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Acid-Catalyzed Condensation of Azulenes with 9-Anthracenecarbaldehyde and the Synthesis of (9-Anthryl)di(1-azulenyl)methyl and (1-Azulenyl)[10-(1-azulenyl)-9-anthryl]methyl Hexafluorophosphates

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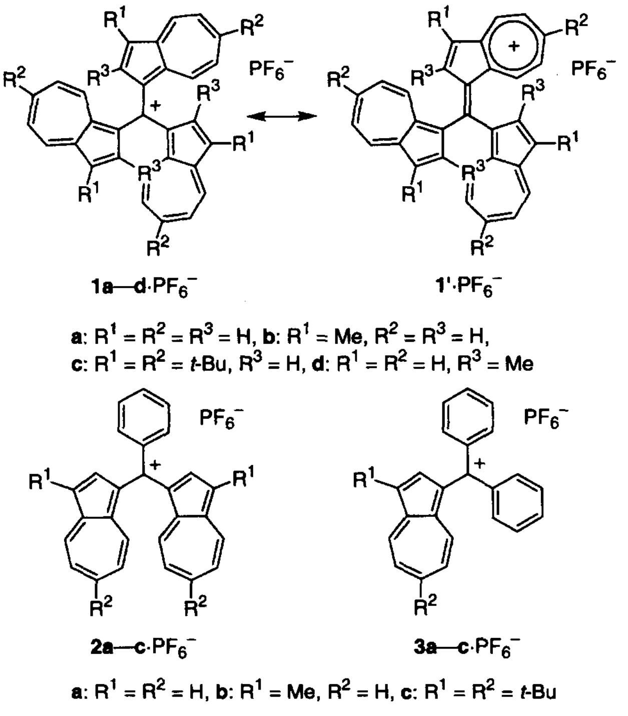
Acid-catalyzed condensations of 1-methyl and 1,6-di-*t*-butylazulenes with 9-anthracenecarbaldehyde led us to unexpected 9-(1-azulenyl)-10-[(1-azulenyl)methylidene]-9,10-dihydroanthracenes **10a** and **10b** as major products, together with (9-anthryl)di(1-azulenyl)methanes **7a** and **7b**. Hydride abstraction from **7a**, **7b**, and **10b** with DDQ afforded substituted (9-anthryl)di(1-azulenyl)methyl and (1-azulenyl)[10-(1-azulenyl)-9-anthryl]methyl hexafluorophosphates **6a**, **6b**$\cdot PF_6^-$ and **11b**$\cdot PF_6^-$, respectively. Their properties were fully characterized. The reaction of the 3-methyl derivatives **10a**, however, did not afford the desired (3-methyl-1-azulenyl)[10-(3-methyl-1-azulenyl)-9-anthryl]methyl hexafluorophosphate (**11a**$\cdot PF_6^-$), due to the low stabilities of **11a**. While cations **6a** and **6b** prepared from **7a** and **7b** showed high stabilities with large pK_{R^+} values (10.7±0.1 and 12.4±0.1, respectively), cation **11b** exhibited relatively low stabilities with the pK_{R^+} value of 5.0±0.1.

We have recently reported the synthesis of a series of (1-azulenyl)methyl cations, i.e., tri(1-azulenyl)methyl, di(1-azulenyl)(phenyl)methyl, and (1-azulenyl)diphenylmethyl hexafluorophosphates (**1a**$\cdot PF_6^-$, **2a**$\cdot PF_6^-$, and **3a**$\cdot PF_6^-$) and their derivatives (e.g., **1b**—**d**$\cdot PF_6^-$, **2b**, **2c**$\cdot PF_6^-$, and **3b**, **3c**$\cdot PF_6^-$) (Chart 1). These cations were readily prepared by hydride abstraction from the corresponding hydrocarbons, which were obtained by acid-catalyzed condensation of azulenes with aldehydes or benzhydroles.[1] These cations showed high stabilities with large pK_{R^+} values (e.g., **1a**; 11.3, **2a**; 10.8, and **3a**; 3.6, respectively).[1d] The high stabilities of these cations are rationalized by the large π-conjugative effect of 1-azulenyl groups with cationic carbons (e.g., **1'**).



1a—d$\cdot PF_6^-$ **1'**$\cdot PF_6^-$

a: $R^1 = R^2 = R^3 = H$, **b**: $R^1 = Me$, $R^2 = R^3 = H$,
c: $R^1 = R^2 = t\text{-Bu}$, $R^3 = H$, **d**: $R^1 = R^2 = H$, $R^3 = Me$

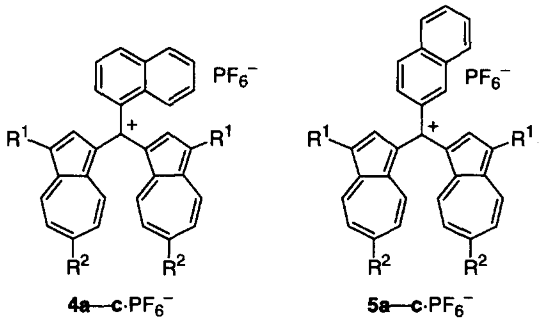
2a—c$\cdot PF_6^-$ **3a—c**$\cdot PF_6^-$

a: $R^1 = R^2 = H$, **b**: $R^1 = Me$, $R^2 = H$, **c**: $R^1 = R^2 = t\text{-Bu}$

Chart 1.

Tris(2-methyl-1-azulenyl)methyl cation (**1d**; pK_{R^+} 13.4) exhibited relatively high stability compared to that of 3,3′,3″-trimethyl derivative **1b** (pK_{R^+} 11.4), although some destabilization could be expected by the increase of the twisting of the three rings due to the steric congestion.[1c,1f] The high stabilities of **1d** could be explained by the destabilization of the corresponding hydroxy derivatives for the equilibrium with the methyl cation **1d** by streic congestion. The large steric congestion in methyl cations might increase the stabilities. 1- and 2-naphthyl derivatives **4a**—**c**$\cdot PF_6^-$ and **5a**—**c**$\cdot PF_6^-$ were also prepared; their dynamic stereochemistry was studied using variable-temperature ^1H NMR spectra (Chart 2).[2] In the cases of **4a**—**c** and **5a**—**c**, 1- and 2-naphthyl substituents did not affect the stabilities of the cations. The pK_{R^+} values of **4a**—**c** (10.7—12.6) and **5a**—**c** (10.3—12.7)[2] were very similar to those of **2a**—**c** (10.5—12.4).[1d]

Further steric congestion might stabilize the methyl cations. We prepared 9-anthryl derivatives, i.e., (9-anthryl)di(1-azulenyl)methyl hexafluorophosphates **6a** and **6b**$\cdot PF_6^-$, to examine their stabilities. In the present paper, we will report the synthesis and properties of the hexafluorophosphates **6a** and **6b**$\cdot PF_6^-$ by hydride abstraction from the corresponding hydrocarbons **7a** and **7b**. Acid-catalyzed condensation of 1-methyl and 1,6-di-*t*-butylazulenes (**8a** and **8b**)[1d] with 9-



