

Supplementary Information

**Precise design of copolymer-conjugated nanocatalysts for active electron transfer**

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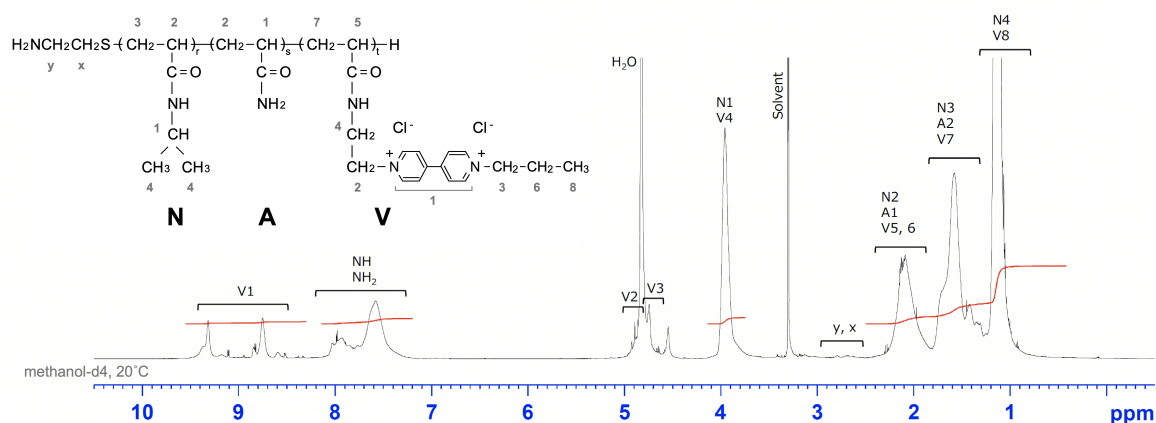
## I. Experimental procedures

**Materials.** *N*-Isopropylacrylamide (NIPAAm) and acrylamide (AAm) (Fujifilm Wako Pure Chemical Industries, Co., Ltd., Osaka, Japan) were purified through recrystallization. *N*-Acrylamidoethyl-*N'*-*n*-propyl-4,4'-bipyridinium bromide chloride (viologen monomer) was synthesized according to the procedures reported in the literatures.<sup>1-2</sup> The counterion of the monomer was exchanged with chloride by an ion-exchange resin (AMBERLITE IRA402BLCL, ORGANO Co., Tokyo, Japan). All the other reagents were used as received without further purification.

**Preparation and characterization of poly(NIPAAm-*co*-AAm-*co*-Viologen) (PNAV).** Semitelechelic poly(NIPAAm-*co*-AAm-*co*-Viologen) with a terminal amino end group (PNAV) was synthesized by the radical telomerization of NIPAAm, AAm, and viologen monomers using 2-aminoethanethiol (AESH) as a chain transfer agent. NIPAAm (6.64 g), AAm (0.24 g), viologen monomer (2.1 g), AESH (0.23 g), AIBN (0.12 g) as an initiator, and HCl (1 M, 5 mL) were dissolved in EtOH/H<sub>2</sub>O (25 mL/20 mL). The ampule containing the solution was degassed by freeze-thaw cycles and subsequently polymerized at 75 °C for 24 h. After dialysis with a 3,500 molecular weight cut-off membrane and freeze-drying, the polymer was obtained. The <sup>1</sup>H-NMR spectra of the copolymer in methanol-*d*<sub>4</sub> were measured (AVANCE<sup>III</sup>-600 with Cryo Probe, Bruker Biospin) (**Fig. S1**). The molecular weight of the polymer was determined using gel permeation chromatography (Pump: Shodex DS-4, Detector: Shodex RI-101; Columns: Shodex OHpak SB806M HQ × 2+SB-802.5 HQ × 1, Showa Denko K.K., calibrated using PS std). The sample with 0.2 wt% solution in DMF was used for the measurement under the given conditions (eluent: 10 mM LiBr in DMF; flow rate: 1.0 mL/min; column temperature: 50 °C; sample injection volume: 100 μL). The molecular weight of the polymer ( $M_w$ ), as determined by gel permeation chromatography, was  $5.02 \times 10^3$  g mol<sup>-1</sup> (polydispersity,  $M_w/M_n = 4.14$ ). The absorption spectra and transmittances of the solutions were measured using a UV-vis spectrometer (V-750, JASCO) (**Fig. S2**). The transmittance as a function of temperature was measured by the spectrometer equipped with an electronically thermo-stated cell holder by raising the temperature at a rate of 0.5 °C min<sup>-1</sup>.

