

Thin Films of a Dimeric Ruthenium Phthalocyanine Complex on Gold

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Abstract

Thin films of a new dimeric ruthenium phthalocyanine complex bearing thioester-functionalized axial ligands were formed on gold surfaces. Characterisation of the thin films by laser ablation-inductively coupled-mass spectrometry and scanning tunneling microscopy revealed that the films do not have any long-range order.

Keywords: Ruthenium / Phthalocyanine / Thin film / Gold

Ruthenium phthalocyanine (PcRu) complexes have been the focus of sustained interest since the first reported synthesis in 1963 [1]. However, only a handful of examples of dimeric PcRu complexes have been reported. The simplest PcRu dimer is that of pure ruthenium phthalocyanine, [(PcRu)₂] [2-6]. Other examples include a nitrido-bridged dimer, [(PcRu)₂N] [3], a μ -carbido dimer, [{PcRu}₂(μ -C)] [7, 8] and an oxo-bridged dimer, [{(NaSO₃)₄PcRuOH}₂O]·8H₂O [9] while a Ru=Ru double bond was identified in the dimeric species [(2,9,16,23-(*t*Bu)₄Pc}Ru(*iso*-quinoline))₂] [10]. In addition, thin films of PcRu complexes on surfaces have been generating increased interest [1, 11] with applications in areas such as photovoltaics [12-15] and sensors [16]. We have recently reported that ruthenium phthalocyanine complexes bearing axial ligands with thioacetate groups can form thin films on gold surfaces [17]. The peripheral and axial ligand substituents on the complexes had a significant effect on their surface coverage and ordering. For example, thin films of a PcRu complex bearing no peripheral substituents contained ordered regions but no ordering was apparent in films of a complex where the Pc ring was substituted with four peripheral tertiary butyl groups. In each case, however, the complexes contained only a single PcRu unit. Here we describe the synthesis and characterization of a new PcRu dimer with a thioacetate functional group that allows binding of the complex to gold surfaces.

<Scheme 1.>

The synthesis of the new dimeric complex, **2**, is shown in Scheme 1 (see Supporting Information for details of the synthesis and characterization). The first step involves the synthesis of the new axially unsymmetrical PcRu complex, **1**, that bears a pyridine ligand functionalized with a thioacetate group to enable binding to gold surfaces, and a pyrazine ligand to enable coordination to a second PcRu unit. Complex **1** was prepared by the axial ligand exchange reaction of [PcRu(PhCN)₂] [18] with the pyridine and pyrazine ligands. Both ligands were added at the same time and so the reaction resulted in a mixture of three complexes; the bis-*S*-(pyridin-4-ylmethyl)ethanethioate and bis-pyrazine complexes, as well as complex **1**. The individual complexes were subsequently separated using silica gel column chromatography. A ten-fold excess of the axial ligands was used to minimize the degree of polymerization that can occur when using pyrazine as an axial ligand, which may coordinate through

both nitrogen atoms and has been employed as a bridging ligand in ruthenium phthalocyanine oligomers [2, 19]. To prepare complex **2**, complex **1** was used as a ligand and the same axial ligand exchange reaction of [PcRu(PhCN)₂] was applied although the two incoming ligands were not used in large excess as neither has the ability to form polymers.

The ¹H NMR spectrum of **1** is typical of axially-substituted ruthenium phthalocyanine phthalocyanine complexes [1]. The macrocyclic protons appear as two AA'BB' patterns at δ 9.19 and 7.93. The pyrazine ligand causes a slight downfield shift in the macrocyclic resonances compared to examples of complexes with two pyridine axial ligands [20]. Protons on the axially coordinated ligands are shielded by the phthalocyanine diamagnetic ring current, with the degree of shielding increasing with proximity to the phthalocyanine ring. For example, resonances arising from the pyrazine protons occur at δ 6.14 and 2.27. The resonance at δ 6.14 is assigned to the protons further from the phthalocyanine ring while the upfield resonance at δ 2.27 is attributed to the pyrazine protons nearer to the macrocycle.

In the spectrum of **2**, the two sets of macrocyclic proton resonances appear as overlapping AA'BB' patterns that are shifted slightly upfield by ~0.3 ppm compared to those of **1** due to shielding by the neighbouring macrocycle. Interestingly, the protons of the bridging pyrazine, sandwiched between the two macrocycles, are shielded to very large extent and the signal appears at δ 0.4, which is a significant upfield shift when compared to ~δ 8.6 for the protons of uncoordinated pyrazine.

<Figure 1.>

The UV-vis spectra of complexes **1** and **2** are shown in Figure 1. The monomeric complex **1** has an electronic spectrum characteristic of ruthenium phthalocyanine complexes. It displays an intense Soret band with a maximum at 314 nm with an accompanying low-energy shoulder, and a Q-band with a maximum at 626 nm and an accompanying high-energy shoulder. Complex **1** also has a broad low intensity absorption band centred at 426 nm. Similar absorption bands have previously been observed in the electronic spectra of [PcRuL₂] complexes where L = (2-oxopropyl)pyridine-4-carboxylate [13] or pyrazine [21] and are attributed to metal-to-ligand charge-transfer (MLCT). The spectrum of the dimeric complex **2** is also dominated by the Q- and Soret bands and the molar absorptivities of these bands are

greatly increased relative to the monomeric complexes due to the two phthalocyanine rings per molecule. The MLCT band appears as a narrower, more intense band and is bathochromically shifted 2060 cm^{-1} compared to **1**.

<Figure 2.>

Thin films of **2** on gold were prepared by immersion of a gold substrate in a dichloromethane solution containing the complex and tetrabutylammonium hydroxide, the latter is included to hydrolyse the acetyl protecting groups. The films were then thoroughly rinsed with dichloromethane and dried under a stream of nitrogen gas. Laser ablation inductively coupled mass spectrometry analysis [17] of thin films of **2** indicate a uniform surface coating across macroscopic regions. Comparison of the data with reported data [17] indicate that **2** has about half the surface density of monolayers of [PcRu(4-*t*Bupy)(4-pyCH₂SAc)] [17]. Both **2** and [PcRu(4-*t*Bupy)(4-pyCH₂SAc)] contain unsubstituted phthalocyanine rings and may therefore be expected to form monolayers of similar density however the low surface density of **2** may be attributed to the dimer molecules forming disordered thin films, reducing the density with which the molecules may adhere to the gold surface. This was confirmed by scanning tunneling microscope (STM) experiments with thin films of **2** on gold (Figure 2), which reveal a lack of ordering of the dimer molecules. Figure 2A displays an STM image of a thin film of **2** on a gold(111) surface. Discreet objects are evident in the higher resolution image shown in Figure 2B however line profile analysis (see Supporting Information) indicates that these objects have diameters in the range 5 to 9 nm. A high resolution image (Figure 2C) reveals that these objects result from aggregation of more than one molecule and that even on this scale, no ordering is apparent.

In conclusion, a new complex containing two ruthenium phthalocyanine units has been prepared that forms thin films on gold via functionalized axial ligands. Thin films of the dimeric complex show no apparent surface ordering.

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Supporting Information Available. Synthesis and characterization data for **1** and **2**. Film formation and characterization data for thin films of **2** on gold.

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