Bridging-arylene effects on spectroscopic and photophysical properties of arylborane–dipyrrinato zinc(II) complexes†

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Novel bis(dipyrrinato)zinc(II) derivatives having 4-[bis(2,4,6-trimethylphenyl)boryl]phenyl (ZnBph) or 4-[bis(2,4,6-trimethylphenyl)boryl]-2,3,5,6-tetramethylphenyl groups (ZnBdu) at the 5-position of the dipyrrinato ligands were designed and synthesized. In ZnBph the smaller dipyrrinato–arylene–dimesitylboryl dihedral angles, an intramolecular charge transfer arising from the presence of the vacant p orbital on the boron atom participates in the ππ* excited state in contrast to the pure ππ* excited state of ZnBdu. The synergistic ππ*/ILCT excited state was weakly fluorescent, and the fluorescence was enhanced upon binding of fluoride to the boron atom.

Introduction

Triarylborane derivatives exhibit a characteristic absorption/fluorescence owing to an intramolecular charge transfer (CT) transition from the π orbital of aryl group to the vacant p orbital on the boron atom (π(aryl)-p(B) CT) and, therefore, various triarylborane derivatives have been reported.1–11 Triarylboranes are also able to tune the spectroscopic and photophysical properties of a metal complex by being introduced to the periphery of its ligand(s). As a pioneering example reported by Kitamura and coworkers, a CHCl3 solution of [Pt(Bph-tpy)Cl]+ (Bph-tpy = 2,2’:6’,2”-terpyridine) showed intense phosphorescence at room temperature (emission quantum yield = 0.011) whereas a metal-to-ligand CT (MLCT) excited state of a [Pt(tpy)Cl]+ (tpy = 2,2’:6’,2”-terpyridine) derivative is typically nonemissive in a solution phase.12 The enhanced emission from [Pt(Bph-tpy)Cl]+ originates in synergistic CT interactions between MLCT in the Pt(tpy)Cl moiety and π(aryl)-p(B) CT in the triarylborane unit. Interestingly, an analogous complex, [Pt(Bdu-tpy)Cl]+ (Bdu-tpy = 4’-[4-[bis(2,4,6-trimethylphenyl)boryl]phenyl]-2,2’:6’,2”-terpyridine), did not exhibit such room-temperature phosphorescence at all. The difference in the phosphorescence ability between the complexes was explained by a disconnection of the CT systems in [Pt(Bdu-tpy)Cl]+ due to the perpendicularly-oriented durylene (2,3,5,6-tetramethylphenylene) group. Thus, the triarylborane has become one of the choices to control photophysical/photochemical properties of a metal complex.13–17 However, the number of the reports focusing on effects of a linker between the triarylborane and metal-complex moieties is still limited.18–20

We recently reported synthesis, spectroscopic and photophysical properties of cyclometalated iridium(II) and platinum(II) complexes with an arylborane-appended dipyrrinato ligand(s).21 These complexes showed intense visible absorption (molar absorption coefficient ε ≥ 104 M–1 cm–1 (M = mol dm–3) at ≈490 nm) and visible–near-IR phosphorescence ascribed to the synergistic MLCT/ππ*/π(aryl)-p(B) CT transition. Dipyrrinato metal complexes exhibiting the CT-type excited states are characteristic at this stage since most of the excited states of dipyrrinato metal complexes are ascribed to ππ* transition in the dipyrrinato ligand.21–22 Especially, two stereoisomers of bis[5-[4-[bis(2,4,6-trimethylphenyl)boryl]phenyl]dipyrrinato]platinum(II), PtBph, possessing the square-planar and distorted tetrahedral geometries show different absorption/emission spectra not only in the MLCT/ππ*/π(aryl)-p(B) CT band but also in the ligand-centered (LC) band. Both crystallographic data and theoretical calculations suggest that a dihedral angle between the dipyrrinate and bridging phenylene moieties in the square-planar isomer is larger than that in the distorted tetrahedral one. The results remind us of the earlier Pt-tpy system and importance of further understanding of the ligand itself in an arylborane-appended metal complex.

