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Influence of Iodine Doping on the Structure, Morphology and Physical Properties of Manganese Phthalocyanine Thin Films

K. Priya Madhuri^{†#}, Neena S. John^{†*}, S. Angappane[†], Pralay K. Santra[†], and F. Bertram[‡]

[†]Centre for Nano and Soft Matter Sciences, Jalahalli, Bengaluru 560 013, India

[#]Department of Chemistry, Mangalore University, Mangalagangothri 574 199, India

[‡]DESY Photon Science, Notkestr. 22607 Hamburg, Germany

*Email: jsneena@cens.res.in

Abstract

Doping with halide ions is a popular method to alter the properties of metal phthalocyanines (MPcs), particularly magnetic and electrical nature of organic semiconductors for applications in spintronic or electronic devices. Doping can cause a structural rearrangement in MPc packing and the physical properties may be correlated with molecular packing. Films of a planar and magnetic MPc, manganese(II)phthalocyanine (MnPc) is chosen for iodine doping study. The optical, magnetic and the electrical properties of pristine and iodine doped MnPc thin films are investigated and can be directly associated with their molecular structure. 2D grazing incidence Synchrotron X-ray diffraction reveals structural disorder in MnPc films upon iodine infusion induced by the reorientation of ordered, edge-on molecular configuration to tilted and face-on configurations in a random fashion. The film morphology changes accordingly, where in the uniform crystallites reorganize in a disordered manner. The ferromagnetic nature of the pristine film gets weakened due to iodine species and favors antiferromagnetic coupling. The study of electrical properties at room temperature by conducting atomic force microscopy reveals that the conductance is enhanced independently of the film thickness due to disorder induced by iodine inclusion.

Introduction

Metal phthalocyanines (MPcs) are considered to be prototype molecular semiconducting materials with envisaged applications in various fields due to their fascinating physical properties. The excellent chemical and thermal stability render them suitable for easy device fabrication and as competitive materials in the field of organic electronics. It is well known that MPcs exhibit polymorphism and the two commonly observed forms of polymorphs are α and β phases. The phases are categorized based on the

stacking angle between the molecular plane and b -axis, 65° and 45° for α and β , respectively.¹ For device applications, thin films of MPcs are employed and various polymorphs formed are governed by the substrate-molecule interactions and intermolecular interactions.² These interactions are influenced by various experimental parameters such as substrate type, substrate temperature and rate of deposition, etc.³ Due to the high anisotropic nature of π -conjugated MPcs, the physical properties like optical absorption and electrical conductivity vary substantially among the above polymorphs with different orientations of molecules with respect to the substrate plane.⁴ Different electronic devices may have different requirements in terms of the molecular orientation of organic molecules, and hence, it is important to fabricate a device for a particular application. For the organic light emitting diodes and solar cells, it is desired that these molecules lie flat on the substrate with extended π stacking in the direction perpendicular to the metal electrodes.⁵ Inorganic field effect transistors (OFETs), the molecular arrangement with standing up configuration becomes important which would facilitate the charge delocalization along the direction parallel to gate dielectric.⁶ Hence, there have been numerous efforts to tailor the molecular organization and orientation to achieve the desired property enhancement in MPc based solar cells and OFETs. Substrate templating with CuI, graphene and other organics have been reported for influencing the face-on or edge-on MPc orientation, and further stacking.^{3,7,8} These molecular semiconductors have other vast applications that include gas sensors, electrocatalysts, supercapacitors, etc. to name a few.^{9,10}

In addition to the structural rearrangement and optoelectronic properties, it has been shown that the magnetic properties of various MPcs hosting transition metal ions with a net spin in the macrocycle cavity are also influenced by the molecular orientations.¹¹ The magnetic ordering can be controlled by the molecular configuration where in ferromagnetic exchange pathways between adjacent atoms become crucial. In a recent article, Serri et al. have demonstrated that CoPc thin films exhibit antiferromagnetic coupling at 100-150 K and the exchange interaction strongly depends on the molecular stacking.¹² It has also been shown that the interface of MnPc and Co films can induce antiferromagnetic ordering in molecular layers.¹³ The magnetic properties of Li-intercalated MnPc powder, an electron-doped MPc system, revealed that Li^+ ions co-ordinate to the pyrrolic nitrogen of the macrocycle and disturb the 1D ferromagnetic Mn-N...Mn interaction, inducing antiferromagnetic ordering.¹⁴ The intercalation of Li is seen to affect the stacking and hence, the magnetic properties as well. Doping or ligation of MPcs with other small molecules like oxygen, carbon monoxide,

halogens can also result in higher or lower spin state along with changes in electrical conductivity.¹⁵ Wackerlin et al. demonstrated that the cobalt porphyrins could be magnetically coupled to a ferromagnetic substrate and a reversible chemical switching is induced by the adsorbed nitric oxide molecule.¹⁶

