

THE FINAL PROJECT REPORT FOR EUROPEAN SCIENCE FOUNDATION

PROGRAMME (ORGANISOLAR)

SELF-ASSEMBLING PHOTOVOLTAIC SYSTEMS INVOLVING LIQUID CRYSTALLINE

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PROJECT REPORT

Introduction

An approach to tuning the properties of materials is the blending of two different discotic compounds [1]. The mixing of two macromolecules that self-assemble into superstructures is complex, since additional interactions between the different components complicate the description of the system [2]. As illustrated in Figure 1, several different supramolecular assemblies can be formed in the mixture. For discotic molecules, which self-assemble in columnar super-structures by π stacking, this ranges from a heterogeneous phase to micro- and even nanoseparation.

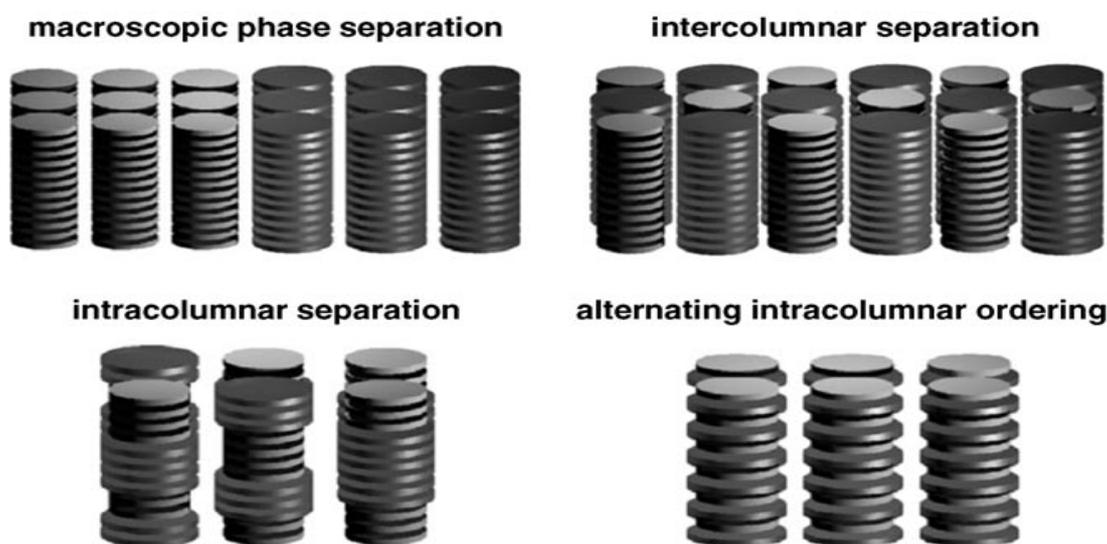


Figure 1. Different possible supramolecular organizations in a mixture of two discotic compounds with different molecular architectures.

π -Stacking is a powerful motif for self-assembly that is ubiquitous in nature and utilized extensively by synthetic chemists to engineer complex supramolecular architectures. Particularly in recent years, having been spurred on by the increasing technological promise of the π -stacks as conducting pathways in organic-based electronics [3]. Important targets include the understanding of the self-assembly of large disc molecules and improving device performance through 1) more specific assembly in solution, 2) further increasing the order in columnar mesophases, and 3) modifying the electronic properties of the discs, in particular, for better hole stabilization. Important targets include the understanding of the self-assembly of large disc molecules and improving device performance through 1)

more specific assembly in solution, 2) further increasing the order in columnar mesophases, and 3) modifying the electronic properties of the discs, in particular, for better hole stabilization.

The goal of our work is to prepare self-organized discotic liquid crystalline materials with using mesogen phthalocyanine derivative as electron donor (D) and mesogen perylene derivative as electron acceptor (A) for efficient charge transport in organic solar cells [4].

Purpose of the visit:

The aim of this short visit was to start a collaboration between the applicant group (Gebze group) and the host group of Prof. Mukundan Thelakkat (Bayreuth group). The main topic of this collaboration is to prepare self-organized discotic liquid crystalline materials with using mesogen phthalocyanine dyes as electron donor and mesogen perylene dyes as electron acceptor to improve device performance of solar cells.

Description of the work carried out during the visit:

In this study, we prepared highly soluble, liquid crystal tetra- and octasubstituted zinc and copper phthalocyanines and perylene derivative. The structures of the compounds were given in Figure 2. The liquid crystalline properties of the phthalocyanines and the perylene derivative were studied by polarizing optical microscopy and differential scanning calorimetry. All of the compounds exhibit thermotropic columnar mesophases. The optical and electrochemical properties of the dyes were also studied.

