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Strategic Design of Anion-Responsive Triarylboranes Exhibiting Colorimetric and Fluorometric Red-Shift for Sensing and Optoelectronic Applications

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Triarylboranes (TABs) have been employed as colorimetric and/or fluorometric anion sensors. The majority of TAB-based anion sensors exhibit blue-shift modes of absorption and photoluminescence (PL) or turn off of PL, attributed to the intrinsic electronic polarity of the trivalent boron unit in their molecular designs. In this *Concept* article, I introduce a novel approach to modulating the photophysical properties of TABs toward a red-

shift mode by balancing the dual, opposing roles of the amine-bridged TAB (phenazaborine). This molecular design strategy enables significant changes in color and emission response to anions, shifting to the lower energy regime in solution. Additionally, this approach is applicable to the solid-state modulation of PL in films and organic light-emitting diodes (OLEDs).

Introduction

Triaryl boranes (TABs) have garnered significant attention for their roles in unique molecular transformations,^[1] catalysis,^[2] optoelectronic materials,^[3] and bio-imaging probes,^[4] owing to the Lewis acidity arising from the vacant p orbital on the trivalent boron and the electro- and photo-active functions arising from the extended π -electron systems. One of the most extensively studied functions of TABs is colorimetric and/or fluorometric anion sensing,^[5] with particular emphasis on fluoride detection, due to its importance in healthcare and environmental monitoring.

Typically, the design of TAB-based anion sensors utilizing boron characteristics can be categorized into three main strategies (Figure 1). The most representative design principle involves the interruption of $p_{\pi}-p_{\pi}^*$ conjugation (Figure 1a).^[6,7] Coordination of fluoride to the trivalent boron center alters the hybridization of boron from sp^2 to sp^3 , thus disrupting the conjugation across the entire molecule in its neutral state. This results in absorption localized to the each isolated aryl π system, leading to a “blue-shift” in absorption and emission quenching^[6] or a blue-shift in both absorption and emission.^[7] Another strategy for modulating the photophysical properties of TABs through fluoride action involves altering the energy transfer (ET) pathway (Figure 1b).^[8] For instance, Takeuchi and Shinkai et al. developed a TAB-phorphyrin conjugate where ET occurs from TAB to porphyrin in a neutral state. The coordination of fluoride to the boron center disrupts the π conjugation, changing the ET pathway and resulting in a ratiometric blue-

and red-shift of absorption and emission spectra. A further approach includes the inhibition of intramolecular charge transfer (ICT) (Figure 1c).^[9–11] The electron-deficient trivalent boron in the TAB structure acts as an electron acceptor when connected to electron-rich units. Within such a donor–acceptor (D–A) structure, ICT from the donor unit to the TAB unit occurs, manifesting ICT absorption and emission from the charge transfer (CT) excited state. However, upon fluoride coordination, ICT is inhibited, due to the saturation of the boron center and an increase in electron density on the TAB unit (the top equation in Figure 1c). Consequently, absorption and emission arise from the local π system, leading to a blue-shift in both absorption and PL.^[9] This principle also applies to through-space CT (TSCT) systems, where a blue-shift of PL is observed (the middle equation in Figure 1c).^[10] Furthermore, long-range ICT from D to A that are linked through an extended π -system are also inhibited by fluoride coordination, resulting in blue-shifted emission from the rigid π -linker and increased PL intensity as a function of the added fluoride amount (the bottom equation in Figure 1c).^[11] From this overview, it is evident that existing TAB-based anion sensing systems primarily exhibit blue-shift modes in absorption and emission or turn-off of emission, due to their underlying molecular design mechanisms. By devising distinct molecular design principles for anion-responsive TABs to modulate photophysical properties in novel ways, new horizons of undeveloped technologies using TAB-based anion-responsive materials can be explored.

Recently, we successfully developed a novel system based on a TAB scaffold that enables significant colorimetric and fluorometric “red-shift” in response to anions, particularly fluoride.^[12,13] The anion-responsive red-shift in photoabsorption and emission offers a significant advantage for anion detection compared to existing methods. In particular, red-shifting into the near-infrared (NIR) region allows for non-invasive anion detection in biological environments, owing to the NIR region’s transparency in biological tissues. This article highlights the underlying molecular design concept.

