Ruthenium Complexes Containing Fully Conjugated Ligands Terminated with Thiol Groups

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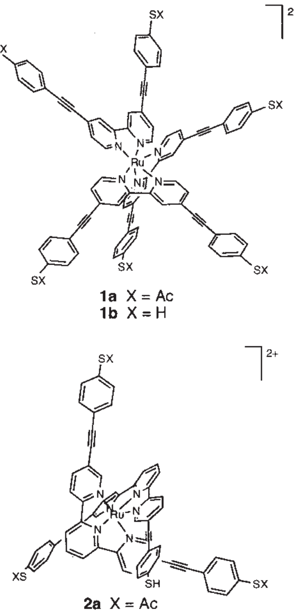
Bipyridine- and terpyridine-based ruthenium complexes containing fully conjugated ligands terminated with thiol groups were prepared and immobilized in self-assembled monolayers of alkanethiolates on gold surface, single molecules of which were observed with scanning tunnelling microscopy.

The advent and rapid development of the scanning probe microscopy (SPM) allow us to probe molecules at a molecular resolution. Small organic conjugated molecules are targets of intense studies by SPM in connection with potential applications in molecular electronics.[1,2] On the other hand, however, small metal complexes have rarely been subjected to measurements at the single molecule level,[3] despite the fact that metal complexes feature well-defined three-dimensional structures and often favourable physical—such as photo-, electro-, and magnetic—properties that are often exploited in solution-phase molecular "devices."[4] Here we report on the synthesis, properties, and preliminary scanning tunnelling microscopy (STM) observations of bipyridine- and terpyridine-based Ru complexes (**1**) and (**2**) designed to be suitable for single molecule characterization.

The ligands in **1** and **2** are fully conjugated and hence rigid. They can be viewed as molecular wires that have a connecting site to a metal ion in the middle. The substitution positions on the pyridine rings were determined such that the phenylethynyl groups stick out along, roughly, the *xyz*-coordinate axes for **1** and in the tetrahedral directions for **2**. These assumptions have been supported by molecular mechanics calculations optimizing the phenylethynyl parts with the $[Ru(bpy)_3]^{2+}$[6] and $[Ru(tpy)_2]^{2+}$[7] cores being locked to the crystallographically known structures (Chart 1). When **1b** or **2b** is placed on an atomically flat surface, it should "stand" on three phenylethynyl arms, leaving remaining arm(s) sticking out upward. Thus our idea was that coordination chemistry might provide a convenient means to construct molecular tripods that stand on their own.[8] The calculation suggests that the height of **1b** standing as such on a surface is about 19 Å.

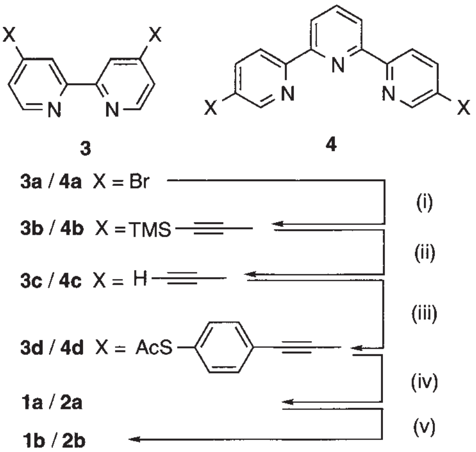
The ligands for these complexes were prepared through the repetitive use of Pd-catalyzed cross-coupling reactions (Scheme 1). Bromopolypyridines **3a**[9]/**4a**[10] were coupled with a TMS-protected acetylene to give **3b**[11]/**4b**. These compounds, after deprotection, were coupled with 4-(acetylthio)iodobenzene[12] to introduce acetyl-protected thiol functionalities to give **3d**/**4d**. The complex formation was facilitated by converting $RuCl_3$ into either $[Ru(DMSO)_4](PF_6)_2$[13] or $[Ru(CH_3COCH_3)_6](BF_4)_2$.[14] The acetyl protected complexes **1a** and **2a** were obtained as PF_6^- salt after purification with silica-gel column chromatography eluted with a mixture of CH_3CN and aqueous KNO_3, whose identity and purity were confirmed with TLC, spectroscopic measurements, and elemental analyses.[15]



1a X = Ac
1b X = H

2a X = Ac
2b X = H

Chart 1. Optimized structures of metal complexes **1** and **2**.