The mixtures of the Pc compound with the perylene derivative were prepared at different molar ratios. The thermal behaviour and optical properties of the blends were studied. Using the blends heterojunction solar cells were prepared on ITO, and analysed with I-V characteristics and morphological characterization using SEM of the cells were done.

μl pans. The differential scanning calorimeter system was calibrated using an indium standard under a nitrogen atmosphere.

Spin coated films: A solution of the material in CHCl_3 , *ca.* 1 ml typically containing 5 mg compound, was added via a glass pipette to a quartz slide revolving at 500 rev min^{-1} on a Headway Spinner. Spinning was continued for 20 s during which time the solvent had evaporated to generate a spin-coated film of the phthalocyanines.

The cyclic voltammetry measurements were carried out using a glassy carbon working electrode in a solution of carefully dried CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) at room temperature. The potentials were measured against Ag/AgNO_3 as the reference electrode and a platinum wire was used as the counter electrode. Each measurement was calibrated with the ferrocene/ferrocenium (Fc) redox system as internal standard. The HOMO and LUMO energy values of the compounds were determined from the first oxidation and the first reduction potentials (E_{ox1} and E_{red1}) respectively, by taking the value of -4.8 eV for the Fc with respect to zero vacuum level.

All SEM images were recorded on a Zeiss 1530 field emission scanning electron microscope (FESEM). The applied voltage was always between 1 kV. To increase the contrast and to improve the uniformity of the images, in some cases a thin layer of platinum (1 nm) was sputtered on the samples with a Bal-tec MED 010 machine under vacuum.

UV-Vis absorption spectroscopy of the compounds:

UV-Vis absorption spectra of the Pcs were measured in CHCl_3 using 6.10^{-6} M solutions. All spectra showed sharp peaks around 677-709 nm (Q band) and in the UV-region around 323-363 nm (Soret-band) originating from $\pi \rightarrow \pi^*$ transitions. Also, the Pcs exhibits the absorption in thin films. It is known that there are four general types of Pc arrangements in aggregates, which one be observed in spin coated films and these are cofacial (C: face-to-face), herringbone (H), edge-to-edge (E) and isolated (I) [5]. The cofacial arrangement of Pc molecules results in a blue-shifted Q-band. For the Pc compounds, Q bands of the spin-coated film are broad and shifted to a shorter wavelength, which indicates that phthalocyanine moieties are in an aggregated form and in a cofacial arrangement (Figure 3).

