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Triazolephthalocyanines: synthesis, supramolecular organization and physical properties

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Contents

Abstract

Different synthetic paths for obtaining triazolephthalocyanines (Tpcs), a new kind of A_3B-type phthalocyanine analogues, are discussed in this paper. An overlook of the structural and characterization features of these compounds is also given. Finally, it is shown why Tpcs are promising targets for the construction of organic molecular materials: they have not only interesting conducting and nonlinear optical properties, but also the capability to be organized in condensed phases such as liquid-crystals and LB-films. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Triazolephthalocyanines; Tribenzhexaazaporphyrins; Phthalocyanine-analogues; Synthesis; Supramolecular organization; Molecular materials

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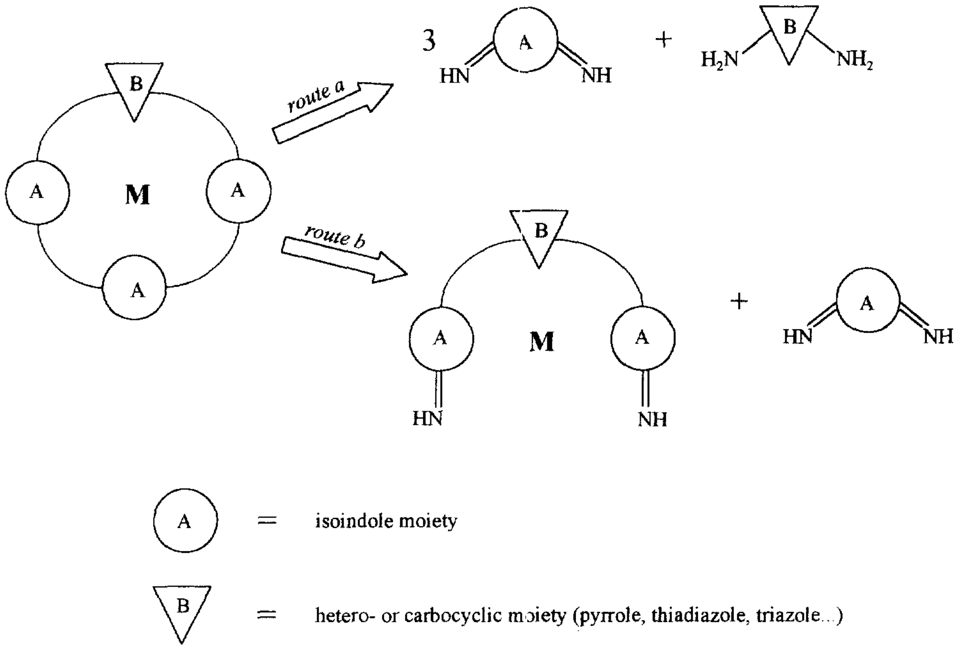
1. Introduction

Phthalocyanines [1,2], aromatic macrocycles constituted by four isoindole subunits bound through aza-bridges, have been widely studied in the last years due to their unusual physical properties [1,3]. These molecules are potential building blocks for the development of new molecular organic materials with applications in opto-electronics [4]. In particular, the design and synthesis of non-centrosymmetrical phthalocyanines and porphyrin derivatives with second order nonlinear optical properties has attracted great attention [5].

In this regard, most of the effort has been focused on the preparation of non-centrosymmetrical phthalocyanines with different substituents in the periphery of the aromatic system [6–8]. Alternatively, the formal substitution of only one isoindole subunit in a phthalocyanine by another conjugated (hetero)cyclic moiety represents also a way to obtain non-centrosymmetrical phthalocyanine analogues that has been less developed. This strategy leads to the formation of aza-bridged phthalocyanine-type macrocycles with an A_3B pattern in which A is an isoindole subunit and B a (hetero)cyclic moiety (benzene, pyridine, pyrrole, thiadiazole, triazole...).

