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Highly Fluorescent Red-Light Emitting Bis(boranils) Based on Naphthalene Backbone

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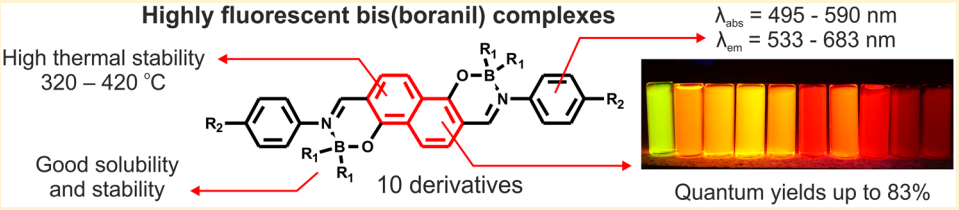
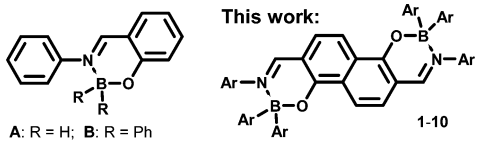
Supporting Information



ABSTRACT: Ten bis(boranils) differently substituted at the boron atom and iminophenyl groups were synthesized from 1,5-dihydroxynaphthalene-2,6-dicarboxaldehyde using a simple one-pot protocol. Their photophysical properties can be easily tuned in a wide range by the variation of substituents. Their absorption and emission spectral bands are significantly red-shifted (λ_{max} = 495−590 nm, λ_{em} = 533−683 nm) when compared with simple boranils, whereas fluorescence quantum yields are strongly improved to reach 83%. The attachment of pendant NO_2 and NEt_2 groups at the opposite positions of the π-conjugated bis(boranil) scaffold resulted in the formation of an unprecedented system featuring push−pull architecture.

Currently, there is an increasing interest in various organoboron compounds due to their specific optoelectronic properties.[1] This enables their wide utilization in materials chemistry with a special emphasis on the construction of optical and optoelectronic devices including organic light emitting diodes (OLEDs), organic field-effect transistors as well as photoresponsive materials.[2] Specifically, boron complexes with (*N*,*O*)-bidentate Schiff base ligands (boranils) have been described as promising fluorescent dyes with potential for biolabeling purposes and suitable emitters for electroluminescent devices (**A**, **B** Scheme 1).[3] Free ligands can be easily obtained by condensation reactions of appropriate salicylaldehydes and anilines. Since the starting materials are readily available, the access to a wide selection of functionalized boranils including multicenter boron complexes is possible in a relatively simple manner.[4] On the other hand the photophysical properties of the reported multiboron Schiff-base complexes are similar to their monoboron analogues with absorption and emission maxima in the range of 350−450 nm and 470−520 nm, respectively, and quantum yields of emission (QY) usually not exceeding 30%.

Scheme 1. Mono- and Mulitiboron Complexes with Salicydeneanilines



A continuous search for related systems with improved optical properties has prompted us to synthesize a group of strongly fluorescent red-light emitting bis(boranils) **1**−**10** derived from a ditopic tetradentate 1,5-dihydroxy-2,6-bis(*N*-phenyliminomethylene)-naphthalene ligand. 1,5-Dihydroxynaphthalene-2,6-dicarboxaldehyde **14** is a key compound en route to targeted Schiff base ligands and final boron complexes. It was obtained from cheap and already accessible substrates (as 1,5-dihydroxynaphthalene) in a four-step protocol with a satisfactory total yield of 56% (Scheme 2). Having the dialdehyde **14** in hand, we have synthesized two referential bis(boranil) complexes bearing substituents frequently encountered at the boron atom−fluorine atoms (**1**) or phenyl groups (**2**). It was expected that the fluorination of *B*-phenyl rings will improve the stability of the complex due to an increased boron Lewis acidity.[5] Thus, we have prepared 2,6-difluorophenyl- (**3**) and pentafluorophenyl (**4**) analogues. Further modification was achieved by rigidifying the organoboron scaffold, which would restrict the rotation of substituents attached to boron atom and limit the fluorescent quenching. Consequently, 10-hydroxyphenoxaborin was used as a precursor for the synthesis of **5**. In addition, the optical properties of the system can be easily tuned by changing the length of the π-conjugated skeleton or by its substitution with electron-withdrawing or electron-donating functional groups. Thus, we have obtained symmetrical complexes **6**−**9** bearing two NO_2 (**6**, **7**) or two NEt_2 (**8**, **9**) groups. Finally, we have also obtained the push−pull system **10** derived from a Schiff base substituted with NO_2 and

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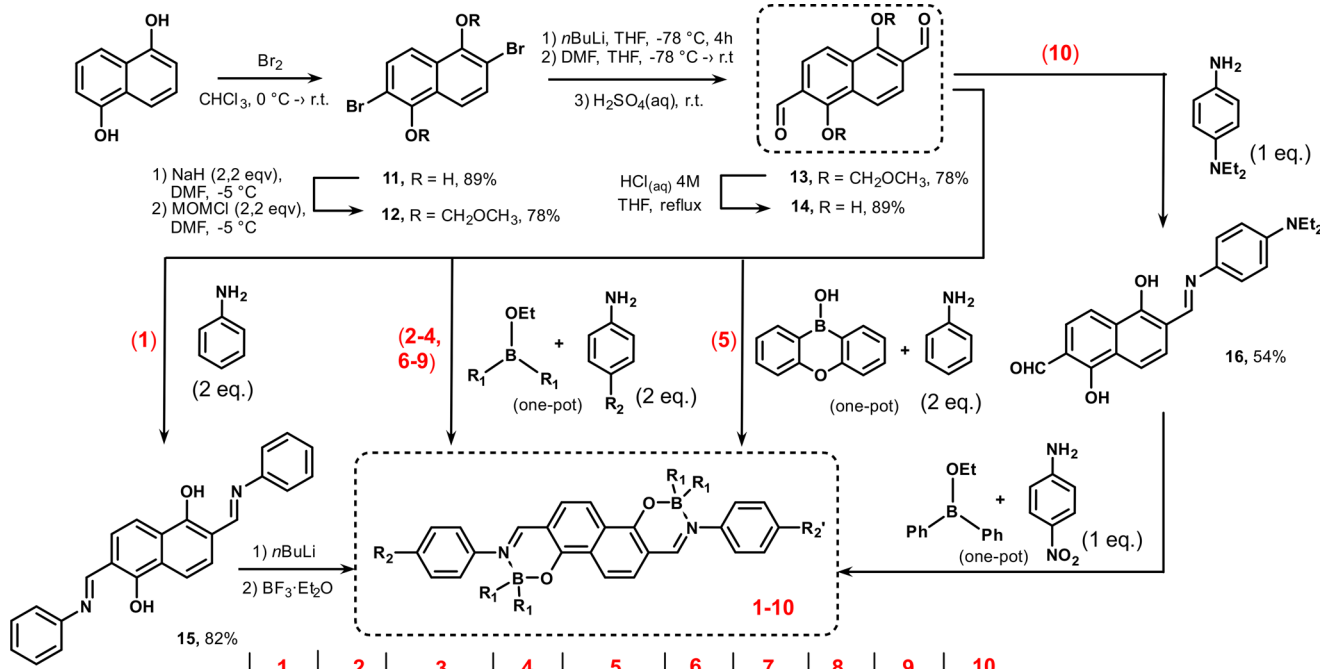
Scheme 2. Synthesis of Bis(boranil) Complexes 1−10



	1	2	3	4	5	6	7	8	9	10
R_1	F	Ph	2,6-$F_2C_6H_3$	C_6F_5		Ph	C_6F_5	Ph	C_6F_5	Ph
R_2 / R_2'	H	H	H	H	H	NO_2	NO_2	NEt_2	NEt_2	NO_2 / NEt_2
Yields:	68%	95%	79%	76%	56%	90%	55%	68%	60%	67%

