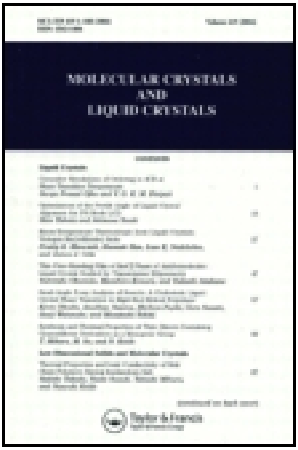

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STUDY ON THE ELECTROCHEMICAL PROPERTIES OF PFVYCFV, PFVDPV AND PFVTPV

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STUDY ON THE ELECTROCHEMICAL PROPERTIES OF PFVYCFV, PFVDPV AND PFVTPV

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The effects of molecular structure on the redox properties are explored by the cyclic voltammetry and spectroscopy using the thin films of organic electroluminescence materials of poly(9,9′-dioctyl-2,7-fluorenediyl vinylene-co-9-cyanamide-2,7-fluorenediyl vinylene); PFVYCFV, poly(9,9′-dioctyl-2,7-fluorenediyl vinylene 2,5-dicyano-1,4-phenyl vinylene); PFVDPV and poly(9,9′-dioctyl-2,7-fluorenediyl vinylene 2,3,5,6-tetracyno-1,4-phenyl vinylene); PFVTPV. The PFVYCFV, PFVDPV and PFVTPV show the UV/visible absorption maxima at 413 nm, 448 nm and 400 nm, respectively. Photoluminescence (PL) of these materials is blue-green color. The measured electrochemical ionization potential and electron affinity of these materials are 5.72 eV/3.19 eV for PFVYCFV, 5.79 eV/3.26 eV for PFVDPV and 5.62 eV/3.48 eV for PFVTPV. The electochemical bisection (oxidation & reduction) energy gaps of PFVYCFV, PFVDPV and PFVTPV about PL onset are 2.93 eV, 2.97 eV and 3.08 eV that are 5.09 eV & 2.97 eV, 5.89 eV & 2.92 eV and 6.17 eV & 3.09 eV with respect to vacuum level, respectively.

Keywords: EA; electroluminescence; IP; PFVYCFV; PFVDPV; PFVTPV; voltammetry

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INTRODUCTION

Ionization potential (IP) and band gap (E_g) of organic materials can be measured by spectroscopic method such as UPS (Ultraviolet Photoelectron Spectroscopy) and UV/visible absorption spectrum. Another method of measuring electrochemical ionization potential and electron affinity uses an oxidation and reduction reaction. A cyclic voltammogram curve shows several peaks as the UV/visible absorption spectrum. While the UV/visible absorption spectrum gives an energy gap between HOMO and LUMO, the electrochemical measurement gives an absolute value of the oxidation and reduction reaction with respect to a vacuum level.

In this study, by comparing the electrochemical rising potential (i.e. the rising point of current due to a reaction of oxidation and reduction) and inflection potential (i.e. the decreasing point of current due to reaction of oxidation and reduction), spectroscopic onset and maxima of PFVYCFV, PFVDPV and PFVTPV, the electrochemical properties such as ionization potential, electron affinity and onset value of PL are analyzed, which are necessary to the study of organic light emitting diodes.

Synthesized molecular structures of PFVYCFV, PFVDPV and PFVTPV are shown in Figure 1. The cyclic voltammograms are measured using the laboratory-made system. We developed new methodology for the electrochemical analysis. The ionization potentials of organic materials are obtained under an indium-tin-oxide (ITO) electrode and the electron affinity with Al electrode. The ITO working electrode and Al working electrode area is $0.5 \times 2.0\,\text{cm}^2$, and the thickness of PFVYCFV, PFVDPV and PFVTPV film on ITO electrode is about 1000 Å, respectively. The ITO coated glass substrate with sheet resistance of $30\,\Omega/\square$ is purchased from Samsung Co.. The Al electrode is evaporated at the pressure of 10^{-6} torr. Acetonitile and DMF are obtained from Johnson Matthey Electronics and are used as received. Tetrabutylammonium perchlolated (Bu_4NClO_4) are obtained from TCI. For cyclic voltammetry, an electrolyte solution of 0.1 M Bu_4NClO_4 in acetonitrile or DMF is used in our experiments. All solutions in the cell are purged with ultrahigh-purity N_2 for 10-15 min before the experiment.

