

## ELECTRONIC SUPPLEMENTARY INFORMATION

# Thioglycerol-capped Mn-doped ZnS quantum dots bioconjugates as efficient two-photon fluorescent nano-probes for bioimaging

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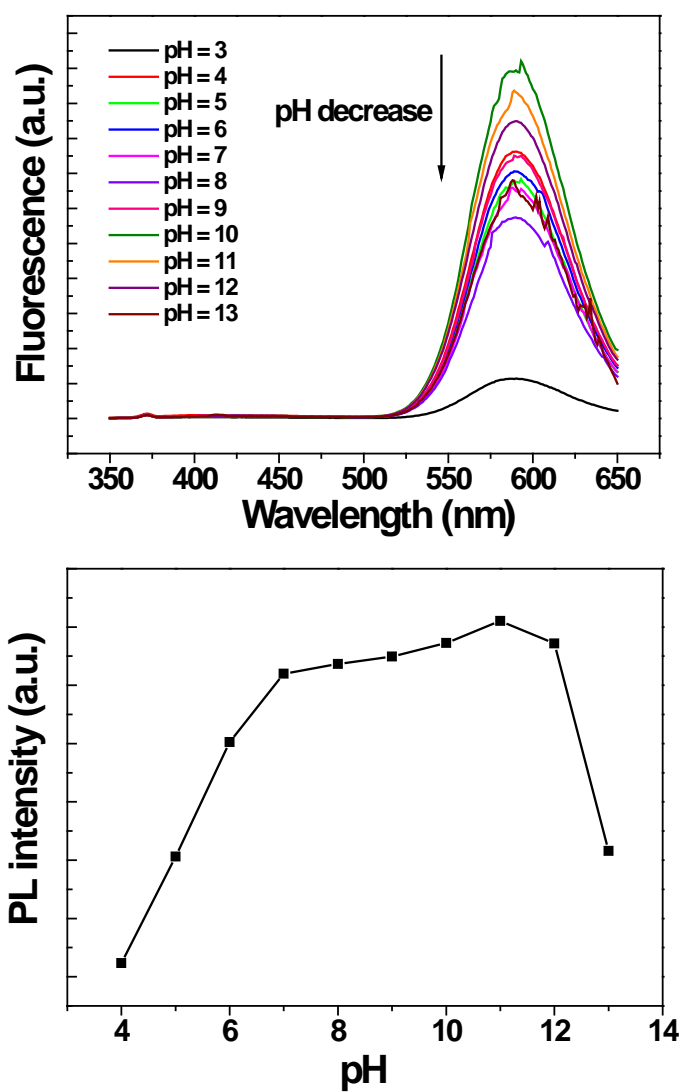
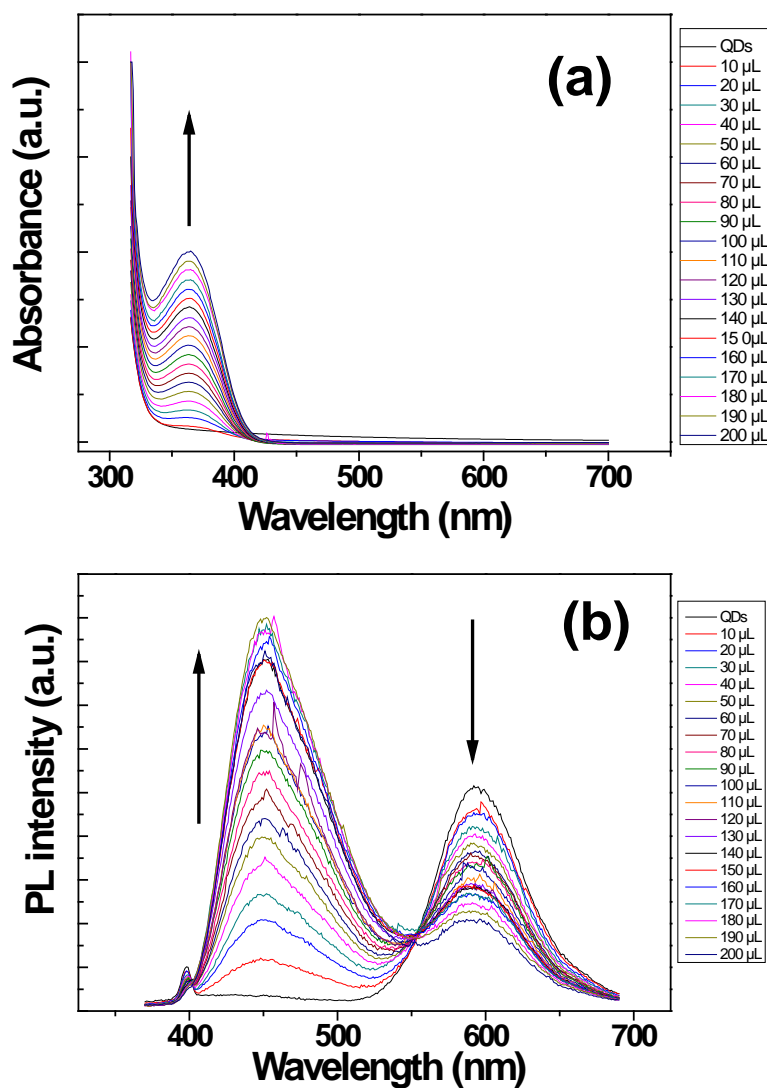
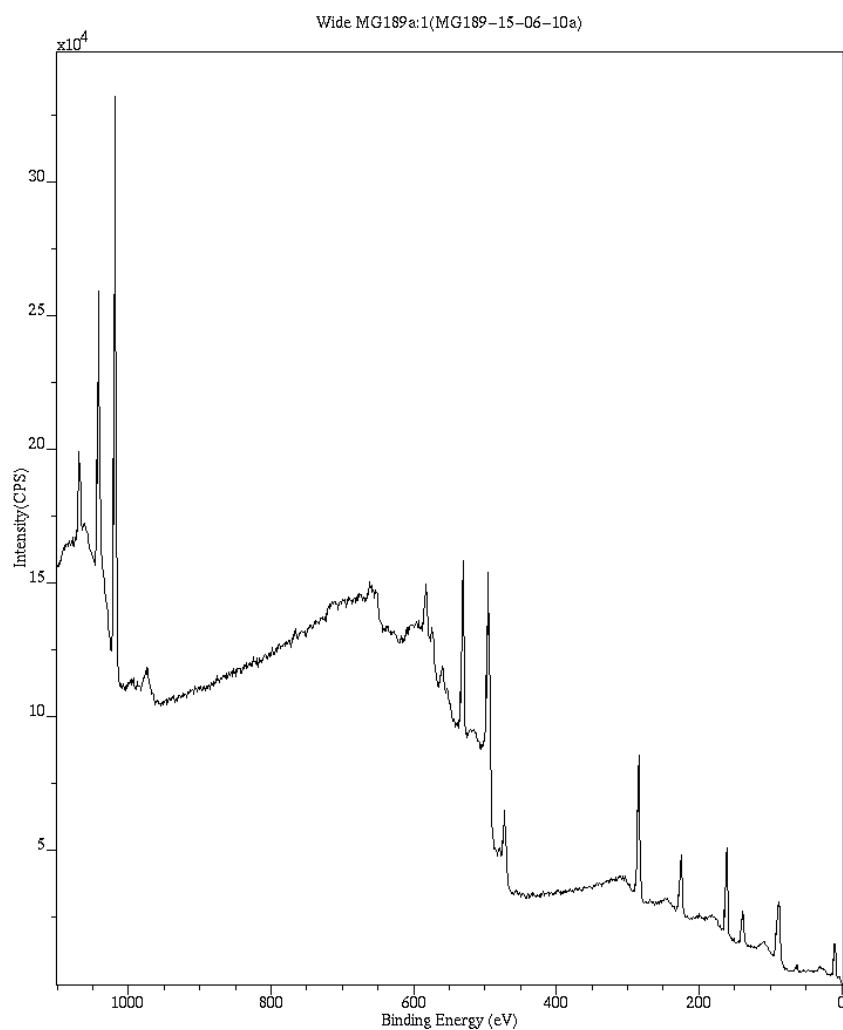


Fig. S1. Influence of pH on the PL intensity of Mn:ZnS@TG d-dots.

