Hemiporphyrazines as Targets for the Preparation of Molecular Materials: Synthesis and Physical Properties

Fernando Fernández-Lázaro and Tomás Torres*

Departamento de Química Orgánica (C-I), Universidad Autónoma de Madrid, Cantoblanco, Madrid 28049, Spain

Bernd Hauschel and Michael Hanack*

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

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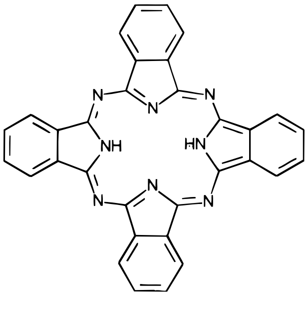
Contents

I. Introduction

Since their casual discovery,[1] the highly aromatic phthalocyanines **1**[2] (Pcs) have attracted much attention because of their unusual characteristics and properties. These are a consequence of the 18 π-electron cloud delocalized over an array of 18 C and N atoms. Such compounds are interesting targets as building blocks for the technology of new molecular organic materials with electrical and nonlinear optical applications.[3] The search for related metallomacrocycles with comparable or improved physicochemical characteristics and higher chemical flexibility from the synthetic point of view has become an important goal during the last years.



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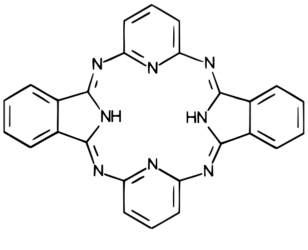
Hemiporphyrazines (Hps) are Pc analogues that, according to Campbell's proposal,[4] could be defined as four-unit macrocycles which bear two opposite-faced pyrrole units and two other (hetero-)aromatic moieties, all bound through aza bridges. The first example of this new class of nonaromatic cross-conjugated compounds was described in 1952 by Elvidge and Linstead while studying the condensation of 1,3-diiminoisoindoline with 2,6-diaminopyridine.[5-7] They obtained a 20 π-electron macrocycle **2**, which displayed completely different properties from those of the related phthalocyanine. This compound, having two pyridine moieties, received in the further literature the particular name of hemiporphyrazine (Hp)[8] as a consequence of a wrong application of Campbell's suggestion.[9] However, the name has been so widely accepted, that in this article we shall refer to other related compounds as hemiporphyrazine derivatives, by introducing the name of the (hetero-)aromatic moiety as a prefix. Indeed, the trivial name triazolehemiporphyrazine (H_2Thp) has been proposed for **3**.[10] Two years later, Linstead and co-workers succeeded in increasing the number of examples of this family by changing the diamino compound that was allowed to react.[11]



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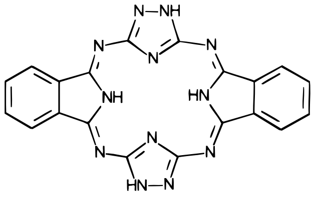

3

A common feature of all these compounds is not only their thermal stability, but also their lability in aqueous acidic media due to their Schiff base or iminic nature.[5]

This review will be devoted to the description of the hemiporphyrazines in a broad sense, and especially to the macrocycles containing two pyridine or two triazole rings, due to the higher attention paid to these two families in the literature.

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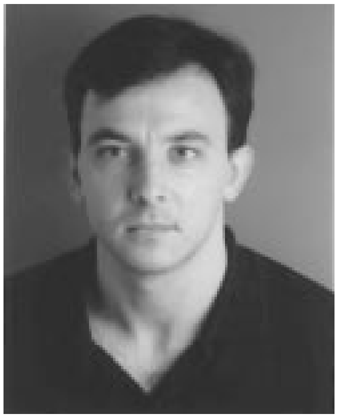


Fernando Fernández-Lázaro was born in Basel, Switzerland, in 1963. He received his diploma (1987) and Ph.D. (1992) from Autónoma University of Madrid (UAM). His doctoral thesis under the supervision of Professor Tomás Torres was concerned with the synthesis of triazolehemiporphyrazines and triazolephthalocyanines, and the study of their properties as new materials. After postdoctoral work with Prof. Dr. Dr. hc Michael Hanack (Universität Tübingen, 1993–1994), Dr. Mingotaud (C.R.P.P.-C.N.R.S., Bordeaux, 1995) and Professor Bruce H. Lipshutz (University of California, Santa Barbara, 1996–1997), he returned to Autónoma University as “Profesor Asociado”. His research interests are mainly directed toward the synthesis of new materials and the study and improvement of their properties.

Born September 21, 1951, Tomás Torres is currently “Profesor Titular” and Vice-Director of the Department of Organic Chemistry at the Autonoma University of Madrid (UAM). He recieved his diploma (1974) and Ph.D. (1978) at the same University, working at the Spanish National Research Council (CSIC) in Madrid (Professor Fariña). After two years (1978–1980) at the Department of Organic Chemistry and Spectroscopy of the Max-Planck-Institute for Biochemistry, in Martinsried bei Muenchen (Germany, Professor Dr. W. Schaefer) as a Max-Planck postdoctoral fellow, he joined (1981) a private company, Abello S.A.-Merck, Sharp and Dohme, as Senior Researcher, in Madrid. In 1985 he was appointed to the staff of the Autónoma University of Madrid. In addition to various aspects of synthetic, heterocyclic and supramolecular chemistry, his current research interests include the preparation and study of electrical and optical properties of molecular materials based on phthalocyanines and related compounds. He is the author of over 100 research papers and patents.

Bernd Hauschel was born in Rottweil in 1968. He studied chemistry in Tübingen where he was awared his diploma in 1994. He received his Ph.D. in 1997 while working in the group of Professor Hanack on the synthesis of hemiporphyrazines and phthalocyanines suitable for repetitive Diels–Alder reactions. During this time, he was supported by a Doktorandenstipendium of the Fonds der Chemischen Industrie. Presently, B.H. is working as a chemist at the Bayer AG in Leverkusen.

Michael Hanack is Professor of Organic Chemistry at the University of Tübingen, Germany. He studied chemistry in Freiburg, Bonn, and Tübingen, and received his Ph.D. in Tübingen while working in the group of Walter Hückel on the kinetics and solvolysis of *p*-toluenesulfonates. He then habilitated in Tübingen in the area of organofluorine compounds and joined the University of the Saarland at Saarbrücken as a Full Professor in 1971. In 1976 he returned to Tübingen where he worked for several years in physical organic chemistry before moving into materials science around 15 years ago. His main interests are the electrical and nonlinear optical properties of phthalocyanines, low bandgap polymers based on polythiophene, and electroluminescence of special organic compounds.

