

Direct Evaluation of Spatial Distribution of Electrons Ejected by Two-Photon Ionization of Aromatic Molecules in Ultrathin Polymer Films

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The spatial distribution of electrons ejected by two-photon ionization of aromatic molecules was directly evaluated using a multi-layered structure of ultrathin polymer films where donor (D) and acceptor (A) layers were separated by spacing layers. The results show that electrons ejected by two-photon ionization are mostly captured by an A layer about 2–3 nm away from the D layer.

The spatial distribution of electron–cation pairs formed by high-energy radiation in a condensed phase has been extensively studied in the fields of radiation chemistry and photochemistry.¹ The decay behavior of electron–cation pairs formed in an irradiated polymer solid has been observed through the charge recombination luminescence of the electron–cation pairs at a fixed temperature, which is called isothermal luminescence (ITL). The ITL decay is determined by the charge recombination rate, which is governed by the separation distance of electron–cation pairs. Hama et al. demonstrated that the initial distribution of electron–cation pairs can be evaluated from the Laplace inverse transformation of an empirical equation of ITL decay.^{2,3} According to Hama's procedure, we also evaluated the spatial distribution of electrons ejected by two-photon excitation of aromatic molecules doped in polymer films. Previously, we found that the photoejected electrons are distributed over 3 nm away from the parent cations.^{4,5} However, this evaluation needs to assume parameters for the charge recombination rate.

Here we report the direct evaluation of the spatial distribution of electrons ejected by two-photon ionization of aromatic molecules. In the present study, electrons ejected by photoionization of D molecules were scavenged by A molecules, not captured by the polymer matrix: ejected electrons were converted into A anions. The electron scavenger are usually used under the condition of totally random distribution where the *average* separation distance of D and A pairs is estimated from concentration of the scavenger. Contrary to this method, our system has the *distinct* separation distance of D and A pairs on a scale of nanometers by using a multi-layered structure of Langmuir–Blodgett polymer film. The number of D and A ion pairs formed by photoionization can be estimated from the charge recombination luminescence. Therefore, we have directly evaluated the spatial distribution of electrons ejected by two-photon ionization by measuring the charge recombination luminescence of D and A ion pairs at various separation distances between the D and A molecules.

For preparation of LB films, three kinds of polymers were used: poly[(2-(9-carbazoly)ethyl methacrylate)-*co*-(isobutyl methacrylate)] (P(Cz-iBMA)), poly(vinyl pentanal acetal) (PVPe), and poly[(vinyl pentanal acetal)-*co*-(methyl vinyl terephthalate)] (P(VPe-MTP)). P(Cz-iBMA) was synthesized

by random copolymerization. PVPe was synthesized by acetalization of poly(vinyl alcohol) (PVA, Wako Pure Chem. Ind., Ltd., degree of polymerization = 2000) with 1-pentanal (Wako Pure Chem. Ind., Ltd.). P(VPe-MTP) was synthesized by esterification of PVPe with terephthalic acid monomethyl ester chloride (Tokyo Kasei Kogyo Co., Ltd.). These polymers were purified by reprecipitation from a benzene solution into methanol three times. Detailed synthetic procedures have been described elsewhere.^{6,7} The compositions of P(Cz-iBMA), PVPe, and P(VPe-MTP) were determined from the carbon fraction measured by elemental analysis and from UV absorption spectra of the chromophoric moiety. P(Cz-iBMA) contains ca. 16-mol% carbazole moiety as an electron donor and P(VPe-MTP) contains ca. 10-mol% terephthaloyl moiety as an electron acceptor. The monolayer thickness is reported to be 1.06 nm for P(Cz-iBMA)⁷ and to be 0.90 nm for PVPe and P(VPe-MTP).⁸

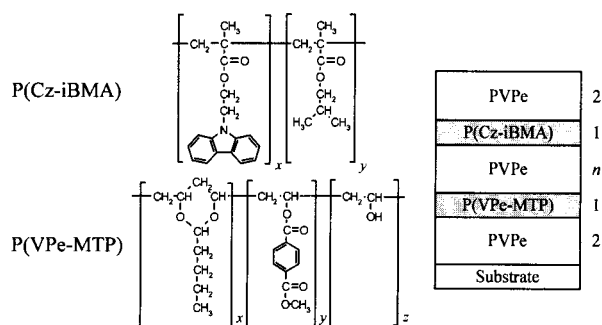


Figure 1. Left; chemical structures of P(Cz-iBMA) and P(VPe-MTP). Right; multi-layered structure of the LB films (D_nA). Shaded layers contain a D or A moiety. The numbers denoted beside the layer structure represent the number of layers.

