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10,9-Oxaboraphenanthrenes as luminescent fluorophores

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ABSTRACT

Reactions of 9-chloro-10,9-oxaboraphenanthrene (**1**) with the phenyl-, *p*-tolyl-, *m*-xylyl-, mesityl-, 2,4,6-tri-*iso*-propylphenyl-, 3,5-bis(trifluoromethyl)phenyl-, and pentafluorophenyl-Grignard reagents resulted in the formation of the corresponding oxaboraphenanthrene derivatives namely 9-phenyl-(**2**), 9-*p*-tolyl-(**3**), 9-(3,5-dimethylphenyl)- (9-*m*-xylyl-) (**4**), 9-mesityl- (**5**), 9-(2,4,6-tri-*iso*-propylphenyl)- (**6**), 9-(3,5-bis(trifluoromethyl)phenyl)- (**7**), and 9-(pentafluorophenyl)-10,9-oxaboraphenanthrene (**8**). 9-Trisyl- (**9**) and 9-supersilyl-10,9-oxaboraphenanthrene (**10**) were obtained selectively employing **1** and Li[C(SiMe₃)₃] or Na[SitBu₃] as reactants. The compounds **4**–**9** were characterized by X-ray crystallog-raphy. The fluorescence measurements of **5**–**9** embedded in PMMA show emission bands with λ_{max} from 341 to 373 nm.

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1. Introduction

10,9-oxaboraphenanthrenes (Fig. 1) are versatile compounds which were first published in 1960 by Dewar and Dietz¹ and since then haven been used as antioxidant additives in lubricants,² as Lewis acids for use in aldol condensations³ or as fungicides.⁴ Later the interest in oxaboraphenanthrenes roses continually since they can be used as precursors for *ortho*-phenylenes which are studied for multiple applications in organic electronics.⁵



Fig. 1. 10,9-oxaboraphenanthrene derivatives (oxaboraphenanthrene).

When regarding oxaboraphenanthrene as a derivative of *ortho*phenylene, the additional B–O bond leads to a planar and rigid structure (Fig. 1).¹ In the heterocyclic ring the electron density is predominantly situated on the electron-rich oxygen atom, explaining why this part of the oxaboraphenanthrene shows no distinct aromaticity.^{1,5}

Due to its structural motif the oxaboraphenanthrene is an asymmetrically-linked donor-acceptor system, whose acceptor properties can be influenced by the substituent R (Fig. 1). Along

with the variation of this donor-acceptor system, a control of the HOMO-LUMO gap is envisioned which is crucial for optoelectronic applications.⁶ Dewar and Dietz's UV/vis investigations of 9-substituted oxaboraphenanthrenes in solution showed several absorption bands, with maxima from the phenyl-substituted oxaboraphenanthrene shifted bathochromically compared to those of a hydroxyl-substituted one.¹ While 9-hydroxy-oxaboraphenanthrene (Fig. 1, R=OH)⁷ is very stable and therefore has found several applications,^{2–4} it shows only an insignificant fluorescence, whereas 9-phenyl-10,9-oxaboraphenanthrene (**Za**) (Fig. 1, R=Ph) fluoresces strongly.¹ Unfortunately **Za** was sensitive to hydrolysis due to the Lewis acidic boron center. Nevertheless, it showed that the fluorescence is tunable depending on the substituent of the oxaboraphenanthrene core.

As the oxaboraphenanthrene unit shows interesting optoelectronic properties we synthesized various 9-substituted BOP derivatives and investigated their stability and luminescence behavior. The emission area would be suitable to use our compounds in UV-OLEDs.^{8,9} Equally an incorporation of them in OLEDs as a host material is conceivable in order to suppress luminescence quenching effects.^{10,11} Recently Hirai et al. published a boroncontaining polycyclic aromatic compound comparable to ours for this purpose.¹²

2. Results and discussion

In this study the 9-substituted oxaboraphenanthrenes were synthesized following a route published by Dewar and Dietz¹ and optimized by Zhou et al.:¹³ By reacting 2-phenylphenol with an





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excess of BCl₃ and catalytic amounts of AlCl₃ in hexane, 9-chloro-10,9-oxaboraphenanthrene (Scheme 1) was obtained for use as the starting compound for further derivatization reactions.



Scheme 1. Synthesis of 9-chloro-10,9-oxaboraphenanthrene (1) in the reaction of 2-phenylphenol with BCl₃ and catalytic amounts of AlCl₃.

2.1. Synthesis of 9-substituted 10,9-oxaboraphenanthrenes

The substitution with bulky groups at the 9-position should on the one hand lead to (hydrolysis-) stable products and on the other enhance their emission. Therefore we synthesized a series of aryland silyl-substituted oxaboraphenanthrenes and investigated their steric shielding effect on the boron atom. As the insertion of an aryl substituent can change the electronic properties of the oxaboraphenanthrene, we tested if there is any effect of electron withdrawing and donating aryl groups on the emission characteristics of the oxaboraphenanthrene (Scheme 2).



Scheme 2. Reaction of 9-chloro-oxaboraphenanthrene (1) with phenyl lithium in THF.

For the substitution reactions on 9-chloro-10.9oxaboraphenanthrene (1) both organolithium as well as Grignard reagents are suitable. Nevertheless, we investigated the case of sterically less demanding aryl substituents, up to *m*-xylyl, and found that the corresponding organolithium species lead to double addition and therefore to product mixtures. For instance, treatment of 1 with 1.1 equiv of Li[Ph] in THF at -78 °C afforded a mixture of 9phenyl-10,9-oxaboraphenanthrene (2a) and the related lithium borate **2b**, as shown in Scheme 2. We identified the borate **2b** by its spectral characteristics and by X-ray structure analysis of single crystals.

