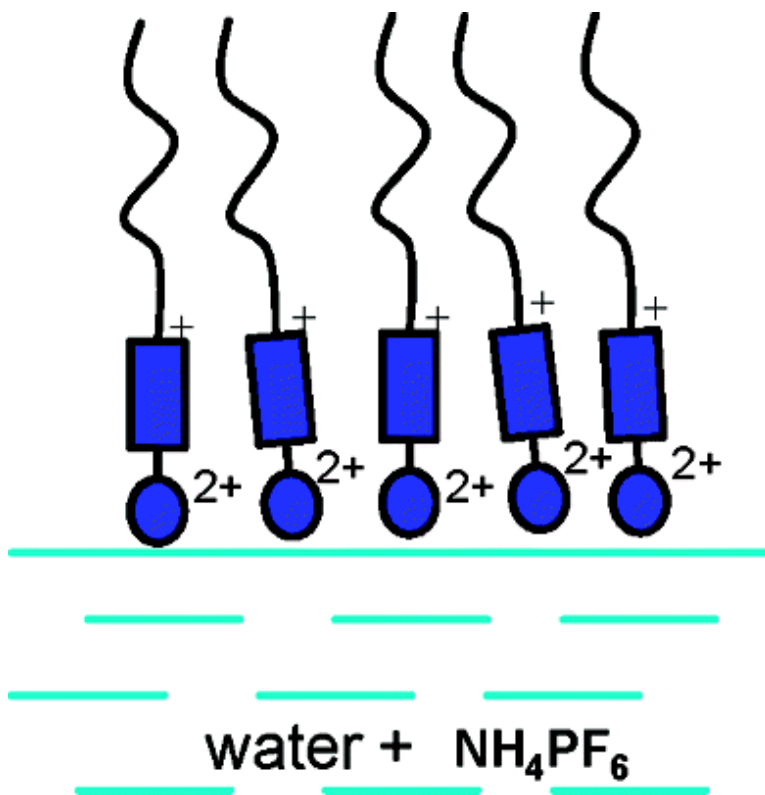Article

Langmuir–Schäfer Films of an Amphiphilic Ruthenium Complex Bearing an "Almost Naked" Multicharged Headgroup

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Langmuir–Schäfer Films of an Amphiphilic Ruthenium Complex Bearing an "Almost Naked" Multicharged Headgroup

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In this paper the preparation and characterization of Langmuir–Schäfer (LS) films of a novel amphiphilic dipolar complex, [Ru^{II}(NH$_3$)$_5$(*N*-dodecyl-4,4′-bpy)](PF$_6$)$_3$ (**1**), are reported. Preparation of these films, otherwise precluded utilizing standard Langmuir procedures, is achieved by using a subphase at relatively high ionic strength, by addition of NH$_4$PF$_6$. The morphology and the spectroscopic features of the floating films are investigated by Brewster angle microscopy and UV–vis reflection spectroscopy at the water–air interface, respectively, whereas LS films are characterized by absorption spectroscopy and atomic force microscopy. The overall results indicate the existence of aggregates of **1** and formation of homogeneous, densely packed layers. The presented approach could represent a general method to achieve Langmuir–Blodgett films of amphiphilic metal complexes having an "almost naked" multicharged headgroup.

Introduction

The Langmuir–Blodgett (LB) technique represents a powerful tool to tailor and prepare molecular assemblies of defined structures.[1] Various classes of molecular materials have been applied as LB films, ranging from simple organic molecules to complex functional systems such as porphyrins, phthalocyanines, calixarenes, etc.[2,3]

Metal complexes are suitable to molecular materials, by virtue of electronic properties associated with the metal center.[4] For instance, dipolar ruthenium(II) ammine complexes of 4,4′-bipyridinium (bpy) ligands possess unique characteristics as functional redox switches.[4,5] Actually, the reversible chemical, electrochemical,[6] or photochemical[7] oxidation of these complexes is accompanied by a dramatic change of their linear and nonlinear optical properties. Moreover, we have recently prepared self-assembled monolayers of these Ru$^{III/II}$ complexes on ultrathin, optically transparent platinum films and demonstrated their reversible redox switching.[8]

