

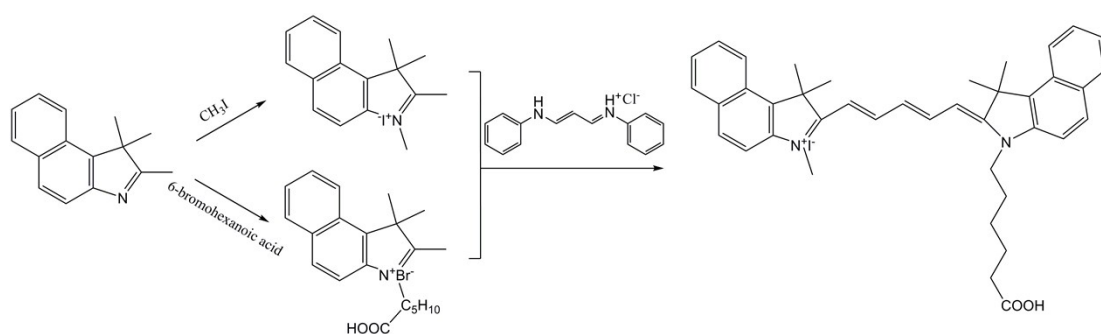
Supporting information for:

**Ultra pH-Sensitive Polypeptide Micelles with Large Fluorescence Off/On Ratio
in Near Infrared Range**

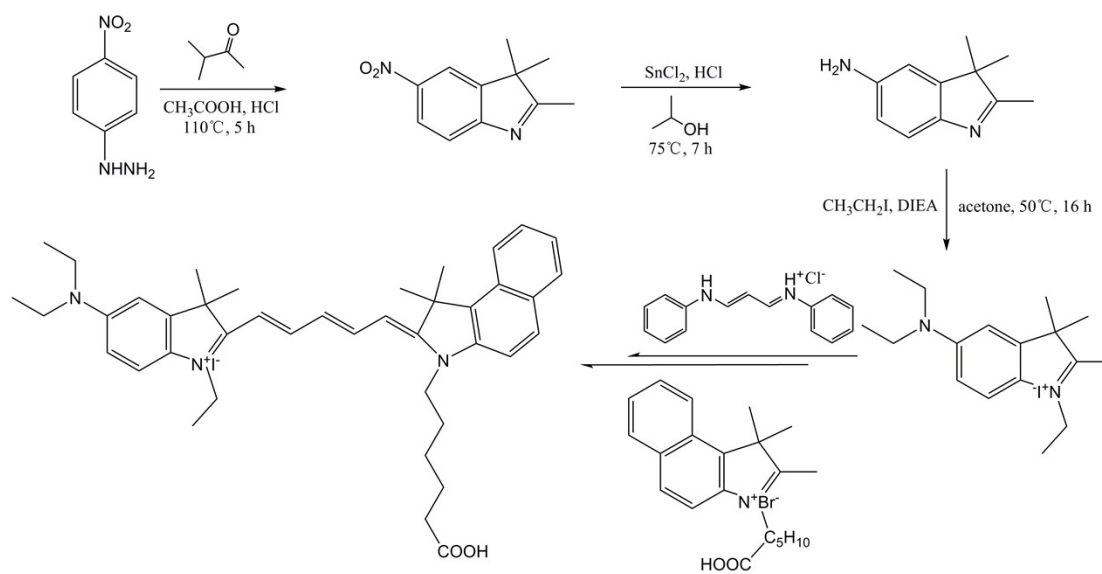
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Scheme S1. Synthesis of Cy5.5.



Scheme S2. Synthesis of the quencher.

