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Design of novel organic thin film transistors for wearable electronics

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The focus of this multidisciplinary, collaborative basic research programme has been on the development of a low cost process technology for depositing high-resolution patterned layers newly custom designed organic macrocyclic compounds – thermotropic liquid crystalline zinc (II) phthalocyanine (ZnPc4) and lutetium (III) bisphthalocyanine (Lu(III)Pc2) derivatives both substituted with individual functional groups at peripheral and non-peripheral positions, respectively. Spin coated films of these molecules were employed as active organic semiconducting layers in the fabrication of organic thin film field-effect transistors (OTFT) and the effect of the grain boundary and interfacial traps at the gate dielectric has been carefully investigated. The radox reactions of (Lu(III)Pc2) films with biological cofactors have spectroscopically been studied for their use in health care. Emphasis is given on easy manufacturability and integration of mechanically flexible sensors over large areas which are suitable for multiple applications including health care, security and fashion industry.

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TABLE OF CONTENTS

ABSTRACT

The focus of this multidisciplinary, collaborative basic research programme has been on the development of a low cost process technology for depositing high-resolution patterned layers newly custom designed organic macrocyclic compounds – thermotropic liquid crystalline zinc (II) phthalocyanine ($ZnPc_4$) and lutetium (III) bisphthalocyanine ($Lu^{(III)}Pc_2$) derivatives both substituted with individual functional groups at peripheral and non-peripheral positions, respectively. Spin coated films of these molecules were employed as active organic semiconducting layers in the fabrication of organic thin film field-effect transistors (OTFT) and the effect of the grain boundary and interfacial traps at the gate dielectric has been carefully investigated. The radox reactions of ($Lu^{(III)}Pc_2$) films with biological cofactors have spectroscopically been studied for their use in health care. Emphasis is given on easy manufacturability and integration of mechanically flexible sensors over large areas which are suitable for multiple applications including health care, security and fashion industry.

LIST OF SYMBOLS USED

Symbols	Description	Page
AFM	Atomic force microscopy	8
β	Constant depending upon the aspect ratio	9
C_i	Gate capacitance per unit area	9
C_8PbPc	Octaoctyllphthalocyaninato lead phthalocyanine	13
C_8H_2Pc	Octaoctyllphthalocyaninato metal free phthalocyanine	13
$I_{D(sat)}$	Saturation current	9
$Lu^{(III)}Pc_2$	bis[octakis(octyl)phthalocyaninato] lutetium(III)	7
NAD^+	Nicotinamide adenine dinucleotide	16
NADH	nicotinamide adenine dinucleotide hydrogen	10
OTFT	Organic thin film transistors	7
PbS	Lead sulphide	13
QD	Quantum dots	16
V_G	Gate voltage	9
V_T	Threshold voltage	9
μ_{sat}	Saturation field effect mobility and	9
ρ	Carrier density	9
T	Room temperature	9
T_C	Characteristic temperature	9
XRD	X-ray diffraction	14
$ZnPcR_4$	tetrasubstituted phalocyaninato Zinc (II)	7

FIGURE CAPTIONS

LIST OF TABLES

SCIENTIFIC AND TECHNOLOGICAL ACHIEVEMENTS

1.0 INTRODUCTION

The investigation of small molecule semiconductors is playing a major role in the current rapid development of organic thin film transistors (OTFTs), a technology that ultimately may enable the low cost production of large area light-weight, low-cost printable plastic electronics. Particular issues involve compound design, the development of commercially adaptable solution processing methods for material deposition on different substrates, control of molecular alignment within the films for optimisation of the electrical properties, and gaining understanding of the fundamental conduction mechanisms. Semiconductivity exhibited by metallated phthalocyanine macrocycles is well documented and this, coupled with their well-established stability, render them interesting compounds for applications in the area of organic electronics. Early p-type semiconductivity data were largely accrued for unsubstituted derivatives, compounds that have limited solubility in most solvents. These materials are formulated as thin films typically by vapour deposition techniques which are not suitable for large area deposition.