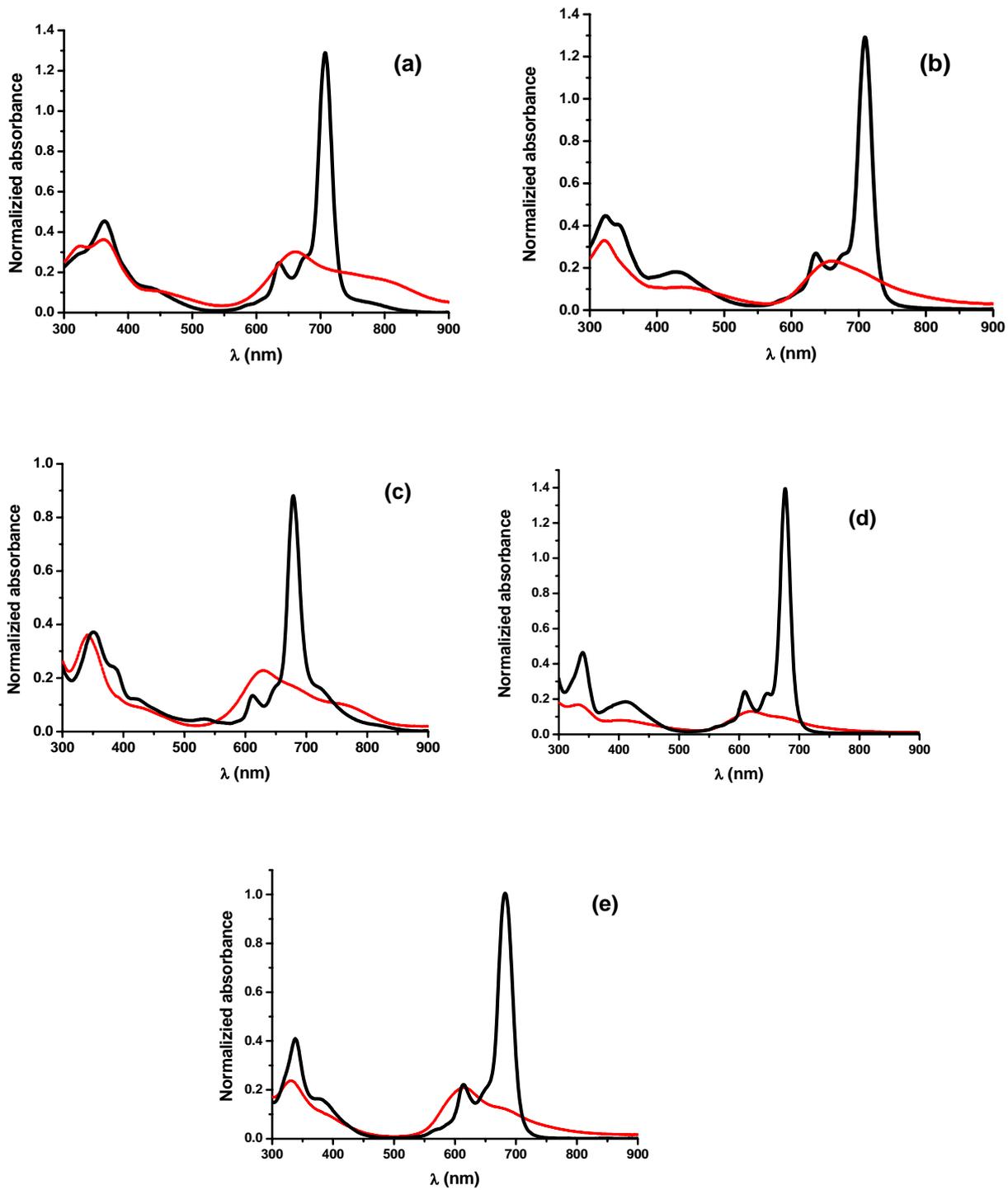


Figure 3. UV-visible absorption spectra in CHCl_3 (black line) and spin-coating film (red line): (a) **Pc1**, (b) **Pc2**, (c) **Pc3**, (d) **Pc4**, (e) **Pc5**.

Mesomorphic properties the Pcs and the perylene:

The mesomorphic behaviour of **Pc1-5 and the perylene** have been investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

All of the Pcs and the perylene display thermotropic mesophase. For **Pc3** and **Pc4**, the exact complete clearing of the mesophase could not be observed in POM as the substances started to decompose at ~ 300 °C, which is additionally verified by thermogravimetric analysis. The compounds show fan-like and dendritic and textures above 130 °C which are characteristic of columnar hexagonal mesophases. On cooling **Pc 1-5** to room temperature, the optical textures of the mesophases are retained. The absence of crystallization can be explained that the compounds are liquid crystalline in wide temperature range including room temperature.

The DSC curves for **Pc1**, **Pc2** and **Pc5** obtained on heating and cooling display one broad, small peak, corresponding to the transitions from discotic mesophases to isotropic liquid phases. No additional peak is observed for these compounds in DSC. The transition to mesophase and from mesophase to partial isotropic state could be seen only POM for **Pc3** and **Pc4**. The **Pc3** and **Pc4** derivative did not give complete clearing to isotropic phase until 300 °C. The thermal stability of the Pcs has been investigated by thermal gravimetric analysis (TGA). The decomposition of the compounds occur above 300°C. The DSC curve of the perylene display three peak, corresponding to the crystal transitions, melting point and clearing point, respectively. Table 2 summarizes the thermal data and Figure 4 shows the textures observed in POM under crossed polarizers.

Table 2. Phase transition temperatures(°C) from the 2nd heating run determined by DSC and mesomorphic transition temperature from POM.

Compound	T/ °C	
	Col _h \longrightarrow I ^a	Col _h \longrightarrow I ^b
Pc1	203	211
Pc2	257	290
Pc3	Not observed	Not observed
Pc4	Not observed	Not observed
Pc5	188	205
Perylene	144	150

^adata determined by DSC. ^bdata determined by POM.

