

Phthalocyanines and Related Compounds: Subunits for the Preparation of Molecular Materials

J. GARCIA, A. GONZALEZ, A. GOULOUMIS, E.M. MAYA
M.D. PEREZ, B.d. REY, P. VAZQUEZ & T. TORRES *

Departamento de Química Orgánica (C-I)
Facultad de Ciencias
Universidad Autónoma de Madrid
28049-Madrid - SPAIN

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The design, synthesis, structural and physical characterization and engineering, and the study of the electrical conductivity and the nonlinear optical properties of phthalocyanines and molecular substances related to them, such as subphthalocyanines, hemiporphyrines and triazolephthalocyanines were reviewed.

Introduction

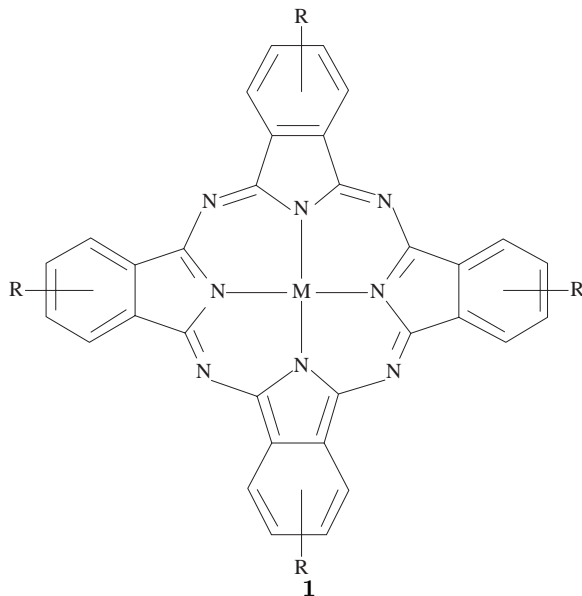
Metallophthalocyanines^{1,2} (Mpcs, **1**) are multipurpose synthetic electroactive materials with particular electronic and structural characteristics which show semiconducting and nonlinear optical properties. The term “Synthetic Electroactive Materials” includes synthetic organic molecules or macromolecules which have a particular activity under either static electric field or electromagnetic field of optical radiation. Charge transfer complexes, polymers, fullerenes, metallomacrocycles and ferroelectric liquid-crystals are examples of this kind of materials.^{3,4}

Phthalocyanines have a two-dimensional 18 π -electron conjugated system, in which more than 70 different metal and also non-metal ions can be incorporated. A number of modifications can be made in the macrocycle either by introduction of different central ions or by substitution of functional groups at the peripheral sites of the ring. Moreover, the formal substitution of one or more isoindole units by another heterocycle affords the phthalocyanine analogues. Phthalocyanines can be also polymerized in one- or two-dimensional arrays. This architectural flexibility facilitates the tailoring of their properties over a very broad range. The preparation properties and applications of phthalocyanines have been recently reviewed.¹

On the other hand, the wide range of condensed phases that they can show, such as monocrystals, mesophases, Langmuir-Blodgett films, etc., has contributed to the development of electronic and electro-optic devices based on these compounds.^{1,3} Therefore, phthalocyanines have a great technological potential

* Address for correspondence: Prof. Tomás Torres Dept. Química Orgánica (C-I) Facultad de Ciencias Universidad Autónoma de Madrid Canto Blanco 280-Madrid, Spain Phone: 341 397 4151 Fax: 341 397 3966 e-mail: tomas.torres at uam.es

in areas related to intrinsic semiconductors and conducting polymers, nonlinear optics, chemical sensors, electrochromic display devices, laser recording materials, information storage systems and liquid-crystal colour display applications, among other.^{1,3-6}



