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# Langmiur–Blodgett studies of silicon(IV) phthalocyanine bis(trihexylsilyoxide) and its optical properties

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ABSTRACT

Although much solution-based research has been carried out on silicon phthalacyanines, little work has been done on Si Pc LB films. In order to attempt studies on thin films, ultrathin Langmuir–Blodgett films of silicon(IV) phthalocyanine bis(trihexylsilyoxide), $C_{68}H_{94}N_8O_2Si_3$ have been studied and characterised. Whilst silicon(IV) phthalocyanine bis(trihexylsilyoxide) is not a traditional LB film forming material, it can be made conducive to deposition by mixing with ideal film forming materials such as calixarenes. Surface pressure–area isotherms revealed an area per molecule of around 7.5 Å$^2$ which indicates that the silicon(IV) phthalocyanine bis(trihexylsilyoxide) forms multi-lamella stacks. Thermal optical polarised spectroscopy revealed the formation of brightly coloured mesophases in films. DSC showed the presence of an irreversible A phase and a reversible T phase.

## 1. Introduction

Phthalocyanines (Pc) are synthetic macrocycles which are related to por-phyrins. They are brightly coloured materials used in dyes and inks [1]. They are simple to synthesise, are highly stable and have strong $\pi$–$\pi^*$ transitions in the visible region. Phthalocyanine derivatives absorb between 600 and 700 nm where light penetrates human tissue effectively and Pcs are easily purified [2]. Their strong absorption in the red (Q-band) overlaps the region of maximum light penetration in tissues thus making them ideal candidates for photodynamic therapy (PDT) [3]. Several silicon phthalocyanines are being researched for photodynamic tumour therapy [4,5] due to their intense absorption in the visible region, high efficiency to generate reactive oxygen species (like singlet oxygen) and low dark toxicity [6]. Phthalocyanine films can be produced by several methods, like spin coating, vacuum sublimation and Langmuir–Blodgett techniques. LB films are highly ordered films and one can make multilayer structures with varying layer composition that can be deposited on a variety of substrates [7]. Due to hydrophobic interactions, stacking of Pcs in aqueous media is particularly strong [8]. Not much research has been carried out on mesophase formation of Pcs, especially in LB films. This work endeavours to focus on the thermal optical polarised spectroscopy studies (mesophase formation) of LB films of Pc dyes which have not been studied in detail before, according to the authors knowledge.

## 2. Experimental

A silicon phthalocyanine purchased from Sigma–Aldrich was the material used. Silicon(IV) phthalocyanine bis(trihexylsilyoxide), $C_{68}H_{94}N_8O_2Si_3$ ($Si_4Pc$; Fig. 1) has a $M_r$ of 1139.78. Surface pressure–area isotherms for $Si_4Pc$ were studied in a clean room environment at room temperature of 20 °C using a 102 M model Nima trough. Deionised pure water from an Elga Purelab water purifier was used as the subphase. Chloroform (Aldrich) was used as the solvent. The $Si_4Pc$ was dispensed from a 100 μl Hamilton syringe drop by drop onto the water subphase. Deposition was carried out on clean glass slides (which were rendered hydrophobic by pretreating them with HMDS) using the Langmuir–Blodgett method which involved vertical dipping of the substrate through the monolayer. A Joyce–Loebl model trough (Mini Trough) was used for deposition. A deposition pressure of 20 mN/m was used and the deposition speed was maintained at 20 mm/min. The compression rate was 100 mm/sec. UV–visible solution spectroscopy for different concentrations was carried out using an Ocean Optics Spectrometer (World Precision Instruments) and similarly solid state spectra studies were

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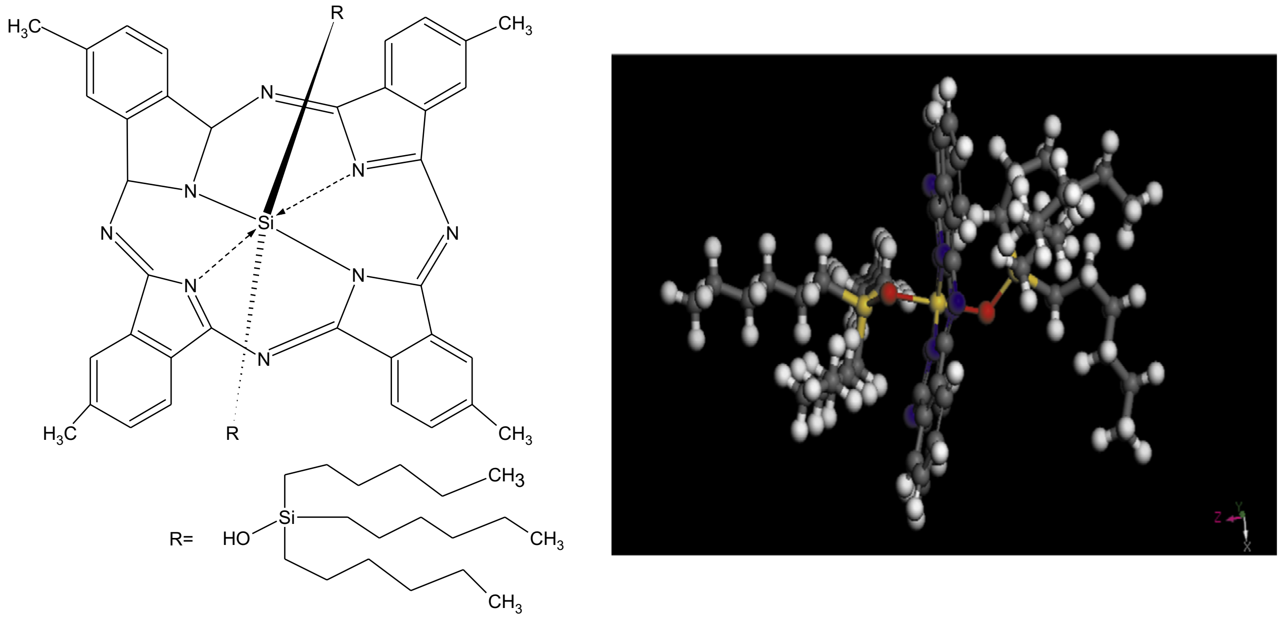

