

## Supporting Information

### **Synthesis of Janus Au@BCP nanoparticles via UV light-initiated RAFT polymerization-induced self-assembly**

Zhenzhong Liu,<sup>a</sup> Chenglin Wu,<sup>b</sup> Yabo Fu,<sup>b</sup> Xinlei Xu,<sup>a</sup> Jialei Ying,<sup>a</sup> Jiansong Sheng,<sup>a</sup>  
Youju Huang,<sup>\*c,d</sup> Chunxin Ma<sup>\*a,e</sup> and Tao Chen<sup>f</sup>

*a. Research Institute of Zhejiang University-Taizhou, Taizhou 318000, P. R. China.*

*b. School of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou 318000, P. R. China.*

*c. College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, P. R. China.*

*d. National Engineering Research Centre for Advanced Polymer Processing Technology, Zhengzhou University, Zhengzhou 450002, P. R. China.*

*e. State Key Laboratory of Marine Resource Utilization in South China Sea, Hainan University, Haikou 570228, P.R. China.*

*f. Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Division of Polymer and Composite Materials, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China.*

*E-mail: yjhuang@hznu.edu.cn, chunxinma@zju.edu.cn*

## Experimental Section

### Materials

Hydrogen tetrachloroaurate trihydrate (99.9 %), sodium citrate tribasic dihydrate were purchased from Aladdin. 4-Vinylpyridine (4VP) was distilled under vacuum after dried with  $\text{CaH}_2$ . Styrene was passed through a column of activated basic alumina prior to use. AIBN was recrystallized from methanol twice and stored at  $3^\circ\text{C}$  prior to use. S-1-dodecyl-S-(a,a'-dimethyl-a''-acetic acid) trithiocarbonate (DDMAT) was synthesized according to the literature reported by Lai *et al.*<sup>1</sup> Methanol was distilled before use. Other reagents were used as received. The UV light source is a UV nail gel curing lamp ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) which equipped with  $4 \times 9 \text{ W}$  bulbs. The intensity of the light was measured as  $2.50 \text{ mW cm}^{-2}$  by a UV radiometer.

### Synthesis of P4VP-CTA

The P4VP-CTA was prepared by thermal initiated RAFT solution polymerization in THF at  $80^\circ\text{C}$ .<sup>2</sup> A typical polymerization procedure is described as follows: 4VP (4.24 g, 40 mmol), DDMAT (72 mg, 0.2 mmol) and AIBN (6.40 mg, 0.04 mmol) were dissolved in 10 mL THF. The solution was degassed by bubbling with nitrogen for 30 min, and then placed in a preheated oil bath at  $80^\circ\text{C}$ . The polymerization was stopped by immersing in liquid nitrogen and exposing to air after 6 h. The resulting polymer was purified by precipitation into excess n-hexane for three times and dried under vacuum at  $40^\circ\text{C}$  overnight. The polymer was characterized by  $^1\text{H}$  NMR and GPC.

### Synthesis of citrate-capped AuNPs

The AuNPs was prepared by sodium citrate reduction of  $\text{HAuCl}_4$ .<sup>3</sup> All glassware was cleaned with aqua regia, repeatedly washed with nanopure water and dried before use. In a typical experiment,  $\text{HAuCl}_4$  aqueous solution (0.246 mL,  $1.22 \times 10^{-4} \text{ mol}$ ) and a sodium citrate aqueous solution (3 mL,  $4.35 \times 10^{-4} \text{ mol}$ ) were added into 100 mL boiling water under vigorously stirring in a 250 mL flask. The mixture was refluxed for 30 minutes until the solution reached a wine red color. After cooled to room temperature, the colloidal suspension was stored at room temperature. The TEM results were shown in Figure S2.

### Preparation of polymer-tethered Au@P4VP

The method is modified by the report in literature.<sup>4,5</sup> A 30 mL of the original citrate-capped AuNPs were centrifuged (8500 rpm, 30 min) to remove the excess sodium citrate. The concentrated AuNPs were redispersed in 2 mL  $\text{H}_2\text{O}$ . Then, a mixture of 25 mg P4VP-CTA dissolved in 15 mL methanol was added to the concentrated AuNPs under sonification at room temperature for 1 h. After incubated for 24 h, the solution was concentrated by centrifugation at 10000 rpm for 30 min. The centrifugation–redispersion procedure was repeated twice in order to exchange the solvent with methanol. Finally, the dispersion was concentrated to 2 mL and stored in refrigerator before use.

