Design and synthesis of β-pyrrole functionalized ferrocenyl BODIPYs

M.Sc. Thesis

by

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY

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Design and synthesis of β-pyrrole functionalized ferrocenyl BODIPYs

A THESIS

Submitted in partial fulfilment of the

Requirements for the award of the degree

Of

Master of science

by

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the thesis entitled **Design and synthesis of *β*-pyrrole functionalized ferrocenyl BODIPYs** in the partial fulfilment of the requirements for the award of the degree of **Master of science** and submitted to the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore,** is an authentic record of my own work carried out during the time period from July 2024 of joining the M.Sc. to May 2025 of M.Sc. Thesis submission under the super vision of Prof. Rajneesh Misra, Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Abhishek Kumar

--अभिषेक कुमार------------

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Prof. Rajneesh Misra

Abhishek Kumar has successfully given his M.Sc. Oral Examination held on May 16/2025.

Signature of Supervisor of M.Sc. thesis

Date: 19/5/25

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Here, it is to be specially mentioned that, none of this would have been possible without the support of my parents and I express my love and gratitude to my family.

Abhishek Kumar

M.Sc. student

DEDICATED TO MY

FAMILY AND FRIENDS.......

ABSTRACT

Ethynyl bridged ferrocenyl functionalized BODIPY **1** was synthesized *via* Sonogashira cross-coupling reaction. Tetracyanobutadiene (TCBD) and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD (DCNQ) incorporated ferrocenyl BODIPYs **2** and **3** were synthesized using [2 + 2] cycloaddition -retroelectrocyclization (CA-RE) reaction, in good yields. BODIPYs **2** and **3** were obtained by reacting BODIPY **1** with strong electron acceptors tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) respectively. The electronic absorption spectra and theoretical calculations have been performed using the UV-visible spectrophotometer and density functional theory at B3LYP/6-31+G** level of theory.

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LIST OF FIGURES, SCHEMES AND TABLE

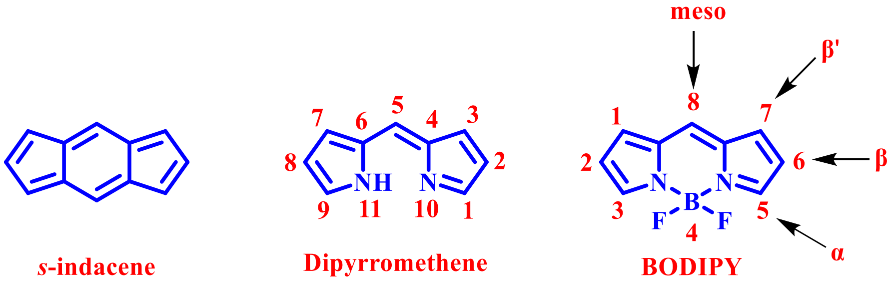
ACRONYMS

HOMO	Highest Occupied Molecular Orbitals
LUMO	Lowest Unoccupied Molecular orbitals
OFETs	Organic Field-Effect Transistors
OLEDs	Organic Light Emitting Diodes
TCNE	Tetracyanoethylene
TCNQ	Tetracyanoquinodimethane
TCBD	Tetracyanobutadiene
DCNQ	Dicyanoquinodi-methane

Chapter 1

INTRODUCTION

π-Conjugated push–pull molecular frameworks have garnered significant attention in recent years due to their tunable optoelectronic features and diverse applications, including inorganic field-effect transistors, nonlinear optical systems, photovoltaic devices, bioimaging, sensors, and organic light-emitting diodes (OLEDs).[1–5] The electronic characteristics and HOMO–LUMO energy gap of these π-conjugated chromophores can be tailored by altering the electron donor (D), acceptor (A), or the π-bridge connecting them. *4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene*, commonly known as BODIPY, has emerged as a prominent chromophore due to its outstanding chemical and photophysical properties. These include intense absorption, high fluorescence quantum yields, large molar extinction coefficients, extended fluorescence lifetimes, and excellent photostability.[6–9] The optoelectronic behaviour of BODIPY derivatives can be finely modulated by extending π-conjugation or by introducing suitable donor or acceptor groups at the pyrrolic (alpha, beta) and meso sites. Consequently, BODIPY-based π-systems have found widespread use in the development of fluorescent probes, molecular switches, chemosensors, laser dyes, OLEDs, photosensitizers, and advanced optoelectronic materials.[10, 11]

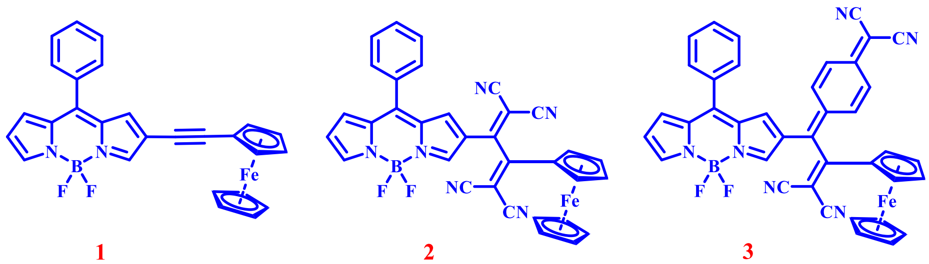


s-indacene Dipyrromethene BODIPY

Figure 1. General structure of s-indacene, dipyrromethene and BODIPY dye.

TCNE and TCNQ are strong electron acceptors that play a crucial role in the [2 + 2] CA-RE reaction, a catalyst-free process known for its high yields. In this reaction, electron-rich alkynes react with TCNE or TCNQ, resulting in the formation of nonplanar push-pull molecules with low HOMO–LUMO gaps.[12] These push-pull systems, particularly those based on TCBD and DCNQ, exhibit pronounced intramolecular charge transfer (ICT), revealing new optical bands at longer wavelengths. The nonplanar nature of these molecules is a key feature, contributing to their unique electronic and optical properties. As a result, TCBD and DCNQ-based push–pull systems have emerged as promising candidates for applications in optoelectronics.[13–15]

Diederich, Michinobu, Shoji, Trolez, and Butenschön et al. have studied the synthesis, photophysical properties, and redox characteristics of TCBD and DCNQ functionalized push-pull chromophores, establishing them as redox-active ICT systems suitable for optoelectronic applications. Recently, our research group has also reported on TCBD and DCNQ functionalized push-pull systems and explored their photophysical and redox properties for potential optoelectronic applications.[16–20]



