Hot Paper

Borylated Subphthalocyanines: Versatile Precursors for the Preparation of Functional Bowl-Shaped Aromatics

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Dedicated to Professor Maurizio Prato on the occasion of his retirement.

The peripheral borylation of porphyrinoids has become a key step to prepare advanced functional materials. This study reports the synthesis, electronic properties, and reactivity of borylated subphthalocyanines. These compounds, which are prepared by Suzuki–Miyaura borylation in excellent yields, are easily purified, display a great stability, and serve as powerful starting materials for the post-functionalization of SubPcs via cross-coupling reactions. Remarkably, this novel approach is more efficient than the methodologies already described and enables the preparation of exotic systems, such as SubPc dimeric species linked by C—C bonds, which are not accessible so far and present promising properties for optoelectronic devices.

Introduction

Subphthalocyanines (SubPcs; Figure 1),[1] bowl-shaped aromatic compounds possessing unique photophysical properties, are receiving much attention because of their potential in state-of-the-art technologies, such as molecular photovoltaics,[2] spintronics[3] or ferroelectric materials.[4] Unlike other π-conjugated materials, SubPcs offer a tremendous functional versatility since their characteristics can be finely tailored by performing chemical modifications. In particular, the peripheral substituents have a crucial impact on the properties of the macrocycle since they are in π-conjugation with the aromatic skeleton. Thus, properties as fundamental as supramolecular organization, band-gap or HOMO–LUMO levels, can be conveniently adjusted by using proper peripheral groups.[1,5] Generally, the peripheral functionalization of SubPcs is tackled following two strategies: (i) using phthalonitriles previously functionalized (SubPc pre-functionalization); or (ii) derivatizing a SubPc
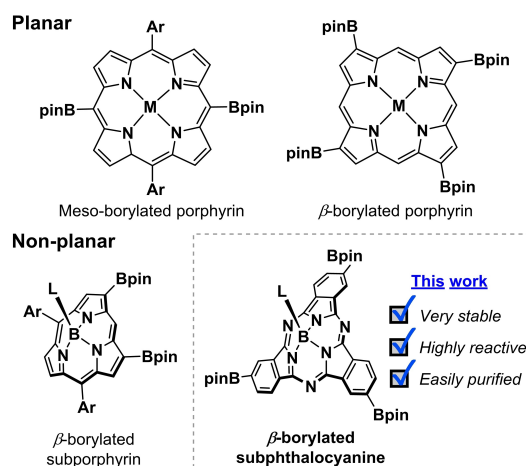

Figure 1. Representative examples of borylated porphyrinoids and borylated subphthalocyanines herein reported.

decorated with functionalizable groups (SubPc post-functionalization). The former is seriously limited because very few functional groups are compatible with the harsh conditions of the cyclotrimerization. By contrast, the method (ii) is a more elegant and efficient approach to convergently prepare modified SubPcs from readily accessible starting materials. In this line, our group and others have reported some palladium-catalyzed Suzuki or Sonogashira cross-coupling reactions starting from iodinated SubPcs.[5a–b,6] Despite these efforts, the development of novel synthetic methods for the peripheral functionalization of SubPcs still remains highly desired.

Over the years, borylated porphyrins have become key building blocks in the synthesis of novel functional porphyrinoids.[7] Along this line, notable is the progress made by the Osuka's group, which by employing meso- and β-borylated (sub)porphyrins has reported multiple π-extended systems with impressive optoelectronic and structural properties (Figure 1). On this basis, the synthesis and manipulation of

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peripherally borylated SubPcs seems to be a promising approach for expanding the chemical space, and thus the functionality, of these materials. As a matter of fact, we recently used a β-borylated SubPc to prepare imide-fused SubPcs, valuable semiconductors for molecular photovoltaics.[2a] Despite these precedents, a detailed study focused on borylated SubPcs have not yet been reported.

