

Electronic Supplementary Information for

Cation Polymer-Induced Aggregation Emission of Au(I)-SR Complexes

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Experimental section

Chemicals

All reagents were of analytical grade and were used as received. Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were obtained from Merck. L-Glutathione in the reduced form (GSH), poly(diallyldimethylammonium chloride) (PDDA, 20 wt.% in H_2O), polyethyleneimine (PEI, 50 wt.% in H_2O), Poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] quaternized (Polyquaternium-2, 62 wt.% in H_2O), 6-mercaptohexanoic acid (MHA) and 3-mercaptopropionic acid (MPA) were purchased from Sigma–Aldrich. The concentration of PDDA was determined by the molecular weight of its repeating unit (161.7 g/mol). Ultrapure Millipore water (18.2 M Ω -cm) was used in the preparation of all aqueous solutions unless otherwise stated.

Synthesis of Au(I)–GSH Complexes

Freshly prepared aqueous solutions of HAuCl_4 (50 mM, 0.20 mL) and GSH (100 mM, 0.20 mL) were mixed with 3.60 mL of ultrapure water under gentle stirring (500 rpm) at 25 °C for 5 min. A precipitate was formed. Then NaOH (1 M) was added to the mixture to bring the pH to 7, 8, 9, 10, 11 and 12. The precipitate was dissolved within seconds, and the solution was aged for ~15 h. The Au(I)–SR complexes formed as such were used without purification and could be stored at 4 °C for 3 days without any changes. Au(I)–GSH complexes under other pH values were synthesized by the same method, but with different NaOH addition.

Synthesis of Au(I)–MHA Complexes

Freshly prepared aqueous solutions of HAuCl_4 (50 mM, 0.20 mL) and MHA (5 mM, 4 mL) were mixed with 0.8 mL of ultrapure water under gentle stirring (500 rpm) at 25 °C for 5 min. Then NaOH (1 M) was added to the mixture to bring the pH to 9, 10, 11 and 12. The precipitate was dissolved within seconds, and the solution was aged for ~10 min.

Synthesis of Au(I)–MPA Complexes

Freshly prepared aqueous solutions of HAuCl_4 (50 mM, 0.20 mL) and MPA (100 mM, 0.20 mL) were mixed with 5 mL of ultrapure water under gentle stirring (500 rpm) at 25 °C for 5 min. Then NaOH (1 M) was added to the mixture to bring the pH to 8, 9, 10, 11 and 12. The precipitate was dissolved within seconds, and the solution was aged for ~20 min.

Materials Characterization

UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Photoluminescence (PL) characterization was performed on a Perkin-Elmer LS-55 system. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker Compact QToFsystem in the positive ion mode. Transmission electron microscopy (TEM) images of Au(I)-GSH@PDDA were taken on a JEOL JEM 2010 microscope operating at 200 kV. Zeta potential measurements were conducted on a Malvern Zetasizer Pro instrument. The absolute quantum yield (QY) was determined by the FLS1000 steady-state transient fluorescence spectrometer at room temperature

Figures

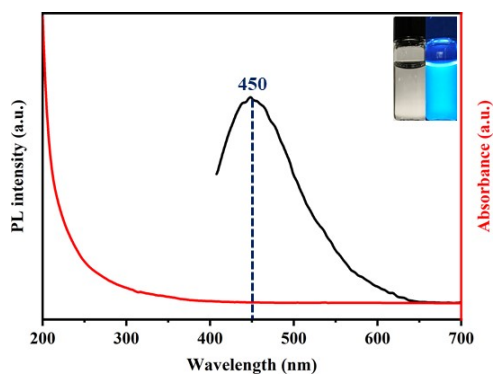


Figure S1 UV-vis absorption (red line) and photoemission (black line, $\lambda_{\text{exc}} = 365 \text{ nm}$) spectra of PDDA solution.

(Inset) Digital photos of PDDA solution under (left) visible and (right) UV light.