1 2 3

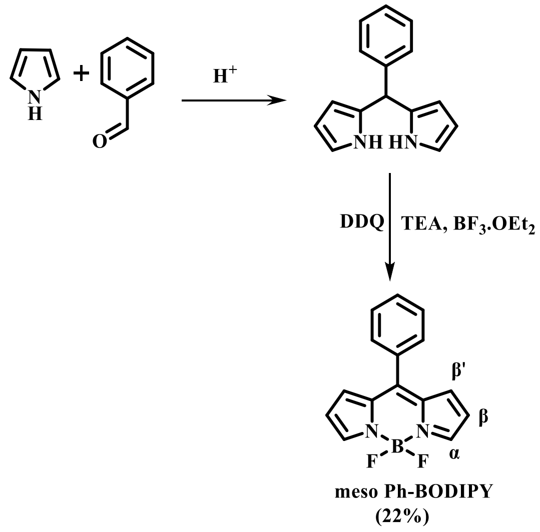
Figure 2. Chemical structure of compounds synthesized.

In this work, we report β-functionalized ferrocenyl BODIPYs **2** and **3**, that are synthesized by the [2 + 2] CA–RE reactions in good yields. [21-22] These molecules were characterized using various spectroscopic techniques, including ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and HRMS spectrometry. Additionally, the effect of TCBD and DCNQ incorporation on the photophysical and computational properties of the ferrocenyl BODIPYs has been investigated. These BODIPY derivatives, with low HOMO–LUMO gap, hold significant potential for application in the field of optoelectronics.

Chapter 2

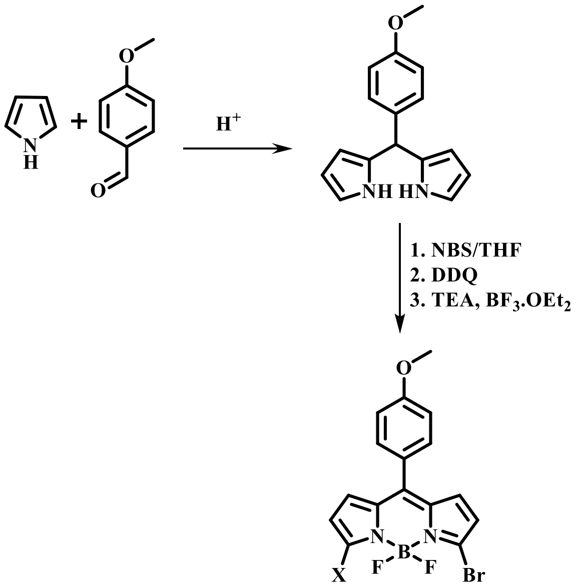
LITERATURE REVIEW

In 1968, the highly fluorescent BODIPY framework was first reported by Treibs and Kreuzer as a serendipitous discovery while attempting to acylate 2,4-dimethylpyrrole using acetic anhydride and $BF_3.OEt_2$. Various methods are reported for synthesizing BODIPYs, among which the Lindsey method involves an acid-catalyzed condensation of pyrrole with benzaldehyde. Further oxidation using DDQ as the oxidant and then complexation using $BF_3.OEt_2$, resulted in the final product in a 22% yield. [23]



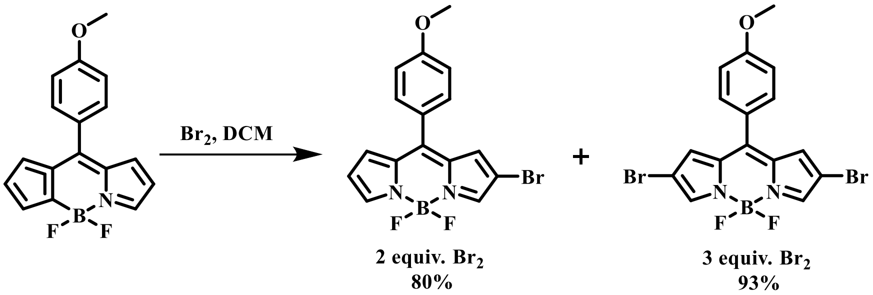
Scheme 1. Lindsey method for the synthesis of BODIPY.

For the bromination of BODIPY at the *α*-pyrrolic position, dipyrromethene (DIPY) was treated with 1 and 2 equivalents of N-bromosuccinimide (NBS), resulting in mono- and di-brominated BODIPYs in 40% and 25% yields respectively.[24-25]



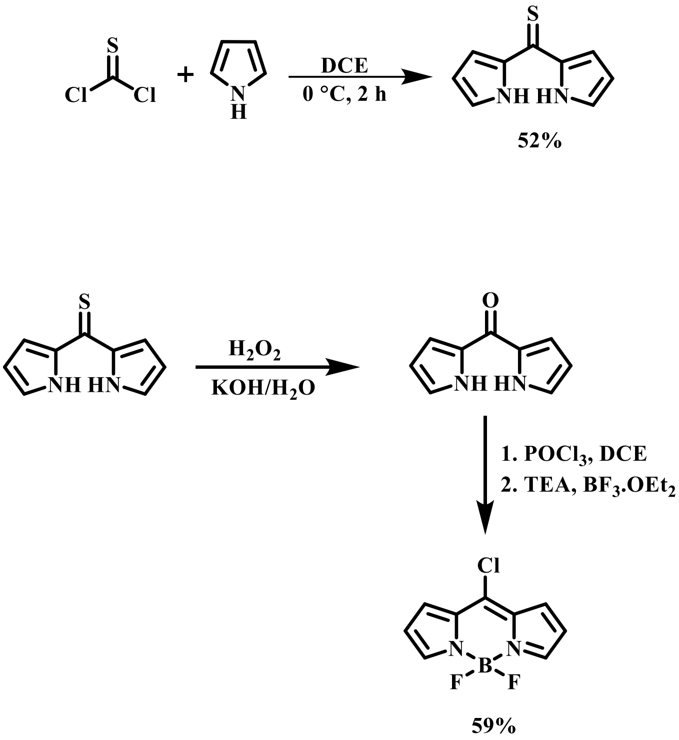
Scheme 2. Synthesis of *α*-halogenated BODIPYs (X=H, 40% and X=Br, 25% yield).

