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Subphthalocyanines: Singular Nonplanar Aromatic Compounds—Synthesis, Reactivity, and Physical Properties

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I. Introduction

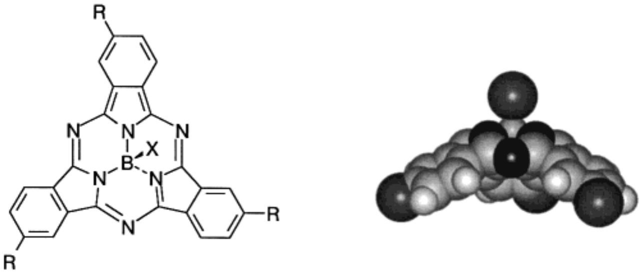

Figure 1. Chemical structure and CPK model of a trisubstituted subphthalocyanine.

Subphthalocyanines (SubPcs, Figure 1) are the lowest homologues of phthalocyanines, well-known two-dimensional 18 π-electron aromatic systems with unusual electrical and optical properties.[1] They are composed of three diiminoisoindole rings *N*-fused around a boron core. Their 14 π-electron aromatic core along with their nonplanar cone-shaped structure, as determined by X-ray crystallography,[2] make them attractive compounds due to their chemical and physical properties. These compounds are only known as boron derivatives.

The serendipitous discovery of subphthalocyanines was made in 1972 by Meller and Ossko,[3] as they were trying to obtain boronphthalocyanine. The condensation reaction of phthalonitrile in the presence of boron trichloride in chloronaphthalene at 200 °C did not lead to the expected cyclotetramerization product. Instead, they observed the formation of a purple compound whose analysis by electron impact mass spectrometry, UV−visible spectrophotometry, and elemental analysis was consistent with the formation of chlorosubphthalocyanine (**1**, Scheme 1). All things being equal, the synthetic method they employed is still the only way to obtain this type of molecular architecture, and chemists are still striving to synthesize the same macrocycle without boron or with another central atom.

The interest of subphthalocyanines is manifold from the purely synthetic point of view to the applied physical properties.

Subphthalocyanines are synthesized in good yields by cyclotrimerization reaction of phthalonitrile precursors in the presence of a boron derivative (typically a boron trihalide of BX_3 type).[4] When the starting dinitrile does not belong to the C_{2v} symmetry group, SubPcs are obtained in fact as a mixture of C_1 and C_3 constitutional isomers.[5] Each of these isomers is in turn a racemic mixture of enantiomers. These enantiomers have been recently resolved by HPLC.[6] Very few C_3 organic compounds have been obtained in optically active forms,[7] and to the best of our knowledge, the resolution of an aromatic chiral

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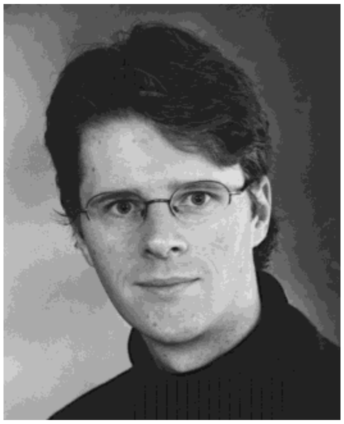


Christian G. Claessens was born in Valenciennes, France, in 1969. He performed his undergraduate education at the Ecole Normale Supérieure de Lyon (ENS Lyon), France. He received his Ph.D. degree in Organic Chemistry from the University of Birmingham, England, in 1997, under the supervision of Professor J. Fraser Stoddart. Following a one-year period as a postdoctoral fellow in the late Professor André Collet's group in the ENS Lyon, he joined Professor Tomás Torres' group at the Autónoma University of Madrid. He now holds a "Ramon y Cajal" fellowship from the Spanish Ministry of Science and Technology. His current research interests include the synthesis, supramolecular aspects, and applications of subphthalocyanines.

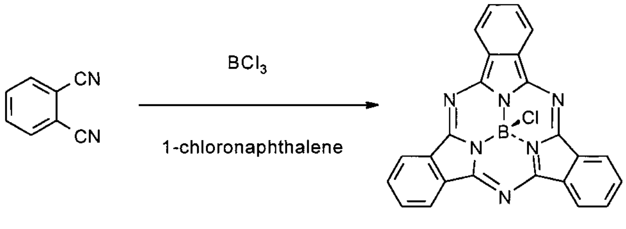
David González-Rodríguez was born in Madrid, Spain, in 1976. He studied Chemistry at the Complutense University of Madrid, where he obtained his Licenciatura (B.Sc.) in 1999. He is currently working on his Ph.D. degree in Organic Chemistry in the research group of Professor Torres. He is studying the chemistry and properties of subphthalocyanines and their assembly into electro- and/or photoactive systems.

C_3 molecule has been described only in the case of a subphthalocyanine. High-symmetry chiral molecules, i.e., compounds with a symmetry number higher than 2, are of special interest for a better understanding of the molecular origins of optical activity.

The constrained structure of subphthalocyanines makes them good synthetic precursors of unsymmetrically substituted phthalocyanines when reacted with appropriate diiminoisoindoline derivatives.[8] SubPcs are usually less stable than their Pc homologues, and they tend to be "reactive" compounds in such a way that the halogen atom (X) in the axial position (Figure 1) can be easily displaced by nucleophiles (mostly by alcohols).[2c,d,f,9] On the other hand, the subphthalocyanine core is robust enough for sustaining chemical modifications of its peripheral substituents (R).[8h,10] Furthermore, subphthalocyanines can be organized at the supramolecular level in liquid crystals[9c,11] and Langmuir–Blodgett films.[9b]

Born in 1951 in Madrid, Tomás Torres is currently Full Professor and Director of the Department of Organic Chemistry at the Autonoma University of Madrid (UAM). He received his Ph.D. degree (1978) at the same University, working at the Spanish National Research Council (CSIC) in Madrid (Professor Fariña). After two years (1978–80) at the Department of Organic Chemistry and Spectroscopy of the Max-Planck-Institute for Biochemistry, in Martinsried near Munich (Germany, Professor Dr. W. Schaefer) as a Max-Planck Society postdoctoral fellow, he joined (1981–85) 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 synthesis of low-symmetry phthalocyanines and the preparation and study of the photophysical and nonlinear optical properties of molecular materials based on phthalocyanines and related compounds. He is now responsible for a research group of two permanent researchers and about 12 graduate students and postdoctoral fellows. He is the author or coauthor of over 180 research papers and patents.

Scheme 1. Preparation of Unsubstituted Subphthalocyanine 1



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Nonlinear optical properties as well as multifunctional molecular materials are attractive fields of increasing research interest. Subphthalocyanines are molecules that show high second-order nonlinear responses as a consequence of their octupolar character[11,12] and could be potentially employed as building blocks to create hybrid inorganic–organic materials that could exhibit combined physical properties (e.g., conducting and nonlinear optical ones).[13] On the other hand, these compounds represent a basis set of chromophore systems for studying electron and excitation transfer processes.[14]

Their purple color are the basis of attractive dyes for electrolithography or for printing.[4b,15] The properties of their excited states make them good photosensitizers with potential applications in photodynamic therapy (PDT).[8e,16b] They were also considered as useful molecules that could act as recording media which could be employed for rewriting at short wavelength.[17]

This review will be devoted to the synthesis and the chemical and physical properties of subphthalo-

Table 1. Subphthalocyanines Obtained by Condensation of a Phthalonitrile Derivative and a Boron Reagent of Type BX_3 or BX_2Y

compound number	type [a]	R peripheral	X axial	yield (%)	ref [b]
1	D	H	Cl	30−64	2a,f,3,4,8b,c,e,f,i- k,12a,b
2	D	H	Br	8	2c,d,f
3	Tm	*tert*-butyl	Br	43−48	8a,16a
4	Tm	SO_2Cl	Br	60	8h,l,u
5	Tm	NO_2	Br	−	17c
6	D	F	Cl	20	2e,24a
7	D	Cl	Cl	−	18
8	H	SC_6H_{13}	Cl	28	8d
9	H	SC_8H_{17}	Cl	26	9c,12e
10	H	$SO_2C_8H_{17}$	Cl	11	9b,12e
11	H	*p*-tolylthio	Cl	28	12e
12	H	*p*-tolylsulfonyl	Cl	25	12e
13	H	$SC_{10}H_{21}$	Cl	14	11,12f,g
14	H	$SC_{12}H_{25}$	Cl	−	11,12f,g
15	H	$SC_{16}H_{33}$	Cl	−	9c,11,12f,g
16	H	$SC_{18}H_{37}$	Cl	−	11,12f,g
17	H	Crown	Cl	3.5	24b
18	Tm	*tert*-butyl	Cl	36	4a,5a,8i,9b,12b
19	Tm	NO_2	Cl	80	4a,12b,c,d,e
20	Tm	I	Cl	45	4a,6a,12d
21	Tm	SC_8H_{17}	Cl	27	9b,12e
22	Tm	$SO_2C_8H_{17}$	Cl	13	9b,12d,e
23	To	NO_2	Cl	6/4 (C_3/C_1)	5b
24	To	I	Cl	7/4 (C_3/C_1)	5b
25	To	SC_3H_7	Cl	1	5b
26	To	$SO_2C_3H_7$	Cl	15	5b
27	D	H	F	20	2f,3
28	D	H	Ph	10	2b,d,f,4a
29	Tm	*tert*-butyl	Ph	43−48	4a,5a
30	H	CH_3	Ph	3	4a
31	H	pentyl	Ph	5	4a
32	H	Crown	Ph	0.4	8p
33	D	H	butyl	< 1	4a

[a] See Figure 2. [b] Selected references in which the compound is mentioned.

cyanines as well as their relatives subazaporphyrins[2b,8p,18] and subnaphthalocyanines.[2b,e,4,8n,p,q,t,9d,16b,18,19] μ-Oxo dimeric subphthalocyanines,[4a,8p,18] fused subphthalocyanines,[16a,20] and subphthalocyanine-based electroactive dyads[14,21] will also be discussed.

II. Synthesis

A. Influence of the Boron Reactant

The boron reagents that have been successfully employed so far in the subphthalocyanine formation are of the BX_3 or BX_2Y types, where X and Y may be butyl, phenyl, fluorine, chlorine, or bromine. The reactivity of these trisubstituted boron compounds toward phthalonitrile derivatives follows, as observed experimentally, the order $B(Alkyl)_3 < BPh_3 < BF_3 < BCl_3 < BBr_3$, which is closely related to their Lewis acidity.[22] The choice of a boron reagent depends on two factors: the first one being the chemical compatibility between the phthalonitrile derivative and the boron reagent and the second one being the purpose of the subphthalocyanine synthesis.

Boron tribromide readily reacts with phthalonitrile derivatives to give[1,2c,d,f,8a,h,17a−c,23] the corresponding bromosubphthalocyanines **2**−**5** (Table 1). This reagent is commercially available as such or as 1 M solutions in dichloromethane, heptane, and hexanes. Bromosubphthalocyanines are fairly unstable with respect to the other axially substituted subphthalocyanines, their purification and characterization being somewhat tedious. Their interest lies in the easy substitution of the axial bromine atom (see below).[2c,d,9a] Only four different Bromo subphthalocyanines **2**−**5** have been described bearing no substituent (**2**) and *tert*-butyl (**3**), sulfonyl (**4**), and nitro (**5**) substituents, respectively.

