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Electronic Supplementary Information

Lighting up the Gold Nanoparticles Quenched Fluorescence by Silver Nanoparticles: A Separation Distance Study

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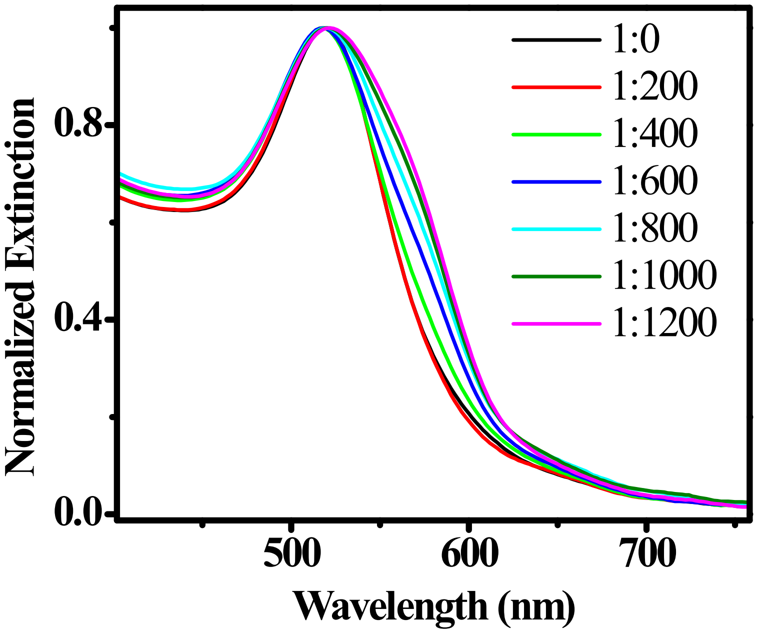

Figure S1 Normalized extinction spectra of Au-RiTC composites with various molar ratios of Au NP to RiTC.

Optimization of Molar Ratio of AuNP to RiTC

The optimal molar ratio of Au NPs to RiTC was determined by investigating the fluorescence intensity as a function of concentration of RiTC in the presence of Au NPs, which is plotted in Fig. S2a. The concentration of AuNPs was fixed at 0.5 nM. The fluorescence intensity increased slowly at lower RiTC concentrations (<0.5 μM) due to the superquenching effect by Au NPs.[1] In our study, lower concentration of RiTC (0.3 μM) was chosen in order to maintain a high RiTC bonding efficiency and meanwhile leave enough active bonding sites for Ag@SiO_2. The quenching efficiency is c.a. 96%, which is consistent with earlier reports.[2, 3]

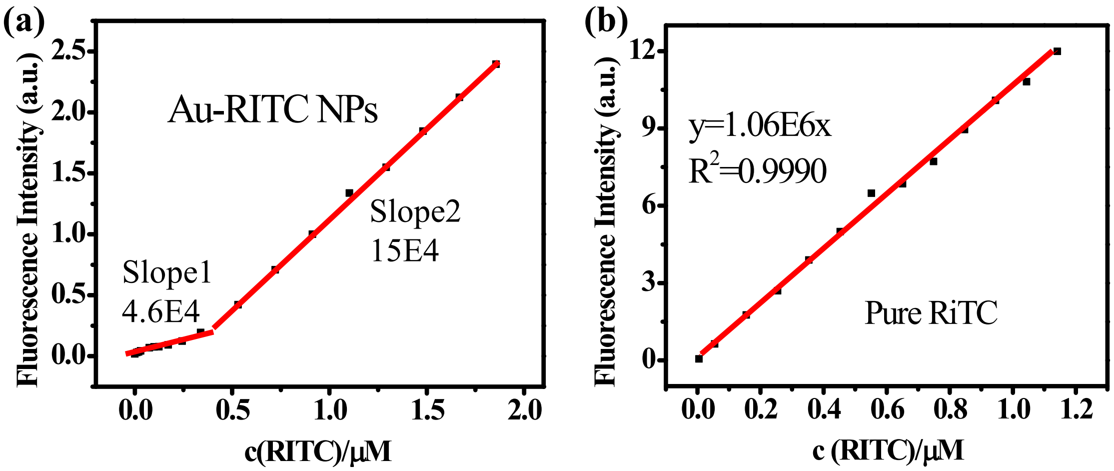

Figure S2 Fluorescence intensity of various concentrations of RiTC in solutions with (a) [Au NPs] = 0.5 nM, (b) [Au NPs] = 0 nM, which was monitored at 580 nm with λ_{EX} = 530 nm.