**Fig. 1.** Structure of a $Si_4Pc$ molecule.

recorded on a Spectromate spectrophotometer (World Precision Instruments). Thermal UV–visible spectroscopy was carried out using an FP80 hot stage and the above mentioned Spectromate Spectrophotometer. An ellipsometer with red light wavelength (633 nm) was used to determine the thickness of the films. The angle at which light was incident on the sample was 70° and silicon wafers were used as substrates. Optical polarised spectroscopy was carried out on different $Si_4Pc$ samples. The slides were placed on the hot stage (FP80) and the video image was captured for required temperatures. Heating and cooling images were recorded. Thermal optical polarised spectroscopy was carried out on the series of materials from temperatures ranging from room temperature to 200 °C. The hot stage was rigged to a spectrometer and the spectrum was recorded. The glass slide was placed on the hot stage (FP40) and the temperature values were programmed every 10 °C while the UV–visible spectra were monitored on the Ocean Optics apparatus. The optical polarised spectroscope also uses a hot stage in conjunction with the polarising microscope. The microscope is fitted with a camera in order to capture the images which are then obtainable via the "studio capture" software. The optical polarised spectroscopy kit used comprised of an Olympus BH2 polarising microscope with a Mettler FP52 and FP82 heating stage and controller and a JVC TK-C1481 colour video camera using Mettler Studio Capture Software, respectively. The Differential Scanning Calorimetry (DSC) unit used was a Perkin Elmer DSC7 with Pyris software and calibrated with indium. A Helium–Cadmium laser with excitation wavelength of 442 nm was used for fluorescence measurements.

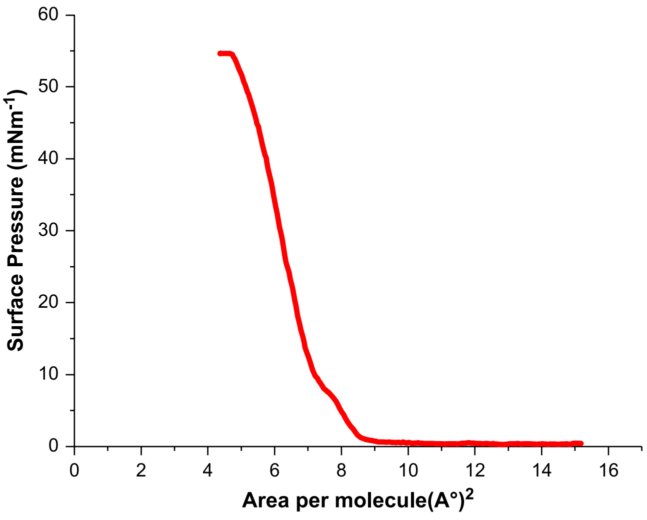

**Fig. 2.** Surface pressure–area isotherm of $Si_4Pc$-calixarene mixture (100:1).

## 3. Results and discussions

### 3.1. *Langmuir–Blodgett films – surface pressure–area isotherms*

$Si_4Pc$ is dissolved in chloroform and gives a dark blue solution. $Si_4Pc$ is not a very stable Langmuir material. When the film is spread on the subphase, it tends to form domains. The morphologies of silicon based Pcs in LB form were analysed using atomic force microscopy and it was shown that domains of dye molecules were formed on the respective LB films. Besides, different Pc dyes gave different morphology domains whose features were dependent on their structures as well as dipping conditions [9]. Pcs with butoxy groups are interesting because this substituent is long enough to yield good solubilities of MPcs in organic solvents, but not too long to avoid steric hindrance by interaction of reactants with the Pcs [10].

The very first time the material was spread on the subphase, it did give a non-collapsible layer, but it could never be reproduced. However, if a minuscule amount of calixarene was added, it remained stable and a layer could be produced. Richardson et al. in their studies have shown calixarene to be an ideal LB material and mixtures with calixarenes have proved to form good LB films [11–13]. Hence calix[8]arene was used to enhance the film stability

