JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b00858 • Publication Date (Web): 30 Jun 2016

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Regioselective and Stepwise Syntheses of Functionalized BODIPY Dyes through Palladium-Catalyzed Cross-coupling Reactions and Direct C-H Arylations

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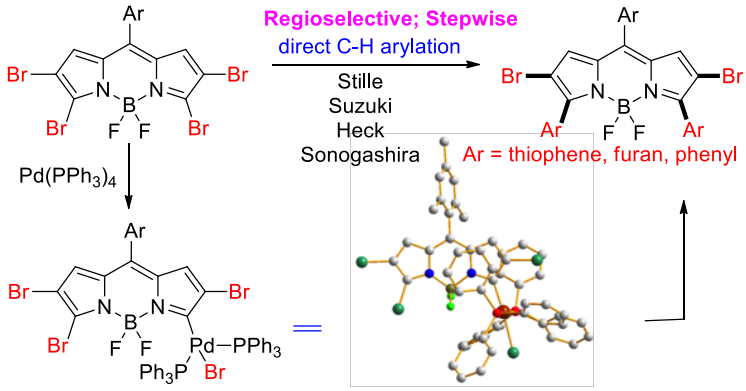
Abstract Graphic



Abstract: Regioselective and stepwise syntheses of a series of functionalized BODIPY dyes through palladium-catalyzed cross-coupling reactions and direct C-H arylations have been developed. In particular, this method allows the straightforward synthesis of 2,6-dibromo-3,5-diarylBODIPYs and 2-bromo-3-arylBODIPYs from polybrominated BODIPYs. The X-ray structure of intermediates **5a**-**c** indicated that the palladium was first inserted into the C-Br bonds at 3,5-positions of brominated BODIPYs. The resulting 2,6-dibromo-substituted BODIPYs are potential long wavelength photosensitizers which are not easily accessible using previous methods.

Introduction

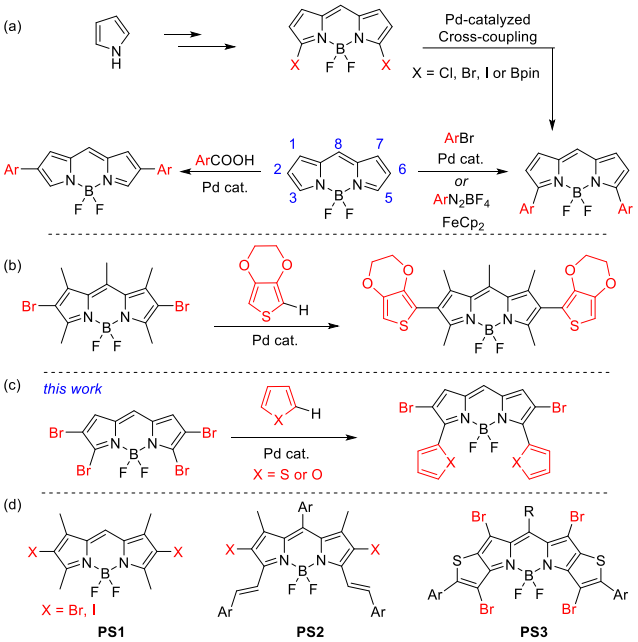
BODIPYs, or 4,4'-difluoro-4-bora-3a,4a-diaza-*s*-indacenes, are valuable fluorophores due to their many excellent properties, such as high stability, strong absorption/emission in the visible spectral range.[1] In recent years, there has been increasing interest in the use of BODIPYs as fluorescent labels and probes,[2] organic electronics/photovoltaics,[3] and photodynamic therapy (PDT) agents.[4] To meet the diverse applications, much investigation is ongoing on the synthesis and functionalization of BODIPYs for fine tuning their photophysical properties such as high fluorescence quantum yields, red/NIR emission, and singlet oxygen quantum yields.[1-5]

Comparing to the total synthesis from functionalized pyrroles, the development of efficient synthetic methods for the facile functionalization of the BODIPY chromophore has thus attracted intense research interests lately[6,7] and modification at α- or β-positions of the BODIPY core is an effective strategy to tune photophysical properties of resulting dyes. Among those, the direct introduction of a variety of functionalities on the BODIPY core through nucleophilic substitutions and metal-catalyzed cross-coupling reactions of the easily accessible core-halogenated BODIPYs[8-11] is particularly attractive. For example, 3- and/or 5-halo-BODIPYs (Scheme 1a) have been used to prepare a series of 3- and/or 5-aryl-, alkenyl- and alkynyl-functionalized BODIPYs through S_NAr[9b,9f,9h] and palladium-catalyzed cross-coupling reactions (e.g. Stille, Negishi, Heck, Suzuki and Sonogashira).[9-11]

Another more efficient method for late-stage modification of BODIPY is the direct C-H activation of which currently only a few examples were reported.[12,13] Direct alkenylation by Burgess et. al[12a] and direct regioselective palladium-catalyzed C-H arylation[12c,f] and recent radical C-H arylation/alkylation[13] at 3- and 3,5-positions of BODIPY by Boens, Dehaen and us were reported

(Scheme 1a), while Wu and You[12g] reported regioselective palladium-catalyzd decarboxylative direct C-H arylation at 2,6-positions of BODIPY (Scheme 1a).

Scheme 1. Summary of synthetic pathways toward arylated BODIPYs



Alternatively, very recently, while we were working in this project, direct C-H arylation on 3,4-ethlenedioxythiophene (EDOT) derivatives with 1,3,5,7,8-pentamethyl-2,6-dibromoBODIPY was recently reported by Yu and coworkers[14a] (Scheme 1b). Previously, our group developed regioselective stepwise brominations of BODIPYs[8a] from which polybrominated BODIPYs, like **2a** in Scheme 2, are easily available. Since the 3,5-positions of BODIPY contain partial positive charge and are subject to nucleophilic addition,[14b] we rationalized that C-Br bonds at the 3,5-position would be highly reactive toward metal catalyzed reactions.

Herein, we report regioselective and stepwise syntheses of a series of functional BODIPY dyes from polybrominated BODIPYs through palladium-catalyzed cross-coupling reactions and direct C-H arylations on thiophene and furans. Previous results by Ortiz and coworkers[8d] on iodinated

BODIPYs showed that the introduction of iodine atoms at 2 and/or 6 positions were critical for the efficiency of $^1O_2$ generation, while iodine atoms at 3 and/or 5 positions did not produce a significant impact.[8d,4b] Our resulting regioselective cross-coupling products (BODIPYs with bromo atoms at 2,6-positions and aryl groups at 3,5-positions) also showed efficient singlet oxygen generation properties due to the enhanced intersystem crossing (ISC) as a result of heavy atom effect. These novel dyes join to the previously reported bromo- and iodo-containing BODIPYs[4,8,15,16] (**PS1-3** in Scheme 1d), orthogonal BODIPY dimers[17] and BODIPY-C_{60} complexes (via intramolecular spin converter)[18] as a new type of potential photosensitizers.

Results and Discussions

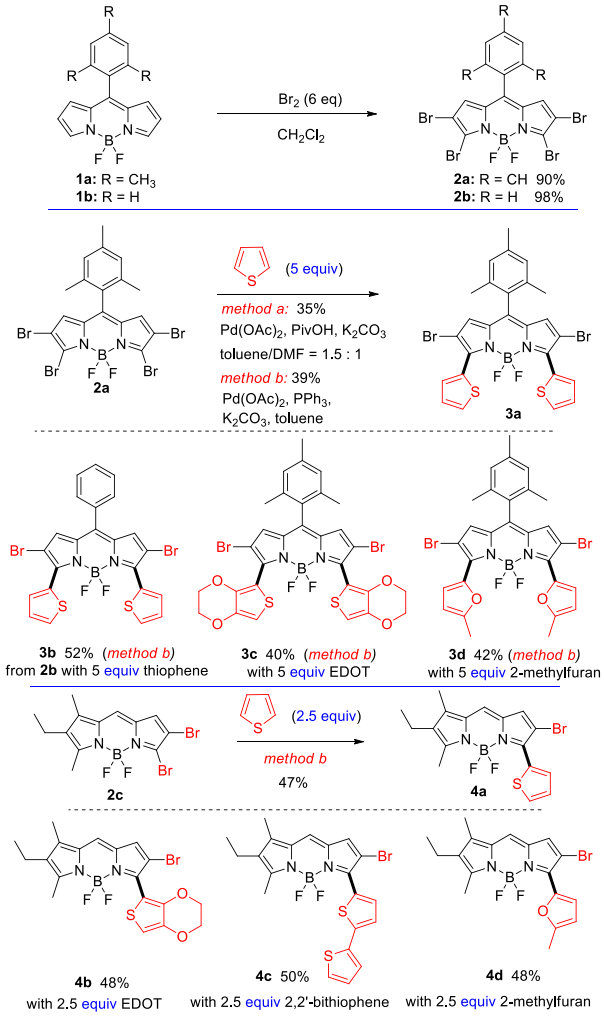
Synthesis:

2,3,5,6-Tetrabromo-substituted BODIPYs **2a**[14b] and **2b**[8a] (Scheme 2) were regioselectively synthesized in over 90% yields using bromine in dichloromethane from the corresponding BODIPYs **1a** and **1b** in one step. We first tested the reaction between **2a/2b** and 5 equiv thiophene in toluene using $Pd(OAc)_2$ as catalyst, PPh_3 as ligand, and K_2CO_3 as base (method b in Scheme 2). The reactions turned bluish quickly and gave mainly one bluish spot on TLC. To our delight, in contrast to many direct C-H arylations which use expensive ligands, such as $PCy_3 \cdot HBF_4$[12f] or P(*o*-Anisyl)$_3$,[14a] this economical reaction conditions were efficient for the arylations of BODIPYs and 3,5-dithiophene-2,6-dibromoBODIPYs **3a** or **3b** in 39% and 52% yields, respectively. The regioselectivity of this reaction was confirmed by the X-ray structure of **3b** (Figure 1) and by the pronounced red-shifted absorption of the resulting thienyl BODIPYs, similar to those reported by Ziessel[19] through total synthesis. Although excess thiophene (5 equiv) was used, no product with thienyl group at 2,6-positions was isolated. Increasing the reaction temperature to 110 ºC, trithienyl

substituted BODIPYs were detected in small amount and no isolation was attempted. Using pivalic acid instead of PPh_3 (method a in Scheme 2) gave similar result.