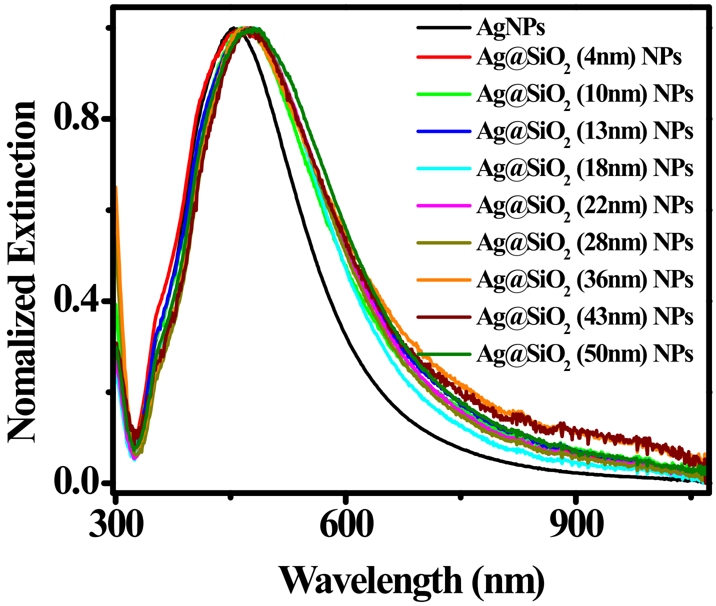

Figure S3 Normalized extinction spectra of silica-coated Ag NPs with different shell thickness.

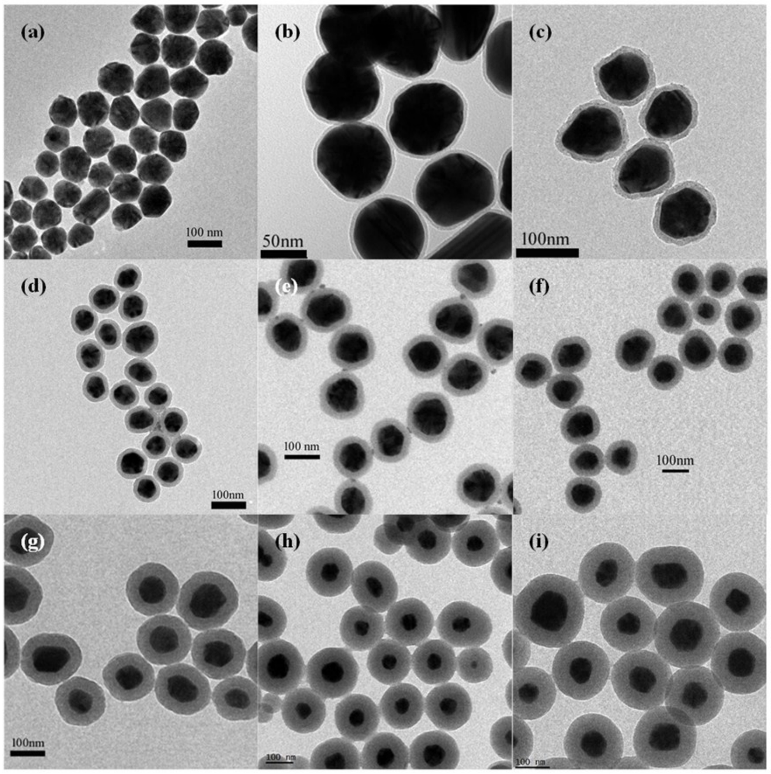

Figure S4 Large area TEM images of core-shell structures Ag@SiO_2 with silica shell thickness of 0 nm (a), 4 nm (b), 10 nm (c), 13 nm (d), 20 nm (e), 25 nm (f), 36 nm (g), 43 nm (h), 50 nm (i)

