JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Planar Subporphyrin Borenium Cations

Eiji Tsurumaki,[†] Shin-ya Hayashi,[†] Fook S. Tham,[‡] Christopher A. Reed*[,‡] and Atsuhiro Osuka*[,†]

[†]Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
[‡]Department of Chemistry, University of California, Riverside, California 92521-0403, United States

S Supporting Information

ABSTRACT: Subporphyrin borenium cations with a carborane counterion have been prepared by treatment of B-methoxy subporphyrins with the silylium reagent $Et_3Si(CH_6B_{11}Br_6)$. In contrast to the distinctly domed subphthalocyanine borenium cation, a nearly planar structure with *sp*^{2} hybridized boron is found in the X-ray structure of the triphenylsubporphyrin borenium cation. The cations exhibit absorption and fluorescence spectra that are quite similar to those of B-methoxy subporphyrins. B-phenyl subporphyrins were prepared in good yield by reaction of subporphyrin borenium cations with phenyllithium.

In recent years, subporphyrins have emerged as a promising class of porphyrinic pigments. These genuinely ring-contracted porphyrins have triangular C_{3v} symmetric shape, a domed 14π-aromatic macrocycle, chemical robustness, bright-green fluorescence, and large nonlinear optical properties.[1−4] Among these attractive attributes, *meso*-aryl-substituted subporphyrins exhibit highly tunable electronic properties due to the large influence of the aryl substituents that can rotate freely.[2c,d] Their singly and doubly reduced congeners, subchlorins and subbacteriochlorins, have also been prepared. They display optical properties that are comparable to those of chlorins and bacteriochlorins,[2f,h] confirming the validity of Gouterman's four orbital theory even for these tripyrrolic porphyrinoids.[5]

What remains unexplored in the chemistry of subporphyrins is the characterization of subporphyrin borenium cations, (SubPor)B$^+$. There is topical interest in the chemistry of boron cations in borinium, borenium, and boronium ions because their strongly electrophilic character and coordinative unsaturation make them effective in cationic polymerization catalysis.[6] Subporphyrins are a nice platform to study borenium cations in terms of a symmetric dianionic tridentate cyclic coordination framework. (SubPor)B$^+$ species are always the main ions detected in positive ion mass spectrometry of boron subporphyrins and these cations are possible intermediates in facile axial ligand exchange reactions under acidic conditions. Typically, simply washing B-methoxy and B-acetoxy subporphyrins with aqueous HCl gives B-hydroxy subporphyrins, and the reverse processes are also facile upon heating in the appropriate solvent (Scheme 1).[1] In contrast, axial ligand exchange reactions of subphthalocyanines typically require more forcing conditions.[7]

Importantly, the solid-state structure of the subphthalocyanine cation, (SubPc)B$^+$, as a salt with a very weakly coordinating carborane anion, $CHB_{11}Me_5Br_6^-$,[8] shows it to be domed with a bowl depth of 1.073 Å. Bowl depth is defined by the distance from the boron atom to the mean plane of the six peripheral β-carbon atoms. Density functional theory (DFT) calculations at the B3LYP/6-31G(d) level also showed the most stable structure of (SubPc)B$^+$ to be domed with a bowl-depth of 0.978 Å. This structure is quite similar to the parent neutral molecule, (SubPc)BCl. In contrast, more nearly planar structures have been calculated for (SubPor)B$^+$: a completely planar structure for the tribenzosubporphine cation and an almost planar structure for the *meso*-triphenylsubporphyrin cation with a bowl-depth of only 0.114 Å (Chart 1).

Herein we report the isolation of (SubPor)B$^+$ as a stable salt using a very weakly coordinating carborane counterion, $CH_6B_{11}Br_6^-$, chosen because of its inertness, excellent crystallizability, and relative ease of preparation.[9] As shown in Scheme 2, a dry toluene solution of *meso*-triphenylsubporphyrin **1a** was treated with $Et_3Si(CH_6B_{11}Br_6)$ at room temperature. After the reaction mixture had stirred for 3 h, hexane was added to complete the precipitation of **2a**, which was isolated by filtration as an orange solid (81%). In a similar manner, salts **2b** and **2c** were obtained in 58 and 91% yields, respectively. Even the quite highly electron-deficient, peripherally brominated salt **2d** was isolated from **1d** (62%). Interestingly, these crystalline salts are moderately stable toward moisture and oxygen and can be stored without decomposition in a glovebox for more than 6 months.

