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Current Mapping of Lead Phthalocyanine Thin Films in the Presence of Gaseous Dopants

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Abstract

The structural organization and its effect on conducting pathways in lead phthalocyanine (PbPc) thin films, a nonplanar phthalocyanine, deposited on Si and highly oriented pyrolytic graphite (HOPG) substrates in the presence of iodine and ammonia vapors are presented. The two-dimensional grazing incidence X-ray diffraction studies revealed that the crystalline ordering in pristine PbPc films on Si and HOPG substrates have undergone a drastic molecular rearrangement and surface reconstruction up on iodine doping. The structural rearrangement leads to morphological changes and higher surface roughness in iodine doped PbPc (I-PbPc) films. An obvious enhancement in the current values of I-PbPc is attributed to the introduction of holes as charge carriers. Nanoscale current mapping reveals the presence of percolation pathways in I-PbPc films, on both Si and HOPG substrates, responsible for the observed high conductance in contrast to the isolated conducting domains in the pristine PbPc system. A broad distribution of current values across various conducting domains on Si is attributed to a mixture of crystalline phases and disordered fractions of I-PbPc while a narrow distribution of current values observed in the case of HOPG is attributed to the majorly disordered PbPc molecules. These films also show enhanced sensitivity towards ammonia by almost four times higher in magnitude than pristine PbPc films. The current maps show that the adsorption of ammonia molecules disrupts the iodine percolation pathways, thereby imposing a detrimental effect on the conductivity of the PbPc films.

Keywords:

Lead phthalocyanine, Conducting-atomic force microscopy, 2D GIXRD, Structural rearrangement.

Introduction

Metal phthalocyanines (MPcs) are *p*-type semiconductors with high near-infrared (NIR) absorption and have recently gained importance in solar cell fabrication and organic photovoltaics.^{1,2} MPcs are relatively inexpensive, flexible, environmentally benign and possess good thermal and chemical stability. These features along with their unique structural, electrical and optical properties render them suitable for applications in various devices such as organic field effect transistors, organic light emitting diodes, gas sensors, supercapacitors, spintronics, electrocatalysis, and so forth.³⁻⁸ Among MPcs, nonplanar phthalocyanines such as lead phthalocyanine (PbPc) or titanyl phthalocyanine (TiOPc) seek special attention since the nonplanar and polar character of the molecules result in a specific molecular arrangement different from that in planar MPc molecules (CuPc, MnPc, etc).^{1,9} Depending on the substrate-molecule interactions, PbPc molecules stack differently to give rise to various crystal structures, monoclinic (space group $P2_1/b$) and triclinic (space group $P\bar{1}$).^{1,10} The monoclinic phase forms columns of 1-D stacks of macrocycles with their molecular plane parallel to each other. These cofacial stacks can orient on the substrate surface in a face-on or edge-on configuration as directed by the substrate-molecule interactions. The triclinic phase consists of concave and convex pairs of nonplanar molecules with significant overlap of adjacent macrocycles and can also orient in both parallel and edge-on arrangements on different substrates.^{1,2,11} Though the intrinsic electronic conductivity in MPc molecules, in general is found to be poor, the crystalline arrangement of molecules with strong π - π interactions along the *b*-axis of the monoclinic domains exhibits enhanced vertical conductivity.¹¹

The conductivity in MPcs (π -electron donors) can also be enhanced by doping of oxidizing species such as halogens. The doping concept has been utilized in various applications such as lithium-ion batteries and oxygen reduction reactions for lowering charge transfer resistance across the electrode/electrolyte interface.^{12,13} Iodine doped organic systems have also been applied in organic photovoltaics to achieve enhanced photocurrent generation and NIR absorption.^{14,15} The semiconducting behavior of these molecules also gets affected significantly due to the presence of different gaseous species in the atmosphere and is exploited for sensing applications. The sensing mechanism involves chemical interactions between the metal centre of the MPc molecule and the analyte, which could be weak forces or redox reactions and is termed as chemiresistive sensing.⁵ These interactions lead to the formation of charge transfer complexes

and the resultant modulation of the Fermi energy level in MPc film gives rise to enhanced conductivity.^{16,17} The magnitude and the reversibility of the conductance in these films depend on the type of the central metal atom and the crystal structure of MPc film. However, sensors based on MPcs have larger response times, poor reversibility and higher operating temperatures.¹⁸ Competitive doping in organic molecules using a secondary dopant is an approach to enhance their sensitivity, response time and selectivity towards better gas sensors wherein the dopants can drastically affect crystallinity, stability, and conductivity of the films.^{19,20} MPcs have been used as a secondary dopant in polypyrrole matrix for improved detection of NO_x species.^{21,22}

