Supporting Information

Self-Assembly of Photoswitchable Diblock Copolymers: Salt-induced Micellization and the Influence of UV Irradiation

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Experimental Section

Materials. 4,4'-Dinonyl-2,2'-bipyridine (dNbpy, 97%), 2-bromo-2-methylpropionyl bromide (98%), 2-bromoethanol (97%), 2,3,3-trimethyl-3H-indole (98%) and 2-hydroxy-5-nitrobenzaldehyde (98%) were purchased from Alfa Aesar, and were used as received. CuBr (Guo Yao Chemical Company, 99.5%) was purified by washing with glacial acetic acid and drying in a vacuum oven at 100 °C. THF (AR grade), DMF (AR grade), MeCN (AR grade), $CHCl_3$ (AR grade) and methanol (AR grade) were purchased from Tianjin Chemical Reagent Company in China. All the solvents were distilled before use.

Characterization. ^{1}H NMR spectra were recorded on a Varian UNITY-plus 400 M nuclear magnetic resonance spectrometer. The apparent molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with a Hitachi L-2130 HPLC pump, a Hitachi L-2350 column oven operated at 40 °C, three Varian PL columns with 1000K−100K (100 000 Å), 100K−10K (10 000 Å), and 100−10K (1000 Å) molecular ranges, and a Hitachi L-2490 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. Molecular weights were calibrated on PS standards. UV-vis absorption spectra were performed on a Shimadzu UV-2450 spectrometer. Fluorescence spectra were collected on a Shimadzu RF-5301PC spectrofluorophotometer. Dynamic light scattering (DLS) measurements were measured on a Zetasizer Nano ZS from Malvern Instruments equipped with a 10 mW HeNe laser at a wavelength of 633 nm. The results were analyzed in CONTIN mode. Transmission electron microscopy (TEM) images were carried out on a Tecnai G2 20 S-TWIN electron microscope equipped with a Model 794 CCD camera. TEM specimens were prepared by dipping copper grids into the micellar solution (about 0.1 mg/mL) and drying in air. The specimens were stained by exposing to the vapor of ruthenium

tetroxide for 1.5 h at room temperature. Mass spectra were collected on a Finnigan Lcqadvantage spectrometer from Thermo Fisher Scientific.

