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Synthesis, Stabilities, and Redox Behavior of Mono-, Di-, and Tetracations Composed of Di(1-azulenyl)methylium Units Connected to a Benzene Ring by Phenyl- and 2-Thienylacetylene Spacers. A Concept of a Cyanine−Cyanine Hybrid as a Stabilized Electrochromic System

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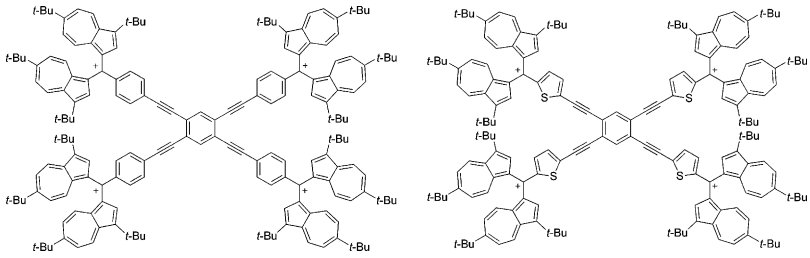

This paper describes the preparation of two tetracations **4a**$^{4+}$ and **4b**$^{4+}$ composed of di(1-azulenyl)-methylium units based on a new structural principle of a cyanine−cyanine hybrid for the design of electrochromic materials with two color changes. Di- and monocations **5a**$^{2+}$, **5b**$^{2+}$ and **6a**$^{+}$, **6b**$^{+}$ composed of di(1-azulenyl)methylium units were also prepared for the purpose of comparison. The pK_R^+ values of the tetracations are rather high despite their tetracationic structure, although the stability of these cations decreases with the increase of the number of the existing cation units. The cyclic voltammetry (CV) of these cations revealed the presumed multielectron redox properties. However, the tetracations did not exhibit the idealized electrochemical behavior, in which subsequent two-electron reduction was presumed as the cyanine−cyanine hybrid, probably due to the less effective electrochemical interaction among the positive charges. The scope of the creation of the novel polyelectrochromic materials taking the new structural principle is demonstrated by these examples.

Introduction

Electrochromism is observed in reversible redox systems, which exhibit significant color changes in different oxidation states.[1] Construction of organic molecules that contain multiple redox-active chromophores is fairly important for the preparation of novel polyelectrochromic materials, which respond to different potentials with a variety of colors.[2] Recently, Hünig et al. proposed a concept of a violene−cyanine hybrid to produce a stabilized organic electrochromic system.[3] The hybrid is constructed by the violene-type redox system containing delo-

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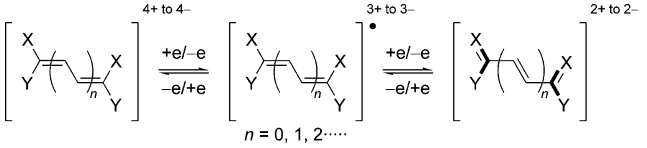
SCHEME 1. General Structure of the Violene−Cyanine Hybrid



calized closed-shell polymethine (e.g., cyanine) dyes as end groups. The hybrid is expected to provide a color of a cyanine dye by an overall two-electron transfer, as illustrated by the general structure in Scheme 1. In contrast to the violene-type redox system, both the colored and the discolored species for the hybrid consist of closed-shell systems. Thus, the persistency for the electrochromic system will be improved by the hybrid system. However, the system will not exhibit multiple color changes important for the construction of polyelectrochromic materials.

Recently, we have proposed the general structure for the construction of the system with multiple color changes, as shown in Schemes 2−4.[4] The system is consistent with the polymethine dye containing the moieties of either one or two polymethine dyes as end groups. In the case of the system illustrated in Scheme 2, the two-step redox reaction is expected by the captodative substituents effect,[5] similar to those of violene-type electrochromics. Di(1-azulenyl)(6-azulenyl)methylium hexafluorophosphates, which were recently reported by us, would exemplify such a system.[4,6]

When both end groups are replaced by the polymethine dyes, a defect of the conjugation will arise in the core cyanine unit because the core subunit is constructed by an odd number of polymethine chains (Scheme 3). The system should also represent the redox properties with color changes. However, such a defect should decrease the stability of the redox cycle. We proposed the connection of two such units by a violene chain to improve the redox stability (Scheme 4). For this reason, the system in Scheme 4 should be called a violene−cyanine−cyanine hybrid. However, we called such a system a cyanine−cyanine hybrid since the colored cyanine system is converted into another cyanine system by two-electron transfer. Both the colored species in Scheme 4 should be represented by the closed-shell systems, from which higher persistency is expected. The scope of this new structural principle is demonstrated by two examples with oxidation levels varying from +4 to 0.

Results and Discussion

Structural Principle. For the construction of the new hybrid system illustrated in Scheme 4, it is very important to select highly colored polymethine end groups with high stability. Recently, we have reported the synthesis of tri(1-azulenyl)methylium hexafluorophosphates (**1**$^+$·PF_6^-) with high thermodynamic stabilities by hydride abstraction of the corresponding hydrocarbon derivatives (Chart 1).[7] The high stability is attributed to the large π-conjugate effect of 1-azulenyl groups with cationic carbon (e.g., **1′**).

We selected di(1-azulenyl)(phenyl- and 2-thienyl)methylium units (**2**$^+$ and **3**$^+$) for the construction of the hybrid system as polymethine end groups, due to their high stability and also the existence of strong absorption in the visible region owing to the contribution of their cyanine substructure. The 2-thienyl derivative **3**$^+$ might further stabilize the presumed two-electron reduction state by the contribution of the thienoquinoid substructure instead of the quinoidal form of benzene rings.[8,9] The *tert*-butyl substituents were introduced into the azulene ring for the improvement of thermodynamic stabilities and the reversibility of both electrochemical reduction and oxidation upon CV. As the central π-electron system, we chose a benzene ring with acetylene spacers for decreasing steric hindrance between the large cationic centers. Thus, tetracations **4a**$^{4+}$ and **4b**$^{4+}$ were designed as the first examples of the cyanine−cyanine hybrid with the general structure in Scheme 4. As illustrated in Scheme 5, tetracations **4a**$^{4+}$ and **4b**$^{4+}$ (Chart 2) exemplify the redox system for the new hybrid system by the presumed two-electron transfer.

In order to examine the effect of the hybrid structure on tetracations **4a**$^{4+}$ and **4b**$^{4+}$, a series of di- and monocations **5a**$^{2+}$, **5b**$^{2+}$ and **6a**$^+$, **6b**$^+$ were also synthesized. Dications **5a**$^{2+}$ and **5b**$^{2+}$ are typical examples for the violene−cyanine hybrid in the point of the connection of two polymethine substructures to the two terminals of the violene-like π-electron core (Chart 3). Monocations **6a**$^+$ and **6b**$^+$ can be considered as the parent compounds of the multicharged methylium compounds (Chart 4).[10]

Synthesis. The reaction of 2 molar amounts of 1,6-di-*tert*-butylazulene (**8**)[11] with 4-ethynylbenzaldehyde (**7a**)[12] and 5-ethynylthiophene-2-carbaldehyde (**7b**),[13] which were prepared starting from 4-bromobenzaldehyde and 5-bromothiophene-2-carbaldehyde, respectively, in acetic acid at room temperature afforded bis(3,6-di-*tert*-butyl-1-azulenyl)(4-ethynylphenyl- and 5-ethynyl-2-thienyl)methanes (**9a** and **9b**) in 82 and 79% yield, respectively (Scheme 6).

Preparation of the corresponding tetrahydro derivatives **11a** and **11b** for the precursors of tetracations was accomplished by a simple one-pot reaction involving repeated Pd-catalyzed alkynylation of 1,2,4,5-tetraiodobenzene (**10**)[14] with **9a** and **9b**

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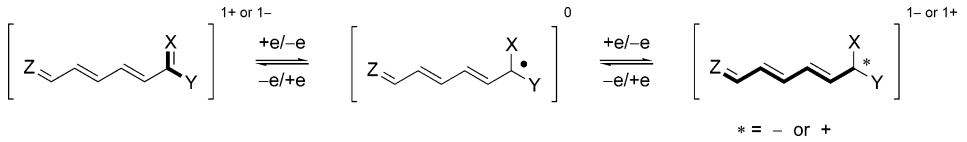
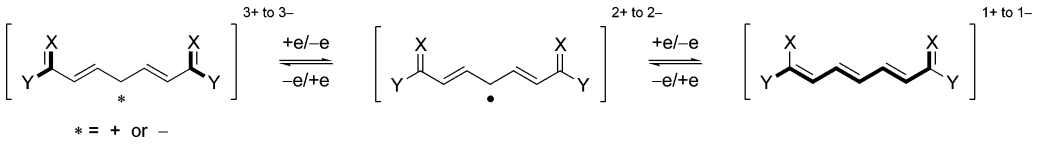
SCHEME 2. General Structure of the Cyanine−Cyanine Hybrid with a Cyanine Unit at One Terminal



SCHEME 3. General Structure of the Cyanine−Cyanine Hybrid with a Cyanine Unit at Both Terminals



SCHEME 4. Improved Structure of the Cyanine−Cyanine Hybrid with a Cyanine Unit at Both Terminals

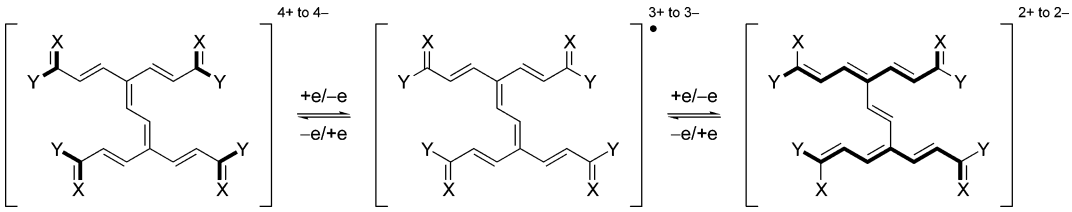
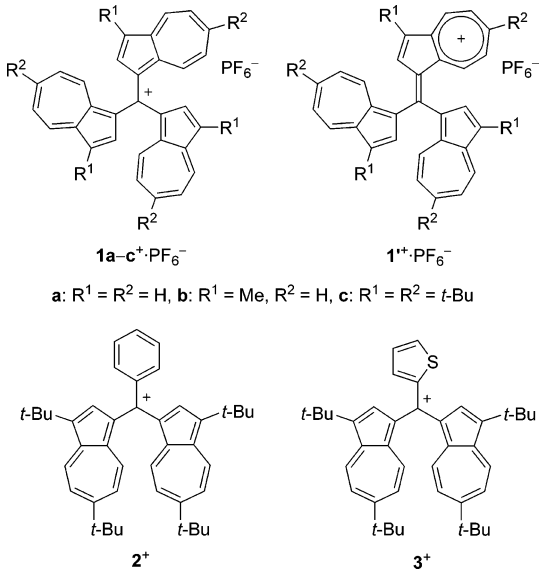


CHART 1



under Sonogashira−Hagihara conditions.[15] The cross-coupling reaction of **10** with **9a** using $Pd(PPh_3)_4$ as a catalyst and subsequent chromatographic purification of the reaction mixture on silica gel afforded the desired **11a** in 33% yield along with trisadduct **12a** in 9% yield (Chart 5). Likewise, the reaction of **10** with **9b** afforded the desired **11b** in 33% yield together with trisadduct **12b** in 21% yield (Chart 5).