Hole doping of MPcs by introducing electron acceptors such as halogens, particularly iodine is a very popular method to enhance the conductivity of organics that possess poor electrical conductivities or higher electronic bandgaps.^{17,18} In the case of MPcs, iodinated MPc crystals are well established to be metallic type conductors wherein iodine exists mainly as triiodide ions forming linear chains causing partial oxidation of the macrocycle.¹⁹ The electronic bands gaps can be considerably tuned by introducing dopants into the lattice sites, and it is also known to cause some structural variations.²⁰⁻²² It is known to increase the solar cell performance by providing more photon harvest due to NIR absorption in organic polymers.²³ Similarly, magnetic properties also get affected due to iodination, and in the case of iodinated CuPc crystals, the magnetic studies indicated coupling of local spins with itinerant electrons.²⁴

A direct correlation of the iodine doping in MPc films with their molecular orientation, morphology and physical properties is clearly lacking. In our earlier study, we have shown that the substrate can influence the molecular packing in a non-planar MPc owing to substrate-molecule interactions. The change in molecular packing substantially influenced the electrical properties of the thin films when measured in the vertical configuration using conducting atomic force microscopy (C-AFM).² Iodination of MPc films can also cause serious changes in molecular orientation and their stacking, which can influence charge transport and magnetic properties. Hence, we have sought to understand the effect of iodine doping in manganese(II)phthalocyanine (MnPc) films, a planar and magnetic MPc, on their molecular rearrangement in relation to the observed physical properties. The molecular packing and orientation of thin films of pristine MnPc and iodine doped MnPc (I-MnPc) studied by 2D grazing incidence Synchrotron X-ray diffraction is presented. The drastic change in the observed MnPc packing upon iodine infusion is reflected in the morphology, magnetic and electrical properties. These studies provide insights into the interplay between the dopants and thin film architecture for the fabrication of MPc based devices.

Experimental Details

MnPc powder (Sigma Aldrich) was taken in a molybdenum boat and evaporated under vacuum onto substrates like quartz, Au/SiO₂/Si and Si(100) using thermal vapor deposition technique. The substrates were cleaned thoroughly with acetone followed by distilled water before use. A thin layer of gold (~40 nm thick) was deposited on to SiO₂/Si by DC sputtering to serve as conductive substrates. MnPc film was deposited at a base pressure of 1×10^{-5} mbar and the substrate was held at 100°C. The rate of deposition was $1\text{--}1.5 \text{ \AA s}^{-1}$, as monitored by quartz crystal microbalance. MnPc films of various thicknesses from 5 to 80 nm were deposited on Au/SiO₂/Si substrates for carrying out electrical measurements. A 50 nm thick MnPc film deposited on the silicon substrate was chosen for magnetic studies and other characterizations. Iodine doping of all the MnPc films was achieved by infusing the vapors from iodine crystals contained in a sealed vessel at a temperature of 60°C for 3 hours. The doped samples turned brownish in color and were quite stable for a period of 25-30 days. The samples were stored in a vacuum desiccator.

The UV-visible spectrum of the as-deposited MnPc film on a quartz substrate was acquired using Perkin-Elmer Lambda 750 spectrophotometer. The crystal structure of thin films on different substrates was investigated by X-ray diffractometer (XRD) (Rigaku Smartlab) equipped with parallel beam optics and monochromatic Cu $k\alpha$ radiation (40 kV, 30mA) was incident at a grazing angle of 0.3°. A more detailed study on the structural arrangement on MnPc molecules before and after doping with iodine on Si substrates was studied with the help of two-dimensional grazing incidence-X-ray diffraction (2D GI-XRD) technique. 2D GI-XRD measurements were performed at PETRA III, Deutsches Elektronen-Synchrotron (DESY) using P08 beamline.²⁵ We performed the measurements at a beam energy of 25 keV ($\lambda = 0.496 \text{ \AA}$) using a flat panel Perkin Elmer 2D detector (2048 × 2048 pixels of size 200 μm), at a fixed detector-to-sample distance (1705 mm). Initially, the detector was calibrated using lanthanum hexaboride sample. The data were analyzed using MATLAB interfaced GIXSGUI software.²⁶ Raman spectra for the films deposited on silicon substrates was acquired using Horiba XploRA PLUS spectrometer with 532 nm laser through a 50X objective. Field emission scanning electron microscopy (FESEM) images were obtained using a TESCAN MIRA3 LM, and the energy dispersive X-ray spectroscopy (EDS) was recorded with Quantax EDS (Bruker) detector. The magnetic properties of the pristine and iodine doped thin films (50 nm) on silicon substrates were studied using a SQUID

