Supporting Information

Experimental

Materials and Chemicals

Tetraethylorthosilicate (TEOS), 3-(aminopropyl)trimethoxysilane (APTS), Tris(2,2'-bipyridyl) dichlororuthenium(II) hexahydrate (Rubpy), Triton X-100 and BSA were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glutaraldehyde (GA) (50 % v/v) was purchased from Alfa (Ward Hill, MA). Cyclohexane, *n*-hexanol, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and NH_4OH (25%) were obtained from Beijing Chemicals Inc. (Beijing, China). Oligonucleotides were synthesized by Sangon Biotechnology Co. (Shanghai, China).

Preparation of fluorescent silica nanoparticles (FNPs)

Rubpy dye-doped nanoparticles were synthesized by the reverse microemulsion method. Briefly, the nanoparticles were synthesized by adding 1.77 g of Triton X-100, 7.5 mL of cyclohexane, and 1.6 mL of *n*-hexanol to a 25 mL glass vial with continuous magnetic stirring. Next, 400 μL of ddH_2O and 80 μL of 0.1 M Rubpy were added. Followed by the addition of 100 μL of TEOS, the materials were stirred for 30 min. To initiate silica polymerization, 65 μL of NH_4OH was added. After 18 h, a postcoating of amino-modified silica was performed by adding 50 μL of TEOS and 50 μL of APTS. This polymerization was allowed to proceed for 18 h. The particles were centrifuged, sonicated, and vortexed three times with 10 mL aliquots of fresh 95% ethanol, followed by a wash two times with 10 mL ddH_2O.[1]

Preparation of magnetic silica microspheres (MSMPs)

The Fe_3O_4 nanoparticles were prepared as previously reported[2] and in size 5 nm in diameter (Figure 1B). To prepare MSMPs, 30 mg Fe_3O_4 nanoparticles were suspended in 1-propanol (90 mL) by sonication for 30 min at room temperature. Then, 200 μL NH_4OH, 3 mL ddH_2O, and 200 μL TEOS were added to the above solution, and the mixture was stirred 10 h. Then 100 μL APTS added to the mixture. The mixture was stirred at room temperature for 10 h and then centrifuged to separate the precipitate. The resulting black precipitate was washed four times with ddH_2O to give the MSMPs.[3, 4]

Modification of FNPs and MSMPs:

For surface activation reaction, 40 mg FNPs or MSMPs was added to 18 ml SSC1 buffer (25 mM sodium citrate,150 mM NaCl, pH 7.4), and sonicated for 1h, then 2 ml GA (50 % v/v) was added. The mixture was stirring for overnight in the constant temperature at 20 ^oC. With the completion of the reaction, the suspension was washed with SSC1 buffer five times to remove excess GA. The DNA modification was carried out by adding 9 mg modified FNPs or MSMPs, 200 μL of 15μM FNP DNA probe or MSMP DNA probe, 2 mL SSC1 buffer. The mixture was stirred in the constant temperature at 20 ^oC for 24 h. Followed by addition of 3 mL BSA (1 mg mL^{-1} in SSC1 buffer), and stirred for 4 h. The mixture was centrifuged, and rinsed with SSC2 buffer (25 mM sodium citrate, 300 mM NaCl, pH 7.4). The final deposition was suspended in 1 mL of SSC2 buffer and stored at 4 ^oC for further use.[5]

Sensor preparation

200 μL Detection probe (15 μM in SSC2 buffer) was added to 1 mL DNA modified

MSMPs (9 mg/mL in SSC2 buffer). This solution was stirred for 12 h at 20 ^{o}C , then 1mL FNPs (9 mg/mL in SSC2 buffer) was added. The mixture was continuously stirred for another 12 h. The complexes were magnetically collected and rinsed with SSC1 buffer. This washing procedure was repeated 5 times to remove the unbound nanoprobes. Finally, the complexes were dispersed in 3 mL of SSC1 buffer and stored at 4 ^{o}C for further use.

Detection of AMP

In AMP detection experiments, 50 μL of the sensor described above was added to 1 mL of concentrated AMP solution (in SSC1 buffer). The mixture was vortexed for 5 min, and then an external magnet was used to separate the MSMPs from the solution. The suspension was collected for fluorescence detection at 20 ^{o}C.