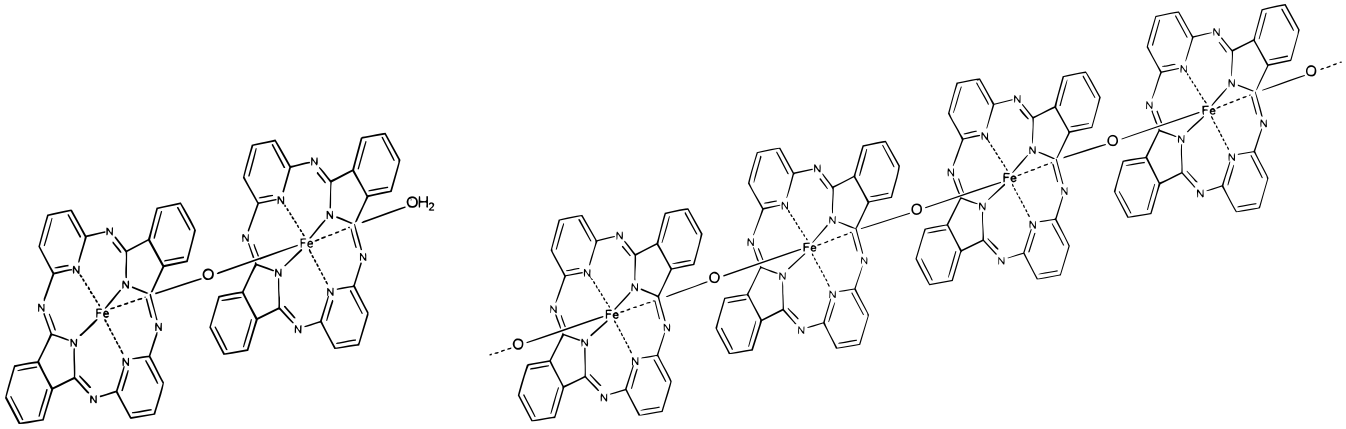
II. Synthesis

A. Hemiporphyrazines

A general procedure for the preparation of hemiporphyrazine **2** (H_2Hp) and some of its transition metal complexes (MHp) has been reported.[4,5,12] The extremely insoluble compounds are oxygen- and moisture-insensitive. Some studies on the electronic structure of this class of compounds have been performed.[13] The magnetic properties[14] and the electrochemical behavior[15] of the metal complexes have been also described.

Early NMR and IR studies on germanium and tin hemiporphyrazines proved the low degree of π-electron delocalization of the Hp ring and the high asymmetry of its ligand core, i.e., the isoindole nitrogens bound to the metal much more strongly than the pyridine ones.[9,16] As a consequence of this, metallohemiporphyrazinates, unlike phthalocyaninates, show an unusual tendency toward axial ligation (even with metals of d^8-d^{10} configuration like nickel, copper, or zinc, for which stable four-coordinated complexes would be expected) giving rise to 1:1 or 1:2 adducts with H_2O, hydrohalic acids and pyridine.[17] Thus, reaction of the metallic acetates with the free base **2** in boiling DMF yields the anhydrous (Ni^{2+}, Cu^{2+}) or the monohydrated (Co^{2+}, Zn^{2+}) derivatives, whereas reaction of the corresponding metallic

Chart 1



4 **5**

halides affords MHp(HX), for Zn^{2+}, or MHp(HX)$_2$, for Ni^{2+}, Co^{2+}, and Cu^{2+}. The bishydrate NiHp(H$_2$O)$_2$ has also been described.[17a]

The thermal stability of the hydrates depends to a great extent on the metallic ion, the nickel complex being the most easily dehydrated (at 100 °C, while the others at 220−240 °C). On the other hand, the hydrohalic adducts are much more stable (~300 °C) in solid state, but they easily dissociate upon solution in hot DMF, cold pyridine, or 0.5 M NaOH. The hydrated and hydrohalic adducts are stabilized by proton−ligand interactions with partial dissociation of the coordinated molecule, i.e., H$_2$O or HX. The spectroscopic data suggest the interaction of the acid protons with the outer nitrogens of the adjacent macrocyclic ligands, while the rest of the coordinated molecule (Cl or O) interact with the metallic ion. Moreover, the 1:1 adducts show six-coordinated geometries, what was explained by assuming either a dimerization of the molecules or the formation of chains with the adduct-molecules acting as bridging ligands.[17a]

This behavior has also been described in Mn^{2+} and Fe^{2+} complexes, showing that manganese complexes are oxygen-insensitive both in solution and solid state, whereas the iron ones are readily oxidized on heating or in solution.[18a]

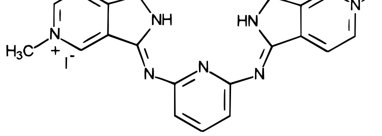
For all six metal series isomorphic forms have been identified. On the other hand, for certain given metallic complexes polymorphs have been described.[17a,18a]

The synthesis of ironhemiporphyrazinates has been the matter of a much deeper study, showing once again that hemiporphyrazines behave quite different from phthalocyanines.[18] Ironphthalocyaninates have a marked tendency to form μ-oxo dimers, which are readily transformed into quite oxygen- and moisture-insensitive L$_2$FePc bisadducts in the presence of nitrogenated bases (N-bases) or isonitriles.[19] In contrast, ironhemiporphyrazinates can afford four different types of μ-oxo dimers depending on the reaction conditions. Thus, treatment of a solution of FeHp·H$_2$O in a N-base solution with oxygen at room temperature can afford either the dimer (FeHpO)$_2$·H$_2$O, **4**, or the polymer (FeHpO)$_n$, **5**, (Chart 1) depending on whether traces of water are present or not. Heating the former compound in vacuo ($T >$ 150 °C) affords the dimer (FeHpO)$_2$ as an amorphous solid, which can be transformed into the polymer by heating at higher temperatures ($T >$ 300 °C). These μ-oxo Fe(III) and Fe(IV) compounds can be reduced in the presence of triphenylphosphine (PPh$_3$) in toluene or nitrobenzene to afford FeHp·H$_2$O, indicating that PPh$_3$ does not form stable adducts with FeHp.

Treatment of Fe(III) μ-oxo dimers with HCl is a classical method to generate chloroferric compounds. However, when the μ-oxo compounds **4** and **5** are treated with HCl in an organic solvent (e.g., DMF), reduction takes place generating FeHp·(HCl)$_2$, whereas in the absence of organic solvents an HCl adduct, (FeHpO)$_2$·HCl, is obtained. Treatment of this compound with water yields **4**, which indicates a weaker bond of the HCl molecule to the dimer than in the case of MHp(HCl)$_2$ (vide supra).[18c] The influence of peripheral alkyl substituents on the kinetic stability of metallohemiporphyrazinates in acidic media has been studied recently.[17d]

N-base bisadducts can be obtained by dissolving in the neat N-base either Fe(II) compounds, e.g., FeHp·H$_2$O or FeHp·(HCl)$_2$, Fe(III) compounds, e.g., **4**, or Fe(IV) compounds, e.g., **5**, under O$_2$-exclusion conditions. These adducts, FeHp·(N-base)$_2$, are readily oxidized, thus forming the μ-oxo dimer hydrate **4** in the presence of O$_2$/H$_2$O, whereas the reaction with O$_2$ under anhydrous conditions leads to the μ-oxo polymer **5**, which in turn decomposes to give **4** when allowed to contact moisture.[18]

The only example described of water-soluble hemiporphyrazine analogues corresponds to the dicationic free base **6** and its copper and nickel complexes, obtained by methylation of the corresponding diazahemiporphyrazine.[15c]



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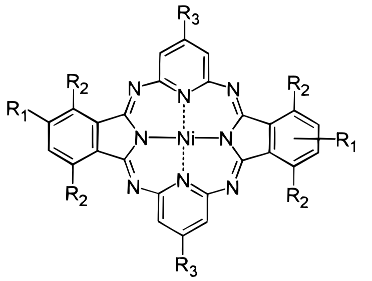
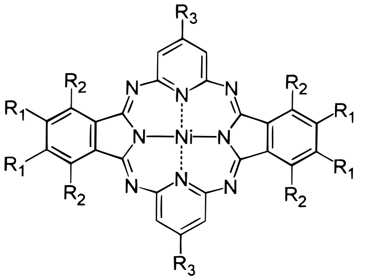


7 - 9

	R_1	R_2	R_3
7	tBu	H	H
8	OC_8H_{17}	H	H
9	tBu	H	OC_8H_{17}



10 - 14

	R_1	R_2	R_3
10	$CH_2OC_6H_{11}$	H	H
11	H	OC_5H_{11}	H
12	H	H	OC_6H_{13}
13	OC_4H_9	H	OC_4H_9
14	H	OC_4H_9	OC_4H_9

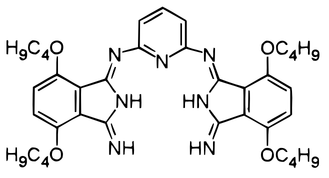
Figure 1.