In this paper we report on the preparation and characterization of films of a novel amphiphilic complex, [Ru^{II}(NH$_3$)$_5$-(*N*-dodecyl-4,4′-bpy)](PF$_6$)$_3$ (**1**) (Chart 1), deposited through a modification of the LB technique, the horizontal lifting or Langmuir–Schäfer (LS) method. This represents one of the few examples of LB films of dipolar complexes having an

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† Università di Catania.
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Chart 1
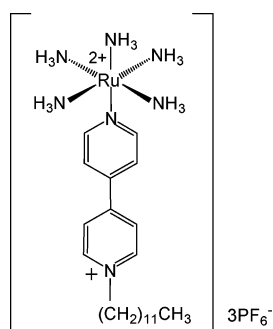
"almost naked" multicharged headgroup. Actually, almost all LB films involving amphiphilic charged complexes are related to species in which the metal cation is generally coordinated with bulky aromatic ligands, i.e. 2,2′-bipyridine, 1,10-phenanthroline, etc., which, shielding the positive charge of the cation, allow the attainment of LB films by standard procedures.[9−11]

In our case, LS films of the amphiphilic ruthenium(II) complex **1** were achieved by a novel, simple approach involving a subphase at relatively high ionic strength. The morphological and spectroscopic features of the floating films were investigated at the water−air interface by Brewster angle microscopy (BAM) and UV−vis reflection spectroscopy, respectively. LS films were characterized by absorption spectroscopy and atomic force microscopy (AFM).

Experimental Section

Materials and Procedures. [Ru^{III}(NH$_3$)$_5$Cl]Cl$_2$ (Strem Chemicals), 1-iodododecane (Aldrich), 4,4′-bipyridine (Aldrich), and NH$_4$PF$_6$ (Aldrich) were used as received. All other reagents were obtained commercially and used as supplied. All solvents used (Carlo Erba) in the isolation and preparation of products were HPLC and analytical grade, respectively.

Physical Measurements. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were recorded on a Varian INOVA 500 spectrometer, with TMS as internal standard. UV−vis spectra were recorded with a Beckman DU 650 spectrophotometer, and λ_{max} values are considered accurate to ±1 nm. ESI MS were recorded on an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 kV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N$_2$ (10 L/min); carrier solvent, methanol (0.4

mL/min). AFM measurements were carried out in air by use of a Dimention 3100S-1 (Digital Instruments) on LS films deposited on hydrophobized Si(100) substrates.

Synthesis of [*N*-Dodecyl-4,4′-bpy]I (1a). A solution of 4,4′-bipyridine (3.00 g, 19.2 mmol) and 1-iodododecane (19 mL, 77.0 mmol) in chloroform (100 mL) was stirred at room temperature for 4 days. The solution was then evaporated under vacuum to dryness. Purification by column chromatography (silica gel, 9:1 dichloromethane/methanol, R_f = 0.45) followed by recrystallization from ethanol gave analytically pure product **1a** as yellow solid (6.05 g, 70%). Anal. Calcd (%) for C$_{22}$H$_{33}$IN$_2$ (452.42): C, 58.41; H, 7.35; N, 6.19. Found: C, 58.22; H, 7.15; N, 5.98; ESI MS *m/z*: 325 ([M − I$^-$]$^+$, 100%); ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.23 (d, *J* = 7.0 Hz, 2H, bpy), 8.86 (d, *J* = 5.5 Hz, 2H, bpy), 8.63 (d, *J* = 7.0 Hz, 2H, bpy), 8.04 (d, *J* = 5.5 Hz, 2H, bpy), 4.62 (t, *J* = 7.5 Hz, 2H, bpy-C*H*$_2$-), 1.94 (2H, m, 2H, bpy-CH$_2$-C*H*$_2$-), 1.22 (br s, 18H, bpy-CH$_2$-CH$_2$-(C*H*$_2$)$_9$-CH$_3$), 0.83 (t, *J* = 7.0 Hz, 3H, CH$_3$).