**Table 1**
Thickness results for the Pcs using Ellipsometry

| LB Film | 1Layer (nm) | 5Layer (nm) |
|---|---|---|
| $Si_4Pc$ | 12.8 | 91 |

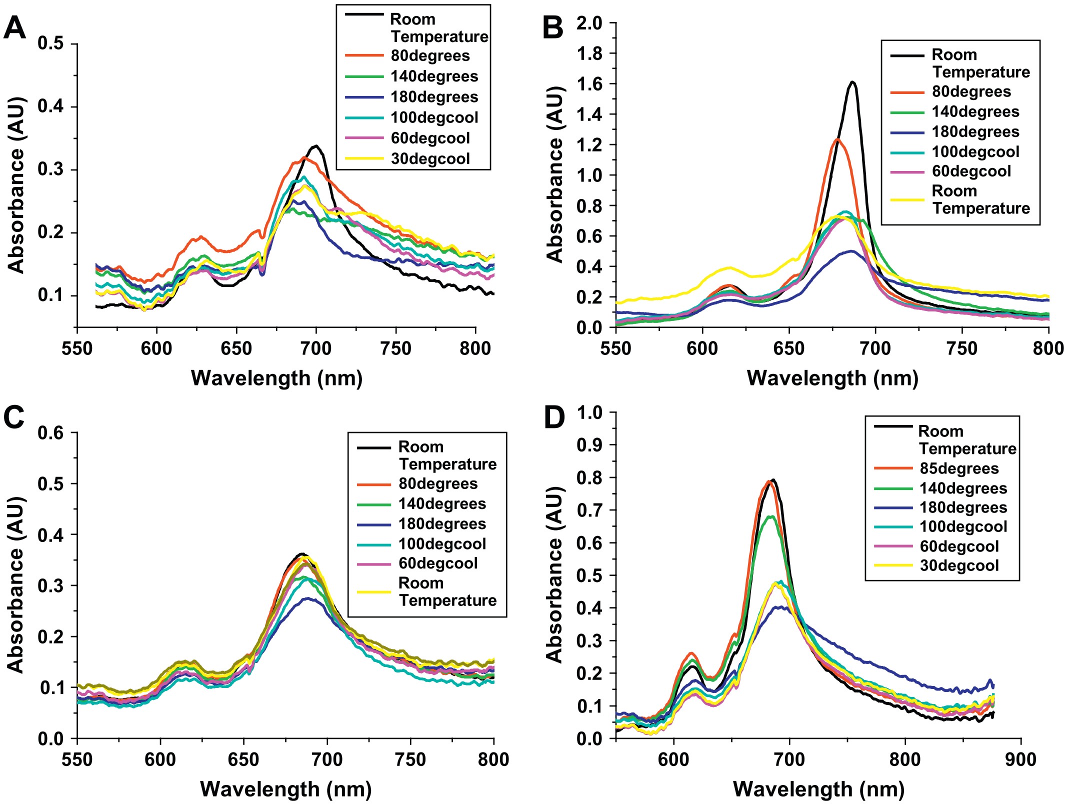

**Fig. 3.** Thermal UV–visible spectroscopy of (A) 50Pc:1calixarene; (B) 2Pc:1calixarene; (C) 10Pc:1calixarene; (D) 100Pc:1calixarene at the relevant temperatures.