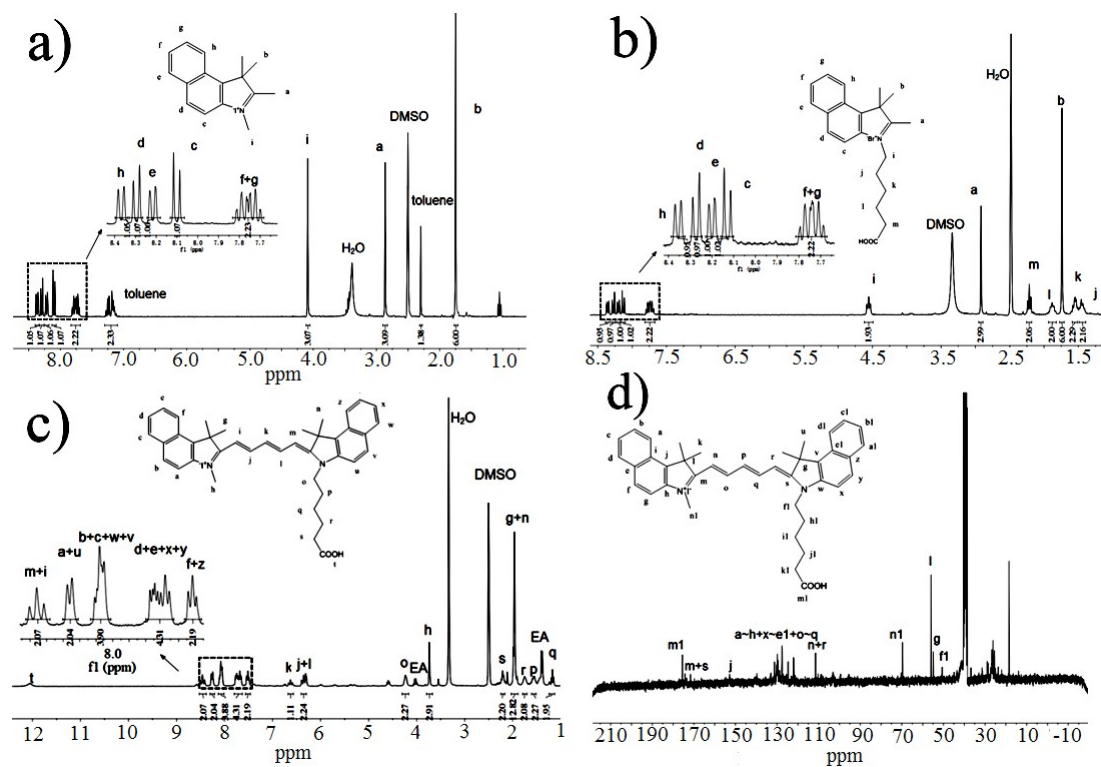


Figure S1. $^1\text{H-NMR}$ spectra of N,2,3,3-tetramethylbenzoindolenium iodide (a), N-(carboxypentyl)-2,3,3-trimethylbenzoindolenium bromide (b) and Cy5.5 (c). $^{13}\text{C-NMR}$ spectrum of Cy5.5 (d).

20160420_HES+FLY-5 #144 RT: 2.06 AV: 1 NL: 3.47E6
T: FTMS +c ESI Full ms [100.00-1800.00]

