Electronic Supplementary Information, *Fine-tuning thermoresponsive functional poly(ε-caprolactone)s to enhance micelle stability and drug loading*

Elizabeth A. Rainbolt, Jason B. Miller, Katherine E. Washington, Suchithra A. Senevirathne, Michael C. Biewer, Daniel J. Siegwart, and Mihaela C. Stefan

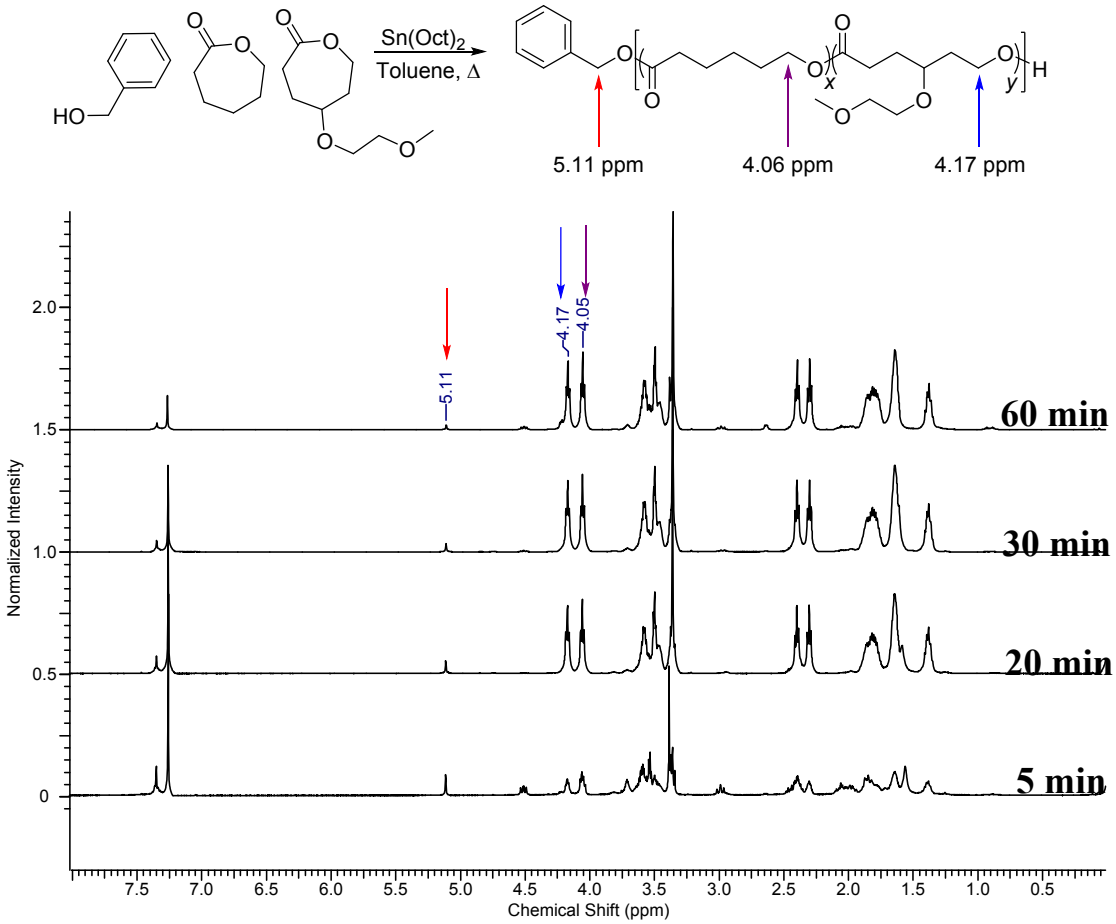

Fig. S1. Copolymerization of ME_1CL and CL: ^1H NMR spectra at different time points in the reaction revealed the incorporation of ME_1CL and CL relative to BnO chain end. Integration of the labeled peaks is shown below in **Table S1**.

