

Research Article

Orientation and Optical Polarized Spectra (380–900 nm) of Methylene Blue Crystals on a Glass Surface

Maja D. Milošević, M. Mihovil Logar, A. Vesna Poharc-Logar, and N. Ljiljana Jakšić

Department of Mineralogy, Crystallography, Petrology and Geochemistry, Faculty of Mining and Geology, University of Belgrade, Djušina 7, 11000 Belgrade, Serbia

Correspondence should be addressed to M. Mihovil Logar; logar@mkpg.rgf.bg.ac.rs

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The crystallographic directions of the crystal toward the vector of polarized light can accurately be positioned, so the information that we gain from polarized spectra can be consistently interpreted according to known crystal structure. The orientation and optical properties of the methylene blue (MB) crystals were analyzed by XRD, XRPD, and polarized VIS-NIR spectroscopy. Cationic dye, MB, was polymerized into crystals on a glass slate. The blue color crystals showed pronounced dichroism, twin lamellar structure and bladed to fibrous habit. According to XRD data, [010] direction lies perpendicular to the crystal surface, so we recognized it as (0k0) face, while [100] and [001] directions coincide with crystal elongation and crystal thickness respectively. In this paper, the polarized spectra of MB crystal are presented, measured with the aim of acquisition of referent values, which could be helpful for the identification of MB molecular aggregation.

1. Introduction

Organic dyes can change color and other properties in accordance with their environment. Changes that occur after interaction of dyes with clay minerals are easily determined and followed by spectrophotometry. The formation, structure, and aggregation of methylene blue (MB) molecules into dimers on the surface of clays have been investigated intensively; hence a large amount of data is available [1–8]. Different types of MB molecular packing upon clays and other materials have also been investigated which led us to new information about properties and applications of MB [9–14], and in due time we have encountered different theoretical studies concerning these questions [15].

In accordance with the literature, depending on the concentration, two absorption maximums in the methylene blue (MB) spectra can be observed. These maximums are the result of dipole electron transitions and their intensities. They are dependent upon monomer-dimer structure in which the degree of dimer growth is a dominant factor. MB solution is predominantly of a monomer structure with a pronounced

absorption maximum at 664 nm and a coefficient of absorption $\epsilon = 95000 \text{ L mol}^{-1} \text{ cm}^{-1}$. At MB concentrations higher than $7 \times 10^{-6} \text{ mol/L}$ in water solutions, formation of dimers occurs. They are identified [7] by an absorption maximum in the short wavelength region, between 570 nm and 600 nm. When the concentration of solution increases, the degree of molecular aggregation also increases leading to the formation of higher polymers. When the concentration is high enough, the final result of aggregation is the formation of the crystal lattice. Since the crystal structure represents a definitively organized form of molecular aggregation, the information that we gain from polarized spectra can be consistently interpreted according to known crystallographic directions and *vice versa*. From the pick intensities we can recognize the orientation of the crystal.

Considering the literature data, we found a lack of information concerning detailed explanation of MB molecular aggregation and orientation which are the fundamental properties of MB and are of a great importance in understanding its interaction with different materials. The objective of this

work was to determine the main features of MB crystals, crystallized on a microscopic glass slate, with spectrophotometry, XRD, and optical microscopy.

2. Experimental

2.1. Materials. Crystallization was carried out from 10^{-2} mol/L concentrated solution (Methylene Blue MERCK ($C_{16}H_{18}ClN_3S \cdot 2H_2O$)). The solution (100 μ L aliquot) was placed on a microscopic glass slate and covered with a microscopic cover glass. After 24 hours at room temperature, the cover glass was removed.

