POlarization-SEnsitive Imaging Detectors with Organic Nanostructured coatings (POSEIDON)

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ABSTRACT
Development of compact on-chip polarization sensitive detectors is crucial for advanced detection systems since polarimetry provides complex information that other techniques cannot give. Using low-cost approaches, POSEIDON aims to add polarimetric capability to color-sensitive imaging cameras introducing organic coatings able to convert the polarization components of the incoming light into different colours. We obtained oriented films of fluorescent organic systems emitting green and red with polarization ratios of about 5. Preliminar tests with commercial colour cameras show promising 20% polarization sensitivity. Evaluation of the performances achievable with different materials will provide potential breakthrough innovation for many scientific and industrial applications.

Keywords: polarimetry; image cameras; organic nanostructures; fluorescence.

1. INTRODUCTION

The polarization state of the light is a probe of the molecular structure and surface texture of the materials involved in light emission and contains information on the properties of the environment where light is propagated through scattering or reflection processes. State of the art imaging systems are unable to analyse the details of the shape of monochrome, highly reflective or transparent objects. However, when light passes through these objects, its polarization changes depending on their shape and transmittance/reflectivity so that a polarization sensitive imaging system can detect the details of the physical properties of these objects. The development of compact on-chip polarization sensitive detectors is therefore crucial for many advanced detection systems since polarimetry provides complex information that other techniques cannot give. As an example, in astronomy the polarization properties of the light contains important information on the physical properties of the sources, as magnetic fields, internal conditions and particle densities. A short overview of the applications of imaging polarimetry can be found in [1].

POSEIDON proposes a new concept of compact on-chip polarimeter. By using innovative organic coatings we add polarimetric capability to imaging cameras in the NUV/optical region, providing simultaneous measurements of the two different polarization states of the light at each pixel without the need of polarizers.

- The use of compact imaging detectors able to simultaneously detect the polarization state of the light at each pixel will minimize and allow controlling the systematic errors of the polarimetric measures leading to substantial breakthrough in these detection systems.
- The low-production cost, low complexity/mass and power budget, along with the versatility of this kind of approach, may have breakthrough innovation potential for a large number of industrial, medical and scientific applications, such as quality control in industrial production lines, remote health monitoring and personalized medicine.
- During the one-year Attract Phase 1 activity, the two research groups of POSEIDON designed and synthesised the organic materials with optimal absorption and emission properties and defined a protocol for their orientation. The good degree of anisotropy in emission (R_{PL} =5) reached by using low cost solution based technologies, provided layers with emission efficiency of 1 and 0.7 for the green and red emissions, respectively. The first tests on coatings, coupled to standard commercial colour cameras via optical layout, provided a promising sensitivity of about 20% to the polarization of the incoming light. The use of fiber optic (FO) faceplates for optimal coupling is in progress to reduce losses due to waveguiding effects.

2. STATE OF THE ART

Imaging polarimeters provide 2D array containing spatially resolved polarization information, pixel-by-pixel for each spatial element. A crucial point is that it is not possible to measure directly the Stokes parameters, which characterize the polarization state of a scene, and multiple images are required to compute them. Since polarimetric data reduction manipulates the same pixel in different frames, the risk of introducing artefacts that might mask the true polarization signature is high. Thus, the ability of controlling and calibrating systematic effects is crucial.

There are many different designs of polarimetric imaging systems (see [2] for a review), each one with their own strengths and drawbacks but, generally speaking, the main architectures are two:

-based on temporally multiplexing the image with an active polarization modulator (a rotating element or a liquid crystal device).

-based on splitting the incident beam in order to make simultaneous measurements of the polarization state (with different sensors or parts of the same sensor).

The first kind is the simpler, but any motion in the scene results in artefacts. To avoid this problem, the images have to be acquired simultaneously, which can be done with the second architecture. However, this approach introduces other artefacts (spatial instead of temporal) since different polarization states are sampled by different sensitive elements. Moreover, mechanical misalignment, as well as optical aberrations, due to separate optical paths, need to be carefully corrected/calibrated. In any case, the use of the multiple sensors or active optical systems means that the polarimetric imagers are often expensive, mechanically complex, heavy and bulky.