BODIPYs undergo electrophilic substitution reactions at the *β*-pyrrolic positions, facilitating halogenation at these sites. Using halogenating agents such as Br_2, *β*-brominated BODIPYs were synthesized with yields of 80% and 93%, respectively.[26-27]



Scheme 3. Synthesis of *β*-halogenated BODIPYs.

Dehaen *et al.* reported the multistep synthesis of 8-chloro BODIPY. The precursor dipyrrolyl ketone was synthesized by treating pyrrole with thiophosgene, followed by oxidation of the intermediate dipyrrolyl thione with H_2O_2. The dipyrrolyl ketone was treated with $POCl_3$, then triethylamine (TEA), followed by complexation with $BF_3{\cdot}OEt_2$, resulting in 8-chloro BODIPY in 59% yield. [28]



Scheme 4. Synthesis of 8-chloro BODIPY.

Chapter 3

EXPERIMENTAL SECTION

3.1 General Methods

All reagents and solvents were used as received unless otherwise specified. Moisture-sensitive reactions were carried out under an argon atmosphere using standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra, including ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{11}B NMR (160 MHz), were recorded in $CDCl_3$ as the solvent. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm) relative to the residual solvent peak ($CDCl_3$, $\delta = 7.26$ ppm). Signal multiplicities are designated as singlet (s), doublet (d), or multiplet (m), and coupling constants (J) are reported in hertz (Hz). ^{13}C NMR chemical shifts are also expressed in ppm with reference to the $CDCl_3$ solvent peak ($\delta = 77.0$ ppm). High-resolution mass spectrometry (HRMS) analyses were performed using electrospray ionization time of flight (ESI-TOF) instrumentation. UV-visible absorption spectra of the BODIPY compounds were recorded in dichloromethane (DCM) using an UV-Visible spectrophotometer (1×10^{-4} M). Theoretical calculations have been done using the density functional theory (DFT).

3.2 Experimental Procedures

3.2.1 Synthesis and characterization of BODIPY 1

β-bromo BODIPY (0.050 g, 0.144 mmol), and ethynyl ferrocene (0.036 g, 0.1734 mmol) were dissolved in THF:DIPEA (diisopropyl ethylamine) (4:1, v/v, 10 mL). The reaction mixture was purged with argon, and $Pd(PPh_3)_4$ (0.008 g, 0.0072 mmol) and CuI (0.0027 g 0.014 mmol) was added, followed by stirring at 60 °C for 12 h. After complete conversion of aryl halide, the reaction mixture was evaporated to dryness, and the crude product was dissolved in CH_2Cl_2 and purified by column chromatography using 100-200 silica bed, hexane/dichloromethane (3/1, v/v) used as eluent to get BODIPY 1 Yield: 81%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.01 (d, 2H, *J* = 16 Hz), 7.60-7.55 (m, 5H), 6.99 (s, 2H), 6.59 (s, 1H), 4.46 (s, 2H), 4.23 (s, 7H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 147.03, 145.9, 145.06, 135.5, 135.1, 134.2, 133.5, 132.1, 131.4, 130.9, 130.4, 128.5, 127.8, 119.0, 115.2, 91.2, 78.2, 71.3, 69.9, 68.9, 64.8. ^{11}B NMR (160 MHz, $CDCl_3$, δ in ppm):d = 0.05, 0.13, 32. HRMS (ESI-TOF) m/z = calculated for $C_{27}H_{19}BF_2N_2Fe$ = 476.0958 $[M]^+$, founded 476.0958 $[M]^+$.

3.2.2 Synthesis and characterization of BODIPY 2

Tetracyanoethylene (TCNE) (26 mg, 0.21 mmol) was added to a solution of compound 1 (100 mg, 0.21 mmol) in DCM (50 mL). The mixture was stirred at RT for 6 h. The solvent was removed in a vacuum, and the product was purified by column chromatography with hexane/dichloromethane (1/1, v/v) as the eluent to yield 2 as a brown colored solid. Yield: 74%.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.24 (s, 1H), 7.84 (s, 1H) 7.63-7.55 (m, 7H), 6.80 (d, 1H, *J* = 4 Hz), 5.38 (s, 1H), 5.02 (s, 1H), 4.87 (s, 1H), 4.59 (s, 1H), 4.47 (s, 5H). ^{13}C

NMR (100 MHz, $CDCl_3$, ppm) δ 172.1, 157.6, 151.8, 148.7, 141.6, 137.8, 136.4, 135.3, 132.2, 130.5, 129.1, 126.8, 123.0, 122.5, 113.5, 112.8, 112.5, 112.1, 78.8, 78.4, 75.8, 75.4, 74.9, 72.5, 72.0, 71.8. ^{11}B NMR (160 MHz, $CDCl_3$, δ in ppm): 0.19, 0.02, 0.16. HRMS (ESI-TOF) m/z = calculated for $C_{33}H_{19}BF_2N_6Fe$ = 604.1083 $[M]^+$, founded 604.1060 $[M]^+$.