On the other hand, the solubility of the parent compound **2** and its metal complexes in organic solvents is very low. For this reason attempts have been made in order to improve it by introduction of peripheral lipophilic chains, either in the isoindole moiety or/and in the pyridine one.

Several alkyl- or alkoxy-substituted nickelhemiporphyrazinates of varying solubility are accessible when the corresponding diiminoisoindolines, diaminopyridines, and nickel acetate are used as starting materials.[20] Figure 1 shows some representative examples.

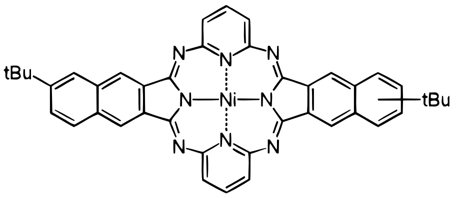
Compounds **7**−**9** are present as a mixture of constitutional isomers exhibiting either C_{2v} or C_{2h} symmetry (ratio ~1:1) due to the relative orientation of the peripheral substituents on the isoindole moiety.

As reported by Elvidge and Linstead, the metal-free macrocycle **2** (H_2Hp) is formed directly during the condensation of unsubstituted 1,3-diiminoisoindoline with 2,6-diaminopyridine.[5] Subsequent metalation is easily achieved by reaction of **2** with, e.g., nickel acetate. However, this two-step synthesis of NiHp is not applicable to the preparation of all the compounds shown in Figure 1. Thus, for example, in the case of 4,7-dialkoxy-1,3-diiminoisoindolines it is supposed that steric hindrance prevents the formation of the macrocycle during the condensation with 2,6-diaminopyridine in the absence of a metal ion. Only acyclic precursors of the corresponding hemiporphyrazine free base, e.g., **15**, are present in the reaction mixtures.[20a] The NiHps depicted in Figure 1 are accessible by reaction of the corresponding acyclic precursors with the appropriate 2,6-diaminopyridine in the presence of nickel acetate, thus using the template effect of the metal ion.

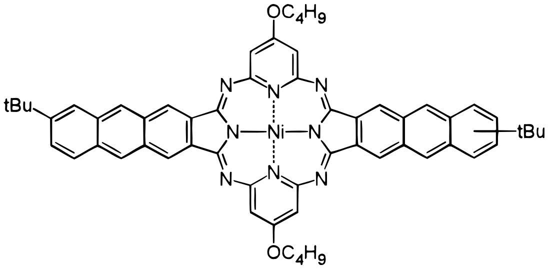


15

Annulated nickelhemiporphyrazinates have also been reported.[20b] In analogy to the NiHps **7**−**9**, compounds **16** and **17** are obtained as a mixture of C_{2h}/C_{2v} isomers (ratio ~1:1).



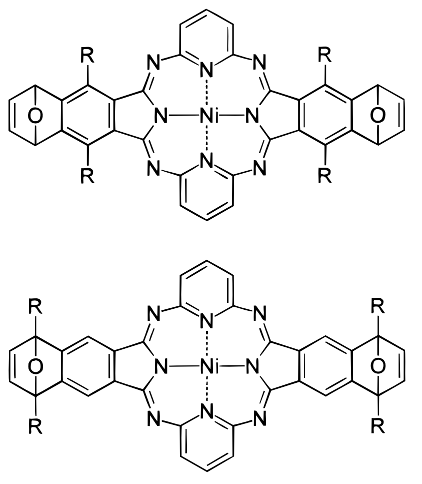
16



17

Metallohemiporphyrazinate-based polymers were prepared according to two different strategies, either following the so-called "shish-kebab" approach or synthesizing ladder polymers via the repetitive Diels−Alder reaction. In both cases, the monomeric units are arranged in a fixed way along the polymer chain, namely either stacked or planar.

The reaction of metallomacrocycles with bidentate ligands to give "shish-kebab" polymers has been widely applied in the case of the related phthalocyanines.[2,3d,21] Polymers consisting of stacked MHp units (M = Si, Ge, Sn) and O^{2-} as bridging ligand are generally prepared by starting from the monomeric dichlorocomplexes $MHpCl_2$. Alkaline hydrolysis of these compounds leads to the corresponding dihydroxides $MHp(OH)_2$, which afford the polymers $[MHpO]_n$ upon thermal treatment.[9,16,22] Reaction of the mentioned dihydroxy complexes with bifunctional alcohols or bisphenols also leads to "shish-kebab" polymers.[23] The related $[FeHpO]_n$ (**5**) is accessible by treating H_2Hp with iron(II) acetate in hot ni-



18 R = OC_4H_9
19 R = OC_6H_{13}
20 R = C_6H_{13}

21 R = C_5H_{11}
22 R = $C_{10}H_{21}$

Figure 2.

trobenzene, whereby the solvent acts as oxidizing agent.[18d]

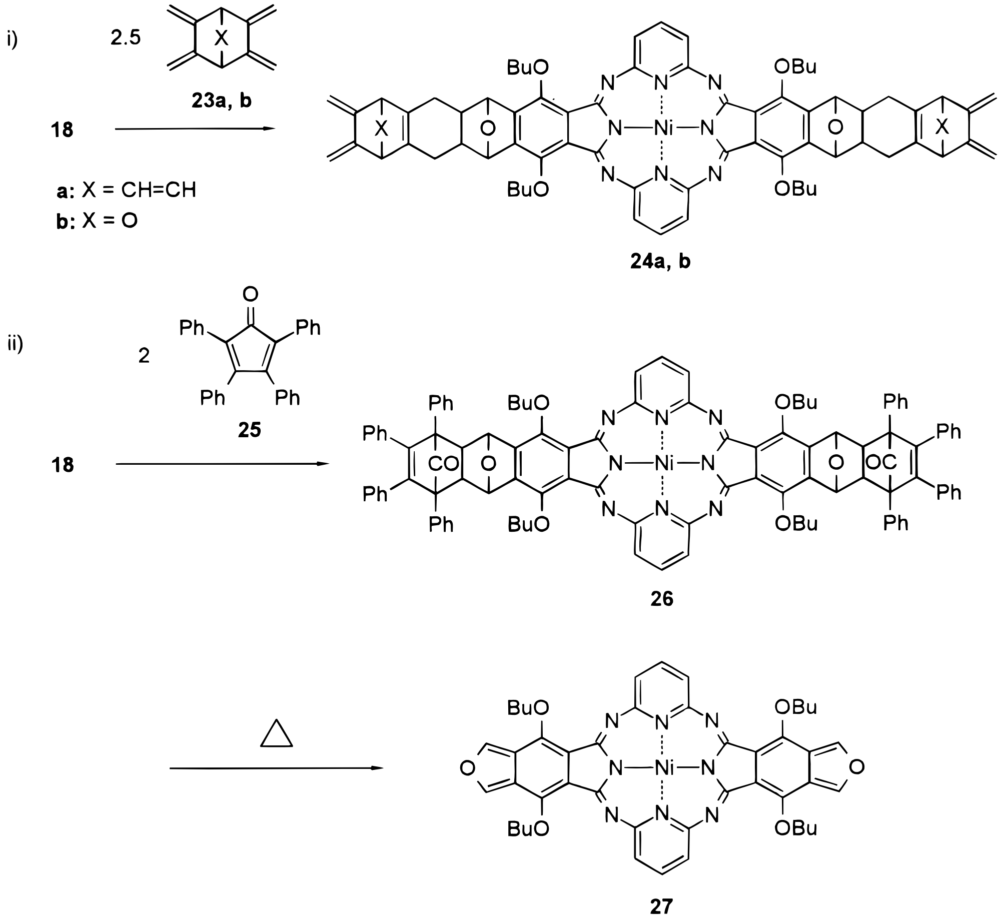
These μ-oxo polymers have been extensively studied with respect to their structures and their magnetic and conducting properties before and after oxidative doping. Results are described in detail in the last two sections of this article.

