High Stabilities of Di(1-azulenyl)(4-hydroxyphenyl)methyl Hexafluorophosphates and Polarized Properties of α,α-Di(1-azulenyl)-1,4-benzoquinone Methides

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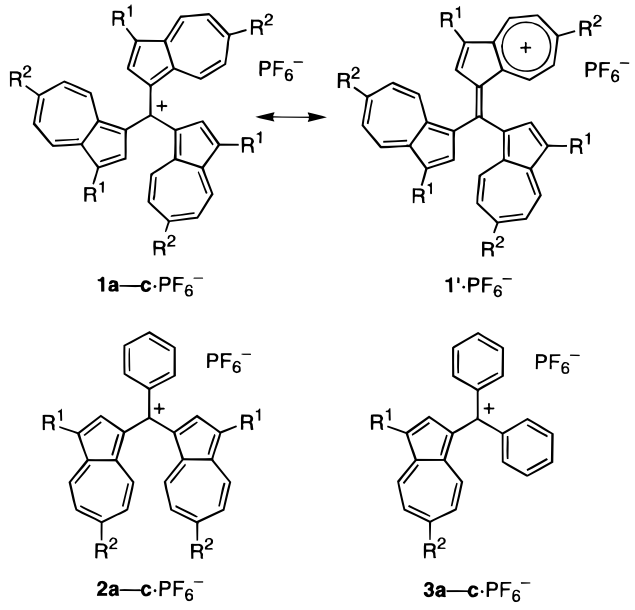
Acid-catalyzed condensation of azulenes **8a**−**c** with 4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde leads to substituted di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methanes **7a**− **f**, which are easily converted into substituted di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl cations **5a**−**f** by oxidation with DDQ. The spectroscopic data are consistent with the protonated cationic structures of **5a**−**f**. The electrochemical reduction of **5a**−**f** showed a reversible wave at −0.74 to −0.86 V (V vs Ag/Ag^+) upon cyclic voltammetry (CV), although **5d** and **5e** showed an irreversible wave at −0.79 V. The relatively high reduction potentials of **5a**−**f**, compared with those of di(1-azulenyl)phenylmethyl cations **2a**−**c**, exhibit the stabilization by 4-hydroxy substituents on the phenyl groups. These salts (**5a**−**f**·PF_6^-) bearing 4-hydroxyl groups on the phenyl rings have been converted by treatment with bases to α,α-di(1-azulenyl)-1,4-benzoquinone methides **6a**−**f**, which revert to **5a**−**f**·PF_6^- upon reprotonation with HPF_6. These quinone methides (**6a**−**f**) are highly polarized by the extreme-electrodonating properties of 1-azulenyl groups. The highly polarized properties of **6a**−**f** reflected to the high pK_a values of their conjugate acids (**5a**−**c**, 6.5−7.1, and **5d**−**f**, 3.4−3.8). The strong solvatochromic effects also provide strong evidence of a large contribution of dipolar forms (**6′**) in the ground state. The relatively low oxidation potentials of **6a**−**f** (+0.35 to +0.47 V vs Ag/Ag^+) reflected facile formation of phenoxy radical cations, stabilized by two 1-azulenyl groups.

Introduction

We have recently reported the synthesis and properties of a series of azulene analogs of triphenylmethyl cation, i.e., tri(1-azulenyl)methyl (**1a**), di(1-azulenyl)phenylmethyl (**2a**), and (1-azulenyl)diphenylmethyl (**3a**) hexafluorophosphate and their derivatives (e.g., **1b**−**c**, **2b**−**c**, and **3b**−**c**) (Chart 1).[1] These cations showed extreme stabilities with high pK_R^+ values (e.g., **1a**, 11.3; **2a**, 10.5; and **3a**, 3.0, respectively).[1a−c,2] In particular, the methyl cations, which were stabilized by three (**1a**−**c**) or two (**2a**−**c**) azulene rings, exhibited extraordinary thermodynamic stabilities. The high stabilities of these cations are rationalized by the large π-conjugative effect of 1-azulenyl groups with the cationic carbon (e.g., **1′**). Thus, the relatively low stability of the cations **1a**−**c**, compared with the expectation based on the stabilities of the cations **2a**−**c** and **3a**−**c**, is explained by the steric effects among the three azulene rings. To enhance the thermodynamic stabilities, the third azulene rings of **1a**−**c** should be replaced with the less hindered substituents. The higher stabilities of di(1-azulenyl)[4-(dimethylamino)phenyl]methyl cations (**4a**−**c**)[11] than **1a** are in accord with these postulations (Chart 2).[3]

Chart 1



In this paper, we report the stabilizing abilities of 4-hydroxyphenyl groups as extra stabilizing groups of di(1-azulenyl)methylium ions, i.e., di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl hexafluorophosphates and their derivatives (**5a**−**f**·PF_6^-) (Chart

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(1) (a) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1991**, *32*, 773−776. (b) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 751−754. (c) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409−1436. (d) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 3723−3726. (e) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2011−2016. (f) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2639−2648. (g) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Chem. Lett.* **1995**, 475−476. (h) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3611−3620. (i) Ito, S.; Kikuchi, S.; Morita, N.; Asao, T. *Chem. Lett.* **1966**, 175−176. (j) Asao, T.; Ito, S. *J. Synth. Org. Chem.* **1996**, *54*, 2−14. (k) Ito, S.; Morita, N.; Asao, T. *J. Org. Chem.* **1996**, *61*, 5077−5082. (l) Ito, S.; Kobayashi, H.; Kikuchi, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3225−3237.

(2) The K_R^+ scale is defined by the equilibrium constant for the reaction $R^+ + 2H_2O = ROH + H_3O^+$ of a carbocation and a water molecule ($K_R^+ = [ROH][H_3O^+]/[R^+]$). The pK_R^+ scales stand for the carbocation in aqueous solution. Thus, $pK_R^+ = -\log K_R^+$. The larger pK_R^+ index indicates a smaller K_R^+ value and in turn a higher stability of the carbocation.

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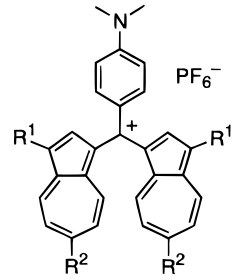
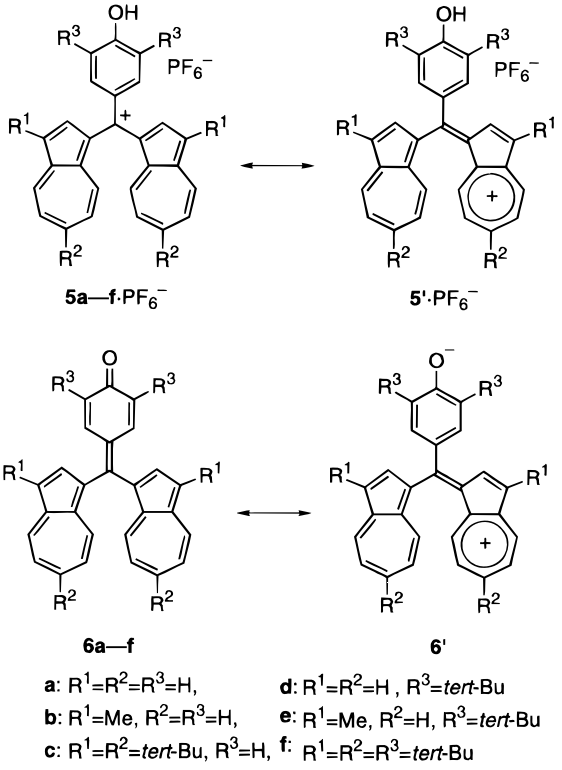
Chart 2



