

Azido-coated Nanoparticles: A Versatile Clickable Platform For The Preparation of Fluorescent Polystyrene Core-PAMAM Shell Nanoparticles

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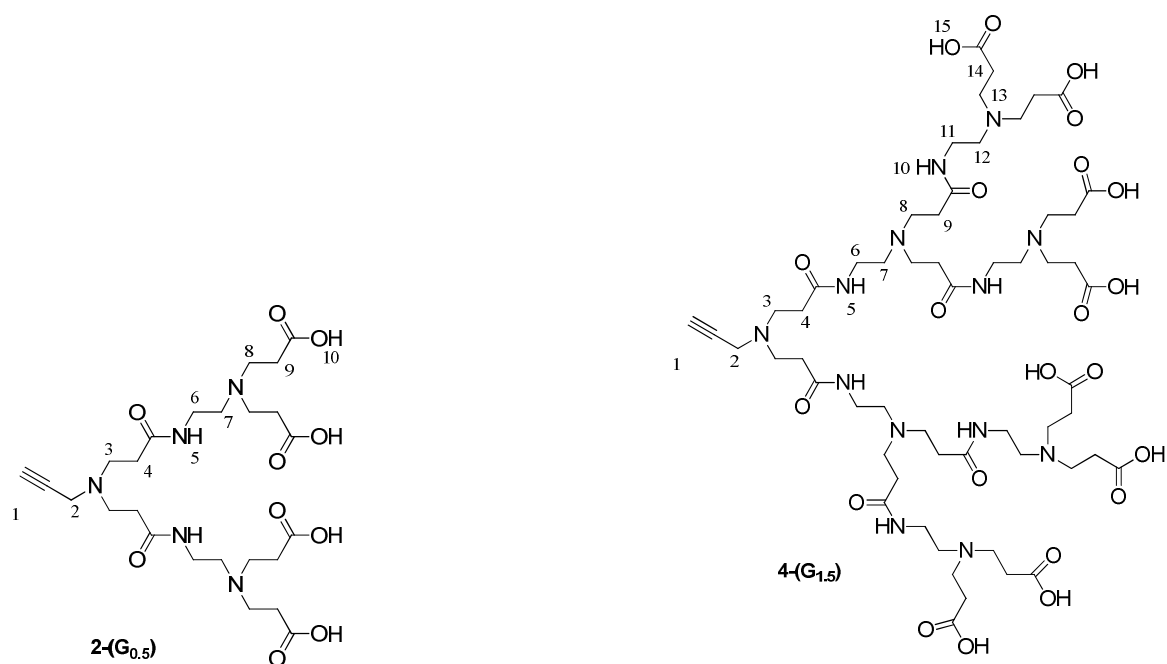


Figure S1. Structures and numbering of propargyl-functionalized acid terminated PAMAM dendrons **2-(G_{0.5})** and **4-(G_{1.5})** used for ¹H NMR signals assignments

Synthesis of functionalized nanoparticles

Materials 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, Acros, 99%) was used as received. Vinylbenzylchloride (VBCl, Aldrich, mixture of isomers *meta* (70%) and *para* (30%), 95%), and divinylbenzene (DVB, Fluka, mixture of isomers *meta* and *para*, 80%) were freed of inhibitors by passing through a LC-Si Solid Phase Extraction tube (Aldrich, cat. no. 57116 and 57133). Styrene (Acros, 99%) was distilled under reduced pressure.

Synthesis of chorobenzyl-functionalized nanoparticles NP_{Cl} A microemulsion was prepared into a reactor by progressive addition, upon gentle magnetic stirring, of a mixture of monomers (styrene / divinylbenzene / vinylbenzylchloride: 3.50 g (33.6 mmol) / 4.51 g (34.7 mmol) / 1.84 g (12.1 mmol), respectively) and DMPA (333 mg, 1.3 mmol) to 220 g of a 15-wt % aqueous solution of DTAB. The resulting microemulsion was degassed with nitrogen for 30 min and the polymerization was then carried out under white light irradiation using two 60 W lamps at room temperature under nitrogen for 18 h. A stable translucent suspension was obtained. Chemical composition of the polymer particles: C, 85.45; H, 7.50; Cl, 1.88; Br, 2.56%. Mean diameter: 15 nm (PDI = 0.069).

