Chapter 4

Anisotropic Study of Electrical and Dielectric Parameters of NiPc

While forming layer-by-layer (LbL) electrostatic assembly of a magnetic organic molecule, namely, nickel phthalocyanine (NiPc), we apply a magnetic field. The field orients the magnetic moment of the molecules on a monolayer along the direction of magnetic field. Such an orientation of the molecules is then electrostatically immobilized with a monolayer of a polycation. By repeating the dipping cycle, we form LbL films with planer NiPc molecules facing a particular direction. With NiPc’s moment perpendicular to the molecular plane, two types of LbL films were formed: (a) NiPc’s molecular plane parallel to the substrate (moment is perpendicular) and (b) molecules perpendicular to the substrate and facing one particular direction, the direction of magnetic field. Such films, with the molecules lying either (a) parallel or (b) perpendicular to the substrate, provide unique systems to study anisotropy of optical, dielectric, and electrical characteristics in these planer organic molecules. The latter film responds to the polarization of incident beam in electronic absorption spectroscopy. Here we show methods to obtain an orientation of molecules in LbL films and study anisotropy of dielectric constant and conductivity of the molecules in ultrathin films.
4.1. Introduction

The initial work on layer-by-layer (LbL) electrostatic assembly of polyanions and polycations¹ in sequence received a momentum when active materials could be adsorbed in thin films.²⁻⁴ Uniform thin films of semiconducting molecules and quantum dots formed an active layer for different optoelectronic and electronic devices ranging from light-emitting diodes to memory elements.⁵⁻¹⁴ The control over thickness in molecular scales has turned the LbL technique to be unique and useful in device fabrication, especially in heterostructures with hole- and electron-transporting materials.

Apart from the control over thickness, the ability to orient molecules in ultrathin films has been of immense interest amongst researchers. Suitable orientation of molecules in thin-films in one hand offers an improved conduction process resulting in higher efficiencies in many devices;¹⁵,¹⁶ such films moreover are ideal systems to study anisotropy of optical and electrical properties of organic molecules.¹⁷⁻²¹ Searches for methods to orient organic molecules in ultrathin-films have hence remained an active area of research.

Some control over the orientation has been achieved in thermally-evaporated thin films. Application of magnetic field near the depositing substrate²² or a control of pressure of the depositing chamber²³ has been a couple of methods to attain a molecular-orientation in such films. In Langmuir monolayers of suitable amphiphilic molecules at the air-water interface, surface pressure plays a major role in imposing a particular orientation of molecules; the orientation has later been translated to Langmuir-Blodgett films through vertical or horizontal lifting.¹⁸,²⁴

In LbL assemblies, some degree of orientation has been achieved through covalent bonding between anionic and cationic monolayers. Azobenzenes²⁵ and bacteriorhodopsins²⁶ are frontrunners in this direction. During the growth of LbL films, an electric field enhances adsorption process;²⁷,²⁸ a magnetic field, on the other hand, can orient the magnetic moment of molecules in a monolayer that in turn can assist LbL electrostatic adsorption process.²⁹ When
the oriented molecules are immobilized through a layer of polyions of opposite charge, the orientation of the molecules becomes frozen in LbL films. Here, we show methods to orient magnetic-molecules in two different directions by orienting its magnetic-moment in each monolayer of LbL films. That is, in this article, we report formation of LbL films of planar nickel (II) phthalocyanine (NiPc) molecules with its molecular plane either parallel to the substrate or perpendicular to it with the molecular-plane facing the direction of magnetic field. In these two types of oriented films, we study anisotropy of optical and electrical properties of the molecules.

4.2. Materials and methods

4.2.1. LbL film deposition: NiPc molecules parallel to the substrate

To deposit conventional LbL films of NiPc, tetrasulfonic acid tetrasodium salt of nickel(II) phthalocyanine (NiPc) and poly(allylamine hydrochloride) (PAH) were used as an anion and a polycation, respectively. PAH had an average molecular weight of 70000 g/mol. To deposit LbL films of copper(II) phthalocyanine (CuPc), tetrasulfonic acid tetrasodium salt of the phthalocyanine was used. All the chemicals were purchased from Aldrich. Concentration of the solutions was 5 mM for both the phthalocyanines; for the polycation, concentration was calculated based on its repeat unit. To deposit conventional LbL films of NiPc and CuPc, suitably treated quartz or indium tin oxide (ITO) coated glass substrates were first dipped in an anionic bath for 15 min. To remove electrostatically unbound moieties from the surface, the substrates were dipped in three separate deionized water baths in sequence for 3, 3, and 2 min respectively. The substrates were then dipped in a polycationic bath for 15 min followed by the same rinsing protocol in a separate set of water baths. This resulted one bilayer of LbL film of a phthalocyanine. The dipping cycle was repeated in sequence to obtain a desired number of bilayers of LbL films.

