Supporting Information

1 Experimental Section

1.1 Reagents and apparatus

All DNA sequences were synthesized and purified by Sangon Biotech Co., Ltd. (Shanghai, China), and their base sequences in detail were as follows: 5′-ATACCAGCTTATTCAATT-3′ (CEA aptamer); 5′-NH_2-AAAAAATTGAA-3′ (modified upon the surface of PFO dots); 5′-CTGGTATAAAA-SH-3′ (modified upon the surface of Au-NPs). Carcinoembryonic Antigen (CEA, from human fluids), the conjugated polymer: poly (9,9-dioctylfluorenyl-2,7-diyl) (PFO; average MW 58200; polydispersity=3.7), the amphiphilic functional polymer poly (styrene-co-maleic anhydride) (PSMA, cumene terminated, average MW ~1700, styrene content 68%) were purchased from Sigma-Aldrich.

Tetrahydrofuran (THF, anhydrous, 99.9%), polyethylene glycol (PEG, MW=3350), 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES buffer), $AuCl_4 \cdot 3H_2O$, sodium citrate dehydrate and filter members were commercially available from local chemical reagent suppliers. And the reagents employed were all of analytical grade.

Ultrapure water was obtained from a Milli-Q Millipore filtration system and used throughout. The fluorescence spectra of PFO dots were measured using a Cary Eclipse fluorescence spectrophotometer (Varian, USA) while the excitation wavelength was set at 380 nm. UV-vis absorption of Au-NPs was characterized by a

UV-vis spectrophotometer (Lambda 750). The morphology and size of the PFO dots were characterized by atomic force microscopy (AFM) with a Nanoscope Multimode IIIa (Veeco Instruments, USA) and dynamic light scattering (DLS, malvern ZEN3690). High resolution transmission electron microscopy (HRTEM) images of the prepared Au-NPs were recorded on an electronic microscopy (Tecnai G2 F20S-TWIN 200KV).

1.2 Preparation of functionalized PFO dots

The PFO dots has been chosen as fluorophore since its emission can be overlapped by the absorbance band of Au-NPs. The PFO dots containing carboxyl groups on the surface was prepared according to Wu *et al*.[31, 32] with slightly alterations. A typical process is briefly presented as follow. The light-harvesting polymer PFO, amphiphilic copolymer PSMA was firstly dissolved in THF to make a stock solution of 1 mg/mL, respectively. Afterward, the two polymer solution were diluted and mixed in THF to produce a solution mixture with a PFO concentration of 50 ppm and a PSMA concentration of 20 ppm. The mixture was sonicated and standing overnight to get a homogeneous solution. In a vigorous bath sonicator, 5 mL mixture solution was quickly added to 10 mL of ultrapure water. The remaining THF was removed by evaporation under vacuum, followed by filtration through a 0.2 μm membrane filter. During nanoparticle formation, the maleic anhydride units of PSMA molecules were hydrolyzed in the aqueous environment, generating carboxyl groups on PFO dots. The PFO dispersions were clear and stable for months without signs of aggregation.

Surface conjugation was performed by utilizing the EDC-catalyzed reaction

between carboxyl PFO dots and the amine-modified ssDNA. In a typical conjugation reaction, 20 μL of PEG (5% w/v) and 20 μL of HEPES buffer (1 M) were added to 1 mL of carboxyl PFO dots solution (50 ppm), resulting in a PFO dots solution in 20 mM HEPES buffer with a pH of 7.4. Then, 10 μL of amine-modified ssDNA (10 μM) was added to the solution and mixed well on a vortex. Last, 20 μL of freshly-prepared EDC solution (5 mg/mL) was added to the solution, and the above mixture was magnetically stirred for 4 hours at room temperature. Finally, the resulting Pdot conjugates were separated from free molecules by Spin-OUT™ GT-1200 ultrafilter column (Sangon Biotech Co., Ltd.)

1.3 Preparation of Au nanoparticles and its DNA functionalized

Au-NPs of 13±2 nm were prepared using the citrate reduction of $HAuCl_4$ method.[33] In brief, $HAuCl_4 \cdot 3H_2O$ (129 μL, 40 mg/mL) was dissolved in ultrapure water (50 mL) and boiled with vigorously stirring at 130℃ for 1 min. Then, sodium citrate dehydrate (1 mL, 1.5% wt/v) was added into the solution by continued stirring. After the solution color change to deep red, the solution was stirred for an additional 15 min, allowed to cool to room temperature and stored at 4℃ for conservation. The concentration of resulting Au-NPs solution was determined by the following absorbance spectra measurement with an appropriate extinction coefficient (521 nm, 2.7×10^8 $M^{-1}cm^{-1}$).[34]

Au-NPs conjugation with DNA was performed mainly according to method of Au-S modification.[35] Although the chemical bond of Au-S provides enough energy to compensate the electrostatic repulsion between the negative charged surface of the

Au-NPs and the ssDNA, the reaction of combining SH group to Au is slow. To overcome this and accelerate the reaction rate, the Au-NP solution was concentrated as high as 500 nM without causing clustering of the Au-NPs, followed by addition of excess thiol-ssDNA for further modification[36]. After incubation the mixture by shaking for 4 h at room temperature, the free thiol-ssDNA was removed by risen twice with PBS.

