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Synthesis, Redox Properties, and Electronic Coupling in the Diferrocene Aza-dipyrromethene and azaBODIPY Donor−Acceptor Dyad with Direct Ferrocene−*α*-Pyrrole Bond

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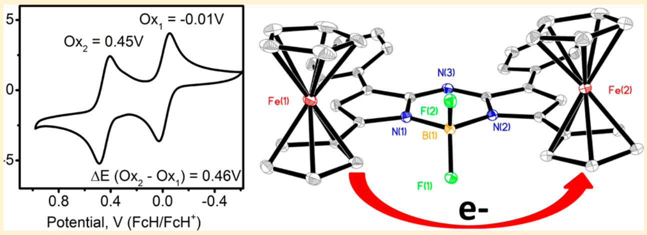
Supporting Information

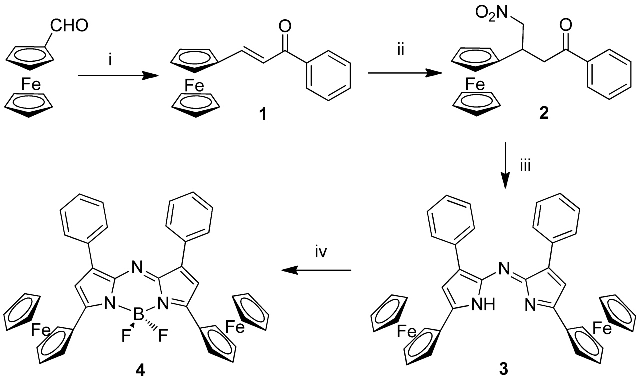
ABSTRACT: 3,3′-Diferrocenylazadipyrromethene (**3**) and corresponding difluoroboryl (azaBODIPY) complex (**4**) were synthesized in several steps from ferrocenecarbaldehyde, following the well-explored chalcone-type synthetic approach. The novel diiron complexes, in which ferrocene groups are directly connected to the *α*-pyrrolic positions were characterized by a variety of spectroscopic techniques, electrochemistry, spectroelectrochemistry, and X-ray crystallography, while their electronic structure, redox properties, and UV−vis spectra were correlated with the density functional theory (DFT) and time-dependent DFT calculations.



■ INTRODUCTION

The preparation of new functional materials that are highly efficient for solar energy conversion is of fundamental interest.[1] Donor−acceptor dyads or donor−antennae−acceptor triads that can generate long-lived highly energetic charge-separated (CS) states have been proposed for applications as soft light-harvesting materials.[2] Because of their well-known absorption properties in the visible electromagnetic spectrum, a large variety of porphyrins and their analogues coupled with organometallic or organic donor groups have been tested as donor−acceptor dyads for organic photovoltaics (OPVs) and dye-sensitized solar cells (DSSCs).[3] Ferrocene-substituents were found to be potentially useful as electron-donating groups for light-harvesting assemblies. Not surprisingly, photophysical as well as redox properties of ferrocene-porphyrins, subphthalocyanines, phthalocyanines, and tetraazaporphyrins have also been intensively investigated in recent years.[4] More recently, dipyrromethenes, azadipyrromethenes, and their borylated derivatives BODIPYs and azaBODIPYs have attracted significant attention because of their specific photophysical properties.[5] During the past decade, several ferrocene-(aza)dipyrromethenes and ferrocene-(aza)BODIPY conjugates in which ferrocene substituent is connected to the chromophoric unit via spacer located at *α*-, *β*-pyrrolic, or *meso*-position were reported.[6] To the best of our knowledge, however, no reports are available on azadipyrromethenes and azaBODIPYs with ferrocene groups connected directly to the heterocyclic chromophore. Thus, in this paper, we report preparation and characterization of the ferrocenyl-containing azadipyrromethene and azaBODIPY donor−acceptor dyads **3** and **4** (Scheme 1) with direct ferrocene-*α*-pyrrole bond.

Scheme 1. Preparation of the Target Azadipyrromethene 3 and azaBODIPY 4[a]



[a]Reagents and conditions: (i) $PhCOCH_3$, NaOH/EtOH, rt/24 h, yield 68%; (ii) CH_3NO_2, NEt_3/EtOH, heat/72 h, yield 70%; (iii) NH_4OAc, EtOH, heat/72 h, yield 4.4%; (iv) $BF_3{\cdot}Et_2O$ DIPEA/CH_2Cl_2 heat/24 h, yield 47%.

