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Orientational Dependence of the Color and Photoconductivity of 1,4-Di-*p*-toluidinoanthraquinone Single Crystals

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Single crystals of 1,4-di-*p*-toluidinoanthraquinone (also known as solvent green 3, SG3) showed different colors and photoconductivity depending on the crystal orientation. Single crystals were grown from the melt in a sandwich cell of indium tin oxide coated glass, where needle-shaped crystals of different colors (mainly blue, yellow-green, and purple) were observed. The absorption spectrum and short-circuit photocurrent of the needle-shaped crystals that appeared blue, yellow-green, and purple were measured with and without a polarizer. Both the absorption spectra and photoconductivity were dramatically different for different crystal orientations, indicating these properties were anisotropic. X-ray diffraction analysis revealed that in the crystal the SG3 molecules were slip-stacked to form a columnar structure. The polarized absorption spectra can be related to the crystal orientation of each needle-shaped crystal. The blue and yellow-green colors are attributed to an intramolecular charge-transfer (CT) transition along, respectively, the long and short molecular axes of the 9,10-anthraquinone molecular framework. The absorption corresponding to the purple color, which was not observed in solution, is proposed to be an intermolecular CT transition between neighboring molecules in the same column. The crystal orientated to show a purple color had the highest photoconductivity, because excitation of the intermolecular CT band facilitates charge separation.

Introduction

The fabrication of optoelectronic devices based on organic materials requires an understanding of the fundamental phenomena that occur in organic solids. For example, recent studies from our laboratory have described large photovoltaic effects[1a] and charge-trapping processes[1b] in porphyrin-based solids. These effects were measured with thin layer (sandwich) cells prepared by capillary filling with molten organic followed by solidification. These studies[1c−e] have emphasized the importance of crystal structure, arrangement, and orientation on the optoelectronic properties.

An important characteristic of many organic molecules is the anisotropy in their molecular and electronic structure which often produces an orientational dependence of the light absorption.[2−5] Because an electronic transition results from the interaction of the electric field component of the light wave with an electron in the molecule, the absorption of polarized light occurs only when molecules are oriented with their transition dipole moments parallel to (or with a component parallel to) the polarizing direction. In ethylene, for example, the electronic transition at 161 nm is allowed only in the direction of the molecular axis and no absorption occurs when the polarizing direction of light is perpendicular to the ethylene double bond.[5] In anthraquinone, which has two orthogonal transition dipole moments corresponding to the directions of the long and short molecular axes,[4] when the exciting light is polarized in a direction parallel to one molecular axis, a transition along the other axis does not occur. Moreover, this molecule absorbs photons at two different wavelengths associated with the two transition dipole moments. Therefore, the molecule shows different colors depending on the relative position between the polarizing direction of light and the orientation of the molecule. This phenomenon, which occurs with a large number of organic molecules, has rarely been used for practical applications because the orientational dependence of light absorption is not seen in systems where the molecules are randomly oriented (e.g., isotropic solutions or amorphous thin films prepared by spin coating or

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

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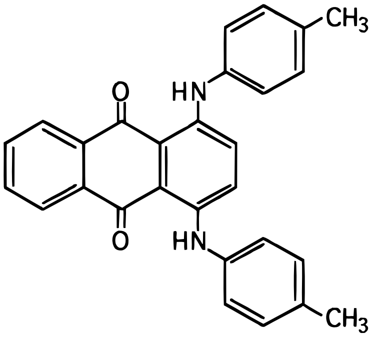
vacuum deposition). Many efforts have been made recently to align dye molecules in a desired direction in a so-called host−guest system for liquid-crystal displays.[6−9] In this case, a very small amount (∼1%) of organic guest molecules are dissolved in a host liquid-crystal medium. An external electric field controls the orientation of the liquid-crystal molecules, forcing the dye molecules to become oriented or partially oriented. In this way, electrically activated segments are colorless while the inactivated segments are the color of the dye, or vice versa, depending on the relative orientation of the dye molecule with respect to the polarizing direction of the light. Mixtures of three different dyes to produce yellow, red, and blue colors have been under active investigation despite many practical challenges.[7,8]

By studying organic single crystals where the anisotropic properties of the individual molecules and the molecular orientations are fixed with respect to specific directions, uncertainties about the exact molecular orientation associated with partially aligned systems are minimized and background interference caused by substrate, host materials, or host−guest interactions are eliminated.[4] Moreover, as compared to samples where a single or a few molecular layers are attached to stretched polymers[4] or liquid-crystal systems,[7−9] molecules are stacked in a single crystal to form well-ordered molecular columns so that the unique optical properties of the individual molecules are amplified to such an extent that the orientational dependence of the light absorption can be seen as sharply different colors with the naked eye, as described in this paper. X-ray diffraction analysis was used to correlate a particular molecular orientation to a specific color. In addition, intermolecular interactions, which have often complicated the interpretations in previous studies,[4] show distinct features in the single-crystal thin films. Such interactions were also probed with optoelectronic measurements. Light-induced charge carrier generation, separation, and transport, as a function of crystal orientation, were studied by monitoring the photocurrent flow through the single crystal. The results are consistent with the optical characterizations and correlate very well with the molecular arrangement in the crystal.

Difficulties are frequently encountered in the growth of large single crystals useful for these types of measurements. For example, single crystals large enough to make electric contacts for photoconductivity experiments are frequently too big for absorption measurements, so that extremely thin single crystals, especially in the UV−visible region, are required.[4] In our previous studies, we have successfully developed a technique for the growth of large (∼1 mm^2 area) organic single-crystal thin films (a few micrometers thick) within two pieces of indium−tin oxide (ITO) coated glass to produce a structure of ITO/crystal/ITO.[1c] This is achieved by capillary filling of the organic substance in its molten state into an empty ITO sandwich cell with a thickness of a few micrometers. ITO serves as a transparent electric contact, so samples prepared this way can be used for both optical and optoelectronic characterization. Electric and optical data can be obtained simultaneously from the same spot on a single crystal with a given orientation. With the help of an optical microscope, the light spot can be focused on a particular site or scanned over the whole sample in order to collect information from different sites on the same single crystal with fixed or variable orientations.

In this paper, we report studies on the optoelectronic properties of 1,4-di-*p*-toluidinoanthraquinone (solvent green 3, SG3) single crystals, a representative dichroic diaminoanthraquinone dye.



