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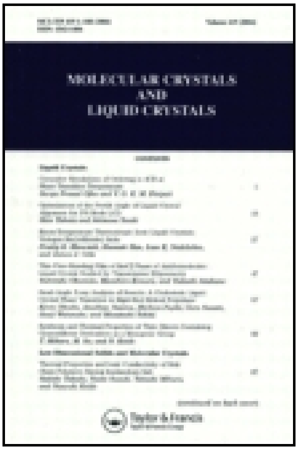

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Excitonic Photoemission in Organic Crystals

Ryuzi Katoh [a] & Masahiro Kotani [a]

[a] Faculty of Science, Gakushuin University Mejiro, Tokyo, 171, Japan

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EXCITONIC PHOTOEMISSION IN ORGANIC CRYSTALS

RYUZI KATOH AND MASAHIRO KOTANI
Faculty of Science, Gakushuin University
Mejiro, Tokyo 171, Japan

Abstract Excitonic photoemission has been studied in aromatic hydrocarbon crystals (anthracene, naphthacene, α-perylene and p-terphenyl). Two mechanisms could be identified: (1) singlet exciton annihilation

$$S_1 + S_1 \longrightarrow e^-$$

and (2) photoionization of singlet exciton

$$S_1 + h\nu \longrightarrow e^- .$$

INTRODUCTION

External photoemission has been studied extensively in organic crystals[1]. Most of them are concerned with single photon excitation. Only a few studies have been reported on photoemission via excited states. Information about unoccupied electronic levels and dynamics of higher excited states can be obtained through this type of measurements. We have made the measurements of external photoemission via excited states using multi-photon or multi-step excitation in anthracene single crystals[2,3]. The mechanism of the photoemission was determined through the measurements of action spectra[2]. When two-color, two-step excitation was applied, the photoemission could be observed from a specific excited state such as the lowest excited singlet state[3]. Here we report the threshold energies for external photoemission via singlet exciton in p-terphenyl and naphthacene crystals. The time profile of the photoemission could be measured in α-perylene crystal.

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EXPERIMENTAL

Measurements of excitonic photoemission were made with pulsed laser excitation. The pressure in the vacuum chamber was 1 x 10^{-7} Torr during the measurements. Emitted electron currents was amplified by an electron multiplier and was processed with a transient digitizer. Time profile of emitted electrons was measured by time-correlated single-electron counting method (Fig.1). The pulse width of the laser was 1ns. The time resolution of the detection system was better than 1ns.

RESULTS AND DISCUSSION

(1) Photoemission by singlet exciton fusion (annihilation)

When an anthracene crystal is excited with a light pulse in the near-UV, external photoemission due to singlet exciton fusion (annihilation) is observed[2]. Similar observation can be made with an α-perylene crystal. Figure 2 shows the time profile of the

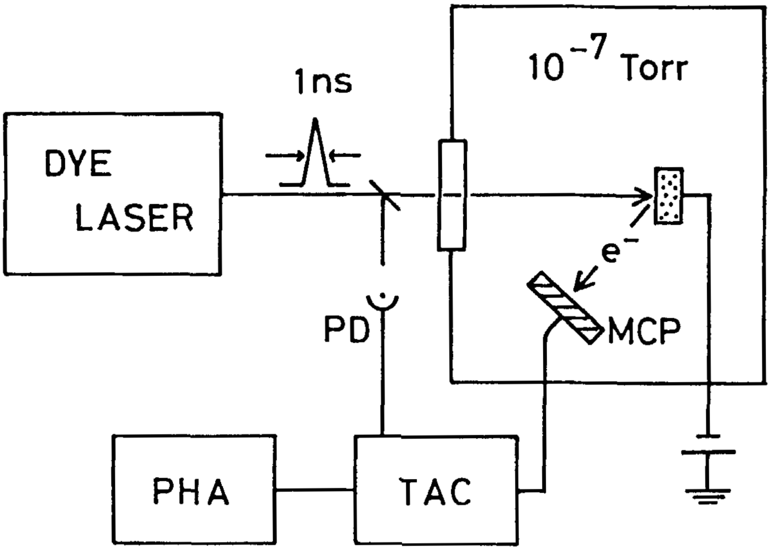

Figure 1 Apparatus for the measurement of time-correlated single-electron counting.