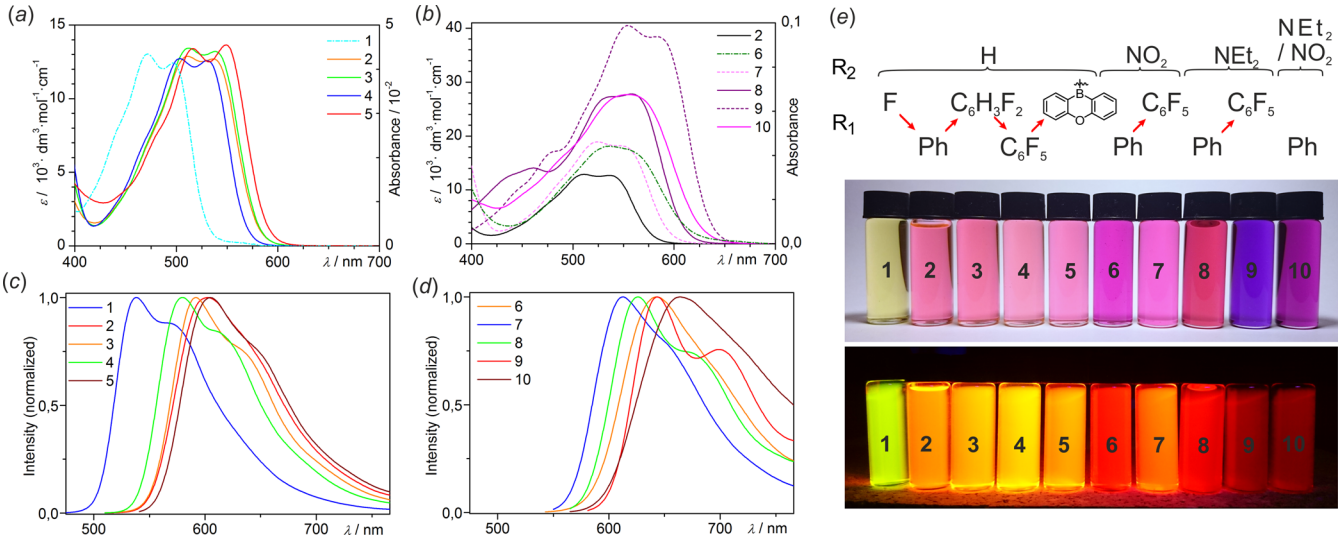


Figure 1. Absorption spectra of **1**−**5** (a) and **6**−**10** (b) in PhMe. Normalized emission spectra of **1**−**5** (c), **6**−**10** (d) recorded in PhMe at room temperature. Photographs of **1**−**10** in DCM (e). Spectra of **1**, 6 are plotted in absorbance scale.

NEt_2 located at the opposite terminal positions of the molecule. Complexes **2**−**9** were obtained in a one-pot three-component reaction between dialdehyde **14**, aniline and diarylborinic ester R_2BOEt (or 10-hydroxyphenoxaborin). The advantage of this procedure over the commonly applied multistep protocol is based on the fact that it omits the isolation of bis(anils) showing very weak solubility in organic solvents which hampers their conversion to targeted bis(boranils). Exceptionally, the synthesis of **1** required the isolation of bis(anil) **15**, which was treated with *n*BuLi and BF_3OEt_2. In the case of push−pull system **10**, the monoimine **16** was isolated in the first step, and it was further reacted in one-pot protocol with 4-nitroaniline and Ph_2BOEt. The isolation of final pure complexes is very simple as they are readily obtained after precipitation from solution in good yields (56−95%).

The proper selection of organic materials for the OLED construction is not simple as there are many parameters that may determine its final performance. The desired emitters

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should be characterized by good optical parameters (high quantum yield), sufficient thermal, hydrolytic and electrochemical stability as well as good solubility. The performed DSC analyses (Figure S2−S21) show that the obtained diboron complexes are thermally stable as evidenced by their high decomposition temperatures (270−440 °C). From the analysis of time-depending UV−vis absorption spectra (Figure S57−S67) it is evident, that the bis(boranil)s are significantly more stable than monoboranils in respective dilute solutions,[3e] although for some complexes the changes in band intensities are observed after few days. This is especially noticeable for nitro complexes **6** and **10**. This naturally comes from the fact that NO_2 functional group decreases the imine nitrogen basicity leading to weakening of N−B dative bond. On the other hand the fluorination of *B*-phenyl groups significantly increases Lewis acidity of boron atoms. Thus, compounds **3**, **4**, **7** and **9** bearing two C_6F_5 or 2,6-$F_2C_6H_3$ substituents at each boron center are stable in solutions as their corresponding UV−vis spectra remain almost time independent. The CV measurements (Figure S22−S26) show that studied bis(boranil) complexes are significantly more stable toward electrochemical oxidation and reduction than monoboranils **A** and **B**. The most stable are diamino complexes **8** and **9** which display reversible two-electron oxidation and reduction waves. The solubility of bis(boranils) strongly varies with the *N*-phenyl and *B*-phenyl substitution pattern ranging from weakly soluble BF_2 complex **1** to well soluble derivatives **4** and **8** (they are soluble even in the low polarity solvents such as PhMe). In general we have found that all complexes are soluble in DMF and pyridine. Furthermore, the introduction of C_6F_5 groups generally improves the solubility, although **9** is less soluble than its nonfluorinated analogue **8**.

The optical properties of obtained complexes were investigated by UV−vis absorption and photoluminescence spectroscopy (Figure 1, Table 1). In order to elucidate the solvatochromic nature of emission bands, the emission spectra were recorded in dichloromethane and PhMe solutions. To provide an additional insight into electronic structures of studied diboron complexes and the features of molecular orbitals involved in the electronic transitions, we have performed TD-DFT calculations on the PBE0[6]/6-31G(d,p)[7] level of theory.

Table 1. Photophysical Data for 1−10 in CH_2Cl_2/PhMe, Respectively

	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	QY[a] (%)
A	368	8100	466	3
B[3e]	400	4600	534	7
1	495/497	14700/−[d]	533/538	52/54
2	529/536	13900/12700	594/602	76/70
3	534/538	14700/13200	585/592	81/76
4	533/531	15400/12600	580/580	80/81
5	545/549	13800/13600	599/605	81/77
6	541(565)[b]/536(570)[b]	16000/−[c]	642/643	48/63
7	553/549	13100/18200	620/613	66/83
8	560(576)[b]/558	35500/27800	644/627	29/40
9	589(604)[b]/584	44500/38400	683/644	10/33
10	560/555	28500/27700	−[d]/664	−[d]/22

[a]Fluorescence standard: Coumarin 153 (**A**, **1**), Rhodamine 6G (**2**−**4**), Rhodamine 101 (**5**−**7**), Cresyl violet (**8**−**10**). [b]Values in brackets obtained after band deconvolution using second derivative method. [c]Due to insufficient solubility, ε values were not determined. [d]It was impossible to obtain the reliable value due to very weak fluorescence.

The studied bis(boranil) complexes present long-wave absorption bands in PhMe and CH_2Cl_2 in range of 495−584 nm and 497−589 nm, respectively. The molar absorption coefficients for **1**−**5** are relatively high ranging from 12 600 to 13 600 M^{-1} cm^{-1} in PhMe and 13 800−15 400 M^{-1} cm^{-1} in CH_2Cl_2, and significantly increase after introduction of NEt_2 groups at the *N*-aryl moieties (up to 38 400 M^{-1} cm^{-1} in PhMe and 44 500 M^{-1} cm^{-1} in CH_2Cl_2). Depending on the substitution pattern the longest-wavelength emission maxima span in range of 538−664 nm in PhMe and 533−683 nm in CH_2Cl_2 with QY reaching 83% in PhMe (**7**) and 81% in CH_2Cl_2 (**5**). Both the absorption and emission bands are significantly red-shifted in comparison with vast majority of reported boranils.[3,4] For instance, the BF_2 (**1**) and BPh_2 (**2**) bis(boranil) complexes absorb and emit at the wavelengths shifted by ca. 130 nm (absorption) and ca. 65 nm (emission) with respect to corresponding monoboron complexes **A** and **B**. The bathochromic shift of absorption and emission bands can be attributed to an increased length of the π-conjugated skeleton. Another important feature of studied bis(boranils) are moderate Stokes shifts (ΔS) values of 1450−2800 cm^{-1}. They are significantly smaller than ΔS values obtained for **A** and **B** monoboranils (ca. 6000 cm^{-1}), reflecting a higher structural rigidity of former complexes.

