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A Family of BODIPY-like, Highly Fluorescent and Unsymmetrical Bis(BF₂) Pyrrolyl-acylhydrazone Chromophore: BOAPY

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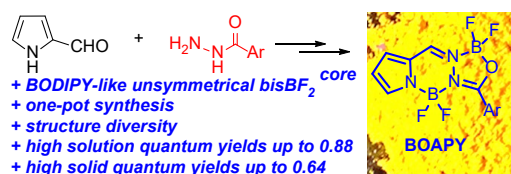
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ABSTRACT: A new family of pyrrolyl-acylhydrazones anchored with two BF₂ units, named BOAPY, has been developed as BODIPY-like and unsymmetrical bisBF₂ chromophore via a simple one-pot reaction. The easily accessible scaffold enjoys excellent diversity owing to the structural versatilities of 2-formylpyrroles and acylhydrazides. BOAPYs exhibit good molar absorption coefficients, large Stokes-shifts, and excellent chem-stability. More importantly, most of them display excellent fluorescence quantum yields both in solution and solid-state (up to 0.88 and 0.64, respectively).

Fluorescent chromophores, especially the novel small-molecule heterocyclic chromophores, have gained wide applications ranging from biological probes in labeling, imaging, sensing and therapy to photovoltaic, and optoelectronics in material science.^{1,2} In recent years, conjugated organic boron fluorophores have been developed as versatile and highly emissive structures.^{3,4} In particular, as one of the most successful fluorophores, boron dipyrromethene (BODIPY, Figure 1), has attracted much attention with significant achievements owing to their structure diversity and tunable photophysical properties.⁵ Nevertheless, in sharp contrast to the often observed strong fluorescence in solvents, most of reported BODIPYs are weakly fluorescent in solid-state because of their self-absorptions, which are closely related with the small Stokes shifts and possible H-type aggregations in solid state. These shortcomings normally lead to their dark and non-radiative excited states in high concentration solution and in solid state, seriously limiting their further applicability of visualizing the cellular environment or making optoelectronic devices.

In 2014, Ziegler, Nemykin and coworkers^{6a} and our group^{7a} reported the highly fluorescent and symmetrical hydrazine inserted bisBF₂-pyrrole chromophores (BOPHY, Figure 1) from stable formylpyrrole and hydrazine. It has received diverse applications in fluorescence energy transfer cascades, solar cells, photodynamic therapy, probes, and cellular imag-

ing.⁶⁻⁸ Several novel chromophores containing more than one BF₂ unit were also developed.⁹ For example, BOIMPYs and aza-BOIMPYs with N-B-N bridges by Werz et. al are a family of red-emissive fluorophores.^{9a,b} BF₂-bridged azafulvene dimers with N-B-O bridge by Wakamiya et. al was developed as a new type of NIR-absorbing dye.^{9c} Recently, our group reported a series of highly fluorescent, unsymmetrical

