Tailorable Degradation of pH-Responsive All Polyether Micelles via Copolymerisation with Varying Acetal Groups

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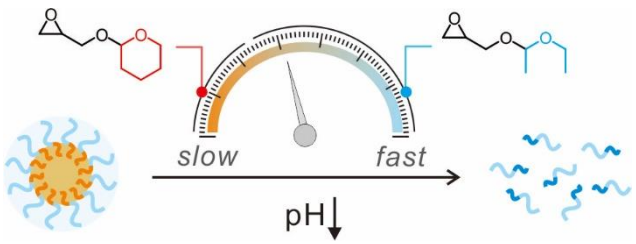

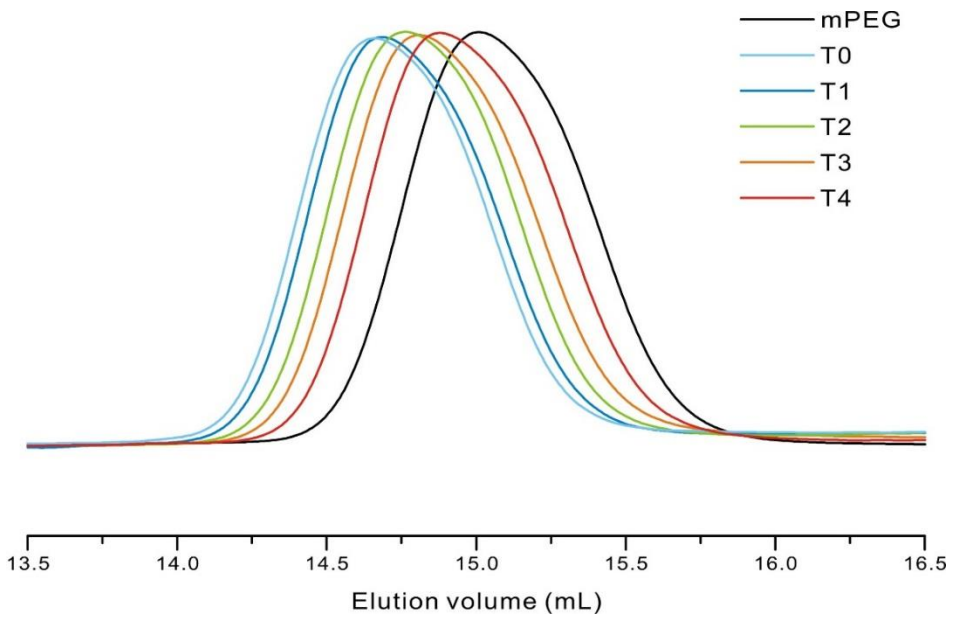

Fig. S1 GPC elution traces in DMF using a RI signal and PMMA as a standard of PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{m/n}$ copolymers (**T0** – **T4**).

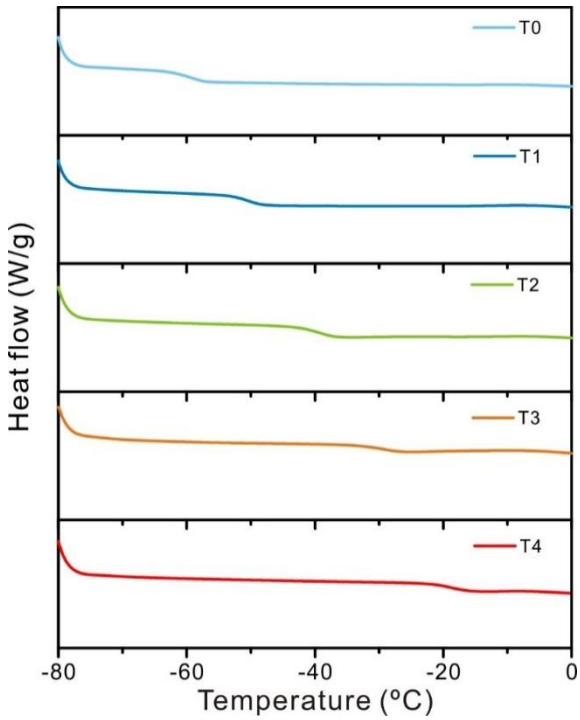

Fig. S2 DSC thermograms for PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{m/n}$ copolymers **(T0 – T4)**. The melting temperature of PEG block was observed at 50 − 54 °C.

