Surface Morphological Study of J-Aggregate Thin Films by Atomic Force Microscopy

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Molecular aggregates formed by polymethine dyes in solutions, at surfaces, and in crystals can be used to modulate the intensity and wavelength of light absorption.[1] The applications for such dye aggregates are manifold: photography, xerography, photovoltaic, molecular photonic, and microelectronic devices.[2] The internal structure of such aggregates is widely perceived as arrays of tightly packed molecules with their molecular planes stacked against each other. Several packing models have been proposed based on the epitaxy match between dye crystalline layers and the lattice of a mica substrate: staircase, brickwork, and ladder structure.[3] A special case of the staircase packing in single crystals of polymethine dye 1,7-bis(dimethylamino)heptamethine perchlorate or $BDH^+ClO_4^-$ is illustrated in Figure 1. The aggregate structure has been quantitatively linked to its spectroscopic properties.[4] The strong coupling of molecular transition dipoles generates excitonic states[4] whose absorption energy is significantly shifted to shorter (H-aggregates) or to longer (J-aggregates) wavelength with respect to the nonaggregated state. When there are two molecular orientations in the unit cell, the molecular transition dipoles, M_1 and M_2, couple with each other as vectors, which results in two excitonic transitions: the Davydov sum, m_+, and difference m_-. These two components are perpendicular to each other.[5] In $BDH^+ClO_4^-$ crystals, the m_+ component parallels [201] and absorbs light at 639 nm, and the m_- component parallels [010] and exhibits an absorption maximum at 592 nm.[6] Both transitions are red-shifted from the monomer absorption at 510 nm. In addition to the exciton propagation, the absorption behavior of three-dimensional dye arrays is also altered by polaritons.[7] The polaritons are generated by the coupling of the light wave with the polarization of
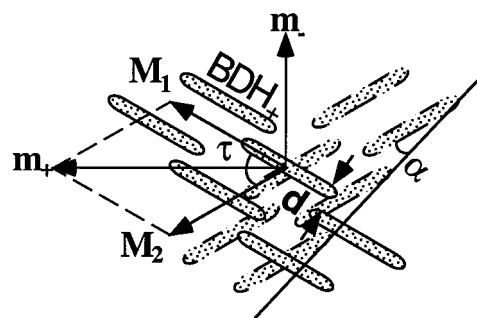

Figure 1. Model of molecular packing in J-aggregates: the distorted herringbone structure of one dimensional staircases in single crystals of $BDH^+ClO_4^-$. Absorption and reflection spectra of J-aggregates depend on the following parameters: the intermolecular distance *d*, the stacking angle α, the angle *τ* between the two molecule directions, the Davydov sum and difference m_+ and m_-, due to coupling of molecular transition dipole moments M_1 and M_2, and the angle $β$ (not shown in the figure) between the molecular axis and the face normal of the crystal.

the medium and lead to a splitting in the longitudinal and transverse exciton energy. The absorption wavelength of the dye crystal varies within the two energy boundaries according to the angle, $β$, between the transition dipole moment and the crystal face normal. It is conceivable that the color of a transparent thin film of three-dimensionally oriented J-aggregates can be tuned precisely if one finds a way to rotate the molecular axis in such thin films.

A method called the thin layer aggregation (TLA) was recently developed to prepare dye films with various color patterns.[8] The TLA method exploits the aggregation of polymethine dyes in strongly undercooled amorphous layers. While the macroscopic properties of the dye layers have been investigated by the UV/vis spectroscopy and thermal analysis, almost nothing is known about the dye thin film surface coverage, roughness, morphology, and molecular packing at the nanoscale. Atomic force microscopy (AFM)[9] has been widely used to study the lattice structure of ordered self-assembled and Langmuir−Blodgett thin films as well as the microstructure of amorphous films and has recently been used to study J-aggregate structure.[10] The goals of this ongoing research are to directly link the color to structure of the aggregate film and to control the film quality and color by intermolecular forces. Structural characterization is carried out by polarized optical spectroscopy and microscopy, X-ray diffraction, and thermal analysis, in addition to AFM.

