



Thermal stability of boron subphthalocyanines as a function of the axial and peripheral substitution

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ABSTRACT

In this work, we have carried out the synthesis and thermogravimetric study of 10 different axially and peripherally substituted boron subphthalocyanines, in order to compare their thermal stabilities under non-oxidizing conditions. We demonstrate that, in general, these compounds enjoy a relatively high thermal stability, a property that is fundamental for future potential applications. The loss of the axial group is usually the first thermal degradation process to occur, and the temperature at which it takes place increases as a function of the nature of this substituent in the order: $\text{Br} < \text{OH} \leq \text{OPh} \sim \text{Cl}$. Peripheral substituents also have an influence on the thermal properties of subphthalocyanines, though their role is somewhat less notable.

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1. Introduction

Organic π -conjugated molecules are very attractive materials for nanotechnological applications in view of their outstanding and tunable electronic properties, their cheap preparation, and the ability to self-organize into different condensed phases, which facilitates their processing for the construction of devices [1]. However, the use of molecular systems in some applications is very often limited due to their low optical, chemical and/or thermal stability. A notable exception is the case of phthalocyanines (Pcs, Fig. 1) [2], which have demonstrated to benefit from remarkable stabilities [3] and have emerged as very reliable candidates for materials of high durability. Pcs are planar macrocycles comprised of four 1,3-diiminoisoindoline units whose central cavity can be occupied by more than 70 different elements in the periodic system. Their chemical and supramolecular versatility, together with their excellent optical and semiconducting properties, renders them as very promising materials in various applied fields, among

which photovoltaics [4] and nonlinear optics [5] are some of the most relevant.

In contrast, their three-unit homologues, the subphthalocyanines (SubPcs, Fig. 1) [6], enjoy very different structural and physicochemical properties. They possess a peculiar conical structure imposed by steric factors and stabilized by the tetrahedral nature of a central boron atom that, to date, is the only element that has been fitted within the central cavity [7]. SubPcs have a 14- π -electron aromatic system that provides them with very interesting electronic properties that have been exploited in nonlinear optics [8], energy and electron transfer [9], and light-emitting diodes [10].

These compounds, however, have shown to lack the chemical stability of Pcs, especially in the case of SubPcs substituted with electron-withdrawing groups. In fact, early work in SubPc chemistry focused on their interest as synthetic precursors of Pcs by a ring-expansion reaction in the presence of diiminoisoindolines [11]. Moreover, the reaction of electron-deficient SubPcs with nucleophiles has been exploited for the development of selective naked-eye sensors of, for instance, CN^- or F^- anions [12].

Very little is known, however, about the optical and thermal stability of these π -conjugated molecules, despite being very important parameters for their successful application in molecular

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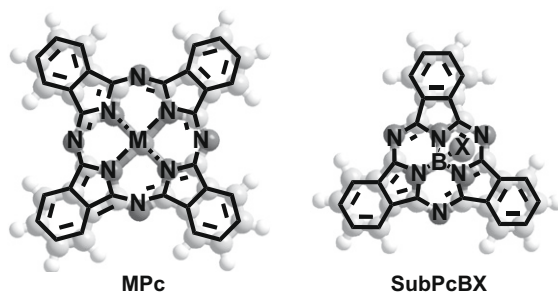


Fig. 1. Structure of a metallophthalocyanine (MPc) and boronsubphthalocyanine (SubPcBX).

materials. In this work, we have made use of thermogravimetric techniques to assess the thermal stability of these macrocycles under non-oxidizing conditions. In addition, we compare the influence of diverse axial and peripheral functional groups, in order to select the best-suited candidates for future applications that demand high stabilities.

