# Self-Assembled Mono- and Multilayers on Gold from 1,4-Diisocyanobenzene and Ruthenium Phthalocyanine

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Self-assembled monolayers of 1,4-diisocyanobenzene on gold were used to bind ruthenium phthalocyanines to the surface by axial ligation of the macrocycle with isocyanide groups pointing out from the SAM. The 1,4-diisocyanobenzene SAM and the RuPc-1,4-diisocyanobenzene bilayer were characterized by ellipsometry, IRRAS, XPS, and SPM. The grafting of RuPc to the SAM is stable. The thickness of the film increases from 10 to 15 Å upon RuPc ligation. IRRAS reveals that both ends of the 1,4-diisocyanobenzene are affected by the N=C to metal interaction occurring at the other end. XPS indicates that each RuPc macrocycle covers  $\sim$ 12 1,4-diisocyanobenzene molecules in the bilayer.

#### Introduction

The possibility of building up designed organic surfaces by self-assembling adequate molecules on various solid substrates has been receiving continuous interest in the past decade<sup>1-3</sup> because such modified surfaces hold much promise in the development of interfaces suitable for use in chemical and biological sensors,<sup>4–8</sup> corrosion prevention,<sup>9</sup> friction control,<sup>10</sup> soiling control,<sup>11</sup> soft lithography,<sup>12,13</sup> and molecular electronics and nanotechnology.<sup>14</sup>

Besides the numerous studies devoted to self-assembled monolayer formation on silica, gold, silver, germanium, platinum, copper, nickel, mica, and silicon, extensive efforts have been dedicated to the formation of multilayers by sequential self-assembly. Multilayers are particularly desirable in optical applications of designed organic surfaces, such as optical waveguides, nonlinear optical elements,<sup>15</sup> display devices, and also in electrochemical devices.<sup>16–18</sup>

The easiest way to build up organic multilayers is the Langmuir–Blodgett (LB) technique,<sup>19</sup> in which a monolayer formed at the air–water interface is sequentially transferred onto a solid substrate. Within LB films, each monolayer is linked to the adjacent one via weak forces, either hydrophobic interactions between aliphatic chains or dipolar interactions between head-groups such as acids, amines, alcohols, etc. This results in a high sensitivity of the lamellar assembly to organic solvents and temperature.

More stable multilayers can be obtained by enhancing the attractive interactions between adjacent monolayers within the lamellar assembly, which is achieved when electrostatic,<sup>20,21</sup> coordination,<sup>22,23</sup> or covalent bonds<sup>24,25</sup> are formed between neighboring layers. The former method is mostly limited to polyelectrolytes since a high density of surface charges is required to promote the adhesion between oppositely charged monolayers. The latter technique generally requires protection—deprotection steps, as in Merrifield's solid phase peptide synthesis. On the contrary, coordination between organic ligands and metal ions is a highly versatile method for building up multilayers by self-assembly: coordination bonds can be strong enough to promote the sequential formation of lamellar systems from solutions and do not require any protection—deprotection steps.

The present paper focuses on the anchoring of a soluble ruthenium phthalocyanine (RuPc) on a gold surface via apical complexation by isocyanide groups present at the surface of a SAM. The primer SAM is formed by 1,4-diisocyanobenzene adsorbed on gold, thus leaving in principle free isocyanide groups on the outer surface of the resulting SAM to coordinate the ruthenium ion. SAM formation with isocyanides has been poorly studied when compared to SAM formation with thiols or disulfides. Following early studies on nickel<sup>26,27</sup> and platinum surfaces,<sup>28</sup> several recent papers were devoted to gold surfaces.<sup>14,29–35</sup> The present study gives a detailed description of a SAM built from 1,4-diisocyanobenzene and its ability to bind ruthenium phthalocyanine.

## **Experimental Section**

General. Proton NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AC200 instrument. Transmission infrared spectra were recorded on a Perkin-Elmer 1725X FTIR spectrometer. Polarization-Modulation Infrared Reflection-Absorption spectroscopy (PM-IRRAS) was performed on a Nicolet Magna 860 FTIR spectrometer, equipped with a step-scan data collector, a photoelastic modulator, a lock-in amplifier, and an MCT detector.<sup>36,37</sup> Ellipsometry measurements were obtained on a SOPRA ES4G spectroscopic ellipsometer. XPS spectra were recorded on a Vacuum Generator ESCALAB 210, using an Al Kα source monochromatized at 1486.6 eV. The radiations were generated at 20 mA under 15 kV, in a system set under UHV at  $10^{-10}$  mbar (1.33  $\times$  10<sup>-8</sup> Pa). We used a hemispheric analyzer working at a pass energy of 50 eV for the global spectrum, and 20 eV when focusing on the sole core levels. All spectra herein, unless noticed, were recorded at a takeoff angle of 90° with respect to the sample plane. The resolution of the apparatus

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was around 0.5 eV. STM imaging was performed at ambient temperature on a custom-made apparatus kindly donated by IBM Zürich Research Laboratory (Rüschlikon, Switzerland). Typical imaging conditions were 150–400 mV bias tip position and 10 pA current set point. Pt/Ir cut tips were used. The AFM apparatus was a Nanoscope IIIa (Digital Instruments), equipped with a scanner capable of scanning a region of  $16.8 \times 16.8$  $\mu$ m. Experiments were done in air at room temperature. The images were recorded in tapping mode using a 125  $\mu$ m long silicon cantilever (rectangular shape, 23 mN/m < k< 65 mN/ m, Nanoprobe GMBH).

