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Organoboron Quinolinolates with Extended Conjugated Chromophores: Synthesis, Structure, and Electronic and Electroluminescent Properties

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Luminescent organoboron complexes featuring substituted 8-quinolinolates as chelating ligands have been synthesized and characterized. Substitution of the quinolinolate has been achieved in the 5 and the 7 positions introducing phenyl, biphenyl, and 9,9′-dihexylfluorenyl substituents by reacting 8-benzyloxy-5,7-dibromoquinoline with the corresponding boronic acid derivatives in a Suzuki-type cross-coupling reaction. Upon deprotection, the 8-quinolinol derivatives have been transformed into the target compounds upon reaction with BPh_3. (κ^2-(*N*,*O*)-5,7-dibromo-8-quinolinolate)diphenylborane (**9**), (κ^2-(*N*,*O*)-5,7-diphenyl-8-quinolinolate)diphenylborane (**10**), (κ^2-(*N*,*O*)-5,7-bis(biphenyl-4-yl)-8-quinolinolate)diphenylborane (**11**), and (κ^2-(*N*,*O*)-5,7-bis(9,9-dihexylfluoren-2-yl)-8-quinolinolate)diphenylborane (**12**) have been investigated by nuclear magnetic resonance and infrared spectroscopy, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, thermal analysis, cyclic voltammetry, UV−vis absorption spectroscopy, and luminescence measurements in solution and in the solid state to retrieve a concise knowledge of the introduced compounds. Special emphasis has been placed on studying the consequences of extension of the conjugated π system of the quinolinolate ligand on materials properties. Small molecule organic light emitting devices (SMOLED) based on compounds **10**, **11**, and **12** give bright yellow to orange electroluminescence with low onset voltages (3.5−3.7 V) and continuous wave luminance intensities exceeding 1000 cd/m^2, while devices based on **9** give poor results, proving **9** to be an unsuitable emissive material.

Introduction

Luminescent organic and organometallic compounds have attracted much interest because of their applications in organic light emitting devices (OLEDs). For the fabrication of full-color flat panel displays, electroluminophores that provide stable red, green, and blue (RGB) emission are needed.[1] Tris(8-quinolinolate)Al(III) (Alq_3) was first reported by Tang and VanSlyke to possess electroluminescent properties and is one of the best known examples of emitting/electron transporting materials in OLEDs.[2] For these aluminum quinolinolates, efficient emission-color tuning can be achieved by attachment of various substituents to the 8-hydroxyquinoline ligand, thus allowing coverage of the entire visible spectrum.[3] Moreover, low cost solution processing becomes possible by incorporating the organometallic compound into a polymer structure.[3e,4] One of the issues with Alq_3 is that it exists in two isomeric forms (the *fac* and *mer* isomers). The possibility of Alq_3 isomerization and the associated changes of material properties are assumed to be a drawback for technological applications and have, therefore, prompted intense theoretical and experimental research.[5] As a potential alternative to aluminum quinolinolates, the

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(1) (a) Shinar, J.; Savvateev, V. In *Organic Light-Emitting Decives: A Survey*; Shinar, J., Ed.; Springer: New York, 2003, Chapter 1. (b) Kelly, S. M. In *Flat Panel Displays: Advanced Organic Materials*; Connor, J. A., Ed.; Royal Society of Chemistry: London, 2000, Chapter 5.

(2) (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* 1987, *51*, 913. (b) Lin, B. C.; Cheng, C. P.; You, Z.-Q.; Hsu, C.-P. *J. Am. Chem. Soc.* **2005**, *127*, 66.

(3) (a) Pohl, R.; Anzenbacher, P., Jr. *Org. Lett.* **2003**, *5*, 2769. (b) Montes, V. A.; Li, G.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. *Adv. Mater.* **2004**, *16*, **2001**. (c) Pohl, R.; Montes, V. A.; Shinar, J.; Anzenbacher, P., Jr. *J. Org. Chem.* **2004**, *69*, 1723. (d) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161. (e) Mayers, A.; Weck, M. *Chem. Mater.* **2004**, *16*, 1183.

(4) (a) Iijima, T.; Yamamoto, T. *Macromol. Rapid Commun.* **2004**, *25*, 669. (b) Meyers, A.; Kimyonok, A.; Weck, M. *Macromolecules* **2005**, *38*, 8671. (c) Meyers, A.; Weck, M. *Macromolecules* **2003**, *36*, 1766. (d) Bae, C.; Lee, S.; Choi, S.-Y.; Kwag, G. *Inorg. Chem.* **2005**, *44*, 7911. (e) Qin, Y.; Pagba, C.; Piotrowiak, P.; Jäkle, F. *J. Am. Chem. Soc.* **2004**, *126*, 7015. (f) Wang, X.-Y.; Weck, M. *Macromolecules* **2005**, *38*, 7219. (g) Qin, Y.; Singh, P.; Pagba, C.; Piotrowiak, P.; Jäkle, F. *Polym. Mater.: Sci. Eng.* **2004**, *91*, 447.

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corresponding organoboron quinolinolates seem to be promising candidates. Organoboron quinolinolates such as (κ^2-(*N*,*O*)-8-quinolinolate)diphenylborane (Ph_2Bq) exhibit efficient luminescence as well as good stability due to the increased covalency of the boron−ligand bonds.[6] They also offer the possibility of incorporation into a polymer backbone and do not form isomers.[4,7] Recent attempts geared at understanding the electronic effects of substituents and ligands in organoboron quinolinolates demonstrated a significant impact on the emission characteristics.[8] Here, we report the synthesis, electronic and electroluminescent properties of highly emissive, stable 5,7-disubstituted organoboron quinolinolates with extended aromatic π systems. These studies give basic insight into the possibilities of tuning the emission characteristics and should lead to the development of new OLED materials for practical applications.

Experimental Section

Unless otherwise noted, materials were obtained from commercial sources (Aldrich, Fluka, or Lancaster) and were used without further purification. Solvents for reactions were freshly distilled over appropriate drying agents prior to use. Reactions were carried out under an inert atmosphere of argon using standard Schlenk techniques. ^{1}H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer at 500 MHz; ^{13}C{^{1}H} NMR spectra were recorded at 125 MHz. Assignment of the peaks was done by DEPT and correlation NMR spectroscopy. Solvent residual peaks were used for referencing the NMR spectra to the corresponding values given in the literature.[9] Fourier transform infrared spectra were obtained from films on NaCl windows with a Perkin-Elmer Spectrum One and a DTGS detector. UV−visible absorption spectra were recorded on a Cary 50 Bio UV−visible spectrophotometer, and fluorescence spectra were recorded on a Perkin-Elmer luminescence spectrometer LS50B. Photoluminescence (PL) quantum yields were measured on a Shimadzu RF-5301PC spectrofluorometer calibrated using a tungsten−halogen light source (Ocean Optics LS-1-CAL) and a Perkin-Elmer Lambda 9 UV/vis/near-infrared spectrophotometer. Combined differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA) measurements were performed with a Polymer Laboratories simultaneous thermal analyzer STA 625 (crucibles: aluminum from Rheometric Scientific). DSC measurements were made with a Perkin-Elmer Pyris Diamond DSC differential scanning calorimeter equipped with a Perkin-Elmer CCA7 cooling system using liquid nitrogen. Mass spectra were recorded with a Micromass TofSpec 2E, equipped with a nitrogen laser (337 nm wavelength, operated at a frequency of 5 Hz) and a time lag focusing unit. Spectra were acquired in reflectron mode at an accelerating voltage of 20 kV. All spectra were recorded in positive ion mode. The analysis of data was done with MassLynx Software 3.4, Micromass, Manchester, U.K. Electrochemical measurements were carried out with an AUTOLAB PGSTAT100 high voltage potentiostat/galvanostat, manufactured by Eco Chemie B.V., Utrecht, The Netherlands. For control, data acquisition, and analysis the provided software, General Purpose Electrochemical System (GPES), version 4.9.004, developed by Eco Chemie, was used. The cyclic voltammograms were recorded in a three-electrode cell, equipped with an argon inlet, a glass-sealed platinum-disk working electrode (diameter 1 mm), a platinum counter electrode, and a silver wire as pseudo-reference electrode.