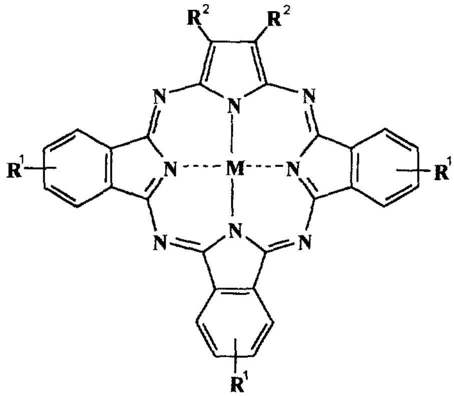
Two main methodologies have been applied for the synthesis of these compounds (Scheme 1). The first one (*route a*) involves the statistical one-step condensation of a 1,3-diiminoisondoline and the diamine of the corresponding (hetero)cyclic moiety



Scheme 1. Retrosynthetic scheme for the synthesis of phthalocyanine-type macrocycles with an A_3B pattern.

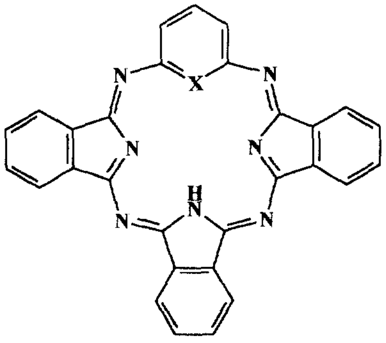
B in a 3:1 molar ratio ($3A + B \rightarrow A_3B$). Alternatively (*route b*), the condensation can be carried out between equimolar amounts of a preformed trimer ABA and a 1,3-diiminoisoindoline ($ABA + A \rightarrow A_3B$).

Thus, compound **1a** ($M = H_2$) was obtained for the first time in 1955 by Elvidge and Lindstead following the *route a* [9]. The metal complexes were obtained by metal insertion reaction to the metal-free macrocycle [10]. Later, it was shown that compound **1a** (as well as compound **1b**) can also be afforded by the ring-expansion reaction of the so-called subphthalocyanine with succinoimidine [11].

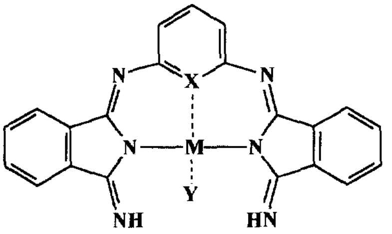


1a $R^1 = R^2 = H$; $M = H_2$, Ni, Co
1b $R^1 = C(CH_3)_3$ $R^2 = H$; $M = H_2$

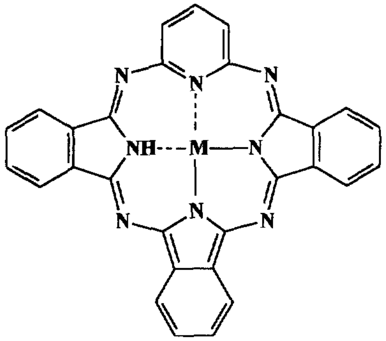
In 1957, Elvidge and co-workers [12,13] obtained the dark-red triisoindole–benzene macrocycle **2a**, by heating the benzene three-unit compound **3a** in boiling ethanol for 12 h in the presence of equimolecular amounts of 1,3-diiminoisoindoline (*route b*, Scheme 1). On the contrary, the pyridine three-unit product **3b** showed to be less reactive than **3a** and could not be converted into compound **2b**. The copper and nickel containing macrocycles **4a,b** were obtained by reacting the corresponding three-unit metal complexes **3c,d** with 1,3-diiminoisoindoline [14]. Both pyridine containing compounds **4a** and **4b** showed to be unstable in acidic and basic media.



2a X = CH
2b X = N (not formed)



3a X=CH; M=H_2; Y=nihil
3b X=N; M=H_2; Y=nihil
3c X=N; M=Cu; Y=H_2O
3d X=N; M=Ni; Y=H_2O



4a M=Cu
4b M=Ni

Recently, the formal substitution of one isoindole subunit in the phthalocyanine ring by a thiadiazole moiety has given rise to compounds **5a**,**b**. These were synthesized using a three-unit metal complex as precursor [15,16], as depicted in Scheme 2. This synthetic method represents a slight variation of *route b* (Scheme 2) since the condensation was carried out starting from the phthalonitrile, which is converted into more reactive intermediates by reaction with the solvent (phenol). The synthesis of such thiadiazole containing A_3B analogues with different substitution patterns is now available since the preparation of substituted three-unit precursors has already been reported [17,18].

