Synthesis, Properties, and Redox Behavior of Di(1-azulenyl)(2- and 3-thienyl)methyl Cations and Dications Composed of Two Di(1-azulenyl)methylium Units Connected with 2,5-Thiophenediyl and 2,5-Thienothiophenediyl Spacers

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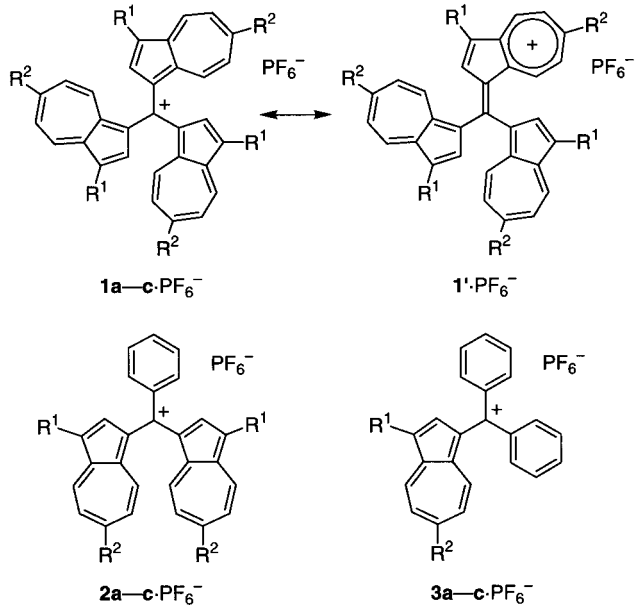
The titled stable monocations, di(1-azulenyl)(2- and 3-thienyl)methyl cations **7a**,**b** and **8a**,**b** and dications composed of two di(1-azulenyl)methylium units connected with 2,5-thiophenediyl and 2,5-thieno[3,2-*b*]thiophenediyl spacers **9a**,**b** and **10a**,**b** were prepared by hydride abstraction of the corresponding methane derivatives. These mono- and dications **7a**,**b**, **8a**,**b**, **9a**,**b**, and **10a**,**b** showed high stability with large pK_R^+ values. The values of monocations **7a**,**b** and **8a**,**b** were 11.2−11.8 ± 0.1 and 11.4−12.4 ± 0.1, respectively. Two cation units in dications **9a**,**b** and **10a**,**b** were neutralized via one step at the pH of 11.1−11.7 ± 0.1, which corresponds to the average of the pK_R^+ values of the dications and half-neutralized monocations. Electrochemical behavior of **7a**,**b**, **8a**,**b**, **9a**,**b**, and **10a**,**b** was examined by cyclic voltammetry (CV). Formation of the thienoquinoid products **18a**,**b** and **19a**,**b** from **9a**,**b** and **10a**,**b** was characterized by UV−vis spectroscopy under electrochemical reduction conditions. Chemical reduction of **9a**,**b** and **10a**,**b** with Zn powder in acetonitrile afforded **18a**,**b** and **19a**,**b** as deep-colored crystals, which exhibited rather high electron-donating ability.

Introduction

We have recently reported the synthesis of a series of (1-azulenyl)methyl cations, i.e., tri(1-azulenyl)methylium, di(1-azulenyl)(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**,**c**·PF_6^-, **2b**,**c**·PF_6^-, and **3b**,**c**·PF_6^-) by hydride abstraction of the corresponding methane derivatives (Chart 1).[1] These cations (**1a**−**c**, **2a**−**c**, and **3a**−**c**) showed high stability with large pK_R^+ values (e.g.: **1a**, 11.3; **2a**, 10.5; and **3a**, 3.0, respectively).[1d] In particular, the methyl cations, which were stabilized by three (**1a**−**c**) or two (**2a**−**c**) 1-azulenyl groups, showed high thermodynamic stability compared with those of **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. Stable cationic multistage redox systems were constructed by a combination of the methylium unit with the ferrocene moiety.[2] Combination of several of the methylium units formed dications of tetraazulenyl-*m*-xylylene **4a**,**b** and tetraazulenyl-*p*-xylylene **5a**,**b** and a trication of hexaazulenyltrimethylbenzene **6**, which also exhibited high thermodynamic stability (Chart 2).[3] However, preparation of quinonoid compounds from the reduction of **5a** and **5b** was not achieved due to instability, ready decomposition, or polymerization of the corresponding reduced species.

Recently, much attention has been focused on multistage redox systems because of their special properties

Chart 1



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(1) (a) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett*. **1991**, *32*, 773. (b) Ito, S.; Morita, N. Asao, T. *Tetrahedron Lett*. **1994**, *35*, 751. (c) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett*. **1994**, *35*, 3723. (d) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 1409. (e) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 2011. (f) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 2639. (g) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Chem. Lett*. **1995**, 475. (h) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 3611. (i) Ito, S.; Kikuchi, S.; Morita, N.; Asao, T. *Chem. Lett*. **1996**, 175. (j) Ito, S.; Kobayashi, H.; Kikuchi, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn*. **1996**, *69*, 3225. (k) Ito, S.; Kikuchi, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn*. **1999**, *72*, 839. (l) Ito, S.; Kikuchi, K.; Morita, N.; Asao, T. *J. Org. Chem*. **1999**, *64*, 5815.

(2) Ito, S.; Morita, N.; Asao, T. *J. Org. Chem*. **1996**, *61*, 5077.

(3) (a) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett*. **1994**, *33*, 3773. (b) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett*. **1992**, *35*, 755. (c) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn*. **2000**, *73*, 1865.

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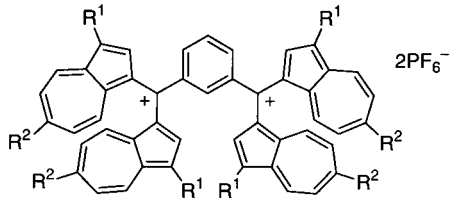
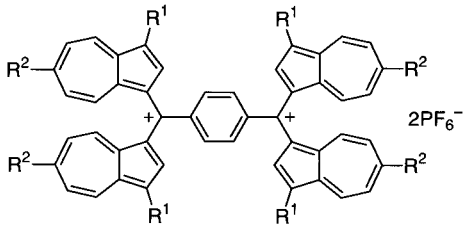
Chart 2

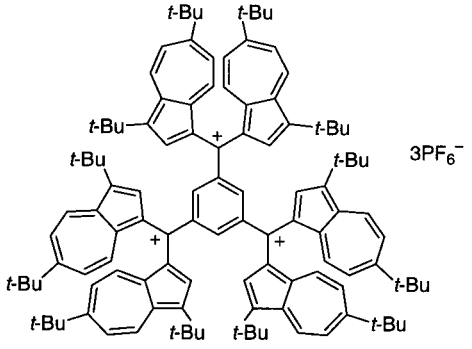


4a, **b**·2PF_6^-



5a, **b**·2PF_6^-

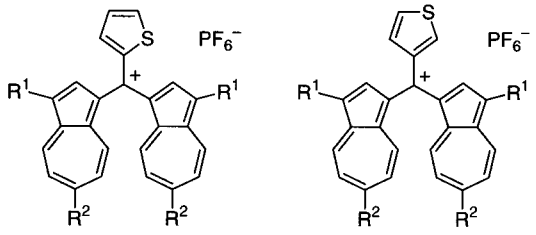
a: R^1 = Me, R^2 = H, **b**: R^1 = R^2 = *t*-Bu



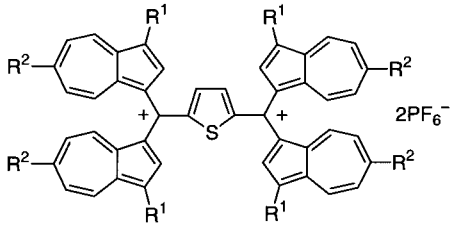
6·3PF_6^-

such as conductivity and organic ferromagnetism.[4] Thiophene and thienothiophene units have been frequently used in thienoquinoid or condensed forms in the design of new molecular skeletons.[5] Aiming at the construction of multistage redox systems with a stabilized carbocation, we have prepared dications composed of two di(1-azulenyl)methylium units connected with 2,5-thiophenediyl and 2,5-thieno[3,2-*b*]thiophenediyl spacers. Incorporation of the thiophene or thieno[3,2-*b*]thiophene as a linking π-bridge could significantly stabilize the quinoid structure in the reduced forms of the dications since the loss of aromaticity of the thiophene and thieno[3,2-*b*]thiophene rings in the thienoquinoid structures is less than that of phenylene bridges. Monocations composed of the di(1-azulenyl)methylium units connected with 2- and 3-thienyl groups have also been prepared for comparison. In the present paper we will report the synthesis and properties of di(1-azulenyl)(2- and 3-thienyl)methyl cations (**7a**,**b** and **8a**,**b**) and 2,5-thiophenediyl- and 2,5-thieno[3,2-*b*]thiophenediylbis[di(1-azulenyl)methylium] (**9a**,**b** and **10a**,**b**) (Chart 3), particularly, their high thermodynamic stability measured spectrophotometrically and their redox behaviors examined by cyclic

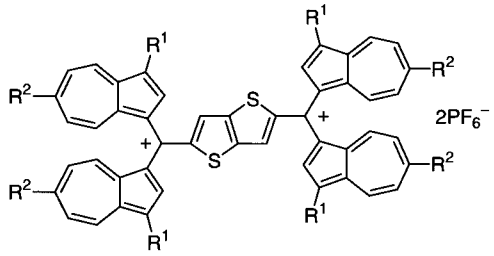
Chart 3



7a, **b**·PF_6^- **8a**, **b**·PF_6^-



9a, **b**·2PF_6^-



10a, **b**·2PF_6^-

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

voltammetry (CV). Electrochromic behavior was also examined with the dications **9a**,**b** and **10a**,**b** that displayed distinct changes in their absorption spectra in different oxidation states. Chemical reduction of the dications **9a**,**b** and **10a**,**b** afforded the closed-shell thienoquinoid compounds, which exhibited high electron-donating ability.

Results and Discussion

Synthesis. The synthesis of monocations **7a**,**b** and **8a**,**b** is outlined in Scheme 1. The key step was the hydride abstraction reaction of di(1-azulenyl)(2- and 3-thienyl)methanes (**12a**,**b** and **13a**,**b**). The synthesis of **12a**,**b** and **13a**,**b** was established by the reaction of 1-methyl- and 1,6-di-*tert*-butylazulenes (**11a** and **11b**)[1d,6] with 2- or 3-thiophenecarbaldehydes in acetic acid at room temperature for 24 h in 79%, 82%, 80%, and 86% yields, respectively. Thus, reaction of **12a**,**b** and **13a**,**b** with DDQ in dichloromethane at room temperature followed by an addition of a 60% aqueous HPF_6 solution yielded di(1-azulenyl)(2- and 3-thienyl)methyl cations (**7a**,**b** and **8a**,**b**) as hexafluorophosphate in 95%, 100%, 95%, and 100% yields, respectively.

Similarly, the reaction of four molar amounts of **11a** and **11b** with 2,5-thiophene- or 2,5-thieno[3,2-*b*]thiophenedicarbaldehydes[7] in acetic acid for 1−2 d afforded 2,5-bis[bis(3-methyl- and 3,6-di-*tert*-butyl-1-azulenyl)methyl]-thiophenes (**14a** and **14b**) and 2,5-bis[bis(3-methyl- and

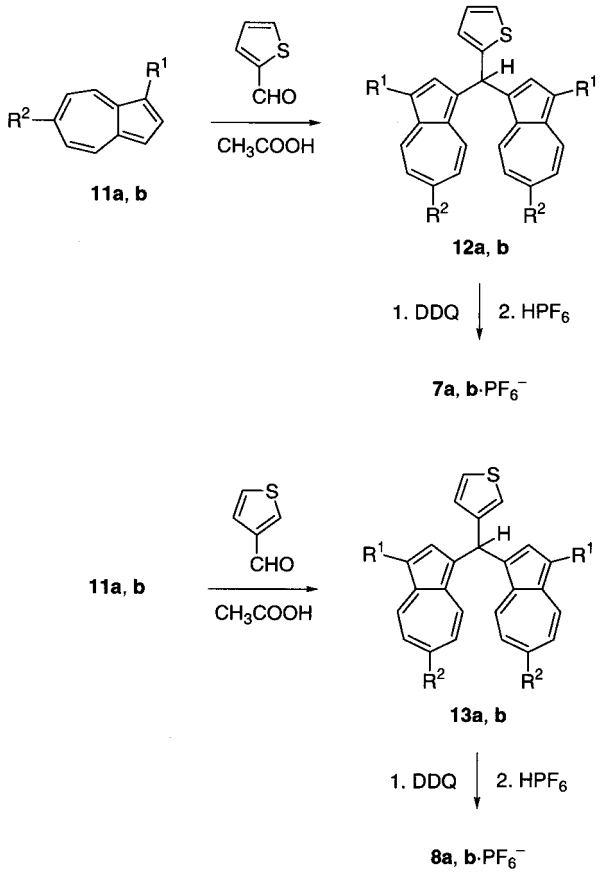
(4) Deuchert, K.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875.

