

# Photoelectron spectrometer equipped with open counter for electronic structures of organic materials

D. Yamashita, Y. Nakajima, A. Ishizaki and M. Uda\*

Riken Keiki Co., LTD., Research Dept., Itabashi-ku Tokyo 174-8744 Japan

\* Institute for Nara Art, Waseda University, Shinjuku-ku, Tokyo 162-8644, Japan

([d-yamashita@rikenkeiki.co.jp](mailto:d-yamashita@rikenkeiki.co.jp))

(Received: November 26, 2007; Accepted: January 08, 2008)

A photoelectron spectrometer equipped with an open counter was prepared. This device is capable of detecting, in the open air, low energy electrons excited by photons. We confirmed performance of the spectrometer using several organic materials. The ionization potential of Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, DPSiO<sub>3</sub> and DPSiO<sub>4</sub> were measured to be 5.39, 6.49 and 6.46 eV, respectively. The near edge electronic structures including density of states at HOMOs of Fe-, Ni-, Cu- and H<sub>2</sub>-phthalocyanines were also investigated by the novel spectrometer successfully.

## 1. Introduction

The electronic structures of organic materials used for semiconductor devices can be analyzed with the aid of "Photo-electron Spectroscopy in Air (PESA)" by estimating the work function (WF), the ionization potential (IP) and the density of states (DOS). For this purpose the "open counter" [1-4] must be employed as a detector, because it can detect and count small numbers of low energy photoelectrons, one by one, in the air under atmospheric pressure.

Compared with such photoelectron spectroscopies as X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), PESA has the unique advantage of measuring high energy-resolution and low photo-excitation energies in a non-vacuum environment. A non-vacuum measurement is very useful for persons engaged in investigations on organic semiconductors in powdered or liquid states. Photoelectron spectra excited with low energy photons are very sensitive to change in the energy of the highest occupied molecular orbital (HOMO) or nearby of a condensed matter. In addition, radiation damage can be ignored when organic materials are lightly irradiated with photons with low energies. Hence, researchers in the field of the organic light emitting devices (OLED) have used PESA spectrometers to measure IPs of OLED materials [5-9].

A PESA measurement was carried out as follows. UV photons emitted from a deuterium lamp were monochromatized by a grating spectrometer and focused on a sample. Photoelectrons emitted from the sample were counted by the open counter. Here, the energies of monochromatized UV photons were shifted at 0.05 eV intervals up to 6.20 eV. This is because UV photons with energies larger than 6.20 eV are much absorbed by air in the pass of UV photons.

In this work, we prepared a new type of PESA, which is operated under irradiation of far UV photons (PESA-FUV). The passage of UV photons in the spectrometer for PESA-FUV was filled with N<sub>2</sub> gas in place of air to reduce absorption of UV photons by oxygen molecules. In order to confirm performance of this newly designed photoelectron spectrometer, we measured IPs of Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, DPSiO<sub>3</sub> and DPSiO<sub>4</sub>. The observed and calculated DOS of Fe-, Ni-, Cu- and H<sub>2</sub>-phthalocyanines were also compared, where calculated DOS was estimated using the DV-X $\alpha$  molecular orbital calculation method [10].

## 2. PESA-FUV

Experimental setup for PESA-FUV is shown in Fig. 1. N<sub>2</sub> gas is introduced into a chamber 1 through an N<sub>2</sub> inlet 2 with a constant flow rate (2 liter/min) and is discharged

through an N<sub>2</sub> gas outlet 3. UV photons emitted from a deuterium lamp 4 are introduced into the chamber 1 through a window 5 made of MgF<sub>2</sub> and are focused on an entrance slit 8 by use of two concave mirrors 6 and 7. The photons thus focused are made parallel by two concave mirrors 9 and 12, and are reflected by a plane mirror 10. The photons are monochromatized with a diffraction grating 11 and come out through an exit slit 13, which are focused on a sample surface 16 by use of a lens 14 made of CaF<sub>2</sub> through a window 15 made of CaF<sub>2</sub>. Here, the CaF<sub>2</sub> window is used to separate inside of the chamber filled with N<sub>2</sub> and the open air. The distance between the CaF<sub>2</sub> window and a sample placed in the open air was 7 mm. Photoelectrons emitted from the sample 16 were counted by the open counter 17.

