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Switchable Three-State Fluorescence of a Nonconjugated Donor−Acceptor Triarylborane

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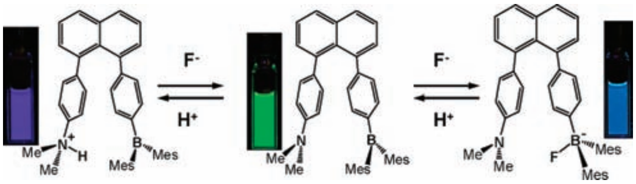
ABSTRACT



A nonconjugated fluorescent molecule with a triarylboron acceptor and an alkylamine donor has been found to display bright green fluorescence due to charge transfer through space, which can be reversibly deactivated by blocking either the donor or acceptor site. Binding of the fluoride ion to boron switches the fluorescence color to sky blue, while protonation of the amine with acid switches the emission color to the purple fluorescence of the acceptor chromophore.

Triarylboranes have been the subject of considerable recent research as selective sensors for fluoride ions, as these Lewis acidic compounds are capable of accepting electrons through the empty p_π orbital on the boron center. When protected by bulky aryl substituents, these materials show high selectivity for F^- binding over other anions such as Cl^- and Br^-, and thus, show promise for applications such as the detection of fluoride in drinking water with reduced interference from other analytes. Furthermore, the electron-accepting boron atom readily promotes intramolecular charge-transfer (CT) luminescence, thereby facilitating rapid visual detection of F^- by visible or fluorescent color change.[1]

Similarly, the electron-accepting ability of the boron center has led to their development as highly efficient electron transport materials and emitters in organic light-emitting diodes (OLEDs).[2] Furthermore, it has recently been demonstrated that fluoride ion binding to a boron center can be used to establish a p−n junction in LED devices.[2f] Since fluoride ions can bind selectively to the boron center and block the empty p_π orbital, a fluoride salt can thus act as a simple probe to determine the impact of the boron moiety, providing insight into the electronic properties of a material.

The luminescent and anion-binding properties of triarylboranes based on a 1,8-naphthyl core have been the subject of several recent reports. When used as anion sensors, the geometry of this linker allows for the preparation of bidentate Lewis acids with greatly increased binding constants over simple triarylboranes (Scheme 1).[3] Also, when donor and acceptor chromophores are connected by this bridge, the rigidity of the linker forces the π-systems of the chro-

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(1) For recent reviews, see: (a) Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbaï, F. P. *Chem. Rev.* **2010**, *110*, 3958. (b) Hudnall, T. W.; Chiu, C.-W.; Gabbaï, F. P. *Acc. Chem. Res.* **2009**, *42*, 388. (c) Hudson, Z. M.; Wang, S. *Acc. Chem. Res.* **2009**, *42*, 1584. (d) Yamaguchi, S.; Wakamiya, A. *Pure Appl. Chem.* **2006**, *78*, 1413. (e) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574. (f) Jäkle, F. *Chem. Rev.* **2010**, *110*, 3985, and references therein.

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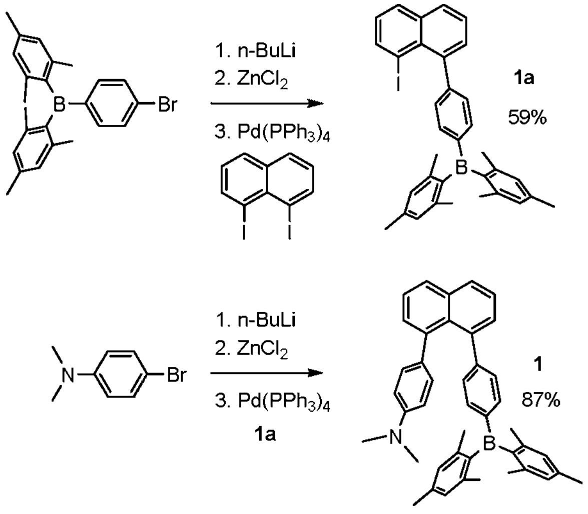
Scheme 1. Synthesis of Compound **1**



mophores out of coplanarity with that of the linker, promoting charge-transfer through-space rather than through a directly conjugated π-system.[4] The fluorescence of these materials is switchable between dual emission pathways, as the charge-transfer fluorescence exhibited by the pure compound can readily be deactivated if fluoride is added. This switches the emission color of the sample, leading to higher-energy $\pi-\pi^*$ fluorescence from the remaining donor chromophore.