To demonstrate the generality of this C-H arylation protocol, BODIPY **2a** was further reacted with 3,4-ethylenedioxythiophene (EDOT) and 2-methylfuran, giving **3c** and **3d** in 40% and 42% yields, respectively (Scheme 2). 2,3-Dibromo-substituted BODIPY **2c** was also reacted with 2.5 equiv thiophene, EDOT, 2,2'-bithiophene and 2-methylfuran, respectively, giving α-arylated BODIPYs **4a**, **4b**, **4c** and **4d** in 47-50% yields (Scheme 2).

Scheme 2. Regioselective direct C-H arylations on thiophenes and furan with BODIPYs 2.



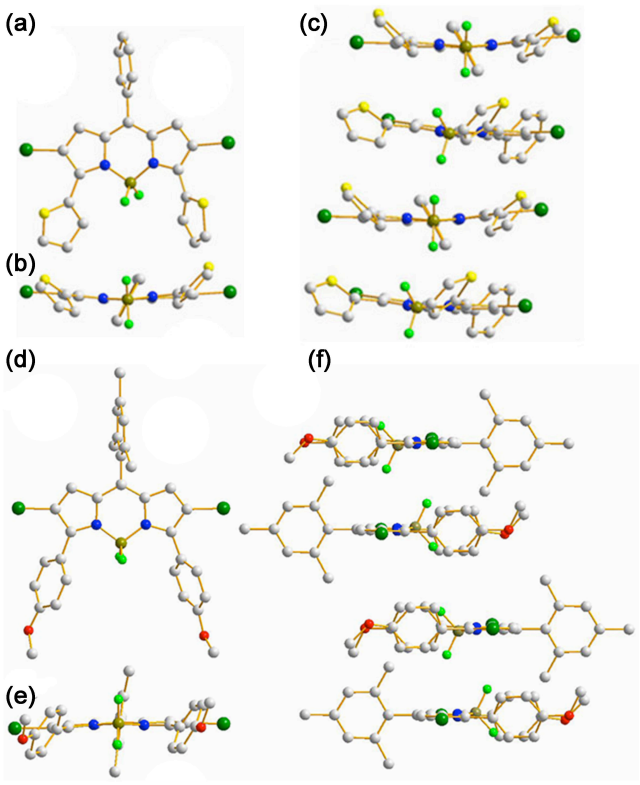
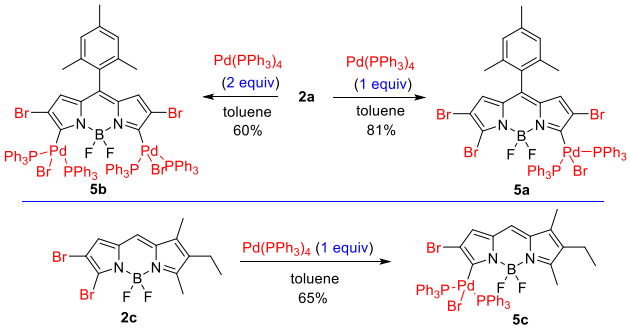


Figure 1. X-Ray structure of **3b** (top) and **3e** (bottom): top (a, d), front (b, e) views and crystal packing (c, f). C, light gray; N, blue; B, dark yellow; F, bright green; Br, green; O, red; S, yellow. Hydrogen atoms were omitted for clarity

The crystals of 2,6-dibromo-substituted BODIPY **3b** suitable for X-ray analysis were obtained by slow evaporation of its dichloromethane solution and confirmed the regioselectivity of the above reaction. The average deviation of the twelve atoms from the mean plane of BODIPY core is only 0.0051 Å and the maximum deviation is 0.1759 Å, indicating that **3b** has an almost planar boron complexed dipyrrin core. The dihedral angle between the idealized *meso*-phenyl ring and the BODIPY core in **3b** is around 62º. The two thienyl rings at the 3,5-positions in **3b** both tilted to the same direction and the dihedral angles between the idealized thienyl rings and the BODIPY core in **3b** are 45º and 46º, respectively. The crystal packing diagram of **3b** in Figure 1c showed that two neighboring molecules form π-stacked dimer structures in a head-to-head arrangement with an intermolecular distance of 4.08 Å between the π-conjugated planes of the neighboring molecules,

where the molecules are longitudinally arranged in a slightly offset fashion to avoid steric repulsion between the *meso*-phenyl rings.

Scheme 3. Regioselective synthesis complexes 5a-c from the reaction of BODIPYs 2 and $Pd(PPh_3)_4$.



Since the initial step of the palladium-catalyzed C-H arylation is the palladium insertion to the C-Br bond, we isolated the intermediates **5a**-**c** (Scheme 3) which may further prove the origin of the high regioselectivity at the 3,5-position. Mixing 2,3,5,6-tetrabromo-substituted BODIPY **2a** and 2,3 -dibromo-substituted BODIPY **2c** with 2 equiv or 1 equiv $Pd(PPh_3)_4$ at 70 ºC regioselectively gave the palladium complexes **5a**-**c** (Scheme 3) in 81%, 60% and 65% yields after silica gel column purification, respectively. No complexes with palladium substituted at 2,6-positions of BODIPY were detected or isolated. Interestingly, the palladium complexes **5a**-**c** are highly stable during the purification, characterization in various solvents with no sign of decomposition.

X-Ray structures of **5a**, **5b** and **5c** are shown in Figure 2. The average and maximum deviations of the twelve atoms from the mean plane of BODIPY core are 0.0059 Å and 0.2857 Å for BODIPY **5a**, 0.0006 Å and 0.0335 Å for BODIPY **5b**, 0.0010 Å and 0.0441 Å for BODIPY **5c**. These results indicate no major deformations of the BODIPY cores due to the presence of $Pd(PPh_3)_2Br$ at 3/5-positons. The Pd-C, Pd-Br and Pd-P distances were found to be respectively, 1.9895(37), 2.4911(7), and 2.3267(12)/2.3353(12) Å for **5a**, and 1.9704(45), 2.4827(8), and

2.3311(17)/2.3405(17) Å for **5c**, and 1.9913(32)/1.9851(34), 2.4949(6)/2.4975(7), and 2.3178(11)-2.3559(12) Å for **5b**.

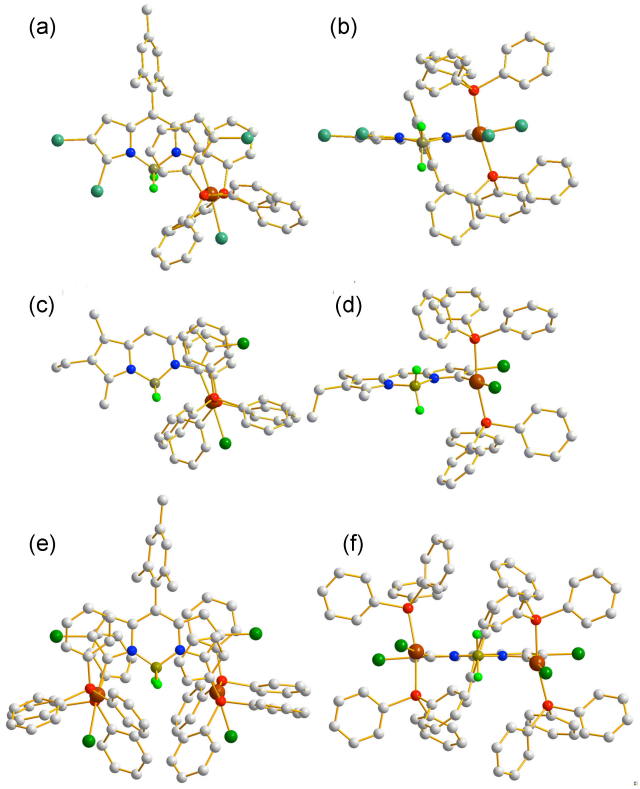
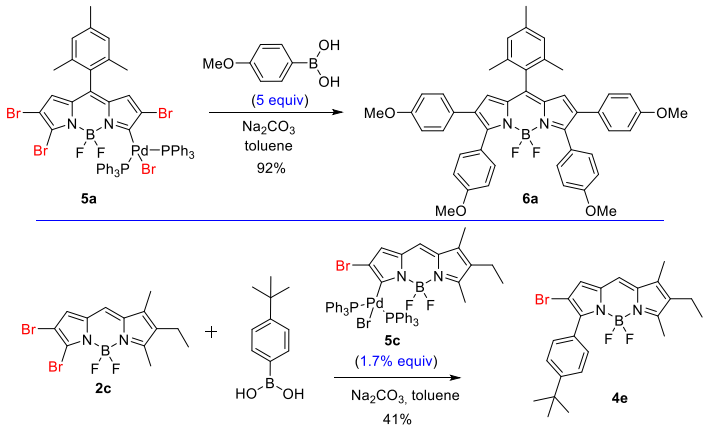


