Supporting information for:

Tuning Polymersome Surfaces:

Functionalization with Dendritic Groups

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Figure S1. Attempt to determine the click reaction yield by ¹H NMR spectroscopy: Polymersome **10** (10 mg/mL, 2 mL) was prepared as described in the experimental section and water was removed on a lyophilizer. The sample was dissolved in CDCl₃ and a ¹H NMR spectrum was collected at 400 MHz on a Varian Inova 400 Spectrometer. Chemical shifts are reported in ppm and are calibrated against residual solvent signals of CDCl₃ (δ 7.27). Appearance of the peak at 8.10 ppm, corresponding to the triazole hydrogen, and decreased intensity of the peaks at 4.33 and 3.93 ppm, corresponding to the starting azide-functionalized polymer (refer to Figure S3 below for a spectrum of the starting polymer PBD-PEO-N₃ (**2**), representing 20 mol% of the polymer composition) supports that the click reaction proceeded. However, quantification of the conjugation yield by integration of the ¹H NMR spectrum proved to be difficult and inaccurate due to the low signal intensity of the above-mentioned peaks relative to the peaks corresponding to the protons on the polymer backbone.



Figure S2. IR spectra of a) PBD-PEO-naked polymersomes (**8**) and b) PBD-PEO-amine polymersomes (**10**) showing the change in the azide stretch integration at 2122 cm⁻¹. The polymersomes were prepared as described in experimental section. Water was then removed using a lyophilizer. Both samples were then dissolved in dichloromethane to give a final polymer concentration of 10 mg/mL. Then, 100 μ L of each solution was cast onto a NaCl plate and the IR spectra were obtained from 400-4000 cm⁻¹ using a Bruker Tensor 27 instrument. This was performed 3 times for each polymersome. The integrations of the peaks at 2122 cm⁻¹ corresponding to the azide stretch were compared, providing a reaction yield of 54 ± 4%.



Figure S3. ¹H NMR spectra comparing PBD-PEO-N₃ (2), the alkyne functionalized rhodamine B derivative 14, and the product rhodamine B labeled copolymer 15. Spectra were obtained at 400 MHz on a Varian Inova 400 Spectrometer. Chemical shifts are reported in ppm and are calibrated against residual solvent signals of CDCl₃ (δ 7.27).