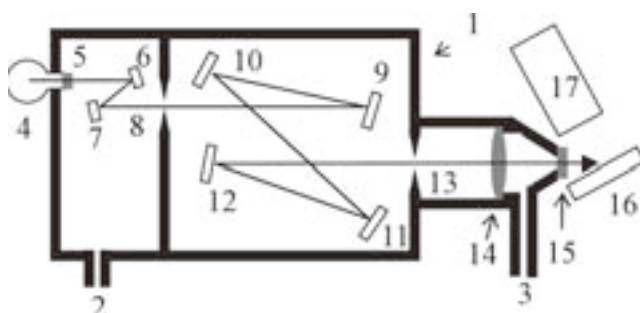


Fig.1 Experimental set up of “photoelectron spectroscopy in air for far UV-photons”.

This apparatus is constructed with the far UV-photon source (1-15), sample or photomultiplier (16) and open counter (17).

1: N<sub>2</sub> chamber, 2: N<sub>2</sub> gas inlet, 3: N<sub>2</sub> gas outlet, 4: deuterium lamp, 5: MgF<sub>2</sub> window, 6, 7: concave mirror, 8: entrance slit, 9: concave mirror, 10: plane mirror, 11: diffraction grating, 12: concave mirror, 13: exit slit 14: CaF<sub>2</sub> lens, 15: CaF<sub>2</sub> window.

The number of counter pulses per second produced at the anode is a function of the number of electrons emitted from the sample. A loss of counts is, however, introduced during the dead time of the counter. Then the number of electrons entered into the counter per second  $N_{in}$  is expressed by a following equation.

$$N_{in} = N_{em} f = \frac{N_{obs}}{1 - \tau N_{obs}} \quad (1)$$

Here,  $N_{em}$  is the number of electrons emitted from the sample per second,  $f$  the fraction of electrons entered into the counter,  $\tau$  the dead time and  $N_{obs}$  the number of observed electrons per second.

The photoelectric quantum yield is derived by dividing

$N_{in}$  by the number of incident photons, which are counted using a phototube (R1080, Hamamatu Photonics) placed at a sample position.

### 3. EXPERIMENTS and RESULTS

Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> was prepared by dropping its solute in ethanol on the indium-tin oxide (ITO)-coated glass substrate. Before the measurement was started, the ethanol in the solute was dried on the substrate at room temperature.

DPSiO<sub>3</sub> and DPSiO<sub>4</sub> were also deposited on an ITO-coated glass. Here Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> has been used for the dye of the Dye-Sensitized Solar Cell (DSC). On the other hand, DPSiO<sub>3</sub> and DPSiO<sub>4</sub> are expected to have high IPs, which have been used for the host material of blue electro-phosphorescence OLEDs. However, their IPs have not yet been investigated using XPS and UPS.

The square roots of photoelectric quantum yields against incident photon energies are shown in Fig. 2 for Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, Fig. 3 for DPSiO<sub>3</sub> and Fig. 4 for DPSiO<sub>4</sub>, respectively. IP of these materials was determined from the energy of an intersecting point between a background line and the extended line of the square root of the photoelectric quantum yield.

IPs of Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, DPSiO<sub>3</sub> and DPSiO<sub>4</sub> were estimated to be 5.88, 6.49 and 6.46 eV, respectively. IP of Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> can be estimated by using a conventional PESA method, where photoexcitation energies up to 6.2 eV are available to use. However, IPs of DPSiO<sub>3</sub> and DPSiO<sub>4</sub> cannot be determined by the method mentioned above because their photoemission threshold energies are larger than 6.2 eV.