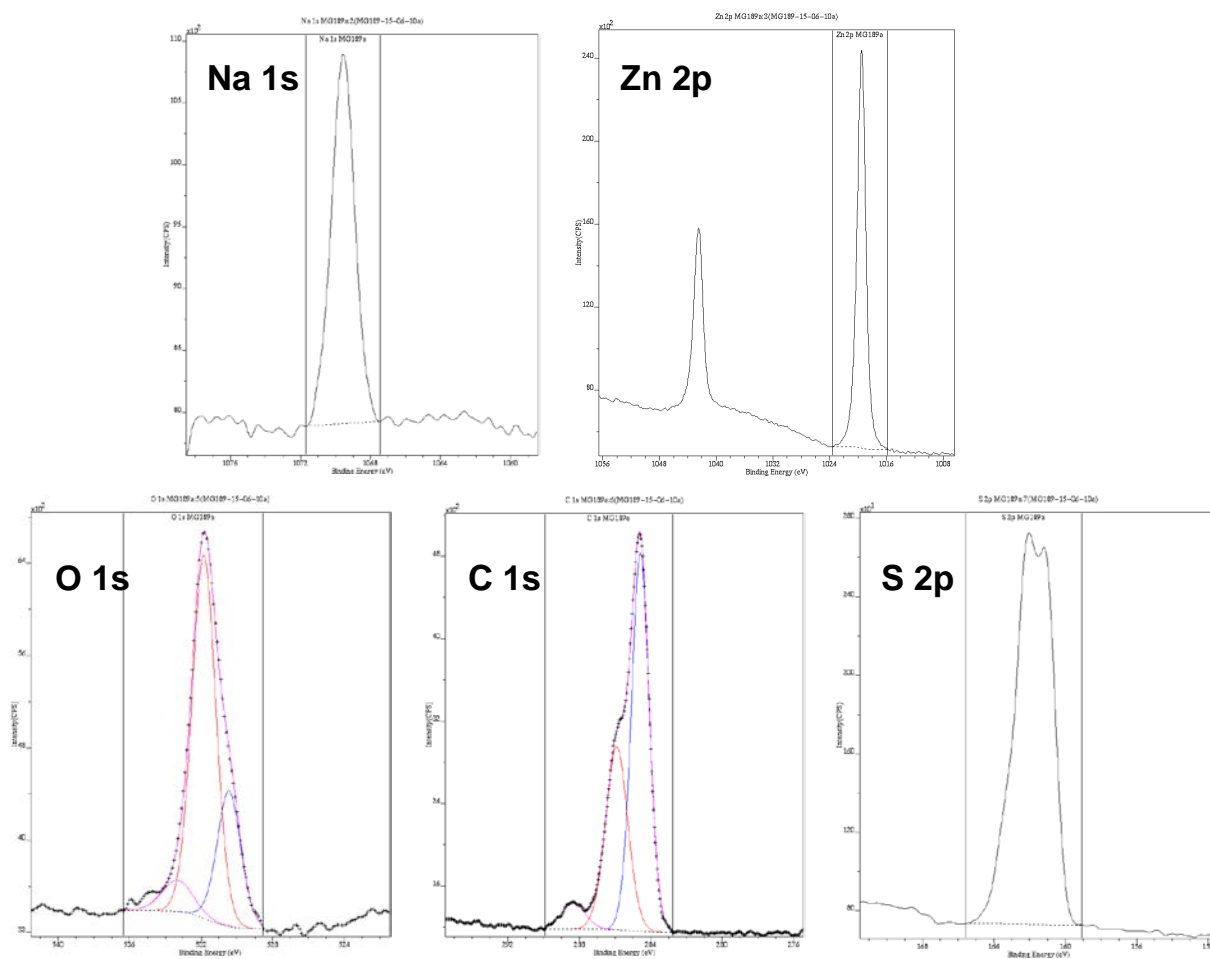


**Fig. S2.** (a) Evolution of photoluminescence spectra of Mn:ZnS@TG dots (1.25 mg in 5 mL borate buffer) upon stepwise addition (with an increment of 10  $\mu\text{L}$ ) of a 2.26 mM folic acid solution in sodium borate buffer. A decrease of PL QY from 13.0 (starting Mn:ZnS@TG dots) to 3.1 % (200  $\mu\text{L}$  of the folic acid solution added) was observed after the addition of the folic acid solution.