4a·PF_6^-: R^1=R^2=H
4b·PF_6^-: R^1=Me, R^2=H
4c·PF_6^-: R^1=R^2=*tert*-Bu

Chart 3



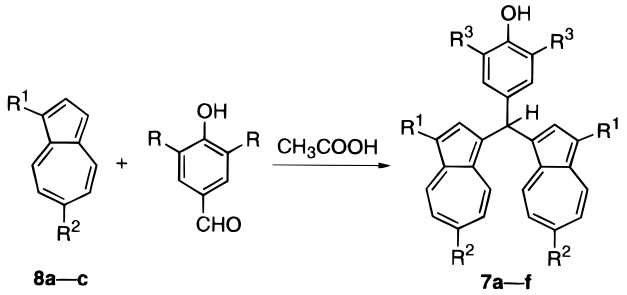
5a—f·PF_6^- **5'**·PF_6^-

6a—f **6'**

a: R^1=R^2=R^3=H, **d**: R^1=R^2=H, R^3=*tert*-Bu
b: R^1=Me, R^2=R^3=H, **e**: R^1=Me, R^2=H, R^3=*tert*-Bu
c: R^1=R^2=*tert*-Bu, R^3=H, **f**: R^1=R^2=R^3=*tert*-Bu

3). Although the stabilizing abilities of the 4-hydroxyphenyl group should be lower than those of the 4-(dimethylamino)phenyl group,[5] the group will also stabilize di(1-azulenyl)methylium ions owing to the mesomeric effect of the 4-hydroxy substituent, effectively. The major distinctions of these cations (**5a**−**f**) may be made as to attain equilibrium with α,α-di(1-azulenyl)-1,4-benzoquinone methides **6a**−**f** under basic conditions. Although numerous substituted quinone methides have been described in the literature,[7] **6a**−**f** will be highly polarized by the extreme-electrodonating properties of 1-azulenyl

Scheme 1



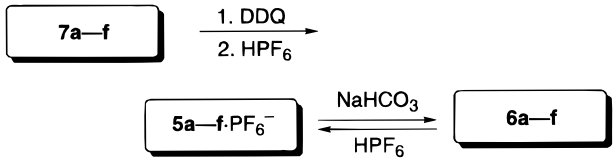
8a—c **7a—f**

groups, which stabilized the protonated forms of **6a**−**f** effectively by the large π-conjugative effect (Chart 3). In this paper, we also report the preparation and the highly polarized properties of **6a**−**f**, which were characterized by large solvatochromic effect, the high pK_a values of their conjugate acids, and their redox behaviors.

Results and Discussion

Synthesis of the Salts 5a−f·PF_6^-. The synthesis of di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl cations **5a**−**f** was accomplished by the hydride abstraction from the appropriate di(1-azulenyl)-(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methanes **7a**−**f** (Scheme 1). The reaction of azulenes **8a**−**c**[1a−c] with 4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxybenzaldehydes in a 4:1 mixture of acetic acid and dichloromethane solution at room temperature for 48 h afforded **7a**−**f** in 18−100% yields, together with diastereomeric mixtures of 1,3-bis[(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl]azulenes (**9a**,**b**, 16%, and **9c**,**d**, 32%), in the case of **8a** (Table 1). The diastereomeric mixture of **9a**,**b** was separable by column chromatography on silica gel (**9a**, 7.7%, and **9b**, 7.0%), whereas that of **9c**,**d**[8] was inseparable by silica gel and by gel permeation chromatography (GPC). Acceleration of the reaction by warming to 60 °C or using high pressure (10 kbar), which gave satisfactory results for the reaction of **8a**−**c** with 4-(dimethylamino)benzaldehyde,[11] decreased the yields of the desired **7a**−**f** and in some cases also afforded undesired byproducts (Chart 4) such as (3-methyl- and 3,6-di-*tert*-butyl-1-azulenyl)(4-hydroxyphenyl)methanes (**10a**,**b**) and α-(3,6-di-*tert*-butyl-1-azulenyl)-3,5-di-*tert*-butyl-1,5-benzoquinone methide (**11**) in considerable yields (Table 1). Hydride abstraction[1] of **7a**−**f** with DDQ in dichloromethane at room temperature followed by the addition of a 60% aqueous HPF_6 solution yielded the salts **5a**−**f**·PF_6^- in 92−100% yield. These new salts **5a**−**f**·PF_6^- were stable deep blue crystals in solution.

Scheme 2



Spectroscopic Properties of the Salts 5a−f·PF_6^-. High-resolution mass spectra of **5a**−**f**·PF_6^- ionized by

(3) Since the pK_R^+ value of tri(1-azulenyl)methyl cation (**1a**) is fairly larger than that of tris[4-(dimethylamino)phenyl]methyl cation (pK_R^+ 9.36),[4] the stabilizing ability of 4-(dimethylamino)phenyl groups must be considerably lower than that of 1-azulenyl groups. However, the pK_R^+ values of **4a** were higher than that of **1a**. This is in accord with these postulations.

(4) (a) Goldacre, R. J.; Phillips, J. N. *J. Chem. Soc.* **1949**, 1724−1732. (b) Deno, N. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3051−3054.

(5) The hydroxyl substituents stabilize carbocations to a considerable extent, e.g., the pK_R^+ value of tris(4-hydoxyphenyl)methyl cation (pK_R^+ 1.97) is fairly larger than that of triphenylmethyl cation (pK_R^+ −6.44):[6] Deno, N. C.; Evans, W. L. *J. Am. Chem. Soc.* **1957**, *79*, 5804−5807.

(6) Arnett, E. M.; Busshick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564−1571.

(7) See, e.g.: (a) Zanarotti, A. *Tetrahedron Lett.* **1982**, *23*, 3815−3818. (b) Becker, H.-D. *J. Org. Chem.* **1967**, *32*, 2943−2947.

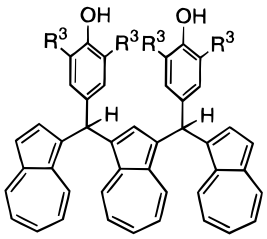
(8) The diastereomeric ratio of **9c**:**9d** was 5:3, which was determined by the ^{1}H NMR spectrum.

Table 1. Acid-Catalyzed Condensation of 8a−c with 4-Hydroxy- and 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde

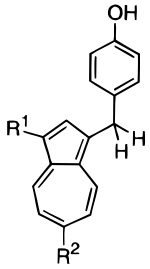
	azulene **8a−c**			aldehyde						recovered
entry	R^1	R^2	mmol	R	mmol	condns[a]	yield[b] (%)			azulene (%)
1	H	H	10	H	5	A	18 (**7a**)	7.7 (**9a**)	7.0 (**9b**)	(27)
2			10		2.5	B	2.0 (**7a**)			(16)
3	Me	H	5	H	5	A	96 (**7b**)			(1.8)
4			5		2.6	B	27 (**7b**)	12 (**10a**)		
5	*t*-Bu	*t*-Bu	5	H	5	A	85 (**7c**)			
6			5		2.6	B	56 (**7c**)			(14)
7			5		5	C	60 (**7c**)	5.8 (**10b**)		
8	H	H	10	*t*-Bu	5	A	34 (**7d**)	32 (**9c**,**d**)		(49)
9			10		2.5	B	15 (**7d**)	16 (**9c**,**d**)		(42)
10	Me	H	5	*t*-Bu	5	A	100 (**7e**)			(21)
11			5		2.6	B	60 (**7e**)			(7.6)
12	*t*-Bu	*t*-Bu	5	*t*-Bu	5	A	80 (**7d**)			
13			5		2.6	B	57 (**7d**)			(48)
14			5		5	C	39 (**7d**)	27 (**11**)		

[a] Conditions A: at room temperature for 48 h in acetic acid/dichloromethane (4:1). Conditions B: at 10 kbar, 30 °C for 24 h in acetic acid/dichloromethane (1:1). Conditions C: at 60 °C for 24 h in acetic acid/dichloromethane (4:1). [b] Isolated yields based on azulenes **8a−c** reacted.

