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Invited Review

Phthalocyanines and Phthalocyanine Analogues: The Quest for Applicable Optical Properties

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Summary. The central subject of this article is the description of the current work of the authors in the context of the Cost Action 518, project DE-1, and the Phthalocyanines Research Training Network, both financed by the European Community. The aim of the above projects is the design, synthesis, and structural and physical characterization of molecular and polymeric materials based on phthalocyanine derivatives with particular optical properties, as well as the study of their technological applications in the sensors field.

Keywords. Films; Liquid crystals; Optical properties; Phthalocyanines; Sensors; Sol-gels.

Introduction

Phthalocyanines (*Pc*s, Fig. 1) and their analogues have been investigated in detail for many years, especially with regard to their properties as dyestuffs, paints, and colours. In the last 20 years phthalocyanine chemistry is undergoing a renaissance because phthalocyanines and many of their derivatives exhibit singular and unconventional physical properties interesting for applications in materials science [1]. Thus, in addition to basic research, the interest in phthalocyanines has been recently expanding, among others, into applied fields such as photovoltaics, electrochromism, optical data storage, laser dyes, liquid crystals, chemical sensors, and photosensitizers for photodynamic therapy [1].

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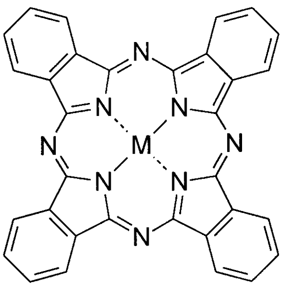

Fig. 1. Metallophthalocyanine

It is well known that substances showing semiconducting or conducting properties or high linear and nonlinear optical responses are currently of great scientific and technological interest for designing electronic or photonic devices. *Pc*s, Metallo-*Pc*s, and their analogues are multipurpose materials applicable in these fields. The relevance of *Pc*s and their analogues results from their variety, architectural flexibility, and exceptional environmental stability. The phthalocyanine molecule has a two dimensional π-electron conjugated system (an aromatic system with 18 π-electrons), and a number of modifications can be made either in the macrocycle by incorporating more than 70 different metal atoms (Fig. 1) or by inserting side groups at the peripheral sites of the macrocycle. Moreover, formal substitution of one or more isoindole units by other heterocycles affords phthalocyanine analogues. Phthalocyanines can also be polymerized in one- or two-dimensional arrays. These changes facilitate the tailoring of electrophysical parameters of metallophthalocyanines over a broad range and, consequently, allow modulating the electrical and optical behaviour of the compounds.

On the other hand, phthalocyanines can present several kinds of condensed phases such as single crystals, polycrystalline films, discotic liquid crystals, and *Langmuir-Blodgett* films. This fact is extremely important *a*) in order to organize the phthalocyanines in a supramolecular architecture to achieve supramolecular properties and *b*) to improve the processability of the compounds for their incorporation in molecular devices.

The objectives of our network [2] are the design, synthesis, structural and physical characterization, and engineering of phthalocyanines and molecular and polymeric substances and the study of their optical, conducting, and magnetic properties as well as their industrial applications, especially in sensor technology. This article intends to give an overview on the past, present, and future research of this network within the field of phthalocyanines and their applications.

Results and Discussion

Optical sensors based on the evanescent wave technique

The optical properties of *Pc*s, even being of great scientific interest, have not been thoroughly explored in many aspects, some of which this network intends to cover. Optical sensors are ideal for being used in environments where electrical isolation

