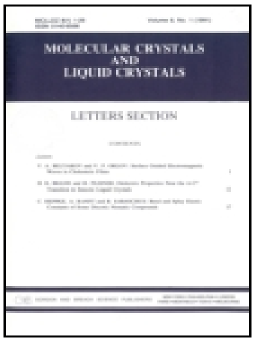

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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Motoyuki Nakano & Atsushi Aoki (2015) Emission Control for Organic Light-emitting Electrochemical Cell Using Ruthenium Complex by Redox Potential, Molecular Crystals and Liquid Crystals, 620:1, 21-25, DOI: 10.1080/15421406.2015.1094612

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1094612

Mol. Cryst. Liq. Cryst., Vol. 620: pp. 21–25, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1094612

Emission Control for Organic Light-emitting Electrochemical Cell Using Ruthenium Complex by Redox Potential

MOTOYUKI NAKANO AND ATSUSHI AOKI*

Materials Science & Engineering, Graduate School of Engineering, Nagoya
Institute of Technology, Gokiso, Showa-ku, Nagoya, Japan

A novel concept for the light-emitting electrochemical transistor (LECT) which consists of the electrochemical light-emitting cell (LEC) and the electrochemical transistor (ECT) was introduced. The four-electrode electrochemical system using interdigitated array (IDA) electrodes was employed to demonstrate the concept of LECT in solution. Cyclic voltammetric (CV) measurement was carried out in solution containing $Ru(bpy)_3(PF_6)_2$ as redox species and a light-emitting material. We confirmed that the light emission was controlled at the electrode potential difference between both fingers of IDA electrodes.

Keywords Light-emitting electrochemical transistor (LECT); Ruthenium complex; Light-emitting electrochemical cell (LEC); Electrochemical transistor (ECT).

Introduction

Organic light-emitting diode (OLED) and organic field effect transistor (OFET) have been developed for the application to display and digital signage, respectively because they have advantages such as high flexibility in shape and low cost fabrication. To make display using such devices, FET is always needed to drive OLED and to control the light emission. So, the emission area of OLED is often restricted by the FET area for driving OLED, resulting the emission intensity becomes low. To overcome this problem, organic light-emitting transistors (OLET) which consist of combination of OLED and OFET have been intensively investigated for application to display. It can control light emission by the gate voltage [1]. So far, we have investigated light-emitting electrochemical cell (LEC) and electrochemical transistor (ECT) independently. LEC has some advantages about a single layer device structure and usage of air-stable metal cathode compared to OLED because of the formation of the electric double layer at the charge injection. ECT also has unique features for lower driving gate voltage than that of OFET as the electrolyte solution and the polyelectrolytes are used as the insulating layer in the ECT whereas the dielectric materials such as SiO_2 in the OFET. Therefore, we introduce a novel concept for light-emitting electrochemical transistor (LECT) consists of combination of LEC and ECT. The LECT

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*Address correspondece to Atsushi Aoki, Materials Science & Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan. E-mail: aaoki@nitech.ac.jp

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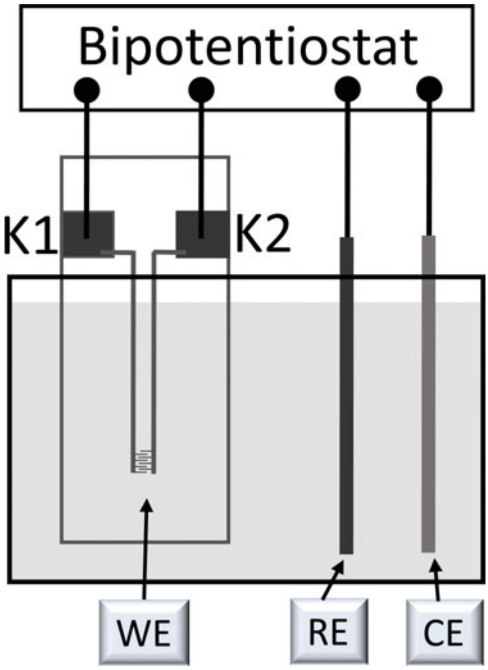

Figure 1. Schematic representation of LECT system.

would be expected to have both attractive properties of LEC and ECT. The LECT has some advantages such as a simple device structure, chemical stability and lower driving gate voltage compared to OLET.

Tris(bipyridine)ruthenium complex ($[Ru(bpy)_3]^{n+}$) is employed as redox species and a light-emitting material. The divalent ruthenium complex Ru(II) can be electrochemically oxidized and reduced to form trivalent Ru(III) and monovalent Ru(I), respectively. When the electron exchange reaction of Ru(III) and Ru(I) takes place, the excited state Ru(II) is produced to emit the light, which is called “electrochemical luminescence”[2].

In order to demonstrate LECT behavior in solution containing the Ru complex, the four-electrode electrochemical system using interdigitated array (IDA) electrodes was employed. We confirmed that the emission from the ruthenium complex was controlled by the voltages applied between the anode and the cathode of IDA electrodes.

Experimental Section

The four-electrode electrochemical system which consists of Pt IDA electrodes (electrode width and interval of electrodes: 2 μm, number of fingers: 65 pairs) purchased from BAS as working electrodes (WE), Ag wire as a reference electrode (RE) and Pt coil as a counter electrode (CE) was carried out under nitrogen atmosphere as shown in Figure 1. K1 stands for one electrode in the IDA electrodes and K2 stands for the other. E1 and E2 are defined as the potential of K1 and K2 electrodes, I1 and I2 are defined as the current of K1 and K2 electrodes, respectively.

