Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Conformations of Poly(propylene imine) Dendrimers in an Ionic Liquid at Different pH

Shilpa Gupta and Parbati Biswas*

Department of Chemistry, University of Delhi, Delhi-110007, India

*E-mail: pbiswas@chemistry.du.ac.in

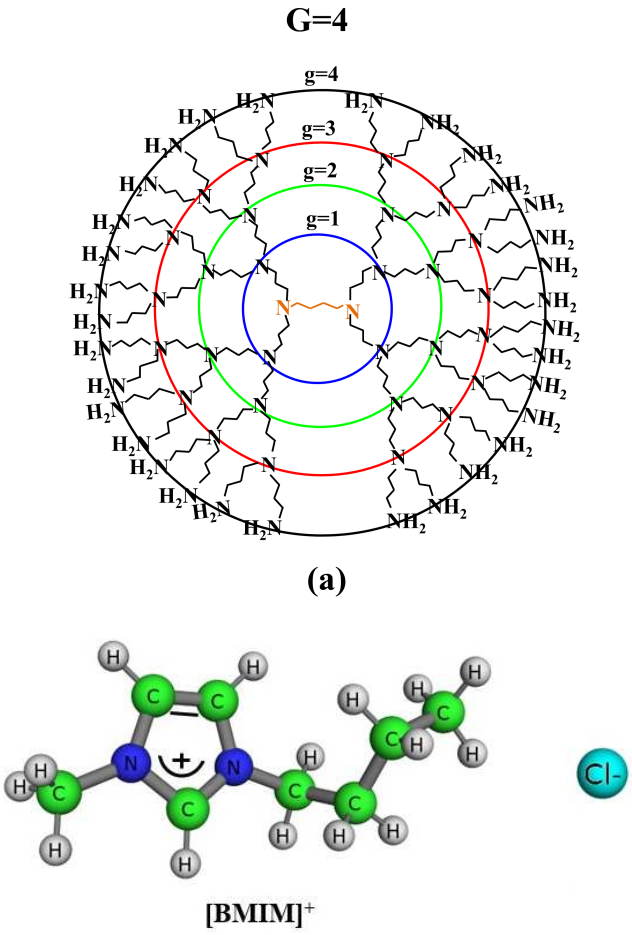

Figure S1: Chemical structure schematics of the (a) $G = 4$ PPI dendrimers and (b) 1-butyl-3-methylimidazolium chloride ([BMIM]Cl).

Table S1: Details of simulated systems for $G = 3$ to $G = 8$ PPI dendrimers in [BMIM]Cl.

Generation	pH	Number of Atoms in Dendrimer	Number of [BMIM]Cl ionic pair	Volume ($\AA^3$)	Dendrimer Charge	Number of Counterions
$G = 3$	High	326	300	$60 \times 60 \times 60$	0	0
	Neutral	346	450	$60 \times 60 \times 60$	20	20
	Low	356	450	$60 \times 60 \times 60$	30	30
$G = 4$	High	678	300	$60 \times 60 \times 60$	0	0
	Neutral	718	450	$70 \times 70 \times 70$	40	40
	Low	740	450	$70 \times 70 \times 70$	62	62
$G = 5$	High	1382	350	$70 \times 70 \times 70$	0	0
	Neutral	1466	550	$80 \times 80 \times 80$	84	84
	Low	1508	550	$80 \times 80 \times 80$	126	126
$G = 6$	High	2790	350	$70 \times 70 \times 70$	0	0
	Neutral	2958	600	$90 \times 90 \times 90$	168	168
	Low	3044	600	$90 \times 90 \times 90$	254	254
$G = 7$	High	5606	450	$80 \times 80 \times 80$	0	0
	Neutral	5946	650	$100 \times 100 \times 100$	340	340
	Low	6116	650	$100 \times 100 \times 100$	510	510
$G = 8$	High	11238	450	$80 \times 80 \times 80$	0	0
	Neutral	11918	650	$110 \times 110 \times 110$	680	680
	Low	12260	650	$110 \times 110 \times 110$	1022	1022

Table S2: Number of Cl^- counterions and solvent Cl^- ions calculated upto radius of gyration for generations $G = 3$ to $G = 8$ PPI dendrimers at high, neutral, and low pH (percentages are shown in brackets).

