Supporting Information

Materials: Multiwalled carbon nanotubes (MWNTs, φ = 10-30 nm) were purchased from Nanotech Port Co. Ltd. (Shenzhen, China). DNA oligomer (anti-lysozyme aptamer, 5'-ATC AGG GCT AAA GAG TGC AGA GTT ACT TAG-3') was synthesized by Sangon Biotechnology Co (Shanghai, China). Tetramethylbenzidine (TMB) and N-Hydroxysulfosuccinimide sodium (sulfo-NHS) were purchased from BBI (Ontario, Canada). H_2O_2 was obtained from Beijing Chemicals Inc (Beijing, China). Poly (allyl amine hydrochloride) (PAH, M_W = 60000), 1-Ethyl-3(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), and N-Hydroxysuccinimide (NHS) were purchased from Alfa Aesar (Ward Hill, MA). Human cyclin A_2 was prepared as described in our previous work.[1] All other proteins (including lysozyme, BSA, HSA and IgG) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Horseradish peroxidase (HRP) was purchased from Sigma-Aldrich, which was of 300 IU mg^{-1} of lyophilised solid. Physical parameters of these proteins were summarized in Table S1. All other regents were of analytical reagent grade. Aqueous solutions were prepared with double-distilled water (ddH_2O) from a Millipore system (>18 MΩ cm).

Synthesis of SP-COOH: The carboxy-containing spiropyran l'-(β-carboxyethyl)-3',3'-dimethyl-6-nitrospiro[indoline-2',2-chromane] (denoted as SP-COOH) was synthesized as the reported method.[2,3] The yield of the final product (SP-COOH) was 70 %. The ^{1}H NMR spectrum of SP-COOH is shown in Figure S1 in the Supporting Information. ^{1}H NMR (400 MHz, deuterated DMSO, 25 ^{o}C, TMS): d=1.0–1.3 (6H;

CH_3), 2.6 (2H; CH_2COO), 3.4–3.5 (2H; CH_2N), 5.9–6.0 (2H; olefinic protons), 6.6–8.2 (aromatic protons), 12.0 ppm (COOH, hydrogen-bonding).

Synthesis of MWNT-COOH: The carboxyl-modified MWNTs were prepared by sonicating the primitive MWNTs in a 3:1 vol/vol solution of concentrated sulfuric acid (98%) and concentrated nitric acid (70%) for 12 h at 35–40 °C, and washed with water, leaving an open hole in the tube side and functionalizing MWNTs with carboxyl group. [4]

Synthesis of MWNT-PAH: 40 mg ml^{-1} MWNT-COOH was firstly dissolved in 3 mL 50 mM MES buffer (pH 6.0). The solution of MWNT-COOH was then added with EDC (76.48 mg, 0.4 mmol) and sulfo-NHS (86.85 mg, 0.4 mmol).[3] After agitating for 24 h at temperature, the solution was added to 100 mg of PAH (20 mL, 50 mM MES buffer , pH 6.0) solution with sonication. The mixture solution was sonicated for 3 h and then stirred at room temperature for 24 h. The resulting solution was centrifuged at 10000 rpm to separate the precipitate. The resulting black precipitate was sonicated and extensively washed several times with ddH_2O.

Synthesis of MWNT-SP: To conjugate the MWNT-PAH with SP-COOH, SP-COOH (20 mg, 0.0526 mmol) was firstly dissolved in 4 mL dimethylformamide (DMF). Then EDC (40.2 mg, 0.21 mmol) and NHS (24.2 mg, 0.21 mmol) were added to the solution.[3] After agitating overnight at temperature in the dark, the solution was mixed with 4 mL MWNT-PAH (10mg mL^{-1} in 50 mM MES buffer, pH 6.0). The resulting solution was stirred at room temperature for 36 h and then centrifuged at 10000 rpm to separate the precipitate. The resulting black precipitate was sonicated and

extensively washed three times with ddH_2O to remove the physisorbed SP-COOH.