In order to extract the molecular/electronic effects of the ligand itself in an arylborane–dipyrrinato metal complex, we chose dipyrrinato zinc(II) complexes. They exhibit intense visible absorption (absorption maximum wavelength λabs ≈ 470–500 nm; ε ≈ (5.0—10) × 104 M–1 cm–1) and fluorescence

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c Electronic supplementary information (ESI) available: 1H and 13C(1H) NMR spectra, crystallographic data of ZnBdu, detailed results of theoretical calculations, fluorescence decay profiles and 1H NMR spectra in the absence and presence of TBAF. CCDC 2035525. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ra09029h
ascribed to pure LC ππ* excited states owing to the inert dπ
nature of the zinc(u) center.51-53 Furthermore, the spectroscopic properties of a dipyrrinato zinc(u) complex are dependent on the substituent group at the 5-position of the dipyrrinato ligand. For example, Lindsey and coworkers revealed that bis[5-(2,4,6-trimethylphenyl)dipyrrinato]zinc(u) (Znmes) showed much higher fluorescence quantum yield (Φf = 0.36) than bis[5-phenyl(dipyrrinato)zinc(u)] (ZnPh, Φf = 0.01) by effects of both fluorescent and nonfluorescent pathways.62 It has also been reported that the fluorescence from Znmes is quenched in a polar solvent by a thermal deactivation of the excited state given intraligand charge transfer (ILCT) character in the excited state and discussed in terms of the molecular geometries obtained by theoretical calculations.

**Experimental section**

**Chemicals**

All the reagents including organic solvents were commercially available and used without further purification. 5-[4-[Bis(2,4,6-trimethylphenyl)boryl]phenyl]dipyrrin was prepared according to the literature methods.54 4-[Bis(2,4,6-trimethylphenyl)boryl]-2,3,5,6-tetramethylbenzaldehyde (2) was synthesized similarly to the phenyl analogue. All the synthetic reactions and subsequent workup manipulations were carried out under air unless otherwise noted.

**Physical measurements and instruments**

NMR spectra were recorded on a JEOL JNM-AL 400 Fourier-transform NMR spectrometers (400 MHz). The chemical shifts of the 1H, 13C{1H}, 11B{1H} and 19F{1H} NMR spectra determined in CDCl3 were given in ppm relative to tetramethylsilane (0.00 ppm for 1H and 13C{1H}) as an internal standard, or boron trifluoride diethyl-ether complex (0.00 ppm for 11B{1H}) and hexafluorobenzene (−164.9 ppm vs. CFCl3 for 19F{1H}) as external standards. High-resolution fast-atom bombardment mass spectrometries (HR-FAB-MS) were carried out on a JEOL JMS-700N spectrometer. Elemental analyses (C, H, N) were performed by a Perkin Elmer 2400II elemental analyzer. UV-vis absorption spectra were recorded on a Jasco V-560 spectrophotometer. The corrected emission spectra were obtained by using a Jasco F-6500 spectrophluorometer (excitation wavelength = 365 nm). Fluorescence decay measurements were conducted by using a Hamamatsu Photonics picosecond fluorescence lifetime measurement system C11200 equipped with picosecond light pulser PLP-10 as a 405 nm excitation light source. Emission quantum yields were determined by using a Hamamatsu Photonics Absolute PL Quantum Yield Measurement System C9920-02 (excitation wavelength = 365 nm). For the photophysical measurements, spectrophotometric-grade toluene was used as supplied.

