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Aza-BODIPY Dyes

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Asymmetric Donor–π-Acceptor-Type Benzo-Fused Aza-BODIPYs: Facile Synthesis and Colorimetric Properties**

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Abstract: *Novel aza-diisoindolylmethene and their BF_2-chelating complexes (benzo-fused aza-BODIPYs) were synthesized on a large scale and in a facile manner from phthalonitrile in tBuOK-DMF solution. The unique asymmetric donor–π-acceptor structure facilitates B–N bond detachment in the presence of trifluoroacetic acid (TFA) in dichloromethane, resulting in sharp color change from red to colorless, with over 250 nm hypsochromic shift in the absorption maximum. This colorimetric process can be reversed by adding a very small amount of proton-accepting solvents or compounds. A ^1H and ^{11}B NMR spectroscopy study and also density functional theory (DFT) calculations suggest that TFA-induced B–N bond cleavage may disrupt the whole π-conjugation of the BODIPY molecule, resulting in significant colorimetric behavior.*

Owning to the prominent photophysical properties,[1] BF_2-chelated dipyrromethene (BODIPY) compounds have found applications in various fields such as chemical sensors,[2] solar cells,[3] or energy-transfer cassettes.[4] Being an important part of BODIPY dyes, aza-BODIPYs show marked red-shifts of absorption and emission energies as compared to other type of BODIPY dyes; these shifts are favorable for some applications such as fluorescence probes in biological imaging[5] and photodynamic therapy.[6] To further lower the absorption and emission energies, BF_2-chelated aza-diisoindolylmethene complexes (benzo-fused aza-BODIPYs) have been recently designed and synthesized.[7] The benzo-fused aza-BODIPY complexes exhibit a significant red-shift in the lowest absorption energy owing to their extended π-conjugation, leading to near-IR-absorbing BODIPY dyes for various applications.[8]

Although numerous aza-BODIPYs have been reported, the methods to prepare these compounds are limited. The present aza-BODIPY compounds are commonly prepared by 1) heating of 1,3-diaryl-4-nitrobutan-1-one or 3-methyl-4-nitro-1-arylbutan-1-one; 2) reacting phthalonitriles with arylmagnesium bromides; or 3) reacting pyrrole with nitrosopyrrole.[1a,7,9] Most of these methods are laborious and/or inefficient. Moreover, the substituents of aza-BODIPY dyes are mainly restricted to aryl substitution on 1,3,5,7-positions in a symmetric manner. Asymmetric aza-BODIPYs still remain scarce owing to the synthetic challenges.[10] Methods (1) and (2) can only afford symmetric aza-BODIPYs. Although asymmetric aza-BODIPYs can be obtained from method (3) through pyrroles or nitrosopyrroles with different substituents, this procedure is infeasible for aza-diisoindolylmethene compounds. To date, there is no report addressing the synthesis and property of asymmetric donor–π-acceptor (D-π-A)-type benzo-fused aza-BODIPYs despite the fact that they might have unique properties and specific applications.

Our group has made continues efforts in the investigation of new aza-BODIPY compounds. We have previously reported the synthesis of aza-BODIPYs by reacting phthalonitriles or naphthalene dicarbonitriles with arylmagnesium bromides.[9] This method is practically useful, since phthalonitrile is commercially available and arylmagnesium bromides can be easily prepared.[11] However, this process can only afford symmetric aza-BODIPYs with aryl substituents on the 3,5-positions. To develop new methods for synthesizing asymmetric aza-BODIPYs, we are engaged to optimize the reaction by varying the solvent and reactant. By accident, we found that an asymmetric aza-diisoindolylmethene (**1a**) can be formed by reacting phthalonitrile with *t*BuOK in DMF solution (Scheme 1). After chelating with $BF_3{\cdot}OEt_2$, an asymmetric D-π-A-type benzo-fused aza-BODIPY (**3a**) was formed.