Preparation and characterization of azide-functionalized nanoparticles NP_{N3}

NP_{N3}-bis Azide-coated nanoparticles were prepared by adding an aqueous solution of sodium azide (7.66 g in 20 mL of water) to 210 g of the freshly prepared crude suspension of **NP_{Cl}** the pH of which was previously adjusted to 7.5. The resulting suspension was stirred at room temperature for one week. The excess of sodium azide was then removed by dialysis through a porous cellulose membrane (MWCO 12000-14000D) toward an aqueous solution of DTAB (15 wt%) leading to a stable translucent aqueous suspension of azide-functionalized nanoparticles (NP_{N3}). Polymer particle content in suspension is 4.36 wt%. Chemical composition: C, 84.71; H, 7.44; N, 1.65 % corresponding to an azide content of 0.39 mmol/g of polymer. Mean diameter (QELS): 16 nm (PDI: 0.036). IR (KBr): 3080, 3052, 3028, 2921, 2852, 2092, 1602, 1512, 1491, 1450, 1262, 1030, 988, 907, 837, 801, 760, 703, 543 cm⁻¹.

Preparation and characterization of acide terminated PAMAM-functionalized nanoparticles NP_PAMAM[CO₂H]_n

NP_PAMAM[CO₂H]₄-bis PAMAM derivative **2-(G_{0.5})** (113 mg, 0.198 mmol) was dissolved in 2 mL of water. The solution was added to 10 g of an aqueous suspension of azide-functionalized nanoparticles **NP_{N3}-bis**. The pH was adjusted to 5.7 by adding NaOH (1M). Then, 2 mL of a freshly prepared aqueous solution of CuSO₄ (77 mg, 0.482 mmol) and sodium ascorbate (178 mg, 0.90 mmol) was added, the pH was again adjusted to 5.7. The resulting suspension was stirred at room temperature for 5 days. 116 mg of cyclam was added and then the suspension was dialyzed against aqueous solution of DTAB (15 wt% to 1 wt%). Polymer particle content in suspension is 8.5 wt%. Chemical composition: C, 81.00; H, 7.82; N, 2.67 % corresponding to a dendron content of 0.15 mmol/g of polymer. Mean diameter (QELS): 16 nm (PDI: 0.067). IR (KBr): 3419, 3080, 3056, 3024, 2923, 2851, 2096, 1653, 1600, 1492, 1451, 1374, 1266, 1182, 1029, 903, 837, 796, 760, 700, 535 cm⁻¹.

NP_PAMAM[CO₂H]₈-bis PAMAM derivative **4-(G_{1.5})** (220 mg, 0.167 mmol) was dissolved in 2 mL of water. The solution was added to 8.25 g of an aqueous suspension of azide-functionalized nanoparticles **NP_{N3}-bis**. The pH was adjusted to 5.7 by adding NaOH (1M). Then, 2 mL of a freshly prepared aqueous solution of CuSO₄ (63 mg, 0.395 mmol) and sodium ascorbate (147 mg, 0.742 mmol) was added, the pH was again adjusted to 5.7. The resulting suspension was stirred at room temperature for 5 days. 96 mg of cyclam was added and then the suspension was dialyzed against aqueous solution of DTAB (15 wt% to 1 wt%). Polymer particle content in suspension is 4.1 wt%. Chemical composition: C, 81.48; H, 7.98; N, 3.14 % corresponding to a dendron content of 0.08 mmol/g of polymer. Mean diameter (QELS): 17 nm (PDI: 0.022). IR (KBr): 3405, 3082, 3057, 3024, 2922, 2851, 2096, 1653, 1600, 1492, 1451, 1374, 1266, 1182, 1029, 903, 832, 796, 760, 700, 539 cm⁻¹.

Table S1. Characterization of azido-coated nanoparticles NP_{N3}

List	Starting suspension	Reactant [x. eq.]	%wt ^c	D (nm) [PDI] ^d	Azide content (meq/g polymer) ^e	n N ₃ per NP ^f
NP _{N3}	NP _{Cl} ^a	NaN ₃ [10]	4.46	18 [0.08]	0.29	560
NP _{N3} -bis	NP _{Cl} ^b	NaN ₃ [10]	4.36	16 [0.036]	0.39	530

^a Chlorobenzyl content in the suspension = 1.04 mmol/g of polymer ; D = 18 nm (PDI = 0.083)