2.2. Methods. X-ray diffraction data was determined using Philips PW 1710 ($CuK\alpha$) in intervals from 4° to $60^\circ 2\theta$. The count rate was 2 seconds per $0.02^\circ 2\theta$. The X-ray data were fitted by Rietveld method using PCW refinement package. As the MB crystals are of very small dimensions, the spectra of two optical directions were obtained including the polarizing microscope (Leitz with Nicol prism) in the optical path of the prism monochromator (Beckman DU), driven by a computer controlled stepper motor. The chopped signal (MC 1000 A Thorlab), synchronized and amplified by lock-in amplifier (LIA100 Thorlab), was recorded to the computer. Between 380 and 1000 nm, 1321 points were measured with the photomultiplier tube (FMI Type 6094A) and Si photo diode (Thorlab DET 36A), using 0.06 mm slit. Crystals were positioned in two different directions. Position *E1* represents that the crystal elongation is parallel to the vibration direction of polarized light (*E*). When the crystal elongation is transversal to *E*, that position is represented as position *E2*. The thickness (*t*) of the crystals has been measured using Taylor-Hobson Talystep profilometer with a diamond needle. Besides that, the thickness was determined measuring the optical path difference (retardation, *D*) between fast and slow polarized beams, using Berek compensator and monochromatic light. The magnitude of retardation depends on the thickness of the crystal (*t*) and the birefringence (*d*). Since $D = t * d$, birefringence (*d*) has been taken from Bodman et al. [16]. Results (*t* (Talystep) = 5.2 μ m; *t* (Berek) = 5.64 μ m) are in the limits of 10% of error. The color of the light transmitted through the crystal that we found is best determined with the CIE standard [17], while adopting the standard source CIE-C as the reference illumination.

3. Results

Methylene blue crystals are mostly of a bladed (Figure 1) habit. Fibrous habit with enormous difference in width-length ratio is also present. Most on the crystals are blue in color, rarely purple or purple with a red hue, depending of the thickness. An intensive blue color appears when the elongation of the crystals coincides with *E*. When *E* is perpendicular to the elongation color disappears or becomes light yellow depending on the thickness. Under "crossed" polarized light we have observed polysynthetic twinning which resembles twinning in feldspar minerals. The term "polysynthetic" corresponds to the case when three or more

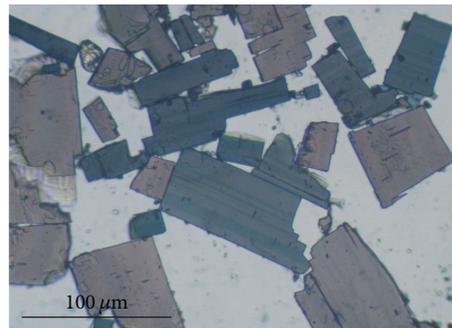


FIGURE 1: MB crystals on microscopic glass slate.

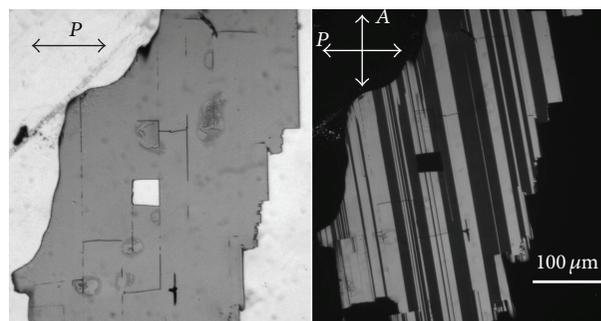


FIGURE 2: Polysynthetic twinning of MB crystals visible under crossed polarized light.

individuals are repeated alternatively on the same twin plane. The lamellas are joined on successive twin planes, parallel with elongation (Figure 2). Relative velocity of the light in two directions of the crystal, parallel and transverse to the elongation, was determined using Berek's compensator.

Since the compensation is achieved when the crystals are oriented at a right angle to the slow ray, we can conclude that the small refractive index is in the direction of crystal elongation. Therefore, MB crystals are optically negative.