2.0 CHARACTERISTICS OF OTFTS

Interest in liquid-crystalline substituted Pc as an active layer in the OTFTs stems from easy solution was also found to be sensitive to the presence of volatile organic compounds in the ppm range based formulation of supramolecular structures with the ability to design the desired mesomorphic properties and to control charge transport along

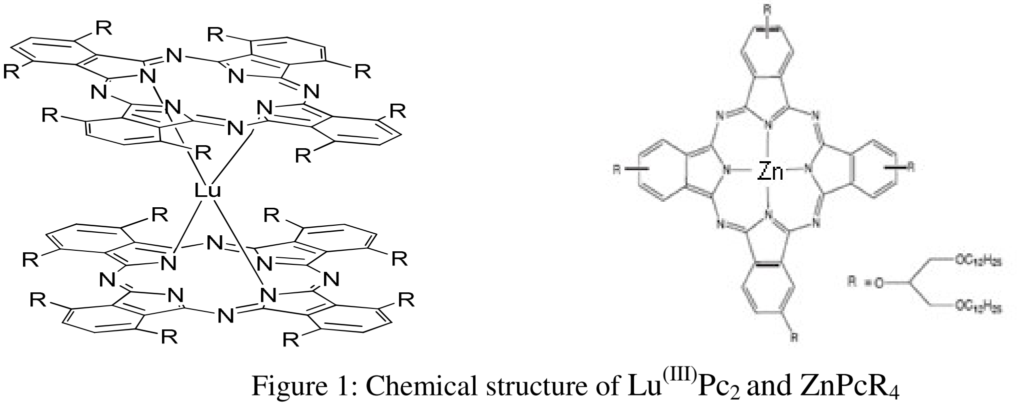


Figure 1: Chemical structure of $Lu^{(III)}Pc_2$ and $ZnPcR_4$

a preferential direction. $Lu^{(III)}Pc_2$ and $ZnPcR_4$ in Figure1 are soluble in most common organic solvents and Bottom-gate, bottom-contact OTFT in Figure 2 have been fabricated using the spun films on pre patterned drain and source electrode systems.

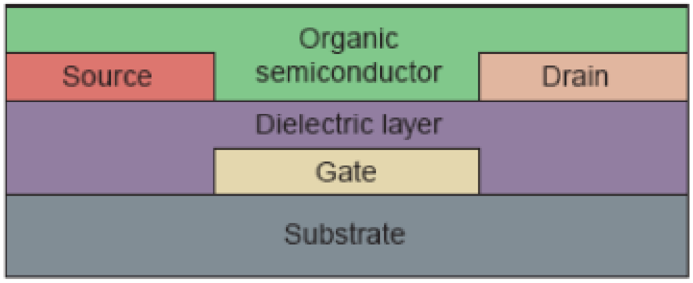


Figure 2: Bottom-gate, bottom-contact OTFT

As shown in Figure 3 of atomic force microscopic (AFM) pictures of $ZnPcR_4$, the active layer is found to be polycrystalline and the electrical performance of OTFT devices is, therefore, expected to be influenced by bulk charge traps, as well as by grain boundary traps of the organic active layer and traps in the interface with the gate insulator. Therefore, the physical interpretation of tranistor characteristics has been made in the present investigation by employing a model in which the saturation field effect mobility is taken to be a charge carrier concentration dependent quantity:

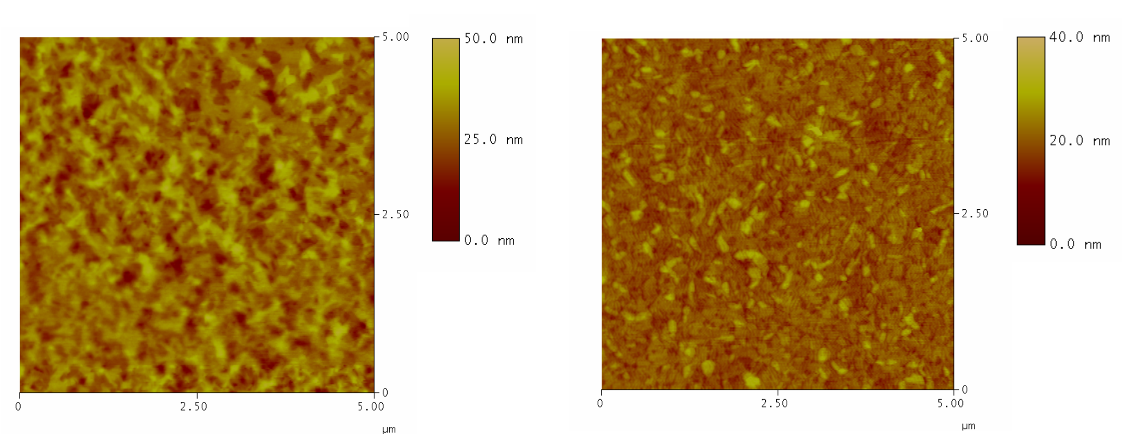


Figure 3. AFM images of the $ZnPcR_4$ films before (a) and after heat treatment.

