Spectroscopic Evidence for Pt−Pt Interaction in a Langmuir−Blodgett Film of an Amphiphilic Platinum(II) Complex

Kentaro Kobayashi,[†] **Hisako Sato,**[‡,§] **Shinobu Kishi,**[||] **Masako Kato,**[||] **Shoji Ishizaka,**[⊥] **Noboru Kitamura,**[⊥] **and Akihiko Yamagishi**[*,‡,§]

Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Division of Material Science, Graduate School of Humanities and Sciences, Nara Women's University, Nara 630-8506, and Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0081, Japan

When a chloroform solution of a dicyano(diimine)platinum(II) complex, [Pt(CN)₂(5,5′-dinonyl-2,2′-bipyridine)], was spread onto pure water, a reversible surface pressure−molecular area curve was obtained. The surface pressure began to increase steeply from 0 at a molecular area of 0.61 nm² molecule⁻¹. On further compression, the monolayer was stable at 0.2 nm² molecule⁻¹ and 30 mN m⁻¹. In such a highly compressed state, the complex was thought to orient its planar ligand 2,2′-bipyridine perpendicular to the water surface. The floating monolayer was vertically deposited onto a hydrophobic quartz substrate as an X-type film. The absorption spectra of the deposited films showed a broad peak at 480 nm, while that band was absent in the solution spectrum. The emission spectra of the films exhibited a broad band around 600 nm. The excitation spectra monitored at 600 nm coincided well with the absorption spectra. The results were interpreted in terms of the formation of the molecular aggregate, in which the platinum complexes were stacked with the overlaying bipyridine moieties. In such an aggregate, the MMLCT state was generated due to the Pt−Pt interaction among the neighboring molecules. On the basis of the model, the absorption band at 480 nm and the emission band at 600 nm were assigned to the ¹MMLCT and ³MMLCT transitions from or to the dσ* orbital of Pt(II) to or from the π* orbital of 2,2′-bipyridine, respectively. The AFM observation showed that the film deposited on a silicon wafer consisted of a grain-shaped aggregate, assisting the intermolecular interactions of composite molecules.

Introduction

Platinum(II)−ammine or −diimine complexes have been attracting extensive attention because of their catalytic property of hydrogen evolution in a photosynthetic model system.[1−3] A key aspect to such a catalytic activity lies in the Pt−Pt interaction in a reduced state of Pt(II), since the intermetallic interaction is thought to be a measure of the stability and reducing ability of a platinum complex. To control such a Pt−Pt interaction, the construction of a well-ordered two-dimensional film of Pt(II) complexes has been attempted by artificial deposition such as the Langmuir−Blodgett (LB) method.[4−6] This approach has the advantage of tuning the extent of intermetallic interaction by changing either the surface density or the mode of layer stacking in the film. So far, however, no attempt has been reported on the successful buildup of molecular films in which there exists a Pt−Pt interaction among component complexes.

In the present work, an amphiphilic Pt(II) complex denoted as [Pt(CN)₂L] with L = 5,5′-dinonyl-2,2′-bipyridine (Figure 1) was synthesized to pursue such a possibility. A nonamphiphilic
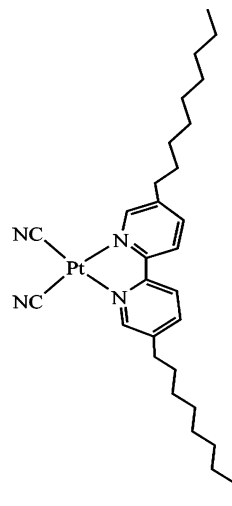
* To whom correspondence should be addressed. Phone: +81-3-5841-4546. Fax: +81-3-5841-4553. E-mail: yamagisi@eps.s.u-tokyo.ac.jp.
† Division of Biological Sciences, Hokkaido University.
‡ The University of Tokyo.
§ Also at CREST, Japan Science and Technology Agency.
|| Nara Women's University.
⊥ Division of Chemistry, Hokkaido University.

