Molecular Dynamics of Poly(L-lysine) Dendrimers with Naphthalene Disulfonate Caps

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Figure S1. (a) The aryl sulfonate group. The atoms for which we created parameters for are shown as **A**, **B** and **C**. (b) The benzhydrylamide group. The atoms for which we created parameters are shown as **D**, **E** and **F**.

Table S1: Symbols used to represent atom types other than the atoms **A**–**F**.

Symbol	Description
C_{am}	an amide carbonyl carbon atom
C_{ar}	an aromatic carbon atom
N_{am}	an amide nitrogen atom
O_{am}	an amide carbonyl oxygen atom
R	an aliphatic carbon atom
X	any atom

Table S2. Non-bonding parameters for the aromatic sulfonate atoms **A**–**C**. The charges *q*(Imp) are those we have implemented in the OPLS-AA force field.

Atom	*q*(MMFF94) (e)	*q*(RESP) (e)	*q*(Imp) (e)	σ(Å)	ε (kcal mol^{-1})
A	-0.009[a]	-0.238	0.000	3.550	0.070
B	1.459	1.632	1.400	3.550	0.250
C	-0.817	-0.798	-0.800	2.960	0.170

[a] -0.008 was used in verification steps due to rounding.

Table S3. Non-bonding parameters for the benzhydrylamide parameters **D**–**F**.

Atom	*q*(IMP) (e)	σ(Å)	ε (kcal mol^{-1})
D	0.200	3.500	0.066
E	0.100	2.420	0.015
F	-0.050	3.550	0.070

Table S4: Bond stretching parameters for the sulfonate and benzhydrylamide groups.

Bond	K_r (kcal mol^{-1} Å^{-2})	r_0 (Å)
A-C_{ar}	469	1.40
A-**B**	340	1.77
B-**C**	700	1.44
D-**E**	340	1.09
D-**F**	317	1.51
F-C_{ar}	469	1.40

Table S5: Angle bending parameters for the sulfonate and benzhydrylamide groups.

Angle	K_θ (kcal mol^{-1} °$^{-2}$)	θ_0 (°)
C_{ar}-**A**-**B**	85.0	119.40
A-**B**-**C**	74.0	107.20
E-**D**-N_{am}	35.0	109.50
F-**D**-**E**	35.0	109.50
F-**D**-N_{am}	80.0	111.20
C_{ar}-**F**-**D**	70.0	120.00

Table S6: Fourier coefficients (kcal mol^{-1}) for torsions in the sulfonate and benzhydrylamide groups.

Torsion	V_1	V_2	V_3	V_4
X-C_{ar}-C_{ar}-**A**	0.000	7.250	0.000	0.000
X-C_{ar}-**A**-**B**	0.000	7.250	0.000	0.000
C_{ar}-**A**-**B**-**C**	0.000	0.000	0.000	0.000
C_{ar}-**F**-**D**-**F**	0.000	0.000	0.000	0.000
C_{ar}-**F**-**D**-**E**	0.000	0.000	0.000	0.000
C_{ar}-**F**-**D**-N_{am}	0.000	0.000	0.000	0.000
X-C_{ar}-**F**-**D**	0.000	7.250	0.000	0.000
X-C_{ar}-C_{ar}-**F**	0.000	7.250	0.000	0.000
H-N_{am}-**D**-**E**	0.000	0.000	0.000	0.000
H-N_{am}-**D**-**F**	0.000	0.000	0.000	0.000
C_{am}-N_{am}-**D**-**E**	0.000	0.000	-0.139	0.000
C_{am}-N_{am}-**D**-**F**	-2.365	0.912	-0.850	0.000
O_{am}-C_{am}-N_{am}-**D**	0.000	6.089	0.000	0.000
R-C_{am}-N_{am}-**D**	2.300	6.089	0.000	0.000

