Supporting information

Multifunctional poly(amine-ester)-type hyperbranched polymers: lipase-catalyzed green synthesis, characterization, biocompatibility, drug loading and anticancer activity

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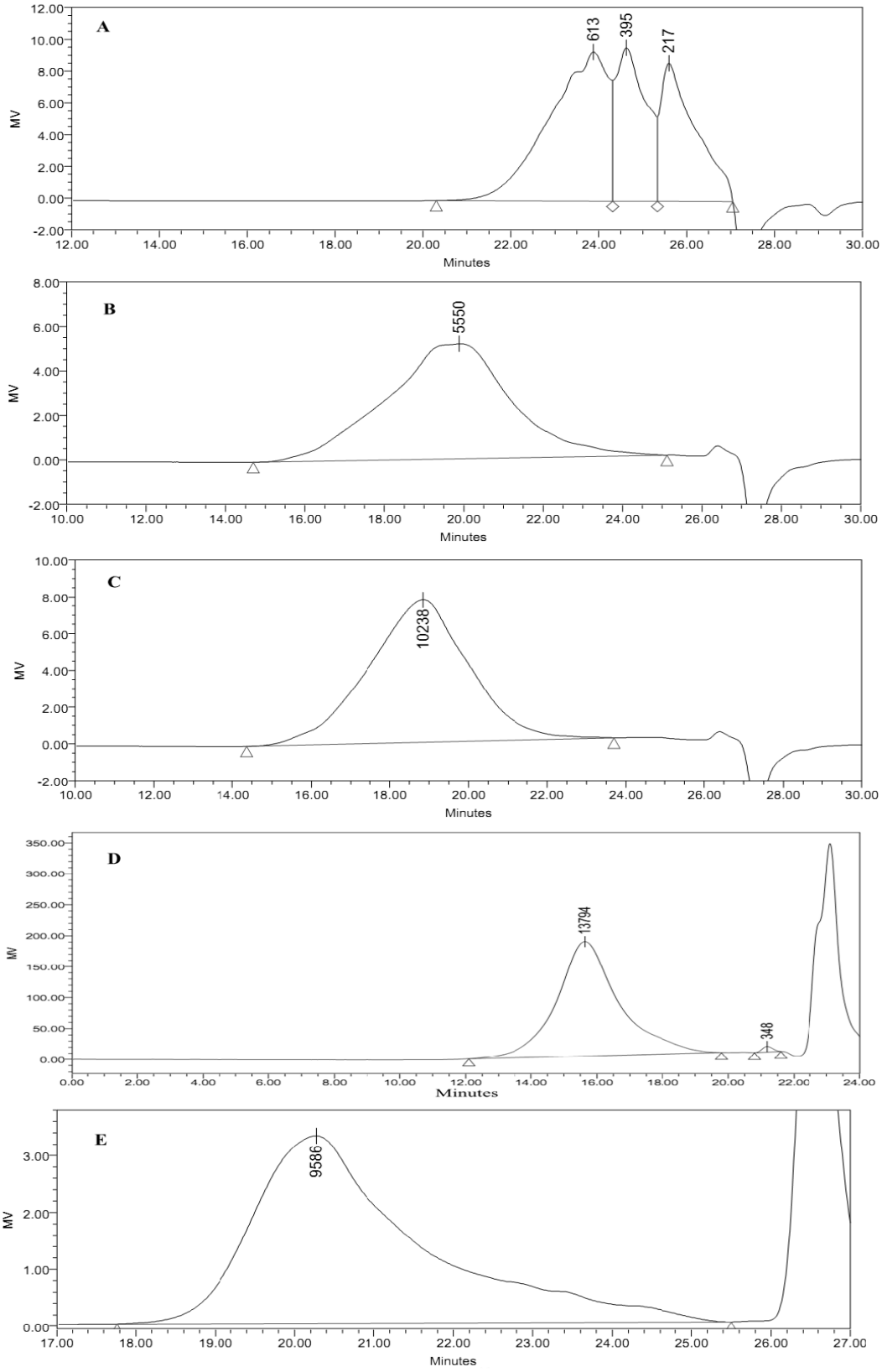

Figure S1. The GPC chromatograms of (A) P1; (B) P2; (C) P3; (D) P4; (E) P5.

