Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Construction and Drug Delivery of A Fluorescent TPE-bridged Cyclodextrin/Hyaluronic Acid Supramolecular Assembly

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Synthesis of **1**[1]

Zinc powder (10 g), 2 mL acetic acid and 50 mL H_2O were mixed and stirred at room temperature for 30 minutes, then the activated zinc powder was gained by filtration and desiccation. Zn dust (3.3 g, 50 mmol) was added to a solution of $TiCl_4$ (2.75 mL, 25 mmol) in 60 ml of dry THF. After refluxing for 2 hours, 1ml pyridine and 4,4'-dimethoxybenzophenone (6.01 g, 25 mmol) in 60 ml THF were added. After refluxing for 20 hours, the reaction was cooled and stopped with K_2CO_3 (5g) aqueous solution. The mixture was extracted by dichloromethane and the organic phase was collected and evaporated under vacuum. Then TPE derivative **1** was gained by recrystallization using dichloromethane and petroleum ether in 90% yield. ^{1}H NMR (400 MHz, CDCl3) δ 6.93 (d, J = 8.7 Hz, 8H), 6.63 (d, J = 8.7 Hz, 8H), 3.74 (s, 12H).

Synthesis of **β-CD azide**[2]

At room temperature, 280 g β-CD, 28 g NaOH and 2 L H_2O were mixed and stirred for 30 minutes. Then 40 g p-toluenesulfonyl chloride in 90 mL CH_3CN was added in 30 minutes, Following by another 2 hours stirring and suction filtration to give a crude p-toluenesulfonyl modified β-CD. Then 15 g NaN_3 and 250 mL H_2O were mixed with the prepared p-toluenesulfonyl modified β-CD and the mixture was stirred at 80 ℃ for 5 hours. After cooling down, the mixture was dropwise added to 1000 mL acetone and then β-CD azide(total yield, 7%) was gained as white solid after filtration.