By contrast the reactions of **1** with the phenyl-, *p*-tolyl-, *m*-xylyl-, mesityl-, 2,4,6-tri-*iso*-propylphenyl-, 3,5-bis(trifluoromethyl)phenyl-, and pentafluorophenyl-Grignard reagent gave only the corresponding oxaboraphenanthrene derivatives, as shown in Scheme 3.

In addition we also investigated the reaction of **1** with the bulky carbanionic reagent Li[C(SiMe₃)₃] (trisyl lithium)^{14,15} and the sterically crowded silanide Na[SitBu₃] (supersilyl sodium),^{16,17} respectively. In both reactions the corresponding 9-substituted-oxaboraphenanthrenes **9** and **10** were formed in good yields (see Scheme 4).

In particular 9-mesityl-oxaboraphenanthrene (**5**), 9-(2,4,6-trisiso-propylphenyl)-oxaboraphenanthrene (**6**), and 9-trisyl-oxaboraphenanthrene (**9**) show an extraordinary stability towards nucleophiles like water. This can be explained using the crystalstructure of**5**,**6**, and**9**: in all these compounds the substituentsshield the boron center from nucleophilic attacks (see Figs. 2–5). The oxaboraphenanthrene **4** was crystallized from a concentrated THF solution at -30 °C, whereas crystals of **5** and **6** were obtained by slow evaporation of hexane solutions at room temperature (see Fig. 2). The compound **4** crystallizes in the orthorhombic space group *Pba2* and **5** in the orthorhombic space group *P2*₁2₁2₁. Both compounds contain two crystallographically independent molecules in the asymmetric unit. Since most structural parameters of molecules **4** as well as **5** are closely similar, in each case the structure of only one molecule of **4** and **5** is shown in Fig. 2. The oxaboraphenanthrene **6** crystallizes in the monoclinic space group *P2*₁/*c*.

The molecular structures of the oxaboraphenanthrenes **7** and **8**, which bear electron withdrawing groups on the B center, are shown in Fig. 3 below. Crystals of **7** (see Fig. 3) were grown from hexane at room temperature and belong to the monoclinic space group $P2_1/c$. X-ray quality crystals of **8** (monoclinic, $P2_1/c$ space group) were obtained from a hexane/diethyl ether solution at room temperature (see Fig. 3).

By slow evaporation of the solvent of a saturated benzene solution, single crystals of **9** were grown, which were suitable for an investigation by X-ray crystallography. The compound **9** crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent molecules in the asymmetric unit. Fig. 4 represents the structure of one of two crystallographically independent molecules of **9** (selected bond lengths in caption of Fig. 4).

Conformation of the aryl-substituted oxaboraphenanthrene derivatives 4-8 are shown in Fig. 5. In contrast to the structures of 5, 6, and 8 (top) the aryl substituent in 4 and 7 (bottom) lies in the plane of the oxaboraphenanthrene units.

While in the oxaboraphenanthrene derivatives **5**, **6**, **8**, and **9** the boron atoms are shielded (Figs. 2–5), in 9–(3,5-bis(trifluoromethyl) phenyl)-oxaboraphenanthrene (**7**) as well as in the moisture-sensitive 9-(m-xylyl)-oxaboraphenanthrene (**4**) the boron center is more accessible (Fig. 5). Nevertheless, **5**, **6**, **8**, and **9** as well as **7** turned out to be relatively stable towards hydrolysis and could be stored for some weeks under air.

2.2. Luminescence investigations of the oxaboraphenanthrene-derivatives 5–9

In general, for application in OLEDs, compounds are preferred which fluoresce with high quantum yields and are oxygen- and moisture-insensitive. Furthermore, they have to form homogeneous layers either alone or in a matrix material, e.g. polymethyl methacrylate (PMMA).^{18,19}

As the oxaboraphenanthrene derivatives 5-9 proved to be airand moisture-stable these compounds were tested for their suitability as emitters for organic electronics. The oxaboraphenanthrenes form homogeneous layers when embedded in PMMA and show an emission in the near-UV area with moderate quantum yields (see the experimental section for more details).

The spectra of **5**–**9** possess almost identical absorption maxima (see Table 1 and Fig. 6). However, the oxaboraphenanthrenes **5**, **6** and **9** with electron donating groups reveal an additional absorption band (see Fig. 6). Even the emission maxima of the oxaboraphenanthrenes **5** and **6** with electron donating groups differ slightly from those of the oxaboraphenanthrenes **7** and **8** with electron withdrawing groups (see Table 2 and Fig. 7). Interestingly, the compounds **5**–**9** emit light of short wavelengths in the range of the near-UV area.

This indicates that electron withdrawing substituents in oxaboraphenanthrenes **7** and **8** effect a bathochromic shift of the emission maximum up to 25 nm compared with these of oxaboraphenanthrenes with electron donating substituents (**5** and **6**). In consequence the oxaboraphenanthrenes **7** and **8** reveal marginally larger Stokes shifts than do **5** and **6**.



Scheme 3. 9-Aryl-substituted oxaboraphenanthrenes synthesized starting from 9-chloro-oxaboraphenanthrene (1) and Grignard-reagents (red: electron withdrawing groups, green: electron donating groups). For the synthesis of 9-phenyl-10,9-oxaboraphenanthrene (2), see Ref. 1.



Scheme 4. 9-Alkyl- and 9-silyl-substituted oxaboraphenanthrenes synthesized starting from 9-chloro-oxaboraphenanthrene (1) and trisilyl lithium and supersilyl sodium.

