

## Supporting Information

### Gold Nanoparticle-Catalysed Photosensitized Water Reduction for Hydrogen Generation

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#### 1. Synthesis and Characterizations

##### Chemicals and Apparatus

Protoporphyrin IX zinc(II) (ZnPP), zinc tetraphenylporphyrin(ZnTPP) triethanolamine (TEOA, >98.0%), rhodium(III) chloride hydrate (Rh: 38-40 %),copper(I) chloride (CuCl, 99.999%), ethyl  $\alpha$ -bromoisobutyrate (EBiB, 98%), trifluoroacetic acid (TFA, 99%) and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%)were bought from Sigma-Aldrich and protoporphyrin disodium salt (PP, >98.0%) from TCI. All of those chemicals were used without further purification. 4-vinylpyridine (4VP) and tertbutyl acrylate (tBA) were dried over CaH<sub>2</sub> and distilled before use. The ligand tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>-TREN) were was synthesized using a literature method.<sup>1</sup> The water used in all experiments was ultrapure water from Milli-Q system (18.2 M $\Omega$ ·cm<sup>-1</sup>). The other reagents and solvents were purchased from commercial sources and used without further purification.

UV-visible absorption, emission and excitation spectra were recorded on a Varian Cary 50 Bio UV-vis spectrophotometer and Varian Cary Eclipse Fluorescence spectrophotometer respectively. Without notice, all of the spectra recorded were used a quartz cuvette (2 mm  $\times$  10 mm). The pH change was measured using apH-meter (Orion 410Aplus). Before measurement, the pH-meter was calibrated with buffer solutions of pH= 7, 10. <sup>1</sup>H NMR spectra were recorded on a Bruker300MHz spectrometer using CDCl<sub>3</sub> as solvent. Gel permeation chromatography (GPC) measurements were performed using a Waters system equipped with a Water 1515 isocratic HPLC pump, a Waters 2414

refractive index detector and a Waters 2998 photodiode array detector, THF being used as eluent (elution rate: 1.0 mL/min) and polystyrene standards used for calibration. Transmission electron microscopy (TEM) observations were carried out using a Hitachi H-7500 microscope at an acceleration voltage of 80 kV. For sample preparation, the solution was dropped and deposited on a TEM copper grid (200meshes, Electron Microscopy Sciences) without staining. The concentration of Au atom in the GSH capped Au NPs solution was assayed by inductively coupled plasma (ICP) spectrometry using an X Series II ICP-MS (Thermo Fisher Scientific).

### **Synthesis of the rhodium trisbipyridine chloride (Rh(bpy)<sub>3</sub>Cl<sub>3</sub>)**

Rh(bpy)<sub>3</sub>Cl<sub>3</sub> was synthesized as the literature method.<sup>2</sup> Rhodium trichloride (0.55 g, 0.21 mmol), bipyridine (0.96 g, 0.62 mmol) and *N*-ethyl morpholine (0.2 ml) were dissolved in 1.2 mL H<sub>2</sub>O and 1.2 mL EtOH mixed solvent in a 10 ml round bottomed flask. And the reaction mixture was heated in oil bath at 80° under stirring for 1 hour. Then the reaction mixture was filtered over Celite and the solvent was removed by rotary evaporator. The final product Rh(bpy)<sub>3</sub>Cl<sub>3</sub> was obtained by recrystallized from ethanol/water/butanol (v/v/v= 50/10/40) with pale yellow crystalline (0.86 g, 57%).

### **Synthesis of glutathione capped gold nanoparticles**

The 2 nm Au NPs was synthesized according to reference reported.<sup>3</sup> Briefly, HAuCl<sub>4</sub>·3H<sub>2</sub>O (62.0 mg, 0.16 mmol) was dissolved in 4.4 mL THF in 25 mL flask in an ice-water bath for 1 h. GSH (250 mg, 0.81 mmol) was slowly added to the flask under a very low stirring speed (60 rpm) and stirred overnight. Then freshly prepared NaBH<sub>4</sub> solution (60 mg, 1.6 mmol, freshly dissolved in 1.5 ml ice-cold ultrapure water) was rapidly added to the flask under very fast stirring speed (1150 rpm) and allowed to further react for over 48 h. Finally the precipitates were collected and washed thoroughly with methanol–water (v/v = 4:1) and dried in vacuum for 24 hrs, obtained Au NPs 33.5 mg which was then dissolved in 6.6 mL ultrapure water. The diameter of the Au NPs was determined to be approximately 2.0±0.7 nm by TEM and the concentration of Au atom was 12.5 mM, which was assayed by ICP-MS.