Ligand Synthesis. Compounds **2**, **3**, **4**, **6**, and **7** were prepared according to literature procedures.[10] Biphenylboronic acid and (9,9-dihexylfluoren-2-yl)boronic acid were synthesized as described elsewhere.[11]

8-Benzyloxy-5,7-bis(9,9-dihexylfluoren-2-yl)quinoline (5). Compound **5** was prepared analogously to a literature procedure.[10b] **2** (100 mg, 0.254 mmol), (9,9-dihexylfluoren-2-yl)boronic acid (300 mg, 0.792 mmol, 3.0 equiv), and Na_2CO_3 (300 mg, 2.830 mmol, 11.1 equiv) were suspended in degassed toluene (3 mL), ethanol (3 mL), and water (3 mL) under an inert atmosphere of argon. After the addition of $Pd(PPh_3)_4$ (25 mg, 0.022 mmol, 0.09 equiv) the reaction mixture was refluxed under argon for 24 h at 95 °C. The product was extracted with CH_2Cl_2, dried over Na_2SO_4, and purified by flash column chromatography on silica (cy:ee = 8:1). Sampling the band at $R_f = 0.7$ (cy:ee = 3:1) and drying in a vacuum yielded 185.0 mg of pure **5** (80.9%). Anal. Calcd for $C_{66}H_{77}NO$ (MW 900.32): C, 88.05; H, 8.62. Found: C, 87.92; H, 8.49. ^{1}H NMR (δ, 20 °C, $CDCl_3$): 9.03 (dd, $^3J_{HH} = 3.9$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, q^2), 8.28 (dd, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, q^4), 7.85 (d, $^3J_{HH}$ =7.8 Hz, 1H, fl_5^{4}), 7.80−7.76 (m, 4H, $\text{fl}_5^{1,5}$, $\text{fl}_7^{4,5}$), 7.69 (s, 1H, q^6), 7.64 (dd, $^3J_{HH} = 6.3$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, fl_5^{3}), 7.51 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, fl_7^{3}), 7.48 (s, 1H, fl_7^{1}), 7.39−7.31 (m, 7H, fl_5^{8}, fl_7^{8}, $\text{bn}^{2,3,4,5,6}$), 7.24−7.22 (m, 2H, fl_5^{6}, fl_7^{6}), 7.18−7.15 (m, 3H, q^3, fl_5^{7}, fl_7^{7}), 5.19 (s, 2H, CH_2), 2.02−1.96 (m, 8H, Hex^1), 1.35−0.95 (m, 24H, $\text{Hex}^{3,4,5}$), 0.78−0.70 (m, 20H, $\text{Hex}^{2,6}$). ^{13}C NMR (δ, 20 °C, $CDCl_3$): 151.3 (1C, q^8), 151.2, 151.1, 150.9, 141.0 (4C, $\text{fl}_5^{8a,9a}$, $\text{fl}_7^{8a,9a}$), 149.8 (1C, q), 143.9 (1C, q^{8a}), 140.8, 140.5, 138.0, 137.2 (4C, $\text{fl}_5^{4a,4b}$, $\text{fl}_7^{4a,4b}$), 137.6 (1C, bn^1), 136.5, 134.9, 134.9, 134.5 (4C, $q^{5,7}$, fl_5^{2}, fl_7^{2}), 134.6 (1C, q^4), 129.8 (1C, q^6), 129.0, 128.7 (2C, fl_5^{8}, fl_7^{8}), 128.6 (2C, $\text{bn}^{3,5}$), 128.1 (2C, $\text{bn}^{2,6}$), 127.7 (1C, bn^4), 127.5 (1C, q^{4a}), 127.4, 127.2, 127.0, 126.9, 124.9, 124.8, 123.2, 123.1 (8C, $\text{fl}_5^{1,4,5,7}$, $\text{fl}_7^{1,4,5,7}$), 121.0 (1C, q^3), 120.0, 119.9, 119.9, 119.6 (4C, $\text{fl}_5^{3,6}$, $\text{fl}_7^{3,6}$), 76.3 (1C, CH_2), 55.4, 55.3

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(5) (a) Kaji, H.; Kusaka, Y.; Onoyama, G.; Horii, F. *J. Am. Chem. Soc.* **2006**, *128*, 4292. (b) Utz, M.; Nandagopal, M.; Mathai, M.; Papadimitrakopoulos, F. *Appl. Phys. Lett.* **2003**, *83*, 4023. (c) Muccini, M.; Loi, M. A.; Kenevey, K.; Zamboni, R.; Masciocchi, N.; Sironi, A. *Adv. Mater.* **2004**, *16*, 861. (d) Braun, M.; Gmeiner, J.; Tzolov, M.; Cölle, M.; Meyer, F.; Milius, W.; Hillebrecht, H.; Wendland, O.; von Schütz, J.; Brütting, W. *J. Chem. Phys.* **2001**, *114*, 9625. (e) Kushto, G. P.; Iizumi, Y.; Kido, J.; Kafafi, Z. H. *J. Phys. Chem. A* **2000**, *104*, 3670. (f) Halls, M. D.; Aroca, R. *Can. J. Chem.* **1998**, *76*, 1730. (g) Malliaras, G. G.; Shen, Y.; Dunlap, D. H.; Murata, H.; Kafafi, Z. H. *Appl. Phys. Lett.* **2001**, *79*, 2582. (h) Curioni, A.; Boero, M.; Andreoni, W. *Chem. Phys. Lett.* **1998**, *294*, 268.

(6) Douglass, J. E. *J. Org. Chem.* **1961**, *26*, 1312.

(7) (a) Wu, Q.; Esteghamatian, M.; Hu, N.-X.; Popovic, Z. D.; Enright, G.; Breeze, S. R.; Wang, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 985. (b) Hassan, A.; Wang, S. *J. Chem. Soc., Chem. Commun.* **1998**, 211. (c) Wu, Q.; Esteghamatian, M.; Hu, N.-X.; Popovic, Z.; Enright, G.; Tao, Y.; D'Iorio, M.; Wang, S. *Chem. Mater.* **2000**, *12*, 79. (d) Anderson, S.; Weaver, M. S.; Hudson, A. J. *Synth. Met.* **2000**, *111*−*112*, 459. (e) Son, H. J.; Jang, H.; Jung, B.-J.; Kim, D.; Shin, C. H.; Hwang, K. Y.; Shim, H.-K.; Do, Y. *Synth. Met.* **2003**, *137*, 1001. (f) Lee, J. E.; Choi, G. C.; Rim, B. O.; Kim, S. M.; Park, N. G.; Ha, Y. K.; Kim, Y. S. *Mater. Sci. Eng., C* **2004**, *24*, 269.

(8) (a) Cui, Y.; Liu, Q.-D.; Bai, D.-R.; Jia, W.-L.; Tao, Y.; Wang, S. *Inorg. Chem.* **2005**, *44*, 601. (b) Chen, H.-Y.; Chi, Y.; Liu, C.-S.; Yu, J.-K.; Cheng, Y.-M.; Chen, K.-S.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H.; Carty, A. J.; Yeh, S.-J.; Chen, C.-T. *Adv. Funct. Mater.* **2005**, *15*, 567. (c) Liu, Q.-D.; Mudadu, M. S.; Thummel, R.; Tao, Y.; Wang, S. *Adv. Funct. Mater.* **2005**, *15*, 143. (d) Teng, Y. L.; Kan, Y. H.; Su, Z. M.; Liao, Y.; Yan, L. K.; Yang, Y. J.; Wang, R. S. *Int. J. Quantum Chem.* **2005**, *103*, 775.

(9) Gottlieb, H. E.; Kotylar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

(10) (a) Shoji, E.; Miyatake, K.; Hlil, A. R.; Hay, A. S.; Maindron, T.; Jousseaume, V.; Dodelet, J. P.; Tao, Y.; D'Iorio, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3006. (b) Kappaun, S.; Sovic, T.; Stelzer, F.; Pogantsch, A.; Zojer, E.; Slugovc, C. *Org. Biomol. Chem.* **2006**, *4*, 1503.

(11) (a) Dingemans, T. J.; Murthy, N. S.; Samulski, E. T. *J. Phys. Chem. B* **2001**, *105*, 8845. (b) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.

(2C, fl$_5^9$, fl$_7^9$), 40.5, 40.4 (4C, Hex^1), 31.7, 29.9, 29.8, 24.0, 24.0, 22.7, 22.7 (16C, Hex^{2,3,4,5}), 14.2, 14.1 (4C, Hex^6). IR (film on NaCl): 3061, 2954, 2927, 2856, 1597, 1498, 1454, 1370, 1339, 1277, 1214, 1098, 1073, 1005, 892, 832, 791, 741, 694 cm^{-1}.