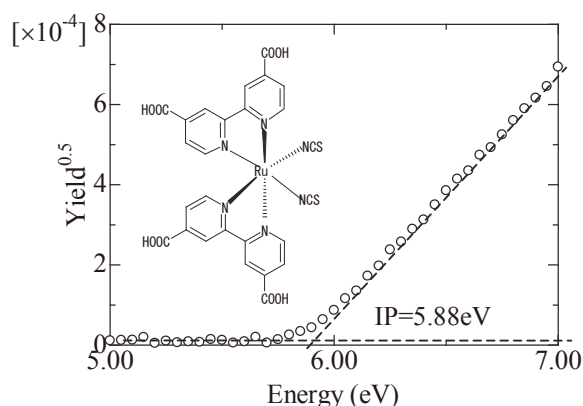


Fig. 2 Square roots of photoelectric quantum yields against incident photon energies for Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> measured by the newly designed photoelectron spectrometer.

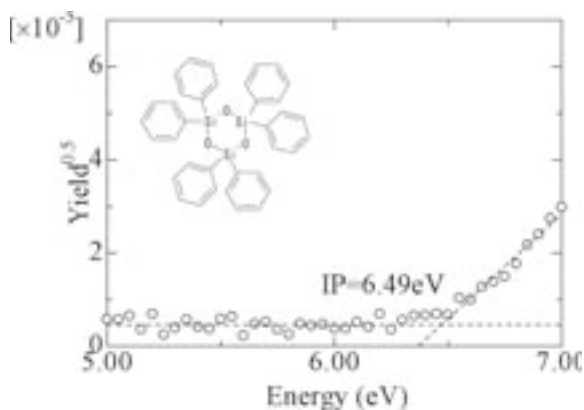


Fig. 3 Square roots of photoelectric quantum yields against incident photon energies for DPSiO<sub>3</sub> measured by the newly designed photoelectron spectrometer.

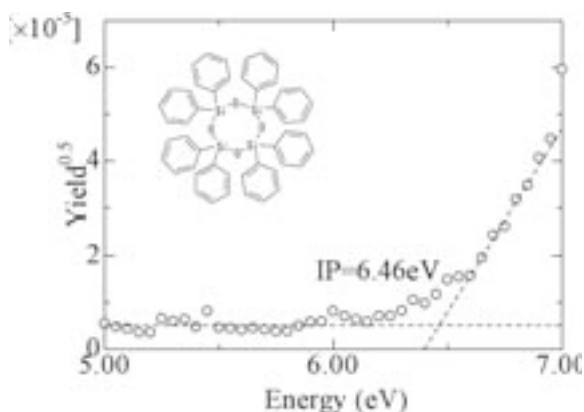


Fig. 4 Square roots of photoelectric quantum yields against incident photon energies for DPSiO<sub>4</sub> measured by the newly designed photoelectron spectrometer.

DOS of Fe-, Ni-, Cu- and H<sub>2</sub>- phthalocyanines was estimated here from PESA-FUV spectra and compared with those obtained from molecular orbital calculations using the DV-X $\alpha$  method [10].

Here, all the phthalocyanines were deposited on an ITO-coated glass. DOS was deduced from differentiating photoelectric quantum yield with incident photon energy. The model used for calculations is shown in Fig. 5. The observed and calculated data are shown in Fig. 6 for Fe-phthalocyanine, Fig. 7 for Ni-phthalocyanine, Fig. 8 for Cu-phthalocyanine, Fig. 9 for H<sub>2</sub>-phthalocyanine, respectively.

Convolution of DOS was carried out adopting the line width of 0.4 eV. The geometries of metallo and metal-free phthalocyanines (MC<sub>32</sub>N<sub>8</sub>H<sub>16</sub> with C<sub>2h</sub> symmetry; M = Fe, Ni, Cu and H<sub>2</sub>) were deduced from an X-ray data [11]. Calculating conditions were as follows: basis sets, 1s - 2p for N, 1s-3p for C, 1s - 2p for O, 1s for H, and 1s - 4p

for Fe, Ni and Cu, and a potential well, 5.0 atomic units in width and -1.0 Hartrees in depth and sampling points, 28500 for all the phthalocyanines. In this calculation, ground state was adopted. Experimentally deduced DOSs were well reproduced by the DV-X $\alpha$  calculations.