Synthesis of [Ru^{II}(NH$_3$)$_5$(*N*-Dodecyl-4,4′-bpy)](PF$_6$)$_3$ (1). A sample of [Ru^{III}(NH$_3$)$_5$Cl]Cl$_2$ (0.40 g, 1.37 mmol) in 10 mL of water, slightly acidified with 4 drops of trifluoroacetic acid, was reduced over Zn−Hg amalgam (1.86 g of Zn, 140 mg of HgCl$_2$, 100 μL of 12 M HCl, and 2 mL of water) at room temperature, with continuous agitation via argon bubbling, until complete dissolution of the starting material with formation of pale yellow solution. After 20 min of reaction, the mixture was allowed to drop down, through the frit supporting the Zn−Hg amalgam, into a flask containing an argon-degassed solution of **1a** (0.62 g, 1.32 mmol) in 36 mL of water and 5 mL of methanol. The resulting deep indigo solution was stirred at 40 °C in the dark under Ar for 2 h. The addition of 5 mL of a saturated solution of NH$_4$PF$_6$ in water, afforded a deep blue precipitate, which was collected by filtration, dried in a vacuum, and purified by recrystallization from methanol/water (0.77 g, 60%). Anal. Calcd (%) for C$_{22}$H$_{48}$F$_{18}$N$_7$P$_3$Ru (946.63): C, 27.91; H, 5.11; N, 10.36. Found: C, 28.60; H, 5.18; N, 9.85. ESI MS *m/z*: 802 [M − PF$_6^-$]$^+$; ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.06 (d, *J* = 7.0 Hz, 2H, bpy), 8.90 (d, *J* = 6.5 Hz, 2H, bpy), 8.70 (d, *J* = 7.0 Hz, 2H, bpy), 7.78 (d, *J* = 6.5 Hz, 2H, bpy), 4.45 (t, *J* = 7.0, 2H, bpy-C*H*$_2$-), 3.46 (s, 3H, *trans*-NH$_3$), 2.39 (s, 12H, *cis*-NH$_3$), 1.94 (m, 2H, bpy-CH$_2$-C*H*$_2$-), 1.24 (br s, 18H, bpy-CH$_2$-CH$_2$-(C*H*$_2$)$_9$-CH$_3$), 0.84 (t, *J* = 7.0, 3H, CH$_3$).

Langmuir Experiments: (A) Film Preparation. Films of **1** on quartz slides (30 × 40 mm^2), previously hydrophobized by exposure for 24 h to a saturated atmosphere of 1,1,1,3,3,3-hexamethyldisilazane, were obtained by the Langmuir−Schäfer method (horizontal lifting) by a KSV 5000 System 3 Langmuir−Blodgett apparatus (subphase surface of 850 cm^2). Chloroform was used in making up the spreading solutions: 0.95 mg of **1** (1.0 × 10^{-3} mmol) was completely dissolved in 10 mL of chloroform. Ultrapure water (resistance larger than 18 MΩ cm^{-1}) from a Milli-Q/Elix3 Millipore system, containing 1.0 mM NH$_4$PF$_6$, was used as the subphase. Under these conditions, the solubility of **1** in the subphase is negligible. The subphase was thermostated at 293 K by a Haake GH-D8 apparatus. Aliquots (200−400 μL) of the spreading solutions were spread onto the subphase. After solvent evaporation, the floating film was compressed at a speed of 5 Å^2 molecule^{-1} min^{-1}.