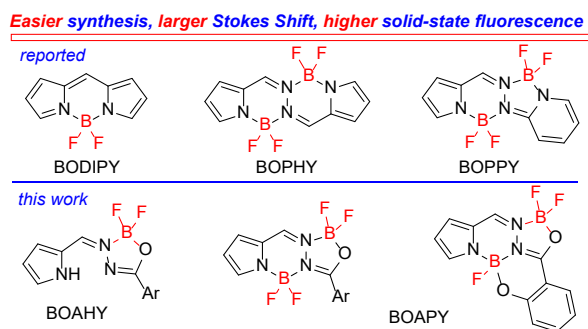
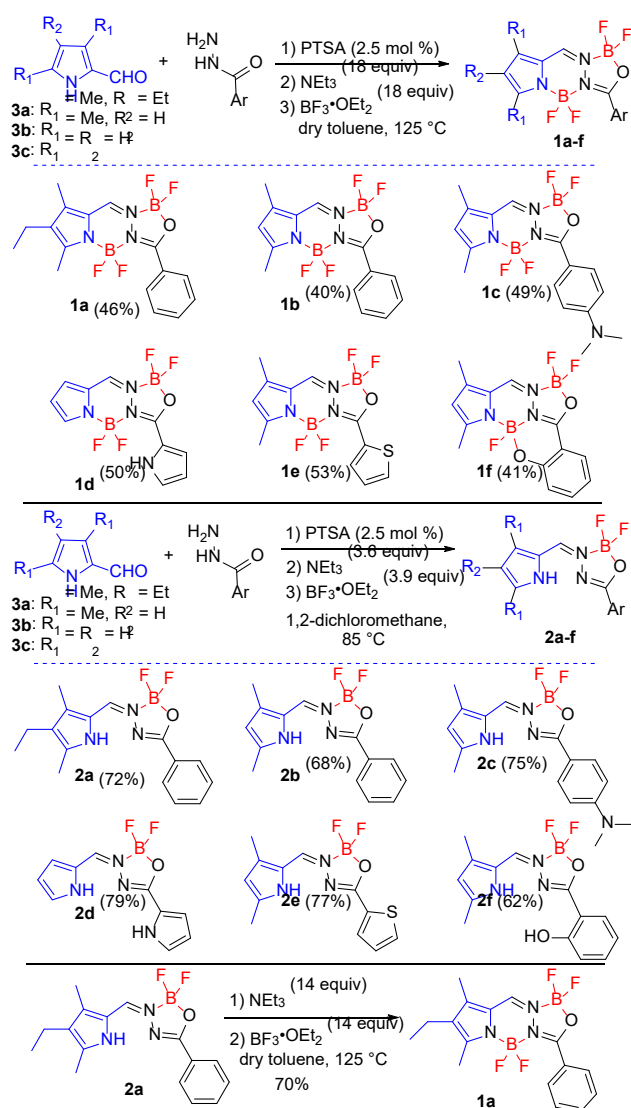


Figure 1. Previously reported BODIPY, BOPHY, BOPPY chromophores, and our BOAHY and BOAPY chromophores based on BF₂ anchored pyrrolyl-acylhydrazones in this work.

and easily accessible BOPPY dyes (Figure 1), which exhibit high solid-state fluorescence and large Stokes shifts, while retaining high molar absorption coefficients, excellent photostability and insensitivity to pH.^{7d} More recently, we have

also developed difluoroboronate anchored acylhydrazones (BOAHYs) as green fluorescent protein chromophore analogues, which exhibit bright fluorescence in solid state and notable aggregation-induced emission (AIE)-active features despite of weak fluorescence in solution.¹⁰ Herein, we hypothesized that pyrrole substituted acylhydrazones, generated *in situ* from the condensation of 2-formylpyrroles and acylhydrazine, could be anchored by two BF₂ units in the presence of NEt₃ to form a novel BOPHY-like bisBF₂ chromophore (Figure 1). With two BF₂ unit rigidifying the pyrrolyl-acylhydrazone skeleton through N–B–N as well as N–B–O bridges, the unsymmetrical core framework would restrict the rotation of their C=N bonds and provide enough rigidity. More importantly, owing to the unsymmetrical structure, this novel BODIPY-like, hydrazine inserted bisboron chromophore might afford higher solid fluorescence efficiency and larger Stokes shifts compared with those of classical BODIPY derivatives.

Scheme 1. Syntheses of BOAPYs **1a-f** and BOAHYs **2a-f** from formylpyrroles **3a-c** and acylhydrazines