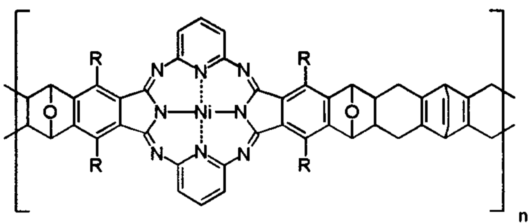
Attempts to prepare ladder-type structures in which the Hp subunits are fused to form a double-stranded polymeric chain were reported by Packham[24] and by Wöhrle.[25] They synthesized a number of different polymers from the corresponding tetranitriles and diamines in polycondensation reactions. The obtained products proved to be insoluble and structure elucidation was therefore limited. However, interchain linkings and incomplete cyclizations are likely to occur during this polycondensations. The thermal stabilities of the obtained products were generally high: decomposition in air started at 350−400 °C. The electrical conductivities of the polymers varied between 10^{-16} and 10^{-8} S cm^{-1} (300 K).

The synthesis of ladder polymers of high structural regularity is possible via the repetitive Diels−Alder reaction.[26] It can be carried out either with bis-dienophiles ("AA-monomers") and bis-dienes ("BB-monomers") or starting from a diendienophile ("AB-monomer"). Various substituted diepoxyhemi*naphtho*porphyrazines, e.g., **18**−**22**, have been prepared as AA-monomers for such a reaction (Figure 2).[27] Again, the introduction of lipophilic side chains is necessary to achieve sufficient solubility of the bis-dienophiles. The 1,6:16,21-tetraalkoxy-substituted Hps **18** and **19** proved to be the best compromise with regard to the yields, the solubility, and the reactivity in Diels−Alder reactions. Due to the relative orientation of the epoxy bridges, compounds **18**−**22** are present as a mixture of syn and anti isomers.

As outlined above, complementary BB-monomers are required for a polymerization, e.g., **24** and **27**. Two strategies have been used to prepare hemiporphyrazine-based bis-dienes (BB-monomers), both starting from **18** (Scheme 1).

Scheme 1





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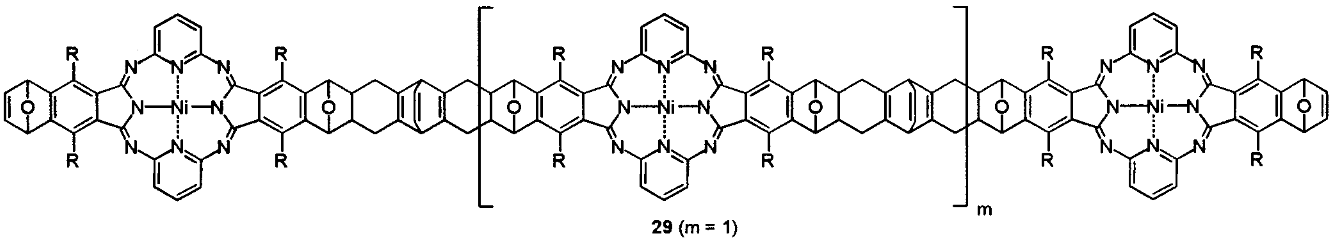
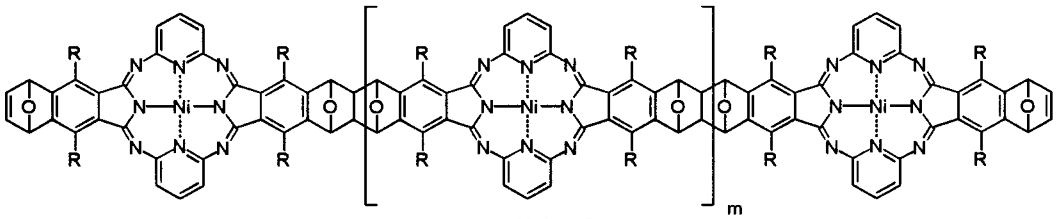


29 (m = 1)
30 (m = 3)
31 (m = 5)
32 (m = 7)



33 (m = 0)
34 (m = 1)

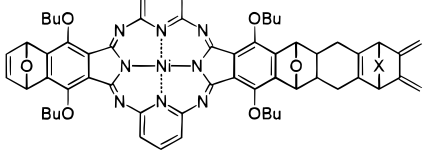
R = OC_4H_9

Figure 3.

The first strategy consisted of treating **18** with an excess of the tetraenes **23a**,**b**. The occurring exo-selective Diels–Alder reactions led to the BB-monomers **24a**,**b** as major products.[27c] Repetitive Diels–Alder reaction of **24a** with an equimolar amount of **18** gave the insoluble polymer **28** (Figure 3). Compounds **18** and **24a** were also used for a stepwise and controlled synthesis of ladder oligomers.[17c] First, trimer **29** was prepared by reaction of **24a** with 2.5 equiv of **18**. To obtain the pentamer **30**, two units of tetraene **23a** were added to the trimer. Subsequent reaction with 2.5 equiv of **18** furnished **30**. The highest oligomer prepared according to this strategy was the still-soluble nonamer **32**.

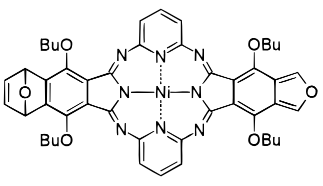
The second route takes advantage of a thermal decomposition reaction of the precursor molecule **26**. It was synthesized by addition of two units of 1,2,3,4-tetraphenylcyclopentadienone (**25**) to **18**.[28] Heat treatment of the precursor **26** (e.g., boiling toluene) led to the bis-diene **27**, whereby loss of CO and 1,2,3,4-tetraphenylbenzene occurred. Compound **27** is a reactive intermediate and is, therefore, always generated in the presence of trapping dienophiles. For example, generation in the presence of an excess of **18** gave rise to the trimer **34**. Exo and endo addition to the isobenzofuran moieties occurred during this double Diels–Alder reaction.

AB-monomers such as **35** and **36** can be prepared by following the above-described routes if the relative amounts of **23** or **25** are chosen appropriately (0.4–1 equiv).[27b,28]



35a, b

a : X = CH=CH
b : X = O



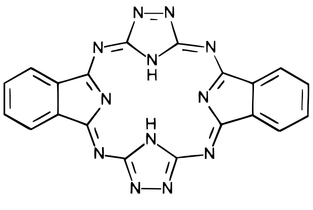
36

Attempts to transform the model compound **34** into its conjugated counterpart by using the Lewis acid $SiMe_3I$ were unsuccessful. A successful route which includes the use of bis-dienes exhibiting two isobenzofuran fragments was reported by Schlüter and coworkers: The mentioned bis-dienes were polymerized with polycyclic aromatic hydrocarbons in a first step. The obtained ladder polymers were then aromatized by full dehydration with *p*-toluenesulfonic acid.[29] The hemiporphyrazine **26** could be subjected to a similar approach if full dehydration works with a Lewis acid or a base, since alkyl- or alkoxy-substituted NiHp are not stable to strong protonic acids.[17d] This approach would afford conjugated ladder polymers consisting of hemiporphyrazine subunits. These hypothetical compounds are expected to combine the advantage of high thermal and mechanical stabilities with extraordinary electrical and optical properties.[30]

