## "Janus-type" Ruthenium Complex Bearing Both Phosphonic Acids and Pyrene Groups for Functionalization of ITO and HOPG Surfaces

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A novel Janus-type ruthenium complex bearing both phosphonic acid and pyrene groups was tethered to both ITO and HOPG surfaces in different tethering modes. On the ITO surface, the phosphonic groups were selectively attached to the ITO, resulting in the hydrophobic surface because of the exposed pyrene groups on the top. On the other hand, on the HOPG surface, pyrene groups interacted with the HOPG surface through noncovalent interaction, resulting in a hydrophilic surface exposing phosphonic acid groups. This selectivity makes it possible to fabricate redoxactive ruthenium complex and graphene composite by layer-bylayer growth of molecular units.

Surface functionalization plays an important role in realizing molecular electronics, catalysts, and photovoltaic technologies. In particular, surface chemistry of self-assembled monolayers has been widely studied with the aim of modulating interfacial properties such as wettability, adhesion, tribology, and biocompatibility.<sup>1,2</sup>

Self-assembly is the spontaneous formation of ordered structures on the basis of the spatial organization of their components, and an effective bottom-up approach for fabricating various functional materials by methods like sequential layer-bylayer growth.<sup>3,4</sup> By selecting a functional anchoring group such as a thiol group, it is possible to selectively immobilize a selfassembling monolayer (SAM) film on gold on an Au/SiO2 patterned electrode. Ruthenium complexes having a carboxylate or phosphonate group can be chemisorbed selectively on the surface of a TiO<sub>2</sub> or indium tin oxide (ITO) electrode, which have been widely studied for numerous applications in dye-sensitized solar cells (DSSCs).<sup>5,6</sup> Recently, nanocarbons such as graphene and carbon nanotubes have been paid much attention from the viewpoint of application as next-generation electrode materials.7-12 In fields such as catalysts and biosensors, therefore, it is becoming necessary to fabricate well-defined structures on nanocarbon. Since nanocarbon is composed of a  $\pi$ -extended system with a hydrophobic surface, a pyrene group is often used for modifying the carbon surface through noncovalent  $\pi$ - $\pi$  interaction.<sup>13</sup> The combination of pyrene groups with hydrophilic phosphonic acid groups in the same molecule forms an amphiphilic molecule, which can be utilized as a surface-tethering molecule. At the same time, phosphonic acid groups can act as a coordination site for the metal ions. It is therefore of great interest to design and synthesize a complex bearing both hydrophilic phosphonate groups and hydrophobic pyrene groups. By utilizing the surface selectivity of such a complex, layer-by-layer growth of a redox-active ruthenium complex together with graphene is feasible for building a multilayer film on highly ordered pyrolytic graphite (HOPG) or graphene.



Scheme 1. Synthetic route of ligand L1 and Ru-1 complex. (i) 1-(4-Bromobutyl)pyrene and  $K_2CO_3$  in DMF and (ii) [Ru(EtL)(CH<sub>3</sub>CN)-Cl<sub>2</sub>] in DMF:*t*-BuOH (1:1)/Me<sub>3</sub>SiBr in DMF and then in MeOH.

In the present study, the synthesis, stability, and electrochemical behaviors of a novel amphiphilic ruthenium complex 1 (Ru-1), as shown in Scheme 1, which consists of phosphonic acids as a hydrophilic group and pyrene as a hydrophobic group, were investigated.

To obtain the target Ru-1, 2,6-bis(*N*-methylbenzimidazol-2-yl)-4-{3,5-bis[4-(1-pyrenyl)butyloxy]phenyl}pyridine (L1) was synthesized by the reaction of the corresponding diol with 1-(4bromobutyl)pyrene. The L1 ligand was first reacted with [Ru(EtL)-(CH<sub>3</sub>CN)Cl<sub>2</sub>] to generate the complex [Ru(EtL)(L1)](PF<sub>6</sub>)<sub>2</sub>. The deprotection reaction of the ethyl group was then promoted by the addition of trimethylsilyl bromide, which produces the desired Ru-1. Similarly, symmetric [Ru(L1)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (Ru-2) was obtained by the reaction of RuCl<sub>3</sub>·3H<sub>2</sub>O with two molar equivalents of L1 in DMF– glycerol (1:1 v/v) (Figure 1). Both complexes were fully characterized by elemental analysis, <sup>1</sup>H NMR, and electrospray-ionization mass spectrometry (ESI-MS) (see Supporting Information).

