Synthesis, Properties, and Redox Behaviors of Di- and Trications Composed of Di(1-azulenyl)methylium Units Connected by *p*- and *m*-Phenylene and 1,3,5-Benzenetriyl Spacers

Shunji Ito,* Noboru Morita, and Toyonobu Asao

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578

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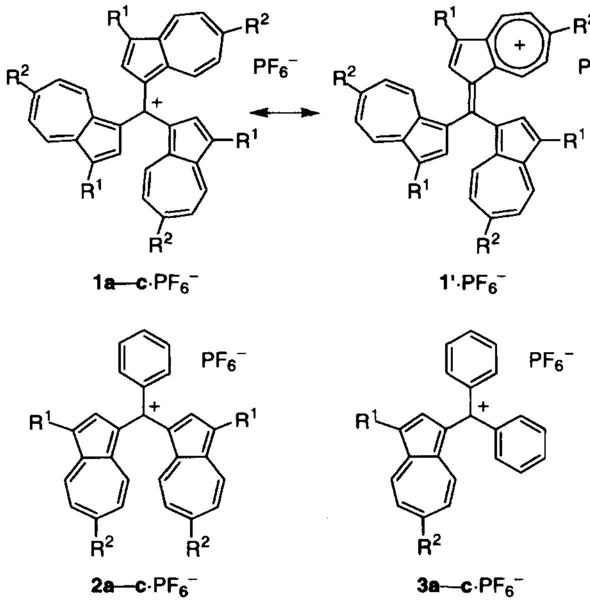
The titled stable di- and trications composed of di(1-azulenyl)methylium units connected by *p*- and *m*-phenylene and 1,3,5-benzenetriyl spacers, i.e., 1,3- and 1,4-phenylenebis[bis(3-methyl- and 3,6-di-*t*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate)s (**4a**, **4b**·$2PF_6^-$ and **5a**, **5b**·$2PF_6^-$), and 1,3,5-benzenetriyltris[bis(3,6-di-*t*-butyl-1-azulenyl)methylium] tris(hexafluorophosphate) (**6**·$3PF_6^-$), were prepared by hydride abstraction of the corresponding hydrocarbons. In spite of di- and tricationic structures, **4a**, **4b**, **5a**, **5b**, and **6** showed high stabilities with large pK_{R^+} values due to the effects of 1-azulenyl substituents. The two cation units in the dications **4a**, **4b** and **5a**, **5b** were neutralized simultaneously at the pH of 11.2—12.1±0.2. The pH correspond to the average of the pK_{R^+} values of dications and half-neutralized monocations. 3,6-Di-*t*-butyl substituents on 1-azulenyl groups increased solubilities and reversibilities of both reduction and oxidation upon cyclic voltammetry (CV). In contrast to the dications, the three cation units in the trication **6** were neutralized stepwise at the pH of 9.1±0.2, 10.9±0.2, and 12.7±0.2, respectively. The electrochemical oxidation of di- and trications **4b**, **5b**, and **6** exhibited a reversible wave at +0.87— +0.89 V (V vs. Ag/Ag^+) upon CV, although dications **4a** and **5a** showed irreversible waves in the similar potential ranges. The electrochemical reduction of *m*-phenylene-connected dications **4a** and **4b** showed two very closely spaced reduction waves at −0.65— −0.82 V upon CV. In the case of *p*-phenylene-connected dications, **5a** and **5b** showed a one-step, two-electron reduction wave at −0.47 and −0.55 V, respectively, upon CV. The reduction wave corresponds to the formation of an unstable closed-shell molecule. The reduction of trication **6** showed irreversible waves in the potential ranges similar to those of dication **4b**.

We have recently reported the synthesis of a series of (1-azulenyl)methylium hexafluorophosphates, i.e, tri(1-azulenyl)methylium, di(1-azuenyl)(phenyl)methylium, and (1-azulenyl)di(phenyl)methylium hexafluorophosphates (**1a**·PF_6^-, **2a**·PF_6^-, and **3a**·PF_6^-) and their derivatives (e.g., **1b**, **1c**·PF_6^-, **2b**, **2c**·PF_6^-, and **3b**, **3c**·PF_6^-) by hydride abstraction of the corresponding hydrocarbons (Chart 1).[1] These cations showed high stabilities with large pK_{R^+} values (e.g., **1a**; 11.3, **2a**; 10.5, and **3a**; 3.0, respectively).[1d] The high stabilities of these cations can be explained by the large π-conjugative effect of 1-azulenyl groups with cationic carbon (e.g., **1′**). In particular, the methyl cations **1a**—**c** and **2a**—**c**, which were stabilized by three or two 1-azulenyl substituents, showed high thermodynamic stabilities compared with those of (1-azulenyl)di(phenyl)methyl cations **3a**—**c**. Combination of di(1-azulenyl)methylium units with other characteristic groups would result in the formation of stable cationic compounds with special properties. In this concept, stable cationic multistage redox systems were constructed by the combination of the methylium unit with ferrocene moiety.[2]



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

Chart 1.

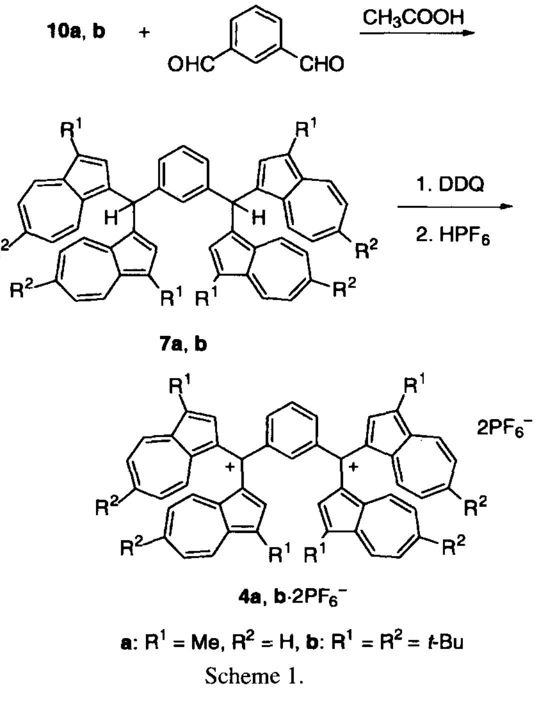
Combination of several of the methylium units would afford polycations with high thermodynamic stabilities. We extended our synthetic method to di- and trications (**4a**, **4b**, **5a**, **5b**, and **6**) composed of the di(1-azulenyl)methylium units connected by *p*- and *m*-phenylene and 1,3,5-benzenetriyl spacers, which will be reported in this paper.[3] Although the methyl substituents on azulene rings slightly stabilized cations **1a**, **2a**, and **3a** by its inductive electronic effect, the *t*-butyl substituents on 1-azulenyl groups effectively stabilized **1a**, **2a**, and **3a** by their steric and also by their inductive electronic effects induced by the contribution of C–C hyperconjugation with π-systems.[1d] In the case of dications, we have prepared both 3-methyl-1-azulenyl and 3,6-di-*t*-butyl-1-azulenyl derivatives to examine the effects of these substituents on 1-azulenyl groups. The *t*-butyl substituents would increase solubilities and also reversibility of both reduction and oxidation upon cyclic voltammetry (CV) compared with those of 3-methyl derivatives.

Results and Discussion

Synthesis. Synthesis of the dications **4a**, **4b** and **5a**, **5b** was accomplished by hydride abstraction from the corresponding hydrocarbon derivatives **7a**, **7b**, **8a**, and **8b** (Schemes 1 and 2).[1] The reaction of four molar amounts of 1-methyl- and 1,6-di-*t*-butylazulenes (**10a** and **10b**)[1d,4] with isophthalaldehyde in acetic acid at room temperature for 12—24 h afforded the desired 1,3-bis[bis(3-methyl- and 3,6-di-*t*-butyl-1-azulenyl)methyl]benzenes (**7a** and **7b**) in 71 and 67% yields, respectively, together with 3-[bis(3-methyl- and 3,6-di-*t*-butyl-1-azulenyl)methyl]benzaldehydes (**11a** and **11b**) in 22 and 24% yields, respectively.

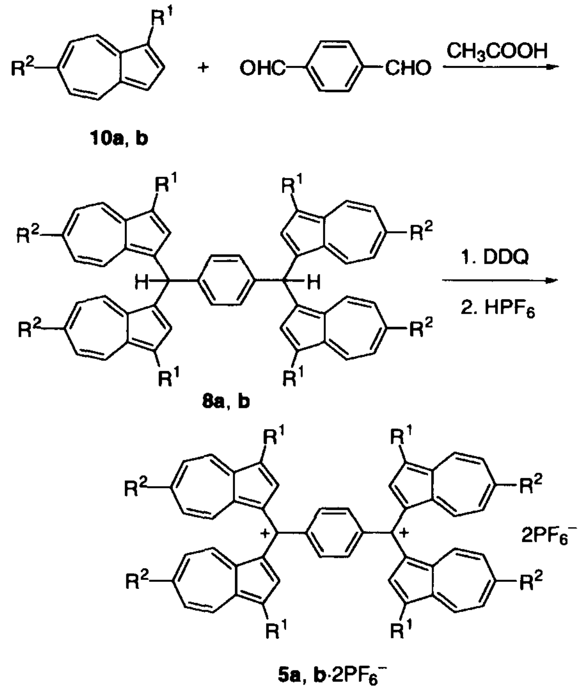
Similarly, the reaction of **10a** and **10b** with terephthalaldehyde yielded 1,4-bis[bis(3-methyl- and 3,6-di-*t*-butyl-1-azulenyl)methyl]benzenes (**8a** and **8b**) in 65 and 80% yields, respectively, together with 4-[bis(3-methyl- and 3,6-di-*t*-butyl-1-azulenyl)methyl]benzaldehydes (**12a** and **12b**) in 23 and 19% yields, respectively (Chart 2).

