Porphyrynilboranes Synthesized via Porphyrynillithiums

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Abstract: As the most nucleophilic porphyrins, meso- or β-lithiated porphyrins were generated by iodine-lithium exchange reactions of the corresponding iodoporphyrins with n-butyllithium at −98 °C. Porphyrynillithiums thus prepared were used for synthesis of dimesitylporphyrynilboranes via reactions with fluordimesitylborane. The boryl groups proved to serve as an electron-accepting unit to alter the photophysical and electrochemical properties. In addition, 5-diallylamin-15-dimethylbor substututed porphyrynilboranes showed increased intramolecular charge-transfer character in the S1 state. Furthermore, the reaction of β-lithiated porphyrin with dichloromesitylborane provided molecules. The first peripheral borylation of porphyrins has been accomplished by Therien and co-workers.[3] The resulting bononates were prepared to be useful building blocks for Suzuki-Miyaura cross-coupling. However, installation of a diarylboryl group directly on the periphery of porphyrins has remained unexplored so far. Reactions of nucleophilic porphyrynilboranes with haloboranes would be a feasible synthetic route to porphyrynilboranes. However, generation of such porphyrynilboranes has not been easy because porphyrin cores are reactive toward nucleophilic species to undergo various transformations.[4]

Recently, we succeeded in preparation of porphyrynil Grignard reagents as a rare example of nucleophilic porphyrin species through iodine-magnesium exchange under cryogenic conditions.[5,6]These Grignard reagents displayed high nucleophilicity toward aldehydes and ketones. Inspired by the success, we embarked on the synthesis of porphyrynilboranes by using porphyrynil Grignard reagents. As an initial attempt, we examined the reaction of a porphyrynil Grignard reagent generated from β-iodoporphyrin 1b[7] (Ar1 = 3,5-di-tert-butylphenyl) with fluordimesitylborane (MesBF). A bulky dimethylboryl group was employed to protect the boron center in the product from moisture and oxygen. However, the reaction was sluggish and gave the desired borylated product 4bNi only in 17% yield. meso-Magnesioporphyrin prepared from meso-iodoporphyrin 1a[8] was entirely unreactive toward MesBF and only decomposition of the Grignard reagent was observed. These disappointing results should stem from the insufficient nucleophilicity of these porphyrynil Grignard reagents.

In recent years, triarylboranes have attracted considerable attention in light of their intriguing features such as high luminescence properties, large nonlinear optical responses, and anion-sensing properties.[1,2] Owing to the high electrophilicity of three coordinate borons, bulky aryl substituents have been often employed to protect the boron center from nucleophilic attack. Considering the rich electrochemical and chemical properties of porphyrins, porphonylboranes that can be regarded as a hybrid of porphyrin and triarylborane would be interesting functional molecules. The first peripheral borylation of porphyrins has been accomplished by Therien and co-workers.[3] The resulting bononates were prepared to be useful building blocks for Suzuki-Miyaura cross-coupling. However, installation of a diarylboryl group directly on the periphery of porphyrins has remained unexplored so far. Reactions of nucleophilic porphyrinylboranes with haloboranes would be a feasible synthetic route to porphyrinylboranes. However, generation of such porphyrinylboranes has not been easy because porphyrin cores are reactive toward nucleophilic species to undergo various transformations.[4]

We then envisioned the preparation of porphonylporphyrinyls as more reactive porphyrinyl nucleophiles via iodine-lithium exchange (Scheme 1). After iodine-lithium exchange between 1a and n-butyllithium at −80 °C, an addition of D2O afforded meso-deuteroporphyrin 3a[9] (57%) along with protodeiodinated product (12%) and meso-butylated product (7%). These results indicated not only the formation of meso-lithiated porphyrin 2a but also the occurrence of undesirable side reactions. Indeed, Senge and co-workers reported that nucleophilic addition of organolithium reagents to porphyrin cores was extremely fast and occurred even at −100 °C in THF.[10] However, after extensive optimization, we found that the iodine-lithium exchange of 1a with n-butyllithium proceeded preferentially over the nucleophilic addition to 1a in THF at −98 °C to give 3a in 81% yield. Generation of β-lithiated porphyrin 2b has been similarly confirmed by the formation of β-deuterated product 3b[8] from 1b in 82% yield under the same conditions.

