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A charge-separated pair in thin crystals of oxotitanium(IV) phthalocyanine revealed by means of femtosecond time-resolved absorption

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Contents

Abstract

The formation and decay of a charge-separated pair in novel polymorphs of thin crystalline oxotitanium(IV) phthalocyanine $(OTiPc)_n$ ($n > 2$) were studied by means of femto-second time resolved absorption spectroscopy. A rapid change of the time-resolved absorption spectrum in the range of 420–620 nm revealed that one-third of the intrinsic exciton of β-OTiPc ‖ exhibiting an absorption maximum around 550 nm was converted within 1 ps to a charge-separated pair exhibiting the absorption bands at 430, 510 and ca. 860 nm, which were assigned to a charge-separated pair. The assignment of cationic is π radical $(OTiPc)_{n-1}^+$ ($n \geq 3$) is based on the dimer formation of cationic radical in a solution of metallo-phthalocyanine. The anionic radical exhibits a similar absorption spectrum to that in a diluted solution. A time-resolved absorption spectrum of an amorphous crystal was also studied.
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Keywords: Thin crystal; Oxotitanium(IV)phthalocyanine; Charge separation; Cation radical; Singlet exciton

1. Introduction

Crystals of oxotitanium(IV) phthalocyanine (OTiPc) are one of the most efficient photo-electric transducers [1]. Crystalline forms of OTiPc are chemically stable and display an intensive and broad absorption band in the

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near infra-red and ultra-violet region. The primary process of photo-induced current generation has been rarely studied since the excited state involved in the charge-separation could be short-lived due to the extremely high efficiency of photon-to-current conversion [2]. More recently, the bi-exponential decay of the fluorescence within 300 ps for the Y-form of crystalline OTiPc was examined under the influence of an electric field [1–3]. The field-dependence of the initial amplitude and the lifetime of the fast decay-component suggested that a portion of the intrinsic excitons with charge-transfer character undergoing carrier generation is converted to another type of mobile exciton exhibiting fast decaying fluorescence. A similar effect by the electric field on the fast decaying fluorescence was observed for the Y-form of OTipc very recently [2,3], while no effect on the initial amplitude of the fast decaying fluorescence was observed for a less active crystalline form of OTiPc (phase I). A Stark-spectroscopy study of the near infra-red absorption band revealed that the lowest band has full charge-transfer character [4]. On the other hand, a study of the Y-form of OTiPc using femtosecond time-resolved absorption spectroscopy showed that a transient species produced by the higher energy laser excitation of the OTiPc disappeared via annihilation within several pico seconds to reduce the photoelectric response [5]. The short-lived species has also been observed for OVPc using femtosecond time-resolved absorption spectroscopy [6,7].

The present authors [8] recently succeeded through vacuum sublimation of heated metal substrates in the preparation of several polymorphs of OTiPc including α-OTiPc ⊥, β-OTiPc ∥ and an amorphous-like form (α-OTiPc). One of the polymorphs, the α-form, which displays an absorption peak at the lowest energy among the polymorphs including the Y-form, exhibits a novel fluorescence with a lifetime of 50 ps in the near infra-red region [9]. The temperature-dependence of the fluorescence quantum yield was investigated to find a short-lived precursor of charge-separated species by means of time-correlated single photon counting technique [9]. A study of femtosecond time-resolved absorption spectroscopy on α-OTiPc ⊥, β-OTiPc ∥ and an amorphous-like form revealed the rise-and-decay of short-lived transient species and the recovery of the ground-state population. Some of the transient species displayed a different absorption spectrum in comparison with that of the dissolved molecules in solution and the others exhibited a similar spectrum to that in solution. A planar molecule is switched to form a dimer, trimer or oligomer in the crystalline solid, which is responsible for the different absorption spectra. In this report, the observed transient species are identified by comparing them with the absorption spectra of the short living intermediates

formed on the photo-excitation of metallo-phthalocyanines (MPcs) in solution.
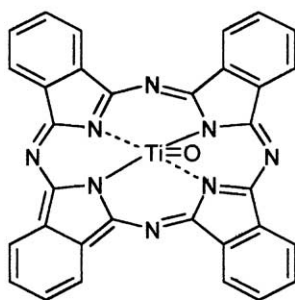
2. Experimental