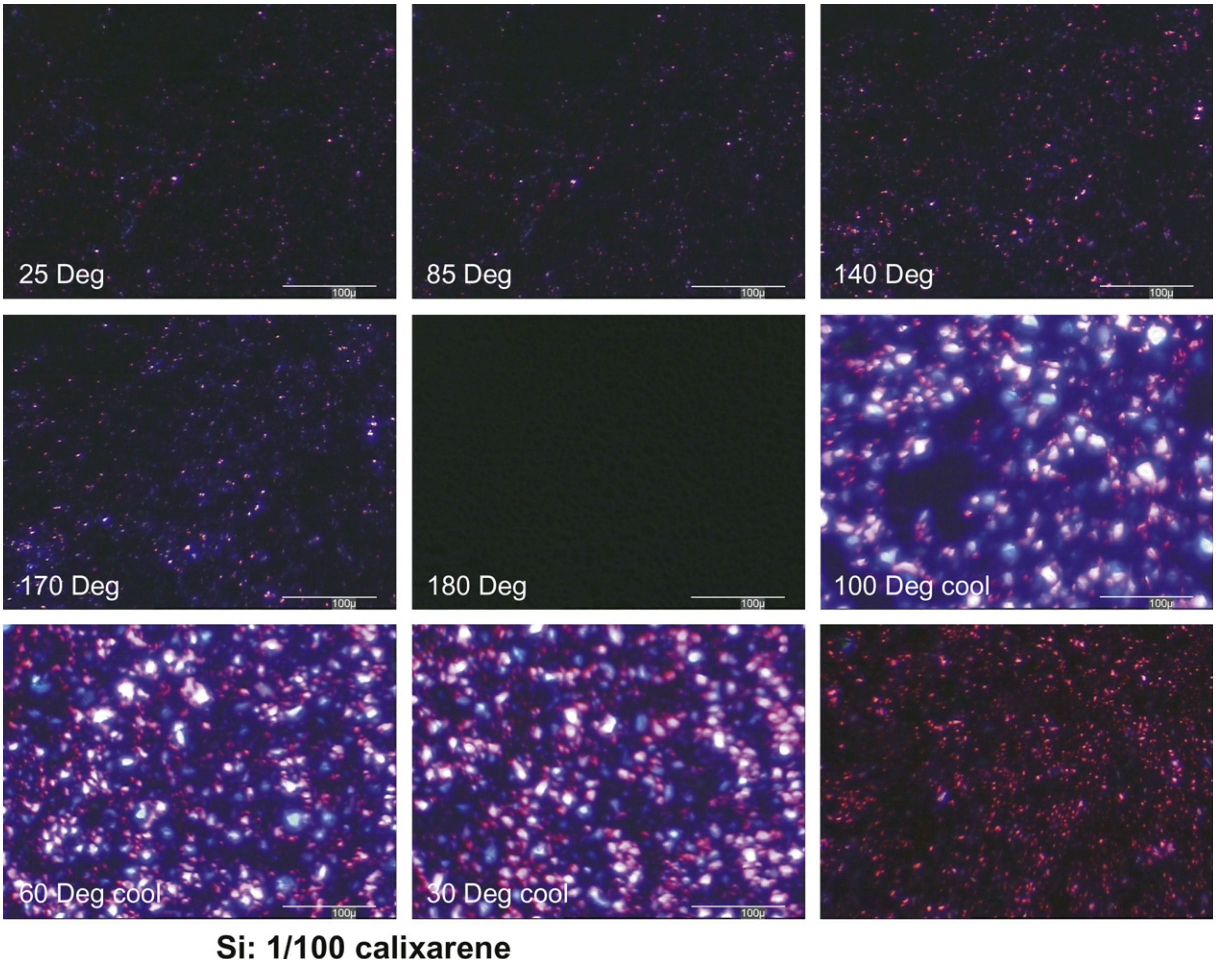

**Fig. 4.** Optical polarised spectroscopy of $100Si_4Pc$:1calixarene five layer film.

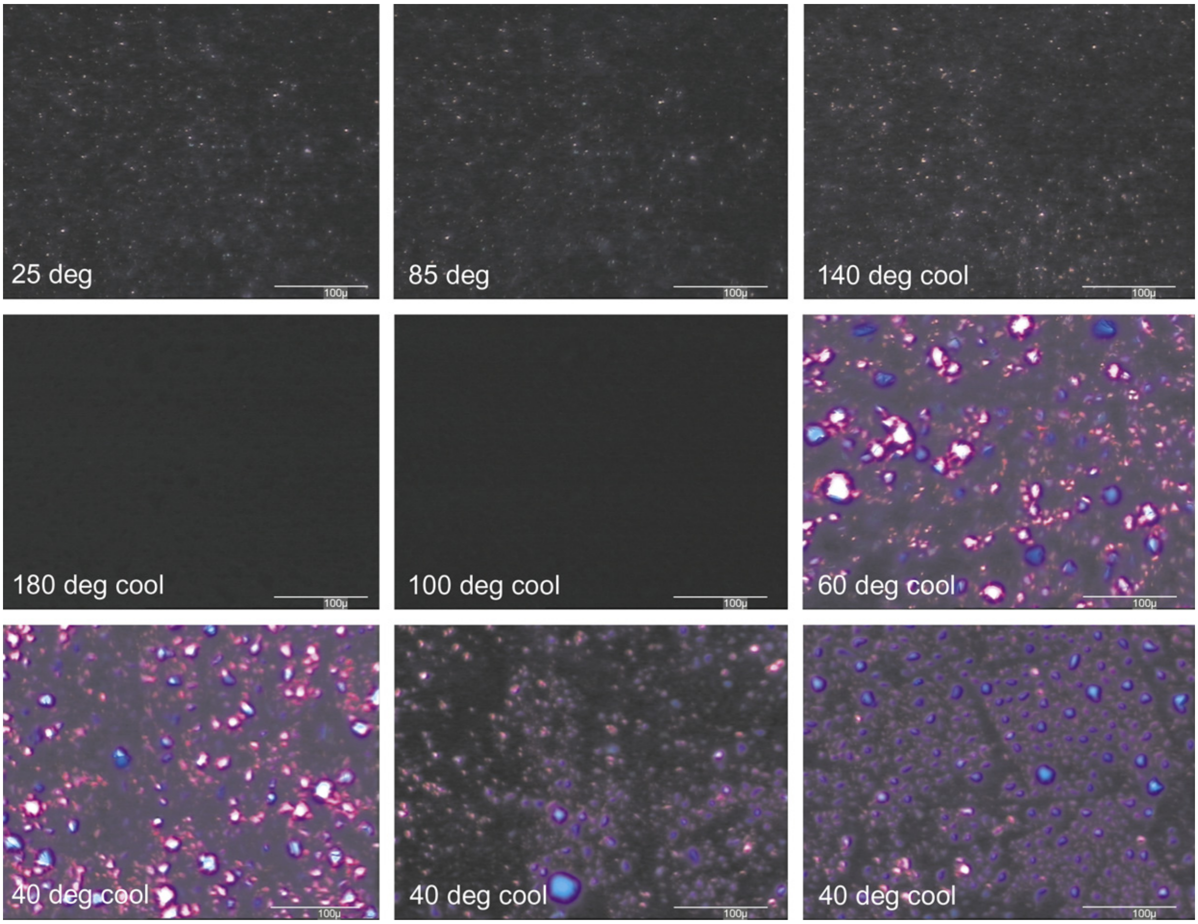

**Fig. 5.** Optical polarised spectroscopy of 50$Si_4Pc$:1calixarene five layer film.

of the traditional non-LB material, $Si_4Pc$. The surface pressure–area isotherm was plotted as seen in Fig. 2. The limiting area per molecule for the $Si_4Pc$ is 7.5 $Å^2$ which is quite striking. This low value for the molecular area is an indication that the $Si_4Pc$ forms stacks and minimise their spreading area. The slides prepared with $Si_4Pc$ and mixtures of calixarenes were bright blue in colour and then the colour began to lighten as the concentration of calixarene was increased. Calixarene was mixed in varied ratios, namely, $Si_4Pc$:calixarene, 100:1, 50:1,10:1 and 2:1, respectively. As the concentration of calixarene in the mixture was increased, the Langmuir film was observed to become quite stable.

The flexible alkyl chains with appropriate lengths prevent the monolayers from being too rigid and enable them to flow smoothly during the dipping process, thus giving high in-plane alignment of the stacking axes. On the other hand, longer alkyl chains are less flexible because of greater mutual interactions, preventing the formation of high in-plane ordering. Also, too short alkyl chains, may not give sufficient fluidity to the monolayer, raising some difficulty in the deposition [14]. Also Mohammed et al. mention that the combination of flexible alkyl moieties and hydrophilic groups on a highly fixed Pc ring is a very important prerequisite to achieve a preferential orientation of the planar macrocyclic compound on the water surface and, after transfer, on the substrate too. Furthermore, films were noted to be stable but consisted of more than one single layer [15]. Ellipsometry measurements were undertaken on silicon substrates ($SiO_2$) whose thickness was found to be 22 Å.