$BDH^+ClO_4^-$ was obtained by exchanging Cl^- with ClO_4^- in BDH^+Cl^-. BDH^+Cl^- was synthesized according to the literature.[11] Single crystals with green golden color were grown by repeated crystallization from acetone. HPLC grade acetone with purity of >99.7% was purchased from Fisher Scientific and used as received. A 20 μL saturated acetone solution of dissolved $BDH^+ClO_4^-$ single crystals was spin-coated on quartz substrates. Later, the film was

(1) Nakatsu, K.; Yoshioka, H.; Morishita, H. *Acta Crystallogr.* **1977**, *B33*, 2181. Daltrozzo, E.; Scheibe, G.; Gschwind, K.; Haimerl, F. *Photogr. Sci. Eng.* **1974**, *18*, 441.

(2) Thirtle, J. R.; Zwick, D. M. *Color Photography* In *Kirk-Othmer: Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley & Sons: New York, 1979; Vol. 6, p 617. Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449. McEvoy, A. J.; Graetzel, M. *Sol. Energy Mater. Sol. Cells* **1994**, *32*, 221. Lovinger, A. J.; Rothberg, L. J. *J. Mater. Res.* **1996**, *11*, 1581.

(3) Czikkely, V.; Försterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 11; *6*, 207.

(4) Kasha, M.; McRae, E. G. In *Physical Processes in Radiation Chemistry*; Augenstein, L., Ed.; Academic Press: New York, 1964; p 23.

(5) Davydov, A. S. *Theory of Molecular Excitons*; McGraw-Hill: New York, 1962; p 23.

(6) Daehne, L.; Horvath, A.; Weiser, G. *Chem. Phys.* **1995**, *196*, 307.

(7) Small, G. J.; Connolly, M. A.; Stevenson, S. H. *Chem. Phys.* **1988**, *157*, 157. Daehne, L.; Reck, G.; Horvath, A.; Weiser, G. *Adv. Mater.* **1996**, *8*, 486.

(8) Daehne, L. *J. Am. Chem. Soc.* **1995**, 117, 12855.

(9) Binnig, G.; Quate, C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986,** *12*, 930.

(10) Higgins, D. A.; Kerimo, J.; Vanden Bout, D. A.; Barbara, P. F. *J. Am. Chem. Soc.* **1996**, *118*, 4049. Shiojiri, M.; Saijo. H. *J. Crystal Growth* **1996**, *166*, 930. Wolthaus, L.; Schaper, A.; Möbius, D. *Chem. Phys. Lett.* **1994**, *225*, 322.

(11) Nikolajewski, H. E.; Dähne, S.; Hirsch, B. *Chem. Ber.* **1967**, 100, 2616.

redissolved in acetone, and from the absorbance of the solution we estimated the film thickness to be approximately 80 nm. The initial film consisted of randomly distributed dye molecules, as indicated by the total light quenching when placed between crossed polarizers. After an induction period, in the range of a few minutes to hours depending on temperature and humidity, circular spots due to sporadic nucleation emerged and expanded. Eventually the growing spheres impinged on their neighbors to form mostly straight grain boundaries, similar to the spherulitic morphology commonly associated with polymeric crystalline films.[12] Under ideal conditions, the spherulites grow to more than 1 cm in diameter. The growth rate of the spherulite and the molecular tilt angle depend strongly on temperature and humidity, whereas the crystal structure of J-aggregates is insensitive to the above parameters.[13] The aggregation at temperatures below 90 °C yields rainbow-like rings within one spherulite, due to a periodic rotation of dye molecules during growth. At temperatures above 90 °C, two optically uniform films with distinct colors were produced which are the focus of this paper. The growth process was performed in an oven with the temperature controlled at either 110 °C and an absolute humidity of 11.5 g/m^3, or at 135 °C and approximately humidity of 100 g/m^3. No decomposition of dye was observed at these temperatures.

