(Supporting Information)

Two-stage Assembly with PEI Induced Emission Enhancement of Au-AgNCs@AMP and the Intrinsic Mechanism

Xu Yu,[‡a] Jiao Liu,[‡b] Hong-Wei Li*[a] and Yuqing Wu[a]

[a]State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University, No.2699 Qianjin Street, Changchun 130012, China. E-mail: lihongwei@jlu.edu.cn.

[b]College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, China.

‡These authors contributed equally to this work.

Experimental Section

Materials and Reagents: Adenosine 5'-monophosphate (AMP, ≥99%) was purchased from TCI (Shanghai) Development Co., Ltd. (China). Polyethyleneimines (PEI, Mw = 10000) and 2-4-(2-Hydroxyethyl)-1-piperazine ethanesulfonic acid (HEPES) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). $HAuCl_4 \cdot 3H_2O$, $AgNO_3$, sodium citrate, NaH_2PO_4 and Na_2HPO_4 were bought from Beijing Chemical Factory (China) and the purities of them were higher than 99% either. Distill water (ρ = 18.2 MΩ·cm, 25 °C) was obtained from a Millipore Milli-Q water purification system. The stock solution of AMP (20 mM) was prepared with distill water and stored in dark at 4 °C. And HEPES-NaOH buffer solution (20 mM, pH=7.4) was prepared with 20 mM HEPES and NaOH in aqueous solution.

Preparation of Au-AgNCs@AMP: The Au-AgNCs@AMP were prepared by following previously reported protocol.[S1]

The assembly of Au-AgNCs@AMP and PEI: 1.0 mL stored solution of Au-AgNCs@AMP (1.0 mM) was diluted with HEPES-NaOH buffer solution (20 mM, pH=7.4) to 20.0 mL and then was divided into 20 parts and removed to EP tubes. The samples were titrated with different amount of PEI and mixed well, respectively. Then the luminescence and Uv-vis absorption spectra were measured to monitor the changes in the process.

Luminescence detections: Luminescence spectra were recorded on a Shimadzu (Japan) RF-5301PC

spectrophotometer. To reduce the fluctuation of excitation intensity during measurement, the lamp was kept on for 0.5 h before the measurement. All spectroscopic measurements were performed in 20.0 mM HEPES-NaOH (pH = 7.4), except for detection in the phosphate buffer solution, and an excitation wavelength at 325 nm was fixed.

Time-resolved fluorescence spectra: Life-times were obtained from the luminescent decay curves recorded by using a time-correlated single photon counting technique with an Edinburgh Analytical Instruments-FLS920. To obtain the luminescent decay curve, the excitation wavelength was fixed at 375 nm for Au-AgNCs@AMP, and the intensity at 490 was collected. Each experiment was repeated three times to obtain more reliable life-times, and the presented result is one selected as a representative. The lifetimes and percentage of them were calculated by exponentially fitting the decay curve with the software including in the Instruments.

UV-vis absorption spectra: The Uv-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer, and all measurements were performed in 0.2 cm × 1.0 cm quartz cuvettes (1.0 mL volume).

Transmission electron microscopy (TEM): TEM images were performed to observe the constitutive nanocrystals of Au-AgNCs by using JEM-2200FS (Jeol Ltd. Japan) at an accelerating voltage of 200 kV. For allowing TEM observations, the sample was suspended in aqueous solution under ultrasonic treatment prior to direct deposition on a copper grid and air-drying.

Field Emission Scanning Electron Microscope (SEM): The morphology of the assembly was characterized using a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) operating at 3.0 kV.

Fourier transform infrared (FT-IR) spectra: All infrared absorption spectra were characterized by using a Vertex 80V vacuum FT-IR spectrometer (Bruker). A pellet is prepared by using ~2 mg of dried sample powder and about 300 mg potassium bromide through a hydraulic pressure. For each spectrum, 64 scans between 4000 and 400 cm^{-1} are recorded, in a resolution of 4 cm^{-1}.

