Supporting Information for

Reduction-Triggered Release of Paclitaxel From *In Situ* Formed Biodegradable Core-Crosslinked Micelles

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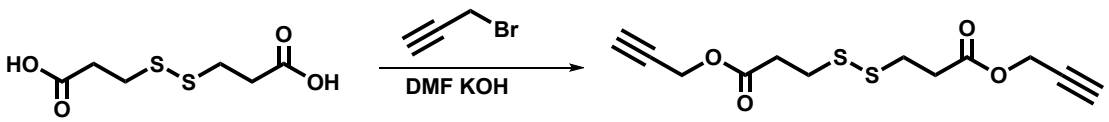
Characterization of propargyl 3,3'-dithiopropionate (Scheme S1)

The ^{1}H NMR spectrum of propargyl 3,3'-dithiopropionate was shown in Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$), d: 2.5 (s, 2H, -CH_2C≡CH), 2.7 (t, 4H, -CH_2CO-), 2.9 (t, 4H, -SCH_2-), 4.7 (m, 4H, -CH_2C≡CH). Unfortunately, the DMF solvent was not removed completely for its high boiling point. However, the amount of DMF in the product could be calculated by the integral ratio of corresponding proton in ^{1}H NMR spectrum and the following "click" reaction was carried out in DMF media, which makes it possible to proceed the "click" reaction precisely.

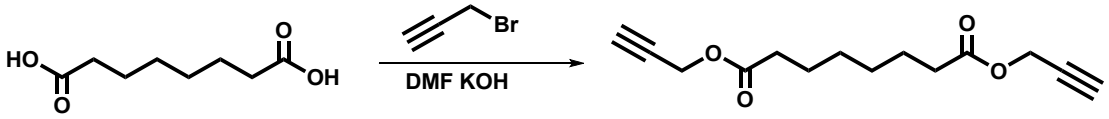
Preparation of PTX-loaded Non-disulfide CCL Micelles

The ^{1}H NMR spectrum of dipropargyl suberate was shown in Fig. S2 with the relevant signals labeled. ^{1}H NMR (400 MHz, $CDCl_3$), d: 1.35 (t, 2H, -$CH_2CH_2CH_2$-), 1.65 (t, 4H, -CH_2CH_2CO-), 2.3 (t, 4H, -CH_2CO-), 2.5 (s, 2H, -$CH_2C{\equiv}CH$), 4.7 (m, 4H, -$CH_2C{\equiv}CH$). Then, 25 mg of mPEG-b-PDATCL (0.062 mmol of azide group), 10 mg of dipropargyl suberate (0.031 mmol) and 2.5 mg of PTX were dissolved in 15 mL of THF and stirred for 0.5 h. Then 15 mL of phosphate buffer (PBS, 0.01 M, pH 7.4) was added dropwise to the solution under stirring. The resulting solution was stirred for 2 h and evaporated to remove THF under vacuum. Then sodium ascorbate (12.3 mg; 0.062 mmol) and copper sulfate (15.4 mg; 0.062 mmol) was added to the reactor under argon atmosphere. The mixture was stirred for 24 h, then dialyzed (MWCO 3500, Fisher Scientific) against PBS (0.01 M, pH 7.4) over 24 h. The final concentration of the micellar solution was adjusted to 1.0 mg/mL.

Determination of the Calibration curves of PTX in PBS with and without DTT. Calibration curves of PTX in ethanol were determined by measuring the absorption of PTX with known concentrations via Shimadzu UV2550 UV-vis spectrophotometer at a wavelength of 227 nm, which is the typical absorption for PTX. The absorption as a function of PTX concentration was recorded to generate the calibration curve, which is shown in Fig S4.



Scheme S1 Synthesis of propargyl 3,3'-dithiopropionate.



Scheme S2 Synthesis of dipropargyl suberate.