Among studied systems compound **1** is characterized by the shortest wavelength of absorption and emission (λ_{abs} = 495 nm, λ_{em} = 533 nm in CH_2Cl_2) accompanied by the smallest Stokes shift value of 1440 cm^{-1}. The introduction of BPh_2 (**2**) leads to the substantial red-shift of absorption and emission bands (λ_{abs} = 529 nm, λ_{em} = 594 nm in CH_2Cl_2).[2c,3d,8] In addition, the fluorescence quantum yield increases from 52% (**1**) to 76% (**2**) in CH_2Cl_2. Importantly, in both cases these QYs significantly exceed the values obtained for respective monoboron complexes **A** (3%) and **B** (7%). According to expectations, the further modification of organoboron core (either by introducing the fluorine substituents or oxaborine scaffold) only slightly influences the absorption and emission wavelengths (Table 1, **2**-**5**). Simultaneously, the QYs are high for these systems (70−81%).

TD-DFT calculations show that for **1**−**5** vertical excitations are observed predominantly due to electron transition from the orbital (usually HOMO) located at the central part of the molecule (naphthalene ring and O−B−N chelate moieties) and LUMO orbital which is delocalized over the entire π-conjugated skeleton. The energy gap of bis(boranils) can be further modified by extending the conjugation with electron-withdrawing NO_2 (**6**, **7**) or electron-donating NEt_2 (**8**, **9**) functional groups attached at the C4-position of the *N*-phenyl ring. The introduction of 4-NO_2 substituent stabilizes the HOMO and LUMO energy levels, but since the LUMO is delocalized over entire skeleton and HOMO is restricted to the center of the molecule, the lowering of LUMO orbital is more pronounced. Thus, HOMO−LUMO energy gap decreases leading to red-shifted absorption and emission with respect to **1**−**5** (**6**: λ_{abs} = 565 nm, λ_{em} = 642 nm in CH_2Cl_2). In turn, the introduction of 4-NEt_2 group (**8**, **9**) pushes the HOMO and LUMO energy levels up, however as HOMO orbital is additionally extended on *N*-(4-NEt_2)Ph groups its elevation is more pronounced than LUMO inducing again a significant red-shift of emission (**8**: λ_{abs} = 576 nm, λ_{em} = 664 nm in CH_2Cl_2).

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The dinitro complexes undergo uncommon blue-shift of emission (22−30 nm) upon the fluorination of *B*-phenyl groups (**6** → **7**).[5] This is accompanied by the sizable increase of QY from 63% to 83% in PhMe, and from 48% to 66% in CH_2Cl_2. In contrast, the replacement of a BPh_2 with a $B(C_6F_5)_2$ groups in diamino complexes (**8** → **9**) induces a sizable red-shift of emission of 17 nm in PhMe and 39 nm in CH_2Cl_2, and reduces QY from 40% to 33% in PhMe and from 29% to 10% in CH_2Cl_2. At this point it is noticeable that these values are high for such red-emitters.

In **10** the location of NO_2 and NEt_2 groups at the terminal parts of a quasi-linear conjugated system leads to the formation of a push−pull rod-type architecture. The TD-DFT calculation show that electron excitation can be interpreted in terms of charge transfer from the naphthalene ring and *N*-(4-NEt_2)Ph group to the *N*-(4-NO_2)Ph group. The absorption maximum of **10** (λ_{abs} = 560 nm, PhMe) is close to the values for corresponding NO_2 (**6**) and NEt_2 (**8**) complexes. In turn, the emission wavelength is red-shifted (λ_{em} = 664 nm, PhMe) with respect to both symmetrical derivatives.

Concerning bis(boranils) **1**−**7**, the solvent polarity only slightly affects their absorption and emission wavelengths, although it is interesting to note that emission is slightly blue-shifted in more polar solvents (Table S6). In turn, amino derivatives undergo sizable red-shift of emission wavelengths with the increase of solvent polarity. This is especially noticeable for red-light emitter **9**, which emission in CH_2Cl_2 (λ_{em} = 683 nm) and THF (λ_{em} = 714 nm) approaches close to the NIR region. According to expectations, the bathochromic shift of emission bands is accompanied by the reduction of QY values. Finally, preliminary results of solid state (powder) photoluminescence of **4** and **7** show that QY are reduced to 13% and 6%, respectively.[9] This is accompanied by red-shift of emission wavelength of ca. 30−35 nm (Figure S55−S56). Both effects are most likely caused by aggregation, thus further studies should be performed (e.g., in blends) to improve solid-state luminescence.

In summary, bis(boranils) derived from a ditopic tetradentate 1,5-dihydroxy-2,6-bis(*N*-phenyliminomethylene)naphthalene ligand are very efficient orange-to-red emitters with QY exceeding 80%. Their photophysical properties are easily tuned in a wide range either by varying the substitution on boron atom or by extending the π-conjugation with electron-withdrawing (NO_2) or electron-donating (NEt_2) functional groups. The introduction of NO_2 and NEt_2 at terminal parts of the molecule gave rise to an unprecedented push−pull system with electron transition possessing charge transfer character. The absorption band for this compound is similar, while emission significantly red-shifted with respect to bis(boranil) bearing two NEt_2 groups. The promising features of obtained bis(boranils), i.e., improved stability (thermal, hydrolytic, electrochemical) and strong fluorescence in a red region of the visible spectrum, would be beneficial for a construction of highly efficient organic red-light emitting diodes. In our opinion, the most appropriate candidate for such applications would be complexes **4** and **8**, as they feature strong red-shifted emission, high stability, and good solubility in most organic solvents.

■ EXPERIMENTAL SECTION

General Comment. All the used reagents were provided by Aldrich Chemical Co.. THF was dried by heating to reflux with sodium or potassium and benzophenone, and distilled under argon. Starting materials (halogenated benzenes, trialkyl borates, *n*-BuLi (10 M in hexane), *t*-BuLi (1.7 M in pentane), DMF, benzoyl chloride, dimethoxymethane) were used as received without additional purification, with exception of 1,5-dihydroxynaphthalene, which was recrystallized from acetonitrile with activated charcoal. Reactions and manipulations involving air and moisture-sensitive reagents were carried out under an argon atmosphere.

Characterization Data. ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance III 300 MHz and Agilent NMR 400 MHz DDR2 spectrometers. ^{1}H and ^{13}C chemical shifts were referenced to TMS using known chemical shifts of solvent residual peaks. ^{11}B and ^{19}F NMR chemical shifts are given relative to $BF_3{\cdot}Et_2O$ and $CFCl_3$, respectively. In the ^{13}C NMR spectra the resonances of boron-bound carbon atoms were not observed in most cases as a result of their broadening by the quadrupolar boron nucleus. HR-MS analyses were performed on a GCT Premiermass spectrometer equipped with EI ion source and a Maldi SYNAPT G2-S HDMS spectrometer equipped with ESI ion source, both spectrometers equipped with TOF mass analyzers. Compound **1** was insufficiently soluble in organic solvents to record reliable ^{13}C spectra even after prolonged acquisition.