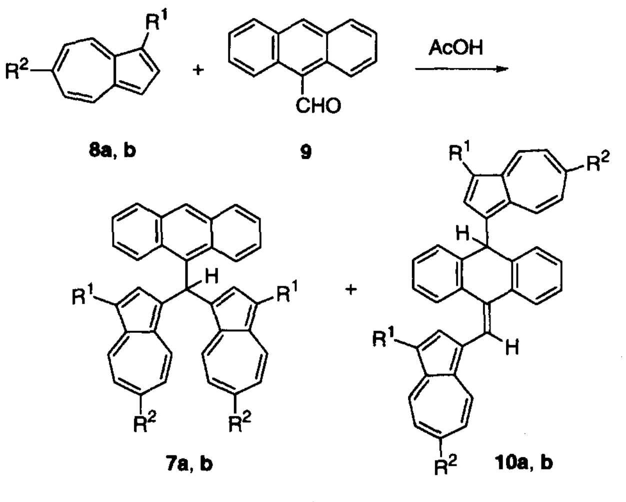
a: $R^1 = R^2 = H$, **b**: $R^1 = Me$, $R^2 = H$, **c**: $R^1 = R^2 = t\text{-}Bu$

Chart 2.

anthracenecarbaldehyde (**9**) led us to condensation products, i.e., 9-(1-azulenyl)-10-[(1-azulenyl)methylidene]-9,10-dihydroanthracenes **10a** and **10b**, as major products, together with (9-anthryl)di(1-azulenyl)methanes **7a** and **7b**. The methyl derivatives **10a** did not lead us to the corresponding hexafluorophosphate **11a**·PF_6^- due to their low stabilities. However, we found that the adducts **10b** gave (3,6-di-*t*-butyl-1-azulenyl)[10-(3,6-di-*t*-butyl-1-azulenyl)-9-anthryl]methyl hexafluorophosphate (**11b**·PF_6^-) in moderate yield. Here we will also report the preparation and properties of the unsymmetrical cation **11b**, together with those of the (9-anthryl)di(1-azulenyl)methyl cations **6a** and **6b**.

Results and Discussion

Acid-catalyzed condensation of azulenes with aldehydes and the hydride abstraction from the condensation products using DDQ were applied for the synthesis of the (9-anthryl)di(1-azulenyl)methyl hexafluorophosphates **6a** and **6b**·PF_6^-.[1] The condensation of **8a** and **8b** with **9** in acetic acid afforded the desired (9-anthryl)di(1-azulenyl)methanes **7a** and **7b** in 5.2 and 11% yields, respectively (Scheme 1). However, the major products of the condensation were 9-(1-azulenyl)-10-[(1-azulenyl)methylidene]-9,10-dihydroanthracenes **10a** and **10b** (24 and 22% yield, respectively). These two types of the condensation products did not show any interconversion under the reaction conditions. Therefore, the formation of the unsymmetrical products **10a** and **10b** can be ascribed to the attack of the second azulene to the C-10 position of the intermediate, i.e., (9-anthryl)(1-azulenyl)methyl cation (**12**).



a: $R^1 = Me$, $R^2 = H$, **b**: $R^1 = R^2 = t\text{-}Bu$

Scheme 1.

The experimental results can be explained in terms of the molecular-orbital coefficients and atomic charge densities of the intermediate cation **12** for the condensation of azulene with **9**. Intermediate cations **13**, **14**, and **12** for the condensation of azulene with benzaldehyde, 1-naphtalenecarbaldehyde, and 9-anthracenecarbaldehyde (**9**) are shown in Chart 3. Optimized structures with LUMO distribution diagrams (MOPAC PM3) of the most stable propeller conformers (heat of formation of **13**; 1123, **14**; 1195, and **12**; 1298 kJ mol^{-1}, respectively) are shown in Fig. 1, although

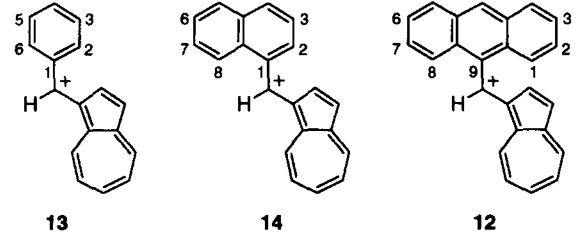


Chart 3.

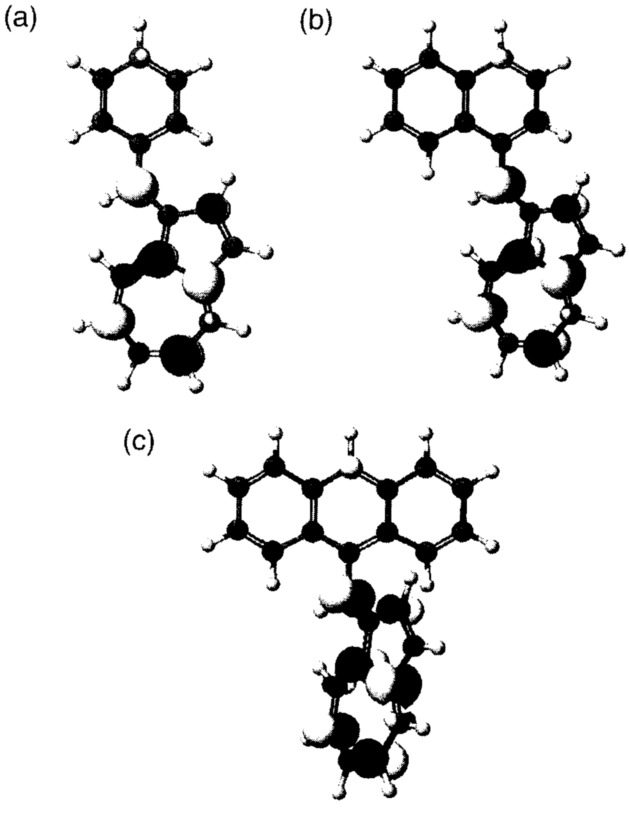
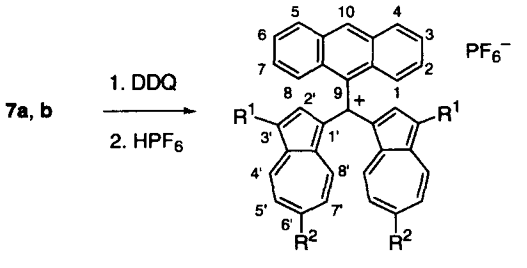


Fig. 1. Optmized ball and stick molecular structures with the LUMO distribution diagrams (MOPAC PM3) of the intermediates of the condensations of azulene with (a) benzaldehyde, (b) 1-naphtalenecarbaldehyde, and (c) 9-anthracenecarbaldehyde (**9**).

several propeller conformations can be expected for these cations.[3] For the LUMO of **13**, **14**, and **12**, the molecular-orbital coefficient on the C-10 atom of **12** (0.200) was slightly larger than that on the C-5 atoms of **13** (0.148) and **14** (0.184). The atomic charge density increased in the order of the C-5 atom of **13** (−0.017), that of **14** (0.024), and the C-10 atom of **12** (0.048), although the densities of cationic carbons of the intermediates **13** (0.180), **14** (0.169), and **12** (0.183) were very similar to each other. The condensations of azulenes with benzaldehyde and 1-naphtalenecarbaldehyde afford only di(1-azulenyl)(phenyl)methanes and di(1-azulenyl)(1-naphtyl)methanes, respectively.[1d,2] Therefore, the relatively large LUMO coefficient and high atomic charge density on the C-10 atom of **12**, compared with those on the C-5 atoms of **13** and **14** must be important factors to determine the reactivities of **12** to produce **10a** and **10b** as major products.