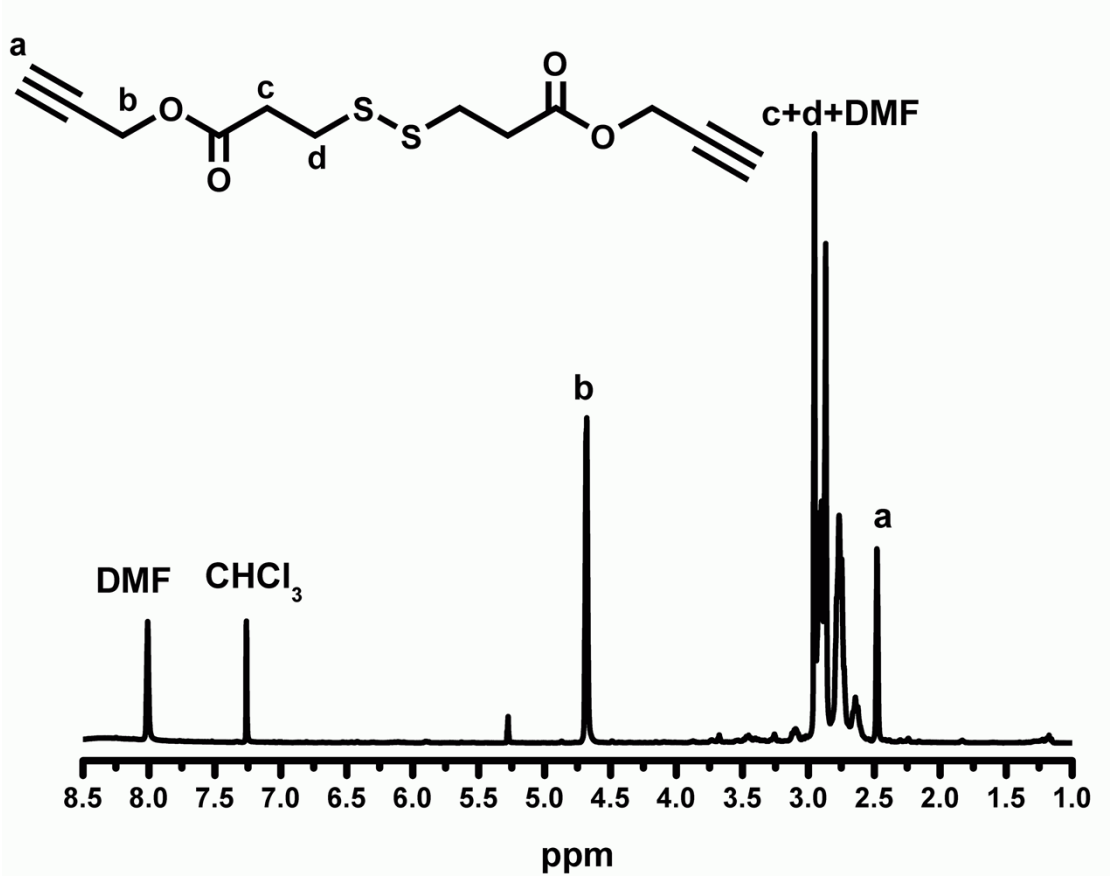


Fig. S1. ^{1}H NMR spectrum of propargyl 3,3'-dithiopropionate.

