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Synthesis and Optical Properties of Salicylaldimine-Based Diboron Complexes

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New salicylaldimine-based diboron complexes 1-3 have been synthesized and characterized by multinuclear NMR spectroscopy, mass spectrometry, and single-crystal X-ray analysis (1 and 3). The photophysical and electrochemical properties of these compounds have been investigated experimentally and with theoretical calculations; their properties suggest that these compounds could have potential applications for the manufacture of optoelectronic devices.

Introduction

In recent years, tri-[1-11] and tetracoordinate[12-14] boron compounds have received immense attention owing to their use as new materials in different fields including organic field-effect transistors, sensor materials, organic light-emitting diodes (OLEDs), and photovoltaics. The overlap of the empty p orbital of the tricoordinate boron atom with the organic π system leads to interesting optoelectronic properties and also enables the detection of anions such as fluoride and cyanide. Recently, efforts have been devoted to the design and synthesis of tetracoordinate boron compounds with N,O-, N,N-, and, N,C-chromophores.^[15-31] Among the tetracoordinate boron compounds, boron dipyrromethene dyes (Figure 1, A)^[32-35] have been studied to a greater extent owing to their potential application in artificial light harvesters, fluorescent sensors, laser dyes, sensitizers for solar cells, and molecular photonic wires. Boron quinolate compounds are analogous to aluminum quinolato compounds (Figure 1, B);^[26,36–42] the photophysical tuning of R_2BQ compounds (Q = substituted quinolate) was recently studied by Wang and co-workers^[40,41] and Jaekle and coworkers.^[43-46] Schiff base boron compounds (Figure 1, C) are yet another type of four-coordinate boron complex that has gained interest owing to their greater stability than tricoordinate boron compounds.^[15,18,24,47-50] For example, Ziessel, Ulrich, and co-workers reported the synthesis and optical properties of Boranil complexes.^[47] Ziessel and Ulrich are also credited for expanding the scope of the Boranil complexes in a model labeling experiment with bovine serum albumin.^[48] More recently, Lee and co-workers re-

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ported a Schiff base route for the synthesis of boron-based stackable pseudo-triphenylenes, which showed interesting increased fluorescence upon aggregation in solution.^[49]



Figure 1. Schematic representation of the skeleton of (A) boron dipyrromethene, (B) boron quinolate, and (C) Schiff base boron compounds.

With advances in the design of different boron fluorophores, researchers are continually trying to synthesize conjugated tetracoordinate diboron or multiboron systems to improve fluorescence and electron-transport properties.^[17,19,51,52] For instance, Yamaguchi and co-workers reported the synthesis of boron-bridged dipyridylvinylenes and dithiazolylvinylenes.^[51] More recently, Gomes and coworkers revealed the synthesis of an iminopyrrolyl diboron complex and its usefulness in nondoped OLEDs.[52] In view of the important potential applications of boron compounds, in particular the use of diboron compounds in transistors, OLEDs, and lasers, the search for alternative fluorescent dyes prompted us to synthesize new salicylaldimine diboron complexes. We expect that a 1,1'-biphenyl backbone will help to increase the conjugation and, thus, result in better luminescent materials. The preparation and structural, photophysical, and electrochemical properties of these compounds have been investigated.

Results and Discussion

The bis-salicylaldimine Schiff bases H_2L1-H_2L3 (Scheme 1) were synthesized by acid-catalyzed condensa-



tion reactions between the dialdehyde^[53] and commercially available anilines in toluene or dichloromethane at reflux temperature. These starting materials were fully characterized by ¹H and ¹³C NMR spectroscopy and LC-MS. As shown in Figure 2, a distinctive H-bonded downfield phenolic proton ($\delta \approx 13-14$ ppm) was observed for all bis-salicylaldimine Schiff bases. All three Schiff bases were also characterized by single-crystal X-ray analysis. The molecular structure of H₂L3 is shown in Figure 2. The metric parameters along with the molecular structures of H₂L1 and H₂L2 are available as Supporting Information. Notably, all three Schiff bases are involved in intramolecular hydrogen bonding to the respective imine nitrogen atoms to form sixmembered rings (Figures 2, S1, and S2). The observed hydrogen-bonding metric parameters (H····N 1.86–1.89 Å; N···O 2.59–2.62 Å; O–H···N 147.7–148.6°) show similar trends to those previously reported for these interacting units.^[54] The Schiff bases were deprotonated by using sodium hydride in anhydrous tetrahydrofuran (THF) at room temperature. The sodium salt of the bis-salicylaldimine reacted with excess BF₃·Et₂O in tetrahydrofuran for 24 h to afford the diboron salicylaldimine complexes in moderate yields.



Scheme 1. Synthesis of 1-4.