Figure 2. X-Ray structure of **5a**, **5c** and **5b**: top (a, c, e) and front (b, d, f) views; C, light gray; N, blue; B, dark yellow; F, bright green; Br, green; Pd, brown; P, red. Hydrogen atoms were omitted for clarity

Scheme 4. **The Suzuki cross-coupling reactions of complexes 5a and 5c.**

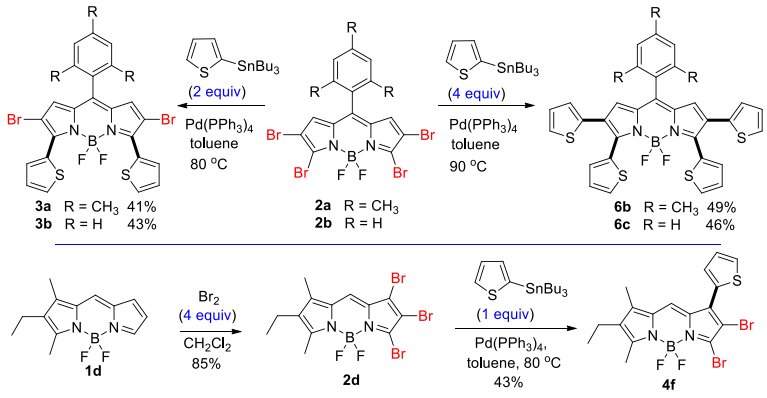


The reactivity of these intermediates **5a** and **5c** was studied. The Suzuki reaction between **5a** and 5 equiv (4-methoxyphenyl)boronic acid gave tetraarylBODIPY **6a** in 92% yield without the

need of additional catalyst (Scheme 4). Notably, **5c** was a good and air-stable catalyst for palladium-catalyzed coupling reactions. For example, **2c** reacted with (4-*tert*-butylphenyl)boronic acid in the presence of only 1.7% mmol **5c**, regioselectively giving BODIPY **4e** in 41% yield (Scheme 4).

Along with this finding, we further extended the palladium catalyzed regioselective reaction to various palladium-catalyzed cross-coupling reactions. Although various palladium-catalyzed coupling reactions have been reported on halogenated BODIPYs, only very recently a few regioselective coupling reactions on polybrominated BODIPYs were reported.[10d,10g,11f] We first tested the Stille coupling reaction on these 2,3,5,6-tetrabromo-substituted BODIPYs since the Stille coupling reaction is highly reactive and does not need base. BODIPYs **2a** or **2b** in toluene with 2 equiv 2-(tributylstannyl)thiophene in the presence of $Pd(PPh_3)_4$ were stirred at 80 °C. The reactions turned bluish quickly and gave mainly 3,5-dithiophene-2,6-dibromoBODIPYs **3a** or **3b** in over 40% yields. Increasing the amount of 2-(tributylstannyl)thiophene to 4 equiv, this Stille coupling reaction at 90 °C gave exclusively 2,3,5,6-tetrathiopheneBODIPYs **6b** or **6c** in around 50% yields (Scheme 5).

Scheme 5. Regioselective Stille coupling reactions of BODIPYs 2.



To further investigate this regioselectivity between the 3/5 and 1/7 positions, 1,2,3-tribromo-substituted BODIPY **2d** was synthesized from bromination of BODIPY **1d** in 85% yield using 4 equiv Br_2, and was applied to the above Stille coupling reaction using with 1 equiv 2-(tributylstannyl)thiophene at 80 ºC (Scheme 5). BODIPY **4f** was observed as a major product and was isolated from this reaction in 43% yield. ^{1}H-NMR, ^{13}C-NMR and HRMS all indicate that **4f** only has one thiophene ring as expected. In order to further confirm its structure, crystals suitable for X-ray structure analysis were obtained by slow diffusion of hexane into its dichloromethane solution. Surprisingly, X-ray structure of **4f** (Figure 3) indicated the above Stille coupling reaction regioselectively occurred at 1-position instead of 3-position of BODIPY core. The thiophene ring is tilted by 35º relative to the BODIPY core. The average root-mean-square deviation of the BODIPY core is 0.0067 Å, indicating that **4f** adopts an almost planar conformation.

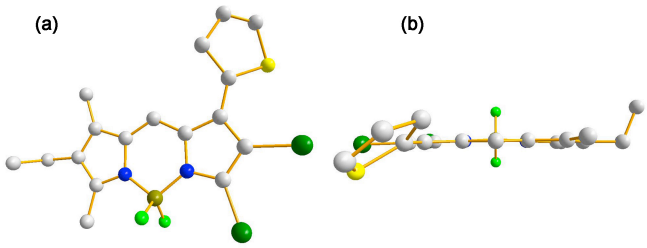
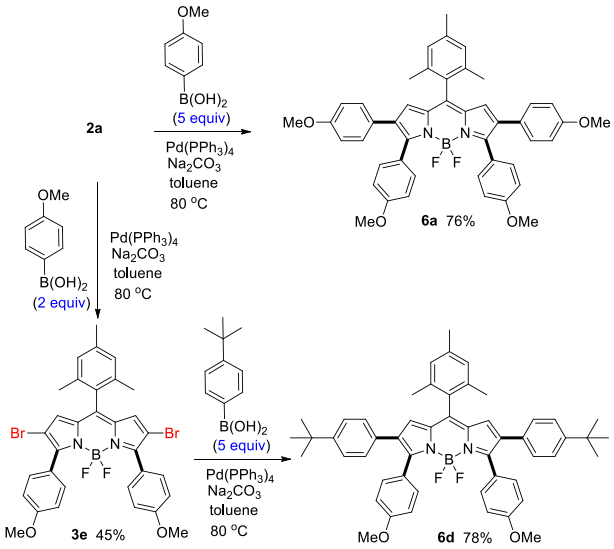


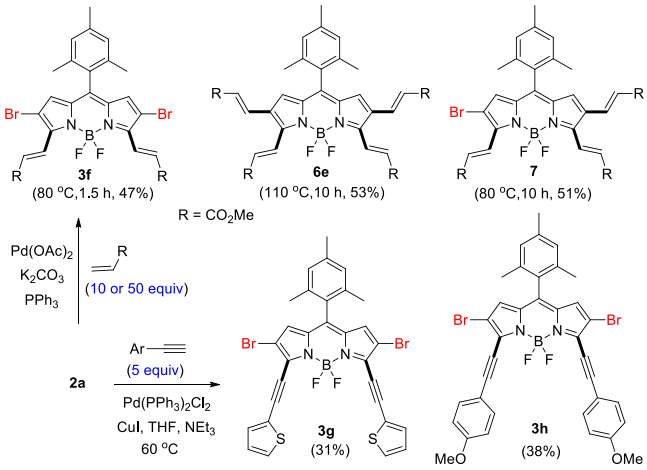
Figure 3. X-Ray structure of **4f**: top (a) and front (b) views. C, light gray; N, blue; B, dark yellow; F, bright green; Br, green, S, yellow. Hydrogen atoms were omitted for clarity

The Suzuki coupling of **2a** with different amount of (4-methoxyphenyl)boronic acid in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 also regioselectively gave 3,5-diarylated BODIPY **3e** (confirmed by the X-ray structure in Figure 1) and 2,3,5,6-tetraarylated BODIPY **6a** in 45% and 76% yields, respectively (Scheme 6). Further Suzuki coupling of 2,6-dibromo-3,5-diarylBODIPY **3e** with 5 equiv (4-tert-butylphenyl)boronic acid under the above Suzuki coupling gave 2,3,5,6-tetraarylBODIPY **6d** having two different sets of substituents at the 3,5- and 2,6-positions, respectively, in 78% yield.

Scheme 6. Regioselective Suzuki cross-coupling reactions of BODIPY 2a.



Scheme 7. Regioselective Heck and Sonogashira cross-coupling of BODIPY 2a.



Similarly, the Heck reaction between **2a** and 10 equiv methyl acrylate in the presence of $Pd(OAc)_2$, PPh_3 and Na_2CO_3 at 80 °C gave mainly 2,6-dibromo-substituted BODIPY **3f** in 47% yield after 1.5 h (Scheme 7). Extending the reaction time to 10 h, the same reaction gave 2,3,5-trialkenyl substituted BODIPY **7** in 51% yield as the major product. Increasing the amount of methyl acrylate to 50 equiv and the reaction temperature to 110 °C, gave exclusively the 2,3,5,6-tetraalkenyl substituted BODIPY **6e** in 51% yield. The palladium-catalyzed regioselective cross-coupling reaction was further extended to the Sonogashira coupling reaction. 2,6-Dibromo-substituted

BODIPYs **3g** and **3h** were thus regioselectively synthesized in 31% and 38% yields under standard condition from 5 equiv 2-ethynylthiophene and 4-ethynylanisole, respectively (Scheme 7).