Strong dopants or oxidizing molecules can also lead to decomposition, fragmentation or surface reconstruction of the film by affecting the molecular organization in MPc structures.^{23,24} In our earlier report, it is shown that the iodine doping in planar MnPc films leads to structural reorganization that can be correlated with the observed magnetic and electrical properties.²⁵ Conducting-atomic force microscopy (C-AFM) is a well-established technique to resolve the conductive domains of molecular electronic materials at a nanoscale level that can be correlated with the morphological features. C-AFM studies have revealed local heterogeneity in organic semiconductor heterojunctions,^{26,27} photocurrent map of doped semiconductors,²⁸ and percolation thresholds in carbon nanostructure-polymer composites,²⁹ and have significant implications on the device properties. C-AFM has also been utilized to investigate noise-source-controlled localized charge transport in reduced graphene oxide and conducting polymer films.^{30,31} In a recent report, the photoresponse and the associated phase changes of perovskite materials in response to temperature variation have also been investigated by C-AFM.³² It would be interesting to visualize the conducting pathways introduced in MPc films due to iodine doping and the impact of other gaseous adsorbates on these domains. In this study, we present the details of structural reorganization in iodine doped nonplanar PbPc films, deposited on different substrates with the help of synchrotron two-dimensional grazing incidence X-ray diffraction (2D GIXRD) technique. Current mapping of the iodinated films is also presented and compared to that of pristine PbPc system, which was reported earlier.¹¹ C-AFM reveals a commendable change in the conduction pathways of iodinated PbPc films for different substrates in comparison with the corresponding pristine systems. The variation in the current distribution across the conductive domains in the case of different substrates can be associated with the

molecular organization in the film. The effect of ammonia on the conducting domains of iodinated films akin to a competitive doping effect is also investigated. The study provides insights into the conduction pathways in doped MPc systems.

Experimental Details

Lead(II)phthalocyanine, PbPc (TCI, dye content > 95.0%), was deposited on to various substrates such as quartz, *n*-type Si, and highly oriented pyrolytic graphite (HOPG) by physical vapor deposition under vacuum. The base pressure of 1×10^{-5} mbar was maintained during PbPc deposition and the substrates were held at 100 °C. The thickness and the rate of deposition were ~ 50 nm and $1 - 1.5 \text{ \AA s}^{-1}$, respectively, as monitored by quartz crystal microbalance. The substrates were subjected to cleaning before mounting in the vacuum chamber. Quartz was cleaned in acetone followed by distilled water, and standard RCA procedure was adopted to clean Si wafer. HOPG substrate was cleaved to expose the fresh surface before deposition. Iodine doping was performed by exposing the deposited PbPc thin films to iodine vapors in a sealed vessel loaded with a few iodine crystals heated to 60 °C for 3 h. After doping, the bluish-green films turned to a brownish color. The iodine doped PbPc films are termed as I-PbPc films, hereafter.

A PerkinElmer (Lambda 20) UV-visible spectrophotometer was used to record absorption spectra of iodinated PbPc film on a quartz substrate. X-ray diffraction (XRD) was performed employing Rigaku Smartlab diffractometer in a parallel beam geometry (grazing angle = 0.3°) using monochromatic Cu K α radiation (40 kV, 30 mA). 2D GIXRD experiments were performed at Deutsches Elektronen-Synchrotron (DESY) PETRA III, P08 beamline using a flat panel Perkin Elmer detector (2048×2048 pixels of the size of $200 \mu\text{m}$) at a beam energy of 25 keV corresponding to $\lambda = 0.496 \text{ \AA}$. The obtained 2D GIXRD images were analyzed with the help of MATLAB interfaced GIXSGUI software.³³ Field-emission scanning electron microscope (FESEM), TESCAN MIRA3 LM was used to obtain morphological features and the elemental composition was acquired through energy dispersive X-ray spectroscopy (EDS) using Quantax EDS Bruker detector. Raman spectra were acquired using Horiba XploRA PLUS spectrometer with 532 nm laser having a 50X objective. An Agilent 5500 atomic force microscope (AFM) was used to obtain the topography and current map of I-PbPc thin films. The topography was acquired by tapping mode using a rectangular probe of resonance frequency 325 kHz and a force

