

Cyclovoltammetric Methods for the Ionization Potential and Electron Affinity of Iridium ppy Derivatives

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Abstract : The effects of molecular structure on the redox properties of the organic electroluminescent materials (Ir(ppy)_3 , Ir(m-ppy)_3 , Ir(p-toly)_3) were studied using cyclic voltammetry and spectroscopy. These iridium complexes show reversible oxidation and reduction on the electrode, which produce the symmetric cyclic voltammogram. It indicates that these materials are very stable under repetitive oxidation/reduction cycles.

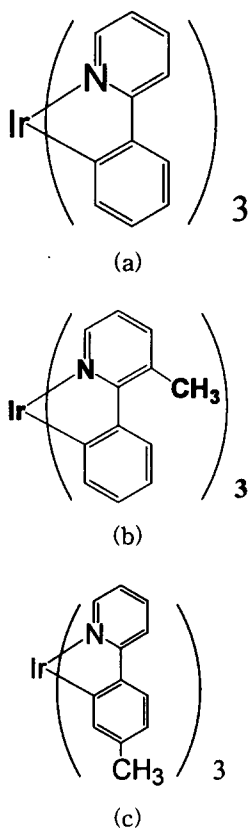
The electrochemically determined ionization potential/electron affinity values are 5.40eV/3.02eV for Ir(ppy)_3 , 5.36eV/2.96eV for Ir(m-ppy)_3 , and 5.35eV/2.97eV for Ir(p-toly)_3 from the SCE(Standard Calomel Electrode). The electrically determined band gaps are 2.38eV (521nm), Ir(ppy)_3 , 2.40eV (517nm), Ir(m-ppy)_3 , and 2.38eV (521nm), Ir(p-toly)_3 , which are similar with the optical band gaps. The position of methyl group on 2-phenylpyridine (ppy) effects do not influence much on the ionization potential, electron affinity, and band gap of Ir(ppy)_3 derivatives.

Keywords : cyclic voltammetry, ITO, Al, IP, EA, Electroluminescence, Ir(ppy)_3 , Ir(m-ppy)_3 , Ir(p-toly)_3

1. Introduction

Significant synthetic efforts have been devoted to the development of organic electroluminescent materials. [1, 2] The optical properties as well as electrical properties such as ionization potential (IP) and electron affinity (EA) have to be considered before applying the luminescent material to the electroluminescent devices. The IP and EA can be measured by cyclic voltammetry, ultraviolet photoelectron spectroscopy and ultraviolet (UV) spectroscopy. [2, 3] The cyclic voltammetry is a dynamic electrochemical method in which the potential applied to an electrochemical cell is scanned

and any resulting changes in cell current are monitored to yield a cyclovoltammogram of the reduction-oxidation properties of the material. The oxidation process corresponds to the removal of electrons from the π -band [highest occupied molecular orbital (HOMO)], whereas the reduction process corresponds to the filling of electrons in the π^* -band [lowest unoccupied molecular orbital (LUMO)]. The difference between the peak potential for the oxidation and reduction provides an estimate of the HOMO-LUMO gap of the compound. These electrochemically determined energy gaps are consistent with UV-visible transition energy, falling between the onset and peak of the $\pi - \pi^*$ transition.



Scheme 1. Molecular structures of (a) $\text{Ir}(\text{ppy})_3$, (b) $\text{Ir}(\text{m-ppy})_3$, (c) $\text{Ir}(\text{p-toly})_3$.

In this paper, we report the electrochemical properties of $\text{Ir}(\text{ppy})_3$, $\text{Ir}(\text{m-ppy})_3$, and $\text{Ir}(\text{p-toly})_3$. The chemical structure of $\text{Ir}(\text{ppy})_3$, $\text{Ir}(\text{m-ppy})_3$, $\text{Ir}(\text{p-toly})_3$ is shown in scheme 1. The metal to ligand charge transfer transition energy can be affected by the ligand structure.

