## **Supporting Information for:**

## From Multi-responsive Tri- and Diblock Copolymers to Diblock-Copolymer-Decorated Gold Nanoparticles: Effect of Architecture on Micellization Behaviors in Aqueous Solutions

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Scheme 1. Synthesis the ATRP initiator DTBE.



Scheme 2. Synthesis of the PDMAEMA-b-PMEO2MA-b-PDMAEMA, PMEO2MA-b-PDMAEMA-b-PMEO2MA triblock



Figure S1. Gel Permeation Chromatography (GPC) traces of polymers.

Polymer	$M_{HNMR}{}^a$	Mn <sup>b</sup>	Mw <sup>b</sup>	PDI <sup>b</sup>
PDMAEMA <sub>54</sub>	8945	8761	10838	1.23
PMEO <sub>2</sub> MA <sub>80</sub> -PDMAEMA <sub>54</sub> -PMEO <sub>2</sub> MA <sub>80</sub>	23233	39180	54981	1.40
PMEO <sub>2</sub> MA <sub>68</sub>	12484	13369	17294	1.29
PDMAEMA46-PMEO2MA68-PDMAEMA46	21119	27748	36869	1.33

Table S1. The Composition, Molecular Weight and Polydispersity of Polymers

<sup>a</sup>As calculated from <sup>1</sup>H NMR spectra.

<sup>b</sup>As measured by GPC with THF as an eluent.



Figure S2. Thermal profile of PMEO<sub>2</sub>MA (black) and PDMAEMA (red) in aqueous solutions as probed by UV-vis



spectra.

Figure S3. UV-vis spectra, size distributions and TEM images of Au NPs and Au@PDMAEMA<sub>27</sub>-b-PMEO<sub>2</sub>MA<sub>80</sub> particles dispersed in aqueous solutions.



Figure S4. Au@PMEO<sub>2</sub>MA<sub>34</sub>-b-PDMAEMA<sub>46</sub> nanoparticles well-dispersed in different solvents (water, THF,

## chloroform and toluene).



Figure S5. (A) Zeta potential of different block copolymers in aqueous solutions at different pHs. (B) Zeta potential of Au@AB and Au@BA NPs at different pHs. The lines are drawn to guide the eye.



Figure S6. Photographs of the phase transfer process for the Au@PMEO<sub>2</sub>MA<sub>34</sub>-b-PDMAEMA<sub>46</sub> system: (A) solventtriggered NP transfer from toluene to the aqueous phase at 4 °C after shaking, (B) acid-triggered NP transfer from toluene to the aqueous phase at 4 °C after shaking, and (C) retention of NPs in the aqueous phase (0.2 M NaCl) upon heating to 50 °C