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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: Br < OH ⩽ OPh ∼ Cl. Peripheral substituents also have an influence on the thermal properties of subphthalocyanines, though their role is somewhat less notable.

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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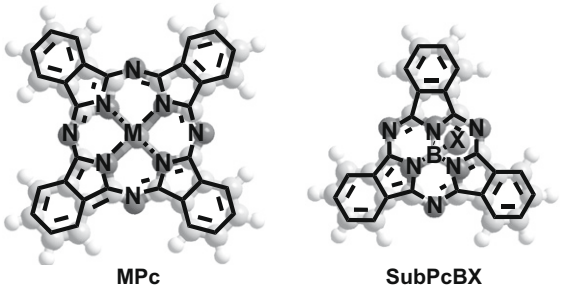


Fig. 1. Structure of a metallophthalocyanine (MPc) and boronsubphthalocyanine (SubPcBX).

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 subtituents placed at the periphery of the macrocycle (H, I, NO_2, 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**, **NO_2–Cl**, and **OPh–Cl** were prepared by cyclotrimerization reaction of the corresponding phthalonitrile in the presence of BCl_3 at reflux of *p*-xylene [13]. Although alkyl ethers are known to cleave in the presence of BCl_3, 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**, **NO_2–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 **NO_2–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 BBr_3. The bromine axial group was then replaced in the presence of SiO_2 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 ^{13}C NMR, LSI-MS and HR-LSI-MS, UV–Vis and IR spectroscopy, and elemental analysis.

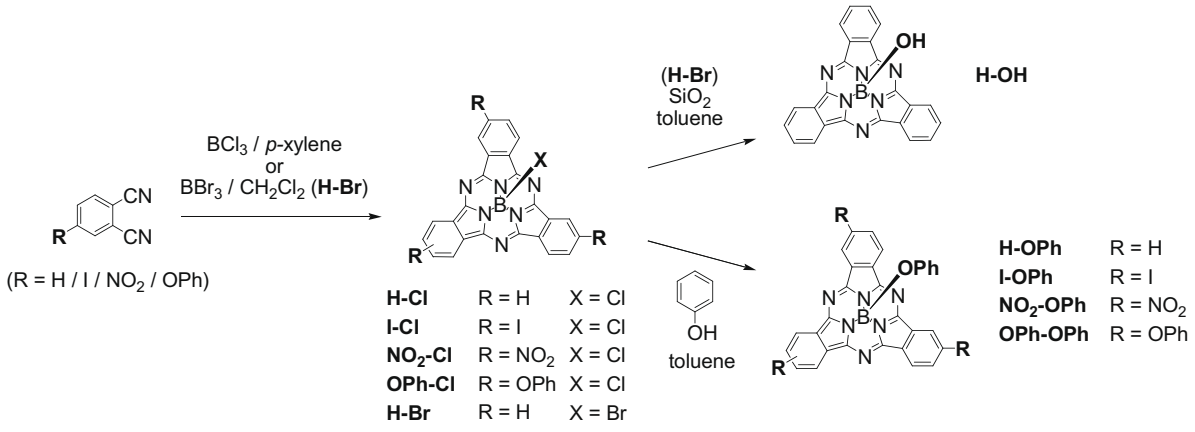
2.2. Thermogravimetric analysis (TGA)

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**, **NO_2–Cl**, and **NO_2–OPh**, two main processes are also observed, the first one occurring again at higher temperatures for the chloro-substituted SubPcs (**I–Cl** and **NO_2–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**, **NO_2–Cl** and **OPh–Cl** samples) the most stable com-



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