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ARTICLE

Synthesis and Spectroscopic Properties of Novel N-N Linked Bis-(diphenylboron) Complexes

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A novel type of five-membered-ring and a six-membered-ring bis-(diphenylboron) complexes, consisting of hydrazine-schiff base linked bispyrrole and two phenyl rings on the boron atoms, are readily synthesized via a facile two-step reaction. Weak intermolecular interactions are observed in the solid state X-ray crystal structures due to replacement of fluoride with phenyl group at the boron atom. Both complexes exhibit high fluorescent in dilute solution with quantum efficiencies in the range of 0.52–0.88. Because of weak intermolecular interactions and large Stokes shifts, the six-membered-ring complex **1** exhibits efficient solid-state fluorescence. Whereas the five-membered-ring complex **2** has small Stoke shifts, resulting in weak fluorescence in the solid state through self-quenching. The structure–property relationships have been analyzed on the basis of X-ray crystallography, optical spectroscopy, and theoretical calculations.

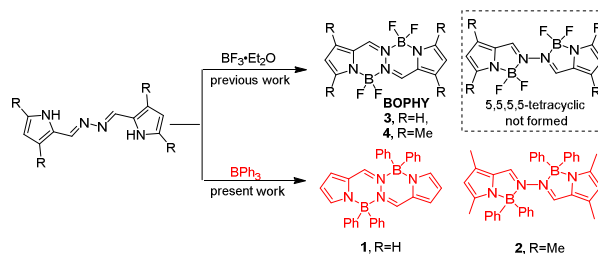
Introduction

The development of highly luminescent fluorophores is great important for applications in biological imaging and organic electronics.¹ Recently, increasing attentions have been paid on the development of novel organoboron dyes with chelating N,N-, N,O-, N,C-chromophores as ligand due to their interesting optical properties that lead to potential uses in organic light-emitting diodes, organic solid-state lasers, organic solid-state sensors and light-emitting electrochemical cells.^{2–6} Among those, BODIPY dyes as the well-known organoboron complexes have been the focus of considerable research interest due to their structural versatility and excellent spectroscopic properties, such as their intense absorption and emission bands, which can be fine-tuned through facile structural modifications, as well as their excellent photostability and high fluorescence quantum yields.^{7–8} Although BODIPY dyes are strongly emissive in solution, they are almost non-emissive in the solid state, owing to the self-absorption enhanced by the small Stokes shifts and strong intermolecular π – π interactions caused by the planar structure.⁹ Much efforts have been devoted to exploring new solid-state emissive organoboron-based fluorophores.¹⁰ Recently, Ziegler and Jiao reported a serial of six-membered-ring bis-(difluoroboron) complexes consisting of hydrazine-schiff base and bispyrrole.¹¹ Although these dyes exhibited

high fluorescence in solution with excellent photostability, relatively weak fluorescence in the solid state were observed due to overlapping π – π interactions between the adjacent fluorophores.^{11b} We conferred that replacing the fluoride atom with larger phenyl groups onto the boron atom might inhibit intermolecular π – π interactions.^{12–13} Therefore, we tried the reaction using triphenylborane with the hydrazine-schiff base linked bispyrrole. Surprisingly, a novel type of five-membered-ring bis-(diphenylboron) complex was exclusively formed by replacement of hydrogen with carbon at 3,5-position of pyrrole. However, six-membered-ring bis-(difluoroboron) complex was obtained using the same precursor.¹¹ Herein, we describe the synthesis, structures and photophysical properties of two types of bis-(diphenylboron) complexes in various solvents and solid states. TD-DFT has been carried out to elucidate the influence of structural modification on the spectroscopic and electronic properties.

Results and discussion

Synthesis



Scheme 1. Synthetic procedure and structures of the bis-(diphenylboron) complexes **1–2** and the bis-(difluoroboron) complexes **3–4**.

