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Synthesis and Studies of Aza-BODIPY-Based π-Conjugates for Organic Electronic Applications

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Aza-boron-dipyromethene (aza-BODIPY) derivatives **1**–**6** were synthesized for the first time by employing the palladium catalyzed Suzuki–Miyaura coupling on dibromo-aza-BODIPY. Photophysical and electrochemical properties of these compounds were studied in solution. Absorption and emission maxima were observed in the near-infrared (NIR) region and were found to extend up to 754 and 751 nm, respectively. NIR fluorescence quantum yields in chloroform were as high as 0.45. Optical band gaps were measured from the onset of absorption spectra in thin films and were found to be low (ca. 1.2–1.4 eV). Electrochemical studies provided insight into the reduction potentials of these compounds and consequently the electron affinity (EA). High electron affinity (ca. 4.5) was observed for these dyes. NIR absorption and emission, good quantum yield, and high electron affinity of these compounds promise their applications in microscope imaging and optoelectronic devices, mainly in solar cells and field-effect transistors.

Introduction

The application of near-infrared (NIR) dyes in biological systems (e.g., bioimaging, sensing of cations and anions, and photodynamic therapy), photovoltaics, organic light-emitting devices and nonlinear optics is very attractive.[1–6] Such applications have encouraged researchers to design and synthesize new materials that incorporate chromophores featuring absorption and emission beyond 700 nm. Based on their physicoelectrochemical properties, applications of these dyes could include microscopic imaging, whereby dyes emitting in the NIR region can provide deeper penetration and high contrast, since it is less absorbed and scattered by biological tissues.[7,8] It is desirable to have high quantum yields of NIR emitting dyes for applications in microscopic imaging. Such NIR dyes can also be used in organic electronic applications, for which the electron-donating (*p*-type) and/or electron-accepting (*n*-type) properties of the dye, absorption and/or emission properties are important.

In organic electronic devices, various electron-donor and electron-acceptor materials have been used, and many organic solar cells use polymer chains such as poly-3-hexylthiophene (P3HT) and fullerene-based molecules {1-[3-(methoxycarbonyl)propyl]-1-phenyl-[6.6]C_{61}, PCBM} as donor and acceptors, respectively.[9] Fullerene-based acceptors do not absorb significantly in the NIR region and hence are unable to harvest photons of these wavelengths.[10] A few attempts have been made to develop alternatives to fullerene-based acceptors.[11–13] Electron-donors such as Cu-phthalocyanine (CuPc), P3HT, and poly[4,8-bis-substituted-benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl-alt-4-substituted-thieno[3,4-*b*]thiophene-2,6-diyl] (PBDTTT)[14] are quite popular in organic solar cells. Very few reports are available on small, solution-processable *n*-type conjugated compounds with low optical band gap.[15] Organic molecules having small energy gap and compatible energy levels can be utilized in organic electronics to harvest NIR photons. Intriguingly, organic solar cells with such molecules could also be operated in the dark.

Here, we explore the chemical modification of aza-BODIPY for *n*-type solution-processable organic materials with low band gaps and high electron affinity. Aza-BODIPY derivatives are particularly interesting because their photophysical and electrochemical properties can be easily adjusted by substituting them with electron-donating and electron-withdrawing groups and by increasing the π-conjugation along the dye molecule (Scheme 1).[15–19] The Suzuki–Miyaura coupling has been successfully employed for the first time on aza-BODIPY to achieve such chemical modifications. These molecules show absorption and emission in the NIR region. Good fluorescence quantum yield in the NIR region and high electron affinities of these compounds make them potential materials for microscope imaging and organic electronic devices.