$ZnPcR_4$ molecules were inhomogeneously distributed at the surface of the as-deposited films as observed from AFM images in Fig. 3. Numerous voids were seen to be present in the films before thermal treatment (Fig. 3 (a)). In contrast, an improved organization of domains in the heated $ZnPcR_8$ layer was evident from AFM images of (Fig. 3(b)), indicating that heat treatment modified the films surface topology. The film roughness decreased from 10.9 to 5.5 nm due to the heating effect.

The transfer characteristics for disordered OTFTs is, therfore, described by the dependence of saturation current $I_{D(sat)}$ on the gate voltage V_G:

$$I_{D(sat)} = \beta(V_G - V_T)^{2T_c/T} \qquad (1)$$

where V_T is the threshold voltage. β is a constant depending upon the aspect ratio, gate capacitance C_i, saturation field effect mobility μ_{sat} and carrier density ρ and T_C is the characteristic temperature associated with the width of the Gaussian or slope of the exponential distribution of traps. The transfer characteristics were analysed and the results are summarised in Table 1.

Table 1. Summary of transistor parameters measured for as-prepared and annealed **$R_{16}LuPc_2$** and $ZnPcR_4$ devices.

	Mobility ($\mu_{(sat)}$) cm^2/Vs	On/off current ratio	Threshold Voltage, (V_T) V	Sub-threshold Voltage, (V/decade)	Interface trap Density, (cm^{-2})	Grain-boundary trap density, (cm^{-2})
$R_{16}LuPc_2$ transistors						
As-prepared	1.5×10^{-3}	~10^3	-25	3.8	2.81×10^{12}	1.2×10^{12}
Annealed	8.0×10^{-3}	~10^5	-12.5	1.6	1.40×10^{12}	7.6×10^{11}
$ZnPcR_4$ transistors						
As-prepared	18 x 10^{-6}	~10^3	-26	3.81	1.06x10^{15}	1.24 x 10^{12}
Annealed	34.0 x 10^{-6}	~10^5	-12	1.64	1.01 x10^{15}	7.62 x 10^{11}

In summary, phthalocyanine molecules that have been investigated during this project can be solution processed on a variety of substrates including flexible substrates, providing economic benefits for *roll-to-roll* plastic substrate-based devices. The enhanced electrical properties achievable by tuning the active layer structure through annealing the devices under specific conditions.

3.0 USE OF PHTHALOCYANINE AS A BIOSENSOR

It can be seen from Table 1 that the mobility of $R_{16}LuPc_2$ transistors is higher than that of $ZnPcR_4$ transistors by three order of magnitudes. For this reason, $R_{16}LuPc_2$ active layers were utilised for quantitative estimation of redox active biomolecules such as nicotinamide adenine dinucleotide hydrogen (NADH) and ascorbic acid (Vitamin C). Solution processed 100nm thick films of newly synthesised $R_{16}LuPc_2$ complexes on ultrasonically cleaned glass substrates exhibit pronounced chemichromic behaviour with potential application in health care. In *situ* kinetic optical absorption spectroscopic measurements show that the phthalocyanine Q-band is red shifted by 60 nm upon oxidation arising from exposure to bromine vapour. Recovery to the original state is achieved by the treatment of the oxidised films with nicotinamide adenine dinucleotide and L-ascorbic acid (vitamin C) in an aqueous solution containing 1.5M lithium perchlorate. The neutralisation process is found to be governed by first order kinetics. The linear increase of the reduction rate with increasing concentration of cofactors provides a basis for calibration of analyte concentrations ranging from 3.5mM down to 0.03mM.

Futher work is now undertaken to determine the active life of the $R_{16}LuPc_2$ biosensors using Raman spectra. As $R_{16}luPc_2^+$-Br_2 is formed, the charge transfer takes place via the metal and from the Pc ring pyrrole C-N bond. This is also indicated by the red shift of 480 band to 586 broad band in optical absorption spectra. Bromine is adsorbed on the film which evaporates out when left in air. The maximum upshift is observable in 1320-1650 cm^{-1} showing the considerable electron shift from the region in agreement with hole localisation. The peak at 1500 cm^{-1} in the neutral form is the marker band for monoradical and the upsift denotes confinement of hole. The Raman peaks with the assignments are listed in Table2. Due to change of electron density the interaction between the macrocycles changes changing the relative intensities of some bonds.