Similar to BODIPY **3b**, BODIPY **3e** also show an almost planar structure for the BODIPY core since the average and maximum deviations of the twelve atoms from the mean plane of BODIPY core are 0.0014 Å and 0.1142 Å. The dihedral angle between the two idealized pyrrole rings in the dipyrrin is 1.9 ^{o} and B-N bond lengths are both around 1.57 Å. The dihedral angle between the *meso*-mesityl group and the BODIPY core in **3e** is around 83^{o} due to the steric hindrance of the methyl groups on the *meso*-mesityl group, while the dihedral angles between the 3,5-phenyl rings and the BODIPY core are around 60^{o}. The crystal packing diagram of **3e** in Figure 1f showed that two neighboring molecules form π-stacked dimer structures in a head-to-tail arrangement with an intermolecular distance of 4.48 Å between the π-conjugated planes of the neighboring molecules. The π-stacked dimer further packed with another dimer in a head-to-tail arrangement with an intermolecular distance of 5.11 Å.

Spectroscopic properties

These palladium catalyzed reactions provided a set of dyes with a variety of substituents at the 2,3,5,6,8-positions of the BODIPY nucleus. The absorption and fluorescence emission spectra of these dyes cover a broad range of visible spectrum (Figure 4) and their optical properties are summarized in Table 1. The α-arylated BODIPYs **3**, **4, 6** and **7** all have red-shifted absorption and emission spectra in relation to BODIPYs **1** and **2**. Electron-rich 2-methylfuran and large π-conjugated 2-ethynylthiophene and 4-ethynylanisole groups, which gave absorption maxima around 670 nm (**3d**, **3g** and **3f**), introduced larger red shifts than those BODIPYs with thiophene and

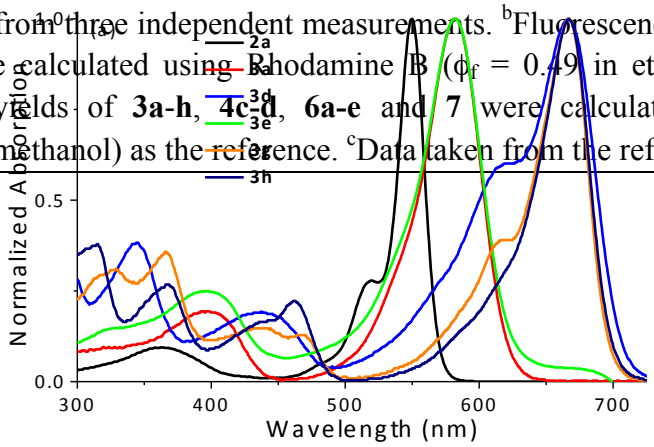
phenyl groups at 3,5-positions (Figure 4). The thienyl BODIPYs **3a-c** and **4a-c** have larger Stokes shift (1304-2257 cm^{-1}) than most of other dyes which have classical small Stokes shift of BODIPYs (Tables 1 and S3).

Table 1. Photophysical properties of BODIPYs **1-7** in dichloromethane at room temperature.

dyes	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	ε ($cm^{-1}M^{-1}$)[a]	Φ[b]	Stokes shift (cm^{-1})
1a[c]	501	520	77600	0.99	729
2a	556	577	92300	0.08±0.006	655
3a	606	658	53500	0.37±0.02	1304
3b	605	662	40300	0.57±0.02	1423
3c	606	649	37000	0.58±0.03	1093
3d	667	689	50100	0.43±0.01	479
3e	582	630	66100	0.34±0.02	1309
3f	612	628	86700	0.64±0.03	416
3g	667	706	72800	0.64±0.03	828
3h	667	697	81900	0.48±0.02	645
4a	523	583	35000	0.51±0.02	1968
4b	529	588	32200	0.60±0.03	1897
4c	560	641	32200	0.60±0.02	2257
4d	580	609	34500	0.58±0.02	821
4e	534	567	43500	0.51±0.01	1090
4f	532	596	29500	0.04±0.004	2018
5a	553	584	49100	0.45±0.01	960
5b	593	608	79700	0.30±0.01	416
5c	559	575	83500	0.44±0.02	498
6a	616	672	49000	0.42±0.02	1353

6b	632	662	48000	0.10±0.01	717
6c	633	662	43400	0.19±0.01	692
6d	604	666	63700	0.62±0.02	1541
6e	634	669	80700	0.79±0.04	825
7	622	655	83500	0.26±0.02	810

[a]Data corresponding to the strongest absorption maximum, the unit for ε is $M^{-1}cm^{-1}$. The standard errors are less than 10% from three independent measurements. [b]Fluorescence quantum yields of **2a**, **4a-b**，**4e** and **5a-c** were calculated using Rhodamine B (ϕ_f = 0.49 in ethanol) as the reference. Fluorescence quantum yields of **3a-h**, **4c-d**, **6a-e** and **7** were calculated using Cresyl violet perchlorate (ϕ_f = 0.54 in methanol) as the reference. [c]Data taken from the reference[14b].



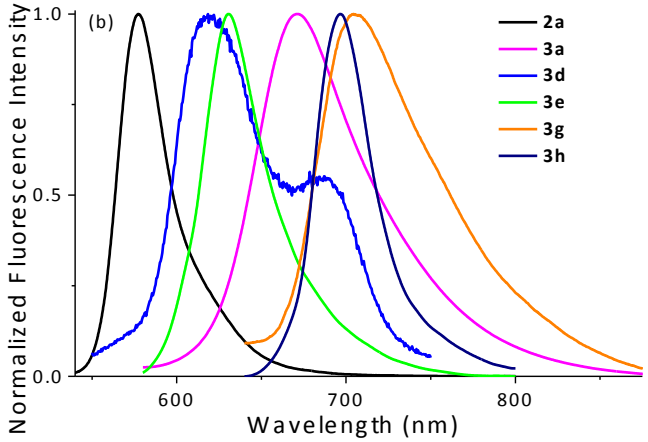


Figure 4. Normalized absorption (left) and emission (right) spectra of dyes **2a, 3a, 3d, 3e, 3f, 3g** and **3h** in dichloromethane.

The solvatochromic effects on most of these new dyes were investigated in hexane, toluene, dichloromethane, tetrahydrofuran, acetonitrile and methanol (Figures S1-S21, Supporting information) and were summarized in Table S3 (Supporting information). The influence of the solvent on λ_{abs}(max) and λ_{em}(max) is minimal. BODIPYs **3a**-**h**, **4a-e** and **6a-e** showed upto 20 nm shifts of both their λ_{abs}(max) and λ_{em}(max) in these different solvents which were often red-shifted with increasing solvent polarizability, similar to previously reported 3,5-diaryl substituted BODIPYs.[12g] For example, λ_{abs}(max) of **3a** moves only 18 nm among these different solvents tested (from 596 nm in acetonitrile to 618 nm in toluene), at the same time as a 14 nm change of λ_{em}(max) is observed (from 652 nm in acetonitrile to 666 nm in toluene).

Although these α-arylated BODIPYs dyes **3**, **4** and **6** have lower fluorescence quantum yields that those of corresponding nonbrominated BODIPYs,[12a] they still showed surprisingly good fluorescence quantum yields in these five solvents (Tables 1 and S3). Only slight variations of fluorescence quantum yields were observed for most of these dyes, except for BODIPY **3c** containing EDOT group and 2,3,5,6-tetrathiopheneBODIPYs **6b** or **6c**. The later three dyes showed a gradual decrease of the fluorescence quantum yields with the increase of the polarity of the solvents. For example, the fluorescence quantum yields for **6b** were 0.42 in hexane, which was gradually reduced to 0.25 (in toluene), 0.10 (in dichloromethane), 0.09 (in tetrahydrofuran) and 0.03 (in acetonitrile).

Interestingly, the palladium complexes **5a**-**c** all showed good fluorescence quantum yields ranging from 0.30 to 0.60 in different solvents as well as good solid state fluorescence due to the presence of bulky substituents (Figure S26 in the Supporting information).