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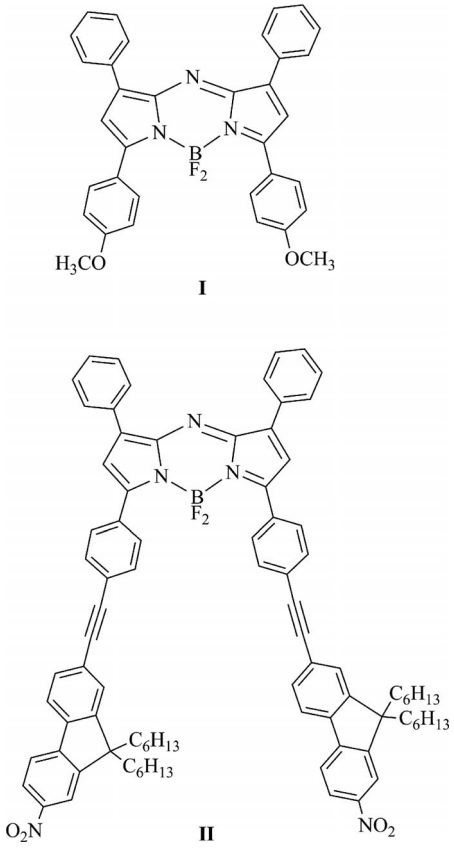
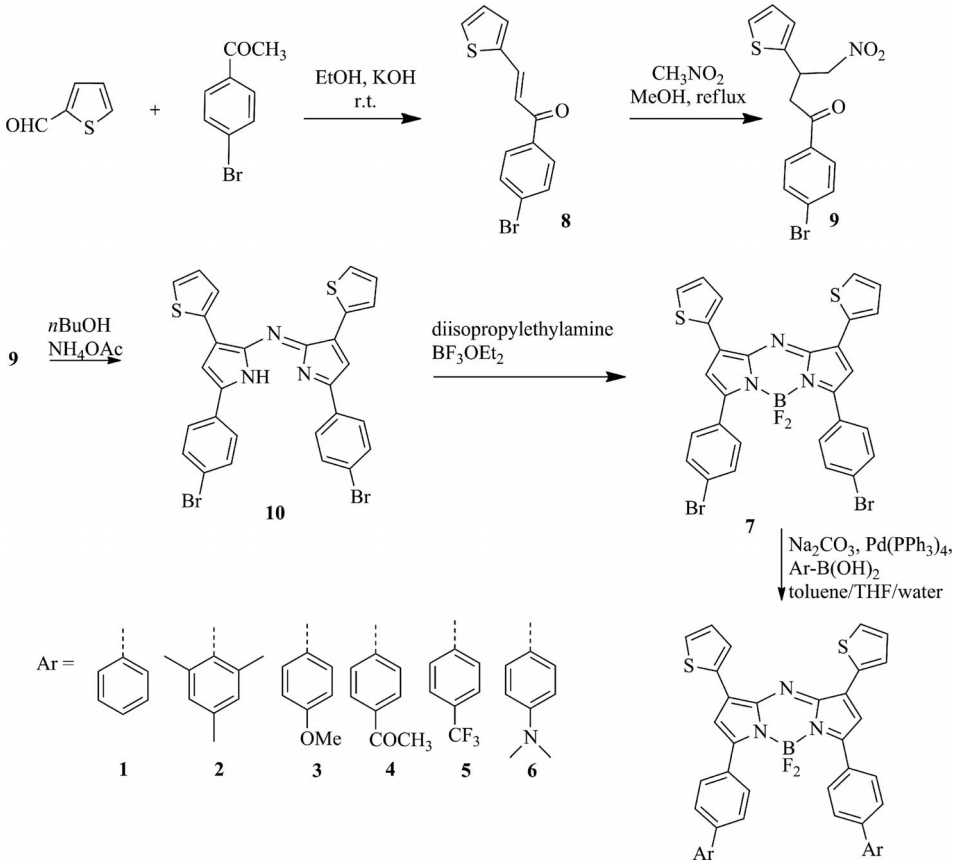


Scheme 1. Structure of substituted aza-BODIPY derivatives **I** and **II** having absorption and emission in the NIR spectral range.

Results and Discussion

Aza-BOBIPY derivatives **1**–**6** were synthesized as shown in Scheme 2. The synthesis of 1,7-dithienyl-3,5-di(4-bromophenyl)borondifluoride-azadipyrromethene (**7**)[16] was carried out by using the classical procedure developed by McDonnell and O'Shea.[17] Chalcone **8** was synthesized by reacting thiophene 2-carbaldehyde with *p*-bromoacetophenone in alcoholic KOH followed by reaction of **8** with nitromethane, leading to the formation of **9** in good yields (52 and 72%, respectively). Compound **9** was treated with excess ammonium acetate at 120 °C in *n*-butanol to give azadipyrromethene **10**, as shown in Scheme 2;[16] the latter was isolated after precipitation in moderate yield, and converted into aza-BODIPY **7** by following a reported method.[16] Thus, azadipyrromethene **10** was dissolved in chloroform, and diisopropylethylamine (10 equiv.) was added dropwise over 1 h, followed by the addition of $BF_3{\cdot}Et_2O$ (15 equiv.). Overnight stirring of the reaction mixture at room temperature and usual work up produced the crude aza-BODIPY **7**, which was purified by column chromatography on silica (dichloromethane/petroleum ether, 1:4) to afford aza-BODIPY **7** as a blue solid in 42% yield. Aza-BODIPY **7** was subsequently used for Suzuki–Miyaura coupling with various substituted aryl boronic acids to prepare aza-BODIPY derivatives **1**–**6** (Scheme 2). The well-known Suzuki–Miyaura coupling conditions [i.e., bromo aza-BODIPY substrate, aryl boronic acids and Pd catalyst with K_2CO_3 and 1,2-dimethoxyethane (DME)/H_2O] did not give



