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1,1′-Biferrocenylenes—The More Redox Stable Ferrocenes! New Derivatives, Corrected NMR Assignments, Redox Behavior, and Spectroelectrochemistry

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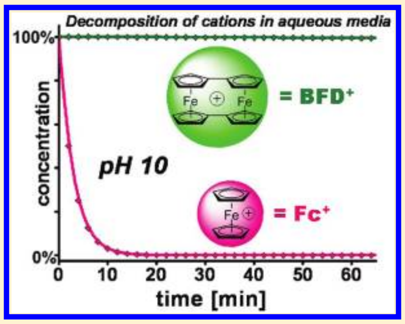
Supporting Information

ABSTRACT: Following an improved protocol, several monosubstituted 1,1′-biferrocenylenes (BFDs) were prepared as a mixture of *α* and *β* constitutional isomers. The isomers were separated and their structures assigned from ^{1}H−^{1}H-COSY and ^{1}H−^{1}H-ROESY NMR data, resulting in a correction of earlier erroneous assignments. Both redox stages (BFD^0/BFD$^+$ and BFD$^+$/BFD^{2+}) were examined by cyclic voltammetry. The reactivity of the parent BFD$^+$ versus that of ferrocenium (Fc$^+$) in aqueous solution was evaluated by UV−vis spectroscopy, suggesting that ferrocene should be replaced by BFD derivatives for redox applications in aqueous media due to their more than 1000-fold higher kinetic stability. Electronic transitions of monoalkylated BFD$^+$ derivatives were measured by thin-layer spectroelectrochemistry, revealing unperturbed mixed-valence class III systems independent of *α* or *β* substitution.



INTRODUCTION

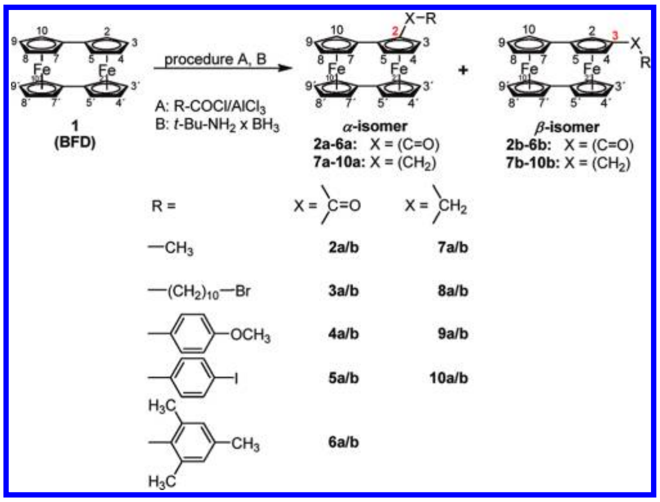
1,1′-Biferrocenylene[1] (BFD, bis(fulvalene)diiron) represents a textbook example of a mixed-valence class III metallocene as defined by Robin and Day,[2] displaying two fully reversible oxidation processes at $^1E_{1/2} = -0.29$ V$_{Fc}$ for BFD/BFD$^+$ and at $^2E_{1/2} = +0.38$ V$_{Fc}$ for BFD$^+$/BFD^{2+}. Despite its interesting redox chemistry, BFD has received almost no attention so far, primarily due to problems with its solubility and its functionalization. Its utility thus remains largely unrecognized, quite in contrast to the situation with ferrocene[3] and even biferrocenes.[4] A comprehensive literature search reveals that altogether only six BFD derivatives have been reported up to now[5,6] and that in case of the five reported monosubstituted BFDs even the assignment of the two possible constitutional isomers is cumbersome.[5]

Herein, we present an improved synthetic protocol to monofunctionalized BFDs and a corrected assignment of their constitutional *α*,*β* isomers using 2D ^{1}H NMR techniques. Results of spectroelectrochemical investigations confirm the mixed-valence class III character for alkylated BFD$^+$ cations as well. Furthermore, the current study establishes the outstanding stability of BFD$^+$ against aqueous basic media, exceeding that of the widely used ferrocenium ion (Fc$^+$) by more than 1000−4000 times. The increased kinetic stability suggests the use of the BFD/BFD$^+$ redox pair in a multitude of aqueous media applications and replacement of the commonly used ferrocene in the fields of bioorganic chemistry,[7] redox sensing,[8,9] redox actuation,[10,11] charge storage,[12,13] and medicinal applications.[14,15]

RESULTS AND DISCUSSION

Synthesis of New BFD Derivatives. As shown in Scheme 1, various monosubstituted 1,1′-biferrocenylenes (BFDs) were prepared by applying a modified Friedel−Crafts acylation protocol. The problem of the limited solubility of the parent BFD in organic solvents was overcome by using a solvent mixture of carbon disulfide and dichloroethane at elevated

Scheme 1. Synthetic Route to BFD Derivatives 2a,b−10a,b



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temperatures, improving the yield to ca. 60% and thus to more than 6 times of what had been reported in the literature so far.[5] All reactions employ an excess of several equivalents of $AlCl_3$ to achieve full conversion and yield a mixture of monosubstituted BFDs in 2- (α isomers **2a−6a**) and in 3-positions (β isomers **2b−6b**) (Table 1). In general, the yield of the β isomer exceeds that of the corresponding α isomer by more than double. Separation of the two constitutional isomers is best achieved at the stage of the acyl derivatives **2a,b−6a,b** (X = C═O) by applying conventional flash chromatography on silica gel. The separation is aided by the large differences of the corresponding R_f values and by the higher solubility of the α-acyl derivatives **2a−6a** in comparison to that of the less soluble β-acyl isomers **2b−6b**. After separation of the isomers, the carbonyl functionality of the acyl derivatives is reduced to $-CH_2-$ by the borane reagent $t\text{-}BuNH_2{\cdot}BH_3$, affording **7a−10a** and **7b−10b** in good yields.

Table 1. Yields of BFD Derivatives 2a,b−10a,b

entry	α/β yield (%)	entry	α/β yield (%)
2a,b	18/40	**7a,b**	70/68
3a,b	20/43	**8a,b**	75/79
4a,b	13/45	**9a,b**	75/73
5a,b	11/33	**10a,b**	71/75
6a,b	18/49		

Structural Identification of α and β Constitutional Isomers. Unambiguous structural identification of the two monosubstituted BFD isomers is derived from characteristic multiplets of their fulvalene ring protons in simple ^1H NMR spectra, which is further ascertained by results from $^1H-^1H$-COSY and $^1H-^1H$-ROESY NMR measurements. Figure 1 gives a top view of the substituted fulvalene system of **2a,b−10a,b** that describes the different multiplet splittings (dt, dd, dd(t), td) as observed in the ^1H NMR. The multiplets are characteristic for either of the two isomers, allowing us to readily differentiate α and β constitutional isomers. For α isomer **3a** the characteristic NMR pattern is displayed in Figure 2.

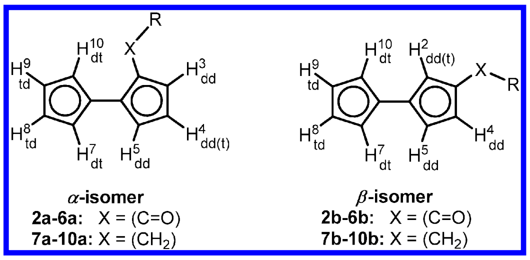

Figure 1. Top view of the substituted fulvalene system of α and β constitutional isomers **2a,b−10a,b**. The different multiplet splittings (dt, dd, dd(t), td) of the ring protons observed in the ^1H NMR spectra are indicated.