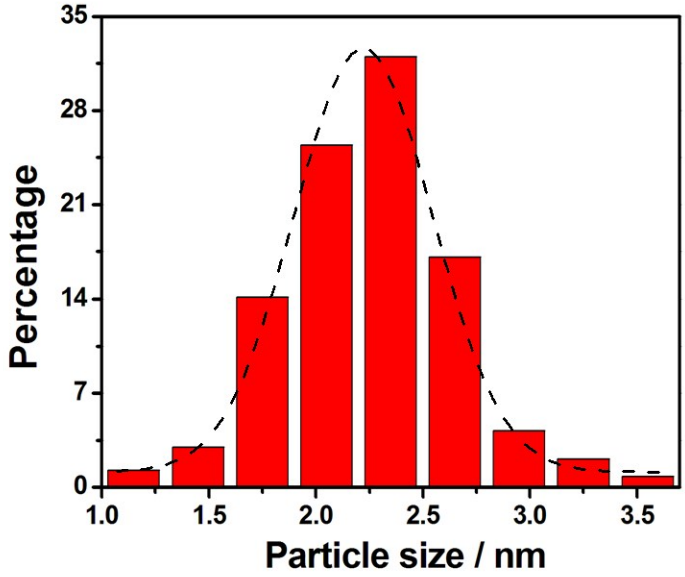

Fig. S1 The size distributions of Au-AgNCs@AMP alone.