The bis-(diphenylboron) complexes **1** and **2** are facilely synthesized via a two-step reaction (Scheme 1). The dipyrrole–imine precursors were prepared by reacting pyrrole-

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2-carboxaldehyde and hydrazine with catalytic amount of acetic acid at room temperature according to the reported literature methods.¹⁴ Complexes **1** and **2** are then obtained by reaction the corresponding dipyrrole-imine with BPh₃ in refluxing toluene in good yields (34% and 61%, respectively). If the same precursors were reacted with BF₃·Et₂O, only six-membered-ring bis-(difluoroboron) complexes could be obtained.¹¹ Five-membered-ring bis-(diphenylboron) complex **2** is the first example of N-N linked dimeric type of BODIPY analogues, which may be formed due to the stability of the five-membered ring and hindrance interaction by the methyl group in the core structure. Both compounds have been characterized by ¹H, ¹³C NMR and MALDI-TOF mass spectroscopy, as well as X-ray single crystal structure analysis. All dyes are well soluble in most organic solvents at room temperature.

X-Ray crystal structure analysis

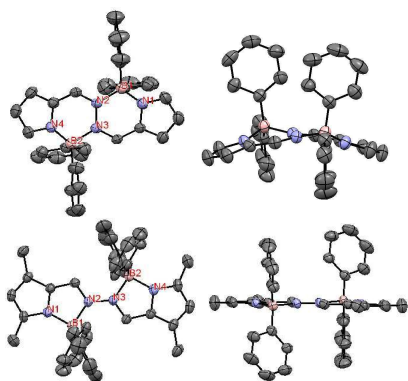


Fig 1. ORTEP drawings of the molecular structures of **1** (top), **2** (bottom). Hydrogen atoms were omitted for clarity. For **1**: B1-N1 1.556, B1-N2 1.633, N2-N3 1.416, N3-B2 1.634, B2-N4 1.551; **2**: B1-N1 1.572, B1-N2 1.639, N2-N3 1.375, N3-B2 1.639, B2-N4 1.572.

X-ray crystallographic analysis was performed to better understand the solid-state emission properties of each compound. Single crystals of **1** were obtained by the slow diffusion of hexane into a CH₂Cl₂ solution at room temperature, single crystals of **2** were obtained by vacuum sublimation. As shown in Fig. 1 (top), the fluorophore core of **1** is composed of four fused rings, with two pyrrole rings at the periphery and two six membered rings in the center, each incorporating two phenyl groups at boron atom. The central core structure of **1** shows a twisted conformation, the dihedral angle between the plane consisting a six-membered-ring and a pyrrole ring with the other symmetrical plane is 24.4° (ESI Fig. 1). In the case of compound **2**, the N-N linked boron pyrrole-imine plane is highly planar with average root mean-square (rms) deviations of 0.046. The boron atom lies within the mean plane and has the typical tetrahedral geometry to form N-B-N fused five-membered ring. The B-N bond lengths are 1.639 (hydrazino-nitrogen atom) and 1.572 Å (pyrrole-nitrogen atom) for compound **2**, 1.634 and 1.551 Å for compound **1**, respectively. The B-N bond lengths in **1** are much longer than that of the B-N (1.599 and 1.515 Å) in the

previously reported bis(BF₂) analogue **3**, this might be due to the twisted conformation of **1** where the boron atoms are slightly deviated out of the indacene plane. The bridged N-N bond length in compound **2** is 1.375 Å, which lies between the single N-N (1.45 Å) and double N-N (1.25 Å) bond length, indicating partially delocalized with the neighbouring aromatic rings.

In the packing diagram (Fig. 2), no face to face or face to head π-π stacking is observed for **1** and **2** due to the large bulky phenyl substituents. For compound **2**, only weak C-H...π (3.44 Å) interactions are found (Fig. 2). Therefore, introducing the phenyl groups efficiently prevent π-π stacking in the solid state structures. This feature will enhance the fluorescence quantum yields in the solid state and facilitate applications for emitting materials.

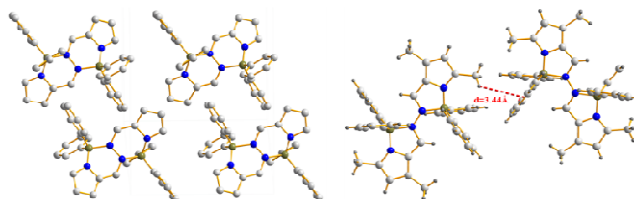


Fig 2. Crystal packing structures of compound **1** (left) and **2** (right).