Herein we describe the synthesis, properties, and reactivity of peripherally borylated SubPcs. Our study starts by assessing the reaction conditions for the peripheral borylation of SubPcs via Suzuki–Miyaura reactions. Then, the properties of the resulting borylated SubPcs are analyzed experimentally and theoretically. Finally, we explore the utility of these borylated SubPcs as synthons for several cross-coupling reactions, as well as for the preparation of SubPc-SubPc dimers linked by single C—C bonds.

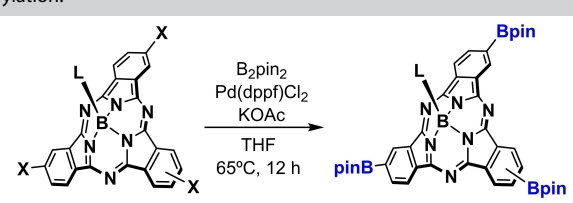## Results and Discussion

Peripheral borylation of SubPcs

The palladium-catalyzed Suzuki–Miyaura borylation is arguably the most common method for the preparation of borylated aromatic compounds.[8] Therefore, we selected this reaction to explore the peripheral borylation of the SubPcs. To this end, the brominated SubPc **1**, which bear an axial aryloxy group to ensure stability and solubility, was prepared. Then, various catalyst, solvents and additives were screened for the palladium-catalyzed borylation. We found that Pd(dppf)Cl$_2$ as the catalyst, potassium acetate as the base, and THF as the solvent afforded the borylated product (**1-Bpin$_3$**) in a 92% yield (Entry 1, Table 1). It should be highlighted that the purification of **1-Bpin$_3$** is carried out just by extraction and a subsequent filtration in hexane. Hereby, **1-Bpin$_3$** is obtained as an easily

manipulable viscous solid presenting a great stability under ambient condition. Importantly, the reaction yield does not depend on the SubPc regioisomer employed (i.e., C_3 or C_1-symmetric) as they present similar reactivities (Entry 2). Consequently, we used C_1-symmetric SubPcs from then on because this regioisomer is obtained in higher yield during the SubPc formation. The influence of the peripheral leaving group on the borylation yield was then explored. Interestingly, the most reactive halogen (i.e., iodine) led to lower yields compared to that of bromine (Entry 3). We hypothesize that undesired reactions, such a homocoupling or dehalogenation, may be facilitated due to the higher reactivity of **2**. On the other hand, the triflated derivative **3** led to a 71% yield, which render them good starting materials for the preparation of borylated SubPcs as well (Entry 4). As expected, significant lower yields are obtained with peripheral chlorine atoms (**4**), which barely reach the 12% yield (Entry 5). Crucially, the borylation reaction is compatible with other axial groups (Entries 6–7), such as chlorine (**5**) or fluorine (**6**). One step further, we investigated whether the borylation could be applied in ortho-substituted SubPcs (**7**), which generally are rather challenging to functionalize.[1] Remarkably, ortho-borylated SubPc (**2-Bpin$_3$**) can also be obtained in moderate yield using our conditions (Figure 2).

Optical and electronic properties of borylated SubPcs

The boryl pinacol fragments possess a partially empty p-orbital and thereby the electronic structure of the aromatic core may be perturbed. Hence, we studied the optoelectronic properties of **1-Bpin$_3$** and **2-Bpin$_3$** by UV/Vis absorption and fluorescence spectroscopy, voltammetry, as well as Density Functional Theory (DFT) calculations. As shown in Figure 3, **1-Bpin$_3$** and **2-Bpin$_3$** exhibit the characteristic Soret and Q bands of SubPcs at ca. 310 nm and 570 nm, respectively. In comparison to those of non-substituted SubPc (hereafter referred as SubPcH$_{12}$), the absorption and emission maxima of **1-Bpin$_3$** and **2-Bpin$_3$** are slightly red-shifted (5-10 nm), suggesting a certain conjugation of the π-skeleton with the peripheral groups. Importantly, both absorption and emission spectra are similar in shape to that of typical SubPcs, which discard additional electronic transitions involving the boryl moieties. In accordance with previous works, **2-Bpin$_3$** displays lower extinction coefficient than that of meta substituted **1-Bpin$_3$**.[9] As determined by time-dependent DFT (TD-DFT; See Supporting Information for further details), the Q

Table 1. Influence of the axial ligand and peripheral groups on the SubPc borylation.