The oxidative hydride abstraction of **7a** and **8a** with DDQ in dichloromethane at room temperature in the presence of aqueous HPF$_6$ solution yielded stable dications **4a** and **5a**, i.e., 1,3- and 1,4-phenylenebis[bis(3-methyl-1-azulenyl)methylium] (**4a** and **5a**) as bis(hexafluorophosphate), in quantitative yields. The hydride abstraction of **7b** and **8b** with DDQ in dichloromethane at room temperature followed by the addition of 60% HPF$_6$ solution yielded stable dications **4b** and **5b**, i.e., 1,3- and 1,4-phenylenebis[bis(3,6-di-*t*-butyl-1-azulenyl)methylium] (**4b** and **5b**), in almost quantitative yields. 3-Methyl derivatives (**4a** and **5a**) of dications exhibited relatively low solubilities as compared with those of 3,6-di-*t*-butyl derivatives (**4b** and **5b**). This prompted us to synthesize a trication **6** using 1,6-di-*t*-butylazulene (**10b**).



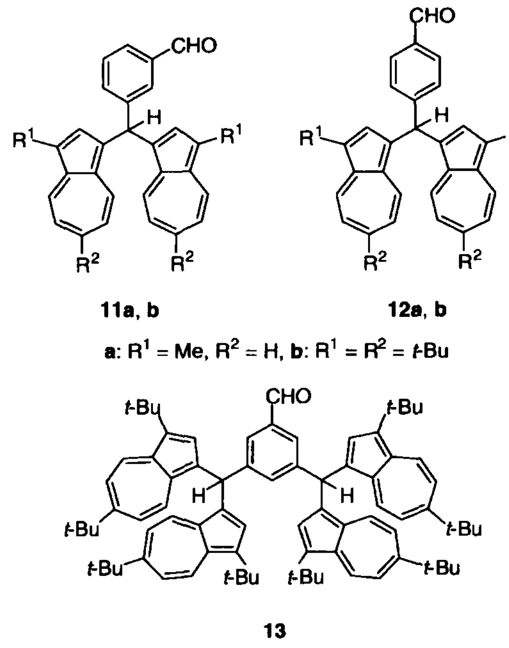
a: R^1 = Me, R^2 = H, b: R^1 = R^2 = *t*-Bu

Scheme 1.



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

Scheme 2.



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

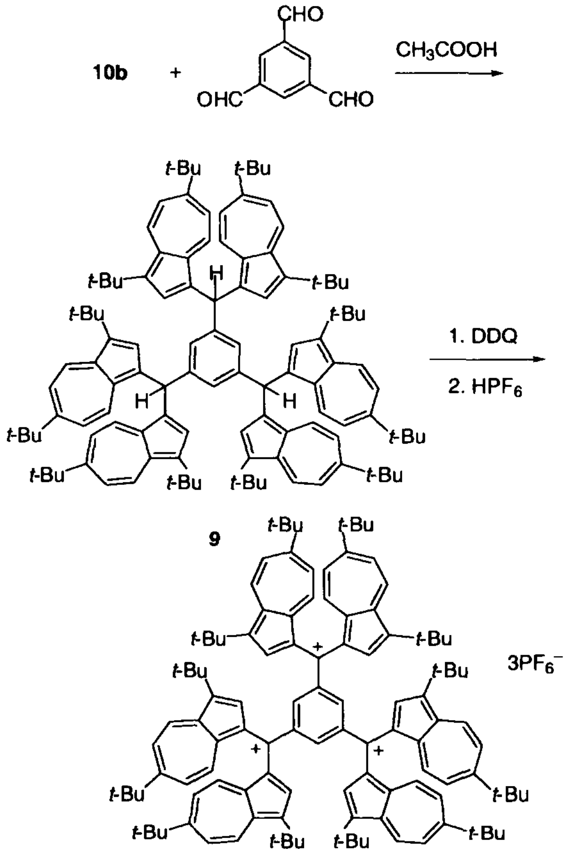
Chart 2.

Trication **6** was synthesized by the hydride abstraction from the corresponding hydrocarbon derivative **9** (Scheme 3). The reaction of six molar amounts of 1,6-di-*t*-butylazulene (**10b**) with 1,3,5-benzenetricarbaldehyde[5] in 50% acetic acid/dichloromethane at room temperature for 24 h afforded the desired 1,3,5-tris[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (**9**) and 3,5-bis[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzaldehyde (**13**) in 55 and 30% yields, respectively (Chart 2). In an acetic acid solution, tetrasubstituted product **13** became a major product (74%) and about two molar amounts of 1,6-di-*t*-butylazulene (**10b**; 31%) was recovered because of the low solubility of the compound **13** in acetic acid. The oxidative hydride abstraction of **9** with DDQ in dichloromethane at room temperature, followed by the addition of 60% HPF_6 solution, yielded a stable trication, 1,3,5-benzenetriyltris[bis(3,6-di-*t*-butyl-1-azulenyl)methylium] (**6**), in 99% yield as tris(hexafluorophosphate).

Spectroscopic Properties. Dications **4a**, **4b** and **5a**, **5b** and a trication **6** were fully characterized by the spectral data, as shown in the Experimental Section. Mass spectra of the bis(hexafluorophosphate)s **4a**, **4b**$\cdot 2PF_6^-$ and **5a**, **5b**$\cdot 2PF_6^-$ ionized by FAB showed M^+-PF_6 and M^+-2PF_6 ion peaks, which indicated their dicationic structures. Similarly, mass spectra of the tris(hexafluorophosphate) **6**$\cdot 3PF_6^-$ exhibited M^+-PF_6, M^+-2PF_6, and M^+-3PF_6 ion peaks. The characteristic bands of hexafluorophosphate were observed at 838—842 (strong) and 558 (medium) cm^{-1} in the IR spectra of dications **4a**, **4b** and **5a**, **5b** and a trication **6**, which also supported their cationic structure assignments.

In the electronic spectra, **4a**, **4b**$\cdot 2PF_6^-$, **5a**, **5b**$\cdot 2PF_6^-$, and **6**$\cdot 3PF_6^-$ showed strong absorption in the visible region in analogy with **2b**$\cdot 2PF_6^-$ and **2c**$\cdot PF_6^-$ and their congeners. UV-vis spectra of dications **4b** and **5b** and trication **6** in acetonitrile, along with those of monocation **2c**, are shown in Figs. 1 and 2. The longest wavelength absorption maxima (nm) and their coefficients (log ε) of the hexafluorophosphates in visible region are summarized in Table 1. Dications **4a**, **4b** and **5a**, **5b** exhibited only a slight bathochromic shift as compared with those of monocations **2b** and **2c**. The extinction coefficients of the dications are almost twice as large as those of monocations **2b** and **2c**, respectively. The trication **6** exhibited a bathochromic shift of 12 nm as compared with that of monocation **2c**. The UV-vis absorption of dications **4a**, **4b**, **5a**, **5b**, and trication **6** reflected the absence of the conjugation among the cation units.

The ^1H NMR chemical shifts of the methine protons of hydrocarbons **7a** and **8a** were observed at a slightly upfield location compared with that of bis(3-methyl-1-azulenyl)(phenyl)methane. Those of **7b**, **8b**, and **9** also exhibited similar slight upfield shift in the methine protons, as compared



Scheme 3.

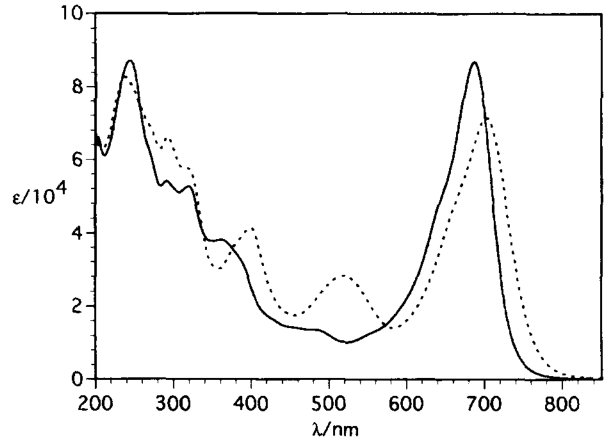


Fig. 1. UV-vis spectra of dications **4b** (solid line) and **5b** (dotted line) in acetonitrile.

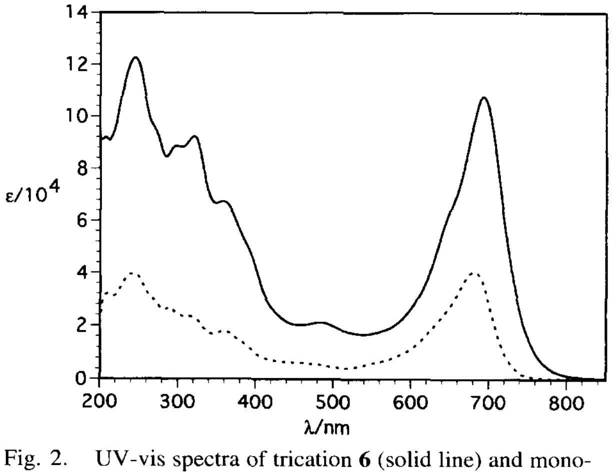


Fig. 2. UV-vis spectra of trication **6** (solid line) and monocation **2c** (dotted line) in acetonitrile.

Table 1. Longest Wavelength Absorption and Their Coefficients of Dications **4a**, **4b** and **5a**, **5b**, Trication **6**, and monocations **2b** and **2c**[1d]

Sample	$\lambda_{\max}$, nm (log ε)	Sample	$\lambda_{\max}$, nm (log ε)
4a	681 (4.67)	**6**	693 (5.03)
4b	687 (4.94)	**2b**	676 (4.53)
5a	681 (4.46)	**2c**	681 (4.61)
5b	703 (4.85)		

with that of bis(3,6-di-*t*-butyl-1-azulenyl)(phenyl)methane. These signals disappeared on the ^{1}H NMR spectra of dications **4a**, **4b**, **5a**, **5b**, and trication **6**. Thus the ^{1}H NMR spectra were also indicating the di- and tricationic structures of these compounds. The chemical shift of central cationic carbons (^{13}C NMR) in dications **4b**, **5b**, and trication **6** (**4b**; 158.85, **5b**; 158.57, and **6**; 156.97 ppm, respectively) were almost comparable with those of analogous monocations (**2b**; 161.58 and **2c**; 161.11 ppm, respectively).