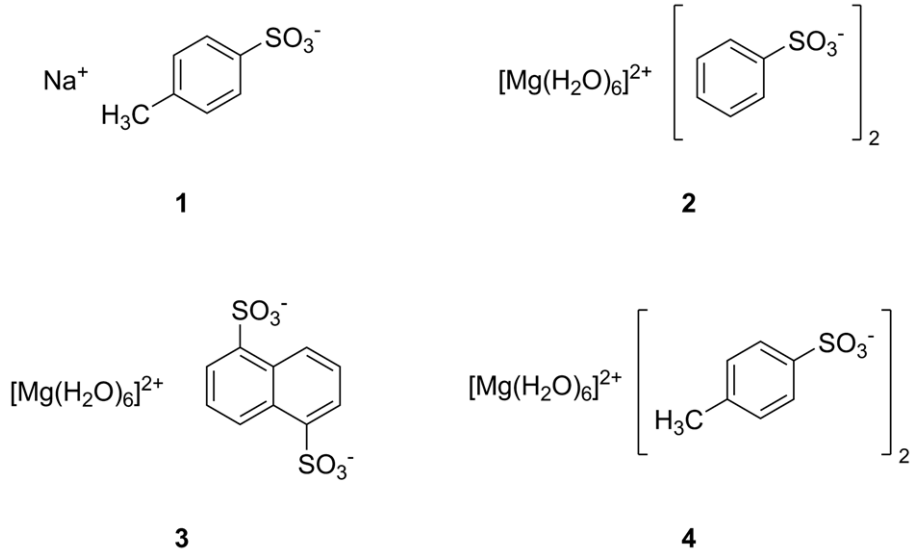

Figure S2: Compounds used to verify aromatic sulfonate parameters.

Table 1: Verification of aromatic sulfonate parameters. Comparison of unit cell dimensions and root mean squared deviations of the compounds **1**–**4** from their reference geometries using MMFF94 charges, RESP charges and implemented charges.

Compound	Parameter set	Unit Cell Dimensions[a]					RMSD
		a (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å^3)	
1	*Reference structure*	*15.4030*	*6.1090*	*8.5360*	*92.7400*	*802.293*	
	Implemented	14.8554	5.9027	8.1009	93.5165	709.006	0.2288
	(% diff.)	3.56%	3.38%	5.10%	0.837%	11.63%	
	MMFF94	14.8685	5.8982	8.0961	93.4950	708.686	0.2273
	(% diff.)	3.47%	3.45%	5.15%	0.814%	11.67%	
	RESP	14.5522	6.0190	8.1653	95.3347	712.098	0.2959
	(% diff.)	5.52%	1.47%	4.34%	2.80%	11.24%	
2	*Reference structure*	*22.6000*	*6.3200*	*6.9400*	*93.6000*	*989.298*	
	Implemented	22.0598	6.0002	6.5992	92.1517	872.875	0.2366
	(% diff.)	2.39%	5.06%	4.91%	1.55%	11.77%	
	MMFF94	21.8889	5.9553	6.6970	90.7697	872.908	0.6411
	(% diff.)	3.15%	5.77%	3.50%	3.02%	11.76%	
	RESP	21.7133	6.0638	6.6813	90.8101	879.606	0.3315
	(% diff.)	3.92%	4.05%	3.73%	2.98%	11.09%	
3	*Reference structure*	*13.1955*	*6.6981*	*9.6616*	*92.3040*	*853.248*	
	Implemented	12.4912	6.3055	10.9927	84.0788	861.202	0.5710
	(% diff.)	5.34%	5.86%	13.8%	8.91%	0.9322%	
	MMFF94	12.4959	6.2957	11.0051	84.0200	861.065	0.5753
	(% diff.)	5.30%	6.01%	13.91%	8.97%	0.9161%	
	RESP	11.4532	6.7637	11.5757	83.0403	890.116	0.9697
	(% diff.)	13.2%	0.979%	19.8%	10.0%	4.321%	
4	*Reference structure*	*6.9481*	*6.2809*	*25.3600*	*91.7720*	*1106.19*	
	Implemented	6.5821	5.9996	24.7537	89.7213	977.511	0.2648
	(% diff.)	5.27%	4.48%	2.39%	2.23%	11.63%	
	MMFF94	6.5839	5.9888	24.7482	89.7266	975.802	0.2665
	(% diff.)	5.24%	4.65%	2.41%	2.23%	11.79%	
	RESP	6.6810	6.0667	24.4491	87.7918	990.226	0.4017
	(% diff.)	3.84%	3.41%	3.59%	4.34%	10.48%	

[a] The internal angles α and γ remain constant at 90°.