^b Halobenzyl content in the suspension = 0.85 mmol/g of polymer ; D = 15 nm (PDI = 0.069)

^c Polymer particle content in suspension

^d Particle diameter determined from QELS

^e Deduced from elemental analysis (nitrogen content)

^f Calculated with the particle diameter obtained from QELS and a polymer density of 1.05

Table S2. Characterization of acid terminated PAMAM-functionalized nanoparticles NP_PAMAM[CO₂H]_n

List	Starting Suspension	Reactant [x. eq.]	%wt ^a	D (nm) [PDI] ^b	Dendron content (meq/g polymer) ^d
NP_PAMAM[CO ₂ H] ₄ -bis	NP _{N3} -bis	2-(G _{0.5}) 1.2	8.5	16 ^c [0.067]	0.15 [40] ^e
NP_PAMAM[CO ₂ H] ₈ -bis	NP _{N3} -bis	4-(G _{1.5}) 1.2	4.1	17 ^c [0.022]	0.08 [20] ^e

^a Polymer particle content in suspension

^b Particle diameter determined from QELS

^c Suspension diluted 50 times in HCl 6.10⁻³ M

^d Deduced from elemental analysis (nitrogen content)

^e In bracket estimation yield from elemental analysis (nitrogen content)

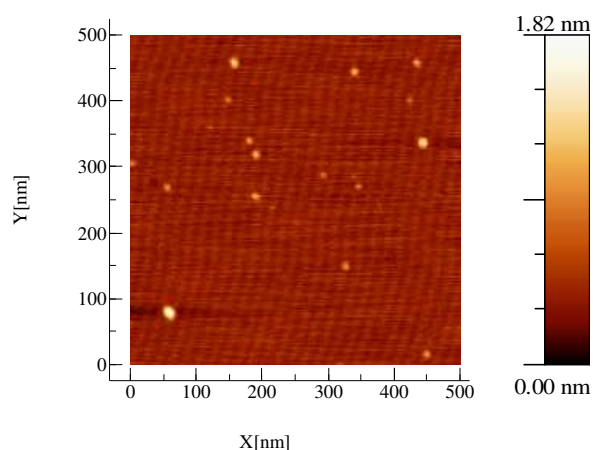


Figure S2. AFM images (amplitude) of a set of NP-Dns-PAMAM[CO₂H]₈ using the tapping mode on mica substrates. The nanolatexes were diluted 4×10^4 times in water (so that the final concentrations of nanoparticles and surfactant were respectively 7.5×10^{-5} g.L⁻¹ and 2.5×10^{-4} g.L⁻¹).

