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Boron Complexes of Oxasmaragdyrin, a Core-Modified Expanded Porphyrin

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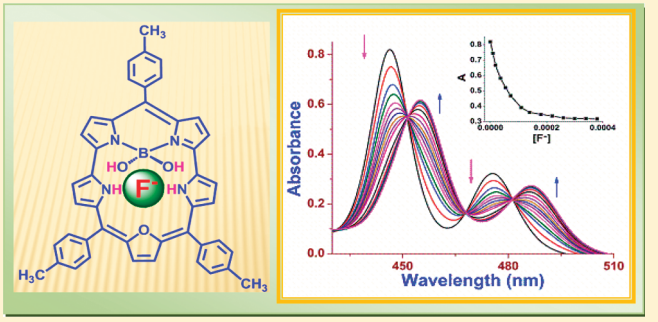
Supporting Information

ABSTRACT: We report the synthesis of first examples of BF_2 and $B(OR)_2$ complexes of oxasmaragdyrin, the expanded core-modified porphyrin, in decent yields under very simple reaction conditions at room temperature. The boron complexation of oxasmaragdyrin alters the electronic properties of the macrocycle significantly as evident by various spectroscopic techniques. Our preliminary studies indicated that the $B(OH)_2$−smaragdyrin complex can act as a selective neutral fluoride ion sensor.



The coordination of boron to a range of polypyrrole containing ligands that includes simple dipyrromethenes (also commonly called as dipyrrins) to large macrocycles such as porphyrins, corroles, and expanded porphyrins has received tremendous attention in recent years.[1] Among these, the most widely utilized class of pyrrolyl boron complexes are boron difluoride dipyrromethenes (BODIPYs) containing the conjugated, monoanionic dipyrromethene ligand.[2] Porphyrins are tetrapyrrolic macrocycles containing dipyrromethene moieties and have been explored for their complexation behavior toward a BF_2 group in recent years.[3] The porphyrin complexes with two BBr_2 or BI_2 groups undergoes spontaneous reductive coupling to give compounds with direct B−B bonds or undergoes hydrolysis and forms B−O−B links inside the porphyrin macrocycle. The expanded porphyrins which contain more than four pyrrole rings[4] and have potential dipyrromethene motifs have been shown very recently to also complex with one or two BF_2 groups.[5] Sessler, Brothers, and others[5] showed that amethyrin, a hexapyrrolic macrocycle, and [32]octaphyrin on reaction with $BF_3 \cdot OEt_2$ gave two products containing one and two BF_2 groups which are stable and does not undergo any hydrolysis. However, to the best of our knowledge, there is no report on boron complexes of core-modified expanded porphyrins to study their electronic properties. Among the various core-modified expanded porphyrins reported in the literature, the oxasmaragdyrins[6] are suitable macrocycles to prepare BF_2 complexes for the following reasons: (1) oxasmaragdyrins possess only one monoanionic dipyrromethene unit; (2) oxasmaragdyrins absorb in the red region with good extinction coefficients; and (3) these are fluorescent compounds with good quantum yield and longer singlet state lifetime. Hence we have chosen the oxasmaragdyrin for the synthesis of first examples of BF_2 (**1**−**4**) and also $B(OR)_2$ (**5**−**8**) complexes of oxasmaragdyrins. We have also demonstrated for the first time that a $B(OH)_2$−smaragadyrin complex can act as an exclusive fluoride anion sensor by using spectral and electrochemical techniques.

The *meso*-substituted oxasmaragdyrins **9**−**12**, the key precursors for target compounds **1**−**4**, were synthesized in very decent yields by adopting the well-established 3 + 2 MacDonald-type condendation of *meso*-aryldipyrromethane with 16-oxatripyrrane under mild acid catalyzed reaction conditions.[6a] The BF_2 complexes of smaragdyrins **1**−**4** were prepared by treating the appropriate free base smaragdyrin **9**−**12** with 40 equiv of triethylamine followed by $BF_3 \cdot OEt_2$ in CH_2Cl_2 at room temperature for 30 min (Scheme 1). After standard workup and chromatographic purification on alumina, the BF_2 complexes **1**−**4** were isolated as green solids in 66−76% yields. The BF_2 complexes **1**−**4** were quite stable and did not undergo any hydrolysis or decomplexation. The complexes **1**−**4** were characterized in detail by HR-MS mass, ^1H, ^{13}C, ^{19}F, ^{11}B NMR spectra and the proton assignments were made based on the correlation observed in the 2D $^1H-^1H$ COSY spectrum recorded for complex **1** (Supporting Information). The BF_2 complex **1** showed four doublets for eight β-pyrrole protons (b, c, d, e) and one sharp singlet for two β-furan protons (a) like its free base smaragdyrin **9** (Figure 1). However, the β-pyrrole and β-furan protons of BF_2 complexes experienced a 0.2 to 0.8 ppm downfield shift compared to their corresponding free base smaragdyrins indicating that the BF_2 complexation altered the π-delocalization of smaragdyrin. Furthermore, on complexation with BF_2, the two inner NH protons of smaragdyrin were