Table 1 gives the layer thickness for the Pc LB films. According to the theoretical calculations, the molecular area of $Si_4Pc = 2.1$ nm. This implies that Pcs deposit in multilayers and probably form stacks, thereby indicating the deposition qualities of the LB films. Though, experimentally we have tried to show that Pcs deposit in multilayers through the thickness calculations, rigorous transfer ratio studies need to be carried out. The onus of this study was to show that appreciable films of $Si_4Pc$ could be deposited and their thermal properties could thereby be studied.

## 4. Silicon phthalocyanines

Silicon phthalocyanine research has been carried out by Bryce et al. [16]. The axial ligands are very effective in sterically isolating the chromophoric Pc rings, by preventing intermolecular interactions between the macrocycles. The presence of the lighter Si atom in the macrocycle leads to lower rates of intersystem crossing (ISC) than those observed in other metallo-Pcs, e.g. zinc derivatives [16]. Hua et al. in their paper, report blue luminescence produced in a metal–insulator–semiconductor (MIS) structure which constituted of a Si Pc deposited as an LB film on a substrate on which high quality ZnSe had been grown by metal organic chemical vapour deposition (MOCVD). The LB layer of the Si Pc was instrumental in producing this peculiar luminescence [17]. Also silicon phthalocyanine oligomers were synthesised as potential templates for organising other electroactive monomers. Syntheses of such LB films are not only exploited for their potential anisotropic conductive properties but also their unique orientational properties can be used to organise other electroactive monomers [18].

### 4.1. Thermal UV–visible spectroscopy

LB films were prepared with various proportions, namely in proportions of $Si_4Pc$:calixarene, 100:1, 50:1, 10:1 and 2:1 ratios,

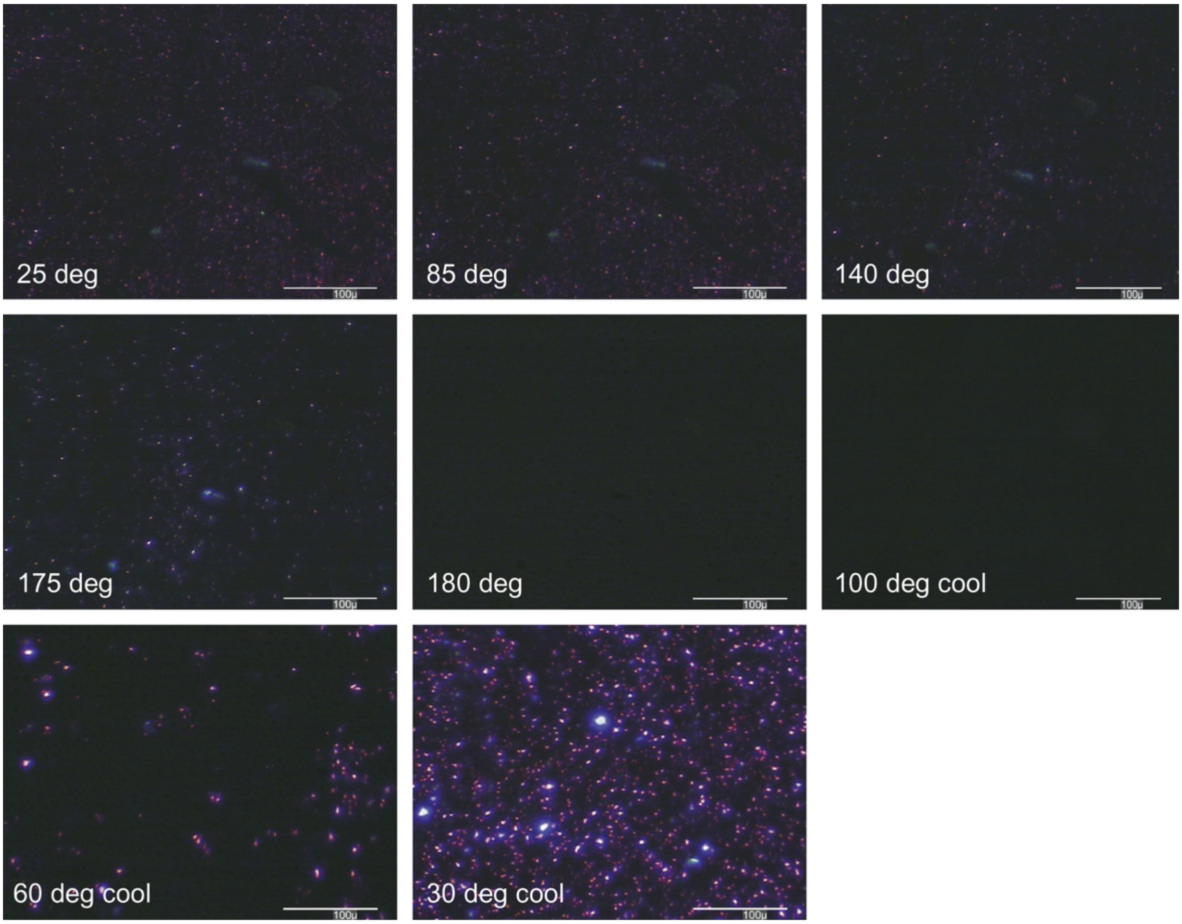

**Fig. 6.** Optical polarised spectroscopy of 10Si$_4$Pc:1calixarene five layer film.

respectively. The Pc was very stable and did not sublime. The UV–visible spectroscopy was undertaken at various different temperatures. Fig. 3 shows the thermal optical spectra for LB films of Si$_4$Pc. The thermal optical spectroscopy shows the dynamics of the spectra when the temperature is raised to 180 °C and then cooled down to room temperature. The process is irreversible as it brings about a change in the structural arrangement of the Pc on the film. Tri and tetra substituted Pcs frequently deposit to form fully, or near fully, cofacial columnar stacks of molecules. These give rise to a blue shift of the visible region absorption band relative to the solution phase spectrum. There is thermally induced reorganisation of the molecular assemblies [19].