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emitted electrons from an α-perylene single crystal with 460nm excitation. The light of this wavelength can excite a lowest singlet exciton only. The emission persists after the excitation is over and decays with a time constant of 7.5ns. This seems to indicate that the external photoemission is due to the fusion of singlet excitons. However, the observed decay is much faster (7.5ns) than the expected decay constant (singlet lifetime/2 = 40ns). The reason of this discrepancy is unclear. One possibility is the quenching of the singlet exciton at the crystal surface. It is interesting to note that twice the energy of a singlet exciton of α-perylene crystal (5eV) is smaller than the threshold energy of external photoemission with one-photon excitation (5.2eV[1]).

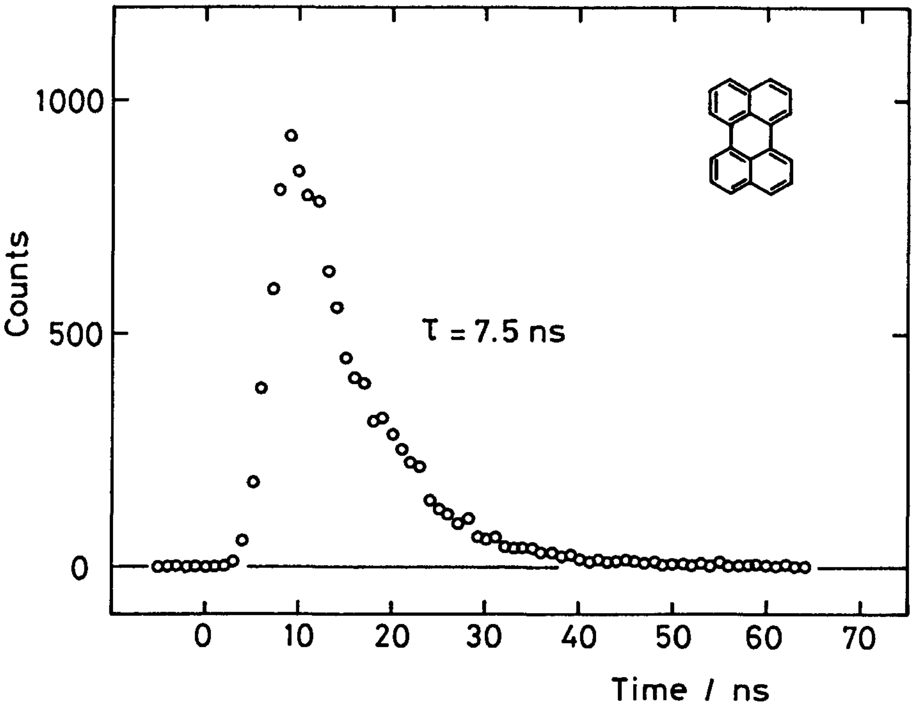

Figure 2 Time profile of the emitted photoelectrons from α-perylene single crystal.

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(2) Photoemission by photoionization of singlet exciton

In anthracene crystal external photoemission is observed with 420nm excitation. It is due to singlet exciton fusion (annihilation)[2]. When the second light around 450-500nm irradiates the sample specimen simultaneously, an enhancement of the photocurrent was observed. This enhancement is due to photoionization of singlet excitons[3]. Figure 3 shows the action spectrum of external photoemission by photoionization of singlet exciton in p-terphenyl single crystal. First-step excitation is made at λ=340nm ($h\nu$=3.69eV) which generates singlet excitons. The photoemission commences at the threshold photon energy of 2.58eV for the second-step excitation. Hence, the threshold energy of the external photoemission via singlet exciton is 6.27eV (=3.69+2.58eV). Figure 4 shows the photocurrent as a

