Stable Boron-Containing Blue-Photoluminescent Radicals

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ABSTRACT: It is highly urgent to develop synthetic strategies to make new category of stable luminescent radicals with desired emission wavelength. In this study, we have isolated two dioxoborocyclic radicals (**3** and **4**) by a direct synthetic route. They were characterized by UV, EPR spectroscopy and SQUID measurements. Their structures were obtained by single-crystal X-ray diffraction. Both radicals produce blue-photoluminescence (458 nm for **3** and 478 nm for **4**) by radiative decay from higher excited states (D_2/D_3) to the ground state (D_0) based on theoretical calculation, breaking Kasha rule. The work records a new kind of radical emitters and the first stable radicals with blue emission bands.

Molecules with luminescence have been extensively investigated for their applications in organic light-emitting diodes (OLEDs) and chemical sensors.¹ Among them, molecules with open-shell doublet ground states recently have gained much attention as they are able to avoid quenching via the spin-forbidden transition from the excited triplet to the ground state and thus provide high-efficiency electroluminescent devices.² Furthermore, the interplay between the magnetic, electronic, and luminescent properties of organic radicals may afford multiply responsive molecular devices.³ Emissive radicals therefore have been targeted as one of the next-generation luminophores. However, in contrast with numerous conventional closed-shell luminescent molecules, neutral emissive organic radicals are restricted to cholorarylmethyl radicals, which were known in 1944 and later developed by Juliá, Nishihara, Li and others.² In addition, the emission wavelengths of cholorarylmethyl radicals are limited to red and NIR regions. Though stable anthracene functionalized dithiadiazolyl radicals with blue emission were reported by Rawson et al., the emission is coming from the anthracene part and the dithiadiazolyl radical part is acting as a fluorescent quencher instead.⁴ It is highly urgent to develop synthetic strategy to make new category of stable luminescent radicals with desired emission wavelength.

Boron-containing radicals have attracted lots of interest for applications as organic synthesis reagents, magnetic system building blocks, polymerization initiators, and chemical sensors.⁵ A number of five-membered diazab-orocyclic⁶ and dioxoborocyclic⁷ radicals recently have been prepared. Stephan et al. have obtained a series of dioxoborocyclic radicals since 2016, by H₂ activation using B(C₆F₅)₃ and diones (4 atm, 110 °C).^{6f,7b,7c,8} We speculate that modification of dioxoborocyclic radicals with donor ligands may lead to photoluminescence. Here we report two stable blue-photoluminescent dioxoborocyclic radicals, which were prepared using a direct method under mild condition.

Dioxoborocyclic radicals **3** and **4** were synthesized in one step from the corresponding diones (**1** and **2**) with chlorobis(perfluorophenyl)borane and potassium graphite in THF, and isolated as deep red crystals in moderate yield (Scheme 1). **3** and **4** are stable in solution and in the solid state under N₂ atmosphere for several weeks. They were characterized by UV, EPR spectroscopy and SQUID measurements. Their crystal structures were determined by single-crystal X-ray diffraction.

Scheme 1 Synthesis of Radicals **3** and **4**, and Photographs of THF Solutions of **3** and **4** in UV (365nm) Light.

Both **3** and **4** are NMR silent. The EPR spectrum of **3** (Figures 1a and S5) displays an octet due to hyperfine coupling with ¹¹B and ¹H atoms with $a_B = 3.17$ G, $a_H = 1.91, 2.47$ G by spectral simulation, suggesting the unpaired electron is delocalized over phenanthrene moiety. Similarly, the sextet of **4** (Figures 1b and S6) arises from coupling with ¹¹B atom and ¹H atoms ($a_B = 2.86$ G, $a_H = 1.86$ G). As shown in Figure 2, the $\chi_M T$ at 300 K for both **3** and **4** is around 0.37 cm³K/mol, consistent with one spin per radical ($\chi_M T = 0.375$ cm³K/mol for $S = 1/2$ spin system). The $\chi_M T$ of **3** shows an increasing susceptibility from 2 to 50 K, indicating an intermolecular antiferromagnetic interaction, while an intermolecular ferromagnetic interaction is observed for **4** below 25 K, but both with small coupling constants ($2J = -44.92$ cal/mol for **3** and 4.5 cal/mol for **4**).

Figure 1 EPR spectra of **3** (a) and **4** (b) in THF at room temperature with simulation, and spin densities of **3** (c) and **4** (d) calculated at the UB3LYP/6-31G(d) level.

Figure 2 $\chi_M T$ versus T curve in the SQUID measurements for the powder of **3** and **4** and the fitting plot obtained with the Bleaney–Bowers equation.⁹

Crystals of **3** and **4** suitable for single crystal X-ray diffraction were grown in the concentrated toluene solution at -20°C . Crystal structures of parent molecules **1** and **2** were also obtained for comparison (Figures S1 and S2, Tables S3 and S4). The crystal structure of **3** exhibits a one-dimensional chain conformation with the shortest intermolecular C–C distances of 3.395 and 3.551 Å between the phenanthrenedione backbones (Figure 3c), while that of **4** shows a π -dimer structure with the shortest C–C distance of 3.465 Å between the neighbouring phenanthrenedione backbones (Figure 3d). The intermolecular C–C distances both in **3** and **4** are close to the sum of sp^2 C–C distance (3.40 Å), indicating weak intermolecular interactions, consistent with the small coupling constants of the magnetic property. Both **3** and **4** feature a planar five-membered BO_2C_2 ring (Figures 3a and 3b), with the B–O distances of 1.549(5), 1.535(5) Å in **3** and 1.511(3), 1.531(3) Å in **4**, and O–B–O angles of $101.2(3)^\circ$ in **3**, $102.23(16)^\circ$ in **4** about the four-coordinate boron atom, respectively (SI). The phenanthrenedione backbones are planar but C1–C2 bond lengths (1.407(5) Å in **3** and 1.409(3) Å in **4**) are shorter than those in **1** (1.536(6) Å) and **2** (1.533(3) Å), while C–O bond lengths (1.332(4), 1.331(4) Å in **3** and 1.319(3), 1.320(3) Å in **4**) are longer than those in **1** (1.213(5), 1.220(5) Å) and **2** (1.214(3), 1.220(3) Å). All other bond parameters of phenanthrenedione backbones basically have no changes from parent molecules to radicals.

