Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Effect of PME Electrostatics

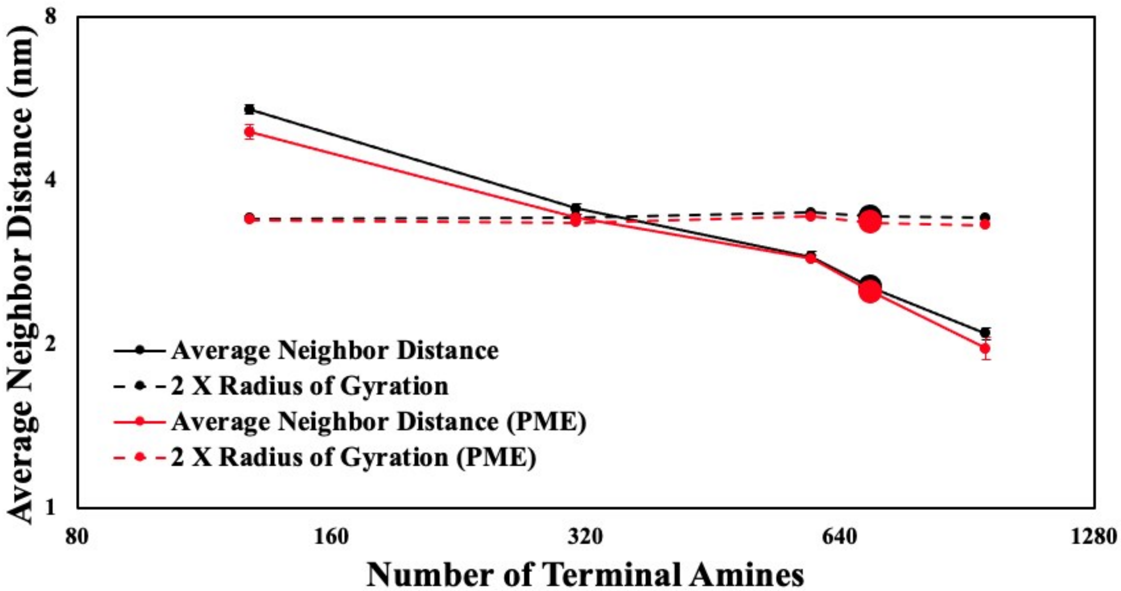


Figure S1: Average spacing of dendrons without PME electrostatics (black lines) and with PME electrostatics (red lines) are compared. The measurement has been conducted on G3 dendrons. The average spacing between dendron grafting points as a function of the number of terminal amines are shown using solid lines. An increase in terminal amines is equivalent to an increase in the relative concentration of the PDAs. The dotted lines denote twice the radius of gyration described by the terminal amines. Both axes are scaled using log of base 2. The enlarged data points represent the critical concentration limit corresponding to the dendron generation.

Equilibrated Bilayer

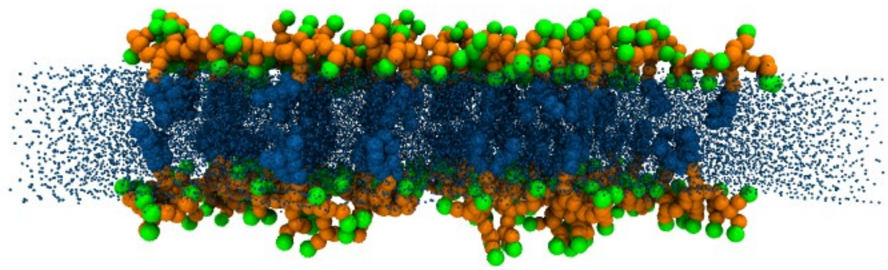


Figure S2. An equilibrated G3 PAMAM dendron-bilayer system has been shown. At this stage of model building, the edges of the bilayer are not exposed to solvent. Color scheme: Blue – DPPC lipids and alkyl tails of PAMAM dendrons, orange – amide groups and tertiary amines in PAMAM dendron branch and green – positively charged terminal amines.