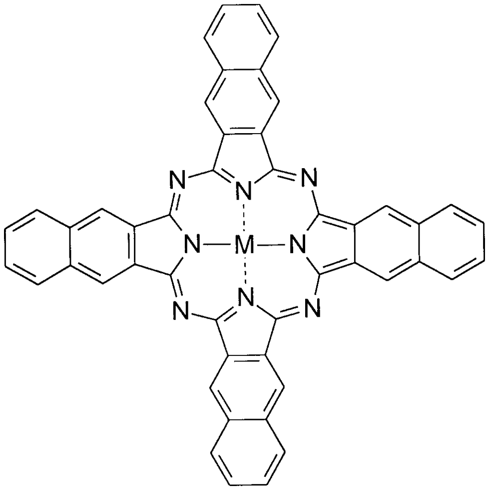

Fig. 2. Metallonaphthalocyanine

and miniaturization of the device are essential. A convenient technology to exploit is one based on a change in absorption or emission properties of a chemically sensitive reagent upon contact with an analyte. Clearly, the reagent must have an unusually high absorption coefficient and exhibit fluorescence emission with a reasonable quantum yield such as the naphthalocyanine shown in Fig. 2.

These are the requirements that render the phthalocyanine nucleus the logical chromophore for optical detection. The macrocycle displays intense visible region absorption (the *Q*-band) and, with appropriate metals in the central cavity, good fluorescence emission. More than 90% of photoreceptors in laser copiers/printers are phthalocyanines. The change of the photoconductivity by a specific surrounding gas is important for gas detection [3–4]. Furthermore, *Pc*s are known to interact with environmentally important gases, such as NO_2, and derivatization of *Pc*s with crown ethers and other ionophores provides compounds able to complex cationic species. Evidence available from solution phase studies indicates that such processes induce a change in the optical properties of the *Pc*. However, for a practical device, it is preferable for the chromophore to be immobilized onto a solid substrate because it is then more convenient and readily addressable. If light is launched down a waveguide (either optical fibre or microscope slide) by internal reflection, a portion of that light will penetrate the outer surface of the waveguide; this is termed the evanescent wave. Thus, the radiation penetrating the waveguide interacts with a *Pc*-type macrocycle deposited onto it. Any variation in the spectroscopic properties of the *Pc* reagent is essential for device application, and to achieve this, self-assembled monolayer (SAM) technology with *Pc*s and incorporation of the *Pc* reagent into a sol-gel [5] or molecular sieve formulation [6] is exploited. This idea may be extended to films on microelectrodes [7].

Sol-gels are constructed by adding a trichlorosilylalkyl-derivatized macrocycle into a sol-gel precursor followed by drying to form glasses or spin coating to form thin glass films. Mercaptoalkyl derivatives are deposited as a SAM onto gold-coated glass or silicon slides by dipping the slide into a solution of the material in an organic solvent. Molecular sieves containing metal phthalocyanines are prepared by either adsorbing a phthalocyanine derivative at silyl-modified molecular sieve walls or by synthesizing a phthalocyanine in the cavities of molecular sieves.

Detection of the analyte can also be carried out by detecting the change of photoconductivity since phthalocyanines belong to the best organic photoconductors [8]. In this case, films of low-molecular-weight phthalocyanines on μ-sized electrode arrays are prepared by vapour deposition or by *in situ* synthesis in the case of polymeric *Pc*s [9].

The films, sol-gels, and molecular sieves are characterized by spectroscopy, in particular fluorimetry, the SAMS by FTIR spectroscopy which is an ideal tool for probing orientations of the macrocyclic molecules in thin film assemblies. Two types of experiments are possible: reflection-absorption IR spectroscopy (RAIRS) and transmission IR. *Pc*-SAM films on gold and, in a preliminary feasibility study, a *Pc*-gold coated waveguide have been enclosed in a flow through cell to allow an analyte gas, NO_2, to interact with the immobilized *Pc* [10]. A laser induced evanescent wave excited the *Pc*, and fluorescence was detected. Upon interaction of the *Pc* with the analyte gas there was a reversible change in the fluorescence intensity. This type of technology is likely to become increasingly important in trace analysis, because fluorimetry is a spectroscopic technique with inherently very high sensitivity.

