

2D Positional Mapping of Casting Condition Driven Microstructural Distribution in Organic Thin Films

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Fabrication of large-area thin films and their swift characterization is highly desired for the commercial aspects of the organic electronic devices. Although a number of techniques have been proposed for the large area thin film fabrication, the microstructural variation is still an issue. In this work, the facile characterization of distribution in thickness and macromolecular ordering in the drop-casted and spin-coated poly(3-hexylthiophene) thin-films have been performed through newly developed 2D-positional mapping technique. Through this technique, a comparative analysis of the absorption spectra in terms of peak absorbance and excitonic bandwidth (W) was performed for the whole sample, the lower value of W observed for the drop-casted thin-film depicts its molecular ordering. Moreover, the difference in W (≈ 10 meV) was noticed between two points (≈ 1 mm apart) on the drop-casted film, which corresponds to the difference in microstructural ordering and it is complicated to characterize through the conventional spectroscopic techniques.

1. Introduction

Organic semiconductors show good solution rheology, environment stability, molecular and energetic tunability which makes them a prominent candidate for roll-to-roll fabrication of flexible printed electronics. [1–4] However, their electrical performance still lags behind the inorganic semiconductors due to their relatively hampered charge transport properties.[5] Charge transport in this class of materials significantly depends on the microstructural distribution present in the thin film. Charge carrier primarily gets transported through the π -conjugated backbones, overlapped π - π stacking and intermolecular as well as inter-domain hopping therefor the controlling the morphological distribution is inevitable to improve the transport efficiency.[6–9] Although high performance organic electronic devices utilizing organic small molecular semiconductors have been achieved through vacuum deposition and growing single-crystals in their thin films but such thin film processing techniques are not suitable for the mass production of organic electronic devices.[10–13] Contrary to this, conjugated polymers (CPs) provide good solution rheology and their quasi 1-dimensional nature qualifies them for enhanced transport, when the macromolecular assembly in the thin films is controlled.[14,15] In the recent past, efforts have been directed for the fabrication of thin films of organic semiconductors considering promotion of self-aggregation, molecular orientations and preparation of large area thin films.[6,15–19] At the same time, issues like ease of film fabrication, material wastage and multilayer thin film fabrication in combination with controlled molecular orientation still need the amicable solution.[20–22] Although the film quality including morphology can be controlled through tuning the parameters of casting techniques, the non-uniform distribution in the film morphology cannot be avoided.[23,24] Therefore, adequate characterization is essential for the large-scale fabrication of flexible electronic devices efficiently.

There are several techniques to probe orientation intensity and backbone conformation of oriented CP films like atomic force microscopy, grazing incidence x-ray diffraction, near edge x-ray absorption fine structure spectroscopy, variable angle spectroscopic ellipsometry, polarized UV-Vis-NIR absorption spectroscopy and polarized Raman spectroscopy etc. but commonly in these systems, a tiny area is scanned.[25,26] Even though for material characterization investigation of the small area sample is adequate, precise characterization of large-area CP films will be rather troublesome. Herein, a new method named 2D positional mapping technique is being utilized for the fast and facile characterization of thickness as well as microstructural distribution in the thin films of regioregular poly (3-hexylthiophene) (RR-P3HT) prepared by different methods.[27]

2. Experimental Section

RR-P3HT, super dehydrated chloroform and super dehydrated 1,2-dichlorobenzene (DCB) were purchased from Sigma Aldrich and used as received. P3HT was dissolved in chloroform and DCB to fabricate thin films by spin-coating and drop-casting methods, respectively. Micro slide glass (25 mm × 10 mm) was used as a substrate for the film fabrication. To fabricate the thin films by drop-cast, the solution of RR-P3HT was prepared in DCB with concentration 0.2 % (w/w) and the surface of the substrate (kept on a flat stage) was covered by the solution. Finally, the thin film was obtained after slow solvent evaporation. On the other hand, to spin-coat, RR-P3HT/chloroform solution with concentration 1 % (w/w) was spun at 2500 rpm for 40 s. The samples were characterized through double beam UV-Visible spectrophotometer (JASCO V-570) and our newly developed 2D positional mapping technique.

