Supporting Information

Photo-Triggered Release of Caged Camptothecin Prodrugs from Dually Responsive Shell Cross-Linked Micelles

Xianglong Hu,[a] Jie Tian,[b] Tao Liu,[a] Guoying Zhang,[a] and Shiyong Liu*,[a]

[a] *CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China*

[b] *Engineering and Materials Science Experiment Center, University of Science and Technology of China, Hefei 230027, China*

* To whom correspondence should be addressed. E-mail: sliu@ustc.edu.cn

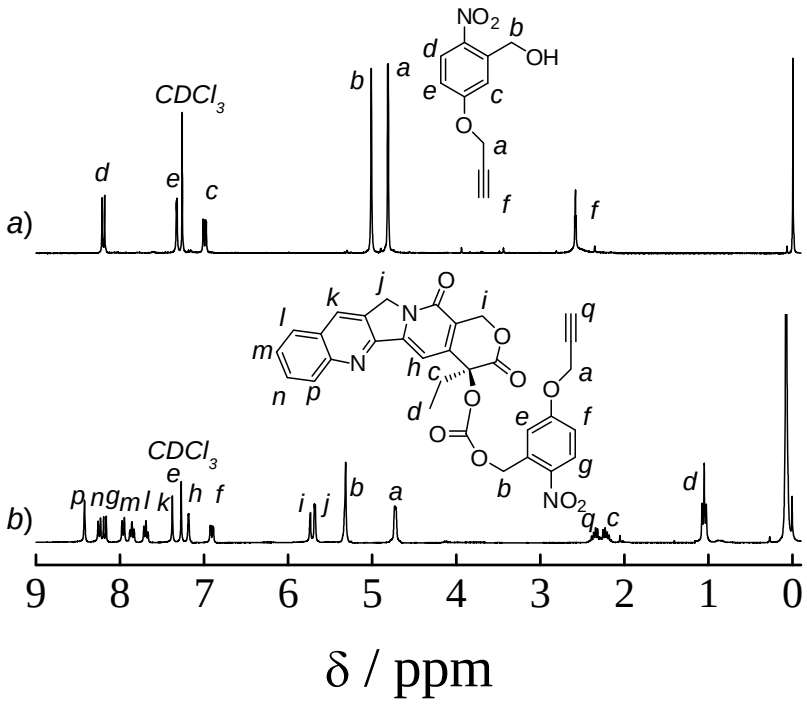

Figure S1. ^{1}H NMR spectra recorded for (a) 2-nitro-5-propargyloxy benzyl alcohol and (b) photocaged CPT prodrug NBCCPT in $CDCl_3$.