Additionally, these results show that oxaboraphenanthrenes with sterically demanding groups show a higher quantum yield even when the concentrations used were lower.²⁰ This effect may be explained with a higher stability of their molecular scaffolds.

3. Conclusion

In summary, convenient access to oxaboraphenanthrenes with sophisticated substituents on the boron center was established. Reactions of 9-chloro-10,9-oxaboraphenanthrene (1) with the *p*-tolyl-, *m*-xylyl-, mesityl-, 2,4,6-tri-*iso*-propylphenyl-, 3,5-bis(trifluoromethyl)phenyl-, and penta-fluorophenyl-Grignard reagent resulted in the formation of the corresponding oxaboraphenanthrene derivatives **3–8**. Under the same conditions, **9** and

10 were obtained by selectively employing **1** and $\text{Li}[C(\text{SiMe}_3)_3]$ or Na[SitBu₃] as reactants. The oxaboraphenanthrene derivatives **4**–**9** were characterized by X-ray crystallography. The UV/vis measurements of **5**–**9** embedded in PMMA show four to five absorption bands. Interestingly, the compounds **5**–**9** emit light of short wavelengths in the range of the near-UV area. In addition to that we observed a dependency between the quantum yields and the steric bulkiness of the substituent. Thus, oxaboraphenanthrenes are considered to be promising candidates for UV-OLED material.

4. Experimental section

4.1. General materials and methods

All reactions and manipulations were carried out under dry, oxygen-free nitrogen by using standard Schlenk ware or in an argon-filled M. Braun glovebox. The solvents THF, Et₂O, Bu₂O, pentane, toluene, benzene and $[D_6]$ -benzene were stirred over sodium/benzophenone and distilled prior to use. CHCl₃ and CH₂Cl₂ were dried over CaH₂ and distilled before use.

The NMR spectra were recorded on *Bruker DPX 250, Avance 300, Avance 400,* and *Avance 500* spectrometers. Elemental analyses were performed at the microanalytical laboratories of the University Frankfurt. The UV/Vis absorption spectra measurements were carried out at a *Varian Cary 500* UV/Vis spectrophotometer, the fluorescence spectra as well as the quantum yields at a *Jasco FP*-8300.

For the luminescence investigations a parent solution was prepared consisting of a mixture of 10 weight percent of the analyte in PMMA, dissolved in methylene chloride (spectrophotometric grade). The results described above are based on parent solutions of 8 mg of the analyte, 72 mg PMMA in 3.6 mL methylene chloride.



Fig. 2. Solid-state structures of **4** (orthorhombic space group *Pba*²; one of two crystallographically independent molecules), **5** (orthorhombic space group *P2*₁/2₁; one of two crystallographically independent molecules), **and 6** (monoclinic space group *P2*₁/2). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) **4**: B(1)–O(1) 1.377(2), B(1)–C(11) 1.562(2), B(1)–C(21) 1.569(3), O(1)–C(1) 1.375(2), C–C_{biphenyl} 1.373(3)–1.416(2), C(2)–C(12) 1.469(2), C–C_{xytyl/aryl} 1.386(3)–1.402(2), O(1)–B(1)–C(11) 115.95(15), O(1)–B(1)–C(21) 111.39(14), C(11)–B(1)–C(21) 132.66(14), C(1)–O(1)–B(1) 124.97(13), O(1)–C(1)–C(6) 116.05(14), O(1)–C(1)–C(2) 121.19(14), C–C–C_{biphenyl} 115.78(14) –124.54(15), C(16)–C(11)–B(1) 124.31(15), C(12)–C(11)–B(1) 118.21(14), C–C–C_{xytyl/aryl} 116.31(15)–122.95(15), C(26)–C(21)–B(1) 126.57(15), C(22)–C(21)–B(1) 117.11(14). **5**: B(1)–O(1) 1.375(4), B(1)–C(11) 1.540(4), B(1)–C(21) 1.568(4), O(1)–C(1) 1.375(3), C–C_{biphenyl} 1.377(4)–1.408(4), C(2)–C(12) 1.475(4), C–C–c_{sytyl/aryl} 1.384(4)–1.409(4); O(1)–B(1)–C(11) 1.79(3), O(1)–B(1)–C(21) 117.2(2), C(11)–B(1)–C(21) 124.9(3), B(1)–O(1) 122.3(2), O(1)–C(1)–B(1) 123.1(2), C(12)–C(11)–B(1) 124.9(3), B(1)–O(1) 122.3(2), O(1)–C(1)–C(1) 115.8(2), O(1)–C(1) 1.533(5), B(1)–O(21) 1.582(4), O(1)–C(11) 1.379(3), C–c_{biphenyl} 1.366(5)–1.419(4), C(2)–C(12) 1.468(5), C–C_{biphenyl} 1.378(3)–1.406(4); O(1)–B(1)–C(11) 118.2(3), O(1)–B(1)–C(21) 118.2(3), C(2)–C(12) 1.468(5), C–C_{biphenyl} 1.378(3)–1.406(4); O(1)–B(1)–C(1) 118.2(3), O(1)–B(1)–C(21) 115.3(3), C(1)–O(1)–B(1) 122.1(5), C–C–C_{biphenyl} 116.2(3)–123.8(3), C(1)–C(11) 1.533(3), C(2)–C(21)–B(1) 122.1(5), C–C–C_{biphenyl} 116.2(3)–123.8(5), O(1)–C(11)–C(12) 121.7(3), O(1)–C(11)-C(12) 121.7(3), O(1)–C(11) 1.62

Into a lying quartz cuvette $(39 \times 11 \times 11 \text{ mm}^3)$ 100 µL of methylene chloride and 10 µL of the parent solution were filled. After evaporation of the solvent a homogeneous layer of PMMA and the luminophore was formed which was analyzed in regard to its luminescence behavior.