3. Results and discussion

In order to perform the comparative study on the effect of film fabrication conditions to control the microstructural distribution, the thin films of RR-P3HT were prepared by spin-coating and drop-casting techniques. Both the coating techniques provide an entirely different condition for the macromolecular arrangement and self-assembly of the CP molecules in the thin film. It is worth to note here that the UV-Vis absorption spectrum of CP thin films provides valuable information pertaining to the film thickness and molecular self-assembly. Value of maximum absorbance corresponds to the film thickness, whereas the relative appearance of different vibronic peaks represents the macromolecular arrangement in the thin film. At the same time, if the thin film has an anisotropic arrangement of CP molecules then the polarized electronic absorption spectroscopy can also be utilized to characterize the orientation direction as well as the extent of optical anisotropy.[6,28] However, in this present work microstructural distribution of the isotropic films has been analyzed.

To characterize the films, custom-made 2D positional mapping (henceforth referred to as mapping) technique has been utilized and schematic representation of the measurement system is shown in **Fig. 1(a)**. [27] To realize the sample characterization, a white light source incident on the sample was used for excitation and the transmitted light was received through the optical fiber cable connected to the photonic multichannel analyzer (PMA, 7473-36,

Hamamatsu Photonics). The PMA consists of a Czerny-Turner type spectrograph where received beam is collimated and dispersed in constituent wavelengths as shown in Fig. 1(b). Further, the whole dispersed optical band is simultaneously received by a set of 1024 back-thinned CCD image sensors function as a multichannel analyzer. In this work, 390 of the total 1024 channels were effectively utilized for simultaneous detection of the optical band from 180 nm – 958 nm with 2 nm resolution, to obtain the absorption spectrum of a point area. Beamwidth of the incident white light was 5 mm and the effective aperture of light-collecting optical fiber (connected to PMA) was of 1 mm diameter, which restricts the minimum area of a point on the sample to 1mm. To improve the resolution, a mask with diameter 0.5 mm was placed between the sample and the detector. A computer-controlled X-Y mobile stage was used to position the sample area for scanning precisely. In this way, the absorption spectrum was measured at collinear point area continuously placed on the sample. Finally, five consecutive data points of the measured spectra were averaged out to improve S/N ratio, as shown in Fig. 1(c, e).

The correlation between the film thickness and the peak absorbance is explained on the basis of the Beer-Lambert law, but the non-uniform thickness imparts the estimation error.[29] More precisely, thickness and corresponding peak absorbance of a set of point area can be analyzed to calculate average extinction coefficient with the range of possible error and further the average extinction coefficient can be utilized to map the thickness distribution throughout the sample.[27] Since the consecutive calculation further leads to the higher value of estimated error so it is better to depict the thickness distribution of the film as a function of corresponding peak absorbance.

In order to visualize the thickness distribution in the spin-coated and drop-casted samples were subjected to 2D positional mapping and the results are shown in **Fig. 2**. To make the mapped results more understandable, the absorption spectra of collinear point areas is shown in Fig. 2(a), the points are scanned along the sample length and the path is marked by a broken line as shown in Fig. 2 (b). Finally, by integrating the peak absorbance value at every point of the sample, distribution in film thickness was estimated. From the perusal of Fig. 2 (b, c), it is clear that in the case of spin-coated film, thickness distribution is highly non-uniform, which can be attributed to the rapid film fabrication step hindering the macromolecular self-assembly. The thickness distribution obtained in this work, for the spin-coated P3HT (dissolved in chloroform) is different from the distribution previously reported

for PBTBT (dissolved in DCB), where the film thickness followed an increasing trend from the spin-center towards the film boundary and beautiful concentric rings were obtained. The reason for the irregular thickness distribution in the present case can be attributed to the more flexible nature of P3HT backbone compared to PBTBT leading to higher inter-molecular entanglement causing the formation of the agglomerated region.