All boron compounds 1–3 were characterized by ¹H and ¹³C NMR spectroscopy; the disappearance of the downfield H-bonded phenolic proton ($\delta \approx 13-14$ ppm) of H₂L1, H₂L2, and H₂L3 gives the first indication for the formation of 1–3. The ¹¹B NMR spectra of the diboron compounds each show a narrow signal at $\delta \approx 0-1$ ppm, which is in agreement with the existence of a four-coordinate boron atom. Furthermore, compounds 1–3 were also characterized by ¹⁹F NMR spectroscopy. The chemical shifts of the fluorine nuclei in the ¹⁹F NMR spectra were not strongly affected



Figure 2. Molecular structure of H_2L3 (top). ¹H NMR spectrum of H_2L3 in C_6D_6 (bottom).

by the substitution. The ¹⁹F NMR signals for **2** and **3** at δ = -137.2 and -137.9 ppm are marginally upfield shifted in comparison to that of **1** (δ = -135.4 ppm). The absence of quartets in the ¹⁹F NMR spectra reveals that there may be fast relaxation of the quadrupolar boron nuclei at room temperature.^[55] Moreover, the proposed structures of the diboron compounds were confirmed by [M + Na]⁺ ion peaks in LC–MS and single-crystal X-ray analysis of **1** and **3**.

The molecular structures of 1 and 3 are shown in Figure 3, and selected bond lengths and angles are listed in the caption. The B-N and B-O bond lengths in 1 and 3 are similar to those of the other reported Schiff base-BF2 complexes.^[21,47] In both structures, the boron atom deviates from the nine-atom plane defined by the six biphenyl carbon atoms and the imino carbon, nitrogen, and oxygen atoms (Figures 4 and S6); the deviation is more pronounced in 1 (0.39 Å for B1 and 0.37 Å for B2) than in 3 (0.30 Å for B1 and 0.18 Å for B2). The dihedral angles between the two planes (planes A and B, Figure S6) are 73.45 and 123.21° in 1 and 3, respectively (Figures 4 and S6). Steric hindrance in 3 plays a major role in this drastic difference, as is also seen from the separation distance between the boron atoms; the B–B distance in 1 is 5.74 Å, whereas in 3 it increases to 7.16 Å. Both boron atoms in 1 and 3 have slightly distorted tetrahedral geometries with angles ranging from 106.1(3) to 111.0(3)° for 1 and 107.30(11) to 110.96(12)° for 3. The interplanar angles between planes A or B (six biphenyl carbon atoms and imino carbon, nitrogen, and oxygen atom) and the N-phenyl rings in 1 are 44.18 and 48.88°, and in 3 these angles are 77.86 and 85.19° (Figure S6).

All three compounds showed limited solubility in nonpolar solvents; hence, the photophysical studies were performed in tetrahydrofuran. The photophysical properties of these compounds were unaffected by solvent change (see Figure S3); this indicates that the interactions of the fluorophores with solvent molecules in the excited state is less significant. The absorption and fluorescence spectra of diboron compounds **1–3** in tetrahydrofuran are shown in Fig-





Figure 3. Molecular structures of 1 and 3. Solvent THF and CH₃CN molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for 1: B1-F1 1.377(5), B1-F2 1.388(5), B2-F3 1.367(5), B2-F4 1.386(4), B1-O1 1.450(5), B2-O2 1.465(5), B1-N1 1.591(5), B2-N2 1.577(5), F1-B1-F2 110.9(3), F1-B1-O1 108.7(3), F2-B1-O1 111.0(3), F1-B1-N1 110.9(3), F2-B1-N1 106.1(3), O1-B1-N1 109.4(3), F3-B2-F4 110.7(3), F3-B2-O2 108.9(3), F4-B2-O2 109.8(3), F3-B2-N2 108.1(3), F4-B2-N2 108.5(3). Selected bond lengths and angles for **3**: B1–F1 1.3640(17), B1-F2 1.3751(18), B2-F3 1.3670(19), B2-F4 1.3723(19), B1-O1 1.4485(17), B2-O2 1.4238(17), B1-N1 1.5905(18), B2-N2 1.5812(17), F1-B1-F2 110.01(12), F1-B1-O1 109.57(11), F2-B1-O1 110.96(12), F1-B1-N1 109.54(11), F2-B1-N1 107.30(11), O1-B1-N1 109.42(10), F3-B2-F4 109.43(12), F3-B2-O2 109.13(12), 110.47(13), F3-B2-N2 109.35(11), F4-B2-N2 F4-B2-O2 108.24(11).