The 6 nm GSH capped Au NPs was synthesized with similar process but reacted in 20 mL ultrapure water. And the small nanoparticles or ligands were removed by washed in MeOH/H<sub>2</sub>O (1:1, v/v) and centrifuged. The Au NPs obtained 2.5 mg was dissolved in 0.5 mL ultrapure water contained 20.3 mM of Au atom. The diameter of the Au NPs was 6.5±1.0 nm

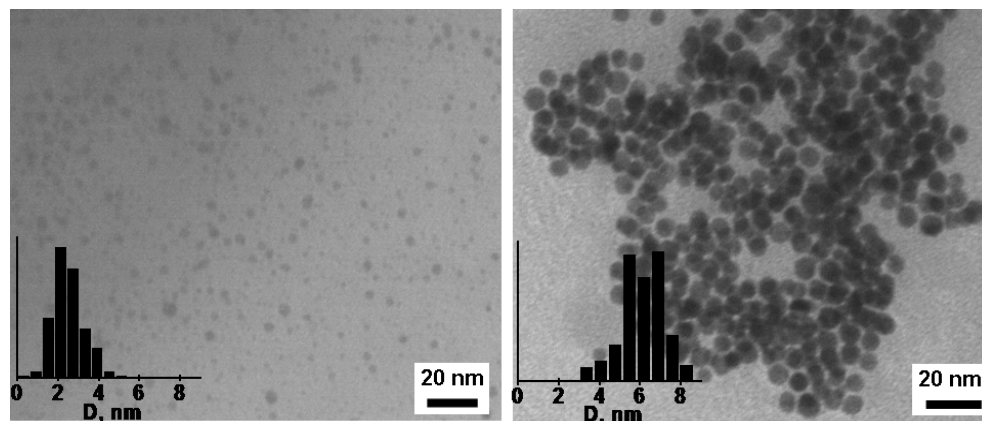
### Synthesis of diblock copolymer PAA<sub>52</sub>-*b*-P4VP<sub>90</sub> by ATRP

Block copolymer PAA<sub>52</sub>-*b*-P4VP<sub>90</sub> was synthesized according to literature.<sup>4,6</sup> Firstly, the macroinitiator PtBA-Cl was synthesized by ATRP of tBA with EBiB as initiator and CuCl/PMDETA as the catalyst. In a typical run, EBiB (0.19 g, 0.98mmol), CuCl (0.10 g, 1mmol), tBA (10.00 g, 0.024 mol), PMDETA (0.17 g, 1mmol) and acetone (12 mL) were added successively into a 25-mL flask. The reaction mixture was degassed by three-pump-thaw cycles, back-filled with N<sub>2</sub> and placed in an oil bath thermostated at 60 °C. After 12 hrs reaction, it was then diluted with THF and passed through a column of neutral alumina to remove the metal salt, then purified by precipitation in a water/methanol mixture (v/v= 1/3) three times, and dried under vacuum. Yield: 7.7 g(77%).  $M_n= 6200, M_w/M_n=1.12$  (SEC) and 52 units of tBA in one polymer (NMR).