The cross-coupling reaction of 1,4-diiodobenzene (**13**) with **9a** and **9b** in the presence of the Pd catalyst afforded bisadducts **14a** (76%) and **14b** (54%), respectively. Compounds **16a** and **16b** for the precursors of monocations were also obtained by the similar Pd-catalyzed reaction of iodobenzene (**15**) with **9a** and **9b** in 64 and 53% yield, respectively (Chart 6). Diacetylene derivatives (**17a** and **17b**) were isolated as byproducts in some reactions because of the homocoupling of the starting acetylenes **9a** and **9b** under the Pd-catalyzed reaction conditions (Chart 7).[16]

SCHEME 5

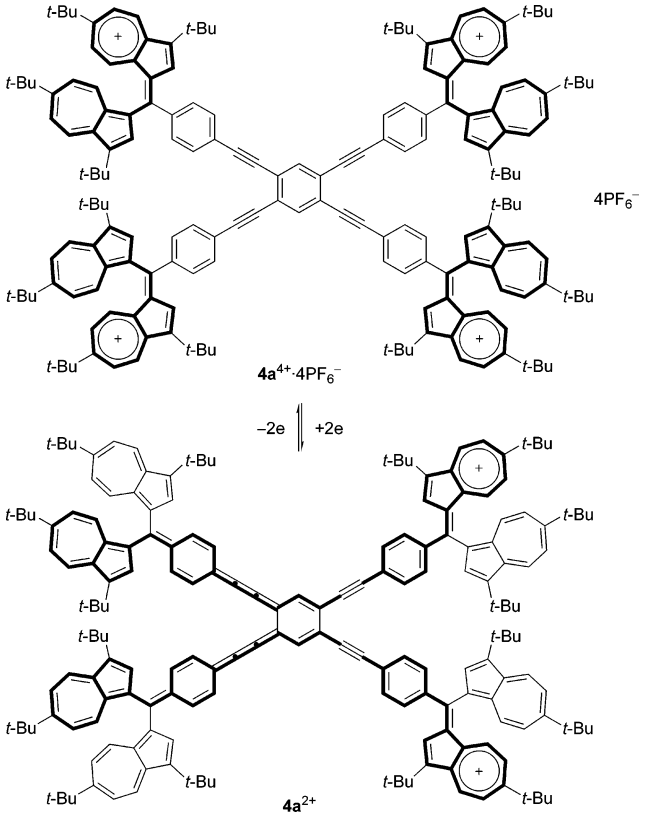


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CHART 2

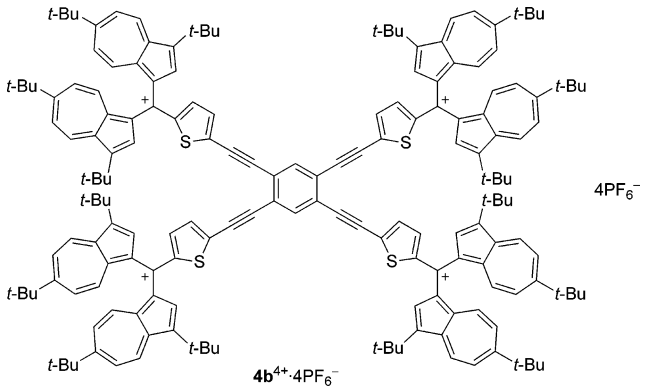


CHART 3

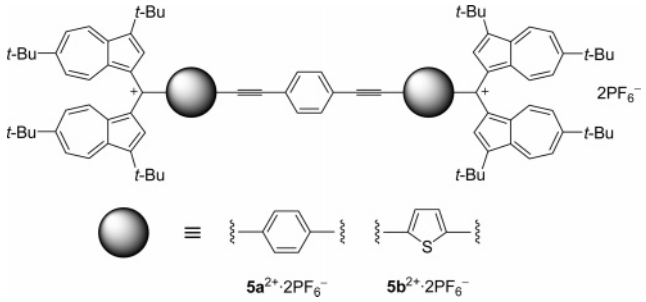
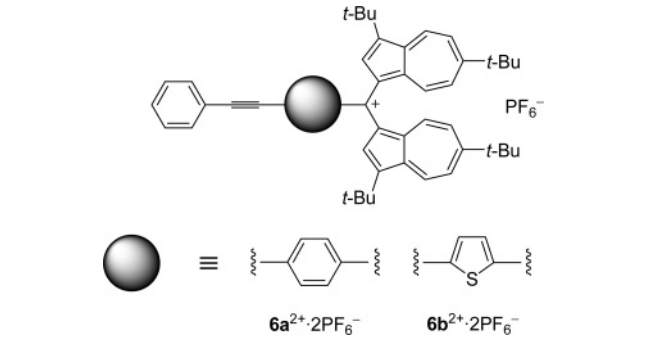
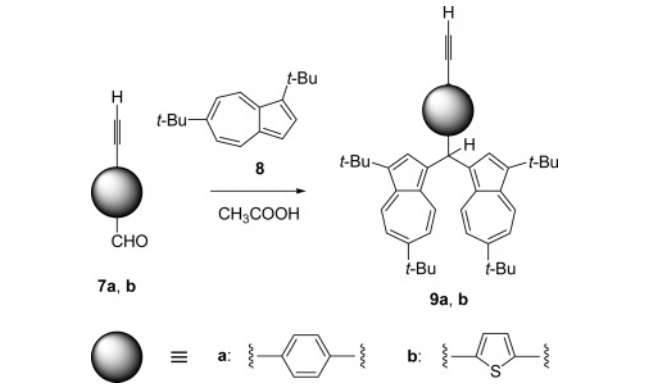


CHART 4



SCHEME 6. Preparation of Bis(3,6-di-*tert*-butyl-1-azulenyl)(4-ethynylphenyl- and 5-ethynyl-2-thienyl)methanes (9a and 9b)



The synthesis of tetra-, di-, and monocations $\mathbf{4a}^{4+}$, $\mathbf{4b}^{4+}$, $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}$, and $\mathbf{6a}^{+}$, $\mathbf{6b}^{+}$ was accomplished by the hydride abstraction from the corresponding hydro derivatives **11a**, **11b**, **14a**, **14b**, and **16a**, **16b**.[7] The reaction of **11a** with 4 molar amounts of DDQ in dichloromethane at room temperature, followed by an addition of a 60% aqueous HPF_6 solution, yielded $\mathbf{4a}^{4+}$ (80%) as tetrakis(hexafluorophosphate). Likewise, the oxidation of **14a** and **16a** with 2 and 1 molar amounts of DDQ, followed by the addition of an HPF_6 solution, afforded the corresponding bis- and mono(hexafluorophosphate)s $\mathbf{5a}^{2+}\cdot 2PF_6^-$ and $\mathbf{6a}^{+}\cdot PF_6^-$ in 78 and 87% yields, respectively. Similarly, the reaction of **11b**, **14b**, and **16b** with DDQ afforded the corresponding tetra-, bis-, and monocations $\mathbf{4b}^{4+}$ (87%), $\mathbf{5b}^{2+}$ (75%), and $\mathbf{6b}^{+}$ (86%) as tetrakis-, bis-, and mono(hexafluorophosphate)s, after the treatment with an HPF_6 solution.

These new salts $\mathbf{4a}^{4+}$, $\mathbf{4b}^{4+}\cdot 4PF_6^-$, $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}\cdot 2PF_6^-$, and $\mathbf{6a}^{+}$, $\mathbf{6b}^{+}\cdot PF_6^-$ are stable, deep-colored crystals and are storable in the crystalline state. Carbocations which have more than four

CHART 5

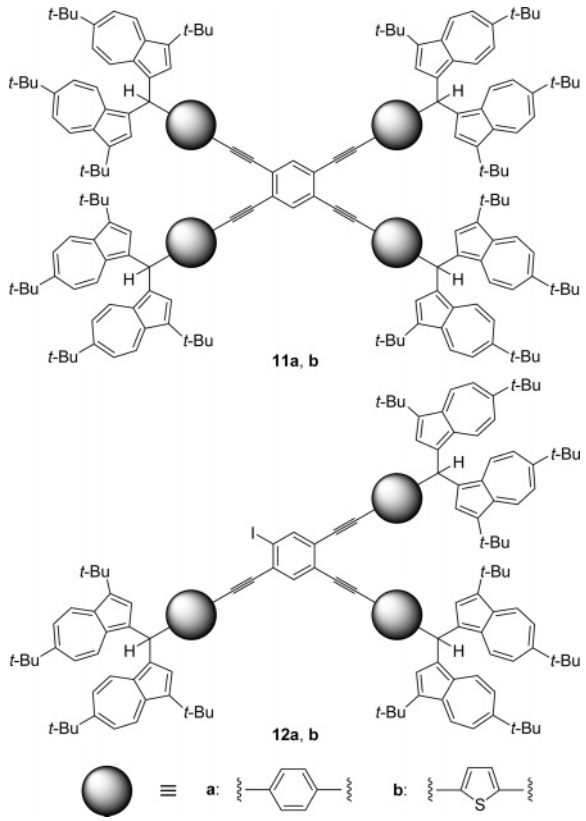


CHART 6

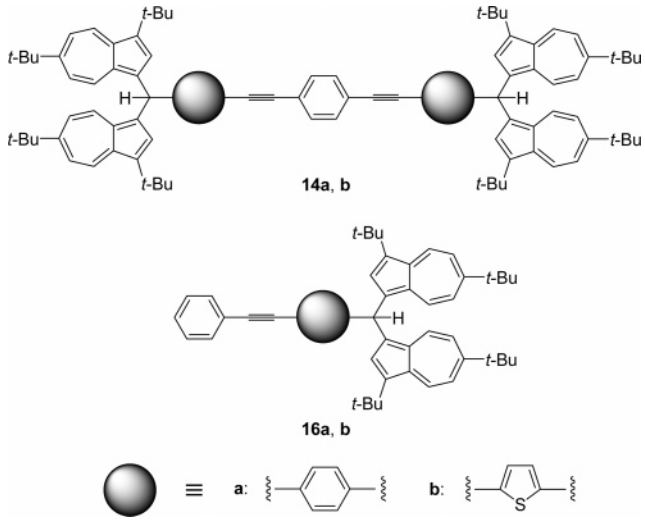
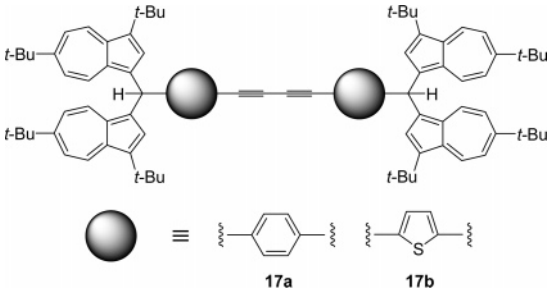


CHART 7



cationic centers are rare species, and isolable compounds are very little. Tetrahedrally arrayed tetracation,[17] which is stable only at low temperature, was generated by Olah et al. The preparation of trications utilizing 2-amino-5-thienyl-substituted methylium units was reported by Hartmann et al.[18] Recently, Rathore et al.[19] prepared isolable tetra- and hexatrityl cations utilizing tetraphenylmethane and hexaphenylbenzene as platforms. The tetracations **4a**$^{4+}$ and **4b**$^{4+}$ are two of a new multicharged methylium compounds with considerably high stability.

Spectroscopic Properties. Tetra-, di-, and monocations **4a**$^{4+}$, **4b**$^{4+}$, **5a**$^{2+}$, **5b**$^{2+}$, and **6a**$^{+}$, **6b**$^{+}$ were fully characterized by the spectral data as shown in the Experimental Section. Mass spectra of monocation salts **6a**$^{+}$·PF_6^- and **6b**$^{+}$·PF_6^- ionized by ESI showed the correct $(M - PF_6)^+$ ion peaks, which indicated the cationic structures of these products. Dication salts **5a**$^{2+}$·$2PF_6^-$ and **5b**$^{2+}$·$2PF_6^-$ showed the correct $(M - PF_6)^+$ and $(M - 2PF_6)^{2+}$ ion peaks. In the case of tetracation salts **4a**$^{4+}$·$4PF_6^-$ and **4b**$^{4+}$·$4PF_6^-$, $(M - 2PF_6)^{2+}$ and $(M - PF_6)^{3+}$ ion peaks were also obtained in addition to the presumed $(M - 4PF_6)^{4+}$ ion peaks. The characteristic bands of hexafluorophosphate were observed at 841−843 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported the cationic structure of these compounds.