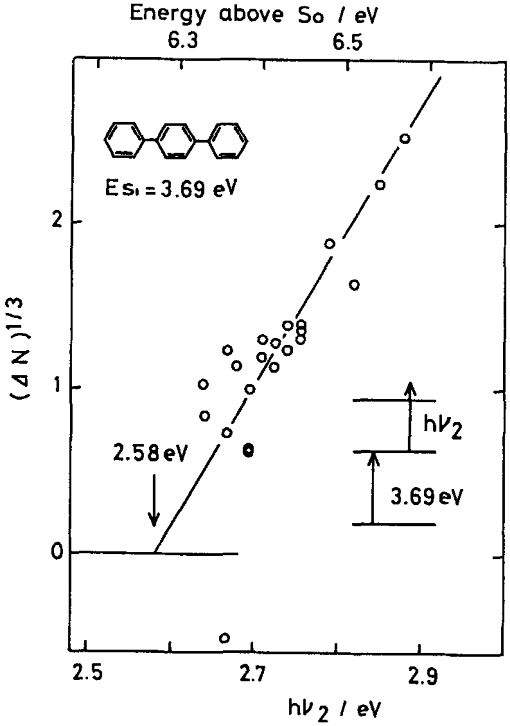

Figure 3 Action spectrum of external photoemission by photoionization of singlet exciton in p-terphenyl single crystal.

function of the photon energy of the second-step excitation in naphthacene crystal. First-step excitation is made at λ=505nm (hν=2.5eV). Threshold energies are summarized in Table 1 for the external photoemission due to photoionization of singlet exciton. The threshold energies for excitonic photoemission (E_{th}^{ex}) are different from those of conventional photoemission, measured with single-photon excitation (E_{th}^{VUV})[1]. It may reflect the difference in the polarization energy between the ground state and a singlet excited state ,and also the relaxation of a singlet exciton.

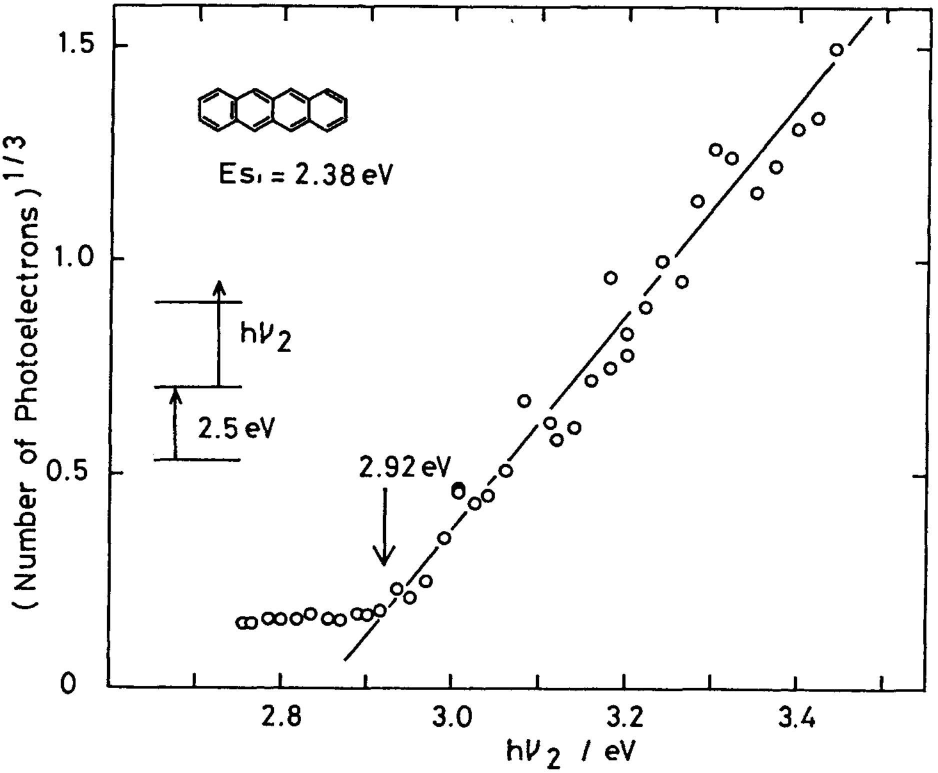

Figure 4 Action spectrum of external photoemission by photoionization of singlet exciton in naphthacene crystal.

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TABLE 1 Threshold energies of excitonic photoemission (E_{th}^{ex})

	E_{th}^{ex} (eV)	E_{th}^{VUV} (eV)
Anthracene	5.50	5.75
Naphthacene	5.30	5.10
p-Terphenyl	6.27	6.1

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