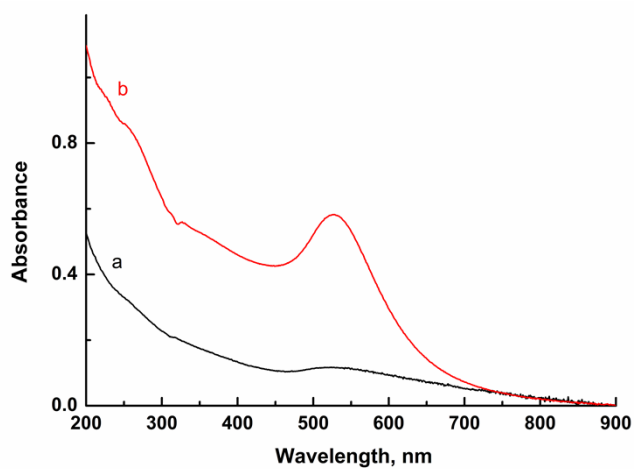
To obtain the diblock copolymer of PtBA<sub>52</sub>-*b*-P4VP<sub>90</sub>, 4VP was polymerized using PtBA-Cl macroinitiator and CuCl/Me<sub>6</sub>-TREN as the catalyst. PtBA-Cl (2.0 g, 0.3mmol), 4VP (5 mL, 45.0 mmol), CuCl (45 mg, 0.45mmol), CuCl<sub>2</sub> (20 mg, 0.15mmol), Me<sub>6</sub>-TREN (0.13 mL, 0.5mmol) and isopropanol (10 mL) were added successively into a 50-mL flask. The reaction mixture was degassed by three-pump-thaw cycles, back-filled with N<sub>2</sub> and placed in an oil bath at 80 °C for 5 h. It was then diluted with THF and passed through a column of neutral alumina to remove the metal salt. The formed PtBA<sub>52</sub>-*b*-P4VP<sub>90</sub> was further purified by precipitation in a water/methanol (v/v= 3/1) mixture three times and dried under vacuum. Yield: 4.2 g (60%).  $M_n= 13519, M_w/M_n=1.25$  (SEC) and 90 units of 4VP in one polymer (NMR).

Finally, the diblock copolymer PAA<sub>52</sub>-*b*-P4VP<sub>90</sub> was obtained by hydrolysis of PtBA<sub>52</sub>-*b*-P4VP<sub>90</sub>. 4.2 g of PtBA<sub>52</sub>-*b*-P4VP<sub>90</sub> and 10 mL of TFA was dissolved into 30 mL of CHCl<sub>3</sub>. After stirring for 20 hrs, the pure PAA<sub>52</sub>-*b*-P4VP<sub>90</sub> was obtained by precipitation of reaction mixture into diethyl ether three times with yield of 4.7 g.

## 2. More Characterization and Measurement Results



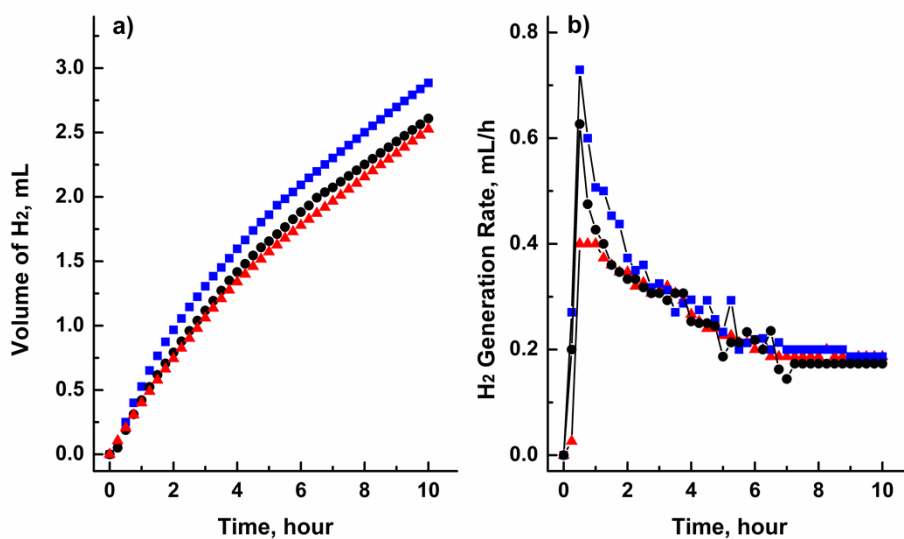
**Figure S1.** TEM image of GSH capped 2 nm (left) and 6 nm AuNPs (right).



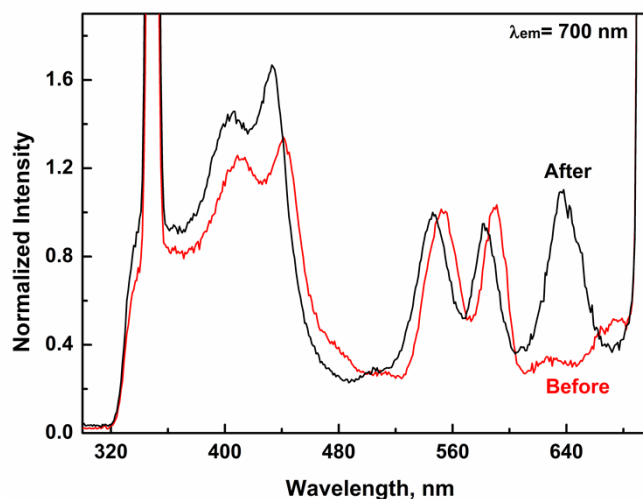
**Figure S2.** Absorption spectra the water solution of GSH capped 2 nm(a: 200  $\mu$ M), 6 nm Au NPs(b: 250  $\mu$ M) in 1 cm optical length.