Each polymer was deposited as a Y or Z-type LB film with a high transfer ratio both in the up and down modes. Detailed procedures of the LB film preparation have been described elsewhere.⁶ Figure 1 shows the chemical structures of polymers used in this study and the layer structure of the LB film, abbreviated as D_nA . The D_nA films were fabricated on the quartz plate in the following sequence: (1) 2 layers of PVPe as the pre-coating layers, (2) 1 layer of P(VPe-MTP) as the electron-accepting layer, (3) n ($= 0, 1, 2, 3, 4, 5$) layers of PVPe as the spacing layers, (4) 1 layer of P(Cz-iBMA) as the electron-donating layer, and (5) 2 layers of PVPe as the protection layers.

The charge recombination luminescence at 20 K (ITL) was measured from 100 to 3000 s after the photoionization by 351-nm light pulses from a XeF excimer laser (Lambda Physik, EMG101MSC; ca. 20 ns fwhm, ca. 30 mJ/cm²). Subsequently, the charge recombination luminescence with increasing temperature (thermoluminescence, TL) was measured from 20 to 340

K at a heating rate of 5 K/min. Details of this measurement apparatus have been described elsewhere.⁴ The steady state emission spectra of the sample films before the photoirradiation were measured at room temperature with a fluorescence spectrophotometer (Hitachi, 850). Both slit widths for excitation and emission were 5 nm. The excitation wavelength was 295 nm where the D moiety was selectively excited.

Intense laser light feeds two photons to D molecules simultaneously⁹ or stepwise via both the excited singlet and triplet states,¹⁰ and then the D molecules are photoionized. In our system, two-photon ionization of the D moiety by 351-nm light (3.5 eV) occurs through the excited triplet state (3.0 eV) as well as the excited singlet state (3.5 eV) as the intermediate. This two-photon ionization produces ejected electrons having an excess energy of ca. 0.5–1 eV, because the ionization potential of the D (Cz) moiety in polymer solids can be estimated to be about 6 eV, considering the polarization energy of D cation to be about 1.5 eV. The ejected electrons are scavenged by A moiety, not by the polymer matrix:¹¹ PVPe can hardly capture ejected electrons contrary to PMMA which can well capture ejected electrons. Although the D and A ion pairs thus formed are stable below the glass transition temperature (T_g) of the matrix polymer, the ion pairs recombine through long-range electron transfer from A anion to D cation even below the T_g .⁵ This charge recombination reproduces the excited states of D moiety and results in emission, i.e., ITL or TL. Thus the number of ion pairs formed in the films can be estimated from the total photon counts of ITL and TL, since the intensity of charge recombination luminescence is proportional to the number of ion pairs formed in the films.

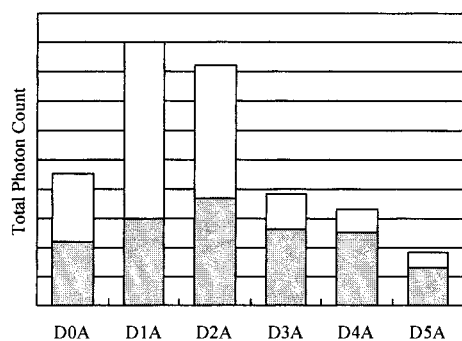


Figure 2. Total photon counts for ITL and TL from the D_nA films. The shaded portion shows the photon counts for ITL from 100 to 3000 s after photoirradiation at 20 K. The open portion shows the photon counts for TL from 20 to 340 K at a heating rate of 5 K/min.

Figure 2 shows the photon counts for ITL and TL: the shaded portion represents the photon count for ITL from 100 to 3000 s after the photoionization at 20 K, and the open portion that for TL from 20 to 340 K. With the heating of the samples up to 340 K, most of the ion pairs formed by two-photon ionization recombined,^{12,13} because the higher temperature (340 K) is above the T_g of PVPe (327 K⁸). The total photon count was maximal for D1A or D2A, and steeply decreased with the increase in the number of spacing layers. This indicates that the number of ion pairs formed is the largest for the D1A or D2A film in which the average separation distance between the D

and A layers is about 2–3 nm. This shows that most of the electrons are ejected about 2–3 nm away from the D layer by two-photon ionization. On the other hand, the total photon count for D0A was less than that for D1A or D2A. This decrease in photon count is probably due to the fluorescence quenching and/or the fast charge recombination of ion pairs whose separation distance is short. The separation distance obtained in this study is in agreement with the distribution peak of electron–cation pairs evaluated from the Laplace inverse transformation of the ITL.⁵ However, the latter evaluation needs to assume two parameters with a frequency factor ν and a damping factor β for the electron transfer rate: $k(r) = \nu \exp(-\beta r)$. The present results were obtained by the direct observation of the separation distance of ion pairs without any assumed parameters.

We conclude that the spatial distribution of electrons ejected by two-photon ionization of aromatic molecules can be directly evaluated by measuring the charge recombination luminescence of D and A ion pairs formed in a multi-layered structure of ultrathin polymer films where the separation distance between the D and A layers is controlled on a scale of nanometers. The results show that electrons ejected by two-photon ionization are distributed about 2–3 nm away from the parent cations.

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