Bilayer-to-Bicelle Transition

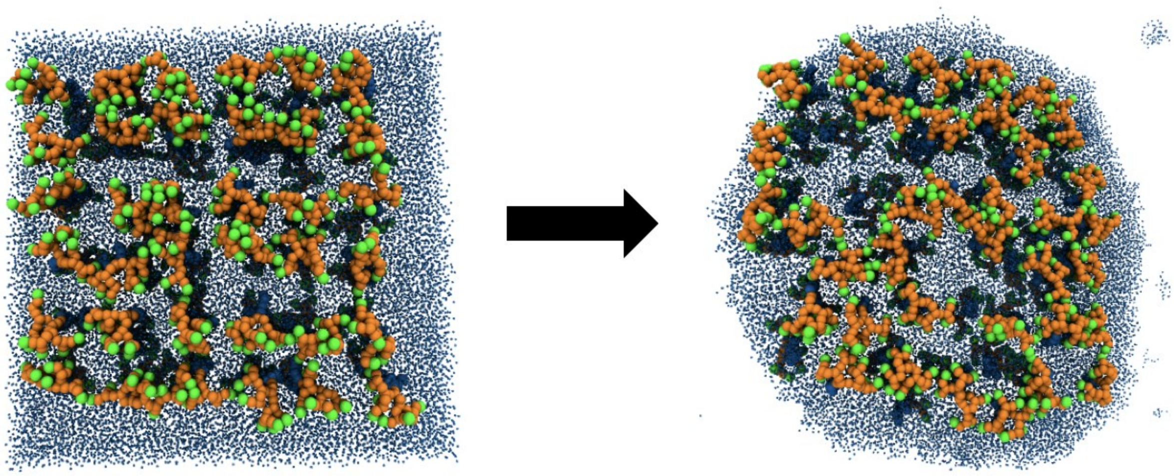
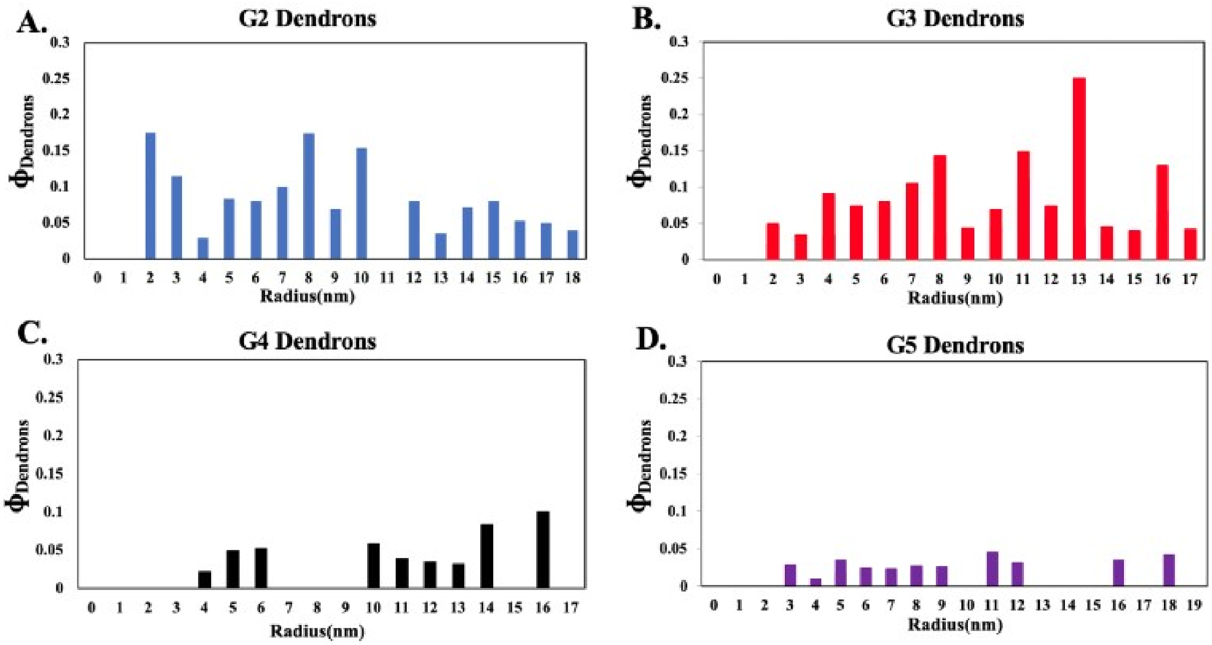


Figure S3. The top view of a bilayer (left) and a bicelle (right) have been shown. Color scheme: Blue – DPPC lipids and alkyl tails of PAMAM dendrons, orange – amide groups and tertiary amines in PAMAM Dendron branch and green – positively charged terminal amines.



E.