Recently, polarimetric image sensors have been introduced in the market (Sony IMX250MZR [3]) based on a pattern of wire-grid polarizers directly deposited on chip, each pixel being provided with a linear polarizer oriented along one of four directions (0°,45°,90°,135°). Thus, each block of 4 pixels provides simultaneous measures along the 4 directions, giving the estimate of 3 Stokes parameters (U, I, Q).

3. BREAKTHROUGH CHARACTER OF THE PROJECT

Imaging polarimeters are already commercially available, but, other than being generally expensive, complex and often with moving parts, they provide measurements of the components of the polarized light sampled at different points in time or space (depending on the scheme adopted), thus introducing artifacts difficult to eliminate, especially when the subjects are moving.

The proposed approach is completely new, based on materials developed and studied for totally different purposes. As in the case of the Sony polarimetric image sensors, it allows a very compact (on-chip) architecture, but with the possibility, for each coating, of measuring simultaneously two orthogonal component (0°and 90°, or 45°and 135°) without splitting the incoming light in two parts. The drawback is that our devices work with monochromatic incident light (the range can be optimized with the choice of the materials used in the coating).

As a first step, during this project we focused on measuring the two orthogonal component at the same time, using standard commercial colour cameras based on filters with Bayer pattern (having mainly in mind the industrial application regarding the detection of surface defects or structural damages in highly reflecting or transparent materials). However, with appropriate filterless sensors, the first image polarimeter really sampling the polarization states of the incident light at the same points both in space and time could be realized, and the design of a Full Stokes polarimeter based on these devices could be studied.

This could open new applications, in particular related to medical diagnostic and polarimetric remote sensing from space, with characterization of atmospheric aerosols.

Moreover, polarimetry is an essential diagnostic tool in astronomy and solar physics, for which could be studied an image polarimeter with very low systematic uncertainty and optimized for spectral lines particularly well suited for diagnosing chromospheric magnetism, i.e. the Ca II H&K lines at 390 nm, and the Mg II H&K lines at 279 nm.

4. PROJECT RESULTS

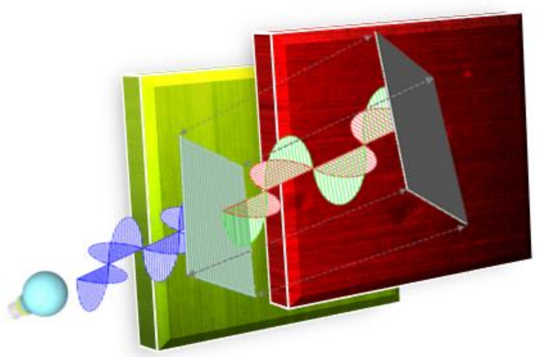
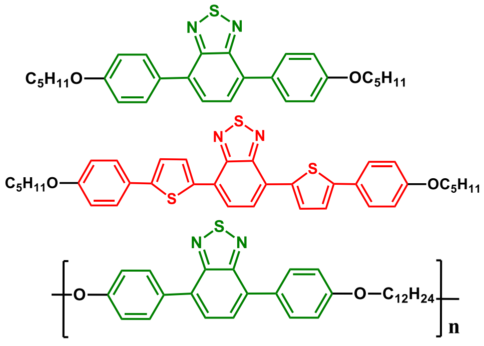


Fig.1 Sketch of the coating for the compact on-chip polarimeter proposed in the POSEIDON project. Two orthogonally oriented emissive layers selectively absorb the two polarization components of the incoming light and convert them into green and red light.



Scheme 1 Chemical structure of molecules **1**, **2** and polymer **3**

Aim of the POSEIDON project is to confer polarimetric capability to standard colour sensitive image detectors by using organic-based coatings able to convert the polarization information of the incoming light into a definite colour, as, sketched in **Fig.1**. In order to prepare the coating we designed and synthetized two molecular and one polymeric system (**1**, **2** and **3**, see **Scheme 1**) by proper functionalization of a class of chromophores already studied in our laboratory [4]. The chemical structures of the conjugated backbones (coloured in **Scheme 1**) provide high extinction coefficients and excellent emission efficiency (η) in the green (**1,3**) and red (**2**) while the linear shape of the backbones grantees high anisotropy of the molecular optical properties.

