Supporting Information

Charge-reversible and pH-responsive biodegradable micelles and vesicles from linear-dendritic supramolecular amphiphiles for anticancer drug delivery

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Scheme S1 Synthetic Routes of (A) Acetal Monomer AEEEMA and (B) Ada-PEG.



Fig. S1 ¹H NMR spectra of (A) VEA and (2) AEEEMA.



Fig. S3 Detailed ¹H NMR spectrum of CD-G1.





Fig. S5 Detailed ¹H NMR spectrum of CD-G3.



Fig. S7 GPC traces of (A) the polyacetal dendrimers with a CD core and (B) the adamantane-terminated poly(sulfobetaine).



Fig. S8 ¹H NMR spectra of (A) Ada-Br and (B) Ada-PEG.



Fig. S9 2D NOESY spectrum of Ada-PEG and CD-G1. The red rectangle showed the correlational peaks between the protons of adamantane groups and the internal protons of CDs.



Fig. S10 DLS profiles of (A) the CD-G1/Ada-PSB₄₀ micelles and (B) the CD-G2/Ada-PSB₄₀ vsicles after being incubated at pH=7.4 for 12 h.



Fig. S11 (A) TEM images and (B) DLS analysis of (a) DOX@CD-G1/Ada-PSB₄₀ and (b) DOX@CD-G2/Ada-PSB₄₀ nanoparticles.

| Sample | <i>M</i> n, calc. | ${}^{a}M$ n, GPC | ${}^{a}M_{ m w}$, GPC | ^a PDI |
|-----------------------|-------------------|------------------|------------------------|------------------|
| CD-G1 | 5986 | 6420 | 6930 | 1.08 |
| CD-G2 | 14736 | 15300 | 17100 | 1.12 |
| CD-G3 | 32236 | 30600 | 35200 | 1.15 |
| Ada-PSB ₄₀ | — | 5170 | 6620 | 1.28 |
| Ada-PSB80 | _ | 9620 | 12800 | 1.33 |

Table S1 MWs of and PDIs of the polyacetal dendrimers with a CD core and the

adamantane-terminated poly(sulfobetaine)

^aMWs and PDIs determined by GPC.

Table S2 Characterizations of the DOX-loaded micelles and vesicles

| Nanoparticle | ^a Size (nm) | ^a PDI | DLC (wt%) | DLE (%) |
|---------------------|------------------------|------------------|-----------|----------------|
| DOX@CD-G1/Ada-PSB40 | 191 | 0.106 | 5.73 | 57.3 |
| DOX@CD-G2/Ada-PSB40 | 231 | 0.119 | 7.22 | 56.1 |

^{*a*}Sizes and PDIs determined by DLS.