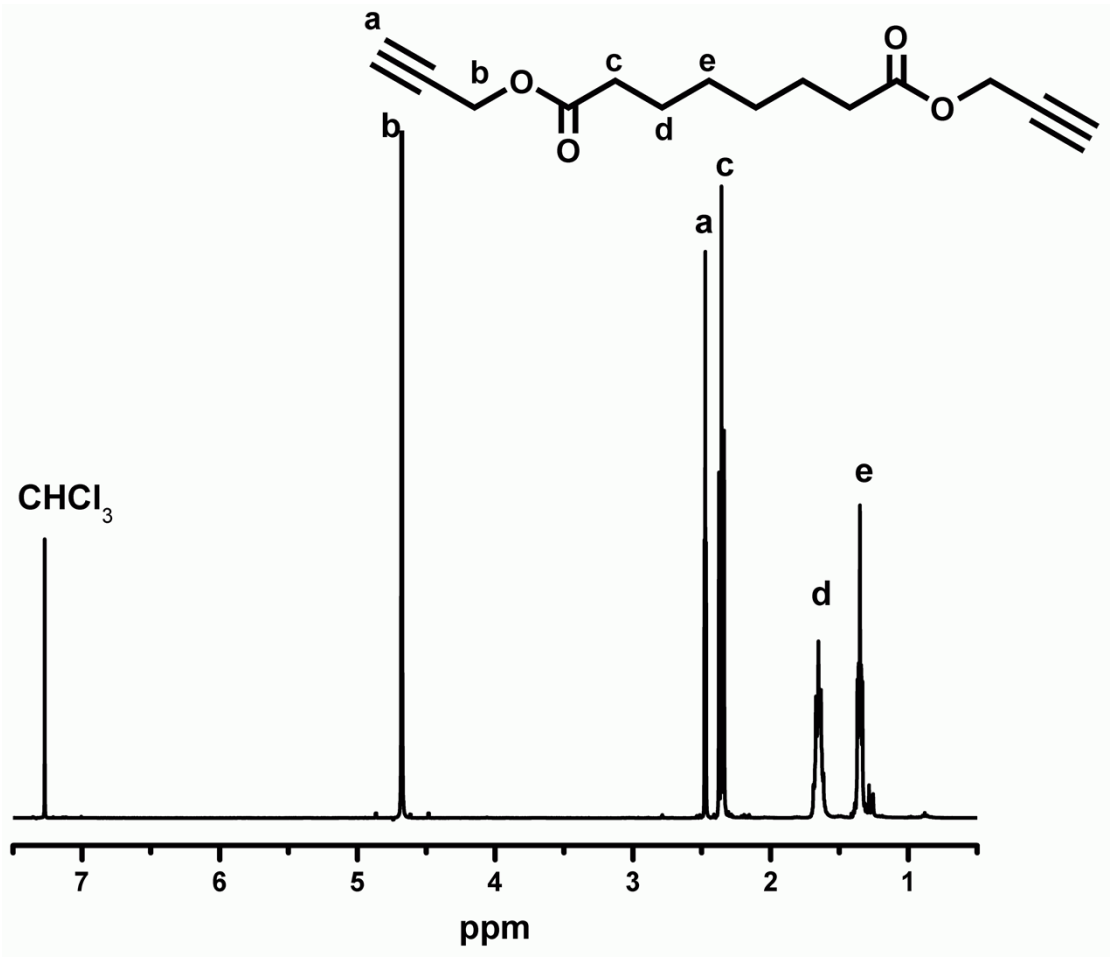


Fig. S2. ^{1}H NMR spectrum of dipropargyl suberate.

