

SUPPORTING INFORMATION

Storing Energy in Biodegradable Electrochemical Supercapacitors

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1. Computational details of supercapacitor simulation

RFL₄FR and EFL₄FE polypeptide sequences (E = Glutamate, F = Phenylalanine, L = Leucine, and R = Arginine) were pre-assembled into nanosheets. We use the -COO and -NH₃ terminations in each peptide, such as the EFL₄FE and RFL₄FR sequences assume a net charge of -2e and +2e, respectively (Figure 1 in main text). XFL₄FX infinite peptide nanosheet was modelled using the CHARMM36 force field.¹ Pre-organized cells were produced by juxtaposition of the XFL₄FX in a regular network of 4x8 monomer. Each nanosheet was carefully pre-assembled to possess virtually the same surface area, 17.8 nm². The nanosheets were placed at the ends of a rectangular box 17 nm long, of which 11.3 nm were used to contain 800 [Ch][Gly] ion pairs. This was done so that the nanosheets held their charged surface in contact with the ionic liquid.

Table S1: Number of sites in each system [total sites], box dimension [in nm] and structural properties: nanosheet thickness (L) and initial length of ionic liquid volume (D) [in nm]. RF represent (RFL₄F[R]⁺²)₃₂ nanosheet and EF represent (EFL₄F[E]⁻²)₃₂ nanosheet. The three different runs used in the simulation are showed at the bottom of the table.

System	EFL ₄ FE RFL ₄ FR [sites]	Ch Gly [sites]	# total sites	X [nm] Y [nm] Z [nm]	Structural Properties [nm]
EF-[Ch][Gly]-RF	32	800	34912	4.176	L _{EF} = 2.9
	32	800		4.255	L _{RF} = 3.2
	[10112]	[24800]		70.000	D = 11.3

MD Simulations	Run 1	Run 2	Run 3
EF-[Ch][Gly]-RF	NVT 10 ns	NPT 10 ns	NVT 50 ns

The EF-[Ch][Gly]-RF system was subjected to carefully equilibration process: a steep-descent minimization process to remove bad contacts and a 10 ns-NVT simulation to cooling the system (Run 1). Then the system was subjected to 10 ns simulated NPT annealing with semiisotropic pressure coupling to obtain the appropriated density of the system. Specifically, the system temperature was gradually increased from initial 350 K to 800 K at the first 2.5 ns and the gradually reduced to the final 350 K at the next 2.5 ns which is followed by a 5 ns equilibration run (Run 2) and a 50 ns-NVT production run (Run 3).

The simulation was performed with $p = 1 \text{ atm}$ e $T = 350 \text{ K}$. The production stage was performed with time step of 2fs. Properties were calculated and the coordinates was collected every 2 ps, which gives a total of 25000 frames for statistical analysis. The system was kept at the appropriate temperature and pressure using velocity rescaling² and semiisotropic Parrinello-Rhman schemes³ with coupling constants of 0.1 and 2.0 ps, respectively. All bond lengths were constrained using the LINCS algorithm.⁴ A potential-shift-Verlet with cutoff lengths of 1.0 nm and 1.2 nm for Lennard-Jones interaction was employed, whereas the Coulomb interactions were treated by using the PME algorithm.⁵

2. Parametrization of the cholinium-glycine [Ch][Gly] ionic liquid.

The force-field parameterization for the liquid liquid [Ch][Gly] was performed in the same protocol used by us in reference⁶. In short, the electrostatic potential (ESP) was computed using the Moller-Plesset second-order perturbation theory, MP2, with precisely the same basis set functions as in wB97XD. The ChelpG scheme with a default grid size in Gaussian 09 was employed to perform charge assignment.⁷ The nuclear geometries (isolated ions and ion pairs) were optimized to correspond to the local minimum configuration of the electron-nuclear system. The electronic structure computations were performed in Gaussian 09, revision D.⁸

We performed three sets of simulations per system per force field (see Table S2). First, enthalpy of vaporization and mass density were determined at room conditions (Run 1). Second, diffusion constants were computed at 350 K using mean-square displacements of all atoms (Run 2). Third, non-equilibrium molecular dynamics simulations were performed at 350 K based on continuous energy dissipation in the liquid (Run 3). The temperatures used in the last two series were smaller than the one used in the original paper since we wanted to reproduce the properties measured experimentally. Figure S1 shows a molecular representation of the ionic pair that makes up the liquid and the simulation box used in the parameterization.

