Supplementary Information

Versatile Types of Polysaccharide-Based Supramolecular Polycation/pDNA Nanoplexes for Gene Delivery

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$^1$H NMR assay

Figure S1. 300 MHz $^1$H NMR spectra of (a$_1$) CD-pDM in D$_2$O, (a$_2$) CD-SS-pDM in D$_2$O, (b$_1$) Dex-Ad in DMSO and (b$_2$) Dex-SS-Ad in DMSO.

Chemical Shift (ppm)
For CD-pDM (Figure S1(a1)), the broad chemical shifts in the wide region of 3.4-4.0 ppm are associated with the inner methylidyne and methylene protons (b, CH-O and CH$_2$-O) on glucose units of CD. The chemical shift associated with the unique methylidyne proton (a, O-CH-O) of glucose units is at about 5.0 ppm. The typical chemical shifts at about 0.98, 1.88, 2.36, 2.71 and 4.08 ppm are mainly attributable to the (1) C-CH$_3$ methyl, (2) C-CH$_2$ methylene, (3) N-CH$_3$ methyl, (4) N-CH$_2$ methylene and (5) CH$_2$-O-C=O methylene protons of the pDMAEMA arms, respectively. Moreover, the obvious signals of β-CD (a, b) and pDMAEMA arms (1, 2, 3, 4, 5) were also observed for CD-SS-pDM (Figure S1(a2)). The signals at about 3.15 and 2.83 ppm correspond to the unique methylene protons adjacent to the amide (c, CH$_2$−NH−C=O) and disulfide bonds (d, CH$_2$−S−S), respectively.

For Dex-Ad (Figure S1(b1)), the four chemical shifts in the region of 4.3-5.0 ppm are associated with the unique methylidyne proton (a’, O-CH-O) and hydroxyl protons (e, C-OH) on glucose units of dextran. The broad chemical shifts in the wide region of 3.1-4.0 ppm are associated with the inner methylidyne and methylene protons (b’, CH-O and CH$_2$-O) on glucose units, except the existence of H$_2$O peak (δ = 3.33 ppm) in DMSO-d6 solvent. Moreover, the three chemical shifts in the region of 1.6-2.1 ppm are mainly associated with them ethylidyne and methylene protons (f: CH$_2$-C and CH-C) on Ad group. As for Dex-SS-Ad, besides the obvious signals of Dextran (a’, b’, e) and Ad (f), the signals at about 3.15 and 2.83 ppm correspond to the unique methylene protons adjacent to the amide (c, CH$_2$−NH−C=O) and disulfide bonds (d, CH$_2$−S−S), respectively. Based on the ratio of peak a’ and peak f, the content of Ad was calculated. The glucose unit/Ad ratios of Dex-Ad and Dex-SS-Ad were 4.9:1 and 5.1:1, respectively.
**Figure S2.** The synthetic route of two types of Ad-pendant dextran (Dex-Ad and Dex-SS-Ad).