Organic Thin Films

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Electrochromism and Stable n-Type Doping of Highly Oriented Thin Films of Tetrakis(thiadiazole)porphyrazine**

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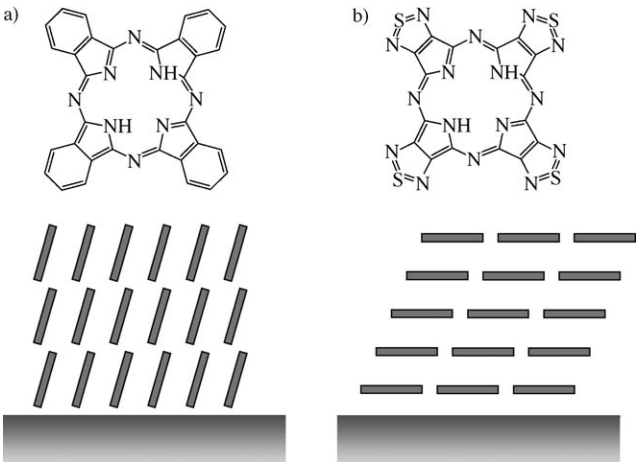
Phthalocyanine (Pc) derivatives (Scheme 1a) have been studied extensively in the last three decades because of their commercial applications as dyes and catalysts, among others.[1,2] The electric, electro-optic, and magnetic properties of metal–phthalocyanine (MPc) derivatives have also attracted recent interest owing to their applications in organic/molecular electronic devices.[3–5] For example, MPc thin films have been utilized as gas sensors; oxidizing gases such as NO_x, HCl, and CO introduce mobile holes in MPc, leading to a significant enhancement in conductivity.[1,6,7] Electrochromism of MPc thin films has also been studied extensively.[8–11] Accordingly, it is important to develop fabrication techniques for these thin films and to elucidate their chemical and physical properties, in addition to performing fundamental studies on the bulk crystals.



Scheme 1. Resolved molecular packing in the thin films of a) H_2Pc and b) H_2TTDPz.

There are two well-known crystal forms for MPc compounds, α and β.[12,13] Both forms consist of a 1D stacking column, in which the molecules have a large π–π overlap. In contrast, intercolumn interactions appear to be hindered by the terminal hydrogen atoms on the benzo ring. Such low dimensionality is disadvantageous for 3D electrical conduction. Seeking multidimensional interactions, Ercolani and coworkers synthesized tetrakis(thiadiazole)porphyrazine (H_2TTDPz, Scheme 1b) and the corresponding metal derivatives, MTTDPz (M = Co, etc.),[14–17] in which intermolecular contacts of the thiadiazole rings were strongly expected in the solid state. In our previous work,[18,19] we carried out the crystal growths, structural analysis, and magnetic measurements on the MTTDPz series. The crystal structure of H_2TTDPz was found to consist of a 2D hexagonal close packing of H_2TTDPz molecules resulting from side-by-side intermolecular S···N contacts (Figure S1 in the Supporting Information). This planar 2D layer is stacked owing to π–π interactions, as in the structure of graphite. Since this crystal structure strongly suggested an application in self-assembling films, we grew thin films from H_2TTDPz and examined their structures and electrochemical properties.

H_2TTDPz thin films of 100-nm thickness were prepared by vacuum vapor deposition. Herein, we focus on the properties of the films of this thickness. This material was found to easily form highly oriented thin films on various substrates with nearly the same structure as that in the bulk crystal. Figure S2 in the Supporting Information shows an AFM image of a thin film on Si(100). The image indicates good overlaps between the grains and a very flat surface; the height difference between the top and bottom on this surface is less than 20 nm. Figure 1 shows the XRD patterns of the thin films on various substrates. They commonly include a peak at $2\theta = 27.3°$, which corresponds to an interlayer separation of 0.33 nm. Since this value is nearly the same as that in the bulk crystal (0.345 nm), it is reasonable to conclude that the thin films of H_2TTDPz consist of a lamellar structure in which the molecular planes are all parallel to the surfaces of the substrate, as shown in Scheme 1b. It is known that H_2Pc thin films show a strong peak at $2\theta = 6.7°$ in the XRD pattern,[1,20] indicating that the molecules are aligned in crystal grains with the molecular plane nearly perpendicular to the substrate surface, as illustrated in Scheme 1a. This type of perpendicular molecular-plane alignment is typical for the thin films of organic π molecules, because this type of structure is advantageous for gaining both π–π stacking stabilization and a high density on a unit area of the

