RESEARCH ARTICLE

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Synthesis, optical, and electrochemical properties, and theoretical calculations of BODIPY containing triphenylamine

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Abstract

The boron dipyrromethene (BODIPY) triads consisting of two triphenylamine units as electron donor (D) and BODIPY core as electron acceptor (A; B3, and B4) have been synthesized using facile palladium cross-coupling reactions to broaden the absorption of the BODIPY dyes. All dyes and intermediates were characterized by ¹H NMR. ¹¹B NMR. ¹³C NMR. and ¹⁹F NMR spectroscopies. UV–Vis spectroscopy. fluorescence spectroscopy, cyclic voltammetry, and time-dependent density functional theory calculations. It was found that an increase in conjugation to the BODIPY core systematically extended the absorption and emission wavelength maxima. As a consequence, **B4** containing the D $-\pi$ -A $-\pi$ -D structure, exhibited the longest absorption and emission maxima at 597 and 700 nm, respectively, with 1.8 eV in optical bandgap. The 96 nm red-shifted absorption of B4 as compared to the unsubstituted BODIPY (B1) indicated the effective electronic communication between triphenylamine and BODIPY. This suggested that the proper alignment of triphenylamine and BODIPY triad could lead to broader absorption and suitable low energy bandgap. Furthermore, the molecular modeling has been employed to analyze the electronic and optical properties of the dyes. We found that the optical, electrochemical, and theoretical bandgaps of all dyes were in good agreement.

1 | INTRODUCTION

Organic dyes have been gaining attention to utilize as photoactive materials in optoelectronic devices including organic light emitting diode (OLED), organic field effect transistors (OFET), organic solar cells (OSC), and dye-sensitized solar cells (DSSC), due to their low cost, versatile synthesis, and ease of fabrication.^[1–5] Over the past decade, progress on design and synthesis of organic-based photoactive materials has been made to understand structure–property relationship that will lead to high device efficiency. There are several factors

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Recently, the panchromatic absorption of the 4,4-difluo ro-4-bora-*3a*,4*a*-diaza-*s*-indacene or boron dipyrromethene (BODIPY) has received more attention.^[11,12] BODIPY possess high molar absorptivity, high quantum yield, and photobleaching resistance because of the rigid and planar structure from the coordination of a boron atom to the dipyrromethene unit. The BODIPY with no substituents exhibited intense absorption with the maxima wavelength around 500 nm.^[13] The BODIPY core has three locations where substituents can be incorporated: (i) the pyrrolic positions, (ii) the *meso*-position, and (iii) the boron atom position. Absorption of BODIPY can be extended to the longer wavelength region by coupling pyrrolic positions, *meso*-position or boron atom of the BODIPY with π -conjugation substitutions through the palladium cross-coupling reactions, Knoevenagel condensations, and nucleophilic substitutions.^[11-14]

Several molecular designs of tunable wavelength BODIPY dyes have been explored. The D–A structure is the most employed structure for tuning absorption of BODIPY. Absorptions of electron-rich groups, such as triphenylamine, carbazole, fluorene and cyclopentadithiophene, combined with electron-deficient BODIPY have been reported.^[11–15] Besides the D–A structure, donor–acceptor–donor (D–A–D) triad is also attractive because it offers the increase in crosssection absorption and nonlinear optical behavior.^[16–19] Thus, we aimed to incorporate the donor groups at the pyrrolic positions of the BODIPY core and to study a correlation between the structure and optoelectronic properties of donor–BODIPY–donor dyes. Triphenylamine groups were employed as the donor functionalities because they are good electron donors and high charge transporting materials.^[16,20]

Here, in our molecular structures, a BODIPY core was designed to elaborate an ethynyl trimethylsilane group at the meso-position. The protected ethynyl functionality was intended to further provide connection of the BODIPY with other building blocks using the Sonogashira coupling reaction or click reaction. The attached building blocks could be p-type or n-type organic semiconductors for using in organic solar cells and carboxylic moieties for making the dye-sensitizers. The 2,6-position of the BODIPY core was functionalized with triphenylamine units to generate the D-A-D triad. Moreover, 4-ethynyl triphenylamine group was attached at the same position of BODIPY to make the D– π –A– π –D system. The influence of the triphenylamine donating units on the optical and electrochemical behaviors was investigated. The computational calculations of the optical properties and electronic structures of the BODIPY dyes were studied, and compared with the experimental absorption.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis

