Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Bio-Cleavable Nanoprobes for Target-Triggered Catalytic Hairpin Assembly Amplification Detection of MicroRNAs in Live Cancer Cells

Daxiu Li,[a] Yulan Wu,[b] Chunfang Gan,[*b] Ruo Yuan[a] and Yun Xiang[*a]

[a] *Key Laboratory of Luminescent and Real-Time Analytical Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, PR China. Email: yunatswu@swu.edu.cn (Y. Xiang); Tel.: +86-23-68252277.*

[b] *College of Chemistry and Materials Science, Guangxi Teachers Education University, Nanning 530001, PR China. Email: ganchunfang2008@126.com (C.F. Gan); Tel.: +86-0771-3908065.*

Supplementary Figure:

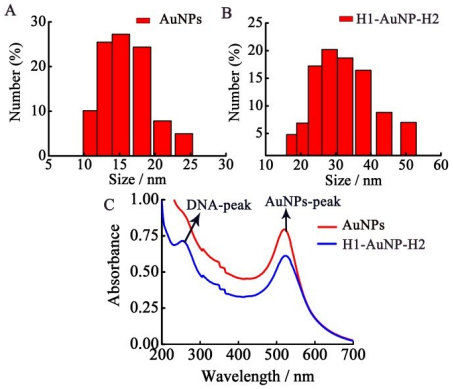

Fig. S1 Dynamic light scattering characterization of (A) AuNPs and (B) the H1-AuNP-H2 nanoprobes. (C) UV-Vis spectra for AuNPs and the H1-AuNP-H2 nanoprobes. Dynamic light scattering and UV-Vis absorption spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan) and a Zetasizer Nano ZS apparatus (Malvern, UK), respectively.

Dynamic light scattering measurements show that the hydrodynamic size of the H1-AuNP-H2 probes is increased from 15.8 to 31.9 nm compared to AuNPs (Fig. S1A and S1B). Also, the UV-Vis absorption spectra show a red shift of the AuNP peak from 520 to 524 nm and a characteristic peak of DNA at 260 nm for the H1-AuNP-H2 probes (Fig. S1C). These results confirmed that the successful preparation of H1-AuNP-H2 probes.

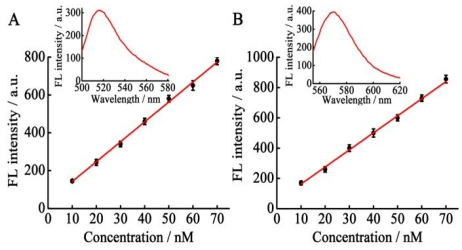

Fig. S2 Standard linear calibration curves of (A) the H1 (with FAM label), (B) H2 (with TAMRA label). Insets: fluorescence spectra of the supernatant collected after

the treatment of H1-AuNP-H2 probes with GSH. Solutions were excited at (A) 488 nm and (B) 543 nm.

The amount of H1 and H2 assembled on AuNPs were determined by incubating the H1-AuNP-H2 probes (1 nM) with GSH (10 mM). After shaking for 12 hours at 25 ºC, the released DNAs were separate through centrifugation. The fluorescence of the supernatant was recorded by a fluorophotometer. From the fluorescence intensity of the supernatant, the concentrations of H1 and H2 are estimated to be ~ 27 nM and ~ 31 nM, respectively. By dividing the concentration of H1 and H2 by the concentration of AuNPs, the average number of H1 and H2 attached to each AuNP is estimated to be ~ 27 and ~ 31 copies, respectively.

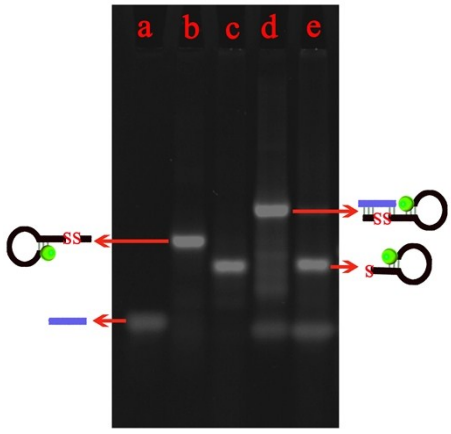

Fig. S3 Degradation of H1 and H1/P1 in the reductive environment: Lane a: P1; Lane b: H1; Lane c: H1 + GSH; Lane d: H1/P1; Lane e: H1/P1 + GSH. The concentrations of H1, P1 and GSH are 250 nM, 250 nM and 5 mM, respectively.

16% native polyacrylamide gel electrophoresis (PAGE) was used to examine whether the disulfide bond can be cleaved by the GSH. Given the fact that the concentration of GSH in cancer cells is normally maintained in the range from 1 to

10 mM,[1] H1 and H1/P1 solutions were mixed with 5 mM GSH for 2 h to cleave the disulfide bond. As shown in Fig. S3, a new band with apparently higher electrophoretic mobility (Lane c) is observed against H1 (Lane b) after treated with GSH. Similar result is obtained for H1/P1 (Lane e vs Lane d). These results indicate that the disulfide bonds incorporated in H1 are efficiently cleaved under reductive environment, and P1 is released from H1/P1 after GSH cleavage.

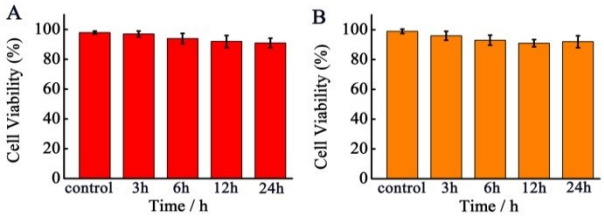

Fig. S4 Cytotoxicity assay of (A) MCF-7 and (B) HeLa cells incubated with the H1-AuNP-H2 probes (2 nM) for 3, 6, 12 and 24 h, respectively, at 37 ºC.

REFERENCES

(1) S. Santra, C. Kaittanis, O. J. Santiesteban and J. M. Perez, *J. Am. Chem. Soc.,* 2011, **133**, 16680-16688.