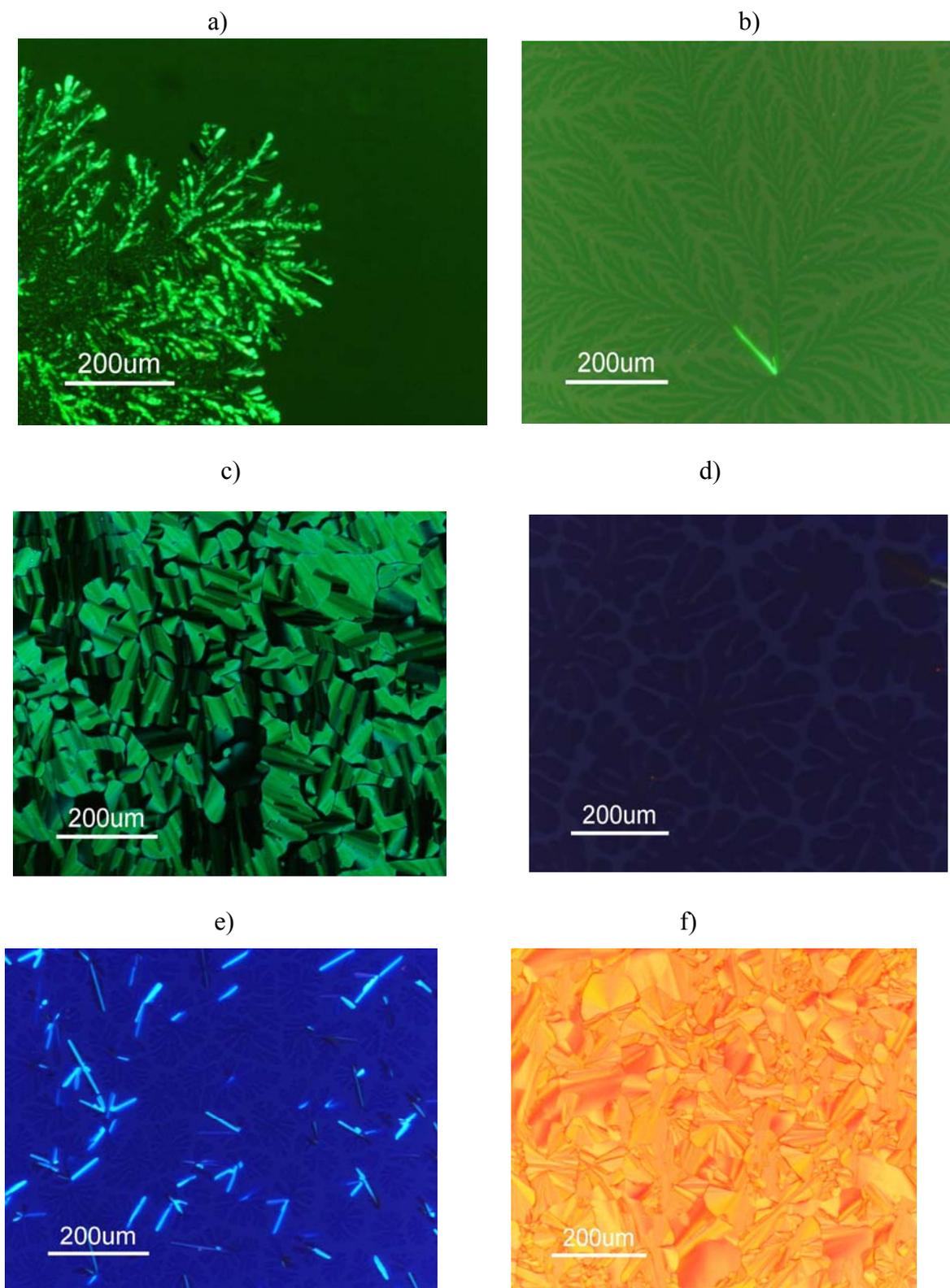


Figure 4. Photomicrographs of typical thermotropic mesophases of the Pcs observed through crossed polarizers: a) dendritic texture of Col_h phase of **Pc1** at 140 °C b) dendritic texture of Col_h phase of **Pc2** at 245 °C c) fan-like texture of Col_h phase of **Pc3** at 270 °C d) dendritic texture of Col_h phase of **Pc4** at 280 °C e) dendritic texture of Col_h phase of **Pc5** at 151 °C f) fine-like texture of Col_h phase of **the perylene** at 138 °C.

Cyclic Voltametry of the Pcs:

The electrochemical stability and reversibility of the redox process of all Pcs were studied using cyclic voltametry (CV) in solution, using a glassy carbon working electrode in a three-electrode assembly and potentiostat set up. The Ag / Ag⁺ was used as reference electrode and dyes were analyzed in dry CH₂Cl₂ containing Bu₄NPF₆ as conducting salt. Each measurement was calibrated with ferrocene redox system as standard and the HOMO/LUMO values were calculated from the HOMO of Fc at -4.8 eV [6].