Boron trichloride is by far the most commonly reported[2a,3,4,8b−f,i−k,o,9c,d,10,11,12b,e,24] boron reagent for subphthalocyanine synthesis; it is commercially available as such or as a 10 wt % solution in 2-chloroethanol and as 1 M solutions in dichloromethane, heptane, hexanes, and *p*-xylene. BCl_3 permitted the synthesis of a wide range of chlorosubphthalocyanines (**1, 6**−**26**, Table 1) in moderate to good yields (20−80%). Peripherally dodeca- (**1**, **6**, and **7**), hexa- (**8**−**17**), and trisubstituted (**18**−**26**) chlorosubphthalocyanines are now readily available in one-step reactions. In the case of the reactions with BCl_3, the choice of a solvent depends on the reactivity of the starting phthalonitrile, i.e., a less reactive one requiring higher reaction temperature. From all the published results, it is not possible to draw a conclusion about the correlation between the reactivity of the phthalonitrile derivative and the donor or acceptor character of its substituents. A wide variety of substituted phthalonitriles has been successfully employed as starting materials [nitro (**19**, **23**), iodo (**20**, **24**), thioethers (**8**, **9**, **11**, **13**−**16**, **21**, **25**), sulfones (**10**, **12**, **22**, **26**), fluorine (**6**), chlorine (**7**), and *tert*-butyl (**18**)]. The introduction of ether groups in the peripheral positions was described[24b] only in very low yields (**17**, $\rho \leq 3.5\%$) as a consequence of their incompatibility with BCl_3. Long alkyl chains could only be introduced by means of thiother and sulfone linkages (**8**−**10**, **13**−**16**, **21**, and **22**). The presence of easily halogenable benzylic positions prevented the synthesis of hexaalkyl-substituted SubPcs using boron trichloride, even at high temperature (>250 °C) or in the presence of a strong base such as DBU.[4a] Preliminary studies showed that dimethyl sulfide complexes of boron trichloride may be employed in subphthalocyanine synthesis.[25] In this way, smoother reaction conditions may be applied so as to get greater compatibility with other functional groups. Low yields are the only drawbacks of this method.[25]

Chlorosubphthalocyanines are stable on the month time-scale in the solid state, while they decompose in a few days in solution in the presence of light. Their relative stability depends very much on the nature of their peripheral substituents, triiodoSubPc **20** being the most stable of all. In contrast to Pcs, chloroSubPcs do not show[9c] aggregation in solution at concentrations ranging from 10^{-5} to 10^{-1} M and show better solubility in most common organic solvents. Substituted SubPcs are quite soluble (0.1 M) in a variety of organic solvents such as aromatics (toluene, benzene, etc), acetone, ethyl acetate, CH_2Cl_2, $CHCl_3$, diethyl ether, THF, and others. They are sparingly soluble in apolar (hexane, etc.) or protic solvents (EtOH, MeOH). Of course, axial or peripheral substitution by different functional groups may dramatically change their solubility. Chlorosubphthalocyanine **1** is commercially available.[26]

Boron trifluoride is much less used since it is more difficult to handle and less reactive than BCl_3 and BBr_3. Homborg et al. reported[2f] the synthesis of SubPc **27** from the etherate $Et_2O{\cdot}BF_3$ in quinoline at reflux. The reaction was performed with both $Et_2O{\cdot}{}^{10}BF_3$ and $Et_2O{\cdot}{}^{11}BF_3$ (see infrared characterization below).

Reactions with triphenylboron are low yielding and, moreover, as a consequence of the low reactivity of BPh_3, have to be carried[2b,d,4a,5a,8n,p,19] out at high temperatures. Interestingly, Hanack et al. reported[2b] the formation of SubPc **28** in naphthalene in the presence of a stoichiometric amount of DBU in 10% yield. More recently, the boron salt $(n\text{-}Bu_4N)[B(C_6H_4)_4]$ was also shown[2f] to yield the desired Phenyl SubPc **28**. Hexaalkyl phenylsubphthalocyanines **30** and **31** could be obtained from the addition of a superbase to the mixture of BPh_3 and of the 4,5-dialkylphthalonitrile precursor.[4a] Thus, $(m\text{-}CH_3)_6$SubPcBPh **30** could be obtained from the corresponding phthalonitrile, while $(m\text{-}C_5H_{11})_6$SubPcBPh **31** was synthesized from the 1,3-diiminoisoindoline, both in very low yields.[4a] The authors would like to mention that it is the only reported subphthalocyanine synthesis starting from 1,3-diiminoisindole derivative. From our own expertise, this method is not general and could not be applied successfully with other boron reagents. BPh_3 was shown to be somewhat compatible with oxygen-substituted phthalonitriles. For example, Kobayashi et al. reported the synthesis of a tris(crown ether)-substituted SubPc **32** with BPh_3 and DBU only in 0.4% yield.[8p] β-Cyclodextrin was shown to complex the phenyl axial ligand of SubPc **32**, while the aggregation in columnar stacks, induced by alkali metal complexation of the crown ether moieties, as in the case of phthalocyanines,[27] does not take place.[8p]

When tributylboron was reacted with phthalonitriles in the presence of DBU or stronger organic bases, no subphthalocyanine was obtained.[4a]

Although there is no doubt about the nature of the axial ligand on the central boron atom of the subphthalocyanine macrocycle when BX_3 is employed, BX_2Y reagents may show some selectivity. In the case of mixed boron halides, such as Ph_2BBr, $BuBBr_2$, $PhBCl_2$, the phenyl or alkyl substituent, being a poorer leaving group, is normally retained in the product formed. Meller and Ossko[3] in 1972 and Kobayashi[16a] in 1991 reported that chloro **1** and bromo **3** axially substituted SubPcs were obtained starting from $PhBCl_2$ and Ph_2BBr, respectively. These results were refuted by Hanack et al. in 1995,[2b] who repeated the syntheses and isolated subphthalocyanines **28** and **29** axially substituted by a phenyl group. However, the same group reported that when $PhBCl_2$ is used, a mixture of subphthalocyanines axially substituted by a phenyl group (**29**) and by a chlorine atom (**18**) was obtained.[5a] The use of mixed boron reagents provided a unique entry into axially butyl-substituted SubPc **33** that could be obtained only with butylboron dibromide in naphthalene.[4a]

Attempts at carrying out the reaction with other boron reagents, which could provide a direct approach for the introduction of other axial substituents (such as borontriiodide, trialkyl borates, boronic esters, boronic thioesters or boronic amides), have been unsuccessful up to now.

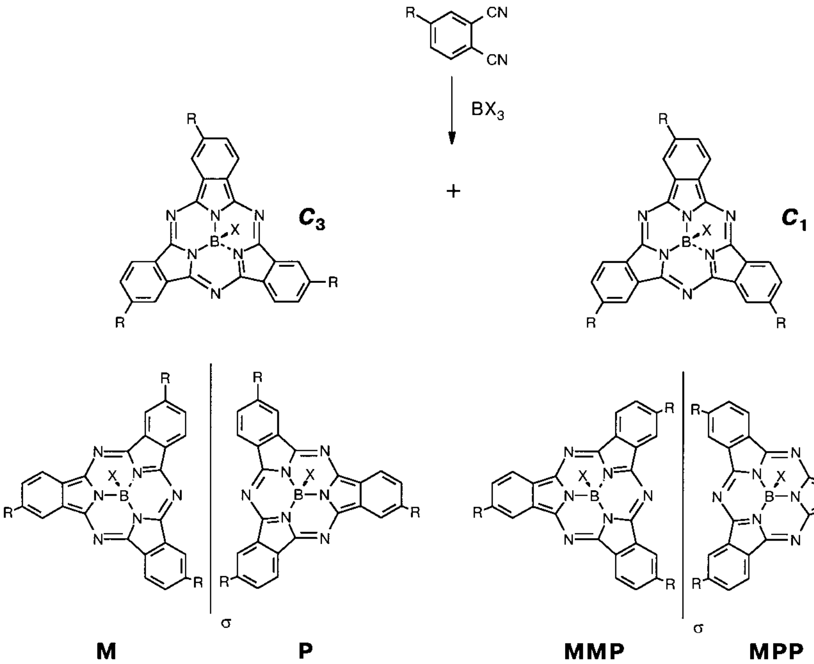
B. Selectivity in Subphthalocyanine Synthesis

While starting phthalonitriles that possess C_{2v} symmetry give rise to single subphthalocyanines, the ones that lack C_{2v} symmetry yield a mixture of two SubPc regioisomers with C_1 and C_3 symmetries (Scheme 2). Moreover, each of these isomers is chiral and is obtained as a racemic mixture of two enantiomers (MMM and PPP for C_3 and MPP and MMP for C_1, see Scheme 2).

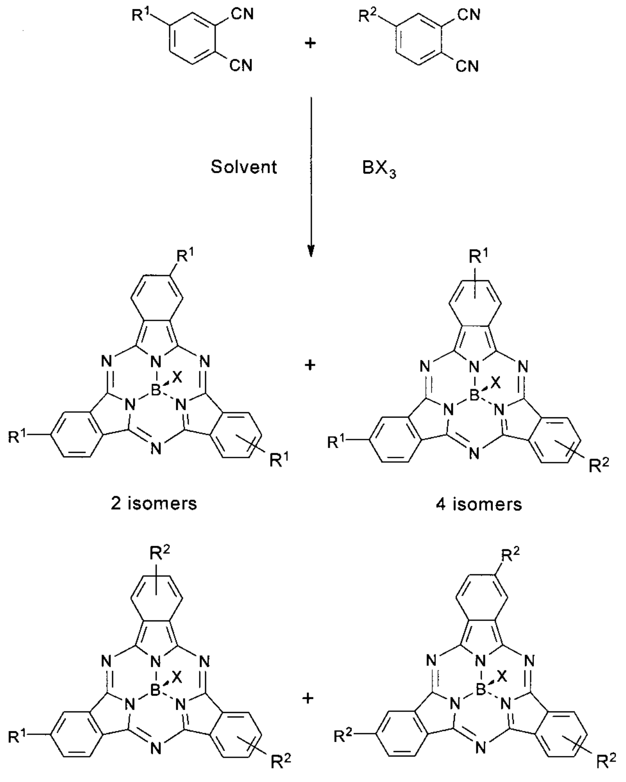
Separation of the C_1 and C_3 constitutional isomers of SubPc **29** was first achieved by Hanack and coworkers[5a] by preparative HPLC. More recently, the separation of the constitutional isomers of a series of 3-substituted[5b] (**23**−**26**) and 4-substituted[6a] (**20**) subphthalocyanines was done by column chromatography on silica gel by Torres and co-workers.

In the case of subphthalocyanines **20** and **29**, the ratio C_3:C_1 does not seem to be influenced by electronic or steric factors and follows a statistical distribution (1:3, respectively). That is no longer the case with *o*-substituted SubPcs **23**−**26**[5b] in which the peripheral substituents are closer to the core of the molecule and steric factors play an important role. Thus, the C_3:C_1 ratio for both SubPcs **23** and **24** was found to be 1.5, while in sharp contrast, the regioisomer ratio for SubPc **26** was 0.11. These experimental results were explained on the basis of the steric characteristics of the substituents. A mecha-

Scheme 2. Subphthalocyanine Regio- and Enantiomers



Scheme 3. Synthesis of Unsymmetrically Substituted Subphthalocyanines (U) and Distribution of the Products



nistic pathway involving a dimeric intermediate made of two aza-fused phthalonitrile units was proposed. This hypothetical species, closely related to the boron β-isoindigo isolated by Engel et al.,[2d] would react with another substituted phthalonitrile to yield the corresponding SubPc.