Herein we report the first synthesis of asymmetric aza-diisoindolylmethenes and their BF_2 complexes. Addition of phthalonitrile to the solution of potassium *tert*-butoxide in dry dimethylformamide (DMF) at 0 °C for 3 h afforded aza-diisoindolymethene **1a** containing an amine group on one side. This asymmetric compound was subsequently reacted with dimethylamine in tetrahydrofuran (THF) to form compound **2a**. The BF_2-chelating complex **3a** was obtained by reaction **2a** with boron trifluoride etherate under basic conditions in dichloromethane (detailed procedures for the preparation of compounds **1a–3a** are provided in the Supporting Information). These dyes were characterized by ^1H NMR (Supporting Information, Figures S1–S3) and ESI-MS spectra. The ^1H NMR spectrum of compound **1a** in

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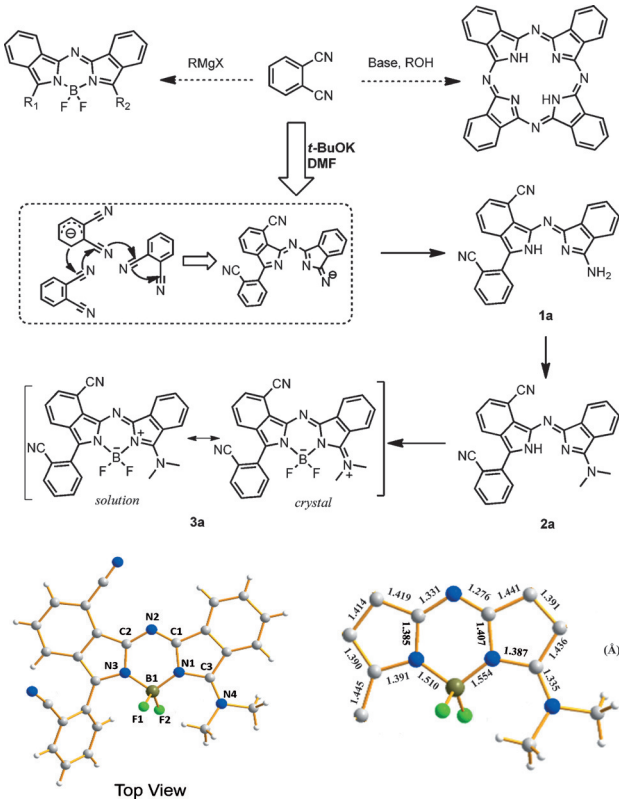
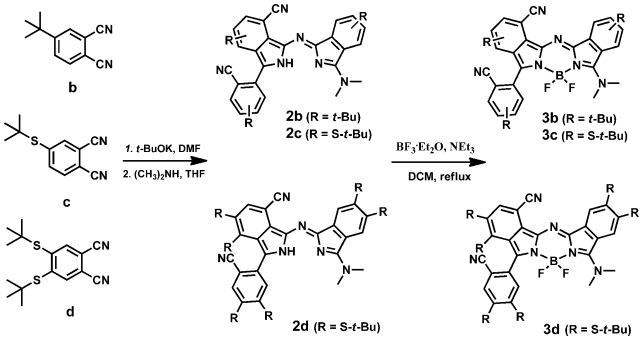


Scheme 1. Synthetic procedure for asymmetric benzo-annulated aza-BODIPY **3a** (see text for details) and its X-ray crystal structure.[19]

potassium *tert*-butoxide in DMF.[12] The deprotonated phthalonitrile would act as a nucleophilic reagent to attack the cyano moiety of a second phthalonitrile molecule, leading to the formation of C–C bond. After further nucleophilic reaction and a two-electron reduction process, aza-diisoindolylmethene with an amino group on one side was obtained. The activation of C–H bond in phthalonitrile and formation of anion with potassium *tert*-butoxide is the key step. Our preparation of the asymmetric benzo-fused aza-BODIPY **3a** can be achieved in a facile and large scale way (> 100 g) with high yield (> 45 %). Moreover, this method can also be extended to prepare other benzo-fused aza-BODIPYs with various functional groups, such as *tert*-butyl or *tert*-butyl thiol (**b–d**) (Scheme 2). The structures of these functional aza-



Scheme 2. Synthetic procedures for aza-diisoindolylmethene derivatives from mono- and bis-substituted phthalonitriles. DCM = CH_2Cl_2.

$(CD_3)_2SO$ showed two broad peaks at 8.8–9.1 ppm, which could be attributed to the two protons of the side amine group, while a wide band at ca. 13.6 ppm could be assigned to the proton of isoindolyl moiety. The N–H proton signal of **2a** (ca. 13.2 ppm) assigned for the isoindolyl moiety disappeared in **3a**, in agreement with the formation of BF_2 complex. The structure of **3a** was further elucidated in a definitive manner by X-ray crystallography (Scheme 1; Supporting Information, Figure S4, Tables S1, S2). Single crystals suitable for X-ray structure analysis were obtained by slow evaporation of dichloromethane/hexane solution. As shown in Scheme 1, the boron atom is coordinated to two nitrogen atoms and two fluorine atoms in a tetrahedral geometry, with B–N bond lengths of 1.554 Å (B–N1) and 1.510 Å (B–N3), and B–F bond lengths of 1.391 Å and 1.394 Å, respectively. The remarkable B–N bonds difference could be attributed to the asymmetric D-π-A type of the molecular structure. Interestingly, the bond length of C3–N4 is 1.334 Å, while the dihedral angle between the BODIPY core plane and the plane of dimethylamine is 21.5°, indicating that dimethylamine group is involved in the π-conjugation with aza-BODIPY core. The results from NMR study and X-ray structure analysis showed that **3a** in crystalline state and solution can be represented by two different resonance structures.

