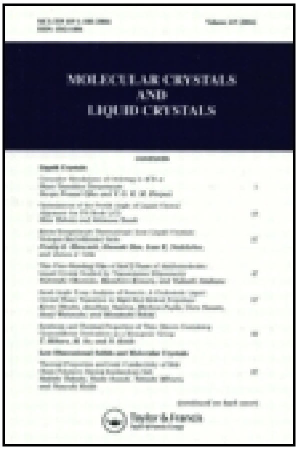


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Organization of One-Dimensional Mixed-Valence Platinum Complexes at the Air-Water Interface and in Langmuir-Blodgett Films

Nobuo Kimizuka [a], Keiji Yamada [a] & Toyoki Kunitake [a]

[a] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, 812-8581

To cite this article: Nobuo Kimizuka, Keiji Yamada & Toyoki Kunitake (2000): Organization of One-Dimensional Mixed-Valence Platinum Complexes at the Air-Water Interface and in Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 103-110

To link to this article: http://dx.doi.org/10.1080/10587250008038252

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 103-110
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Organization of One-Dimensional Mixed-Valence Platinum Complexes at the Air-Water Interface and in Langmuir-Blodgett Films

NOBUO KIMIZUKA, KEIJI YAMADA and TOYOKI KUNITAKE

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812–8581

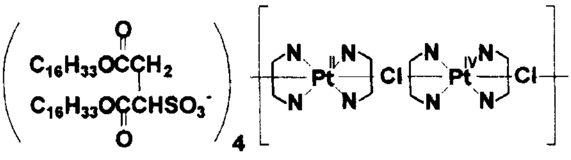
Surface monolayers consisting of cationic, halogen-bridged linear platinum complex and anionic amphiphiles are formed at the air-water interface. Lipophilic polyion complex prepared from lipid and one-dimensional platinum complex is dispersed in chloroform as an indigo-colored solution, which color is ascribed to charge transfer (CT) absorption of the halogen-bridged complex ($Pt^{II} \rightarrow Pt^{IV}$). Upon heating the solution, the indigo color disappeared due to dissociation of the linear complex into molecular unit complexes. Oriented surface monolayer is formed on water by spreading the colorless chloroform solution. Appearance of the CT band in reflectance spectra of monolayers indicates that the one-dimensional halogen-bridged complex is reformed at the air-water interface. The present technique opens an avenue to dimension-controlled organization of linear halogen-bridged complexes.

Keywords: halogen-bridged mixed-valent complex; platinum; thermochromism; surface monolayer; Langmuir-Blodgett film

INTRODUCTION

Manipulation of dimension-controlled inorganic materials by the use of organic molecular assemblies is emerging as a fertile area in nano-chemistry.[1,2] Halogen-bridged complexes of $Pt(en)_2PtX_2(en)_2$ (en, ethylenediamine, X = Cl, Br, I) belongs to pseudo one-dimensional metal complexes, which are attracting much interests due to their charge density wave (CDW) states,[3] strong intervalence absorption[4] and non-linear optical properties.[5] Though these one-dimensional structures are obtainable only in the crystalline states,[3-5] isolation of these molecular chains in solution phase and their organization in desired dimensions would provide a new research field of nano-chemistry.

We recently have developed a novel approach to disperse these molecular wires in organic media, via polyion complexation with an anionic amphiphile **1**.[6] In the present paper, we describe two-dimensional organization of the polyion complex $[Pt(en)_2][PtCl_2(en)_2]$ $(\mathbf{1})_4$ as a monolayer at the air-water interface. Formation of their 3D-assembly by the use of Langmuir-Blodgett technique was also investigated.



$[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$

EXPERIMENTAL METHOD

Indigo-colored complex of $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ was prepared as reported previously.[6] The complex was dissolved in chloroform as an indigo-colored solution by hand shaking (solution I , concentration, 0.1 unit mM). This color is ascribed to the CT absorption ($Pt^{II} \rightarrow Pt^{VI}$, λ_{max} at 600 nm) of chloro-bridged, mixed-valent platinum complex.[6] Interestingly, when this indigo solution is heated up to ca. 60 ℃, the color disappeared as a result of dissociation into molecular unit complexes of $[Pt(en)_2](\mathbf{1})_2$ and $[PtCl_2(en)_2](\mathbf{1})_2$ (solution II).[7] The solution II remained colorless within 30 minutes after cooling to room temperature, whereas the indigo color was recovered upon further standing, due to self-assembly of the linear complex in the solution.[7] Taking this reversibility in consideration, spreading of the colorless solution II on pure water (Milli Q system, Millipore Co., subphase temperature at 26 ℃) was conducted immediately after cooling the solution to room temperature. The surface pressure-area isotherms (π - A curve) were obtained with a computer-controlled film balance (USI system, model FSD-300). Reflectance spectra of surface monolayers were measured with a photodiode array–equipped spectrometer (Otsuka electronics, model MCPD-7000. light source, I_2-lamp). The experimental details were given before.[8] Hydrophobic quartz plates prepared by the use of dimethylpolysiloxane (siliconize L-25, Fuji Systems. Co.) were used as substrates for deposition.