8-Hydroxy-5,7-bis(9,9-dihexylfluoren-2-yl)quinoline (8). 8 was prepared referring to the modified procedure of Vankar and Rao.[10b,12] A suspension of **5** (210 mg, 0.233 mmol) and KI (1.011 g, 6.090 mmol, 26.1 equiv) in CH_3CN (25 mL) was carefully degassed. After adding $BF_3{\cdot}Et_2O$ (0.7 mL, 5.5 mmol, 23.7 equiv) the reaction mixture was heated for 24 h under an inert atmosphere of argon at 80 °C. Quenching with water and adding aqueous $Na_2S_2O_3$ (10%, 4 mL) and aqueous HCl (10%, 2 mL) gave the crude product after extraction with CH_2Cl_2 and drying over Na_2SO_4. The product was recrystallized from hot methanol yielding 20.0 mg of **8** (10.6%). Anal. Calcd for $C_{59}H_{71}NO$ (MW 810.20): C, 87.46; H, 8.83. Found: C, 87.23; H, 9.00. ^{1}H NMR (δ, 20 °C, $CDCl_3$): 9.10−8.80 (bs, 1H, O*H*), 8.78 (d, $^3J_{HH}$ = 3.9 Hz, 1H, q^2), 8.29 (d, $^3J_{HH}$ = 8.3 Hz, 1H, q^4), 7.80−7.18 (m, 16H, q^{3,6}, fl$_5^{1,3,4,5,6,7,8}$, fl$_7^{1,3,4,5,6,7,8}$), 1.97−1.91 (m, 8H, Hex^1), 1.08−0.94 (m, 24H, Hex^{3,4,5}), 0.71−0.66 (m, 20H, Hex^{2,6}). ^{13}C NMR (δ, 20 °C, $CDCl_3$): 151.4 (1C, q^8), 151.2, 151.1, 151.0, 150.8, 141.2, 141.0 (6C, q^{2,8a}, fl$_5^{8a,9a}$, fl$_7^{8a,9a}$), 140.8, 140.8, 140.7, 140.6, 140.5, 137.9, 136.2, 131.4 (8C, q^{5,7}, fl$_5^{2,4a,4b}$, fl$_7^{2,4a,4b}$), 130.3 (1C, q^4), 129.0, 128.3, 127.4, 127.1, 127.0, 126.9, 126.8, 124.8, 124.3, 123.1, 123.1 (11C, q^6, fl$_5^{1,4,5,7,8}$, fl$_7^{1,4,5,7,8}$), 127.1 (1C, q^{4a}), 121.4 (1C, q^3), 120.0, 120.0, 119.7, 119.7 (4C, fl$_5^{3,6}$, fl$_7^{3,6}$), 55.3 (2C, fl$_5^9$, fl$_7^9$), 40.5 (4C, Hex^1), 31.7, 31.6, 29.9, 29.8, 24.0, 24.0, 22.7 (16C, Hex^{2,3,4,5}), 14.2 (4C, Hex^6). IR (film on NaCl): 2954, 2927, 2856, 1578, 1500, 1465, 1449, 1411, 1375, 1325, 1276, 1260, 1166, 1099, 831, 791, 740, 722 cm^{-1}.

General Procedure for the Preparation of 5,7-Disubstituted Organoboron Quinolinolates. According to Wu and co-workers,[7] the corresponding 8-hydroxyquinoline derivate (**1**, **6**, **7**, and **8**) was dissolved in dry CH_2Cl_2 under an inert argon atmosphere. The reaction mixture was stirred for 24 h at room temperature after a solution of triphenylborane in tetrahydrofuran (THF) had been added. Quenching with water, extraction with CH_2Cl_2, drying over Na_2SO_4, and precipitation from CH_2Cl_2/MeOH gave the pure products **9**, **10**, **11**, and **12**. Although **9** has already been published in a patent, we want to report our findings on this compound for a better demonstration of the influence of the conjugation length on the material properties.[13]

(κ^2-(*N*,*O*)-5,7-Dibromo-8-quinolinolate)diphenylborane (9). The preparation of **9** could be achieved by the treatment of **1** (105 mg, 0.347 mmol) with BPh_3 (1.6 mL, 0.25 M in THF, 0.4 mmol, 1.2 equiv) in dry CH_2Cl_2 (6 mL) under an inert atmosphere of argon according to the general procedure yielding 97.9 mg of a yellow-greenish solid (60.3%). Anal. Calcd for $C_{21}H_{14}BBr_2NO$ (MW 466.96): C, 54.01; H, 3.02. Found: C, 54.22; H, 3.28. ^{1}H NMR (δ, 20 °C, DMSO-d_6): 9.29 (d, $^3J_{HH}$ = 5.4 Hz, 1H, q^2), 8.75 (d, $^3J_{HH}$ = 8.3 Hz, 1H, q^4), 8.25 (s, 1H, q^6), 8.07 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, q^3), 7.36−7.18 (m, 10H, ph$_1^{2,3,4,5,6}$, ph$_2^{2,3,4,5,6}$). ^{13}C NMR (δ, 20 °C, DMSO-d_6): 155.8 (1C, q^8), 146.6 (2C, ph$_1^1$, ph$_2^1$), 144.2 (1C, q^2), 140.4, 137.2 (2C, q^{4,6}), ca. 138.5 (1C, q^{8a}), 132.2, 128.2 (8C, ph$_1^{2,3,5,6}$, ph$_2^{2,3,5,6}$), 127.6 (2C, ph$_1^4$, ph$_2^4$), 127.2 (1C, q^{4a}), 126.5 (1C, q^3), 105.0, 101.6 (2C, q^{5,7}). MALDI-MS (*m*/*z*): [M$\cdot$Na$^+$] 487.9424 (calcd 487.9437).

(κ^2-(*N*,*O*)-5,7-Diphenyl-8-quinolinolate)diphenylborane (10). 6 (100 mg, 0.336 mmol) and BPh_3 (1.5 mL, 0.25 M in THF, 0.4 mmol, 1.2 equiv) were stirred in dry CH_2Cl_2 under an inert atmosphere of argon for 24 h following the general procedure. A total of 108.1 mg of the product could be isolated as a yellow solid (69.7%). Anal. Calcd for $C_{33}H_{24}BNO$ (MW 461.36): C, 85.91; H, 5.25. Found: C, 86.12; H, 5.40. ^{1}H NMR (δ, 20 °C, $CDCl_3$): 8.63 (d, $^3J_{HH}$ = 4.9 Hz, 1H, q^2), 8.52 (d, $^3J_{HH}$ = 8.3 Hz, 1H, q^4), 8.20 (d, $^3J_{HH}$ = 7.3 Hz, 2H, ph$_7^{2,6}$), 7.99 (s, 1H, q^6), 7.56−7.20 (m, 19H, q^3, ph$_1^{2,3,4,5,6}$, ph$_2^{2,3,4,5,6}$, ph$_5^{2,3,4,5,6}$, ph$_7^{3,4,5}$). ^{13}C NMR (δ, 20 °C, $CDCl_3$): 155.2 (1C, q^8), ca. 147.3 (2C, ph$_1^1$, ph$_2^1$), 139.7 (1C, q^2), 138.6, 138.3 (2C, ph$_5^1$, ph$_7^1$), 137.7, 132.9 (2C, q^{4,6}), 136.3 (1C, q^{8a}), 132.2, 127.7 (8C, ph$_1^{2,3,5,6}$, ph$_2^{2,3,5,6}$), 129.8, 129.1, 128.8, 128.5, 127.1 (10C, ph$_5^{2,3,4,5,6}$, ph$_7^{2,3,4,5,6}$), 127.8 (2C, ph$_1^4$, ph$_2^4$), 126.9, 126.2, 122.0 (4C, q^{4a,5,7}), 122.5 (1C, q^3). IR (film on NaCl): 3034, 2927, 1600, 1491, 1465, 1443, 1379, 1338, 1199, 1148, 1105, 903, 881, 818, 757, 735, 702 cm^{-1}. MALDI-MS (*m*/*z*): [M$\cdot$Na$^+$] 484.1794 (calcd 484.1855).

(κ^2-(*N*,*O*)-5,7-Bis(biphenyl-4-yl)-8-quinolinolate)diphenylborane (11). Referring to the general procedure, **7** (190 mg, 0.423 mmol) and BPh_3 (1.9 mL, 0.25 M in THF, 0.5 mmol, 1.1 equiv) were stirred in dry CH_2Cl_2 (10 mL) under an inert atmosphere of argon for 24 h yielding 127.4 mg of a yellow solid (49.1%). Anal. Calcd for $C_{45}H_{32}BNO$ (MW 613.26): C, 88.09; H, 5.26. Found: C, 88.33; H, 5.44. ^{1}H NMR (δ, 20 °C, $CDCl_3$): 8.58 (d, $^3J_{HH}$ = 4.9 Hz, 1H, q^2), 8.52 (d, $^3J_{HH}$ = 8.3 Hz, 1H, q^4), 8.25 (d, $^3J_{HH}$ = 8.8 Hz, 2H, bp$_7^{2,6}$), 8.02 (s, 1H, q^6), 7.71−7.17 (m, 27H, q^3, ph$_1^{2,3,4,5,6}$, ph$_2^{2,3,4,5,6}$, bp$_5^{2,3,5,6,2',3',4',5',6'}$, bp$_5^{3,5,2',3',4',5',6'}$). ^{13}C NMR ($\delta$, 20 °C, $CDCl_3$): 155.4 (1C, q^8), ca. 147.3 (2C, ph$_1^1$, ph$_2^1$), 140.9, 140.7, 140.6, 140.4, 138.7, 137.2, 135.2 (7C, q^{8a}, bp$_5^{1,1'}$,4, bp$_7^{1,1'}$,4), 139.8 (1C, q^2), 137.8, 132.6 (2C, q^{4,6}), 132.2, 127.8 (8C, ph$_1^{2,3,5,6}$, ph$_2^{2,3,5,6}$), 130.2, 129.1, 129.0, 128.8, 127.8, 127.6, 127.5, 127.3, 127.2, 127.1 (20C, ph$_1^4$, ph$_2^4$, bp$_5^{2,3,5,6,2',3',4',5',6'}$, bp$_7^{2,3,5,6,2',3',4',5',6'}$), 126.5, 126.3, 121.7 (3C, q^{4a,5,7}), 122.6 (1C, q^3). IR (film on NaCl): 3027, 1600, 1499, 1488, 1463, 1432, 1381, 1261, 1199, 1148, 1007, 903, 841, 801, 764, 735, 699 cm^{-1}. MALDI-MS (*m*/*z*): [M$\cdot$Na$^+$] 636.2474 (calcd 636.2482).