Figure 1. Molecular structure of [Pt(CN)₂L] with L = 5,5′-dinonyl-2,2′-bipyridine.

analogue of this compound, [Pt(CN)₂(bpy)] (bpy = 2,2′-bipyridine), is known to have emissive properties with a broad peak around 600 nm in both the solution and solid states.[7−11] The peak is assigned to the emission from the ³MMLCT state on the basis of the electronic excitation from dσ* arising from the Pt−Pt interaction to π* of the bpy ligand. The presence of

this emission band is considered to be evidence for the Pt–Pt interaction within a distance of 0.33–0.35 nm.[7,12,13]

We have investigated the spectroscopic properties of an LB film of [Pt(CN)$_2$L]. Our main attention was focused on revealing the relation between molecular packing and the extent of intermetallic interaction. As a result, the deposited LB film of [Pt(CN)$_2$L] showed an absorption peak at 480 nm which was not seen in the solution spectrum of the same complex. The film was also found to emit luminescence around 600 nm, which was assigned to the ^{3}MMLCT transition due to the Pt–Pt interaction. This was initial evidence for the Pt–Pt interaction in an LB film. The results may motivate the use of the LB films of amphiphilic Pt complexes for energy conversion of light-induced water decomposition.

Experimental Section

Materials. [Pt(CN)$_2$L] with L = 5,5′-dinonyl-2,2′-bipyridine was prepared by refluxing [Pt(CN)$_2$] with L in a 1:1 (v/v) mixture of aqueous ammonia (28%) and dimethylformamide overnight.[7,13] After the mixture was filtered, the precipitate was washed with methanol. The product was identified by ^{1}H NMR and FT-IR measurements. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 0.88 (m, CH$_3$, 3H), 1.27 (br, CH$_2$, 14H), 2.78 (t, CH$_2$, 2H), 8.01(br, 3,4-py, 1H), 9.23 (s, 6-py, 1H). IR (KBr, cm^{-1}): ν(alkyl) 2956, 2924, 2854; ν(CN) 2141. Milli-Q SP reagent water (Millipore) was used as a subphase. A hydrophilic quartz glass plate was prepared by treatment with a 7:3 (v/v) mixture of hydrogen peroxide (30%) and concentrated sulfuric acid. A hydrophobic quartz glass plate was prepared from the hydrophilic one by immersion in a 2% (v/v) toluene solution of octyltrichlorosilane for 2 h. A silicon wafer was treated with a 3:2 (v/v) mixture of hydrogen peroxide (30%) and aqueous ammonia (28%) solutions.

Instruments. A floating monolayer was formed with a Langmuir trough (USI System, Japan) whose area was 10.0 cm × 13.0 cm. An LB film was prepared by the vertical dipping method at a dipping rate of 2 mm min^{-1}. The measurements of infrared reflection–absorption spectra were carried out at a resolution of 8 cm^{-1} with a JIR7000 spectrometer (JEOL, Japan) equipped with an MCT detector. A sample was deposited onto a gold-coated glass substrate. The incident angle of the monitoring light was 80° from the normal direction. Atomic force microscopy (AFM) images were recorded at room temperature under air with a Nanoscope scanning probe microscope (DI Instruments). Nanoprobe integral cantilevers (Si) were used, having tips with a spring constant of 42 N m^{-1}. AFM images were obtained in the tapping mode with the filters off. The "j" scan head was used, which has a maximum scan range of 125 μm × 125 μm × 5 μm. Emission spectra were recorded with a fluorescence spectrometer, F-4500 (Hitachi, Japan).

