Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supplementary Information (ESI)

Co-caged Gold-Nanoclusters and Methyl-Motifs Lead to Detoxification of Dendrimers and Allow Cytosolic Access for siRNA Transfection

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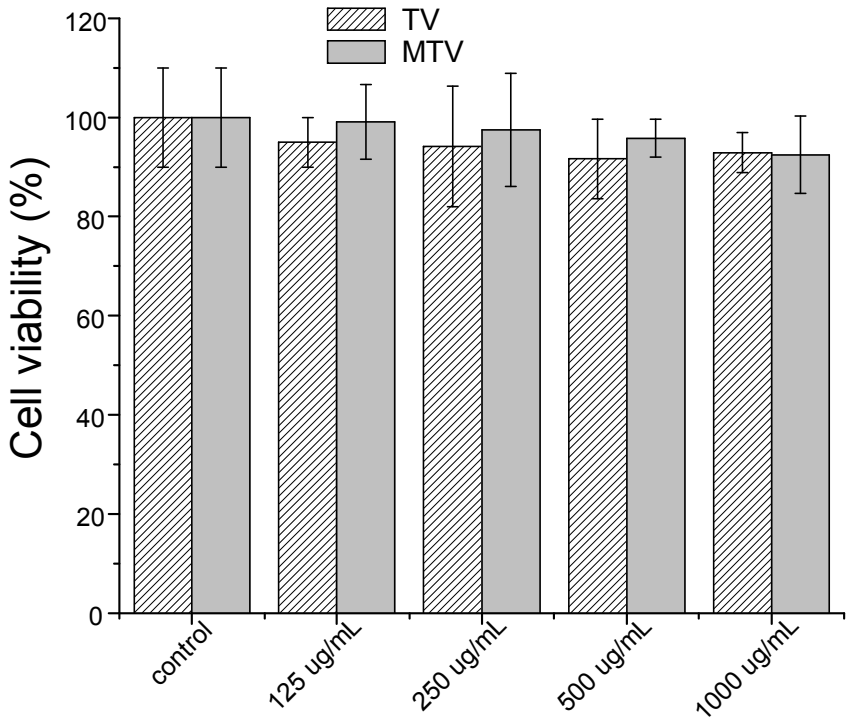


Fig. S1 The cytotoxicity of DCs was evaluated by WST-1 assay after treatment with TV and MTV for 24 h.

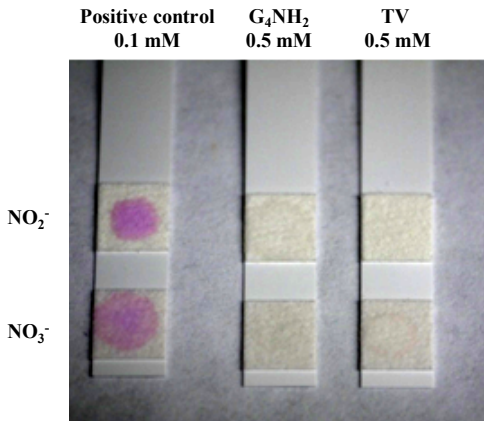


Fig. S2 To examine the oxidization possibility of 1°-amines form dendrimers.