Table S1. Summary of PME_1CL-*co*-PCL

Time (min)	δ (ppm)		
	5.11 (BnO)	**4.17 (ME_1CL)**	**4.06 (CL)**
5	1.0	2.7	3.6
20	1.0	15.9	15.5
30	1.0	25.5	25.5
60	1.0	33.9	35.7

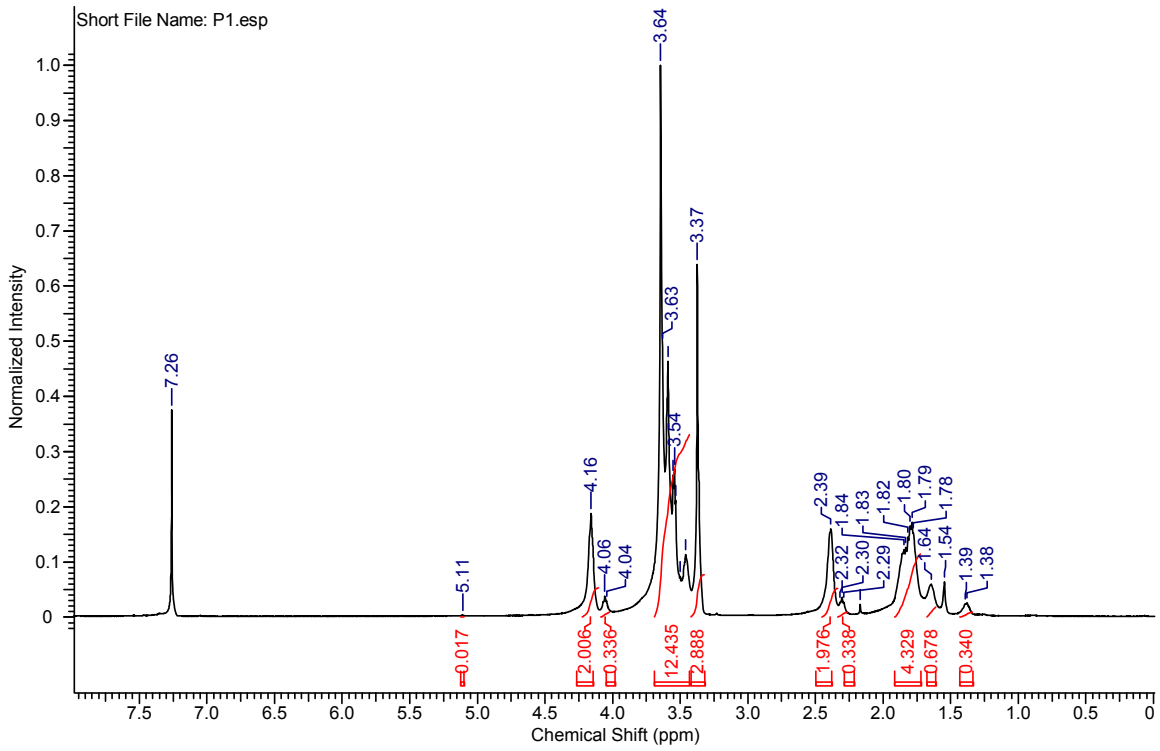

Fig. S2. ^{1}H NMR spectrum of **P1**.