Spectroscopic properties in solution

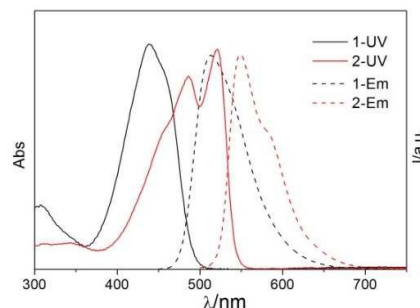


Fig 3. The absorption and emission spectra of **1** and **2** in DCM ($\lambda_{\text{exc}} = 430\text{nm}$ for **1**, $\lambda_{\text{exc}} = 475\text{nm}$ for **2**).

Table 1. Spectroscopic and photophysical properties of **1-2** in various solvents and **3**^{11b} in CH₂Cl₂ at 298K.

| Solvents | λ_{abs} nm | ϵ_{max} | λ_{em} nm | Φ_{F} | τ_{f} ns | K_{r} 10^8 s^{-1} | K_{nr} 10^8 s^{-1} |
|----------|---------------------------------|-------------------------|-----------------------------|-------------------|-------------------------|---|--|
| 1 | Hexane | 436 | 32800 | 509 | 0.70 | 5.34 | 1.31 |
| | Toluene | 440 | 35800 | 513 | 0.80 | 4.91 | 1.63 |
| | CH ₂ Cl ₂ | 438 | 34800 | 513 | 0.69 | 5.12 | 1.35 |
| | THF | 436 | 34800 | 512 | 0.88 | 4.69 | 1.88 |
| | CH ₃ CN | 437 | 34900 | 511 | 0.67 | 5.64 | 1.19 |
| 2 | Hexane | 486,520 | 50500 | 543 | 0.63 | 5.02 | 1.25 |
| | Toluene | 490,523 | 56900 | 550 | 0.53 | 4.75 | 1.12 |
| | CH ₂ Cl ₂ | 486,521 | 52600 | 547 | 0.52 | 4.71 | 1.10 |
| | THF | 487,521 | 58500 | 547 | 0.57 | 5.28 | 1.08 |
| | CH ₃ CN | 485,517 | 54000 | 545 | 0.53 | 5.06 | 1.05 |
| 3 | CH ₂ Cl ₂ | 423 | 39800 | 468 | 1.00 | | |

Photophysical properties of **1** and **2** are measured in hexane, toluene, dichloromethane, tetrahydrofuran and acetonitrile solution at a concentration of 10^{-5} M, and the related data are

summarized in Table 1. In CH_2Cl_2 , the six-membered-ring complex **1** exhibits similar absorption band at 438 nm compared with the reported bis(BF_2) complex **3** (423 nm).¹¹ However, the five-membered-ring complex **2** displays two red-shifted absorption peaks at 486 and 521 nm. The absorption maxima of **1** and **2** are almost independent of solvent polarity with only 2–4 nm variation from CH_3CN to hexane (Table 1 and Fig. 2 in ESI), indicating a small ground-state dipole moment, which is similar to the general behaviour of BODIPY chromophores.^{2d} The emission spectra in CH_2Cl_2 show a maximum peak at 513 nm for **1** and 547 nm for **2**, respectively. Both complexes are strongly emissive with quantum yield in the range of 0.52–0.88 in the investigated solvents. Compound **1** possess larger Stokes shift (3338 cm^{-1}) than that of **2** (912 cm^{-1}) in CH_2Cl_2 solution, indicating the large geometry relaxation at the excited state. Large Stokes shift can eliminate the spectral overlap between absorption and emission and allows reliable detection of fluorescence from reducing interference.¹⁵ The small k_{nr} values of complexes **1** and **2**, which may due to less efficient internal conversion or intersystem crossing, lead to the significant improvement in their quantum efficiencies. In addition, complexes **1** and **2** exhibit slight changes in the emission maxima and intensity in different polar solvents. The fluorescence decay profiles can be described by a single-exponential fit with lifetimes in the range of 4.71–5.64 ns in all of the solvents investigated, similar to the lifetime data of the conventional BODIPYs and analogues published in the literature.⁹

Spectroscopic properties in the solid states

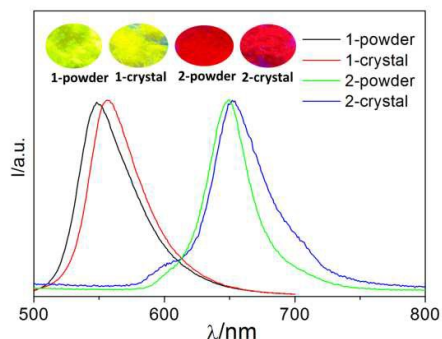


Fig 4. Fluorescent spectra of **1** and **2** in powder and crystal. Inset: The photo pictures of **1** and **2** in powder and crystal excited at 365 nm using a UV lamp.