In general, the 15 protons of the monosubstituted BFDs show up as two discrete sets of signals in the ^1H NMR. One set is shifted downfield (range 6.1−5.1 ppm) and the other to the upfield region (range 4.4−3.6 ppm). In the course of assigning all of them, we realized that the inner protons of the unsubstituted cyclopentadienyl rings (7-H, 10-H, 7′-H, 10′-H, 2′-H, 5′-H) show up as doublets of triplets (dt, $^3J \cong 2$ Hz, $^4J \cong 1$ Hz) in the downfield region, whereas the outer protons (8-H, 9-H, 8′-H, 9′-H, 3′-H, 4′-H) appear as triplets of doublets (td, $^3J \cong 2$ Hz, $^4J \cong 1$ Hz) in the upfield region of the ^1H NMR. The introduction of a substituent leads to significant shifts of the respective cyclopentadienyl ring protons and changes in their multiplet character. In the case of the α isomers (Figures 1 and 2), proton 4-H now appears as a pseudotriplet (dd(t) = doublet of doublets appearing as triplet, with $^3J \cong 3$ Hz) at 4.40 ppm and proton 3-H as a doublet of doublets (dd) at 4.21 ppm, both located within the set of upfield-shifted protons. In contrast, the signal of proton 5-H shows up as a doublet of doublets (dd) in the downfield region. Regarding the corresponding β isomers, it is proton 2-H that is split into a pseudotriplet (dd(t), $^4J \cong 2$ Hz), appearing together with the signal of 5-H (dd) in the downfield region of the ^1H NMR. Reciprocally, the upfield-shifted proton 4-H exhibits a doublet of doublets (dd, $^3J = 3$ Hz, $^4J = 2$ Hz). The correlation of the proton signals within the cyclopentadienyl rings was fully confirmed by $^1H-^1H$-COSY measurements. In the $^1H-^1H$-COSY NMRs of the BFD derivatives **2a,b−6a,b** (see the Supporting Information) with an acyl functionality (X = C═O), the correlations consistently display the inner protons 2-H, 5-H, 7-H, 10-H, 2′-H, 5′-H, 7′-H, 10′-H shifted downfield, as can be rationalized by the added deshielding effects of two neighboring cyclopentadienyl rings. In contrast, all outer β protons of BFD (3-H, 4-H, 8-H, 9-H, 3′-H, 4′-H, 8′-H, 9′-H) experience deshielding effects from only one aromatic cyclopentadienyl ring and thus appear more upfield in the ^1H NMR spectra.

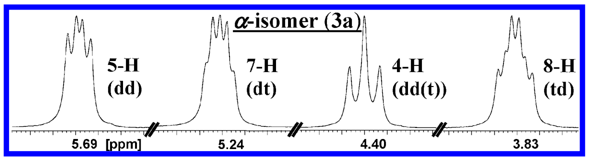

Figure 2. Selected characteristic ^1H NMR multiplets of four protons of **3a**. This pattern is analogous for all α constitutional isomers.

In order to allow for an accurate assignment of all individual protons in the BFD system, in particular also those at the unsubstituted cyclopentadienyl rings, the $^1H-^1H$-ROESY technique was applied. As an example, Figures 3 and 4 display the $^1H-^1H$-ROESY NMRs of the α and β constitutional BFD derivatives **3a,b**. In the case of α isomer **3a** intense cross signals are detected between protons 5-H(dd) and 7-H(dt), 5′-H(dt) and 7′-H(dt), and 2′-H(dt) and 10′-H(dt), which enabled a reliable assignment of protons at the neighboring cyclopentadienyl rings. In compliance with the expected doublet of triplets, using the multiplicity of the inner protons 2′-H, 5′-H, 7-H, 7′-H, 10′-H and cross-checking the $^1H-^1H$-ROESY assignments with the respective $^1H-^1H$-COSY correlations, the individual proton positions can be assigned over the whole BFD system. In the same manner, the proton assignments were made for β isomer **3b**. Corroborating the suggested structure of **3b**, the multiplet of 4-H is now a doublet of doublets (dd, $^3J \cong 3$ Hz, $^4J \cong 2$ Hz). In addition, a strong cross-peak is detected between 2-H(dd(t)) and 10-H(dt) by $^1H-^1H$-ROESY. Additional cross-checking with corresponding $^1H-^1H$-COSY correlations confirmed the complete assignments of all protons.

As described in Synthesis of New BFD Derivatives, the reduction of the carbonyl functionality in α derivatives **2a−5a** and β derivatives **2b−5b** leads to the corresponding saturated α and β isomers **7a−10a** and **7b−10b**. Equally for the latter, the protons show up as two distinct sets of downfield- and upfield-shifted ^1H NMR signals. Unfortunately, due to strong signal

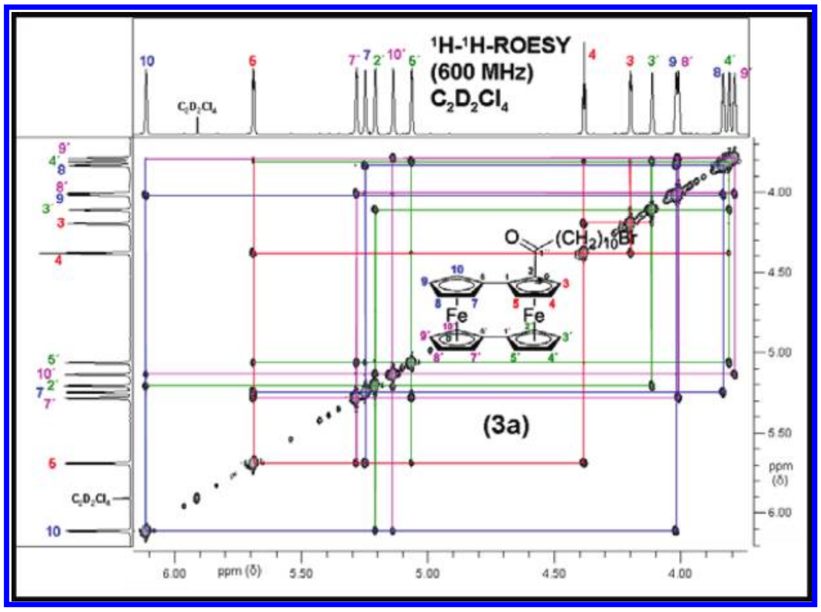

Figure 3. ^{1}H−^{1}H-ROESY NMR of *α* isomer **3a** (the region of the BFD proton signals is shown).

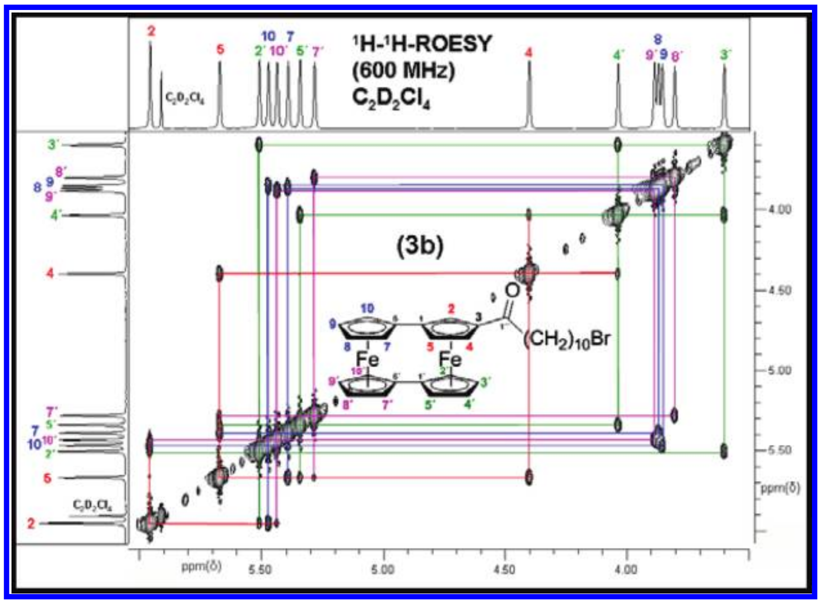

Figure 4. ^{1}H−^{1}H-ROESY NMR of *β* isomer **3b** (the region of the BFD proton signals is shown).

overlap not all protons within the two different sets (see ^{1}H−^{1}H-COSY NMR of **8a,b** and **7a,b** in the Supporting Information) are clearly resolved, making it difficult to unambiguously assign all protons equally for alkyl-substituted BFDs.

Our assignment of the constitutional isomers is reversing that used so far in the literature.[5] Concerning the acetyl-substituted BFDs **2a,b** (X = C═O, R = CH_3) two references assume for assignment that the inner *α* protons next to the bridge between the two cyclopentadienyl rings ought to appear upfield in ^{1}H NMR, because they “experience greater diamagnetic anisotropy” in the vicinity of the two iron centers.[5] In contrast, the outer *β* protons were supposed to appear more downfield, due to the reduced shielding by only one iron atom. It was concluded that *α*-monosubstituted BFD systems should exhibit seven protons shifted upfield in the ^{1}H NMR, whereas the *β*-monosubstituted BFD isomers are assumed to display eight upfield protons.

