Aggregation Induced Emission Enhancement by Plasmon Coupling of Noble Metal Nanoparticles

Jiangling He,^{a,b} Shuang Li,^c Da Lyu,^{a,b} Dingfeng Zhang,^c Xiao Wu,^c and Qing-Hua Xu*a,^b

^aDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543 ^bNational University of Singapore (Suzhou) Research institute, Suzhou 215123, P. R. China ^cInstitute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China



Figure S1 Absorption and fluorescence spectra of RiTC aqueous solution.



Figure S2: Extinction spectra of Au@Ag NPs and Au@Ag-RiTC NPs with different Ag shell thicknesses. Ag shell thicknesses is 0 nm (a), 1.3 nm (b), 2.1 nm (c), 3.2 nm (d), 4.5 nm (e), and 5.6 nm (f).



Figure S3 (a-c) and (d-f) Typical TEM images of monodisperse Au-RiTC NPs and aggregated Au-RiTC NPs at different magnifications, respectively.



Figure S4 FT-IR spectra of (a-b) Au-RiTC NPs and (c-d) Au@Ag(5.6 nm)-RiTC NPs before and after aggregations, respectively.



Figure S5 (a) and (c) Emission spectra of as-prepared Au@Ag(5.6 nm)-RiTC sample after introduction of cysteine molecules at various pH values and various NaCl concentrations (mol/L), respectively. (b) and (d) Integrated fluorescence intensity of this sample versus pH values and versus [NaCl], respectively.



Figure S6 (a) Simulated electric field of Au@Ag NPs with shell thicknesses of 0, 1.3, 2.1, 3.2, 4.5, and 5.6 nm from bottom to top. (b) and (c) Simulated electric field of Au NPs (19 nm) and Au@Ag(5.6 nm) NPs monomer, dimmer, trimer, and tetramer, respectively. The wavelength of 520 nm was chosen to mimic the experimental results.

Finite-Difference Time-Domain (FDTD) simulation: The numerical simulations were conducted by Lumerical FDTD solution. The optical materials of Au and Ag were taken from Au (Gold)-Palik and Ag (Siliver)-Palik (0-2 μ m), respectively. The gap between metal NPs was 1 nm. The background refractive index was set to 1.0 representing aqueous solution, and Boundary condition was stretched coordinate PML, Total-field Scattered-field Source (TFSF Source) was used as source.



Figure S7 (a)-(f) Exhibit fluorescence lifetime curves of free RiTC, isolated Au@Ag-RiTC NPs and coupled Au@Ag-RiTC NPs with different Ag shell thicknesses: 0 nm (a), 1.3 nm (b), 2.1 nm (c), 3.2 nm (d), 4.5 nm (e), and 5.6 nm (f).



Figure S8 (a) Fluorescence emission spectra of Au@Ag-RiTC NPs solution upon addition of different concentrations of cysteine in the low concentration range. Inset is the corresponding enhancement factor I/I₀ versus [cysteine], where I₀ and I represent the fluorescence intensity of Au@Ag-RiTC NPs without and with addition of cysteine. (b) Emission spectra of as-presented method to couple Au@Ag-RiTC NPs with addition of different coupling agents. All these measurements were conducted in the laboratory tap water.

Ag shell thickness (nm)	0	1.3	2.1	3.2	4.5	5.6
Quenching ratio	8.1	5.8	4.6	5.6	5.8	5.9
Compared to free RiTC	3.0	5.6	6.8	7.1	7.3	7.6
Compared to pre-quenched	24.3	32.0	31.3	39.6	42.8	44.8

Table S1 Optimum enhancements factor of Coupled Au@Ag NPs with different Agshell (0, 1.3, 2.1, 3.2, 4.5, and 5.6 nm) versus pre-quenched and free RiTC molecules