Generation	High pH (pH>12)	Neutral pH (pH∼7)	Low pH (pH<3)
$G = 3$	3(1%)	11(2%)	18(5%)
$G = 4$	0(0%)	27(5%)	11(2%)
$G = 5$	2(0.5%)	44(7%)	63(9%)
$G = 6$	1(0.3%)	47(6%)	131(15%)
$G = 7$	2(0.4%)	163(16%)	236(20%)
$G = 8$	1(0.2%)	302(23%)	473(28%)

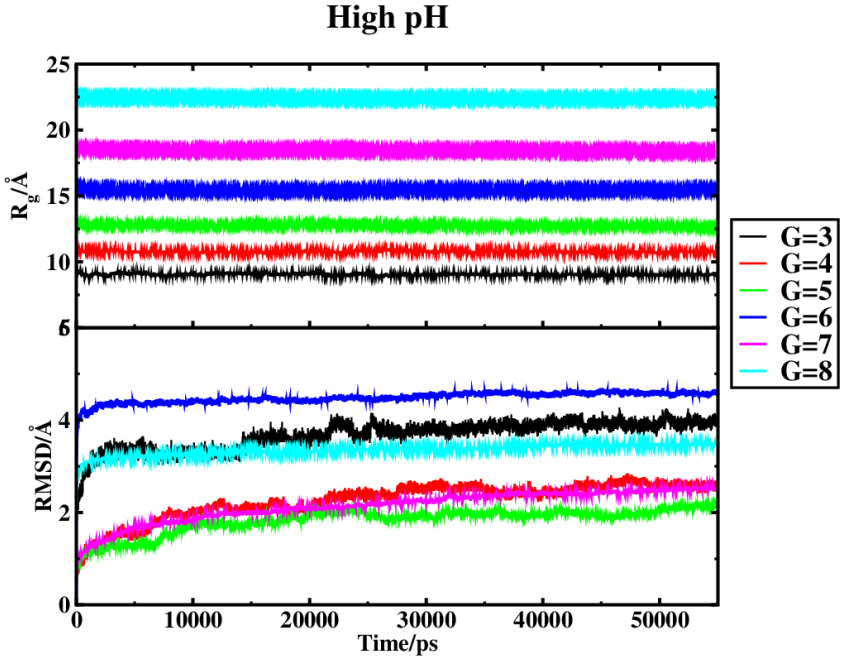

Figure S2: The radius of gyration (R_g) and the root-mean-square deviation (RMSD) of all atoms with respect to their initial structures (t=0) as a function of simulation time at high pH.

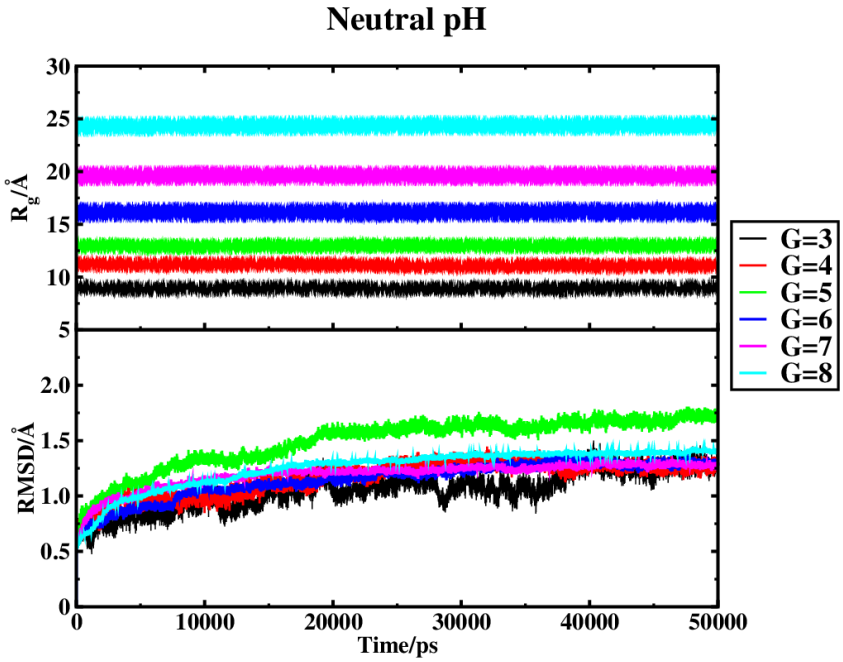

Figure S3: The radius of gyration (R_g) and the root-mean-square deviation (RMSD) of all atoms with respect to their initial structures (t=0) as a function of simulation time at neutral pH.