Table 2. Emission maxima and the absolute quantum yields of **1–2** in crystal and in powder.

| | | Powder | Crystal |
|----------|---------------------------------|----------|---------------------------------|
| | | 1 | $\lambda_{\text{em}}/\text{nm}$ |
| | Φ_{F} | 0.28 | 0.36 |
| 2 | $\lambda_{\text{em}}/\text{nm}$ | 650 | 652 |
| | Φ_{F} | 0.05 | 0.04 |

The emission spectra of **1** and **2** in powder and crystal are shown in Fig. 4, and corresponding data are summarized in Table 2. Compared with the emission spectra measured in solution, the emission band of both complexes are red-shifted in the solid state. The absorption spectra of dyes **1** and **2** in crystal form display a

largely broad shape with unclear peak, which can be attributed to the strong intermolecular interaction in the crystal state (Fig. 3 in ESI). Complex **1** shows efficient solid-state fluorescence with a quantum yield of 0.36, 0.28 in the crystal and powder state, respectively, which is stronger than that of the corresponding BF_2 complex **3** (0.12 in powder form),^{11b} suggesting that introduction of phenyl groups on the boron atom significantly inhibit the π - π stacking interactions, thus enhance the solid-state fluorescence quantum yield. However, the quantum yield of **2** in the solid state is much lower than the corresponding fluorescence in solution, probably due to its small Stokes shift which cause a large overlap between the absorption and emission spectra, leading to self-quenching of the fluorescence.

DFT Calculation

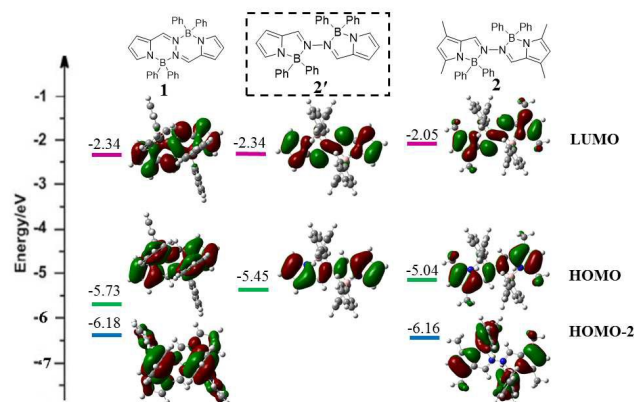


Fig 5. Energy level diagram of the frontier π -MOs of **1**, **2'** and **2** using the B3LYP functional and 6-31G(d) basis sets. The angular nodal patterns are shown at an isosurface value of 0.02 a.u.

Table 3. Calculated electronic excitation energies, oscillator strengths, and eigenvectors for the TD-DFT spectra of **1** and **2** carried out using the B3LYP functional and 6-31G(d) basis sets.

| | State ^[a] | $E^{[b]}$ [eV] | λ [nm] | $f^{[c]}$ | Wavefunction ^[d] |
|----------|----------------------|-------------------|-------------------|-----------|-------------------------------------|
| 1 | S1 | 2.96 | 418 | 0.222 | HOMO→LUMO (90%) HOMO-2→LUMO (7%) |
| | S4 | 3.27 | 384 | 0.152 | HOMO-2→LUMO(90%) HOMO→LUMO (7%) |
| | 2 | S1 | 2.82 | 438 | 0.764 |
| | S3 | 3.52 | 352 | 0.046 | HOMO-2→LUMO (99%) |

[a] Excited state, [b] Energy of excited state, [c] Oscillator strength, $f < 0.02$ are not included, [d] MOs involved in the transitions.

