Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

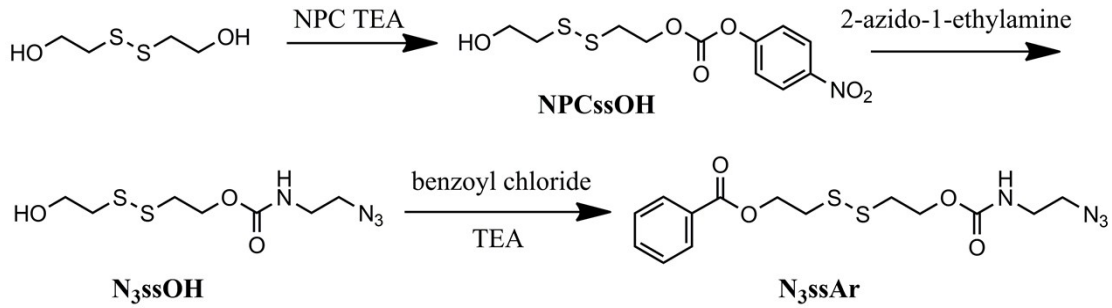
Support Information

Synthesis of N_3ssAr

The functional monomer was synthesized according to Scheme S1. 2-hydroxyethyl disulfide (10 g, 64.8 mmol) and triethylamine (9 ml, 64.8 mmol) were codissolved in dry THF (100 ml) and cooled to 0 ^oC. A solution of NPC (11.8 g, 58.3 mmol) in 40 ml THF was added dropwise into the solution over 30 min. Subsequently, the mixture was stirred at RT for another 6 h. The resulted white precipitant was removed by filtration and the filtrate was concentrated with rotary evaporation. Then, the concentrated solution was charged with 150 ml DCM, washed sequentially with saturated $NaHCO_3$ solution (3*150 ml) and brine (3*100). The organic layer was collected, dried with anhydrous Na_2SO_4 and concentrated to get the crude product. Finally, the crude product was purified by column chromatography with hexane/ethyl acetate (3:1) to get the desired material NPCssOH (8.7 g, yield 42%).

2-azido-1-ethylamine (3.5 g, 41.0 mmol) in 20 ml THF was added dropwise into the THF solution (50 ml) of NPCssOH (8.7g, 27.3 mmol) which was left to stir at RT for 4 h. Then the solvent was removed by rotary evaporation. The obtained residue was dissolved in 100 ml CH_2Cl_2, which was washed with saturated $NaHCO_3$ solution (3*100 ml), brine (3*100 ml) and dried with anhydrous Na_2SO_4 over night. After removing the solvent, the resulted crude product was purified by column chromatography with hexane/ethyl acetate to achieve N_3ssOH (6.0 g, yield 83%) (Figure S1).

N_3ssOH (6.0 g, 22.7 mmol) and triethylamine (4.6 g, 45.4 mmol) were dissolved in 70 ml dry THF in a round bottom flask. This flask was immersed into ice bath and benzoyl chloride (3.9 ml, 34.1 mmol) in 20 ml THF was added slowly into the flask. Then, the flask was allowed to stir at RT for 6 h. The solvent was removed and 100 ml CH_2Cl_2 was added. The solution was washed with saturated $NaHCO_3$ solution (3*100 ml) and brine (3*100), concentrated to obtain the N_3ssAr. (7.3 g, yield 78%) (Figure S2).



Scheme S1 Synthesis routes of N_3ssAr.