(B) Reflection Spectroscopy and Brewster Angle Microscopy. Reflection spectroscopy and Brewster angle microscopic analysis were carried out on a NIMA 601BAM apparatus, at a compression speed of 5 Å^2 molecule^{-1} min^{-1}. The reflection data (ΔR) were obtained by an NFT RefSpec instrument. They were acquired under

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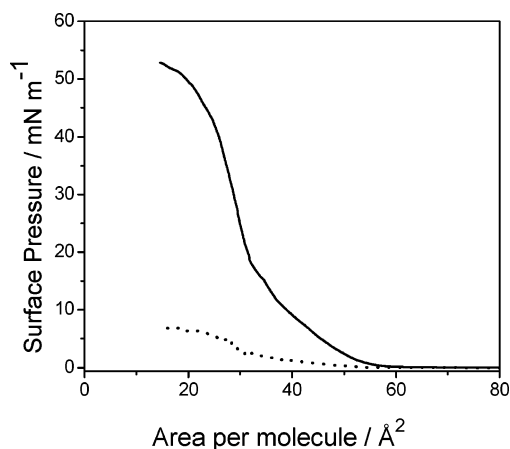
Figure 1. Surface pressure−area (Π−A) curve of **1** at 293 K (solid line). The dotted line shows the behavior observed with pure water as subphase.

normal incidence of radiation according to the description given in ref 12 and correspond to the difference between the reflectivities of the floating film/liquid interface and the clean air/liquid interface. All reflection spectra were obtained at 293 K. BAM measurements were carried out on an NFT BAM2*plus* system with a lateral resolution of 2 μm.

Results and Discussion

Complex **1** (Chart 1) was synthesized by a two-step approach based on the preparation of [*N*-dodecyl-4,4′-bpy]I, followed by chloride substitution in the [Ru^{III}(NH$_3$)$_5$Cl]$^{2+}$ salt, yielding **1**. Purity and composition of **1** were confirmed by ^{1}H NMR spectroscopy, ESI-MS, and elemental analysis.

The saltlike nature of the polar headgroup in **1** poses some problems in preparing LS films. Despite the presence of a C$_{12}$ chain and two aromatic rings, the hydrophile−lipophile balance does not satisfy the requirements for a completely amphiphilic substance. In fact, the compression of the floating film involves only a slight increase of the pressure, up to a constant, trifling value of ca. 5−6 mN/m, which is not modified by changing either the concentration of the spreading solution or the spread volume (Figure 1). This finding can be related to the presence of three "almost naked" positive charges in the polar headgroup of **1**, which may induce a partial transfer of the complex in the water subphase, even at low surface pressure. Consistent with this picture, compression leads to a further transfer of **1** in the water subphase (Scheme 1a), giving rise to an insignificant Langmuir curve behavior. This characteristic performance is consistent with a sort of "phase transition" of the complex, from the air−water interface to the bulk of the subphase, promoted by surface pressure increasing values exhibiting, under our experimental conditions, a "threshold" value of about 5 mN m^{-1}.