■ RESULTS AND DISCUSSION

The precursor to the azadipyrromethene modified with ferrocene at the *α*-pyrrolic positions is the chalcone **1**, which can be synthesized via an aldol condensation with ferrocenecarbaldehyde.

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The chalcone **1** was further modified with nitromethane by using a Michael addition to afford compound **2**, which is then reacted with ammonium acetate in refluxing ethanol to produce azadipyrromethene **3**. The corresponding ferrocene-containing azaBODIPY **4** can be generated by reaction of **3** with $BF_3 \cdot Et_2O$ in the presence of a base (DIPEA). Organometallic azadipyrromethene **3** and azaBODIPY **4** are stable in the solid state in air and can be purified by conventional chromatographic methods, but slowly degrade upon prolonging standing in solution under ambient atmosphere. Structures of the target compounds **3** and **4** were confirmed by the X-ray diffraction analysis (Figure 1 and Tables S1−2) and further elucidated by ^1H and ^{13}C NMR spectroscopy (Supporting Information), UV−vis spectra (Figure 2), and elemental analyses.

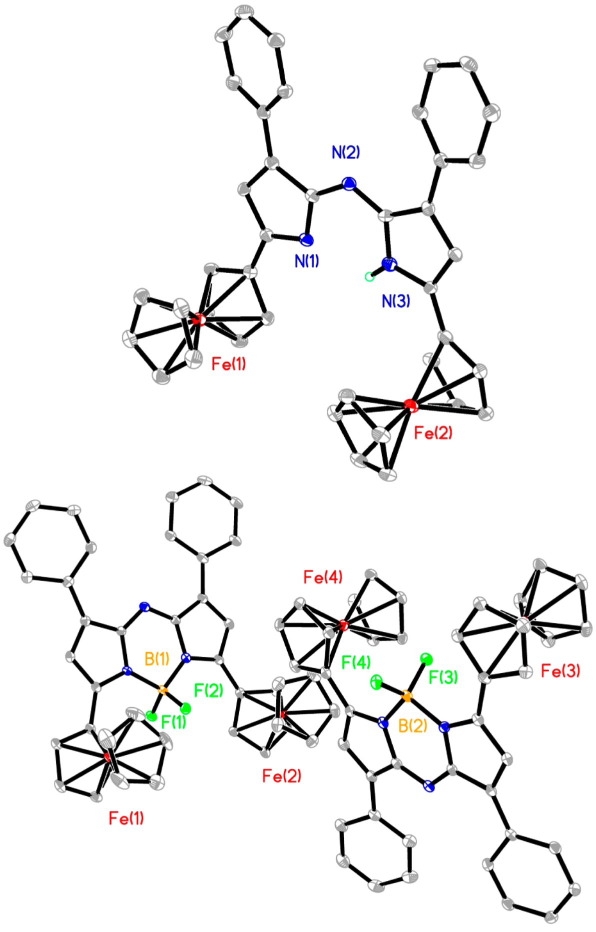

Figure 1. X-ray crystal structure of **3** (top) and two crystallographically independent molecules of **4** (bottom).

Experimental crystal structures of **3** and **4** are shown in Figure 1, while their detailed descriptions are provided in Supporting Information Tables S1 and S2. In the X-ray crystal structures of both complexes **3** and **4**, ferrocene groups were found in a syn conformation. The torsion angles between the ferrocene and pyrrole fragments vary between 7.63° and 20.25° in **3**, while they are significantly smaller in the case of complex **4** (1.25−4.54°). The torsion angles between the phenyl and pyrrole groups follow the same trend: they are larger in complex **3** (19.81−21.25°) compared to those in complex **4** (12.07−20.38°). Because of the larger ferrocene to pyrrole torsion angle, the crystallographic Fe−Fe distance in complex **3** is smaller (6.827 Å) than those in **4** (7.125−7.401 Å).