Characterization and measurement

TEM was performed using a JEOL 1011 transmission electron microscope at an accelerating voltage of 100 kV. Fluorescence measurements were carried out on a JASCO FP-6500 spectrofluorometer.[6-8]

References

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Supporting Figures

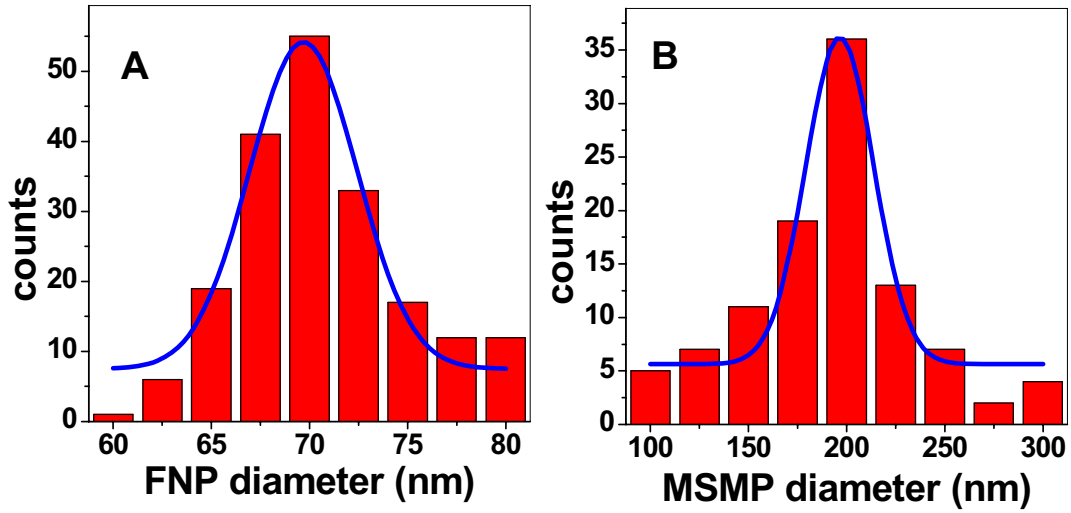

Figure S1 Particle size distribution of (A) FNPs and (B) MSMPs.

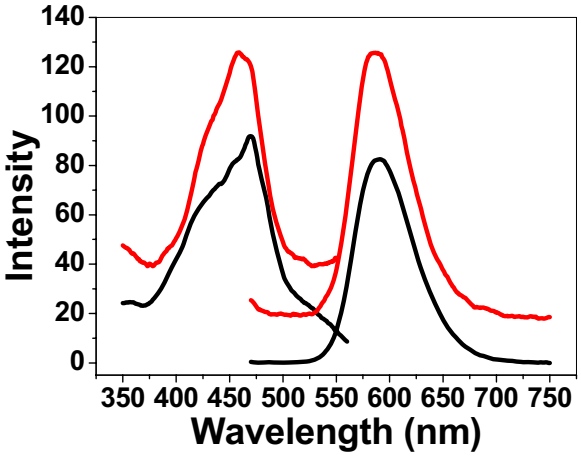

Figure S2 Fluorescence excitation (left, Em=586 nm) and emission (right, Ex=458 nm) spectra recorded in the aqueous phase for the pure Rubpy (black) and FNPs (red).

