DOI: 10.1002/ejoc.201100186

Electronic Structure Manipulation of (Benzothiazole)zinc Complexes: Synthesis, Optical and Electrochemical Studies of 5-Substituted Derivatives

Somnath Dey,*[a] Alexander Efimov,[a] Chandan Giri,[b] Kari Rissanen,[b] and Helge Lemmetyinen[a]

Keywords: Conducting materials / Cross-coupling / Voltammetry / Fluorescence / N,O ligands / Zinc / Borylation

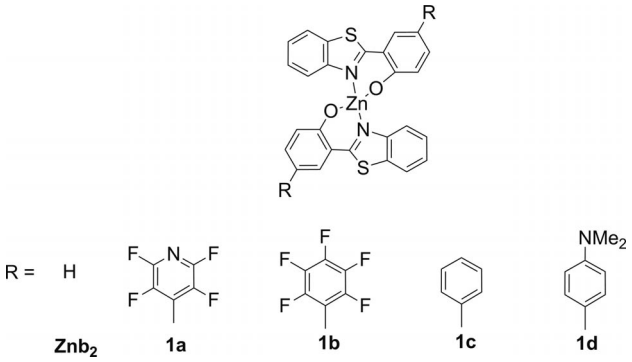
The electronic properties of bis[2-(2-hydroxyphenyl)benzothiazolato]zinc(II) complexes were tuned by attachment of electron-withdrawing and -donating aryl groups through the Suzuki–Miyaura coupling reaction. Optimization studies of the borylation reaction and Suzuki coupling of protected benzothiazoles were performed to maximize the yields of the target compounds. The absorption, emission, and electrochemical properties of the newly synthesized complexes were found to correlate to the electronic nature of the attached aryl group. Whereas the LUMO levels are less dependent on the substituents, the HOMO levels are very sensitive to the nature of the substituent, thus providing an array of organometallic complexes with gradual changes in redox potentials.

Introduction

Since Tang and VanSlyke[1,2] demonstrated the use of tris(8-hydroxyquinoline)aluminum (Alq_3) as an electron-transporting and emissive layer in organic light-emitting diodes (OLEDs), intense research has been ongoing in this area, and a number of metal-organic complexes have been studied.[3] Variable photophysical properties, high stability, and ease of fabrication resulted in considerable attention in the academic field and allowed the organic metal chelates to be used both in OLEDs as electroluminescent material and in organic solar cells as electron-transporting and buffer layers.[4] However, Alq_3 remains one of the best-known and most-used compounds because of its high electron mobility and good photophysical properties. Recently, Zhu et al. have shown that bis[2-(2-hydroxyphenyl)benzothiazolato]zinc(II) (Znb_2) has better electron mobility and can be used instead of Alq_3 in OLEDs[5] or as buffer layers in organic solar cells. Surprisingly, Znb_2 has received little attention and has been studied by only a few groups.[6,7]

Light emission from the Znb_2 complex originates from the π–π* transition in the benzothiazole ligand. Theoretical computational studies have shown that that HOMOs are mainly localized on the phenoxide part, and LUMOs are localized on the thiazole part of the benzothiazole ligand, whereas the metal atom has only a small contribution.[8] Thus, it is possible to increase or decrease the HOMO–LUMO energy gap of Znb_2 by attaching suitable electron-withdrawing or -donating groups either in the phenoxide or in the thiazole ring without changing the core structure. For tuning the emission color and redox potentials of Znb_2, we present a method that involves the introduction of electron-withdrawing and -donating aryl groups in the 5-position of the benzothiazole ligand, which ultimately modifies the HOMO energy levels and thus the HOMO–LUMO energy gap.

In this paper, the synthesis of [2-(5-aryl-2-hydroxyphenyl)benzothiazole]zinc derivatives with various aromatic substituents is reported. The Znb_2 compounds **1a**–**d**, with electron-donating and -withdrawing groups are shown in Scheme 1. In addition to the optimization of the synthetic procedures, the photophysical and electrochemical proper-



Scheme 1. Structures of bis[2-(2-hydroxyphenyl)benzothiazolato]-zinc(II) complexes.

[a] Department of Chemistry and Bioengineering, Tampere University of Technology,
P. O. Box 541, 33101 Tampere, Finland
Fax: +358-331-152-108
E-mail: somnath.dey@tut.fi
[b] Department of Chemistry, University of Javäskylä,
P. O. Box 35, 40014 Jyväskylä, Finland

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100186.

ties of the newly synthesized complexes were studied in detail. Moreover, (hydroxyphenyl)benzothiazoles exhibit excited-state proton phenomena,[9] which can also be useful and will be investigated further in a separate study.