To further understand the electronic structures of these π -systems, density functional theory (DFT) calculations at the B3LYP/6-31G(d) level were carried out.¹⁶ The plots and data of HOMOs and LUMOs are shown in Fig. 5 and table 3. The general trend of the calculated HOMO/LUMO levels and energy gaps agrees with the experimentally observed trend. The calculated ground states, mainly consisting of HOMO→LUMO transition, have energies of 2.96 eV (418 nm, $f = 0.222$) for **1** and 2.82 eV (438 nm, $f = 0.764$) for **2**, respectively. For **1**, the LUMO is delocalized on the entire π -conjugated skeleton, and the HOMO is localized on the central

benzene ring and entire π -conjugated skeleton. Compared with **1**, the HOMO and LUMO levels of **2** are both raised. However, it is not rational to simply attribute the variation of HOMO/LUMO levels to the effect of methyl groups because of their different core skeletons. Therefore, a model structure **2'**, which have a similar structure of **2** without methyl groups, is calculated in order to give a reasonable explanation. For **2'**, the HOMO slightly destabilized while the LUMO unchanged with respect to that of **1**. Compare with **2'**, the HOMO and LUMO levels of **2** are both destabilized due to the electron-donating effect of the methyl groups on the pyrrole ring. There is a red shift of the absorption bands of **2**, since the destabilization of the HOMO is greater than that of the LUMO. In the energy optimized structures, the bridging N-N band length in **2** is 1.366 Å, which correlates well with that observed in the single crystal structure (1.375 Å).

Conclusions

In summary, a novel five-membered-ring and a six-membered-ring bis-(diphenylboron) complexes have been prepared through a facile two step reaction. Both complexes exhibit high fluorescence quantum yields in solution. The six-membered-ring bis-(diphenylboron) complex **1** exhibits excellent solid-state fluorescence because of less intermolecular π - π stacking interactions, together with large Stokes shifts. The five-membered-ring bis-(diphenylboron) complex **2** has a small Stokes shift, resulting in fluorescent quenching in the solid states through self-quenching.

Experimental section

Synthesis and characterization

Synthesis of compound **1**.

(1E,2E)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine (186 mg, 1.0 mmol), triphenyl borane (500 mg, 2.06 mmol) were dissolved in dry toluene (25 mL) under nitrogen atmosphere. The resulting mixture was refluxed for 16 h. After cooling to room temperature, the solvent was removed under vacuum. The residue was purified by column chromatography using petroleum ether/dichloromethane (v:v; 4:1) as eluent to afford the desired product. Compound **1**, yellow solid (petroleum ether: dichloromethane = 4: 1, v: v). Yield: 34 %. ^1H NMR (500 MHz, CDCl_3): δ 7.65 (s, 2 H), 7.19-7.16 (m, 4 H), 7.10-7.07 (m, 8 H), 7.03-7.02 (m, 4 H), 6.88-6.87 (m, 8 H), 6.45 (dd, $J_1=J_2=2.1$ Hz, 2H). ^{13}C NMR (125 Hz, CDCl_3): δ 145.40, 139.22, 133.26, 127.72, 127.10, 126.01, 125.73, 115.02. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 438 nm ($34800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).MALDI-TOF: calcd ($[\text{C}_{34}\text{H}_{28}\text{B}_2\text{N}_4+\text{Na}]^+$) m/z = 537.2, found m/z = 537.4. Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{B}_2\text{N}_4$: C, 79.41; H, 5.49; N, 10.90. Found: C, 79.19; H, 5.68; N, 11.05.

Compound **2** was obtained as a red solid in 61% yield by following a procedure similar to that of **1**. ^1H NMR (500 MHz, CDCl_3): δ 8.10 (s, 2 H), 7.26-7.24 (m, 20 H), 5.85 (s, 2 H), 2.07 (s, 6 H), 1.84 (s, 6 H). ^{13}C NMR (125 Hz, CDCl_3): δ 144.18, 141.00, 134.85, 133.96, 131.23, 129.73, 129.45, 128.09, 128.03, 127.72, 117.44, 14.27, 11.68. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 521 nm ($52600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).MALDI-TOF: calcd ($[\text{C}_{38}\text{H}_{36}\text{B}_2\text{N}_4]^+$) m/z = 570.3, found m/z = 570.6. Anal.

Calcd for $\text{C}_{38}\text{H}_{36}\text{B}_2\text{N}_4$: C, 80.02; H, 6.36; N, 9.82. Found: C, 79.79; H, 6.60; N, 9.91.