In contrast, we present herein convincing evidence from ^{1}H NMR, ^{1}H−^{1}H-COSY, and ^{1}H−^{1}H-ROESY NMR analysis that the formerly reported ^{1}H NMR assignments of *α*- and *β*-substituted BFD isomers need to be corrected and reversed. On the basis of the presented ^{1}H NMR multiplet assignments and ^{1}H−^{1}H-COSY as well as ^{1}H−^{1}H-ROESY NMR correlations, any *α*-monosubstituted BFD may be identified rather easily by the appearance of a set of seven downfield-shifted (*δ* 6.1−5.0 ppm) and a second set of eight upfield-shifted (*δ* 4.4−3.1 ppm) BFD protons in the ^{1}H NMR. In contrast, *β* monosubstitution is recognized by a set of eight downfield-shifted (*δ* 6.9−5.3 ppm) and a second set of seven upfield-shifted proton (*δ* 4.4−3.4 ppm) signals. This simple ^{1}H NMR assignment protocol will facilitate the exact identification and precise assignment of the different BFD derivatives in upcoming applications.

Table 2. Oxidation Potentials of BFD Derivatives **2a,b**−**10a,b**[a]

entry	$^1E_{1/2}$ (V_{Fc})	$^2E_{1/2}$ (V_{Fc})	ΔE^b (V)	$K_c{}^c$	entry	$^1E_{1/2}$ (V_{Fc})	$^2E_{1/2}$ (V_{Fc})	ΔE^b (V)	$K_c{}^c$
1	−0.29	0.38	0.67	2.3×10^{11}					
2a	−0.15	0.51	0.66	1.5×10^{11}	**7a**	−0.29	0.39	0.68	3.4×10^{11}
2b	−0.13	0.54	0.67	2.3×10^{11}	**7b**	−0.32	0.35	0.67	2.3×10^{11}
3a	−0.16	0.51	0.67	2.3×10^{11}	**8a**	−0.29	0.38	0.67	2.3×10^{11}
3b	−0.14	0.52	0.66	1.5×10^{11}	**8b**	−0.32	0.35	0.67	2.3×10^{11}
4a	−0.20	0.49	0.69	5.0×10^{11}	**9a**	−0.27	0.40	0.67	2.3×10^{11}
4b	−0.14	0.51	0.65	1.0×10^{11}	**9b**	−0.30	0.36	0.66	1.5×10^{11}
5a	−0.17	0.51	0.68	3.4×10^{11}	**10a**	−0.25	0.41	0.66	1.5×10^{11}
5b	−0.10	0.55	0.65	1.0×10^{11}	**10b**	−0.28	0.37	0.65	1.0×10^{11}
6a	−0.15	0.56	0.71	1.1×10^{12}					
6b	−0.10	0.56	0.66	1.5×10^{11}					

[a]Conditions: CH_2Cl_2, 0.1 M NBu_4PF_6, scan rate 0.1 V s^{-1}. [b]$\Delta E = {}^2E_{1/2} - {}^1E_{1/2}$. [c]$K_c = 10^{\Delta E/0.059\ V}$.

Electrochemical Investigations. The results of the cyclic voltammetry investigations on derivatives **2a,b**−**10a,b** and the parent BFD (**1**) in dichloromethane are summarized in Table 2. As typical mixed-valence class III compounds, all BFD systems display two well-separated redox waves. In the case of **1**, the monocationic state (BFD^0/BFD^+) at $^1E_{1/2} = -0.29\ V_{Fc}$ and the dicationic state (BFD^+/BFD^{2+}) at $^2E_{1/2} = +0.38\ V_{Fc}$ are separated by a potential difference of 670 mV, furnishing a large comproportionation constant K_c of 2.3×10^{11}, very typical for a mixed-valence class III compound.[16] The K_c values of all derivatives **2a,b**−**10a,b** are found in the same regime without notable deviations. Thus, the pronounced mixed-valence character of the parent BFD system remains intact upon substitution. According to the criteria of Nicholson and Shain,[17] **2a,b**−**10a,b** proved to be fully reversible redox systems as for the parent BFD. The influence of a carbonyl group in **2a,b**−**6a,b** entails a distinct anodic shift of both redox waves: for example, in the case of the alkanoyl derivatives **2a,b** and **3a,b**, an anodic shift of ca. 140−150 mV. A slightly stronger anodic shift is exerted by acyl substituents attached at the β position (**2b**−**6b**) than by those at the α position (**2a**−**6a**). When the carbonyl group was replaced by a methylene unit (**7a,b**−**10a,b**), both redox waves were found at almost the same positions as those of the parent BFD (**1**). However, as with all acyl BFDs, equally in the alkyl derivatives, a β substituent exerts a greater influence on the redox potential than an α substituent.

Stability of BFD^+ vs Fc^+ Ion in Aqueous Solution. To provide a comparison with the reported rapid decomposition of Fc^+ (ferrocenium ion) in basic aqueous solution,[18] we investigated the stability of the BFD^+ monocation under identical conditions. The stability of $BFD^+PF_6^-$ and $Fc^+PF_6^-$ in various aqueous buffer solutions at pH 7−12 was determined by following the decrease of their characteristic UV−vis absorptions at 596 and 617 nm, respectively. Table 2 shows the half-life times ($t_{1/2} = \ln 2/k$) at different pH values averaged over a total duration of 3 half-lives. Pseudo-first-order kinetics during the decomposition process was assumed, allowing us to read out k as the slope in the absorbance plot of $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs time. Due to the extremely large lifetime of $BFD^+PF_6^-$ at pH 7 ($t_{1/2}$ = 168 000 min = 117 days) data acquisition was restricted to 1 half-life in this case. Initial concentrations of $BFD^+PF_6^-$ and $Fc^+PF_6^-$ were adjusted to 1 and 2 mM in an acetonitrile/buffer mixture (50/50 v/v), respectively, to obtain a reasonable absorbance at the beginning. The results of the measurements are summarized in Table 3 and attest to the superior stability of the BFD^+ vs that of the Fc^+ ion at all pH values. At pH 7, the stability of BFD^+ exceeds that of Fc^+ by 1400 times and at pH 10 by up to 3600 times. In previous literature reports addressing the low stability of Fc^+ in the presence of nucleophiles, the iron center was identified as the primary target in the decomposition: e.g., the iron center is attacked by HO^- with formation of $Fe(OH)_3$, in particular, in the case of an alkaline aqueous solution.[18] One can rationalize the significantly higher stability of BFD^+ by two contributors: (i) delocalization of the positive charge over two iron centers in the mixed-valence class III system renders the BFD^+ less electrophilic with only 0.5 positive charge per iron center, and (ii) the more extended fulvalene units in the BFD system contribute to a more effective shielding of the iron atoms against nucleophilic attack.

Table 3. Half-Life ($t_{1/2}$, min) of $BFD^+PF_6^-$ vs $Fc^+PF_6^-$ in Aqueous Buffer Solution

entry	pH 7[c]	pH 8[d]	pH 9[e]	pH 10[e]	pH 11[d]	pH 12[f]
$BFD^+PF_6^{-a}$	168 000	72 000	42 000	7 200	660	120
$Fc^+PF_6^{-b}$	120	50	9	2	<1	<1

[a]1 mM in acetonitrile/buffer (50/50 v/v). [b]2 mM in acetonitrile/buffer (50/50 v/v). [c]KH_2PO_4/Na_2HPO_4. [d]H_3BO_3/NaOH/HCl. [e]$Na_2B_4O_7$/NaOH. [f]Na_2HPO_4/NaOH.

The relative stability gain of BFD^+ vs Fc^+ was determined at different pH values: pH 7 (1400×), pH 8 (1440×), pH 9 (4670×), and pH 10 (3600×). While the error is considered to be ±10% at pH 7 and pH 8, the very rapid decay of Fc^+ at pH 9 and pH 10 leads to an error of ±30%. Accordingly, the different relative stabilities at distinct pH values may be simply due to the larger errors in the kinetic measurement at high pH.