In addition, the films of vapour deposited and *in situ* prepared low-molecular and polymeric phthalocyanines are under investigation for the change of their photoconductivity. Because the range of the value of the photoconductivity depends greatly on the analyte gas molecules, the response can be characteristic of the analyte.

Chiroptical sensors

In connection with the sensing properties, a target of our network is the technological application of chiral liquid crystals based on *Pc*s. Recently, different *Pc* compounds with branched side chains containing chiral centres have been synthesized [11]. When such compounds are prepared as single enantiomers, in which all side chains are either in the *R* or the *S* configuration, they form a chiral liquid crystalline phase [12] and micrometer-long helical fibres by self-assembly in organic solvents. It has been shown that the helicity of these fibres is very sensitive to alkaline cations. Binding of metal ions strongly influences the pitch of the helices as can be detected by different techniques, *e.g.* circular dichroism or, when combined with a nematogenic compound, as a change in the cholesteric pitch that is even visible to the naked eye. This property can be used for sensing purposes.

When *Pc*s include a dihydrosilicon unit in the centres of the molecules (Fig. 3) they can be polymerized to form axial polysiloxanes [13]. These compounds represent a novel class of chiral polymers based on *Pc*s (Fig. 4). The aim of this network is to make use of chiral phthalocyanines, in particular crown ether functionalized *Pc*s, in order to detect metal ions with the help of chiroptical techniques.

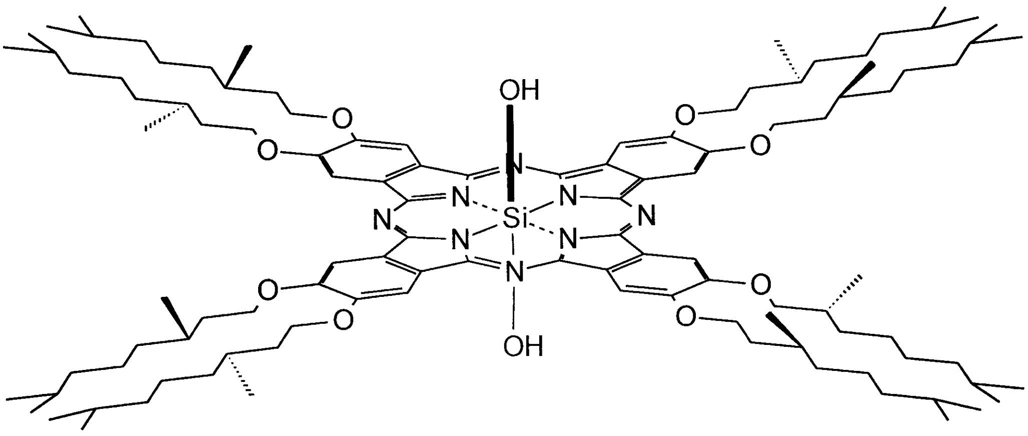

Fig. 3. Chiral dihydroxysiliconaphthalocyanine

Fig. 4. Schematic representation of a chiral *shish-kebab* polymer

Second harmonic generation (SHG) and third harmonic generation (THG)

In the last few years, *Pc*s have also been studied as targets for SHG, THG, and optical limiting devices [14, 15]. Moreover, non-resonant sub-picosecond response times and small absorption losses as well as thermal and environmental stability are important characteristics that make them promising candidates to be incorporated into devices. Most of the NLO studies with *Pc*s have focused on third-order applications since they have concerned centrosymmetric compounds. Detailed up-to-date reviews on the nonlinear optical behaviour of *Pc*s and related compounds can be found in recent reports [15]. In this regard, much less effort has been devoted to the SHG response of *Pc* derivatives, mainly due to the difficulty in preparing non-centrosymmetric *Pc*s. Therefore, we are actively working on the expansion of the properties of *Pc*s from THG to SHG. This network is also interested in making advances in this field by *a*) rationalizing the effect of the extension of the conjugation in *Pc*s and analogues and the influence of supramolecular order achieved in organized condensed phases of *Pc*s on the NLO properties and *b*) designing, synthesizing, and studying octupolar *Pc* derivatives (Fig. 5) in order to enrich the span of molecular symmetries and offer additional parameters for the optimization of the nonlinear response.