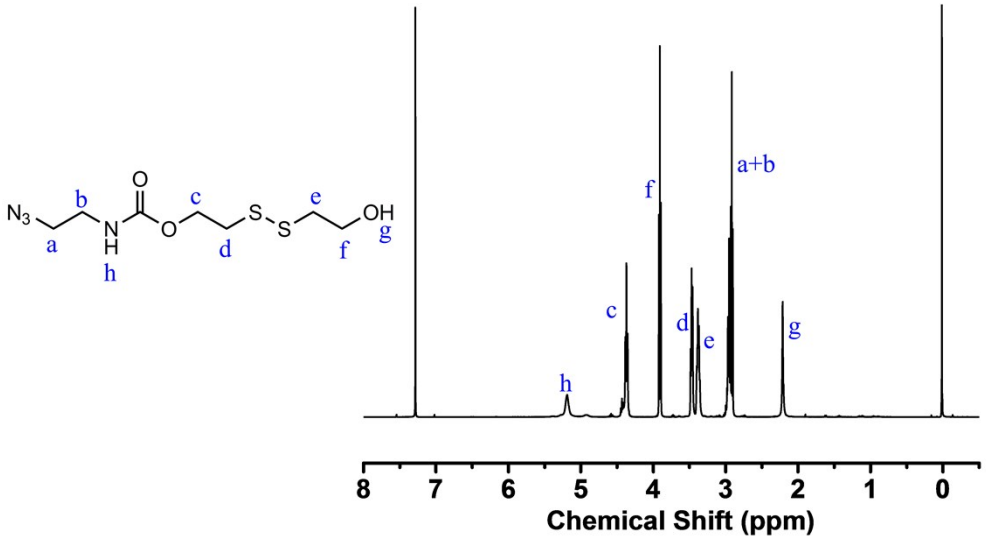


Figure S1 The ^{1}H NMR spectrum of N_3ssOH in $CDCl_3$.

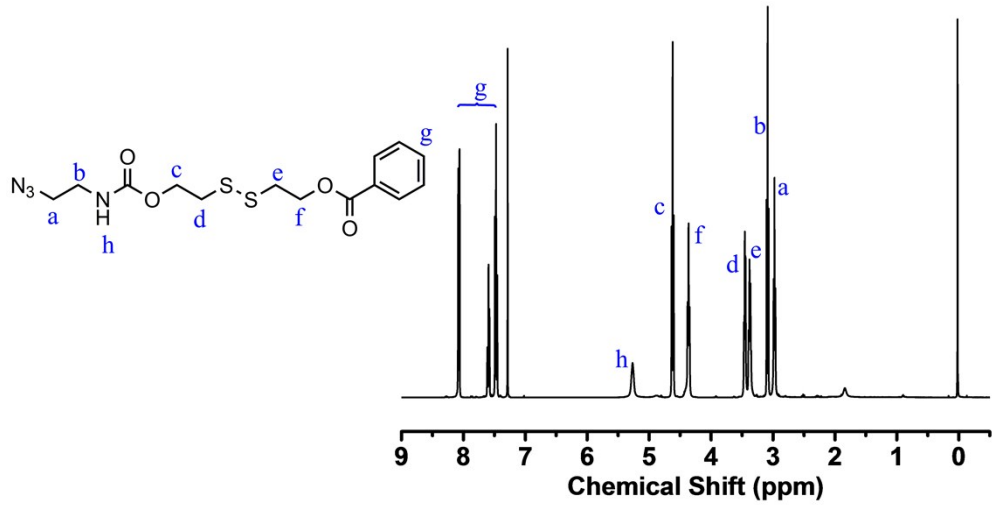


Figure S2 The ^{1}H NMR spectrum of N_3ssAr in $CDCl_3$.