UV−vis spectra of **4a**$^{4+}$, **4b**$^{4+}$, **5a**$^{2+}$, **5b**$^{2+}$, and **6a**$^{+}$, **6b**$^{+}$ in acetonitrile are shown in Figure 1. As expected by their polymethine substructures, these salts showed characteristic charge-transfer absorption in the visible region. Their absorption maxima (nm) and coefficients (log ϵ) are summarized in Table 1. The UV−vis spectra of **4b**$^{4+}$, **5b**$^{2+}$, and **6b**$^{+}$ in the visible region were characterized by two strong absorption bands, although **4a**$^{4+}$, **5a**$^{2+}$, and **6a**$^{+}$ exhibited an absorption band in this region. The longest wavelength absorption of **4b**$^{4+}$, **5b**$^{2+}$, and **6b**$^{+}$ showed a bathochromic shift of 7, 11, and 11 nm, respectively, compared to those of **4a**$^{4+}$, **5a**$^{2+}$, and **6a**$^{+}$, similar to the results of the carbocations between **2**$^{+}$ and **3**$^{+}$ stabilized by 1-azulenyl groups. Dications **5a**$^{2+}$ and **5b**$^{2+}$ and tetracations **4a**$^{4+}$ and **4b**$^{4+}$ exhibited only a slight bathochromic shift compared to those of monocations **6a**$^{+}$ and **6b**$^{+}$. The extinction coefficients of the dications **5a**$^{2+}$ and **5b**$^{2+}$ and tetracations **4a**$^{4+}$ and **4b**$^{4+}$ are approximately 2- and 4-fold as large as those of monocations **6a**$^{+}$ and **6b**$^{+}$, respectively.

Thermodynamic Stability. As a measure of the thermodynamic stability of the carbocations, the pK_R^+ values of tetra-, di-, and monocations were determined spectrophotometrically in a buffer solution prepared in 50% aqueous acetonitrile. The K_R^+ scale is defined by the equilibrium constant for the reaction of a carbocation with a water molecule ($K_R^+ = [ROH][H_3O^+]/[R^+]$). Therefore, the larger pK_R^+ index value (p$K_R^+ = -\log K_R^+$) indicates higher stability of the carbocation.

The values are summarized in Table 2. The pK_R^+ value of **6a**$^{+}$ is almost equal to that of **2**$^{+}$ (p$K_R^+ = 12.4$).[7a] In contrast to the stabilizing ability of the 2-thienyl substituent, monocation **6b**$^{+}$ is less stable than the corresponding benzylcation **6a**$^{+}$,

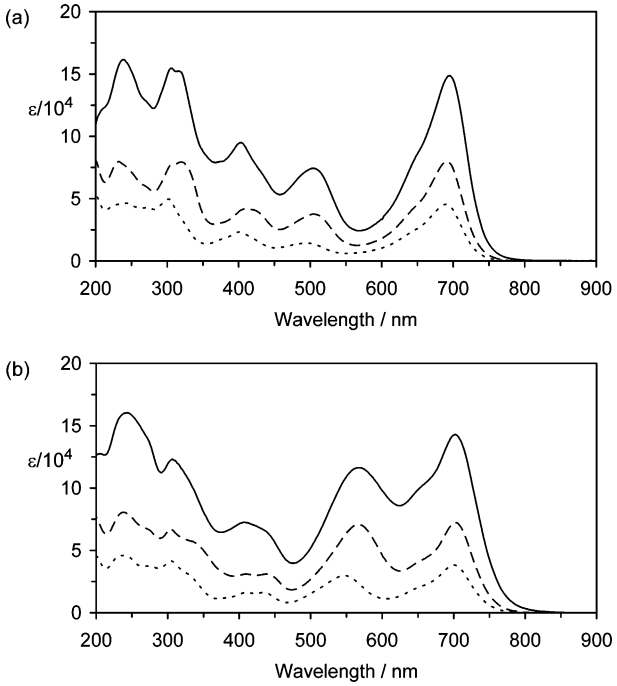


FIGURE 1. UV−vis spectra of (a) **4a**$^{4+}$ (solid line), **5a**$^{2+}$ (broken line), and **6a**$^{+}$ (dotted line); (b) **4b**$^{4+}$ (solid line), **5b**$^{2+}$ (broken line), and **6b**$^{+}$ (dotted line) in acetonitrile.

TABLE 1. Longest Wavelength Absorption Maxima (nm) and Their Coefficients of Cations 4a^{4+}, 4b^{4+}, 5a^{2+}, 5b^{2+}, and 6a^{+}, 6b^{+} in Acetonitrile

sample	λ_{max} (log ϵ)	sample	λ_{max} (log ϵ)	ref
4a^{4+}	692 (5.17)	**6a**$^{+}$	687 (4.65)	
4b^{4+}	565 (5.07), 699 (5.15)	**6b**$^{+}$	544 (4.47), 698 (4.58)	
5a^{2+}	689 (4.90)	**2**$^{+}$	681 (4.61)	7a
5b^{2+}	564 (4.85), 700 (4.86)	**3**$^{+}$	687 (4.56)	8

TABLE 2. pK_R^+ Values[a] and Redox Potentials[b] of Tetra-, Di-, and Monocations 4a^{4+}, 4b^{4+}, 5a^{2+}, 5b^{2+}, and 6a^{+}, 6b^{+}

sample	pK_R^+ [c]	E_1^{red}	E_1^{ox}
4a^{4+}	8.7 ± 0.1 (7%)	−0.68 (−0.65)	+0.93 (+0.91)
4b^{4+}	8.1 ± 0.1 (7%)	−0.61 (−0.58)	+0.95 (+0.93)
5a^{2+}	10.8 ± 0.1 (6%)	−0.70 (−0.68)	+0.93 (+0.92)
5b^{2+}	9.6 ± 0.1 (3%)	−0.63 (−0.62)	+0.96 (+0.94)
6a^{+}	12.3 ± 0.1 (21%)	−0.70 (−0.68)	+0.93 (+0.91)
6b^{+}	11.4 ± 0.1 (5%)	−0.65 (−0.63)	+0.96 (+0.94)

[a] The pK_R^+ values were determined spectrophotometrically in a buffered solution prepared in 50% aqueous acetonitrile. [b] Redox potentials were measured by CV and DPV [V vs Ag/$AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (i.d.: 1.6 mm), scan rate = 100 mV s^{-1}, and Fc/Fc^+ = +0.15 V]. The peak potentials measured by DPV 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.

(17) (a) Head, N. J.; Prakash, G. K. S.; Bashir-Hashemi, A.; Olah, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 12005−12006. (b) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7351−7354.
(18) Noack, A.; Schröder, A.; Hartmann, H.; Rohde, D.; Dunsch, L. *Org. Lett.* **2003**, *5*, 2393−2396.
(19) Rathore, R.; Burns, C. L.; Guzei, I. A. *J. Org. Chem.* **2004**, *69*, 1524−1530.

similar to the results of the cations between $\mathbf{2}^+$ and $\mathbf{3}^+$ ($pK_R^+ = 11.8$)[8] stabilized by 1-azulenyl groups.

In the case of the dications, the two cation units could be neutralized by two steps because of the through-bond electrostatic repulsion of the two positively charged units. However, the two cation units in the dications $\mathbf{5a}^{2+}$ and $\mathbf{5b}^{2+}$ were neutralized simultaneously at pH 10.8 ± 0.1 and 9.6 ± 0.1, respectively, although the titration curve for the neutralization caused some fluctuation, probably due to the instability of the neutralized species. The pH should correspond to the average of the pK_R^{2+} values and the pK_R^+ values of the dications $\mathbf{5a}^{2+}$ and $\mathbf{5b}^{2+}$. Thus, dications $\mathbf{5a}^{2+}$ and $\mathbf{5b}^{2+}$ exhibit still high thermodynamic stability like those of the corresponding monocations $\mathbf{6a}^+$ and $\mathbf{6b}^+$, although some destabilization is observed.

In the case of the tetracations $\mathbf{4a}^{4+}$ and $\mathbf{4b}^{4+}$, four cation units were neutralized simultaneously at pH 8.7 ± 0.1 and 8.1 ± 0.1, respectively. The pH should correspond to the average of the values pK_R^{4+}, pK_R^{3+}, pK_R^{2+}, and pK_R^+ of the tetracations $\mathbf{4a}^{4+}$ and $\mathbf{4b}^{4+}$. Thus, tetracations $\mathbf{4a}^{4+}$ and $\mathbf{4b}^{4+}$ are even more destabilized than monocations $\mathbf{6a}^+$ and $\mathbf{6b}^+$ by 3.6 and 3.3 p*K* units and dications $\mathbf{5a}^{2+}$ and $\mathbf{5b}^{2+}$ by 1.5 and 1.8 p*K* units. The destabilization in dications and tetracations could be explained by the existence of some intramolecular interaction that arises from the conjugation among the cation units through the central benzene ring, although it might be attributable to the difference of solvation to the sterically congested positive site in dications and tetracations.

The neutralization of these cations was not completely reversible. This is attributable to the instability of the neutralized products under the conditions of the pK_R^+ measurement. After the measurement, acidification of the alkaline solutions of $\mathbf{4a}^{4+}$, $\mathbf{4b}^{4+}$, $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}$, and $\mathbf{6a}^+$, $\mathbf{6b}^+$ with HCl regenerated the characteristic absorption in the visible region in 3−21% (Table 2).

Redox Potentials. To clarify the electrochemical property, the redox behavior of tetra-, di-, and monocations $\mathbf{4a}^{4+}$, $\mathbf{4b}^{4+}$, $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}$, and $\mathbf{6a}^+$, $\mathbf{6b}^+$ was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The first redox potentials (in volts vs $Ag/AgNO_3$) of $\mathbf{4a}^{4+}$, $\mathbf{4b}^{4+}$, $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}$, and $\mathbf{6a}^+$, $\mathbf{6b}^+$ are summarized in Table 2. The redox potentials observed at higher potentials are summarized in the Supporting Information. The first oxidation and reduction waves of $\mathbf{4a}^{4+}$ and $\mathbf{4b}^{4+}$ are shown in Figures 2 and 3, and those of $\mathbf{5a}^{2+}$, $\mathbf{5b}^{2+}$ and $\mathbf{6a}^+$, $\mathbf{6b}^+$ are summarized in the Supporting Information.

As seen from Table 2, the electrochemical reduction of monocation $\mathbf{6a}^+$ showed a reversible wave at −0.70 V and an irreversible wave at −1.54 V upon CV due to the formation of a radical and an anionic species. The reduction potentials of tetracation $\mathbf{4a}^{4+}$ ($E_1^{red} = -0.68$ V) and dication $\mathbf{5a}^{2+}$ ($E_1^{red} = -0.70$ V) are almost equal to those of monocation $\mathbf{6a}^+$, in contrast to the decreasing pK_R^+ values with increasing cation units. Apparently, the CV waves of tetracation $\mathbf{4a}^{4+}$ and dication $\mathbf{5a}^{2+}$ exhibit more current compared to the first reduction wave of monocation $\mathbf{6a}^+$ in the same concentration. Therefore, the first reduction wave of tetracations $\mathbf{4a}^{4+}$ and dication $\mathbf{5a}^{2+}$ could be concluded to four- and two-electron transfer in one step (at a constant potential) to generate neutral species.