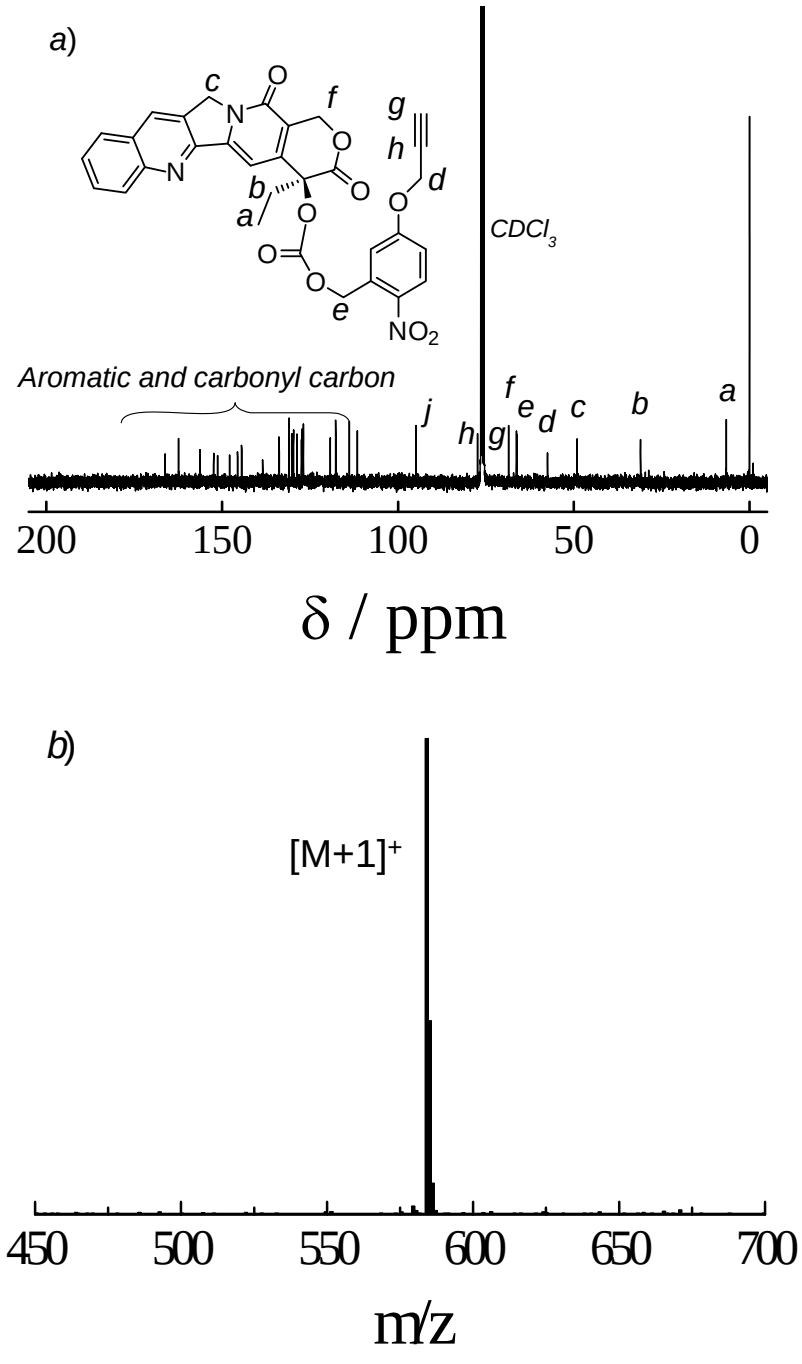

Figure S2. (a) ^{13}C-NMR spectrum obtained in $CDCl_3$ and (b) ESI-MS spectrum recorded for the photocaged CPT prodrug NBCCPT (Calculated for: $[M]^+$ = 581.5; found :$[M+H]^+$ = 582.5).

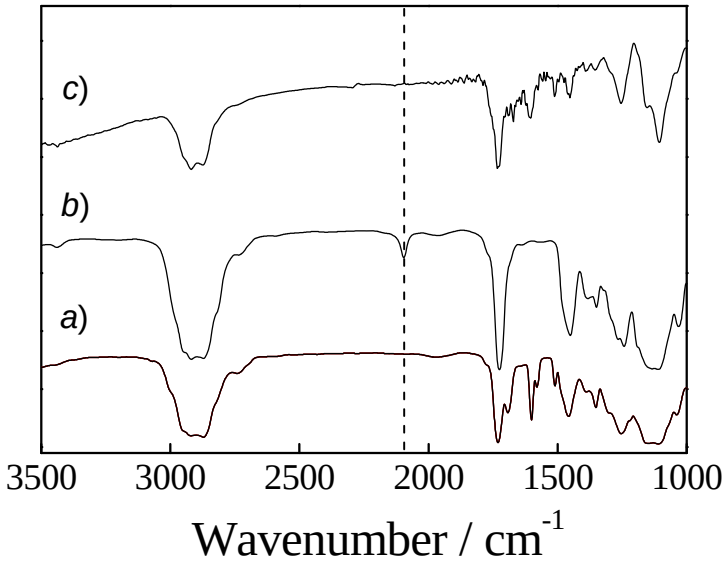

Figure S3. FT-IR spectra recorded for (a) P(CL-*co*-CLBr)-*b*-P(OEGMA-*co*-MAEBA), (b) the azidation product of (a), P(CL-*g*-N_3)-*b*-P(OEGMA-*co*-MAEBA)-N_3, and (c) P(CL-*g*-CPT)-*b*-P(OEGMA-*co*-MAEBA)-CPT amphiphilic diblock copolymers.