Results and Discussion

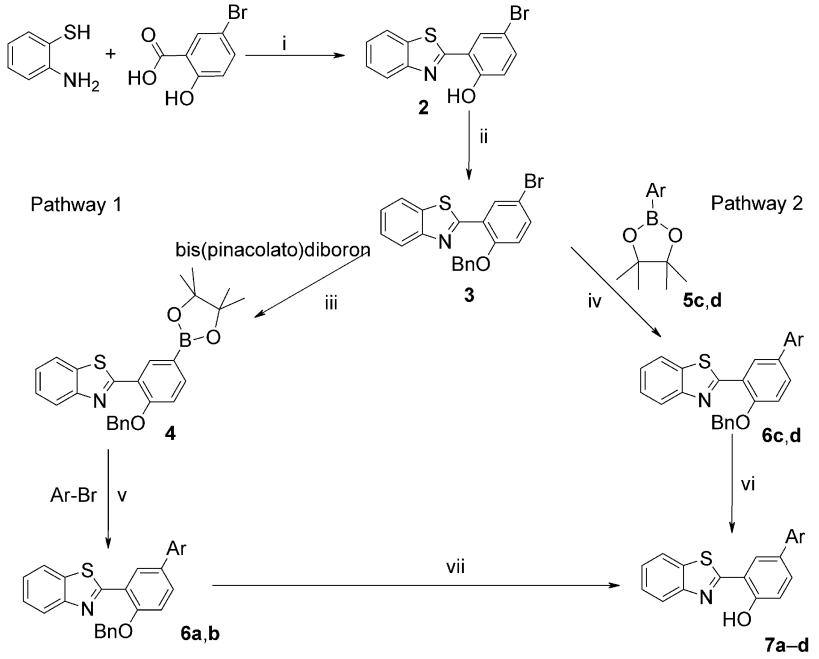
Synthesis and Characterization

The synthetic routes to the benzothiazole derivatives are shown in Scheme 2. The preparation of 2-(5-bromo-2-hydroxyphenyl)benzothiazole (**2**) was achieved by using a literature procedure,[10] with some modifications. Compound **2** was subsequently converted into protected benzothiazole **3**. Suzuki coupling normally requires two components, an arylboronic derivative and a haloarene. The choice of components depends on the nature of substituents in the aromatic ring. Thus, because pinacolborane derivatives of electron-withdrawing aryl compounds are not commercially available and are difficult to synthesize, we therefore devised two different routes for the Suzuki coupling of bezothiazole **3** with electron-withdrawing and -donating arenes. The synthesis of benzothiazole derivatives bearing electron-withdrawing groups was performed according to Pathway 1, whereas Pathway 2 was employed for the synthesis of 2-(5-arylphenyl)benzothiazoles bearing electron-donating groups.

In Pathway 1, 2-[5-(benzyloxy)phenyl]benzothiazole **3** was first converted into pinacolatoboronate ester **4** by reaction with bis(pinacolato)diboron using $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (5 mol-%) catalyst [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene] and 2 equiv. of potassium acetate in dimethyl sulfoxide (DMSO) at 80 °C.[11] Further Suzuki–Miyaura coupling reaction of pinacolatoboronate **4** and electron-withdrawing aryl bromides was performed in a toluene/water biphasic mixture by using $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (5 mol-%), tetrabutylammonium chloride (TBACl; 10 mol-%) and a 1 M aqueous solution of potassium carbonate to produce benzyl-protected 2-(5-arylphenyl)benzothiazoles **6a** and **6b**.

In Pathway 2, aryl bromides were first converted into aryl pinacolatoboronate esters **5c** and **5d** under borylation reactions condition similar to those used for the preparation of benzothiazole **4**. Protected benzothiazole **3** was coupled with aryl pinacolatoboronate esters **5c** and **5d** under reaction conditions similar to those used in Pathway 1, thus producing benzyl-protected 2-(5-arylphenyl)benzothiazoles **6c** and **6d**, respectively.

For all the Suzuki–Miyaura coupling reactions, the reaction times and yields are shown in Table 1. The reactions were optimized to give yields of more than 75% in all cases. The deprotection of 2-[5-(benzyloxy)phenyl]benzothiazoles **6c** and **6d**, having election-donating aryl groups, was performed by using Pd/C (1 wt.-equiv.) and ammonium formate (1 equiv.) in a tetrahydrofuran (THF)/methanol (1:1) mixture, producing the corresponding unprotected benzothiazoles **7c** and **7d**, respectively. The same method was not successful for the deprotection of 2-[5-(benzyloxy)phenyl]-benzothiazoles **6a** or **6b**, bearing election-withdrawing aryl groups. In these cases, deprotections were achieved by using