The compounds exhibited similar electrochemical behaviour and all compounds show two reversible reduction steps. Table 3 summarizes the measured potentials and the determined HOMO and LUMO levels.

Table 3. Electrochemical properties of the phthalocyanine derivatives **Pc1-Pc5**

Compound	E _{red1} vs. Fc/V	LUMO /eV	E _{oxd1} vs. Fc/V	HOMO /eV	E _g ^{ec} /eV	E _g ^{opt} /eV
Pc1	-1,469	3,411	0,252	5,132	1,721	1.88
Pc2	-1,561	3,239	0,216	5,016	1,777	1.87
Pc3	-1,296	3,504	-	-	-	1.95
Pc4	-1,374	3,426	-	-	-	1.96
Pc5	-1,324	3,476	-	-	-	1.94

E_{ox1} and E_{red1}- first oxidation and reduction potentials, respectively.

E_g^{ec}-electrochemical band gap taken as the difference between HOMO/LUMO values. Fc: Ferrocene

As expected, in all of the Pc compounds, the reduction and oxidation potentials do not vary much. The HOMO values are about 5 eV and LUMO values are around 3.4-3.5 eV. This is in full agreement with reported values in literature [7]. The oxidation peaks could not be clearly observed for both **Pc3**, **Pc4** and **Pc5** under our measuring conditions. This indicates that the oxidation potentials may be shifted to higher potentials, that lie outside the measurable region in our set up. The favourable HOMO values around 5 eV and absorption in the long wavelength region up to 700 nm make these compounds highly favourable materials for application in solar cells, both as dyes and hole conductors.

Blend preparation:

The Blends of the Pc compound with the perylene derivative were prepared at different molar ratios [1:3 (**Blend 1**), 1:1 (**Blend 2**) and 3:1 (**Blend 3**)]. **Pc5** and the **perylene derivatives** were solved in benzene separately. The mixture was stirred to obtain homogenize solution in benzene and cooled in liquid nitrogen. After the cooling step, the solvent was removed with vacuum distillation ($3 \cdot 10^{-3}$ mbar).

UV-Vis absorption spectroscopy of the Blend films:

In UV-visible absorption spectra, the spin-coating films of the blends were all highly transparent and exhibited a range of coloration from red to blue, characteristic of charge-transfer interactions (Figure 5).

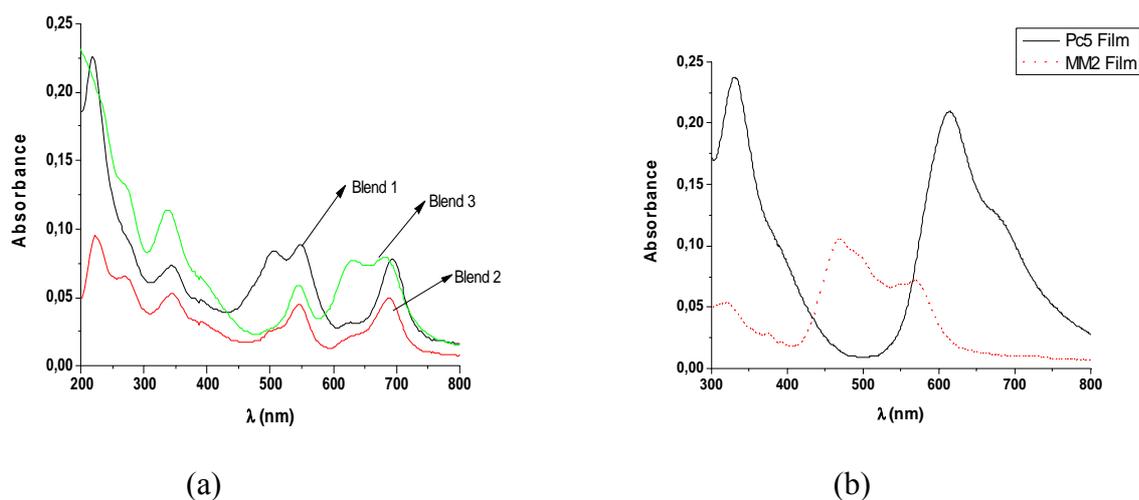


Figure 5. UV-visible absorption spectra of the spin-coating films (a) Blend 1, Blend 2 and Blend 3 (b) Pc5 and the perylene derivative.