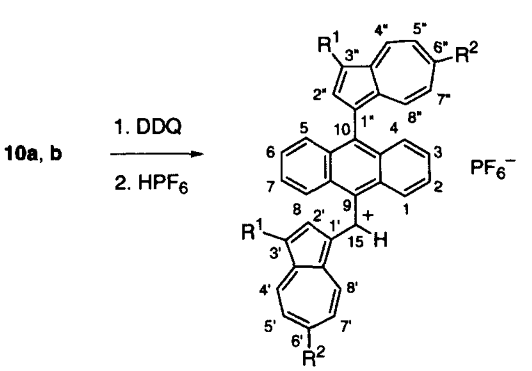
Hydride abstraction from the methanes **7a** and **7b** with DDQ in dichloromethane at room temperature, followed by an addition of 60% aqueous HPF_6, yielded the desired (9-anthryl)di(1-azulenyl)methyl hexafluorophosphates **6a** and **6b**·PF_6^- in 74 and 77% yield, respectively (Scheme 2). Hydride abstraction from the unsymmetrical adduct **10b** also afforded the corresponding hexafluorophosphate **11b**·PF_6^- in 48% yield after the treatment of 60% aqueous HPF_6 (Scheme 3). However, **10a** did not afford the desired salt **11a**·PF_6^- in pure form by this method due to its low stability. These new salts **6a**, **6b**·PF_6^- and **11b**·PF_6^- were stable, deeply colored crystals.



6a, b·PF_6^-

a: R^1 = Me, R^2 = H, b: R^1 = R^2 = *t*-Bu

Scheme 2.



11a, b·PF_6^-

a: R^1 = Me, R^2 = H, b: R^1 = R^2 = *t*-Bu

Scheme 3.

Mass spectra of **6a**, **6b**·PF_6^- and **11b**·PF_6^- ionized by FAB showed the correct M^+-PF_6 ion peaks, which indicated the cationic structure of these compounds. The characteristic bands for the counter ion (PF_6^-) were observed at 839 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported the ionic structure of these compounds. These salts showed strong absorption in the visible region, in analogy with the salts **2b**, **2c**·PF_6^- and **4b**, **4c**·PF_6^-, etc.[1,2] The absorption maxima (nm) and the coefficients (log ε) of these salts in the visible region are summarized in Table 1. UV-vis spectra of **6b** and **11b** in acetonitrile, along with that of the related analogous benzyl cation **2c**, are shown in Fig. 2. The strong absorption of **6a** and **6b** in the visible region [**6a**; 690 (log ε 4.53) and **6b**; 692 nm (4.79)] exhibited a bathochromic shift by 14 and 11 nm, respectively, compared with those of **2b** and **2c**. The absorption maxima of the cation **11b** were completely different from those of **2c**, **4c**, and **6b**. That of **11b** [649 (log ε 4.11)] showed an hypsochromic shift by 43 nm, compared with that of **6b** and the absorption tailed up to over 850 nm.

As one criterion of thermodynamic stabilities, the pK_{R^+} values of these cations **6a**, **6b**, and **11b** were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous acetonitrile.[1d,4] The values are summarized in Table 2, along with those of analogous benzyl and 1-naphthylmethyl cations **2b**, **2c** and **4b**, **4c**.[1d,5] The *t*-butyl substituents on azulene rings slightly increased the pK_{R^+} values (**6b**; 12.4±0.1), which is higher by 1.7 p*K* units than that of **6a** (10.7±0.1). However, there is little difference between the pK_{R^+} values of the 9-anthrylmethyl cations **6a** and **6b** and those of the analogous benzyl and 1-naphthylmethyl cations **2b**, **2c** and **4b**, **4c**. 9-Anthrylmethyl cations **6a** and **6b** did not show any expected stabilization by the steric congestion of the 9-anthryl group. However, the values of **6a** and **6b** are rather high for a methyl cation substituted with

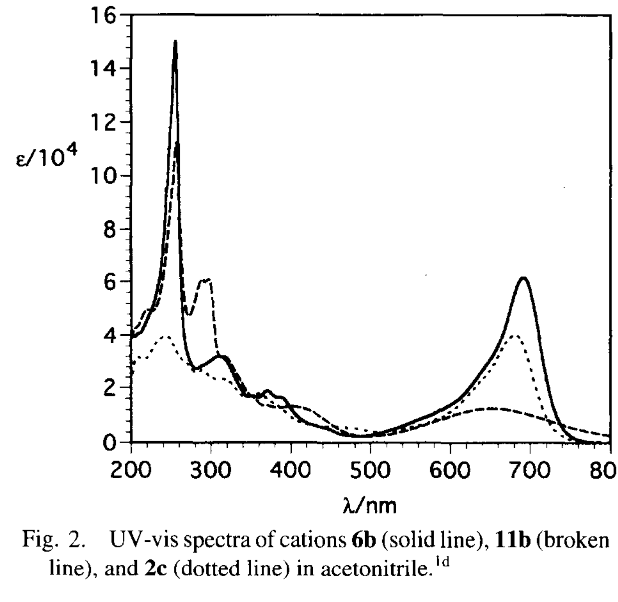


Fig. 2. UV-vis spectra of cations **6b** (solid line), **11b** (broken line), and **2c** (dotted line) in acetonitrile.[1d]

Table 1. Longest Wavelength Absorption and Their Coefficients of **6a**, **6b**, and **11b** and those of **2b**, **2c** and **4b**, **4c** for Comparison[1d,2]

Sample	$\lambda_{\max}$/nm (log ε)	Sample	$\lambda_{\max}$/nm (log ε)	Sample	$\lambda_{\max}$/nm (log ε)
6a	690 (4.53)	**2b**	676 (4.53)	**4b**	684 (4.70)
6b	692 (4.79)	**2c**	681 (4.61)	**4c**	686 (4.78)
11b	649 (4.11)				

Table 2. p$K_{\mathrm{R^+}}$ Values and Redox Potentials[a)] of **6a**, **6b**, and **11b** and those of **2b**, **2c** and **4b**, **4c** for Comparison[1d,2]

Sample	p$K_{\mathrm{R^+}}$	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}
6a	10.7±0.1	+0.88	(+1.20)	(−0.69)	
6b	12.4±0.1	+0.87	(+1.15)	−0.76	(−1.66)
11b	5.0±0.1	+0.56	(+0.92)	(−0.53)	
2b	10.8	(+0.90)		−0.70	(−1.57)
2c	12.4	+0.88	(+1.38)	−0.78	(−1.64)
4b	11.0	(+0.88)		−0.69	(−1.59)
4c	12.6	+0.87	(+1.38)	−0.77	(−1.64)

a) The redox potentials were measured by cyclic voltammetry (V vs. Ag/Ag$^+$, 0.1 mol dm^{-3} Et$_4$NClO$_4$ in acetonitrile, Pt electrode, and scan rate 100 mV s^{-1}, Fc$^+$/Fc = 0.08 V). In the case of irreversible waves, which were shown in parentheses, E^{ox} and E^{red} were calculated as E_{pa} (anodic peak potential) − 0.03 and E_{pc} (cathodic peak potential) + 0.03 V, respectively.

only hydrocarbon groups.