A series of BODIPY dyes (**B1–B4**) derived from a BODIPY core were prepared as illustrated in Scheme 1. Condensation

of 2,4-dimethylpyrrole with 4-iodobenzaldehyde in the presence of trifluoroacetic acid provided dipyrromethane. Then, dipyrromethane was consequently oxidized by DDQ to form dipyrromethene that was coordinated with BF_3OEt_2 to yield corresponding BODIPY (1). Ethynyltrimethylsilane was incorporated with iodine atom of compound 1 using the Sonogashira coupling reaction to yield dye **B1** as an orange powder. The 2,6-positions of **B1** were iodinated to give **B2** as a red powder with 65% yield. **B2** was then incorporated with electron-rich triphenylamine using the Suzuki coupling reaction to yield corresponding **B3** as a maroon solid. Next, 4-ethynyltriphenylamine (7) was coupled with **B2** using the Sonogashira cross-coupling reaction to provide **B4** as a deep blue solid in 22% yield.

The chemical structures of all compounds were confirmed with ¹H NMR, ¹³C NMR, ¹¹B NMR, ¹⁹F NMR, and TOF-HRMS (as reported in experimental and supporting information). For the unsubstituted BODIPY, B1, the two protons of the pyrrole rings appeared at 5.97 ppm as singlet peak. The four protons of phenyl ring appeared at 7.05 and 7.85 ppm as doublet peak with coupling constant of 8 Hz. The nine protons of trimethylsilyl moiety appeared at 0.28 ppm. The 2,6-diiodo substituted BODIPY, B2, was confirmed via disappearance of two pyrrolic protons. The spectral of B3 and **B4** dyes showed aromatic proton of triphenylamine rings at 6.98–7.27 ppm. The disubstitution of triphenylamine moieties were identified using a ratio of aromatic protons of triphenylamine versus triemethysilyl protons. The ¹³C NMR spectrum of **B3** showed peaks at -0.12, 13.1, 95.7-104.2 and 122-154 ppm indicating the corresponding of trimethylsilyl carbons (Si-C-(CH₃)₃, methyl carbons, alkyne carbons, and aromatic carbon, respectively. The ¹³C NMR spectrum of **B4** exhibited similar NMR pattern. The presence of BF2 unit of all BODIPY derivatives has been evaluated using ¹¹B NMR and ¹⁹F NMR. The ¹¹B NMR showed a triplet peak around 0.6–0.8 ppm with coupling constant (J_{B-F}) is 32 Hz that corresponding to presence of BF₂ group. The ¹⁹F NMR exhibited a quartet peak at -147 ppm with similar J_{B-F} of 33 Hz, indicating that fluorine atoms were coupled with a boron atom. Examples of ¹¹B-NMR and ¹⁹F-NMR spectrum of B1 have shown in Fig. 1.

2.2 | Optical properties

Linear absorption spectra and fluorescence spectra of the BODIPY derivatives concentration of 10^{-5} M were measured in dichloromethane solution to study the effect of chemical structures on the optical properties. The photophysical parameters including absorption maxima, molar extinction coefficient, emission maxima, and absorption onset were determined (Table 1). The optical bandgap was calculated from the onset of the lower energy absorption edge $(E_{\rm g,opt} = 1240/\lambda_{\rm onset})$.



SCHEME 1 Synthetic route of B1–B4

The solution-state absorption maxima of dyes (B1-B4) were readily tuned from approximately 500 to 600 nm as shown in Fig. 2. B1 exhibited the characteristic narrow spectral band in the visible region with strong absorption maxima (λ_{max}) at 503 nm.