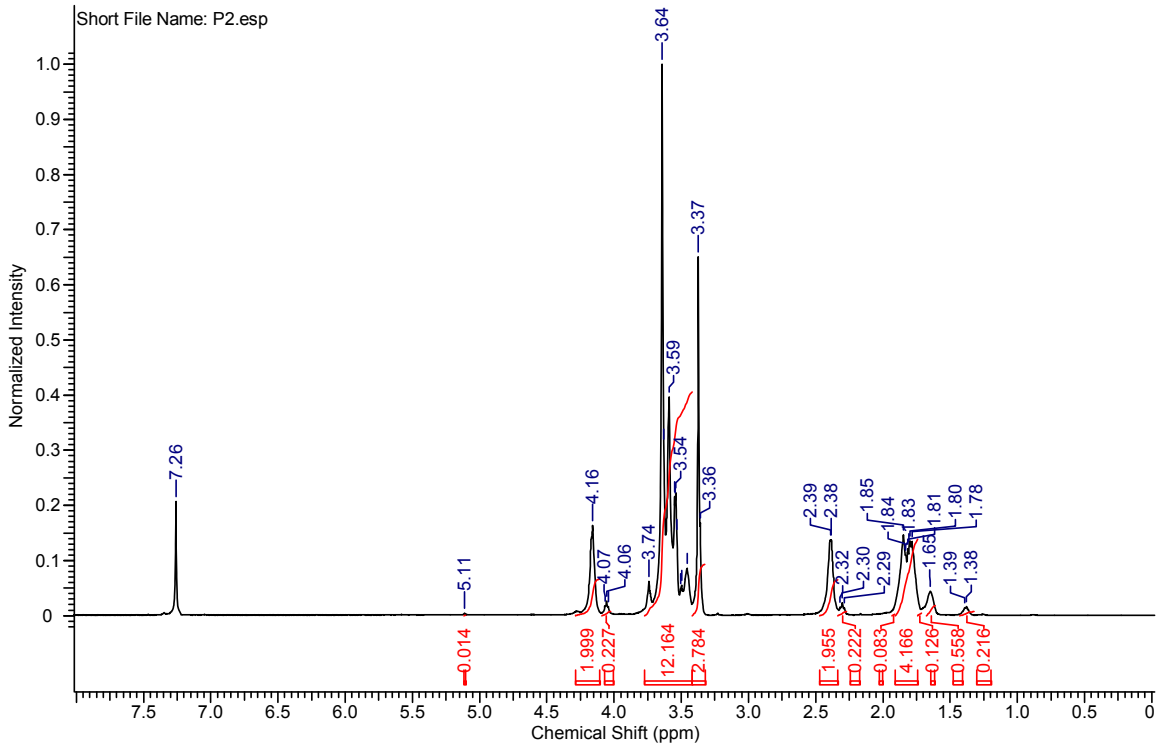

Fig. S3. ^{1}H NMR spectrum of **P2**.

