Electronic Supplementary Information


Nanoparticles as scaffolds for FRET-based Ratiometric Detection of Mercury Ions in Water with QDs as Donors

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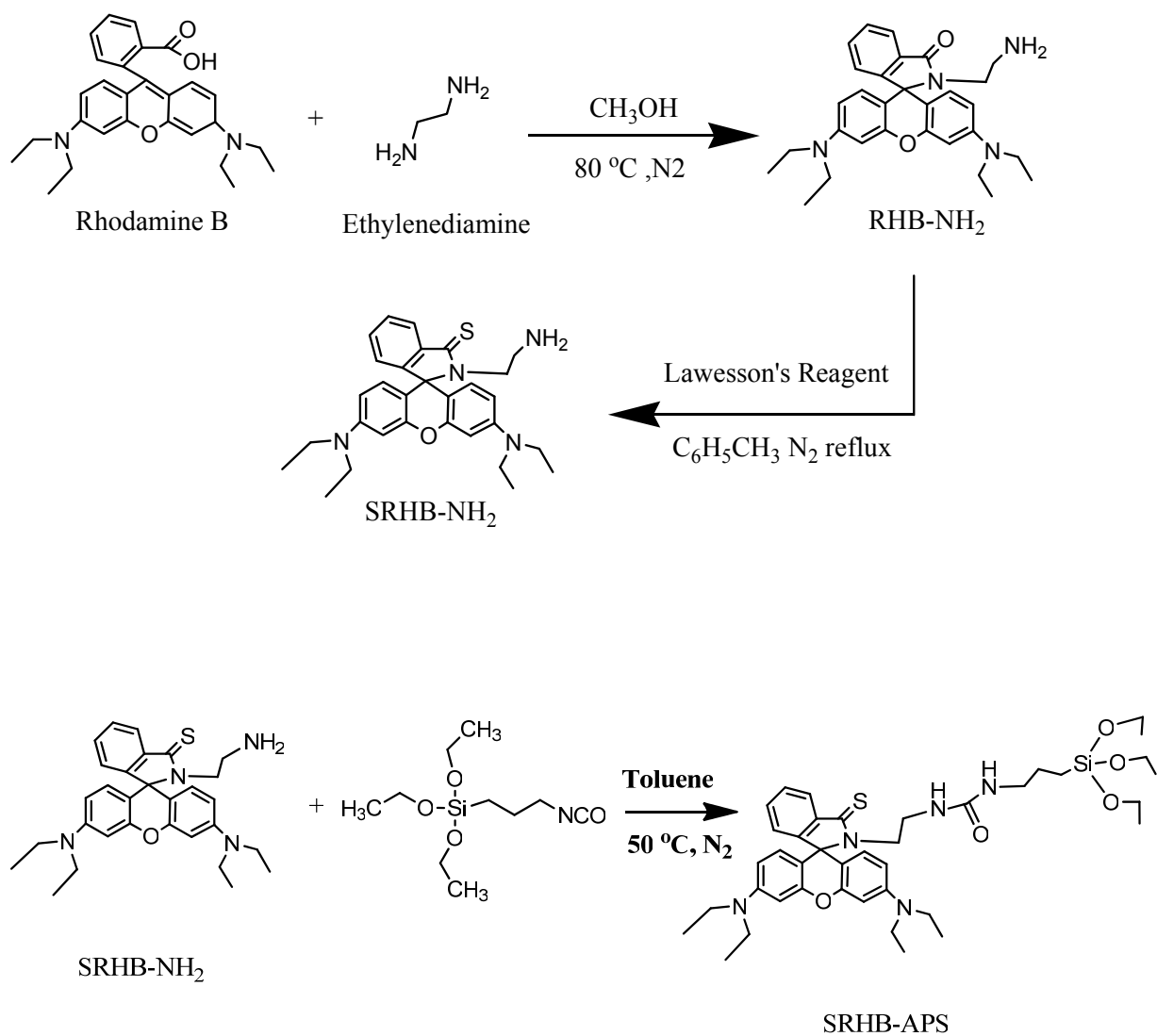
Scheme S1. Synthetic route of the Hg^{2+} probe (SRhB-NH$_2$) and ethoxysilane-linked probe (probe precursor).
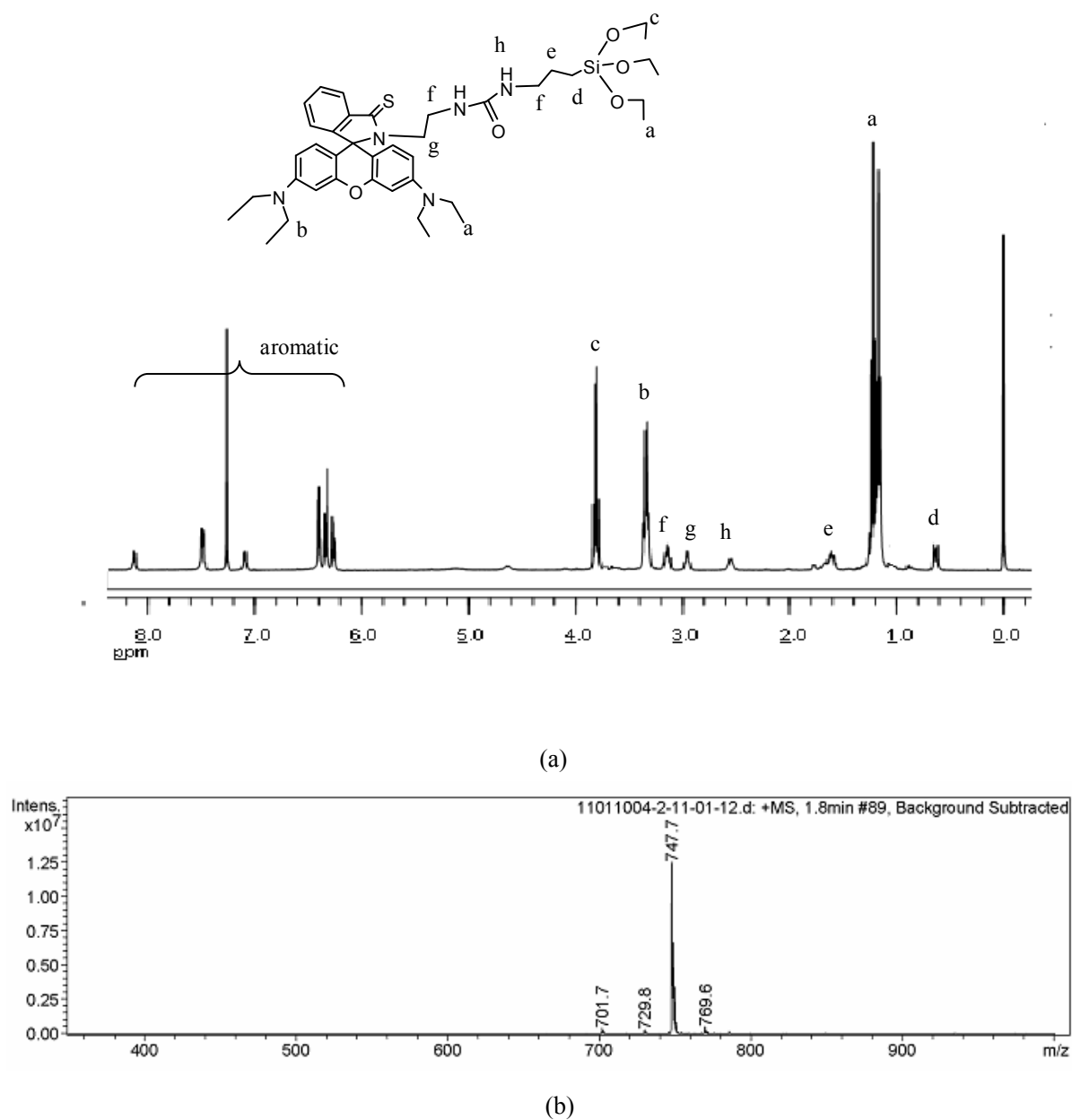
(a)

