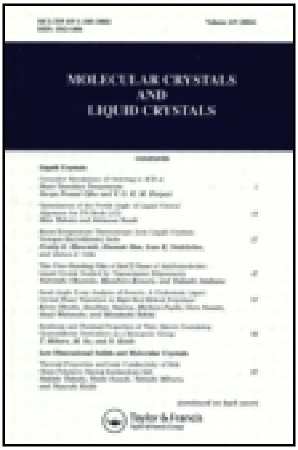

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Ultrafast Excitation Energy Transfer in Multilayered Ultrathin Films of Copper Phthalocyanine and 1,4,5,8-Naphthalenetracarboxylic Dianhydride Revealed by Femtosecond Transient Absorption Spectroscopy

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ULTRAFAST EXCITATION ENERGY TRANSFER IN MULTILAYERED ULTRATHIN FILMS OF COPPER PHTHALOCYANINE AND 1,4,5,8-NAPHTHALENETETRACARBOXYLIC DIANHYDRIDE REVEALED BY FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY

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Relaxation dynamics of photoexcited states in ultrathin multilayered films composed of copper phthalocyanine (CuPc) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA), were investigated by femtosecond absorption spectroscopy. Absorption bands due to an electronically excited state and a vibrationally excited state of electronically ground state of CuPc were measured for the excitation at 390 nm and 780 nm. Furthermore, an additional absorption band was observed when excited at 390 nm, which was assigned to an NTCDA excited state. Ultrafast energy transfer from NTCDA to CuPc takes place with the time scale of 1 ps at the interface between NTCDA and CuPc layers.

Keyword: femtosecond absorption spectroscopy; organic multilayered ultrathin film; ultrafast energy transfer; copper phthalocyanine; 1,4,5,8-naphthalenetetracarboxylic dianhydride

INTRODUCTION

Space-limited structures of organic molecular associates have attracted much attention, because migration of excitons, holes and electrons in their structures is different from that in bulk materials in order to limited freedom of the motion. The migration behavior was studied for evaporated thin films, Langmuir-Blodgett films, etc. [1]. Multilayered ultrathin films, fabricated by organic molecular beam deposition (OMBD) technique, have an advantage for investigating exciton dynamics in space limited structure because of variable thicknesses of layers. In this work, we have applied femtosecond transient absorption spectroscopy to the multilayered films, composed of CuPc and NTCDA with the unit layer thickness of a few nanometor. Photophysics of phthalocyanines has been studied quite widely in view of scientific interest and its potential application. Recently, in our laboratory, ultrafast excitation energy relaxation processes in CuPc solid have been revealed by transient regular reflection spectroscopy [2 - 5]. On the other hand, NTCDA was chosen as a molecule to fabricate alternatively with CuPc, as NTCDA has small lattice mismatch for CuPc. The excited state dynamics in the multilayered film with different unit layer thickness is discussed.

EXPERIMENTS

CuPc/NTCDA multilayered film (ML(*d*)) with several unit layer thicknesses of *d* nm was fabricated on (100)-cleaved plane of a potassium chloride single crystal by using an OMBD technique described in a previous paper [6], and layer number was varied for each sample to keep almost the same optical path length. The first layer of the multilayered film on the crystal was CuPc, and afterward NTCDA and CuPc layers were alternatively deposited. The multilayered structure was confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy. A CuPc film and a NTCDA film, whose thicknesses are 10.5 nm, were also fabricated by the OMBD technique under similar condition.

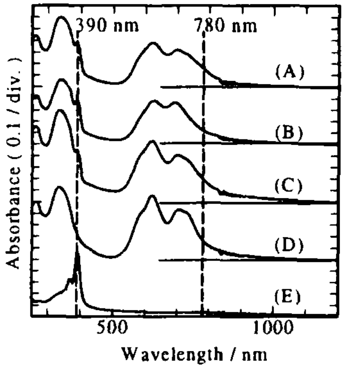
Details of our femtosecond absorption spectroscopic measurement have been described in previous reports [7, 8]. Fundamental light (780 nm) or second harmonic (390 nm) of Ti: sapphire laser system (3-4 mJ/pulse, FWHM 150 fs, 10 Hz) was used as an excitation light source. The induced transient absorption change was probed by the femtosecond white light continuum. All measurements were performed under vacuum condition at room temperature (23 ℃).

