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Femtosecond time-resolved two-photon photoemission study of organic semiconductor copper phthalocyanine film

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Abstract

We have carried out a femtosecond two-photon photoemission study of organic semiconductor copper phthalocyanine (CuPc) film. Furthermore, we have carried out the photoemission (PES) and inverse photoemission (IPES) studies. From the simultaneous PES and IPES measurements, the lowest unoccupied molecular orbital, highest occupied molecular orbital, and ionization potential of CuPc film have been directly determined. From the detailed time-resolved two-photon photoemission measurements, it is found that the relaxation lifetime of excited state is extremely short (all below 50 fs) and monotonously became faster with increasing excitation energy. From these results, we discuss the electronic structure and excited-state dynamics in the organic semiconductor CuPc film.

Key words:
Organic semiconductor, Cooper phthalocyanine, Excited-state dynamics, Electronic structure, Time-resolved two-photon photoemission, Photoemission, Inverse photoemission

Organic semiconductors are recently attracting much interest from the viewpoints of both device and fundamental physics. These organic semiconductors are considered to be important constituents of the future devices, such as organic light-emitting diode, organic field effect transistor, and organic solid-state laser [1, 2]. In order to elucidate their detailed physical properties and to develop the future devices, it is indispensable to understand their excited-state dynamics as well as their electronic structures. The femtosecond time-resolved two-photon photoemission (TR-2PPE) spectroscopy is attracting much interest because of its capability to observe the energy-resolved excited electron dynamics [3]. In this work, we have carried out a TR-2PPE study of the organic semiconductor copper phthalocyanine (CuPc) film. Furthermore, we have investigated the detailed electronic structure of CuPc film using ultraviolet photoemission (UPS) and inverse photoemission (IPES) spectroscopies. The family of phthalocyanines have been of considerable interest as materials to be used in electronic and nonlinear optical devices, since they have the high chemical and thermal stability

besides the nature of two-dimensional π-electron conjugation.

TR-2PPE measurements were performed with an ADES 500 (VG Mictrotech Co.) photoelectron spectrometer and a femtosecond self-mode locked Ti:sapphire laser (Tsunami, Spectra Physics Co.). The experimental set-up has been described in detail elsewhere [4]. A CuPc film with a thickness of 100 nm was prepared by vacuum evaporating on Au-coated Si substrate cleaned by Ar^+ sputtering. The output of fundamental light from the Ti:sapphire laser has a pulse width of about 50 fs, pulse energy of about 9 nJ, wavelength of about 750 nm, and a repetition frequency of 82 MHz. The frequency-doubled light with photon energy of 3.3 eV was split into two beams with equal intensities by a beam splitter. One beam was used as a pump pulse to generate the excited-electron in the sample, while the other beam was used as a probe pulse to photoemit the excited-electrons. After one of the beams was passed through the variable delay line, the two beams were recombined to make coaxial beams in order to obtain the both spatial and temporal overlap on the sample surface. The two beams were cross-polarized using a half-wave plate in order to eliminate coherent artifacts due to the coherent two-photon excitation [5]. The pulse width of the frequency-doubled light was about 80 fs and was obtained by deconvolution of a pump-probe scan (cross-correlation trace) of a transition-metal tantalum reference, in which the lifetime of the excited-electron is negligible far above the Fermi level (E_F) (> 3.0 eV) [6]. In order to reduce the effects of stray fields and to extend the range of detection angle being collected, the sample was biased with –10 V. The additional UPS measurement was performed with the He I resonance line ($h\nu$=21.2 eV) as the excitation source. Moreover, IPES measurement was performed using a custom-made spectrometer, composed of an electron gun (ELG-2, Kimball Physics Co.) and a band-pass photon detector. This band-pass photon detector will detect the photons around 9.7 eV, since the high- and low-energy cutoffs are determined by the characteristic absorption of CaF_2 window around 10.1 eV and the ionization potential of multichannel plate coating above 9 eV. All measurements were performed at room temperature.

