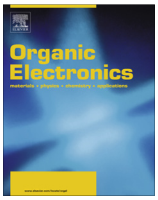
Organic Electronics 20 (2015) 24–30

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Electron affinities of organic materials used for organic light-emitting diodes: A low-energy inverse photoemission study

Hiroyuki Yoshida [a,*], Kei Yoshizaki [b]

[a] *Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
[b] *Idemitsu Kosan Co. Ltd., 1280 Kami-izumi, Sodegaura, Chiba 299-0293, Japan*

ARTICLE INFO

Article history:
Received 22 December 2014
Received in revised form 29 January 2015
Accepted 29 January 2015
Available online 4 February 2015

Keywords:
Low-energy inverse photoemission spectroscopy
Electron affinity
LUMO level
Organic light-emitting diode

ABSTRACT

The electron affinity (EA) of an organic semiconductor is a measure of the electron transport level. Although reliable values of the EA are required for designing the device architecture of organic light-emitting diodes (OLED), there were no appropriate methods. Recently we have developed low-energy inverse photoemission spectroscopy which enables us to determine the EA of organic materials in solid with the precision required for research of OLED. Using this new technique, we precisely determined EA of typical OLED materials, TCTA, CBP, Ir(ppy)$_3$, BCP, Alq$_3$ and Liq as well as a newly developed dopant 4CzIPN. The obtained electron affinities are generally smaller by about 1 eV than the commonly believed values urging the reconsideration of the electron injection/transport mechanisms in OLED. We also compare EAs determined by various experimental and calculation methods for 29 materials. The results show that the reduction potential gives a reasonable estimate rather than the optical gap and ionization energy.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Organic light-emitting diodes (OLED) are a promising new technology for flat-panel displays and interior lighting. Since the first report of the electroluminescence in organic material in 1960s [1], external quantum efficiency and operating voltage are markedly improved by harvesting the triplet exciton [2–7], controlling the molecular orientation of emitter molecule [7–9] and introducing multilayer structures [10–13]. Particularly, multilayer devices can decrease the carrier injection barriers at the interfaces and efficiently confine the carriers into the emissive layer. Following the monumental development of the two layer structure by Tang which lowered the operating voltage to 10 V and achieved the brightness of 1000 cd cm^{-2} [10], doping emitting material in host [11], insertion of exciton and hole block layer [12], and electron transport layer [13] has been demonstrated. Now as many as 5 or 7 layers are common.

Designing an efficient multilayer structure requires knowing the precise energy of the hole and electron transport levels of constituent materials [12,14], corresponding to the highest occupied molecular orbital-derived levels (HOMO levels) and the lowest unoccupied molecular orbital-derived levels (LUMO levels), respectively. While the HOMO levels have been examined extensively using photoemission spectroscopy (PES) and photoemission yield spectroscopy (PYS), there was no appropriate method available to accurately measure the LUMO levels. While the reduction potentials measured using cyclic-voltammetry in solution are often used to estimate the electron affinity (the bottom of the LUMO level with respect to the vacuum level), the value measured in solution is inherently different from the electron affinity of solid materials. The electron affinity is also frequently estimated by adding

---

* Corresponding author. Tel.: +81 774 38 3083; fax: +81 774 38 3084.
E-mail address: yoshida@e.kuicr.kyoto-u.ac.jp (H. Yoshida).

http://dx.doi.org/10.1016/j.orgel.2015.01.037
1566-1199/© 2015 Elsevier B.V. All rights reserved.

the optical gap and the ionization energy (the top of the HOMO level with respect to the vacuum level). The optical gap is usually smaller than the transport gap by an amount of 0.2–1.0 eV which is interpreted as the exciton binding energy [15–17], causing the electron affinity to be overestimated.

In principle, inverse photoemission spectroscopy (IPES) can give the electron affinity relevant to the electron transport in the solid material [16,18]. Actually the electron affinity determined by IPES is often regarded as the reference value [19,20]. In this technique, an electron is introduced to the surface of sample material and a photon is emitted due to the radiative transition to the unoccupied levels. From the onset of the photon signal, the electron affinity is determined. The uncertainty involved is, however, often assumed to ±0.35 eV [19], substantially higher than PES, its complementary method for determining the ionization energy. The fundamental problem originates from the low cross section of IPES process which is five orders of magnitude smaller than PES [21]. A high intensity electron beam is required to gain sufficient signal intensity resulting in serious damage to organic samples [22,23], and the weak photon signal have to be detected using specially designed photon detector with a high sensitivity and an inadequate energy resolution [24].

