Self-Assembled Nanowires of Lipid-packaged Halogen-bridged Platinum Complexes Formed by One-pot Oxidation of $Pt(en)_2$ complexes by Au(III) Ions

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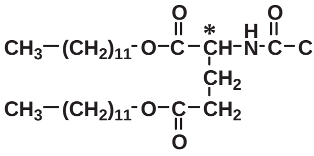
A solution-phase synthesis of lipid-packaged mixed valence platinum complexes is newly developed. Addition of aqueous $HAuCl_4$ or $AuBr_3$ to $Pt(en)_2[\mathbf{1}]_2$ complex dissolved in dichloromethane affords halogen-bridged linear complexes $[Pt(en)_2][Pt(en)_2X_2][\mathbf{1}]_4$ (X = Cl or Br). Formation of self-assembled nanowires was confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy.

Self-assembly of electronically conjugated nanoarchitectures in solution is a promising area of research that provides bottom-up manipulation of functional nanomaterials.[1,2] We have developed supramolecular nanowires that consist of cationic, one-dimensional halogen-bridged complexes $[Pt(en)_2][PtCl_2(en)_2]$ (en = 1,2-diaminoethane) and anionic amphiphiles.[3–8] Preparation of these ternary complexes requires the synthesis of both $Pt(en)_2$ and $PtCl_2(en)_2$ complexes, followed by polyion complexation with anionic lipids. In this study, we developed a one-pot solution route to synthesize chloro- or bromo-bridged $[Pt(en)_2][Pt(en)_2X_2](\mathbf{1})_4$ (X = Cl, Br) complexes by stoichiometric oxidation of $[Pt(en)_2](\mathbf{1})_2$ by $HAuCl_4$ or $AuBr_3$ ions.



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The divalent complex $[Pt(en)_2]Cl_2$ was synthesized according to the literature.[9] Aqueous dispersion of lipid **1** (L-form, counter ion, Na^+, concentration, 20 mM, 50 mL) was prepared by ultrasonication (Branson Sonifier Model 185, sonic power 30 W, 5 min). To the aqueous dispersion, $[Pt(en)_2]Cl_2$ in water (1.0 M, 0.5 mL) was added at room temperature. Colorless precipitate of $[Pt(en)_2](\mathbf{1})_2$ was collected by filtration, washed with pure water and dried in vacuo.[10]

To $[Pt(en)_2](\mathbf{1})_2$ dissolved in dichloromethane (0.6 mM, 0.5 mL), an aq solution of $HAuCl_4$ (50 mM, 1–6 µL) was added at a molar ratio of $r = Pt^{II}/Au^{III}$ at 5 °C. Within 5 minutes, the color of dichloromethane phase turned into purple or indigo blue, depending on the mixing ratio r. These intense colors are characteristic of the charge-transfer absorption (CT, $Pt^{II}/Pt^{IV} \rightarrow Pt^{III}/Pt^{III}$) of halogen-bridged complexes $[Pt(en)_2][PtCl_2(en)_2]$.[1,11,12] UV–vis spectra for these mixtures are shown in Figure 1. A CT absorption peak was observed at 585 nm ($r = 3$, indigo blue color), 582 nm ($r = 4.5$), and at 529 nm ($r = 6$, purple). The color of reaction mixtures prepared at mixing ratio of $r = 2$–6 are stably maintained. On the other hand, those prepared at $r = 1$ showed gradual fading from indigo blue to pale red. The fading was accompanied by precipitation of Au(0) clusters within an hour. In the inset of Figure 1, the absorbance observed at the maximum absorption wavelength is plotted against the mixed molar ratio r. The CT absorption intensity reaches a maximum at $r = 3$ ($\varepsilon_{585} = 4.43 \times 10^4$ unit $M^{-1}cm^{-1}$). The maximum absorption wavelength of 585 nm observed at $r = 3$ is identical with that of $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ prepared according to the previously reported method[8] ($\varepsilon_{585} = 3.43 \times 10^4$ unit $M^{-1}cm^{-1}$ at 5 °C). An Au(III) ion is known as a strong electron acceptor ($Au^{3+} + 3e^- = Au$, $E^\circ = +1.52$ V vs SHE), and the stoichiometry of $r = 3$ showing the largest absorbance strongly suggests that $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ was formed according to Eq 1. It is anticipated that a half of six $Pt(II)(en)_2$ complexes are oxidized by two $AuCl_4^-$ ions, to give three $Pt(IV)(en)_2$ complexes. Chloride ions released from $AuCl_4^-$ ions would be trapped by $Pt(IV)(en)_2$ as axial ligands. As a result, the mixed valence platinum complex of $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ was formed.

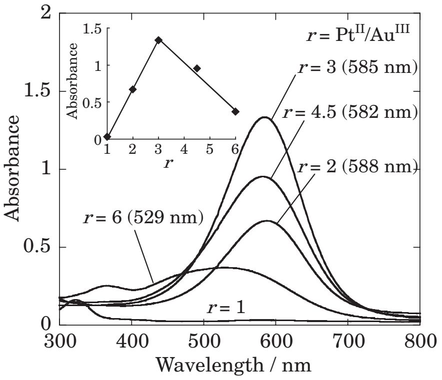

Figure 1. UV–vis spectra of reaction mixtures. $[Pt(en)_2](\mathbf{1})_2$ = 0.6 mM. Inset, dependence of the maximum absorption intensity on the mixing ratio $r = Pt(II)/Au(III)$. In dichloromethane, 5 °C.

$$6[Pt(en)_2][\mathbf{1}]_2 + 2HAuCl_4 = 3[Pt(en)_2][PtCl_2(en)_2][\mathbf{1}]_4 + 2Au^0 + 2HCl \qquad (1)$$

