

Supporting Information

Using Block Copolymers to Enhance Photosensitized Water Reduction for Hydrogen Gas Generation

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1. Synthesis

Materials. Prior to use, tetrahydrofuran (THF, 99%) was refluxed with sodium and a small amount of benzophenone and distilled, triethylamine (TEA) (Aldrich, $\geq 99\%$) was refluxed with *p*-toluenesulfonyl chloride (Fluka, $\geq 99\%$) and distilled, dichloromethane (DCM) was distilled from CaH_2 . Copper(I) chloride (CuCl , 99.999%), α -bromoisobutyryl bromide (98%), trifluoroacetic acid (TFA, 99%) and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used directly. 4-vinylpyridine (4VP) and tertbutyl acrylate (tBA) were dried over CaH_2 and distilled before use. Tris[2-(dimethylamino)ethyl]amine ($\text{Me}_6\text{-TREN}$) was synthesized using a literature method.¹ Rhodium tris-bipyridine chloride was also synthesized by using a literature method.² All reagents were purchased from commercial sources and used without further purification.

Synthesis of PtBA-Cl ATRP macroinitiator. PtBA-Cl was firstly synthesized by ATRP of tBA with propargyl 2-bromoisobutyrate as initiator and CuCl/PMDETA as the catalyst. In a typical run, propargyl 2-bromoisobutyrate (0.06g, 0.3 mmol), CuCl (30.0 mg, 0.3 mmol), tBA (3.1 g, 0.024 mol), PMDETA (51.0 mg, 0.3 mmol) and acetone (4.0 mL) were added successively into a 10-mL flask. The reaction mixture was degassed by three-pump-thaw cycles, back-filled with N_2 and placed in an oil bath thermostated at 60 °C for 12 h. It was then diluted with THF and passed through a column of neutral alumina to remove the metal salt. The macroinitiator was then purified by precipitation in a water/methanol mixture (1/3 v/v) three times, and dried under vacuum. Yield: 68%. $M_n=7950$ and $M_w/M_n=1.15$ (SEC).

Synthesis of PtBA-*b*-P4VP. To obtain the diblock copolymer of PtBA-*b*-P4VP, 4VP was polymerized using PtBA-Cl macroinitiator and $\text{CuCl/Me}_6\text{-TREN}$ as the catalyst. In a typical example, PtBA-Cl (1.0 g, 0.13 mmol), 4VP (1.6 g, 15.0 mmol), CuCl (16 mg, 0.16 mmol), $\text{Me}_6\text{-TREN}$ (36.8 mg, 0.16 mmol) and DMF (4.0 mL) were added successively into a 10-mL flask. The reaction mixture was degassed by three-pump-thaw cycles, back-filled with N_2 and placed in an oil bath thermostated at 80 °C for 16 h. It was then diluted with THF and passed through a column of neutral alumina to remove the metal salt. The formed PtBA-*b*-P4VP was further purified by precipitation in a water/methanol mixture (1/3 v/v) three times and, and dried under vacuum. Yield: 60%. $M_n=16100$ and $M_w/M_n=1.16$ (SEC).

Synthesis of PAA-*b*-P4VP. The hydrolysis of tBA groups of PtBA-*b*-P4VP gives rise to the amphiphilic diblock copolymer PAA-*b*-P4VP. Typically, 1.0 g of PtBA-*b*-P4VP was firstly dissolved into 8.0 mL of DCM. Then 1.5 mL of TFA was added into the polymer solution to hydrolyze the PtBA segment for 5 h, after that, the pure PAA-*b*-P4VP was obtained by precipitation of the reaction mixture into diethyl ether three times. Yield: 86%.

2. Characterizations

NMR Spectra. ^1H NMR spectra in pyridine d_5 were recorded on a Bruker spectrometer (300MHz, AC300), while those in D_2O were obtained with an Oxford spectrometer (400MHz, AS400). Pyridine d_5 : $\delta = 8,7$ ppm; $\delta = 7,6$ ppm; $\delta = 7,2$ ppm; D_2O : $\delta = 4,5$ ppm.

Photophysical Measurements. UV-vis absorption spectra were recorded on a Varian 50 Bio Cary spectrophotometer. Steady-state fluorescence emission spectra were recorded on a Varian Cary Eclipse spectrometer.

Photoinduced Hydrogen Generation. We used a 500W mercury lamp with UV cut-off filter (Oriel Thermo 66902) for the illumination experiments. After a given illumination time, hydrogen gas was sampled by using a Valco series A2 syringe. The amount of hydrogen gas was obtained through analysis using a GC-TCD Hewlett Packard 5890 Series II, the column being packed with 5 Å molecular sieves (2 meter long).

Preparation of Samples for Hydrogen Generation. A solution was first prepared by directly adding ZnPP, copolymer, TEOA and K_2PtCl_4 together in distilled water (typically a volume of 7 mL). A second aqueous solution of bipyridine and rhodium trisbipyridine chloride (typically a volume of 2 mL) was also prepared and heated to 80°C for 5 min to solubilize the chemicals. When the latter solution was cooled to room temperature, the two solutions were mixed under vigorous stirring. We set pH to 7.5 with sulfuric acid (1 M), added the phosphate buffer and corrected the volume to 10 mL. Finally, the solution was bubbled with argon for 30 min prior use.

¹ D. Landini and F. Rolla, *J Org Chem*, 1980, **45**, 3527.

² M. Kirch, J.M. Lehn and J.P. Sauvage, *Helvetica Chimica Acta*, 1979, **62**, 1345-1381.