Initially, formylpyrrole **3a** and benzoylhydrazine were condensed with a catalytic amount of *p*-toluenesulfonic acid (PTSA) (Scheme 1). The resultant condensation product

was not isolated and directly used to react with BF₃·OEt₂ in 1,2-dichloroethane for the boron complexation. According to TLC, the reaction mainly gave two products, which were then isolated and identified to be bisBF₂ BOAPY **1a** and mono-BF₂ BOAHY **2a**, and were further confirmed by the X-ray single crystal diffraction analysis (Figure 2). However, **2a** was the major product despite strong fluorescence of the reaction mixture after adding BF₃·OEt₂. After optimizing the reaction condition with temperature, equiv of BF₃·OEt₂ and solvents, it was found that **1a** could be generated exclusively in dry toluene in a sealed reaction tube in an oil bath at 125 °C overnight (Scheme 1). This optimized one-pot reaction gave expected **1a** in 46% yield. Similarly, **1b** was also obtained in 40% yield starting from 3,5-dimethyl-1H-pyrrole-2-carboxaldehyde **3b** and benzoylhydrazine. Furthermore, commercially available 4-(dimethylamino)benzoylhydrazide, 1H-pyrrole-2-carbohydrazide, thiophene-2-carbohydrazide and salicylhydrazide were then applied for the above “two step one-pot” reaction with formylpyrroles **3a-b**, respectively. These reactions gave expected BOAPYs **1c-f** in 41-53% yields as shown in Scheme 1. Interestingly, in **1f**, the additional phenol group was also complexed with the boron atom through an O–N–B linked six-membered ring to form a N₂O-type BF complex.^{4c,d} Furthermore, the corresponding mono-BF₂ anchored BOAHYs **2a-f** have been also efficiently synthesized in 62-77% yields requiring only 3.9 equiv of BF₃·OEt₂ in refluxing 1,2-dichloroethane. BOAHY was able to generate BOAPY via further BF₂ complexation. For example, **1a** was obtained from **2a** in 70% yield (Scheme 1). All these BOAPYs and BOAHYs are stable in toluene and solid-state under air toward 365 nm UV and daylight. They were also stable during the silica column chromatography purification and further recrystallization from dichloromethane and hexane. All of them were well characterized by various NMR spectroscopy (¹H, ¹³C, ¹¹B, and ¹⁹F NMR, respectively) and exact mass spectroscopy. Similar to BOPPY, these BOAPYs showed two kinds of boron signals in ¹¹B NMR and gave two sets of signals around -136 and -147 ppm in ¹⁹F NMR, which indicated their unsymmetrical structure features. What to be mentioned is that the signals of the boron and fluorine in the six-membered-ring are observed to have a downfield shift than those in the five-membered-ring.

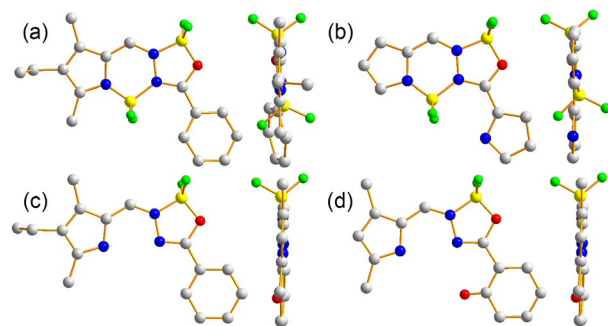


Figure 2. X-Ray crystal structures of **1a** (a), **1d** (b), **2a** (c) and **2f** (d). C, light grey; N, blue; O, red; B, yellow; F, green. All hydrogen atoms were removed for clarity.

X-Ray single crystal structure analysis of BOAPYs **1a**, **1d** and BOAHYs **2a**, **2f** elucidated the structural distinctions for this chromophore (Figures 2 and S1-S5 in the Supporting Information (SI)). All the boron atoms are coordinated to form slightly distorted tetrahedral geometries by N–N (or N–

O) and two fluorine atoms. All the B-O bond length is around 1.48(2) Å (Table S1, SI). Among the three types of B-N bonds, the B-N bond between boron atom and nitrogen atom of pyrrolic ring has the shortest bond length (1.506(3) Å for **1a**, Table S1), while the other two B-N bonds are in the range of 1.55-1.62 Å (Table S1). In BOAPYs **1a** and **1d**, there are three rigid and almost planar rings of the pyrrolic ring, the six-membered BC₂N₃ ring in the center, and a neighboring BCN₂O five-membered ring.