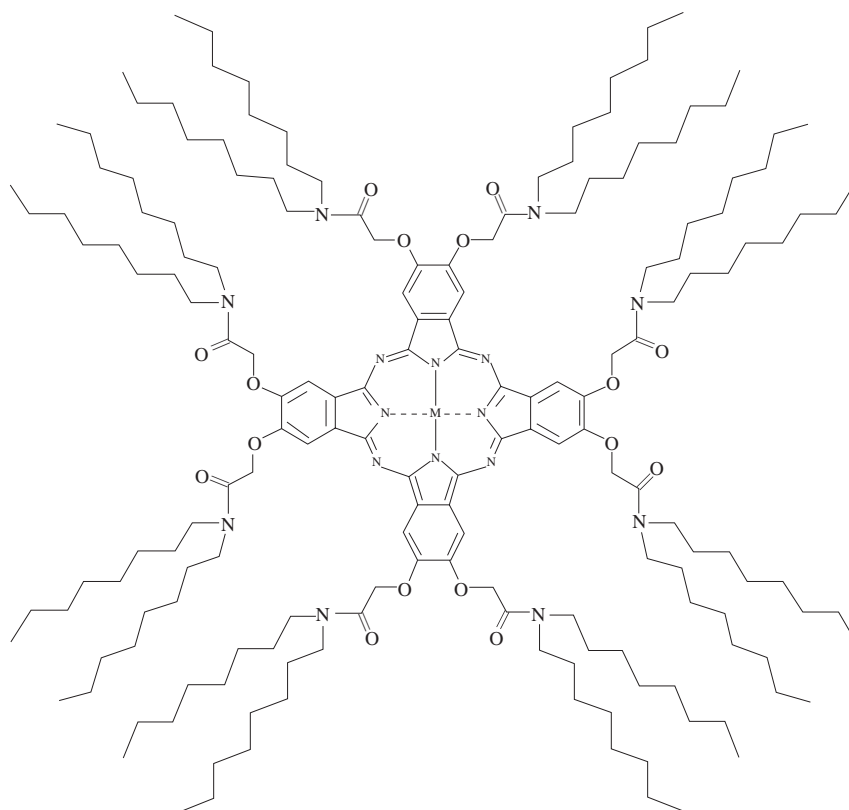
The goals of our research group are the design, synthesis, structural and physical characterization and engineering, and the study of the Electrical Conductivity and the Nonlinear Optical Properties of phthalocyanines and molecular substances related to them. Through structural modifications of phthalocyanines that include, among others, an adequate non-centrosymmetric functionalization of the systems with acceptor/donor or hydrophilic/lipophilic substituents, and the formal substitution of one or more isoindole subunits by another nitrogenated heterocycle in order to create unsymmetric systems, it is intended to obtain new azoporphyrins with useful electrical and optical behavior. Phthalocyanines, subphthalocyanines, hemiporphyrines and triazolephthalocyanines are the main targets of our research. The compounds are formulated as liquid crystals or spin-coated, evaporated and Langmuir-Blodgett films. Our major interest lies in the organization of the macrocycles at supramolecular level in order to improve the conducting and nonlinear optical properties as well as their potential applications to the fabrication of sensors and optoelectronic devices.

Phthalocyanines

One of our contributions to the field of the phthalocyanines is the preparation of highly soluble substituted Pcs, such as **2**. These compounds form stable columnar hexagonal mesophases between room temperature and temperatures near 100°C.⁷ The steric hindrance between the lateral chains avoids the aggregation of the compounds even at relatively high concentrations (10^{-3} M).⁸

The two-dimensional π -conjugated metallophthalocyanines are interesting materials, tailor-made for third-order nonlinear optics, which offer additional features to optimize the nonlinear response. Thus, besides the $\pi-\pi^*$ transitions of the conjugated system, they present charge transitions from ligand to metal (LMCT) and from metal to ligand (MLCT), as well as metal to metal transitions, which provide enhanced possibilities for tailoring the $\chi^{(3)}$ susceptibilities.⁹

The third order nonlinear optical properties (THG) of compounds **2** and related ones in solution, as well as the dependence of the NLO response as a function of the central ion have been studied by us.¹⁰ In all cases, the cobalt derivatives show the largest gamma THG values. We have also prepared Langmuir Blodgett films with these compounds. The goal was in this case to organize the molecules in stacks, in order to promote a nonlinear optical supramolecular property. The third order NLO properties of these films have been studied by us,¹¹ and preliminary data show an increase of the nonlinear response as a function of the organization.

