

Intermolecular Interaction by Apical Oxygen in Titanyl Phthalocyanine

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Local charge distribution around the titanium atom of amorphous and α -crystalline TiOPc films was investigated using Ti 2*p* X-ray absorption and emission spectroscopy. The X-ray emission spectra show two characteristic features that correspond to charge transfer states that result from in-plane Ti–N and apical Ti–O hybridizations. In the amorphous phase, the Ti–O charge transfer state has both localized and delocalized properties, whereas in the α -crystalline phase it has only the delocalized property. These different properties evidence the role of the oxygen atom in forming a network with a neighboring molecule and in balancing the total dipole moment in the α -crystalline phase. [DOI: 10.1143/JJAP.44.L1147]

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Titanyl phthalocyanine (TiOPc) is known for its high sensitivity to near-infrared (IR) photoexcitation and the high quantum efficiency of subsequent free carrier generation.¹⁾ It exhibits the following types of polymorphism in a solid phase, depending on the molecular configurations:^{2–4)} phase I (A-form or β -form TiOPc) is monoclinic and less active to near-IR photoexcitation and it is similar to an amorphous or molecular phase in solution; phase II (B-form or α -form TiOPc) is triclinic and near-IR active; and Y-form TiOPc is monoclinic and is characterized by very high sensitivity to near-IR photoexcitation. The sensitivity to near-IR photoexcitation of the Y-form is highly dependent on humidity.¹⁾

The origin of the high sensitivity of TiOPc to near-IR photoexcitation has been extensively discussed. Saito *et al.* suggested a redshift in their electroabsorption spectra in terms of a J-aggregate-like interaction and intermolecular charge transfer (CT) excitation.^{5,6)} Mizuguchi *et al.* adopted a molecular-based approach in which the presence of molecular distortion due to an interplanar π – π interaction was ascribed as the origin of the redshift.⁷⁾ They excluded the possibility of the intermolecular CT excitation through π – π stacking. They also inferred that the macrocycle of shuttlecock-shaped molecules such as TiOPc could be reasonably deformed due to intermolecular interactions in the solid state. Gulbinas *et al.* attained a transient absorption spectra of photoexcited TiOPc, which they explained by a splitting of the degenerate Q-absorption band without excluding the possibilities of intermolecular CT exciton and intramolecular distortion.⁸⁾ Since the intrinsic exciton by valence photoexcitation should be a precursor of free carriers that contribute to the carrier quantum yield, several experiments adopting various methods have been conducted to elucidate the character of the intrinsic exciton.^{5–18)} Since the origin of the intrinsic exciton is considered to be the π – π^* excitation of phthalocyanine, the role of an apical oxygen atom has not been extensively discussed. However, the apical oxygen atom induces the characteristic shuttlecock shape of TiOPc, which should play an important role in the variation of stacking, i.e., polymorphism. The manner of

stacking may depend on the presence and/or absence of intermolecular hybridization between the electronic structure of the oxygen atom and that of a neighboring molecule.

In this report, we demonstrate different properties of Ti–O CT states between amorphous and α -crystalline TiOPc using Ti 2*p* X-ray absorption (XAS) and emission (XES) spectroscopy. Further, we discuss the role of the oxygen atom in the electronic structure and molecular stacking. Ti 2*p* XAS provides information regarding unoccupied valence electronic states. It is sensitive to the valency of the titanium atom as well as to the ligand fields of neighboring nitrogen and oxygen atoms. Ti 2*p* XES provides information on the occupied valence electronic states around the centrally located titanium atom. At resonant excitations, the profile of the XES spectra shows dramatic dependence on the excitation energy that is specific to the localization of the excited electron.^{19,23)} In the case of TiOPc, the occupied valence electronic states are well characterized by CT states through interactions between Ti 3*d* states and neighboring N 2*p* and O 2*p* states. Thus, we expect Ti 2*p* XES to be a measure of the localization of the CT states by resonant excitation through the Ti 2*p* absorption edge.

TiOPc was prepared by the reaction of tetra-*n*-butyl orthotitanate with 1,3-diiminoisindoline in quinoline at 180°C for 3 h. The crude precipitates were successively washed with hot *N,N*-dimethylformamide and hot methanol, and subsequently purified by sublimation (5 mmHg, 500°C). The analytically calculated mass ratio was 66.68% for C, 2.80% for H, 19.44% for N, and the product was 66.76% for C, 2.79% for H, 19.41% for N. The chemical structure of the TiOPc molecule is shown in Fig. 1. TiOPc films were deposited at a pressure of approximately 10^{–5} Torr by vacuum deposition from a tantalum crucible onto a hydrogen-terminated Si(100) substrate at room temperature. The deposition rate of the organic materials ranged between 2 and 5 Å·s^{–1}. The thickness of each film was determined to be 75 nm by monitoring with a quartz crystal oscillator. The morphology of TiOPc was translated from amorphous to α -crystalline by exposing the cell to ethanol vapor for 2 h. After exposure, the cell was dried in vacuo (at 10^{–3} Torr) for 5 h in order to remove any remaining ethanol.