The cone-shaped structure of subphthalocyanines makes them intrinsically noncentrosymmetric as opposed to their phthalocyanine analogues. This noncentrosymmetry may induce chirality, in case the subphthalocyanine is made of noncentrosymmetric subunits. This chirality is similar to the one that may be found in fullerene or fullerene fragments.[28] Subphthalocyanine enantiomers were described by means of the helical descriptors M and P, considering the necessary Cl−B−N−C key dihedric angles: the subphthalocyanine molecule is treated as if it were a superimposition of three chiral helices. This leads to four different isomers M, P and PMM, PPM that are in fact the enantiomers of the C_3 and C_1 regioisomers, respectively. Only very recently, the enantiomers of the C_1 and C_3 isomers of SubPc **20** were separated by Torres and co-workers on an analytical scale by chiral HPLC.[6a] The careful analysis of the circular dichroism of each enantiomer combined with theoretical calculations would allow the determination of their absolute configuration.[1e,6b]

Fine-tuning of the physical properties of SubPc derivatives can be achieved by lowering the symmetry of the macrocycle. Starting from two different phthalonitrile derivatives, a statistical cyclotrimerization reaction results in a mixture of SubPcs that differ in the nature, number, and position of the peripheral substituents (Scheme 3). Condensation of 4-nitrophthalonitrile and 4-*tert*-butylphthalonitrile in a 6:1 M ratio gave a mixture of SubPcs, consisting of mononitro SubPc (45%), dinitro SubPc (45%), and trinitro SubPc (10%) (**38** in Table 2).[8o] The complete separation of all the possible compounds and regioisomers, resulting from the statistical condensation of 3-iodophthalonitrile and 4-octylthiophthalonitrile (**39** in Table 2) and 3-iodophthalonitrile and 4,5-dioctylthiophthalonitrile (**40** in Table 2), was achieved very recently by column chromatography.[24c] Thorough characterization of the different compounds obtained was made possible by ^{1}H NMR spectroscopy by careful analysis of the symmetry environment experienced by each aromatic proton. The mixed condensation of 2,3-dicyanonaphthalene and tetra-

Table 2. Naphthalocyanines (N), Unsymmetrically (U) Substituted SubPcs, and Subazaporphyrazines (SAP)

compound number	type[a]	R peripheral	X axial	yield (%)	ref[e]
34	N	H	Ph	<1	2b,4a
35	N	*tert*-butyl	Ph	<1	2b,4a
36	N	H	Cl	35−53	2e,9d,16b
37	N	H	Br	28−35	8p,9a
38	U[b]	NO_2(4)/ *tert*-butyl (4)	Cl		8o
39	U[b]	I(3) / SC_8H_{17} (4)	Cl		23c
40	U[b]	I(3) / SC_8H_{17} (4,5)	Cl		23c
41	U[b]	F(3,4,5,6) / 2,3-dicyano naphthalene	Cl		2e
42	U[b]	H(3,4,5,6) / dicyano naphthalene	Cl		9d
43	SAP[c]	*c*	Cl	15	2b
44	SAP[d]	*d*	Br	2	8p,18

[a] See Figure 3. [b] Unsymmetrically substituted SubPcs as defined in Scheme 3; A(X)/B(Y) means that we are considering the reaction between a phthalonitrile substituted by the group A in position X and a phthalonitrile substituted by the group B in position Y. [c] Starting material: (*E*)-di(4-*tert*-butylphenyl)fumaronitrile. [d] Starting material: 1-(1,2,2-tricyanoethenyl)-2-trifluoromethylbenzene. [e] References in which the compound is mentioned.

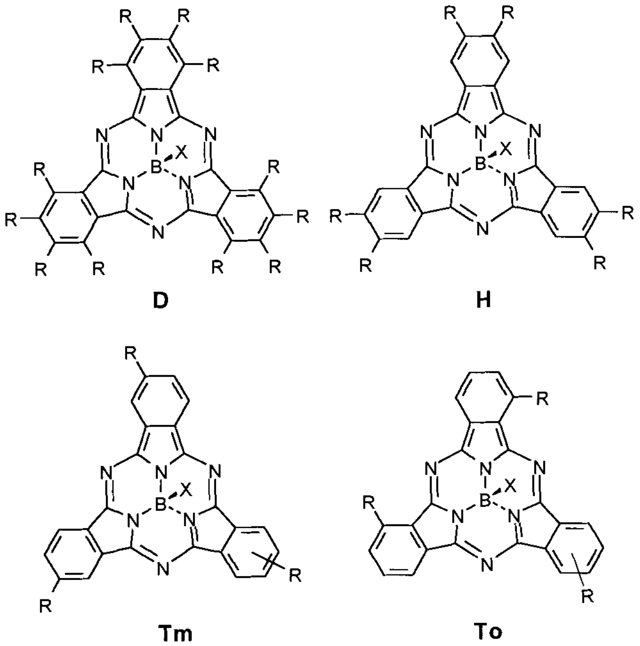


Figure 2. Acronyms used in this review for different types of substituted subphthalocyanines (D, dodecasubstituted; H, Hexasubstituted; Tm, trisubstituted in meta position; To, trisubstituted in ortho position).

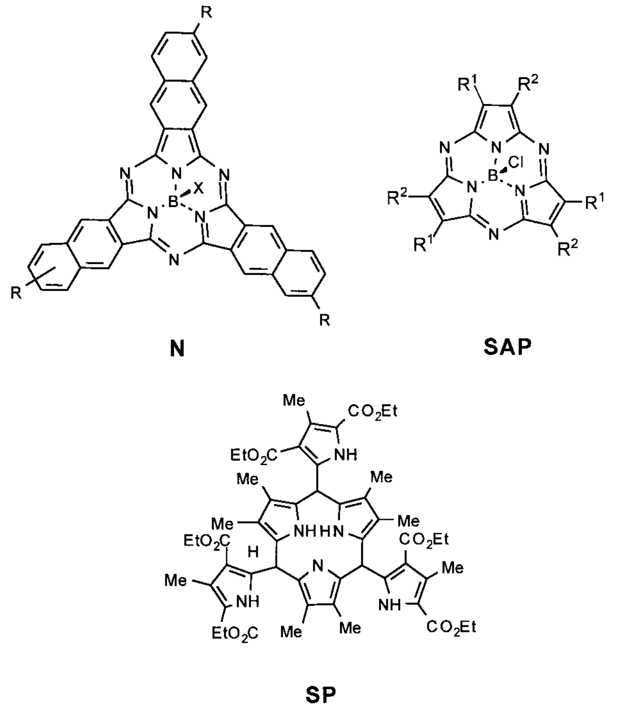


Figure 3. Acronyms used in this review for different subphthalocyanine-related compounds (N, subnaphthalocyanine; SAP, subazaporphyrazin; SP, subporphyrin analog).

fluorophthalonitrile[2e] or phthalonitrile,[9d] respectively, produces a mixture of the four possible compounds (**41** and **42** in Table 2).

It is clear from the previous results that the selectivity in the formation of unsymmetrically substituted SubPcs depends on steric factors and also on the relative reactivity of the phthalonitrile precursors toward the boron reagent.

C. Subphthalocyanine-Related Compounds

As in the case of phthalocyanines and their higher naphthalocyanine homologues,[29] it was interesting to increase the conjugation of the SubPcs in order to alter their electronic properties. The most important representatives of this group are the subnaphthalocyanines (Figure 3). Hanack, in 1995, reported the first synthesis of a subnaphthalocyanine **34** (SubNc)[2b] whose synthesis follows exactly the same pattern as the one of SubPcs. Reaction between 2,3-dicyanonaphthalene and $BPhCl_2$ in naphthalene resulted in the blue subnaphthalocyanine **34** in 0.1% yield (Table 2).[4a] A peripherally tri-*tert*-butylated SubNc **35** was prepared by the same method and also in low yield. Torres et al. managed to synthesize **36** in 35% yield using BCl_3 instead of $PhBCl_2$ in a mixture of chlorobenzene and toluene.[16b] This yield was improved (53%) very recently using 1,2-dichlorobenzene as solvent.[9d] The course of this reaction is very critical and depends very much on the reaction conditions; some authors have pointed out the ease with which the naphthalene ring may be chlorinated in the presence of BCl_3.[2e] SubNc **37** containing bromide as an axial ligand has also been obtained in acceptable yield (28%) by condensation of 2,3-dicyanonaphthalene with BBr_3.[9a] Boron sub-2,3-naphthalocyanine chloride **36** is commercially available (with 75% purity).[30] Subnaphthalocyanines seem to differ from their SubPc counterpart in their fairly low stability both in the solid state and in solution.

Table 3. Subphthalocyanines Obtained by Axial Substitution (45−67) or by Functionalization on the Axial Ligand (68−72)

starting SubPc	type [a]	R peripheral	X axial	reaction product	axial X product	yield (%)	ref [b]
2	D	H	Br	**45**	OCH_3	5	2c,d
2	D	H	Br	**46**	OC_2H_5	15	2c
2	D	H	Br	**47**	O*tert*butyl	7	2c,f
2	D	H	Br	**48**	OPhenyl	18	2c,f
2	D	H	Br	**49**	$OCH(CH_3)_2$	−	2f
2	D	H	Br	**50**	OCOH		2f
2	D	H	Br	**51**	$OCOCH_3$		2f
2	D	H	Br	**52**	$OCOCH_2Cl$		2f
2	D	H	Br	**53**	$OCOCH_2C_6H_5$		2f
2	D	H	Br	**54**	$OCOCl_3$		2f
2	D	H	Br	**55**	$OCOCF_3$		2f
2	D	H	Br	**56**	$OCOC_6H_5$		2f
2	D	H	Br	**57**	$OSi(C_6H_{13})_3$		2d
2	D	H	Br	**1**	Cl		2f
4	Tm	SO_2Cl	Br	**58**	OH[d]	60	8h,l,u
37	N	H	Br	**59**	OMe	20	9a
37	N	H	Br	**60**	OEt	18	9a
1	D	H	Cl	**61**	OH	2	2f,4a
1	D	H	Cl	**28**	Ph		4a
9	H	SC_8H_{17}	Cl	**62**	OH		9b,9c
15	H	$SC_{16}H_3$	Cl	**63**	OH		9c
20	Tm	I	Cl	**64**	OH	55	4a
21	Tm	SC_8H_{17}	Cl	**65**	OH	92−97	9c
36	N	H	Cl	**66**	$OSi(C_6H_{13})_3$		9d
42	U[c]	H (3,4,5,6)/2,3-dicyano naphthalene	Cl	**67**	$OSi(C_6H_{13})_3$		9d
61	D	H	OH	**68**	$OSi(tBu)Me_2$		2d
62	H	SC_8H_{17}	OH	**69**	$OSi(Et)_3$		9c
63	H	$SC_{16}H_{33}$	OH	**70**	$OSi(Et)_3$		9c
64	Tm		OH	**71**	$OSi(C_2H_5)_3$	22	4a
65	Tm	SC_8H_{17}	OH	**72**	$OSi(C_6H_{13})_3$	39−40	9b

[a] See Figures 2 and 3. [b] Selected references in which the reaction is mentioned. [c] Unsymmetrically substituted SubPcs as defined in Scheme 3 and Table 2. [d] The peripheral $SOCl_2$ groups were functionalized to $SO_3[PyH]$ during the same reaction.