Thermodynamic Stability. As a measure of thermodynamic stability, the $\mathrm{p}K_{\mathrm{R^+}}$ values of the dications **4a**, **4b** and **5a**, **5b** were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous acetonitrile.[6] The two cation units in the dications **4a**, **4b** and **5a**, **5b** were neutralized simultaneously at the pH of 11.2—12.1 ±0.2. The pH correspond to the average of the $\mathrm{p}K_{\mathrm{R^+}}$ values of the dications and half-neutralized monocations. The values of dications **4a**, **4b** and **5a**, **5b** are summarized in Table 2 along with those of monocations **2b** and **2c**.[1d] The $\mathrm{p}K_{\mathrm{R^+}}$ values of **4a**, **4b** and **5a**, **5b** are extremely high for dications substituted with only hydrocarbon groups. These values are 19.3—22.6 pK units higher than those of corresponding analogous phenyl derivatives **14** and **15** (**14**; $\mathrm{p}K_{\mathrm{R^{++}}}$ -9.9 and $\mathrm{p}K_{\mathrm{R^+}}$ -7.9, **15**; $\mathrm{p}K_{\mathrm{R^{++}}}$ -10.5 and $\mathrm{p}K_{\mathrm{R^+}}$ -8.1, respectively) (Chart 3).[7]

Dications **4a**, **4b** and **5a**, **5b** are as stable as monocations **2b** and **2c**, although dications **14** and **15** exhibit destabilization by the through-bond electrostatic repulsion of the two positively charged units.[8] The *t*-butyl substituents on azulene rings in the case of dication **5b** slightly stabilized cations by their steric and also by their inductive electronic effects induced by the C–C hyperconjugation with the π-systems. The $\mathrm{p}K_{\mathrm{R^+}}$ values of the *t*-butyl derivatives **5b** are higher by 0.9 pK units than that of **5a**. Dications **4a**, **4b** and **5a**, **5b** are also as stable as 1,2 : 3,4 : 5,6-tris(bicyclo[2.2.2]octeno)-tropylium ion connected by *m*- and *p*-phenylene spacer (*m*-; $\mathrm{p}K_{\mathrm{R^{++}}}$ 12.2 and $\mathrm{p}K_{\mathrm{R^+}}$ 10.4, *p*-; average of the $\mathrm{p}K_{\mathrm{R^+}}$ value 11.5, respectively).[9]

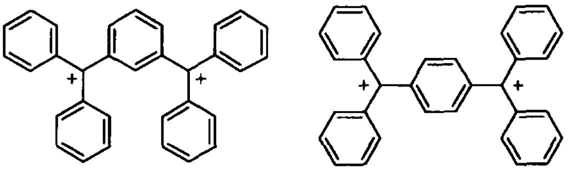

14 **15**

Chart 3.

The $\mathrm{p}K_{\mathrm{R^+}}$ values of trication **6** were also determined spectrophotometrically in a buffer solution prepared in 50% aqueous acetonitrile. In the case of trication **6** three cation units were neutralized stepwise at the pH of 9.1±0.2, 10.9±0.2, and 12.7±0.2, respectively. Thus, trication **6** itself is even more destabilized than monocation **2c** by 3.3 pK units and *m*-phenylene-connected dication **4b** by 2.4 pK units. The average (11.8) of the $\mathrm{p}K_{\mathrm{R^{++}}}$ and $\mathrm{p}K_{\mathrm{R^+}}$ values of trication **6** was comparable with that of dication **4b**. The $\mathrm{p}K_{\mathrm{R^+}}$ values of **6** exhibited that the neutralized monocation of **6** was as stable as monocation **2c**.

The neutralization of these dications **4a**, **4b** and **5a**, **5b**, and trication **6** is not completely reversible due to the instability of the neutralized products under the conditions of the $\mathrm{p}K_{\mathrm{R^+}}$ measurement. After the measurement, acidification of the alkaline solutions of **4a**, **4b**, **5a**, **5b**, and **6** with HCl regenerated the characteristic absorption of dications and trication **4a**, **4b**, **5a**, **5b**, and **6** in the visible region in 17—26%. Rather large errors of the $\mathrm{p}K_{\mathrm{R^+}}$ values are due to the low solubilities and poor reversibility under the conditions of the $\mathrm{p}K_{\mathrm{R^+}}$ measurement, which cause fluctuation in the absorption of the UV-vis spectra.

Redox Potentials. The reduction potentials (V vs. Ag/Ag$^+$) of dications **4a**, **4b** and **5a**, **5b** and trication **6** determined by CV in acetonitrile are summarized in Table 2

Table 2. $\mathrm{p}K_{\mathrm{R^+}}$ Values[a)] and Redox Potentials[b)] of Dications **4a**, **4b** and **5a**, **5b**, Trication **6**, and Monocations **2b** and **2c**[1d]

Sample	$\mathrm{p}K_{\mathrm{R^+}}$[c)]	E_1^{red}	E_2^{red}	E_3^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}
4a	11.5±0.2 (24%)	(−0.65)	(−0.73)	(−2.13)	(+0.91)	(+1.90)	
4b	11.5±0.1 (17%)	−0.72	−0.82	(−1.70)	+0.88	(+1.52)	(+2.00)
5a	11.2±0.1 (26%)	(−0.47)	(−1.84)		(+0.90)	(+1.87)	
5b	12.1±0.2 (20%)	(−0.55)	(−2.00)		+0.87	(+1.41)	(+1.87)
6	9.1±0.2 10.9±0.2 12.7±0.2 (18%)	(−0.77)	(−1.61)	(−1.71)	+0.89	(+1.50)	(+2.00)
2b	10.8	−0.70[d)]	(−1.57)[d)]		(+0.90)[d)]	(+1.79)[d)]	
2c	12.4	−0.78[d)]	(−1.64)[d)]		+0.88[d)]	(+1.38)[d)]	(+1.82)[d)]

a) The $\mathrm{p}K_{\mathrm{R^+}}$ values were determined by spectrophotomerically at 25 °C in a buffered solution prepared in 50% aqueous MeCN. b) The redox potentials were measured by cyclic voltammetry (V vs. Ag/Ag$^+$, 0.1 M $\mathrm{Et_4NClO_4}$ in MeCN, Pt electrode, and scan rate 500 mV s^{-1}, Fc/Fc^+ = 0.07 V). Irreversible processes were shown in parentheses. c) Regenerated absorption maxima (%) of the cations in visible region by immediate acidification of the alkaline solution with HCl were shown in parentheses. d) Scan rate 100 mV s^{-1}.

together with those of the corresponding monocations **2b** and **2c**. 3,6-Di-*t*-butyl substituents on each 1-azulenyl group in dications increased reversibility of both reduction and oxidation upon CV, except for the dication **5b**. *m*-Phenylene-type dications **4a** and **4b** are expected to give a non-Kékule-type electronic structure upon two-electron reduction. Dication **4b** in acetonitrile exhibited the voltammogram upon CV and differential pulse voltammogram (DPV) as shown in Figs. 3a and 4a, respectively. The voltammogram of **4b** upon CV was characterized by a barely separated two-step reduction wave at $E_{1/2}$ −0.72 and −0.82 V, which was almost reversible at the scan rate 500 mV s^{-1}. The voltammogram of **4b** upon DPV also exhibited a barely separated two-step reduction wave at −0.71 and −0.78 V. 3-Methyl derivatives **4a** also exhibited barely separated two-step reduction waves at $E_{1/2}$ −0.65 and −0.73 V, which showed poor reversibility upon CV even at the scan rate of 500 mV s^{-1}.

The CV of **5b** in acetonitrile exhibited voltammograms upon CV and DPV, as shown in Figs. 3b and 4b, respectively. The cathodic peak potentials of **5a** (E_{pc} −0.50 V) and **5b** (E_{pc} −0.58 V) are less negative by 0.17—0.27 V than those of dications **4a** and **4b** and monocations **2b** and **2c**. The waves correspond to a one-step, two-electron reduction of dications **5a** and **5b**. Less negative reduction potentials of **5a** and **5b** are attributable to the destabilization arising from the through-bond electrostatic repulsion of the two positively charged units. The voltammograms of **5a** and **5b** upon DPV also exhibited a wave at −0.45 and −0.53 V, respectively.

The cyclic scan of dication **5b** exhibited that the anodic peak positively shifted by 0.11 V from the cathodic peak, although the peak of monocations **2b** and **2c** showed positive shift by 0.06 V in these conditions. Formation of a closed-shell covalent molecule **16** (Chart 4) is expected by the positive shift of the anodic peak of dication **5b**, because the propeller conformation of dication **5b** becomes a planer quinodimethane structure **16** by the reduction. Some extra energy would be required upon the oxidation of the completely reduced species **16** back to the dication **5b** with propeller conformation. The reduction of dications **4a**, **4b** and **5a**, **5b** also exhibited other reduction waves at −2.13, −1.70, −1.84, and −2.00 V, respectively, upon CV after these reduction waves.

The formation of a closed-shell hydrocarbon from **5b** was examined by UV-vis spectroscopy under the condition of electrochemical reduction (Fig. 5). The deep blue color of the solution of **5b** changed to a brown one under the reduction conditions. Absence of the isosbestic point suggests the decomposition of the fully reduced one of **5b** in these conditions. Chemical reduction of dication **5b** with Zn powder in acetonitrile also did not afford satisfactory results. Thus, the preparation of the fully reduced one **16** was not achieved by its instability, ready decomposition or polymerization.

The CV of trication **6** in acetonitrile exhibited the voltammograms upon CV and DPV as shown in Figs. 3c and 4c, respectively. The voltammogram upon CV of **6** was characterized by an irreversible reduction wave at −0.77 V, which showed poor reversibility even at the scan rate 500 mV s^{-1}.