constant of 40 N m^{-1} (MikroMasch, USA). C-AFM was performed in contact mode using a conductive probe (MikroMasch, USA) with Cr/Au coating (diameter $< 35 \text{ nm}$ and force constant $= 0.18 \text{ N m}^{-1}$). The substrates such as *n*-type Si or HOPG served as the bottom electrode while the conductive Au tip scanning the film served as the top electrode in a vertical configuration. The Au tip is held at ground, and the substrate is swept through positive or negative potentials. For C-AFM experiments in the presence of gas, the environmental chamber of AFM was purged with ammonia vapors under saturated conditions and imaging of thin films of pristine PbPc and I-PbPc were performed. The conductivity of the films was calculated using the formulae given by Lu et al.,³⁴ considering effective contact area of the C-AFM tip.

Results and Discussion

1. Effect of iodine doping on molecular organization

2D GIXRD was performed to glean details of the structural rearrangement and molecular orientation in PbPc films upon iodine doping. In our earlier report, conventional XRD (θ - 2θ geometry) showed that pristine PbPc films on Si exhibited an ordered (100) triclinic phase while on HOPG, PbPc attained an ordered (320) monoclinic packing directed by substrate-molecule interactions.¹¹ This is further substantiated with molecular orientation information obtained from the 2D GIXRD analysis presented in this report. Figure 1a shows 2D GIXRD image for pristine PbPc film deposited on a Si substrate. A bright spot at q_z , $0.5 \text{ \AA}^{-1}$ can be deconvoluted into two peaks (Figure 1e), the peak at $0.49 \text{ \AA}^{-1}$ can be assigned to (001) triclinic phase or (200) monoclinic (blue curve) with $d = 12.82 \text{ \AA}$ ($2\theta = 6.88^\circ$). The second peak at $0.52 \text{ \AA}^{-1}$ corresponding to (100) triclinic (green curve) has $d = 12.08 \text{ \AA}$ ($2\theta = 7.44^\circ$). The faint appearance of (320) monoclinic phase can also be spotted at q_z , $0.89 \text{ \AA}^{-1}$ with $d = 7.03 \text{ \AA}$ ($2\theta = 12.69^\circ$). The intensity ratio of the triclinic to monoclinic peak is 57:1, indicating that the majority of the crystalline phase on Si is triclinic. All these peaks also appear faintly in different azimuthal angles (Figure S1). The two main peaks, (001) and (100) (with $d \geq 12 \text{ \AA}$) corresponding to triclinic fractions reveal that the molecules are in standing-up or edge-on configuration.³⁵ The presence of weak peaks with lower d -spacing indicates that a few molecular crystallites possess tilted or lying down configuration. In literature, it has been shown that the intramolecular interactions dominate with increasing thickness leading to minor disorder in the molecular arrangement.³⁵

Figure 1. 2D GIXRD images of PbPc thin films on various substrates (a) pristine PbPc on Si, (b) pristine PbPc on HOPG, (c) I-PbPc on Si, (d) I-PbPc on HOPG (e) profile sections along the q_z directions for pristine PbPc and I-PbPc on Si; Blue and green curves show the deconvoluted peaks for pristine PbPc and red curve indicate I-PbPc (f) profile sections along the q_z directions for pristine PbPc and I-PbPc on HOPG.

In the case of pristine PbPc film on HOPG, a distinct out of plane feature is seen at q_z , 0.89 $\text{\AA}^{-1}$ (Figures 1b and 1f) corresponding to (320) monoclinic PbPc with $d = 7.03$ $\text{\AA}$ ($2\theta =$

12.69°).³⁵ The (320) plane of monoclinic phase in a q_z plane can be attributed to the face-on packing of PbPc molecules. This confirms our observation in the earlier report that PbPc film on HOPG has an ordered stacking with monoclinic domains lying parallel to the substrate plane. The graphite layers promote cofacial π - π stacking of the PbPc domains along their b -axis, thereby enhancing vertical charge transport in PbPc.¹¹ A less intense (320) peak due to monoclinic fraction is observed in the q_y plane at different azimuthal angles (Figure S2) indicating that the arrangement of monoclinic domains also exists in lateral direction on HOPG. A few weak signatures of triclinic moieties are also observed at $0.96 \text{ \AA}^{-1}$ ($2\theta = 13.4^\circ$, $d = 6.54 \text{ \AA}$) along the q_z plane corresponding to triclinic ($1\bar{2}1$) and $0.52 \text{ \AA}^{-1}$ along q_y corresponding to triclinic (100) with molecular orientation parallel to the substrate.³⁵