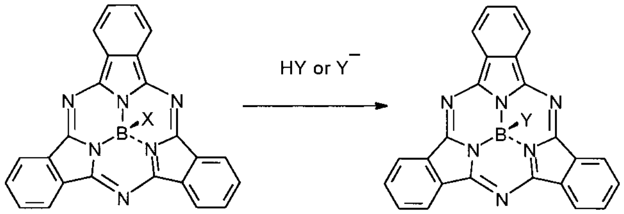
Two subazaporphyrins have been prepared by condensation of (*E*)-di(4-*tert*-butylphenyl)fumaronitrile with BCl_3 and by condensation of 1-(1,2,2-tricyanoethenyl)-2-trifluoromethylbenzene with BBr_3 (**SAP** in Figure 3). The yellow-green products were obtained in very low yields (2%).[2b,8p,18]

Surprisingly, subporphyrins are still to be synthesized. An example of a hexapyrrole trimer (**SP** in Figure 3) that possesses an interesting structure and that could be an entry into subporphyrin chemistry was described in 1975 by Fleiderman et al. Condensation of two differently substituted pyrroles leads to this colorless compound that was characterized by MS and elemental analysis.[31]

III. Reactivity of Subphthalocyanines

Due to the functional group limitation imposed by the use of boron reagents, the development of synthetic modifications of SubPcs at both the levels of the boron atom and of the peripheral aromatic units is of utmost importance. This approach may allow, for example, the fine-tuning of their physical properties, the modification of their solubility characteristics, the extension of their π-conjugation, the incorporation of these units into other electroactive systems, or their organization in supramolecular assemblies. In this sense, SubPc reactivity was divided in three different sections: axial reactivity (A), peripheral reactivity (B), and ring expansion reactions (C). The three of them differ in the reactive center: the central boron atom (A), the peripheral functional groups on the aromatic carbon atoms (B), or the imine-type core (C), respectively. Both axial and peripheral reactions produce modified subphthalocyanines, while ring expansion results in the loss of the SubPc skeleton and the formation of a low-symmetry phthalocyanine.

Scheme 4. Axial Reactivity of Subpthalocyanines



A. Axial Reactivity

Bromo- and chloroSubPcs were reacted with a wide range of oxygen nucleophiles to give rise to axially substituted SubPcs **45**−**67** (Scheme 4, Table 3). It was shown that peripheral donor groups increase the rates and the yields of substitution, probably by stabilization of an eventual positive charge on the boron atom.[25] Thus, column chromatography of SubPcs **9** and **15** over silica gel yields significant amounts of axially hydroxy-substituted SubPcs **62** and **63**, respectively. In many cases, phthalimide, a product of subphthalocyanine hydrolysis, was also obtained.[25] As a general trend, the nucleophilic substitution readily takes place in the case of bromoSubPcs, whereas it may require harsher conditions in the case of chloroSubPcs.[2c,d,9a]

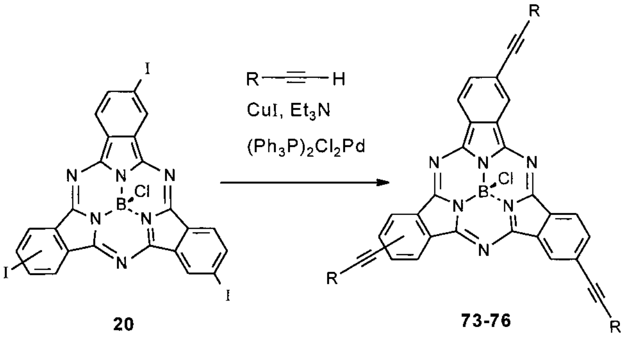
Different methods allow the substitution of the axial halide by a hydroxy group (Table 3, compounds

Table 4. Reaction on the Peripheral Positions of SubPcs

starting SubPc	type [a]	R peripheral	X axial	reactionproduct	R peripheral	yield (%)	ref [b]
4	Tm	SO_2Cl	Br	**58**	$SO_3[PyH]$[c]	60	8h,l,u
20	Tm	I	Cl	**73**	$-C{=}CTMS$[d]	28	10
20	Tm	I	Cl	**74**	$-C{=}CC_3H_7$	28	10
20	Tm	I	Cl	**75**	$-C{=}CCH_2OCH_3$	26	10
20	Tm	I	Cl	**76**	p-$NO_2(C_6H_4)C{=}C-$	29	10

[a] See Figure 2. [b] References in which the reaction is mentioned. [c] The axial Br atom was substituted by OH during the same reaction; Py means pyridine. [d] TMS means trimethylsylil.

Scheme 5. Peripheral Reactivity of Subphthalocyanines



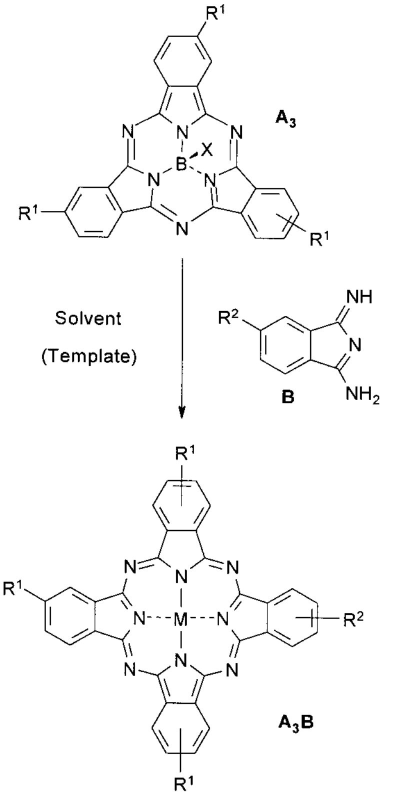
58, **61**−**65**). The simplest procedure consists of refluxing a suspension of the SubPc in water,[9b] pyridine/water,[2f,8h] or acetonitrile/water.[9c] The axial exchange with OH groups has also been achieved on an ion-exchange resin[8p] or by phase-transfer catalysis with 18-Crown-6.[4a] The axial substitution reaction on SubPcs was also performed with aliphatic and aromatic alcohols so as to obtain SubPcs **45**−**49**, **59**, and **60**. The reactions were performed in a SubPc solution of the corresponding alcohol or of a pyridine/alcohol mixture. Carboxilic acids were also reacted[2f,4b] with SubPcs to yield compounds **50**−**56**. Typically, the subphthalocyanine is heated with the organic acid at the boiling or the melting point, depending on the acid.

The substitution with other types of nucleophiles is much less common. Only two attempts to carry out this reaction with carbon nucleophiles have been made.[4a] PhenylSubPc **28** (Table 1) was obtained by reacting an excess phenyllithium with a solution of chloroSubPc **1** in toluene. On the contrary, SubPc **1** was found to decompose in the presence of butyllithium.[4a] Finally, halogen exchange was performed[2f,4b] by reacting SubPc **2** with thionyl chloride. Trialkylsilyloxy SubPcs **68**−**72** were obtained by further functionalization of the OH derivatives **61**−**65**, respectively, by reaction with trialkylchlorosilanes.[2d,4a,9b,c]

B. Peripheral Reactivity

The peripheral reactivity of subphthalocyanines has been much less studied than the axial one (Table 4). Water-soluble SubPc salt **58** (Table 3) was obtained by refluxing SubPc **4** in pyridine/water.[8h] The well-known Sonogashira palladium-mediated cross-coupling reaction of alkynes with aryl iodides was applied by Torres et al. to synthesize highly conjugated SubPcs **73**−**76** (Scheme 5, Table 4) from compound **20**.[10] Reaction yields were quite good (30%) taking into account that three C−C bonds had to be formed for each SubPc molecule.

Scheme 6. Synthesis of Phthalocyanines by Ring Expansion Reaction of a Subphthalocyanine



This palladium-catalyzed reaction has been performed more recently in the coupling of an alkynyl-substituted phthalocyanine to a series of unsymmetrically substituted monoiodo SubPcs to yield phthalocyanine-subphthalocyanine dyads.[21]

C. Ring Expansion Reaction

While symmetrical phthalocyanines (represented by four identical isoindole subunits as $\mathbf{A_4}$) are readily available by cyclotetramerization reaction of phthalonitriles or diiminoisoindolines (**A**),[1] unsymmetrically substituted Pcs of the $\mathbf{A_3B}$ type are usually difficult to obtain. The most common method is the statistical condensation of two different phthalonitriles or diiminoisoindolines **A** and **B** and, subsequently, their tedious chromatographical purification. In this context, several selective methods were developed.[32]

The ring expansion reaction[8] of subphthalocyanines (Scheme 6) is one of the most elegant synthetic pathways, devised by Kobayashi et al., for obtaining unsymmetrically substituted Pcs of the $\mathbf{A_3B}$ type, otherwise unattainable.[8f] The geometrically constrained SubPc ($\mathbf{A_3}$) is reacted with 1,3-diiminoisoindoline derivatives (**B**) to form the **A$_3$B** phthalocyanine. This method was claimed to have several advantages over the statistical cyclotetramerization: (i) high yields (8−20%), (ii) selectivity, and (iii) simple purification procedure since there are no byproducts.[8a] After much work,[8b−u] it is now clear that the selectivity of this procedure depends dramatically on (i) the nature of the peripheral substituents of the SubPc, (ii) the reactivity of the diiminoisoindoline derivative, (iii) the solvent, and (iv) the reaction temperature.

Typical ring expansion reactions were carried out in DMSO/1-chloronaphthalene or dichlorobenzene (1:4 to 4:1) or in (dimethylamino)ethanol at 80−100 °C for 5−12 h.

Since, so far, only SubPcs **1**, **3**, **8**, **18**, **19**, **38**, and **58** (Tables 1−3) have been employed in the preparations of Pcs by this method, it is still too early to draw conclusions about the effect of the peripheral substituents of the SubPc starting material on the ring expansion. Nevertheless, it seems that strong withdrawing groups such as sulfonyl allow the reaction to be carried out at relatively low temperatures (from room temperature to 70 °C) and provide higher selectivity in Pc formation.[8h,l] The axial substituent on SubPc seems to have no effect on the rate or on the outcome of the reaction, as reported by some authors.[8,e,n]

The nature of the starting diiminoisoindoline has proved to be a very important factor for the selectivity of the reaction. Donor substituents such as amino, amido bis(octyltriiodo), or *tert*-butyl on the diiminoisoindoline reduce its reactivity and avoid its self-condensation. The reaction of these compounds with SubPc in suitable conditions is very selective, and only small amounts of undesired unsubstituted Pc were observed.[8f,i] On the other hand, diiminoisoindolines bearing electron-withdrawing substituents (nitro, sulfoxide, and sulfone), being more reactive, have a stronger tendency to react with themselves yielding higher amounts of di-, tri-, and tetrasubstituted Pcs.[8d,i] The formation of these undesired Pcs may be, to some extent, prevented by changing the relative proportion of starting SubPc/diiminoisoindoline, which conventionally lies between 1:3 and 1:9. Less reactive phthalonitrile derivatives were successfully employed to form monosubstituted Pcs,[8e] even if the reaction yielded high amounts of nondesired di-, tri-, and tetrasubstituted Pcs, whose proportion could be reduced by means of catalytic amounts of DBU and pentanol. Attempts at performing this reaction with different precursors, such as 1-imino-3-thioisoindoline, were unsuccessful.[8e,h,l]

The use of a transition metal salt template (Zn(OAc)$_2$,[8e,f] FeSO$_4$, or NiCl$_2$[8i]) increases the yield of the expected unsymmetrical Pc but also leads to a higher amount of the other statistical distribution compounds. It was demonstrated that in the presence of transition metal salts, SubPcs undergo spontaneous ring opening leading to the symmetrical Pc.

A mechanistic pathway of the ring expansion reaction that involves three main routes has been proposed.[8f,i]

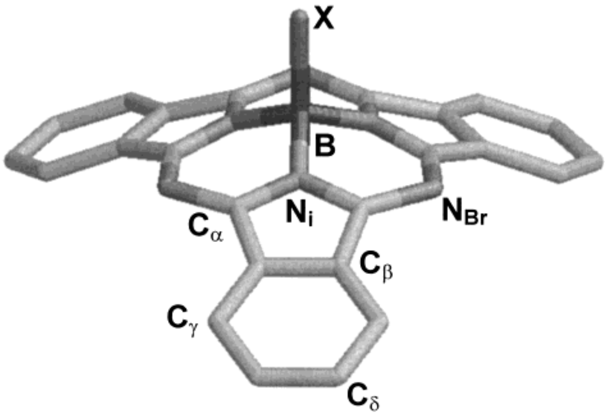


Figure 4. Stick representation of a subphthalocyanine showing the atom labels.