All systems were simulated in the constant-pressure constant-temperature ensemble. The equations of motion were propagated with a time-step of 2.0 fs. The electrostatic interactions were simulated using direct Coulomb law up to 1.2 nm of separation between the interaction sites. The electrostatic interactions beyond 1.2 nm were accounted for by computationally efficient Particle-Mesh-Ewald (PME) method.⁵ The Lennard-Jones-12-6 interactions were smoothly brought down to zero from 1.1 to 1.2 nm using the classical shifted force technique. The constant temperature (298 and 350 K) was

maintained by the Bussi-Donadio-Parrinello velocity rescaling thermostat (with a time constant of 0.5 ps).² The constant pressure was maintained by the Parrinello-Rahman barostat³ with a time constant of 4.0 ps and a compressibility constant of $4.5 \times 10^{-5} \text{ bar}^{-1}$. All molecular dynamics trajectories were propagated using the GROMACS 2016.⁹

Table S2: Composition of the simulated system and time simulation used in the parametrization.

	# ion pairs	# interaction centers	Run 1	Run 2	Run 3
[Ch][Gly]	100	3100	10 ns	50 ns	50 ns

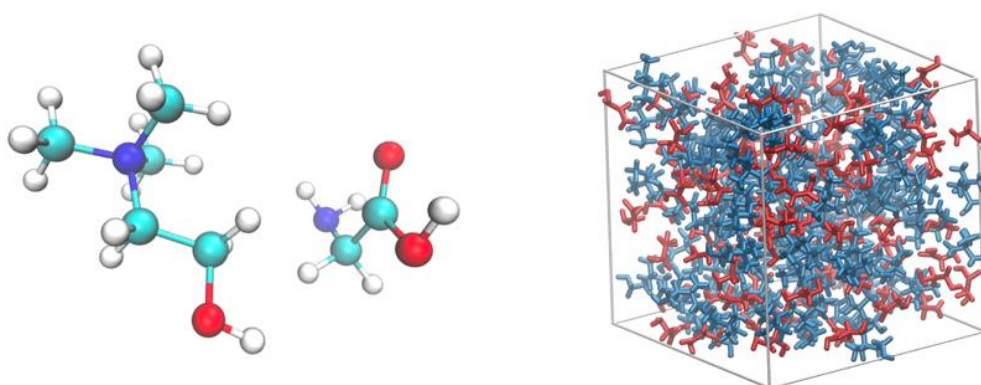


Figure S1. Molecular representation of the ion pair [Ch][Gly] and the simulation box used in the parameterization.

Table S3: Simulated and experimental properties of ionic liquid [Ch][Gly].

	Simulated	Experimental ^a
$d \text{ (g cm}^{-3}\text{)}$	1.196	1.145
$\Delta H_{\text{vap}} \text{ (kJ mol}^{-1}\text{)}$	135	-
$\eta \text{ (mPa.s)}$	1.2	3.5

^a) Tao, et. al. ¹⁰

Cartesian coordinates were saved every 5 ps and thermodynamic quantities were saved every 0.02 ps. Self-diffusion coefficients were computed from mean-square displacements of atomic positions. Shear viscosity was calculated using cosine-shape acceleration of all atoms of all ions.¹¹ The first nanosecond of the simulation was used for an accelerated ionic flow to be established. The subsequent 19 ns were used for the viscosity calculation. Further discussion on the force field derivation can be found in reference ⁶. The values obtained for the heat of vaporization, ΔH_{vap} , mass density, d , and

shear viscosity, η , are found in good agreement with the corresponding experimental values, as shown at Table S3.^{10, 12}

This force field derived here and ready-to-use topology input files for the GROMACS molecular dynamics simulation package are available free of charge upon e-mail to fileti@gmail.com.

3. Stability of the peptide-based nanosheet in ionic liquid [Ch][Gly]

We recently investigated the EFL₄FE and RFL₄FR nanosheets in water and observed a high level of structuring and stability. Since the electrostatic nature of pure water and ionic liquids are very different, it is not obvious that the nanosheets are stable in ionic liquid. Thus, we re-analyzed such stability considering these nanosheets immersed in ionic liquid [Ch][Gly]. The XFL₄FX nanosheets pre-structured for the construction of the capacitor electrodes were simulated separately embedded in ionic liquid [Ch][Gly]. The simulation process was performed using the same initial criteria used for the supercapacitor (see Section 1). Figure S2 and Table S4 presented below confirm the structural stability of the EFL₄FE e RFL₄FR nanosheets in the ionic liquid.