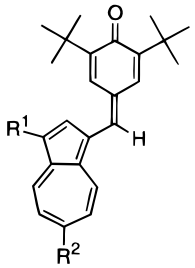
Chart 4



9a,**b**: R^3=H
9c,**d**: R^3=*tert*-Bu



10a: R^1=Me, R^2=H
10b: R^1=R^2=*tert*-Bu



11: R^1=R^2=*tert*-Bu

FAB showed the correct $M^+ - PF_6$ ion peaks, which indicated the ionic structure of these products. The characteristic bands for the counter ion PF_6^- were observed at 841−843 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported the ionic structure of these compounds (**5a**−**f**·PF_6^-).[1] UV−vis spectra of **5a** in acetonitrile along with those of the related phenyl analogs **2a** was shown in Figure 1. The strong absorptions of **5a**−**f** in the visible region exhibited a hypsochromic shift by 15−19 nm, compared with those of **2a**−**c**.[1c] The ^{1}H NMR chemical shift of the methine protons of **7a**−**f** was slightly upfield compared with those of di(1-azulenyl)phenylmethane and its related derivatives. The signals disappeared on the ^{1}H NMR spectra of **5a**−**f**. Thus, the ^{1}H NMR spectra also indicated a ionic structure of these compounds. These results are in accordance with the spectroscopic properties of di(1-azulenyl)[4-(dimethylamino)phenyl]methyl cations **4a**−**c**. The spectroscopic properties exhibited the protonated ionic structures of quinone methides **6a**−**f**.

Redox Properties of the Cations 5a−f. As a criterion of high stabilities of the cations **5a**−**f**, the redox potentials (V vs Ag/Ag^+) are measured by cyclic voltammetry (CV). The redox potentials of **5a**−**f** and those of the comparative compounds **1a**−**c** and **2a**−**c** are summarized in Table 2.[1c] The redox behavior of **5a**−**f** is almost identical to the behavior of the phenyl analogs

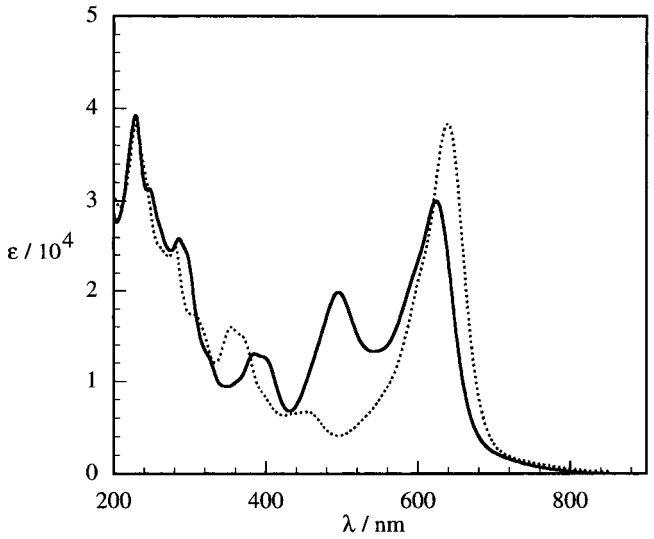


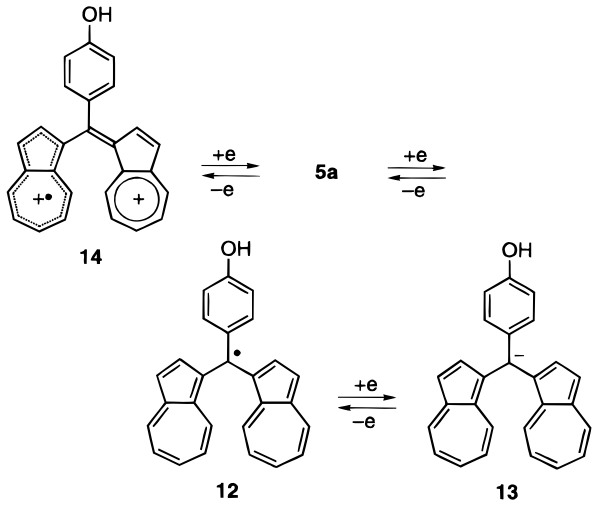
Figure 1. UV−vis spectra of cation **5a** (solid line) and cation **2a** (broken line) in acetonitrile.

Table 2. pK_R^+ Values and Redox Potentials[a] of the Cations 5a−f, 1a−c, and 2a−c[1c]

	pK_R^+	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}
5a		−0.74	(−1.62)	(+1.02)	
5b		(−0.79)		(+0.89)	
5c		−0.85	(−1.76)	+0.87	(+1.33)
5d		−0.74	(−1.50)	(+0.98)	
5e		(−0.79)		(+0.90)	
5f		−0.86	(−1.69)	(+0.92)	
1a	11.3	−0.78	(−1.56)	(+0.98)	(+1.07)
1b	11.4	−0.82	(−1.59)	(+0.85)	(+0.94)
1c	14.3	−0.91	(−1.72)	+0.84	+0.95
2a	10.5	−0.66	(−1.52)	(+1.04)	
2b	10.8	−0.77	(−1.57)	(+0.90)	
2c	12.4	−0.78	(−1.64)	+0.88	(+1.38)

[a] The redox potentials were measured by cyclic voltammetry (V vs Ag/Ag^+, 0.1 M Et_4NClO_4 in acetonitrile, Pt electrode, and scan rate 100 mV s^{-1}). In the case of irreversible waves, which are shown in parentheses, E^{ox} and E^{red} were calculated as E_{pa} (anodic peak potential) −0.03 and E_{pc} (cathodic peak potential) +0.03 V, respectively.

Scheme 3



2a−**c**, except for the enlargement of the reduction potentials owing to the stabilization by the 4-hydroxyl substituents. The reduction of **5a**−**f** in acetonitrile showed a reversible wave at −0.74 to −0.86 V and an irreversible wave at −1.50 to −1.76 V upon the CV, except for **5b** and **5e**, which showed an irreversible wave at −0.79 V. These two waves are ascribed to the formation of a radical and an anion species such as **12** and **13**, respectively (Scheme 3). The more negative reduction potentials of **5a**−**f** compared to those of **2a**−**c** by 0.02−0.08 V indicate the stabilization of the methyl cations by the 4-hydroxy substituent on the phenyl groups. The most negative reduction potential of the *tert*-butyl derivatives (**5c**, −0.85 V, and **5f**, −0.86 V) among these compounds corresponds to their high electrochemical stability. The potentials are comparable with those of the tri(1-azulenyl)methyl cations **1a**−**c**. Although the thermodynamic stabilities (pK_R^+ values) of these cations **5a**−**f** could not be determined due to the equilibrium with the quinone methides **6a**−**f**, the redox potentials of **5a**−**f** indicate that the 4-hydroxy substituents on the phenyl groups stabilize the cations effectively by their mesomeric effects. The high stabilities of **5a**−**f** are attributable to the high contribution of the azulenium ion structures (**5′**) in addition to the electron-donating properties of the less hindered 4-hydroxyphenyl groups.[5]