ure 5. As shown in Figure 5 and Table 1, all three compounds exhibit absorption at ca. 370-380 nm and emission at ca. 460-490 nm. Both the absorption and the emission of 1 are redshifted in comparison to those of 2 and 3. Compounds 1-3 showed moderate quantum yields (12, 28, and 16% respectively); however, a remarkably higher quantum yield was observed for 2 compared to those of 1 and 3. To gain more insight into the effect of the biphenyl moiety in our design, we also synthesized the salicylaldimine monoboron complex 4 (Scheme 1 and Supporting Information) and studied its photophysical properties. The mononuclear compound 4 showed substantial blueshifts both in absorption (20 nm) and in emission (18 nm) when compared to those of the diboron compound 3 (Figures S4 and S5); this might be because of the decreased conjugation length, and such a trend is similar to that reported by Gomes and coworkers in their study of iminopyrrolyl boron complexes.^[52]

Density functional theory $(DFT)^{[56]}$ computations were performed to model the photophysical properties of the diboron compounds. The geometries of **1**–**3** were optimized by DFT [B3LYP, 6-31G(d)] calculations, and the excitation energies were computed by using time-dependent DT (TD-DFT) calculations. The computed results are consistent with the experimental results, although the absolute excitation data deviate significantly (Table 2). Figure 6 shows plots of the highest occupied molecular orbitals (HOMOs)



Figure 4. Illustration of the boron deviation from the nine-atom plane (defined by the six biphenyl carbon atoms and the imino carbon, nitrogen, and oxygen atoms) and the dihedral angle between the planes for 1 (top) and 3 (bottom).



Figure 5. Normalized absorption (top) and fluorescence emission (bottom) spectra of 1-3.



Table 1. Experimental photophysical data of 1-3.

	$\lambda_{\max}^{[a]} [nm]$	ε [L/mol cm]	$\lambda_{\rm em}^{[a,b]} [nm] (\Phi)^{[c]}$
1	380	13500	490 (0.12)
2	373	8700	464 (0.28)
3	375	15548	460 (0.16)

[a] Concentrations were $4.35\times10^{-5}\,{\rm M}$ in THF. [b] Excited at the absorption maximum. [c] Quantum yield.

and lowest unoccupied molecular orbitals (LUMOs) of 1–3; according to the theoretical calculations, the lowest energy excitation corresponds to a π - π * transition for all three compounds. The HOMOs are mainly contributed to by the π orbitals of the biphenyl and oxygen moieties, whereas the LUMOs are composed of π * orbitals of the biphenyl and imine moieties (Tables S4 and S5). There is a clear difference in the electron distribution of 1 and those of 2 and 3. For 2 and 3, the electron distribution in the LUMO is confined to the biphenyl and oxygen moieties, whereas the electron distribution in the LUMO of 1 shows a delocalized

Table 2. Calculated electronic transitions for 1–3 from TD-DFT (B3LYP) calculations.

	Transition	MO contribution	Energy gap [eV] ([nm])	Oscillator strength (f)
1	$S_0 \rightarrow S_1$	HOMO→LUMO	3.01 (411)	0.2030
	$S_0 \rightarrow S_2$	HOMO→LUMO+1	3.09 (400)	0.0001
	$S_0 \rightarrow S_3$	HOMO–2→LUMO+1	3.54 (350)	0.0142
	0 0	HOMO–1→LUMO		
2	$S_0 \rightarrow S_1$	HOMO→LUMO	3.16 (391)	0.1325
	$S_0 \rightarrow S_2$	HOMO→LUMO+1	3.19 (387)	0.0000
	$S_0 \rightarrow S_3$	HOMO–6→LUMO+1	3.71 (333)	0.0080
		HOMO–5→LUMO		
		HOMO–4→LUMO+1		
		HOMO–1→LUMO		
3	$S_0 \rightarrow S_1$	HOMO→LUMO	3.16 (391)	0.1324
	$S_0 \rightarrow S_2$	HOMO→LUMO+1	3.19 (387)	0.0000
	$S_0 \rightarrow S_3$	HOMO–3→LUMO+1	3.67 (337)	0.0103
		HOMO–2→LUMO		
		$HOMO-1 \rightarrow LUMO+1$		

feature. Owing to this π conjugation, the LUMO level of **1** is lowered and this helps to decrease the band gap and, thus, results in a redshift. Pronounced twists of the *N*-phenyl rings were observed in **2** and **3** [the rings in **3** are twisted by 77.86 and 85.19°, whereas the rings in **1** are twisted by 48.88 and 44.18° (from X-ray data)] and may be responsible for restricted electronic communication in **2** and **3**.

The electron-accepting abilities of the diboron compounds were studied by cyclic voltammetry in dimethylformamide (DMF). All compounds 1–3 exhibit two separate reduction waves. The redox potentials for 1 at $E_{1/2}(1)$ = -1.63 V and $E_{1/2}(2)$ = -1.83 V are slightly less negative than those of 2 and 3 [$E_{1/2}(1)$ = -1.83 V, $E_{1/2}(2)$ = -2.03 V for 2; $E_{1/2}(1)$ = -1.81 V, $E_{1/2}(2)$ = -2.0 V for 3 (Figure 7)], maybe because of the presence of electron-donating groups in 2 and 3.^[57] The first reduction potentials of diboron compounds 1–3 are comparable with those of the diboron flu-



Figure 7. Cyclic voltammogram of **3** with 0.1 M $Bu_4N(PF_6)$ in DMF as the supporting electrolyte (scan rate 100 mV/s). Referenced relative to Fc/Fc⁺ couple.