Similar to typical unsubstituted BODIPY dyes, the intense absorption is attributed to the S_0 - S_1 transition.^[11] Attachment of two iodine atoms at the pyrrolic positions gave λ_{max} of **B2** to locate at 534 nm. For B3 dye, incorporation of BODIPY

with two triphenylamine units exhibited two absorption peaks at 305 and 541 nm with the onset at 640 nm, respectively. The first peak in the UV region corresponded to the absorption of the triphenylamine moiety, while the second broad peak corresponded to the energy transition of BODIPY core. The extended absorption is due to the intramolecular charge transfer from the electron-rich triphenylamine unit to the BODIPY chromophore. Indeed, the molar absorptivity is increased as compared to that of B1. Moreover, the insertion

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of ethynyl linker between BODIPY and triphenylamine of **B4** provided significant redshifted at 597 nm with the onset at 690 nm. In comparison with triad **B3**, addition of triple bond



FIGURE 1 ¹¹B-NMR (160 Hz) spectrum and ¹⁹F-NMR (470 Hz) spectrum of **B1** in CDCl₃

spacer resulted in 56 nm redshift of the absorption maxima. This indicates that efficient π -conjugation linker and more planar alignment of the donor/acceptor enhances the electronic communication. As the result, **B4** exhibited the lowest optical energy bandgap of 1.80 eV that relatively close to the near IR energy bandgap (1.60 eV). The low bandgap of small organic compound was known for photon absorption improvement that could lead to enhance photovoltaic efficiency.^[21] Therefore, **B4** could be considered as a suitable light absorber for organic solar cells. In addition, the λ_{max} of **B3** and **B4** could be further extended to via conjugation of the ethynyl unit at the *meso*-position.

The normalized fluorescence spectra of **B1–B4** in CH_2Cl_2 solution at the room temperature were depicted in Fig. 3. The emission maxima covered in a wide range from 515 to 700 nm and followed the trend of the absorption spectra: **B4** (700 nm) > **B3** (637 nm) > **B2** (555 nm) > **B1** (515 nm). The substitution of the triphenylamine functionalities on the BODIPY core results in a substantial bathochromic shift in the emission maxima. In addition, 2,6-triphenylamine-substituted BODIPY or **B3** showed large Stokes shift of 96 nm as compared to the small Stokes shift of the unsubstituted BODIPY, **B1** (30 nm). The relatively large Stokes shift may be attributed to the large geometry relaxation at the excited state. Similar result of 2,6-thiophene-substituted BODIPY

TABLE 1 Summary of optical absorption maxima, absorption coefficients, absorption onset, emission maxima, and the optical bandgaps of B1-B4

	Absorbance			Fluorescence		
Compounds	λ_{\max} (nm)	$\varepsilon_{\rm max}~(imes 10^4~{ m M}^{-1}~{ m cm}^{-1})$	λ_{onset} (nm)	λ_{emiss} (nm)	$E_{\rm g,opt} ({\rm eV})$	
B1	503	6.60	533	515	2.32	
B2	534	6.06	580	555	2.14	
B3	308, 541	7.68, 7.45	640	637	1.93	
B4	346, 597	10.15, 8.57	690	700	1.80	



FIGURE 2 UV–Vis spectra of **B1–B4** in CH_2Cl_2 solution and the solution's color

was also reported by Chen et al.^[22] and this only occurred with the 2,6-substituted BODIPYs. Interestingly, the Stokes shift of **B4** was further increased to 103 nm by addition of the ethynyl spacer.



FIGURE 3 Normalized fluorescence spectra of **B1–B4** in CH_2Cl_2 solution



FIGURE 4 Cyclic voltammograms of **B1–B4**

TABLE 2 Summary of electrochemical data of B1-B4

2.3 | Electrochemical properties

The redox properties of BODIPY dyes were studied using cyclic voltammetry with an electrochemical system utilizing a three-electrode system. BODIPYs at concentration of 10^{-4} M in anhydrous CH₂Cl₂ were prepared. The oxidation and reduction potentials were approximated from the onset of the oxidation and reduction peaks. All voltammograms were normalized to half-wave potential of ferrocene/ferrocenium redox couple ($E_{1/2}$ (Fc/Fc+)) as shown in Fig. 4. The HOMO and LUMO energy levels were calculated using the following relationship; HOMO = $-(E_{\text{red,onset}} + 4.8) \text{ eV}$.^[23] The onset oxidation and reduction potentials, the HOMO and LUMO energy levels and the estimated electrochemical bandgaps are summarized in Table 2.