Since BODIPY dyes possess a set of ideal optical properties, including high molar absorption coefficients, low dark toxicities, efficient cellular uptake and excellent photostability that are characteristics of photosensitizers,[4] several halogenated BODIPYs have been reported as photosensitizers.[15,16] However, currently only limited types of them show strong near infrared (NIR) absorption. Representative examples are **PS2** (Figure 1) one by Akkaya and others[15b,c] and **PS3** (Figure 1) by You[15d] and Shen[15e]. With a series of 2,6-dibromo-substituted BODIPYs in hand, the singlet oxygen generation properties of representative 2,6-dibromo-substituted BODIPYs **3d**, **3f** and **3g** with long wavelength absorption maxima above 600 nm were selected and studied. A comparative study of the relative singlet oxygen generating efficiency of these dyes (1×10^{-5} M) was performed in air-saturated dichloromethane under broad band light (> 590 nm, at 2 mw/cm^2) irradiation condition using 1,3-diphenylisobenzofuran (DPBF, 8×10^{-5} M) as a trap molecule. A well-known photosensitizer methylene blue (1×10^{-5} M) was used as reference, which has a singlet oxygen quantum yield of 0.57 in air-saturated dichloromethane.[20] The decrease of the absorbance band of DPBF at 415 nm was monitored (Figure 5). The calculated singlet oxygen quantum yields in dichloromethane are 0.14, 0.35 and 0.19 for **3d**, **3f** and **3g**, respectively, using methylene blue as the reference. Nevertheless, the singlet oxygen quantum yields of **3d**, **3g** and **3h** in dichloromethane are lower than those known BODIPY based photosensitizers **PS1-3** (Figure 1).[15]

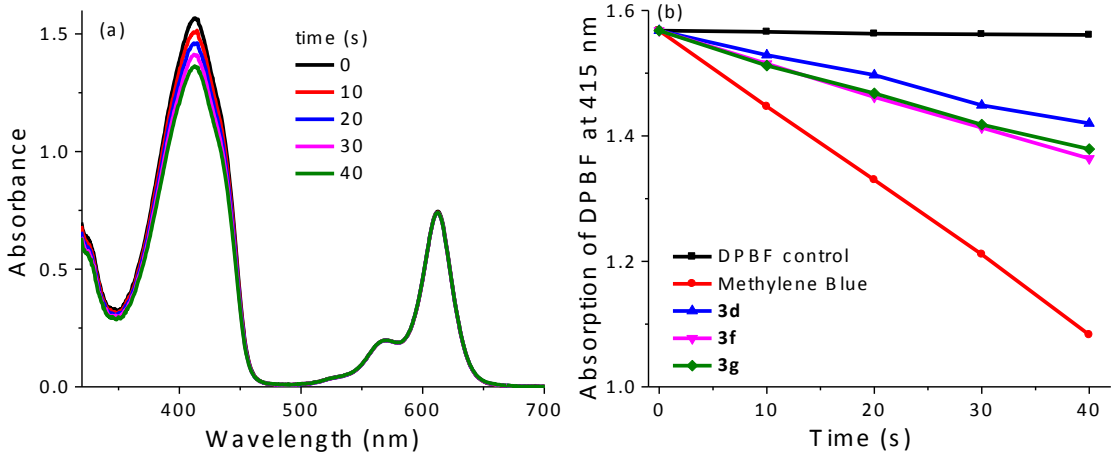


Figure 5. (a) Absorption spectra of DPBF (8×10^{-5} M) upon irradiation in the presence of BODIPY **3f** (1×10^{-5} M) in dichloromethane. (b) Comparative DPBF degradation profiles (absorbance changes at 415 nm) in dichloromethane by BODIPYs **3d**, **3f** and **3g** (1×10^{-5} M). Methylene Blue (1×10^{-5} M) was used as reference. Filtered light > 590 nm was used at 2 mw/cm^2.

Conclusion

In conclusion, a versatile, general method for regioselective functionalization of brominated BODIPYs using palladium-catalyzed direct C-H arylations on furans and thiophenes as well as cross-coupling reactions was developed. The resulting dyes showed strong bathochromically shifted absorption and emission compared to the starting BODIPYs. With this fast and efficient reaction, new fluorophores with interesting photophysical properties can be synthesized, avoiding the tedious total synthesis of pyrrole precursors and unstable intermediates.

Experimental Section

General. Reagents and solvents were used as received from commercial suppliers unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless otherwise stated, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (HSGF 254) for thin-layer chromatography (TLC). Flash column chromatography was performed using silica gel (200−400 mesh). ^{1}H and ^{13}C NMR were recorded on a 300 MHz or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ or DMSO-d_6 (7.26 ppm for ^{1}H, 77 ppm and 40 ppm for ^{13}C) or to internal TMS. High-resolution mass spectra (HRMS) were obtained using APCI (or ESI)-TOF in positive mode.

Photophysical Measurements. UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (190-870 nm scan range) at room temperature (10 mm quartz cuvette). Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various organic solvents with with Rhodamine B (Φ= 0.49 in ethanol)[21a] and Cresyl violet perchlorate (Φ= 0.54 in methanol)[21b]. Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions (0.01<A<0.05) were used to minimize the reabsorption effects. Quantum yields were determined using the equation (1)[22]:

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1-10^{-A_r(\lambda_{ex})}}{1-10^{-A_x(\lambda_{ex})}} \times \frac{n_x^2}{n_r^2} \qquad (1)$$

Where the subscripts *x* and *r* refer respectively to our sample *x* and reference (standard) fluorophore *r* with known quantum yield Φ_r in a specific solvent, *F* stands for the spectrally corrected, integrated fluorescence spectra, $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength λ_{ex}, and *n* represents the refractive index of the solvent (in principle at the average emission wavelength).

Singlet oxygen quantum yield (Φ) determinations were carried out using the chemical trapping method[20]. Typically, a 3 mL portion of the respective photosensitizer solutions (1×10^{-5} M) that contained 8×10^{-5} M diphenylisobenzofuran (DPBF) was irradiated at > 590 nm (2.0 mW/cm^3) in air saturated dichloromethane. Φ_{Δ} value was obtained by the relative method using methylene blue as the reference equation (2):

$$\Phi_{\Delta} = \Phi_{\Delta}^{ref} \frac{K}{K^{ref}} \frac{\int_{590}^{750} A^{ref}}{\int_{590}^{750} A} \qquad (2)$$

Φ_{Δ}^{ref} is the singlet oxygen quantum yield for the standard (methylene blue = 0.57)[20a,20c], K and K^{ref} are the DPBF photo-bleaching rate constants in the presence of the respective samples and standard, respectively; $\int_{590}^{750} A$ and $\int_{590}^{750} A^{ref}$ are the integration of light absorption at the irradiation wavelength from 590 nm to 750 nm by the samples and standard, respectively.

Crystallography. Crystals of **3b**, **3e**, **4f**, **5a**, **5b** and **5c** suitable for X-ray analysis were obtained by slow diffusion of hexane into their dichloromethane solutions or slow evaporation of their dichloromethane solutions. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Crystal diffraction suitable for X-ray analysis was performed on a CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K, with φ and ω scan techniques. An empirical absorption correction was applied using the SADABS program.[23] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package.[24] The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual

electron densities were of no chemical significance. CCDC-1431320 (**3b**), CCDC-1431321 (**3e**), CCDC-1485940 (4f), CCDC-1431322 (**5a**), CCDC-1443083 (**5b**) and CCDC-1431323 (**5c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis. BODIPYs **1a** and **1b**[25], **2a**,[8a] **2b**,[14b] and **2d**[8a] were synthesized according to literatures.

Synthesis of BODIPY **2c:** To compound 4,5-dibromo-1H-pyrrole-2-carbaldehyde (1 mmol, 253 mg) in 50 mL of CH_2Cl_2 was added 3-ethyl-2,4-dimethyl-1H-pyrrole (1.2 mmol) in 1 mL of CH_2Cl_2 and $POCl_3$ (50 μL, 0.5 mmol), respectively, at ice-cold condition under argon. The reaction mixture was stirred at ice-cold condition for 3 h, and Et_3N (1.5 mL) was added into the reaction mixture. The mixture was further stirred for 10 mins, then $BF_3{\cdot}OEt_2$ (1.8 mL) was added through a syringe. The reaction mixture was left stirring for 10 h, poured into 50 mL of water, and extracted with 30 mL of CH_2Cl_2. Organic layers were combined, and solvent was removed under vacuum. The crude product was purified by chromatography (silica gel, petroleum ether / dichloromethane = 3/1, v/v) to give the desired compound **2c** as a brown powder in 52% yield (211 mg). mp 140-141 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.73 (s, 1H), 2.57 (s, 3H), 2.40 (q, J = 7.5 Hz, 2H), 2.15 (s, 3H), 1.08 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 142.1, 137.0, 136.4, 132.3, 124.6, 123.1, 121.0, 106.3, 17.3, 14.0, 13.6, 9.5. HRMS (APCI) calcd. for $C_{13}H_{13}BBr_2FN_2$ $[M\text{-}F]^+$ 386.9502, found 386.9505.

Synthesis of BODIPY **2d:** To 1,3-dimethyl-2-ethylBODIPY **1d** (49 mg, 0.2 mmol) in 16 mL of dry CH_2Cl_2 was added liquid bromine (45 μL, 0.8 mmol) in CH_2Cl_2 (4 mL). The mixture was left stirring for 30 min at room temperature, then poured into an aqueous solution of sodium thiosulfate, and extracted by CH_2Cl_2. Organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated to dryness under vacuum. The crude product was purified by chromatography (silica gel, dichloromethane as eluent) to give the desired **2d** as brown solids in 85% yield (82 mg). mp

185-189 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 1H), 2.58 (s, 3H), 2.42 (q, *J* = 7.0 Hz, 2H), 2.21(s, 3H), 1.10 (t, 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 142.5, 137.5, 137.0, 131.1, 122.2, 119.0, 114,1, 108.9, 17.3, 13.9, 13.8, 9.6. HRMS (APCI) calcd. for $C_{13}H_{14}Br_3N_2$ $[M-BF_2+2H]^+$ 436.8687, found 436.8719.

