Fluorescent Dyes

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# Regiospecific N-Heteroarylation of Amidines for Full-Color-Tunable Boron Difluoride Dyes with Mechanochromic Luminescence**

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In recent years, a large number of powerful transition-metal-catalyzed coupling reactions have been developed. Because of the modular and highly efficient features of these coupling reactions, it is usually possible to assemble a versatile molecular library in a single step.[1] Arguably, transition-metal-catalyzed coupling methods provide a unique opportunity to access new skeletons, and understand and manipulate the specific properties of molecular structures.[2] In contrast, it still remains challenging to develop new chromophores synchronously possessing diverse fluorescent characteristics.[3] Herein, we report the discovery of multifunctional fluorescent molecular libraries through the rational design of molecular structures as well as target-directed development of transition-metal-catalyzed coupling reactions.

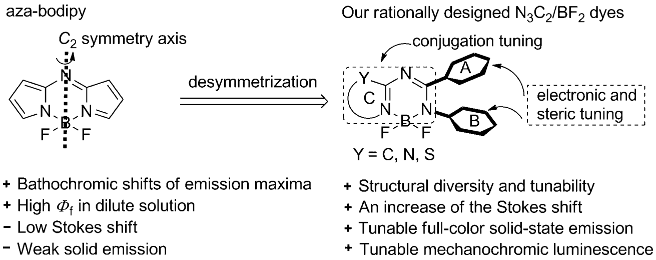
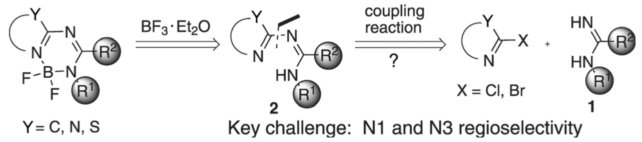


***Figure 1.*** Design of fluorescent framework containing a staggered class of $N_3C_2/BF_2$ cores.

Boron difluoride dyes are one of the most popular fluorescent dyes.[4] Among these organoboron dyes, the aza-bodipy fluorophores are well known because of their inherent bathochromic shifts for absorption and emission maxima, and high fluorescence quantum yields in dilute solution (Figure 1).[5] However, most of these molecules feature planarity to some extent, and this planarity normally causes certain intermolecular interactions (e.g., π–π stacking, weak excimer formation, etc.) resulting in significant quenching of the emission in the aggregated state. In addition, the aza-bodipy core, having a staggered $N_3C_2$ framework and a $C_2$ symmetry axis, typically exhibits a low Stokes shift (5–30 nm, in most cases). In this study, one of two pyrrole units present in an aza-bodipy dye is replaced by a variety of N-heteroarenes, thus leading to a fluorescence library of structurally diverse molecules. The other pyrrole ring is replaced by two aromatic rings, A and B, at the C2 and N1 positions, respectively, and could lead to an unsymmetric propeller-shaped conformation to trigger high fluorescent efficiency in the solid-state, and luminescent mechanochromism as a result of the crowded environment (Figure 1).[6] Furthermore, the resulting desymmetrization of the staggered $N_3C_2$ framework would render the ground and excited states more distinct, and thus may induce an increase of the Stokes shift.[7]

To achieve the diversity-oriented library of $BF_2$/amidine molecules, the development of a versatile and common method for the synthesis of various precursors (**2**) was required (Scheme 1). We envisaged that these amindine-based precursors could be accessed in one step by the regiospecific N-heteroarylation of a 1,2-disubstituted amidine (**1**) with an N-heteroaryl halide. However, in spite of the remarkable progress made in the palladium-catalyzed N-arylation over the last decades, the palladium-catalyzed regiospecific N-heteroarylation of 1,2-disubstituted amidines with N-heteroaryl halides is still less developed. Potential challenges include the generation of N1 and N3 regioisomers and/or bi-heteroarylated products owing to the presence of two nucleophilic nitrogen centers (N1-H and N3-H) and the general reluctance of heteroaryl halides to undergo coupling.[8]