Recently, we developed low-energy inverse photoemission spectroscopy (LEIPS) which solves the both issues [25,26]. The kinetic energy of electron is lowered below 5 eV, the damage threshold of most organic materials [27]. By decreasing the electron energy, the photons in the near ultraviolet range emit which can be analyzed using a high-resolution bandpass filter. So far we have applied LEIPS to various organic materials [26,28–32] demonstrating that the electron affinities are determined with the precision similar to PES without damaging the organic samples.

In this study, we determine the electron affinities of organic materials relevant to OLEDs, including a hole transport material, tris(4-carbazoyl-9-ylphenyl)amine (TCTA), a host material, 4,4′-bis(carbazol-9-yl)biphenyl (CBP) [3], a phosphorescent material, tris(2-phenylpyridinato)iridium(III) ($Ir(ppy)_3$) [3], electron transport materials, (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) (BCP) [3,33], 8-hydroxyquinolinolato-lithium (Liq) [34] and tris(8-hydroxyquinolinato)aluminum (Alq_3) [10], a hole injection material, 2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexaazatriphenylene (HAT-CN) and a recently developed thermally activated delayed-fluorescent material (TADF), 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) [6]. In addition to these most frequently used materials, we determine electron affinities of 22 materials designed and developed specially for the OLED application by Idemitsu Kosan Co., Ltd. The values determined by LEIPS are compared with those obtained by other commonly used experimental methods, such as the reduction potential and the difference between the ionization energy and optical gap as well as calculated values of the LUMO orbital energy, the electron affinity, and the sum of the ionization energy and singlet excitation energy based on the density functional method.

2. Experimental

The thin films were prepared by vacuum deposition method on a 100-nm-thick indium-tin oxide (ITO) film or an 80-nm-thick Al film on a glass plate at a pressure lower than 10^{-5} Pa. Prior to the vacuum deposition, the ITO coated glass was treated by the UV ozone followed by Ar plasma. The thicknesses of the films were 5, 25 and 50 nm while the deposition rate was kept to 0.1 nm s^{-1} monitored by a quartz micro balance.

The prepared films were exposed to air and introduced to the LEIPS apparatus evacuated to lower than 10^{-7} Pa. The detail of the experimental apparatus is described elsewhere [35]. Mono-energetic electron beam was introduced to the sample surface with the sample current between 0.4 and 0.5 μA. Under this condition, any spectral change due to the sample degradation was not observed. The emitted photons are collected and focused using a quartz lens into the photon detector consisting of a bandpass filter and photomultiplier tube. The bandpass filters with the following nominal center wavelengths (the corresponding photon energies in the parenthesis) were used: 254 nm (4.885 eV), 260 nm (4.785 eV), 280 nm (4.455 eV), 285 nm (4.377 eV), 335 nm (3.713 eV), 387 nm (3.203 eV), 434 nm (2.859 eV). Overall energy resolution was about 0.3 eV.

The ionization energies were measured using PYS in air on Riken Keiki AC-3 for the 50-nm-thick films on the ITO glass at the light intensity of 1 nW. The square root of photoemission yield is plotted against the photon energy and the ionization energy is determined as the onset of the spectrum. The optical gaps were measured in toluene solution with the concentration of about 10^{-5} mol L^{-1} on Hitachi UV–vis spectrometer U3310. Cyclic voltammetry were performed using a potentiostat (ALS Co., Ltd., Model 2325). The sample was dissolved in N,N-dimethylformamide (DMF) and tetrabutylammonium perchlorate ($t\text{-}Bu_4NClO_4$) was mixed as a supporting electrolyte. Glass carbon, Pt, and Ag/AgCl were used as the working electrode, the counter electrode and the reference electrode, respectively. The first oxidation potential of ferrocene was used as a reference.

3. Calculation

The density functional (DFT) calculations were performed for a single molecule using the hybrid density functional B3LYP with the 6-31G(d) basis set on Gaussian 09 program package [36]. The adiabatic electron affinity was obtained as the energy difference between the anion and neutral molecule at the optimized geometry for each state. The singlet excitation energy is calculated with time-dependent DFT (TD-DFT) at the same level.

4. Results and discussion

The aim of this work is to determine the electron affinities of organic materials as a measure of electron transport levels in OLED. This means that the obtained values should

Download English Version:

https://daneshyari.com/en/article/1263724

Download Persian Version:

https://daneshyari.com/article/1263724

Daneshyari.com