Although the oxidation of 4-(dimethylamino)phenyl derivatives **4a**−**c** exhibited voltammograms that were characterized by a barely separated two-step oxidation wave at +0.75 to +0.87 and +0.89 to +1.01 V,[11] **5a**−**f** exhibited similar oxidation properties with those of the corresponding phenyl derivatives **2a**−**c**.[1c] The oxidation potentials of **5a**−**f** were also comparable with those of **2a**−**c**. The oxidation of **5a**−**f** showed a wave at +0.87 to +1.02 V, which is ascribed to the oxidation of an azulene ring to give dication radical species such as **14** (Scheme 3). The *tert*-butyl substituents on the azulene rings also stabilize the oxidation states of these cations, as indicated by the oxidation of **5c**. The oxidation of **5c** exhibited an irreversible E_2^{ox} wave at +1.33 V, which is in the potential range comparable with those of **2c**. The oxidation properties of **5a**−**f** did not show any evidence of the contribution of (4-methylidene-2,5-cyclohexadien-1-ylidene)oxonium structures.[9]

Neutralization of the Salts 5a−**f·PF$_6^-$.** These salts **5a**−**f**·PF_6^- cause a deprotonation upon a treatment with bases, forming α,α-di(1-azulenyl)-1,4-benzoquinone methides **6a**−**f**. Neutralization of **5a**−**f**·PF_6^- with 5% aqueous $NaHCO_3$ solution afforded the quinone methides **6a**−**f** in 78−92% yield (Scheme 2). All new quinone methides **6a**−**f** are stable crystalline compounds of dark brown color. Protonation of **6a**−**f** with HPF_6 regenerated the corresponding (4-hydroxyphenyl)methyl hexafluorophosphates **5a**−**f**·PF_6^- in 92−100% yield.

Table 3. pK_a Values[a] of the Protonated Cations 5a−f and Redox Potentials[b] of the Quinone Methides 6a−f

	pK_a		E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}
5a	6.5	**6a**	−1.38	(−1.75)	(+0.45)	
5b	7.1	**6b**	−1.39	(−1.80)	(+0.41)	
5c	7.0	**6c**	−1.41	(−1.93)	(+0.36)	
5d	3.4	**6d**	(−1.55)		+0.47	(+0.95)
5e	3.7	**6e**	(−1.56)		+0.40	(+0.72)
5f	3.8	**6f**	−1.57	(−2.03)	+0.35	(+0.74)

[a] The pK_a values were determined by spectrophotometrically at 25 °C in a buffered solution prepared in 50% aqueous acetonitrile. [b] Determined as indicated in Table 2.

pK_a Values of the Conjugate Acids of the Quinone Methides 6a−f. The high pK_a values of the conjugate acids of **6a**−**f** provide a criterion of high stabilities of the protonated forms of **6a**−**f** and of a large contribution of polar canonical forms **6′**. The pK_a values of the conjugate acids **5a**−**f** were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous acetonitrile.[1c,10] The pK_a values of **5a**−**f**, particularly those of **5a**−**c** (pK_a 6.5−7.1), are appreciably high (Table 3).[11] The values exhibit that the protonation of **6a**−**c** causes in almost neutral conditions. This provides strong evidence of a large contribution of dipolar forms (e.g., **6′**) of **6a**−**f** in the ground state. The relatively low pK_a values for **5d**−**f**, compared with those of **5a**−**c**, indicate the steric effects of the *tert*-butyl substituents on the six-membered rings, which hinder the protonation of the quinone methides **6a**−**f**. As expected, the 3-methyl and 3,6-di-*tert*-butyl substituents on the azulene rings slightly increase the pK_a values by 0.3−0.6 pK units. The protonation and the neutralization of these compounds **6a**−**f** are approximately reversible. Neutralization of the acidic solutions of **6a**−**f** with NaOH regenerated the absorptions of the quinone methides in the visible region quantitatively.

Solvatochromic Properties of the Quinone Methides 6a−f. The large solvatochromic effects of **6a**−**c** also provides strong evidence of a large contribution of dipolar forms (e.g., **6′**) of **6a**−**f** in the ground state, although **6d**−**f** showed rather weak solvatochromic effects for the steric reasons of the *tert*-butyl substituents on the six-membered rings, which hinder the solvation of the protic solvents as well as the protonation. Compounds **6a**−**c** form solutions that appear deep red in dichloromethane but deep blue in methanol. The marked

(9) The electrochemical oxidation of di(1-azuenyl)[4-(dimethylamino)phenyl]methyl cations **4a**−**c** exhibited voltammograms that were characterized by a barely separated two-step oxidation wave at +0.75 to +0.87 and +0.87 to +1.01 V. This provides the strong evidence of the contribution of dimethyl(4-methylidene-2,5-cyclohexadien-1-ylidene)ammonium structures for **4a**−**c**, which faciliated the oxidation of the two azulene rings.[11]

(10) The pK_a values for **5a**−**f** were determined in a similar manner as the determination of the pK_R^+ values for carbocations: (a) Kerber, R. C.; Hsu, H. M. *J. Am. Chem. Soc.* **1973**, *95*, 3239−3245. (b) Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470−2479.

(11) The pK_a values for the conjugate acid of the majority of carbonyl compounds lie between 0 and −10. For example, the pK_a value for the protonation of acetone is reported as −7.2: Arnett, E. M. *Progr. Phys. Org. Chem.* **1963**, *1*, 223−403.

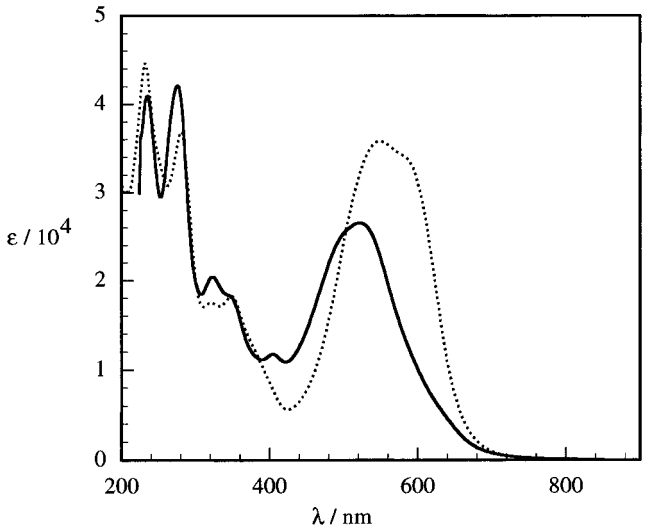


Figure 2. UV−vis spectra of the quinone methide **6a** in dichloromethane (solid line) and in methanol (broken line).

Table 4. Solvatochromic Data for the Longest Wavelength Absorption of 6a−f

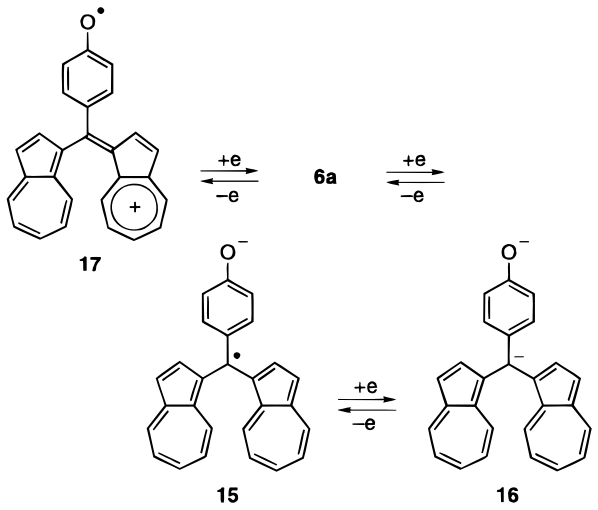
	CH_2Cl_2		MeOH	
	λ_{max}, nm	log ϵ	λ_{max}, nm	log ϵ
6a	522	(4.43)	549	(4.55)
6b	534	(4.49)	594	(4.57)
6c	537	(4.50)	599	(4.47)
6d	507	(4.42)	521	(4.45)
6e	523	(4.43)	529	(4.47)
6f	534	(4.46)	536	(4.26)