We have herein extended this concept to a fluorescent material switchable between triple emission pathways, incorporating donor and acceptor fluorophores both capable of acting as receptor sites (compound **1**, Scheme 1). Using a more basic dimethylarylamine unit, this compound can be readily protonated to block the filled p orbital of the donor group. In this way, blocking of either the donor group with acid or the acceptor group with fluoride disrupts through-space charge-transfer fluorescence, causing the material to emit with the color of an alternate chromophore. In this way, these simple stimuli allow for facile switching between three emissive excited states.

This material is best prepared by sequential Negishi coupling of the donor and acceptor chromophores to 1,8-diiodonaphthalene, involving one-pot metal−halogen exchange and formation of an organozinc intermediate, followed by palladium-catalyzed C−C bond formation with the appropriate aryl halide. This method was found to proceed in a much higher yield than more commonly used Suzuki coupling reactions, and it is possible that the steric demands of the substrate play a role in the efficiency of this coupling step. The steric congestion in this molecule is apparent from the crystal structure of **1**, with torsion angles of 57.2° and 47.4° and bend angles of 118.02° and 115.22° between the naphthyl linker and the phenyl rings of the donor and acceptor chromophores, respectively (Figure 1). Incorporation of a rigid linker forces the donor and acceptor atoms into close proximity, with a B···N separation distance of 5.55 Å.

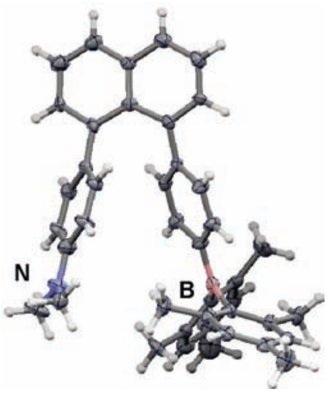


Figure 1. Crystal structure of **1** with 35% thermal ellipsoids.

The through-space donor−acceptor charge-transfer transition may be observed as a weak low-energy band centered at ~386 nm in the UV−visible absorption spectrum of **1** in CH_2Cl_2 (see Supporting Information, SI). This spectrum also features an intense band at 333 nm, attributed to charge transfer from the filled π-orbitals on the mesityl and naphthyl rings to the boron center. These assignments have been corroborated by theoretical absorption spectra calculated using time-dependent density functional theory (TD-DFT, see SI), confirming that the intense absorption band is not in fact due to donor−acceptor charge transfer as is commonly seen in directly conjugated systems.[5] Due to the ambipolar nature of **1**, this compound undergoes both reversible reduction and oxidation by cyclic voltammetry, at potentials of $E_{1/2}^{\mathrm{red}} = -2.41$ V and $E_{1/2}^{\mathrm{ox}} = +0.34$ V vs $\mathrm{FeCp_2}^{0/+}$ in DMF.

Compound **1** exhibits bright green charge-transfer fluorescence ($\lambda_{\max} = 529$ nm in CH_2Cl_2) with a quantum efficiency of 0.43, the highest observed to date for a molecule displaying through-space charge transfer to boron (Figure 2). The charge-transfer fluorescence is supported by the strong solvent-dependence of the emission spectrum (e.g., $\lambda_{\mathrm{em}} = 450$ nm in hexanes, 560 nm in acetone; see SI). The considerable increase in quantum efficiency over previously reported nonconjugated donor−acceptor triarylboron compounds is likely due to both the improved donor strength of

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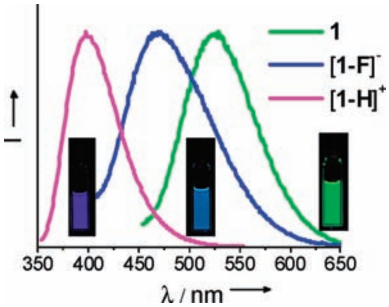

Figure 2. Normalized fluorescent emission spectra of **1** and its acid and fluoride adducts. Inset: Photographs of the corresponding solutions at 10^{-5} M in CH_2Cl_2, $\lambda_{ex} = 365$ nm.

the dialkylamine as well as the close donor−acceptor spacing imposed by the naphthyl linker.

