Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Theranostic Unimolecular Micelles of Highly Fluorescent Conjugated Polymer Bottlebrushes for Far Red/Near Infrared Bioimaging and Efficient Anticancer Drug Delivery

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Table S1 Experimental details for synthesis of polymer brushes PFTB-*b*-POEGMA and PFTB-*g*-(PCL-*b*-POEGMA) via ATRP

Polymer bottlebrushes	Macroinitiator	[monomer]/ [initiator]	[monomer] [M]	Toluene /mL	[initiator]/ [CuBr]/ [PMDETA]
$(PFTB\text{-}g\text{-}(POEGMA_6)_2)_{10}$	$PFTB_{10}$-Br	100:1	0.5	4	1:1:1
$(PFTB\text{-}g\text{-}(PCL_8\text{-}b\text{-}POEGMA_{16})_2)_{10}$	$(PFTB\text{-}g\text{-}(PCL_8\text{-}Br)_2)_{10}$	100:1	0.5	4	1:1:1
$(PFTB\text{-}g\text{-}(PCL_{35}\text{-}b\text{-}POEGMA_{29})_2)_{10}$	$(PFTB\text{-}g\text{-}(PCL_{35}\text{-}Br)_2)_{10}$	100:1	0.4	4.5	1:1:1
$(PFTB\text{-}g\text{-}(PCL_{35}\text{-}b\text{-}POEGMA_{118})_2)_{10}$	$(PFTB\text{-}g\text{-}(PCL_{35}\text{-}Br)_2)_{10}$	200:1	0.4	3	1:1:1
$(PFTB\text{-}g\text{-}(PCL_{59}\text{-}b\text{-}POEGMA_{36})_2)_{10}$	$(PFTB\text{-}g\text{-}(PCL_{59}\text{-}Br)_2)_{10}$	150:1	0.15	20	1:1:1

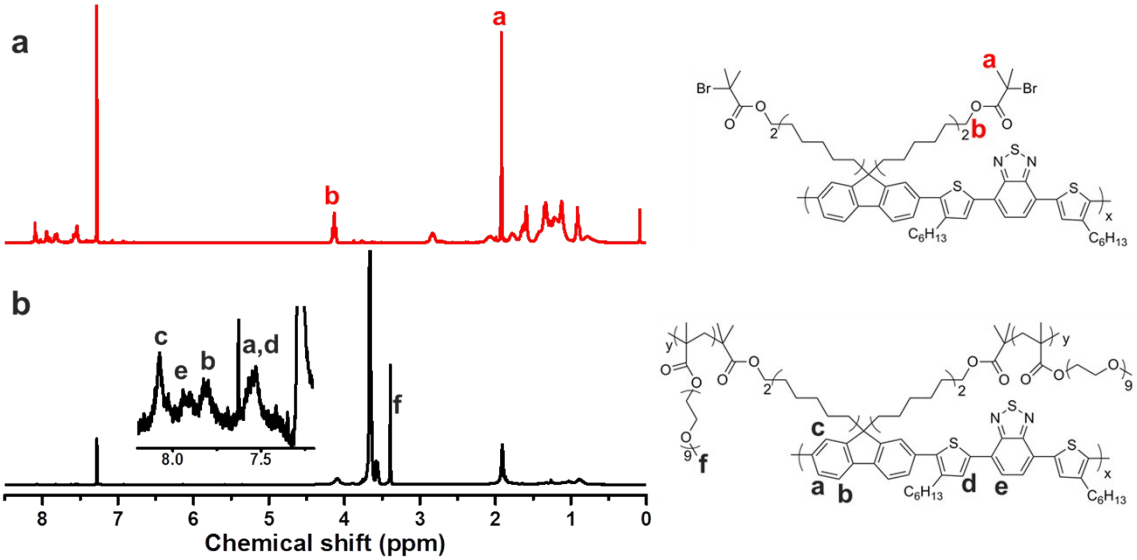

Figure S1 ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of $PFTB_{10}$-Br (a), (PFTB-*g*-$(POEGMA_{27})_2)_{10}$ (b).