By adding the parent solution in 10 μ L steps dissolved in methylene chloride onto the existing layer and evaporating the solvent thicker layers can be formed and analyzed.

9-Chloro-10,9-oxaboraphenanthrene,⁸ Li[C(SiMe₃)₃] · 2 THF,^{14,15} and Na[SitBu₃]^{16,17} were synthesized following literature known methods.

4.2. Synthesis protocols and characterization data

4.2.1. Synthesis of the lithium borate of **2**. To a solution of (0.541 g, 2.52 mmol, 1.0 equiv) 9-chloro-oxaboraphenanthrene (**1**) in THF (20 mL) a phenyl lithium solution (1.8 mL, 1.52 M in Bu₂O; 2.77 mmol, 1.1 equiv) was added (90 min) at -90 °C and the

resulting reacting mixture was additionally stirred for 1 h at -90 °C. After warming to room temperature, the yellow suspension was filtered and the white precipitate was washed with hexane (3×2 mL). All volatiles were removed from the combined organic layers in vacuo. According to the ¹¹B NMR spectrum 9-phenyl-10,9-oxaboraphenanthrene (**2a**) and the borate **2b** were thereby formed (integral ratio of the signals: **2a**: **2b**=3: 7). The residue was a yellow oil from which X-ray quality crystals were obtained at room-temperature after approx. 3 weeks under nitrogen atmosphere (yield: 34%, 0.482 g, 0.85 mmol).²¹

¹H NMR (300.0 MHz, C₆D₆): δ =8.06 (m, 5H), 7.95 (m, 1H), 7.55 (m, 2H), 7.50 (m, 4H), 7.27 (m, 4H), 7.10 (m, 2H), 3.46 (m, 12H, OCH₂), 1.10 (m, 12H, CH₂); ¹¹B NMR (96.3 MHz, C₆D₆): δ =3.3; elemental Anal. Calcd (%) for C₃₈H₄₀BLiO₃ (562.45): 81.14, H, 7.17; found: C 81.04, H 7.24.

4.2.2. Synthesis of 9-p-tolyl-10,9-oxaboraphenanthrene (**3**). To a solution of (0.523 g, 2.43 mmol, 1.0 equiv) 9-chloro-



Fig. 3. Solid-state structures of **7** (monoclinic space group *P*2₁/*c*) and **8** (monoclinic space group *P*2₁/*c*). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) **7**: O(1)–C(1) 1.370(3), O(1)–B(1) 1.377(4), B(1)–C(11) 1.549(4), B(1)–C(21) 1.585(4), C–C_{biphenyl} 1.376(4)–1.424(4), C(2)–C(12) 1.475(4), C–C_{phenyl} 1.383(4)–1.402(4); C(1)–O(1)–B(1) 124.6(2), O(1)–B(1)–C(11) 117.2(2), O(1)–B(1)–C(21) 110.7(2), C(11)–B(1)–C(21) 132.0(2), O(1)–C(1)–C(6) 116.5(2), O(1)–C(1)–C(2) 121.0(2), C–C–C_{biphenyl} 116.2(3)–124.0(2). **8**: O(1)–B(1) 1.361(2), O(1)–C(11) 1.383(2), B(1)–C(11) 1.533(3), B(1)–C(21) 1.585(2), C–C_{biphenyl} 1.373(3)–1.419(2), C(2)–C(12) 1.472(3), C–C_{phenyl} 1.374(3)–1.397(2), B(1)–O(1)–C(11) 122.26(14), O(1)–C(1) 119.60(15), O(1)–B(1)–C(21) 114.60(15), C(1)–B(1)–C(21) 125.77(16), C–C–C_{biphenyl} 116.38(17)–123.36(16), C(6)–C(1)–B(1) 123.75(16), C(2)–C(1)–B(1) 117.55(16), O(1)–C(11)–C(16) 115.96(16), O(1)–C(11)–C(12) 121.45(16).



Fig. 4. Solid-state structure of **9** (monoclinic space group *P*₂₁/*c*). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) of one of two crystallographically independent molecules: Si-C_{Me} 1.867(4) – 1.886(3), Si-C(7) 1.919–1.933(3), B(1)–O(1) 1.384(4), B(1)–C(1) 1.561(4), B(1)–C(7) 1.580(4), O(1)–C(11) 1.373(4), C(1)–C(6) 1.403(4), C-C_{biphenyl} 1.366(5)–1.424(4), C(2)–C(12) 1.457(5); C-Si-C 102.21(16)–107.22(16), C-Si-C(7) 109.96(14) –117.17(16), O(1)–B(1)–C(1) 114.3(3), O(1)–B(1)–C(7) 114.0(3), C(1)–B(1)–C(7) 131.4(3), C(1)–0(1)–B(1) 126.0(2), C-C-C_{biphenyl} 115.7(3)–122.7(3), C(6)–C(1)–B(1) 123.5(3), C(2)–C(1)–B(1) 119.1(3), B(1)–C(7)–Si 106.6(2)–114.4(2), Si–C(7)–Si 107.77 (14)–111.60(14), O(1)–C(11)–C(16) 116.4(3), O(1)–C(11)–C(12) 120.9(3).

oxaboraphenanthrene (**1**) in THF (5 mL) a *p*-tolyl-Grignard solution (0.8 mL, 0.30 \times in THF; 2.80 mmol, 1.1 equiv) was added (10 min) at room temperature and the resulting reacting mixture was stirred for 1 h at 60 °C. After cooling to room temperature, the colorless suspension was filtered and the white precipitate was washed with hexane (3×2 mL). All volatiles were removed from the combined organic layers in vacuo. The product was obtained as

a yellowish, hydrolysis-sensitive powder in 88% (0.580 g, 2.15 mmol) yield.