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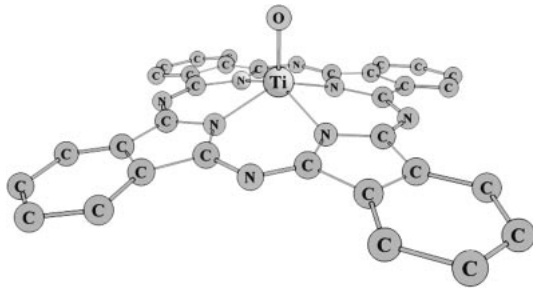


Fig. 1. Chemical structure of a TiOPc molecule (phase II).²⁾

Ti 2*p* XAS and XES measurements for the amorphous and α -crystalline TiOPc films were performed at the figure-8 undulator beamline BL27SU in SPring-8.^{20,21)} The absorption spectra were obtained by collecting the total photon yield (TPY) using a 1500-Å-thick Al-filtered Si photodiode. Since the electronic structure of TiOPc in the surface region is considered to be quite different from that in its bulk,⁸⁾ it is important to use a TPY that is more bulk sensitive than the total electron yield (TEY). In fact, the result measured using the TEY had a problem with regard to reproducibility. The emission spectra were measured using a flat-field-type soft X-ray emission spectrometer.²²⁾ The incident beam was focused with a spot size of approximately 10 μm (vertical) \times 150 μm (horizontal) on the sample. The incidence angle was fixed at 60° with respect to the sample normal. During exposure to soft X-rays, the samples were automatically scanned at a rate of 200 $\mu\text{m}/\text{min}$ in the vertical direction to exclude the influence of radiation damage on the experimental results. All the experiments were carried out at room temperature. The energy resolution of an incident photon at 450 eV was set at 0.05 eV for absorption and 0.2 eV for emission measurements. The total energy resolution for the emission measurement was approximately 0.5 eV.

Figure 2 shows the Ti 2*p* absorption spectra of the amorphous and α -crystalline TiOPc. Vertical bars on the absorption spectrum indicate the excitation energies used for the Ti 2*p* XES measurement. The profile of the Ti 2*p* absorption spectra is similar to that of rutile TiO₂,²³⁾ which represents the 3*d*⁰ *O_h* symmetry. The similarity is derived from the dominant role of localized core excitons in the Ti 2*p* absorption spectra, which makes them insensitive to the characteristic square pyramidal structure of TiOPc. In contrast, the valency of the titanium ion is strongly reflected in the Ti 2*p* absorption spectra. Thus, the Ti⁴⁺(3*d*⁰) state is expected for the amorphous and α -crystalline TiOPc.

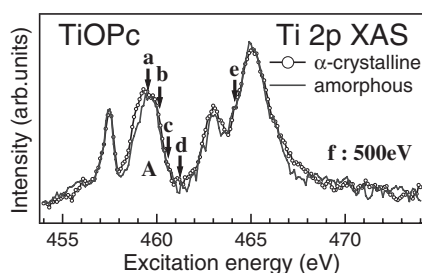


Fig. 2. Ti 2*p* absorption spectra of the amorphous and α -crystalline TiOPc.

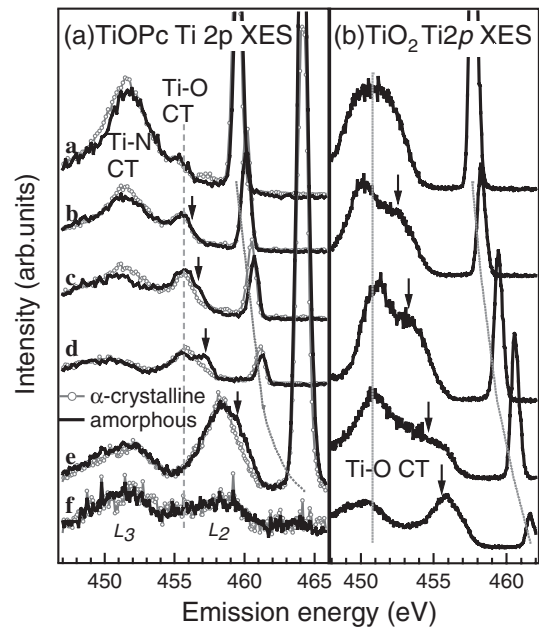


Fig. 3. (a) Ti 2*p* emission spectra of the amorphous and α -crystalline TiOPc. The dotted and dashed lines are guides for the elastic line and the delocalized Ti–O CT states, respectively. The arrows indicate the localized Ti–O CT states. (b) Ti 2*p* emission spectra of TiO₂ showing a similar excitation energy dependence of the Ti–O CT states to that of TiOPc.

Figure 3(a) shows the Ti 2*p* emission spectra of the amorphous and α -crystalline TiOPc. The symmetric peak guided by the dotted line, termed the elastic line, corresponds to the excitation energy. As mentioned above, the profile of the Ti 2*p* XES spectra below the elastic line primarily reflects the CT states between Ti 3*d* and the ligand valence states.