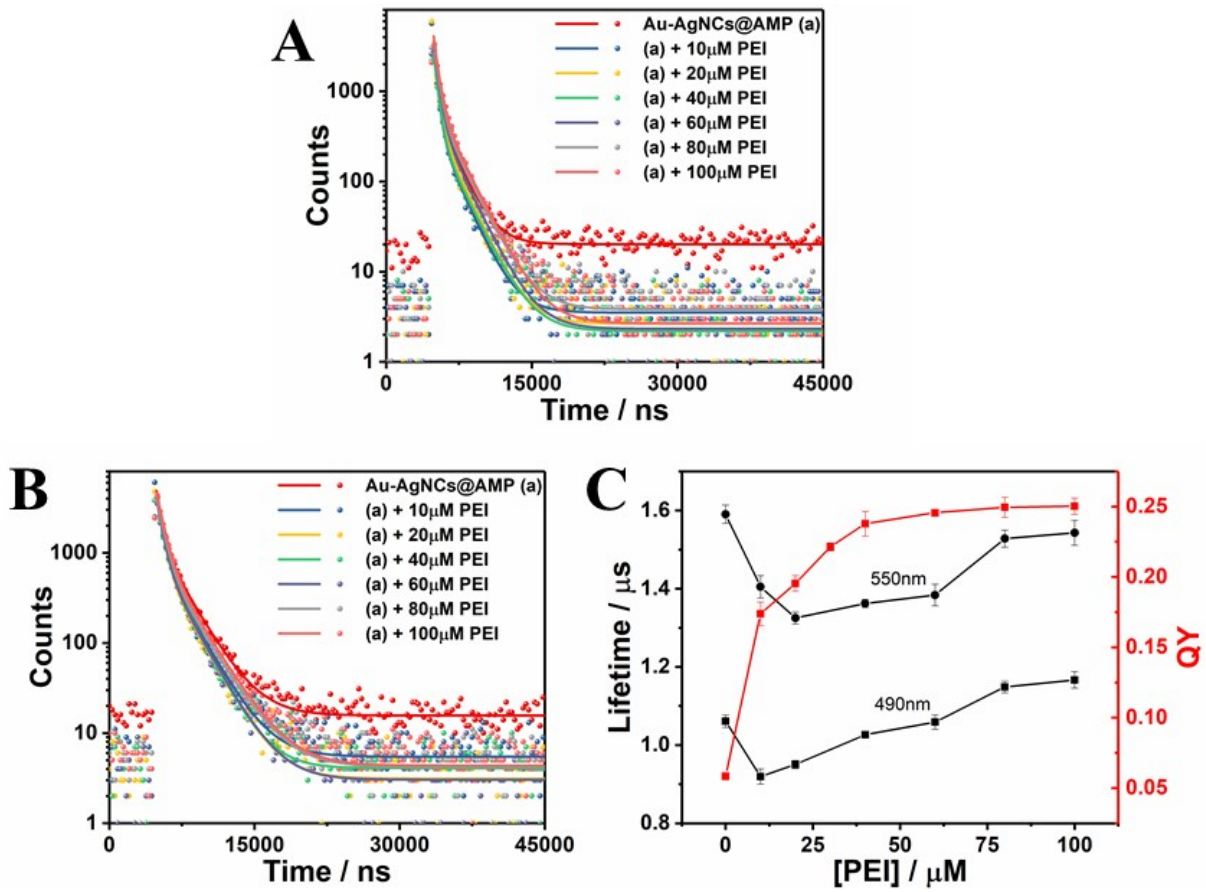

Fig. S2 The time-resolved luminescence spectra of Au-AgNCs@AMP before and after adding different amount of PEI (10.0 – 100 μM) at 490 nm (A) and 550 nm (B) respectively; (C) Average lifetime and luminescence QY changes of Au-AgNCs@AMP upon adding different amount of PEI (0 – 100 μM).

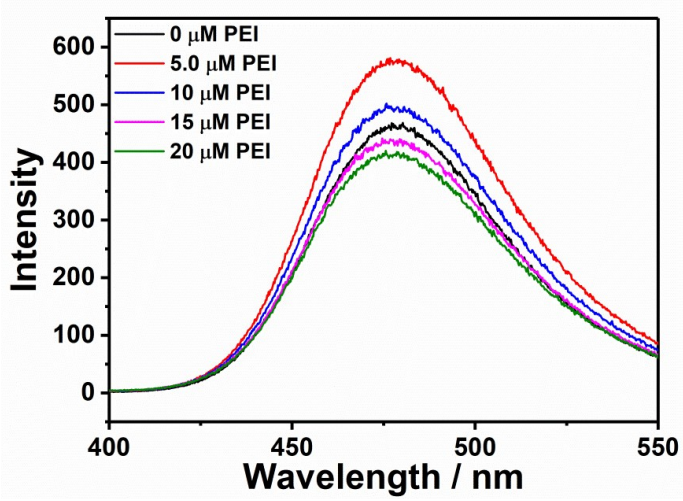

Fig. S3 Luminescence spectra of AuNCs@AMP (50 μM) in the presence of different amount of PEI (0, 5.0, 10, 15, 20 μM).

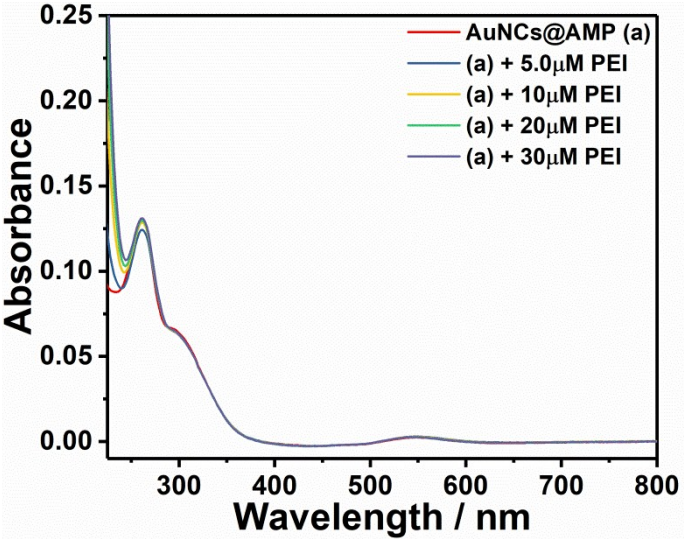

Fig. S4 Uv-vis absorption spectra of AuNCs@AMP (50 μM) in the presence of different amount of PEI (0, 5.0, 10, 15, 20 μM).