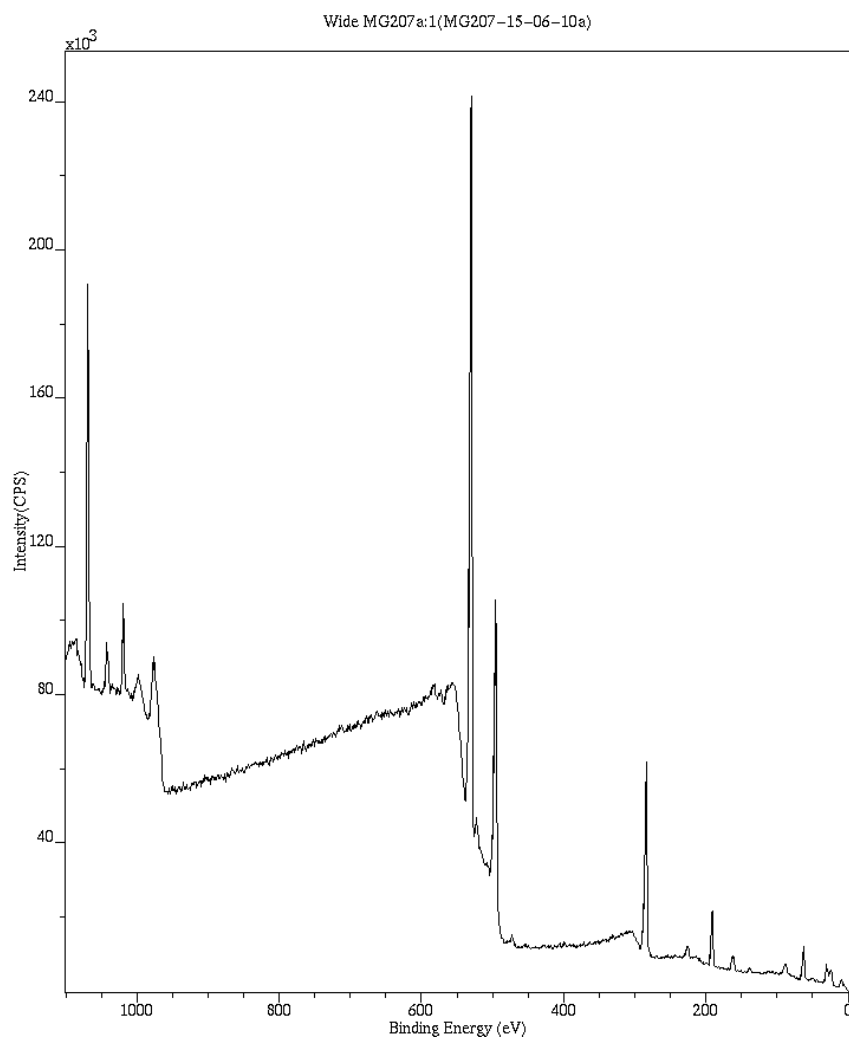


<i>Peak</i>	<i>Position BE (eV)</i>	<i>FWHM (eV)</i>	<i>Raw Area (CPS)</i>	<i>RSF</i>	<i>Atomic Mass</i>	<i>Atomic Conc %</i>	<i>Mass Conc %</i>
<i>Na 1s MG189a</i>	<i>1069.600</i>	<i>1.496</i>	<i>4858.3</i>	<i>1.685</i>	<i>22.990</i>	<i>4.21</i>	<i>4.22</i>
<i>Zn 2p MG189a</i>	<i>1019.500</i>	<i>1.361</i>	<i>31075.8</i>	<i>3.726</i>	<i>65.387</i>	<i>12.75</i>	<i>36.33</i>
<i>O 1s MG189a</i>	<i>531.800</i>	<i>2.083</i>	<i>8017.8</i>	<i>0.780</i>	<i>15.999</i>	<i>18.23</i>	<i>12.71</i>
<i>C 1s MG189a</i>	<i>284.650</i>	<i>1.876</i>	<i>7797.0</i>	<i>0.278</i>	<i>12.011</i>	<i>50.14</i>	<i>26.24</i>
<i>S 2p MG189a</i>	<i>162.000</i>	<i>2.396</i>	<i>5164.1</i>	<i>0.668</i>	<i>32.065</i>	<i>14.67</i>	<i>20.50</i>