solvent dependence of the electronic spectra of **6a**−**f** is illustrated by the data in Table 4, showing the absorption maxima for the lowest-energy electronic transition, and by the spectra of **6a** in Figure 2. The strong absorption of **6a**−**c** in the visible region exhibited an appreciable bathochromic shift by 27, 60, and 62 nm, respectively, on changing the solvent from dichloromethane to methanol. In contrast to the large solvatochromic effects of **6a**−**c**, the longest wavelength absorption of **6d**−**f** showed a slight bathochromic shift within 2−14 nm on changing the solvents. The solvatochromic effects of **6a**−**c** can be rationalized by the stabilization of the excited state by the hydrogen bonding of the quinone methides with the protic solvents. The *tert*-butyl substituents on the six membered rings of **6d**−**f** hinder the solvation of the quinone methides with the polar solvents. This reflects the rather weak solvatochromic effects of **6d**−**f**. In conclusion, the charge-separated ionic forms (**6′**) with "di-(1-azulenyl)methylium ion" character make a remarkable contribution to the resonance hybrid for the ground state.[12]

Redox Properties of the Quinone Methides 6a−f. The redox potentials (V vs Ag/Ag^+) of **6a**−**f** measured by CV in dimethylformamide (DMF) are summarized in Table 3. The redox potentials of **6a**−**f** were apparently distinct from those of **5a**−**f**, as expected. The redox properties of **6a**−**f** can be characterized by rather high reduction potentials and by rather low oxidation potentials, compared with those of their conjugate acids **5a**−**f**. The reduction of **6a**−**f** in DMF showed a reversible

(12) For interesting similar situations for solvatochromic effect of diarylquinocyclopropenes see: (a) Wellman, D. E.; West, R. *J. Am. Chem. Soc.* **1984**, *106*, 355−360. (b) West, W.; Zecher, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 155−161.

Scheme 4



wave at −1.38 to −1.57 V and an irreversible wave at −1.75 to −2.03 V upon the CV, except for **6d** and **6e**, which showed an irreversible wave at −1.55 to −1.56 V. These two waves are ascribed to the formation of a radical and an anion species such as **15** and **16**, respectively (Scheme 4). The more negative reduction potentials of **6d**−**f** than those of **6a**−**c** by about 0.2 V corresponds to the high electrochemical stabilization by the 3′,5′-di-*tert*-butyl substituents on their phenyl groups. The reduction potentials for **6a**−**f** are affected little by the substituents on their azulene rings.

The oxidation of **6a**−**f** showed a wave at +0.35 to +0.47 V, which corresponds to the oxidation of the quinone methide moieties to form phenoxy radical cations such as **17** (Scheme 4). The reversibilities of the waves for **6d**−**f** are due to the stabilization of the phenoxy radicals by the adjacent 3′,5′-di-*tert*-butyl substituents on the phenyl rings. The oxidation of **6d**−**f** also exhibited an irreversible E_2^{ox} wave at +0.72 to +0.95 V.

Conclusions. The stabilities of the cations **5a**−**f** were examined by the redox potentials measured by CV. These cations (**5a**−**f**) exhibited high stabilities with high reduction potentials, which were comparable with those of the tri(1-azulenyl)methyl cations **1a**−**c**. The high stabilization of **5a**−**f** by the 4-hydroxyphenyl groups is attributable to the high contribution of the azulenium ion structures (**5′**) in addition to the electron-donating properties of the less hindered 4-hydroxyphenyl groups.[5] The large solvatochromic effects of **6a**−**c** provide strong evidence of a large contribution of a dipolar form of **6a**−**c** in the ground state, although **6d**−**f** showed little effect due to the steric effect of the *tert*-butyl substituents on the six-membered rings. The dipolar structures of the quinone methides **6a**−**f** also reflect the high pK_a values of their conjugate acids **5a**−**f** owing to the contribution of azulenium ion structures such as **6′**. The high pK_a values for **5a**−**f** are consistent with the high electrochemical stabilities of **5a**−**f**. The relatively low oxidation potentials for **6a**−**f**, compared with those of **5a**−**f**, which correspond to the oxidation of the quinone methide moieties to form phenoxy radical cations, reflect to facile formation of phenoxy radical cations **17**, stabilized by two 1-azulenyl groups.

Experimental Section

General Procedures. Melting points were determined on a micro melting point apparatus and are uncorrected. Mass spectra were usually obtained at 70 eV. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded at 90 MHz (22.5 MHz), at 400 MHz (100 MHz), and/or at 600 MHz (150 MHz). Voltammetry measurements were carried out with an electrochemical workstation equipped with Pt working and auxiliary electrodes, and a reference electrode formed from Ag/$AgNO_3$ (0.01 M) and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte, at the scan rate of 100 mV s^{-1}. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

General Procedure for the Reaction of Azulenes 8a−c with 4-Hydroxy- or 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde at Atmospheric Pressure. A solution of the appropriate azulenes **8a**−**c** (5−10 mmol) and 4-hydroxy- or 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (5 mmol) in a 4:1 mixture of acetic acid and CH_2Cl_2 (50−100 mL) was stirred at room temperature for 48 h or at 60 °C for 12 h under an Ar atmosphere (Table 1). The solvent was removed in vacuo. The residue was diluted with CH_2Cl_2. The organic layer was washed with 5% aqueous $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated in vacuo. The residue was then purified by column chromatography on silica gel and/or GPC to afford the di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methanes **7a**−**f**. The product was further purified by recrystallization.

General Procedure for the High-Pressure Reaction of Azulenes 8a−c with 4-Hydroxybenzaldehyde or 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde. A solution of the appropriate azulenes **8a**−**c** (5 mmol) and 4-hydroxy- or 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (2.5−2.6 mmol) in a 1:1 mixture of acetic acid and CH_2Cl_2 (3.7 mL) was pressurized up to 10 kbar at 30 °C for 24 h (Table 1). The crude material was then purified by column chromatography on silica gel and/or GPC to afford the di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methanes **7a**−**f**.

Di(1-azulenyl)(4-hydroxyphenyl)methane (7a). The general procedure was followed using azulene **8a** (1.28 g, 10.0 mmol) and 4-hydroxybenzaldehyde (612 mg, 5.01 mmol) at room temperature for 48 h. Column chromatography on silica gel with ethyl acetate/CH_2Cl_2 and GPC with $CHCl_3$ afforded the recovered **8a** (348 mg, 27%), the methane **7a** (241 mg, 18%), and a diastereomeric mixture of 1,3-bis[(1-azulenyl)(4-hydroxyphenyl)methyl]azulene (**9a** and **9b**) (236 mg, 16%), which was separable by column chromatography on silica gel with ethyl acetate/CH_2Cl_2 (**9a:** 110 mg, 7.7%; **9b:** 101 mg, 7.0%). When the general procedure was followed using **8a** (1.28 g, 10.0 mmol) and the benzaldehyde (307 mg, 2.51 mmol) in a 50% acetic acid solution of CH_2Cl_2 (9.1 mL) at 10 kbar for 24 h, column chromatography afforded the recovered **8a** (207 mg, 16%) and the methane **7a** (30 mg, 2.0%).