Among crystals, thickness variations appeared and their values were in range from 1 to 20 μ m. Thickness above 10 μ m is related to crystal aggregates which appear as radiated or felted masses. X-ray diffraction (XRD) analysis was carried out in an effort to identify structure (Figure 3(a)) and orientation of MB crystals (Figure 3(b)).

Powder diffraction data was fitted according to the structural model for methylene blue powder [18]. Diffraction band profiles and lattice parameters have only been fitted, while atomic positions have been left unchanged. The achieved *R* factors ($R_p = 20.54$, $R_{wp} = 29.08$, and $R_{exp} = 19.04$) are acceptable. The agreement with the structural model of MB pentahydrate is obvious since the difference between model's and the calculated unit cell dimensions is within the error limits (Table 1).

XRD of MB crystals on a glass slate (Figure 3 right) exhibits dominant (0*k*0) reflections and those with a small angle regarding (0*k*0) plane ($(\bar{1}13.1)$, $(\bar{1}42)$). Therefore *b*-axis is positioned upward regarding the glass slate. The wide maximum around $24^\circ 2\theta$ originates from the glass slate.

TABLE 1: Unit cell dimension.

Unit cell (Å)	Calculated	Marr et al. [18]
a_o	9.642 (7)	9.646 (9)
b_o	31.134 (21)	31.106 (17)
c_o	6.987 (5)	6.992 (2)
β_o	96.71 (8)	96.70 (6)
V_o (Å ³)	2083	2083

TABLE 2: The color specification (CIE 1931) of the MB crystals.

	X	Y	d_c (nm)	P_c (%)
MB1				
E1	0.2679	0.2827	481	19.01
E2	0.3154	0.3309	565	5.42
MB2				
E1	0.2329	0.2516	480	35.25
E2	0.3165	0.3350	565	6.85

Polarized absorption spectra (400–900 nm) were obtained from two crystals with different thickness (MB1 = 1.3 μm and MB2 = 3.3 μm). Spectrum deconvolution was carried out with GaussAmp function (Origin program). Seven absorption bands (Figure 4) were observed in the spectra with maximums near 406, 475, 573, 645, 728, 746, and 825 nm (24630, 21040, 17442, 15490, 13732, 13397, and 12117 cm^{-1}).

Variations in peak positions are very small, but a pronounced polarization dependence is obvious. The most noticeable is for the bands 406, 570, and 645 nm. Other bands exhibit more or less the same absorption intensities in both positions. The intensities of bands near 570 and 645 decrease in position *E2*, while the band intensity at 406 nm increases in position *E2*. The color of the crystals is a consequence of absorbance in the 400–700 nm region. Crystals exhibit prominent dichroism: from blue ($d_c = 480$ nm) to slightly yellow ($d_c = 565$ nm) (Table 2). Thicker crystals can be slightly purple-red as a product of intensified band at 406 nm. The dominant wavelength of the crystal's color (d_c) changes depending on the position against the vibration direction of the polarized light.

When *E* is parallel to the elongation, the color is blue ($d_c = 480$ nm), changing the saturation or purity (p_c) depending on crystal thickness. In the other position, *E2*, the color is changed to yellow ($d_c = 565$ nm) but with a considerable decrease in the purity. The d_c is practically the same for both crystals, but the purity of the color (p_c) in *E1* depends of the crystal thickness. The p_c of slightly yellow color in *E2* direction does not depend on the thickness. The absorption coefficients (ϵ_s) of the methylene blue crystals are different than the absorption coefficients calculated for MB solution. The absorbance values were taken for all peaks appearing in *E1* except for the one at 406 nm which appears in *E2* orientation (Table 3).