Mesomorphic properties the Blends:

The investigation of the thermal behaviour by POM and DSC that all prepared mixtures formed a macroscopic, homogenous phase. Table 4 summarizes the thermal data. The DSC curves for the Blends obtained on heating and cooling display one broad, small peak, corresponding to the transitions from discotic mesophases to isotropic liquid phases. No additional peak is observed for these compounds in DSC.

The new supramolecular structure in the blends significantly affected the thermal behaviour and

the morphology. When mixtures of **Pc5** and the perylene were cooled down from the isotropic phase between two glass slides, a homogenous film was obtained; this would be characteristic for a homeotropic phase (Figure 6). All blends revealed a homeotropic alignment suggesting an identical intracolumnar packing of the two discotics.

Table 4. Phase transition temperatures(°C) from the 2nd heating run determined by DSC and mesomorphic transition temperature from POM.

Compound	T/ °C	
	Col _h → I ^a	Col _h → I ^b
Blend 1	231	270
Blend 2	284	291
Blend 3	277	283

^adata determined by DSC. ^bdata determined by POM.

According to POM and DSC data, the isotropic transition temperatures are shifted to higher temperatures as compared to pure **Pc5** and the perylene consist of 188 and 144 °C, respectively (Table 4). This effect was observed early for the other discotic compounds and is due to an additional charge-transfer interaction and promotion of ordered supersstructures in donor-acceptor mixtures [8, 9].