**Fig. S3.** XPS survey spectrum of Mn:ZnS@TG dots.

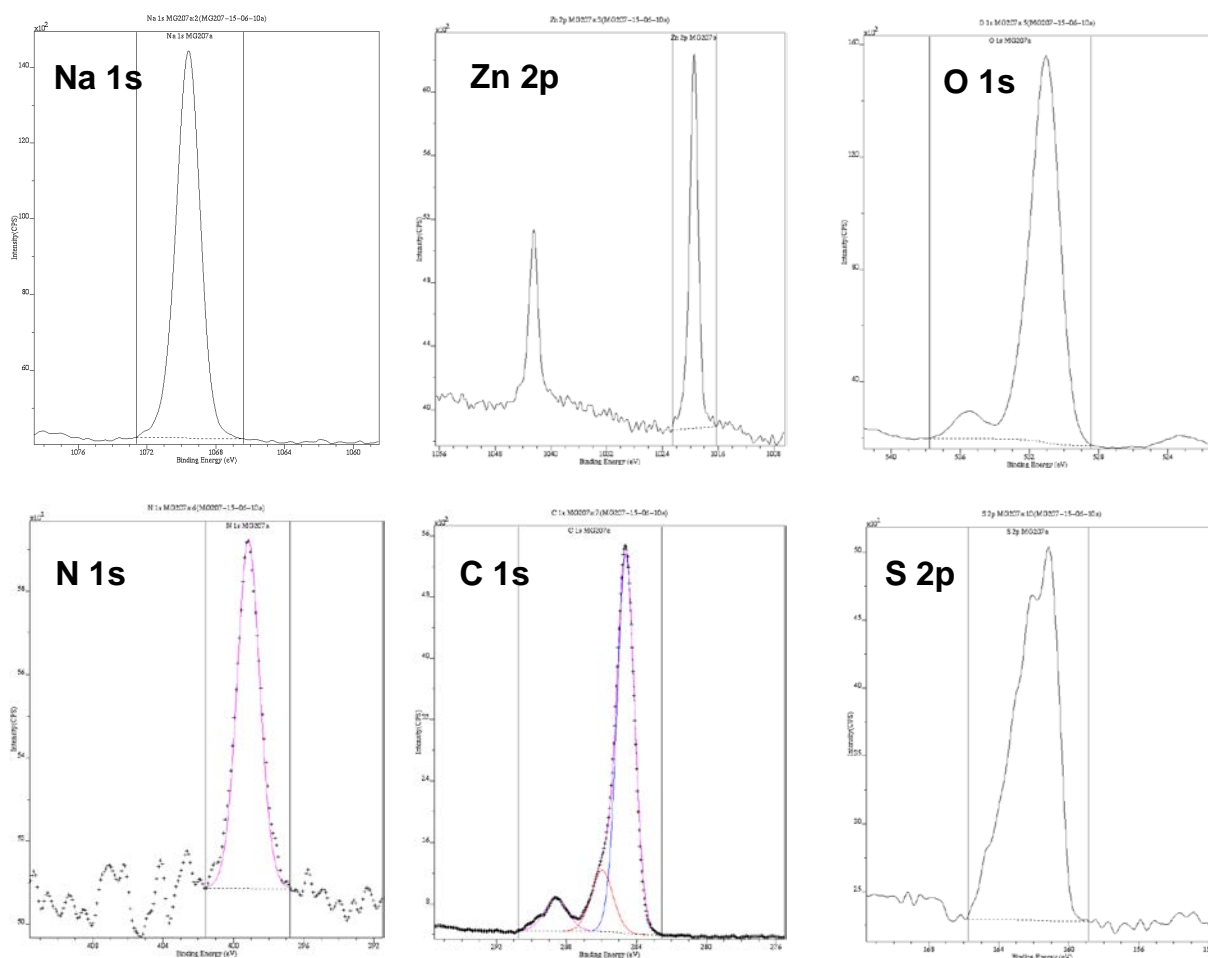


**Fig. S4.** High-resolution XPS spectra of Mn:ZnS@TG dots.

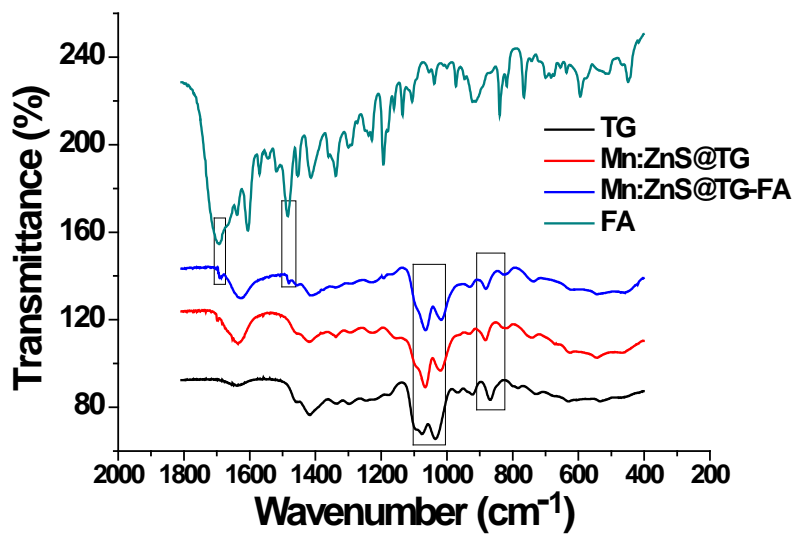


<i>Peak</i>	<i>Position BE (eV)</i>	<i>FWHM (eV)</i>	<i>Raw Area (CPS)</i>	<i>RSF</i>	<i>Atomic Mass</i>	<i>Atomic Conc %</i>	<i>Mass Conc %</i>
<i>Na 1s MG207a</i>	<i>1069.550</i>	<i>1.580</i>	<i>17774.5</i>	<i>1.685</i>	<i>22.990</i>	<i>9.00</i>	<i>13.58</i>
<i>Zn 2p MG207a</i>	<i>1019.450</i>	<i>1.346</i>	<i>3779.7</i>	<i>3.726</i>	<i>65.387</i>	<i>0.91</i>	<i>3.89</i>
<i>O 1s MG207a</i>	<i>531.050</i>	<i>1.931</i>	<i>31395.2</i>	<i>0.780</i>	<i>15.999</i>	<i>41.71</i>	<i>43.80</i>
<i>N 1s MG207a</i>	<i>399.150</i>	<i>1.591</i>	<i>145.4</i>	<i>0.477</i>	<i>14.007</i>	<i>0.32</i>	<i>0.29</i>
<i>C 1s MG207a</i>	<i>284.650</i>	<i>1.227</i>	<i>8256.6</i>	<i>0.278</i>	<i>12.011</i>	<i>31.03</i>	<i>24.46</i>
<i>B 1s MG207a</i>	<i>192.050</i>	<i>1.390</i>	<i>2295.1</i>	<i>0.159</i>	<i>10.823</i>	<i>15.68</i>	<i>11.14</i>
<i>S 2p MG207a</i>	<i>161.150</i>	<i>2.879</i>	<i>811.0</i>	<i>0.668</i>	<i>32.065</i>	<i>1.35</i>	<i>2.84</i>

Fig. S5. XPS survey spectrum of Mn:ZnS@TG-FA dots.