Figure 6. Computed orbitals for 1-3.

orophores reported by Zhang et al.^[17] but notably less negative than that of AlQ₃.^[58] The HOMO and LUMO energy levels were also calculated from the onset absorption and onset reduction potentials (Table 3). The HOMO–LUMO gaps from these measurements are in agreement with the results obtained from the TD-DFT computations.

Table 3. Frontier orbital energies [eV] derived from UV/Vis onset absorption and electrochemical data.

	HOMO–LUMO gap ^[a]	LUMO ^[b]	HOMO ^[c]
1	2.91	-3.28	-6.19
2	2.98	-3.11	-6.09
3	2.97	-3.18	-6.15

[a] Estimated from the absorption onset of the longest-wavelength UV band. [b] Calculated from $E_{\rm pc}$ of the first reduction wave referenced to Fc/Fc⁺. [c] Calculated from the HOMO–LUMO gap and the LUMO.

Conclusions

We have designed and synthesized new salicylaldiminebased diboron fluorophores by a simple synthetic procedure. All three boron compounds showed high thermal stability and interesting photophysical and electrochemical properties. We expect that the new diboron complexes reported here will have potential applications in optoelectronic devices. Further studies on the modification of conjugated diboron system are in progress.

Experimental Section

Reagents were used as received unless otherwise noted. THF and toluene were distilled from Na/benzophenone prior to use. Chlorinated solvents were distilled from CaH₂. 2,2'-Dihydroxybiphenyl-3,3'-dicarbaldehyde was prepared according to a literature procedure.^[53] All ¹H (400 MHz), ¹³C (100 MHz), ¹¹B (128 MHz), and ¹⁹F (376 MHz) NMR spectra were recorded with a Bruker ARX 400 spectrometer. All ¹H and ¹³C NMR spectra were referenced internally to solvent signals. ¹¹B NMR spectra were referenced externally to BF₃·Et₂O in CDCl₃ ($\delta = 0$ ppm), and ¹⁹F NMR spectra were referenced to α, α, α -trifluorotoluene (0.05% in CDCl₃; δ = -63.73 ppm). All NMR spectra were recorded at ambient temperature. Elemental analyses of C, H, and N were performed with a Perkin-Elmer 240C elemental analyzer. ESI mass spectra were recorded with a Bruker microTOF-QII mass spectrometer. The absorbance spectra were recorded with a Perkin-Elmer Lambda 750 UV/Visible spectrometer. The fluorescence spectra were recorded with a Perkin-Elmer LS-55 Fluorescence Spectrometer and corrected for the instrumental response. Quinine sulfate was used as the standard for the determination of the quantum yields.

Electrochemical measurements were performed with a conventional three-electrode cell and an electrochemical workstation (CH Instrument 1100A). The three-electrode system consisted of a glassy carbon working electrode, a Pt wire as the secondary electrode, and a Ag wire as the reference electrode. The voltammograms were recorded with ca. 1.0×10^{-3} M solutions in DMF containing Bu₄N(PF₆) (0.1 M) as the supporting electrolyte. The scans were referenced after the addition of a small amount of ferrocene as the internal standard.

Single-crystal X-ray diffraction data were collected with a Bruker KAPPA APEX-II four angle rotation system with Mo- K_a radiation (0.71073 Å). The crystallographic data for 1, 3, H₂L1, H₂L2 and H₂L3 and details of the X-ray diffraction experiments and crystal structure refinements are given in the Supporting Information. SADABS^[59] absorption corrections were applied. Structures were solved by direct methods and completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures on reflection intensities (*F*2). All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL (v. 5.10) program package.^[60]

CCDC-932528 (for 1), -932529 (for 3), -942656 (for H_2L1), -942657 (for H_2L2), and -942655 (for H_2L3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. DFT calculations were performed with the Gaussian03 program.^[52] Excitation data were determined by TD-DFT (B3LYP) calculations.