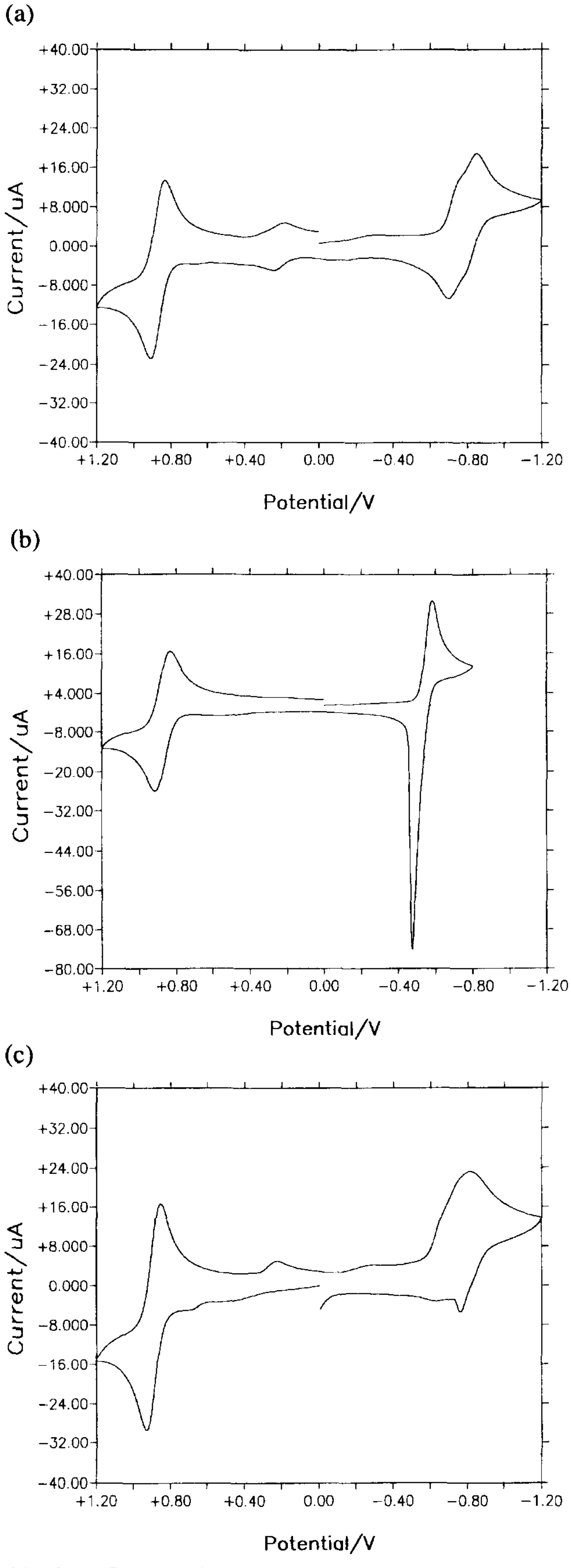


Fig. 3. Cyclic voltammograms of (a) **4b**·$2PF_6^-$, (b) **5b**·$2PF_6^-$, and (c) **6**·$3PF_6^-$ (1 mM) in MeCN containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate, 500 mV s^{-1}.

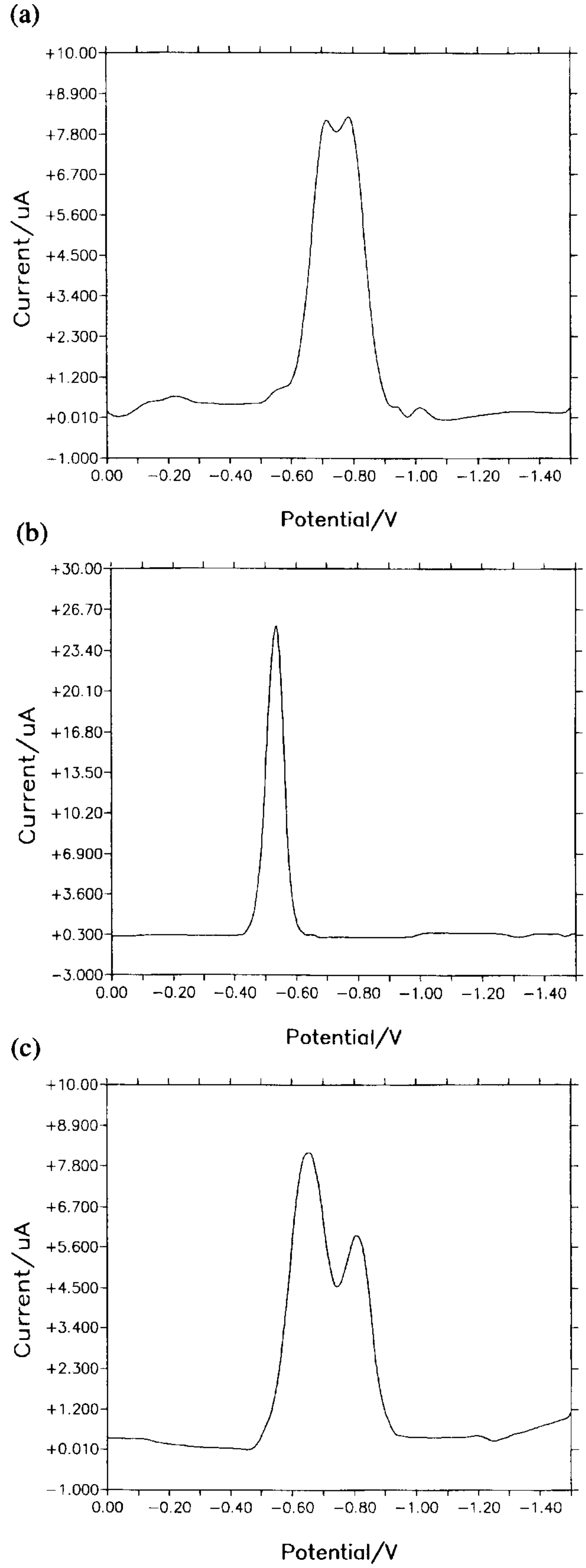


Fig. 4. Differential pulse voltammograms of the reduction of (a) **4b**$\cdot$2PF$_6^-$, (b) **5b**$\cdot$2PF$_6^-$, and (c) **6**$\cdot$3PF$_6^-$ (1 mM) in MeCN containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte.

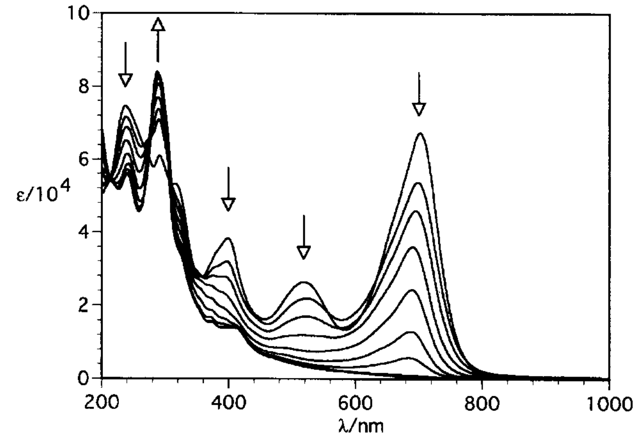
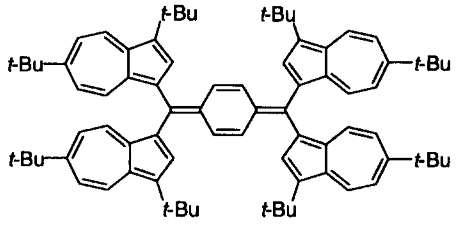


Fig. 5. Change of the UV-vis spectra of the electrochemical reduction of **5b**$\cdot$2PF$_6^-$ in MeCN at room temperature.



16

Chart 4.

The reduction potential of **6** was in the potential range of those of dication **4b**. Thus, the waves correspond to three-electron reduction of trication **6**. The waves could be divided to two barely separated waves at −0.66 (large) and −0.82 V (small) by DPV measurement. Therefore, the reduction waves observed upon CV of trication **6** consist of two processes. The reduction of **6** upon CV also exhibited another irreversible waves at −1.61 and −1.71 V, after the irreversible waves.

The oxidation of dications **4b**, **5b** and trication **6** exhibited a reversible wave at +0.87— +0.89 V (V vs. Ag/Ag$^+$) upon CV, although **4a** and **5a** showed irreversible waves in the similar potential ranges. The waves were ascribed to the oxidation of two or three azulene rings to generate a tetra- and a hexacationic species, respectively, since the waves were in the similar potential ranges with those of monocations **2b** and **2c**. The electrochemical oxidation of dications **4a**, **4b** and **5a**, **5b** also showed one or two other irreversible oxidation waves (**4a**; +1.90 V, **4b**; +1.52 and +2.00 V, **5a**; +1.87 V, and **5b**; +1.41 and +1.87 V, respectively) upon CV. The oxidation of trication **6** exhibited two similar irreversible waves at +1.50 and +2.00 V, after the reversible oxidation wave.

These dications **4a**, **4b** and **5a**, **5b** and trication **6** showed high stabilities with large pK_{R^+} values in spite of di- and tricationic structures. These results indicate that the combination of the di(1-azulenyl)methylium units could produce larger polycationic species with high stabilities. Preparations of the polycationic species using the di(1-azulenyl)methylium units are now in progress.

Experimental

General. Melting points were determined on a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. 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 Hitachi R-90H at 90 MHz (22.5 MHz), a JEOL GSX 400 at 400 MHz (100 MHz), a JEOL JNM A500 at 500 MHz (125 MHz), or a Bruker AM 600 spectrometer at 600 MHz (150 MHz). Gel permeation chromatography (GPC) purification was performed using Showadenko Shodex K2001 and K2002. Voltammetry measurements were carried out with a BAS100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes, a reference electrode formed from Ag/AgNO$_3$ (0.01 M, 1 M = 1 mol dm^{-3}), and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte, at the scan rate of 500 mV s^{-1}. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

1,3-Bis[bis(3-methyl-1-azulenyl)methyl]benzene (7a). A solution of 1-methylazulene (**10a**) (1.43 g, 10.0 mmol) and isophthalaldehyde (338 mg, 2.52 mmol) in acetic acid (50 ml) was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was diluted with CH_2Cl_2. The organic solution was washed with 5% $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/CCl_4 to afford the benzene **7a** (1.19 g, 71%), 3-[bis(3-methyl-1-azulenyl)methyl]benzaldehyde (**11a**) (219 mg, 22%), and the recovered **10a** (265 mg, 19%).