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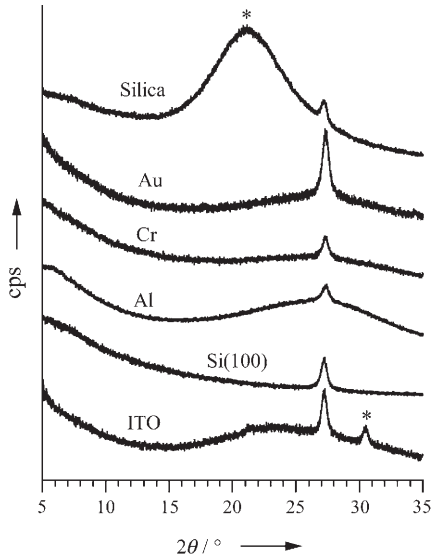

Figure 1. XRD patterns ($2\theta/\theta$ scan) of H_2TTDPz thin films on various substrates. The asterisks indicate peaks from the substrates. cps = counts per second.

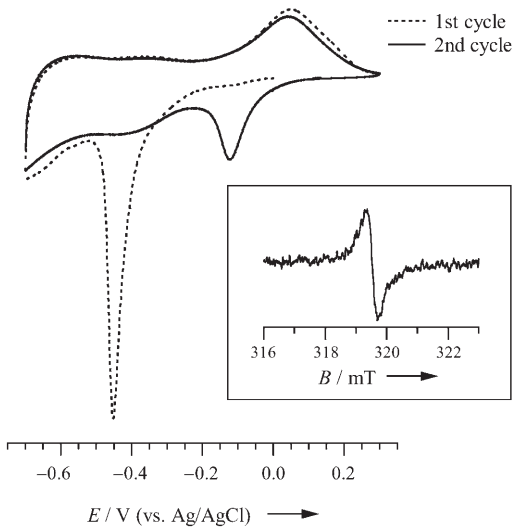

Figure 2. Cyclic voltammogram of H_2TTDPz thin film on Au substrate. Scanning rate: 10 $mV s^{-1}$. The inset shows an EPR signal of the reduced thin film at $E = -0.7$ V at room temperature.

substrates.[21] In other words, the structure of H_2TTDPz thin films, namely, parallel molecular plane alignment with respect to the substrate surface, is very unusual and is indicative of the strong propensity of H_2TTDPz to self-assemble into a 2D sheet structure.

The cyclic voltammetry (CV) of H_2TTDPz films on Au was measured in 0.1 mol dm^{-3} aqueous solutions of various electrolytes. H_2TTDPz films exhibited only a reduction peak, reflecting that this material is an acceptor having electronegative thiadiazole rings on its molecular skeleton. The repeatability of the redox cycle significantly depended on the electrolytes; the thin films exhibited a repeatable redox cycle in the solutions of KCl and NH_4Cl, while they gradually dissolved or peeled off in LiCl solution within a few cycles. Figure 2 depicts the CV curves in aqueous NH_4Cl solution. In the first cycle, a sharp reduction peak appeared at −0.45 V, but in the second or later cycles, the reduction took place at −0.12 V with good reproducibility. The CV peak shape in the first cycle was dependent on the area size of the indium tin oxide (ITO) electrode; the peak became broader and/or split into two when larger electrodes were used. This type of overpotential, as compared to the peak position on all subsequent scans, was often observed in the various thin-film samples, and was recognized as a memory effect,[22] caused by an irreversible penetration of counterions into the film for charge balancing, a surface process such as film restructuring, and/or surface resistance change during the first CV cycle.[9–11] In the oxidation scans, on the other hand, an oxidation peak always appeared at 0.05 V.