[1,1'-Biphenyl]-2,2'-diol-3,3'-bis(phenylimino)methyl (H₂L1): Aniline (0.88 mL, 9.70 mmol) and 2,2'-dihydroxybiphenyl-3,3'-dicarbaldehyde (1.12 g, 4.62 mmol) were dissolved in anhydrous toluene (20 mL). To this solution a catalytic amount of p-toluenesulfonic acid was added. The reaction mixture was heated to reflux for 15 h under Dean-Stark reaction conditions. The reaction mixture was cooled to room temperature, the solvent was removed under vacuum, and the solid was purified by crystallization in chloroform and ethanol, yield 1.50 g, 83%, m.p. 169 °C. ¹H NMR (400 MHz, C_6D_6): $\delta = 6.85-6.9$ (m, 6 H, ArH), 6.95-6.99 (m, 4 H, ArH), 7.02-7.07 (m, 4 H, ArH), 7.73 (dd, J = 1.6, 8 Hz, 2 H, ArH), 8.07 (s, 2 H, CH=N), 13.97 (s, 2 H, ArOH) ppm. ¹³C NMR (100 MHz, C_6D_6): δ = 118.54, 119.83, 121.56, 126.74, 126.92, 129.43, 132.26, 135.95, 148.97, 159.96 (ArC), 163.34 (CH=N) ppm. HRMS (ESI): calcd. for $C_{26}H_{20}N_2O_2 [M + H]^+$ 393.1598; found 393.1595. $C_{26}H_{20}N_2O_2$ (392.46): calcd. C 79.57, H 5.14, N 7.14; found C 79.31, H 5.22, N 7.01.

[1,1'-Biphenyl]-2,2'-diol-3,3'-bis({[2,6-bis(methyl)phenyl]imino}methyl) (H₂L2): 2,6-Dimethylaniline (0.63 mL, 5.16 mmol), 2,2'-dihydroxybiphenyl-3,3'-dicarbaldehyde (0.50 g, 2.06 mmol), and formic acid (0.1 mL) were dissolved in anhydrous dichloromethane (15 mL). The reaction mixture was heated to reflux for 15 h and then cooled to room temperature. The solvent was removed under vacuum, and the solid was purified by crystallization in chloroform and ethanol, yield 0.65 g, 70%, m.p. 175 °C. ¹H NMR (400 MHz, C_6D_6): $\delta = 1.95$ (s, 12 H, CH₃), 6.85 (t, J = 8 Hz, 2 H, ArH), 6.90– 6.93 (m, 8 H, ArH), 7.71 (s, 2 H, CH=N), 7.73 (d, J = 8 Hz, 2 H, ArH), 13.72 (s, 2 H, ArOH) ppm. ¹³C NMR (100 MHz, C_6D_6): $\delta =$ 18.45 (CH₃), 118.54, 119.42, 125.14, 126.73, 128.58, 128.63, 132.16, 136.19, 148.74, 159.91 (ArC), 167.50 (CH=N) ppm. HRMS (ESI): calcd. for $C_{30}H_{28}N_2O_2$ [M + H]⁺ 449.2224; found 449.2234. C30H28N2O2 (448.56): C 80.33, H 6.29, N 6.25; found C 80.12, H 6.01, N 6.08.

[1,1'-Biphenyl]-2,2'-diol-3,3'-bis({[2,6-bis(methylethyl)phenyl]imino}methyl) (H₂L3): By a similar procedure as that for H₂L2, the reaction of 2,6-diisopropyl aniline (1.94 mL, 10.32 mmol) and biphenol dialdehyde (1.00 g, 4.13 mmol) gave a yellow solid, which was purified by recrystallization, yield 2.00 g, 86%, m.p. 192 °C. ¹H NMR (400 MHz, C₆D₆): $\delta = 1.04$ (d, J = 8 Hz, 24 H, CH₃), 2.93–3.03 (m, 4 H, CH), 6.82 (t, J = 8 Hz, 2 H, ArH), 6.96 (d, J =8 Hz, 2 H, ArH), 7.09–7.10 (m, 6 H, ArH), 7.74 (d, J = 8 Hz, 2 H, ArH), 7.99 (s, 2 H, CH=N), 13.75 (s, 2 H, ArOH) ppm. ¹³C NMR



(100 MHz, C_6D_6): $\delta = 23.60$ (CH₃), 28.53 (CH), 118.75, 119.36, 123.56, 125.87, 126.60, 132.21, 136.46, 139.08, 147.00, 159.88 (ArC), 167.58 (CH=N) ppm. HRMS (ESI): calcd. for $C_{38}H_{44}N_2O_2$ [M + H]⁺ 561.3476; found 561.3441. $C_{38}H_{44}N_2O_2$ (560.78): calcd. C 81.39, H 7.91, N 5.00; found C 81.23, H 7.99, N 4.92.