Results

π–A Curves of a Floating Monolayer of [Pt(CN)$_2$L]. A chloroform solution of [Pt(CN)$_2$L] (4.0 × 10^{-4} M) was spread onto pure water at 20 °C. After 30 min, the surface was compressed at a rate of 10 cm^2 min^{-1}. As shown by the π–A isotherm in Figure 2, the surface pressure began to increase from 0 around a molecular area of 0.6 nm^2 molecule^{-1}. On further compression, the surface pressure increased steeply, and no collapse of the film was observed at 0.2 nm^2 molecule^{-1}, where the surface pressure attained a value as high as 30 mN m^{-1}. The π–A isotherm was found to be nearly reversible when the compression–expansion cycle was repeated several times.
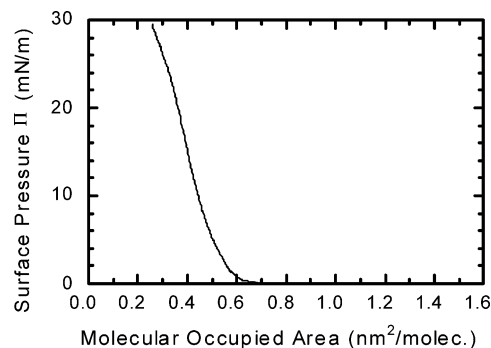

Figure 2. A surface pressure versus molecular area curve of [Pt-(CN)$_2$L]. The subphase was pure water. The temperature was 20 °C.

Absorption and Emission Properties of the Deposited Monolayers of [Pt(CN)$_2$L]. An attempt was made to transfer a floating film of [Pt(CN)$_2$L] onto a solid substrate by the vertical dipping method. No transfer of the film was possible onto a hydrophilic glass plate in the X-, Y-, and Z-modes. Onto a hydrophobic quartz glass plate was deposited a monolayer of the complex as an X-type film. The transfer ratio was within the range of 0.90 ± 0.10.

Figure 3A shows the absorption spectra of a five-layered X-type film. There was a broad peak observed at 480 nm in addition to a sharp peak at 260 nm and a shoulder around 330 nm. A solution spectrum of the same complex exhibited the two main peaks at 260 and 325 nm, which are assignable to the $\pi\pi^*$ transitions of the bipyridine moiety (Figure 3B). These two corresponded to the peak at 260 nm and the shoulder at 330 nm in the film, respectively. Thus, the peak at 480 nm was particular to an LB film. The intensity of the peak increased with an increase of the deposition pressure or the molecular density in the film as shown in Figure 3C.

Figure 4A shows the emission spectra of a five-layered X-type film. The excitation wavelength was 320 nm. The deposition pressure was changed from 2 to 24 mN m^{-1}. All spectra were normalized so that the fluorescence intensity took the same value at 470 nm. The spectra consisted of two components or a vibronic peak around 450 nm and a broad single peak around 600 nm. Figure 4B shows the plot of the intensity at 600 nm as a function of the molecular density of the film. The increase in the intensity was by a factor of about 4 in comparison to the increase of the molecular density by a factor of about 2. A change of the deposition pressure (from 2 to 24 mN m^{-1}) resulted in a red shift of the peak position from 605 to 615 nm (Figure 4C).

Figure 5 is the excitation spectra of the same film. When the emission was monitored at 600 nm, the excitation spectrum showed a sharp peak at 260 nm, a shoulder at 330 nm, and a broad band at 480 nm. These peaks corresponded to the absorption spectrum as observed in Figure 3A.

The effect of intervening molecules on the emission properties was studied by adding palmitic acid in a film. Figure 6 shows the emission spectra when a mixed monolayer of [Pt(CN)$_2$L] and palmitic acid was deposited as an X-type film onto a hydrophobic quartz glass plate at various mixing ratios. In this figure, too, each spectrum was normalized at the intensity at 470 nm. The intensity of the peak at 600 nm decreased in comparison to that of the vibronic band around 450 nm remarkably with an increase of the molar ratio of palmitic acid in the mixed films. The peak position was displaced toward shorter wavelength on dilution with palmitic acid.

