Supramolecular Assemblies Comprised of One-Dimensional Mixed Valence Platinum Complex and Anionic Amphiphiles in Organic Media

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A novel class of one-dimensional supramolecular assembly dispersed in organic media was prepared from halogen-bridged mixed valence platinum complex and anionic amphiphiles. Their intervalence absorption characteristics and nanostructures varied depending on the chemical structure of amphiphiles.

Fabrication of low-dimensional inorganic structures based on organic molecular assembly is an issue of great importance in nanochemistry.[1,2] They have been known as basic structural motifs of three dimensional solids, and a technique to molecularly disperse these structural motifs would lead to a new class of inorganic nanomaterials.

A family of pseudo one-dimensional halogen-bridged mixed valence complexes $[Pt^{II}(en)_2][Pt^{IV}X_2(en)_2](ClO_4)_4$ (en ; 1,2-diaminoethane, X = Cl, Br or I) are attracting much interests because of their unique physicochemical properties such as intense intervalence ($Pt^{II}/Pt^{IV} \rightarrow Pt^{III}/Pt^{III}$) charge-transfer (CT) absorption,[3] semiconductivity,[4] and large third-order nonlinear optical susceptibilities.[5] These one-dimensional structures have not been possible to be maintained in solution.

We developed a novel strategy for dispersing one-dimensional halogen bridged platinum complexes *in organic media*, by using dialkyl sulfosuccinates as lipophilic counterions.[6] Very recently, we found that the molecular structure of lipophilic counterion was crucial to formation of the one-dimensional structure. We describe this dependence in this communication.

Complexes of $[Pt(en)_2]Cl_2$, *trans*-$[PtCl_2(en)_2]Cl_2$, and $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ were prepared according to the literature.[7] Amphiphiles 1-4 were used as organic counter anions.[8] An equimolar mixture of $[Pt(en)_2]Cl_2$ and *trans*-$[PtCl_2(en)_2]Cl_2$ was dissolved in deionized water ($[Pt]_{total} = 100$ mM, 0.2 ml). To this colorless solution, aqueous dispersions of 1-3 (Na salt, 20 mM, 2 ml, 40 °C) were added at room temperature. Yellow precipitates were immediately formed for 1(n =12). 1(n=16) afforded colorless precipitates, which turned yellow upon keeping the reaction mixture for a few minutes at 60 °C. When single-chained phosphate 2 was used, colored precipitates were not formed at any temperature. In contrast, purple precipitates were immediately formed, when
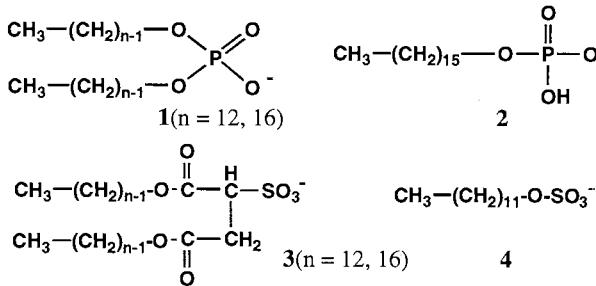
double-chained sulfonates 3 (n = 12, 16) were added to the aqueous platinum complex. Addition of aqueous sodium dodecyl sulfate 4 (80 mM, 0.5 ml) to the Pt complex resulted in formation of yellow precipitates. Elemental analysis of these powders indicated the formation of ternary complexes $[Pt(en)_2][PtCl_2(en)_2](1, 3$ or $4)_4$ for the colored products. These colors are typical of the intervalence absorption of one-dimensional halogen-bridged Pt^{II}/Pt^{IV} complexes,[3-5] and such a visible absorption band is present neither for $[Pt(en)_2]Cl_2$ and *trans*-$[PtCl_2(en)_2]Cl_2$, nor for the lipid complexes of $[Pt(en)_2](1)_2$ and *trans*-$[PtCl_2(en)_2](1)_2$.

