Supporting Information

Nanoscale PDA disassembly in ionic liquids: structure-property relationships underpinning redox tuning.

Marianna Ambrico,[a]* Paola Manini,[b]* Paolo F. Ambrico,[a] Teresa Ligonzo,[c] Giuseppe Casamassima,[c] Paola Franchi,[d] Luca Valgimigli,[d] Andrea Mezzetta,[e] Cinzia Chiappe,[e] Marco d'Ischia[b]

a. CNR– Istituto per la Scienza e Tecnologia dei Plasmi, Via Amendola 122/D, Bari, Italy. email: marianna.ambrico@cnr.it
b. Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia 4, Napoli,Italy. email: pmanini@unina.it
c. Dipartimento Interateneo di Fisica, Università degli Studi di Bari, Via Orabona 4, Bari, Italy
d. Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via S. Giacomo 11, Bologna,Italy
e. Dipartimento di Farmacia, Universita' degli Studi di Pisa, via Bonanno Pisano 6, Pisa, Italy

Materials

1-Butyl-3-methylimidazolium (98%), trioctylmethyl-ammonium [N8881] (98%) methylcarbonate methanol solutions (30% and 54%, respectively) were purchased from Proionic GmbH. Oleic acid was purchased from Fluka, tested according to Ph. Eur. Choline chloride (99%), trimethylphosphate (99%), dimethyl methylphosphonate and dimethyl phosphite were purachased from Sigma.Aldrich. All reagents were used as received, without further purification.

Nyquist Plots representation via electrical circuit

Electrical Impedance Spectroscopy data can be expressed via the Nyquist Plots (NyPs) i.e. *ReZvs –ImZ*. NyPs are generally examined by fitting the experimental data with the NyP returned by a properly designed electrical equivalent circuits.

The equivalent circuit is generally constitute by a combination of a resistive *R*, a pure capacitive *C*, and peculiar like the constant phase (Z_{CPE}) and diffusion (Z_W) elements that are properly assembled in order to represent the overall AC electrical carrier transport mechanisms. Moreover, each circuital element combination can be assigned to a specific interaction in specific AC frequency signal range.

The constant phase element Z_{CPE} is expressed by:

$$Z_{CPE} = \frac{1}{Q_0\,(j\omega)^n}$$

and is a phenomenological element introduced in order to simulate a non-perfect capacitive element. The n – parameter plays the main role since if it is close to zero the impedance element behaves more like a resistor, while when it is close to 1 it acts like a pure capacitor.

The diffusion element (Z_W) is given by:

$$Zw = \frac{A_W}{\omega^{1/2}} - j\frac{A_W}{\omega^{1/2}}$$

and is generally represented in NyPs through a straight line whose slope is equals to 0.5. If the diffusion element is represented in the NyPs by a straight line with slope different (higher / lower) than 0, the circuital element is substituted by a constant phase element and we refer it to an anomalous diffusion or CPE-limited diffusion mechanisms[36]

A commonly adopted circuit for representing carrier transport mechanisms occurring when a electronic/ionic material is placed in between two metallic electrode is the Randles circuit generally made up of a resistor (the contact resistance) in series with the parallel of a constant phase element or a capacitor (representing the charge double layer) with the series of a resistance (defined as the charge transfer resistance) and the diffusion element.

Figure S1. Nyquist plots (NyPs) derived from EIS data readouts on PDA-T and PDA-C in the full set of ILs (**IL 1-9)**. The inset is a magnification of the same data in the high frequency region. The continuous lines represent the best fit curves obtained via the equivalent circuit shown in the sketch in Fig.2 of the main text.