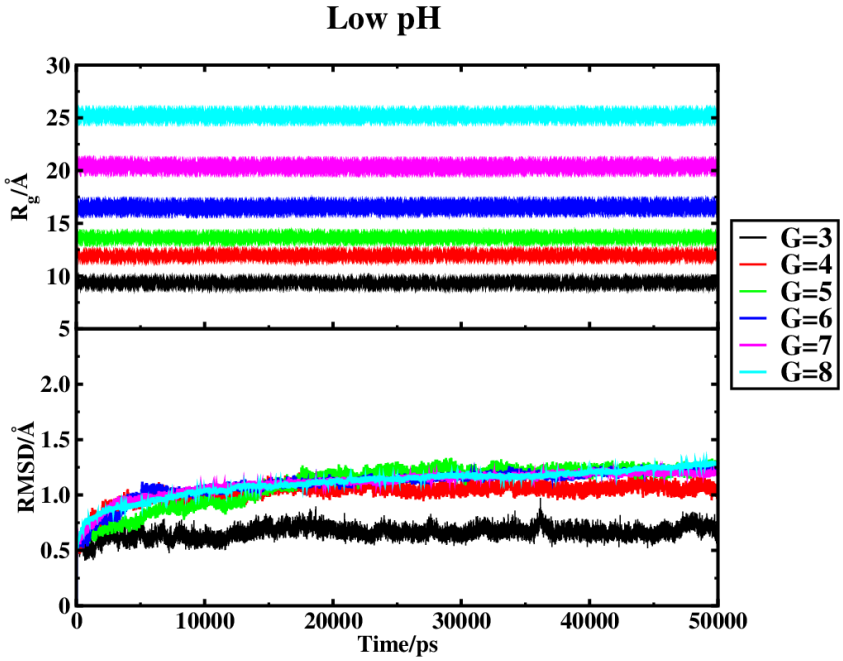

Figure S4: The radius of gyration (R_g) and the root-mean-square deviation (RMSD) of all atoms with respect to their initial structures (t=0) as a function of simulation time at low pH.

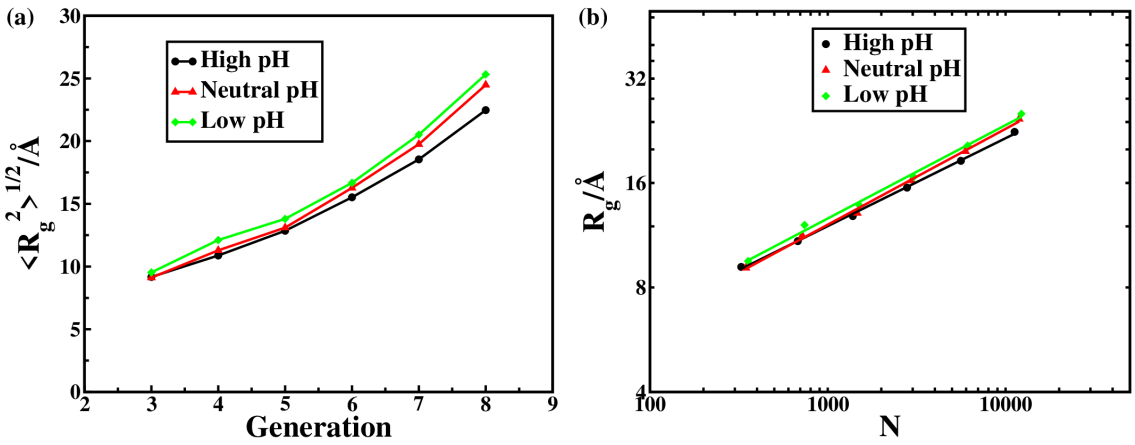

Figure S5: Radius of gyration of the DAB-dendr-$(NH_2)_x$ as a function of (a) the generations and (b) the total number of atoms in double logarithmic scales at all three pH conditions in [BMIM]Cl.

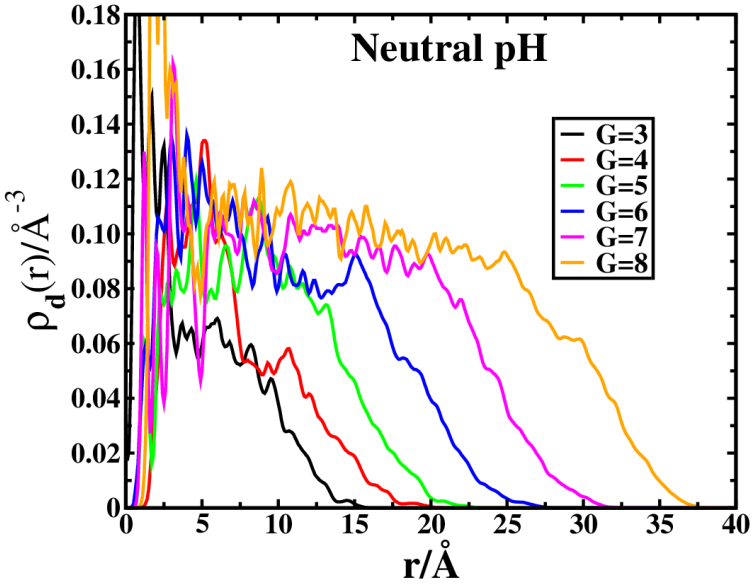

Figure S6: Radial atomic density distribution, $\rho_d(r)$ for the PPI dendrimers from generations $G = 3$ to $G = 8$ as a function of the distance, r from the center of mass at neutral pH in [BMIM]Cl.