Since magnetic moment of NiPc is directed perpendicular to its plane, we could orient the molecules in a monolayer with a suitable magnetic field followed by immobilization of the
orientation with a PAH layer through electrostatic binding. In practice, after adsorption of a monolayer of NiPc, we applied a field (330 mT) perpendicular to the substrate with the substrate suspending in an empty beaker. Magnetic moment of NiPc now directs towards the external field. After 2 min, PAH solution was poured in the beaker so that the film became completely immersed in the solution. Electrostatic adsorption of PAH was allowed to continue for 15 min. The magnetic field was then switched off and the film was removed from the polycation solution. The same rinsing protocol was followed to remove unbound polycations from the substrates. This completed deposition of a bilayer of NiPc LbL film with molecules parallel to the substrate. The dipping cycle was repeated in sequence to obtain a desired number of LbL layers. Here, magnetic field was applied after adsorption of each monolayer of NiPc. In the rest of the article, we will term such films as “molecules parallel to the substrate” case. A schematic representation of the dipping sequence is shown in figure 4.1.(a).

![Figure 4.1](image_url)

**Figure 4.1.** Schematic representation of LbL deposition process with magnetic field (a) perpendicular and (b) parallel to the substrate.
4.2.2. LbL film deposition: NiPc molecules perpendicular to the substrate

To deposit films with such an orientation of the molecules, the monolayer was placed in a magnetic field in such a manner that the field was parallel to the substrate. Since magnetic moment of NiPc is perpendicular to the molecular plane, loosely bound molecules on the monolayer became perpendicular to the substrate and tentatively face the direction of magnetic field. As earlier, a layer of PAH was adsorbed to immobilize the molecules with such an orientation. With rinsing procedure remaining the same as before, this formed one bilayer of NiPc with the NiPc molecules perpendicular to the substrate and facing one particular direction. Here also, the dipping cycle was repeated in sequence to obtain a desired number of LbL layer and magnetic field was applied after adsorption of each monolayer of NiPc. In the rest of the article, we will term such films as “molecules perpendicular to the substrate” case. A schematic representation of the dipping cycle is shown in figure 4.1.(b).

4.2.3. Characterization of films and devices

Electronic absorption of LbL films, measured with Shimadzu 2550 UV Spectrometer, was recorded after adsorption of each bilayer. For both types of films, polarized absorption spectroscopy was recorded with polarizers placed at both sample and reference optical-paths. For films with NiPc molecules perpendicular to the substrate and its normal aligning one particular direction, polarized absorption spectroscopy was carried out with the plane of polarization parallel and normal to the expected plane of the molecule. Dichroic ratio was calculated for films after adsorption of each bilayer. Atomic force microscopy (AFM) images of the films were recorded with a Nanosurf atomic force microscope. From the AFM image of an intentional scratch on a film, thickness of each of the films was estimated from the depth profile of the scratch. The AFM topographies also gave roughness of the surface of the films. Orientation of magnetic moments in the films was recorded by magnetic force microscopy (MFM) images. The MFM images were recorded with a Veeco CPII; a magnetized tip recognized magnetic phases of the films. The images were scanned in an amplitude-lift mode. Spectroscopic ellipsometry data in the 1.5 – 4.0 eV range have been measured with Jobin Yvon.
UVISEL elliposometer. For the measurement of current-voltage \((I-V)\) characteristics and impedance spectroscopy, LbL films were deposited on ITO coated glass substrates. Aluminium as a top electrode was grown on LbL films via thermal evaporation under vacuum to form sandwiched device structures. While \(I-V\) characteristics were recorded with a Keithley 6517 Electrometer, Solartron 1260 Impedance Analyzer measured complex impedance in the 10 Hz to 500 kHz region.