The surface of an ITO electrode was immobilized by the immersion of the substrate into a pH-5 aqueous DMF mixed solution of Ru-1 (50  $\mu$ M) (see Supporting Information). Typical cyclic voltammograms of the Ru-1 on the ITO electrode is shown in Figure 2a. The Ru(II/III) peak was clearly observed at +0.47 V vs. Fc/Fc<sup>+</sup>, and linear dependence of the peak current on the scan rate suggested that the Ru-1 was immobilized on the ITO electrode. The temporal change of surface coverage  $\Gamma$  was monitored by cyclic voltammetry of the modified ITO electrode in CH<sub>3</sub>CN (0.1 M TBAPF<sub>6</sub>), and the result is shown in Figure 2b. The surface adsorption of Ru-1 followed the kinetic Langmuir equation:

$$\Gamma(t) = \Gamma(s)\{1 - \exp(-kCt)\}$$
(1)

where  $\Gamma(t)$ ,  $\Gamma(s)$ , k, C, and t are the surface coverage amounts, saturated surface coverage, rate constant, the concentration in the bulk solution, and time, respectively. The saturated surface



Figure 1. Structure of the complex, Ru-2.



**Figure 2.** (a) Typical cyclic voltammograms of Ru-1 on the ITO electrode in CH<sub>3</sub>CN (0.1 M TBAPF<sub>6</sub>) at various scan rates. (0.1, 0.2, 0.3, 0.4, and  $0.5 \text{ V s}^{-1}$ ). (b) Temporal change of surface coverage of Ru-1 in DMF on ITO electrode by use of the CV method. The simulated curve by eq 1 is shown in dotted line.

coverage of Ru-1 on the ITO surface was obtained as  $2.5 \times 10^{-11}$  mol cm<sup>-2</sup>. Similarly, a HOPG electrode was immersed in the same solution of Ru-1. This modified HOPG electrode showed an adsorbed Ru(II/III) oxidation peak at +0.45 V vs. Fc/Fc<sup>+</sup> with surface coverage of  $1.94 \times 10^{-11}$  mol cm<sup>-2</sup> in CH<sub>3</sub>CN (0.1 M TBAPF<sub>6</sub>). However, this oxidative peak decreased under desorption rate of  $6.8 \times 10^{-7}$  s<sup>-1</sup> in fresh CH<sub>3</sub>CN solution since the nonbonded Ru-1 molecules were slowly desorbed from HOPG surface, particularly in an easily soluble solvent for Ru-1. Several examples of pyrene-anchored redox-active molecules have been reported.<sup>8,11-14</sup> In these examples, the desorption rate of the nonbonded redox-active complexes was employed as a measure of the adsorption stability of the complexes on a nanocarbon surface through noncovalent  $\pi$ - $\pi$  interactions.<sup>14</sup> Compared with the reported desorption rates, that of the present Ru-1 is much slower, indicating Ru-1 is relatively stable on an HOPG surface.



Figure 3. Proposed surface-tethered structures for the Ru-1 monolayer on ITO and HOPG. A bilayer connected by Zr-phosphonate bond on HOPG.