RESULTS AND DISCUSSION

Figure 1 displays π -A curves of $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ on pure water obtained by spreading chloroform solutions I (a) and II (b), respectively. $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ spread from the indigo-colored solution I

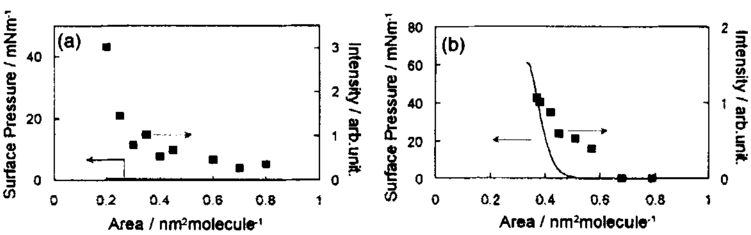


FIGURE 1. Surface pressure-area isotherms. (a) Monolayer spread from solution I. (b) monolayer spread from solution II. Filled squares indicate peak intensities of reflectance spectra measured *in situ*. Subphase, pure water, 26 ℃.

showed no increase in surface pressure, during compression from a molecular area of 0.86 $nm^2 \cdot molecule^{-1}$ to 0.19 $nm^2 \cdot molecule^{-1}$ (Figure 1a). On the other hand, when $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ was spread from the colorless solution II, surface pressure started to rise at a surface area of 0.5 $nm^2 \cdot molecule^{-1}$, and a condensed π-A isotherm with a molecular cross sectional area of ca. 0.43 $nm^2 \cdot molecule^{-1}$ was obtained (Figure 1b, solid line). This molecular area is comparable to that of the densely packed double-chained amphiphile **1**,[9] and apparently oriented surface monolayer is formed by spreading the dissociated unit complexes of $[Pt(en)_2](\mathbf{1})_2$ and $[PtCl_2(en)_2](\mathbf{1})_2$.

Figure 2 shows reflectance spectra of surface monolayers prepared from the solution I (a) and II (b), respectively. Their peak intensities are plotted as filled squares in Figure 1a and 1b. In Figure 2a, reflectance spectrum with a maximum at 620 nm was observed at a molecular area of 0.45 nm^2 $molecule^{-1}$ (curve e), and the peak intensity increased upon further compression (Figures 1a, 2a). The observed spectra are close to that observed for solution I, indicating maintenance of the linear mixed-valence platinum complex at the air-water interface. As this complex did not show any rise in surface pressure, increase in the reflectance intensity must be ascribed to piling up of the hydrophobic polyion complexes as schematically shown in

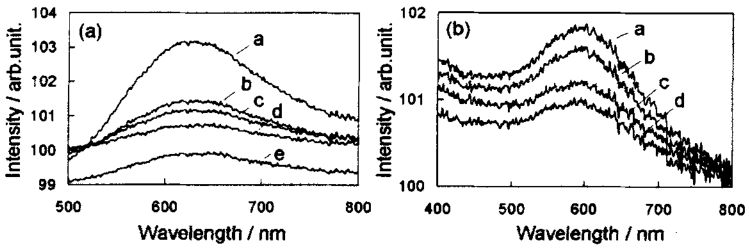


FIGURE 2. Reflectance spectra at the air-water interfaces. (a) monolayer spread from solution I. a, at 0.2 nm^{2}molecule^{-1}, b, at 0.25 nm^{2}molecule^{-1}, c, at 0.35 nm^{2}molecule^{-1}, d, at 0.4 nm^{2}mole-cule^{-1}, e, at 0.45 nm^{2}molecule^{-1}. (b) monolayer spread from solution II. a, at 20 mNm^{-1}, b, at 10 mNm^{-1}, c, at 4 mNm^{-1}, d, at 1.2 mNm^{-1}.

Figure 3a.

On the other hand, when the colorless solution II was spread on pure water, no reflectance peak was observed initially at the molecular area of 0.8 nm$^2\cdot$molecule^{-1} (Figure 1b). Then a charge transfer band at 600 nm appeared, after compression of the monolayer to the surface area of ca. 0.6 nm$^2\cdot$molecule^{-1}. This spectral maximum is identical to that observed for $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ in chloroform, and its intensity increased with the rise in surface pressure (Figures 1b, 2b). As the colorless stock solution II contained dissociated unit complexes of $[Pt(en)_2](\mathbf{1})_2$ and $[PtCl_2(en)_2](\mathbf{1})_2$, they must be re-assembled into linear, mixed-valent platinum complexes at the air-water interface. Schematic illustration of the polyion-complexed surface monolayer $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ is given in Figure 3b.