Phthalocyanines have shown to exhibit excellent nonlinear optical response for both second and third-order effects. General rules for molecular opto-electronics

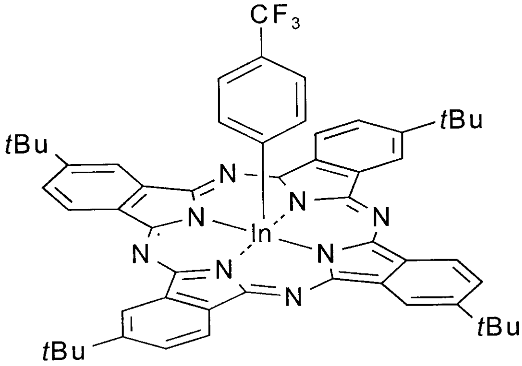

Fig. 5. Indiumphthalocyanine

have been obtained and need to be refined substantially before this material class can find its way into general applications.

The second order NLO properties of specially designed *Pc*s are being studied with the main aim of evaluating their potential for high-speed electro-optic switching and data processing as well as in telecommunication systems. In order to produce low-symmetry *Pc*s, two main strategies will be followed: *a*) peripheral substitution of the macrocycle with donor and acceptor groups and *b*) structural modification of the *Pc* itself into subpthalacyanine or triazolehemiporphyrazine (Fig. 6) in order to reduce the symmetry.

The resulting non-centrosymmetric compounds (*e.g.* subphthalocyanines [16] or triazolehemiporphyrazines [17]) present rich charge-flow patterns that permit variable degrees of dipolarity/octupolarity in the nonlinear response. The second-order NLO properties are being studied by *Hyper-Rayleigh* scattering (HRS) to obtain information at the molecular level and by electro-optic modulation spectroscopy in poled polymer matrix for switching device application evaluation.

The third-order NLO properties are being investigated by *Z*-scan, optical limiting, time resolved ultrafast spectroscopy, and degenerate four-wave mixing (DFWM) experiments in solution and films in order to integrate complementary

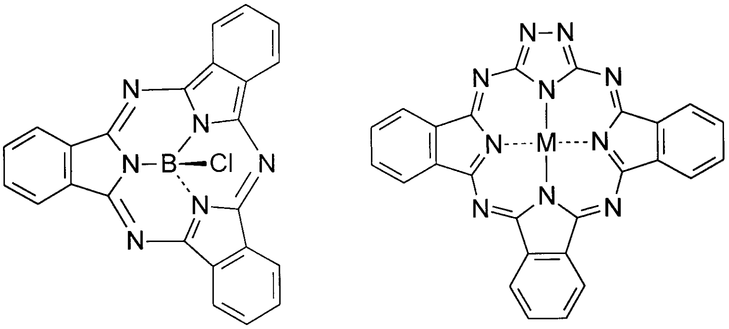

Fig. 6. Subphthalocyanine (left) and triazolephthalocyanine (right)