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Design Strategy

To achieve anion-responsive colorimetric and fluorometric red-shift using a TAB scaffold, we focused on the nitrogen-bridged TAB structure, specifically phenazaborine (PAzB) (Figure 2a). PAzB is a B,N-isoelectronic analogue of anthracene, possessing 14 π electrons and adopting a planar structure, due to the delocalization of π electrons across the entire ring systems.^[14] Since PAzB contains both an electron-deficient trivalent boron and an electron-rich trivalent nitrogen within the same unit, it can function simultaneously as a Lewis acid and an electron donor (D) when an appropriate electron deficient unit (A) is connected to the nitrogen atom (Figure 2a). In an ideal D–A system, a subtle ICT occurs from the PAzB to the A unit in its neutral form, resulting in absorption and PL in the visible-light region. The formation of a fluoroborate complex upon coordination with an anion enhances the ICT, leading to a substantial red-shift in absorption and PL. To realize this concept, we selected dibenzo[*a,j*]phenazine (DBPHZ) as the acceptor, originally developed by our research team (Figure 2b).^[15] The DBPHZ is electron-deficient and luminescent,^[16] making it an excellent electron acceptor. Utilizing these characteristics, we demonstrated that the DBPHZ-cored donor–acceptor–donor (D–A–D) scaffold serves as an exceptional platform for a wide variety of photofunctions, including thermally activated delayed fluorescence (TADF),^[17,18] external stimuli-responsive luminochromism,^[18–20] room temperature phosphorescence (RTP),^[21] and more.^[22] A notable structural feature of the D–A–D system with planar D units is the perpendicular orientation of the D–A unit, likely due to steric repulsion between the *ortho* hydrogen atoms. This orthogonal structure is crucial for realizing red-shifts in absorption and emission in D–A–D type TABs (Figure 2b). The orthogonal arrangement allows for the disconnection of direct electronic interaction between DBPHZ and PAzB, enabling DBPHZ to withdraw electrons from the PAzB unit through the N–C σ bond, thus enhancing the Lewis acidity of the PAzB unit. Additionally, this twisted D–A–D structure permits spatial separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), facilitating the manifestation of TADF function. The



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separation of HOMO and LUMO was confirmed by density functional theory (DFT) calculations. According to the design blueprint, we have developed two DBPHZ-linked PAzB derivatives (**B-Mes-PAzB-DBPHZ** and **B-Tipp-PAzB-DBPHZ** in Figure 2).^[12] As designed, both compounds adopt orthogonal D–A–D structures, revealed by the single crystal X-ray crystallographic analysis.

Red-Shift Modulation of Absorption and PL in Response to Anions in Solution

As a proof of concept, we investigated the photophysical properties of **B-Mes-PAzB-DBPHZ** and **B-Tipp-PAzB-DBPHZ** in solution in response to addition of variety of anions (Figure 3). UV-vis absorption spectrum of **B-Mes-PAzB-DBPHZ** in its neutral state in THF (c 10⁻⁵ M) exhibited absorption λ_{abs} at around 419 nm (Figure 3a). Addition of fluoride drastically caused a red-shift of the absorption spectrum (λ_{abs} ca. 500 nm), which is attributable to ICT transition. This resulted in a colorimetric change from pale yellow to pink (photographs in Figure 3a). Other anions such as acetate, hydroxide, cyanate, and cyanide also caused colorimetric red-shift. In response to the red-shift in UV-vis absorption, PL spectrum also showed red-shift in the presence of anions, moving from λ_{em} 539 nm to λ_{em} 592 nm (Figure 3b). NMR experiments clearly showed the formation of fluoroborate when the addition of fluoride to the solution of **B-Mes-PAzB-DBPHZ**. Importantly, the UV-vis titration experiments revealed that association constants K_1 and K_2 against fluoride are larger in one order when compared with the N-phenyl PAzB (Figure 3c). This finding clearly supports the validity of the molecular design aimed at increasing the Lewis acidity of the PAzB unit by connecting it with DBPHZ in an orthogonal orientation. Furthermore, the significantly lower association constants of **B-Tipp-PAzB-DBPHZ** (on the order of 10⁴ M⁻¹) reinforce the notion that the binding event occurs at the boron center. The larger steric hinderance introduced by the isopropyl (*i*-Pr) group makes fluoride coordination unfavorable both kinetically and thermodynamically.