However, the role of low boiling-point solvent should also be considered because during spinning the solution move away from the center and solvent also starts to evaporate rapidly. Generally, in a very small interval between solution pouring and spinning steps the contact with substrate and solution leads to the formation of nucleation centers and this is more distributed in case of low boiling-point solvents causing enhanced non-uniformity in the film thickness. In contrast, drop-casting is a slow coating technique with high boiling point solvent, CP molecules get sufficient time to rearrange and adopt a more thermodynamically stable conformation, nonetheless, the improved film crystallinity has also been reported with this technique.[30,31] The positional mapping of the drop-casted film shows the thickness distribution in the shape of a quarter section of concentric rings with the position of center around one corner, which can be attributed to the presence of slope in the stage, where the solution covered samples were kept, as shown in Fig. 2 (c). The film thickness has an increasing trend from the ring-boundary towards the center. The component of the gravitational force along the substrate surface guides the solution movement along a downward slope. Moreover, the solution-substrate contact is also get dragged leading to capillary flow related to the coffee-ring effect and brings the polymer-solution towards the contact line.[30,32–34] The solvent evaporation from the polymer-solution interface can also cause evaporative cooling effect at the interface, which introduces a temperature gradient at the solution surface. The effective temperature gradient act as binary solvent mixtures and may lead to Marangoni flows from the outer surface toward the solution bulk. All of these processes are interrelated and occur simultaneously leading to uniform thickness along the concentric rings. Further, distribution in the macromolecular arrangement in the film was demonstrated through the comparative analysis of the vibronic structure of the positional distribution in the electronic absorption spectra.

Electronic absorption spectra have been most widely used for characterization of thin films of CPs, where the shift in absorption maxima, the appearance of vibronic peaks and spectral width have been utilized for the analysis of macromolecular self-assembly. A perusal

of solid-state electronic absorption of spectra of the thin film of RR-P3HT clearly corroborates that there is pronounced vibronic peaks in the drop-casted film in comparison to spin-coated one as shown in the **Fig. 3** (a), which can be attributed to better self-ordering in drop-casted film. This is the clear evidence of slow growth of the crystalline domain in RR-P3HT, which is known to promote the appearance of lower vibronic modes and arises due to the fibrous crystalline domain formation.[16,35–37] Especially, the growth of 0-0 modes in RR-P3HT is discussed by Spano in detail correlating with the electronic structure of excitonic bandwidth (W) with intermolecular coupling transition energy, E_p , by Equation 1 as shown below.[38]

$$\frac{A_{0-0}}{A_{0-1}} \approx \left(\frac{1 - 0.24 \frac{W}{E_p}}{1 + 0.073 \frac{W}{E_p}} \right)^2 \quad (1)$$

Where A_{0-0} and A_{0-1} refers to respective intensities of 0–0 and 0–1 transitions.

Spanos model was applied for the detailed and quantitate analysis of inter and intramolecular ordering.[38] E_p denotes the vibrational energy at 0.18 eV.[39,40] The value of W was calculated for both of the pristine spin-coated and drop-casted films by deconvolution of individual spectra. The value of W for RR-P3HT, when spin coated was found to be 521.36 meV, whereas substantial decreases in its value was observed for drop-casted sample i.e. 453.98 meV. This clearly reflects the promotion of high intermolecular ordering in between RR-P3HT macromolecules and they maintain rather well stretched conformation owing to the relatively slow solvent evaporation in in drop casting process.

In order to visualize the distribution in macromolecular assembly throughout the thin films, the vibronic peaks of positional absorption spectra obtained through the mapping technique were analyzed in the light of Spano's model as discussed above and have been shown in the Fig. 3(b). The calculated values of W are summarized in the Table-I. From the perusal of Table-I, it is clear that the central region of the spin-coated film possesses higher intermolecular ordering as compared to the region near the boundary. However, in the drop-casted sample, the increasing value of W follows the decreasing trend, when observed from one corner ((0 mm, 0 mm) point on the film as shown in Fig. 2 (c)) and moving towards the other corner diagonally. Therefore, it is evidenced that macromolecular ordering increases