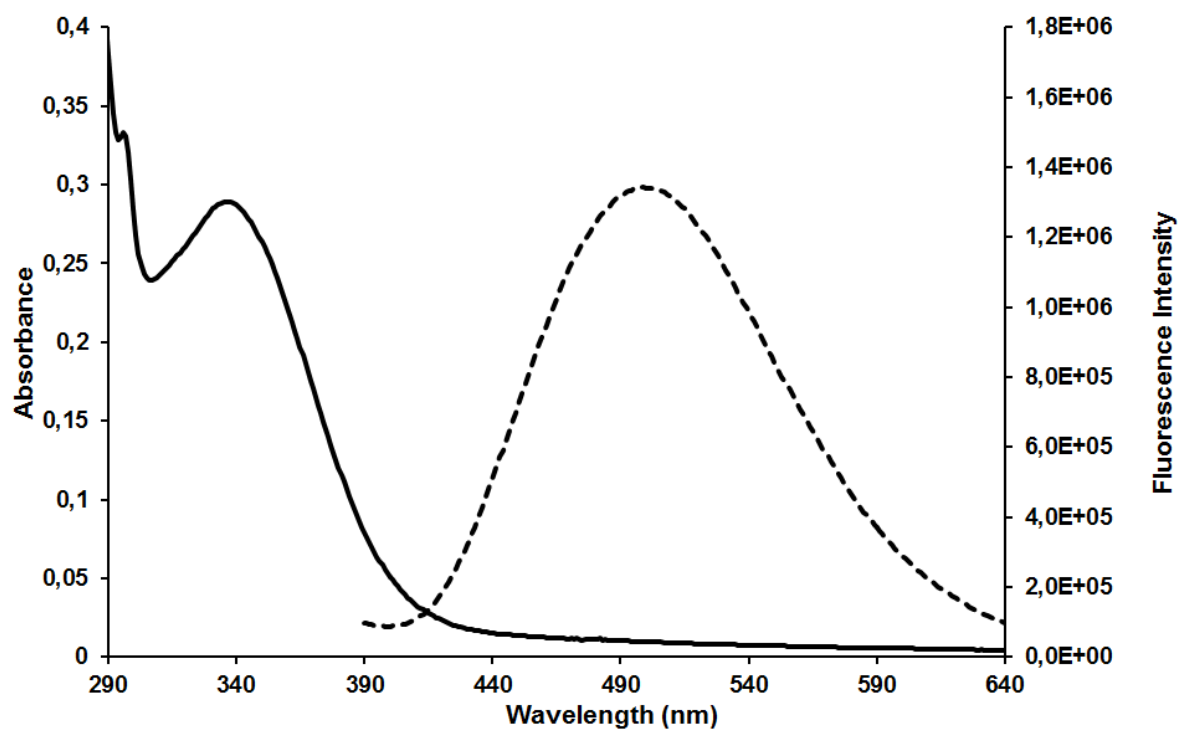


Figure S3. Absorption (Full, diluted 10 times, 0.5 wt% DTAB content) and fluorescence emission spectra (long-dash, diluted 160 times, $\lambda_{exc} = 336$ nm, 0.03 wt% DTAB content) of aqueous suspension of NP_Dns_PAMAM[CO₂H]₈

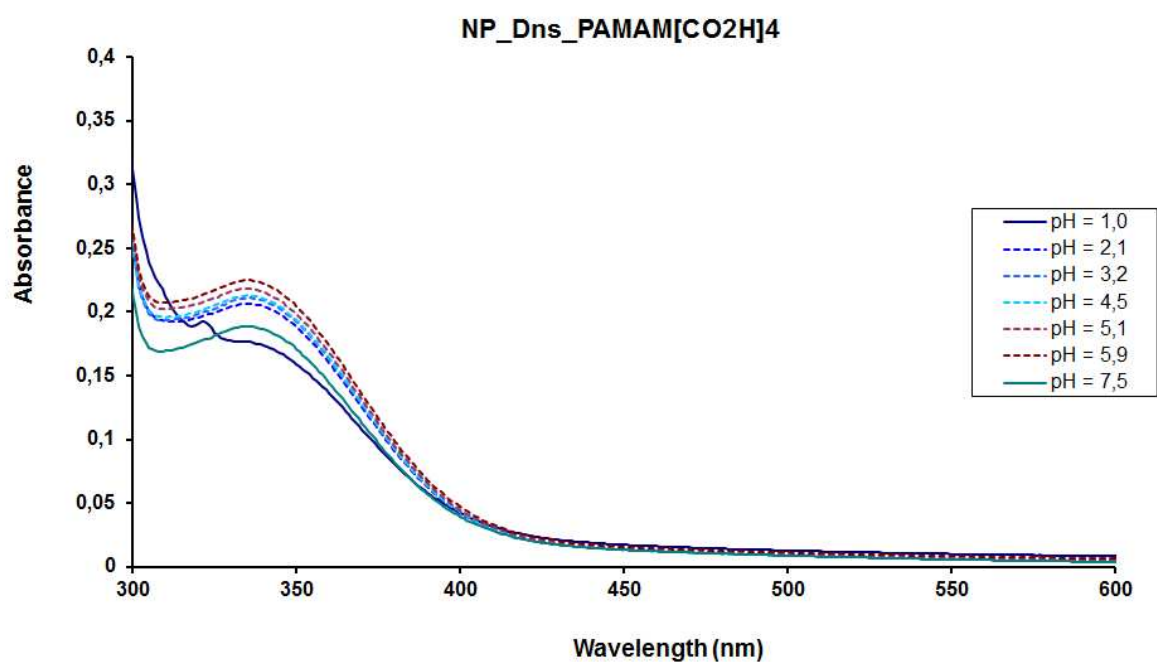


Figure S4. Absorption spectral changes of aqueous suspension of NP_Dns_PAMAM[CO₂H]₄ with increasing pH values. Suspensions were diluted 7.5 times (0.7 wt% DTAB content).