B. Triazolehemiporphyrazines

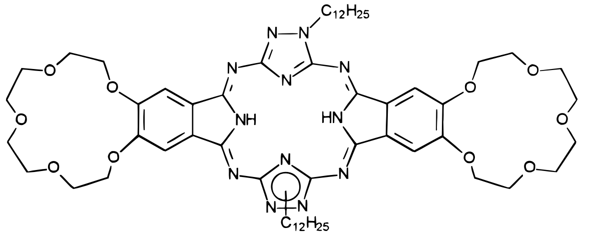
The first synthesis of this class of compounds was carried out by Campbell by reacting *o*-dicyanobenzene and 3,5-diamino-1,2,4-triazole (guanazole) to afford **3**.[4] In this patent, up to seven different substituted triazolehemiporphyrazines (H_2Thp) and some metalcomplexes (Co, Mg, Zn, Pb, and Fe) are described, but it offered neither chemical nor analytical proofs other than elemental analyses to corroborate the structures. Almost 15 years later, Smirnov et al. described the unsubstituted compound by reaction of diiminoisoindoline and guanazole and prepared the Cu, Ni, Co, Zn, and Cd complexes, presenting only the IR and the UV−vis spectra in this and in a subsequent paper.[31]

However, the first detailed study on triazolehemiporphyrazines was published in 1989.[32] The parent compound was synthesized by both the dinitrile and the diiminoisoindoline methods. Two triazole-substituted macrocycles were also reported, namely the diphenyl- and the didodecyltriazolehemiporphyrazines, the first being already described in Campbell's patent.[4] The compounds were characterized by means of IR, UV−vis, FAB-MS, ^{1}H− and ^{13}C NMR, and ^{13}C CP/MAS. Attempts to oxidize **3** to the corresponding aromatic form **37**, isoelectronic with phthalocyanine, by both chemical and electrochemical methods proved to be unsuccessful.[33] Moreover, a MNDO study was performed to answer the question of whether these molecules could become aromatic.[32] The results showed the antiaromatic compound **3** to be much more stable than the hypothetical aromatic one, **37**. The explanation lies in the instability of the substructure of 1,2,4-triazoline-3,5-diimine that one triazole ring must adopt for the aromatization of the whole molecule. Recent theoretical calculations corroborate this fact.[34] The further preparation of related aromatic compounds having only one triazole moiety also reinforced the explanation given above.[35]


37

In view of the extreme insolubility of the triazolehemiporphyrazines in nonacidic media,[10] which prevents further studies on these compounds (vide infra), several attempts have been carried out to introduce lipophilic substituents either in the triazole[32,36] or in the isoindole moieties.[37] While the former way enhances the solubility of the corresponding compounds in chloroform, the latter proved to be insufficient to ensure enough solubility.

Once it was shown that N-triazole substitution is the determinant key for high solubilities, the efforts were directed to obtain specifically designed soluble targets such as **38**[38] and **39**.[39]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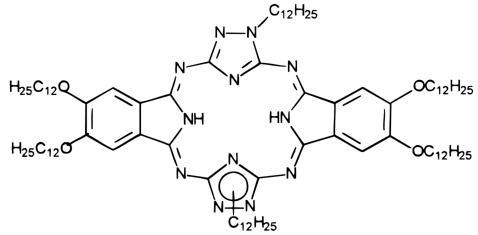
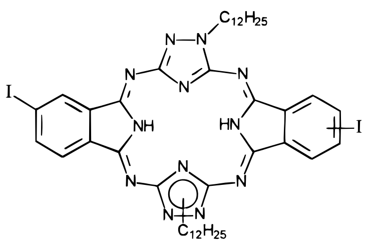

39

^{1}H NMR and UV−vis experiments performed on **38** have shown significant changes in the corresponding spectra on addition of large alkali metal ions such as K^+, Rb^+, and Cs^+.[38] Cooperative cofacial interactions between different molecules promoted by intermolecular cation complexation of the crown units, i.e., aggregation phenomena, have been proposed in this case.[40]

Compound **38** has been deposited in LB films (vide infra), while the liquid crystalline character of **39** has been recently studied.[39b]

The statistical reaction of substituted diamino(hetero)aromatic compounds with diiminoisoindolines is not regioselective. Mixtures of regioisomers are obtained when one of the reagents or both are unsymmetrically substituted. Thus, for example, compound **38** is actually a mixture of two isomers in a 60:40 ratio as determined by HPLC. On the other hand, triazolehemiporphyrazine **40** has shown to be a mixture of four structural isomers difficult to separate.[41]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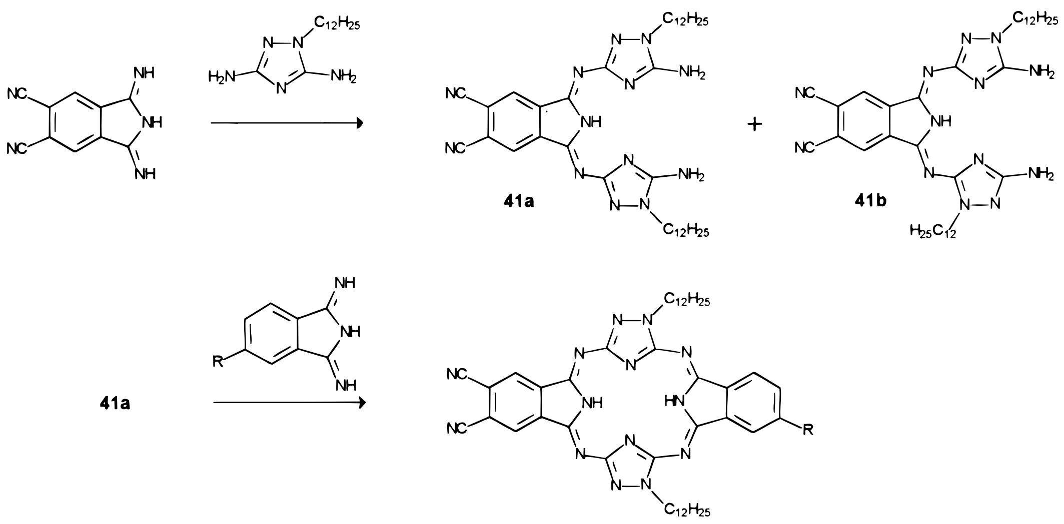
The general trend observed is that the more insoluble the macrocycle, the higher the yield. Thus, the unsubstituted (**3**) and the isoindole-tetrasubstituted compounds can be prepared in high amounts

Scheme 2

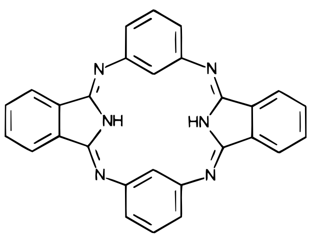


in 75–85% yield, while the triazole-disubstituted and the triazole-isoindole-hexasubstituted ones (e.g., **38**) are obtained in 35–45%, these results pointing out to the insolubility of the intermediate/macrocycles as one of the major driving forces in the reaction. On the other hand, the purification is more easily achieved in the soluble compounds (chromatography and/or recrystallization from DMF, heptane, etc.) than in the insoluble ones (trituration in hot methanol, eventual recrystallization from TFA losing material).

The only regioselective approach described up to now is depicted in Scheme 2 and represents a general stepwise methodology.[42] The reaction of 5,6-dicyano-1,3-diiminoisoindoline with 1-dodecyl-3,5-diamino-1,2,4-triazole afforded a mixture of the three-unit isomeric compounds **41a** and **41b** in a 7:1 ratio. After chromatographic separation, the major component **41a** was reacted with different monosubstituted diiminoisoindolines to afford the unsymmetrically substituted triazolehemiporphyrazines in good yields.