Infrared Reflection–Absorption Spectra of the Deposited Films of [Pt(CN)$_2$L]. Infrared reflection–absorption spectra

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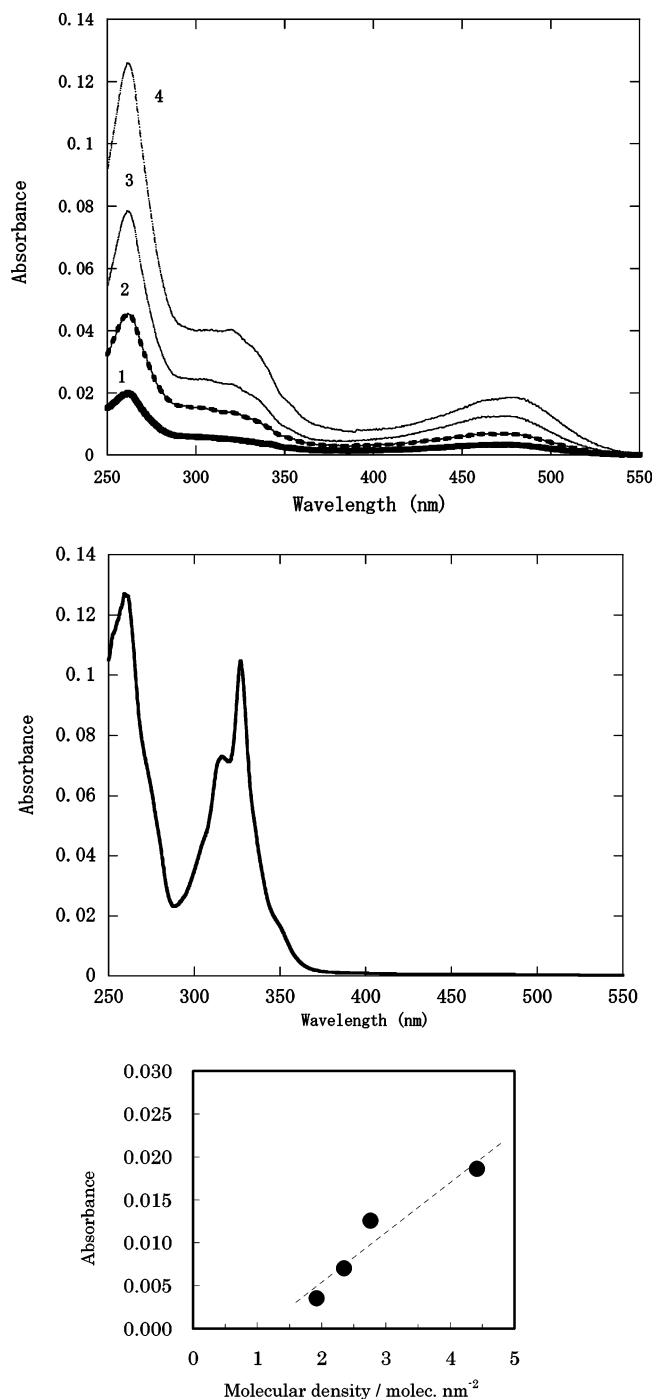*J. Phys. Chem. B, Vol. 108, No. 48, 2004* **18667**

Figure 3. (A, top) Absorption spectra of the films deposited at various surface pressures. Curves 1−4 are for the films deposited at 2, 6, 16, and 24 N m⁻¹, respectively. The films were prepared by depositing five layers of an X-type monolayer. (B, middle) Absorption spectrum of [Pt(CN)₂L] with L = 5,5′-dinonyl-2,2′-bipyridine in chloroform at room temperature. (C, bottom) Dependence of the absorption intensity at 480 nm on the molecular density of the film.