Scheme 2. Synthetic scheme for compounds **1**–**10**.

the aryl-substituted aza-BODIPY. Under these conditions, cleavage of the BF_2 linkages of aza-BODIPY was observed. It has been reported that BF_2 linkages in aza-BODIPY cleave when reacted under Sonogashira coupling conditions.[18,20] The Suzuki–Miyaura coupling conditions were therefore slightly modified, and aza-BODIPY **7** and the respective aryl boronic acid were degassed with argon gas for 5 min. A mixture of tetrahydrofuran (THF), toluene and water (1:1:1) was added to the reaction flask and the mixture was stirred under argon gas. $Pd(PPh_3)_4$ was used as catalyst and Na_2CO_3 as base to initiate the coupling of aryl boronic acid with aza-BODIPY **7**. After 2 h stirring at 80 °C, analysis of the reaction by TLC clearly indicated the formation of a new spot corresponding to aryl coupled aza-BODIPY along with the reactant. For the completion o which we attribute to the formation of mono- and di-aryl-substituted products. The reaction mixture was cooled and successively washed with brine and water. The organic layers were dried with anhydrous sodium sulfate and the solvent was evaporated. The crude product was purified by chromatography on silica column to afford di-substituted aza-BODIPY derivatives **1**–**6** as blue solids in 35–65% yield. In addition to compounds **1**–**6**, we also collected small amounts of mono-substituted products and some unidentified product in trace amounts.

All compounds were found to be reasonably soluble in common organic solvents such as chloroform, dichloromethane, acetonitrile and dimethyl formamide. The identities of the compounds were confirmed by HRMS analysis, and by ^1H, ^{13}C and ^{19}F NMR spectroscopy (see the Supporting Information). The ^1H NMR spectra of compounds **1**–**6** showed characteristic NMR signals corresponding to the aza-BODIPY core with additional aryl proton signals of substituted aryl groups. A representative ^1H NMR spectrum for compound **1** recorded in $CDCl_3$ is shown in Figure 1. Three sets of signals were obtained for the thienyl group present at the 1- and 7-positions of aza-BODIPY at δ = 7.22, 7.58 and 7.96 ppm. A singlet was observed for *beta* protons of pyrrole at δ = 7.06 ppm. The biphenyl groups attached at the 3- and 5-position of aza-BODIPY exhibited five sets of signals with three doublets at δ = 7.65, 7.71 and 8.14 ppm corresponding to six aryl protons and two multiplets at δ = 7.37 and 7.45 ppm corresponding to four aryl protons. The ^1H NMR spectra for compounds **2**–**6** were found to be similar, with slight changes due to the presence of substituents attached to the aryl group. ^{13}C NMR spectroscopic analysis of compounds **1**, **3** and **7** were recorded in $CDCl_3$. Unfortunately, clear homogeneous solutions of **2** and **4**–**6** in $CDCl_3$ of the required concentration for ^{13}C NMR could not be obtained, so we were unable to record good quality spectra for these compounds. Melting points were not observed up to 220 °C in silicone oil.

Compounds **1**–**6** were studied by absorption, fluorescence, and electrochemical techniques in solution. The absorption spectra were recorded in chloroform and are shown in Figure 2, and the data were compared with those of reference aza-BODIPY;[18] the results are summarized in

