Electronic Supplementary Material (ESI) for Soft Matter.

Machine Learning Enabled Quantification of the Hydrogen Bonds Inside the Polyelectrolyte Brush Layer Probed Using All-Atom Molecular Dynamics Simulations: Supplementary Information

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S1. Force field parameters and other details for the MD simulations

In Fig. S1, we have provided a partial schematic representation of the fully ionized poly(2-methacryloyloxy)-ethyl-trimethylammonium (PMETAC) molecule.

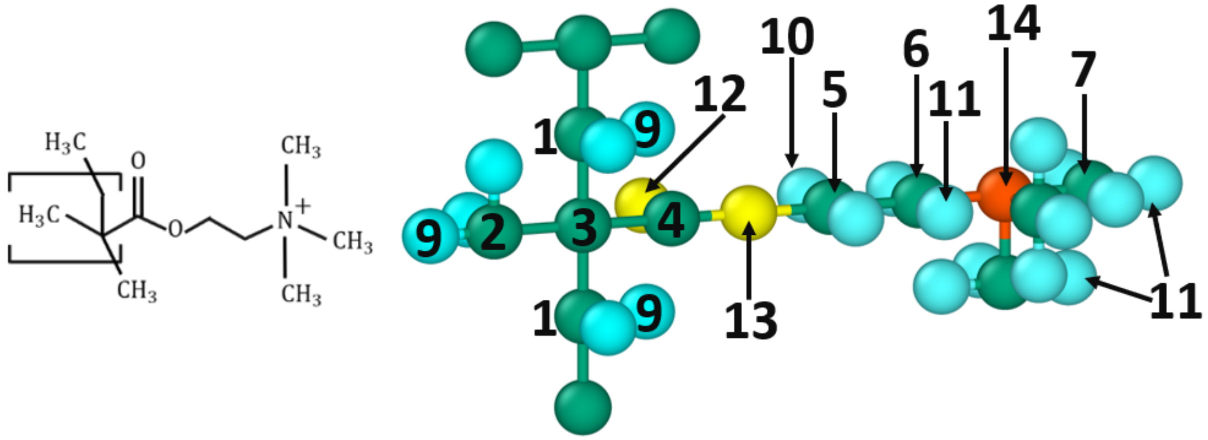

Figure S1. A partial schematic representation of the fully ionized PMETAC molecule. Definition of these atoms and their parameters have been provided in table S1.

Nonbonded Potentials and Corresponding Parameters

We have used the OPLS-AA [1] force field to model the PMETAC molecules and used the parameters from Joung *et al.* [2] for calculating the potentials for the counterions.

The Lennard-Jones (LJ) potential (U_{LJ}) used in the simulations is:

$$U_{LJ} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], \quad \text{(S1)}$$

while the Coulombic pairwise interaction (U_{Coul}) used in the simulation is:

$$U_{Coul} = \frac{q_i q_j}{4\pi\in_0\in_1 r_{ij}}. \quad \text{(S2)}$$

In these equations, ϵ_{ij} is the depth of the LJ potential well between atoms i and j, σ_{ij} is the distance between atoms i and j, q_i and q_j are charges of the i^{th} and j^{th} atoms respectively, r_{ij} is the distance between atoms i and j, $\in_0$ is the permittivity of a vacuum and $\in_1$ the relative permittivity of the background (used as 1). The geometric mixing rules were used for calculating the LJ interactions between dissimilar atoms, except for the mobile ion-ion and ion-water interactions. For these ion-ion and ion-water interactions, we used Lorentz-Berthelot mixing rules to be consistent with the paper of Joung *et al.* [2]. We have used VMD [3] and Gromacs [4] (when not found in VMD) database for obtaining the OPLS parameters.

The values for these parameters [needed for eqs.(S1,S2)] for all atom types, shown in Fig. S1, have been summarized in Table S1.

