

The Nature of Titanylphthalocyanine Y-form Crystals in Photoreceptors

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Abstract

Molecular dynamics calculations and several experiments were performed to investigate the physical properties of the titanylphthalocyanine Y-form crystal. The proposed crystal structure by Oka et al. is confirmed as stable at room temperature. It is suggested that the dependence of the photosensitivity on the humidity is caused by the water molecules on the surface of the Y-form. A mechanism for the phase transition from the Y- to A-form is proposed. At about 250 °C the water molecules observed in the Y-form in this study begin to jump from one space to another in the crystal through the channels connecting them and as a result are expelled out of the crystal. After the water molecules go out of the internal spaces, the phase transition to the A-form occurs by changing the molecular arrangement to shrink these spaces. It has been proposed that the high photosensitivity of the Y-form is due to its molecular arrangement in terms of the transition moment. Since the photosensitivity is raised by the water molecules on the surface, these observed inside of the Y-form might also contribute to increase the photosensitivity.

Introduction

Phthalocyanine crystals have been used as photosensitive materials in photocopiers and printers. The photosensitivity of these crystals depends on the crystal polymorph as well as the molecular structure. Several polymorphs of titanylphthalocyanine (TiOPc), which has a titanium atom at the center of the molecule and has an oxygen atom connected to the titanium atom (Fig.1), have been synthesized and crystallized. The structures of two stable polymorphs of TiOPc called A- and B-form, respectively were determined using single crystal analyses⁽¹⁾. Recently, another polymorph called Y-form was crystallized and found to have extremely high photosensitivity to infrared light. The properties of this crystal form have been investigated⁽²⁾⁻⁽⁵⁾.

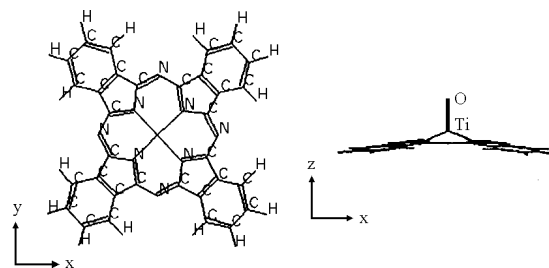


Figure 1. Molecular structure of TiOPc.

The TiOPc Y-form crystal is metastable and no sufficiently large crystal has yet been obtained for single-crystal analysis. The crystal structure proposed by Oka et al. was obtained with Monte Carlo and Rietveld methods by fitting the powder X-ray diffraction pattern⁽⁶⁾. The estimated lattice energy of the proposed Y-form has been reported to be as low as that of the A-form. However, the proposed crystal structure has not been confirmed as stable at room temperature. The characteristics of the Y-form crystal structure are that it has spaces between the TiOPc molecules (see Fig. 2 in Reference 6) and these spaces are connected to each other via small channels. The dependence of the photosensitivity on the humidity⁽²⁾⁻⁽⁵⁾ and the phase transition to the A-form⁽⁵⁾ have been reported. In this study molecular dynamics (MD) calculations and several experiments were performed to investigate the stability, the phase transition and the behavior of the water molecules in the Y-form.

Molecular Dynamics

All the MD calculations were performed under constant pressure and constant temperature conditions with an MD program developed by Mauro Ferrario. The pressures of all the systems were kept at 1.0 atm. The temperatures were changed from 27 °C to 1027 °C to

observe the stability of the Y-form, the phase transition and the movement of the water molecules. The commonly used three-dimensional periodic boundary condition was applied to realize the infinite size crystal. The details of the MD calculations performed in this study are presented in Reference 7.

Experiments

The differential scanning calorimetry (DSC) measurements were performed with DSC3100 (Mac Science Inc.) to observe the detachment of the water molecules from the Y-form and the phase transition. X-ray diffraction patterns were obtained with MPX18 (Mac Science Inc.) to monitor the phase transition. The amount of the water detached from the sample were measured with KF06 (Mitsubishi Chemical Corporation) based on the Karl Fischer method.