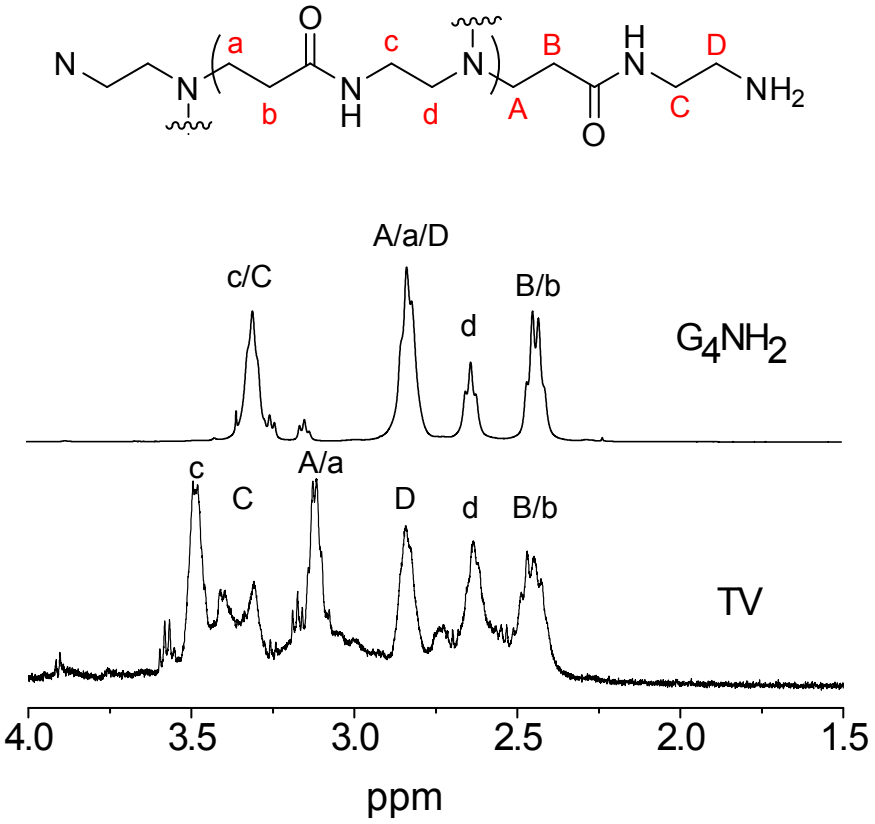


Fig. S3 Top panel: a schematic representation of G_4NH_2 from the core to the branch. Bottom panel: the ^1H NMR spectra of G_4NH_2 and TV, respectively. Note that the assignment of G_4NH_2 was referenced a previous paper (J. Am. Chem. Soc. 2013, 135, 11513-11516).