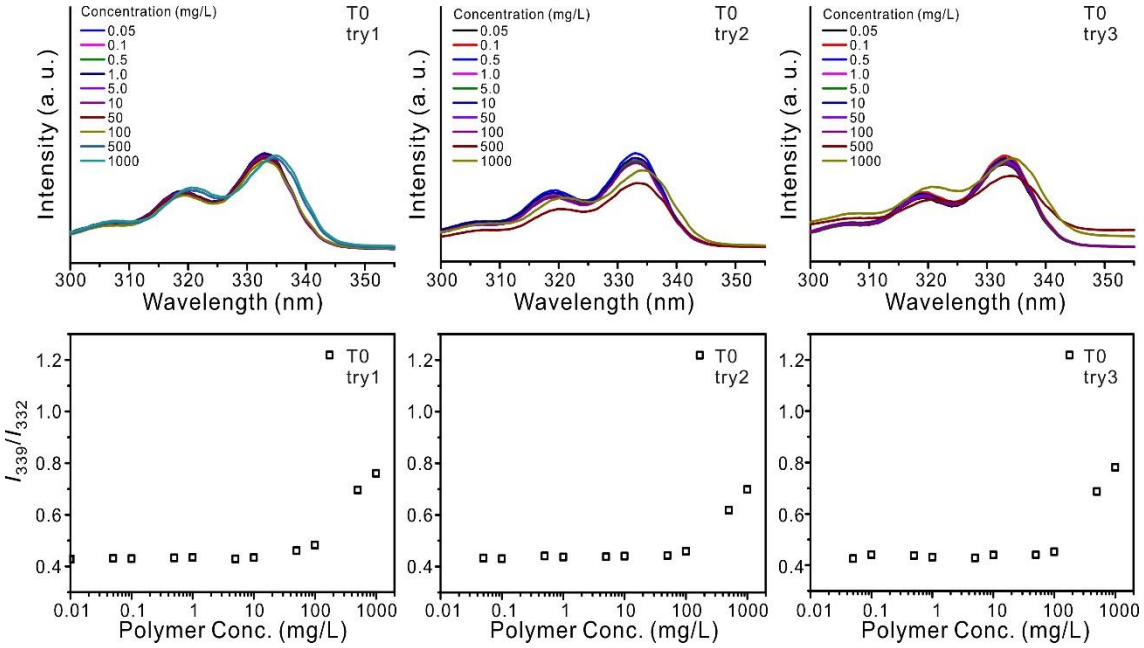

Fig. S3 Excitation spectra of pyrene in aqueous solution and determination of CMC for PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{27/0}$ (**T0**) micelles (λ_{em} = 372 nm). CMC was calculated *via* measurements of I_{339}/I_{332} as a function of polymer concentration using the fluorescence excitation spectra of pyrene.

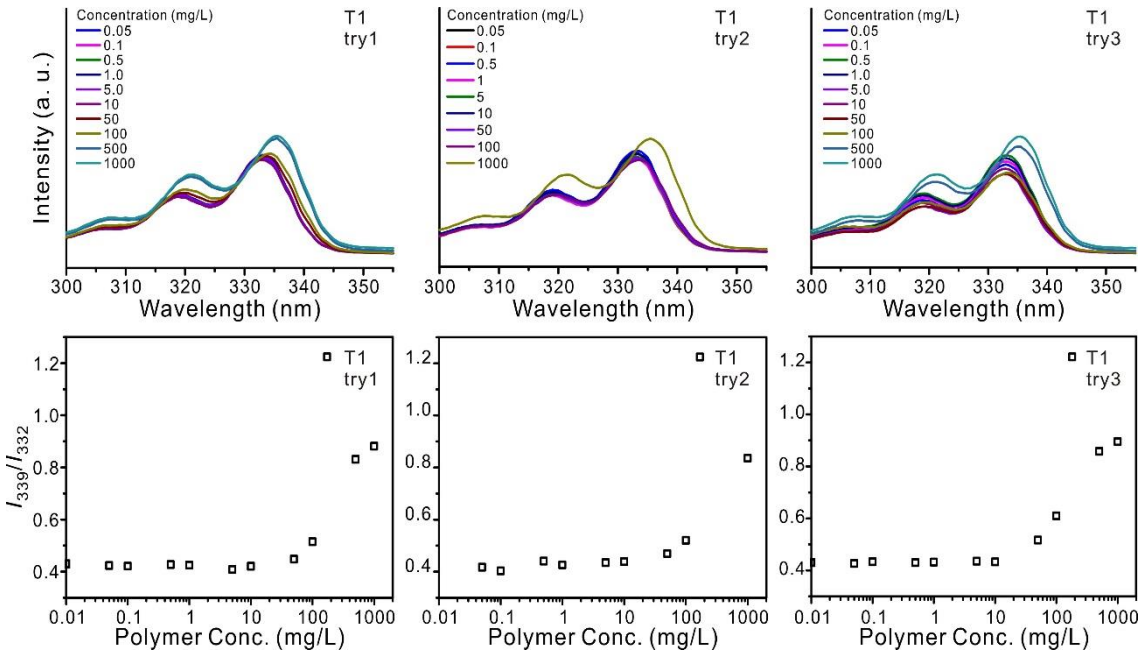

Fig. S4 Excitation spectra of pyrene in aqueous solution and determination of CMC for PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{21/6}$ (**T1**) micelles (λ_{em} = 372 nm). CMC was calculated *via* measurements of I_{339}/I_{332} as a function of polymer concentration using the fluorescence excitation spectra of pyrene.