(5) See e.g., (a) Takahashi, K.; Nihira, T. *Tetrahedron Lett.* **1989**, *30*, 5903. (b) Takahashi, K.; Nihira, T.; Tomitani, K. *J. Chem. Soc., Chem. Commun.* **1993**, 1617.

(6) Yasunami, M.; Miyoshi, S.; Kanegae, N.; Takase, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 892.

(7) Lunazzi, L.; Pedulli, G. F.; Tiecco, M.; Vincenzi, C.; Veracini, C. A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 751.

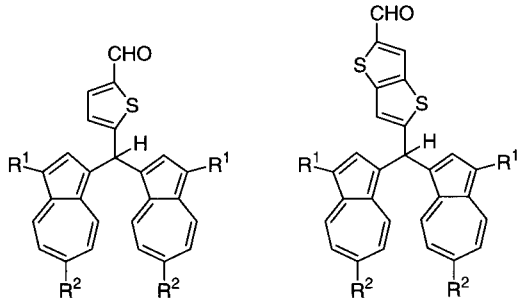
Scheme 1



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

3,6-di-*tert*-butyl-1-azulenyl)methyl]thieno[3,2-*b*]thiophenes (**15a** and **15b**) in 57%, 50%, 79%, and 71% yields, respectively, together with 5-bis(3-methyl- and 3,6-di-*tert*-butyl-1-azulenyl)methylthiophene-2-carbaldehydes (**16a** and **16b**) and 5-bis(3-methyl- and 3,6-di-*tert*-butyl-1-azulenyl)methylthieno[3,2-*b*]thiophene-2-carbaldehydes (**17a** and **17b**) in 32%, 9.6%, 35%, and 9.7% yields, respectively (Chart 4). Hydride abstraction reaction of **14a**,**b** and **15b** with two molar amounts of DDQ in

Chart 4



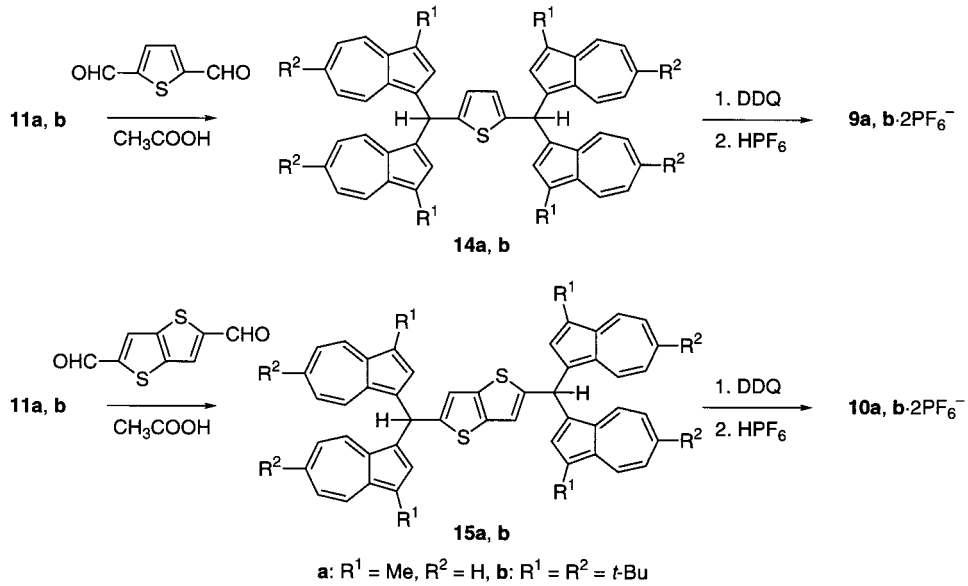
a: R^1 = Me, R^2 = H, **b**: R^1 = R^2 = *t*-Bu

dichloromethane afforded the corresponding dications **9a**,**b** and **10b**. After exchanging the counteranion to PF_6^- by the addition of an aqueous HPF_6 solution, dications **9a**,**b** and **10b** were isolated as bis(hexafluorophosphate) in 97%, 100%, and 86% yields, respectively, as a stable dark-brown powder. The oxidative hydride abstraction of **15a** with DDQ in dichloromethane in the presence of aqueous HPF_6 solution yielded the dication **10a** in 67% yield (Scheme 2).

Spectroscopic Properties. Monocations **7a**,**b** and **8a**,**b** and dications **9a**,**b** and **10a**,**b** were fully characterized by the spectral data as shown in the Experimental Section. Mass spectra of **7a**,**b**·PF_6^-, **8a**,**b**·PF_6^-, **9a**,**b**·$2PF_6^-$, and **10a**,**b**·$2PF_6^-$ ionized by FAB showed correct $M^+ - PF_6$ and $M^+ - 2PF_6$ ion peaks, which indicated the cationic and dicationic structures of these compounds. The characteristic bands of the hexafluorophosphate were observed at 837−843 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported the cationic structure of these compounds.

In the electronic spectra **7a**,**b**, **8a**,**b**, **9a**,**b**, and **10a**,**b** showed strong absorption in the visible region in analogy with **1a**−**c**, **2a**−**c**, and **3a**−**c**. The absorption maxima (nm) and their coefficients (log ϵ) of these compounds in the visible region are summarized in Table 1 along with those of monocations **2b**,**c** and dications **5a**,**b**. UV−vis spectra of monocations **7b** and **8b** in acetonitrile along with that of monocation **2c** are shown in Figure 1.

Scheme 2



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

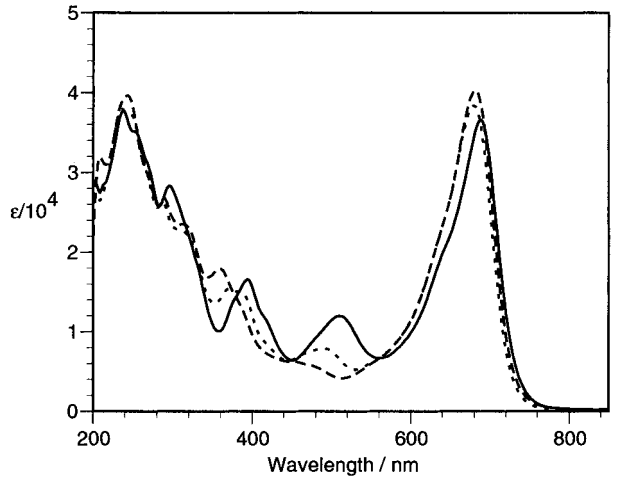


Figure 1. UV−vis spectra of monocations **7b** (solid line), **8b** (dotted line), and **2b** (broken line) in acetonitrile.

Table 1. Longest Wavelength Absorption and Their Coefficients of Monocations 7a,b, 8a,b, and 2b,c[1b] and Dications 9a,b, 10a,b, and 5a,b[3]

sample	λ_{max}, nm (log ϵ)	sample	λ_{max}, nm (log ϵ)	
7a	683 (4.51)	**9a**	602 (4.62)	724 (4.66)
7b	687 (4.56)	**9b**	594 (4.63)	729 (4.71)
8a	673 (4.58)	**10a**	631 (4.79)	713 (4.72)
8b	679 (4.59)	**10b**	618 (4.84)	718 (4.85)
2b	676 (4.53)	**5a**		681 (4.46)
2c	681 (4.61)	**5b**		703 (4.85)

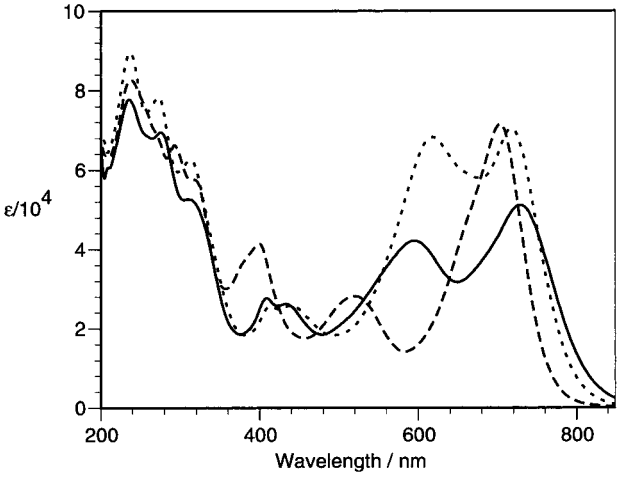


Figure 2. UV−vis spectra of dications **9b** (solid line), **10b** (dotted line), and **5b** (broken line) in acetonitrile.

Absorption maxima of **7a** and **7b** exhibited slight bathochromic shift by 6−7 nm compared with those of **2b** and **2c**. Those of **8a** and **8b** showed slight hypsochromic shift by 3 nm compared with those of **2b** and **2c**.

UV−vis spectra of dications **9b** and **10b** in acetonitrile along with that of dication **5b** are shown in Figure 2. The UV−vis spectra of dications **9a**,**b** and **10a**,**b** in the visible region were characterized by two strong absorptions at 594−631 (log ϵ 4.62−4.84) and 713−729 nm (4.66−4.85), although dications **5a** and **5b** exhibited an absorption in this region. The longest wavelength absorption of **9a**,**b** and **10a**,**b** showed an appreciable bathochromic shift by 41, 42, 40, and 39 nm, respectively, compared with those of monocations **7a**,**b** and **8a**,**b**. The bathochromic shift may be attributed to the extra positive charge at the central carbon, similar to the effect of the central carbon in dications **5a** and **5b**.

^{1}H NMR chemical shifts of the methine protons of **12a**,**b** and **13a**,**b** were slightly upfield compared with those of the corresponding di(1-azulenyl)(phenyl)-methanes.[1d] These signals disappeared on the ^{1}H NMR spectra of monocations **7a**,**b** and **8a**,**b**. Thus, the ^{1}H NMR spectra of cations **7a**,**b** and **8a**,**b** also indicate the cationic structure of these compounds. The chemical shift of cationic carbon (^{13}C NMR) for **7a**,**b** and **8a**,**b** (**7a**, 151.8; **7b**, 151.6; **8a**, 153.7; and **8b**, 153.7 ppm, respectively) showed significant upfield shift compared with those for the corresponding benzyl cations **2b** and **2c** (**2b**, 161.6 and **2c**, 161.1 ppm, respectively).

Methine signals of **14a**,**b** and **15a**,**b** also disappeared on the ^{1}H NMR spectra of dications **9a**,**b** and **10a**,**b**. Thus, the ^{1}H NMR spectra of dications **9a**,**b** and **10a**,**b** also exhibit the dicationic structure of these compounds. The chemical shift of cationic carbons for dications **9a**,**b** (**9a**, 149.3 and **9b**, 149.3 ppm) and **10b** (150.8 ppm) also showed significant upfield shift compared with those for the corresponding dications **5a** and **5b** (**5a**, 159.0 and **5b**, 158.6 ppm, respectively) and were comparable with those of the corresponding monocations **7a**,**b** and **8b**. The relatively low solubility of dication **10a** did not allow determination of the ^{13}C chemical shift of its cationic carbons.

Thermodynamic Stability. As a measure of the thermodynamic stability, the pK_R^+ values of monocations **7a**,**b** and **8a**,**b** and dications **9a**,**b** and **10a**,**b** were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous acetonitrile as described in the Experimental Section.[1d,8] The pK_R^+ scales stand for the carbocation in aqueous solution. The K_R^+ scale is defined by the equilibrium constant for the reaction of a carbocation with a water molecule (K_R^+ = [ROH][H_3O^+]/[R^+]). Thus, the pK_R^+ = −log K_R^+. Therefore, the larger pK_R^+ index indicates a smaller K_R^+ value and, in turn, a higher stability of the carbocation.