(κ^2-(*N*,*O*)-5,7-Bis(9,9-dihexylfluoren-2-yl)-8-quinolinolate)diphenylborane (12). Stirring of **8** (131 mg, 0.162 mmol) in dry CH_2Cl_2 (10 mL) with BPh_3 (0.8 mL, 0.25 M in THF, 0.2 mmol, 1.2 equiv) for 24 h under an inert atmosphere of argon gave the orange product in a yield of 62.0 mg (39.3%). Anal. Calcd for $C_{71}H_{80}BNO$ (MW 974.21): C, 87.53; H, 8.28. Found: C, 87.91; H, 8.59. ^{1}H NMR (δ, 20 °C, $CDCl_3$): 8.65 (d, $^3J_{HH}$ = 4.9 Hz, 1H, q^2), 8.48 (d, $^3J_{HH}$ = 8.3 Hz, 1H, q^4), 8.26 (s, 1H, fl$_7^1$), 8.18 (d, $^3J_{HH}$ = 7.8 Hz, 1H, fl$_7^3$), 8.10 (s, 1H, q^6), 7.83−7.70, 7.54−7.48, 7.36−7.19 (m, 22H, ph$_1^{2,3,4,5,6}$, ph$_2^{2,3,4,5,6}$, fl$_5^{1,3,4,5,6,7,8}$, fl$_7^{4,5,6,7,8}$), 7.44 (s, 1H, q^3), 2.06−1.92 (m, 8H, Hex^1), 1.12−0.97 (m, 24H, Hex^{3,4,5}), 0.77−0.65 (m, 20H, Hex^{2,6}). ^{13}C NMR (δ, 20 °C, $CDCl_3$): 155.1 (1C, q^8), 151.6, 151.6, 151.1, 151.1, 141.0, 140.9, 140.8, 140.6 (8C, fl$_5^{8a,9a,4a,4b}$, fl$_7^{8a,9a,4a,4b}$), 147.7 (2C, ph$_1^1$, ph$_2^1$), 139.7 (1C, q^2), 138.7 (1C, q^{8a}), 137.7 (1C, q^4), 136.9, 135.0 (2C, fl$_5^2$, fl$_7^2$), 134.9, 132.6, 128.6, 128.1, 127.5, 127.2, 127.1, 127.0, 126.9 (12C, ph$_1^4$, ph$_2^4$, fl$_5^{1,4,5,7,8}$, fl$_7^{1,4,5,7,8}$), 127.4, 126.3 (2C, q^{5,7}), 132.0, 127.7 (8C, ph$_1^{2,3,5,6}$, ph$_2^{2,3,5,6}$), 124.3, 123.1, 123.1, 122.2, 120.2, 120.0 (6C, q^{3,6}, fl$_5^{3,6}$, fl$_7^{3,6}$), 122.8 (1C, q^{4a}), 55.3, 55.3 (2C, fl$_5^9$, fl$_7^9$), 40.6, 40.5, (4C, Hex^1), 31.7, 31.6, 30.0, 29.9, 24.1, 24.0, 22.7 (16C, Hex^{2,3,4,5}), 14.2, 14.1 (4C, Hex^6). IR (film on NaCl): 3048, 3007, 2955, 2928, 2855, 1618, 1504, 1488, 1466, 1450, 1432, 1378, 1336, 1261, 1199, 1149, 1096, 1021, 927, 902, 881, 801, 739, 701 cm^{-1}. MALDI-MS (*m*/*z*): [M$\cdot$Na$^+$] 996.6194 (calcd 996.6242).

X-ray Diffraction. Single crystals of **9** were obtained from ether diffusion into a saturated CH_2Cl_2 solution. X-ray data were collected on a Bruker AXS Smart charge-coupled device (CCD) area detector diffractometer at 173(2) K using graphite monochromatized Mo Kα radiation, λ = 0.710 73 Å, and 0.3° ω scan frames covering a complete sphere of the reciprocal space. After data integration with the SAINT program, corrections for absorption, the λ/2 effect of

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(12) Vankar, Y. D.; Rao, C. T. *J. Chem. Res.* **1985**, 232.

(13) Heuer, H.-W.; Wehrmann, R.; Elschner, A. European Patent 969531, 2000.

the detector, and crystal decay were applied to the data using the SADABS program.[14] The structure was solved by direct methods using the SHELXS97 program. Structure refinement on F^2 was carried out with the SHELXL97 program.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Final R indices [$4303I > 2\sigma(I)$, 232 parameters] are R1 = 0.0251 and wR2 = 0.0589. Salient crystal data for **9** are $C_{21}H_{14}BBr_2NO$, $M = 466.96$, monoclinic, $P2_1/n$, $a = 8.9807(4)$, $b = 18.1461(9)$, $c = 11.2254(5)$ Å, $\beta = 101.851(1)°$, $V = 1790.35(14)$ Å^3, and $Z = 4$; atomic coordinates, thermal displacement parameters, bond lengths, and bond angles of **9** are given in a CIF (see Supporting Information).

Mass Spectroscopy. Solid samples were dissolved in THF (0.5−1 mg/mL); 1,8,9-trihydroxyanthracene was used as the matrix (10 mg/mL in THF), and sodium trifluoroacetate was used as the ionizing agent (1 mg/mL in THF). Solutions were mixed in the cap of a microtube in the ratio of 1 μL:5 μL:0.5 μL, and 0.5 μL of the resulting mixture was spotted onto the target and allowed to air-dry. Calibration was carried out with appropriately selected oligoethyleneglycols.

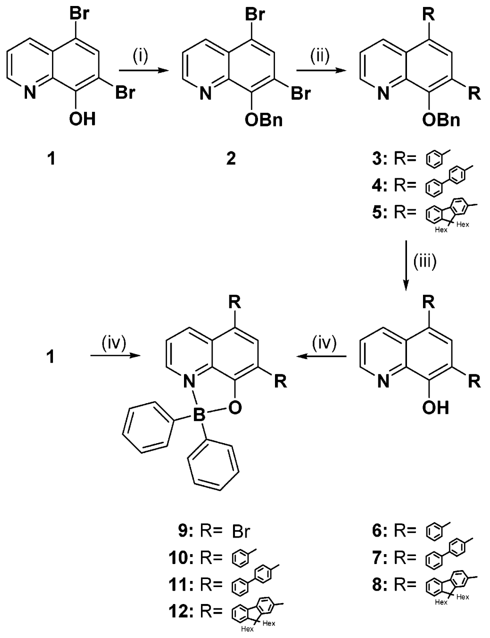
Thermal Properties. Thermal properties were determined in aluminum pans with a heat rate of 10 °C/min in a nitrogen flow of approximately 35 mL/min in the case of the combined DSC/TGA experiments. DSC measurements of compound **12** were performed in aluminum pans with heating rates of 20 and 10 °C/min in a nitrogen flow of 20 mL/min.

Absorption and Fluorescence Measurements. For solution investigations the corresponding compound was dissolved in and diluted with $CHCl_3$. UV/vis absorption and PL spectra were recorded using quartz cuvettes of 1 cm path length. PL spectra were obtained by irradiation with UV light at 348 nm. PL quantum yields of compounds **9**−**12** were determined in diluted $CHCl_3$ solutions at room temperature using quinine sulfate dihydrate in 0.1 N H_2SO_4 as the standard with excitation wavelengths of 420, 435, 440, and 450 nm, respectively. Samples for film investigations were prepared by spin coating (1000 rpm) of solutions of **9**−**12** (1 g/L) in $CHCl_3$ onto quartz plates.