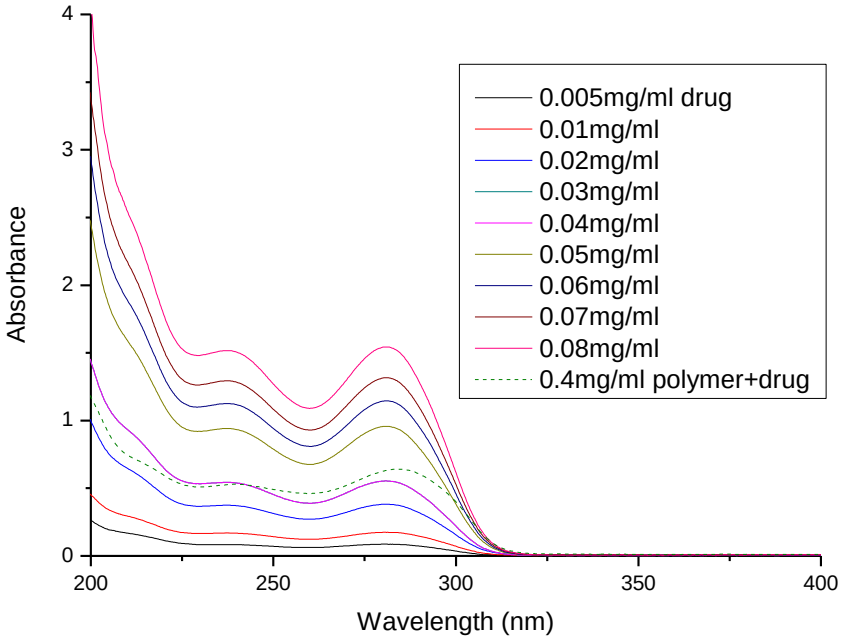

Figure S2. UV absorption spectra of 5'-O-vinyladipoyl-fluorodeoxyuridine solution with different concentrations and drug packaged Poly(TEOA1-DMSE1) micelles water solution.

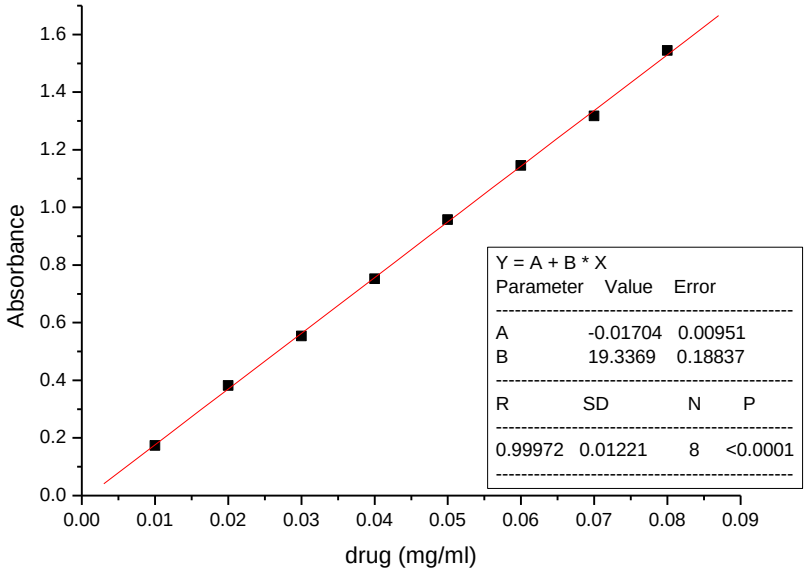

Figure S3. Linear relationship between UV absorbance and the concentrations of 5'-O-vinyladipoyl-fluorodeoxyuridine. The fitted equation was: Absorbance=19.3×drug concentration-0.02.