Characterization: ^{1}H NMR experiments were carried out on a 400 MHz Bruker Avance NMR spectrometer at 20 ^oC. TEM was performed using a JEOL 1011 transmission electron microscope at an accelerating voltage of 100 kV. FTIR characterization was carried out on a BRUKE Vertex 70 FTIR spectrometer. UV-vis absorbance measurements and time course experiments were carried out on a Jasco—V550 UV/Vis spectrophotometer. Thermogravimetric analysis (TGA) was recorded on a PE TGA-7 thermal analyzer at 10 $^oC \cdot min^{-1}$ in an N_2 atmosphere. The dynamic light scattering (DLS) measurements and the zeta potential of MWNT-MC in solution (~0.05 mg/mL) was determined using a Zeta PALS, zeta potential analyzer (Brookhaven Instruments Corp. Holtsville, NY). The photoinduced isomerization reactions of MWNT-SP were performed in the UV using a Cole Parmer 97500-50 Transilluminator (365 nm, 7000 $\mu W/cm^2$) or in the visible with a visible lamp. For kinetic measurement, the sample was irradiated with UV light for 5 min before measurement.

Bioassay: The samples of MWNT-SP were irradiated with UV light until the photostationary distribution was reached. Kinetic measurements were performed on a Jasco-V550 UV/Vis spectrophotometer in time-course mode at 652 nm.[5] Experiments were carried out by using MWNT-SP or MWNT-MC in Na_2HPO_4 buffer (25 mM, pH 5.0, reaction volume 500 mL), in the absence or presence of 10 $ng \cdot ml^{-1}$ HRP, with TMB (80 μM) as the substrate. The H_2O_2 concentration was 0.5 mM, the pH was 5.0, and the temperature was 20 ^oC, unless otherwise stated.

For lysozyme detection, the sample of MWNT-SP was firstly irradiated by UV light for 5 min then added with DNA aptamer and lysozyme. The solution was kept in dark for 20 min, added with HRP for time course measurement. The time-course measurements for each sample were repeated at least three times. Primary data were transferred to the graphics program Origin for plotting and analysis.[5]

References

1. X. H. Wang, C. Y. Wang, K. G. Qu, Y. J. Song, J. Ren, D. Miyoshi, N. Sugimoto, X. Qu, *Adv. Funct. Mater* 2010, **20**, 3967.

2. J. Chen, F. Zeng, S. Z. Wu, Q. M. Chen, Z. Tong, *Chem. Eur. J.* 2008, **14**, 4851.

3. A. Fissi, O. Pieroni, G. Ruggeri, F. Ciardelli, *Macromolecules* 1995, **28**, 302.

4. (a) X. Li, Y. H. Peng, X. Qu, *Nucleic Acids Res* 2006, **34**, 3670; (b) X. Li, Y. H. Peng, J. Ren, X. Qu, *Proc. Natl Acad. Sci. USA* 2006, **103**, 19658.

5. (a) Y. J. Song, X. H. Wang, C. Zhao, K. G. Qu, J. Ren, X. Qu, *Chem. Eur. J.* 2010, **16**, 3617. (b) Y. J. Song, K. G. Qu, C. Xu, J. Ren, X. Qu, *Chem. Commun.* 2010, **46**, 6572. (C) Y. J. Song, K. G. Qu, C. Zhao, J. Ren, X. Qu, *Adv. Mater.* 2010, **22**, 2206.