***Scheme 1.*** Design of a target-directed coupling reaction for the proposed $N_3C_2/BF_2$ dyes.

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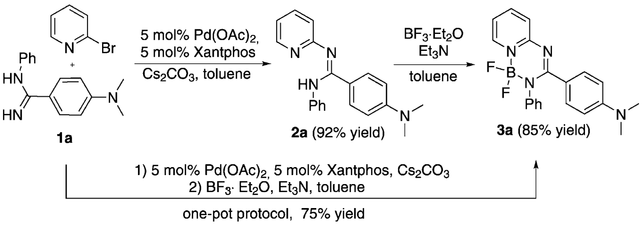
We began the investigation of the regiospecific N-heteroarylation of 4-(dimethylamino)-*N*-phenylbenzimidamide (**1a**) with 2-bromopyridine. After screening several parameters (e.g., solvents, bases, palladium sources, and ligands), the optimized reaction conditions afforded the desired compound **2a** in 92 % yield with complete N1 selectivity (Scheme 2). The precursor **2a** reacted readily with boron trifluoride diethyl etherate in the presence of triethylamine to yield the BF$_2$/amidine-based complex **3a** in 85 % yield. We were also pleased to find that this two-step process could be shortened to a sequential one-pot synthesis with the same yield and without the isolation of **2a**.

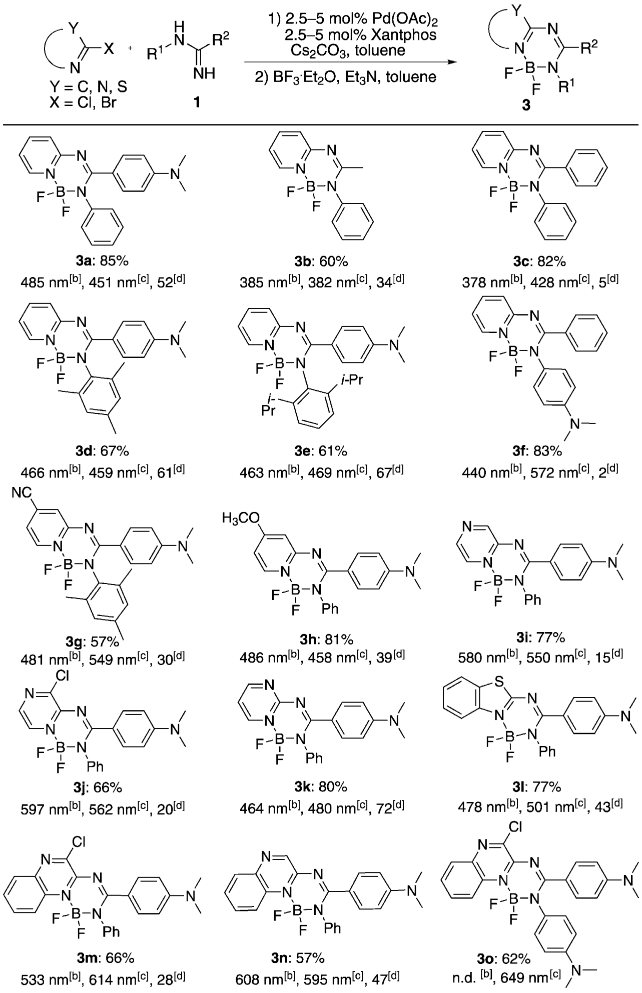


***Scheme 2.*** Regiospecific N-heteroarylation of **1a** with 2-bromopyridine to give the BF$_2$/amidine-based complex **3a**. Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

Following our molecular design concept, we created a diversity-oriented library based on the N$_3$C$_2$/BF$_2$ core, bearing distinct degrees of conjugation, and electronic and steric characteristics, by using the regiospecific coupling reactions with a variety of 2-halo-N-heteroarenes and amidines (**1**; Table 1). 2-Halo-substituted pyridines bearing the electron-donating or electron-withdrawing groups reacted smoothly with various amidines (**3a–h**). Other five- or six-membered 2-halo-N-heteroarenes including 2-halopyrazines, 2-haloquinoxalines, 2-halopyrimidines, and 2-halobenzothiazoles could also selectively react with a variety of amidines to afford the BF$_2$/amidine-based complexes in satisfactory yields (**3i–o**).