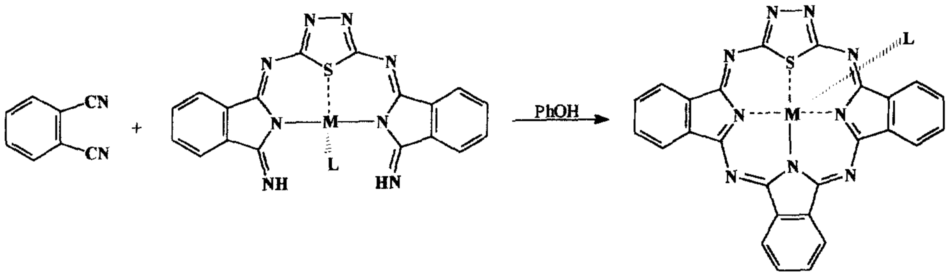
Among the A_3B phthalocyanine analogues, those in which one isoindole subunit has been replaced by a 1,2,4-triazole (Scheme 3) have received the trivial name of triazolephthalocyanines (Tpc) [19]. These azaporphyrins in which, beside the four *meso* nitrogen atoms, there are two further nitrogen atoms in β-position can also be formally designed as tribenzhexaazaporphyrins.

2. Synthesis of triazolephthalocyanines (Tpcs)

The two general synthetic methodologies previously discussed have been applied for obtaining the Tpcs (Scheme 3): a single-step metal template method (*route a*), and a two-step one (*routes b1* and *b2*).

The former allows the preparation of Tpcs bearing the same substituents in the three isoindole moieties. The latter represents a good strategy for the preparation of unsymmetrically substituted Tpcs.

Moderate yields (40–60%) are reached with *route a* [19], a statistical reaction in which the corresponding 1,3-diiminoisoindoline and the 3,5-diamino-1,2,4-triazole (guanazole) are reacted in a 3:1 molar ratio in the presence of a metal salt (acetate, tetrafluorborate or bromide) in refluxing 2-ethoxyethanol. Triazolehemiporphyrazine and phthalocyanine are side-products whose amounts are reduced by controlling the stoichiometry of the reaction, which is critical. Thus, a molar ratio

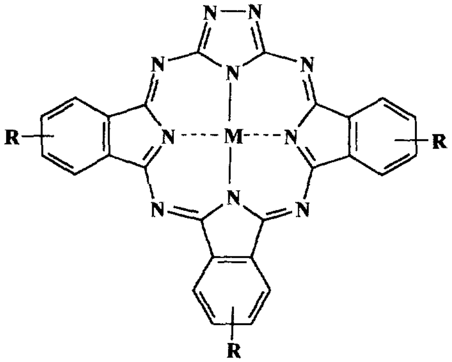


5a M=Zn, L = OH
5b M=Al, L = OH

Scheme 2.

1:1 of both reagents affords the corresponding triazolehemiporphyrazine as the only reaction product [20], whereas the employment of 5:1 as molar ratio causes an increase of the phthalocyanine formation.

