

Solvatochromic Nanowires Self-assembled from Cationic, Chloro-bridged Linear Platinum Complexes and Anionic Amphiphiles

Chang-Soo Lee and Nobuo Kimizuka*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
6-10-1, Hakozaki, Higashi-ku, Fukuoka 812-8581

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A newly developed lipid-packaged one-dimensional complex of platinum shows solvatochromism in organic media. The use of anionic lipids as counter anions is indispensable for the solvent-dependent control of one-dimensional electronic states, aggregate morphology and thermal stability.

There has been an increasing interest in fabricating conjugated nanowires because of their potential application in nanodevices. The handling of "bulk" inorganic low-dimensional structures as soluble nanowires is one of the promising direction in nanotechnology.¹ Quasi-one dimensional, halogen-bridged mixed-valence metal complexes $[M(en)_2][M'X_2(en)_2](ClO_4)_4$ (M, M' : Pt, Pd, Ni, X: Cl, Br, I, en; 1,2-diaminooctane) have been attracting much interest on account of their conjugated electronic states with strong intervalence charge transfer (CT) absorption² and large nonlinear susceptibilities.³ However, these halogen-bridged chains have been available only in bulk crystals, and they have never been considered as candidates for the independent nano- or molecular wires.

We have recently developed a supramolecular strategy to solubilize these one-dimensional complexes in organic media, by packaging them with anionic amphiphiles.⁴⁻⁸ The $[M(en)_2][M'Cl_2(en)_2](lipid)_4$ complexes display aggregate morphology and CT absorption characteristics which are dependent on the amphiphilic chemical structures^{4,5} and metal species.⁶ In addition, some of the complexes display thermochromism, as a result of the reversible dissociation and reassembly of the nanowires in solution.⁵⁻⁸ In this study, we report on solvatochromism observed for the newly synthesized complex $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$.

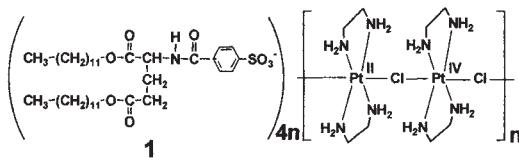


Chart 1.

A phenyl group was introduced in the anionic amphiphile **1** since aromatic stacking can enhance the thermal stability of mixed valence chains in solution.⁹ Aqueous dispersion of **1** (10 mM, 20 mL) was prepared by ultrasonication (Branson Sonifier Model 185, sonic power 45 W, 5 min). It was added to colorless aqueous solution of $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ at room temperature ($[Pt]_{total} = 10$ mM, 4 mL). An orange precipitate immediately formed was collected by centrifugation. After washing with pure water, it was dried in vacuo.¹⁰

The obtained powdery sample was soluble in organic

media by hand-shaking. When $[Pt_2(en)_2][Pt_2Cl_2(en)_2](\mathbf{1})_4$ is dissolved in chloroform (concentration, 0.6 unit mM, 1 unit = $[Pt_2(en)_2][Pt_2Cl_2(en)_2](\mathbf{1})_4$), it showed the same orange color as the solid (Figure 1a inset). On the other hand, when $[Pt_2(en)_2][Pt_2Cl_2(en)_2](\mathbf{1})_4$ was dissolved in dichloromethane, a red solution was unexpectedly obtained (Figure 1b inset). These intense colors are typical to the charge transfer (CT, $Pt^{II}/Pt^{IV} \rightarrow Pt^{III}/Pt^{III}$) absorption of the chloro-bridged mixed valence complexes,^{1,2} and their maintenance in solutions indicates that the one-dimensional complexes are dispersed as lipophilic superstructures.

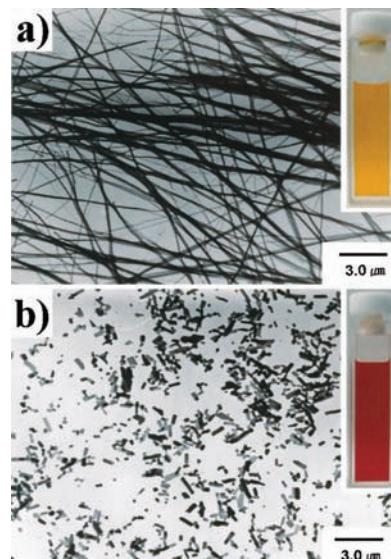


Figure 1. Transmission electron microscopy of $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ and the color of dispersions. (a) in chloroform, (b) in dichloromethane. 0.6 unit mM, 15 °C. Samples are not stained.

Transmission electron microscopy (TEM) was conducted for the samples dropped on carbon-coated copper grid at 15 °C. In the orange chloroform solution, developed nanowires (length, more than 20 μ m, width 20–100 nm) are abundantly seen (Figure 1a). On the other hand, short rectangular nanocrystals (length, 200–300 nm, width, 100 nm) were observed in dichloromethane (Figure 1b). As the observed widths of these nanowires and nanocrystals are larger than the bimolecular length of amphiphile **1** (ca. 5 nm by CPK model), these architectures must be consisting of layered aggregates of $[Pt_2(en)_2][Pt_2Cl_2(en)_2](\mathbf{1})_4$. It is noteworthy that the solvents influence both on the CT absorption and on the aggregate nanostructures.