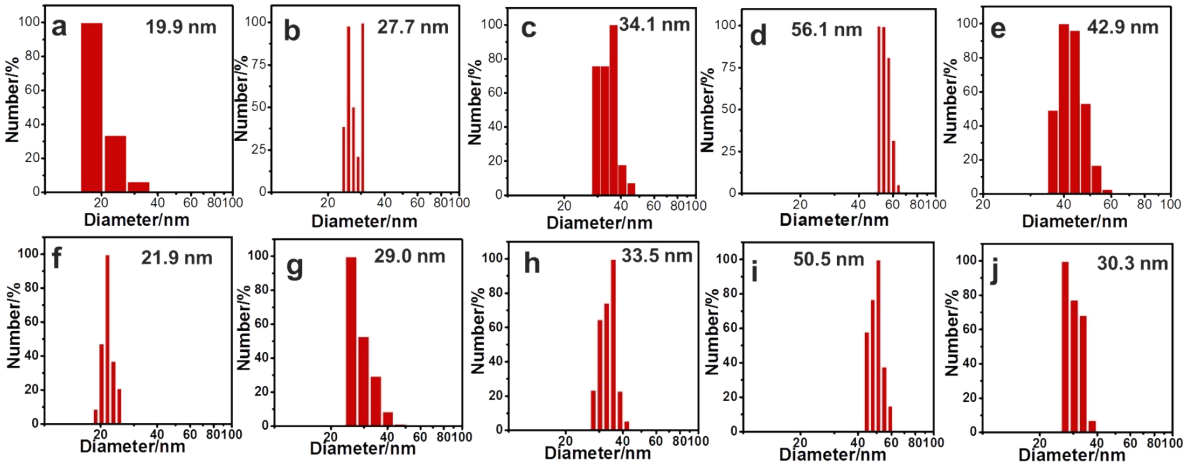

Figure S2 DLS histograms of UMs formed in THF: (a) UM-P0, (b) UM-P1, (c) UM-P2, (d) UM-P3, (e) UM-P4; and UMs in aqueous medium after being stored at 5 ^{o}C for over three months: (f) UM-P0, (g) UM-P1, (h) UM-P2, (i) UM-P3, (j) UM-P4.

Table S2 Comparison of hydrodynamic diameters between unimolecular micelles in water and THF from DLS results

D_h (nm)	P0	P1	P2	P3	P4
Water	20.2	26.8	30.6	54.2	32.3
THF	19.9	27.7	34.1	56.1	42.9