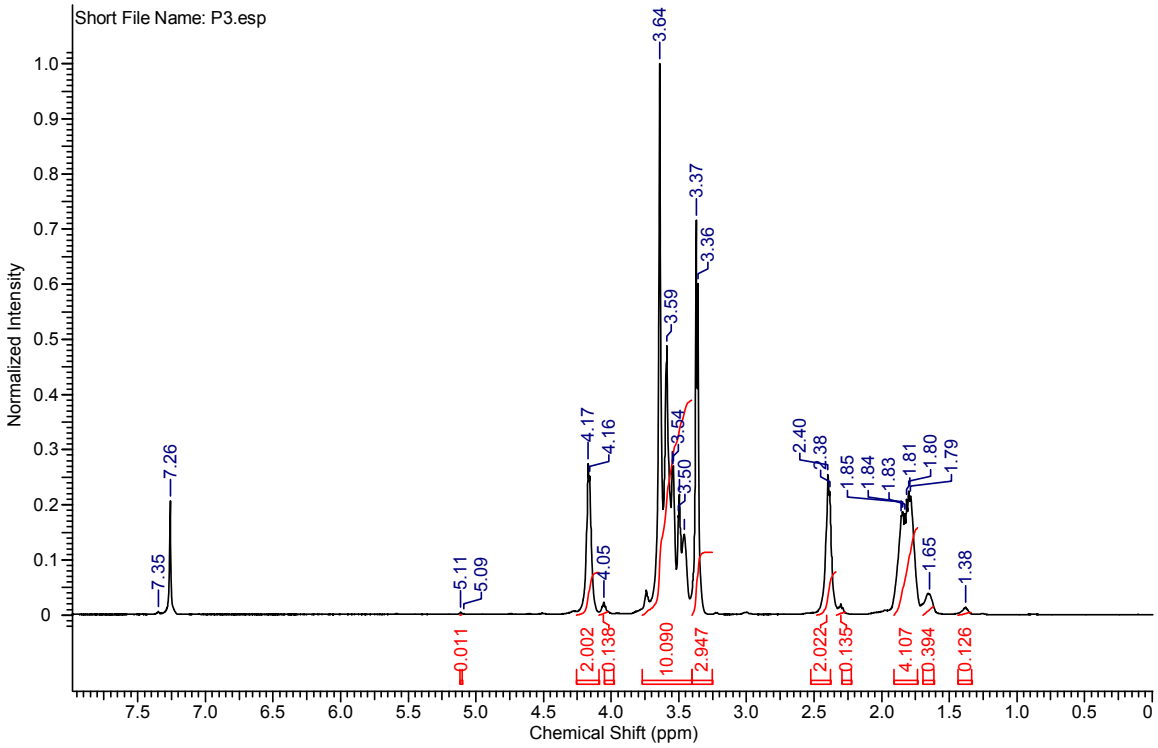

Fig. S4. ^{1}H NMR spectrum of **P3**.

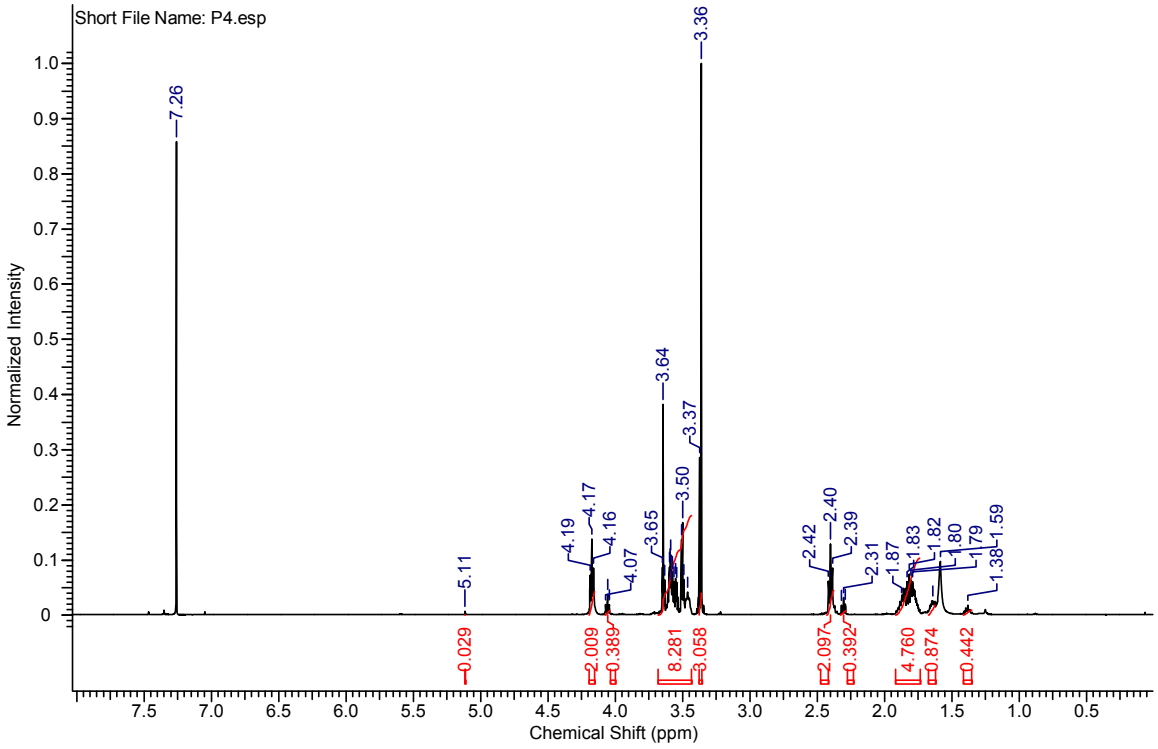

Fig. S5. ^{1}H NMR spectrum of **P4**.