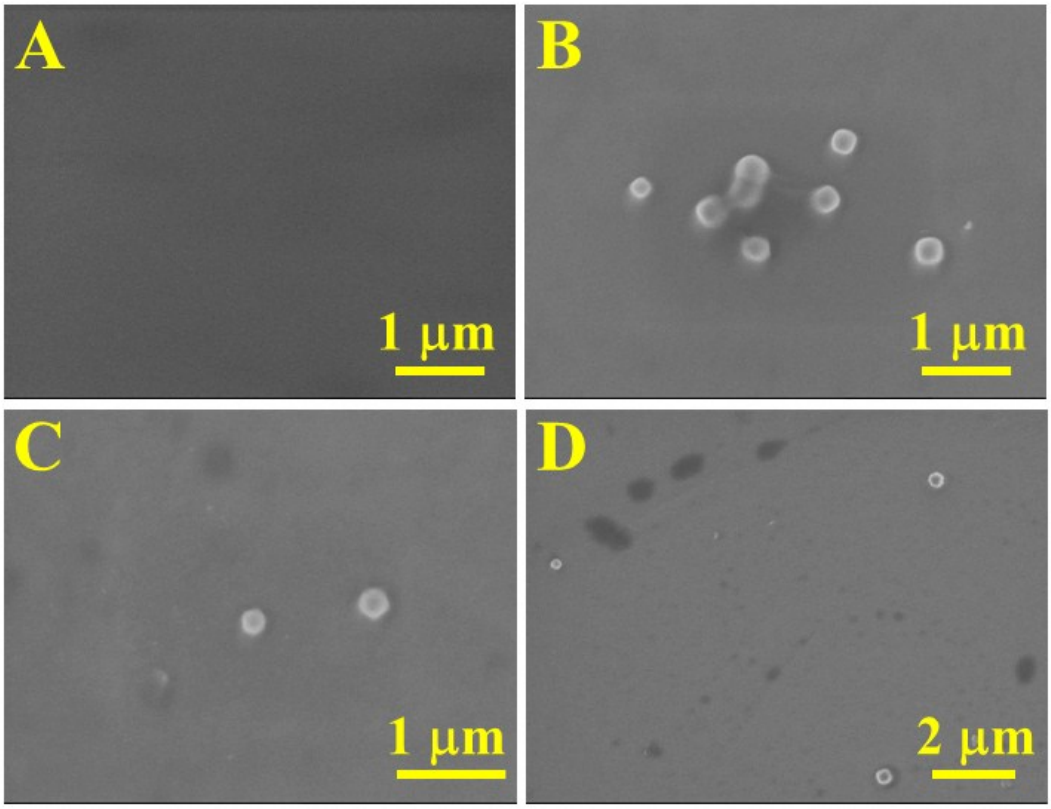

Fig. S5 Typical SEM images of AuNCs@AMP (50 μM) in the absence (A) and presence of (B) 10, (C) 20 μM and (D) 30 μM PEI, respectively.