To our delight, we have found that porphonylporphyrinyls 2a and 2b are reactive enough toward fluordimesitylborane to give 4aNi and 4bNi in 52% and 70% yields, respectively (Scheme 2). Importantly, these dimesitylporphonylporphyrinyls are tolerable under basic and acidic conditions owing to the sterically protected boron center. Thanks to their high stability, 4aNi and 4bNi underwent reductive denickelation with 4-tolylmagnesium bromide[10] followed by zincation to yield 4aZn and 4bZn, respectively. The solid-state structures of 4aNi and 4bNi have been revealed by X-ray crystallographic analysis (Figure 1). The boron center on meso-borylporphyrin 4aNi shows a propeller-like structure with C––B bonds of 1.57–1.58 Å, which are typical lengths for sterically crowded triarylboranes.[11] The boron atom is embedded in a completely planar geometry with the sum of ∠C–B–C angles to be 360°. The dihedral angle between the

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Supporting information for this article is given via a link at the end of the document.
Scheme 2. Synthesis of porphyrinylboranes 4aM, 4bM, 8M, and 9Ni and structures of reference compounds 10M and 11M. a) n-BuLi (1.5 equiv), THF, –98 ºC, then fluoro(dimesityl)boryl (1.5 equiv), r.t.; b) 4-TolMgBr (10 equiv), toluene, 60 ºC (for 4aNi and 8Ni) or 40 ºC (for 4bNi), then Zn(OAc)₂, CH₂Cl₂/MeOH, r.t.; c) NBS (1.0 equiv), pyridine, CHCl₃, 0 ºC; d) Ni(acac)₂, toluene, reflux; e) di(4-tert-butylphenyl)amine (3 equiv), Pd-PEPPSI-IPr/NaOᵗBu conditions. Di(4-tert-butylphenyl)amine was employed as a coupling partner to avoid competitive halogenation on the diarylamino segment in the next reaction. 

The free meso-position of 6Ni was iodinated with iodine/bis(trifluoroacetoxy)iodobenzene (PIFA)[8] via more electron-rich free-base porphyrin 6H₂ to furnish 7Ni in 64% yield. 7Ni was subjected to the same iodine-lithium exchange conditions followed by treatment with Mes₂BF to give 8Ni in 39% yield. Ni⁺ porphyrin 8Ni was further converted to the corresponding Zn²⁺ porphyrin 8Zn via denickelation with 4-tolylmagnesium bromide and subsequent zincation in 47% yield. 

The structure of 8Ni has been revealed by X-ray crystallographic analysis to possess planar geometries both at the boron and nitrogen atoms, as indicated by the sums of 180°—B—C and

dimesitylboryl plane and the porphyrinic plane is 43°, suggesting a moderate stereoelectronic interaction between the boron atom and the porphyrin π-plane. In contrast, the structure of β-boryl 4bNi shows a smaller dihedral angle between the boron unit and the porphyrinic plane (25.2°) and a shorter C—B bond (1.552 Å), which suggest a more effective p-π interaction between the β-boryl group and porphyrin network owing to the sterically less hindered nature of β position.