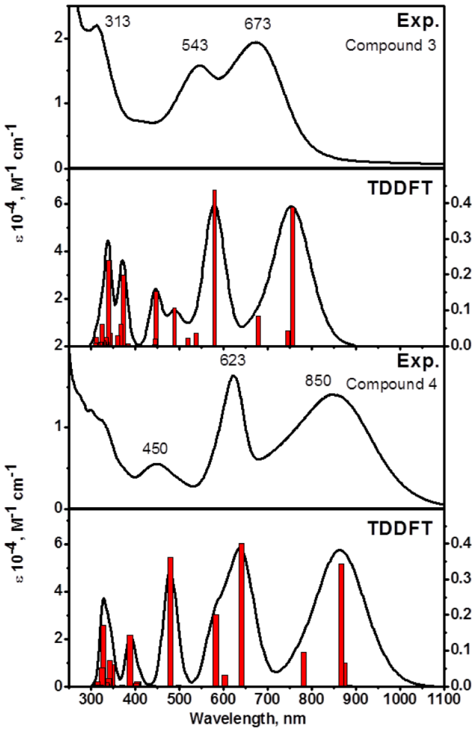

Figure 2. Experimental (CH_2Cl_2) and PCM-TDDFT predicted UV−vis spectra of **3** (top) and **4** (bottom).

In agreement with the other ferrocene-BODIPY dyads, complexes **3** and **4** have two major bands in the visible region with the lower energy band being broader compared to the higher energy band (Figure 2). These bands in ferrocenyl-containing azadipyrromethene derivative **3** (546 and 673 nm) were observed at significantly higher energies compared to those in azaBODIPY **4** (623 and 850 nm). Steady-state fluorescence measurements in **3** and **4** are indicative of complete quenching in both systems and agree well with the standard quenching mechanism in ferrocene-containing compounds.[7] According to this mechanism, electron-transfer from the low-spin iron(II) center in ferrocene to the photoexcited azadipyrromethene or azaBODIPY core is predominantly responsible for the fluorescence quenching.

The redox properties of diiron compounds **3** and **4** were studied using electrochemical CV and DPV methods (Figure 3 and Supporting Information Table S3). In both cases two reversible oxidations of ferrocene substituents were observed. The difference in potential between the first and the second oxidations waves is 340 and 460 mV for complexes **3** and **4**, respectively, in CH_2Cl_2/0.05 M TBAF system (TBAF = tetrabutylammonium tetrakis

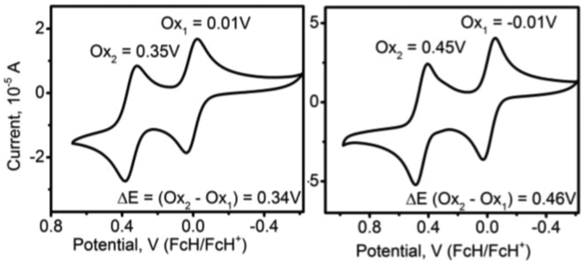

Figure 3. Room-temperature CV data on compounds **3** (left) and **4** (right) in CH_2Cl_2/0.05 M TBAF system.

(pentafluorophenyl)borate, which is indicative of their electronic coupling (Figure 3).[8] Although electronic coupling in one diferrocene BODIPY system has been previously described,[6c] the magnitude of electronic communication between the ferrocene units in compounds **3** and **4** is unprecedented. Oxidation of the azaBODIPY core was not observed for both compounds **3** and **4** within electrochemical window, while irreversible (compound **3**) and reversible (compound **4**) reduction was observed at −1.42 and −1.15 V, respectively.

To clarify the nature of redox-active species in oxidized forms of **3** and **4**, we have conducted spectroelectrochemical oxidation and reduction experiments (Figure 4 and Supporting Information Figures S5 and S6). In the case of azaBODIPY **4**, during the first oxidation process, both major bands in visible region lose their intensity and three new bands at 639, 760, and 996 nm appear in the spectrum. In addition, new broad NIR band appears in the spectrum (Figure 4). This band spans between ∼1700 and 2650 nm and is centered outside of the accessible range for our spectrometer. The appearance of the NIR bands in 4^+ is clearly suggestive of its mixed-valence character and resembles the ferrocenyl-containing mixed-valence porphyrins discussed earlier.[4l−o] During the second oxidation, all NIR bands lose their intensities and new intensive band at 697 nm appears in the visible region (Figure 4). Similar behavior has been also observed for $3 \rightarrow 3^+ \rightarrow 3^{2+}$ transformation under spectroelectrochemical conditions (Supporting Information Figure S6). It is important to note that 4^{2+} cation generated under spectroelectrochemical oxidation conditions can be easily reduced back to the neutral **4**.