Experimental Procedures: General Comment. The synthesis of BF_2 monoboranil **A** has not been described and it is given below whereas another referential compound **B** was obtained according to the published procedure.[3e] Complexes **2**-**10** were synthesized according to a protocol developed by us recently which involves a one-pot three-component reaction between dialdehyde **14**, aniline and diarylborinic esters Ar_2BOR ($Ph_2B(OEt)$, $(2,6\text{-dF-Ph})_2B(OiPr)$, $(C_6F_5)_2B(OEt)$).[3e] The latter components were generated in situ from aryllithium and corresponding dialkyl arylboronates $ArB(OR)_2$.[3e] An intermediate borinic ate-complex $[R_2B(OR)_2]^-Li^+$ was quenched with TMSCl or 2 M ethereal HCl affording diarylborinic ester Ar_2BOR. Diphenylborinic ester Ph_2BOEt was isolated and purified by distillation whereas fluorinated analogues were unstable at elevated temperatures and therefore, they were prepared and used without isolation. In the case of **5**, 10-phenoxaborin was used as a boron precursor.[10] Complex **1** was obtained from bis(anil) **15**, which was treated with *n*BuLi and $BF_3{\cdot}Et_2O$. The synthesis of bis(boranil) **10** required the isolation of mono(imine) **16** in the first step, which was further reacted in one-pot protocol with 1 equiv of 4-nitroaniline and diphenylborinic ester Ph_2BOEt.

Synthesis of Substrates. *2,6-Dibromo-1,5-dihydroxynaphthalene (**11**).* To a suspension of 1,5-dihydroxynaphthalene (10.0 g, 62.4 mmol) in $CHCl_3$ (200 mL), a solution of bromine (20.0 g, 125 mmol) in $CHCl_3$ (15 mL) was added dropwise at 0 °C. A mixture was warmed up to room temperature and stirred for 3 h. A solid product was filtered, washed with $CHCl_3$ (50 mL) and hexane (50 mL), and dried under vacuum to give pure 2,6-dibromo-1,5-dihydroxynaphthalene as a beige powder (17.7 g, yield 89%). mp 213−215 °C (decomposition is observed). ^{1}H NMR (400 MHz, Acetone-d_6) δ = 8.55 (s, OH), 7.74 (d, J = 8.9 Hz, 2H, naph), 7.58 (d, J = 8.9 Hz, 2H, naph) ppm; $^{13}C\{^{1}H\}$ NMR (75 MHz, Acetone-d_6) δ = 150.2, 130.4, 126.8, 116.3, 105.9 ppm. Anal. Calcd for $C_{10}H_6Br_2O_2$: C, 37.77; H, 1.90. Found: C, 37.64; H, 1.95.

*1,5-Bis(methoxymethoxy)-2,6-dibromonaphthalene (**12**).* To a suspension of NaH (60% oil dispersion, 3.36 g, 84 mmol) in anhydrous DMF (10 mL), a solution of **11** (12.1 g, 38 mmol) in anhydrous DMF (20 mL) was added dropwise at −5 °C. After ca. 1 h a gas evolution ceased, and a solution of chloromethyl methyl ether MOMCl (6,79 g, 84 mmol) in Et_2O (20 mL) was added dropwise over 1 h at −5 °C. During the addition a mixture thickened and was diluted with Et_2O (50 mL). The mixture was stirred for 5 h at 0 °C. A beige slurry was poured onto vigorously stirred ice cold water (40 mL). CH_2Cl_2 (110 mL) was added to dissolve suspended solids. Phases were separated. Water layer was extracted twice with CH_2Cl_2 (2 × 25 mL). Combined organic phases were washed with 5% $NaHCO_3$ (50 mL) and brine (50 mL) and dried with $MgSO_4$. Volatiles were removed under vacuum to obtain a brown solid. It was washed with hexane (30 mL) and dried under vacuum to give pure 1,5-bis(methoxymethoxy)-2,6-dibromonaphthalene as a beige crystal-

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line solid (12.04 g, yield 78%). mp 115−116 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ = 7.97 (d, J = 8.9 Hz, 2H, naph), 7.77 (d, J = 8.9 Hz, 2H, naph), 5.31 (s, 4H, −OCH_2O−), 3.69 (s, 6H, -OCH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6) δ = 152.1, 132.0, 131.2, 121.3, 114.5, 101.3, 58.4 ppm. Anal. Calcd for $C_{14}H_{14}Br_2O_4$: C, 41.41; H, 3.48. Found: C, 41.24; H, 3.59.

*1,5-Bis(methoxymethoxy)naphthalene-2,6-dicarboxaldehyde (**13**).* A solution of **12** (10.20 g, 25 mmol) in anhydrous THF (150 mL) was added dropwise to a stirred solution of *n*BuLi (10 M, 6.3 mL, 63 mmol) in anhydrous THF (100 mL) over 40 min at −70 °C. After 3.5 h anhydrous DMF (5 mL, 65 mmol) was added dropwise at −70 °C. A mixture was slowly warmed up to 0 °C and H_2SO_4 (1.5 M) was added to reach pH = 4. The precipitated solid was filtered, washed with cold EtOH (2 × 10 mL), Et_2O (2 × 15 mL), hexane (15 mL) and dried under vacuum to give pure 1,5-bis(methoxymethoxy)-naphthalene-2,6-dicarboxaldehyde as a bright yellow powder (6.7 g, 88%). mp 151−153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.55 (s, 2H, −CHO), 8.08 (d, J = 8.8 Hz, 2H, naph), 7.98 (d, J = 8.8 Hz, 2H, naph), 5.28 (s, 4H, −OCH_2O−), 3.67 (s, 6H, -OCH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 190.2, 159.1, 133.1, 128.2, 124.1, 120.4, 102.3, 58.5 ppm. Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 62.88; H, 5.15.

*1,5-Dihydroxynaphthalene-2,6-dicarboxaldehyde (**14**).* A suspension of **13** (6.32 g, 21 mmol) in THF (100 mL) and hydrochloric acid (6 M, 100 mL) was refluxed for 4 h. The mixture was cooled to 0 °C. The obtained solid was filtered, washed with water to reach a neutral pH. Then it was washed with cold ethanol (15 mL), hexane (20 mL), and dried under vacuum to give pure 1,5-dihydroxynaphthalene-2,6-dicarboxaldehyde as a yellow crystalline solid (4.14 g, 91% yield). mp 240−245 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 12.42 (s, 2H, −OH), 10.06 (s, 2H, −CHO), 8.00 (d, J = 8.5 Hz, 2H, naph), 7.61 (d, J = 8.5 Hz, 2H, naph); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 197.0, 160.4, 128.9, 127.1, 117.2, 115.3 ppm. Anal. Calcd for $C_{12}H_8O_4$: C, 66.67; H, 3.73. Found: C, 66.57; H, 3.79.

*2,6-Bis(N-phenyliminomethyl)-1,5-dihydroxynaphthalene (**15**).* A mixture of aniline (0.30 mL, 3.3 mmol), **14** (325 mg, 1.5 mmol) and TsOH (19 mg) in PhMe (10 mL) was refluxed in a Dean−Stark apparatus for 6 h. After cooling to room temperature the mixture was filtered and the precipitate was washed with cold Et_2O (2 × 10 mL) and dried under vacuum to give pure **15** as a brown crystalline solid (0.45 g, yield 82%). mp 208−210 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 14.93 (d, J = 4.5 Hz, 2H, OH), 9.10 (d, J = 4.5 Hz, 2H, N = CH), 7.65 (d, J = 8.6 Hz, 2H, naph), 7.60−7.47 (m, 10H, Ar), 7.38−7.30 (m, 2H, Ph) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ = 165.5, 160.6, 144.2, 129.7, 129.0, 128.0, 127.0, 120.5, 114.3, 112.1, 39.5 ppm. Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N 7.65. Found: C, 78.51; H 4.83; N 7.69.

