Electronic Supplementary Information

Plasmonic Vesicles with Tailored Collective Properties

Hui Sun^{a,b} and Jianzhong Du^{*a,b}

^a Department of Orthopedics, Shanghai Tenth People's Hospital, Tongji University

School of Medicine, Shanghai 200072, China. E-mail: jzdu@tongji.edu.cn; Fax: +86-

21-6958 0239; Tel: +86-21-6958 0239

^b Department of Polymeric Materials, School of Materials Science and Engineering,
Tongji University, 4800 Caoan Road, Shanghai 201804, China.

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



Fig. S1. ¹H NMR spectrum of 2-(dodecylthiocarbono-thioylthio)-2-methyl propanoic acid (DDMAT) in CDCl₃.



Fig. S2. ¹H NMR spectrum of 4-hydroxyethoxy azobenzene in CDCl₃.



Fig. S3. ¹H NMR spectrum of Azo-DDMAT in CDCl₃.



Fig. S4. ¹H NMR spectrum of Azo-PEEA in CDCl₃.



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



Fig. S6. DLS studies of Azo-PEEA vesicle in water.



Fig. S7. ¹H NMR spectrum of Azo-PEEA vesicles in D_2O .



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.



Fig. S10. DLS studies of plasmonic vesicles at different temperatures.

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:

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 radiuses 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.