Following the assignments previously reported by Kera *et al.*,²⁵⁾ the structure at lower energies around 451 eV is assigned to the Ti 3*d*–N 2*p* CT (referred to as Ti–N CT hereafter) states, and at higher energies around 456 eV, to the Ti 3*d*–O 2*p* CT (Ti–O CT) states. The bandwidth of the Ti–N and Ti–O CT states reflects the degree of localization. The Ti–O CT states are fairly localized as compared with the Ti–N CT states, as expected from the molecular structure. The profile and intensity of these structures indicate remarkable dependence on the excitation energy. When the excitation energy is tuned across peak A (Ti 3*d*: nearly *e_g*), emissions to the Ti–N CT states are enhanced when tuned to the top of the peak, whereas emissions to the Ti–O CT states increase at higher excitation energies. Between the amorphous and α -crystalline phases, the profiles of the emission spectra are different for both the Ti–N and Ti–O CT states. In particular, we observed a gradual increase in new Ti–O CT states in the amorphous phase by increasing the excitation energy. A single peak around 456 eV in spectrum a splits into double peaks as the excitation energy increases; one remains around 456 eV while the other follows the excitation energy. The latter is observed even in spectrum e, where it overlaps a strongly enhanced Ti *L*₂ emission. In the α -crystalline phase, we observed only a single peak at around 456 eV. The stationary peak around 456 eV converges with emission spectrum f obtained by excitation

energies much greater than the ionization energy, often termed X-ray fluorescence or normal X-ray emission, even though it severely overlaps the Ti L_2 emission spectrum. The peculiar dependence of the XES spectra on the excitation energy is also exhibited in the Ti $2p$ XES of a TiO_2 single crystal.^{23,26,27} We compare the corresponding spectra of TiO_2 and TiOPc in Fig. 3. TiO_2 has Ti $3d$ states that are strongly hybridized with delocalized O $2p$ valence states, having both localized and delocalized properties. The delocalized property yields a stationary peak (that does not linearly follow the excitation energy), whereas the localized property yields a resonant emission line that linearly follows the excitation energy,¹⁹ which is thought to be the origin of the splitting of the peak of TiO_2 around 451 eV. In the same manner, the splitting of the Ti–O CT peak in the amorphous phase may be interpreted as the appearance of both localized and delocalized properties. To summarize the experimental result, we found narrow Ti–O CT states above the broad Ti–N CT states. The Ti–O CT states exhibited both localized and delocalized properties in the amorphous phase, whereas only the delocalized property was exhibited in the α -crystalline phase.

There are two possible reasons for the existence of different properties of the Ti–O CT states in the amorphous and α -crystalline phases. One is the difference in the strength of hybridization between the Ti $3d$ and O $2p$ states in the amorphous and α -crystalline phases (intramolecular effect). The other is the presence (absence) of hybridization among the Ti–O CT states and the electronic states of a neighboring molecule that is stacked in the Ti–O bond direction (intermolecular effect).

Since no regular stacking of a neighboring molecule is expected in the amorphous phase, the presence of the delocalized property of the Ti–O CT states is explained only by the contribution from strong Ti–O hybridization within a molecule. However, we face the following problem: what makes the Ti–O CT states more delocalized in the α -crystalline phase? As indicated by Mizuguchi *et al.*, in the α -crystalline phase the plane of each end phenyl ring is tilted against the plane of the four central nitrogen atoms due to the periodic stacking of TiOPc molecules.⁷ This distortion may possibly induce a change in the effective electric dipole in a molecule in the direction of the molecular stacking, which minimizes the total energy. However, it is not expected that this will induce a significant change in Ti–O hybridization since the distortion of the end phenyl rings is very small and it occurs at a distance from the Ti–O bond. Instead, it is more likely that a new hybridization occurs between a neighboring molecule and the oxygen atom, which explains the difference in the Ti–O hybridization, i.e., the disappearance of the localized property in the α -crystalline phase. This phenomenon appears to be rather similar to the one that occurs when the J-aggregate-like interaction due to π – π stacking is introduced.^{5,6} However, our discussion is regarding the fairly localized Ti–O bonding states that have a larger binding energy than the π states in the macrocycle. The proposed intermolecular hybridization by the oxygen atom may play an important role in stabilizing the structure of the π – π stacking and allow an effective charge transfer by π – π^* excitations, which results in an

extremely high photocurrent by near-IR excitations.²⁸ Thus, we suggest that the oxygen atom is not only a point charge that extracts a titanium ion from the macrocycle to form the well-known shuttlecock structure but also a charge storage that controls the electric dipole along the molecular stacking by intermolecular hybridization. There have been no reports that focus on the role of the apical oxygen atom in TiOPc and phthalocyanine complexes. This work revealed, for the first time (although qualitatively) the role of the apical oxygen in TiOPc via a change in the property of the Ti–O CT states.

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