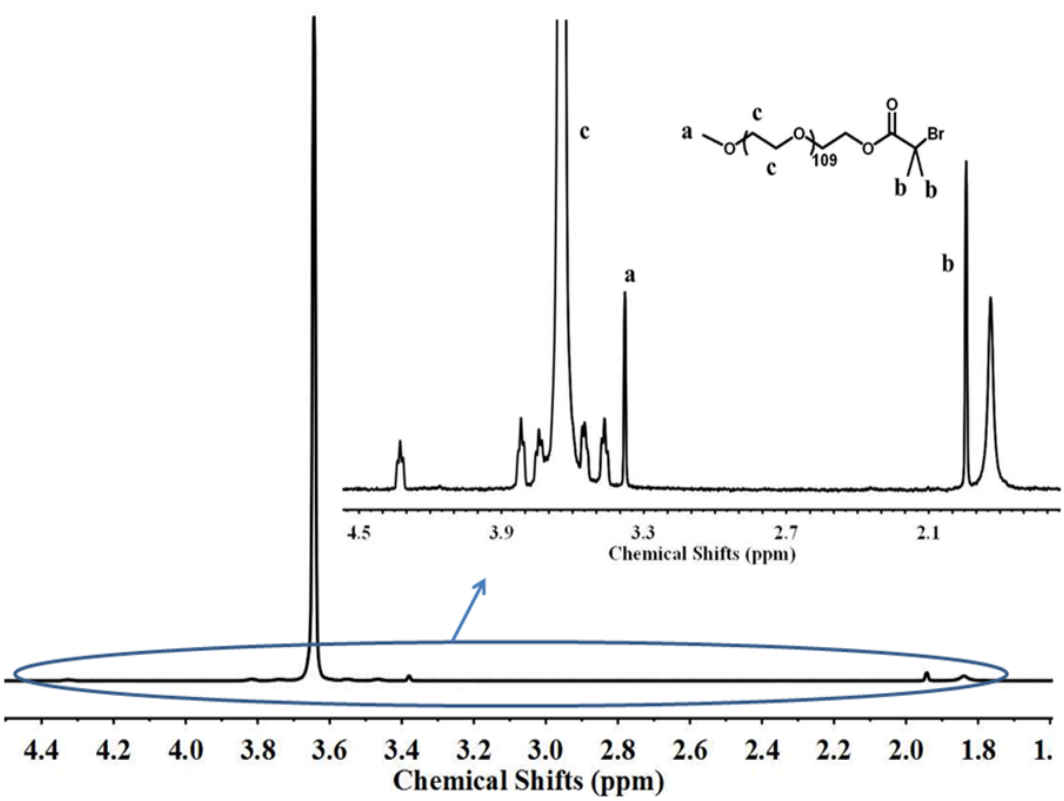

Figure S1. ^{1}H NMR spectrum of macroinitiator PEG-Br. The spectrum was collected in $CDCl_3$.

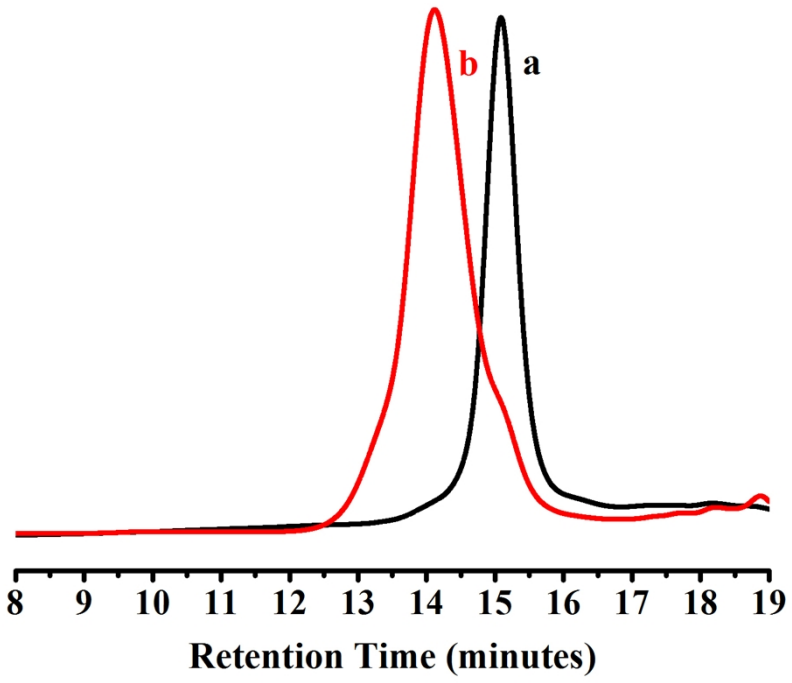

Figure S2. GPC traces of (a) macroinitiator PEG-Br and (b) PEG-b-$PSPMA_{20}$ block copolymer.