Cyclic voltammograms of **B1** and **B2** exhibited quasireversible oxidation wave and the reversible reduction wave, similar to other BODIPYs in the literature.^[11,24] The HOMO energy levels of **B1**, **B2**, **B3**, and **B4** were -5.35, -5.55, -4.95, and -4.85 eV, respectively, while the corresponding LUMO energy levels ranged from -3.15 to -3.55 eV. Incorporation of triphenylamine moieties to the BODIPY core (B3 and B4) resulted in significant decreased in the HOMO energy level and the slightly increased of the LUMO energy level. This revealed that the electron-rich triphenylamine units destabilized the HOMO that led to the smaller HOMO-LUMO bandgaps. It was also found that the electrochemical bandgaps and the optical bandgaps were comparable. In addition, **B3** and **B4** could be considered as a p-type semiconductor for organic solar cell since the LUMO energy level of **B3** and **B4** were higher than that of [6,6]-phenylC₆₁ butyric acid methyl ester or PCBM (-4.3 eV).^[25] Thus, both of B3 and B4 can make charge transfer to PCBM.

2.4 | Theoretical calculation

The time-dependent density functional theory (TD-DFT) was performed to gain a deeper insight into the electronic structures, electronic transition energies, and the spectroscopic properties of BODIPY derivatives **B1–B4**. All calculations were performed with Gaussian 09 package.^[26] Ground-state

Compounds	Е (V)	HOMO (eV) ^a	F (V)	LUMO (eV) ^b	E (eV) ^c
compounds			² red (1)		g,elec (C+)
B1	+0.80	-5.35	-1.33	-3.15	2.2
B2	+1.20	-5.55	-0.80	-3.55	2.0
B3	+0.45	-4.95	-1.25	-3.30	1.8
B4	+0.50	-4.85	-1.20	-3.25	1.75

^aHOMO = $-(E_{\text{ox,onset}} + 4.8)^{[23]}$.

 $^{b}LUMO = -(E_{red,onset} + 4.8)^{[23]}.$

 ${}^{c}E_{g,elec} = LUMO-HOMO.$

	Calculations		Experiment			
Dyes	Band assignment	Energy (eV)	λ (nm)	f	λ (nm)	$\varepsilon (\mathrm{M}^{-1} \mathrm{cm}^{-1})$
B1	H-0->L+0(70%)	2.80	443	0.670	503	66 000
	H-6->L+0(20%), H-1->L+1(65%)	4.82	257	1.131		
B2	H-0->L+0(70%)	2.68	463	0.835	534	60 620
	H-3->L+0(64%), H-2->L+0(12%)	3.82	325	0.108		
	H-1->L+1(56%)	4.76	260	0.992		
B3	H-0->L+0(50%)	2.61	475	1.183	541	74 520
	H-4->L+0(45%), H-2->L+0(23%), H-0->L+0(28%)	3.96	362	0.212		
	H-4->L+0(13%), H-1->L+5(44%), H-0->L+4(46%)	4.22	293	0.817		
B4	H-2->L+0(38%), H-0->L+0(58%)	2.41	514	1.630	595	85 777
	H-4->L+0(17%), H-2->L+0(18%), H-0->L+2(47%)	3.74	331	1.969		

geometry optimizations were calculated with B3LYP functional.^[27–29] 6-31G(d)^[30,31] basis set was used for all atoms except for iodine atom that used the LANL2DZ basis set.^[32,33] The TD-DFT was performed with 10 singlet excited states using CAM-B3LYP functional^[34] and 6-311+G(d) basis set^[35,36] except for iodine atom that used the LANL2DZ basis set. Conductor like polarizable continuum model (CPCM)^[37] was used with CH₂Cl₂ parameters. Molecular orbitals were plotted with Jimp2 visualizing program.^[38,39] UV–Vis absorption spectra were simulated using SpecDis.^[40]

The calculated absorption spectra were blue-shifted from those of the measured absorption spectra, as commonly reported in the literature.^[41,42] The sequence of the maximum absorption wavelengths and the relative magnitude of their oscillator strengths (*f*) were relatively agreed with the experimental absorption wavelength and the molar extinction coefficients (ε). The considerable difference between D–A–D (**B3**) and D– π –A– π –D (**B4**) dyes was the increase of the oscillator strength (1.18 vs 1.63) due to the insertion of ethynyl spacer, as shown in Table 3.