### 4.2. *Phthalocyanine mesophases: optical polarised spectroscopy*

Optical polarised microscopy of Si$_4$Pc gives very interesting results. The LB films when heated, show characteristic images as seen in Figs. 4–7. Fig. 4 has a minimum amount of calixarene and is reflective of the actual Si$_4$Pc mesophase. Fig. 5 is not much different from Fig. 4. As the concentration of calixarene increases, as seen in Figs. 6 and 7, the mesophases become less intense. Little work has been done on the mesomorphic phases pertaining to LB films. If the films are reheated and recooled, the image structure remains the same. There is no increase in brightness. It retains the same texture that was conferred during the first cooling. So it is obvious that there is a structural rearrangement with increase in temperature in the first heating cycle which is irreversible.

### 4.3. *Differential scanning calorimetry*

The differential scanning calorimetry of Si$_4$Pc was undertaken as seen in Fig. 8. The sample was scanned in two cycles of each heating and cooling. The clearing point temperature was approximately 175 °C. Two phase changes are visible: A and T phases, of which A phase is irreversible. Peaks are seen at 85 and 175 °C whilst the sample is heated. However, when the sample is reheated, the peak at 85 °C is absent indicating the presence of an irreversible phase. The recrystallisation peak is seen at 140 °C. There is a change in the shape in this peak. On second heating this peak is longer and sharper indicating some kind of reorganisation. So DSC studies on Si$_4$Pc show a transition at 85 °C which is in accordance with the thermal optical spectroscopy results. In Fig. 4, there is a shift observed at approximately 80 °C temperature from the room temperature peak. However, the effects in the optical polarised spectroscopy profiles are more subtle at these temperatures and more detailed temperature studies need to be carried out.

## 5. Fluorescence studies

Singlet molecular oxygen, ($^1O_2$), is a metastable excited state of ground state molecular oxygen and a highly reactive form of molecular oxygen [20]. The production of the excited state of molecular oxygen $O_2$ ($^1\Delta_g$) involves energy transfer from an electronically excited triplet state of molecular oxygen of sensitiser molecule S to the ground state of molecular oxygen, $O_2$ ($^3\sum^-{}_g$). Pcs have absorption spectra that show maxima in the red spectral region [21].