*6-[N-(4′-(N′,N′-Diethylamino)phenyliminomethyl)]-1,5-dihydroxynaphthalene-2-carboxaldehyde (**16**).* A solution of 4-(*N*,*N*-dietylamino)aniline (1.30 g, 7.9 mmol) in PhMe (100 mL) was added dropwise over 6 h to refluxed mixture of **16** (1.50 g, 6.9 mmol) in PhMe (300 mL). Water released during reaction was removed using Dean−Stark apparatus. A mixture was stirred and refluxed for 2 h and cooled to rt. A brown precipitate was filtered off on a Büchner funnel, washed with PhMe (2 × 50 mL), hexane (10 mL) and dried under vacuum to obtain bis(anil), 2,6-bis[*N*-(4′-(*N*′,*N*′-diethylamino)-phenyliminomethyl)]-1,5-dihydroxynaphthalene (**16**; 0.69 g). The filtrate was concentrated on a rotary evaporator to obtain the crude product as a red solid (2.11 g). It was purified by recrystallization from PhMe-hexane (v/v = 5:1) and dried under vacuum. The pure imine **16** was isolated as red needles (1.36 g, 54%). Decomposition starts at 154 °C (mp 190 °C). ^{1}H NMR (300 MHz, Acetone-d_6) δ = 15.67 (s, 1H, OH), 12.53 (s, 1H, OH), 10.13 (s, 1H, CHO), 8.96 (s, 1H, N═CH), 7.98 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 9.1 Hz, 2H), 6.81 (d, J = 9.1 Hz, 2H), 3.46 (q, J = 7.0 Hz, 4H, NCH_2), 1.19 (t, J = 7.0 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6) δ = 209.9, 198.7, 156.4, 128.9, 127.4, 123.1, 117.2, 115.7, 112.9, 112.8, 45.1, 12.9 ppm. Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 72.79; H, 6.24; N, 7.78.

Ethoxydiphenylborane (Ph_2BOEt). Bromobenzene (13.5 mL, 86 mmol) was added dropwise to a stirred solution of *n*BuLi (9.0 mL, 90 mmol) in THF (120 mL) at −78 °C. A white suspension of PhLi was formed. After 1 h of stirring diethyl phenylboronate ($PhB(OEt)_2$) (15.10 g, 85 mmol) dissolved in Et_2O (15 mL) was added dropwise at −78 °C. The resulting thick white slurry was stirred for ca. 30 min and then allowed to reach room temperature. A mixture was treated with TMSCl (13 mL, 100 mmol) and heated to 40 °C. After 15 min LiCl precipitated from the solution. A mixture was stirred for 2 h and then volatiles were removed under vacuum. Et_2O (30 mL) was added and the obtained slurry was filtered under argon atmosphere. The precipitate was washed three times with Et_2O (3 × 30 mL) and the combined colorless filtrate was concentrated in vacuo. A crude product was purified by distillation under reduced pressure to give ethoxydiphenylborane as a colorless liquid boiling at 90−101 °C (1 Tr) (15.4 g, 86%). It is air and moisture sensitive, so it should be stored and handled under an inert atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94−7.75 (m, 4H, Ph), 7.70−7.45 (m, 6H, Ph), 4.38 (q, J = 7.0 Hz, 2H, OCH_2), 1.52 (t, J = 7.0 Hz, 3H, CH_3) ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ = 45.4 ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 134.2, 130.1, 127.7, 63.7, 17.8 ppm.

Synthesis of Boranils. *Difluoroboron Salicylideneaniline Complex (**A**).* *n*BuLi (10 M, 0.50 mL, 5.0 mmol) was added dropwise to a solution of salicylideneaniline (0.97 g, 4.9 mmol) in THF (20 mL) at −70 °C. Mixture was warmed up to −50 °C and stirred for 30 min. Then it was cooled to −70 °C and $BF_3{\cdot}Et_2O$ (0.61 mL, 5.0 mmol) was added dropwise. A cooling bath was removed and a mixture was left to warm up to the room temperature. After 2 h a mixture was cooled to 0 °C and filtered. The solid was washed with water (3 × 10 mL), cold EtOH (2 × 5 mL) and hexane (15 mL), and dried under vacuum to obtain pure compound A as a light yellow powder (0.85 g, 69%). mp 226−228 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 9.20 (s, 1H, N═CH), 7.83 (ddd, J = 7.7, 1.8, 0.6 Hz, 1H, Ar), 7.75 (ddd, J = 8.3, 7.3, 1.8 Hz, 1H, Ar), 7.71−7.64 (m, 2H, Ar), 7.62−7.48 (m, 3H, Ar), 7.17−7.09 (m, 2H, Ar) ppm; ^{11}B NMR (96 MHz, DMSO-d_6) δ = 0.56 (t, J_{BF} = 16.1 Hz) ppm; ^{19}F NMR (282 MHz, DMSO-d_6) δ = −132.28 to −132.54 (m) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6) δ = 166.4, 158.4, 142.1, 139.0, 133.7, 129.4, 129.0, 123.6, 120.4, 118.3, 116.1 ppm. Anal. Calcd for $C_{13}H_{10}BF_2NO$: C, 63.72; H, 4.11; N, 5.72. Found: C, 63.56; H, 3.94; N, 5.85.

*2,6-Bis(N-phenyliminomethyl)-1,5-dihydroxynaphthalene bis-(difluoroboron) complex (**1**).* **15** (0.45 g, 1.2 mmol) was dissolved in anhydrous PhMe (45 mL) at 50 °C. A dark red solution was rapidly cooled in dry ice−acetone bath and *n*BuLi (10M, 0.25 mL, 2.5 mmol) was added dropwise at −78 °C. A cooling bath was removed and a mixture was slowly warmed up to 50 °C, and stirred for 4 h, then cooled and left overnight with stirring at room temperature. The obtained orange slurry was cooled to −78 °C and $BF_3{\cdot}Et_2O$ (0.30 mL, 2.5 mmol) was added, the mixture become darker. It was slowly warmed to room temperature and then gently refluxed for 4 h. The formation of a bright orange precipitate was observed. It was cooled to room temperature and filtered. The obtained solid (very fine powder) was washed with PhMe (2 × 7 mL) and acetone (10 mL), and dried in air flow. A crude product was transferred to small beaker and stirred vigorously with water for 20 min. Then it was filtered, washed with EtOH (50%, 2 × 5 mL), EtOH (100%, 2 × 5 mL) and Et_2O (3 × 5 mL), and dried under vacuum. **1** was obtained as a fine orange powder (0.39 g, yield 68%). Decomposition >430 °C (does not melt). ^{1}H NMR (300 MHz, DMSO-d_6) δ = 9.38 (s, 1H, N═CH), 8.04 (d, J = 8.6 Hz, 1H, naph) 7.90 (d, J = 8.6 Hz, 1H, naph), 7.75 (d, J = 7.2 Hz, 2H, NPh), 7.67−7.52 (m, 3H, NPh) ppm; ^{11}B NMR (96 MHz, DMSO-d_6) δ = 0.9 ppm; ^{19}F NMR (282 MHz, DMSO-d_6) δ = −130.43 ppm; FTIR (ATR) ν = 3071, 3043, 1621, 1580, 1494, 1487, 1435, 1361, 1249, 1197, 1113, 1092, 1207, 980, 720, 687, 604 cm^{-1}; HRMS (EI) calcd. for $C_{24}H_{16}B_2F_4N_2O_2$ $[M]^+$ 462.1334, found 462.1332.

*2,6-Bis(N-phenyliminomethyl)-1,5-dihydroxynaphthalene bis-(diphenylborinic) complex (**2**).* Ethoxydiphenylborane (Ph_2BOEt) was dissolved in EtOH (10 mL) followed by the addition of aniline (0.40 mL, 4.4 mmol) and **14** (0.43 g, 2.0 mmol). Immediately, the

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resulting solution turned red. A mixture was stirred for 15 h and the precipitation of the bis(boranil) was observed. The obtained thick orange slurry was filtered. The solid was washed with water (20 mL), EtOH (30 mL), Et_2O (10 mL) and hexane (20 mL). A crude product was transferred to a small flask, stirred vigorously with Et_2O (20 mL) for 4 h. Then it was filtered, washed with Et_2O (20 mL) and dried under vacuum to give **2** as an orange powder (1.32 g, 95% yield). mp 299−301 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ = 9.04 (s, 2H, N=CH), 7.81 (d, J = 8.6 Hz, 2H, naph), 7.60 (d, J = 8.6 Hz, 2H, naph), 7.49−7.42 (m, 8H, Ph), 7.28 (s, 10H, Ph), 7.15−7.03 (m, 12H, Ph) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ = 165.2, 161.8, 146.7, 134.6, 132.2, 129.6, 129.2, 129.1, 128.1, 127.7, 127.2, 125.7, 117.3, 115.3 ppm; FTIR (ATR) ν = 3069, 3047, 3008, 1611, 1565, 1490, 1475, 1432, 1423, 1349, 1182, 1144, 1097, 981, 879, 718, 702, 690, 596, 555 cm^{-1}; HRMS (EI) calcd. for $C_{48}H_{36}B_2N_2O_2$ [M]$^+$ 694.2963, found 694.2958.