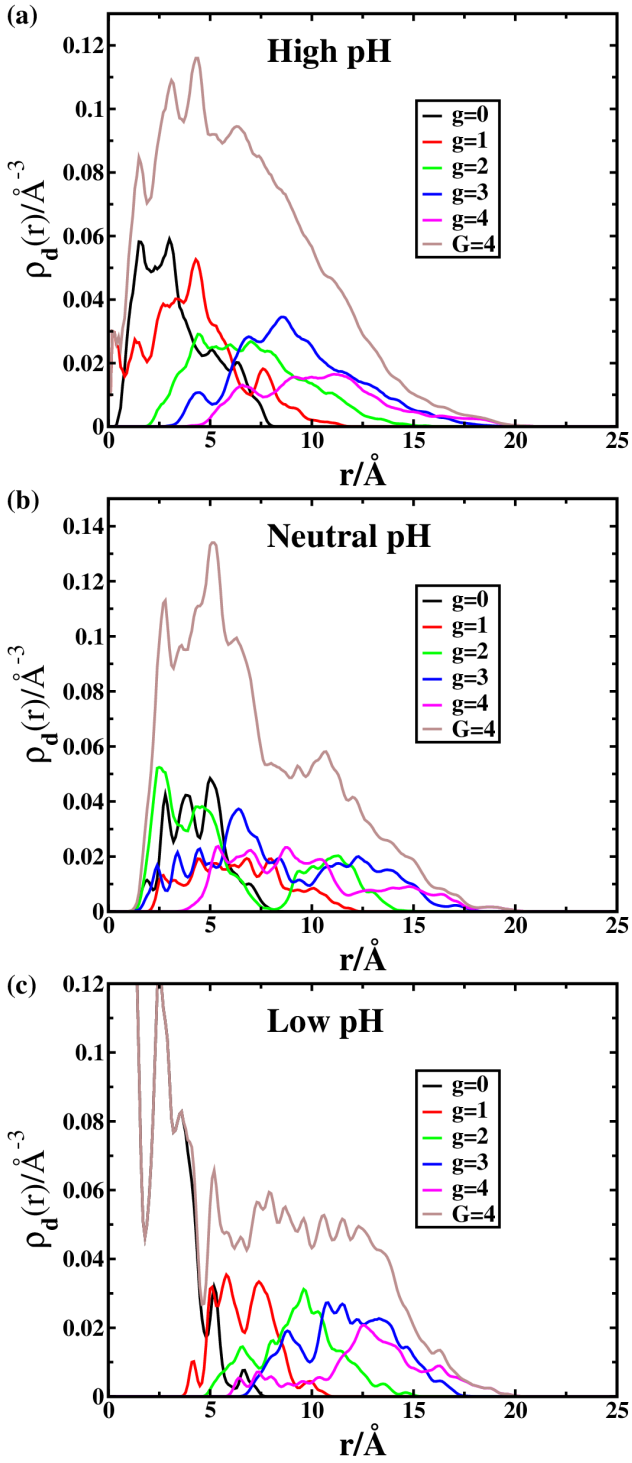

Figure S7: Plots of Radial atomic density versus the distance from the center of mass for each inner generations of $G = 4$ PPI dendrimers at (a) high pH, (b) neutral pH, and (c) low pH in [BMIM]Cl.