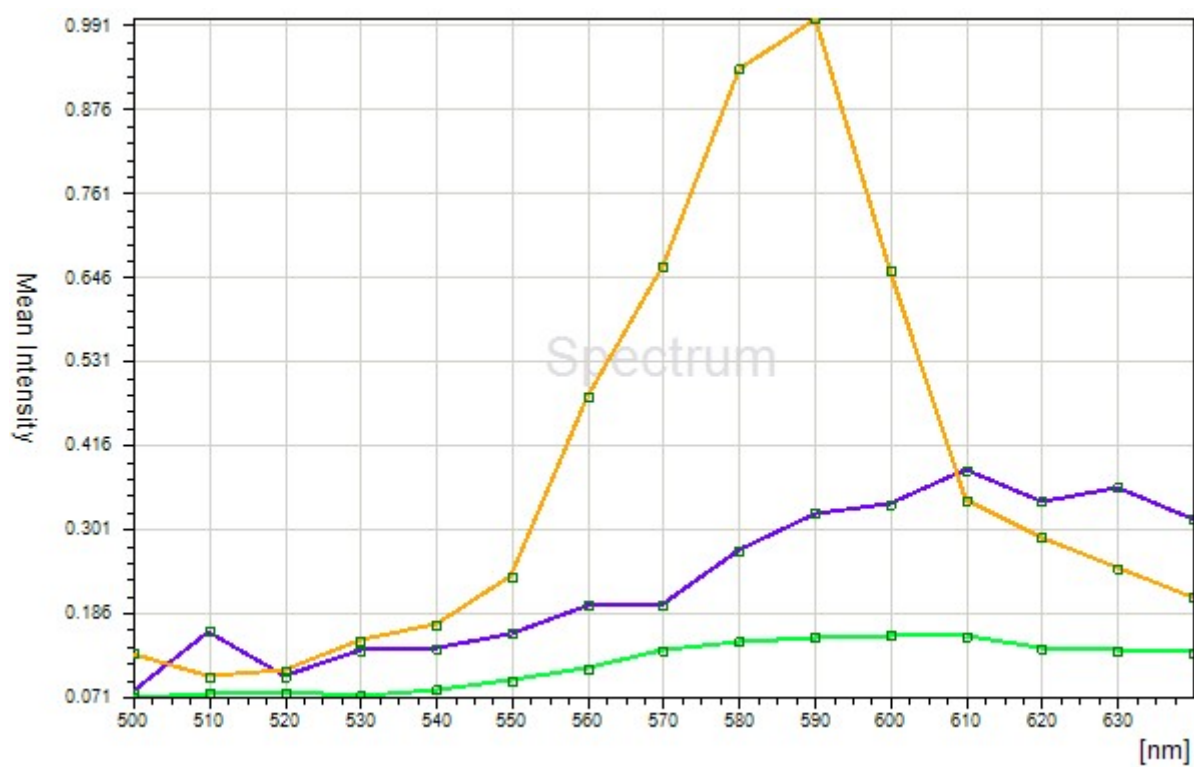


**Fig. S6.** High-resolution XPS spectra of Mn:ZnS@TG-FA dots.

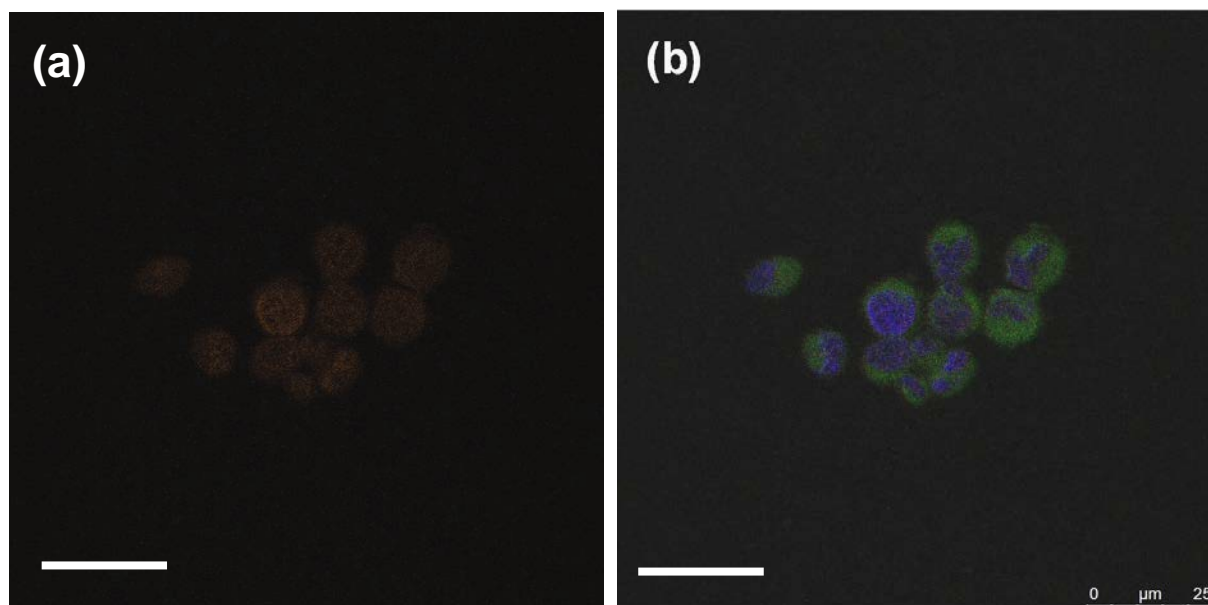


**Fig. S7.** FT-IR spectra of thioglycerol (TG), of Mn:ZnS@TG and Mn:ZnS@TG-FA d-dots, and of folic acid (FA).

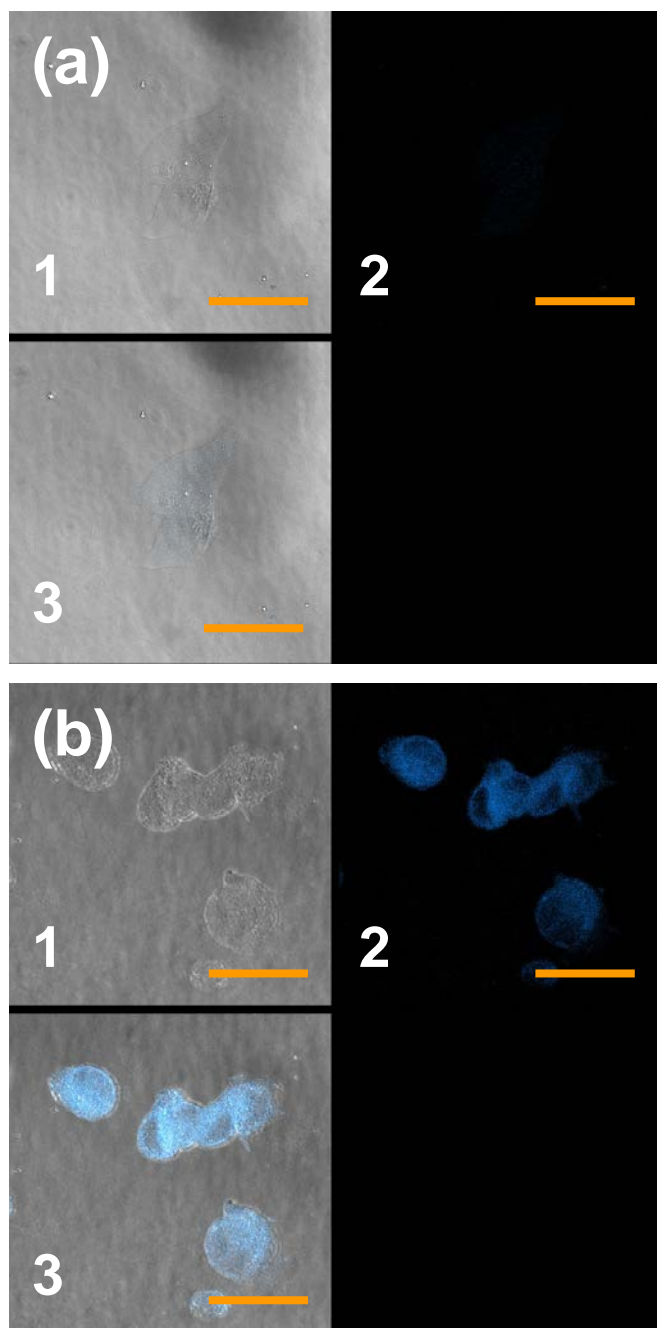




**Fig. S8.** Fluorescence emission spectra of Mn:ZnS@TG d-dots after biphotonic excitation at 720 nm (the sample was scanned from 500 to 640 nm).



**Fig. S9.** Confocal fluorescence imaging of human T47D cells labelled with (a) Mn:ZnS@TG dots, and (b) Hoechst and JC1 organic dyes. Scale bar = 25  $\mu\text{m}$ .



**Fig. S10.** Confocal microscopic images of T47D cells treated with Mn:ZnS@TG-FA dots. Cells in (a) were saturated with free FA for 2 h before treatment with the dots, while cells in (b) were not saturated with free FA. Images “1” are the transmission images, “2” are the corresponding fluorescence images, and “3” the overlays of fluorescence and transmission images. Two-photon confocal microscopy images were obtained with laser excitation at 800 nm. All fluorescence images are presented in false color. Scale bar = 10  $\mu\text{m}$ .