In solution, the observed intensity-averaged emission lifetimes $\langle \tau \rangle$ are on the order of nanoseconds across all solvents. Considering the radiative rate k_r in the range of 10⁶–10⁷ s⁻¹, the emission in solution is predominantly attributed to prompt fluorescence.

Red-Shift Modulation of PL in Solid-State

The modulation of the photophysical properties of emissive materials in the solid state is fundamentally important for optoelectronic applications such as organic light-emitting diodes (OLEDs) and other devices. As discussed in the previous section, PAzB compounds linked to DBPHZ unit exhibit significant colorimetric and fluorometric red-shifts in response to anions in solution. We hypothesized that the evaporation of a mixed solution containing the TAB compound, fluoride, and

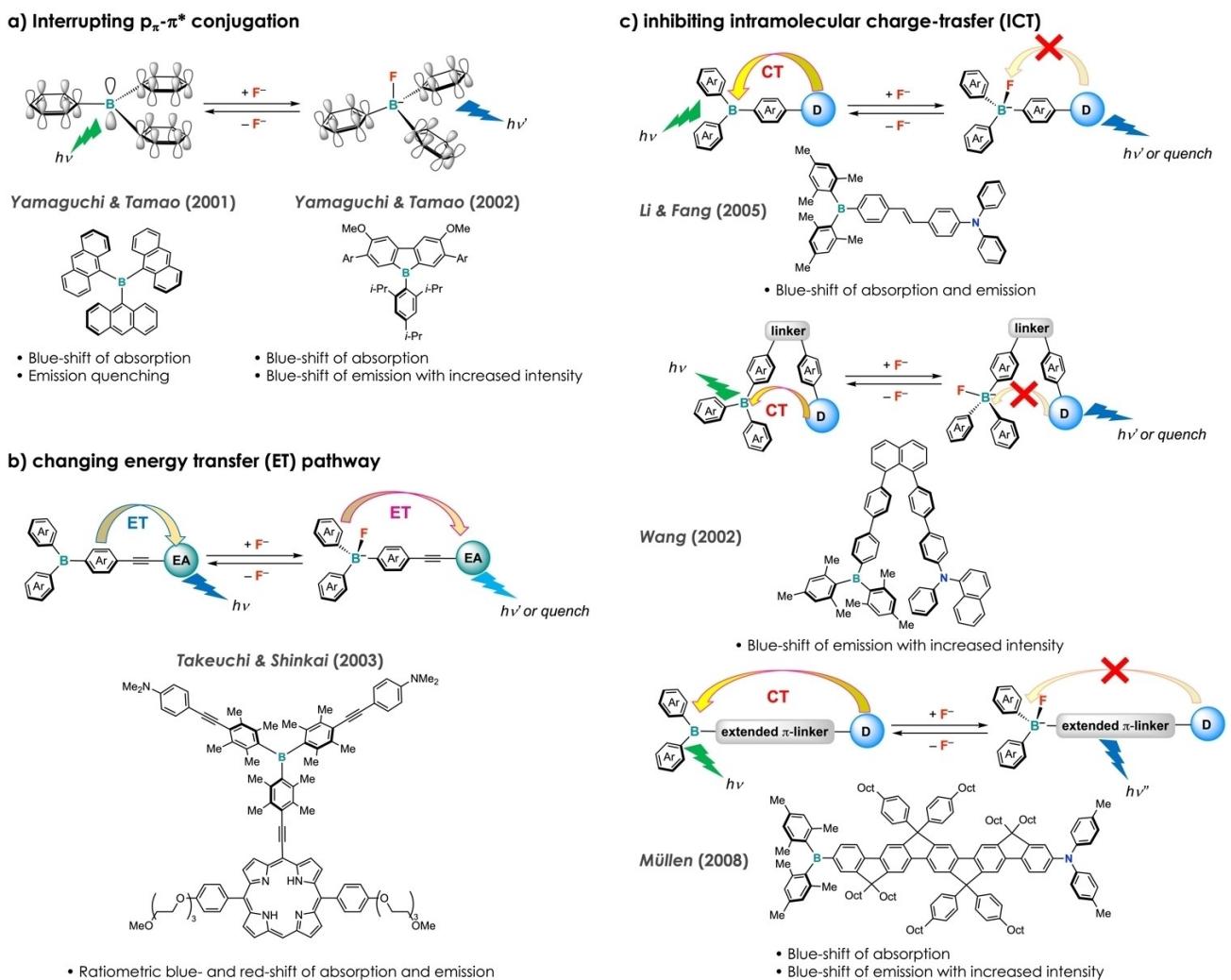


Figure 1. Previous approaches to modulate photophysical properties of TABs with anion (Adapted with permission.^[12] Copyright 2024, Wiley-VCH).