The ^{1}H NMR spectrum of **2a** in $CDCl_3$ at room temperature displays a singlet due to the peripheral β-pyrrolic protons at 8.96 ppm, downfield shifted from that of **1a** at 8.12 ppm. Consistent with these results, the β-pyrrolic protons of **1a** and its cation **2a** are calculated by DFT calculations using the GIAO method to be 7.49−8.20 and 8.96−9.05 ppm, respectively. As with (SubPc)B$^+$,[8] it was difficult to detect a ^{11}B NMR signal of **2a**. The ^{1}H and ^{11}B NMR spectra of **2b** and **2c** are similar to those of **2a**.

The formation of the borenium cation from **1a** under acidic conditions was followed by ^{1}H NMR analysis. The spectrum of **1a** in a 1:1 mixture of $CDCl_3$ and trifluoroacetic acid-*d* (TFA-*d*) displays a singlet due to the β-pyrrolic protons at 8.89 ppm. Under these conditions, a ^{11}B NMR signal was detected as a broad singlet at $\delta = -0.8$ ppm with full width at half height of 382 Hz. This is considerably downfield shifted compared to **1a** in $CDCl_3$ ($\delta = -15.3$ ppm) but is rather high compared with other borenium cations,[6] probably reflecting a diatropic ring current of the subporphyrin or a strongly electron-donating subporphyrin ligand. In line with these experimental observations, DFT calculations predict the ^{11}B NMR chemical shifts of **1a** and of its cation to be −17.8 and 2.3 ppm, respectively.[10] The ^{1}H NMR

Received: June 17, 2011
Published: July 16, 2011

dx.doi.org/10.1021/ja2056566 | *J. Am. Chem. Soc.* 2011, 133, 11956–11959

Scheme 1. Axial Ligand Exchange Reactions of *meso*-Aryl-Subporphyrins

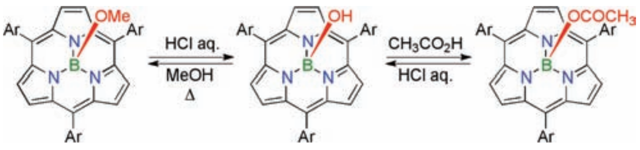
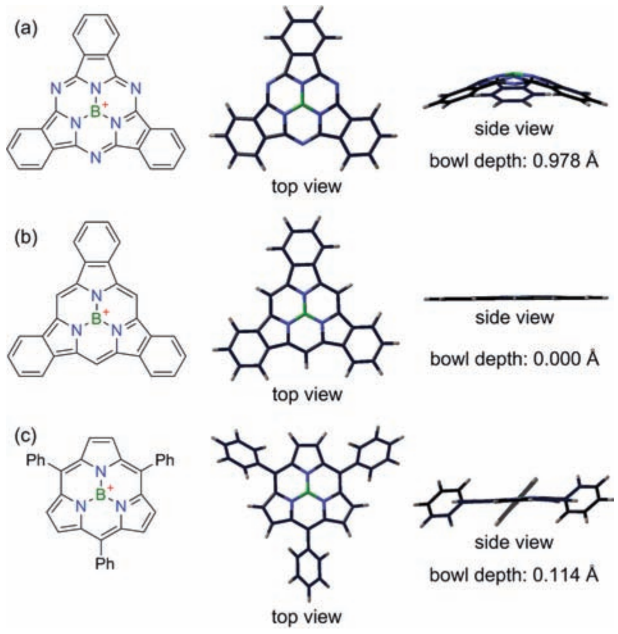
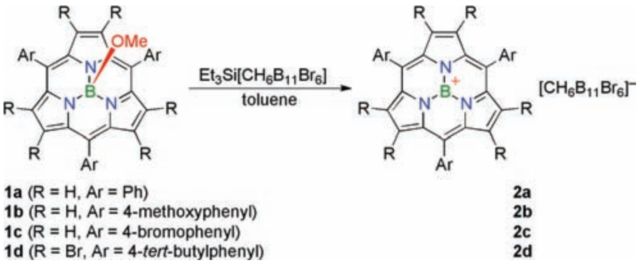


