Supplementary Information for

Dendroids, Discrete Covalently-Crosslinked Dendrimer Superstructures

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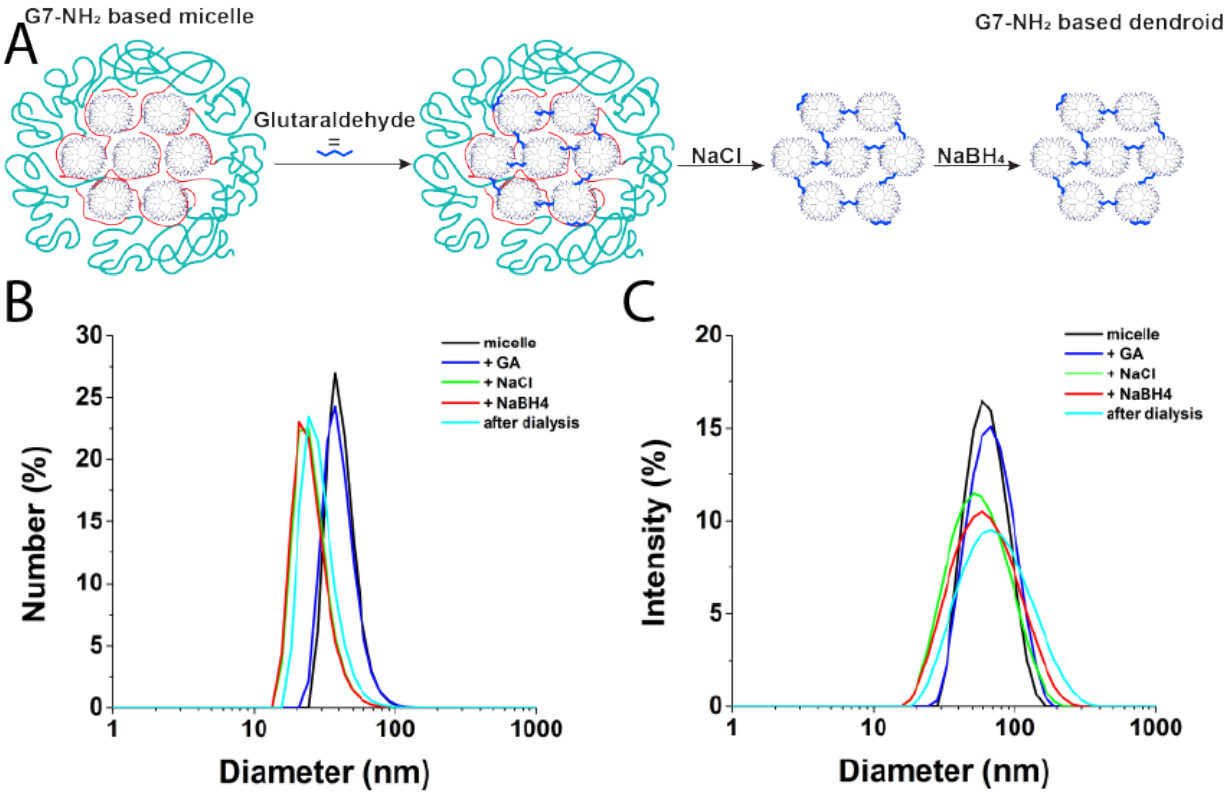

Figure S1: (A) Stepwise scheme of G7-E based dendroid formation. After dendrimicelle formation, the dendrimers inside the micellar core are crosslinked with glutaraldehyde. Then the ionic strength is increased to a NaCl concentration of 0.8 M to remove the block copolymer from the crosslinked core, resulting in dendroids. The imide bonds are subsequently reduced by the addition of $NaBH_4$ to amide bonds. Finally, the dendroids are purified by dialysis. (B) Number averaged DLS plots and (C) Intensity DLS plots after each step for dendroid formation (ratio PAMAM : glutaraldehyde is 1 : 60). After micelle formation (black) a size of 43 nm was determined. The size did not change significantly after the addition of glutaraldehyde (dark blue). After the addition of NaCl (green) the size decreased to 24 nm suggesting the removal of the block copolymer corona. The addition of $NaBH_4$, in a ratio of 1 : 10, (red) and purification with dialysis (light blue) did not influence the size significantly.

