Electronic Supplementary Information (ESI)

for

Precise Modular Synthesis and Structure-Property Study of Acid-Cleavable Star-Block Copolymers for pH-Triggered Drug Delivery

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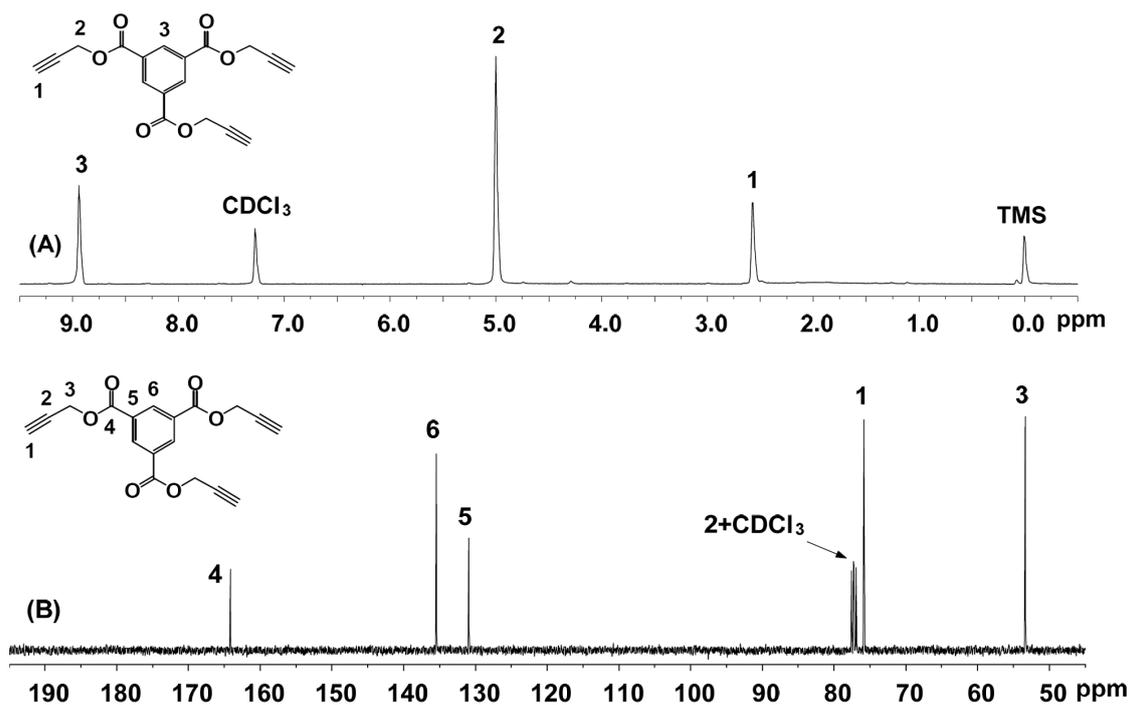and   Jinlin   He   (E-mail: jlhe@suda.edu.cn)