**4.3. Results and discussion**

**4.3.1. LbL adsorption processes**

We have grown LbL films of NiPc with PAH. Three types of films were grown: (a) after adsorption of a monolayer of NiPc, a magnetic field was applied perpendicular to the substrate for 2 min before the oriented monolayer was electrostatically immobilized with a monolayer of the polycation, (b) magnetic field was applied parallel to the substrate before immobilization of the molecules, and (c) conventional LbL films, where no magnetic film was applied at any stage of deposition to induce an orientation. It may be noted that since the direction of magnetic moment of NiPc is perpendicular to the molecular plane, the film (a) would yield molecules lying parallel to the substrate leading to a film exhibiting magnetic moments perpendicular to the plane of the substrate. In film (b), the molecular planes will be perpendicular to the substrate with the normal pointing towards the direction of applied magnetic field. During adsorption process in film (c), molecules face only the conventional electrostatic force of attraction. In figure 4.2, we have plotted electronic absorption spectra of the films after deposition of each bilayer. Plots, illustrating spectra for all the three types of films, show that the absorption band representing NiPc molecules increases as the film grows layer after layer. The increase in absorbance is higher in LbL films when each NiPc monolayer was aligned parallel to the substrate.
To summarize the spectra, we have plotted absorbance at 616 nm as a function of number of bilayers. The plot, presented in figure 4.2.(d), shows that for each of the films the increase of absorbance is monotonic with the number of deposited bilayers. The series of experiments were carried out for at least four times. Standard deviation of the results, included in the figure as error bars, has been low. When we compare the spectra of the three types of films, we observe that absorbance of any bilayered film was higher for the “molecules parallel to the substrate” case as compared to the unoriented films or the films with “molecules perpendicular to the substrate”. This occurs due to augmented adsorption during LbL assembly process in subsequent monolayers. That is, when NiPc molecules in a monolayer lie parallel to the substrate, their magnetic moment points towards the growth direction, which is perpendicular to the plane of the substrate; the oriented magnetic moments supplement electrostatic adsorption process of the next monolayer of NiPc. In other words, each layer of NiPc is now assembled due to two forces: (i) electrostatic force that is conventional in LbL deposition and (ii) magnetic force appearing from aligned moments of oriented NiPc molecules. The aligned moments can be evidenced from MFM images of the films, as will be discussed in the next section. This method of LbL deposition can hence be termed as magnetic-moment assisted electrostatic adsorption process. Due to this assistance from magnetic moments, a better surface coverage is achieved in a monolayer; the absorbance corresponding to NiPc increased at a higher rate as the LbL deposition process progressed.

In film (b) with H parallel to the substrate, the molecules are adsorbed with its plane perpendicular to the substrate. Magnetic moment of the planer molecules face the direction of magnetic field (both are parallel to the substrate). Hence the magnetic moment of the molecules would not augment LbL deposition process. Absorbance increased at the conventional rate as the LbL deposition progressed. The plot of absorbance versus number of bilayers matched the one for conventional LbL film that was deposited without any magnetic field. In film (c) too, surface coverage of molecules would not be augmented. While MFM tip may not detect any moment in the surface of film (b), electronic absorption spectrum would become polarized due to the perpendicular orientation of molecular planes on the substrate.
Figure 4.2. Electronic absorption spectra of different bilayers of NiPc LbL films deposited (a) by applying magnetic field perpendicular to the substrate, (b) by applying magnetic field parallel to the substrate, and (c) without any magnetic field. (d) Absorbance at 616 nm versus number of deposited-bilayers for the three cases. Error bars show the degree of reproducibility in each type of depositions. Inset of (c) shows chemical structure of NiPc.
4.3.2. Magnetic force microscopy (MFM)