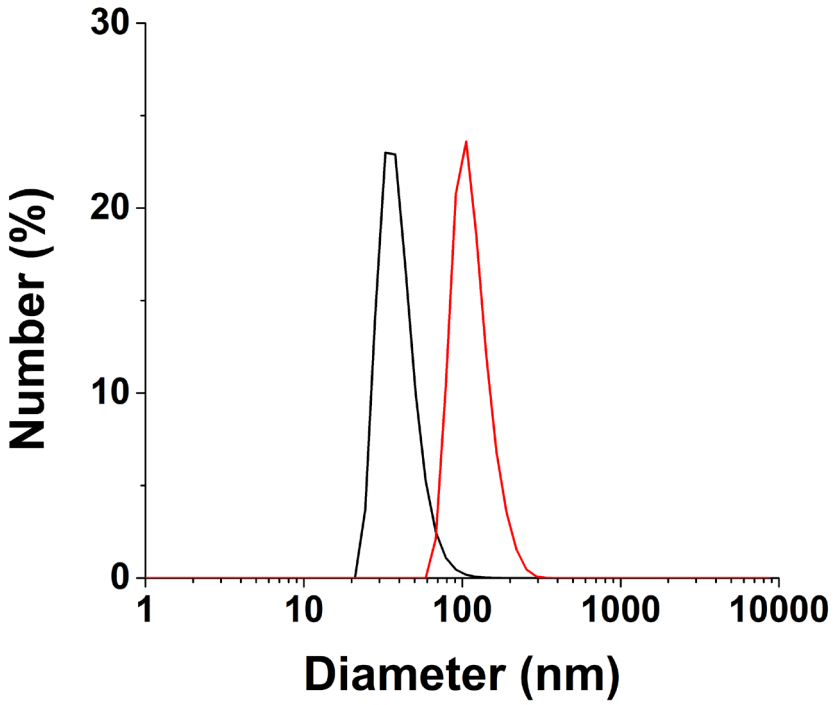

Figure S2: DLS number averaged plot of G7-E based micelles before (black) and after (red) the addition of NaCl (final concentration of 0.8 M).

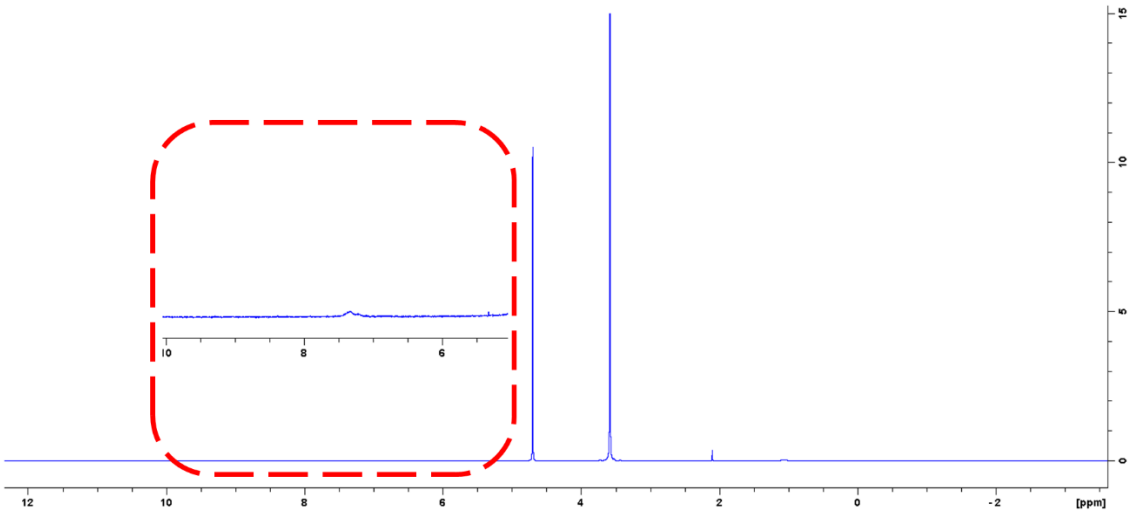

Figure S3: Proton NMR spectrum of the block copolymer, pMAA64PEO885, functionalised with 6 aminofluorescein., with higher intensity highlight of the aromatic (fluorescein) region (red box). In D_2O, rt)