It is important to note that there are other ways to stabilize ferrocene-type cations in comparison to the parent system: e.g., by permethylation as well as by donor substituents such as in biferrocene[4] and oligoferrocenes. For example, decamethylferrocenium showed an improved stability vs the ferrocenium cation in neutral and acidic aqueous medium.[19]

Spectroelectrochemistry of 8a,b. UV−vis−near-IR absorption spectra of the alkyl-substituted BFD derivatives **8a,b** in dichloromethane at both the monocation and dication oxidation state are shown in Figure 5. The band region at 5000−10 000 cm^{-1} is characteristic for the BFD monocation as a typical class III mixed-valence system. Absorption maxima are located at 6300 cm^{-1} (shoulder at 8020 cm^{-1}) and at 6550 cm^{-1} (shoulder at 8140 cm^{-1}) for **8a**$^+$ and **8b**$^+$, respectively, and are attributed to intervalence charge resonance (IVCR)[20,21] transitions,[22] as supported by recent TD-DFT calculations (Table 4).[23] Observed differences in the IVCR bands of both

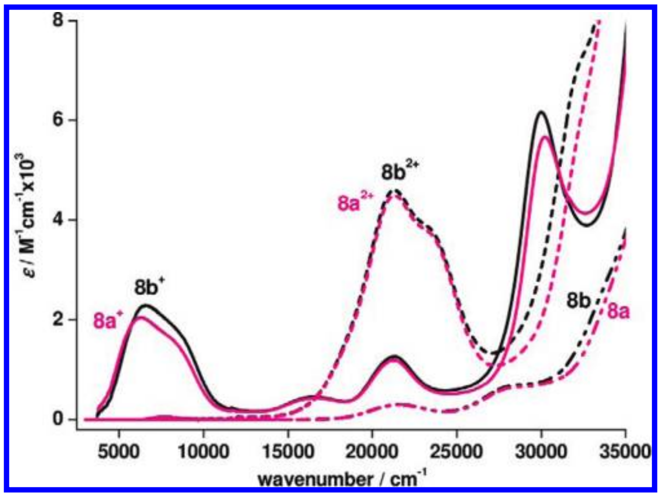

Figure 5. UV−vis−near-IR spectra of **8a** (neutral, red —··—; monocation, red —; dication, red - - -) and **8b** (neutral, black —··—; monocation, black —; dication, black - - -) in dichloromethane at 298 K.

isomeric derivatives **8a**$^+$ and **8b**$^+$ are very small. In both cases, the position and the shape of the measured IVCR bands are in full compliance with results in the literature on the parent BFD$^+$PF$_6^-$ measured in acetonitrile.[23] During anodic preparation of the dications **8a**$^{2+}$ and **8b**$^{2+}$, the IVCR bands vanish completely while simultaneously a new band at 21 300 cm^{-1} (shoulder at 23 000 cm^{-1}) appears. As expected for a BFD^{2+} dication, the mixed-valence class III character is lost. From a comparison of the IVCR spectra of **8a**$^+$ and **8b**$^+$ and that of the parent BFD$^+$PF$_6^-$ in CH$_2$Cl$_2$, it can be concluded that IVCR bands keep their position and shape almost invariant of alkyl vs H substitution. Apparently, alkyl substitution in positions 2 or 3 of the BFD system does not affect the mixed-valence class III character of the BFD$^+$ cation. Thus, the mixed-valence class III property should be a part of other alkyl-substituted BFD derivatives as well, opening interesting venues for future applications.

■ CONCLUSIONS

The notoriously difficult functionalization of BFD was improved by applying a modified Friedel−Crafts acylation protocol, allowing us to access several new BFD derivatives in reasonable yields. α and β constitutional isomers of various monosubstituted BFD systems were separated by chromatography and fully assigned by ^{1}H−^{1}H-COSY and ^{1}H−^{1}H-ROESY NMR, leading to a correction of previous erroneous assignments. In a kinetic study, the superior stability of the BFD$^+$ monocation vs the ferrocenium ion (Fc$^+$) in aqueous solution becomes apparent, a feature that is related to the pronounced mixed-valence class III property of BFD$^+$-type monocations. Spectroelectrochemical investigations indicate that alkyl substitution at position 2 or 3 of BFD will not decrease the mixed-valence class III character; thus, it is suggested to utilize BFD$^+$ and its derivatives in known and future water-based applications instead of Fc$^+$. A fundamental prerequisite to any wide use of BFD systems in practical applications, however, will be the facile availability of not only mono- but even difunctionalized BFD derivatives, a challenge that hopefully will find some solution in the near future.

■ EXPERIMENTAL SECTION

General Remarks. The atom-numbering system used for the BFD system was proposed by Goldberg and Matteson.[24] 11-Bromoundecanoic acid chloride was prepared by reaction of the corresponding acid with oxalyl chloride in dichloromethane (CH$_2$Cl$_2$) and was used without distillation. *p*-Iodobenzoic acid chloride (Aldrich), *p*-methoxybenzoic acid chloride, *sym*-trimethylbenzoic acid chloride, acetyl chloride, and *t*-BuNH$_2$·BH$_3$ (Acros) were purchased and used without further purification. Copper powder for synthesis (1−5 μm) was received from Aldrich and used without activation. AlCl$_3$ was purified by sublimation. Carbon disulfide (CS$_2$) was dried over P$_2$O$_5$, dichloromethane (CH$_2$Cl$_2$) and 1,2-dichloroethane (C$_2$H$_4$Cl$_2$) were dried over CaH$_2$. ***Cautionary warning on the handling of 1,2-dichloroethane and carbon disulfide!*** 1,2-Dichloroethane (C$_2$H$_4$Cl$_2$) may cause cancer and kidney damage. Carbon disulfide (CS$_2$) is toxic to kidneys, the nervous system, and liver by all routes of exposure and is very hazardous in case of skin contact (permeator). Wear impervious protective clothing and eye protection and work only in well-ventilated hoods. BFD$^+$PF$_6^-$ and Fc$^+$PF$_6^-$ were prepared according to a modified literature procedure (see the Supporting Information).[25,28]

Instrumental Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer or on a 600 MHz Varian spectrometer. The chemical shifts (δ) are reported in ppm and are referenced with regard to the residual protiated solvent: tetrachloroethane-d_2, δ 5.91 (^{1}H) and δ 74.2 (^{13}C); chloroform-*d*, δ 7.26 (^{1}H) and δ 77.0 (^{13}C); benzene-d_6, δ 7.15 (^{1}H) and δ 128.0 (^{13}C). The following abbreviations were utilized to describe NMR peak splitting: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; dd(t), doublet of doublets with two identical coupling constants; td, triplet of doublets.

For all cyclic voltammetry measurements (EG&G 2273 potentiostat/galvanostat), a conventional three-electrode setup was used, with a 1 mm platinum-disk working electrode, a platinum-wire counter electrode, and a silver wire as pseudoreference electrode. Tetra-*n*-butylammonium hexafluorophosphate (TBA$^+$PF$_6^-$) served as supporting electrolyte, and decamethylferrocene ($E_{1/2}$ = −0.54 V$_{Fc}$) was used as the internal standard. Spectroelectrochemical measurements were performed on a Perkin-Elmer Lambda 750 UV−vis−near-IR spectrometer. Spectroelectrochemistry was carried out in transmission mode by using a thin-layer cell that has been already described in detail,[26] with a transparent gold minigrid serving as the working electrode. The molar extinction coefficients ε_M (M^{-1} cm^{-1}) of the neutral BFD derivatives **8a,b** and of the BFD$^+$PF$_6^-$ salt in dichloromethane were determined in a 1 cm cuvette and were averaged over three measurements, leading to an accuracy of at least ±0.7%.

Table 4. UV−Vis−Near-IR Absorption Bands of 8a,b and BFD$^+$PF$_6^-$ in Dichloromethane, As Measured in a Transparent Gold-Minigrid Thin-Layer Cell

	UV−vis−near-IR abs/cm^{-1} (ε_M/M^{-1}·cm^{-1})					
		monocation				
entry	neutral	IVCR	band II	band III	LMCT	dication
BFD$^+$PF$_6^-$		6450 (2090)	16 670 (380)	21 370 (1120)	30 120 (5540)	
8a	21 645 (296)	6300 (2050)	16 560 (430)	21 280 (1180)	30 200 (5670)	21 280 (4500)
8b	21 550 (298)	6550 (2300)	16 560 (450)	21 280 (1260)	29 990 (6160)	21 280 (4600)

1,1′-Biferrocenylene (1). 1,1′-Biferrocenylene was prepared via Ullmann coupling of 1,1′-diiodoferrocene[27] according to a literature procedure.[28] A mixture of 17.2 g (39.3 mmol) of 1,1′-diiodoferrocene, 25.0 g (393 mmol) of copper powder, and 400 g of biphenyl was heated at 180 °C for 18 h. The reaction mixture was filtered hot through a Büchner funnel into *n*-hexane (1.5 L). The reddish brown precipitate was filtered off and purified by sublimation (240 °C at 0.07 mbar). The yield ranged between 1.80 and 2.70 g (25−37%). ^{1}H NMR (400 MHz, C_6D_6): δ 5.23 (m, 8H), 3.75 (m, 8H). Anal. Calcd for $C_{20}H_{16}Fe_2$: C, 65.27; H, 4.38. Found: C, 65.45; H, 4.29.