**Synthesis of 4-iodo-2,3,5,6-tetramethylphenyl]bis(2,4,6-trimethylphenyl)boran (1)**

Synthesis was performed with minor changes in the reported procedures.37 An oven-dried Schlenk tube was evacuated and filled subsequently with an argon gas. 1,4-Diiodo-2,3,5,6-tetramethylbenzene (2.8 g, 7.2 mmol) and dry diethyl ether (20 mL) was added, then, cooled to −78 °C in a dry-ice bath. n-Butyllithium in n-hexane (1.6 M, 5.2 mL, 8.3 mmol) was added to the reaction mixture at −78 °C. After stirring at −78 °C for 1 h, the reaction mixture became a pale-yellow suspension. Bis(2,4,6-trimethylphenyl)boron fluoride (2.1 g, 7.9 mmol) dissolved in dry diethyl ether (20 mL) was added to the reaction mixture, then, the mixture allowed to warm to room temperature and continuously stirred overnight. The reaction mixture became a yellow suspension. After an addition of HCl(aq) (1 M, 20 mL), the mixture was extracted with diethyl ether (30 mL × 2). The combined organic extract was washed with water (50 mL), dried over anhydrous Na2SO4 and concentrated under reduced pressure. The crude product was washed with n-hexane (50 mL) to give pure 1 (2.0 g, 59%) as a colorless solid.37 1H NMR (400 MHz, CDCl3) δ: 6.73 (4H, s, m-Ar-H of mesityl), 2.43 (6H, s, 2,6-CH₃ of duryl), 2.26 (6H, s, p-CH₃ of mesityl), 2.09 (6H, s, 3,5-CH₃ of duryl), 1.94 ppm (12H, s, o-CH₃ of mesityl).

**Synthesis of 4-[bis(2,4,6-trimethylphenyl)boryl]-2,3,5,6-tetramethylbenzaldehyde (2)**

An oven-dried Schlenk tube was evacuated and filled subsequently with an argon gas. 1 (2.0 g, 4.9 mmol) and dry tetrahydrofuran (20 mL) was added, then, cooled to −78 °C in an acetone/dry-ice bath. n-Butyllithium in n-hexane (1.6 M, 4.4 mL, 7.0 mmol) was added to the reaction mixture at −78 °C. After stirring at −78 °C for 1 h, the reaction mixture became an orange suspension. Dry N,N-dimethylformamide (2.0 mL) was added to the reaction mixture at −78 °C.
for 1 h, the reaction mixture became a yellow solution. Then, HCl(aq) (1 M, 50 mL) was added and stirred for another 4 h. The reaction mixture was extracted with ethyl acetate (30 mL x 2). The combined organic extract was washed with water (50 mL), dried over anhydrous MgSO4 and concentrated under reduced pressure. The crude product was purified by recrystallization from ethyl acetate to give pure 2 (1.3 g, 65%) as a pale-yellow solid. 
1H NMR (400 MHz, CDCl3): δ: 10.7 (1H, s, CHO), 6.75 (4H, s, m-CH3 of mesityl), 2.31 (6H, s, 2,6-CH3 of duryl), 2.27 (6H, s, p-CH3 of mesityl), 2.02 (6H, s, 3,5-CH3 of duryl), 1.95 ppm (12H, s, o-CH3 of mesityl).

Synthesis of 5-{4-[bis(2,4,6-trimethylphenyl)boryl]boryl}-2,3,5,6-tetramethylphenyl)dipyrrin (3)

2 (501.4 mg, 1.22 mmol) was dissolved in neat pyrrole (25 mL) and degassed by a nitrogen-gas bubbling for 30 min. Tri-fluoroacetic acid (20 µL, 0.23 mmol) was then added, and stirred at room temperature for 10 min. The reaction mixture was further diluted with CH2Cl2 (50 mL), washed with NaOH(aq) (1 M, 50 mL) and dried over anhydrous MgSO4. After removing MgSO4 by filtration and evaporation of CH2Cl2 under reduced pressure, the remaining pyrrole was removed by vacuum distillation with heating (40 °C). Then, the product was added to a solution of p-chloranil (500 mg, 2.04 mmol) in CH2Cl2 (50 mL). The solution color changed from yellow to dark yellow-green. The solution was stirred overnight and, then, filtered and evaporated to remove resultant insolubles and CH2Cl2 respectively. The reaction mixture was processed by precipitation (CH2Cl2/hexane) and silica-gel column chromatography, eluting with CH2Cl2. Recrystallization from CH2Cl2/methanol afforded pure ZnBdu (80.8 mg, 61%) as a yellow-brown solid. 
1H NMR (400 MHz, CDCl3): δ: 7.50 (4H, s, 1,9-Ar-H of dipyrrinate), 6.79 (8H, d, J = 6.8 Hz, m-CH3 of mesityl), 6.57 (4H, d, J = 4.0 Hz, 2,8-Ar-H of dipyrrinate), 6.38 (4H, d, J = 4.2 Hz, 3,7-Ar-H of dipyrrinate), 2.30 (12H, s, p-CH3 of mesityl), 2.10 (12H, s, 2,6-CH3 of durylene), 2.05 (12H, s, 3,5-CH3 of durylene), 2.02 ppm (24H, s, o-CH3 of o-mesityl).