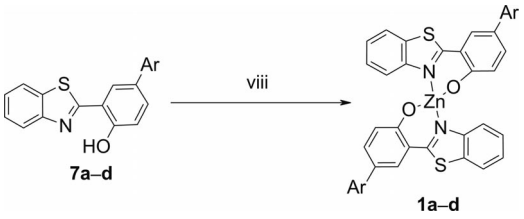
Scheme 2. Synthetic route to 2-(5-arylphenyl)benzothiazoles. Reagents and conditions: (i) polyphosphoric acid (PPA), 140 °C, 24 h; (ii) BnBr, acetone, K_2CO_3, 60 °C, 3 h; (iii) $[PdCl_2(dppf)]$, KOAc, DMSO, 80 °C, 4 h; (iv) $[PdCl_2(dppf)]$, toluene, 1 M K_2CO_3, TBACl, 90 °C; (v) $[PdCl_2(dppf)]$, toluene, 1 M K_2CO_3, TBACl, 90 °C; (vi) Pd/C, HCO_2NH_4, THF/MeOH, 60 °C, 3 h; (vii) Pd/C, HCO_2NH_4 (20 equiv.), THF/H_2O, 60 °C, 3 h.

Table 1. Summarized reaction conditions for all Suzuki–Miyaura coupling reaction.

Boronic acid pinacol ester	Aryl halide	Time [h]	Yield [%]
4	4-bromo-2,3,5,6-tetrafluoropyridine	16	81
4	1-bromo-2,3,4,5,6-pentafluorobenzene	14	79
Phenylboronic acid pinacol ester	**3**	24	78
[4-(Dimethylamino)phenyl]boronic acid pinacol ester	**3**	30	76

Pd/C (1 wt.-equiv.) and aqueous ammonium formate (20 equiv.) in THF, which gave the corresponding unprotected benzothiazoles **7a** and **7b** in good yields.

Finally, zinc complexes **1a**–**d** were obtained by treating ligands **7a**–**d** with zinc acetate in ethanol,[12] as shown in Scheme 3. All the complexes were purified by vacuum sublimation and were characterized by FTIR spectroscopy and elemental analysis. The low solubility of the synthesized complexes in common NMR solvents precluded NMR analysis of **1a**–**d**.



Scheme 3. Synthesis of benzothiazole–zinc complex derivatives. Reagents and conditions: (viii) zinc acetate, EtOH, 70 °C; reaction times for **1a**–**d**: 16, 22, 36, and 48 h, respectively.

In addition to the synthesis of (benzothiazole)zinc complexes, the borylation reaction of protected benzothiazole **3** was studied in detail. Standard literature methods involve long reaction times, which gave low yields in our case. The low yields of the target compounds were mainly due to efficient formation of cross-coupled benzothiazole dimers (30–60%). Thus, we systematically varied the catalysts, solvents, bases, and reaction times to maximize the yield of boronic esters with no or negligible amounts of side products. The optimization studies are summarized in Table 2.

Table 2. Reaction conditions for the synthesis of **4**.

Entry	Base	Solvent	Catalyst	Temp. [°C]	Time [h]	Yield [%]
1	Et_3N[a]	dioxane	$Pd(OAc)_2$	90	24	–
1	Et_3N[a]	toluene	$Pd(OAc)_2$	110	48	11
3	Et_3N[a]	dioxane	$PdCl_2(dppf)$	90	24	17
4	Et_3N[b]	THF	$PdCl_2(dppf)$	100	36	60
5	Et_3N[a]	THF	$Pd(PPh_3)_4$	100	36	35
6	KOAc[b]	DMSO	$PdCl_2(dppf)$	80	24	38
7	Et_3N[a]	DMSO	$PdCl_2(dppf)$	80	12	42
8	KOAc[b]	DMSO	$PdCl_2(dppf)$	80	12	57
9	KOAc[b]	DMSO	$PdCl_2(dppf)$	80	4	74

[a] The reactions were carried out with pinacolborane. [b] The reactions were carried out with bis(pinacolato)diboron.

It was found that by using bis(pinacolato)diboron as reactant, $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (5 mol-%) as catalyst, 2 equiv. of potassium acetate as base, and DMSO as solvent at 80 °C for 4 h, nearly 75% yield of the borylated product could be obtained with only a small amount of cross-coupled dimer. From the optimization studies, it is evident that a solvent with high polarity (DMSO > 1,4-dioxane > THF > toluene) and a weak base (Et_3N > KOAc) were needed to avoid dimerization.

Spectroscopic Studies

For all zinc complexes **1a**–**d**, the absorption and emission spectra, fluorescence quantum yields, oxidation and reduction potentials, and HOMO–LUMO energies were measured or calculated as described in the Experimental Section. The absorption and emission spectra were measured in chloroform. The results are summarized in Table 3. Emission spectra of the compounds **1a**–**d** are shown in Figure 1. The fluorescence quantum yields Φ_F were determined by using quinine sulfate (in 0.1 N H_2SO_4, quantum yield = 0.55) as a standard.[13]

Table 3. Summarized spectroscopic and electrochemical data of complexes **1a**–**d**.

