Supplementary Material (ESI) for Journal of Materials Chemistry This journal is [©] The Royal Society of Chemistry 2011

Ultrasensitive Ratiometric Fluorescent pH and Temperature Probes Constructed from Dye-Labeled Thermoresponsive Double Hydrophilic

Block Copolymers

Jinming Hu, Xiaozheng Zhang, Di Wang, Xianglong Hu, Tao Liu, Guoying Zhang,* and Shiyong Liu*

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China

* To whom correspondence should be addressed.

Email: sliu@ustc.edu.cn; gyzhang@ustc.edu.cn.

Table S1. Molecular Parameters of Polymer Precursors and Dye-Labeled DoubleHydrophilic Block Copolymers (DHBCs) Synthesized in this Work.

| Samples ^{<i>a</i>} | $M_{\rm n}{}^b$ (Da) | $M_{ m w}/M_{ m n}^{\ b}$ |
|---|----------------------|---------------------------|
| P(OEGMA-co-RhBAM) ₉₀ | 36,200 | 1.10 |
| P(NIPAM-co-APMA) ₃₆ -b-P(OEGMA-co-RhBAM) ₉₀ | 41,500 | 1.23 |
| P(NIPAM-co-FITC) ₃₆ -b-P(OEGMA-co-RhBAM) ₉₀ | 41,700 | 1.24 |
| POEGMA ₈₇ | 35,100 | 1.08 |
| P(NIPAM-co-APMA) ₃₄ -b-POEGMA ₈₇ | 39,900 | 1.17 |
| P(NIPAM-co-FITC) ₃₄ -b-POEGMA ₈₇ | 40,100 | 1.19 |

^{*a*} DPs of POEGMA and PNIPAM blocks were determined by ¹H NMR analysis in CDCl₃. ^{*b*} Obtained from GPC analysis using DMF as eluent. APMA is *N*-(3-aminopropyl)methacrylamide hydrochloride.



Figure S1. (a) Fluorescence emission spectra and (b) relative fluorescence intensity changes at 582 nm recorded for 0.1 g/L aqueous solution of P(NIPAM-*co*-APMA)₃₆-*b*-P(OEGMA-*co*-RhBAM)₉₀ diblock copolymer (25 °C, $\lambda_{ex} = 550$ nm; slit widths: Ex. 5 nm, Em. 5 nm) in the pH range of 2-10. *I*₀ represents the fluorescent intensity measured at pH 10.



Figure S2. (a) Fluorescence emission spectra and (b) relative fluorescence intensity changes at 522 nm recorded for 0.1 g/L aqueous solution of P(NIPAM-*co*-FITC)₃₄-*b*-POEGMA₈₇ diblock copolymer (25 °C, λ_{ex} = 495 nm; slit widths: Ex. 5 nm, Em. 5 nm) in the pH range of 2-10. *I*₀ represents the fluorescent intensity measured at pH 2.



Figure S3. Changes in fluorescence emission intensity recorded for 0.1 g/L aqueous solution of (a) P(NIPAM-*co*-APMA)₃₆-*b*-P(OEGMA-*co*-RhBAM)₉₀ ($\lambda_{ex} = 550$ nm; slit widths: Ex. 5 nm, Em. 5 nm) and (b) P(NIPAM-*co*-FITC)₃₄-*b*-POEGMA₈₇ diblock copolymer ($\lambda_{ex} = 495$ nm; slit widths: Ex. 5 nm, Em. 5 nm) at 25 °C when the solution pH was cycled between 3 and 7.



Figure S4. (a) Normalized fluorescence emission spectrum recorded for 0.1 g/L aqueous solution (pH 7) of P(NIPAM-*co*-FITC)₃₄-*b*-POEGMA₈₇ diblock copolymer (25 °C, $\lambda_{ex} = 495$ nm; slit widths: Ex. 5 nm, Em. 5 nm) and (b) normalized absorbance spectrum recorded for 0.1 g/L aqueous solution (pH 3) of P(NIPAM-*co*-APMA)₃₆-*b*-P(OEGMA-*co*-RhBAM)₉₀ diblock copolymer.



Figure S5. (a) Fluorescence emission spectra and (b) fluorescence intensity changes at 582 nm recorded for 0.1 g/L aqueous solution of P(NIPAM-*co*-APMA)₃₆-*b*-P(OEGMA-*co*-RhBAM)₉₀ diblock copolymer (pH 2, $\lambda_{ex} = 550$ nm, slit widths: Ex. 5 nm, Em. 5 nm) in the range of temperature 25-60 °C.



Figure S6. (a) Fluorescence emission spectra and (b) fluorescence intensity changes at 522 nm recorded for 0.1 g/L aqueous solution of P(NIPAM-*co*-FITC)₃₄-*b*-POEGMA₈₇ diblock copolymer (pH 10, λ_{ex} = 495 nm, slit widths: Ex. 5 nm, Em. 5 nm) in the range of temperature 25-60 °C.