Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis of Poly[(propargylamine/*n*-butylamine)phosphazene] (PPBP)

Propargylamine (1.0 mL or 1.2mL, 14.6 mmol or 17.5 mmol), n-butylamine (1mL, 10.1 mmol) and triethylamide (TEA) (5 mL, 35.9 mmol) were dissolved in 50 mL THF with stirring, followed by dropwise addition of 1.5 g Poly(dichlorophosphazene) (12.9 unit mmol) to the stirred solution. The stirring was continued for 24 hours at room temperature and then the mixture was filtered to remove any insoluble salts. The resultant polymer was purified via precipitation of the concentrated reaction mixture with water. Further purification was achieved by re-dissolution in THF (three times) and precipitation by hexane. ^{1}HNMR (DMSO): δ (ppm): 3.5-3.8 (N***H***C***H***$_2$C≡CH, N***H***CH$_2$CH$_2$CH$_2$CH$_3$), 2.6-2.9 (NHCH$_2$-C≡C***H***, NHC***H***$_2$CH$_2$CH$_2$CH$_3$), 1.40 (NHCH$_2$C***H***$_2$CH$_2$CH$_3$), 1.28 (NHCH$_2$CH$_2$C***H***$_2$CH$_3$), 0.86 (NHCH$_2$CH$_2$CH$_2$C***H***$_3$).

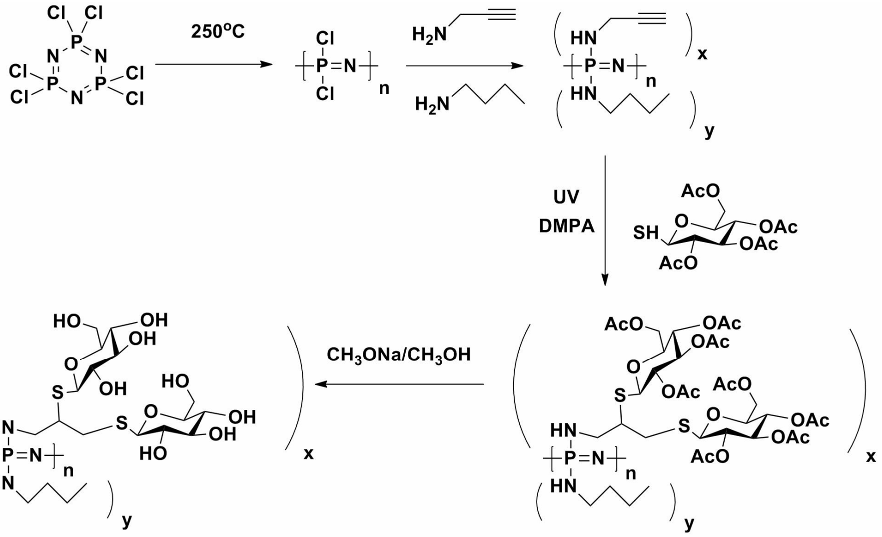

Fig. S1 Schematic representation of click reaction between PPBP and the SH-GlcAc$_4$.

Clicking SH-GlcAc$_4$ to PPBP via the thiol-yne reaction

SH-GlcAc$_4$ (0.7 g, 2.0 mmol) was added to a solution of PPBP (20 mL, C≡C 0.5 mmol), followed by the initiator DMPA (3.2 mg, 0.012 mmol). The reaction was photo-initiated under UV irradiation (λmax=365 nm) at room temperature for a total of 4 hours. A 1:1 H$_2$O/THF solution was used to precipitate the pure poly[(*β*-D-glucose/*n*-butylamine)phosphazene]. Deprotected polyphosphazene was also synthesized using the similar method. For deprotected resultants, ^{1}H NMR (DMSO): 3.5-3.8 ($\mathrm{N}\boldsymbol{H}\mathrm{CH_2}$), 3.3-3.4 ($\mathrm{O}\boldsymbol{H}$), 2.6-2.9 ($\mathrm{NHCH_2C{\equiv}C}\boldsymbol{H}$, $\mathrm{NHC}\boldsymbol{H_2}\mathrm{CH_2CH_2CH_3}$, $\mathrm{NHC}\boldsymbol{H_2}\mathrm{C}\boldsymbol{H}\mathrm{(SR)C}\boldsymbol{H_2}\mathrm{(SR)}$), 1.4 ($\mathrm{NHCH_2C}\boldsymbol{H_2}\mathrm{CH_2CH_3}$), 1.3 ($\mathrm{NHCH_2CH_2C}\boldsymbol{H_2}\mathrm{CH_3}$), 0.86 ($\mathrm{NHCH_2CH_2CH_2C}\boldsymbol{H_3}$). The 4.0-5.5 represented carbohydrate protons. In case of P-37%, the peaks at 2.6-2.9 ($\mathrm{NHCH_2C{\equiv}C}\boldsymbol{H}$) and 5.8-6.2 ($\mathrm{NHCH_2C}\boldsymbol{H}\mathrm{{=}C}\boldsymbol{H}\mathrm{(SR)}$) disappeared, which confirmed that every alkyne group on PPBP underwent the two–step “thiol-yne” click reaction. As illustrated in Fig. S3, due to the large fraction of alkynyl group on PPBP and steric hindrance of glucosyl group, most alkynyl group (49%) completed the two-step click reaction with the introduction of two glycosyl groups to single alkyne group, while the rest (9%) was converted to alkene.