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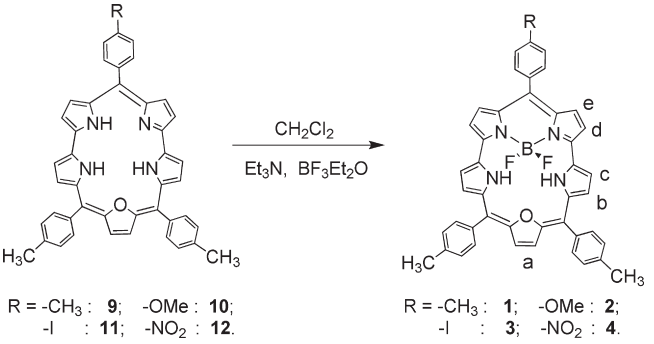
localized and appeared as an unresolved triplet at very upfield. This is due to strong hydrogen bonding with the two fluoride ions of the BF_2 unit, which exposes the inner NH protons to experience the strong ring current effect of the macrocycle. This kind of hydrogen bonding was also noted by Sessler and co-workers in the crystal structure solved for the BF_2 complex of amethyrin.[5] The hydrogen bonding and π-delocalization effect were also noted in ^{19}F and ^{11}B NMR spectra of complexes **1**−**4** (Supporting Information). The geometry optimized structure of compound **1** also supports the presence of strong BF···H hydrogen bonding (Supporting Information).

The BF_2 complexes **1**−**4** showed two clear well-separated absorption bands in the Soret region at 447 and 475 nm in addition to absorption bands present in the visible region. The most interesting feature of BF_2 complexes **1**−**4** is the strong absorption band at 702 nm, which is three times more intense than the absorption band of free base smaragdyrin **9** present in the same region (Supporting Information). The BF_2−smaragdyrins **1**−**4** exhibited one fluorescence band that was bathochromically shifted by 10−15 nm and their fluorescent quantum yields are two times higher than those of free base smaragdyrins.

The BF_2 complexes **1**−**4** showed two reversible oxidations and one reversible reduction and one irreversible reduction. The comparison of BF_2 complexes such as **1** with its corresponding free base smaragdyrin **9** reveal the following: (1) the oxidation potentials of BF_2 complexes **1**−**4** were shifted toward more positive by ~500 mV compared to that of free base smaragdyrin **9** (Supporting Information) indicating that the BF_2 smaragdyrins are difficult to oxidize; (2) the first reduction potential of **1**−**4** shifted toward less negative by ~450−500 mV compared to that of free base smaragdyrin **9**, indicating that the BF_2 complexes are easier to reduce. Thus, BF_2 complexation of smaragdyrins makes the resulting macrocyles more electron deficient than free base smaragdyrins.

Although BF_2−smaragdyrins exhibited interesting spectral and electrochemical properties, these complexes cannot be used for chemical sensor applications. This is because the fluorides of the BF_2 moiety are involved in strong hydrogen bonding with inner NH protons hence the inner NH protons are not freely

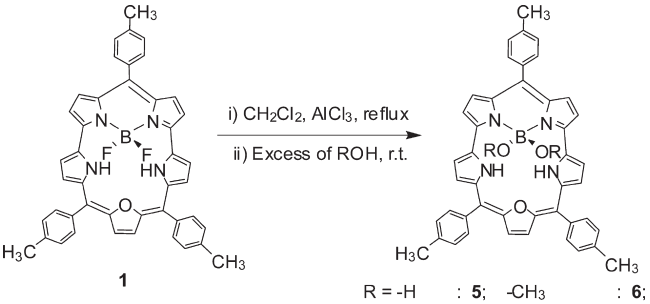
Scheme 1. Synthesis of BF_2−Smaragdyrin Complexes 1−4



R = -CH_3 : **9**; -OMe : **10**; -I : **11**; -NO_2 : **12**.