Entry	L	X	Starting SubPc	Regioisomer	Yield[a]
1	O^{t}BuPh	Br	1	C_1	92%
2	O^{t}BuPh	Br	C_3-1	C_3	94%
3	O^{t}BuPh	I	2	C_1	56%
4	O^{t}BuPh	OTf	3	C_1	71%
5	O^{t}BuPh	Cl	4	C_1	12%
6	Cl	Br	5	C_1	90%
7	F	Br	6	C_1	92%

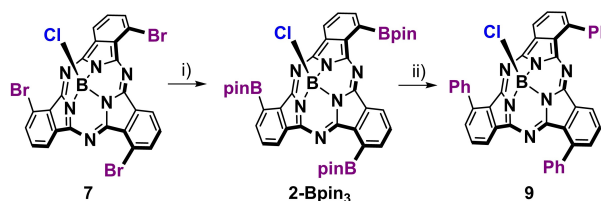[a] Yields were determined after purification.

Figure 2. Borylation and Suzuki-Miayura cross-coupling of a ortho-substituted SubPc. Reagents and conditions: (i) B$_2$pin$_2$, Pd(dppf)Cl$_2$, KOAc, THF, 65 °C, 12 h, 54% (ii) Ph—Br, Pd(dppf)Cl$_2$, Cs$_2$CO$_3$, THF, r. t., 12 h, 47%.

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Table 2. Electrochemical oxidation and reduction potentials of SubPcH$_{12}$, 1-Bpin$_3$ and 2-Bpin$_3$ obtained by cyclic voltammetry in THF.

	E^{Red} [V]	E^{Ox} [V]	HOMO [eV]	LUMO [eV]	λ_{abs} [nm]	λ_{em} [nm]
SubPcH$_{12}$	−1.51	0.57	−5.75	−3.59	563	578
1-Bpin$_3$	−1.48	0.63	−5.76	−3.62	575	590
2-Bpin$_3$	−1.41	0.67	−5.81	−3.69	568	583