7a: blue prisms; mp 187.0−188.0 °C; MS (70 eV) *m*/*z* (rel inten) 360 (M^+, 100), 359 (37), 267 (27), 265 (40), 231 (38); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.58), 278 (4.87), 350 (4.02), 366 (3.93), 601 (2.83), 655 (2.74); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.271 (d, J = 9.4 Hz, 2H), 8.248 (d, J = 9.7 Hz, 2H), 7.501 (dd, J = 9.9, 9.7 Hz, 2H), 7.440 (d, J = 3.9 Hz, 2H), 7.271 (d, J = 3.9 Hz, 2H), 7.075 (dd, J = 9.7, 9.4 Hz, 2H), 7.008 (d, J = 8.7 Hz, 2H), 6.986 (dd, J = 9.9, 9.7 Hz, 2H), 6.692 (d, J = 8.7 Hz, 2H), 6.685 (s, 1H), 4.773 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.608 (s), 141.023 (s), 138.241 (d), 138.065 (s), 137.331 (d), 136.713 (d), 134.913 (s), 133.683 (d), 133.558 (s), 129.889 (d), 122.485 (d), 121.924 (d), 116.552 (d), 115.045 (d), 41.932 (d). Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 90.10; H, 5.78.

9a (fast eluate): blue crystals; mp 168.0−172.0 °C; MS (70 eV) *m*/*z* (rel inten) 592 (M^+, 1.6), 360 (25), 128 (100); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 239 (4.71), 281 (5.00), 346 (4.13), 366 (4.10), 604 (2.93); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.218 (d, J = 9.7 Hz, 2H), 8.200 (d, J = 9.8 Hz, 2H), 8.150 (d, J = 9.8 Hz, 2H), 7.482 (dd, J = 9.8, 9.8 Hz, 2H), 7.391 (t, J = 9.8 Hz, 1H), 7.318 (d, J = 3.8 Hz, 2H), 7.189 (d, J = 3.8 Hz, 2H), 7.120 (s, 1H), 7.047 (dd, J = 9.8, 9.7 Hz, 2H), 6.930 (dd, J = 9.8, 9.8 Hz, 2H), 6.877 (dd, J = 9.8, 9.8 Hz, 2H), 6.872 (d, J = 8.4 Hz, 4H), 6.601 (s, 2H), 6.574 (d, J = 8.4 Hz, 4H), 4.694 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.449 (s), 141.047 (s), 139.694 (d), 138.206 (d), 137.855 (s), 137.372 (d), 137.227 (d), 136.659 (d), 135.748 (s), 134.929 (s), 133.823 (d), 133.583 (d), 133.338 (s), 132.053 (s), 129.793 (d), 122.421 (d), 121.778 (d), 121.620 (d), 116.459 (d), 114.896 (d), 41.849 (d). Anal. Calcd for $C_{44}H_{32}O_2 \cdot 2H_2O$: C, 84.05; H, 5.77. Found: C, 84.24; H, 5.43.

9b (second eluate): blue crystals; mp 158.0−160.0 °C; MS (70 eV) *m*/*z* (rel inten) 592 (M^+, 1.1), 360 (28), 128 (100); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 239 (4.69), 281 (4.96), 350 (4.11), 365 (4.08), 605 (2.91); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.179 (d, J = 9.7 Hz, 2H), 8.163 (d, J = 9.9 Hz, 2H), 8.139 (d, J = 9.7 Hz, 2H), 7.439 (dd, J = 9.9, 9.9 Hz, 2H), 7.356 (t, J = 9.9 Hz, 1H), 7.275 (d, J = 3.8 Hz, 2H), 7.140 (d, J = 3.8 Hz, 2H), 7.050 (s, 1H), 7.014 (dd, J = 9.9, 9.7 Hz, 2H), 6.885 (dd, J = 9.9, 9.7 Hz, 2H), 6.881 (d, J = 8.5 Hz, 4H), 6.841 (dd, J = 9.9, 9.9 Hz, 2H), 6.585 (s and d, J = 8.5 Hz, 6H), 5.061 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.351 (s), 140.978 (s), 139.715 (d), 138.198 (d), 137.910 (s), 137.365 (d), 137.236 (d), 136.623 (d), 135.721 (s), 134.857 (s), 133.753 (d), 133.629 (d), 133.216 (s), 132.137 (s), 129.797 (d), 122.402 (d), 121.799 (d), 121.608 (d), 116.371 (d), 114.951 (d), 41.863 (d). Anal. Calcd for $C_{44}H_{32}O_2 \cdot 1/2H_2O$: C, 87.82; H, 5.53. Found: C, 88.17; H, 5.76.

Bis(3-methyl-1-azulenyl)(4-hydroxyphenyl)methane (7b). The general procedure was followed using 1-methylazulene (**8b**) (719 mg, 5.06 mmol) and 4-hydroxybenzaldehyde (611 mg, 5.00 mmol) at room temperature for 48 h. Column chromatography on silica gel with CH_2Cl_2 afforded the recovered **8b** (13 mg, 1.8%) and the methane **7b** (923 mg, 96%). When the general procedure was followed using **8b** (712 mg, 5.01 mmol) and the benzaldehyde (318 mg, 2.60 mmol) in a 50% acetic acid solution of CH_2Cl_2 (3.7 mL) at 10 kbar for 24 h, column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded the methane **7b** (264 mg, 27%) and (3-methyl-1-azulenyl)(4-hydroxyphenyl)methane (**10a**) (78 mg, 12%).

7b: blue crystals; mp 179.0−181.0 °C; MS (70 eV) *m*/*z* (rel inten) 388 (M^+, 100), 373 (39), 279 (23), 245 (20), 231 (31); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 241 (4.50), 281 (4.84), 357 (3.98), 374 (3.96), 631 (2.84); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.11 (d and d, J = 9.5 Hz, 4H), 7.40 (dd, J = 10.6, 9.7 Hz, 2H), 7.28 (s, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.93 (dd, J = 9.7, 9.5 Hz, 2H), 6.82 (dd, J = 10.6, 9.5 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 6.61 (s, 1H), 4.60 (br, 1H), 2.55 (s, 6H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 153.44 (s), 139.29 (d), 138.19 (s), 137.13 (d), 136.94 (s), 134.99 (s), 133.47 (d), 132.98 (d), 131.91 (s), 129.78 (d), 124.47 (s), 120.94 (d), 120.66 (d), 114.99 (d), 41.54 (d), 12.73 (q). Anal. Calcd for $C_{29}H_{24}O$: C, 89.65; H, 6.23. Found: C, 89.29; H, 6.34.

10a: blue needles; mp 96.0−97.5 °C; MS (70 eV) *m*/*z* (rel inten) 248 (M^+, 100), 247 (23), 233 (77), 155 (35); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 240 (4.24), 286 (4.68), 354 (3.71), 371 (3.60), 629 (2.52); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.153 (d, J = 9.5 Hz, 1H), 8.112 (d, J = 9.5 Hz, 1H), 7.508 (s, 1H), 7.435 (dd, J = 9.8, 9.8 Hz, 1H), 7.030 (d, J = 8.3 Hz, 2H), 6.952 (dd, J = 9.8, 9.5 Hz, 1H), 6.922 (dd, J = 9.8, 9.5 Hz, 1H), 6.692 (d, J = 8.3 Hz, 2H), 4.972 (s, 1H), 4.306 (s, 2H), 2.599 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.55 (s), 138.95 (d), 137.34 (d), 136.80 (s), 135.83 (s), 134.16 (s), 133.38 (d), 132.97 (d), 129.62 (d), 127.95 (s), 124.86 (s), 120.76 (d), 120.61 (d), 115.17 (d), 32.48 (t), 12.55 (q). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.90; H, 6.72.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(4-hydroxyphenyl)-methane (7c). The general procedure was followed using 1,6-di-*tert*-butylazulene (**8c**) (1.20 g, 5.00 mmol) and 4-hydroxybenzaldehyde (612 mg, 5.01 mmol) at room temperature for 48 h. Column chromatography on silica gel with CH_2Cl_2 afforded the methane **7c** (1.24 g, 85%). When the general procedure was followed using **8c** (1.20 g, 5.00 mmol) and the benzaldehyde (612 mg, 5.01 mmol) at 60 °C for 12 h, column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded the methane **7c** (884 mg, 60%) and (3,6-di-*tert*-butyl-1-azulenyl)(4-hydroxyphenyl)methane (**10b**) (100 mg, 5.8%). When the general procedure was followed using **8c** (1.20 g, 5.01 mmol) and the benzaldehyde (318 mg, 2.60 mmol) in a 50% acetic acid solution of CH_2Cl_2 (3.7 mL) at 10

kbar for 24 h, column chromatography on silica gel with ethyl acetate/CH_2Cl_2 afforded the recovered **8c** (174 mg, 14%) and the methane **7c** (708 mg, 56%).