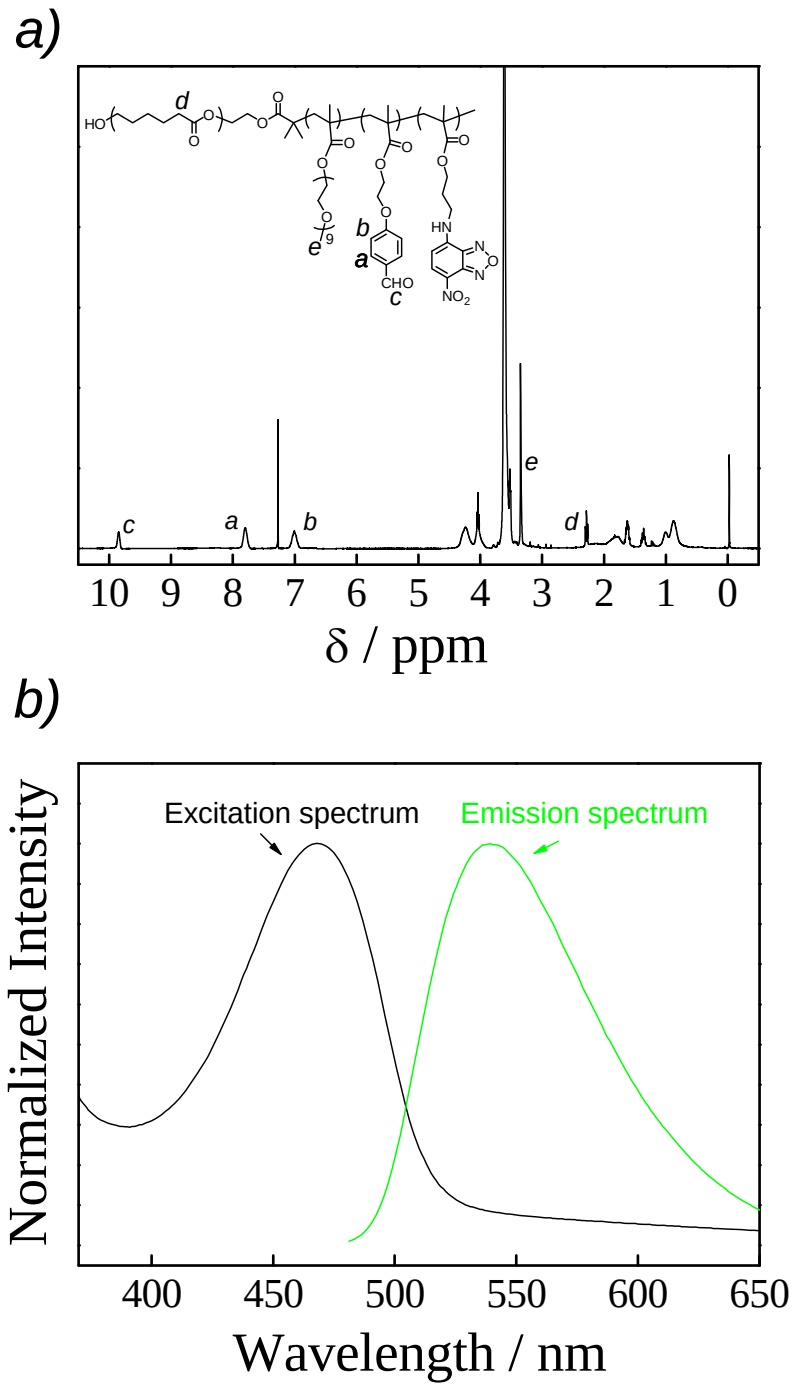

Figure S4. Characterization of NBD-labeled diblock copolymer, PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-NBD). (a) ^{1}H NMR spectrum recorded in $CDCl_3$. (b) Normalized fluorescence excitation and emission spectra recorded for PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-NBD) micelles in aqueous media (slit widths: Ex. 5 nm, Em. 5 nm).

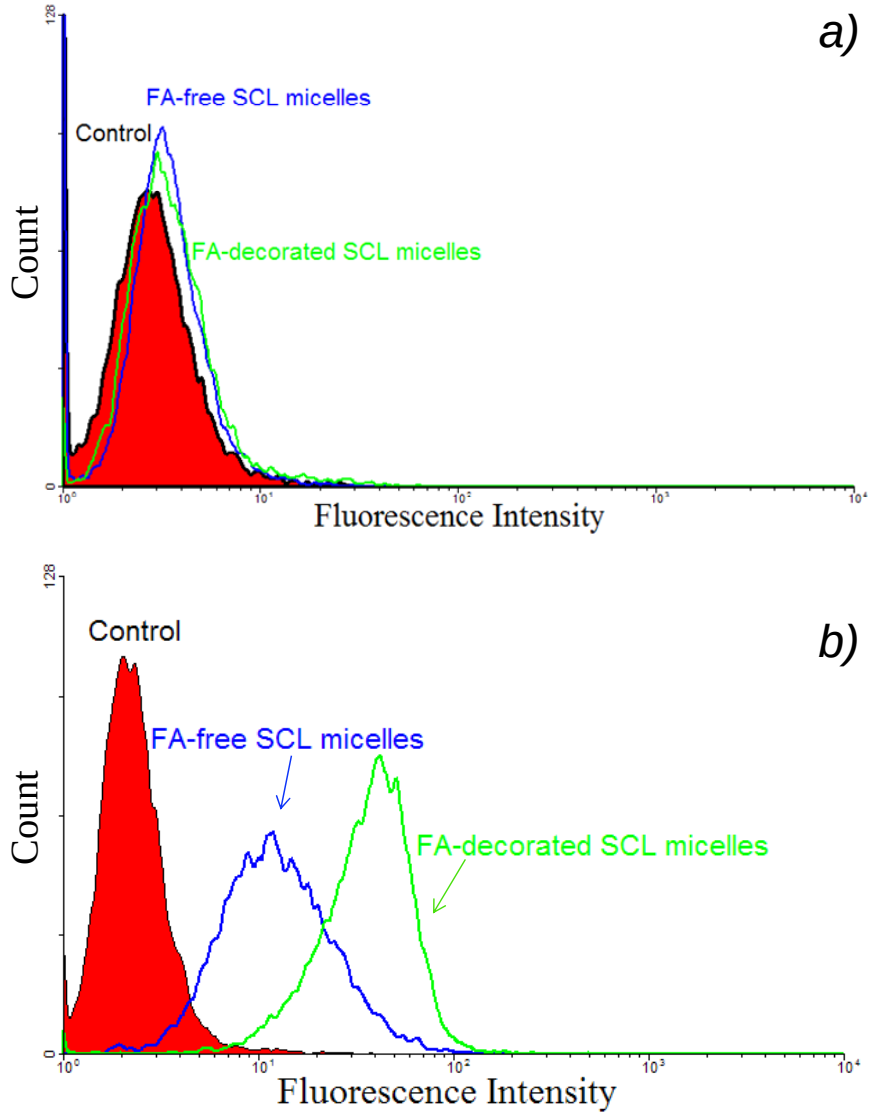

Figure S5. Flow cytometry results of A549 cells after incubation with FA-decorated SCL micelles or FA-free SCL micelles for 1 h at (a) 4 ºC and (b) 37 ºC by measuring cellular fluorescence of NBD channel. FA-decorated and NBD-labeled SCL micelles were fabricated from a mixture of PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-FA) and PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-NBD) (1/1, wt/wt), whereas FA-free and NBD-labeled SCL micelles were fabricated from PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-AzPMA) and PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-NBD) (1/1, wt/wt).