In contrast to the high stabilities of **6a** and **6b**, cation **11b** exhibited relatively low stabilities with the p$K_{\mathrm{R^+}}$ value of 5.0±0.1. The value of **11b** was quite similar to those of (1-azulenyl)diphenylmethyl cations **3a**—**c**, which were stabilized by an azulenyl group, e.g., the p$K_{\mathrm{R^+}}$ value of **3c** is 4.6.[1d] The low stabilities of **11b** are suggesting that the positive charge does not effectively delocalize on two azulene rings, but localizes on only one ring. ^{13}C NMR spectra of **11b** provide added support for this suggestion. The chemical shifts of C-1′, 3′, 3a′, 5′, 6′, 7′, and 8a′ positions of 1-azulenyl group on C-15 atom of **11b** showed significant down field shifts over 13.8 ppm, compared with those of the corresponding hydrocarbon **10b**. The chemical shifts of 1-azulenyl group on C-10 atom also exhibited down field shifts. However, the shifts were within 4.1 ppm, except for the up field shift (6.75 ppm) at C-1″ position. This indicates that the positive charge of the cation **11b** localized on the 1-azulenyl group on C-15 atom (Chart 4). In contrast to the ^{13}C NMR spectra of the cation **11b**, those of cations **6a** and **6b** were symmetrical about two 1-azulenyl groups. The chemical shifts of C-3′, 3a′, 5′, 7′, and 8a′ positions of **6a** and **6b** exhibited significant down field shifts over 11.8 ppm, compared with those of **7a** and **7b**. This observation indicates that the cation of **6a** and **6b** was effectively stabilized by two 1-azulenyl groups. This is in agreement with the high stabilities of these two cations **6a** and **6b**.

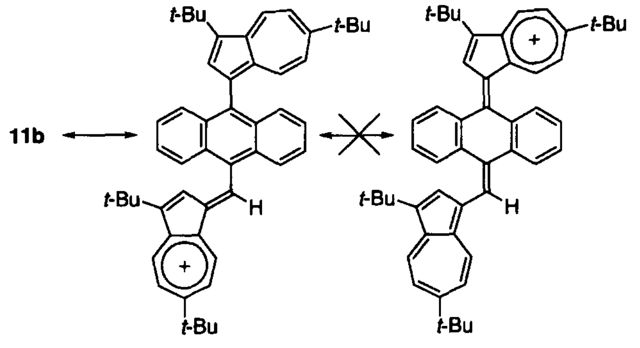


Chart 4.

The redox potentials (V vs. Ag/Ag$^+$) of **6a**, **6b**, and **11b** measured by cyclic voltammetry (CV) in acetonitrile are also summarized in Table 2, together with those of benzyl and 1-naphthylmethyl cations **2b**, **2c** and **4b**, **4c**.[1d,2] The cyclic voltamograms of **6b** and **11b** are shown in Fig. 3. The electrochemical oxidation of the cations **6a** and **6b** showed a reversible one-electron oxidation wave at +0.88 and +0.87 V upon CV due to the oxidation of an azulene ring to give a dication radical. The electrochemical reduction of **6a** and **6b** showed an irreversible wave at −0.69 V and a reversible wave at −0.76 V, respectively, to afford a neutral radical species. The cation **6b** also exhibited an irreversible second reduction wave at −1.66 V, which corresponds to the formation of an anion species. These redox potentials are almost equal to those of benzyl and 1-naphthylmethyl cations **2b**, **2c** and **4b**, **4c**. The redox properties of unsymmetrical cation **11b** were characterized by relatively less positive oxidation (+0.56 V) and less negative reduction potentials (−0.53 V), compared with those of **2c**, **4c**, and **6b**. The less negative reduction potential of the cation **11b** is in agreement with its low stability. The reduction potential of the cation **11b** was comparable with that of (3,6-di-*t*-butyl-1-azulenyl)diphenylmethyl cation (**3c**; −0.59 V).[1d] The less positive oxidation potential for the oxidation of an azulene ring of the cation **11b** also added support to the suggestion that the positive charge of the cation **11b** localized on an azulenyl ring.

Experimental

General Procedures. Melting points were determined on a Yanagimoto micro melting point apparatus MP-S3 and are un-