3.2.3 Synthesis and characterization of BODIPY 3

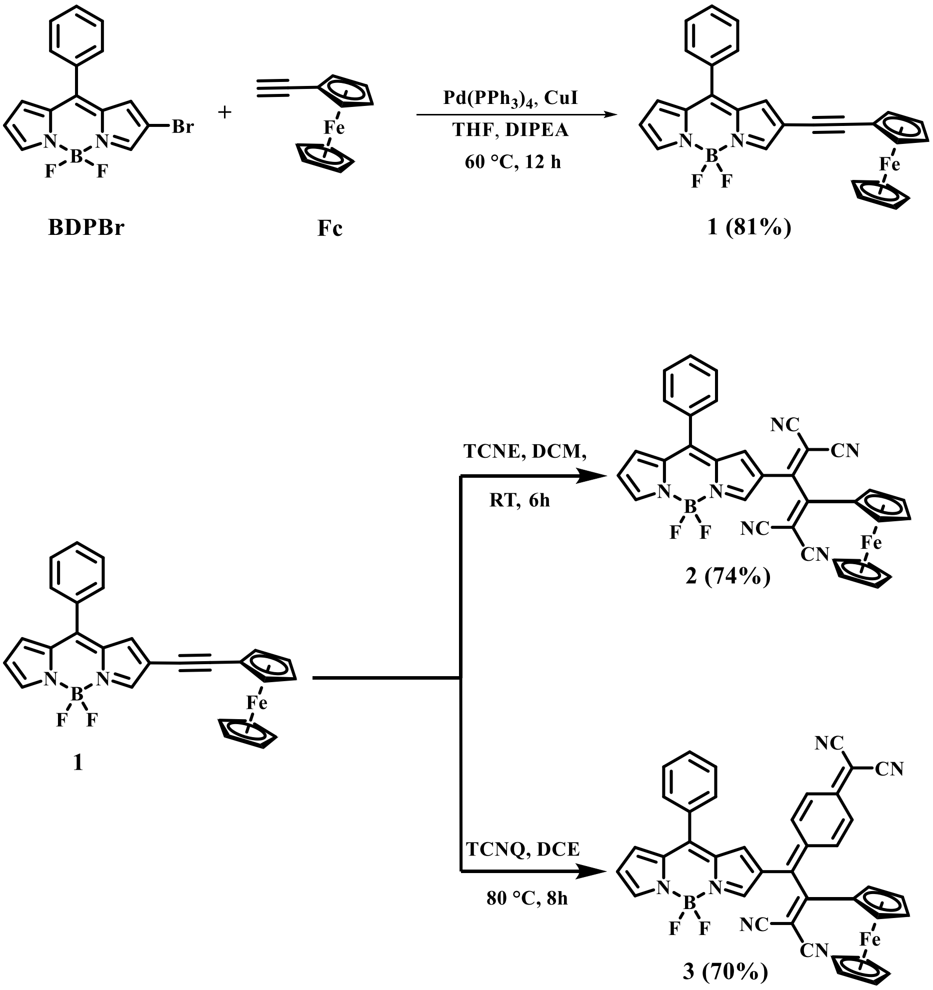
Tetracyanoquinodimethane (TCNQ) (42 mg, 0.21 mmol) was added to a solution of compound 1 (100 mg, 0.21 mmol) in DCE (dichloroethane) solvent (50 mL). The mixture was stirred at 80 °C for 8 h. The solvent was removed in a vacuum, and the product was purified by column chromatography with hexane/dichloromethane (1/4, v/v) as the eluent to yield 3 as a dark brown colored solid. Yield: 70%.

^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.31 (d-d, 1H, J= 4 Hz), 8.21 (s, 1H), 7.77 (s, 1H), 7.71-7.67 (m, 1H) 7.63-7.55 (m, 5H), 7.49-7.46 (m, 1H), 7.24-7.16 (m, 2H), 6.77 (t, 2H, J=8 Hz), 4.99 (s, 1H), 4.85 (s, 1H), 4.45 (s, 1H), 4.38 (s, 4H). ^{11}B NMR (160 MHz, $CDCl_3$, δ in ppm): 0.21, 0.04, 0.13. HRMS (ESI-TOF) m/z = calculated for $C_{39}H_{23}BF_2FeN_6$ = 681.1475 $[M + H]^+$, founded 681.1489 $[M + H]^+$.

Chapter 4

RESULTS AND DISCUSSION

4.1 Synthesis



Scheme 5. Synthesis route of **BODIPY** dyes **1–3**.

The BODIPY **1** was synthesized *via* the Pd(II)-catalyzed Sonogashira cross-coupling reaction in 81% yield. [29] The push–pull BODIPY **2** and **3** were synthesized by the [2 + 2] CA-RE reaction of BODIPY **1** with strong acceptor TCNE and TCNQ units. The push–pull BODIPY **2** was synthesized by the reaction of BODIPY **1** with TCNE at room temperature for 6 h in DCM in 74% yield. Similarly, BODIPY **3** was synthesized by the reaction of BODIPY **1** with TCNQ in DCE at 80 °C for 8 h which resulted in 70% yield (Scheme 5).

The push–pull BODIPYs **2** and **3** and control compound **1** were purified by silica-gel column chromatography (silica-gel size = 100-200 mesh) using hexanes /DCM as a solvent. The ^{1}H NMR, ^{13}C NMR,^{11}B NMR and HRMS techniques were used to characterize the molecular structures of the push–pull BODIPYs.

4.2 Photophysical properties

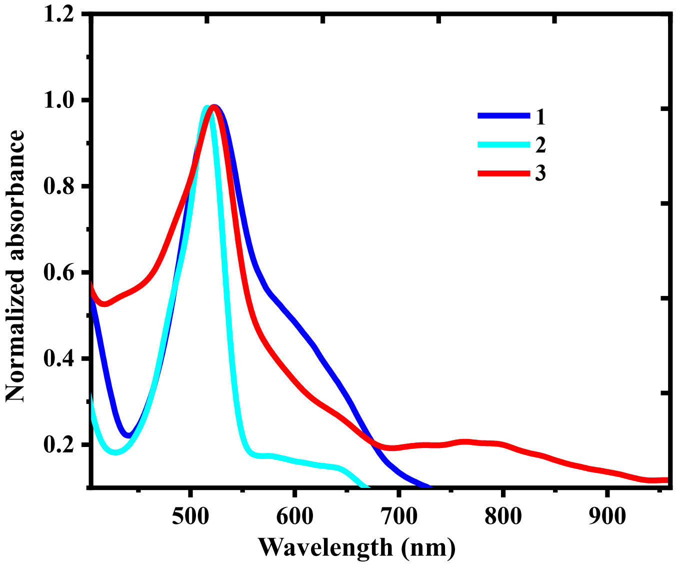


Figure 3. Normalized electronic absorption spectra of *β*-ferrocenyl substituted BODIPYs **1**–**3** in DCM (1×10^{-4} M).

Electronic absorption spectra of the ferrocenyl BODIPYs **1**–**3** were recorded in DCM at 10^{-4} M concentration (Figure 3). BODIPYs show absorption bands around 500–530 nm with a broad shoulder at higher energy region. The *β*-ferrocenyl substituted BODIPYs 1–3 exhibit absorption maxima at 527 nm, 517 nm and 526 nm respectively corresponding to the $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition of the BODIPY unit.[30-31] Compound **3** displays an additional broad absorption band ranging from 650 to 850 nm, due to the intramolecular charge transfer from donor to acceptor unit of the molecule. BODIPYs

1–3 displays molar extinction coefficient values of 18000, 24000 and 26000 $M^{-1}.cm^{-1}$ respectively.

