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<th>Direct formation of a 2D redox-active adlayer based on a bisterpyridine derivative and Co$^2+$ on a Au(…</th>
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The direct assembly of single component 4′,4″′-(1,4-phenylene)bis(2,2‴:6′,2‴′-terpyridine) (PTPy) and Co2+ and PTPy mixed arrays was examined on a Au(111) surface by a simple immersion method. A redox active 2D adlayer consisting of a bisterpyridine derivative and cobalt ions was found to form directly on Au(111) from solution, suggesting that new nanostructures and/or adlayers with electrochemical activity can be precisely designed and controlled by selection of the metal ion and ligand.

Recently, metal–organic frameworks (MOFs) composed of metal ions and organic compounds have been extensively studied in the context of hydrogen storage, catalysis, and local magnetism applications because of their high porosity.1,2 From the viewpoint of surface science, two-dimensional (2D) MOFs with open-spaced adlayers have been extensively investigated on metal single crystal surfaces such as Au, Ag, and Cu under ultrahigh vacuum (UHV).3–8 The 2D structures of these MOFs have been characterized by scanning tunneling microscopy (STM). In contrast to UHV studies, there have been few investigations of 2D MOFs in solution.9–16 Surface MOFs are often used as host frameworks for small organic molecules, such as fullerene.3,4 On the other hand, coordination assemblies of metal ions with organic ligands, such as pyridine and carboxylic groups, are very attractive in the surface electrochemistry field12–22 because direct coordination assembly on a surface may enable the design of new nanostructures with characteristic electrocatalytic activities by controlling the redox potentials of the coordinated metal ions.15–19 PTPy is often used as a molecular building block for both metallosupramolecular assemblies and molecular wires in the field of coordination chemistry.17,18

Herein, we focus on the self-organization of 4′,4″′-(1,4-phenylene)bis(2,2‴:6′,2‴′-terpyridine) (PTPy) (see Scheme 1).

The direct assembly of Co2+ and PTPy mixed arrays was examined on a Au(111) surface by a simple immersion method, and the adlayer was characterized in 0.1 M HClO4 by cyclic voltammetry (CV) and electrochemical (EC-) STM. To understand the interaction between PTPy and Co2+, several different types of electrochemical characterization were carried out in 0.1 M HClO4.