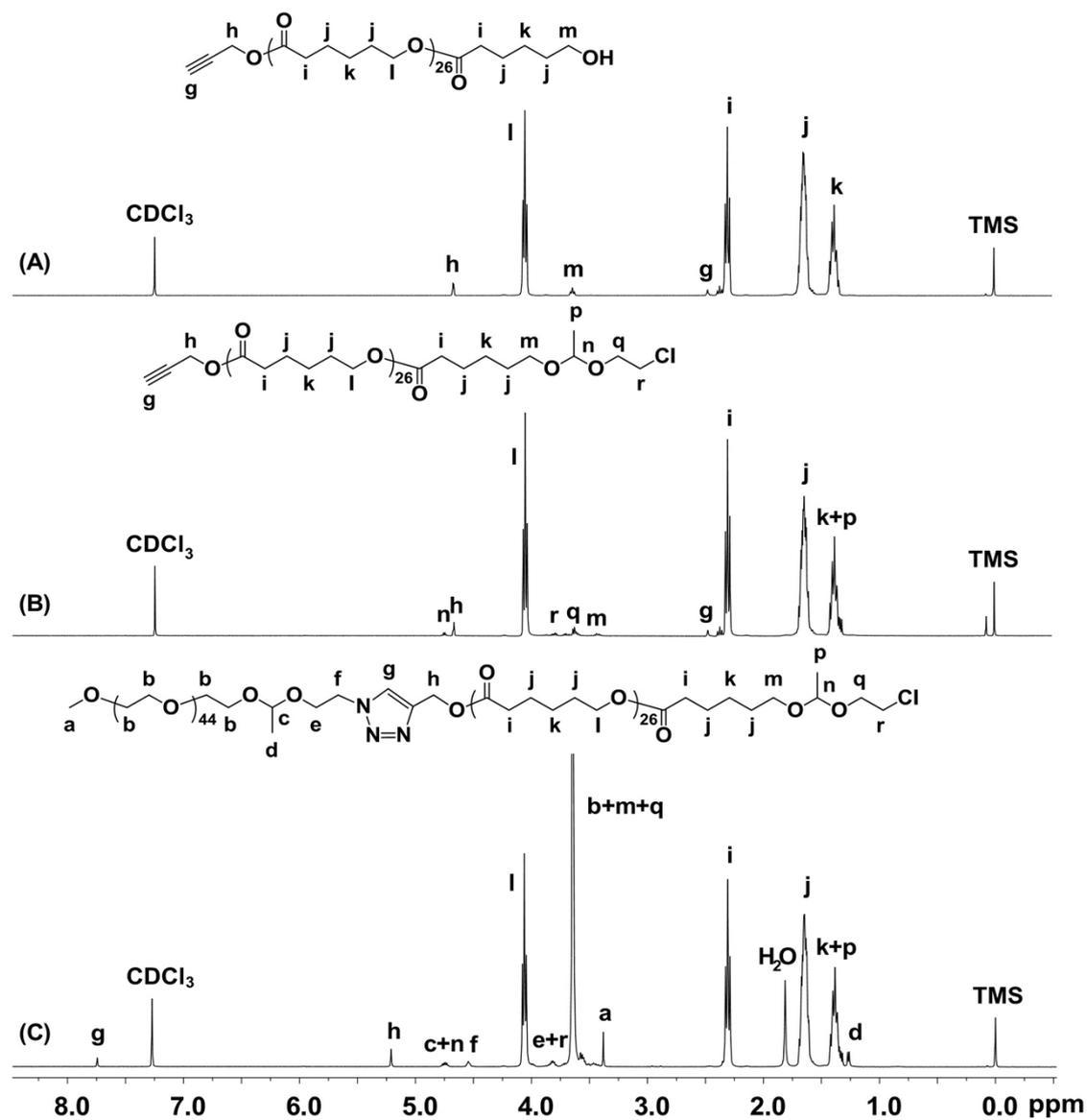**Fig. S1.** (A) ^{1}H NMR and (B) ^{13}C NMR spectra of TPBTC in CDCl$_3$.

Fig. S2. ^{1}H NMR spectra of (A) PA-PCL$_{27}$, (B) PA-PCL$_{27}$-a-Cl and (C) mPEG$_{45}$-a-PCL$_{27}$-a-Cl in CDCl$_3$.