All these BOAPYs **1a-f** and BOAHYs **2a-f** show excellent optical properties with intense broad absorption in common organic solvents studied as summarized in Tables 1 and S3, Figures 3 and S6-S18. For example, **1b** gives intense absorption maxima at 397 nm in toluene (Figures 3a, S6 and S8), with molar extinction coefficients of $3.55 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ (Table S3). Similar absorption is observed for **1e** (Figures 6 and S11). In obvious contrast with **1b** and **1e**, other BOAPYs developed dual absorption. For example, **1c** displays dual absorption bands with maxima at 432 and 453 nm, and molar extinction coefficients of 2.95×10^4 and $3.16 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, respectively.

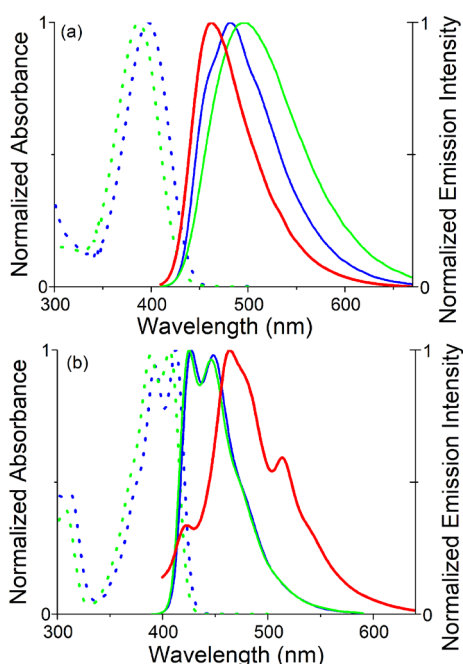


Figure 3. Normalized absorption (dot lines) and emission spectra (solid lines) of BOAPYs **1b** (a) and **1d** (b) in toluene (blue), acetonitrile (green) and solid-state (red).

Most of the BOAPYs manifest dual emission shape with bright sky blue or blue fluorescence. For example, **1b** in toluene gave splitted emission band with maximum at 481 nm and a shoulder peak of 460 nm (Figure 3a), with a quantum yield of 0.77 (Tables 1 and S3). These BOAPY dyes give Stokes shifts of 2453-5773 cm^{-1} (Table S3), which are significantly larger than those of typical BODIPY dyes.⁵ Attachments of electron-donating groups on their pyrrolic positions or the aryl group of arylhydrazide segment gradually redshifted the absorption and emission bands of these BOAPYs (Table 1). For example, in comparison with 2,4-dimethylpyrrole substituted **1b**, the emission band for **1a** with additional ethyl group was redshifted to 510 nm in acetonitrile. **1c** with 4-(dimethylamino)phenyl group showed redshifted emission maxima at 471 and 494 nm in toluene (Figure S6). Compared with BOAPYs **1a-f**, BOAHYs **2a-f** showed very weak fluores-

cence in organic solvents due to the free rotation of the uncoordinated pyrrolic rings (Figure S13-S18). However, **2a-f** present obvious AIE-active features (Figures S27-S29) and have strong solid-state fluorescence because of restricted intramolecular free rotation (Figures S25 and S26, Table S3).

The absorption and emission spectra of these BOAPYs were further studied in various solvents of different polarities. In general, BOAPYs showed blue-shifted absorption bands in solvents from toluene, dichloromethane to acetonitrile (Table S3). However, with increasing the solvent polarity, BOAPYs exhibited a gradually redshifted emission maxima and decreased fluorescence quantum yields (Table S3). The variable emission of our BOAPY species might be attributed to rapid solvent-dependent relaxation pathways in the excited state.