When tetrabutylammonium fluoride (TBAF) is added to a solution of **1**, the emission color is observed to rapidly switch from green to sky blue with similar quantum efficiency ($\lambda_{max} = 469$ nm, $\Phi = 0.42$). This is accompanied by an increase in intensity of the strong 333 nm band in the UV−visible spectrum of **1**, likely due to a reduction in the CT contributions of this transition and increase in $\pi-\pi^*$ character, improving the overall overlap between participating MOs. Approximately 20 equiv of fluoride are required to achieve complete color switching, a higher level than in the case of most organoboranes but comparable to similar sterically congested materials reported previously,[4,6] corresponding to a binding constant K of $(1.7 \pm 0.5) \times 10^4$ M^{-1}. ^1H and ^{19}F NMR titrations of **1** with TBAF indicate the quantitative conversion of **1** to $[\mathbf{1{\cdot}F}]^-$ without intermediates.

While the selectivity of dimesitylboranes for fluoride ions over Cl^-, Br^-, and others is well documented, these compounds are well-known to be responsive to cyanide ions as well.[7] Titration with tetraethylammonium cyanide (TEACN) in CH_2Cl_2 thus triggers a similar fluorescent spectral change to that induced by F^- ($\lambda_{max} = 466$ nm, $K = (1.6 \pm 0.5) \times 10^4$ M^{-1}). As the response to both anions is similar, further detailed studies will focus on fluoride as a trigger for fluorescent change here.

Conversely, addition of a strong acid (HBF_4 or $HBAr^F_4$) to a CH_2Cl_2 solution of **1** results in quantitative protonation after addition of ∼1.5 equiv of acid, switching the emission color of the sample to bright purple ($\lambda_{max} = 398$ nm). This is accompanied by a large increase in the quantum yield of the sample ($\Phi = \sim 1.0$), which is consistent with other triarylboron compounds conjugated to highly electron-rich π-systems.[6,8] As with $[\mathbf{1{\cdot}F}]^-$, NMR data indicate clean formation of $[\mathbf{1{\cdot}H}]^+$ on addition of acid.

DFT calculations on compound **1** and its H^+ and F^- adducts at the B3LYP/6-31G* level of theory provide insight into the nature of fluorescence in each of these emissive states. Calculations indicate that the donor and acceptor chromophores make the largest contributions to the HOMO and LUMO, respectively, consistent with through-space p(N) ← p(B) charge transfer as the lowest-energy emission pathway. However, once the p orbital on boron is blocked using fluoride, the lowest energy transition of $[\mathbf{1{\cdot}F}]^-$ becomes a charge transfer from the (F)$BMes_2$-phenyl (HOMO) to the naphthyl (LUMO), producing blue fluorescence. If instead the filled p orbital on nitrogen is blocked using acid, the lowest energy transition of $[\mathbf{1{\cdot}H}]^+$ is from the $BMes_2$phenyl-naph (HOMO) to the phenyl-naph (LUMO), producing purple fluorescence with some charge transfer character. The trend of the emission energy observed for these species agrees with that of the calculated HOMO−LUMO gap shown in Figure 3.

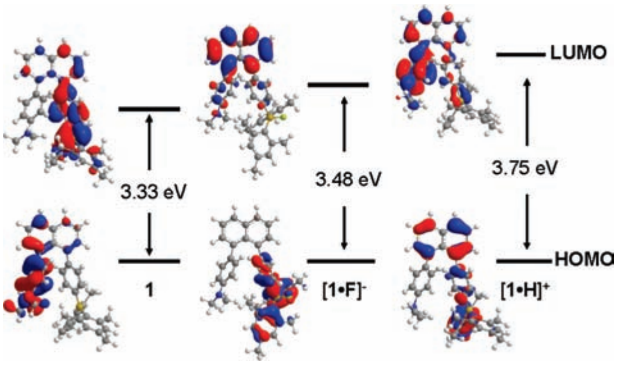

Figure 3. HOMO−LUMO diagrams of **1**, $[\mathbf{1{\cdot}F}]^-$, and $[\mathbf{1{\cdot}H}]^+$.