**Materials.** Gold (99.99%) was obtained from Engelhard-Clal (Paris, France). Chromium (99.996%) was obtained from Johnson-Matthey (Paris, France). Silicon wafers were purchased from ACM (Villiers, France). Chloroform used for SAM formation was distilled under nitrogen and degassed with nitrogen bubbling.

**Substrates.** Gold films (100 nm thick) were thermally evaporated on glass slides that had been primed with chromium (2 to 4 nm) to promote gold adhesion. STM experiments were done on flat gold [111] surfaces on mica prepared by evaporation of 1000 Å of gold on a mica substrate heated at 350 °C.

**Bis-benzonitrile Phthalocyaninatoruthenium(II), RuPc**-( $\phi$ CN)<sub>2</sub>. RuPc( $\phi$ CN)<sub>2</sub> was synthesized as already described<sup>38</sup> by refluxing bis-ammine phthalocyaninatoruthenium(II) RuPc-(NH<sub>3</sub>)<sub>2</sub> under a nitrogen atmosphere and in the dark for 24 h in pure benzonitrile, then for 1 h in a 3/2 mixture of benzonitrile and chloroform. The complex was precipitated in the dark by addition of methanol, then rinsed with ethanol and dried. The product was isolated in a 60% yield. UV-vis (chloroform)  $\lambda_{max}$ -(log $\epsilon$ ) 643 nm (5.03), 311 nm (5.04). IR (KBr) 3050 cm<sup>-1</sup> (weak,  $\nu_{C-H}$ ), 2237 (weak,  $\nu_{C=N}$ ), 1607–1446 (weak,  $\nu_{C=C}$  and  $\nu_{C=N}$ ), 1122 (strong,  $\beta_{C-H}$ ), 754–735 (strong,  $\gamma_{C-H}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 9.30 (dd, 3 Hz, 8H), 7.90 (dd, 3 Hz, 8H), 6.83 (t, 7.6 Hz, 2H), 6.5 (dd, 7.6 Hz, 4H).

**1,4-Diisocyanobenzene.** 1,4-diisocyanobenzene (dib) was prepared as already described,<sup>32</sup> except that it was purified by chromatography on silica (elution dichloromethane) before use.

**Bis(1,4-diisocyanobenzene)** Phthalocyaninatoruthenium-(**II**), **RuPc(dib)**<sub>2</sub>. *RuPc(\phiCN)*<sub>2</sub> was dispersed in degassed acetonitrile. A 15-fold excess of dib was added and the mixture was refluxed for 24 h. The mixture was filtered and the RuPc-(dib)<sub>2</sub> complex washed several times with acetonitrile. RuPc-(dib)<sub>2</sub> was isolated in a 73% yield. UV-vis (chloroform)  $\lambda_{max}$ (log  $\epsilon$ ) 643 nm (5.30), 583 nm (4.62), 307 nm (5.10). IR (KBr) 3057 cm<sup>-1</sup> (weak,  $\nu_{C-H}$ ), 2102 and 2093 (weak,  $\nu_{C=N}$ ), 1632– 1488 (weak,  $\nu_{C=C}$  and  $\nu_{C=N}$ ), 1119 (strong,  $\beta_{C-H}$ ), 754–730 (strong,  $\gamma_{C-H}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 9.31 (dd, 3 Hz, 8H), 8.01 (dd, 3 Hz, 8H), 6.83 (t, 7.6 Hz, 2H), 6.46 (dd, 6.8 Hz, 4H), 5.23 (d, 6.8 Hz, 4H). Those results are similar to the results already published.<sup>39</sup>

**Room Temperature Exchange between**  $\phi$ **CN and dib.** The lability of the benzonitrile axial ligand and its easy replacement for the stronger ligand dib at room temperature was checked. RuPc( $\phi$ CN)<sub>2</sub> was dissolved in chloroform, together with a large excess of dib. The exchange was followed by UV-vis spectroscopy. The Q-band at 643 nm became thinner and more intense upon the exchange: the final extinction coefficient was 2.02 × 10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup> (1.07 × 10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup> for the starting RuPc( $\phi$ CN)<sub>2</sub>), and the final width at mid-height was 20 nm (35 nm for the starting RuPc( $\phi$ CN)<sub>2</sub>). The exchange was complete after 24 h.