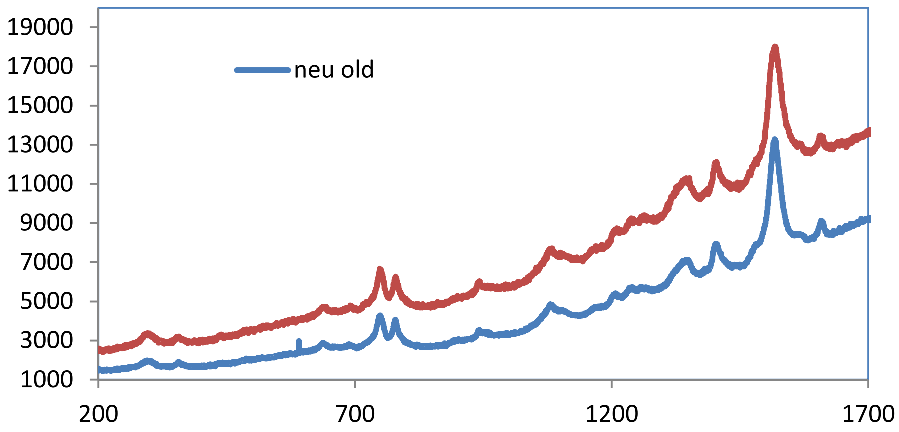


Figure 4: Raman spectra of the neutral and oxidised film which is used and left in air for 3 months.

The Raman spectra in Figure 4 show similar shift of positions due to oxidation of the film but the relative intensities of neutral and oxidised film do not show same pattern as fresh one due to the structural distortion.

Table 2: Wavenumber locations of characteristic Raman bands of neutral and oxidised $R_{16}LuPc_2$.

Fresh film		**3 months old film**		**Assignment**
Neutral	**Oxidised**	**Neutral**	**Oxidised**	
637	639	631	634	Pc ring breathing
688	694	687	----	Pc ring breathing
748	751	749	749	Aromatic C-H wag
777	780	775	778	C=N aza stretching
942	942	932		Pc ring breathing
1078	1081	1076	1079	Aromatic C-H bending
1167				Aromatic C-H bending
1209	1204	1203	1203	Aromatic C-H bending
1230	1237	1229		Aromatic C-H bending
1259				Aromatic C-H bending
1335	1352	1325	1345	pyrrole stretching
1402	1406	1403	1405	isoindole stretching
1510	1519	1511	1519	Coupling of C=C pyrrole and aza C=N stretching
1603	1609	1592	1608	benzene stretching

4.0 CATHODIC ELECTRODEPOSITION OF ANATASE HIGH DİELECTRIC CONSTANT TITANIA

Polycrystalline titania (TiO_2) films were prepared on the indium tin oxide glass substrate on high temperature annealing of TiO_2 hydrates electrodeposited from the chemical bath of titanyl sulphate at room temperature and above. The film grew in thickness monotonically with the rise in bath temperature. The bath temperature was found to be important for the extent to the anatase phase was achieved for a given set of annealing temperature and time The Raman spectra of the annealed films which was deposited at the bath temperature of 336K exhibited distinct anatase phase. Full description of this is available from one of our recent publication (Cruz Blanco et al 2012 Journal of the Electrochemical Society **159(2**) E30-E36. DOI: 10.1149/2.016202jes).