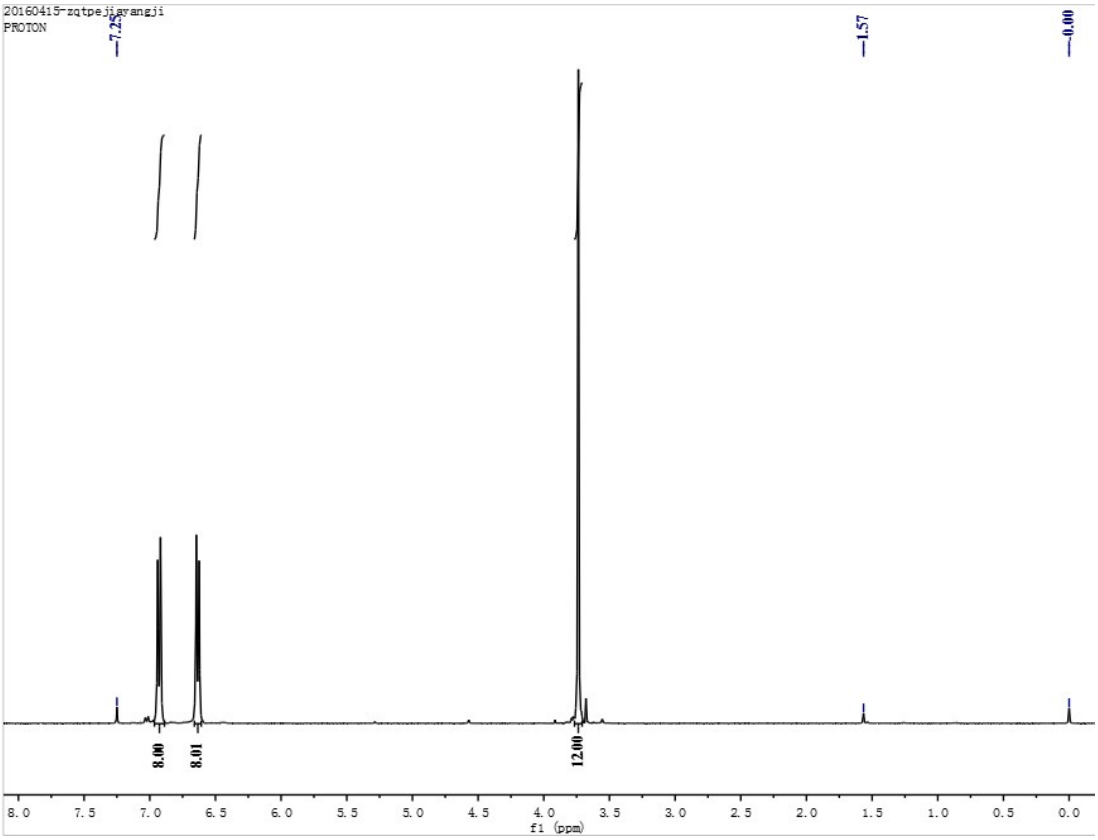

Figure S1. ^{1}H NMR of TPE derivative **1**

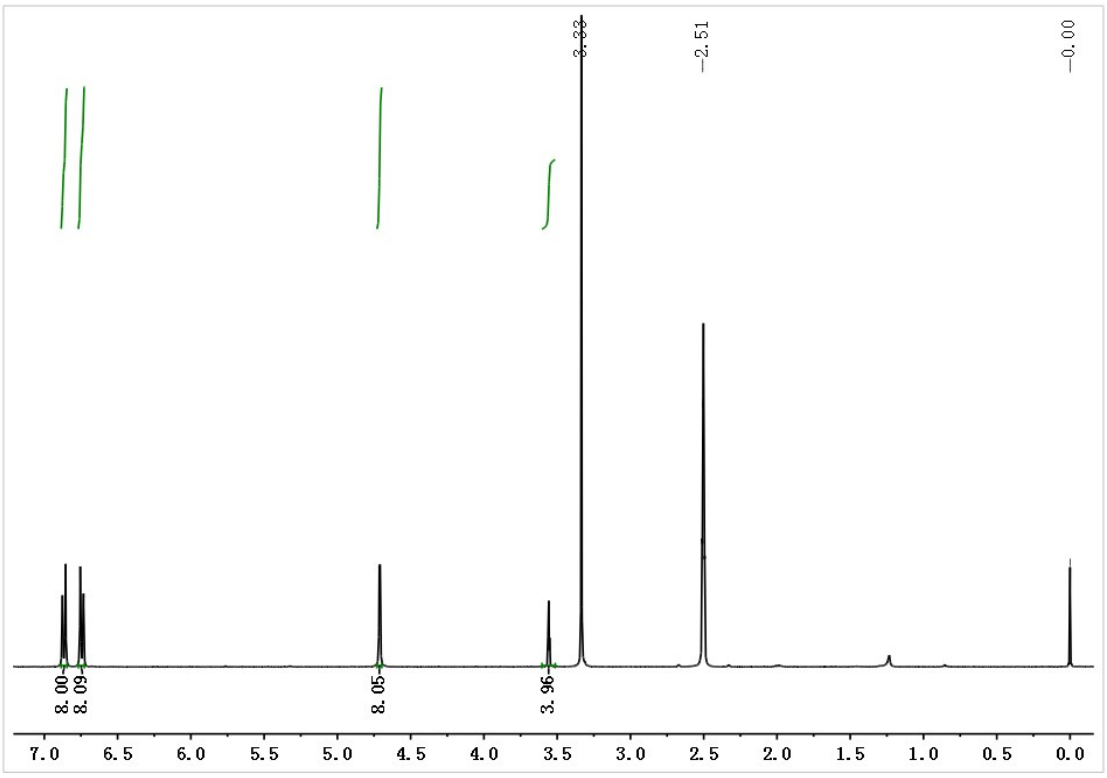

Figure S2. ^{1}H NMR of TPE derivative **2**

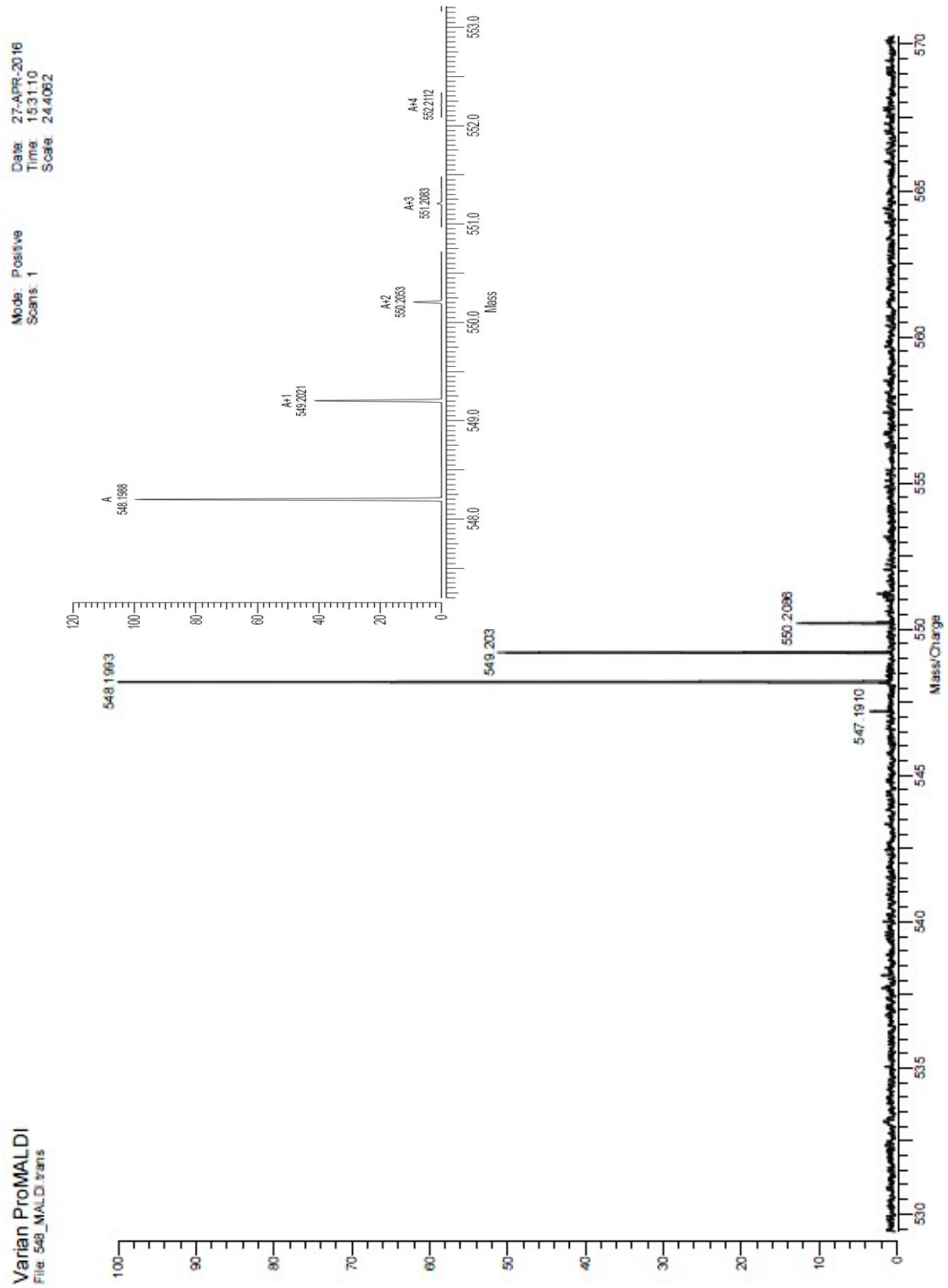

Figure S3. HRMS of TPE derivative **2**(insert: simulated spectrum)