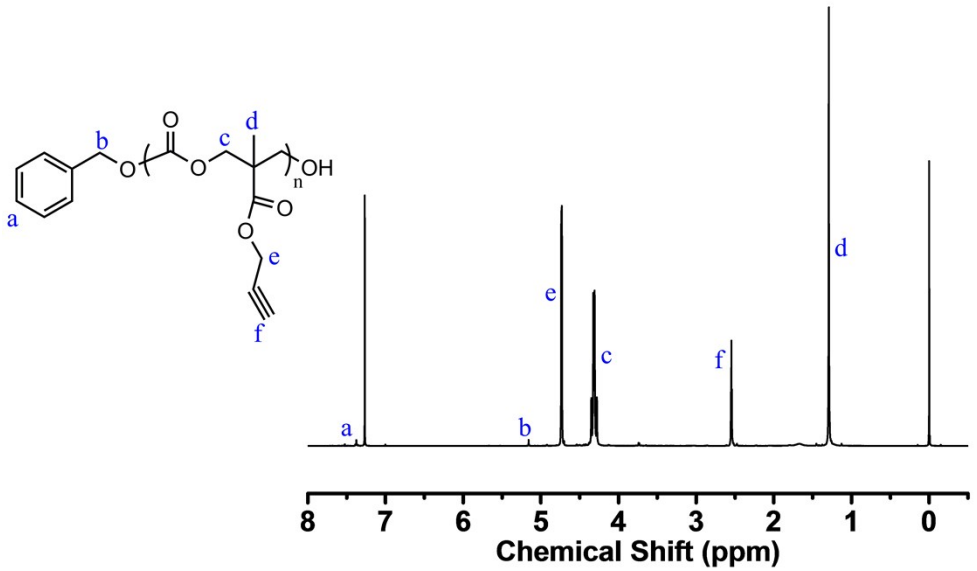


Figure S3 The ^{1}H NMR spectrum of PMPC in $CDCl_3$

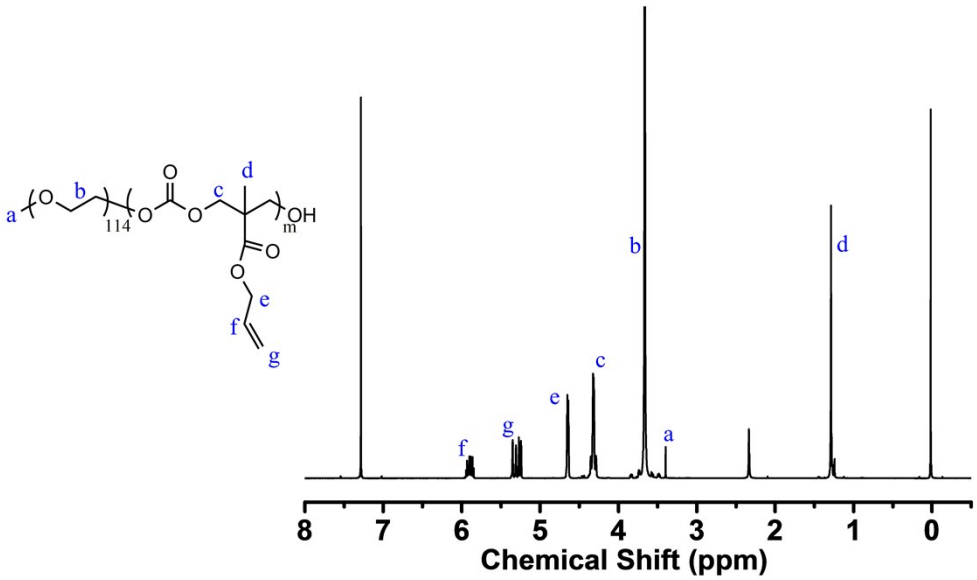


Figure S4 The ^{1}H NMR spectrum of PEG-PMAC in $CDCl_3$.

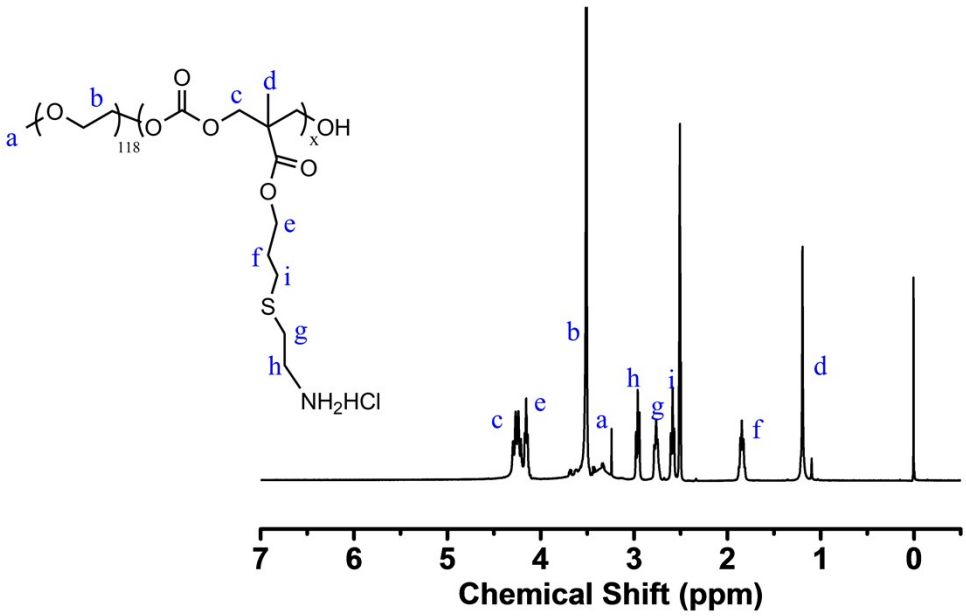


Figure S5 The ^{1}H NMR spectrum of PEG-PCNH$_2$ in d_6-DMSO.