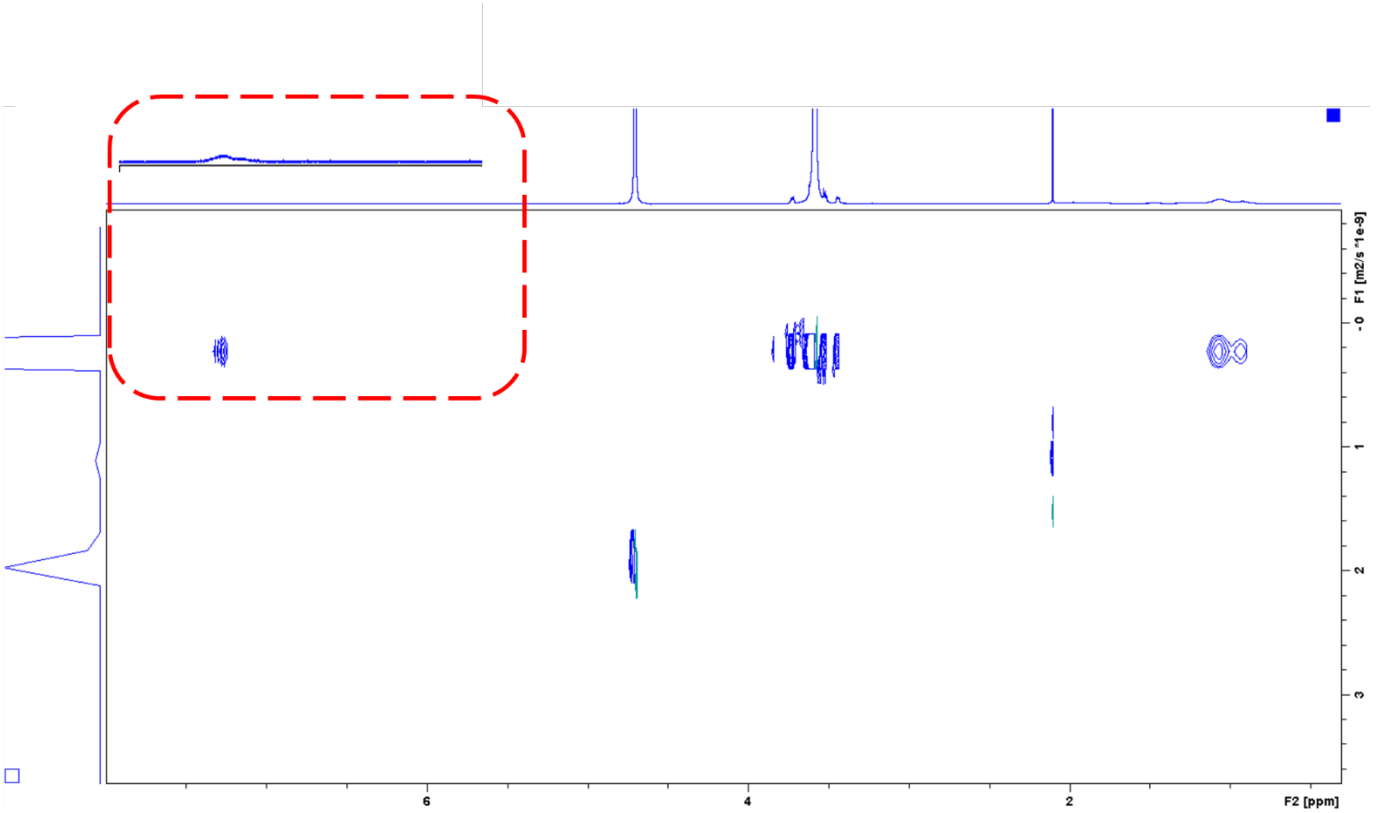

Figure S4: (A) Full DOSY NMR spectrum of the block copolymer, pMAA64PEO885, functionalised with 6 aminofluorescein., with higher intensity insert of the 1D and DOSY peak of the aromatic region (red box). In D_2O, rt. The signals in the aromatic fluorescein region, the PEO region (3.5 ppm) and PMAA (1 ppm) all show the same diffusion coefficient, corroborating the conjugation of the fluorophore and polymer.

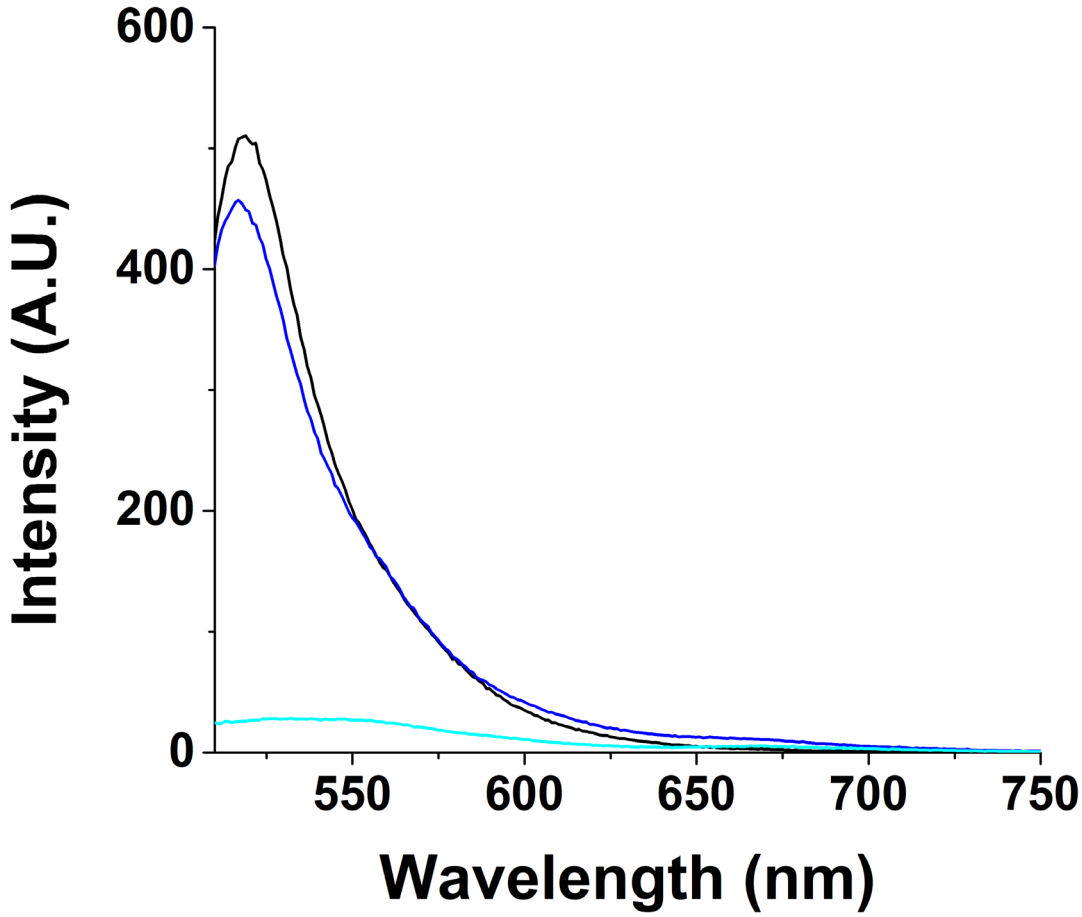

Figure S5: Fluorescence emission of micelles based on G7-E dendrimers and pMAA64pEO885-AF (black), the same sample after crosslinking and addition of NaCl and $NaBH_4$ (dark blue) and the same sample after 3 days of dialysis against 1 M NaCl (light blue). Excitation wavelength is 495 nm.

