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Synthesis and Properties of Ferrocenylmethylene-Bridged Calix[4]azulene and a New Example of Bis(1-azulenyl)ferrocenylmethylium Ion

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Ferrocenylmethylene-bridged calix[4]azulene derivative **3** and bis(1-azulenyl)ferrocenylmethane derivative **4** were obtained by the reaction of 6-*tert*-butylazulene (**6**) with ferrocenecarbaldehyde (**7**) in acetic acid. The new bis(1-azulenyl)ferrocenylmethylium ion **5**$^+$ was also generated by the hydride abstraction reaction of the corresponding hydro derivative **4** with DDQ. The novel ferrocene-substituted calix[4]azulene derivative **3** exhibit a reversible one-step multi-electron oxidation upon cyclic voltammetry.

Introduction

Calixarenes are molecular scaffolds that are used extensively in the field of host–guest chemistry.[1,2] A variety of sophisticated host molecules consisting of a calixarene skeleton have been synthesized by using the regio- and stereoselective functionalization methods that have been developed for the synthesis of this class of compounds during the last few decades.

Azulene ($C_{10}H_8$) has attracted the interest of many research groups owing to its unusual properties as well as its blue color.[3] Previously, we reported the synthesis of 2,2′,2′′,2′′′-tetramethoxycalix[4]azulene (**1**) starting from the reaction of 2-methoxyazulene with paraformaldehyde. Our methodology for the preparation of **1** included a multistep reaction and therefore the overall yield of the product was rather low.[4] A one-pot procedure did not improve the yield of the desired **1** in solution. Recently, Colby and Lash reported the Florisil-mediated reaction of the parent azulene with paraformaldehyde, which gave calix[4]azulene (**2**) in a good yield.[5] The yield of the desired cyclic product **2** was significantly improved by using the solid support. They also reported the reactions with other carbonyl compounds, such as acetone, hexachloroacetone, 1,3-dichloroacetone, cyclopentanone, and propionaldehyde, but the expected cyclic products were never obtained under their conditions (Figure 1).

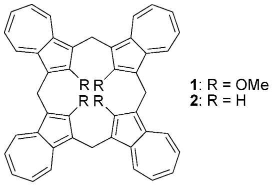

Figure 1. Calix[4]azulene derivatives **1** and **2**.

We found that the condensation reaction of 6-*tert*-butylazulene with ferrocenecarbaldehyde as the carbonyl compound under acidic conditions afforded the expected cyclic product in a moderate yield in solution. The successful preparation of the calix[4]azulene derivative using the functionalized carbonyl compound provides a new and efficient functionalization strategy for the synthesis of calix[4]azulene derivatives. Herein, we report the efficient preparation of the novel ferrocenylmethylene-bridged calix[4]azulene **3** and the new bis(1-azulenyl)ferrocenylmethylium ion derivative **5**$^+$, which was formed by the hydride abstraction reaction of the corresponding hydro derivative **4** with DDQ. The properties of these new products were characterized by electrochemical analysis and absorption spectroscopy.

Results and Discussion

Synthesis

We recently reported the synthesis of bis(1-azulenyl)ferrocenylmethylium hexafluorophosphates with high thermodynamic stabilities by the hydride abstraction reaction of the corresponding hydrocarbon derivatives.[6] We ex-

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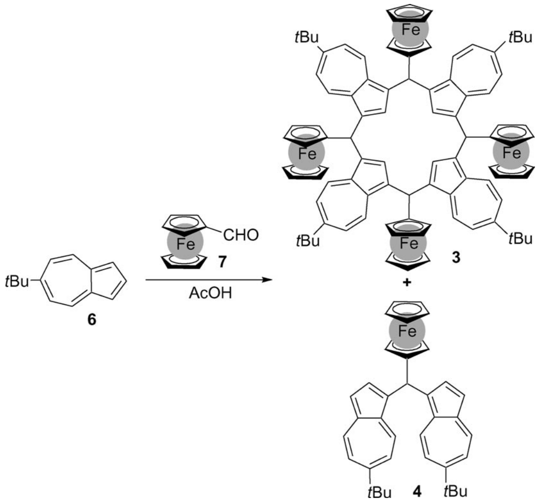
amined the reaction of 6-*tert*-butylazulene (**6**) with ferrocenecarbaldehyde (**7**) in acetic acid under similar reaction conditions to those reported by us previously. In this reaction we eventually discovered that ferrocenylmethylene-bridged calix[4]azulene derivative **3** was obtained as the main product along with bis(6-*tert*-butyl-1-azulenyl)ferrocenylmethane (**4**; Scheme 1). The yields of the products **3** and **4** were affected by the proportions of the reagents. The results are summarized in Table 1.