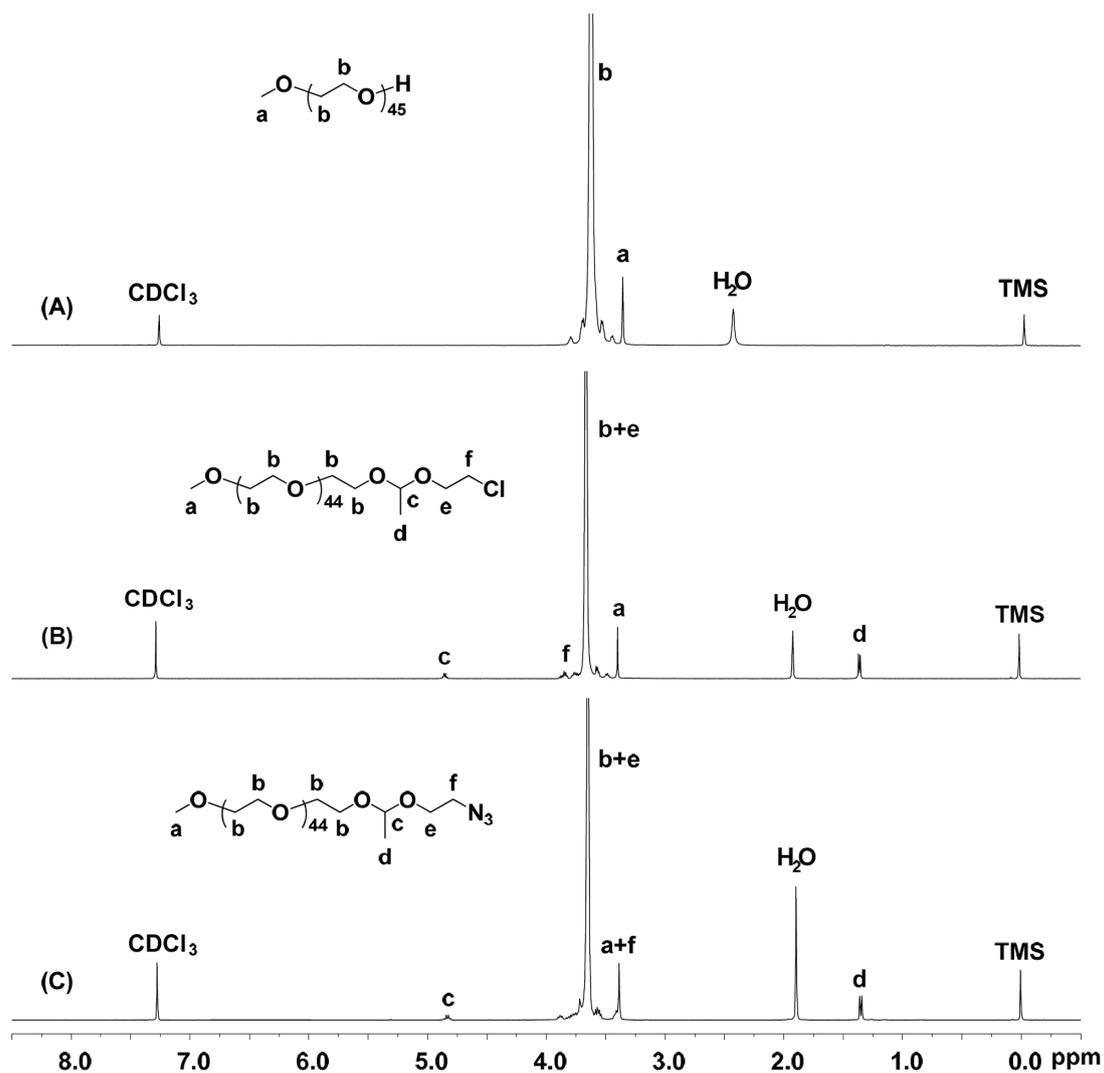
Fig. S3. ^{1}H NMR spectra of (A) mPEG$_{45}$, (B) mPEG$_{45}$-a-Cl, and (C) mPEG$_{45}$-a-N$_3$ in CDCl$_3$.
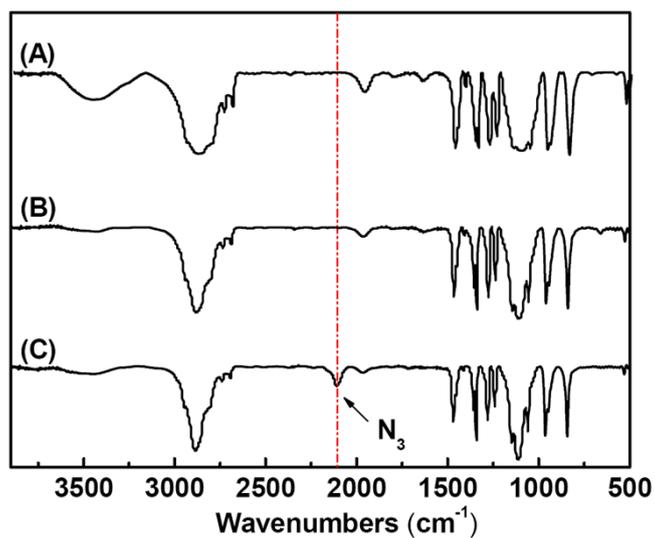
Fig. S4. FT-IR spectra of (A) mPEG$_{45}$, (B) mPEG$_{45}$-a-Cl, and (C) mPEG$_{45}$-a-N$_3$.