An orthorhombic coordinate system was used to label directions and planes within a spherulite. The radial and growth direction, R, in the plane of the film surface, originates from the center of the spherulite toward its boundary. The tangential direction, T, is perpendicular to R and also lies in the plane of the film. The third axis is the film face normal, N, which is perpendicular to both R and T. Under linearly polarized white light, one spherulitic region was red when light was polarized in the tangential direction and colorless when light was polarized in the radial direction (region RC). The other type of spherulites was blue for polarization along the tangential direction and colorless for polarization along the radial direction (region BC). The dichroic absorption spectra of the aggregated films were measured by polarized UV/vis microspectroscopy and compared with the absorption spectra of the components m_+ and m_- of the BDH$^+$ClO$_4^-$ single crystals.[13] The tangential transition in region RC with an absorption peak at 574 nm matches that of Davydov difference m_- in the single crystal, and the tangential transition at 628 nm in region BC matches that of Davydov sum m_+. The similarity in absorption spectra between dye thin films and single crystals suggests that the molecular orientation in region RC resembles the (201) face of the single crystal which contains m_-, and the molecular orientation in region BC resembles the (010) face which contains m_+. No light was absorbed in the radial direction in either regions; therefore this direction must be perpendicular to both Davydov components. However, it cannot be concluded based only on optical data that the structure in thin films is exactly that of the single crystal.

The amorphous BDH$^+$ClO$_4^-$ film and regions BC and RC were investigated by tapping mode AFM (Digital Instruments). The amorphous film appeared to be molecularly smooth and continuous over the whole substrate surface. AFM measured a surface roughness of 1.2 ± 0.8 nm only. Scan damages were observed at high tip forces and prolonged scanning, indicating a soft
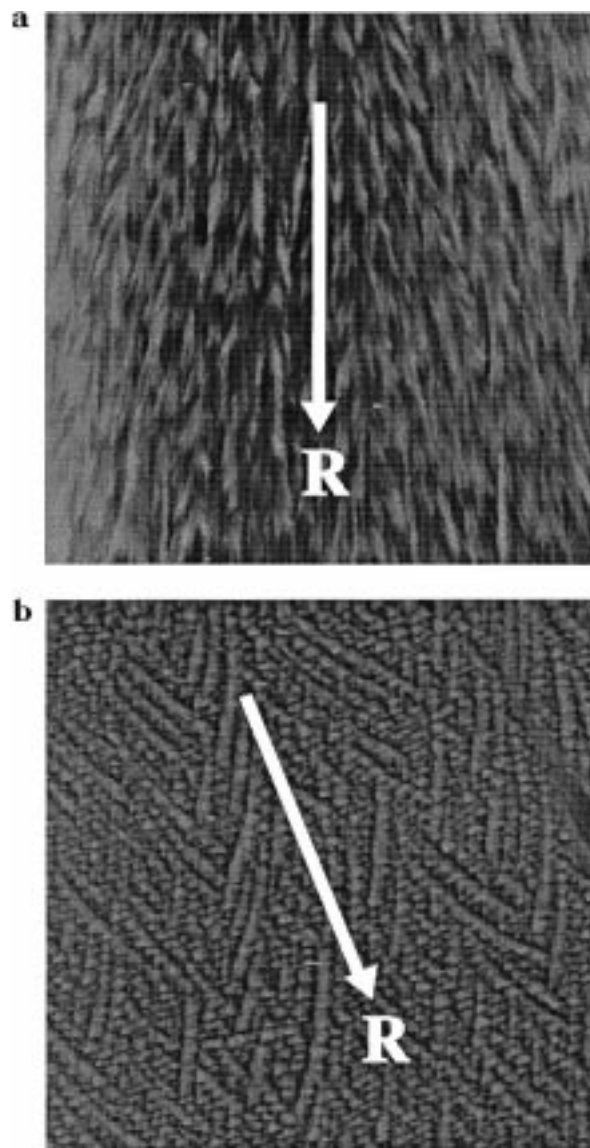
(12) Sperling, L. H. *Introduction to Physical Polymer Science*, 2nd ed.; John Wiley and Sons: New York, 1992; p 218.