Table S1: Sizes of G7-E based dendrimicelles and resulting dendrimer aggregates determined with DLS. Different ratios between G7 PAMAM dendrimer and glutaraldehyde were tested. Ratios below 1 : 40 show a dramatic increase or decrease in size after the addition of salt, suggesting that no dendroids were formed due to insufficient crosslinks. Ratios of 1 : 40 and above show the characteristic decrease in size after the addition of salt, suggesting that dendroids were successfully formed.

Ratio G7-E : glutaraldehyde	**micelles diameter (nm)**	**dendrimer aggregates diameter (nm)**
1 : 10	48	4
1 : 20	43	756
1 : 30	43	852
1 : 40	42	34
1 : 60	42	35
1 : 80	43	29
1 : 100	48	35
1 : 120	46	32
1 : 140	46	32
1 : 160	42	29
1 : 180	42	29
1 : 200	41	31
1 : 300	41	28
1 : 400	42	30
1 : 500	47	34

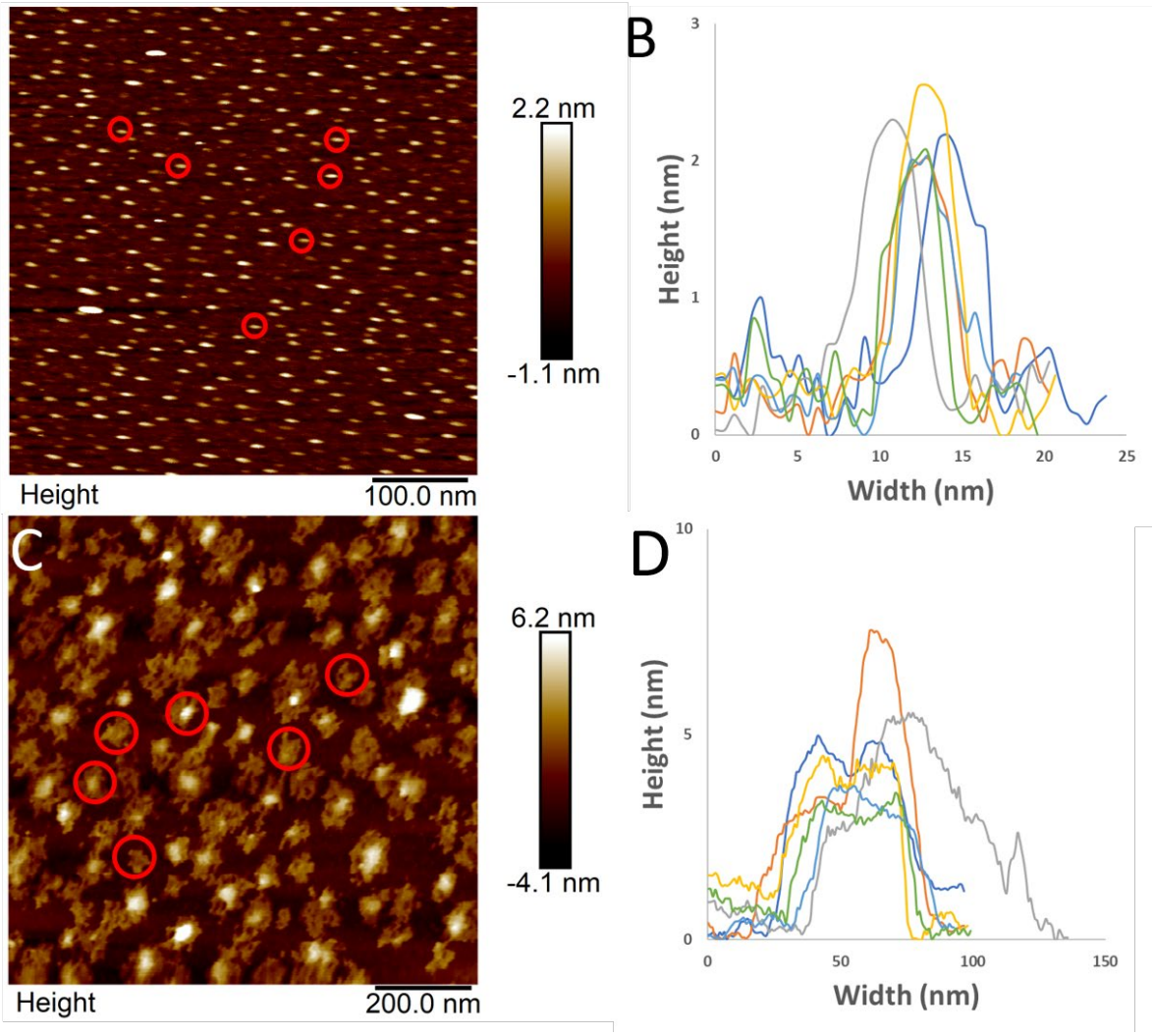

Figure S6: AFM pictures and corresponding height profiles of selected particles (highlighted with a red circle) of (A),(B) G7-E dendrimers and (C),(D) G7-E micelles. The average height of single G7-E dendrimers is 2 nm and the average height of G7-E micelles is 5 nm. The AFM of the dendrimicelles sample clearly shows that the micelles are not stable in a dried state.

