Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Thermo- and pH-Responsive Poly(N-isopropylacrylamide)-Mn-ZnS Nanocomposite for Controlled Release and Real-Time Photoluminescence Tracking of Doxorubicin

Ruo-Mei Wang,[a] Qian Liu,[b] Yu Zhang,[a] Zhangyong Hong[b] and He-Fang Wang*[a,b]

[a]Research Center for Analytical Sciences, College of Chemistry, Nankai University. [a]Key Laboratory of Biosensing and Molecular Recognition, [b]State Key Laboratory of Medicinal Chemical Biology, [a]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), 94 Weijin Road, Tianjin 300071, China

E-mail: wanghefang@nankai.edu.cn

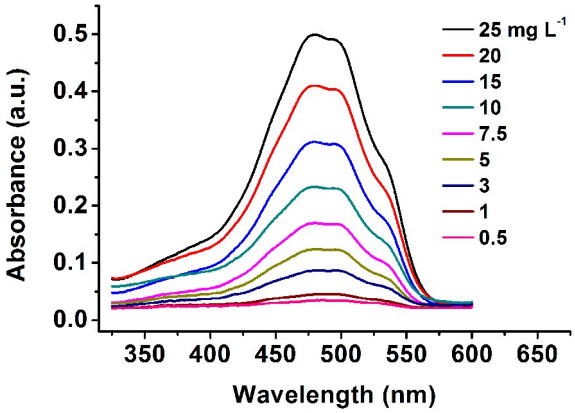

Fig. S1. The UV-vis spectra of standard Dox·HCl solutions.