Upon iodine doping, conventional XRD pattern(θ - 2θ geometry) shows that the crystalline peaks due to PbPc on Si and HOPG substrates disappear entirely except for the weak peak of (320) monoclinic fraction that evolved in the case of Si substrate (Figure S3). This indicates that iodine doping causes a rearrangement in the PbPc molecular packing. 2D GIXRD data after iodine doping gives detailed information on molecular orientation and are given in Figures 1c and 1d. I-PbPc film on Si substrate (Figure 1c) shows three sharp crystalline peaks along the q_z meridian at positions 0.53 , 0.67 and $0.89 \text{ \AA}^{-1}$. The doublet at $0.5 \text{ \AA}^{-1}$ in pristine PbPc, appears as a single peak at $0.53 \text{ \AA}^{-1}$ corresponding to (100) triclinic fraction in I-PbPc (Figure 1e, red curve). The peak at $0.67 \text{ \AA}^{-1}$ ($d = 9.38 \text{ \AA}$ and $2\theta = 9.41^\circ$) has newly evolved and the lower d -spacing indicates that certain fraction of standing-up PbPc molecules lie inclined to the substrate owing to the rearrangement after iodine doping. We also find that there is an increase in (320) peak of monoclinic fractions seen at $0.89 \text{ \AA}^{-1}$. The intensity ratio of the triclinic to monoclinic peak is 11:1 indicating that the majority of the triclinic moieties have been rearranged to form monoclinic domains. Further, all these peaks present faint diffraction patterns at different azimuthal angles (Figure S4) indicating increased randomness in the arrangement of PbPc molecules after iodine doping. On HOPG, I-PbPc film does not exhibit any crystalline ordering and (320) peak observed in the pristine case has disappeared as confirmed by 2D GIXRD (Figures 1d and 1f). Table 1 gives the various peak positions with intensity variations observed for pristine and I- PbPc films from 2D GIXRD data.

Table 1. 2D GIXRD peak positions and intensity variations observed for pristine and I-PbPc films on Si and HOPG substrates.

Substrate	Peak position q_z ($\text{\AA}^{-1}$)	Peak intensity	
		Pristine PbPc	I-PbPc
Si	0.49	Strong	Absent
	0.52	Strong	Strong
	0.67	Absent	Weak
	0.89	Weak	Medium
HOPG	0.53	Weak	Absent
	0.89	Strong	Absent
	0.96	Strong	Absent

2. Effect of iodine doping on optical and structural properties

The inclusion of iodine in PbPc films is confirmed by optical absorption and Raman spectroscopy. The UV-Vis absorption spectra of pristine PbPc and I-PbPc films on quartz substrates (Figure S5) show typical B and Q bands of PbPc with intensity variations after iodine doping. The peak intensity in the visible region is seen enhanced after iodine doping indicating the formation of a charge transfer complex. The Q band at 650 nm associated with monoclinic fractions seems to increase in intensity while that at 900 nm associated with triclinic component seems to decrease after iodine doping. Such intensity changes in optical spectra due to molecular rearrangement have been observed during annealing of PbPc films and exploited to improve the solar cell efficiency.¹

Raman spectra are acquired to understand the type of iodine species present in I-PbPc films (Figure 2). The peak at 108 cm^{-1} corresponds to antisymmetric stretching of I_3^- species (Figure 2a). It has been reported that in the case of iodinated MPc crystals (NiPcI), iodine exists as a linear chain of triiodide ions (I_3^-) in the MPc lattice and is responsible for metallic type conductivity.^{36,37} For I-PbPc films, the overtones of 108 cm^{-1} vibrations are not observed indicating the absence of linear I_3^- chains.^{36,37} Further, the peak at 185 cm^{-1} may correspond to I_5^- wherein I_2 molecules are coordinated to a Lewis base such as I_3^- due to high doping concentrations. In the region $1000 - 1600\text{ cm}^{-1}$, the various stretching and bending modes of different moieties constituting the phthalocyanine macrocycle are seen (Figure 2b).¹¹ It is

observed that the intensity of vibrational signatures is considerably enhanced after iodine doping due to a resonance Raman effect similar to the case of our previous report on iodinated MnPc.²⁵ Peaks due to isoindole (1450 cm^{-1}) and pyrrole stretching (1340 cm^{-1} of C-C pyrrole stretch and 1500 cm^{-1} of C-N pyrrole stretch) of PbPc molecules are observed (Figure 2b). These particular peaks are sensitive to the disordered arrangement of molecules giving rise to additional high frequency vibrations associated with the fundamental peak. It can be observed from Figure 2b that in the case of I-PbPc on HOPG, the C-N stretching of pyrrole moiety at 1511 cm^{-1} is accompanied by another peak at 1540 cm^{-1} and the strong intensity of the high frequency peak is indicative of a highly disordered film.³⁸