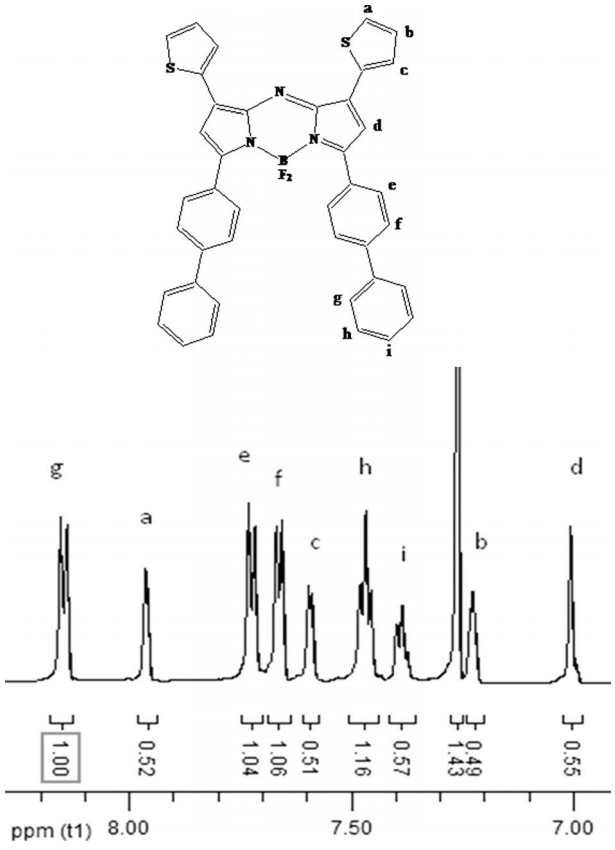


Figure 1. ^1H NMR spectrum of **1** recorded in $CDCl_3$.

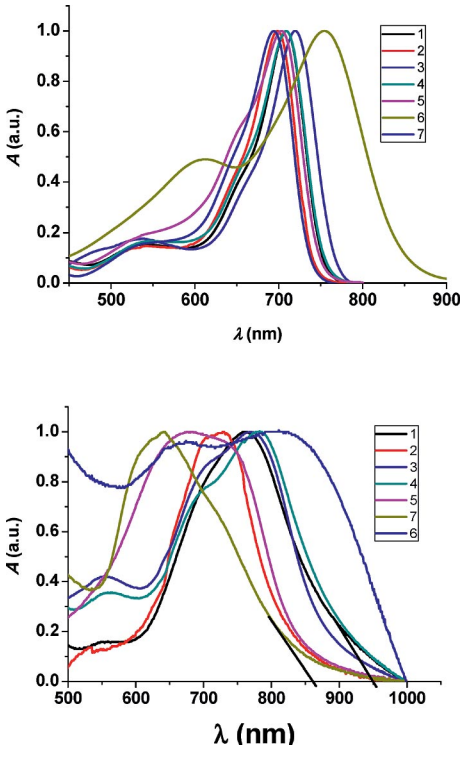


Figure 2. Normalized absorption spectra for **1**–**7** in $CHCl_3$ (top) and in thin films (bottom).

Table 1. Photophysical data for **1**–**7** recorded in $CHCl_3$.

	λ_{abs} [nm]	log ε	λ_{em} [nm]	f[a]	τ [ns][a]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]	λ_{abs} [nm][b]
I	661	4.5	689	0.36	–	–	–	–
1	708	4.7	738	0.27	1.20	2.25	6.08	761
2	698	4.2	722	0.38	1.16	3.27	5.34	725
3	719	4.3	751	0.45	1.72	2.61	3.19	770
4	708	4.7	738	0.22	1.17	1.88	6.66	782
5	702	4.3	730	0.21	1.12	1.87	7.05	680
6	754	4.4	–	–	–	–	–	823
6+TFA	707	4.4	730	0.10	–	–	–	–
7	693	4.7	723	0.17	0.93	1.82	8.92	641

[a] Relative quantum yields were calculated by using aza-BODIPY **I** as reference ($CHCl_3$, f = 0.36). [b] Absorption maxima recorded in drop-cast films, τ is fluorescence lifetime, k_r and k_{nr} are radiative and nonradiative constants, respectively.

Table 1. The absorption spectra of **1**–**6** showed two major bands, one strong $S_0 \rightarrow S_1$ transition at lower energy and a second weak $S_0 \rightarrow S_2$ transition at higher energy. The reference aza-BODIPY **7** showed $S_0 \rightarrow S_1$ transition at 693 nm, which was shifted to longer wavelengths in **1**–**6** by 5–60 nm. Absorption maxima for **1**–**6** were observed at 698–754 nm with high extinction coefficients. Thin-film absorption spectra of **1**–**6** were recorded with a drop cast film on glass surface. Compounds **1**–**6** showed broad and redshifted absorption in thin films compared with solution spectra (Figure 2). Optical band gaps were calculated from the onset of thin-film absorption spectra and are tabulated in Table 2.

Table 2. Electrochemical data for **1**–**7** recorded in $CHCl_3$.