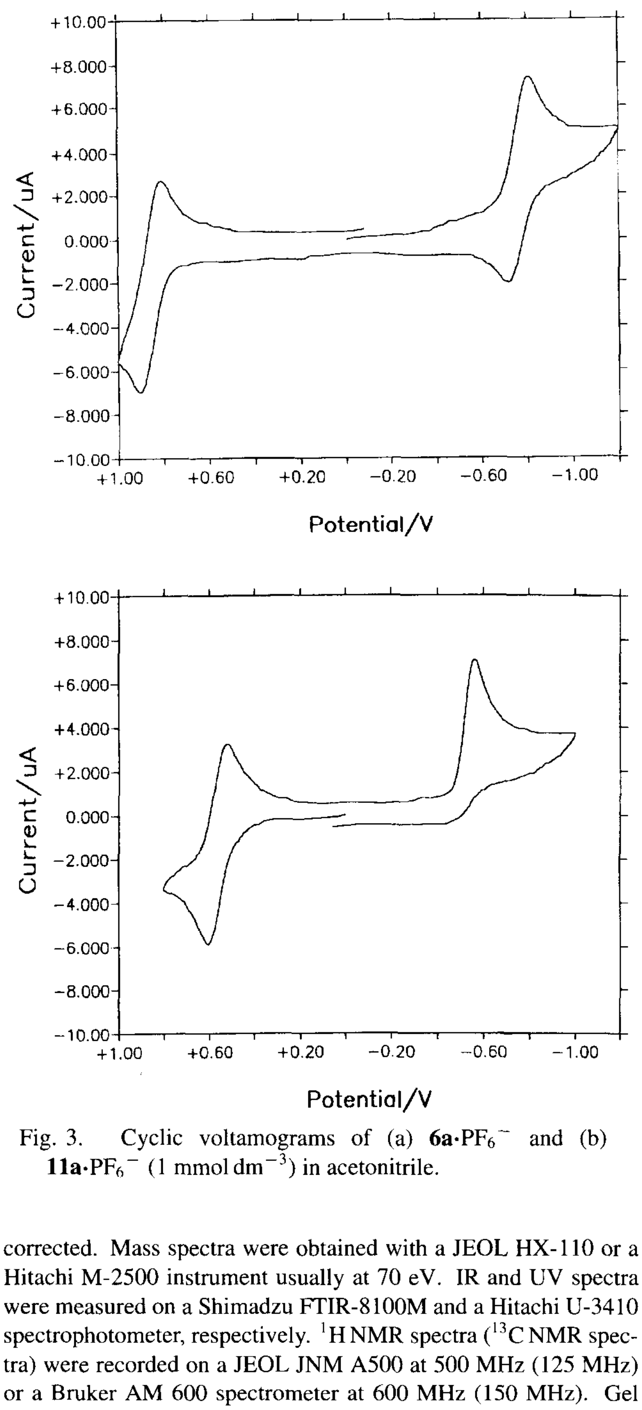


Fig. 3. Cyclic voltamograms of (a) **6a**$\cdot$PF$_6^-$ and (b) **11a**$\cdot$PF$_6^-$ (1 mmol dm^{-3}) in acetonitrile.

corrected. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. IR and UV spectra were measured on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL JNM A500 at 500 MHz (125 MHz) or a Bruker AM 600 spectrometer at 600 MHz (150 MHz). Gel permeation chromatography (GPC) purifications were performed on a TSKgel G2000H$_6$. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

Acid-Catalyzed Condensation of 1-Methylazulene (8a) with 9-Anthracenecarbaldehyde (9). A solution of **8a** (1.42 g, 10.0 mmol) and **9** (1.03 g, 5.01 mmol) in acetic acid (60 ml) was stirred at room temperature for 24 h under an Ar atmosphere. The solvent was removed in vacuo. The residue was diluted with CH$_2$Cl$_2$. The organic layer was washed with 5% aqueous NaHCO$_3$ and water, dried over MgSO$_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$ and GPC with CHCl$_3$ to afford (9-anthryl)bis(3-methyl-1-azulenyl)methane (**7a**) (124 mg, 5.2%), 9-(3-methyl-1-azulenyl)-10-[(3-methyl-1-azulenyl)methylidene]-9,10-dihydroanthracene (**10a**) (570 mg, 24%), and the recovered **8a** (186 mg, 13%).

7a: Greenish blue crystals; mp 282.0—285.0 °C decomp (toluene/hexane); MS (70 eV) *m/z* (rel intensity) 472 (M$^+$; 100), 330 (28), 329 (21), 315 (41), and 279 (24); IR (KBr disk) $\nu_{\max}$ 1572, 1429, 1362, 745, and 729 cm^{-1}; UV (CH$_2$Cl$_2$) $\lambda_{\max}$, nm (log ε) 258 (5.08), 287 (4.83), 359 (4.15), 376 (4.18), 399 (3.91), and 633 (2.86); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.44 (s, 1H, H$_{10}$), 8.34 (d, J = 9.1 Hz, 2H, H$_{1,8}$), 8.13 (d, J = 9.5 Hz, 2H, H$_{4'}$), 8.08 (s, 1H, CH), 8.00 (d, J = 8.4 Hz, 2H, H$_{4,5}$), 7.82 (d, J = 9.5 Hz, 2H, H$_{8'}$), 7.36 (dd, J = 9.9, 9.8 Hz, 2H, H$_{6'}$), 7.35 (dd, J = 8.4, 6.3 Hz, 2H, H$_{3,6}$), 7.31 (s, 2H, H$_{2'}$), 7.20 (dd, J = 9.1, 6.3 Hz, 2H, H$_{2,7}$), 6.95 (dd, J = 9.7, 9.5 Hz, 2H, H$_{5'}$), 6.66 (dd, J = 9.9, 9.5 Hz, 2H, H$_{7'}$), and 2.50 (s, 6H, 3′-Me); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 139.88 (d, C$_{2'}$), 137.30 (s, C$_{3'a}$), 137.19 (s, C$_9$), 137.12 (d, C$_{6'}$), 135.21 (s, C$_{8'a}$), 133.50 (d, C$_{4'}$), 133.29 (d, C$_{8'}$), 131.98 (s, C$_{11,12}$), 131.36 (s, C$_{1'}$), 130.57 (s, C$_{13,14}$), 129.17 (d, C$_{4,5}$), 127.22 (d, C$_{10}$), 125.51 (d, C$_{1,8}$), 125.31 (d, C$_{2,7}$), 124.60 (d, C$_{3,6}$), 124.53 (s, C$_{3'}$), 121.00 (d, C$_{7'}$), 120.75 (d, C$_{5'}$), 38.59 (d, CH), and 12.68 (q, 3′-Me). Found: C, 93.72; H, 6.26%. Calcd for C$_{37}$H$_{28}$: C, 94.03; H, 5.97%.