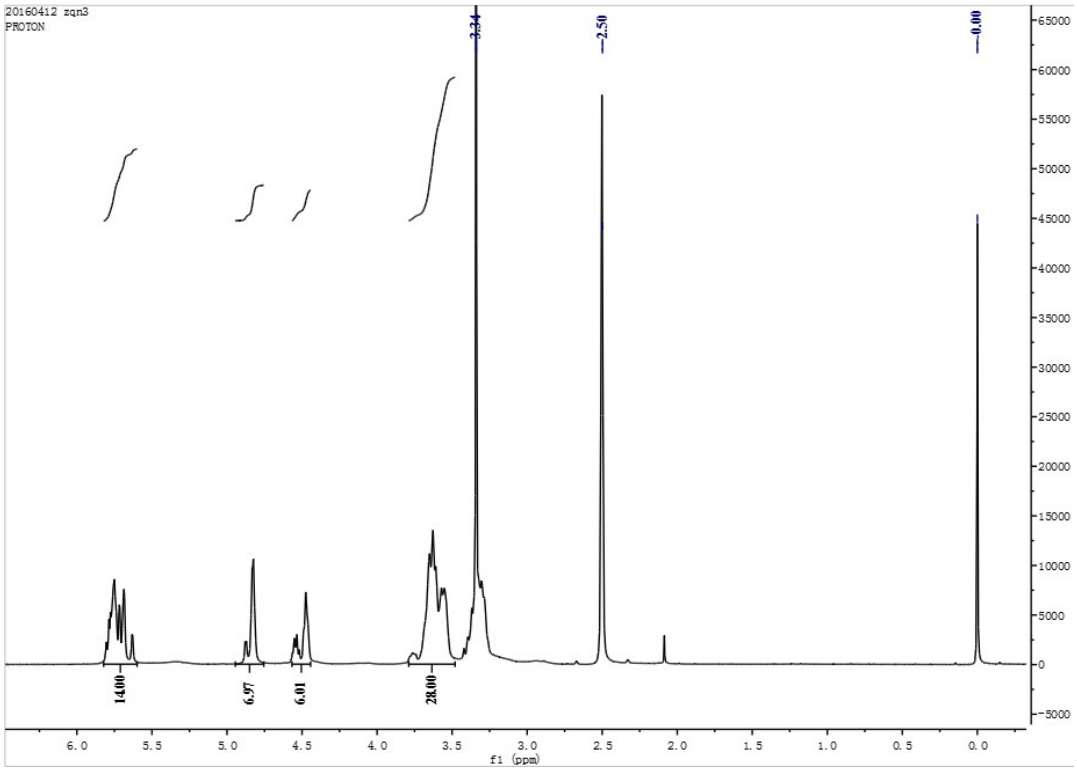

Figure S4. ^{1}H NMR of N_3-β-CD

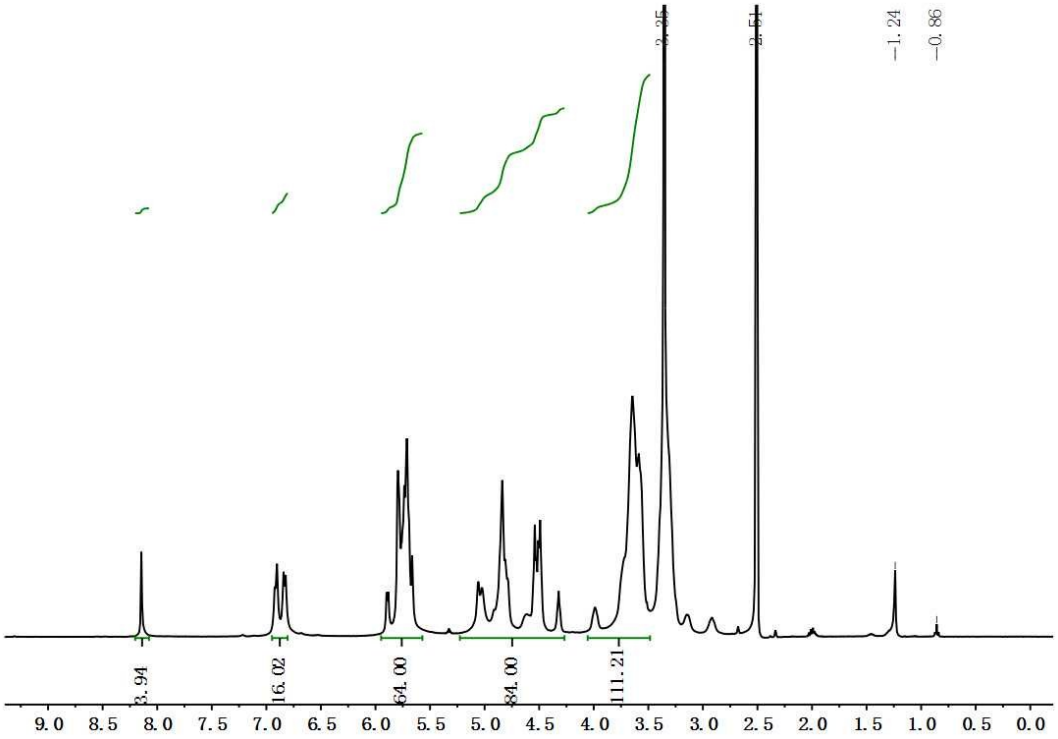

Figure S5. ^{1}H NMR of TPECD

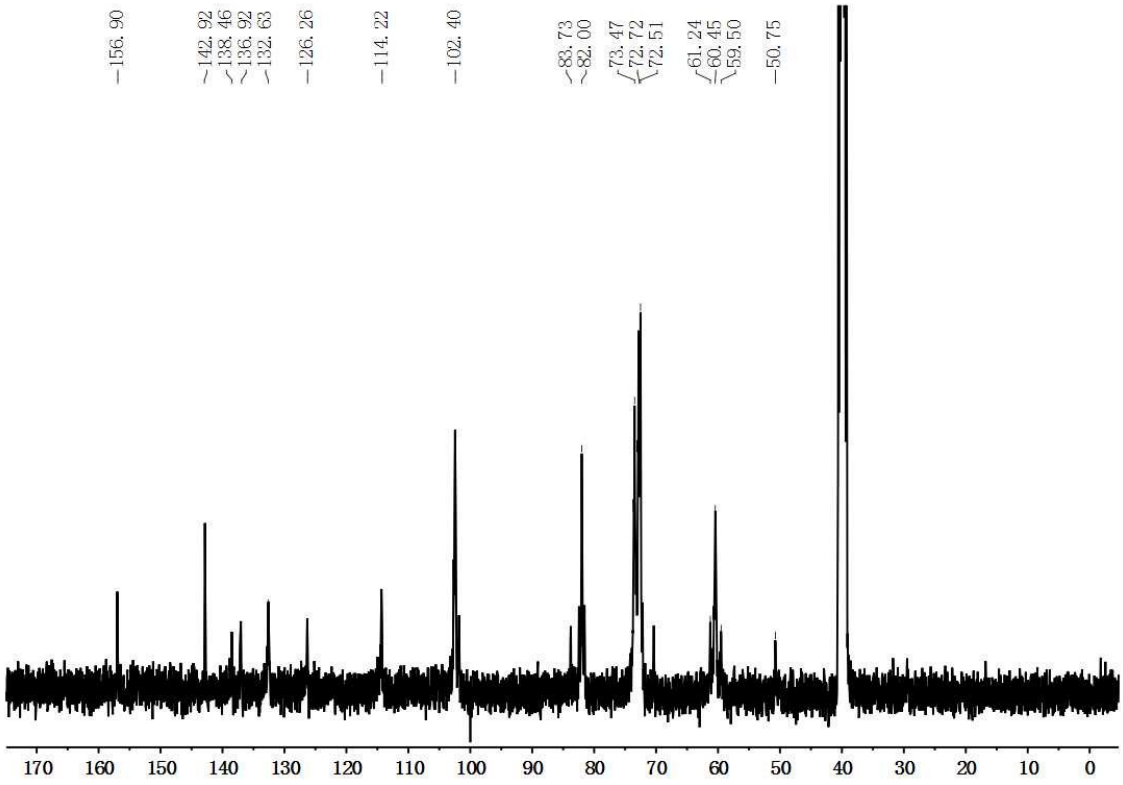