2. Results and discussion

2.1. Synthesis

We have prepared 10 different SubPcs that can be classified depending on the substituents placed at the periphery of the macrocycle (H, I, NO₂, or OPh) or on the axial position (Cl, Br, OH, or OPh). For the sake of clarity, the references of the different SubPcs will follow the pattern: “Peripheral substituents-axial group”, as indicated in Scheme 1. ChloroSubPcs **H-Cl**, **I-Cl**, **NO₂-Cl**, and **OPh-Cl** were prepared by cyclotrimerization reaction of the corresponding phthalonitrile in the presence of BCl₃ at reflux of *p*-xylene [13]. Although alkyl ethers are known to cleave in the presence of BCl₃, the diphenyl ether moiety in 4-phenoxyphthalonitrile was stable enough to survive the harsh reaction conditions. Substitution of the axial chlorine atom in these SubPcs by phenol afforded the respective phenoxySubPcs **H-OPh**, **I-OPh**, **NO₂-OPh**, and **OPh-OPh**. These reactions were typically carried out using a small excess of phenol in boiling toluene, except in the case of less activated substrates, like **NO₂-Cl**, which was prepared in molten phenol [13].

In addition to these chloro- and phenoxy-axial substituents, we prepared SubPcs bearing bromo- and hydroxy-groups. SubPc **H-Br** was directly synthesized by condensation of phthalonitrile in the presence of BBr₃. The bromine axial group was then replaced in the presence of SiO₂ in boiling toluene to yield compound **H-OH**,

a method that was found quite efficient for the synthesis of hydroxySubPcs.

All compounds were fully purified and characterized by ¹H and ¹³C NMR, LSI-MS and HR-LSI-MS, UV-Vis and IR spectroscopy, and elemental analysis.

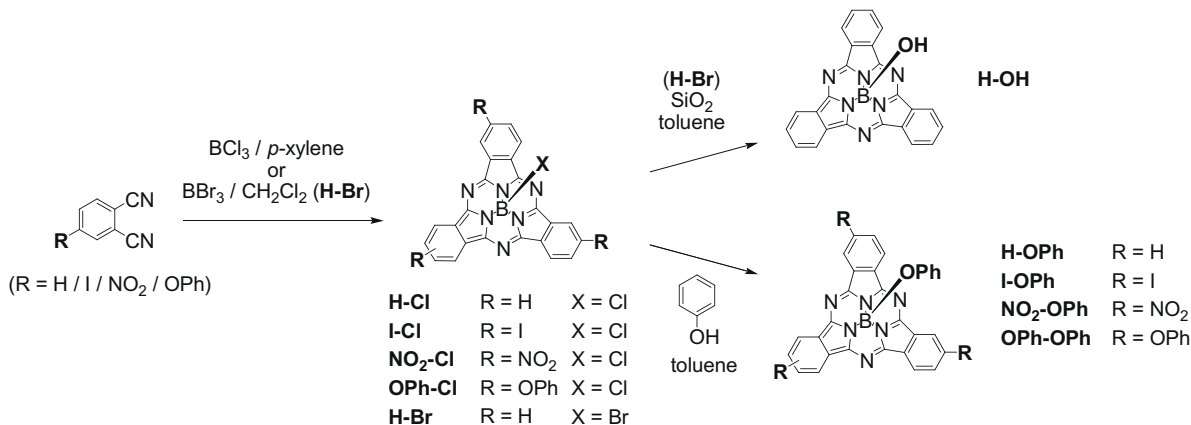
2.2. Thermogravimetric analysis (TGA)

Fig. 2 shows the multifit gaussian of the compounds in the unsubstituted SubPc (**H-**) group: **H-Cl**, **H-Br**, **H-OH** and **H-OPh**, where the only difference comes from the axial substituent attached to the boron atom (Cl, Br, OH, or OPh, respectively). In general, the first mass loss processes occur at temperatures well above 300 °C, which underscores the high thermal stability of these macrocycles. The thermal behavior of SubPcs **H-Cl**, **H-OH** and **H-OPh** can be described by two separate processes. For compound **H-Cl**, the first process takes place above 350 °C and the second one starts around 400 °C. In the case of SubPcs **H-OH** and **H-OPh** the initial degradation processes occur at similar temperatures (~300 °C), but the **H-OPh** degradation process is slower and consequently reaches higher temperatures. It is interesting to note that the mass loss during the first thermal degradation process follows the mass of the axial substituent (**H-OPh** (35%) > **H-Cl** (20%) > **H-OH** (13.6%)), while the mass loss in the second process is very similar for all the compounds, suggesting that it stems from the common SubPc core. Compound **H-Br**, in contrast, shows a more complicated pattern with four different processes, the first one occurring after 220 °C (see Fig. 3).