Contact angles of water droplet on both the ITO and HOPG surfaces modified by Ru-1 were measured. The measured contact angles on the Ru-1-modified ITO and HOPG surfaces were 75 and 51.8°, respectively. Since the contact angles on bare ITO and HOPG are 52.8 and 61.5°, we concluded that the surface property with respect to hydrophilicity-hydrophobicity reversed after the surface immobilization of Ru-1. Phosphonic groups were selectively attached to the ITO surface, thereby producing a hydrophobic surface. Furthermore, pyrene groups can be indirectly immobilized on the HOPG surface through noncovalent  $\pi$ - $\pi$ interaction, resulting in the appearance of the exposed phosphonic acid groups with a hydrophilic property on the HOPG surface. While the selective adsorption of Ru-1 is obvious, further study on the molecular orientation of the Ru-1 adlayers is indispensable in due course. Ru-1 possesses double-faced properties; therefore, it is hereafter called a "Janus-type complex."

Layer-by-layer (LbL) assembly to fabricate well-defined nanostructures for molecular functional devices on a surface has received much attention.<sup>15</sup> As shown in Figure 3, the Janus-type complex (Ru-1) was used as a primer layer to fabricate novel multilaver structures of redox-active Ru complexes on the HOPG. Since free phosphonic acid groups are present on the uppermost layer of the Ru-1-modified HOPG, a method of metal-phosphonate bonding developed by Mallouk and others<sup>16</sup> was used to construct a multilayer structure. At first, a HOPG electrode was immersed in an aqueous DMF solution of the Ru-1 complex (50 µM) for six hours, after which it was rinsed with copious ultrapure water. Next, the HOPG substrate was dipped in a 20 mM aqueous solution of ZrOCl<sub>2</sub> for 30 min, rinsed with water, and immersed in the Ru-1 solution again. A cyclic voltammogram of the resulting bilayer film showed an oxidative wave at +0.49 V vs. Fc<sup>+</sup>/Fc with a surface coverage of  $2.83 \times 10^{-11} \text{ mol cm}^{-2}$  in



**Figure 4.** UV–vis spectral monitoring of successive LbL fabrication of (graphene-flake/Ru-2)<sub>n</sub> above Ru-1 adlayer on ITO. The Ru-1 film was referred to 1 layer and "*n*" stands for the number of the paired layers (n = 0–4); (blue) Ru layer on the top and (green) graphene on the top.



**Figure 5.** (a) Plots of absorbance (red: Ru on the top; black: graphene on the top) and (b) surface coverage obtained from CV in Figure S3 vs. the number of layers for (graphene-flake/Ru-2)<sub>n</sub> above Ru-1 adlayer on ITO (The number of paired layers, n = 0-4).

CH<sub>3</sub>CN (0.1 M TBAPF<sub>6</sub>), which is 1.5 times larger than that of the Ru-1 monolayer on the HOPG surface. Furthermore, the contact angle was  $80.6^{\circ}$ , which indicates that a bilayer structure was formed and pyrene groups were exposed to the uppermost layer after the formation of Zr–phosphonate bonds.

To obtain the LbL films of Ru complexes segregated with graphene, the Ru-1-modified ITO electrode was used. A LbL multilayer film composed of Ru-1, Ru-2, and graphene were fabricated on an ITO surface by successive formation of layers (see Supporting Information and Figure S2);<sup>17</sup> namely, at first a graphene suspension was spin coated at 800 rpm onto the Ru-1modified ITO electrode and dried in nitrogen flow. Secondly, this graphene-modified ITO electrode was immersed in a DMF solution of Ru-2 (50 µM) for six hours and dried. The resulting substrate was treated by spin-coating with the graphene suspension at 800 rpm. While these successive layering processes were carried out, the UV-vis spectra and CV of the modified ITO substrate were monitored. Change of UV-vis spectra and CVs for LbL films with different numbers of lavers are shown in Figure 4 and Figure S3, respectively. The Ru-1 and Ru-2 complexes exhibited the MLCT band at 500 and 520 nm, respectively. Upon successive graphene immobilization on the top of Ru-1 or Ru-2, the absorption peak at 345 nm and the broad peak around 540 nm increased linearly. These increases correspond to the reported graphene absorption bands. In addition, upon increase of the number of layers of Ru-2, the absorption peak around 520 nm, which corresponds to the MLCT band from Ru-2 and graphene, increased linearly, as shown in Figure 5a. At the same time, the Ru(II/III) oxidative peak current at +0.47 V increased with increasing the number of Ru-2 layers, as shown in Figure S3. The plots of surface coverage vs. number of