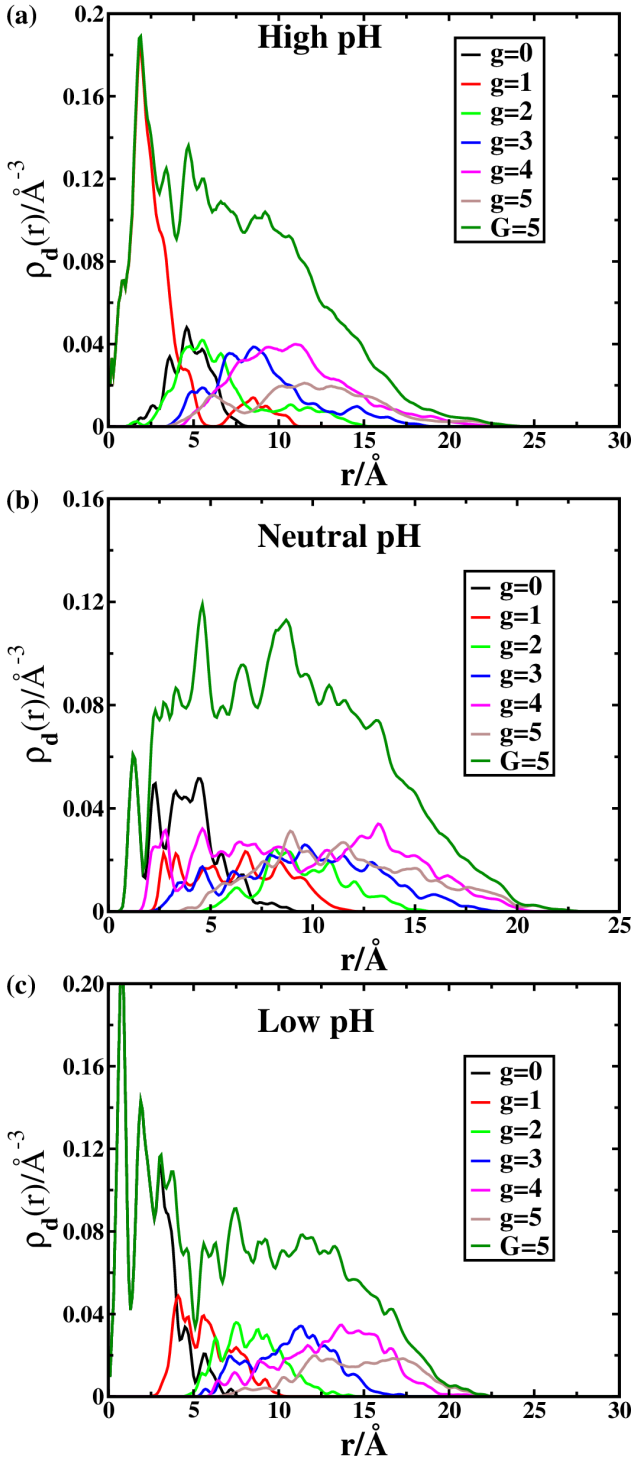

Figure S8: Plots of Radial atomic density versus the distance from the center of mass for each inner generations of $G = 5$ PPI dendrimers at (a) high pH, (b) neutral pH, and (c) low pH in [BMIM]Cl.

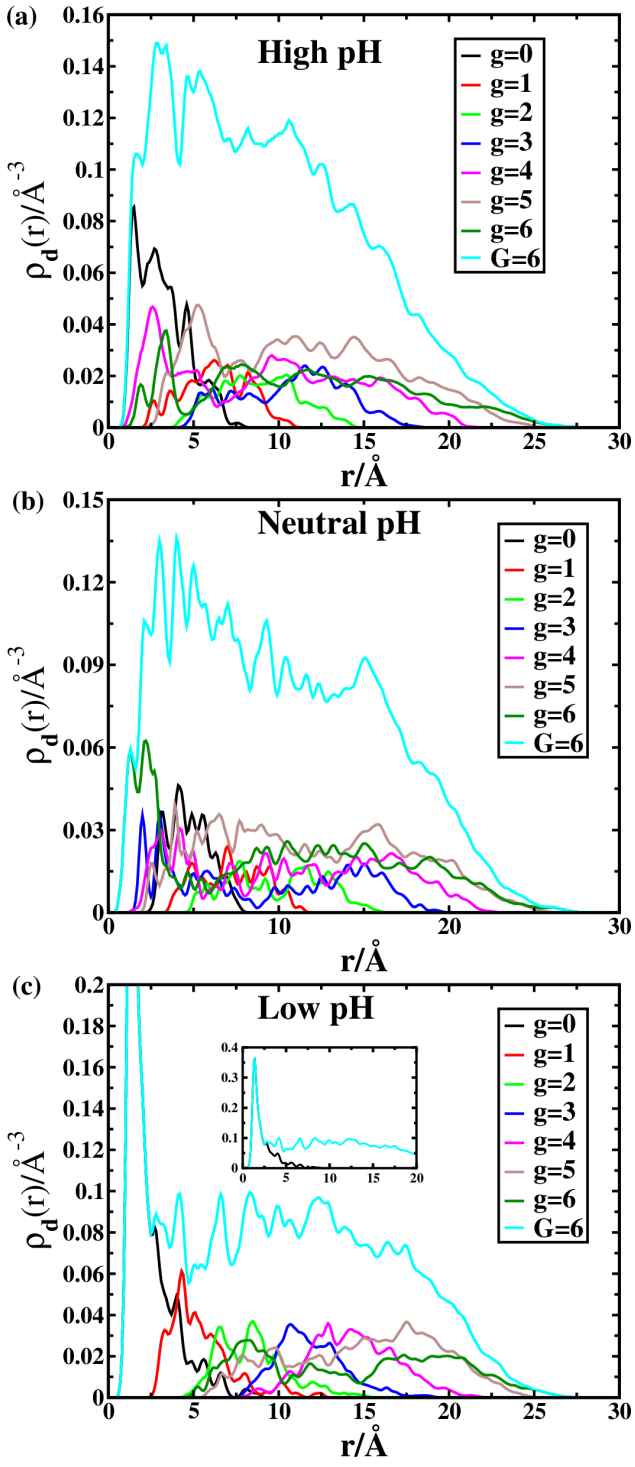

Figure S9: Plots of Radial atomic density versus the distance from the center of mass for each inner generations of $G = 6$ PPI dendrimers at (a) high pH, (b) neutral pH, and (c) low pH in [BMIM]Cl. The radial atomic density distribution for $G = 6$ and $g = 0$ at small r is shown in inset of Figure (c).