This set of measurements indicates that the loss of the axial group is the first thermal degradation process to occur in SubPcs, and that the overall thermal stability of these molecules strongly depends on the nature of this axial ligand, increasing in the order: Br < OH ≤ OPh ~ Cl.

In the case of the peripherally substituted SubPcs some similarities are observed. For instance, for **I-Cl**, **I-OPh**, **NO₂-Cl**, and **NO₂-OPh**, two main processes are also observed, the first one occurring again at higher temperatures for the chloro-substituted SubPcs (**I-Cl** and **NO₂-Cl**). Triphenoxy-SubPcs (**OPh-Cl** and **OPh-OPh**) show in contrast a quite different behaviour from the rest of the compounds studied. The thermal degradation of **OPh-OPh** can be well described by only one process above 300 °C while five processes, occurring above 120 °C, are necessary to describe the degradation of **OPh-Cl**. In some of these samples we observed as well the presence of an additional low-mass process that takes place around 200 °C (see Fig. 4).

The comparison between the diverse types of peripheral substituents leads to several conclusions. Among the chloroSubPcs (**H-Cl**, **I-Cl**, **NO₂-Cl** and **OPh-Cl** samples) the most stable com-



Scheme 1. Synthesis and chemical structure of the SubPc compounds employed in this work.

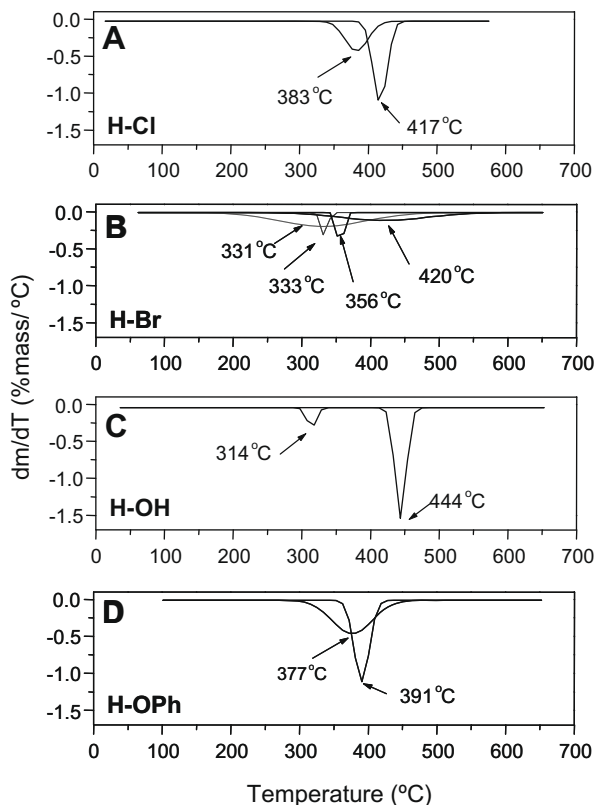


Fig. 2. Fits of the differential thermogravimetric curves of (A) **H-Cl**, (B) **H-Br**, (C) **H-OH**, (D) **H-OPh**.