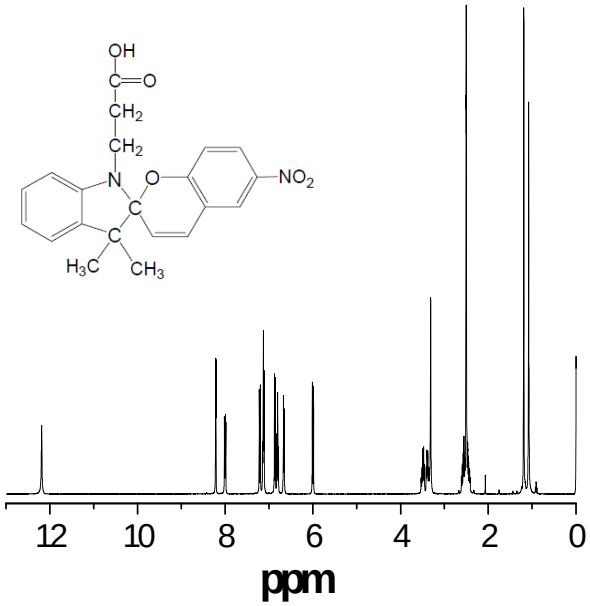

Fig. S1 ^{1}H NMR spectrum of SP-COOH.

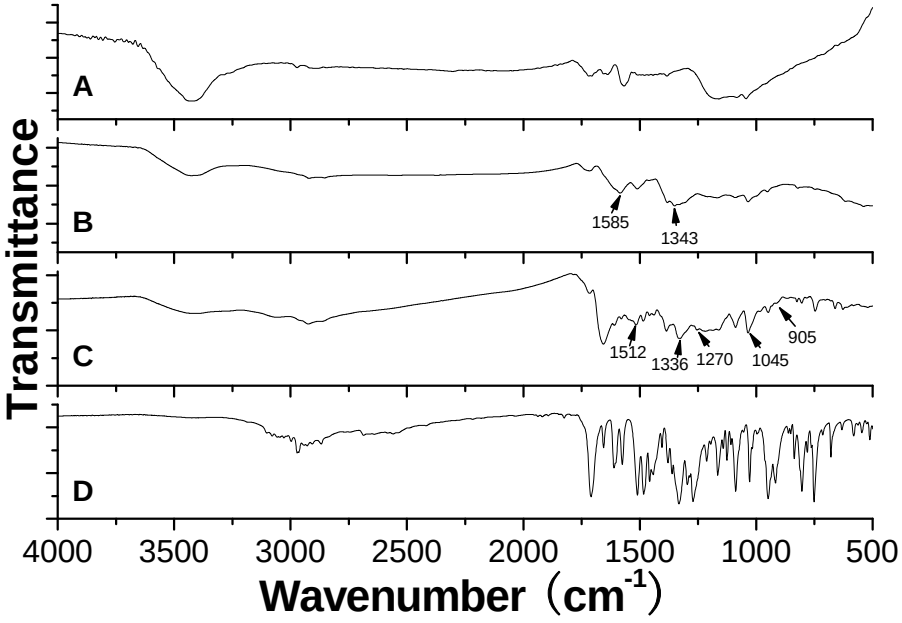

Fig S2 FTIR of (A) MWNT-COOH, (B) MWNT-PAH, (C) MWNT-SP and (D) SP-COOH.