**Monolayer Formation.** The primer SAM was formed in a nitrogen-filled inert atmosphere and in the dark by immersing



**Figure 1.** PM-IRRAS spectrum recorded on a gold sample covered by a 1,4-diisocyanobenzene SAM (403 scans). An automatic baseline correction was applied to the crude PM-IRRAS spectrum within the chosen wave number range.

gold substrates which have just been cleaned by UV-ozone treatment in a freshly filtered 15 mmol  $L^{-1}$  THF solution of the aryldiisocyanide. The solution was stirred during the experiment, which lasted 1 h. Then the substrate was rinsed with acetone, dried and immediately studied by PM-IRRAS. The resulting sample will be called [Au-dib] in the following text.

**RuPc Deposition.** The gold substrates covered with the 1,4diisocyanobenzene SAM were immersed for 35 min in a 1.5 mmol L<sup>-1</sup> solution of RuPc( $\phi$ CN)<sub>2</sub> in chloroform at 20 °C.<sup>40</sup> The substrates were then rinsed three times with pure chloroform and dried under nitrogen. The resulting sample will be called the [Au-dib-RuPc] bilayer in the following text.

# **Results and Discussion**

Formation of a SAM with Aryldiisocyanides on Gold. The theoretical and experimental thicknesses (obtained by ellipsometry) of the [Au-dib] SAM are 9.9 and 10 Å, respectively. The theoretical thickness of the SAMs was calculated from simple space filling models of the aryldiisocyanides obtained with the Cambridge Scientific Chem3D software. The Au-C=N bond length was fixed at 1.9 Å according to experimental and theoretical results.<sup>14,41</sup> Our results are consistent with published results<sup>32</sup> and thus support the hypothesis that the molecules stand up on the gold surface, offering one free isocyanide group for subsequent chemical reactions.

Our PM-IRRAS results reveal some features which were not given by previous authors, as shown in Figure 1.

First, the  $\nu N \equiv C$  stretching bands for the bonded and free isocyanide groups were found at 2176 and 2122 cm<sup>-1</sup>, respectively. These figures are consistent with the values given by Robertson<sup>29</sup> and Henderson<sup>32</sup> on similar 4,4'-arylene diisocyanide molecules. We observed a very slight shift from 2180 to 2176 cm<sup>-1</sup> when the sample was immersed several times in the 1,4-diisocyanobenzene solution. A similar shift toward lower frequencies has already been described by Ontko and attributed to the completion of the monolayer beyond the 70% surface coverage limit.<sup>33</sup> According to Ontko's results, we consider that monolayers exhibiting  $\nu N \equiv C$  stretching bands at those frequencies (2176 and 2122 cm<sup>-1</sup>) are close packed.

Second, an additional peak at 2272 cm<sup>-1</sup> was observed (see Figure 1) when the sample was immersed in very diluted solutions of 1,4-diisocyanobenzene for short times (typically 15 min in  $10^{-4}$  mol L<sup>-1</sup> solutions). The peak at 2272 cm<sup>-1</sup> was not changed by rinsing with acetone, but disappeared almost

completely when the same sample was immersed for 80 min in a  $10^{-3}$  mol L<sup>-1</sup> solution of the same 1,4-diisocyanobenzene solution. This transient peak may arise either (i) from some nitrile impurities within the isonitrile solution, (ii) from a low-coverage configuration in which the molecule lies parallel to the gold surface, or (iii) from some peculiar aggregated form of the 1,4-diisocyanobenzene.

As regards the former explanation, the hypothesis of nitrile impurities present in the initial compound can be ruled out, since no significant nitrile stretching band was observed in the infrared spectrum of dib in the solid state. Although one cannot strictly exclude the possibility of an isocyanide  $\rightarrow$  nitrile isomerization taking place on the surface upon deposition, this mechanism is known to have an activation energy significantly higher than what thermal agitation can afford, and we feel it is not prevailing in our case.

The second hypothesis, which implies that the isocyanide groups interact with the gold surface in a  $\eta^2$  state is most likely to occur in dilute solutions. Such a  $\eta^2$  configuration has already been observed for acetone<sup>42</sup> and acetonitrile<sup>43</sup> on Pt(111). But the  $\eta^2$  configuration was not evidenced for methylisocyanide on Pt(111), Ni(111), and Rh(111)<sup>28</sup> and was never observed for isocyanides on gold. The only observed configuration for isocyanide bond perpendicular to the gold surface. The  $\eta^2$ -configuration is thus very unlikely in our case. Moreover, the  $\eta^2$  configuration is IRRAS-silent, since the C=N dipole is parallel to the gold surface.<sup>44</sup> The peak at 2272 cm<sup>-1</sup> observed in our PM-IRRAS spectrum cannot be accounted for by a configuration in which the benzene ring lies parallel to the gold surface.