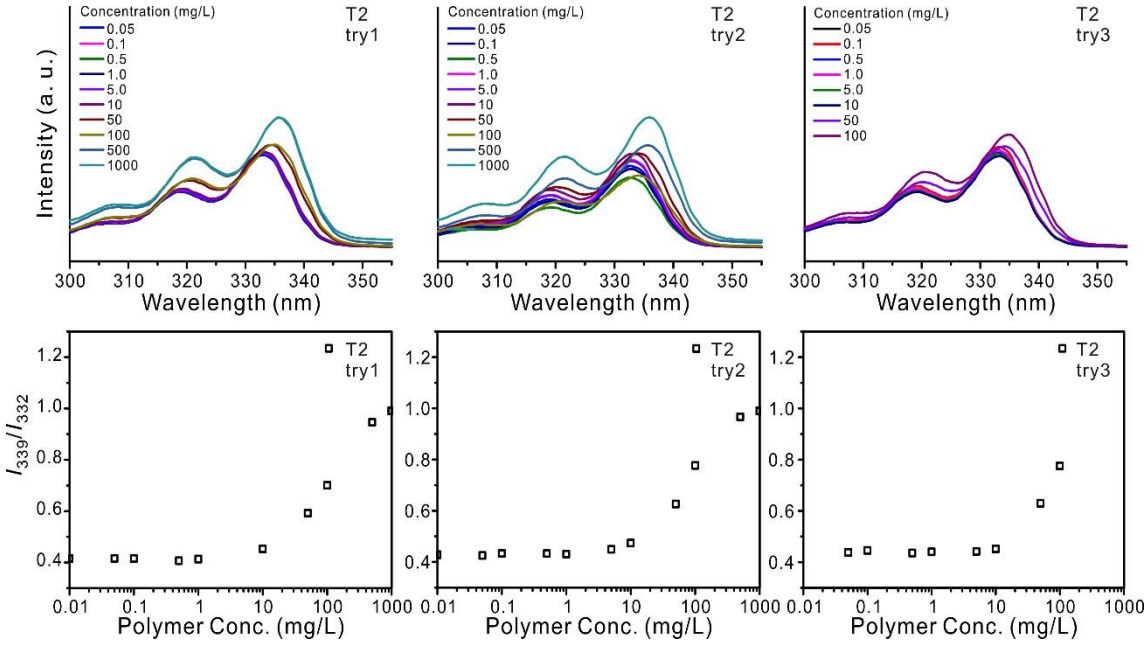

Fig. S5 Excitation spectra of pyrene in aqueous solution and determination of CMC for PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{14/14}$ (**T2**) micelles (λ_{em} = 372 nm). CMC was calculated *via* measurements of I_{339}/I_{332} as a function of polymer concentration using the fluorescence excitation spectra of pyrene.

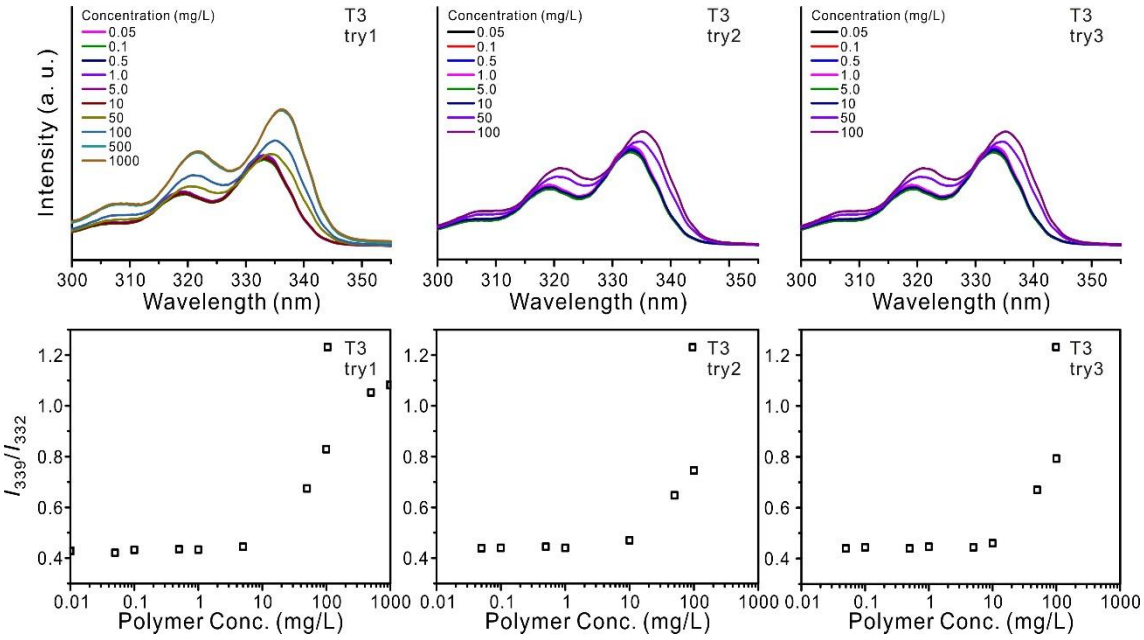

Fig. S6 Excitation spectra of pyrene in aqueous solution and determination of CMC for PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{7/19}$ (**T3**) micelles (λ_{em} = 372 nm). CMC was calculated *via* measurements of I_{339}/I_{332} as a function of polymer concentration using the fluorescence excitation spectra of pyrene.