Since $\epsilon_s = A/c * t$, where A (absorption) is known from the spectra, t (thickness) is measured value, and the concentration ($c = 0.797$ mol/L) was calculated using unit cell volume (2083 Å³) and calculated density (1.31 g/cm³)

TABLE 3: Absorption coefficients of methylene blue crystals in different peak positions.

nm	Peak position		ϵ_s (L/mol*cm)		
	Cm^{-1}	MB1	MB2	Mean	
406	24631	3616	3719	3667	
475	21053	467	393	430	
573	17452	1617	1786	1701	
646	15480	1775	1455	1615	
728	13736	258	250	254	
746	13405	183	219	201	
825	12121	775	616	696	

of MB pentahydrate ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+\text{Cl}^- * 5\text{H}_2\text{O}$); the calculated ϵ_s is in good agreement with the crystal's thickness (MB1 = $1.29 * 10^{-4}$ cm, MB2 = $3.35 * 10^{-4}$ cm) in the limits which do not exceed 10% of average value.

4. Discussions

According to XRD data, the *b*-axis lies perpendicular to the crystal surface. In other words, the *b*-axes are oriented in the direction of the optical system axes. So, we are observing the (0*k*0) crystal's plane. Therefore, we expect that the values of absorption coefficient of the bands in the 550–700 nm region should be a little bit different compared to MB solutions and thin films [3, 14]. The first question is the direction of *x*-axis ([100]) and *z*-axis ([001]). We have observed that each individual lamella has an extinction angle at 6.5° in regard to crystal elongation. The alternative way of lamellar extinction indicates specific twin structure. The twin plane is at the same time a symmetry plane which produces mirror transformation between neighboring lamellas. This is represented by two adjacent elementary cells and a corresponding crystal structure projected on (010) plane (Figures 5, 1, and 2). Comparison with the structure indicates that when the boundaries of elementary cells, along [100], are parallel with the *E*, lamellas are in an optical intermediate position and the benzol rings are at $\pm 6.5^\circ$ inclination.

But when the crystal position is adjusted in such a way that the lamella boundaries are at $\pm 6.5^\circ$ inclination to the *P*, the extinction appears in the alternative group of lamellas, depending on the left or right rotation. Extinction appears in the lamellas when the plate MB molecules are parallel to the *P*. Therefore elongation of the crystal coincides with the *x*-axis ([100]) (Figure 5). Crystal growth is pronounced in the [100] direction (crystal elongation), less pronounced in [001] direction (crystal width), which coincides with the twin axis and least in the [010] direction (crystal thickness). Polysynthetic twinning has, according to the structure, an extinction angle of 6.5 degrees (Figure 5), very close to the angle ($\beta - 90^\circ$). The dipole transition moment due to the exocyclic N oriented in the direction of [010] in the crystal structure does not get excited. This arises from the fact that the [010] coincides with the optical axis of the measuring equipment. The dipole transition moment that gets excited is oriented in the direction of [100] or [001] depending