2.1. Preparation of thin crystals of OTiPc

OTiPc was synthesized according to a method developed by one of the present authors and then purified by repeated vacuum sublimation under Ar atmosphere [8,10]. Semitransparent metal-on-glass were obtained by evaporating Au of 20 nm thickness on 1 mm thick Corning 7059 glass plates (20×20 mm^2) at 0.2 nm s^{-1} under 1×10^{-13}–10^{-5} Pa and by sputtering Pt onto the glass plate at 0.1 nm s^{-1}. Polymorphs of the OTiPc crystal were prepared on various metals by means of sublimation at various temperatures with a depositing rate of 0.05 nm s^{-1}. α-Form crystal (phase II) with 150–200 nm thickness in which OTiPc molecules are aligned with the molecular plane 'standing' with respect to the substrate surface (α-OTiPc ⊥), was prepared on Pt at 150 °C under 10^{-3}–4×10^{-4} Pa as is shown in Fig. 1. Another α-form of 400 nm thickness which OTiPc molecules are aligned with the molecular plane 'lying' with respect to the substrate surface (α-OTiPc ∥), was formed on Pt metal at 150 °C under 2.7×10^{-5} Pa. The β-form (phase I) with 100 nm thickness with orientation lying of the molecular plane with respect to the substrate surface (β-OTiPc ∥) was formed on Au at 150 °C. Amorphous-like forms were prepared at ambient temperature.

2.2. Femtosecond time-resolved absorption spectroscopy

Laser pulses with a repetition rate of 200 Hz were generated by a Ti^{3+}:sapphire based on oscillator and a regenerative amplifier (Tsunami and Spitfire, Spectra Physics, Inc.). The pulse length of the amplified laser is about 200 fs with a wavelength centered at 800 nm and a pulse energy of 0.4 mJ. The fundamental pulse is frequency doubled using a 1 mm BBO crystal yielding a 400 nm pulse which was used to excite the sample. The remainder of the fundamental pulse was focused into a 8 mm flow cell containing water, and thereby generating a white light continuum [9]. The energy of a typical pump pulse is about 25 μJ per pulse with a focus diameter of 1 mm at the sample. The signal beam through the sample and the reference beam were detected by a couple of image sensors (Hamamatsu S4805-512) attached to polychromators (Chromex 250IS). The full width at the half maximum of the instrument response function (IRF) is about 300 fs.

Structure of oxotitanium phthalocyanine(OTiPc)

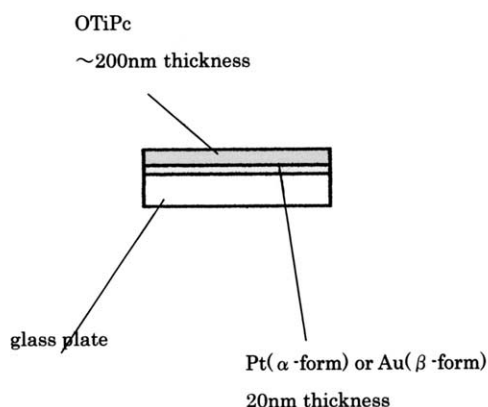## Schematic drawing of thin crystals of OTiPc

OTiPc
~200nm thickness

glass plate

Pt(α-form) or Au(β-form)
20nm thickness

Fig. 1. Structure of oxotitanium phthalocyanine (OTiPc) and schematic drawing of thin crystal of OTiPc.