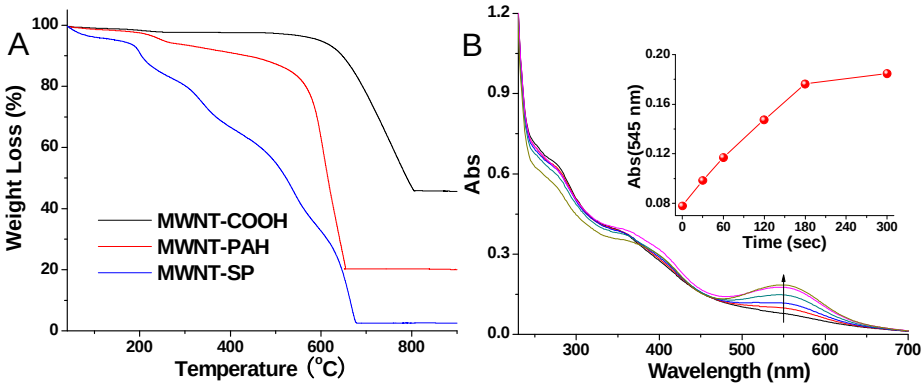

Fig. S3 (A) Thermogravimetric analysis for MWNT-COOH (black), MWNT-PAH (red) and MWNT-SP (blue) in N_2 atmosphere with a ramp of 10 °C/min. (B) UV/Vis spectra of MWNT-SP irradiated by UV light for different time. (Inset) The absorption at 545 nm is depended on the time of irradiation.

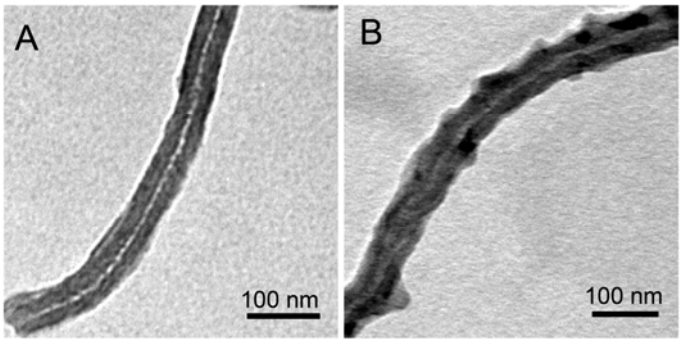

Fig. S4. High resolution transmission electron microscopy (HRTEM) images of (A) MWNT-COOH and (B) MWNT-MC.

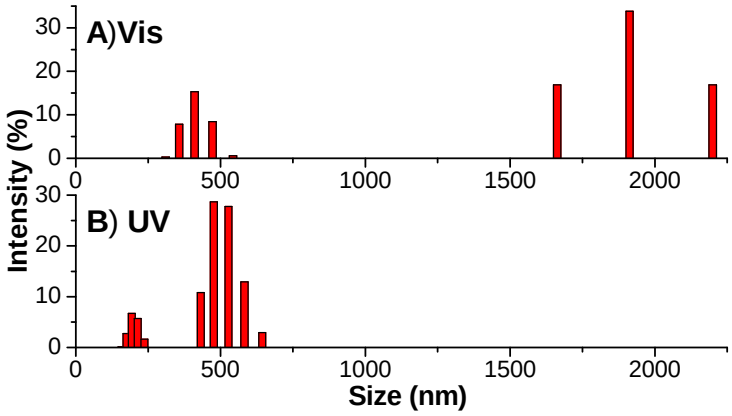

Fig. S5 Size distribution determined by dynamic light scattering (DLS): (A) MWNT-SP and (B) MWNT-MC.

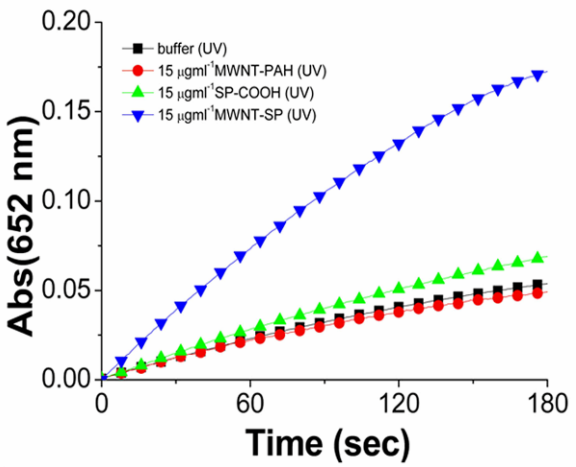

Fig. S6 The time-dependent absorbance changes at 652 nm in the absence (■, buffer was irradiated by UV light, then added with 10 ng·ml^{-1} HRP) or presence of MWNT-PAH (●, buffer was firstly irradiated by UV light, then added with 10 ng·ml^{-1} HRP), SP-COOH (▲, 15 μg·ml^{-1}SP-COOH was firstly irradiated by UV light, then added with 10 ng·ml^{-1} HRP) and MWNT-SP (▼, 15 μg·ml^{-1} MWNT-SP solution was firstly irradiated by UV light, then added with 10 ng·ml^{-1} HRP) at room temperature.