### Preparation of Janus Au@P4VP-*b*-PS nanoparticles

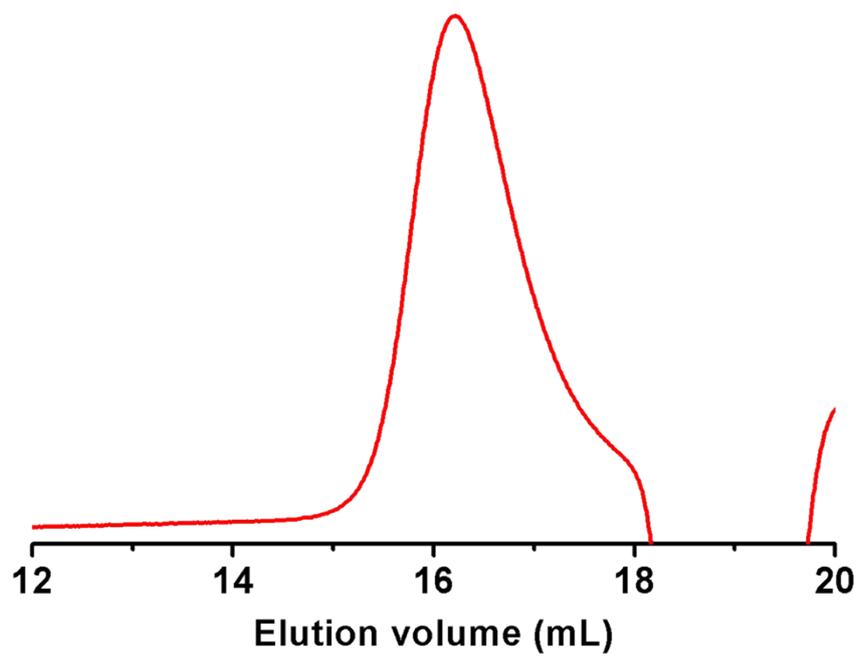
In UV light-initiated RAFT polymerization, the glass bottle charged with reaction mixture was placed in a UV curing lamp, which was equipped with a magnetic stirring apparatus and a blowing air device for keeping constant temperature. The reaction mixture was deoxygenated by three freeze-pump-thaw cycles and filled with N<sub>2</sub> gas. Then the mixture was irradiated under UV irradiation. A typical experiment was conducted as follows: Au@P4VP (200 μL), P4VP (4.0 mg, 5.88 × 10<sup>-4</sup> mmol), styrene (0.909 g, 8.7 mmol), AIBN (0.02 mg, 1.21 × 10<sup>-4</sup> mmol) with a molar ratio of P4VP/St/AIBN = 5:14800:1 were dissolved in 3.2 mL methanol. The polymerization was conducted under UV light for 9 h and then stopped by exposing to air.

For the kinetics study, the hybridization process of Janus Au@P4VP-*b*-PS via UV light-initiated RAFT PISA was monitored by TEM, *in situ* UV-vis spectroscopy and *in situ* <sup>1</sup>H NMR spectroscopy. The evolution of Janus Au@BCPs during photopolymerization was recorded by TEM observation at timed intervals (e.g., 1 h, 3 h, 4 h, 5 h, 7 h and 9 h). The evolution of the UV-vis absorption spectra of the mixture with the molar ratio of P4VP/St/AIBN = 5:14800:1 in methanol were recorded after the solution exposed to the UV light at different time intervals. The evolution of <sup>1</sup>H NMR spectra of the mixture in *d*<sub>4</sub>-methanol during the polymerization was recorded at different time intervals after a NMR tube exposed to the UV light.