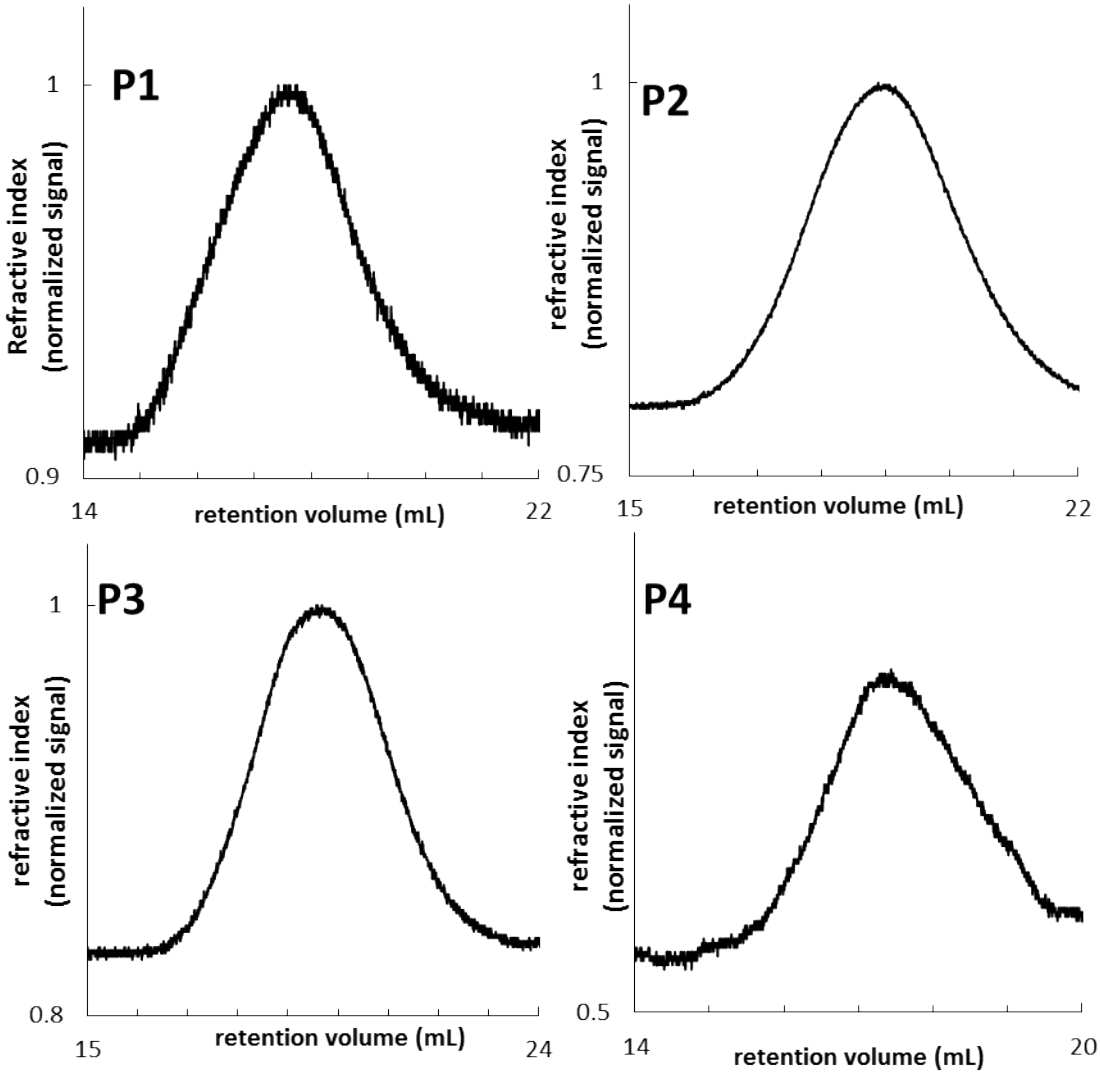

Fig. S6 Size exclusion chromatography (SEC / GPC) traces of copolymers **P1** – **P4**.

