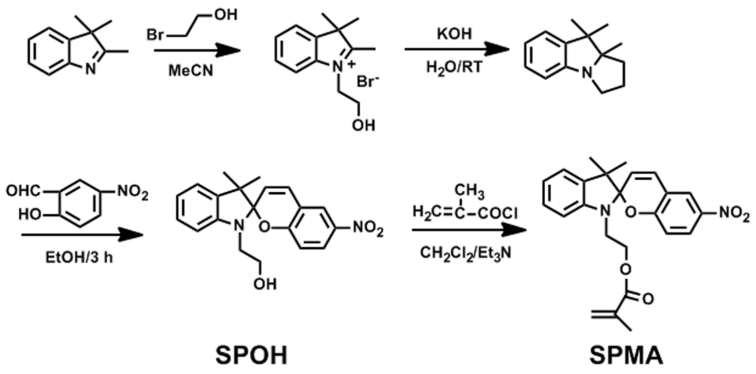
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Light-responsive amphiphilic copolymer coated nanoparticles as nanocarrier and real-time monitor for controlled drug release

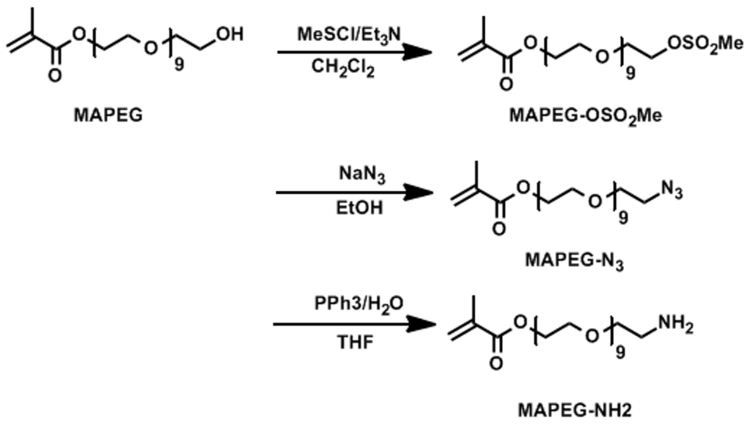
Qingjian Xing [a], Najun Li* [a,b], Dongyun Chen [a], Wenwei Sha [a], Yang Jiao [c], Xiuxiu Qi [a], Qingfeng Xu [a,b] and Jianmei Lu* [a,b]

[a] Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123 China.
[b] State Key Laboratory of Treatments and Recycling for Organic Effluents by Adsorption in Petroleum and Chemical Industry, Suzhou, 215123 China.
[c] School of Radiation Medicine and Protection, Medical College of Soochow University, Suzhou, Jiangsu 215123, China.
* E-mail: linajun@suda.edu.cn, lujm@suda.edu.cn; Tel./Fax: +86 (0) 512-6588 0367.

Supplementary Information



Scheme S1 The synthesis route of SPMA



Scheme S2 The synthesis route of MAPEG-NH_2

Synthesis of MAPEG Methanesulfonate (MAPEG-OSO_2Me)

MAPEG (5.26 g, 10 mmol) was dissolved in dry CH_2Cl_2 (20 mL) under argon while cooling in an ice bath. Triethylamine (3.06 mL, 22 mmol) was added, followed by dropwise additional of a solution of methanesulfonyl chloride (1.55 mL, 20 mmol) in dry CH_2Cl_2 (10 mL). The mixture was allowed to stir at room temperature over night. The resulting mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ (twice) and brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness to give MAPEG methanesulfonate as yellow oil (4.92 g, 81%)

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.03 (m, 1H), 5.69 (m, 1H), 4.30 (t, *J*= 4.4 Hz, 2H), 4.21 (t, *J*= 4.8 Hz 2H), 3.67 (m, 4H), 3.51 (m, 32H), 3.18 (s, 3H), 1.89 (s, 3H).

Synthesis of MAPEG Azide (MAPEG-N_3)

MAPEG methanesulfonate (2.76 g, 5 mmol) was dissolved in DMF (10 mL). Sodium azide (0.65 g, 10 mmol) was added and the mixture was stirred at room temperature for 5 days. The resulting

mixture was diluted with water and extracted with CH_2Cl_2 (twice). The organic layers were washed with saturated KCl, dried over $MgSO_4$, filtered, and evaporated to give MAPEG azide as a yellow liquid (2.20 g, 80 %).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.11(m, 1H), 5.57 (m, 1H), 4.28 (t, *J*= 4.8 Hz, 2H), 3.73 (m, 2H), 3.63 (m, 32H), 3.39 (t, *J*= 4.4 Hz, 2H), 3.10 (s, 2H), 1.93 (s, 3H).