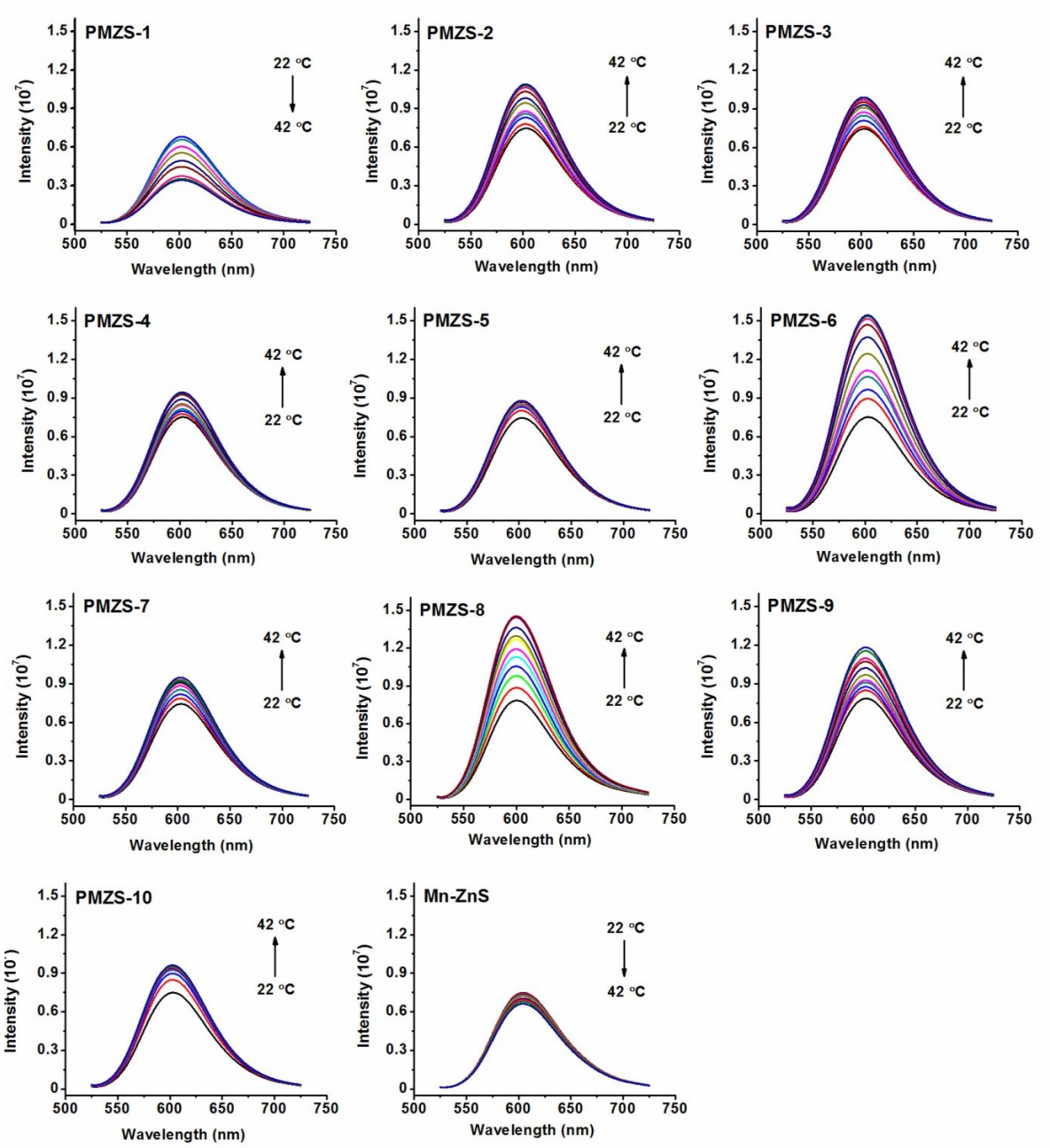

Fig. S2. Temperature-dependent PL spectra of PMZS nanocomposites (with equivalent Mn-ZnS of 0.015 g L^{-1}) and raw Mn-ZnS (0.015 g L^{-1}) in MES-Tris buffers (10 mM, pH 6.5) excited at 320 nm.

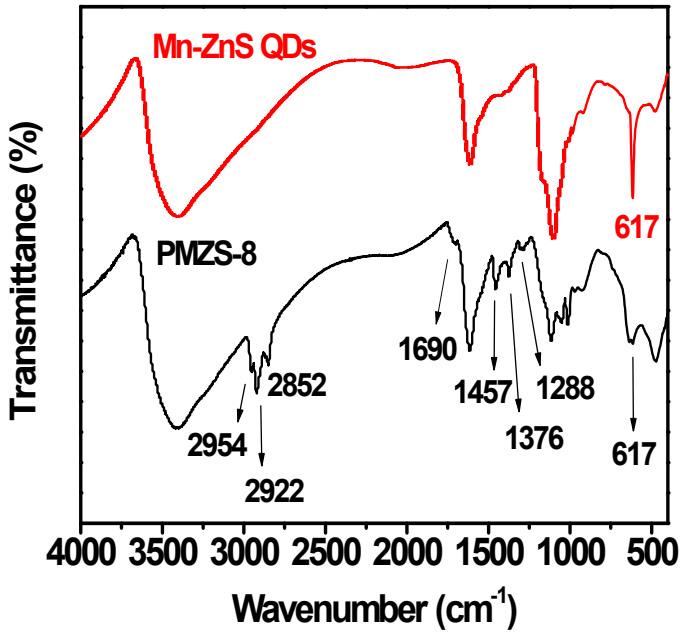

Fig. S3. FT-IR spectra of PMZS-8 and raw Mn-ZnS QDs.