Complex	λ_{max} [nm] (ε [$mol^{-1}cm^{-1}$])	λ_F [nm]	Φ_F	E^{ox} [V]	E^{red} [V]	HOMO–LUMO [eV]
Znb_2	346 (1.3×10^4)	534	0.132	0.90	–1.93	2.83
1a	337 (3.1×10^4)	505	0.194	1.16	–1.87	3.03
1b	341 (2.9×10^4)	509	0.213	1.12	–1.88	3.00
1c	356 (1.7×10^4)	556	0.111	0.83	–1.93	2.76
1d	364 (1.9×10^4)	583	0.076	0.56	–1.94	2.50

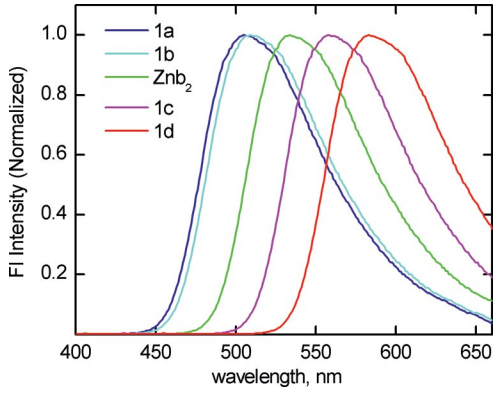


Figure 1. Emission spectra of compounds **1a**–**d** and Znb_2 in chloroform.

UV/Vis absorption spectra show shifts in the absorption maxima of complexes **1a** and **1b** to shorter wavelengths by 5–9 nm, whereas those of complexes **1c** and **1d** shift by 10–18 nm to longer wavelengths, compared to the parent Znb_2 (Table 3). The attachment of aryl moieties presumably extends the conjugation of the benzothiazole chromophore; however, the blueshift for complexes **1a** and **1b** clearly indicates the participation of inductive effects and a reduction in the contribution from mesomeric effects. For the same reason, considerable blueshifts (25–29 nm) were observed in the fluorescence spectra of these compounds (Figure 1, **1a** and **1b**).

The redshift caused by electron-donating aryl groups is mainly due to the extended conjugation caused by the additional phenyl ring. Thus, redshifts of 22–49 nm were observed in the emission spectra of complexes **1c** and **1d**. In addition, the dimethylaniline substituents in **1d** extend the conjugation further, resulting in the largest redshift of 49 nm.

The Stokes shifts for all the compounds are relatively large (160–220 nm). As expected, complexes having electron-donating groups show redshifted fluorescence spectra with decreased fluorescence quantum yields, and complexes bearing electron-withdrawing groups show blueshifted fluorescence spectra with increased emission efficiencies.

Electrochemical Studies

To better understand the effects of electron-donating and -withdrawing groups of zinc complexes **1a**–**d**, differential pulse voltammetry (DPV) measurements were performed in dichloromethane at room temperature by using the ferrocene/ferrocenium redox couple as internal standard. HOMO–LUMO energy gaps were calculated (Figure 2) from the DPV data by calibrating the scale of reference to the Fermi level.[14]

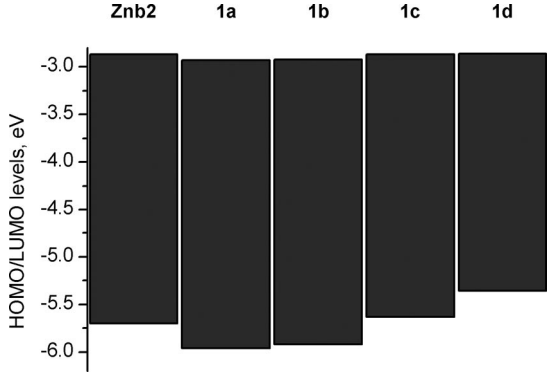


Figure 2. HOMO/LUMO energy levels calculated from the redox potentials of compounds **1a**–**d** and Znb_2.

As expected, E^{red} remains constant around –1.9 V for all the complexes, whereas E^{ox} varies from 0.56 to 1.16 V (Table 3). For complexes with the most blueshifted emissions (**1a** and **1b**), the oxidation process becomes more difficult, which is in accordance with the expected behavior.

The results shows that the electronic properties of the aryl moieties attached to the 2-phenylbenzothiazole ligand of Znb_2 derivatives change the HOMO energy levels. Because the aryl groups are attached to the phenoxide part of the ligand, which is believed to contain the HOMO,[8] it is understandable that HOMO energy levels of the benzothiazole will be more affected by the aryl attachement than the LUMO energy levels. Although it was expected that changes to the substituents might also affect the LUMO energy levels, surprisingly the LUMO levels remained largely unaffected for all the Znb_2 derivatives (Figure 2). Thus, the electron-donating properties of (benzothiazole)zinc complexes can be selectively tuned without affecting its electron-accepting capabilities. This pecularity could be beneficial for the application of (benzothiazole)zinc complexes as charge-transporting materials in organic electronic devices, for which a proper match between the redox potentials of the subsequent functional layers is of crucial importance for the efficiency of the interlayer charge transfer and thus for the overall performance of the device.