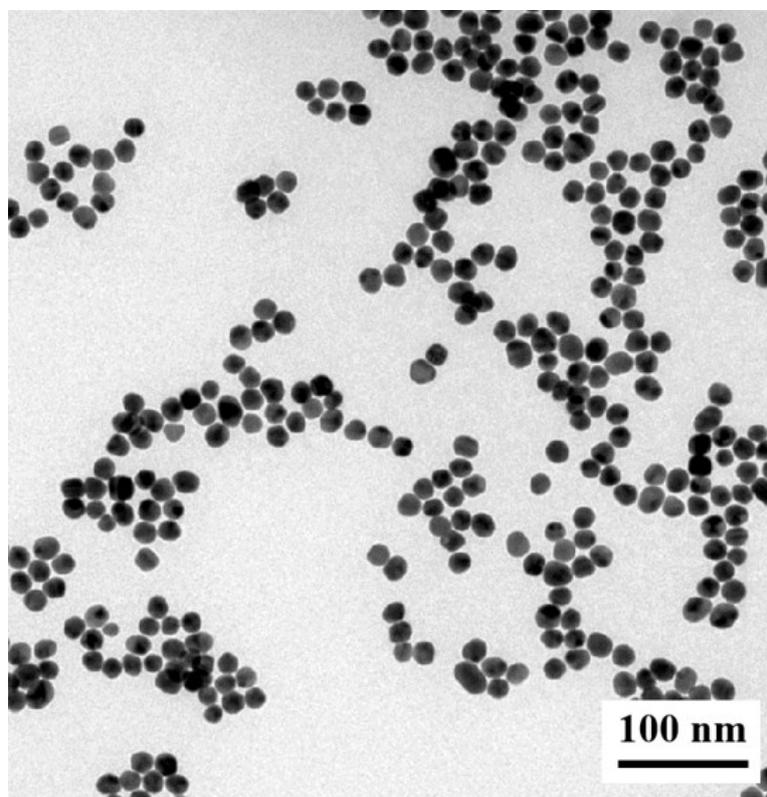
### Characterizations

The <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> using tetramethylsilane as an internal reference at room temperature on a Bruker AVANCE III 400 MHz NMR spectrometer in 5 mm diameter tubes. The number average molecular weight (*M<sub>n</sub>*) and molecular weight distributions (*M<sub>w</sub>*/*M<sub>n</sub>*) were assessed by Waters 1515 GPC equipped with refractive index detector at 40 °C. DMF was used as eluent at a flow rate of 1.0 mL/min. TEM images were performed with a JEOL JEM-2100F microscope at an accelerating voltage of 200 kV. SEM images were captured on a S4800 at an accelerating of 5 kV. The UV-vis absorption spectra were conducted on a Perkin Elmer Lambda 950 with wavelength from 300 nm to 800 nm. The XPS measurements were carried out using an XPS Kratos Axis Ultra<sup>DL</sup>D instrument. The power was 120 W and the X-ray spot size was set to 700×300 μm. The XPS spectra were calibrated relative to the reference energy value of the C 1s core level at 284.8 eV.

