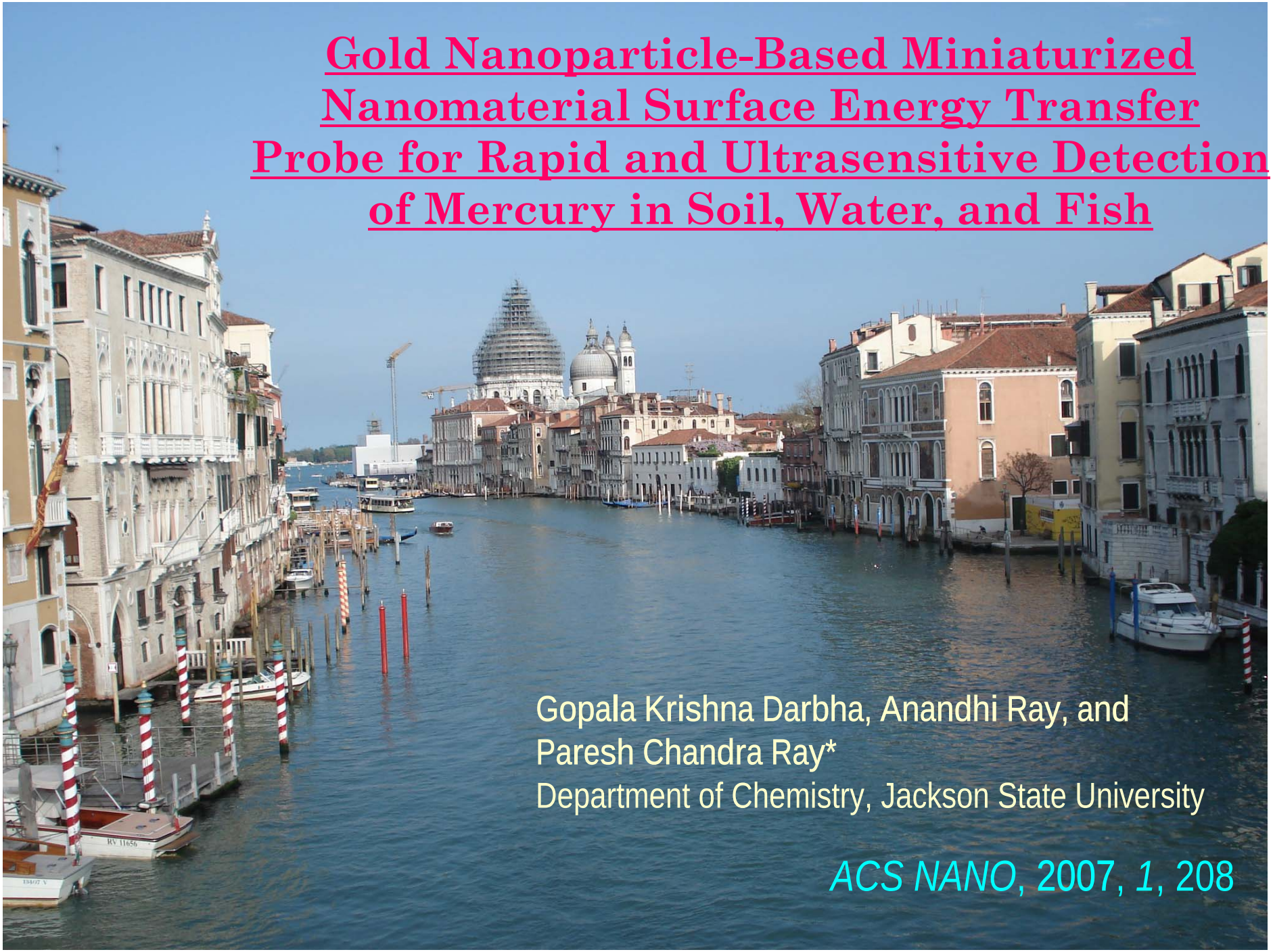

Gold Nanoparticle-Based Miniaturized Nanomaterial Surface Energy Transfer Probe for Rapid and Ultrasensitive Detection of Mercury in Soil, Water, and Fish

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MERCURY POLLUTION

- coal-burning power plants,
- Oceanic and volcanic emissions,
- gold mining,
- solid waste incineration

- Needed

  extremely high sensitive, cost-effective Hg sensor that can provide real-time determination of Hg levels in the environment, water, and food.

- Existing methods

  provide low detection limits

  time-consuming

  laborious

  lack the procedural simplicity for on-site analysis

- Alternative approaches using fluorescence based molecular sensors

  drawbacks -such as the lack of water solubility, cross-sensitivity toward other metal ions, weak fluorescence enhancement factors, and short emission wavelengths

FRET based techniques

The efficiency of FRET is very sensitive to the distance between the donor and an acceptor. The length scale is limited to the order of 100 Å.