(b)

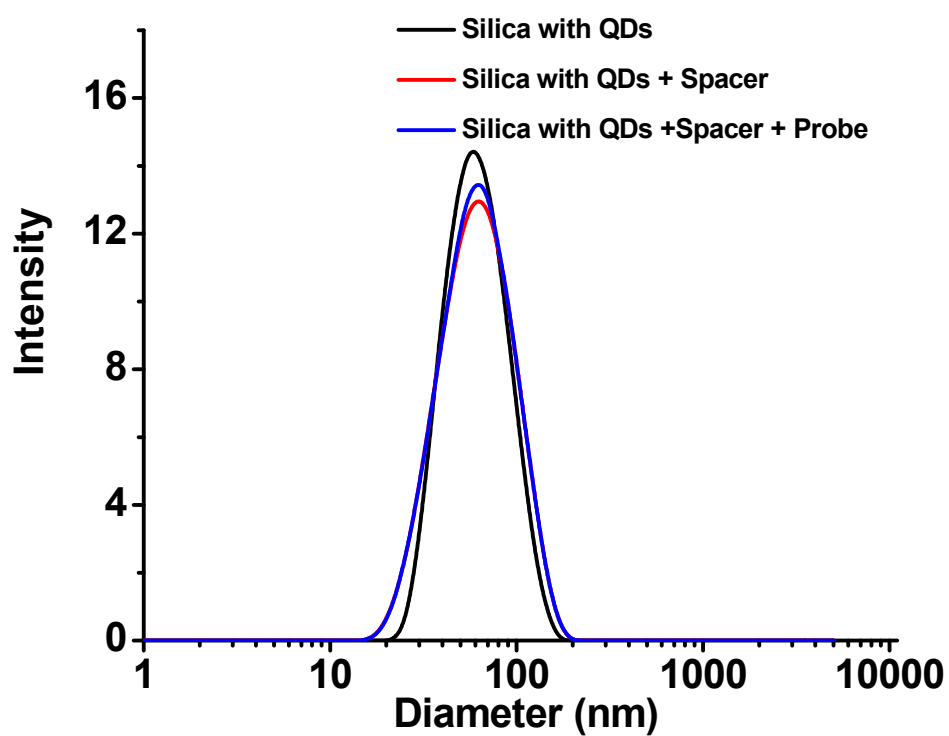**Fig. S1.** ^{1}H NMR and MS spectra for probe precursor.

Fig. S2. Diameter distribution for QDs/silica composite NPs at different synthesis stages. From the distribution curves, the averaged diameters for the particles were calculated as 58 nm, 61 nm and 61 nm. Coating a probe layer onto the Qds/silica particles could not cause detectable increase in the particle diameter. The thickness of the spacer layer can thus be estimated as 1.5 nm.
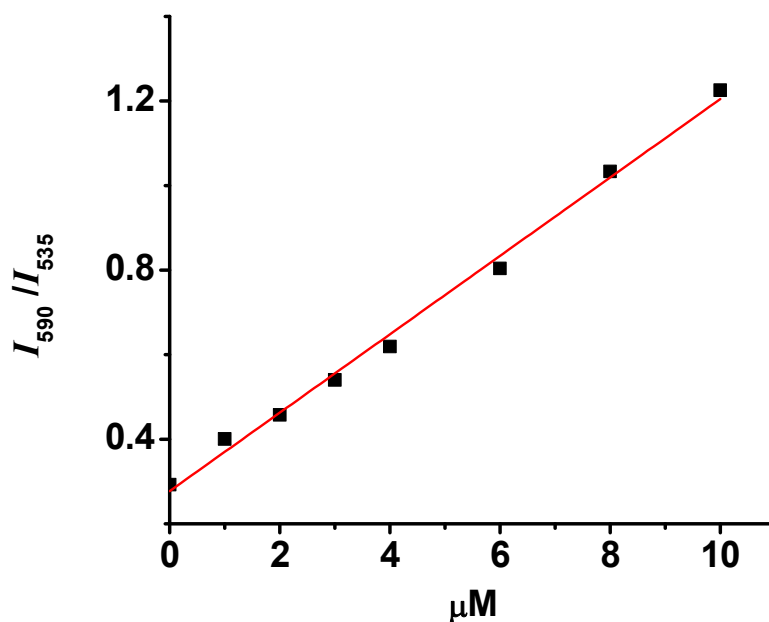
Fig. S3. The fluorescence intensity ratio of QDs-based sensor (probe concentration: 5.6×10^{-5} M) as a function of Hg(II) concentration in pH 7.0 HEPES buffered water. Hg(II) concentration: 0 - 10 μM. (λexc = 410 nm).