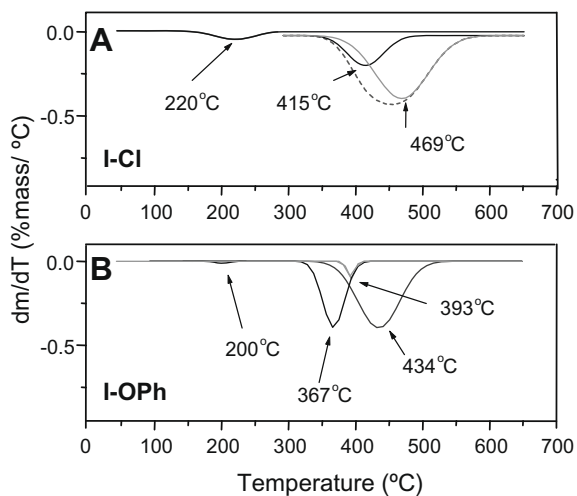


Fig. 3. Fits of the differential thermogravimetric curves of (A) **I-Cl**, (B) **I-OPh**.

compound is **H-Cl** which does not have any substituent on the core structure. Among the phenoxySubPcs (**H-OPh**, **I-OPh**, **NO₂-OPh** and **OPh-OPh** samples) the most stable compound is, in contrast, **OPh-OPh**, whose thermogravimetric curve suggests that the thermal degradation can be initiated either in the central or external phenoxy groups, and needs relatively high activation energies ($T > 325$ °C). We do not know if the higher symmetry of this compound, having four identical substituents placed at the tetrahedral vertexes, might account for this behaviour. The differences in stability among the compounds studied in this work are, however, not very substantial and, in general, it can be said that all the SubPcs

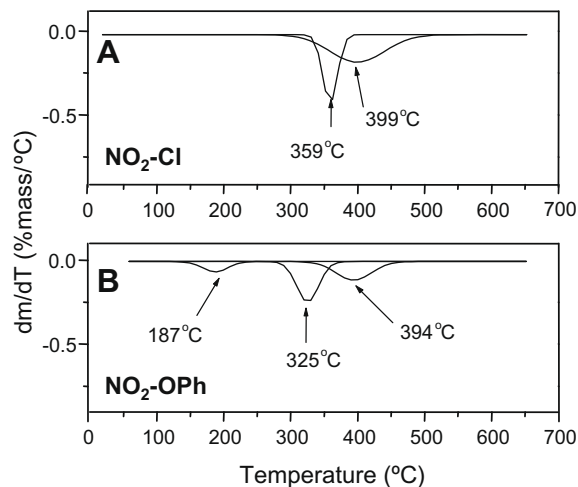


Fig. 4. Fits of the differential thermogravimetric curves of (A) **NO₂-Cl**, (B) **NO₂-OPh**.

enjoy a relatively high thermal stability under non-oxidizing conditions (see Fig. 5).

2.3. Total mass loss

Table 1 shows the total mass loss of the different compounds obtained by this thermogravimetric technique under heating until 650 °C.

For the **H-series**, the total mass loss is very similar, though it increases slightly in the series **H-Cl** < **H-Br** < **H-OH** < **H-OPh**. Probably, this result is related to the influence of the axial groups and their capacity to produce secondary products with low thermal degradability. In addition, it is important to observe that if we compare separately the different chloroSubPcs (**-Cl** series) and the different phenoxySubPcs (**-OPh** series), three of the compounds present very similar total mass loss values (ca. 60–70%). The only exceptions are seen in the trinitroSubPcs (**NO₂-Cl** and **NO₂-OPh**), that show extremely low mass loss values (ca. 35–40%). This suggests that the presence of the peripheral nitro groups promotes secondary reactions with a rearrangement of the structure, resulting in compounds with high thermal stability and low total mass

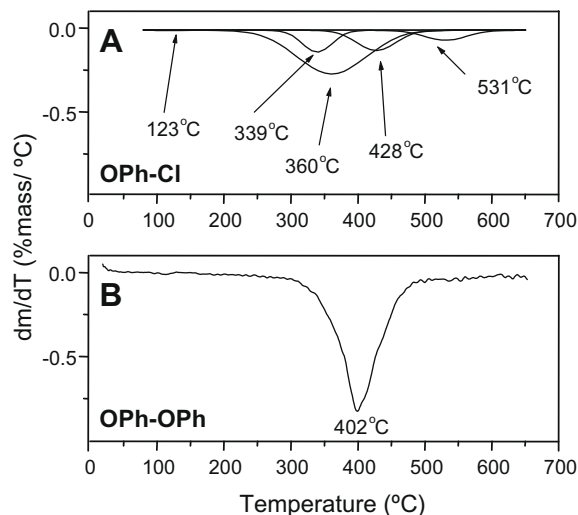


Fig. 5. Fits of the differential thermogravimetric curves of (A) **OPh-Cl**, (B) **OPh-OPh**.