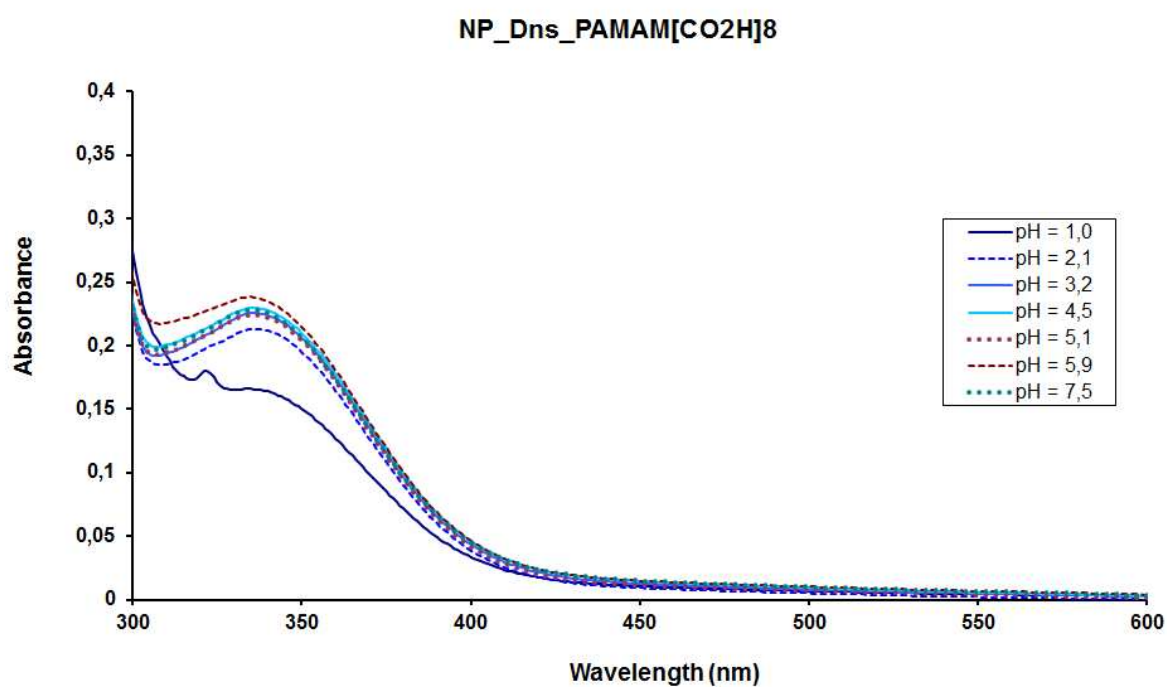


Figure S5. Absorption spectral changes of aqueous suspension of NP_Dns_PAMAM[CO₂H]₈ with increasing pH values. Suspensions were diluted 15 times (0.35 wt% DTAB content).