Cyclic Voltammetry. The electrochemical properties of **9**−**12** were probed by cyclic voltammetry with a scan rate of 0.1 V/s in solutions of tetrabutylammonium perchlorate in dry CH_2Cl_2 (0.7 M) under an inert atmosphere of argon with an analyte concentration of 1 mM. Ferrocene was used for referencing and quantification of the obtained cyclic voltammograms.

Device Fabrication. OLEDs were fabricated on glass substrates with transparent indium tin oxide (ITO) anodes in a commonly used sandwich structure. First, the samples were cleaned in an ultrasonic bath using a series of different organic solvents. Subsequently, they were etched for 10 min in an oxygen plasma. Then poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) was applied by spin coating under ambient conditions (approximate thickness 50 nm). After annealing the samples in a vacuum oven at a temperature of 160 °C for at least 20 min, followed by cooling to room temperature over 40 min, the samples were transferred directly to an evaporation chamber. At a base pressure lower than 2×10^{-6} mbar, 40 nm of *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD) followed by 40 nm of the boron containing compound were evaporated by conductive heating in a quartz tube. Ca top electrodes and an Al capping layer were evaporated at the same base pressure in an evaporation chamber located in an Ar glovebox (exposure to air between the evaporation processes in the two chambers was kept at a minimum). Devices were tested in an Ar atmosphere to avoid oxidation. Device characteristics were recorded using a customized setup. While current/voltage characteristics were measured using a Keithley 236 source measure unit, a photodiode mounted in an integrating sphere and connected to a Keithly 181 nanovoltmeter was used to measure the emission intensity. To obtain luminance values (for devices operated in continuous wave (cw) mode), the setup was calibrated using a luminance meter LS100 (Minolta) near the maximum emission intensity. Electroluminescence (EL) spectra were obtained with a DB401 UV CCD detector (Andor) mounted on an Oriel 77400 grid spectrometer. The spectral sensitivity was calibrated with an Ocean Optics LS-1-CAL tungsten−halogen lamp.

Scheme 1. Synthesis of 5,7-Disubstituted Organoboron Quinolinolates[a]



[a] (i) Benzyl bromide, KOH, EtOH, H_2O, 100 °C, 20 h; (ii) boronic acid, $[Pd(PPh_3)_4]$, Na_2CO_3, toluene, EtOH, H_2O, Ar, 95 °C, 24 h; (iii) $BF_3 \cdot Et_2O$, KI, CH_3CN, Ar, 80 °C, 24 h; (iv) BPh_3 in THF, CH_2Cl_2, Ar, room temperature, 24 h. Bn = benzyl.

Results and Discussion

Synthesis. We have recently reported a general procedure for the preparation of 5,7-disubstituted 8-hydroxyquinoline derivatives starting from commercially available 5,7-dibromo-8-hydroxyquinoline (**1**) as depicted in Scheme 1.[10b] Benzylation of the starting material by refluxing **1** with an excess of benzyl bromide in EtOH, water, and KOH for 20 h gave analytically pure 8-benzyloxy-5,7-dibromoquinoline (**2**) after column chromatography on silica in 43% yield.[10a] For the extension of the π-conjugation length, **2** was converted into 8-benzyloxy-5,7-diphenylquinoline (**3**), 8-benzyloxy-5,7-bis(biphenyl-4-yl)quinoline (**4**), and 8-benzyloxy-5,7-bis(9,9-dihexylfluoren-2-yl)quinoline (**5**) via a Suzuki cross-coupling reaction using the catalyst tetrakis(triphenylphospine)palladium $[Pd(PPh_3)_4]$. The C,C-cross-coupling reaction of **2** with the corresponding boronic acid was performed within 24 h at 95 °C in a solvent mixture of toluene, EtOH, and water using Na_2CO_3 as the base (yield

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(14) *SMART*, version 5.625; *SAINT*, version 6.22; *SADABS*, version 2.10; *XPREP*, version 6.12; *SHELXTL*, version 6.12. Bruker AXS, Inc.: Madison, WI.

(15) Sheldrick, G. M. *SHELXS97*; *SHELXL97*. University of Göttingen, Göttingen, 1997.

30−80%).[10] The removal of the benzyloxy group was achieved by refluxing a suspension of the corresponding 5,7-disubstituted 8-benzyloxy compound (**3**−**5**), KI, and $BF_3 \cdot Et_2O$ in CH_3CN. The 5,7-disubstituted 8-hydroxyquinoline derivatives were obtained after precipitation from hot methanol in moderate yields (11−41%).[10b,12]

For the synthesis of organoboron quinolinolates several methods are described in the literature. Most commonly used is the exchange of an alkyloxy group in dialkoxyorganoboranes or the esterification of organoboronic acids. An alternative way of preparation is the alcoholysis of triorganoboranes under the cleavage of one organic substituent.[4e] The latter one was our method of choice because of the commercial availability and ease of handling of the triphenylborane solution in THF. The organoboron quinolinolates (κ^2-(*N*,*O*)-5,7-dibromo-8-quinolinolate)diphenylborane (**9**), (κ^2-(*N*,*O*)-5,7-diphenyl-8-quinolinolate)diphenylborane (**10**), (κ^2-(*N*,*O*)-5,7-bis(biphenyl-4-yl)-8-quinolinolate)diphenylborane (**11**), and (κ^2-(*N*,*O*)-5,7-bis(9,9-dihexylfluoren-2-yl)-8-quinolinolate)diphenylborane (**12**) were prepared by dropwise addition of a BPh_3 solution (0.25 M in THF) to a solution of the corresponding 5,7-disubstituted 8-hydroxyquinoline derivative (**1**, **6**−**8**) in dry CH_2Cl_2 under an inert atmosphere of argon.[7]

Stirring for 24 h at room temperature, evaporating off the solvent, and precipitation from CH_2Cl_2/MeOH gave the products in pure form (yield 39−70%). It is worth noting that **9**−**11** could be readily precipitated from these solvents in a solid crystalline form, whereas **12** was obtained as a waxy solid. Attempts to overcome the three-step ligand synthesis for the preparation of **10** by reacting phenylboronic acid with **9** under otherwise identical conditions for the Suzuki cross-coupling reaction failed. Compounds **9**−**12** were characterized by ^{1}H,^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS to determine the exact mass. All four compounds are air-stable both in the solid state and in solution. Thermal behavior and stability were further studied by simultaneous thermal analysis (STA) and DSC measurements (see below).

The ^{1}H NMR spectrum of **9** exhibits peaks equivalent of 1 proton each at 9.29, 8.75, 8.25, and 8.07 ppm as well as a signal with an intensity of 10 protons in the range of 7.36−7.18 ppm. The first four signals can be easily assigned to the protons 2, 4, 6, and 3 (in order of appearance from low to high field) of the quinolinolate moiety based on their multiplicity (cf. Experimental Section) and chemical shift, while the signal at higher field corresponds to the two phenyl rings bonded to the boron atom. The indicative quinolinolate protons in **10**, **11**, and **12** are shifted to higher field compared to that of **9**. As an example, the signals corresponding to proton 2 of the quinolinolate appear at 8.63 (in **10**), 8.58 (in **11**), and 8.65 ppm (in **12**). Particularly indicative for the π-extended derivatives is the appearance of signals for two protons at a comparatively low field around 8.20 ppm. These peaks were assigned to the ortho protons of the aromatic substituent in the 7 position of the quinolinolate core. ^{13}C NMR spectra were also in agreement with the proposed structure. Interestingly, the carbon 8 of the quinolinolate moiety (i.e., C^8−O) is hardly shifted in all four compounds under investigation. Corresponding C^8 signals are 155.8 (in **9**), 155.2 (in **10**), 155.4 (in **11**), and 155.1 ppm (in **12**). As expected, the C^1 carbons of the two phenyl substituents of the boron atom are very low in intensity and broadened. Resonances were obtained in the range of 147.6−146.6 ppm.

To obtain further data to confirm the identity of the prepared complexes, exact masses were determined using MALDI-TOF MS. Among the expected pseudo-molecular ions $[9\text{-Na}]^+$ − $[12\text{-Na}]^+$, fragment ions with a mass corresponding to $[9\text{-}C_6H_5]^+$ − $[12\text{-}C_6H_5]^+$ were also detected. These fragmentation processes became more important within the series **9**−**12** (cf. Supporting Information). For **12**, $[12\text{-}C_6H_5]^+$ is clearly the base peak. Hohaus and Riepe[16] reported that the ratio of $[M]^+/[M-C_6H_5]^+$ observed in electron impact mass spectra of comparable compounds can be used as an estimate for the stability of 8-quinolinolate−boron chelates. Higher intensities of the $[M-C_6H_5]^+$ peak indicate a stronger binding of the chelate ligand. Applying this argument, an increase of the relative stability of the chelation of the quinolinolate ligands upon extension of the π system was obtained. To ensure the identity of the prepared compounds, finally, elemental analyses were performed, which were in agreement with the expected data.