Table 1
Total mass loss of the different SubPc samples.

Sample	Total mass loss (%)
H-Cl	61.29
H-Br	63.79
H-OH	64.32
H-OPh	72.57
I-Cl	59.96
I-OPh	61.73
NO ₂ -Cl	42.95
NO ₂ -OPh	34.89
OPh-Cl	61.82
OPh-OPh	70.24

loss. We are currently carrying out SEM, TEM, IR and micro-Raman spectroscopic measurements in order to analyze the nature of the carbonaceous residue.

3. Conclusion

The results of the thermogravimetric studies carried out in this work suggest that SubPcs have, in general, a high thermal stability, a property that is fundamental for future potential applications. Compared to Pcs, nonetheless, the thermal degradation of these molecules starts at lower temperatures (by ca. 100 °C) [3c]. The loss of the axial group seems to be usually the first thermal degradation process, and the temperature at which it occurs increases as a function of the nature of this substituent in the order: Br < OH ≤ OPh ~ Cl. On the other hand, the influence of the peripheral substitution on the thermal stability of SubPcs is less significant role, and seems to be sometimes coupled to the nature of the axial substituent.

4. Experimental

4.2. Synthesis and characterization

4.2.1. General methods

Melting points (m.p.) were determined in a Büchi 504392-S equipment and are uncorrected. UV-Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. LSI-MS and HRMS spectra were determined on a VG AutoSpec apparatus. NMR spectra were recorded with a BRUKER AC-300 instrument. Elemental analyses were performed with a Perkin-Elmer 2400 CHN equipment. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F₂₅₄ (E. Merck). Chemicals were purchased from commercial suppliers and used without further purification. Phthalonitrile and 4-nitrophthalonitrile were purchased from Aldrich, while 4-iodophthalonitrile [14] and 4-phenoxyphthalonitrile [15] were prepared from 4-nitrophthalonitrile using the reported procedures. The synthesis and characterization of SubPcs H-Cl [11b,16], I-Cl [17], NO₂-Cl [8a], H-OPh [18], I-OPh [9a,b], H-Br [18a], and H-OH [11d,17,18b,19] has been previously reported in the literature. The synthesis of H-OH is described here following a novel method. All the trisubstituted SubPcs were used as approximately 1:3 mixtures of their C₃ and C₁ regioisomers [20].

4.2.1.1. Chloro-[2,9,16(17)-triphenoxy-7,12:14,19-diimino-21,5-nitrilo-5H-tribenzo[*c,h,m*][1,6,11]triazacyclopentadecinato-(2)-kN²², kN²³, kN²⁴]-boron(III) (OPh-Cl; 1:2.9 mixture of C₃:C₁ regioisomers). In a 25 mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, BCl₃ (5 mL, 1M solution in *p*-xylene) was added to 4-phenoxyphthalonitrile (1.10 g; 5 mmol) under argon atmosphere. The reaction mixture was