10a: Green crystals; mp 215.5—217.5 °C (toluene/hexane); MS (70 eV) *m/z* (rel intensity) 472 (M$^+$; 100), 315 (20), and 83 (24); IR (KBr disk) $\nu_{\max}$ 1568, 1447, 1429, 770, 737, and 727 cm^{-1}; UV (CH$_2$Cl$_2$) $\lambda_{\max}$, nm (log ε) 238 (4.59), 290 (4.80), 329 (4.35), 354 (4.34), 372 (4.26), 424 (4.34), and 629 (2.83); ^{1}H NMR (600 MHz, 50% CD$_2$Cl$_2$/CS$_2$) δ = 8.50 (d, J = 9.6 Hz, 1H, H$_{8''}$), 8.38 (d, J = 9.6 Hz, 1H, H$_{8'}$), 8.06 (d, J = 9.4 Hz, 1H, H$_{4''}$), 8.01 (d, J = 9.3 Hz, 1H, H$_{4'}$), 7.92 (dd, J = 7.8, 1.0 Hz, 1H, H$_8$), 7.77 (s, 1H, H$_{2'}$), 7.63 (dd, J = 7.8, 1.2 Hz, 1H, H$_1$), 7.56 (s, 1H, H$_{15}$), 7.54 (s, 1H, H$_{2''}$), 7.47 (dd, J = 9.7, 9.7 Hz, 1H, H$_{6''}$), 7.44 (dd, J = 9.7, 9.7 Hz, 1H, H$_{6'}$), 7.27 (ddd, J = 7.8, 7.2, 1.4 Hz, 1H, H$_7$), 7.18 (dd, J = 7.7, 1.3 Hz, 1H, H$_4$), 7.14 (dd, J = 7.6, 1.4 Hz, 1H, H$_5$), 7.09 (ddd, J = 7.6, 7.2, 1.0 Hz, 1H, H$_6$), 7.06 (ddd, J = 7.7, 7.3, 1.2 Hz, 1H, H$_3$), 7.02 (dd, J = 9.7, 9.6 Hz, 1H, H$_{7''}$), 6.99 (dd, J = 9.7, 9.3 Hz, 1H, H$_{5'}$), 6.97 (dd, J = 9.7, 9.4 Hz, 1H, H$_{5''}$), 6.95 (dd, J = 9.7, 9.6 Hz, 1H, H$_{7'}$), 6.92 (ddd, J = 7.8, 7.3, 1.3 Hz, 1H, H$_2$), 5.85 (s, 1H, H$_{10}$), 2.51 (s, 3H, 3′-Me), and 2.45 (s, 3H, 3″-Me); ^{13}C NMR (150 MHz, 50% CD$_2$Cl$_2$/CS$_2$) δ = 142.46 (s, C$_{11}$), 140.24 (s, C$_{3'a}$), 140.17 (s, C$_{12}$), 140.04 (s, C$_{13}$), 138.98 (d, C$_{2''}$), 138.81 (d, C$_{6'}$), 138.37 (s, C$_{8'a}$), 138.32 (d, C$_{2'}$), 138.28 (d, C$_{6''}$), 138.14 (s, C$_{3''a}$), 135.86 (s, C$_{14}$), 135.61 (s), 134.43 (s), 134.23 (d, C$_{8'}$), 134.16 (d, C$_{4''}$), 133.99 (d, C$_{4'}$), 133.57 (d, C$_{8''}$), 131.92 (s, C$_{1''}$), 128.92 (d, C$_1$), 128.67 (d, C$_4$), 128.48 (d, C$_5$), 128.22 (d, C$_3$), 127.50 (d, C$_7$), 127.37 (d, C$_6$), 127.25 (s, C$_{3'}$), 126.45 (s, C$_{3''}$), 126.17 (d, C$_2$), 125.51 (s, C$_{1'}$), 124.16 (d, C$_8$), 123.50 (d, C$_{5''}$), 122.86 (d, C$_{7'}$), 122.13 (d, C$_{7''}$), 121.94 (d, C$_{5'}$), 120.50 (d, C$_{15}$), 45.23 (d, C$_{10}$), 13.42 (q, 3′-Me), and 13.39 (q, 3″-Me). Found: C, 94.40; H, 6.06%. Calcd for C$_{37}$H$_{28}$: C, 94.03; H, 5.97%.

Acid-Catalyzed Condensation of 1,6-Di-*t*-butylazulene (8b) with 9-Anthracenecarbaldehyde (9). The same procedure as for the acid-catalyzed condensation of **8a** with **9** was adopted here. The condensation of **8b** (1.30 g, 5.41 mmol) with **9** (526 mg, 2.55 mmol) in 30 ml acetic acid afforded (9-anthryl)bis(3,6-di-*t*-butyl-1-azulenyl)methane (**7b**) (195 mg, 11%), 9-(3,6-di-*t*-butyl-1-azulenyl)-10-[(3,6-di-*t*-butyl-1-azulenyl)methylidene]-9,10-dihydroanthracene (**10b**) (395 mg, 22%), and the recovered **8b** (169 mg, 13%).

7b: Greenish blue crystals; mp 283.5—286.0 °C decomp (hexane); MS (70 eV) *m/z* (rel intensity) 668 (M$^+$; 55), 612 (55), 611 (100), 371 (25), 279 (22), 225 (40), 167 (23), 149 (52), 69 (27), and 57 (52); IR (KBr disk) $\nu_{\max}$ 2963, 2953, 2903, 2869, 1574, 1460, 1420, 1389, 1362, 1225, 833, and 729 cm^{-1}; UV (CH$_2$Cl$_2$)

λ_{max}, nm (log ε) 258 (5.10), 294 (4.88), 303 (4.89), 360 (4.19), 376 (4.18), and 618 (2.81); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.51 (d, *J* = 10.6 Hz, 2H, $H_{4'}$), 8.47 (d, *J* = 9.1 Hz, 2H, $H_{1,8}$), 8.40 (s, 1H, H_{10}), 8.03 (s, 1H, CH), 7.99 (d, *J* = 8.4 Hz, 2H, $H_{4,5}$), 7.81 (d, *J* = 10.5 Hz, 2H, $H_{8'}$), 7.35 (dd, *J* = 8.4, 6.9 Hz, 2H, $H_{3,6}$), 7.33 (s, 2H, $H_{2'}$), 7.22 (br dd, *J* = 9.1, 6.9 Hz, 2H, $H_{2,7}$), 7.11 (dd, *J* = 10.6, 1.8 Hz, 2H, $H_{5'}$), 6.81 (dd, *J* = 10.5, 1.8 Hz, 2H, $H_{7'}$), 1.41 (s, 18H, 3′-*t*-Bu), and 1.34 (s, 18H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.06 (s, $C_{6'}$), 137.64 (s, C_9), 137.31 (s, $C_{3'}$), 137.00 (d, $C_{2'}$), 134.75 (s, $C_{8'a}$), 134.39 (s, $C_{3'a}$), 134.28 (d, $C_{4'}$), 132.53 (d, $C_{8'}$), 132.03 (s, $C_{11,12}$), 130.67 (s, $C_{13,14}$), 130.39 (s, $C_{1'}$), 129.03 (d, $C_{4,5}$), 126.91 (d, C_{10}), 125.99 (d, $C_{1,8}$), 124.90 (d, $C_{2,7}$), 124.52 (d, $C_{3,6}$), 119.07 (d, $C_{7'}$), 118.26 (d, $C_{5'}$), 38.46 (d, CH), 38.08 (s, 6′-*t*-Bu), 33.15 (s, 3′-*t*-Bu), 32.20 (q, 3′-*t*-Bu), and 31.75 (q, 6′-*t*-Bu). Found: C, 91.22; H, 8.53%. Calcd for $C_{51}H_{56}$: C, 91.56; H, 8.44%.