Transmission electron microscope (TEM) images of $[Pt(en)_2](\mathbf{1})_2$ and dispersions prepared at $r = 6$, 3, and 2 are shown in Figure 2. These specimens were prepared by dropping the reaction mixture on a carbon-coated copper grid at 5 °C and were observed without staining. $[Pt(en)_2](\mathbf{1})_2$ in colorless dichloromethane dispersion gives irregular microcrystalline aggregates (Figure 2a). On the other hand, the purple reaction mixture at $r = 6$ showed nanowires with an average length of ca. 5–20 µm and a width of ca. 340 nm (Figure 2b). Upon increasing the Au(III) concentration, the length of nanowires was in the range of ca. 10–30 µm at $r = 4.5$. The most developed nano-

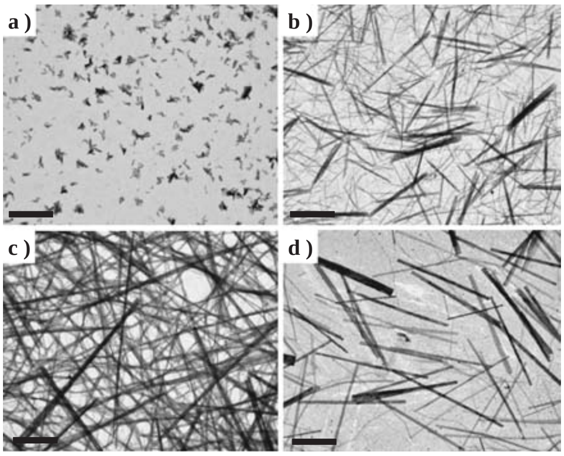

Figure 2. TEM images of dichloromethane dispersions. (a) $[Pt(en)_2](\mathbf{1})_2$, (b) mixtures at $r = 6$, (c) $r = 3$, (d) $r = 2$. Scale bars, 10 µm. Temperature, 5 °C.

wires were observed from the indigo-blue reaction mixture at $r = 3.0$ (lengths, ca. 30–100 µm, width, ca. 670 nm, Figure 2c). Upon further increasing the Au(III) concentration, nanowires became shorter ($r = 2$, lengths, ca. 10–30 µm, Figure 2d). Apparently, the presence of equimolar Pt(II) and Pt(IV) units leads to the most developed nanowires.[13]

Formation of polymeric mixed valence complexes $[Pt(en)_2][Pt(en)_2Cl_2](\mathbf{1})_4$ is further confirmed by X-ray photoelectron spectroscopy (XPS, instrument, ESCA-5000, ULVAC-PHI).[14] Figure 3 shows Pt(4f) XPS spectra for specimens prepared at $r = 6$, 3, and 1. At $r = 6$, the XPS spectrum is mainly ascribed to Pt(II) species (Figure 3a, $4f_{7/2}$ and $4f_{5/2}$), whereas the spectra at $r = 1$ indicated Pt(IV) species (Figure 3c, Au(III) in excess). At $r = 3$, fitting curves indicate that Pt(II) and Pt(IV) components are present almost at an equivalent molar ratio. These results obviously support that the mixed valence complex $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ was quantitatively formed by electron transfer to Au(III) ions.

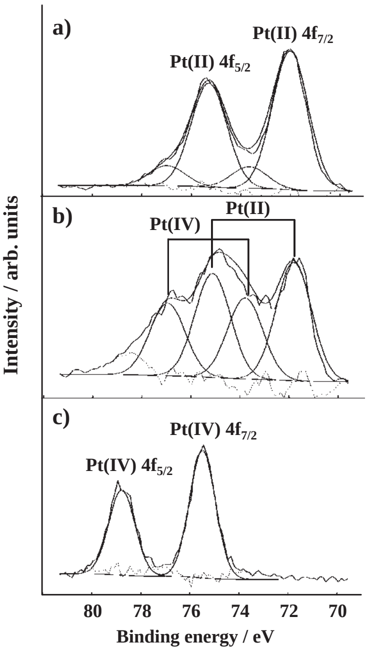

Figure 3. X-ray photoelectron spectra of the mixtures at the Pt 4f region. (a) $r = 6$, (b) $r = 3$, (c) $r = 1$.

It is interesting that the shorter nanowires display blue-shifted CT absorption (529 nm at $r = 6$, 582 nm at $r = 4.5$) compared to the longest nanowires (585 nm at $r = 3$, Figure 1). It is likely that delocalization of the CT excitation, i.e., increase in the conjugation length, is most notable in the nanowires prepared at $r = 3$, since increased conjugation lengths generally leads to smaller HOMO–LUMO band gaps.[15]

The present technique is also applicable to the synthesis of $[Pt(en)_2][PtBr_2(en)_2](\mathbf{1})_4$. When an aqueous solution of $AuBr_3$ was added to $[Pt(en)_2](\mathbf{1})_2$ in dichloromethane, pale blue dispersion showing a maximum CT absorption intensity at 1560 nm ($\mathcal{E} = 6.10 \times 10^4$ unit $M^{-1}cm^{-1}$, $r = 3$) was obtained. The red-shifted CT band compared to $[Pt(en)_2][Pt(en)_2Cl_2](\mathbf{1})_4$ is typical to bromo-bridged complexes.[8,11] Formation of developed nanowires similar to Figure 2c was also confirmed by TEM.

In conclusion, the in situ oxidation of $[Pt(en)_2](\mathbf{1})_2$ complexes by Au(III) ions allows formation of lipid-packaged nanowires of $[Pt(en)_2][Pt(en)_2X_2](\mathbf{1})_4$ with the control over both nanostructures and one-dimensional electronic states. This technique is simple, and will be widely applied to the synthesis of nanosized mixed valence complexes in solution.

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References and Notes

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