3. Result and discussion

3.1. Absorption and fluorescence spectra

The intense absorption band of OTiPc at 14,510 cm^{-1} in CH_2Cl_2 solution is considerably broadened and shifted to lower energy in the crystalline of OTiPc, α-OTiPc $\perp$ (11,630 cm^{-1}), β-OTiPc $\parallel$ (13,160 cm^{-1}) and a-OTiPc (14,100 cm^{-1}). The OTiPC crystal fluor-escences at 10,420 cm^{-1} for α-OTiPc $\perp$, 11,900 cm^{-1} for β-OTiPc $\parallel$ and at 11,000 cm^{-1} for a-OTiPc as Table 1 and Fig. 2 show; these are lower in energy by more than 3000 cm^{-1} than in a solution. The formation of a wide absorption band confirms an existence of a transition dipole–transition dipole interaction [4,10]. Moreover, the fluorescence band of the α-form having a larger width (700 cm^{-1}) than that (400 cm^{-1}) in the solution suggests the presence of various dipole–dipole interac-

Table 1
Energies of optical transitions and yield and lifetime of fluorescence for the crystalline samples and the CH_2Cl_2 solution at 298 K [a]

Samples	α-OTiPc $\perp$	β-OTiPc $\parallel$	a-OTiPc	CH_2Cl_2
Lowest absorption peak (cm^{-1})	11,630	13,160	14,100	14,510
Emission peak (cm^{-1})	10,420 [b]	10,400, 11,900	~11,000	14,230
Yield of emission	0.0036, 0.022 [b], 0.002 [c]	0.0042		0.20
Lifetime of emission (ps)	53 [d], 100 [e], 53 [b], 416 [c]	21 [f], 58 [g]		4000

[a] Ref. [9]
[b] The short-lived component at 77 K.
[c] The long-lived component at 77 K.
[d] The short-lived component at 298 K.
[e] The long-lived component at 298 K.
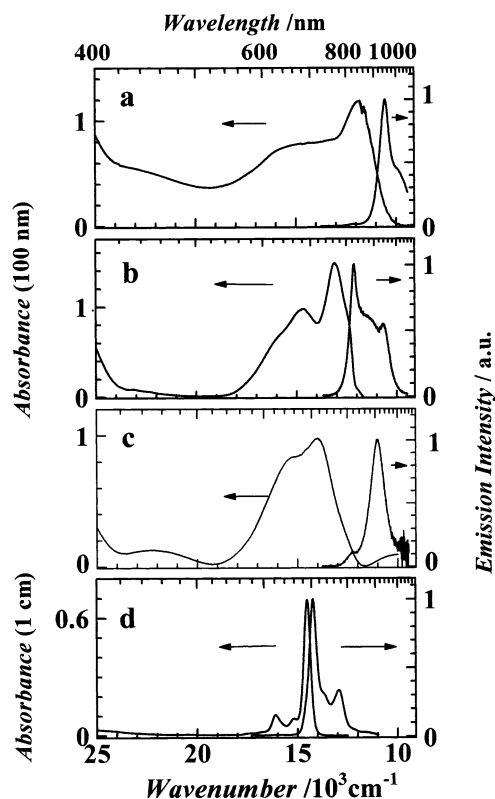[f] Fluorescence at 10,400 cm^{-1}.
[g] Fluorescence at 11,900 cm^{-1}.

Fig. 2. Absorption and fluorescence spectra of α-OTiPc ⊥, β-OTiPc ∥, a-OTiPc and OTiPc in CH₂Cl₂.

tions due to the imperfect structure of the crystal. The fluorescence of the α-form is different from that reported for the Y-form; the peak energies (10,420 cm^{-1} for α-OTiPc ⊥) are much lower than 11,760 cm^{-1} of the Y-form [1,5]. The crystal of β-OTiPc ∥ emits a higher-energy fluorescence with a maximum at 11,900 cm^{-1} in addition to that at 10,420 cm^{-1}.
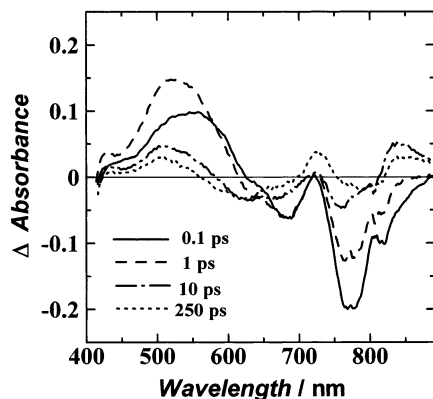