In order to produce films able to absorb only one component of linearly polarized light, the molecular anisotropy has to be transferred to the macroscopic scale by orienting all the molecules in the same direction. Molecular orientation is a standard procedure in the case of Liquid Crystal (LC) molecules [5] while orientation of conjugated molecules or polymers has been reported in few cases for systems possessing some LC property [6-8]. Here we introduce the alkoxy (OC_5H_{11}) flexible chains at the head-tail positions of the rigid backbones of **1** and **2** in order to impart them LC character [9]. Differential scanning calorimetry (DSC) analysis evidences several thermal events, typical of a LC behaviour, for molecule **1**, while compound **2** does not display LC properties. We then orient films of **1** by rubbing with a rotating cylinder covered by velvet (see **Fig.2a**) [10]. As shown in **Fig.2b** the rubbed film of **1** (about 50-80 nm thick) displays high optical anisotropy along the rubbing direction.

To obtain films with the same properties in absorption but different emission colours we take advantage of energy transfer processes and we add a small amount of **2** (2%w/w) to **1**. The films so obtained, hereafter called **1:2**, display an absorption spectrum identical to **1** and emission very similar to **2** when dissolved in solution, well satisfying the requests of our project (see **Tab.1**). In addition, the photoluminescence (PL) efficiency η (70%) of **1:2** increased with respect to compound **2** (23%) thanks to the efficient resonant

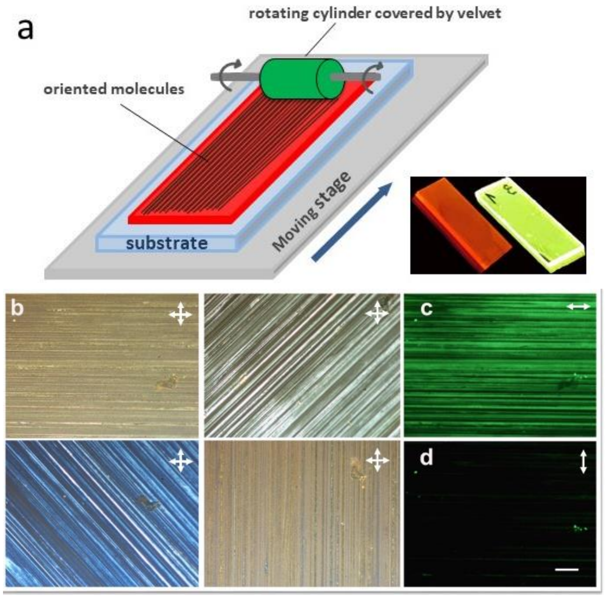


Fig. 2 a) Schematic diagram of the rubbing process with the picture of films of **1:2** (left) and **1** (right) under UV illumination. **b)** Cross polarized optical microscopy images of an oriented film of compound **1** upon 45° rotation of the film: high sample contrast is observed when the film is at 45° with respect to the polarizer and analyser axis, as a result of the anisotropy of the film along the rubbing direction. Fluorescence images by excitation with blue light polarized parallel (**c**) or orthogonal (**d**) to the rubbing direction: the oriented film display high emission contrast in response to the polarization of the incident light. White arrows indicate the polarizer axis direction. The bar scale is 40 µm.

Foerster energy transfer from **1** to **2**. The film of **1:2** have been aligned following the same procedure of **1**. **Fig.2c,d** and **Fig.3** show the fluorescence microscopy images of the films excited with polarized blue light, evidencing the response in the emission intensity when the polarization of the incident light is switched from parallel to orthogonal with respect to the rubbing direction. Polymer **3** possesses the same optical and LC properties of **1** but it lacks the low temperature phase transition. Its higher thermal stability allows annealing treatments to increase the anisotropy [6]. Films obtained with polymer **3** and **3:2** (2%w/w of **2**), after orientation with the same rubbing procedure, show similar anisotropies and higher stability. The lower η of these films is related to some impurities due to the polymerization process, whose optimization is now in progress.