X-ray crystal structure determinations

Diffraction data were collected at −180 °C under a stream of cold N2 gas on a Rigaku RA-Micro7 HFM instrument equipped with a Rigaku Saturn724+ CCD detector by using graphite-monochromated Mo Kβ radiation. The frame data were integrated using a Rigaku CrystalClear program package, and the data were corrected for absorption using a REQAB program. The calculation was performed with a CrystalStructure software package except for refinement, which was performed using SHELXLI Version 2018/3. The structures were solved by direct methods and refined on F2 by the full-matrix least-squares methods. Anisotropic refinement was applied to all non-hydrogen atoms with the exception of the crystal solvents. All hydrogen atoms were put at calculated positions.

Computational methods

Theoretical calculations for the complexes were conducted with Gaussian 16W software (Revision A.03). Optimizations of the ground-state geometries of the complexes were performed by using the B3LYP density functional theory (DFT). The LanL2DZ19,20 and 6-31G(d,p)21 basis sets were used to treat the geometrical structures of the zinc and all other atoms, respectively. Time-dependent DFT (TD-DFT) calculations were then performed to estimate the energies and oscillator strengths of electronic excitation transitions generating the 50 lowest-energy singlet excited states. All of the calculations were carried out in toluene by using a polarizable continuum model (PCM). Optimized geometries, Kohn–Sham molecular orbitals and
natural transition orbitals (isovalue = 0.03 e Å⁻³) were visualized by GaussView 5.²⁸

Results and discussion
Synthesis and characterization

Novel dipyrirnato zinc(II) complexes ZnBph and ZnBdu were successfully synthesized in moderate yields (45% for ZnBph, 61% for ZnBdu) by mixing Zn(OAc)₂ · 2H₂O and dipyrrin in a dichloromethane/methanol mixture at room temperature. The complexes were identified by the ¹H and ¹³C{¹H} NMR spectroscopies, HR-FAB-MS and elemental analysis. In the ¹H NMR spectra of ZnBph and ZnBdu (see Fig. S3 and S4), four protons at 1- and 9-positions of dipyrrinate moiety were observed as singlet at 7.50–7.54 ppm which was shifted to upfield upon the complexation. Two doublets ascribed to protons at 2,8- and 3,7-positions were observed at 6.38–6.68 ppm. The trends are similar to other bis(dipyrirnato)zinc(II) complexes.²⁴ Single crystals of ZnBdu suitable for X-ray crystallographic analysis were obtained from CH₂Cl₂/n-pentane. The X-ray structure of ZnBdu is shown in Fig. 1(a), whose crystallographic data is summarized in Table S1.¹ The zinc center takes a tetrahedral geometry with a dihedral angle for two Zn–N₂(dipyrirnato) planes being 90°. The distance between the zinc center and each pyrrolic nitrogen is 1.983 Å, which are similar to those in Znph (1.973–1.988 Å).²⁴ The dihedral angle between a dipyrrinato ligating and bridging phenylene moieties was 77.9°. The value is similar to those of the previous iridium(m) and platinum(II) complexes (80.7° and 88.7°).²² The boron atoms in the aryloborane groups take a planar sp²-like configuration with B–C bond lengths being 1.57–1.58 Å and C–B–C angles being ~120°. Dihedral angle between the durylene and BC₄ plane was 54.1°. These structural characteristics of ZnBdu in the crystalline phase are indicative of the conjugation between the dipyrrinato moiety and boron atom in the ligand. The structures of the complexes were compared on the basis of the DFT calculations because single crystals of ZnBph suitable for X-ray structural analysis were not obtained in spite of many efforts for recrystallization from various conditions. Optimized geometries of ZnBph and ZnBdu are shown in Fig. 1(b) and (c), respectively. The zinc centers in both complexes take tetrahedral geometries, and zinc–nitrogen distances are in the range of 2.059–2.063 Å. The dihedral angle between dipyrirnato ligating moiety and bridging phenylene group (θ₁) in ZnBph (64.1°–64.3°) is smaller than that in ZnBdu (89.0°–89.2°). Similar tendency was also observed for the tilt angle between arylene group and the BC₄ plane in the aryloborane moiety (θ₂ = 21.7°–25.6° and 57.1°–57.7° for ZnBph and ZnBdu, respectively). On the basis of these angles, (cos θ₁ × cos θ₂) values as measures of the conjugation between the π