stirred under vigorous reflux for 15 min. The purple solution was then allowed to reach room temperature and flushed with argon. The solvent was removed by vacuum distillation and the resulting red-brown solid was subjected to column chromatography on silica gel using a 4:1 mixture of hexane/ethyl acetate as eluent. SubPc OPh-Cl was further purified by precipitation from methanol/water (20:1), yielding 400 mg of a reddish solid (34%). M.p. > 250 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.83 (d, J_o = 8.8 Hz), 8.82 (d, J_o = 8.8 Hz), 8.77 (d, J_o = 8.8 Hz), 8.75 (d, J_o = 8.8 Hz), 8.36 (d, J_m = 2.3 Hz), 8.32 (d, J_m = 2.3 Hz), 8.30 (d, J_m = 2.3 Hz), 8.29 (d, J_m = 2.3 Hz), 7.63 (dd, J_o = 8.8 Hz, J_m = 2.3 Hz), 7.61 (dd, J_o = 8.8 Hz, J_m = 2.3 Hz), 7.59 (dd, J_o = 8.8 Hz, J_m = 2.3 Hz), 7.58 (dd, J_o = 8.8 Hz, J_m = 2.3 Hz), 7.5–7.0 (m). ¹³C NMR (75.5 MHz, CDCl₃): δ (ppm) = 160.3, 160.2, 160.1, 159.9 (3C; C-2, C-9, C-17), 156.2, 156.1 (3C; C-22), 150.4, 149.9, 149.3, 148.8, 148.8, 148.7, 148.2 (6C; C-5, C-7, C-12, C-14, C-19, C-21), 133.2, 133.0, 132.9, 132.8 (3C; C-7a, C-18a, C-21a), 130.0, 129.9 (6C; C-24), 126.1, 126.0, 125.9 (3C; C-4a, C-11a, C-14a), 124.6, 124.5 (3C; C-25), 124.0, 123.9, 123.8, 123.4 (3C; C-4, C-11, C-15), 121.7, 121.6 (3C; C-3, C-10, C-16), 119.9, 119.8 (6C; C-23), 110.2, 110.1, 110.0 (3C; C-1, C-8, C-18). MS (LSI-MS, *m*-NBA): *m/z* = 706 [M]⁺ (15%), 688 [M-18]⁺ (30%), 671 [M-Cl]⁺ (30%). HRLSI-MS (C₄₂H₂₄N₆O₃BCl) [M]⁺: Calculated: 706.1691. Found: 706.1639. UV-Vis (CHCl₃): λ_{max} (nm) (log ε (dm³ mol⁻¹ cm⁻¹)) = 574 (4.5), 528 (sh), 338 (4.2), 316 (4.2), 272 (4.5). Elemental Anal. Calc. for C₄₂H₂₄N₆O₃BCl: C, 71.36; H, 3.42; N, 11.89. Found: C, 70.97; H, 3.64; N, 12.10%.

4.2.1.2. Hydroxy-[7,12:14,19-diimino-21,5-nitrilo-5H-tribenzo[*c,h,m*][1,6,11]triazacyclopentadecinato-(2)-kN²², kN²³, kN²⁴]-boron(III) (H-OH). In a 25 mL round-bottomed flask, equipped with a condenser and a magnetic stirrer, 500 mg of silica gel (230–400 mesh) and bromoSubPc H-Br (118 mg; 0.25 mmol) were placed. Toluene (3 mL) was added and the mixture was stirred and heated to reflux for 1 h. After that time, the reaction was allowed to reach room temperature and the mixture was directly poured onto a silica gel column and eluted with toluene/THF (10:1). Hydroxysubphthalocyanine H-OH was obtained as a pink solid which was further purified washing with hexane (84.5 mg; 82%). M.p. > 250 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.75–8.65 (AA'BB' system, 6H), H-1, H-4, H-8, H-11, H-15, H-18), 7.88–7.78 (AA'BB' system, 6H), –0.58 (s (broad), 1H; OH). ¹³C NMR (75.5 MHz, CDCl₃): δ (ppm) = 150.9, 130.8, 129.6, 122.0. MS (LSI-MS, *m*-NBA): *m/z* = 412 [M]⁺ (40%). HRLSI-MS (C₂₄H₁₃N₆O) [M]⁺: Calculated: 412.1243. Found: 412.1222. UV-Vis (CHCl₃): λ_{max} (nm) (log ε (dm³ mol⁻¹ cm⁻¹)) = 562 (4.5), 530 (sh), 303 (4.1), 272 (4.2). FT-IR (KBr), ν (cm⁻¹): 1460, 1392, 1284, 1192, 1138, 1097 (B-O), 1070, 762, 735. Elemental Anal. Calc. for C₂₄H₁₃N₆O: C, 69.93; H, 3.18; N, 20.39. Found: C, 69.87; H, 3.27; N, 20.34%.