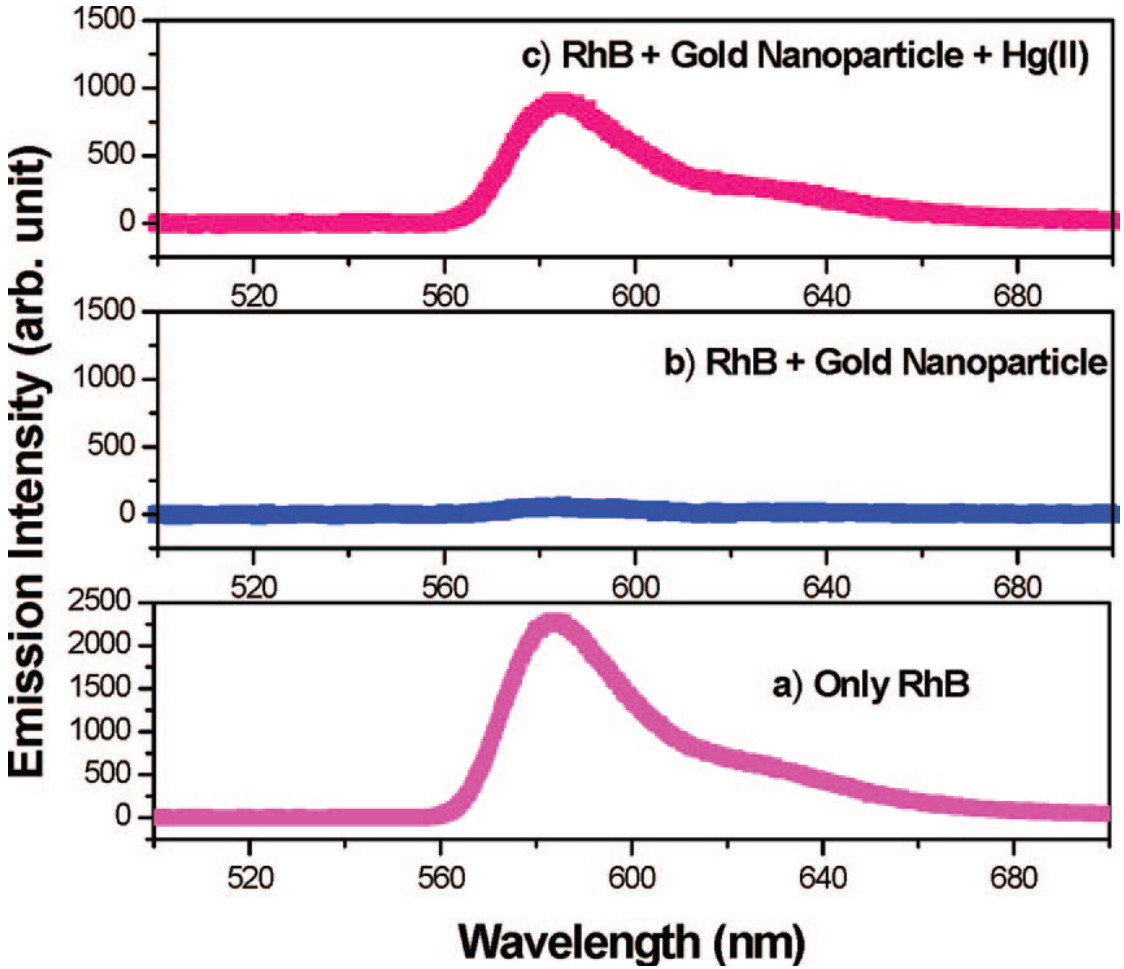
Nanomaterial surface energy transfer (NSET) based technique

capable of measuring distances nearly twice as far as FRET in which energy transfer from a donor molecule to a nanoparticle surface follows a predictable distance dependence. NSET differs from FRET theoretically in that the distance dependence of quenching is related to the inverse fourth power rather than the inverse of the sixth power of the separation distance ($1/R^4$ rather than $1/R^6$).

Gold nanoparticle-based NSET

gold nanoparticle surface acts as an acceptor and organic dye acts as a donor- provides high sensitivity for the detection of metal ions because of their unique property of superquenching chromophores through both energy-transfer and electron-transfer processes.

How it is working?

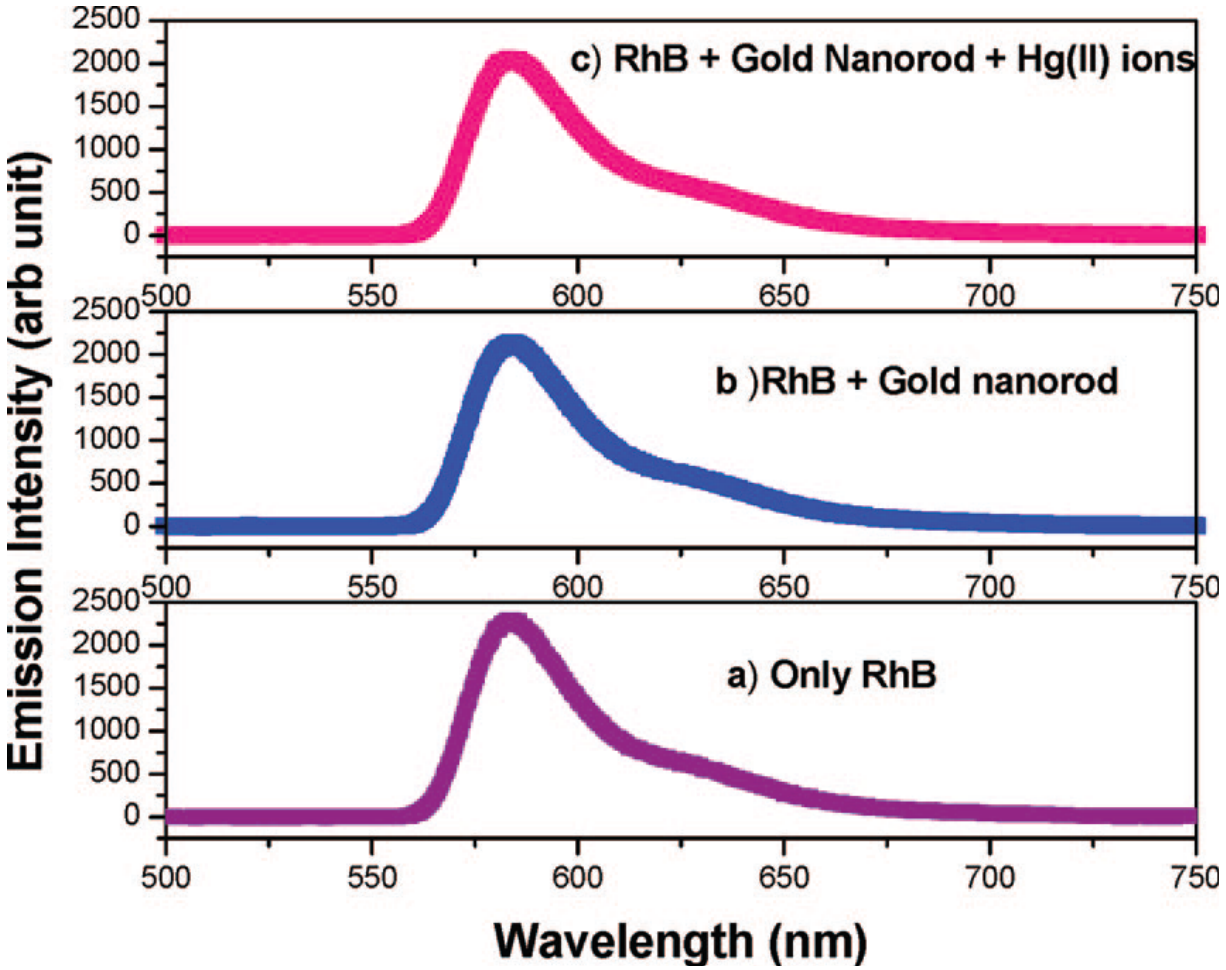


energies for surface adsorption of organic dyes onto gold are usually in the range of 8–16 kcal/mol, much smaller than the binding energies involved in rhodamine B and mercury binding (80–100 kcal/mol),