Atom Type	**Charge (e)**	**Mass (amu)**	**ϵ (Kcal/mole)**	**σ** (Å)
1 ; C1	-0.12	12.011	0.066	3.50
2 ; C2	-0.18	12.011	0.066	3.50
3 ; C3	0.0	12.011	0.066	3.50
4 ; C4	0.51	12.011	0.105	3.75
5 ; C5	0.19	12.011	0.066	3.50
6 ; C6	0.05	12.011	0.066	3.50
7 ; C7	-0.05	12.011	0.066	3.50
8 ; end carbon	-0.18	12.011	0.066	3.50
9 : H1	0.06	1.008	0.030	2.50
10 ; H2	0.03	1.008	0.015	2.42
11 : H3	0.1	1.008	0.030	2.50
12 ; O1	-0.430	15.999	0.210	2.960
13 ; O2	-0.330	15.999	0.170	3.000
14 ; N	0.0	14.007	0.170	3.250
O_w (H_2O)	-0.8476	15.999	0.155354	3.166
H_w (H_2O)	0.4238	1.008	0	0
Cl	-1.00	35.453	0.012785	4.83
Continuous LJ Wall (Parameters remain unchanged for	0.00	15.00794	0.1947	3.00 (LJ cut off length is 3.36 Å)

interaction with all atom types)				

Table S1: Charge, mass and LJ parameters for all the different atom types shown in Fig. S1.

Bonded Potentials and Corresponding Parameters

Harmonic bond style is used to calculate the potential energy for bond which expressed as:

$$U_{bond} = K_b(r - r_0)^2. \qquad \text{(S3)}$$

Here, r_0 is the equilibrium bond length and K_b is the bond stiffness. The values for r_0 and K_b for all bond types are given in Table S2.

Bond Type **(Participating atoms)**	$\boldsymbol{K_b}, (\frac{\boldsymbol{Kcal}}{\boldsymbol{mol.}\text{Å}^{\boldsymbol{2}}})$	$\boldsymbol{r_0}$, (Å)
1_9	340	1.09
1_3	268	1.529
2_3	268	1.529
2-9	340	1.09
3_4	317	1.522
4_12	570	1.229
4-13	214	1.327
5_13	320	1.41
5_6	268	1.529
5_10	340	1.09
6-11	340	1.09

6_14	367	1.471
7-14	367	1.471
7_11	340	1.09
8-3	268	1.529
8_9	340	1.09
15-16	0	1

Table S2: Bond parameters used in the simulations

The potential energy for the angle between different bonds is calculated using the following harmonic equation:

$U_{angle} = K_a(\theta - \theta_0)^2$. (S4)

Here, θ_0 is the equilibrium value of the angle and K$_a$ is the angle stiffness. The values for θ_0 and K$_a$ for different angles are provided in Table S3.

Angle Type	$\boldsymbol{K_{a}}, (\frac{\boldsymbol{Kcal}}{\boldsymbol{mol.rad^2}})$	$\boldsymbol{\theta_0(deg)}$
9_1_9	33	107.8
9_1_3	37.5	110.7
9_8_9	33	107.8
9_8_3	37.5	110.7
1_3_2	58.35	112.7
1_3_1	58.35	112.7
3_1_3	58.35	112.7

1_3_4	63	111.1
2_3_4	63	111.1
8_3_2	58.35	112.7
8-3_1	58.35	112.7
8_3_4	63	111.1
9-2_3	37.5	110.7
9-2_9	33	107.8
3_4_12	80	120.4
3-4-13	81	111.4
12_4_13	83	123.4
4_13-5	83	116.9
10_5_13	35	109.5
6_5_13	50	109.5
10_5_10	33	107.8
10_5_6	37.5	110.7
5_6_11	37.5	110.7
5_6_14	80	111.2
11_6_14	35	109.5
6_14_7	50	113
11_6_11	33	107.8
11_7_11	33	107.8
11_7_14	35	109.5

7_14_7	50	113
16_15_16	0	109.47

Table S3: Angle parameters used in the simulations

The potential energy for the 4-atom dihedral torsion interactions is given by

$$U_{dihedral} = \frac{1}{2}K_1[1+\cos(\emptyset)] + \frac{1}{2}K_2[1-\cos(2\emptyset)] + \frac{1}{2}K_3[1+\cos(3\emptyset)] + \frac{1}{2}K_4[1-\cos(4\emptyset)]. \qquad \text{(S5)}$$

Here, K_1, K_2, K_3 and K_4 are the four Fourier coefficients for torsional interactions, and $\emptyset$ is the torsional angle. Values of K_1, K_2, K_3 and K_4 are provided in Table S4.