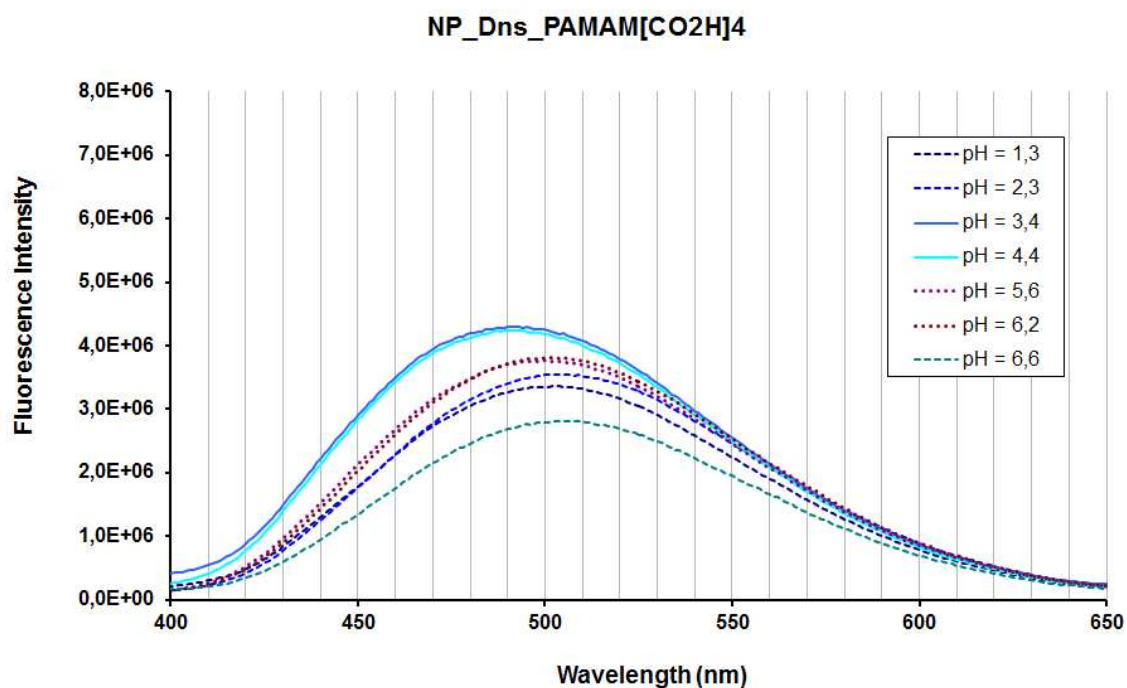


Figure S6. Fluorescence emission spectra of aqueous suspension of NP_Dns_PAMAM[CO₂H]₄ for pH values ranging from 1.3 to 6.6. Suspensions were diluted 37.5 times (0.14 wt% DTAB content). Dansyl was excited at 335 nm.

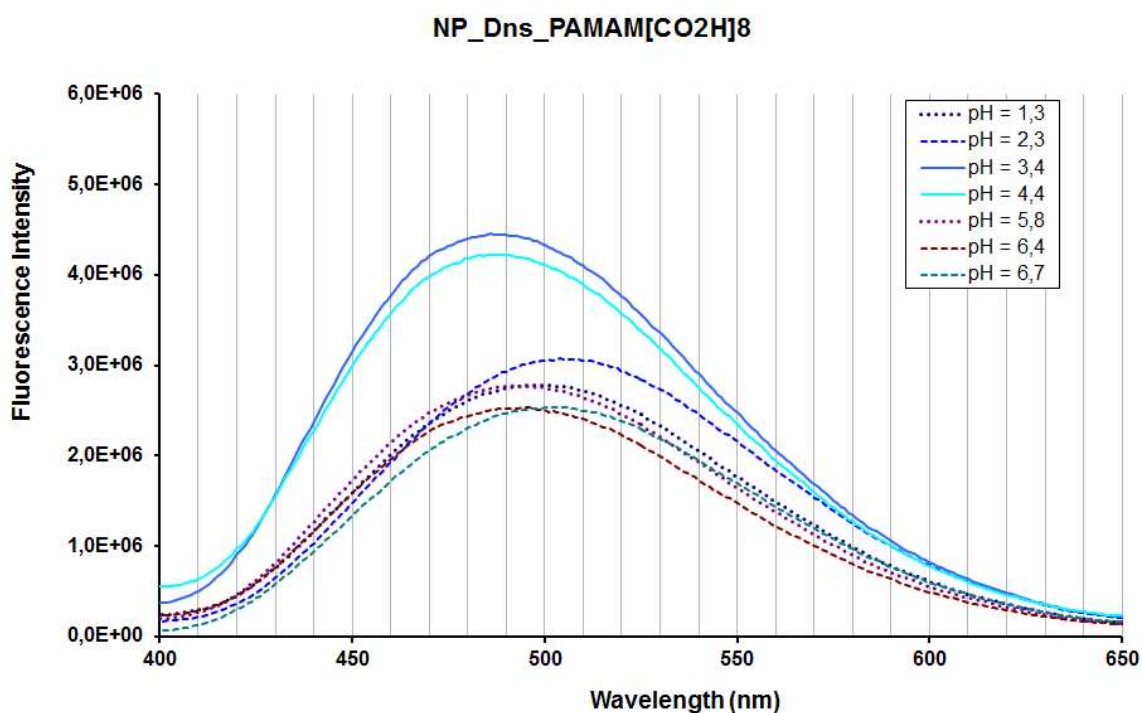


Figure S7. Fluorescence emission spectra of aqueous suspension of NP_Dns_PAMAM[CO₂H]₈ for pH values ranging from 1.3 to 6.7. Suspensions were diluted 75 times (0.07 wt% DTAB content). Dansyl was excited at 335 nm.