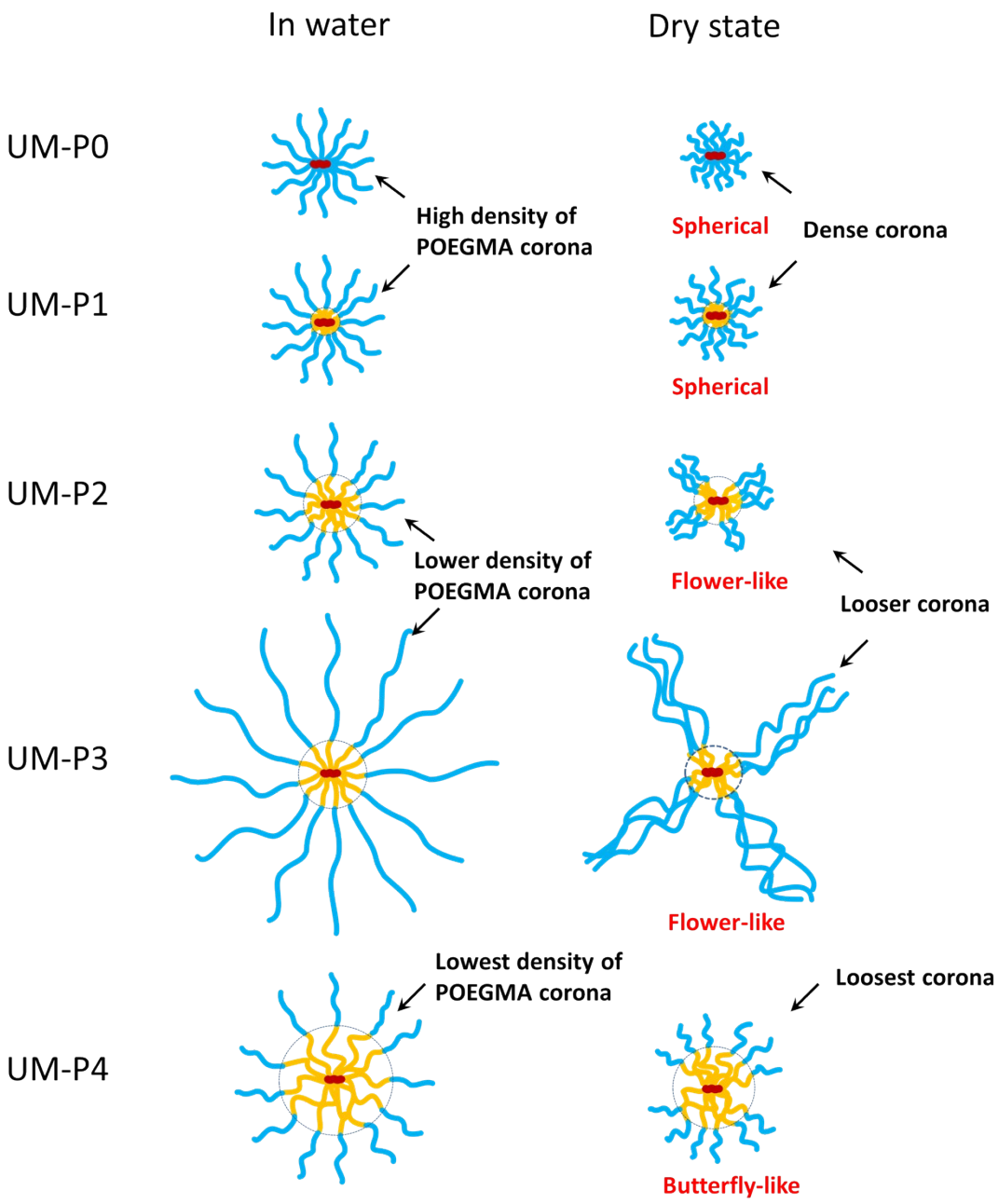

Figure S3. Schematic presentation of the morphological transition of UMs from aqueous solution to solid states.