The values of **7a**,**b**, **8a**,**b**, **9a**,**b**, and **10a**,**b** are summarized in Table 2 along with those of **2b**,**c** and **5a**,**b**. In contrast to the stabilizing ability of the thienyl substituent, the values of monocations **7a**,**b** and **8a**,**b** are comparable with those of the analogous benzyl cations **2b** and **2c**. *tert*-Butyl substituents on the azulene rings at the 3,3′,6,6′-positions slightly stabilized these methyl cations by their steric and also by their inductive electronic effects induced by C−C hyperconjugation. The pK_R^+ values of the *tert*-butyl derivatives **7b** and **8b** are higher by 0.6−1.0 pK units than those of **7a** and **8a**.

Similarly to the neutralization of dications **5a** and **5b**, two cation units in dications **9a**,**b** and **10b** were neutralized via one step at the pH of 11.1−11.7 ± 0.1, which corresponds to the average of the pK_R^+ values of dications and half-neutralized monocations. Low solubility of dication **10a** under the conditions did not allow determination of the pK_R^+ value. The pK_R^+ values of dications **9a**,**b** and **10b** are almost as large as those of monocations **7a**,**b** and **8a**,**b** and dications **5a**,**b**. In the case of dications, *tert*-butyl substituents on the azulene rings also slightly increased the pK_R^+ values. Dications **9a**,**b** and **10b** exhibited high thermodynamic stability like those of the

(8) (a) Kerber R. C.; Hsu, H. M. *J. Am. Chem. Soc.* **1973**, *95*, 3239. (b) Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470.

Table 2. pK_R^+ Values[a] and Redox Potentials[b] of Monocations 7a,b, 8a,b, and 2b,c and Dications 9a,b, 10a,b, and 5a,b

sample	pK_R^+ [c]	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}
7a	11.2 ± 0.1 (72%)	−0.64	(−1.55)	(+0.92)	(+1.51)
7b	11.8 ± 0.1 (29%)	−0.74	(−1.64)	+0.91	(+1.37)
8a	11.4 ± 0.1 (73%)	−0.72	(−1.59)	(+0.90)	(+1.66)
8b	12.4 ± 0.1 (50%)	−0.80	(−1.66)	+0.88	(+1.35)
2b[e]	10.8	−0.70	(−1.57)	(+0.90)	(+1.79)
2c[e]	12.4	−0.78	(−1.64)	+0.88	(+1.38)
9a	11.1 ± 0.1 (27%)	−0.22	(−1.80)	(+0.98)	(+1.56)
9b	11.7 ± 0.1 (25%)	−0.30	(−1.92)	+0.98	(+1.42)
10a[d]		−0.36	(−1.84)	(+0.87)	(+1.00)
10b	11.7 ± 0.1 (21%)	(−0.43)	(−1.94)	+0.89	(+1.28)
5a[f]	11.2	(−0.47)	(−1.84)	(+0.90)	(+1.87)
5b[f]	12.1	(−0.55)	(−2.00)	+0.87	(+1.41)

[a] The pK_R^+ values were determined 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 Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mVs^{-1}, and $F_c/F_c^+ = 0.07$ V). Irreversible processes are shown in parentheses. [c] Regenerated absorption maxima (%) of the cations in the visible region by immediate acidification of the alkaline solution with HCl are shown in parentheses. [d] The potentials were measured in DMF ($F_c/F_c^+ = 0.06$ V). [e] Data from ref 1d. [f] Data from ref 3.

corresponding monocations **7a**,**b** and **8a**,**b** and dications **5a**,**b**, although the dications were expected to show destabilization due to the through-bond electrostatic repulsion of two positively charged units.

The neutralization of monocations **7a**,**b** and **8a**,**b** and dications **9a**,**b** and **10b** is not completely reversible due to the instability of the neutralized products under the conditions of the pK_R^+ measurement, similarly to that of monocations **2b**,**c** and dications **5a**,**b**. After the measurement, acidification of the alkaline solutions of **7a**,**b**, **8a**,**b**, **9a**,**b**, and **10b** with HCl regenerated the characteristic absorption of the cations in the visible region in 21−73%.

Redox Properties. Observed redox potentials (V vs Ag/Ag^+) of monocations **7a**,**b** and **8a**,**b** and dications **9a**,**b** and **10a**,**b** are summarized in Table 2 together with those of **2b**,**c** and **5a**,**b**. Low solubility of dication **10a** did not allow measurement of the redox potentials under the same conditions.

The electrochemical reduction of **7a**,**b** and **8a**,**b** showed a reversible wave at −0.64 to −0.80 V and an irreversible wave at −1.55 to −1.66 V upon CV due to the formation of a radical and an anion species. The electrochemical oxidation of cations **7b** and **8b** showed a reversible wave at +0.88 to +0.91 V and an irreversible wave at +1.35 to +1.37 V, due to the oxidation of an azulene ring to give a dication radical and a tricationic species. The electrochemical oxidation of cations **7a** and **8a** exhibited irreversible waves at +0.90 to +0.92 V and +1.51 to +1.66 V. These redox potentials are almost equal to those of analogous benzyl cations **2b** and **2c**, comparable with the results of pK_R^+ values (Table 2).

CV of dications **9b** and **10b** in acetonitrile exhibited the voltammograms as shown in Figure 3. In contrast to the high pK_R^+ values, dications **9a**,**b** and **10a**,**b** (−0.22 to −0.43 V) exhibited less negative first reduction potentials as compared with those of monocations **7a**,**b** and **8a**,**b**. The less negative reduction potentials of dications **9a**,**b** and **10a**,**b** are attributable to the destabilization arising from the through-bond electrostatic repulsion of the two positively charged units. The first reduction wave of dications **9a**,**b** and **10a**,**b** corresponds to the reduction of two cation units by a one-step, two-electron reduction

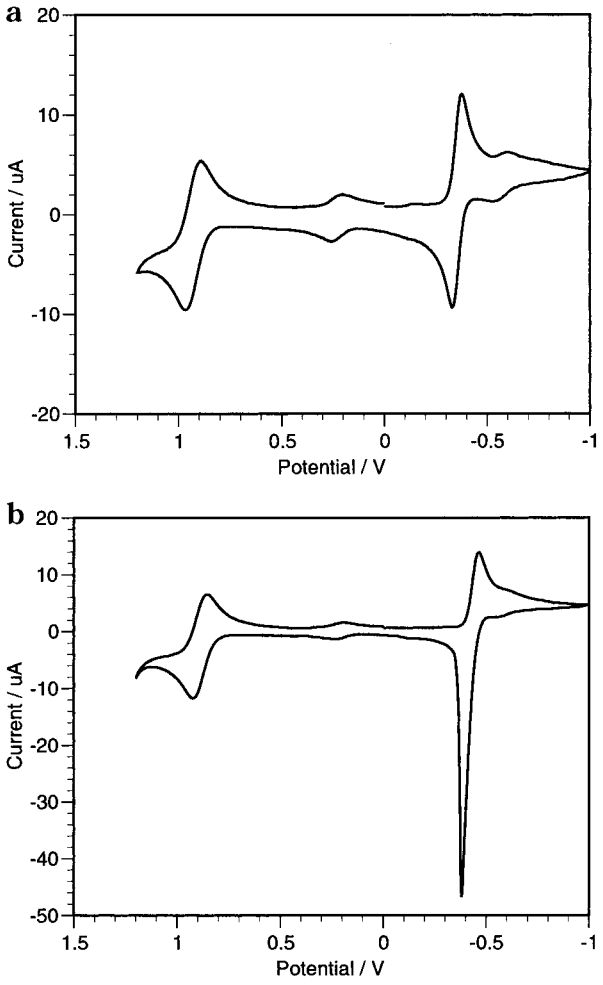


Figure 3. Cyclic voltammograms of (a) **9b** and (b) **10b** (1 mM) in MeCN containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate, 100 mV s^{-1}.

to form thienoquinoid products **18a**,**b** and **19a**,**b**. The less negative reduction potentials of dications **9a**,**b** and **10a**,**b** by 0.12−0.25 V than those of dications **5a** and **5b** exhibited the stabilization of thienoquinoid products **18a**,**b** and **19a**,**b** compared with those from dications **5a** and **5b**. The reduction of the dications also exhibited another reduction wave at −1.80 to −1.94 V.

Electrochemical oxidation of dications **9a**,**b** and **10a**,**b** exhibited a wave at +0.87 to +0.98 V upon CV. The wave was ascribed to the oxidation of two azulene rings to generate a tetracationic species, since the waves were in similar potential ranges with those of monocations **7a**,**b** and **8a**,**b** and dications **5a**,**b**. The electrochemical oxidation of dications **9a**,**b** and **10a**,**b** also showed another irreversible oxidation wave at +1.00 to +1.56 V upon CV.

Electrochromic Behavior of the Dications. Two-electron reduction of dications **9a**,**b** and **10a**,**b** was examined to clarify the formation of radical cations and a fully reduced species by UV−vis spectroscopy under the electrochemical reduction conditions. When the UV−vis spectra of **9a**,**b** and **10a**,**b** were measured under the reduction conditions in acetonitrile at room temperature, the strong absorptions of **9a**,**b** and **10a**,**b** in the visible region gradually decreased as shown in Figure 4. On slight reduction of **9a**,**b** and **10a**,**b** a band developed at 537, 544, 582, and 593 nm, respectively, together with a very broad one at around 900 nm. From the very broad band the existence of a radical cationic species in a low

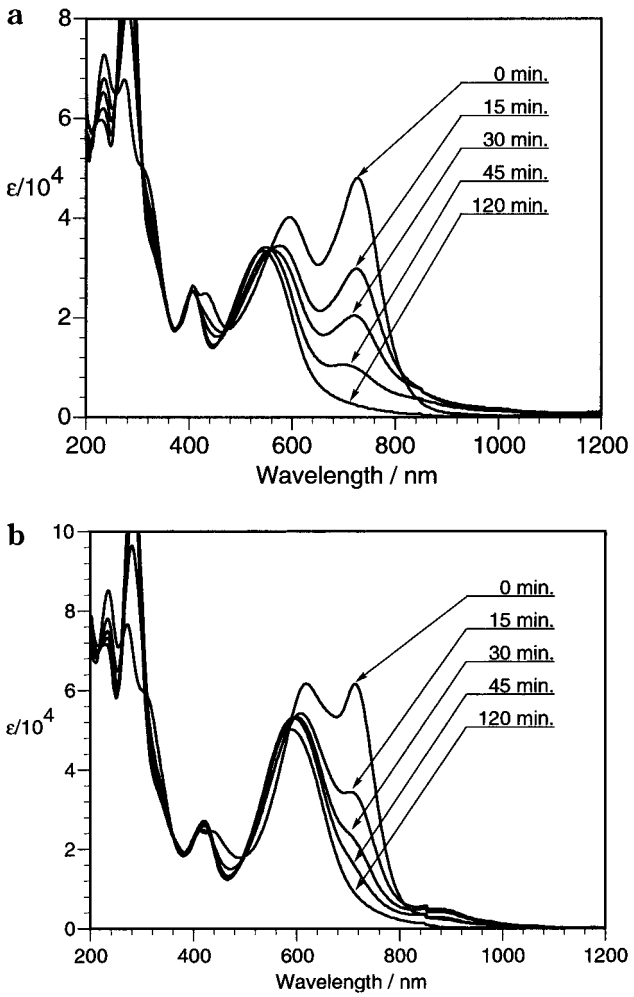
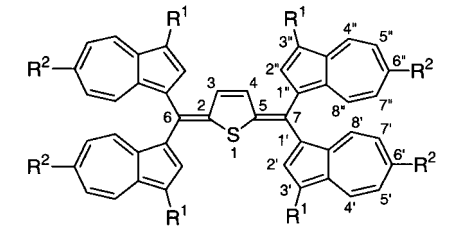


Figure 4. Change in UV−vis spectra of (a) **9b**·$2PF_6^-$ (10 mL; 1.05×10^{-5} mol dm^{-3}) and (b) **10b**·$2PF_6^-$ (10 mL; 1.06×10^{-5} mol dm^{-3}) in MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 upon constant-current electrochemical reduction (5 μA).