peaks, which is probably associated with a lower redox stability. Further insights into the electronic structure of **1-Bpin$_3$** and **2-Bpin$_3$** were obtained by inspection of the DFT calculated frontier molecular orbitals. As shown in Figure 3b–c, the HOMO, HOMO-1, LUMO and LUMO + 1, which are the orbitals governing either the Q band or first oxidation/reduction processes, are mainly located at the π-core and a negligible participation of the peripheral boron atoms is noticeable. This finding is in nice agreement with the experimental fact that the SubPc optoelectronic properties remain almost unaltered after peripheral borylation.
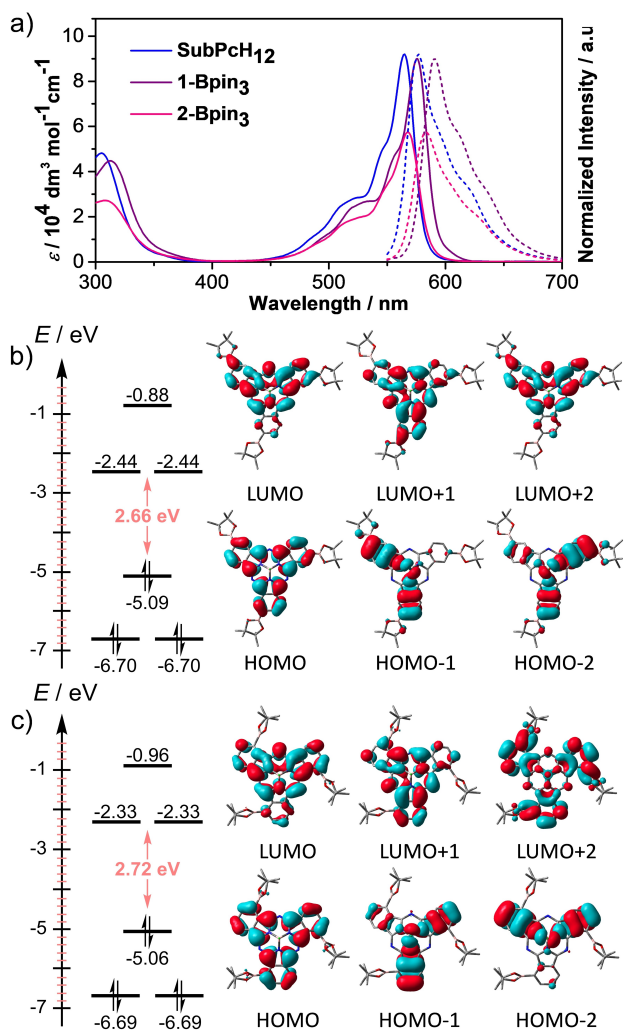
Figure 3. Optical and electrochemical properties of **1-Bpin$_3$** (purple) and **2-Bpin$_3$** (pink). a) UV/Vis-NIR and fluorescence (λ_{ex} = 550 nm) spectra in THF at room temperature. (2.0×10^{-5} M for UV-Vis-NIR and 1.0×10^{-6} M for fluorescence). Selected molecular orbitals and their energy levels calculated by DFT at the B3LYP/6-31G(d) level of theory for b) **1-Bpin$_3$** and c) **2-Bpin$_3$**. Isosurface value = 0.02. Hydrogen atoms are omitted for clarity.

Post-functionalization reactions of borylated SubPcs

The excellent formation yield and great stability of **1-Bpin$_3$** encouraged us to explore their use as synthetic precursor for Suzuki–Miyaura reactions with bromo-unsaturated compounds. To this end, bromobenzene (Ph–Br) was selected as model substrate. After extensive screening, we found that the coupling reaction of **1-Bpin$_3$** with Ph–Br using Pd(dppf)Cl$_2$ and Cs$_2$CO$_3$ in THF at room temperature gave **8** in an 86% yield (Figure 4). Notably, the reaction is compatible with chlorine as axial ligand which, despite being more labile than aryloxy, is preferred for technological applications. Importantly, these catalytic conditions can be also applied for the post-functionalization of ortho derivatives by employing **2-Bpin$_3$**, which affords **9** (Figure 2). With the optimized conditions in hand, we studied the reaction
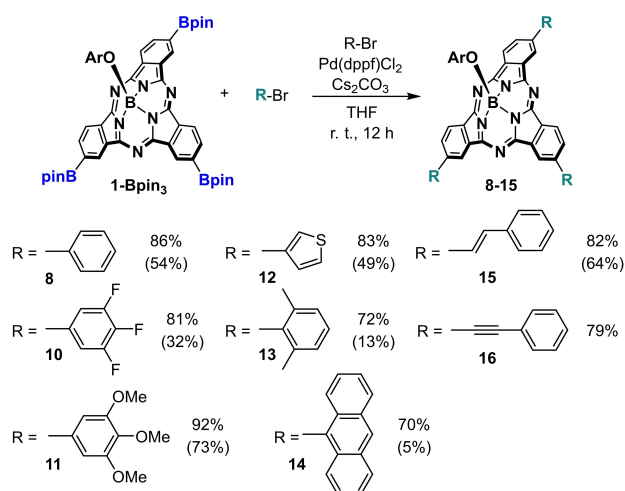
band of both **1-Bpin$_3$** and **2-Bpin$_3$** are mainly derived from HOMO→LUMO and HOMO→LUMO + 1 transitions (f = 0.71 and 0.88, respectively, see Supporting Information for further details). Regarding the emission properties, both **1-Bpin$_3$** and **2-Bpin$_3$** exhibit strong fluorescence peaking at 590 and 583 nm, with a quantum yield of 0.41 and 0.35, respectively, and Stokes shifts in the range of typical SubPcs (ca. 15 eV).