magnetometer (MPMS-5XL) at 300 K and 10 K. The magnetic field was applied parallel to the substrate plane. The topography of the thin films on various substrates was acquired using an atomic force microscope (AFM, Agilent 5500) operating in dynamic mode equipped with a rectangular probe having a resonance frequency of 65 kHz and a force constant of 0.6 N m^{-1} (Mikromasch, USA). For electrical measurements, MnPc films are deposited on Au coated SiO_2/Si substrates that served as a bottom contact. Current versus voltage characteristics of MnPc films on Au/ SiO_2/Si substrates were acquired using C-AFM using a conductive Au tip that serves as a top contact. The tip was also sputtered with Au layer with a thickness of approximately 20 nm, prior to the measurements to enable good contact with the films. In these experiments, the Au probe is at the ground, and the sample bias is swept positive or negative. At positive bias, the holes are injected from the bottom Au electrode into the MnPc film and vice versa at negative bias.

Results & Discussion

1. Optical Properties

Figure 1: UV-Visible spectra of MnPc and I-MnPc thin films deposited on quartz substrates.

UV-visible spectra of pristine MnPc film and I-MnPc films on the quartz substrates are given in Figure 1. Various absorption bands observed at 272, 362, 528, and 738 nm in pristine MnPc film are attributed to B and Q bands, characteristic features of the metal-centered phthalocyanine system. In the case of iodine infused MnPc films, the above bands are seen red-shifted to 280, 388, 570, and 874 nm, respectively. We can see the broadening of B band around the region of 480 nm which indicates the presence of iodide species.¹⁸ Further, the Q bands observed are largely shifted towards NIR region. The shift in the Q bands could

be due to the narrowing of the HOMO-LUMO orbitals by forming a new charge transfer complex. A new peak at 636 nm is also observed, which could be arising from the introduction of dopant levels by iodine species.^{27,28} These shifts may also indicate the formation of a different polymorph due to the structural modifications in the pristine MnPc film upon iodine exposure.

2. Structural Properties

The structural features of MnPc before and after doping with iodine are studied using XRD technique (Figure 2). The diffraction peak at 7.03° corresponds to (100) plane of β phase in the case of pristine MnPc film deposited on silicon substrate. In β polymorph, the stacking angle between the molecular plane and the b-axis in the herringbone structure is lower than its α counterpart.¹ The high-intensity peak indicates a (100) oriented or textured film. After doping with iodine, 7.03° peak intensity has diminished and broadened indicating that the structural organization of the β phase is disrupted. It is also known from the literature that the increased iodine doping concentration proportionately decreases the crystallinity in the film by increasing amorphous nature.^{21,22} A similar trend was also observed in the case of pristine and I-MnPc films when deposited on HOPG, and Au coated SiO_2 substrates (Figure S1). This structural reorganization giving rise to different molecular orientations may also account for the absorbance variations in Q bands with doping (Figure 1).

Figure 2: XRD pattern of 50 nm thick, pristine MnPc and I-MnPc films deposited on silicon substrates. The inset shows the expanded region of interest for I-MnPc.

To further investigate the structural changes in MnPc layers deposited on Si substrate associated with iodine exposure, 2D GI-XRD was employed. This tool is extensively

employed to study the molecular orientation and crystalline quality of thin films.^{29,30} Figure 3a is the 2D GI-XRD of pristine MnPc film, which shows that there is a single diffraction peak at a q_z of $0.5 \text{ \AA}^{-1}$ corresponding to 2θ , 7.03° and d -spacing of $12.56 \text{ \AA}$ arising from (100) plane of β polymorph. The single diffraction peak indicates that the film on Si substrate is highly oriented and ordered in q_z direction. The peak is quite sharp and intense confirming the crystalline nature of MnPc film as shown in the line-cut profile along the q_z direction represented in figure 3c. We can also find another bright spot in q_y plane $0.5 \text{ \AA}^{-1}$ with an azimuthal angle $\sim 0^\circ$, which indicates that the MnPc molecules are ordered not only in the vertical direction but also in the lateral direction of the substrate. The obtained d -spacing of $12.56 \text{ \AA}$ corresponding to (100) plane also indicates that MnPc molecules are arranged in standing up configuration with parallel alignment of (100) plane with the substrate. In the case of CuPc thin film grown on a glass substrate, single sharp peak concentrated along the q_z meridian, $0.5 \text{ \AA}^{-1}$ and $q_{xy} = 0$, corresponds to (100) plane lying parallel to the substrate surface and it has been attributed to the edge-on the configuration of CuPc molecules.⁷

Figure 3: 2D GI-XRD of 50 nm MnPc films deposited on a silicon substrate (a) pristine MnPc and (b) I-MnPc (c) Plot of line-profiles (normalized with areas) along q_z direction indicating the Bragg peaks.