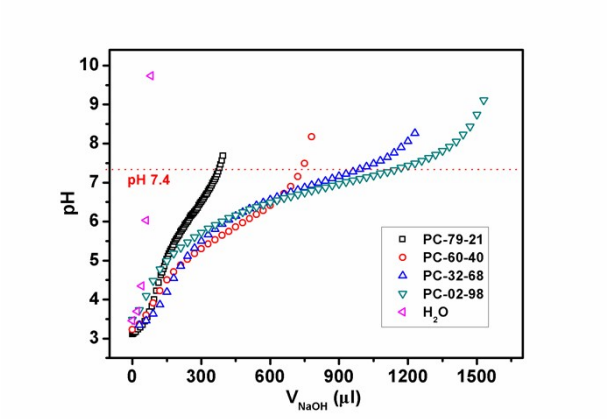
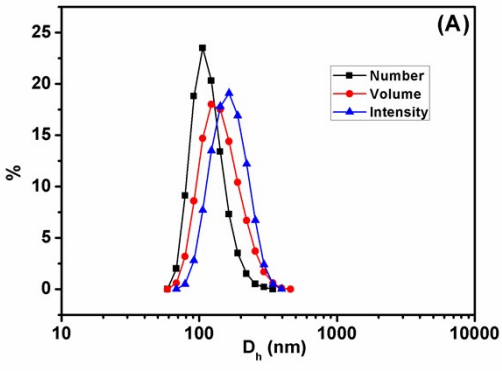


Figure S6 Titration curves of PC(Arss-N2CH$_3$)s in water.



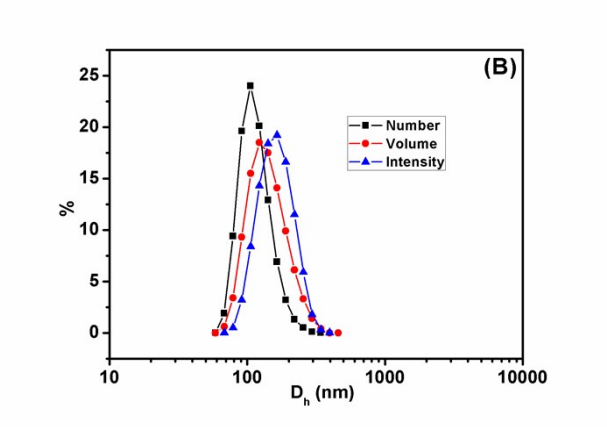
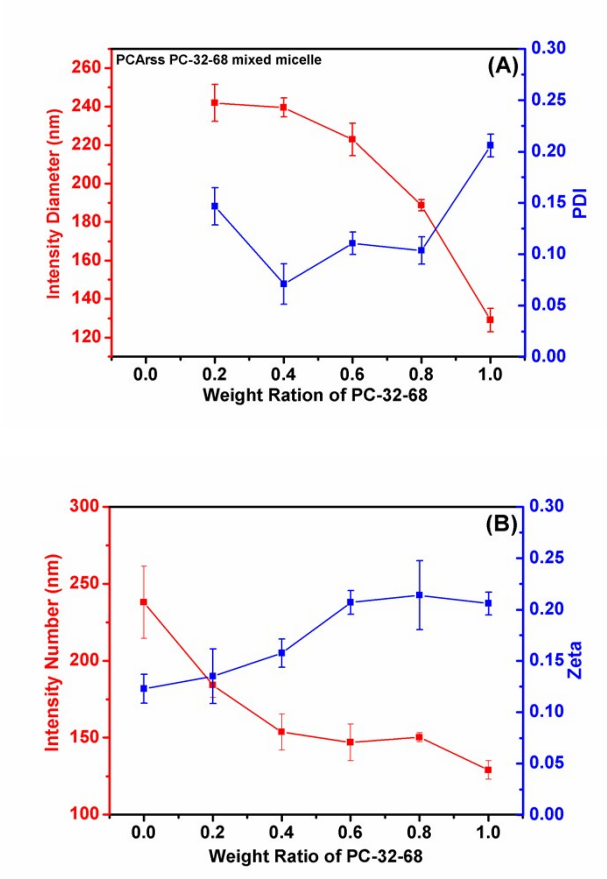


Figure S7 DLS data showing the distribution of (A) PC-79-21 PC-32-68 4-1 and (B) PC-79-21 PC-32-68 3-2 mixed core micelles.