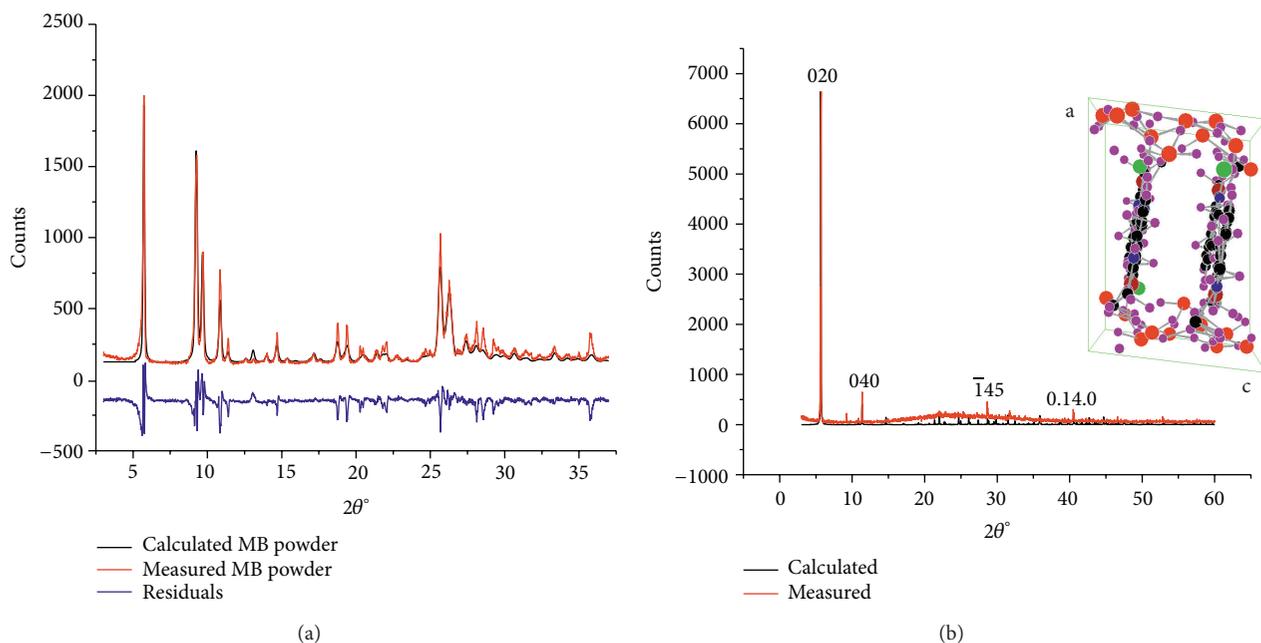


FIGURE 3: XRPD of MB (a) and XRD of MB crystal on the glass plate. Insert: MB structure cross-section according to the XRD data, *b*, perpendicular to glass plate.