Results and Discussion

Stability and Phase Transition of Y-form

The stability and the phase transition of the proposed Y-form crystal structure mentioned above are examined with MD calculations by changing the temperature. In the calculations, the phase transition is not observed up to 327 °C showing that the Y-form is stable at room temperature. This supports the notice that the proposed crystal structure of the Y-form is realistic.

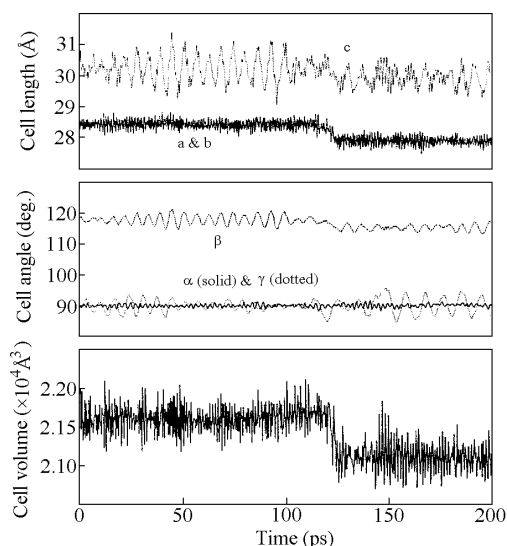


Figure 2. Time evolution of cell parameters and volume.

The time evolution of cell volume and cell parameters at 327 °C (first 100 ps) and 377 °C (last 100 ps) are shown in Fig. 2. A phase transition is observed after the temperature is changed to 377 °C. Watanabe et al. Reported that the Y-form transformed to the stable A-form at about 255 °C⁽³⁾. The calculated powder X-ray diffraction patterns of the Y-form, the A-form and the crystal obtained from the MD calculations (X-form) are shown in Fig. 3. The X-form

is clearly different from the A-form, which is also verified with computer graphics. The results of the DSC measurement and the X-ray diffraction patterns at several temperatures are shown in Fig. 4 and 5, respectively. The origin of the endothermic peak at about 70 °C is discussed later. The exothermic peak at about 250 °C corresponds to the phase transition. The phase transition of the Y-form to the A-form is seen between 200 °C and 270 °C in Fig. 4. As the temperature goes up the degree of crystallinity of the A-form increases. This implies that the phase transition starts at about 250 °C and continues up to 450 °C, which probably corresponds to the fluctuation of the DSC curve between 250 °C and 450 °C in Fig. 4. Unfortunately, the phase transition to the A-form is not observed in the MD calculations. However, some important information can still be obtained by analyzing the nature of the phase transition to the X-form. During the phase transition to the X-form the spaces where we think water molecules might exist are shrank. The same mechanism could be applied to the phase transition to the A-form.

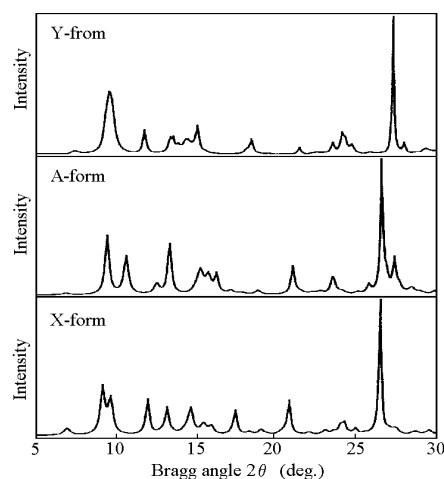


Figure 3. X-ray diffraction patterns of TiOPc Crystals.

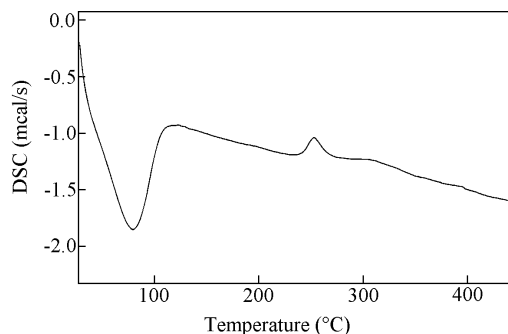


Figure 4. Differential scanning calorimetry.