Conclusions

Two synthetic pathways based on the Suzuki–Miyuara coupling reaction were devised to synthesize Znb_2 derivatives with both electron-withdrawing and -donating aryl groups attached to the 5-position of the 2-hydroxyphenyl group of the benzothiazole ligand. The reaction conditions for both borylation and Suzuki coupling steps were varied systematically to maximize the yields of the target compounds.

Notable changes in both the absorption and emission wavelenghs of all the complexes strongly suggests electronic interaction between the benzothiazole moitey and the 5-arylphenyl groups. The blueshifts in both the absorption and emission spectra for complexes with electron-withdrawing aryl groups attached to the 2-hydroxyphenyl group of the benzothiazole ligand is mainly due to the negative inductive effect, whereas for complexes with electron-donating aryl groups, the redshift is mainly due to extended conjugation of the benzothaizole chromophore and the attached aryl groups. Moreover, DPV measurements show that substituents at the 5-position of the 2-hydroxyphenyl group have significant influence on the HOMO energy but negligible effects on the LUMO energy, as expected. It is proposed that the synthesized (benzothiazole)zinc complexes can be used for applications in multilayered organic electronic devices as charge-transporting and buffer layers. Inverted organic solar cell experiments involving the newly synthesized compounds are underway, and the results will be published as a separate paper.[15] Detailed studies on the photophysical properties of the benzothiazole ligands **7a**–**d** are also in progress.

Experimental Section

General Remarks: All the reagents used in the syntheses were purchased from Sigma–Aldrich Co. and used as received. The solvents

were of HPLC grade, purchased from VWR, and used without further purification. The sorbents for column chromatography (Silica 60, Silica 100), and TLC plates (aluminum sheet Silica gel 60 F_{254}) were purchased from Merck. ^{1}H NMR spectra were recorded with a Varian Mercury 300 MHz spectrometer in $CDCl_3$ at room temperature. All chemical shifts are quoted relative to TMS (δ = 0.0 ppm); shifts (δ values) are given in ppm, and J values are given in Hz. Melting points were measured with a Stuart SMP 10 apparatus. Mass spectra were measured with a Waters LCT Premier XE ESI-TOF benchtop mass spectrometer. Elemental analyses were performed with an Elementar Analysensysteme GmbH VarioEL instrument. Differential pulse voltammetry experiments were performed with a Faraday MP instrument (Obbligato Objectives Inc.) by using a three-electrode, single-compartment cell consisting of platinum in glass as working electrode, Ag/AgCl as reference electrode, and graphite as a counter electrode. Dichloromethane containing 0.1 M $TBAPF_6$ was used as solvent. The measurements were conducted under a continuous flow of nitrogen. All potentials were internally referenced to the Fc/Fc^+ couple. Under these conditions, the ferrocene/ferrocenium couple potential was determined to be +0.16 V. The measurements were carried out in both directions: toward the positive and negative potential. The scan rate of the measurements was 2.5 mV/s. Reduction and oxidation potentials were calculated as an average of the two scans. HOMO and LUMO energy levels were calculated by using a standard procedure[16] through the following equations:

$$HOMO = -(E^{ox} + 4.8)\ eV$$

$$LUMO = -(E^{red} + 4.8)\ eV$$

in which E^{ox} and E^{red} are the redox potentials referenced against ferrocene. The value for Fc with respect to the zero vacuum level is estimated to be –4.8 eV, determined from –4.6 eV for the standard electrode potential $E°$ of the normal hydrogen electrode (NHE) on the zero vacuum level, and 0.2 V for Fc vs. NHE. If not indicated otherwise, all the spectroscopic measurements were carried out at room temperature. The absorption spectra were recorded with a Shimadzu UV-2501PC spectrophotometer, and the fluorescence spectra were recorded with a Fluorolog-3 (SPEX Inc.) fluorimeter. The emission spectra were corrected by using a correction function supplied by the manufacturer.