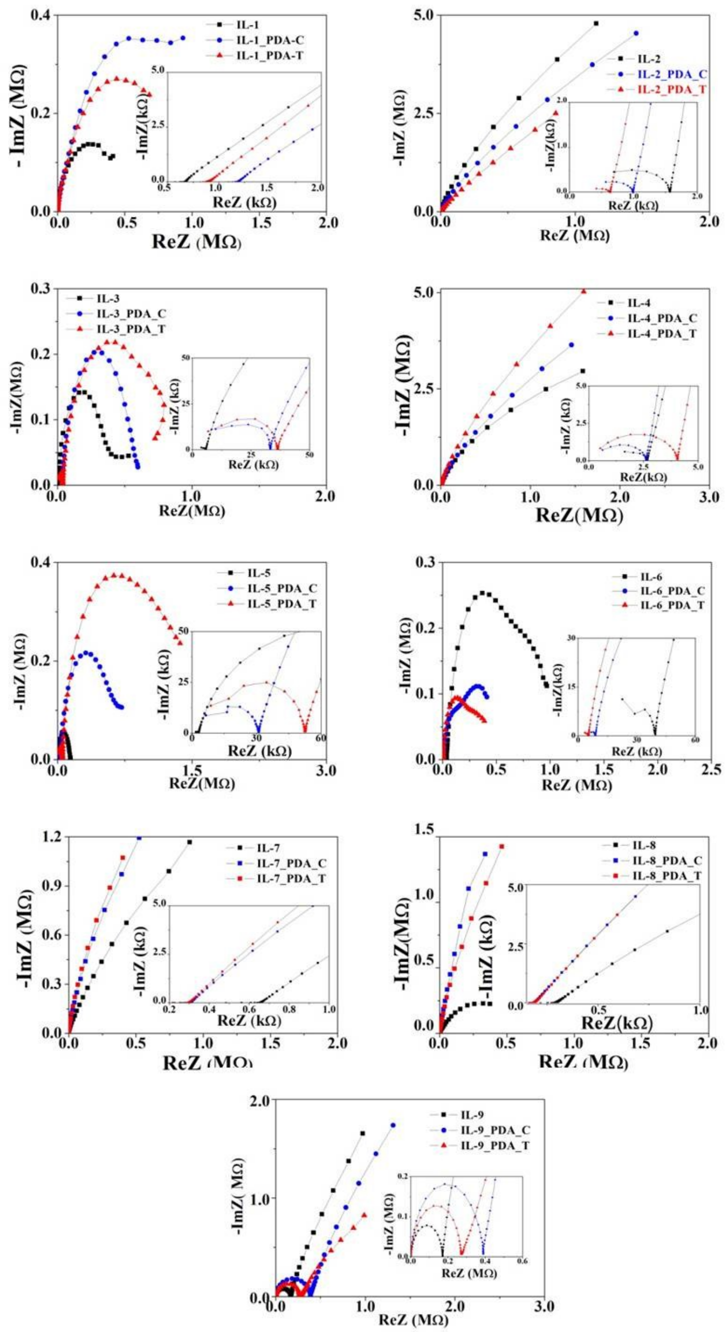

Table S1. Summary of the best fit parameters for all ILs and PDA-T and PDA-C in the different ILs as extracted from Nyquist plots by using the EIS analyzer free downloadable program. The equivalent best fit circuit and device configuration have been reported in the main text

Ionic Liquid	R_{HF} (kΩ)	R_{CT}(MΩ)	Z_W [a)]	$Z_{CPE,HF}$,n [b)]	$Z_{CPE,dl}$,n [b)]
IL1	177	0.25	-	0.69, 0.8	2.22, 0.9
IL1-PDA_C	49	1.00	24184	0.51,0.9	0.55, 0.8
IL1-PDA_T	34	0.71	62931	0.43,0.9	0.60, 0.8
IL2	778	35.0	-	0.34,1.0	1.12, 0.9
IL2-PDA_C	297	20.0	-	0.52, 0.9	1.94, 0.9
IL2-PDA_T	198	5.70	-	0.71, 0.9	1.48, 0.9
IL3	135	0.25	-	0.16, 0.9	1.31, 0.8
IL3-PDA_C	32	0.54	-	$2.0\ 10^{-6}$, 0.9	0.09, 0.8
IL3-PDA_T	36	0.62		$1.0\ 10^{-6}$, 0.9	0.12, 0.8
IL4	2.7	10.1	-	$2.0\ 10^{-6}$, 1.0	0.39, 0.9
IL4-PDA_C	1.9	2.61	$5.2\ 10^{6}$	$2.2\ 10^{-5}$, 1.0	0.3, 0.9
IL4-PDA_T	3.4	25.0	-	$1.1\ 10^{-5}$, 1.0	0.26, 0.9
IL5	3.0	0.13	$3.5\ 10^{3}$	$1.8\ 10^{-6}$, 1.0	0.35,0.9
IL5-PDA_C	233	0.42	45478	$1.2\ 10^{-6}$, 0.7	$8.8\ 10^{-2}$, 0.7
IL5-PDA_T	643	0.82	-	$1.2\ 10^{-2}$, 0.8	0.6, 0.7
IL6	499	0.52	-	$3.3\ 10^{-2}$, 0.9	0.7, 0.7
IL6-PDA_C	125	0.35	-	0.13, 0.9	1.5, 0.7
IL6-PDA_T	178	0.18	-	0.16, 0.9	2.2, 0.8
IL7	-	0.064	$1.8\ 10^{6}$		0.3, 0.9
IL7-PDA_C	-	0.93	$1.8\ 10^{6}$	-	0.8, 0.9
IL7-PDA_T	-	0.85	$1.7\ 10^{6}$	-	$1.0\ 10^{-6}$
IL8	32	0.54	-	2.8, 0.9	2.8, 0.9
IL8-PDA_C	-	0.39	$4.6\ 10^{6}$	-	0.9, 0.9