Upon exposing the pristine MnPc thin film to iodine vapors, we can see from figure 3b that there is a change in the structural arrangement of molecules. The line-cut profile along the q_z direction is represented in Figure 3c. The peak around $0.5 \text{ \AA}^{-1}$ appears to be broad, and upon resolving, it is found that in addition to the peak at $0.5 \text{ \AA}^{-1}$ corresponding to (100) plane, there are peaks positioned 0.56 and $0.63 \text{ \AA}^{-1}$ (Figure S2). The $0.56 \text{ \AA}^{-1}$ has a d -spacing of $11.22 \text{ \AA}$, and the lowered d -spacing could imply that the phthalocyanine rings tend to incline towards the substrate surface from the standing up configuration. A similar trend in the decreased d -spacing of ZnPc molecules after annealing treatment is reported by Ahn et al. This change has been indicated to the macrocycles rings inclining to the substrate surface.³¹ The peak with a q_z value of $0.63 \text{ \AA}^{-1}$ corresponds to a d -spacing of $9.97 \text{ \AA}$. This closely matches with $(10\bar{2})$ diffraction plane of β polymorph, $2\theta = 9.2^\circ$. The $(10\bar{2})$ plane lies mostly in the q_y plane at an azimuthal angle, 20° , along with a small fraction oriented in q_z plane. The spread along a particular azimuthal angle indicates that there is a change in the ordered stacking of MnPc molecules and the crystallites are arranged in a random fashion to some extent. In addition to the above peaks, a prominent peak is noticed at $1.4 \text{ \AA}^{-1}$, which is highly crystalline in q_z plane along with small fractions in q_y plane. This corresponds to (110) plane with a 2θ value of 19.87° and d -spacing of $4.48 \text{ \AA}$. The lowered d -spacing can be an indication towards the MnPc molecules arranged in a lying down configuration with some degree of tilt. The 2D GI-XRD studies indicate that pristine MnPc film is a single crystalline β polymorph having a highly oriented (100) diffraction plane. Upon exposing the MnPc film to the iodine vapors, there is a significant structural rearrangement among MnPc molecules rendering the film polycrystalline in nature. The iodine has induced a reorientation of molecules leading to decreased d -spacing along with the formation of $(10\bar{2})$ and (110) crystal structures after rearrangement. The size of crystallites for pristine MnPc and I-MnPc has been calculated from the (100) peak plotted in figure 3c by applying Debye-Scherrer equation with the value of dimensionless factor, K equal to 0.9 assuming spherically shaped crystallites. The average crystallite size of pristine MnPc is $\sim 42 \text{ nm}$ and for I-MnPc, the size ranges from 25-35 nm.

Confocal Raman spectra were acquired from the pristine and iodine doped MnPc films at an excitation wavelength of 532 nm to identify the iodide species. The intensity of Raman signals of MnPc is seen amplified after exposing the films to iodine vapors (Figure 4a). This could be due to the resonance Raman Effect originating from the high absorption of I-MnPc at 500 nm close to Raman excitation wavelength as seen in UV-Vis spectra (Figure 1).

Janczak et al. show that the majority of the iodinated MPc crystals contain triiodide ions which can be identified using resonance Raman methods.³² The signatures of I_3^- is generally observed at 110 cm^{-1} and 140 cm^{-1} due to antisymmetric I_3^- stretching, and the overtone frequencies at 220 and 330 cm^{-1} are indicative of the presence of linear chains of symmetric I_3^- ions. These peaks are indicative of the unequivocal presence of I_3^- ions. The presence of linear chains of triiodide ions is eventually responsible for the metallic character in iodinated MPc crystals. In the present case of MnPc films, Raman signal seen at 109 cm^{-1} (Figure 4b) is due to the antisymmetric stretching of I_3^- ions. However, the absence of overtone frequencies at 220 and 330 cm^{-1} rule out the presence of triiodide chains though isolated species are present in the system. Signatures due to other iodine species such as I_2 molecule and I_5^- ions are seen at 195 cm^{-1} and 162 cm^{-1} , respectively.

Figure 4: Raman spectra of 50 nm thick MnPc and I-MnPc films on silicon substrate obtained with 532 nm laser (a) spectra in the region 100-1700 cm^{-1} , (b) and (c) show the expanded regions of interest for I-MnPc film.