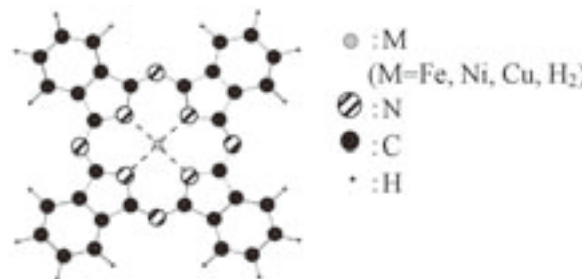


Fig. 5 Geometry of phthalocyanines used for present calculations, where a central metal atom M is substituted with Fe, Ni, Cu and H<sub>2</sub>.

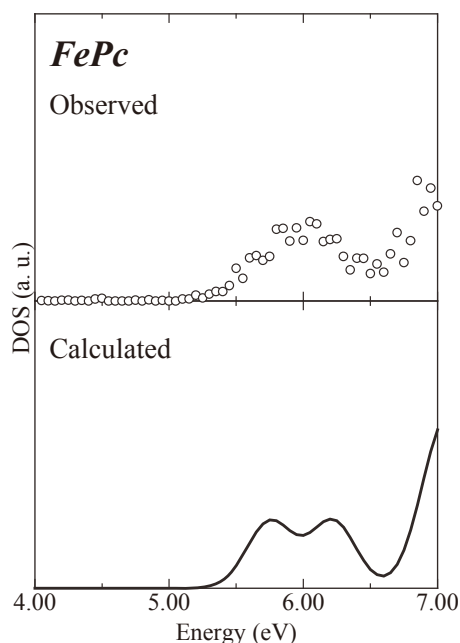


Fig. 6 Comparison of the observed DOS of Fe-phthalocyanine (dots) with the calculations (solid line).

#### 4. CONCLUSIONS

We prepared an apparatus for PESA-FUV which can detect, in the open air, low energy electrons excited with photons with energies up to 7.0 eV using the spectrometer filled with N<sub>2</sub> gas in place of air. Expected performance of the apparatus was obtained by using several kinds of organic materials.

The photoemission threshold energies of Ru(dcbpyH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, DPSiO<sub>3</sub> and DPSiO<sub>4</sub> were successfully estimated to be 5.88, 6.49 and 6.46 eV, respectively

by the PESA-FUV spectrometer. The near edge structures including DOSs in HOMOs of Fe-, Ni-, Cu- and H<sub>2</sub>-phthalocyanines were also deduced from the observed PESA data, which were reproduced by DV-X $\alpha$  molecular orbital calculations.

Such measurements will provide important contribu-

tions to the studies of electronic structures of organic materials.

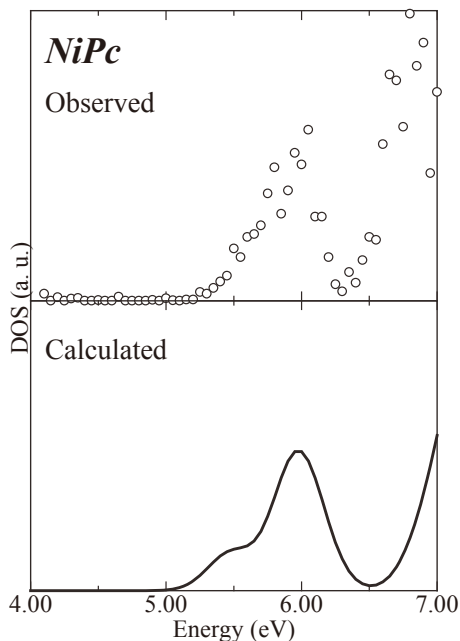


Fig. 7 Comparison of the observed DOS of Ni-phthalocyanine (dots) with the calculations (solid line).