1,4-di-p-toluidinoanthraquinone (SG3)

In SG3 the two *N*-phenylamino groups act as electron donors and the two carbonyl groups as electron acceptors, so that an intramolecular charge-transfer (CT) transition is observed in the visible region.[10]

Experimental Section

SG3 was purchased from Aldrich and purified by repeated recrystallization from a toluene−2-propanol (1:2) solution. ITO-coated glass was obtained from Donnelly Applied Film Corporation (Boulder, CO) and was cut into 1 cm × 2 cm pieces. Symmetrical sandwich cells of ITO/SG3/ITO were fabricated according to a previously reported method.[1] Briefly, a small amount of solid SG3 was placed at the opening between the ITO sheets (Figure 1a). The cells were filled by capillary action when they were placed in an oven at ∼225 °C, slightly above the melting point of the dye. The cells with the molten layer of SG3 were allowed to cool at room temperature very slowly, and crystals of SG3 formed within the cell. The thickness of the dye layer was about 6 μm, as estimated by the comparison of the absorbance at 580 nm with that of another sandwich cell whose gap was already known. Electrical contacts to the cell were made to the exposed ITO surfaces with silver paint for photoconductivity measurements. Large single crystals for X-ray diffraction measurements were grown from a highly concentrated toluene solution in Pyrex round-bottom tubes, which were left undisturbed for the duration of the crystallization process. All the crystals obtained were needle-shaped, about 10−30 mm long, 0.1−2 mm wide, and 10−100 μm thick. The needle-shaped crystals grew along the glass wall from top to bottom, with the wider side facing the glass wall.

In the photocurrent measurements (Figure 1b), the ITO/SG3/ITO sandwich cell was fixed on the stage of an optical microscope (Olympus Model BHTU). A small spot (∼150 μm in diameter) of the selected individual needle-shaped crystal was irradiated through the microscope with an external halogen lamp (300 W). The steady-state short-circuit photocurrent was detected by a home-built high-sensitivity amplifier

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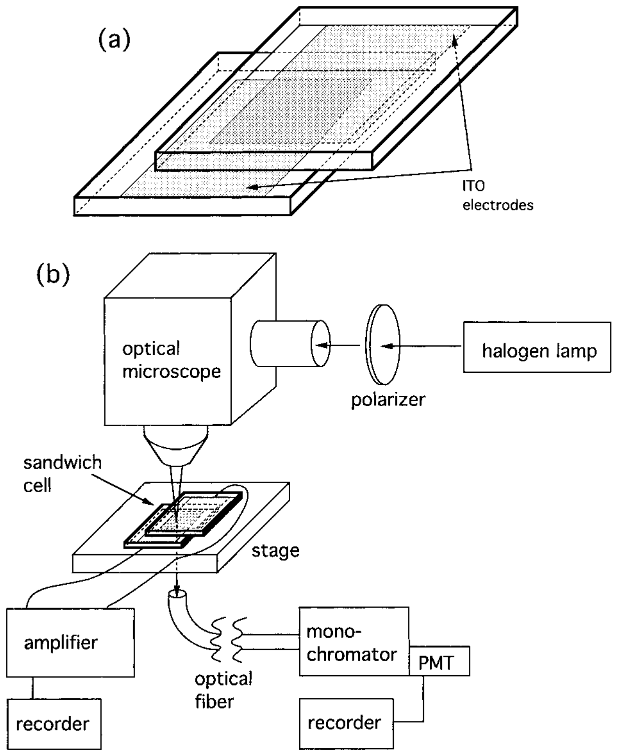

Figure 1. Schematic diagrams of (a) a sandwich cell and (b) the microscopic photocurrent and absorption measurement system.

circuit. No bias voltage was applied to the cell. The cell was covered with aluminum foil to minimize external electrical noise. When polarized light was used, a dichroic sheet polarizer (ORIEL, 27345) was placed between the halogen lamp and the microscope.

The absorption spectra of the colored needle-shaped crystals were measured as follows (Figure 1b). A halogen lamp (650 W) was employed as the external light source of the optical microscope. The ITO/SG3/ITO sandwich cell was fixed on the stage of the microscope, and an individual needle-shaped crystal was selected. The light spot (top irradiation) was ~150 μm in diameter. The light through the sample cell was passed into a monochromator with a glass optical fiber and then detected with a photomultiplier (Hamamatsu, R374). In polarized absorption measurements, the dichroic sheet polarizer was placed between the halogen lamp and the microscope.

X-ray diffraction measurements were carried out with a conventional diffractometer (Siemens, P4). The detailed procedures and results are given in the Supporting Information and will be published separately.[11]

In a time-of-flight measurement, an ITO/SG3/ITO sandwich cell (area, 4.5×10^{-5} m^2; distance between the ITO electrodes, 6.3 μm) was excited by a 532 nm light pulse of a YAG laser (pulse width, ~5 ns) through one electrode. The photoinduced current signal was terminated with a 1 MΩ resistor and then detected with an oscilloscope using the charge integration method.[12]

Results and Discussion

Effect of Crystal Orientation on Color Display. After filling with molten SG3 and cooling to room temperature, ITO/SG3/ITO symmetrical sandwich cells showed a number of needle-shaped crystals in the organic layer upon microscopic examination. Each crystal needle completely filled the spacing of ~6 μm in the cell, and the needles did not appear to overlap. The needles were typically 150−300 μm wide and up to 3 mm long (the cell length), their size being limited by collision during solidification with growing neighboring crystals. These micrometer-thick organic layers were thus composed of single crystals as determined with polarized optical microscopy. The SG3 samples showed several different colors even without a polarizer (Figure 2a). All crystals were of the same needle shape. Moreover, their color changed with polarized light (Figure 2b,c). However, in the same domain of a given crystal that showed one homogeneous color without a polarizer, a strained part appeared as a different color under polarized light. This indicates that the different colors are caused not by different polymorphs but rather by different orientations of the same crystal structure with respect to the polarizing direction of light as observed previously in our laboratory with a different organic single-crystal thin film.[1c] As will be discussed in detail later, blue, yellow-green, and purple are the three basic colors corresponding to three nearly orthogonal transition dipole moments in the organic single crystal. When a particular crystal needle was oriented so that only one of the three basic transition dipole moments was parallel or nearly parallel to the direction