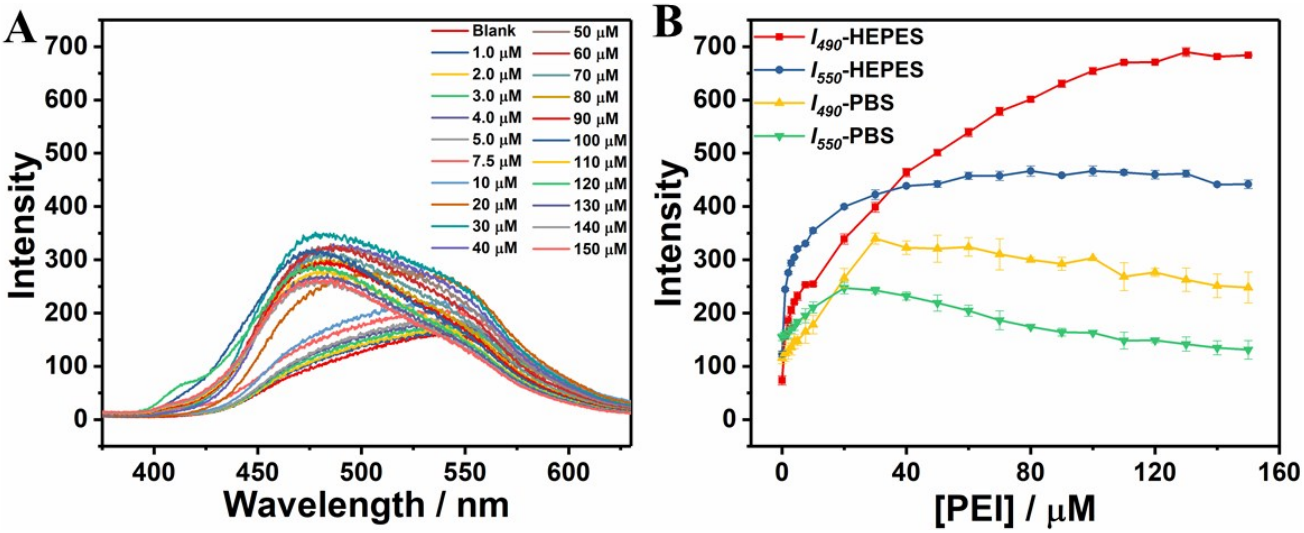

Fig. S6 A) The fluorescence spectra of Au-AgNCs@AMP (50 μM) in absence and presence of different amounts of PEI (1.0−150 μM) in the PBS buffer solution (pH = 7.4, λ_{ex} = 325 nm); B) The plot of the corresponding fluorescence intensities and the corresponding result in HEPES-NaOH buffers upon the addition of PEI.

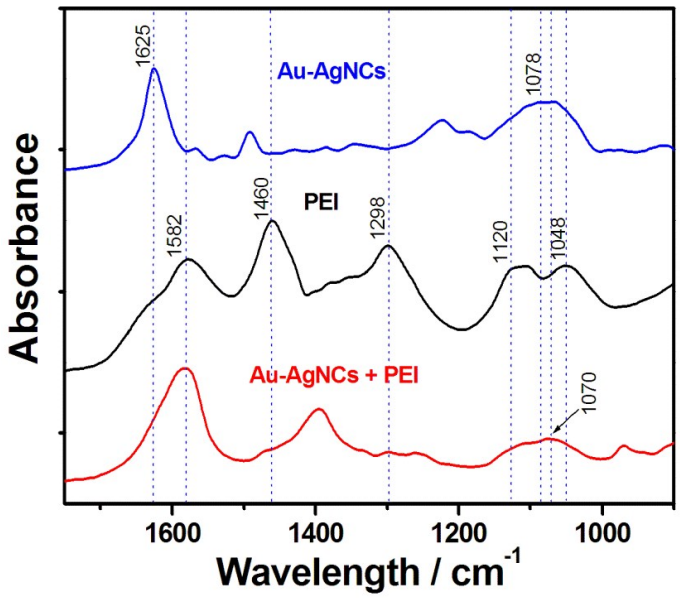

Fig. S7 FT-IR spectra of Au-AgNCs@AMP, PEI and the assembly of them.