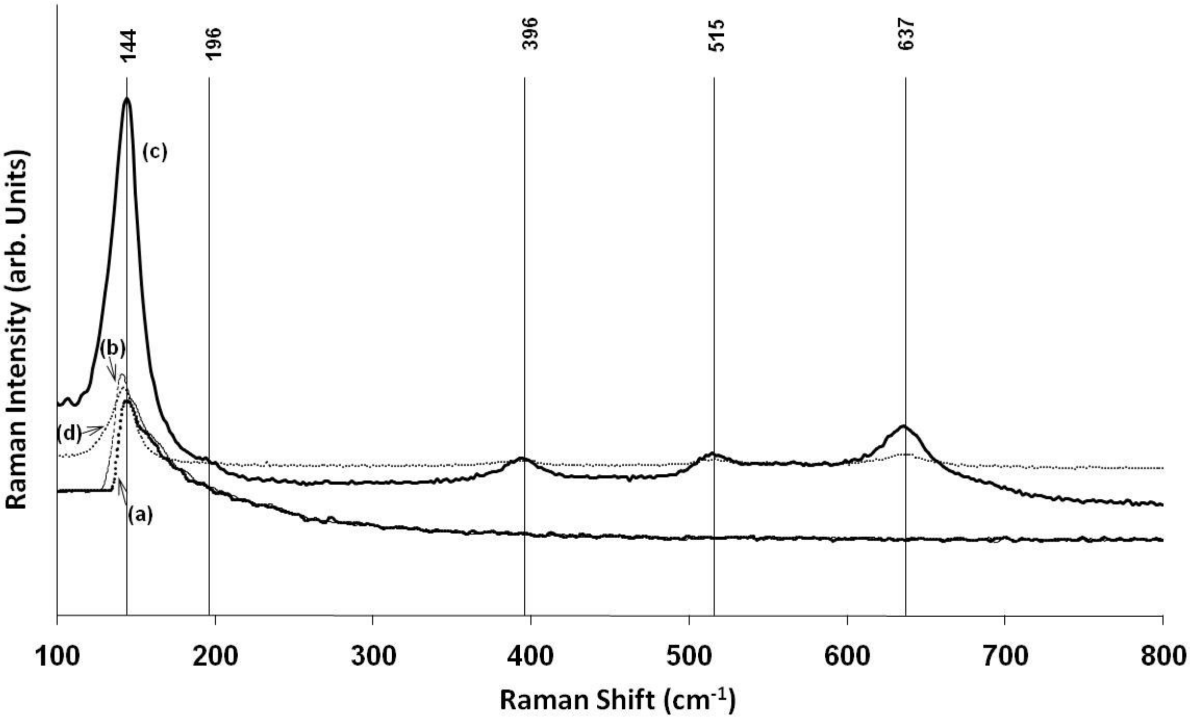
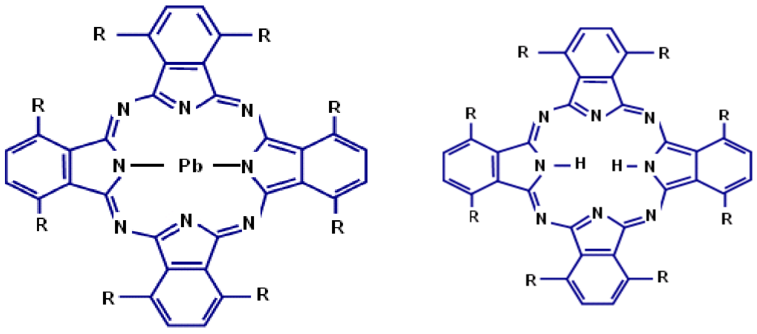


Figure 5. Raman Spectra for TiO2 films electrodeposited at temperatures: (a) 296K, (b) 318K, (c) 336K and (d) 353K. The Raman values for anatase peaks are shown for reference (anatase powder from Aldrich)

4.0 NANOCOMPOSITE LEAD SULPHIDE EMBEDDED IN PHTHALOCYANİNE MATRIX

Lead sulphide (PbS) nanoparticles have been used in photodetectors, photovoltaics and many other electronic and optoelectronic devices depending on the adjustable band gap and size. PbS quantum dots of approximately 7 nm in size have been embedded into metal free phthalocyanine (C_8PbPc, R= C_8H_{17}), by exposing lead phthalocyanine(C_8PbPc) in H_2S gas for approximately 12 hours. The completion of reaction was indicated by a colour change, from green to blue-green. The Raman spectra of C_8PbPc before and after passing H_2S were studied and then compared with one obtained for pure C_8H_2Pc. Existence of PbS nanoparticles and its size were also estimated by X-Ray Diffraction pattern. In nanocomposite materials the composition and the interaction between the components influence the optical and electrical properties. In this investigation, Raman spectra of nanocomposite and pure C_8H_2Pc do not show any significant changes of peak positions. This observation indicates no interfacial interaction in Raman bands of C_8H_2Pc with nanoparticles. FTIR spectroscopic study produces the similar results. This will be presented in the forthcoming international conference on Raman spectra.