Complex 1: Under nitrogen, H₂L1 (0.40 g, 1.02 mmol) was added to a suspension of NaH (0.056 g, 2.34 mmol) in anhydrous tetrahydrofuran (15 mL) at 0 °C with stirring. The reaction mixture was warmed to room temperature and stirred at that temperature for 2 h. The resulting solution was added to a solution of BF₃·Et₂O (2.51 mL, 20.40 mmol) in tetrahydrofuran, and the mixture was stirred for 24 h. The reaction mixture was filtered through Celite, and the resulting filtrate was concentrated to yield a pale yellow solid, which was purified by recrystallization in acetonitrile, yield 260 mg, 52%, m.p. 297–303 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ = 7.17 (t, J = 4 Hz, 2 H, ArH), 7.47–7.58 (m, 12 H, ArH), 8.05 (d, J = 8 Hz, 2 H, ArH), 8.49 (s, 2 H, CH=N) ppm. ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 116.61, 120.40, 123.78, 126.15, 129.49,$ 129.84, 132.43, 142.01, 142.56, 157.65 (ArC), 163.84 (CH=N) ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -135.44 (br) ppm. ¹¹B NMR (128 MHz, CDCl₃): $\delta = 1.01$ (s) ppm. Quantum yield (Φ) = 0.12. IR (KBr): $\tilde{v} = 3030$ (w), 2944 (m), 2872 (s), 1622 (s), 1589 (m), 1567 (m), 1454 (s), 1391 (m), 1335 (m), 1255 (s), 1201 (s), 1126 (m), 1048 (s) cm⁻¹. HRMS (ESI): calcd. for $C_{26}H_{18}B_2F_4N_2O_2$ $[M + Na]^+$ 511.1392; found 511.1321. $C_{26}H_{18}B_2F_4N_2O_2$ (488.05): calcd. C 63.99, H 3.72, N 5.74; found C 64.27, H 3.79, N 5.63.

Complex 2: Compound 2 was prepared by following a similar procedure to that used for 1. The reaction of imine (0.20 g, 0.44 mmol), NaH (0.026 g, 1.11 mmol), and BF₃·Et₂O (2.7 mL, 22.30 mmol) in anhydrous tetrahydrofuran gave the product as a white solid, which was purified by recrystallization, yield 0.183 g, 75%, m.p. >310 °C (stable to 310 °C). ¹H NMR (400 MHz, CDCl₃): δ = 2.31 (s, 12 H, CH₃), 7.15–7.22 (m, 8 H, ArH), 7.50 (d, J = 8 Hz, 2 H, ArH), 8.14 (d, J = 8 Hz, 2 H, ArH), 8.26 (s, 2 H, CH=N) ppm. ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 18.30 (\text{CH}_3), 116.54, 120.35, 126.20,$ 128.74, 128.92, 132.18, 133.56, 141.15, 142.16, 157.67 (ArC), 167.65 (CH=N) ppm. ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -137.15$ (br) ppm. ¹¹B NMR (128 MHz, CDCl₃): δ = 0.89 (s) ppm. Quantum yield (Φ) = 0.28. IR (KBr): \tilde{v} = 3032 (w), 2965 (m), 2870 (m), 1626 (s), 1581 (m), 1567 (s), 1436 (s), 1385 (s), 1316 (s), 1245 (s), 1218 (s), 1188 (s), 1048 (m) cm⁻¹. HRMS (ESI): calcd. for $C_{30}H_{26}B_2F_4N_2O_2$ [M + Na]⁺ 567.2019; found 567.2064. C₃₀H₂₆B₂F₄N₂O₂ (544.16): calcd. C 66.22, H 4.82, N 5.15; found C 65.94, H 4.42, N 5.38.

Complex 3: Compound 3 was prepared by following a similar procedure to that used for 1. The reaction of imine (1.00 g, 1.78 mmol), NaH (0.107 g, 4.46 mmol), and BF₃·Et₂O (11 mL, 89.16 mmol) in anhydrous tetrahydrofuran (30 mL) gave the product as a white solid, which was purified by recrystallization, yield 1.05 g, 90%, m.p. >310 °C (stable to 310 °C). ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (d, J = 8 Hz,12 H, CH₃), 1.29 (d, J = 8 Hz, 12 H, CH₃), 3.03–3.1 (m, 4 H, CH), 7.18 (t, J = 8 Hz, 2 H, ArH), 7.26–7.28 (m, 4 H, ArH), 7.40 (t, J = 8 Hz, 2 H, ArH), 7.48 (d, J = 8 Hz, 2 H, ArH), 8.15 (d, J = 8 Hz, 2 H, ArH), 8.24 (s, 2 H, CH=N) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 23.37 (CH₃), 25.61 (CH₃), 28.60 (CH), 116.35, 120.44, 124.48, 126.17, 129.48, 132.22, 137.87, 142.31, 144.21, 157.63 (ArC), 167.02 (CH=N) ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -137.94 (br) ppm. ¹¹B NMR (128 MHz, CDCl₃): $\delta = 0.80$ (s) ppm. Quantum yield (Φ) = 0.16. IR (KBr): \tilde{v} = 3065 (w), 2975 (s), 2872 (m), 1626 (s), 1592 (w), 1568 (s), 1465 (m), 1439 (s), 1386 (s), 1311 (s), 1254 (s), 1238 (s), 1183 (s), 1151 (m), 1111 (m), 1057 (m) cm⁻¹. HRMS (ESI): calcd. for

 $C_{38}H_{42}B_2F_4N_2O_2\ [M + Na]^+$ 679.3273; found 679.3211. $C_{38}H_{42}B_2F_4N_2O_2\ (656.37):$ calcd. C 69.54, H 6.45, N 4.27; found C 69.83, H 6.31, N 4.11.