10b: Green crystals; mp 249.5—252.0 °C decomp (hexane); MS (70 eV) *m/z* (rel intensity) 668 (M^+; 100); IR (KBr disk) ν_{max} 2963, 2953, 2903, 2867, 1574, 1460, and 1362 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 294 (4.86), 304 (4.90), 357 (4.43), 428 (4.41), and 618 (2.90); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.55 (d, *J* = 10.7 Hz, 1H, $H_{8''}$), 8.48 (d, *J* = 10.5 Hz, 1H, $H_{4''}$), 8.46 (d, *J* = 10.5 Hz, 1H, $H_{4'}$), 8.44 (d, *J* = 11.0 Hz, 1H, $H_{8'}$), 7.95 (dd, *J* = 7.8, 1.2 Hz, 1H, H_8), 7.84 (s, 1H, $H_{2'}$), 7.72 (s, 1H, $H_{2''}$), 7.69 (dd, *J* = 7.7, 1.3 Hz, 1H, H_1), 7.61 (s, 1H, H_{15}), 7.29 (ddd, *J* = 7.8, 7.4, 1.2 Hz, 1H, H_7), 7.27 (dd, *J* = 7.8, 1.2 Hz, 1H, H_5), 7.24 (dd, *J* = 10.7, 1.9 Hz, 1H, $H_{7''}$), 7.23 (dd, *J* = 7.6, 1.3 Hz, 1H, H_4), 7.21 (dd, *J* = 11.0, 1.9 Hz, 1H, $H_{7'}$), 7.19 (dd, *J* = 10.5, 1.9 Hz, 1H, $H_{5'}$), 7.16 (dd, *J* = 10.5, 1.9 Hz, 1H, $H_{5''}$), 7.13 (ddd, *J* = 7.8, 7.4, 1.2 Hz, 1H, H_6), 7.08 (ddd, *J* = 7.6, 7.4, 1.3 Hz, 1H, H_3), 6.94 (ddd, *J* = 7.7, 7.4, 1.3 Hz, 1H, H_2), 5.89 (s, 1H, H_{10}), 1.46 (s, 9H, 6′-*t*-Bu), 1.45 (s, 9H, 6″-*t*-Bu), 1.42 (s, 9H, 3′-*t*-Bu), and 1.32 (s, 9H, 3″-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.17 (s, $C_{6''}$), 160.42 (s, $C_{6'}$), 141.94 (s, C_{11}), 139.75 (s, C_{12}), 139.68 (s, C_{13}), 139.03 (s, $C_{3'}$), 138.57 (s, $C_{3''}$), 136.98 (s, $C_{3'a}$), 136.53 (s, $C_{8'a}$), 135.42 (s, C_{14}), 135.10 (d, $C_{2''}$), 134.92 (d, $C_{2'}$), 134.41 (s, $C_{8''a}$), 134.28 (d, $C_{4'}$ or $C_{4''}$), 134.25 (d, $C_{4'}$ or $C_{4''}$), 134.13 (s, $C_{3''a}$), 133.63 (s, C_9), 132.34 (d, $C_{8'}$), 131.81 (d, $C_{8''}$), 130.19 (s, $C_{1''}$), 128.27 (d, C_1), 127.84 (d, C_4), 127.59 (d, C_5), 127.24 (d, C_3), 126.35 (d, C_7), 126.26 (d, C_6), 124.77 (d, C_2), 123.71 (s, $C_{1'}$), 123.37 (d, C_8), 120.55 (d, $C_{7'}$), 119.73 (d, $C_{5'}$), 119.52 (d, C_{15}), 119.46 (d, $C_{7''}$), 118.27 (d, $C_{5''}$), 44.58 (d, C_{10}), 38.23 (s, 6′- or 6″-*t*-Bu), 38.20 (s, 6′- or 6″-*t*-Bu), 33.15 (s, 3″-*t*-Bu), 33.13 (s, 3′-*t*-Bu), 32.12 (q, 3″-*t*-Bu), 31.93 (q, 3′-*t*-Bu), 31.83 (q, 6′- or 6″-*t*-Bu), and 31.73 (q, 6′- or 6″-*t*-Bu). Found: C, 91.53; H, 8.52%. Calcd for $C_{51}H_{56}$: C, 91.56; H, 8.44%.

(9-Anthryl)bis(3-methyl-1-azulenyl)methyl Hexafluorophosphate (6a·PF_6^-). DDQ (41 mg, 0.18 mmol) was added at room temperature to a solution of (9-anthryl)bis(3-methyl-1-azulenyl)methane (**7a**) (58 mg, 0.12 mmol) in CH_2Cl_2 (15 ml). After the solution was stirred at the same temperature for 5 min, 60% HPF_6 (1.5 ml) was added. After stirring at room temperature for an additional 5 min, water (15 ml) was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (3 ml) and added to ether (50 ml). The precipitated crystals were collected by filtration, washed with ether, and dried in vacuo to give the salt **6a**·PF_6^- (56 mg, 74%). Deep blue powder; mp 179.0—186.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 471 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1480, 1441, 1310, 1283, 1073, 839, and 558 cm^{-1}; UV (MeCN) λ_{max}, nm (log ε) 254 (5.15), 287 (4.44), 352 (4.13), 371 (4.19), 390 (4.18), and 690 (4.53); ^{1}H NMR (500 MHz, $(CDCl_2)_2$, 100 °C) δ = 8.78 (s, 1H, H_{10}), 8.57 (d, *J* = 9.5 Hz, 2H, $H_{4'}$), 8.13 (d, *J* = 8.6 Hz, 2H, $H_{4,5}$), 8.00 (dd, *J* = 9.6, 9.5 Hz, 2H, $H_{6'}$), 7.94 (dd, *J* = 9.5, 9.5 Hz, 2H, $H_{5'}$), 7.93 (d, *J* = 9.5 Hz, 2H, $H_{8'}$), 7.56 (s, 2H, $H_{2'}$), 7.46 (dd, *J* = 8.6, 6.7 Hz, 2H, $H_{3,5}$), 7.45 (d, *J* = 8.6 Hz, 2H, $H_{1,8}$), 7.39 (dd, *J* = 9.5, 9.5 Hz, 2H, $H_{7'}$), 7.27 (dd, *J* = 8.6, 6.7 Hz, 2H, $H_{2,7}$), and 2.55 (s, 6H, 3′-Me); ^{13}C NMR (125 MHz, $(CDCl_2)_2$, 100 °C) δ = 158.35 (s, C^+), 152.54 (s, $C_{3'a}$), 147.71 (s, $C_{8'a}$), 145.07 (d, $C_{2'}$), 143.27 (d, $C_{6'}$), 138.56 (d, $C_{8'}$), 138.18 (d, $C_{4'}$), 136.74 (s, $C_{3'}$), 135.39 (d, $C_{5'}$), 135.30 (d, $C_{7'}$), 134.47 (s), 134.41 (s, $C_{1'}$), 131.74 (s, $C_{13,14}$), 131.26 (d, C_{10} and s), 129.04 (d, $C_{4,5}$), 128.15 (d, $C_{2,7}$), 126.01 (d, $C_{3,6}$), 124.87 (d, $C_{1,8}$), and 12.72 (q, 3′-Me). Found: C, 71.72; H, 4.42%. Calcd for $C_{37}H_{27}\cdot PF_6$: C, 72.08; H, 4.41%.

