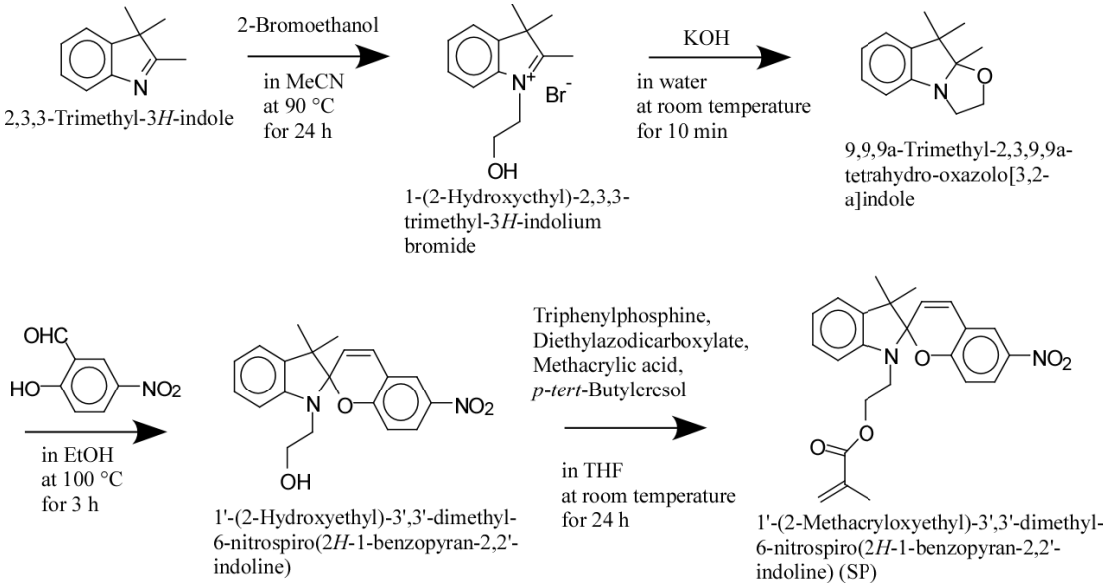
Electronic Supplementary Material (ESI) for Soft Matter

Aqueous Polymeric Micelles of Poly[*N*-isopropylacrylamide-*b*-sodium 2-(acrylamido) -2-methylpropanesulfonate] with Spiropyran Dimer Pendant: Quadruple Stimuli-responsivenes

Supporting Information



Scheme S1. Synthetic Route of SP

1-(2-Hydroxyethyl)-2,3,3-trimethyl-3*H*-indolium bromide

A solution of 2,3,3-trimethyl-3*H*-indole (25.0 g, 0.157 mol) and 2-bromoethanol (24.5 g, 0.196 mol) were dissolved in acetonitrile (192 mL). The solution was heated at 90 °C for 24 h under Ar atmosphere. After cooling down to ambient temperature, the solvent was evaporated under reduced pressure. The crude product was recrystallized from a mixed solvent of *n*-hexane (100 mL) and $CHCl_3$ (50 mL). The product was further recrystallized from a mixed solvent of methanol (50 mL) and diethylether (150 mL) to obtain 1-(2-hydroxyethyl)-2,3,3-trimethyl-3*H*-indolium bromide (32.8 g, 73.6 %) as a pink solid. mp = 195 °C; ^{1}H NMR (500 MHz, D_2O): δ 1.56 (6H, s), 2.79 (3H, s), 4.10 (2H, t), 4.62 (2H, t), 7.59-7.74 (4H, m).

9,9,9a-Trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a]indole

A solution of 1-(2-hydroxyethyl)-2,3,3-trimethyl-3*H*-indolium bromide (32.8 g, 0.116 mol) and KOH (10.3 g, 0.184 mol) in water (560 mL) was stirred at ambient temperature for 10 min, and then it was extracted with diethylether (3 × 200 mL). The organic layer was evaporated under

reduced pressure to obtain 9,9,9a-trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a]indole (23.3 g, 99.0 %) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (3H, s), 1.40 (3H, s), 1.44 (3H, s), 3.51-3.87 (4H, m), 6.77-7.17 (4H, m).