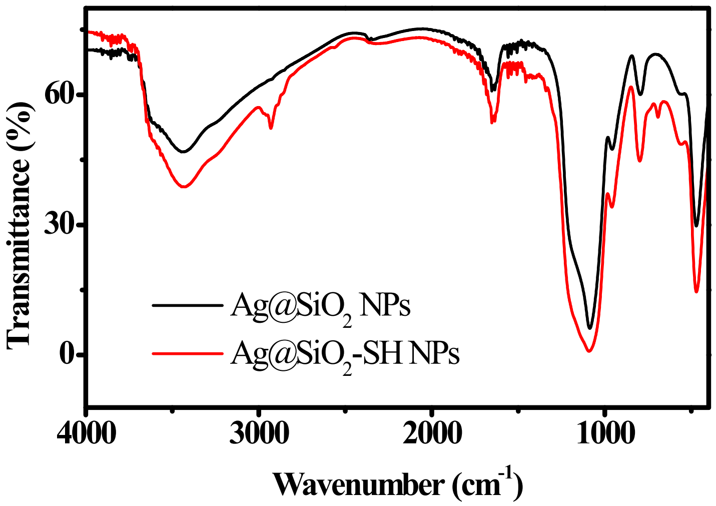

Figure S5 FTIR spectra of Ag@SiO_2 power before and after MPTMS condensation.

Characterization of -SH on SiO_2

The surface modification of thiol group was achieved by condensation of the siloxane groups with MPTMS to form a siloxane bond (Si-O-Si) ($-Si-OH + HS(CH_2)_3Si-OCH_3 \rightarrow -Si-O-Si-(CH_2)_3-SH + CH_3OH$). This surface modification was verified by FTIR analysis. The strong absorption peak at 1091 cm^{-1} in both spectra before and after MPTMS condensation is assigned to the asymmetric stretching vibrations of the Si-O-Si from silica shells. Peaks obtained at 468 cm^{-1}, 798 cm^{-1}, 1220 cm^{-1} originated from Si-O-Si are also associated with the formation of the condensed silica. Peak obtained at 3452 cm^{-1} appeared for O-H stretching of the surface silanol groups (Si-OH) before and after -SH modification, which indicates the as-prepared nanoparticles will be well dispersed in water and ethanol.

In thiol capped $Ag@SiO_2$, the presence of the mercaptopropyl groups in the sample is evidenced by observation of a new peak obtained at 2929 cm^{-1} which is attributed to C-H stretching vibrations. S-H stretches were found at about 2550 cm^{-1}, which are typically very weak and convoluted by contamination of the CO_2 stretching bands from the background.[4]

Two-Photon Photoluminescence Measurements of Coupled Nanostructures

Two-photon photoluminescence (2PPL) measurements were performed by using a femtosecond Ti: sapphire oscillator (Avesta TiF-100M) with output laser pulses centered at 820 nm and average power of 100 mW as the excitation source. The laser pulses have pulse duration of 100 fs and repetition rate of 84.5 MHz. The laser beam was focused onto the sample that was contained in a cuvette with path length of 1.0 cm. The increased two-photon photoluminescence of $Ag@SiO_2$-Au-RiTC NPs upon the attaching the Au-

RiTC NPs to the surface of Ag@SiO_2 NPs confirmed Plasmon coupling interactions between the core Ag NP and surrounding Au NPs within each Ag@SiO_2-Au-RiTC NPs.