4.2.1.3. Phenoxy-[2,9,16(17)-trinitro-7,12:14,19-diimino-21,5-nitrilo-5H-tribenzo[*c,h,m*][1,6,11]triazacyclopentadecinato-(2)-kN²², kN²³, kN²⁴]-boron(III) (NO₂-OPh; 1:3.1 mixture of C₃:C₁ regioisomers). In a 10 mL round-bottomed flask, equipped with a magnetic stirrer and rubber seal, phenol (94 mg; 1 mmol) and SubPc NO₂-Cl (113 mg; 0.2 mmol) were placed. The mixture was heated to the melting point of phenol and stirred at that temperature for 6 h. The reaction mixture was cooled down to room temperature and the solid residue was washed with a 4:1 mixture of methanol/water and subjected to column chromatography on silica gel using a 10:1 mixture of toluene/THF as eluent. Compound NO₂-OPh was further purified washing with hexane, obtaining 72 mg of a deep magenta solid (58%). M.p. > 250 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.80 (d, J_m = 2.0 Hz), 9.78 (d, J_m = 2.0 Hz), 9.72 (d, J_m = 1.8 Hz), 9.09 (d, J_o = 8.5 Hz), 9.07 (d, J_o = 8.5 Hz), 9.02 (d, J_o = 8.8 Hz), 8.88 (dd, J_o = 8.5 Hz, J_m = 2.0 Hz), 8.86 (dd, J_o = 8.5 Hz,

$J_m = 2.0$ Hz), 8.85 (dd, $J_o = 8.5$ Hz, $J_m = 2.0$ Hz), 8.81 (dd, $J_o = 8.8$ Hz, $J_m = 1.8$ Hz), 6.80 (dd, $J_o = J'_o = 7.6$ Hz), 6.70 (t, $J'_o = 7.6$ Hz), 5.38 (d, $J_o = 7.6$ Hz). ^{13}C NMR (75.5 MHz, CDCl_3): δ (ppm) = 152.0, 151.9, 151.7, 151.6, 151.4, 150.9, 150.8, 150.4, 149.0, 148.9, 134.2, 134.1, 133.9, 131.1, 130.9, 130.8, 129.6, 129.3, 125.4, 125.2, 125.1, 125.0, 123.6, 123.5, 123.4, 122.4, 122.3, 118.8, 118.7. MS (LSI-MS, *m*-NBA): $m/z = 623$ $[\text{M}]^+$ (10%). HRLSI-MS ($\text{C}_{30}\text{H}_{14}\text{N}_9\text{O}_7\text{B}$) $[\text{M}]^+$: Calculated: 623.1109. Found: 623.1129. UV-Vis (CHCl_3): λ_{max} (nm) ($\log \epsilon$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)) = 588 (4.4), 571 (4.4), 547 (4.1), 526 (4.1), 303 (4.3), 280 (sh). FT-IR (KBr), ν (cm^{-1}): 1622, 1596, 1530 (NO_2 , asym), 1462, 1341 (NO_2 , sym), 1327, 1260, 1233, 1179, 1139, 1058, 909, 857, 843, 753, 699. Elemental Anal. Calc. for $\text{C}_{30}\text{H}_{14}\text{N}_9\text{O}_7\text{B}$: C, 57.81; H, 2.26; N, 20.22. Found: C, 57.97; H, 2.47; N, 20.34%.