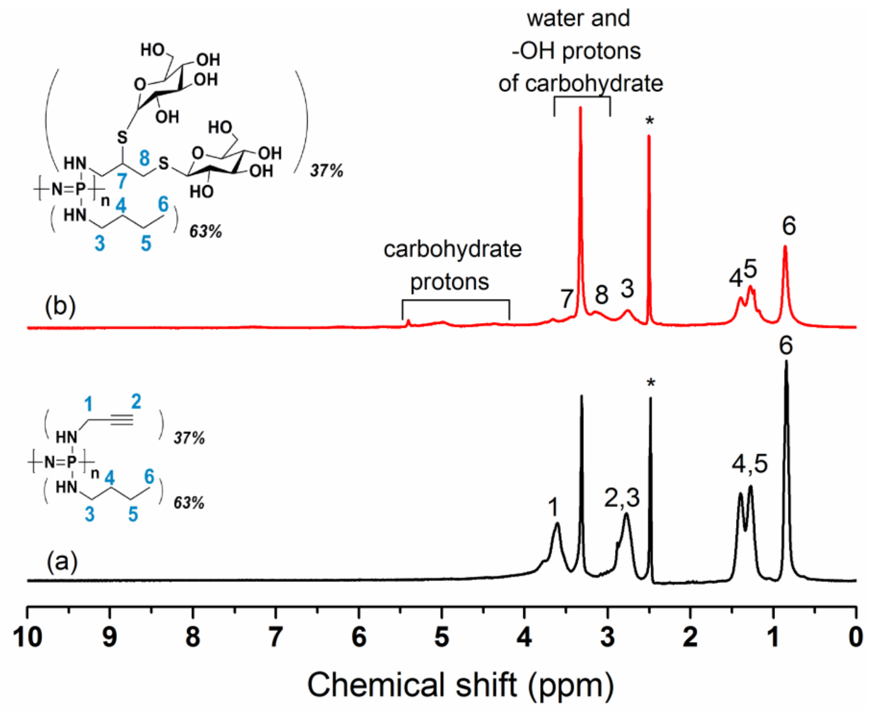

Fig. S2 ^{1}H NMR spectra for P-37%– (a) before, and (b) after glycosylation.

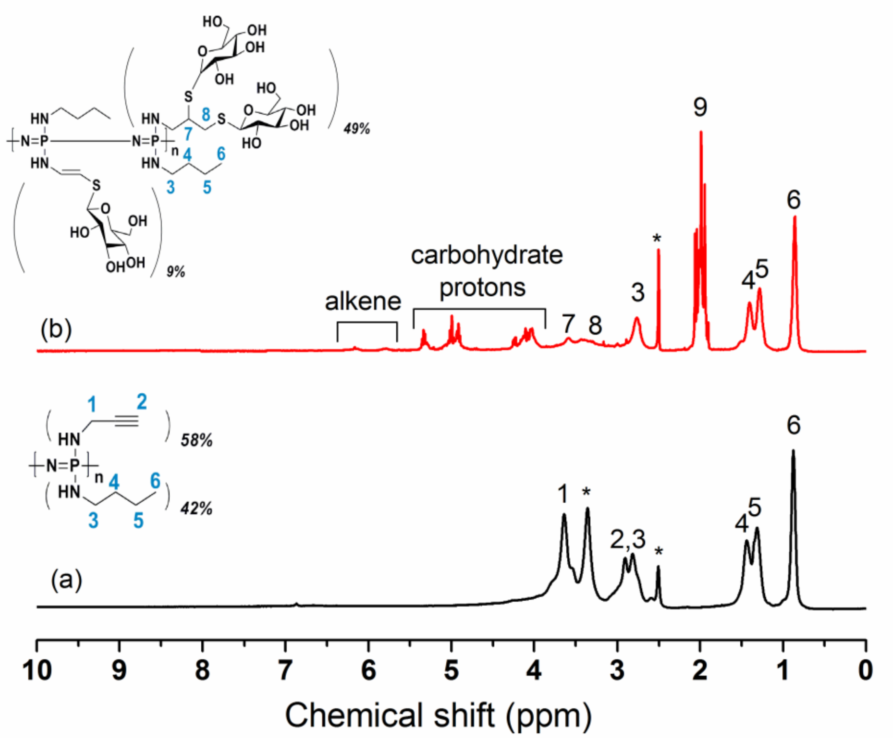

Fig. S3 ¹H NMR spectra for P-58%– (a) before, and (b) after glycosylation.