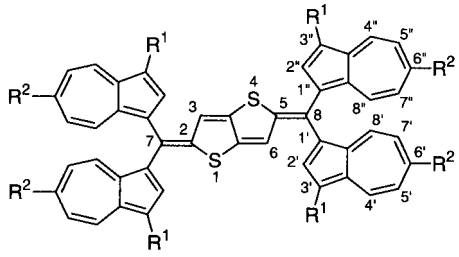
concentration during the electrochemical reduction is presumed, although the reduction upon CV suggests that the two cation units of dications are reduced in one step. On further reduction the NIR band maintained its weak strength, but it finally vanishes. This change is accompanied with an increase of the new band and the decrease of bands of dications. The color of the solution of **9a**,**b** and **10a**,**b** gradually changed to violet and blue, respectively, during the electrochemical reduction. The color change of the solutions is attributed to the formation of a thienoquinoid species under electrochemical reduction conditions. The rather well-developed isosbestic points in the UV−vis spectra suggested the formation of stable new closed-shell molecules **18a**,**b** and **19a**,**b** in solution (Chart 5). The development of new absorptions in the visible region by the electrochemical reduction is a contrastive result with that of dication **5b**, which affords only a brown solution under similar reaction conditions. Absence of the isosbestic point for the reduction of **5b** suggests the instability of the quinoid compound from the reduction of **5b** under the conditions.[3c]

Formation of the Thienoquinoid Species. In an attempt to obtain more information about the structure of the closed-shell molecules **18a**,**b** and **19a**,**b**, dications **9a**,**b** and **10a**,**b** were chemically reduced. Thus, the reaction of **9a**,**b** and **10a**,**b** with Zn powder in acetonitrile

Chart 5



18a, b



19a, b

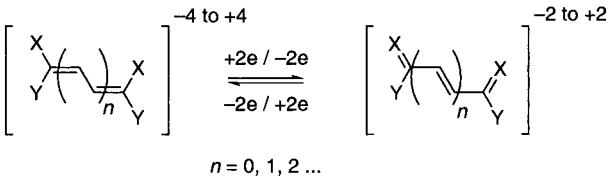
a: R^1 = Me, R^2 = H, **b**: R^1 = R^2 = *t*-Bu

under ultrasonication afforded **18a**,**b** and **19a**,**b** in 57%, 62%, 47%, and 71% yields, respectively, as brown crystals. The formation of the closed-shell molecules **18a**,**b** and **19a**,**b** is a contrastive result with the reduction of dications **5b**, which did not afford satisfactory results by similar reactions.[3c] The products **18a**,**b** and **19a**,**b** showed violet and blue color in solution, respectively, and exhibited electronic absorption at the same region (λ_{max} 550−556 (log ϵ 4.44−4.56) and 596−601 nm (4.72−4.72), respectively) in CH_2Cl_2 in analogy with those of electrochemical reduction products. The compounds **18a**,**b** and **19a**,**b** were relatively unstable in solution, but could be fully characterized by the spectral data as shown in the Experimental Section.

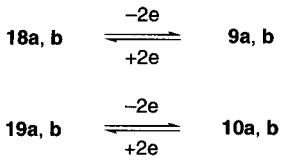
Mass spectra of **18a**,**b** and **19a**,**b** showed correct M^+ ion signals. The characteristic bands of the hexafluorophosphate of dications **9a**,**b** and **10a**,**b** disappeared in their IR spectra, which are consistent with the structure of these compounds. Compounds **18a**,**b** and **19a**,**b** showed significant signal broadening in $CDCl_3$ upon ^1H NMR. The signal broadening in $CDCl_3$ is probably due to equilibrium with the protonated species of **18a**,**b** and **19a**,**b**. However, **18a**,**b** and **19a**,**b** exhibited well-resolved signals in C_6D_6. ^1H NMR spectra of **18a**,**b** and **19a**,**b** in C_6D_6 at room temperature were comprised of two sets of 1-azulenyl proton signals with equal intensities. The two sets of signals in the azulene region exhibit the restricted rotation of the thiophene and thienothiophene moieties. These phenomena are attributed to the thienoquinoid structure of these compounds. The redox behavior of **18b** and **19b** was examined to confirm the reversibility of these compounds under the electrochemical conditions. Electrochemical oxidation of **18b** and **19b** showed a one-step, two-electron wave at −0.35 and −0.41 V, respectively, upon CV due to the regeneration of dications **9b** and **10b**. The redox behaior of **18b** and **19b** fairly corresponded with those of dications **9b** and **10b**.

Recently, Hünig et al. have proposed the concept of violene/cyanine hybrids as stabilized organic electrochromics.[9] The hybrids contain the moieties X=C−Y, which represent "cyanine"-type structure in fully reduced or oxidized form, as end groups of violene. This system

Scheme 3



Scheme 4



provides highly colored closed-shell systems as cyanine dyes by an overall two-electron transfer (Scheme 3).

Dications **9a**,**b** and **10a**,**b** contain the delocalized closed-shell 1-azulenylium dye as both end groups, which could be assumed by polymethine dyes (cyanine-type structures). The redox system of the central thienoquinoid structures can be illustrated in Scheme 4. Electrochemical reduction of **9a**,**b** and **10a**,**b** produced closed-shell compounds **18a**,**b** and **19a**,**b**. As anticipated from the electrochemical behavior, the radical cations are unimportant in these cases so that the changes in absorption are mostly due to the closed-shell species throughout. Dications **9a**,**b** and **10a**,**b** showed significant changes in their absorption spectra in the different oxidation states by electrochemical reductions. Therefore, the electrochromic behavior of both dications **9a**,**b** and **10a**,**b** is assumed as that of a violene/cyanine hybrid in which the four end groups X and Y in the general structure are azulenes connected to the central thienoquinoid structure in their reduced form.

Conclusion. We have synthesized monocations **7a**,**b** and **8a**,**b** and dications **9a**,**b** and **10a**,**b** and clarified their high thermodynamic stability. The electrochemical reduction of dications **9a**,**b** and **10a**,**b** as well as chemical reduction with Zn powder in acetonitrile afforded the stable closed-shell molecules **18a**,**b** and **19a**,**b** in contrast to the reduction of dications of tetraazulenyl-*p*-xylylene **5a**,**b**. The highly electron-donating properties of **18a**,**b** and **19a**,**b** are noteworthy. These extremely stable dications **9a**,**b** and **10a**,**b** may be exploited in construction of new multistage redox systems, including their electrochromic behavior in different oxidation states.

Experimental Section

General. Melting points were determined on a micro melting point apparatus and are uncorrected. Voltammetry measurements were carried out with an electrochemical workstation equipped with Pt working and auxiliary electrodes, a reference electrode formed from $Ag/AgNO_3$ (0.01 M), and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

General Procedure for the Synthesis of 12a,**b and 13a**,**b.** A solution of azulene (**11a** or **11b**) and 2- or 3-thiophenecarbaldehyde in acetic acid (30 mL) was stirred at room temperature for 24 h. The blue solution turned into a blue suspension. The solvent was rotary evaporated, and 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. The product was further purified by recrystallization.

Bis(3-methyl-1-azulenyl)-2-thienylmethane (12a). The general procedure using **11a** (717 mg, 5.04 mmol) and 2-thiophenecarbaldehyde (283 mg, 2.52 mmol) afforded **12a** (758 mg, 79%). Green prisms; mp 198−199 °C (ethyl acetate/hexane); MS (70 eV) *m*/*z* (rel intensity) 378 (M^+, 100); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 241 (4.59), 280 (4.86), 356 (4.01), 373 (3.99), 627 (2.84); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.22 (d, J = 9.6 Hz, 2H, $H_{8'}$), 8.15 (d, J = 9.5 Hz, 2H, $H_{4'}$), 7.49 (s, 2H, $H_{2'}$), 7.43 (dd, J = 9.9, 9.8 Hz, 2H, $H_{6'}$), 7.13 (dd, J = 5.1, 1.2 Hz, 1H, H_5), 6.98 (dd, J = 9.9, 9.5 Hz, 2H, $H_{5'}$), 6.90 (dd, J = 9.9, 9.6 Hz, 2H, $H_{7'}$), 6.89 (s, 1H, CH), 6.88 (dd, J = 5.1, 3.5 Hz, 1H, H_4), 6.65 (ddd, J = 3.5, 1.2, 1.2 Hz, 1H, H_3), 2.58 (s, 6H, 3′-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 150.5 (C_2), 138.7 ($C_{2'}$), 137.3 ($C_{6'}$), 137.1 ($C_{3'a}$), 134.8 ($C_{8'a}$), 133.7 ($C_{4'}$), 132.8 ($C_{8'}$), 131.3 ($C_{1'}$), 126.4 (C_4), 125.3 (C_3), 124.7 ($C_{3'}$), 123.7 (C_5), 121.2 ($C_{7'}$), 121.0 ($C_{5'}$), 37.3 (CH), 12.7 (3′-Me). HRMS calcd for $C_{27}H_{22}S$, 378.1442; found, 378.1440. Anal. Calcd for $C_{27}H_{22}S$: C, 85.67; H, 5.86. Found: C, 85.63; H, 6.07.

Bis(3,6-di-*tert*-butyl-1-azulenyl)-2-thienylmethane (12b). The general procedure using **11b** (1.21 g, 5.03 mmol) and 2-thiophenecarbaldehyde (290 mg, 2.59 mmol) afforded **12b** (1.18 g, 82%). Blue crystals; mp 134−137 °C (hexane); MS (70 eV) *m*/*z* (rel intensity) 574 (M^+, 18); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.56), 286 (2.94), 303 (4.85), 358 (4.04), 375 (3.95), 612 (2.83); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.55 (d, J = 11.0 Hz, 2H, $H_{4'}$), 8.25 (d, J = 10.8 Hz, 2H, $H_{8'}$), 7.57 (s, 2H, $H_{2'}$), 7.16 (dd, J = 11.0, 1.8 Hz, 2H, $H_{5'}$), 7.12 (dd, J = 5.3, 1.1 Hz, 1H, H_5), 7.10 (dd, J = 10.8, 1.8 Hz, 2H, $H_{7'}$), 6.85 (dd, J = 5.3, 3.5 Hz, 1H, H_4), 6.81 (s, 1H, CH), 6.58 (ddd, J = 3.5, 1.1, 1.1 Hz, 1H, H_3), 1.51 (s, 18H, 3′-*tert*-Bu), 1.41 (s, 18H, 6′-*tert*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 160.1 ($C_{6'}$), 151.0 (C_2), 137.5 (s), 135.5 ($C_{2'}$), 134.4 ($C_{4'}$), 134.2 (s), 131.7 ($C_{8'}$), 130.0 (s), 126.0 (C_4), 125.0 (C_3), 123.4 (C_5), 119.3 ($C_{7'}$), 118.3 ($C_{5'}$), 38.1 (s, 6′-*tert*-Bu), 37.1 (CH), 33.2 (s, 3′-*tert*-Bu), 32.2 (q, 3′-*tert*-Bu), 31.8 (q, 6′-*tert*-Bu). HRMS calcd for $C_{41}H_{50}S$, 574.3633; found, 574.3627. Anal. Calcd for $C_{41}H_{50}S$: C, 85.66; H, 8.76. Found: C, 85.17; H, 8.34.

Bis(3-methyl-1-azulenyl)-3-thienylmethane (13a). The general procedure using **11a** (718 mg, 5.05 mmol) and 3-thiophenecarbaldehyde (282 mg, 2.52 mmol) afforded **13a** (766 mg, 80%). Green plates; mp 197−198 °C (ethyl acetate/hexane); MS (70 eV) *m*/*z* (rel intensity) 378 (M^+, 100); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.55), 281 (4.87), 356 (4.01), 373 (3.98), 628 (2.84); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.19 (d, J = 9.5 Hz, 2H, $H_{8'}$), 8.14 (d, J = 9.6 Hz, 2H, $H_{4'}$), 7.43 (dd, J = 9.8, 9.8 Hz, 2H, $H_{6'}$), 7.38 (s, 2H, $H_{2'}$), 7.22 (dd, J = 5.0, 3.0 Hz, 1H, H_5), 6.97 (dd, J = 9.8, 9.6 Hz, 2H, $H_{5'}$), 6.70 (dd, J = 5.0, 1.3 Hz, 1H, H_4), 6.88 (dd, J = 9.8, 9.5 Hz, 2H, $H_{7'}$), 6.69 (s, 1H, CH), 6.65 (ddd, J = 3.0, 1.3, 1.2 Hz, 1H, H_2), 2.57 (s, 6H, 3′-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 146.8 (C_3), 138.9 ($C_{2'}$), 137.3 ($C_{6'}$), 137.0 ($C_{3'a}$), 134.9 ($C_{8'a}$), 133.6 ($C_{4'}$), 132.9 ($C_{8'}$), 131.4 ($C_{1'}$), 128.7 (C_4), 125.0 (C_5), 124.6 ($C_{3'}$), 121.8 (C_2), 121.0 ($C_{7'}$), 120.8 ($C_{5'}$), 37.8 (CH), 12.7 (3′-Me). HRMS calcd for $C_{27}H_{22}S$, 378.1442; found, 378.1441. Anal. Calcd for $C_{27}H_{22}S$: C, 85.67; H, 5.86. Found: C, 85.32; H, 6.05.