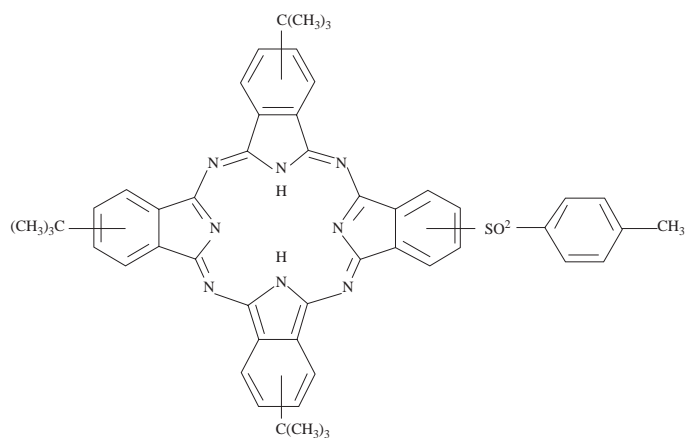


M=H₂, Cu(II), Ni(II), Co(II)

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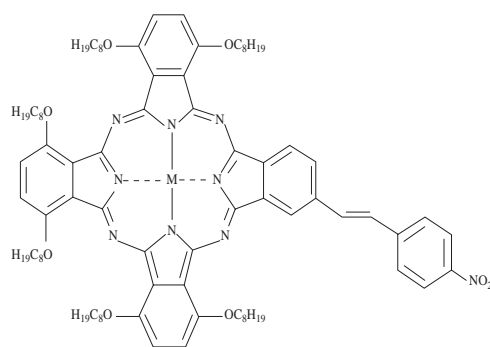
There is also considerable current interest in non-centrosymmetric organic molecules with π -electron systems and asymmetric charge distribution because of their potential applications in second-order nonlinear optics, e.g. Second Harmonic Generation (SHG). Unsymmetric phthalocyanines substituted by both electron donor and electron acceptor groups have been suggested as promising targets for SHG.^{12,13}

The NLO properties at molecular level of a family of unsymmetrically substituted metal-free phthalocyanines,¹⁴ for example **3**, specially designed to present quadratic polarizabilities have been studied for the first time.¹⁵ NLO characterization has been performed by Electric Field-Induced Second Harmonic (EFISH) Generation and Third Harmonic Generation (THG) experiments in solution. The NLO response has been investigated for different types of substituents. Although no experimental evidence of first-order hyperpolarizability (β) contribution to γ_{THG} has been obtained, a significant influence of intramolecular charge transfer (ICT) on the cubic nonlinear response has been evidenced and correlated to the relative strengths of donor and acceptor substituents using Hammett parameters.¹⁵

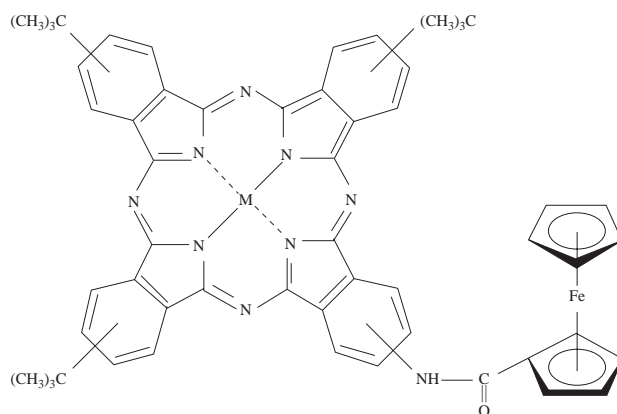


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Other non-centrosymmetric phthalocyanines such as **4**,¹⁶ and **5**, with the possibility of electron-delocalization and potential second order NLO properties are being presently studied.