¹H NMR (300.0 MHz, C₆D₆): δ =8.10 (d, ³*J*_{HH}=7.8 Hz, 1H), 8.31 (d, ³*J*_{HH}=7.4 Hz, 4H), 7.79 (d, ³*J*_{HH}=7.4 Hz, 1H), 7.64 (m, 2H), 7.34 (m, 2H), 7.04 (m, 2H), 2.10 (s, 3H, CH₃); ¹¹B NMR (96.3 MHz, C₆D₆): δ =42.6 (br, *h*_{1/2}=530 Hz); ¹³C NMR (75.5 MHz, C₆D₆): δ =141.5, 135.4, 135.1, 130.2, 129.2, 128.9, 128.4, 125.8, 125.3, 123.7, 123.2, 122.7, 112.35, 21.2; elemental Anal. Calcd (%) for C₁₉H₁₅BO (270.13): 84.48, H 5.60; found: C 84.45, H 5.47.

4.2.3. Synthesis of 9-m-xylyl-10,9-oxaboraphenanthrene (4). To a solution of (0.723 g, 3.36 mmol, 1.0 equiv) 9-chloro-oxaboraphenanthrene (1) in THF (15 mL) 10.0 mL (0.27 m in THF; 4.00 mmol, 1.2 equiv) of an m-xylyl-Grignard solution were added (5 min) at room temperature. The resulting yellow reaction mixture was heated for 2.5 h at -70 °C and was filtered after cooling to room temperature over Celite using Schlenk technique. The filtrate was concentrated whereupon colorless plates appropriate for X-ray crystallography were obtained by storing the saturated THF solution of the product at -30 °C overnight. After evaporation of the solvent under reduced pressure the product was obtained as a colorless powder in a yield of 52% (0.521 g, 1.75 mmol).

¹H NMR (300.0 MHz, C₆D₆): δ =8.44 (m, 1H), 7.74 (m, 2H), 7.55 (m, 1H), 7.45 (m, 1H), 7.23 (m, 3H), 7.10 (m, 2H), 7.04 (m, 1H), 2.26 (m, 6H, 2 CH₃); ¹¹B NMR (96.3 MHz, C₆D₆): δ =44.3 (br, $h_{1/2}$ =780 Hz); ¹³C NMR (75.5 MHz, C₆D₆): δ =152.1, 139.8, 137.8, 137.2, 133.0, 132.8, 132.2, 130.2, 129.3, 128.5, 127.3, 126.4, 123.9, 123.7, 123.5, 122.1, 120.8, 21.5 (2 CH₃); elemental Anal. Calcd (%) for C₂₀H₁₇BO (284.16): C 84.53; H, 6.03; found: C 84.55, H 6.87.

4.2.4. Synthesis of 9-mesityl-10,9-oxaboraphenanthrene (**5**). To a solution of (0.526 g, 2.45 mmol, 1.0 equiv) 9-chloro-oxaboraphenanthrene (**1**) in THF (10 mL) 3.8 mL (0.67 M in THF; 2.55 mmol, 1.2 equiv) of a mesityl-Grignard solution were added (2 min) at room temperature. The resulting colorless suspension was stirred for 30 min at room temperature, mixed with water (50 mL) and the layers were separated. The aqueous layer was treated with diethyl ether (3×20 mL), the combined organic layers



Fig. 5. Conformation of aryl-substituted oxaboraphenanthrene derivatives 4-8.

Table 1Absorption data of 5–9 in PMMA films

	5	6	7	8	9
Wavelengths/nm	262	262	259	260	262
	271	272	269	269	271
	293	293	295	296	295
	309	308	308	307	309
	321	319			322



Fig. 6. Absorption spectra of **5–9** from PMMA layers of same thickness and same weight percent content of the analyte see Table 1.

 Table 2

 Data for the emission measurements of 5–9 in PMMA films which showed no emission itself in the observed wavelengths area

	Excitation λ _{ext} nm	Emission λ _{em} nm	Concentration mmol/L	Substance 10 ⁻⁶ mmol	ϕ_{max} %
5	268	348	7.4	0.148	25.2
6	262	341	5.8	0.058	34.8
7	266	373	5.6	0.224	29.5
8	266	361	6.4	0.064	16.1
9	260	344	5.4	0.011	47.3

dried over MgSO₄ and the solvent evaporated under reduced pressure. The oxaboraphenanthrene **5** was obtained as a colorless powder with a yield of 92% (0.678 g, 2.27 mmol). Slow evaporation of a saturated hexane solution of **5** over *Granopent* lead to colorless crystal blocks which were suitable for an investigation by X-ray crystallography.

¹H NMR (300.0 MHz, C₆D₆): δ =8.03 (m, 2H), 7.86 (d, ³J_{HH}=6.8 Hz, 1H), 7.55 (dd, ³J_{HH}=8.1 Hz, ⁴J_{HH}=1.1 Hz, 1H), 7.42 (m, 1H), 7.20–7.07 (m, 3H), 6.87 (s, 2H), 2.26 (s, 3H, CH₃), 2.18 (s, 6H, 2 CH₃); ¹¹B NMR (96.3 MHz, C₆D₆): δ =46.1 (br, $h_{1/2}$ =730 Hz); ¹³C NMR (75.5 MHz, C₆D₆): δ =152.4, 140.3, 139.1, 138.1, 137.7, 133.5, 129.3, 127.8, 127.7, 124.9, 123.7, 123.7, 121.9, 121.0, 22.6 (2 CH₃), 21.4 (1 CH₃); elemental Anal. Calcd (%) for C₂₁H₁₉BO (298.15): C 84.59, H 6.42; found: C 84.55, H 6.87.