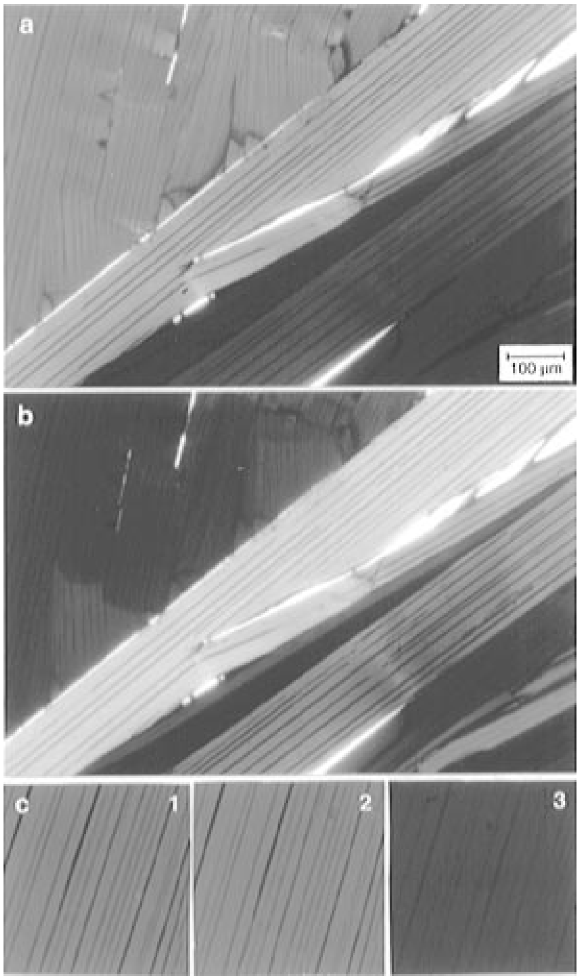

Figure 2. Micrographs of SG3 single crystals between two pieces of ITO-coated glass (~6 μm thick; area of view, 1 mm × 0.67 mm) (a) without and (b) with polarizer. The direction of polarized plane of light was rotated by (b) 140° clockwise from the vertical position. (c) The color of a purple spot (unpolarized light) with polarizer at (1) 60°, (2) 90°, and (3) 150°.

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of polarized light, the corresponding color would dominate, while the other two colors were almost absent. For a crystal needle with a different orientation, however, none of the three dipole moments were parallel to the polarizing direction, and a combination of the three basic colors would appear. Since there were many possible orientations of the crystal needles, many different colors were experimentally observed depending on which of the basic colors made the largest contributions. This was further confirmed with individual SG3 single-crystal needles grown from a solution. In this case, the color of the crystals changed upon rotation of the single-crystal needle. In the discussion that follows, the stated color of a given crystal implies only the orientation of that crystal with respect to the irradiating light.

Another striking characteristic of the organic single-crystal needles is the many thin parallel lines that appear in each crystal domain (Figure 2), similar to those discussed previously.[1c] These are slip lines[1c,13] or stacking faults[14] caused by a relative sliding along certain crystal planes due to the weak van der Waals interactions between molecular columns (described below in a discussion of the crystal structure). These slip lines are useful indicators of crystal orientation. A domain showing only straight lines (oriented in one direction) is a true single-crystal domain with a fixed orientation; the color of that domain will change upon sample rotation between two crossed polarizers, and the color will always be the same everywhere within that domain at any given position. The domain showing a yellow color in Figure 2b is such an example. In other cases the slip lines may be curved or bent to a certain degree at some points as can be seen in the upper-left corner in Figure 2a which shows a purple color. In that corner, each independent direction of the slip line represents a particular crystal orientation that is clearly distinguishable with polarized light as showing different colors (Figure 2b) corresponding to transition dipole moments in different directions. Note that one has to be cautious in using those slip lines to compare crystal orientations. When two single-crystal domains show slip lines running in two different directions, the crystal orientations in these two domains must be different. However, when slip lines in two separate single-crystal domains run parallel to each other, these two crystal domains may or may not have the same orientation depending on which crystal faces (i.e., *ab* or *bc* plane) show the slip lines. Nevertheless, slip lines provide a convenient way to differentiate crystal orientations at variable single-crystal domains.

Effect of Crystal Orientation on Photocurrent. Short-circuit photocurrents are produced in symmetrical cells containing molecular crystals (ITO/molecular crystal/ITO) when these are irradiated through one of the transparent ITO electrodes.[1a] These have been analyzed in terms of different rates of electron and hole injection into the irradiated electrode and the photoconductivity of the single crystal.[1] Upon irradiation, photons are absorbed by a molecule when at least one of its transition dipole moments is along a component of the electric field of the incident beam. This produces an excited state which can lead to the production of free charge carriers in the crystal. A photocurrent is observed if the free charge carriers can travel through the organic layer and enter the external circuit. The magnitude of the photocurrent depends on the efficiency of charge carrier generation and the mobility of charge carriers. Thus, the photocurrent is sensitive to the orientation of the molecule and the transition dipole moment for the charge generation as well as the structural orientation of the single crystal for charge transport. A very strong dependence of photocurrent on the orientation of a porphyrin single-crystal thin film was recently observed in our laboratory;[1c] this was attributed to the anisotropic nature of the organic molecular crystal. The preferential electron injection at the illuminated interface produces a steady-state short-circuit photocurrent (I_{sc}). Figure 3 shows the I_{sc} produced from a number of SG3 needle-shaped single-crystal domains. In this case, the unpolarized light spot was focused to about 150 μm in diameter on different colored crystals in the ITO/SG3/ITO sandwich cell without bias. I_{sc} was significantly larger in crystal domains that showed a purple color than in those of other colors under identical experimental conditions (including the light intensity). The fluctuations of I_{sc} generated from those crystal domains of similar color were much smaller and are probably caused mainly by small variations in color in different crystal domains of the same apparent color. The larger photocurrent in

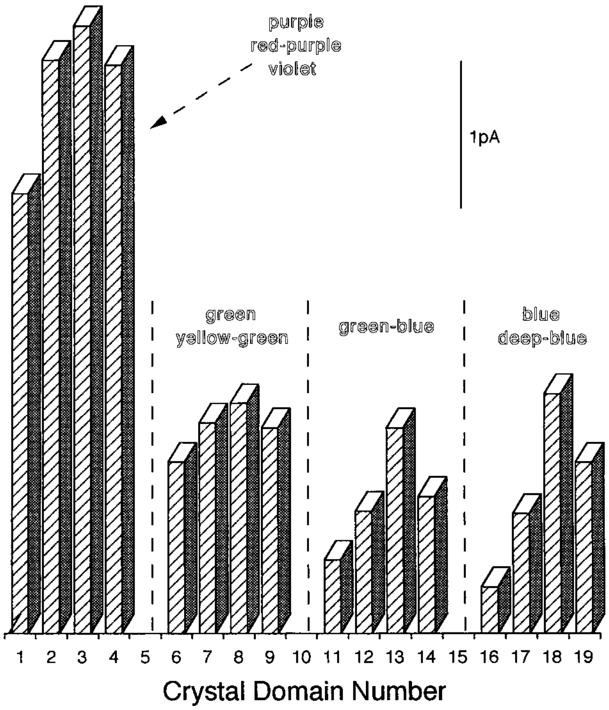

Figure 3. Steady-state short-circuit photocurrents generated at different colored single-crystal domains in an ITO/SG3/ITO sandwich cell. Each of the 16 separate domains showed only one particular color under an optical microscope. Different colors represent the different orientations of the SG3 single crystal and therefore the different directions of the transition dipole moments in the solid. The crystal domains are numbered arbitrarily.