Chart 1. Optimized Structures Calculated at the B3LYP/6-31G(d) Level; (a) (SubPc)B$^+$, (b) Tribenzoporphine Cation, and (c) *meso*-Triphenylsubporphyrin Cation



Scheme 2. Synthesis of B(SubPor)$^+$ as Carborane Anion Salt 2



spectrum of **2d** in $CDCl_3$ exhibits a pair of doublets at 7.82 and 7.73 ppm for *meso*-aryl protons, which is again quite similar to that of **1d** in a 1:1 mixture of $CDCl_3$ and TFA-*d* (7.70 and 7.66 ppm),[11] indicating the D_{3h} symmetric planar borenium cation.

Single crystals of **2a** suitable for X-ray analysis were obtained by slow recrystallization from a mixture of 1,2-dichlorobenzene and hexane. Diffraction analysis revealed a slightly ruffled but almost planar structure with a bowl-depth of 0.114 Å (Figure 1). Importantly, the B−N bond lengths for **2a** are 1.369(3), 1.372(3) and 1.372(3) Å, which are significantly shorter than those of **1a** (1.494(4), 1.486(4), and 1.507(4) Å), reflecting the positive charge and the hybridization change of the central boron from sp^3 to sp^2. In line with these structural features, the planar triangular coordination is revealed by the sum of NBN angles of 359.9°. On the other hand, the other C−C and C−N bond lengths of **2a** are not significantly changed from those of **1a**. Thus, the detachment of the methoxy group from **1a** causes a hybridization change at the central boron and a concurrent bowl-to-planar structural change but has almost no structural influence in the remainder of the molecule. The carborane anion sits above the cation with its electronegative brominated end directed toward the cation but without any specific coordinating interaction. The closest approaches between Br atoms and the central B and N(1) atoms are 3.441 and 3.273 Å, respectively, close to the sum of the van der Waals radii. These data indicate that the borenium cation and the carborane anion are both free ions associated only by Coulombic attraction. An aromatic solvent molecule, 1,2-dichlorobenzene, is located on the other side of the cation at 3.314−3.454 Å, suggesting a $\pi-\pi$ interaction. Two other single crystals of **2a** were obtained from different solvent systems, but the structures differed only in the nature of the solvate molecule, chlorobenzene or toluene.

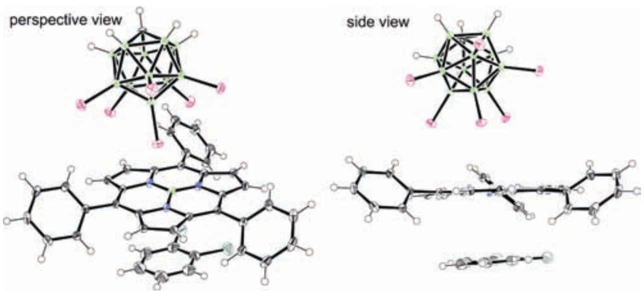


Figure 1. Crystal structure of **2a** at 50% probability of thermal ellipsoids (boron: light green, carbon: black, hydrogen: white, nitrogen: blue, bromine: reddish purple, chlorine: green).

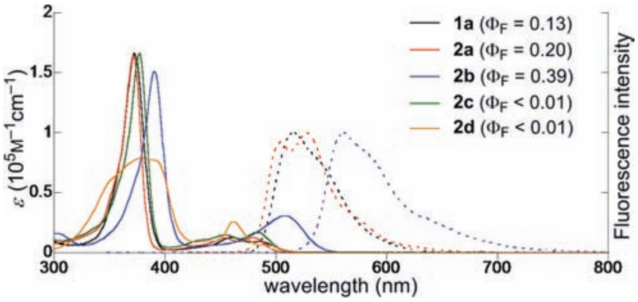
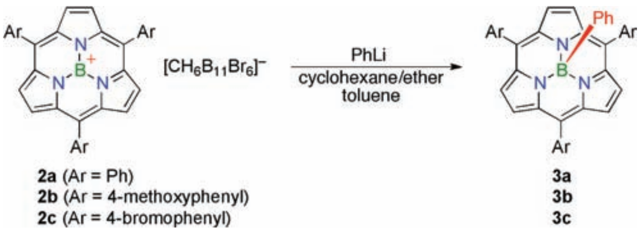


Figure 2. UV−vis absorption (solid) and fluorescence (dashed) spectra of **1a** and **2a**−**d** in CH_2Cl_2.