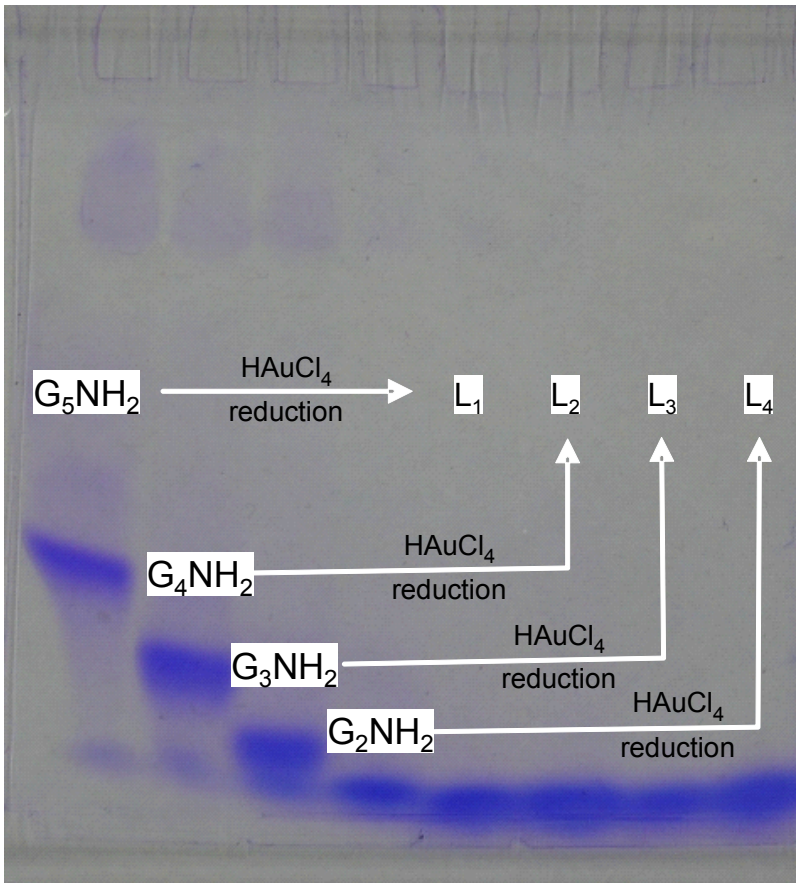


Fig. S4 A comparison of the sizes of various TVs derived form dendrimers with smaller and larger generations.