Supporting Information (see footnote on the first page of this article): Synthesis of **4**, additional experimental and analytical details.

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- [1] C. D. Entwistle, T. B. Marder, Chem. Mater. 2004, 16, 4574.
- [2] J. D. Hoefelmeyer, M. Schulte, M. Tschinkl, F. P. Gabbai, Coord. Chem. Rev. 2002, 235, 93.
- [3] C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbai, *Chem. Rev.* 2010, 110, 3958.
- [4] S. Yamaguchi, A. Wakamiya, Pure Appl. Chem. 2006, 78, 1413.
- [5] F. Jaekle, Coord. Chem. Rev. 2006, 250, 1107.
- [6] N. Matsumi, Y. Chujo, Polym. J. 2008, 40, 77.
- [7] A. Lorbach, A. Hubner, M. Wagner, *Dalton Trans.* 2012, 41, 6048.
- [8] H. Braunschweig, A. Damme, J. O. C. Jimenez-Halla, C. Hoarl, I. Krummenacher, T. Kupfer, L. Mailaender, K. Radacki, J. Am. Chem. Soc. 2012, 134, 20169.
- [9] L. Weber, J. Halama, V. Werner, K. Hanke, L. Böhling, A. Chrostowska, A. Dargelos, M. Maciejczyk, A.-L. Raza, H.-G. Stammler, B. Neumann, *Eur. J. Inorg. Chem.* 2010, 5416.
- [10] A. L. Korich, P. M. Iovine, Dalton Trans. 2010, 39, 1423.
- [11] K. Parab, K. Venkatasubbaiah, F. Jaekle, J. Am. Chem. Soc. 2006, 128, 12879.
- [12] Y.-L. Rao, H. Amarne, S. Wang, Coord. Chem. Rev. 2012, 256, 759.
- [13] K. Tanaka, Y. Chujo, *Macromol. Rapid Commun.* 2012, 33, 1235.
- [14] J. F. Araneda, W. E. Piers, B. Heyne, M. Parvez, R. McDonald, Angew. Chem. 2011, 123, 12422; Angew. Chem. Int. Ed. 2011, 50, 12214–12217.
- [15] D. Frath, S. Azizi, G. Ulrich, R. Ziessel, Org. Lett. 2012, 14, 4774.
- [16] J. Massue, D. Frath, G. Ulrich, P. Retailleau, R. Ziessel, Org. Lett. 2012, 14, 230.
- [17] Z. Zhang, H. Bi, Y. Zhang, D. Yao, H. Gao, Y. Fan, H. Zhang, Y. Wang, Y. Wang, Z. Chen, D. Ma, *Inorg. Chem.* **2009**, 48, 7230.
- [18] Q. Hou, L. Zhao, H. Zhang, Y. Wang, S. Jiang, J. Lumin. 2007, 126, 447.
- [19] D. Li, Z. Zhang, S. Zhao, Y. Wang, H. Zhang, *Dalton Trans.* 2011, 40, 1279.
- [20] H. Zhang, C. Huo, K. Ye, P. Zhang, W. Tian, Y. Wang, *Inorg. Chem.* 2006, 45, 2788.
- [21] F. P. Macedo, C. Gwengo, S. V. Lindeman, M. D. Smith, J. R. Gardinier, *Eur. J. Inorg. Chem.* 2008, 3200.
- [22] B. J. Liddle, R. M. Silva, T. J. Morin, F. P. Macedo, R. Shukla, S. V. Lindeman, J. R. Gardinier, J. Org. Chem. 2007, 72, 5637.
- [23] Y. Ren, X. Liu, W. Gao, H. Xia, L. Ye, Y. Mu, Eur. J. Inorg. Chem. 2007, 1808.
- [24] M. Rodriguez, J. L. Maldonado, G. Ramos-Ortiz, O. Dominguez, M. E. Ochoa, R. Santillan, N. Farfan, M.-A. Meneses-Nava, O. Barbosa-Garcia, *Polyhedron* 2012, 43, 194.
- [25] Q. D. Liu, M. S. Mudadu, R. Thummel, Y. Tao, S. Wang, Adv. Funct. Mater. 2005, 15, 143.
- [26] S. L. Hellstrom, J. Ugolotti, G. J. P. Britovsek, T. S. Jones, A. J. P. White, New J. Chem. 2008, 32, 1379.