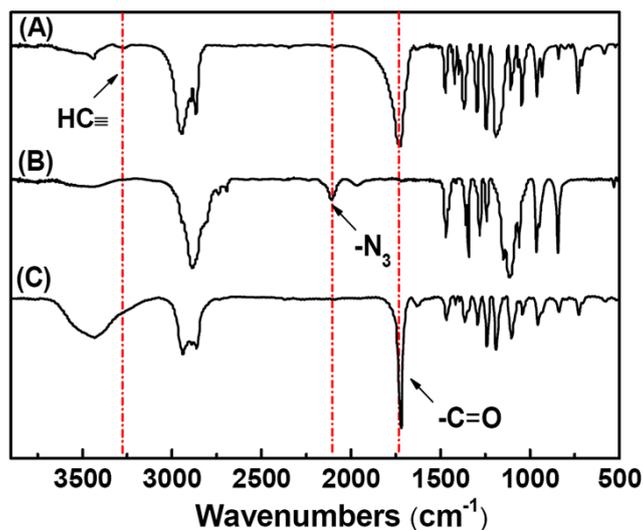
Fig. S5. FT-IR spectra of (A) PA-PCL$_{27}$-a-Cl, (B) mPEG$_{45}$-a-N$_3$ and (C) mPEG$_{45}$-a-PCL$_{27}$-a-Cl.
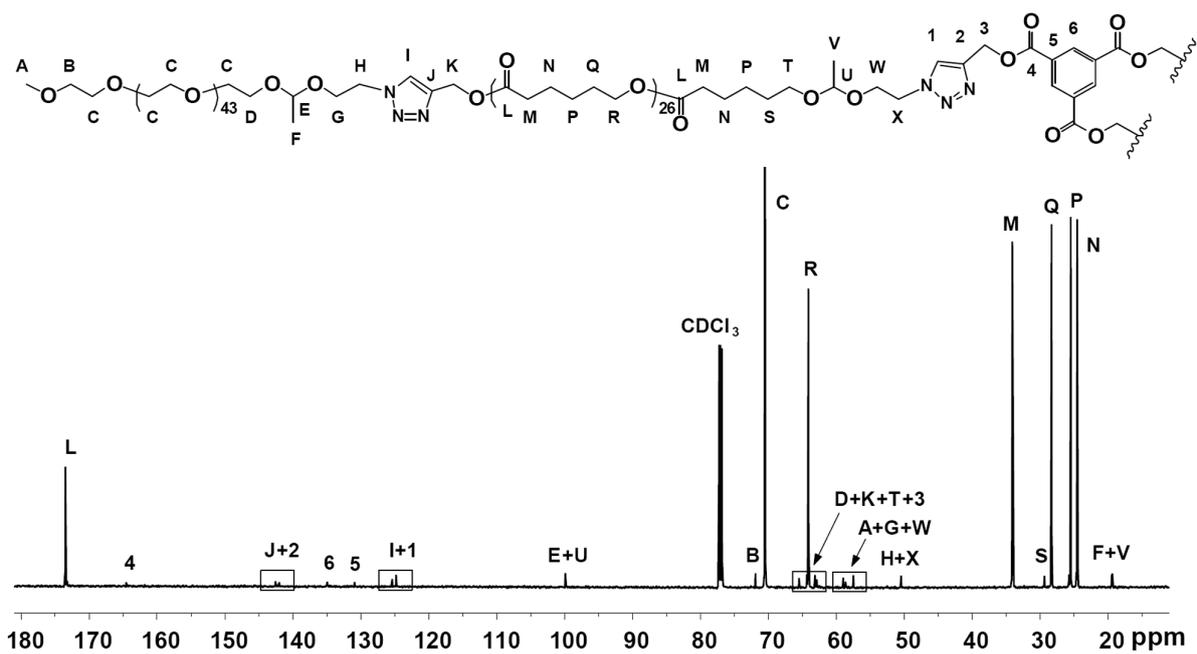
Fig. S6. ^{13}C NMR spectrum of (mPEG$_{45}$-a-PCL$_{27}$-a-)$_3$ in CDCl$_3$.