Figure 2 shows UV−vis absorption and fluorescence spectra of **1a** and **2a**−**d** in dry CH_2Cl_2. Surprisingly, the absorption spectra of **2a** and **2c** are nearly the same as those of **1a** and **1c**, respectively. On the other hand, the cation **2b** exhibits a red-shifted Soret-like band and Q-like band probably due to increased charge-transfer interactions. The fluorescence spectrum of **2a** is also similar to that of **1a** except for split peaks at 504 and 528 nm, an enhanced fluorescence quantum yield ($\Phi_F = 0.20$), and a smaller Stokes shift (992 cm^{-1}), while that of **1a** exhibits a peak at 516 nm, $\Phi_F = 0.13$, and a Stokes shift of 1282 cm^{-1}. MO

Scheme 3. Synthesis of B-Phenyl-Substituted Subporphyrin 3



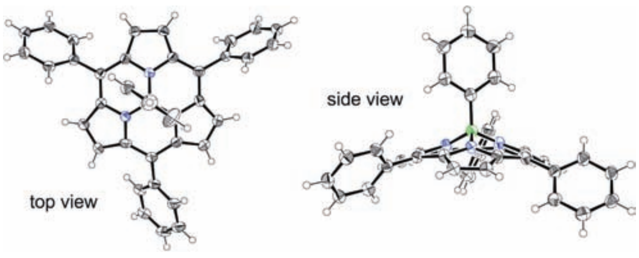


Figure 3. Crystal structure of **3a** at 50% probability of thermal ellipsoids (boron: light green, carbon: black, hydrogen: white, nitrogen: blue).

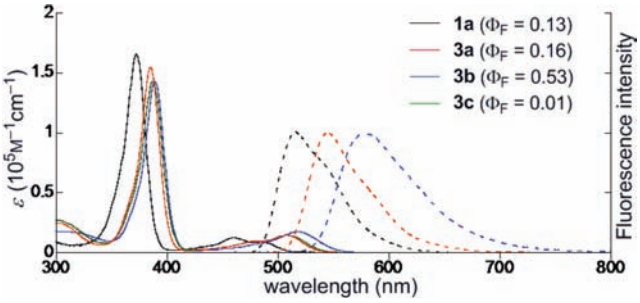


Figure 4. UV−vis absorption (solid) and fluorescence (dashed) spectra of **1a** and **3a**−**c** in CH$_2$Cl$_2$.

calculations indicated that the energy levels of LUMO+1, LUMO, HOMO, and HOMO−1 of **2a** without a counterion were typically stabilized from those of **1a** by ∼3.6 eV, but the relative energies and orbital characteristics were not much changed. Peripherally hexabrominated **2d** shows a characteristic broad Soret-like band that is drastically changed from that of **1d**, indicating significant changes in the molecular orbitals of **2d**. MO calculations reveal intense stabilization of a$_1$ and a$_2$ orbitals of the subporphyrin macrocycle due to the peripheral hexabromo-substituents and the cationic boron center. Consequently, the occupied orbitals derived from *meso*-aryl groups shift between a$_1$ and a$_2$ orbitals. This is probably the reason for the broadening of the Soret-like band of **2d**.[12]

