Electronic Supplementary Information

Plasmonic Vesicles with Tailored Collective Properties

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Scheme S1. Synthesis of Azo-DDMAT chain transfer agent and Azo-PEEA homopolymer by RAFT.

Fig. S1. $^1$H NMR spectrum of 2-(dodecylthiocarbo-no-thioylthio)-2-methyl propanoic acid (DDMAT) in CDCl$_3$. 

in CDCl$_3$. 
Fig. S2. $^1$H NMR spectrum of 4-hydroxyethoxy azobenzene in CDCl$_3$.

Fig. S3. $^1$H NMR spectrum of Azo-DDMAT in CDCl$_3$. 
**Fig. S4.** $^1$H NMR spectrum of Azo-PEEA in CDCl$_3$.

**Fig. S5.** THF GPC trace of Azo-PEEA homopolymer.

$M_n = 2800$

$D = 1.17$
Fig. S6. DLS studies of Azo-PEEA vesicle in water.

Fig. S7. $^1$H NMR spectrum of Azo-PEEA vesicles in D$_2$O.
Fig. S8. High resolution TEM image of gold nanoparticles. The inter-planar spacing of (111) is 2.36 Å.

The indices of crystal face were determined by measuring the distance of the diffraction rings and comparing to the theoretical values. The enlarged high resolution TEM image in Fig. S8 demonstrates the indices of crystal face of (111) of gold nanoparticles, while the inter-planar spacing of (111) is 2.360 Å, corresponding to the classical X-ray diffraction results (2.355 Å).

Fig. S9. The stability of plasmonic vesicles at different pH values and salt concentrations at 15 °C, as monitored by DLS.
Calculation of compactness and distance between gold nanoparticles on plasmonic vesicles:

The numbers of gold nanoparticles on the plasmonic vesicles are 202 ± 34, 579 ± 87 and 1148 ± 187 at 15, 25 and 35 °C, respectively, while the diameters of the plasmonic vesicles are 168 ± 38, 246 ± 61 and 335 ± 75 nm at 15, 25 and 35 °C. Assuming that the diameters of plasmonic vesicles are the same either in solution or on the carbon grid, the density of gold nanoparticles on the plasmonic vesicles is as follows:

\[
\text{Number of gold nanoparticles per plasmonic vesicle} = \frac{\text{Number of gold nanoparticles}}{\text{Surface area of plasmonic vesicle}}
\]

So the ratio of the density of gold nanoparticles on the plasmonic vesicles at 15, 25 and 35 °C is as follows:

\[
\frac{202}{4\pi R_1^2}, \frac{579}{4\pi R_2^2}, \frac{1148}{4\pi R_3^2}
\]

While \( R_1, R_2 \) and \( R_3 \) are the corresponding radiiuses of plasmonic vesicles. Putting in the numbers, the ratio is calculated to be 1:1.34:1.44, while the ratio of the average distances of gold nanoparticles on the plasmonic vesicles at 15, 25 and 35 °C is inversely proportional to the ratio of the density of gold nanoparticles, calculated as 1:0.75:0.69.
Fig. S11. Hydrodynamic diameters and UV-vis absorption peaks of fused plasmonic vesicles (heated to 35 °C) at different pH values.

Fig. S12. Hydrodynamic diameters and UV-vis absorption peaks of fused plasmonic vesicles (heated to 35 °C) at different salt concentrations.
Fig. S13. Hydrodynamic diameters and UV-vis absorption peaks of fused plasmonic vesicles (heated to 35 °C) at different temperatures.