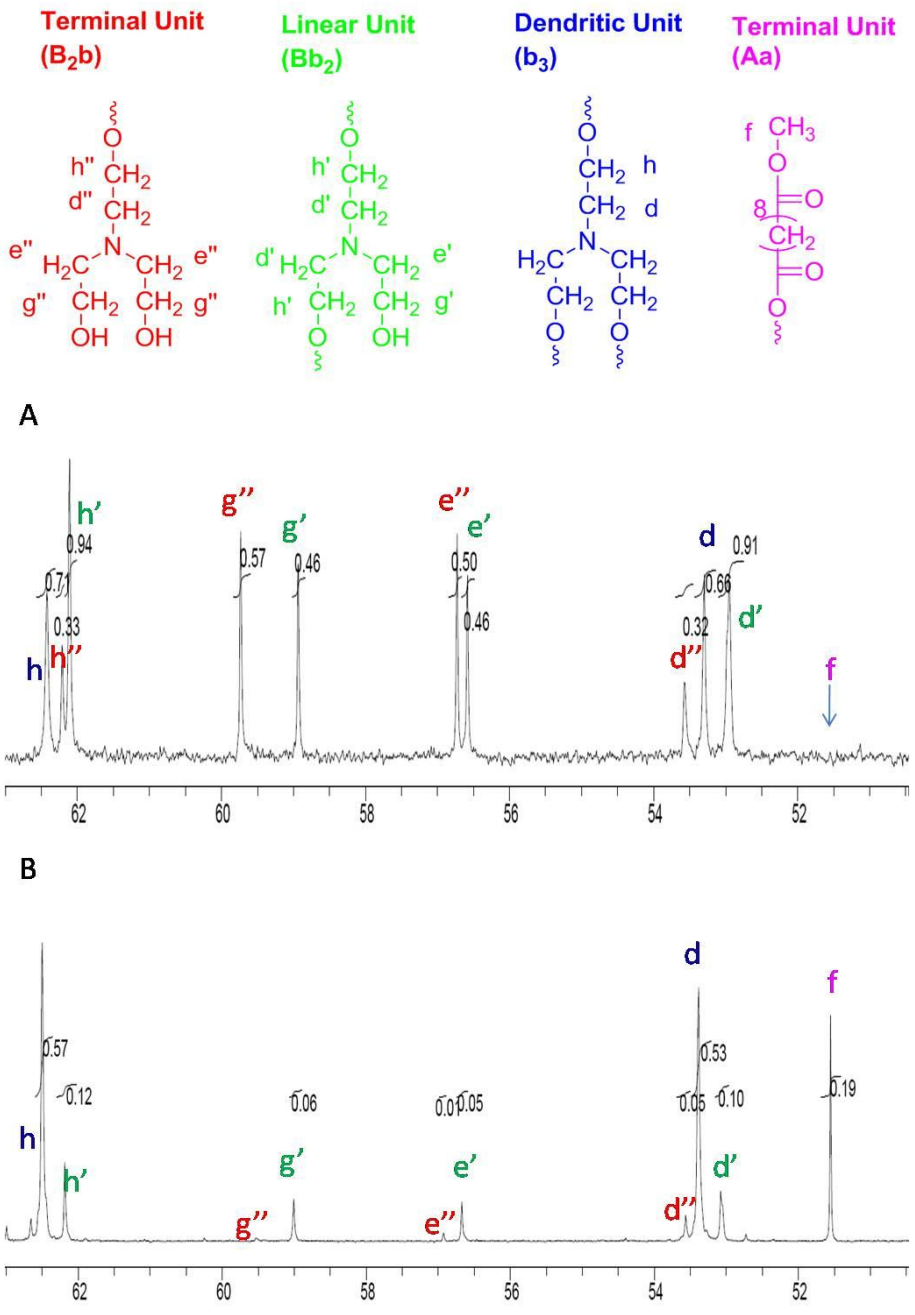

Figure S4. Possible structural units and comparison of ^{13}C NMR subspectra of Poly(TEOA1-DMSE1) (A) and Poly(TEOA1-DMSE2) (B).