The frontier molecular orbitals of the model compounds have been shown in Fig. 5. Our DFT calculations exhibited that the HOMO and the LUMO were resided in the BODIPY core of **B1** and **B2**. However, in the case of **B3**, the HOMO was predominantly delocalized along the triphenylamine– BODIPY–triphenylamine backbone, while the LUMO was only confined in the BODIPY core. This indicated that the HOMO of **B3** was destabilized because of the triphenylamine incorporation and the electronic transition from HOMO to LUMO related to the charge transfer process. For **B4**, the HOMO was further destabilized with respect to **B3**, due to the ethynyl linker that provides effective conjugation. It was also observed in cyclic voltammograms where the oxidation potentials of **B3** and **B4** were lowered. Therefore, the extended π -conjugation of **B4** results in the longest wavelength absorption and the lowest bandgap. In addition, the predicted bandgap energies and spectral properties were similar to that of optical and redox properties discussed above.

3 | CONCLUSIONS

In summary, triphenylamine-substituted BODIPYs have been synthesized via Pd-catalyzed cross-coupling reactions. It was found that 4-ethynyl triphenylamine functionalized BODIPY (B4) exhibited the most red-shifted absorption with 1.8 eV of optical energy bandgap. The enhancement of electronic conjugation of **B4** also increases the emission maxima with the largest Stokes shift. Electrochemical studies revealed that triphenylamine units lowered the oxidation potentials of the dyes. TD-DFT calculations also suggested that triphenylamine donating unit can destabilize the HOMO of B3 and B4. As a result, $D-\pi-A-\pi-D$ structure of B4 exhibited the lowest optical (1.80 eV), electrochemical and theoretical bandgaps. Thus, **B4** could be potential alternative photoactive chromophore which can be used in organic solar cell device. Currently, works focusing on the fabrication of organic solar cells and works focusing on tuning the optical properties through the ethynyl unit at the meso-position of B3 and **B4** are in progress. These studies will be disseminated in future publications.

4 | EXPERIMENTAL

4.1 | General materials

4-Iodobenzaldehyde, 2,4-dimethylpyrrole, trifluoroacetic acid, 2,3-dichloro-5,6-dicyano-1,4-benzoquin one, boron trifluoride etherate (BF₃OEt₂), ethynyltrimethylsilane, *N*-iodosuccinimide, 4-(diphenyllamino)



FIGURE 5 Frontier molecular orbitals of B1-B4

phenyl boronic acid pinacol ester, 4-bromotriphenylamine, copper iodide, and 1,8-diazabicycloundec-7-ene were purchased from Aldrich. The palladium catalysts including tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), [1,1'-bis(diphenylphosphine)ferrocene]dichoropalladium(II) (Pd(dppf)Cl₂), and bis(triphenylphosphine)palladium(II) dichloride PdCl₂(PPh₃)₂ were purchased form Aldrich. HPLC grade toluene, dichloromethane (CH₂Cl₂), ethyl acetate (EtOAc), methanol (MeOH), dioxane, anhydrous *N*, *N'*-dimethylformamide (DMF), and triethylamine were purchased from Fisher. Deuterated chloroform (CDCl₃) was purchased from Cambridge Isotope Laboratories. Silica gel for column chromatography was purchased from Silicycle. All chemicals were used as received.

4.2 | Instrumentations

¹H NMR, ¹¹B NMR, ¹³C NMR, and ¹⁹F NMR spectra were measured in CDCl₃ solution at 500 MHz, 160 MHz, 125 MHz, and 470 MHz, respectively, on Bruker NMR spectrometers. The spectra were reported in ppm and peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. The chemical shift (δ) of ¹H NMR and ¹³C NMR spectra were recorded using the residual proton and carbon signal of the deuterated solvent as the internal standard. The chemical shift of ¹¹B NMR and ¹⁹F NMR were measured using BF₃OEt₂ ($\delta = 0$ ppm) and $C_6H_5CF_3$ ($\delta = -64$ ppm) as the external standards, respectively. UV-visible absorption spectra of all compounds were recorded on a Thermo Scientific UV-Genesys 10s spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-2500 fluorescence spectrophotometer. Cyclic voltammetric (CV) studies were carried out on a Metrohm Autolab potentiostat with an electrochemical system utilizing a three-electrode configuration consisting of a glassy carbon electrode, platinum wire electrode and a silver/silver chloride electrode. The cyclic voltammograms of BODPIPYs were recorded in anhydrous CH₂Cl₂ with 0.1 M terabutylammonium hexafluorophosphate (TBAPF₆) at a scan rate of 50 mV s⁻¹. Theoretical calculations were performed with Gaussian 09 package.

