

## Article

# Physisorption of Cyclic Poly(ethylene glycol) on Platinum Nanoparticles for Dispersion Stabilization and Catalytic Applications

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## Abstract

Dispersion stabilization of nanoparticles for catalytic reactions is an important issue. However, dispersing agents should be carefully selected not to hinder catalytic performance. In the present study, physisorption of cyclic poly(ethylene glycol) (*c*-PEG) onto platinum nanoparticles (PtNPs) was investigated in comparison with unmodified PtNPs (PtNPs/No PEG), PtNPs mixed with linear PEG (PtNPs/HO-PEG-OH), and PtNPs chemisorbed with HS-PEG-OMe (PtNPs/HS-PEG-OMe). DLS showed a significant increase in the particle size for PtNPs/*c*-PEG and PtNPs/HS-PEG-OMe compared to PtNPs/No PEG and PtNPs/HO-PEG-OH.  $\zeta$ -potential measurements revealed values around  $-30$  mV for PtNPs/No PEG and PtNPs/HO-PEG-OH, whereas PtNPs/*c*-PEG and PtNPs/HS-PEG-OMe approached 0 mV, which indicated that *c*-PEG and HS-PEG-OMe adsorb onto PtNPs to form a shielding layer. Moreover, PtNPs/*c*-PEG and PtNPs/HS-PEG-OMe were stable in a phosphate-buffered saline (PBS) solution, but PtNPs/No PEG and PtNPs/HO-PEG-OH immediately aggregated. This suggests that high dispersion stability by *c*-PEG is comparable to ordinary surface modification using HS-PEG-OMe. Furthermore, the catalytic ability of PtNPs/*c*-PEG and PtNPs/HS-PEG-OMe was compared in various reactions. As a result, physisorbed PtNPs/*c*-PEG showed suitable catalytic activities, whereas chemisorbed PtNPs/HS-PEG-OMe was significantly hampered by the blocking of the catalytic sites with thiol in some reactions. Thus, physisorption of *c*-PEG endows PtNPs with dispersion stability and maintains the catalytic ability, leading to an alternative way of modifying metal nanoparticles.

**Keywords:** cyclic polymer; poly(ethylene glycol); platinum nanoparticle; catalysis



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## 1. Introduction

Platinum is one of the most precious metals, as a much smaller amount exists than gold and is extensively used, especially in catalytic applications [1]. Platinum nanoparticles (PtNPs) exhibit high catalytic activity due to their large surface area, where the surface area per unit mass also contributes to reducing the consumption of

the scarce resource and are widely used in industrial catalysts, including for purifying automobile exhaust gases [2]. In this connection, dendritic PtNPs exhibit high catalytic activity and functionality due to their fine structures, which greatly increase their surface area [3]. Furthermore, platinum aggregates with certain numbers of atoms were reported to demonstrate extremely high activity, where the highest activity was observed in platinum clusters with 19 atoms [4].

In order to synthesize metal nanoparticles including gold and platinum, various methods have been developed [5,6]. Many compounds, including citric acid, thiols, and polymers, have been used as capping agents to stabilize metal nanoparticles [7,8]. Because thiols have a great affinity for metal nanoparticles, their introduction marked a significant advancement in the formation of small nanoparticles with long-term stability [9]. However, because of the blocking of the catalytically active sites on the surface and their high ligand packing density, which prevent substrate access, the stability and catalytic activity of the metal nanoparticles are generally incompatible [8,10]. As a result, an alternative methodology that produces stable metal nanoparticles with high reactivity for a range of catalytic processes is desired.

In the meantime, cyclic polymers exhibit various physical and chemical properties distinct from those of linear counterparts of identical composition [11,12]. For example, because cyclic polymers lack highly mobile chain ends, they have a higher glass transition temperature compared to linear counterparts of the same molecular weight. However, as the molecular weight increases, the proportion of chain ends decreases, reducing this difference. Furthermore, cyclic polymers have a smaller hydrodynamic volume than linear counterparts. These characteristics, known as *topology effects*, play a crucial role in thermal, optical, and biological applications [13–15].

In this connection, modifying nanoparticle surfaces with polymers to impart dispersion stability enables their various applications. Gold nanoparticles (AuNPs) are widely used nanomaterials and are often stabilized via gold–thiol bonds using linear PEG with a thiol group (HS-PEG-OMe) [16,17]. Our group previously reported that cyclized PEG (*c*-PEG), derived from linear PEG with hydroxyl groups at both ends (HO-PEG-OH), physisorbs onto AuNPs and silver nanoparticles (AgNPs), conferring stability against stimuli such as heating, freeze-drying, and physiological conditions [18,19]. Especially, under heating conditions, *c*-PEG-modified AuNPs exhibited stability surpassing even that of HS-PEG-OMe. Since physisorption by *c*-PEG does not involve chemical modification on the nanoparticle surface, it is expected to have broader applications, including serving as a catalyst in environments where nanoparticles alone cannot maintain dispersion stability.

As previously mentioned, complexes formed with nanoparticles via chemisorption by HS-PEG-OMe cover the active sites on the metal nanoparticle surface, making them difficult to apply as catalysts [20]. In contrast, physisorption of *c*-PEG, which does not alter the nanoparticle surface, is expected to offer potential for catalyst applications. Therefore, this study focused on preserving the catalytic ability through dispersion stabilization by the physisorption of *c*-PEG onto PtNPs (Figure 1a). Using three types of polymers—HO-PEG-OH, *c*-PEG, and HS-PEG-OMe, with three molecular weights between 2 and 10 kg/mol—the particle size and  $\zeta$ -potential of the complexes formed with PtNPs were examined via DLS and UV–Vis measurements for dispersion stability. Furthermore, the catalytic activity of the complexes was studied, revealing significantly better activity observed for the physisorption of *c*-PEG than the chemisorption of HS-PEG-OMe in certain reactions.