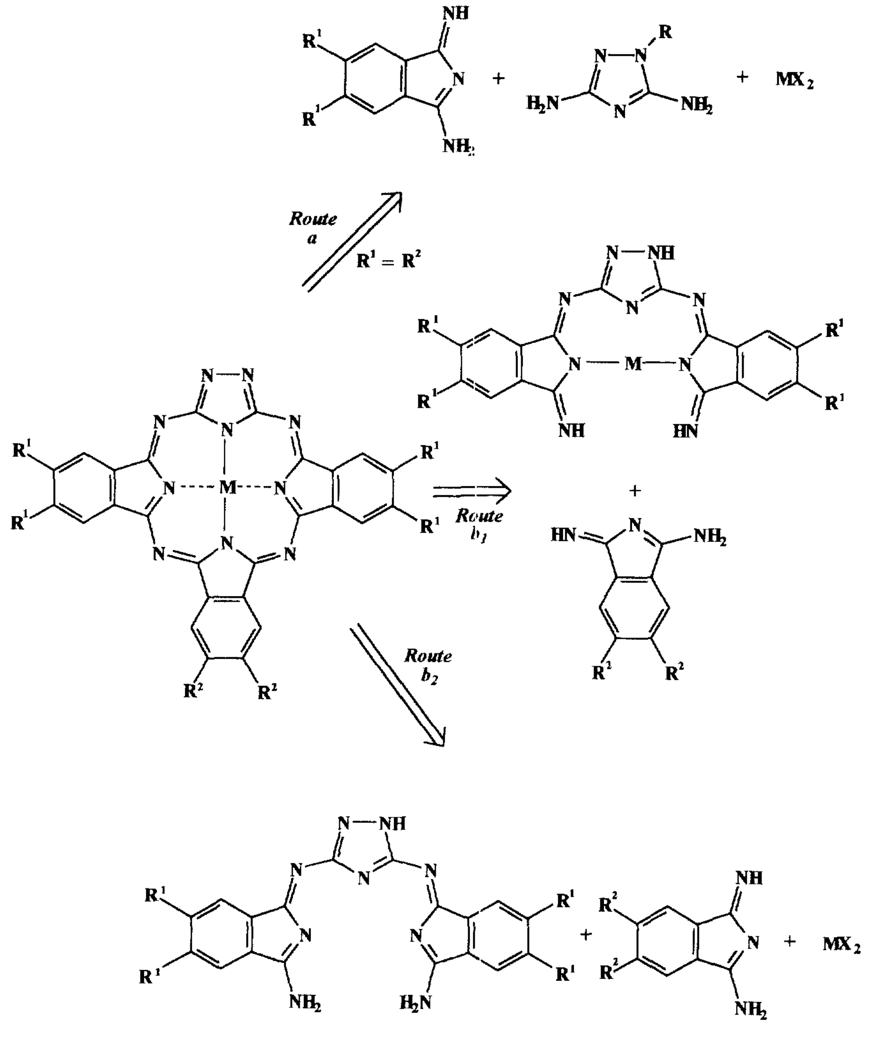
Non-substituted Tpcs have then been obtained with different inner metals such as Ni, Cu, Mg and Co (**6b**–**e**) [19,21] as well as Zn and Al [22] following the *route a*. Their purification showed to be tedious, due to the high insolubility of the macrocycles, as well as of the side-products: repeated trituration in hot alcoholic solvents (e.g. 2-ethoxyethanol) was necessary. The metal-free compound of this series (**6a**) could not be obtained by a direct non-template reaction [19]. However, demetallation of the magnesium complex (**6e**) when treated with trifluoroacetic acid afforded the free-base form, which was detected by FAB-MS but not isolated [21].



6 a $M = H_2$ $R = H$
b $M = Ni(II)$ $R = H$
c $M = Cu(II)$ $R = H$
d $M = Co(II)$ $R = H$
e $M = Mg(II)$ $R = H$
f $M = Ni(II)$ $R = OC_8H_{17}$

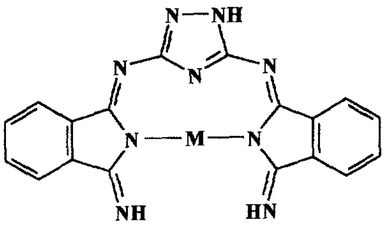
This one-step methodology was also applied for the preparation of nickel Tpcs **6f** and **8g** (the first obtained as a mixture of regioisomers) which bear the same substituents in all three isoindole units. The presence of alkyl or alkoxy chains in the isoindole rings gives rise to better solubilities, thus allowing chromatographic purification.