Crystal Structure. To further confirm the structural identities of the formed organoboron quinolinolates, we tried to grow single crystals from ether diffusion into saturated CH_2Cl_2 solutions of **9**−**12**. Only compound **9** could be crystallized by this method, while attempts to prepare single crystals of **10**, **11**, and **12** by the above-mentioned methodology and alternatively by layering of CH_2Cl_2 solutions with *n*-pentane were unsuccessful. According to literature, the growth of single crystals suitable for X-ray diffraction of this class of materials is somewhat difficult.[7c] To our knowledge only a few successful examples of X-ray structure determinations of organoboron quinolinolates have been hitherto reported in the literature.[7c,8a] The boron center in **9** displays a typical tetrahedral geometry, as shown in Figure 1. The quinolinolate ligand is chelated to the boron to form a five-membered ring. Selected bond lengths and angles are given in the caption of Figure 1. The B−N, B−O, and B−C bond lengths as well as the characteristic angles are similar to those reported previously for related compounds.[7c,17]

Thermal Properties. To determine the thermal properties, especially the thermal stability of compounds **9**−**12**, heat flux DSC/TGA measurements were performed. As described by Wu and co-workers, significant effects on the melting points of organoboron quinolinolates are obtained by enhancing the intermolecular π−π interactions.[7c] In the case of 8-quinolinolatodiethylborane, 8-quinolinolatodiphenylborane, and 8-quinolinolatodi(2-naphthyl)borane, an increase

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(16) (a) Hohaus, E.; Riepe, W. *Z. Naturforsch.* **1973**, *28B*, 440. (b) Hohaus, E.; Riepe, W. *Z. Naturforsch.* **1976**, *31B*, 324.

(17) (a) Liu, S.-F.; Seward, C.; Aziz, H.; Hu, N.-X.; Popovic, Z.; Wang, S. *Organometallics* **2000**, *19*, 5709. (b) Niedenzu, K.; Deng, H.; Knoeppel, D.; Krause, J.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 3162. (c) Hsu, L. Y.; Mariategui, J. F.; Niedenzu, K.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 143. (d) Kiegel, W.; Lubkowitz, G.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1991**, *69*, 1217. (e) Dal Negro, A.; Ungaretti, L.; Perotti, A. *Dalton Trans.* **1972**, *15*, 1639.

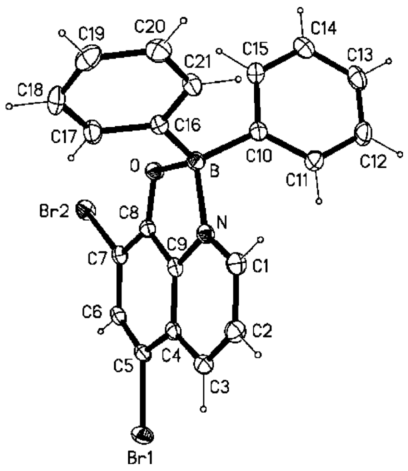

Figure 1. ORTEP of **9** (40% ellipsoids). Selected bond lengths (Å) and angles (deg): B−N, 1.629(2); B−O, 1.542(2); B−C(10), 1.604(3); B−C(16), 1.600(3); Br(1)−C(5), 1.889(2); Br(2)−C(7), 1.883(2); C(8)−O−B, 110.3(1); C(1)−N−C(9), 119.3(1); C(1)−N−B, 132.8(1); C(9)−N−B, 107.9(1); O−B−C(16), 111.7(1); O−B−C(10), 108.6(1); C(10)−B−C(16), 117.0(1); and O−B−N, 98.4(1).

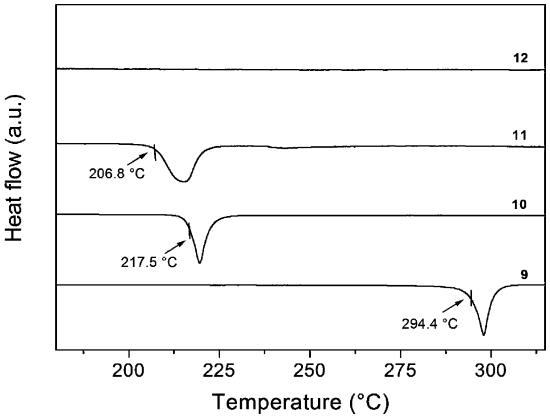

Figure 2. Measurement of the melting points by heat flux DSC.

of the melting point of 45 °C to above 200 °C was observed.[7c] Our measurements (Figure 2) revealed the inverse effect by extension of the π-conjugation length of the 8-hydroxyquinoline ligand. While **9** exhibits the onset of the melting point at 295 °C, the melting points of **10** and **11** are reduced to 218 °C and 207 °C, respectively. For **12**, we succeeded in the preparation of a semicrystalline sample analyzed by power-compensated DSC revealing a T_g value of 52.2 °C and a melting point of 160 °C. It should be noted that the melting point of **12** could only be detected in the first heating run which can be rationalized by the fact that **12** does not readily recrystallize under the conditions of the DSC experiment. These results clearly indicate a decreased possibility of intermolecular interactions and demonstrate the impact of modifying the ligand on the material properties.

Concerning practical applications it is known that materials with good thermal stability improve device lifetimes.[18] The thermal stability of compounds **9**−**12** was evaluated by TGA measurements under a nitrogen atmosphere. As shown in Figure 3, all materials exhibit excellent thermal stability up to 290 °C. While **9** decomposes immediately after melting, compounds **10**−**12** exhibit enlarged thermal stability above their melting points. The temperature at a weight loss of 5% was chosen as a measure for the thermal stability of the four compounds under investigation. From the corresponding temperature values (343 °C for **10**, 387 °C for **11**, and 377 °C for **12**), an increased thermal stability of the aryl substituted derivatives compared to that of the dibromo derivative **9** (310 °C) is evident. Furthermore, findings of the MALDI-TOF MS investigation discussed above are corroborated by these data. It is worth noting that thermal stability is also crucial for an application in thermal evaporation processes. Our results and the results of Wu et al. provide a convenient method for tuning the thermal properties of organoboron quinolinolates.[7c]

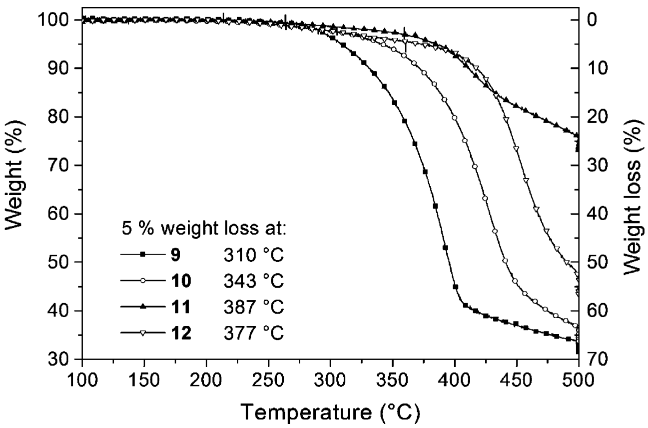

Figure 3. TGA thermograms of compounds **9**−**12**.

Electrochemical Properties. The electrochemical properties of the organoboron quinolinolates **9**−**12** were studied, and the energy levels of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were estimated. The oxidation of compound **9** in CH_2Cl_2/Bu_4NClO_4 (Figure 4a) at a platinum disk electrode shows a strong irreversible oxidation peak at 1.31 V (peak potential) versus ferrocene/ferrocenium (Fc/Fc$^+$). The latter redox couple was used as an internal standard to calibrate the potential of the silver pseudo-reference electrode and, because of its ideally reversible one-electron transfer, for the estimation of the number of electrons transferred in the electrochemical reactions of the investigated compounds **9**−**12**. Compared to the peak height of an equimolar Fc/Fc$^+$ couple the oxidation of **9** is close to a three-electron transfer. Compared to **9**, compounds **10**−**12** show an additional irreversible peak at lower oxidation potentials. The peak potentials are 0.98, 0.96, and 0.86 V, respectively. The peaks have approximately the same height as that of Fc/Fc$^+$ which indicates a one-electron transfer. The facilitated oxidation of compounds **9**, **10**, and **11**, compared to **9**, can be rationalized by the extension of the aromatic π system of the quinolinolate moiety (cf. Figure 4a). On reduction, compound **9** has a broad wave starting at −1.2 V and a distinct irreversible one-electron reduction peak with a peak potential of −1.73 V (see Figure 4b). Compounds **10**−**12** show a similar behavior with a broad wave between approximately −1.1 V and −1.8 V; then a sharp one-electron reduction peak appears at −1.97, −1.95, and −1.99 V, respectively, which is slightly reversible at the scan rates of 0.1 V/s. A distinct influence of the substituents R cannot be

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(18) Kim, Y. H.; Ahn, J. H.; Shin, D. C.; Kwon, S. K. *Polymer* **2004**, *45*, 2525.