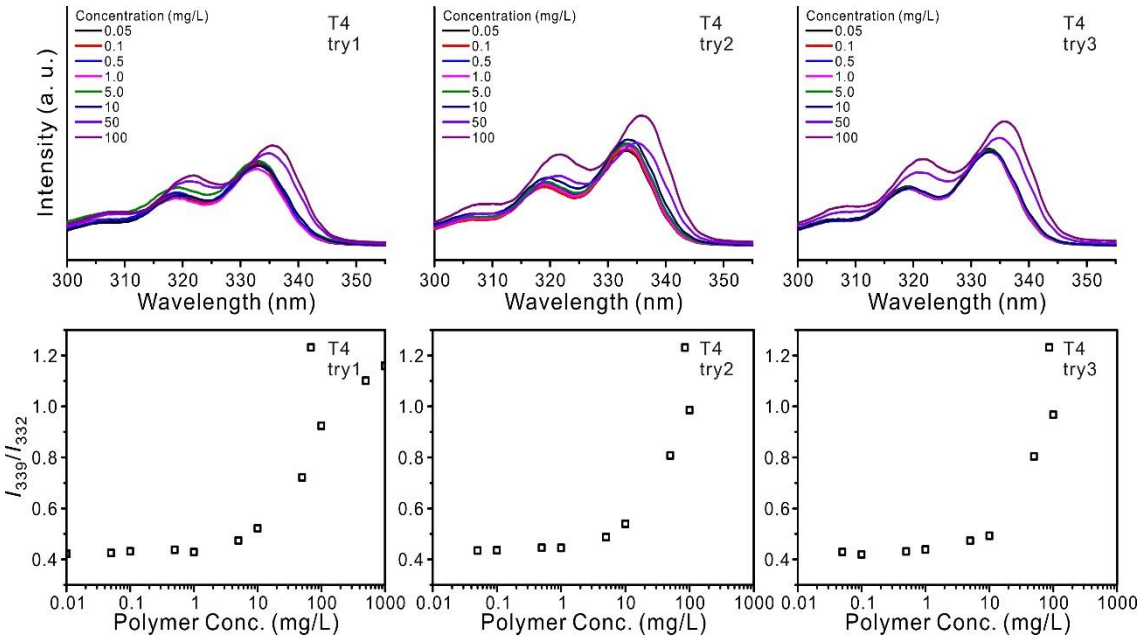

Fig. S7 Excitation spectra of pyrene in aqueous solution and determination of CMC for PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{0/27}$ (**T4**) micelles (λ_{em} = 372 nm). CMC was calculated *via* measurements of I_{339}/I_{332} as a function of polymer concentration using the fluorescence excitation spectra of pyrene.

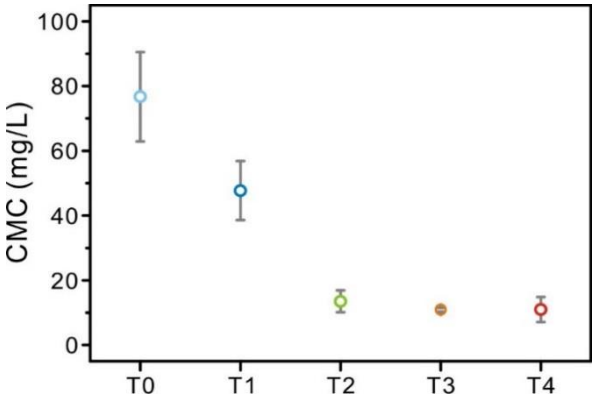

Fig. S8 Relationship of CMC values with respect to the PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{m/n}$ copolymer (**T0** – **T4**) micelles.

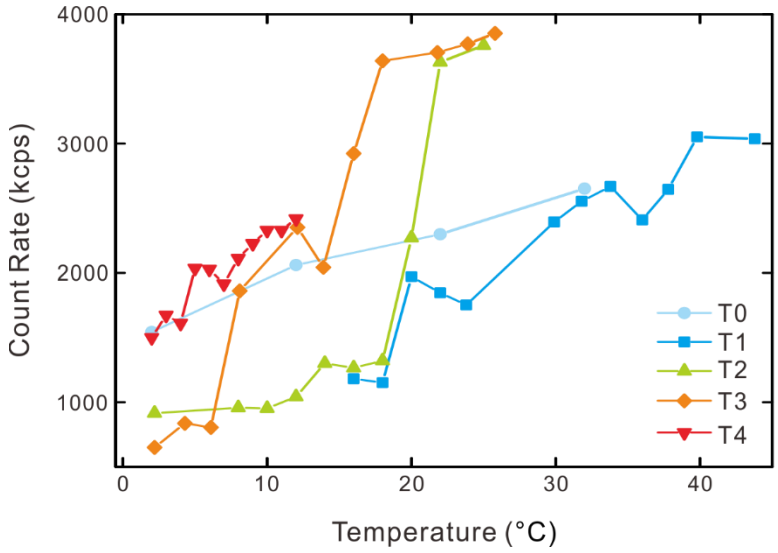

Fig. S9 Temperature-dependent count rate for all micelles (**T0** – **T4)** measured by DLS.