C. Other Hemiporphyrazines

The preparation of hemiporphyrazinic systems other than those described above has been much less developed. Thus, few examples of symmetrical hemiporphyrazines have been described. Among them, compound **42**,[25,43,44] bearing two benzene units, has been the most widely studied and was cited in 1954 by Elvidge and Linstead for the first time.[11]

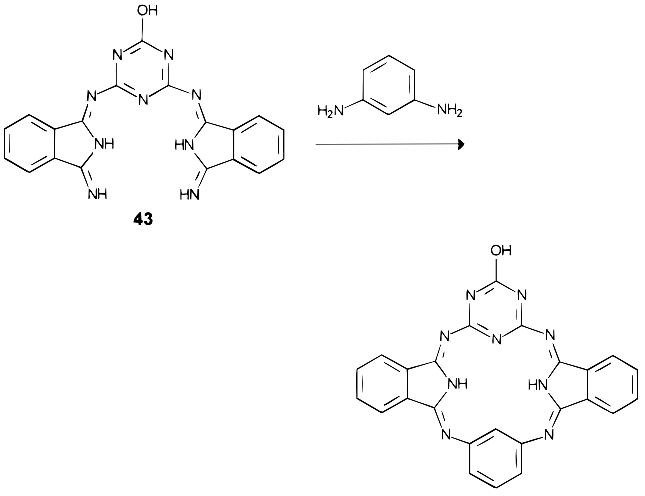


42

Other symmetrical hemiporphyrazines have been obtained by reaction of diiminoisoindoline with 2,7-diaminonaphthalene,[11] 2,8-diaminoacridine,[11] 3,5-diaminopyridine,[11] 2,4-diamino-6-chloropyrimidine,[31a] 2,4-diamino-6-chloro-*s*-triazine,[31b] 2,4-diaminotoluene,[43a] 2,5-diaminothiadiazol,[45] 2,7-diaminofluorene,[46] 2,7-diaminodiphenylene sulfone,[46] 2,4-diamino-3,4-dicyanothiophene,[47] and bis(5-amino-1,3,4-thiadiazole-2) disulfide,[48a] among others.[48b] On the other hand, there are two routes to achieve the synthesis of mixed hemiporphyrazines containing two different (hetero-)aromatic moieties placed face-to-face, namely the statistical and the stepwise ways, the latter being the most widely used.

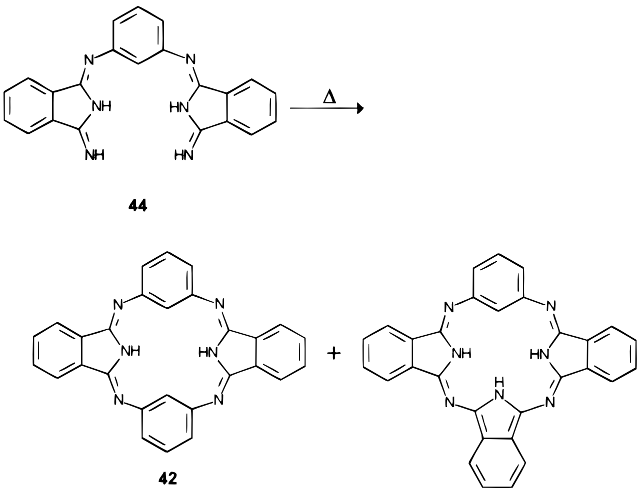
Although the stepwise way was already described to afford symmetric hemiporphyrazines,[43,44a] the first successful attempts to obtain mixed hemiporphyrazines using the stepwise method were carried out by Russian authors.[44a,49] Thus, for example, they claimed the synthesis of mixed triazinohemiporphyrazines in 25–60% yield by reaction of the three-unit compound **43** (Scheme 3) with equimolar amounts of different diaminocompounds (1,3-diaminobenzene, 2,6-diaminopyridine, and 2,6-diaminochloropyrimidine). The corresponding metal complexes were obtained by treatment of the free bases with metallic salts.

Scheme 3



In a similar way, these and other authors have described a variety of mixed hemiporphyrazines with the couples benzene−thiophene (obtained from the benzene three-unit compound in 53% yield),[47] benzene−thiadiazole (obtained from the same compound in 52% yield),[50] pyridine−thiadiazole (obtained from the pyridine three-unit compound in 63% yield),[50] and benzene−triazole (obtained from the benzene and triazole three-unit derivatives in 47% and 52% yield, respectively).[51] In all cases, the authors provided UV−VIS and/or IR data and elemental analyses to confirm the structures of the compounds. However, they did not describe the formation of any symmetrically substituted hemiporphyrazines as byproducts. The last point is extremely striking, taking into account previous works by Baguley and Elvidge,[43b] in addition to the thermal lability of some three-unit compounds related to **44** (Scheme 4).[52] Some more recent works describe the reaction of three-unit derivatives with diamino compounds to yield mixtures of the mixed and the two possible symmetric hemiporphyrazines.[10,52] Thus, for example, the reaction of the triazole compound **45** with 1,3-diaminobenzene afforded a mixture of the macrocycles **46**, **3**, and **42** in 26%, 36% and 23% yield, respectively (Scheme 5). A mechanism has been proposed[52] in which three different pathways operate simultaneously: the diamine could either react with the two "outer" iminic bonds or split the three-unit compound in two dimeric structures by reaction with an "inner" imino group,[43b] the third pathway being the thermal cleavage of the three-unit compound.[43a] In the same paper it was also pointed out that the statistical synthesis, although also giving a mixture of the three products, leads to a better yield of the mixed hemiporphyrazine **46** (42%).

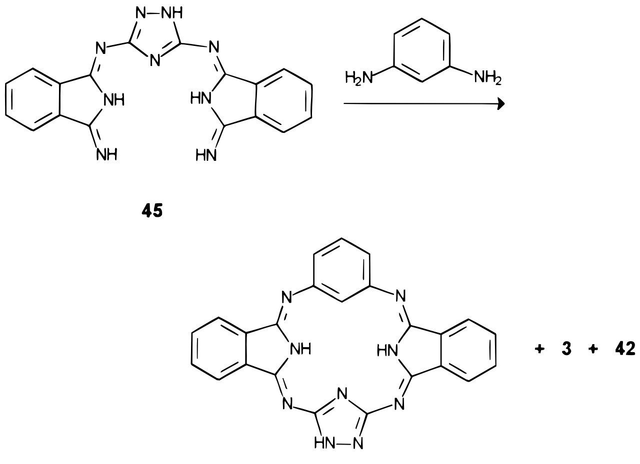
Scheme 4



44

42

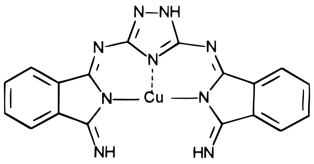
Scheme 5



45

46

On the other hand, attempts to stabilize the three-unit compounds by introduction of a metallic ion have led to less reactive metal complexes such as **47**, being unsuccessful until now the efforts for obtaining metallotriazolehemiporphyrazines from them by reaction with diamino derivatives.[52] However, the reaction of this kind of three-unit compounds with diiminoisoindolines has succeeded in the preparation of other metallomacrocycles.[53]



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The statistical method of preparing hemiporphyrazines has been much less studied, although it has been described that this method provides better yields of mixed hemiporphyrazines in some cases where mixtures of products are obtained by the stepwise method. This is the case, for example, of the pyridine−triazole and benzene−triazole hemiporphyrazines.[52]

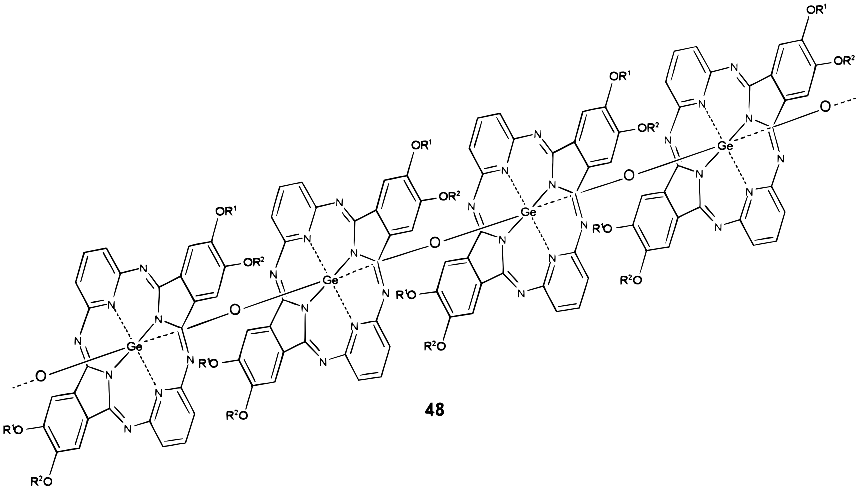
III. Molecular Organization of Hemiporphyrazines in Condensed Phases

The potential nonconventional physical properties of hemiporphyrazines are expected, as in the case of phthalocyanines,[2] to be highly dependent on the organization of the metallomacrocycles at supramolecular level.