Table 1. Photophysical properties of ***β***-ferrocenyl substituted BODIPYs **1–3**.

BODIPY	**λ_{abs} (nm)^a**	**ε ($M^{-1}.cm^{-1}$)^a**	**E_g^{b}**
1	527	18000	2.34
2	517	24000	2.52
3	526	26000	2.21

[a]Absorbance measured in dichloromethane at 1 × 10^{-4} M concentration, ε: extinction coefficient; [b]HOMO–LUMO band gap obtained from DFT calculation.

Expanded TCBD incorporated BODIPY **3** shows absorption at longer wavelength compared to **1** and **2**. This could be due to strong electron deficient characteristics of DCNQ unit.

4.3 Density functional theory

The density functional theory (DFT) calculation was carried out to understand the geometry and electronic structure of the ferrocenyl substituted BODIPYs 1–3 using the Gaussian 09W program. The DFT calculation was performed at the B3LYP/6-31+G** for C, H, O, N, B, F and Lanl2DZ for Fe level of theory and geometry optimization was carried out in the gas phase. The frontier molecular orbitals are displayed in Figure 4.[32] The optimized structures of the push–pull BODIPYs **1**–**3** exhibit twisted geometry due to the incorporation of ferrocene and strong acceptor TCBD and DCNQ.

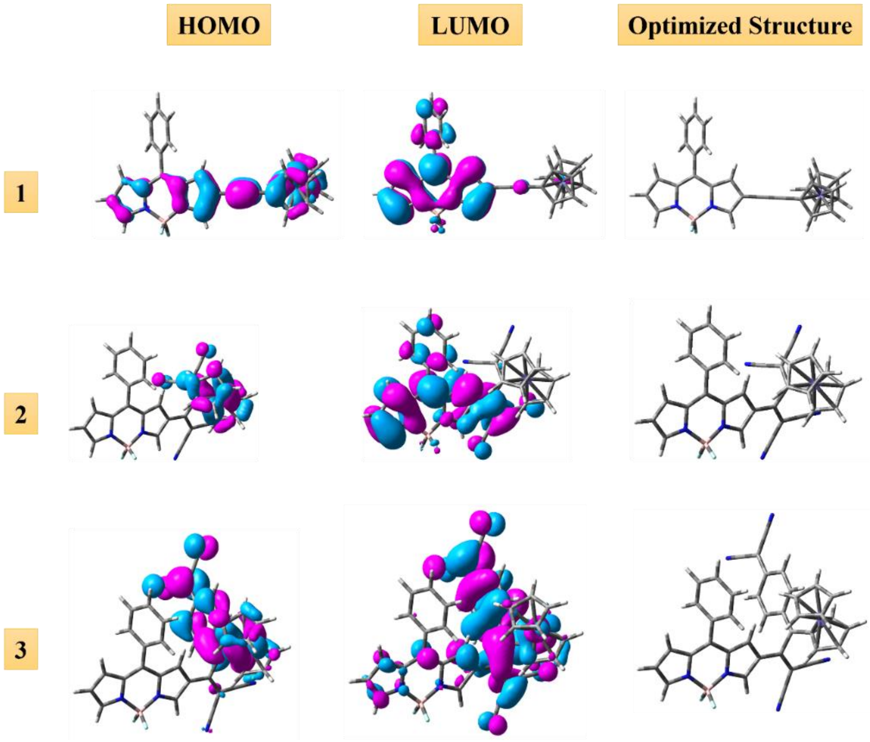


Figure. 4 The frontier molecular orbitals of the ***β***-ferrocenyl BODIPYs 1–3.

The LUMOs of the ***β***-ferrocenyl substituted BODIPY 1 are concentrated on BODIPY unit, whereas the HOMOs are distributed over the ferrocenyl and BODIPY units. The HOMOs of the TCBD substituted BODIPY 2 is localized on ferrocenyl unit whereas the LUMO orbital is distributed over BODIPY and TCBD units. In case of DCNQ incorporated BODIPY 3 HOMO is concentrated on ferrocenyl unit, whereas the LUMO is distributed over DCNQ and BODIPY units.

The DFT-predicted energy level diagram is shown in figure **5**. BODIPY **1** shows band gap of 2.34 eV, BODIPY **2** shows band gap of 2.52 eV whereas, BODIPY **3** exhibits the lowest band gap of 2.34 eV among all the ferrocenyl BODIPYs. The push–pull BODIPY **3** exhibits the lowest HOMO–LUMO gap and signifies that the DCNQ unit acts as a strong acceptor compared to the TCBD unit. The theoretically predicted HOMO energy levels of the push–pull BODIPYs **1–3** are –5.32, –5.93 and –5.74 eV, and the associated LUMO levels are –2.98, –3.41, and –3.53 eV, respectively. The trend in the LUMO energy level of BODIPYs **1–3** follows the order 1 > 2 > 3. The computationally calculated HOMO–LUMO gap values of push–pull BODIPYs **1–3** is 2.34, 2.52, and 2.21 eV, respectively.

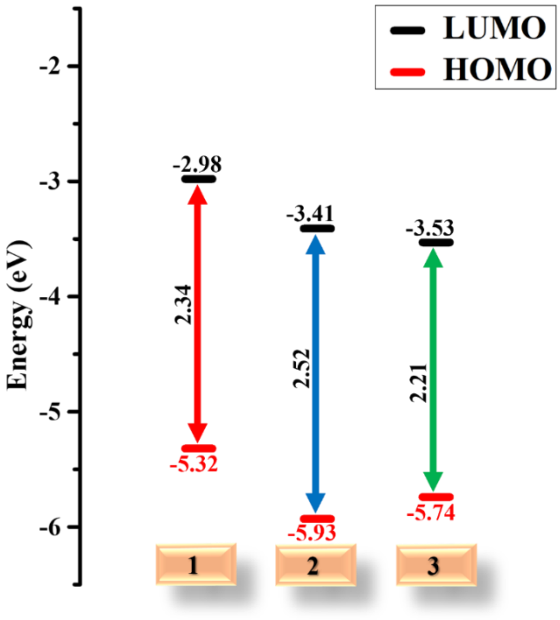


Figure 5. Energy level diagram of BODIPY dyes **1–3**.