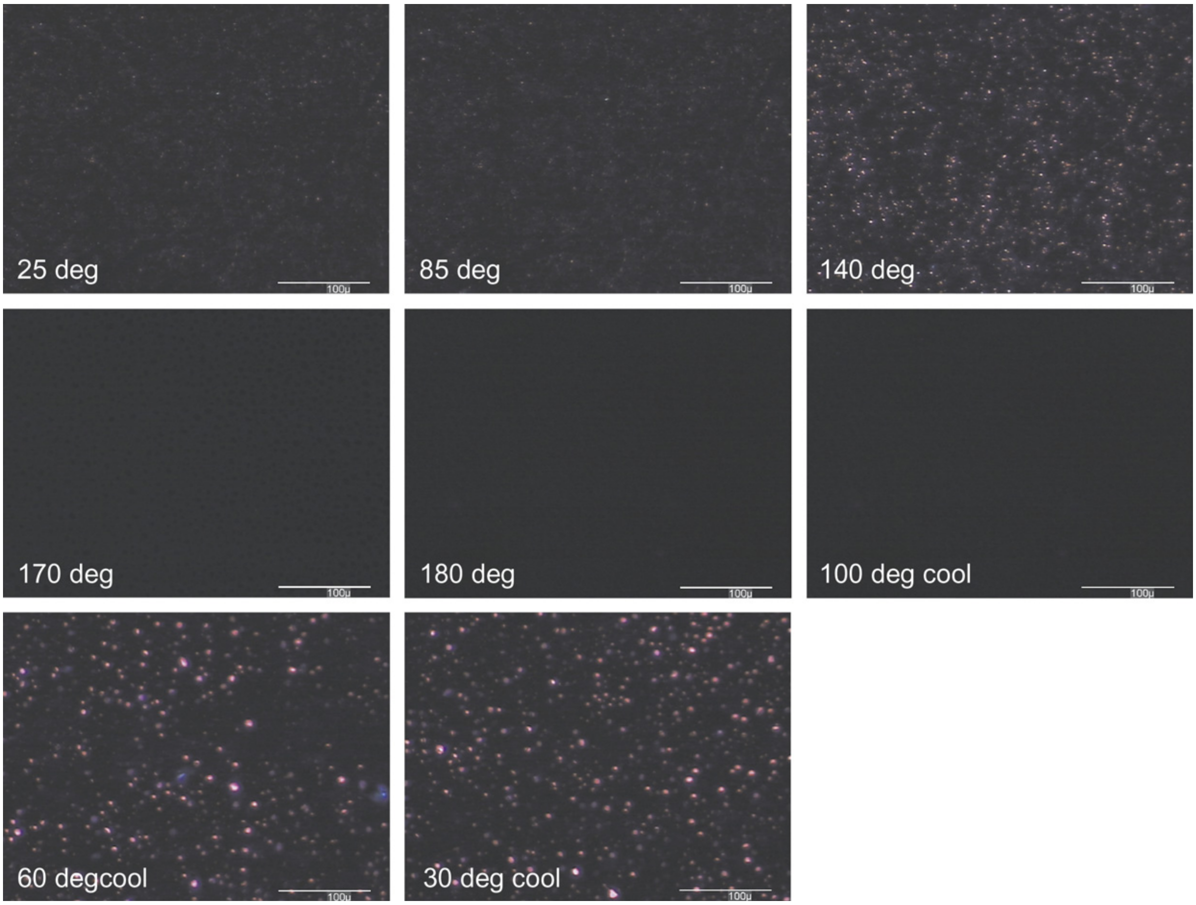

**Fig. 7.** Optical polarised spectroscopy of $2Si_4Pc$:1calixarene five layer film.

The group IV metal Pcs are of particular interest for PDT partly because their axial ligands can be varied and hence their properties can be tuned. Excitation in the absorption region of a Pc yields the excited singlet state ($^1PS^*$) and then by intersystem crossing (ISC), the excited triplet state ($^3PS^*$). Then the spin allowed triplet–singlet energy transfer from $^3PS^*$ to triplet oxygen ($^3O_2$, $^3\sum^-{}_g$) gives singlet oxygen ($^1O_2$, $^1\Delta_g$).

Singlet oxygen plays a key role in photooxidation reactions. Thermodynamically, the energy transfer from $^3PS^*$ to $^3O_2$ is possible with phthalocyanines [10].

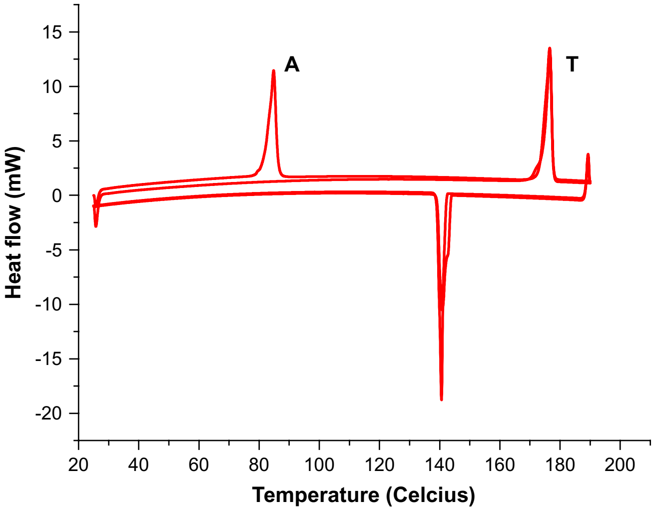

**Fig. 8.** DSC results of $Si_4Pc$.

### 5.1. *Interface dynamics for fluorescence*

$Si_4Pc$ interacts with atmospheric oxygen and hence the fluorescence dynamics can be applied to the Pc. The nature of the environment at the gas/solid interface affects the spectral pattern of the ground state absorption of adsorbed molecules. The surface broadening of the absorption bands is a general observation which is interpreted as the consequence of the inhomogeneous environment of the adsorbed molecules. The role of surface oxygen seems to increase in aggregated samples. Another aspect of the photophysics and photochemistry of the organic molecule-$O_2$ system at the gas/solid interface is the generation of the singlet molecular oxygen followed by the reaction between the $^1O_2$ and organic molecule [22]. An important aspect of gas/solid interface is that the adsorption of organic molecules onto the solid surfaces may provide spatially restricted environments and inhomogeneous distribution of reactants as well as specific surface reactive sites giving an opportunity to promote selectively some processes with participation of particular intermediates which do not occur in solution [23].

### 5.2. *Discussion on fluorescence studies*

Solution fluorescence was carried out using the Ocean Optics apparatus using a red filter at 650 nm. Light was emitted by the $Si_4Pc$ as shown in Fig. 9. Photoluminescence studies undertaken on $Si_4Pc$-calixarene showed intense emission as seen in Fig. 10.

The fluorescence peak for the $Si_4Pc$-calixarene mixture is 785.96 nm. The peak is sharp with a satellite peak at 722 nm. In a study carried out by Anula et al. [24] on silicon Pcs, the axial ligands of the compounds investigated are tethered to the central silicon