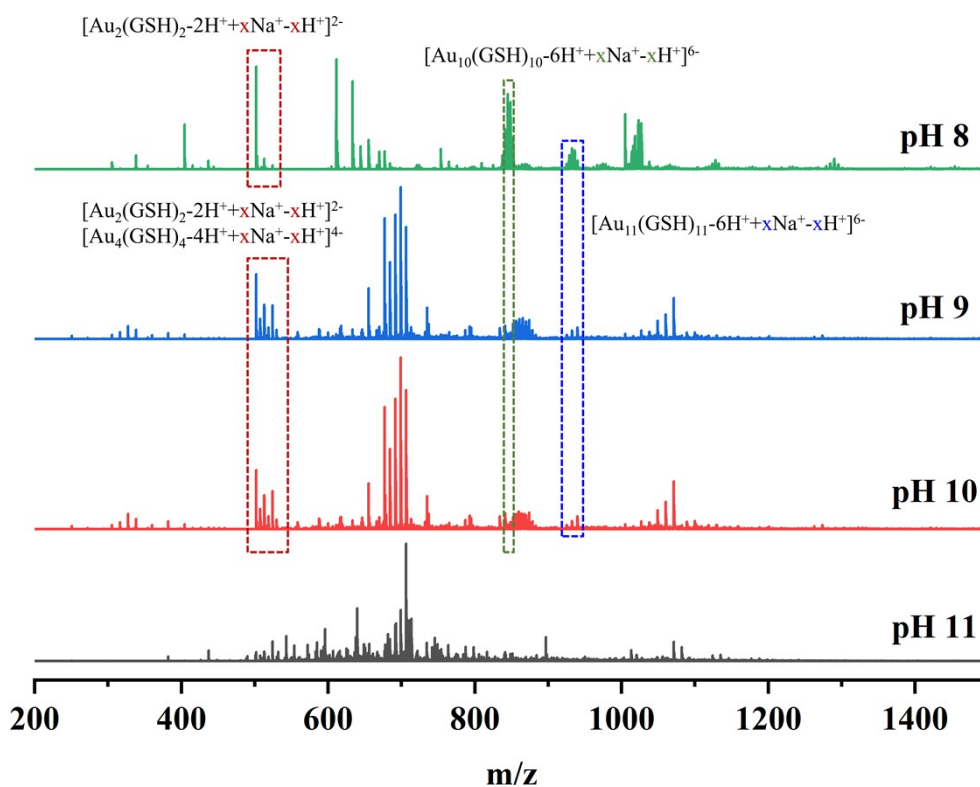


Figure S2 ESI-MS analysis of Au(I)-GSH complexes under different pH value. With pH increased, the negative charge density on the Au(I)-GSH surface is increased, which will increase the intra-cluster repulsion in longer complexes and reduce their stability. The dominant large species at pH 8, $\text{Au}_{11}(\text{GSH})_{11}$, quickly decreased with pH value increasing.

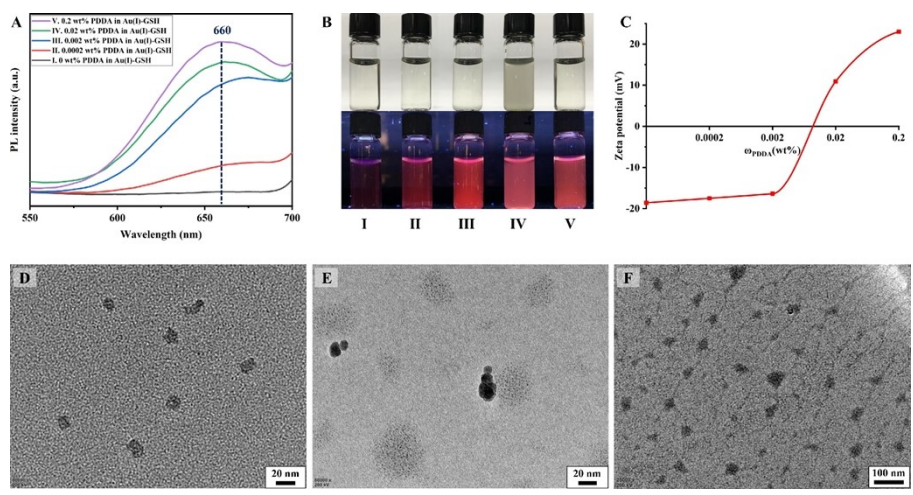


Figure S3 Photoemission spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) of Au(I)-GSH@PDDA (pH 12, 2 mM Au(I)-GSH complexes mixed with PDDA of different concentration) (A) and corresponding digital photos under visible (top row) and UV (bottom row) light (B). (C) Zeta potential of the mixture of Au(I)-GSH and PDDA of different concentrations. TEM images of Au(I)-GSH@PDDA: (D) 2 mM Au(I)-GSH complexes mixed with 0.002 wt% PDDA (Sample III); (E) 2 mM Au(I)-GSH complexes mixed with 0.02 wt% PDDA (Sample IV); (F) 2 mM Au(I)-GSH complexes mixed with 0.2 wt% PDDA (Sample V).