IL8-PDA_T	-	0.27	2.9 10^{6}	-	1.0, 0.9
IL9	169	8.70	-	1.2 10^{-5}, 0.9	0.7, 0.8
IL9-PDA_C	386	11.0	-	1.2 10^{-5}, 0.9	0.7, 0.8
IL9-PDA_T	274	4.45	.	1.7 10^{-5}, 0.9	1.2, 0.7

[a]$Z_W = (\Omega\ s^{-0.5})$; [b]$Z_{CPE} = (\mu F \cdot s^{(n-1)})$

Table S2. Summary of the dielectric strengths (Δ_i, i = 1, 2, 3) and peak times ($\tau_{i,}$ i = 1, 2, 3) of the dielectric relaxation mechanisms of the HN functions as resulting from the best fit of the permittivity data by using WINFIT 2.0 Novocontrol Software.

Ionic Liquid	**1st process**		**2nd process**		**3rd process**	
	$\Delta_1(10^3)$	τ_1 (ms)	$\Delta_2(10^3)$	τ_2 (ms)	$\Delta_3(10^3)$	τ_1 (μs)
IL1	246	467	179	16	68.9	103
IL1-PDA-C	17.6	381	372	10.6	30.0	104
IL1-PDA-T	23.5	397	41	11.6	36.2	97
IL2	1.57	323	6.6	7.3	73.1	278
IL2-PDA-C	1.78	308	6.7	8.6	4.99	156
IL2-PDA-T	1.93	291	7.0	6.9	5.63	718
IL3	41.3	489	17.5	14	24.9	375
IL3-PDA-C	103	557	93.4	15	42.4	810
IL3-PDA-T	97.6	550	40.1	14	26.8	726
IL4	3.25	293	18.4	8.2	65.7	459
IL4-PDA-C	26.0	267	10.9	8.9	631	410
IL4-PDA-T	1.54	265	7.68	7.5	52.0	537
IL5	113	461	8.9	18	73.1	278
IL5-PDA-C	23.7	435	13.0	15	12.7	415
IL5-PDA-T	12.7	415	8.9	14	57.3	861
IL6	17.1	439	8.94	18	37.1	375
IL6-PDA-C	43.5	389	32.8	17	14.1	341
IL6-PDA-T	40.7	380	26.3	26	7.9	312
IL7	12.1	283	34.6	12	82.1	137
IL7-PDA-C	8.4	267	39.0	9.3	217	159
IL7-PDA-T	8.2	264	38.6	9.3	260	185
IL8	13.5	340	48.6	9.6	250	94

IL8-PDAC	4.9	216	37.4	8.6	250	114
IL8-PDAT	5.9	251	34.0	8.7	224	103
IL9	10.0	228	30.6	20	0.068	820
IL9-PDAC	11.9	203	12.9	18	0.17	6200
IL9-PDAT	18.9	258	17.9	19	0.065	2000

Fig.S2. Calculated HN1 functions in the corresponding frequency range by using the Winfit 2.0 best fit parameters and the term with i= 1 in Eq.4 (main text): (left:1a,1c,1e) HN1 functions for IL 1, IL2 and IL3 and corresponding ILX-PDA-(T/C) suspensions; (right: 1b,1d,1f) HN1 function values normalized to the ILX (X=1,2,3) HN1 function values (1b,1d,1f). The EPR spin numbers N_s = Nxspin/L (10^{-6}) (N= Avogadro's number) have been inserted for comparison.