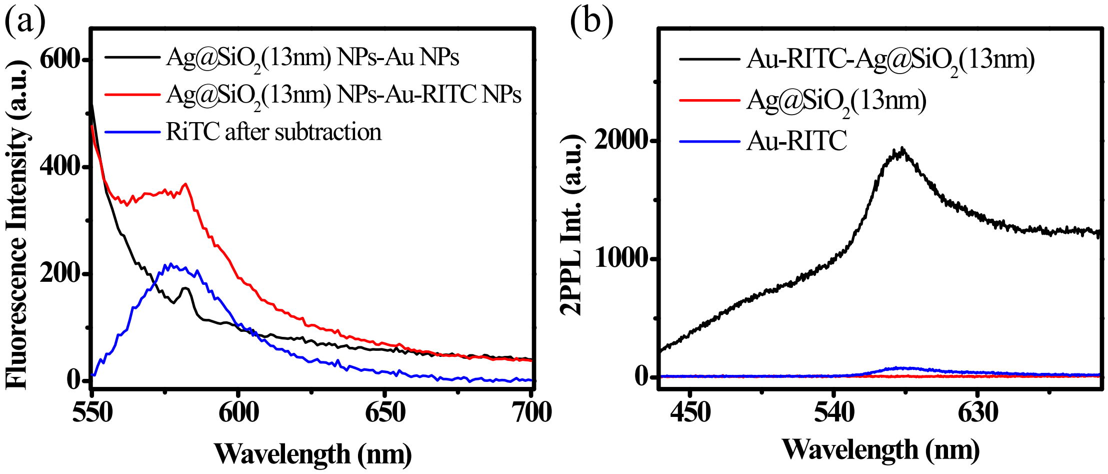

Figure S6 (a) Emission spectra of Ag@SiO_2(13nm)-Au-RiTC NPs (red curve), Ag@SiO_2(13nm)-Au NPs (black curve) and emission intensity difference between these two composites; (b) Two-photon photoluminescence (2PPL) of Au-RiTC NPs (blue), Ag@SiO_2(13nm)-SH NPs (red) and Ag@SiO_2(13nm)-Au-RiTC NPs (black).

DTT Treatment

The particle phase and solution phase were separated after formation of Ag@SiO_2-Au-RiTC NPs. The fluorescence intensity of the solution state is negligible, as shown by the black curve in Fig. S7, which indicating that no RiTC molecules were detached from the Au NR surface during the treatment. We further utilized DTT treatment to quantify the number of molecules bound to the surface of Au NPs due to the strong affinity between Au and thiol groups of DTT. The sediment was re-dispersed into the solution before adding DTT to detach RiTC from the surface of Au NPs. The particle phase was removed by centrifugation and the fluorescence of the rest solution was measured. The fluorescence of the solution is comparable to that of control (the same amount of free RiTC), which means the amount of RiTC detached from Au NPs during the binding interactions with Ag@siO2 is negligible.

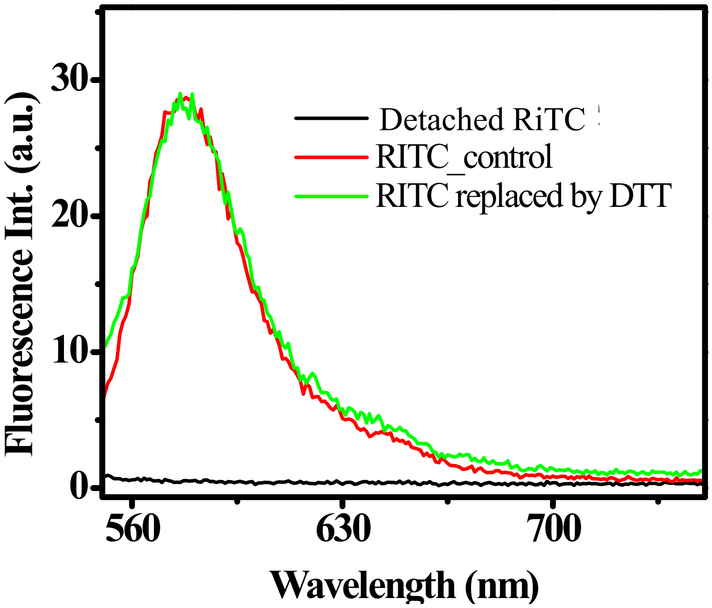

Figure S7 Investigation of free RITC in Ag@SiO$_2$-Au-RiTC NPs dispersion.

Fluorescence Lifetime measurement

Fluorescence lifetime measurements of different samples were carried out using a time-correlated single photon counting (TCSPC) method. The second harmonic generation of an Avesta TiF-100M femtosecond Ti:sapphire oscillator with output laser pulse at 810 nm give laser pulses at 405 nm, which was used the excitation source. Emission from the sample at 580 nm was collected at 90° angle with respect to the excitation beam by an optical fiber that was connected to a monochromator (Acton, Spectra Pro 2300i) coupled photomultiplier tubes (PMT) (PicoQuant, Berlin, Germany). The fluorescence signals were processed by a TCSPC module (PicoQuant, PicoHarp 300) with an instrument response function of 100 ps. The spectral resolution was set as 10 nm and full-width at half-maximum (FWHM) of the instrument response function (IRF) is c.a. 200 ps, which gives a temporal resolution of c.a. 100 ps after deconvolution. The signals were processed by a TCSPC module (PicoQuant, PicoHarp 300). Rhodamine B was chosen as the reference to test the lifetime measurement. Rhodamine B gives a longer lifetime about