Table S4: Number of molecules in each system [total sites], box dimension [in nm] and structural properties: nanosheets thickness (L) [in nm].

MD runs	XFL ₄ FX [sites]	Ch Gly [sites]	All sites	X [nm] Y [nm] Z [nm]	Structural Properties [nm]
(EFL ₄ FE) ₃₂ in [Ch][Gly]	32	560		4.176	
	[4768]	560	22128	4.255	L _{EF} = 2.64
		[17360]		10.480	
(RFL ₄ FR) ₃₂ in [Ch][Gly]	32	560		4.176	
	[5344]	560	22704	4.255	L _{RF} = 2.67
		[17360]		10.844	

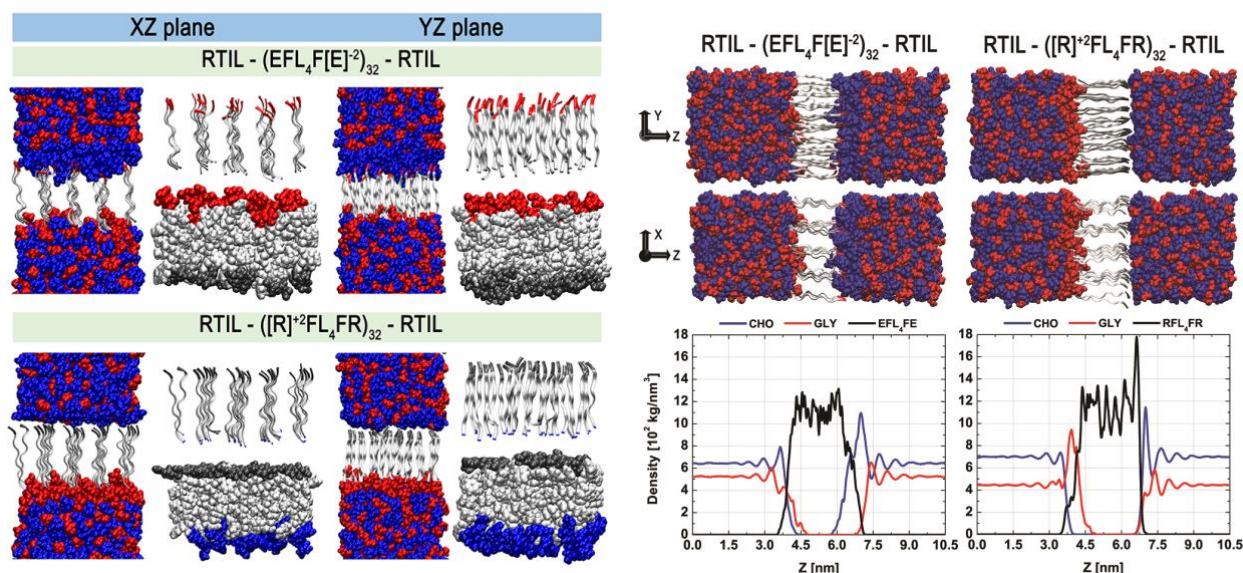


Figure S2: At left, molecular representation of the EFL₄FE and RFL₄FR nanosheets in the ionic liquid [Ch][Gly]. Cholinium cation, [Ch]⁺, and glycine anion [Gly]⁻, are shown as blue and red vdW spheres, respectively. EFL₄FE and RFL₄FR nanosheet are in red-white-grey and grey-white-blue ribbons/vdW representation, respectively. At right, mass density profiles for the EFL₄FE and RFL₄FR systems. At top are presented a representative molecular configuration (YZ and XZ plane) for each system.

4. Planar gold electrode supercapacitor

The planar gold supercapacitor was simulated to provide reference values that allowed to evaluate the performance of the peptide-based supercapacitor. For this simulation, we use the same parameters used in the main simulations. The gold electrode was modeled as four monolayers of area 20.9 nm² using the force field developed by Heinz and co-workers.¹³ To obtain the same potential difference determined for the peptide supercapacitor (namely 3.1V) we performed a series of simulations varying the surface density of charges between 4.8 μC cm⁻² and 9.6 μC cm⁻². The charges were uniformly distributed over all the atoms of the innermost monolayers (in contact with the ionic liquid). The density of 7.2 μC cm⁻² was the one that produced the target potential difference across the supercapacitor.