The colored complexes were placed in 1 ml of chloroform or of methylcyclohexane, and were ultasonicated to give dispersions of ca. 1 unit mM (Branson Sonifier 5210). $[Pt(en)_2][PtCl_2(en)_2](1)_4$ (n = 12, 16) gave yellow colloidal dispersions in methylcyclohexane, and an yellow dispersion was also obtained for 1(n = 16) in chloroform. The Pt complexes with 1(n = 12) dispersed in chloroform showed pale-yellow color which is characteristic of that of non-coordinated *trans*-$[PtCl_2(en)_2]$. In contrast, $[Pt(en)_2][PtCl_2(en)_2](3)_4$ gave clear chloroform solutions with indigo (n = 16) or purple color (n = 12), while $[Pt(en)_2][PtCl_2(en)_2](4)_4$ gave yellow, colloidal dispersions in chloroform. Observation of such intense yellow, purple or indigo colors in organic media clearly indicates that one-dimensional mixed-valence chains of $[Pt(en)_2][PtCl_2(en)_2]$ remain intact as lipophilic polyion complexes.[6]

Figure 1 displays a transmission electron micrograph of $[Pt(en)_2][PtCl_2(en)_2](1)_4$ in methylcyclohexane (n = 12, 0.5 mM) (a) and that of $[Pt(en)_2][PtCl_2(en)_2](3)_4$ (n = 12, 0.1 mM) (b), $[Pt(en)_2][PtCl_2(en)_2](4)_4$ (0.5 mM) in chloroform (c). $[Pt(en)_2][PtCl_2(en)_2](1)_4$ gives aggregates with rod-like structures (width, ca. 125 nm), whereas fragmented tapes (width, ca. 80 - 400 nm, length, ca. 200 nm - 2800 nm) are seen for $[Pt(en)_2][PtCl_2(en)_2](3)_4$.[9] These aggregate morphologies are not
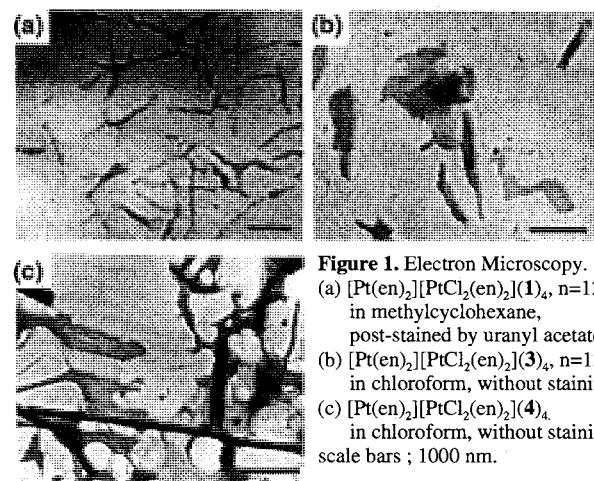
Figure 1. Electron Microscopy.
(a) $[Pt(en)_2][PtCl_2(en)_2](1)_4$, n=12, in methylcyclohexane, post-stained by uranyl acetate.
(b) $[Pt(en)_2][PtCl_2(en)_2](3)_4$, n=12, in chloroform, without staining.
(c) $[Pt(en)_2][PtCl_2(en)_2](4)_4$ in chloroform, without staining. scale bars ; 1000 nm.

CH_3—$(CH_2)_{n-1}$—O, O / P / O, O$^-$ 1(n = 12, 16)

CH_3—$(CH_2)_{15}$—O—P(=O)(O$^-$)—OH   2

CH_3—$(CH_2)_{n-1}$-O-C(=O)—CH(H)—SO$_3^-$
CH_3—$(CH_2)_{n-1}$-O-C(=O)—CH$_2$ 3(n = 12, 16)

CH_3—$(CH_2)_{11}$-O-SO$_3^-$ 4

dependent on alkyl chain length of **1** and **3**. On the other hand, both of rods (width, 100 – 120 nm) and fragmented tapes are found for $[Pt(en)_2][PtCl_2(en)_2](4)_4$.