R = -CH_3 : **1**; -OMe : **2**; -I : **3**; -NO_2 : **4**.

Scheme 2. Synthesis of $B(OR)_2$−Smaragdyrin Complexes 5−8



R = -H : **5**; -CH_3 : **6**; -C_2H_5 : **7**; -CH_2CH_2OH : **8**

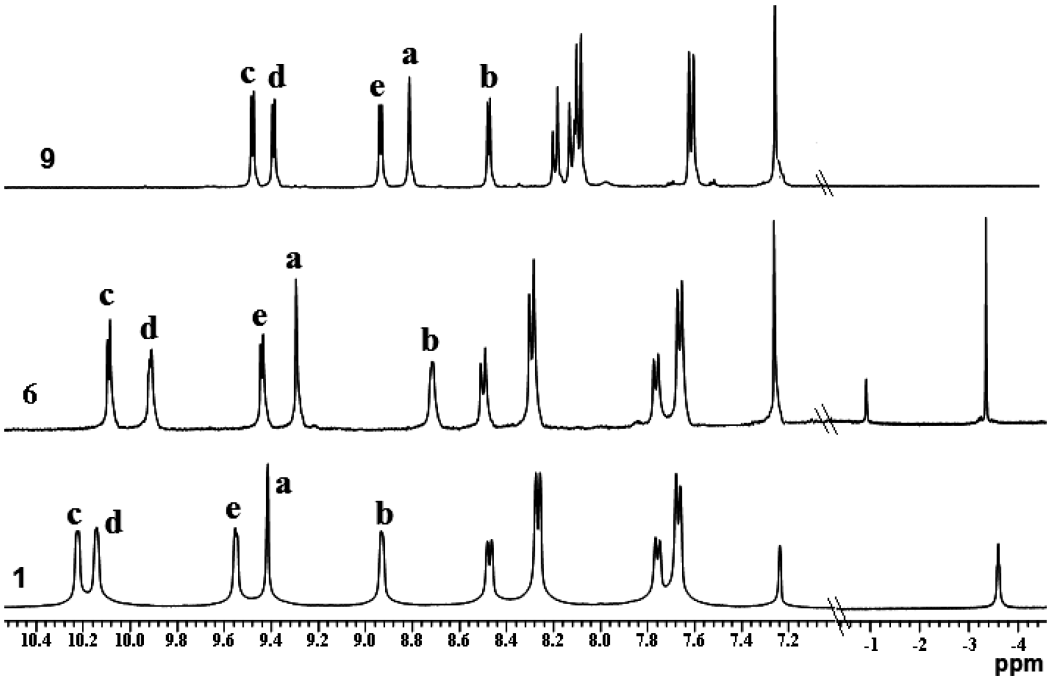


Figure 1. Comparison of ^1H NMR spectra of BF_2 and $B(OCH_3)_2$−smaragdyrins **1** and **6** along with free base smaragdyrin **9**.

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accessible. To overcome this problem, we attempted to replace the fluoride ions with hydroxy and alkoxy groups using simple reaction conditions. We anticipated that these groups on the boron atom would further tune the electronic properties of macrocycle, and particularly the $B(OH)_2$ complex of smaragdyrin with four available hydrogens can be used for sensor applications. With this idea in mind, we prepared $B(OR)_2$ complexes from BF_2 complex **1** using the reaction conditions developed by Bonnet and co-workers recently.[7] The $B(OH)_2$−smaragdyrin complex **5** was prepared by treating **1** with $AlCl_3$ in CH_2Cl_2 at refluxing temperature for **5** min (Scheme 2) followed by column chromatographic purification to afford **5** as a green solid in 60% yield. The alkoxy substituted $B(OR)_2$−smaragdyrin complexes **6**−**8** were prepared by treating BF_2−smaragdyrin **1** with $AlCl_3$ in the presence of an appropriate alcohol such as methanol, ethanol, and glycol in excess amount under similar reaction conditions. The ^{1}H NMR spectral features of complexes **5**−**8** are almost identical with those of BF_2−smaragdyrin complex **1** in the 7−10 ppm region (Supporting Information). The interesting ^{1}H NMR spectral features of $B(OR)_2$−smaragdyrins **5**−**8** were clearly evident in the high-field region. In BF_2−smaragdyrin complex **1**, because of the hydrogen bonding between inner NH protons and fluoride ions as well as the macrocyclic ring current effect, the inner NH signal appeared as an unresolved triplet very upfield (−3.7 ppm). However, in $B(OR)_2$−smaragdyrin complexes, this kind of strong hydrogen bonding is not possible hence the inner NH protons experienced downfield shift and appeared as a sharp singlet at −0.6 ppm. Furthermore, the hydroxy or alkoxy groups present on the boron atom also experience the ring current effect of the macrocycle and appear at very high field. In ^{11}B NMR spectra, complexes **5**−**8** showed a sharp singlet at ca. −11.5 ppm, which experiences a slight downfield shift compared to those for BF_2−smaragdyrin complexes **1**−**4**. The absorption and fluorescence spectral studies of $B(OR)_2$−smaragdyrin complexes **5**−**8** showed the same spectral features as BF_2−smaragdyrin complexes **1**−**4**. However, the electrochemical studies of $B(OR)_2$−smaragdyrins **5**−**8** showed some different features from those of BF_2−smaragdyrins **1**−**4** because of the electron donating nature of alkoxy substituents, which makes the macrocycle in **5**−**8** easier to oxidize but difficult to reduce.