Figure 3 Thermal ellipsoid drawings (at 50% probability) with selected bond lengths (Å) of molecules and crystal packings of **3** (a, c) and **4** (b, d). Hydrogen atoms and solvent molecules are omitted for clarity.

The UV-Vis absorption spectrum of **3** in dilute THF solution displays an intense absorption band at 420 nm with an additional absorption band at 476 nm (Figure 4a). The absorption bands of **4** (437, 572 nm) are red-shifted compared to those of **3**, which can be attributed to the electron-donation of two -OMe substituent groups at the 3, 6 positions of the phenanthrenedione backbone in **4**. Solution fluorescence studies on **3** and **4** revealed emissions at 458 and 478 nm in THF, respectively (Figure 4b). Red-shift of the emissions of **3** and **4** in DCM are observed due to the solvent polarity (Figure S9). The excited-state luminescence lifetime (τ) of **3** is estimated to be 3.9 ns, and 7.7 ns for **4** (Figure 4c). The photoluminescence quantum yield (PLQY) of **3** and **4** are measured to be 0.30% and 1.03%, respectively. Both radicals exhibit photochemical stability with the half-life ($t_{1/2}$) of 123 min for **3** and 175 min for **4** (Figures 4d, S10 and S11).

Figure 4 (a) UV/Vis absorption spectra of **3** and **4** in THF at room temperature. (b) Fluorescence spectra excited at 372 nm of **3** and 360 nm of **4** in THF at room temperature. (c) Fluorescence decay of **3** and **4** following excitation at 365 nm for **3** and **4**. (d) Photostability analysis of **3** and **4** under irradiation (365 nm) for different times. A/A_0 represents the ratio of absorbance before and after irradiation for the corresponding time.

To gain further insights into photoluminescence mechanism, quantum chemical calculations were carried out using the Gaussian 16 series of programs.¹⁰ The ground state molecular configurations (Figure S12) optimized by the unrestricted Kohn-Sham density functional theory¹¹ (UKS-DFT) are consistent with that in the crystal structures. Due to the existence of an unpaired electron, the ground states of **3** and **4** are doublet (D_0). The spin-up unpaired electron is located on 154 α and 170 α orbitals in **3** and **4**, respectively, namely the single electron occupied molecular orbital (SOMO), while other orbitals with

lower energy are all occupied by two electrons, displayed in Figures 5a and 5b. The nature of electronic excited state can be revealed by time dependent DFT (TDDFT) calculation.¹² As shown in Tables S5 and S6, the lowest excited state (D_1) is mainly attributed to beta electron (spin-down) transition from HOMO to SOMO. Its oscillator strengths of both excitation ($f=0.0057$ in **3**, 0.0002 in **4**) and emission ($f=0.0079$ in **3**, 0.0022 in **4**) are all close to zero, which means the “dark state” nature¹³ of D_1 restraining photoluminescence. Meanwhile, higher excited states have large oscillator strength, therefore valence electrons are prone to jump to higher excited state after photoexcited. However, electrons excited to D_2 or other higher excited state relax to D_1 state hardly. As expected, D_2 and D_3 excited states almost overlap owing to a minimal energy difference (0.2 eV in **3**, almost 0 eV in **4**) but a large energy gap (1.43 eV in **3**, 1.36 eV in **4**) between D_2 and D_1 even more than 1 eV, which brings about internal conversion (IC) slowly.¹⁴ In addition, D_3 state are formed by the alpha electron (spin-up) transition from SOMO to LUMO in **4**. Due to the opposite electronic spin orientation, the IC process from D_3 to D_1 is almost transition forbidden. At the same time, there is also the transition contribution of alpha electron in D_2 and D_3 states of **3**. Unexpectedly, the UKS-TDDFT calculations for D_2 and D_3 reach consensus on fluorescence emission spectra: theoretical, D_2 : 430 nm, D_3 : 423 nm, experimental, 458 nm in **3**; theoretical, D_2 : 503 nm, D_3 : 502 nm, experimental, 478 nm in **4**. Hence, different excited state formation upon photoexcitation, higher excited states (D_2 and D_3) deactivate to D_1 through IC process laboriously and they only return to the ground state through emission. The corresponding schematic diagrams are exhibited in Figure 5c. These theoretical results rationalize that emission obeys anti-Kasha rules.

Figure 5 Quantum chemical results for the monoradical. Energy levels and wavefunctions for the ground state frontier molecular orbitals of **3** (a) and **4** (b), calculated at UB3LYP/6-31G(d,p) level of theory. (c) Schematic diagram of photophysical process after doublet excitation identified by theoretical calculations.

In summary, we have isolated two dioxoborocyclic radicals **3** and **4**. They have been characterized by SQUID, EPR spectroscopy and single-crystal X-ray diffraction analysis. The structure and SQUID measurements indicates an intermolecular antiferromagnetic interaction for **3** and an intermolecular ferromagnetic interaction for **4**. Both **3** and **4** are blue-photoluminescent radical emitters with anti-Kasha doublet emission. Our work provides a new kind of radical emitter species and paves the way toward blue-light radical emitters. Further work about high efficient blue-light radical emitters is continuous in our lab.

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