Finally, in expectation of their high electrophilicity, we have examined B-phenylation reactions of **2a**−**c** (Scheme 3). The salts **2a**−**c** were treated with 5 equiv of 1 M PhLi/cyclohexane/ether in dry toluene at 0 °C for 1 h. B-Phenylation proceeded nicely to provide subporphyrins **3a**−**c** in 96, 75 and 57% yields, respectively. These are, to the best of our knowledge, the first examples of subporphyrins bearing an axial B−C bond.[13] The ^{1}H NMR spectrum of **3a** in CDCl$_3$ shows characteristic high-field shifts of the B-phenyl protons at 4.57 (ortho), 6.34 (meta), 6.48 (para) ppm, reflecting a diatropic ring current of the subporphyrin macrocycle. X-ray analysis of **3a** revealed a bowl-shaped structure with the bowl-depth of 1.41 Å and a B−C bond length of 1.611(4) Å (Figure 3). The UV−vis absorption spectra of **3a**−**c** in CH$_2$Cl$_2$ exhibit Soret-like bands at 385, 389, and 387 nm and the Q-like bands at 508, 518, and 509 nm, respectively, which are red-shifted compared with that of **1a** (Figure 4). The fluorescence spectra of **3a** and **3b** were observed as mirror images of the Q-like bands at 545 and 577 nm with Φ_F = 0.16 and 0.53, while **3c** was practically nonfluorescent due to the internal heavy atom effect. The observed large Φ_F of **3b** is notable, in that it is close to the highest value among those reported so far (5,10-(4-(*N*,*N*-dibenzylamino)phenyl)-15-phenylsubporphyrin: Φ_F = 0.60).[1] The first oxidation and reduction potentials of **3a**−**c** vs ferrocinium/ferrocene were measured to be 0.58, 0.42, and 0.71 V, and −2,01, −2.10, and −1.86 V, respectively, which are all higher than those of **1a.**[1] Thus, B-phenylation is an effective means to modulate the optical and electronic properties of subporphyrins.

In summary, the subporphyrin borenium cations have been isolated for the first time as stable salts with a carborane anion, CH$_6$B$_{11}$Br$_6$$^-$. X-ray analysis revealed an almost planar structure for the borenium cation in **2a**, consistent with DFT calculations. Curiously, the optical properties of **2a** are quite similar to those of **1a** despite the structural difference. The formation of borenium cations from B-methoxy subporphyrins under mildly acidic conditions have been observed by ^{1}H- and ^{11}B NMR spectra and UV/vis absorption spectra. Hence, subporphyrin borenium cations may be involved in the facile boron axial ligand exchange reactions via an S$_N$1 mechanism. Further work is currently under way to study the detailed mechanisms of these exchange reactions and explore new uses of subporphyrin borenium cations in synthesis and/or catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, characterization data, physical properties, and crystallographic data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

osuka@kuchem.kyoto-u.ac.jp; chris.reed@ucr.edu

■ ACKNOWLEDGMENT

Work at Kyoto was supported by Grants-in-Aid (Nos. 22245006 (A) and 20108001 "pi-Space") for Scientific Research from MEXT. E.T. acknowledges JSPS Fellowship for Young Scientists. Work at Riverside was supported by NSF Grant CHE 0841428.

■ REFERENCES

(1) (a) Inokuma, Y.; Osuka, A. *Dalton Trans.* **2008**, 2517. (b) Torres, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2834. (c) Osuka, A.; Tanaka, T.; Tsurumaki, E. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 679.

(2) (a) Inokuma, Y.; Kwon, J. H.; Ahn, T. K.; Yoon, M.-C.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 961. (b) Inokuma, Y.; Yoon,

Z. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 4747. (c) Inokuma, Y.; Easwaramoorthi, S.; Yoon, Z. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2008**, *130*, 12234. (d) Inokuma, Y.; Easwaramoorthi, S.; Jang, S. Y.; Kim, K. S.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4840. (e) Hayashi, S.; Inokuma, Y.; Osuka, A. *Org. Lett.* **2010**, *12*, 4148. (f) Tsurumaki, E.; Saito, S.; Kim, K. S.; Lim, J. M.; Inokuma, Y.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2008**, *130*, 438. (g) Hayashi, S.; Inokuma., Y.; Easwaramoorthi, S.; Kim, K. S.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 321. (h) Hayashi, S.; Tsurumaki, E.; Inokuma, Y.; Kim, P.; Sung, Y. M.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2011**, *133*, 4254. (i) Tsurumaki, E.; Inokuma, Y.; Easwaramoorthi, S.; Lim, J. M.; Kim, D.; Osuka, A. *Chem.—Eur. J.* **2009**, *15*, 237.