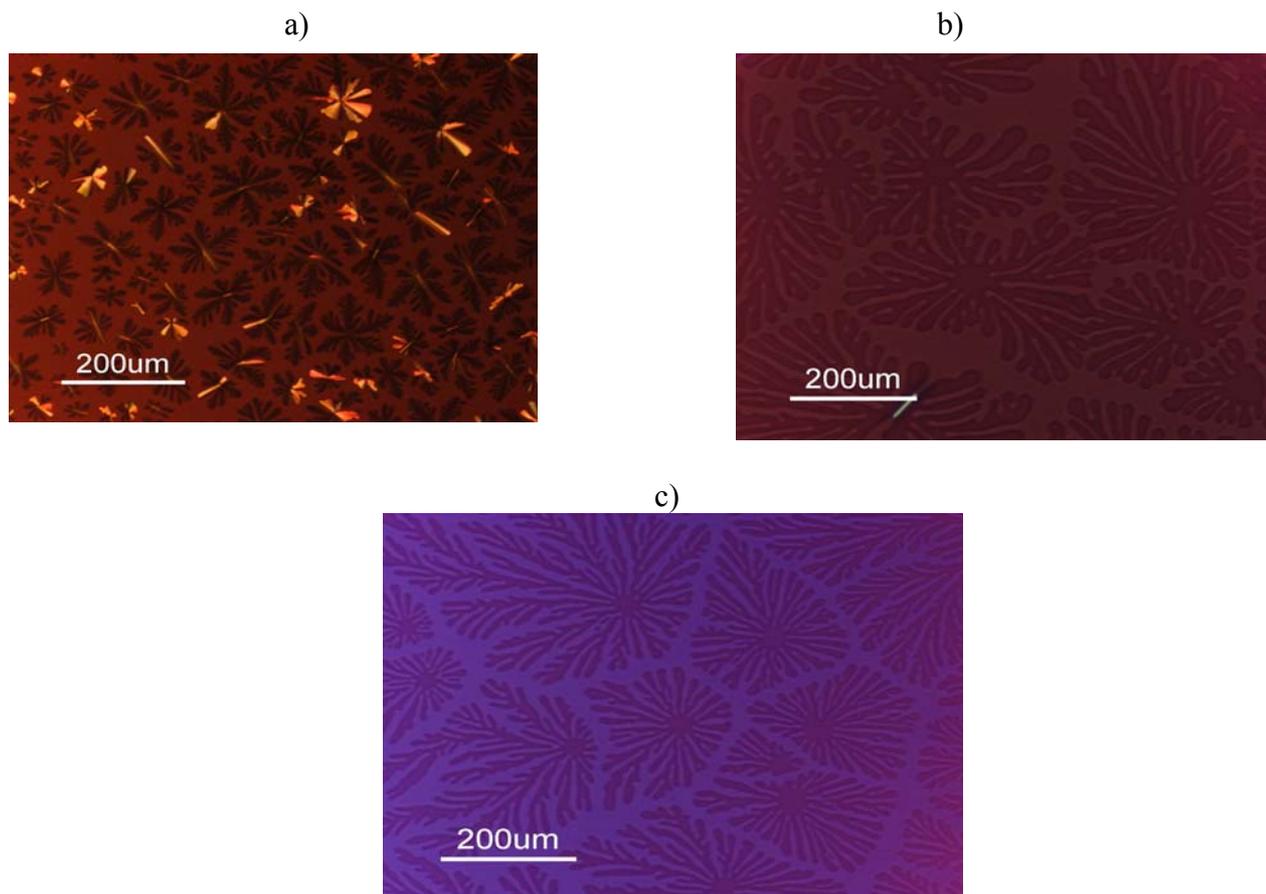


Figure 6. Photomicrographs of typical thermotropic mesophases of the Blends observed through crossed polarizers: a) dendritic texture of Col_h phase of **Blend 1** at 221 °C b) dendritic texture of Col_h phase of **Blend 2** at 270 °C c) dendritic texture of Col_h phase of **Blend 3** at 265 °C.

Solar cell preparation and characterization:

The ITO coated glass sheets were first cut into quadratic plates of 2.5 cm width. Approximately 15 mm need to be covered accurately with a Tesa® Tape. On the remaining part a thin layer of Zn powder is spread and the etch process is initiated by dropping 15 % HCl slowly upon. After a reaction time of at least 2 minutes the procedure is repeated, ensuring an efficient etching. To wipe off the residue the plates were washed thoroughly under running water. The final cleaning is subdivided into several steps, guaranteeing the complete removal of organic and inorganic impurities. For this purpose all samples were sonicated in several solvents, according the following procedure:

1. 10 min in Acetone
2. 10 min in Ethanol
3. 20 min in 2 % Helmanex® solution
4. washing at least 10 times with demineralised water
5. 10 min in demineralised water
6. 10 min in Ethanol

For a dry and clean storage of the samples they were kept under vacuum.

For the preparation of the solar cells, pre-etched and cleaned ITO substrates with a sheet resistance of $10 \Omega/\square$ were used. A 30 nm thin layer of PEDOT:PSS (Aldrich, electronic grade) was deposited by spin-coating a 1:1 mixture of the filtered dispersion and deionized water at 2000 r/min. The active layer was obtained on top of this layer by spin-coating 0.5 wt.-% chloroform solutions of the block copolymers at 2000 r/min, resulting in 70 nm thin films then dried at 120 °C for 10 minutes. **Blend 1** solution was prepared in CHCl_3 . The concentrations were 8 mg/0.1 ml and 5mg/0.1 ml. The **Blend 1** solution were spin coated onto PEDOT:PSS coated substrates at 500 rev min^{-1} , resulting in 130 nm thin films. Al electrodes were evaporated at 10^{-6} mbar, the active area of a single device was 0.18 cm^2 . Figure 7 shows the scheme of prepared solar cells. *I-V*-characteristics were measured under a simulated AM 1.5 spectrum (77 mW/cm^2 , Oriel setup with 150 W xenon arc lamp and suitable filters) in a N_2 atmosphere. SEM images of the solar cells were recorded (Figure 8). The SEM image displays the layers of the cell and indicates that the aluminium layer is not smooth. In respect of *I-V* characteristic of the cells, the cells do not work (Figure 8) due to that the aluminium layer is roughness of aluminium layer.