	E_{red} [V]	E_g [eV][a]	E_{LUMO} or (–EA) [eV][b]	E_{HOMO} [eV][c]
1	–0.413	1.28	–4.58	–5.86
2	–0.426	1.38	–4.57	–5.95
3	–0.415	1.33	–4.57	–5.90
4	–0.383	1.26	–4.62	–5.88
5	–0.394	1.44	–4.61	–6.05
6	–0.434	1.18	–4.57	–5.75
7	–0.427	1.39	–4.65	–6.04

[a] Optical band gap, calculated from absorption spectrum recorded in drop-cast films. [b] E_{LUMO} were calculated from onset of reduction potentials vs. ferrocene. [c] $E_{HOMO} = E_{LUMO} - E_g$.

The fluorescence spectra of **1**–**6** were recorded in chloroform and are shown in Figure 3; the data is presented in Table 1. Compounds **1**–**5** showed strong emission peaks in the range 722–751 nm. Compound **6** did not show any fluorescence. Absorption and fluorescence spectra of **1**–**7** were not mirror images of each other as in the case of BODIPY dyes. Furthermore, it was found that these compounds possess considerable Stoke's shift. This observation could be accounted for by the possible differences in the ground and excited state geometries of compounds **1**–**7**. The fluorescence quantum yields of **1**–**5** in chloroform were calculated by using **I** as reference compound (Scheme 1),[18] and it was found that these compounds showed varying fluorescence quantum yields (0.21–0.45). Recently, Maury et al. reported that 3,5-nitrofluorenylethynyl-substituted aza-BODIPY (**II**) showed emission at 740 nm with a high quantum yield of 0.36.[18] They attributed this redshift in the emission for compound **II** to the longer π-conjugated skeleton (Scheme 1). Emission wavelengths and quantum yields of **1**–**7** are comparable to those of **II**. To the best of our knowledge, there is no other report of infrared emission and high quantum yields of aza-BODIPY in the literature. Among all the compounds **1**–**5**, aza-BODIPY **3** showed that highest emission maxima (751 nm) with a high quantum yield of 0.45. The aza-BODIPY **6** was completely nonfluorescent due to electron transfer from the *N*,*N*-dimethylamine group to the aza-BODIPY core. However, compound **6** became fluorescent upon the addition of trifluoroacetic acid (TFA), as shown previously by McDonnell and O'Shea,[17] with a quantum yield of 0.1 (see Figure S14 in the Supporting information).

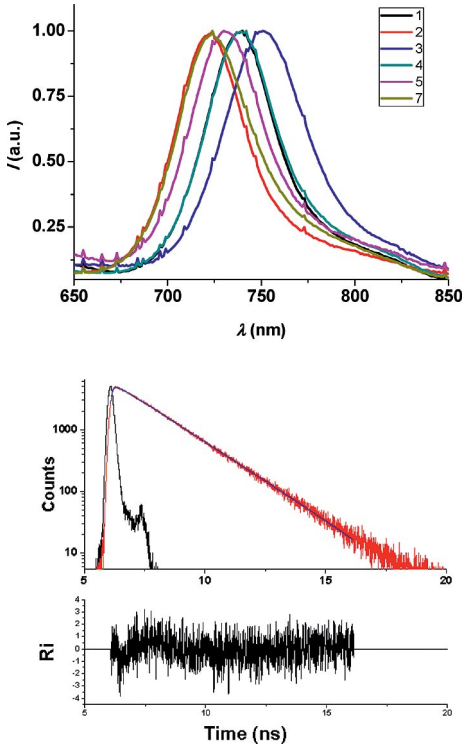


Figure 3. Normalized emission spectra for **1**–**5** and **7** recorded in $CHCl_3$ (top) and fluorescence decay profile and weighted, residual distribution fit of **3** in $CHCl_3$ (bottom). The excitation wavelength used was 635 nm and emission was detected at 751 nm.

Fluorescence lifetime studies were carried out on **1**–**5** to understand their fluorescence properties in detail; the results are presented in Table 1, and the fluorescence decay profile for **3** is shown in Figure 3 (see also the Supporting

Information SI 15). Compounds **1**–**5** showed a single exponential decay in $CHCl_3$ solvent. The fluorescence lifetime, nonradiative and radiative decay constants for compounds **1**–**5** were consistent with their fluorescence quantum yields.