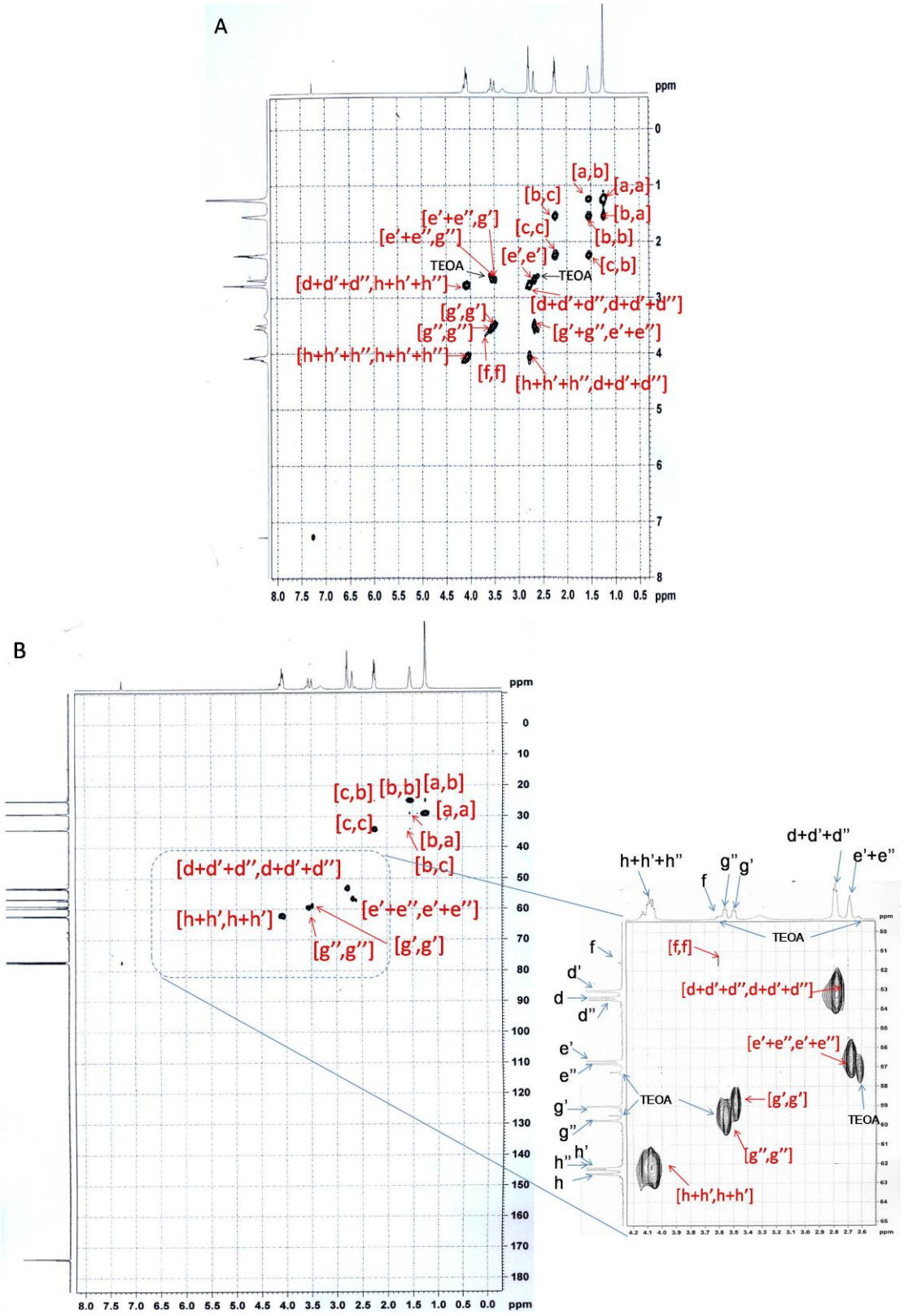

Figure S5. 2D-NMR of Poly(TEOA1-DMSE1) in $CDCl_3$, ^1H, ^1H-COSY spectrum (A) and ^{13}C, ^1H-HSQC spectrum (B)

The DB calculation of HBPs

DB of Poly(TEOA1-DMSE2): The peak at 2.8ppm in Figure 1A relating with the methylene groups attached to N atoms in b_3, Bb_2, B_2b units (d+d'+d'') can provide the equation of "$6b_3+4Bb_2+2B_2b=2.9$". And the peak g' in Figure 1A relates with the methylene groups of hydroxy terminals in Bb_2 ("$2Bb_2=0.26$"), while the peak relating with the methylene groups of hydroxyl terminals in B_2b units is absent which means "$B_2b=0$". From the above three equations, we can obtain: $b_3=0.40$, $Bb_2=0.13$, and $B_2b=0$. According to the following equation:

$$DB = \frac{2D}{2D+L} = \frac{2(b_3)}{2(b_3)+(Bb_2)}$$

The DB of Poly(TEOA1-DMSE2) was about 86.0%. It can be found that very few hydroxyl terminals and linear units exist in the hyperbranched Poly(TEOA1-DMSE2), while the ester terminal units (3aA=1.46) had the highest percentage.