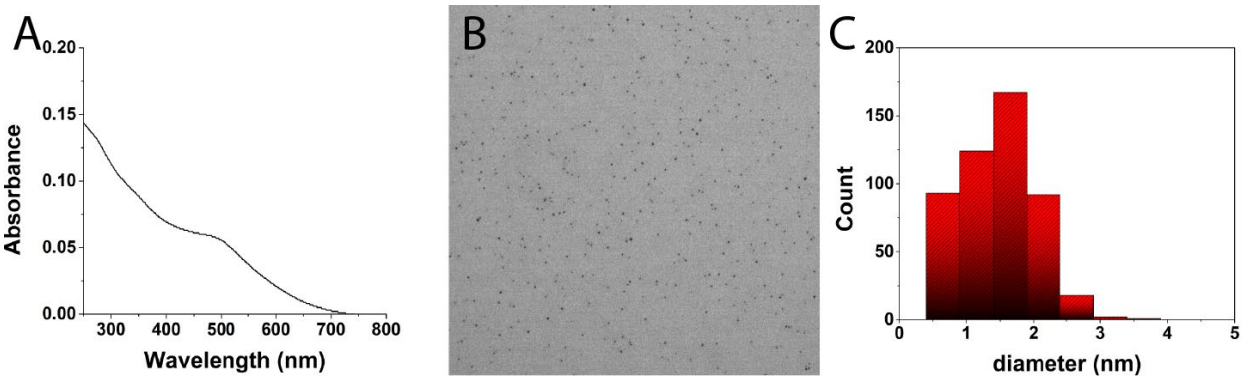

Figure S7: (A) UV-Vis spectrum and (B) TEM picture of dendrimer encapsulated gold nanoparticles in Generation 7 PAMAM dendrimers. (C) Histogram of G7-Au DENs in solution. The average size is 1.5 ± 0.5 nm based on 497 particles.

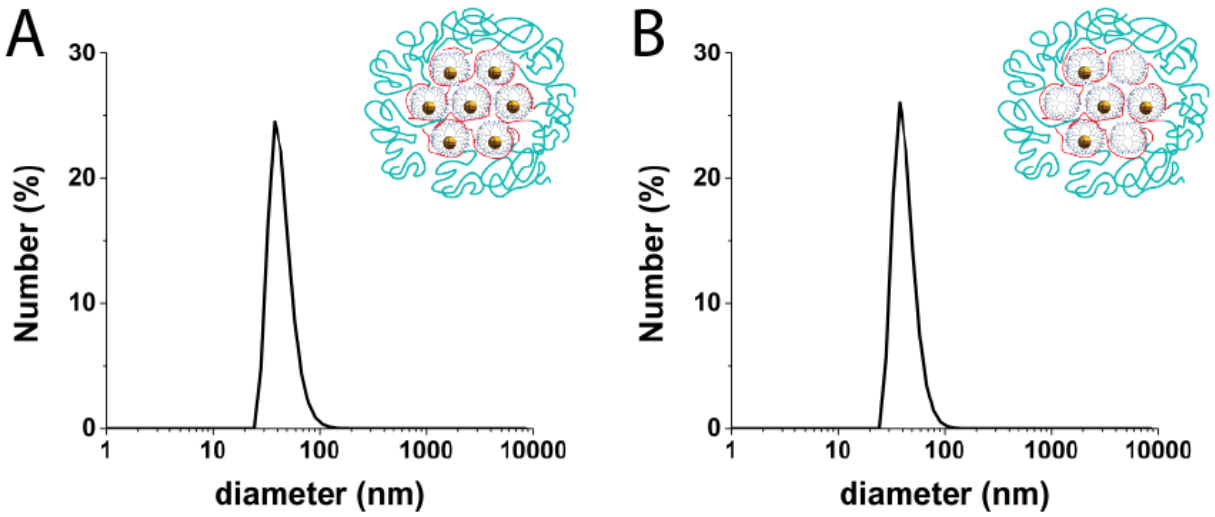

Figure S8: DLS Number averaged plots of (A) G7-Au based dendrimicelles and (B) G7-AuE based dendrimicelles. The sizes determined by DLS are 46 nm and 43 nm, respectively.

Table S2: DLS data of G7-E, G7-Au and G7-AuE based micelles and corresponding dendroids before dialysis. Values of G7-E dendroids after dialysis do not change much.

Sample	Diameter (nm)	St.dev. (nm)	PDI
G7-E micelle	43	11	0.14
G7-E dendroid	26	8	0.21
G7-Au micelle	41	11	0.15
G7-Au dendroid	34	10	0.34
G7-AuE micelle	51	14	0.16
G7-AuE dendroid	36	12	0.25