Figure S6.^{13}C NMR of TPECD

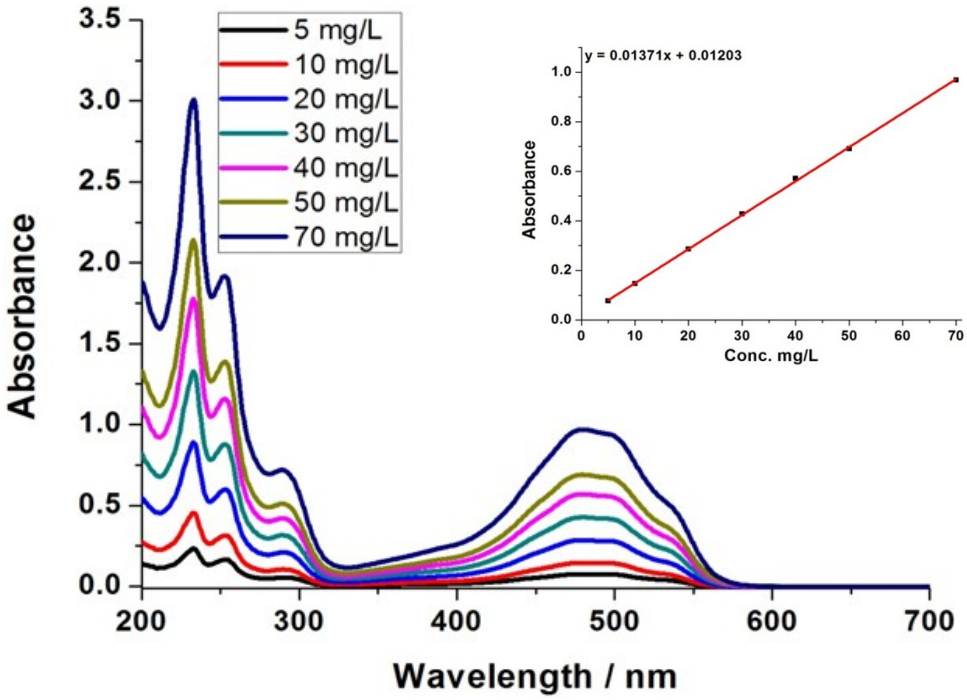

Figure S7. UV-Vis spectra of a series of concentrations of DOX in H_2O (Insert: Standard curve of DOX at 481nm)