In the next step, we attempted to synthesize a donor-acceptor type porphyrin bearing a diarylamino group and a diarylboryl group on the porphyrin periphery. meso-Amination of 5 was accomplished via meso-bromination with N-bromosuccinimide followed by Pd-catalyzed Buchwald-Hartwig amination under Pd-PEPPSI-IPr/NaOᵗBu conditions. Di(4-tert-butylphenyl)amine was employed as a coupling partner to avoid competitive halogenation on the diarylamino segment in the next reaction. The free meso-position of 6Ni was iodinated with iodine/bis(trifluoroacetoxy)iodobenzene (PIFA) via more electron-rich free-base porphyrin 6H₂ to furnish 7Ni in 64% yield. 7Ni was subjected to the same iodine-lithium exchange conditions followed by treatment with Mes₂BF to give 8Ni in 39% yield. Ni⁺ porphyrin 8Ni was further converted to the corresponding Zn²⁺ porphyrin 8Zn via denickelation with 4-tolylmagnesium bromide and subsequent zincation in 47% yield. 

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Figure 1. X-ray crystal structures of (a) 4aNi (b) 4bNi, and (c) 8Ni. The thermal ellipsoids are scaled to 50% probability. Solvent molecules and tert-butyl groups are omitted for clarity.
Absorption and fluorescence spectra were taken to investigate the electronic properties of porphyrinylboranes (Figure 2). The absorption spectrum of meso-borylated 4aZn showed a sharp and intense Soret band at 432 nm and weak Q bands at 558 and 601 nm. Both bands were red-shifted by ca. 20 nm compared to those of the corresponding triaryl ZnII-porphyrin (10Zn). β-borylated 4bZn exhibited almost the same absorption spectrum as that of 4aZn. 4aZn and 4bZn exhibited slightly enhanced fluorescence representing mirror images of their Q bands. The absorption spectrum of 5-diarylamino-15-dimesitylboryl porphyrin 8Zn exhibited a characteristically broad Soret band similar to meso-diaminoporphyrin (11Zn) with a bathochromic shift in its Q band by 20 nm. Porphyrin 8Zn shows relatively large Stokes shifts that depend on solvent polarity; 623 cm⁻¹ in hexane, 828 cm⁻¹ in toluene, 883 cm⁻¹ in CHCl₃, 1079 cm⁻¹ in CH₂Cl₂, and 1164 cm⁻¹ in nitromethane (see Figures S31, S2 in SI). These data suggest increased charge transfer character in the S₁ state. The charge transfer character of 8Zn was also supported by theoretical calculation (see Figures S34 in SI). While the orbital coefficients are almost localized on the porphyrin unit in the frontier orbitals, 8Zn shows delocalised orbitals over the diarylamino and dimesitylboryl moieties in the HOMO and LUMO, respectively.

Upon addition of tetrabutylammonium fluoride (TBAF), the absorption of 4aNi and 4bNi were blue-shifted (see Figure S33 in SI) by disruption of the π-π interaction by B-F coordination. In order to make this coordination effect clearer, we designed a boron-bridged porphyrin dimer 9Ni, which is supposed to show π-conjugation between two porphyrin units through the vacant π-orbital on the boron atom. Thanks to the high reactivity of β-lithiated porphyrin 2b, two-fold nucleophilic substitution of dichloromesitylboryl (14) successfully provided 9Ni in 25% yield. 9Ni were quickly purified by silica-gel column chromatography because 9Ni gradually decomposed under ambient conditions. The instability toward moisture or oxygen implies insufficient kinetic stabilization at the boron center. High-resolution atmospheric-pressure-chemical-ionization-time-of-flight (HR-APCI-TOF) mass spectrum of 9Ni exhibited the ion peak at [M+Cl]⁻ = 2024.0659 (calcd. for C₁₃₃H₁₃₅N₃⁵B₁₀Cl₂₀N₂₀₂. 2024.0731). The ¹H NMR spectrum of 9Ni showed two singlets and six doublets in the range of 9.82–8.54 ppm due to the meso- and β-protons and three singlets at 7.11, 2.53, and 2.49 ppm due to the protons of the mesityl group. The dimer 9Ni exhibited a rather broad Soret band over 390–470 nm and red-shifted Q bands, owing to the conjugative electronic interaction between two porphyrins via the vacant π-orbital of the boron atom. Upon addition of TBAF, the Soret band became sharpened (13) as a consequence of the disruption of the conjugative interaction between two porphyrins.