Dendron Generation	Average Position (nm)	Standard Deviation
G2	8.7	2.4
G3	10	2
G4	10.6	1.1

Migration of Dendrons towards Bicelle edge

Figure S4. The spatial distribution of dendrons have been plotted w.r.t the center of the bicelle (radius = 0 nm). A: G2 (small) dendrons; B and C: G3 and G4 (intermediate) dendrons; D: G5 (large) dendrons; E: The mean and standard deviations of the spatial distributions for G2, G3 and G4 dendrons.

We plot the spatial distribution of dendrons (Φ = number of dendrons/total number of dendrons and DPPC lipids at a distance from the center of the bicelle) along the radial direction of the bicelle. The complete population of dendrons is represented as a histogram. We note that the concentration of large dendrons (see Figure S4.D) is not significant enough to make any conclusions.

Figure S4.E shows the average position of dendrons on the bicelle. A higher value suggests that dendrons may be migrating towards the edge of the bicelle. We observe that larger dendron generations (for example: G3 and G4 dendrons) may have a tendency to migrate towards the edge of the bicelle. It is difficult to resolve this trend with certainty given the statistical variability in the results.

Asymmetric distribution of dendrons in the DV Bilayer

The process of membrane closing may generate asymmetric distributions of dendrons across the DV bilayer. The ratio between dendrons on the upper and lower monolayer is evaluated and termed as the asymmetric ratio. A value of 1 would indicate that the number of dendrons on both monolayers are the same. A value larger than 1 would mean that there are higher number of dendrons on the outer monolayer. A value less than one is rarely observed as the inner monolayer is volumetrically constrained. Table S1 highlights two interesting features:

1. The G2 and G3 dendrons have the same critical concentrations (5%). This seems to be non-intuitive as typically larger dendrons have lower critical concentrations. However, as the larger dendrons (G3) have a relatively symmetric distribution of dendrons (1.2), as compared to the smaller dendrons (G2). This means that DVs with G3 dendrons incur relatively lower asymmetric stresses, permitting incorporation of a higher number of dendrons without vesicle rupture.

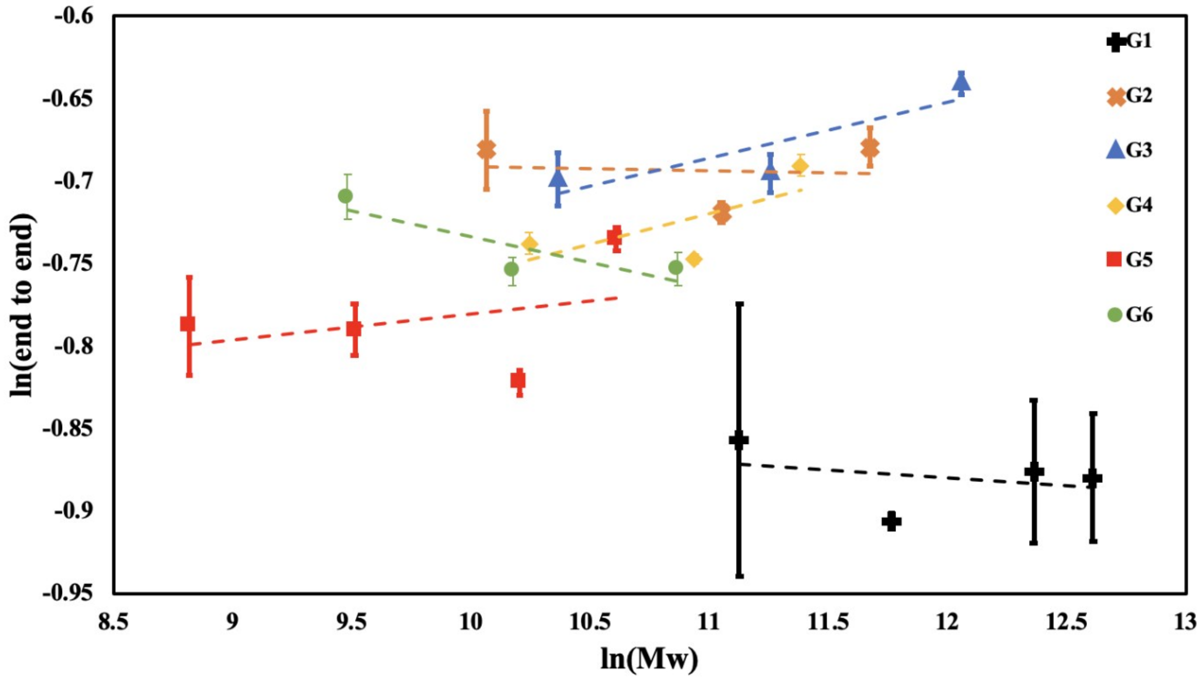
2. The values of asymmetric ratios for large dendrons (G5 and G6) do not have error bars. Due to an extremely low concentration of dendrons, the distribution of dendrons of the initial configuration (asymmetric ratio =1) is retained across every large dendron simulation.