Bis(3,6-di-*tert*-butyl-1-azulenyl)-3-thienylmethane (13b). The general procedure using **11b** (1.21 g, 5.03 mmol) and 3-thiophenecarbaldehyde (287 mg, 2.56 mmol) afforded **13b** (1.25 g, 86%). Blue crystals; mp 221−224 °C decomp (hexane); MS (70 eV) *m*/*z* (rel intensity) 574 (M^+, 10); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.52), 286 (4.95), 303 (4.78), 358 (4.04), 375 (3.95), 613 (2.83); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.54 (d, J = 10.8 Hz, 2H, $H_{4'}$), 8.21 (d, J = 10.8 Hz, 2H, $H_{8'}$), 7.45 (s, 2H, $H_{2'}$), 7.16 (dd, J = 5.3, 2.2 Hz, 1H, H_5), 7.14 (dd, J = 10.8, 1.8 Hz, 2H, $H_{5'}$), 7.07 (dd, J = 10.8, 1.8 Hz, 2H, $H_{7'}$), 6.86 (dd, J = 5.3, 1.1 Hz, 1H, H_4), 6.61 (s, 1H, CH), 6.59 (dd, J = 2.2, 1.1 Hz, 1H, H_2), 1.50 (s, 18H, 3′-*tert*-Bu), 1.41 (s, 18H, 6′-*tert*-

(9) (a) Hünig, S.; Kemmer, M.; Wenner, H.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Gescheid, G. *Chem.*−*Eur. J.* **1999**, *5*, 1969. (b) Hünig, S.; Kemmer, M.; Wenner, H.; Barbosa, F.; Gescheidt, G.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Peters, K. *Chem.*−*Eur. J.* **2000**, *6*, 2618. (c) Hünig, S.; Perepichka, I. F.; Kemmer, M.; Wenner, H.; Bäuerle, P.; Emge, A. *Tetrahedron* **2000**, *56*, 4203.

Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 160.0 ($C_{6'}$), 147.1 (C_3), 137.5 (s), 135.7 ($C_{2'}$), 134.3 ($C_{4'}$), 134.1 (s), 131.8 ($C_{8'}$), 130.2 (s), 128.7 (C_4), 124.5 (C_5), 121.4 (C_2), 119.0 ($C_{7'}$), 118.1 ($C_{5'}$), 38.1 (s, 6′-*tert*-Bu), 37.6 (CH), 33.2 (s, 3′-*tert*-Bu), 32.2 (q, 3′-*tert*-Bu), 31.8 (q, 6′-*tert*-Bu). HRMS calcd for $C_{41}H_{50}S$, 574.3633; found, 574.3630. Anal. Calcd for $C_{41}H_{50}S$: C, 85.66; H, 8.76. Found: C, 85.32; H, 8.72.

General Procedure for the Preparation of 7a,b·PF_6^- and 8a,b·PF_6^-. DDQ was added at room temperature to a solution of **12a**,**b** or **13a**,**b** in CH_2Cl_2 (100 mL). The blue solution turned deep blue. After the solution was stirred at the same temperature for 5 min, 60% HPF_6 (10 mL) was added to the mixture. After the solution was stirred 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, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL), then poured into ether or hexane (100 mL). The precipitated crystals were collected by filtration, washed with ether or hexane, and dried in vacuo to give **7a**,**b**·PF_6^- and **8a**,**b**·PF_6^-.

Bis(3-methyl-1-azulenyl)(2-thienyl)methylium Hexafluorophosphate (7a·PF_6^-). The general procedure using **12a** (379 mg, 1.00 mmol) and DDQ (274 mg, 1.21 mmol) gave **7a**·PF_6^- (498 mg, 95%). Dark brown powder; mp 221−222 °C (CH_2Cl_2/ether); MS (FAB) *m*/*z* 377 ($M^+ - PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 236 (4.65), 289 (4.46), 397 (4.32), 520 (4.18), 683 (4.51); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 9.7 Hz, 2H, $H_{4'}$), 8.17 (dd, *J* = 4.9, 0.8 Hz, 1H, H_5), 8.03 (dd, *J* = 9.7, 9.7 Hz, 2H, $H_{6'}$), 7.95 (dd, *J* = 9.7, 9.7 Hz, 2H, $H_{5'}$), 7.95 (s, 2H, $H_{2'}$), 7.78 (d, *J* = 9.8 Hz, 2H, $H_{8'}$), 7.52 (dd, *J* = 3.9, 0.8 Hz, 1H, H_3), 7.49 (dd, *J* = 4.9, 3.9 Hz, 1H, H_4), 7.44 (dd, *J* = 9.8, 9.7 Hz, 2H, $H_{7'}$), 2.72 (s, 6H, 3′-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 151.8 (C^+), 151.2 ($C_{3'a}$), 148.3 ($C_{8'a}$), 145.2 (C_2), 144.8 ($C_{2'}$), 143.3 ($C_{6'}$), 139.6 (C_5 and C_3), 138.6 ($C_{8'}$), 138.5 ($C_{4'}$), 135.0 ($C_{3'}$), 134.1 ($C_{5'}$), 133.8 ($C_{7'}$), 131.2 ($C_{1'}$), 130.2 (C_4), 13.0 (3′-Me). HRMS calcd for $C_{27}H_{21}S$, 377.1364; found, 377.1380. Anal. Calcd for $C_{27}H_{21}SPF_6$: C, 62.07; H, 4.05. Found: C, 62.25; H, 4.24.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(2-thienyl)methylium Hexafluorophosphate (7b·PF_6^-). The general procedure using **12b** (575 mg, 1.00 mmol) and DDQ (274 mg, 1.21 mmol) gave **7b**·PF_6^- (719 mg, 100%). Dark brown powder; mp 194−195 °C (CH_2Cl_2/hexane); MS (FAB) *m*/*z* 573 ($M^+ - PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 238 (4.58), 295 (4.45), 333 (4.24), 394 (4.22), 510 (4.08), 687 (4.56); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.05 (d, *J* = 11.0 Hz, 2H, $H_{4'}$), 8.17 (dd, *J* = 4.2, 1.9 Hz, 1H, H_5), 8.14 (dd, *J* = 11.0, 1.8 Hz, 2H, $H_{5'}$), 7.86 (d, *J* = 10.8 Hz, 2H, $H_{8'}$), 7.73 (s, 2H, $H_{2'}$), 7.63 (dd, *J* = 10.8, 1.8 Hz, 2H, $H_{7'}$), 7.51−7.49 (m, 2H, $H_{3,4}$), 1.60 (s, 18H, 3′-*tert*-Bu), 1.45 (s, 18H, 6′-*tert*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.9 ($C_{6'}$), 151.6 (C^+), 148.6 ($C_{3'a}$), 148.0 ($C_{8'a}$), 147.0 ($C_{3'}$), 144.6 (C_2), 142.2 ($C_{2'}$), 139.3 ($C_{4'}$), 139.1 (C_5), 138.8 (C_3), 138.1 ($C_{8'}$), 131.8 ($C_{5'}$), 131.3 ($C_{7'}$), 130.7 ($C_{1'}$), 130.2 (C_4), 39.4 (s, 6′-*tert*-Bu), 33.3 (s, 3′-*tert*-Bu), 31.5 (q, 6′-*tert*-Bu), 31.2 (q, 3′-*tert*-Bu). HRMS calcd for $C_{41}H_{49}S$, 573.3555; found, 573.3536. Anal. Calcd for $C_{41}H_{49}SPF_6 \cdot {}^1/_2H_2O$: C, 67.66; H, 6.92. Found: C, 67.79; H, 6.55.

Bis(3-methyl-1-azulenyl)(3-thienyl)methylium Hexafluorophosphate (8a·PF_6^-). The general procedure using **13a** (378 mg, 1.00 mmol) and DDQ (273 mg, 1.20 mmol) gave **8a**·PF_6^- (494 mg, 95%). Dark brown powder; mp 214−215 °C (CH_2Cl_2/ether); MS (FAB) *m*/*z* 377 ($M^+ - PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 234 (4.66), 283 (4.45), 374 (4.26), 500 (3.99), 673 (4.58); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 9.4 Hz, 2H, $H_{4'}$), 8.04 (dd, *J* = 9.2, 9.2 Hz, 2H, $H_{6'}$), 7.97 (dd, *J* = 9.4, 9.2 Hz, 2H, $H_{5'}$), 7.85 (d, *J* = 9.0 Hz, 2H, $H_{8'}$), 7.82 (s, 2H, $H_{2'}$), 7.66 (br s, 1H, H_2), 7.63 (d, *J* = 3.4 Hz, 1H, H_5), 7.49 (dd, *J* = 9.2, 9.0 Hz, 2H, $H_{7'}$), 7.19 (d, *J* = 3.4 Hz, 1H, H_4), 2.71 (s, 6H, 3′-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 153.7 (C^+), 151.3 ($C_{3'a}$), 148.2 ($C_{8'a}$), 145.1 ($C_{2'}$), 143.8 (C_3), 143.3 ($C_{6'}$), 138.8 ($C_{8'}$), 138.4 ($C_{4'}$), 137.8 (C_2), 135.1 ($C_{3'}$), 134.2 ($C_{5'}$), 134.0 ($C_{7'}$), 132.1 (C_4), 131.5 ($C_{1'}$), 127.6 (C_5), 12.9 (3′-Me). HRMS calcd for $C_{27}H_{21}S$, 377.1364; found, 377.1354. Anal. Calcd for $C_{27}H_{21}SPF_6$: C, 62.07; H, 4.05. Found: C, 62.28; H, 4.30.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(3-thienyl)methylium Hexafluorophosphate (8b·PF_6^-). The general procedure using **13b** (575 mg, 1.00 mmol) and DDQ (272 mg, 1.20 mmol) gave **8b**·PF_6^- (719 mg, 100%). Dark brown powder; mp 184−186 °C (CH_2Cl_2/hexane); MS (FAB) *m*/*z* 573 ($M^+ - PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 236 (4.58), 287 (4.42), 371 (4.19), 490 (3.90), 679 (4.59); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.04 (d, *J* = 11.0 Hz, 2H, $H_{4'}$), 8.14 (dd, *J* = 11.0, 1.8 Hz, 2H, $H_{5'}$), 7.90 (d, *J* = 10.7 Hz, 2H, $H_{8'}$), 7.68−7.65 (m, 6H, $H_{2,5,2',7'}$), 7.21 (d, *J* = 4.6 Hz, 1H, H_4), 1.60 (s, 18H, 3′-*tert*-Bu), 1.47 (s, 18H, 6′-*tert*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.0 ($C_{6'}$), 153.7 (C^+), 148.8 ($C_{3'a}$), 148.2 ($C_{8'a}$), 147.2 ($C_{3'}$), 143.6 (C_3), 142.4 ($C_{2'}$), 139.2 ($C_{4'}$), 138.4 ($C_{8'}$), 136.6 (C_2), 132.0 ($C_{5'}$), 131.8 (C_4), 131.6 ($C_{7'}$), 131.3 ($C_{1'}$), 127.8 (C_5), 39.4 (s, 6′-*tert*-Bu), 33.3 (s, 3′-*tert*-Bu), 31.5 (q, 6′-*tert*-Bu), 31.2 (q, 3′-*tert*-Bu). HRMS calcd for $C_{41}H_{49}S$, 573.3555; found, 573.3538. Anal. Calcd for $C_{41}H_{49}SPF_6$: C, 68.50; H, 6.87. Found: C, 68.45; H, 6.81.

2,5-Bis[bis(3-methyl-1-azulenyl)methyl]thiophene (14a). The same procedure as for the preparation of **12a** was adopted here. The condensation reaction of **11a** (719 mg, 5.06 mmol) with 2,5-thiophenedicarbaldehyde (178 mg, 1.27 mmol) in acetic acid (30 mL) for 2 d and the column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded **14a** (484 mg, 57%) and 5-[bis(3-methyl-1-azulenyl)methyl]-2-thiophenecarbaldehyde (**16a**) (167 mg, 32%).

