Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Gold Nanoclusters-Based Light-Controlled Molecular Switch

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Materials. Chitosan (M_w=50000, D.D=95%) and $HAuCl_4 \cdot 4H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Mercaptoethylamine were purchased from Sigma-Aldrich. *N*-hydroxysuccinimide (NHS) was received from ACROS (New Jersey, USA). *N*-ethyl-*N*-[(dimethylamino)propyl] carbodiimide (EDC) were from Avocado Research Chemicals Ltd. (Lancashire, UK). While the carboxyl-containing spiropyran l-(b-carboxyethyl)-3(,3(-dimethyl-6-nitrospiro(indoline-2(,2[2H-1] benzopyran) (referred to as SPCOOH) was synthesized according to a procedure reported in reference 1.

The water used in this work is double-distilled water, and other chemicals used here are of analytical reagent grade, used as received.

Synthesis of Au NCs: 1mL of chitosan solutions ($C_{chitosan}$=0.2mg/mL, Dissolved with HCl solution) and 50μL of $HAuCl_4$ solution(C_{HAuCl4}=0.02M) were mixed together, and added water to 50mL, then added the mixed solution to a hydrothermal reactor and sealed, heated at 90° for 12 hours.

The estimation of the concentration of the Au NCs: using the concentration of $HAuCl_4$ in the first preparation solution divide the number of atoms of the Au NCs, because the amount of Au_8 is the most in the as-prepared Au NCs, the number used here is 8.

Synthesis of the thiolated spiropyrans: The thiolated spiropyrans were synthesized according the following method: the carboxyl-containing spiropyran was first activated by 15 mM *N*-hydroxysuccinimide (NHS) and 50 mM *N*-ethyl-*N*′- [(dimethylamino)propyl]carbodiimide (EDC) in ethanol for 30 min, and then the activated spiropyrans were modified by adding equal amount of 50 mM mercaptoethylamine ethanol solution.

Preparation of molecular switch composed of the Au NCs and Spiropyran: Syntheses of spiropyran-bound Au NCs were carried out by mixing desired ratios of the thiol-containing spiropyran (SP) ethanol solution and the Au NCs aqueous solution, and stirred for two days under dark. And the SP/Au NCs mixed solutions were dialyzed against ethanol for 2 times, and stocked for future use under dark at 2~8 ^{o}C.

Instrumentation: Fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. UV-visible spectra were recorded with a Perkin-Elmer Lambda 25 instrument.

UV-vis spectrum of the chitosan-stabilized Au NCs:

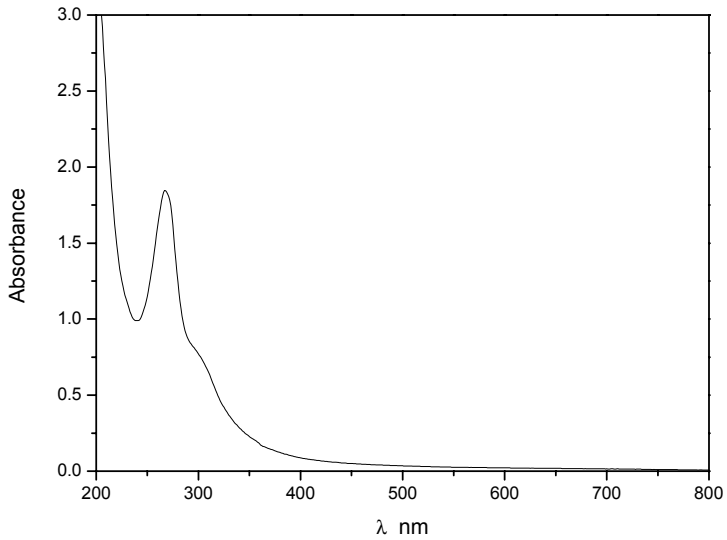

Figure S1. UV-vis spectrum of aqueous solution of chitosan-stabilized Au clusters.

Overlap of the emission and absorption spectra of the donor (Au NCs) and acceptor (the open-ring state McH):

