## Electrochemical and Photophysical Study in Solution and on Ruthenium(II) Polypyridyl Complexes Containing Thiophenylethynylphenanthrolines Self-assembled on Gold Surfaces

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Novel ruthenium(II) polypyridyl complexes with diethynylphenanthrolines containing acetylthiophenyl unit(s) have been prepared and characterized by photophysical measurements. These complexes showed the MLCT and the lowest energy  $\pi - \pi^*$  absorption bands, and also intensive broad emission bands assignable to a triplet MLCT transition were observed in the deaerated solution. The electrochemistry of these complexes in the solution and on self-assembled monolayers on the gold electrode clearly showed Ru(II)/R(III) redox waves.

Research regarding various types of molecular assemblies on metallic and semiconductor surfaces continues to be carried out because the anchoring of molecules on surfaces is the first step toward the construction of molecular-based electric devices.<sup>1-3</sup> Stable electro- and photo-active molecules, and in particular thiol derivatives, have been investigated to understand their important role in charge injection and as conductive bodies from molecules to the electrode surface in the recent past.<sup>2-4</sup> Even though most of the reported systems are organic systems, some investigations of self-assembly on conductive surfaces with metal-polypyridyl complex systems containing ruthenium, platinum, and osmium ions have been carried out by several groups.<sup>3–5</sup> We have previously reported the preparation as well as the photophysical and electrochemical properties of ruthenium(II) polypyridyl supramolecular complexes containing 3-ethynylphenanthroline linked by a gold(I) cation and by a platinum(II) bis-tributylphosphine organometallic system, because these systems suggest the possibility of a molecular wire by charge injection from the ruthenium center to the wire skeleton, which contains two ethynyl-substituted phenanthrolines under photoexcitation.<sup>6</sup> The self-assembled monolayers (SAMs) of these ruthenium(II) polypyridyl supramolecular complexes on the conductive surface have not been investigated with regard to their electrochemical and photophysical properties compared with those in the solution, although the electrochemical properties of some ruthenium(II) polypyridyl mononuclear complexes on the platinum and ITO surfaces have been reported.4,5

We, therefore, became interested in the electrochemical properties of ruthenium(II) polypyridyl complexes containing diethynylphenanthrolines with a thiophenyl substituent for the creation of SAM on a gold surface as a first step toward the construction of supramolecular complex-based electric devices. In this paper, we report the synthesis and photophysical properties of ruthenium(II) polypyridyl complexes containing diethynylphenanthrolines bonded with one or two acetylthiophenyl unit(s): specifically, a  $[Ru(AcL1)(bpy)_2](PF_6)_2$  (1) and  $[Ru(AcL2)(bpy)_2](PF_6)_2$  (2) (AcL1: acetyl-protected 3-(4-thiophenylethynyl)-8-ethynylphenanthroline, AcL2: acetyl-protected 3,8-bis(4-thiophenylethynyl)phenanthroline) (Figure 1). This



Figure 1. Schematic representation and structure of novel compounds.

study has also focused on the electrochemical properties of acetyl-deprotected complexes  $[Ru(L1)(bpy)_2](PF_6)_2$  (3) and  $[Ru(L2)(bpy)_2](PF_6)_2$  (4) on the self-assembled gold surface compared to 1 and 2 in the solution. In particular, the electrochemical data for these compounds on the gold surface showed rare redox peaks of  $Ru^{3+}/Ru^{2+}$  couples under these experimental conditions, although previous research regarding ruthenium(II) polypyridyl complexes with phenanthroline or bipyridine derivatives has rarely resulted in the observation of redox peaks of  $Ru^{3+}/Ru^{2+}$  couples of SAM on the gold surface.<sup>5</sup>

Novel phenanthroline derivatives (Figure 1), AcL1 and AcL2, were synthesized from 3,8-diethynylphenanthroline and 1-acetylthio-4-iodobenzene using a Sonogashira cross-coupling reaction,<sup>7</sup> and the separation of AcL1 and AcL2 was performed by column chromatography, while ruthenium(II) complexes 1 and 2 were prepared by the usual method.<sup>6,8,9</sup> These compounds were characterized by <sup>1</sup>H NMR, IR, UV-vis spectroscopy, and elemental analysis (See Supporting Information).<sup>10</sup> The ruthenium(II) complexes were further measured by electrospray ionization mass spectroscopy, and the data showed a good agreement with a satisfactory isotopic matching to the simulated pattern of our supposed molecular formula. The IR spectral data of these compounds clearly indicate the structural difference of the C $\equiv$ C bond at both ends in AcL1 and AcL2 (Figure 1). Two characteristic  $\nu(C \equiv C)$  bands were observed at around 2100 and 2200 cm<sup>-1</sup> for AcL1 and 1, while only one  $\nu$ (C=C) band was observed at around  $2200 \text{ cm}^{-1}$  for AcL2 and 2. The structural differences between AcL1 and AcL2 were further supported by the <sup>1</sup>H NMR measurement; all six proton signals of phenanthro-