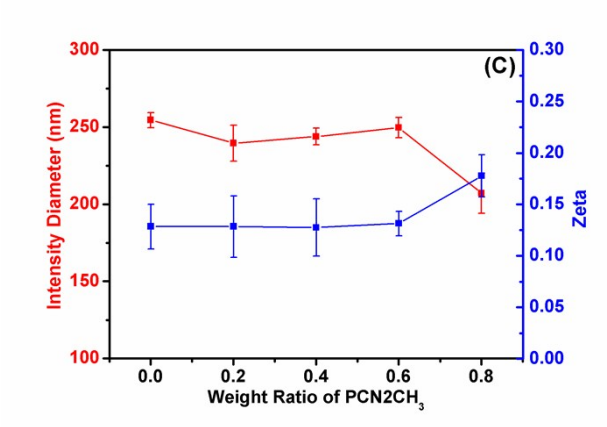


Figure S8 Size and PDI changes of the mixed micelle combined with (A) PC-100 and PC-32-68, (B) PC-60-40 and PC-32-68 (C) PC-60-40 and $PCN2CH_3$ in 10 mM pH 7.4 PBS. The micelle concentration was set as 0.3 mg/ml.

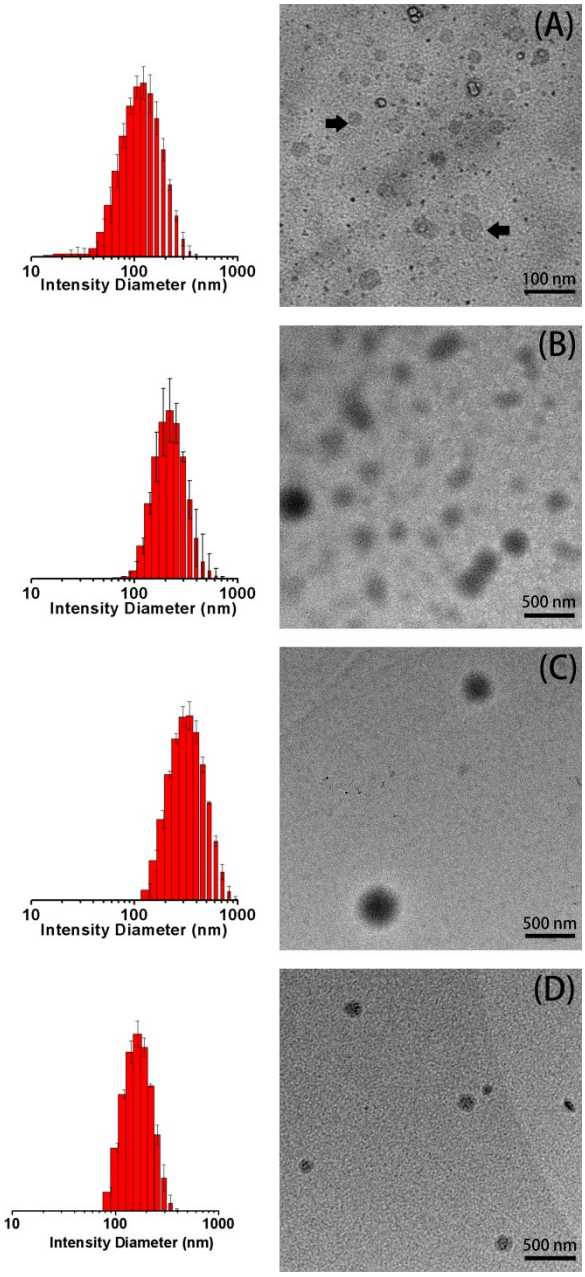
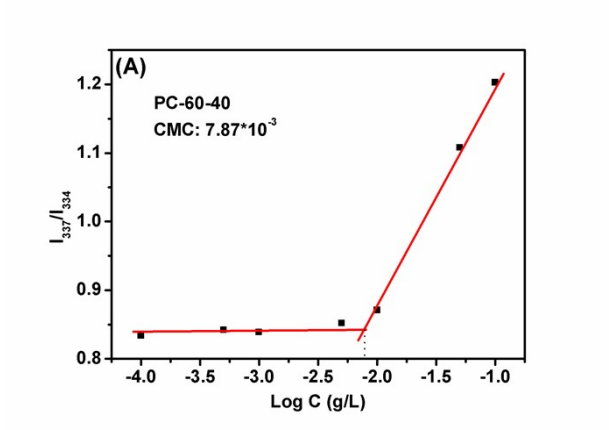
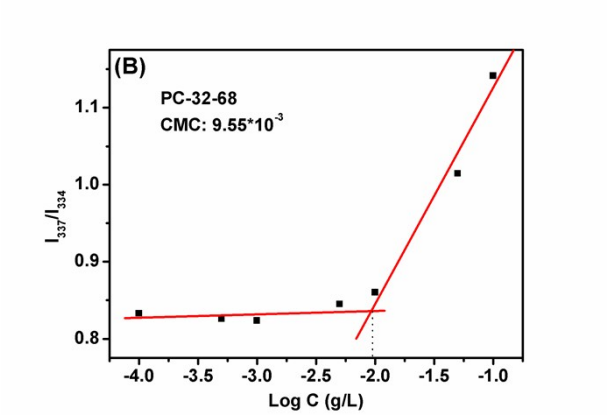
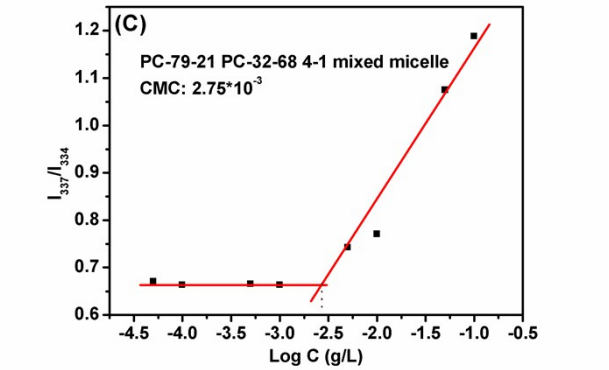
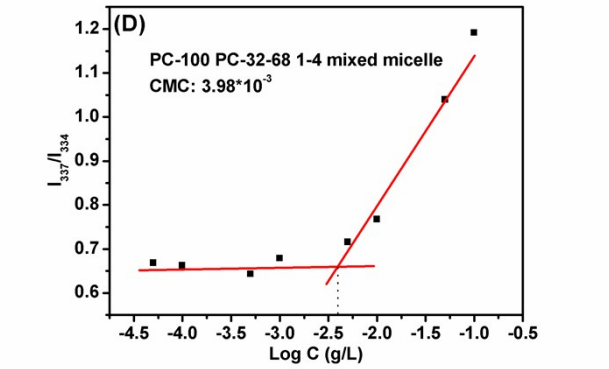