The method for determining the detection limit (LOD):
First the calibration curve was obtained from the plot of fluorescence intensity ratio, I_{590}/I_{535}, as a function of the analyte concentration (Hg^{2+}). The regression curve equation was then obtained.
The detection limit $= 3 \times S.D./k$
where k is the slope of the curve equation, and S.D. represents the standard deviation for intensity ratio of the sensor dispersion in the absence of mercury ion.

$I_{590}/I_{535} = 0.28 + 9.3$ E5 [Hg(II)] (R = 0.997)
LOD $= 3 \times 0.082 / 9.3$ E5 $= 260$ (nM)

References:
V. Thomsen, D. Schatzlein, D. Mercuro, *Spectroscopy* **2003***, 18,* 112-114.
A. D. McNaught, A. Wilkinson, *IUPAC Compendium of Chemical Terminology,*
1997.

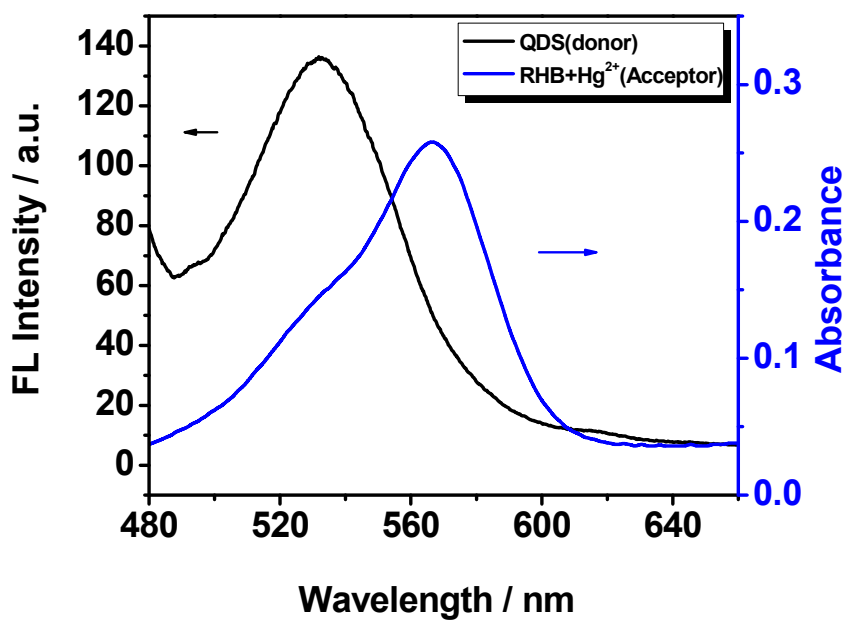**Fig. S4.** Overlap of QDs' emission band and acceptor's (RhB+Hg^{2+}) absorption band for the QDs/silica composite system.
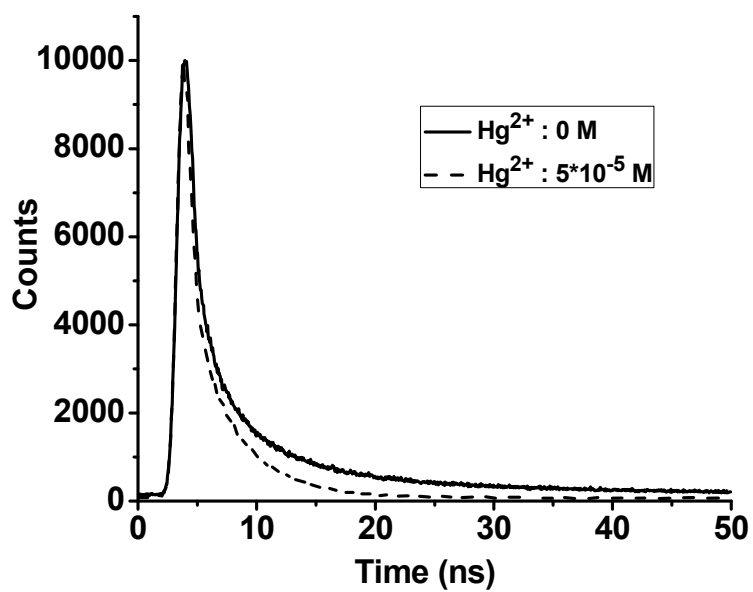
Fig. S5. Fluorescence intensity decay curves for CdTe QDs in the composite NPs with or without Hg^{2+}.