Scheme 1.

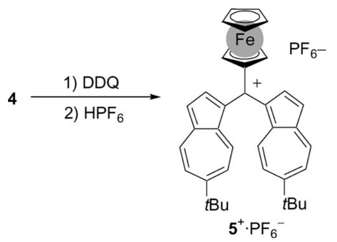
Table 1. Synthesis of ferrocenylmethylene-bridged calix[4]azulene **3**.

Entry	Ratio **6**/**7**	Reaction time [h]	Yield [%]	
			3	**4**
1	1:1	48	38	2
2	1:1	170	37	0
3	1:3	48	49	15
4	1:5	48	33	29

The reaction of equimolar amounts of **6** with **7** in acetic acid at room temperature for 48 h afforded the cyclic product **3** in 38% yield along with **4** in 2% yield (Table 1, entry 1). Compounds **3** and **4** possess fair solubility in common organic solvents such as chloroform and dichloromethane. Moreover, these compounds are stable and show no decomposition even after several weeks at room temperature. Increasing the reaction time to 170 h had little effect on the yields of the products (entry 2). The reaction of **6** with the 3 mol-equiv. of **7** improved the yields of both **3** and **4** (**3**: 49%; **4**: 15%; entry 3), but the yield of **3** was reduced when 5 mol-equiv. of **7** was used in this reaction (entry 4).

We have already reported the reaction of several azulene derivatives with various aldehydes.[7] However, calixazulene derivatives have only ever been obtained by reaction with paraformaldehyde. This can be attributed to the characteristic reactivity between 6-*tert*-butylazulene (**6**) and ferrocenecarbaldehyde (**7**) in the cyclization reaction to give a calixazulene derivative. We also investigated the Florisil-mediated reaction of **6** with **7** under similar conditions to those reported by Colby and Lash.[5] However, the desired cyclic product was not produced, only the starting materials were recovered.

The methylium ion $\mathbf{5}^+$ was synthesized by the hydride abstraction reaction of the corresponding hydro derivative **4**. The reaction of **4** with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in dichloromethane at room temperature followed by the addition of a 60% aqueous HPF_6 solution yielded the expected monocation $\mathbf{5}^+$ as the hexafluorophosphate salt in 93% yield (Scheme 2). The $\mathbf{5}^+\cdot PF_6^-$ salt was obtained as stable, deep-colored crystals and can be stored in the crystalline state at room temperature. The reaction of **3** with DDQ was also examined, but under similar reaction conditions the reaction generated an inseparable complex mixture. HRMS analysis of the mixture did not reveal the molecular-ion peak of the expected tetracationic species. Recently, the generation of the tetracationic species of the methylene-bridged calix[4]azulene derivative by reaction with DDQ was reported.[8] Therefore, it would seem that the ferrocene substituents in the ferrocenylmethylene-bridged calix[4]azulene affect the hydride abstraction reaction with DDQ.



Scheme 2.

Spectroscopic Properties

Compounds **3**, **4**, and $\mathbf{5}^+\cdot PF_6^-$ were fully characterized by spectroscopic data, which are presented in the Exp. Sect. The mass spectra of **3** and **4** showed the correct molecular-ion peaks. The high-resolution mass spectrum of the salt $\mathbf{5}^+\cdot PF_6^-$ ionized by ESI showed the correct $[M - PF_6^-]^+$ ion peaks, which indicates the ionic structure of the salt $\mathbf{5}^+\cdot PF_6^-$. The characteristic stretching–vibration bands of the hexafluorophosphate in the salt $\mathbf{5}^+\cdot PF_6^-$ were observed at 839 (strong) and 557 (medium) cm^{-1} in its IR spectrum. These results are consistent with the structures of these products. The cyclic structure of the product **3** was also characterized by ^1H NMR spectroscopy (see the Supporting Information); its spectrum revealed a highly symmetrical structure, which is attributable to the formation of a single symmetrical stereoisomer. However, the stereochemistry of the product **3** could not be determined because we were unable to obtain crystals suitable for crystal structure analysis.