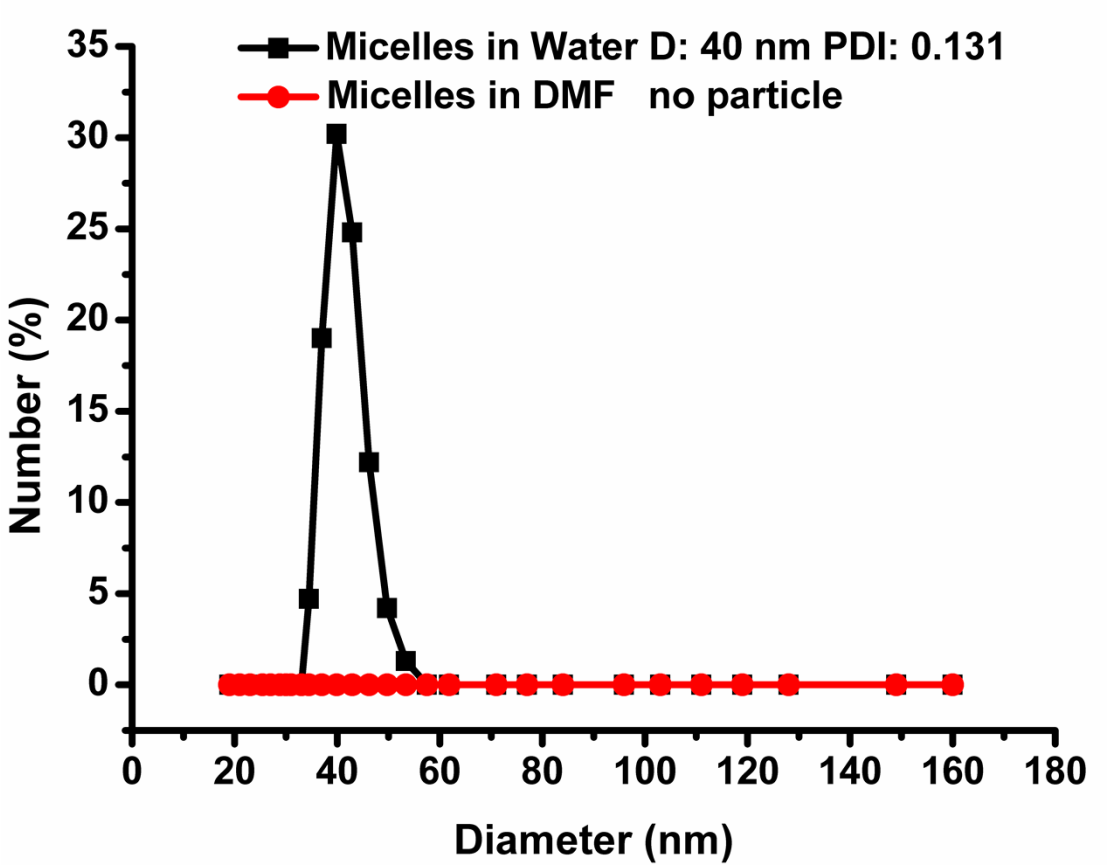


Fig. S3. Particle size of non-crosslinked micelles in water and DMF by DLS.

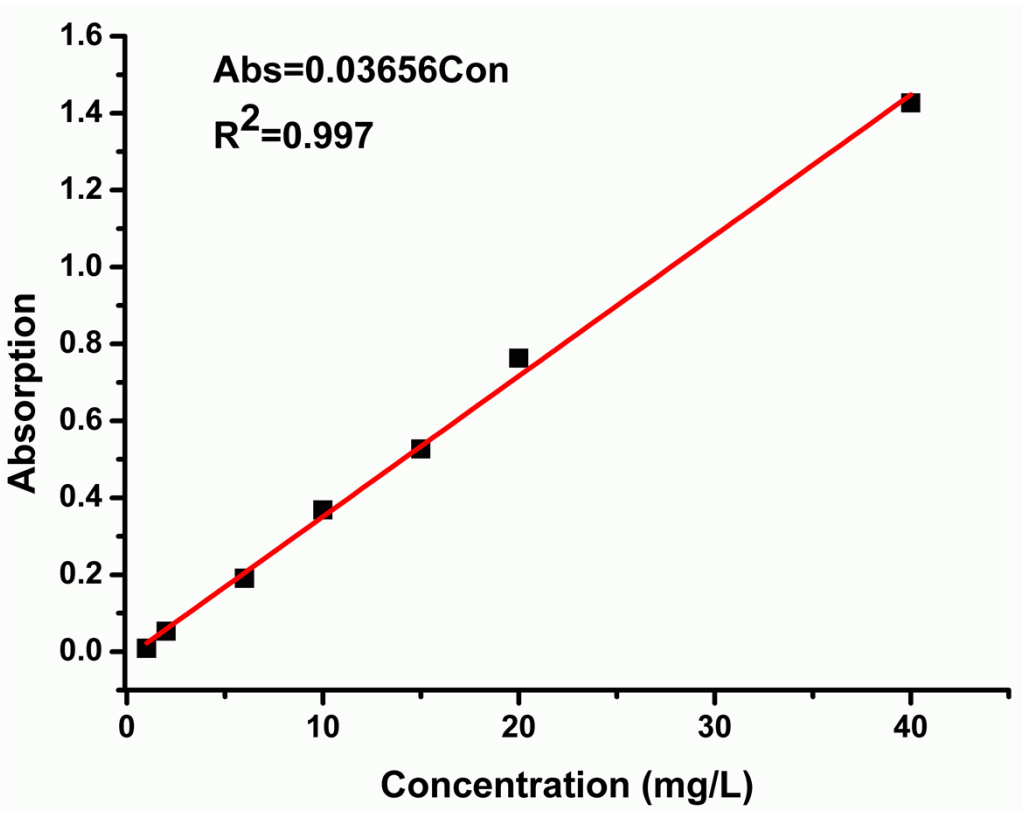


Fig. S4. Calibration curves of PTX in ethanol.