Compounds 2a,b−6a,b. General Procedure A: Friedel−Crafts Acylation of BFD (1). Under nitrogen, 1,1′-biferrocenylene (1.80 g, 4.89 mmol) in 150 mL of dry CS_2 was heated to 50 °C. A solution of the respective acid chloride (4.89 mmol) and $AlCl_3$ (1.50 g, 11.2 mmol, 2.3 equiv) in dry dichloroethane (120 mL) was added rapidly to the reaction mixture. After 3 as well as 12 h an additional portion of solid $AlCl_3$ (1.50 g, 11.2 mmol) was added. After a further 12 h, the reaction mixture was cooled to room temperature and water (100 mL) was added. The separated aqueous layer was acidified with hydrochloric acid to pH 1 and extracted with 100 mL of CH_2Cl_2. The combined organic layers were washed twice with saturated $NaHCO_3$ solution and water and finally dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the solid was purified by flash column chromatography.

Compounds 7a,b−10a,b. General Procedure B: Carbonyl Reduction of BFD Derivatives. To a suspension of $AlCl_3$ (600 mg, 4.50 mmol) in CH_2Cl_2 (60 mL) was added *t*-BuNH$_2$·BH$_3$ (783 mg, 9.00 mmol) at 0 °C. After the mixture was stirred for 15 min, a solution of 1.50 mmol of the respective carbonyl compound (**2a**,**b**−**5a**,**b**) in CH_2Cl_2 (50 mL) was added dropwise to the mixture. After completion of the addition, stirring was continued for 1 h at room temperature. Finally, the reaction mixture was quenched carefully with 0.1 M hydrochloric acid (50 mL). After extraction of the aqueous layer with 50 mL of CH_2Cl_2, the combined organic layers were washed twice with 50 mL of brine and dried over Na_2SO_4. After solvent evaporation under reduced pressure the residue was purified by flash column chromatography over silica (*n*-hexane/CH_2Cl_2).

*2-Acetyl-1,1′-biferrocenylene (**2a**).* Flash chromatography (silica: dichloromethane; R_f = 0.29). Yield: 0.36 g (18%). Mp: 222 °C. IR (KBr, cm^{-1}): 3088 (C−H$_{Ar}$, w), 1663 (C═O, s), 1499 (w), 1431 (m), 1399 (m), 1352 (m), 1270 (w), 1245 (s), 1206 (w), 1157 (w), 1112 (w), 1051 (m), 1031 (s), 999 (m), 930 (w), 897 (w), 853 (m), 809 (s), 694 (w), 635 (w), 584 (w), 546 (m), 504 (s), 484 (s), 422 (w). ^{1}H NMR (600 MHz, $C_2D_2Cl_4$): δ 6.08 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.71 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.29 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 5.25 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.23 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.13 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.07 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 4.41 (dd(t), ^3J = 3 Hz, 1H, 4-H), 4.19 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 3-H), 4.13 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 4.02 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 4.01 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.83 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.82 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.78 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 2.65 (s, 3H, 2″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 203.7 (C═O), 98.5, 94.5, 92.6, 92.2, 80.2, 75.7, 73.8, 72.4, 72.3, 72.0, 71.3, 71.1, 69.8, 69.7, 69.2, 68.6, 68.2, 68.1, 66.6, 66.3, 29.9. Anal. Calcd for $C_{22}H_{18}Fe_2O$: C, 64.44; H, 4.42. Found: C, 64.65; H, 4.26.

*3-Acetyl-1,1′-biferrocenylene (**2b**).* Flash chromatography (silica: dichloromethane/ethyl acetate, 95/5 v/v; R_f = 0.52). Yield: 0.80 g (40%). Mp: 260 °C dec. IR (KBr, cm^{-1}): 3098 (C−H$_{Ar}$, w), 2922 (w), 2856 (w), 1665 (C═O, s), 1450 (s), 1409 (m), 1355 (m), 1295 (m), 1269 (m), 1237 (m), 1176(w), 1115 (w), 1047 (s), 1031 (s), 1008 (m), 966 (w), 901 (w), 850 (m), 808 (s), 630 (w), 551 (w), 524 (m), 506 (s), 484 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 5.96 (dd(t), ^4J = 2 Hz, 1H, 2-H), 5.68 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.51 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.46 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.44 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.39 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.35 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.28 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 4.38 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 4-H), 4.06 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.89 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 3.88 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.85 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 3.80 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.60 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 2.25 (s, 3H, 2″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 202.4 (C═O), 100.9, 97.8, 93.2, 93.0, 77.7, 73.5, 70.19, 70.21, 69.8, 69.7 (2 C), 69.4, 69.4, 69.0, 67.9 (2 C), 67.4, 67.2, 67.0, 66.7, 27.7. Anal. Calcd for $C_{22}H_{18}Fe_2O$: C, 64.44; H, 4.42. Found: C, 64.72; H, 4.32.

*2-(11″-Bromoundecanoyl)-1,1′-biferrocenylene (**3a**).* Flash chromatography (silica: dichloromethane/*n*-hexane, 60/40 v/v; R_f = 0.32). Yield: 0.61 g (20%). Mp: 117 °C. IR (KBr, cm^{-1}): 3089 (C−H$_{Ar}$, w), 2921 (s), 2848 (m), 1679 (C═O, s), 1466 (m), 1428 (m), 1409 (m), 1374 (w), 1342 (m), 1271 (m), 1249 (w), 1224 (m), 1087 (w), 1047 (m), 1029 (m), 1000 (m), 927 (m), 858 (m), 808 (s), 756 (w), 726 (m), 640 (m), 552 (w), 501 (s), 412 (w). ^{1}H NMR ($C_2D_2Cl_4$): δ 6.09 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.69 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.28 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 5.24 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.21 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.12 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.06 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 4.40 (dd(t), ^3J = 3 Hz, 1H, 4-H), 4.21 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 3-H), 4.12 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 4.02 (m, 2H, 9-H, 8′-H), 3.83 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.81 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.78 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 3.36 (t, ^3J = 7 Hz, 2H, 11″-H), 3.10 (ddd, ^2J = 16 Hz, ^3J = 8 Hz, ^3J = 6 Hz, 1H, 2″-H$_a$), 2.80 (ddd, ^2J = 16 Hz, ^3J = 8 Hz, ^3J = 6 Hz, 1H, 2″-H$_b$), 1.79 (m, 4H, 3″-H, 10″-H), 1.36 (m, 8H, 4″-H, 5″-H, 8″-H, 9″-H), 1.27 (m, 4H, 6″-H, 7″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 206.1 (C═O), 98.1, 94.3, 92.3, 91.8, 80.6, 75.7, 74.1, 72.7, 72.3, 71.4, 71.1, 71.1, 70.0, 69.8, 69.1, 68.6, 68.2, 67.9, 66.4, 66.2, 41.4, 35.0, 33.1, 29.9 (2C), 29.8, 29.8, 29.1, 28.5, 25.4. Anal. Calcd for $C_{31}H_{55}BrFe_2O$: C, 60.52; H, 5.73. Found: C, 60.59; H, 5.65.

*3-(11″-Bromoundecanoyl)-1,1′-biferrocenylene (**3b**).* Flash chromatography (silica: dichloromethane; R_f = 0.29). Yield: 1.28 g (43%). Mp: 190 °C. IR (KBr, cm^{-1}): 3100 (C−H$_{Ar}$, m), 2914 (s), 2851 (m), 1670 (C═O, s), 1453 (m), 1409 (w), 1344 (w), 1292 (m), 1270 (m), 1225 (w), 1175 (w), 1089 (w), 1048 (m), 1030 (s), 900 (w), 851 (m), 823 (m), 806 (s), 714 (w), 644 (m), 551 (w), 509 (s), 483 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 5.95 (dd(t), ^4J = 2 Hz, 1H, 2-H), 5.67 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.50 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.47 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.43 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.39 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.34 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.28 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 4.40 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 4-H), 4.03 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.88 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 3.87 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.85 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 3.80 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.60 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 3.34 (t, ^3J = 7 Hz, 2H, 11″-H), 2.55 (m, 2H, 2″-H), 1.77 (m, 2H, 10″-H), 1.56 (m, 2H, 3″-H), 1.33 (m, 2H, 9″-H), 1.22 (m, 10H, 4″-H, 5″-H, 6″-H, 7″-H, 8″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 205.0 (C═O), 100.6, 97.7, 93.3, 93.1, 77.6, 73.3, 70.1, 69.8, 69.7, 69.7, 69.6, 69.4, 69.4, 68.8, 67.8, 67.5, 67.3, 67.2, 67.0, 66.8, 39.8, 35.0, 33.1, 29.8, 29.8, 29.7 (2C), 29.1, 28.5, 24.9. Anal. Calcd for $C_{31}H_{55}BrFe_2O$: C, 60.52; H, 5.73. Found: C, 60.79; H, 5.69.