Chapter 5

Conclusion

In conclusion we have synthesized ***β***-ferrocenyl substituted BODIPY 1 *via* Sonogashira cross-coupling reaction and its TCBD and DCNQ functionalized derivatives 2 and 3 *via* [2+2] CA-RE reaction. The effect of the TCBD and DCNQ acceptor units on the photophysical and computational properties of the ferrocenyl BODIPYs were investigated. BODIPY 3 exhibited the most red-shifted absorption in 650 to 850 nm region due to the intra molecular charge transfer from donor to acceptor part of the molecule. Computational studies reveal that BODIPY 3 exhibits lowest HOMO–LUMO band gap which could be due to the strong electron deficient characteristics of the DCNQ unit. The theoretically obtained results are in good agreement with the photophysical observations. Absorption in Vis-NIR region and low HOMO-LUMO energy gap makes these BODIPYs potential candidates for various optoelectronic applications.

Chapter 6

SUPPORTING INFORMATION

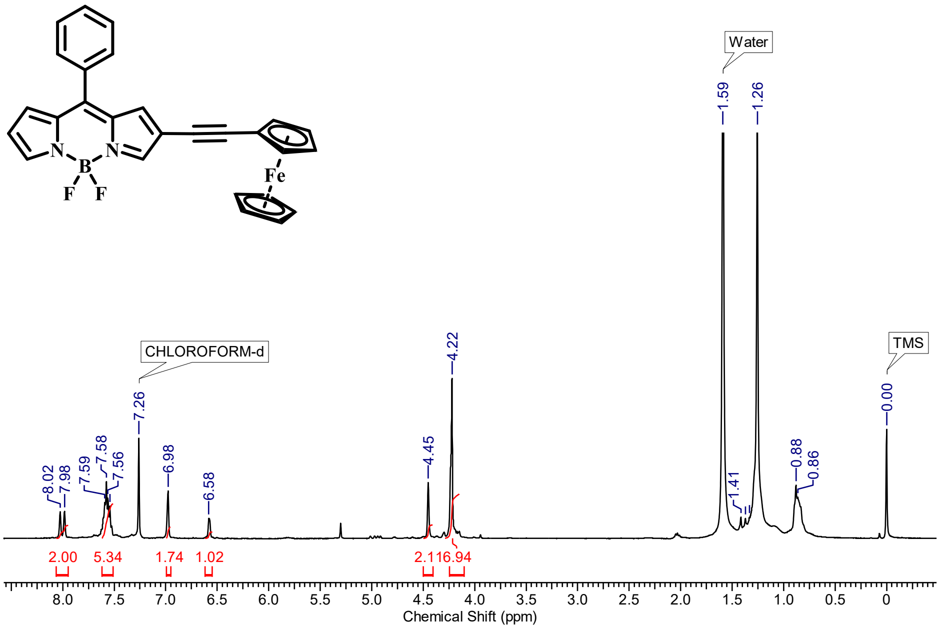


Figure 6. ${}^{1}H$ NMR of BODIPY **1.**

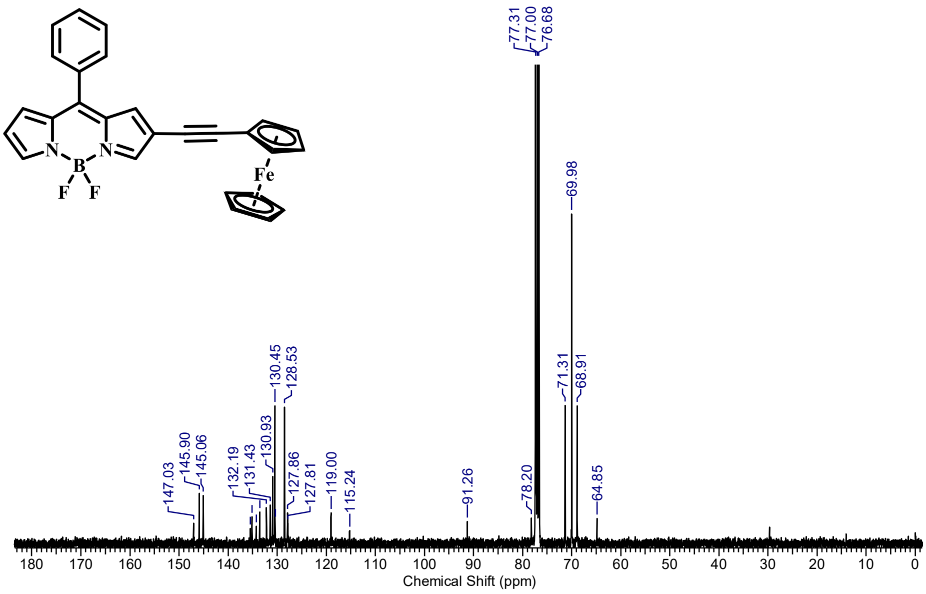


Figure 7. ^{13}C NMR of BODIPY **1.**

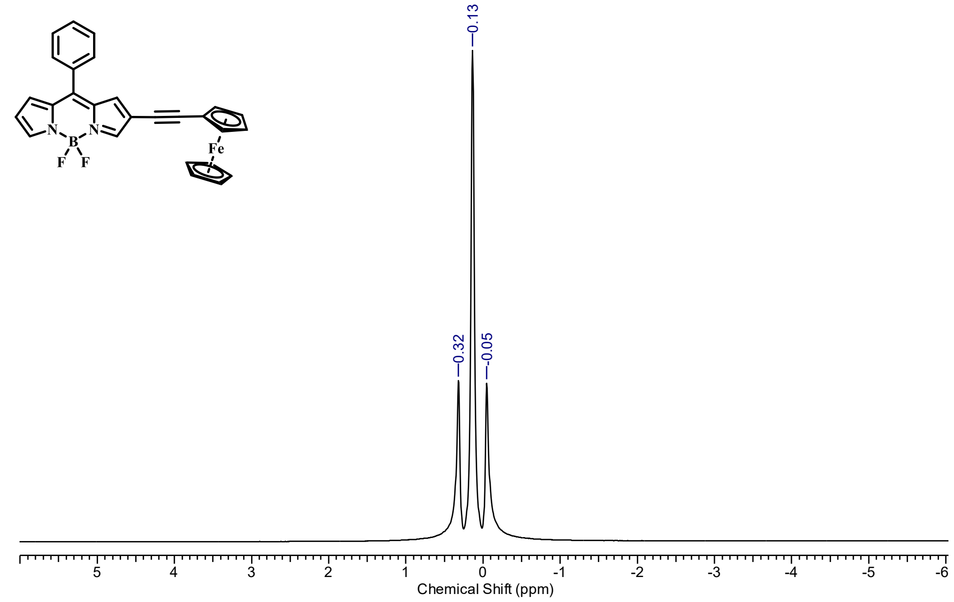


Figure 8. ^{11}B NMR of BODIPY **1.**

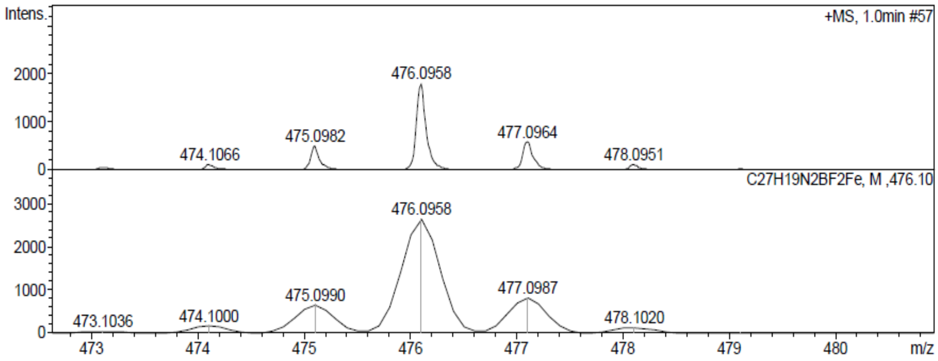