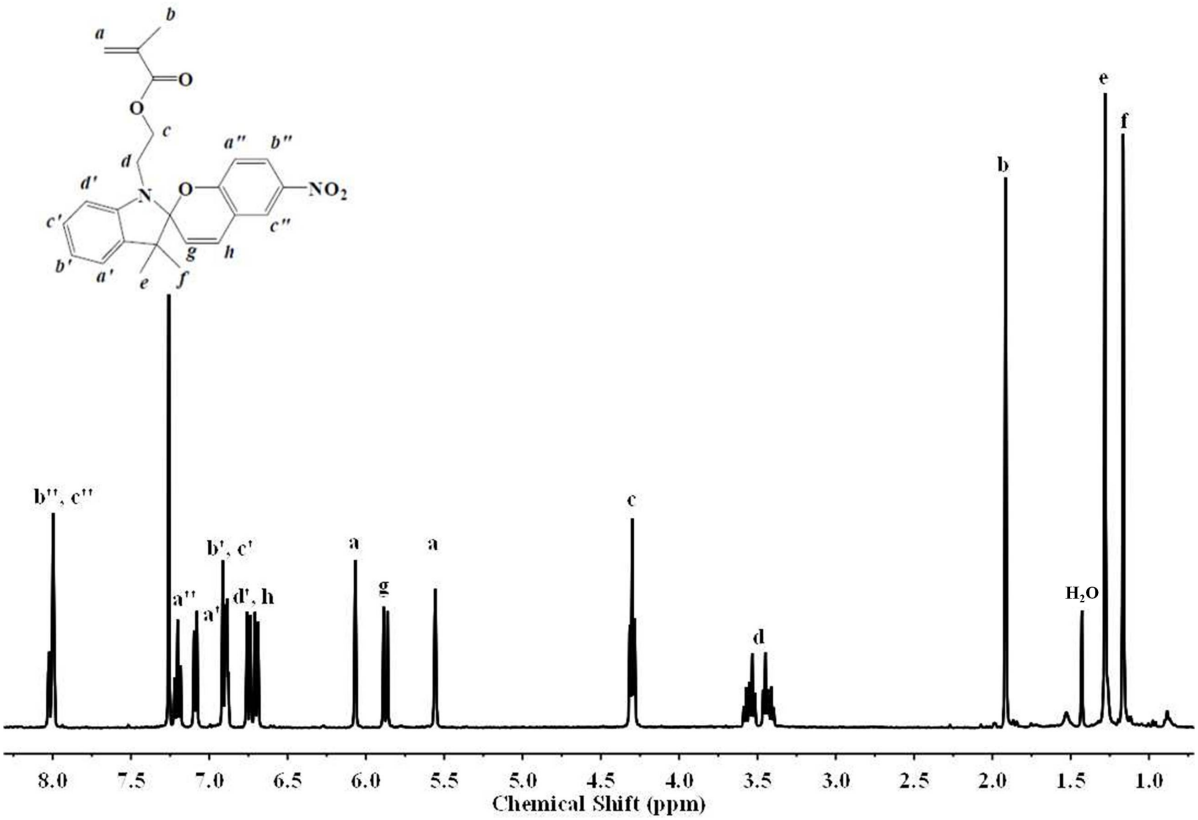

Figure S3. ^{1}H NMR spectrum of SPMA monomer. The spectrum was collected in $CDCl_3$.