To circumvent this drawback, we used a subphase at relatively high ionic strength by addition of NH$_4$PF$_6$. Under these conditions, a typical surface pressure−area (Π−A) Langmuir curve is obtained (Figure 1). These results suggest a complete inhibition of the transfer process as a consequence of the insolubility of **1** in the subphase (Scheme 1b).
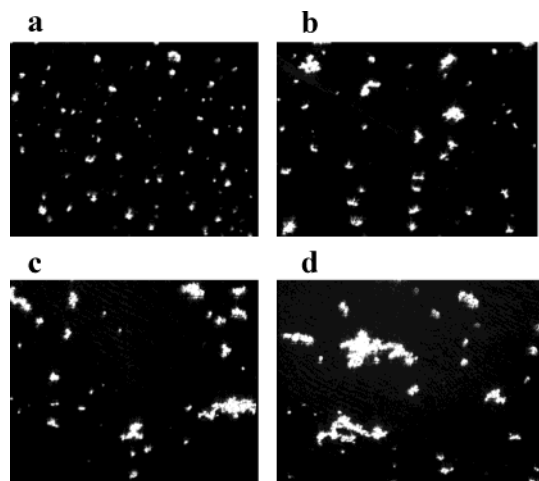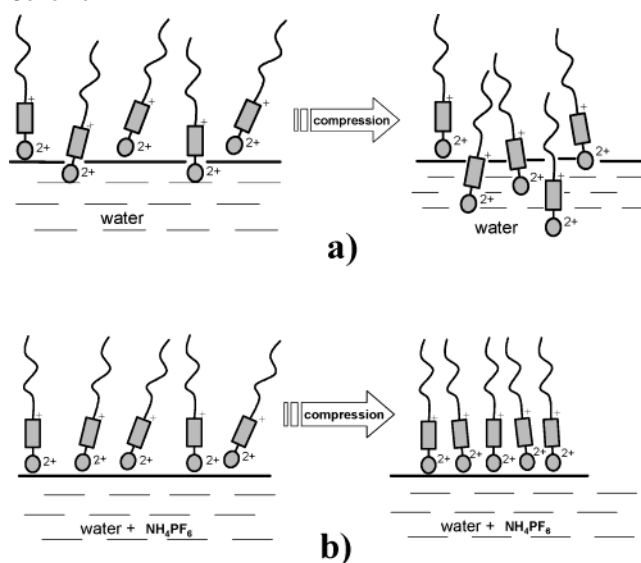
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Figure 2. Brewster angle microscopic images of the floating layer of **1** at different surface pressures: (a) Π = 0 mN m^{-1}; (b) Π = 5 mN m^{-1}; (c) Π = 20 mN m^{-1}; (d) Π = 50 mN m^{-1}. The field of view along the *x*-axis is 430 μm.

Scheme 1

The Langmuir curve (Figure 1) shows a sort of gaseous phase (Π < 1 mN m^{-1}) for areas per molecule larger than 55 Å^2, although BAM investigations (vide infra) indicate the coexistence of condensed 3D aggregates and uncovered water surface, even for such low surface pressure values. A steep and rigid region for surface pressure larger than 10 mN m^{-1} is exhibited in the Langmuir curve. The limiting area per molecule, $A_{\Pi \to 0}$, as obtained by extrapolation of the steepest portion of the curve to 0 mN m^{-1} pressure, is 35 Å^2. However, formation of 3D aggregates, as evidenced by the BAM analysis (vide infra), precludes any consideration related to the molecular orientation on the subphase based on the limiting area per molecule.

BAM images were recorded during the compression of the floating layers, representative examples of which are displayed in Figure 2.

They provide evidence for the presence of aggregates on the water surface, even at low surface pressure. In fact, the simultaneous coexistence of aggregate islands and clean water surface is observed starting from 0 mN m^{-1} (Figure

Figure 3. UV−Vis reflection spectra of **1** at the air−water interface at different surface pressures.
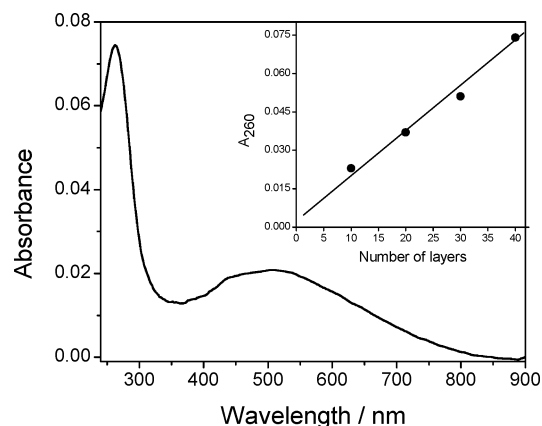

Figure 4. Absorption spectrum of a typical LS film of **1** (40 layers) on quartz. The inset shows the plot of absorbance at 260 nm as a function of deposited layers of **1**.

2a). It is possible to distinguish bright regions of **1** aggregates and dark region of pure water surface. During the compression, aggregate islands coalesce into broader and larger domains that, however, do not generate a continuous and homogeneous floating film (Figure 2b−d). Eventually, such 3D structures can even be about 100 µm long along the direction of the compression. The presence of such aggregates floating on the water surface is further confirmed by AFM analysis (vide infra).