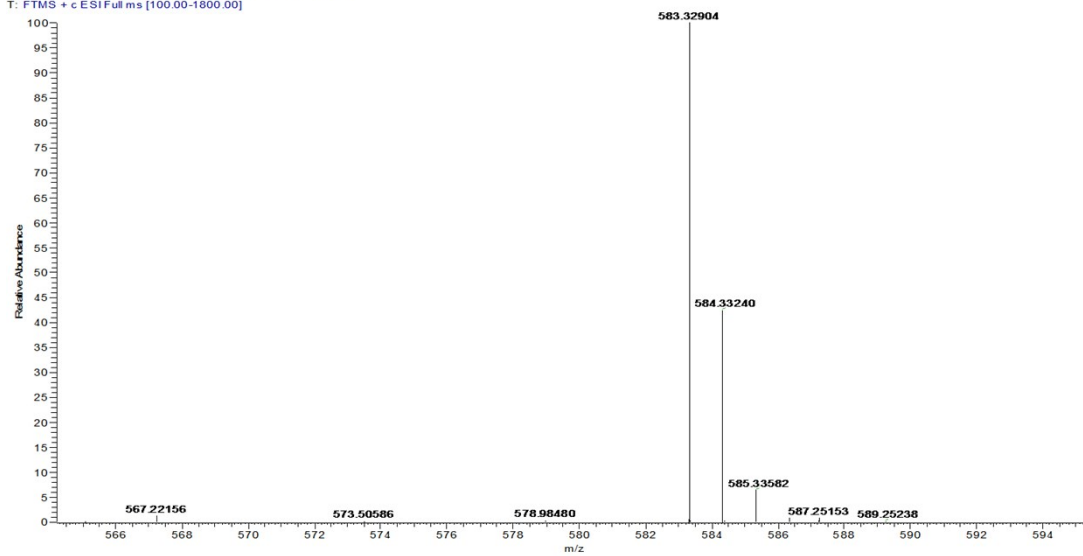


Figure S2. The mass spectrum of Cy5.5.