## Data analysis



**Figure S1.** The GPC curve of P4VP in DMF elution.

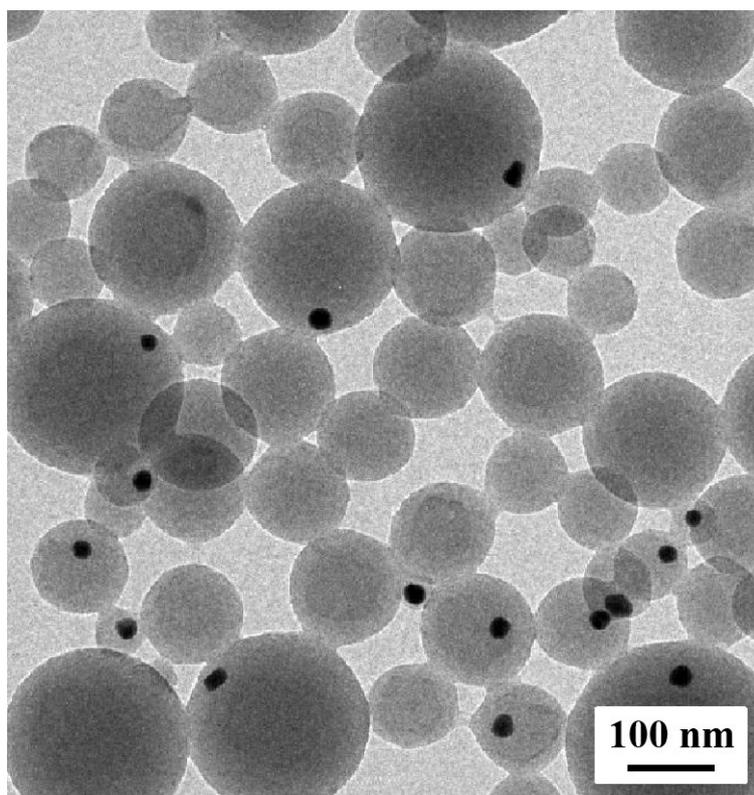


**Figure S2.** TEM image of citrate-capped AuNPs.

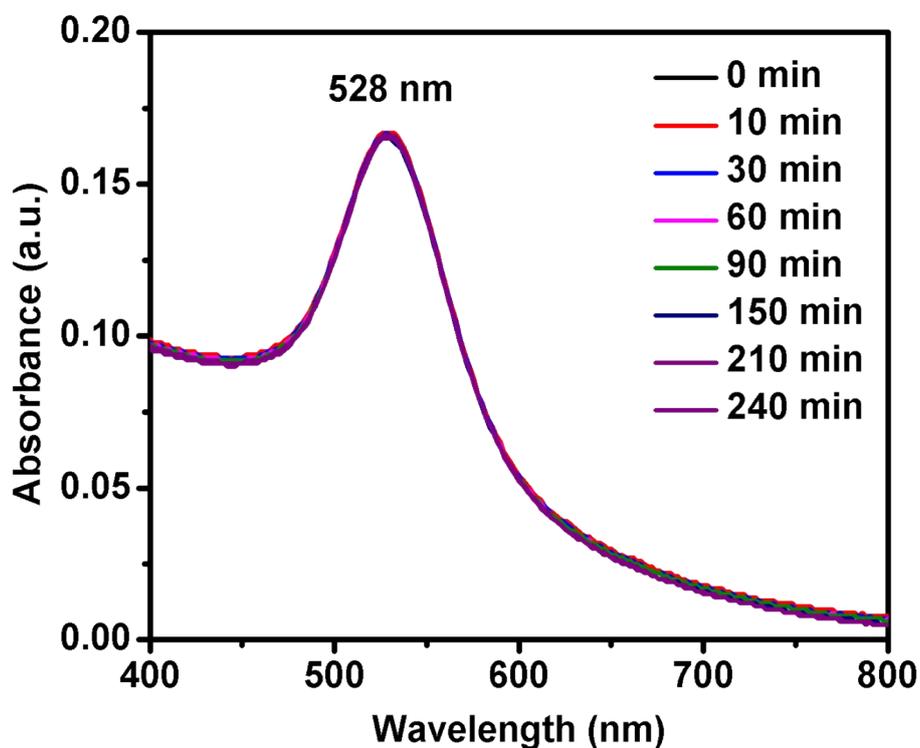
**Table S1.** Experimental recipe using citrate-capped AuNPs as seeds to prepare hybrid nanoparticles by UV-light initiated RAFT PISA.

entry	Au@citrate <sup>a</sup>	P4VP	St	AIBN	methanol
1	200 $\mu$ L	4 mg	0.1 mL	0.02 mg	3.2 mL

<sup>a</sup>The citrate-decorated AuNPs is concentrated in water and stored at 5 °C before use. Experimental condition: UV light intensity:  $I_{365\text{ nm}} = 2.50\text{ mW cm}^{-2}$ , irradiation time: 9 h, 25 °C.