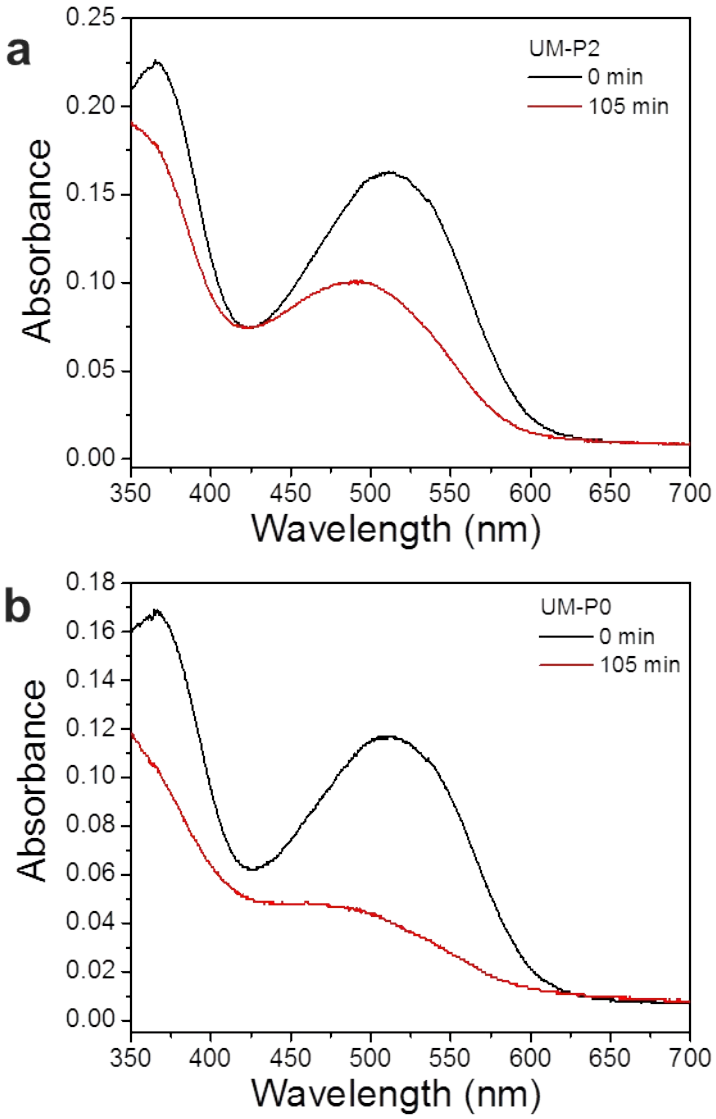

Figure S4. (a) Absorption spectra of UM-P2 for different irradiation time using LED light; (b) absorption spectra of UM-P0 for different irradiation times using white LED light.

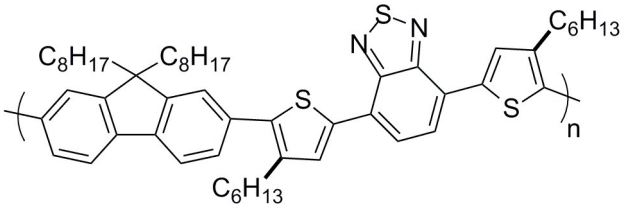

Figure S5. Chemical structure of PFTB reported in our previous work.[1]

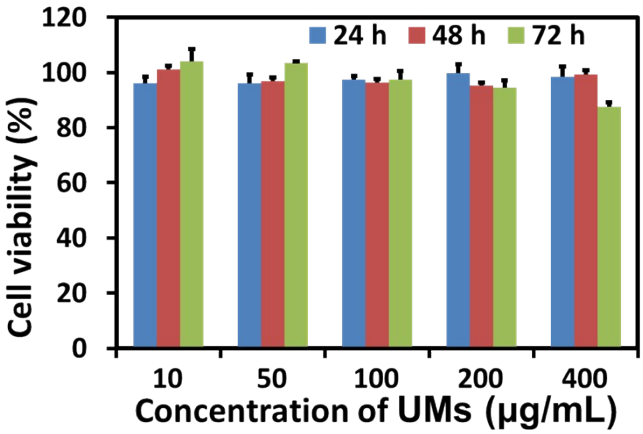

Figure S6. Metabolic viability of L929 cancer cells after incubation with UM-P1 at different concentrations for 24, 48 and 72 h, respectively.

Table S3 Loading content (LC) and encapsulation efficiency (EE) of UM-P1, UM-P2 and UM-P4

Sample	UM-P1	UM-P2	UM-P4
LC (%)	7.3	9.9	9.5
EE (%)	44.6	55.3	59.7

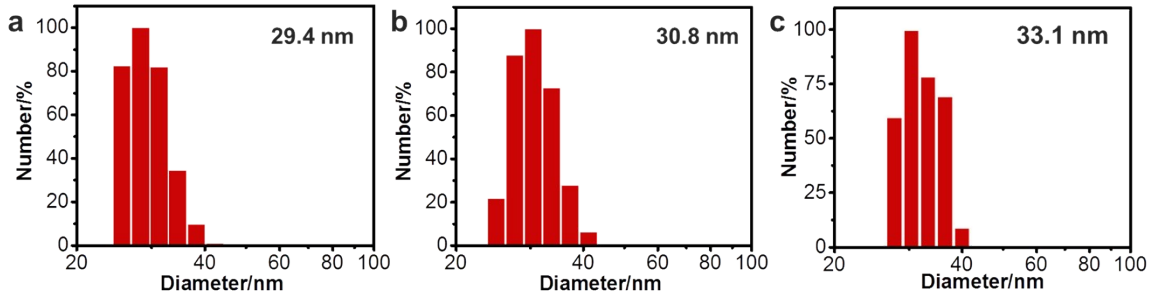

Figure S7. DLS results of DOX@UMs in aqueous media: (a) DOX@UM-P1, (b) DOX@UM-P2, (c) DOX@UM-P4.