The first reduction potentials of $\mathbf{4b}^{4+}$, $\mathbf{5b}^{2+}$, and $\mathbf{6b}^+$ are slightly less negative compared to those of $\mathbf{4a}^{4+}$, $\mathbf{5a}^{2+}$, and $\mathbf{6a}^+$; this indicates the electrochemical destabilization of the methyl cations by the 2-thienyl substituents as similar to the results on the pK_R^+ measurements. Thus, all the cation units up to

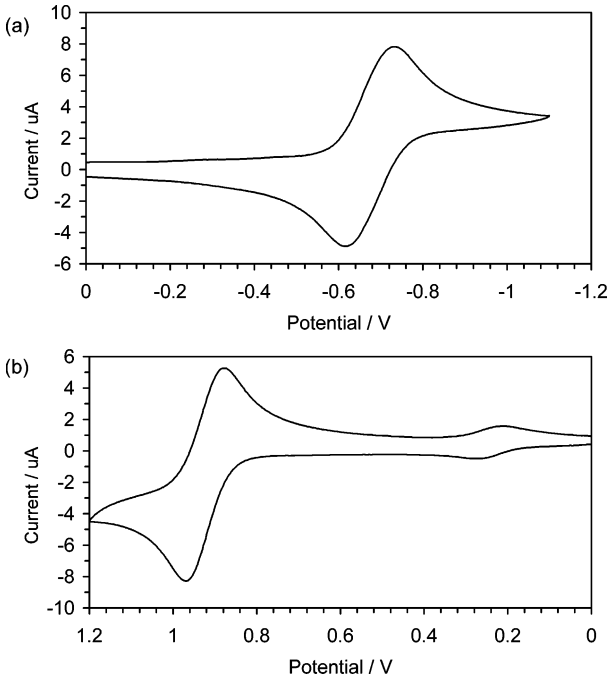


FIGURE 2. Cyclic voltammograms of (a) reduction and (b) oxidation of tetracation $\mathbf{4a}^{4+}$ (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

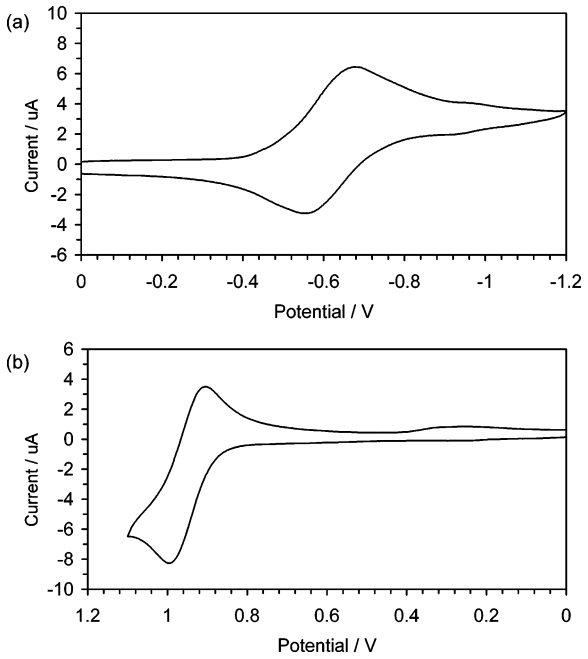


FIGURE 3. Cyclic voltammograms of (a) reduction and (b) oxidation of tetracation $\mathbf{4b}^{4+}$ (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

tetracations were reduced in one step upon CV and DPV; this indicates that the presumed redox interaction among the cation units should be rather small.

The electrochemical oxidation of monocation $\mathbf{6a}^+$ showed a reversible wave at +0.93 V upon CV, due to the oxidation of an azulene ring to give a dication radical. These redox potentials are almost equal to those of analogous benzyl cation $\mathbf{2}^+$ ($E_1^{ox} = +0.87$ V),[7a] comparable with the results of pK_R^+ values (Table 2). The oxidation of tetracations $\mathbf{4a}^{4+}$ and dication $\mathbf{5a}^{2+}$

also exhibited a wave at +0.93 V upon CV. The wave should be ascribed to the oxidation of four and two azulene rings to generate octa- and tetracationic species, respectively, since the wave is in similar potential ranges with those of monocation **6a**$^+$ and exhibits more current compared to the first oxidation wave of monocation **6a**$^+$ in the same concentration. The first oxidation potentials of **4b**$^{4+}$, **5b**$^{2+}$, and **6b**$^+$ are slightly more positive compared to those of **4a**$^{4+}$, **5a**$^{2+}$, and **6a**$^+$, similar to those of cations **2**$^+$ and **3**$^+$ (E_1^{ox} = +0.91 V)[8] stabilized by 1-azulenyl groups.

Electrochromic Analysis. Visible spectra of **4a**$^{4+}$, **4b**$^{4+}$, **5a**$^{2+}$, **5b**$^{2+}$, and **6a**$^+$, **6b**$^+$ were monitored to clarify the formation of a colored cyanine-type substructure under the electrochemical reduction conditions, although the CV analysis revealed the less effective electrochemical interaction among all the cation units in the dications and tetracations. A constant-current reduction was applied to the solutions of **4a**$^{4+}$, **4b**$^{4+}$, **5a**$^{2+}$, **5b**$^{2+}$, and **6a**$^+$, **6b**$^+$ with a platinum mesh for working electrode and a wire counter electrode.

When the visible spectra of **4a**$^{4+}$ were measured in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte at room temperature under the electrochemical reduction conditions, the strong absorption at 692 nm in the visible region of **4a**$^{4+}$ was gradually decreased (see Supporting Information). The color of the solution of **4a**$^{4+}$ gradually changed from dark green to yellow during the electrochemical reduction. However, the reverse oxidation of the pale-colored solution did not regenerate the spectrum of the tetracation **4a**$^{4+}$ (regeneration 35%) completely, although good reversibility was observed upon CV. Several acetylenes with pyridinyl end groups have been reported to afford extremely sensitive reduction products.[20] Therefore, the instability of the reduced species might be attributable to the facile polymerization of the neutral radical formed by the electrochemical reduction with acetylene spacers.

The dark green color of the solution of **5a**$^{2+}$ and **6a**$^+$ also changed to a yellow one under the reduction conditions. Absence of the isosbestic point suggests the decomposition of the fully reduced ones of **5a**$^{2+}$ and **6a**$^+$ under the electrochemical conditions. The reverse oxidation of the yellow-colored solution slightly regenerated the UV−vis spectra of the deep-colored **5a**$^{2+}$ (regeneration 13%) and **6a**$^+$ (regeneration 4%), respectively. Therefore, the color change of the solution should correspond to the formation of radical species in multiple-electron transfer, as observed upon CV.

We also tried electrochemical reduction of **4b**$^{4+}$, **5b**$^{2+}$, and **6b**$^+$ under visible spectral monitoring. We anticipated that the formation of the thienoquinoid forms during the redox reaction might improve the reversibility. In these cases, however, we could not also obtain any evidence of the formation of a colored cyanine-type structure in the two-electron reduction of tetracation **4b**$^{4+}$. Low reversibility for all the reduction of **4b**$^{4+}$ (regeneration 30%), **5b**$^{2+}$ (regeneration 22%), and **6b**$^+$ (regeneration 10%) also suggests the formation of the neutral radical species for the presumed reduction products under the conditions of the visible spectral measurements.

Conclusion

The first examples for the cyanine−cyanine hybrid prepared by the general structure in Scheme 4 did not exhibit the presumed multiple color change during the electrochemical reduction. However, these cations represented multiple-electron transfer as a function of the substituted di(1-azulenyl)methylium units and also exhibited color change during the electrochemical reduction, although the reversibility of the redox reaction upon electrochromic measurements was rather low for all cases. The electrochemical behavior was not ideal for the presumed cyanine−cyanine hybrid, probably due to the less effective electrochemical interaction among the positive charges. This might be attributable to the disadvantage of conjugation of the positively charged units by the central benzene ring, although measurement of the pK_R^+ value of dications and tetracations exhibited the existence of some interaction among the cation units. However, tetracations which we have prepared are highly stable despite their tetracationic structure. Thus, the use of di(1-azulenyl)methylium units as stabilized redox-active polymethine units would be highly effective in the point of their high stability and their strong absorption in the visible region with their redox activity. Preparations of the polycationic species using the di(1-azulenyl)methylium units with different π-electron core systems are now in progress.

Experimental Section

General. For general and electrochemical measurement details, see Supporting Information. The peak assignment of ^{1}H and ^{13}C NMR spectra reported was accomplished by decoupling, H−H COSY, NOE, HMQC, and/or HMBC experiments.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(4-ethynylphenyl)methane (9a). A mixture of 1,6-di-*tert*-butylazulene (**8**) (1.37 g, 5.70 mmol) and 4-ethynylbenzaldehyde (**7a**) (371 mg, 2.85 mmol) in acetic acid (34 mL) was stirred at room temperature for 24 h. The reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with a 5% $NaHCO_3$ solution and water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **9a** (1.39 g, 82%): blue crystals; mp 155.6−158.1 °C dec (CH_2Cl_2/methanol); MS (ESI negative) *m*/*z* (relative intensity) 592 (M^-, 100%), 591 (M^- − H, 62); HRMS calcd for $C_{45}H_{52}^-$ 592.4075, found 592.4017; IR (KBr disk) ν_{max} 3320 (m, C≡C−H), 3303 (w, C≡C−H), 2965, 2109 (w, C≡C), 1578, 1364, 1229, 835 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 245 (4.63), 285 (4.90), 302 (4.87), 341 sh (3.96), 345 sh (3.99), 356 (4.05), 374 (3.98), 560 sh (2.68), 609 (2.82), 664 sh (2.74), 744 sh (2.22); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (d, 2H, J = 10.7 Hz, H_4), 8.13 (d, 2H, J = 10.6 Hz, H_8), 7.35 (d, 2H, J = 7.8 Hz, $H_{3',5'}$), 7.34 (s, 2H, H_2), 7.17 (dd, 2H, J = 10.7, 1.9 Hz, H_5), 7.07 (d, 2H, J = 7.8 Hz, $H_{2',6'}$), 7.06 (dd, 2H, J = 10.6, 1.9 Hz, H_7), 6.62 (s, 1H, CH), 3.00 (s, 1H, H_β), 1.49 (s, 18H, 3-*t*-Bu), 1.40 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 147.4, 137.7, 136.1, 134.7, 134.6, 134.2, 132.1, 132.0, 129.7, 128.8, 119.3, 119.1, 118.4, 84.1, 76.4, 42.0, 38.2, 33.2 (2C), 31.8. Anal. Calcd for $C_{45}H_{52}$: C, 91.16; H, 8.84. Found: C, 91.10; H, 9.00.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(5-ethynyl-2-thienyl)-methane (9b). The same procedure as for the preparation of **9a** was adopted here. The reaction of **8** (1.84 g, 7.65 mmol) with 4-ethynylthiophene-2-carbaldehyde (**7b**) (520 mg, 3.82 mmol) in acetic acid (46 mL) at room temperature for 24 h followed by column chromatography on silica gel with hexane and toluene afforded **9b** (1.81 g, 79%): blue crystals; mp 143.5−146.2 °C dec (methanol/water); MS (ESI negative) *m*/*z* (relative intensity) 597 (M^- − H, 100%); HRMS calcd for $C_{43}H_{50}S^-$ − H 597.3560, found 597.3565; IR (KBr disk) ν_{max} 3310 (w, C≡C−H), 3279 (w, C≡C−H), 2965, 2101 (w, C≡C), 1578, 1364 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 245 (4.52), 287 (4.90), 301 sh (4.86), 340 sh (4.03), 347 (4.05), 356 (4.07), 374 (3.99), 560 sh (2.67), 606 (2.78), 660 sh (2.69), 731 sh (2.20); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, 2H, J = 10.6 Hz, H_4), 8.22 (d, 2H, J = 10.6 Hz, H_8), 7.54

(20) Hünig, S.; Berneth, H. *Top. Curr. Chem.* **1980**, *92*, 1−44.

(s, 2H, H_2), 7.19 (dd, 2H, J = 10.6, 1.8 Hz, H_5), 7.12 (dd, 2H, J = 10.6, 1.8 Hz, H_7), 7.06 (d, 1H, J = 3.7 Hz, $H_{4'}$), 6.77 (s, 1H, CH), 6.47 (d, 1H, J = 3.7 Hz, $H_{3'}$), 3.24 (s, 1H, H_β), 1.51 (s, 18H, 3-*t*-Bu), 1.41 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.6, 154.2, 137.8, 135.5, 134.7, 134.4, 134.3, 132.9, 131.8, 129.2, 125.0, 119.8, 119.6, 118.7, 80.5, 77.8, 38.2, 37.4, 33.2, 32.2, 31.8. Anal. Calcd for $C_{43}H_{50}S$: C, 86.23; H, 8.41; S, 5.35. Found: C, 86.15; H, 8.59; S, 5.30.