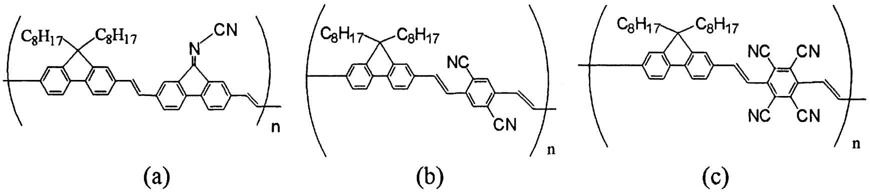


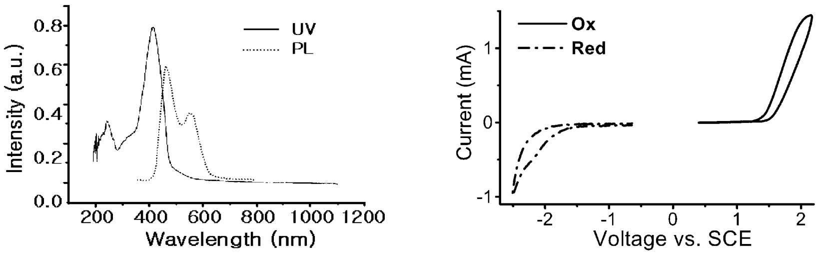
FIGURE 1 Molecular structures of (a)PFVYCFV, (b)PFVDPV and (c)PFVTPV.

A three-electrode compartment electrochemical cell consisted of ITO or Al as the working electrode in sample grafted, a platinum wire of 0.6 mm as the counter electrode, and Ag/Ag^+ (0.1 M $AgNO_3$ solution) is used as a reference electrode. The cyclic voltammograms are obtained with a voltage scan rate of 150 ~ 100 mV/s. The IP and EA analysis of PFVYCFV, PFVDPV and PFVTPV are performed in three steps. First, the preparation of compound films is spin-coated on the working electrode (ITO and Al). Second, this working electrode is put in the electrochemical cell (the electrolyte, counter electrode and reference electrode), and oxidation/reduction potential of the Ag/Ag^+ reference electrode is measured and analyzed with cyclic voltammetry. Finally, a potential conversion of the reference electrode is carried out by criterion materials. In this potential conversion, ferrocene and Alq_3 are used as criterion materials.

A potential conversion constant of SCE reference electrode vs. Ag/Ag^+ reference electrode is +0.31 V with DMF or +0.41 V with acetonitrile, and potential conversion constant of SCE reference electrode vs. ionization potential, electron affinity of electrochemical potential is +4.8 [1–8]. The UV/visible absorption spectra of are obtained using the Hewlett Packard 8425A spectrometer. PL is obtained using the Perkin Elmer LS50B in air. Thickness measurements of various films are carried out with α-step 200 profilometer and ellipsometer. All processing steps and characterization measurements are carried out under the air at room temperature.

RESULTS AND DISCUSSION

The UV/visible absorption and PL spectra of PFVYCFV films are shown in Figure 2(a). The UV/visible absorption spectrum shows the peak at the wavelengths of 240 nm and 413 nm, which lead the edge of 490 nm from the peak of 413 nm. The π-π^* optical band gap (E_g) has λ_{edge} = 490 nm. The PL



(a) (b)

FIGURE 2 (a)UV/visible and PL spectra, and (b) cyclic voltammogram of PFVYCFV.

spectrum shows the peaks at the wavelengths of 454 nm and 546 nm, which lead the onset of 418 nm. The cyclic voltammogram and potentials of PFVYDFV are shown in Figure 2(b) and Table 1. First rising potentials of the oxidation and reduction are appeared at +0.92 V and −1.61 V with respect to the SCE electrode, respectively. Then the electron removal energy (Inonization Potential; IP), electron addition energy (Electron Affinity; EA) and bisection energy gap (band gap; E_g) yields 5.72 eV, 3.19 eV and 2.53 eV. The optical and electrical band gaps are agreed with 2.53 eV (490 nm). The inflection potentials about the first rising potentials (+0.92 V and −1.61 V) are appeared at +1.14 V (5.94 eV) and −1.83 V (2.97 eV) that yields the electrical UV_{Max} (electrical potential gap) of 2.97 eV (418 nm). Second rising potentials of the oxidation and reduction leads to +1.10 V and −1.83 V that yield the bisection energy gap of 2.93 eV (423 nm). The inflection potentials of the oxidation and reduction with respect to the second rising potentials are measured to be +1.28 V and −1.98 V that yield the electrical UV_{Max} (electrical potential gap) of 3.26 eV (380 nm). Third and fourth rising potentials of the oxidation/reduction are measured to be +1.24 V/−1.94 V and +1.38 V/−2.12 V which yield the bisection energy gap of 3.18 eV (376 nm) and 3.50 eV (3.54 nm). The

TABLE 1 The Potentials of PFVYCFV, PFVDPV and PFVTPV.