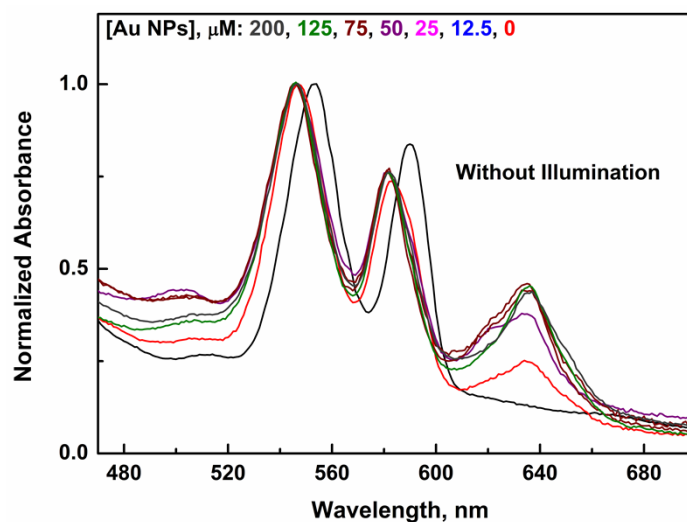
**Figure S3.** Photos of the water splitting solution without ZnPP after irradiation for 3 hours. [Au NPs] = 125  $\mu$ M; [PAA<sub>52</sub>-*b*-P4VP<sub>90</sub>] = 2 mg/mL; [Rh(bpy)<sub>3</sub>Cl<sub>3</sub>] = 2 mM; [bpy] = 3 mM; [TEOA] = 0.3 M, at pH=7.5 (10 mM phosphate buffer) at 25°C.



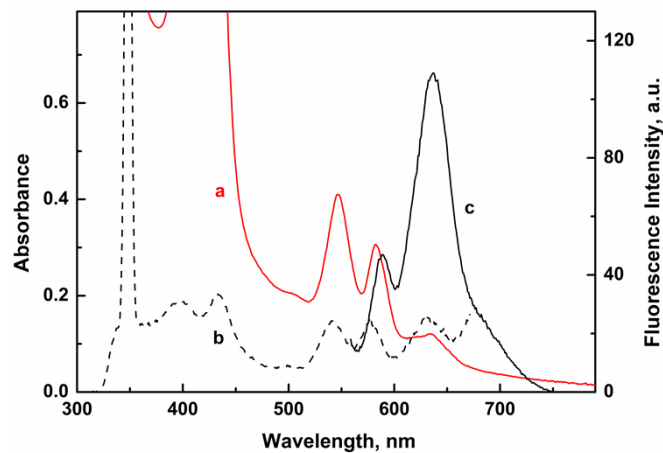
**Figure S4.** Accumulative hydrogen generation quantity (a) and average hydrogen generation rate (b) from three separate experiments using water splitting solutions containing 125  $\mu$ M 2 nm Au NPs.