Some efforts have been made to study the organization of hemiporphyrazines in macroscopic assemblies and condensed phases, namely in crystals, liquid crystals, and Langmuir−Blodgett films.

The first crystal structure reported for a hemiporphyrazine was NiHp by Speakman in 1953.[54] The compound was described as nonplanar, unlike Pcs. This structure was reinvestigated later[55] together with the free ligand monohydrate $H_2Hp \cdot H_2O$.[55,56] Both compounds have a marked nonplanar saddle shaped geometry and present similar column-like packing, the hydrogen bonding in $H_2Hp \cdot H_2O$ playing an important role in these properties. In contrast, the anhydrous ligand form, H_2Hp, and the metal complex monohydrates, $MHp \cdot H_2O$ (M = Mn(II), Co(II), Cu(II), Zn(II)), all have a planar geometry formed by the metal ion and the macrocyclic ring.[57] In compounds $MHp \cdot H_2O$ a water molecule in axial position leads to a square-pyramidal geometry. The molecules in the case of H_2Hp are parallel stacked with an interplanar spacing of 3.36 Å, comparable to those of phthalocyanine (3.38 Å). This is not the

Chart 2



48

case of the metal complexes MHp·H_2O which show a noncolumnar packing due to weak hydrogen bonding between the water molecules and two nitrogen atoms of the aza bridges.

Crystallographic data of axially disubstituted compounds such as bis(pyridine)nickelhemiporphyrazinate,[17b] α-difluorogermaniumhemiporphyrazinate,[58] and bis(ethylene glycol monoethyl ether)germaniumhemiporphyrazinate[59] have been also reported. In the last compound, for example, the hemiporphyrazinic system is completely planar with noncolumnar molecular packing in the crystal. Similar results have been obtained for the *trans*-bis(3,3-dimethyl-1-butynyl)germaniumhemiporphyrazinate which show a mostly planar GeHp moiety, but in this case the Hp ligands are parallel stacked.[60]

More recently, the crystal structure of the unsymmetric linear (*μ*-oxo)hemiporphyrazinatoiron(III) dimer **4** containing six- and five-coordinated iron atoms (one of them linked to a water molecule) has been described.[18b] The dimers are paired coaxially to form tetramers, which are in turn connected via a two-dimensional net of hydrogen bonds.

The crystal structure of the first polymeric *μ*-oxo-bridged iron complex **5**, *catena*-(*μ*-oxo)(hemiporphyrazinato)iron(IV) $(FeOHp)_n$, was determined in 1984[18d] from single-crystal, three-dimensional X-ray diffraction counter data. Distorted FeHp units stack along the *b* axis and are linked into polymeric, uniformly spaced, linear chains by axially bound oxygen bridges. Mössbauer spectral studies at different temperatures revealed that there are two iron sites in the chain as a result of the disorder of the oxygen atoms. Magnetic susceptibility studies indicated that the iron ions are antiferromagnetically coupled in an alternating chain. The severe distortion or saddle shape of the FeHp units, that probably arises from the space requirements of the central iron atom, is in sharp contrast to the planar GeHp moiety in other above-mentioned complexes.[60] Two adjacent chains of $(FeOHp)_n$ are packed according to an antiparallel arrangement.[18d]

Until now no examples of crystal structures for triazolehemiporphyrazines have been reported; however, very recently the liquid-crystal behavior of adequately substituted triazolehemiporphyrazines was described for the first time.[39b] Thus, compound **39** and its copper and nickel complexes present diffraction patterns, at 50 °C, unambiguously characteristic of a mesomorphic phase. The data are consistent with a columnar hexagonal network with a lattice constant (shortest distance between neighboring column axes) of ~31 Å. A sharp maximum at about 3.3 Å in each case corresponds to the short-range correlation between stacked molecules. Finally, a diffuse maximum at about 4.5−4.6 Å corresponds to interferences between the conformationally disordered aliphatic chains. These data are equivalent to those found in related phthalocyanines[2] and point out the possibility of inducing organization in appropriately designed hemiporphyrazines.

The study of the Langmuir−Blodgett film[61] properties of hemiporphyrazines has been delayed because of the slow development of soluble compounds. Indeed, there are only three reports on this matter.[62,63] On the one side, substituted triazolehemiporphyrazines **38** have shown to originate well-ordered defect-free multilayers.[62a] By using IR linear dichroism and ESR experiments it has been pointed out that the molecules are arranged in aggregates of ~50 molecules on average, possessing a high degree of in-plane orientation. Taking into account the experimental data, a stack-of-cards model has been proposed for these molecular aggregates, induced during the deposition process.[62a] Besides, it has been shown that shearing of a Langmuir film of triazolehemiporphyrazines by a rotating disk can induce orientation of surfactant molecules at the gas−water interface. By this method, in-plane-oriented Langmuir−Blodgett films of triazolehemiporphyrazine **38** have been obtained.[62b]

On the other hand, the deposition behavior of the polygermanoxanehemiporphyrazinate **48** has been studied[63] (Chart 2). After careful analyses (including X-ray investigations and IR and UV dichroisms) it was demonstrated that the oligomers are deposited with their main axes parallel to the dipping direction, although it seems that the consecutive macrocycles are rotated to an eclipsed conformation along the Ge−O−Ge axis.

Both reports point out a hypothetic organization of crown-ether supporting hemiporphyrazine polymers, which would lead to a supramolecular architecture of ionic channels in LB films.

IV. Hemiporphyrazines as Units for Molecular Organic Materials

The chemical flexibility of metallohemiporphyrazines described before provides an excellent opportunity to vary the electronic structure through ligand and metal modifications, thus allowing a systematic correlation of these changes with the modification of the properties. Hemiporphyrazines have received little attention as building blocks for new materials most probably due to the fact that they display lower chemical stability than phthalocyanines and to the nonavailability of soluble compounds until recent times.

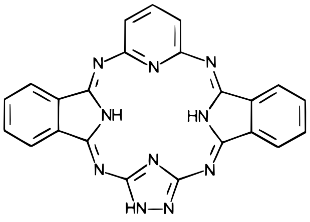
Works in this field have been mainly focused in two directions, namely electrical conductivity and NLO (nonlinear optical) properties.