Having established a structurally diverse library of boron complexes, we first evaluated their photophysical properties. The absorption maxima, photoluminescence (PL) emission maxima, PL quantum yields ($\Phi_f$), and excited-state lifetimes of these complexes in both the solid state and CH$_2$Cl$_2$ solution are shown in Table 1, as well as Tables S1 and S2 in the Supporting Information. It is worth noting that all these BF$_2$ amidines were stable in light, humidity, and air. The fluorescence intensities of their CH$_2$Cl$_2$ solutions showed negligible roll-off over 1 hour under constant excitation at ambient atmosphere. Taking **3d** as a representative example, its fluorescence intensity remained stable over a 5 hour period (see Figure S1). Under photoexcitation, these BF$_2$ amidines could emit fluorescence covering the entire visible region, and formed a palette of colors in both CH$_2$Cl$_2$ solution ($\lambda_{em}$: 378–608 nm) and in the solid state ($\lambda_{em}$: 382–649 nm; Table 1 and Figure 2a). As far as $\Phi_f$ is concerned, most of the BF$_2$-amidine-based complexes showed quite low fluorescence efficiencies in CH$_2$Cl$_2$ solution, whereas their solid and 1 % dye-doped poly(methylmethacrylate) (PMMA) film samples showed enhanced PL efficiencies (see Table S1 in the Supporting Information). This enhancement might stem from the restriction of intramolecular rotation (RIR) of the A and B rings of the complexes in the aggregate state or in a rigid matrix, as it has been proposed to be a crucial element for the high emission efficiency in the condensed state.[6]

***Table 1:*** Catalytic regiospecific N-heteroarylation and photophysical data of the resulting catalytic products.[a]



**3a**: 85%
485 nm[b], 451 nm[c], 52[d]

**3b**: 60%
385 nm[b], 382 nm[c], 34[d]

**3c**: 82%
378 nm[b], 428 nm[c], 5[d]

**3d**: 67%
466 nm[b], 459 nm[c], 61[d]

**3e**: 61%
463 nm[b], 469 nm[c], 67[d]

**3f**: 83%
440 nm[b], 572 nm[c], 2[d]

**3g**: 57%
481 nm[b], 549 nm[c], 30[d]

**3h**: 81%
486 nm[b], 458 nm[c], 39[d]

**3i**: 77%
580 nm[b], 550 nm[c], 15[d]

**3j**: 66%
597 nm[b], 562 nm[c], 20[d]

**3k**: 80%
464 nm[b], 480 nm[c], 72[d]

**3l**: 77%
478 nm[b], 501 nm[c], 43[d]

**3m**: 66%
533 nm[b], 614 nm[c], 28[d]

**3n**: 57%
608 nm[b], 595 nm[c], 47[d]

**3o**: 62%
n.d. [b], 649 nm[c]

[a] For detailed reaction conditions, see the Supporting Information. [b] Emission maximum in CH$_2$Cl$_2$. [c] Emission maximum in the solid state. [d] Fluorescence quantum yield (%) in doped PMMA film with 1 % of the BF$_2$-amidine-based dye. Absolute quantum yield was determined with a calibrated integrating sphere system. n.d. = not detected because of the weak emission intensity.

According to the RIR mechanism, the $\Phi_f$ values of the compounds in solution could be enhanced by internally hindering intramolecular rotation at the molecular level.[9] Therefore, by incorporation of bulky groups into the B ring of **3a**, we constructed **3d** and **3e** whose intramolecular rotation (IMR) process should be suppressed effectively. The steric effect of these bulky groups was observed to greatly influence the molecular fluorescence. The $\Phi_f$ values of **3a**, **3d**, and **3e** increased from < 1 to 75 to 86 %, respectively, in CH$_2$Cl$_2$ (Figure 2b). The phenomena are in good accordance with the calculated rotation barrier ($E_R$) values (see Table S3). The

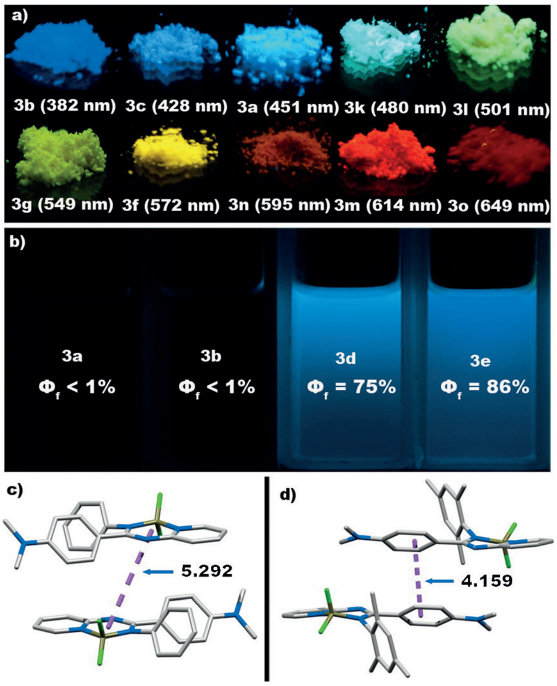


***Figure 2.*** a) Fluorescence images of the $BF_2$/amidine-based complexes in the solid state under UV light ($\lambda_{ex} = 365$ nm). The emission maximum is given within parentheses. b) RIR mechanism for the control of the molecular photoluminescence. c,d) The X-ray structures of the crystals **3a** and **3d**, respectively.