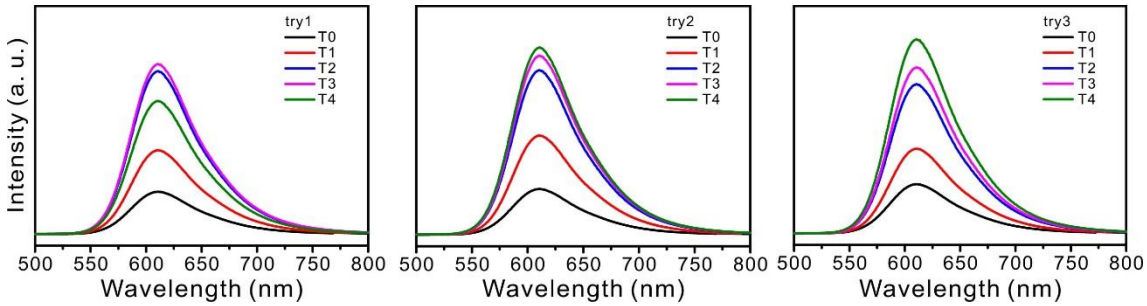

Fig. S10 Emission spectra of Nile Red in acetone after freeze-drying of aqueous solution of all **T0** – **T4** micelles for the calculation of encapsulation efficiency (λ_{ex} = 480 nm).

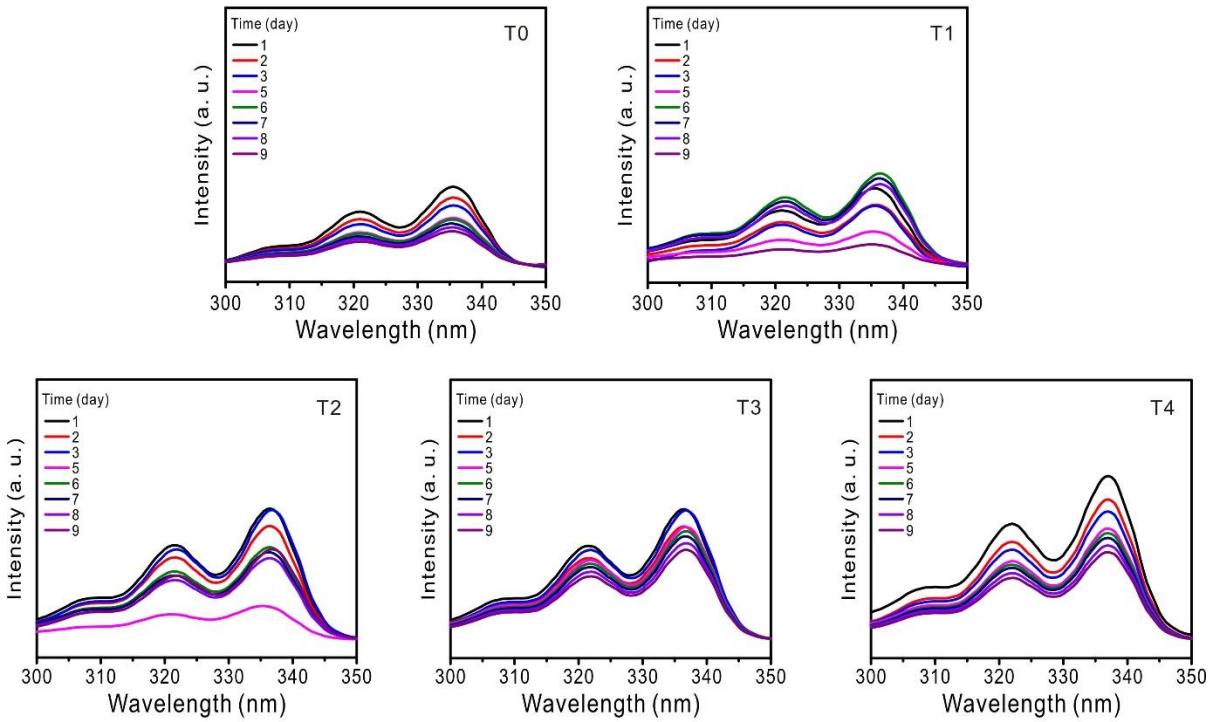

Fig. S11 Changes in excitation spectra of pyrene encapsulated by **T0** – **T4** micelles in pH 7.4 condition. The concentrations of all polymers are fixed to 0.10 mg/mL.