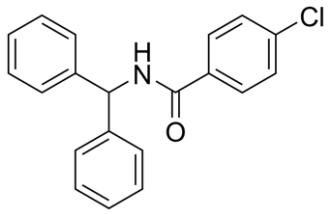

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Figure S3: The compound used to verify parameters for the benzhydrylamide group.

Table 2: Verification of parameters for the benzhydrylamide group. Alteration of unit cell dimensions and root mean squared deviation of the compound **5** from its reference geometry using implemented charges.

Compound	Parameter set	Unit Cell Dimensions[a]					RMSD
		a (Å)	*b* (Å)	*c* (Å)	β	*V* (Å^3)	
5	*Reference structure*	26.3540	5.1630	23.6540	91.2000	3217.79	
	Implemented	26.1000	4.9710	23.9485	89.2608	3106.89	0.2509
	(% diff.)	0.964%	3.72%	1.25%	2.13%	3.45%	

[a] The internal angles α and γ remain constant at 90°.

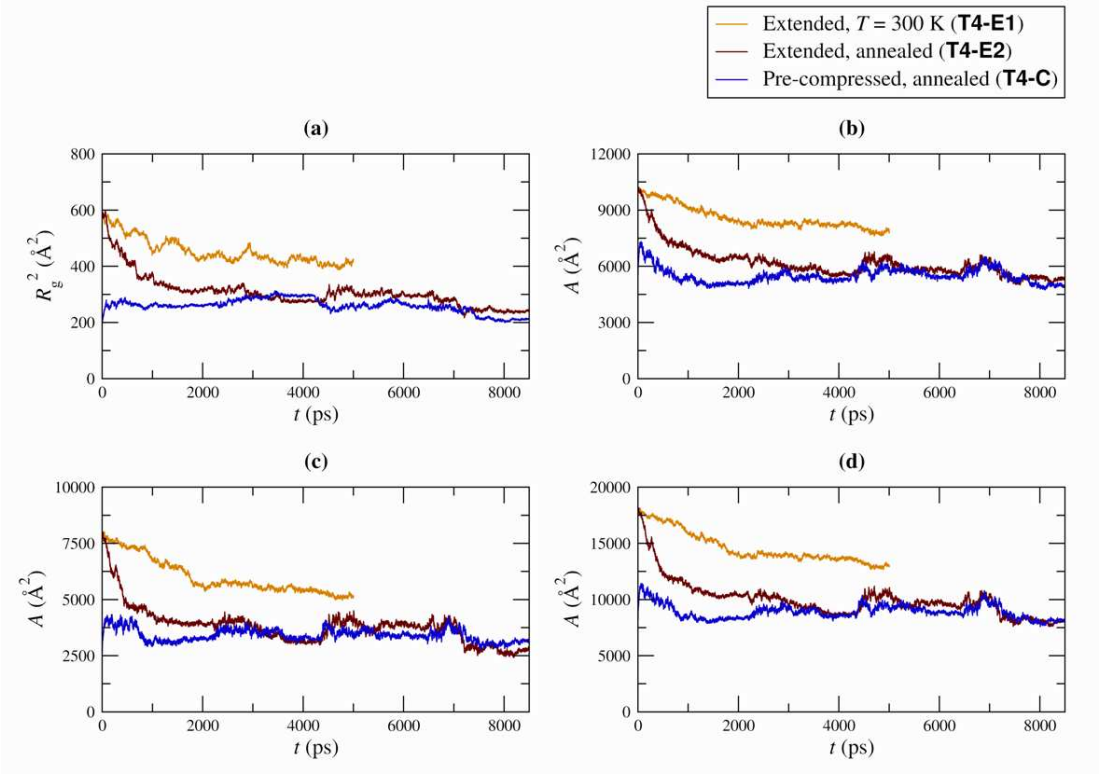

Figure S4: Comparison of dendrimer sizes over three different equilibration protocols. (a) Mean-squared radius of gyration. (b) Polar solvent-accessible surface area. (c) Non-polar solvent-accessible surface area. (d) Total solvent-accessible surface area.

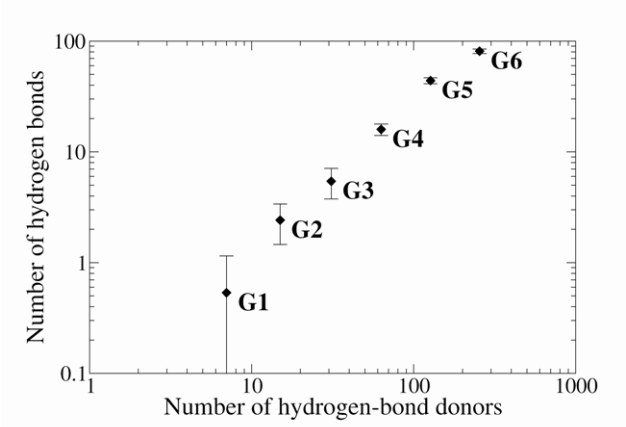

Figure S5: Number of hydrogen bonds in the simulated dendrimers. Error bars indicate one standard deviation each side of the mean.