2. Experimental

The cyclic voltammograms were obtained from a homemade system. The ionization potential was measured with the indium-tin-oxide (ITO) electrode and the electron affinity was measured with Al

electrode. The iridium complex thin films on the electrodes were prepared by the organic molecular beam deposition (OMBD) method. The area of the electrodes was $0.5 \times 2.0 \text{ cm}^2$. The thickness of iridium complex thin films on the electrodes was 1000 Å. The iridium complex layer was fabricated under vacuum, 10–8 torr, and the deposition rate was typically 0.1–0.2 nm/sec. The sheet resistance of ITO glass substrate was $30 \Omega/\text{m}^2$ and was purchased from Samsung Corning Co. Al electrode was evaporated under the pressure of 10⁻⁶ torr.

Acetonitrile (ultra pure, 99+%) and dimethylformamide (DMF, ultra pure, 99+%) were obtained from Johnson Matthey Electronics. Tetrabutylammonium perchlorate (Bu^4NClO_4) was obtained from TCI. For cyclic voltammetry, 0.1M Bu^4NClO_4 in acetonitrile or DMF was used. The solutions were slowly purged with high-purity N_2 for 10–15 minutes before each experiment. A three-electrode compartment electrochemical cell is consisted of ITO or Al electrode as a working electrode, a platinum wire 0.6mm as a counter electrode, and Ag/Ag^+ (0.1M AgNO_3 solution) was used as a reference electrode. The cyclic voltammograms were obtained at a scanning rate of 150~100mV/sec.

UV/visible absorption spectra of Iridium complexes were obtained using a Hewlett Packard 8425A spectrometer. Photoluminescence (PL) spectra were obtained from a Perkin Elmer LS50. Thickness measurements of various films were carried out with α -step 200 profilometer and ellipsometer. The solid-state spectra of Iridium complexes were obtained from the films made with OMBD on the quartz plate with the size of $2.02 \times 0.2 \text{ cm}^2$.

Electrochemical analysis of ionization potentials and electron affinity of Iridium complexes proceeded through three steps. Iridium complexes were deposited on the working electrode (ITO or Al electrodes),

which located in the cell. The oxidation/reduction potentials of Iridium complexes are measured with the Ag/Ag⁺ reference electrode. The bias potential of reference electrode measured with the reference materials. For the bias potential conversion, Ferrocene and AlQ₃ were used as a reference material. The bias potential between SCE and Ag/Ag⁺ reference electrode was + 0.31V when it measured in DMF and +0.41V in acetonitrile. The bias electrochemical potential of electron affinity was + 4.8V.^[1-8]

3. Results and Discussion

The UV/visible absorption and PL spectra of Ir(ppy)₃ film are shown in Fig. 1 (a). The absorption spectra exhibit absorption maxima at 248nm, 294nm and 389nm. The absorption edges of 463nm (2.68eV) and 532nm (2.33eV) are resolved from the absorption maxima of 389nm and 488nm. Therefore, the $\pi-\pi^*$ optical band gap (E_g) is 463nm (2.68eV). PL spectrum shows the fluorescence maxima at 447nm and 523nm and the onsets at 410nm and 476nm (2.61eV).

Cyclic voltammogram of Ir(ppy)₃ is shown in Figure 1(b). The initial oxidation-reduction was appeared at +0.60V, and 1.78V about the SCE electrode, respectively. The IP, EA and E_g were estimated to be 5.40eV, 3.02eV and 2.38eV (521nm) from the cyclic voltammogram. Because the oxidation-reduction reactions are symmetric, Ir(ppy)₃ shows reversible characteristic and is very stable. The inflection points of cyclovoltammogram were appeared at +0.67V and 2.13V. The electrically determined transition energy is 2.80eV (443nm). The second starting points of cyclovoltammogram are estimated to be +0.67V and 2.03V, which yield the second E_g = 2.70eV (459nm). The second inflection points of cyclovoltammogram are measured to be +0.80V and 2.46V, which

generates the electrically determined transition energy of 3.26eV (380nm). The difference of the optically determined band gap and electrically determined one is 532nm (2.33eV) 521nm (2.38eV) = 11nm (0.05eV).