1'-(2-Hydroxyethyl)-3',3'-dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-indoline)

A solution of 2-hydroxy-5-nitorobenzaldehyde (25.0 g, 0.150 mol) and 9,9,9a-trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a]indole (20.7 g, 0.102 mol) in ethanol (238 mL) was heated at 100 °C for 3 h under Ar atmosphere. After cooling down to ambient temperature, the mixture was filtrated. The resulting solid was washed with ethanol (100 mL) and dried to obtain 1'-(2-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-indoline) (34.3 g, 95.4 %) as a purple solid. mp = 171 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (3H, s), 1.31 (3H, s), 3.33-3.50 (2H, m), 3.71-3.82 (2H, m), 5.98 (1H, d), 6.68-7.22 (6H, m), 8.00-8.04 (2H, m)

1'-(2-Methacryloxyethyl)-3',3'-dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-indoline) (SP)

A solution of 1'-(2-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-indoline) (18.7 g, 52.9 mmol) and triphenylphosphine (25 g, 95.3 mmo) in THF (792 mL) was cooled to 0 °C under Ar atmosphere. Diethylazodicarboxylate (16.4 g, 94.3 mmol) was added, and the mixture was stirred for 10 min. Following the addition of methacrylic acid (8.21 g, 95.4 mmol) and a trace of *p-tert*-butylcresol, and the solution was stirred for 24 h at ambient temperature. The solvent was evaporated under reduced pressure. The crude product was purified with silica gel column chromatography using $CHCl_3$. The first fraction was collected and recrystallized from *n*-hexane to obtain 1'-(2-methacryloxyethyl)-3',3'-dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-indoline) (SP) (12.6g, 56.7 %) as a pale green solid. mp = 104 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.17 (3H, s), 1.29 (3H, s), 1.93 (3H, s), 3.41-3.95 (2H, m), 4.31 (2H, t), 5.57 (1H, m), 5.87 (1H, d), 6.08 (1H, m), 6.71-7.23 (6H, m), 8.00 (2H, m).

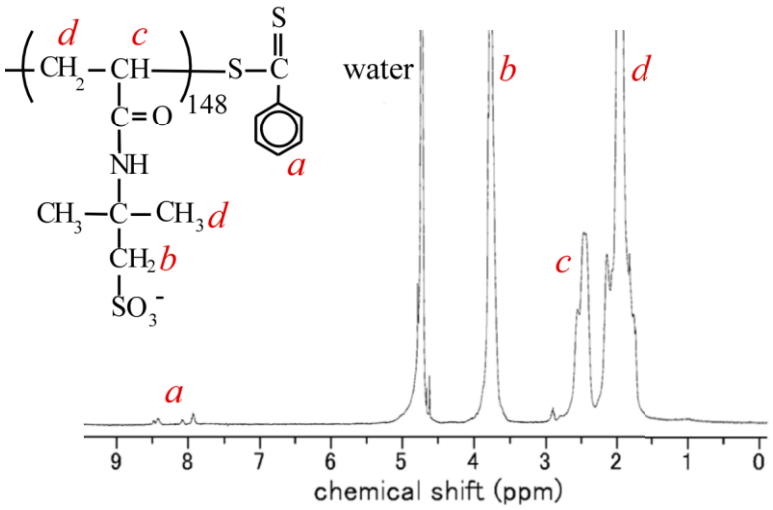


Fig. S1 ^{1}H NMR spectrum for CTA-$APMS_{148}$ in D_2O at room temperature.

Fig. S1 shows ^{1}H NMR spectrum for CTA-APMS$_{148}$ in D_2O. The resonance bands observed at 1.7-2.8 ppm are attributed to the sum of the main chain and pendent methyl groups. The resonance band at 3.7 ppm is attributed to the pendent methylene groups. DP and M_n(NMR) of CTA-APMS$_{148}$ were calculated from the intensity ratio of the resonance bands due to the pendent methylene protons at 3.7 ppm and terminal phenyl protons at 7.8-8.5 ppm.

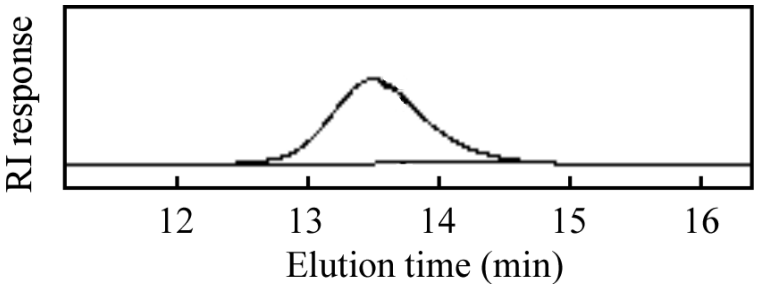
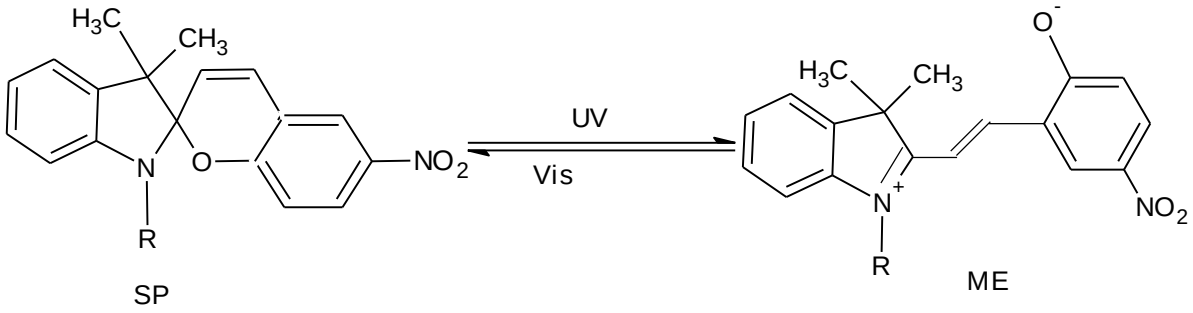


