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Supramolecular solvatochromism. Effect of solvents on the self-assembly and charge transfer absorption characteristics of lipid-packaged, linear mixed-valence platinum complexes

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Abstract

Lipid-packaged, mixed-valence linear platinum complexes are dispersed in chloroform, chlorocyclohexane and in methylcyclohexane. They show indigo-colors, which are identical to solid samples. These lipid-complexes display supramolecular thermochromism, resulting from heat-induced dissociation and recovery of coordination chains. Unexpectedly, reassembled samples show altered CT absorption spectra. In chloroform, the reassembled complex gives indigo-color, while the chlorocyclohexane and methylcyclohexane dispersions show blue and red-colors, respectively. These color changes indicate enhanced solvation of lipid-packaged platinum complexes after the heat treatment. The thermal re-assembly also affects the aggregate morphology, and leads to the formation of nanowires, nanofibers and nanoparticles depending on the solvents employed. The conversion of pseudo one-dimensional (1D) inorganic complexes to lipophilic supramolecular assemblies thus gives solvatochromic properties, which are elements not existing in the conventional solid-state inorganic chemistry.

Keywords: Nanowire; One-dimensional metal complex; Mixed-valence; Self-assembly; Charge transfer; Solvatochromism; Neuromorphic; Molecular informatics

1. Introduction

Controlled formation of conjugated electronic structures based on self-assembly provides a basis for the development of self-wiring, neuromorphic devices [1]. Molecular wires are indispensable elements for fabricating nanocircuits, and π-conjugated oligomers or polymers have been taking the mainstream of research [2]. However, covalent polymers are devoid of reversible polymerization/de-polymerization properties, and hence they do not provide conjugated electronic structures which are formed in response to self-assembly. To develop self-assembling molecular wires, we devised supramolecular strategies to disperse linear metal complexes as nanowires in organic media [3–13]. Quasi-1D, halogen-bridged 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-diaminoethane) are attracting much interest due to their *d–p* conjugated electronic structures with charge density wave state [14] and large nonlinear optical susceptibilities [15]. These 1D chains have been available only as a basic structural motif in bulk crystals, and consequently they were not considered as candidates for molecular wires. We have reported that introduction of lipid counter anions coverts these 1D complexes to nanowires dispersed in organic media. The solvophobic $[Pt(en)_2][PtCl_2(en)_2]$ chains are surrounded by solvophilic lipid alkyl chains, giving amphiphilic superstructures. The $[Pt(en)_2][Pt(en)_2Cl_2][Lipid]_4$ complexes display aggregate morphology and charge transfer (CT, $Pt^{II} \rightarrow Pt^{IV}$) absorption characteristics which vary depending on metal ions [5,7], bridging halogen ions [8], solvents [9] and lipid chemical structures [3,4,7]. Some of the complexes display supramolecular thermochromism, as a result of reversible dissociation and reassembly of coordination chains in solution [4–11]. Thus, lipid-modified linear metal complexes allow solubilization

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and self-assembly of molecular wires in organic media, giving a new research field of neuromorphic nanomaterials. As our basic strategy is based on the conversion of solid pseudo-1D metal complexes to amphiphilic supramolecular assemblies, it is particularly important to develop functions which are not available in the solid state. In this work, we focus on the solvatochromic nature of lipid/chloro-bridged Pt(II)/Pt(IV) complexes. Solvents exert a decisive role in determining the LUMO-HOMO band gap, and their relevance to thermal morphology changes is discussed.

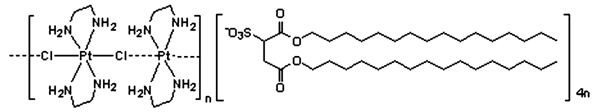
2. Experimental section

2.1. Materials

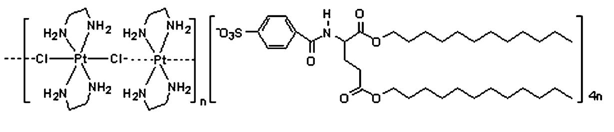
Chloroform, chlorocyclohexane and methylcyclohexane were of spectral grade (Kishida Chemical Co. Ltd. or Tokyo Chemical Industry Co. Ltd.) and were used as received. $[Pt^{II}(en)_2]Cl_2$, *trans*-$[Pt^{IV}Cl_2(en)_2]Cl_2$ were prepared according to the literature [16]. Amphiphilic sulfonate **1** was selected as an organic counter-anion, and the complex $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ (Chart 1) was synthesized as described previously [3,4]. Aqueous dispersions of anionic amphiphiles **1** (Na^+ salt, 20 mM, 2 mL) were added to equimolar solutions containing $[Pt(en)_2]Cl_2$ and *trans*-$[PtCl_2(en)_2]Cl_2$ in deionized water (0.2 mL, $[Pt]_{total} = 100$ mM). Indigo-colored precipitates immediately formed were collected by centrifugation and washed with pure water to remove sodium chloride. The samples were then dried in vacuo. Elementary analysis for $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$: Calcd. for $C_{152}H_{308}N_8S_4Pt_2Cl_2$: C, 55.56; H, 9.45; N, 3.41. Found: C, 54.92; H, 9.44; N, 3.33.