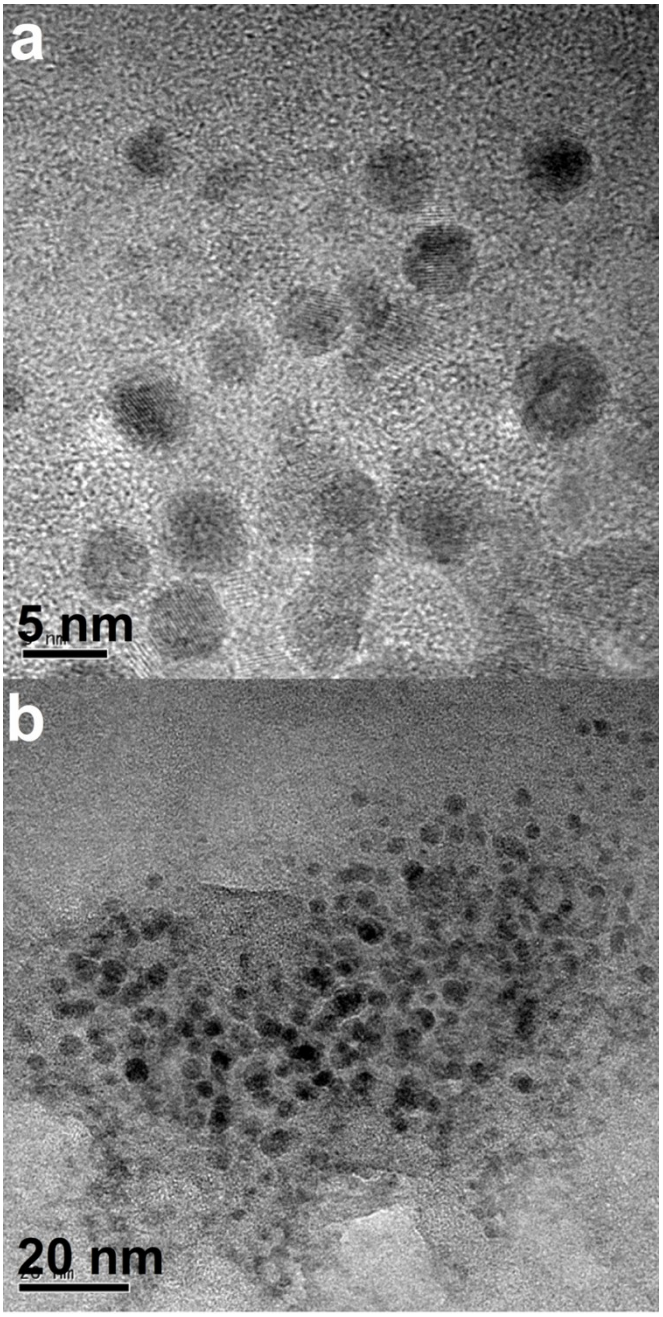

Fig. S4. TEM images of PMZS-8.