- [27] H. Y. Chen, Y. Chi, C. S. Liu, J. K. Yu, Y. M. Cheng, K. S. Chen, P. T. Chou, S. M. Peng, G. H. Lee, A. J. Carty, S. J. Yeh, C. T. Chen, *Adv. Funct. Mater.* 2005, *15*, 567.
- [28] T.-R. Chen, R.-H. Chien, M.-S. Jan, A. Yeh, J.-D. Chen, J. Organomet. Chem. 2006, 691, 799.
- [29] Z. Zhang, D. Yao, S. Zhao, H. Gao, Y. Fan, Z. Su, H. Zhang, Y. Wang, *Dalton Trans.* 2010, 39, 5123.
- [30] H. Zhang, C. Huo, J. Zhang, P. Zhang, W. Tian, Y. Wang, *Chem. Commun.* 2006, 281.
- [31] Y. Liu, J. Guo, H. Zhang, Y. Wang, Angew. Chem. 2002, 114, 190; Angew. Chem. Int. Ed. 2002, 41, 182.
- [32] A. Loudet, K. Burgess, Chem. Rev. 2007, 107, 4891.
- [33] G. Ulrich, R. Ziessel, A. Harriman, Angew. Chem. 2008, 120, 1202; Angew. Chem. Int. Ed. 2008, 47, 1184.
- [34] N. Boens, V. Leen, W. Dehaen, Chem. Soc. Rev. 2012, 41, 1130.
- [35] S. Madhu, M. Ravikanth, Inorg. Chem. 2012, 51, 4285.
- [36] S. Kappaun, S. Rentenberger, A. Pogantsch, E. Zojer, K. Mereiter, G. Trimmel, R. Saf, K. C. Mouller, F. Stelzer, C. Slugove, *Chem. Mater.* 2006, 18, 3539.
- [37] A. Nagai, S. Kobayashi, Y. Nagata, K. Kokado, H. Taka, H. Kita, Y. Suzuri, Y. Chujo, J. Mater. Chem. 2010, 20, 5196.
- [38] F. Cheng, F. Jaekle, Chem. Commun. 2010, 46, 3717.
- [39] Y. Nagata, Y. Chujo, Macromolecules 2007, 40, 6.
- [40] Q. Wu, M. Esteghamatian, N.-X. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio, S. Wang, *Chem. Mater.* 2000, 12, 79.
- [41] Y. Cui, Q.-D. Liu, D.-R. Bai, W.-L. Jia, Y. Tao, S. Wang, *Inorg. Chem.* 2005, 44, 601.
- [42] S. Anderson, M. S. Weaver, A. J. Hudson, Synth. Met. 2000, 111–112, 459.
- [43] Y. Qin, I. Kiburu, S. Shah, F. Jaekle, *Macromolecules* 2006, 39, 9041.
- [44] Y. Qin, I. Kiburu, S. Shah, F. Jaekle, Org. Lett. 2006, 8, 5227.
- [45] F. Cheng, E. M. Bonder, F. Jaekle, *Macromolecules* 2012, 45, 3078.
- [46] H. Li, F. Jaekle, Macromolecules 2009, 42, 3448.
- [47] D. Frath, S. Azizi, G. Ulrich, P. Retailleau, R. Ziessel, Org. Lett. 2011, 13, 3414.
- [48] D. Frath, S. Azizi, G. Ulrich, R. Ziessel, Org. Lett. 2012, 14, 4774.
- [49] J. A. Riddle, S. P. Lathrop, J. C. Bollinger, D. Lee, J. Am. Chem. Soc. 2006, 128, 10986.

- [50] Y.-K. Lim, S. Wallace, J. C. Bollinger, X. Chen, D. Lee, *Inorg. Chem.* 2007, 46, 1694.
- [51] Q. Zhao, H. Zhang, A. Wakamiya, S. Yamaguchi, Synthesis 2009, 127.
- [52] D. Suresh, C. S. B. Gomes, P. T. Gomes, R. E. Di Paolo, A. L. Macanita, M. J. Calhorda, A. Charas, J. Morgado, M. T. Duarte, *Dalton Trans.* 2012, 41, 8502.
- [53] H.-C. Zhang, W.-S. Huang, L. Pu, J. Org. Chem. 2000, 66, 481.
- [54] T. Steiner, Angew. Chem. 2002, 114, 50; Angew. Chem. Int. Ed. 2002, 41, 48.
- [55] N. N. Shapetko, L. N. Kurkovskaya, V. G. Medvedeva, A. P. Skoldinov, L. K. Vasyanina, *Zh. Strukt. Khim.* **1969**, *10*, 936.
- [56] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, rev. C.02, Gaussian, Inc., Wallingford, CT, 2009.
- [57] Another possibility is the extended conjugation seen in 1 (*N*-phenyl and biphenyl) might have altered the orbital energy levels; further studies are under progress to elucidate the origin of the same.
- [58] I. Shinar, Organic light-emitting devices: a survey, Springer, New York, 2003.
- [59] G. M. Sheldrick, SADABS, v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI.
- [60] G. Sheldrick, Bruker XRD, Madison, WI.

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