The two-step synthetic method was developed in order to achieve unsymmetrically substituted triazolephthalocyanines [23]. The preparation of the three-unit nickel complex **7a** was published by Torres and co-workers [24]. This compound can react with different substituted 1,3-diiminoisoindolines in equimolar amounts at relatively low temperature (55°C) to afford the corresponding triazolephthalocyanines in 35–60% yield [23] (Scheme 3, *route b1*). Alternatively, the reaction can be



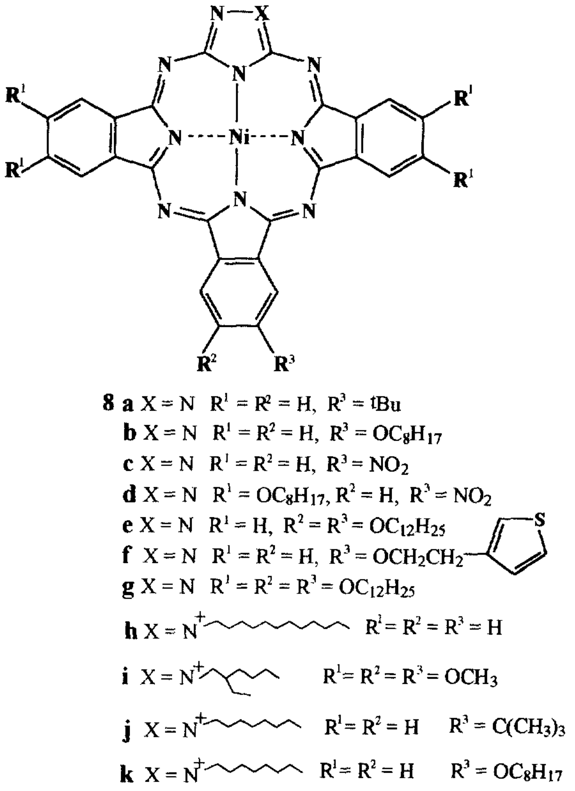
Scheme 3. Retrosynthetic scheme for the synthesis of triazolephthalocyanines.

undertaken by successive treatment of the corresponding metal-free three-unit compound **7b** [25] with nickel(II) acetate at 80°C and then with the adequate 1,3-diiminoisoindoline at lower temperature (55°C) (*route b2*). Yields are comparable for *routes b1* and *b2*.



7a $M = Ni$
7b $M = H_2$

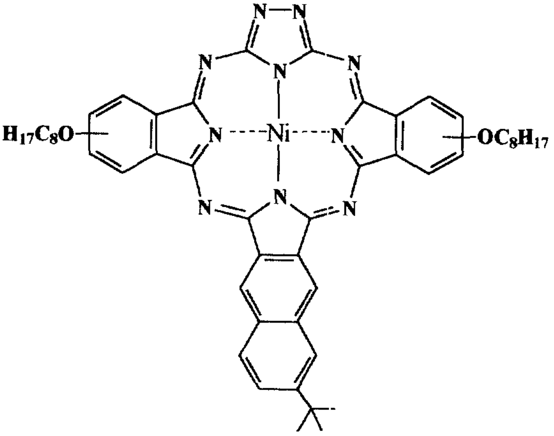
All compounds **8a–g** were prepared following this stepwise methodology [21,23,26]. The Tpcs bearing a single substituent, as well as the ones bearing nitro groups are moderately soluble in organic solvents, their purification being done by extracting them with hot chloroform and grinding them afterwards in methanol. Macrocycles bearing more than one alkyl or alkoxy substituent present good solubilities and can be purified by chromatography.



8 a $X = N$ $R^1 = R^2 = H$, $R^3 = {}^tBu$
b $X = N$ $R^1 = R^2 = H$, $R^3 = OC_8H_{17}$
c $X = N$ $R^1 = R^2 = H$, $R^3 = NO_2$
d $X = N$ $R^1 = OC_8H_{17}, R^2 = H$, $R^3 = NO_2$
e $X = N$ $R^1 = H$, $R^2 = R^3 = OC_{12}H_{25}$
f $X = N$ $R^1 = R^2 = H$, $R^3 = OCH_2CH_2$–
g $X = N$ $R^1 = R^2 = R^3 = OC_{12}H_{25}$
h $X = N^+$ $R^1 = R^2 = R^3 = H$
i $X = N^+$ $R^1 = R^2 = R^3 = OCH_3$
j $X = N^+$ $R^1 = R^2 = H$ $R^3 = C(CH_3)_3$
k $X = N^+$ $R^1 = R^2 = H$ $R^3 = OC_8H_{17}$

Substituted copper triazolephthalocyanines can be obtained in the same manner as the nickel compounds without difficulty [27]. However, the preparation of substituted metallated Tpcs other than the nickel and copper derivatives seems to need higher reaction temperatures and is still not well controlled [27].