Electrochemical experiments further confirm a slight electronic communication between the boryl groups and the SubPc π-system. As shown in Figure S6.1, **1-Bpin$_3$** presents one-electron oxidation and reduction peaks at −1.48 V and 0.63 V, respectively. Likewise, **2-Bpin$_3$** reveals these peaks at −1.41 V and 0.63 V, respectively. From these values and comparing with SubPcH$_{12}$ (Table 2), it can be concluded that the borylation does not significantly vary either the redox properties of SubPcs or their HOMO–LUMO energy levels. However, the reduction peaks in borylated SubPcs are broader and composed of smaller

Figure 4. Suzuki-Miyaura reactions of **1-Bpin$_3$**.

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using bromoaryls with different electronic nature and bulkiness, as well as heterocyclic compounds or even bromo-alkenes and -alkynes. Fortunately, our catalytic system proved to be very effective for coupling both 3,4,5-fluorophenyl, 3,4,5-metoxy-phenyl and 3-thiophene, providing **10**, **11** and **12** in excellent yields. Moreover, we also succeeded when using the bulky anthracene and ortho-dimethylphenyl brominated precursors, which gave rise to **13** and **14** in ca. 70% yield. On the other hand, the use of phenylalkene and phenylalkyne bromides, enabled the peripheral functionalization with Csp^2 and Csp^3 groups (**15** and **16**). It is noteworthy that the reported palladium-catalyzed Suzuki–Miyaura cross-couplings over SubPcs requires high temperatures (70-100 °C) and the reactions yields are moderate. In stark contrast, the methodology herein reported provides outstanding yields at room temperature. To get a direct comparison with the reported conditions, we performed the same cross-couplings using iodinated SubPcs and boronic esters/acids (the corresponding yields are indicated in brackets; Figure 4). In all cases, the reaction yields observed are significantly lower than those of the method employing borylated SubPcs. Furthermore, higher temperatures (100 °C) were required. Based on these results, we can conclude that SubPcs are excellent precursors for the post-functionalization of SubPcs.

We then explored the utility of borylated SubPcs to prepare exotic SubPc-based systems. Oligomeric porphyrinoids are known to display intriguing properties, such as NIR absorption/emission or high electronic conductivity.[10] Hence, we turned our attention to the synthesis of the SubPc dimers linked together by single C–C bond, which so far can be only prepared by on-surface chemistry.[11] To this end, we prepared two key mono-substituted SubPcs, **17** and **18** (Figure 5). The synthesis of **17** was carried out by statistical cyclotrimerization of phthalonitrile and 4-bromophthalonitrile followed by the regioisomers separation. **18** was then obtained from **17** by Suzuki–Miyaura borylation. With these compounds in hand, we conducted their cross-coupling reaction employing our optimized conditions. Fortunately, this reaction afforded the SubPc dimer **19** in a 79% yield. Due to the chirality of both **17** and **18** (M and P enantiomers), this dimer is based on two regioisomers, homochiral and heterochiral. The former, in turn, coexist as a mixture of enantiomers (MM and PP).