A possible mechanism for the formation of **1a** is shown in Scheme 1. The reaction was initiated by deprotonation of phthalonitrile at the *ortho* position of the CN group using

diisoindolylmethene compounds have been confirmed by ^{1}H NMR, MS, elemental analysis, and absorption spectra. It should be noted that the reaction time is important for these substituted phthalonitrile. Side reactions are inevitable for long-time stirring owing to the strong base conditions and possible existence of radicals in *t*BuOK-DMF.[13] Normally, the yields of aza-diisoindolylmethene compounds drop to a low value or zero after reacting overnight. Therefore, the reactions should be monitored by UV/Vis spectra to ensure the highest yields. It is well known that phthalocyanine compounds synthesized from mono-substituted phthalonitriles have multiple isomers.[14] Isomers of aza-diisoindolylmethenes are also obtained from mono-substituted phthalonitriles **b** and **c**. Bis-substituted phthalonitrile produces one conformation of aza-diisoindolylmethene derivatives, according to the ^{1}H NMR spectra of **2d** and **3d** (Supporting Information, Figures S5, S6).

The absorption spectrum of **3a** in CH_2Cl_2 shows a broad maximum at 591 nm with full-width at half-maximum (FWHM) of 92 nm (Figure 1); the detailed spectroscopic data are summarized in the Supporting Information, Table S3. The solvent effect of the photophysical properties of **3a** is typical for BODIPYs. The fluorescence spectrum of **3a** exhibits moderate emission at 654 nm ($\Phi_F = 0.34$) with a Stokes shift of 63 nm (Supporting Information, Figure S7). The larger Stokes shifts of **3a** can be attributed to the asymmetric molecular structure, which increase the energy differences between the ground and excited states.[15] The

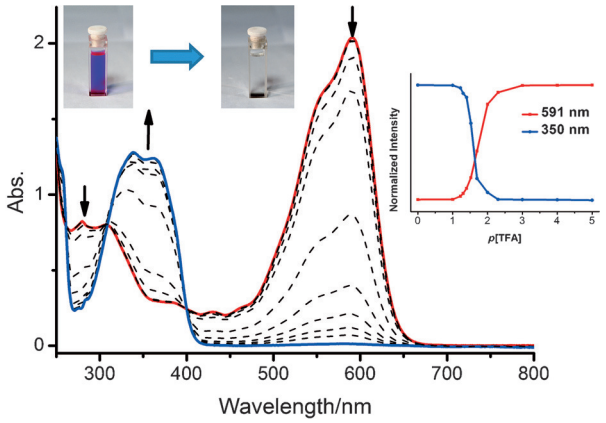


Figure 1. Absorption spectra changes of **3a** in CH_2Cl_2 titrated with increasing concentration of TFA. Inset: Changes of the absorption intensity at 591 nm and 350 nm vs. *p*[TFA] in CH_2Cl_2. (*p*[TFA] = $-\log C_{TFA}$).

photophysical properties of substituted aza-diisoindolylmethene complexes (**3b–d**) were also investigated in CH_2Cl_2 (Supporting Information, Figure S7, Table S4). There is no apparent difference in the spectra with different substituted groups, as they contain the same electronic structure of the central π-conjugation system.

Upon addition of TFA, the absorption maximum at 591 nm gradually decreases while the peaks in the 300–400 nm region increase progressively, with a clear isosbestic point at 400 nm, suggesting a conversion between two distinct forms. Meanwhile, the fluorescence intensity is quenched (Supporting Information, Figure S8). A similar spectra change can be observed in toluene solution (Supporting Information, Figure S9).