More importantly, these unsymmetrical BOAPYs **1a-f** showed intense emission in solid-state with maxima ranging from 462 to 533 nm (Table 1, Figures 3b and S19-S24) and attractive solid-state fluorescence quantum yields of 0.09-0.64 (Figures S30 and S31). Their fluorescence emission bands in solid-state are tunable via the variation of substituents on the pyrrolic or aryl group. For example, **1a**, **1b** and **1c** each showed strong solid-state fluorescence with maxima at 456, 508 nm ($\phi = 0.32$), 462 nm ($\phi = 0.64$), and 507, 533 nm ($\phi = 0.33$), respectively. For most of these BOAPYs, the obtained solid-state fluorescence emission bands are redshifted, comparing with their emission spectra in organic solvents. For instance, **1e** has fluorescence maxima at 507 and 533 nm with an absolute fluorescence quantum yield of 0.33 in solid state (Tables 1 and S3), whereas **1e** displays maxima fluorescence peaks at 472 and 500 nm with a fluorescence quantum yield of 0.65 in toluene. However, **1b** discloses a different appearance. **1b** in toluene emits maxima at 481 nm with a shoulder peak at 460 nm, but its solid, unexpectedly, emits maxima at 462 nm.

The crystal packing of BOAPYs also indicate their attractive solid-state emission (Figure 4a). For example, both **1a** and **1d** show multiple intermolecular C-H...F hydrogen bonds and head-to-tail packings. Importantly, no corresponding intermolecular π - π stackings are observed for these two BOAPY dyes (Figures S2 and S3). More importantly, they both adopt coplanar inclined arrangements with slip angles of 18.3-50.4° for their transition dipoles (Figures 4b, S2 and S3). These arrangements and the strong fluorescence features in solid-state for BOAPY dyes are in good agreement with Kasha's molecular exciton model, corresponding to the textbook cases of *J*-type ($\theta < 54.7^\circ$).¹¹

Table 1. Selected photophysical data of BOAPYs **1a-f** and BOAPYs **2a-f** in toluene and solid-state (as powders) at rt.^a

dyes	toluene		solid powder
	$\lambda_{\text{abs}}^{\text{max}}/\text{nm}^b$ ($10^{-4}\epsilon^c$)	$\lambda_{\text{em}}^{\text{max}}/\text{nm}^b$ (ϕ^d)	$\lambda_{\text{em}}^{\text{max}}/\text{nm}$ (ϕ^d)

1a	399, 411 (2.29)	494 (0.54)	508 (0.32)
1b	397 (3.55)	481 (0.77)	462 (0.64)
1c	432, 453 (3.16)	471, 494 (0.76)	473, 531 (0.09)
1d	393, 412 (3.09)	427, 449 (0.74)	464, 514 (0.22)
1e	418 (3.98)	500 (0.65)	507, 533 (0.33)
1f	405 (1.86), 421	451, 470 (0.78)	485, 521 (0.20)
2a	395 (2.24), 415	435, 462 (0.02)	473, 502 (0.16)
2b	388 (1.91), 408	433, 457 (0.03)	493, 537 (0.08)
2c	412 (3.81), 434	460 (0.03)	539, 563 (0.12)
2d	383 (2.29), 404	412, 435 (0.02)	472, 543 (0.04)
2e	400 (2.95), 421	437, 460 (0.03)	485, 518 (0.48)
2f	394 (3.55), 412	435, 508 (0.02)	553 (0.09)

^a For full data, see Table S3. ^b Data correspond to the strongest absorption (or emission) peaks. ^c Extinction coefficient (ϵ) in $M^{-1}cm^{-1}$. ^d Absolute fluorescence quantum yields

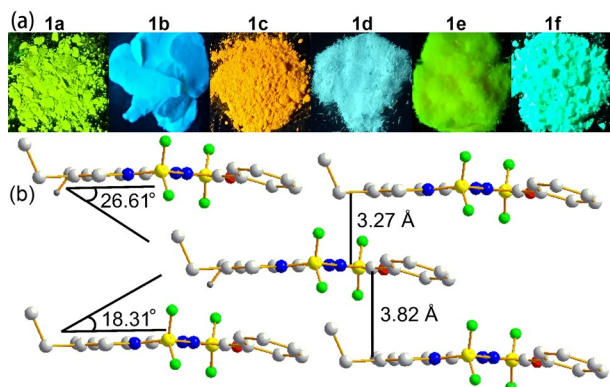


Figure 4. (a) Photos of solid fluorescence of BOAPYs **1a-f** under a handheld UV (365 nm) lamp. (b) Crystal packing patterns of BOAPY **1a**.