Fig. S2 GPC elution profile for CTA-APMS$_{148}$ (M_n(GPC) = 2.48 × 10^4, M_w/M_n = 1.18) at 40 °C detected by refractive index (RI) eluted with a phosphate buffer (pH 9) containing 10 vol % acetonitrile.

Fig.S2 shows GPC elution profile for CTA-APMS$_{148}$ eluted with a phosphate buffer (pH 9) containing 10 vol % acetonitrile. M_n(GPC) and M_w/M_n were 2.48 × 10^4 and 1.18, respectively, estimated from GPC.



Scheme S2 Light induced isomerization between SP and ME.

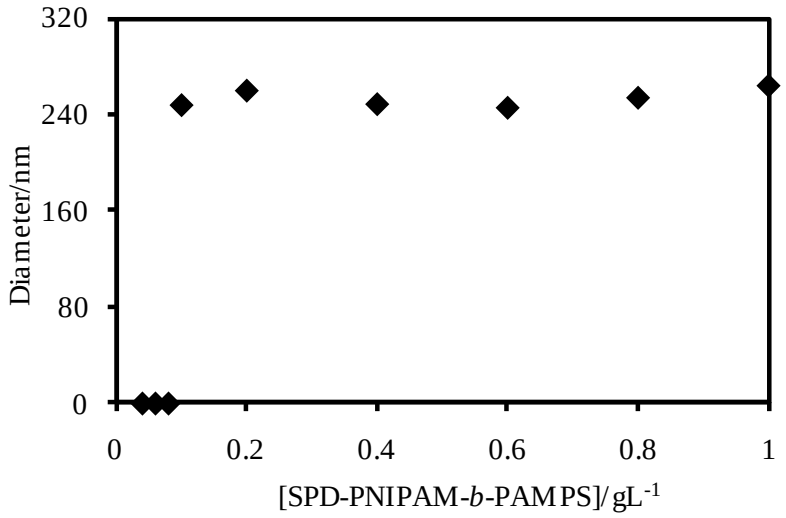


Fig. S3 Hydrodynamic diameter of the micelles of SP_2-$PNIPAM_{154}$-*b*-$PAMPS_{148}$ as a function of polymer concentration at 24 ºC.

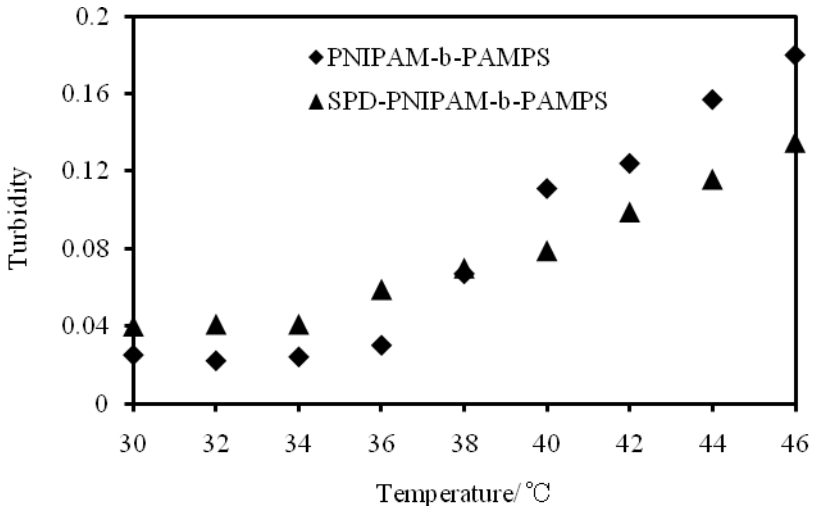


Fig. S4 Turbidity of aqueous solutions of $NIPAM_{154}$-*b*-$AMPS_{148}$ (◆) and SP_2-$NIPAM_{154}$-*b*-$AMPS_{148}$ (▲) as a function of temperature. Concentration of polymer is 1 gL^{-1} in both the cases.