100%-Quenching

Figure 1. Plot of fluorescence intensity *vs* wavelength: (a)rhodamine B (RhB) dye in water solution (5.6 M); (b) RhB self-adsorbed onto gold nanoparticles in 5 nM solution; (c)130 ppb Hg(II) added to solution (b) (RhB-adsorbed goldnanoparticle solution).

whether the changes of the rhodamine B fluorescence observed on the gold nanoparticle surface are due mainly to NSET?



strong longitudinal plasmon band at 700 nm and a very weak transverse plasmon band at 510 nm

10%-Quenching

Figure 2. Plot of fluorescence intensity *vs* wavelength: (a) rhodamine B (RhB) dye in water solution (5.6 M); (b) RhB self-adsorbed on gold nanorods in 5 nMsolution; (c) 130 ppb Hg(II) added to solution (b) (RhB-adsorbed gold nanorod solution).

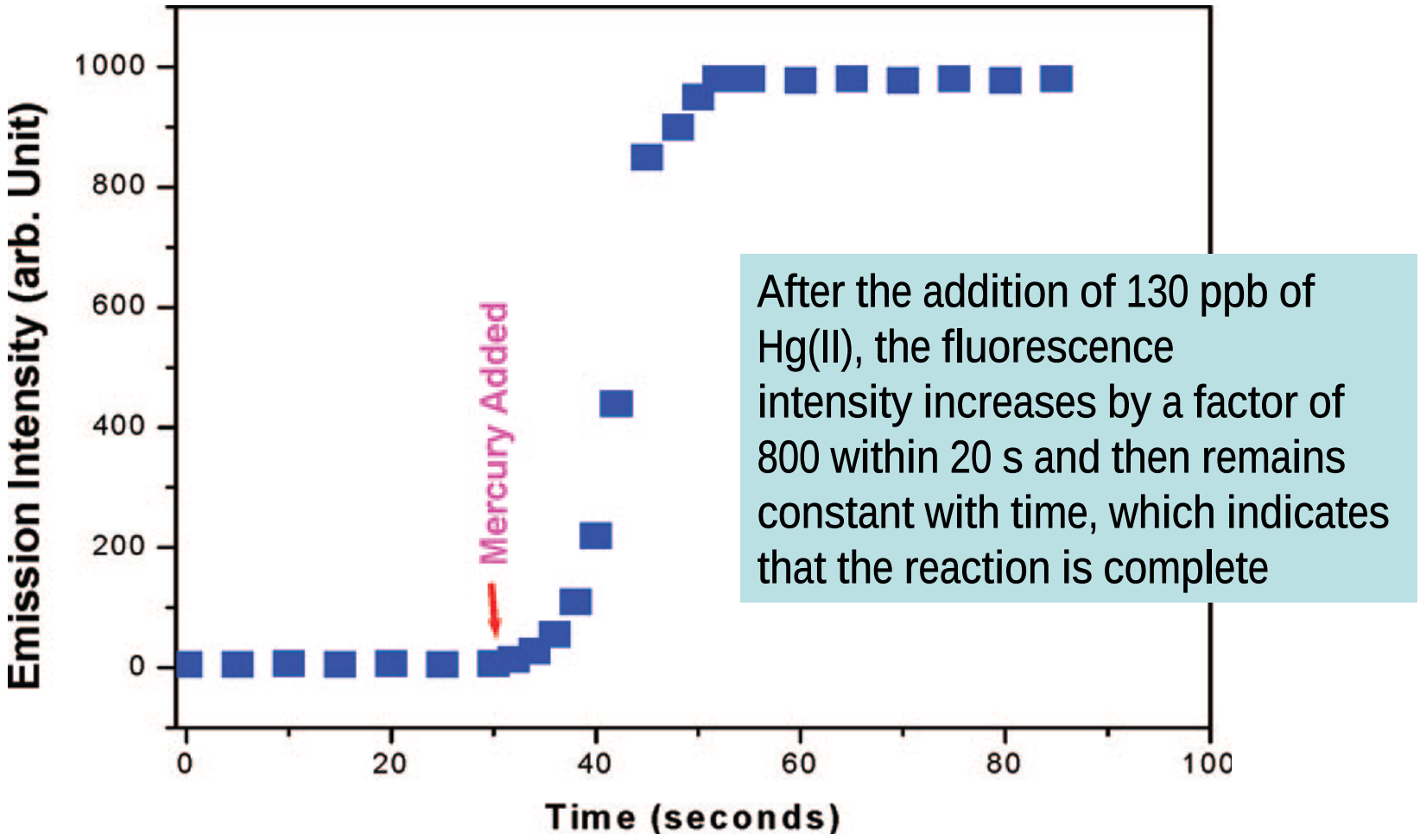


Figure 3. Plot of fluorescence intensity *vs* time (in seconds) upon the addition of 130 ppb Hg(II) to RhB-adsorbed gold nanoparticle solution. The arrow indicates the initial time of mercury addition.

