

# Supporting Information

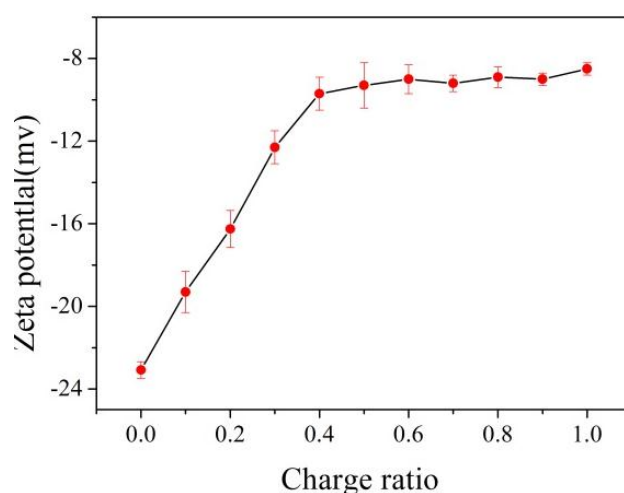
## Constructing Asymmetric Polyion Complex Vesicles via Template Assembling Strategy: Formulation Control and Tunable Permeability

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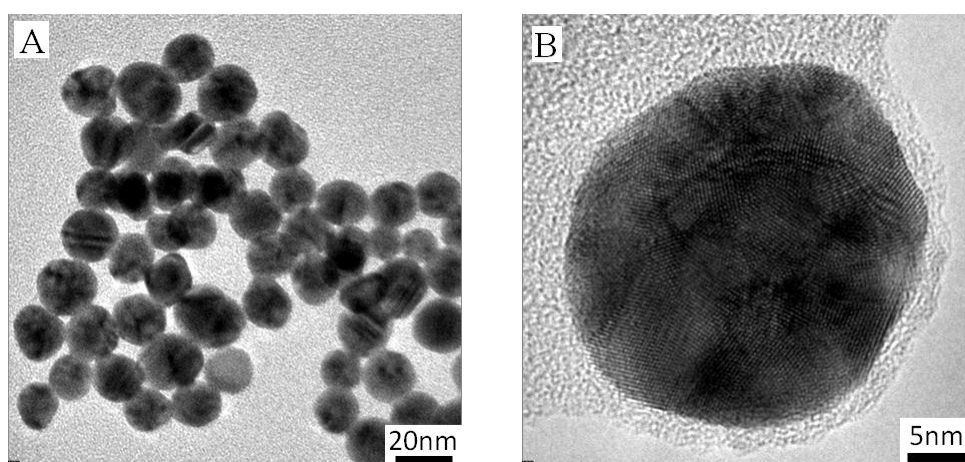
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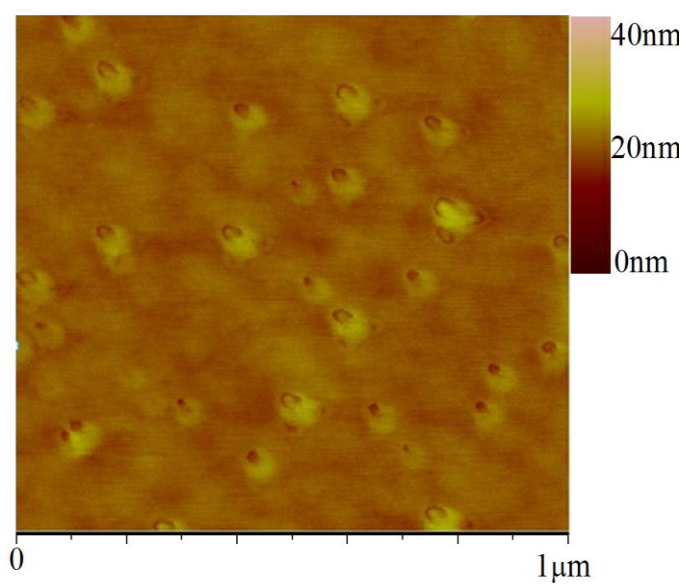
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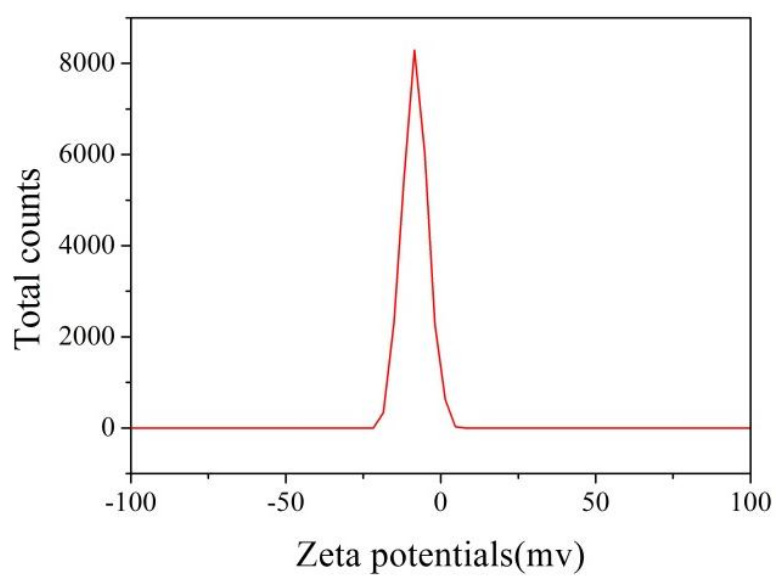
**Figure S1.** Zeta potentials of PMAA-*b*-PNIPAm-@-Au NPs complex with PEG-*b*-PMMPImB at various charge ratios (PMMA to PMMPImB). Values represent mean ( $\pm$  SD ( $n = 3$ ))