![Fig. 1](image1.png)

Fig. 1 Perspective view of crystal structure for ZnBdu (a) 50% probability ellipsoids) and DFT optimized geometries of ZnBph (b), ZnBdu (c) and ZnBph 2F⁻ (d): carbon (gray), nitrogen (blue), boron (red), zinc (orange) and fluorine (green). Hydrogen atoms are omitted for clarity.

![Fig. 2](image2.png)

Fig. 2 UV–vis absorption (broken lines) and fluorescence spectra (solid lines) of ZnBph (red) and ZnBdu (blue) in toluene at 298 K. The integrations of the fluorescence spectra in a wavenumber scale correspond relatively to the fluorescence quantum yields of the complexes. Inset: normalized fluorescence spectra.
orbital of the dipyrrinate moiety and the vacant p orbital on the boron atom via the bridging arylene moiety in ZnBph and ZnBdu were calculated to be 40 and 1%, respectively. The smaller dihedral angle in ZnBph than in ZnBdu strongly indicates enhanced electronic interactions between the dipyrrinato zinc(II) complex and the arylborane moieties, and therefore larger contribution of the arylborane moieties to the spectroscopic/photophysical properties of a complex are expected.

Absorption spectra

Fig. 2 shows absorption spectra of ZnBph and ZnBdu in toluene at 298 K, and the spectroscopic properties are summarized in Table 1. The complexes exhibited intense/narrow and weak/broad absorption bands at around 487 and 334 nm, respectively. According to the DFT calculations (vide infra), the former band is assigned to the typical $\pi\pi^*$ transitions in a dipyrrinato ligand and the latter is ascribed to $\pi$(aryl)–$p$(B) CT transitions in an arylborane moiety, similarly to other arylborane–dipyrrinato metal complexes. The absorption maximum wavelengths of ZnBph and ZnBdu ($\lambda_{abs} = 487$ and 486 nm, respectively) are comparable with those of Znph and Znmes ($\lambda_{abs} = 485$ nm and 487 nm, respectively) without any arylborane substituents. Interestingly, the molar absorption coefficients ($\epsilon$) at the maximum wavelength ($\lambda_{abs}$) of the low-energy band of the complexes ($9.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for ZnBph and $1.32 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for ZnBdu) were larger than those of the arylborane–dipyrrinato iridium(III) and platinum(II) complexes ($\epsilon = 7.4 \times 10^4$ and $2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively) whose $\pi\pi^*$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{abs}$/nm ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)</th>
<th>$\lambda_{f}$/nm</th>
<th>$\Phi_f$</th>
<th>$\tau_d$/ns</th>
<th>$k_{\text{f}}$/s$^{-1}$</th>
<th>$k_{\text{nr}}$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBph</td>
<td>334 (4.3), 487 (0.9)</td>
<td>517</td>
<td>0.01</td>
<td>1.3</td>
<td>$7.7 \times 10^6$</td>
<td>$7.6 \times 10^4$</td>
</tr>
<tr>
<td>ZnBdu</td>
<td>333 (4.4), 486 (13.2)</td>
<td>504</td>
<td>0.34</td>
<td>2.7</td>
<td>$1.3 \times 10^8$</td>
<td>$2.4 \times 10^4$</td>
</tr>
<tr>
<td>ZnBph$^{2F}$</td>
<td>383 (1.6), 481 (0.94)</td>
<td>503</td>
<td>0.02</td>
<td>0.2</td>
<td>$1 \times 10^8$</td>
<td>$5 \times 10^9$</td>
</tr>
<tr>
<td>Znph$^a$</td>
<td>485</td>
<td>500</td>
<td>0.006</td>
<td>0.09</td>
<td>$7 \times 10^7$</td>
<td>$1 \times 10^10$</td>
</tr>
<tr>
<td>Znph$^b$</td>
<td>322 (1.4), 482 (11.5)</td>
<td>500</td>
<td>0.36</td>
<td>2.7</td>
<td>$1.3 \times 10^8$</td>
<td>$2.4 \times 10^8$</td>
</tr>
<tr>
<td>Znmes$^a$</td>
<td>487</td>
<td>501</td>
<td>0.36</td>
<td>2.7</td>
<td>$1.3 \times 10^8$</td>
<td>$2.4 \times 10^8$</td>
</tr>
<tr>
<td>Znmes$^b$</td>
<td>345, 485</td>
<td>501</td>
<td>0.36</td>
<td>2.7</td>
<td>$1.3 \times 10^8$</td>
<td>$2.4 \times 10^8$</td>
</tr>
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</table>