The third hypothesis is based on former calculations on intermolecular interactions in liquid acetonitrile: significant shifts in the stretching frequencies of nitriles have already been attributed to antiparallel dimer arrangements of acetonitrile molecules.45-47 It has been shown, in particular, that these pairing effects stem from both the high magnitude of the local dipole moments of the CN groups (>4D) and the intrinsic polarizabilities of these groups interacting with their counterpart. As isocyanide groups have similar electronic properties, similar phenomena may take place between 1,4-diisocyanobenzene molecules already linked to the gold surface and 1,4-diisocyanobenzene molecules coming from the solution. Preliminary calculations carried out at the semiempirical level reveal that, as observed in the case of acetonitrile, the antiparallel dimer configuration leads to an hypsochromic shift of the stretching frequency of the triple bond.<sup>48</sup> Upon completion of the 1,4diisocyanobenzene SAM, the formation of antiparallel dimers between 1,4-diisocyanobenzene molecules already linked to the gold surface and 1,4-diisocyanobenzene molecules coming from the solution becomes sterically impossible, which results in the vanishing of the peak at 2272 cm<sup>-1</sup> at high coverage.

Third, the intensity of the  $\nu N \equiv C$  stretching bands was slightly decreased upon ultrasonic treatment of the samples for 2 min in chloroform. This modification can be attributed to removal of weakly bonded 1,4-diisocyanobenzene molecules located in high roughness areas of the gold surface.

Except for this observation, the spectrum remained almost unchanged upon ultrasonic treatment of the samples in chloroform.

Figure 2 exhibits the  $N_{1s}$  region of the XPS spectrum recorded on a high coverage sample of the [Au-dib] SAM. The decomposition of the spectrum clearly indicates the presence of two types of nitrogen atoms on the gold surface, namely one



**Figure 2.** XPS spectra of a [Au-dib] SAM (solid line). Only the  $N_{1s}$  region of the spectrum is given. The decomposition of the spectrum exhibits the isonitrile peak (dashed line) and the imine peak (dotted line).

at about 400.0 eV, and the other one at about 398.5 eV. When the sample was tilted at grazing incidence, the intensity of the latter peak increased with respect to that of the former one (Figure 1 in Supporting Information). This result indicates that the atoms responsible for the peak centered at 400.0 eV are located closer to the gold surface than the atoms responsible for the peak centered at 398.5 eV. This result allows us to rule out the obvious interpretation of the XPS spectrum that would assign the 400.0 eV peak to the free isocyanide group and the 398.5 eV peak to the bonded isocyanide group. Our proposal is rather that the peak at 398.5 eV arises from polyimine impurities stacked on top of the 1,4-diisocyanobenzene monolayer. This assumption relies on three arguments: (i) the 1,4diisocyanobenzene molecule is quite unstable and prone to chemical degradation. A green colored material spontaneously develops within the 1,4-diisocyanobenzene powder, even in the dark. This colored impurity is separated by chromatography but forms again on storage. The spontaneous formation of similar polyimine moieties in the chloroform solution used for the formation of 1,4-diisocyanobenzene SAMs is likely. (ii) According to our decomposition, the peak at 398.5 eV accounts for less than 20% of the whole N<sub>1s</sub> signal. This low value might account for nitrogen atoms bound to the gold surface and buried deeply inside the monolayer, but our grazing incidence XPS experiments rule out this hypothesis. Thus, the peak at 398.5 eV arises from a distinct moiety. (iii) The UPS spectrum of the same monolayer (see Figure 2 in Supporting Information) exhibits a large and featureless peak centered at 7 eV, which is characteristic of the presence of nitrogen lone pairs, such as with imine functions in polyimine structures.49 Preliminary quantum chemistry based calculations have been carried out at the restricted Hartree-Fock level using a 6-31G\*\* basis set on geometry-optimized structures<sup>50</sup> on both the isocyanide and a dimeric model of the presumed polyimine polymer. They reveal that the energy of the isocyanide is expected to give a peak at a binding energy 0.8 to 1.0 eV lower than that of the dimeric polyimine. Note that this shift is of the same order of magnitude as the one observed between nitriles and imines (0.8 eV experimental, 0.5 to 1.5 eV theoretical).<sup>50</sup> This shift is clearly higher than the resolution of the UPS experiment and suggests that the isocyanide is unlikely to contribute to a peak most plausibly attributable to the polyimine.

Thus, if we assume that the peak centered at 398.5 eV arises from imine impurities stacked on top of the monolayer, the large peak centered at 400.0 eV accounts for the two nitrogen atoms of the 1,4-diisocyanobenzene molecule. Contrary to the PM-IRRAS measurements, it was impossible to discriminate the two nitrogen atoms, although one is linked to the gold surface and the other belongs to a free isocyanide group. The peak is quite large (WMH  $\sim$ 2 eV) and probably stems from several components, but our proposal is that the two nitrogen atoms of the isocyanide groups are unresolved, essentially because of the large conjugated  $\pi$  system connecting them.