Figure 1 shows the simultaneous UPS and IPES spectra of CuPc film with a thickness of 100 nm. The inset

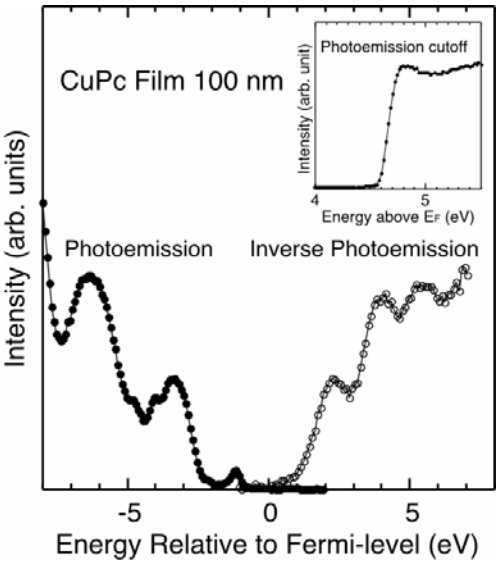

Fig. 1. Combined UPS and IPES spectra of CuPc film with a thickness of 10 nm at room temperature.

of Fig. 1 shows the cutoff the UPS spectrum of CuPc film due to the vacuum level. These spectra are almost same as the previously reported one by Hill *et al.* [7]. The observed UPS spectrum is the representation of the filled states of a molecular cation resulting from the photoemission process modified by the relaxation (polarization). We have defined the onset of photoemission from the highest occupied molecular orbital (HOMO) in the UPS spectrum as the HOMO position, at 0.7 eV below E_F. We have also found the lowest unoccupied molecular orbital (LUMO) position at 1.0 eV above the E_F from the onset of emission from LUMO in the IPES spectrum. This result is consistent with the common observation of a *p*-type-like behavior of CuPc. The energy difference between the HOMO and LUMO positions is almost same as an injection gap or optical gap of about 1.7 eV. From the cutoff of the UPS spectrum as shown in the inset of Fig. 1 and the above HOMO position, it is found that the ionization potential of CuPc film is about 5.3 eV.

Figure 2 shows the two-photon photoemission (2PPE) spectrum of the CuPc film measured with photon energy of 3.3 eV at zero pump-probe delay. As shown in Fig. 2, the observed 2PPE spectrum exhibits a broad feature. From the comparison with the experimental energy structure determined by the above UPS and IPES measurements, it is found that the high-energy edge and low-energy cutoff of the present 2PPE spectrum correspond to the 2PPE from the HOMO and the cutoff due to the vacuum level, respectively. From the measured kinetic energy of the photoelectron (E_k), the corresponding intermediate-state energy (E_i) can be determined by $E_i - E_{HOMO} = I_p + E_k - h\nu$, where I_p is the ionization potential of CuPc film. As shown in Fig. 2, the intermediate-states observed in the 2PPE spectrum correspond to the energy region between 2.0 and 3.3 eV above HOMO. In Fig. 2, there is no spectral intensity in the higher intermediate-state energy region beyond the high-energy edge of the 2PPE spectrum, indicating that there is no 2PPE from electronic states between the Fermi-level and HOMO. This means that there is no midgap state below the Fermi-level in the present CuPc film.

TR-2PPE measurements were carried out by monitoring the number of photoelectrons at a given kinetic energy as a function of delay time between the pump and probe pulses. This pump-probe scan directly

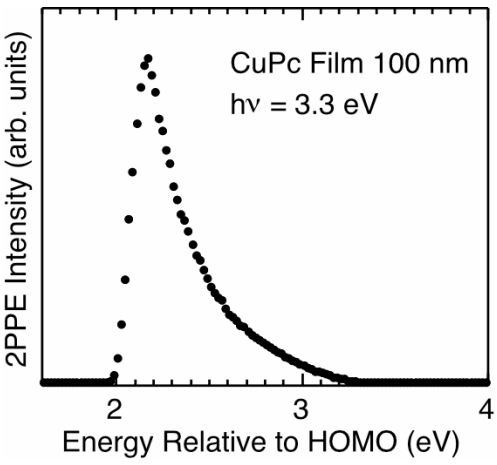

Fig. 2. Two-photon photoemission spectrum of CuPc film measured with a photon energy of 3.3 eV at zero pump-probe delay. Horizontal-axis corresponds to the intermediate-state energy with respect to HOMO.