7a: Blue crystals; mp 174.0—175.5 °C (EtOAc); MS (70 eV) *m/z* (rel intensity) 666 (M$^+$; 17), 295 (62), 279 (35), 265 (30), 142 (67), and 141 (100); IR (KBr disk) ν_{max} 1574, 1436, 1362, 740, and 726 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 241 (4.75), 285 (5.09), 357 (4.23), 374 (4.21), and 631 (3.06); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, J = 9.5 Hz, 4H, $H_{4'}$), 8.04 (d, J = 9.5 Hz, 4H, $H_{8'}$), 7.39 (dd, J = 9.8, 9.8 Hz, 4H, $H_{6'}$), 7.19 (s, 4H, $H_{2'}$), 7.11 (t, J = 7.6 Hz, 1H, H_5), 7.07 (t, J = 1.8 Hz, 1H, H_2), 6.95 (dd, J = 7.6, 1.8 Hz, 2H, $H_{4,6}$), 6.94 (dd, J = 9.8, 9.5 Hz, 4H, $H_{5'}$), 6.77 (dd, J = 9.8, 9.5 Hz, 4H, $H_{7'}$), 6.55 (s, 2H, CH), and 2.51 (s, 12H, 3′-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.62 (s, $C_{1,3}$), 139.39 (d, $C_{2'}$), 137.09 (d, $C_{6'}$), 136.92 (s, $C_{3'a}$), 135.05 (s, $C_{8'a}$), 133.44 (d, $C_{4'}$), 133.15 (d, $C_{8'}$), 131.83 (s, $C_{1'}$), 129.55 (d, C_2), 128.10 (d, C_5), 126.42 (d, $C_{4,6}$), 124.40 (s, $C_{3'}$), 120.89 (d, $C_{7'}$), 120.59 (d, $C_{5'}$), 42.54 (d, CH), and 12.64 (q, 3′-Me). HRMS Calcd for $C_{52}H_{42}$: M, 666.3287. Found: *m/z* 666.3289. Found: C, 90.06; H, 6.65%. Calcd for $C_{52}H_{42}\cdot 3/2H_2O$: C, 90.01; H, 6.54%.

11a: Blue needles; mp 183.0—187.0 °C (hexane); MS (70 eV) *m/z* (rel intensity) 400 (M$^+$; 100), 385 (23), and 295 (26); IR (KBr disk) ν_{max} 1696, 1576, 1434, 1364, and 732 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 244 (4.57), 281 (4.84), 356 (3.95), 373 (3.94), and 628 (2.80); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.90 (s, 1H, 1-CHO), 8.17 (d, J = 9.5 Hz, 2H, $H_{4'}$), 8.13 (d, J = 9.5 Hz, 2H, $H_{8'}$), 7.72 (ddd, J = 6.6, 1.9, 1.9 Hz, 1H, H_6), 7.68 (br s, 1H, H_2), 7.45 (dd, J = 9.8, 9.8 Hz, 2H, $H_{6'}$), 7.42 (ddd, J = 7.5, 1.9, 1.9 Hz, 1H, H_4), 7.39 (dd, J = 7.5, 6.6 Hz, 1H, H_5), 7.26 (s, 2H, $H_{2'}$), 7.00 (dd, J = 9.8, 9.5 Hz, 2H, $H_{5'}$), 6.88 (dd, J = 9.8, 9.5 Hz, 2H, $H_{7'}$), 6.76 (s, 1H, CH), and 2.57 (s, 6H, 3′-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.65 (d, 1-CHO), 147.18 (s, C_3), 139.17 (d, $C_{2'}$), 137.45 (d, $C_{6'}$), 137.10 (s, $C_{3'a}$), 136.51 (s, C_1), 135.14 (s, $C_{8'a}$), 134.89 (d, C_4), 133.83 (d, $C_{4'}$), 132.92 (d, $C_{8'}$), 130.54 (s, $C_{1'}$), 130.20 (d, C_2), 128.95 (d, C_5), 127.25 (d, C_6), 124.77 (s, $C_{3'}$), 121.25 (d, $C_{7'}$), 121.07 (d, $C_{5'}$), 42.10 (d, CH), and 12.66 (q, 3′-Me). HRMS Calcd for $C_{30}H_{24}O$: M, 400.1827. Found: *m/z* 400.1834. Found: C, 89.71; H, 6.35%. Calcd for $C_{30}H_{24}O$: C, 89.97; H, 6.04%.

1,3-Bis[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (7b). A solution of 1,6-di-*t*-butylazulene (**10b**) (1.21 g, 5.03 mmol) and isophthalaldehyde (170 mg, 1.27 mmol) in acetic acid (25 ml) was stirred at room temperature for 24 h. The solvent was rotary-evaporated, and the residue was diluted with CH_2Cl_2. The solution was washed with 5% $NaHCO_3$ and water. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford the benzene **7b** (891 mg, 67%) and 3-[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzaldehyde (**11b**) (182 mg, 24%).

7b: Blue crystals; mp 294.0—296.0 °C decomp (CH_2Cl_2/hexane); MS (FAB) *m/z* 1059 (M$^+$); IR (KBr disk) ν_{max} 2963, 1576, 1460, 1364, 1229, and 833 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 243 (4.79), 289 (5.23), 304 (5.19), 359 (4.35), 376 (4.27), and 615 (3.12); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.49 (d, J = 10.6 Hz, 4H, $H_{4'}$), 8.11 (d, J = 10.6 Hz, 4H, $H_{8'}$), 7.28 (s, 4H, $H_{2'}$), 7.23—6.95 (m, 4H, $H_{2,4,5,6}$), 7.10 (dd, J = 10.6, 1.8 Hz, 4H, $H_{5'}$), 6.97 (dd, J = 10.6, 1.8 Hz, 4H, $H_{7'}$), 6.52 (s, 2H, CH), 1.42 (s, 36H, 3′-*t*-Bu), and 1.37 (s, 36H, 6′-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 159.77 (s, $C_{6'}$), 145.62 (s, $C_{1,3}$), 137.23 (s), 136.11 (d, $C_{2'}$), 134.37 (s), 134.09 (d, $C_{4'}$), 133.97 (s), 131.96 (d, $C_{8'}$), 130.77 (s), 129.34 (d, C_2), 127.75 (d, C_5), 125.98 (d, $C_{4,6}$), 118.82 (d, $C_{7'}$), 117.90 (d, $C_{5'}$), 42.20 (d, CH), 38.02 (s, 6′-*t*-Bu), 33.11 (s, 3′-*t*-Bu), 32.20 (q, 3′-*t*-Bu), and 31.77 (q, 6′-*t*-Bu). HRMS Calcd for $C_{80}H_{98}$: M, 1058.7671. Found: *m/z* 1058.7660. Found: C, 90.16; H, 9.41%. Calcd for $C_{80}H_{98}$: C, 90.68; H, 9.32%.

11b: Blue crystals; mp 153.5—155.0 °C (CH_2Cl_2/hexane); MS (70 eV) *m/z* 596 (M$^+$; 100), 540 (24), and 539 (53); IR (KBr disk) ν_{max} 2963, 1701, 1578, 1364, 1227, and 833 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 246 (4.62), 286 (4.96), 303 (4.92), 357 (4.07), 375 (4.00), and 612 (2.86); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 9.89 (s, 1H, 1-CHO), 8.57 (d, J = 10.8 Hz, 2H, $H_{4'}$), 8.16 (d, J = 10.8 Hz, 2H, $H_{8'}$), 7.72—7.63 (m, 2H, $H_{2,6}$), 7.39—7.32 (m, 3H, $H_{4,5,2'}$), 7.18 (dd, J = 10.8, 1.8 Hz, 2H, $H_{5'}$), 7.06 (dd, J = 10.8, 1.8 Hz, 2H, $H_{7'}$), 6.71 (s, 1H, CH), 1.50 (s, 18H, 3′-*t*-Bu), and 1.39 (s, 18H, 6′-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 192.36 (d, 1-CHO), 160.35 (s, $C_{6'}$), 147.39 (s, $C_{3'}$), 137.60 (s), 136.20 (s), 135.77 (d, $C_{2'}$), 134.64 (s), 134.49 (d, C_4 and $C_{4'}$), 134.06 (s), 131.84 (d, $C_{8'}$), 130.25 (d, C_2), 129.22 (s), 128.58 (d, C_5), 126.59 (d, C_6), 119.22 (d, $C_{7'}$), 118.36 (d, $C_{5'}$), 41.77 (d, CH), 38.08 (s, 6′-*t*-Bu), 33.14 (s, 3′-*t*-Bu), 32.14 (q, 3′-*t*-Bu), and 31.71 (q, 6′-*t*-Bu). HRMS Calcd for $C_{44}H_{52}O$: M, 596.4018. Found: *m/z* 596.4017. Found: C, 88.25; H, 8.95%. Calcd for $C_{44}H_{52}O$: C, 88.54; H, 8.78%.

1,4-Bis[bis(3-methyl-1-azulenyl)methyl]benzene (8a). A solution of 1-methylazulene (**10a**) (1.43 g, 10.1 mmol) and terephthalaldehyde (336 mg, 2.50 mmol) in acetic acid (50 ml) was stirred at room temperature for 24 h. The precipitated crystals were collected by filtration, washed with CH_2Cl_2, and dried in vacuo to give the benzene **8a** (1.09 g, 65%). The filtrate was concentrated in vacuo. The residue was diluted with CH_2Cl_2. The organic solution was washed with 5% $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford 4-[bis(3-methyl-1-azulenyl)methyl]benzaldehyde (**12a**) (227 mg, 23%).