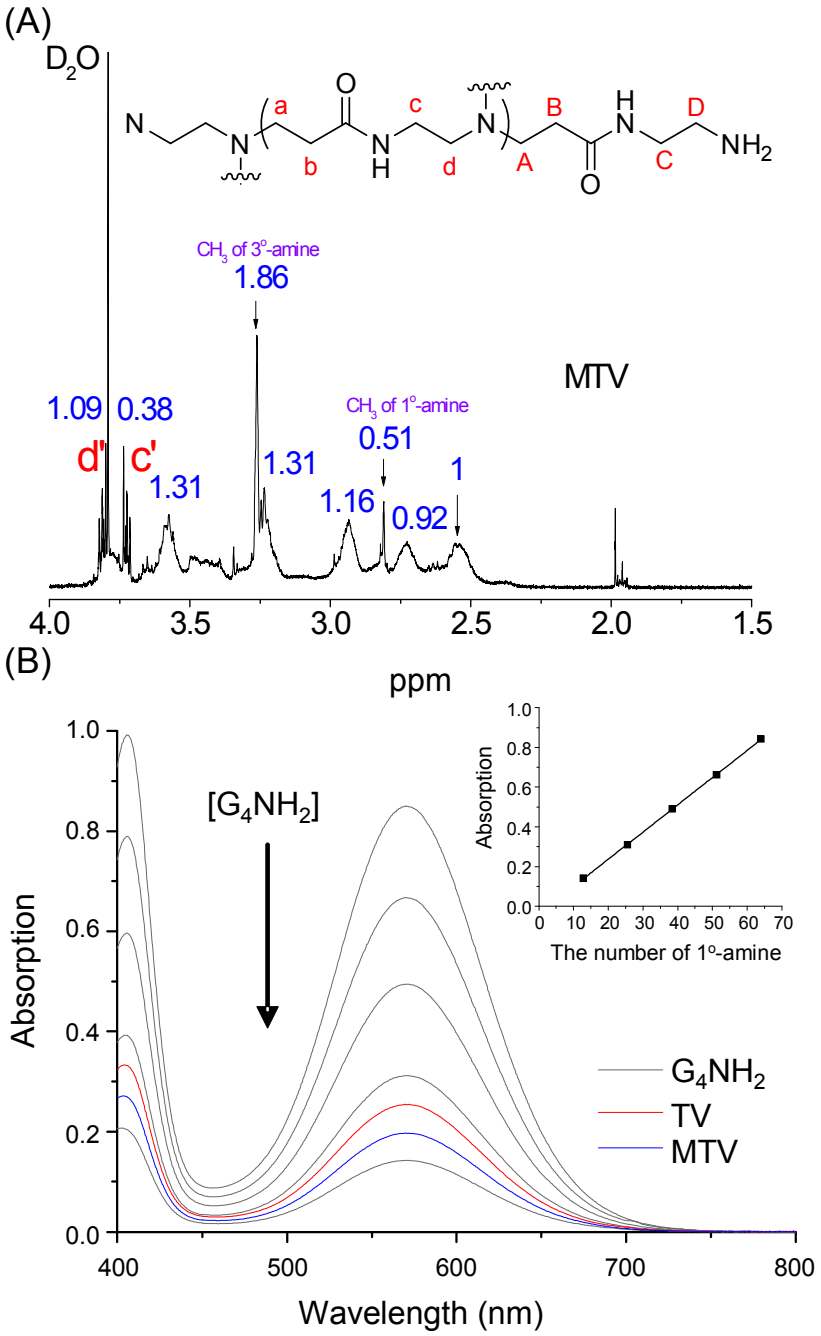


Fig. S5 (A) ^{1}H NMR spectrum of MTV. The values are labeled to represent the relative integral of protons. (B) The result of the ninhydrin test. The inset shows a plot of the absorption of ninhydrin dye versus the number of 1°-amine of dendrimers.

Table S1 A summary of the percentage and number of 1°-amine from TV and MTV

	TV	MTV
Absorption at λ = 560 nm	0.2528	0.19623
Percentage (%)	33	27
Number of 1°-amine	21	17

According to the Figure S3, the calculations are shown below:

H_{number} of 3°-amine : H_{number} of 1°-amine = (1.86-1.31) : 0.51 = 1.08 : 1

N_{number} of 3°-amine : N_{number} of 1°-amine = (1.86/3) : (1/9) = X : (21-17)

N_{number} of 3°-amine = X = 13

Percentage of 3°-amine with methyl-motifs = 13/62 = 21 %

Percentage of 1°-amine with methyl-motifs = 4/21 = 19 %

Table S2 Calculation and comparison of the buffer capacity of the TV and MTV.

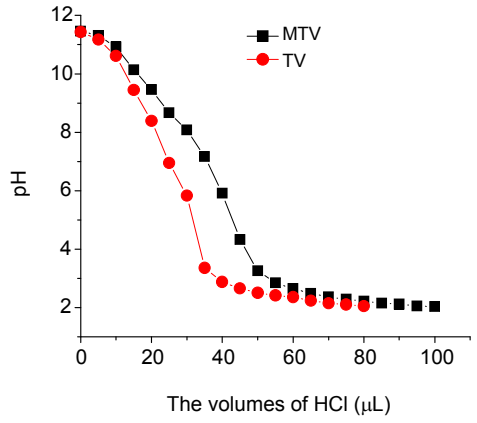
	TV	MTV
(1) Molecular weight	15786	18312
(2) weight	5 mg	5 mg
(3) mole	3.17×10^{-7}	2.73×10^{-7}
(4) total protons of 1°-amine	21	17
(5) total protons of 3°-amine	62	49
(6) total mole of amines (mol N)	2.63×10^{-5}	1.80×10^{-5}
(7) titration volume (ΔV)*	8.7 μL	7.9 μL
(8) concentration of HCl	1.0 M	1.0 M
(9) Buffer capacity (%) $\frac{\Delta V \times 1.0M}{mol\ N} \times 100\%$	33.1 %	43.9 %

Note :

mol N = (21 + 62) x 3.17×10^{-7} = 2.63 x 10-5 for TV

mol N = (17 +49) x 2.73×10^{-7} = 1.80×10^{-5} for MTV

* $\Delta V = V_{pH\ (at\ 7.4)} - V_{pH\ (at\ 5.1)}$, the titration volume is adopted from the following figure:



Reference: M. Piest; Engbersen J. F. J., *J. Controlled Release* **2010,** *148*, 83-90.