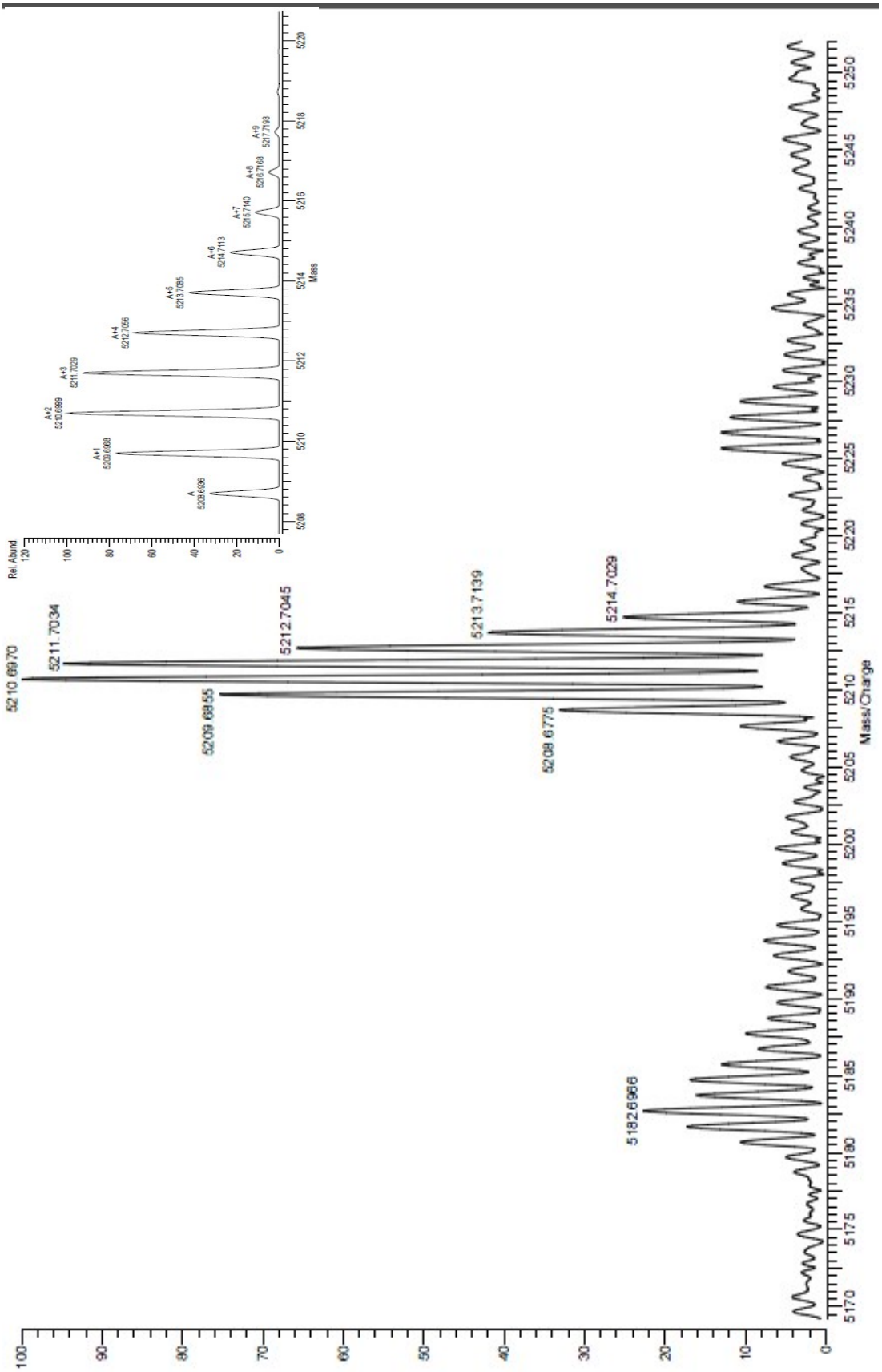

Figure S8. HRMS of TPECD (insert: simulated spectrum)