Macrocycle deformation and isoindole ring deformations exhibit Raman shift in the range of 200-500 cm^{-1} . Peaks appearing in the frequency ranges of 500-1000 cm^{-1} correspond to benzene ring deformation and the macrocycle breathing (expansion and contraction)^{33,34} of MnPc molecules. Regions from 1100 to 1300 arise due to the C-H bending and pyrrole ring stretching. The peaks at 1450 and 1530 cm^{-1} are due to the isoindole stretching and pyrrole stretching vibrations.³⁵ These peaks are accompanied by higher frequency peaks (Figure 4c) indicating disorders in molecular packing.^{2,36} Hence, Raman spectra support the observations from XRD that iodine infusion in MnPc films causes stacking disorder in the system.

Figure 5: Schematic showing the rearrangement in MnPc molecules after exposure to iodine vapors.

Based on the above observations, we can represent the schematic of the molecular arrangement in pristine MnPc molecules and subsequent molecular rearrangement upon doping with iodine as shown in Figure 5. XRD indicates the formation of highly oriented (100) plane of MnPc β polymorph. Upon iodine doping, the (100) peak diminishes with the appearance of weak and broad reflections of other planes of β polymorph as discussed before. Further to complement this observation, we also see a highly oriented single crystalline Bragg peak at 0.5 $\text{\AA}^{-1}$ along the q_z plane from 2D GI-XRD. This single crystalline (100) peak in pristine MnPc film having a d -spacing value of 12.56 $\text{\AA}$ coincides with the standing up the configuration of MnPc molecules with b -axis parallel to the substrate plane. Further, the appearance of (100) plane in both $\chi = 90^\circ$ and 0° angles (Figure S3a) shows the ordered edge-on arrangement of the molecules. The diffraction patterns of the iodine treated MnPc film shows new crystal planes associated in both q_z and q_y directions at different azimuthal angles (Figure S3b) indicating the tilted and lying down molecular orientations causing randomness in crystalline packing. Raman studies show the signatures of iodine and triiodide ions and some degree of disorder in the microcrystalline domains from high-frequency isoindole and pyrrole stretching around 1450 and 1530 cm^{-1} . Based on this, we can hypothesize that the iodine molecules enter the interstitial site of the MnPc lattice and destroy

the orderliness in molecular packing. The intervention of iodine causes the nanocrystallites to attain different configurations such as a few crystallites lying parallel to the substrate with face-on orientation while other molecules have tilted standing up or lying down orientations. The schematic agrees well with the predictions of the diffraction and Raman studies clearly indicating that the iodine infusion causes a significant rearrangement in molecular packing. This topotactic reaction of MPc with iodine has been confirmed previously through other techniques like high-resolution electron microscopy.²⁰

3. Morphological Studies

Figure 6: (a) and (b) FESEM images, (c) and (d) 1 $\mu\text{m} \times 1 \mu\text{m}$ AFM images, (e) and (f) corresponding profile sections showing grain size and roughness variation of pristine MnPc film (left column) and I-MnPc film (right column) deposited on silicon substrates.

The morphology of the pristine MnPc and I-MnPc thin films deposited on silicon substrates were examined under FESEM and AFM. Figure 6a shows the FESEM image of pristine MnPc thin film consisting of uniform nanocrystallites covering the entire substrate indicating that the thermal evaporation of MnPc has resulted in a uniform deposition. Upon iodine doping of the films, a significant change in morphology can be noticed with a change in grain size and shape (Figure 6b). Table 1 gives the EDS analysis in detail indicating the percentage composition of the different elements. The amount of iodine is seen in appreciable quantity after iodine infusion. AFM analysis (Figure 6c and 6d) complements the morphology variations observed for pristine and doped MnPc films in FESEM. Pristine MnPc exhibits a uniformly evaporated film with spherical grains of size in the range of 35-40 nm, which matches with the crystallite size obtained from 2D GI-XRD measurements. The film roughness in the pristine MnPc film (root mean square value) is estimated to be 0.729 nm.

Table 1: EDS analysis showing the percentage of composition of different elements

Sample	C		N		Mn		I	
	Wt. %	At. %	Wt. %	At. %	Wt. %	At. %	Wt. %	At. %
MnPc	49.18	59.06	35.95	37.03	14.87	3.90	-	-
I-MnPc	28.73	62.35	12.84	23.89	6.52	3.09	51.91	10.66

After iodine doping, MnPc films show a drastic change in morphology with flat grains of various sizes (larger ones with 150-200 nm size) oriented randomly, increasing the surface roughness of the film to 3.73 nm. The smaller average crystallite size for I-MnPc obtained from 2D GI-XRD data indicates that the grains consist of randomly arranged smaller nanocrystallite domains. The varying surface features are shown as a profile plot in Figure 6e and 6f. The increase in the roughness can be correlated with the increase in disorder due to nanocrystallites orienting in various directions caused by iodine diffusion. We have also observed such roughness variation in the case of substrate influence on PbPc stacking.² The change in morphology from smaller spherical grains to flat grains can be associated with the alteration of molecular orientation from the edge-on to lying down and other tilted configurations of MnPc upon iodine doping as shown in the schematic (Figure 5).