5. Aqueous mixtures as electrolyte

Some molar fractions (MF) of water were inserted into the ionic liquid to evaluate the behaviour of the supercapacitor. Table S5 shows the amount of water and ionic pairs as

well as the properties of the system with water addition. In total, 5 molar fractions of 10%, 20%, 30%, 40%, and 50% were simulated.

Table S5: Analyses for EFL₄FE and RFL₄FR nanosheet and cholyne (Ch) and glycine (Gly) ionic liquid (RTIL=[Ch][Gly]). Number of atoms in each system [total sites], box dimension [in nm] and structural properties: nanosheet thickness (L) and initial length of mixture volume (D) [in nm]. We simulated system with water molecules mixed with ionic liquid (RTIL/H₂O). The RTIL/H₂O system was simulated with Molar Fraction (MF) range between FM=0.00 (no water molecules = pure ionic liquid) and FM=0.50 (# CH+GLY molecules = # water molecules).

MD runs	EFL ₄ FE RFL ₄ FR [sites]	Ch Gly [sites]	H ₂ O [sites]	All sites	X [nm] Y [nm] Z [nm]	Structural Properties [nm]
EF-RTIL-RF Model MF=0.00	32 32 [10112]	800 800 [24800]	--	34912	4.176 4.255 70.000	L _{EF} = 2.94 L _{RF} = 3.22 D = 11.34
EF-RTIL/H ₂ O-RF Model MF=0.10	32 32 [10112]	783 783 [24273]	87 [261]	34646	4.520 4.637 70.000	L _{EF} = 3.78 L _{RF} = 4.06 D = 8.40
EF-RTIL/H ₂ O-RF Model MF=0.20	32 32 [10112]	776 776 [24056]	194 [582]	34750	4.520 4.637 70.000	L _{EF} = 3.92 L _{RF} = 3.78 D = 8.54
EF-RTIL/H ₂ O-RF Model MF=0.30	32 32 [10112]	763 763 [23653]	327 [981]	34746	4.520 4.637 70.000	L _{EF} = 3.92 L _{RF} = 3.92 D = 8.40
EF-RTIL/H ₂ O-RF Model MF=0.40	32 32 [10112]	744 744 [23058]	498 [1494]	34664	4.520 4.637 70.000	L _{EF} = 3.78 L _{RF} = 3.92 D = 8.40
EF-RTIL/H ₂ O-RF Model MF=0.50	32 32 [10112]	725 725 [22475]	725 [2175]	34762	4.520 4.637 70.000	L _{EF} = 3.78 L _{RF} = 4.06 D = 8.26

Figure S3 shows the final configuration obtained for each water molar fraction compared to that for pure ionic liquid.