C8PbPc C8H_2Pc

Figure 6: 1-, 4-, 8-, 11-, 15-, 18-, 22-, 25-octaoctyllphthalocyaninato lead (C8PbPc) and (b) 1-, 4-, 8-, 11-, 15-, 18-, 22-25-octaoctylphthalocyanine metal free (C8H_2 Pc) molecules.

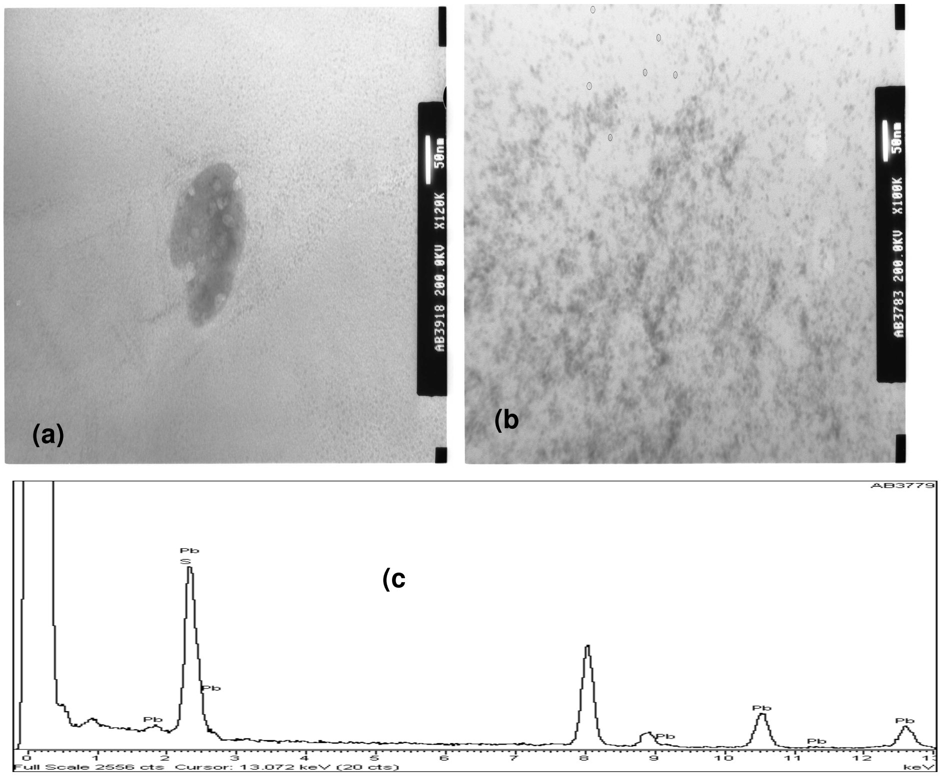


Figure 7: TEM of (a) PbPc, (b) PbS nanoparticles, (c) EDAX of PbS nanoprticles.

The average particle size of PbS is estimated to be similar to 5.8±1nm from be the TEM data (fig.7b). This value is in agreement with the one determined from the X-ray diffraction (XRD) pattern. The consistency of particle size in TEM and XRD shows non aggregated feature of the PbS nanoparticles in this route. DC conductivity study of both pure C8H$_2$Pc and nanocomposite material was performed on interdigitated gold electrode in dark and vacuum condition inside a cryostat from 0 to 50 volt. From 5 to 50 volt. Values of Ohmic Dc conductivity are estimated to be 1.8×10^{-10}S and 3×10^{-10}S for C8H$_2$Pc and nanocomposite material. The activation energy(ΔE) of both pure and composite H2Pc was carried out from 87K-430K temperature region. From 87K to room temperature the ΔE value of pure C$_8$H$_2$Pc was found to be .02 eV where as nanocomposite material shows two different conductance characters in these regions. Upto 240 K there is no significant change of conductivity with temperature indicating quantum tunnelling occurring in this low temperature region. > 240K show ΔE value as 0.2 eV. The quantum tunnelling upto 240K agrees with the higher conductivity of nancomposite material at room temperature. In 240K-340K conductance by hopping mechanism takes place in presence of PbS quantum dots which can be attributed to impurity conduction.