4. Magnetic Properties

MnPc possesses highest spin state with Mn(II) in the central cavity bearing a net spin of 3/2 and thus, MnPc can be expected to have larger magnetic moment compared to other

Figure 7: $M - H$ plots of (a) pristine MnPc and (b) I-MnPc thin film on Si substrates at 300 K and 10 K; Insets show expanded view of low field region at 10 K.

MPcs. The magnetic field (H) dependence of the magnetization, M at 300 K and 10 K for the pristine MnPc are shown in Figure 7a. The applied magnetic field is parallel to the substrate. The magnetization of the films is found to increase with an increase in the strength of the external magnetic field. The $M - H$ curve for pristine MnPc film begins saturation at 4 kOe. The saturation magnetization (M_s) obtained is 39.77 and 40.81 emu cm^{-3} at 300 K and 10 K, respectively, for pristine MnPc films. The saturating nature of $M - H$ curves indicates the ferromagnetic nature due to the weak inter-chain interactions. The hysteresis loop becomes pronounced at a low temperature indicating the increase of spin polarization at low temperatures (inset of Figure 7a). Figure 7b shows the magnetization curves for iodine doped MnPc thin films. A large decrease in the magnetization in the case of I-MnPc is observed. Due to very low values of M , diamagnetic correction for silicon substrate is applied. The reduction in values could be attributed to the destruction in the ferromagnetic interaction pathways among the crystallites caused due to iodine doping. M_s values are 5.12 and 5.24 emu cm^{-3} for I-MnPc at 300 K and 10 K. The structural change caused by iodine doping could disturb the inter-chain interactions and thus, rendering lower M_s . This is also

concurrent with the observation that iodine is disrupting the ordered molecular stacking of MnPc films.

Figure 8: ZFC and FC curves for (a) pristine MnPc ($H = 200$ Oe) and (b) I-MnPc ($H = 500$ Oe) thin films on silicon substrates.

In order to understand the magnetic interactions among the molecules, both zero field cooled (ZFC) and field cooled (FC) magnetization as a function of temperature down to 10 K at an applied field of 200 Oe for pristine MnPc, and 500 Oe for I-MnPc films are acquired and are given in figure 8. For pristine MnPc films (Figure 8a), FC magnetization increases with a decrease in temperature, whereas ZFC magnetization shows broad maxima around 175 K and starts decreasing indicating blocking temperature. This decrease may be due to the freezing of ferromagnetic clusters. The divergence of FC and ZFC indicates magnetic anisotropy. Figure 8b shows the ZFC and FC curves for I-MnPc thin films. The negative values are due to the diamagnetic contribution from the substrate. The huge decrease in magnetization is due to the presence of diamagnetic iodine that shields the external magnetic field and the disorder caused in the MPc stacking gives rise to antiferromagnetic

interactions.³⁷ As the temperature is decreased, around 50 K, the magnetization starts increasing, which may be attributed to paramagnetic impurities.

In pristine β -MnPc films, the ordered molecular stacking favors ferromagnetic interactions at room temperature, which further goes to strong ferromagnetic ordering at lower temperatures. The introduction of iodine doping introduces disorder (Figure 5) and the observed magnetic property in these systems is probably attributed to the nanocrystalline regions possessing possibly reduced ferromagnetic exchange pathways, and antiferromagnetic interactions play the main role in the disordered film structure. A large decrease in magnetization and antiferromagnetic interactions in disordered MnPc thin films has been reported by Yamada et al.¹¹ This is explained in terms of the differences in superexchange interactions due to variation in the stacking arrangement of molecules. The high-temperature antiferromagnetism has been recently reported in the case of CoPc films arising from a strong exchange coupling. Possibly, there exists a superexchange interaction between Mn^{2+} ions, which strongly depends on the Mn-Mn distance and stacking angle as in the case of CoPc. At lower temperatures, the nanocrystalline regions having isolated spins can also contribute to paramagnetic behavior.¹²

5. *Electrical Properties*

The electrical characteristics of the deposited MnPc thin films are studied by employing the C-AFM technique. The thicknesses of the films were confirmed by AFM cross section profiles across the film edge. The experimental setup is depicted in the inset of Figure 9a. Figure 9a shows $I - V$ characteristics for pristine MnPc films of various thicknesses acquired from C-AFM. The $I - V$ curves are non-linear and symmetrical in nature. The output current and the threshold voltage required to produce a specific current varies with thickness variation from 5 nm to 80 nm. It is known that the conductance across the organic film is highly dependent on the thickness of the material.³⁸ It is seen that at 7.5 V, the current value is 1.5 nA for 80 nm film, 3 nA for 60 nm film, 8 nA for 40 nm film and about 35 nA for 20 nm film. The $I - V$ nature for a 5 nm film of MnPc exhibits the highest current value reaching 100 nA at 1.9 V.