*2,6-Bis(N-phenyliminomethyl)-1,5-dihydroxynaphthalene bis-[bis(2,6-difluorophenyl)-borinic] complex (**3**).* 1,3-Difluorobenzene (0.37 mL, 3.8 mmol) was added dropwise to a stirred solution of *n*BuLi (0.38 mL, 3,8 mmol) in Et_2O (20 mL) at −78 °C. After ca. 30 min diethyl 2,6-difluorophenylboronate (0.81 g, 3.8 mmol) was added dropwise. The mixture was stirred for ca. 30 min. A cooling bath was removed and a mixture was allowed to warm up to −10 °C. It was treated with the ethereal HCl (2 M, 1.9 mL, 3.8 mmol) resulting in the formation of ethoxybis(2,6-difluorophenyl)borane. A mixture was warmed up to 30 °C. After 1 h aniline (0.40 mL, 4.4 mmol) and **14** (0.39 g, 1.8 mmol) were added, resulting in a red coloration of the mixture. The mixture was stirred for 10 h at 60 °C. An orange precipitate was formed. It was cooled to ca. 0 °C; an orange precipitate was filtered and washed with hexane (20 mL). The crude product was transferred to a small flask and stirred vigorously with Et_2O (30 mL) for 3 h. Precipitate was filtered, washed with water (20 mL), EtOH (20 mL) and hexane (20 mL), and dried under vacuum to give **3** as a bright orange powder (1.33 g, 79% yield). mp 353−355 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 9.29 (s, 2H, N=CH), 7.68 (d, J = 8.7 Hz, 2H, naph), 7.62 (d, J = 8.7 Hz, 2H, naph), 7.44 (m, 4H, Ar), 7.40−7.26 (m, 6H, Ar), 7.23−7.08 (m, 4H, Ar), 6.72 (t, J = 8.4 Hz, 8H, Ar) ppm; ^{1}H NMR (400 MHz, DMF-d_7) δ 9.36 (s, 2H, N=CH), 7.79 (d, J = 8.7 Hz, 2H, naph), 7.74 (d, J = 8.7 Hz, 2H, naph), 7.61 (d, J = 7.7 Hz, 4H, Ar), 7.43−7.36 (m, 4H, Ar), 7.36−7.31 (m, 2H, Ar), 7.18 (tt, J = 8.2, 6.5 Hz, 4H, Ar), 6.74 (t, J = 8.4 Hz, 8H, Ar) ppm. ^{19}F NMR (282 MHz, DMSO-d_6) δ = −103.29 (t, J = 7.1 Hz) ppm; ^{13}C{^{1}H} NMR (101 MHz, DMF-d_7) δ = 166.3 (dd, J_{CF} = 243.5, 14.7 Hz), 164.5, 162.4, 159.6, 144.8, 131.1, 130.0, 129.9 (t, J_{CF} = 11.5 Hz), 128.9, 127.8, 123.7, 116.2, 114.6, 110.9 (d, J_{CF} = 29.8 Hz). FTIR (ATR) ν = 3069, 3041, 1611, 1560, 1492, 1478, 1479, 1442, 1351, 1247, 1218, 1183, 1095, 977, 916, 871, 783, 714, 692, 589, 510 cm^{-1}; HRMS (EI) calcd. for $C_{48}H_{28}B_2F_8N_2O_2$ [M]$^+$ 838.2209, found 838.2221.

*2,6-Bis(N-phenyliminomethyl)-1,5-dihydroxynaphthalene bis-[bis(pentafluorophenyl)-borinic] complex (**4**).* Pentafluorobromobenzene (0.50 mL, 4.0 mmol) was added dropwise to a stirred solution of *n*BuLi (0.42 mL, 4.2 mmol) in Et_2O (20 mL) at −78 °C. After ca. 20 min diethyl pentafluorophenylboronate ($C_6F_5B(OEt)_2$) (1.18 g, 4.4 mmol) was added dropwise. Subsequently the mixture was stirred for ca. 40 min and the ethereal HCl (2 M, 2.1 mL, 4.2 mmol) was added. A cooling bath was removed and a mixture was allowed to slowly reach room temperature and was stirred for 1 h to give ethoxybis-(pentafluorophenyl)borane ($(C_6F_5)_2BOEt$. In the next step, aniline (0.38 mL, 4.2 mmol) and **14** (0.41 g, 1.9 mmol) were added. A mixture was stirred for 24 h at room temperature. Then it was cooled to −50 °C, an orange precipitate was filtered and washed with hexane (20 mL). A crude product was transferred to a small flask and stirred vigorously with water (20 mL) for 0.5 h. The product was filtered, washed with warm EtOH (50 mL) and hexane (20 mL), and dried under vacuum to give **4** as a bright orange powder (1.51 g, yield 76%). mp 350−353 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ = 9.37 (s, 2H, N=CH), 7.85 (d, J = 8.8 Hz, 2H, naph), 7.82 (d, J = 8.8 Hz, 2H, naph), 7.59−7.51 (m, 4H, NPh), 7.50−7.38 (m, 6H, NPh) ppm; ^{11}B NMR (96 MHz, Acetone-d_6) δ = 1.7 ppm; ^{19}F NMR (282 MHz, Acetone-d_6) δ = −135.15 (dd, J = 23.4, 9.2 Hz, 8F), −157.90 (t, J = 20.0 Hz, 4F), −165.41 (ddd, J = 23.4, 20.0, 9.2 Hz, 8F) ppm; ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ = 166.5, 159.6, 150.8−147.8 (m), 144.8, 142.8−139.8 (m), 139.5−136.2 (m), 132.0, 130.5, 130.4, 120.0, 124.4, 117.1, 116.6 ppm; FTIR (ATR) ν = 1646, 1610, 1545, 1517, 1458, 1347, 1292, 1283, 1185, 1113, 1094, 983, 966, 774, 718, 690, 557 cm^{-1}; HRMS (ESI) calcd. for $C_{48}H_{16}B_2F_{20}N_2O_2$ [M]$^+$ 1054.1079, found 1054.1062.

*2,6-Bis(N-phenyliminomethyl)-1,5-dihydroxynaphthalene bis-(phenoxaborin) complex (**5**).* To a solution of 10-hydroxyphenoxaborin (0.667 g, 3.4 mmol) in acetone (5 mL), aniline (0.40 mL, 4.4 mmol) and solution of **14** (0.371 g, 1.7 mmol) in acetone (25 mL) were added. An immediate coloration of the mixture was observed. The mixture was stirred for 18 h at room temperature, resulting in the formation of a bright red precipitate. The precipitate was filtered, washed with acetone (20 mL) and Et_2O (20 mL). A crude product was transferred to a small flask and stirred vigorously with Et_2O (20 mL) for 1.5 h. The pure product was filtered, washed with Et_2O (10 mL) and dried under vacuum to give **5** as a bright orange powder (0.70 g, 56%). mp 402−410 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 9.09 (s, 2H, N=CH), 7.60 (d, J = 8.7 Hz, 2H, naph), 7.57 (dd, J = 7.4, 1.8 Hz, 4H, oxaborin), 7.51 (d, J = 8.7 Hz, 2H, naph), 7.25 (ddd, J = 8.3, 7.1, 1.8 Hz, 4H, oxaborin), 7.20−7.15 (m, 6H, NPh), 7.05 (dd, J_{HH} = 8.3, 0.7 Hz, 4H, oxaborin), 6.99−6.90 (m, 8H, NPh, oxaborin) ppm; ^{1}H NMR (400 MHz, Pyridine-d_5) δ = 8.90 (s, 2H, N=CH), 7.98 (dd, J = 7.6, 0.8 Hz, 4H, oxaborin), 7.75 (d, J = 8.8 Hz, 2H, naph), 7.49 (d, J = 8.7 Hz, 2H, naph), 7.39−7.34 (m, 8H, Ar), 7.17−7.02 (m, 14H, Ar) ppm; ^{13}C{^{1}H} NMR (101 MHz, pyridine) δ = 165.0, 160.8, 157.2, 146.2, 133.9, 132.4, 127.6, 124.9, 124.2, 124.0, 123.7, 123.3, 116.8, 115.4, 114.6 ppm.; FTIR (ATR) ν = 3066, 3009, 1616, 1594, 1565, 1491, 1428, 1345, 1296, 1279, 1217, 1198, 1181, 1165, 1145, 1088, 997, 900, 815, 784, 753, 725, 691, 556 cm^{-1}; HRMS (EI) calcd. for $C_{48}H_{32}B_2N_2O_4$ [M]$^+$ 722.2548, found 722.2521.