The expanded porphyrins are effective anion receptors because of their large cavity and availability of more inner NH/CH protons for bonding interactions with anions. Sessler et al.[8] have shown that the pyrrole containing expanded porphyrins have high affinity for various anions. Chandrashekar and co-workers[9] tested the anion binding affinity of core-modified analogues. However, most of the expanded porphyrins bind anions only in their protonated form and they also lack the specificity toward anion. Thus, it is required to develop a neutral expanded porphyrin that can bind anions selectively. We explored the anion sensing properties of **5** with various anions such as F^-, Cl^-, Br^-, I^-, HSO_4^-, and ClO_4^- and studies showed that compound **5** can act as an exclusive sensor for F^- ion among these anions. In **5**, the presence of −OH and −NH protons would help in binding anions through hydrogen bonding interactions. We used various spectral and electrochemical techniques to demonstrate the fluoride anion specificity of **5**.

The fluoride anion binding to **5** was first followed by ^{1}H NMR titration with increasing amounts of fluoride anion in $CDCl_3$ (Supporting Information). Since **5** exhibits four clear doublets for pyrroles and a singlet for furan protons in ^{1}H NMR, we followed the changes in the chemical shifts of these protons by addition of increasing amounts of tetrabutylammonium fluoride. The pyrrole and furan proton signals of **5** experienced slight downfield shifts on increasing amounts of fluoride ion. For example, the β-pyrrole protons which appeared as a doublet at 8.69 ppm slowly disappeared with the appearance of a new doublet at 8.79 ppm, and finally after addition of 10 equiv of anion, a new doublet appeared at 8.79 ppm. Similarly, the furan signal that appeared as a singlet at 9.25 ppm in **5** completely disappeared and a new singlet for furan protons appeared at 9.35 ppm (Supporting Information). Thus, the trends observed in ^{1}H NMR spectra on addition of increasing amounts of anion support that **5** binds the fluoride ion. Under the same experimental conditions, **5** did not show any changes in chemical shifts of pyrrole and furan protons on addition of various other anions such as Cl^-, Br^-, I^-, HSO_4^-, and ClO_4^- (Supporting Information).

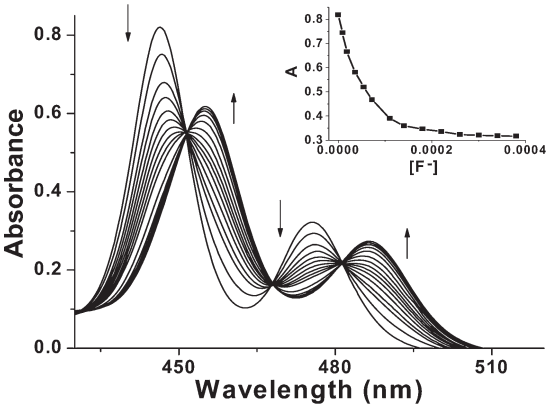

Figure 2. The absorption spectra of **5** (5 μM) in the region 400−525 nm in the presence of F^- in CH_2Cl_2. The F^- concentration is 0, 9, 18, 27, 36, 45, 54, 63, 72, 81, 90, 99, and 108 μM, respectively.