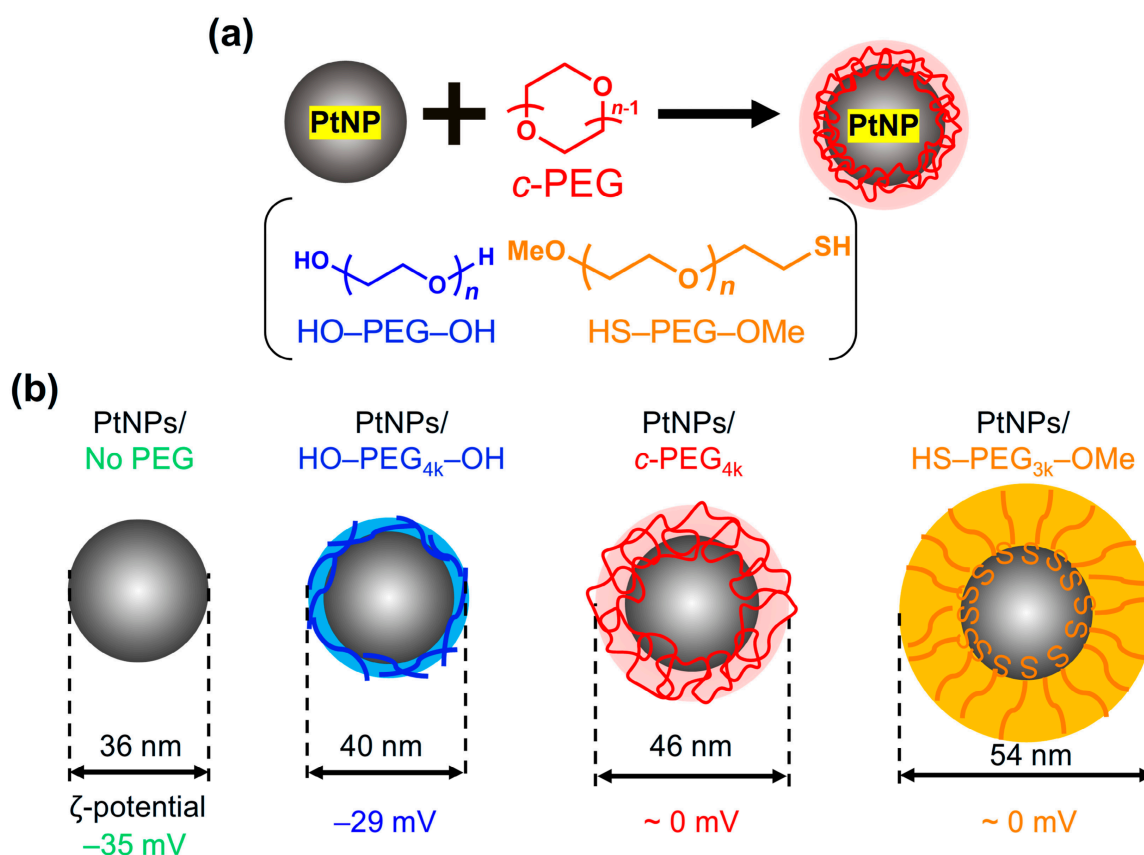


**Figure 1.** (a) Formation of PtNPs/HO-PEG-OH, PtNPs/c-PEG, and PtNPs/HS-PEG-OMe. (b) Schematic illustrations of PtNPs/No PEG, PtNPs/HO-PEG<sub>4k</sub>-OH, PtNPs/c-PEG<sub>4k</sub>, and PtNPs/HS-PEG<sub>3k</sub>-OMe. The measured DLS size and ζ-potential are shown.

## 2. Materials and Methods

### 2.1. Materials

c-PEG was synthesized according to the previous reports [21,22]. Platinum nanoparticles (PtNPs) with a diameter of 30 nm (platinum nanospheres, citrate, Nanoxact, 0.05 mg/mL in aqueous 2 mM sodium citrate, nanoComposix, San Diego, CA, USA), 4-toluenesulfonyl chloride (TsCl) (>98.0%, Junsei Chemical, Tokyo, Japan), sodium chloride (NaCl) (>99.0%, Kanto Chemical, Tokyo, Japan), potassium hydroxide (KOH) (>85.5%, Kanto Chemical), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) (>99.0%, Kanto Chemical), methanol (MeOH) (>99.5%, Kanto Chemical), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (>99.0%, Kanto Chemical) for workup, chloroform (CHCl<sub>3</sub>) (>99.0%, Kanto Chemical), diethyl ether (>99.5%, Kanto Chemical) for reprecipitation, benzene (>99.9%, Sigma-Aldrich Japan, Tokyo, Japan) for lyophilization, mPEG-SH (HS-PEG-OMe) (Biopharma PEG Scientific, Watertown, MA, USA), and 10× PBS buffer (pH 7.4 ± 0.2, NaCl 1370 mM, Na<sub>2</sub>HPO<sub>4</sub> 81 mM, KCl 26.8 mM, KH<sub>2</sub>PO<sub>4</sub> 14.7 mM, NIPPON GENE, Tokyo Japan) were used as received. *n*-hexane (>99.0%, Kanto Chemical) was purified by distillation. Tetrahydrofuran (THF), dehydrated stabilizer free (>99.5%, Kanto Chemical), and dehydrated dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (>99.5%, Kanto Chemical) for synthesis were purified by a solvent purification system (MB-SPS-Compact, MBRAUN Garching, Germany). Poly(ethylene glycol) (HO-PEG-OH) (*M<sub>n</sub>* ~ 2000, 4600, and 10,000; Sigma-Aldrich Japan) was purified by reprecipitation in diethyl ether.

### 2.2. Preparation of PtNPs/HO-PEG-OH, PtNPs/HS-PEG-OMe, and PtNPs/c-PEG

Complexes of PtNPs and various PEG represented as PtNPs/HO-PEG-OH, PtNPs/HS-PEG-OMe, and PtNPs/c-PEG were prepared using a similar method to the case of AuNPs

and AgNPs [18,19]. Typically, *c*-PEG<sub>4k</sub> (0.5 mg), where the subscript indicates the molecular weight of PEG, was added to a PtNPs dispersion (0.2 mL) in a 2.0 mL vial, and PEG was dissolved to form PtNPs/*c*-PEG<sub>4k</sub> with a PEG concentration of 2.5 wt%. The mixture was left standing for 12 h or longer.

### 2.3. Dispersion Stability in PBS

PtNPs/No PEG, PtNPs/HO-PEG<sub>10k</sub>-OH, PtNPs/HS-PEG<sub>9k</sub>-OMe, or PtNPs/*c*-PEG<sub>10k</sub> (0.54 mL) was placed in a micro quartz cuvette to measure an absorption spectrum. Subsequently, a tenfold-concentrated PBS solution (0.06 mL) was added to the cuvette, and the resulting mixture was 0.6 mL.

### 2.4. DLS and $\zeta$ -Potential

Zetasizer Nano ZS (Malvern Panalytical, Worcestershire, UK) with a high-precision micro quartz cuvette (ZEN2112, Hellma Analytics, Müllheim, Germany) and Zetasizer nano cells (DTS1060, Malvern Panalytical) were used to measure the size and  $\zeta$ -potential, respectively. All measurements were performed at 25 °C with up to 20 scans with a 30 s equilibration time.

### 2.5. UV-Vis Spectroscopy

UV-Vis spectra were measured on a JASCO Ubset V-670 spectrophotometer at 25 °C using a micro quartz cell (M25-UV-2, GL Science, Tokyo, Japan).

### 2.6. Catalytic Reactions of 4-Nitrophenol, *Trans*-Cinnamic Acid, and Benzophenone

For reduction of 4-nitrophenol, a 1.0 mM substrate solution was prepared by dissolving 62 mg of 4-nitrophenol in 7.0 mL of deionized water. A 15 mM NaBH<sub>4</sub> aqueous solution was prepared by dissolving 8.5 mg of NaBH<sub>4</sub> in 3 mL of deionized water. Then, 0.30 mL of the 1.0 mM 4-nitrophenol solution, 1.0 mL of the 15 mM NaBH<sub>4</sub> aqueous solution, 1.4 mL of deionized water, and 0.30 mL of a PtNPs catalyst dispersion (0.050 mg/mL of Pt and 1.0 mg/mL of PEG by weight) were added to a 3 mL quartz cell, and a time-course UV-Vis measurement was performed for 1000 min while stirring at a speed of 100 rpm.

For hydrogenation of *trans*-cinnamic acid, 1.0 mM of substrate solution was prepared by dissolving 2.96 mg of *trans*-cinnamic acid in 1.0 mL of ethanol and diluting the mixture 20-fold. A 150 mM NaBH<sub>4</sub> solution was prepared by dissolving 5.7 mg of NaBH<sub>4</sub> in 1.0 mL of ethanol. A 150 mM acetic acid solution was prepared by dissolving 8.6  $\mu$ L of acetic acid in 1.0 mL of ethanol [23]. PtNPs/*c*-PEG and PtNPs/HS-PEG-OMe dispersions (0.050 mg/mL of Pt and 1.0 mg/mL of PEG by weight) were diluted 150-fold with water. Then, 0.30 mL of the 1.0 mM *trans*-cinnamic acid solution, 0.10 mL of the 150 mM NaBH<sub>4</sub> solution, 2.3 mL of ethanol, and 0.18 mL of a 150-fold diluted PtNPs/*c*-PEG or PtNPs/HS-PEG-OMe dispersion were added to a 3 mL quartz cell, and a time-course UV-Vis measurement was performed while stirring at a speed of 100 rpm.