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the purple regions suggests that the rates of charge carrier generation or transport are higher in these domains. As shown below, X-ray diffraction analysis and other evidence suggests that light absorption in the purple crystal domains occurs by an intermolecular electron transfer that is much more efficient in free charge carrier generation, while in other colored domains only intramolecular electron transfer occurs upon irradiation. In the latter case, excited states decay more rapidly to the ground states, leading to a lower photocurrent.[15]

In these measurements, the difference in the absorbance of the different colored crystals did not affect the magnitude of the photocurrent very much, because each absorption band was broad and the peak absorbance was larger than unity for all three. The quartz halogen lamp had relative intensities of about 1:7:100 at 400:500:600 nm. In fact, a blue spot showed a larger absorbance than a purple one, and the light intensity is also larger at the wavelengths absorbed by the blue spots. The behavior of I_{sc} as a function of time was also different in those crystal domains that produced the five smallest photocurrents shown in Figure 3, i.e., domains 11, 12, 14, 16, and 17. Representative curves of these two kinds of behavior are shown in Figure 4, where curve a was obtained from a purple crystal needle (domain 3, Figure 3) and curve b a blue crystal (domain 16, Figure 3). In addition to the large difference in I_{sc}, an initial negative transient photocurrent spike was seen in curve b. This type of spike was observed in five different crystal domains that produced the smallest I_{sc} values. This spike is not caused by an electrical transient triggered by interruption of the light source because the lamp was on during all of the measurements and was turned on and off by manual blocking of the light beam. Even when the light intensity was intentionally reduced with neutral density filters so that the magnitude of I_{sc} obtained in the purple crystal domains (in the range 0.26−4.14 pA) became comparable or smaller than those in domains 11 and 16 (Figure 3), no evidence of the negative transient I_{sc} was seen. In fact, systematic investigations of I_{sc} as a function of light intensity in purple, green-blue, and blue domains indicated that the negative transient I_{sc} did not depend on the magnitude of I_{sc} and was never observed in purple crystal domains. The negative I_{sc} spike is probably an indication of a charge carrier trapping/detrapping process. Trapping sites such as structural defects or impurities were empty in the dark and had to be filled during irradiation before an anodic steady-state current was established. During dark periods, trapped charges were released back to the ground state, giving rise to a cathodic transient whenever the light was turned on. The trapping and detrapping led to a much smaller steady-state photocurrent in regions which showed the cathodic transient.

This explanation was further confirmed by the studies of those crystal domains where grain boundaries or turns of the slip lines were seen. These obvious structure defects should enhance the trapping/detrapping activities. Indeed, the negative I_{sc} spikes obtained in these regions were significantly larger than those generated from apparent defect-free domains and even exceeded the magnitude of the steady-state current. These results are consistent with previous ones produced from porphyrin single-crystal thin films.[1c] In general, the conductivity is sensitive to the crystal orientation, especially for organic substances, many of which are optically and electronically anisotropic. When charge carriers hop along an unfavorable direction in a crystal, the possibility of being trapped is higher. The photocurrent measurements suggested that the orientation for the purple crystals within the single-crystal thin film is much better for charge carrier transport than in the other crystals. This explanation was supported by other experimental data, discussed later, as well as the X-ray diffraction analysis which revealed a molecular column structure in the SG3 crystal. The directions for observing colors other than purple are perpendicular to the molecular columns. In these, charge carriers hop between the columns, and this is inherently slower than hopping within a column. Trap sites may also exist in those domains showing purple color but not to such an extent as to reverse the I_{sc} flow at any time.

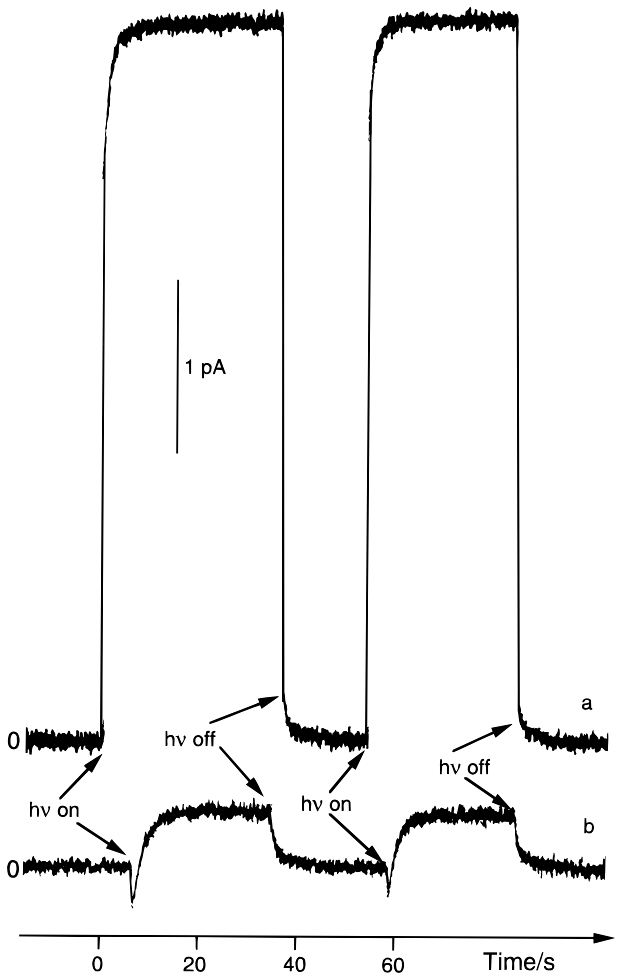

Figure 4. Short-circuit photocurrent, as a function of time, generated in the crystal domains numbered (a) 3 and (b) 16 in Figure 3. The same shape as curve b was seen in those domains that produced the five smallest I_{sc} (domains 11, 12, 14, 16, and 17 in Figure 3), while the other domains generated I_{sc} vs t curves similar to a. The zero current level is indicated in both curves which are shifted for clarity.