*2-(p-Methoxybenzoyl)-1,1′-biferrocenylene (**4a**).* Flash chromatography (silica: dichloromethane; R_f = 0.39). Yield: 0.33 g (13%). Mp: 156 °C. IR (KBr, cm^{-1}): 3084 (C−H$_{Ar}$, w), 1642 (C═O, s), 1599 (s), 1574 (m), 1508 (m), 1428 (s), 1332 (m), 1254 (s), 1162 (s), 1028 (s), 914 (m), 899 (m), 844 (s), 808 (s), 769 (m), 621 (m), 501 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.87 (d, ^3J = 9 Hz, 2H, 3″-H, 7″-H), 6.81 (d, ^3J = 9 Hz, 2H, 4″-H, 6″-H), 5.72 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.61 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.57 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.41 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 5.32 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.27 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.10 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 4.34 (dd(t), ^3J = 3 Hz, 1H, 4-H), 4.23 (td, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 3′-H), 4.02 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.99 (dd, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3-H), 3.91 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 3.78 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.77 (s, 3H, 8″-H) 3.71 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.70 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 198.0 (C═O), 163.2, 132.4, 131.9, 113.7, 97.9, 94.8, 93.3, 93.2, 85.7, 73.4, 72.3, 71.8, 71.6, 71.3, 71.3, 69.9, 69.4, 69.4, 69.2, 68.3, 68.1, 67.0, 66.0, 65.5, 55.9. Anal. Calcd for $C_{28}H_{22}Fe_2O_2$: C, 66.97; H, 4.42. Found: C, 67.18; H, 4.37.

3-(p-Methoxybenzoyl)-1,1′-biferrocenylene (***4b***). Flash chromatography (silica: dichloromethane/ethyl acetate, 95/5 v/v; R_f = 0.63). Yield: 1.10 g (45%). Mp: 300 °C dec. IR (KBr, cm^{-1}): 3095 (C−H$_{Ar}$, w), 1624 (C═O, s), 1601 (s), 1510 (m), 1438 (m), 1406 (m), 1321 (m), 1271(s), 1253 (s), 1173 (m), 1155 (m), 1079 (w), 1030 (m), 843 (m), 807 (m), 770 (m), 623 (m), 511 (s), 482 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.82 (d, ^3J = 9 Hz, 2H, 3″-H, 7″-H), 6.91 (d, ^3J = 9 Hz, 2H, 4″-H, 6″-H), 6.11 (dd(t), ^4J = 2 Hz, 1H, 2-H), 5.76 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.56 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.51 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.46 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.43 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.36 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.29 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 4.48 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 4-H), 4.06 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.89 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 3.88 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.86 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 3.82 (s, 3H, 8″-H), 3.80 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.57 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 197.7 (C═O), 162.6, 132.4, 130.7, 113.8, 100.9, 97.9, 93.3, 93.3, 77.0, 73.5, 71.1, 70.6, 70.5, 69.9, 69.8, 69.6, 69.5, 69.4, 69.3, 68.2, 67.4, 67.2, 67.0, 66.7, 55.9. Anal. Calcd for $C_{28}H_{22}Fe_2O_2$: C, 66.97; H, 4.42. Found: C, 67.28; H, 4.32.

2-(p-Iodobenzoyl)-1,1′-biferrocenylene (***5a***). Flash chromatography (silica: dichloromethane/*n*-hexane, 80/20 v/v; R_f = 0.60). Yield: 0.32 g (11%). Mp: 200 °C. IR (KBr, cm^{-1}): 3082 (C−H$_{Ar}$, w), 1648 (C═O, s), 1579 (m), 1480 (w), 1423 (m), 1383 (m), 1339 (m), 1255 (m), 1182 (w), 1105 (w), 1059 (m), 1031 (m), 1001 (m), 985 (m), 898 (w), 850 (s), 826 (m), 810 (s), 757 (m), 729 (w), 687 (w), 602 (w), 551 (w), 503 (s), 489 (m). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.73 (d, ^3J = 8 Hz, 2H, 3″-H, 7″-H), 7.61 (d, ^3J = 8 Hz, 2H, 4″-H, 6″-H), 5.80 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.74 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.49 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.40 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 5.29 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 2H, 10′-H, 7-H), 5.07 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 4.41 (dd(t), ^3J = 3 Hz, 1H, 4-H), 4.19 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 4.04 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.96 (m, 2H, 9-H, 3-H), 3.77 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.75 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.73 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 199.6 (C═O), 139.3, 137.7, 130.8, 100.1, 98.6, 95.6, 92.8, 92.7, 82.7, 73.8, 73.6, 72.3, 72.3, 72.0, 71.5, 70.3, 69.0, 69.6, 69.4, 68.6, 68.3, 67.4, 66.1, 65.8. Anal. Calcd for $C_{27}H_{19}Fe_2IO$: C, 54.23; H, 3.20. Found: C, 54.31; H, 3.00.

3-(p-Iodobenzoyl)-1,1′-biferrocenylene (***5b***). Flash chromatography (silica: dichloromethane; R_f = 0.35). Yield: 0.98 g (33%). Mp: 235 °C dec. IR (KBr, cm^{-1}): 3099 (C−H$_{Ar}$, w), 1628 (C═O, s), 1578 (m), 1555 (w), 1443 (m), 1409 (m), 1385 (w), 1347 (w), 1312 (m), 1293 (m), 1271 (w), 1250 (m), 1177 (m), 1108 (w), 1080 (m), 1050 (m), 1033 (m), 1006 (s), 969 (m), 854 (s), 834 (s), 806 (s), 757 (s), 683 (w), 609 (w), 572 (w), 500 (s), 484 (s), 431 (w). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.78 (d, ^3J = 8 Hz, 2H, 3″-H, 7″-H), 7.49 (d, ^3J = 8 Hz, 2H, 4″-H, 6″-H), 6.07 (dd(t), ^4J = 2 Hz, 1H, 2-H), 5.79 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.54 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.50 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.45 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.42 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.35 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.28 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 4.45 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 4-H), 4.05 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.90 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 3.89 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.86 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 3.80 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.58 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 198.5 (C═O), 139.1, 137.9, 129.8, 101.8, 99.1, 98.3, 93.0, 92.9, 76.0, 74.1, 71.1, 70.5, 70.3, 69.9, 69.8, 69.7, 69.7, 69.5, 69.4, 68.3, 67.5, 67.3, 67.1, 66.8. Anal. Calcd for $C_{27}H_{19}Fe_2IO$: C, 54.23; H, 3.20. Found: C, 54.29; H, 3.02.

2-(sym-Trimethylbenzoyl)-1,1′-biferrocenylene (***6a***). Flash chromatography (silica: dichloromethane/*n*-hexane, 50/50 v/v; R_f = 0.37). Yield: 0.45 g (18%). Mp: 225 °C. IR (KBr, cm^{-1}): 3096 (C−H$_{Ar}$, w), 2952 (w), 2918 (w), 2854 (w), 1659 (C═O, s), 1609 (m), 1428 (s), 1375 (w), 1339 (m), 1250 (m), 1188 (w), 1060 (m), 1030 (m), 999 (w), 888 (w), 839 (s), 810 (s), 734 (w), 629 (w), 549 (w), 502 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 6.82 (s, 2H, 4″-H, 6″-H), 6.41 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.95 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.51 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.47 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.37 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.33 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 4.95 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 4.44 (dd(t), ^3J = 3 Hz, 1H, 4-H), 4.20 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 4.15 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 4.14 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.76 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.75 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H),3.63 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.58 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 3-H), 2.26 (s, 9H, 8″-H, 9″-H, 10″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 206.5 (C═O), 139.9, 138.5, 134.3, 128.8, 98.8, 96.4, 93.3, 92.5, 82.3, 75.6, 73.4, 73.2, 73.1, 71.7, 71.6, 71.0, 69.6, 69.5, 69.0, 68.9, 68.7, 67.2, 65.7, 65.3, 21.5, 20.3. Anal. Calcd for $C_{30}H_{26}Fe_2O$: C, 70.07; H, 5.10. Found: C, 70.14; H, 5.04.