The absorption maxima and extinction coefficients ($\log\varepsilon$) of compounds **3**, **4**, and the cation $\mathbf{5}^+$ together with those of $\mathbf{8}^+$–$\mathbf{10}^+$ (Figure 2) are summarized in Table 2. The UV/Vis spectra of **3**, **4**, and $\mathbf{5}^+$ are shown in Figure 3. Compounds **3** and **4** show characteristic absorptions arising from the azulene system at 615 and 590 nm, respectively, in dichloromethane in the visible region. The extinction coefficients increase with the number of substituted azulene rings. The longest wavelength absorption band of **3** showed bathochromic shifts of 37 and 77 nm compared with those of the methylene-bridged calix[4]azulene derivatives **1** and **2**, respectively [**1**: 578 nm (logε = 2.85);[4] **2**: 538 nm (logε = 3.15)[5]], even though the π conjugation between the azulene and ferrocene rings is shielded by an sp^3 carbon atom. The UV/Vis spectrum of **5**$^+$ in acetonitrile displays strong absorptions in the visible region that extend up to the infrared region. The absorption maxima of **5**$^+$ are comparable to those of **8**$^+$. However, compound **5**$^+$ exhibits a hypsochromic shift of 26 and 28 nm, respectively, compared with the corresponding 1-alkylazulene derivatives **9**$^+$ and **10**$^+$. Therefore, for these carbocations the absorption maxima are little dependent on the substituents at the 6-position of the azulene ring, but are affected by the substituents at the 1-position.

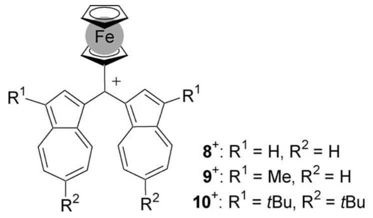


Figure 2. Bis(1-azulenyl)ferrocenylmethylium ion derivatives **8**$^+$–**10**$^+$.

Table 2. Absorption maxima for **3**, **4**,[a] **5**$^+$, and **8**$^+$–**10**$^{+[b]}$ and their coefficients.

Sample	λ_{max} [nm] [log(ε/M^{-1}cm^{-1})]
3	395 sh [4.25], 615 [3.09], 660 sh [3.01], 734 sh [2.52]
4	550 sh [2.64], 590 [2.75], 640 sh [2.67], 711 sh [2.20]
5$^+$	400 [4.41], 471 [4.08], 629 [4.29], 722 [3.95], 884 [3.81]
8$^{+[c]}$	395 sh [4.15], 447 sh [4.14], 467 [4.16], 591 sh [4.10], 621 [4.20], 746 [3.84]
9$^{+[c]}$	468 sh [3.89], 497 [3.96], 629 sh [4.18], 655 [4.23], 711 sh [4.09]
10$^{+[c]}$	461 sh [4.00], 486 [4.03], 657 [4.31], 693 sh [4.28]

[a] The UV/Vis spectra of **3** and **4** were recorded in dichloromethane. [b] The UV/Vis spectra of **5**$^+$ and **8**$^+$–**10**$^+$ were recorded in acetonitrile. [c] See ref.[6]

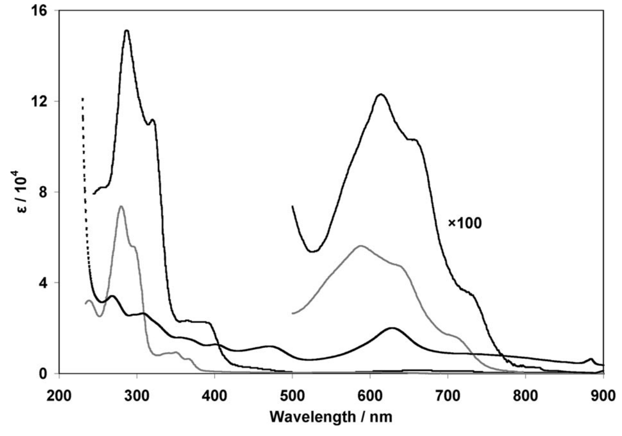


Figure 3. UV/Vis spectra of **3** (black line) and **4** (gray line) in dichloromethane and **5**$^+$ (broken line) in acetonitrile.