To obtain more insight about anion binding with **5**, spectrophotometric titration experiments were carried out systematically with various anions. The absorption spectral titrations of **5** with the addition of the fluoride ion is shown in Figure 2. It is clear from Figure 2 that the intensity of the absorption bands of **5** at 446, 475, and 705 nm decreased on addition of increasing amounts of F^- ion and new bands at 455, 487, and 720 nm appeared with four isosbestic points at 451, 468, 482, and 713 nm. The expected 1:1 stoichiometry, suggested by the presence of isosbestic points, was further confirmed by Job's plot analysis (Supporting Information). From the Benesi−Hildebrand equation, the binding constant of 13 000 M^{-1} was evaluated for receptor−anion complex formation. Because complex **5** is fluorescent with a strong emission band at 713 nm, we carried out the anion binding studies of **5** by following fluorescence spectral changes in CH_2Cl_2 (Supporting Information). Addition of increasing amounts of tetrabutylammonium fluoride to **5** resulted in the quenching of the emission band at 713 nm with a slight red shift and broadening suggesting that the fluoride ion was bound to **5**. However, we did not observe any change in the absorption and fluorescence spectral profile of **5** on addition of other anions. Thus, NMR, absorption, and fluorescence spectral studies supported that **5** is an exclusive receptor for fluoride ion.

We also probed the changes in the redox potentials of **5** on addition of increasing amounts of F^- ion by cyclic as well as square wave voltammetry and Figure 3 shows the systematic changes in the oxidation waves of receptor on increasing addition

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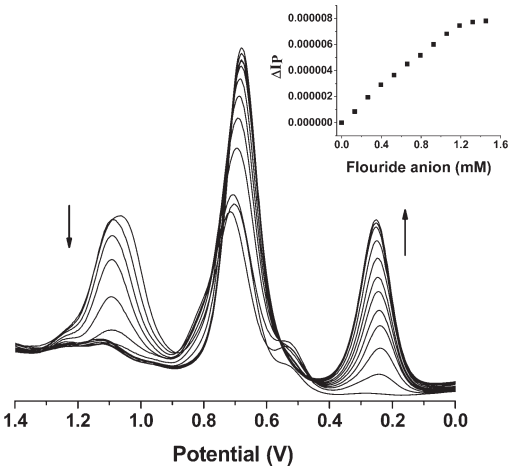

Figure 3. Square wave voltammograms of **5** (0.59 mM) in the presence of F^- ion. The F^- concentration is 0, 0.14, 0.28, 0.42, 0.56, 0.70, 0.84, 0.98, 1.12, 1.26, 1.40, and 1.54 mM, respectively.

of fluoride anion. The addition of increasing amounts of fluoride anion to the solution of **5** resulted in the decrease of current intensity of the oxidation wave at 1.06 V, which gradually disappears, and at the same time the appearance of new oxidation with gradual increase in current intensity at 0.300 V was observed. However, the oxidation wave at 0.700 V experienced negligible shift in the potential on increasing the addition of fluoride ion to **5**. Furthermore, no changes in oxidation potentials of **5** was observed when we added other anions. All these results indicate that **5** can also be used as a specific electrochemical sensor for fluoride ion.

To understand the mode of binding of **5** with various anions, we carried out the geometry optimizations performed at the B3LYP/6-31G* level (Supporting Information). The optimization studies indicated that th F^- ion binds to **5** by using three hydrogen bonds with high complexation energy (59.06 kcal/mol) compared to other anions such as Cl^- which binds **5** with one hydrogen bond and moderate to very low complexation energy (Supporting Information).

In conclusion, we synthesized BF_2 complexes of oxasmragdyrin in decent yields under very simple reaction conditions. The BF_2−smaragdyrin complexes exhibit very interesting spectral and electrochemical properties which are different from those of free base smaragdyrins. We also synthesized the first examples of $B(OR)_2$ complexes of smaragdyrin by reacting the BF_2−smaragdyrins with alcohols in the presence of $AlCl_3$. We showed that $B(OH)_2$−smaragdyrin can be used as an exclusive sensor for fluoride ion.