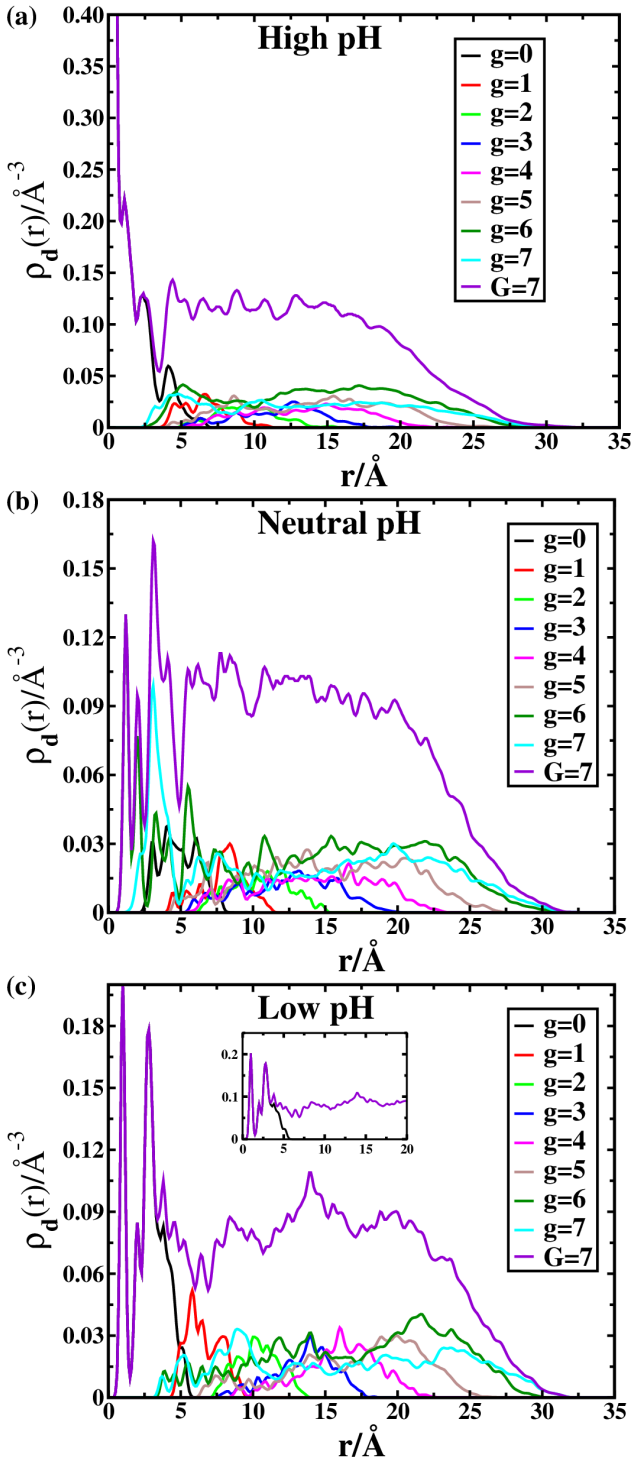

Figure S10: Plots of Radial atomic density versus the distance from the center of mass for each inner generations of $G = 7$ PPI dendrimers at (a) high pH, (b) neutral pH, and (c) low pH in [BMIM]Cl. The radial atomic density distribution for $G = 7$ and $g = 0$ at small r is shown in inset of Figure (c).