Electrochemical properties were revealed by cyclic voltammetry (Table 1). The parent unsubstituted ZnII triarylporphyrin 10Zn shows first oxidation potential of 0.36 V, and first reduction potential of −1.86 V. The reduction potentials of 4aZn and 4bZn were positively shifted by ca. 0.1 V. 8Zn also shows a positively shifted reduction wave compared to 11Zn. Thus, their electrochemical HOMO–LUMO gaps (ΔEHL), decreased by ca. 0.1 eV owing to their enhanced electron-accepting characters.

Table 1. Redox potentials of 4aZn, 4bZn, 8Zn, 10Zn, and 11Zn.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Eox₁ (V)</th>
<th>Eox₂ (V)</th>
<th>Redox (V)</th>
<th>ΔEHL (eV)</th>
</tr>
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<tbody>
<tr>
<td>4aZn</td>
<td>0.64</td>
<td>0.35</td>
<td>−1.78</td>
<td>2.13</td>
</tr>
<tr>
<td>4bZn</td>
<td>0.67</td>
<td>0.36</td>
<td>−1.77</td>
<td>2.13</td>
</tr>
<tr>
<td>10Zn</td>
<td>0.66</td>
<td>0.36</td>
<td>−1.86</td>
<td>2.22</td>
</tr>
<tr>
<td>8Zn</td>
<td>0.46</td>
<td>0.26</td>
<td>−1.77</td>
<td>2.00</td>
</tr>
<tr>
<td>11Zn</td>
<td>0.48</td>
<td>0.27</td>
<td>−1.83</td>
<td>2.10</td>
</tr>
</tbody>
</table>

[a] The redox potentials were measured by cyclic voltammetry in anhydrous CH₂Cl₂ with 0.1 M Bu₄NPF₆ as supporting electrolyte and Ag/AgClO₄ as reference electrode. Fc/Fc⁺ was used as external reference.
In summary, porphyrinyllithiums were successfully generated by iodine-lithium exchange reactions of the corresponding iodoporphyrins with n-butyllithium at –98 °C. The porphyrinyllithiums were useful for synthesis of a series of porphyrinyllaboranes via reactions with suitable halaboranes. The boryl groups proved to serve as an electron-accepting unit to alter photophysical and electrochemical properties. Boron-substituted donor-acceptor porphyrin showed increased intramolecular charge-transfer character in the S1 state and boron-bridged porphyrin dimer exhibited a conjugative interaction between the two porphyrin units through the vacant p-orbital at the boron atom. Further applications of porphyrinyllithiums and investigations on boron-containing porphyrinoids are currently underway.

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Keywords: porphyrin • halogen-lithium exchange • borylation • triarylboration • donor-acceptor porphyrin


[9] Use of BuLi (2.5 equiv) instead of nBuLi under the same conditions led to formation of a rather complicated reaction mixture including 3a (36%) protodeiodinated product (19%), and unidentified by-products.


[15] Probably because of its highly crowded nature, a meso-to-meso boron-bridged dimer was not formed under the same reaction conditions using meso-lithiated porphyrin 2a.

[16] Upon addition of TBAB, the full width at half maximum (fwhm) of the Soret band of 9Ni was decreased from 3320 cm−1 to 1860 cm−1. The Soret band of 9Ni-F is still larger than that (fwhm = 1190 cm−1) of 10Ni due to the exciton coupling interaction.
Porphyrinyllithiums were generated by iodine-lithium exchange of the corresponding iodoporphyrins. The porphyrinyllithiums were useful for synthesis of a series of porphyrinylboranes via reactions with suitable haloboranes. The boryl groups proved to serve as an electron-accepting unit to alter photophysical and electrochemical properties. B,N-substituted donor-accepter porphyrin showed increased intramolecular charge-transfer character in the $S_1$ state. Boron-bridged porphyrin dimer exhibited a conjugative interaction between two porphyrin units through the vacant p-orbital at the boron atom.