Figure 9: (a) *I* - *V* curves obtained from C-AFM and inset of C-AFM setup (b) double logarithmic *J* - *V* plots for pristine MnPc films of different thickness.

In order to understand the charge transport characteristics, the *I* - *V* curves were plotted on a double logarithmic scale as shown in Figure 9b. The slope obtained for the lower voltage regions is found to be ~1 indicating Ohmic behavior and transforms into a space charge limited regime at higher voltages, whose slope values are >3. Thickness dependence of current density can be used to verify space charge limited conduction (SCLC) mechanism, which follows Mott-Gurney formalism.^{39,40} For macroscopic planar device measurements, the Mott-Gurney law is represented as shown in Eq. (1),

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{L^3} \dots (1)$$

where *J* is the current density (effective area of the electrode is considered according to the Hertz model⁴¹), ϵ_0 and ϵ are the permittivity of free space and the dielectric constant of the active material, μ is the mobility of the charge carriers, *V* is the applied voltage and *L* is the thickness of the device under investigation.

Reid et al.⁴² hypothesized that the current density obtained in C-AFM measurements exhibit a different dependence on the sample thickness when compared to the planar macroscopic measurements. Thus the thickness dependent current densities for MnPc thin films at a fixed potential of 10 V was plotted, and it was fit in a power law. The fit yields an Eq. (2) as follows as that obtained from the plot in Figure 10a. The resulting value is in agreement with the proposed values in the literature.⁴²

$$J = kL^{-1.45} \dots (2)$$

The dependence of the threshold voltage variation on the thickness is also represented in figure 10b. The voltage required to observe the specific onset of the current varies linearly with the thickness. The observations are in agreement with the previously reported literature.⁴³

Thus for C-AFM measurements, the modified Mott-Gurney Eq. (3) proposed by Reid et al.⁴² is used to calculate the hole mobilities,

$$J = \alpha \epsilon \epsilon_0 \mu e^{0.89 \gamma \left(\frac{V}{L}\right)^{1/2} \frac{V^2}{L^3} \delta \left(\frac{L}{d}\right)^{1.6 \pm 0.1}} \dots (3)$$

where α is the prefactor determined by numerical calculations and is found to have a value of 8.2, δ is an empirical dimensionless parameter having a value of 7.8, d is the diameter of the tip-substrate contact area (cm), J is current density (A cm⁻²), ϵ_0 and ϵ are the permittivity of free space (8.854×10^{-14} F cm⁻¹) and the dielectric constant of the active material (3.3×10^{-2} F cm⁻¹ for MnPc), μ is the mobility of the charge carriers (cm² V⁻¹ s⁻¹), V is the applied voltage (V), γ expresses the field dependent mobility and L is the active layer thickness (cm).

The plot of $\ln\left(\frac{J L^{1.4} d^{1.6}}{V^2}\right)$ vs $\left(\frac{V}{L}\right)^{\frac{1}{2}}$ for different thicknesses of MnPc films were extracted from the high voltage regime of the SCLC region of the $I - V$ curves (Figure S4). The linear fit gives a straight line with the intercept equal to $\ln(\alpha \epsilon \epsilon_0 \mu \delta)$ from which the values of mobility can be extracted. The calculated mobility values for 5, 20, 40, 60 and 80 nm thick MnPc films are $1.08 \times 10^{-4} \pm 3.55 \times 10^{-6}$, $7.81 \times 10^{-5} \pm 1.53 \times 10^{-5}$, $1.96 \times 10^{-5} \pm 6.09 \times 10^{-6}$, $6.95 \times 10^{-6} \pm 1.96 \times 10^{-6}$ and $5.99 \times 10^{-6} \pm 1.76 \times 10^{-6}$ cm² V⁻¹ s⁻¹, respectively. The trend in the decreasing mobility values for increasing thickness from 5 nm up to 80 nm is observed. Obtained mobility values are comparable to the reported data for a 10 nm thick MnPc film, 1.5×10^{-4} cm² V⁻¹ s⁻¹.⁴³

Figure 10: (a) Plot of calculated current density at 10 V sample bias as a function of thickness (b) Variation of threshold voltage as a function of thickness.