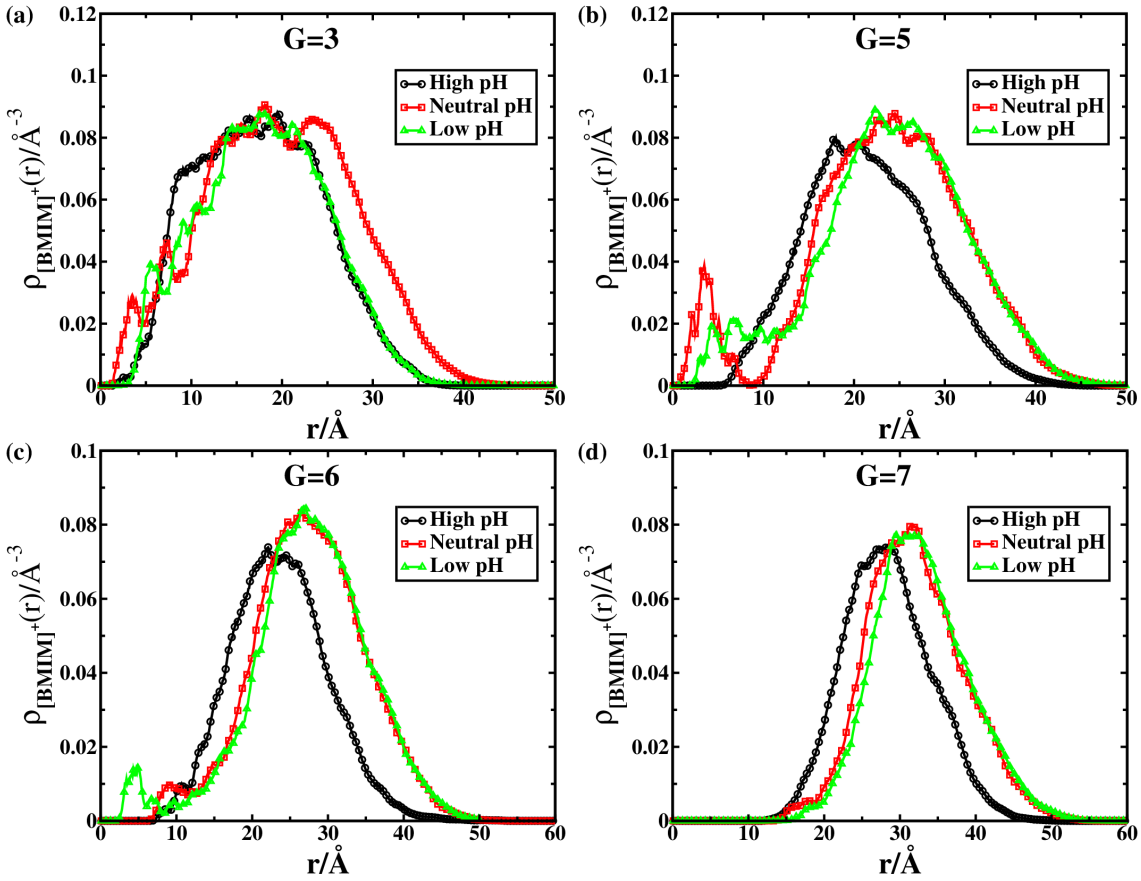

Figure S11: Radial density distribution of [BMIM] cations from the center of mass of the PPI dendrimer for (a) $G = 3$, (b) $G = 5$, (c) $G = 6$, and (d) $G = 7$ dendrimers.