Scheme 1. Synthesis of complexes **1** and **2**. (i) TMSCCH, $(PPh_3)_2PdCl_2$, CuI, *i*-Pr_2NH, THF. (ii) KF or K_2CO_3, MeOH. (iii) 4-(acetylthio)iodobenzene, $(PPh_3)_2PdCl_2$, CuI, *i*-Pr_2EtN, THF. (iv) For **1**, $Ru(DMSO)_4Cl_2$, $AgPF_6$; for **2**, $Ru(CH_3COCH_3)_6(BF_4)_2$. (v) Au substrate, Et_2NH, DMF.

The complex **1a** exhibits a broad and large metal-to-ligand charge-transfer absorption band. In CH_3CN, the λ_{max} (485 nm) is red-shifted by as large as 35 nm from that of $[Ru(bpy)_3]^{2+}$ and the molar absorption coefficient ($4.4 \times 10^4\,M^{-1}\,cm^{-1}$) is threefold larger than that of the model complex ($1.4 \times 10^4\,M^{-1}\,cm^{-1}$), owing to the extended ligand π systems in **1a**.[16] The luminescence from **1a** is also red-shifted by ca. 30 nm compared with that from the model. The luminescence quantum yield is twice that of the model in air-saturated CH_3CN. Hence, the complex **1a** is a significant improvement from the standard $[Ru(bpy)_3]^{2+}$ as a photosensitiser. On the other hand, the visible absorption of **2a** shows a broadening without a significant red-shift compared from the model complex $[Ru(tpy)_2]^{2+}$. Cyclic voltammetry of **1a** in CH_3CN shows a redox couple at 0.99 V vs. Fc^+/Fc corresponding to Ru^{2+}/Ru^{3+}, which is more positive by 0.10 V than that of $[Ru(bpy)_3]^{2+}$. Similarly, the oxidation wave for Ru^{2+}/Ru^{3+} in **2a** appears at 1.00 V vs. Fc^+/Fc, which is more positive than the model $[Ru(tpy)_2]^{2+}$ by 0.11 V.

Immobilized samples of **1b/2b** on a Au surface were prepared by immersing a gold wire (Nilaco) into a millimolar solution of **1a/2a** in DMF with a drop of Et_2NH for 10–20 min, followed by washing with solvents and drying with a flow of N_2. Et_2NH removes the acetyl groups to bare the thiol moieties that anchor onto the gold surface. The immobilization was confirmed by alkaline desorption measurements in 0.5 M aqueous KOH. Upon sweeping the potential of the Au electrode treated with **1b/2b** as described above to a negative potential, a broad desorption peak was observed in the range of -0.9–-1.0 V vs. Ag/AgCl.[17] This potential is less negative than the case for a self-assembled monolayer (SAM) consisting of octanethiol, whose sharper peak was centered at -1.02 V vs. Ag/AgCl. These observations suggest that the attachment of **1b/2b** on Au surface is rather inhomogeneous and there is little organization that reinforces the assembly.

More defined samples for single-molecule observation were prepared by using an alkanethiolate monolayer matrix.[18] Exposure of a SAM of dodecanethiolate formed in advance on Au to a millimolar solution of **1a** in DMF in the presence of Et_2NH for 2 h resulted in the isolated complexes adsorbing at existing SAM defect sites.[19] A typical example of such complexes is shown in Figure 1. The $(\sqrt{3}\times\sqrt{3})R30^\circ$ crystalline domains of the host dodecanethiolates are clearly observed. The bright spot is apparently higher than the dodecanethiolate host by several angstroms as shown by the height profile in the figure. This value is comparable with the difference of the geometrical height of **1b** and the dodecanthiolate monolayer (14 Å). The width of the bright spot is 14 Å, which matches the calculated dimension of the complex **1b**, providing unequivocal evidence that the spot is a single molecule of **1b**.

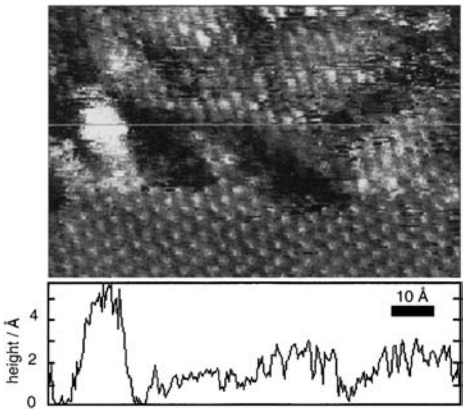


Figure 1. An STM image and its height profile of a single molecule of **1b** immobilized in a host SAM of dodecanethiolate on Au(111).

In summary, we successfully immobilized and observed single molecules of fully conjugated metal complexes on Au surface. Ru complexes are photo- and redox-active. Hence, some sort of switching phenomena may be envisaged in response to photon and/or electron input, which are being pursued in our laboratories with various techniques of SPM.[20]

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