$^a$ Calculated by the equation, $\Phi_f = \frac{k_{\text{f}}}{(k_{\text{f}} + k_{\text{nr}})} = k_{\text{f}} \tau_f$. $^b$ Data in toluene compiled from ref. 62. $^c$ Data in CH$_2$Cl$_2$ compiled from ref. 54.
transitions synergistically interact with MLCT and/or \( \pi(aryl)-p(B) \) CT ones. Such differences in the \( \epsilon \) values indicates that an introduction of the charge-transfer character to the \( \pi\pi^* \) transition in a dipyrrinato-metal complex decreases the relevant oscillator strength. Thus, smaller \( \epsilon \) value of \( \text{ZnBph} \) suggests the existence of the \( \pi \) interactions throughout the ligand presumably owing to the smaller dihedral angles between dipyrrinate–phenylene and phenylene–dimesitylboryl moieties. These discussions were theoretically supported by TD-DFT calculations as summarized in Tables S2–S5.† For both complexes, intense absorption bands at \( \lambda \approx 487 \) nm appeared as electronic transitions generating third (\( S_3 \)) and forth excited states (\( S_4 \)). Fig. 3 shows natural transition orbitals (NTOs) for the \( S_3 \) and \( S_4 \) states of the complexes. Both \( S_3 \) and \( S_4 \) states of \( \text{ZnBph} \) originate in electronic transitions from the dipyrrinate moiety to the whole ligand, gaining the \( \pi(aryl)-p(B) \) CT character, whereas those of \( \text{ZnBdu} \) are assignable to the pure \( \pi\pi^* \) transitions in a 5-duryldipyrrinate moiety.

**Fluorescence spectra and photophysical properties**

As shown in Fig. 2, the fluorescence from \( \text{ZnBph} \) (\( \Phi_f = 0.01 \) in toluene at 298 K) was significantly weak compared with that from \( \text{ZnBdu} \) (\( \Phi_f = 0.34 \)). Furthermore, the fluorescence spectrum of \( \text{ZnBph} \) (maximum wavelength \( \lambda_f = 517 \) nm) was broadened and shifted to lower-energy compared with those of \( \text{ZnBdu} \) (504 nm), \( \text{Znph} \) (501 nm)\(^{62} \) and \( \text{Znmes} \) (500 nm)\(^{62} \) see Table 1. The spectroscopic data of \( \text{ZnBph} \) indicate a partial contribution of a CT character arising from the low-energy p(B) to the fluorescent excited state and energetic stabilization of the excited state by the solvation. In practice, the radiative rate constant (\( k_r \)) of \( \text{ZnBph} \) (7.7 \( \times \) \( 10^6 \) s\(^{-1} \), see Table 1) was 17-times smaller than that of \( \text{ZnBdu} \) (1.3 \( \times \) \( 10^8 \) s\(^{-1} \)) owing to a decreased wavefunction overlap between the excited and ground states.