Synthesis of folate NHS ester (FA-NHS)

Folic acid (2.0 g) was dissolved in dry DMF (50 mL). Dicyclohexylcarbodiimide (0.62 g) and NHS (0.51 g) were added to the solution. The mixture was stirred for 12 h at room temperature in the dark. Then the solution was filtered off and precipitated in diethyl ether. The obtained yellow powder was washed several times with anhydrous ether and dried under vacuum.

Table S1 Properties of PRMS with different feed ratio

Feed ratio[a] RBM:MAPEG:SPMA=x:y:z	Mn (g/mol)	PDI	Polymer Composition(x:y:z)[b]
3:100:300	15360	1.520	3:130:325
1:100:100	8790	1.410	1:128:110
1:300:100	11600	1.243	1:370:105

[a]The molar ratio between RBM and SPMA was chosen according to the previous literature[1]. According to the literature, the molar ratio between RBM and SPMA should be 1:30 at least to realize an obvious decline of fluorescence emission in the FRET process.

[b]Determined by ^{1}H NMR.

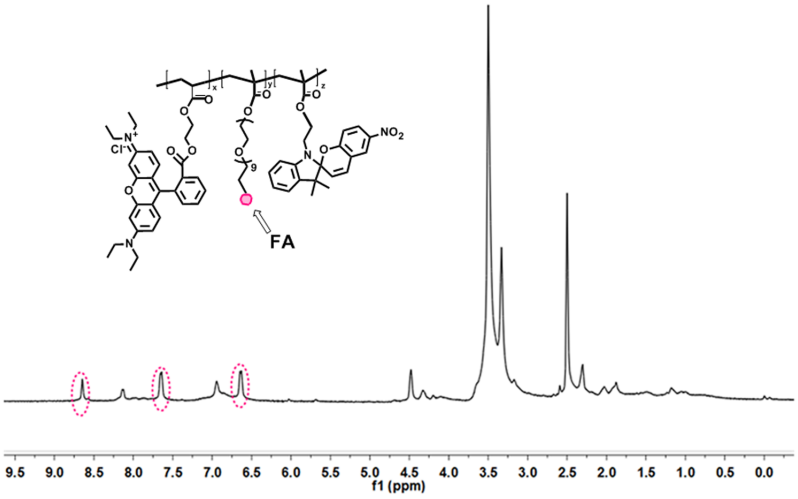


Fig. S1 ^{1}H NMR spectrum (DMSO, 400MHz) of copolymer PRMS-FA

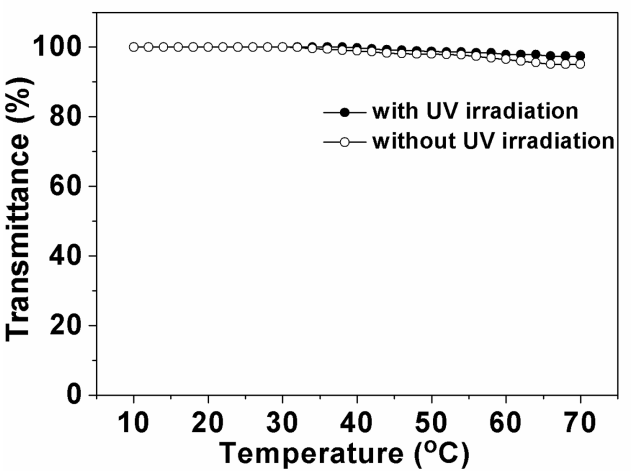


Fig.S2 Transmittance versus temperature for copolymer solution (concentration at 1mg/ml) with and without UV irradiation.

The transmittance measurement was used to measure the LCST of PRMS-FA. The measurement was carried out by using a polymer concentration of 1 mg/mL and the transmittance data were taken at 750 nm that is sufficiently apart from the absorptions of the chromophores. The solution heating rate was about 1 °C/min. And at each temperature, the solution was equilibrated for 2 min before the taking of the UV-Vis absorption spectrum. The results were summarized in Fig. S2. And a small transmittance change could be observed upon solution heating above 40 °C before UV irradiation compared to the samples treated with UV irradiation. Indeed, the photoisomerization resulted in an increase in LCST (about 5 °C) for PRMS-FA and to some extent, enhanced its solubility.