**Figure S3.** SEM image of nanoparticles obtained using citrate-capped AuNPs as seeds in methanol.

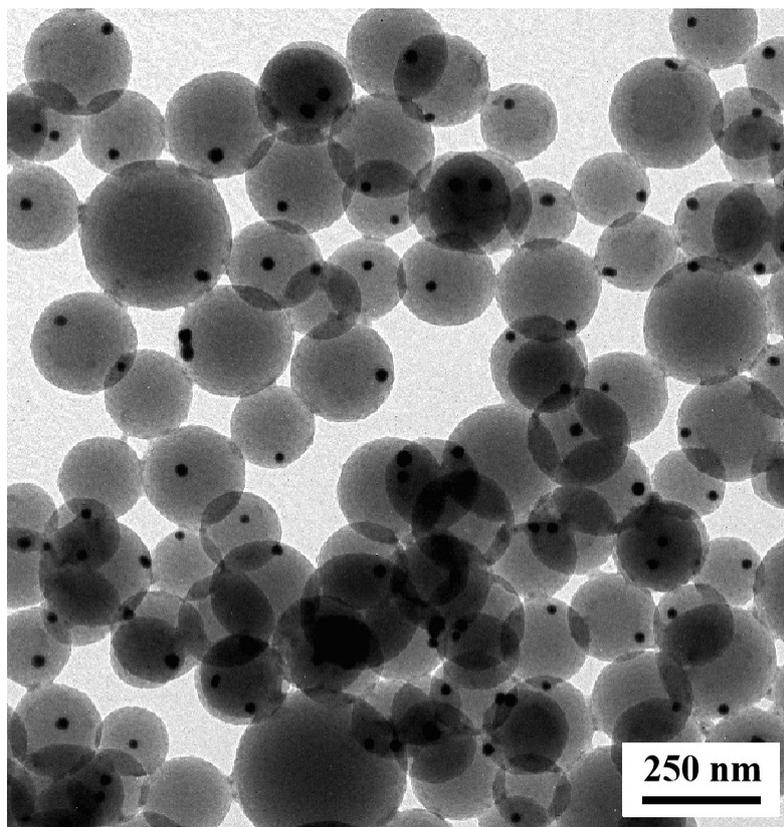


**Figure S4.** The evolution of UV-vis spectra of Au@P4VP upon UV irradiation at different times in methanol.

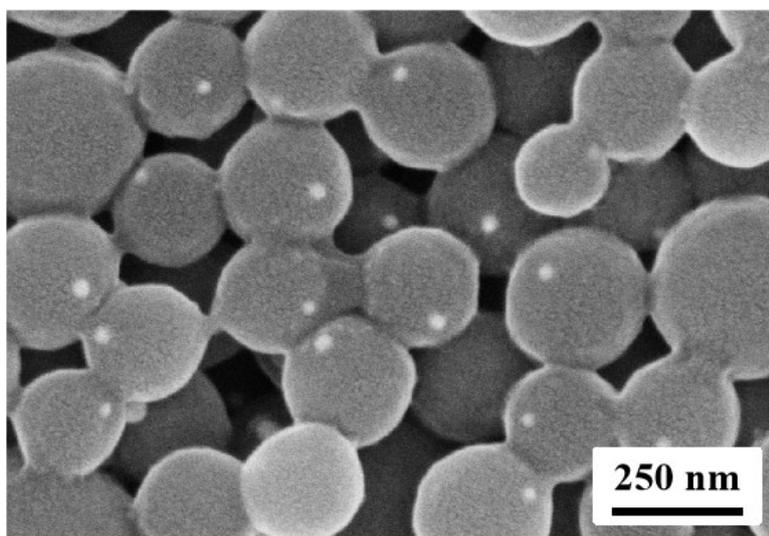
**Table S2.** Experimental recipes using Au@P4VP as seeds to prepare hybrid nanoparticles by UV-light initiated RAFT PISA.

entry	Au@ P4VP <sup>a</sup>	P4VP	St	AIBN	methanol
1	200 $\mu$ L	4 mg	0.1 mL	0.02 mg	3.2 mL

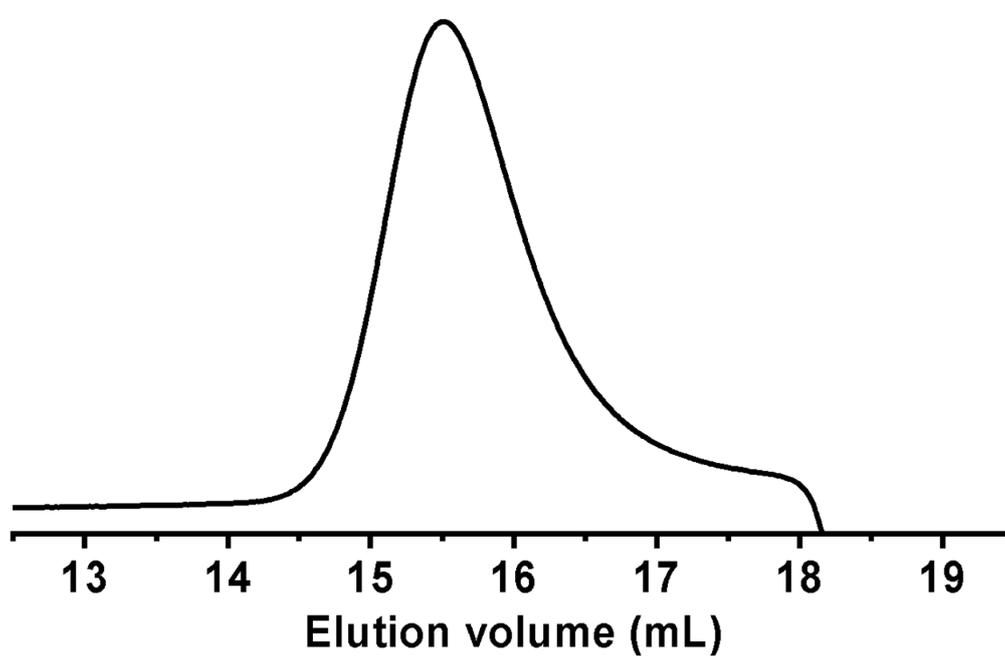
<sup>a</sup> The Au@P4VP is dispersed in methanol and stored at 5 °C before use. Experimental condition: UV light intensity:  $I_{365\text{ nm}} = 2.50\text{ mW cm}^{-2}$ , irradiation time: 9 h, 25 °C.