The n values for the reductions of H_2TTDPz in the first and second cycles were determined to be 0.86 and 0.63, respectively, by chronocoulometry.[23] The difference between the two values is probably due to the fact that some of the countercations (NH_4^+) that penetrated into the film in the reduction scan remained even after the oxidation scan. The n value for the oxidation was determined to be 0.70. This value was in fairly good agreement with the value for the reduction in the second cycle. To support one-electron reduction, we measured X-band EPR for reduced thin films at $E = -0.7$ V on ITO after removing the samples from the solutions, rinsing with water, and then drying. Although the sample was exposed to air once in these measurements, the color of the thin films indicated that H_2TTDPz was still in the reduced state (see Figure 4a). The inset of Figure 2 shows the spectrum at room temperature. While the neutral thin film was EPR-silent before reduction, a single-line absorption appeared at $g = 2.0032$, indicating the presence of an anion radical species, which was consistent with the results of the chronocoulometry. Notably, this EPR signal was persistent even in air, indicating the stability of the anion radical of H_2TTDPz.

In situ resistance measurements on the H_2TTDPz thin films were performed during the redox scan with the electrochemical apparatus depicted in the inset of Figure 3, following the method reported previously.[24] The gap width of the two-

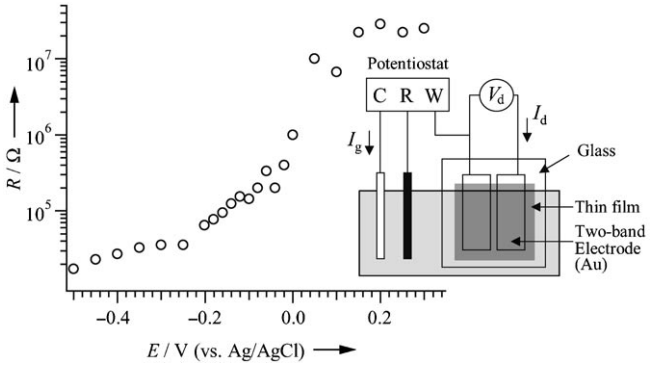

Figure 3. In situ resistance of H_2TTDPz thin film. The inset shows the apparatus. C = counter electrode, R = reference electrode, W = working electrode.

band electrodes (Au) was 0.1 mm, and the film thickness was 100 nm. The measurement details are described in the experimental section. The results are shown in Figure 3. It is notable that these results depended little on the redox cycle number. This is probably due to the fact that we waited for attainment of equilibrium in the in situ resistance measurements. The resistance R of the initial thin film was on the order of $10^7\ \Omega$ in NH_4Cl solution. Upon reduction, the R value suddenly decreased by three orders of magnitude at $E = 0$ V. Since this critical voltage is roughly coincident with the CV reduction peak (−0.12 V) in the second cycle or later, the enhancement of conductivity would have been caused by the generation of unpaired electrons that became charge carriers. Even after the drastic decrease in R, the values of R slightly decreased further below $E = 0$ V. While we confirmed the reproducibility, it was hard to conclude this weak dependence, owing to the experimental difficulty of these in situ measurements; the drain current I_d was affected by the gate current I_g, which exhibited an increase with an increase in $|E|$ (see also the Experimental Section). Upon oxidation, a sudden increase of R was found with little hysteresis (not shown). The in situ resistance measurements clearly indicated an enhancement of conductivity at the reduction point. The electrochemical method can be utilized in the charge control of MTTDPz thin films, which is a key to obtaining the desired electrical properties.