2.94 ns in ethanol and a short fluorescence lifetime about 1.64 ns in water, which is excellently agreed with the early report.[5] Long living emission of pure RiTC in methanol is characterized by a lifetime of 2.44 ns. In aqueous, RiTC shows a short living emission with a lifetime about 1.49 ns.

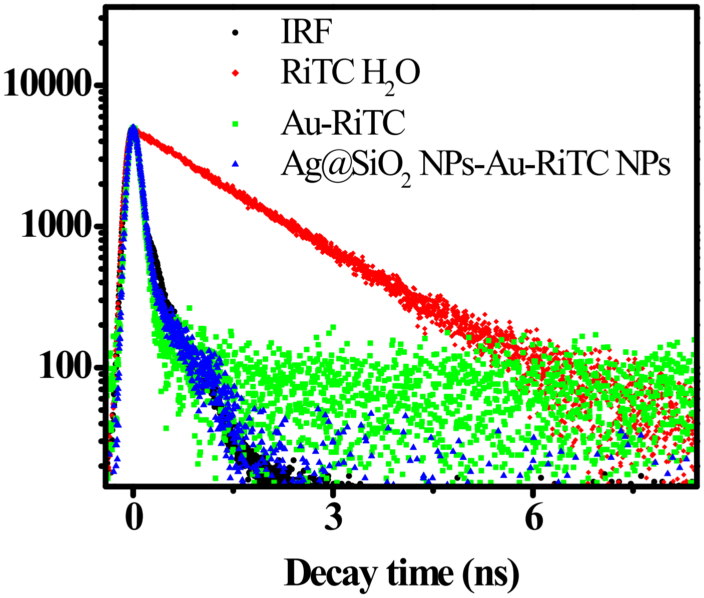

Figure S8 Time-resolved fluorescence intensity decays of Au-RiTC NPs and Au-RiTC-Ag@SiO$_2$ NPs and free RiTC dye molecules in aqueous solution.