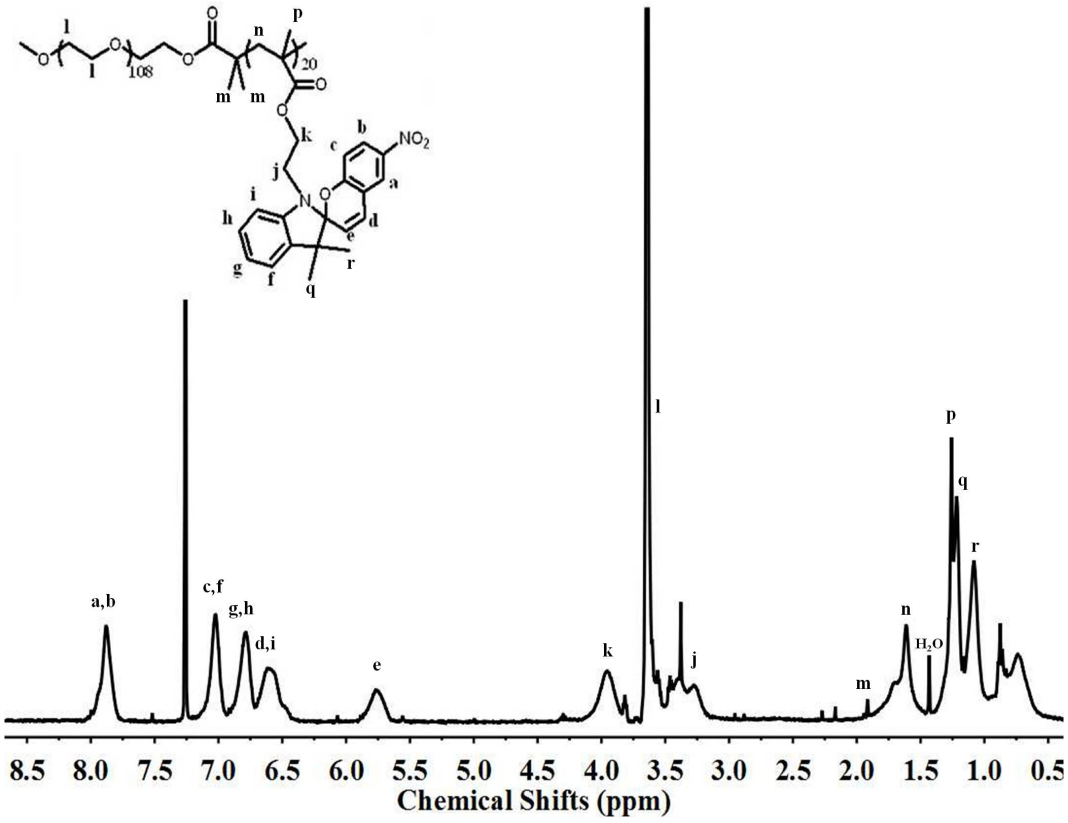

Figure S4. ^{1}H NMR spectrum of PEG-b-PSPMA$_{20}$ block copolymer. The spectrum was collected in $CDCl_3$.

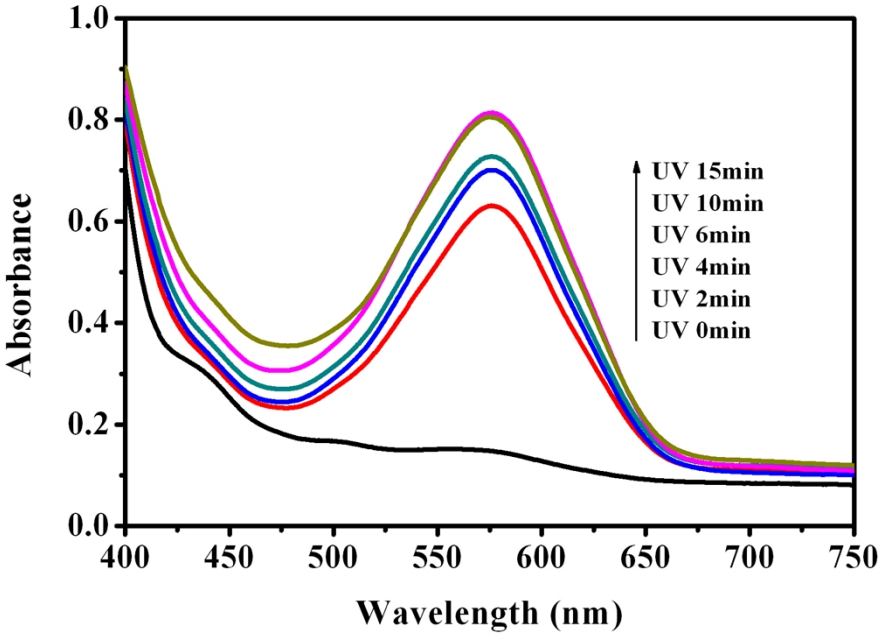

Figure S5. Absorption spectra of PEG-b-PSPMA$_{31}$ in DMF upon UV irradiation (365 nm) for different exposure time intervals.