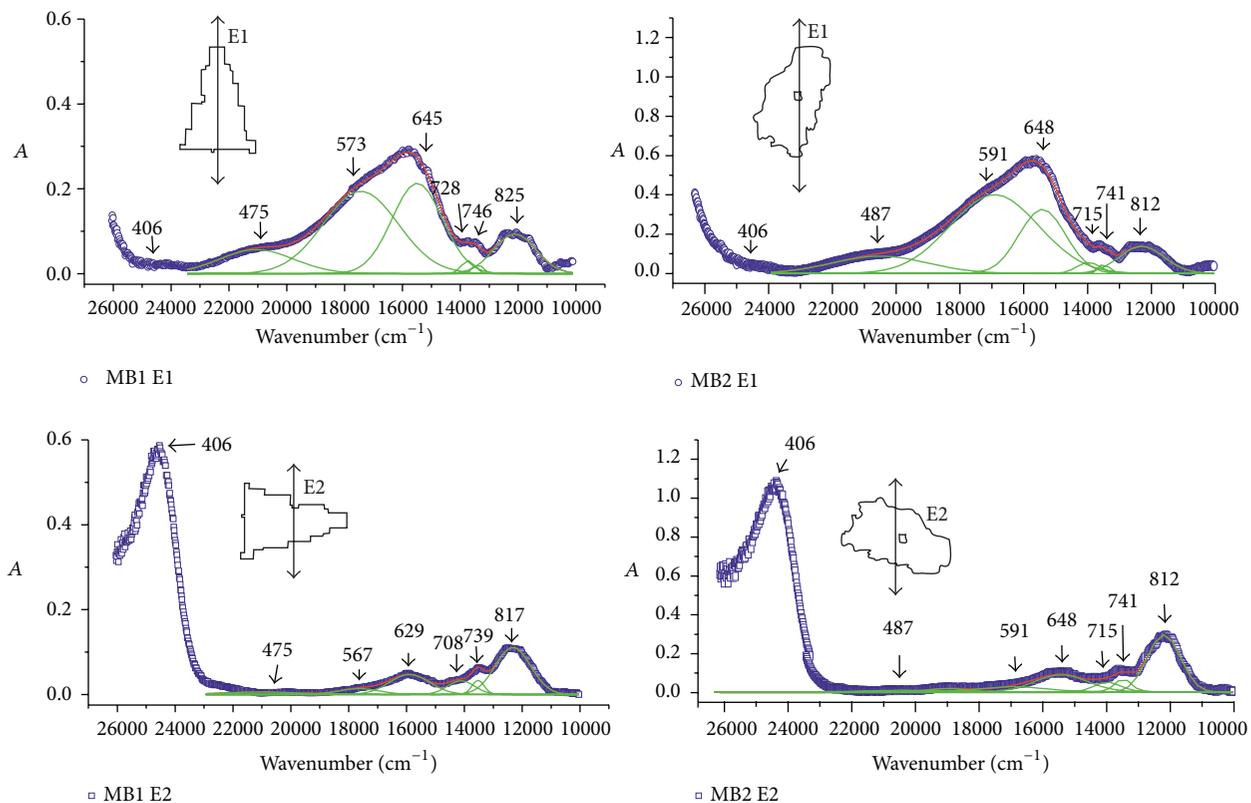


FIGURE 4: Peak positions given in nm scale.

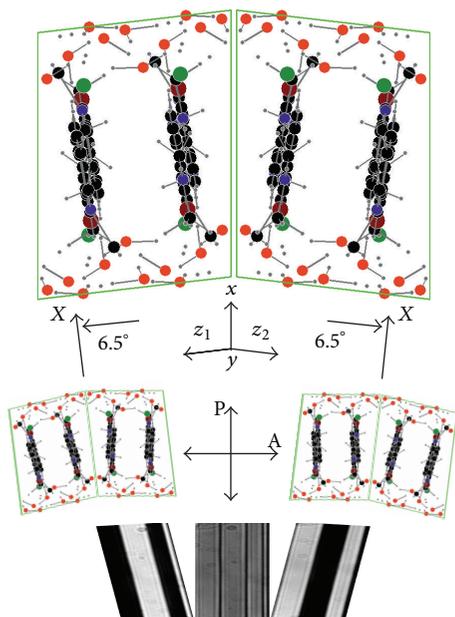


FIGURE 5: Comparison of the structure (010) projection with twinned MB crystal. P and A are the vibration directions of bottom and upper Nicol prisms.

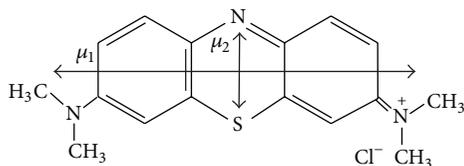


FIGURE 6: Dipole structure of MB molecule. μ_1 , μ_2 -main and assumed dipole transition vector, respectively.

on coincidence with E . When $E = [100]$, the resonance is localized only to the central ring where the dipole transition moment is oriented in direction of μ_2 (assumed dipole transition vector) (Figure 6). In the region of 570–670 nm ($17544\text{--}14925\text{ cm}^{-1}$), all observed absorption bands can be connected with transitions due to the molecular aggregation. It can be expected that energies of these transitions are higher in crystal than in thin films or solutions. In comparison with ϵ (absorption cross-section in m^2/mol) values from Kobayashi et al. [14] for MB water solution (ϵ (604 nm) = $4.9 \times 10^3\text{ m}^2/\text{mol}$) and MB thin film (monolayer ϵ (604 nm) = $1.3 \times 10^3\text{ m}^2/\text{mol}$), our values at 573 nm and 646 nm of $0.1831 \times 10^3\text{ m}^2/\text{mol}$ and $0.1550 \times 10^3\text{ m}^2/\text{mol}$, respectively, are lower. However, absorption coefficient [14] for 15.7 layer ($\epsilon = 0.3 \times 10^3\text{ m}^2/\text{mol}$) is much more closer to our values. Results indicate that with increasing molecular aggregation in distinct crystallographic directions, more precisely, with the increase of molecular preferred orientation, absorption coefficient values decrease. Therefore, Kobayashi et al. [14]