were measured on a cast film and five-layered X-type LB films deposited at 6 and 18 mN m⁻¹. The results are shown in Figure 7A. The absorption band at 2300−2400 cm⁻¹ was due to CO_2 molecules in the atmosphere. For all the films, the absorption peaks around 3000 cm⁻¹ arose from the symmetric and antisymmetric stretching vibrations of methylene and methyl groups. The peak at 2180 cm⁻¹ was assigned to the CN stretching vibration. The appearance of these bands indicated that the transition moment of these absorptions had at least a
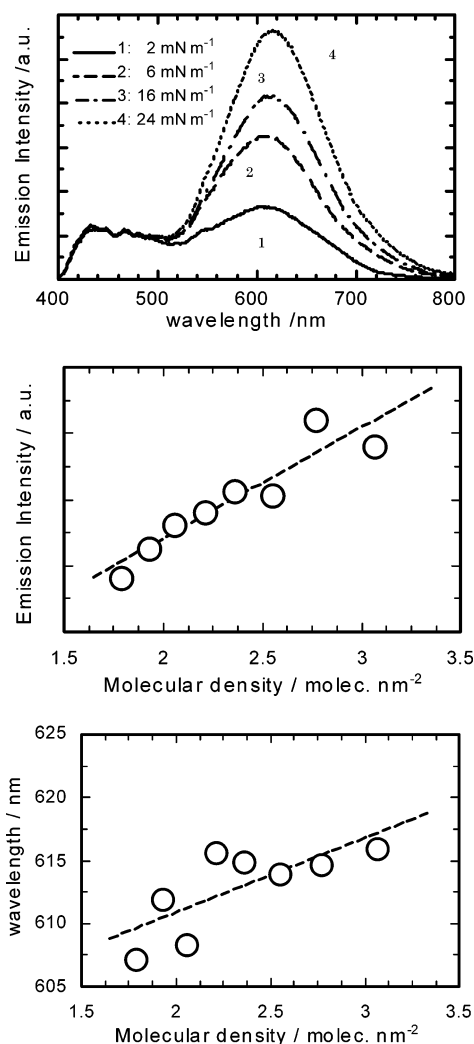

Figure 4. (A) Emission spectra of the films deposited at various surface pressures. Curves 1−4 are for the films deposited at 2, 6, 16, and 24 N m⁻¹, respectively. (B, middle) Dependence of the emission intensity at 600 nm on the molecular density. The films were prepared by depositing five layers of an X-type monolayer. (C, bottom) Dependence of the peak position of the emission on the molecular density. The films were prepared by depositing five layers of an X-type monolayer.

component perpendicular to the substrate surface as shown in Figure 7B (right).

AFM Observation of the Deposited Films of [Pt(CN)₂L]. A floating film of the complex was deposited onto a hydrophilic silicon wafer as a Z-type film. Figure 8 shows a 5 μm × 5 μm image of the film deposited at 2 mN m⁻¹. The surface was not uniform, but it consisted of grainlike aggregates of nearly the same size (10 nm × 100 nm). Its height was estimated to be 1.5 ± 0.4 nm from the bare surface of the silicon wafer. When the deposition pressure increased to 8 mN m⁻¹, no remarkable change of the size or shape of an aggregate was noted except for the decrease of the empty spaces. Thus, the grainlike aggregates might form simultaneously even at low deposition pressure, and an increase of the deposition pressure resulted in an increase of the surface density of such aggregates.

Discussion

The measurement of the π−A curve confirmed the reversible formation of a monolayer of the present complex, [Pt(CN)₂L], at an air−water interface. The surface pressure began to increase steeply from 0 at a molecular area of 0.61 nm² molecule⁻¹. On
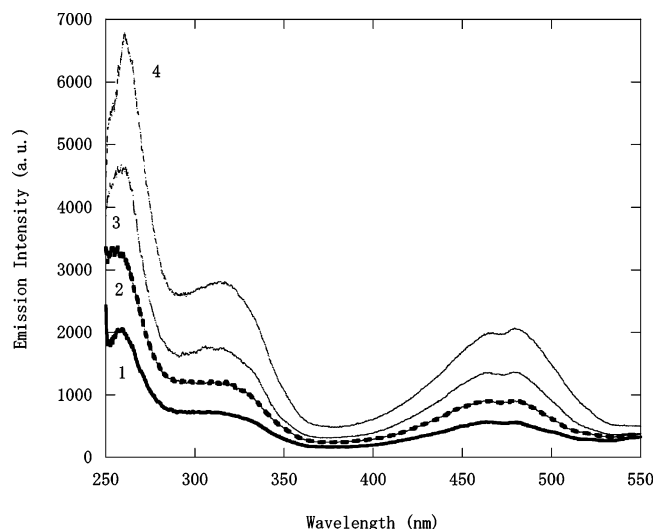
Figure 5. Excitation spectra of the films deposited at various surface pressures. Curves 1−4 are for the films deposited at 2, 6, 16, and 24 N m^{-1}, respectively. The emission was monitored at 600 nm. The films were prepared by depositing five layers of an X-type monolayer.
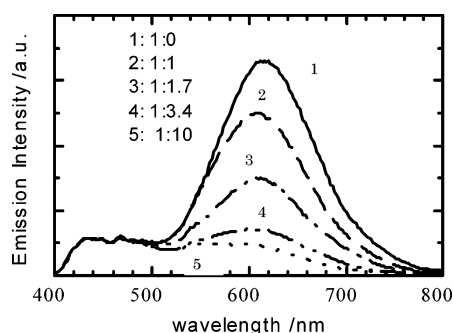