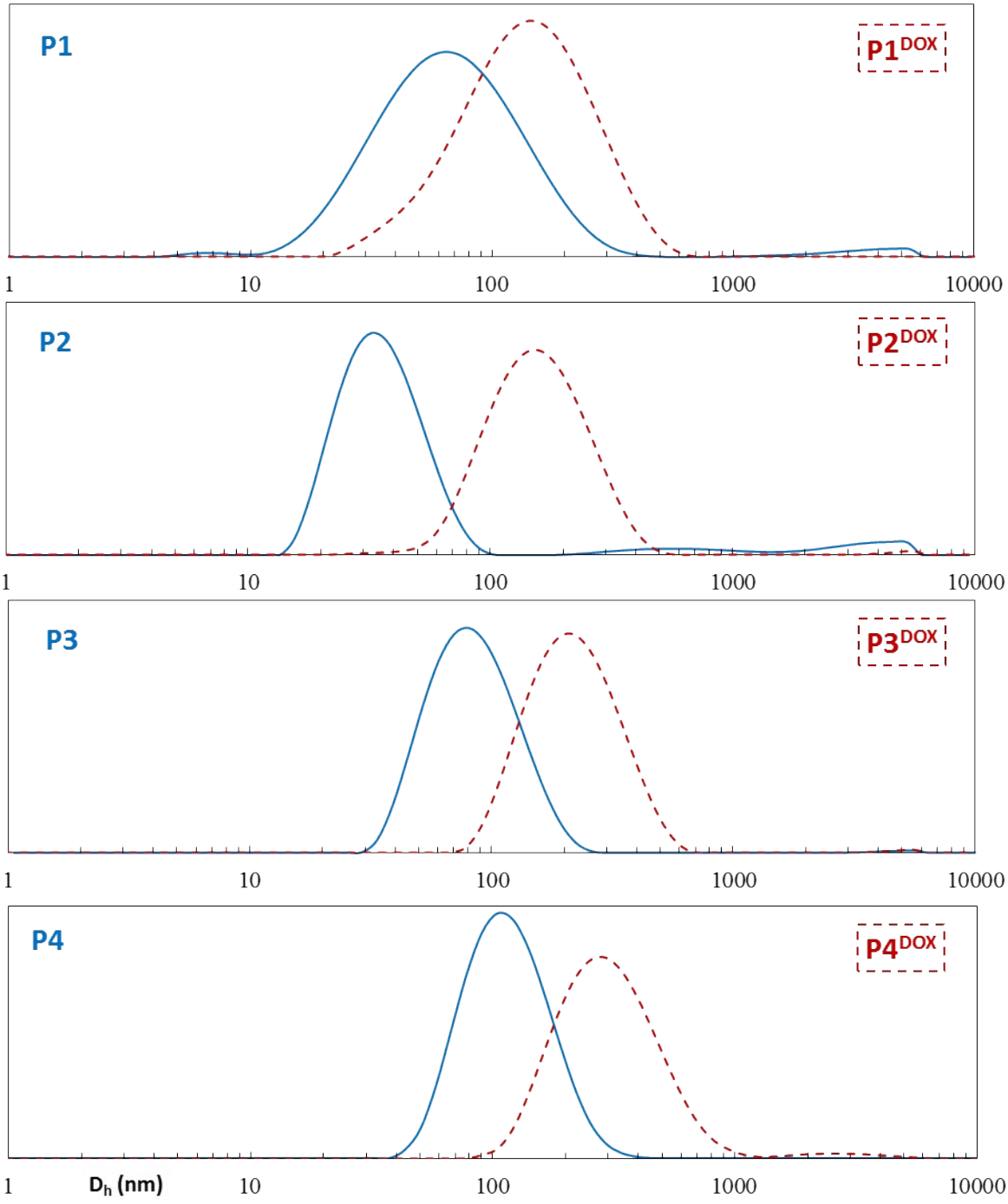

Fig. S7. DLS measurements: hydrodynamic diameters (D_h) of empty (blue, solid) and DOX-loaded (red, dashed) micelles of **P1** – **P4**.