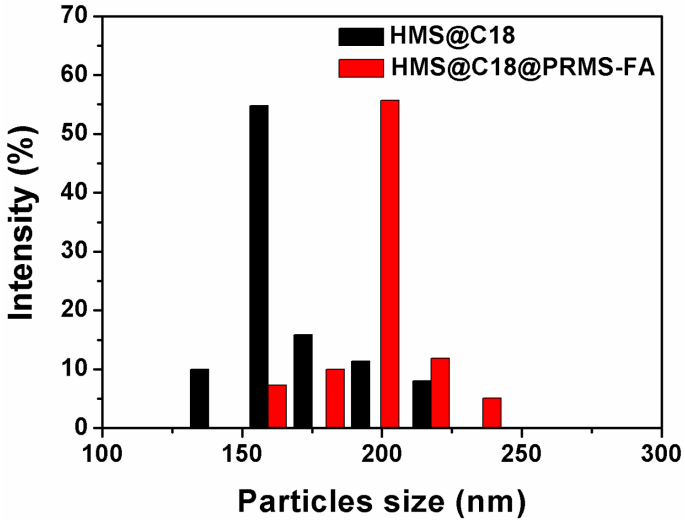


Fig.S3 DLS of HMS@C18 and HMS@C18@PRMS-FA.

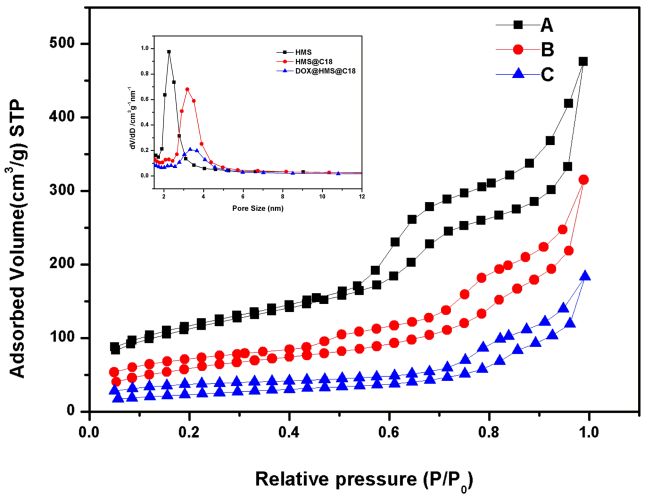


Fig. S4 N_2 adsorption-desorption isotherm of (A) HMS, (B) HMS@C18 and (C)DOX@HMS@C18

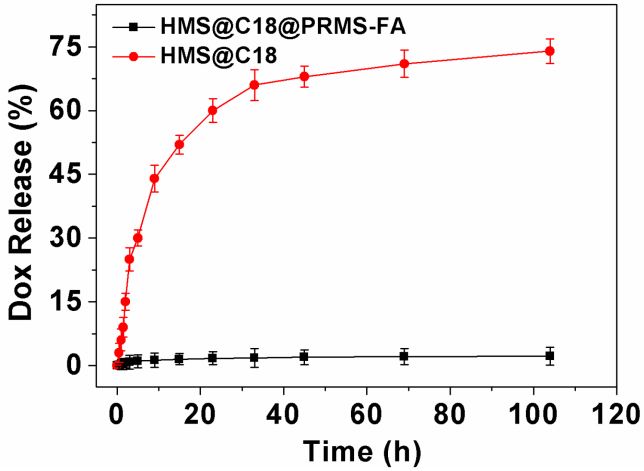


Fig.S5 Release of DOX from HMS@C18 and HMS@C18@PRMS-FA

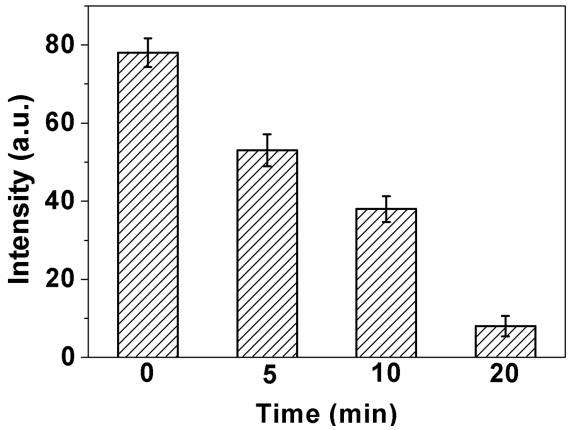


Fig. S6 Mean fluorescence intensity of KB cells at different time with UV irradiation

References:

1. F. May, M. Peter, A. Hütten, L. Prodi and J. Mattay, *Chem. Eur. J.*, 2012, **18**, 814.
2. I. Vlassiouk, C. D. Park, S. A. Vail, D. Gust and S. Smirnov, *Nano Lett.*, 2006, **6**, 1013.