Figure S9 Size distribution and TEM images of (A) PC-32-68, (B) PC-60-40, (C) PC-79-21 and (D) PC-79-21 PC-32-68 4-1 mixed micelle.


(A)
PC-60-40
CMC: 7.87*10-3
I337/I334
Log C (g/L)


(B)
PC-32-68
CMC: 9.55*10-3
I337/I334
Log C (g/L)


(C)
PC-79-21 PC-32-68 4-1 mixed micelle
CMC: 2.75*10-3
I337/I334
Log C (g/L)


(D)
PC-100 PC-32-68 1-4 mixed micelle
CMC: 3.98*10-3
I337/I334
Log C (g/L)

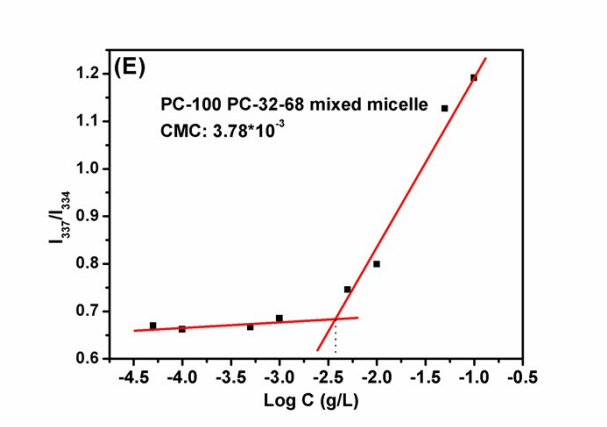


Figure S10 Plots of I339/I335 ratio of pyrene excitation spectra in pH 7.4 PBS as a function of the concentration of (A) PC-60-40, (B) PC-32-68, (C) PC-79-21 PC-32-68 4-1, (D) PC-100 PC-32-68 1-4 and (E) PC-100 PC-32-68 2-3.