Figure 2. UV–vis absorption (left) and emission (right) spectra upon excitation at 425 nm of 1 (solid line) and 2 (dash line) at room temperature in acetonitrile.

line ring were detected in AcL1 and 1, respectively, while the observed phenanthroline proton signals for AcL2 and 2 were three sets of signals corresponding to the protons of the symmetric diethynylphenanthroline skeleton.<sup>10</sup>

Figure 2 shows the absorption spectra of Ru(II) complexes 1 and 2 in CH<sub>3</sub>CN at room temperature. The absorption bands in the 400-550 nm region of these complexes were assigned to typical MLCT transitions observed for ruthenium(II) polypyridyl complexes with bipyridine and/or phenanthroline derivatives. The absorption bands in the 300-400 nm region were primarily assigned to  $\pi - \pi^*$  (diethynylphenanthroline) transitions, and this assignment was supported by UV-vis absorption spectra of novel ligands, AcL1 and AcL2, as shown in Figure S1.<sup>10</sup> The spectrum of **2** shows the lowest energy  $\pi - \pi^*$ (AcL2) transition band near 370 nm. A similar absorption band for 1 was detected at 340 nm, and the molar extinction coefficient ( $\varepsilon$ ) for the lowest  $\pi - \pi^*$ (AcL1) absorption of 1 was found to be smaller than that for 2. This red shift and high  $\varepsilon$  of the lowest energy  $\pi - \pi^*$ absorption in 2 is likely due to greater electron delocalization by the two acetylthiophenyl substitutions on the diethynylphenanthroline skeleton in the AcL2 ligand compared with AcL1.<sup>5,11</sup>

The emission spectra of 1 and 2 in Figure 2 show similar phosphorescent bands assignable to the triplet MLCT transition in the long wavelength region (1: 638 nm, 2: 671 nm) at room temperature. These complexes have a higher emission quantum yield ( $\phi$ ) (1:  $\phi = 0.156$ , 2:  $\phi = 0.113$ ) than standard ruthenium(II) complexes, [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> ( $\phi = 0.095$ ).<sup>9</sup> Furthermore, these emissions at 77 K display the phosphorescent bands with weak vibronic progressions assignable to the triplet MLCT transition in the short wavelength region (1: 594 nm, 2: 631 nm) (Figure S2).<sup>10</sup>

The electrochemical properties of ruthenium(II) complexes **1** and **2** were investigated by cyclic voltammetry in acetonitrile. The resulting electrochemical data are collected in Table 1. These complexes exhibited reversible oxidation waves and reversible first reduction waves in the potential range +1.50 to -1.50 V versus SCE. The oxidation potentials ( $E_{1/2}(x)$ ) of two

Table 1. The electrochemical data of 1 and  $2^a$ 

Compound	<i>E</i> <sub>1/2</sub> (ox) /V	$E_{1/2}(\text{red})$ /V	$\Delta E_{1/2}$ /V
1	1.29	-1.06	2.35
2	1.31	-1.02	2.33
[Ru(bpy) <sub>2</sub> (phen)]	1.25	-1.37	2.62
[Ru(bpy) <sub>3</sub> ]	1.26	-1.36	2.62

<sup>a</sup>Cyclic voltammograms for all compounds were measured in 1.0 mM acetonitrile solutions containing  $0.1 \text{ M Bu}_4\text{NPF}_6$ , using a Ag/AgNO<sub>3</sub>/CH<sub>3</sub>CN reference electrode (+0.37 V vs. SCE; calibrated with Fc<sup>0/+</sup>) and Pt working electrode.

complexes near +1.3 V are typical for the  $\text{Ru}^{3+/2+}$  couple of ruthenium(II) polypyridyl complexes with bipyridine and/or phenanthroline derivatives, while the first reduction potentials  $(E_{1/2}(red))$  are assigned to the first reduction process of the phenanthroline or bipyridine ligands. An interest finding is that the  $E_{1/2}$  (red) values of two complexes (1: -1.06 V, 2: -1.02 V) have a higher potential than those of  $[Ru(bpy)_3](PF_6)_2(-1.36 \text{ V})$ or  $[Ru(bpy)_2(phen)](PF_6)_2$  (-1.37 V) under the same measurement conditions. These first reduction potentials of compounds might indicate that the first reduction occurred at the phenanthroline derivative ligands, AcL1 and AcL2, in these complexes; in addition, it means that the diethynylphenanthroline in the complex accepts the electron from a ruthenium center under the photoexcited MLCT state. The validity of this explanation is supported by our previously reported results.<sup>6,11</sup> Furthermore, the relation between the emission energy of maximum intensity and potential difference,  $\Delta E_{1/2}$ , listed in Table 1 was consistent with the relation in many ruthenium(II) polypyridyl complexes reported in our previous article.<sup>6</sup> The second reduction potentials of novel ruthenium(II) complexes were observed at near -1.3 V and these reduction might be assigned the reduction of one of bpy ligands in these complexes. However, the reversibility on the multiple sweeping in present complexes was very low, and the EC reaction must be occurred after the second reduction of these complexes.