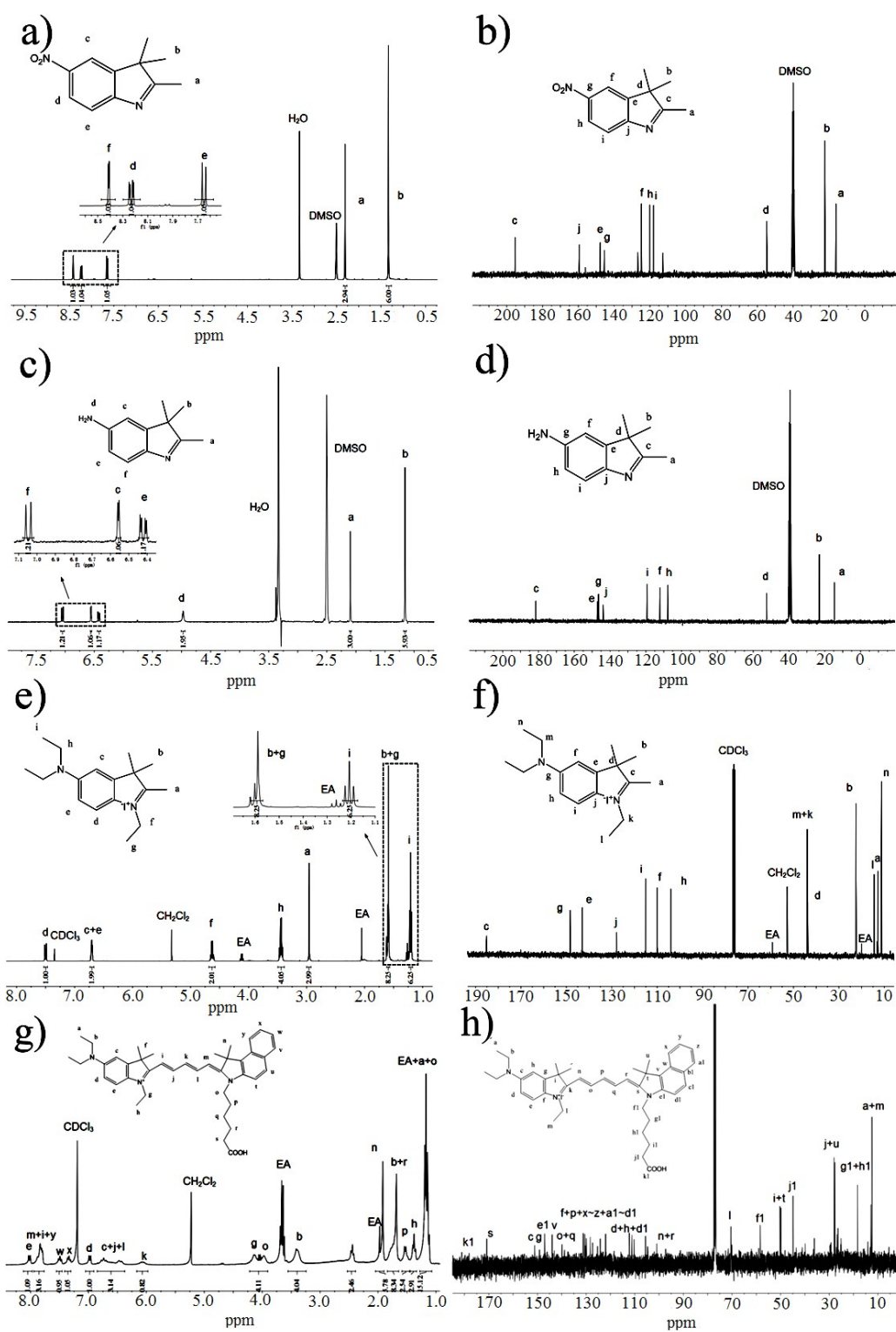


Figure S3. ^1H -NMR and ^{13}C -NMR spectra of 2,3,3-trimethyl-5-nitroindole (a, b), 2,3,3-trimethyl-5-aminoindole (c, d), N,N',N'-triethyl-2,3,3-trimethyl-5-aminoindolenium iodide (e, f) and the quencher (g, h).

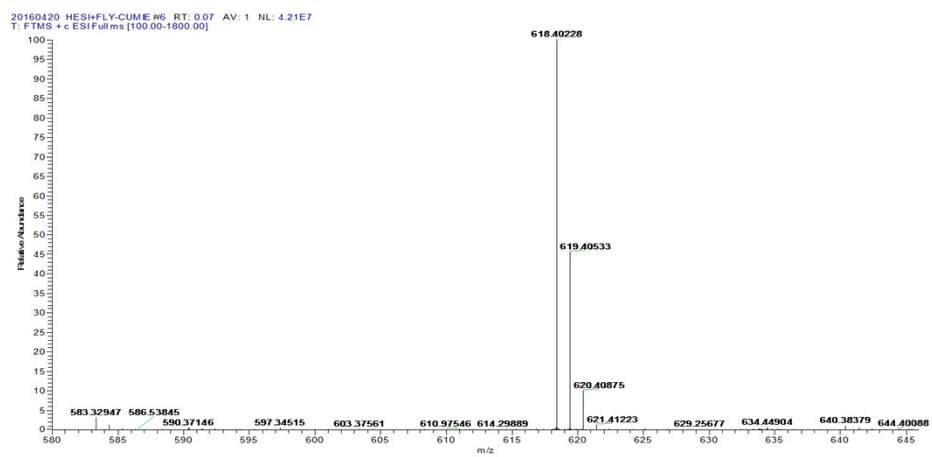


Figure S4. The mass spectrum of the quencher.