Remarkably, the fluorescent responses to both acid and fluoride in this system are fully reversible by applying the opposite trigger. Despite possessing receptor sites for both ions, the compound exists instead as free **1** when treated with both stimuli, and the green fluorescence is preserved. Similarly, after treatment of **1** with excess acid or fluoride, the CT emission can be restored by titration with the other trigger (Figure 4b and 4d). No sample degradation is observed in either case, and these processes can be cycled several times in either direction without loss of fluorescent intensity. These results are in constrast with previous studies, in which it was shown that protonation of a proximal tertiary amine could promote hydrolysis of an adjacent triarylborane.[9] The removal of fluoride ions from triarylboranes using protic acids including water has been reported previously.[10]

^1H and ^{19}F NMR titrations of $[\mathbf{1{\cdot}F}]^-$ with acid or $[\mathbf{1{\cdot}H}]^+$ with fluoride provide insight into these processes. While

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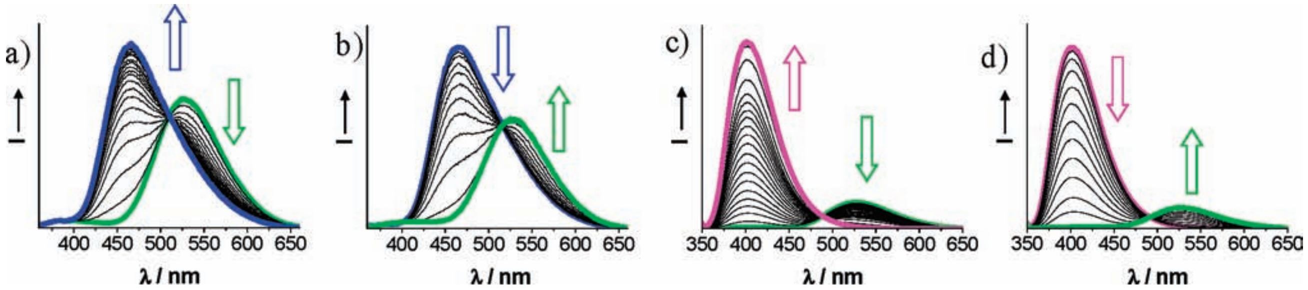

Figure 4. Fluorescent titration spectra for 1.0×10^{-5} M solutions of **1** in CH_2Cl_2 ($\lambda_{ex} = 365$ nm): (a) **1** titrated with 20 equiv of TBAF; (b) 21 equiv of TBAF added to **1** and then titrated with 14 equiv of HBF_4; (c) **1** titrated with 1.8 equiv of HBF_4; (d) 1.8 equiv of HBF_4 added to **1** and then titrated with 3.0 equiv of TBAF.

chelation of HF by a compound with spatially proximate phosphine and borane groups has been recently reported,[11] the 5.55 Å B···N separation distance in this case is too long to support chelation of HF in the presence of both analytes. Instead, it appears that fluoride abstraction from **[1·F]**$^-$ occurs via a B−F···H intermediate when acid is added, as evidenced by the appearance of a broad peak from −146 to −153 ppm in the ^{19}F NMR spectrum of **[1·F]**$^-$ on titration with HBF_4. This is similar in chemical shift to previously studied hydrogen bond adducts of fluoride.[12] Once sufficient acid is added to completely switch the emission color back to green, this peak disappears, indicating restoration of the material to the original form of **1**.

A similar intermediate is observed in the ^{19}F NMR spectrum of [**1·H**]$^+$ titrated with F$^-$, though the peak is much sharper, appearing further upfield between −181 to −185 ppm and likely arising from a N−H···F intermediate (see SI). Once again, after a sufficient amount of fluoride has been added, compound **1** is restored to its original form. Though the deprotonation of a dialkylarylamine by fluoride may not seem intuitively favorable due to their stronger basicities in water, this is in fact consistent with the dramatically higher basicity of fluoride in anhydrous aprotic solvent.[13]

In summary, we have demonstrated a highly luminescent, nonconjugated donor−acceptor triarylboron compound that can rapidly and reversibly be switched between three fluorescent states using either acid or fluoride. Moreover, each of these stimuli can also be used to reverse the effects of the other, making it possible to cycle compound **1** between the three fluorescent colors using only two simple triggers.

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Supporting Information Available: Synthetic details, absorption spectra, TD-DFT data, ^{1}H and ^{19}F NMR titrations of **1** with acid and fluoride, UV−visible and fluorescence titration data for the reaction of **1** with CN$^-$, and complete X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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