*2,6-Bis[N-(4′-nitrophenyl)iminomethyl)]-1,5-dihydroxynaphthalene bis(diphenyl-borinic) complex (**6**).* To solution of ethoxydiphenylborane (Ph_2BOEt) (0.66 g, 3.1 mmol) in anhydrous 2-MeTHF (15 mL), **14** (0.22 g, 1.0 mmol) and 4-nitroaniline (0.30 g, 2.2 mmol) were added. The mixture was warmed up to 50 °C and stirred for 24 h. After cooling a pink precipitate was filtered, washed with Et_2O (5 × 5 mL) and hexane (2 × 5 mL), and dried under vacuum. The pure compound **6** was obtained as a pink, fine powder (0.70 g, 90%). mp 326−328 °C. ^{1}H NMR (400 MHz, DMF-d_7) δ = 9.42 (s, 2H), 8.28−8.19 (m, 4H), 7.78 (d, J = 8.9 Hz, 2H), 7.76−7.68 (m, 6H), 7.54−7.47 (m, 8H), 7.23−7.08 (m, 12H) ppm. ^{13}C NMR (101 MHz, DMF-d_7) δ = 166.7, 161.4, 150.8, 147.0, 134.0, 131.5, 127.3, 126.8, 126.5, 124.4, 117.2, 114.6, 112.9 ppm. FTIR (ATR) ν = 3067, 3004, 1606, 1557, 1520, 1473, 1342, 1294, 1196, 1177, 1141, 1094, 1070, 992, 984, 904, 881, 738, 704, 603, 550, 444 cm^{-1}. HRMS (EI) calcd. for $C_{48}H_{34}B_2N_4O_6$ [M]$^+$ 784.2664, found 784.2679. Anal. Calcd for $C_{48}H_{34}B_2N_4O_6$: C, 73.50; H, 4.37; N, 7.14. Found: C, 73.65; H, 4.64; N, 7.05.

*2,6-Bis[N-(4′-nitrophenyl)iminomethyl)]-1,5-dihydroxynaphthalene bis[bis(penta-fluorophenyl)borinic] complex (**7**).* Compound **7** was prepared as described for **4** using pentafluorobromobenzene (0.79 g, 3.1 mmol), *n*BuLi (10 M, 0.31 mL, 3.1 mmol), Et_2O (20 mL), diethyl pentafluorophenylboronate (0.84 g, 3.1 mmol), HCl/Et_2O (2 M, 1.55 mL, 3.1 mol), **14** (0.32 g, 1.5 mmol) and 4-nitroaniline (0.45, 3.3 mmol) in anhydrous 2-MeTHF (65 mL). The mixture was stirred at room temperature for 24 h and concentrated on rotary evaporator. The precipitate was washed with Et_2O (3 × 5 mL), water (2 × 5 mL), EtOH (5 mL) and Et_2O (5 mL) to give pure **7** as a dark pink powder (1.03 g, yield 60%). mp 338−340 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ = 9.59 (s, 2H, N=CH), 8.38−8.30 (m, 4H, naph), 7.91−7.82 (m, 8H, NAr) ppm; ^{1}H NMR (400 MHz, Pyridine-d_5) δ = 10.02 (s, 2H, N=CH), 8.44 (d, J = 8.8 Hz, 4H, Ar), 8.22 (d, J = 8.9 Hz, 2H, naph), 8.05 (d, J = 8.9 Hz, 4H, Ar), 7.90 (d, J = 8.8 Hz, 2H, naph) ppm ^{11}B NMR (96 MHz, Acetone-d_6) δ = 2.0 (s) ppm; ^{19}F NMR (282 MHz, Acetone-d_6) δ = −135.20 (dd, J = 23.4, 9.2 Hz, 8F), −157.17 (t, J = 23.4 Hz, 4F), −164.92 (ddd, J = 23.4, 20.0, 9.2 Hz, 8F) ppm; ^{13}C{^{1}H} NMR (101 MHz, Pyridine-d_5) δ = 168.1, 160.6, 148.9, 148.6, 148.4−147.6 (m), 143.0−139.7 (m), 139.5−136.4 (m), 132.5,

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128.9, 125.9, 125.5, 124.2, 117.4, 117.3 ppm. FTIR (ATR) ν = 1646, 1610, 1561, 1531, 1518, 1549, 1346, 1291, 185, 1092, 970, 860, 718, 689, 532, 438 cm^{-1}; HRMS (ESI) calcd. for $C_{48}H_{14}B_2F_{20}N_4O_6$ $[M]^+$ 1144.0780, found 1144.0807.

*2,6-Bis[N-(4′-(N′,N′-diethylaminophenyl)iminomethyl)]-1,5-dihydroxynaphthalene bis(diphenylborinic)complex (**8**).* Compound **8** was prepared as described for **6** using ethoxydiphenylborane Ph_2BOEt (0.43 g, 2.0 mmol), anhydrous THF (15 mL), **14** (0.19 g, 0.9 mmol) and 4-(*N*,*N*-diethylamino)aniline (0.35 g, 2.1 mmol). The mixture was stirred at 50 °C for 48 h and filtered. The obtained product was washed with THF (2 × 10 mL) and Et_2O (2 × 10 mL), and dried under vacuum to give **8** as a brown powder (0.51 g, yield 68%). mp 315−316 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.33 (s, 1H, N═CH), 7.86 (d, J = 8.6 Hz, 1H, naph), 7.52−7.45 (m, 4H, Ar), 7.24−7.09 (m, 7H, Ar), 7.00−6.88 (m, 2H, Ar), 6.45−6.36 (m, 2H), 3.29 (q, J = 7.1 Hz, 4H, NCH_2), 1.11 (t, J = 7.1 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 160.6, 159.2, 147.6, 134.3, 133.8, 131.2, 127.0, 126.3, 126.0, 125.5, 115.7, 115.1, 110.9, 44.5, 12.6 ppm; FTIR (ATR) ν = 3066, 3041, 3012, 2972, 2931, 2891, 1609, 1590, 1567, 1514, 1350, 1267, 1193,1140, 1093, 982, 881, 820, 701, 607, 530 cm^{-1}; HRMS (ESI) calcd. for $C_{56}H_{54}B_2N_4O_2$ $[M + H]^+$ 837.4511, found 837.4530.