X-ray structure determination

The X-ray diffraction data were collected on a Bruker Smart 85 Apex CCD diffractometer with graphite monochromated Mo-K α radiation (λ = 0.71073 Å) using the ω -2 θ scan mode. The structure was solved by direct methods and refined on F^2 with full-matrix least-squares methods using SHELX programs.¹⁷ All calculations and molecular graphics were carried out using the SHELX-97 program package and the Diamond program.

1: $\text{C}_{34}\text{H}_{28}\text{B}_2\text{N}_4$; a yellow block-like crystal of approximate $0.27 \times 0.25 \times 0.22 \text{ mm}^3$ dimensions was measured. Space group C2/c, a = 27.194(4) Å, b = 10.9496(13) Å, c = 19.143(2) Å, α = 90°, β = 100.772(4)°, γ = 90°, V = 5599.6(12) Å³, Z = 8, $F(000)$ = 2160, ρ = 1.220 g/cm³, R_1 = 0.1262, wR_2 = 0.1537, GOF = 0.982.

2: $\text{C}_{38}\text{H}_{36}\text{B}_2\text{N}_4$; a red block-like crystal of approximate $0.28 \times 0.26 \times 0.22 \text{ mm}^3$ dimensions was measured. Space group P21/n, a = 11.471(3) Å, b = 22.263(5) Å, c = 12.598(3) Å, α = 90°, β = 94.037(4)°, γ = 90°, V = 3207.0(12) Å³, Z = 4, $F(000)$ = 1208, ρ = 1.181 g/cm³, R_1 = 0.1145, wR_2 = 0.1399, GOF = 1.006.

CCDC No. 1435544 for **1**, 1435545 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Spectroscopic Measurements

UV-Vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The solid state UV-vis spectra were recorded on Perkin Elmer Lambda 950 UV/Vis/NIR Spectrometer at room temperature. Fluorescence spectra were measured on a Hitachi F-4600 FL spectrophotometer with a xenon arc lamp as light source. Samples for absorption and emission measurements were contained in 1 cm \times 1 cm quartz cuvettes. For all measurement, the temperature was kept constant at (298 ± 2) K. Dilute solution with an absorbance of less than 0.05 at the excited wavelength was used for the measurement of fluorescent quantum yields, The luminescence quantum yields in solution were measured by using fluorescein with excited wavelength 489 nm (Φ_F = 0.79 in 0.1M NaOH) as a reference.¹⁸ The quantum yield Φ as a function solvent polarity is calculated using the following equation.

$$\Phi_{\text{sample}} = \Phi_{\text{std}} \left[\frac{I_{\text{sample}}}{I_{\text{std}}} \right] \left[\frac{A_{\text{std}}}{A_{\text{sample}}} \right]^2 \quad (1)$$

Where subscript sample and std denote the sample and standard, respectively, Φ is quantum yield, I is the integrated emission intensity, A stands for the absorbance, n is refractive index.

The fluorescence lifetimes of the samples were determined with a Horiba JobinYvonFluorolog- 3 spectrofluorimeter. Absorption and emission measurements were carried out in 1 \times 1 cm quartz cuvettes. The absolute quantum yields and emission spectra in the solid state were measured in Horiba JobinYvon Fluorolog-3 spectrofluorimeter with integrating sphere. The goodness of the fit of the single decays as judged by reduced chi-squared (χ^2_R) and autocorrelation function $C(j)$ of the residuals was below $\chi^2_R < 1.2$.

When the fluorescence decays were monoexponential, the rate constants of radiative (k_f) and nonradiative (k_{nr}) deactivation were

calculated from the measured fluorescence quantum yield (Φ_f) and fluorescence lifetime (τ) according to eqs 2 and 3:

$$k_f = \Phi_f/\tau \quad (2)$$

$$k_{nr} = (1-\Phi_f)/\tau \quad (3)$$

Computational details

The ground state structures of compounds **1**, **2'** and **2** are optimized using the density functional theory (DFT) method with B3LYP. 6-31G (d) basis set was assigned to the elements, which guarantees a reasonable balance of the computational cost and the reliability of the results. The absorption properties were predicted by time-dependent (TD-DFT) method with the same basis set. All of the calculations were performed with the Gaussian09 program package.

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GRAPHIC ABSTRACT

A novel five-membered-ring and a six-membered-ring bis-(diphenylboron) complexes were reported.