polymer material would enable the fabrication of films incorporating fluoroborate and allow for the modulation of PL emission in a red-shift manner. Figure 4a presents the PL spectra of **B-Mes-PAzB-DBPHZ** as a function of fluoride added in polystyrene (PS) films containing the TAB compound. In the absence of fluoride, the TAB compound exhibits sky-blue PL (λ_{em} 465 nm) (Figure 4a). PS films containing 10 equivalents of TBAF displayed a new emission band at λ_{em} 576 nm, while the PL intensity of the blue emission decreased (Figure 4a). As the amount of fluoride increased, the intensity ratio of the red to blue emission increased. With more than 100 equivalents of TBAF, almost exclusively red PL emission at λ_{em} 620 nm was observed (Figure 4a). This ratiometric behavior facilitates the modulation of the PL color of the film from sky-blue to orange (Figure 4b). Additionally, with an appropriate amount of fluoride, warm-white emission with *Commission Internationale de l'Eclairage* (CIE) coordinates of (0.39, 0.33) was achievable (Figure 4b). This modularity is advantageous for lighting applications utilizing a single molecule.^[23] The emission band of **B-Mes-PAzB-DBPHZ** exhibits substantial overlap with the excitation spectrum of fluoroborate in PS films, suggesting that

Förster resonance energy transfer (FRET) could be responsible for this ratiometric red-shifting behavior. Furthermore, the PL emission in films can be tuned by simply altering the polarity of the polymer materials (Figure 4c). In a polymer with higher polarity than PS (polymethyl methacrylate: PMMA), the PL emissions from **B-Mes-PAzB-DBPHZ** and its fluoroborate were significantly red-shifted (λ_{em} 621 nm and λ_{em} 684 nm, respectively) compared to those in PS (Figure 4c). This effect is likely due to the stabilization of the CT excited state through dipole-dipole interactions. This demonstrates the modulation of the emission properties of a single molecule by merely changing the anion concentration and polymeric material.

Modulation of EL in the OLED Devices

The tunability of PL through anion addition in polymeric matrices led us to explore the tuning of electroluminescence (EL) colors via fluoride addition.^[13] Time-resolved spectroscopic analysis of the emitters embedded in matrices (Zeonex® and CBP) revealed that both emitters exhibit complex delayed

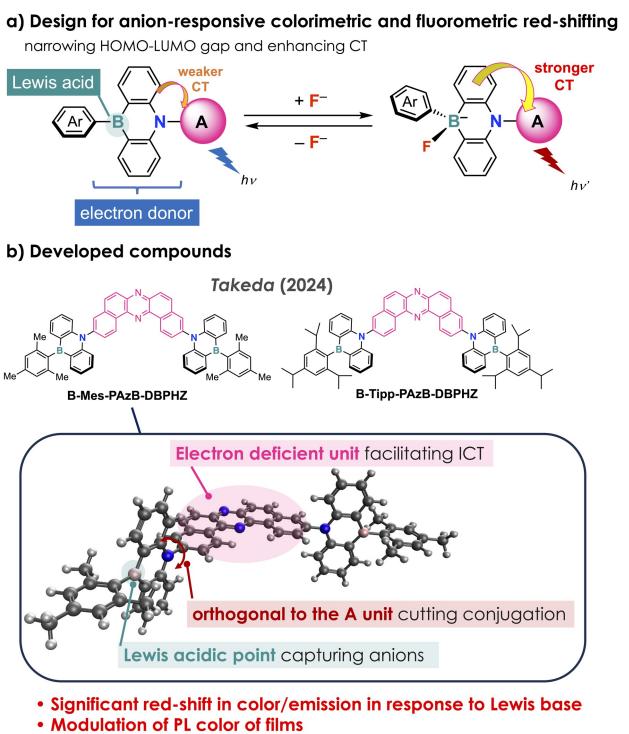


Figure 2. a) Design concept for anion-responsive colorimetric and fluorometric red-shift and b) developed compounds by our group.