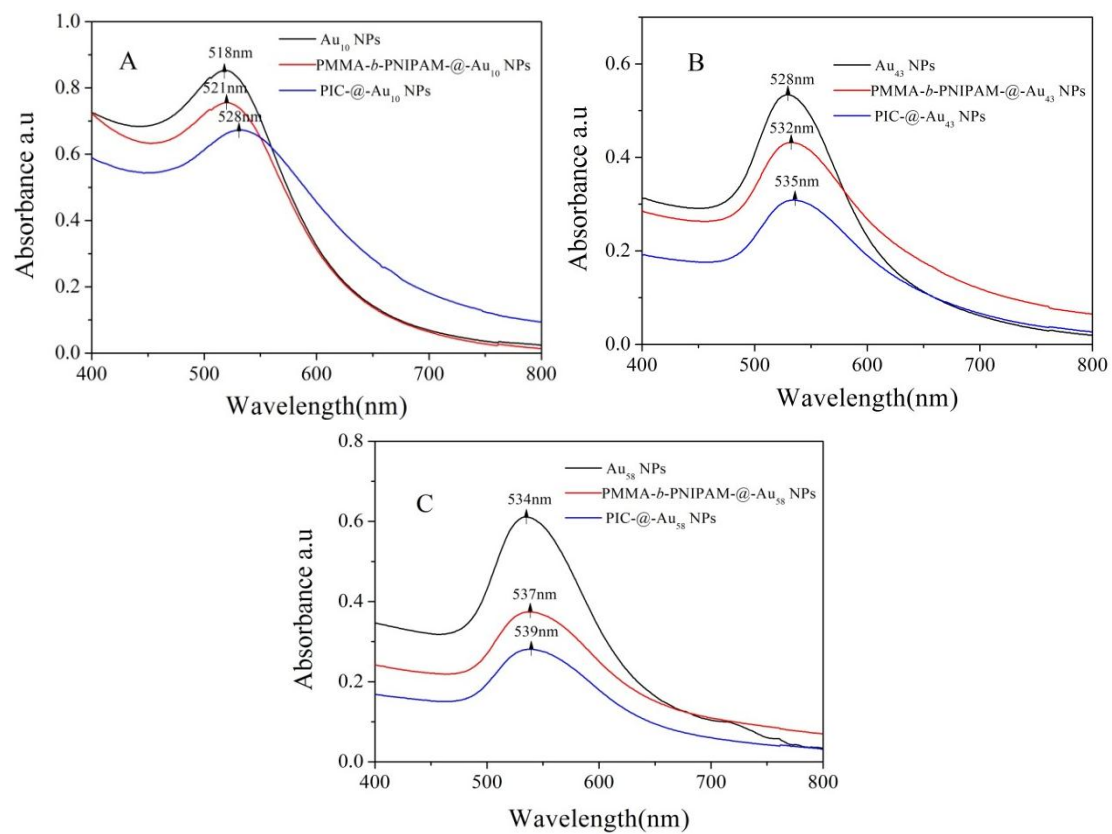
**Figure S2.** The TEM image of Au 20 NPs(A) and PMAA-*b*-PNIPAm-@-Au<sub>20</sub> NPs(B)