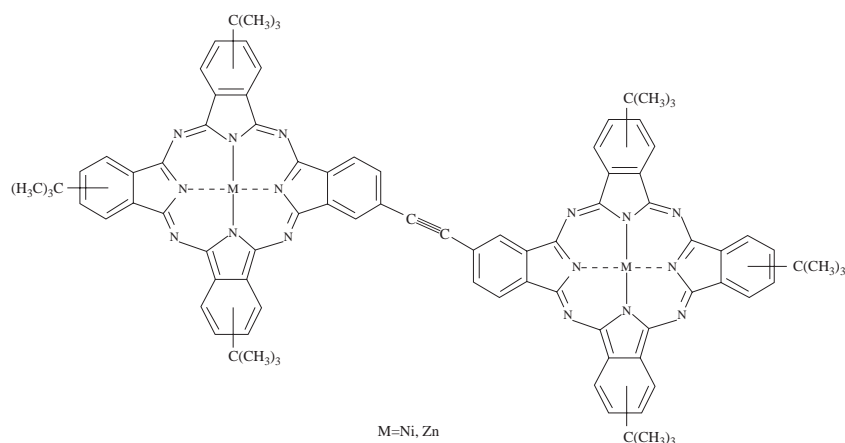


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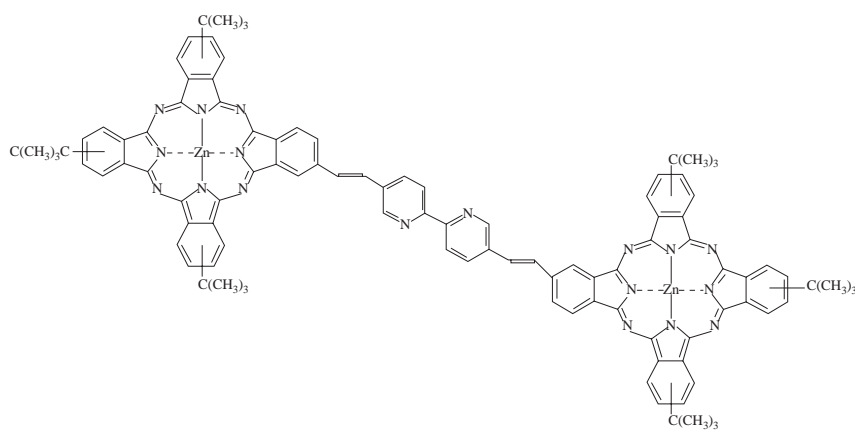


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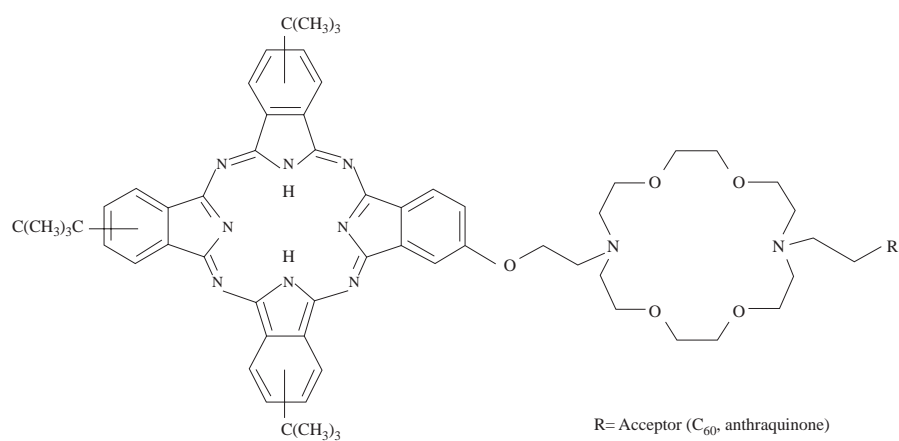
Binuclear phthalocyanines, such as **6**¹⁷ and **7**,¹⁸ and unsymmetrically substituted phthalocyanines, for example **8**, have been recently prepared by us in order to study energy and electron transfer processes, as well as their NLO properties.