RESULTS AND DISCUSSION

Ground state absorption spectra

The spectral shape of the ground state absorption in visible region (500-800 nm) depends on the unit layer thickness, as shown in Figure 1. It is known that visible absorption spectrum due to Q-band of CuPc is sensitive to a molecular stacking manner [9], hence it is suggested that stacking structure changes a little depending on *d*.

CuPc layers are excited by 780 nm pulse, while NTCDA layers are mainly excited by 390 nm pulse even for ML(*d*).



Type	Layer number
(A) ML(4.0)	5
(B) ML(1.8)	11
(C) ML(0.9)	21
(D) CuPc film	
(E) NTCDA film	

FIGURE 1. Ground state absorption spectra of (A - C) ML(*d*), (D) CuPc, and (E) NTCDA films.

Transient absorption spectra of the CuPc film and the NTCDA film

Figure 2 shows transient absorption spectra of the CuPc film excited at 390 nm and 780 nm. Excitation wavelength dependence of spectral shapes was not observed at each delay time. The transient spectra contain two species; a short lifetime species with the positive band at 520 nm and a long lifetime species with the band at 670 nm.

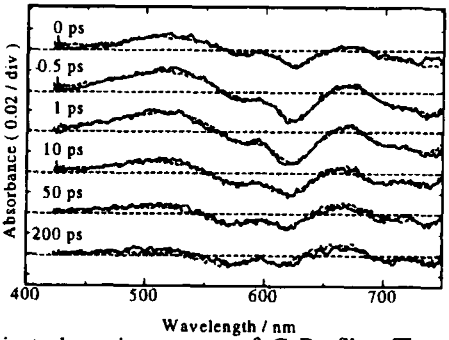


FIGURE 2. Transient absorption spectra of CuPc film. The spectra by 780 nm excitation (broken line) and those by 390 nm excitation (solid line) are normalized at 520 nm.

From the results of previous investigation [2-5, 10], it is considered that short and long lifetime species are due to an electronically excited state (exciton) and vibrationally excited state of the electronically ground state (hot band), respectively. The hot band may be formed via exciton-exciton annihilation, which is already considered as one of the relaxation processes of excited CuPc film [11].

Transient absorption spectra of the NTCDA film by 390 nm excitation show that, after rapid decay of the broad absorption band in the range shorter than 570 nm, the positive bands around 450 nm and 650 nm were remained over several nanoseconds. A flat absorption observed at 1 - 4 ps can be reproduced by a sum of early and late components as simulated in Figure 3. This means that only two transient species are responsible to transient absorption spectra of the NTCDA film. The short lifetime species with the band around 550 nm is considered as an electronically excited state of NTCDA, because the band was observed immediately after excitation.

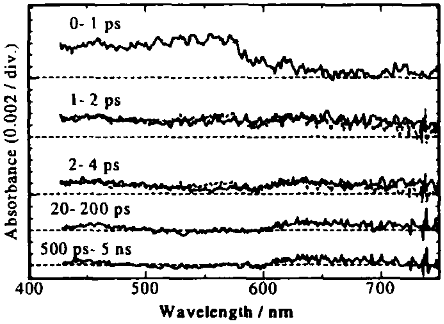


FIGURE 3. Transient absorption spectra of NTCDA film by 390 nm excitation (solid line), and least square fitted spectra (broken line) using two component spectra; the transient absorption spectrum at 0 - 1 ps, and that at 20 - 200 ps in the NTCDA film.