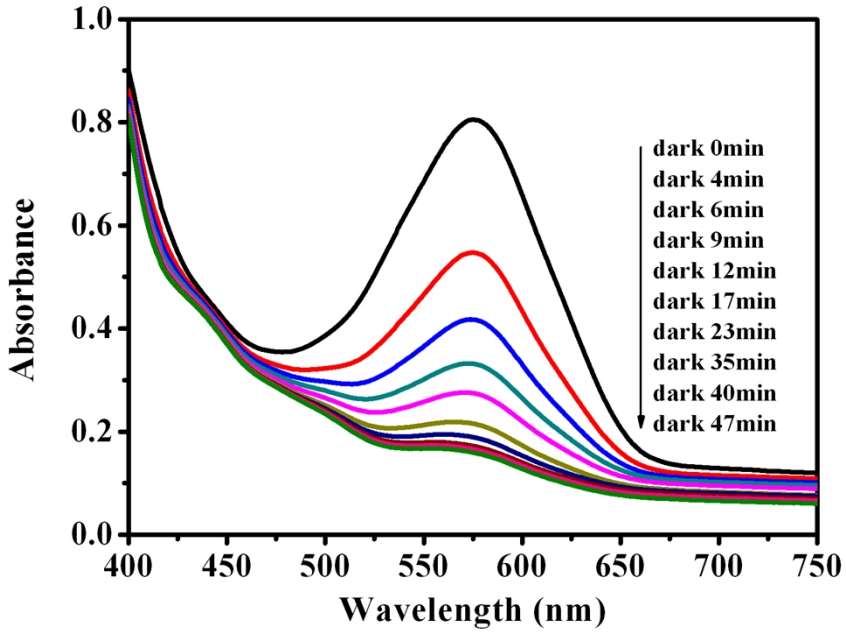

Figure S6. Back-photoisomerization process of PEG-b-PSPMA$_{31}$ in DMF solution in the dark recorded at various times.

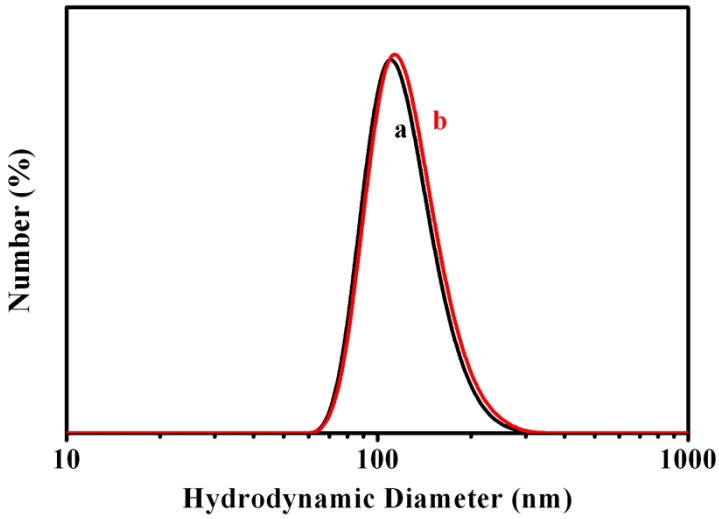

Figure S7. (a) DLS curves of PEG-b-PSPMA$_{20}$ micelles induced by $FeCl_3$ in 10:1 DMF/H_2O mixture after 30 min UV irradiation. The molar ratio of SP to Fe^{3+} is 3:1. (b) DLS curves of the micelles standing by in the dark overnight.

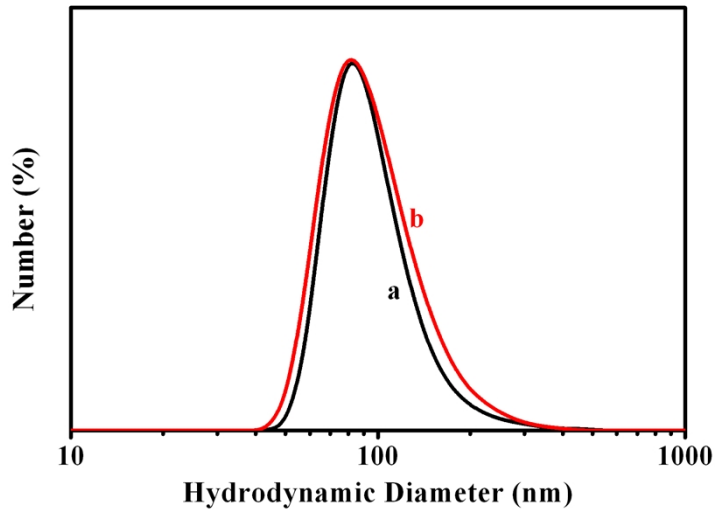

Figure S8. (a) DLS curves of PEG-b-PSPMA$_{20}$ micelles induced by $Zn(Ac)_2$ in 10:1 DMF/H_2O mixture after 30 min UV irradiation. The molar ratio of SP to Zn^{2+} is 2:1. (b) DLS curves of the micelles standing by in the dark overnight.