4.3 | Synthesis details

4.3.1 | Synthesis of compound 1

4-Iodobenzaldehyde (1.14 g, 4.90 mmol) was dissolved in dichloromethane (DCM; 400 mL). To this solution,

2,4-dimethylpyrrole (1 mL, 9.70 mmol) was added and the solution mixture was degassed for 10 minutes by purging nitrogen (N₂). Trifluoroacetic acid (TFA; 0.20 mL) was added and the reaction was allowed to proceed at room temperature for 3 hours. A solution of 2,3-dichloro-5,6-dicyano-1,4-ben zoquinone (DDQ; 1.10 g, 4.90 mmol) in toluene (10 mL) was then added to the solution mixture. After 12 hours, trimethylamine (Et₂N; 5 mL) was added and the reaction was allowed to proceed for 1 hour. Boron trifluoride etherate (5 mL) was then added and the reaction was stirring at room temperature for another 12 hours. The reaction mixture was washed in water several times. The organic layer was dried over sodium sulfate (Na2SO4) and concentrated under reduced pressure to yield a viscous dark red solution. The crude product was purified by flash chromatography over silica using ethyl acetate (EtOAc)/hexane as the eluents. The product was a bright orange solid (0.39 g, 18%). ¹H NMR (500 MHz, CDCl₃): δ (ppm), 7.84 (d, J = 8 Hz, 2H, CH_{AR}), 7.04 (d, J = 8 Hz, 2H, CH_{AR}), 5.99 (s, 2H, NH) 2.55 (s, 6H, CH₃), 1.41 (s, 6H, CH₃); ¹³C NMR (125 MHz, CDCl₃): δ (ppm), 155.88, 142.91, 140.05, 138.34, 134.55, 131.12, 129.94, 121.43, 94.72, 14.64; ¹¹B NMR (160 MHz, CDCl₃): δ (ppm), 0.61 (t, 1B, J_{B-F} = 32 Hz); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm), -147.38 (q, 2F, J_{B-F} = 33 Hz); MALDI-TOF MS (m/z) calculated for $C_{19}H_{18}BF_2N_2I$ [M + Na], 473.07; found 473.04.

4.3.2 | Synthesis of compound 2 (B1)

BODIPY (1; 0.30 g, 0.67 mmol) was dissolved in toluene (20 mL). The reaction mixture was degassed for 10 minutes. Pd(PPh₃)₄ (0.05 g, 0.04 mmol) and copper iodide (CuI; 0.007 g, 0.04 mmol) were added, followed by addition of trimethylsilylacetylene (0.1 g, 1.0 mmol). The reaction mixture was stirred at room temperature for 30 minutes, followed by addition of Et₃N (0.2 g, 3.02 mmol). The reaction mixture was refluxed under N2 for 48 hours. The mixture was filtered and the solid was washed with DCM. The reaction mixture was then concentrated under reduced pressure and extracted with DCM and water. The organic layers were dried over Na₂SO₄ and concentrated using a rotary evaporator. The crude mixture was then purified by column chromatography over silica with EtOAc/hexane as an eluent to give the product **2** as an orange powder (0.22 g, 78%). ¹H NMR (500 MHz, CDCl3): δ (ppm), 7.59 (d, J = 8 Hz, 2H, CH_{AR}), 7.22 (d, J = 8 Hz, 2H, CH_{AR}), 5.97 (s, 2H, NH) 2.54 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 0.28 (s, 9H, Si(CH₃)₂); ¹³C NMR $(500 \text{ MHz}, \text{CDCl}_2)$: δ (ppm), 155.74, 142.97, 135.18, 132.69, 131.13, 128.05, 123.91, 121.32, 104.17, 95.80, 14.56, -0.13; ¹¹B NMR (160 MHz, CDCl₃): δ (ppm), 0.88 (t, 1B, $J_{B_{-}}$ $_{\rm F} = 32$ Hz); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm), -147.40 (q, 2F, J_{B-F} = 33 Hz); MALDI-TOF MS (*m*/*z*) calculated for $C_{24}H_{27}BF_2N_2Si [M + Na], 443.37;$ found 443.19.