Redox Behavior

To clarify the electrochemical properties, the redox behavior of **3**, **4**, and **5**$^+$ was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Measurements were carried out using a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as the supporting electrolyte with platinum wire as the auxiliary and working electrodes. All measurements were carried out under argon and the potentials were measured relative to an Ag/AgNO$_3$ reference electrode with Fc/Fc$^+$ as the internal reference, which discharges at +0.15 V under these conditions. The redox potentials (in V vs. Ag/AgNO$_3$) of **3**, **4**, and **5**$^+$ are summarized in Table 3, along with those of the related **8**$^+$–**10**$^+$.

Table 3. Redox potentials [V vs. Ag/AgNO$_3$][a] for **3**, **4**, **5**$^+$, and **8**$^+$–**10**$^+$.

Sample	Method	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}
3	CV			+0.08	
	(DPV)	(–2.15)		(+0.06)	(+0.86)
4	CV			+0.03	
	(DPV)	(–2.04)	(–2.18)	(+0.01)	(+0.42)
5$^+$	CV	–0.82		+0.48	
	(DPV)	(–0.80)	(–1.96)	(+0.46)	(+1.02)
8$^{+[b,c]}$	CV	–0.76	(–1.58)	+0.47	(+1.08)
9$^{+[b,c]}$	CV	–0.79	(–1.65)	+0.43	(+0.95)
10$^{+[b,c]}$	CV	–0.87	(–1.74)	+0.42	(+0.95)

[a] Redox potentials were measured by CV and DPV [V vs. Ag/AgNO$_3$, 1 mM in benzonitrile containing Et$_4$NClO$_4$ (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mV s^{-1}, and Fc/Fc$^+$ = +0.15 V]. In the case of reversible waves, half-wave potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses. [b] Redox potentials measured in acetonitrile for **8**$^+$–**10**$^+$. Irreversible processes are shown in parentheses. [c] See ref.[6]

Ferrocene derivatives have attracted interest due to their redox properties, with their lower oxidation potentials to form stabilized radical cationic states, that is, ferrocenium ions. The azulene derivatives with multiple ferrocenyl moieties are expected to show multiple-electron oxidation with reversible redox properties. Electrochemical reduction of **3** showed an irreversible wave upon CV, attributable to the generation of an unstable radical anion by the reduction of azulene moieties of **3**. The first reduction potential was determined by DPV to be –2.15 V. A reversible oxidation wave was observed at +0.08 V for **3** upon CV, which can be ascribed to the electrochemical oxidation of the four ferrocenyl moieties of **3** in one step to form the tetracationic species (Figure 4). The oxidation potential of **3** is slightly less positive than that of the parent ferrocene (+0.15 V), which is attributable to the electron-donating nature of the methylene moieties substituted by two azulene rings. These results indicate the strong π-donating ability, that is, the higher HOMO level, of the calix[4]azulene derivative **3** compared with the parent ferrocene. Although **3** contains multiple ferrocenyl groups, its CV displayed only a single anodic process with features of chemical reversibility. These results should be reflected by a less effective electrochemical intramolecular interaction between the ferrocenyl groups and the azulene rings.

The electrochemical reduction of **4** also exhibited irreversible waves, which are attributable to the reduction of the azulene ring of **4** upon CV. The oxidation potentials were determined at –2.04 and –2.18 V by DPV. The oxidation potential of **4** (+0.03 V) was observed upon CV to be at a less positive potential than that of the parent ferrocene, similarly to that of **3**. These results are also ascribed to the electron-donating nature of the alkyl moiety connected by two 1-azulenyl groups.