$E_R$ values for **3d** (>8.619 a.u.) and **3e** (>8.955 a.u.) are approximately 36 times higher than those for **3a** (>0.2430 a.u.). In spite of high quantum efficiency of **3d** and **3e** in $CH_2Cl_2$, their solid-state emission intensities significantly decreased in comparison with that of **3a**. To elucidate the distinct emissive behavior, single crystals of **3a** and **3d** were obtained.[10] The dye **3a** showed a strikingly twisted molecular conformation, and the parallel $N_3C_2/BF_2$ frameworks of adjacent molecules were far away from each other (5.29 Å, Figure 2c), and thus might lead to inactive rotation and prevent close packing in the solid state. As a result, **3a** had a relatively high solid-state light-emitting efficiency (for crystal, $\lambda_{em} = 452$ nm, $\Phi_f = 22\%$). In contrast, **3d** exhibited a reduced light-emission efficiency in the solid state (for crystal, $\lambda_{em} = 454$ nm, $\Phi_f = 7.5\%$). The shorter distance between the *p*-dimethylaminophenyl planes of neighboring molecules of **3d** (4.16 Å, Figure 2d) indicated a potential π–π stacking.

Subsequently, DFT calculations [B3LYP/6-31G(d) level] indicated that for most of these dyes, the highest occupied molecular orbital (HOMO) was primarily localized over the dimethylaminophenyl moiety, and the lowest unoccupied molecular orbital (LUMO) was mainly centered on the $BF_2$-containing heterocycle framework (for details, see the Supporting Information, Part VI). These observations implied that this type of dye might exhibit intramolecular charge-transfer (ICT) character.[7d,11] To confirm the presence of ICT processes, solvatochromic effects were investigated to estimate the dipole moment change ($\Delta\mu = \mu_e - \mu_g$) between the fluorescent excited state and ground state.[11e,12] Considering that the excited-state lifetimes of dyes in solution must be much longer than the solvent orientational relaxation times to ensure the accuracy of solvatochromic experiments,[12d,13] **3d** and **3e** were chosen to evaluate their solvatochromic effects because of their nanosecond grade lifetimes. For both **3d** and **3e**, switching to various solvents had little effect on their absorption spectra, but led to significant red-shifts in the fluorescence spectra in line with the increasing solvent polarity (see Figure S3). The good linear correlations between Stokes shifts and the solvent polarity allowed us to determine the dipole moment changes ($\Delta\mu$) of the compounds from ground to excited states (for **3d**, 14.76 D; for **3e**, 14.72 D; For details, see the Supporting Information, Part VII). Such large values of $\Delta\mu$ clearly indicated a substantial contribution of ICT character in the excited state of **3d** and **3e**. The intramolecular charge-transfer transition for **3d** and **3e** might have occurred from the dimethylaminophenyl moiety to the $BF_2$-containing heterocycle framework.[7d,11]

Mechanofluorochromic materials have great potential for various applications including sensors, memory devices, and security systems, etc.[14] However, the molecular design strategy for mechanochromic dyes still remains obscure so far. The examples describing piezochromic properties are limited, and most documented cases have occurred as single isolated events. Herein, we surprisingly found most of the $BF_2$/amidine-based dyes (e.g., **3e**, **3d**, **3h**, **3a**, **3i**, **3j**, and **3m**) exhibited piezochromic fluorescence and constituted a full-color-tunable piezochromic fluorescent molecular library upon grinding and annealing treatments. All of emission peaks of these mechanofluorochromic materials were clearly red-shifted by grinding (Figure 3a and Figure S5).