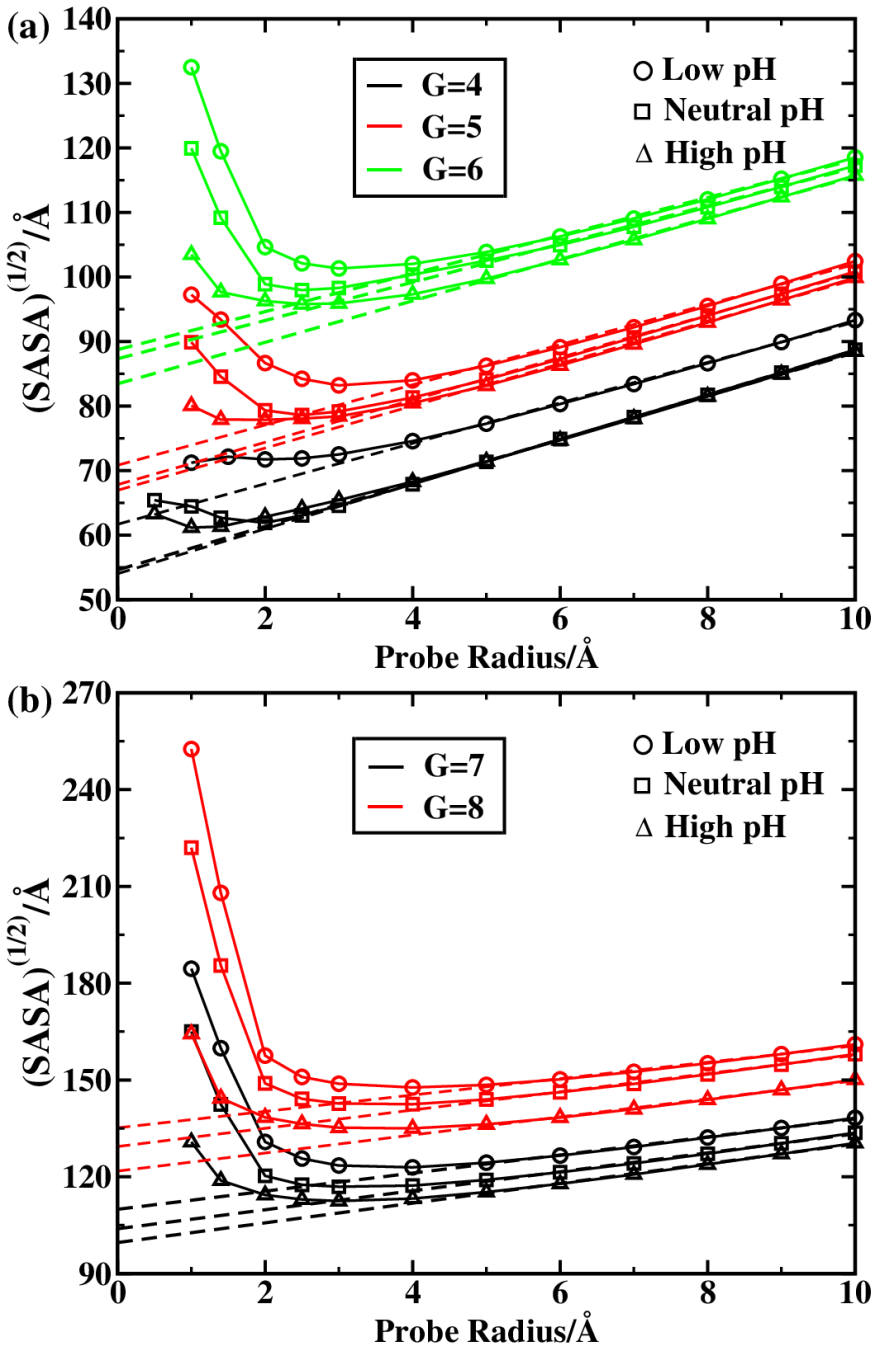

Figure S12: Solvent accessible surface area (SASA) for (a) $G = 4$ to $G = 6$ and (b) $G = 7$ and $G = 8$ are plotted as a function of probe radius at three different pH conditions.

Table S3: Solvent excluded volume (SEV), van der Waals volume, void volume, packing density, and percentage free space for $G = 3$ to $G = 8$ DAB-dendr-$(NH_2)_x$ in [BMIM]Cl.

Generation	pH	Solvent Excluded Volume ($Å^3$)	van der Waals Volume ($Å^3$)	Void Volume ($Å^3$)	Packing Density	Free Space/ Void Space (Percentage)
$G = 3$	High	2168.89	1857.22	311.67	0.856	14.4
	Neutral	2303.37	1914.64	388.74	0.831	16.9
	Low	2251.68	1937.38	314.30	0.860	14
$G = 4$	High	4782.98	3850.02	932.96	0.805	19.5
	Neutral	4886.56	3961.35	925.21	0.810	18.9
	Low	5352.50	4027.34	1325.16	0.752	24.7
$G = 5$	High	10145	7833.43	2311.57	0.772	22.8
	Neutral	11236	8095.31	3140.69	0.720	28
	Low	12422.17	8193.89	4228.28	0.659	34
$G = 6$	High	21182	15788.40	5393.60	0.745	25.5
	Neutral	24216	16309.70	7906.30	0.673	32.6
	Low	25109.70	16525.60	8584.10	0.658	34.2
$G = 7$	High	43678.30	31636	12042.30	0.724	27.6
	Neutral	51980.80	32764.30	19216.50	0.630	37
	Low	55380.50	33194.10	22186.40	0.599	40
$G = 8$	High	88308.50	63343	24965.5	0.717	28.3
	Neutral	105156	65433.70	39722.30	0.622	37.8
	Low	116143	66540.30	49602.70	0.573	42.7

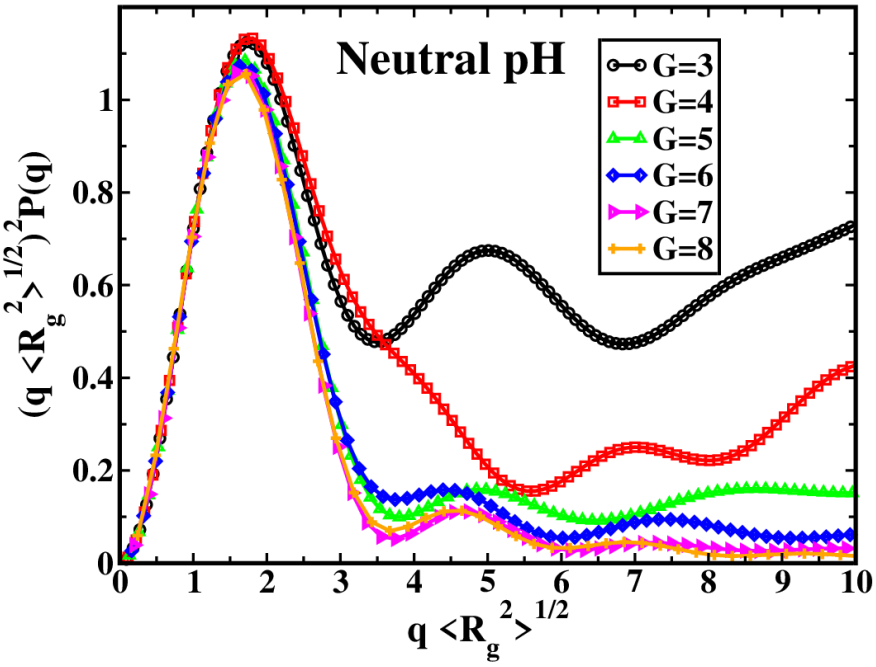

Figure S13: Kratky plot of the structure factor, $P(q)$, versus $q\langle {R_g}^2 \rangle^{\frac{1}{2}}$ at neutral pH.