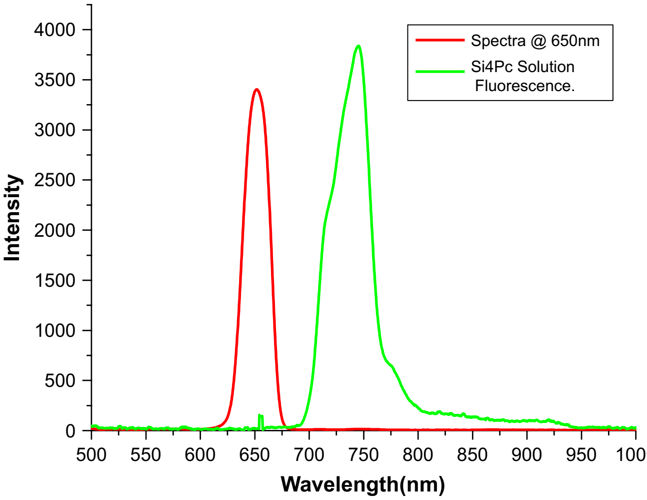

**Fig. 9.** $Si_4Pc$ solution excited at 650 nm showing fluorescence.

atom of the Pc π systems by linker chains of variable length (one to six $CH_2$ units). Thus upon photoexcitation, the $(^1\pi, \pi^*)$ state of the Pc residue and a probable (putative) quenching amine residue are in relative proximity because of the tether linking them. The tether is solely a σ-bonded skeleton and is therefore flexible, allowing a multiplicity of conformation states to be visited by the electron donor entity (the amine) and the $S_1$ state of the π system (the putative acceptor). Thus the intrinsic structure of the molecule and the flexible nature of the linkers convey the possibility of an intramolecular charge transfer quenching process, perhaps via the formation of an intramolecular complex. This, in turn, depends critically on the chemical nature of the amine residues and on the length of the tether. To apply this theory to the $Si_4Pc$ mesophase formation is plausible. It is likely that there is a kind of interaction of the Pc with atmospheric oxygen and the nature of the interaction can be described as intramolecular charge transfer between tethered donor and acceptor moieties undergoing restricted diffusion through an ensemble of conformational states. In all probability, this charge transfer interaction involves a formation of an intramolecular complex which keeps shifting from different energy levels [24]. There is a strong indication of singlet oxygen presence in the $Si_4Pc$ complex. Future work will involve conducting experiments to detect the presence of singlet oxygen (flash photolysis experiments and IR spectroscopy in emission mode). Fluorescence lifetime measurements will also be carried out to determine lifetimes.

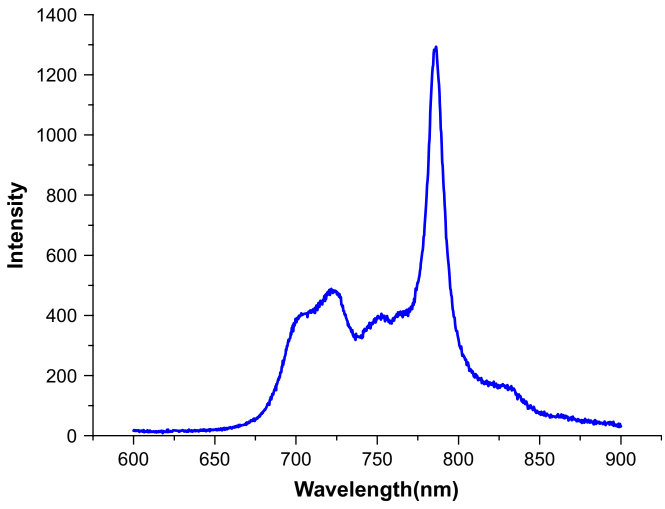

**Fig. 10.** Fluorescence measurements of $100Si_4Pc$:1calixarene five layer film at 442 nm.

## 6. Explanation of occurrence of phthalocyanine mesophases

The fluorescence measurements performed on the Pcs offer a strong indication of the presence of the oxygen singlet state. Ground state oxygen has a triplet state which is the stable state (two unpaired electrons with parallel spins). Addition of energy can activate the triplet state of oxygen and it can be transformed into the singlet state which is a reactive species. Singlet oxygen state constitutes a pair of opposite spins, which is highly reactive. When the Pc is heated, the adsorbed oxygen becomes excited and goes into the singlet state. And when singlet oxygen relaxation takes place, this energy is transferred to the Pc which in turn gives rise to the unique textures in the visible region, when the material is allowed to cool. Formation and decay of singlet oxygen gives rise to a red glow (red chemiluminescence) [25]. The $Si_4Pc$ interacts with the oxygen, more strongly at higher temperature. Since Pc molecules sit in stacks, there are oxygen excitations, which give rise to such phases. It is possible that heating effects also influence the orientation of the $Si_4Pc$ molecules on the substrate, thus enabling the singlet oxygen to interact more actively with the $Si_4Pc$. There is structural reorganisation taking place after thermal exposure. The thermal effects are irreversible, as also indicated in the DSC measurements. This implies that a structural change has taken place. Also when thermal optical spectroscopy was repeated on the sample, it does not show any intense mesophase formation. There is a strong case that the presence of singlet oxygen may instigate the formation of mesophases as there is an indication of emission as well. Work is ongoing to determine the reasons for such occurrences.

## 7. Conclusions

Dyes like $Si_4Pc$, which are not traditional LB forming materials can form monolayers conducive to deposition by mixing them with ideal LB film forming materials are discussed. The highlight of this study was the formation of brightly coloured mesophases during thermal optical polarised spectroscopy in LB films. There is molecular reorganisation taking place on exposure to heat. $Si_4Pc$ is unique in the sense that it shows two distinct phases, the irreversible A phase and the reversible T phase in the DSC scans of this material. Also, this Pc dye shows emission spectra. One of the plausible reasons for the formation of the mesophases is the probability of singlet oxygen interacting with the material giving rise to excitation in the visible region and when the films are heated, structural reorganisation takes place, which is irreversible. LB films of these Pcs open up a fascinating study on mesophase formation and between them, UV–visible spectroscopy, thermal polarised spectroscopy and differential scanning calorimetry show very good correlations. Future work will involve X-ray studies in order to determine how the orientations of the molecules on the LB film change with respect to exposure to temperature. In-depth fluorescence studies will be carried out by doing time resolved spectroscopy. The presence of singlet oxygen will also be investigated. To conclude, thermal studies of LB films of phthalocyanine dyes are a potential topic which shows interesting results.

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