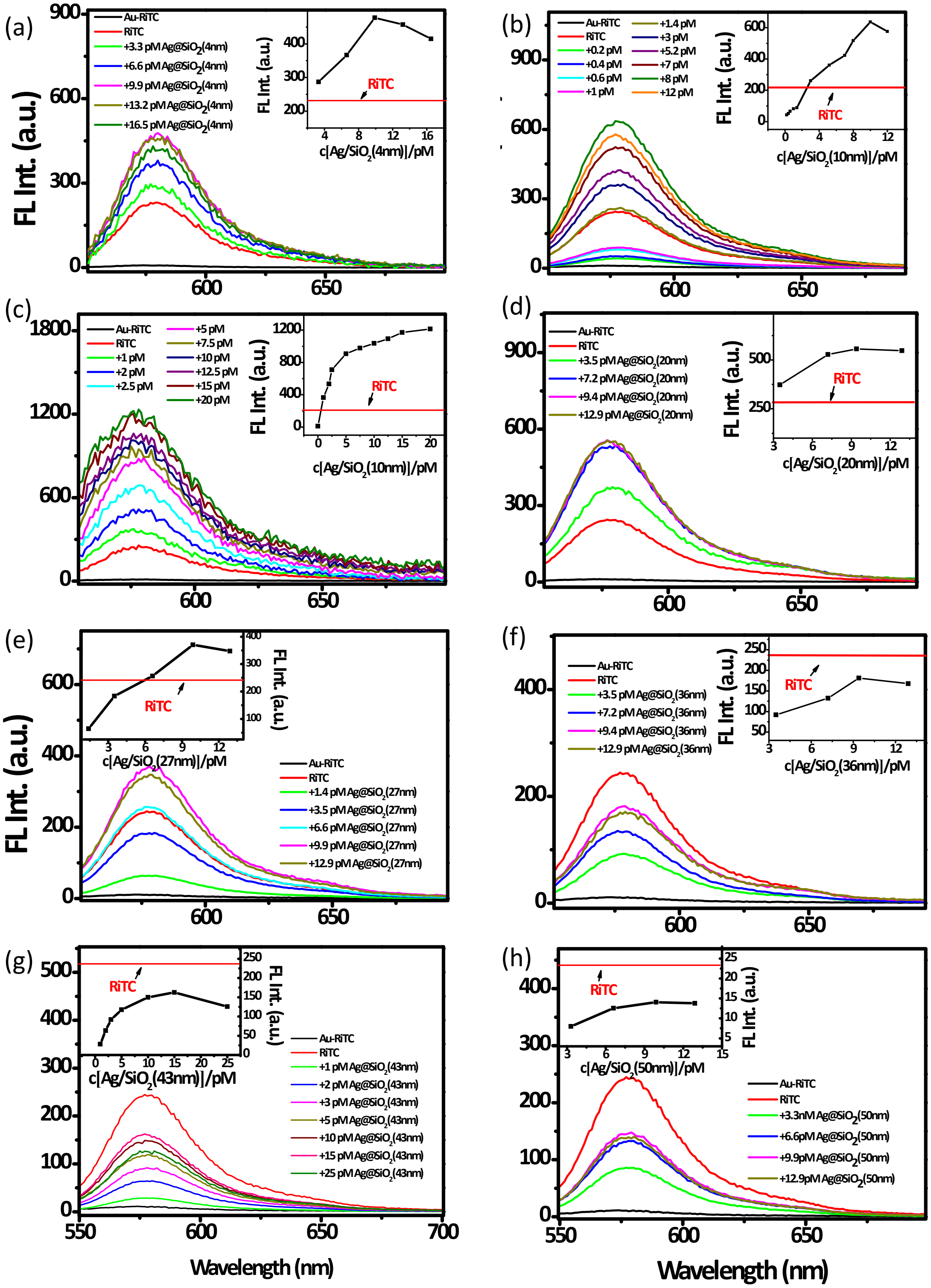

Figure S9 Fluorescence recovery/enhancement of Au-RiTC NPs with various concentrations of Ag@SiO$_2$ NPs at different separation distances: 4 nm (a), 10 nm (b), 13 nm (c), 20nm (d), 25 nm (e), 36 nm (f), 43 nm (g) and 50 nm (h).

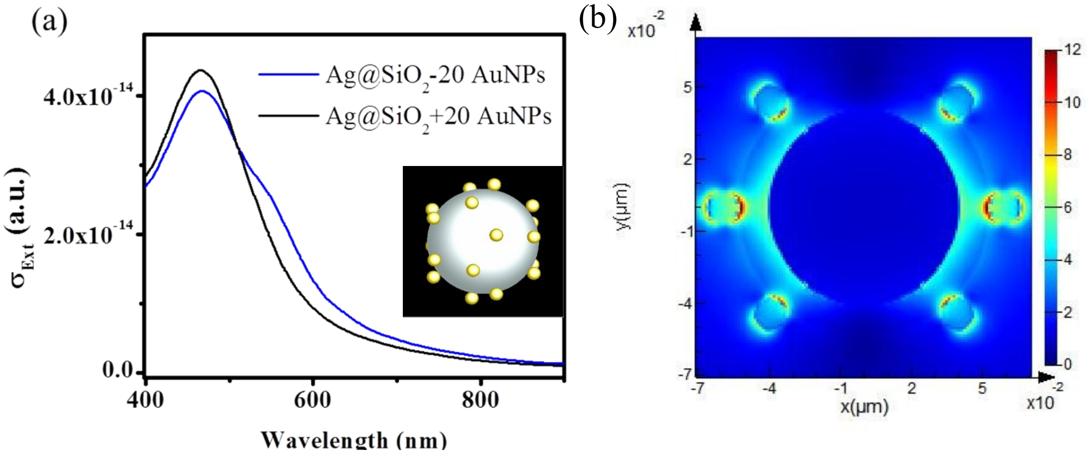

Figure S10 (a) Simulated extinction spectra of coupled Ag@SiO$_2$-Au NPs (blue curve) structure compared to that w/o coupling with molar ratio of Au:Ag = 20 :1. (b) Simulated electrical field profile at 530 nm around the coupled nanostructure.