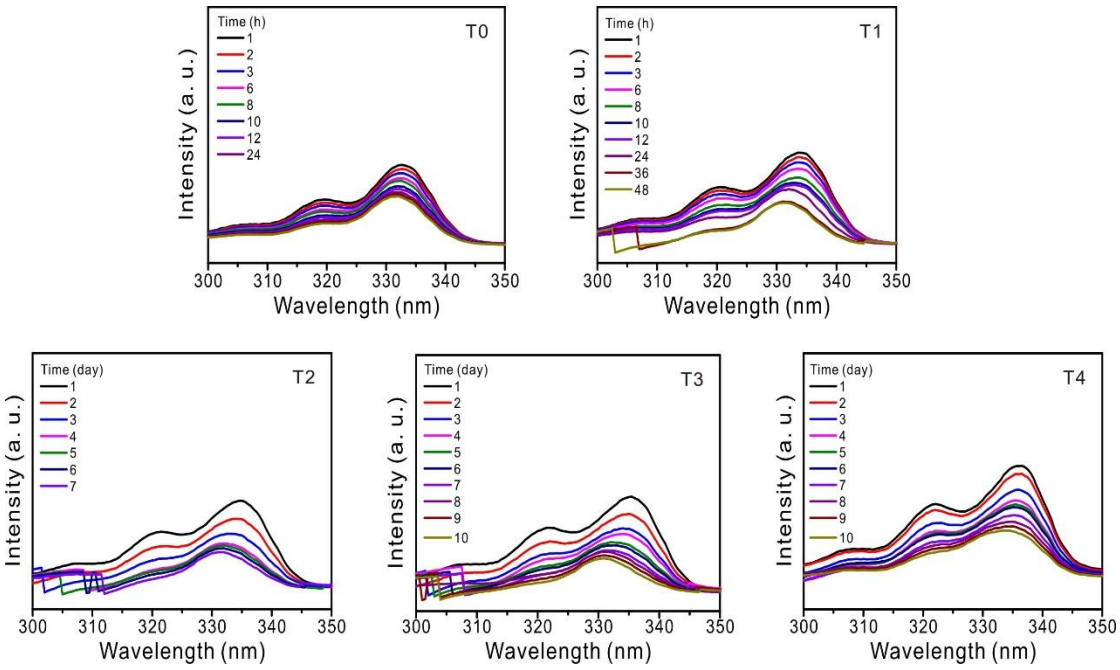

Fig. S12 Changes in excitation spectra of pyrene encapsulated by **T0** – **T4** micelles in pH 5.0 condition. The concentrations of all polymers are fixed to 0.10 mg/mL.

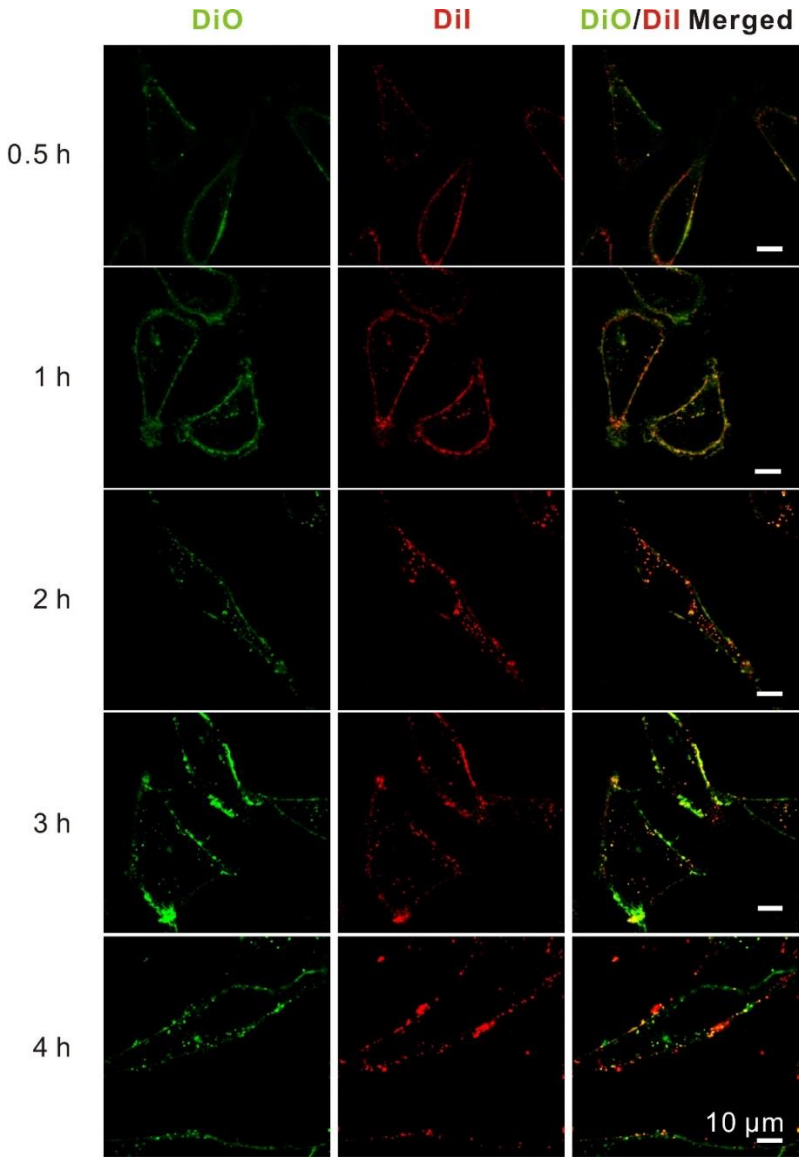

Fig. S13 *In vitro* FRET studies for **T2** micelle after incubation in different time by live imaging in HeLa cells. The green and red colours represent DiO and DiI signals, respectively, and the yellow colour indicates overlapped signals of the both FRET dyes. Excitation and emission wavelength for DiO was 488 nm and 535 nm, and that for DiI was set to 543 nm and 620 nm, respectively. Scale bars: 10 μm.