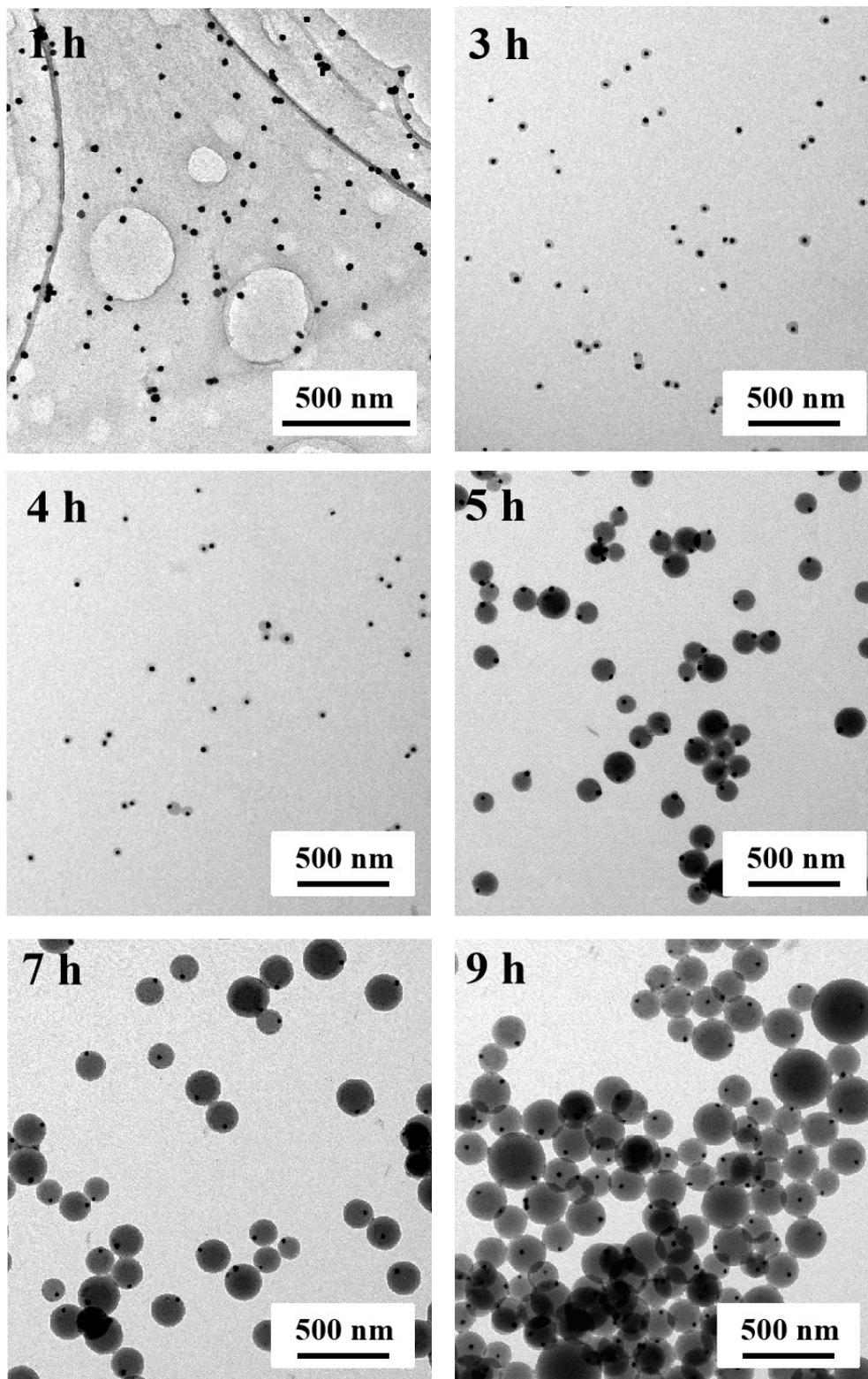
**Figure S5.** TEM image of Janus Au@P4VP-*b*-PS nanoparticles obtained using polymer-tethered Au@P4VP as seeds in methanol after 9 h polymerization.