For reduction of benzophenone, 0.55 mM of substrate solution was prepared by dissolving 1.2 mg of benzophenone in 12 mL of ethanol. A 150 mM NaBH<sub>4</sub> solution was prepared by dissolving 5.7 mg of NaBH<sub>4</sub> in 1.0 mL of ethanol. PtNPs/*c*-PEG and PtNPs/HS-PEG-OMe dispersions (0.050 mg/mL of Pt and 1.0 mg/mL of PEG by weight) were diluted 150-fold with water. Then, 0.55 mL of a 0.55 mM benzophenone solution, 0.10 mL of the 150 mM NaBH<sub>4</sub> solution, 2.3 mL of ethanol, and 0.18 mL of a 150-fold diluted PtNPs/*c*-PEG or PtNPs/HS-PEG-OMe dispersion were added to a 3 mL quartz cell, and a time-course UV-Vis measurement was performed while stirring at a speed of 100 rpm.

### 3. Results and Discussion

#### 3.1. Synthesis of *c*-PEG

The series of *c*-PEG with various molecular weights were synthesized and purified according to the previous work [21,22]. Thus, *c*-PEG was formed from linear HO-PEG-OH by the ring-closure strategy in high dilution; the hydroxyl end of HO-PEG-OH was converted to a leaving group (tosylate, OTs), and cyclization was driven by intramolecular etherification under dilute conditions to minimize intermolecular reactions.

From the size-exclusion chromatography (SEC) measurement of *c*-PEG<sub>2k</sub>, the number-average molecular weight,  $M_n$ , was 1440 g/mol, the peak-top molecular weight,  $M_p$ , was 1420 g/mol, and the molecular weight distribution,  $M_w/M_n$ , was 1.04 (Table 1). Furthermore, for *c*-PEG<sub>4k</sub>,  $M_n$  was 3230 g/mol,  $M_p$  was 3230 g/mol, and  $M_w/M_n$  was 1.06; for *c*-PEG<sub>10k</sub>,  $M_n$  was 7570 g/mol,  $M_p$  was 7870 g/mol, and  $M_w/M_n$  was 1.14. In SEC, substances with smaller hydrodynamic volumes elute more slowly. Therefore, the smaller apparent molecular weight determined by SEC confirmed that cyclization had proceeded. For example,  $M_n$  for *c*-PEG<sub>4k</sub> was 3230 g/mol, whereas that for HO-PEG<sub>4k</sub>-OH was 4300 g/mol (Figure 2a). Furthermore, comparing the <sup>1</sup>H and <sup>13</sup>C NMR spectra of linear HO-PEG-OH and *c*-PEG revealed that the signals from the chain ends in HO-PEG-OH were absent in *c*-PEG (Figure 2b,c). This can be interpreted as the formation of highly symmetrical defect-free *c*-PEG. Furthermore, MALDI-TOF-MS measurements were performed on HO-PEG-OH and *c*-PEG. The presence of peaks with an interval of  $m/z = 44$ , corresponding to the PEG repeating unit, and a decrease in the molecular weight by one water molecule ( $m/z = 18$ ) compared to HO-PEG-OH also indicate cyclization. Moreover, the observed peaks at  $m/z = 4710.7$  and  $4692.8$  match the calculated values of  $4709.7$  for  $[\text{HO}(\text{C}_2\text{H}_4\text{O})_{106}\text{H} + \text{Na}]^+$  and  $4691.8$  for  $[(\text{C}_2\text{H}_4\text{O})_{106} + \text{Na}]^+$ , respectively.

**Table 1.** SEC results of HO-PEG-OH, *c*-PEG, and HS-PEG-OMe used in the present study.

|                              | $M_n$ (g/mol) <sup>a</sup> | $M_p$ (g/mol) <sup>a</sup> | $M_w/M_n$ |
|------------------------------|----------------------------|----------------------------|-----------|
| HO-PEG <sub>2k</sub> -OH     | 1850                       | 1950                       | 1.03      |
| <i>c</i> -PEG <sub>2k</sub>  | 1440                       | 1420                       | 1.04      |
| HS-PEG <sub>2k</sub> -OMe    | 1590                       | 1740                       | 1.08      |
| HO-PEG <sub>4k</sub> -OH     | 4300                       | 4220                       | 1.06      |
| <i>c</i> -PEG <sub>4k</sub>  | 3230                       | 3230                       | 1.06      |
| HS-PEG <sub>3k</sub> -OMe    | 3200                       | 3420                       | 1.16      |
| HO-PEG <sub>10k</sub> -OH    | 9250                       | 9060                       | 1.14      |
| <i>c</i> -PEG <sub>10k</sub> | 7570                       | 7870                       | 1.14      |
| HS-PEG <sub>9k</sub> -OMe    | 9070                       | 9370                       | 1.05      |

<sup>a</sup> Determined by SEC in DMF using PEG standards.

#### 3.2. Formation of PtNPs/PEG Complexes and DLS Size and $\zeta$ -Potential

PtNPs/PEG complexes were prepared by adding various PEG to PtNPs dispersions (0.050 mg/mL) to achieve a PEG concentration of 2.5 mg/mL (Figure 1a). The particle sizes measured by DLS for the PEG<sub>4k</sub> series are shown in Figure 1b. The z-average size of unmodified PtNPs was 36 nm, and those for PtNPs/HS-PEG-OMe were 50, 54, and 72 nm for 2, 3, and 9 kg/mol, respectively, showing a clear molecular weight dependence (Figure 3a). Similarly, for the complexes with HO-PEG-OH and *c*-PEG, the particle size was largest when using 10 kg/mol PEG (45 nm for HO-PEG<sub>10k</sub>-OH and 53 nm for *c*-PEG<sub>10k</sub>). The *c*-PEG layer was thinner than that of HS-PEG-OMe, which was consistent with the case of AuNPs, arising from the fact that *c*-PEG interacts with the nanoparticle surface by multiple points, thereby forming a “flattened” conformation, whereas HS-PEG-OMe attached to the surface at one point, forming an “upright” conformation [14]. HO-PEG-OH also interacted to some degree, especially with high molecular weight [24].