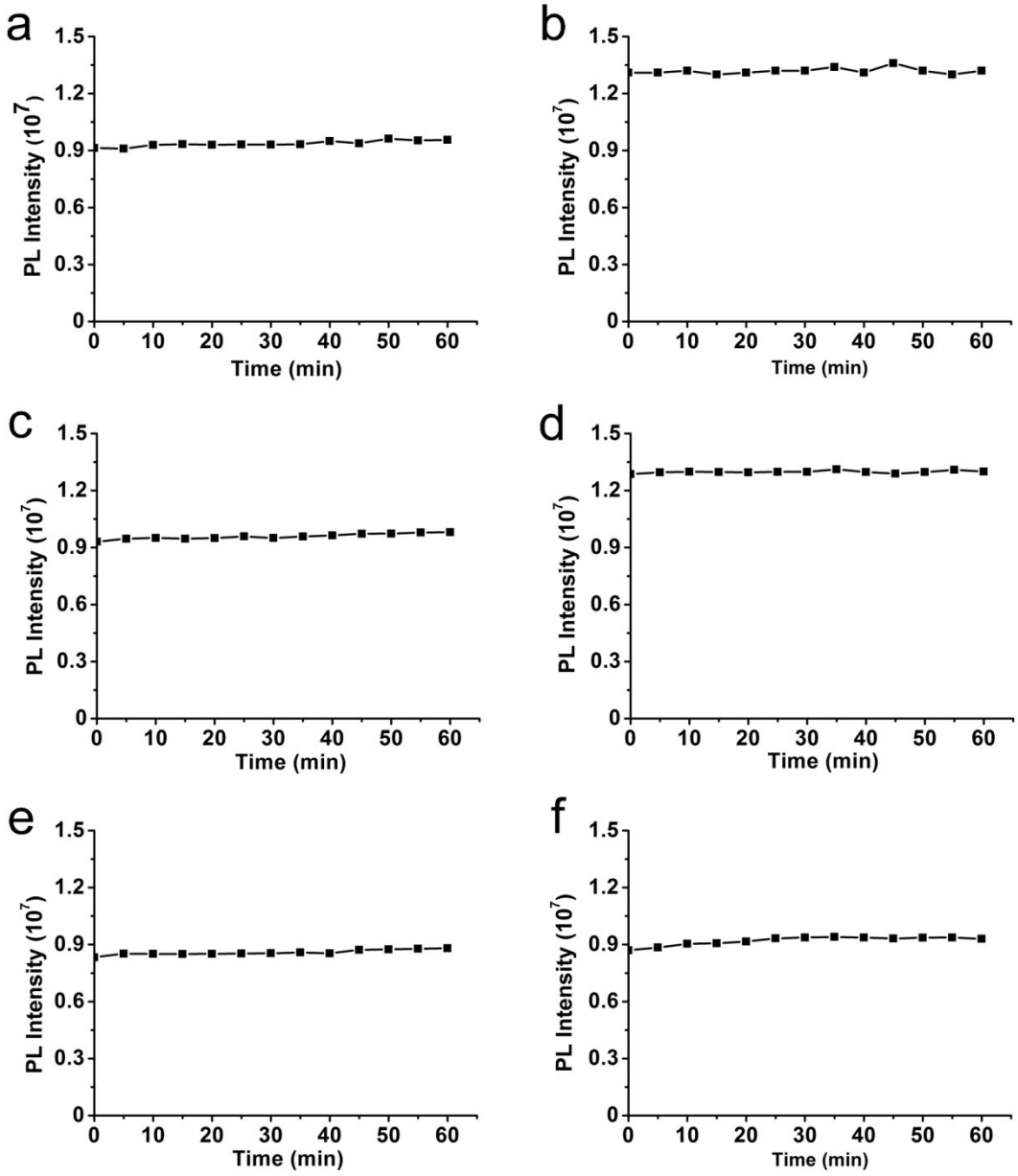

Fig. S5. Stability of 600 nm emission of PMZS-8 (0.06 g L^{-1}) at 25 ^{o}C in (a) pH 5.5; (c) pH 6.5; (e) pH 7.4 and 37 ^{o}C in (b) pH 5.5, (d) pH 6.5, (f) pH 7.4 MES-Tris buffer (10 mM)

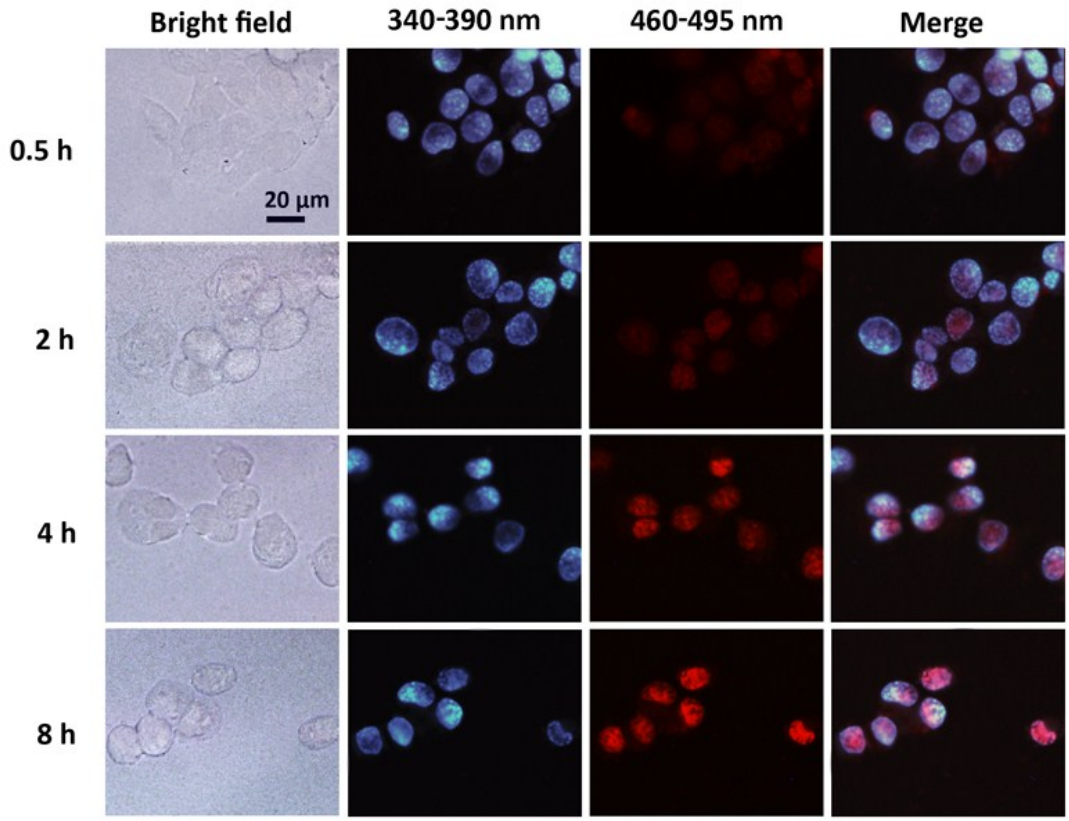

Fig. S6. Fluorescence imaging of 4T1 cells exposed to free Dox (5 µM) for 0.5, 2, 4 and 8 h. The pictures were taken by a fluorescence microscope in bright field, under excitation of 340-390 nm (for DAPI) and 460-495 nm (for Dox).