reflects the temporal evolution of the excited-state population at a given intermediate-state. The present TR-2PPE spectra were measured with a pair of cross-polarized laser pulses. In this case, the temporal profile of the observed cross-correlation trace is described by the convolution of the autocorrelation function of the two laser pulses (Gaussian instrumental function) and the exponential decay function $\exp(-|t|/\tau)$ of the excited states, where τ is the relaxation lifetime of the excited state [5]. Using this expression, we can derive the relaxation lifetimes of excited states at various excitation energies from the experimental cross-correlation traces. In the inset of Fig. 3, we show a cross-correlation trace at the excited-state energy of 2.03 eV relative to HOMO and the exponential fit to experimental result. As shown in the inset of Fig. 3, the observed cross-correlation trace is reproduced fairly well by the convoluted function of a single exponential decay function with the autocorrelation function of the two laser pulses. Figure 3 shows the measured relaxation lifetimes of excited states as a function of excited-state energy relative to HOMO. As shown in Fig. 3, it is found that the relaxation lifetimes of excited states in the present CuPc films are very short (all below 50 fs) and monotonously become faster with increasing excitation energy. In general, the relaxation process can be classified into several processes, which is distinguished by the duration and interaction energies involved [8]. The first process is very fast process and results from the interaction of electron and hole with polarization

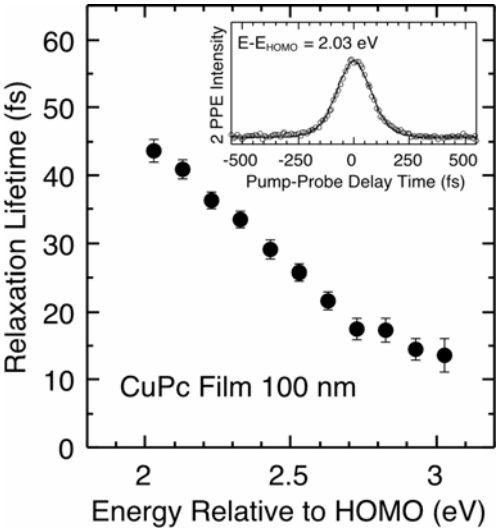

Fig. 3. Relaxation lifetime of excited state as a function of excited-state energy relative to HOMO for CuPc film. The inset shows the cross-correlation trace measured at the excited-state energy of 2.03 eV relative to HOMO.

fluctuations of the medium. In the second process, the excited molecule will undergo a rapid internal conversion process from the highly excited state to the lower levels. This is then followed by a fast vibrational relaxation of these lower levels. However, the relaxation due to the valence electron polarization effects of the medium is extremely fast (0.4-0.5 fs) [8]. On the other hand, in general, the relaxation time due to a radiative decay is several hundreds picoseconds or a few nanoseconds in organic semiconductor films. Therefore, the observed relaxation times can be related to the rapid internal conversion process. Here, the pump pulse with photon energy of 3.3 eV excites the molecule to the excited states, which is isoenergetic with the highly excited vibrational levels of lower-lying states. As a result, the

internal conversion process can be extremely fast.

In summary, we have performed a femtosecond TR-2PPE, PES, and IPES studies of organic semiconductor CuPc film with a thickness of 100 nm. From the simultaneous PES and IPES measurements, the HOMO, LUMO, and ionization potential of CuPc film have been directly determined. From the TR-2PPE measurements, it is found that the relaxation lifetimes of excited states in the present CuPc films are very short (all below 50 fs) and monotonously become faster with increasing excitation energy. We attribute this extremely fast relaxation process of photoexcitation to a rapid internal conversion process.

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