Fig. 3. Time-resolved difference absorption spectra of β-OTiPc ∥ referred to the ground state. The delay times are shown after the laser excitaiton.
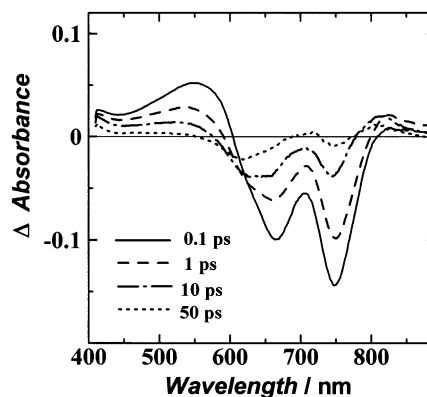

Fig. 4. Time-resolved difference absorption spectra of an amorphous-like crystal, a-OTiPc, referred to the ground state. The decay times are shown after the laser excitation.

3.2. Time-resolved absorption spectra of β-OTiPc ∥, α-OTiPc ⊥ and a-OTiPc

3.2.1. Intrinsic exciton

Time-resolved absorption spectra of β-OTiPc ∥ at various delay times from the excitation of 400 or 800 nm laser consist of the bleaching of ground-state absorption band in a wide range from 600 to 890 nm and the formation of a broad absorption band in the range of 420–620 nm as shown in Fig. 3. The sudden bleach at 755 nm immediately after the laser excitation linearly increases with the increase of the laser intensity. The peak of the absorption band formed just after the laser excitation was shifted from 560 to 520 nm within 1 ps. A similar peak shift of the time-resolved absorption band was observed for the α-OTiPc ⊥ with laser excitation of 400 nm. The time-resolved absorption spectra of the amorphous-like crystal (Fig. 4) are similar to those of β-OTiPc ∥ and α-OTiPc ⊥ except for a weak band in the red region. The initial difference absorption spectrum of the major intermediate with the peak at 560 nm is similar to that of the singlet excited state of MPc in solution [11] and of the short-lived exciton of crystalline OVPc [5] and CuPc [12]. Therefore, the primary intermediate of β-OTiPc ∥, α-OTiPc ⊥, and a-OTiPc is assigned to a singlet exciton.

The laser intensity was not sufficiently large to excite all the ground-state molecules of β-OTiPc ∥ to the exciton state. Fifty-two percent of the original ground-state absorption at 770 nm was bleached, while the bleached absorption at 650 nm was only 26% of the original one. It can be estimated that the molar absorption coefficient of exciton is about one half of the ground-state absorption in the 600–720 nm region, provided that the molar coefficient of the exciton is null at 770 nm. The formation of the exciton is estimated to be 2.2×10^{13} molecules per shot from the bleached absorption at 755 nm using the molar extinction coefficient (57,000 mol^{-1} dm^3 cm^{-1}). The quantum

yield of the exciton formation is calculated to be 0.9 assuming that the absorbed quanta of a laser pulse are about 2.5×10^{13}. The large yield of the bleaching implies that the exciton did not escape from the measurement. A difference absorption band with a peak at 560 nm can also be identified as the singlet exciton, since the intensity of the absorption band emerging without any delay is linear to the laser intensity as that of the bleached band at 755 nm.