3-(sym-Trimethylbenzoyl)-1,1′-biferrocenylene (***6b***). Flash chromatography (silica: dichloromethane/*n*-hexane, 80/20 v/v; R_f = 0.55). Yield: 1.23 g (49%). Mp: 264 °C dec. IR (KBr, cm^{-1}): 3098 (C−H$_{Ar}$, w), 2962 (w), 2918 (w), 2854 (w), 1644 (C═O, s), 1611 (m), 1439 (s), 1380 (w), 1346 (w), 1308 (m), 1294 (m), 1272 (w), 1240 (m), 1172 (w), 1075 (w), 1031 (m), 1013 (m), 968 (w), 845 (s), 810 (s), 725 (w), 625 (w), 525 (w), 498 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 6.81 (s, 2H, 4″-H, 6″-H), 5.74 (dd(t), ^4J = 2 Hz, 1H, 2-H), 5.68 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 5-H), 5.54 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.42 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.30 (m, 2H, 7-H, 2′-H), 5.24 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.21 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7′-H), 4.29 (dd, ^3J = 3 Hz, ^4J = 2 Hz, 1H, 4-H), 4.04 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 4.00 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9′-H), 3.94 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 9-H), 3.88 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.85 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 3.84 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 2.27 (s, 3H, 10″-H), 2.08 (s, 6H, 8″-H, 9″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 205.6 (C═O), 138.7, 138.2, 134.6, 128.9, 100.2, 96.9, 92.7, 92.4, 79.6, 73.1, 71.0, 70.5, 70.1 (4C), 69.8 (2C), 69.5, 67.8, 67.6, 67.4, 67.2, 67.1, 21.5, 20.3. Anal. Calcd for $C_{30}H_{26}Fe_2O$: C, 70.07; H, 5.10. Found: C, 70.23; H, 5.02.

2-Ethyl-1,1′-biferrocenylene (***7a***). Flash chromatography (silica: dichloromethane/*n*-hexane, 50/50 v/v; R_f = 0.81). Yield: 0.42 g (70%). Mp: 175 °C. IR (KBr, cm^{-1}): 3097 (C−H$_{Ar}$, w), 2965 (w), 2848 (w), 1460 (w), 1407 (w), 1381 (w), 1267 (m), 1140 (w), 1075 (m), 1048 (m), 1030 (m), 998 (m), 953 (w), 848 (m), 806 (m), 686 (w), 640 (w), 570 (w), 501 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 5.48 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-H), 5.40 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 7-H), 5.35 (m, 2H, 7′-H, 5-H), 5.30 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.27 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.00 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 3.95 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 3.90 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8-H), 3.87 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 8′-H), 3.85 (m, 2H, 9-H, 9′-H), 3.83 (dd(t), ^3J = 2.4 Hz, 1H, 4-H), 3.78 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.73 (dd, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3-H), 3.48 (dq, ^2J = 15 Hz, ^3J = 8 Hz, 1H, 1″-H$_a$), 3.25 (dq, ^2J = 15 Hz, ^3J = 8 Hz, 1H, 1″-H$_b$), 1.40 (t, ^3J = 8 Hz, 3H, 2″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 95.5, 95.2, 95.1, 92.4, 91.7, 72.5, 70.4, 70.3, 69.7, 69.5, 69.3, 68.8, 67.2, 66.9, 66.7, 66.6, 66.3, 66.2, 65.7, 65.1, 23.2, 15.5. Anal. Calcd for $C_{22}H_{20}Fe_2$: C, 66.71; H, 5.09. Found: C, 66.95; H, 5.03.

3-Ethyl-1,1′-biferrocenylene (***7b***). Flash chromatography (silica: dichloromethane; R_f = 0.97). Yield: 0.40 g (68%). Mp: 210 °C. IR (KBr, cm^{-1}): 3098 (C−H$_{Ar}$, w), 2964 (w), 2845 (w), 1524 (w), 1469 (w), 1407 (w), 1378 (w), 1324 (w), 1300 (w), 1268 (m), 1108 (w), 1080 (w), 1027 (s), 918 (w), 847 (s), 807 (s), 638 (w), 607 (w), 508 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 5.41 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 2′-H), 5.34 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10′-H), 5.32 (m, 2H, 2-H, 7′-H), 5.31 (m, 2H, 10-H, 7-H), 5.29 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5′-H), 5.24 (dd, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 5-H), 3.87 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4′-H), 3.81 (m, 4H, 8-H, 8′-H, 9-H, 9′-H), 3.75 (dd, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 4-H), 3.58 (td, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 3′-H), 2.14 (m, 2H, 1″-H), 1.07 (t, ^3J = 8 Hz, 3H, 2″-H). ^{13}C NMR ($C_2D_2Cl_4$): not recorded due to solubility problems. Anal. Calcd for $C_{22}H_{20}Fe_2$: C, 66.71; H, 5.09. Found: C, 66.50; H, 4.91.

2-(11″-Bromoundecyl)-1,1′-biferrocenylene (***8a***). Flash chromatography (silica: dichloromethane/*n*-hexane, 50/50 v/v; R_f = 0.77). Yield: 0.68 g (75%). Mp: 109 °C. IR (KBr, cm^{-1}): 3082 (C−H$_{Ar}$, w), 2922 (m), 2847 (m), 1465 (m), 1268 (m), 1045 (m), 1027 (m), 996 (m), 850 (m), 831 (m), 807 (s), 724 (m), 699 (w), 646 (m), 566 (w), 500 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 5.46 (dt, ^3J = 2 Hz, ^4J = 1 Hz, 1H, 10-

H), 5.38 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 7-H), 5.35 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 7′-H), 5.34 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 5-H), 5.30 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 10′-H), 5.25 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 5′-H), 4.99 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 2′-H), 3.95 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 3′-H), 3.88 (m, 2H, 8-H, 8′-H), 3.86 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 9-H), 3.83 (m, 2H, 9′-H, 4-H), 3.75 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 4′-H), 3.69 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 3-H), 3.39 (ddd, ^{2}J = 15 Hz, ^{3}J = 10 Hz, ^{3}J = 7 Hz, 1H, 1″-H$_a$), 3.37 (t, ^{3}J = 7 Hz, 2H, 11″-H), 3.25 (ddd, ^{2}J = 15 Hz, ^{3}J = 10 Hz, ^{3}J = 7 Hz, 1H, 1″-H$_b$), 1.80 (m, 2H, 10″-H), 1.66 (m, 2H, 2″-H), 1.49 (m, 2H, 3″-H), 1.36 (m, 4H, 4″-H, 9″-H), 1.27 (m, 8H, 5″-H, 6″-H, 7″-H, 8″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 95.5, 95.2 (2C), 92.3, 90.3, 72.6, 70.4, 70.3, 69.6, 69.5, 69.2, 68.8, 67.4, 67.3, 67.0, 66.7, 66.2, 66.1, 65.7, 65.2, 35.0, 33.1, 31.4, 30.3, 30.3, 30.0, 30.0, 29.9, 29.8, 29.1, 28.5. Anal. Calcd for $C_{31}H_{57}BrFe_2$: C, 61.93; H, 6.20. Found: C, 62.29; H, 6.18.

*3-(11″-Bromoundecyl)-1,1′-biferrocenylene (**8b**).* Flash chromatography (silica: dichloromethane/*n*-hexane, 80/20 v/v; R_f = 0.76). Yield: 0.71 g (79%). Mp: 185 °C. IR (KBr, cm^{-1}): 3100 (C−H$_{Ar}$, w), 2925 (m), 2849 (m), 1523 (w), 1471 (m), 1269 (m), 1080 (w), 1027 (s), 939 (w), 847 (m), 806 (s), 713 (w), 506 (s), 485 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 5.43 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 2′-H), 5.35 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 10′-H), 5.32 (m, 4H, 10-H, 7′-H, 2-H, 7-H), 5.29 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 5′-H), 5.24 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 5-H), 3.87 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 4′-H), 3.81 (m, 4H, 8-H, 8′-H, 9-H, 9′-H), 3.74 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 4-H), 3.54 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 3′-H), 3.36 (t, ^{3}J = 7 Hz, 2H, 11″-H), 2.20 (ddd, ^{2}J = 15 Hz, ^{3}J = 9 Hz, ^{3}J = 6 Hz, 1H, 1″-H$_a$), 2.04 (ddd, ^{2}J = 15 Hz, ^{3}J = 9 Hz, ^{3}J = 6 Hz, 1H, 1″-H$_b$), 1.78 (m, 2H, 10″-H), 1.37 (m, 4H, 2″-H, 9″-H), 1.21 (m, 12H, 3″-H, 4″-H, 5″-H, 6″-H, 7″-H, 8″-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 95.2, 95.1, 94.6, 94.1, 88.5, 70.4, 69.9, 69.6, 69.2 (2C), 69.1 (2C), 68.7, 68.1, 66.8, 66.5 (2C), 66.4, 66.4 (2C), 35.0, 33.1, 31.4, 29.9 (3C), 29.8 (2C), 29.2, 29.1, 28.5. Anal. Calcd for $C_{31}H_{57}BrFe_2$: C, 61.93; H, 6.20. Found: C, 62.11; H, 6.21.