The electrochemical properties of **1**–**7** were investigated by cyclic voltammetry and differential pulse voltammetry in $CHCl_3$ at a scan rate of 50 mV/s with tetrabutylammoniumhexafluorophosphate (TBAHFP) as supporting electrolyte. Compounds **1**–**7** were not oxidized under these experimental conditions and only reduction waves were observed. A comparison of the first reduction wave of compounds **4**, **5**, and **7** is shown in Figure 4 and the data for **1**–**7** are presented in Table 2. The 3,5-diaryl-substituted aza-BODIPY derivatives **1**–**6** are easier to reduce than **7**, which is clearly evident from data presented in Table 2. The E_{LUMO} of compounds **1**–**7** were calculated by using the reduction potential onset and by using the Fc/Fc^+ value at 5.1 eV vs. vacuum. E_{HOMO} was calculated by using the E_{LUMO} and optical band gap for respective compounds **1**–**7** (Figure 2). The E_{LUMO} of organic compounds is generally considered as electron affinity (EA) or, in other words, it reflects how easily they can accept electrons. Electron affinity of more than 4.0 eV is considered to be high. The E_{LUMO} values for **1**–**7** were observed at ca. –4.6 eV and because E_{LUMO} also reflects the EA, we can say that these compounds have high electron affinity.

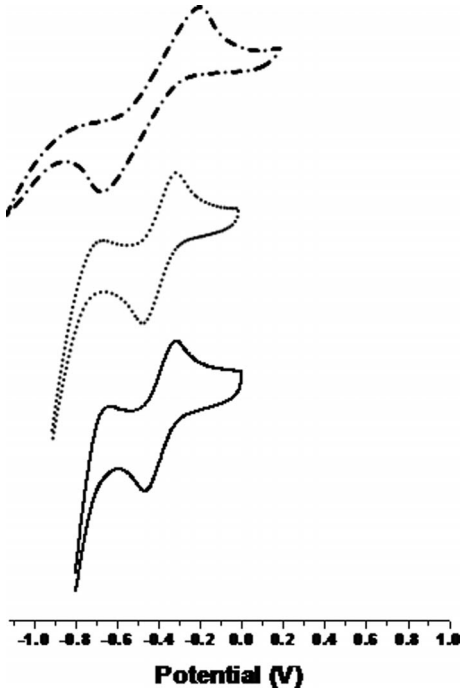


Figure 4. Cyclic voltammograms of **5** (–), **4** (···) and **7** (–·–·–) in $CHCl_3$.

Conclusions

We have demonstrated the substitution of aza-BODIPY at the 3- and 5-positions by various aryl groups having electron-donating and electron-withdrawing properties. To the best of our knowledge, this is the first example of Suzuki–Miyaura coupling of aza-BODIPY. Absorption and emission maxima of these compounds are bathochromically shifted and are in the near-infrared region. Extinction coefficients and fluorescence quantum yields are found to be high. Electrochemical properties of compounds **1**–**5** and **7** exhibited one reversible reduction wave. HOMO and LUMO energy levels of these compounds were calculated by using the onset of reduction potential and optical band gaps. E_{LUMO} values suggest that these compounds have high electron affinity and have potential applications in organic field-effect transistors (OFET). Furthermore, we believe that the photophysical and electrochemical parameters of these compounds could be exploited for use in organic solar cells. We are in the process of establishing a facility to explore the possible applications of these compounds in organic solar cells and OFET.

Experimental Section

Chemicals: All general chemicals and solvents were procured from SD Fine Chemicals, India, or Sigma–Aldrich. Column chromatography was performed using silica gel and basic alumina obtained from Sisco Research Laboratories, India. Tetrabutylammoniumhexafluorophosphate was purchased from Aldrich and used without further purifications. Solvents such as dichloromethane, chloroform, tetrahydrofuran (THF), and toluene were purified and distilled by standard procedures.

Instrumentation: ^1H and ^{13}C NMR spectra (δ in ppm) were recorded with a Varian 600 MHz spectrometer. ^{19}F NMR spectra were recorded with a Bruker Avance III 376 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference for recording ^1H NMR spectra (residual proton; δ = 7.26 ppm) in $CDCl_3$. HRMS spectra were recorded with a Q-Tof micromass spectrometer. UV/Vis spectra were acquired at room temperature with a Shimadzu 1800 instrument. Fluorescence emission measurements were carried out at room temperature with a Horiba Fluoromax 4 instrument. Cyclic voltammetry measurements were carried out with an electrochemical analyzer (620 D, CH Instruments Co.) at room temperature by utilizing the three-electrode configuration consisting of glassy carbon (working electrode), platinum wire (auxiliary electrode), and Ag/AgCl (reference electrode) electrodes. The experiments were performed in anhydrous chloroform with 0.1 M tetrabutylammoniumhexafluorophosphate as the supporting electrolyte. Fluorescence decay measurements were carried out at the magic angle with a picosecond-diode-laser-based, time-correlated single-photon-counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decays were fitted to a single exponential.