The extension of the conjugated system is expected to allow the modulation of the triazolephthalocyanine electronic properties. Thus, new structural modifications have been successfully undertaken through the replacement of one to three benzene rings by naphthalene units, leading to compounds such as **9** [28].



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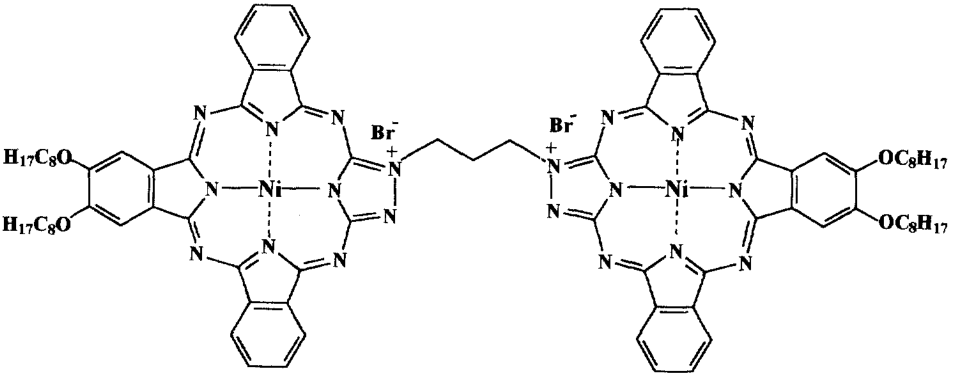
Soluble Tpcs substituted in the triazole moiety and so bearing a positive charge on the nitrogen atom (Tpcs **8h–k**) can be prepared in two ways: either by direct *N*-alkylation of the preformed macrocycle (**8h**–**k**) [27] or by template condensation of the corresponding *N*-substituted guanazole and the 1,3-diiminoisoindoline in a 3:1 molar ratio (**8h, 8i**) [19,21,27].

Tpc dimers have also been already prepared by connecting two Tpcs through their triazole subunits. This has been accomplished through *N*-alkylation reaction of two Tpcs with an aliphatic dihalide (see structure **10**) [28]. Such dimers can be seen as parents of binuclear phthalocyanines covalently linked through two to four-atom bridges, which are known for their electrocatalytic activity [29,30].



10

3. Structure and characterization of Tpcs

The molecular geometry of the non metallated triazolephthalocyanine **6a** was optimized by Ortí et al. [31] using the semiempirical AM1 method with the unrestricted Hartree–Fock (UHF) formalism. The interaction between the N–N bonds and the central methineimine macrocycle was calculated to be very weak, suggesting that the Tpc must be seen as 18-π carbon–nitrogen macrocycle connected to three peripheral benzenes and one N=N unit. On the other hand, the electronic structure was calculated at the HF ab initio 3–21G level. Due to the electronegative character of the triazole subunit, the HOMO is stabilized in going from the Pc to the Tpc and the oxidation potential is therefore increased. The introduction of the triazole ring also breaks the degeneracy between the LUMO and the LUMO + 1 since the LUMO, mainly determined by the triazole moiety, is more stabilized than the LUMO + 1. This feature leads the authors to expect well separated Q_x and Q_y absorption bands for this non metallated Tpc (**6a**). The stabilization of the LUMO also suggests that Tpcs are more easily reduced than Pcs. Unfortunately, experimental data are not available for comparison since until now the H_2Tpc has not been isolated [21]. Semi-empirical calculations (MNDO/d and Zindo approaches) concerning substituted and non substituted metallated Tpcs, for which experimental data are in fact available, are at this moment in progress [32].