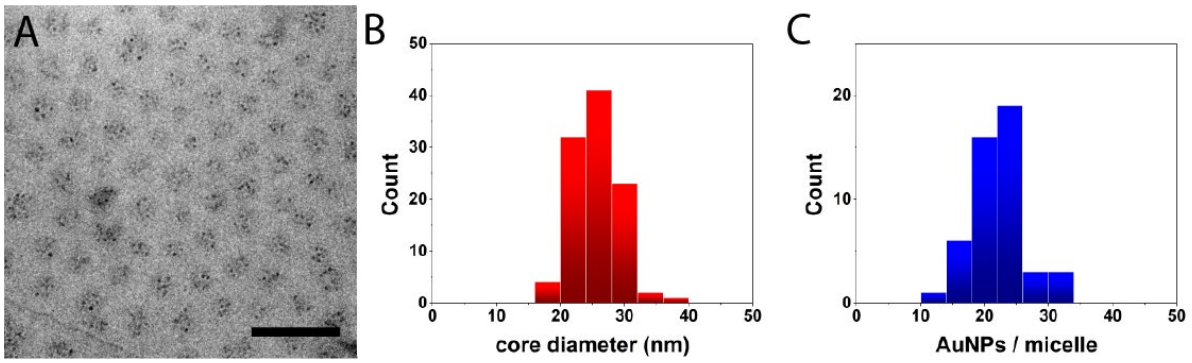

Figure S9: Dendrimicelles based on AuDENs. (A) Cryo-TEM picture of G7-Au based dendrimicelles. Scale bar represents 100 nm. (B) Histogram showing the core diameter of the micelles. The average core size is 26 ± 3 nm (103 micelles analysed). (C) Histogram showing the number of AuNPs per micelle. That is 22 ± 4 (48 micelles analysed)

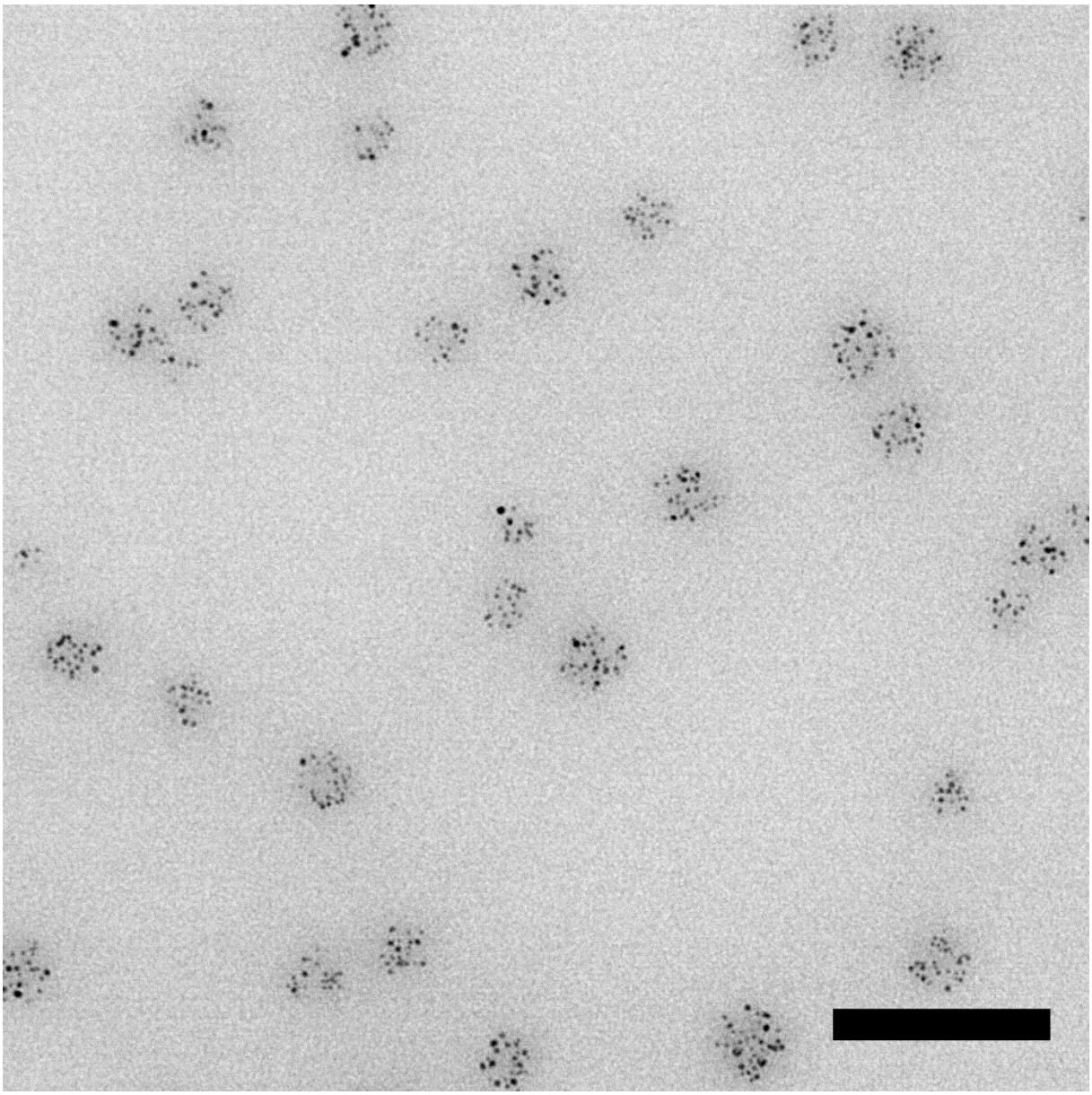

Figure S10: TEM picture of G7-Au based dendroids. Scale bar represents 100 nm.