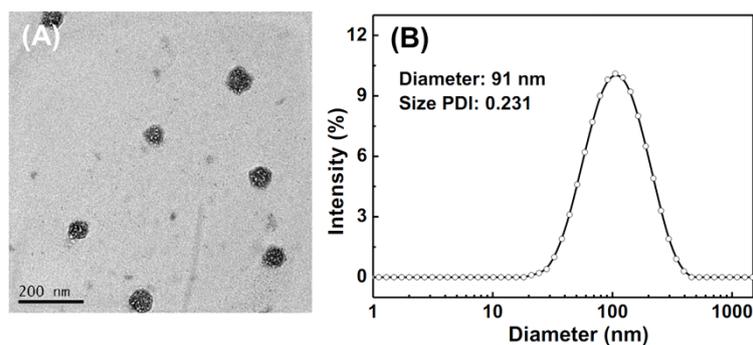
Fig. S7. (A) TEM image and (B) particle size distribution curve of the aggregates self-assembled from $(mPEG_{45}\text{-}a\text{-}PCL_{18}\text{-}a\text{-})_3$. The polymer concentration was 80 mg L^{-1}, bar = 200 nm.
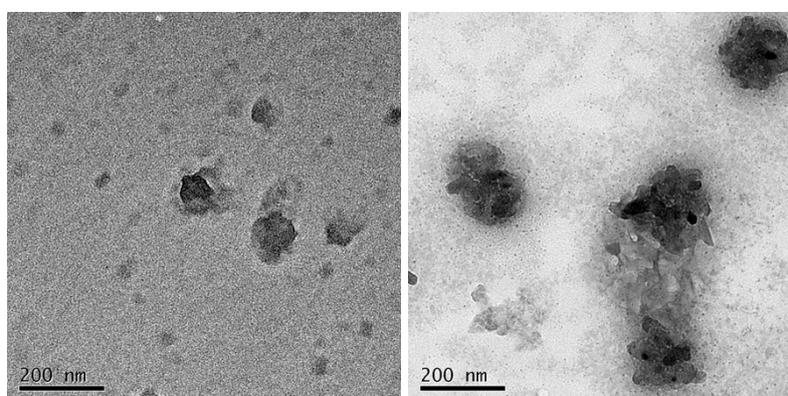
Fig. S8. TEM images of $(mPEG_{45}\text{-}a\text{-}PCL_{27}\text{-}a\text{-})_3$ aggregates after incubation at pH 5.0 for 48 h (bar = 200 nm). The concentration of sample was 80 mg L^{-1}.
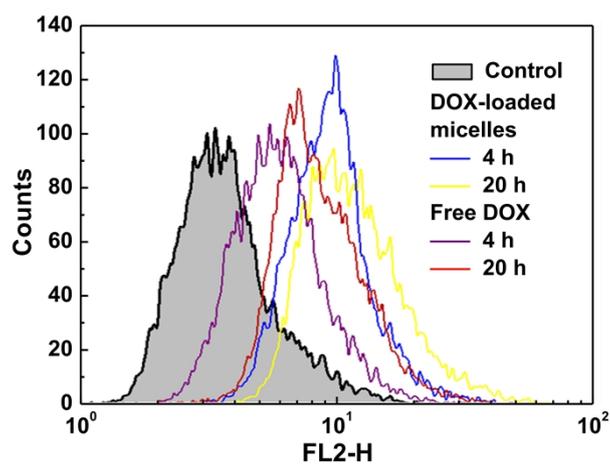
Fig. S9. Flow cytometry histogram profiles of HeLa cells incubated with DOX-loaded $(mPEG_{45}\text{-}a\text{-}PCL_{27}\text{-}a\text{-})_3$ micelles and free DOX for different times. The dosage of DOX was 0.1 mg L^{-1}.