General Procedure for the Synthesis of Substituted Aza-BODIPY Dyes 1–6

Compound 1: A 25 mL round-bottomed flask fitted with reflux condenser was filled with argon for 5 min. Compound **7** (0.1 g, 0.15 mmol), phenylboronic acid (0.055 g, 0.45 mmol) and Na_2CO_3 (0.063 g, 0.60 mmol) in water/THF/toluene (1:1:1, 15 mL) were stirred under argon for 5 min. $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol) was added and the reaction mixture was heated to reflux at 80 °C. After completion of the reaction as judged by TLC analysis, the reaction mixture was diluted with water (5 mL) and extracted with dichloromethane. The combined organic layers were washed with water and

brine, then dried with Na_2SO_4. The solvent was evaporated and the crude product was purified on a silica gel column (petroleum ether/dichloromethane, 80:20) to afford **1** (65%, 0.065 g) as a dark solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.06 (s, 2 H, Py), 7.22–7.32 (m, 2 H, Th), 7.37–7.39 (m, 2 H, Ph), 7.45–7.48 (m, 4 H, Ph), 7.58 (d, J = 4.5 Hz, 2 H, Th), 7.65 (d, J = 7.5 Hz, 4 H, Ph), 7.71 (d, J = 7.9 Hz, 4 H, Ph), 7.96 (s, 2 H, Th), 8.14 (d, J = 8 Hz, 4 H, Ph) ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$): δ = 116.75, 126.80, 127.12, 127.19, 127.89, 128.25, 128.82, 129.61, 130.02, 130.18, 130.31, 133.28, 134.70, 140.06, 142.21, 143.46, 158.66, 161.66 ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$,): δ = –130.4 (q, $J_{B–F}$ = 64.0 Hz) ppm. HRMS: calcd. for $C_{40}H_{26}BF_2N_3S_2$ + K^+ 700.1248; found 700.1268.

Compound 2: Compound **7** (0.1 g, 0.15 mmol), mesitylboronic acid (0.074 g, 0.45 mmol), and Na_2CO_3 (0.063 g, 0.60 mmol) in water/THF/toluene (1:1:1, 15 mL) were stirred under argon for 5 min. $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol) was added and the reaction mixture was heated to reflux at 80 °C. After completion of the reaction and purification of the crude product on silica gel column (petroleum ether/dichloromethane, 70:30), compound **2** (38%, 0.047 g) was afforded as a dark solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.04 (s, 12 H, CH_3), 2.34 (s, 6 H, CH_3), 6.95 (s, 4 H, Mesityl), 7.05 (s, 2 H, Ph), 7.22–7.24 (m, 2 H, Th), 7.27–7.29 (m, 4 H, Ph), 7.58 (d, J = 4.9 Hz, 2 H, Th), 7.96 (d, J = 3.4 Hz, 2 H, Th), 8.15 (d, J = 8.0 Hz, 4 H, Ph) ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = –131.3 (q, $J_{B–F}$ = 60.2 Hz) ppm. HRMS: calcd. for $C_{46}H_{38}BF_2N_3S_2$ + K^+ 784.2208; found 784.2211.

Compound 3: Compound **7** (0.10 g, 0.15 mmol), 4-anisylphenylboronic acid (0.068 g, 0.45 mmol), and Na_2CO_3 (0.063 g, 0.60 mmol) in water/THF/toluene (1:1:1, 15 mL) were stirred under argon for 5 min. $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol) was added and the reaction mixture was heated to reflux at 80 °C for 18 h. Workup as described above and purification of the crude product on silica gel column (petroleum ether/dichloromethane, 40:60) gave **3** (45%, 0.049 g) as a dark solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.87 (s, 6 H, OCH_3), 6.93–7.0 (m, 6 H, Py+Ph), 7.22 (s, 2 H, Th), 7.57 (d, J = 4.6 Hz, 2 H, Th), 7.60 (d, J = 8.1 Hz, 4 H, Ph), 7.67 (d, J = 7.9 Hz, 4 H, Ph), 7.95 (s, 2 H, Th), 8.12 (d, J = 7.9 Hz, 4 H, Ph) ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$): δ = 55.56, 114.54, 117.02, 126.89, 128.47, 129.77, 130.31, 130.41, 159.92 ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = –130.5 (q, $J_{B–F}$ = 60.2 Hz) ppm. HRMS: calcd. for $C_{42}H_{30}BF_2N_3O_2S_2$ + K^+ 760.1467; found 760.1479.