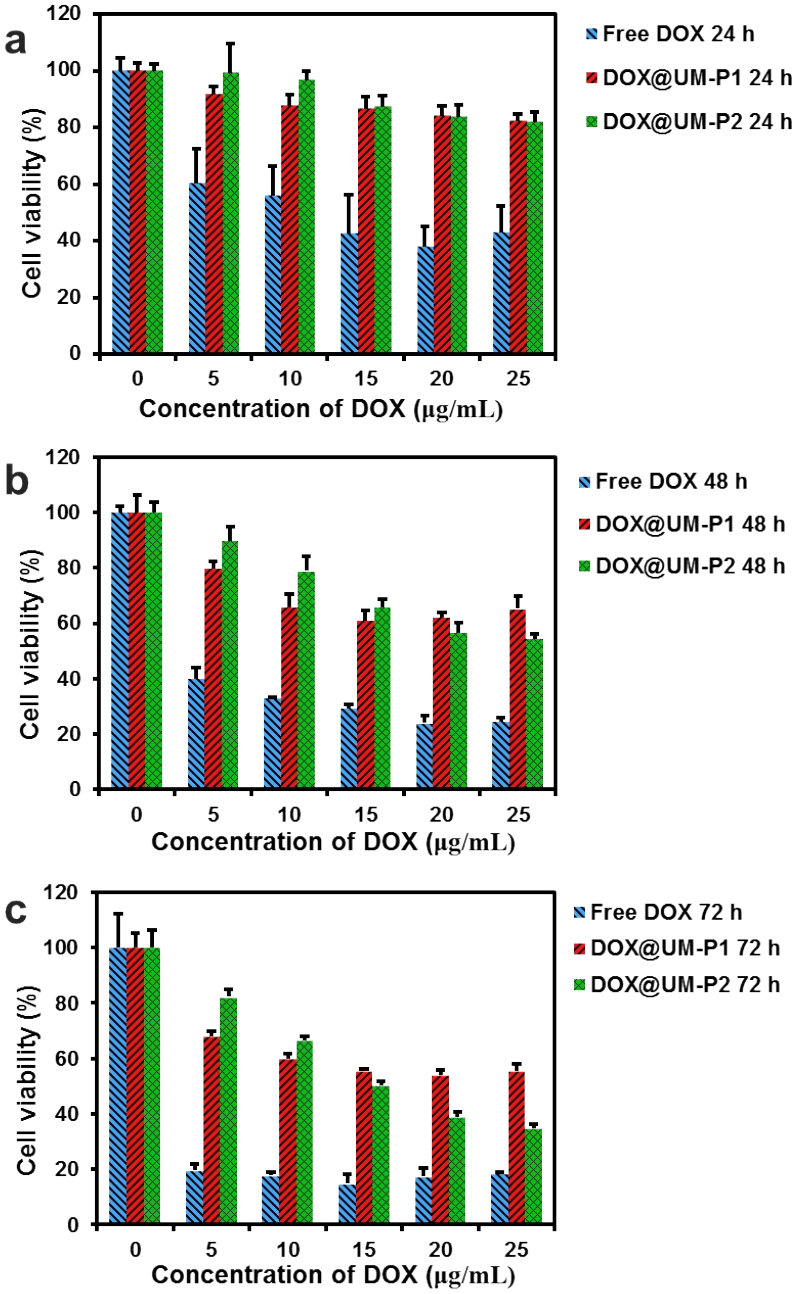

Figure S8. Viability of L929 cells incubated for 24 h (a), 48 h (b) and 72 h (c) with free DOX, DOX@UM-P1 and DOX@UM-P2 in aqueous solution at various DOX concentrations.