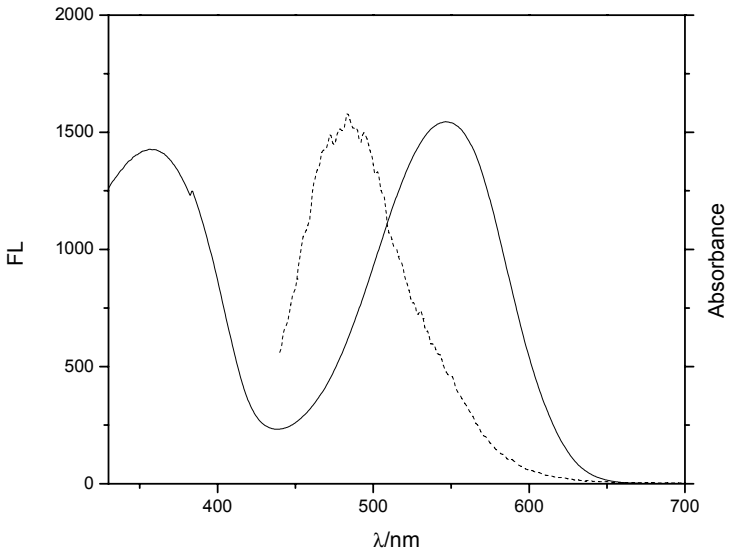

Figure S2. The Fluorescence spectrum when excited at 420 nm of Au NCs (Dashed) and the Uv-vis absorption spectrum of McH (Solid) in the ethanol.

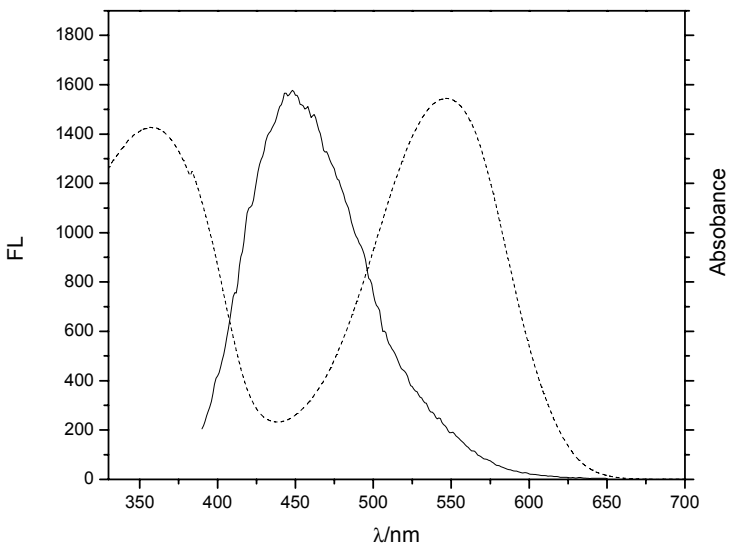

Figure S3. The Fluorescence spectrum when excited at 370 nm of Au NCs (Solid) and the UV-vis absorption spectrum of McH (Dashed) in the ethanol.

Data supporting FRET process:

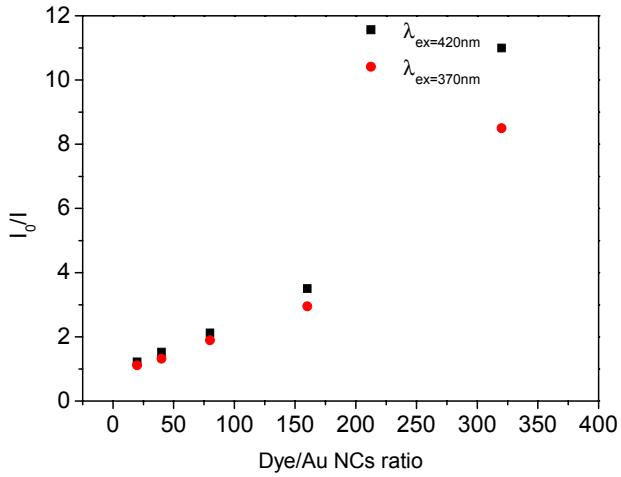

Figure S4. The dependence of observed quenching efficiency of the Au NCs in the hybrid system upon the amounts of bound spiropyran when excitation at 370 nm and 420 nm respectively.

Figure S4 is the dependence of observed quenching efficiency of the Au NCs in the hybrid system upon the amounts of bound spiropyran when used 370 nm and 420 nm wavelength to excite. As can be seen, with increase of the concentration of the dye, the quenching efficiency is increased, and about 320 bound dye molecules were required to attain maximal quenching. At the same time, it can be found that the quenching efficiency when exciting with 370nm wavelength is always lower than that using 420 nm wavelength to excite. The fluorescence emission when excitation at 370 nm of the Au NCs should mostly come from Au_8, while most of the fluorescence emission of the Au NCs in the hybrid system when exciting with 420 nm wavelength should come from the Au NCs with bigger size. The emission bands of the Au_8 overlap less strongly the absorption band of the merocyanine than does the Au NCs with bigger size (Figure S2 and S3). Therefore, it indicates that the quenching mechanism should be FRET.

Reference

1 Chen J.; Zeng F., Wu S.; Chen Q.; Tong Z.; Chem. Eur. J. 2008, 14,4851.