4.2.5. Synthesis of 9-(2,4,6-tri-iso-propylphenyl)-10,9-oxaboraphenanthrene (**6**). To a solution of (0.522 g, 2.43 mmol, 1.0 equiv) 9-chloro-oxaboraphenanthrene (**1**) in THF (10 mL) a 2,4,6-tri-iso-propylphenyl-Grignard solution (0.20 M in THF;



Fig. 7. Emission spectra of **5–9**. Measurement with the highest obtained quantum yield with normalized intensities see Table 2.

2.93 mmol, 1.2 equiv) was added (1 h) at room temperature and stirred for 2 h at 60 °C. After cooling to room temperature, the reaction solution was quenched with water (30 mL) and the layers were separated. The aqueous layer was treated with diethyl ether (3×20 mL) and the combined organic layers were dried with MgSO₄. After evaporation of the solvent in vacuo, the product was obtained as a colorless powder with a yield of 79% (0.737 g, 1.93 mmol). By slow evaporation colorless crystal blocks which were suitable for an investigation by X-ray crystallography were grown from a saturated hexane solution of **6**.

¹H NMR (300.0 MHz, C₆D₆): δ =8.02 (m, 2H), 7.86 (d, ³J_{HH}=7.4 Hz, 1H), 7.58 (d, ³J_{HH}=8.0 Hz,1H), 7.41 (t, ³J_{HH}=7.6 Hz, 1H), 7.24 (s, 2H, *m*-PhH), 7.20–7.07 (m, 3H), 2.93 (m, 1H, CH-*i*Pr), 2.77 (m, 2H, CH-*i*Pr), 1.34 (d, 6H, CH₃-*i*Pr), 1.22 (d, 6H, CH₃-*i*Pr) 1.16 (d, 6H, CH₃-*i*Pr); ¹¹B NMR (96.3 MHz, C₆D₆): δ =46.7 (br, $h_{1/2}$ =1700 Hz); ¹³C NMR (75.5 MHz, C₆D₆): δ =152.4, 140.3, 139.1, 138.1, 137.7, 133.5, 129.3, 127.8, 127.7, 124.9, 123.7, 123.7, 121.9, 121.0, 22.6 (2 CH₃), 21.4 (1 CH₃); elemental Anal. Calcd (%) for C₂₇H₃₁BO (382.35): C 84.82, H 8.17; found: C 84.66, H 8.14.

4.2.6. Synthesis of 9-(3,5-bis(trifluoromethyl)phenyl)-10,9oxaboraphenanthrene (7). To a solution of (0.824 g, 3.84 mmol, 1.0 equiv) 9-chloro-oxaboraphenanthrene (1) in toluene (40 mL) 20.0 mL (0.23 M in THF; 4.52 mmol, 1.2 equiv) of a 3,5bis(trifluoromethyl)phenyl-Grignard solution were added (30 min) at room temperature, whereby the reddish solution of 9chloro-oxaboraphenanthrene (1) immediately turned yellow. After adding the entire dose of the Grignard solution the brown reaction mixture was stirred for 2.5 h at 70 °C. The now clear yellow reacting solution was cooled to room temperature and quenched with water (50 mL). The separated aqueous layer was treated with diethyl ether (3×20 mL), the combined organic layers were dried over MgSO₄ and the solvent removed in vacuo which resulted in a brownish oil. After some hours at room temperature colorless crystal needles of 7 could be obtained from the oil which were suitable for X-ray crystallography. Analytically pure 7 was obtained by crystallization in hexane at room temperature in a yield of 93% (1.401 g, 3.57 mmol).

¹H NMR (300.0 MHz, C_6D_6): δ =8.0 (s, 2H), 7.77–7.67 (m, 4H), 7.22–7.13 (m, 2H), 7.01–6.86 (m, 3H); ¹¹B NMR (96.3 MHz, C_6D_6): δ =40.4 (br., $h_{1/2}$ =590 Hz); ¹³C NMR (75.5 MHz, C_6D_6): δ =151.3, 140.0, 136.6, 134.4 (br.), 133.7, 131.4, 131.0, 129.6, 127.7, 126.1, 124.1, 123.9, 123.7, 123.7, 123.6, 123.5, 122.5, 122.3, 120.8; ¹⁹F NMR (282.3 MHz, C_6D_6): δ = -62.5 (2CF₃); elemental Anal. Calcd (%) for $C_{20}H_{11}BF_{6}O$ (392.10): C 61.26, H 2.83; found: C 61.26, H 3.00.

4.2.7. Synthesis of 9-(pentafluorophenyl)-10,9-oxaboraphenanthrene (8). To a solution of (0.701 g, 3.27 mmol, 1.0 equiv) 9-chloro-oxaboraphenanthrene (1) in toluene (20 mL) 20.0 mL (0.18 M in THF: 3.59 mmol. 1.1 equiv) of a pentafluorophenyl-Grignard solution were added (30 min) at room temperature, whereby the reddish 9chloro-oxaboraphenanthrene (1) solution turned immediately yellow. After the entire dose of the Grignard reagent the mixture was stirred for 2 h at room temperature and quenched with water (50 mL). The layers were separated, the aqueous layer was treated with diethyl ether (3×20 mL) and the combined organic layers were dried over MgSO₄. Removing the solvent under reduced pressure the crude product was obtained as a brownish crystalline solid. By elution of the solid in hexane (20 mL) and the dropwise addition of diethyl ether (ca. 2 mL) until the solid was completely dissolved and after slow evaporation of the solvent at room temperature colorless crystal blocks of 8 were obtained in a yield of 85% (0.961 g, 2.77 mmol) which were suitable for X-ray crystallography.