3.2.2. Charge-separated pair

A difference absorption spectrum derived from the laser excitation of β-OTiPc ∥, α-OTiPc ⊥ and a-OTiPc was slightly changed to one with new peaks at 420, 510 and ca. 830 nm within 2 ps as is shown in Figs. 3 and 4. The last one decayed in 50 ps and then was almost unchanged between 50 and 240 ps as shown in Fig. 3. The difference absorption spectrum at 2 ps with a peak at 510 nm and two weak peaks around 420 and 830 nm can be attributed to the formation of $(OTiPc)_{n-1}^{+}$ ($n \geq 3$) and OTiPc^{-} by comparing with the absorption spectra of (MPc_{2}^{+}) (M = Mg^{2+} and Zn^{2+}) [13,14] and OTiPc^{-} in solution (Table 2). Even in a diluted solution of MPc, the cation radical (MPc^{+}) are able to form dimer cation radicals (MPc$_{2}^{+}$) [13,14]. It is known that cation radicals of aromatic compounds (Ar^{+}) form dimer cation radicals (Ar$_{2}^{+}$) in solution with a concentration larger than 10^{-3} M, exhibiting an intense charge-resonance band in near infra-red region [15]. The absorption spectra of (MPc_{2}^{+}) exhibit intense bands at 510 and 730 nm in solution [13,14], while intense bands at 420, 510 and 840 nm are ascribed to the monomer cation radical of MPc (M = Mg^{2+}, Zn^{2+}, $AlCl^{2+}$ and InCl^{2+}) in solution [13,14,16,17]. Formation of the absorption band at 730 nm due to the dimer cation radical $((OTiPc)_{n-1}^{+}, n \geq 3)$ might be hidden by the bleaching of the ground-state absorption. Hence the distinct band at 510 nm can be ascribed to the formation of $(OTiPc)_{n-1}^{+}$, $n \geq 3$ in the crystal. The absorption spectrum of the reduced species, meanwhile, might resemble that of OTiPc^{-}, because anionic π-radical do

not dimerize in solution. The characteristic absorption peaks of the anionic π-radical of MPc^{-} (M = Mg^{2+}, Zn^{2+}, Al^{3+}, Fe^{+}) [16–18] around 600 nm were not observed for the thin crystal of OTiPc exposed to the laser. To observe an absorption spectrum of a reduced species of OTiPc, a photo-excitation of OTiPc in CH$_2$Cl$_2$ containing 1 M 1,2,4-trimethoxybenzene (TMB) and in 1-chloronaphthalene containing 1 M diphenylamine (DPA) was performed using the third harmonics (355 nm) of a mode-locked Nd^{3+}:YAG laser. Two bands at 430 and 460 nm were measured upon its laser excitation, of which the former cannot be ascribed to a π-radical of OTi^{IV}Pc but to a σ-radical of OTi^{III}Pc and the latter band at 460 nm to TMB^{+} [18,19]. The absorption band at 430 nm was also detected together with DPA^{+}, which displayed a broad band with the peak around 670 nm [20].

The difference spectrum at 240 ps exhibits a broad band with peaks at 420 and 500 nm for β-OTiPc and a sigmoidal band at wavelengths longer than 600 nm with positive peaks at 730 and 850 nm and with negative peaks at 620 and 780 nm for β-OTiPc ∥ and α-OTiPc ⊥. The absorption intensity at the 420 and 500 nm in the time region of 50–240 ps following the 400 nm excitation of β-OTiPc ∥ did not decay, while the fluorescence disappeared and the ground-state absorption was completely recovered at 100 ps after the laser excitation. The formation of the absorption band is ascribed to some spectral change of Au thin layer (20 nm thick) on which β-OTiPc is prepared. The absorption intensity at 510 nm at 240 ps increased with decrease in the thickness of OTiPc layer and remained for the Au layer without OTiPc.

No effect of the excitation wavelength on the intensity of sigmoidal difference band at 240 ps around 800 nm implies that the sigamoidal difference band in the red region is produced than other mechanism as mentioned below.

The origin of the sigmoidal difference band might be ascribed to the thermal broadening of the structured spectrum due to the laser excitation. An sigmoidal difference-spectrum was produced on heating the sample of α-OTiPc ⊥: a negative and positive peaks were produced for the peak and the valley of an original absorption band due to thermal broadening of the structured bands, respectively. Such a difference absorption spectrum at long time delay was observed for the crystal of OVPc excited by using a high energy laser [7].