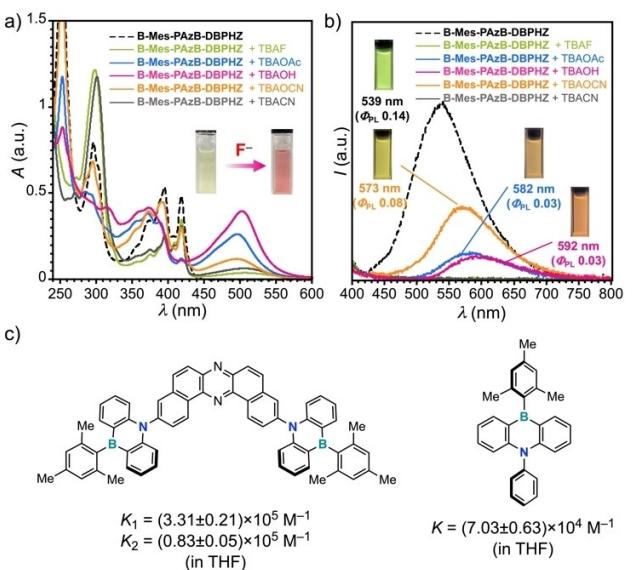


Figure 3. a) Absorption and b) developed compounds by our group. (Adapted with permission.^[12] Copyright 2024, Wiley-VCH).

emission profiles, including triplet-triplet annihilation (TTA) and RTP, attributed to a large singlet-triplet energy splitting (ΔE_{ST}) ranging from 270 to 470 meV (Figure 5a). In contrast, the film prepared from a mixed solution of fluoride and the emitter exhibited a significant red-shift in emission and enabled TADF, due to a narrowed ΔE_{ST} of 160 to 240 meV (Figure 5b). The observation of delayed emission with lifetimes ranging from microseconds to milliseconds is in stark contrast to that

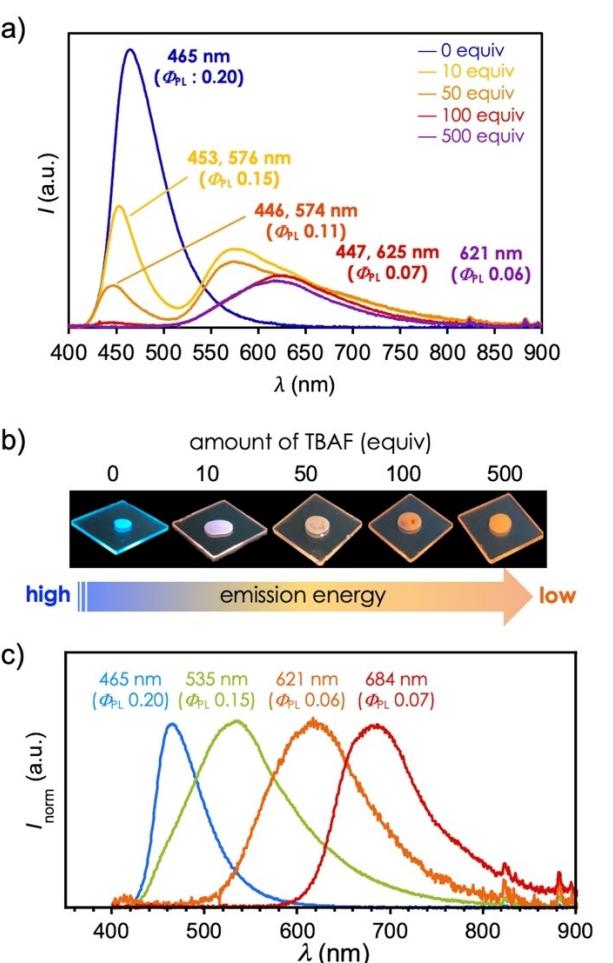


Figure 4. a) PL spectra of B-Mes-PAzB-DBPHZ in PS films (1 wt %) containing a varied amount of TBAF ($\lambda_{\text{ex}} = 365 \text{ nm}$); b) photographs of B-Mes-PAzB-DBPHZ with varied TBAF content in polystyrene films taken under the irradiation of a UV lamp ($\lambda_{\text{ex}} = 365 \text{ nm}$); c) PL spectra of B-Mes-PAzB-DBPHZ (1 wt %) in matrices: in PS (sky blue); in PMMA (moth green); in PS with TBAF (500 equiv) (orange); in PMMA with TBAF (100 equiv) (red) ($\lambda_{\text{ex}} = 365 \text{ nm}$). (Adapted with permission.^[12] Copyright 2024, Wiley-VCH).

