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SUPPORTING MATERIAL

Graphene/Ionic Liquid Ultracapacitors: Does Ionic Size Correlate with Storage Energy Performance?

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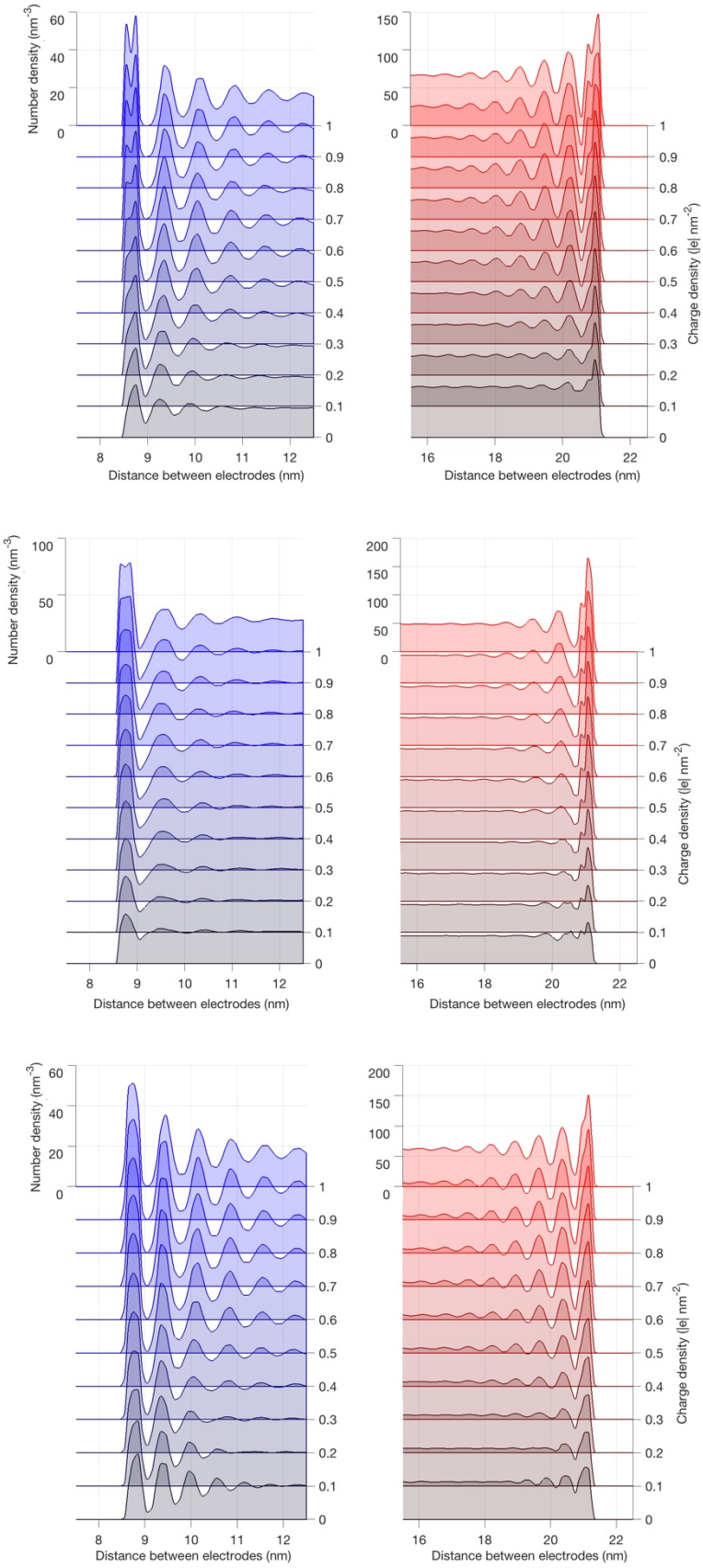

Figure S1: Number ion densities (in nm^{-3}) of anions near positive electrode (blue area) and cations near negative electrode (red area) near the charged electrodes. PYR-PF6, BMA-TFSI and BMA-PF6 at top, middle and bottom, respectively. The distributions are presented as a function of the charge density magnitude ($|e|\,nm^{-2}$) and of distance between electrodes (nm).