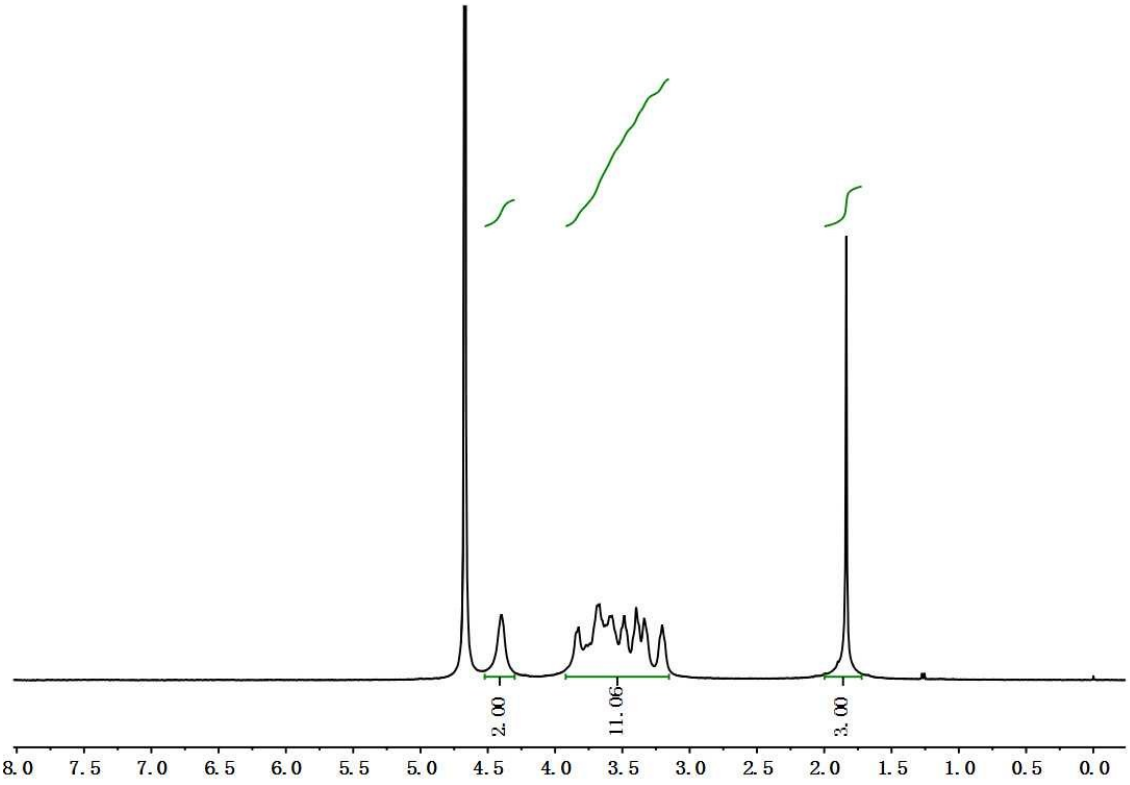

Figure S9. ^{1}H NMR of HA

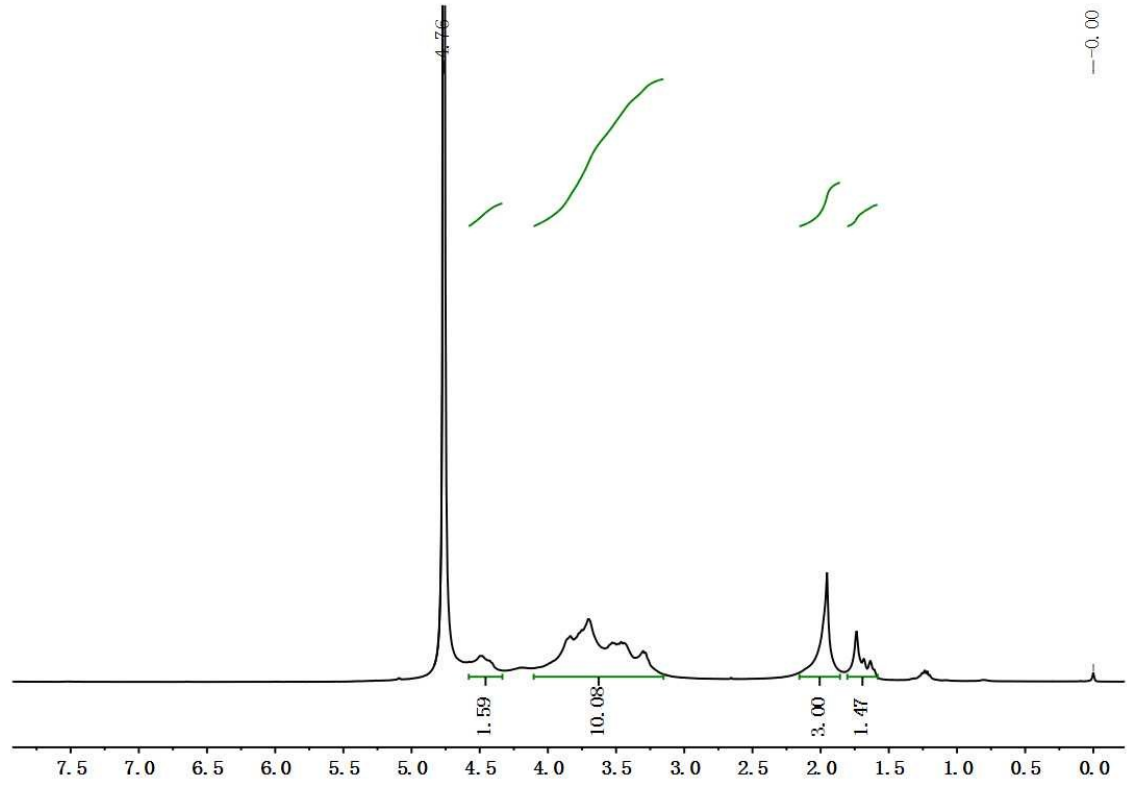

Figure S10.^{1}H NMR of HAAD

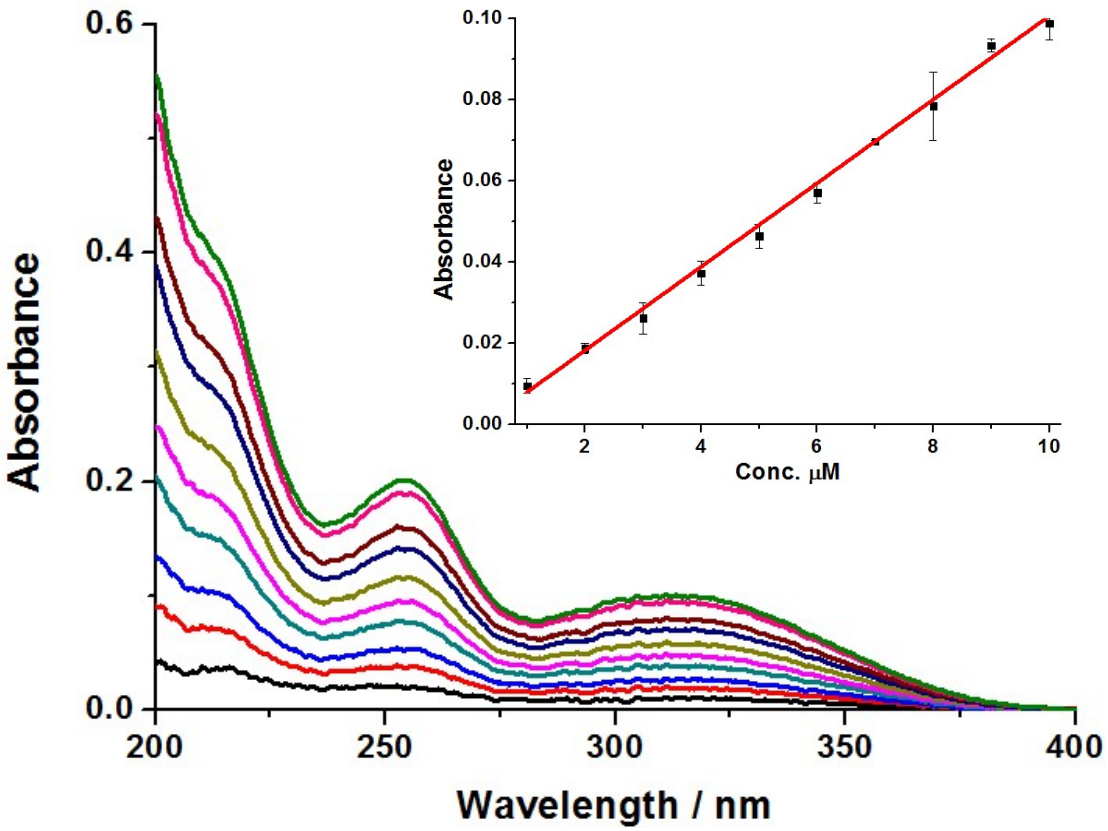

Figure S11. Concentration-dependent UV-Vis spectra (insert: liner fitting of absorption at 316 nm)

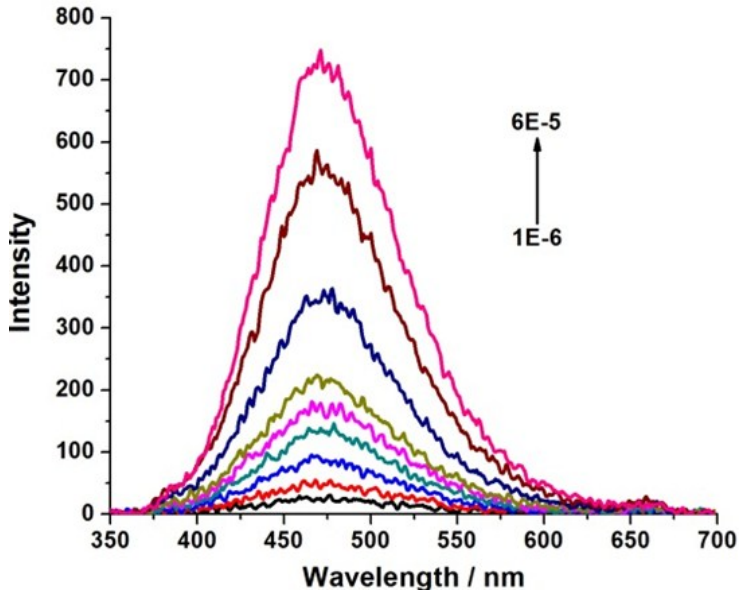