Generation	**Asymmetric Ratio**
G1	1.3 ± 0.1
G2	1.6 ± 0.2

G3	1.2 ± 0.2
G4	1.02 ± 0.04
G5	1
G6	1

Table S1. The ratio of dendrons in the outer and lower monolayer in DV bilayers for each dendron generation. Asymmetric ratios have been averaged across all values of relative concentration for each generation.

Scaling Exponents for Qualitative comparison against Polymer Theory



1. Log (end-to-end distance) vs log (molecular weight of PAMAM dendron)

Figure S5. The normalized end-to-end distance between terminal amines and corresponding grafting points have been plotted against the total molecular weight of the dendrons. (Total molecular weight of dendrons = number of dendrons in the model × molecular weight of 1 dendron).

Generation	Scaling Exponent
G1	-0.01 ± 0.01
G2	-0.004 ± 0.002
G3	0.017 ± 0.002
G4	0.018 ± 0.001
G5	0.013 ± 0.005
G6	-0.024 ± 0.001

Table S2. The scaling exponent (mean ± standard error) of linear trendlines for all generations shown in Figure S5. The final 100 ns of trajectory data is extracted from 4 independent simulations and compiled into a single dataset. The mean and standard error of this dataset is reported in this table.

2. Log (dendron height) vs log (molecular weight of PAMAM dendron)

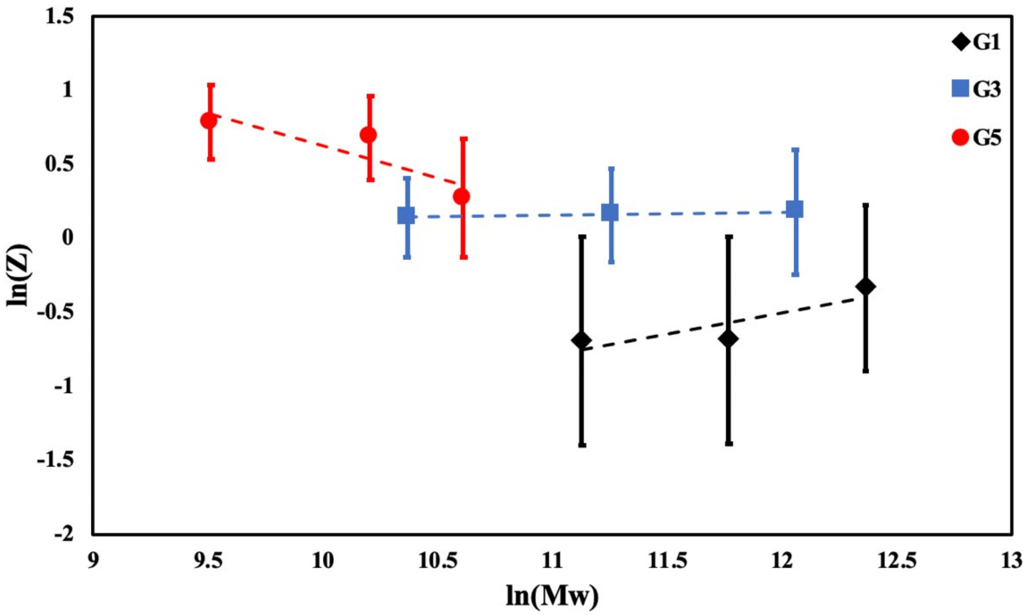


Figure S6. The dendron heights for generation 1, 3 and 5 have been plotted against corresponding total molecular weights of dendrons. (Total molecular weight of dendrons = number of dendrons in the model × molecular weight of 1 dendron).

Generation	**Scaling Exponent**
G1	0.3 ± 0.3
G3	0.0 ± 0.1
G5	-0.4 ± 0.2

Table S3. The scaling exponent (mean ± standard error) of linear trendlines for dendrons shown in Figure S6. The final 100 ns of trajectory data is extracted from 4 independent simulations and compiled into a single dataset. The mean and standard error of this dataset is reported in this table.