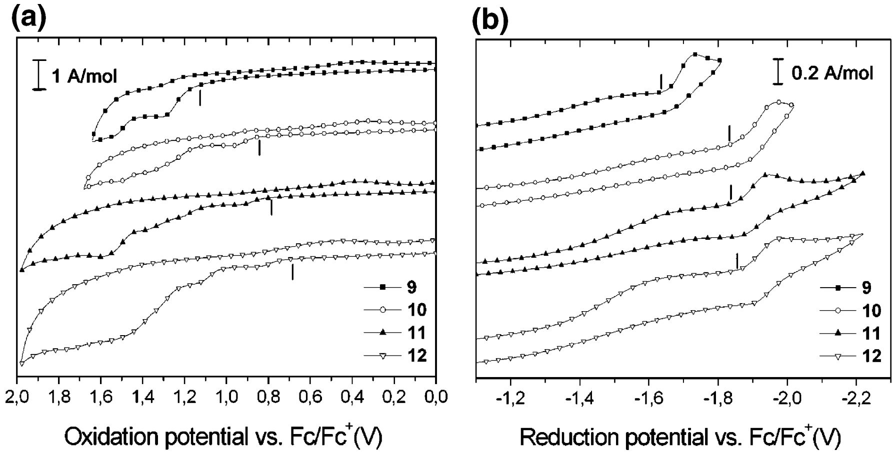

Figure 4. (a) Cyclic voltammograms of compounds **9**−**12** (anodic runs) and (b) cyclic voltammograms of compounds **9**−**12** (cathodic runs), both performed in CH_2Cl_2/Bu_4NOCl_4. The ticks mark the onsets used for the calculation of HOMO and LUMO energy levels.

Table 1. Absorption, Emission, and Electrochemical Data for Compounds 9−12

compd	abs[a] $\lambda_{abs}(\epsilon)$, nm (L mol^{-1} cm^{-1})	HOMO/LUMO[b] band gap (eV)	PL$_{sol}$[c] λ_{max}, nm (energy, eV)	Q.Y.[d] ϕ, %	PL$_{film}$[e] $\lambda_{max,film}$, nm (energy, eV)
Ph_2Bq	396, 264, 242 [7c]		504 (2.46) [7c]	30 [7c]	505 (2.46)[7d], 495 (2.51)[7c]
9	420 (1870), 348 (1720), 334 (1680), 276 (22120)	−5.92/−3.17 2.75	519 (2.39)	24 ± 2	535 (2.32)
10	435 (3530), 365 (3740), 352 (3580), 299 (36100)	−5.63/−2.97 2.66	550 (2.25)	30 ± 2	564 (2.20)
11	441 (3390), 365 (5920), 316 (40990)	−5.59/−2.97 2.62	559 (2.22)	27 ± 2	577 (2.15)
12	452 (3790), 330 (41060)	−5.48/−2.94 2.54	578 (2.15)	22 ± 2	579 (2.14)

[a] Measured in $CHCl_3$. [b] HOMO and LUMO levels with respect to zero vacuum level were estimated from cyclic voltammograms performed in CH_2Cl_2/Bu_4NPF_6. The substrate concentration was 1 mM, the scan rate was 0.1 V/s, the currents were normalized to the concentration; and the potential was calibrated versus the redox couple Fc/Fc$^+$ as internal standard. [c] In $CHCl_3$, upon excitation at the absorption maximum of the absorption band at lowest energy. [d] In $CHCl_3$, at room temperature, under ambient conditions, quinine sulfate dihydrate in 0.1 N H_2SO_4 as the reference. [e] Measured on quartz substrates.

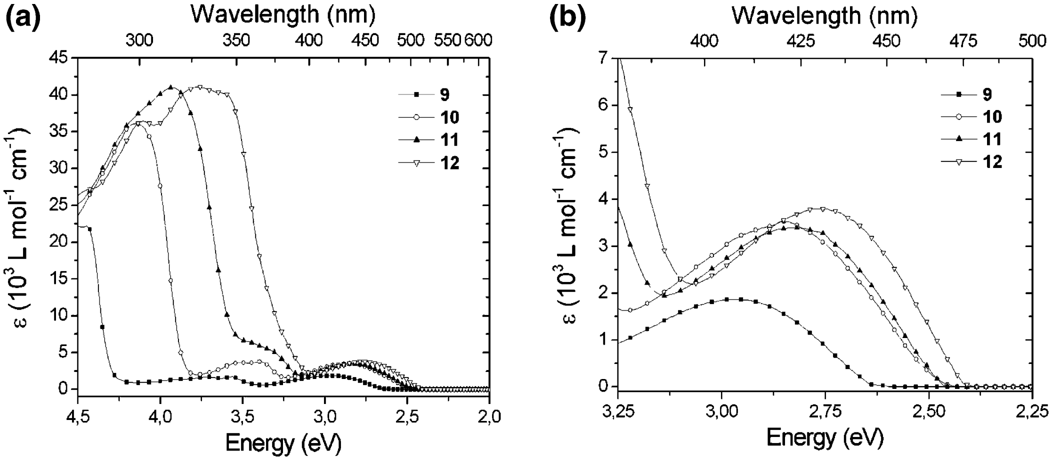

Figure 5. (a) UV−vis absorption spectra of compounds **9**−**12** in $CHCl_3$ solutions. (b) Enlarged UV−vis absorption spectra of compounds **9**−**12** in the low-energy region.

seen; we suggest that the reduction is dominated by electron transfer to the organoboron quinolinolate skeletal structure. With some restrictions the reduction and oxidation onsets of the cyclic voltammetry peaks can be used to estimate the electron affinity ($E_A \approx$ LUMO energy) and the ionization potential ($I_P \approx$ HOMO energy) of the compounds. The calculations were done assuming that the absolute level of the Fc/Fc$^+$ redox pair is 4.8 eV below the vacuum level.[19] The HOMO energy level rises with extension of conjugation of the quinolinolate core from −5.92 eV for **9** to −5.48 eV for **12**. The same accounts for the LUMO energy level, which rises from −3.17 eV to −2.94 eV within the series **9**−**12** (cf. Table 1).

Absorption. UV−vis absorption and PL spectra were recorded in diluted solutions of $CHCl_3$ at room temperature under ambient conditions. In Figure 5a, the UV−vis absorption spectra of compounds **9**−**12** are shown. All complexes exhibit similar absorption characteristics featuring absorption peaks with large extinction coefficients in the UV and absorption peaks with significantly smaller extinction coef-

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(19) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

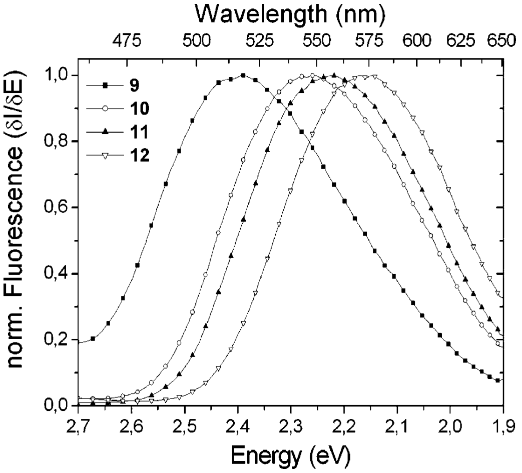

Figure 6. PL of compounds **9**−**12** in $CHCl_3$ solutions.

ficients (see Figure 5b) in the visible range. While the strongest absorbing peaks are significantly red-shifted upon extension of the π-conjugation length (from 276 nm in **9** to 330 nm in **12**, cf. Table 2), comparably small influence on the absorption bands at lower energies was noted. A similar trend was found studying the absorption of related π-extended 8-benzyloxyquinolines, and this could be related to different degrees of delocalization of the excited states onto the substituents at the 5 position.[20] The optical properties of compounds **9**−**12** are summarized in Table 1.

Luminescent Properties. Irradiation of the organoboron quinolinolates **9**−**12** with UV light results in bright greenish-yellow to orange-yellow emission in solution. As shown in Figure 6, **9** exhibits its emission maximum at 519 nm, and **10**, **11**, and **12** emit with maxima at 550, 559, and 578 nm, respectively. While the emission characteristics are considerably influenced by modifications of the 8-hydroxyquinoline ligand, PL quantum yields determined in $CHCl_3$ solutions at room temperature under ambient conditions (ranging between 22% and 30% using quinine sulfate dihydrate in 0.1 N H_2SO_4 as the standard; see Table 1) are hardly affected. For comparison, the corresponding values for Ph_2Bq are reported to be 504 nm (λ_{max} of emission) with a PL quantum yield of 30% (in this case measured relative to 9,10-diphenylanthracene in CH_2Cl_2 at room temperature).[8a] Consistent with absorption measurements and with literature data for aluminum quinolinolates with extended chromophores,[3c,10a] extension of the π system of the quinolinolate chromophore leads to a red shift of emission. PL spectra in film were determined using samples prepared by spin-coating solutions of **9**−**12** in $CHCl_3$ (1 mg/mL) onto quartz substrates (a figure showing the corresponding emission spectra can be found in the Supporting Information). Emission maxima were determined to be 535 nm (2.32 eV), 564 nm (2.20 eV), 577 nm (2.15 eV), and 579 nm (2.14 eV), respectively.