Route a: The reaction between the diiminoisoindoline derivative and the SubPc yields an open four-unit compound which could evolve through three alternative ways, depending on the reaction conditions. (i) It may form directly the desired unsymmetrically substituted Pc. (ii) It may be cleaved in smaller fragments, either thermally or by attack of a solvent molecule, to afford diiminoisoindoline or diiminoisoindoline dimers. (iii) The open tetramer may be cleaved by another diiminoisoindoline molecule, thus yielding trimers and dimers.

Route b: Opening of the Subpc macrocycle that further reacts with the diiminoisoindoline or will be cleaved into smaller units.

Route c: Self-condensation of the diiminoisoindoline unit leads first to a dimeric species that may react with products formed in Routes a and b.

All the intermediates coming from Routes a−c may further react and lead to a statistical mixture of all the possible symmetrically and unsymmetrically substituted Pcs. The relative importance of each of the mechanistic pathways depends on the experimental conditions and the nature of the reactants. To obtain high yields of the desired unsymmetrically substituted Pc, SubPc should be selectively opened by the reacting 1,3-diiminoisoindoline while the resulting four-unit open tetramer should close into a Pc macrocycle without further fragmentation.

From our point of view, the ring expansion reaction is a very promising procedure for the selective synthesis of A$_3$B phthalocyanines, but work has still to be done in the search for proper reaction parameters.

IV. Characterization

A. X-ray Structure Determination

The most striking common feature for all X-ray crystal structures of subphthalocyanines[2] is their cone-shaped geometry (Figure 4, Table 5), as opposed to the flat or nearly flat structure of their parent phthalocyanines. Nevertheless, one has to bear in mind that Zn and Pb Pcs or metal Pcs bearing an extra ligand on the metal center sustain[33] some concave deformation. In the case of subphthalocyanines, the macrocyclic core is extremely rigid, in such a way that $N_{i,a}$ and $C_{\alpha,\beta,\gamma,\delta\_}$ atom positions are

Table 5. Selected Structural Data of SubPcs from X-ray Analysis

SubPc[a]	N_i−B−N_i	N_i−B−X	B−X	B−N_i	C−C	C−N_i	C−N_{Br}	P[b]	ref
1	105.2	113.8 112.8	1.863	1.467	1.460	1.369	1.344	0.59	2a
46	103.2 117.5 110.5	117.7	1.418	1.502	1.458	1.375	1.336-	0.64	2c
41	105.3	113.4	1.875	1.455 1.490					2e
61	102.9	116.5 115.6 116.6	1.438	1.494	1.469	1.365	1.340	0.66	2f
61 · 2 H_2O	102.9	118.7 113.1 114.7	1.426	1.495	1.460	1.363	1.355	0.64	2f
28	102.6	116.5 117.2 113.2	1.605	1.504	1.454	1.364	1.345	0.65	2b
47	102.7	117.0 108.0 121.2	1.420	1.502	1.452	1.363	1.348	0.65	2d
51· 0.5 $H_2O·C_2H_5OH$	104.5	116.1 108.7 117.3	1.461	1.493	1.446	1.363	1.344	0.61	2f
51· 0.4 H_2O· 1.1 C_5H_5N	104.5	115.8 108.7 117.0	1.473	1.492	1.455	1.367	1.344	0.60	2f

[a] See Tables 1 and 3. [b] Distance between the boron atom and the plane defined by the 3 N_i atoms (Figure 4).

virtually independent of the peripheral or axial substitution.

As a rule, the main geometric changes brought by the change of X ligand on the boron atom remain confined to the $X(N_i)_3$ tetrahedron. The boron atom lies from 0.59 to 0.66 Å above the plane ***P*** (defined by the three N_i atoms) depending on the axial X ligand. The B−X bond length varies from 1.418 Å for SubPc **28** (Table 1, X = phenyl) to 1.863 Å for SubPc **1** (Table 1, X = Cl). The angles involving the boron atom are somewhat slightly deformed with respect to the ideal tetrahedron, N_i−B−N_i and Cl−B−N_i angles ranging from 103° to 105° and from 109° to 118°, respectively. As a general trend, the pyramidality of SubPc increases with the electronegativity of the atom of the X ligand directly linked to the boron atom. The X-ray crystal structure of acyloxy-substituted SubPcs **51** (Table 3) shows further desymmetrization at the tetrahedron level since the B−O bond is not perpendicular to the ***P*** plane. The B−O bond is slightly tilted toward one of the pyrrole rings by a little less than 10°. All three B−N_i distances are identical within the error margin and possess an average value of 1.467 Å, significantly shorter than the standard B−N single bond length (1.611 Å).[34] A shortening of this bond by π conjugation would be impossible since the boron atom is already tetracoordinated. This very short B−N bond may be a consequence of the steric effects at the level of the above-mentioned tetrahedron, since a larger distance would deform it even more.

The geometric parameters within the subphthalocyanine family vary much less than those of the phthalocyanine macrocycles (Table 5). Most bonds are comparable in length even if the C_α−N_i bonds are generally slightly smaller, while those of the C_α−N_{br} are slightly longer. Larger differences are found in the C_α−N_i−C_α bond angles (ca. 112°) that are typically larger for subphthalocyanines than those found in Pcs (ca. 108°), indicating that the coordination of a boron atom to the isoindole nitrogen N_i forces it away from the ***P*** plane (parameter ***P***, Table 5). As a consequence, the C_α−N_{Br}−C_α and the N_i−C_α−N_{Br} angles in SubPcs are smaller than those in Pcs. The deviation of the benzene ring from planarity does not exceed 0.02 Å. The N_i−C_α and N_{Br}−C_α lengths are 1.366 and 1.345 Å, respectively, the former being always somewhat longer than the latter, showing the partial loss of their single- and double-bond characters, respectively.

The pyrrole rings are not planar; the N_i nitrogen atom is located above the plane formed by the four carbon atoms by about 0.16 Å so as to be located closer to the boron atom. The perpendicular line to the plane formed by the four carbon atoms of the pyrrole ring forms an angle of 21.2° with respect to the B−X bond axis.

The perpendicular to the benzene rings forms an angle of about 24° with the same axis. The C_α and C_β carbon atoms of the isoindole groups do not lie in the same plane as the C_γ and C_δ benzene ones, the pyrrole ring being bent by about 3° with respect to the adjacent benzene ring. The C_β−C_γ, C_γ−C_δ, and C_δ−C_δ bond lengths in the benzene rings are fairly standard (1.395 Å), while the common bond C_β−C_β between benzene and pyrrole rings is slightly longer (1.418 Å).

B. ^{1}H NMR Spectroscopy Characterization

Subphthalocyanines yield very informative and well-defined ^{1}H NMR spectra unlike those obtained for phthalocyanines that are usually broad due to the tendency of their π-systems to form aggregates.

SubPcs do not form aggregates, and their protons chemical shifts do not depend on the samples' concentration. The effect of strong ring currents in the macrocyclic aromatic core was observed in (i) the low-field chemical shifts (from 7.8 to 9.9 ppm) corresponding to the protons attached to the C_γ and C_δ carbon atoms (Figure 4) and (ii) in the high-field chemical shifts corresponding to protons on the axial ligand pointing toward the macrocycle.[2b,d,4a,5a,8n,p,14,19] While the peripheral substitution does influence the aromatic protons chemical shifts in a predictable way (according to the nature of the substituents), the influence of the axial substituent is not as simple. The ^{1}H NMR chemical shifts follow the order δ_{Harom} **2** (X = Br) > δ_{Harom} **45**/**46** (X = O) > δ_{Harom} **1** (X = Cl) (Table 3), showing that there is communication between the aromatic macrocycle and the axial substituents through the boron atom and the aromatic macrocyclic core. ^{11}B NMR spectroscopy gave results in accordance with the expected chemical shifts for a tetrasubstituted boron atom.[2f,4a] In all cases the boron atom gave rise to a sharp singlet located between −17.7 and −19.6 ppm.

C. Mass Spectrometry Characterization

The characterization of the first subphthalocyanine **1** by Meller and Ossko was made possible mostly by electron impact mass spectroscopy.[3] The fragmentation pattern was unambiguously characteristic of a compound containing both a boron and a chlorine atom as well as three diiminoisoindole units. LSIMS or FAB and MALDI mass spectrometries usually yield very clean spectra including the molecular ion as the major peak. However, the presence of peaks corresponding to the loss of the axial ligand (SubPc-boron cation) is quite commonly observed. These peaks appear to be more intense in the case of subphthalocyanines substituted by donor groups in the peripheral positions,[35] which is consistent with a marked ionic character of the B−X bond.

D. Infrared Spectroscopy Characterization

The infrared spectra of SubPcs can be interpreted mostly on the bases of the bending and stretching of the C−C and C−N bonds of the macrocycle and, therefore, are similar to those of phthalocyanines. We will then focus on the assignment of the stretching band corresponding to the B−X bond that was made possible by substituting the boron atom in the subphthalocyanines with ^{10}B and monitoring the changes.[2f] A decrease of the wavenumber was observed within the halogen series 1063 (**27**, X = F, Table 1), 960 (**1**, X = Cl), and 622 cm^{-1} (**2**, X = Br) in accordance with the electronegativity of the ligand. In the case of alkoxy SubPcs **47**−**49** (Table 3), the B−O stretching was found at 1119 (**47**, R = C_4H_9), 1107 (**49**, R = C_3H_7), and 1052 cm^{-1} (**48**, R = Ph). The comparison of ν(C−O) and ν(C=O) stretching in the IR spectrum of SubPc **51** (Table 3) (R = CH_3, 1702 and 1277 cm^{-1}, respectively) revealed a hypsochromic shift of about 100 cm^{-1} with respect to metalloacetates and a bathochromic shift of about 80 cm^{-1} with respect to acetic acid.[2f] The difference ν(C=O) − ν(C−O) = 425 cm^{-1} is not compatible with a bidentate coordination, which has to be smaller than 200 cm^{-1}. These results are in accordance with the monodentate ligand character also found in the crystal structure of **51**. In all cases, the vibration frequencies are in total accordance for both carboxylates and alkoxy series with the inductive effects brought by the substituents on the ligands. With the increase in the polarity of the B−O bond, there is a decrease of the covalent character of the bond. In the μ-oxo dimer (see section VI), a band at 1069 that shifts to 1087 cm^{-1} upon substitution by ^{10}B was assigned to the asymmetric B−O−B vibration.