*2-(p-Methoxybenzyl)-1,1′-biferrocenylene (**9a**).* Flash chromatography (silica: dichloromethane/*n*-hexane, 50/50 v/v; R_f = 0.42). Yield: 0.55 g (75%). Mp: 220 °C. IR (KBr, cm^{-1}): 3098 (C−H$_{Ar}$, w), 1612 (w), 1582 (w), 1514 (m), 1465 (w), 1438 (w), 1381 (w), 1317 (w), 1300 (m), 1242 (m), 1175 (m), 1132 (w), 1107 (m), 1071 (w), 1027 (m), 998 (m), 967 (w), 932 (w), 875 (w), 847 (m), 808 (m), 759 (m), 730 (m), 583 (m), 531 (m), 510 (s), 449 (m). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.14 (d, ^{3}J = 9 Hz, 2H, 3″-H, 7″-H), 6.77 (d, ^{3}J = 9 Hz, 2H, 4″-H, 6″-H), 5.41 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 7-H), 5.40 (m, 2H, 10-H, 5-H), 5.36 (m, 2H, 10′-H, 7′-H), 5.30 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 5′-H), 5.11 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 2′-H), 4.90 (d, ^{2}J = 16 Hz, 1H, 1″-H$_a$), 4.56 (d, ^{2}J = 16 Hz, 1H, 1″-H$_b$), 3.94 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 3′-H), 3.91 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 8-H), 3.87 (m, 3H, 8′-H, 4-H, 9′-H), 3.81 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 9-H), 3.79 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 4′-H), 3.70 (s, 3H, 8″-H), 3.61 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 3-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 158.0, 133.7, 129.7, 114.1, 95.3, 95.0, 94.9, 92.8, 88.5, 72.7, 70.8, 70.5, 69.8, 69.7, 69.4, 69.0, 68.6, 67.3, 67.1, 66.8, 66.4, 66.4, 66.2, 65.7, 55.6, 35.4. Anal. Calcd for $C_{28}H_{24}Fe_2O$: C, 68.89; H, 4.96. Found: C, 69.05; H, 4.88.

*3-(p-Methoxybenzyl)-1,1′-biferrocenylene (**9b**).* Flash chromatography (silica: dichloromethane/*n*-hexane, 75/25 v/v; R_f = 0.74). Yield: 0.53 g (73%). Mp: 197 °C. IR (KBr, cm^{-1}): 3098 (C−H$_{Ar}$, w), 1610 (m), 1583 (w), 1511 (s), 1462 (m), 1436 (w), 1319 (w), 1300 (m), 1269 (m), 1244 (s), 1175 (m), 1107 (w), 1078 (w), 1035 (s), 1012 (m), 943 (w), 847 (s), 808 (s), 762 (m), 635 (w), 684 (w), 609 (w), 555 (w), 505 (s), 488 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 6.99 (d, ^{3}J = 9 Hz, 2H, 3″-H, 7″-H), 6.74 (d, ^{3}J = 9 Hz, 2H, 4″-H, 6″-H), 5.41 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 5.31 (m, 5H, 2-H), 5.28 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 5.27 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 5-H), 3.87 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 3.81 (m, 4H), 3.76 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 4-H), 3.70 (s, 3H, 8″-H), 3.61 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 3.55 (d, ^{2}J = 15 Hz, 1H, 1″-H$_a$), 3.32 (d, ^{2}J = 15 Hz, 1H, 1″-H$_b$). ^{13}C NMR ($C_2D_2Cl_4$): δ 157.9, 133.9, 129.7, 114.0, 94.9, 94.8, 94.7, 94.6, 87.4, 70.7, 70.0, 69.8, 69.4, 69.3 (2C), 69.3, 69.0, 68.6, 66.9 (2C), 66.6 (2C), 66.6, 66.5, 55.6, 34.8. Anal. Calcd for $C_{28}H_{24}Fe_2O$: C, 68.89; H, 4.96. Found: C, 68.71; H, 4.81.

*2-(p-Iodobenzyl)-1,1′-biferrocenylene (**10a**).* Flash chromatography (silica: dichloromethane/*n*-hexane, 50/50 v/v; R_f = 0.74). Yield: 0.62 g (71%). Mp: 219 °C dec. IR (KBr, cm^{-1}): 3078 (C−H$_{Ar}$, w), 1483 (m), 1434 (w), 1397 (m), 1267 (m), 1256 (m), 1101 (w), 1054 (m), 1031 (m), 1008 (m), 876 (w), 843 (s), 807 (s), 727 (w), 631 (w), 505 (s). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.52 (d, ^{3}J = 8 Hz, 2H, 3″-H, 7″-H), 6.95 (d, ^{3}J = 8 Hz, 2H, 4″-H, 6″-H), 5.41 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 5.39 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 5-H), 5.34 (m, 2H), 5.30 (m, 2H), 5.08 (dt, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 4.93 (d, ^{2}J = 16 Hz, 1H, 1″-H$_a$), 4.52 (d, ^{2}J = 16 Hz, 1H, 1″-H$_b$), 3.91 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 3.90 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 3.86 (m, 2H, 4-H), 3.85 (m, 1H), 3.79 (m, 2H), 3.58 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 3-H). ^{13}C NMR ($C_2D_2Cl_4$): δ 141.3, 137.7, 130.9, 95.5, 94.7 (2 C), 92.9, 91.6, 87.2, 72.6, 71.0, 70.6, 69.7, 69.7, 69.5, 69.1, 68.6, 67.3, 67.1, 66.8, 66.5 (2 C), 66.3, 65.8, 35.8. Anal. Calcd for $C_{27}H_{21}Fe_2I$: C, 55.52; H, 3.62. Found: C, 55.60; H, 3.42.

*3-(p-Iodobenzyl)-1,1′-biferrocenylene (**10b**).* Flash chromatography (silica: dichloromethane/*n*-hexane, 80/20 v/v; R_f = 0.94). Yield: 0.66 g (75%). Mp: 225 °C dec. IR (KBr, cm^{-1}): 3082 (C−H$_{Ar}$, w), 1523 (w), 1482 (m), 1400 (w), 1378 (w), 1292 (w), 1268 (m), 1206 (w), 1195 (m), 1108 (w), 1079 (w), 1035 (s), 1006 (s), 944 (m), 845 (s), 802 (s), 739 (m), 678 (w), 634 (w), 528 (w), 506 (s), 484 (s), 452 (w). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.51 (d, ^{3}J = 8 Hz, 2H, 3″-H, 7″-H), 6.82 (d, ^{3}J = 8 Hz, 2H, 4″-H, 6″-H), 5.41 (m, 1H), 5.32 (m, 2H), 5.31 (m, 1H), 5.29 (m, 4H), 3.86 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 3.82 (m, 2H), 3.80 (m, 2H), 3.75 (dd, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H, 4-H), 3.59 (td, ^{3}J = 2 Hz, ^{4}J = 1 Hz, 1H), 3.56 (d, ^{2}J = 16 Hz, 1H, 1″-H$_a$), 3.32 (d, ^{2}J = 16 Hz, 1H, 1″-H$_b$). ^{13}C NMR ($C_2D_2Cl_4$): δ 141.4, 137.6, 130.8, 95.2, 95.0, 94.7, 94.4, 91.5, 86.1, 70.6, 69.9, 69.8, 69.4, 69.3 (2C), 69.2, 69.0, 68.7, 67.0 (2C), 66.7, 66.7, 66.7, 66.5, 35.2. Anal. Calcd for $C_{27}H_{21}Fe_2I$: C, 55.52; H, 3.62. Found: C, 55.58; H, 3.41.

■ ASSOCIATED CONTENT

Supporting Information

Figures and text giving additional ^{1}H−^{1}H-COSY NMR and ^{1}H−^{1}H-ROESY NMR spectra of the BFD derivatives **2a**,**b**−**8a**,**b** and details of the preparation of BFD^{+}PF$_6^{-}$ and Fc^{+}PF$_6^{-}$. 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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