**Fig. 4** UV-vis absorption and fluorescence spectral changes upon an addition of TBAF (0–4.0 equiv.) in toluene: \( \text{ZnBph} \) ((a and b) red to green) and \( \text{ZnBdu} \) ((c and d) blue to yellow).
Furthermore, the CT character in the excited state accelerated thermal deactivation to the ground state as the nonradiative decay rate constant \((k_{nr})\) of \(\text{ZnBph}\) \((7.6 \times 10^8 \text{ s}^{-1})\) was three-times larger than that of \(\text{ZnBdu}\) \((k_{nr} = 2.4 \times 10^8 \text{ s}^{-1})\). It should be larger than \(k_r\) and \(k_{nr}\) values of \(\text{ZnBdu}\) are comparable to those of \(\text{Znmes}\) \((k_r = 1.3 \times 10^8 \text{ s}^{-1} \text{ and } k_{nr} = 2.4 \times 10^8 \text{ s}^{-1})\). Thus, the strong fluorescence from \(\text{ZnBdu}\) would originate in the pure \(\pi\pi^*\) excited state and suppressed nonradiative decay processes owing to the presence of the bulky durenyl bridging units. On the other hand, the \(k_r\) and \(k_{nr}\) values of \(\text{ZnBph}\) are significantly smaller than those of \(\text{Znp}\) \((k_r = 7 \times 10^7 \text{ s}^{-1} \text{ and } k_{nr} = 1 \times 10^8 \text{ s}^{-1})\), suggesting the existence of CT interactions in the excited state. As results, the fluorescence from \(\text{ZnBph}\) was well characterized by the \(\pi\pi^*/\text{ILCT}\) excited state, and the participation of the ILCT character in the excited state of a complex was revealed by varying the extent of \(\pi\)-conjugation between the dipyrrinate and aryloborane moieties.

**Spectroscopic responses to fluoride**

Since the electron-deficient boron atom in an aryloborane derivative can bind with a small Lewis base such as fluoride (Chart 2) with a binding constant being \(\sim 10^6 \text{ M}^{-1}\), we carried out the fluoride-addition experiments for the complexes. Fig. 4 shows absorption and fluorescence spectra of the complexes in the absence and presence of tetra-n-butylammonium fluoride (TBAF) in toluene. The absorbances of each spectrum were divided by the total concentration of the complex \((c_0)\) and optical path length \((l)\) so that the vertical axis corresponds to the molar absorption coefficient. Upon an addition of TBAF to \(\text{ZnBph}\), the \(\pi\text{(aryl)}-\text{p}(\text{B})\) CT absorption band at around 334 nm disappeared, and a broad absorption band at around 383 nm appeared with an isosbestic point at 360 nm. In addition, the fluoride binding shortened the maximum wavelength of the lowest-energy \(\pi\pi^*/\text{ILCT}\) absorption band of \(\text{ZnBph}\) from 487 nm to 481 nm, similarly to that observed for the relevant cyclometalated iridium(II) complex.9 Complete disappearance of the \(\pi\text{(aryl)}-\text{p}(\text{B})\) CT band and the complicated spectral changes in the absorption band at \(\sim 480 \text{ nm}\) indicate successive bindings of two fluoride, affording a \(1:1\) adduct, followed by a \(1:2\) adduct, \(\text{ZnBph} - 2\text{F}^-\). The spectroscopic changes arising from the binding of fluoride to the boron atom were strongly evidenced by \(^1\text{H}, \text{ }^{11}\text{B}[^1\text{H}]\) and \(^{19}\text{F}[^1\text{H}]\) NMR measurements as shown in Fig. S8, S10 and S13,† respectively. The \(^{11}\text{B}\) NMR signal of \(\text{ZnBph}\) was drastically shifted from 75.7 ppm to 5.5 ppm upon the addition of fluoride as TBAF. The broad signal was also observed at \(\sim 174.41 \text{ ppm}\) for the \(^{19}\text{F}\) NMR spectrum of \(\text{ZnBph}\) in the presence of TBAF \((4.0 \text{ eq.})\) owing to the coupling to \(^{10}\text{B} (I = 3)\) and \(^{11}\text{B} (I = 3/2)\), indicating the formation of a B-F bond with \(\text{ZnBph}\). In addition, the absence of the signal at \(\sim 84.04 \text{ ppm}\) (corresponding to the signal of DCDF\(_2\) generated by the reaction of fluoride with solvent molecule DCDF\(_2\)) in the \(^{19}\text{F}\) NMR spectrum of \(\text{ZnBph}\) suggests that fluoride quickly binds to the boron atom before proceeding the exchange reaction of fluoride with chloride in the solvent molecule. Consequently, the binding of fluoride to the boron atom in \(\text{ZnBph}\) increased electron density around the boron atom.