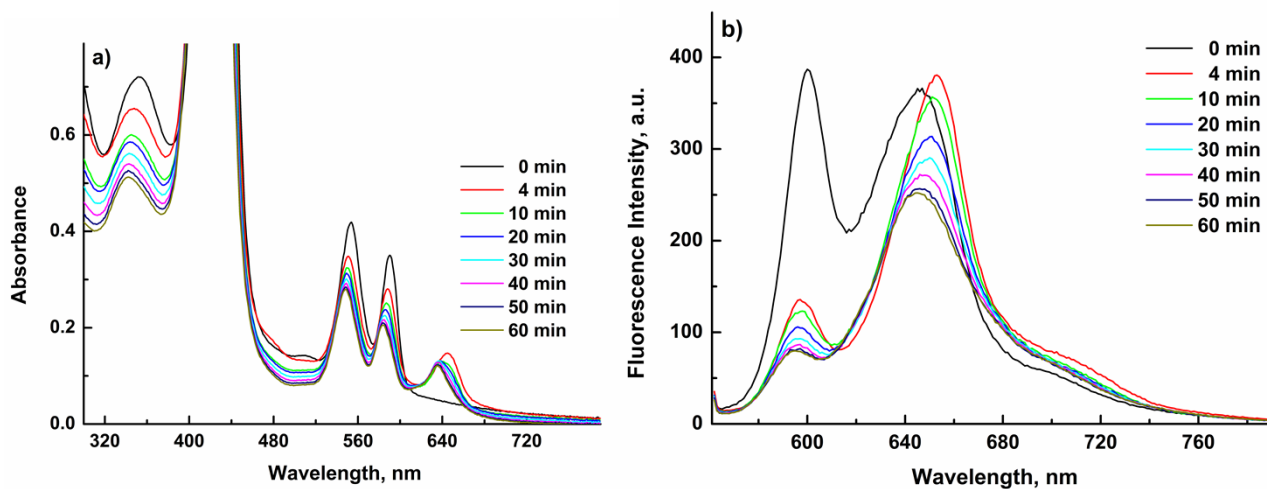
**Figure S5.** Normalized excitation spectra (a,  $\lambda_{em} = 700$  nm) of the water splitting solution containing 200  $\mu\text{M}$  AuNPs before (in red) and after (in black) irradiation for 10 hrs.



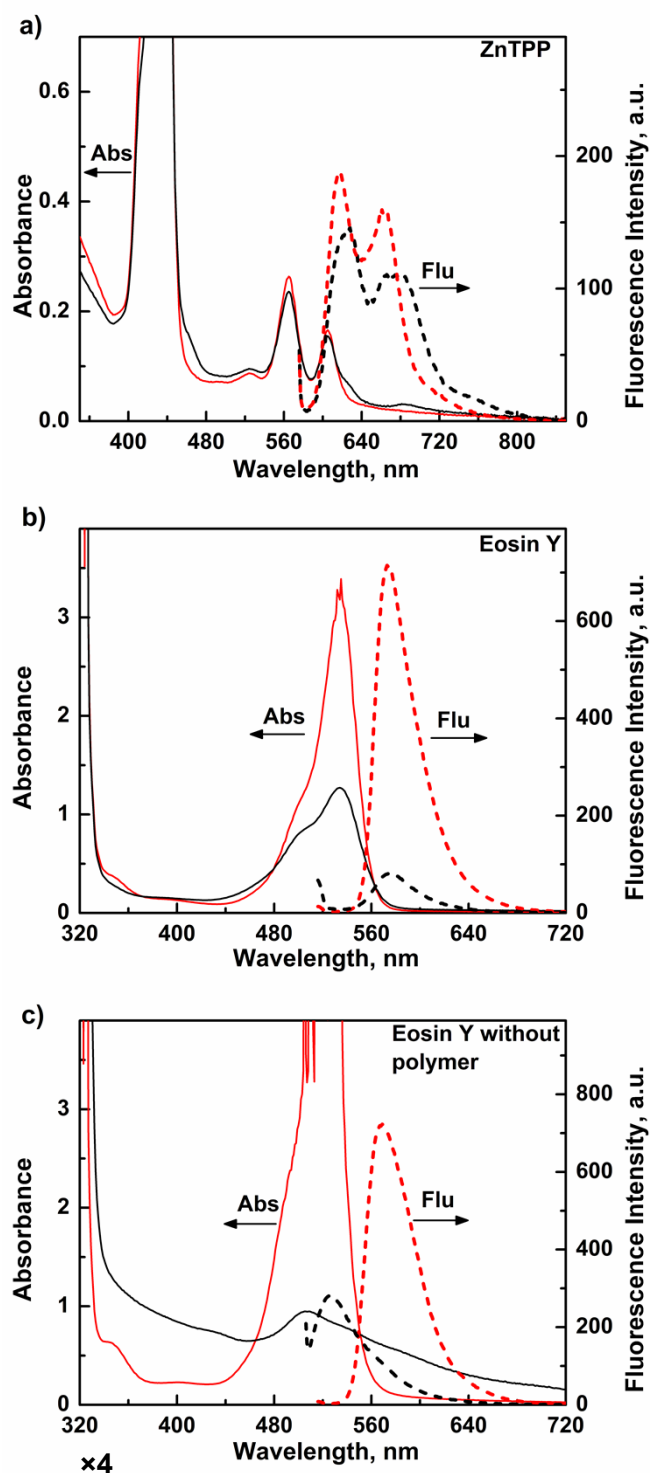
**Figure S6.** Normalized absorption spectra of the water splitting solution without AuNP catalyst before irradiation (—) or containing different concentrations of AuNPs after irradiation. [AuNPs],  $\mu\text{M}$ : —: 200, —: 125, —: 75, —: 50, —: 25, —: 12.5, —: 0.