Figure 9. HRMS of BODIPY **1.**

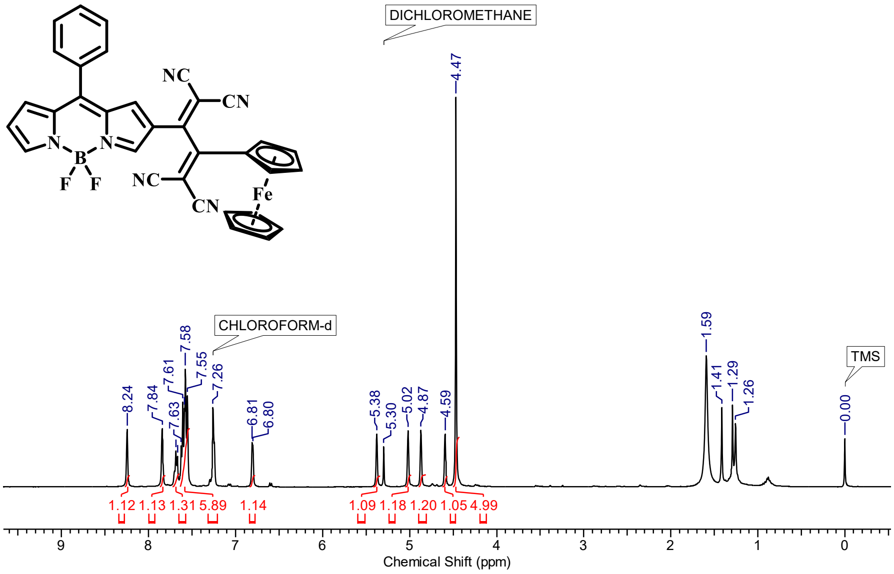


Figure 10. ^{1}H NMR of BODIPY **2.**

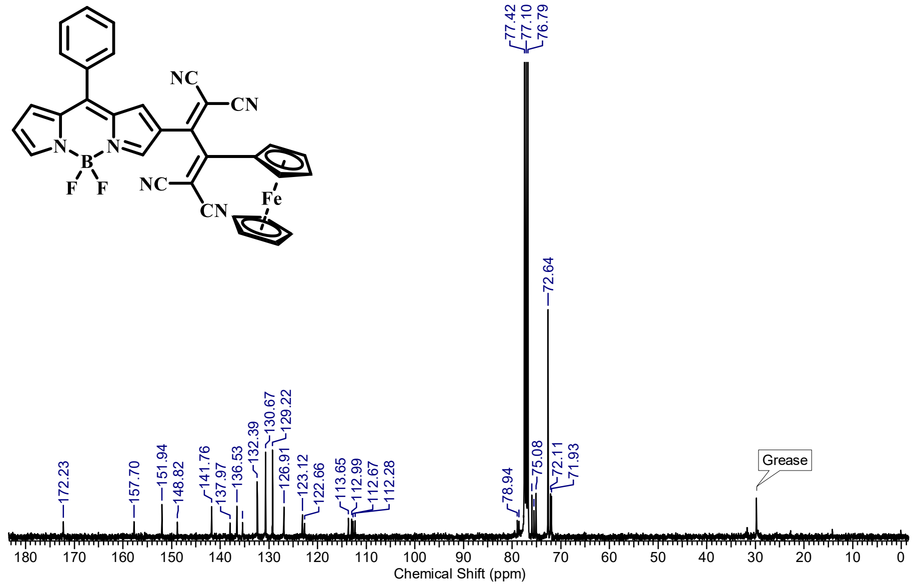


Figure 11. ^{13}C NMR of BODIPY **2.**

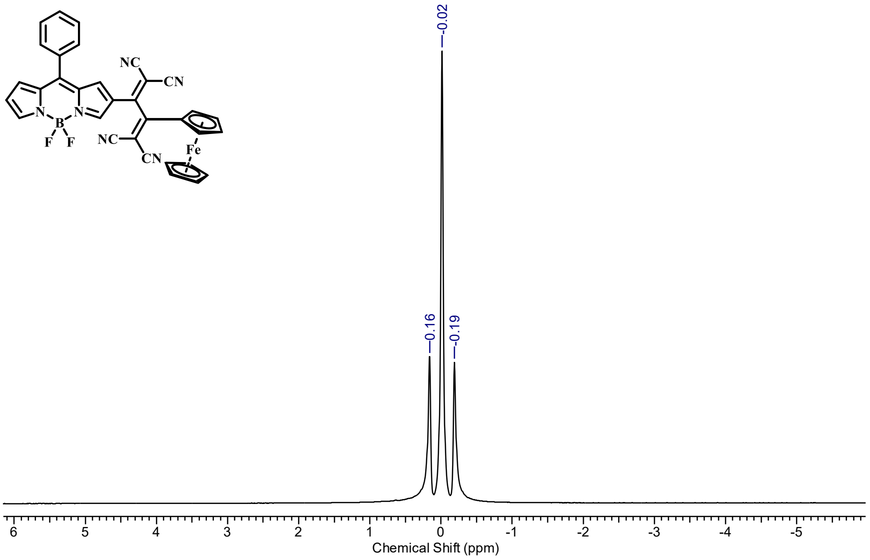


Figure 12. ^{11}B NMR of BODIPY **2.**

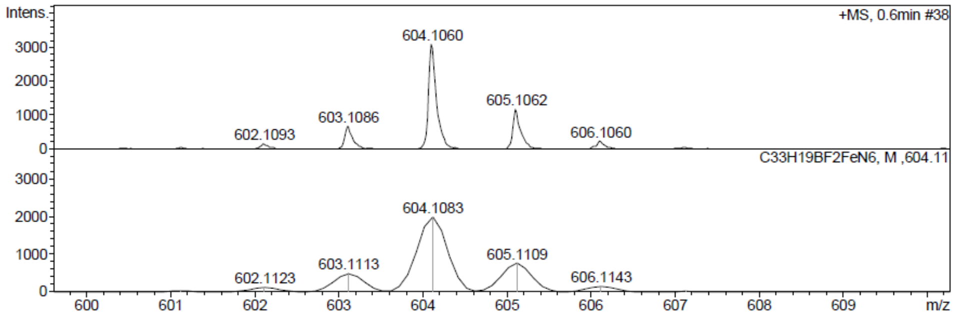


Figure 13. HRMS of BODIPY **2.**

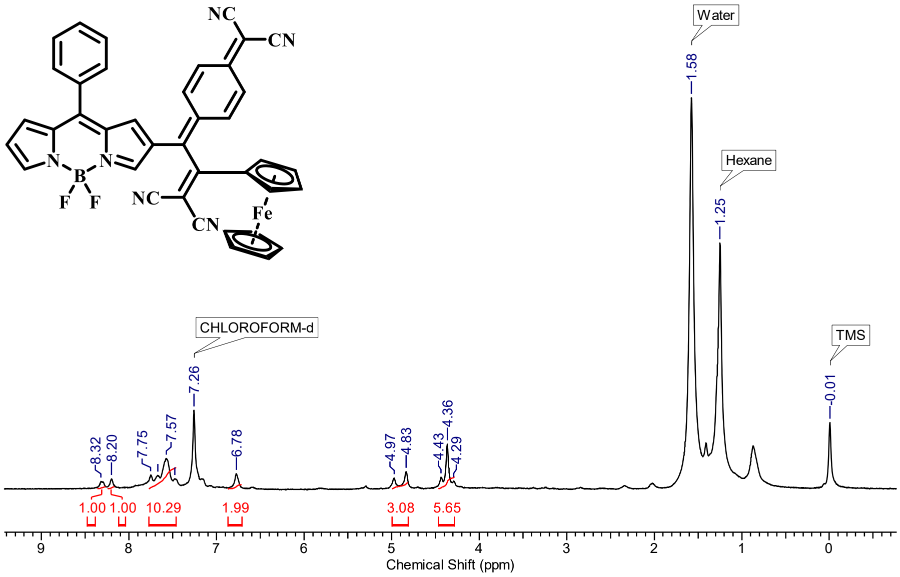


Figure 14. ^{1}H NMR of BODIPY **3.**

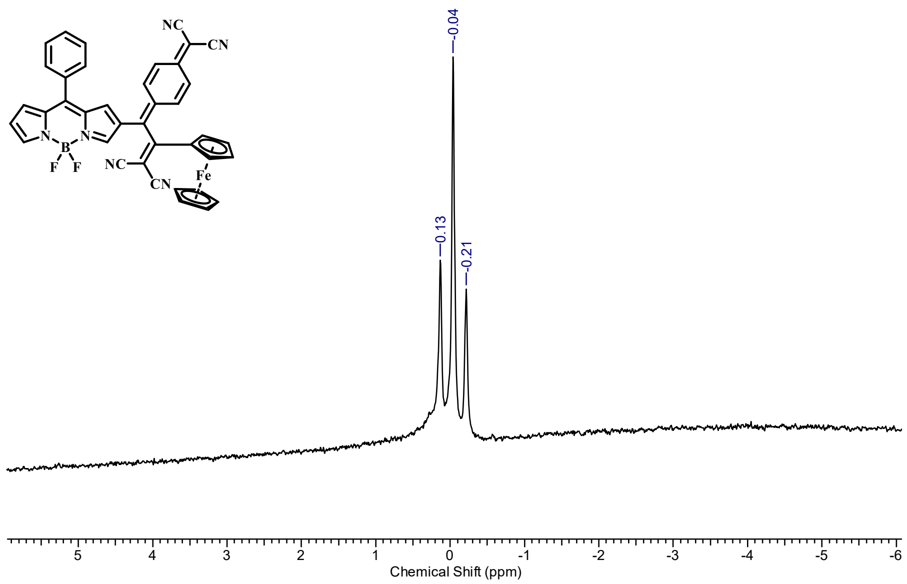


Figure 15 ^{11}B NMR of BODIPY **3.**

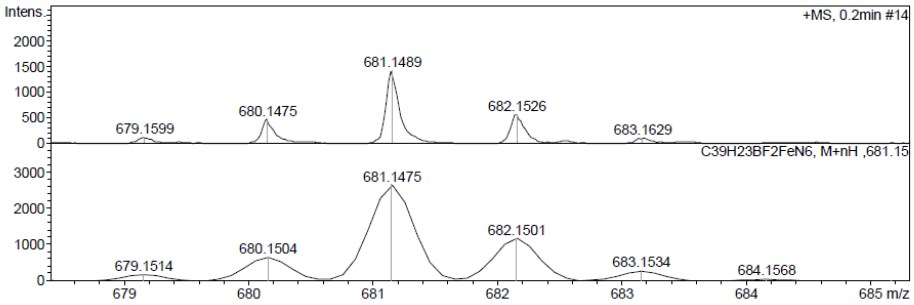


Figure 16. HRMS of BODIPY **3.**

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