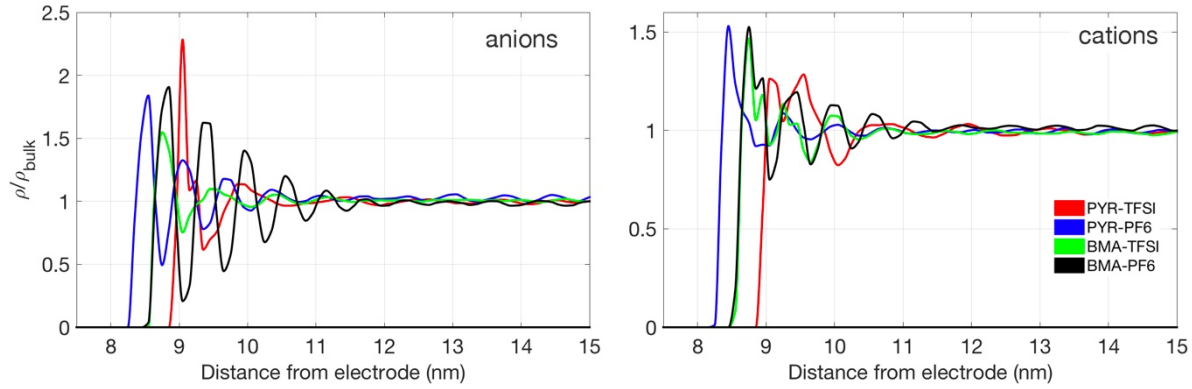

Figure S2: Comparison of the positions of the first peak of the distributions of anions (at left) and cations (at right) in the unloaded supercapacitor. The distance was measured in relation to the position of the electrode: (at z = 8.55 nm or z = 21.5 nm)

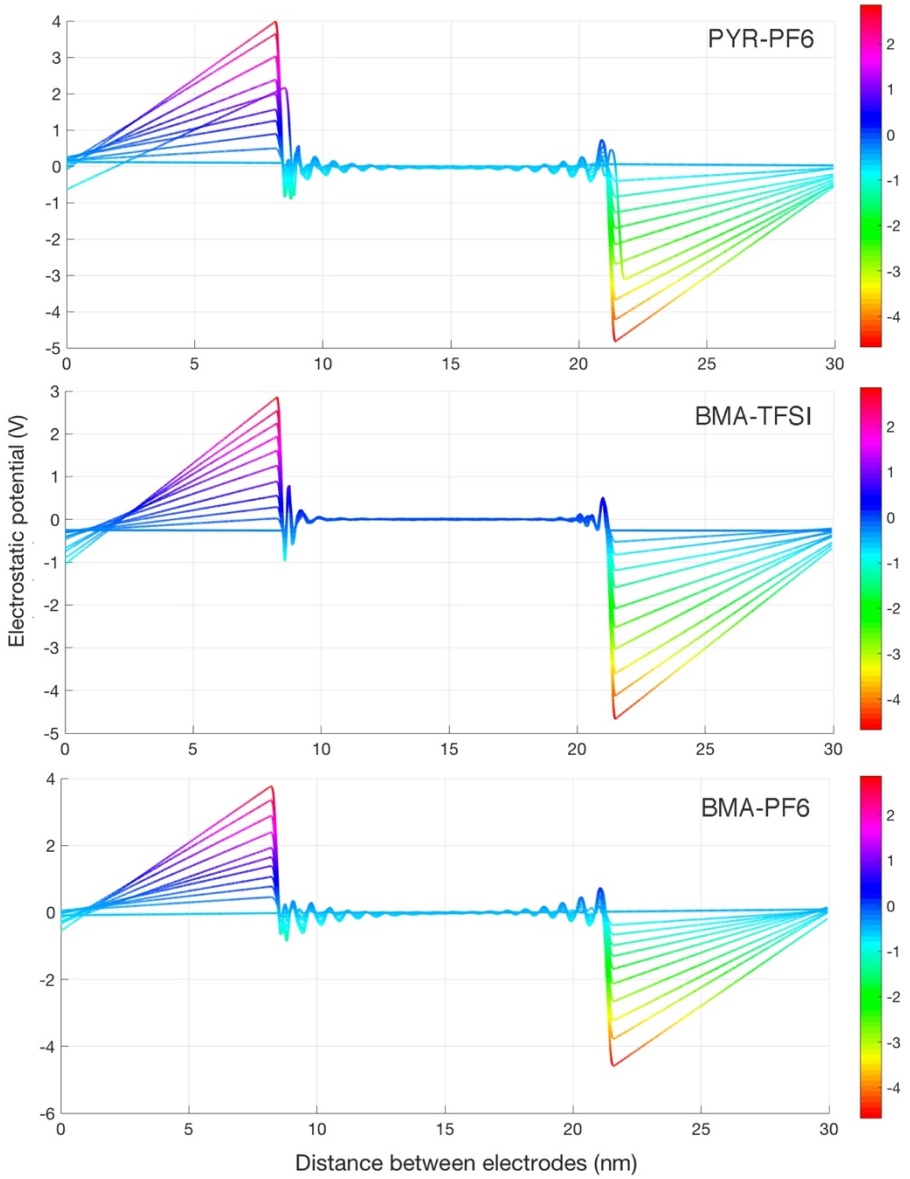

Figure S3: Electrostatic potential profile (V) for the PYR-PF6, BMA-TFSI and BMA-PF6 ultracapacitors as a function of the distance (nm) from the electrodes. The superimposed profiles are presented for all charge densities.