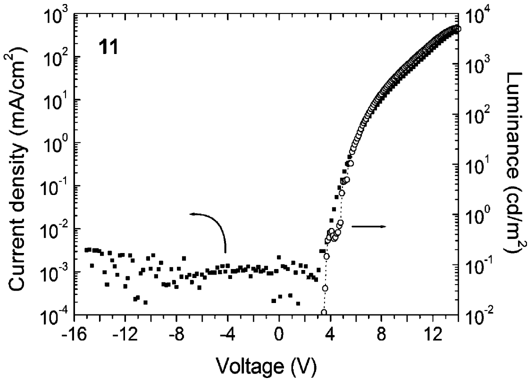

Figure 7. Current density−voltage characteristics of a device with **11** as the emissive layer.

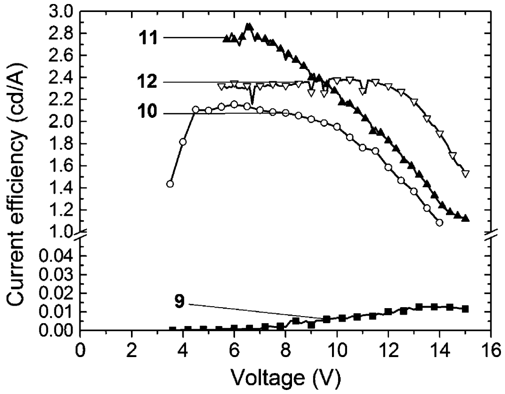

Figure 8. Current efficiency−voltage characteristics of devices with **9**−**12** as the emissive layers.

The red shift compared to solution data is attributed to intermolecular interactions in the films (solid-state effects). Although the concentrations in the spin coating process have been kept low enough to achieve very thin films with emission intensity close to the detection limit of the setup, self-absorption processes can also not be fully excluded. For comparison, Anderson et al. reported a solid-state luminescence for Ph_2Bq peaking at 505 nm,[7d] albeit a discrepancy with data from Wu et al. has to be noted. These authors report a blue shifted emission maximum in the solid state (λ_{max} = 495 nm).[7c]

Electroluminescence. EL devices using **9**, **10**, **11**, or **12** as the emitter were fabricated in a multilayer architecture consisting of ITO/PEDOT/PSS (50 nm)/TPD (40 nm)/**9**, **10**, **11**, or **12** (40 nm)/Ca (30 nm)/Al (300 nm), where TPD acts as hole-transport/electron blocking layer. TPD, the boron quinolinolates, and the metal cathodes were applied by vacuum deposition. As a representative example, the current−voltage and luminance−voltage characteristics of the device containing **11** are shown in Figure 7 (for the respective curves of the other devices, see Supporting Information). The onset voltages[21] were between 3.5 and 3.7 V for **10**, **11**, and **12** with cw luminance intensities exceeding 1000 cd/m². The materials possess good hole blocking capabilities as evidenced by the low reverse leaking currents. Current efficiencies of the devices are shown in Figure 8. While the efficiency of **9** was very low (vide infra), the maximum efficiencies of the devices fabricated with **10**, **11**, and **12** as emissive materials range from close to 2.2 cd/A for **10** to 2.8 cd/A for **11**. Interestingly, the current efficiency of the

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(20) A detailed description of absorption and emission spectra based on quantum chemical calculations of 8-benzyloxy-5,7-(diphenyl)quinoline and 8-benzyloxy-5,7-di(biphenyl-4-yl)quinoline can be found in ref 10b.

(21) Onset voltages are defined by the voltage where, in the semilogarithmic plot, the luminance rises from the background noise and where the tangent to the luminance−voltage curve is close to vertical.

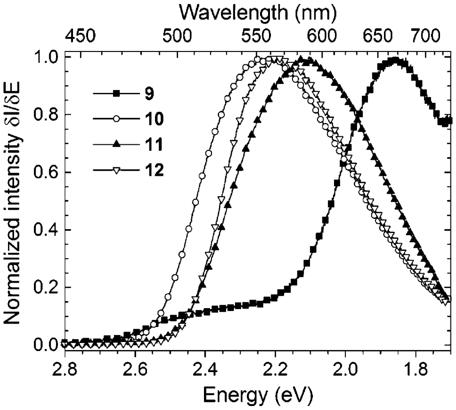

Figure 9. EL spectra of devices with **9**−**12** as the emissive layers.

device containing **12** remained virtually constant up to a bias voltage of 11.5 V; also for **10**, the decrease in current efficiency was relatively gradual.

The EL spectra of the devices containing **10**, **11**, and **12** (Figure 9) were strongly reminiscent of the PL spectra with peaks at 556 nm (2.23 eV) for **10**, 587 nm (2.11 eV) for **11**, and 566 nm (2.19 eV) for **12**. No bias-voltage dependence or change of emission spectra during operation of the devices was observed.

In sharp contrast to the devices described above, OLEDs fabricated with the dibromo derivative **9** as the emitting material showed poor performance. cw luminance remained below 25 cd/m^2, and a low current efficiency of only 0.03 cd/A at 8 cd/m^2 was achieved. The EL maximum at 667 nm (1.86 eV) is strongly red-shifted relative to the PL peak (519 nm in solution and 535 nm in the film). Moreover, the EL spectrum changed during operation with a broad shoulder growing around 2.4 eV. To ensure the chemical integrity of the used batch of **9**, a second series of devices was built using the same type of device structure but newly synthesized **9**. The results presented above were in principle reproduced (0.01 cd/A at 8 cd/m^2). To ensure that the molecule is not adversely affected by the evaporation process, PL measurement on an evaporated sample of **9** was performed, yielding the same spectra as for the spin-cast film. Therefore, the origin of the red-shifted emission in EL is not understood yet. It could be related to interaction with other materials in the multilayer structure (a similar red-shifted emission of Ph_2Bq had been attributed to exciplex formation by others)[7c] or be due to an increased influence of defects in EL caused, for example, by charge carrier trapping. The latter might be related to the reduced thermal stability of **9** or to defect states at grain boundaries. These could play a more pronounced role in **9**, as can be inferred from the more grainy structure for films consisting of this material compared to films made from **10**−**12** (a corresponding photograph can be found in Supporting Information). The results with **9** in electroluminescence lines up with the description of detrimental effects of Br groups on the EL properties of devices made of polymeric materials.[22]

Conclusion

In the present study, we have established synthetic procedures for preparing 5,7-disubstituted diphenylborane-quinolinolates. As the substituents, phenyl, biphenyl, and 9,9-dihexylfluorenyl have been introduced. The molecules display increasing thermal stability within the series **9**−**12**, with approximately the same thermal stability for **11** and **12**. Melting points, on the other hand, are decreasing within the series from 294 °C in the case of **9** to 160 °C in the case of **12**. All organoboron quinolinolates under investigation are emissive exhibiting PL quantum yields of 22−30% in solution. Emission wavelengths are progressively shifted to the red upon extension of the aromatic π system of the quinolinolate ligand. Light emitting devices based on compounds **10**, **11**, and **12** give bright yellow to orange EL with attractive onset voltages (3.5−3.7 V) and cw luminance intensities exceeding 1000 cd/m^2, while devices based on **9** give poor results, proving **9** to be an unsuitable emissive material.

Our results line up with recent reports that boron containing compounds are useful electroluminescent materials and interesting alternatives to other, widely used quinolinolate complexes such as Alq_3.[6−8,23] The influence of enlarging the aromatic π system of the quinolinolate moiety on the thermal and electro- and photochemical properties discussed here offers a rational tool for the fine-tuning of organoboron quinolinolates toward particular needs.

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Supporting Information Available: MALDI-TOF MS data and ^1H and ^{13}C NMR spectra of **9**−**12**, PL of films made of **9**−**12**, photograph of a film of **9**, and current density−voltage characteristics of devices made of **9**, **10**, and **12** (PDF), as well as crystallographic data for **9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Yang, X. H.; Yang, W.; Yuan, M.; Hou, Q.; Huang, J.; Zeng, X, R.; Cao, Y. *Synth. Met.* **2003**, *135−136*, 189.

(23) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.