8a: Green crystals; mp > 300 °C (CH_2Cl_2 wash); MS (70 eV) *m/z* (rel intensity) 666 (M^+; 78), 400 (30), 142 (69), and 141 (100); IR (KBr disk) ν_{max} 1576, 1438, 1364, 738, and 728 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 242 (4.80), 285 (5.17), 357 (4.30), 374 (4.27), and 631 (3.08); ^1H NMR (400 MHz, 50% $CDCl_3/CS_2$) δ = 8.06 (d, *J* = 9.5 Hz, 4H, $H_{8'}$), 8.05 (d, *J* = 9.5 Hz, 4H, $H_{4'}$), 7.37 (dd, *J* = 9.8, 9.8 Hz, 4H, $H_{6'}$), 7.23 (s, 4H, $H_{2'}$), 6.97 (s, 4H, $H_{2,3,5,6}$), 6.91 (dd, *J* = 9.8, 9.5 Hz, 4H, $H_{5'}$), 6.80 (dd, *J* = 9.8, 9.5 Hz, 4H, $H_{7'}$), 6.56 (s, 2H, CH), and 2.53 (s, 12H, 3′-Me); ^{13}C NMR (100 MHz, 50% $CDCl_3/CS_2$) δ = 142.95 (s, $C_{1,4}$), 139.42 (d, $C_{2'}$), 136.96 (d, $C_{6'}$), 136.92 (s, $C_{3'a}$), 134.98 (s, $C_{8'a}$), 133.25 (d, $C_{4'}$), 132.90 (d, $C_{8'}$), 131.83 (s, $C_{1'}$), 128.55 (d, $C_{2,3,5,6}$), 124.25 (s, $C_{3'}$), 120.82 (d, $C_{7'}$), 120.58 (d, $C_{5'}$), 41.86 (d, CH), and 12.63 (q, 3′-Me). HRMS Calcd for $C_{52}H_{42}$: M, 666.3287. Found: *m/z* 666.3320. Found: C, 92.29; H, 6.58%. Calcd for $C_{52}H_{42}\cdot 1/2H_2O$: C, 92.40; H, 6.41%.

12a: Blue needles; mp 199.0—200.5 °C (EtOAc/hexane); MS (70 eV) *m/z* (rel intensity) 400 (M^+; 100), 385 (28), and 295 (24); IR (KBr disk) ν_{max} 1698, 1604, 1576, 1436, 1362, 1210, and 726 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 246 (4.55), 282 (4.89), 356 (4.01), 374 (4.02), and 628 (2.80); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.95 (s, 1H, 1-CHO), 8.17 (d, *J* = 9.8 Hz, 2H, $H_{4'}$), 8.12 (d, *J* = 9.8 Hz, 2H, $H_{8'}$), 7.76 (d, *J* = 8.2 Hz, 2H, $H_{2,6}$), 7.45 (dd, *J* = 9.8, 9.8 Hz, 2H, $H_{6'}$), 7.31 (d, *J* = 8.2 Hz, 2H, $H_{3,5}$), 7.27 (s, 2H, $H_{2'}$), 7.01 (dd, *J* = 9.8, 9.8 Hz, 2H, $H_{5'}$), 6.88 (dd, *J* = 9.8, 9.8 Hz, 2H, $H_{7'}$), 6.74 (s, 1H, CH), and 2.57 (s, 6H, 3′-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.01 (d, 1-CHO), 153.22 (s, C_4), 139.15 (d, $C_{2'}$), 137.50 (d, $C_{6'}$), 137.10 (s, $C_{3'a}$), 135.17 (s, $C_{8'a}$), 134.50 (s, C_1), 133.85 (d, $C_{4'}$), 132.94 (d, $C_{8'}$), 130.20 (s, $C_{1'}$), 129.88 (d, $C_{2,6}$), 129.41 (d, $C_{3,5}$), 124.78 (s, $C_{3'}$), 121.30 (d, $C_{7'}$), 121.13 (d, $C_{5'}$), 42.60 (d, CH), and 12.65 (q, 3′-Me). HRMS Calcd for $C_{30}H_{24}O$: M, 400.1827. Found: *m/z* 400.1833. Found: C, 89.38; H, 6.30%. Calcd for $C_{30}H_{24}O$: C, 89.97; H, 6.04%.

1,4-Bis[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (8b). The same procedure as for the preparation of **7b** was adopted here. The condensation of 1,6-di-*t*-butylazulene (**10b**) (1.21 g, 5.03 mmol) with terephthalaldehyde (169 mg, 1.26 mmol) in acetic acid (25 ml) afforded the benzene **8b** (1.07 g, 80%) and 4-[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzaldehyde (**12b**) (141 mg, 19%).

8b: Blue crystals; mp 289.5—291.0 °C decomp (CH_2Cl_2/hexane/EtOH); MS (FAB) *m/z* 1059 (M^+); IR (KBr disk) ν_{max} 2963, 1576, 1364, 1227, and 833 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 243 (4.78), 289 (5.22), 304 (5.18), 359 (4.34), 376 (4.25), and 615 (3.10); ^1H NMR (90 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 11.0 Hz, 4H, $H_{4'}$), 8.14 (d, *J* = 10.8 Hz, 4H, $H_{8'}$), 7.34 (s, 4H, $H_{2'}$), 7.11 (dd, *J* = 11.0, 1.8 Hz, 4H, $H_{5'}$), 7.01 (dd, *J* = 10.8, 1.8 Hz, 4H, $H_{7'}$), 6.97 (s, 4H, $H_{2,3,5,6}$), 6.57 (s, 2H, CH), 1.47 (s, 36H, 3′-*t*-Bu), and 1.39 (s, 36H, 6′-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 159.86 (s, $C_{6'}$), 143.15 (s, $C_{1,4}$), 137.30 (s), 136.23 (d, $C_{2'}$), 134.43 (s), 134.16 (d, $C_{4'}$), 133.97 (s), 132.02 (d, $C_{8'}$), 130.86 (s), 128.30 (d, $C_{2,3,5,6}$), 118.85 (d, $C_{7'}$), 117.93 (d, $C_{5'}$), 41.71 (d, CH), 38.05 (s, 6′-*t*-Bu), 33.17 (s, 3′-*t*-Bu), 32.20 (q, 3′-*t*-Bu), and 31.77 (q, 6′-*t*-Bu). HRMS Calcd for $C_{80}H_{98}$: M, 1058.7640. Found: *m/z* 1058.7671. Found: C, 90.10; H, 9.34%. Calcd for $C_{80}H_{98}$: C, 90.68; H, 9.32%.

12b: Blue crystals; mp 145.0—148.0 °C (MeOH); MS (70 eV) *m/z* (rel intensity) 596 (M^+; 100) and 539 (43); IR (KBr disk) ν_{max} 2963, 1703, 1576, 1364, and 833 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 247 (4.59), 287 (4.99), 302 (4.92), 358 (4.12), 376 (4.07), and 612 (2.85); ^1H NMR (90 MHz, $CDCl_3$) δ = 9.91 (s, 1H, 1-CHO), 8.57 (d, *J* = 11.0 Hz, 2H, $H_{4'}$), 8.15 (d, *J* = 10.8 Hz, 2H, $H_{8'}$), 7.72 (d, *J* = 8.1 Hz, 2H, $H_{2,6}$), 7.36 (s, 2H, $H_{2'}$), 7.29 (d, *J* = 8.1 Hz, 2H, $H_{3,5}$), 7.18 (dd, *J* = 11.0, 1.8 Hz, 2H, $H_{5'}$), 7.07 (dd, *J* = 10.8, 1.8 Hz, 2H, $H_{7'}$), 6.70 (s, 1H, CH), 1.50 (s, 18H, 3′-*t*-Bu), and 1.39 (s, 18H, 6′-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDlC_3$) δ = 191.69 (d, 1-CHO), 160.41 (s, $C_{6'}$), 153.52 (s, C_4), 137.63 (s), 135.80 (d, $C_{2'}$), 134.58 (s), 134.52 (d, $C_{4'}$), 134.16 (s), 134.09 (s), 131.84 (d, $C_{8'}$), 129.55 (d, $C_{2,6}$), 129.19 (d, $C_{3,5}$), 128.94 (s), 119.28 (d, $C_{7'}$), 118.45 (d, $C_{5'}$), 42.32 (d, CH), 38.11 (s, 6′-*t*-Bu), 33.17 (s, 3′-*t*-Bu), 32.17 (q, 3′-*t*-Bu), and 31.71 (q, 6′-*t*-Bu). HRMS Calcd for $C_{44}H_{52}O$: M, 596.4018. Found: *m/z* 596.4018. Found: C, 88.40; H, 8.75%. Calcd for $C_{44}H_{52}O$: C, 88.54; H, 8.78%.

1,3,5-Tris[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (9). The same procedure as for the preparation of **7b** was adopted here. The condensation of 1,6-di-*t*-butylazulene (**10b**) (1.21 g, 5.03 mmol) with 1,3,5-benzenetricarbaldehyde (137 mg, 0.845 mmol) in acetic acid (15 ml) and CH_2Cl_2 (15 ml) afforded the benzene **9** (551 mg, 55%), 3,5-bis[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzaldehyde (**13**) (274 mg, 30%), and the recovered **10b** (284 mg, 23%). The condensation of **10b** (1.22 g, 5.08 mmol) with 1,3,5-benzenetricarbaldehyde (135 mg, 0.833 mmol) in acetic acid (30 ml) afforded the benzene **9** (88 mg, 9.7%), **13** (673 mg, 74%), and the recovered **10b** (378 mg, 31%).

9: Blue crystals; mp 247.0—248.5 °C decomp (CH_2Cl_2/hexane/EtOH); MS (FAB) *m/z* 1549 (M^+); IR (KBr disk) ν_{max} 2963, 1576, 1460, 1364, 1246, 1229, and 831 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 243 (4.97), 290 (5.40), 303 (5.34), 359 (4.51), 376 (4.42), and 616 (3.28); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.43 (d, *J* = 10.5 Hz, 6H, $H_{4'}$), 8.03 (d, *J* = 10.5 Hz, 6H, $H_{8'}$), 7.09 (s, 6H, $H_{2'}$), 7.07 (dd, *J* = 10.5, 1.7 Hz, 6H, $H_{5'}$), 6.97 (s, 3H, $H_{2,4,6}$), 6.92 (dd, *J* = 10.5, 1.7 Hz, 6H, $H_{7'}$), 6.37 (s, 3H, CH), 1.37 (s, 54H, 6′-*t*-Bu), and 1.29 (s, 54H, 3′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.68 (s, $C_{6'}$), 145.24 (s, $C_{1,3,5}$), 137.22 (s, $C_{3'}$), 136.25 (d, $C_{2'}$), 134.36 (s, $C_{8'a}$), 134.09 (d, $C_{4'}$), 134.03 (s, $C_{3'a}$), 132.05 (d, $C_{8'}$), 131.28 (s, $C_{1'}$), 127.00 (d, $C_{2,4,6}$), 118.76 (d, $C_{7'}$), 117.85 (d, $C_{5'}$), 42.26 (d, CH), 38.04 (s, 6′-*t*-Bu), 33.00 (s, 3′-*t*-Bu), 32.17 (q, 3′-*t*-Bu), and 31.84 (q, 6′-*t*-Bu). Found: C, 90.19; H, 9.48%. Calcd for $C_{117}H_{144}$: C, 90.64; H, 9.36%.