**Figure 6.** SEM images of (a) graphene monolayer on Ru-1 complex and (b) graphene uppermost layer on 7 layers on ITO.

layers show a linear relationship (Figure 5b), which suggests a uniform layer structure is formed during the LbL process. The surface morphology of each graphene uppermost layered film was measured by SEM (Figure 6 and Figure S4). A relatively flat surface packed with graphene flakes is seen in the SEM images. While the present graphene flakes used are not a pure single layer, a Ru-2 complex (having two pyrene groups at both ends) is strongly adsorbed on the graphene surface and connects two interlayers of graphenes. As a result, the Ru complexes immobilized in each layer became redox-active. The fabricated graphene–Ru-complex multilayer films are applicable to functional devices such as super capacitors and photoelectrochemical solar cells.

In conclusion, a "Janus-type" ruthenium complex bearing both phosphonic acid and pyrene groups was tethered on both ITO and HOPG surfaces in different tethering modes. The Ru complex was directly attached on ITO surface by phosphonate groups, while indirect attachment of the Ru complex was feasible through noncovalent  $\pi$ - $\pi$  interaction of pyrene groups on the HOPG surface.

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Supporting Information is available electronically on J-STAGE.

## References

- 1 B. Xin, J. Hao, Chem. Soc. Rev. 2010, 39, 769.
- 2 Y. Liu, L. Mu, B. Liu, J. Kong, Chem.-Eur. J. 2005, 11, 2622.
- 3 B. A. Grzybowski, C. E. Wilmer, J. Kim, K. P. Browne, K. J. M. Bishop, *Soft Matter* 2009, 5, 1110.
- 4 G. Katsukis, C. Romero-Nieto, J. Malig, C. Ehli, D. M. Guldi, *Langmuir* 2012, 28, 11662.
- 5 G. V. Dubacheva, C.-K. Liang, D. M. Bassani, *Coord. Chem. Rev.* 2012, 256, 2628.
- 6 M. Haga, K. Kobayashi, K. Terada, Coord. Chem. Rev. 2007, 251, 2688.
- 7 V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, *Chem. Rev.* 2012, *112*, 6156.
- 8 J. D. Blakemore, A. Gupta, J. J. Warren, B. S. Brunschwig, H. B. Gray, J. Am. Chem. Soc. 2013, 135, 18288.
- 9 J. A. Mann, W. R. Dichtel, J. Phys. Chem. Lett. 2013, 4, 2649.
- 10 G. Modugno, Z. Syrgiannis, A. Bonasera, M. Carraro, G. Giancane, L. Valli, M. Bonchio, M. Prato, *Chem. Commun.* 2014, 50, 4881.
- 11 B. Reuillard, A. Le Goff, S. Cosnier, Chem. Commun. 2014, 50, 11731.
- 12 E. W. McQueen, J. I. Goldsmith, J. Am. Chem. Soc. 2009, 131, 17554.
- 13 A. Le Goff, B. Reuillard, S. Cosnier, Langmuir 2013, 29, 8736.
- 14 J. A. Mann, J. Rodríguez-López, H. D. Abruña, W. R. Dichtel, J. Am. Chem. Soc. 2011, 133, 17614.
- 15 K. Ariga, Y. Yamauchi, G. Rydzek, Q. Ji, Y. Yonamine, K. C.-W. Wu, J. P. Hill, *Chem. Lett.* **2014**, *43*, 36.
- 16 H.-G. Hong, T. E. Mallouk, Langmuir 1991, 7, 2362.
- 17 A. A. Green, M. C. Hersam, Nano Lett. 2009, 9, 4031.