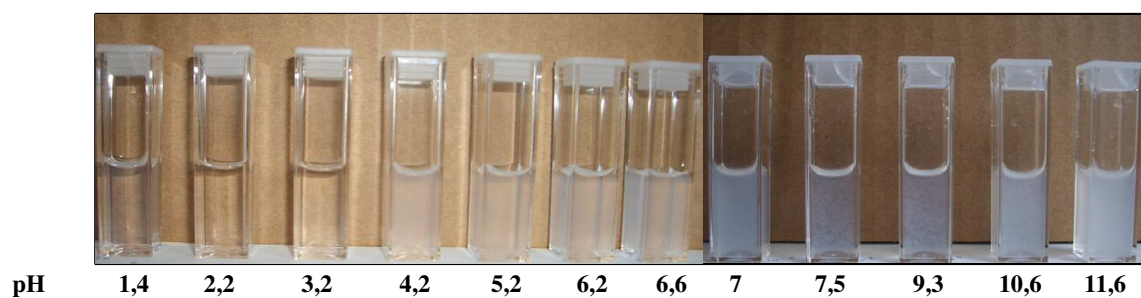


Figure S8. Pictures depicting the colloidal stability of NP_PAMAM[CO₂H]₄-bis versus pH

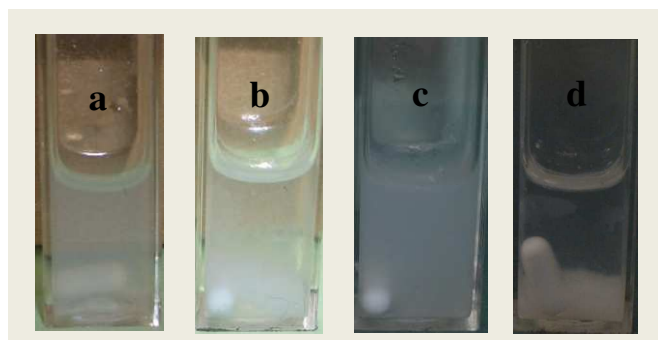


Figure S9. Photographs of NP_PAMAM[CO₂H]₈-bis (0.02 wt% DTAB content) after standing 24h: from the starting suspension (initial pH 2.0) after the first sequence final pH 2.0 (a), solution from picture **a** after basification pH 12.0 (b), from the starting suspension after three sequences final pH 2.0 (c), solution from picture **c** after basification pH 12.0 (d).



Figure S10. Photographs of the switched forms of NP_PAMAM[CO₂H]₈ in acidic and basic media after standing for two weeks.

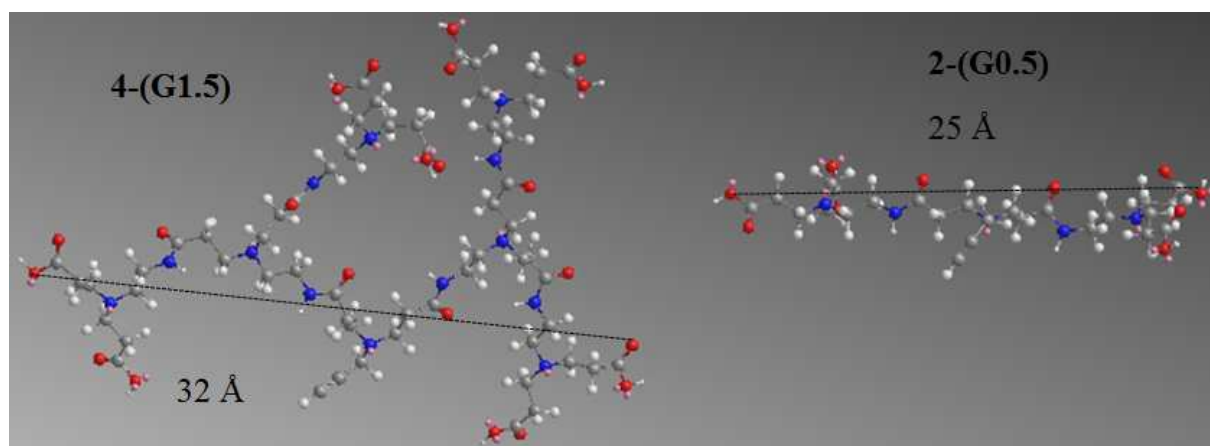


Figure S11. Estimation of the radius of propargyl-functionalized acid terminated PAMAM dendrons **2-(G_{0.5})** and **4-(G_{1.5})** using Chem Bio3D Ultra 11.0 (MM2 calculation) software.