Spreading of the heat-dissociated lipid complexes is prerequisite to form oriented monolayer with linear mixed-valence platinum complex. When the anionic amphiphile **1** (Na^+ salt) was spread on aqueous subphase containing equimolar $[Pt(en)_2]Cl_2$ and $[PtCl_2(en)_2]Cl_2$ (concentration, 1 mM), reflectance spectra due to the formation of

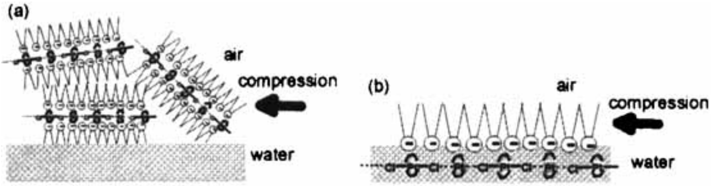


FIGURE 3. Schematic illustration of surface monolayers.
(a) squeezed up monolayer formed by spreading solution I.
(b) oriented polyion-complex monolayer formed from solution Ⅱ.

mixed-valence complex was not observed, regardless of the appearance of condensed π -A isotherm (data not shown). It is possible that $Pt(en)_2$ and $PtCl_2(en)_2$ complexes are adsorbed to the monolayer **1** in non-equimolar ratio, and this prohibited the formation of extended, linear mixed-valence complexes.

Formation of polyion-complexes at the air-water interface has been reported to stabilize charged monolayers, and it facilitates fabrication of their LB films.[8,10] When $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ was spread from solution I, however, vertical dipping and withdrawal of a quartz plate (molecular area, at 0.3 $nm^2 \cdot molecule^{-1}$) were not accompanied by appearance of the CT band on quartz plate (Figure 4, filled triangle). Apparently, the polyion-complex spread from solution I is not transferable onto the substrate. On the other hand, when surface monolayer prepared form colorless solution Ⅱ was deposited on a quartz plate, absorption intensity at 600 nm increased linearly with repeating dipping cycles (Figure 4, filled squares. surface pressure at 20 $mN \cdot m^{-1}$). Thus, multilayered Langmuir-Blodgett (LB) film is obtained only for the oriented polyion complex monolayer. These observations clearly indicate that two- and three- dimensionally controlled organization of halogen-bridged linear mixed-valence complexes can be realized by the use of surface monolayer/LB

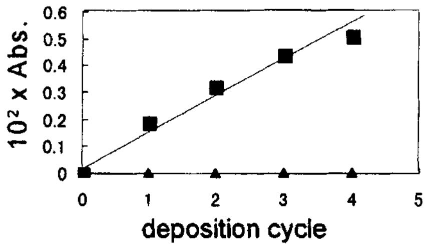


FIGURE 4. Absorption peak intensity changes of LB films with the repetition of deposition. Filled triangle; monolayer was spread from solution I and deposition was conducted at a molecular area of 0.3 $nm^2 molecule^{-1}$. Filled square; monolayer was spread from solution II and deposited at a surface pressure of 20 mNm^{-1}. Substrate, hydrophobized quartz plate. Subphase, pure water, 26 ℃.

techniques.

To date, synthesis and organization of inorganic nanomaterials such as colloid nanoparticles,[11] metal oxides,[12] and cyano-bridged mixed-valence complexes[13] has been exploited by the use of surface monolayers. However, preparation of monolayers containing one-dimensional inorganic complexes has been unprecedented. The present strategy is widely applicable to control organization of low-dimensional inorganic complexes, and it provides a new perspective in inorganic nanochemistry.

References

[1] N. Kimizuka and T. Kunitake *Adv. Mater.*, **8**, 89 (1996).

[2] G. A. Ozin *Adv. Mater.*, **4**, 612 (1992).

[3] H. Okamoto, T. Mitani, K. Toriumi and M. Yamashita, *Mater. Sci. Eng.* **B13**, L9 (1992).

[4] H. Okamoto and M. Yamashita, *Bull. Chem. Soc. Jpn.* **71**, 2023 (1998) and references therein.

[5] Y. Iwasa, E. Funatsu, T. Hasegawa, T. Koda and M. Yamashita, *Appl. Phys. Lett.*, **59**, 2219 (1991).

[6] N. Kimizuka, N. Oda and T. Kunitake *Chem. Lett.*, 695 (1998).

[7] (a) N. Kimizuka, N. Oda and T. Kunitake, *Polymer Preprints. Jpn.*, **46**, 3273 (1997).
(b) L. Sang Ho, N. Kimizuka, T. Kunitake, *Angew. Chem. Int, Ed. Engl.*, in press.

[8] (a) N. Kimizuka and T. Kunitake, *Colloids and Surfaces*, **38,** 79 (1989). (b) N. Kimizuka and T. Kunitake, *Chem. Lett.*,827 (1988).

[9] For example, T. Kawahara, K. Kurihara and T. Kunitake, *Chem. Lett.*, 1839 (1992).

[10] (a) M. Shimomura and T. Kunitake, *Thin Solid Films*, **132,** 243 (1986). (b) N. Higashi and T. Kunitake *Chem. Lett.*, 105 (1986).

[11] For example, X. K. Zhao, S. Xu and J. H. Fendler, *Langmuir*, **7,** 520 (1991).

[12] I. Moriguchi, H. Maeda, Y. Teraoka and S. Kagawa, *J. Am. Chem. Soc.* **117,** 1139 (1995).

[13] N. Kimizuka, T. Asai, S. Ohno, K. Fujiyoshi and T. Kunitake, *Surface Science*, **386,** 245 (1997).