Compound 4: Compound **7** (0.1 g, 0.15 mmol), 4-acetylphenylboronic acid (0.074 g, 0.45 mmol), and Na_2CO_3 (0.063 g, 0.60 mmol) in water/THF/toluene (1:1:1, 15 mL) were stirred under argon for 5 min. $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol) was added and the reaction mixture was heated to reflux. Upon completion of the reaction, the crude product was purified on a silica gel column (petroleum ether/dichloromethane, 40:60) to afford **4** (60%, 0.07 g) as a dark solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.65 (s, 6 H, $COCH_3$), 7.0 (s, 2 H, Py), 7.23 (s, 2 H, Th), 7.60 (d, J = 4.5 Hz, 2 H, Th), 7.74–7.76 (m, 8 H, Ph), 7.96 (d, J = 3.1 Hz, 2 H, Th), 8.05 (d, J = 7.8 Hz, 4 H, Ph), 8.15 (d, J = 7.8 Hz, 4 H, Ph) ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = –130.2 (q, $J_{B–F}$ = 64.0 Hz) ppm. HRMS: calcd. for $C_{44}H_{30}BF_2N_3O_2S_2$ + Na^+ 768.1725; found 768.1740.

Compound 5: Compound **7** (0.1 g, 0.15 mmol), 4-(trifluoromethyl)-phenylboronic acid (0.085 g, 0.45 mmol) and Na_2CO_3 (0.063 g, 0.60 mmol) in water/THF/toluene (1:1:1, 15 mL) were stirred under argon for 5 min. $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol) was added and the reaction mixture was heated to reflux at 80 °C. On completion and usual work up of the reaction mixture, the crude product was purified on silica gel column (petroleum ether/dichloromethane, 95:5) to afford **5** (35%, 0.042 g) as a dark solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.0 (s, 2 H, Py), 7.23–7.24 (m, 2 H, Th), 7.61 (d, J = 4.5 Hz, 2 H, Th), 7.71–7.78 (m, 12 H, Ph), 7.96–7.97 (m, 2 H, Th), 8.15 (d, J = 8.0 Hz, 4 H, Ph) ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = –130.2 (q, $J_{B–F}$ = 64.0 Hz), –62.45 (s) ppm.

Compound 6: Compound **7** (0.1 g, 0.15 mmol), 4-(dimethylamino)-phenylboronic acid (0.074 g, 0.45 mmol), and Na_2CO_3 (0.063 g, 0.60 mmol) in water/THF/toluene (1:1:1, 15 mL) were stirred under argon for 5 min. $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol) was added and the reaction mixture was heated to reflux at 80 °C. After completion of the reaction, the crude product was purified on a silica gel column (petroleum ether/dichloromethane, 50:50) to afford **6** (43%, 0.048 g) as a dark solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.01 (s, 12 H, CH_3), 7.01 (s, 2 H, Py), 7.20 (m, 2 H, Th), 7.48 (d, J = 6.9 Hz, 4 H, Ph), 7.55 (d, J = 4.9 Hz, 2 H, Th), 7.60 (d, J = 8.6 Hz, 4 H, Ph), 7.68 (d, J = 8.3 Hz, 4 H, Ph), 7.94 (d, J = 3.4 Hz, 2 H, Th), 8.12 (d, J = 8.3 Hz, 4 H, Ph) ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = –130.6 (q, $J_{B–F}$ = 64.0 Hz) ppm. HRMS: calcd. for $C_{44}H_{36}BF_2N_5S_2$ + K^+ 786.2105; found 786.2112.

Compound 7: Compound **7** was synthesized according to a reported procedure.[16] Yield 53%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.8 (s, 2 H, Py), 7.20–7.22 (m, 2 H. Th), 7.60–7.66 (m, 6 H, Th + Ph), 7.86 (d, ^3J = 8 Hz, 4 H, Ph), 7.93 (s, 2 H, Th) ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$): δ = 116.41, 125.79, 128.34, 129.95, 130.69, 130.82, 131.84, 134.48, 138.70, 145.06 ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = –130.2 (q, $J_{B–F}$ = 64.0 Hz) ppm.

Supporting Information (see footnote on the first page of this article): NMR, mass spectra, and fluorescence decay profile of selected compounds.

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