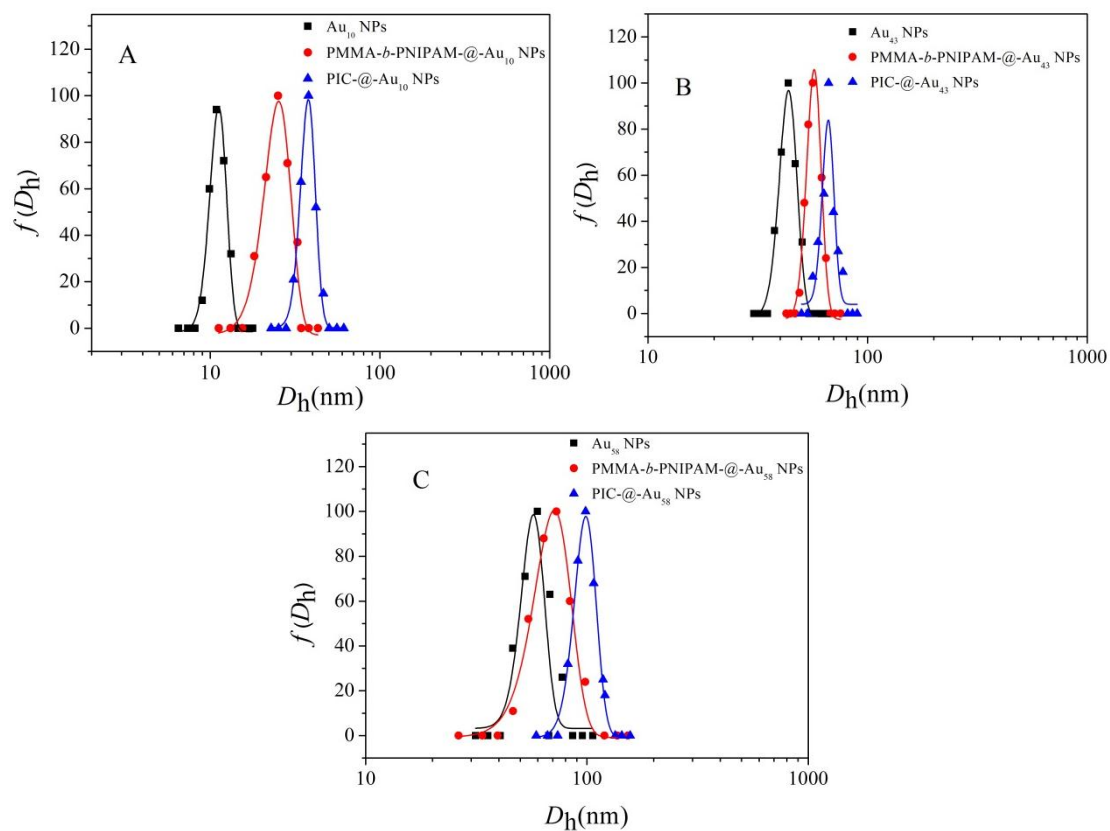
**Figure S3.** Height profile of PICsomes corresponding to Figure 3C.



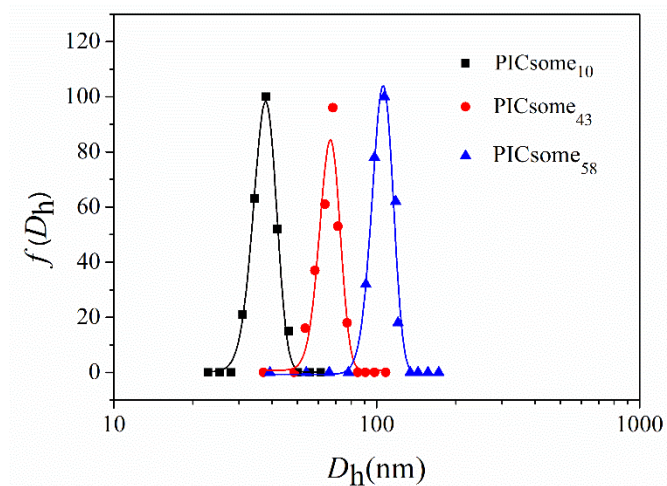
**Figure S4.** The  $\zeta$ -potential distribution curves for PICsomes.



**Figure S5.** UV-Vis spectra of Au NPs, PMMA-*b*-PNIPAm-@-Au and PIC-@-Au NPs with different size of the Au template, where A is 10nm, B is 43nm and C is 58 nm.



**Figure S6.** Hydrodynamic diameter distributions of Au NPs, PMAA-*b*-PNIPAm-@-Au and PIC-@-Au NPs with different size of the Au template, where A is 10nm, B is 43nm and C is 58nm.



**Figure S7.** Hydrodynamic diameter distributions of PICsome<sub>10</sub>, PICsome<sub>43</sub> and PICsome<sub>58</sub>, where the subscript corresponds to the size of the Au template.