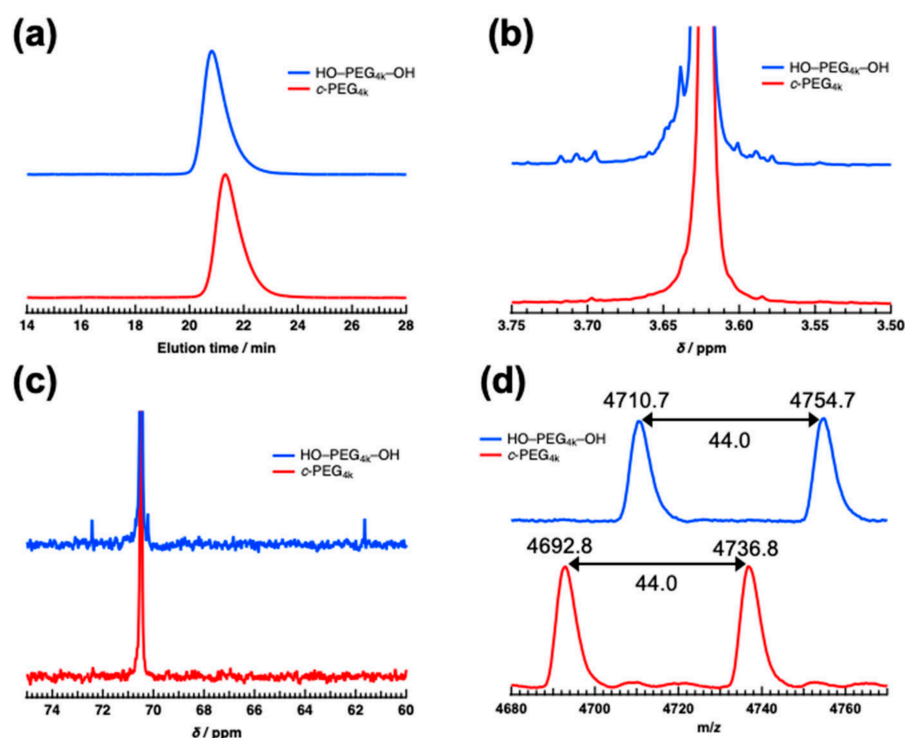


**Figure 2.** (a) SEC traces, (b)  $^1\text{H}$  NMR spectra, (c)  $^{13}\text{C}$  NMR spectra, and (d) MALDI-TOF mass spectra of HO-PEG $_{4k}$ -OH (blue) and *c*-PEG $_{4k}$  (red).

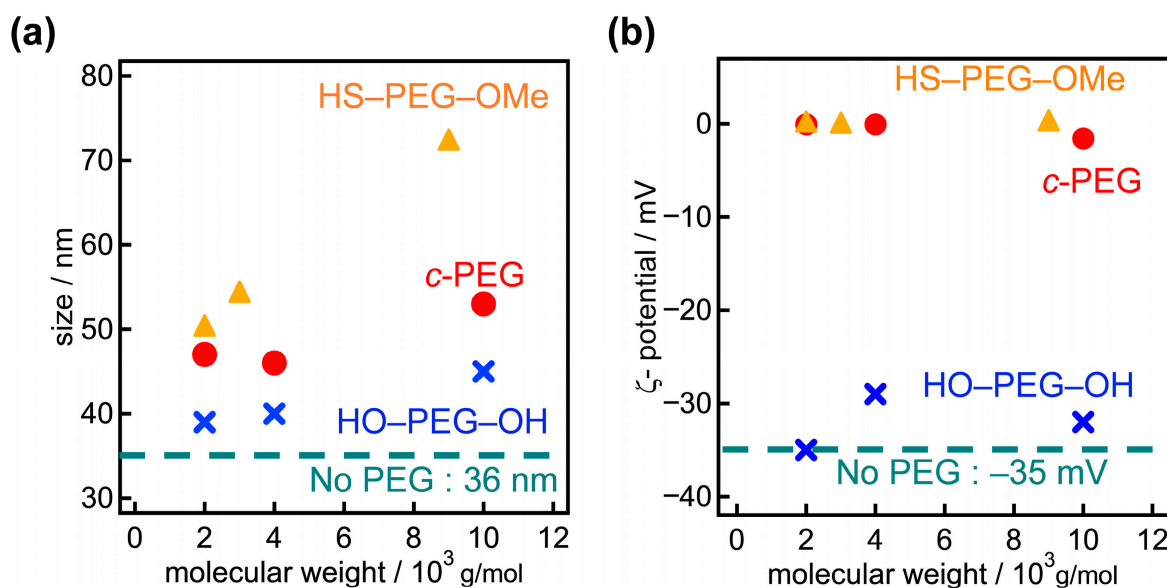


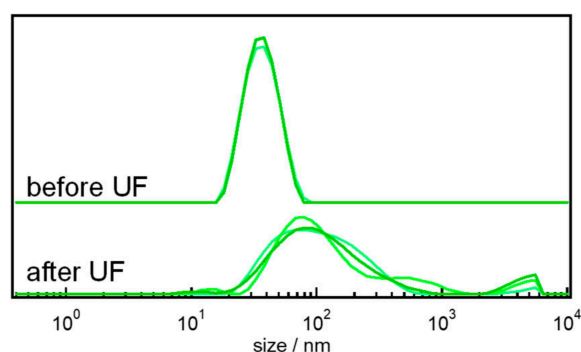
**Figure 3.** (a) DLS z-average size and (b)  $\zeta$ -potential of PtNPs/No PEG, PtNPs/HO-PEG-OH, PtNPs/*c*-PEG, and PtNPs/HS-PEG-OMe with various molecular weights.

Moreover, the  $\zeta$ -potential of these complexes was evaluated. For PtNPs/No PEG and PtNPs/HO-PEG-OH, the  $\zeta$ -potential was approximately  $-30$  mV, indicating that the surface charge, arising from the capping citrate anions, was not shielded (Figures 1b and 3b). In contrast, values close to  $0$  mV were observed for PtNPs/HS-PEG-OMe and PtNPs/*c*-PEG regardless of the molecular weight, confirming the formation of an adsorption layer, which shields the surface charge, similar to the cases of AuNPs and AgNPs [18,19].

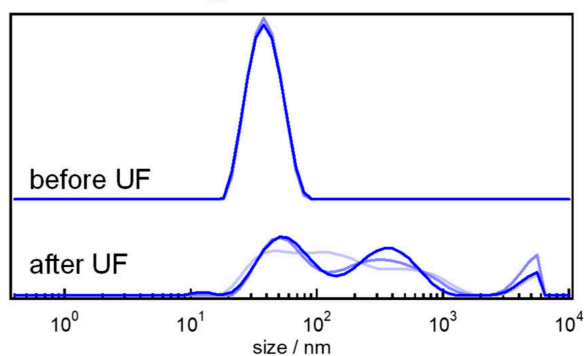
In order to test the dispersion stability, the size distribution by intensity of these complexes both before and after undergoing multiple ultrafiltration cycles was compared

by DLS; this experiment specifically examined how different types of PEG influence the dispersion stability of the nanoparticles. The average size by intensity of PtNPs/No PEG increased from 37 to 125 nm after ultrafiltration six times, suggesting a certain degree of aggregation takes place (Figure 4a). More importantly, the dispersions became mostly colorless, which is indicative that a large proportion of PtNPs precipitated. PtNPs/HO-PEG<sub>4k</sub>-OH also suffered from significant aggregation, where the size distribution became multimodal with peaks centered at 59 and 396 nm, suggesting that HO-PEG<sub>4k</sub>-OH caused interparticle interactions (Figure 4b). In the meantime, PtNPs/*c*-PEG remained remarkably stable; aggregation was mostly prevented, where the size increased from 44 nm to only 59 nm after ultrafiltration six times (Figure 4c). UV-Vis spectra were recorded to show that only PtNPs/*c*-PEG remained dispersed, exhibiting scattering from the nanoparticles (Figure 5a). This experiment also highlighted the superiority of *c*-PEG in maintaining uniform dispersion stability after repeated purification cycles, and the usefulness of *c*-PEG.

**(a) PtNPs/No PEG**



**(b) PtNPs/HO-PEG<sub>4k</sub>-OH**



**(c) PtNPs/*c*-PEG<sub>4k</sub>**

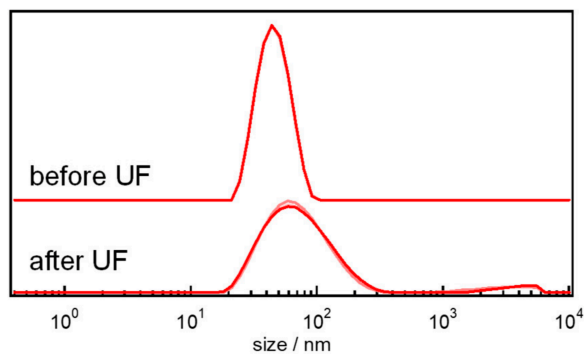


**Figure 4.** DLS size distribution by intensity before and after ultrafiltration (UF) six times (left) and photograph after UF for (a) PtNPs/No PEG, (b) PtNPs/HO-PEG<sub>4k</sub>-OH, (c) PtNPs/*c*-PEG<sub>4k</sub>, and PtNPs/HS-PEG<sub>3k</sub>-OMe.