**Preparation and characterization of PNAV-Pt nanoparticles.** The PNAV-conjugated Pt nanoparticles (NPs) were prepared by liquid reduction method at ambient temperature (approximately 25 °C). An aqueous solution of hydrogen hexachloroplatinate(IV) hexahydrate (1.2 mM, 15.0 mL) was placed in a round-bottomed flask and the prepared PNAV (48.8 mg) was added and sonicated for 30 min. Subsequently, NaOH aq. (0.1 M, 1 mL) was added to the solution under vigorous stirring, and a reducing agent of NaBH<sub>4</sub> aq. (55 mM, 2.5 mL) was added dropwise to the solution and stirred for 30 min. The color of the solution changed from yellowish to dark brown after reduction with NaBH<sub>4</sub>. The polymer concentration in the aqueous solution was 2.6 mg/mL. To remove the unconjugated polymers and salts from the synthesized PNAV-Pt colloidal solution, the sample was purified using a dialysis membrane with a 100 K molecular weight cutoff (Amicon ultra-0.5, Merck) and centrifuged (15,000 rpm, 15 min, three times) (**Fig. S4**). After centrifugation, the precipitates were redispersed in the same volume of pure water as the sample before dialysis. The composition ratios of PNAV and Pt were determined by the elemental analysis of sulfur (S) and platinum (Pt) by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8800) (**Table S1, and Fig. S6**). The samples were dried on a grid and observed using a transmission electron microscope (H-7650, HITACHI). The transmittance as a function of temperature for the PNAV-Pt colloidal solution was measured similarly to the PNAV solutions. Viologen redox changes in the purified PNAV-Pt colloidal solution were confirmed using Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> as a reducer (**Fig. S7 and S8**).

## II. Characterization of poly(NIPAAm-co-AAm-co-Viologen)



**Fig. S1.** <sup>1</sup>H-NMR spectrum of the semitelechelic poly(NIPAAm-co-AAm-co-Viologen) with amino end group.

When the proton signals of several monomer units overlap in one range, the peak area of each monomer unit must be subtracted from the total peak area in that region.

Specifically, the following procedure was used to determine the molar ratio of PNAV.

1. The peak (V1) around 9 ppm (8.00), which is derived from the heterocyclic ring, indicates the viologen integral.

$$\text{Integral (V1)} = 8.00$$

2. The N1 integral was obtained by subtracting the viologen-derived integral from the integral of the peak (N1, and V4) around 4 ppm (22.611), which is derived from the proton of the carbon chain directly attached to the amine nitrogen.

$$\text{Integral (N1)} = 22.611 - \text{Integral (V4)} = 22.611 - 8.00 \times 2/8 = 20.611$$

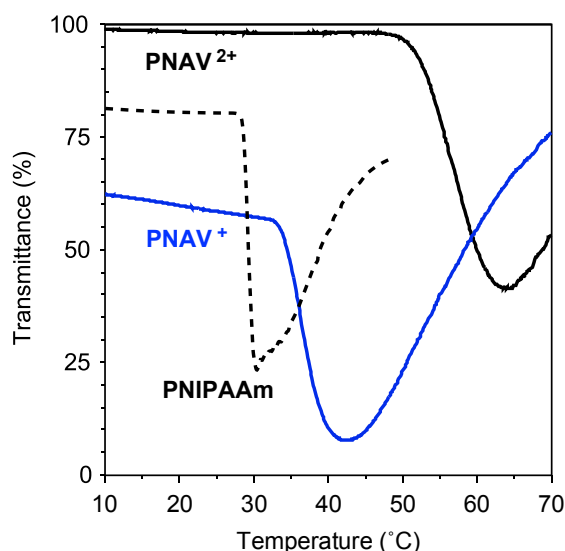
3. In the same way, integrals of A1 and A2 were obtained by subtracting integrals derived from NIPAAm and viologen from the integrals between 0.5 and 2.5 ppm.