(3) (a) Kobayashi, N.; Takeuchi, Y.; Matsuda, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 758. (b) Takeuchi, Y.; Matsuda, A.; Kobayashi, N. *J. Am. Chem. Soc.* **2007**, *129*, 8271. (c) Xu, T.; Lu, R.; Liu, X.; Chen, P.; Qiu, X.; Zhao, Y. *Eur. J. Org. Chem.* **2008**, 1065.

(4) For other ring-contracted porphyrins: (a) Myśliborski, R.; Latos-Grażyński, L.; Szterenberg, L.; Lis, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3670. (b) Kim, K. S.; Lim, J. M.; Myśliborski, R.; Pawlicki, M.; Latos-Grażyński, L.; Kim, D. *J. Phys. Chem. Lett.* **2011**, *2*, 477. (c) Xue, Z.-L.; Shen, Z.; Mack, J.; Kuzuhara, D.; Yamada, H.; Okujima, T.; Ono, N.; You, X.-Z.; Kobayashi, N. *J. Am. Chem. Soc.* **2008**, *130*, 16478.

(5) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.

(6) (a) Kölle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399. (b) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016.

(7) (a) Claessens, C. G.; González-Rodríguez, D.; Torres, T. *Chem. Rev.* **2002**, *102*, 835. (b) Claessens, C. G.; González-Rodríguez, D.; del Rey, B.; Torres, T.; Mark, G.; Schuchmann, H.-P.; von Sonntag, C.; MacDonald, J. G.; Nohr, R. S. *Eur. J. Org. Chem.* **2003**, 2546. (c) Shibata, N.; Das, B.; Tokunaga, E.; Shiro, M.; Kobayashi, N. *Chem.—Eur. J.* **2010**, *16*, 7554.

(8) Kato, T.; Tham, F. S.; Boyd, P. D. W.; Reed, C. A. *Heteroatom Chem.* **2006**, *17*, 209.

(9) (a) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133. (b) Reed, C. A. *Acc. Chem. Res.* **2010**, *43*, 121. (c) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922.

(10) The formation of a borenium cation was also indicated from ^{1}H NMR spectral analysis of methoxo(5,10,15-tris(2,4,6-trimethoxyphenyl)-subporphyrinato)boron(III). While this subporphyrin exhibited three singlet signals due to the *meso*-aryl-methoxy protons at 3.98, 3.79, and 3.32 ppm in the ^{1}H NMR spectrum in $CDCl_3$, reflecting the restricted rotation of the *meso*-aryl substituents, only two singlets were observed at 4.12 and 3.71 ppm in a ratio of 1:2 in a 1:1 mixture of $CDCl_3$/TFA-*d*. For more details see Supporting Information.

(11) The ^{1}H NMR spectrum of **1d** in $CDCl_3$ showed considerably broad signals at room temperature but showed four sharp doublets for the *ortho*- and *meta*-protons of the *meso*-aryl groups at δ = 8.00, 7.70, 7.46 and 7.11 ppm at −40 °C, indicating the restricted rotation of the *meso*-aryl substituent.

(12) The absorption spectra of **1a**−**d** in TFA were essentially the same as those of **2a**−**d** in CH_2Cl_2., respectively, indicating the formation of the borenium cations in TFA.

(13) Several examples have been reported for subphthalocyaines bearing axial B−C bond: (a) Rauschnabel, J.; Hanack, M. *Tetrahedron Lett.* **1995**, *36*, 1629. (b) Geyer, M.; Plenzig, F.; Rauschnabel, J.; Hanack, M.; del Rey, B.; Sastre, A.; Torres, T. *Synthesis* **1996**, 1139. (c) Camerel, F.; Ulrich, G.; Retailleau, P.; Ziessel, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 8876. (d) Yamasaki, Y.; Mori, T. *Chem. Lett.* **2010**, *39*, 1108. (e) Guilleme, J.; González-Rodríguez, D.; Torres, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 3506.