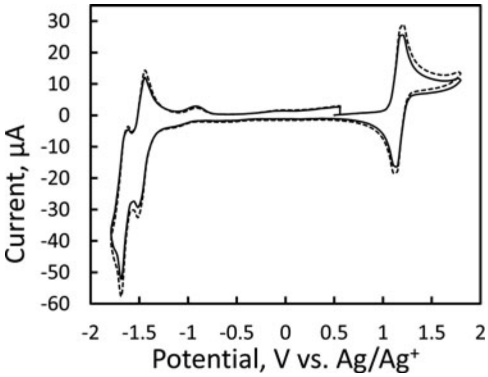

Figure 2. Cyclic voltammograms at both K1 (dotted line) and K2 (solid line) swept at the scan rate of 50 mV/s.

CV measurement was carried out in anhydrated acetonitrile solution containing 1.0 mM $[Ru(bpy)_3](PF_6)_2$ and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). First, both E1 and E2 were swept with the same potential. Then, E1 was swept and E2 was fixed at 0 V vs Ag/Ag^+, where Ru(I) is oxidized and Ru(III) is reduced to produce Ru(II). Furthermore, E2 was fixed at 1.5 V vs Ag/Ag^+, where Ru(I) and Ru(II) are oxidized to produce Ru(III). The background measurement was also carried out under the following conditions: Pt wire as WE in anhydrated acetonitrile solution containing 0.1 M $TBAPF_6$.

Results and Discussion

The voltammograms at K1 and K2 where the both of the electrode potential were swept were shown in Figure 2. The similar redox behavior of the Ru complex was observed at each K1 and K2 independently. The redox potential was determined to be +1.1, −1.4 and −1.6 V vs Ag/Ag^+ for Ru(II/III), Ru(II/I) and Ru(I/0) redox couples, respectively. The voltammogram at K2 where E2 was fixed at 0 V vs Ag/Ag^+ and the voltammogram at K1 where E1 was swept were shown in Figure 3. No current was observed at K1 and K2 electrodes in the E1

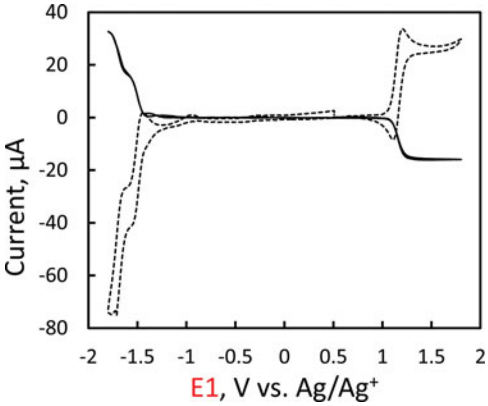

Figure 3. Cyclic voltammograms at K2 (solid line) fixed at 0 V vs Ag/Ag^+ and at K1 (dotted line) swept at the scan rate of 50 mV/s.

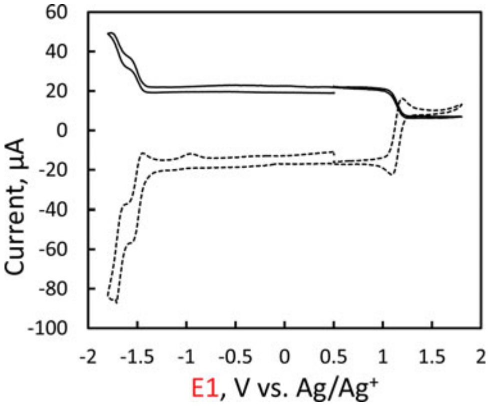

Figure 4. Cyclic voltammograms at K2 (solid line) fixed at +1.5 V vs Ag/Ag$^+$ and K1 (dotted line) swept at the scan rate of 50 mV/s.

range from +1.0 to -1.2 V vs Ag/Ag$^+$ as the same as Figure 2. The steady state oxidation and reduction current was observed at K1 and K2 electrodes, respectively in the E1 range of higher than +1.2 V vs Ag/Ag$^+$, indicating that Ru(III) generated at K1 electrode was transported to K2 electrode by diffusion and it was re-reduced to be Ru(II) at K2 electrode, so called "redox cycling". The opposite current was observed in the E1 range of lower than -1.3 V vs Ag/Ag$^+$.

The voltammogram at K2 where E2 was fixed at +1.5 V vs Ag/Ag$^+$ and the voltammogram at K1 where E1 was swept were shown in Figure 4. The steady state oxidation current in K1 and K2 were observed with the almost same current magnitude in the E1 range of higher than +1.2 V vs Ag/Ag$^+$. Ru(II) transported from the bulk solution by two-dimensional diffusion is oxidized to produce Ru(III) at K1 and K2 electrodes. The steady state reduction and oxidation current was observed at K1 and K2, respectively in the E1 range of 1.0∼−1.3 V. Ru(II) and Ru(III) were generated on K1 and K2, respectively. Meanwhile, Ru(I) was formed at K1 in the E1 range of −1.3∼−1.6 V. The light emission was observed in this condition. Because the excited state Ru(II) was produced by electron exchange reaction of Ru(I) and Ru(III) produced at K1 and K2 electrodes, respectively. Therefore, we demonstrate that the light-emitting electrochemical transistor would be constructed in the near future by control of the voltage difference between E1 and E2. However, the emission was weak, and disappeared after several potential cycles, probably due to some contaminants in the solution. Ru(I) would form quencher by reaction with water [3].

Conclusions

In order to confirm the concept of LECT using Ru complex, CV was carried out in the four-electrode electrochemical solution system. The light emission was controlled by the redox voltage of the Ru complex, but it was weak and disappeared after repeated measurements.

Acknowledgment

This work was partly supported by Grant-in-Aid for Scientific Research (C) (25410249) from Japan Society for the Promotion of Science.

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