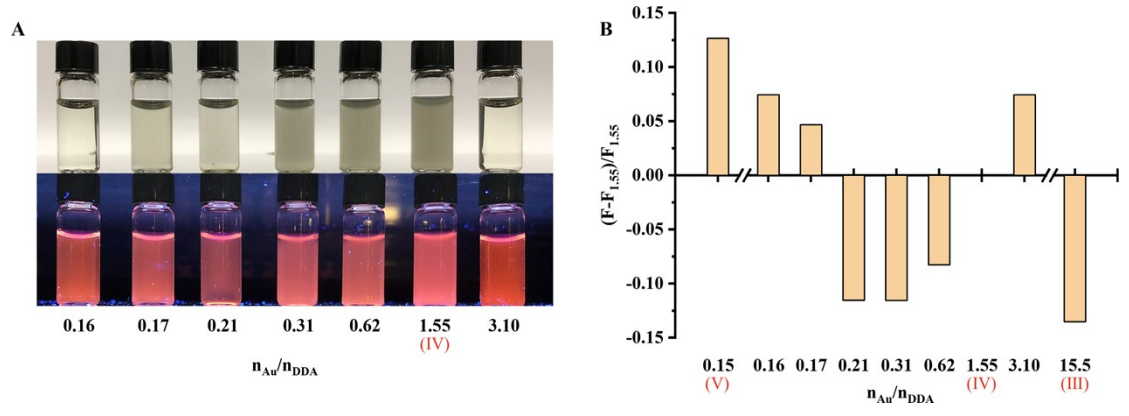


Figure S4 (A) Digital photos of the mixture of Au(I)-GSH complexes and PDDA in different ratios under visible (top row) and UV (bottom row) light. (B) Fluorescence intensity of the mixtures compared with Sample IV. The sedimentation phenomenon occurs when the ratio of n_{Au} to n_{PDDA} is 0.17 to 1.55 and the ratio of n_{Au} to n_{PDDA} in sample IV is 1.55.

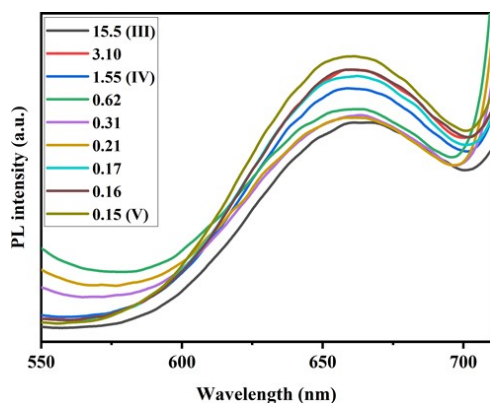


Figure S5 Photoemission spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) of samples with different molar ratio of Au and DDA. The fluorescence intensity of the samples decreased slightly with the increase of precipitation. When $n_{\text{Au}}/n_{\text{DDA}}$ is 0.21 and 0.31, the fluorescence intensity reached the lowest in this range, indicating that the precipitation reach the maximum at these two ratios. Then the intensity recovered as the precipitation decreased ($n_{\text{Au}}/n_{\text{DDA}} = 0.62$). The samples at these ratios all show stronger fluorescence intensity than sample III ($n_{\text{Au}}/n_{\text{DDA}} = 15.5$).

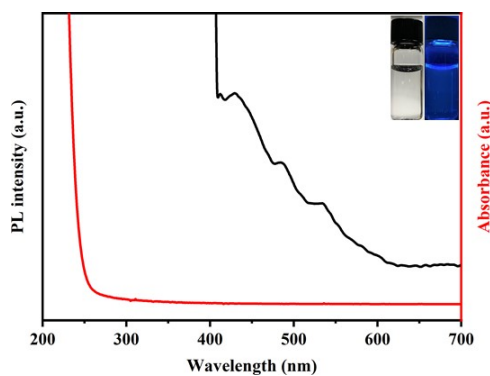


Figure S6 UV-vis absorption (red line) and photoemission (black line, $\lambda_{\text{ex}} = 365 \text{ nm}$) spectra of PEI solution. (Inset) Digital photos of PEI solution under (left) visible and (right) UV light.

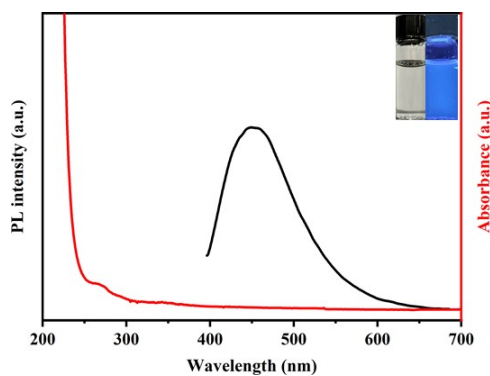


Figure S7 UV-vis absorption (red line) and photoemission (black line, $\lambda_{\text{ex}} = 365 \text{ nm}$) spectra of polyquaternium-2

solution. (Inset) Digital photos of polyquaternium-2 solution under (left) visible and (right) UV light.