Bis{2-[2-hydroxy-5-(2,3,5,6-tetrafluoropyridyl)phenyl]benzothiazolato}zinc(II) (1a). Typical Procedure: A solution of zinc acetate (0.020 g, 0.110 mmol) in ethanol (2 mL) was added dropwise to a solution of 2-[2-hydroxy-5-(2,3,5,6-tetrafluoropyridyl)phenyl]-benzothiazole (0.081 g, 0.215 mmol) in ethanol (10 mL). The resulting mixture was stirred at 70 °C for 16 h. The yellow precipitate was collected by filtration, washed with water, and dried overnight. Purification was achieved by recrystallization (ethanol and acetone) and further by vacuum sublimation to give compound **1a** as a yellow powder (0.065 g, 74%); m.p. >310 °C. HRMS (ESI-TOF): calcd. for $C_{36}H_{14}F_8N_4O_2S_2Zn$ $[M + H]^+$ 814.9794; found 814.9819. FTIR (KBr): $\tilde{\nu}$ = 3058, 1638, 1605, 1504, 1457, 1409, 1324, 1208, 1152 cm^{-1}. $C_{36}H_{14}F_8N_4O_2S_2Zn$ (816.02): calcd. C 52.99, H 1.73, N 6.87; found C 53.12, H 1.68, N 6.76.

Bis{2-[2-hydroxy-5-(2,3,4,5,6-pentafluorophenyl)phenyl]benzothiazolato}zinc(II) (1b): Yield: 73%; m.p. >310 °C. HRMS (ESI-TOF): calcd. for $C_{38}H_{14}F_{10}N_2O_2S_2Zn$ $[M + H]^+$ 848.9701; found 848.9728. FTIR (KBr): $\tilde{\nu}$ = 3059, 1610, 1506, 1474, 1419, 1321, 1272, 1199, 1152 cm^{-1}. $C_{38}H_{14}F_{10}N_2O_2S_2Zn$ (850) calcd. C 53.69, H 1.66, N 3.14; found C 53.62, H 1.72, N 3.14.

Bis[2-(2-hydroxy-5-phenylphenyl)benzothiazolato]zinc(II) (1c): Yield: 71%; m.p. >310 °C. HRMS (ESI-TOF): calcd. for $C_{36}H_{24}N_2O_2S_2Zn$ $[M + H]^+$ 669.0643; found 669.0675. FTIR (KBr): $\tilde{\nu}$ = 2929, 1726, 1610, 1524, 1444, 1424, 1397, 1313, 1210, 1151 cm^{-1}. $C_{36}H_{24}N_2O_2S_2Zn$ (646): calcd. C 68.11, H 3.61, N 4.18; found C 68.29, H 3.66, N 4.21.

Bis(2-{5-[4-(dimethylamino)phenyl]-2-hydroxyphenyl}benzothiazolato)zinc(II) (1d): Yield: 68%; m.p. >310 °C. HRMS (ESI-TOF): calcd. for $C_{42}H_{34}N_4O_2S_2Zn$ $[M + H]^+$ 755.1487; found 755.1505. FTIR (KBr): $\tilde{\nu}$ = 2929, 1727, 1610, 1524, 1493, 1311, 1278, 1208, 1137 cm^{-1}. $C_{42}H_{34}N_4O_2S_2Zn$ (756): calcd. C 66.70, H 4.53, N 7.41; found C 66.83, H 4.59, N 7.36.

5-Bromo-2-hydroxybenzothiazole (2): 5-Bromosalicylic acid (0.870 g, 4 mmol) and 2-aminothiophenol (0.500 g, 4 mmol) were added to PPA (25 mL) and stirred at 140 °C for 24 h. The mixture was cooled, poured into cold water, and neutralized with dilute sodium hydroxide to pH = 5. The precipitate was filtered, extracted with ethyl acetate, and dried with anhydrous sodium sulfate. The solvent was removed, and the crude product was purified by silica gel column chromatography (chloroform/hexane, 1:2) to give **2** as a white powder (0.735 g, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.00 (d, J = 8.7 Hz, 1 H), 7.43 (m, 2 H), 7.52 (m, 1 H), 7.79 (d, J = 2.4 Hz, 1 H), 7.91 (d, J = 8.1 Hz, 1 H), 7.99 (d, J = 8.1 Hz, 1 H), 12.56 (s, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{13}H_9BrNOS$ $[M + H]^+$ 305.9588 and 307.9568; found 305.9584 and 307.9561.

2-[2-(Benzyloxyl)-5-bromophenyl]benzothiazole (3): 2-(5-Bromo-2-hydroxyphenyl)benzothiazole (0.610 g, 1.99 mmol) was dissolved in acetone (30 mL), then benzyl bromide (0.376 g, 2.2 mmol) and potassium carbonate (0.690 g, 5 mmol) were added, and the reaction mixture was stirred at 60 °C for 3 h. After cooling, the mixture was filtered, and the filtrate was concentrated to dryness. The crude material was purified by silica gel column chromatography (chloroform/hexane, 1:4), to give **3** as a brown powder (0.733 g, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.32 (s, 2 H), 6.97 (d, J = 8.9 Hz, 1 H), 7.39 (m, 4 H), 7.48 (m, 4 H), 7.87 (d, J = 8.2 Hz, 1 H), 8.08 (d, J = 8.1 Hz, 1 H), 8.70 (d, J = 2.5 Hz, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{13}H_9BrNOS$ $[M + H]^+$ 396.0058; found 395.9882.