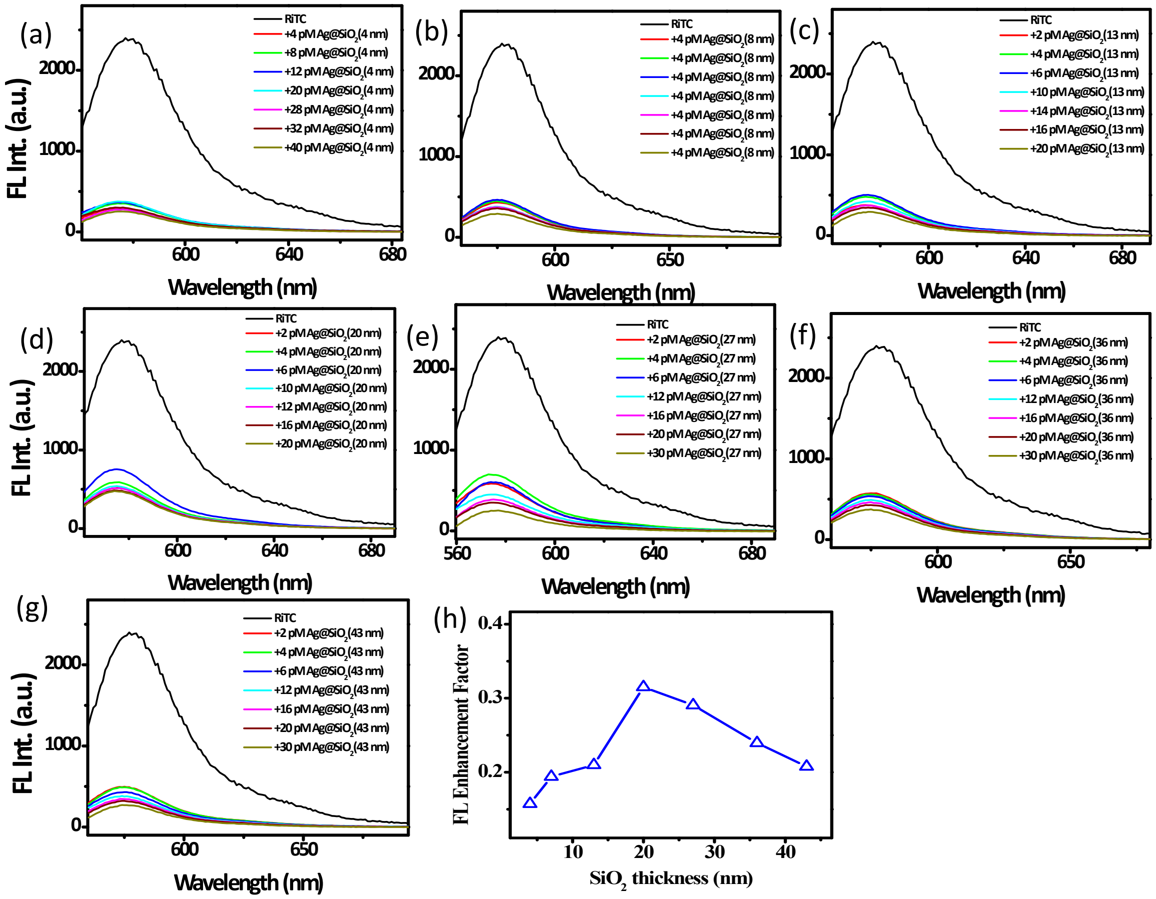

Figure S11 (a-g) Fluorescence spectra of RiTC upon gradual addition Ag@SiO$_2$ with different SiO$_2$ thickness: 4 nm (a), 10 nm (b), 13 nm (c), 20nm (d), 25 nm (e), 36 nm (f), and 43 nm (g). The optimum fluorescence intensity of Ag@SiO$_2$ - RiTC for different SiO$_2$ thickness with respect of free RiTC are summarized in (h).

References

1. Z. Guan, L. Polavarapu and Q.-H. Xu, *Langmuir*, 2010, **26**, 18020-18023.
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4. P. Bladon, *Org. Magn. Resonance*, 1969, **1**, 277-277.