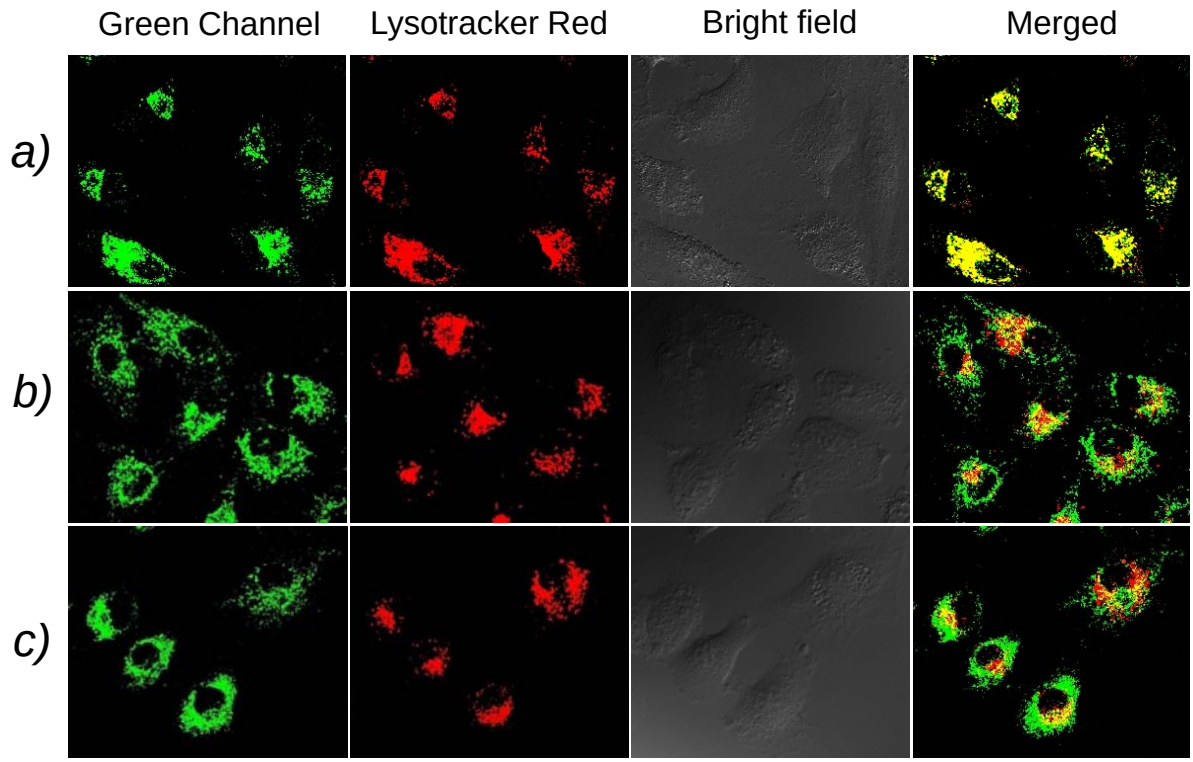

Figure S6. CLSM images recorded for A549 cells after incubation with FA-decorated SCL micelles fabricated from a mixture of PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-FA) and PCL-*b*-P(OEGMA-*co*-MAEBA-*co*-NBD) (1/1, wt/wt) for (a) 4 h, (b) 8 h, and (c) 12 h. Late endosomes and lysosomes were stained with Lysotracker Red (Red).