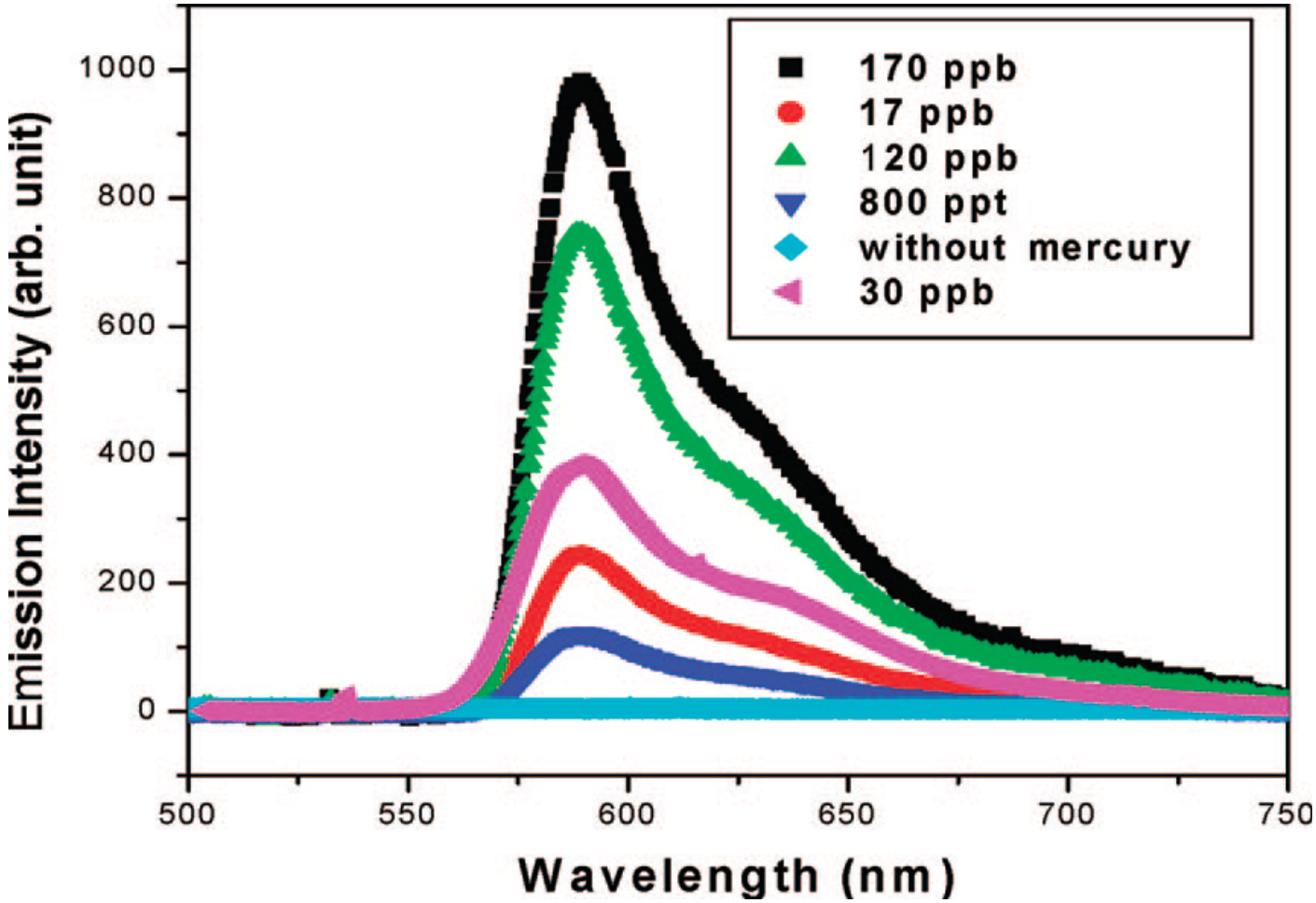
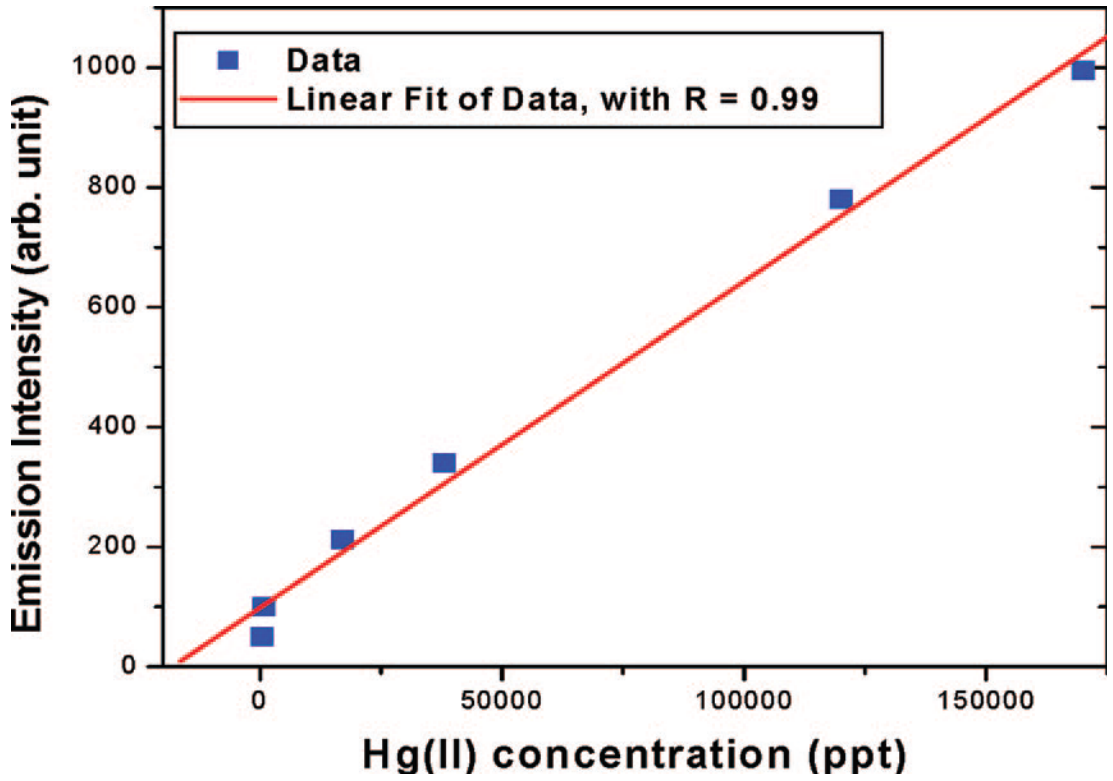