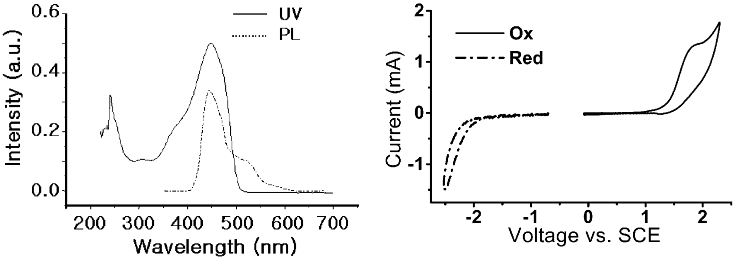
	Rising potentials (E_g)[1]	Inflection potentials (UV_{Max})[2]
PFCYVEV		
First	+0.92 V & −1.61 V = 2.53 eV	+1.14 V & −1.83 V = 2.97 eV
Second	+1.10 V & −1.83 V = 2.93 eV	+1.28 V & −1.98 V = 3.26 eV
Third	+1.24 V & −1.94 V = 3.18 eV	+1.42 V & −2.14 V = 3.56 eV
Fourth	+1.38 V & −2.12 V = 3.50 eV	+1.62 V & −2.39 V = 4.01 eV
PFVDPV		
First	+0.99 V & −1.54 V = 2.53 eV	+1.18 V & −1.70 V = 2.88 eV
Second	+1.09 V & −1.88 V = 2.97 eV	+1.44 V & −2.04 V = 3.48 eV
Third	+1.30 V & −2.00 V = 3.30 eV	+1.89 V & −2.21 V = 4.10 eV
Fourth	+1.90 V & −2.17 V = 4.07 eV	–
PFVTPV		
First	+0.82 V & −1.32 V = 2.14 eV	+1.00 V & −1.48 V = 2.48 eV
Second	+1.02 V & −1.43 V = 2.45 eV	+1.29 V & −1.55 V = 2.84 eV
Third	+1.11 V & −1.54 V = 2.65 eV	+1.52 V & −1.72 V = 3.24 eV
Fourth	+1.37 V & −1.71 V = 3.08 eV	+1.81 V & −1.91 V = 3.72 eV

[1] Rising potential: the rising point of current due to a reaction of oxidation and reduction.

[2] Inflection potentials: the decreasing point of current due to a reaction of oxidation and reduction.

inflection potentials of the oxidation and reduction with respect to the third and fourth rising potentials are measured to be +1.42 V/−2.14 V and +1.62 V/−2.39 V which yields the electrical UV_{Max} (electrical potential gap) of 3.56 eV (348 nm) and 4.01 eV (309 nm). The electrical hole gap (difference between +1.14 V and +0.92 V) and electron gap (difference between −1.83 V and −1.61 V) with respect to the first rising and inflection potentials are obtained to be 0.22 eV. Thus this materials is identified to be the supply of electron and hole with respect to the first rising and inflection potentials.

The UV/visible absorption and PL spectra and PFVDPV films are shown in Figure 3(a). The UV/visible absorption spectrum shows the peak at the wavelengths of 240 nm of 448 nm, which lead the edge of 495 nm from the peak of 448 nm. The π-π^* optical E_g has $\lambda_{edge} = 495$ nm. The PL spectrum shows the peaks at the wavelengths of 440 nm and 530 nm, which lead the onset of 410 nm. The cyclic voltammogram of PFVDPV is shown in Figure 3(b) and Table 1. First rising potentials of the oxidation and reduction are appeared at +0.99 V and −1.54 V with respect to the SCE electrode, respectively. Then the electron removal energy (IP), electron addition energy (EA) and bisection energy gap (E_g) yield 5.79 eV, 3.26 eV and 2.53 eV (490 nm). The inflection potentials about the first rising potentials are appeared at +1.18 V and −1.70 V that yields the electrical UV_{Max} of 2.88 eV (431 nm). The difference of optical and electrical UV_{Max} is 448 nm − 431 nm = 17 nm. Second rising potentials of the oxidation and reduction are lead to +1.09 V and −1.88 V that yields the bisection energy gap of 2.97 eV (418 nm). The inflection potentials of the oxidation and reduction about +1.09 V and −1.88 V are measured to be +1.44 V and −2.04 V that yields the electrical UV_{Max} of 3.48 eV (356 nm). Third rising potentials of the oxidation and reduction are measured to be +1.30 V and −2.00 V that yields the bisection energy gap of 3.30 eV (376 nm). The inflection potentials of the oxidation and reduction about +1.30 V and