Thus concerning metallated MTpcs, the experimental UV–vis spectrum of the nickel *tert*-butyltriazolephthalocyanine **8a** in chloroform is typical of soluble MTpcs [23] and is represented in Fig. 1, besides the spectrum of the same compound in trifluoroacetic acid and the spectrum of the nickel tetra-*tert*-butylphthalocyanine, for comparative purposes.

Compound **8a** presents in chlorofom solution a Q band at 623 nm that is quite blue-shifted in relation with the phthalocyanine Q band, due to the lower degree of charge delocalization. This blue shift has already been observed for other A_3B phthalocyanine analogues like the tribenzotetraazaporphyrin [11]. Another interesting difference between phthalocyanines and triazolephthalocyanines is that the latter show absorption bands between 470 and 580 nm and that the B band, which appears around 370 nm, is comparatively more intense for the Tpcs. When the spectrum of **8a** is registered in trifluoroacetic acid, the Q band at 650 nm drastically decreases and shifts to lower wavelengths (ca. 590 nm), while the B band broadens and undergoes a batochromic shift. The protonation of the basic triazole subunit should be responsible for these changes.

Concerning the IR features, triazolephthalocyanines give several characteristic vibrational bands [23]: one located at 1600 cm^{-1} (middle intensity) and three more between 1450 and 1500 cm^{-1} attributed to the C=N bonds, more intense than those which appear for the phthalocyanines in the same region. The *N*-alkylation of the Tpcs (**8h–k**) gives rise to new vibrational bands located at 1534 and 1573 cm^{-1}.

Proton magnetic resonance of the soluble nickel Tpcs can be recorded in chloroform and shows broad signals between 6.2 and 7.6 ppm for the aromatic

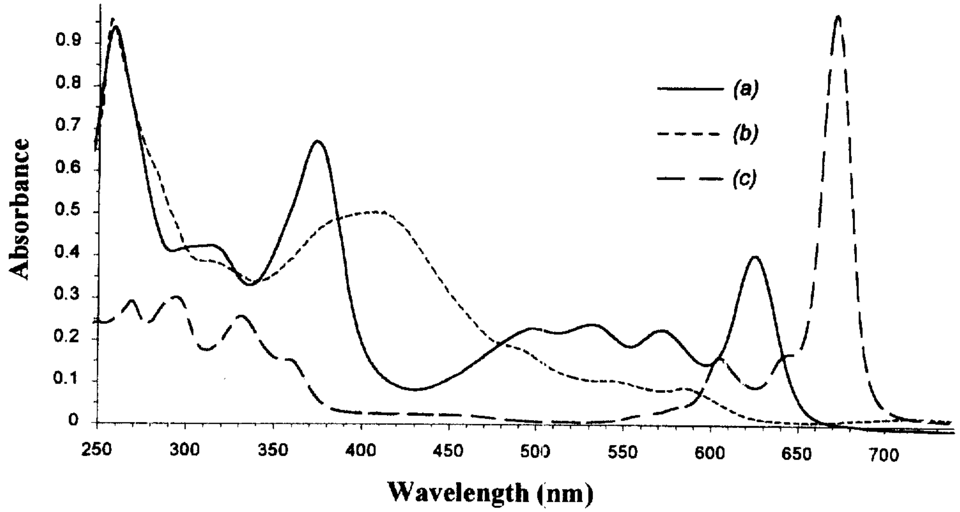


Fig. 1. UV–vis spectra of (a) **8a** in chloroform, $c = 2.1 \times 10^{-5}$ mol l^{-1}, (b) **8a** in trifluoroacetic acid, $c = 2 \times 10^{-5}$ mol l^{-1} and (c) nickel tetra-*tert*-butylphthalocyanine in chloroform, $c = 3.4 \times 10^{-6}$ mol l^{-1}.

isoindole protons. Aromatic hydrogens located in the *ortho*-position to the alkoxy substituents experience a strong shielding [23]. The broadening and low resolution of the signals may be explained by the fact that the central nickel atom probably facilitates the relaxation of the proximal nuclei. This effect can also be observed for nickel phthalocyanines [33]. The protonation of the macrocycle in the presence of some trifluoroacetic acid drops produces a shift of aromatic signals to lower fields (8.2–7.3 ppm).