Table S1: Properties of the ultracapacitor of PYR-TFSI as a function of the module of the electrode surface charge density (in e nm^{-2}). $V^{(+)}$ and $V^{(-)}$ are the drop potentials near the positive and negative electrode surfaces (in Volts). $C^{(+)}$ and $C^{(-)}$ are the electrode capacitances (in μF cm^{-2}). V^T and C^T are the total drop potential across the ultracapacitor and its total capacitance. U and u are the surface and volumetric energy densities.

PYR-TFSI								
σ(e nm^{-2})	$V^{(+)}$ (V)	$V^{(-)}$ (V)	V^T(V)	$C^{(+)}$(μF cm^{-2})	$C^{(+)}$(μF cm^{-2})	C^T (μF cm^{-2})	U (μ J cm^{-2})	u (J cm^{-3})
0.0	-0.3	-0.3	0.02	0.000	0.000		0.00	0.0
0.1	0.0	-0.8	0.78	4.577	1.470	2.05	0.62	0.5
0.2	0.3	-1.1	1.44	4.782	2.241	2.23	2.31	1.8
0.3	0.7	-1.5	2.21	4.758	2.584	2.17	5.31	4.1
0.4	1.0	-1.9	2.90	4.818	2.874	2.21	9.29	7.1
0.5	1.3	-2.3	3.58	5.038	3.023	2.24	14.34	11.0
0.6	1.5	-2.9	4.38	5.310	2.976	2.19	21.05	16.1
0.7	2.2	-3.1	5.27	4.504	3.260	2.13	29.55	22.6
0.8	2.5	-3.6	6.11	4.513	3.261	2.10	39.15	29.9
0.9	2.9	-4.0	6.91	4.464	3.322	2.09	49.81	38.1
1.0	3.3	-5.0	8.27	4.413	3.023	1.94	66.24	50.6

Table S2: Properties of the ultracapacitor of PYR-PF6 as a function of the module of the electrode surface charge density (in e nm^{-2}). $V^{(+)}$ and $V^{(-)}$ are the drop potentials near the positive and negative electrode surfaces (in Volts). $C^{(+)}$ and $C^{(-)}$ are the electrode capacitances (in μF cm^{-2}). V^T and C^T are the total drop potential across the ultracapacitor and its total capacitance. U and u are the surface and volumetric energy densities.

PYR-PF6								
σ(e nm^{-2})	$V^{(+)}$ (V)	$V^{(-)}$ (V)	V^{total} (V)	$C^{(+)}$(μF cm^{-2})	$C^{(+)}$(μF cm^{-2})	C^T (μF cm^{-2})	U (μ J cm^{-2})	u (J cm^{-3})
0.0	0.1	0.1	0.03	0.000	0.000		0.00	0.0
0.1	0.5	-0.4	0.89	2.835	1.393	1.80	0.71	0.5
0.2	0.9	-0.8	1.73	3.320	2.015	1.85	2.77	2.1
0.3	1.3	-1.3	2.53	3.600	2.379	1.90	6.08	4.6
0.4	1.6	-1.7	3.27	3.895	2.616	1.96	10.48	8.0
0.5	2.0	-2.2	4.15	3.860	2.762	1.93	16.62	12.7
0.6	2.4	-2.7	5.09	3.899	2.786	1.89	24.46	18.7
0.7	2.2	-3.2	5.36	5.017	2.839	2.09	30.05	23.0
0.8	3.3	-3.1	6.41	3.797	3.320	2.00	41.08	31.4
0.9	3.7	-4.2	7.88	3.871	2.895	1.83	56.81	43.4
1.0	4.0	-4.8	8.82	3.941	2.871	1.82	70.65	54.0

Table S3: Properties of the ultracapacitor of BMA-TFSI as a function of the module of the electrode surface charge density (in e nm^{-2}). $V^{(+)}$ and $V^{(-)}$ are the drop potentials near the positive and negative electrode surfaces (in Volts). $C^{(+)}$ and $C^{(-)}$ are the electrode capacitances (in μF cm^{-2}). V^T and C^T are the total drop potential across the ultracapacitor and its total capacitance. U and u are the surface and volumetric energy densities.