$$\text{Integral (A1, and A2)}$$

$$= 200.910 - \text{Integral (N2, N3, and N4)} - \text{Integral (V5, V6, V7, and V8)}$$

$$= 200.910 - 20.611 \times 9/1 - 8.00 \times 8/8 = 7.411$$

4. The molar ratio was obtained from the integral ratio of the signal.



**Figure S2.** Temperature dependence of transmittances of polymer solutions. PNIPAAm and PNAV: 0.05 wt%; Tris-HCl buffer solution (500 mM);  $\lambda = 700$  nm.  $\text{Na}_2\text{S}_2\text{O}_4$  (50 mM) for reducing viologen,  $\text{PNAV}^+$ .

After a drastic decrease in the transmittance with increasing temperature, the transmittance gradually increased. This is because hydrophobic polymers flocculate with each other and exhibit phase separation. PNIPAAm with  $M_n$  of  $5.5 \times 10^3$  was used for the transmittance measurement to compare the temperature dependencies of  $\text{PNAV}^{2+/+}$ .



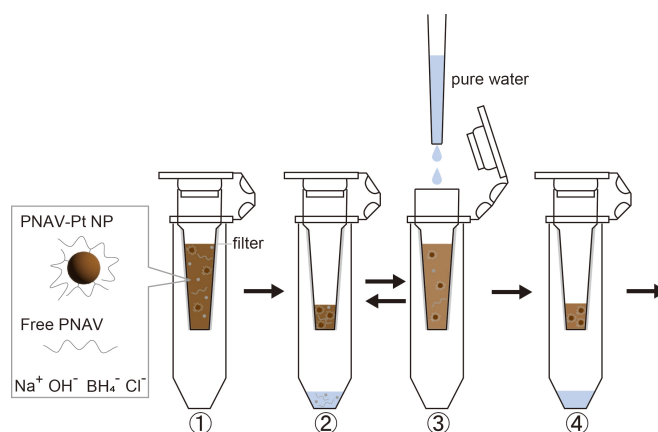
**Fig. S3. Schematic of PNAV as a linear chain, calculated with the values in polymer properties.** A specific case of the monomer sequence of 36 NIPAAm, 4 AAm, and 2 viologen having the longest distance between the AAm and viologen: all of AAm monomers and all of viologen monomers are arranged on the terminal end points.

This specific case means that 4 AAm monomers and 2 viologen monomers can be separated by 36 NIPAAm (**Fig. S3**). It is certainly possible, and the probability is obtained by the following equation.

$$\frac{4! \times 36! \times 2! \times 2}{42!} \times 100 = 2.54 \times 10^{-6} (\%)$$

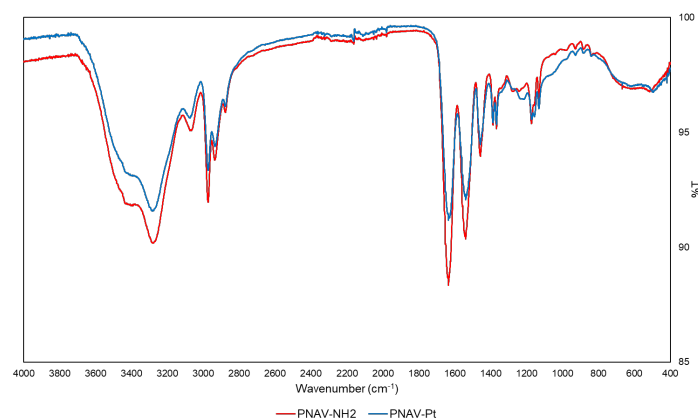
This calculation means that the existence possibility of such a specific copolymer is rare. Even if the copolymer like a triblock copolymer exists in the sample, the typical copolymer shown in **Fig. 2B** would mainly conjugate on the Pt NP because they are the very high percentage of cases. The statistical probability guarantees the distance between viologen and AAm within 2 nm.