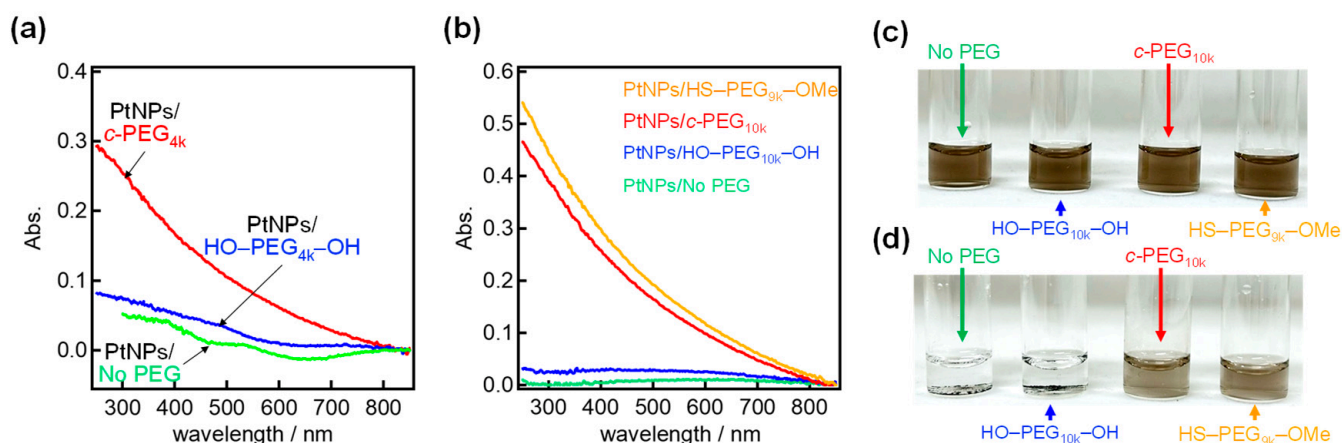


**Figure 5.** UV-Vis spectra (a) after ultrafiltration six times and (b) after the addition of PBS (10×). Appearance of PtNPs/No PEG, PtNPs/HO-PEG<sub>10k</sub>-OH, PtNPs/*c*-PEG<sub>10k</sub>, and PtNPs/HS-PEG<sub>9k</sub>-OMe (c) before and (d) after the addition of PBS (10×).

### 3.3. Dispersion Stability Under Physiological Conditions

For AuNPs and AgNPs, stability under physiological conditions was investigated in composites with various PEG [18,19]. It has been reported that the nanoparticles modified with *c*-PEG maintain dispersion stability under various conditions, unlike uncoated nanoparticles and complexes with HO-PEG-OH. PtNPs are also reported to have various applications in biological fields [25]. Here, concentrated PBS (10×) was added to four complexes (PtNPs/No PEG, PtNPs/HO-PEG<sub>10k</sub>-OH, PtNPs/HS-PEG<sub>9k</sub>-OMe, PtNPs/*c*-PEG<sub>10k</sub>) to test their stability against physiological conditions. The stability was evaluated based on absorption spectra and DLS size before and after addition of PBS (10×). The appearance of the samples before and 17 h after addition is shown in Figures 5c and 5d, respectively. The absorption spectra are shown in Figure 5b, and the DLS sizes are shown in Figure 6, which suggest a significant increase in size, corresponding to aggregation after PBS (10×) addition for PtNPs and PtNPs/HO-PEG<sub>10k</sub>-OH. A slight increase from 72 to 82 nm was observed for PtNPs/HS-PEG<sub>9k</sub>-OMe, while PtNPs/*c*-PEG<sub>10k</sub> showed almost no change (before, 57 nm; after, 58 nm). This confirmed the aggregation-inhibiting effect of *c*-PEG adsorbed on PtNPs. Furthermore, the appearance of the samples shown in Figure 5d became completely colorless after 17 h for PtNPs/No PEG and PtNPs/HO-PEG<sub>10k</sub>-OH, while PtNPs/HS-PEG<sub>9k</sub>-OMe and PtNPs/*c*-PEG<sub>10k</sub> remained nearly unchanged. Based on these results, PtNPs/*c*-PEG is considered to have an anti-aggregation effect under the physiological conditions.

Transmission electron microscopy (TEM) images of various PtNPs were recorded without and with PBS (10×) to visualize the aggregation (Figure 7). Based on the TEM images, PtNPs/No PEG and PtNPs/HO-PEG<sub>10k</sub>-OH were aggregated to some degree even before the addition of PBS (10×) (Figure 7a,b). In the meantime, PtNPs/HS-PEG<sub>9k</sub>-OMe and PtNPs/*c*-PEG<sub>10k</sub> were well dispersed (Figure 7c,d). No visible PEG layer was observed on PtNPs due to the large difference in the electron densities between PEG and Pt. After the addition of PBS (10×), the formation of larger clusters was observed for PtNPs/No PEG and PtNPs/HO-PEG<sub>10k</sub>-OH (Figure 7e,f). This state was significantly different from particles functionalized with *c*-PEG<sub>4k</sub> or HS-PEG<sub>3k</sub>-OMe, which successfully maintained their individual dispersion and did not aggregate when exposed to the same PBS environment (Figure 7g,h). The microscopic views highlighted that PEGylation with *c*-PEG and HS-PEG-OMe is effective at maintaining their dispersibility.