DB of Poly(TEOA1-DMSE1): The calculation of DB of Poly(TEOA1-DMSE1) is similar to Poly(TEOA1-DMSE2). From the ^{1}H NMR shown in Figure 1B, we can get three equations: $6b_3+4Bb_2+2B_2b=3.99$; $2Bb_2=1.03$; $4B_2b=1.13$. Thus, we can obtain: $b_3=0.23$, $Bb_2=0.52$ and $B_2b=0.28$. The DB of Poly(TEOA1-DMSE2) was about 46.9%.

DB values of Poly(TEOA1-DMAD2) and Poly(TEOA1-DMAZ2): The DB values of Poly(TEOA1-DMAD2) and Poly(TEOA1-DMAZ2) also can be calculated from their corresponding ^{1}H NMR spectra shown in Figure S6-S7. They were 89.7% and 84.6%, respectively.

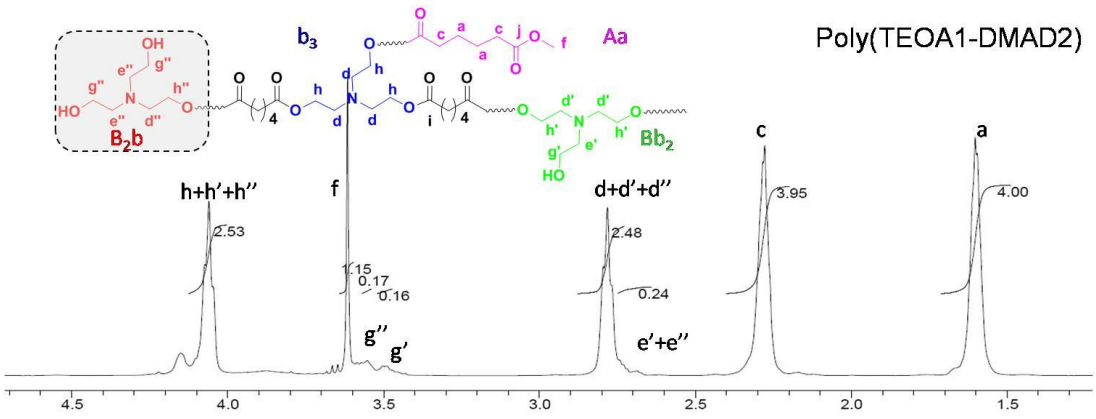

Figure S6. ^{1}H NMR spectrum of Poly(TEOA1-DMAD2) for calculation of DB

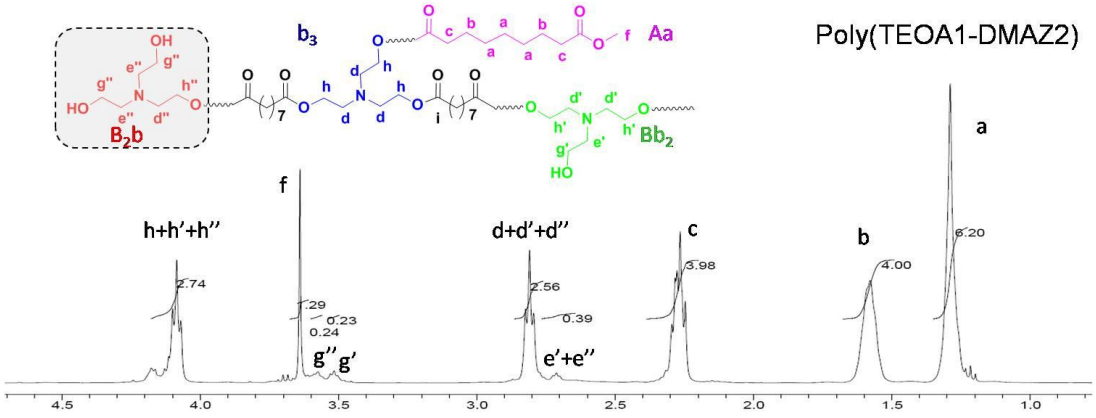

Figure S7. ^{1}H NMR spectrum of Poly(TEOA1-DMAZ2) for calculation of DB