During the CV redox process, H_2TTDPz thin films underwent a significant color change. Figure 4a shows the photographs of the thin film in the KCl solution ($0.1\ mol\,dm^{-3}$) at the three potentials. This material was initially light blue, and turned first to purple and then to brown during the reduction. This color change was reversible over many cycles, and was essentially independent of the electrolytes. Figure 4b depicts the in situ absorption spectra in NH_4Cl solution ($0.1\ mol\,dm^{-3}$), indicating a systematic change with three isosbestic points. The presence of these points indicated the stability of this thin film upon reduction. Before reduction ($E = 0$ V), the so-called Q band and Soret band appeared at 2.0 and 4.0 eV, respectively. With a decrease of the potential, new bands came out at 2.3 and 2.8 eV. Since their intensities were similar to that of the original Q band, they can be ascribed to the bands of this character. The Soret band appeared to exhibit a high-energy shift after reduction. The new weak band at 1.3 eV is probably ascribable to an intermolecular charge-transfer (CT) band. The structure of the thin film is expected to include an interlayer π–π overlap, so that it would be reasonable to expect a magnification of CT after reduction. This view is also consistent with the enhancement of conductivity after reduction. Upon oxidation, we observed a reversible spectral change (not shown). The black dotted curve shows the absorption of the oxidized sample at $E = 0$ V, which has experienced the potential of $E = +0.2$ V once. This curve is similar in features to that of the original sample (black solid curve), but does not agree with it completely. This result suggests that a small number of the penetrated countercations still remain even after oxidation in the film.

These changes in optical absorption are much more gradual than those in CV and resistivity. This result was probably due to the inhomogeneous redox reaction in the optical samples; the area size of the thin film for the optical measurements was much larger than for the others.

Figure 5 shows the XRD pattern change of the H_2TTDPz thin film around $2\theta = 27°$ in the redox cycle. These are not the results of in situ measurements; we measured the XRD patterns after removing the samples from the solutions, rinsing with water, and then drying. The black curve in Figure 5 shows the pattern of the original thin film, which exhibits a peak at $2\theta = 27.3°$. The red curve shows the results on the reduced film deposited at $E = -0.7$ V. The peak position was shifted to 27.5° with a significant decrease in intensity. The peak shift is small, but is larger than the

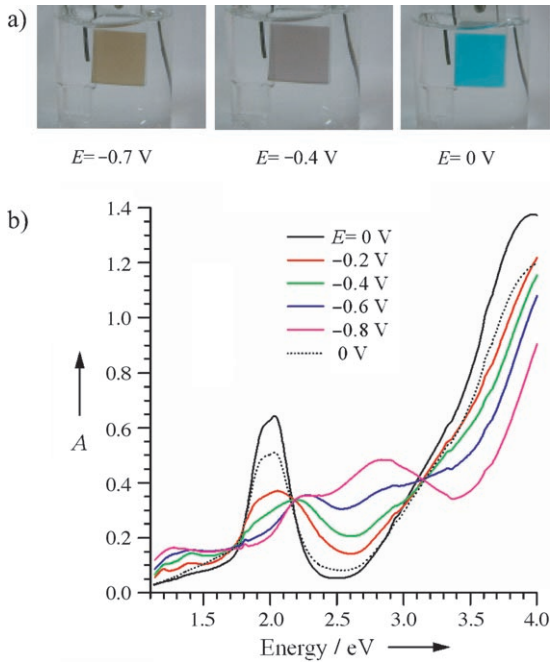

Figure 4. a) Color change and b) in situ UV/Vis spectra for H_2TTDPz thin film on ITO at several potentials.