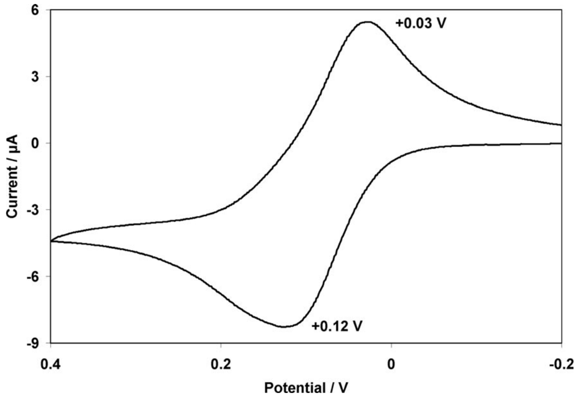


Figure 4. Cyclic voltammogram of the oxidation of **3** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate = 100 mV s^{-1}.

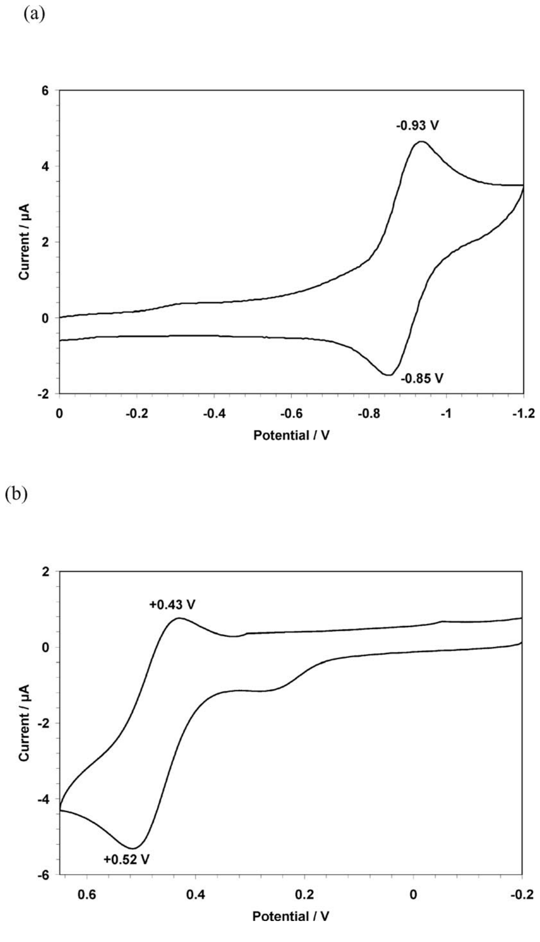


Figure 5. Cyclic voltammograms of (a) the reduction and (b) the oxidation of $\mathbf{5}^+$ (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate: 100 mV s^{-1}.

The cyclic voltammograms for the reduction and the oxidation of monocation $\mathbf{5}^+$ are shown in Figure 5. The electrochemical reduction of $\mathbf{5}^+$ showed a reversible wave at –0.82 V upon CV and an irreversible wave at –1.96 V upon DPV due to the formation of a neutral radical and an anionic species, respectively. The first reduction potential of $\mathbf{5}^+$ is slightly more negative than those of $\mathbf{8}^+$ and $\mathbf{9}^+$. This might be attributable to the *tert*-butyl substituents at the 6-positions of the azulene rings, which stabilize the cationic state by their electron-donating nature. The electrochemical oxidation of $\mathbf{5}^+$ also showed a reversible wave at +0.48 V. This clearly indicates the generation of a dicationic species by oxidation of the ferrocene ring of $\mathbf{5}^+$. The first oxidation potential of $\mathbf{5}^+$ is more positive than that of the parent ferrocene by 0.33 V. These results are attributable to the reduced π-donating ability of $\mathbf{5}^+$, that is, the lower HOMO level, which results from the electron-withdrawing nature of the attached carbocation unit.

Conclusions

The novel ferrocenylmethylene-bridged calix[4]azulene derivative **3** was obtained as a single stereoisomer in a moderate yield by the one-pot reaction of 6-*tert*-butylazulene (**6**) with ferrocenecarbaldehyde (**7**) in acetic acid. The new bis(1-azulenyl)ferrocenylmethylium ion $\mathbf{5}^+$ was also prepared by the hydride abstraction reaction of the corresponding hydro derivative **4** with DDQ. CV and DPV analyses revealed that compound **3** exhibits a reversible one-step oxidation process with a less positive oxidation potential than the parent ferrocene even though compound **3** contains multiple ferrocenyl groups in its structure. Cation $\mathbf{5}^+$ displayed amphoteric redox properties upon CV, which are attributable to both the oxidation of the ferrocene ring and the reduction of the cationic moiety of $\mathbf{5}^+$.