General Procedure for the Pd-Catalyzed Reaction of 9a and 9b with Aryl Iodides (10, 13, and 15). To a degassed solution of **9a** and **9b**, aryl iodides (**10**, **13**, and **15**), and CuI in triethylamine and toluene was added tetrakis(triphenylphosphine)palladium(0). The resulting mixture was stirred at room temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into a 5% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The products were isolated by column chromatography on silica gel and/or gel permeation chromatography (GPC) with $CHCl_3$.

1,2,4,5-Tetrakis{4-[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]-phenylethynyl}benzene (11a). The general procedure was followed by using **9a** (400 mg, 0.675 mmol), 1,2,4,5-tetraiodobenzene (**10**) (98 mg, 0.17 mmol), CuI (14 mg, 0.073 mmol), tetrakis(triphenylphosphine)palladium(0) (40 mg, 0.035 mmol), triethylamine (8 mL), and toluene (18 mL) at room temperature for 24 h. Chromatographic purification on silica gel with 50% CH_2Cl_2/hexane and GPC afforded **11a** (136 mg, 33%), 1-iodo-2,4,5-tris{4-[bis-(3,6-di-*tert*-butyl-1-azulenyl)methyl]phenylethynyl}benzene (**12a**) (30 mg, 9%), and 4,4′-bis[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]-diphenyldiacetylene (**17a**) (71 mg, 18%).

11a: blue crystals; mp 217.7−220.6 °C dec (toluene/hexane); MS (MALDI TOF) m/z 2439.61 (M^+), found 2439.44; IR (KBr disk) ν_{max} 2963, 2205 (w, C≡C), 1576, 1364, 833 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 241 (5.12), 284 (5.41), 288 sh (5.41), 300 (5.42), 323 (5.21), 346 sh (5.01), 356 (5.00), 373 (4.93), 397 sh (4.59), 563 sh (3.27), 609 (3.40), 663 sh (3.31), 746 sh (2.79); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (d, 8H, J = 10.7 Hz, $H_{4''}$), 8.12 (d, 8H, J = 10.6 Hz, $H_{5''}$), 7.70 (s, 2H, $H_{3,6}$), 7.41 (d, 8H, J = 8.3 Hz, $H_{2',6'}$), 7.33 (s, 8H, $H_{2''}$), 7.15 (dd, 8H, J = 10.7, 1.8 Hz, $H_{5''}$), 7.08 (d, 8H, J = 8.3 Hz, $H_{3',5'}$), 7.05 (dd, 8H, J = 10.6, 1.8 Hz, $H_{7''}$), 6.60 (s, 4H, CH), 1.46 (s, 72H, 3″-*t*-Bu), 1.39 (s, 72H, 6″-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4, 147.3, 137.7, 136.2, 135.2, 134.7, 134.5, 134.2, 132.1, 131.6, 129.8, 128.9, 125.0, 120.1, 119.3, 118.3, 95.7, 87.2, 42.1, 38.2, 33.2, 32.2, 31.8. Anal. Calcd for $C_{186}H_{206}$·H_2O: C, 90.83; H, 8.52. Found: C, 90.74; H, 8.70.

12a: blue crystals; mp 209.6−211.0 °C (hexane/ethanol); MS (MALDI TOF) m/z 1975.12 (M^+), found 1974.86; IR (KBr disk) ν_{max} 2963, 2213 (w, C≡C), 1576, 1364, 833 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.93), 286 sh (5.28), 291 (5.28), 303 (5.30), 345 sh (4.81), 355 (4.82), 375 (4.71), 558 sh (3.10), 610 (3.25), 663 sh (3.16), 741 sh (2.58); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.56 (d, 2H, J = 10.7 Hz, $H_{4''}$), 8.54 (d, 4H, J = 10.7 Hz, $H_{4''}$), 8.15 (d, 2H, J = 10.7 Hz, $H_{8''}$), 8.12 (d, 4H, J = 10.7 Hz, $H_{8''}$), 8.00 (s, 1H, H_3 or H_6), 7.61 (s, 1H, H_3 or H_6), 7.44 (d, 2H, J = 8.3 Hz, $H_{2',6'}$), 7.40 (d, 4H, J = 8.3 Hz, $H_{2',6'}$), 7.35 (s, 2H, $H_{2''}$), 7.32 (s, 4H, $H_{2''}$), 7.17 (dd, 2H, J = 10.7, 1.4 Hz, $H_{5''}$), 7.16 (dd, 4H, J = 10.7, 1.4 Hz, $H_{5''}$), 7.11 (d, 2H, J = 8.3 Hz, $H_{3',5'}$), 7.09 (d, 2H, J = 8.3 Hz, $H_{3',5'}$), 7.08 (d, 2H, J = 8.3 Hz, $H_{3',5'}$), 7.07 (dd, 2H, J = 10.7, 1.4 Hz, $H_{7''}$), 7.05 (dd, 4H, J = 10.7, 1.4 Hz, $H_{7''}$), 6.64 (s, 1H, CH), 6.61 (s, 1H, CH), 6.60 (s, 1H, CH), 1.49 (s, 18H, 3″-*t*-Bu), 1.47 (s, 18H, 3″-*t*-Bu), 1.46 (s, 18H, 3″-*t*-Bu), 1.41 (s, 18H, 6″-*t*-Bu), 1.40 (s, 36H, 6″-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.4 ($C_{6''}$), 147.6 ($C_{1'}$ or $C_{4'}$), 147.5 ($C_{1'}$ or $C_{4'}$), 147.4 ($C_{1'}$ or $C_{4'}$), 141.5 (C_3 or C_6), 137.7 ($C_{3''}$), 136.2 ($C_{2''}$), 134.7 (1C and/or 1C, $C_{4''}$, $C_{8''a}$, and/or C_3 or C_6), 134.6 (3C and/or 1C, $C_{4''}$, $C_{8''a}$, and/or C_3 or C_6), 134.5 (2C and/or 1C, $C_{4''}$, $C_{8''a}$, and/or C_3 or C_6), 134.2 ($C_{3''a}$), 132.1 ($C_{8''}$), 131.6 (2C, $C_{2',6'}$), 131.5 ($C_{2',6'}$), 129.8 ($C_{1''}$), 129.7 (2C, $C_{1''}$), 129.3 (C_2, C_4, or C_5), 128.9 ($C_{3',5'}$), 126.0 (C_2, C_4, or C_5), 125.5 (C_2, C_4, or C_5), 119.9 ($C_{1'}$ or $C_{4'}$), 119.8 ($C_{1'}$ or $C_{4'}$), 119.7 ($C_{1'}$ or $C_{4'}$), 119.3 ($C_{7''}$), 118.4 ($C_{5''}$), 99.3 (C_1), 96.5 (C_β), 95.5 (C_β), 95.3 (C_β), 90.6 (C_α), 86.5 (C_α), 86.3 (C_α), 42.1 (CH), 38.2 (s, 6″-*t*-Bu), 33.2 (s, 3″-*t*-Bu), 32.2 (q, 3″-*t*-Bu), 31.8 (q, 6″-*t*-Bu). Anal. Calcd for $C_{141}H_{155}I$·1/2H_2O: C, 85.29; H, 7.92. Found: C, 85.20; H, 8.10.

17a: blue crystals; mp 222.5−224.9 °C dec (methanol); MS (ESI negative) m/z (relative intensity) 1182 (M^- − H, 100%); HRMS calcd for $C_{90}H_{102}^-$ − H 1181.7909, found 1181.7911; IR (KBr disk) ν_{max} 2965, 2213 (w, C≡C), 2145 (w, C≡C), 1576, 833 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.80), 288 (5.08), 301 (5.08), 345 sh (4.55), 356 (4.51), 374 (4.37), 563 sh (2.99), 609 (3.12), 663 sh (3.03), 743 sh (2.47); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (d, 4H, J = 10.7 Hz, $H_{4'}$), 8.12 (d, 4H, J = 10.6 Hz, $H_{8'}$), 7.37 (d, 4H, J = 8.2 Hz, $H_{2,6}$), 7.33 (s, 4H, $H_{2'}$), 7.17 (dd, 4H, J = 10.7, 1.8 Hz, $H_{5'}$), 7.07 (d, 4H, J = 8.2 Hz, $H_{3,5}$), 7.07 (dd, 4H, J = 10.6, 1.8 Hz, $H_{7'}$), 6.61 (s, 2H, CH), 1.49 (s, 36H, 3′-*t*-Bu), 1.40 (s, 36H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 147.9, 137.8, 136.1, 134.7, 134.6, 134.2, 132.3, 132.1, 129.6, 128.9, 119.3, 118.9, 118.4, 81.8, 73.5, 42.1, 38.2, 33.2, 32.2, 31.8. Anal. Calcd for $C_{90}H_{102}$·$2H_2O$: C, 88.62; H, 8.76. Found: C, 88.56; H, 8.84.

1,2,4,5-Tetrakis{5-[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]-2-thienylethynyl}benzene (11b). The general procedure was followed by using **9b** (404 mg, 0.675 mmol), **10** (98 mg, 0.17 mmol), CuI (13 mg, 0.068 mmol), tetrakis(triphenylphosphine)palladium(0) (39 mg, 0.034 mmol), triethylamine (4 mL), and toluene (8 mL) at room temperature for 24 h. Chromatographic purification on silica gel with 50% toluene/hexane and GPC afforded **11b** (137 mg, 33%) and 1-iodo-2,4,5-tris{5-[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]-2-thienylethynyl}benzene (**12b**) (69 mg, 21%).

11b: green crystals; mp 212.4−214.6 °C dec (hexane/ethanol); MS (MALDI TOF) m/z 2463.44 (M^+), found 2463.25; IR (KBr disk) ν_{max} 2965, 2197 (w, C≡C), 1578, 1364, 833 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (5.10), 283 (5.42), 300 (5.39), 347 sh (5.07), 357 (5.13), 373 sh (5.01), 408 sh (4.77), 429 sh (4.65), 562 sh (3.40), 605 (3.50), 660 sh (3.42), 739 sh (2.96); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (d, 8H, J = 10.6 Hz, $H_{4''}$), 8.20 (d, 8H, J = 10.6 Hz, $H_{8''}$), 7.51 (s, 8H, $H_{2''}$), 7.45 (s, 2H, $H_{3,6}$), 7.15 (dd, 8H, J = 10.6, 1.7 Hz, $H_{5''}$), 7.10 (dd, 8H, J = 10.6, 1.7 Hz, $H_{7''}$), 6.98 (d, 4H, J = 3.7 Hz, $H_{3'}$), 6.75 (s, 4H, CH), 6.41 (d, 4H, J = 3.7 Hz, $H_{4''}$), 1.47 (s, 72H, 3″-*t*-Bu), 1.39 (s, 72H, 6″-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 154.6, 137.8, 135.5, 134.7, 134.4, 134.3, 133.8, 132.5, 131.9, 129.3, 125.7, 124.2, 120.8, 119.6, 118.6, 91.0, 89.5, 38.2, 37.6, 33.2, 32.2, 31.8. Anal. Calcd for $C_{178}H_{198}S_4$: C, 86.70; H, 8.09; S, 5.20. Found: C, 86.41; H, 8.12; S, 5.10.