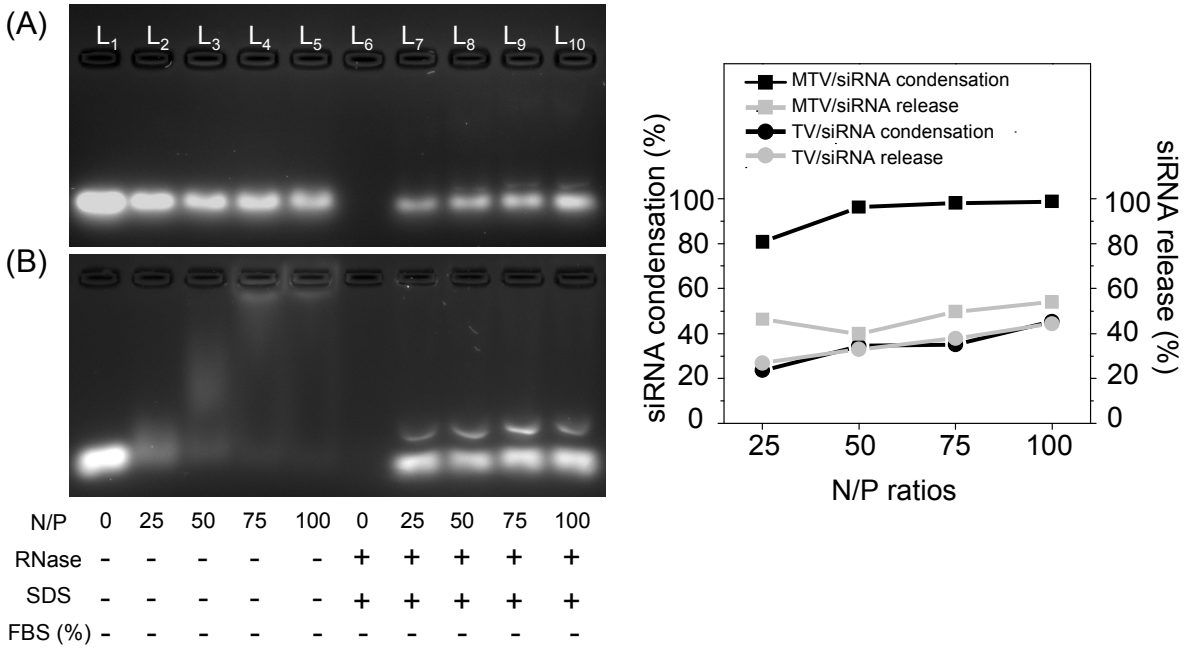


Fig. S6 The efficiency of siRNA condensation and release was evaluated. Panels (A) and (B) represent the agarose gel electrophoresis of TV/siRNA complexes and MTV/siRNA complexes, respectively. The efficiency of siRNA protection and release from two sets of complexes were plotted at various N/P ratios as a function showing in the right lower panel.

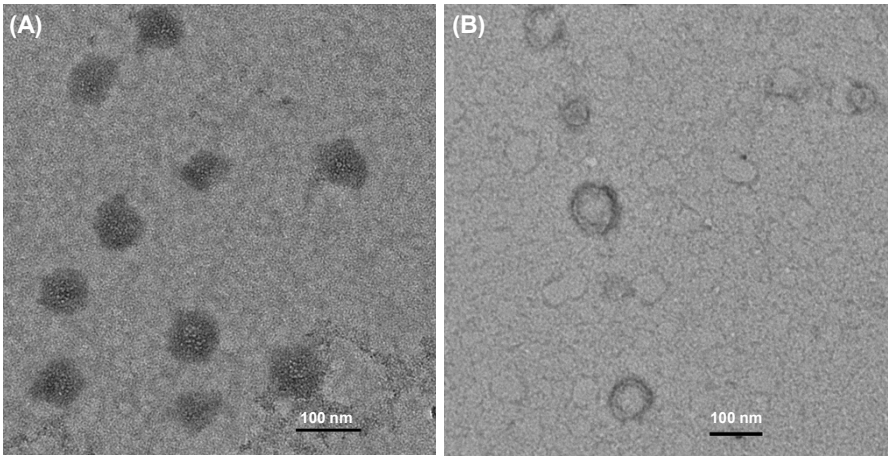


Fig. S7 TEM photographs of (A) TV/siRNA and (B) MTV/siRNA complexes. The samples were deposited on the carbon coated grid and then stained with 2% phosphortungsten acid.