Electronic Supplementary Information

pH-Responsive Assembly of Metal Nanoparticles and Fluorescent Dyes by Diblock Copolymer Micelles

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The extinction property of Au NP in PS-PAA micelles

In general, the extinction spectrum of a given metal NP is the sum of its absorption and scattering spectra, each of which is interconnected to fluorescence quenching and enhancement.[1-3] For instance, small metal NPs usually quench fluorescence, as their extinction is mostly composed of the absorption, while larger NPs tend to enhance fluorescence due to their superior scattering factor.[1-3] In this context, we calculated the extinction spectrum of Au NP in the core of PS-PAA micelles with open-source Mieplot v4400 program4 by specifying the value of diameter of Au NP (11.0 nm in Figure 1a) and the refractive index of the medium (n = 1.59 for PS block). Calculation with Mie theory in Figure S1 clearly shows that Au NPs in this study have a dominant absorption (σ_{abs}) with negligible scattering (σ_{scat}) in their extinction spectrum (σ_{ext}). Therefore, they can quench the fluorescence of R123 as discussed in the main text.

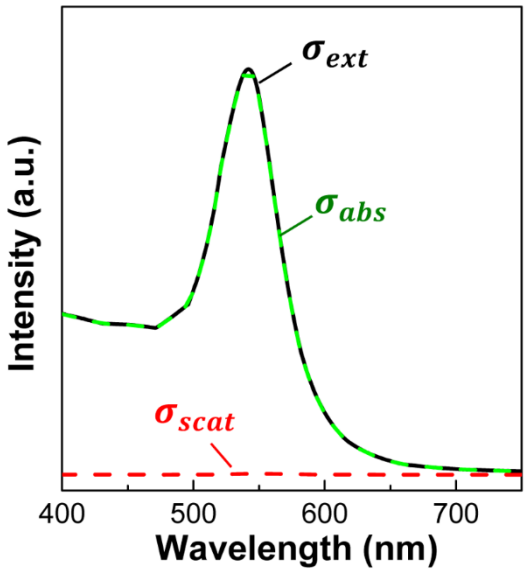

Figure S1. Calculated extinction (black solid), absorption (green dotted), and scattering (red dotted) spectra of Au NP in the core of PS-PAA micelles.

The contribution of empty micelles and plasmonic effect to the quenched R123 fluorescence

To prepare empty PS-PAA micelles, a 0.1 wt% DMF solution of PS-PAA copolymers was first prepared, into which deionized water was continuously added by a syringe pump (~ 8.0 μL / min). The concentration of H_2O in the total solution was ~30 vol%. Subsequently, the resulting solution was dialyzed against H_2O to remove DMF. It needs to be noted that the concentrations of [-COOH] in the empty micelles and Au@PS-PAA micelles have to be the same in order to assess the effect of empty micelle. However, the exact concentration of [-COOH] in Au@PS-PAA micelles was unknown because of numerous centrifugation- and dialysis-based purification processes. Hence, we titrated Au@PS-PAA micelles and empty micelles with 0.1 M HCl solution to determine their concentration, the results of which are shown in Figure S2. Note, pHs of both solutions were pre-adjusted to 10.0 by using 0.1 M NaOH before titration. In the titration curve, the volume of HCl solution between two peaks in the 1st derivative plot $(\Delta pH/\Delta V)$ is proportional to the concentration of [-COOH]. Therefore, we diluted the aqueous solution of empty micelle by using deionized water until the concentration of [-COOH] in the empty micelles becomes the same as that in the Au@PS-PAA micelles.

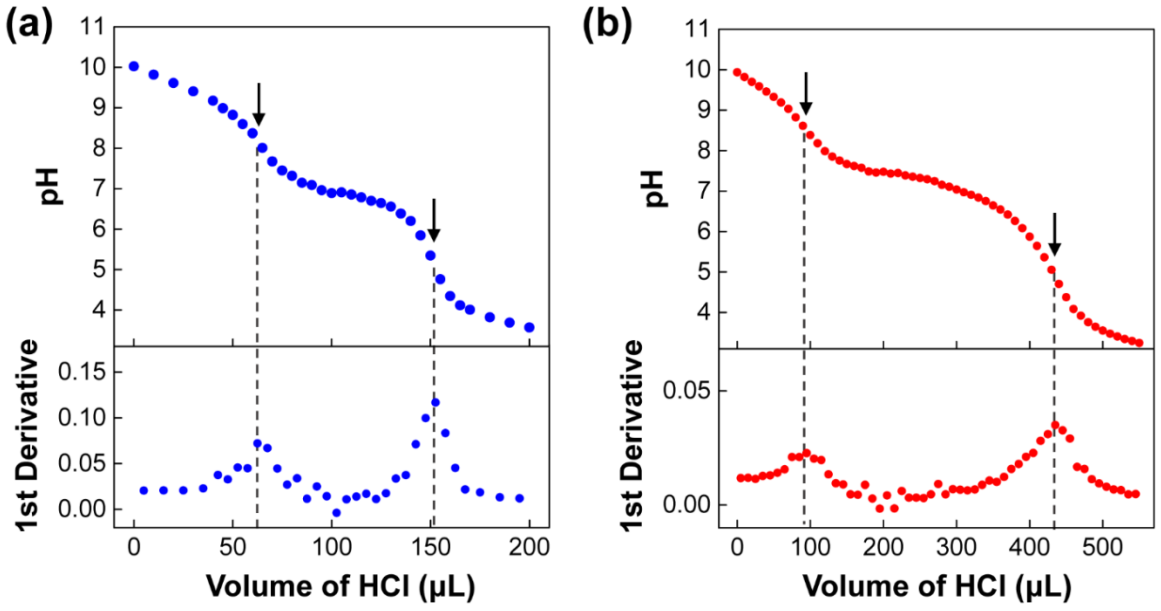

Figure S2. Titration results of Au@PS-PAA micelles (a) and empty PS-PAA micelles (b) with 0.1M HCl. The first derivative, $\Delta pH/\Delta V$, of the titration curve is also included in each case.