The colorimetric process can be reversed when bases such as triethylamine and diisopropylamine are added. Interestingly, upon adding trace amount of proton-accepting solvents, such as acetonitrile, THF, or DMSO, the absorption and fluorescence spectra of **3a** can also be recovered. DMSO is the most effective solvent among these (Supporting Information, Figure S10). For substituted derivatives **3b–3d**, the TFA-induced spectra changes are also investigated (Supporting Information, Figure S11). The addition of TFA leads to the bleaching of the red solution of *tert*-butyl substituted **3b**. However, BODIPY with thiol group shows slightly different change in spectra. The band at 599 nm disappeared, while a strong absorption in 300–400 nm and a weaker band in 400–500 nm was observed. The colorimetric processes are also reversible by adding trace amount of proton-accepting solvents, rendering them applicable for distinguishing molecules containing proton-accepting N or O atoms in certain conditions (Supporting Information, Figure S12).

To understand the mechanism for such a unique colorimetric process, ^{1}H- and ^{11}B NMR spectra of **3a** before and after addition of TFA in CD_2Cl_2 were studied. The ^{1}H NMR spectra shown in Figure 2a provide evident information for the structure changes: the singlet proton signal of the side NMe_2 at 3.7 ppm is downfield shifted and split into three peaks with the integration ratio of 3:1.29:1.71 accounting for 6H, while two new singlet peaks appear at 6.55 and 6.93 ppm

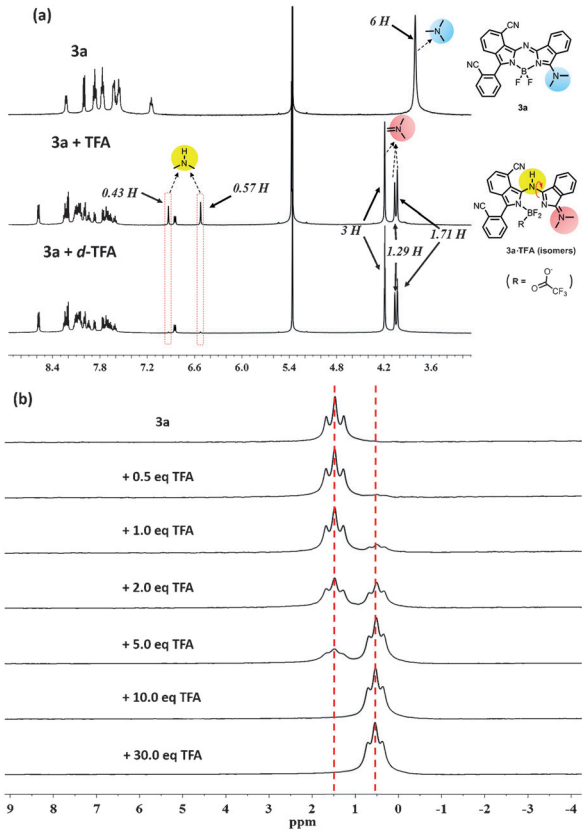
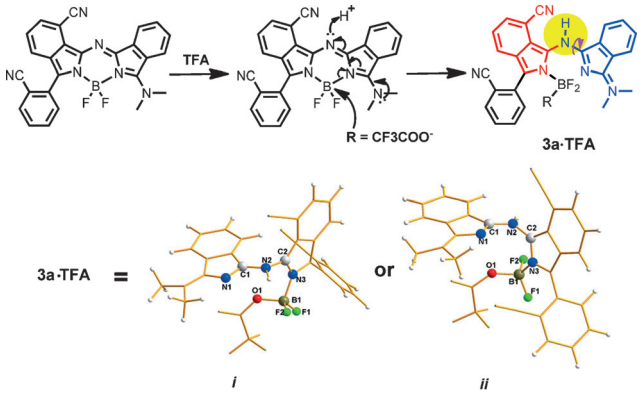


Figure 2. a) Changes in the ^{1}H NMR (500 MHz) spectra of **3a** in the presence of excess amount of TFA or deuterated TFA. b) Changes in the ^{11}B NMR (160 MHz) spectra of **3a** upon addition of TFA.