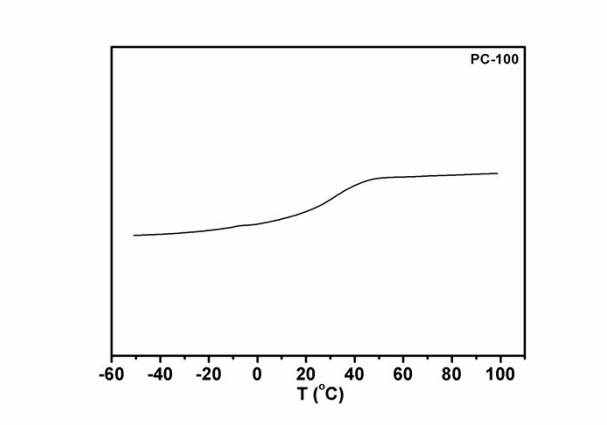


Figure S11 The DSC curve of PC-100.

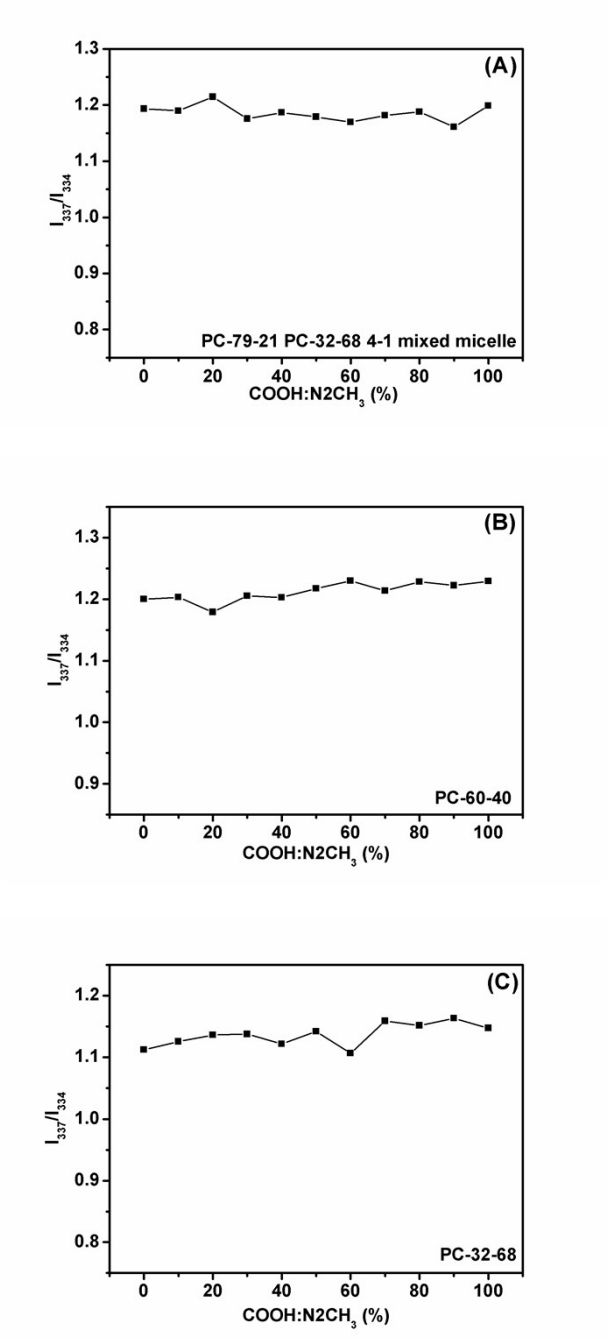


Figure S12 Pyrene excitation spectra of (A) PC-79-21 PC-32-68 4-1, (B) PC-60-40 and (C) PC-32-68 with the titration of PEG-PCDCA in pH 7.4, 10 mM PBS.