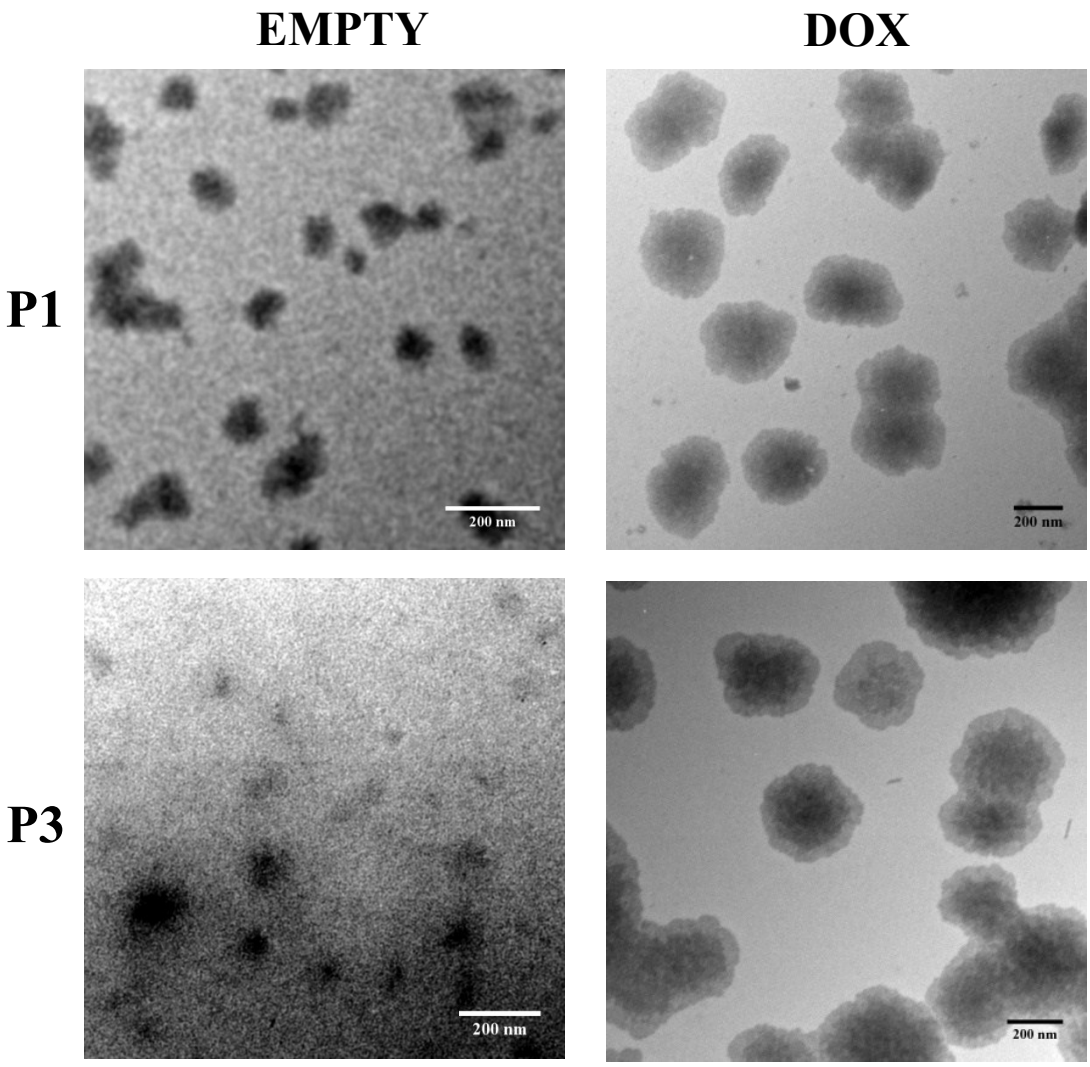

Fig. S8. TEM images of **P1** and **P3** empty micelles (left); and $\mathbf{P1}^{\mathbf{DOX}}$ and $\mathbf{P3}^{\mathbf{DOX}}$ (right); micelles deposited on copper mesh grid and stained with phosphotungstic acid; scale bars 200 nm.