The floating layers at the air−water interface were also investigated by reflection spectroscopy. In particular, the reflection of light under normal incidence at a water surface covered with a floating film of **1** was studied. This method is well-suited to investigate the chromophore behavior on the water surface because only chromophores at the interface contribute to the enhanced reflection.[13] The difference in reflectivity (ΔR) from the floating layer of **1** on the subphase and reflectivity from the bare subphase was monitored as a function of the wavelength. The corresponding reflection spectra from **1** on the water surface at different fixed surface pressures after reaching equilibrium are shown in Figure 3.

A quasimonotonic reflection enhancement upon compression, as a result of the average surface density growth, accompanied by an essentially unchanged profile is observed. This finding suggests an unchanged nature of aggregates even at high surface pressure.

Films of **1** were prepared by the Langmuir−Schäfer method (horizontal lifting). In this approach, hydrophobized quartz slide substrates were lowered horizontally until their contacted the floating film on the water surface. Following this procedure, a different number of runs were accomplished on the substrate at the surface pressure of 15 mN m^{-1}. The UV/vis absorption spectrum of a LS film of **1** obtained after 40 runs is reported in Figure 4. It shows the typical optical absorption band centered at ca. 510 nm, associated with the low-energy [d_π(Ru^{II}) → π*(bpy)] MLCT transition. This absorption maximum is slightly (ca. 20 nm) blue-shifted in
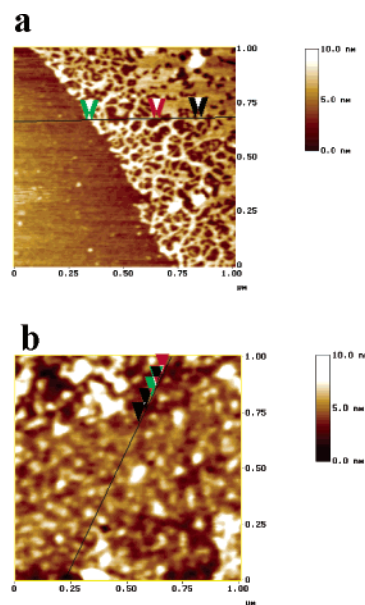
Figure 5. Two-dimensional tapping-mode AFM images of films obtained after one (a) and five (b) deposition runs of **1** on silicon substrates. The marked lines indicate where the section analysis was performed.

comparison with that observed for self-assembled monolayers of an analogous *N*-alkyl-derivatized Ru^{II}(NH$_3$)$_5$(4,4′-bpy) complex.[8b] This can be related to the aggregate nature of **1** in the LS films vs noninteracting molecules generally involved in self-assembled monolayers.[14] The good linear relation of the absorbance against the number of deposited layers (see inset in Figure 4) indicates the uniformity and reproducibility of the transfer process.

AFM measurements were performed on films of **1** on silicon substrates, obtained after one and five deposition runs. After the first horizontal lifting, AFM analysis indicates the presence of both uncovered substrate surface and transferred material. Figure 5a displays a detail of the film−substrate edge. The film exhibits areas of large interconnected aggregates (hundreds of nanometers in lateral size, 5 nm height) that are edged by a network of nanowires, 15−30 nm in diameter and 2−5 nm in height. The measured root-mean-square (RMS) roughness of the films area is ca. 1.8 nm.

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The film obtained after five deposition runs (Figure 5b) exhibits an improved flatness as compared with the previous one. In particular, it is characterized by homogeneous and densely packed aggregates having lateral dimensions and height ranging between 50 and 70 nm and 0.8 and 1.1 nm, respectively, and RMS roughness of 0.8 nm.

Conclusion

In this work we have obtained homogeneous, densely packed LS films of a novel amphiphilic Ru(II) complex. Preparation of these films, otherwise precluded utilizing standard Langmuir procedures, has been achieved by using a subphase at relatively high ionic strength. This simple approach could represent a general method to achieve Langmuir−Blodgett films of amphiphilic metal complexes with "almost naked" multicharged headgroups.

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