EXPERIMENTAL SECTION

General. All NMR spectra (δ values, ppm) were recorded with 300 or 400 MHz spectrometers. Tetramethylsilane (TMS) was used as an external reference for recording ^1H (of residual proton; δ = 7.26 ppm) and ^{13}C (δ = 77.0 ppm) spectra in $CDCl_3$. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with an electrochemical system utilizing a three-electrode configuration consisting of a glassy carbon (working) electrode, platinum wire (auxiliary) electrode, and a saturated calomel (reference) electrode. The experiments were performed in dry CH_2Cl_2 with 0.1 M TBAP as the supporting electrolyte. Half-wave potentials were measured with DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials.

Details of Anion Binding Studies. All the anion salts used for the titrations were as their tetrabutylammonium salts. All the solvents used were of analytical grade and were purified and dried by routine procedures immediately before use. Stock solutions of the anions (10 mM) and a stock solution of **5** (1 mM) were prepared in CH_2Cl_2. For absorption measurements, the stock solution of **5** was diluted to 5 μM. Titration experiments were performed by placing 2.5 mL of solution **5** (5 μM) in a quartz cuvette of 1 cm path length and various amounts of anions were added incrementally by means of a micropipet. For fluorescence measurements, excitation was provided at 420 nm, and emission was collected from 500 to 800 nm. The association constant of the anion complex formed in the solution has been estimated by using the standard Benesi−Hildebrand equation, viz.,

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K_a[A^-]}$$

where I_0 is the intensity of **5** before addition of anion, I is the intensity in the presence of A^-, I_1 is intensity upon saturation with A^-, and K_a is the association constant of the complex formed. All square-wave voltammetric experiments were carried out in distilled anhydrous and degassed CH_2Cl_2 at 0.59 mM concentration of the sensor and 0.1 M TBAP was present as the supporting electrolyte. The typical setting for SWV experiments was as follows: freq = 15 Hz, increment = 4 mV, amplitude = 25 mV.

Smaragdyrin−BF_2 Complexes 1−4. A sample of smaragdyrin **9**−**12** (0.157 mmol) was taken in CH_2Cl_2 (30 mL) and triethylamine (6.28 mmol) was added at room temperature. After 5 min $BF_3 \cdot Et_2O$ (7.85 mmol) was added, and stirring was continued at room temperature for 30 min. The reaction mixture was diluted with CH_2Cl_2 and washed thoroughly with 0.1 M NaOH solution and water. The organic layers were combined, dried over Na_2SO_4, and filtered, and solvent was removed on a rotary evaporator under vacuum. The resulting crude product was purified by column chromatography on alumina, using petroleum ether/dichloromethane (70:30), and afforded pure compounds **1**−**4** as a green powder.

1: 81 mg, 76%; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) −3.60 (t, 2H; −NH), 2.76 (s, 9H; Tol), 7.66 (d, 4H, ^3J(H,H) = 7.0 Hz; Ar), 7.75 (d, 2H, ^3J(H,H) = 7.0 Hz; Ar), 8.26 (d, 4H, ^3J(H,H) = 6.7 Hz; Ar), 8.46 (d, 2H, ^3J(H,H) = 6.7 Hz; Ar), 8.92 (dd, 2H, ^3J(H,H) = 4.4 Hz, ^4J(H,H) = 1.4 Hz; Py), 9.41 (s, 2H; Fur), 9.52 (d, 2H, ^3J(H,H) = 7.0 Hz; Py), 10.15 (dd, 2H, ^3J(H,H) = 4.4 Hz, ^4J(H,H) = 1.4 Hz; Py), 10.20 (d, 2H, ^3J(H,H) = 7.0 Hz; Py); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm) −149.6 (bs); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −12.04 (bs); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 21.7, 21.8, 107.0, 120.1, 120.5, 121.7, 123.7, 124.8, 125.0, 128.4, 129.4, 130.7, 131.1, 132.0, 134.4, 134.8, 136.2, 138.0, 138.1, 139.7, 149.9; HRMS calcd for $C_{44}H_{33}BF_2N_4O$ 682.2715, found 682.2682.