The cyclic voltammetry of BOAPYs **1a-f** show irreversible reductions, respectively, with E_{pc} of -1.90, -1.77, -2.09, -1.72, -1.77 and -1.83 V (Figure 5 and Table S4). The reversible oxidations for **1a**, **1c** and **1e** were found and their half-wave potentials are 0.92, 0.80 and 0.93 V, respectively. Compared to **1b**, the introduction of electron donating dimethylamino substituent on the *para*-position of the phenyl group shifted both oxidation and reduction of **1c** to low potentials. In addition, **1f** with B-O-Ph structure showed negative shift of its reduction potential.

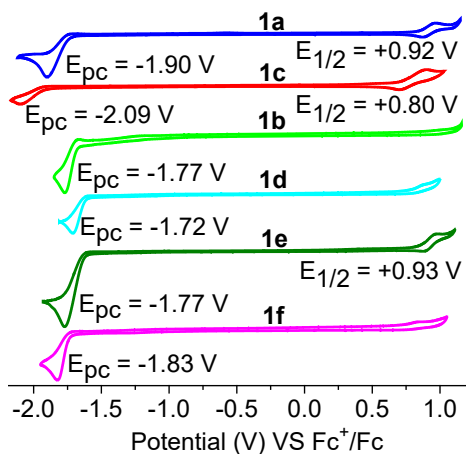


Figure 5. Cyclic voltammograms of BOAPYs **1a-f** in anhydrous dichloromethane.

To better understand the electronic properties of these BOAPYs **1a-f**, their ground state geometries were optimized at B3LYP/6-31+G(d,p) level of the density functional theory

(DFT) (Figure 6). Their HOMOs and LUMOs are well distributed over the chromophore. Their energy band gaps were estimated to be 3.57, 3.61, 3.21, 3.63, 3.40 and 3.61 eV for **1a-f**, respectively. These data have similar trend with the above absorption data and electrochemical results. TD-DFT analysis refers the main absorptions peak to $S_0 \rightarrow S_1$ transitions, which have good oscillator strength (f) values ranging from 0.43 to 0.89 (Table S5). Similar to BOPHY dyes, the dual absorption bands for BOAPYs might be ascribed to vibronic progressions of the same S_1 excited state.^{6a,7c}

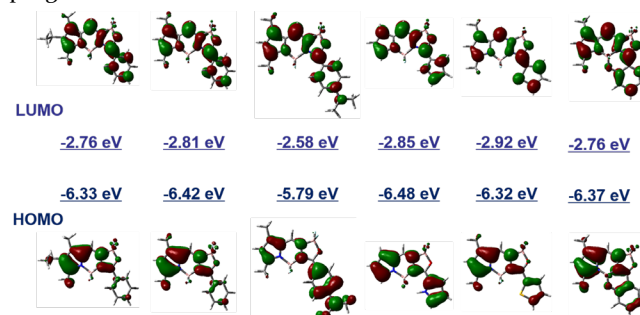


Figure 6. The frontier molecular orbitals and the relative energies of BOAPYs **1a-f**.

In conclusion, a series of novel BODIPY-like and unsymmetrical BOAPY dyes from commercially available 2-formylpyrroles and acylhydrazides *via* a simple one-pot procedure was reported. The reaction is diversity-oriented and efficient. Our BOAPYs developed here show intriguing photophysical properties, such as large Stokes shifts, intense fluorescence both in solution and solid-state. The excellent diversity of BOAPYs and their tuneable photophysical properties were rendered due to the easily accessible starting pyrrole derivatives and aryl hydrazide building blocks. Further synthesis and applications for these BODIPY-like unsymmetrical BOAPY dyes will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

Experimental details, NMR, additional photophysical data and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes

CCDC 1987211-1987213 and 1543022 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing da_ta_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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