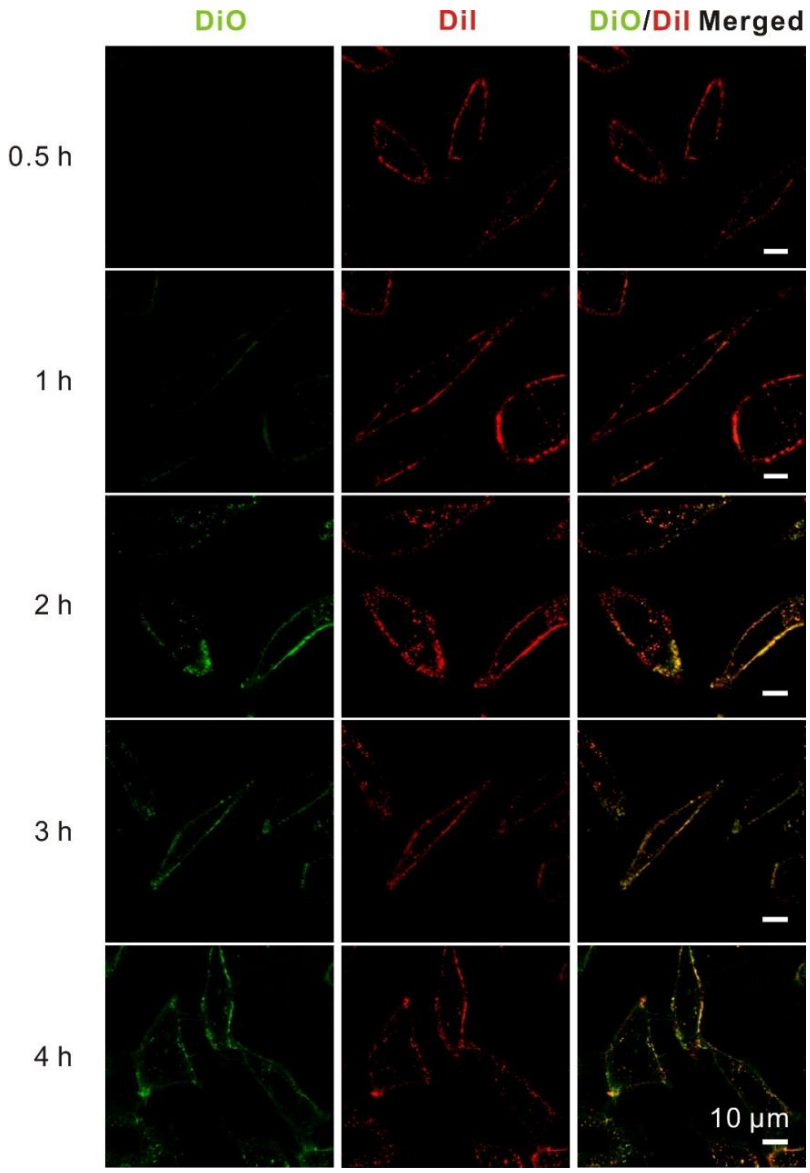

Fig. S14 *In vitro* FRET studies for **T3** micelle after incubation in different time by live imaging in HeLa cells. The green and red colours represent DiO and DiI signals, respectively, and the yellow colour indicates overlapped signals of the both FRET dyes. Excitation and emission wavelength for DiO was 488 nm and 535 nm, and that for DiI was set to 543 nm and 620 nm, respectively. Scale bars: 10 μm.