2: 74 mg, 69%; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) −3.53 (t, 2H; −NH), 2.76 (s, 6H; Tol), 4.12 (s, 3H; $-OCH_3$), 7.48 (d, 2H, ^3J(H,H) = 8.4 Hz; Ar), 7.67 (d, 4H, ^3J(H,H) = 7.8 Hz; Ar), 8.24 (d, 4H, ^3J(H,H) = 7.8 Hz; Ar), 8.49 (d, 2H, ^3J(H,H) = 8.4 Hz; Ar), 8.91 (dd, 2H, ^3J(H,H) = 4.3 Hz, ^4J(H,H) = 1.5 Hz; Py), 9.39 (s, 2H, Fur), 9.52 (d, 2H, ^3J(H,H) = 4.4 Hz; Py), 10.12 (dd, 2H, ^3J(H,H) = 4.2 Hz, ^4J(H,H) = 1.8 Hz; Py), 10.20 (d, 2H, ^3J(H,H) = 4.4 Hz; Py); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm) −149.28 (bs); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −11.91 (bs); HRMS calcd for $C_{44}H_{33}BF_2N_4O_2$ 698.2665, found 698.2631.

3: 77 mg, 72%, mp >300 °C; ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) −3.90 (t, 2H; −NH), 2.79 (s, 6H; Tol), 7.69 (d, 4H, ^3J(H,H) = 7.7 Hz; Ar), 8.26−8.32 (m, 8H; Ar), 9.00 (m, 2H; Py), 9.49 (s, 2H; Fur), 9.55 (d, 2H, ^3J(H,H) = 4.4 Hz; Py), 10.22 (m, 2H; Py), 10.31 (d, 2H, ^3J(H,H) = 4.4 Hz; Py); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in

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ppm) −149.68 (bs); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −12.54 (bs); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 29.8, 107.2, 117.5, 120.5, 120.9, 122.1, 123.8, 124.1, 125.2, 128.4, 130.8, 131.0, 131.5, 134.4, 136.5, 137.7, 138.1, 138.8, 139.6, 150.0; HRMS calcd for $C_{43}H_{30}BF_2IN_4O$ 794.1526, found 794.1541.

4: 71 mg, 66%, mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −4.25 (t, 2H; −NH), 2.81 (s, 6H; Tol), 7.72 (d, 4H, ^3J(H,H) = 7.7 Hz; Ar), 8.32 (d, 4H, ^3J(H,H) = 8.0 Hz; Ar), 8.83 (d, 4H, ^3J(H,H) = 7.7 Hz; Ar), 9.10 (dd, 2H, ^3J(H,H) = 4.4 Hz, ^4J(H,H) = 1.4 Hz; Py), 9.59−9.60 (m, 4H; Py + fur), 10.32 (dd, 2H, ^3J(H,H) = 4.4 Hz, ^4J(H,H) = 1.4 Hz; Py), 10.43 (d, 2H, ^3J(H,H) = 4.4 Hz; Py); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm) −149.5 (bs); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −12.70 (bs); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 29.7, 107.4, 114.6, 120.9, 121.6, 122.7, 123.3, 123.5, 124.0, 125.3, 128.3, 128.4, 130.0, 131.2, 134.4, 135.5, 137.7, 138.1, 139.4, 146.4, 147.6, 150.0; HRMS calcd for $C_{43}H_{30}BF_2N_5O3$ 713.2410, found 713.2401.

Smaragdyrin−B(OR)$_2$ Complexes 5−8. Smaragdyrin **1** (50 mg, 0.733 mmol) was dissolved in dry CH_2Cl_2 (20 mL) in the presence of aluminum chloride (15 mg, 1.09 mmol) under argon. The resulting mixture was refluxed for 5 min prior to addition of the corresponding alcohol (5 mL) and the reaction mixture was stirred for an additional 5 min. Then the crude mixture was concentrated under reduced pressure, and pure compounds **5**−**8** were isolated by column chromatography on basic alumina, using petroleum ether/CH_2Cl_2 (60:40) to afford a green solid.

5: 30 mg, 60%, mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −7.43 (s, 2H; −OH), −0.07 (s, 2H; −NH), 2.77 (s, 9H; Tol), 7.67 (d, 4H, ^3J(H,H) = 7.6 Hz; Ar), 7.75 (d, 2H, ^3J(H,H) = 7.6 Hz; Ar), 8.25 (d, 4H, ^3J(H,H) = 7.6 Hz; Ar), 8.45 (d, 2H, ^3J(H,H) = 7.6 Hz; Ar), 8.69 (dd, 2H, ^3J(H,H) = 3.8 Hz, ^4J(H,H) = 1.8 Hz; Py), 9.28 (s, 2H; Fur), 9.40 (d, 2H, ^3J(H,H) = 4.3 Hz; Py), 9.89 (dd, 2H, ^3J(H,H) = 3.8 Hz, ^4J(H,H) = 1.8 Hz; Py), 10.06 (d, 2H, ^3J(H,H) = 4.3 Hz; Py); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −12.10 (s); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 29.9, 107.0, 118.9, 119.3, 121.4, 122.8, 124.1, 124.4, 124.8, 125.4, 128.3, 128.4, 130.6, 131.5, 132.4, 134.4, 134.7, 137.7, 140.2, 150.0; HRMS calcd for $C_{44}H_{35}BN_4O_3$ 674.2489, found 674.2487 $(M-4)^+$.