Water Molecules in Y-form

The endothermic peak at about 70 °C observed in the DSC measurement in Fig. 4 is attributed to the detachment

of water molecules from the surface of the Y-form. The dependence of the photosensitivity on the humidity supports the existence of the water molecules on the surface of the Y-form. In order to confirm this and to investigate the behavior of the water molecules, one sample was used in successive DSC measurements changing the experimental environment.

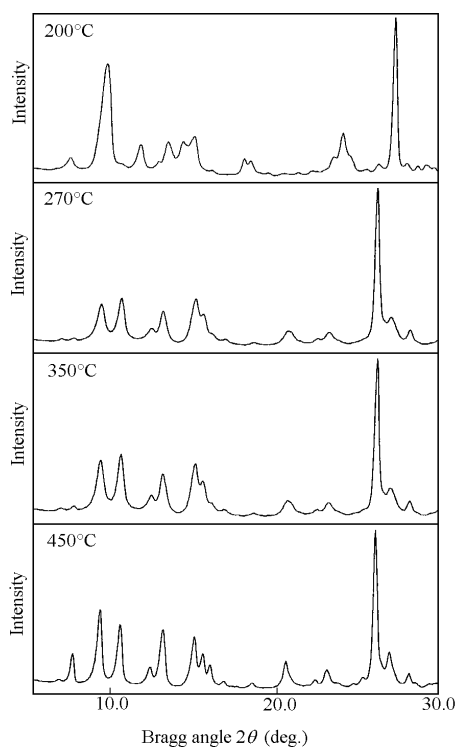


Figure 5. X-ray diffraction patterns showing the phase transition.

First, the sample was heated up to 120 °C in air, which is well below the phase transition temperature. The endothermic peak was observed at about 70 °C. The sample was then cooled down to ambient temperature. After leaving the sample for 1 hr. in air the sample was heated up to 120 °C in nitrogen flow where the humidity was zero. The endothermic peak was observed again. The sample was then cooled down to ambient temperature and left in the nitrogen flow for 1 hr. The sample was again heated up to 120 °C in the nitrogen flow and this time the endothermic peak was not observed. This indicates that some substance that was detached from the Y-form by heat did not attach in the nitrogen flow. The substance was confirmed to be water molecules with the experiment explained later. The sample that was cooled down to ambient temperature and left in air for 1 hr. was heated up to 120 °C in air. The endothermic peak was observed again. This shows that the water molecules re-attached to the Y-form when it was left in air. From the series of the DSC measurements it is observed that the water molecules detach from the Y-form when heated and attach to the Y-form in air at room temperature. With the results of the MD calculations that the insertion of the

water molecules in the Y-form is unfavorable and they did not diffused at low temperature, it is suggested that the water molecules observed at around 70 °C are on the surface of the Y-form adsorbed via weak intermolecular interactions.

As mentioned before, experimentally the Y-form transformed to A-form at about 250 °C. The DSC measurement was performed using the sample that is heated up to 450 °C, where the sample is in the A-form. The endothermic peak shown at about 70 °C for the Y-form was not observed for the A-form. That is, the water molecules are not attached to the A-form. We have not figured out the reason why the water molecules are attached to only the Y-form. The water molecules might be attracted at some particular parts of the TiOPc molecules or regions in the molecular arrangements of the Y-form, which are exposed on the surface of the Y-form but not that of the A-form.

In the discussion above we assumed that the water molecules exist on the surface of the Y-form. However, as yet we have not examined whether or not the substance to detach and attach is water. We have employed the moisture content measurement based on the Karl Fischer method. Water was detected between 60 °C and 90 °C, which corresponds to the endothermic peak observed in the DSC measurement (Fig.4), and also between 200 °C and 300°C, which corresponds to the exothermic peak. So, we confirmed that the substance to detach and attach at about 70 °C were water molecules. We also confirmed that the water molecules were expelled at the phase transition to the A-form. This supports the proposed mechanism of the phase transition. The amount of water measured between 60 °C and 90 °C probably depends on the humidity. About 0.07 wt% of water was detected between 200 °C and 270 °C. This indicates that only one water molecule is contained per 45 TiOPc molecules.