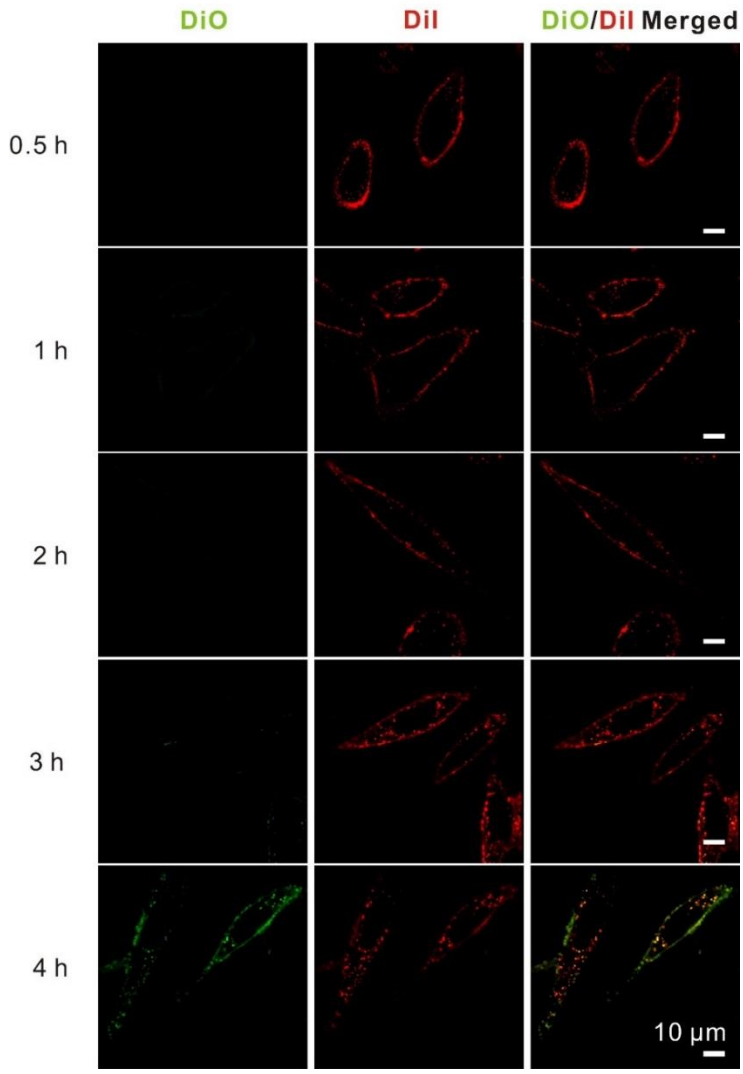

Fig. S15 *In vitro* FRET studies for **T4** micelle after incubation in different time by live imaging in HeLa cells. The green and red colours represent DiO and DiI signals, respectively, and the yellow colour indicates overlapped signals of the both FRET dyes. Excitation and emission wavelength for DiO was 488 nm and 535 nm, and that for DiI was set to 543 nm and 620 nm, respectively. Scale bars: 10 μm.

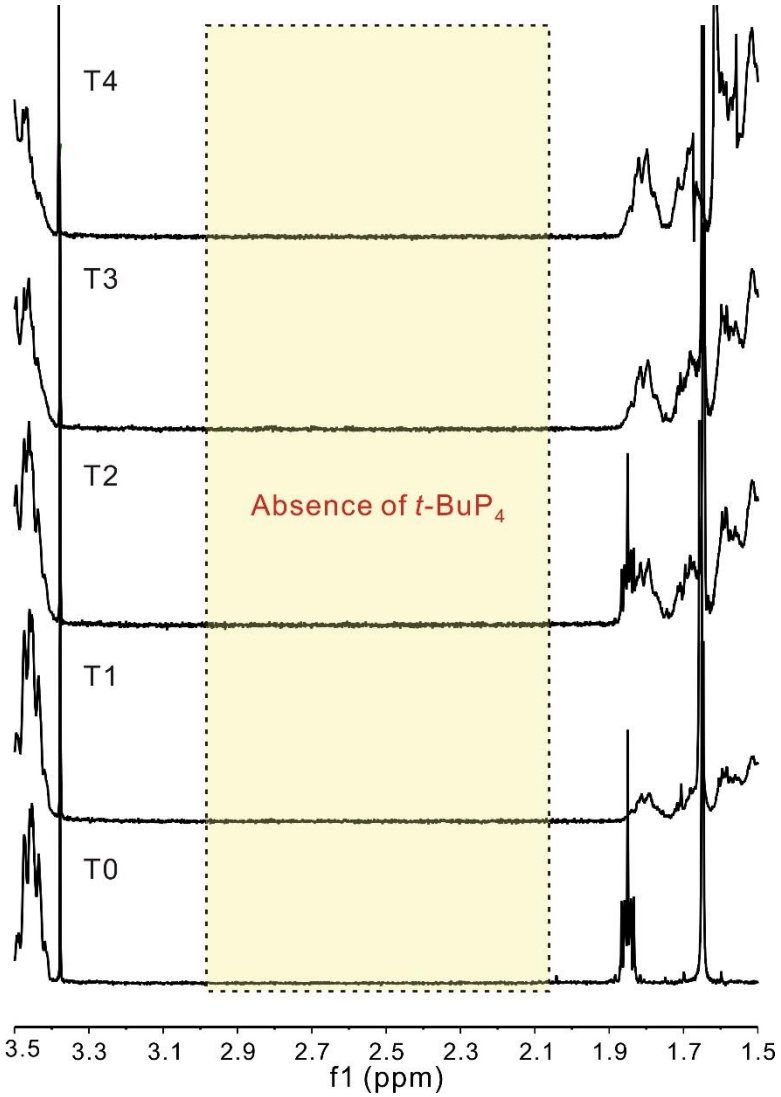

Fig. S16 Expanded ^{1}H NMR spectra of PEG_{114}-*b*-P(EEGE-*co*-TGE)$_{m/n}$ copolymers (**T0** –**T4**), displaying the clear disappearance of the residual phosphazene base, *t*-BuP_4.