Figure 2. (a) Raman spectra of pristine PbPc and I-PbPc films on HOPG substrate (a) 100 - 300 cm^{-1} (b) 1000 - 1600 cm^{-1} .

Based on the inferences from 2D GIXRD and Raman spectra, the structural rearrangements in PbPc films on Si and HOPG substrates before and after iodine doping can be represented as shown in Figure 3. The ordered (100) triclinic phase of PbPc having edge-on orientation on Si surface undergoes structural transformation up on iodine doping to give rise to a fraction of molecules with (320) face-on monoclinic configuration along with other orientations. Additionally, a few PbPc triclinic moieties incline towards the substrate plane with lowered d -spacing. On the other hand, (320) monoclinic phase of PbPc with a face-on orientation on HOPG undergo structural transformation drastically up on iodine doping to give rise to randomly arranged PbPc units without any crystalline ordering. In both the cases, the iodine species (I_3^- and I_5^-) are found amidst the PbPc lattice causing the rearrangement and disorder.

Figure 3. Schematic of the structural rearrangement in PbPc films on Si and HOPG substrates up on iodine doping.

3. Effect of iodine doping on morphology

The morphological features of I-PbPc films on different substrates were studied with the help of FESEM and AFM and the images are shown in Figure 4. The details of morphological features of pristine PbPc films on Si and HOPG substrate have been presented in our previous report.¹¹ There is a considerable difference in the morphology among pristine and I-PbPc thin films (comparison is given in Figures S6a - 6d). It is seen that the I-PbPc films contain variously shaped grains distributed over the film surface (Figures 4a - 4d). The spherically shaped and uniformly distributed PbPc crystallites are modified to form larger elongated and flat features after iodine doping, particularly in the case of Si and smaller individual nanocrystallites are found to be present beneath the larger features. The particle size of the pristine PbPc grains on HOPG increases from 50 nm (80 nm on Si) to 175 nm (250 nm on Si) up on iodine doping. Accordingly, the surface roughness (RMS values) of the pristine PbPc film on HOPG changes from 2.89 nm (3.58 nm on Si) to 25.3 nm (11.3 nm on Si) in I-PbPc thin films. Figures 4e and 4f are the profile sections of I-PbPc film on Si and HOPG substrates showing the height variations, which can be compared with the pristine PbPc thin films (Figures S6e and 6f). To prove that the morphological changes and the increased surface roughness of the I-PbPc are exclusively due to iodine doping in the PbPc films, the pristine PbPc films were heated at 60 °C for 3 h in the absence of iodine and examined using FESEM. The morphological features before and after annealing are found to be similar (Figures S7a - 7d). Further, I-PbPc films were heated at 100 °C

for 1 h in an argon atmosphere with an intention to oust iodine molecules and to see the effect on the morphology. Figures S8a and 8b show the FESEM morphology of I-PbPc films on Si and HOPG substrates after the annealing process. It is seen that there is no significant change in the morphology and the surface features are comparable to those before annealing. The EDS analyses (Table S1) also indicate the presence of iodine in the thin films even after annealing.

Figure 4. FESEM images of I-PbPc films on substrates (a) Si, (b) HOPG, 3 μm × 3 μm AFM images of I-PbPc films on substrates (c) Si, (d) HOPG, (e) and (f) are the profile sections across the marked lines in (c) and (d).