13: Blue crystals; mp 296.0—298.0 °C decomp (CH_2Cl_2/hexane); MS (FAB) *m/z* 1087 (M^+); IR (KBr disk) ν_{max} 2963, 1703, 1576, 1460, 1364, 1227, and 833 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε) 244 (4.79), 287 (5.18), 304 (5.15), 358 (4.31), 375 (4.23), and 612 (3.08); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.79 (s, 1H, 1-CHO), 8.51 (d, *J* = 10.8 Hz, 4H, $H_{4'}$), 8.08 (d, *J* = 10.5 Hz, 4H, $H_{8'}$), 7.50 (s, 3H, $H_{2,6}$ and H_4), 7.19 (s, 4H, $H_{2'}$), 7.14 (dd, *J* = 10.8, 2.0 Hz, 4H, $H_{5'}$), 7.02 (dd, *J* = 10.5, 2.0 Hz, 4H, $H_{7'}$), 6.58 (s, 2H, CH), 1.391 (s, 36H, 6′-*t*-Bu), and 1.388 (s, 36H, 3′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.18 (s, 1-CHO), 160.36 (s, $C_{6'}$), 147.24 (s, $C_{3,5}$), 137.63 (s, $C_{3'}$), 136.45 (s, C_1), 135.89 (d, $C_{2'}$), 135.66 (d, C_4), 134.57 (d, $C_{4'}$), 134.54 (s, $C_{8'a}$), 134.16 (s, $C_{3'a}$), 131.99 (d, $C_{8'}$), 129.71 (s, $C_{1'}$), 127.67 (d, $C_{2,6}$), 119.23 (d, $C_{7'}$), 118.41 (d, $C_{5'}$), 42.03 (d, CH), 38.16 (s, 6′-*t*-Bu), 33.12 (s, 3′-*t*-Bu), 32.18 (q, 3′-*t*-Bu), and 31.81 (q, 6′-*t*-Bu). Found: C, 88.75; H, 9.01%. Calcd for $C_{81}H_{98}O$: C, 89.45; H, 9.08%.

1,3-Phenylenebis[bis(3-methyl-1-azulenyl)methylium] Bis(hexafluoroposphate) ($4a\cdot 2PF_6^-$). DDQ (275 mg, 1.21 mmol) was added at room temperature to a mixture of 1,3-bis[bis(3-methyl-1-azulenyl)methyl]benzene (**7a**) (334 mg, 0.501 mmol), CH_2Cl_2 (100 ml), concentrated HPF_6 (10 ml), and water (100 ml). After the solution was stirred at the same temperature for 10 min, 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 (10 ml) and Et_2O (100 ml) was added to the solution. The precipitated crystals were collected by filtration, washed with Et_2O, and dried in vacuo to give the salt **4a**·$2\mathrm{PF_6}^-$ (472 mg, 99%). Black powder; mp > 300 °C ($\mathrm{CH_2Cl_2}$/ether); MS (FAB) *m/z* 809 ($\mathrm{M^+-PF_6}$) and 664 ($\mathrm{M^+-2PF_6}$); IR (KBr disk) ν_{max} 1488, 1444, 1412, 1348, 1314, 1288, 1072, 838, and 558 $\mathrm{cm^{-1}}$; UV-vis (MeCN) λ_{max}, nm ($\log\varepsilon$) 234 (4.83), 284 (4.64), 367 (4.47), 496 (4.04), and 681 (4.67); ^{1}H NMR (500 MHz, $\mathrm{(CDCl_2)_2}$, 80 °C) δ = 8.57 (d, J = 9.6 Hz, 4H, $\mathrm{H}_{4'}$), 8.02 (dd, J = 9.8, 9.8 Hz, 4H, $\mathrm{H}_{6'}$), 7.91 (dd, J = 9.8, 9.6 Hz, 4H, $\mathrm{H}_{5'}$), 7.81 (t, J = 8.4 Hz, 4H, H_5), 7.80 (d, J = 9.8 Hz, 1H, $\mathrm{H}_{8'}$), 7.74 (d, J = 8.4 Hz, 2H, $\mathrm{H}_{4,6}$), 7.67 (s, 4H, $\mathrm{H}_{2'}$), 7.48 (dd, J = 9.8, 9.8 Hz, 4H, $\mathrm{H}_{7'}$), 7.41 (s, 1H, H_2), and 2.61 (s, 12H, 3′-Me); ^{13}C NMR (125 MHz, $\mathrm{(CDCl_2)_2}$, 80 °C) δ = 159.12 (s, C^+), 152.38 (s, $\mathrm{C}_{3'\mathrm{a}}$), 149.11 (s, $\mathrm{C}_{8'\mathrm{a}}$), 145.22 (d, $\mathrm{C}_{2'}$), 143.81 (d, $\mathrm{C}_{6'}$), 143.07 (s, $\mathrm{C}_{1,3}$), 139.39 (d, $\mathrm{C}_{8'}$), 138.99 (d, C_2), 138.74 (d, $\mathrm{C}_{4'}$), 138.49 (d, $\mathrm{C}_{4,6}$), 136.55 (s, $\mathrm{C}_{3'}$), 135.27 (d, $\mathrm{C}_{5'}$), 135.13 (d, $\mathrm{C}_{7'}$), 132.94 (s, $\mathrm{C}_{1'}$), 130.03 (d, C_5), and 13.12 (q, 3′-Me). Found: C, 65.42; H, 4.52%. Calcd for $\mathrm{C_{52}H_{40}\cdot 2PF_6}$: C, 65.41; H, 4.22%.

1,3-Phenylenebis[bis(3,6-di-*t*-butyl-1-azulenyl)methylium] Bis(hexafluoroposphate) (4b·$2\mathrm{PF_6}^-$). DDQ (273 mg, 1.20 mmol) was added at room temperature to a solution of 1,3-bis[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (**7b**) (529 mg, 0.499 mmol) in $\mathrm{CH_2Cl_2}$ (50 ml). After the solution was stirred at the same temperature for 5 min, concentrated $\mathrm{HPF_6}$ (10 ml) was added. After stirring at room temperature for an additional 5 min, water (100 ml) was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, washed with water, dried with $\mathrm{MgSO_4}$, and concentrated under reduced pressure. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (5 ml), then poured into hexane (100 ml). The precipitated crystals were collected by filtration, washed with hexane, and dried in vacuo to give the salt **4b**·$2\mathrm{PF_6}^-$ (673 mg, 100%). Dark green powder; mp 249.0—253.0 °C ($\mathrm{CH_2Cl_2}$/hexane); MS (FAB) *m/z* 1202 ($\mathrm{M^+-PF_6}$) and 1057 ($\mathrm{M^+-2PF_6}$); IR (KBr disk) ν_{max} 2961, 1478, 1333, 1312, 1244, 1117, 839, and 558 $\mathrm{cm^{-1}}$; UV-vis (MeCN) λ_{max}, nm ($\log\varepsilon$) 244 (4.94), 291 (4.73), 319 (4.72), 362 (4.58), and 687 (4.94); ^{1}H NMR (600 MHz, $\mathrm{(CDCl_2)_2}$, 78 °C) δ = 8.94 (d, J = 11.0 Hz, 4H, $\mathrm{H}_{4'}$), 8.08 (dd, J = 11.0, 1.8 Hz, 4H, $\mathrm{H}_{5'}$), 7.90 (br d, J = 10.5 Hz, 4H, $\mathrm{H}_{8'}$), 7.84 (br t, J = 7.2 Hz, 1H, H_5), 7.78 (br d, J = 7.2 Hz, 2H, $\mathrm{H}_{4,6}$), 7.64 (br d, J = 10.5 Hz, 4H, $\mathrm{H}_{7'}$), 7.60 (br s, 1H, H_2), 7.47 (br s, 4H, $\mathrm{H}_{2'}$), 1.47 (s, 36H, 3′-*t*-Bu), and 1.41 (s, 36H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $\mathrm{(CDCl_2)_2}$, 78 °C) δ = 170.11 (s, $\mathrm{C}_{6'}$), 158.85 (br s, C^+), 149.90 (br s, $\mathrm{C}_{3'\mathrm{a}}$), 148.68 (br s, $\mathrm{C}_{8'\mathrm{a}}$), 148.43 (s, $\mathrm{C}_{3'}$), 143.00 (br s, $\mathrm{C}_{1,3}$), 142.31 (br d, $\mathrm{C}_{2'}$), 139.54 (d, $\mathrm{C}_{4'}$), 138.67 (d, $\mathrm{C}_{8'}$), 137.61 (br d, $\mathrm{C}_{4,8}$), 137.13 (d, C_2), 133.01 (d, $\mathrm{C}_{5'}$), 132.67 (d, $\mathrm{C}_{7'}$), 132.15 (br s, $\mathrm{C}_{1'}$), 130.10 (d, C_5), 39.65 (s, 6′-*t*-Bu), 33.50 (s, 3′-*t*-Bu), 31.73 (q, 6′-*t*-Bu), and 31.29 (q, 3′-*t*-Bu). HRMS Calcd for $\mathrm{C_{80}H_{96}}^+$: M, 1056.7512. Found: *m/z* 1056.7400. Found: C, 69.87; H, 6.52%. Calcd for $\mathrm{C_{80}H_{96}\cdot 2PF_6\cdot 2H_2O}$: C, 69.45; H, 7.28%.