For the electrochemistry of SAM with ruthenium complexes on a gold electrode, a precleaned highly flat gold thin film sheet on mica was used to form a thiol-bonded monolayer by immersion of this gold sheet into an acetonitrile solution of 1.0 mM 1 or 2. An acetate-protecting group on the thiophenyl substituent in the ligand was removed in situ by adding NH<sub>3</sub>(aq) to obtain the thiol complexes 3 or 4. After 1 day of immersion, the SAM of the ruthenium complex on the gold surface was firmly developed and the sheet was thoroughly rinsed with acetonitrile. Details regarding preparation of the self-assembled ruthenium complex monolayer on the gold electrode are described in the Supporting Information.<sup>10</sup> The cyclic voltammograms of SAM with 3 and 4 on gold sheet electrodes were measured with different scan rates and referenced against SCE with a silver wire as a quasi-reference electrode under similar conditions to those used for the acetyl-protected ruthenium complexes 1 and 2 in the solution described above. Reversible oxidation waves of  ${\bf 3}$  and  ${\bf 4}$  for the  $Ru^{3+/2+}$  redox process occurred near +1.3 V, very similar to the values obtained in solutions of 1 and 2. Self-assembled complex 3 on the gold surface exhibited the characteristic electrochemical behavior of surface-confined species with small peak separation (example



**Figure 3.** (a) Cyclic voltammograms of SAM of **3** on gold sheet electrode in the 0.1 M TBAPF<sub>6</sub> of acetonitrile solution. Scan rates 0.1 (red), 0.2 (green), 0.4 (blue), and  $0.8 \text{ V s}^{-1}$  (black). (b) Cyclic voltammograms of **1** (0.1 mM) in the 0.1 M TBAPF<sub>6</sub> of acetonitrile solution. Scan rates 0.1 (red), 0.4 (green), 1.6 (blue), 6.4 V s<sup>-1</sup> (black).

for **3**: 40 mV, **1**: 77 mV at 100 mV s<sup>-1</sup> scan rate) at all scan rates (Figure 3). Furthermore, peak current values were linearly dependent on the scan rate in the case of **3** on the SAM, while they were linearly dependent on the root of the scan rate in the solution of **1**, as shown in Figure 3 and Figure S3,<sup>10</sup> which means the process is diffusion-controlled. Almost the same correlation between **4** on gold surface and **2** in the solution was obtained under the same condition (Figure S4).<sup>10</sup> This electrochemical behavior of the present complexes on the gold surface is consistent with previous electrochemical behavior of some ruthenium(II) polypyridyl complexes with phenanthroline or bipyridine derivatives on a platinum electrode.<sup>5</sup>

Novel phenanthroline ligands and ruthenium(II) polypyridyl complexes, **1** and **2**, were synthesized and characterized by some spectroscopic means. Ruthenium complexes show an intense emission assignable to the triplet MLCT transition. The electrochemical properties of ruthenium(II) complexes in the solution and self-assembled ruthenium(II) complex monolayers of **3** and **4** on the gold sheets suggest that new ruthenium(II) complexes have almost the same electrical behavior both in the solution state and on the metal surface. We are currently extending synthetic work on a novel ruthenium(II)–platinum(II) supramolecular system with complex **1** and [Ru(bpy)<sub>2</sub>(3,8-diethynyl-phenanthroline)](PF)<sub>6</sub> linked by platinum(II) bis-tributylphosphine organometallics and further preparation of SAM of this supramolecular complex system on a gold surface.