Direct C-H arylation on thiophenes and furan

Syntheses of BODIPY **3a:**

Method a: To a dry round-bottom flask loaded with compound **2a** (0.1 mmol, 62 mg), trimethylacetic acid (0.12 mmol, 12 mg), K_2CO_3 (0.25 mmol, 35 mg), $Pd(OAc)_2$ (0.01 mmol, 3 mg) and thiophene (1 mmol, 82 mg) in 3 mL of toluene were added through a syringe into the mixture. Freeze-pump-thaw cycle was carried out three times. After that, the mixture was warmed to 80 ^{o}C under argon and stirred for 10 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Then the solvent was removed under vacuum. The crude product was purified by chromatography (silica gel, petroleum ether/dichloromethane = 4/1, v/v) to give the desired compound **3a** as brown solid in 35% yield (23 mg). mp 213-215 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 3.4 Hz, 2H), 7.60 (d, *J* = 5.0 Hz, 2H), 7.23 – 7.14 (m, 2H), 6.99 (s, 2H), 6.75 (s, 2H), 2.38 (s, 3H), 2.19 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 149.1, 142.3, 139.3, 136.7, 135.0, 133.3, 130.6, 130.4, 129.9, 129.1, 128.4, 127.4, 110.1, 21.2, 20.2. HRMS (APCI) calcd. for $C_{26}H_{20}BF_2N_2S_2Br_2$ $[M+H]^+$ 632.9475, found 632.9464.

Method b: To a dry round-bottom flask loaded with compound **2a** (0.1 mmol, 62 mg), K_2CO_3 (0.25 mmol, 35 mg), $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3 (0.04 mmol, 10 mg) and thiophene (1 mmol, 84 mg) in 3 mL of toluene were added through a syringe into the mixture. Freeze-pump-thaw cycle was carried out three times. After that, the mixture was warmed to 80 ^{o}C under argon and stirred for 10 h. After cooling to room temperature, the reaction mixture was

extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Then the solvent was removed under vacuum. The crude product was purified by chromatography (silica gel, petroleum ether/dichloromethane = 4/1, v/v) to give the desired compound **3a** as brown solid in 39% yield (26 mg).

BODIPY **3b** was obtained as brown solid in 51% yield (31 mg) using *method b* from compound **2b** (0.1 mmol, 58 mg), K_2CO_3 (0.25 mmol, 35 mg), $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3 (0.04 mmol, 10 mg) and thiophene (0.5 mmol, 42 mg) in 3 mL of toluene. mp 236-238 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 3.6 Hz, 2H), 7.64 – 7.52 (m, 7H), 7.17– 7.20 (m, 2H), 6.99 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 142.3, 134.7, 133.4, 133.3, 133.3, 132.1, 130.8, 130.4, 129.9, 128.7, 127.5, 117.0, 110.0. HRMS (APCI) calcd. for $C_{23}H_{14}BF_2N_2S_2Br_2$ $[M+H]^+$ 590.9000, found 590.8991.

BODIPY **3c** was obtained as brown solid in 40% yield (30 mg) using *method b* from compound **2a** (0.1 mmol, 62 mg), K_2CO_3 (0.25 mmol, 35 mg) , $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3 (0.04 mmol, 10 mg) and EDOT (0.5 mmol, 71 mg) in 3 mL of toluene. mp 231-232 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.71 (s, 2H), 6.62 (s, 2H), 4.22 – 4.27 (m, 8H), 2.37 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 143.2, 142.3, 140.9, 139.2, 136.7, 135.4, 129.9, 129.0, 128.3, 128.2, 111.7, 104.6, 64.7, 64.3, 21.1, 20.2. HRMS (APCI) calcd. for $C_{30}H_{23}BBr_2FN_2O_4S_2$ $[M-F]^+$ 728.9523, found 728.9515.

BODIPY **3d** was obtained as brown solid in 42% yield (26 mg) using *method b* from compound **2a** (0.1 mmol, 62 mg), K_2CO_3 (0.25 mmol, 35 mg), $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3 (0.04 mmol, 10 mg) and 2-methylfuran (0.5 mmol, 41 mg) in 3 mL of toluene . mp 200-202 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 3.4 Hz, 2H), 6.95 (s, 2H), 6.62 (s, 2H), 6.27 (d, J = 3.0 Hz, 2H), 2.47 (s, 6H), 2.36 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 143.3, 142.9, 138.9, 136.9, 135.0,

130.5, 129.6, 128.3, 119.6, 119.5, 119.4, 109.6, 21.1, 20.0, 14.0. HRMS (APCI) calcd. for $C_{28}H_{23}BBr_2FN_2O_2$ $[M-F]^+$ 609.0183, found 609.0181.

BODIPY **4a** was obtained as brown solid in 47% yield (19 mg) using *method b* from **2c** (0.1 mmol, 40 mg), K_2CO_3 (0.25 mmol, 35 mg), $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3 (0.04 mmol, 10 mg) and thiophene (0.25 mmol, 21 mg) in 3 mL of toluene. mp 158-160 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 3.3 Hz, 1H), 7.51 (d, *J* = 4.2 Hz, 2H), 7.17 (d, *J* = 3.9 Hz, 1H), 7.00 (s, 1H), 6.92 (s, 1H), 2.53 (s, 3H), 2.40 (q, *J* = 15.0 Hz, 2H), 2.19 (s, 3H), 1.08 (t, *J* = 9.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 135.9, 132.2, 131.3, 131.2, 131.2, 131.1, 128.3, 126.9, 126.3, 124.7, 121.6, 121.0, 17.3, 14.0, 13.5, 9.5. HRMS (APCI) calcd. for $C_{17}H_{16}BFN_2SBr$ $[M-F]^+$ 389.0295, found 389.0300.

BODIPY **4b** was obtained as brown solid in 48% yield (22 mg) using *method b* from compound **2c** (0.1 mmol, 40 mg), K_2CO_3 (0.25 mmol, 35 mg), $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3 (0.04 mmol, 10 mg) and EDOT (0.25 mmol, 36 mg) in 5 mL of toluene. mp 258-260 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.89 (s, 1H), 6.55 (s, 1H), 2.53 (s, 3H), 2.39 (q, *J* = 15.0 Hz, 2H), 2.19 (s, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.7, 143.0, 141.7, 141.2, 141.0, 132.7, 132.6, 126.5, 125.5, 123.89, 123.9, 123.8, 102.6, 64.8, 64.6, 17.1, 14.3, 13.7, 9.7. HRMS (APCI) calcd. for $C_{19}H_{19}BF_2N_2O_2SBr$ $[M+H]^+$ 467.0412, found 467.0411.

BODIPY **4c** was obtained as brown solid in 50% yield (25 mg) using *method b* from compound **2c** (0.1 mmol, 40 mg), K_2CO_3 (0.25 mmol, 35 mg), $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3(0.04 mmol, 10 mg) and 2,2'-bithiophene (0.5 mmol, 83 mg) in 5 mL of toluene. mp 104-105 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 3.9 Hz, 2H), 7.23 (d, *J* = 3.9 Hz, 1H), 6.98 – 7.04 (m, 3H), 6.92 (s, 1H), 2.55 (s, 3H), 2.40 (q, *J* = 15 Hz, 2H), 2.19 (s, 3H), 1.08 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 137.1, 132.5, 132.3, 132.2, 130.7, 127.9, 127.8, 126.6, 125.0, 124.8, 124.2, 124.0,

123.8, 121.4, 121.2, 17.3, 14.1, 13.5, 9.5. HRMS (APCI) calcd. for $C_{21}H_{18}BFN_2S_2Br$ $[M-F]^+$ 471.0172, found 471.0172.

BODIPY **4d** was obtained as brown solid in 48% yield (20 mg) using *method b* from compound **2c** (0.1 mmol, 40 mg), K_2CO_3 (0.25 mmol, 35 mg) , $Pd(OAc)_2$ (0.01 mmol, 3 mg), PPh_3 (0.04 mmol, 10 mg) and 2-methylfuran (0.25 mmol, 21 mg) in 3 mL of toluene. mp 108-109 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 3.3 Hz, 1H), 6.93 (s, 1H), 6.89 (s, 1H), 6.18 (d, *J* = 3.3 Hz, 1H), 2.57 (s, 3H), 2.48 – 2.34 (m, 5H), 2.17 (s, 3H), 1.08 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 139.9, 127.9, 127.3, 121.2, 120.9, 116.1, 116.1, 116.0, 115.1, 109.7, 109.6, 108.6, 17.3, 14.1, 13.9, 13.3, 9.4. HRMS (APCI) calcd. for $C_{18}H_{18}BBrFN_2O$ $[M-F]^+$ 387.0680, found 387.0682.

Intermediates 5a, 5b and 5c from BODIPYs 2 and $Pd(PPh_3)_4$.