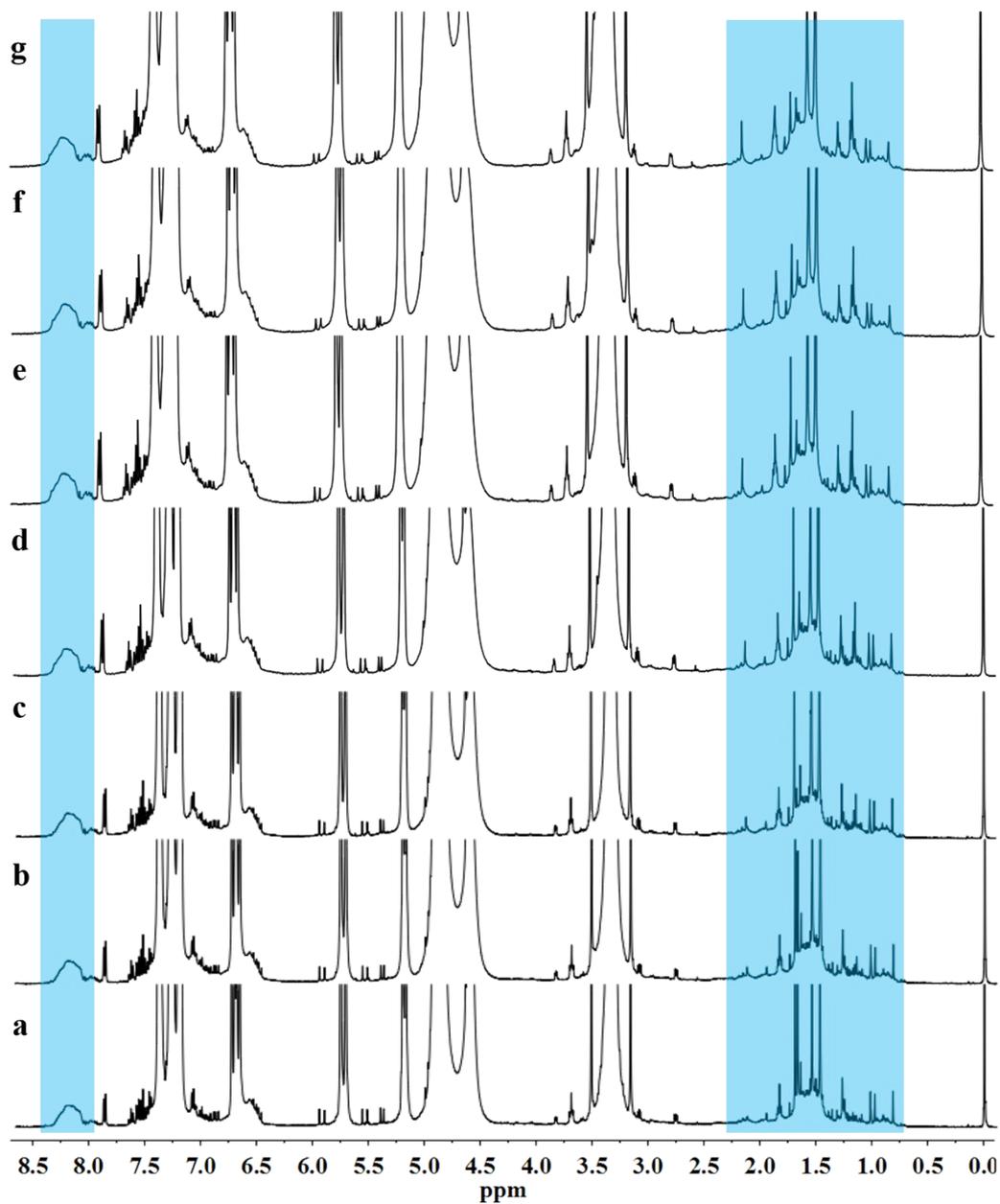
**Figure S6.** SEM image of Janus Au@P4VP-*b*-PS nanoparticles obtained using polymer-tethered Au@P4VP as seeds in methanol after 9 h polymerization. (Note: those nanoparticles which only see the micelles part is because the Au@P4VP part is displayed on the bottom side.)



**Figure S7.** The GPC curve of P4VP-*b*-PS obtained by Janus Au@BCPs in DMF elution.



**Figure S8.** TEM images of the intermediates obtained at different polymerization times: 1 h, 3 h, 4 h, 5 h, 7 h and 9 h.