Experimental Section

General: Melting points were determined with a Yanagimoto MP-S3 micro melting apparatus and are uncorrected. Mass spectra were obtained with a Hitachi M-2500 or Bruker APEX II spectrometer. IR and UV/Vis spectra were measured with a Shimadzu FT-IR 8100M spectrometer and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded with a Bruker Avance 400 spectrometer at 400 MHz (100 MHz) or with a Bruker AM 600 spectrometer at 600 MHz (150 MHz). Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from Ag/AgNO$_3$ (0.1 M) in a solution of tetrabutylammonium perchlorate (0.1 M) in acetonitrile. Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Reaction of 6-*tert*-Butylazulene (6) with Ferrocenecarbaldehyde (7): A solution of **6** (544 mg, 3.00 mmol) and **7** (214 mg, 1.00 mmol) in acetic acid (10 mL) was stirred at room temperature for 48 h under Ar. The reaction mixture was poured into water and extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and Bio-Beads® with CH_2Cl_2 as eluent to give **3** (189 mg, 49%) as green crystals and **4** (85 mg, 15%) also as green crystals.

3: M.p. 260.0–265.0 °C (decomp.). IR (KBr disk): $\tilde{\nu}_{max}$ = 3029 (w), 2963 (s), 2905 (m), 2870 (m), 1719 (m), 1578 (s), 1549 (m), 1516 (m), 1478 (m), 1458 (m), 1443 (m), 1428 (m), 1391 (m), 1364 (m), 1312 (m), 1281 (m), 1243 (m), 1198 (m), 1183 (w), 1071 (m), 1038 (w), 926 (w), 831 (m), 768 (w), 675 (w), 617 (w), 536 (w), 448 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/$M^{-1}cm^{-1}$)] = 288 [5.15], 321 [5.00], 395 (sh) [4.25], 615 [3.09], 660 (sh) [3.01], 734 (sh) [2.52] nm. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.38 (d, J = 11.2 Hz, 8 H, 4,8-H), 8.07 (s, 4 H, 2-H), 7.14 (d, J = 11.2 Hz, 8 H, 5,7-H), 6.34 (s, 4 H, CH), 4.11 (d, J = 1.9 Hz, 8 H, 2,5-H of Fc), 4.07 (d, J = 1.9 Hz, 8 H, 3,4-H of Fc), 3.91 (s, 20 H, Cp), 1.38 (s, 36 H, *t*Bu) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3 (C-6), 136.6 (C-2), 133.3 (C-3a,8a), 132.2 (C-1,3), 131.4 (C-4,8), 119.0 (C-5,7), 96.4 (C-1 of Fc), 68.7 (Cp), 68.6 (C-3,4 of Fc), 67.1 (C-2,5 of Fc), 38.2 (s, *t*Bu), 34.1 (CH), 31.8 (q, *t*Bu) ppm. MS (MALDI-TOF): calcd. for $C_{100}H_{96}Fe_4$ $[M]^+$ 1520.4909; found 1520.2870. $C_{100}H_{96}Fe_4$ (1521.3): calcd. C 78.95, H 6.36; found C 78.93, H 6.48.