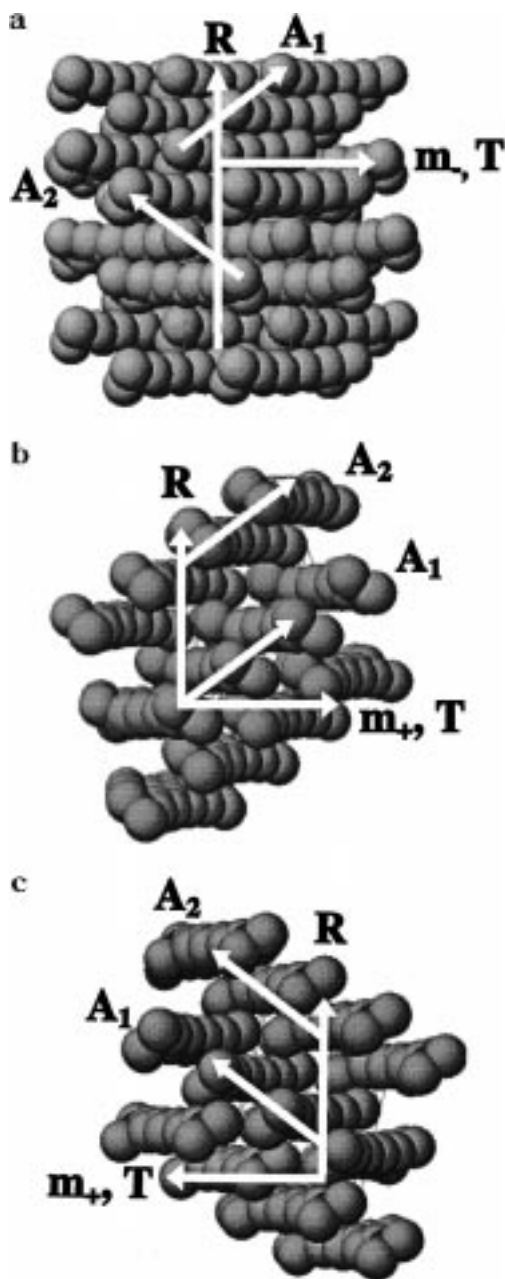(13) Daehne, L.; Biller, E.; Baumgaertel, H. Submitted to *Adv. Mater.*

Figure 2. Tapping mode AFM height images of BDH$^+$ClO$_4^-$ dye thin films: (a) region RC and (b) region BC with a scan size of 45 × 45 μm^2. The radial growth direction is indicated by R.

and viscous film, consistent with the amorphous nature of the initial spin-coated film. After the self-organization process, two distinctive spherulites were imaged by AFM, corresponding to optical regions RC and BC. Centrally radiating threadlike features were observed in both regions. No scan damages were observed after J-aggregate formation indicating a solid-like robust film. Figure 2a depicts the surface of region RC, where the threads are much more diffuse and less defined in shape than those in region BC shown in Figure 2b. Region RC has a surface roughness of 4.3 ± 1.2 nm, significantly less than the film thickness of 80 nm. Contrary to region RC, the edges of radiating threads and individual grains within a thread in region BC were clearly defined. Region BC exhibited a higher surface roughness of 18.0 ± 1.0 nm. The thickness of a thread oscillates along the radial direction, and results in a characteristic surface pattern of a long range order. Furthermore, in contrast to the straight threads in region RC, the threads in region BC have a strong tendency to bend, more pronounced for layers prepared at higher humidity and/or temperature. Domains of left-handed only branches and right-handed only branches have also been observed.