Calculation of Förster Critical Radius (R_0) [1-3]

Calculation of the Förster radii (R_0) [1-3]

The Förster's distance or critical distance R_0 is the characteristic distance, at which the efficiency of energy transfer is 50%. The magnitude of R_0 is dependent on the spectral properties of the donor and the acceptor molecules. If the wavelength λ is expressed in nanometers, then $J(\lambda)$ is in units of $M^{-1}cm^{-1}nm^4$ and the Forster distance, R_0 in angstroms (Å), is expressed as follows [Eq. (1)]:

$$R_0 = 0.2108 \times \left[\kappa^2 \times \Phi_D \times n^{-4} \times J(\lambda)\right]^{1/6} \quad \text{[Eq. (1)]}$$

K^2 is the orientation factor for the emission and absorption dipoles and its value depends on their relative orientation, n is the refractive index of the medium and Φ_D is the quantum yield of the donor. $J(\lambda)$ is the overlap integral of the fluorescence emission spectrum of the donor and the absorption spectrum of the acceptor (Figure S4) [Eq. (2)].

$$J(\lambda) = \int_0^\infty F_D(\lambda) \times \varepsilon_A(\lambda) \times \lambda^4 \times d\lambda \quad \text{[Eq. (2)]}$$

$F_D(\lambda)$ is the fluorescence intensity of the donor in the absence of acceptor normalized so that $\int_0^\infty F_D(\lambda)d\lambda = 1$; $\varepsilon_A(\lambda)$ is molar extinction coefficient of the acceptor, λ is wavelength. In current experimental conditions, for QD containing dispersion system, the $J(\lambda)$ was calculated to be 1.3×10^{14} $M^{-1}cm^{-1}nm^4$. The Förster distance (R_0) has been calculated assuming random orientation of the donor and acceptor molecules taking $K^2 = 2/3$, $n = 1.54$ (silica), and determined $\Phi_D = 0.20$.

For QD (donor) and SRhB/Hg^{2+} (acceptor) in current experimental situation, by using a commercial software Origin 8.0 as the integral tool, we calculated $R_0 = 24.0$Å. Energy transfer will be effective for 12.0 Å$\le d \le 36.0$ Å ($R_0 \pm 50\% R_0$).

Reference:

(1) Gouanve, F.; Schuster, T.; Allard, E.; Meallet-Renault, R.; Larpent, C. *Adv. Funct. Mater.* **2007**, *17*, 2746-2756.

(2) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*: Plenum, New York, 1999.

(3) Valeur, B. *Molecular Fluorescence: Principles and Applications*: Wiley-VCH**:** NewYork, **2002.**

Estimation of number of QDs per silica nanoparticle:

The number of QDs per silica particle was estimated according to the following steps:

1. The diameter of CdTe QDs was estimated according to the following empirical fitting function: [1,2]

$$D = (9.8127 \times 10^{-7}) \lambda^3 - (1.7147 \times 10^{-3}) \lambda^2 + (1.0064) \lambda - 194.84 \quad \text{[Eq. (3)]}$$

Where D (nm) is the diameter of CdTe QDs and λ (nm) is the wavelength of the first absorption peak of the sample (in this study $\lambda = 514$ nm, for aqueous solution of QDs), and D was estimated as 2.69 nm.

2. Determination of total number of QDs:

Based on the weight of dried QD, the concentration for the QD solution (the stock solution for preparing QDs/silica NPs) was determined as 3.22×10^{-2} M. During the synthesis of QDs/silica NPs, 0.4 ml of QD stock solution was added into the medium, and the total weight of QDs can be determined as 3.09×10^{-3} g, and total volume of QDs was determined as 4.5×10^{-4} cm^3 (density of CdTe: 6.8 g/cm^3). Then, total number of QDs was estimated as 4.41×10^{16}.

3. Estimation of number of QDs per silica NP

Upon dialysis and drying, the weight of silica NPs was determined as 0.134 g. The total number of silica NPs was then determined (based on their average diameter of 61 nm) as 5.13×10^{14}. Thus, the average number of QDs per silica NP was finally estimated as 86.

References:

1. W.W. Yu, et al., *Chem. Mater.*, 2003, **15**, 2854-2860.

2. W.W. Yu, et al., *Chem. Mater.*, 2004, **16**, 560-560.