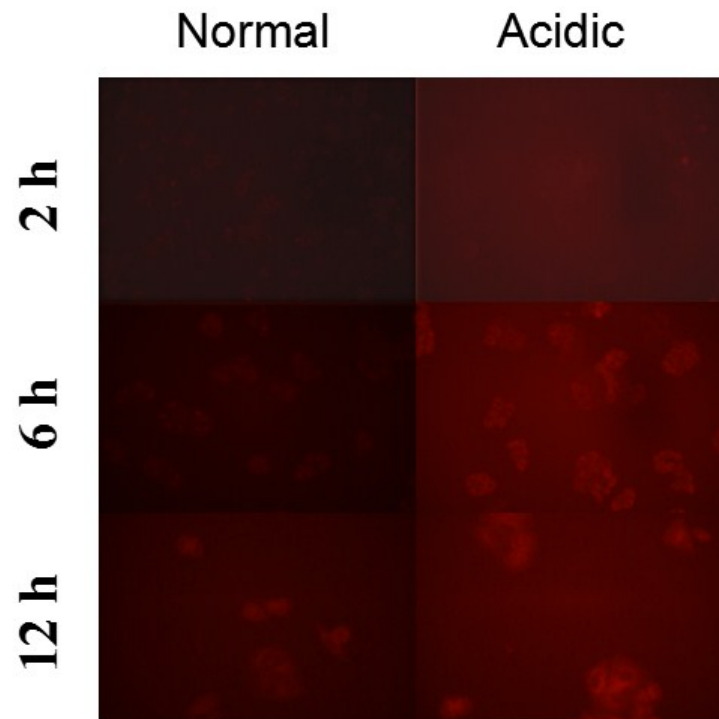


Figure S5. Images of fluorescence microscope of HepG2 cells cultivated with the mixed micelles which were or weren't acidized with diluted hydrochloric acid before observation at 2 h, 6 h and 12 h.

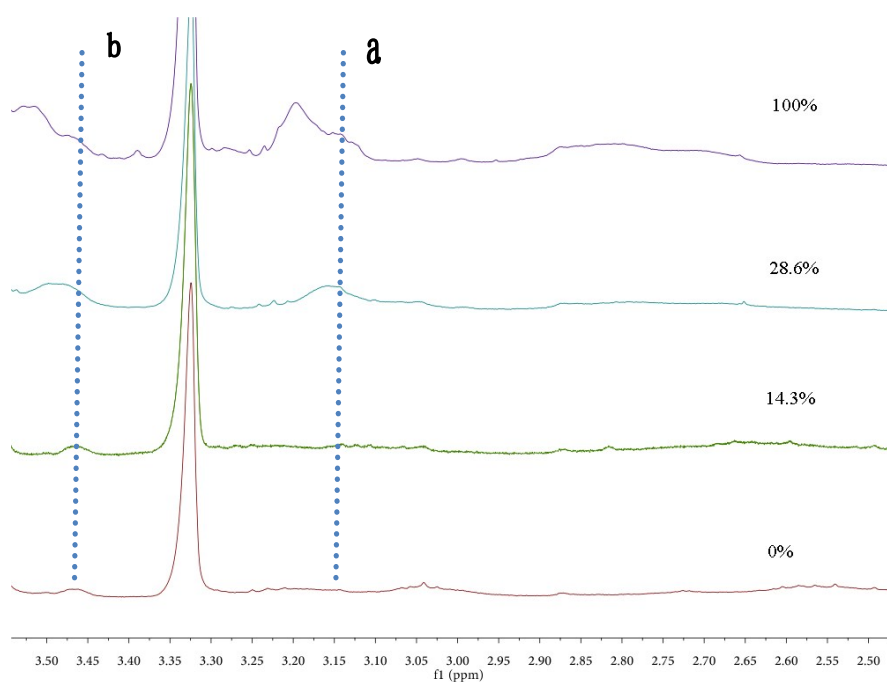


Figure S6. $^1\text{H-NMR}$ spectra (in D_2O) of butyl (a) and isopropyl (b) protons in the copolymer adjacent to nitrogen atoms at different protonation degrees.

As the increase of protonation degree, the chemical shifts of the peaks at about 3.5ppm (corresponding to the hydrogen atom linked to the carbon atom next to the nitrogen atom on the isopropyl group) and 3.15ppm (corresponding to the hydrogen atom linked to the carbon atom next to the nitrogen atom on the n-butyl group) hardly changed, and the integration of the peaks increased. It illustrated that the polymers we synthesized could form micelles and similar pH cooperativity like the result of Li et al. [1] is observed.

Reference

1. Y. Li, T. Zhao, C. Wang, Z. Lin, G. Huang, B. D. Sumer, J.M. Gao. *Nat. Commun.* 2016, DOI: 10.1038/ncomms13214.