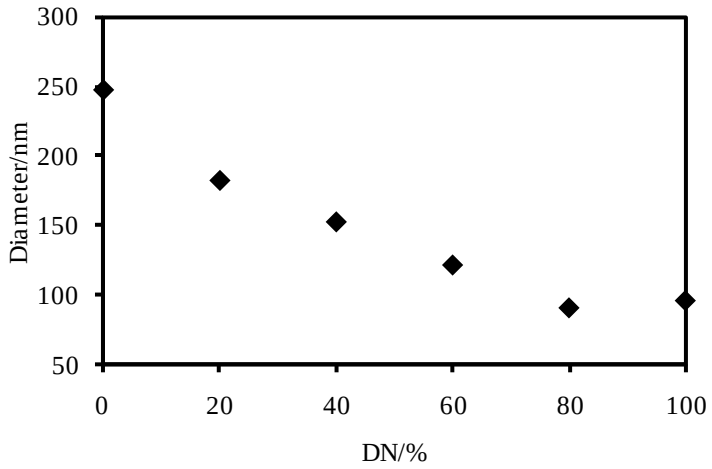


Fig. S5 Hydrodynamic diameter of the micelles with SP/AMPS-core as a function of DN. The Fe^{3+} is used as the counter ion to insolubilize the AMPS block.

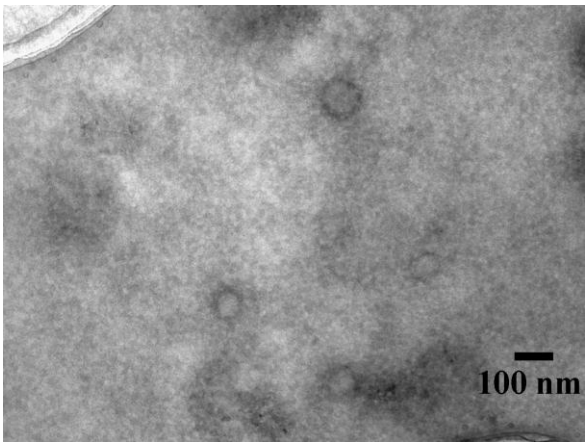


Fig. S6 TEM image of the SP_2-*b*-$NIPAM_{154}$-*b*-$AMPS_{148}$ micelles in the presence of Fe^{3+} at 60% DN. The TEM sample was prepared from the solution with a polymer concentration of 0.4 gL^{-1}.

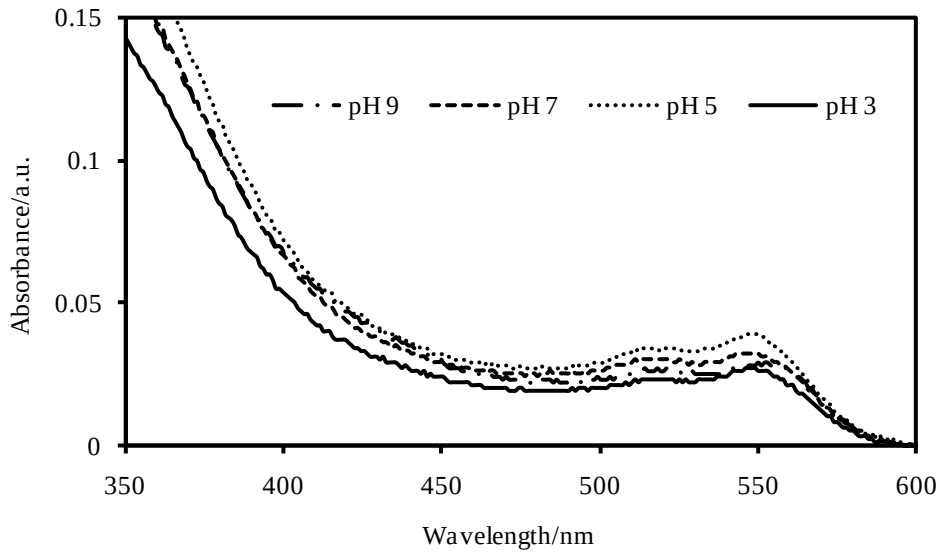


Fig. S7 UV/Vis spectra of polymeric micelles at different pHs.