Syntheses of BODIPY **5a:** To a dry round-bottom flask loaded with compound **2a** (0.05 mmol, 31 mg) and $Pd(PPh_3)_4$ (0.05 mmol, 55.0 mg) were added toluene (5.0 mL). Freeze-pump-thaw cycle was carried out three times. After that, the mixture was heated to 60 ^{o}C under argon and stirred for 8 h. After cooling to room temperature, the mixture was evaporated under vacuum. The residue was purified through column chromatography (silica, petroleum ether/ethyl acetate = 2/1, v/v) to afford **6** as orange crystals in 81% yield (51 mg). mp 162-164 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 13H), 7.33 (s, 17H), 6.80 (s, 2H), 6.04 (s, 1H), 5.85 (s, 1H), 2.26 (s, 3H), 1.87 (s, 6H). HRMS (APCI) calcd. for $C_{54}H_{43}BBr_3F_2N_2P_2Pd$ $[M-Br]^+$: 1176. 9507, found 1176.9525.

BODIPY **5b** was obtained as purple crystals in 60% yield (31 mg) using the above method from compound **2a** (0.03 mmol, 18 mg) and $Pd(PPh_3)_4$ (0.06 mmol, 66 mg). mp 243-244 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 8.15 (s, 15H), 7.44 (s, 18H), 7.26 – 7.29 (m, 7H), 6.89 (s, 5H), 6.79 (s, 2H), 6.70 (s, 8H), 6.49 (s, 7H), 5.58 (s, 2H), 2.26 (s, 3H), 1.95 (s, 6H). HRMS calcd. for

$C_{54}H_{43}BBr_3F_2N_2P_2Pd$ [M-Pd(PPh_3)$_2$Br]$^+$: 1176.9507, found 1176.9490. HRMS (APCI) calcd. for $C_{54}H_{44}BBr_2F_2N_2P_2Pd$ [M-Pd(PPh_3)$_2$-2Br+H]$^+$: 1097.0422, found 1097.0422.

BODIPY **5c** was obtained as orange crystals in 65% yield (47 mg) using the above method from compound **2c** (0.05 mmol, 20 mg) and $Pd(PPh_3)_4$ (0.05 mmol, 55 mg). mp 228-230 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 13H), 7.28 (s, 17H), 6.33 (s, 1H), 5.82 (s, 1H), 2.27 – 2.35 (m, 5H), 2.04 (s, 3H), 1.02 (t, *J* = 7.5 Hz, 3H). HRMS (APCI) calcd. for $C_{49}H_{42}BBr_2F_2N_2P_2Pd$ [M-H]$^+$: 1035.0265, found 1035.0267.

The Suzuki coupling reaction for 4e catalyzed by BODIPY 5c. To a dry round-bottom flask loaded with compound **2c** (0.28 mmol, 112 mg), BODIPY **5c** (5 mg, 0.0048 mmol), (4-*tert*-butylphenyl)boronic acid (0.4 mmol, 60 mg), Na_2CO_3 (0.6 mmol, 63 mg) were added toluene (5 mL). Freeze-pump-thaw cycle was carried out three times. After that, the mixture was heated to 80 ^{o}C under argon and stirred for 15 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, petroleum ether/ethyl acetate = 5/1, v/v) to afford purple powder **4e** in 41% yield (53 mg). mp 196-198 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.03 (s, 1H), 6.94 (s, 1H), 2.49 (s, 3H), 2.39 (q, *J* = 7.6 Hz, 2H), 2.19 (s, 3H), 1.37 (s, 9H), 1.07 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 151.8, 150.2, 140.7, 136.0, 135.3, 131.9, 130.1, 128.1, 126.3, 125.2, 124.6, 122.1, 34.8, 31.3, 17.3, 14.1, 13.4, 9.4. HRMS (APCI) calcd. for $C_{23}H_{26}BBrFN_2$ [M-F]$^+$ 439.1356, found 439.1346.

The Suzuki coupling reaction for 6a from BODIPY 5a. To a dry round-bottom flask loaded with compound **5a** (0.02 mmol 25 mg), (4-methoxyphenyl)boronic acid (0.1 mmol, 15 mg), Na_2CO_3 (0.04 mmol, 4 mg) were added toluene (5 mL). Freeze-pump-thaw cycle was carried out three times. After that, the mixture was heated to 80 ^{o}C under argon and stirred for 8 h. After

cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, petroleum ether/ethyl acetate = 6/1, v/v) to afford purple powder in 92% yield (17 mg). mp 264-265 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 4H), 7.00 (s, 2H), 6.91 (d, J = 8.0 Hz, 4H), 6.85 (d, J = 7.9 Hz, 4H), 6.69 (d, J = 7.9 Hz, 4H), 6.64 (s, 2H), 3.82 (s, 6H), 3.74 (s, 6H), 2.39 (s, 6H), 2.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 158.5, 155.8, 141.9, 138.5, 137.0, 134.7, 134.1, 132.1, 130.6, 129.5, 128.2, 126.7, 126.1, 124.4, 113.6, 113.4, 55.2, 55.1, 21.2, 20.3. HRMS (APCI) calcd. for $C_{46}H_{42}BF_2N_2O_4$ $[M+H]^+$ 735.3206, found 735.3197.

The Stille coupling reaction

Syntheses of BODIPY **3a:** To a dry round-bottom flask loaded with compound **2a** (0.1 mmol, 62 mg), 2-(tributylstannyl)thiophene (0.2 mmol, 75 mg) and $Pd(PPh_3)_4$ (0.01 mmol, 11 mg) were added toluene (6 mL). Freeze-pump-thaw cycle was carried out three times. After that, the mixture was heated to 80 □ under argon and stirred for 14 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, petroleum ether/dichloromethane = 4/1, v/v) to afford **3a** as a brown solid in 41% yield (26 mg).

BODIPY **3b** was obtained as brown solids in 43% yield (25 mg) using the above method from compound **2b** (0.1 mmol, 58 mg), 2-(tributylstannyl)thiophene (0.2 mmol, 75 mg) and $Pd(PPh_3)_4$ (0.01 mmol, 11 mg).

BODIPY **6b** was obtained as brown crystals in 49% yield (31 mg) using the above method at 90 □ from compound **2a** (0.1 mmol, 62 mg), 2-(tributylstannyl)thiophene (0.4 mmol, 149 mg) and $Pd(PPh_3)_4$ (0.015 mmol, 16 mg). mp 267-268 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 3.6

Hz, 2H), 7.50 (d, *J* = 5.0 Hz, 2H), 7.17 (d, *J* = 5.0, Hz, 2H), 7.10 (d, *J* = 5.0 Hz, 2H), 7.01 (s, 2H), 6.89 (d, *J* = 5.0 Hz, 2H), 6.72 (d, *J* = 3.6 Hz, 2H), 6.69 (s, 2H), 2.40 (s, 3H), 2.26 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 143.5, 138.9, 136.8, 135.3, 135.2, 132.3, 130.9, 129.8, 129.6, 129.1, 128.3, 127.2, 127.2, 126.4, 126.3, 125.5, 21.2, 20.3. HRMS (APCI) calcd. for $C_{34}H_{26}BF_2N_2S_4$ $[M+H]^+$ 639.1035, found 639.1023.

BODIPY **6c** was obained as brown crystals in 46% yield (27 mg) using the above method at 90 □ from compound **2b** (0.1 mmol, 58 mg), 2-(tributylstannyl)thiophene and (0.4 mmol, 149 mg) and $Pd(PPh_3)_4$ (0.015 mmol, 16 mg). mp 253-255℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (m, 5H), 7.55 (d, *J* = 3.3 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.20 (d, *J* = 5.1 Hz, 2H), 7.11 (dd, *J* = 6 Hz, 2H), 6.95 (s, 2H), 6.92 (d, *J* = 5.0 Hz, 2H), 6.76 (d, *J* = 3.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 159.8, 149.1, 143.4, 135.2, 135.1, 133.9, 132.3, 130.9, 130.6. HRMS (APCI) calcd. for $C_{31}H_{20}BF_2N_2S_4$ $[M+H]^+$ 597.0565, found 597.0562.

BODIPY **4f** was obtained as brown solids in 43% yield (41 mg) using the above method at 80 ℃ from compound **2d** (0.2 mmol, 92 mg), 2-(tributylstannyl)thiophene (0.2 mmol, 75 mg) and $Pd(PPh_3)_4$ (0.02 mmol, 22 mg). mp 189-191 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.0 Hz, 1H), 7.31 (d, 3.0 Hz, 1H), 7.22 (s, 1H), 7.20 (brs,, 1H), 2.60 (s, 3H), 2.42 (q, J = 8.0 Hz, 2H), 2.17 (s, 3H), 1.09 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 141.7, 137.1, 136.2, 132.3, 128.7, 127.8, 127.6, 124.6, 120.3, 114.1, 106.7, 17.3, 14.0, 13.5, 9.5. HRMS (APCI) calcd. for $C_{17}H_{16}BBrF_2N_2S$ $[M-Br+H]^+$ 408.0279, found 408.0299.