A recent article by Yao et al.³⁹ has discussed the step-wise structural transformations induced by different dosages of iodine, perturbing the self-assembly of CoPc film deposited on

Au surface. The scanning tunneling microscopy images revealed that a few iodine atoms get embedded among the CoPc molecules and with increased iodine dosage, the periphery of each CoPc molecule gets surrounded by iodine atoms. These arrangements can extrapolate in thicker films to give rise to disordered molecular stacking of MPc molecules causing different morphological characteristics. Iodine doping in other organic polymers such as P3HT, polyterphenol, etc is also known to affect the surface morphology and roughness of the films.⁴⁰ These morphological studies support the surface reconstruction in PbPc films after iodine exposure leading to considerable change in surface roughness. This type of rearrangement and disorder has been visualized in iodine-doped NiPc structures through high-resolution electron microscopy imaging.²⁴ Similar morphological changes were mapped in planar MnPc thin films in which the uniformly distributed small spherical MnPc particles rearrange to give rise to larger flat grains among the individual nanocrystallites upon iodine doping, thereby increasing the surface roughness.²⁵ The increase in roughness values of PbPc films is drastically high after iodine doping when compared to that of MnPc. This may be due to the difference in packing of nonplanar PbPc molecules possessing a shuttle-cock structure compared to planar MnPc, the former being more sensitive to any perturbation. 2D GIXRD also supports a drastic molecular reorganization in both cases of PbPc deposited on Si and HOPG after iodine doping. Higher degree of disorder is observed in the case of HOPG and accordingly, a higher roughness increase is observed.

4. Effect of iodine doping on current response

The current imaging of I-PbPc films on Si and HOPG are performed to understand the local current distribution upon iodine doping using C-AFM technique. Figures 5a and 5b show the topography and current map of I-PbPc film on Si, obtained at a sample bias of 1 V. Compared with our earlier report on pristine PbPc obtained on Si,¹¹ the current values of I-PbPc are seen enhanced due to iodine doping (pristine PbPc data is shown in Figure S9 for comparison). While the lesser conducting domains in pristine PbPc exhibited a maximum current value of 10 pA (Figure S9b), the conductive domains of I-PbPc (Figure 5b) exhibited the highest current value of 600 pA under 1 V bias. The enhancement in current values for I-PbPc films is almost 60 times more than that for pristine PbPc film. The enhancement is as expected for halogen doping in *p*-type organic semiconductors. However, the current mapping reveals that the isolated and lesser conducting domains seen in the case of pristine PbPc have largely been

modified upon iodine doping. The height and current variation across the I-PbPc films is represented in Figure 5c. On comparison with topography, it can be seen that the large crystallites that appear bright (protruded) in the height image of I-PbPc, are less conducting. The higher conduction is achieved through smaller crystallites establishing percolation networks in I-PbPc films, as revealed by nanoscale mapping. The current profile of I-PbPc films (Figure 5c) also show continuous and interconnected conducting domains in contrast to the isolated domains in case of pristine PbPc (Figure S9c). The above observation is more evident from the histograms of current distribution across domain population generated from the current images of pristine PbPc and I-PbPc films on Si substrate (Figures 5d and 5e). Majority of the domains show current values in the range of 2 pA for pristine PbPc film with a narrow distribution while a tiny fraction shows higher current values in the range 6 - 10 pA. For I-PbPc film, the current values have increased over a broad distribution of conducting domains. The major fraction of the domains exhibits current values in the range of 200 pA and a significant fraction shows high current values in the 100 pA range. Further, a moderate fraction shows higher current values > 250 pA. The difference in the current distribution for pristine and I-PbPc films is evident from the histograms. Histograms reveal that higher current observed in I-PbPc is gained through a larger population of grains contributing to conducting domains with higher current values, however, with considerable heterogeneity in the current distribution. The conductivity is found to be $8.16 \times 10^{-7} \text{ S cm}^{-1}$ and $7.18 \times 10^{-4} \text{ S cm}^{-1}$ for pristine PbPc and I-PbPc on Si, respectively, with three orders of enhancement.

Figure 5. (a) 2 $\mu\text{m} \times 2 \mu\text{m}$ AFM topography and (b) corresponding current map obtained at 1 V for I-PbPc film on Si (c) profile sections of (a) and (b) across the marked lines showing the height and current variations in I-PbPc film on Si. Histograms showing the population percent vs. current distribution in (d) pristine PbPc film (derived from Figure S9b) and (e) I-PbPc films on Si substrate (from 5b).