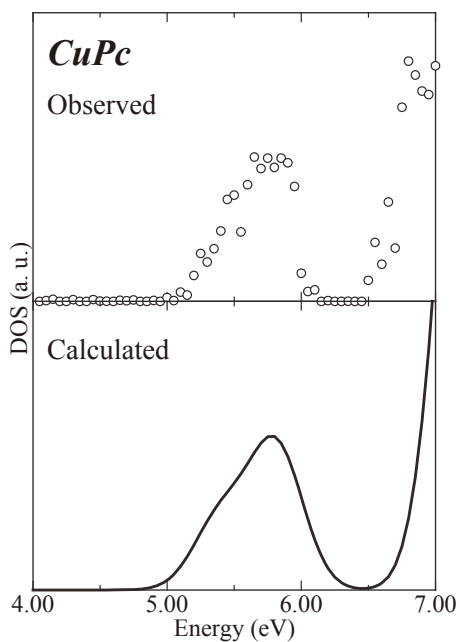


Fig. 8 Comparison of the observed DOS of Cu-phthalocyanine (dots) with the calculations (solid line).

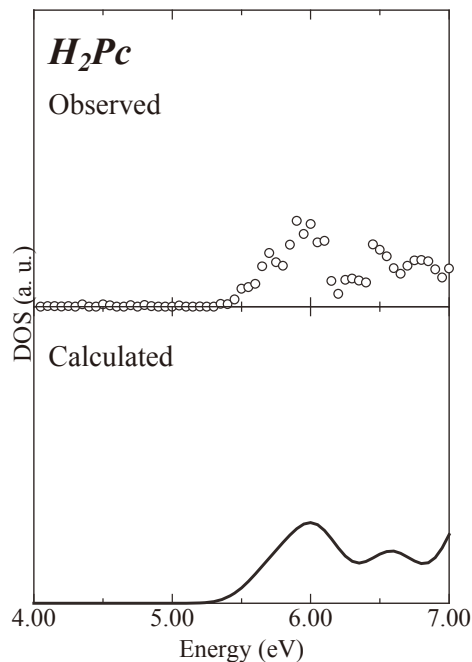


Fig. 9 Comparison of the observed DOS of H<sub>2</sub>-phthalocyanine (dots) with the calculations (solid line).

## 5. REFERENCES

- [1] H. Kirihata, and M. Uda, Rev. Sci. Instr. 52, 68 (1981).
- [2] M. Uda, Jpn. J. Appl. Phys. 24, 284 (1985).
- [3] T. Noguchi, S. Nagashima, and M. Uda, Nucl. Instr. Meth. Phys.Res. A342, 521 (1994).
- [4] S. Nagashima, T. Tsunekawa, N. Shiroguchi, H.Zenba, and M. Uda, Nucl. Instr. Meth. Phys. Res. A373, 148 (1996).
- [5] Y. Nakajima, M. Hoshino, D. Yamashita, and M. Uda, Adv. Quantum Chem. 42, 399 (2003).
- [6] C. Hosokawa, H. Higashi, and T. Kusumoto, Appl. Phys. Lett. 62, 3238 (1993)
- [7] Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H.Nakada, Y.Yonemoto, S. Kawami, and K. Imai, Appl. Phys. Lett. 65, 807 (1994)
- [8] J. Kido, H. Shionoya, and K. Nagai, Appl. Phys. Lett. 67, 2881 (1995)
- [9] C. Adachi, K. Nagai, and N Tamoto, Appl. Phys. Lett. 66, 2679 (1995)
- [10] H. Adachi, M. Tsukada, C. Satoko, J. Phys. Soc. Jpn. 49, 875 (1978).
- [11] K. Yase, N. Yasuoka, T. Kobayashi and N. Uyeda, Acta Cryst. C44, 514 (1988)