MFM images of the films supported such an orientation of the molecules in LbL films. Figure 4.3.(a) shows such an image of a 15-bilayer film where a perpendicular magnetic field (to the substrate) was applied during adsorption of NiPc molecules so that the planer molecules remain parallel and their magnetic moment perpendicular to the substrate. The image captures the magnetic moment due to the molecules. For comparison, MFM images were recorded for the other films, namely, LbL films with “molecules perpendicular to the substrate” and films deposited without any magnetic field. Such images have been presented in figures 4.3.(b) and 4.3.(c), respectively. In films presented in figure 4.3.(b), magnetic moment of the molecules lie parallel to the substrate and align the direction of magnetic field. Hence, the MFM tip could not “see” the magnetic moment of molecules. In figure 4.3.(c) representing a film where no magnetic field was applied during the adsorption process, some degree of orientation of the molecules is visible. This could be due to the fact that usual LbL assembly process may induce some orientation in films with the molecular core lying parallel to the substrate.20

![MFM Images](image)

**Figure 4.3.** Magnetic force microscopy images (amplitude-lift mode scan) of 15-bilayer LbL films of NiPc (a) with molecules parallel to the substrate (b) with molecules perpendicular to the substrate, and (c) without any preferred orientation. Area of each MFM images was 600 nm x 600 nm.
4.3.3. Polarized absorption spectroscopy

Absorption spectrum of film (a), that is, the film with “molecules parallel to the substrate”, was not polarized. In the other film, namely in film (b), where magnetic field was applied parallel to the substrate during LbL deposition, electronic absorption spectrum was polarized. This was due to the orientation of NiPc molecules. We recorded absorption spectra of such films with incident light polarized parallel and normal to the molecular plane that we expect to have formed in the film. Such spectra were recorded for films of different number of LbL bilayers. In figure 4.4.(a), we present polarized absorption spectra of a 15-bilayer film along with a spectrum of the film with unpolarized light. Absorbance has been more for a particular polarization of incident light as compared to that recorded with a polarization orthogonal to it. With unpolarized light, absorbance values are intermediate to the polarized cases. This implies that the molecules had a preferred orientation in the films. We find that molecular planes face the direction of the magnetic field that was applied during the LbL adsorption process.

Dichroic ratio ($d$), the ratio between absorbances with the electric field perpendicular to the molecular plane and that with the field parallel to the plane, is a measure of the orientation of rod-like molecules in films. We applied the formula for the planar molecules; a spectrum of the ratio for a 15-bilayer film is plotted in figure 4.4.(b). The ratio reached about 0.64 at 616 nm, which is the absorption band maximum of NiPc molecules. Dichroic ratio responded to the film thickness. In figure 4.4.(c), we plot the ratio at 616 nm as a function of number of LbL bilayers. With an increase in film thickness, dichroic ratio of the film reached a steady value. For thinner films, the value of the ratio was 0.25 that corresponds to a mean titling angle ($\phi$) of 35° that has been calculated from equation $d = \frac{1}{2} \tan^2 \phi$.

It may be recalled that this equation is applicable to films of rod-like molecules where only the tilt angle with respect to the axis of polarization is calculated. In the present case with planar molecules,
two types of titling will affect the polarized absorption spectra: tilt of the molecule along the two axes of the molecular plane. That is, tilt of the molecular plane with respect to both the substrate as well as the axis of polarization is involved here. Tilt of the plane only with respect to the substrate may actually be much less than 35°.

**Figure 4.4.** (a) Polarized electronic absorption spectra of 15-bilayered NiPc LbL films deposited with magnetic field parallel to the substrate. Here, the molecules are perpendicular to the substrate and are facing one particular direction (the direction of applied magnetic field). Schematic representation of the molecules on the substrate was shown in figure 4.1.(b). In addition to spectra with unpolarized light, the figure shows plots with plane of polarization parallel and perpendicular to the molecular plane. (b) Dichroic ratio versus wavelength plot as derived from the two polarized spectra. (c) Dichroic ratio at 616 nm as a function of number of LbL bilayers.

The thesis of orientating molecules with a magnetic field in LbL films gains support by depositing the films with different magnitude of the magnetic field. Since an individual molecule has a relatively low magnetic moment, a reasonably high field was required to orient the molecules. We chose different (magnitude of) magnetic field for the LbL deposition process and continued for 15 bilayers. For each of the cases, we recorded polarized electronic absorption spectra to determine the degree of orientation of the molecules in LbL films. In figure 4.5., we plot dichroic ratio as a function of magnetic field that was applied to each monolayer during the LbL adsorption process. The ratio decreased above a certain field. The
plot shows that a minimum field was necessary to orient NiPc molecules. Also, with an increase in magnetic field, the degree of orientation tends to reach a limit or saturation.