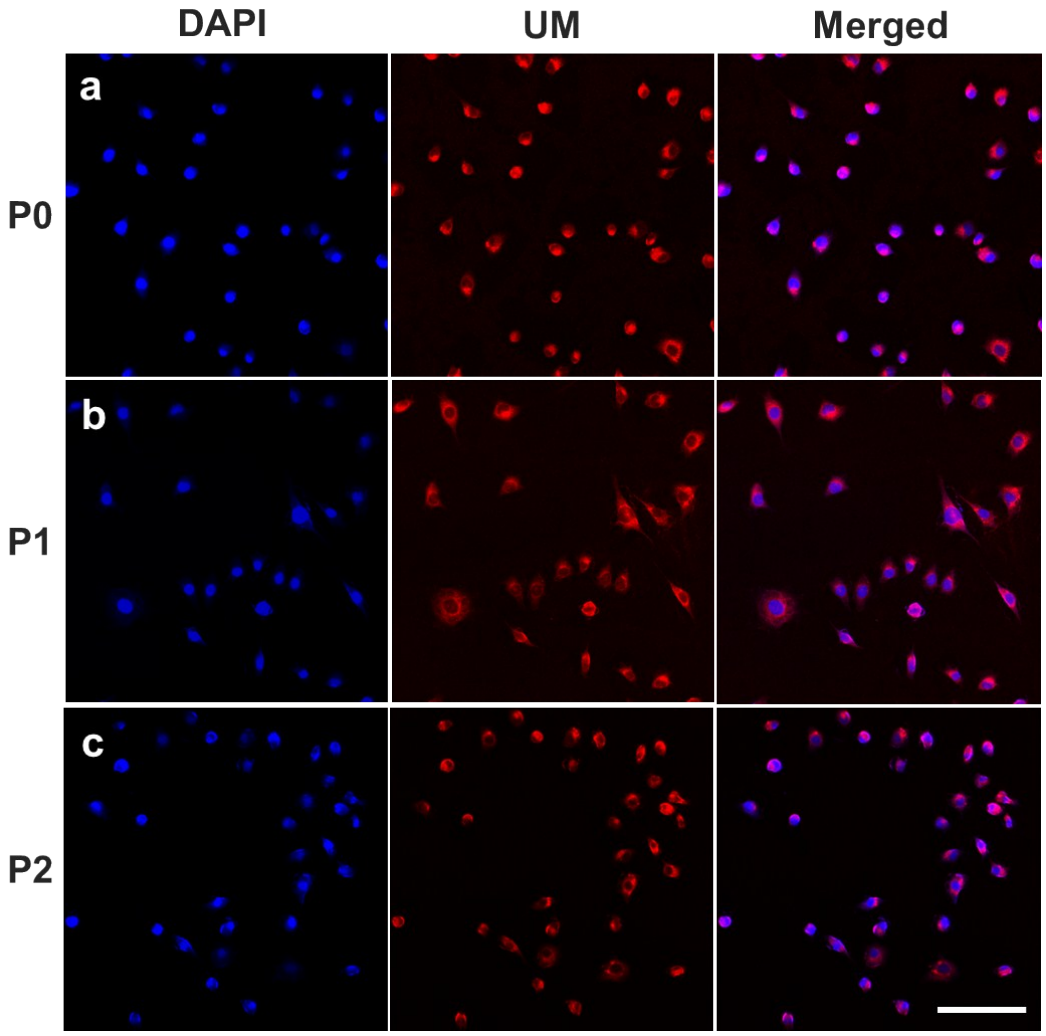

Figure S9. Confocal fluorescence microscope images of L929 cells stained with (a) UM-P0, (b) UM-P1, (c) UM-P2. The concentration of UMs is 50 μg/mL. The fluorescence of DAPI and UMs is pseudo-labeled with blue and red, respectively. The scale bar represents 100 μm.

Reference

1. X. Wang, K. Wang and M. Wang, *Polym. Chem.*, 2015, **6**, 1846-1855.