14a. Green needles; mp 173−175 °C decomp (toluene/hexane); MS (FAB) *m*/*z* 672 (M^+); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.81), 283 (5.14), 373 (4.25), 628 (3.11); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 9.5 Hz, 4H, $H_{8'}$), 8.12 (d, *J* = 9.5 Hz, 4H, $H_{4'}$), 7.49 (s, 4H, $H_{2'}$), 7.43 (dd, *J* = 9.8, 9.8 Hz, 4H, $H_{6'}$), 6.96 (dd, *J* = 9.8, 9.5 Hz, 4H, $H_{5'}$), 6.89 (dd, *J* = 9.8, 9.5 Hz, 4H, $H_{7'}$), 6.77 (s, 2H, CH), 6.38 (s, 2H, $H_{3,4}$), 2.56 (s, 12H, 3′-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.4 ($C_{2,5}$), 138.9 ($C_{2'}$), 137.2 ($C_{3'a}$ and $C_{6'}$), 134.7 ($C_{8'a}$), 133.6 ($C_{4'}$), 132.9 ($C_{8'}$), 131.4 ($C_{1'}$), 124.6 ($C_{3,4}$ and $C_{3'}$), 121.1 ($C_{7'}$), 120.9 ($C_{5'}$), 37.7 (CH), 12.7 (3′-Me). HRMS calcd for $C_{50}H_{40}S$, 672.2850; found, 672.2839. Anal. Calcd for $C_{50}H_{40}S \cdot {}^3/_2H_2O$: C, 85.80; H, 6.19. Found: C, 86.15; H, 5.81.

16a. Green crystals; mp 169−170 °C (ethyl acetate/hexane); MS (70 eV) *m*/*z* (rel intensity) 406 (M^+, 100); IR (KBr disk) ν_{max} 1661 (s, C=O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.55), 294 (4.89), 356 (4.08), 373 (4.07), 624 (2.87); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 9.76 (s, 1H, 5-CHO), 8.18 (d, *J* = 9.2 Hz, 2H, $H_{8'}$), 8.16 (d, *J* = 8.8 Hz, 2H, $H_{4'}$), 7.55 (d, *J* = 3.7 Hz, 1H, H_4), 7.46 (dd, *J* = 9.7, 9.7 Hz, 2H, $H_{6'}$), 7.46 (s, 2H, $H_{2'}$), 7.01 (dd, *J* = 9.7, 8.8 Hz, 2H, $H_{5'}$), 6.90 (dd, *J* = 9.7, 9.2 Hz, 2H, $H_{7'}$), 6.90 (d, *J* = 0.9 Hz, 1H, CH), 6.81 (dd, *J* = 3.7, 0.9 Hz, 1H, H_3), 2.57 (s, 6H, 3′-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 182.6 (5-CHO), 162.5 (s), 141.8 (s), 138.2 ($C_{2'}$), 137.5 ($C_{6'}$), 137.2 (s), 136.4 (C_4), 134.8 (s), 133.9 ($C_{4'}$), 132.5 ($C_{8'}$), 129.4 (s), 126.6 (C_3), 124.8 (s), 121.4 ($C_{7'}$), 121.3 ($C_{5'}$), 38.3 (CH), 12.7 (3′-Me). HRMS calcd for $C_{28}H_{22}SO$, 406.1391; found, 406.1391. Anal. Calcd for $C_{28}H_{22}SO$: C, 82.72; H, 5.45. Found: C, 82.35; H, 5.53.

2,5-Bis[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]thiophene (14b). The same procedure as for the preparation of **12a** was adopted here. The condensation reaction of **11b** (1.21 g, 5.03 mmol) with 2,5-thiophenedicarbaldehyde (177 mg, 1.26 mmol) in acetic acid (30 mL) for 2 d and column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded **14b** (673 mg, 50%) and 5-[bis(3,6-di-*tert*-butyl-1-azulenyl)-methyl]-2-thiophenecarbaldehyde (**16b**) (73 mg, 9.6%).

14b. Blue crystals; mp 200−205 °C decomp (hexane/EtOH); MS (FAB) *m*/*z* 1065 (M^+); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 244 (4.82), 288 (5.23), 359 (4.36), 375 (4.25), 612 (3.13); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 10.5 Hz, 4H, $H_{4'}$), 8.22 (d, *J* = 10.5 Hz, 4H, $H_{8'}$), 7.56 (s, 4H, $H_{2'}$), 7.12 (dd, *J* = 10.5, 1.8 Hz, 4H, $H_{5'}$), 7.07 (dd, *J* = 10.5, 1.8 Hz, 4H, $H_{7'}$), 6.70 (s, 2H, CH), 6.28 (s, 2H, $H_{3,4}$), 1.49 (s, 36H, 3′-*tert*-Bu), 1.40 (s, 36H, 6′-*tert*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1 ($C_{6'}$), 148.6 ($C_{2,5}$), 137.6 ($C_{3'}$), 135.8 ($C_{2'}$), 134.4 ($C_{4'}$), 134.3 ($C_{8'a}$), 134.2 ($C_{3'a}$), 131.8 ($C_{8'}$), 130.4 ($C_{1'}$), 124.4 ($C_{3,4}$), 119.2 ($C_{7'}$), 118.2 ($C_{5'}$), 38.1 (s, 6′-*tert*-Bu), 37.3 (CH), 33.2 (s, 3′-*tert*-Bu), 32.2 (q, 3′-*tert*-Bu), 31.8 (q, 6′-*tert*-Bu). HRMS calcd for $C_{78}H_{96}S$, 1064.7233; found, 1064.7280. Anal. Calcd for $C_{78}H_{96}S$: C, 87.91; H, 9.08. Found: C, 87.47; H, 9.18.

16b. Blue crystals; mp 146−149 °C (hexane); MS (70 eV) *m*/*z* (rel intensity) 602 (M^+, 100); IR (KBr disk) ν_{max} 1669 (s, C=O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 244 (4.52), 303 (4.96), 356 (4.12), 375 (4.04), 607 (2.86); ^1H NMR (90 MHz, $CDCl_3$) δ = 9.77 (s, 1H, 5-CHO), 8.58 (d, J = 10.8 Hz, 2H, $H_{4'}$), 8.21 (d, J = 10.8 Hz, 2H, $H_{8'}$), 7.56 (d, J = 4.0 Hz, 1H, H_4), 7.53 (s, 2H, $H_{2'}$), 7.21 (dd, J = 10.8, 1.8 Hz, 2H, $H_{5'}$), 7.14 (dd, J = 10.8, 1.8 Hz, 2H, $H_{7'}$), 6.84 (s, 1H, CH), 6.79 (d, J = 4.0 Hz, 1H, H_3), 1.52 (s, 18H, 3′-*tert*-Bu), 1.42 (s, 18H, 6′-*tert*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 182.8 (5-CHO), 163.7 (s), 160.8 (s), 141.7 (s), 137.9 (s), 136.6 (C_4), 135.2 ($C_{2'}$), 134.9 ($C_{4'}$), 134.5 (s), 134.4 (s), 131.7 ($C_{8'}$), 128.4 (s), 126.6 (C_3), 119.8 ($C_{7'}$), 118.9 ($C_{5'}$), 38.3 (s, 6′-*tert*-Bu), 38.2 (CH), 33.3 (s, 3′-*tert*-Bu), 32.3 (q, 3′-*tert*-Bu), 31.9 (q, 6′-*tert*-Bu). HRMS calcd for $C_{42}H_{50}SO$, 602.3582; found, 602.3600. Anal. Calcd for $C_{42}H_{50}SO$: C, 83.67; H, 8.36. Found: C, 83.22; H, 8.26.

2,5-Bis[bis(3-methyl-1-azulenyl)methyl]thieno[3,2-*b*]thiophene (15a). A solution of **11a** (712 mg, 5.01 mmol) and 2,5-thieno[3,2-*b*]thiophenedicarbaldehyde (247 mg, 1.26 mmol) in acetic acid (15 mL) and CH_2Cl_2 (15 mL) was stirred at room temperature for 24 h. The precipitated green crystals were separated by filtration, washed with CH_2Cl_2, and dried in vacuo to give **15a** (467 mg, 79%). The filtrate was worked up and following column chromatography on silica gel with CH_2Cl_2 afforded 5-[bis(3-methyl-1-azulenyl)methyl]-2-thieno[3,2-*b*]thiophenecarbaldehyde (**17a**) (201 mg, 35%) and then recovered **11a** (252 mg, 35%).

15a. Green crystals; mp 260−263 °C; MS (FAB) *m*/*z* 728 (M^+); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.79), 287 (5.14), 356 (4.37), 373 (4.30), 625 (3.13); ^1H NMR (600 MHz, $CDCl_3$) δ = 8.24 (d, J = 9.5 Hz, 4H, $H_{8'}$), 8.16 (d, J = 9.5 Hz, 4H, $H_{4'}$), 7.53 (s, 4H, $H_{2'}$), 7.46 (dd, J = 9.8, 9.8 Hz, 4H, $H_{6'}$), 7.00 (dd, J = 9.8, 9.5 Hz, 4H, $H_{5'}$), 6.92 (dd, J = 9.8, 9.5 Hz, 4H, $H_{7'}$), 6.88 (s, 2H, CH), 6.63 (d, J = 0.9 Hz, 2H, $H_{3,6}$), 2.58 (s, 12H, 3′-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 151.2 ($C_{2,5}$), 138.8 ($C_{2'}$), 137.4 ($C_{6'}$), 137.2 ($C_{3a,6a}$ and $C_{3'a}$), 134.8 ($C_{8'a}$), 133.8 ($C_{4'}$), 132.8 ($C_{8'}$), 130.7 ($C_{1'}$), 124.7 ($C_{3'}$), 121.3 ($C_{7'}$), 121.1 ($C_{5'}$), 118.0 ($C_{3,6}$), 38.3 (CH), 12.7 (3′-Me). HRMS calcd for $C_{52}H_{40}S_2$, 728.2571; found, 728.2592. Anal. Calcd for $C_{52}H_{40}S_2 \cdot 2H_2O$: C, 81.64; H, 5.80. Found: C, 81.53; H, 5.85.

17a. Green crystals; mp 192−193 °C (CH_2Cl_2/hexane); MS (70 eV) *m*/*z* (rel intensity) 464 (M^+, 100); IR (KBr disk) ν_{max} 1660 (s, C=O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.58), 279 (4.82), 297 (4.83), 329 (4.54), 624 (2.87); ^1H NMR (600 MHz, $CDCl_3$) δ = 9.88 (s, 1H, 5-CHO), 8.24 (d, J = 9.5 Hz, 2H, $H_{8'}$), 8.20 (d, J = 9.4 Hz, 2H, $H_{4'}$), 7.77 (d, J = 0.6 Hz, 1H, H_6), 7.52 (s, 2H, $H_{2'}$), 7.49 (dd, J = 9.9, 9.9 Hz, 2H, $H_{6'}$), 7.05 (dd, J = 9.9, 9.4 Hz, 2H, $H_{5'}$), 6.96 (dd, J = 9.9, 9.5 Hz, 2H, $H_{7'}$), 6.95 (s, 1H, CH), 6.86 (dd, J = 1.1, 0.6 Hz, 1H, H_3), 2.60 (s, 6H, 3′-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 183.2 (5-CHO), 161.1 (C_2), 145.7 (C_{3a}), 143.8 (C_5), 138.5 ($C_{2'}$), 138.2 (C_{6a}), 137.7 ($C_{6'}$), 137.3 ($C_{3'a}$), 134.9 ($C_{8'a}$), 134.1 ($C_{4'}$), 132.7 ($C_{8'}$), 129.5 (C_6 and $C_{1'}$), 124.9 ($C_{3'}$), 121.6 ($C_{7'}$), 121.5 ($C_{5'}$), 118.5 (C_3), 38.9 (CH), 12.7 (3′-Me). HRMS calcd for $C_{30}H_{22}S_2O$, 462.1112; found, 462.1124. Anal. Calcd for $C_{30}H_{22}S_2O \cdot {}^1/_2H_2O$: C, 76.40; H, 4.92. Found: C, 76.44; H, 5.07.