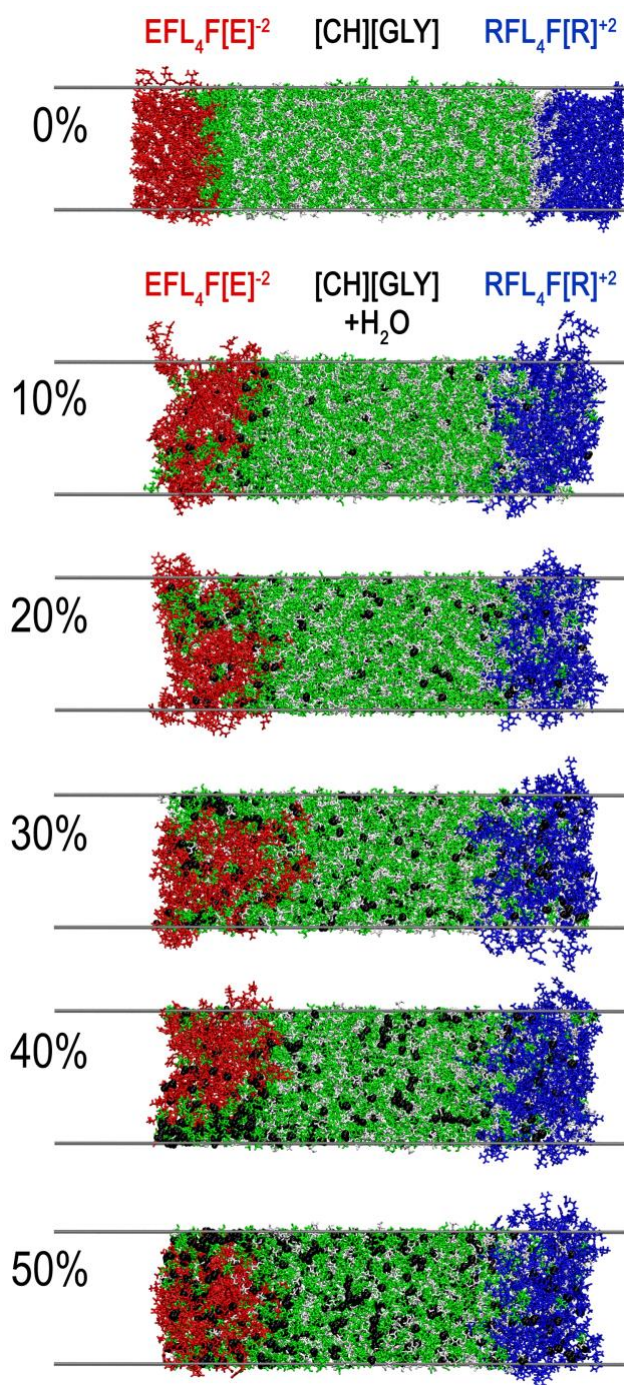


Figure S3: EF-[Ch][Gly]-RF supercapacitors. Each X% system was simulated with molar fraction between 0.0 (pure ionic liquid) and 0.5 (1:1 mixture). Black sphere represents water molecules.

6. References

- (1) Best, R. B.; Zhu, X.; Shim, J.; Lopes, P. E.; Mittal, J.; Feig, M.; Mackerell, A. D., Jr. Optimization of the additive CHARMM all-atom protein force field targeting improved sampling of the backbone phi, psi and side-chain chi(1) and chi(2) dihedral angles. *J Chem Theory Comput* **2012**, 8, 9, 3257-3273.
- (2) Bussi, G.; Donadio, D.; Parrinello, M. Canonical sampling through velocity rescaling. *J. Chem. Phys.* **126** **2007**, 126, 014101-014108.
- (3) Parrinello, M.; Rahman, A. Polymorphic transitions in single crystals: A new molecular dynamics method. *J. Appl. Phys.* **1981**, 52, 7182-7192.
- (4) Hess, B.; Bekker, H.; Berendsen, H. J. C.; Fraaije, J. G. E. M. LINCS: A linear constraint solver for molecular simulations. *J. Comp. Chem.* **1997**, 18, 1463.
- (5) Darden, T.; York, D.; Pedersen, L. Particle mesh Ewald: An N·log(N) method for Ewald sums in large systems. *J. Chem. Phys.* **1993**, 98, 10089-10099.
- (6) Fileti, E. E.; Chaban, V. V. The scaled-charge additive force field for amino acid based ionic liquids. *Chemical Physics Letters* **2014**, 616-617, 205-211.
- (7) Breneman, C. M.; Wiberg, K. B. Determining Atom-Centered Monopoles From Molecular Electrostatic Potentials - The Need For High Sampling Density In Formamide Conformational-Analysis *Journal Of Computational Chemistry* **1990**, 11.
- (8) Frish, M. J.; al., e. *Gaussian 09*, Gaussian, Inc.: Wallingford CT, 2009.
- (9) Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. . *SoftwareX* **2015**, 1–2, 19–25.
- (10) Tao, D.-J.; Cheng, Z.; Chen, F.-F.; Li, Z.-M.; Hu, N.; Chen, X.-S. Synthesis and Thermophysical Properties of Biocompatible Cholinium-Based Amino Acid Ionic Liquids. *Journal of Chemical & Engineering Data* **2013**, 58, 6, 1542-1548.
- (11) Hess, B. Determining the shear viscosity of model liquids from molecular dynamics simulations. *J. Chem. Phys.* **2002**, 116, 209-217.
- (12) Hou, X. D.; Liu, Q. P.; Smith, T. J.; Li, N.; Zong, M. H. Evaluation of toxicity and biodegradability of cholinium amino acids ionic liquids. *PLoS One* **2013**, 8, 3, e59145.
- (13) Heinz, H.; Vaia, R. A.; Farmer, B. L.; Naik, R. R. Accurate Simulation of Surfaces and Interfaces of Face-Centered Cubic Metals Using 12–6 and 9–6 Lennard-Jones Potentials. *The Journal of Physical Chemistry C* **2008**, 112, 44, 17281-17290.