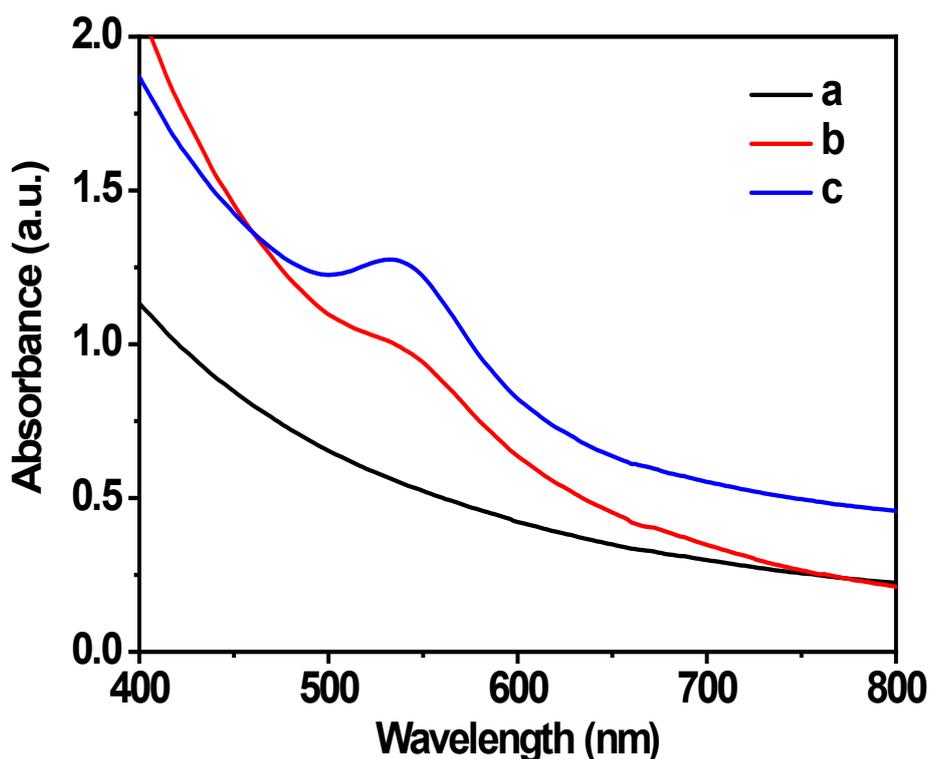


**Figure S9.** The evolution of  $^1\text{H}$  NMR spectra during UV light-initiated RAFT PISA in  $d_4$ -methanol at (a) 0 h, (b) 1 h, (c) 3 h, (d) 4 h, (e) 5 h, (f) 7 h and (g) 9 h.

**Table S3.** Experimental recipes by tuning concentrations of Au@P4VP seeds, P4VP and styrene to prepare hybrid nanoparticles by UV-light initiated RAFT PISA.

entry	Au@ P4VP <sup>a</sup>	P4VP	St	AIBN	methanol
1	200 $\mu$ L	5 mg	0.15 mL	0.02 mg	3.2 mL
2	200 $\mu$ L	4 mg	0.10 mL	0.02 mg	3.2 mL
3	400 $\mu$ L	4 mg	0.10 mL	0.02 mg	3.2 mL

<sup>a</sup> The Au@P4VP is concentrated in methanol and stored at 5 °C before use. Experimental condition: UV light intensity:  $I_{365\text{ nm}} = 2.50\text{ mW cm}^{-2}$ , irradiation time: 9 h, 25 °C.



**Figure S10.** UV-vis spectra of hybrid nanoparticles obtained via UV light-initiated RAFT PISA with different recipes: (a) the mixture of Janus Au@BCPs and free micelles, (b) the bigger Janus Au@BCPs and (c) the smaller Janus Au@BCPs.

## References

1. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.
2. W. M. Wan, C. Y. Hong and C. Y. Pan, *Chem Commun*, 2009, **39**, 5883-5885.
3. H. Wang, X. Song, C. Liu, J. He, W. H. Chong and H. Chen, *ACS Nano*, 2014, **8**, 8063-8073.
4. A. M. Percebom, J. J. Giner-Casares, N. Claes, S. Bals, W. Loh and L. M. Liz-Marzán, *Chem Commun*, 2016, **52**, 4278-4281.
5. N. Guarrotxena, O. Garcia and I. Quijada-Garrido, *Scientific reports*, 2018, **8**, 5721.