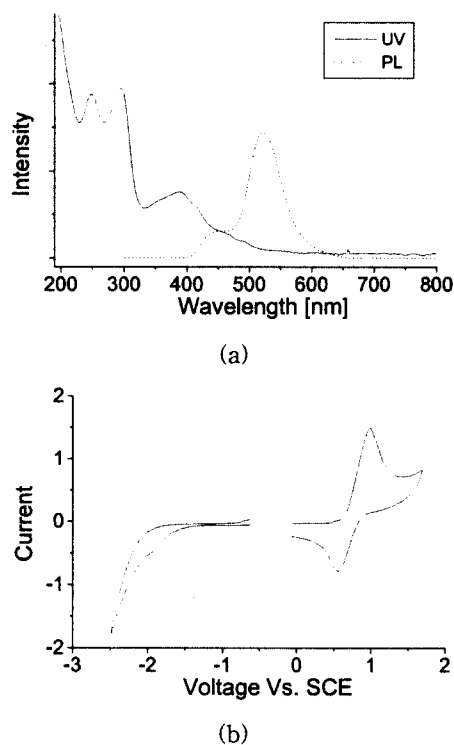


Fig. 1. UV-visible absorption spectra and PL spectra (a), and cyclovoltammogram (b) of Ir(ppy)₃.

The absorption spectrum of Ir(m-ppy)₃ film shown in Figure 2(a) exhibits the absorption maxima at 248nm, 294nm, 389nm, and 488nm. The absorption edge of 520nm (2.38eV) was resolved from the absorption band with the maximum at 488nm. The PL spectrum shows the fluorescence maximum at 528nm, from which 482nm (2.57eV) onset was resolved.

Cyclic voltammogram and constant current potentiogram of Ir(m-ppy)₃ are shown in Figure 2 (b). The IP, EA and the first E_g were 5.36eV, 2.96eV and 2.40eV (517nm) determined from the initial oxidation-reduction

potential at +0.56V and 1.84V about the SCE electrode. The electrical determined transition energy was 2.92eV (425nm) based on the first inflection potentials observed at +0.64V, and 2.28V. The second oxidation-reduction potentials were measured at +0.62V and 1.92V, which yielded the second transition energy of 2.54eV (488nm). The second transition energy was 3.21eV (386nm) based on the first inflection potentials observed at +0.87V and 2.34V. The difference of the optical and electrical band gap is 520nm (2.38eV) 517nm (2.40eV) = 3nm (0.02eV).

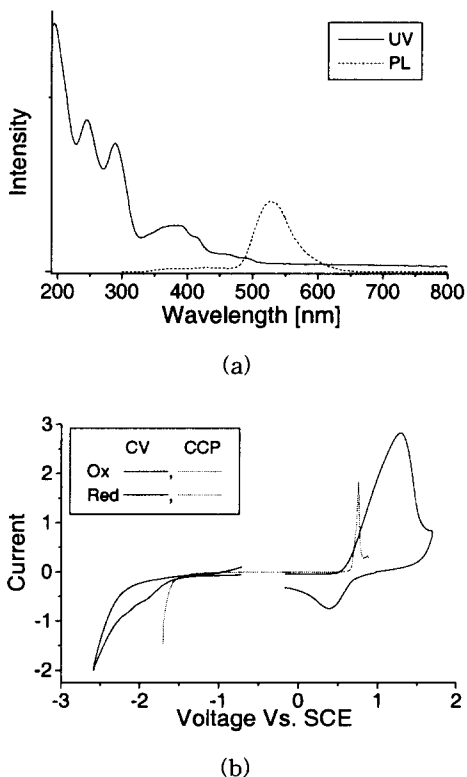


Fig. 2. UV-visible absorption spectra and PL spectra (a), and cyclic voltammogram (b) of Ir(m-ppy)₃.