12b: green crystals; mp 201.9−206.4 °C dec (ethanol/water); MS (MALDI TOF) m/z 1992.99 (M^+), found 1992.76; IR (KBr disk) ν_{max} 2963, 2197 (w, C≡C), 1578, 1364 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.95), 284 (5.29), 301 (5.26), 345 (4.89), 356 sh (4.88), 374 (4.82), 413 sh (4.57), 559 sh (3.15), 605 (3.29), 661 sh (3.19), 738 sh (2.60); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.56 (d, 2H, J = 10.6 Hz, $H_{4''}$), 8.54 (d, 2H, J = 10.6 Hz, $H_{4''}$), 8.53 (d, 2H, J = 10.6 Hz, $H_{4''}$), 8.23 (d, 2H, J = 10.6 Hz, $H_{8''}$), 8.20 (d, 4H, J = 10.6 Hz, $H_{8''}$), 7.85 (s, 1H, H_3 or H_6), 7.55 (s, 2H, $H_{2''}$), 7.51 (s, 4H, $H_{2''}$), 7.43 (s, 1H, H_3 or H_6), 7.19 (dd, 2H, J = 10.6, 1.6 Hz, $H_{5''}$), 7.16 (dd, 4H, J = 10.6, 1.6 Hz, $H_{5''}$), 7.13 (dd, 2H, J = 10.6, 1.6 Hz, $H_{7''}$), 7.11 (dd, 4H, J = 10.6, 1.6 Hz, $H_{7''}$), 7.11 (d, 1H, J = 3.6 Hz, $H_{3'}$), 7.00 (d, 2H, J = 3.6 Hz, $H_{3'}$), 6.79 (s, 1H, CH), 6.76 (s, 2H, CH), 6.51 (d, 1H, J = 3.6 Hz, $H_{4'}$), 6.42 (d, 2H, J = 3.6 Hz, $H_{4'}$), 1.51 (s, 18H, 3″-*t*-Bu), 1.48 (s, 18H, 3″-*t*-Bu), 1.47 (s, 18H, 3″-*t*-Bu), 1.41 (s, 18H, 6″-*t*-Bu), 1.40 (s, 36H, 6″-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.6 (2C, $C_{6''}$), 160.5 ($C_{6''}$), 155.2 ($C_{2'}$ or $C_{5'}$), 155.0 ($C_{2'}$ or $C_{5'}$), 154.7 ($C_{2'}$ or $C_{5'}$), 140.7 (C_3 or C_6), 137.8 ($C_{3''}$), 135.5 ($C_{2''}$), 134.7 ($C_{4''}$), 134.4 ($C_{3''a}$ or $C_{8''a}$), 134.3 ($C_{3''a}$ or $C_{8''a}$), 133.7 (C_3 or C_6), 132.7 ($C_{3'}$), 132.6 ($C_{3'}$), 132.5 ($C_{3'}$), 131.8 ($C_{8''}$), 129.3 ($C_{1''}$), 129.2 (2C, $C_{1''}$), 129.0 (C_2, C_4, or C_5), 125.7 (2C, $C_{4'}$), 125.6 ($C_{4'}$), 125.3 (C_2, C_4, or C_5), 124.8 (C_2, C_4, or C_5), 120.6 ($C_{2'}$ or $C_{5'}$), 120.5 ($C_{2'}$ or $C_{5'}$),

120.3 ($C_{2'}$ or $C_{5'}$), 119.6 ($C_{7''}$), 118.6 ($C_{5''}$), 98.4 (C_1), 94.2 (C_α or C_β), 90.4 (C_α or C_β), 90.2 (C_α or C_β), 90.1 (C_α or C_β), 89.3 (C_α or C_β), 89.2 (C_α or C_β), 38.2 (s, 6″-*t*-Bu), 37.6 (d, CH), 37.5 (2C, d, CH), 33.2 (s, 3″-*t*-Bu), 32.2 (q, 3″-*t*-Bu), 31.8 (q, 6″-*t*-Bu). Anal. Calcd for $C_{135}H_{149}IS_3$: C, 81.29; H, 7.53; S, 4.82. Found: C, 81.45; H, 7.57; S, 4.72.

1,4-Bis{4-[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]-phenylethynyl}benzene (14a). The general procedure was followed by using **9a** (202 mg, 0.341 mmol), 1,4-diiodobenzene (**13**) (57 mg, 0.17 mmol), CuI (6.5 mg, 0.034 mmol), tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.017 mmol), triethylamine (3 mL), and toluene (6 mL) at room temperature for 24 h. Chromatographic purification on silica gel with 50% CH_2Cl_2/hexane afforded **14a** (163 mg, 76%): blue crystals; mp 243.9−245.7 °C dec (toluene/hexane); MS (ESI negative) *m*/*z* (relative intensity) 1258 (M^- − H, 91%); HRMS calcd for $C_{96}H_{106}^-$ − H 1257.8222, found 1257.8228; IR (KBr disk) ν_{max} 2965, 2217 (w, C≡C), 1576, 1516, 1364, 833 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.79), 244 sh (4.77), 285 sh (5.09), 290 sh (5.10), 301 (5.12), 330 sh (4.82), 339 sh (4.78), 356 sh (4.70), 374 sh (4.48), 559 sh (2.95), 609 (3.08), 665 sh (2.99), 746 sh (2.49); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, 4H, *J* = 10.7 Hz, $H_{4''}$), 8.14 (d, 4H, *J* = 10.6 Hz, $H_{5''}$), 7.44 (s, 4H, $H_{2,3,5,6}$), 7.38 (d, 4H, *J* = 8.2 Hz, $H_{2',6'}$), 7.35 (s, 4H, $H_{2''}$), 7.17 (dd, 4H, *J* = 10.7, 1.5 Hz, $H_{5''}$), 7.10 (d, 4H, *J* = 8.2 Hz, $H_{3',5'}$), 7.07 (dd, 4H, *J* = 10.6, 1.5 Hz, $H_{7''}$), 6.63 (s, 2H, CH), 1.49 (s, 36H, 3″-*t*-Bu), 1.40 (s, 36H, 6″-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4, 147.1, 137.7, 136.2, 134.7, 134.6, 134.2, 132.1, 131.5, 131.4, 129.8, 128.9, 123.1, 120.1, 119.3, 118.4, 91.6, 88.6, 42.1, 38.2, 33.2, 32.2, 31.8. Anal. Calcd for $C_{96}H_{106}\cdot H_2O$: C, 90.23; H, 8.52. Found: C, 90.54; H, 8.73.

1,4-Bis{5-[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]-2-thienylethynyl}benzene (14b). The general procedure was followed by using **9b** (200 mg, 0.334 mmol), **13** (55 mg, 0.17 mmol), CuI (6.4 mg, 0.034 mmol), tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.017 mmol), triethylamine (4 mL), and toluene (8 mL) at room temperature for 24 h. Chromatographic purification on silica gel with 50% toluene/hexane and GPC afforded **14b** (113 mg, 54%): blue crystals; mp 222.8−226.3 °C dec (methanol); MS (ESI negative) *m*/*z* (relative intensity) 1270 (M^- − H, 100%); HRMS calcd for $C_{92}H_{102}S_2^-$ − H 1269.7350, found 1269.7357; IR (KBr disk) ν_{max} 2963, 2201 (w, C≡C), 1578, 1364, 833 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 241 (4.79), 284 (5.08), 301 (5.06), 344 sh (4.76), 357 (4.82), 374 sh (4.77), 385 sh (4.67), 559 sh (3.04), 605 (3.15), 658 sh (3.07), 739 sh (2.57); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, 4H, *J* = 10.7 Hz, $H_{4''}$), 8.23 (d, 4H, *J* = 10.6 Hz, $H_{8''}$), 7.56 (s, 4H, $H_{2''}$), 7.35 (s, 4H, $H_{2,3,5,6}$), 7.18 (dd, 4H, *J* = 10.7, 1.7 Hz, $H_{5''}$), 7.13 (dd, 4H, *J* = 10.6, 1.7 Hz, $H_{7''}$), 7.06 (d, 2H, *J* = 3.7 Hz, $H_{3'}$), 6.79 (s, 2H, CH), 6.52 (d, 2H, *J* = 3.7 Hz, $H_{4'}$), 1.51 (s, 36H, 3″-*t*-Bu), 1.41 (s, 36H, 6″-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.6, 154.4, 137.8, 135.5, 134.7, 134.4, 134.3, 132.0, 131.8, 131.1, 129.3, 125.4, 122.8, 120.9, 119.6, 118.6, 92.4, 85.4, 38.2, 37.5, 33.2, 32.2, 31.8. Anal. Calcd for $C_{92}H_{102}S_2$: C, 86.88; H, 8.08; S, 5.04. Found: C, 86.63; H, 8.33; S, 5.07.

Bis(3,6-di-*tert*-butyl-1-azulenyl)[4-(phenylethynyl)phenyl]-methane (16a). The general procedure was followed by using **9a** (151 mg, 0.255 mmol), iodobenzene (**15**) (51 mg, 0.25 mmol), CuI (4.7 mg, 0.025 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg, 0.013 mmol), triethylamine (3 mL), and toluene (6 mL) at room temperature for 24 h. Chromatographic purification on silica gel with 50% toluene/hexane and GPC afforded **16a** (107 mg, 64%) and **17a** (12 mg, 8%).

16a: blue crystals; mp 142.5−144.7 °C dec (methanol); MS (ESI negative) *m*/*z* (relative intensity) 667 (M^- − H, 100%); HRMS calcd for $C_{51}H_{56}^-$ − H 667.4309, found 667.4308; IR (KBr disk) ν_{max} 2965, 2217 (w, C≡C), 1576, 1509, 1364, 833, 754 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.53), 289 (4.90), 296 (4.89), 302 (4.90), 339 (4.06), 345 sh (4.05), 356 (4.08), 374 (4.01), 563 sh (2.72), 609 (2.85), 663 sh (2.76), 747 sh (2.25); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, 2H, *J* = 10.6 Hz, H_4), 8.15 (d, 2H, *J* = 10.6 Hz, H_8), 7.51−7.48 (m, 2H, $H_{2'',6''}$), 7.39 (d, 2H, *J* = 8.3 Hz, $H_{3',5'}$), 7.36 (s, 2H, H_2), 7.33−7.26 (m, 3H, $H_{3'',4'',5''}$), 7.17 (dd, 2H, *J* = 10.6, 1.8 Hz, H_5), 7.10 (d, 2H, *J* = 8.3 Hz, $H_{2',6'}$), 7.07 (dd, 2H, *J* = 10.6, 1.8 Hz, H_7), 6.63 (s, 1H, CH), 1.50 (s, 18H, 3-*t*-Bu), 1.41 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4, 146.9, 137.7, 136.2, 134.7, 134.5, 134.2, 132.1, 131.5 (2C), 129.9, 128.8, 128.3, 128.0, 123.5, 120.3, 119.3, 118.4, 89.8, 88.8, 42.0, 38.2, 33.2, 32.2, 31.8. Anal. Calcd for $C_{51}H_{56}$: C, 91.56; H, 8.44. Found: C, 91.34; H, 8.68.

Bis(3,6-di-*tert*-butyl-1-azulenyl)[5-(phenylethynyl)-2-thienyl]-methane (16b). The general procedure was followed by using **9b** (152 mg, 0.254 mmol), **15** (52 mg, 0.25 mmol), CuI (4.5 mg, 0.024 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg, 0.013 mmol), triethylamine (3 mL), and toluene (6 mL) at room temperature for 24 h. Chromatographic purification on silica gel with 50% toluene/hexane and GPC afforded **16b** (91 mg, 53%) and 5,5′-bis[bis(3,6-di-*tert*-butyl-1-azulenyl)methyl]di(2-thienyl)-diacetylene (**17b**) (14 mg, 9%).

16b: blue crystals; mp 137.2−138.4 °C dec (methanol); MS (ESI negative) *m*/*z* (relative intensity) 673 (M^- − H, 100%); HRMS calcd for $C_{49}H_{54}S^-$ − H 673.3873, found 673.3873; IR (KBr disk) ν_{max} 2963, 1576, 1364 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.42), 283 sh (4.72), 290 sh (4.73), 302 (4.75), 338 sh (4.25), 355 sh (4.05), 374 (3.88), 554 sh (2.66), 604 (2.78), 656 sh (2.71), 736 sh (2.24); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (d, 2H, *J* = 10.6 Hz, H_4), 8.24 (d, 2H, *J* = 10.6 Hz, H_8), 7.56 (s, 2H, H_2), 7.42−7.45 (m, 2H, $H_{2'',6''}$), 7.27−7.29 (m, 3H, $H_{3'',4'',5''}$), 7.19 (dd, 2H, *J* = 10.6, 1.7 Hz, H_5), 7.13 (dd, 2H, *J* = 10.6, 1.7 Hz, H_7), 7.07 (d, 1H, *J* = 3.6 Hz, $H_{4'}$), 6.80 (s, 1H, CH), 6.52 (d, 1H, *J* = 3.6 Hz, $H_{3'}$), 1.52 (s, 18H, 3-*t*-Bu), 1.42 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.6, 154.0, 137.8, 135.5, 134.7, 134.4, 134.3, 131.8 (2C), 131.3, 129.4, 128.3, 128.1, 125.3, 123.2, 121.1, 119.6, 118.6, 92.5, 83.5, 38.2, 37.5, 33.3, 32.2, 31.8. Anal. Calcd for $C_{49}H_{54}S$: C, 87.19; H, 8.06; S, 4.75. Found: C, 87.21; H, 8.33; S, 4.60.