**Figure S7.** Absorption spectra (a), excitation (b,  $\lambda_{em}=700$  nm) and emission ( $\lambda_{ex}=550$  nm, solid line) spectra of the water splitting solution containing  $200 \mu\text{M}$   $\text{K}_2\text{PtCl}_4$  after irradiation for 10 hrs.



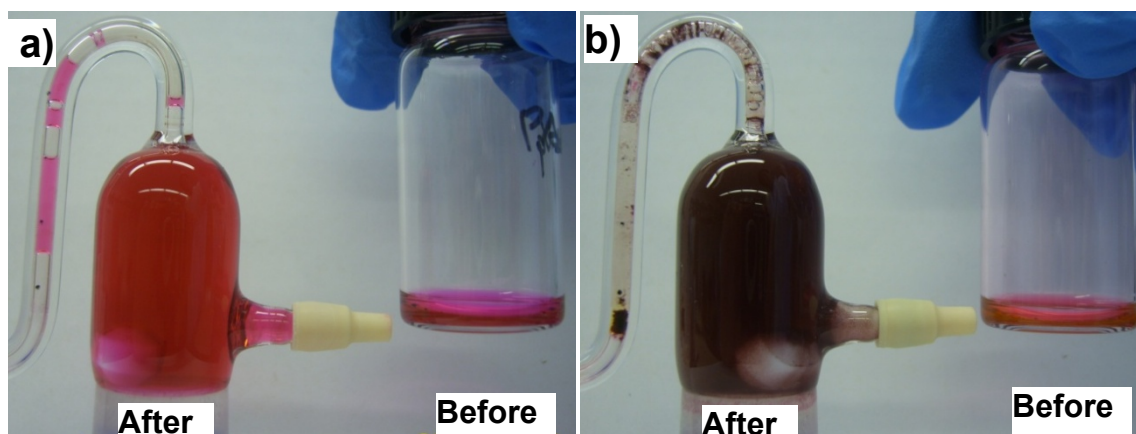
**FigureS8.** Absorption (a) and emission (b,  $\lambda_{ex}=550$  nm) spectra of the solution containing ZnPP (0.1 mM), PAA<sub>52</sub>-*b*-P4VP<sub>90</sub> (2 mg/mL) and TEOA (0.3 M) after irradiation at pH=7.5 (10 mM phosphate buffer) at 25°C.



**FigureS9.** Absorption (solid line, 0.2 cm optical length) and emission (a:  $\lambda_{\text{ex}}=565$  nm; b, c:  $\lambda_{\text{ex}}=516$  nm; dash line) spectra of the solution using ZnTPP (a, with polymer) or Eosin Y (b, with polymer; c, without polymer) as photosensitizer for water splitting before irradiation (in red line) and after irradiation (in black line).  $[\text{PAA}_{52}\text{-}b\text{-P4VP}_{90}] = 2$  mg/mL;  $[\text{Rh}(\text{bpy})_3\text{Cl}_3] = 2$  mM;  $[\text{bpy}] = 3$  mM;



[TEOA]= 0.3 M; [Au NPs]= 125  $\mu$ M, at pH=7.5 (10 mM phosphate buffer) at 25°C. Dye: [Eosin Y]= 0.2 mM or [ZnTPP]= 0.1mM.



**FigureS10.** Photos of the solution containing Eosin Y as photosensitizer with polymer (a) or without polymer (b) before and after irradiated for 6 hours. [AuNPs]= 125  $\mu$ M; [Eosin Y]= 0.2 mM; [PAA<sub>52</sub>-*b*-P4VP<sub>90</sub>]= 2 mg/mL; [Rh(bpy)<sub>3</sub>Cl<sub>3</sub>]= 2 mM; [bpy]= 3 mM; [TEOA]= 0.3 M, at pH=7.5 (10 mM phosphate buffer) at 25°C.

## References

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