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## **References and Notes**

- a) Z. Li, E. Borguet, J. Am. Chem. Soc. 2012, 134, 63. b) W. Hong, D. Z. Manrique, P. Moreno-García, M. Gulcur, A. Mishchenko, C. J. Lambert, M. R. Bryce, T. Wandlowski, J. Am. Chem. Soc. 2012, 134, 2292. c) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, Chem. Rev. 2005, 105, 1103. d) J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, Science 1999, 286, 1550. e) J. G. Kushmerick, C. M. Whitaker, S. K. Pollack, T. L. Schull, R. Shashidhar, Nanotechnology 2004, 15, S489. f) C. Joachim, J. K. Gimzewski, A. Aviram, Nature 2000, 408, 541. g) J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McEuen, D. C. Ralph, Nature 2002, 417, 722. h) F. Minisci, Synthesis 1973, 1. i) G. A. Olah, T. D. Ernst, J. Org. Chem. 1989, 54, 1203. j) H. Takeuchi, T. Adachi, H. Nishiguchi, J. Chem. Soc., Chem. Commun. 1991, 1524. k) S. Seko, N. Kawamura, J. Org. Chem. 1996, 61, 442.
- 2 a) C. Vericat, M. E. Vela, G. Benitez, P. Carro, R. C. Salvarezza, *Chem. Soc. Rev.* 2010, *39*, 1805. b) B. Ulgut, H. D. Abruña, *Chem. Rev.* 2008, *108*, 2721. c) K. Yokota, M. Taniguchi, M. Tsutsui, T. Kawai, *J. Am. Chem. Soc.* 2010, *132*, 17364. d) J. M. Mativetsky, G. Pace, M. Elbing, M. A. Rampi, M. Mayor, P. Samori, *J. Am. Chem. Soc.* 2008, *130*, 9192. e) S. Wu, M. T. González, R. Huber, S. Grunder, M. Mayor, C. Schönenberger, M. Calame, *Nat. Nanotechnol.* 2008, *3*, 569. f) K. Yokota, M. Taniguchi, T. Kawai, *J. Am. Chem. Soc.* 2007, *129*, 5818. g) J. G. Kushmerick, J. Lazorcik, C. H. Patterson, R. Shashidhar, D. S. Seferos, G. C. Bazan, *Nano Lett.* 2004, *4*, 639.
- 3 a) K. Seo, A. V. Konchenko, J. Lee, G. S. Bang, H. Lee, J. Am. Chem. Soc. 2008, 130, 2553. b) W. Huang, L. Wang, H. Tanaka, T. Ogawa, Eur. J. Inorg. Chem. 2009, 1321. c) T.-Y. Dong, C. Huang, C.-P. Chen, M.-C. Lin, J. Organomet. Chem. 2007, 692, 5147. d) N. Tuccitto, V. Ferri, M. Cavazzini, S. Quici, G. Zhavnerko, A. Licciardello, M. A. Rampi, Nat. Mater. 2009, 8, 41. e) Z. Ng, K. P. Loh, L. Li, P. Ho, P. Bai, J. H. K. Yip, ACS Nano 2009, 3, 2103. f) T. Albrecht, A. Guckian, J. Ulstrup, J. G. Vos, Nano Lett. 2005, 5, 1451.
- 4 a) G. Tsekouras, O. Johansson, R. Lomoth, *Chem. Commun.* 2009, 3425. b) Y. S. Obeng, A. J. Bard, *Langmuir* 1991, 7, 195. c) P. Bertoncello, E. T. Kefalas, Z. Pikramenou, P. R. Unwin, R. J. Forster, *J. Phys. Chem. B* 2006, *110*, 10063.
- 5 a) S. Ramachandra, K. C. Schuermann, F. Edafe, P. Belser, C. A. Nijhuis, W. F. Reus, G. M. Whitesides, L. De Cola, *Inorg. Chem.* 2011, 50, 1581. b) Y. Sato, K. Uosaki, *J. Electroanal. Chem.* 1995, 384, 57. c) A. D'Aléo, R. M. Williams, Y. Chriqui, V. M. Iyer, P. Belser, F. Vergeer, V. Ruiz, P. R. Unwin, L. De Cola, *Open Inorg. Chem. J.* 2007, 1, 26.
- 6 a) M. Shiotsuka, N. Nishiko, K. Keyaki, K. Nozaki, *Dalton Trans.* 2010, *39*, 1831. b) M. Shiotsuka, Y. Tsuji, K. Keyaki, K. Nozaki, *Inorg. Chem.* 2010, *49*, 4186.
- 7 D. L. Pearson, J. M. Tour, J. Org. Chem. 1997, 62, 1376.
- 8 G. H. Allen, R. P. White, D. P. Rillema, T. J. Meyer, J. Am. Chem. Soc. 1984, 106, 2613.
- 9 K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi, S. Tobita, *Phys. Chem. Chem. Phys.* 2009, 11, 9850.
- 10 Supporting Information is available electronically on the CSJ-Journal Web Site, http://www.csj.jp/journals/chem-lett/index. html.
- 11 M. Shiotsuka, Y. Inui, Y. Sekioka, Y. Yamamoto, S. Onaka, J. Organomet. Chem. 2007, 692, 2441.