Effect of Crystal Orientation on the Absorption Spectra. Upon irradiation, the transition probability and thus the absorbance is maximized when the transition dipole moment of the molecules lies along the

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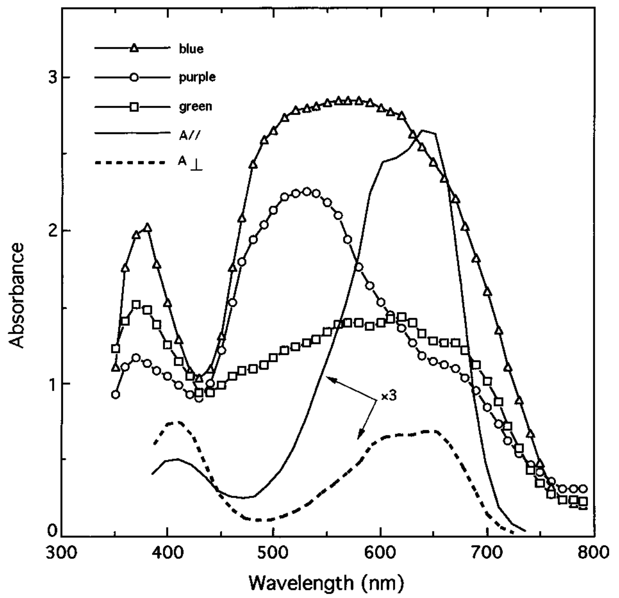

Figure 5. Absorption spectra of (a) purple, (b) blue, and (c) yellow-green spots (~150 μm in diameter) of SG3 single crystals in an ITO/SG3/ITO sandwich cell (thickness, ~6 μm). $A_{\parallel}$ and $A_{\perp}$ are the absorption spectra of SG3 in a nematic liquid crystal with light polarized parallel and perpendicular to the nematic director, respectively.[16]

electric vector of the light and vanishes when it is perpendicular to it. The physical nature of the transition dipole moment is related to oscillations in the molecular charge density induced by the interaction with the electric field of the light wave.[4] Therefore, light absorption (polarized and unpolarized) can be used to determine the molecular and crystal orientation when its structure is known. For an SG3 single crystal, X-ray diffraction analysis indicated that the molecules are regularly stacked to form molecular columns leading to a one-dimensional needle structure.[11] The anisotropy of the individual molecules leads to an optical anisotropy in the crystal. It is therefore useful to correlate the alignment of the molecules in the single crystals to their absorption spectra to determine the crystal orientation of each color seen from the needle-shaped crystal. Experimentally, we measured the absorption spectra of SG3 single-crystal thin films by using a microscopic absorption measurement system (Figure 1); the results are shown in Figure 5. In this case, each colored spot (~150 μm in diameter) showed a distinctive absorption spectrum. In a previous study, Clark and Saunders[16] studied the polarized absorption spectra of aligned individual SG3 molecules in a nematic liquid-crystal medium and reported the absorption spectra using polarized light parallel and perpendicular to the nematic director, i.e., the absorption spectra due to transitions along the long and short molecular axes of SG3 (solid and dashed lines in Figure 5). The absorption spectra of crystals that appeared blue and yellow-green are quite similar to those due to the transition along the long and short molecular axes, respectively. We can thus identify the directions of the crystal orientations showing blue and yellow-green colors as transitions along the long and short molecular axes, respectively. Inoue et al. identified the dominant visible absorption band around 600 nm of 1,4-diaminoanthraquinone as an intramolecular CT transition associated with the charge transfer from the amino groups to the carbonyl groups by means of polarized absorption spectra measurements and theoretical calculations.[10] Therefore, we identify the transition due to the blue color of SG3, which is parallel to the long molecular axis, as an intramolecular CT transition. The transition corresponding to the yellow-green color is less clear. In the case of 1,4-di-*p*-*tert*-butylanilinoanthraquinone, whose structure is quite similar to that of SG3, similar transitions corresponding to the blue and yellow-green colors perpendicular to each other were observed.[17] Note that in the case of a 1,4-di-*n*-butylaminoanthraquinone (solvent blue 35) single crystal, no greenish-color was observed even with a polarizer. In general, 1,4-*N*,*N*-diarylaminoanthraquinones show a greener color than the corresponding dialkylaminoanthraquinones due to the presence of a shorter wavelength absorption band around 400 nm.[17] This implies that the nature of the electron donor group at the 1 and 4 positions affects the shorter wavelength transition, namely, the yellow-green color. An absorption spectrum corresponding to that of the crystal orientation showing a purple color was not observed in either a liquid-crystal medium[16] or solution. The SG3 molecule has two orthogonal transition moments which correspond to the blue and yellow-green colors.[16] The presence of a third absorption band corresponding to the purple color, only observed in the crystal, suggests that this transition involves an intermolecular interaction between spatially arranged molecules.

Color and Photoconductivity vs Polarized Light. As described previously, the crystal changes its color with rotation of the polarizer. Under an optical microscope with a polarizer, a given crystal needle at a fixed orientation changed color from purple to blue or from yellow-green to blue with about a 90° rotation of the polarizer, suggesting that the corresponding three transition dipole moments were essentially perpendicular to one another, as discussed further in the next section. The apparent color of a crystal in a given orientation consists of contributions from all three basic transitions with one dominating; this leads to a rather broad absorption band as shown in Figure 5. Indeed, at a fixed spot on a given crystal needle, the absorption spectra changed with the polarizer angle. When the polarizer angle was adjusted so that the crystal appeared blue, the spectrum matched the absorption spectrum for a crystal that looked blue in unpolarized light. The same was true for the polarizer adjusted to produce yellow-green or purple colors. Since the direction of the purple transition was different by about 90° from those of the monomer transitions, the purple absorption is an intrinsically independent one and is not caused by the Davydov effect.[3,19] Note that the SG3 molecule has both donor and acceptor groups, so that the intermolecular charge-transfer transition was stronger than that of usual homomolecular systems such as tetracene or pentacene.