(9-Anthryl)bis(3,6-di-*t*-butyl-1-azulenyl)methyl Hexafluorophosphate (6b·PF_6^-). The same procedure as for the preparation of **6a**·PF_6^- was adopted here. The hydride abstraction reaction of (9-anthryl)bis(3,6-di-*t*-butyl-1-azulenyl)methane (**7b**) (134 mg, 0.20 mmol) with DDQ (55 mg, 0.24 mmol) in CH_2Cl_2 (20 ml) gave the salt **6b**·PF_6^- (125 mg, 77%). Deep blue powder; mp 292.0—293.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 812 (M^+) and 667 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1478, 1416, 1368, 1331, 1310, 1244, 1179, 839, and 558 cm^{-1}; UV (MeCN) λ_{max}, nm (log ε) 255 (5.18), 310 (4.51), 352 (4.23), 371 (4.28), and 692 (4.79); ^{1}H NMR (600 MHz, $(CDCl_2)_2$, 90 °C) δ = 8.91 (d, *J* = 10.9 Hz, 2H, $H_{4'}$), 8.77 (s, 1H, H_{10}), 8.12 (d, *J* = 8.2 Hz, 2H, $H_{4,5}$), 8.03 (dd, *J* = 10.9, 1.2 Hz, 2H, $H_{5'}$), 7.80 (br, 2H, $H_{8'}$), 7.49 (br, 2H, $H_{2'}$), 7.44 (dd, *J* = 8.2, 5.7 Hz, 2H, $H_{3,6}$), 7.44 (d, *J* = 8.0 Hz, 2H, $H_{1,8}$), 7.38 (br, 2H, $H_{7'}$), 7.24 (dd, *J* = 8.0, 5.7 Hz, 2H, $H_{2,7}$), 1.46 (s, 18H, 3′-*t*-Bu), and 1.36 (s, 18H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $(CDCl_2)_2$, 90 °C) δ = 169.51 (s, $C_{6'}$), 157.70 (s, C^+), 149.96 (s), 149.10 (s, $C_{3'}$), 147.83 (s), 142.51 (d), 139.16 (d, $C_{4'}$), 137.85 (d), 134.39 (s), 134.08 (s), 132.94 (d, $C_{5'}$), 132.68 (d, $C_{7'}$), 132.14 (s, $C_{13,14}$), 131.56 (d, C_{10}), 131.48 (s, $C_{11,12}$), 129.27 (d, $C_{4,5}$), 128.12 (d, $C_{2,7}$), 126.17 (d, $C_{3,6}$), 125.25 (d, $C_{1,8}$), 39.46 (s, 6′-*t*-Bu), 33.50 (s, 3′-*t*-Bu), 31.64 (q, 6′-*t*-Bu), and 31.28 (q, 3′-*t*-Bu). Found: C, 75.23; H, 6.86%. Calcd for $C_{51}H_{55}\cdot PF_6$: C, 75.35; H, 6.82%.

(3,6-Di-*t*-butyl-1-azulenyl)[10-(3,6-di-*t*-butyl-1-azulenyl)-9-anthryl]methyl Hexafluorophosphate (11b·PF_6^-). The same procedure as for the preparation of **6a**·PF_6^- was adopted here. The hydride abstraction reaction of 9-(3,6-di-*t*-butyl-1-azulenyl)-10-[(3,6-di-*t*-butyl-1-azulenyl)methylidene]-9,10-dihydroanthracene (**10b**) (134 mg, 0.200 mmol) with DDQ (55 mg, 0.24 mmol) in CH_2Cl_2 (20 ml) gave the salt **11b**·PF_6^- (78 mg, 48%). Deep blue powder; mp 274.0—276.5 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 812 (M^+) and 667 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 2965, 1595, 1580, 1553, 1464, 1443, 1312, 1237, 870, 839, and 558 cm^{-1}; UV (MeCN) λ_{max}, nm (log ε) 211 (4.70), 256 (5.05), 287 (4.79), 297 (4.79), 317 (4.51), 403 (4.13), and 649 (4.11); ^{1}H NMR (600 MHz, $(CDCl_2)_2$) δ = 9.58 (s, 1H, H_{15}), 9.47 (d, *J* = 10.7 Hz, 1H, $H_{8'}$), 9.04 (d, *J* = 11.0 Hz, 1H, $H_{4'}$), 8.84 (dd, *J* = 10.7, 2.0 Hz, 1H, $H_{7'}$), 8.76 (d, *J* = 10.8 Hz, 1H, $H_{4''}$), 8.71 (dd, *J* = 11.0, 2.0 Hz, 1H, $H_{5'}$), 8.28 (d, *J* = 8.8 Hz, 2H, $H_{1,8}$), 7.86 (s, 1H, $H_{2''}$), 7.66 (d, *J* = 8.8 Hz, 2H, $H_{4,5}$), 7.57 (d, *J* = 10.7 Hz, 1H, $H_{8''}$), 7.53 (dd, *J* = 8.8, 7.5 Hz, 2H, $H_{2,7}$), 7.52 (s, 1H, $H_{2'}$), 7.36 (dd, *J* = 10.8, 2.0 Hz, 1H, $H_{5''}$), 7.33 (dd, *J* = 8.8, 7.5 Hz, 2H, $H_{3,6}$), 7.02 (dd, *J* = 10.7, 2.0 Hz, 1H, $H_{7''}$), 1.64 (s, 9H, 3″-*t*-Bu), 1.57 (s, 9H, 6′-*t*-Bu), 1.39 (s, 9H, 3′-*t*-Bu), and 1.34 (s, 9H, 6″-*t*-Bu); ^{13}C NMR (150 MHz, $(CDCl_2)_2$) δ = 174.26 (s, $C_{6'}$), 162.32 (s, $C_{6''}$), 158.28 (s, $C_{3'a}$), 157.61 (s, $C_{3'}$), 155.04 (s, $C_{8'a}$), 144.93 (d, C_{15}), 143.55 (d, $C_{5'}$), 143.26 (s), 142.75 (d, $C_{7'}$), 141.14 (d, $C_{4'}$), 139.32 (s, $C_{1'}$), 139.27 (s, $C_{3''}$), 138.97 (d, $C_{8'}$), 138.79 (d, $C_{2'}$), 138.54 (s, $C_{8''a}$), 138.35 (d, $C_{2''}$), 136.01 (d, $C_{4''}$), 135.70 (s, $C_{3''a}$), 135.04 (d, $C_{8''}$), 131.93 (s, $C_{11,12}$), 131.73 (s, $C_{13,14}$), 129.71

(d, $C_{4,5}$), 128.75 (d, $C_{2,7}$), 127.74 (s), 126.53 (d, $C_{3,6}$), 125.05 (d, $C_{1,8}$), 123.44 (s, $C_{1''}$), 121.81 (d, $C_{7''}$), 120.56 (d, $C_{5''}$), 40.74 (s, 6′-*t*-Bu), 38.70 (s, 6″-*t*-Bu), 33.86 (s, 3′-*t*-Bu), 33.73 (s, 3″-*t*-Bu), 32.70 (q, 3″-*t*-Bu), 32.10 (q, 6″-*t*-Bu), 31.78 (q, 6′-*t*-Bu), and 30.01 (q, 3′-*t*-Bu). Found: C, 75.29; H, 6.81%. Calcd for $C_{51}H_{55}\cdot PF_6$: C, 75.35; H, 6.82%.

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3 PM3 semiemprical MO calculations in Fig. 1 were performed by the MOPAC version 94 on a Tektronix CAChe WorkSystem 4.02.

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5 Neutralization of these cations **6a**, **6b**, and **11b** was not completely reversible due to the instability of the neutralized products under basic conditions. Acidification of the alkaline solution of **6a**, **6b**, and **11b** with HCl regenerated the absorption maxima in the visible region in 85, 27, and 93%, respectively.