The [Au-dib] SAM was studied by AFM and STM. Inspection of the AFM images recorded on the [Au-dib] SAM (see Supporting Information, Figure 3) confirm that the whole surface is covered. The roughness (rms) of the layer, measured on a gold terrace, is 6.5 Å, and a texture made of flattened grains of average diameter in the range 5-20 nm was observed. This texture is confirmed by the STM inspection (see Supporting Information, Figures 5a and 5b). It should be noted that STM investigation of these layers was difficult at least at ambient conditions: no molecular resolution could be obtained, and most of the time the images were noisy, likely because the layer is hydrophilic. At some relatively rare places, the layer appeared to follow the substrate more closely with holes that resembles those commonly observed on alkanethiol layers (the height of the holes is exactly equal, but for small experimental uncertainties, to the height of a gold [111] step, Figure 5b, Supporting Information). Without molecular resolution, it was not possible to ascertain the presence of 1,4-diisocyanobenzene molecules in the holes. A conservative conclusion arising from the SPM and ellipsometry investigation of the 1,4-diisocyanobenzene SAM is that it is homogeneous on a large scale and of maximum height corresponding to two 1,4-diisocyanobenzene monolayers.

**Grafting a Ruthenium Phthalocyanine Monolayer via Axial Ligation.** As already described,<sup>22,51</sup> ruthenium macrocycles can be chemically linked to monolayers by a ligand exchange reaction: the outer ligand of the self-assembled monolayer replacing the weaker ligand bonded to the ruthenium ion in solution. We applied the same strategy on ruthenium phthalocyanine with benzonitrile as sacrificial axial ligand. Benzonitrile was chosen because (i) it makes the macrocycle soluble in organic solvents without any need for chemical modification on the periphery of the macrocycle, and (ii) it is easily replaced by pyridine-based ligands or isocyanides in the axial positions of the complex.

Thus, a gold sample covered by a monolayer of 1,4diisocyanobenzene prepared as described above was immersed for 35 min in a 1.5 mmol L<sup>-1</sup> solution of RuPc( $\phi$ CN)<sub>2</sub> in chloroform at 20 °C. After several rinsing steps with chloroform, the sample was dried in a nitrogen flow and stored under a nitrogen atmosphere.

Figure 3 gives the imaginary part of the measured and fitted polarizabilities of the [Au-dib-RuPc] bilayer, measured using the ellipsometer as a spectrophotometer.<sup>52</sup> The Q-band typical of the phthalocyanine ring can be observed at 640 nm. This absorption is resistant to thorough rinsing of the sample and thus does not concern nonspecifically deposited RuPc molecules. This result indicates that some RuPc has actually been chemically grafted on the [Au-dib] SAM.

Ellipsometry performed on the same sample gives an overall thickness of 15 Å for the [Au-dib-RuPc] bilayer, which is consistent with the claimed geometry. The onset from the pristine [Au-dib] SAM is around 5 Å, which is a reasonable figure for a flat-lying Pc macrocycle bearing an extra axial ligand (the second benzonitrile, which has not been replaced<sup>53</sup>) on its outer surface. As the benzonitrile molecule is regularly scattered on the surface and does not form a uniform and close-packed layer, it cannot be fully taken into account in the



**Figure 3.** Imaginary part of the measured and fitted polarizabilities of a [Au-dib-RuPc] bilayer using the ellipsometer as a reflection spectrophotometer.<sup>52</sup> The solid line is the experimental curve, the dotted line the fitting curve.



**Figure 4.** PM-IRRAS spectrum recorded on a [Au-dib-RuPc] bilayer (500 scans). The spectrum in Figure 1 is also given in dotted line for comparison. An automatic baseline correction was applied to the crude PM-IRRAS spectra within the chosen wave number range.

measured thickness. The benzonitrile molecules are thus taking part in the experimental roughness.<sup>54</sup>

Figure 4 gives the PM-IRRAS spectrum recorded on the [Audib-RuPc] bilayer. Significant changes in the spectrum are related to the chemical grafting of RuPc to the monolayer: first, the free isocyanide stretching band at 2122 cm<sup>-1</sup> significantly decreased; second the Au-bonded isocyanide stretching band at 2175 cm<sup>-1</sup> decreased; third, an additional peak appeared at 2155 cm<sup>-1</sup>; fourth, a large shoulder grew around 2100 cm<sup>-1</sup>.