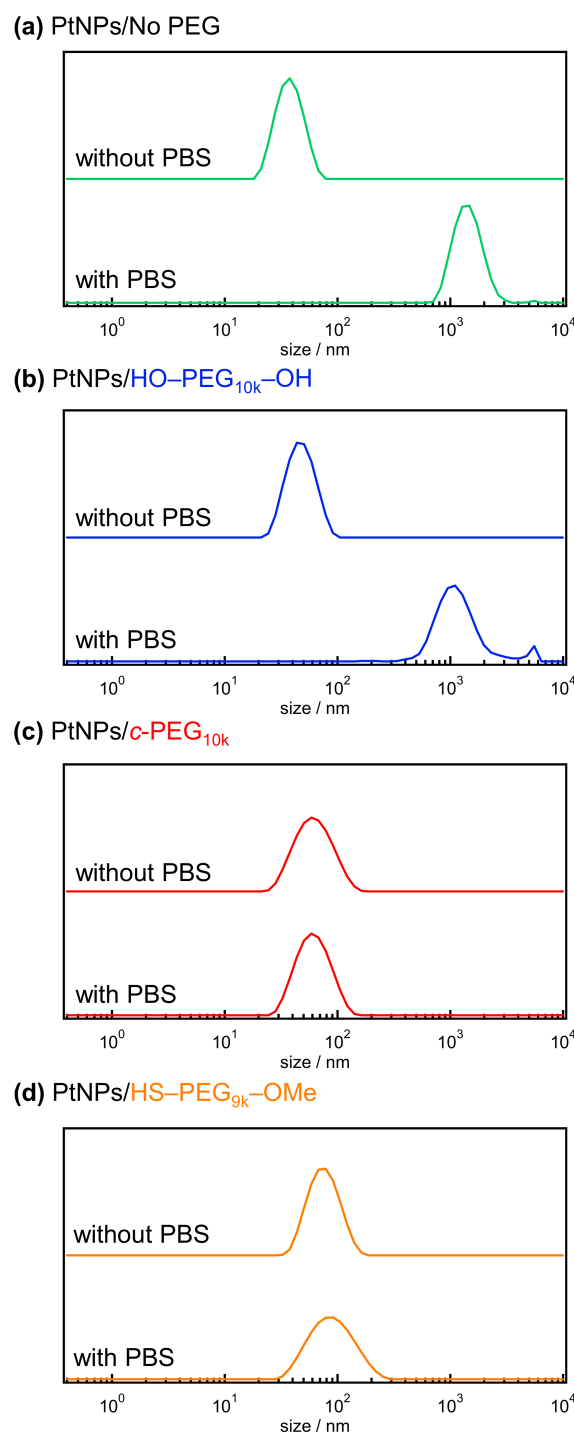


**Figure 6.** DLS size distribution by intensity without and with PBS for (a) PtNPs/No PEG, (b) PtNPs/HO-PEG<sub>10k</sub>-OH, (c) PtNPs/*c*-PEG<sub>10k</sub>, and (d) PtNPs/HS-PEG<sub>9k</sub>-OMe.

### 3.4. Application to Catalysis

Finally, PtNPs/PEG complexes were used to evaluate the catalytic activity in various reactions (Scheme 1). These three were selected to verify the applicability of the PtNPs/*c*-PEG complex to catalyze reactions based on the different mechanisms (electron transfer, hydrogenation, and hydride reduction). Figures 8–10 show photographs, the time-dependent absorption spectra of samples containing 4-nitrophenol, NaBH<sub>4</sub>, and either PtNPs/HS-PEG<sub>3k</sub>-OMe or PtNPs/*c*-PEG<sub>4k</sub>, along with plots of the absorption ratio versus time. When PtNPs/HS-PEG<sub>3k</sub>-OMe was used, the peak intensity at 400 nm originating from 4-nitrophenol remained almost unchanged, suggesting that nearly no reaction pro-

ceeded. In contrast, the reaction using PtNPs/*c*-PEG<sub>4k</sub> showed a significant decrease in peak intensity, confirming the progress of the reaction. The logarithm of the absorption ratio at 400 nm ( $\ln A/A_0$ ) was plotted against time to determine the rate constant ( $k$ ). PtNPs/*c*-PEG<sub>4k</sub> had a  $k$  value of  $4.0 \times 10^{-3} \text{ min}^{-1}$ . On the other hand, that for PtNPs/HS-PEG<sub>3k</sub>-OMe notably decreased to  $0.51 \times 10^{-3} \text{ min}^{-1}$ . The conversion for PtNPs/*c*-PEG<sub>4k</sub> under this condition was 62% after 700 min, whereas that for PtNPs/HS-PEG<sub>3k</sub>-OMe was drastically suppressed to only 11% (Table 2). A control experiment without PtNPs was also performed to show no conversion of the substrate. These suggest that, unlike PtNPs/HS-PEG<sub>3k</sub>-OMe, where the catalytic sites are inactivated by thiol and/or high grafting density of HS-PEG<sub>3k</sub>-OMe, PtNPs/*c*-PEG<sub>4k</sub> successfully maintained catalytic activity due to the physisorption of *c*-PEG.

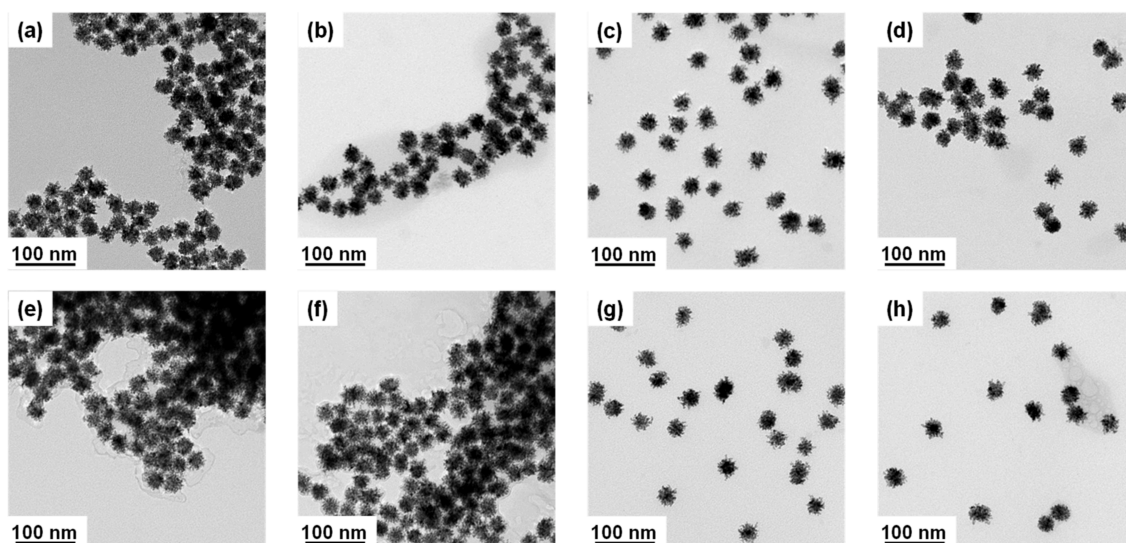
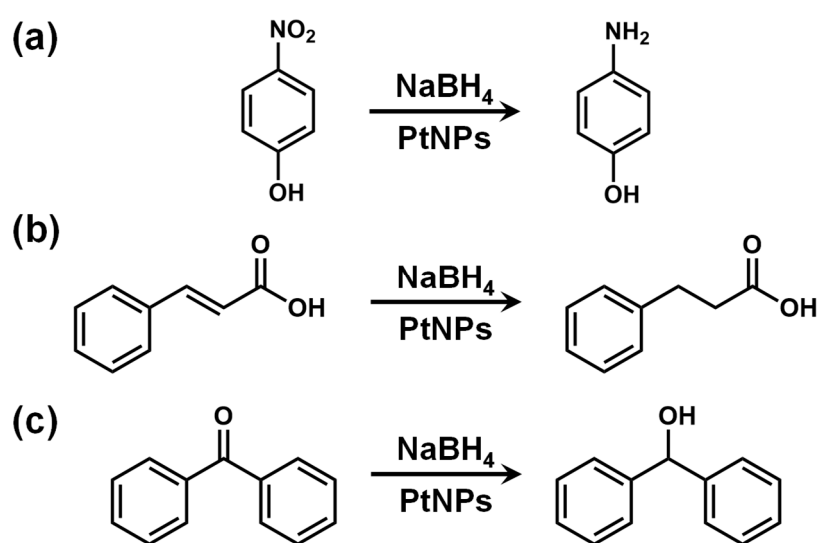


**Figure 7.** TEM images of (a) PtNPs/No PEG, (b) PtNPs/HO-PEG<sub>4k</sub>-OH, (c) PtNPs/HS-PEG<sub>3k</sub>-OMe, and (d) PtNPs/*c*-PEG<sub>4k</sub> before the addition of PBS (10 $\times$ ). TEM images of (e) PtNPs/No PEG, (f) PtNPs/HO-PEG<sub>4k</sub>-OH, (g) PtNPs/HS-PEG<sub>3k</sub>-OMe, and (h) PtNPs/*c*-PEG<sub>4k</sub> after the addition of PBS (10 $\times$ ).