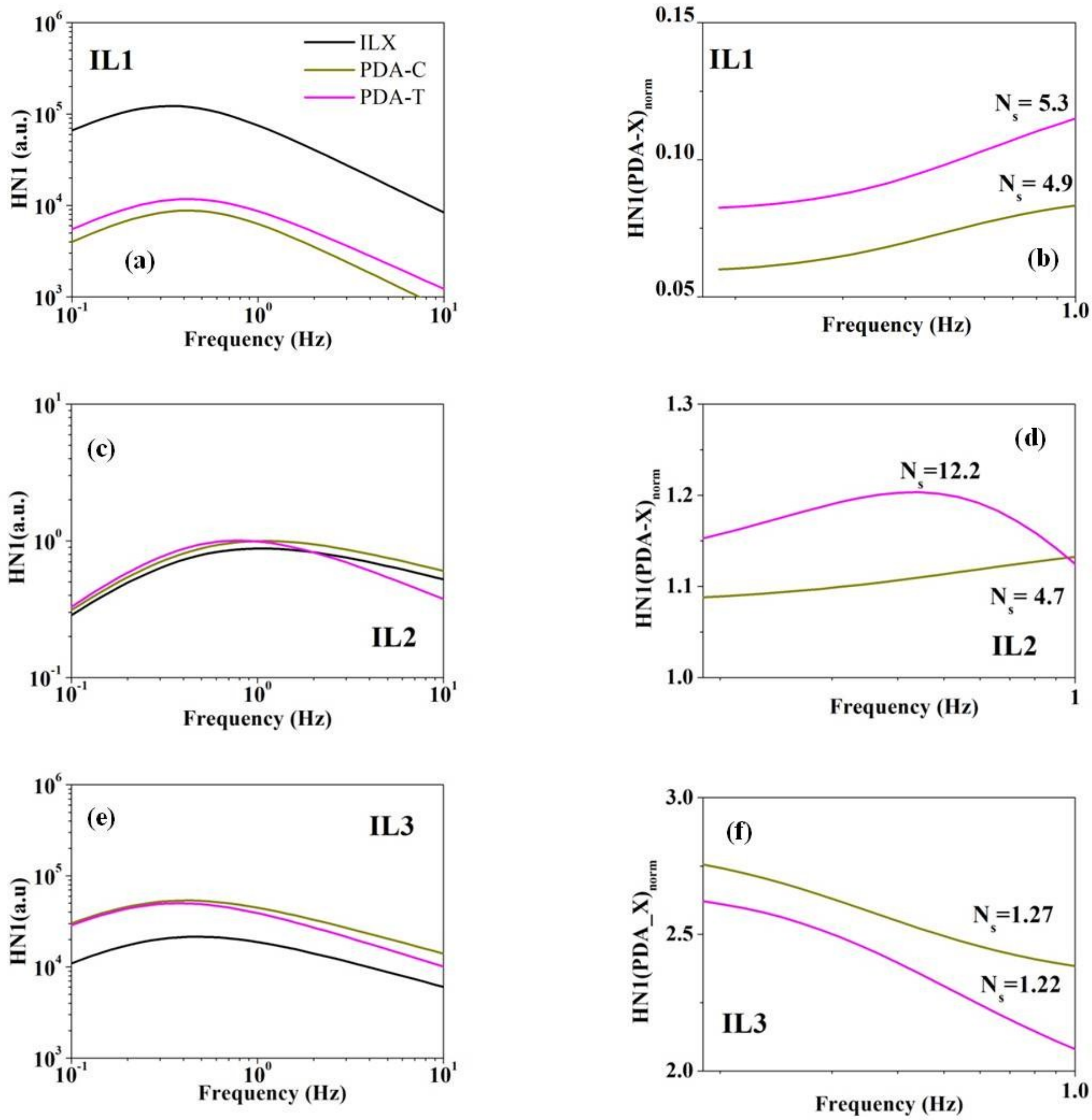

Fig.S3 Calculated HN1 functions in the corresponding frequency range by using the Winfit 2.0 best fit parameters and Eq.4 (main text): (left:1a,1c,1e) HN1 functions for IL4, IL5 and IL6 and corresponding ILX-PDA-(T/C) suspensions; (right: 1b,1d,1f) HN1 function values normalized to the ILX (X=4,5,6) HN1 function values (1b,1d,1f). The EPR spin numbers N_s = Nxspin/L (10^{-6}) (N= Avogadro's number) have been inserted for comparison.