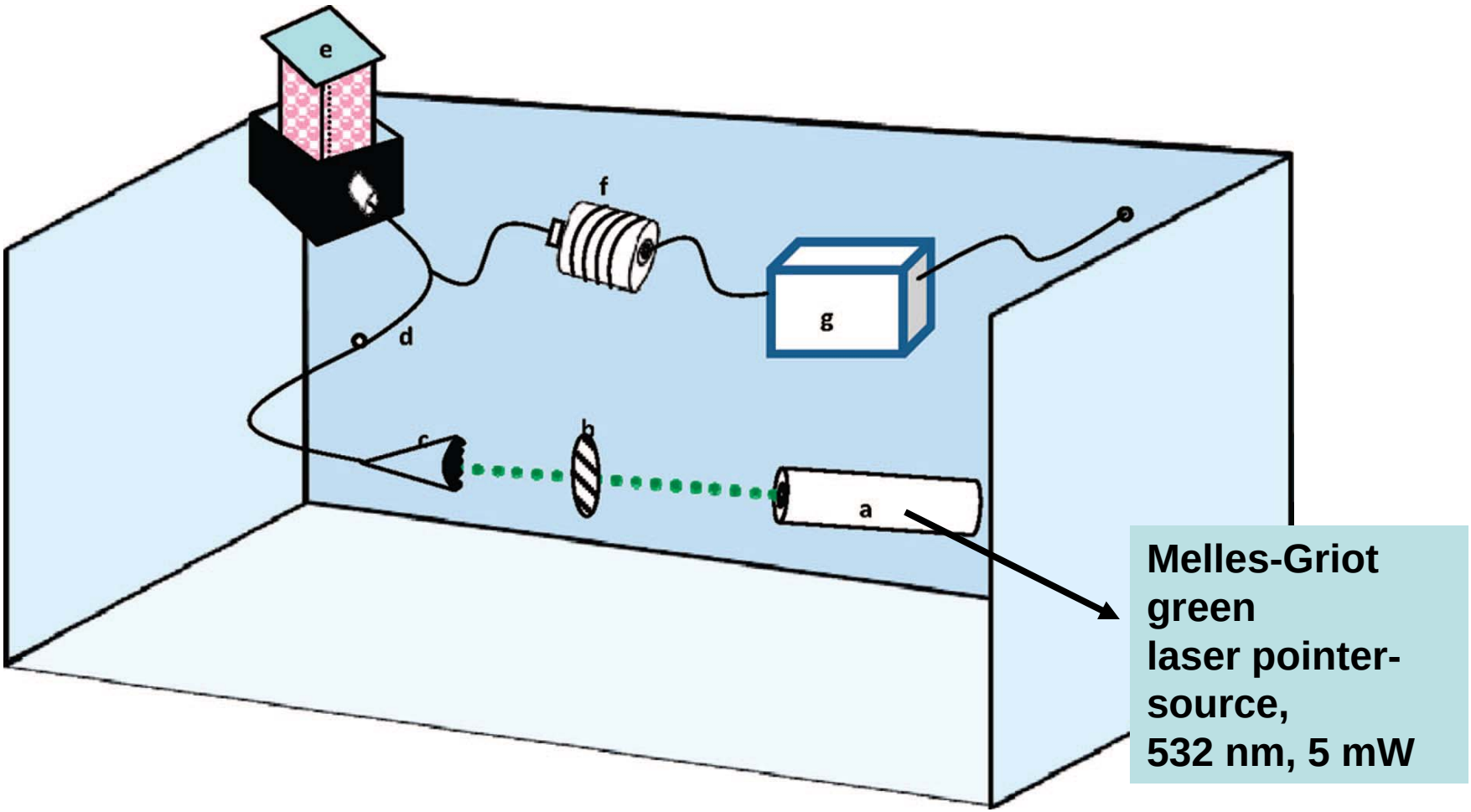
Figure 4. Fluorescence response of RhB adsorbed onto gold anoparticles in 5 nM solution upon addition of different concentrations of Hg(II) ions (800 ppt, 17 ppb, 30 ppb, 120 ppb, and 170 ppb).



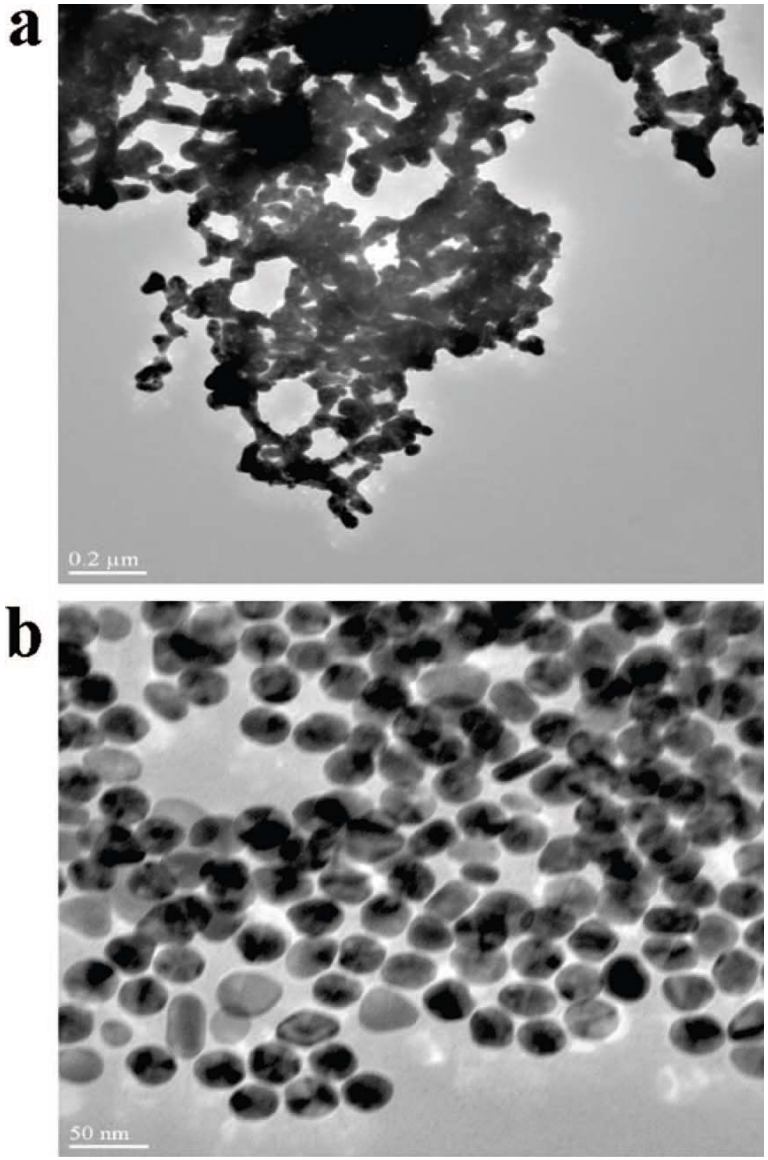
NSET emission intensity is highly sensitive to the concentration of Hg(II) ions, and the intensity increased linearly with concentration of Hg(II) ions. A linear correlation was found between the emission intensity and concentration of Hg(II) ions over the range of 0.8–170 ppb

Figure 5. Plot of fluorescence intensity *vs* Hg(II) concentration in parts-per-trillion. A linear correlation exists over the range of 0.8–170 ppb, with *R* 0.99.