*2,6-Bis[N-(4′-(N′,N′-diethylaminophenyl)iminomethyl)]-1,5-dihydroxynaphthalene bis[bis(pentafluorophenyl)borinic)] complex (**9**).* Compound **9** was prepared as described for **4** using pentafluorobromobenzene (0.74 g, 3.0 mmol), *n*BuLi (10 M, 0.30 mL, 3.0 mmol), THF (70 mL), diethyl pentafluorophenylboronate (0.89 g, 3.3 mmol), HCl/Et_2O (2M, 1.50 mL, 3.0 mol), **14** (0.22 g, 1.0 mmol) and 4-(*N*,*N*-diethylamino)aniline (0.36 g, 2.2 mmol). A mixture was stirred at room temperature for 72 h. The precipitation of the product was not observed. Solvents were removed under vacuum to obtain a dark solid. CH_2Cl_2 was added with stirring and after 20 min a brown solid was filtered off. It was washed with water (2 × 10 mL), EtOH (2 × 5 mL) and Et_2O (2 × 5 mL). After drying under vacuum pure compound **9** was obtained as a brown powder (0.76 g, yield 60%). mp 303−305 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.38 (s, 2H, N═CH), 7.81 (d, J = 8.7 Hz, 2H, naph), 7.35 (d, J = 8.7 Hz, 2H, naph), 7.09 (d, J = 9.0 Hz, 4H, Ar), 6.50 (d, J = 9.0 Hz, 4H, Ar), 3.34 (q, J = 7.2 Hz, 8H, NCH_2), 1.15 (t, J = 7.2 Hz, 12H, CH_3) ppm; ^1H NMR (300 MHz, Pyridine-d_5) δ = 9.41 (s, 2H, N═CH), 8.20 (d, J = 8.7 Hz, 2H, naph), 7.73 (d, J = 8.7 Hz, 2H, naph), 7.64−7.53 (m, 4H, Ar), 6.69 (d, J = 9.2 Hz, 4H, Ar), 3.11 (q, J = 6.9 Hz, 8H, NCH_2), 0.91 (t, J = 6.9 Hz, 12H, CH_3) ppm.; ^{19}F NMR (376 MHz, $CDCl_3$) δ = −134.83 (dd, J = 23.6, 9.0 Hz, 2F), −156.30 (t, J = 20.4 Hz, 1F), −163.58 to −163.89 (m, 2F) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, Pyridine-d_5) δ = 160.8, 158.3, 149.2, 148.8−148.5 (m), 142.5−139.4 (m), 139.3−136.4 (m), 131.4, 127.9, 125.1, 116.9, 116.6, 111.8, 44.8, 12.8 ppm.; FTIR (ATR) ν = 2974, 2937, 2874, 1646, 1613, 1591, 1569, 1517,1459, 1352, 1286, 1274, 1194, 1093, 977, 919, 815, 684 cm^{-1}; HRMS (ESI) calcd. for $C_{56}H_{34}B_2F_{20}N_4O_2$ $[M + H]^+$ 1197.2627, found 1197.2646.

*2-[N-(4′-Nitrophenyl)iminomethyl)]-6-[N′-(4″-(N″,N″-diethylaminophenyl)-iminomethyl)]-1,5-dihydroxynaphthalene bis-(diphenylborinic) complex (**10**).* To solution of ethoxydiphenylborane $((C_6F_5)_2BOEt)$ (0.66 g, 3.1 mmol) in anhydrous 2-MeTHF (25 mL) compound **16** (0.36 g, 1.0 mmol) was added. The mixture was warmed to 50 °C and stirred for 17 h. Then 4-nitroanilne (0.15 g, 1.05 mmol) was added and a mixture was stirred for 22 h at 50 °C. Volatiles were removed under reduced pressure to obtain a dark solid. Et_2O was added with stirring and after 20 min a dark precipitate was filtered. It was washed with Et_2O (5 × 10 mL) and hexane (2 × 10 mL), and dried under vacuum. The pure compound **10** was obtained as a violet powder (0.54 g, 67%). mp 270−275 °C. ^1H NMR (400 MHz, Acetone-d_6) δ = 9.20 (s, 1H, N═CH), 8.92 (s, 1H, N═CH), 8.20−8.12 (m, 2H, Ar), 7.78 (d, J = 8.7 Hz, 2H, naph), 7.63−7.53 (m, 4H, Ar), 7.51−7.42 (m, 8H, Ar), 7.19−7.03 (m, 14H, Ar), 6.57−6.49 (m, 2H, Ar), 3.35 (q, J = 7.0 Hz, 4H, NCH_2), 1.09 (t, J = 7.0 Hz, 6H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 163.01, 162.98, 160.3, 158.8, 150.5, 147.8, 146.9, 134.1, 133.8, 133.6, 132.3, 131.1, 127.4, 127.3, 127.0, 126.8, 126.5, 125.9, 125.8, 125.5, 124.4, 116.8, 115.9, 115.2, 115.1, 110.9, 44.5, 12.6 ppm; HRMS (ESI) calcd. for $C_{52}H_{44}B_2N_4O_4$ $[M + H]^+$ 811.3627, found 811.3638.

Optical Properties. The UV−vis absorption spectra were recorded using a Hitachi UV-2300II spectrometer. The emission spectra were recorded using a Hitachi F-7000 spectrofluorometer, equipped with a photomultiplier detector, calibrated using Spectral Fluorescence Standard Kit certified by BAM Federal Institute for Materials Research and Testing.[11] The measurements were performed at room temperature, according to published procedures.[12] Suprasil quartz cuvettes (10.00 mm) were used. 1.5 nm slits were used for absorption and 2.5 nm slits were used for emission spectra. To eliminate any background emission, spectrum of pure solvent was subtracted from the samples' spectra. QY were determined in diluted solutions (A < 0.1 for longest wavelength band) by comparison with known standards: Coumarin 153 in ethanol ($c = 4 \times 10^{-6}$ mol dm^{-3}), Rhodamine 6G in ethanol ($c = 9 \times 10^{-7}$ mol dm^{-3}), Rhodamine 101 in methanol ($c = 3 \times 10^{-7}$ mol dm^{-3}) and Cresyl violet perchlorate in ethanol ($c = 1 \times 10^{-6}$ mol dm^{-3}). Concentration of bis(boranil) solutions were in the range of 1−3 × 10^{-6} mol dm^{-3} (concentration was adjusted to reach absorbance similar to that for reference solution at the excitation wavelength). To calculate the QY the following formula was used:

$$QY_x = QY_{st} \times \frac{F_x}{F_{st}} \times \frac{1 - 10^{-A_{st}}}{1 - 10^{-A_x}} \times \frac{n_x^2}{n_{st}^2}$$

where F is the relative integrated photon flux of sample (x) and standard (st), A is the absorbance at the excitation wavelength, n is the refractive index of used solvents.

$$F = \int I_c \, d\lambda_{em} = \int \frac{I(\lambda_{em})\lambda_{em}}{s(\lambda_{em})} \, d\lambda_{em}$$

Photon fluxes (F) were calculated by integration of corrected spectra (I_c), obtained by multiplication of intensity of emission spectra (I) by photon energy and division by the spectral responsivity (s) in corresponding wavelengths (λ_{em}). All measurements were carried out at room temperature. For compound **A**, **1** referenced standards were used: Coumarine 153 (QY_r = 0.38); **2**−**4**: Rhodamine 6G (QY_r = 0.95); **5**−**7**: Rhodamine 101 (QY_r = 1.00); **8**−**10** Cresyl violet perchlorate (QY_r = 0.56). The QY for these standards were adopted from IUPAC report.[13] The following excitation wavelengths (nm) were used: 370 (**A**), 400 (**B**), 440 (**1**, DCM), 465 (**1**, toluene), 500 (**2**−**4**, toluene), 503 (**2**−**4**, DCM), 531 (**5**, toluene), 533 (**5**−**7**, DCM; **6**, toluene), 540 (**7**, toluene), 550 (**8**, **10**, DCM), 555 (**7**, **10**, toluene), 563 (**9**, DCM), 571 (**9**, toluene).

Absolute fluorescence quantum yields of **4** and **7** in solid state (powders) were determined using FLS980 (Edinburgh Instruments) fluorescence spectrometer, equipped with an integrating sphere, with BENFLEC inside coating, from Edinburgh Instruments.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01001.

Detailed information regarding X-ray structures of complexes **4** and **9**, DSC, electrochemical measurements, spectroscopic measurements, time-dependent UV−vis experiments, computational studies, copies of NMR spectra (PDF)

Crystal data (CIF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Tadeusz Marek Krygowski on the occasion of his 80th birthday.

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