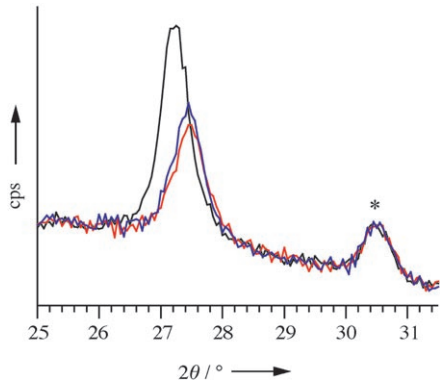

Figure 5. XRD patterns ($2\theta/\theta$ scan) of H_2TTDPz thin film on ITO; the black, red, and blue curves represent the patterns before reduction, after reduction, and after reoxidation, respectively. The asterisk indicates the peaks from the substrate.

experimental error. This observation is supported by the fact that the XRD peaks from ITO at 30.5° in the three curves (asterisk in Figure 5) are in precise agreement. The interlayer distance in the reduced thin film was calculated to be 0.325 nm, which is slightly shorter than that before reduction. The presence of a lamellar structure in the reduced thin film was unexpected, because thin film reduction (or oxidation) was believed to be accompanied by penetration of countercations (or anions) into the films for charge balancing. The persistence of the lamellar structure in H_2TTDPz thin films is considered to be due to the strong self-assembling ability of this molecule. It was also considered that the countercations, penetrated into the film, only break the in-plane structure and/or that the penetration depth of the cations is not very deep, and thus only breaks the structure in the vicinity of the surface.

The sample represented by the red curve was reset in the electrochemical cell and oxidized at $E = 0.2$ V. The blue curve in Figure 5 shows the XRD pattern of this reoxidized thin film. Although the color and resistivity were nearly the same as those of the original thin film, the compressed structure was still maintained after oxidation. This observation suggests that, after a structural modification in the first reduction that is accompanied by the CV overpotential (see Figure 2), the modified structure is maintained in the following redox processes.

In summary, we prepared thin films of H_2TTDPz with a thickness of 100 nm. They were found to include a high and unusual orientation of the molecular planes; the planes are all parallel to the substrate surface, reflecting the strong self-assembling ability of H_2TTDPz. The electrochemical reduction of H_2TTDPz thin films produced reversible electrochromism and n-type carrier doping with an enhancement of conductivity in nearly the same lamellar structure.

Experimental Section

H_2TTDPz was prepared as described in the literature.[14] The Au, Cr, and Al substrates were prepared by generating their evaporation films (100 nm in thickness) on glasses, and the others were commercially obtained. Before deposition, the substrates were cleared by washing ultrasonically with 2-propanol, acetone, and chloroform. The thin films of H_2TTDPz with a thickness of 100 nm were prepared by vacuum vapor deposition at 565 °C under 3×10^{-4} Pa at a rate of 2–6 nm min^{-1} by using a ULVAC VPC-260FN. The film thickness was monitored during deposition by a quartz crystal microbalance located adjacent to the sample position within the bell jar.

Electrochemical measurements of the thin films were carried out at room temperature in 0.1 mol dm^{-3} aqueous solutions of various electrolytes. All the electrolytes were of reagent grade and were used without further purification. Aqueous solutions were prepared using distilled water. A platinum wire and a Ag/AgCl electrode were used as a counter electrode and as a reference electrode, respectively. Electrochemical measurements were performed on an ALS Electrochemical Analyzer Model 600 A.

Thin-film X-ray diffraction was recorded on a Rigaku RINT2000 diffractometer. AFM images were taken using an SII SPI3800 atomic force microscope. EPR measurements were done on a JEOL JES-FA200 spectrometer. In situ absorption spectra were recorded on a JASCO V-570 spectrophotometer; the CV scan was stopped at several potentials. In situ resistance measurements were carried out with the apparatus shown in the inset of Figure 3. The deposit was first brought to the desired potential (gate potential, V_g) by a three-electrode potentiostat, while maintaining the drain voltage at $V_d = 0$ V. After attainment of equilibrium (constant gate current, I_g), the drain current (I_d) was recorded. Then a small-amplitude dc voltage, $V_d = 20$ mV, was applied between the two bands, and the stable excess drain current (ΔI_d) was recorded. The resistance (R) was calculated as $R = V_d/\Delta I_d$. We confirmed the linearity of I_d with respect to V_d in the range 5–20 mV.

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