Dihedral type	$\boldsymbol{K_1}$, $(\boldsymbol{Kcal/mole})$	$\boldsymbol{K_2}$, $(\boldsymbol{Kcal/mole})$	$\boldsymbol{K_3}$, $(\boldsymbol{Kcal/mole})$	$\boldsymbol{K_4}$, $(\boldsymbol{Kcal/mole})$
009_001_003_001	0	0	0.3	0
009_001_003_002	0	0	0.3	0
009_008_003_001	0	0	0.3	0
009_008_003_002	0	0	0.3	0
009_001_003_004	0	0	-0.076	0
009_008_003_004	0	0	-0.076	0
001_003_001_003	1.3	-0.05	0.2	0
001_003_002_009	0	0	0.3	0
001_003_004_012	-0.2777	1.228	-0.694	0
001_003_004_013	0	0	-0.553	0
008_003_001_003	1.3	-0.05	0.2	0

008_003_002_009	0	0	0.3	0
008_003_004_012	-0.2777	1.228	-0.694	0
008_003_004_013	0	0	-0.553	0
009_002_003_004	0	0	-0.076	0
002_003_004_012	-0.2777	1.228	-0.694	0
002_003_004_013	0	0	-0.553	0
002_003_001_003	1.3	-0.05	0.2	0
003_001_003_004	-1.697	-0.456	0.585	0
003_004_013_005	4.669	5.124	0	0
012_004_013_005	0	5.124	0	0
04_013_005_010	0	0	0.198	0
004_013_005_006	-1.22	-0.126	0.422	0
013_005_006_011	0	0	0.468	0
013_005_006_014 (from ref. 4)	1.2997	-0.05	0.2	0
010_005_006_011	0	0	0.3	0
010_005_006_014	0	0	0.384	0
005_006_014_007	1.4379	-0.1238	0.2639	0
011_006_014_007	0	0	0.3017	0
011_007_014_007	0	0	0.3017	0
006_014_007_011	0	0	0.3017	0
009_001_003_008	0	0	0.3	0

Table S4: Dihedral parameters used in the simulations

The potential energy for the improper torsional dihedrals is calculated by using the harmonic function:

$U_{improper} = K_i(\varphi - \varphi_0)^2$.   (S6)

Here, φ_0 represents the equilibrium value of the improper torsional angle and K_i is the improper torsional stiffness. Their values for the C1-O-C-O system is provided in Table S6.

Improper Type	$\boldsymbol{K_i}\ (\frac{\boldsymbol{Kcal}}{\boldsymbol{mol.rad^2}})$	$\boldsymbol{\varphi_0(deg)}$
4-13-3-12	10.5	180

Table S5: Improper dihedral parameters used in the simulations

S2. Water Density:

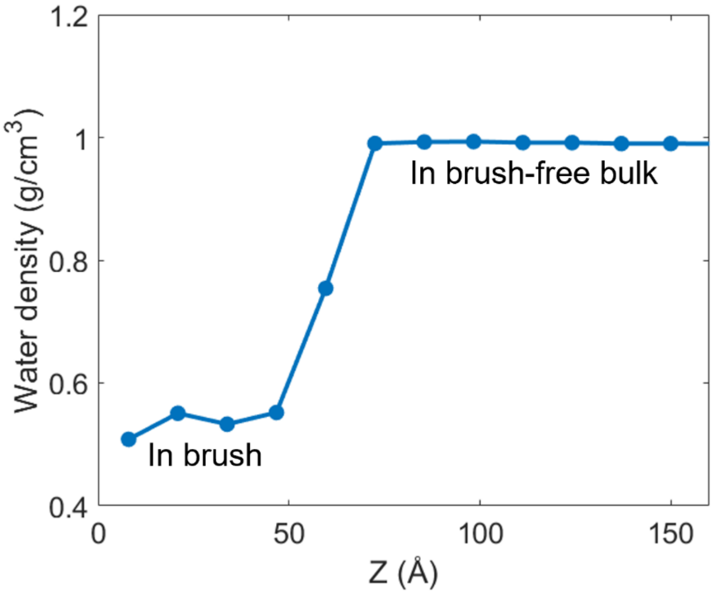

Figure S2. Density of water along simulation box.

References:

1. Jorgensen, W.L.; Maxwell, D.S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. J. Am. Chem. Soc. 1996, 118, 11225–11236.
2. Joung, I.S.; Cheatham, III, T.E. Determination of Alkali and Halide Monovalent Ion Parameters for use in Explicitly Solvated Biomolecular Simulations. J. Phys. Chem. B. 2008, 112, 9020–9041.
3. https://github.com/thatchristoph/vmd-cvs-github/tree/master/plugins/bossconvert
4. https://github.com/gromacs/gromacs/tree/main/share/top/oplsaa.ff