**Figure 4.5.** Dichroic ratio at the absorption band maximum (616 nm) versus magnetic field that was applied to orient the NiPc molecules perpendicular to the substrate and facing one particular direction (the direction of applied magnetic field). Schematic representation of the molecules on the substrate was shown in an earlier figure, namely figure 4.1.(b).

### 4.3.4. Control experiments

As a control experiment, we continued with magnetic field assisted LbL deposition with CuPc molecules. Here, the LbL deposition processes without or with a magnetic field (either parallel or perpendicular to the depositing substrate) did not differ. In other words, LbL deposition process of CuPc with magnetic field did neither become augmented nor yield an oriented film. Plots of absorbance at any wavelength versus number of layers did not differ in the films; absorption spectra of the films neither depended on the polarization of incident light.
This was in contrast to the results presented for NiPc LbL films. This is expected due to non-magnetic nature of CuPc molecules. The results hence show that for a magnetic organic molecule, a magnetic field applied at a suitable stage of LbL deposition protocol can augment the monolayer adsorption process and enforce an orientation of molecules in LbL films. The method moreover would allow any particular orientation of magnetic organic molecules in ultrathin LbL films by selecting the direction of magnetic field with respect to the substrate.

**Figure 4.6.** (a) Typical AFM image of a scratched 16-bilayer LbL film deposited with a magnetic field parallel to the substrate (molecules perpendicular to the substrate) along with (b) the depth profile of the scratch. The area of the AFM image was about 50 μm x 50 μm. (c) Film thickness versus number of deposited-bilayers of NiPc for the three types of films (as shown in legends).
4.3.5. Thickness of different films

Thickness of NiPc LbL films with different molecular orientations has been estimated with AFM topography. Here, film surfaces with an intentional scratch on the films were scanned; depth profile of the topography was a measure of the thickness of the films. A typical topography and its corresponding depth profile are shown in figures 4.6.(a) and 4.6.(b), respectively. It is interesting to compare the thickness of NiPc LbL films deposited in different methods. In figure 4.6.(c), we summarize plots of thickness versus number of LbL layers for the three types of films. We find that the thickness of the film is more when the LbL deposition was carried out with a magnetic field parallel to the substrate as compared to the other two cases, where either magnetic field was perpendicular to the substrate or no magnetic field was applied. That is, the film thickness depends on the orientation of the molecules. Since the NiPc molecules are planer in nature, the results support that a magnetic field parallel to the substrate enforces a particular orientation of the molecules in LbL films. Since the molecular plane lie perpendicular to the substrate (and face the direction of magnetic field), such films return a higher thickness as compared to the other two cases. That is, the dimension along the plane of the molecules contributes or adds up to the thickness in film (b). In film (c), during the usual LbL assembly process without any magnetic field, the planer NiPc molecules may become adsorbed through as many of its anionic moieties as possible with the tiny molecular magnets in anti-parallel configurations. Hence, LbL adsorption process of the subsequent layer has not become augmented. Thickness of the films (a) and (c), on the other hand, remained the same, since both the films have molecular cores parallel to the substrate.

In film (a) with molecules assembling parallel to the substrate, a higher absorbance along with the invariance in film thickness may appear conflicting. A closer analysis reveals that the films with molecules assembling parallel to the substrate meant a more-compact film. It may be stated here that LbL deposition process does not always provide complete coverage in a monolayer (number of free ionic moieties dictates the coverage). Due to this assistance from magnetic moments of the molecules in a monolayer, the surface density of NiPc or
coverage in the subsequent monolayer is more in film (a) as compared to that in films (b) and (c). Hence, absorbance corresponding to NiPc increased at a higher rate as the LbL deposition process progressed. But the thickness of film (a) remained the same since electrostatic adsorption process ensured deposition of only one monolayer in one dipping. That is, a more compact film was deposited leading to an enhancement in electronic absorption as shown in figure 4.2.(d). Film (c) neither has compact architecture nor contains molecules with a particular orientation.