Figures 6a and 6b show the topography and the current images acquired for I-PbPc films deposited on HOPG substrate under 1 V bias. The surface features of I-PbPc film have been mostly modified to form randomly arranged crystallites of varied sizes (200 - 500 nm) yielding

higher roughness as described earlier (Figure 6a). The average current value from the conducting surface features is about 175 pA with maximum current value reaching 500 pA for I-PbPc (Figure 6b). In the case of pristine PbPc on HOPG (Figure S10b) the average current values of the grains are 50 pA with few domains showing current values as high as 100 pA. Similar to I-PbPc film on Si, an interconnected percolating network of conducting domains is observed for I-PbPc on HOPG in contrast to isolated domains of pristine PbPc on HOPG (see Figure S10). The higher current in pristine PbPc film on HOPG, when compared to PbPc on Si, is attributed to the enhanced vertical charge transport arising from the ordered cofacial molecular packing, which was reported earlier.¹¹ Figure 6c shows the height and the current profiles across I-PbPc film and it can be noticed that the smaller grains that constitute the film show enhanced current than the larger morphological features. Figures 6d and 6e show the histograms of the domain population versus current distribution obtained from the current images for pristine PbPc and I-PbPc films on HOPG substrates. The histogram of pristine PbPc shows a broad distribution with the majority of the conducting domains having current values in 50 - 70 pA range and a significant fraction with 100 pA current. For the case of I-PbPc, the majority of the domains exhibit current in the range of 200 pA and highest current value up to 800 pA. After iodine doping, the current distribution is narrower with most of the domain population contributing to the higher current value of 200 pA and the domain population with enhanced current values has increased. The conductivity of the pristine PbPc and I-PbPc film on HOPG is calculated to be $7.29 \times 10^{-5} \text{ S cm}^{-1}$ and $4.37 \times 10^{-3} \text{ S cm}^{-1}$, respectively. There is two order increment in conductivity in the case of HOPG substrate.

Figure 6. $2\ \mu\text{m} \times 2\ \mu\text{m}$ AFM topography (a) and corresponding current map (b) obtained at 1 V of I-PbPc film on HOPG, (c) profile sections of (a) and (b) across the marked lines showing the height and current variations in I-PbPc film on HOPG. Histograms showing the population percent vs. current distribution in (d) pristine PbPc (derived from Figure S10b) and (e) I-PbPc films on HOPG (from 6b).

In general, it can be seen that iodine doping causes increase in the concentration of the hole carriers and establish percolation pathways, thereby, enhancing the charge transport. This was also supported by our earlier observation of increase in hole mobility upon iodine doping in

MnPc irrespective of the film thickness.²⁵ In the case of PbPc film on Si substrate, the enhancement in the current values upon iodine doping is three orders higher compared to pristine film while in the case of HOPG, the corresponding enhancement is only two orders high. This is because of the low intrinsic conductivity of pristine PbPc films on Si substrate, as the obtained triclinic configuration does not favor vertical charge transport while the cofacial stacking with lying-down configuration of pristine PbPc achieved on HOPG already shows enhanced conductance.¹¹ The current enhancement in I-PbPc films in both cases of substrates is governed by the hole charge carriers introduced due to iodide species and the resulting conducting pathways. Molecular packing is no longer greatly influenced by the substrate, and hence, the current value is observed to be similar for I-PbPc films on Si and HOPG. However, the heterogeneity of the conducting domains and current value distribution seems to be different for I-PbPc films on the given substrates. The histograms and current maps show that the population of domains contributing to higher current values is more abundant in the case of HOPG than Si and the current distribution is broad in the case of Si after iodine doping. This can be associated with the structural rearrangement of PbPc on Si and HOPG after iodine doping.

From 2D GIXRD, we observe that iodine doping causes a major fraction of standing-up PbPc (triclinic crystallites) to tilted and lying-down orientations (monoclinic crystallites) on Si with some degree of disorder while mostly disordered PbPc fractions are observed in the case of HOPG. Hence, in the current map of I-PbPc on Si, we see a broad distribution of current values across various molecular orientations. The retained triclinic crystallites and tilted edge-on oriented molecules may give rise to lesser current response as they are not favorable for vertical conduction in C-AFM configuration.¹¹ In the case of HOPG, the disordered fractions establish percolation networks of conducting domains more effectively. Similar C-AFM studies and histogram analysis was reported by Wolski et al. in which the enhanced surface conductivity due to iodine doping in polymer brushes was mapped. The observations from the histograms were correlated to the different polymer grafting densities affecting conductance and different thicknesses leading to charged ladder-like brushes with conjugated chains.^{41,42} The histograms obtained in our study mainly emphasize on the current distribution before and after doping the PbPc films. Local conductive domains mapped in pristine and I-PbPc films give a clear representation of isolated and percolating conductive networks through which the charges are transported. This property at nanoscale gets manifested in bulk electrical properties of thin films.