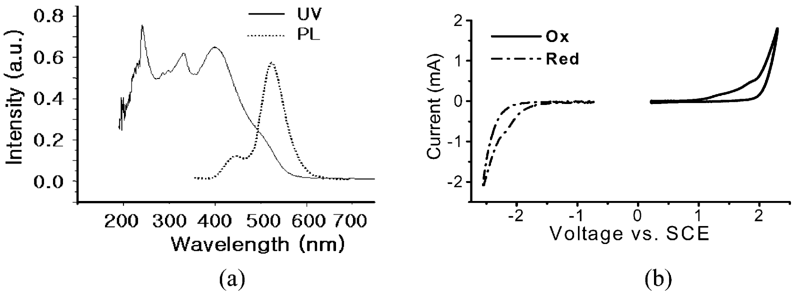


(a) (b)

FIGURE 3 (a) UV/visible and PL spectra, and (b) cyclic voltammogram of PFVDPV.

−2.00 V are measured to be +1.89 V and −2.21 V that yields the electrical UV_{Max} of 4.10 ev (302 nm). The electrical hold gap (difference between +1.18 V and +0.99 V) and electron gap of (difference between −1.70 V and −1.54 V) with respect to the first rising and inflection potentials are obtained to be 0.19 eV and 0.16 eV. Thus this material is a little better supplied with hole than electron with respect to the first rising and inflection potentials.

The UV/visible absorption and PL spectra of PFVTPV films are shown in Figure 4(a). The UV/visible absorption spectrum shows the peak at the wavelengths of 286 nm and 298 nm, 332 nm and 400 nm. The edge leads 560 nm around to 490 nm peak. The π-π^* optical E_g has $\lambda_{edge} = 560$ nm. The PL spectrum shows the peaks at the wavelengths of 440 nm and 525 nm, which lead the onset of 410 nm. The cyclic voltammogram of PFVTPV is shown in Figure 4(b) and Table 1. First rising potentials of the oxidation and reduction are appeared at +0.82 V and −1.32 V with respect to the SCE electrode, respectively. Then the electron removal energy (IP), electron addition energy (EA) and bisection energy gap (E_g) yields 5.62 eV, 3.48 eV and 2.14 eV (579 nm). The inflection potentials with respect to the first rising potentials are appeared at +1.00 V and −1.48 V that yields the electrical UV_{Max} of 2.48 eV (500 nm). Second rising and inflection potentials of the oxidation and reduction are measured to be +1.02 V/−1.43 V and +1.29 V/−1.55 V which yields the bisection energy gap of 2.45 eV (506 nm) and electrical UV_{Max} of 2.84 eV (437 nm). Third rising and inflection potentials of the oxidation and reduction are measured to be +1.11 V/ −1.54 V and +1.52 V/−1.72 V which yields the bisection energy gap of 2.65 eV (468 nm) and electrical UV_{Max} of 3.24 eV (383 nm). Fifth rising and inflection potentials of the oxidation and reduction are measured to be +1.37 V/−1.71 V and +1.81 V/−1.91 V which yields the bisection energy gap of 3.08 eV (403 nm) and electrical UV_{Max} of 3.72 eV (333 nm).



(a) (b)

FIGURE 4 (a) UV/visible and PL spectra, and (b) cyclic voltammogram of PFVTPV.

The bisection energy gap of 3.08 eV is similar to PL onset of 3.02 eV (410 nm). The electrical hole gap of (difference between +1.00 V and +0.82 V) and electron gap of (difference between −1.48 V and h−1.32 V) with respect to the first rising and inflection potentials are obtained to be 0.18 eV and 0.16 eV. Thus this material is a little better supplied with hole than electron with respect to the first rising and inflection potentials.

CONCLUSION

We have performed the electrochemical analysis of the organic luminescence materials of PFVYCFV, PFVDPV and PFVTPV. The measured electrochemical IP and EA are 5.72 eV & 3.19 eV for PFVYCFV, 5.79 eV & 3.26 eV for PFVDPV and 5.62 eV & 3.48 eV for PFVTPV with respect to the SCE electrode. The electrical bisection energy gap of 2.14 eV and UV/visible absorption E_g of 2.21 eV of PFVTPV are smaller than those of PFVYCFV (2.53 eV & 2.53 eV), PFVDPV (2.53 eV & 2.51 eV). And the PL peaks wavelength of PFVDPV and PFVTPV is longer than that of PFVYCFV.

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