The structure of \(\text{ZnBph} - 2\text{F}^-\) was theoretically investigated by the DFT calculation and the optimized geometry is shown in Fig. 1(d). Each boron atom possesses a tetrahedral geometry, and the dihedral angles between a dipyrrinate ligating moiety and bridging phenylene group \((\theta_1)\) were reduced to \(56.8^\circ - 58.7^\circ\). The structural and electronic changes increased the transition energy of the lowest-energy absorption band through efficient electron donation from the fluorinated aryloborane group to the dipyrrinate moiety, leading to the decrease of electron density on the dipyrrinate moiety and therefore the downfield-shift of proton signals in the pyrrole rings (see Fig. S15† for HOMO and HOMO-1). The fluorescence from \(\text{ZnBph}\) was shifted to higher-energy with a slight decrease in intensity and then enhanced largely upon a continuous addition of TBAF as shown in Fig. 4(b). The maximum wavelength \((\lambda_{max} = 503 \text{ nm})\) and band shape in the presence of \(\equiv 3.0\) equivalence of fluoride were almost identical to those of \(\text{ZnBdu}\), and the \(k_c\) value of \(\text{ZnBph} - 2\text{F}^- (1 \times 10^8 \text{ s}^{-1})\) was also similar to that of \(\text{ZnBdu}\). Owing to these fluorescence characteristics, it can be expected that the fluoroscence excited state of \(\text{ZnBph} - 2\text{F}^-\) possesses the pure \(\pi\pi^*\) character. Significantly smaller \(\theta_1 (0.02)\) of \(\text{ZnBph} - 2\text{F}^-\) than that of \(\text{ZnBdu}\) can be explained by enhanced thermal deactivation \((k_{nr} = 5 \times 10^9 \text{ s}^{-1})\) via a rotation of the phenylene moiety as reported for \(\text{Znp}\) and \(\text{Znmes}\) \((k_{nr} = 1.1 \times 10^{10} \text{ and } 3.2 \times 10^8 \text{ s}^{-1} \text{ in toluene, respectively})\). On the other hand, there was no experimental evidence of the fluoride binding to \(\text{ZnBdu}\) in the absorption, fluorescence and \(^1\text{H}, \text{ }^{11}\text{B}[^1\text{H}]\) and \(^{19}\text{F}[^1\text{H}]\) NMR spectra as shown in Fig. 4(c) and (d), S9, S11 and S14† presumably due to the steric hindrance of the durenyl moieties. Thus, fluoride binding affinity of an aryloborane–dipyrrinate zinc(II) complex was controllable by the bridging arylene moiety and, upon the fluoride binding, the excited-state electronic structure of \(\text{ZnBph}\) was switched from \(\pi\pi^*/\text{ILCT}\) to pure \(\pi\pi^*\).

**Conclusions**

The bridging arylene moieties in novel bis(dipyrrinate)zinc(II) derivatives having the aryloborane groups at 5-position of the dipyrrinate ligands had significant impacts on the absorption/fluorescence spectra and fluoride-binding affinity of the complex. The theoretical calculations suggest that \(\text{ZnBph}\) with the phenylene linkers possesses smaller dihedral angles between dipyrrinate–phenylene and phenylene–dimesitylboryl moieties than the relevant values of \(\text{ZnBdu}\) with the durenyl linkers. The smaller dihedral angles in \(\text{ZnBph}\) afford the \(\pi\)-conjugation in the entire of the ligand and, therefore, the electron-withdrawing aryloborane groups participate in the electronic structure of the complex. As a result, the excited state of \(\text{ZnBph}\) was best characterized by the synergistic \(\pi\pi^*/\text{ILCT}\), whereas that of \(\text{ZnBdu}\) was the pure \(\pi\pi^*\). \(\text{ZnBph}\) could bind with fluoride, and the excited state was switched from \(\pi\pi^*/\text{ILCT}\) to pure \(\pi\pi^*\) upon the fluoride binding owing to the disappearance of the electron-withdrawing ability of the dimesitylboryl moieties. Thus, we revealed the importance of the
molecular design including the linker structure in metal complexes with an arylborane group(s). Tuning of the extent of the CT character in an excited-state metal complex will be an important factor to control spectroscopic and photophysical properties of metal complexes.

Conflicts of interest

The authors declare no competing financial interest.

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References