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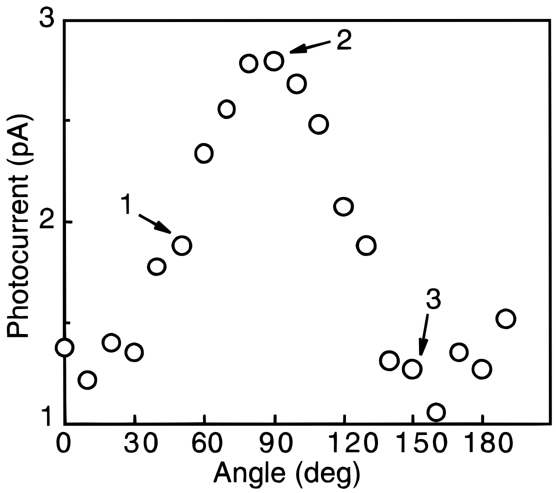


Figure 6. Plot of short-circuit photocurrent versus angle between the direction of the polarized plane of light and the needle direction in a purple spot (~150 μm in diameter) of SG3 single crystals in an ITO/SG3/ITO sandwich cell. Points 1−3 correspond to the colors shown in Figure 2c.

We also investigated how the photoconductivity changed with color while rotating the polarizer at exactly the same crystal location. This eliminates any potential uncertainties that would arise from differences in crystal quality when comparing photocurrents obtained with different crystal needles, which might have different crystal defects or impurities. Figure 6 shows a plot of photocurrent intensity versus the angle between the plane of polarized light and the needle direction. The photocurrent intensity strongly changed when the polarizer was rotated. From the polarized absorption spectra, we confirmed that the total absorbance in the visible region did not change much with rotation of the polarizer. Therefore, the change of photocurrent intensity is inherent to the photoconduction process. The excitation of the absorption band corresponding to the 90° angle between needle and polarized light facilitates the photoconduction much more effectively (roughly three times) than that of the absorption band corresponding to a 160° orientation. This result is consistent with that of the photocurrent measurement of each colored crystal described in Figures 3 and 4. The photoconduction process consists of both charge generation and charge-transport processes. In this case, the charge-transport process should not change by rotating the polarizer, since the photocurrents were measured at exactly the same spot on a given crystal needle. Thus it is the charge generation process that is affected; i.e., the excited state formed by excitation in the absorption band corresponding to the purple color is more efficient in the charge generation process.

Color and Photoconductivity vs Crystal Structure. Details of the crystal structure of SG3 needle-shaped single-crystal grown from toluene solution and determined by X-ray diffraction analysis will be reported elsewhere.[11] The crystal structure, depicted in Figure 7, is characterized by the planes of the two phenyl groups not being parallel to that of the anthraquinone skeleton. The phenyl groups produce large steric hindrance so that the SG3 molecules are slip-stacked with equally directed *N*-phenylamino groups, resulting in a packing which is reflected in the needle shape of the crystal (Figure 7a). The needle direction is perpendicular to the *bc* plane, which is tilted versus the *a* axis by about 5°. The molecular plane of anthraquinone skeleton is tilted with respect to the *a* axis by about 60° (Figure 8). The direction of the long molecular axis is offset by 27° between neighboring columns. Figure 7b shows the overlap of adjacent molecules in the same column. The amino groups of one molecule overlap the carbonyl groups of the molecule directly below it. The distance between nitrogen and oxygen is quite short (3.5−3.6 Å), suggesting the possibility of an intermolecular CT transition. If the purple color is assigned to the intermolecular CT transition, the transition moments corresponding to the blue, yellow-green, and purple colors are nearly perpendicular to each other. This situation can explain the observed effects, because one color among the three would be dominant when two of them are contained in the plane nearly parallel to the direction of viewing.

To investigate the direction of the transition moment corresponding to the purple color, we measured the polarized absorption spectrum of a thin crystal film of SG3, which was obtained on the glass by the same technique as the preparation method of the large single crystal. We chose a small spot (~750 μm diameter) of the thin crystal film and measured the absorbance while rotating the polarizer. The length and width of the thin needle-shaped crystal were 5−8 mm and 300−700 μm, respectively. The thickness was about 3 μm as estimated from its absorbance. From X-ray diffraction analysis, the needle direction is perpendicular to the *bc* plane and tilts by 5° against the longest axis, *a*, the second longest is the *c* axis and the shortest is the *b* axis. Thus in the crystal structure, the molecules stack most tightly almost along the *a* axis and most poorly along the *b* axis (Figure 7a). We assume, therefore, that the SG3 needles lie on the glass with the *b* axis oriented perpendicular to the glass, so that absorption along the *b* axis should be observed in this measurement. This situation is displayed in Figure 8. The transition moment along the long molecular axis, which shows the blue color, is expected to tilt against the *a* axis by 60° (or 120°). The transition moment corresponding to the yellow-green color should be nearly perpendicular to the glass substrate, so that the contribution from this transition should be small in this measurement. In fact, the yellow-green color appeared only when the thin crystal film was tilted to make the needle direction nearly parallel to the viewing direction. A line drawn from nitrogen to oxygen between the closest molecules (dashed line in Figure 8) is tilted versus the needle direction by about 35°. If the transition corresponding to the purple color is the intermolecular CT transition, this absorption would show a maximum at an angle of 35° between the polarized plane of the light and the needle direction. To investigate the direction of these transition moments, we measured the change of the absorbance of the absorption bands corresponding to the purple and blue color near the peak wavelength position of these absorption bands while rotating the polarizer. The results obtained are summarized in Table 1. The absorption band corresponding to the blue color showed a maximum at about 140−150°, which is close to the angle expected between the needle direction and the molecular plane of the anthraquinone skeleton. This is consistent with the blue color attributable to the