Figure S12. Fluorescence spectra (right, λ_{ex}=330nm) of TPECD at different concentrations.

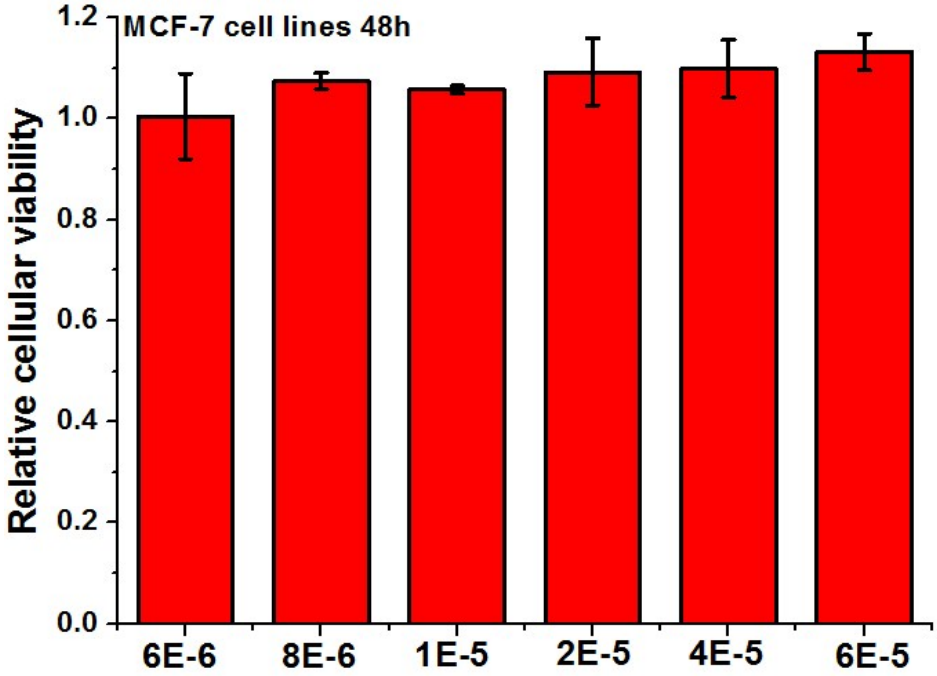

Figure S13. Relative cellular viability of MCF-7 cell lines after 48h of treatment with TPECD-HAAD of a series concentrations(calculated according to TPECD).