E. UV−Vis and MCD Spectroscopy Characterization

UV−Vis spectra of subphthalocyanines are comparable to the ones obtained for phthalocyanines in that they both show a Q-band and a Soret B band as in other aza aromatic macrocyclic compounds. In the case of SubPcs there is a tendency for both the Soret band (300 nm) and the Q-band (560 nm) to shift to shorter wavelength with respect to Pcs as a consequence of the decrease of the π-conjugation system (Figure 5). Absorption coefficients (ϵ) in both the Soret band and the Q-band also decrease on going from Pcs to SubPcs. For example, the ϵ values of the Q-bands of SubPcs are (5−6) × 10^4 dm^3 mol^{-1} cm^{-1}, and those for most Pcs are in the range 8−24 × 10^4 dm^3 mol^{-1} cm^{-1}. The smaller Q-band intensity of SubPcs compared to that of Pcs may be attributed to their nonplanar structure.[8p,16a] Peripheral donor and acceptor substituents tend to shift the Q-band of SubPcs toward longer wavelengths, while axial substituents have no or only a very small effect on the position of the bands (Table 6). Absorption spectra of alkoxy-, sulfonyl-, or thioether-substituted SubPcs **4**, **8**−**10**, **13**−**17**, **21**, **22**, **25**, **26**, and **32** (Table 1) differ from those of the rest of SubPcs in that another band that may be an n−π transition attributable to the oxygen or sulfur atoms, observed at ca. 400 nm.[12e]

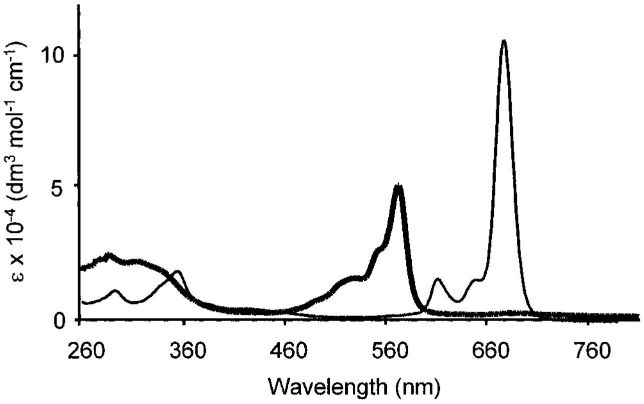


Figure 5. UV−vis spectrum of subphthalocyanine **1** (thick line) compared to the one of nickel phthalocyanine (thin line), both in chloroform.

Magnetic circular dichroism (MCD) is usually employed, as a complementary technique to UV−Vis spectroscopy, to retrieve valuable information about the nature of UV−Vis transitions such as the position

Table 6. λ_{max} Corresponding to the Q Band of Some Selected SubPcs

SubPc	type [a]	R peripheral	X axial	λ_{max}	solvent
1	D	H	Cl	565	$CHCl_3$
2	D	H	Br	567	$CHCl_3$
6	D	F	Cl	570	CH_3CN
28	D	H	Ph	566	toluene
33	D	H	butyl	566	$CHCl_3$
45	D	H	OMe	561	$CHCl_3$
46	D	H	OEt	561	$CHCl_3$
47	D	H	O*tert*-butyl	562	$CHCl_3$
48	D	H	OPh	562	$CHCl_3$
61	D	H	OH	562	$CHCl_3$
34	N	H	Ph	650	toluene
37	N	H	Br	667	ODC[b]
9	H	SC_8H_{17}	Cl	603	$CHCl_3$
10	H	$SO_2C_8H_{17}$	Cl	579	$CHCl_3$
18	Tm	*tert*-butyl	Cl	570	$CHCl_3$
19	Tm	NO_2	Cl	580	$CHCl_3$
20	Tm	I	Cl	574	$CHCl_3$
21	Tm	SC_8H17	Cl	584	$CHCl_3$
22	Tm	$SO_2C_8H_{17}$	Cl	570	$CHCl_3$

[a] See Figure 2. [b] ODC = *ortho*-dichlorobenzene.

(energy) and number of transitions to the degenerate excited states. In SubPcs **1**, **3**, and **7** (Table 1), it was oberved that the positions of MCD peaks or troughs in the Q-band region are approximately the same as those of absorption shoulders or a peak. From these studies it can be concluded that the Q_{0-0} band corresponds to a transition to an orbitally degenerate state that could only be fitted with a Faraday A term. On the other hand, the Soret region is composed of three bands that correspond to three transitions to nondegenerate states (Faraday B terms).[8p,16a,18]

F. Redox Properties

The first oxidative or reductive half-wave potentials of SubPcs are both one-electron processes and are generally observed at around 1 and −1 V, respectively (Table 7). The oxidation is quasi-reversible and appears to be accompanied by some decomposition, while on the other hand, the reduction appears to be reversible on the cyclic voltammetry time scale. For comparison, the corresponding redox potentials of chloroaluminumphthalocyanine (AlClPc) appear at 1.1 and −0.5 V, which is roughly consistent with the fact that the Q-band of SubPcs (ca. 570 nm) is shifted to shorter wavelengths with respect to that of AlClPc (670 nm).

The substitution in an axial position does not change[2c,f] significantly the reduction and oxidation potentials (Table 7). It seems that the redox properties of SubPcs are mostly driven by the nature of the macrocyclic aromatic core.

On the other hand, the nature of the peripheral substituents on the macrocycle may alter dramatically the redox properties of the overall molecule.[12e,24a] The oxidation and reduction potentials follow the trend one would anticipate from the substitution pattern, the fluoro and nitro derivatives **6** and 1**9**, respectively, being the easiest to reduce by ca. 500 mV relative to unsubstituted SubPc **1**, followed by sulfonyl derivatives **22** and **12** (by 350 and 270 mV, respectively). The oxidation potentials follow the same trend.

The spectrum of the anion radical of subPc **6**, which was obtained by spectroelectrochemistry,[24a] showed a broad absorption centered at 490 nm very different from the one of the neutral species.

G. Molecular Modeling

Theoretical studies of subphthalocyanines at Hartree−Fock and density functional theory levels using STO-3G and 6-31G basis sets yielded geometrical parameters that agree well with the experimental data obtained by X-ray diffraction, although the AM1 method gave bond distances significantly larger (0.1 Å) than the experimental ones.[8p,18,36] No substantial changes with respect to unsubstituted SubPc **1** in the geometrical parameters were observed when peripheral substituents were introduced in the SubPc core (SubPcs **18** and **19**).[36a,b] On the other hand, it was found[36c] that the nature of the axial ligand alters dramatically the geometry of the tetrahedron formed by the four atoms $(N_i)_3$−X as already observed in the X-ray crystal structures.

The experimental and theoretical dipole moments[36a,b] (AM1 method) are in good agreement for compounds **1**, **2**, **20**, **21**, and **22**. Deviations

Table 7. Known Redox Potentials of SubPcs

SubPc	type [a]	R	X	ox.	red.	solvent
1	D	H	Cl	1.04	−1.05	CH_2Cl_2
2	D	H	Br	1.03Epa	−1.06Epc	CH_2Cl_2
6	D	F	Cl	1.50	−0.53	CH_3CN
45	D	H	OMe	1.05Epa	−1.10	CH_2Cl_2
46	D	H	OEt	1.06	−1.11	CH_2Cl_2
47	D	H	O*tert*-butyl	1.03	−1.11(−1.03)	CH_2Cl_2
48	D	H	OPh	1.09Epa	−1.05	CH_2Cl_2
51	D	H	$OCOCH_3$	1.01	−1.08	CH_2Cl_2
53	D	H	$OCOCH_2Ph$	1.05	−1.08	CH_2Cl_2
55	D	H	$OCOCF_3$	1.08	−0.98	CH_2Cl_2
11	H	*p*-tolylthio	Cl	1.02	−0.97	CH_2Cl_2
12	H	*p*-tolylsulfonyl	Cl	1.29	−0.78	CH_2Cl_2
18	Tm	*tert*-butyl	Cl	0.98	−1.11	CH_2Cl_2
19	Tm	NO_2	Cl	1.34	−0.57	CH_2Cl_2
20	Tm	I	Cl	1.13	−0.92	CH_2Cl_2
21	Tm	SC_8H_{17}	Cl	0.95	−1.09	CH_2Cl_2
22	Tm	$SO_2C_8H_{17}$	Cl	1.27	−0.70	CH_2Cl_2

[a] See Figure 2.

between the experimental and calculated dipole moments are found in compounds **9** and **10**, bearing six long lipophilic chains, where the experimental values are higher than the calculated ones, probably as a consequence of the aggregation of the lipophilic chains. Finally, the major discrepancy was found in **19**, where the computed values are very different for C_1 and C_3 isomers.

The MO calculations[8p] of the Q-bands and Soret bands of SubPcs, within the framework of the Pariser–Parr–Pople (PPP) approximation, were found to be in good correspondence with the experimental observations in both energy and strength.

Theoretical calculations were performed so as to explain the origin of the reactivity of the SubPc in its ring expansion reaction. The first one, using DFT/natural bond orbital treatment, discarded the strained structure as a possible cause and rather proposed that the reactivity comes from a lack of donor–acceptor stabilization in the $B-N_i$ bonds.[8p] On the other hand, it was suggested,[36c] according to DFT/6-31G calculations, that the reactivity and unstability of SubPcs may come from the exceptionally polar nature of the B–X bond.

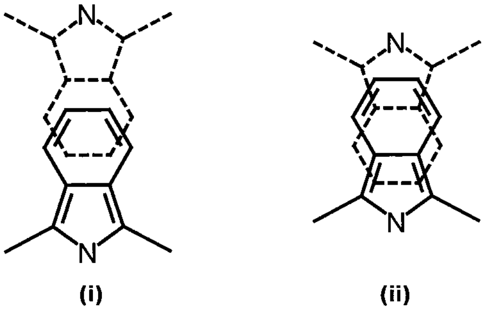
V. Subphthalocyanines as Building Blocks for Molecular Materials

A. Organization of Subphthalocyanines in Condensed Phases

The potential nonconventional physical properties of subphthalocyanines are expected, as in the case of phthalocyanines, to be highly dependent on the organization of the macrocycle at supramolecular level.

1. Organization in the Solid State

The packing in the solid state usually gives valuable information about the type of intermolecular interactions that sustain the cohesion between identical molecules, and its study may help further design of materials in which these interactions could play a significant role. In the case of subphthalocyanines, independently of the different crystal structures and of the packing of the molecules, the presence of pairs of SubPcs in van der Waals contact is one of the most striking features of their X-ray crystal structures.[2d,f] Two types of pairs were found (Figure 6) depending on the axial substituent on the boron atom: (i) in the case of SubPc **1**, the concave faces, which correspond to the hollow part of the molecule, of SubPcs within a pair overlap very little whereas (ii) in the case of SubPcs **46**, **47**, and **61** (Table 3), the overlapping between the isoindole units is much more pronounced. UV–Vis spectrophotometry, performed in the solid state, is consistent with the two different packings observed in the X-ray crystal structures in that the broadening of the spectra observed for SubPcs **46**, **47**, and **61** is not observed in the case of SubPc **1**. In a secondary organization, the SubPc pairs form a sheet in which the concave faces point inward and the X axial groups point outward toward the next sheets. The intersheet separation mostly depends on the steric hindrance brought by the X axial groups. It is worth mentioning the presence of N_i-H-O and O–H–O hydrogen bonds in the hydrated crystals of **61** and **51**.[2f]



(i) (ii)

Figure 6. Two types of interactions between SubPc molecules in the crystal.

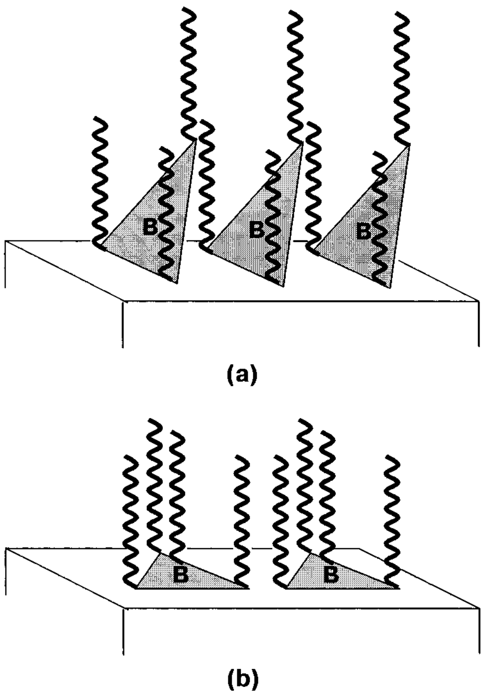


Figure 7. Two different types of organizations within the subphthalocyanines' Langmuir–Blodgett films.