**Scheme 1.** Catalytic reactions using various PtNPs complexes. (a) Reduction of 4-nitrophenol, (b) hydrogenation of *trans*-cinnamic acid, and (c) reduction of benzophenone.

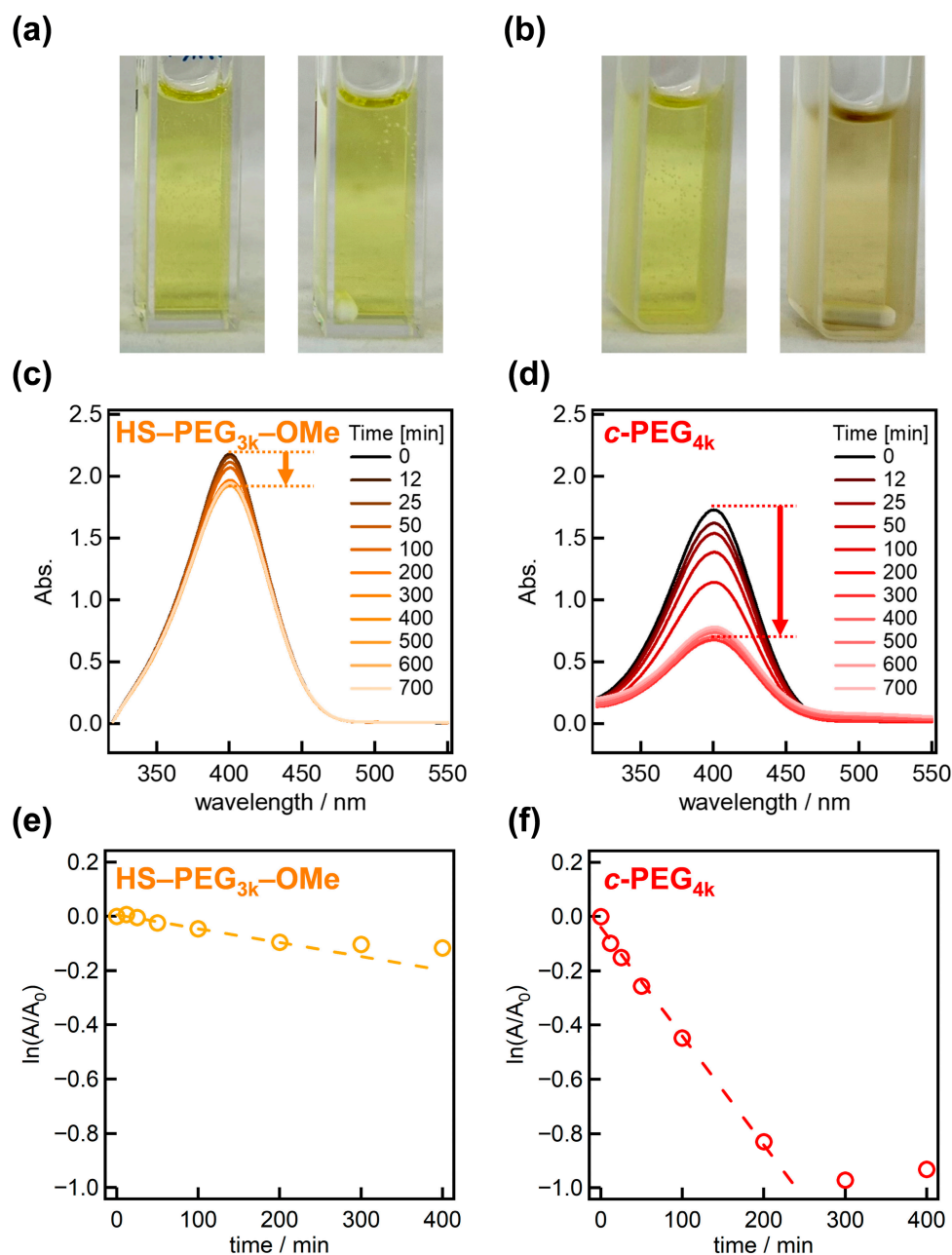


**Figure 8.** Appearance of the reaction mixtures for reduction of 4-nitrophenol at 0 min (**left**) and at 700 min (**right**) catalyzed by (a) PtNPs/HS-PEG<sub>3k</sub>-OMe and (b) PtNPs/c-PEG<sub>4k</sub>. Change in the absorption spectra during the reduction using (c) PtNPs/HS-PEG<sub>3k</sub>-OMe and (d) PtNPs/c-PEG<sub>4k</sub>. Plots of the logarithm of the absorption ratio at 400 nm ( $\ln A/A_0$ ) versus time for (e) PtNPs/HS-PEG<sub>3k</sub>-OMe and (f) PtNPs/c-PEG<sub>4k</sub>.

**Table 2.** Rate constant ( $k$ ,  $\text{min}^{-1}$ ) and conversion for catalytic reactions using various PtNPs.

|                             | PtNPs/c-PEG <sub>4k</sub> |                         | PtNPs/HS-PEG <sub>3k</sub> -OMe |                         | No PtNPs                  |                         |
|-----------------------------|---------------------------|-------------------------|---------------------------------|-------------------------|---------------------------|-------------------------|
| Substrate                   | $k$ ( $\text{min}^{-1}$ ) | Conversion <sup>a</sup> | $k$ ( $\text{min}^{-1}$ )       | Conversion <sup>a</sup> | $k$ ( $\text{min}^{-1}$ ) | Conversion <sup>a</sup> |
| 4-nitrophenol               | $4.0 \times 10^{-3}$      | 62%                     | $0.51 \times 10^{-3}$           | 11%                     | -                         | -                       |
| <i>trans</i> -cinnamic acid | $1.8 \times 10^{-3}$      | 14%                     | $0.36 \times 10^{-3}$           | 2.7%                    | -                         | -                       |
| benzophenone                | 0.22                      | 97%                     | 0.15                            | 97%                     | 0.021                     | 77%                     |

<sup>a</sup> Conversion was determined at 700, 140, and 25 min for 4-nitrophenol, *trans*-cinnamic acid, and benzophenone, respectively.