4: M.p. 95.0–100.0 °C. IR (KBr disk): $\tilde{\nu}_{max}$ = 3081 (w), 3027 (w), 2963 (s), 2903 (m), 2867 (m), 1578 (s), 1551 (m), 1493 (m), 1478 (m), 1460 (m), 1402 (s), 1362 (m), 1306 (w), 1250 (w), 1237 (m), 1198 (w), 1105 (w), 1057 (w), 1040 (w), 1024 (w), 1001 (m), 922 (w), 895 (m), 837 (s), 820 (w), 754 (m), 723 (w), 706 (w), 675 (w), 617 (w), 536 (w), 490 (m), 451 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/$M^{-1}cm^{-1}$)] = 239 [4.51], 280 [4.87], 298 (sh) [4.74], 342 (sh) [3.96], 351 [3.96], 368 [3.80], 550 (sh) [2.64], 590 [2.75], 640 (sh) [2.67], 711 (sh) [2.20] nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 10.4 Hz, 2 H, 8-H), 8.14 (d, J = 10.4 Hz, 2 H, 4-H), 7.72 (d, J = 3.6 Hz, 2 H, 2-H), 7.22 (dd, J = 10.4, 1.6 Hz, 2 H, 7-H), 7.19 (d, J = 3.6 Hz, 2 H, 3-H), 7.18 (dd, J = 10.4, 1.6 Hz, 2 H, 5-H), 6.40 (s, 1 H, CH), 4.08 (br. s, 4 H, 2,3,4,5-H of Fc), 3.90 (s, 5 H, Cp), 1.38 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 140.0, 137.2, 136.0, 134.4, 133.5, 132.9, 120.7, 120.3, 116.6, 97.0, 69.4, 69.1, 67.6, 38.9, 37.1, 32.4 ppm. HRMS (ESI): calcd. for $C_{39}H_{40}Fe + Na^+$ $[M + Na]^+$ 587.2372; found 587.2371. $C_{39}H_{40}Fe\cdot\frac{1}{4}H_2O$ (564.6 + 4.5): calcd. C 82.31, H 7.17; found C 82.23, H 7.23.

Bis(6-*tert*-butyl-1-azulenyl)ferrocenylmethylium Hexafluorophosphate ($5^+\cdot PF_6^-$): DDQ was added at room temperature to a solution of **4** (139 mg, 0.25 mmol) in CH_2Cl_2 (25 mL). The solution was stirred at the same temperature for 5 min and a 60% aqueous HPF_6 solution (5 mL) was then added to the reaction mixture. After stirring the solution at room temperature for an additional 5 min, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and then Et_2O was added to the solution. The precipitated crystals were collected by filtration, washed with Et_2O, and dried in vacuo to give $\mathbf{5^+}\cdot PF_6^-$ (165 mg, 93%) as a deep-blue powder; m.p. 198.0–205.0 °C (decomp.). HRMS (ESI): calcd. for $C_{39}H_{39}Fe^+$ $[M]^+$ 563.2396; found 526.2393. IR (KBr disk): $\tilde{\nu}_{max}$ = 3115 (w), 2963 (m), 2922 (w), 2870 (w), 1576 (m), 1460 (s), 1429 (s), 1379 (m), 1356 (m), 1325 (s), 1294 (s), 1246 (m), 1219 (m), 1194 (m), 1109 (m), 1076 (m), 1061 (m), 1055 (m), 1018 (w), 974 (w), 924 (w), 839 (s), 775 (w), 743 (w), 708 (w), 669 (w), 617 (w), 594 (w), 557 (w), 500 (w), 482 (w) cm^{-1}. UV/Vis (CH_3CN): λ_{max} [log(ε/$M^{-1}cm^{-1}$)] = 268 [4.53], 300 (sh) [4.41], 308 [4.42], 360 (sh) [4.20], 400 [4.41], 471 [4.08], 629 [4.29], 722 [3.95], 884 [3.81] nm. ^1H NMR (400 MHz, CD_3CN): δ = 8.68 (d, J = 10.4 Hz, 2 H, 8-H), 8.62 (d, J = 4.4 Hz, 2 H, 2-H), 8.04 (d, J = 10.4 Hz, 2 H, 7-H), 7.71 (d, J = 4.4 Hz, 2 H, 3-H), 7.59 (d, J = 10.4 Hz, 2 H, 4-H), 7.41 (d, J = 10.4 Hz, 2 H, 5-H), 5.41 (dd, J = 2.4, 2.4 Hz, 2 H, 2,5-H of Fc), 5.13 (dd, J = 2.4, 2.4 Hz, 2 H, 3,4-H of Fc), 4.50 (s, 5 H, Cp), 1.30 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 173.2, 169.6, 151.6, 146.6, 144.0, 141.3, 139.4, 133.9, 132.3, 131.4, 125.4, 119.3, 86.5, 79.6, 78.6, 74.3, 40.4, 32.1 ppm. $C_{39}H_{39}F_6FeP$ (708.6): calcd. C 66.11, H 5.55; found C 65.98, H 5.77.

Supporting Information (see also the footnote on the first page of this article): ^1H NMR spectrum of compound **3**.

Acknowledgments

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