Figure 2 compares absorption spectra of lipid complexes dispersed in chloroform (0.5 unit mM, 1 mm cell). $[Pt(en)_2]$ $[PtCl_2(en)_2](1)_4$ (n =16) gave absorption λ_{max} at 460 nm (2.67 eV, ε : 9380 $M^{-1}cm^{-1}$), which is close to that observed for the single crystal of $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (λ_{max} at 456 nm, 2.72 eV).[10] It is likely that $[Pt(en)_2][PtCl_2(en)_2](1)_4$ dispersed
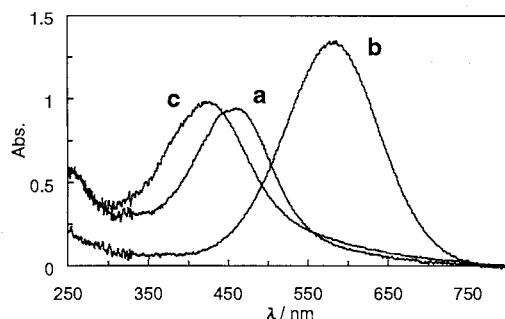
Figure 2. UV-Vis absorption spectra in chloroform.
a, $[Pt(en)_2][PtCl_2(en)_2](1)_4$ (n=16).
b, $[Pt(en)_2][PtCl_2(en)_2](3)_4$ (n=16).
c, $[Pt(en)_2][PtCl_2(en)_2](4)_4$.
[Pt]total = 1 mM, 1 mm cell, 20 °C.

in chloroform possesses halogen bridged Pt^{II}-Pt^{IV} structure similar to that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$, due to structural similarlity between the phosphate head group of **1** and ClO_4 anion. $[Pt(en)_2][PtCl_2(en)_2](4)_4$ showed a blue-shifted λ_{max} at 420 nm (2.95 eV, ε : 9810 $M^{-1}cm^{-1}$), while the indigo-colored solution of $[Pt(en)_2][PtCl_2(en)_2](3)_4$ (n =16) gave a much red-shifted absorption band centered at 580 nm (2.15 eV, ε :13400 $M^{-1}cm^{-1}$) with enhanced molar extinction coefficient. CT exciton energy of halogen-bridged, mixed-valence $Pt(en)_2$ polymers in the crystalline state is related to the energy-gap caused by the lattice distortion, i.e, the magnitude of off-center displacement of halogen ions.[3b,10] If this relationship is applicable to the present system, the spectral red shift observed for $[Pt(en)_2][PtCl_2(en)_2](3)_4$ implies that the bridging Cl ion is located more to the center of Pt^{II}-Pt^{IV} separation, compared to that for $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ in which chloride ions are positioned closer to Pt^{IV}. This positional shift is attributable to the bulky molecular cross-section of double-chained sulfonate **3**, since such a spectral shift has not been observed for $[Pt(en)_2][PtCl_2(en)_2](4)_4$ that possess single-chained counteranion. The blue shift observed for the latter compound, on the other hand, is indicative of decreased Pt^{II}-Pt^{IV} distance and/or increased off-center displacement of chloride ions.[3b,10]

As the dimension of nanostructures observed in electron microscopy are larger than bi-molecular lengths of the corresponding amphiphiles, we presume that TEM figures consist of bundles of supramolecular polyion complexes schematically shown in Figure 3. It is noteworthy that solubility and spectral characteristics of the one-dimensional mixed-valence Pt^{II}/Pt^{IV} complexes in organic media are affected by the chemical structure of amphiphiles. They not only provide
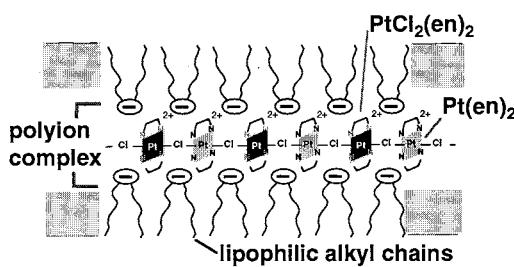

Figure 3. Schematic illustration of supramolecular polyion complex formed from platinum complexes and anionic amphiphiles.

solubility in organic media but also exert influence on intra-chain Pt^{II}-Pt^{IV} distance and/or off-center displacement of bridging chloride ions. Enhanced solubility of $[Pt(en)_2][PtCl_2(en)_2](3)_4$ implies that this mixed-valence polymer chain is dispersed without chain aggregation. Though contribution of such interactions on intervalence absorption spectra are generally ignored,[3] the observed large red shift might reflect an effect of chain isolation as well.

To date, structural modification of halogen-bridged, one dimensional metal complexes has been conducted for crystalline samples, and are limited to the substitution of metal components, bridging-halogen ions, organic ligands, and of counter anions.[3-5,10-12] The present system is widely applicable for regulation of low-dimensional inorganic structures in organic media. Together with amphiphilic hydrogen bond networks we have developed,[13] it constitutes a new family of mesoscopic supramolecular assemblies.

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