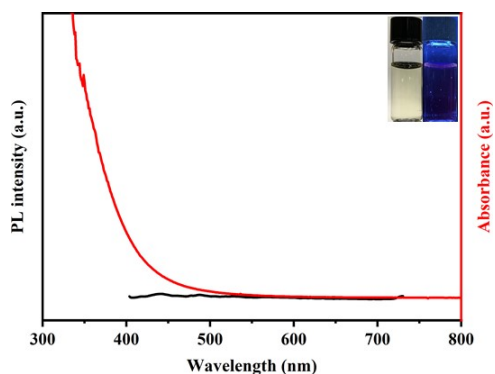


Figure S8 UV-vis absorption (red line) and photoemission (black line, $\lambda_{\text{ex}} = 365 \text{ nm}$) spectra of Au(I)-MHA complexes. (Inset) Digital photos of Au(I)- MHA complexes under (left) visible and (right) UV light.

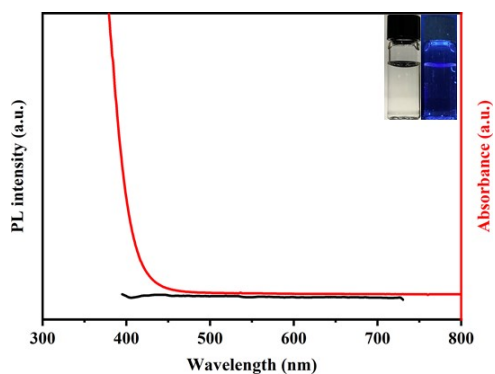


Figure S9 UV-vis absorption (red line) and photoemission (black line, $\lambda_{\text{ex}} = 365 \text{ nm}$) spectra of Au(I)-MPA complexes. (Inset) Digital photos of Au(I)- MPA complexes under (left) visible and (right) UV light.

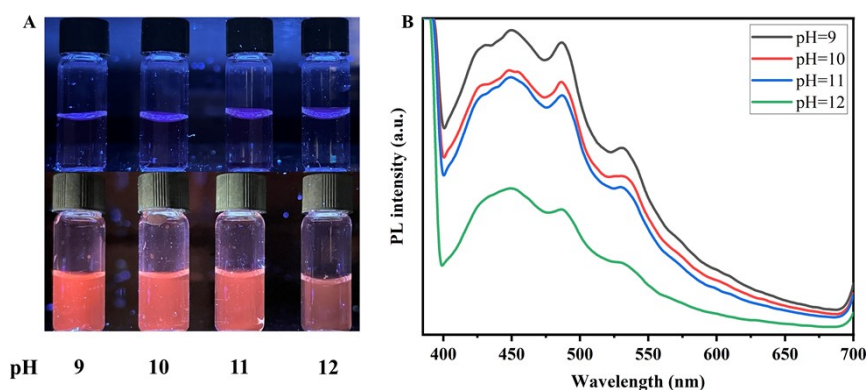


Figure S10 (A) Digital photos of Au(I)-MHA complexes at different pH value in water (top row) and Au(I)-MHA@PDDA (0.02 wt% PDDA in 2 mM Au(I)-MHA complexes) at different pH value (bottom row) under UV light; (B) Corresponding photoemission spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) of Au(I)-MHA@PDDA at different pH value.

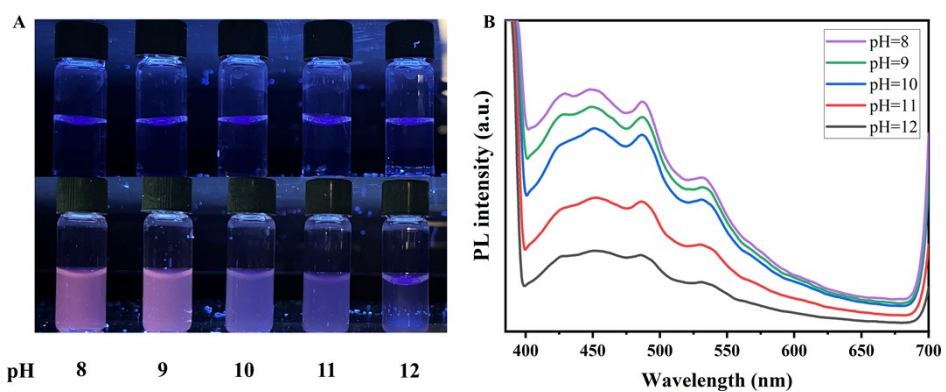


Figure S11 (A) Digital photos of Au(I)-MPA complexes at different pH value in water (top row) and Au(I)-MPA@PDDA (0.02 wt% PDDA in 2 mM Au(I)-MHA complexes) at different pH value (bottom row) under UV light; (B) Corresponding photoemission spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) of Au(I)-MPA@PDDA at different pH value.