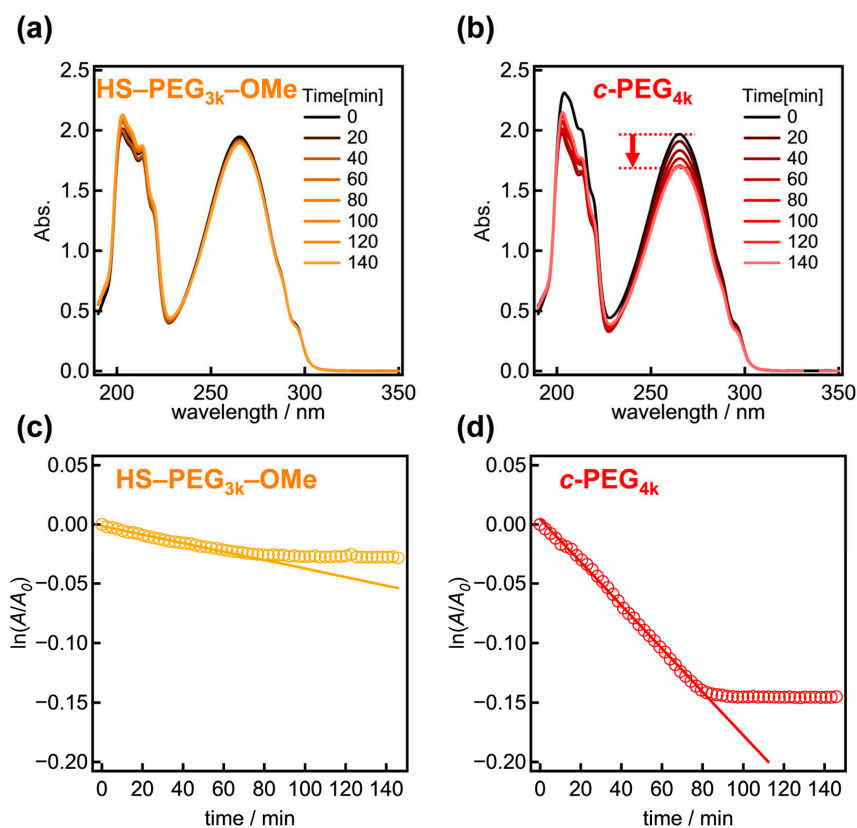


**Figure 9.** Change in the absorption spectra during hydrogenation of *trans*-cinnamic acid using (a) PtNPs/HS-PEG<sub>3k</sub>-OMe and (b) PtNPs/*c*-PEG<sub>4k</sub>. Plots of the logarithm of the absorption ratio at 400 nm ( $\ln A/A_0$ ) versus time using (c) PtNPs/HS-PEG<sub>3k</sub>-OMe and (d) PtNPs/*c*-PEG<sub>4k</sub>.

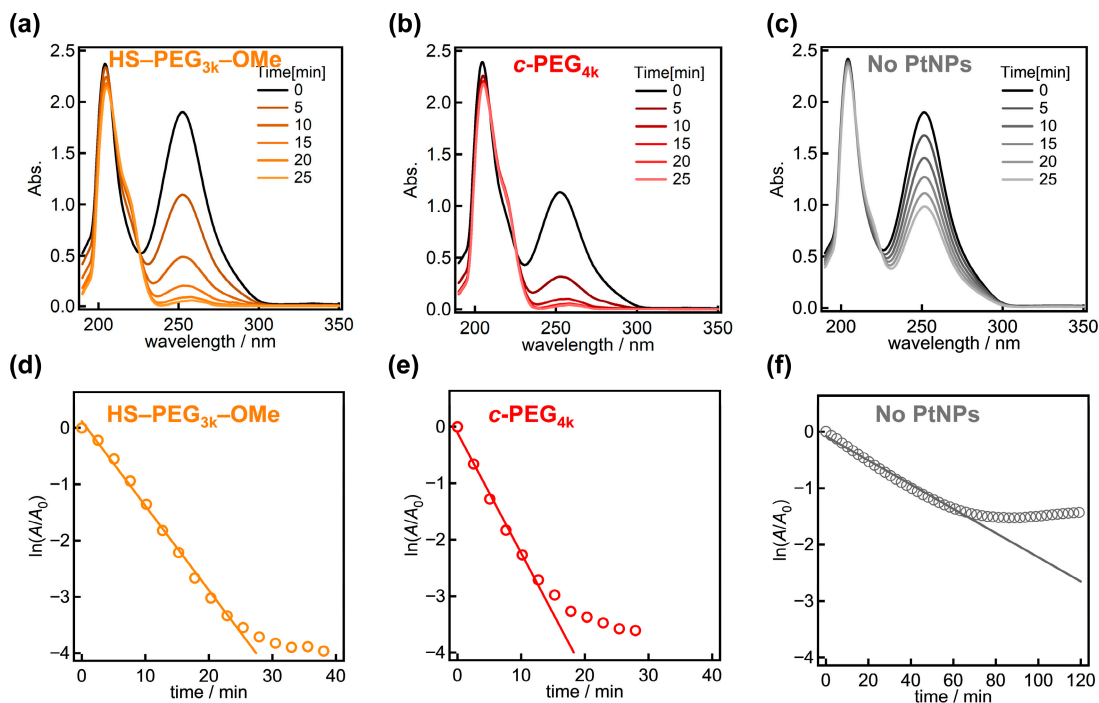


**Figure 10.** Change in the absorption spectra during reduction of benzophenone using (a) PtNPs/HS-PEG<sub>3k</sub>-OMe, (b) PtNPs/*c*-PEG<sub>4k</sub>, and (c) no PtNPs. Plots of the logarithm of the absorption ratio at 400 nm ( $\ln A/A_0$ ) versus time using (d) PtNPs/HS-PEG<sub>3k</sub>-OMe, (e) PtNPs/*c*-PEG<sub>4k</sub>, and (f) no PtNPs.

Moreover, the PtNPs complexes were applied to the hydrogenation of *trans*-cinnamic acid (Scheme 1b) [23] and reduction of benzophenone (Scheme 1c). Similarly, PtNPs/*c*-PEG<sub>4k</sub> had relatively large  $k$  ( $1.8 \times 10^{-3} \text{ min}^{-1}$ ), but a reduced value was observed for PtNPs/HS-PEG<sub>3k</sub>-OMe ( $0.36 \times 10^{-3} \text{ min}^{-1}$ ) for *trans*-cinnamic acid (Table 2). Therefore, HS-PEG<sub>3k</sub>-OMe modified the surface through chemical bonding with platinum, thereby occupying the reaction sites and rendering them unavailable, thus lacking catalytic activity. In contrast, the *c*-PEG complex modifies the surface through physical adsorption. This allowed PtNPs to potentially maintain activity without covering the catalytic sites. This suggests that even under conditions where unmodified nanoparticle catalysts lose dispersion stability and become deactivated without PEG stabilization—such as high temperatures or high substrate concentrations—the *c*-PEG complex can maintain catalytic activity by stabilizing the nanoparticle catalyst dispersion.

In the reduction of benzophenone, the  $k$  values were comparable for PtNPs/*c*-PEG<sub>4k</sub> ( $0.22 \text{ min}^{-1}$ ) and PtNPs/HS-PEG<sub>3k</sub>-OMe ( $0.15 \text{ min}^{-1}$ ). The undisturbed catalytic reaction by HS-PEG-OMe suggests that the binding site for thiol and the catalytic site on PtNPs are different [26]. It is also proposed that NaBH<sub>4</sub> acts not only as a direct reducing agent for the substrate, but also that PtNPs promote the hydrolysis of NaBH<sub>4</sub>, and the resulting active hydrogen species (Pt-H) attacks the carbonyl group of the ketone [27]. Furthermore, conditions have been established for the efficient reduction of ketones to alcohols using a Pt/C catalyst using hydrogen gas at room temperature and atmospheric pressure [28]. Thus, the reduction of benzophenone was attempted without PtNPs, resulting in a smaller  $k$  of  $0.021 \text{ min}^{-1}$ , showing the effectiveness of the PtNPs catalysts.

#### 4. Conclusions

*c*-PEG physisorbed onto PtNPs in the same manner as AuNPs and AgNPs, and the complexes were characterized and applied for catalytic reactions. The size of the complex increased with the molecular weight of *c*-PEG, and the ultrafiltration and PBS addition experiments showed that PtNPs/*c*-PEG exhibited minimal changes in the size and absorption spectra, indicating notable dispersion stabilization. Furthermore, PtNPs/*c*-PEG was successfully applied for various catalytic reactions. In contrast, traditional modification via chemisorption of HS-PEG-OMe blocked the reactive sites, resulting in deterioration of the catalytic capability in certain reactions.

The present technique ensured nanoparticles remained well dispersed in solution while simultaneously preserving their catalytic efficiency. Ultimately, this approach offers a promising alternative for modifying nanomaterials without compromising their functional performance. Such advancements could be significant and have the potential to resolve challenging issues for improving practical applications in various scientific and industrial fields.

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