The isocyanide stretching band at  $2122 \text{ cm}^{-1}$  was attributed to the "free" isocyanide group pointing out from the surface. Upon axial complexation of RuPc by some of those free isocyanide groups, the stretching vibration of the isocyanide bond is expected to shift, as already observed with numerous organometallic complexes.<sup>55–63</sup>

Indeed, the effect of metal complexation on the stretching frequency of the isocyanide bond has already been well documented. The balance between  $\sigma$ -accepting and  $\pi$ -donating abilities of the metallic ions mainly accounts for the location of the  $\nu N \equiv C$  stretching band: hypsochromic shifts from the pure 1,4-diisocyanobenzene spectrum have been reported when the  $\sigma$ -accepting character of the metallic ion is dominating the N $\equiv$ C to metal bonding, as in gold(I) complexes,<sup>60</sup> but bathochromic shifts are more often observed since N $\equiv$ C to metal bonding is generally dominated by the  $\pi$ -back-bonding from the metallic ion to the isocyanide group, as in Rh(I), W(0), W(II) or Ru(II) complexes.<sup>39,56,57,63,64</sup> In the particular case of ruthenium phthalocyanines, a 35 to 40 cm<sup>-1</sup> bathochromic shift has

been reported upon axial complexation with 1,4-diisocyanobenzene, indicating that  $\pi$ -back-bonding from the ruthenium ion to the isocyanide group is strong.<sup>39</sup>

The adsorption of isocyanides on metal surfaces has also been studied and, as for organometallic complexes, the isocyanide stretching band is strongly affected by the  $\sigma-\pi$  balance in its bonding with the metal surface. For example, methylisocyanide was found to adsorb very strongly to Ni(111), via a chemisorption state involving more than a single nickel atom. The  $\nu$ N=C stretching band was observed around 1700 cm<sup>-1</sup>, indicating an imine-like structure ( $\eta^2$  configuration).<sup>27</sup> Similar results were obtained on Pt(111) at high coverage, but the  $\nu$ N=C stretching band at 2265–2240 cm<sup>-1</sup> was also observed on that surface by HREELS at low coverage, indicating a terminal-bonded configuration.<sup>28</sup> In the same way, on-top adsorption of cyanide formed by high-temperature dissociation of acetonitrile on Pt(111) exhibits a  $\nu$ N=C stretching band at 2073 cm<sup>-1</sup>, 30 cm<sup>-1</sup> higher than the parent molecule.

Isocyanides clearly prefer to adsorb on platinum rather than on gold when offered both surfaces at the same time,<sup>65</sup> but are able to form stable monolayers on gold powder or gold films.<sup>32–35</sup> The adsorption site is generally assumed to be of on-top type and results in a  $\nu N \equiv C$  stretching band dominated by the  $\sigma$ -attracting character of the metal surface. IR adsorption values of 2190 cm<sup>-1</sup> (for aryl isocyanides which adsorb around 2130 cm<sup>-1</sup> in the bulk solid state) to 2220 cm<sup>-1</sup> (for alkyl isocyanides which adsorb around 2150 cm<sup>-1</sup> in the bulk solid state) were reported. It is thus clear that the isocyanide-to-gold bonding results in a hypsochromic shift of the  $\nu N \equiv C$  stretching frequency.

Our case is quite unusual because the bis(isocyanide) molecule is chemically bound to *two different* metal centers, the gold surface on one end and the ruthenium ion complexed by a phthalocyanine on the other end of the molecule. As indicated above, opposite effects are expected to be experienced by the  $\nu N \equiv C$  stretching frequency upon bonding to these metallic sites since the gold surface induces hypsochromic shifts whereas the RuPc gives bathochromic shifts to the  $\nu N \equiv C$  stretching band.

Very few examples of conjugated bis(isocyanide) molecules bound to two different metal centers can be found in the literature, all involving tungsten complexes.57,61,64 The two latter references are devoted to 1,4-diisocyanobenzene-W(0) polymers, which are partially oxidized with iodine. The resulting mixed valence polymers exhibit both  $\nu N \equiv C$  stretching bands arising from the tungsten(0) and the tungsten(II) complexes. It is, however, impossible from that study to extract any unambiguous information on pure mixed valence W(0)-4,4'-phenyldiisocyanide-W(II) moieties since the iodine oxidation may be heterogeneously distributed over the treated sample, leading to domains containing only symmetrical bimetallic arrangements. Bennett's work<sup>64</sup> is more instructive since well-defined mixed valence bridged complexes of the W(0)-dib-W(II) type were synthesized and compared to symmetrical analogues W(0)dib-W(0) and W(II)-dib-W(II). The results clearly indicate that the ligand  $\pi$  system of the 1,4-diisocyanobenzene molecule transfers any modification at one isocyanide end to the other end. For example, the  $\nu N \equiv C$  stretching frequency of the isocyanide end ligated to a W(II) complex shifts from 2083 to 2092 cm<sup>-1</sup> when the other isocyanide end of the molecule is changed from the same W(II) complex to a W(0) complex. In the same way, the  $\nu N \equiv C$  stretching frequency of the isocyanide end ligated to a W(0) complex shifts from 2132 to 2141  $cm^{-1}$ when the other isocyanide end of the molecule goes from the same W(0) complex to a W(II) complex. Similar "information transfer" through the benzene ring was also observed by Kubiak<sup>66</sup> who studied the electrochemical reduction of trinuclear nickel clusters capped by isocyanide molecules. When the aryl isocyanide ligand bears a nitrile group as ancillary substituent, the reduction of the trinuclear nickel cluster can be followed by the infrared behavior of the nitrile group: the reduction of the trinuclear nickel cluster in a significant increase in the electron density on the phenyl ring, experienced by the nitrile ancillary group.