![Figure 4.7](image_url)

**Figure 4.7.** Spectrum of ellipsometric parameters, real and imaginary parts of complex dielectric function, for the two types of NiPc films (as shown in legends).
4.3.6. Anisotropy of dielectric parameters

The ability to form ultrathin molecular films with planer NiPc molecules oriented parallel or perpendicular to the substrate forms systems that are ideal to study anisotropy of optical and electrical properties. We have recorded ellipsometric spectroscopy of the two films. For each of two orientations, films with three different thicknesses were characterized. Their corresponding dielectric functions are shown in figure 4.7. The results depended on the orientation of molecules in the films. Ellipsometric spectroscopy data, both real and imaginary components of dielectric function, show anisotropy in the two orientations. The real part, $\varepsilon_1$, is higher for films with the planer molecules lying parallel to the substrate as compared to that with molecules oriented perpendicular to the substrate. The line shape of imaginary component ($\varepsilon_2$) showed signatures of NiPc. While the Q band appears 2.0 eV, the Soret or B band appears at 3.6 eV. Both the transitions are known to be of $\pi-\pi^*$ in nature for NiPc. The Q band corresponds to the absorption band of NiPc films as shown in figure 4.2. The ellipsometric spectra, both real and imaginary components of dielectric function, did not depend on the thickness; the invariance is due to the fact that dielectric functions are intrinsic parameters of the material on the active layer.

Impedance spectroscopy in the 10 Hz to 500 kHz range has been carried out for devices based on the two types of films, that is, films where molecules lie parallel or perpendicular to the base electrode. The top electrode has been Al in both the cases. For each type of molecular orientations, real and imaginary component of impendence have been measured for devices with three different thicknesses. Instead of conventional Cole-Cole plots (plots between real and imaginary components of complex impedance), we plotted dielectric constant versus frequency spectrum (figure 4.8.). This was done due to the fact that thickness of a device depends on the orientation of the molecule and would have affected both components of complex impedance. The dielectric constant of the material, on the other hand, does not depend on the thickness of active layer.
Figure 4.8. Dielectric constant, as derived from impedance spectroscopy, for different NiPc films (as shown in legends). Results from devices with three thicknesses for each of the cases are shown in the figure.

Figure 4.8. evidences anisotropy in dielectric properties in ultrathin films of NiPc. That is, the dielectric constant of the films has depended on the orientation of the molecules on the base electrode. In ultrathin films with the planer molecules lying parallel to the substrate, the dielectric constant was lower than that in films with molecules having another orientation (perpendicular to the substrate and facing one particular direction). For comparison, we have included results from devices based on films deposited without any specific orientation, that is, without applying any magnetic field during LbL deposition. The value of the dielectric constant for film (c) remained intermediate to that of films (a) and (b). The plots further show that such anisotropy in dielectric properties is observed irrespective of the number of molecular layer or thickness of the active material adding credence to our results.
4.3.7. Anisotropy of electrical properties

While recording current-voltage characteristics of devices based on the two types of orientations (of the molecules), we have observed anisotropy in conductivity. Plots of current density versus electric field have depended on the orientation of NiPc molecules in the active layer. Figure 4.9 shows such plots for three thicknesses (for each type of orientations). For comparison, characteristics from devices with conventional (unoriented) LbL films of NiPc have been included in the figure. The results show that films with molecules lying parallel to the base electrode offer low resistivity probably due to close-packing of the molecules and improved molecule-to-molecule conduction process. When the molecules are perpendicular to the substrate and face one particular direction, hopping conduction still prevails as compared to films where the molecules do not have any specific organization or orientation. Conductivity
of ultrathin films expectedly did not depend on the thickness of the active layer for both types of oriented films and the unoriented one (figure 4.9).

4.4. Conclusions

In conclusion, during the LbL assembly of NiPc molecules, we oriented the molecules in each monolayer with a magnetic field and immobilized their orientation. We could form multilayered LbL films with NiPc molecules in each layer lying (a) parallel to the substrate or (b) perpendicular to it with the molecular plane facing one particular direction. Formation of such molecular orientations was confirmed by (polarized) electronic absorption spectroscopy and magnetic force microscopy. Since such films are ideal to study anisotropy of physicochemical properties of the molecule itself, we measured dielectric functions and conductivity of molecular films in the two orientations of the molecules. Ultrathin films with the molecules lying parallel to the substrate have a lower dielectric constant and a higher conductivity than that having the other orientation of the molecules in LbL films.
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