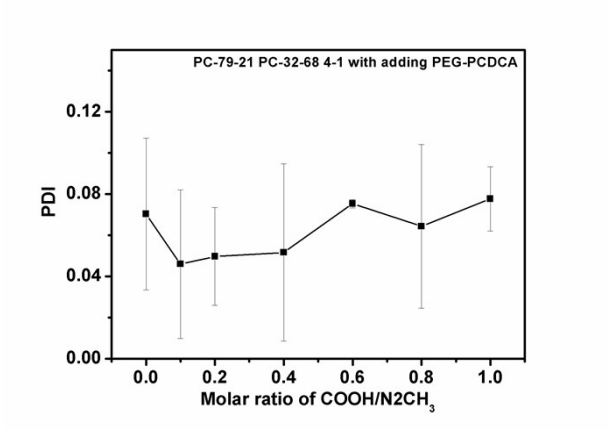


Figure S13 The PDI changes of PC-79-21 PC-32-68 4-1 with adding PEG-PCDCA

Table S1 Characteristics of NR Loaded micelles

Drug	Micelle	Size1[a] (nm)	PDI[b]	Drug/Polymer[c]	LC(%)[d]	EE(%)[d]	Size 2[e] (nm)	PDI[f]
NR	PC-32-68	129	0.210	0.1	1.97	20.1	145	0.206
	PC-60-40	238	0.127	0.1	4.27	44.6	226	0.129
	PC-79-21 PC-32-68 4-1	170	0.083	0.1	5.69	60.3	217	0.073
	PC-79-21 PC-32-68 4-1	170	0.083	0.15	7.42	53.5	203	0.081
	PC-79-21 PC-32-68 4-1	170	0.083	0.2	11.7	66.0	195	0.062
	PC-79-21 PC-32-68 4-1	170	0.083	0.3	4.38	15.3	184	0.082
	PC-79-21 PC-32-68 2-3	150	0.091	0.3	4.94	17.3	180	0.100
	PC-79-21 PC-32-68 3-2	169	0.072	0.3	3.68	12.7	191	0.089
	PC-100 PC-32-68 2-3	223	0.124	0.3	3.91	13.7	263	0.106
	PC-100 PC-32-68 3-2	239	0.118	0.1	4.81	50.5	274	0.135
	PC-100 PC-32-68 3-2	239	0.118	0.3	3.75	13.0	291	0.109

[a] Empty micelles with no drugs, the size was determined by DLS.

[b] The PDI of blank micelle.

[c] The weight of drug to polymer.

[d] Determined by UV measurement.

[e] Drug loaded micelle.

[f] The PDI of drug loaded micelle.

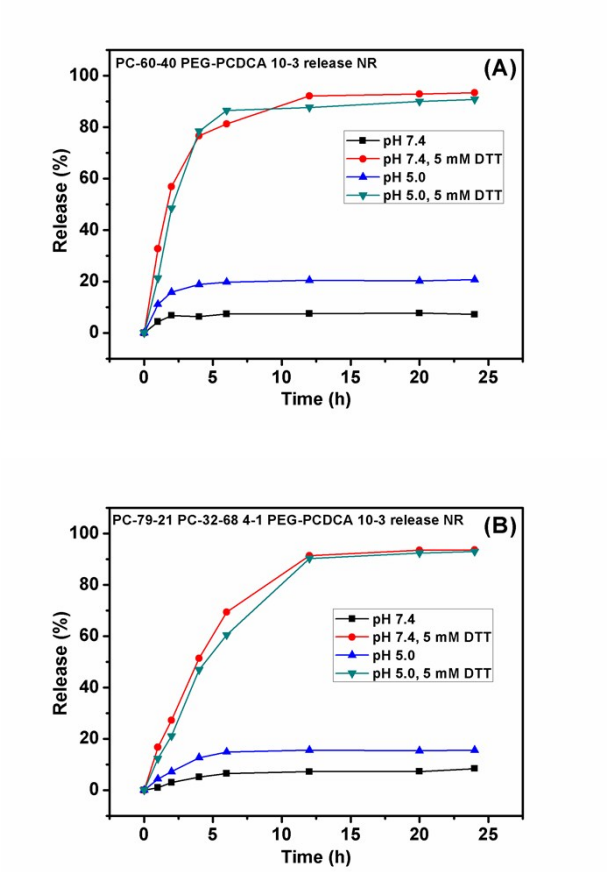


Figure S14 pH and/or redox-triggered release of NR at 37 °C from (A) PC-60-40 PEG-PCDCA 10-3 (B) PC-79-21 PC-32-68 4-1 PEG-PCDCA 10-3 core shell mixed micelles.