Transient absorption spectra of CuPc/NTCDA multilayered films

Figure 4 shows transient absorption spectra of ML(1.8). Roughly, the spectral shape and their time evolution obtained by both excitation looked similar to those of the CuPc film, however, transient absorption spectra by 390 nm excitation and those by 780 nm excitation were different around 520 nm within a few picoseconds after excitation, which is ascribed to a characteristic transient species of ML(1.8) only generated by 390 nm excitation.

The transient absorption spectral shapes of CuPc solid are partly determined by the spectral shape of bleaching due to the ground state absorption [12]. The difference between transient absorption spectra of the CuPc film and those of ML(1.8) may be due a difference between their ground state absorption spectra. Therefore, it is reasonable to consider that the transient absorption spectra by 780 nm excitation at the early time are assigned to the CuPc excited state as only CuPc can be excited.

On the other hand, NTCDA is mainly excited with 390 nm light and the difference between transient spectra of ML(1.8) and those of the CuPc film was in good agreement with the band of NTCDA excited state shown in Figure 3. Thus, it is considered that the additional band by 390 nm excitation is assigned to the NTCDA excited state.

Furthermore, there is a possibility that the band induced by 390 nm light is due to a NTCDA anion. To confirm assignment of this band, we measured transient absorption spectra of NTCDA solutions. The spectral shape of 550 nm band of the NTCDA film was in good agreement with the transient spectra of the NTCDA solution in tetrahydrofuran, although the different transient spectrum was observed in the xylene solution. Since xylene is a good electron donor compared with tetrahydrofuran, the former should be due to excited state and the latter NTCDA anion. Thus, the band induced by 390 nm excitation cannot be ascribed to the NTCDA anion.

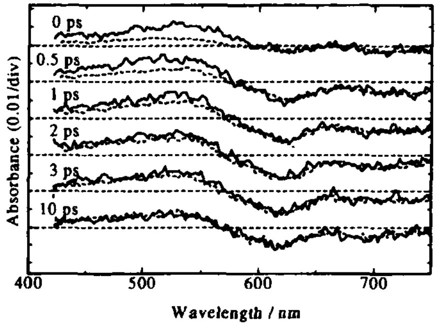


FIGURE 4. Transient absorption spectra of ML(1.8). The spectra by 780 nm excitation (broken line) and those by 390 nm excitation (solid line) are normalized at 620 nm.

Figure 5 shows time profiles of transient absorption of the CuPc film and ML(*d*) obtained with excitation at 390 nm. For ML(1.8), the rise at 620 nm delayed in comparison with that at 520 nm with decreasing the unit layer thickness, although both rises of CuPc film coincide with each other. The NTCDA excited state appeared in the range shorter than 550 nm as shown in Figure 3, while the early time evolution of the negative band in ML(d) around 620 nm represents the population of the CuPc excited state. The delayed rise at 620 nm indicates that the CuPc excited state is not directly generated by the 390 nm light. Therefore it is concluded that the energy of NTCDA excited states is transferred to CuPc with the time scale of 1 ps, although the corresponding decay of the NTCDA excited state at 520 nm was not observed because of spectral overlap with the band of the CuPc excited state. Furthermore, from the fact that the rise at 620 nm of ML(5) coincided nearly with that of CuPc film, it is considered that the ultrafast energy transfer takes place in the NTCDA layer of about 2 nm at the CuPc/NTCDA interface.

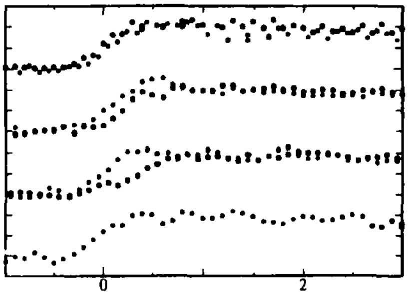


FIGURE 5. Time profiles of the positive band at 520 nm (●) and of the bleaching at 620 nm (○): (A) CuPc film, (B) ML(5), (C) ML(1.8), and (D) ML(1.8). Excitation wavelength was 390 nm.

Acknowledgments

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