To get a preliminary idea about the electronic communication between the SubPc cores in **19**, we analyzed the UV/Vis spectra and DFT calculated molecular orbitals. Interestingly, **19** display a Q-band composed of two intense bands peaking at 568 and 594 nm, respectively. As shown in Figure 6, the orbital distribution of **19** is rather unusual for a SubPc system since, in
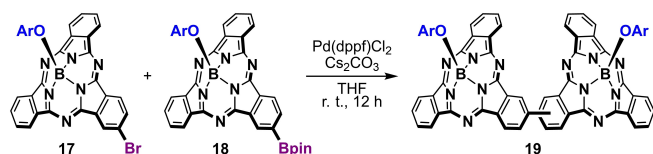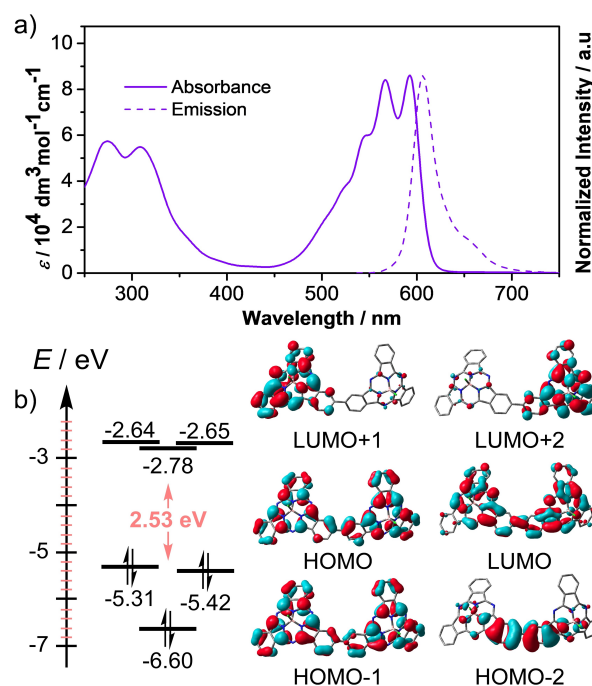

Figure 6. Optical and properties. a) UV/Vis-NIR and fluorescence ($\lambda_{ex} = 530$ nm) spectra of **19** in THF at room temperature. (2.0×10^{-5} M for UV-Vis-NIR and 1.0×10^{-6} M for fluorescence). b) Selected molecular orbitals of **19** and their energy levels calculated by DFT at the B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.

contrast to common SubPcs where the LUMO and LUMO+1 are energetically degenerate, **19** presents the LUMO more stabilized than the LUMO+1 and LUMO+2 which, in turn, are energetically degenerate. Furthermore, the HOMO and HOMO-1 present similar energy, while in common SubPcs the HOMO is significantly less stable than HOMO-1 and HOMO-2. Remarkably, the LUMO is delocalized over the two SubPc units, while the LUMO+1 and LUMO+2 are located at one of the two macrocycles. Similarly, the energetically degenerate HOMO and HOMO-1 are well extended over both SubPcs. As supported by TD-DFT calculations, two transitions in the range of the Q-band are now possible, one derived from HOMO→LUMO transitions, and other resulting from transitions between four orbitals: HOMO-1, HOMO, LUMO+1 and LUMO+2 transitions. These interesting findings render oligomeric SubPc promising for the design of NIR-absorbing materials and n-type semiconductors.

Conclusions

In summary, a very efficient and versatile method for the preparation of borylated SubPcs in excellent yields has been developed. Despite being in conjugation with the aromatic core, the peripheral boryl groups do not perturb the electronic properties of the macrocycle. These borylated compounds, which exhibit an excellent stability and can be easily purified, were used for the post-functionalization of SubPcs via Suzuki–Miyaura cross-coupling reactions. Remarkably, this method provided higher yields than those previously described, thus

Figure 5. Synthesis of SubPc dimer **19** via Suzuki-Miyaura cross-coupling starting from **17** and **18**.

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rendering it a powerful approach for the preparation of more complex SubPc derivatives. As a proof of concept, this methodology was then exploited for the preparation of a SubPc dimer exhibiting a broad, red-shifted absorption and an extended π-conjugated skeleton. Applications of borylated SubPcs for fabricating more elaborated SubPc oligomers are actively in progress in our laboratory.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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