towards the center of the drop-casted ring-patterns. It is worth to mention here that the distribution in the microstructural ordering, obtained follows the expected trend based on conventional fluid dynamic[30] but the variation in the magnitude of W , especially in the case of drop-casted sample was noted and presently it is attributed to the application of different illumination source (Megalight 100, Schott, IBE SMT Equipment, Magnolia) whose intensity was manually controlled, for the conventional UV-Vis slandered illumination source is utilized depending on the setup. Although the shape of absorbance spectra measured through both the techniques are almost similar in this report as well as our previous report, the magnitude of peak absorbance some-times varies, this may also lead to the deviation in the magnitude of W . [27] However the mapped distribution of relative thickness and the macromolecular ordering can lead to the better selection thin film for optimum deice performance.

4. Conclusions

The fabrication of large-area organic thin-film is essential for next-generation printable electronics. Although there are numerous techniques to cast such thin films, the qualitative variation in the film is still a big issue. The facile characterization of the microstructural distribution in the thin film is crucial to control the variation. In this work, the distribution in thickness and macromolecular ordering in the RR-P3HT thin film has been mapped through the 2D positional mapping technique. Through the relative analysis of positional absorption spectra, it was observed that the central region of the spin-coated thin film exhibited more thickness uniformity and high macromolecular ordering. Moreover, the drop-casted thin film shown the thickness distribution in the shape of concentric rings with a uniform thickness along the periphery of individual ring and the value of W was also decreased towards the center of the ring. Moreover, the clear variation in W (≈ 10 meV) was possible to characterize between two closely located points (≈ 1 mm apart) on the drop-casted film, which corresponds to the difference in microstructural ordering and it is complicated to characterize through the conventional spectroscopic techniques. Hence, the 2D positional mapping technique can be successfully utilized to characterize the morphological distribution in the large-area organic thin films in order to attain efficient casting control and cost-effective utilization of the resources.

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Figure Captions

Fig. 1. Schematic illustration of developed measurement system for the 2D positional of mapping (a) and schematic illustration for working mechanism of spectrograph inside PMA (b). The measured spectra for a point with diameter 0.5 mm (c) on the RR-P3HT (d) thin film and the corresponding smoothed data after taking average of five consecutive data points (e).

Fig. 2. Spectral profile along the single line with a continuous array of point areas represented by the broken line (a) on the mapped thickness profile of the spin-coated film (b) and mapped thickness profile of the drop-casted film (c) measured through 2D positional mapping technique.

Fig. 3. Normalized absorption spectra of drop-casted and spin-coated films measured by conventional UV-Vis spectrophotometer (a) and position-dependent variation in the shape of absorption spectra in terms of the appearance of relative vibronic peak (b). Each spectrum represents the microstructural arrangement in the film corresponding to the point area with diameter 0.5 mm, the spectra are measured through 2D positional mapping technique.