Figure 6. Emission spectra of a mixed film of [Pt(CN)$_2$L] and palmitic acid. Curves 1−5 are for the films at mixing ratios of 1:0 (metal complex only), 1:1, 1:1.7, 1:3.4, and 1:10, respectively. The films were prepared by depositing two layers of an X-type monolayer at 15 N m^{-1}.

compression of the surface, the monolayer showed a molecular area of 0.2 nm^2 molecule^{-1} at 30 mN m^{-1}. Since the molecular area of a Pt(II)−bipyridine moiety is estimated to be 0.60 nm^2, the complex was thought to orient its bpy ligand vertical to the water surface at this molecular area.

The monolayer was deposited as an X-type film onto a hydrophobic glass. The absorption spectra showed a broad band at 480 nm. Such a band is absent in the spectrum of the same complex in a dilute chloroform solution. Comparing the present results with the previous works on Pt(II)−polypyridyl complexes in a solution, the broad peak is considered to be evidence for the formation of an aggregate of Pt(II) complexes in which the platinum complexes are stacked with overlaying bipyridine moieties.[12−14] Neighboring molecules can interact through the d-orbital interaction of Pt(II) metal ions. The absorption at 480 nm was assigned to the ^{1}MMLCT transition from dσ^* to π^*. The transition energy and probability depend on the degree of Pt(II)−Pt(II) interaction. This was consistent with the observation that the intensity of the band increased with an increase of the molecular density of the film (Figure 3C).

The emission spectra (Figure 4A) consisted of two components or a vibronic peak around 450 nm and a broad single peak around 600 nm. The peak around 450 nm was assigned to the $^3(\pi−\pi^*)$ band of a bpy ligand, while the peak at 600 nm was assigned to the emission from the ^{3}MMLCT state of an aggregate.[7] The excitation spectra (Figure 5) are identical with
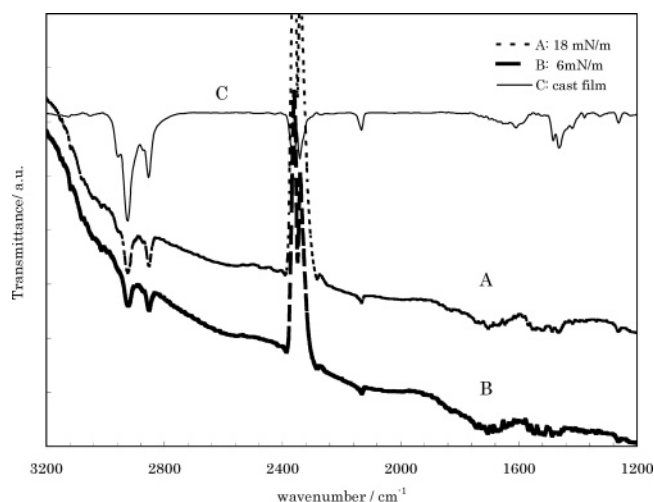