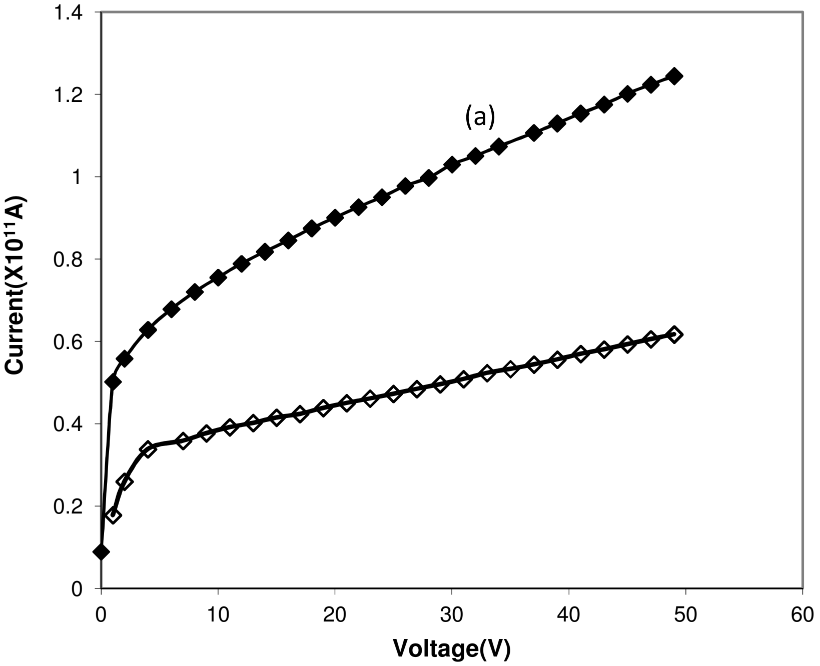


Figure 8: Dc conductivity in dark of (a) C8 H_2Pc-PbS nanocomposite, (b). H_2Pc films

6.0 SCOPE OF EXPLOITATION AND APPLICATIONS

Metallophthalocyanines have proven to be of great interest following their development in the early 1930's. They have a long standing commercial role as pigments and dyes but are now also widely regarded as important functional materials with potential or realized applications that include their use as gas sensors and biosensors. Whereas most metallophthalocyanines are 1:1 complexes of a metal ion or metalloid element and the phthalocyanine ligand there is a smaller but interesting series of 2:1 complexes, , in which a metal ion, most commonly a lanthanide (Ln), is sandwiched between two ligands. The π-π interaction between two phthalocyanine ligands in such sandwich structures add interesting complexity over and above that of the simpler monoligand compounds. The different energy levels of the HOMO and LUMO in different redox states of the phthalocyanine rings are responsible for electrochromic properties.

Nicotinamide adenine dinucleotide (NAD^+) is found in all living systems and takes part in many oxidoreductase reactions. The ratio of NAD^+ to NADH may often indicate the metabolic state associated with several age-related diseases such as diabetes, cancers and neurodegenerative diseases. Several spectroscopic, chromatographic and electrochemical studies have been proposed for rapid, cost-effective sensing of NADH at varying concentrations in order to meet the pharmaceutical requirements. Exploitation of electrochromic properties of $Lu^{(III)}Pc_2$ films for the determination of NADH in a buffer water solution is, therefore, of practical importance as a cheap, disposable biosensor.

The bulk PbS has a small band gap and optically applicable in near infrared (around 3500 nm) region, but strong quantum confinement in PbS QDs allows to tune the band gap energy and thus their applications in a wide spectral region from visible to infrare. In fact, by increasing the size of PbS QDs from about 4 nm to near 20 nm, the energy gap decreases from about 2 to 0.41 eV in PbS, leading to adjust the optical properties of PbS QDs for different applications in the corresponding region. PbS QDs have also demonstrated multiple exciton generation, in which more than one exciton is generated per each absorbed photon. Typically when a photon with energy higher than the band gap energy hits a bulk, a part of its energy is used to excite an electron and the rest is dissipated by another form of energy such as heat. But in nanoscale size, the light with energy more than twice of the band gap can generate two excitons, and so on. Moreover, the long lifetime exciton, about 1 μs, has been observed in PbS QDs. Comparing to other quantum dots, such as CdSe with exciton lifetime about 10 ns, the lifetime of excited states is long enough to allow the excited states to be swapped to the interface and dissociate there before recombination. These phenomena directly enhance the efficiency of photovoltaic devices.