U.S. Environmental Protection Agency (EPA) standard for the maximum allowable level of Hg(II) in drinking water is 2 ppb



Scheme 1. Schematic diagram of our NSET probe. It consists of several components: (a) (18 Lab 181), (b) neutral density filter, (c) plano-convex lens, (d) optical fiber, (e) sample holder, (f) 532 nm cut-off filter, and (g) Ocean Optics QE65000 spectrometer.



To detect Hg(II) ions selectively, the surface of the gold nanoparticle was modified with mercaptopropionic acid (MPA) and homocystine and added a chelating ligand, 2,6-pyridinedicarboxylic acid (PDCA), to the solution

Figure 6. TEM images of a gold nanoparticle–MPA solution (a) in the presence and (b) in the absence of 130 ppm Hg(II) ions.

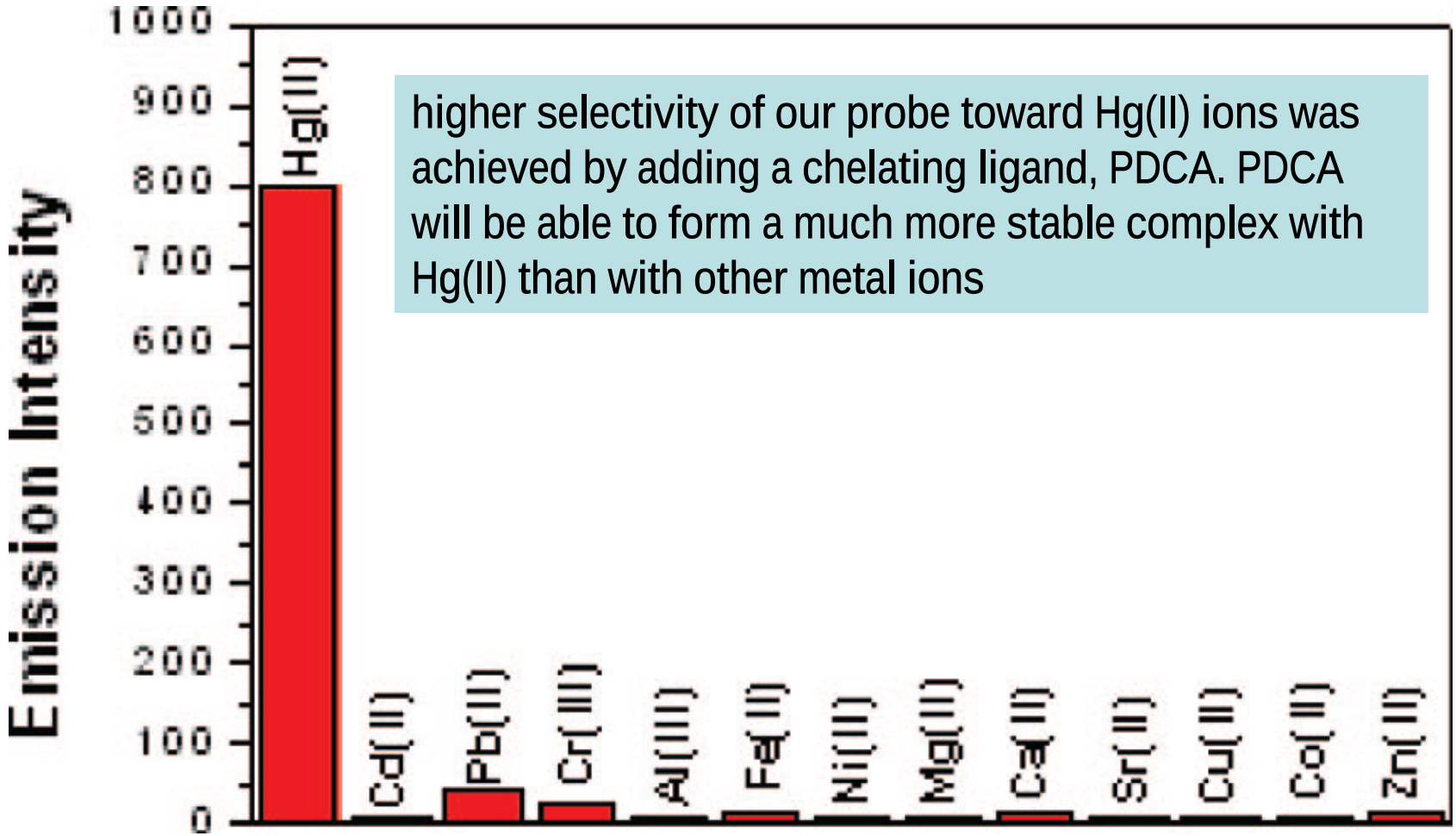
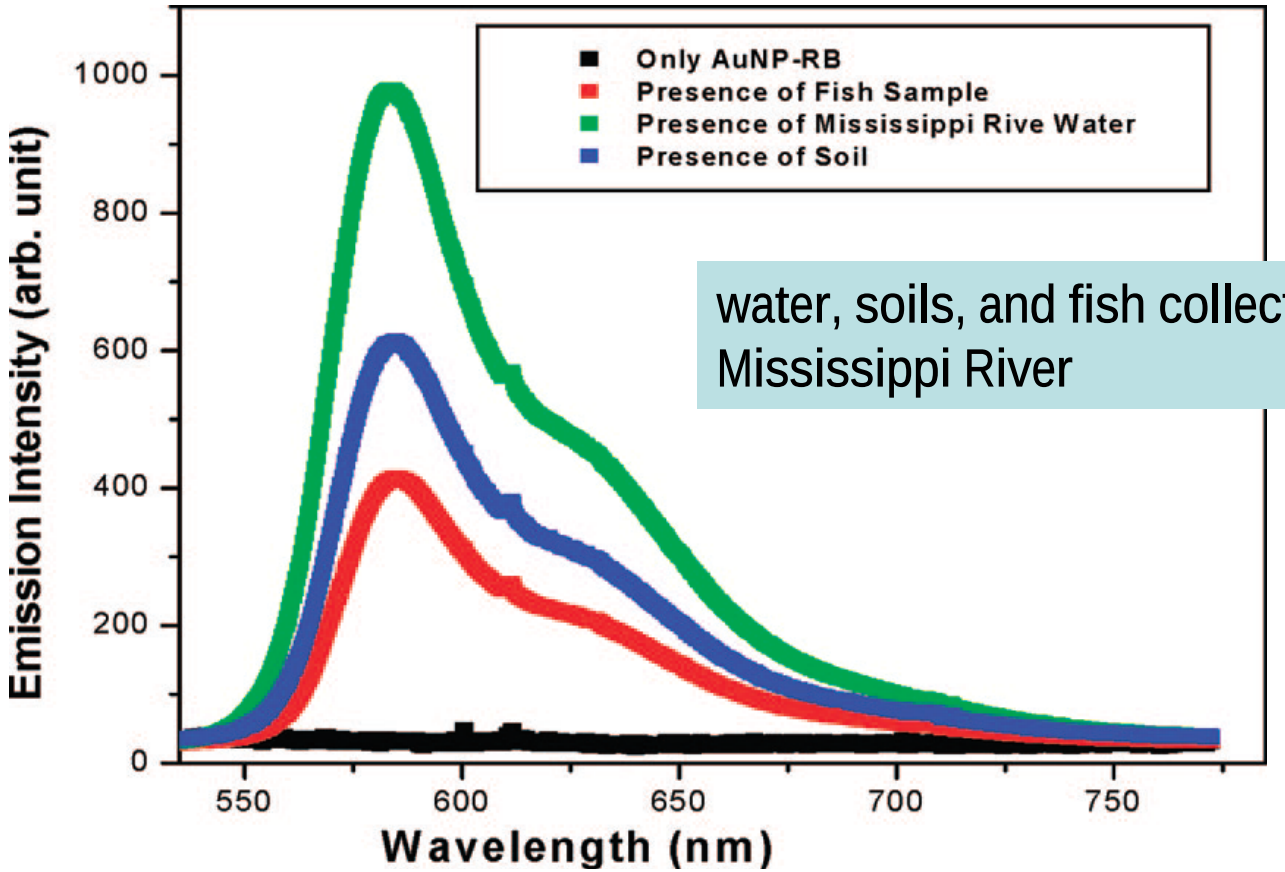