Termogravimetric studies of substituted and non-substituted triazolephthalocyanines [34], have shown a high stability for these macrocycles, with decomposition temperatures above 550°C for the non-substituted compounds. The results are similar to those obtained for the corresponding substituted and non-substituted phthalocyanines.

4. Triazolephthalocyanines: potential building blocks for molecular organic materials

Interesting physical properties are expected for this new series of phthalocyanine analogues that we have called triazolephthalocyanines. However, for a real development of improved molecular Tpc-based materials, the formation of organized condensed phases is of great importance. In this regard, one may think that the aromaticity and the disk-like shape of these molecules could provide the ability shown by phthalocyanines to form columnar aggregates [35]. This would favour organization of triazolephthalocyanines at a supramolecular level in the construction of, for example, LB films. On the other hand, the replacement of one of the isoindole subunits by the polar 1,2,4-triazole moiety provides the amphiphilic features required for LB films construction [26,36,37]. Actually, those Tpcs presenting long aliphatic chains (such as **8e**, **6f** and others [27]), in which Van der Waals interactions and π–π ones are adequately balanced, give rise to Langmuir monolayers where the macrocycles stand perpendicular to the air–water interface, leaving the triazole subunit in contact with the water. On the other hand, substitution of the side-isoindole subunits by large groups (octyloxy) is not a favorable molecular structure for Langmuir film formation. Deposition by the vertical dipping method onto calcium fluoride substrates, made hydrophobic by previous deposition of three layers of fatty acid, is of Y-type and leads to in-plane oriented LB films when nickel(II) acetate is introduced in a 10^{-3} molar concentration in the water subphase [36].

Preliminary studies [26] revealed that Tpcs are promising materials for the development of electronic devices, since six-layer LB films made from compounds **8e** and **8f** showed a conductivity around $10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Resistance–temperature dependence experiments were performed for **8f**, showing a semiconducting behaviour and allowing the deduction of the activation energy, which was found to be around 0.15 eV. This low level explains the good conductivity of this compound. Moreover, for high temperatures (50–80°C), there was no irreversible increase of the resistance, opposite to other related phthalocyanines. It was also proved that, whereas the material in the LB film remains chemically unaltered, the presence of the gold electrode induces with time structural changes followed by an increase of the resistance value.

Finally, since triazolephthalocyanines are intrinsically non-centrosymmetrical compounds, they can be considered good targets for second harmonic generation [4,5]. In fact, the high value of the dipolar moments measured for several Tpcs (ca. 14 Debyes) [27] reveals an important asymmetry in the electronic distribution of those macrocycles, which is due to the acceptor character of the triazole ring. Within preliminary studies [38], third order polarizabilities in chloroform solution were measured by the EFISH technique for compounds **6f**, **8a**, **8b**, **8g**, **8i**. The absolute values of γ^{EFISH} at 1.907 μm fall in the range of $1–3 \times 10^{-33}$ esu, which is comparable to that obtained for non-centrosymmetrical phthalocyanines [4]. Second order non-linear polarizabilities (β) were deduced from the γ^{EFISH} values and also measured by the Hyper–Rayleigh Light Scattering technique at 1.34 μm. Typical values are in the range of $30–140 \times 10^{-30}$ esu. The results are, again, comparable to those of unsymmetrical phthalocyanines. The ratio $\beta^{\mathrm{EFISH}}/\beta^{\mathrm{HRS}}$ changes when varying the donor strength of the substituents at the isoindole ring; this result is promising with regard to the control of the non-linear response through chemical manipulation of the Tpc. Anyway, the high β and γ values, combined with the high dipolar moments, make Tpcs of great interest for being macroscopically organized by the presence of an external electrical field.

In conclusion, triazolephthalocyanines represent a new kind of porphyrin-like metallomacrocycles which can be easily prepared, structurally modified by conventional organic synthesis and organized at supramolecular level. Moreover, they show interesting performances as building blocks for the construction of molecular materials.

Acknowledgements

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