2.2. Measurements

The lipid complex $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ was dispersed in organic solvents by vigorous hand shaking (as-dispersed samples). UV-vis spectra were measured for 0.1 unit mM dispersions (JASCO V-570). Transmission electron microscopy (TEM) was conducted on a JEOL JEM-2010 instrument (120 kV). Samples were prepared by placing a drop of chloroform, chlorocyclohexane, or methylcyclohexane solution on a carbon-coated TEM grid placed on a filter paper. The drops immediately penetrated into the filter paper, and the grids dried in air were observed without negative staining.



$[Pt^{II}(en)_2][Pt^{IV}(en)_2Cl_2][\mathbf{1}]_4$



$[Pt^{II}(en)_2][Pt^{IV}(en)_2Cl_2][\mathbf{2}]_4$

Chart 1. Chemical structures of $[Pt^{II}(en)_2][Pt^{IV}(en)_2Cl_2][1]_4$ and $[Pt^{II}(en)_2][Pt^{IV}(en)_2Cl_2][2]_4$.

3. Results and discussion

The indigo-colored dispersion of $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ in chloroform show a CT absorption peak at ca. 597 nm (2.08 eV, line a in Fig. 1(a), 20 °C), indicating that the halogen-bridged mixed-valence chain is maintained in solution. The observed CT peak is considerably red-shifted compared to that of crystalline perchlorate compound $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (yellow solid, 456 nm, 2.72 eV) [17]. It indicates the enhanced delocalization of photoexcited states in main chains, as a result of larger Pt–Pt interactions [10,18]. Densely positioned anionic charges of lipid layers in $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ give periodical electrostatic potential that makes $Pt(en)_2$ and $PtCl_2(en)_2$ complexes to coordinate in shorter Pt(II)–Cl–Pt(IV) distances, compared to that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$. This is supported by single crystal X-ray diffraction analysis conducted for $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ with shorter chained lipids [18], where Pt(II)–Cl–Pt(IV) distance (5.27 Å) in the lipid complex is shortened compared to that in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (5.43 Å) [19]. The decrease in interplatinum Pt(II)–Cl–Pt(IV) distances allows larger overlap between $d_z{}^2$ and p_z orbitals of Pt and Cl ions, leading to the smaller HOMO-LUMO band gap. It facilitates the charge transfer along the coordination chains (supramolecular band gap engineering) [8,10]. $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ dispersed in chlorocyclohexane and methylcyclohexane also showed indigo colors whose CT absorption peaks are observed at 597 and 596 nm, respectively.

When these dispersions were heated to ca. 60 °C (chloroform), 80 °C (chlorocyclohexane) and to 90 °C (methylcyclohexane), colors originated from CT absorption peaks disappeared. UV-Vis spectra of samples immediately after cooling to 20 °C are shown in Fig. 1(lines b in (a)–(c)). The disappearance of CT absorption peaks by heating is ascribed to the dissociation of chloro-bridged structures [4,7,10]. On the other hand, upon keeping these dispersions at 20 °C, absorption intensities were gradually recovered. In chloroform, CT absorption after standing 1 h showed a slightly blue-shifted CT peak at 563 nm (2.20 eV, line c in Fig. 1(a)), and the peak intensity increased with time (line d). Finally, indigo-colored dispersion was obtained as shown in Fig. 2(a). The spectral shift observed for reassembled $[Pt(en)_2][PtCl_2(en)_2]$ complex reflects changes in the LUMO-HOMO band gap, i.e., 1D electronic structure of chloro-bridged mixed valence chains. It is sensitive to molecular structure of anionic lipids and their molecular organization [3,4,7].

Transmission electron micrographs of $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ dispersed in chloroform before and after the heat treatment are shown in Fig. 3a and b, respectively. The as-dispersed sample gave fragmented