7c: blue crystals; mp 217.0−218.0 °C dec; MS (70 eV) *m/z* (rel inten) 584 (M^+, 85), 528 (42), 527 (97), 277 (21), 57 (100); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.49), 287 (4.90), 304 (4.86), 359 (4.04), 376 (3.96), 611 (2.91); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.53 (d, J = 10.8 Hz, 2H), 8.15 (d, J = 10.8 Hz, 2H), 7.36 (s, 2H), 7.13 (dd, J = 10.8, 1.9 Hz, 2H), 7.04 (dd, J = 10.8, 1.9 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 6.56 (s, 1H), 3.73 (br, 1H), 1.49 (s, 18H), 1.40 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 160.15 (s), 153.26 (s), 138.65 (s), 137.55 (s), 136.21 (d), 134.56 (s), 134.38 (d), 134.14 (s), 132.13 (d), 130.81 (s), 129.81 (d), 119.11 (d), 118.16 (d), 114.87 (d), 41.27 (d), 38.22 (s), 33.31 (s), 32.33 (q), 31.91 (q). Anal. Calcd for $C_{43}H_{52}O$: C, 88.30; H, 8.96. Found: C, 88.34; H, 9.07.

10b: blue crystals; mp 155.0−156.0 °C; MS (70 eV) *m/z* (rel inten) 346 (M^+, 66), 332 (28), 331 (100), 107 (42); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.25), 290 (4.74), 300 (4.74), 356 (3.80), 373 (3.58), 613 (2.55); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.527 (d, J = 10.5 Hz, 1H), 8.119 (d, J = 10.5 Hz, 1H), 7.533 (s, 1H), 7.149 (dd, J = 10.5, 1.8 Hz, 1H), 7.116 (dd, J = 10.5, 1.8 Hz, 1H), 7.039 (d, J = 8.3 Hz, 2H), 6.693 (d, J = 8.3 Hz, 2H), 4.852 (s, 1H), 4.294 (s, 2H), 1.544 (s, 9H), 1.415 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.61 (s), 153.45 (s), 137.83 (s), 135.91 (d), 135.40 (s), 134.45 (d), 134.36 (s), 133.93 (s), 132.30 (d), 129.58 (d), 126.61 (s), 119.09 (d), 118.23 (d), 115.09 (d), 38.19 (s), 33.22 (s), 32.54 (t), 32.22 (q), 31.80 (q). Anal. Calcd for $C_{25}H_{30}O$: C, 86.65; H, 8.72. Found: C, 86.72; H, 8.78.

Di(1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)-methane (7d). The general procedure was followed using azulene (**8a**) (1.28 g, 10.0 mmol) and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (1.17 g, 5.00 mmol) at room temperature for 48 h. Column chromatography on silica gel with CH_2Cl_2/CCl_4 and GPC with $CHCl_3$ afforded the recovered **8a** (630 mg, 49%), the methane **7d** (405 mg, 34%), and an unseparable diastereomeric mixture of 1,3-bis[(1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl]azulene (**9c** and **9d**) (439 mg, 32%) in a ratio of 5:3. When the general procedure was followed using **8a** (1.28 g, 10.0 mmol) and the benzaldehyde (587 mg, 2.51 mmol) in a 50% acetic acid solution of CH_2Cl_2 (9.1 mL) at 10 kbar for 24 h, column chromatography afforded the recovered **8a** (538 mg, 42%), the methane **7d** (211 mg, 15%), and a diastereomeric mixture of **9c** and **9d** (236 mg, 16%).

7d: blue plates; mp 182.0−183.0 °C; MS (70 eV) *m/z* (rel inten) 472 (M^+, 100), 471 (21), 415 (26), 267 (28), 265 (30); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 239 (4.59), 278 (4.88), 351 (4.02), 367 (3.92), 602 (2.83), 657 (2.74); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.286 (d, J = 9.7 Hz, 2H), 8.249 (d, J = 9.4 Hz, 2H), 7.498 (d, J = 3.9 Hz, 2H), 7.485 (dd, J = 10.0, 9.9 Hz, 2H), 7.270 (d, J = 3.9 Hz, 2H), 7.050 (dd, J = 9.9, 9.4 Hz, 2H), 7.023 (s, 2H), 6.982 (dd, J = 10.0, 9.7 Hz, 2H), 6.641 (s, 1H), 5.021 (s, 1H), 1.320 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.804 (s), 141.012 (s), 138.197 (d), 137.122 (d), 136.481 (d), 135.706 (s), 135.341 (s), 134.873 (s), 134.420 (s), 133.657 (d), 125.444 (d), 122.237 (d), 121.729 (d), 116.536 (d), 42.610 (d), 34.269 (s), 30.330 (q). Anal. Calcd for $C_{35}H_{36}O$: C, 88.94; H, 7.68. Found: C, 88.48; H, 7.89.

9c and **9d:** blue crystals; mp 225.0−227.0 °C dec; MS (70 eV) *m/z* (rel inten) 816 (M^+, 80), 473 (21), 472 (66), 471 (77), 345 (38), 128 (100); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 239 (4.76), 281 (5.05), 350 (4.21), 366 (4.18), 607 (2.97). Anal. Calcd for $C_{60}H_{64}O_2 \cdot H_2O$: C, 86.29; H, 7.96. Found: C, 86.70; H, 8.18. **9c (major product):** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.332 (d, J = 9.4 Hz, 2H), 8.233 (d, J = 9.7 Hz, 2H), 8.216 (d, J = 9.6 Hz, 2H), 7.461 (dd, J = 9.8, 9.8 Hz, 2H), 7.432 (d, J = 3.8 Hz, 2H), 7.418 (t, J = 9.8 Hz, 1H), 7.279 (s, 1H), 7.212 (d, J = 3.8 Hz, 2H), 7.037 (dd, J = 9.8, 9.6 Hz, 2H), 6.925 (dd and dd, J = 9.8, 9.4 Hz and J = 9.8, 9.7 Hz, 4H), 6.593 (s, 2H), 4.928 (s, 1H), 1.156 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.646 (s), 141.017 (s), 138.978 (d), 138.023 (d), 137.096 (d and d), 136.467 (d), 135.467 (s), 135.383 (s), 135.100 (s), 134.928 (s), 134.405 (s), 133.519 (d), 133.034 (d and s), 125.340 (d), 122.204 (d), 121.739 (d), 121.313 (d), 116.440 (d), 41.930 (d), 34.100 (s), 30.180 (q). **9d (minor product):** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.241 (d, J = 9.7 Hz, 2H), 8.203 (d, J = 9.6 Hz, 2H), 8.143 (d, J = 9.4 Hz, 2H), 7.477 (dd, J = 9.8, 9.8 Hz, 2H), 7.341 (t, J = 9.8 Hz, 1H), 7.317 (d, J = 3.8 Hz, 2H), 7.181 (s, 1H), 7.178 (d, J = 3.8 Hz, 2H), 7.032 (dd, J = 9.8, 9.6 Hz, 2H), 6.944 (dd, J = 9.8, 9.7 Hz, 2H), 6.935 (s, 2H), 6.849 (s, 2H), 6.815 (dd, J = 9.8, 9.4 Hz, 2H), 6.552 (s, 2H), 4.949 (s, 1H), 1.240 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.646 (s), 140.982 (s), 139.506 (d), 138.084 (d), 137.018 (d), 136.967 (d), 136.394 (d), 135.647 (s), 135.422 (s), 135.153 (s), 134.684 (s), 134.501 (s), 133.736 (d), 133.541 (d), 132.731 (s), 125.340 (d), 122.133 (d), 121.580 (d), 121.176 (d), 116.462 (d), 42.785 (d), 34.189 (s), 30.326 (q).