4.2.1.4. *Phenoxy-[2,9,16(17)-triphenoxy-7,12:14,19-diimino-21,5-nitrilo-5H-tribenzo[*c,h,m*][1,6,11]triazacyclopentadecinato-(2)- κN^{22} , κN^{23} , κN^{24}]-boron(III) (OPh-OPh; 1:3 mixture of $\text{C}_3\text{:C}_1$ regioisomers). In a 25 mL round-bottomed flask, equipped with a condenser and a magnetic stirrer, phenol (235 mg; 2.5 mmol) and SubPc OPh-Cl (353 mg; 0.5 mmol) were refluxed in toluene (2 mL) for 2 h. The reaction mixture was cooled down to room temperature, the solvent was evaporated and the solid residue was washed with a 4:1 mixture of methanol/water and subjected to column chromatography on silica gel using a 3:1 mixture of hexane/ethyl acetate as eluent. Compound OPh-OPh was further purified washing with cold hexane, obtaining 306 mg of a red solid (80%). M.p. > 250 °C. ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.83 (d, $J_o = 8.8$ Hz), 8.82 (d, $J_o = 8.8$ Hz), 8.76 (d, $J_o = 8.8$ Hz), 8.72 (d, $J_o = 8.8$ Hz), 8.36 (d, $J_m = 2.3$ Hz), 8.30 (d, $J_m = 2.3$ Hz), 8.29 (d, $J_m = 2.3$ Hz), 7.63 (dd, $J_o = 8.8$ Hz, $J_m = 2.3$ Hz), 7.61 (dd, $J_o = 8.8$ Hz, $J_m = 2.3$ Hz), 7.58 (dd, $J_o = 8.8$ Hz, $J_m = 2.3$ Hz), 7.56 (dd, $J_o = 8.8$ Hz, $J_m = 2.3$ Hz), 7.5–7.0 (m), 6.76 (dd, $J_o = J'_o = 8.2$ Hz), 6.20 (t, $J'_o = 8.2$ Hz), 5.16 (d, $J_o = 8.2$ Hz). ^{13}C NMR (75.5 MHz, CDCl_3): δ (ppm) = 160.4, 160.3, 160.1, 159.9, 156.3, 156.14, 156.08, 152.5, 152.3, 150.9, 150.8, 150.2, 149.9, 149.0, 148.8, 148.7, 148.5, 133.3, 133.1, 132.9, 132.8, 130.2, 130.0, 129.9, 129.0, 128.9, 126.0, 125.9, 124.6, 124.5, 124.4, 124.1, 123.9, 123.7, 122.0, 121.7, 121.6, 121.5, 121.3, 120.0, 119.8, 119.7, 118.9, 110.2, 110.1, 110.0. MS (LSI-MS, *m*-NBA): $m/z = 765$ $[\text{M}]^+$ (5%), 671 $[\text{M}-\text{axial group}]^+$ (35%). HRLSI-MS ($\text{C}_{48}\text{H}_{29}\text{N}_6\text{O}_4\text{B}$) $[\text{M}]^+$: Calculated: 764.2343. Found: 764.2337. UV-Vis (CHCl_3): λ_{max} (nm) ($\log \epsilon$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)) = 572 (4.5), 524 (sh), 335 (4.2), 273 (4.5). FT-IR (KBr), ν (cm^{-1}): 1618, 1549, 1460, 1389, 1253, 1138, 1069, 1040 (B-O), 862, 803, 737, 705. Elemental Anal. Calc. for $\text{C}_{48}\text{H}_{29}\text{N}_6\text{O}_4\text{B}$: C, 75.40; H, 3.82; N, 10.99. Found: C, 75.17; H, 3.97; N, 10.82%.*

4.3. Thermogravimetric analysis (TGA)

All compounds were analysed using a TGA 2050 Thermogravimetric Analyser, Module TGA 1000 °C (TA Instruments). The analysis was carried out using around 3.0 mg of the dry samples directly weighed on the platinum pans at a heating rate of 20 K min^{-1} . Analyses performed using a heating rate of 10 K min^{-1} showed similar results. The measurements were performed under nitrogen continuous flow (100 mL/min) in the temperature range between 20 °C and 650 °C. In order to analyse the obtained thermograms, the least square fit procedure of MULTIGAUSSIAN functions was used. The well-known Marquard algorithm for multifunctional fits permitted to analyse the overall degradation process in the partial processes.

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Appendix A. Supplementary material

Original thermogravimetric spectra for each SubPc compound, displayed following the same classification as in the text. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.055.

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