Tab. 1. Absorption and emission properties of oriented films (τ, PL lifetime)

film	abs λ_{max}	R_{ab} 450nm	PL λ_{max}	R_{PL}	τ ns	η
1	416	4.8	535	3.7	8.9	1.00
1:2	415	4.4	650	5.0	6.4	0.70
3	422	4.8	542	5.5	1.3	0.15
3:2	422	4.6	654	4.3	3.5	0.35

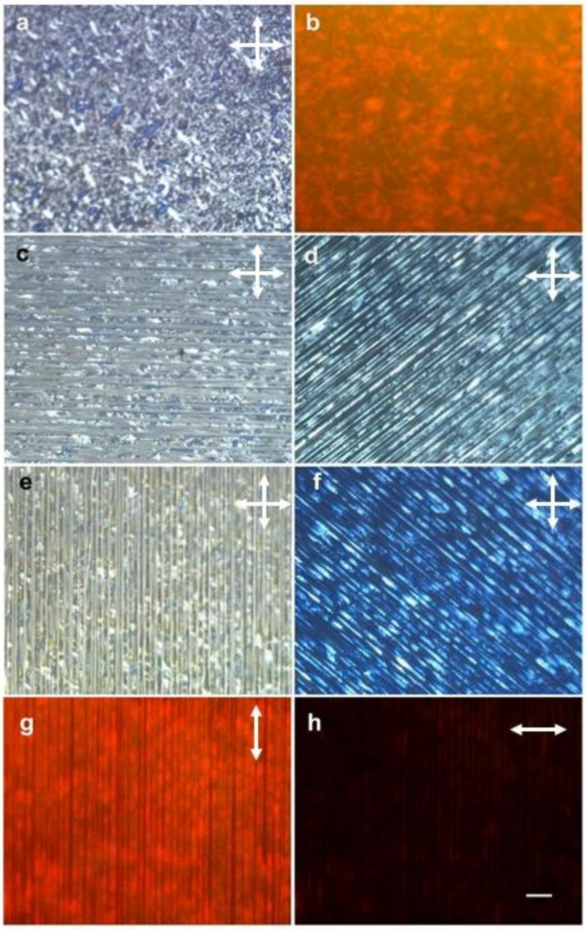


Fig. 3 Cross polarized optical microscopy images of a film of compound **1:2** before (**a**) and after rubbing(**c-f**) upon 45° rotation of the film. Fluorescence images by excitation with blue light before (**b**) and after rubbing with light polarized parallel (**g**) or orthogonal (**h**) to the rubbing direction. White arrows indicate the polarizer axis direction. The bar scale is 25 μm.

The spectroscopic characterization of the rubbed films provides anisotropies $R_{ab} > 4$ in the blue and $R_{PL} \approx 5$ in emission (see **Tab.1)**. As shown in **Fig.4** the optical absorption of the oriented films displays a band centred at about 415 nm, polarized parallel to the rubbing direction. The emission colours of the films **1, 3** and **1:2**, **3:2** are green and red, respectively, with R_{PL} similar to the absorption, that do not show variation with the exciting wavelength in the region 400-450nm.

The high emission efficiency of the oriented **1** and **1:2** films and their good anisotropy motivated us to optically couple these two oriented films to an image detector. We used a commercial camera (SInC by Sanitas EG), selected for the possibility of easily changing the image sensor. As sensor, we used the colour CMOS CMV4000 (**Fig.5**, **Tab.2**) produced by CMOSIS (now AMS [11]).

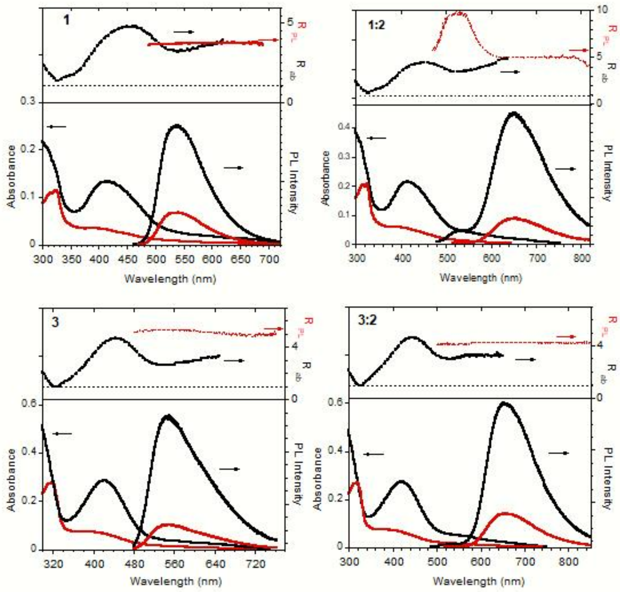


Fig. 4. Polarized absorption and emission spectra (bottom) of oriented layers of **1**, **1:2**, **3** and **3:2** and their anisotropy ratios (top). Absorbance and PL spectra are obtained with light polarized parallel (black) and orthogonal (red) to the rubbing direction.