state that the dipole transition moment (μ) in the $[010]$ direction is standing vertically to the substrate surface. Since

$$\epsilon \propto \mu^2 (\sin^2 \xi \cos^2 \varphi), \quad (1)$$

where ξ is the tilt angle of the dipole transition against the normal of the surface and φ is the azimuthal angle, the absorption coefficient (ϵ) becomes zero when ξ approaches 0° and/or $\varphi 90^\circ$. It follows that ϵ becomes zero when the vector of dipole transition moment coincides with the vertical axis ($\xi = 0^\circ$), more explicitly, when it coincides with the optical axis of the instrument, regardless of the φ value. However, regarding the MB crystals, this statement is incomplete, because the angle ξ is zero, but absorption still occurs especially when the E is parallel the crystal elongation ($[100]$). Having in mind that charge distribution is not “distortingly anisotropic” in the MB molecule [18], there is a possibility that in our spectra we observe μ_2 dipole transition (Figure 6).

The μ_2 dipole transition coincides with $[100]$; therefore it is excited when E is parallel to crystal elongation. Crystallographic directions of the crystal toward vector of polarized light can accurately be positioned, so ξ and φ are strictly defined. Since the thin films have a random orientation regarding to φ and partially random regarding ξ , we cannot expect a congruence of absorption's peak positions and intensities with our results. When the crystal is in the position $E1$, two absorption bands are dominant in the spectrum: near 650 nm band with a shoulder at ~ 570 nm (which have been observed in the literature [1, 7, 19] as monomer and dimer H -aggregates). The absorption spectra of crystal are not comparable with a solution because the molecule orientation in solutions is random. Monomeric structure, which is present in solutions, does not exist in crystal structure. Therefore the origin of absorption bands in the crystal spectra cannot be assigned to the monomer resonance. However, analogy with dimeric and trimeric molecular aggregation in solutions can be included in the interpretation of the crystal spectra because MB crystal lattice is the definitive mode of molecular aggregation. So, the band at 650 nm (with a shoulder at ~ 570) corresponds to the dimer spectrum being positioned on the slightly higher energy. When the crystal is in the position $E2$, the very intensive absorption band at ~ 406 nm appears. This absorption band has a high polarization dependence, but it has not been noticed in the literature. It can be a result of interactions that are occurring in the crystal structure along $[001]$. J -aggregation is also visible in the spectrum and its dominant bands are at 730 nm and 750 nm. The absorption band at ~ 820 nm was observed as MB fluorescence band in solutions [20], but this data is not confirmed for crystals of MB.

5. Conclusions

Based on the given results, crystal growth on relatively neutral surface is preferred in the direction of $[100]$, slower in $[001]$ and quite restrictive in the $[010]$, direction. The usual crystal dimension scale is $y : z : x \approx 1 : 10 : 100$. Therefore, with the development of the polymerization, molecular aggregates take more and more the μ_1 direction (Figure 6) vertically

oriented towards the surface. The excitation probability of this dipole transition decreases because the vibrational direction of polarized light is parallel with the substrate. The final result of polymerization is the formation of crystal lattice whereby the natural position of the crystal is that (0k0) plane lies on the surface of the substrate. Since the light beam is directed perpendicular to the surface, the main dipole transition (μ_1) is forbidden. The appearance of absorption bands in the vicinity of known energies for *H* and *J* aggregates in solutions, although on much lower intensity, occurs when the vibration direction of the polarized light (*E*) is parallel to the molecular plane (001). Since in this case *E* coincides with $[100] \pm 6.5^\circ$, it can be assumed that the absorption bands are originating from the excitation of dipole transitions *N-S* in the central ring of MB molecules (μ_2). Positions of these bands in the spectrum of the crystal are on somewhat higher energies than in solutions, which is normal for a high level of polymerization.

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