17b: green crystals; mp 175.3−178.3 °C dec (hexane/methanol); MS (ESI negative) *m*/*z* (relative intensity) 1194 (M^- − H, 100%); HRMS calcd for $C_{86}H_{98}S_2^-$ − H 1193.7037, found 1193.7041; IR (KBr disk) ν_{max} 2963, 2136 (w, C≡C), 1578, 1364 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.84), 286 (5.18), 296 sh (5.16), 301 (5.17), 340 sh (4.64), 348 sh (4.65), 358 (4.67), 374 (4.59), 392 sh (4.35), 558 sh (2.97), 606 (3.11), 663 sh (3.01), 736 sh (2.47); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, 4H, *J* = 10.6 Hz, $H_{4'}$), 8.21 (d, 4H, *J* = 10.7 Hz, $H_{8'}$), 7.53 (s, 4H, $H_{2'}$), 7.18 (dd, 4H, *J* = 10.6, 1.8 Hz, $H_{5'}$), 7.12 (dd, 4H, *J* = 10.7, 1.8 Hz, $H_{7'}$), 7.08 (d, 2H, *J* = 3.8 Hz, H_3), 6.76 (s, 2H, CH), 6.46 (d, 2H, *J* = 3.8 Hz, H_4), 1.50 (s, 36H, 3′-*t*-Bu), 1.41 (s, 36H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.7, 155.7, 137.9, 135.4, 134.8, 134.4, 134.3, 134.2, 131.8, 129.1, 125.5, 120.0, 119.6, 118.7, 77.6, 77.4, 38.2, 37.6, 33.2, 32.2, 31.81. Anal. Calcd for $C_{86}H_{98}S_2$: C, 86.38; H, 8.26; S, 5.36. Found: C, 86.07; H, 8.28; S, 5.19.

General Procedure for the Preparation of Hexafluorophosphate Salts ($4a^{4+}$, $4b^{4+}\cdot 4PF_6^-$, $5a^{2+}$, $5b^{2+}\cdot 2PF_6^-$, and $6a^+$, $6b^+\cdot PF_6^-$). DDQ was added at room temperature to a solution of the corresponding hydro derivatives (**11a**, **11b**, **14a**, **14b**, and **16a**, **16b**) in CH_2Cl_2. After the solution was stirred at the same temperature for 30 min, a 60% HPF_6 solution was added to the mixture. After stirring at room temperature for an additional 15 min, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was crystallized from CH_2Cl_2 and Et_2O. The precipitated crystals were collected by filtration, washed with Et_2O, and dried in vacuo to give the corresponding methyl cations (**4a**$^{4+}$, **4b**$^{4+}$, **5a**$^{2+}$, **5b**$^{2+}$, and **6a**$^+$, **6b**$^+$) as hexafluorophosphate salts.

1,2,4,5-Tetrakis(phenylethynyl)benzene-4′,4″,4‴,4⁗-tetrayl-tetrakis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] tetrakis-(hexafluorophosphate) ($4a^{4+}\cdot 4PF_6^-$). The general procedure was followed by using DDQ (27 mg, 0.12 mmol), **11a** (60 mg, 0.025

mmol), and 60% HPF_6 (1.0 mL) in CH_2Cl_2 (10 mL). Recrystallization from CH_2Cl_2/ether gave **4a**$^{4+}$·$4PF_6^-$ (59 mg, 80%): black powder; mp 208.4−209.1 °C dec (CH_2Cl_2/ether); MS (ESI positive) *m/z* (relative intensity) 1363 ($M^{2+} - 2PF_6$, 13%), 860 ($M^{3+} - 3PF_6$, 38), 609 ($M^{4+} - 4PF_6$, 38); HRMS calcd for $C_{186}H_{202}P_2F_{12}^{2+}$ 1362.7540, found 1362.7538; HRMS calcd for $C_{186}H_{202}PF_6^{3+}$ 860.1811, found 860.1812; HRMS calcd for $C_{186}H_{202}^{4+}$ 608.8946, found 608.8943; IR (KBr disk) ν_{max} 1478, 1418, 1335, 1314, 1242, 841 (s, PF_6^-), 558 (m, PF_6^-) cm^{-1}; UV−vis (CH_3CN) λ_{max}, nm (log ϵ) 236 (5.21), 268 sh (5.11), 304 (5.19), 314 (5.18), 371 sh (5.00), 400 (4.97), 425 sh (4.88), 502 (4.87), 644 sh (4.90), 692 (5.17); ^{1}H NMR (600 MHz, $CDCl_3$, 55 °C) δ =8.97 (d, 8H, J = 11.0 Hz, $H_{4''}$), 8.09 (dd, 8H, J = 11.0, 1.4 Hz, $H_{5''}$), 8.04 (s, 2H, $H_{3,6}$), 7.89 (d, 8H, J = 11.0 Hz, $H_{8''}$), 7.88 (d, 8H, J = 6.7 Hz, $H_{2',6'}$ or $H_{3',5'}$), 7.64 (br dd, 8H, J = 11.0, 1.4 Hz, $H_{7''}$), 7.52 (s, 8H, $H_{2''}$), 7.52 (d, 8H, J = 6.7 Hz, $H_{2',6'}$ or $H_{3',5'}$), 1.52 (s, 72H, 3″-*t*-Bu), 1.43 (s, 72H, 6″-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 168.8 ($C_{6''}$), 159.6 (br, C^+), 149.2 ($C_{3''a}$), 148.4 (br, $C_{8''a}$), 147.4 ($C_{3''}$), 142.8 (br, $C_{2''}$), 141.9 (br, $C_{1'}$ or $C_{4'}$), 139.0 ($C_{4''}$), 138.6 ($C_{8''}$), 136.5 ($C_{3,6}$), 134.8 ($C_{2',6'}$ or $C_{3',5'}$), 132.3 ($C_{2',6'}$ or $C_{3',5'}$ and $C_{5''}$), 132.0 ($C_{7''}$), 131.7 (br, $C_{1''}$), 127.1 ($C_{1'}$ or $C_{4'}$), 125.4 ($C_{1,2,4,5}$), 95.9 (C_β), 91.4 (C_α), 39.4 (s, 6″-*t*-Bu), 33.3 (s, 3″-*t*-Bu), 31.5 (q, 6″-*t*-Bu), 31.0 (q, 3″-*t*-Bu). Anal. Calcd for $C_{186}H_{202}P_4F_{24}$·$2H_2O$: C, 73.16; H, 6.80. Found: C, 72.87; H, 6.83.

1,2,4,5-Tetrakis(2-thienylethynyl)benzene-5′,5″,5‴,5⁗-diyltetrakis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] tetrakis(hexafluorophosphate) (4b^{4+}·$4PF_6^-$). The general procedure was followed by using DDQ (31 mg, 0.14 mmol), **11b** (69 mg, 0.028 mmol), and 60% HPF_6 (1.1 mL) in CH_2Cl_2 (11 mL). Recrystallization from CH_2Cl_2/ether gave **4b**$^{4+}$·$4PF_6^-$ (74 mg, 87%): black powder; mp 247.2−250.4 °C dec (CH_2Cl_2/ether); MS (ESI positive) *m/z* (relative intensity) 1375 ($M^{2+} - 2PF_6$, 11%), 868 ($M^{3+} - 3PF_6$, 46), 615 ($M^{4+} - 4PF_6$, 27); HRMS calcd for $C_{178}H_{194}S_4P_2F_{12}^{2+}$ 1374.6668, found 1374.6698; HRMS calcd for $C_{178}H_{194}S_4PF_6^{3+}$ 868.1230, found 868.1227; HRMS calcd for $C_{178}H_{194}S_4^{4+}$ 614.8510, found 614.8510; IR (KBr disk) ν_{max} 1476, 1418, 1335, 868, 843 (s, PF_6^-), 558 (m, PF_6^-) cm^{-1}; UV−vis (CH_3CN) λ_{max}, nm (log ϵ) 240 (5.20), 269 sh (5.15), 304 (5.09), 405 (4.86), 434 sh (4.82), 565 (5.07), 652 sh (5.00), 699 (5.15); ^{1}H NMR (600 MHz, CD_3CN, 70 °C) δ = 9.05 (d, 8H, J = 11.0 Hz, $H_{4''}$), 8.15 (d, 8H, J = 11.0 Hz, $H_{5''}$), 7.92 (br s, 2H, $H_{3,6}$), 7.82 (s, 8H, $H_{2''}$), 7.79 (d, 8H, J = 10.9 Hz, $H_{8''}$), 7.65 (d, 4H, J = 3.4 Hz, $H_{3'}$), 7.64 (d, 8H, J = 10.9 Hz, $H_{7''}$), 7.38 (d, 4H, J = 3.4 Hz, $H_{4'}$), 1.54 (s, 72H, 3″-*t*-Bu), 1.38 (s, 72H, 6″-*t*-Bu); ^{13}C NMR (150 MHz, CD_3CN, 70 °C) δ = 169.4 ($C_{6''}$), 149.3 (C^+), 149.1 ($C_{3''a}$), 148.7 ($C_{8''a}$), 147.8 ($C_{3''}$), 147.7 ($C_{2'}$), 141.7 ($C_{2''}$), 139.7 ($C_{4''}$), 139.1 ($C_{4'}$), 138.5 ($C_{8''}$), 135.7 ($C_{3'}$), 135.5 ($C_{3,6}$), 133.5 ($C_{5'}$), 132.6 ($C_{5''}$), 132.2 ($C_{7''}$), 131.4 ($C_{1''}$), 125.3 ($C_{1,2,4,5}$), 96.2 (C_α), 89.9 (C_β), 39.3 (s, 6″-*t*-Bu), 33.3 (s, 3″-*t*-Bu), 30.9 (q, 6″-*t*-Bu), 30.6 (q, 3″-*t*-Bu). Anal. Calcd for $C_{178}H_{194}S_4P_4F_{24}$·$2H_2O$: C, 69.47; H, 6.48; S, 4.17. Found: C, 69.34; H, 6.49; S, 3.83.