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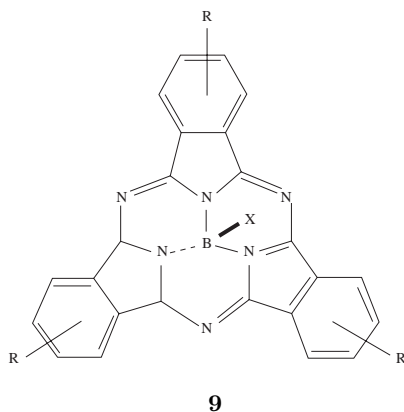
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Subphthalocyanines

Subphthalocyanines (SubPcs, **9**)¹⁹ are non-planar coned-shaped (saddle shaped) aromatic molecules with 14 π electrons and a trigonal geometry. The UV visible spectrum of subphthalocyanines is quite similar to that

of phthalocyanines with a Q-band at ca. 600 nm. We have also studied the second order nonlinear optical properties of adequately substituted subphthalocyanines having dipolar and octupolar character, such as the trinitro derivative **9** ($R = \text{NO}_2$), by Hyper Raleigh Scattering.²⁰ The second order polarizabilities (β) found in these compounds are remarkable.

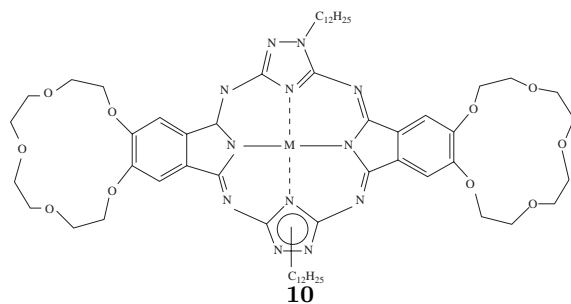
Recently we were successful in the organization of these kind of octopolar compounds in spincoated films, using a corona poling method.²¹ On the other hand, unsubstituted SubPc have been investigated in sublimated thin films for THG, and χ^3 values three times higher than those obtained for phthalocyanines in the same frequency range have been measured.



Hemiporphyrazines

Despite the structural similarities with phthalocyanines, metallohemiporphyrazines²² and related compounds are virtually not investigated, most probably due to the fact that all hemiporphyrazines described are “non-Hckel” systems and display lower chemical stability than phthalocyanines. The most recent advances in this field are due to Hanack and coworkers²³ who have described the preparation of soluble ladder-polymers (oligomers) based on the hemiporphyrazine moiety and, Wagner and co. who have reported the Langmuir-Blodgett film organization of soluble rod-like polymers based on cofacially joined metallohemiporphyrazines.²⁴

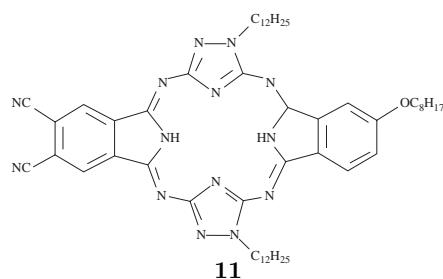
On the other hand, our group has developed during the last years the preparation and study of properties of what we have called triazolehemiporphyrazines. Triazolehemiporphyrzines^{25–31} (Thp, **10**) are highly conjugated 20 π electron systems which have several structural features in common with phthalocyanines. They are formally originated by the substitution of two face-to-face isoindole rings of a phthalocyanine by two triazole units.



The most striking features of these compounds are: Their chemical flexibility from the synthetic point of view (higher than that of Pcs), the high complexing ability towards transition metal ions of the triazole subunits, the electron-withdrawing character of the triazole moieties (able to facilitate an unsymmetric charge distribution in some cases), their high thermal stability, but also their lower chemical stability (for example in acidic media) in comparison with that of Pcs as a consequence of their lack of aromaticity (actually these compounds are Schiff bases).