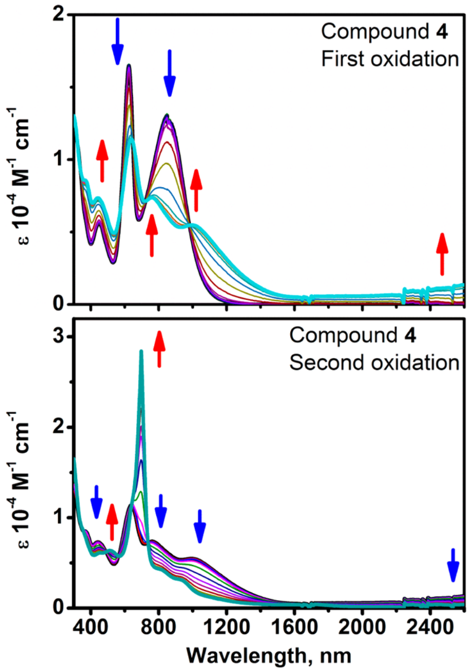

Figure 4. Room-temperature spectroelectrochemical oxidation of **4** at first (top) and second (bottom) oxidation potentials in CH_2Cl_2/0.15 M TBAF system.

The electronic structure and the vertical excitation energy calculations for compounds **3** and **4** (Figures 2 and 5 and Supporting Information) correlate well with the experimental results. First, DFT calculations suggest that the energies and electronic structures of syn and anti conformations of **3** and **4** are very close to each other. In agreement with the electrochemical data, HOMO−HOMO−5 MOs in complexes **3** and **4** are predominantly ferrocene-centered, while HOMO−6 and HOMO−7 are π-orbitals centered on heterocyclic core. In addition, HOMO and HOMO−4 in **3** and **4** have substantial (∼20−40%) π-character. The LUMO in both compounds is predominantly heterocycle-centered π*-orbital and energetically well separated from the LUMO+1. Such electronic structure results in appearance of numerous low-energy ferrocene-to-chromophore MLCT transitions predicted by the TDDFT calculations (Figure 2). MLCT transitions, which originate from almost pure ferrocene MOs (HOMO−1 to HOMO−3) to LUMO are predicted to have low intensities, while similar transitions from the mixed ferrocene-chromophore HOMO and HOMO−4 to LUMO are predicted to be intense (Supporting Information). TDDFT calculations also correctly predict low-energy shifts of the major bands in UV−vis spectra going from **3** to **4** (Figure 2). The major reason for such a shift is the substantial stabilization of LUMO in **4** compared to **3**.

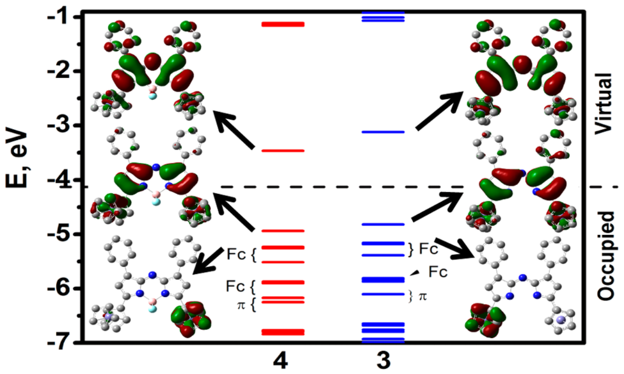

Figure 5. DFT-PCM (TPSSh/6-311G(d)) calculated orbital energies for complexes **3** and **4** with pictorial representation of the frontier MOs.

■ CONCLUSIONS

In conclusion, we have synthesized and characterized the first azadipyrromethene and azaBODIPY complexes with ferrocene substituents directly connected to the α-pyrrolic carbon atom position. The ferrocene units in these compounds are electronically coupled to each other. The DFT and TDDFT calculations on target systems **3** and **4** are in reasonable agreement with the experimental data and suggesting of the predominantly ferrocene-centered MOs in the HOMO region and chromophore π*-character LUMO.