2. Organization in Thin Films

Langmuir–Blodgett Films. The Langmuir–Blodgett technique is one of the best ways for obtaining well-defined multilayers of an organic compound on a solid support.[37]

The organization of SubPcs **10**, **18**, **21**, **22**, and **72** (Tables 1 and 3) in Langmuir films revealed[9b] the films to possess a very low collapse pressure, indicative of the poor stability of the monolayer, as opposed to that corresponding to their parent phthalocyanine. The axial X ligand prevents the molecules from interacting efficiently via $\pi-\pi$ interactions as observed in the case of phthalocyanines.[38] According to the comparison between calculated and experimental areas per molecules, SubPcs **10** and **72** were found to lie flat on the surface (**a** in Figure 7), whereas SubPcs **18**, **21**, and **22** possess an edge-on disposition at the gas/water interface (**b** in Figure 7). These results suggest that the orientation of SubPcs on air/water interface can be chemically modulated by increasing the number of polar groups in the periphery or by adding bulky groups in the axial position.

LB films of SubPc **22** made of up to 50 layers could be obtained by transfer onto glass substrates. Infrared linear dichroism of the films showed a very small preferential alignment with respect to the dipping direction, 1 order of magnitude smaller than that found for some Pc derivatives in LB films.[38] The analysis of such a dichroism suggests that various transition dipoles of SubPcs are tilted versus the normal to the substrate with an angle of ca. 60°, indicating that the macrocycle is tilted in the LB film (Figure 7).

X-ray diffraction and ellipsometry experiments suggested that the lamellar structure is not perfectly well-defined and demonstrated that LB films of SubPc **22** are formed of interpenetrated layers of Y-type with a well-defined layer thickness of ca. 16 Å.

Evaporated Films. SubPc **5** films obtained by vacuum deposition on single-crystal silicon substrates were studied by spectroscopic ellipsometry to determined their refractive index, dielectric constants, and absorption coefficients.[17c] The position of the maximum of refractive index at 630 nm and the low value of the extinction coefficient *k* in this wavelength range ($k < 0.05$) clearly indicate that SubPc thin films are advantageous for the applications in DVD-recordable (DVD-R). Several patents have also demonstrated the advantages of SubPcs thin films for high-density optical data storage.[17d−i] Submonolayers of SubPc **1** onto silicon Si(111)−(7 × 7) were obtained[39] by vapor deposition in a deposition chamber. Scanning tunneling microscopy (STM) of these submonolayers clearly revealed the site-dependent molecular physisorption as well as dissociative chemical reaction of the SubPc molecules on the silicon surface. At room temperature, single molecules are discriminated to physisorb only in one specific site on the triangular subunit cell of the Si surface: the axial chlorine atom is anchored onto one Si restatom, and the N_i and N_{Br} atoms sit closer to the surrounding Si adatoms. In this case the SubPc molecule appears as three bright spots corresponding to the more electron-dense benzene rings. A lateral displacement from this position results in a breakup of the molecules into low-molecular components containing one or two aromatic units, probably as a consequence of the electrophilic attack at the more reactive Si adatom "dangling" bonds on the active molecular site of the SubPc.

3. Organization in Liquid Crystals

SubPcs have been long considered as potential columnar mesogens as a consequence of their cone-shaped geometry. SubPcs **13**−**16** (Table 1) show[11] enantiotropic liquid crystalline behavior as revealed by differential scanning calorimetry (DSC), polarizing optical microscopy, and X-ray diffraction. DSC revealed compounds **13** and **14** to possess mesomorphic behavior at room temperature. SubPc **15** shows a phase transition from crystalline to mesophase near room temperature and transforms into an isotropic liquid at 75 °C. Furthermore, SubPc **16** is a solid at room temperature and melts at 43 °C to form a mesophase, which turns into an isotropic liquid phase at 70 °C. Polarizing optical microscopy performed on compounds **13**−**16** showed that these compounds exhibit pseudo-focal conic textures, which are characteristic of columnar mesophases. X-ray diffraction suggested that the bowl-shaped mesogens may be stacked in a head-to-tail fashion to form a polar column which in turn forms a hexagonal array with random polarity.

Despite their similar structure to SubPcs **13**−**16** mentioned above, it was unambiguously demonstrated that hexaalkylthiohydroxy and -silyloxy axially substituted subphthalocyanines **62**, **63**, **65**, and **69**−**72** (Table 3) do not show any liquid crystalline behavior.[9c] On the contrary, these SubPcs were the first ones to show an isotropic liquid character. The nature of the axial substituents seems then to be crucial as far as the organization of the molecules in columnar stacks is concerned.

B. Physical Properties

1. Excited States

The cone-shaped structure of SubPcs provides a chromophore with distinctive photophysical properties that compare favorably to those shown by related planar phthalo- and naphthalophthalocyanines. The development of second-generation compounds for photodynamic therapy with improved properties is currently the subject of major research efforts.[40] Mostly all the candidate compounds possess a planar skeleton, a feature that leads to stacking in biological media and loss of photosensitizing effectiveness. Subphthalocyanines, with their cone-shaped structure, do not form aggregates, and they have higher triplet and singlet oxygen quantum yields, which makes them amenable to cytotoxicity for exploring their use in photodynamic therapy applications.

Subphthalocyanines are fluorescent[12e,16a,24a] (emission and excitation spectra of being in a mirror image relationship) with quantum yields, Φ_F, ca. 0.25, about one-half the value observed for related phthalocyanines, e.g., $\Phi_F = 0.58$ for AlPcCl. Clearly, nonradiative deactivation channels, i.e., internal conversion and intersystem crossing, are more efficient for SubPcs than for Pcs. The low quantum yield observed for triiodo SubPc is characteristic of the highly efficient intersystem crossing of heavy atom substituted aromatic compounds (Table 8). The lifetimes of the excited singlet state, τ_S, are ca. 3 ns for all compounds, about one-half the value for phthalocyanines. SubPcs have larger triplet quantum yields than Pcs. The triplet-state lifetime is in the 100 μs time range, long enough for efficient oxygen quenching. The singlet to triplet energy gap (30−40 kJ mol^{-1}) is significantly smaller than that of phthalocyanines (50−70 kJ mol^{-1}). Consistent with this, the intersystem crossing rate constants and quantum yields are larger. Small singlet−triplet energy gaps in combination with high triplet quantum yields were also encountered in other nonplanar aromatic molecules such as C_{60} ($\Phi_T = 0.62$).[41] The SubPcs are excellent photosensitizers (quantum yield ranging

Table 8. Known Photophysical Data for SubPcs

SubPc [a]	type [b]	R	X	E_S[c] kJ mol^{-1}	Φ_F [d]	τ_S [d] ns	E_T [e] kJ mol^{-1}	Φ_T [d]	τ_T [f] μs	k_qO_2 [d] 10^9 M^{-1} s^{-1}	Φ_Δ [d]
1	D	H	Cl	209	0.25	3.3	175	0.62	82	1.79	0.61
6	D	F	Cl		0.66	2.6					
28	D	H	Ph		0.14						
45	D	H	OCH_3		0.37						
68	D	H	OSi(tBu)Me_2		0.21						
11	H	*p*-tolylthio	Cl	195	0.24	2.9	164	0.69	157	1.18	0.64
12	H	*p*-tolylsulfonyl	Cl	200	0.23	2.9	152	0.42	132	1.17	0.30
32	H	Crown	Ph		0.135						
3	Tm	*tert*-butyl	Br		0.61	2.1					
18	Tm	*tert*−butyl	Cl	209	0.16	2.8	166	0.55	127	0.88	0.47
19	Tm	NO_2	Cl	203	0.20	3.2	154	0.49	109	1.33	0.46
20	Tm	I	Cl	208	0.013	<0.5	169	0.77	56	1.15	0.74
21	Tm	SC_8H_{17}	Cl	202	0.25	2.8	173	0.62	130	1.46	0.61
22	Tm	$SO_2C_8H_{17}$	Cl	207	0.18	3.1	162	0.25	144	0.95	0.23
34	N	H	Ph		0.094						
36	N	H	Cl	179	0.22	2.5	130	0.68	95	2.5	0.68

[a] See Tables 1−3. [b] See Figure 2. [c] E_S is the energy of the first excited singlet state. [d] As defined in the text. [e] E_T is the energy of the first excited triplet state. [f] τ_T is the lifetime of the first excited triplet state.

Table 9. Known Physical Data Representative of the Nonlinear Optical Properties of SubPcs

SubPc [a]	type [b]	R	X	μ_0 (D)	$\langle\gamma_{EFISH}\rangle(2\omega)$ ($\times 10^{-34}$ esu) 1.34 nm	$\langle\gamma_{EFISH}\rangle(2\omega)$ ($\times 10^{-34}$ esu) 1.9 nm	$\langle\gamma_{THG}\rangle(2\omega)$ ($\times 10^{-33}$ esu) 1.34 nm	$\langle\beta^2_{HRS}\rangle^{1/2}(2\omega)$ ($\times 10^{-30}$ esu) 1.46 nm	$\langle\beta^2_{HRS}(0)\rangle^{1/2}$ ($\times 10^{-30}$ esu)[c]
1	D	H	Cl	0	−60			296	71
9	H	SC_8H_{17}	Cl	15	13	−3	−106	40	10
10	H	$SO_2C_8H_{17}$	Cl	14.8	80	−15	−27	260	
11	H	*p*-tolylthio	Cl	4.8	13.6	−8	−70	64.3	
12	H	*p*-tolylsulfonyl	Cl	8.6	130	−13.4	−1.6	211.5	
13−16	H	SC_nH_{2n+1}	Cl					190[d]	21 ± 3
18	T	*tert*-butyl	Cl	1.3	−30			380	86
19	T	NO_2	Cl	5.5	16	−8.5	−13	144.3	
20	T	I	Cl	5.3	4.3	−7.3	−5.8	164.5	
21	T	SC_8H_{17}	Cl	6.7	9.7	−3.7	−23.4	76.5	
22	T	$SO_2C_8H_{17}$	Cl	7.6	22.3	−6.6	−18	168.5	
77	T	$C\equiv C(C_6H_4)NO_2$	Cl	10.1	7	−6	−14	38	

[a] See Tables 1 and 3. [b] See Figure 2. [c] $\langle\beta^2_{HRS}(0)\rangle^{1/2}$ values were calculated according to a three-level model.[d] $\langle\beta^2_{HRS}\rangle^{1/2}(2\omega)$ value obtained at 1.3 nm.

from 0.23 to 0.75) and produce singlet oxygen, $O_2(^1\Delta_g)$, in large quantities. Singlet oxygen production occurs by exothermic energy transfer from the highly populated, long-life triplet state. SubPcs are interesting candidates for use in photosensitization processes, especially in situations where absorption in the red part of the spectrum is not required. Unfortunately, since they are transparent to light above 600 nm, the region of highest tissue penetration, they are not suitable for PDT. Subnaphthalocyanine, on the other hand, could meet all the requirements needed for PDT since they do not aggregate in solution (as they possess the same cone-shaped structure as SubPcs) and have their λ_{max} at around 650 nm. SubNc absorbs in the red part of the spectrum and has substancial fluorescence (Φ_F = 0.22). Significant for photodynamic therapy applications, energy transfer from the triplet state to molecular oxygen occurs with high rate constant and singlet molecular oxygen $O_2(^1\Delta_g)$ is produced with quantum yield $\Phi_\Delta = 0.68$.[16b]

2. Nonlinear Optical Properties

Recently, theoretical and experimental considerations have demonstrated the great potential of conjugated “multipolar” molecules in the field of nonlinear optics.[12,42] In this context, subphthalocyanines, which are of both aromatic and octupolar character, present an extraordinary interest.