### III. Characterization of PNAV-Pt nanoparticles



**Fig S4.** Methodology of purification of PNAV-conjugated Pt colloidal solution using ultra-filter device, Amicon ultra.

1. Add 300  $\mu\text{L}$  of sample to the ultra-filter device and cap it.
2. Centrifuge at 15,000 rpm for 15 minutes to separate the salt and unreacted copolymer.
3. Add 300  $\mu\text{L}$  of pure water to the supernatant.
4. Repeat 2 and 3 three times to obtain purified solution.
5. Re-disperse by adding the appropriate amount of pure water.



**Fig. S5.** FT-IR spectra of PNAV before and after conjugation onto Pt.

The red line means the PNAV spectrum before the conjugation onto Pt, and the blue line means the PNAV-Pt spectrum after the conjugation. The spectra were measured in the wavelength range of 400—4000  $\text{cm}^{-1}$  using solid samples on Spectrum 100 (PerkinElmer). The samples were prepared by precipitating with ethanol in the aqueous solution, and dried under the reduced pressure. The peak intensity around 1600  $\text{cm}^{-1}$  originating from the bending adsorption of the amine in the PNAV decreases after the conjugation onto Pt. This result strongly suggests that the amine is consumed for the binding on Pt.

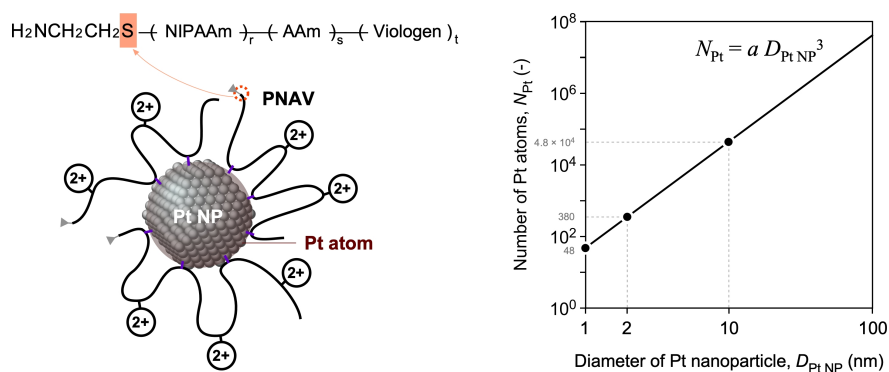
The samples for ICP-MS measurements were prepared as follows. After purification using an Amicon Ultra dialysis membrane, the sample was diluted into 10 times the original volume with the addition of pure water. This diluted sample was used for ICP-MS measurements.

**Table S1. Quantitative analysis for elemental ratio by ICP-MS**

n	Elemental concentration ( $\mu\text{g/g}$ )	
	S	Pt
1	0.2511	9.684
2	0.2561	9.512
Average	0.25	9.6

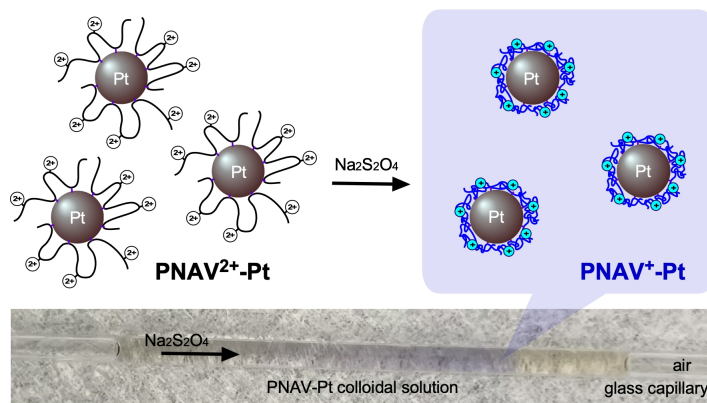
Based on the molecular weights (S = 32.066 (g/mol) and Pt = 195.084 (g/mol)), the molar ratio in the sample was calculated as follows:

$$\text{S (mol): Pt (mol)} = 0.25 (\mu\text{g/g})/32.066 (\text{g/mol}) : 9.6 (\mu\text{g/g})/195 (\text{g/mol}) = 1 : 6.314$$



**Fig. S6.** Estimation of number of PNAV chain on a Pt nanoparticle.

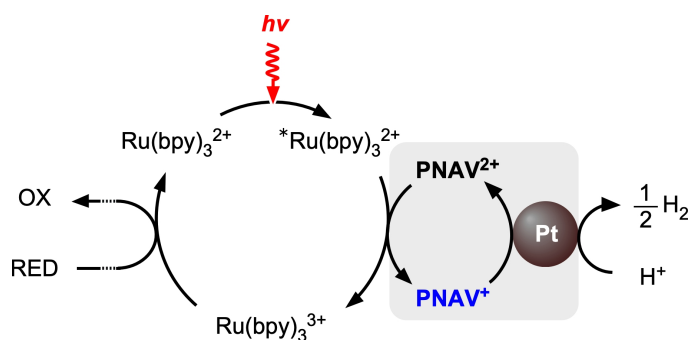
The number of PNAV chains on one Pt nanoparticle can be estimated using the elemental ratio between S in PNAV and Pt (**Table S1**) and the size of the Pt nanoparticles (**Fig. S4**). When the average values of  $a = 47.8$  and  $D_{\text{Pt NP}} = 1.85$  nm were introduced, the number of Pt atoms ( $N_{\text{Pt NP}}$ ) was estimated to be an average of  $47.8 \times 1.85^3 = 303$ .



**Fig. S7. Reduction of viologen in PNAV-Pt aqueous solution.** Addition of aqueous  $\text{Na}_2\text{S}_2\text{O}_4$  solution of a reducer into purified PNAV-Pt colloidal solution.

We confirmed that the purified PNAV-Pt colloidal solution exhibited a violet color when  $\text{Na}_2\text{S}_2\text{O}_4$  solution was added as a reducer. This color change indicates that the viologen in PNAV-Pt is capable of changing from an oxidized to a reduced state.

In the PNAV-Pt reduction reaction using the reductant,  $\text{Na}_2\text{S}_2\text{O}_4$  shown in **Fig. S7**, the violet color of the solution similar with the  $\text{PNAV}^+$  solution returned to its initial state of  $\text{PNAV}^{2+}$ -Pt after the reductant was consumed. Moreover, neither the polymeric flocculation nor Pt NPs precipitation were observed even in the high salt concentration. These results suggest that the amine group is stably conjugated onto Pt even after the progress of air oxidation. This stability of PNAV-Pt NPs in high salt concentration is totally different from that of surfactant-dispersed Pt NPs which easily precipitate in a high salt solution.<sup>3</sup>



**Fig. S8. Photoinduced electron transferring circuit for  $\text{H}_2$  generation.** Typical example using  $\text{Ru}(\text{bpy})_3^{2+}$  as photosensitizer, viologen as an electron acceptor, and Pt nanoparticle as a catalyst. RED/OX means a sacrificial reductant such as EDTA, or an  $\text{O}_2$  generating catalyst from  $\text{H}_2\text{O}$  such as  $\text{RuO}_2$ .

Optimized conditions will be explored by tuning the molar ratio of PNAV, the chain length of PNAV, particle size of Pt NPs, ratio of PNAV and Pt, *etc.*, to realize the  $\text{H}_2$  generation with high overall quantum efficiency.

## References

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