The Suzuki coupling reaction

Syntheses of BODIPY **3e**: To a dry round-bottom flask loaded with compound **2a** (0.1 mmol, 62 mg), (4-methoxyphenyl)boronic acid (0.2 mmol, 30 mg), Na_2CO_3 (5 mml, 1 M) and $Pd(PPh_3)_4$ (0.01 mmol, 11 mg) were added toluene (5 mL). Freeze-pump-thaw cycle was carried out three times. After that, the mixture was heated to 80 ^{o}C under argon and stirred for 10 h. After cooling

to room temperature, the reaction mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, petroleum ether/ethyl acetate = 4/1, v/v) to afford **3e** as a blackish green crystal in 45% yield (31 mg). mp 247-248 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J = 8.7 Hz, 4H), 7.01 – 6.92 (m, 6H), 6.74 (s, 2H), 3.83 (s, 6H), 2.38 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 156.0, 143.0, 139.1, 136.7, 134.4, 131.98, 130.1, 129.3, 128.3, 122.3, 113.4, 109.5, 55.2, 21.2, 20.2. HRMS (APCI) calcd. for $C_{32}H_{28}BF_2N_2O_2Br_2$ $[M+H]^+$ 681.0553, found 681.0554.

BODIPY **6a** was obtained as fuchsia solids in 76% yield (55 mg) using the above method from compound **2a** (0.1 mmol, 62 mg), (4-methoxyphenyl)boronic acid (0.5 mmol, 76 mg), Na_2CO_3 (5 mml, 1 M) and $Pd(PPh_3)_4$ (0.01 mmol, 11 mg). mp > 250 ℃ ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 4H), 7.00 (s, 2H), 6.91 (d, J = 8.0 Hz, 4H), 6.85 (d, J = 7.9 Hz, 4H), 6.69 (d, J = 7.9 Hz, 4H), 6.64 (s, 2H), 3.82 (s, 6H), 3.74 (s, 6H), 2.39 (s, 6H), 2.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 158.5, 155.8, 141.9, 138.5, 137.0, 134.7, 134.1, 132.1, 130.6, 129.5, 128.2, 126.7, 126.1, 124.4, 113.6, 113.4, 55.2, 55.1, 21.2, 20.3. HRMS (APCI) calcd. for $C_{46}H_{42}BF_2N_2O_4$ $[M+H]^+$ 735.3206, found 735.3197.

BODIPY **6d** was obtained as fuchsia solids in 78% yield (60 mg) using the above method from compound **3e** (0.1 mmol, 68 mg), (4-*tert*-butylphenyl)boronic acid (0.3 mmol, 45 mg), Na_2CO_3 (3 mml, 1 M) and $Pd(PPh_3)_4$ (0.01 mmol, 11 mg). mp > 300 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 5.0 Hz, 4H), 7.15 (d, J = 10.0 Hz, 4H), 6.99 (s, 2H), 6.92 (d, J = 10.0 Hz, 4H), 6.86 (d, J = 5.0 Hz, 4H), 6.69 (s, 2H), 3.83 (s, 6H), 2.39 (s, 3H), 2.27 (s, 6H), 1.24 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 156.0, 149.7, 138.5, 137.0, 134.8, 134.2, 132.1, 131.2, 128.1, 127.8, 126.7, 125.0, 124.4, 113.4, 55.2, 34.4, 31.3, 21.2, 20.3. HRMS (APCI) calcd. for $C_{52}H_{53}BFN_2O_2$ $[M-F]^+$ 767.4184, found 767.4190.

The Heck coupling reaction

Syntheses of BODIPY **3f:** To a 50 mL dry Schlenk flask were added BODIPY **2a** (65 mg, 0.1 mmol), $Pd(OAc)_2$ (1.6 mg, 0.008 mmol), PPh_3 (28 mg, 0.14 mmol) and K_2CO_3 (78 mg, 0.57 mmol). Freeze-pump-thaw cycle was carried out three times. Methyl acrylate (90 μL, 1 mmol) in 8 mL toluene was added through a syringe into the mixture. Freeze-pump-thaw cycle was carried out three times again. The mixture was stirred at 80 ^oC for 1.5 h under argon, cooled to room temperature. The reaction mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The organic layers were combined and evaporated under vacuum. The residue was purified through column chromatography (silica, petroleum ether/ethyl acetate = 5/1, v/v) to give the desired compound **3f** as dark blue solid in 47% yield (29 mg). mp 284-285 ℃. ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 16.4 Hz, 2H), 7.32 (d, J = 16.5 Hz, 2H), 6.98 (s, 2H), 6.74 (s, 2H), 3.89 (s, 6H), 2.37 (s, 3H), 2.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 147.9, 144.1, 139.0, 135.5, 135.4, 130.7, 130.4, 127.7, 127.5, 127.0, 109.3, 51.4, 20.3, 19.2. HRMS (ESI) calcd. for $C_{26}H_{24}BBr_2F_2N_2O_4$ $[M+H]^+$: 635.0164, found 635.0162.

BODIPY **6e** was obtained as dark blue solids in 53% yield (33 mg) using the above method from BODIPY **2a** (65 mg, 0.1 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), PPh_3 (30 mg, 0.15 mmol) and K_2CO_3 (82 mg, 0.6 mmol). mp 290-291 ℃. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 16.4 Hz, 2H), 7.63 (d, J = 15.8 Hz, 2H), 7.02 (s, 2H), 6.84 (s, 2H), 6.60 (d, J = 16.4 Hz, 2H), 6.23 (d, J = 15.8 Hz, 2H), 3.89 (s, 6H), 3.78 (s, 6H), 2.40 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 165.8, 152.1, 147.0, 139.8, 137.1, 136.3, 134.0, 131.7, 130.6, 128.8, 128.7, 128.6, 127.1, 121.0, 52.3, 51.8, 21.1, 20.1. HRMS (APCI) calcd. for $C_{34}H_{33}BFN_2O_8$ $[M-F]^+$: 627.2314, found 627.2303.

BODIPY **7** was obtained as dark blue solids in 51% yield (32 mg) using the above method from BODIPY **2a** (65 mg, 0.1 mmol), $Pd(OAc)_2$ (1.6 mg, 0.008 mmol), PPh_3 (28 mg, 0.14 mmol) and

K_2CO_3 (78 mg, 0.57 mmol). mp 273-274 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 16.4 Hz, 2H), 7.62 (d, *J* = 15.8 Hz, 1H), 7.33 (d, *J* = 16.4 Hz, 1H), 6.79 (d, *J* = 14.9 Hz, 2H), 6.59 (d, *J* = 16.4 Hz, 1H), 6.21 (d, *J* = 15.8 Hz, 1H), 3.89 (s, 6H), 3.77 (s, 3H), 2.39 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 166.2, 165.8, 151.8, 148.9, 146.0, 139.8, 136.7, 136.3, 134.0, 131.7, 131.1, 130.4, 128.7, 128.5, 127.9, 127.0, 120.9, 110.5, 52.2, 52.2, 21.1, 20.1; HRMS (ESI) calcd. for $C_{30}H_{29}BBrF_2N_2O_6$ $[M+H]^+$: 641.1270, found 641.1262.

The Sonagashira coupling reaction

Syntheses of BODIPY **3g:** To a 50 mL dry Schlenk flask were added BODIPY **2a** (126 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 3 mmol%) and CuI (13 mg, 7 mmol%) in 5 mL of freshly distilled THF. After freeze-pump-thaw three times, Et_3N (0.4 mL) and 2-ethynylthiophene (100 μL, 1 mmol) in 1 mL of THF were added through a syringe into the mixture, respectively. The mixture was stirred at 60 ^{o}C for 6 h, cooled to room temperature, and filtrated through celite, and then the cake was washed with CH_2Cl_2 (3 × 20 mL). The crude product was purified by chromatography (silica gel, petroleum ether/dichloromethane = 3/1, v/v) to give the desired compound **3g** as golden yellow solids in 31% yield (42 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 3.6 Hz, 2H), 7.50 (d, *J* = 5.0 Hz, 2H), 7.11 (t, *J* = 4.3 Hz, 2H), mp 181-183 ℃. 6.96 (s, 2H), 6.65 (s, 2H), 2.36 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 139.4, 137.8, 136.6, 136.2, 135.2, 130.7, 128.9, 128.8, 128.4, 127.7, 121.7, 113.3, 100.6, 85.6, 21.1, 20.1. HRMS (APCI) calcd. for $C_{30}H_{20}BF_2N_2S_2Br_2$ $[M+H]^+$ 678.9490, found 678.9491.

BODIPY **3h** was obtained as golden yellow solids in 38% yield (55 mg) using the above method from BODIPY **2a** (126 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 3 mmol%), CuI (13 mg, 7 mmol%), Et_3N (0.4 mL) and 4-ethynylanisole (144 μL, 1 mmol). mp 210-211 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.9 Hz, 4H), 6.97 – 6.92 (m, 6H), 6.64 (s, 2H), 3.88 (s, 6H), 2.36 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2, 140.1, 139.3, 138.3, 136.7, 135.9, 134.5, 129.0,

128.7, 128.4, 114.2, 114.0, 113.0, 108.0, 81.2, 55.5, 21.1, 20.1. HRMS (APCI) calcd. for $C_{36}H_{28}BF_2N_2O_2Br_2$ $[M+H]^+$ 727.0573, found 727.0584.

Supplementary Information (SI) available: Crystal structure data and CIF files, additional photophysical data and spectra, copies of NMR spectra and high resolution mass spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgements

We thank the National Nature Science Foundation of China (Grants Nos. 21372011, 21402001 and 21472002), Nature Science Foundation of Anhui Province (Grants No 1508085J07) for supportting this work.

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