2-[2-(Benzyloxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]benzothiazole (4): A screw-cap flask was loaded with 2-[2-(benzyloxy)-5-bromophenyl]benzothiazole (0.200 g, 0.51 mmol), potassium acetate (0.149 g, 1.52 mmol), and anhydrous DMSO (5 mL). The solution was purged with argon for 10 min, then bis-(pinacolato)diboron (0.291 g, 2.28 mmol) and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (0.021 g, 0.026 mmol) were added, and the reaction mixture was stirred at 80 °C for 4 h. After cooling, water (20 mL) and chloroform (20 mL) were added, and the organic phase was separated and washed with water (2 × 10 mL). The organic phases were collected, combined, and dried with anhydrous sodium sulfate and the solvents evaporated. Purification was achieved by silica gel column chromatography (ethyl acetate/toluene, 1:20) to give **4** as a brown powder (0.178 g, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (s, 12 H), 5.35 (s, 2 H), 7.08 (d, J = 8.4 Hz, 1 H), 7.43 (m, 4 H), 7.53 (m, 3 H), 7.89 (d, J = 8.3 Hz, 2 H), 8.08 (d, J = 8.2 Hz, 1 H), 8.81 (d, J = 2.1 Hz, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{26}H_{27}BNO_3S$ $[M + H]^+$ 443.1810; found 443.1904.

***N*,*N*′-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (5d):** Prepared as described for compound **4**. Yield: 69%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.32 (s, 12 H), 2.97 (s, 6 H), 6.68 (d, J = 8.8 Hz, 2 H), 7.69 (d, J = 8.8 Hz, 2 H) ppm. HRMS (ESI-TOF): calcd. for $C_{14}H_{22}BNO_2$ $[M + H]^+$ 248.1824; found 248.1846.

2-[2-(Benzyloxy)-5-(2,3,5,6-tetrafluoropyridyl)phenyl]benzothiazole (6a): 2-[2-(Benzyloxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]benzothiazole (0.400 g, 0.903 mmol), 4-bromo-2,3,5,6-tetrafluoropyridine (0.208 g, 0.903 mmol), tetrabutylammonium chloride (0.025 g, 0.09 mmol), and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (0.037 g, 0.045 mmol) were added to a two-phase mixture of toluene (20 mL) and aqueous 1 M potassium carbonate solution (20 mL). The reaction mixture was vigorously stirred at 90 °C under argon for 16 h, then the organic layer was separated, and the aqueous phase was extracted with toluene (3 × 20 mL). The organic layers were combined, washed with water (2 × 20 mL), dried with anhydrous sodium sulfate and the solvents evaporated. Purification was achieved by silica gel column chromatography (ethyl acetate/toluene, 1:25) to give **6a** as a yellowish powder (0.341 g, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.42 (s, 2 H), 7.25 (d, J = 8.9 Hz, 1 H), 7.42 (m, 4 H), 7.56 (m, J = 7.6 Hz, 2 H), 7.75 (dd, J = 2.4, 7.6 Hz, 1 H), 7.89 (d, J = 7.9 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 8.80 (s, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{25}H_{15}F_4N_2OS$ $[M + H]^+$ 467.0841; found 467.0856.

2-[2-(Benzyloxy)-5-(2,3,4,5,6-pentafluorophenyl)phenyl]benzothiazole (6b): Prepared as described for compound **6a**. Yield: 79%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.41 (s, 2 H), 7.23 (d, J = 8.9 Hz, 1 H), 7.42 (m, 5 H), 7.56 (dd, J = 2.3, 7.6 Hz, 2 H), 7.76 (d, J = 7.7 Hz, 1 H), 7.89 (d, J = 7.9 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 8.80 (s, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{26}H_{14}F_5NOS$ $[M + H]^+$ 484.0794; found 484.0767.

2-[2-(Benzyloxy)-5-phenylphenyl]benzothiazole (6c): 2-[2-(Benzyloxy)-5-bromophenyl]benzothiazole (0.400 g, 1.01 mmol), pinacol phenylboronate (0.206 g, 1.01 mmol), tetrabutylammonium chloride (0.028 g, 0.101 mmol), and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (0.041 g, 0.051 mmol) were added to a two-phase mixture of toluene (20 mL) and aqueous 1 M potassium carbonate (20 mL). The reaction mixture was vigorously stirred at 90 °C under argon for 24 h. The organic layer was separated, and the aqueous phase was extracted with toluene (3 × 20 mL). The organic layers were combined, washed with water (2 × 20 mL), and dried with anhydrous sodium sulfate and the solvents evaporated. Purification was achieved by silica gel column chromatography (ethyl acetate/toluene, 1:25) to give **6c** as a yellowish powder (0.310 g, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.33 (s, 2 H), 7.13 (d, J = 8.9 Hz, 1 H), 7.35 (m, 5 H), 7.45 (m, 4 H), 7.60 (m, 2 H), 7.66 (d, J = 7.1 Hz, 2 H), 7.86 (s, J = 8.1 Hz, 1 H), 8.10 (s, J = 8.1 Hz, 1 H), 8.92 (s, J = 2.4 Hz, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{26}H_{19}NOS$ $[M + H]^+$ 394.1266; found 394.1196.