■ EXPERIMENTAL SECTION

Materials. Chemicals were obtained commercially and used without further purification. Basic alumina (50−200 μm) was purchased from Sorbent Technologies. The tetrabutylammonium tetrakis-(pentafluorophenyl)borate (TBAF) was used in anhydrous DCM for electrochemical studies, after preparation according to literature procedures.[8a]

Instrumentation. UV−vis data were obtained on Jasco-720 spectrophotometer. Electrochemical measurements were conducted using a CH Instruments electrochemical analyzer utilizing a three-electrode scheme with platinum working, auxiliary, and Ag/AgCl reference electrodes in a 0.05 M solution of TBAF in DCM with redox potentials corrected using an internal standard (decamethylferrocene, FcH*) in all cases. The redox potentials were then corrected to ferrocene using appropriate oxidation potentials for FcH*/FcH*⁺ versus FcH/FcH^+ in the CH_2Cl_2/0.05 M TBAF system. NMR spectra were recorded on a Varian Mercury 300 MHz and Varian NMRS 500 MHz spectrometers with a 500 MHz frequency for protons and 125 MHz for carbon. Chemical shifts were reported in parts per million (ppm) with respect to residual solvent peaks as internal standard

(^{1}H CDCl$_3$, δ = 7.26 ppm, DMSO-d6, δ = 2.50 ppm; ^{13}C CDCl$_3$, δ = 77.36 ppm, DMSO-d6, δ = 39.7 ppm) and referenced to tetramethylsilane [Si(CH$_3$)$_4$]. FTIR spectra were recorded on a Nicolet iS5 spectrometer using NaCl disks. Elemental analyses were performed by Atlantic Microlab of Norcross, GA 30091. Electrospray MS (ES-MS; positive mode) spectra were recorded using a Bruker HCT-ultra ETD II Ion Trap mass spectrometer.

Computational Aspects. All computations were performed using Gaussian 09 software running under Windows or UNIX OS.[9] Molecular orbital contributions were compiled from single point calculations using the VMOdes program.[10] In all calculations, TPSSh hybrid (10% of Hartree−Fock exchange)[11] exchange correlation functional was used because it was found in a set of model gas-phase calculations that it is superior over standard GGA (BP86)[12] and hybrid B3LYP[13] exchange-correlation functionals. Indeed, use of hybrid B3LYP exchange-correlation functional results in HOMO, which is purely azaBODIPY centered MO in disagreement with experimental data, while calculated using BP86 exchange-correlation functional vertical excitation energies for MLCT transitions were found to be severely underestimated. In all calculations, Wachter's full-electron basis set for iron and 6-311G(d) basis set for all other atoms were employed.[14] Solvent effects were modeled using PCM approach.[15] In all TDDFT calculations, the lowest 40 excited states were calculated to cover experimentally observed transitions in UV−vis region.

Synthesis. *Compound 1.* This compound has been previously synthesized.[16] An ethanolic solution of 1.00 g of acetylferrocene (4.4 mmol) and 0.44 mL of benzaldehyde (4.4 mmol) were mixed in a 250 mL Erlenmeyer flask and 2 mL of a 30% aqueous NaOH solution was added dropwise after mixing. The reaction mixture turned dark orange upon addition of the base. After 24 h of reaction, an excess amount of cold water was added with vigorous stirring to the flask until a solid precipitate was observed. The solid was collected, washed with cold water, and air-dried. The purity of the crude product was determined at this point using TLC and ^{1}H NMR spectroscopy. The spectral characteristics were in good agreement with those found in the literature. Yield: 1.3 g (68%). ^{1}H (CDCl$_3$): δ (ppm) 7.82 (d, 1H, J = 15 Hz, trans H); 7.67 (s, 2H, H on benzene); 7.43 (s, 3H, H on benzene); 7.15 (d, 1H, J = 15 Hz, trans H); 4.93 (s, 2H, Cp on ferrocene); 4.61 (s, 2H, Cp on ferrocene); 4.23 (s, 5H, Cp on ferrocene).

Compound 2. Compound **1** (1.00 g, 2.4 mmol), nitromethane (0.64 mL, 12 mmol), and triethylamine (3.01 mL, 21.6 mmol) were combined in 30 mL of ethanol and heated to reflux for 72 h. The ethanol was removed, and the resulting oil extracted with CH$_2$Cl$_2$ (50 mL) and water (50 mL). The organic layer was washed with DI water (2 × 50 mL), and the organic fractions were dried over anhydrous magnesium sulfate. The solvent was removed, and the resulting brown oily product used in the next step without further purification. Yield: 0.81 g (70%).

