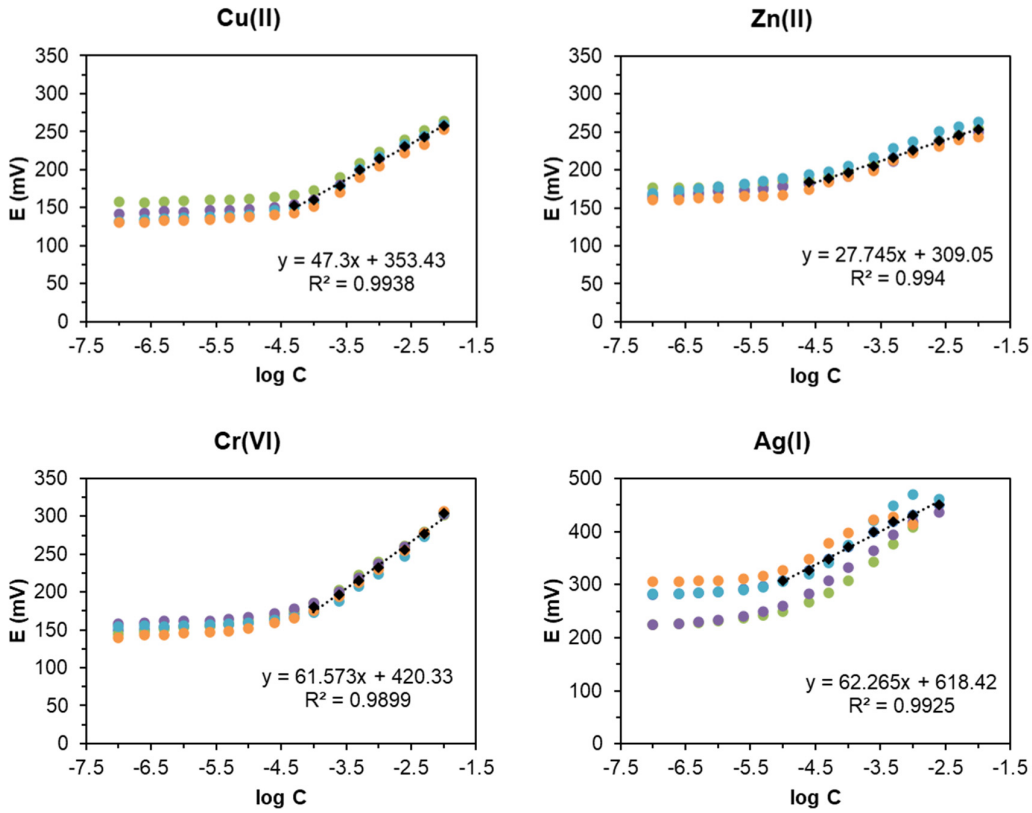
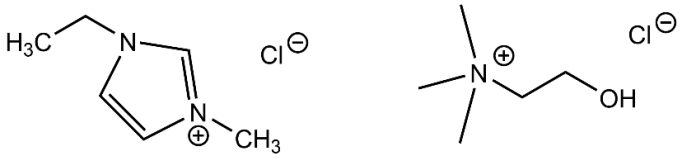


Figure S4. -Calibration curves LS-based PU composite membrane sensor doped with 1% w/w MWCNTs towards four selected cations (four calibration curves – coloured dots – for each cation and the re-spective average response slope with linear trendline – black).



(**a**) (**b**)

Figure S5. Chemical structure of the ILs studied: (a) 1-ethyl-3-methylimidazolium chloride and (b) choline chlorid**e.**

Table S1. Assignment of bands in FTIR-ATR spectra of purified LS from eucalypt thick sulphite pulping liquor and LS-based PU undoped (LS-PU) and doped with 1% w/w MWCNTs (LS-PU-CNT) [1,2,11,3–10].

LS (cm^{-1})	**LS-PU/ LS-PU-CNT (cm^{-1})**	**Assignment**
3356	3298	O-H stretching, H-bonded
2940/2848	2966/2916/ 2860	C-H stretching in methyl, methylene and O-CH_3 groups
-	1722	C=O stretching (urethane group)
1604		Aryl ring stretching, symmetric
-	1530	N-H bending (secondary amine in urethane group)
1510		Aryl ring stretching, asymmetric
1460		C-H bending in O-CH_3 groups, asymmetric
1426		Aromatic skeletal vibration combined with C-H bending in O-CH_3 groups, asymmetric in-plane
1330		C_{aryl}-O vibrations, SO_3H groups (S=O stretching vibration)
-	1220	C-N stretching (urethane group)
1210		C_{aryl}-O vibrations, C-C, C-O, C=O stretching, metallic salt of SO_3H groups (S=O stretching vibration)
1154		Aromatic C-H in-plane deformation, SO_3H groups
1112		Aromatic C-H in-plane deformation, C-O-C groups, metallic salt of SO_3H groups
-	1086	C-O-C vibration (polyether bridges)
1034		Aromatic C-H in-plane deformation related with C-O, C-C stretching and C-OH stretching, SO_3H groups, C_{alkyl}-O ether vibrations (O-CH_3 and β–O-4)
914/818		C-H deformation out-of-plane, aromatic ring
650/630		SO_3H groups (S-O stretching vibration/C-S stretching vibration)
630		SO_3H groups (C-S stretching vibration)

Table S2. Sensitivity characteristics of LS-based PU membrane sensor doped with 1% *w/w* MWCNTs at pH 7.

Cation	Slope (mV/decade)	Detection limit (M)	Linear range (M)
Cu(II)	47.3 ± 2.1	4.6×10^{-5}	5.0×10^{-5}–1×10^{-2}
Cd(II)	20.3 ± 2.5	4.2×10^{-6}	5.0×10^{-6}–1×10^{-2}
Zn(II)	27.2 ± 0.7	1.2×10^{-5}	1.5×10^{-5}–1×10^{-2}
Hg(II)	40.9 ± 5.7	3.3×10^{-5}	5.0×10^{-5}–1×10^{-2}
Cr(VI)	61.6 ± 3.6	6.1×10^{-5}	1.0×10^{-4}–1×10^{-2}
Cr(III)	68.3 ± 1.8	6.2×10^{-5}	1.0×10^{-4}–1×10^{-2}
Ag(I)	62.1 ± 15.5	4.9×10^{-6}	1.0×10^{-5}–2.2×10^{-3}

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