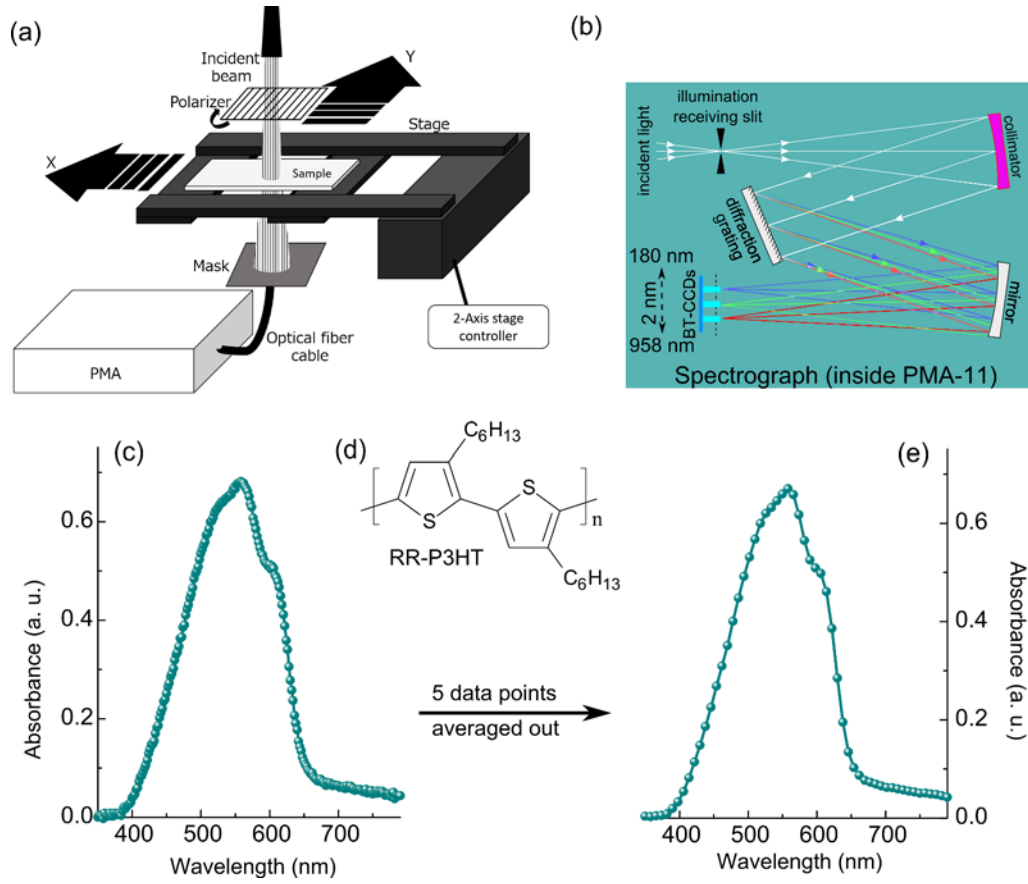


Fig. 1

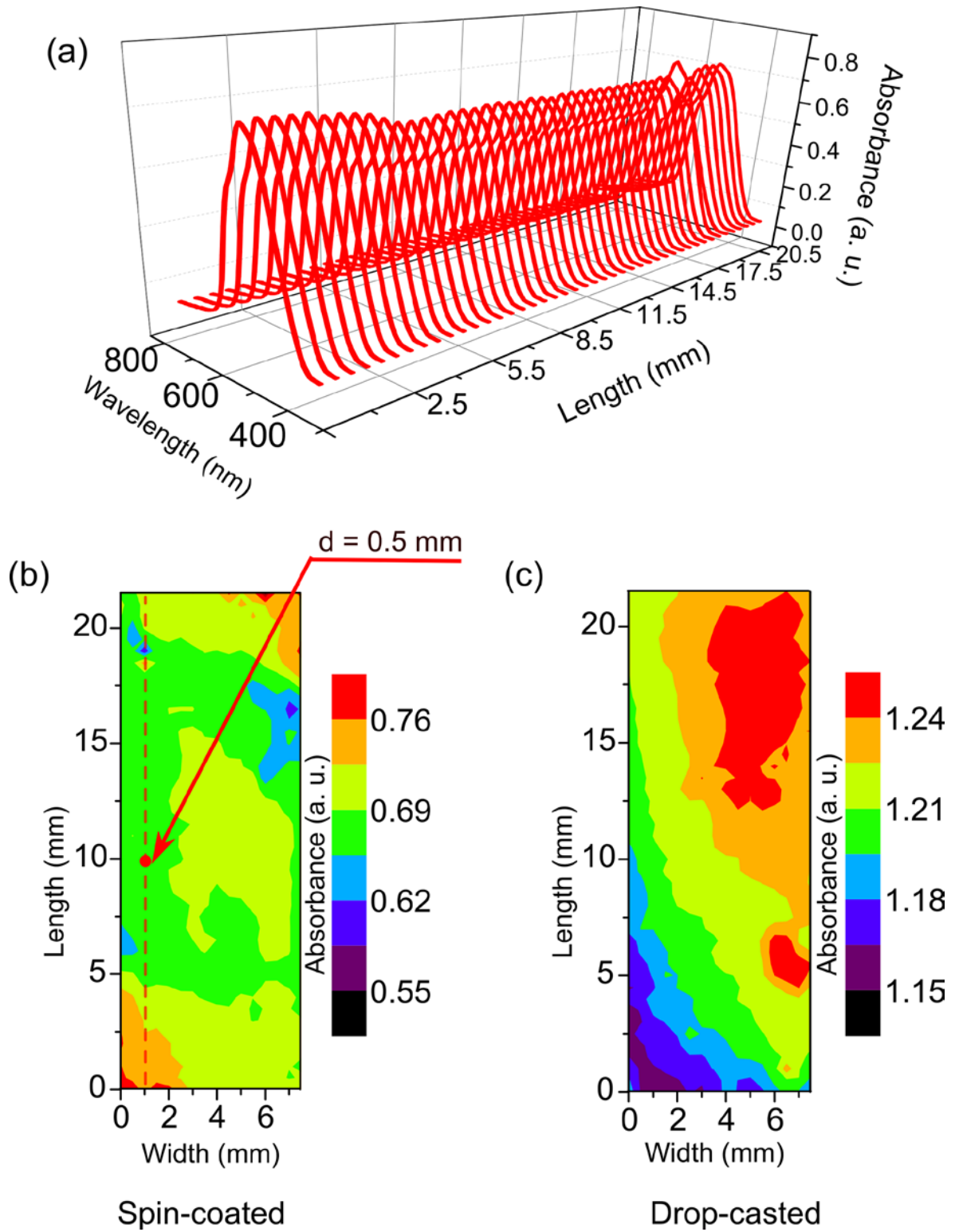


Fig. 2

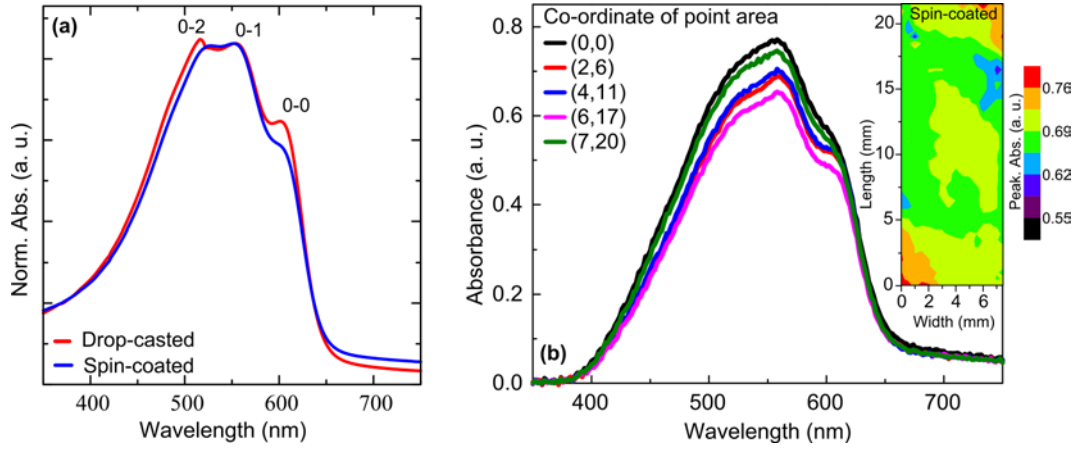


Fig. 3

Table I. The value of excitonic bandwidth (W) at different location of the spin-coated (SC) and drop-casted (DC) films, as shown in Figure 2 and 3. The position dependent absorption spectrum was measured through 2D positional mapping technique.

Point location (SC)	W (meV)	Point location (DC)	W (meV)
(0, 0)	556.41	(0, 0)	394.05
(2, 6)	492.01	(0.5, 1.5)	382.34
(4, 11)	491.83	(1.5, 4.5)	379.07
(6, 17)	433.04	(2.5, 7)	379.02
(7, 20)	537.74	(3, 8.5)	371.88
		(3.5, 10.5)	355.48
		(4, 11.5)	354.76
		(5.5, 16.5)	357.15
		(7, 20)	355.01
		(7.5, 21.5)	353.34