The UV spectrum of Ir(p-toly)₃ films shown in Figure 3(a) exhibits the absorption maxima of 246nm, 295nm, 362nm, and 485nm.

The absorption edge of 528nm (2.35eV) was resolved from the absorption band with the maximum at 485nm. The PL spectrum shows the fluorescence maximum at 525nm, from which 484nm (2.56eV).

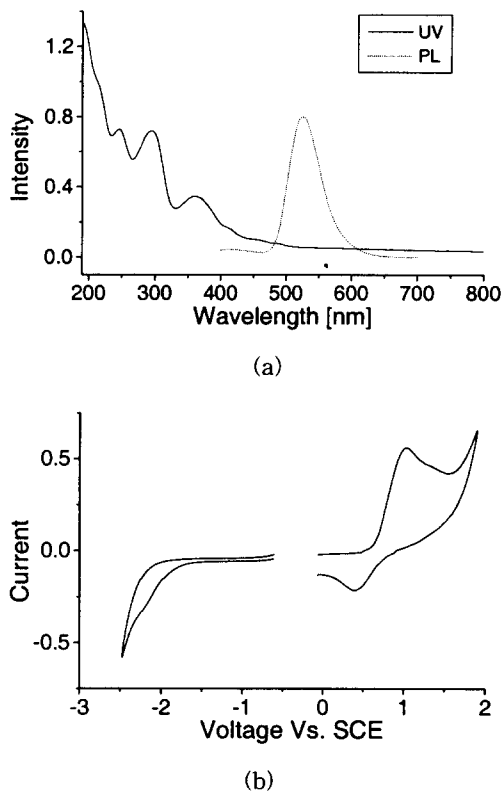


Fig. 3. UV-visible absorption spectra and PL spectra (a), and cyclic voltammogram (b) of Ir(p-toly)₃.

Cyclic voltammogram of Ir(ppy)₃ was shown in Figure 3 (b). The IP, EA and the first Eg were 5.35eV, 2.97eV and 2.38eV (521nm) determined from the initial oxidation-reduction potential at +0.55V, and 1.83V about the SCE electrode. The electrically determined transition energy was 2.59eV (479nm) based on the first inflection potentials observed at +0.64V, and 1.95V. The second oxidation-reduction potentials were measured at +0.64V and 1.88V, which yielded the second transition energy of 2.52eV

Table 1. Transition Energy, Ionization Potential, Electron Affinity and Band Gap of Iridium Complexes

	Ir(ppy) ₃	Ir(m-ppy) ₃	Ir(p-toly) ₃
Absorption lowest transition energy	2.54	2.54	2.55
Fluorescence energy (max.)	2.37	2.34	2.36
IP	5.40	5.36	5.35
EA	3.02	2.96	2.97
Band gap	2.38	2.40	2.38

(492nm). The second transition energy was 3.09eV (401nm) based on the first inflection potentials observed at +0.91V and 2.18V. The difference of the optical and electrical band gap is 528nm (2.35eV) - 521nm (2.38eV) = 7nm (0.03eV).

The transition energy and band gap were summarized in the Table 1.

4. Conclusions

In summary, we have reported the redox properties of Ir(ppy)₃, Ir(m-ppy)₃, and Ir(p-toly)₃ measured by cyclic voltammetry and optical absorption. The electrochemically determined electron affinity and ionization potential values of the Iridium complexes were 5.40eV/3.02eV for Ir(ppy)₃, 5.36eV/2.96eV for Ir(mppy)₃, and 5.35eV/2.97eV for Ir(p-toly)₃ from the SCE. The band gaps obtained from cyclic voltammetry agree with the optical band gaps of absorption spectrum.

References

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