After the axial ligation of RuPc by the free isocyanide group pointing out from the [Au-dib] SAM, we observed a global bathochromic shift of the isocyanide infrared signature, consistent with the bonding of the external isocyanide end of the molecule with a ruthenium phthalocyanine. We believe that the large shoulder appearing around 2100 cm<sup>-1</sup> arises from the isocyanide bound to RuPc. Although weak and large, the peak is consistent with published values on similar complexes.<sup>39</sup> Additionally, the peak of the former "free" isocyanide group centered at 2122 cm<sup>-1</sup> significantly decreased. It did not completely disappeared since all of the 1,4-diisocyanobenzene molecules of the SAM are not involved in a chemical bond with RuPc. An estimation of the stoichiometry of the bilayer from XPS experiments will be given later in this paper.

A second peak grows in our IRRAS spectrum, centered at 2155 cm<sup>-1</sup>. We assume that this peak comes from the isocyanide groups bound to the gold surface within the 1,4-diisocyanobenzene molecules that are bound both to the gold surface and to RuPc. As shown above, the whole molecule experiences any interaction occurring on any of its two isocyanide ends; hence, the  $\nu C \equiv N$  bond of the isocyanide group linked to the gold surface experienced a slight weakening measured by the 20 cm<sup>-1</sup> shift in the PM-IRRAS spectrum upon ligation of RuPc on the other end of the conjugated ligand. Moreover, the peak arising from the pristine gold-1,4-diisocyanobenzene bond at 2175 cm<sup>-1</sup> decreased but did not disappeared completely, as explained above for the peak at 2122 cm<sup>-1</sup>. Finally, two sets of peaks are visible in the PM-IRRAS spectrum (Figure 4, solid line): [2122, 2175 cm<sup>-1</sup>] for the "free" and bonded-to-gold isocyanide groups of the 1,4-diisocyanobenzene molecules not linked to RuPc, and [2100, 2155 cm<sup>-1</sup>] for the bonded to RuPc and bonded-to-gold isocyanide groups of the 1,4-diisocyanobenzene molecules *linked* to RuPc.<sup>67</sup>

The XPS spectrum of the [Au-dib-RuPc] bilayer is given in Figure 5. Figure 5a compares the  $N_{1s}$  signal of the pristine [Au-dib] SAM to that stemming from the [Au-dib-RuPc] bilayer. An additional XPS signal appears as a shoulder at lower binding energy than the pristine signal. It is clear from Figure 5a that the [Au-dib-RuPc] bilayer is significantly richer in imino-type nitrogens than the pristine [Au-dib] SAM. Figure 5b, and c gives the XPS  $N_{1s}$  and  $Ru_{3d}$  signals from the [Au-dib-RuPc] bilayer, together with the corresponding fitting curves. It was possible to get information on the quality and the stoichiometry of the bilayer from the XPS spectra.

First, the ratio between the low binding energy  $N_{1s}$  signal (centered at 398.6 eV) and the  $Ru_{3d}$  signal at 281 eV equals 8. As demetalation of the RuPc ring is very unlikely, even under the XPS experimental conditions, this result shows that all of the imino-type nitrogen atoms that are responsible for the low binding energy  $N_{1s}$  signal centered at 398.6 eV belong to Pc rings. It appears that the polyimine impurities observed on the XPS spectrum of the pristine [Au-dib] SAM were washed out during the formation of the [Au-dib-RuPc] bilayer. The very



**Figure 5.** XPS spectra of a pure gold film (dashed line), the [Au-dib] SAM (solid line), and the [Au-dib-RuPc] bilayer (dotted line) in the  $N_{1s}$  region (Figure 5a); XPS spectrum in the  $N_{1s}$  region of the [Au-dib-RuPc] bilayer, together with the fitting curves and the attribution of each peak (Figure 5b); XPS spectrum in the  $Ru_{3d}$  region of the [Au-dib-RuPc] bilayer, together with the fitting curve (Figure 5c).

high affinity of RuPc for the isocyanide group might explain this observation.

Second, by comparing (i) the high binding energy  $N_{1s}$  signal (centered at 399.9 eV, stemming from the isocyanide groups) and the low binding energy  $N_{1s}$  signal (centered at 398.6 eV, stemming from the phthalocyanine imino groups) or (ii) the high binding energy  $N_{1s}$  signal to the  $Ru_{3d}$  signal at 281 eV, it was possible to derive the dib/RuPc ratio. In both cases, the 1,4-diisocyanobenzene to RuPc ratio was found close to 12. Assuming an ideal geometry of the bilayer, i.e., a perfectly flat lying phthalocyanine ring (projected area 200 Å<sup>2</sup>) over a close packed SAM of 1,4-diisocyanobenzene molecules standing perpendicularly to the gold surface (projected area 18 Å<sup>2</sup> per isocyanide), the theoretical ratio would be 11. Our XPS results thus indicate that the phthalocyanine layer is almost close packed.