Figure 3. Space-filling model of the BDH$^+$ClO$_4^-$ crystal structure viewed along (a) [201], (b) [010], and (c) [01̄0]. R is the radial growth direction of the spherulite, T is the tangential direction, A_1 and A_2 are the two aggregate directions in a distorted herringbone structure, m_+ and m_- are the Davydov sum and difference components. These figures are a computer simulation based on the data from single crystal, rather than experimental data obtained for the film.

In both types of films, no macroscopic crystalline faces were exposed. This observation agrees with the fact that neither the (010) nor the (201) face is a low-energy crystal face, and both are absent in single crystals. The lack of large crystalline faces at the film surface has so far prevented the molecular resolution by AFM, and direct probing of the BDH$^+$ orientation within the layer. However, the known molecular structure of BDH$^+$ClO$_4^-$ crystals offers clues to the difference in surface morphology between the two color regions. Figure 3 depicts space-filling molecular models viewed along different directions using the CAChe program based on X-ray diffraction data of the single crystal. The single crystal structure is used to describe the molecular packing in thin films based on

the matching of optical absorption spectra between single crystal and thin film. Figure 3a displays the topview of the (201) face, corresponding to region RC. m_- is parallel to the tangential direction T. The projections of the two dye aggregate directions, A_1 and A_2, onto the (201) plane, are symmetrical with respect to the growth direction R. Symmetrical growth along the radial direction was expected in region RC which was indicated by straight threads and smaller surface roughness.

Region BC, dominated by the (010) and (01̄0) faces, has the same crystal structure and growth direction as region RC, except that its crystal lattice is rotated by 90° around R. This leads to a lack of mirror symmetry with respect to the growth direction as shown in the topview of the (010) face (Figure 3b) and (01̄0) face (Figure 3c). At the (010) face, both A_1 and A_2, project onto the right side of the radial direction, whereas at the (01̄0) face, both aggregate directions project toward the left side of R. We believe that the difference in aggregate directions resulted in the right- and left-handed branches competing and coexisting with each other in region BC. In order to expose the (010) face, molecules in the amorphous phase attach to the right hand side of the growth direction yielding a bent growth to the right of the radial direction. When the amorphous layer is more mobile and liquid-like at higher temperature or humidity, bent branches are allowed to grow longer than when the layer is more viscous and solid-like. In the solid-like amorphous layer, straight threads are more likely due to the more frequent formation of parasitic nuclei or crystal twins at the interface between crystalline and amorphous phases. The higher surface roughness in region BC may be a result of the competition between (010) and (01̄0) faces. Another possible cause for increased surface roughness is a higher degree of molecular translation and rotation in the phase transformation process of forming (010) and (01̄0) planes. The reason for the deviation of the growth direction from the aggregate direction is not clear. The main growth direction was expected to be parallel to the bisector between the aggregate directions A_1 and A_2. The growth direction observed was always perpendicular to the polymethine chain. BDH$^+$ molecules probably prefer to attach themselves in the configuration which is parallel to the phase boundary.

Conclusions

AFM and optical study of the thin polymethine dye films has shown that aggregation of dye molecules from an undercooled melt produces two optically uniform regions: region BC and region RC. This is a remarkable phenomenon since the physical size of J-aggregates within the two regions is limited to submicron range. Each color pattern displays a characteristic surface texture which must be related to the slight difference in growth conditions (temperature gradient, humidity, defect type) and variation in molecular orientations. The straight growth in region RC and the bent growth in region BC seem to reflect the different symmetry between the radial growth direction and the two molecular stacking directions. The spin-coated films generally exhibit a higher order as shown by the optical micrographs and a smoother surface as shown by AFM images than those produced by evaporation or epitaxy. The TLA method provides a potential means for the color tuning of dye films by intermolecular interactions and for the further study of the structure and directional dependence of collective properties of dye aggregates. For a deeper understanding of the J-aggregation process, it is necessary to further investigate the internal structure of J-aggregates.

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