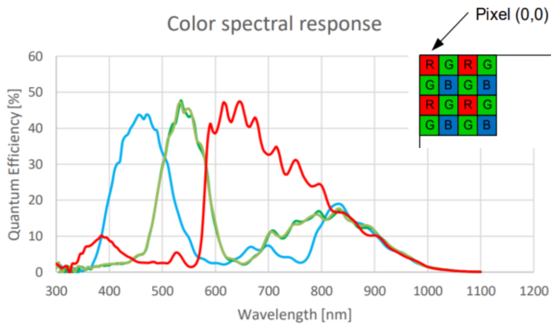


Fig. 5. Typical spectral response of CMV4000 with RGB colour filters, and Bayer pattern [11].

In order to allow quick testing of multiple coatings, the film has been deposited on a planar transparent substrate and then coupled to the sensor via optical layout. We used a quartz light source with a B Johnson filter (central λ=442 nm, FWHM=97.6nm) to provide Blue illumination, then a rotating linear polarizer was inserted between the source and the film.

Tab. 2. Image sensor parameters.

Resolution	**2048(H) x 2048 (V) pixels**
Pixel size	5.5μm x 5.5μm
Maximum frame rate	180fps (10-bit mode) and 37fps (12-bit mode)
Full Well Capacity	13.5 Ke-
Dark noise	13 e- rms
Maximum SNR	41.3 dB

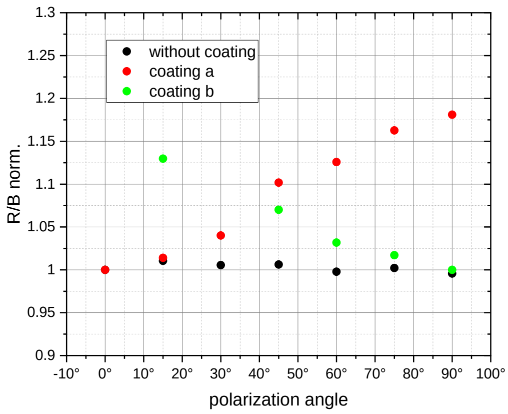


Fig. 6. Response of standard image camera coupled to orthogonally oriented films of **1** (coating b) and **1:2** (coating a) in the green (green points) and red (red points), as a function of the polarization angle of the incoming blue light. Films of **1** and **1:2** are oriented at 0° and 90°, respectively, with respect to the light polarization when the polarizer is positioned at 0°.

Colour images have been acquired for different polarization angles. The ratio of the signal measured in Red (absorbed and re-emitted light) and Blue filter (unprocessed light) has been computed and results are shown in **Fig.6**. The R/B ratio shows a monotone variation with the polarization angle, reaching its maximum value when the polarization of the incident light is parallel to the film orientation. The device performances can be easily increased by using FO faceplates that reduce losses due to waveguide effects induced by the planar structure of the substrates [12]. In fact, these effects strongly reduce the intensity of the emission coupled to the sensor.

5. FUTURE PROJECT VISION

5.1. Technology Scaling

ATTRACT Phase 1 allowed us to bring our ideas to experimental proof-of-concept TRL 3, while we are still working on TRL 4 validation. To bring our technology to TRL 5-7, in ATTRACT Phase 2 a scaling-up of the laboratory synthetic methodology, also introducing well defined purification protocols, is mandatory.