¹H NMR (300.0 MHz, C₆D₆): δ =7.92–7.89 (m, 2H), 7.78–7.75 (m, 1H), 7.47–7.38 (m, 2H), 7.20 (td, ³J_{HH}=7.4 Hz, ⁴J_{HH}=1.0 Hz, 1H), 7.17–7.03 (m, 2H); ¹¹B NMR (96.3 MHz, C₆D₆): δ =41.1 (br., $h_{1/2}$ =450 Hz); ¹³C NMR (75.5 MHz, C₆D₆): δ =151.5, 139.7, 137.1, 134.4, 133.9, 132.6, 129.6, 129.1, 127.7, 124.4, 124.0, 123.4, 122.8, 123.7, 122.1, 121.8, 120.8, 120.0; ¹⁹F NMR (282.3 MHz, C₆D₆): δ =–131.30 (m, 2 *o*-PhF), –151.93 (*p*-PhF), –161.53 (2 *m*-PhF); elemental Anal. Calcd (%) for C₁₈H₈BF₅O (346.06): C 62.47, H, 2.33; found: C 62.43, H 2.58.

4.2.8. Synthesis of 9-trisyl-10,9-oxaboraphenanthrene (**9**). To a slurry of (1.357 g, 2.87 mmol) Li[C(SiMe₃)₃] \cdot 2 THF in toluene at $-78 \degree C$ (0.502 g, 2.34 mmol) **1** in toluene (20 mL) was added over a period of 1.5 h and the colorless suspension was warmed to room temperature overnight. The solvent was removed under reduced pressure, the precipitate eluted with hexane (20 mL) and the resulted slurry filtered over Celite. After removal of the solvent **9** was obtained as a colorless powder 65% (0.624 g, 1.52 mmol). By slow evaporation of a saturated benzene solution colorless crystal blocks were grown, which were suitable for X-ray crystallography.

¹H NMR (300.0 MHz, C₆D₆): δ =8.54 (dd, ³*J*_{HH}=7.7 Hz, ⁴*J*_{HH}=1.1 Hz, 1H)), 7.94 (t, ³*J*_{HH}=8.3 Hz, 2H), 7.48 (dd, ³*J*_{HH}=8.1 Hz, ⁴*J*_{HH}=1.1 Hz, 1H), 7.41–7.31 (m, 1H), 7.30–7.22 (m, 1H), 7.20–7.11 (m, 1H), 7.06–6.99 (m, 1H), 0.40 (s, 27H, 9 CH₃); ¹¹B NMR (96.3 MHz, C₆D₆): δ =45.1 (br., *h*_{1/2}=550 Hz); ¹³C NMR (75.5 MHz, C₆D₆): δ =151.3, 138.9, 138.6, 132.4, 129.3, 129.3, 128.6, 125.7, 123.9, 123.3, 123.0, 122.3, 119.7, 6.6 (9 CH₃); ²⁹Si NMR (59.6 MHz, C₆D₆): δ = –1.4 (3 SiMe₃) elemental Anal. Calcd (%) for C₂₂H₃₅BOSi₃ (410.58): C 64.36; H, 8.59, found: C 64.03, H 8.51.

4.2.9. Synthesis of 9-supersilyl-10,9-oxaboraphenanthrene (**10**). To a solution of (2.67 mmol, 1.1 equiv) Na[SitBu₃]·2 THF in 7 mL toluene at $-78 \degree C$ (0.520 g, 2.42 mmol, 1.0 equiv) **1** in toluene (20 mL) was added over a period of 1.5 h and the yellow solution was warmed to room temperature overnight. The solvent was removed under reduced pressure, the precipitate eluted with benzene (15 mL) and the resulted slurry filtered over Celite. By concentrating the filtrate **10** was obtained as colorless, dendritic crystals (yield: 90%, g, 2.18 mmol).

¹H NMR (300.0 MHz, C₆D₆): δ =8.74 (d, ³*J*_{HH}=7.6 Hz, 1H), 7.99 (t, ³*J*_{HH}=9.1 Hz, 2H), 7.58 (dd, ³*J*_{HH}=8.1 Hz, 1H), 7.40 (t, ³*J*_{HH}=7.5 Hz, 1H), 7.32 (t, ³*J*_{HH}=7.3 Hz, 1H), 7.20–7.13 (m, 1H), 7.07 (t, ³*J*_{HH}=7.6 Hz, 1H), 1.42 (s, 27H, 9 CH₃); ¹¹B NMR (96.3 MHz, C₆D₆): δ =54.0 (br, *h*_{1/2}=500 Hz); ¹³C NMR (75.5 MHz, C₆D₆): δ =151.6, 139.9 (2C), 137.1, 132.9, 129.2, 126.8, 123.0, 123.8, 123.0, 122.2, 120.3, 32.6 (9 CH₃), 23.1 (3 CMe₃); ²⁹Si NMR (59.6 MHz, C₆D₆): *n*,b; elemental