Here we see that the $J - V$ characteristics depend on the thickness of the device. The number of charge carriers available for conduction is lesser and current decreases exponentially as the thickness of the MnPc film increases. It is well known that the anisotropic nature of π conjugated molecules like MPcs give rise to different electronic conductivities in in-plane and out-of-plane with respect to the substrate due to their molecular packing. The decrease in mobility values can thus be attributed to the edge-on stacking of MPcs on the surface of the substrate where the overlap of π orbitals are less favored vertically.⁴⁴ As the thickness of the film increases, the electronic pathway between the successive molecular columns is reduced and thus the out-of-plane conductivity measurements with progressing thickness results in decreasing conductance and hence mobility.

I - *V* characteristics of iodine exposed MnPc films with different thicknesses acquired by C-AFM are given in Figure 11. It is observed that the current achieved for all the thicknesses is 100 nA. Although we have not observed ohmic conduction as reported in the literature for bulk NiPc(I), a great enhancement in conductance for I-MnPc films is evident when compared to pristine ones. This enhancement is due to the partial oxidation of MnPc molecules by highly oxidizing iodine species increasing the concentration of hole carriers in the bulk of the film.⁴⁵ As a representative case, the hole mobility was calculated for 80 nm film by linear fitting of SCLC region (Figure S5). A value of $1.94 \times 10^{-2} \pm 1.93 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, four orders of magnitude higher than the mobility in pristine MnPc film is estimated. An increase of two orders of magnitude in hole mobility (from 10^{-9} to $10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for 700 nm thick iodine doped zinc phthalocyanine film is reported by Sharma et al.⁴⁶ In addition to partial oxidation of MnPc film, the presence of iodide moieties also form conducting percolation pathways linking the nanocrystallite domains through which the charges are transported to the collecting electrodes efficiently.⁴⁷

Figure 11: *I* - *V* curves of I-MnPc films for different thicknesses from 5 nm to 80 nm obtained employing C-AFM.

Hole doping into MPc was first demonstrated, and the electronic and physical properties such as magnetism were successfully studied by obtaining highly conducting molecular solid NiPc(I).¹⁹ Iodine acts as an electron acceptor species since it is known for its high oxidizing property. There are various studies on the effect of iodine doping on thiophene,^{44,48} graphene,⁴⁹ polyaniline^{50,51} and quite a few polymer films, where in the conductivity is found to be ohmic due to the formation of conducting iodine percolation network. In the case of I-MnPc, though a similar enhancement is observed, we do not observe

a thickness dependent variation as observed in pristine MnPc cases. The iodine has been infused under saturation conditions and the disorder introduced in the MnPc molecular orientation irrespective of the thickness could result in the conductance being dominated by the charge hopping due to iodide ions.

Conclusions

We have studied the influence of iodine infusion on the structural rearrangement and crystallinity of MnPc thin films deposited on silicon substrate. Doping by iodine is confirmed by energy dispersive X-ray spectroscopy and also from the presence of charge transfer bands in UV-Vis spectra and iodide vibrational modes in Raman spectra. The pristine MnPc films have a highly ordered molecular packing with a preferred orientation of (100) plane of β polymorph and edge-on molecular orientation. Iodination causes complete structural reorganization and disorder in MnPc packing with a change in edge-on molecular orientation to inclined edge-on and face-on configurations. The change in molecular orientation is supported by the observed decrease in d -spacing and appearance of other diffraction planes. The structural reorganization and disorder upon iodine doping are also reflected as a change in morphology from spherical to randomly oriented flat grains with an increase in film roughness. The magnetic studies indicate that the pristine MnPc film having a ferromagnetic character transform to antiferromagnetic under iodine treatment. The presence of iodine in the lattice of MnPc disrupts the ferromagnetic exchange pathways and also decreases the spin value on MnPc with the decreased magnetic moment. On the other hand, the presence of iodine in MnPc films improves electrical conductivity as studied by conducting AFM. The conductivity follows a decreasing trend with increasing thickness for pristine films and is attributed to the reduced charge transport across the film. The hole mobility is found to increase substantially with iodine doping independent of the film thickness. Iodine partially oxidizes MPcs and forms the conductive percolation pathways in the disordered nanocrystallites irrespective of the thickness. This study reveals the importance of understanding the structural modifications caused by dopants in MPc films in order to relate to the physical properties of the system and various applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

XRD patterns for films deposited on HOPG and Au/SiO₂ substrates, Line-cut profiles of 2D GI-XRD in different azimuthal angles and Semiempirical Mott–Gurney fit for C-AFM plots.

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