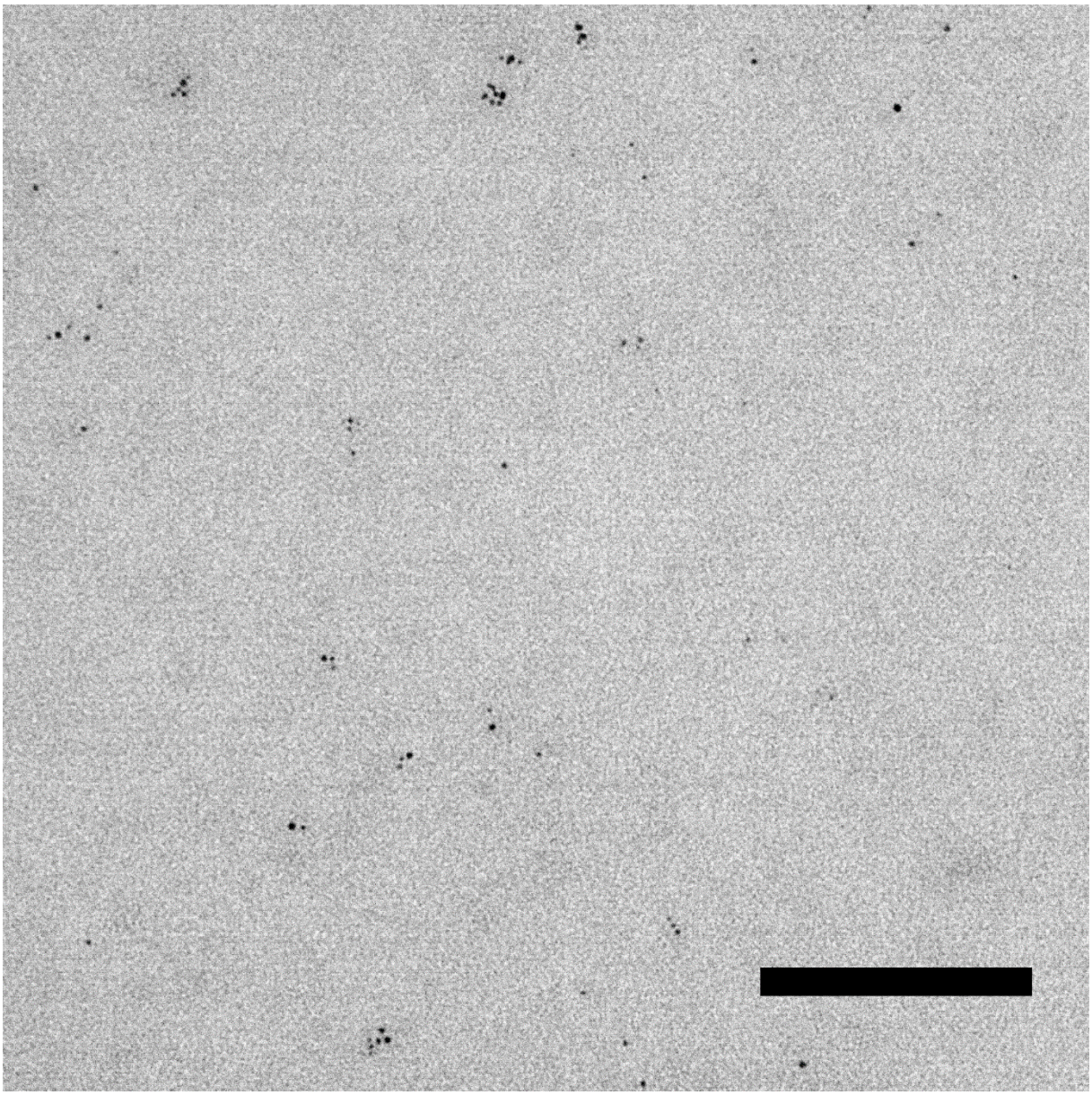

Figure S11: TEM picture of G7-Au based micelles after NaCl addition to a final concentration of 0.8 M. Only small clusters and single DENs are visible suggesting that the micelles are disrupted at this salt concentration. Scale bar represents 100 nm.