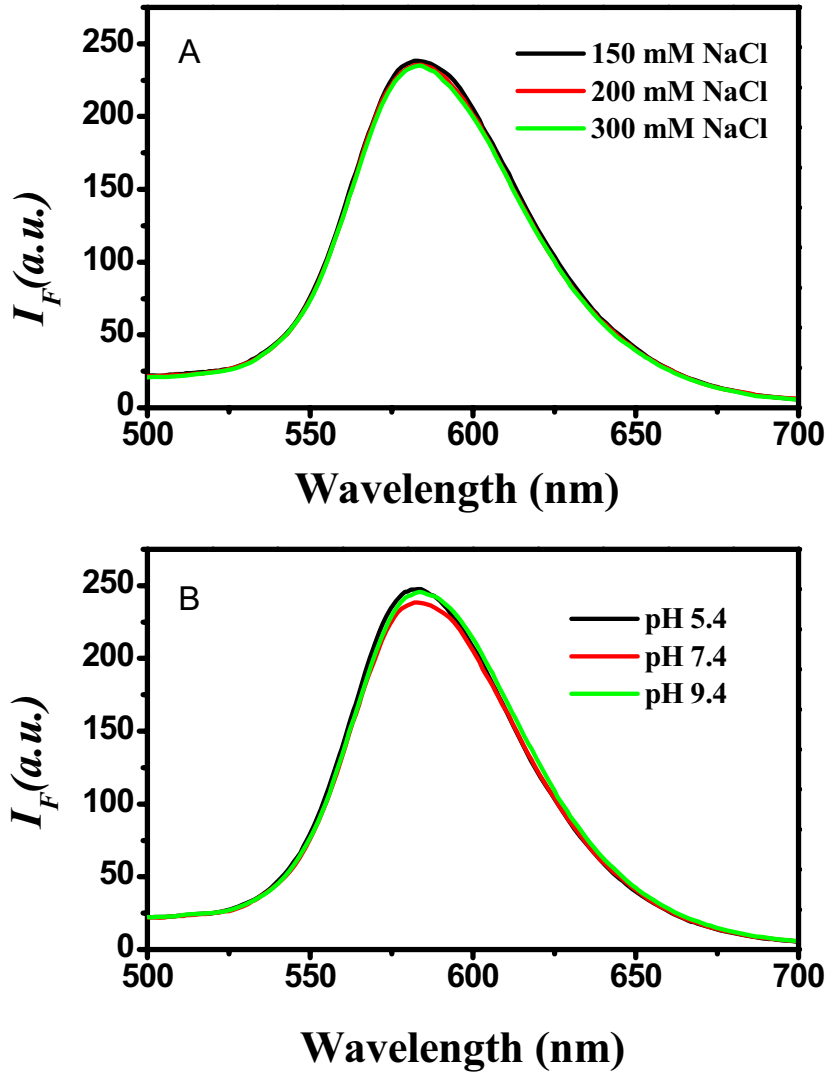

Figure S3 In the absence of AMP, fluorescence emission spectra of 10 mgmL^{-1} FNPs at different [NaCl]: A) 150 mM NaCl (black line), 200 mM NaCl (red line), 300 mM NaCl (green line); or at different pH: B) pH 5.4 (black line), pH 7.4 (red line), pH 9.4 (green line).

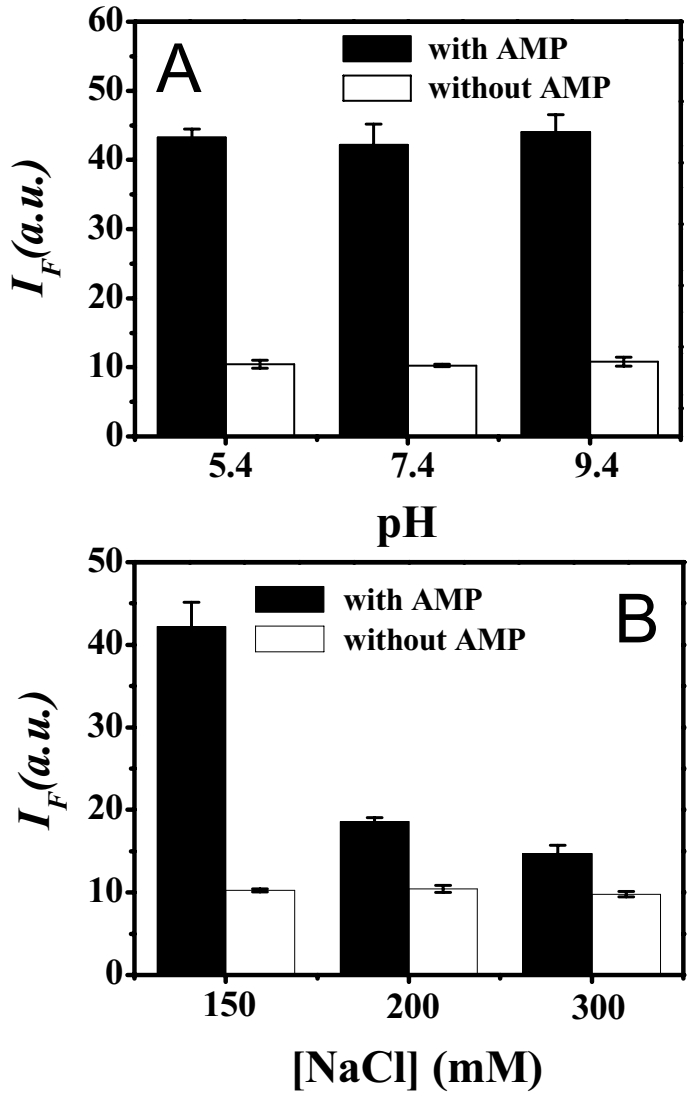

Figure S4 A) pH effect on the sensor fluorescence signal. NaCl concentration was 150 mM and AMP concentration was 1 μM for all the experiments; B) Salt effect on the sensor fluorescence signal. pH was 7.4 and AMP concentration was 1 μM for all the experiments. Temperature was 20 ^{o}C. Fluorescence measurements were carried out as described in Figure 2.