6: 34 mg, 69%, mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −3.42 (s, 6H; $-OCH_3$), −0.99 (s, 2H; −NH), 2.77 (s, 9H; Tol), 7.66 (d, 4H, ^3J(H,H) = 7.6 Hz; Ar), 7.75 (d, 2H, ^3J(H,H) = 7.6 Hz; Ar), 8.28 (d, 4H, ^3J(H,H) = 7.6 Hz; Ar), 8.48 (d, 2H, ^3J(H,H) = 7.6 Hz; Ar), 8.71 (m, 2H; Py), 9.29 (s, 2H; Fur), 9.44 (d, 2H, ^3J(H,H) = 4.3 Hz; Py), 9.91 (m, 2H; Py), 10.09 (d, 2H, ^3J(H,H) = 4.3 Hz; Py); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −11.06 (s); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 29.7, 106.8, 114.1, 119.6, 119.9, 120.3, 121.6, 123.6, 124.6, 124.9, 128.3, 130.6, 131.0, 131.4, 134.2, 135.8, 137.9, 139.6, 149.8; HRMS calcd for $C_{46}H_{39}BN_4O_3$ 706.3115, found 706.3142.

7: 35 mg, 70%, mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −3.85 (t, 6H, ^3J(H,H) = 7.0 Hz; $-CH_3$), −3.46 (q, 4H, ^3J(H,H) = 7.0 Hz; $-OCH_2$), −0.11 (s, 2H; −NH), 2.72 (s, 9H; Tol), 7.60 (d, 4H, ^3J(H,H) = 7.6 Hz; Ar), 7.70 (d, 2H, ^3J(H,H) = 7.6 Hz; Ar), 8.22 (d, 4H, ^3J(H,H) = 7.6 Hz; Ar), 8.44 (d, 2H, ^3J(H,H) = 7.6 Hz; Ar), 8.62 (m, 2H; Py), 9.23 (s, 2H; Fur), 9.35 (d, 2H, ^3J(H,H) = 4.2 Hz; Py), 9.82 (dd, 2H, ^3J(H,H) = 4.2 Hz, ^4J(H,H) = 1.4 Hz; Py), 10.01 (d, 2H, ^3J(H,H) = 4.2 Hz; Py); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −11.85 (s); HRMS calcd for $C_{48}H_{43}BN_4O_3$ 734.3428, found 734.3436.

8: 31 mg, 63%, mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −4.99 (s, 2H; −OH), −3.32 (s, 4H; $-CH_2$), −1.06 (s, 2H; −NH), −1.05 (s, 2H; $-CH_2$), 2.80 (s, 9H; Tol), 7.79 (d, 2H, ^3J(H,H) = 7.9 Hz; Ar), 7.89 (m, 4H; Ar), 8.39 (m, 4H; Ar), 8.50 (d, 2H, ^3J(H,H) = 7.9 Hz; Ar), 8.72 (dd, 2H, ^3J(H,H) = 3.8 Hz, ^4J(H,H) = 1.8 Hz; Py), 9.30 (s, 2H; Fur), 9.49 (d, 2H, ^3J(H,H) = 4.2 Hz; Py), 9.97 (dd, 2H, ^3J(H,H) = 3.8 Hz, ^4J(H,H) = 1.8 Hz; Py), 10.13 (d, 2H, ^3J(H,H) = 4.2 Hz; Py); ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm) −11.58 (s); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 29.8, 58.3, 58.2, 107.1, 119.5, 119.7, 121.6, 124.2, 124.6, 125.2, 127.7, 128.2, 129.0, 130.0, 131.1, 132.2, 133.1, 134.6, 134.8, 136.3, 138.2, 142.7, 149.8; HRMS calcd for $C_{48}H_{43}BN_4O_5$ 766.3327, found 766.3305.

■ ASSOCIATED CONTENT

Supporting Information. Characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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