Fig. 1a shows typical CV profiles of the single PTPy-modified and the PTPy and Co2+ coadsorbed Au(111) electrodes under an Ar atmosphere. No redox couples were observed in the same potential region when the modification was carried out in ethanolic solution without Co2+. In contrast, a characteristic redox couple was seen in the potential region between 0.80 and 1.10 V, suggestive of a redox reaction from Co(n) to Co(III) in the cobalt ions located between PTPy molecules. Indeed, the peak current is proportional to scan rate, as shown in the inset of Fig. 1a. Based on the peak area of the redox couple, the transferred electronic charge is estimated to be approximately 1.4 μC cm–2, corresponding to a surface excess of (1.5 ± 0.3) × 10–11 mol cm–2 assuming a one-electron transfer reaction. This result is consistent with a previous report on a Co2+ and terpyridine complex.19 Furthermore, electrochemical reduction of O2 on the PTPy and Co2+ coadsorbed Au(111) electrode was examined in 0.1 M HClO4 saturated with O2. Electrocatalytic activity for O2 was observed at 0.28 V vs. RHE, which agrees well with previously reported data on Co(ii) porphyrin adlayers, such as tetraphenyl porphyrin (CoTPP) and octaethyl porphyrin (CoOEP) on Au(111).23,24 The CV profile obtained for the PTPy and Co2+ coadsorbed Au(111) electrode shows a very similar O2 reduction occurring near 0.30 V vs. RHE, as shown in Fig. 1b. These results suggest that a complex adlayer...
The structure of PTPy is a square adlattice with dimensions of $3.16 \times 3.16 \text{ nm}^2$ that incorporates four PTPy molecules. The model structure for a highly-ordered array of PTPy is proposed in Fig. 2c. Taking the pyridine ring-inverted form into consideration, the alternating-row structure of the PTPy adlayer on Au(111) can be readily explained. As reported in previous papers, pyridine N and H atoms on nearest neighbor molecules can weakly interact with one another (the distance between pyridine N and H atoms is approximately 0.25 nm). Therefore, the proposed model depicted in Fig. 2c is a reasonable model for the 2D PTPy adlayer. Based on the adlattice of PTPy molecules, the surface excess of the PTPy adlayer formed on Au(111) is calculated to be $6.7 \times 10^{-11} \text{ mol cm}^{-2}$. Note that it is an incommensurate structure between PTPy array and Au(111) lattice because of the formation of hydrogen bonding between PTPy molecules. Therefore, it is difficult to propose a structural model for the underlying Au(111) lattice. The single component adlayer of PTPy was stable in the potential region between 0 and 1.00 V. By contrast, when the mixed system composed of PTPy and Co(ClO$_4$)$_2$ was examined at a Au(111) electrode surface in ethanolic solution, the STM image was completely different from the image of the sample prepared in the absence of Co$^{2+}$. Only disordered arrays of PTPy were found on the terrace, as shown in Fig. 2d. However, a careful inspection revealed that bright spots could be seen between PTPy molecules. A close-up view of the disordered adlayer of PTPy is shown in Fig. 2e. In this high-resolution STM image, individual bright spots were often found along the long axis of the PTPy molecules rather than the short axis. Based on the STM image shown in Fig. 2e, particularly the area of the image within the dotted circle, we propose in Fig. 2f that the adsorbed PTPy is mainly orientated as form 2 depicted in Scheme 1. Careful inspection of the adlayer revealed that each bright spot was located not at the central part of PTPy’s flanks, but at either right or left position of the flanks, indicating that the Co$^{2+}$ ion interacts weakly with the Py moiety in the PTPy molecule. The structural model of the Co$^{2+}$ and PTPy mixed array strongly supports the theory that the characteristic PTPy adlayer is formed through hydrogen bonding between nearest neighbor molecules. It should be noted that Co ions are stably trapped by the presence of PTPy molecules in such a strong acidic solution.

In addition, to confirm the insertion of cobalt ions in the mixed adlayer on Au(111), XPS measurements were carried out. Fig. 3 shows an XPS result in the region of Co 2p$_{3/2}$ spectra after the insertion of Co ions. Two peaks were clearly found at 782.1 eV in the Co spectrum by the immersion into Co$^{2+}$ and PTPy mixed ethanolic solution. Therefore, bright spots in the Co$^{2+}$ and PTPy mixed adlayer are assigned to be cobalt ions. The result is consistent with XP spectra of Co2p$_{3/2}$ for the insertion of Co ion onto a free-base porphyrin adlayer on Au(111), as reported by Bai et al.$^{27}$ Unfortunately, we could not see a clear difference in the coordination between Co ions and PTPy molecules in the N1s spectrum. However, based on the results from CVs shown in Fig. 1, it is surely the case that Py moieties in each PTPy molecule interact with Co ions and act as a complex. It is noteworthy that the insertion of cobalt ions was examined by the PTPy-modified...
Au(111) electrode in an ethanolic solution containing Co\(^{2+}\) for 1 min after the highly-ordered PTPy adlayer was formed on the Au(111) electrode. However, the change in the PTPy adlayer could not be observed in the CV profile and STM image, i.e., Co\(^{2+}\) ions could not be inserted in the highly-ordered PTPy adlayer on Au(111), indicating that the PTPy adlayer is stable due to the formation of hydrogen bonding between N and H atoms.

In conclusion, self-assemblies of PTPy molecules and a PTPy adlayer incorporated with Co\(^{2+}\) were clearly characterized at the molecular level. The coordination-like assembly between PTPy and Co\(^{2+}\) can be directly formed on a Au(111) surface by inverting the pyridine rings in PTPy. The PTPy adlayer formation with Co\(^{2+}\) can act as a 2D complex adlayer with redox properties and is created by a simple immersion method.

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Notes and references