Table S1

Decay Parameters of PMZS-8 at Different Temperatures Obtained by 2-Exponential Fitting [a]

T (°C)	τ_1 (μs)	A_1 (%)	τ_2 (μs)	A_2 (%)	X^2	τ_{av} (μs)
25	500.6±36.2	70.5±3.4	2884±207	29.5±1.9	0.9313	1205±87
30	434.7±37.1	71.8±4.7	2525±181	28.2±1.9	0.8431	1024±78
34	483.6±27.2	75.9±2.3	3381±322	24.1±1.2	1.068	1181±98
37	487.5±44.2	73.1±4.0	2731±287	26.9±2.5	0.9987	1090±110

[a] $F(t) = A_1e^{-t/\tau1} + A_2e^{-t/\tau2}$

The decay curve of the RTP emission of 0.06g L^{-1} PMZS-8 at different temperatures was excited by N_2 laser at 320 nm, and scanned three times of emission at 600 nm (300 channels). The emission slit at 20 nm with integration time of 25 μs.

Table S2

The Loading Capacity, Release Condition and Accumulative Release Amount of Dox by Some PNIPAm-Based Nanocarriers

Nanocarriers	Loading capacity (%)	Release condition	Accumulative Release amount (%)	Ref
PNIPAm-Mn-ZnS	15.20	pH 5.5, 37 ^{o}C, 24 h	81.50	This Work
UCNPs@mSiO_2-P(NIPAm-MAA)	8.60	pH 5.0, 45 ^{o}C, 20 h	52.20	1
MSN-NH_2@colipid	29.51	pH 5.5, 37 ^{o}C, 24 h	76.80	2
PNDGPs	20.70	pH 5.5, 37 °C, 48 h	~33.00	3
POEGMA-b-P(NIPAm-NBA-Gd)	4.90	pH 5.0, 37 ^{o}C, UV, 12 h	~73.00	4
M-MSN-P(NIPAm-MAA)	21.50	pH 5.0, 37 ^{o}C, 24 h	80.20	5
Au-nanocage@mSiO_2@PNIPAm	23.50	pH 5.0, NIR, 8 h	78.90	6
P(MAA-DVB)-g-PNIPAm	12.90	pH 5.6, 37 ^{o}C, 72 h	~50.00	7

UCNPs@mSiO_2-P(NIPAm-MAA): $NaYF_4$:Yb^{3+}/Er^{3+} core (UCNPs) with poly(N-isopropylacrylamide-co-methacrylic acid) gated mesoporous silica shell

MSN-NH_2@colipid: soyphosphatidylcholine-poly(N-isopropylacrylamide-co-methacrylic acid-co-octadecyl acrylate) bilayer coated mesoporous silica nanoparticales

PNDGPs: amphiphilic polyphosphazenes with poly(N-isopropylacrylamide-co-N,N-dimethylacrylamide) and ethyl glycinate side groups

POEGMA-b-P(NIPAm-NBA-Gd): poly[oligo(ethylene glycol) monomethyl ether methacrylate]-b-poly(N-isopropylacrylamide-co-o-nitrobenzyl acrylate-co-Gd^{3+}) diblock copolymer

M-MSN-P(NIPAm-MAA): poly(N-isopropylacrylamide-co-methacrylic acid) coated magnetic mesoporous silica nanoparticles

Au-nanocage@mSiO_2@PNIPAm: gold nanocages core with poly(N-isopropylacrylamide) coated mesoporous silica shell

P(MAA-DVB)-g-PNIPAm: nanocapsule with poly(methacrylic acid-co-divinylbenzene) inner shell and poly(N-isopropylacrylamide) grafted chain

Reference

1 X. Zhang, P. Yang, Y. Dai, P. a. Ma, X. Li, Z. Cheng, Z. Hou, X. Kang, C. Li and J. Lin, *Adv. Funct. Mater.*, 2013, **23**, 4067-4078.

2 X. Wu, Z. Wang, D. Zhu, S. Zong, L. Yang, Y. Zhong and Y. Cui, *Acs Appl. Mater. Interfaces*, 2013, **5**, 10895-10903.

3 L. Y. Qiu, X. L. Wu and Y. Jin, *Pharmaceut. Res.*, 2009, **26**, 946-957.

4 Y. Li, Y. Qian, T. Liu, G. Zhang and S. Liu, *Biomacromolecules*, 2012, **13**, 3877-3886.

5 B. Chang, X. Sha, J. Guo, Y. Jiao, C. Wanga and W. Yang, *J.Mater. Chem.*, 2011, **21**, 9239-9247.

6 J. Yang, D. Shen, L. Zhou, W. Li, X. Li, C. Yao, R. Wang, A. M. El-Toni, F. Zhang and D. Zhao, *Chem. Mater.*, 2013, **25**, 3030-3037.

7 L. Chen, Z. Peng, Z. Zeng, Y. She, J. Wei and Y. Chen, *J. Polym. Sci. Pol. Chem.*, 2014, **52**, 2202-2216.