1.4 Fluorescence intensity measurement

Firstly, the ssDNA modified PFO dots and Au-NPs were incubated with the CEA aptamer for 30min with a slightly shaking. After sufficient hybridization of ssDNA with each other forming the stable sandwich structure, the fluorescence intensity of mixture solution was measured as well as the equal concentration of PFO dots solution as blank. Then, various concentration of CEA was added into the above solution and incubated for 1 hour with a slightly shaking. Soon afterward, the fluorescence intensity of mixture solution was measured again as results for CEA quantification. During these experiments, the excitation wavelength was 380 nm.

2. Characterization of PFO dots and Au-NPs.

The morphology and size of the PFO dots were firstly characterized by AFM (see Fig. S1a). Results show that the prepared PFO dots presented in a homogeneous status. Then the size distribution of particles were measured and statistics analyzed by DLS, which revealed that the particles possessed an average diameter of 52 nm (Fig. S1b). In addition, the TEM image of the the Au-NPs was shown in Fig. S1c. Finally, we

investigated the spectral properties of PFO dots and Au-NPs respectively. Au-NPs have a big absorbance band from 400 nm to 550 nm, which well overlap the emission of PFO at about 440 nm, as shown in Fig.S1d, this indicated that the emission of PFO dots could be absorbed by Au-NPs.

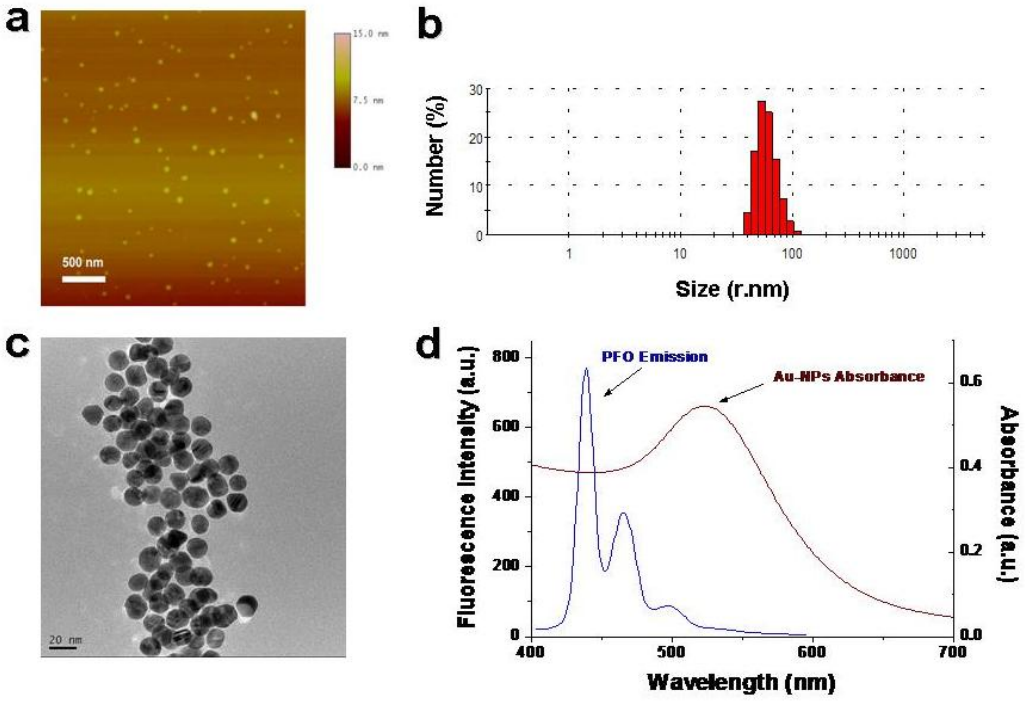

Fig. S1 Characterizations of PFO dots and Au-NPs. (a) AFM image of PFO dots. (b) Size distribution of PFO dots. (c) TEM image of Au-NPs (diameter=13±2 nm). (d) Overlap between the emission of PFO dots (5 ppm) and the absorbance of Au-NPs (20 nM).