The influence of empty micelle on R123 fluorescence was then examined under the same condition as in the main text. Again, an equal amount of empty micelle (0.2 mL) was continuously added to an aqueous solution of R123 (3.0 mL, 1.0×10^{-5} M). Note, pHs of all the solutions were pre-adjusted to 9.0. Upon successive addition of empty micelles, R123 fluorescence was progressively quenched as in Figure S3. This empty-micelle effect could be attributed to dye-dye interactions and/or dye-micelle interactions.[5,6] For instance, upon binding to empty micelles, the local concentration of R123 molecules on the micellar corona significantly increases, which can facilitate dye-dye interaction such as homo-FRET (Fluorescence Resonance Energy Transfer).[5] In addition, the binding event itself also can affect the fluorescence by a complex formation.[5-6] Taken together, these interactions could strongly quench fluorescence intensity.

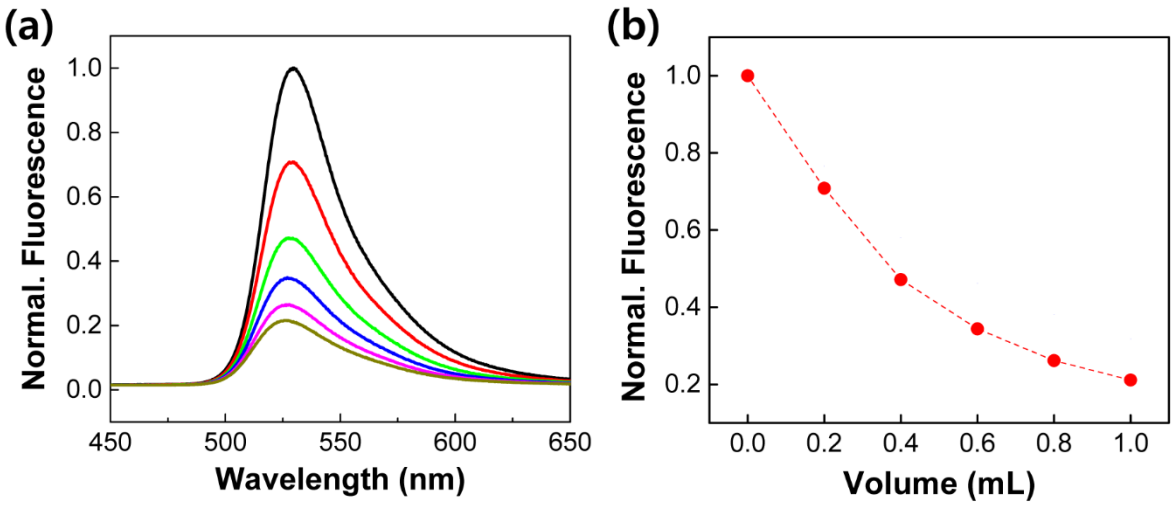

Figure S3. Normalized fluorescence spectra (a) and maximum fluorescence intensity (b) of R123 molecules with the successive addition of empty micelles at pH = 9.0.

Therefore, it can be validated that the effect of Au@PS-PAA micelles in the main text arises from both (plasmonic) NP effect and (empty) micelle effect. However, the observed fluorescence quenching caused by Au@PS-PAA micelle could not be a simple addition of the two effects because the overall photochemical processes of R123 molecules are modified upon binding to Au@PS-PAA

micelles. In a more analytical expression, the total decay rates of pure R123 (k_{tot}^{0}), R123 bound to the empty micelle (k_{tot}^{mic}), and R123 bound to Au@PS-PAA micelle (k_{tot}^{Au}) can be expressed as

$$k_{tot}^{0} = k_{rad}^{0} + k_{nr}^{0} \quad \cdots\cdots(S1)$$

$$k_{tot}^{mic} = k_{rad}^{0} + k_{nr} + k_{dye}^{0} + k_{mic}^{0} \quad \cdots\cdots(S2)$$

$$k_{tot}^{Au} = k_{rad}^{Au} + k_{nr}^{Au} + k_{dye}^{Au} + k_{mic}^{Au} + k_{NET} \quad \cdots\cdots(S3)$$

where, $k_{rad}^{0}\ and\ k_{nr}^{0}$ are the radiative and non-radiative decay rates of pure R123, respectively. In general, $k_{rad}^{0}$is essentially constant for any given fluorophores, while $k_{nr}^{0}$is easily modified by quenching effect.[6] In equation (S2), we specified the quenching effect arose from dye-dye and dye-micelle interactions with additional rate constants of $k_{dye}^{0}\ and\ k_{mic}^{0}$, respectively.

Moreover, the presence of Au NP in the core of micelle can potentially affect all of the decay processes.[1-3,5,7] In this sense, we expressed the NP effect with the superscript "Au" in equation (S3). Also, new decay channel such as non-radiative energy transfer to Au NPs is newly included with a rate constant of k_{NET}. Equation (S3) may represent the complex nature in the near-field interactions among R123, Au NPs and micelles. Indeed, it is quite difficult to quantify the actual contribution of each decay process to the quenched R123 fluorescence in the presence of Au@PS-PAA micelle. However, in this study, we did not pursue precise quantification of the photochemical processes. Otherwise, we are mainly interested in the fluorescence change along with the pH-dependent organization of R123 and Au@PS-PAA micelles. Hence, considering that the fluorescence change in this study reflects the overall changes in the photochemical processes, the exact quantification on the photochemical processes would not be crucial for discussing the result.

References

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