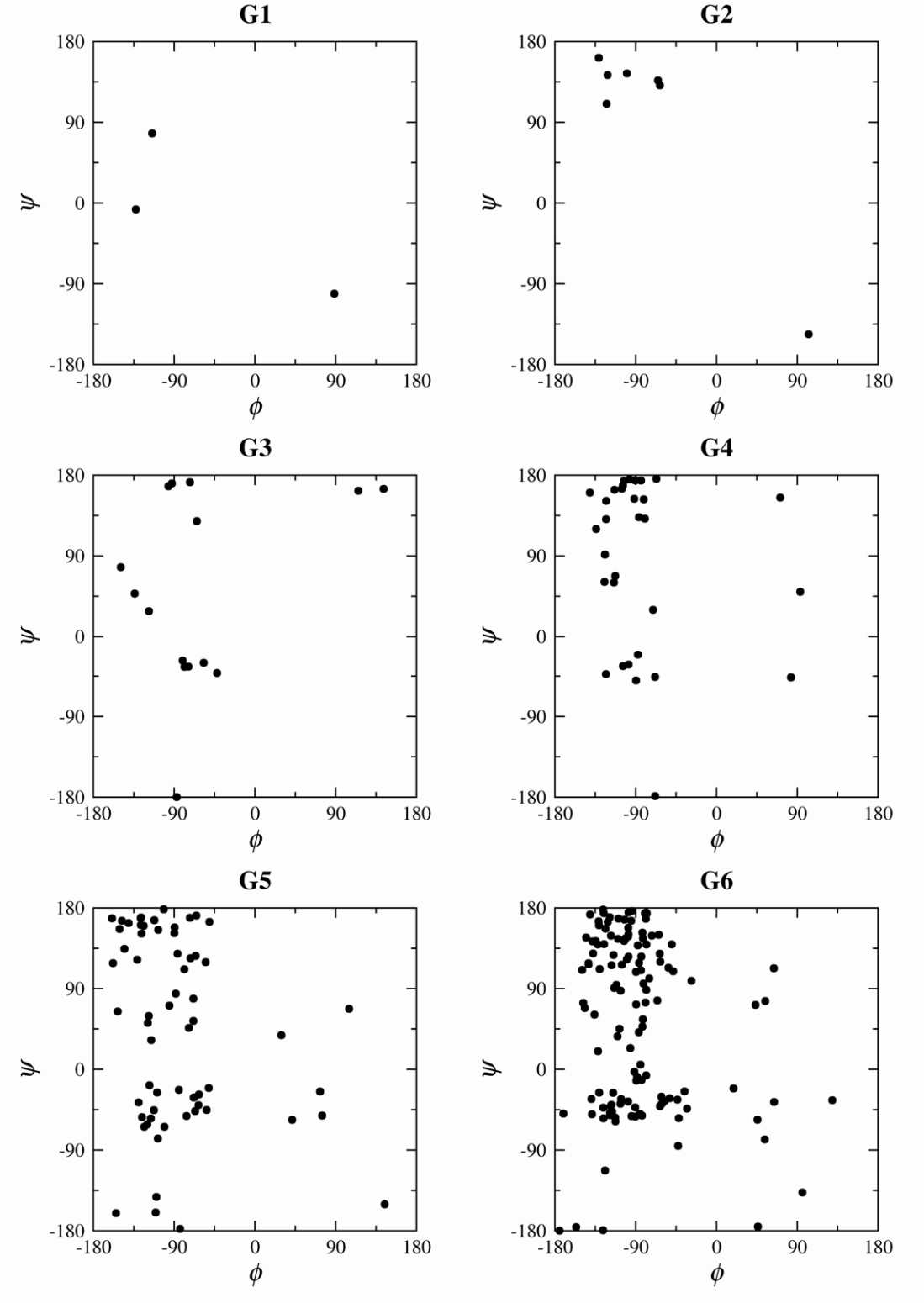

Figure S6: Ramachandran plots of dendrimers G1 to G6 at the final frames of the simulations.

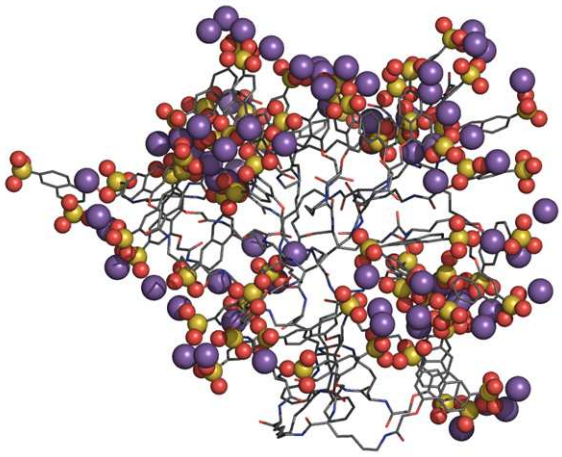

Figure S7: The final frame of the simulation of G4, showing all sodium ions within 4 Å of any dendrimer atom (except hydrogen atoms). Sodium ions are shown as purple spheres. Sulfonate groups are shown as yellow spheres (sulphur) and red spheres (oxygen).

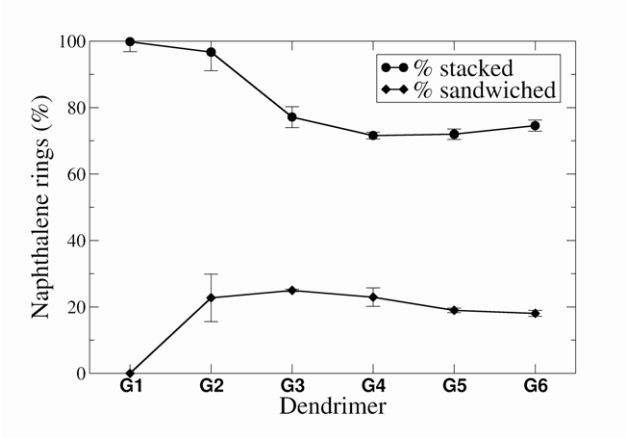

Figure S8: Average extent of stacking and sandwiching in the dendrimers **G1** to **G6**. Error bars are one standard deviation either side of the mean. The lines between points are shown to guide the eye.