observed in solution. The rigidification of molecular motions may suppress nonradiative pathways to the ground state. These findings demonstrate a novel approach to modulate excited state energy and ΔE_{ST} via external factors (Figure 5c), providing a versatile method for tuning the photophysical properties of TAB-based emissive materials. To demonstrate this concept, OLED devices were fabricated using B-Mes-PAzB-DBPHZ and B-Tipp-PAzB-DBPHZ through solution process, both with and without the presence of fluoride. As expected, the EL emission colors shifted dramatically from approximately $\lambda_{\text{em}} = 510 \text{ nm}$ (Dev 1, B-Mes-PAzB-DBPHZ without fluoride) to $\lambda_{\text{em}} = 650 \text{ nm}$ (Dev 2, B-Mes-PAzB-DBPHZ with fluoride) (Figure 5d).

Summary and Outlook

In summary, this Concept article highlights the design and development of anion-responsive TABs that exhibit colorimetric

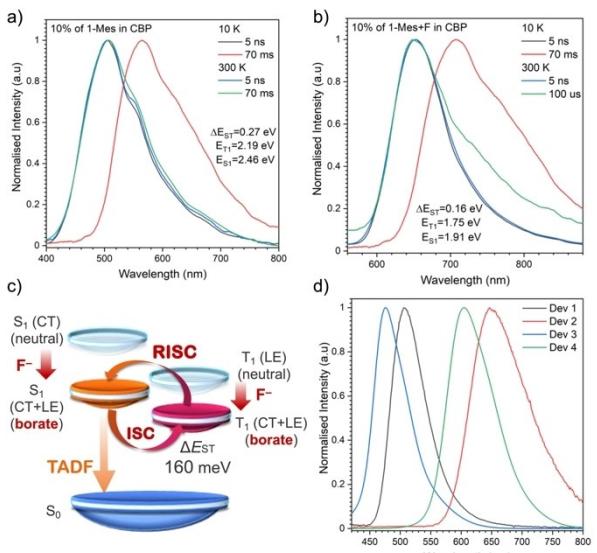


Figure 5. Time-resolved PL spectra of a) B-Mes-PAzB-DBPHZ and b) B-Mes-PAzB-DBPHZ with fluoride in CBP matrix. c) Schematic illustration of energy diagrams and photophysical fates of B-Mes-PAzB-DBPHZ without and with fluoride in CBP. d) EL spectra of OLED devices fabricated with phenazaborine emitters (DEV1: 10% B-Mes-PAzB-DBPHZ in CBP; DEV2: 10% B-Mes-PAzB-DBPHZ + fluoride in CBP; DEV3: 10% B-Tipp-PAzB-DBPHZ; DEV4: B-Tipp-PAzB-DBPHZ + fluoride) (Adapted with permission.^[13] Copyright 2024, American Chemical Society).

and fluorometric red-shift properties, a novel strategy in contrast to the traditionally observed blue-shift modes. This system also demonstrates tunable photophysical properties in the solid states, making it highly suitable for applications in OLEDs and anion sensing technologies. The molecular design presents new opportunities for advanced sensing and optoelectronic devices, particularly in anion detection and customizable light emitting applications such as OLEDs. Future research may focus on further optimizing this system for real-world applications, including smart materials, bio-imaging technologies, and energy-efficient lighting solutions.

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Conflict of Interests

The authors declare no conflict of interest.

Keywords: Boron · Charge transfer · Donor-acceptor systems · Lewis acids · Photophysics

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CONCEPT

This Concept article presents a novel design strategy for anion-responsive triarylboranes that exhibit red-shifted colorimetric and fluorometric properties. With potential applications in organic light-emitting diodes and sensing technologies, this approach opens new possibilities for the development of advanced optoelectronic devices.



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1 – 6

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