In the case of graphene-polymer composites, C-AFM mapping has revealed the percolation thresholds associated with the amount of graphene doping.⁴³

5. Effect of ammonia on current response

We have also explored the effect of ammonia on the electrical response of pristine and I-PbPc films on HOPG using C-AFM under saturated ammonia atmosphere. For this, the ammonia vapors were introduced into the environmental chamber of AFM and C-AFM was performed. Ammonia acts as an electron donor and neutralizes the hole carriers, thereby reducing the conductance of MPcs. The decrease in current response upon ammonia exposure was mapped using C-AFM for I-PbPc films akin to a secondary doping effect studied in other systems such as conducting organic polymers²¹ and compared with that of pristine PbPc. Figures 7a and 7b show the topography of I-PbPc and pristine PbPc films after exposure to ammonia vapors. There is no noticeable change in morphological features of PbPc films after ammonia exposure. However, Figures 7c and 7d present considerable difference in the current exhibited by PbPc films under ammonia atmosphere. Figure 7c shows the current map of I-PbPc in the presence of ammonia vapors. For comparison, the current image of pristine PbPc exposed to ammonia vapors is given in Figure 7d and it can be seen that there is a drastic reduction in current values in both the cases.⁴⁴ The current values decreased from 400 pA to less than 4 pA even after applying a higher sample bias of 3 V in the case of I-PbPc after ammonia exposure.

The histogram of the current values of I-PbPc is given in Figure 7e and shows that the majority of the domains have a current of 1 pA. The current map of I-PbPc after ammonia exposure shows that almost all the conducting domains have diminished current response with values in the range of 0.5 - 3 pA. Importantly, from Figure 7c, it can be seen that the percolation networks established by iodine doping are disrupted by ammonia molecules. For the case of pristine PbPc, the domain population versus current values shows that the majority of the domains exhibit a current of 1.5 pA (Figure 7f). From these studies, it is revealed that the current value observed for I-PbPc film is four times higher compared to the pristine film due to iodine doping and accordingly, there is a four-fold increase in the sensitivity upon exposure to ammonia, as estimated from the ratio of $\left(\frac{I_{air}}{I_{NH_3}}\right)$ obtained for I-PbPc film and pristine PbPc film. The sensitivity enhancement for I-PbPc film can be attributed to the disruption of conducting domain network on exposure to ammonia vapors.

Figure 7: (a) 2 $\mu\text{m} \times 2 \mu\text{m}$ AFM topography of I-PbPc film on HOPG (b) 1 $\mu\text{m} \times 1 \mu\text{m}$ AFM topography of pristine PbPc film on HOPG (c) corresponding current image of I-PbPc after ammonia exposure (d) current image of pristine PbPc after ammonia exposure at 3 V sample bias; Histograms showing the population percent vs. current distribution after ammonia exposure in (e) I-PbPc and (f) pristine PbPc films.

Conclusions

The study presents the structural reorganization caused by iodine doping in ordered nonplanar PbPc films deposited on Si and HOPG substrates and its influence on the conducting

domains. 2D GIXRD studies of pristine and iodine doped films reveal that upon iodine doping, a significant fraction of ordered triclinic PbPc crystallites in standing-up configuration goes to tilted and lying-down orientations with some degree of disorder in the case of Si while on HOPG, the significant fraction of PbPc molecules in lying-down configuration with cofacial stacking has undergone reorganization leading to complete disorganization. The imaging of conducting domains employing C-AFM shows that the iodine doping enhances the conductivity in the system by establishing a percolation network of conductive domains in contrast to the isolated domains in pristine films. The heterogeneity in conduction domains is broader in the case of iodine doped films on Si compared to HOPG and can be associated with the various crystallites having different molecular configuration in the former case. In the latter case, major molecular fractions are disordered that contribute to more percolation pathways for charge transport. The current mapping also reveals that the response of iodine doped films towards ammonia is higher compared to pristine films since the percolation pathways are disrupted. Thus the secondary doping caused by iodine can aid in enhancing the electrical properties of PbPc molecules for improvement in the detection and sensitivity of other gaseous dopants.

Conflicts of Interest

There are no conflicts of interest to declare.

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TOC graphics

Iodine doping in nonplanar Pb(II)phthalocyanine causes drastic structural reorganization and enhanced conductance with nanoscale conducting pathways and better sensitivity towards other gaseous adsorbates.