Figure 2 shows temperature dependence of UV-vis spectra of

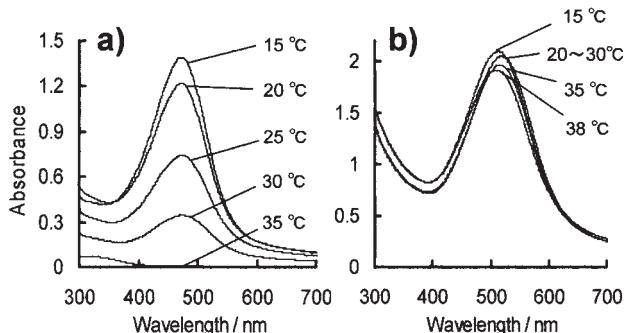


Figure 2. UV-vis spectra of $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$ and their temperature dependence. (a) in chloroform, (b) in dichloromethane. 0.6 unit mM, 1 mm cell.

$[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$ in chloroform (a) and in dichloromethane (b). In chloroform, an intense intervalence CT absorption was observed at 473 nm (\mathcal{E} : 13846 units $\text{M}^{-1} \text{cm}^{-1}$, temperature, 15 °C), which is red shifted by 17 nm compared to that observed for the single crystal $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ (λ_{max} , 456 nm).¹¹ On the other hand, the red dichloromethane solution gave λ_{max} at 513 nm (\mathcal{E} : 15017 units $\text{M}^{-1} \text{cm}^{-1}$, temperature, 15 °C), which is red-shifted by 40 nm compared to that in chloroform. As solvent evaporation of the red dichloromethane solution leaves the original orange powders, the red color requires the presence of dichloromethane. The presence of lipid counterion **1** is essential to the observed solvatochromism, since it is not observed for crystalline $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\text{ClO}_4)_4$ immersed in these solvents.

Interestingly, the yellow nanowires in chloroform and red nanocrystals in dichloromethane show different thermal stability. In chloroform, the intensity of CT absorption is decreased upon heating and the solution becomes colorless at 35 °C (Figure 2a). This change is typical to the thermally induced dissociation of the halogen-bridged mixed valence complexes.^{1,5,6,8} In contrast, the red dichloromethane solution showed almost no changes upon heating to 38 °C (Figure 2b). The nanocrystals formed in dichloromethane are thermally intact, indicating that the phenyl group-containing lipids **1** are less-solvated and are tightly packed in the assemblies.

Figure 3 displays the dependence of CT absorption on the solvent composition of binary chloroform-dichloromethane

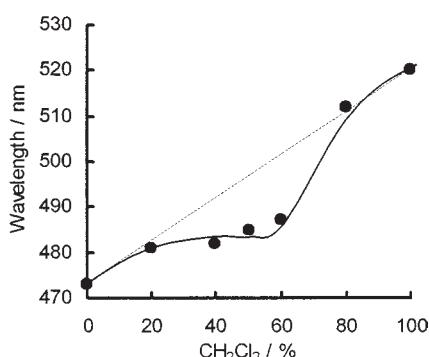


Figure 3. Dependence of charge transfer absorption maxima on the volume fraction of dichloromethane in the binary dichloromethane-chloroform mixture. Temperature, 15 °C.

mixture. The λ_{max} values showed large deviation from the linear relationship at the dichloromethane content of 40–60 vol%. This indicates that the solvatochromism in the mixed solvent is not directly respond to the changes in bulk polarity. At dichloromethane content of 20 vol%, however, the fibrous nanowires are totally changed to the rectangular nanocrystals similar to those in dichloromethane (data not shown). Thus, the aggregate morphology is much more sensitive to the presence of dichloromethane, which enhances aggregate's crystallinity.

The nonlinear dependence of CT absorption on solvent composition is indicative of the contribution of lipid molecular orientations in determining the coordination structure. The charge transfer absorption of $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2]$ complex is known to be sensitive to the size and chemical structure of anionic species.^{4,5,12} In the red nanocrystals, the densely packed sulfonate groups would direct the electrostatically bound $\text{Pt}(\text{en})_2$ and $\text{PtCl}_2(\text{en})_2$ complexes to polymerize in higher density. Contraction of the interplatinum ($\text{Pt}^{\text{II}}-\text{Cl}-\text{Pt}^{\text{IV}}$) distance is accompanied by the enhanced overlap between d_{z^2} and p orbitals, and it would promote the excitation delocalization along the chain. The concomitant decrease in the LUMO-HOMO band gap may be a possible account for the observed red-shift in charge transfer absorption.⁸

In summary, $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$ displays solvatochromism which has not been observed for the halogen-bridged platinum complexes. The lipid-packaging is indispensable for achieving the solvent-dependent control of electronic states, aggregate morphology and thermal stability. It may be utilized to develop new sensory systems.

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