As for the [Au-dib] SAM, it was still very difficult to obtain good resolution AFM and STM images of the [Au-dib-RuPc] bilayer (see Supporting Information, Figures 4, 5c and 5d). However, a fine texture was found in these images which was absent in the images taken before adsorption of the RuPc phthalocyanines (compare Figure 5b and Figure 5d, Supporting Information). This fine texture is superimposed on the larger one already existing in the images of the [Au-dib] SAM. It is composed of objects of average diameter of ca. 2-2.5 nm, which we believe to be the individual phthalocyanines. The fine texture is found all over the image which indicates that the RuPc adlayer is dense. No order was found inside this adlayer.

We could not get confirmation from the SPM investigation of the [Au-dib-RuPc] bilayer, that the RuPc adlayer is actually a monolayer. However, we found no evidence against this possibility. We only noted some deposits of matter (5-10 nm high) scattered on the samples that we attribute to unbound RuPc resisting the mild rinsing performed on the samples prepared specially for the SPM experiments.

### Conclusion

We show that metal phthalocyanines can be grafted to a solid substrate by axial ligation using isonitriles as apical ligands. The thickness, compactness, and stoichiometry of the [Au-dib-RuPc] bilayer is fully consistent with the expected supramolecular assembly. However, from the SPM images, it is clear that the [Au-dib] SAM and the [Au-dib-RuPc] bilayer appear quite unordered at least on large scales. It is obviously a point to improve in the future implementation of this layer-by-layer assembling strategy.

Indeed, as isonitriles are very strong  $\pi$ -accepting ligands of the ruthenium ion, the other axial ligand bound on the other side of the planar macrocycle can be easily removed and replaced. It should thus be possible to follow this strategy to produce regular multilayers by a step-by-step grafting of metal phthalocyanines.

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**Supporting Information Available:** Five figures: Grazing incidence XPS and UPS spectra recorded on [Au-dib] SAM and AFM and STM images recorded on [Au-dib] and [Au-dib-RuPc]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(51) Li, D.; Moore, L. W.; Swanson, B. I. Langmuir 1994, 10, 1177. (52) Ellipsometry measures at each wavelength the complex ratio of the reflected field amplitudes along the polarization axes (which amounts to 2 real parameters). The spectra can then be conveniently analyzed by modelling the species with unknown refractive indices by a collection of oscillators defined by their frequency, line width, and amplitude. Better fits are usually obtained in solids with Gaussian shaped lines corresponding to a heterogeneous widening rather than damping. The refractive index is computed by "adding-up" the polarizabilities using the Lorentz-Lorenz formula:  $(n^2 + 1)/(n^2 + 2) =$  Sum (density\*alpha), with alpha the polarizability. A single oscillator in the far UV usually accounts for non absorbing media. The spectra can therefore be fitted with a minimum number of unknown parameters. We report in the figure the imaginary part of the measured and fitted polarizabilities of the layer. The real part of the polarizability (not shown) was fitted with the same set of parameters. The asymmetric peak observed in Figure 3 clearly indicates the relevance of two absorption lines.

(53) We have no direct evidence that the second benzonitrile ligand remains on the outer surface of the [Au-dib-RuPc] bilayer. No specific signal from the nitrile bond was observed either in the PM-IRRAS spectrum or in the N<sub>1s</sub> XPS spectrum. This lack of signal is not surprising since (i) the nitrile signature is often very weak in infrared spectra and (ii) our N1s XPS signal is quite broad. However, we performed a SIMS analysis on similar architectures built on glass with pyridine groups pointing out from the surface as anchoring axial ligands. The presence of the remaining benzonitrile ligand on the outer surface of the bilayer was clearly evidenced on the SIMS spectrum.

(54) The roughness arising from a perfectly ordered film exhibiting protruding benzonitrile ligands regularly scattered over a close packed RuPc monolayer can be estimated as 3 Å. This figure is lower than the expected roughness of our substrates.

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(67) All our attempts to synthesize the dissymmetrical RuPc complex bearing one benzonitrile molecule on one face and one 1,4-diisocyanobenzene molecule on the other apical position of the macrocycle were unsuccessful. Mixtures containing the symmetrical RuPc(dib)2 molecule and linear oligomers based on the same monomer were invariably obtained, which prevented us to measure the stretching frequency of isocyanide groups embedded in a dissymmetrical RuPc complex. In the symmetrical RuPc-(dib)<sub>2</sub> complex, the stretching vibration of the free isocyanide group appears at 2100 cm<sup>-1</sup>, and the stretching vibration of the isocyanide group bonded to the Ru ion is observed at 2090 cm<sup>-1</sup>. This result confirms that the coordination of the isocyanide group to RuPc results in a weakening of the isocyanide bond.