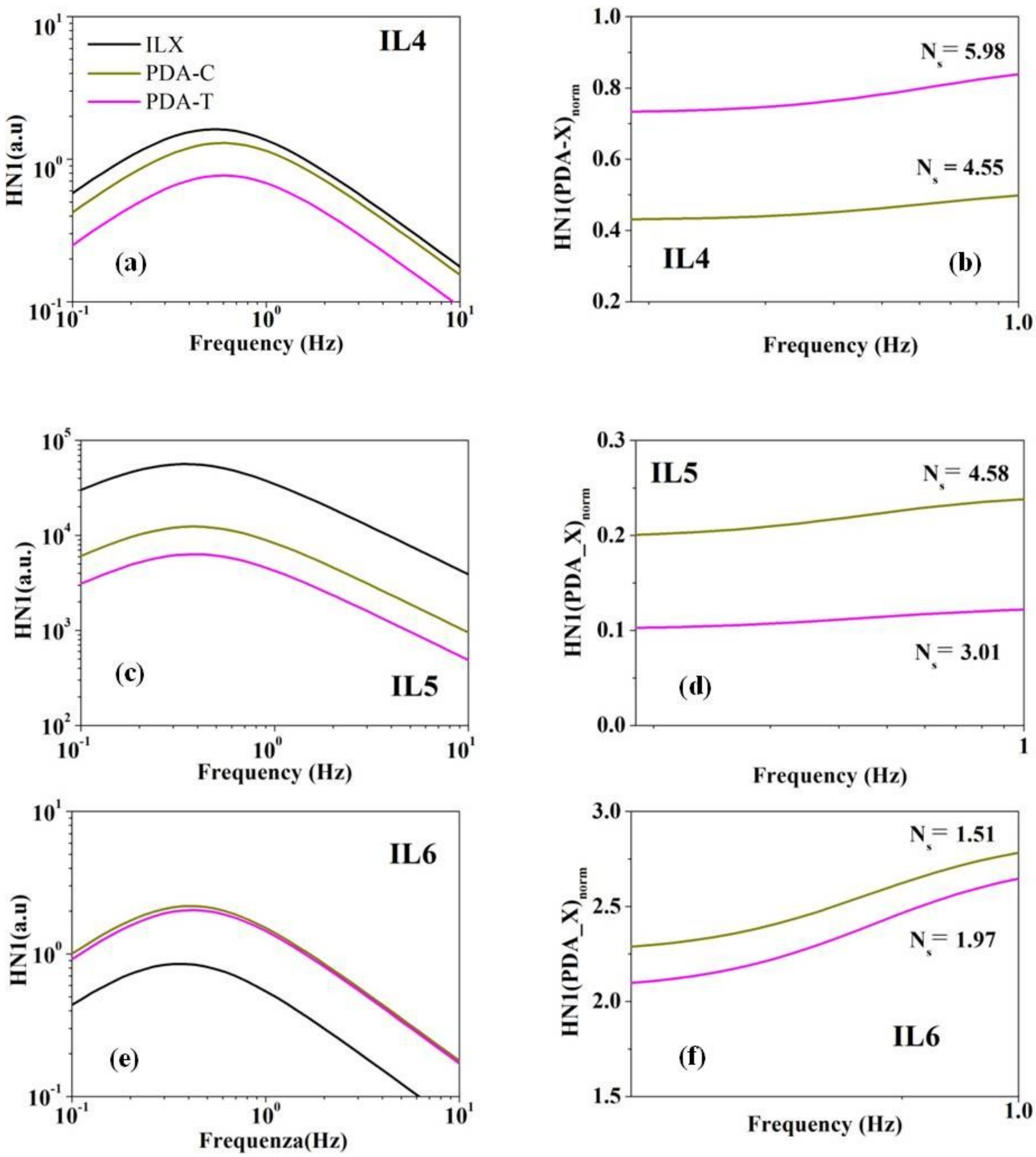

Figure S4. Calculated HN1 functions in the corresponding frequency range by using the Winfit 2.0 best fit parameters and Eq.4 (main text): (left:1a,1c,1e) HN1 functions for IL7, IL8 and IL9 and corresponding ILX-PDA-(T/C) suspensions; (right: 1b,1d,1f) HN1 function values normalized to the ILX (X=7,8,9) HN1 function values (1b,1d,1f). The EPR spin numbers N_s = Nxspin/L (10^{-6}) (N= Avogadro's number) have been inserted for comparison