The first report on the electrical conductivity of Hps established in 1972 their insulating character, with σ values, at 100 °C, between 10^{-7} and 10^{-17} S cm^{-1} for **2**, **42** and some other Hps.[64] Moreover, the variation of the conductivity of hemiporphyrazine **2** and its copper complex thin films compared to other macrocycles, on exposure to different gases, have been investigated. This study concluded that both compounds are inert to N_2, O_2, CO, CH_4, SO_2, CO_2, H_2, NH_3, H_2S, N_2O, NO_2/N_2O_4, NO, Cl_2, and HCl. Only I_2 vapors were able to enhance the conductivity of the metallomacrocycles, although the σ_{RT} values remained in the isolator range. These results were attributed to a poor bulk sorption and to the lack of surface chemisorption.[65]

To answer the question of whether this insulating character of the hemiporphyrazines is due to a problem of the supramolecular architecture or to an intrinsic deficiency of the basic unit, Marks et al. studied the electrical conductivities of cofacial assemblies based on silicon and germanium hemiporphyrazines ($[SiHpO]_n$ and $[GeHpO]_n$).[22] They achieved the synthesis of polyoxometallohemiporphyrazinates with average degrees of polymerization (determined by radiochemical end-group analysis) of ~25 and 60 units for silicon and germanium compounds, respectively. However, the conductivities of these stacked molecules were found to be less than 10^{-11} S cm^{-1}. Moreover, treatment of these compounds with iodine led to insulating materials ($\sigma = 10^{-10}-10^{-12}$ S cm^{-1}) rather than to the expected electrically conductive arrays of cofacial π-radical cations. This result was attributed to the destruction of the polymeric M−O−M backbone by analogy with $[SnPcO]_n$. A previous work[23] on polymeric hemiporphyrazinatogermanium compounds, although having O−R−O spacers, had already led to extreme low conductivity values ($\sigma_{RT} < 10^{-15}$ S cm^{-1}). On the other hand, linear polymerization in hemiporphyrazines and benzenehemiporphyrazines has also led to insulators ($\sigma_{RT} = 10^{-8}-10^{-16}$).[25]

Theoretical calculations performed by Honeybourne on closed-shell conjugated macrocyclic ligands placed in perfectly linear columnar stacks, with an interplanar spacing of 0.373 nm, pointed out that both metal-free phthalocyanines and hemiporphyrazines, because of the large bandgaps, must show low σ values at room temperature when undoped, i.e., they will not act as intrinsic semiconductors.[66] However, these results are extremely distance-dependent, and narrower bandgaps and larger bandwidths could be obtained by reducing the interplanar distance. Moreover, by taking into account the fact that the conductivity of the macrocycles is usually very low until donor−acceptor interactions occur, the studies were extended to open-shell (radical ions) systems.[67] The calculations for two spacing distances (0.373 and 0.332 nm) showed that the metal-free phthalocyanine displays larger bandwidths and narrower bandgaps than the corresponding hemiporphyrazines. Indeed, the H_2Thp radical anion does not have at 0.373 nm the minimum bandwidth required to ensure enough mobility of the charge carriers.

A more recent study on triazolehemiporphyrazines confirmed this previous result. Two series of first-row metal complexes of both the triazolehemiporphyrazine **3** and the pyridinotriazolehemiporphyrazine **49** showed σ_{RT} values ranging between 10^{-12} and 10^{-9} S cm^{-1}.[10,37]



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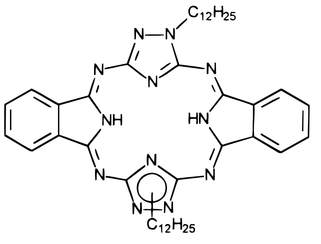
Only after iodine doping did the authors succeed in increasing the σ values to $10^{-6}-10^{-8}$ S cm^{-1}, just in the semiconducting border.[10]

More recently, cofacially joined irontriazolehemiporphyrazines prepared using the "shish-kebab" approach[3d,21] have also been described in an attempt to improve the conducting properties by organization of the metallomacrocycles. Thus, cofacial assemblies of type $[FeR_6ThpL]_n$, L = pyrazine or diisocyanobenzene, have been reported.[39a] In this way conductivity values in the range of $10^{-10}-10^{-7}$ S cm^{-1} were achieved, which could be increased to 10^{-5} S cm^{-1} after iodine doping. These low values are attributed to the low degree of polymerization (measured by the MALDI/TOF-MS technique) and the broad distribution of the chain lengths. The iodine doping results also showed to be highly dependent on the bridging ligand nature. More extensive synthetic studies are required in order to obtain longer chain polymers from metallohemiporphyrazines (iron, ruthenium, etc.) able to display higher electrical conductivities.

Hemiporphyrazines with their delocalized π-conjugated systems are also potentially useful as third-order nonlinear optical materials.[68] Thus, two families of triazolehemiporphyrazines, **38** and **50**, have been the subject of NLO studies by using the THG (third harmonic generation) technique on chloroform solutions.[36,69] While in the latter case only the real



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part of the third-order polarizability γ $(3\omega{:}\omega,\omega,\omega)$ has been determined due to the limited solubility of the compounds,[36] in the former case[69] both the real (γ') and the imaginary (γ'') parts of γ ($\gamma = \gamma' + i\gamma''$) have been determined from the concentration dependence of the macroscopic THG susceptibilities $\chi^{(3)}$ $(3\omega{:}\ \omega,\omega,\omega)$ at two different fundamental wavelengths, 1.904 and 1.340 μm. For both families, the real part of the γ values are about 1 order of magnitude lower than that measured by THG at 1.904 μm for the aromatic related compound silicon naphthalocyanine, this result being in accord with the lower π delocalization in the hemiporphyrazines. It is also noteworthy that for the free base **38** and its zinc complex γ has only a real component, whereas manganese, iron, cobalt, nickel, and copper complexes have an important imaginary (γ'') contribution.[69]

As already described for the Pcs, the NLO response of the Thps is highly metal-dependent. Thus, γ' in the cobalt-containing derivative is more than 1 order of magnitude higher than in the nonmetalated compound **38**, while γ values for zinc complexes are close to those of the metal free compounds. To account for this metal-induced enhancement of γ, a three-level model for the free bases and a four-level model for the complexes with unfilled d-shell metal ions have been used, both involving one photon forbidden and two photons allowed levels. Moreover, a relationship between the IR d−d transitions and the variation of γ for the metal complexes has been also proposed.

A next goal in this area would be to determine a relationship between the microscopic third-order polarizability (γ) and the corresponding macroscopic susceptibility (χ^3). From a theoretical point of view, this would contribute to a better understanding of the influence of structure and order parameters over the microscopic phenomena, i.e., the nexus between single-molecule properties and supramolecular architecture. On the other hand, from a practical point of view, it would measure the real possibilities of the Thps as NLO materials.

V. Concluding Remarks

The present review reflects the resurgent interest in hemiporphyrazine chemistry, since recent work has provided an initial basis for the use of this kind of compounds as building blocks for the preparation of molecular materials.

The high synthetic versatility of hemiporphyrazines in comparison with that of related metallomacrocycles, e.g., phthalocyanines, opens a vast field for fine-tuning of specific physical properties such as electrical and, specially, nonlinear optical ones.

These compounds are also very promising for the preparation of two-dimensional metal−organic polymers (ladder polymers) involving the coupling of different metallohemiporphyrazine subunits in homo- or heteronuclear arrays with potential electrical and magnetic properties. Much synthetic work is needed in the forthcoming years to develop all the possibilities of this fascinating family of molecules.

VI. Acknowledgments

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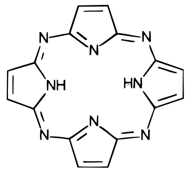
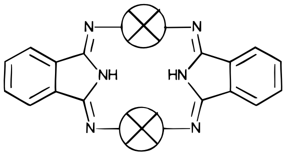
(6) Campbell's patent[4] appeared in 1956 (although the application year was 1952) claiming the invention of a new class of coloring compounds obtained by reaction of aromatic ortho dinitriles with nonpyrrolic diamino heterocyclic compounds. He coined the term hemiporphyrazine to encircle all these new macrocycles taking into account Linstead's definition of porphyrazine.[7]



Porphyrazine



Hemiporphyrazine

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