Figure 7. The scheme of the solar cell

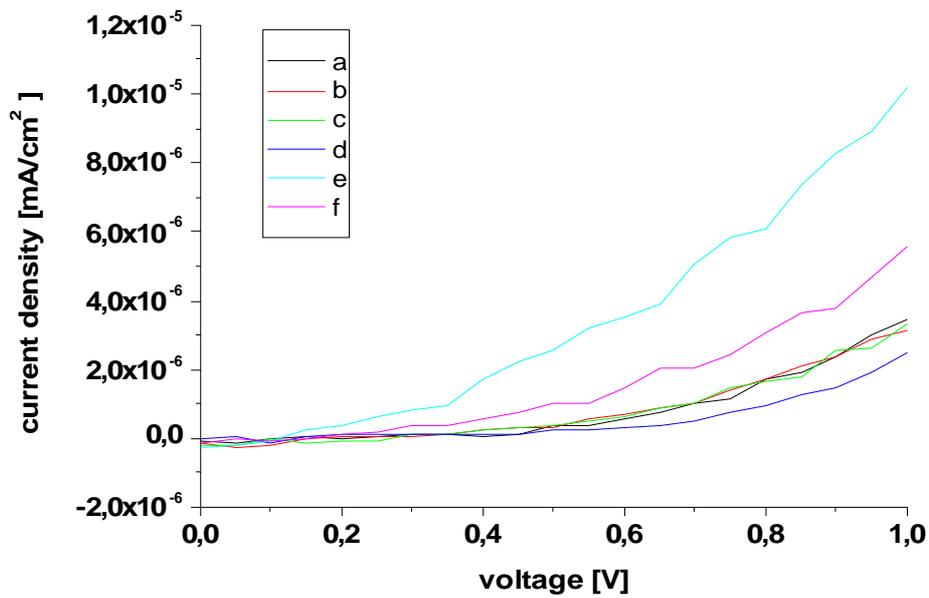


Figure 8. IV-characteristics of the solar cells (a) thickness of Blend 1:300 nm, annealing at 150 °C ; (b) thickness of Blend 1:300 nm, annealing at 90 °C; (c) thickness of Blend 1: 500 nm, annealing at room temperature; (d) thickness of Blend 1:300 nm annealing at room temperature; (e) thickness of Blend 1: 500 nm, annealing at 150 °C; (f) thickness of Blend 1: 500 nm, annealing at 90 °C

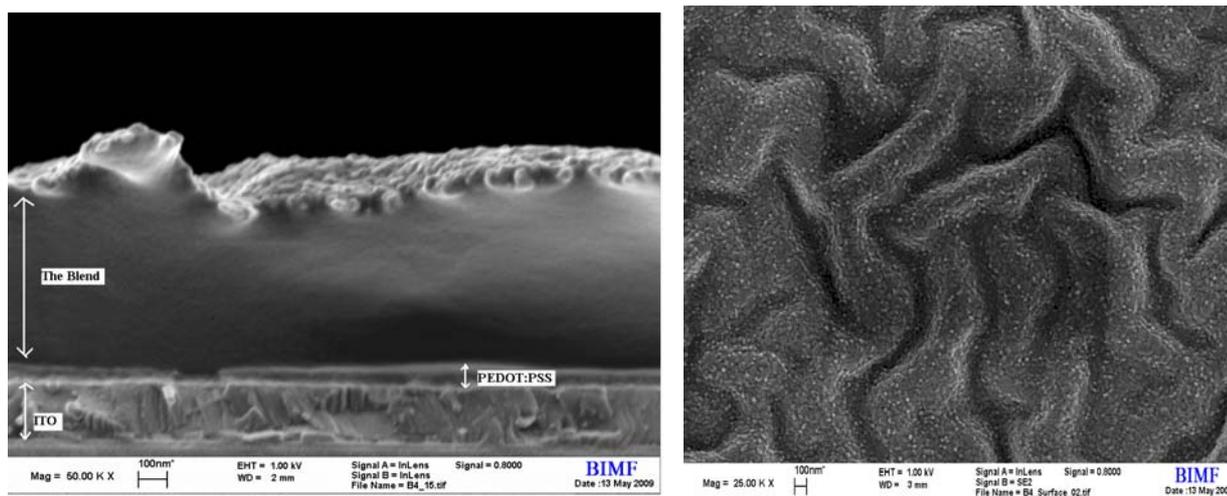


Figure 9. SEM cross-section images of the solar cell based on the phthalocyanine:the perylene blend

Conclusion:

Novel mesogen zinc and copper phthalocyanines containing ethyleneoxy groups as substituents, which are soluble in common organic solvents, were synthesized. The pcs were characterized using different spectroscopic techniques (NMR, UV-Vis, FT-IR and MS). The phthalocyanine derivatives (**Pc1-Pc5**) exhibit a hexagonal columnar (Col_h) structure. The optical and electrochemical properties of the Pcs were investigated. Self-organized liquid crystalline materials (phthalocyanine and perylene derivative) has been used to improve device performance of solar cells and heterojunction solar cells based the blend on ITO were prepared, analysed with I-V characteristics and morphological characterization of thin films was done using SEM.

Our further studies is to improve the aluminium layer on the cell with using different method for solar cell preparation. To gain more detailed insight into supramolecular arrangement of the mixtures, x-ray diffraction measurements will be performed.

Future collaborations:

Future collaboration between the two groups in Bayreuth and Gebze is to prepare bilateral project which is attending on this study

Projected publications:

We are planning to include the experimental results from this visit into one of our future publications on the subject.

Acknowledgements:

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