3.3. Rise-and-decay of transient absorption

The decay dynamics of the difference absorption of α-OTiPc ∥ at 510, 614 and 755 nm could not be fitted by a mono-exponential function on the 400 nm excitation. Bi-exponential fit yields the rate constants of 31×10^{11} and 4.5×10^{11} s^{-1} for the absorption-band at 510 and

Table 2
Absorption peaks of the photo-produced intermediates (λ_{max}^{obs}) for the thin crystals and a dilute solution of MPc

Species	λ_{max}^{obs} of monomer	λ_{max}^{obs} of dimer	λ_{max}^{obs} of crystal [e]
Singlet exciton	560 [a]	–	550
Cation radical	430, 510, 730, 860 [b]	510, 730 [c]	510, 830
Anion radical	420, 590, 610 [d]	No dimer band	430

[a] Ref. [12].
[b] Refs. [13,14,16,17].
[c] Refs. [13,14].
[d] Refs. [16,17].
[e] This work.

614 nm. The first and the second recoveries of the ground-state absorption at 755 nm occurred with a rate-constant of 35×10^{11} and 5.4×10^{11} s^{-1}, respectively. Sixty-nine percent of the bleached ground state absorption were recovered with the first rate constant and the remaining (31%) were recovered with the second rate constant. The difference absorption in the range of 450–620 nm decays more slowly than the major recovery of the bleached absorbance. As for the amorphous-like form with a weak absorption in a longer wavelength region than 800 nm, a weak band at 830 nm is ascribed to the charge-separated pair because of the slow decay rate (1.3×10^{11} s^{-1}).

Judging from the recovery of the ground-state absorption during the decay of the singlet exciton, the recovery of the ground-state population occurred more efficiently than the formation of charge-separated pair. The nascent exciton, $^1(OTiPc)_n^{**}$, is considered to undergo charge separation because of the rapid conversion to the charge-separated pair within 1 ps. Probably, the nascent excitons produce charge-separated pairs with various separation distances, of which the closely separated pairs, $[(OTiPc)_{n-1}^+ \bullet OTiPc^-]$, disappear in 1 ps and the longer separated ones, $(OTiPc)_{n-1}^+ \cdots OTiPc^-$, exhibit as long a lifetime as 5 ps. The characteristics of the nascent exciton are absolutely different from that of the long-lived fluorescent exciton which may be localized as a kind of trap. Since the high reactivity of the nascent exciton was observed for the 800 nm laser excitation the high reactivity could not be characteristic the vibrationally excited exciton but of the nascent exciton. The major and short-lived exciton was named as 'an intrinsic exciton' [1].

The presence of a linear relation between the transient absorption at 3 ps and the laser pumping intensity confirms that a majority of the intrinsic exciton disappeared in the uni-molecular decay of the intrinsic exciton.

$$^1(OTiPc)_n^{**} \rightarrow (OTiPc)_{n-1}^+ \cdots OTiPc^-$$

If the bimolecular annihilation of the exciton could produce the charge-separated pair as in the case of OVPc [6,7], the amount of the secondary intermediate, the charge-separated pair, should reach a plateau value with increasing energy of the laser. This is not the case.

4. Conclusion

The crystalline forms of OTiPc, α-OTiPc ⊥, β-OTiPc ∥ and a-OTiPc, were observed to exhibit a broad absorption band with a peak at much lower energy (11,630 and 13,160 cm^{-1}, respectively) compared with that in the solution. The study of femtosecond time-resolved absorption spectroscopy on the chemistry of the photo-excited crystal revealed that the intrinsic exciton exhibits a difference absorption between 420 and 620 nm with bleaching of the ground-state absorption in the red region. The intrinsic exciton is assumed to be converted into charge-separated pairs, $(OTiPc)_{n-1}^+ \cdots OTiPc^-$ within 1 ps, showing absorption peaks at 430, 510 nm and ca. 830 nm with a lifetime of 5 ps. A majority of the intrinsic exciton was not converted to the long-living and fluorescent exciton resulting in the recovery of the bleached ground-state absorption within10 ps. The absorption spectrum of the anion radical in the crystal is different from that of the monomer in solution, while the cation radical in the crystal exhibits a similar absorption spectrum to that of the dimer cation radical in the solution.

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