BMA-TFSI								
σ(e nm^{-2})	$V^{(+)}$ (V)	$V^{(-)}$ (V)	V^{total} (V)	$C^{(+)}$(μF cm^{-2})	$C^{(+)}$(μF cm^{-2})	C^T (μF cm^{-2})	U (μ J cm^{-2})	u (J cm^{-3})
0.0	-0.3	-0.3	-0.002	0.000	0.000		0.00	0.0
0.1	0.0	-0.5	0.55	5.006	6.965	2.91	0.44	0.3
0.2	0.3	-0.8	1.12	5.431	6.045	2.86	1.79	1.4
0.3	0.6	-1.2	1.74	5.654	5.400	2.76	4.18	3.2
0.4	0.9	-1.6	2.48	5.385	4.967	2.58	7.95	6.1
0.5	1.3	-2.1	3.35	5.135	4.475	2.39	13.42	10.2
0.6	1.6	-2.5	4.13	5.059	4.310	2.33	19.85	15.2
0.7	1.9	-3.0	4.96	5.029	4.108	2.26	27.81	21.2
0.8	2.2	-3.6	5.85	5.046	3.872	2.19	37.49	28.6
0.9	2.5	-4.1	6.67	5.077	3.764	2.16	48.08	36.7
1.0	2.9	-4.7	7.53	5.070	3.666	2.13	60.32	46.1

Table S4: Properties of the ultracapacitor of BMA-PF6 as a function of the module of the electrode surface charge density (in e nm^{-2}). $V^{(+)}$ and $V^{(-)}$ are the drop potentials near the positive and negative electrode surfaces (in Volts). $C^{(+)}$ and $C^{(-)}$ are the electrode capacitances (in μF cm^{-2}). V^T and C^T are the total drop potential across the ultracapacitor and its total capacitance. U and u are the surface and volumetric energy densities.

BMA-PF6								
σ(e nm^{-2})	$V^{(+)}$ (V)	$V^{(-)}$ (V)	V^{total} (V)	$C^{(+)}$(μF cm^{-2})	$C^{(+)}$(μF cm^{-2})	C^T (μF cm^{-2})	U (μ J cm^{-2})	u (J cm^{-3})
0.0	0.0	0.0	0.04	0.000	0.000		0.00	0.0
0.1	0.5	-0.4	0.83	3.338	4.577	1.93	0.66	0.5
0.2	0.8	-0.7	1.43	4.056	5.006	2.24	2.29	1.8
0.3	1.1	-1.0	2.04	4.450	5.006	2.36	4.90	3.7
0.4	1.4	-1.3	2.68	4.577	5.006	2.39	8.59	6.6
0.5	1.7	-1.7	3.33	4.796	4.825	2.41	13.34	10.2
0.6	1.9	-2.1	4.06	4.929	4.555	2.37	19.51	14.9
0.7	2.4	-2.7	5.05	4.653	4.248	2.22	28.32	21.6
0.8	2.9	-3.2	6.11	4.419	3.993	2.10	39.15	29.9
0.9	3.4	-3.8	7.13	4.278	3.835	2.02	51.40	39.3
1.0	3.8	-4.6	8.36	4.227	3.505	1.92	66.96	51.2

Table S5: Tables below are the raw data, obtained directly from simulations, on the interaction energy between the ions (in the tables named by PYR, TFS BMA and PF6) and the electrodes (GRP(positive) and GRN(negative)). The components of Coulomb (Coul-SR) and van der Waals (LJ-SR) are presented separately. Considering the large volume of data, we present here only the results for the highest charge density employed in the work (σ = 1.0 e nm^{-2}). For the other densities the analysis presented in the text follows the same trend.

PYR-TFSI (σ = 1.0 e nm^{-2})

Energy	Average	Err.Est.	RMSD	Tot-Drift	
Coul-SR:GRP-PYR	47.522	1.2	8.23591	5.56026	(kJ/mol)
Coul-SR:GRP-TFS	-739.818	4.4	20.9973	-26.0488	(kJ/mol)
Coul-SR:GRN-PYR	-442.181	8.6	21.772	-53.0856	(kJ/mol)
Coul-SR:GRN-TFS	13.2632	1.1	3.67134	-5.68081	(kJ/mol)
Total	-1121.21	12	--	-79.255	(kJ/mol)

Energy	Average	Err.Est.	RMSD	Tot-Drift	
LJ-SR:GRP-PYR	-199.326	2.1	25.0901	10.4279	(kJ/mol)
LJ-SR:GRP-TFS	-1015.86	15	44.9325	-105.201	(kJ/mol)
LJ-SR:GRN-PYR	-979.487	27	62.7248	-161.338	(kJ/mol)
LJ-SR:GRN-TFS	-44.5879	9.1	24.5814	49.6513	(kJ/mol)
Total	-2239.26	30	--	-206.46	(kJ/mol)