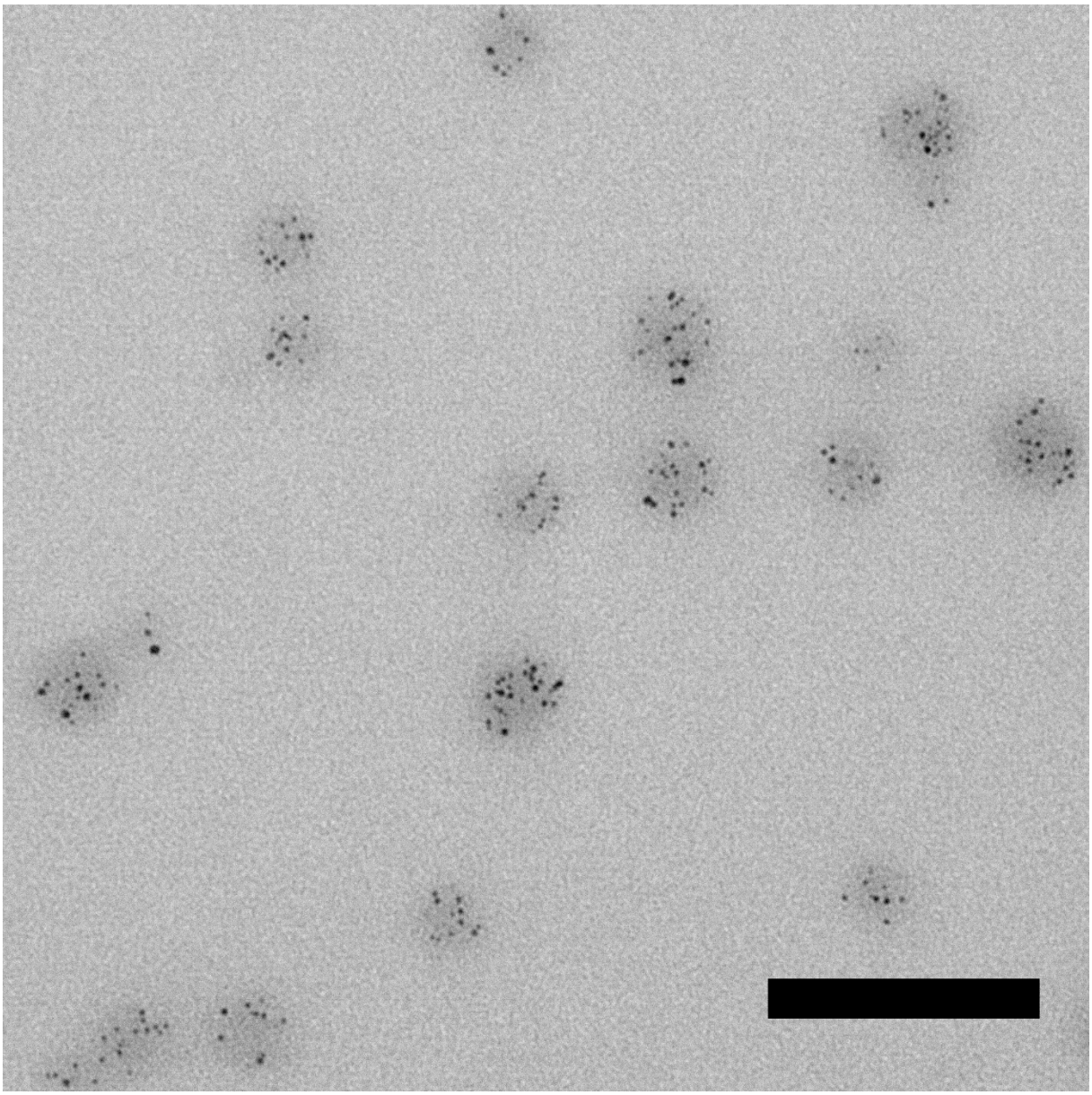

Figure S12: TEM picture of G7-AuE based dendroids. So half of the dendrimers in a dendroid is empty, and the other half is filled with Au-DENs. Scale bar represents 100 nm.

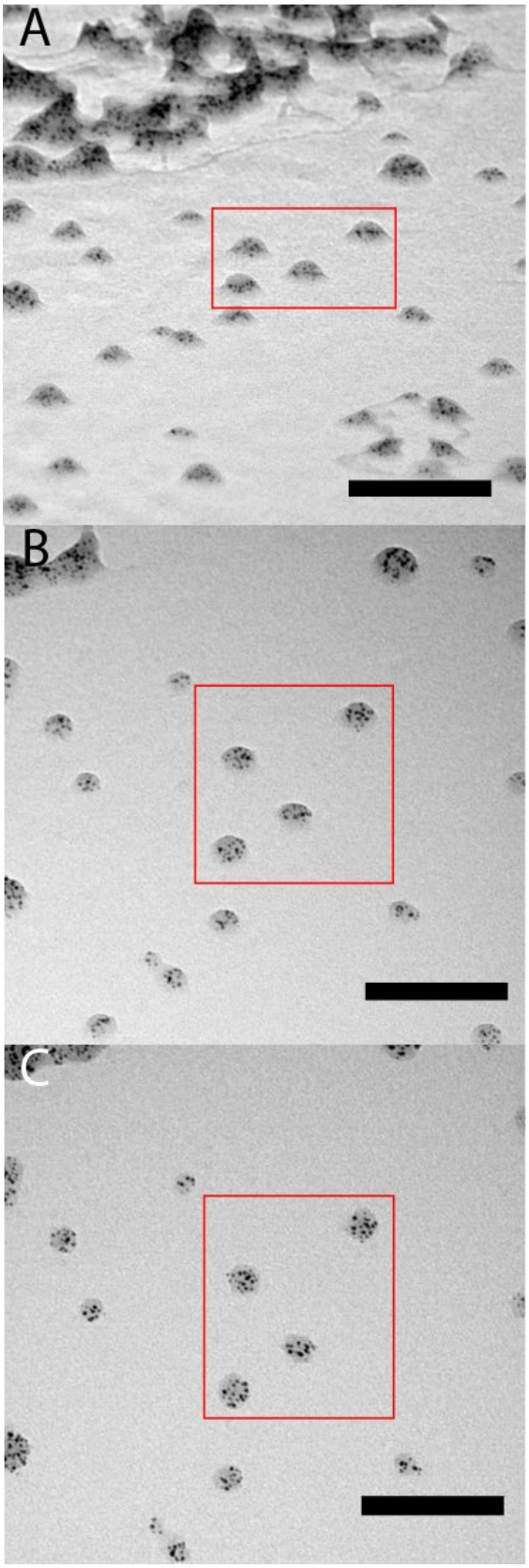

Figure S13: Enlarged TEM pictures of G7-Au based dendroids at (A) +70 degree, (B) +35 degree and (C) 0 degree tilt angles. Red squares indicate the dendroids used for reconstruction. Scale bars represent 100 nm.

Figure S14: Tomography reconstruction of G7-Au based DENdroids.(A) XZ isosurface, (B) YZ isosurface, (C) XY isosurface. Scale bars represent 25 nm.