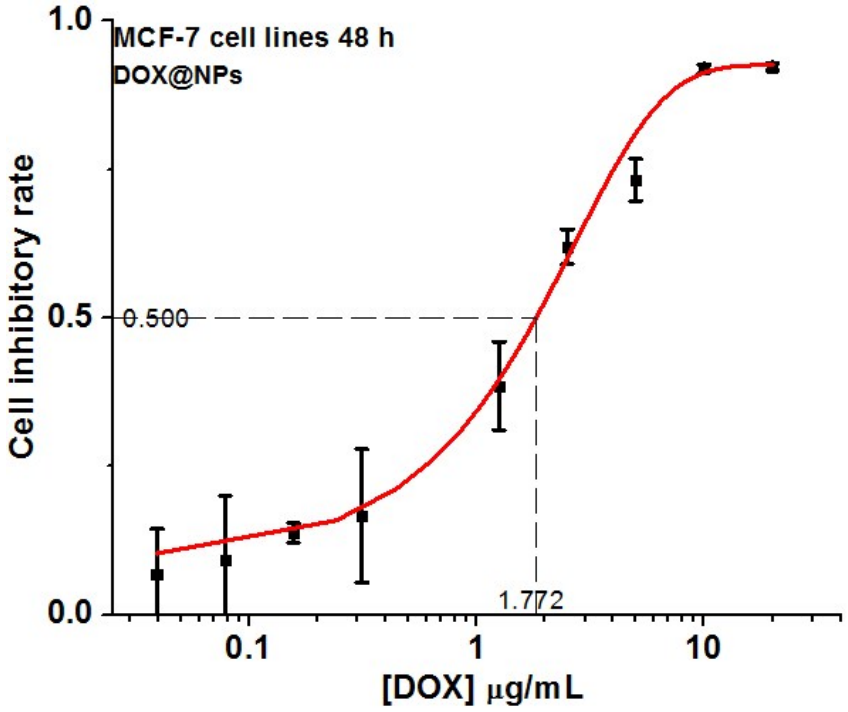

Figure S14. The inhibitory rate of MCF-7 cells at different concentrations of DOX@NPs after incubation for 48 h.

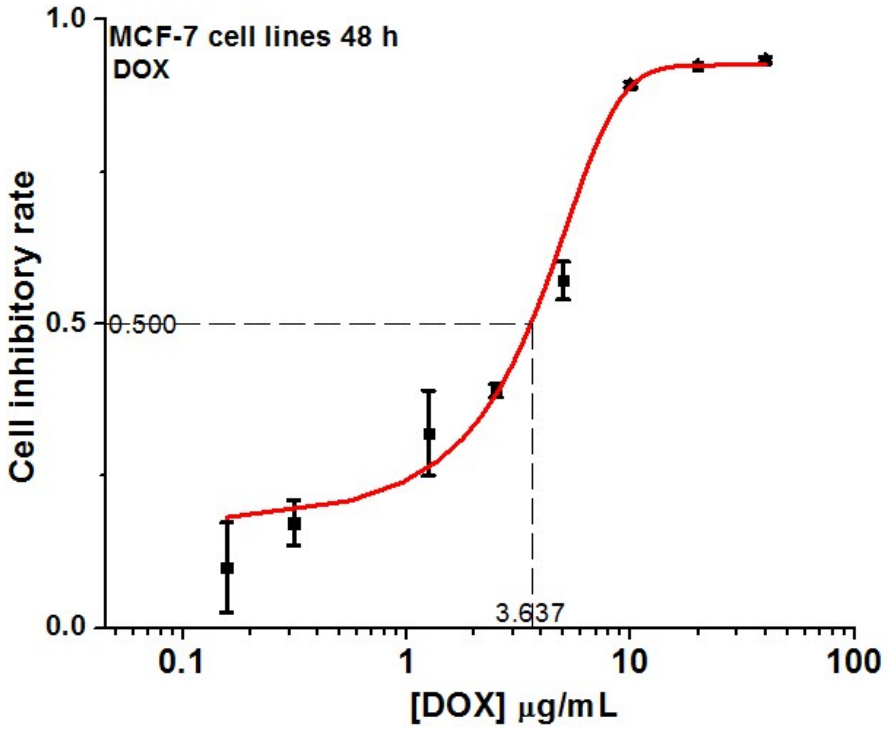

Figure S15. The inhibitory rate of MCF-7 cells at different concentrations of DOX after incubation for 48 h.

1. X.-M. Hu, Q. Chen, J.-X. Wang, Q.-Y. Cheng, C.-G. Yan, J. Cao, Y.-J. He and B.-H. Han, *Chem. Asian J.*, 2011, 6, 2376.

2. M. Sun, H.-Y. Zhang, X.-Y. Hu, B.-W. Liu and Y. Liu, *Chin. J. Chem.*, 2014, 32, 771.