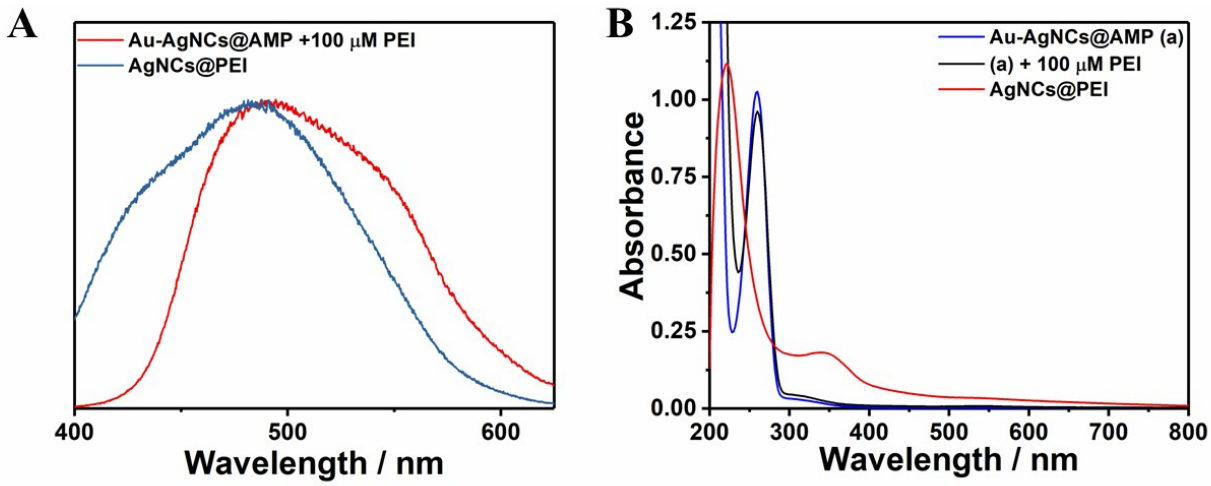

Fig. S8 A) The fluorescence spectra of AgNCs@PEI (50 μM) and the assembly of Au-AgNCs and PEI in the HEPES-NaOH buffer solution (pH = 7.4, λ_{ex} = 325 nm); B) the Uv-vis absorption spectra of Au-AgNCs@AMP (50 μM) in the absence and presence of PEI (100 μM) and AgNCs@PEI (50 μM) in HEPES-NaOH buffer solution.

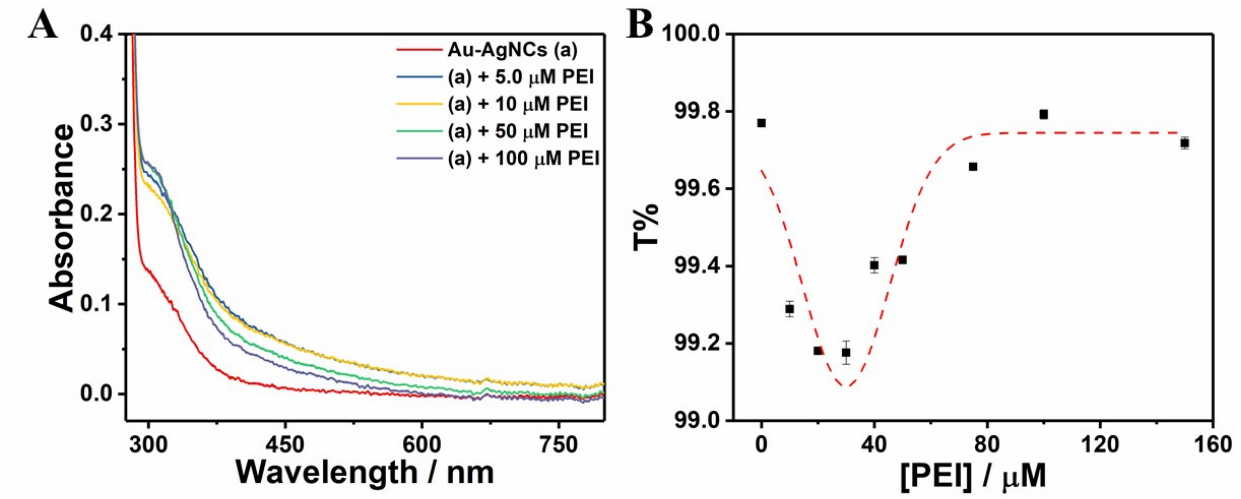

Fig. S9 (A) UV-vis absorption spectra of Au-AgNCs@AMP (50 μM) in the absence and presence of different amount PEI; (B) Transmission changes of Au-AgNCs@AMP in titrating with different amount of PEI.