Taking **3a** as a representative example, the mechanofluorochromic process was studied in greater detail. Its emission could be reversibly switched between two different states by grinding/heating cycles with no obvious fatigue response (Figures 3b,c). A differential scanning calorimetry (DSC) experiment of the unground **3a** did not exhibit any endothermic or exothermic peaks at 20-170 °C (Figure 3d). In contrast, the ground **3a** presented an obvious exothermic peak at relatively lower temperature (approximately 97 °C), thus indicating a transition from a disordered phase to a well-organized phase. Thus, DSC analysis clearly indicated that the grinding could convert a thermodynamically stable crystal into a metastable state, and could be restored to the original crystalline state through an exothermic process (Figure 3d). The PXRD patterns of the unground solid of **3a** exhibited sharp and intense reflections, whereas the profile of the ground solid became broader with weaker reflection peaks. After heating at 120 °C, the sharp peaks in the PXRD patterns were recovered (Figure 3e). These observations manifested a morphological transition between crystalline and amorphous phases upon every grinding/heating cycle. We rationalized that the mechanochromism should be attributed to the desymmetric propeller-like configuration in our luminogens. The highly twisted conformation most likely results in the weak intermolecular interactions and relatively loose packing, which is susceptible to external perturbation to endow a chromic response.

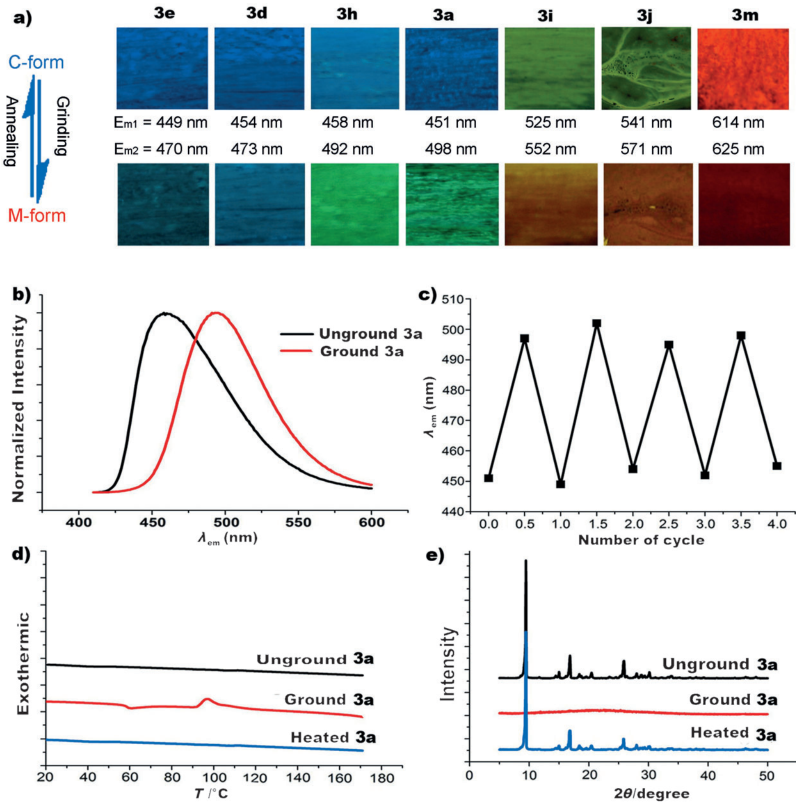


***Figure 3.*** a) Photographs of piezochromic fluorescence of the library under UV light ($\lambda_{ex}=365$ nm) upon grinding and heating treatments. b) Fluorescence emission spectra of unground and ground **3a**. c) Reversible switching of emission of **3a** by repeated grinding/heating cycles. d) DSC trace of **3a** in different states. e) XRD patterns of **3a** in different states. Traces in (d) and (e) are stacked vertically.

In conclusion, we have developed unsymmetric $N_3C_2/BF_2$ dyes through the rational design of molecular structures involving the target-directed development of transition-metal-catalyzed coupling reactions. From the perspective of the discovery of methodology, we disclose a palladium-catalyzed regiospecific N-heteroarylation of amidines with various 2-halo-N-heteroarenes. As viewed from a dye discovery point of view, this concise and highly regiospecific N-heteroarylation provides a modular route to assemble the structurally diverse $BF_2$/amidine-based complexes. These boron difluoride dyes with a desymmetric configuration not only present full-color-tunable solid-state emissions ($\lambda_{em}$: 382–649 nm), but also exhibit the tunable mechanofluorochromic nature.

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