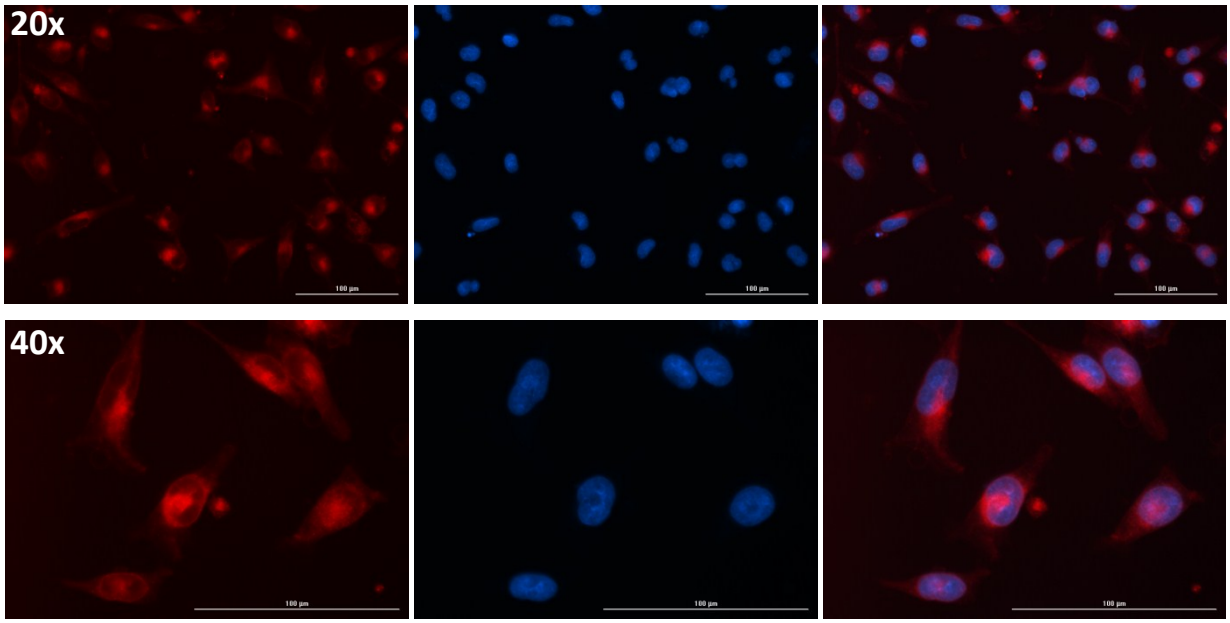

Fig. S9. Digital fluorescence microscopy showing the uptake of DOX-loaded micelles **P3^{DOX}**: left, DOX shown in red; center, DAPI-stained cell nuclei in blue; right, overlay of red and blue channels; scale bars signify 100 μm.