5.2. Project Synergies and Outreach

Synergies with other organizations are needed to bring POSEIDON polarimetric technology to TRL 5-7:
- Chemical companies for large scale production of the identified LC organic molecules and polymers;
- Companies operating in LC display fabrication for the orientation of the coatings;
- SMEs (in particular Sanitas EG and R4P who already expressed interest in this R&D) operating in industrial quality control to validate the final device in real industrial applications with continuous and long lasting operation
- the availability of filter-less image color sensors to sample the polarization at the same point in space and time, would be of great interest. IMASENIC Advanced Imaging, involved in the ATTRACT Projet Low-cost, large area X-ray colour image sensors (XCOL), is working on this topic and expressed interest in a collaboration in ATTRACT Phase 2;
- In ATTRACT Phase 2 we plan to extend the POSEIDON concept of linear polarimetry towards compact image sensors sensitive to circularly polarized light for the development of medical diagnostic tools, as proposed by the ATTRACT SmartOpsy. As discussed with SmartOpsy coordinator, in ATTRACT Phase 2 the consortium will include all the teams of POSEIDON and SmartOpsy.

In ATTRACT Phase 1 a master thesis has been assigned on the synthesis of materials and their orientation, the student was inserted in our team and took part with great enthusiasm to all the project activities. The involvement of young researchers in the team, in particular a post-doc working on the polymerization, has been very advantageous for the project growth. In ATTRACT Phase 2 we intend to involve as much as possible master students, PhD students and post-docs with the aim of disseminate, also through their Universities, the results obtained in the project. We will organize three-month meetings among the consortium teams and exchanges of young researchers in the different laboratories. Thematic conferences will be organized to share the project results with the international community and with industries at mid-term and at end of the project.

5.3. Technology application and demonstration cases

Added value for Scientific Research: Polarimetry is an essential diagnostic tool in solar physics, due to the crucial importance of the magnetic fields in both active and quiet regions. A high resolution, high efficiency, compact polarimeter, allowing very low systematic uncertainty and optimized for spectral lines suited for the diagnosis of chromospheric magnetism (Ca II H&K lines at 390 nm and Mg II H&K lines at 279 nm). Such an instrument could play a very important role in future scientific payloads on stratospheric balloons or spacecraft.
Added value for society in health: remote health monitoring and personalized medicine will be favored by quantifying structural and functional malformations within optically dense biological tissues with compact devices, by monitoring the circular polarization of the light scattered in biological tissues.
Added value for society in health and environment: monitoring the quality of the atmosphere from space, with polarimetry it will be possible to characterize the

atmospheric aerosols that affect climate, the atmospheric chemistry, visibility and, at the end also human health. Solar magnetism is also responsible for solar activity and space weather events, some of which affect our modern civilization

Added value for society in industry: analysis of polarized light allows to detect defects or structural damages in highly reflecting or transparent materials, and this is very difficult to do with standard image sensors, the polarization information will be crucial to identify stress and defects in structures. The use of compact polarimeters will provide an effective and compact solution to the quality control in industrial production lines.

5.4. Technology commercialization

We have received interest from two SMEs operating in quality control of products in industrial production lines. Such SMEs will be part of the ATTRACT Phase 2 consortium for the compact polarimeters test in real industrial applications with continuous and long lasting operation.

5.5. Envisioned risks

The core risks the project will face in a potential ATTRACT Phase 2 project are i) the insufficient sensitivity of the polarimeters in the whole visible spectral region and the need to extend the response out of the visible range, in particular towards the NIR. We will explore different class of materials, comprising quantum rods and hybrid host-guest systems, to increase the sensitivity of the coating. ii) the constrast might be low. Higher film anisotropy will be obtained by annealing treatments of polymer **3** or by using other polymers possessing good thermal stability [6]. Another strategy will be to use photoalignment layers on the substrates [8] that do not alter the absorption properties of the coating.

5.6. Liaison with Student Teams and Socio-Economic Study

Following the successful inclusion of a master student and a postdoc in the team of ATTRACT Phase 1 POSEIDON, we intend to include master students in the Phase 2 also by implementing the relationships with Universities through seminars and stages directly related to the project activity. To this aim we plan to hire a post-doc that will take care of organizing seminars and stages with the involvement of undergraduate students, while PhD students teach-to-learn actions will be promoted.

In ATTRACT Phase 2, any expert-driven socio-economic study of the ATTRACT initiative and ecosystem will benefit from the contributions of the whole team members, through a person responsible of this task.

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