Compound 3. An ethanolic solution of **2** (2 g, 4.14 mmol) and ammonium acetate (9.57 g, 124.2 mmol) was refluxed for 48 h. After the solution was cooled to room temperature, the solvent was removed and crude product was dissolved in CH$_2$Cl$_2$ and washed with water. The CH$_2$Cl$_2$ layer was collect, dried over Na$_2$SO$_4$, and evaporated to dryness. The collected dark solution was purified by column chromatography using basic alumina and CH$_2$Cl$_2$ as the mobile phase. The pure product is purple solid. Yield 0.12 g (4.35%, based on **1**). Purple crystals were obtained from CH$_2$Cl$_2$ solution. ^{1}H NMR (CDCl$_3$) δ: 8.09 (d, 2H, J = 6 Hz), 7.35−7.43 (m, 3H), 6.82 (s, 1H), 4.89 (s, 2H, Cp on ferrocene), 4.61 (s, 2H, Cp on ferrocene), 4.23 (s, 5H, Cp on ferrocene). Anal. Calcd for **3**·0.7H$_2$O C$_{40}$H$_{31}$Fe$_2$N$_3$(H$_2$O)$_{0.7}$: C, 70.86; H, 4.82; N, 6.20%. Found: C, 70.73; H, 4.66; N, 6.24%.

Compound 4. Compound **3** (0.04 g, 0.06 mmol) was dissolved in CH$_2$Cl$_2$ (40 mL). Diisopropylethylamine (0.021 mL, 0.12 mmol) and boron trifluoride diethyl etherate (0.015 mL, 0.12 mmol) were added and the mixture was stirred at room temperature for 24 h. The mixture was washed with water and the organic layer was separated, dried over Na$_2$SO$_4$, and evaporated to dryness. The residue was purified by column chromatography (basic alumina) with CH$_2$Cl$_2$ to give the product as a green solid. Yield: 0.02 g (47%). Green crystals were obtained from CH$_2$Cl$_2$/hexane solution. ^{1}H NMR (CDCl$_3$) δ: 8.10 (d, 2H, J = 6 Hz), 7.44−7.47 (m, 3H), 6.95 (s, 1H), 5.40 (s, 2H, Cp on ferrocene), 4.83 (s, 2H, Cp on ferrocene), 4.27 (s, 5H, Cp on ferrocene). Anal. Calcd for **4**·0.26H$_2$O·1.8(CH$_2$Cl$_2$) C$_{40}$H$_{30}$Fe$_2$N$_3$BF$_2$(H$_2$O)$_{0.26}$(CH$_2$Cl$_2$)$_{1.8}$: C, 57.73; H, 3.96; N, 4.83%. Found: C, 57.82; H, 4.13; N, 4.64%.

X-ray Crystallography. X-ray intensity data for compound **3** was measured on a CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (Mo Kα radiation, λ = 0.71073 Å) operated at 2000 W power. Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystal. A specimen of **3** approximate dimensions 0.22 mm × 0.13 mm × 0.09 mm was used for the X-ray crystallographic analysis. Data were acquired using three sets of Omega scans at different Phi settings. The frame width was 0.5°. The structure was solved and refined using the Bruker SHELXTL Software Package,[17] using the space group $P_{2(1)}/c$, with Z = 4 for the formula unit, C$_{40}$H$_{31}$Fe$_2$N$_3$. Hydrogen atoms were assigned ideal positions and refined isotropically as riding atoms.

X-ray intensity data for **4** was collected on a CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu Kα radiation, λ = 1.54178 Å). Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K. A specimen of **4** approximate dimensions 0.26 mm × 0.32 mm × 0.59 mm, was used for the X-ray crystallographic analysis. The integration of the data using a triclinic unit cell yielded a total of 35640 reflections to a maximum θ angle of 62.99° (0.87 Å resolution), of which 9559 were independent (average redundancy 3.728) The structure was solved and refined using the Bruker SHELXTL Software Package,[17] using the space group $P\bar{1}$, with Z = 4 for the formula unit, C$_{40}$H$_{30}$BF$_2$Fe$_2$N$_3$. Hydrogen atoms were assigned ideal positions and refined isotropically as riding atoms. Crystal data and structure refinement parameters for **3** and **4** are summarized in Supporting Information Table S2. CCDC reference numbers: CCDC 986211 (**3**) and CCDC 986212 (**4**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic and DFT data for target compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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