Table 1 Cell parameters and energies of systems with water molecules. •Energy : kJ/mol•

	H ₂ O 1 mol	H ₂ O 8 mol	H ₂ O 16 mol	H ₂ O 0 mol
a (Å)	1.413	1.410	1.412	1.414
b (Å)	1.414	1.413	1.412	1.414
c (Å)	1.500	1.509	1.506	1.500
α (deg.)	90.0	89.8	89.8	90.0
β (deg.)	118.0	118.1	117.8	118.0
γ (deg.)	90.0	89.7	90.7	90.0
ρ (g/cm ³)	1.450	1.458	1.466	1.447
E(total)	-176.6	-148.5	-130.2	-181.7
E(vdW)	-215.7	-182.3	-156.0	-221.7
E(Coulomb)	-9.54	-11.24	-12.42	-9.41

The MD calculations of four systems with various numbers of water molecules inside of the Y-form were performed at ambient temperature. The water molecules were put in the spaces in the Y-form mentioned above. The cell parameters and energies of these systems are listed in Table 1. The cell parameters of the equilibrated systems with water molecules are almost same as those without one.

However, the total intermolecular interaction energies are increased by the insertion of the water molecules. This implies that the spaces in the Y-form are not large enough for water molecules although the sizes of the MD cells are little changed.

The MD calculations with water molecules in the Y-form were performed by increasing the temperature. When one molecule is put in the MD cell at the empty space the phase transition to X-form occurred at 477 °C, which is 100 K higher than the system without one. When more than eight water molecules are put in the MD cell the phase transition is not observed up to 1027 °C, where the MD calculation was stopped owing to the deformation of the MD cell. This suggests that the existence of the water molecules in the spaces to be shrunk prevent the phase transition to the X-form. Suppose the same mechanism can be applied to the actual phase transition to the A-form, the existence of the water molecules inside of the crystal prevents the phase transition of the Y-form.

It is interesting that the water molecules prevent the phase transition though the existence of the water molecules increases the total intermolecular interaction energy. The Y-form is usually crystallized well in aqueous solutions or the solutions containing a small portion of the water. We suggest that the water molecules play an important role to favor crystallization of the Y-form and are trapped in it occasionally to prevent the phase transition.

Movement of Water Molecules

Movement of the water molecules inside of the Y-form in the MD calculations was monitored with a graphic tool. Up to 627 °C the water molecules moved around in the particular spaces in the crystal. When the temperature was raised to 727 °C the water molecules began to jump from one space to another through the channels connecting them. The jumps occur stochastically depending on the movement of the water molecules as well as that of the TiOPc molecules. The jumps could not be observed at 250 °C in the MD calculations, because the MD calculation time is very short compared with the real time. In reality the same type of jump motion might be activated at the phase transition temperature. Water molecules go out of the Y-form through the channels, since the existence of the water molecules is energetically unfavorable. As mentioned before, the phase transition occurs mainly at about 250 °C and continues until at 450 °C increasing the crystallinity. This delay of the phase transition might happen due to the difference in the size, concentration and diffusion rate of the water molecules for the individual crystals.

Conclusion

The MD calculations and experiments were utilized to investigate the physical properties of the TiOPc Y-form crystal. The Y-form was shown to be stable at room temperature. We have proposed the mechanisms of the

phase transition of the Y- to the A-form and the roles of the water molecules in and on the Y-form. That is, the phase transition occurs by shrinking the spaces in the Y-form at about 250 °C after the water molecules are expelled from the spaces to the outside of the crystal through the channels connecting them. It seems that the dependence of the photosensitivity on the humidity comes from the water molecules on the surface of the Y-form. It has been proposed that the high photosensitivity of the Y-form is due to its molecular arrangement of the nearest two molecules in terms of the transition moment⁽⁸⁾. Since the photosensitivity is raised by the existence of the water molecules on the surface, these observed in the Y-form might also contribute to increase the photosensitivity.

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Biography

Okimasa Okada received his B.S. in Metallurgy from the University of Tokyo in 1988 and his M.S. in chemistry from the University of Pennsylvania in 1995. He joined Fuji Xerox Co., Ltd. in 1988 working on molecular simulations. His current interests are in dynamics of polymers and in interactions of molecules in ink.

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