Table 3

Crystal data and refinement details for oxaboraphenanthrenes 4-9

Empirical formula C ₂₀ H ₁₇ BO C ₂₁ H ₁₉ BO C ₂₇ H ₃₁ BO C ₂₀ H ₁₁ BF ₆ O C ₁₈ H ₈ BF ₅ O C ₂₂	22H35BOSi3
Formula weight 284.15 298.17 382.33 392.10 346.05 410	10.58
T/K 173(2) 173(2) 293(2) 173(2) 173(2) 173	73(2)
المحمد المحم	loK _α , 0.71073 Å
Crystal system Orthorhombic Orthorhombic Monoclinic Monoclinic Monoclinic Monoclinic Mo	Ionoclinic
Space group Pba2 P21212 P21/c P21/c P21/c P21/c P21/c	$2_1/n$
a/Å 15.2162(5) 9.4804(5) 9.0884(7) 12.1297(12) 15.7080(11) 16.	6.5118(8)
b/Å 35.4853(14) 13.7252(6) 32.123(2) 5.4293(4) 7.2722(4) 8.7	.7803(4)
c/Å 5.5091(2) 25.3586(11) 8.5689(6) 25.144(3) 12.5481(10) 33.	3.5288(16)
α,/° 90 90 90 90 90 90 90 90	0
$\beta/^{\circ}$ 90 90 110.9690(10) 96.922(8) 96.140(6) 99.	9.209(4)
$\gamma/^{\circ}$ 90 90 90 90 90 90 90 90	0
$V/Å^3$ 2974.65(19) 3299.7(3) 2336.0(3) 1643.8(3) 1425.17(17) 475	798.3(4)
Z 8 8 4 4 4 8	
Density calculated g cm ⁻³ 1.269 1.200 1.087 1.584 1.613 1.1	.137
F(000) 1200 1264 824 792 696 177	776
$Index ranges -16 \le h \le 18 -11 \le h \le 11 -10 \le h \le 10 -14 \le h \le 14 -19 \le h \le 16 -2$	-20≤h≤20
$-42 \le k \le 42$ $-16 \le k \le 13$ $-38 \le k \le 38$ $-6 \le k \le 6$ $-8 \le k \le 8$ -11	10≤k≤10
$-6 \le l \le 6$ $-25 \le l \le 30$ $-10 \le l \le 10$ $-29 \le l \le 30$ $-15 \le l \le 15$ -3	-31 <i>≤l</i> ≤41
Crystal size/mm ³ 0.23×0.15×0.10 0.48×0.46×0.46 0.65×0.50×0.15 0.35×0.32×0.27 0.28×0.15×0.02 0.4	.42×0.27×0.13
No. of reflections collected 32,715 12,830 22,779 8072 10,868 35,	5,581
R1, wR2 [<i>l</i> >2σ(<i>l</i>)] 0.0387, 0.0943 0.0487, 0.1298 0.0878, 0.2010 0.0638, 0.1509 0.0422, 0.0992 0.0	.0620, 0.1570
Data/restraints/parameter 5518/1/402 5765/0/421 4119/9/261 3016/37/265 2664/0/226 910	108/0/515
GOOF on F^2 0.9901.0271.1141.0510.9461.0	.033
R1, wR2 (all data) 0.0455, 0.0976 0.0513, 0.1320 0.1168, 0.2165 0.0801, 0.1603 0.0616, 0.1067 0.0	.0791, 0.1665
largest diff peak and hole/eÅ $^{-3}$ 0.168, -0.140 0.0167, -0.220 0.0255, -0.283 0.602, -0.547 0.254, -0.253 0.3	.322, -0.507

Anal. Calcd (%) for C₂₄H₃₅BOSi (378.43): 76.17, H, 9.32, found: C 76.09, H 9.57.

4.3. X-ray structure determination

The data for **6** were collected on a Siemens SMART three-circle diffractometer using MoK_{α} radiation (λ =0.71073 Å) and were scaled using the program SADABS.²²

The data for the remaining structures were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK_α radiation (λ =0.71073 Å) and were scaled using the frame scaling procedure in the *X*-AREA program system.²³

The structures were solved by direct methods using the program *SHELXS* and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL-97* (see Table 3).²⁴

Due to the absence of anomalous scatterers, the absolute structure of **4** and **5** could not be determined.

The crystal of **6** was measured at room temperature, because the crystals did not survive being cooled. One isopropyl group is disordered over two positions with a site occupation factor of 0.570 (15) for the major occupied site. The disordered atoms were isotropically refined.

One trifluoromethyl group in **7** is disordered over three positions with site occupation factors of 0.447(3), 0.303(3), and 0.250(3). Bond lengths and angles of the disordered atoms were restrained to be equal to those of the non-disordered trifluoromethyl group. The disordered atoms were isotropically refined.

One trimethylsilyl group in 9 is disordered over two positions with a site occupation factor of 0.644(8) for the major occupied site. The disordered atoms were isotropically refined.

CCDC deposition numbers: 1410266 (lithium borate **2b**×**3** THF), 1403456 (**4**), 1403457 (**5**), 1403458 (**6**), 1403459 (**7**), 1403460 (**8**), 1403461 (**9**).

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- 21. **2b**×3 THF ($C_{38}H_{40}BLiO_3$) crystallizes in the 'monoclinic' system, space group 'P $2_1/n'$ with a=9.7010(8) Å, b=19.0850(11) Å, c=17.7489(15) Å, $\alpha=90^{\circ}$, $\beta=101$. 416(7)°, $\gamma=90^{\circ}$, V=3221.1(4), M=562.45, Z=4, and Dc=1.160 g cm⁻³. 24799 reflections (6030 unique) were collected in the range of 3.393–25.703° at 173 K giving a final residual value of R1=0.1021 (all data) wR2=0.1721 ($[I>2\sigma(I)]$); CCDC 1410266.
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