4.3.3 | Synthesis of compound 3 (B2)

BODIPY (2; 0.20 g, 0.4 mmol) was dissolved in DCM (20 mL) and the flask was purged with N₂. A solution of Niodosuccinimide (NIS; 0.19 g, 0.9 mmol) in anhydrous DMF (4 mL) was slowly added to a solution mixture. The reaction mixture was stirred at room temperature for 48 hours. After that, the crude mixture was extracted with DCM and water. The organic layers were dried over Na₂SO₄ and concentrated using a rotary evaporator. The crude mixture was then purified by column chromatography over silica with DCM/hexane as an eluent to give the product 3 as a red solid (0.19, 65%). ¹H NMR (500 MHz, CDCl3): δ (ppm), 7.63 (d, J = 8.8 Hz, 2H, CH_{AR}), 7.20 (d, J = 8.8 Hz, 2H, CH_{AR}), 2.64 (s, 6H, CH₃), 1.40 (s, 6H, CH₃), 0.28 (s, 9H, Si(CH₃)₂); ¹³C NMR (125 MHz, CDCl₂): δ (ppm), 157.30, 145.50, 135.18, 132.69, 131.13, 128.05, 123.91, 121.32, 104.17, 95.80, 14.56, -0.13; ¹¹B NMR (160 MHz, CDCl₃): δ (ppm), 0.68 (t, 1B, $J_{B-F} = 32$ Hz); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm), -146.82 (q, 2F, $J_{B-F} = 33$ Hz); MALDI-TOF MS (*m/z*) calculated for $C_{24}H_{25}BF_2N_2I_2Si + Na$, 695.17; found 695.43.

4.3.4 | Synthesis of compound 4 (B3)

2,6-Diiodo-BODIPY (3; 0.05 g, 0.07 mmol) and 4-(diphenyl amino) phenyl boronic acid pinacol ester (0.14 g, 0.02 mol) were dissolved in dioxane (10 mL). The reaction mixture was degassed for 10 minutes. Pd(dppf)Cl₂ (0.07 g, 7 µmol) and K₂CO₃ (2M) were added. The reaction mixture was stirred under reflux for 36 hours. The reaction mixture extracted with DCM and water. The organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was then purified by column chromatography over silica using DCM/hexane as the eluents to yield 4 (0.02 g, 33%) as a maroon solid. ¹H NMR (500 MHz, CDCl₃): δ (ppm), 7.62 (d, J = 8 Hz, 2H, CH_{AR}), 7.32 (d, J = 8 Hz, 2H, CH_{AR}) 7.27–7.25 (m, 4H, CH_{AR}), 7.12–6.98 (m, 24H, CH_{AR}) 2.56 (s, 6H, CH₃), 1.35 (s, 6H, CH₃), 0.28 (s, 9H, Si(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃): δ (ppm), 154.63, 147.61, 146.77, 138.74, 133.53, 132.772, 130.81, 129.27, 128.24, 127.14, 124.58, 123.03, 122.92, 104.25, 95.79, 13.52, 13.10, -0.12; ¹¹B NMR (160 MHz, CDCl₃): δ (ppm), 0.86 (t, 1B, J_{B-F} = 32 Hz); ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm), -147.07 (q, 2F, J_{BF} = 33 Hz); HRMS (MALDI-TOF MS) (m/z) calculated for C₆₀H₅₃BF₂N₄Si, 906.41; found 906.41.

4.3.5 | Synthesis of compound 5 (B4)

BODIPY (**3**; 0.05 g, 0.07 mmol) was dissolved in dry toluene (15 mL). The reaction mixture was degassed for 10 minutes. $Pd(PPh_3)_4$ (10 mg, 7 µmol) and CuI (3 mg, 3.5 µmol) were added, followed by addition of 4-ethynyltriphenylamine