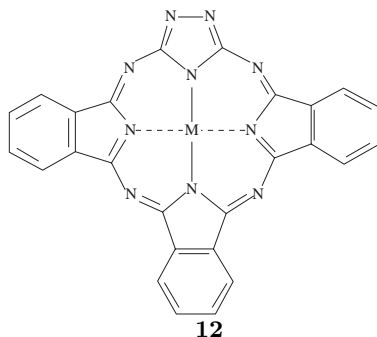
With regard to their electrical properties, we have described triazolehemiporphyrazines with a semi-conducting character after oxidative doping²⁶ and we have studied the polymerization of the iron derivatives with suitable bridge ligands to improve the conductivity.²⁹ We have also prepared Langmuir-Blodgett films of "crowned" triazolehemiporphyrazines (**10**).³⁰ The macrocycles aggregate into elongated strands comprising about 50 molecules.³¹

Metallotriazolehemiporphyrazines have shown third order nonlinear optical properties^{32,33} which depend on the central ion, comparable to those presented by phthalocyanines. Recently³⁴ we have described for the first time a regioselective stepwise procedure for the preparation of unsymmetrically substituted triazolehemiporphyrazines (**11**) for NLO purposes.



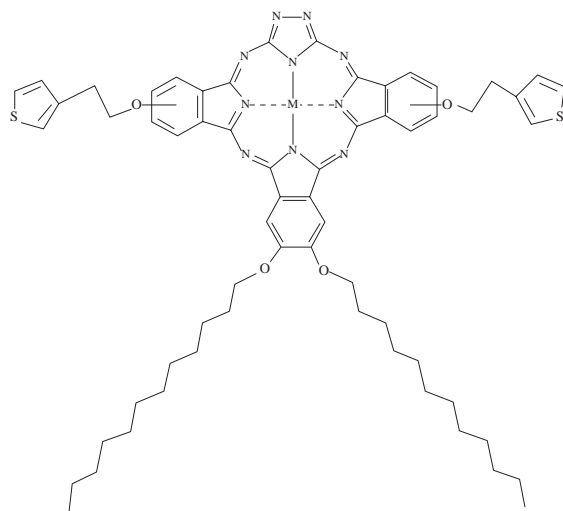
Triazolephthalocyanines

We have described the preparation of a new kind of Pc analogues to which we have assigned the trivial name Triazolephthalocyanines (TPc, **12**). These compounds are the first examples of porphyrin or phthalocyanine analogues in which one pyrrole or isoindole subunit has been replaced by a polyazole, such as 1,2,4-triazole. Triazolephthalocyanines³⁵ are aromatic compounds having an 18 π electron system, isoelectronic to phthalocyanines.



These new kinds of unsymmetric azaporphyrins lacking symmetry center could represent an important entry into the development of improved materials for nonlinear optical applications. Thus, the electron

acceptor character of the triazole ring, together with an adequate peripheral substitution on the isoindole moieties, provides an electronic disymmetry in compounds, giving a net dipolar moment which would be potentially useful for the second harmonic generation.¹³ We have recently³⁶ reported on a stepwise, widely applicable strategy for the preparation of unsymmetrically substituted triazolephthalocyanines (**13**) soluble in organic solvents.



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In plane oriented Langmuir films of some of these triazolephthalocyanines have been obtained when Ni^{2+} ions were introduced into the aqueous subphase to complex the 1,2,4-triazole moiety. By transferring the Langmuir-monolayer to hydrophobic substrates, in plane oriented Langmuir-Blodgett films were obtained with molecular planes preferentially oriented perpendicularly to the dipping direction.³⁷ These LB films have semiconducting character³⁸ with conductivity values of $10^{-3} \text{ S/cm}^{-1}$. The application of LB-films of these compounds as gas detectors are being presently studied.

Acknowledgements

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