2,5-Bis[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]thieno[3,2-*b*]thiophene (15b). The same procedure as for the preparation of **12a** was adopted here. The condensation reaction of **11b** (1.24 g, 5.16 mmol) with 2,5-thieno[3,2-*b*]-thiophenedicarbaldehyde (249 mg, 1.27 mmol) in acetic acid (15 mL) and CH_2Cl_2 (15 mL) for 24 h and the column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded **15b** (1.03 g, 71%) and 5-[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]-2-thieno[3,2-*b*]thiophenecarbaldehyde (**17b**) (164 mg, 9.7%).

15b. Blue crystals; mp 228−230 °C decomp (hexane); MS (FAB) *m*/*z* 1120 (M^+); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 244 (4.81), 291 (5.20), 304 (5.19), 359 (4.41), 375 (4.28), 608 (3.14); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.53 (d, J = 10.5 Hz, 4H, $H_{4'}$), 8.26 (d, J = 10.5 Hz, 4H, $H_{8'}$), 7.61 (s, 4H, $H_{2'}$), 7.16 (dd, J = 10.5, 1.8 Hz, 4H, $H_{5'}$), 7.10 (dd, J = 10.5, 1.8 Hz, 4H, $H_{7'}$), 6.82 (s, 2H, CH), 6.53 (s, 2H, $H_{3,6}$), 1.49 (s, 36H, 3′-*tert*-Bu), 1.40 (s, 36H, 6′-*tert*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4 ($C_{6'}$), 151.6 ($C_{2,5}$), 137.8 ($C_{3'}$), 137.1 ($C_{3a,6a}$), 135.7 ($C_{2'}$), 134.6 ($C_{4'}$), 134.4 ($C_{8'a}$), 134.3 ($C_{3'a}$), 131.8 ($C_{8'}$), 129.6 ($C_{1'}$), 119.5 ($C_{7'}$), 118.5 ($C_{5'}$), 118.0 ($C_{3,6}$), 38.2 (s, 6′-*tert*-Bu), 38.1 (CH), 33.2 (s, 3′-*tert*-Bu), 32.2 (q, 3′-*tert*-Bu), 31.8 (q, 6′-*tert*-Bu). Anal. Calcd for $C_{80}H_{96}S_2$: C, 85.66; H, 8.62. Found: C, 85.47; H, 8.40.

17b. Green crystals; mp 211−213 °C decomp (CH_2Cl_2/hexane/EtOH); MS (70 eV) *m*/*z* (rel intensity) 658 (M^+, 91); IR (KBr disk) ν_{max} 1669 (s, C=O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.54), 285 (4.88), 305 (4.91), 606 (2.85); ^1H NMR (90 MHz, $CDCl_3$) δ = 9.87 (s, 2H, 5-CHO), 8.59 (d, J = 10.8 Hz, 2H, $H_{4'}$), 8.26 (d, J = 10.8 Hz, 2H, $H_{8'}$), 7.77 (s, 1H, H_6), 7.59 (s, 2H, $H_{2'}$), 7.22 (dd, J = 10.8, 1.8 Hz, 2H, $H_{5'}$), 7.15 (dd, J = 10.8, 1.8 Hz, 2H, $H_{7'}$), 6.88 (s, 1H, CH), 6.78 (s, 1H, H_3), 1.52 (s, 18H, 3′-*tert*-Bu), 1.42 (s, 18H, 6′-*tert*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 183.0 (5-CHO), 161.8 (s), 160.8 (s), 145.6 (s), 143.5 (s), 138.2 (s), 137.9 (s), 135.4 ($C_{2'}$), 134.9 ($C_{4'}$), 134.5 (s), 134.4 (s), 131.7 ($C_{8'}$), 129.4 (C_6), 128.3 (s), 119.8 ($C_{7'}$), 118.9 ($C_{5'}$), 118.3 (C_3), 38.8 (CH), 38.3 (s, 6′-*tert*-Bu), 33.3 (s, 3′-*tert*-Bu), 32.3 (q, 3′-*tert*-Bu), 31.9 (q, 6′-*tert*-Bu). HRMS calcd for $C_{44}H_{50}S_2O$, 658.3303; found, 658.3304. Anal. Calcd for $C_{44}H_{50}S_2O$: C, 80.19; H, 7.65. Found: C, 79.79; H, 7.94.

2,5-Thiophenediylbis[bis(3-methyl-1-azulenyl)methylium] Bis(hexafluorophosphate) (9a·2PF$_6^-$). The same procedure as for the preparation of **7a**·2PF_6^- was adopted here. The hydride abstraction reaction of **14a** (338 mg, 0.502 mmol) with DDQ (272 mg, 1.20 mmol) gave **9a**·2PF_6^- (469 mg, 97%). Dark brown powder; mp 217−219 °C (CH_2Cl_2/ether); MS (FAB) *m*/*z* 815 ($M^+ - PF_6$), 670 ($M^+ - 2PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 253 (4.91), 413 (4.48), 602 (4.62), 724 (4.66); ^1H NMR (600 MHz, MeCN-d_3, 50 °C) δ = 8.83 (d, J = 9.8 Hz, 4H, $H_{4'}$), 8.19 (dd, J = 9.8, 9.6 Hz, 4H, $H_{6'}$), 8.19 (s, 4H, $H_{2'}$), 8.08 (dd, J = 9.8, 9.6 Hz, 4H, $H_{5'}$), 8.08 (d, J = 9.7 Hz, 4H, $H_{8'}$), 7.91 (s, 2H, $H_{3,4}$), 7.64 (dd, J = 9.8, 9.7 Hz, 4H, $H_{7'}$), 2.77 (s, 12H, 3′-Me); ^{13}C NMR (150 MHz, MeCN-d_3, 50 °C) δ = 155.8 ($C_{2,5}$), 152.2 ($C_{3'a}$), 149.3 (C^+), 148.9 ($C_{8'a}$), 144.8 ($C_{2'}$), 143.8 ($C_{6'}$), 139.9 ($C_{3,4}$), 139.4 ($C_{8'}$), 138.9 ($C_{4'}$), 136.3 ($C_{3'}$), 135.0 ($C_{5'}$), 134.8 ($C_{7'}$), 132.3 ($C_{1'}$), 12.2 (3′-Me). Anal. Calcd for $C_{50}H_{38}SP_2F_{12} \cdot {}^1/_2H_2O$: C, 61.92; H, 4.05. Found: C, 61.99; H, 4.08.

2,5-Thiophenediylbis[bis(3,6-di-*tert*-butyl-1-azulenyl)-methylium] Bis(hexafluorophosphate) (9b·2PF$_6^-$). The same procedure as for the preparation of **7a**·2PF_6^- was adopted here. The hydride abstraction reaction of **14b** (533 mg, 0.500 mmol) with DDQ (272 mg, 1.20 mmol) gave **9b**·2PF_6^- (677 mg, 100%). Dark brown powder; mp 240−241 °C (CH_2Cl_2/hexane); MS (FAB) *m*/*z* 1208 ($M^+ - PF_6$), 1063 ($M^+ - 2PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 236 (4.89), 276 (4.84), 311 (4.72), 409 (4.44), 433 (4.42), 594 (4.63), 729 (4.71); ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ = 8.98 (d, J = 11.0 Hz, 4H, $H_{4'}$), 8.07 (d, J = 11.0 Hz, 4H, $H_{5'}$), 8.00 (br d, J = 9.3 Hz, 4H, $H_{8'}$), 7.89 (br s, 4H, $H_{2'}$), 7.80 (br s, 2H, $H_{3,4}$), 7.74 (br d, J = 9.3 Hz, 4H, $H_{7'}$), 1.60 (s, 36H, 3′-*tert*-Bu), 1.44 (s, 36H, 6′-*tert*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C) δ = 169.3 ($C_{6'}$), 155.4 ($C_{2,5}$), 149.3 (C^+), 149.1 ($C_{3'a}$), 148.7 ($C_{8'a}$), 147.9 ($C_{3'}$), 141.8 ($C_{2'}$), 139.7 ($C_{3,4}$), 139.2 ($C_{4'}$), 138.7 ($C_{8'}$), 132.4 ($C_{7'}$), 132.2 ($C_{5'}$), 131.7 ($C_{1'}$), 39.4 (s, 6′-*tert*-Bu), 33.4 (s, 3′-*tert*-Bu), 31.5 (q, 6′-*tert*-Bu), 31.1 (q, 3′-*tert*-Bu). HRMS calcd for $C_{78}H_{94}S$, 1062.7076; found, 1062.6970. Anal. Calcd for $C_{78}H_{94}SP_2F_{12} \cdot H_2O$: C, 68.30; H, 7.05. Found: C, 68.27; H, 6.68.

2,5-Thieno[3.2-*b*]thiophenediylbis[bis(3-methyl-1-azulenyl)methylium] Bis(hexafluorophosphate) (10a·2PF$_6^-$). DDQ (114 mg, 0.502 mmol) was added at room temperature to a mixture of **15a** (148 mg, 0.203 mmol), CH_2Cl_2 (40 mL), 60% HPF_6 (4 mL), and water (40 mL). After the mixture was stirred at room temperature for 10 min, the reaction mixture was worked up. The residue was crystallized from MeCN/ether (1:1) to give **10a**·2PF_6^- (138 mg, 67%). Dark brown powder; mp 236−238 °C decomp; MS (FAB) *m*/*z* 871 ($M^+ - PF_6$), 726 ($M^+ - 2PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 235 (4.86), 268 (4.75), 300 (4.62), 417 (4.38), 631 (4.79), 713 (4.72); ^1H NMR (600 MHz, MeCN-d_3) δ = 8.84 (dd, J = 9.8, 1.0 Hz, 4H, $H_{4'}$), 8.17 (s, 4H, $H_{2'}$), 8.16 (dd, J = 9.7, 9.7 Hz, 4H, $H_{6'}$), 8.06 (dd, J = 9.8, 9.7 Hz, 4H, $H_{5'}$), 8.03 (s, 2H, $H_{3,6}$), 7.99 (d, J = 9.8 Hz, 4H, $H_{8'}$), 7.55 (dd, J = 9.8, 9.7 Hz, 4H, $H_{7'}$), 2.79 (d, 12H, 3′-Me); ^{13}C NMR (150 MHz, MeCN-d_3) δ = 151.5 (s), 149.2 ($C_{3'a}$), 148.5 ($C_{8'a}$), 144.5 ($C_{2'}$), 143.4 ($C_{6'}$), 139.0 ($C_{8'}$), 138.7 ($C_{4'}$), 135.6 ($C_{3'}$), 134.4 ($C_{5'}$), 134.2 ($C_{7'}$), 131.9 ($C_{3,6}$), 131.8 ($C_{1'}$), 12.0 (3′-

Me). Anal. Calcd for $C_{52}H_{38}S_2P_2F_{12}\cdot 2H_2O$: C, 59.32; H, 4.02. Found: C, 58.82; H, 3.76.

2,5-Thieno[3.2-*b*]thiophenediylbis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] Bis(hexafluorophosphate) (10b·2PF$_6^-$). The same procedure as for the preparation of **7a**·2PF$_6^-$ was adopted here. The hydride abstraction reaction of **15b** (561 mg, 0.500 mmol) with DDQ (273 mg, 1.20 mmol) gave **10b**·2PF$_6^-$ (607 mg, 86%). Dark brown powder; mp 263−266 °C decomp (CH_2Cl_2/ether); MS (FAB) *m*/*z* 1263 ($M^+ - PF_6$), 1118 ($M^+ - 2PF_6$); UV−vis (MeCN) λ_{max}, nm (log ϵ) 237 (4.95), 272 (4.89), 313 (4.80), 412 (4.41), 440 (4.41), 618 (4.84), 718 (4.85); ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ = 9.00 (d, *J* = 11.0 Hz, 4H, H$_{4'}$), 8.11 (br d, *J* = 10.3 Hz, 4H, H$_{8'}$), 8.08 (dd, *J* = 11.0, 2.0 Hz, 4H, H$_{5'}$), 7.86 (s, 2H, H$_{3,6}$), 7.82 (br d, *J* = 10.3 Hz, 4H, H$_{7'}$), 7.81 (br s, 4H, H$_{2'}$), 1.61 (s, 36H, 3′-*tert*-Bu), 1.47 (s, 36H, 6′-*tert*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C) δ = 169.1 (C$_{6'}$), 150.9 (s), 150.8 (C$^+$), 149.8 (s), 148.8 (C$_{3'a}$), 148.3 (C$_{8'a}$), 147.6 (C$_{3'}$), 142.4 (C$_{2'}$), 139.1 (C$_{4'}$), 138.8 (C$_{8'}$), 132.3 (C$_{7'}$), 131.8 (C$_{5'}$), 131.5 (C$_{1'}$), 131.3 (C$_{3,6}$), 39.5 (s, 6′-*tert*-Bu), 33.4 (s, 3′-*tert*-Bu), 31.6 (q, 6′-*tert*-Bu), 31.2 (q, 3′-*tert*-Bu). Anal. Calcd for $C_{80}H_{94}S_2P_2F_{12}$: C, 66.16; H, 6.72. Found: C, 67.81; H, 6.39.

pK_R^+ Value. A sample solution of **7a**,**b**·PF$_6^-$, **8a**,**b**·PF$_6^-$, **9a**,**b**·2PF$_6^-$, and **10b**·2PF$_6^-$ was prepared by dissolving the compounds in a glycine (0.1 M) solution (50 mL) and made up to 100 mL by adding MeCN, and the sample solution with lower acidity was made by further alkalification with 20% aqueous NaOH. The pH of each sample was made on a pH meter calibrated with standard buffers before use. The observed absorbances at the specific absorption maxima of cations **7a**,**b**, **8a**,**b**, **9a**,**b**, and **10b** were plotted against the pH, giving classical titration curves whose midpoints were taken as the pK_R^+ values.