(0.08 g, 0.28 mmol), followed by addition of Et_3N (1 mL). The reaction mixture was refluxed under N₂ for 36 hours. The mixture was filtered and the solid was washed with DCM. The reaction mixture was then concentrated under reduced pressure and extracted with DCM and water. The organic layers were dried over Na2SO4 and concentrated using a rotary evaporator. The crude mixture was then purified by column chromatography over silica with DCM/hexane to yield 5 (0.015 g, 22%) as a dark blue solid. ¹H NMR (500 MHz, CDCl₂): δ (ppm), 7.65 (d, 2H, CH_{AR}), 7.30–7.24 (m, 14H, CH_{AR}), 7.10 (d, 8H, CH_{AR}), 7.03 (d, 4H, CH_{AR}), 6.99 (d, 4H, CH_{AR}), 2.69 (s, 6H, CH₃), 1.52 (s, 6H, CH₃), 0.29 (s, 9H, Si(CH₂)₃); ¹³C NMR (125 MHz, CDCl₂)): δ (ppm) 158.61, 147.86, 147.17, 143.21, 132.86, 132.29, 129.51, 128.03, 124.91, 123.52, 122.40, 116.18, 96.84, 80.59, 29.68, 13.70, -0.13; ¹¹B NMR (160 MHz, CDCl₃): δ (ppm), 0.79 (1B, $J_{\rm B-E} = 32$ Hz); ¹⁹F NMR (470 MHz, CDCl₂): δ (ppm), -147.59 (2F, $J_{R-F} = 33$ Hz); HRMS (ESI) (*m/z*) calculated for C₆₄H₅₃BF₂N₄Si, 954.41; found 954.41.

4.3.6 | Synthesis of compound 6

4-Bromotriphenylamine (1.0 g, 3.0 mmol) was dissolved in toluene (30 mL). The reaction mixture was degassed for 10 minutes. PdCl₂(PPh3)₂ (0.1 g, 0.1 mmol) and CuI (0.03 g, 0.1 mmol) were added, followed by addition of trimethylsilylacetylene (0.45 g, 4.6 mmol). The reaction mixture was stirred at room temperature for 30 minutes, followed by addition of 1.8-diazabicycloundec-7-ene (DBU; 0.9 g, 6.2 mmol). The reaction mixture was refluxed under N₂ and the completion of the reaction was followed by thin layer chromatography (TLC). The mixture was filtered and the solid was washed with DCM. The reaction mixture was then concentrated under reduced pressure and extracted with DCM and water. The organic layers were dried over Na_2SO_4 and concentrated using a rotary evaporator. The crude mixture was then purified by column chromatography over silica with EtOAc/hexane to afford 4-(trimethylsilyl)ethynyl triarylamine 6 (0.25 g, 26%) as a viscous brown liquid. ¹H NMR (500 MHz, CDCl_3): δ (ppm) 7.29 (m, 2H, CH_{AR}), 7.24 (m, 4H, CH_{AR}), 7.03–7.08 (m, 6H, CH_{AR}), 6.94 (d, 2H, CH_{AR}), 0.23 (s, 9H, Si(CH₃)₂); ¹³C NMR (125 MHz, CDCl₃): δ (ppm), 148.06, 147.17, 132.92, 129.34, 124.91, 123.49, 122.17, 115.97, 105.39, 98.05, 0.06; MALDI-TOF MS (m/z) calculated for $C_{23}H_{23}NSi$, 341.15; found 342.16 (M + H).

4.3.7 | Synthesis of compound 7

4-(Trimethylsilyl)ethynyl triarylamine (0.25 g, 0.7 mmol) was mixed with KOH (0.20 g, 3 mmol) in 20 mL MeOH. The mixture was refluxed under N_2 atmosphere for 48 hours. The reaction mixture was concentrated under reduced pressure. A quantity of 1N HCl (10 mL) was added and the reaction

mixture was extracted with DCM and water. The organic layer was dried over Na₂SO₄ and concentrated using a rotary evaporator. The crude mixture was then purified by column chromatography over silica with EtOAc/hexane to yield 4-ethynyltriphenylamine **7** (0.17 g, 85%) as a brown solid. ¹H NMR (125 MHz, CDCl₃): δ (ppm) 7.29 (m, 2H, CH_{AR}), 7.22 (d, 6H, CH_{AR}), 6.91–7.12 (m, 6H, CH_{AR}), 3.03 (s, 1H, \equiv C–H); ¹³C-NMR (500 MHz, CDCl₃): δ (ppm) 148.36, 147.25, 133.06, 129.42, 125.05, 123.64, 122.05, 114.74, 83.93; EIS MS (*m*/*z*) calculated for C₂₀H₁₅N, 269.12 founded; 270.12 (M + H).

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