Figure 7. (A, top) Infrared reflection−absorption spectra of the five-layered X-type films deposited at 18 (A) and 6 mN m^{-1} (B) and a cast film (C). (B, bottom) Models of orientation of molecules adsorbed onto a solid substrate.
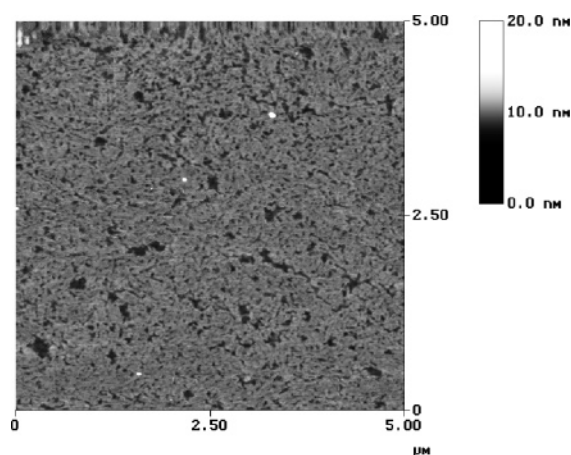

Figure 8. A 5 μm × 5 μm AFM image of the monolayer film deposited onto a silicon wafer at 2 mN m^{-1}.

the absorption spectra (Figure 3A). Thus, it was a species with an absorption band at 450 nm that was responsible for the emission at 600 nm. The species was assigned to an aggregate formed through Pt(II)−Pt(II) interaction, since an isolated molecule in solution did not give an absorption band at 450 nm (Figure 3B).[8,9,13] As exhibited in Figure 4C, the peak position around 600 nm showed a tendency to shift, depending on the deposition surface pressure or the molecular density of the film. The results are consistent with the view that the peak of the ^{3}MMLCT band is sensitive to the Pt−Pt distance.[11,13] In other words, the emission peak corresponding to the ^{3}MMLCT emission was red-shifted since the molecules were stacked more closely at higher surface density.

As shown in Figure 6, the intensity of the peak at 600 nm decreased with the addition of palmitic acid molecules in the film. The result was consistent with the view that the Pt−Pt interaction took place in the same layer and that the possibility of such an interaction was reduced by dilution with palmitic

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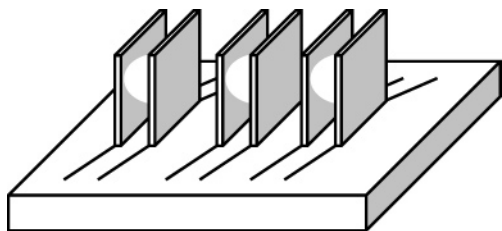

Figure 9. A model of an aggregate in a deposited film.

acid molecules. The previous structural studies have confirmed that the proximity of two neighboring Pt atoms is a requisite for the formation of an aggregate.[7,15]

The AFM observation showed that the deposited film of this complex consisted of grainlike aggregates (Figure 8). Such aggregates were thought to be formed spontaneously even at low surface pressure (<2 mN m^{-1}). The height of the aggregates was nearly equal to that of the complex when it oriented a Pt(II) plane vertically. It is suspected that, inside the aggregates, the planes of the bpy ligands face each other, orienting perpendicularly to the substrate surface. Figure 9 shows such a stacking model. By raising the deposition pressure, the surface density of the aggregates increased to result in the closer stacking of bpy ligands in an aggregate. This reflects the change of the emission peak as shown in Figure 4C. In these ways, the intermolecular interaction is tuned. The results of the reflection−absorption infrared spectra suggested that the CN ligands oriented perpendicularly to the surface (Figure 7). This is also consistent with the model postulated above.

In this work, the Pt−Pt interaction among the Pt(II) complexes has been initially evidenced by the appearance of a new peak at 450 nm in the deposited states. So far no such peak has been reported for crystalline and solution states even when the emission assigned to $d\sigma^*(Pt) \rightarrow \pi^*(bpy)$ transition is observed.[11−13] The present finding may be utilized to develop a molecular film system that achieves efficient conversion of light energy to chemical energy for decomposition of water molecules. We are now making an attempt by hybridizing the present Pt(II) film with a molecular film of photosensitive polypyridyl−Ru(II) complexes.

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