1,4-Bis(phenylethynyl)benzene-4′,4″-diylbis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate) (5a^{2+}·$2PF_6^-$). The general procedure was followed by using DDQ (35 mg, 0.15 mmol), **14a** (82 mg, 0.065 mmol), and 60% HPF_6 (0.6 mL) in CH_2Cl_2 (6 mL). Recrystallization from CH_2Cl_2/ether gave **5a**$^{2+}$·$2PF_6^-$ (79 mg, 78%): black powder; mp 248.6−253.4 °C dec (CH_2Cl_2/ether); MS (ESI positive) *m/z* (relative intensity) 1402 ($M^+ - PF_6$, 4%), 628 ($M^{2+} - 2PF_6$, 84); HRMS calcd for $C_{96}H_{104}PF_6^+$ 1401.7774, found 1401.7793; HRMS calcd for $C_{96}H_{104}^{2+}$ 628.4064, found 628.4059; IR (KBr disk) ν_{max} 1476, 1335, 1314, 1242, 870, 841 (s, PF_6^-), 558 (m, PF_6^-) cm^{-1}; UV−vis (CH_3CN) λ_{max}, nm (log ϵ) 231 (4.90), 240 sh (4.89), 268 sh (4.78), 305 sh (4.89), 317 (4.90), 407 (4.62), 420 sh (4.61), 502 (4.57), 643 sh (4.62), 689 (4.90); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.04 (d, 4H, J = 11.0 Hz, $H_{4''}$), 8.16 (dd, 4H, J = 11.0, 1.4 Hz, $H_{5''}$), 7.90 (br d, 4H, J = 10.7 Hz, $H_{8''}$), 7.77 (br d, 4H, J = 6.8 Hz, $H_{2',6'}$ or $H_{3',5'}$), 7.68 (br dd, 4H, J = 10.7, 1.4 Hz, $H_{7''}$), 7.65 (s, 4H, $H_{2,3,5,6}$), 7.54 (br s, 4H, $H_{2''}$), 7.48 (br d, 4H, J = 6.8 Hz, $H_{2',6'}$ or $H_{3',5'}$), 1.58 (s, 36H, 3″-*t*-Bu), 1.47 (s, 36H, 6″-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 169.1 ($C_{6''}$), 159.5 (br, C^+), 149.3 ($C_{3''a}$), 148.4 (br, $C_{8''a}$), 147.5 ($C_{3''}$), 142.6 (br, $C_{2''}$), 141.4 (br, $C_{1'}$ or $C_{4'}$), 139.2 ($C_{4''}$), 138.6 ($C_{8''}$), 134.6 ($C_{2',6'}$ or $C_{3',5'}$), 132.4 ($C_{5''}$), 132.1 ($C_{2',6'}$ or $C_{3',5'}$ and $C_{7''}$), 132.0 ($C_{2,3,5,6}$), 131.6 (br, $C_{1''}$), 127.7 (br, $C_{1'}$ or $C_{4'}$), 123.1 ($C_{1,4}$), 93.7 (C_α), 91.1 (C_β), 39.5 (s, 6″-*t*-Bu), 33.4 (s, 3″-*t*-Bu), 31.6 (q, 6″-*t*-Bu), 31.1 (q, 3″-*t*-Bu). Anal. Calcd for $C_{96}H_{104}P_2F_{12}$·H_2O: C, 73.64; H, 6.82. Found: C, 73.32; H, 6.95.

1,4-Bis(2-thienylethynyl)benzene-5′,5″-diylbis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium]bis(hexafluorophosphate) (5b^{2+}·$2PF_6^-$). The general procedure was followed by using DDQ (21 mg, 0.093 mmol), **14b** (50 mg, 0.039 mmol), and 60% HPF_6 (0.8 mL) in CH_2Cl_2 (8 mL). Recrystallization from CH_2Cl_2/ether gave **5b**$^{2+}$·$2PF_6^-$ (46 mg, 75%): black powder; mp 222.5−227.1 °C dec (CH_2Cl_2/ether); MS (ESI positive) *m/z* (relative intensity) 1414 ($M^+ - PF_6$, 4%), 634 ($M^{2+} - 2PF_6$, 84); HRMS calcd for $C_{92}H_{100}S_2PF^+$ 1413.6903, found 1413.6917; HRMS calcd for $C_{92}H_{100}S_2^{2+}$ 634.3628, found 634.3626; IR (KBr disk) ν_{max} 1476, 1420, 1335, 841 (s, PF_6^-), 558 (m, PF_6^-) cm^{-1}; UV−vis (CH_3CN) λ_{max}, nm (log ϵ) 236 (4.91), 268 sh (4.83), 302 (4.82), 333 sh (4.76), 407 (4.49), 436 (4.49), 564 (4.85), 650 sh (4.61), 700 (4.86); ^{1}H NMR (600 MHz, CD_3CN) δ = 9.09 (d, 4H, J = 11.0 Hz, $H_{4''}$), 8.16 (dd, 4H, J = 11.0, 2.1 Hz, $H_{5''}$), 7.85 (d, 4H, J = 10.8 Hz, $H_{8''}$), 7.84 (s, 4H, $H_{2''}$), 7.67 (dd, 4H, J = 10.8, 2.1 Hz, $H_{7''}$), 7.65 (d, 2H, J = 4.0 Hz, $H_{3'}$), 7.56 (s, 4H, $H_{2,3,5,6}$), 7.53 (d, 2H, J = 4.0 Hz, $H_{4'}$), 1.58 (s, 36H, 3″-*t*-Bu), 1.39 (s, 36H, 6″-*t*-Bu); ^{13}C NMR (150 MHz, CD_3CN) δ = 169.7 ($C_{6''}$), 150.4 (C^+), 149.6 ($C_{3''a}$), 149.2 ($C_{8''a}$), 148.1 ($C_{3''}$), 147.6 ($C_{2'}$), 142.6 ($C_{2''}$), 140.4 ($C_{4''}$), 140.2 ($C_{4'}$), 139.2 ($C_{8''}$), 136.1 ($C_{3'}$), 135.4 ($C_{5'}$), 133.1 ($C_{5''}$), 132.9 ($C_{7''}$), 132.8 ($C_{2,3,5,6}$), 131.9 ($C_{1''}$), 123.7 ($C_{1,4}$), 99.4 (C_α), 85.7 (C_β), 40.0 (s, 6″-*t*-Bu), 34.1 (s, 3″-*t*-Bu), 31.6 (q, 6″-*t*-Bu), 31.3 (q, 3″-*t*-Bu). Anal. Calcd for $C_{92}H_{100}S_2P_2F_{12}$: C, 70.84; H, 6.46; S, 4.11. Found: C, 71.04; H, 6.67; S, 3.93.

Bis(3,6-di-*tert*-butyl-1-azulenyl)[4-(phenylethynyl)phenyl]-methylium hexafluorophosphate (6a$^+$·PF_6^-). The general procedure was followed by using DDQ (20 mg, 0.088 mmol), **16a** (50 mg, 0.075 mmol), and 60% HPF_6 (0.8 mL) in CH_2Cl_2 (8 mL). Recrystallization from CH_2Cl_2/hexane gave **6a**$^+$·PF_6^- (53 mg, 87%): black powder; mp 279.6−279.9 °C (CH_2Cl_2/hexane); MS (ESI positive) *m/z* (relative intensity) 667 ($M^+ - PF_6$, 100%); HRMS calcd for $C_{51}H_{55}^+$ 667.4298, found 667.4298; IR (KBr disk) ν_{max} 1476, 1335, 1314, 1242, 868, 841 (s, PF_6^-), 558 (m, PF_6^-) cm^{-1}; UV−vis (CH_3CN) λ_{max}, nm (log ϵ) 224 sh (4.65), 240 (4.67), 270 (4.63), 301 (4.70), 374 sh (4.24), 398 (4.36), 419 sh (4.27), 493 (4.16), 640 sh (4.36), 687 (4.65); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.05 (d, 2H, J = 11.0 Hz, H_4), 8.17 (dd, 2H, J = 11.0, 1.9 Hz, H_5), 7.89 (br d, 2H, J = 10.7 Hz, H_8), 7.75 (br d, 2H, J = 7.4 Hz, $H_{2',6'}$ or $H_{3',5'}$), 7.67 (br dd, 2H, J = 10.7, 1.9 Hz, H_7), 7.62−7.60 (m, 2H, $H_{2'',6''}$), 7.53 (br s, 2H, H_2), 7.46 (br d, 2H, J = 7.4 Hz, $H_{2',6'}$ or $H_{3',5'}$), 7.42−7.41 (m, 3H, $H_{3'',4'',5''}$), 1.58 (s, 18H, 3-*t*-Bu), 1.46 (s, 18H, 6-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 169.1 (C_6), 159.5 (br, C^+), 149.3 (C_{3a}), 148.4 (br, C_{8a}), 147.5 (C_3), 142.5 (br, C_2), 141.1 (br, $C_{1'}$ or $C_{4'}$), 139.3 (C_4), 138.6 (C_8), 134.6 ($C_{2',6'}$ or $C_{3',5'}$), 132.5 (C_5), 132.1 (C_7 and $C_{2',6'}$ or $C_{3',5'}$), 131.9 ($C_{2'',6''}$), 131.6 (br, C_1), 129.1 ($C_{4''}$), 128.6 ($C_{3'',5''}$), 128.1 (br, $C_{1'}$ or $C_{4'}$), 122.5 ($C_{1''}$), 94.2 (C_β), 88.8 (C_α), 39.5 (s, 6-*t*-Bu), 33.4 (s, 3-*t*-Bu), 31.5 (q, 6-*t*-Bu), 31.1 (q, 3-*t*-Bu). Anal. Calcd for $C_{51}H_{55}PF_6$·1/$2H_2O$: C, 74.52; H, 6.87. Found: C, 74.64; H, 7.10.

Bis(3,6-di-*tert*-butyl-1-azulenyl)[5-(phenylethynyl)-2-thienyl]-methylium hexafluorophosphate (6b$^+$·PF_6^-). The general procedure was followed by using DDQ (18 mg, 0.079 mmol), **16b** (44 mg, 0.065 mmol), and 60% HPF_6 (0.7 mL) in CH_2Cl_2 (7 mL). Recrystallization from CH_2Cl_2/ether gave **6b**$^+$·PF_6^- (46 mg, 86%): black powder; mp 209.3−212.2 °C (CH_2Cl_2/ether); MS (ESI positive) *m/z* (relative intensity) 673 ($M^+ - PF_6$, 100%); HRMS calcd for $C_{49}H_{53}S^+$ 673.3862, found 673.3862; IR (KBr disk) ν_{max} 1474, 1420, 1335, 841 (s, PF_6^-), 558 (m, PF_6^-) cm^{-1}; UV−vis (CH_3CN) λ_{max}, nm (log ϵ) 236 (4.66), 270 (4.57), 303 (4.62), 330 sh (4.48), 383 sh (4.08), 407 (4.21), 430 (4.20), 544 (4.47), 649 sh

(4.29), 698 (4.58); ^{1}H NMR (600 MHz, CD_3CN) δ = 9.08 (d, 2H, J = 10.9 Hz, H_4), 8.15 (dd, 2H, J = 10.9, 1.1 Hz, H_5), 7.85 (d, 2H, J = 10.7 Hz, H_8), 7.82 (br s, 2H, H_2), 7.66 (br d, 2H, J = 10.7 Hz, H_7), 7.61 (br s, 1H, $H_{4'}$), 7.55−7.52 (br m, 2H, $H_{2'',6''}$), 7.50 (br s, 1H, $H_{3'}$), 7.47−7.40 (br m, 3H, $H_{3'',4'',5''}$), 1.57 (s, 18H, 3-*t*-Bu), 1.38 (s, 18H, 6-*t*-Bu); ^{13}C NMR (150 MHz, CD_3CN) δ = 169.7 (C_6), 150.6 (C^+), 149.5 (C_{3a}), 149.1 (C_{8a}), 148.0 (C_3), 147.0 ($C_{5'}$), 142.7 (C_2), 140.3 (C_4), 140.2 ($C_{3'}$), 139.2 (C_8), 136.1 ($C_{2'}$), 135.6 ($C_{4'}$), 133.0 (C_5), 132.8 (C_7), 132.5 ($C_{2'',6''}$), 131.8 (C_1), 130.8 ($C_{4''}$), 129.9 ($C_{3'',5''}$), 122.6 ($C_{1''}$), 100.2 (C_β), 83.1 (C_α), 40.0 (s, 6-*t*-Bu), 34.1 (s, 3-*t*-Bu), 31.6 (q, 6-*t*-Bu), 31.3 (q, 3-*t*-Bu). Anal. Calcd for $C_{49}H_{53}SPF_6$: C, 71.86; H, 6.52; S, 3.92. Found: C, 71.66; H, 6.66; S, 3.69.

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Supporting Information Available: General and electrochemical measurements details, details of CV data, CV waves of **5a**$^{2+}$, **5b**$^{2+}$ and **6a**$^+$, **6b**$^+$, spectroelectrograms of **4a**$^{4+}$, **4b**$^{4+}$, **5a**$^{2+}$, **5b**$^{2+}$, and **6a**$^+$, **6b**$^+$, and copies of ^{1}H and ^{13}C NMR spectra of reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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