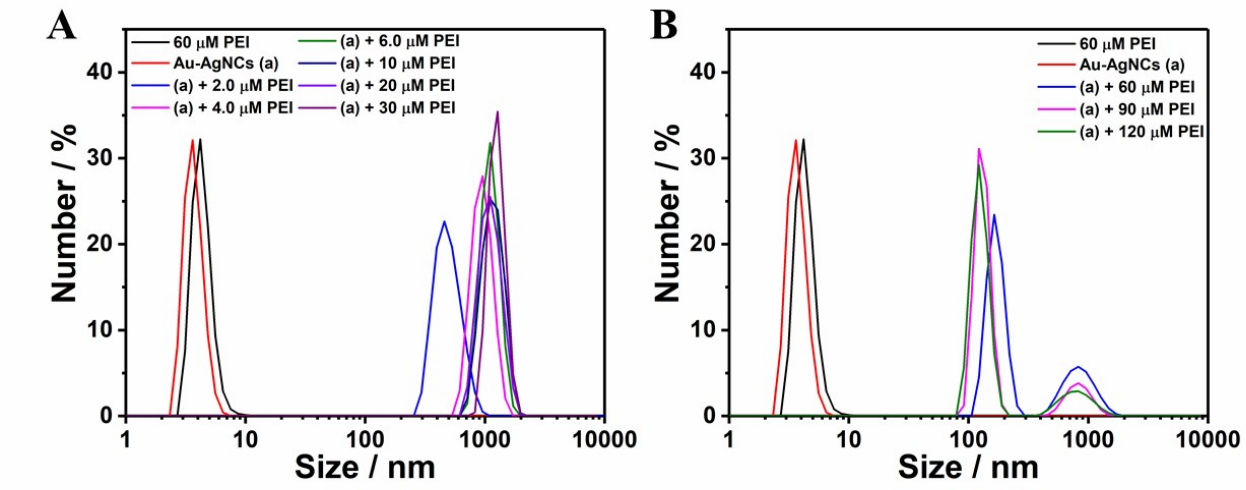

Fig. S10 DLS measurement of Au-AgNCs@AMP (50 μM), PEI (60 μM) and the assembly of Au-AgNCs@AMP (50 μM) and different amount of PEI in HEPES-NaOH buffer solution, where in the presence of (A) 2.0, 4.0, 6.0, 10.0, 20.0, 30.0 μM PEI and (B) 60.0, 90.0, 120 μM PEI in the system.

Table S1 The life-times and percentages changes of Au-AgNCs@AMP at 490 nm and 550 nm, respectively, in the absence and presence of different amount of PEI.

[PEI] / μM	$I_{490\ nm}$					I_{550nm}				
	τ_1 / μs	Rel / %	τ_2 / μs	Rel / %	$\tau_{Average}$ / μs	τ_1 / μs	Rel / %	τ_2 / μs	Rel / %	$\tau_{Average}$ / μs
0	0.292	40.71	1.589	59.29	1.061	0.500	39.08	2.290	60.92	1.590
10	0.362	59.10	1.725	40.90	0.919	0.568	49.62	2.228	50.38	1.405
20	0.380	60.23	1.814	39.77	0.950	0.552	53.57	2.217	46.43	1.325
40	0.398	59.05	1.933	40.95	1.027	0.524	46.61	2.094	53.39	1.362
60	0.432	57.16	1.895	42.84	1.059	0.585	51.44	2.230	48.56	1.384
80	0.447	53.95	1.971	46.05	1.149	0.665	52.58	2.485	47.42	1.528
100	0.445	53.06	1.982	46.94	1.166	0.687	52.14	2.475	47.86	1.543

Reference

S1 J. Liu, X. X. Yuan, H. W. Li and Y. Q. Wu, *J. Mater. Chem. C*, 2017, **5**, 9979-9985.