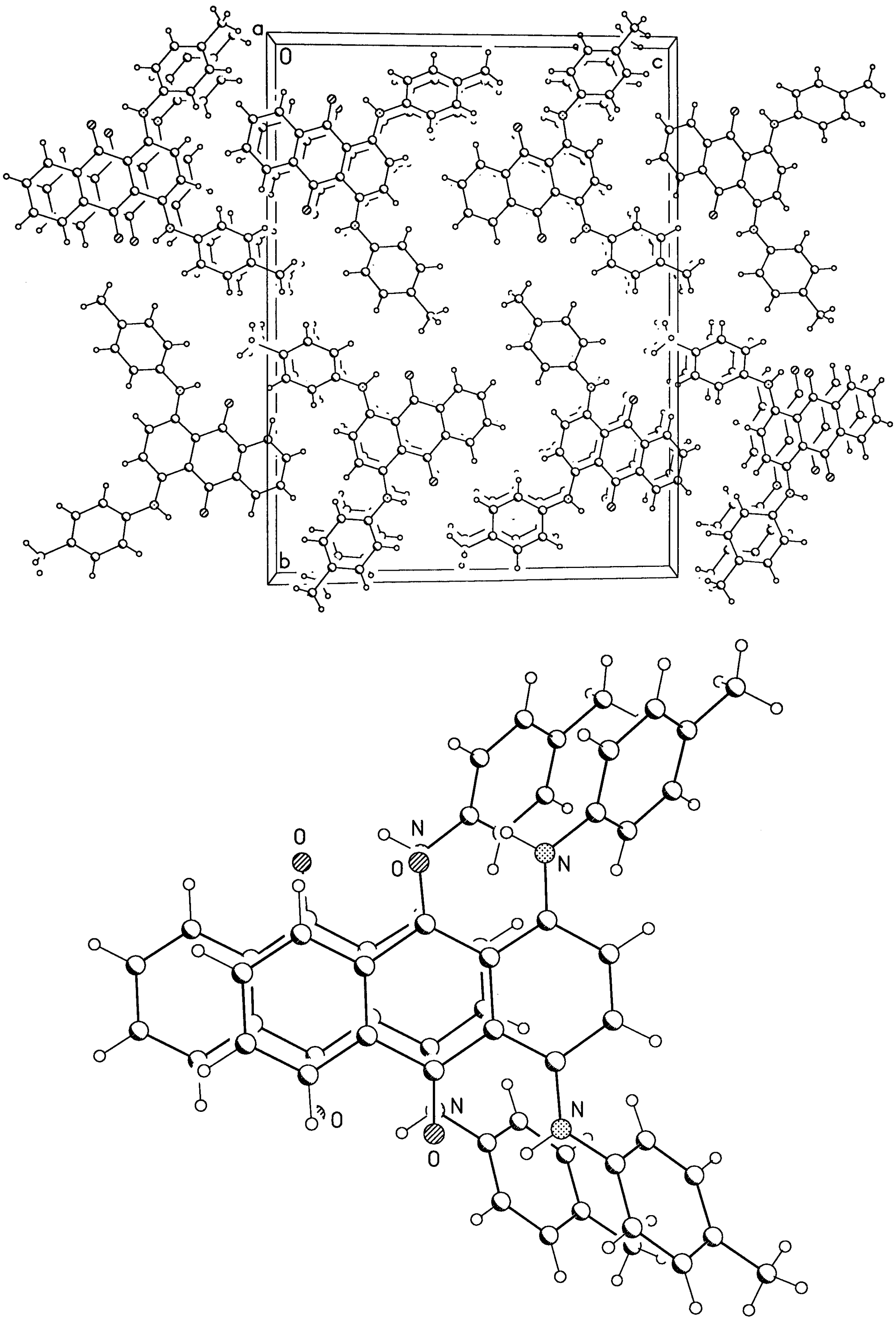


Figure 7. Crystal structure of the SG3 single-crystal determined by X-ray diffraction analysis. (a, top) View along the needle direction (perpendicular to page); the *a* axis is at a 5° angle to the needle direction and (b, bottom) overlap of the adjacent molecules.

intramolecular CT transition. The absorption band corresponding to the purple color showed a maximum at about 70–90°, depending slightly on the wavelength. This dependence might be due to the overlap with another absorption band, probably that corresponding to the blue color, which has a different polarization. In this case, therefore, the value obtained at the shorter wavelength is more likely to be close to the true one. However, this angle (35°) is inconsistent with that of the intermolecular CT transition assuming a transition

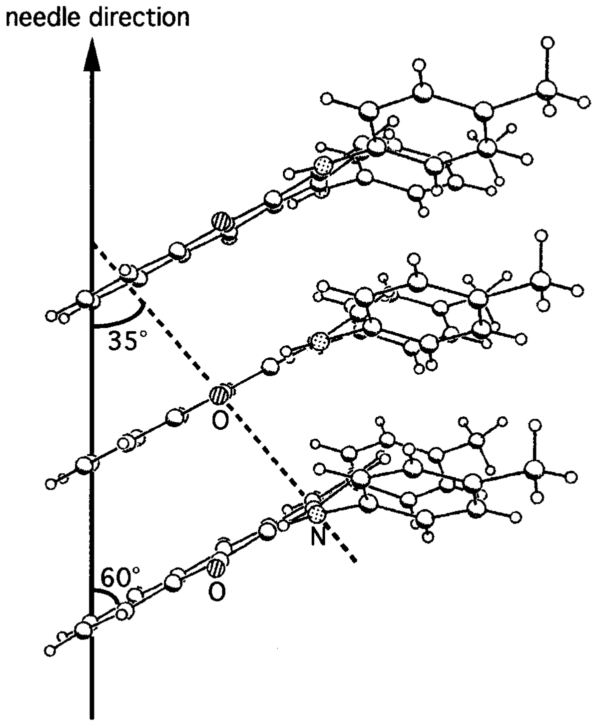


Figure 8. Crystalline packing structure of SG3 viewed parallel to the *b* axis (the *b* axis is perpendicular to the plane of the page). The dashed line is drawn from nitrogen to oxygen between the closest neighboring molecules.

Table 1. Angle between the Plane of Polarized Light and the Needle Direction at Which the Absorption Shows a Maximum and Minimum in a Purple Spot of the SG3 Crystal Thin Film

	angle (deg) of absorption	
wavelength (nm)	maximum	minimum
470	70	160
500	80	170
530	90	180
600	140	50
630	150	60

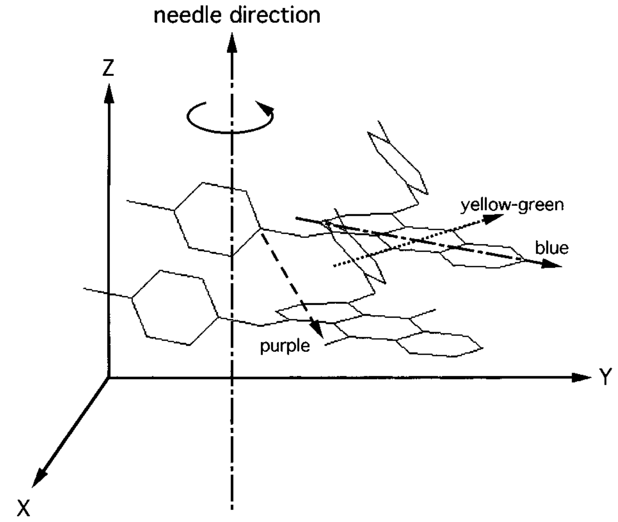
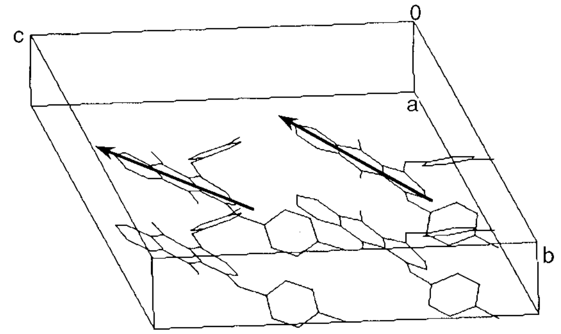
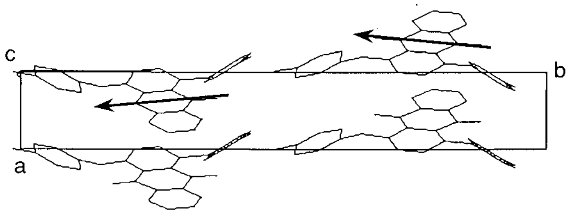