Quadratic hyperpolarizabilities β values, as determined from HRS (hyper Raleygh scattering) at λ = 1.46 μm,[12e] compared well with the best values obtained so far with organic molecules.[43] The highest values ($\beta_{HRS} \approx 2-10^{-28}$ esu) were reached for SubPcs containing acceptor substituents in their periphery. Recently, it was shown that femtosecond modulated HRS may be employed[12f−h] to suppress multiphoton fluorescence, which tends to increase artificially the β values.[12b] The EFISH (electric field induced second harmonic) technique was also applied for determining quadratic hyperpolarizabilities of SubPcs but did not yield fully reliable data as a consequence of the unknown contribution of the electronic part of the cubic hyperpolarizability (γ_e) to the β tensor.

It was found that[12e] the cubic hyperpolarizabilities γ_{EFISH} of SubPcs at 1.34 μm were also strongly dependent on the donor−acceptor character of the peripheral substituents and reach a remarkable value for SubPcs **10** and **12** (Table 9). Both γ_{THG} and γ_{EFISH} values are in the same range as those reported for some unsymmetrically substituted phthalocyanines and markedly lower than those of symmetrical Pcs.[42c] As opposed to the results obtained by the EFISH technique, the highest γ_{THG} values were obtained for SubPcs **9**, **11**, and **21** containing donor substituent groups. This behavior may be due to the large red shift of the Q optical absorption band that should increase the resonant behavior at 2ω. Moreover, these compounds show an additional band at ca. 400 nm (assigned as a thioether n$-\pi$ band) that is strongly resonant at the third harmonic frequency and so should contribute to the enhancement of the NLO response.

The second harmonic generation[12c] (SHG) yield of both evaporated and spin-coated films of subphthalocyanine **19**, **20**, and **22** has been measured. Partial molecular ordering in the spin-coated films was achieved by the corona poling technique. For the evaporated films the ordering is obtained through the evaporation process itself. Values close to 10^{-9} esu have been obtained for the highest $\chi^{(2)}{}_{31}$ component of the spin-coated films containing SubPc **22**. For the evaporated films the susceptibility values are somewhat higher, indicating a significant degree of molecular ordering.

χ^3 (THG) three times bigger than those obtained for phthalocyanines in the same frequency range (0.95$-$2.00 μm) have been measured in thin films of SubPc **5** prepared by vacuum sublimation over amorphous silica plates.[12a] A four-level model, including the ground state and three excited states associated to bands observed in the linear absorption spectrum, has been successfully used to explain the nonlinear behavior of the compound. This model fits well the magnitude and phase of the THG susceptibility.

To get more information concerning the influence of the organization within the LB film on the SHG response, alternated Langmuir$-$Blodgett from SubPc **22** and behenic acid were deposited onto a silica substrate. Preliminary SHG experiments at $\lambda = 1.064$ μm on LB films made of 100 layers of SubPc **22** revealed a strong increase of the SHG response and much broader angular spectra with respect to the nonalternated LB films. Therefore, it may be concluded that layer alternation induces the noncentrosymmetric ordering in the LB films of SubPcs and its potentiality for second-order NLO applications.

VI. New Trends in Subphthalocyanines

A. μ-Oxo Subphthalocyanine Dimers

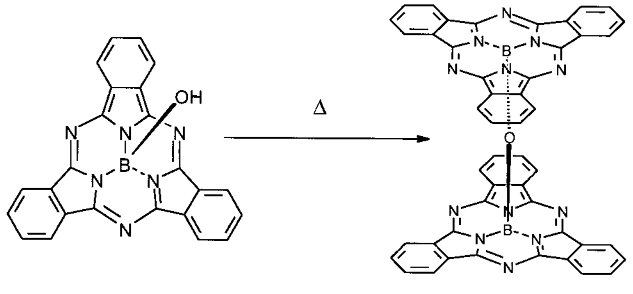
μ-Oxobissubphthalocyanine **77** (Scheme 7) formed by two SubPcs fused through a μ-oxo bridge between the two boron atoms was first isolated in 1996.[4a] It can be synthesized by heating SubPc **61** (Table 3) at 300 °C for 3 h under vacuum[4a] or by refluxing a nitrobenzene solution of SubPc **61** containing molecular sieves.[8p] The dimer was best purified from unreacted material by gel permeation chromatography.

Other axially linked subphthalocyanine dimers have been recently described.[44] They are composed of two identical subphthalocyanines linked by an aromatic diol, such as hydroquinone, catechol, resorcinol, and 1,1′-bis-2-naphthol.

B. Fused SubPc Dimers and Larger Species

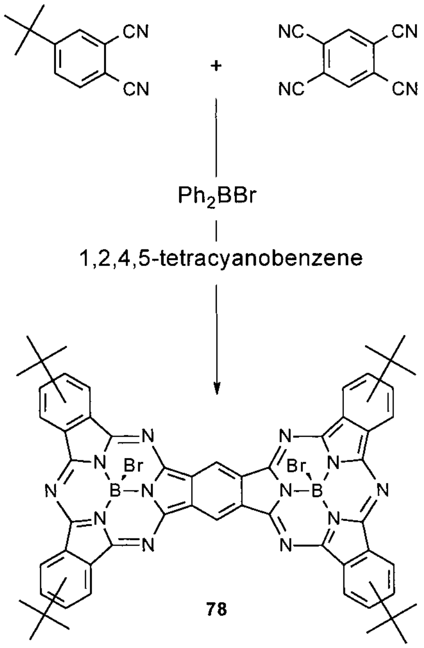
An extension of the π-conjugation of the SubPc aromatic core was exemplified by Kobayashi in 1991 in the synthesis of the subphthalocyanine fused dimer.[16] The condensation of an excess of 4-*tert*-butylphthalonitrile and 1,2,4,5-tetracyanobenzene with diphenylboron bromide yielded, after purification by gel permeation chromatography, a compound to which the structure **78** depicted in Scheme 8 was assigned.

Scheme 7. μ-Oxobissubphthalocyanine Synthesis



61 **77**

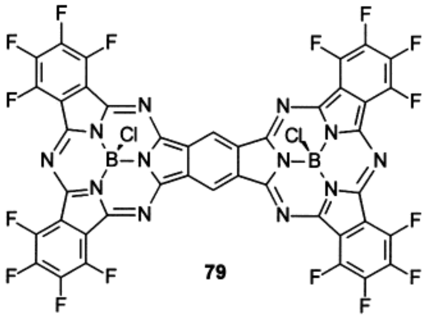
Scheme 8. Synthesis of the Fused Subpthalocyanine Dimer 79



78

However, this work has been recently revisited. Thus, Torres et al. described and fully characterized compound **79** and pointed out that, as a consequence of the concave nature of the Subpc macrocycle, this fused dimer exists as two topological isomers syn and anti represented in Figure 8. These topoisomers have been separated by column chromatography.[20]

From the careful observation of the curved structure of topoisomer syn and also from the geometrical parameters obtained from the X-ray crystal structures of SubPcs (see above), one may consider the subphthalocyanine moiety as a C_3 aromatic supramolecular synthon.[45] Thus, the SubPc macrocycle may be potentially employed for the construction of larger, nanometer-sized fully aromatic molecular architecture that could be coined “heterofullerenoids”.[46] For example, the condensation of decacyanocorannulene with boron trichloride could lead to the sphere containing 20 suphthalocyanines as depicted in Scheme 9.



79

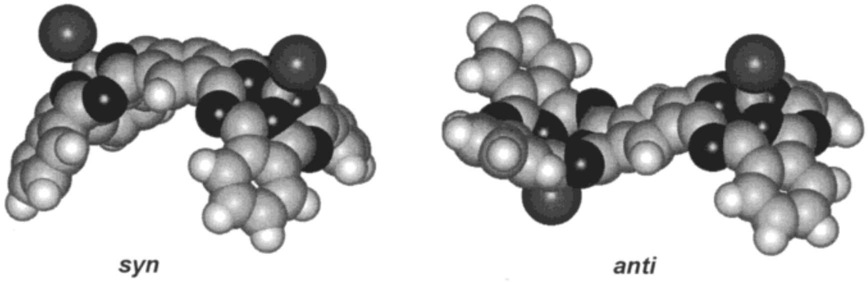
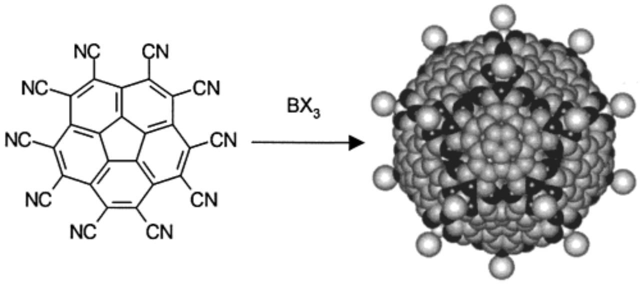


Figure 8. Syn and anti topoisomers of the fused subpthalocyanine dimer **79**.

Scheme 9. Proposed Synthesis of a Subpthalocyanine Molecular Sphere from Decacyanocorannulene



VII. Concluding Remarks

This review has pointed out the interest of subphthalocyanines in many basic and applied areas. The accomplishments achieved so far in subphthalocyanine chemistry and properties are very important, but they are by no means complete.

Thus, for example, further work needs to be done to find alternative synthetic pathways which lead to SubPc-free bases and allow the preparation of SubPcs with other guest central atoms different from boron. New developments will most probably require this new type of compounds. On the other hand, efforts should be made toward the development of chemo-, regio-, and stereoselective methods for the preparation of suitably functionalized systems. The development of a stepwise synthetic approach to subphthalocyanines that could solve some of the problems outlined above remains a challenging task for the future.

There is also a need for mechanistic investigations on the basis of spectroscopic techniques and kinetic studies, either in the boron template cyclotrimerization reaction of phthalonitriles to afford SubPcs or in the ring enlargement reaction of subphthalocyanines in the presence of diiminoisoindolines to yield unsymmetrically substituted phthalocyanines.

Some trends that are beginning to emerge are coming from the particular three-dimensional structure of these compounds. Thus, the preparation of chiral versions of SubPcs and the cone-shaped structure of these azaporphyrins, which allow using them as building blocks for constructing concave aromatic large systems, are aspects that will deserve much attention in the near future.

The optical properties of novel subphthalocyanines will be no doubt intensively investigated. The possibilities of SubPc chromophores for electron and energy transfer are of increasing interest. Adequately substituted subnaphthalocyanines could be targets for photosensitizers with applications in photodynamic therapy. Nonlinear optics is also a field where SubPcs could play an important role.

Regarding industrial applications, subphthalocyanines are especially interesting. In this respect SubPc derivatives and related compounds constitute an important challenge in the photodynamic therapy and high-density optical data storage areas, in which we predict a high development of these compounds, providing that the limitation for applications caused by the instability of some SubPcs at light could be overcome. In this connection there is need for significant improvements in the understanding of the photophysical and photochemical behavior of these compounds.

In summary, we are convinced that the field of SubPcs will grow vigorously in the time to come.

VIII. Acknowledgments

The contributions of those who have developed the research that is described are partially acknowledged by the references to their publications. Particularly, we express our great appreciation to the co-workers and colleagues who have worked in our subphthalocyanine project since 1994 and whose names are recorded in the references. This work was supported by CICYT (Spain) and the European Union through grants MAT-99-0180 and HPRN-CT-2000-00020, respectively.

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