1,4-Phenylenebis[bis(3-methyl-1-azulenyl)methylium] Bis(hexafluoroposphate) (5a·$2\mathrm{PF_6}^-$). The same procedure as for the preparation of **4a**·$2\mathrm{PF_6}^-$ was adopted here. The hydride abstraction reaction of 1,4-bis[bis(3-methyl-1-azulenyl)methyl]benzene (**8a**) (334 mg, 0.501 mmol) with DDQ (293 mg, 1.29 mmol) in $\mathrm{CH_2Cl_2}$ (100 ml) gave the salt **5a**·$2\mathrm{PF_6}^-$ (475 mg, 99%). Black powder; mp > 300 °C ($\mathrm{CH_2Cl_2}$/ether); MS (FAB) *m/z* 809 ($\mathrm{M^+-PF_6}$) and 664 ($\mathrm{M^+-2PF_6}$); IR (KBr disk) ν_{max} 1488, 1442, 1412, 1346, 1316, 1288, 1070, 842, and 558 $\mathrm{cm^{-1}}$; UV-vis (MeCN) λ_{max}, nm ($\log\varepsilon$) 230 (4.81), 347 (4.24), 398 (4.31), 518 (4.18), and 681 (4.46); ^{1}H NMR (500 MHz, $\mathrm{(CDCl_2)_2}$, 80 °C) δ = 8.61 (d, J = 9.8 Hz, 4H, $\mathrm{H}_{4'}$), 8.04 (dd, J = 9.8, 9.8 Hz, 4H, $\mathrm{H}_{6'}$), 7.94 (dd, J = 9.8, 9.8 Hz, 4H, $\mathrm{H}_{5'}$), 7.89 (d, J = 9.8 Hz, 4H, $\mathrm{H}_{8'}$), 7.79 (s, 4H, $\mathrm{H}_{2'}$), 7.61 (s, 4H, $\mathrm{H}_{2,3,5,6}$), 7.51 (dd, J = 9.8, 9.8 Hz, 4H, $\mathrm{H}_{7'}$), and 2.68 (s, 12H, 3′-Me); ^{13}C NMR (125 MHz, $\mathrm{(CDCl_2)_2}$, 80 °C) δ = 158.99 (s, C^+), 152.43 (s, $\mathrm{C}_{3'\mathrm{a}}$), 149.17 (s, $\mathrm{C}_{8'\mathrm{a}}$), 145.68 (d, $\mathrm{C}_{1,4}$), 145.58 (s, $\mathrm{C}_{2'}$), 143.77 (d, $\mathrm{C}_{6'}$), 139.37 (d, $\mathrm{C}_{8'}$), 138.68 (d, $\mathrm{C}_{4'}$), 136.72 (s, $\mathrm{C}_{3'}$), 135.27 (d, $\mathrm{C}_{2,3,5,6}$ and $\mathrm{C}_{5'}$), 135.06 (d, $\mathrm{C}_{7'}$), 133.07 (s, $\mathrm{C}_{1'}$), and 13.10 (q, 3′-Me). Found: C, 63.35; H, 4.18%. Calcd for $\mathrm{C_{52}H_{40}\cdot 2PF_6\cdot 2H_2O}$: C, 63.03; H, 4.48%.

1,4-Phenylenebis[bis(3,6-di-*t*-butyl-1-azulenyl)methylium] Bis(hexafluoroposphate) (5b·$2\mathrm{PF_6}^-$). The same procedure as for the preparation of **4b**·$2\mathrm{PF_6}^-$ was adopted here. The hydride abstraction reaction of 1,4-bis[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (**8b**) (530 mg, 0.500 mmol) with DDQ (272 mg, 1.20 mmol) in $\mathrm{CH_2Cl_2}$ (100 ml) gave the salt **5b**·$2\mathrm{PF_6}^-$ (600 mg, 89%). Dark brown powder; mp 285.0—287.0 °C ($\mathrm{CH_2Cl_2}$/ether); MS (FAB) *m/z* 1202 ($\mathrm{M^+-PF_6}$), 1057 ($\mathrm{M^+-2PF_6}$), and 528 (($\mathrm{M^+-2PF_6}$)/2); IR (KBr disk) ν_{max} 2963, 1480, 1333, 1312, 1244, 839, and 558 $\mathrm{cm^{-1}}$; UV-vis (MeCN) λ_{max}, nm ($\log\varepsilon$) 238 (4.92), 293 (4.82), 319 (4.76), 399 (4.62), 520 (4.45), and 703 (4.85); ^{1}H NMR (600 MHz, $\mathrm{(CDCl_2)_2}$, 78 °C) δ = 8.99 (d, J = 11.0 Hz, 4H, $\mathrm{H}_{4'}$), 8.09 (dd, J = 11.0, 1.8 Hz, 4H, $\mathrm{H}_{5'}$), 7.93 (br d, J = 10.5 Hz, 4H, $\mathrm{H}_{8'}$), 7.69 (br s, 4H, $\mathrm{H}_{2,3,5,6}$), 7.62 (br d, J = 10.5 Hz, 4H, $\mathrm{H}_{7'}$), 7.59 (br s, 4H, $\mathrm{H}_{2'}$), 1.58 (s, 36H, 3′-*t*-Bu), and 1.43 (s, 36H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $\mathrm{(CDCl_2)_2}$, 78 °C) δ = 169.81 (s, $\mathrm{C}_{6'}$), 158.57 (br s, C^+), 149.79 (s, $\mathrm{C}_{3'\mathrm{a}}$), 148.73 (br s, $\mathrm{C}_{8'\mathrm{a}}$), 148.39 (s, $\mathrm{C}_{3'}$), 145.55 (br s, $\mathrm{C}_{1,4}$), 142.67 (br d, $\mathrm{C}_{2'}$), 139.44 (d, $\mathrm{C}_{4'}$), 138.78 (d, $\mathrm{C}_{8'}$), 134.83 (d, $\mathrm{C}_{2,3,5,6}$), 132.78 (d, $\mathrm{C}_{5'}$), 132.51 (d, $\mathrm{C}_{7'}$), 132.34 (br s, $\mathrm{C}_{1'}$), 39.60 (s, 6′-*t*-Bu), 33.59 (s, 3′-*t*-Bu), 31.75 (q, 6′-*t*-Bu), and 31.37 (q, 3′-*t*-Bu). HRMS Calcd for $\mathrm{C_{80}H_{96}}^+$: M, 1056.7512. Found: *m/z* 1056.7520. Found: C, 71.26; H, 7.38%. Calcd for $\mathrm{C_{80}H_{96}\cdot 2PF_6}$: C, 71.30; H, 7.18%.

1,3,5-Benzenetriyltris[bis(3,6-di-*t*-butyl-1-azulenyl)methylium] Tris(hexafluoroposphate) (6·$3\mathrm{PF_6}^-$). The same procedure as for the preparation of **4b**·$2\mathrm{PF_6}^-$ was adopted here. The hydride abstraction reaction of 1,3,5-tris[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (**9**) (518 mg, 0.334 mmol) with DDQ (272 mg, 1.20 mmol) in $\mathrm{CH_2Cl_2}$ (100 ml) gave the salt **6**·$3\mathrm{PF_6}^-$ (656 mg, 99%). Black powder; mp 265.5—268.0 °C ($\mathrm{CH_2Cl_2}$/ether); MS (FAB) *m/z* 1836 ($\mathrm{M^+-PF_6}$), 1691 ($\mathrm{M^+-2PF_6}$), and 1546 ($\mathrm{M^+-3PF_6}$); IR (KBr disk) ν_{max} 2965, 1480, 1333, 1310, 1246, 839, and 558 $\mathrm{cm^{-1}}$; UV-vis (MeCN) λ_{max}, nm ($\log\varepsilon$) 245 (5.09), 299 (4.95), 320 (4.97), 358 (4.83), 485 (4.33), and 693 (5.03); ^{1}H NMR (600 MHz, $\mathrm{(CDCl_2)_2}$, 100 °C) δ = 8.92 (d, J = 11.1 Hz, 6H, $\mathrm{H}_{4'}$), 8.04 (br d, J = 11.1 Hz, 6H, $\mathrm{H}_{5'}$), 8.01 (s, 3H, $\mathrm{H}_{2,4,6}$), 7.80 (br d, J = 9.1 Hz, 6H, $\mathrm{H}_{8'}$), 7.61 (br d, J = 9.1 Hz, 6H, $\mathrm{H}_{7'}$), 7.57 (s, 6H, $\mathrm{H}_{2'}$), 1.47 (s, 54H, 3′-*t*-Bu), and 1.38 (s, 54H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $\mathrm{(CDCl_2)_2}$, 100 °C) δ = 170.14 (s, $\mathrm{C}_{6'}$), 156.97 (br s, C^+), 149.86 (s, $\mathrm{C}_{3'\mathrm{a}}$), 149.32 (br s, $\mathrm{C}_{8'\mathrm{a}}$), 148.76 (s, $\mathrm{C}_{3'}$), 143.51 (s, $\mathrm{C}_{1,3,5}$), 141.31 (br d, $\mathrm{C}_{2'}$), 139.97 (br d, $\mathrm{C}_{2,4,6}$), 139.48 (d, $\mathrm{C}_{4'}$), 138.95 (d, $\mathrm{C}_{8'}$), 133.14 (d, $\mathrm{C}_{7'}$), 132.97 (br s, $\mathrm{C}_{1'}$), 132.89 (d, $\mathrm{C}_{5'}$), 39.59 (s, 6′-*t*-Bu), 33.47 (s, 3′-*t*-Bu), 31.67 (q, 6′-*t*-Bu), and 31.39 (q, 3′-*t*-Bu). Found: C, 69.89; H, 6.92%. Calcd for $\mathrm{C_{117}H_{141}\cdot 3PF_6}$: C, 70.89; H, 7.17%.

p$K_{\mathrm{R^+}}$ Value. The sample solution of the salts **4a**, **4b**·$2\mathrm{PF_6}^-$, **5a**, **5b**·$2\mathrm{PF_6}^-$, and **6**·$3\mathrm{PF_6}^-$ were prepared by dissolving in a glycine (0.1 M) solution (50 ml) and the mixture was made up to 100 ml by adding MeCN; the sample solution with lower acidity was made by further alkalification with 20% aqueous NaOH. The pH of each sample solution was measured on a Horiba pH meter F-13 calibrated with standard buffers before use. The observed absorbances at the specific absorption maxima of dications **4a**, **4b**·$2\mathrm{PF_6}^-$ and **5a**, **5b**·$2\mathrm{PF_6}^-$ were plotted against the pH, giving a classical titration curve whose midpoint was taken as the p$K_{\mathrm{R^+}}$ value for **4a**, **4b**·$2\mathrm{PF_6}^-$ and **5a**, **5b**·$2\mathrm{PF_6}^-$. The observed absorbances of trication **6**· $3\mathrm{PF_6}^-$ were also plotted against the pH, giving a three-step titration curve, and each midpoint was taken as the pK_{R^+} values for **6**$\cdot 3PF_6^-$.

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