3. Log (dendron height) vs log (average neighbor distance)

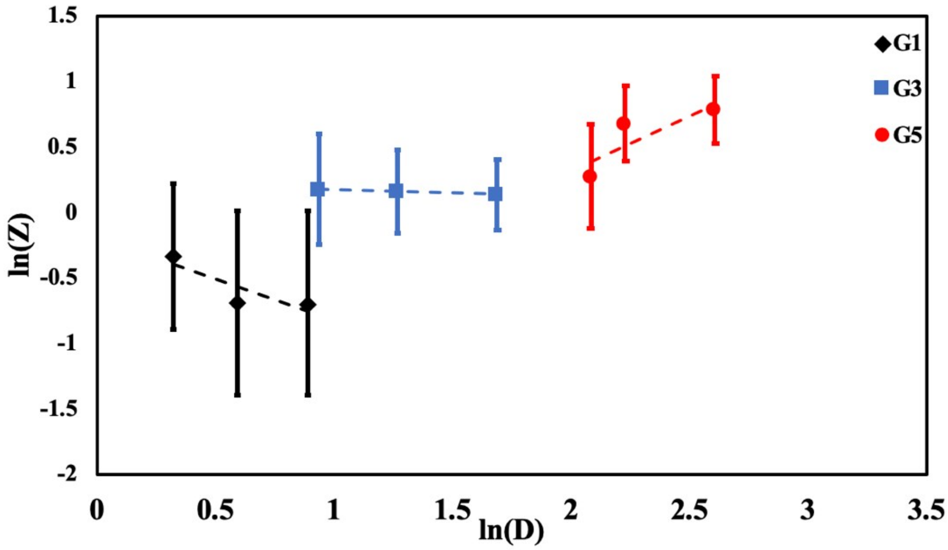


Figure S7. The dendron heights of generation 1, 3 and 5 have been plotted against the corresponding average neighbor distance (D) between dendron grafting points.

Generation	**Scaling Exponent**
G1	-0.7 ± 0.3
G3	-0.0 ± 0.2
G5	0.8 ± 0.2

Table S4. The scaling exponent (mean ± standard error) of linear trendlines for dendrons shown in Figure S7. The final 100 ns of trajectory data is extracted from 4 independent simulations and compiled into a single dataset. The mean and standard error of this dataset is reported in this table.

Packing Factor Calculations

Generation	Relative Dendron Concentration	Packing factor of Outer Monolayer	Packing Factor of Inner Monolayer	Stability of Vesicle
G1	5 %	1.023 ± 0.002	0.6054 ± 0.0009	Stable
	10 %	1.0402 ± 0.0009	0.6026 ± 0.0004	Stable
	17 %	1.054 ± 0.003	0.603 ± 0.002	Stable
	20%	1.07185 ± 0.002	0.599 ± 0.001	Stable
G2	1 %	1.06 ± 0.02	0.62 ± 0.02	Stable
	2.5 %	1.047 ± 0.001	0.6016 ± 0.0002	Stable
	5 %	1.001 ± 0.004	0.611 ± 0.002	Stable
	6 %	0.752 ± 0.006	0.608 ± 0.003	Unstable
G3	1 %	1.014 ± 0.006	0.610 ± 0.002	Stable
	2.5 %	1.002 ± 0.004	0.615 ± 0.002	Stable
	4 %	0.988 ± 0.002	0.607 ± 0.002	Stable
	5 %	0.991± 0.007	0.614 ± 0.006	Stable

	7 %	0.92 ± 0.01	0.614 ± 0.003	Unstable
G4	0.5 %	0.988 ± 0.002	0.6076 ± 0.0004	Stable
	1 %	0.977 ± 0.001	0.6068 ± 0.0003	Stable
	1.5 %	1.017 ± 0.002	0.6015 ± 0.0003	Stable
	2 %	1.016 ± 0.003	0.6022 ± 0.0003	Stable
	2.5 %	0.82 ± 0.09	0.62 ± 0.01	Unstable
G5	0.00065 %	1.0147 ± 0.0009	0.6098 ± 0.0003	Stable
	0.00131 %	1.022 ± 0.005	0.609 ± 0.002	Stable
	0.00263 %	1.009 ± 0.002	0.6137 ± 0.0003	Stable
	0.00394 %	0.997 ± 0.003	0.6001 ± 0.0006	Stable
	0.00592 %	0.993 ± 0.002	0.6069 ± 0.0003	Unstable
G6	0.00065 %	1.015 ± 0.002	0.608 ± 0.002	Stable
	0.00131 %	1.014 ± 0.002	0.605 ± 0.001	Stable
	0.00263 %	1.018 ± 0.004	0.616 ± 0.002	Stable

Table S5. The packing factor of the outer and inner monolayer of all DVs have been reported.