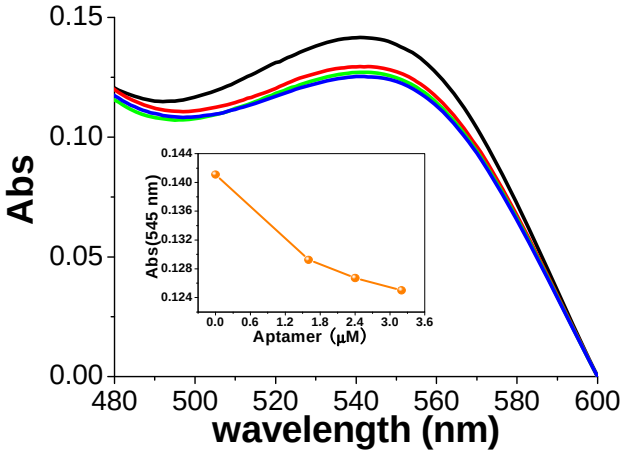

Fig. S7. UV/Vis spectra of MWNT-MC in the absence (black) or presence of 1.6 μM (red), 2.4 μM (green) and 3.2 μM (blue) lysozyme aptamer.（Inset）Calibration curve corresponding to the absorbance value at 545 nm of MWNT-MC upon analyzing variable concentration of DNA aptamer.

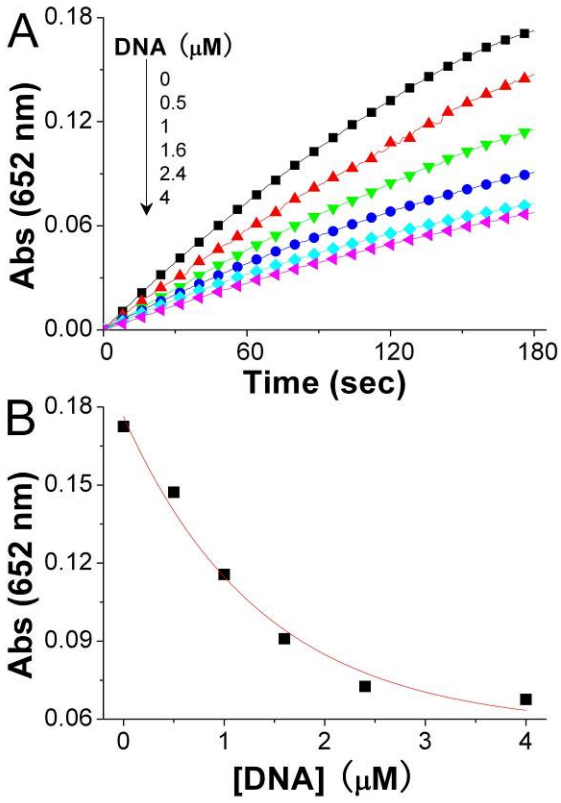

Fig. S8 (A) Time-dependent absorbance changes of 15 μg·ml^{-1} MWNT-MC and 10 ng·ml^{-1} HRP upon adding different concentration of DNA aptamer. (B) Calibration curve corresponding to the absorbance upon analyzing variable concentration of DNA aptamer after a fixed time interval of 3 min.

Table S1. Physical properties of proteins probe.

	Mw (Da)	pI	ε_{280} (M^{-1} cm^{-1})
Lysozyme	14307	11	37640
Cyclin A_2	49588	6.2	38830
BSA	66430	4.7	43824
HSA	66437	4.7	36600
IgG	151000	6.1-6.5	203850