General Procedure for the Reduction of 9a,b·2PF$_6^-$ and 10a,b·2PF$_6^-$. Zn powder was added to a solution of **9a**,**b**·2PF$_6^-$ or **10a**,**b**·2PF$_6^-$ in acetonitrile. The resulting mixture was stirred at room temperature under ultrasonication for 10 min. During the ultrasonication, the deep blue color of the mixture turned violet or blue. After an addition of CH_2Cl_2 and 5% aqueous $NaHCO_3$ solution to the mixture, the excess Zn powder was removed by filtration. The organic layer was separated, washed with 5% aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on Al_2O_3 with CH_2Cl_2 to afford **18a**,**b** and **19a**,**b**.

2,5-Bis[bis(3-mehtyl-1-azulenyl)methylene]-2,5-dihydrothiophene (18a). The general procedure using **9a**·2PF$_6^-$ (59 mg, 0.061 mmol) and Zn powder (998 mg, 15.3 mmol) in acetonitrile (50 mL) afforded **18a** (23 mg, 57%). Brown crystals; mp 208−212 °C decomp (CH_2Cl_2/hexane); MS (70 eV) *m*/*z* (rel intensity) 670 (M^+, 100); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.69), 279 (4.87), 409 (4.32), 550 (4.44); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.26 (d, *J* = 9.5 Hz, 2H, H$_{8''}$), 8.10 (s, 2H, H$_{2'}$), 8.02 (d, *J* = 9.8 Hz, 2H, H$_{8'}$), 7.87 (d, *J* = 9.3 Hz, 2H, H$_{4''}$), 7.69 (d, *J* = 9.3 Hz, 2H, H$_{4'}$), 7.68 (s, 2H, H$_{2''}$), 7.04 (dd, *J* = 10.0, 9.8 Hz, 2H, H$_{6''}$), 6.91 (dd, *J* = 9.8, 9.8 Hz, 2H, H$_{6'}$), 6.91 (s, 2H, H$_{3,4}$), 6.60 (dd, *J* = 10.0, 9.3 Hz, 2H, H$_{5''}$), 6.54 (dd, *J* = 9.8, 9.3 Hz, 2H, H$_{5'}$), 6.53 (dd, *J* = 9.8, 9.5 Hz, 2H, H$_{7''}$), 6.37 (dd, *J* = 9.8, 9.8 Hz, 2H, H$_{7'}$), 2.37 (s, 6H, 3″-Me), 2.20 (s, 6H, 3′-Me); ^{13}C NMR (100 MHz, C_6D_6) δ = 144.4 (s), 140.9 (C$_{2''}$), 140.8 (C$_{2'}$), 139.8 (s), 139.5 (s), 137.9 (d), 137.6 (d), 136.7 (s), 136.3 (d), 135.8 (s), 133.9 (d), 133.8 (C$_{3,4}$), 133.7 (d), 131.7 (s), 131.4 (s), 126.0 (C$_{3'}$), 125.7 (C$_{3''}$), 122.3 (d), 122.0 (d), 12.6 (3″-Me), 12.5 (3′-Me). Anal. Calcd for $C_{50}H_{38}S\cdot{}^1/_2H_2O$: C, 88.33; H, 5.78. Found: C, 88.41; H, 5.92.

2,5-Bis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylene]-2,5-dihydrothiophene (18b). The general procedure using **9b**·2PF$_6^-$ (207 mg, 0.153 mmol) and Zn powder (2.22 g, 33.9 mmol) in acetonitrile (100 mL) afforded **18b** (101 mg, 62%). Brown crystals; mp 208−214 °C decomp (MeOH/water); MS (FAB) *m*/*z* 1062 (M^+); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.78), 287 (5.04), 413 (4.42), 556 (4.56); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.61 (s, 2H, H$_{2'}$), 8.51 (d, *J* = 10.5 Hz, 2H, H$_{4''}$), 8.41 (d, *J* = 10.8 Hz, 2H, H$_{8''}$), 8.38 (d, *J* = 10.8 Hz, 2H, H$_{4'}$), 7.96 (d, *J* = 10.8 Hz, 2H, H$_{8'}$), 7.88 (s, 2H, H$_{2''}$), 6.96 (dd, *J* = 10.5, 1.3 Hz, 2H, H$_{5''}$), 6.87 (dd, *J* = 10.8, 1.3 Hz, 2H, H$_{7''}$), 6.84 (s, 2H, H$_{3,4}$), 6.83 (dd, *J* = 10.8, 1.4 Hz, 2H, H$_{5'}$), 6.56 (dd, *J* = 10.8, 1.4 Hz, 2H, H$_{7'}$), 1.54 (s, 18H, 3′-*tert*-Bu), 1.48 (s, 18H, 3″-*tert*-Bu), 1.19 (s, 18H, 6″-*tert*-Bu), 1.00 (s, 18H, 6′-*tert*-Bu); ^{13}C NMR (100 MHz, C_6D_6) δ = 161.1 (C$_{6''}$), 160.8 (C$_{6'}$), 144.3 (s), 138.8 (C$_{3''}$), 138.5 (C$_{3'}$), 137.8 (C$_{2'}$ and C$_{2''}$), 137.0 (s), 136.8 (s), 136.7 (s), 136.6 (s), 135.8 (C$_{8''}$), 135.6 (C$_{8'}$), 135.1 (C$_{4''}$), 134.9 (C$_{4'}$), 133.8 (C$_{3,4}$), 130.8 (C$_{1'}$), 130.7 (C$_{1''}$), 122.5 (s), 120.9 (C$_{7'}$ and C$_{7''}$), 119.9 (C$_{5'}$), 119.6 (C$_{5''}$), 38.0 (s, 6″-*tert*-Bu), 37.8 (s, 6′-*tert*-Bu), 33.5 (s, 3′-*tert*-Bu), 33.4 (s, 3″-*tert*-Bu), 32.4 (q, 3′-*tert*-Bu), 32.3 (q, 3″-*tert*-Bu), 31.7 (q, 6″-*tert*-Bu), 31.5 (q, 6′-*tert*-Bu). Anal. Calcd for $C_{78}H_{94}S\cdot H_2O$: C, 86.61; H, 8.95. Found: C, 86.40; H, 9.25.

2,5-Bis[bis(3-mehtyl-1-azulenyl)methylene]-2,5-dihydrothieno[3.2-*b*]thiophene (19a). The general procedure using **10a**·2PF$_6^-$ (52 mg, 0.051 mmol) and Zn powder (1.08 g, 16.5 mmol) in acetonitrile (50 mL) afforded **19a** (17 mg, 47%). Brown crystals; mp > 300 °C (CH_2Cl_2/hexane); MS (70 eV) *m*/*z* (rel intensity) 726 (M^+, 100); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.79), 278 (4.98), 424 (4.39), 596 (4.72); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.10 (d, *J* = 9.5 Hz, 2H, H$_{8''}$), 8.09 (d, *J* = 9.5 Hz, 2H, H$_{8'}$), 7.93 (s, 2H, H$_{2'}$), 7.85 (d, *J* = 9.5 Hz, 2H, H$_{4''}$), 7.83 (d, *J* = 9.5 Hz, 2H, H$_{4'}$), 7.64 (s, 2H, H$_{2''}$), 7.02 (dd, *J* = 10.1, 9.8 Hz, 2H, H$_{6'}$), 6.99 (dd, *J* = 10.1, 9.8 Hz, 2H, H$_{6''}$), 6.65 (dd, *J* = 10.1, 9.5 Hz, 2H, H$_{5'}$), 6.64 (dd, *J* = 10.1, 9.5 Hz, 2H, H$_{5''}$), 6.55 (s, 2H, H$_{3,6}$), 6.48 (dd, *J* = 9.8, 9.5 Hz, 2H, H$_{7'}$), 6.39 (dd, *J* = 9.8, 9.5 Hz, 2H, H$_{7''}$), 2.38 (s, 6H, 3′-Me), 2.37 (s, 6H, 3″-Me). Anal. Calcd for $C_{52}H_{38}S_2\cdot 2H_2O$: C, 81.85; H, 5.55. Found: C, 81.75; H, 5.51.

2,5-Bis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylene]-2,5-dihydrothieno[3.2-*b*]thiophene (19b). The general procedure using **10b**·2PF$_6^-$ (206 mg, 0.146 mmol) and Zn powder (2.06 g, 31.4 mmol) in acetonitrile (100 mL) afforded **19b** (113 mg, 71%). Brown crystals; mp 244−247 °C decomp (MeOH/water); MS (70 eV) *m*/*z* (rel intensity) 1118 (M^+, 100); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.83), 285 (5.07), 427 (4.46), 601 (4.72); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.50 (d, *J* = 10.5 Hz, 2H, H$_{4''}$), 8.45 (d, *J* = 10.5 Hz, 2H, H$_{4'}$), 8.36 (s, 2H, H$_{2'}$), 8.33 (d, *J* = 10.8 Hz, 2H, H$_{8''}$), 8.01 (d, *J* = 10.8 Hz, 2H, H$_{8'}$), 7.82 (s, 2H, H$_{2''}$), 6.96 (dd, *J* = 10.5, 1.9 Hz, 2H, H$_{5''}$), 6.91 (dd, *J* = 10.5, 1.9 Hz, 2H, H$_{5'}$), 6.71 (dd, *J* = 10.8, 1.9 Hz, 2H, H$_{7''}$), 6.68 (dd, *J* = 10.8, 1.9 Hz, 2H, H$_{7'}$), 6.43 (s, 2H, H$_{3,6}$), 1.56 (s, 18H, 3′-*tert*-Bu), 1.47 (s, 18H, 3″-*tert*-Bu), 1.14 (s, 18H, 6″-*tert*-Bu), 1.10 (s, 18H, 6′-*tert*-Bu); ^{13}C NMR (100 MHz, C_6D_6) δ = 161.4 (C$_{6''}$), 161.2 (C$_{6'}$), 149.7 (s) 147.2 (s), 139.0 (C$_{3''}$), 138.8 (C$_{3'}$), 138.1 (C$_{2'}$), 137.8 (C$_{2''}$), 137.3 (C$_{3'a}$), 137.1 (C$_{3''a}$), 136.7 (C$_{8'a}$), 136.5 (C$_{8''a}$), 136.0 (C$_{8'}$), 135.7 (C$_{8''}$), 135.1 (C$_{4'}$ and C$_{4''}$), 130.7 (C$_{1'}$), 130.5 (C$_{1''}$), 122.1 (s), 121.4 (C$_{7''}$), 121.1 (C$_{7'}$), 120.0 (C$_{5'}$), 119.8 (C$_{5''}$), 118.4 (C$_{3,6}$), 38.1 (s), 38.0 (s), 33.4 (s, 3′- and 3″-*tert*-Bu), 32.3 (q, 3′- and 3″-*tert*-Bu), 31.6 (q, 6′- and 6″-*tert*-Bu). Anal. Calcd for $C_{80}H_{94}S_2\cdot{}^1/_2H_2O$: C, 85.13; H, 8.48. Found: C, 85.10; H, 8.76.

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