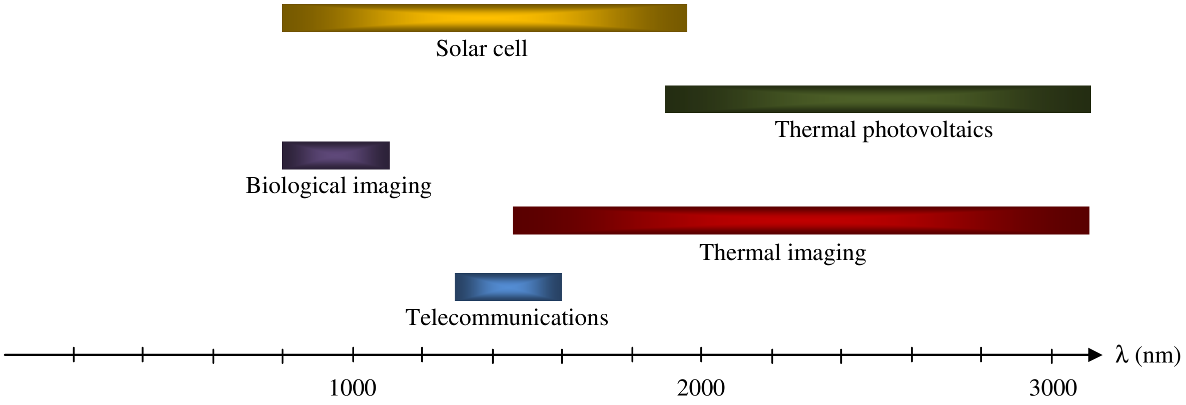


Figure 9 Illustration of active frequency region for various applications.

Project students:

Mrs Chandana Pal MSc is registered with Brunel University for PhD degree in Materials Engineering as of 2011. The title of the project is 'Study of Optical and Electrical Properties of Novel Substituted Phthalocyanine molecules in Thin Film Formulations'.

The experimental investigation of interaction between lanthanide phthalocyanine derivatives with redox biomolecules like NADH (nicotinamide adenine dinucleotide phosphate) and vitamin C will be undertaken in term of optical absorption and voltammetric process. Phthaiocyanine is a macrocyclic compound that is widely used in dyeing, gas sensors, biosensors, photography and laser printing. NADH is important cofactor in metabolism and Vitamin C is an antioxidant. Determination of concentration of these cofactors is relevant to diagnosis of diseases.

Miss Tsegie Mariam Faris B Eng is registered with Brunel University for M Phil degree in Materials Engineering as of 2011 on the project of “Modelling of Phthalocyanine based thin film organic transistors”. Experimental data on output and transfer characteristics were obtained for tetrasubstituted zinc phthalocyanine ($ZnPc_4$) organic thin film transistors. Physical models have been developed to examine the effects of grain boundary, traps in the interface between gate and semiconducting layers and the contact resistances in the source and drain.

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PUBLICATIONS

1. Chaure N. B., Basova, T., Zahedi M., Ray, A.K. Sharma A. K, Durmuş M. and Ahsen V., 2010 **Slution processed tetrasubstituted zinc phthalocyanine as an active layer in organic field effect transistors**. *J. Appl. Phys* **107 (11):**114503 - 114503-5.

2. Cruz Blanco, C. F., Pal, C., Ojeda, J. J., Ray, A.K. and Sharma A. K, 2012 **Morphological and Elemental Studies on Titania Thin Films Electrodeposited at Different Bath Temperatures**. *Journal of the Electrochemical Society* **159(2***)* E30-E36. DOI: 10.1149/2.016202jes

3. Pal, C. Cammidge A.N., Cook M. J, Sosa-Sanchez, J. L., Sharma A. K, . and Ray, A.K. 2012 ***In situ* chemichromic studies of interactions between a lutetium bis-octaalkyl substituted phthalocyanine and selected biological cofactors**. *Journal of the Royal Society Interface* ***9(66)*** 183-189. DOI: 10.1098/rsif.2010.0726.

4. Pal, C., Ojeda, J. J., Cook M. J, Sharma A. K, . and Ray, A.K. 2012 **Raman Spectroscopic Study of Interfacial Interaction in Lead sulphide/Phthalocyanine Nanocomposite Film.** *23rd International Conference on Raman Spectroscopy, Bangalore, India* - **ICORS 2012**, August 12 - 17, 2012.