with the integration ratio being 0.43:0.57 account for 1H, which disappear if deuterated TFA is added instead. The other signals from the aryl rings in the lower field are downfield shifted and split into more peaks. This information suggest that TFA may induce partial B–N cleavage in **3a** to generate lower symmetric products. Two sets of unequal methyl proton signals in NMe_2 can be ascribed as a resonant structural transform from C3–N4Me_2 to C3=N4Me_2 in the presence of TFA. The new singlet peaks at 6.55 and 6.93 ppm may come from the protonated *meso*-N. The structure changes can be more clearly revealed from the ^{1}H NMR spectra of **3d** with two sets of peaks after addition of TFA (Supporting Information, Figure S13). The ^{11}B NMR spectra of **3a** without and with TFA are compared (Figure 2b). The triplet signal at 1.47 ppm is transformed to a new triplet peak with downfield shift of 0.53 ppm. This indicates the change of coordination environment of BF_2.[16] Generally the B–N bond in a six-membered central core structure of BODIPY is very stable, whereas it can be detached by the nucleophiles, such as F^- and CN^-, in a seven-membered expanded BODIPY analogue.[17] In our system, the molecule is polar and asymmetric, resulting in two non-equivalent B–N bonds as evidenced by two different bond lengths in the X-ray structure. The longer B–N bond is labile to be attacked by nucleophilic reagent, especially when the *meso*-N atom is protonated and the positive charge is delocalized on the N=C–N=C–N moiety, thus weakening the electron density of N

atom coordinated to B atom. The trifluoroacetic acid anion will then act as a nucleophilic agent to attack the boron atom, resulting in the cleavage of one weaker B–N bond and formation of a B–O(CF_3COO^-) bond (Scheme 3). Since the



Scheme 3. Proposed mechanism for the colorimetric process of **3a** and optimized structures of proposed products.

rigid central BN2 coordination six-membered ring is cleaved, the two isoindole rings can rotate freely. Moreover, the two *meso* C–N bonds are transformed to single bond; therefore, the π-conjugation in the whole BODIPY is disrupted and causes the absorption at 591 nm decreases significantly. When base or a proton-accepting molecule is added to remove $CF_3CO_2^-$, the added compound is then dissociated from B atom, which allows it to coordinate with an N atom of the isoindole to form a rigid six-membered ring again, and thus the fading process is reversed (Supporting Information, Scheme S1). Therefore, the cleavage and restoration of the B–N bond leads to the color change. It is noteworthy that such novel colorimetric phenomena of **3a–d** are closely related to their unique structures. The presence of the N=C–N=C–N moiety leads to electron redistribution upon protonation, while the two nonequivalent B–N bond ensures that only one B–N bond is fragile. Therefore, the cleavage and restoration of B–N bond is accessible and reversible.

We also optimized the structure of the additive compound between the CF_3COO^- anion and the protonated complex **3a** using DFT calculations. By including the CF_3COO^- anion into structure optimization, two lowest energy conformations of the additive compounds are obtained (Scheme 3). In these two structures, the B–N bonded six-membered ring is cleaved, which allows the free rotation of the two isoindole moieties to form two stable conformations. The dihedral angles between the two moieties are 77.6° and 77.9°, respectively in two stable isomers. The isomers (***i*** and ***ii***) along the C1=N2 double bond induce two sets of ^{1}H NMR response, while these two structures have a similar energy level. TDDFT calculations predict low-energy absorptions at 633 and 667 nm, which can be assigned to intramolecular charge transfer (Supporting Information, Figures S14, S15). However, these transitions have very small oscillator strengths and will not be observed. The second lowest energy absorption is predicted to be at 385 and 401 nm, respectively, corresponding to the enhanced band observed in the absorption spectra between 300–400 nm.

Meanwhile, simple protonation of an aza-nitrogen is unlikely to cause the significant colorimetric effect. The NBO charge population analysis showed that the *meso*-N atom of **3a** is more electronegative than other protonation sites and therefore have the best proton accepting ability (Supporting Information, Figure S16). Moreover, the meso-N protonated structure has the lowest energy among four possible N-atom protonated products (Supporting Information, Figure S17).[18] However, the meso-N protonated complex **3a** show red-shifted lowest-energy absorption at ca. 610 nm, which is contradictory to the observed huge blue-shift (Supporting Information, Figures S18, S19).

In conclusion, we describe herein a facile synthetic strategy for asymmetrically substituted benzannulated aza-BODIPY dyes from commercially available phthalonitrile in *t*BuOK-DMF solution. Our method can be achieved on a large scale with a high yield. Moreover, this method can also be extended to obtain other benzo-fused aza-BODIPYs with various substituted groups. Owing to the unique asymmetric and D-π-A structures, these aza-BODIPYs show novel colorimetric properties in TFA; the reversible color change upon adding electron-donating molecules suggests potential applications such as colorimetric probes for specific solvents.

Keywords: aza-BODIPY · C–H activation · colorimetry · dyes

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[19] CCDC 1047636 (**3a**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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