BMA-TFSI (σ = 1.0 e nm^{-2})

Energy	Average	Err.Est.	RMSD	Tot-Drift	
Coul-SR:GRP-BMA	22.693	0.42	5.3903	-2.50197	(kJ/mol)
Coul-SR:GRP-TFS	-705.693	2.3	17.2292	-12.0172	(kJ/mol)
Coul-SR:GRN-BMA	-450.772	0.38	9.79341	0.658105	(kJ/mol)
Coul-SR:GRN-TFS	19.8185	0.12	3.04868	0.39063	(kJ/mol)
Total	-1113.95	2.8	--	-13.4705	(kJ/mol)

Energy	Average	Err.Est.	RMSD	Tot-Drift	
LJ-SR:GRP-BMA	-101.509	3.3	22.6319	22.8159	(kJ/mol)
LJ-SR:GRP-TFS	-1095.53	10	37.9682	-57.1667	(kJ/mol)
LJ-SR:GRN-BMA	-1042.2	3.2	35.1384	7.46774	(kJ/mol)
LJ-SR:GRN-TFS	-62.9156	0.56	14.5159	-2.69434	(kJ/mol)
Total	-2302.16	8.6	--	-29.5774	(kJ/mol)

PYR-PF6 (σ = 1.0 e nm^{-2})

Energy	Average	Err.Est.	RMSD	Tot-Drift
Coul-SR:GRP-PYR	50.6192	0.8	5.51145	4.8014 (kJ/mol)
Coul-SR:GRP-PF6	-520.716	3.4	13.4996	-20.5146 (kJ/mol)
Coul-SR:GRN-PYR	-445.383	0.41	10.215	-1.26212 (kJ/mol)
Coul-SR:GRN-PF6	8.72468	0.022	1.3836	-0.158195 (kJ/mol)
Total	-906.755	2.9	--	-17.1335 (kJ/mol)

LJ-SR:GRP-PYR	-229.109	2.1	26.7487	12.2825 (kJ/mol)
LJ-SR:GRP-PF6	-437.206	3.8	27.9868	-23.0418 (kJ/mol)
LJ-SR:GRN-PYR	-975.125	0.34	26.767	1.7598 (kJ/mol)
LJ-SR:GRN-PF6	-21.5955	0.049	2.12663	0.288996 (kJ/mol)
Total	-1663.03	2	--	-8.71045 (kJ/mol)

BMA-PF6 (σ = 1.0 e nm^{-2})

Energy	Average	Err.Est.	RMSD	Tot-Drift
Coul-SR:GRP-BMA	47.8517	0.61	5.16157	3.70956 (kJ/mol)
Coul-SR:GRP-PF6	-548.144	2.5	13.5651	-15.9726 (kJ/mol)
Coul-SR:GRN-BMA	-435.853	0.4	9.92095	-0.716667 (kJ/mol)
Coul-SR:GRN-PF6	14.4628	0.081	1.74725	-0.00770944 (kJ/mol)
Total	-921.682	2.1	--	-12.9874 (kJ/mol)

Energy	Average	Err.Est.	RMSD	Tot-Drift
LJ-SR:GRP-BMA	-201.27	3.4	29.1803	3.79236 (kJ/mol)
LJ-SR:GRP-PF6	-474.638	3.4	28.3594	-19.753 (kJ/mol)
LJ-SR:GRN-BMA	-997.062	0.41	32.4176	2.82424 (kJ/mol)
LJ-SR:GRN-PF6	-31.8702	0.12	2.62337	0.0959939 (kJ/mol)
Total	-1704.84	3.8	--	-13.0404 (kJ/mol)

Table S6: Charge density of graphene electrode (in *e* nm^{-2} and μC nm^{-2}), total charge at the electrode, Q, (in *e*) and C-atom charge, q, (in *e*). q = Q/N where N = 448.

σ (*e* nm^{-2})	**σ (μC cm^{-2})**	**Q**	**q**
0	0	0.0	0.00000
0.1	1.6	1.2	0.00260
0.2	3.2	2.3	0.00520
0.3	4.8	3.5	0.00780
0.4	6.4	4.7	0.01040
0.5	8	5.8	0.01300
0.6	9.6	7.0	0.01560
0.7	11.2	8.2	0.01820
0.8	12.8	9.3	0.02080
0.9	14.4	10.5	0.02340
1	16	11.7	0.02600