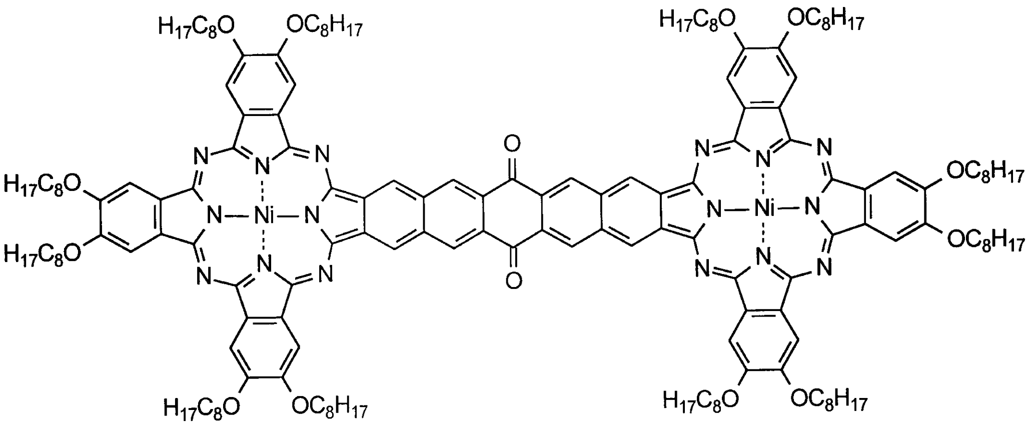

Fig. 7. Nickelphthalocyanine-based ladder-type dimer

techniques in an effective way. The influence of the conjugation and self-organisation on the second- and third-order NLO properties will be investigated. For this goal, supramolecular electronic structures such as ladder polymers [18] (Fig. 7) and *shish-kebab* polymers [13] (Fig. 4) based on *Pc*s will be prepared. If the size and speed of the nonlinearity appears promising for all-optical switching applications, tests in waveguides at 1.3 and 1.55 µm wavelength will be carried out in a guest-polymer host or another thin film geometry.

Optical limiting

Optical limiting is a nonlinear effect consisting in a decrease in the transmittance of a sample under high intensity or fluence illumination. Ideally, the transmitted intensity should remain constant (or even decrease to a small value) above a certain illumination threshold. Consequently, the initial constant transmittance should linearly decrease to zero above the threshold. The optical limiting effects find useful applications in sensor technology (*e.g.* CCD) and protection of the human eye. Phthalocyanine derivatives have received a great deal of attention as reverse saturable absorbers [19]. Optical limiting with *Pc*s was first reported for chloroaluminum *Pc* (*CAP*). Experiments have been performed on many *Pc*s in solution, particularly *CAP*, and much information is available. Much effort is still being devoted to determining the main physical parameters and understanding the relevant mechanisms. The role of metal substitution and molecular stacking is being actively investigated. The best results obtained so far concern indium phthalocyanine (Fig. 5) [19].

In the field of optical limiting properties at the microscopic levels of indium phthalocyanines have been recently reported [19]. The present network intends to extend these studies at the supramolecular level using suitable macroscopic sol-gel systems. Dimetallic binuclear phthalocyanines are being designed and synthesized also for optical limiting purposes. In this case, a cooperative effect between the two halves of the molecules is expected.

The nonlinear optical properties of the materials designed for optical limiting will be determined by means of laser spectroscopic methods. Time-resolved experiments including spectroscopically resolved transient absorption (TA) and degenerate four-wave mixing (DFWM) studies will be employed to measure the dynamics of the nonlinear optical responses. The *Z*-scan technique will be used to evaluate the different contributions of both nonlinear absorption and refraction to the nonlinear response of the *Pc*s. The change of the relative transmission will be measured as a function of both incident fluence and wavelength. This will allow the determination of the nonlinear absorption coefficient α_{NL} of the materials and the threshold for optical limiting. Finally, the materials that fulfil the requirements, such as low threshold, ability to limit a large range of fluences over a broad spectral range, and high photochemical stability will be further tested for practical devices.

Conclusions

This network [3] intends to cover a broad range of techniques for improving the characteristics of phthalocyanines and their derivatives in the fields of linear and nonlinear optics for sensors, switches, or optical limiting applications. We believe that the efforts of this scientific community will lead in near future to real-life applications. Another very important topic that is not included within the scope of the network but still could have profound consequences is the use of phthalocyanines in photodynamic therapy (PDT) [20]. The same physical characteristics used for linear and nonlinear optical applications may also be of importance in medicine.

Acknowledgements

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