2-{2-(Benzyloxy)-5-[4-(dimethylamino)phenyl]phenyl}benzothiazole (6d): Prepared as described for compound **6c**. Yield: 76%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.33 (s, 2 H), 6.82 (d, J = 6.8 Hz, 2 H), 7.08 (d, J = 8.9 Hz, 1 H), 7.45 (m, 6 H), 7.59 (m, 4 H), 7.90 (d, J = 8.1 Hz, 1 H), 8.10 (d, J = 8.1 Hz, 1 H), 8.78 (d, J = 2.4 Hz, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{28}H_{24}N_2OS$ $[M + H]^+$ 437.1643; found 437.1636.

2-[2-Hydroxy-5-(2,3,5,6-tetrafluoropyridyl)phenyl]benzothiazole (7a): 2-[2-(Benzyloxy)-5-(2,3,5,6-tetrafluoropyridyl)phenyl]benzothiazole (0.320 g, 0.67 mmol) and 10% Pd/C (0.320 g) were added to THF (25 mL), and aqueous ammonium formate (2.0 mL, 0.844 g, 13.4 mmol) was added. The reaction mixture was heated at reflux for 3 h; then, after cooling, the mixture was filtered, and the filtrate was concentrated. Purification was achieved by silica gel column chromatography (ethyl acetate/toluene, 1:30) to give **7a** as a white powder (0.207 g, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 (d, J = 8.6 Hz, 1 H), 7.49 (m, 1 H), 7.58 (m, 2 H), 7.94 (m, 2 H), 8.04 (d, J = 8.3 Hz, 1 H), 13.00 (s, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{18}H_9F_4N_2OS$ $[M + H]^+$ 377.0372; found 377.0395.

2-[2-Hydroxy-5-(2,3,4,5,6-pentafluorophenyl)phenyl]benzothiazole (7b): Prepared as described for **7a**. Yield: 84%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.23 (d, J = 8.7 Hz, 1 H), 7.45 (m, 2 H), 7.55 (m, 1 H), 7.76 (s, 1 H), 7.92 (d, J = 7.9 Hz, 1 H), 8.03 (d, J = 8.1 Hz, 1 H), 12.83 (s, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{19}H_8F_5NOS$ $[M - H]^+$ 392.0168; found 392.0182.

2-(2-Hydroxy-5-phenylphenyl)benzothiazole (7c): 2-[2-(Benzyloxy)-5-phenylphenyl]benzothiazole (0.130 g, 0.30 mmol), 10% Pd/C (0.130 g), and ammonium formate (0.019 g, 0.30 mmol) were added to a mixture of THF (15 mL) and methanol (15 mL), and the reaction mixture was heated at reflux for 3 h. After cooling, the mixture was filtered, and the filtrate was concentrated. Purification was achieved by silica gel column chromatography (chloroform) to give **7c** as a white powder (0.084 g, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.15 (d, J = 8.7 Hz, 1 H), 7.41 (m, 3 H), 7.50 (m, 2 H), 7.58 (m, 3 H), 7.84 (d, J = 2.4 Hz, 1 H), 7.87 (d, J = 8.1 Hz, 1 H), 7.96 (d, J = 8.3 Hz, 1 H), 12.56 (s, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{19}H_{14}NOS$ $[M + H]^+$ 304.0796; found 304.0791.

2-{5-[4-(Dimethylamino)phenyl]-2-hydroxyphenyl}benzothiazole (7d): Prepared as described for **7c**. Yield: 82%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.01 (s, 6 H), 6.84 (d, J = 8.9 Hz, 2 H), 7.15 (d, J = 8.5 Hz, 1 H), 7.51 (m, 6 H), 7.83 (d, J = 2.2 Hz, 1 H), 7.93 (d, J = 8.5 Hz, 1 H), 8.01 (d, J = 8.5 Hz, 1 H), 12.45 (s, 1 H) ppm. HRMS (ESI-TOF): calcd. for $C_{21}H_{18}N_2OS$ $[M + H]^+$ 347.1218; found 347.1235.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of all synthesized compounds and absorption spectra (in chloroform solution), DPV graphs, and FTIR spectra of all zinc complexes.

Acknowledgments

Financial support from the Academy of Finland is greatly acknowledged.

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Received: February 9, 2011
Published Online: August 31, 2011