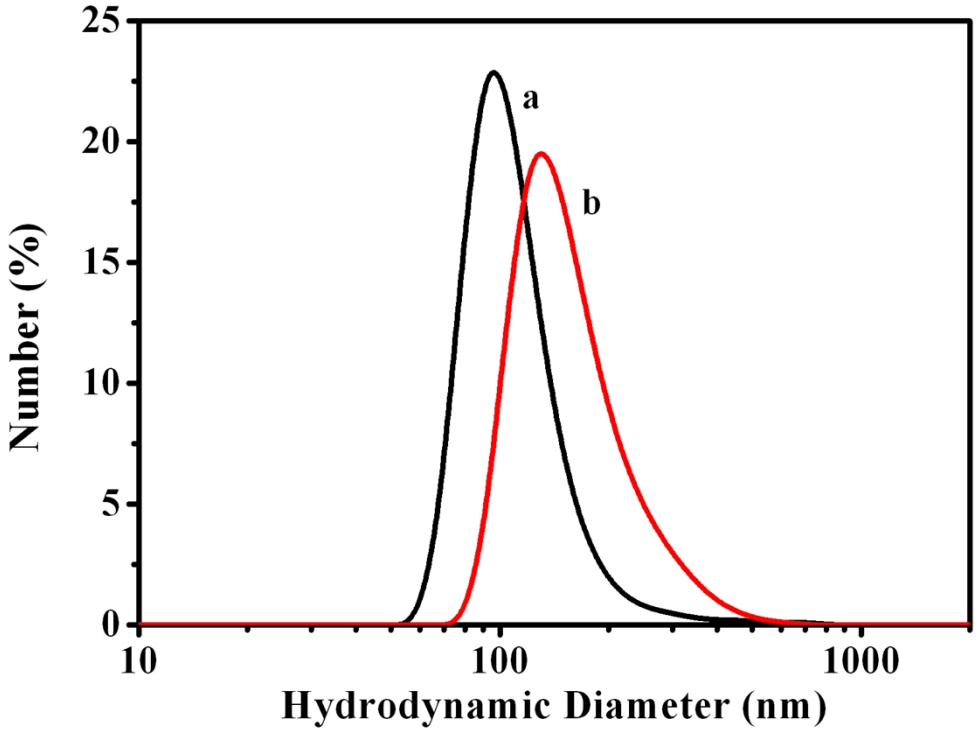

Figure S9. DLS curves of $CuCl_2$-induced PEG-b-$PSPMA_{31}$ micelles in 10:1 DMF/H_2O mixture after 30 and 60 min UV irradiation. The diblock polymer concentration in the solution is 0.01 wt%.

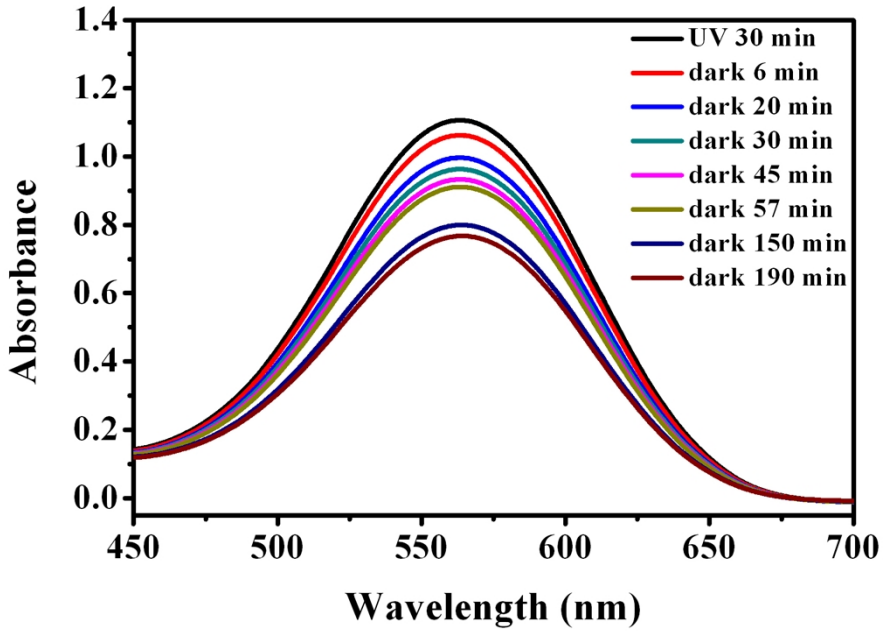

Figure S10. Back-photoisomerization process of micelles formed by PEG-b-$PSPMA_{20}$ in aqueous solution in the dark.