Figure 7. Fluorescence response upon the addition of 130 ppb of different metal ions on RhB-adsorbed gold nanoparticle–MPA–PDCA solution (5 nM).

NSET probe can detect Hg(II) ions from environmental samples



water, soils, and fish collected from the Mississippi River

Figure 8. Fluorescence response of RhB-adsorbed 5 nM gold nanoparticle–MPA–PDCA solution in the absence and in the presence of different environmental samples (fish, water, and soil) of the same amount.

the mercury level in the Mississippi River is quite high and the level of mercury in drinking and tap water samples is much less than the EPA limit of 2 ppb

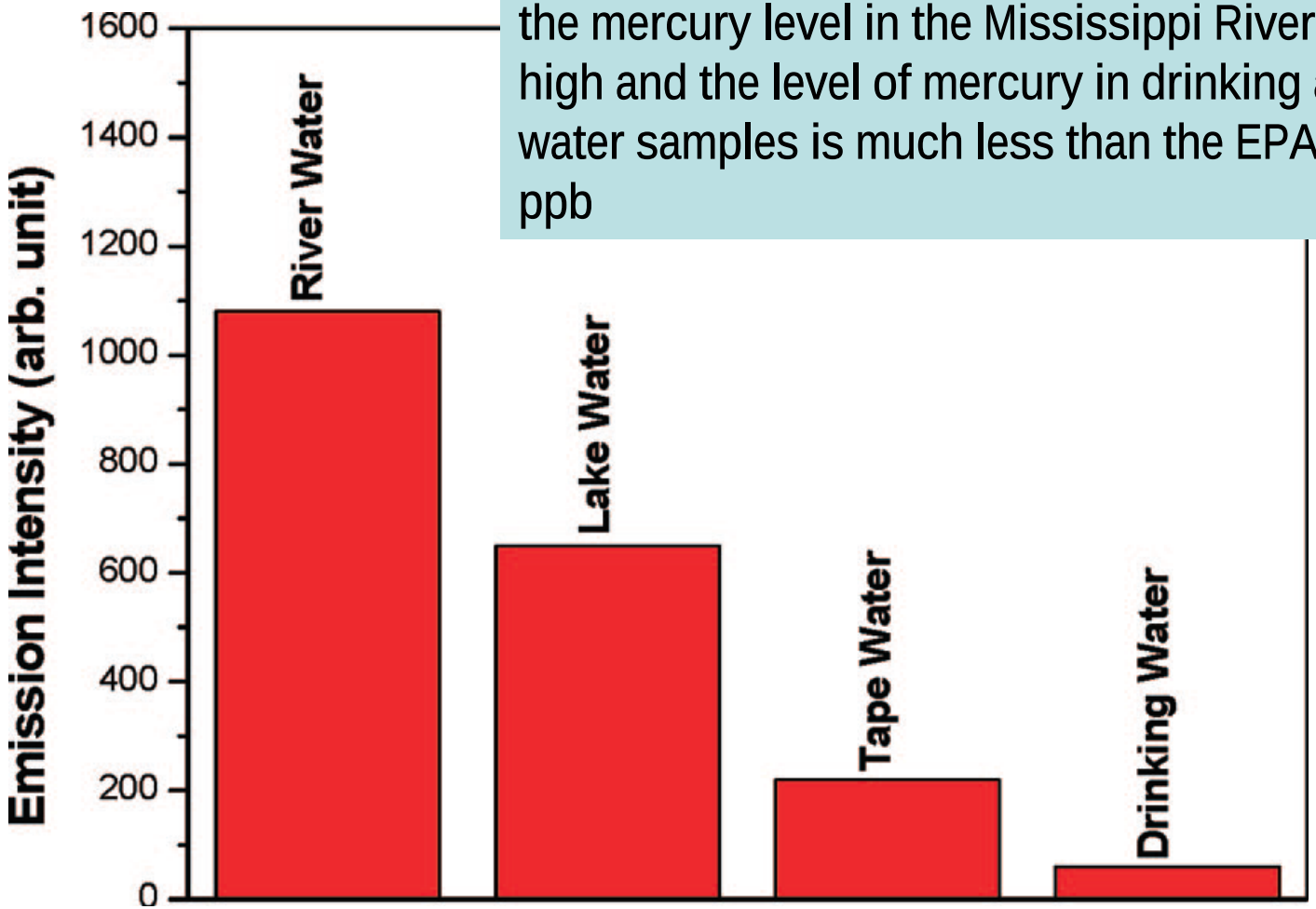


Figure 9. Fluorescence response of RhB-adsorbed 5 nM gold nanoparticle–MPA–PDCA solution upon the addition of water samples (300 L) from different sources.

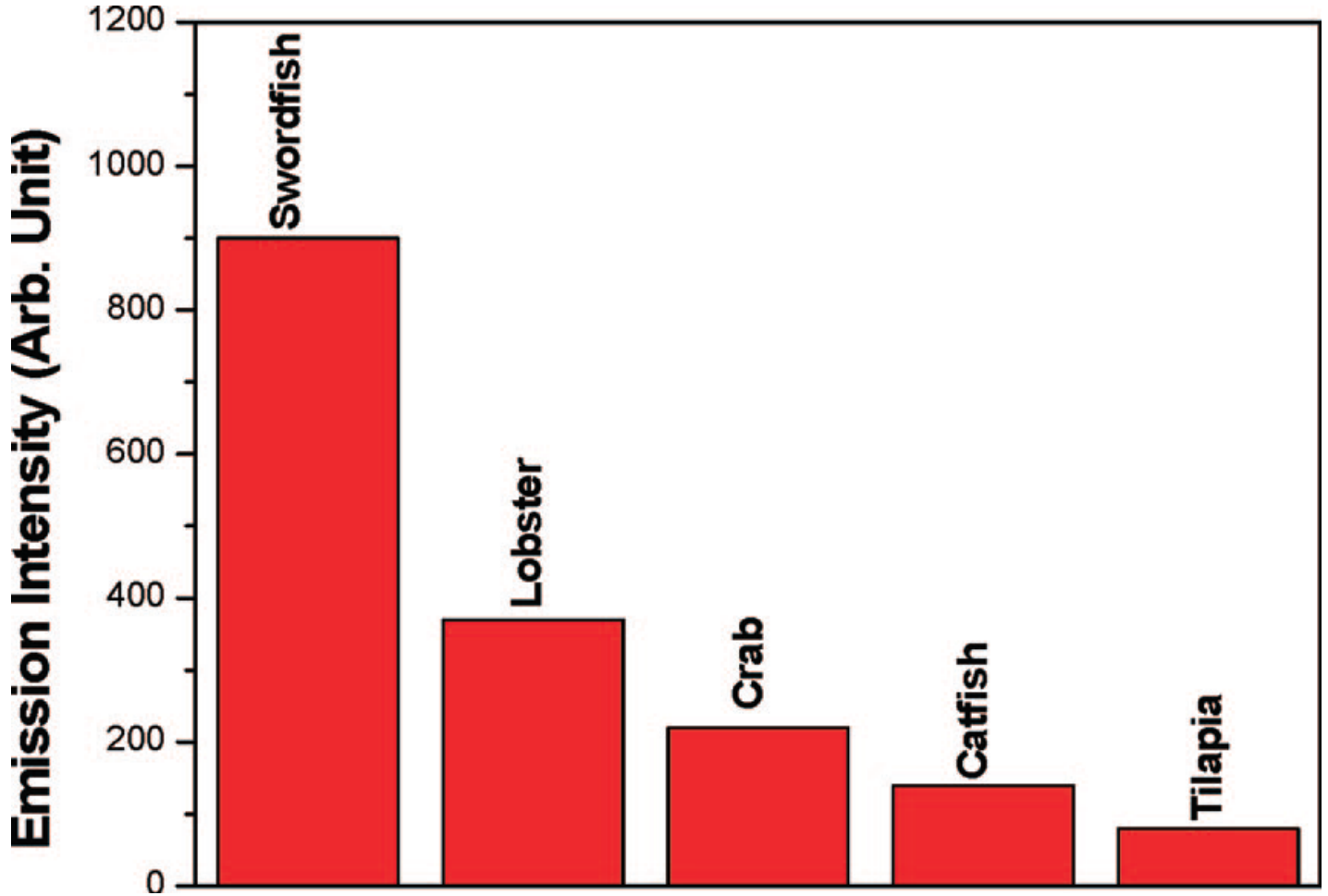


Figure 10. Fluorescence response of RhB-adsorbed 5 nM gold noparticle–MPA–PDCA solution upon the addition of different fish samples in the same amounts (100 g).

Conclusion

In conclusion, in this article we have reported a miniaturized, inexpensive, and battery-operated ultrasensitive gold nanoparticle-based NSET probe for screening mercury levels in soil, fish, and water with excellent sensitivity (2 ppt) and selectivity for Hg(II) over competing analytes.

Our probe exhibits the largest fluorescenceenhancement to date for sensing Hg(II) in water. Furthermore, the sensitivity of our probe to detect mercury levels in soil, water, and fish is about 2–3 orders of magnitude higher than the EPA standard limit.

We have shown that our probe is suitable to screen the amount of mercury in different fish, shellfish, and water samples from various commercial sources.

Though we have demonstrated this only for soil, water, and fish samples, we believe that our probe provides a useful starting point for the development of a practical nanosensor for screening mercury from a wide range of biological, toxicological, and environmental samples.