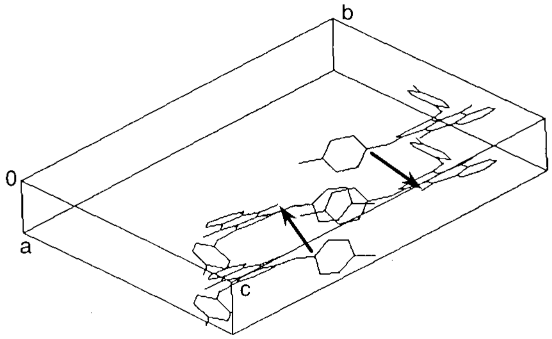
Figure 9. Stacking of SG3 molecules and the directions of their transition moments. The colors which each transition brings are indicated in the figure. *X*, *Y*, and *Z* are experimental coordinates.



(a) blue spot



(b) yellow-green spot



(c) purple spot

Figure 10. Predicted crystal orientation of (a) blue, (b) yellow-green, and (c) purple spots of an ITO/SG3/ITO sandwich cell. The ITO electrodes are parallel to the paper plane. The dominant transition moments are indicated by arrows.

from the N-atom to the O-atom. However, the highest occupied molecular orbital (HOMO) does not involve localization on the nitrogen atom but is delocalized over the phenyl group. Indeed, in the case of arylamines, such delocalization of the HOMO is well-known.[18] If the delocalization of the HOMO extends to the phenyl group in SG3, the direction of the transition moment of the intermolecular CT transition between neighboring molecules in the same column will be tilted much more than an angle of 35°. For example, a line drawn from the center of the phenyl ring to the oxygen of a neighboring molecule is oriented with respect to the needle direction by about 62°, which is quite close to the experimentally obtained angle. MO calculations (AM1 method) confirm that the HOMO is delocalized over the phenyl group and the lowest unoccupied molecular orbital (LUMO) is also delocalized in the anthraquinone skeleton. We conclude, therefore, that the transition corresponding to the purple color, which is observed only in the crystal, can be attributed to an intermolecular CT transition. This is consistent with the finding that excitation into the absorption band corresponding to the purple color produced the largest short-circuit photocurrent. This intermolecular CT excited state promotes an electron to the neighboring molecule, leading to a more effective charge separation than an intramolecular process. Since a special conformation is necessary for the intermolecular CT transition to occur, this transition is observed only in the crystal.

The proposed transition moments are indicated in Figure 9. Consider that we are looking at the crystal along the X axis. In this case, the color of the crystal depends on the projection of each of the transition moments against the yz plane. These projections obviously depend on the rotation of the crystal around the needle direction, leading to the crystal orientation dependence of the color of the crystal.

Since the three transition moments are nearly perpendicular to each other, one of them dominates the color of the crystal as the others become nearly parallel to the viewing direction. Considering that the transition corresponding to the color of each spot should be dominant, we can predict the crystal orientation of each of the colored locations of the ITO/SG3/ITO sandwich cell (Figure 10). In Figure 10, the viewing direction is perpendicular to the plane of the paper. In blue and yellow-green spots, the transition moments along the longer and shorter molecular axes should be nearly perpendicular to the viewing direction, respectively. In both spots the other transition moments should have much smaller components perpendicular to the viewing direction, while at a purple spot, the transition moment due to intermolecular CT transition should have a much larger component perpendicular to the viewing direction than the other two transition moments. At a purple spot, the needle direction does not appear to be parallel to the ITO electrodes, which would facilitate the charge transport process between two ITO electrodes because of better $\pi-\pi$ stacking or intermolecular CT interaction along the needle direction.

We determined the mobility of holes perpendicular to the needle direction as 4×10^{-3} cm^2/Vs by a conventional time-of-flight measurement technique. This mobility is rather small compared to the mobility of holes in crystals, generally within a range of 0.1−10 cm^2/V s.[19] Probably intercolumnar charge hopping is slow. Unfortunately, we could not determine the mobility along the needle direction because of experimental difficulties. We would expect a value in the range 0.1−10 cm^2/V s because of the better $\pi-\pi$ overlap or intermolecular CT interaction along the needle direction. For example, for 1-phenylazo-2-naphthol single crystals, which have a similar needle shape, a large anisotropy in the conductivity between that parallel and perpendicular to the needle direction was observed.[20] It is likely, therefore, that the SG3 crystal is anisotropic not only in its optical properties but also in its electrical properties, including photoconductivity.

Conclusions

We have investigated optical and electrical properties of 1,4-di-*p*-toluidinoanthraquinone (SG3) single crystals. The crystals show three colors (blue, yellow-green, and purple), which are attributed to different orientations of the crystals. The transition producing the purple color, which is not observed in solution, is assigned to an intermolecular CT transition between the *N*-phenylamino group of one molecule to the carbonyl group of a neighboring molecule in the same column. The blue color is attributed to an intramolecular CT transition. Thus, in the SG3 crystal both intra- and intermolecular CT transitions occur. The photocurrent also depends on the crystal orientation. Excitation at the absorption band corresponding to the purple color produced the largest relative photocurrent, because the intermolecular CT excited state formed leads to better charge separation compared with the intramolecular CT excited state. Overall the SG3 crystal shows unique anisotropy in its optical and electrical properties, which may be of interest in the fabrication of novel optoelectronic devices.

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Supporting Information Available: Experimental details for the X-ray diffraction measurements, tables of positional and thermal parameters, bond lengths, angles, torsion angles, and figures (14 pages); lists of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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