Bis(3-methyl-1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane (7e). The general procedure was followed using 1-methylazulene (**8b**) (715 mg, 5.03 mmol) and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (1.17 g, 5.00 mmol). Column chromatography on silica gel with CH_2Cl_2/CCl_4 afforded the recovered **8b** (147 mg, 21%) and the methane **7e** (1.00 g, 100%). When the general procedure was followed using **8b** (712 mg, 5.01 mmol) and the benzaldehyde (610 mg, 2.60 mmol) in a 50% acetic acid solution of CH_2Cl_2 (3.7 mL) at 10 kbar for 24 h, column chromatography afforded the recovered **8b** (54 mg, 7.6%) and the methane **7e** (754 mg, 60%). **7e:** blue prisms; mp 208.0−209.0 °C; MS (70 eV) *m/z* (rel inten) 500 (M^+, 100), 485 (23), 141 (25), 57 (50); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 241 (4.52), 280 (4.85), 358 (3.98), 374 (3.95), 632 (2.79); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.16 (d, J = 9.2 Hz, 2H), 8.10 (d, J = 9.2 Hz, 2H), 7.40 (dd, J = 9.5, 9.0 Hz, 2H), 7.35 (s, 2H), 7.00 (s, 2H), 6.92 (dd, J = 9.2, 9.0 Hz, 2H), 6.82 (dd, J = 9.5, 9.2 Hz, 2H), 6.56 (s, 1H), 4.99 (s, 1H), 2.57 (s, 6H), 1.32 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 151.64 (s), 139.20 (d), 136.91 (d), 135.85 (s), 135.27 (s), 134.99 (s), 133.22 (d), 132.95 (d), 132.70 (s), 125.39 (d), 124.44 (s), 120.72 (d), 120.42 (d), 42.24 (d), 34.38 (s), 30.44 (q), 12.79 (q). Anal. Calcd for $C_{37}H_{40}O$: C, 88.75; H, 8.05. Found: C, 88.33; H, 8.70.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane (7f). The general procedure was followed using 1,6-di-*tert*-butylazulene (**8c**) (1.20 g, 5.01 mmol) and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (1.17 g, 5.00 mmol) at room temperature for 48 h. Column chromatography on silica gel with CCl_4 afforded the methane **7f** (1.39 g, 80%). When the general procedure was followed using **8c** (1.21 g, 5.03 mmol) and the benzaldehyde (1.17 g, 5.01 mmol) at 60 °C for 12 h, column chromatography on silica gel with CH_2Cl_2/CCl_4 and GPC with $CHCl_3$ afforded the methane **7f** (684 mg, 39%) and α-(3,6-di-*tert*-butyl-1-azulenyl)-3,5-di-*tert*-butyl-1,4-benzoquinone methide (**11**) (474 mg, 21%). When the general procedure was followed using **8c** (1.20 g, 5.00 mmol) and the benzaldehyde (610 mg, 2.60 mmol) in a 50% acetic acid solution of CH_2Cl_2 (3.7 mL) at 10 kbar for 24 h, column chromatography on silica gel with CH_2Cl_2/CCl_4 and GPC with $CHCl_3$ afforded the recovered **8c** (573 mg, 48%) and the methane **7f** (522 mg, 57%).

7f: blue crystals; mp 255.0−256.0 °C dec; MS (70 eV) *m/z* (rel inten) 696 (M^+, 100), 640 (32), 639 (59); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.48), 285 (4.92), 359 (4.01), 377 (3.93), 618 (2.80); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.50 (d, J = 10.8 Hz, 2H), 8.25 (d, J = 10.8 Hz, 2H), 7.45 (s, 2H), 7.11 (dd, J = 10.8, 1.8 Hz, 2H), 7.05 (dd, J = 10.8, 1.8 Hz, 2H), 7.00 (s, 2H), 6.52 (s, 1H), 4.96 (s, 1H), 1.50 (s, 18H), 1.40 (s, 18H), 1.32 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 159.90 (s), 151.52 (s), 137.43 (s), 136.12 (d and s), 134.99 (s), 134.47 (s), 134.14 (d and s), 131.97 (d), 131.67 (s), 125.57 (d), 119.01 (d), 117.89 (d), 41.57 (d), 38.19 (s), 34.41 (s), 33.34 (s), 32.36 (q), 31.91 (q), 30.47 (q). Anal. Calcd for $C_{51}H_{68}O$: C, 87.83; H, 9.83. Found: C, 87.61; H, 10.02.

11: greenish brown plates; mp 130.5−133.0 °C; MS (70 eV) *m/z* (rel inten) 456 (M^+, 100), 441 (56), 399 (24), 57 (42); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 232 (4.39), 258 (4.35), 292 (4.31), 301 (4.30), 355 (4.13), 505 (4.69); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.628 (d, J = 11.0 Hz, 1H), 8.487 (d, J = 11.0 Hz, 1H), 8.183 (s, 1H), 7.982 (d, J = 2.2 Hz, 1H), 7.668 (s, 1H), 7.462 (dd, J = 11.0, 1.8 Hz, 1H), 7.451 (dd, J = 11.0, 1.8 Hz, 1H), 7.174 (d, J = 2.2 Hz, 1H), 1.614 (s, 9H), 1.470 (s, 9H), 1.404 (s, 9H), 1.385 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.58 (s), 163.57 (s), 148.00 (s), 145.80 (s), 142.44 (s), 141.14 (s), 138.62 (s), 136.06 (d), 135.83 (d), 135.78 (d), 134.76 (d), 133.11 (d), 128.92

(d), 127.54 (s), 123.76 (d), 123.43 (s), 123.24 (d), 38.56 (s), 35.49 (s), 34.98 (s), 33.28 (s), 31.68 (q), 31.67 (q), 29.64 (q). Anal. Calcd for $C_{33}H_{44}O$: C, 86.79; H, 9.71. Found: C, 86.90; H, 9.94.

General Procedure for the Synthesis of Di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl Hexafluorophosphates 5a−f·PF_6^-. DDQ was added at room temperature to a solution of di(1-azulenyl)(4-hydroxy- and 3,5-di-*tert*-butyl-4-hydroxyphenyl)methanes **7a**−**f** in CH_2Cl_2 (100 mL). The solution was stirred at the same temperature for 5 min. A 60% aqueous HPF_6 solution (10 mL) was added to the reaction mixture. After the mixture was stirred at room temperature for an additional 5 min, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and hexane (100 mL) was added to the solution. The precipitated crystals were collected by filtration, washed with hexane, and dried in vacuo to give the hexafluorophosphates **5a**−**f**·PF_6^-. The product was further purified by recrystallization from CH_2Cl_2/hexane.

Di(1-azulenyl)(4-hydroxyphenyl)methyl Hexafluorophosphate (5a·PF_6^-). The general procedure was followed using DDQ (273 mg, 1.20 mmol) and di(1-azulenyl)(4-hydroxyphenyl)methane (**7a**) (361 mg, 1.00 mmol). Recrystallization from CH_2Cl_2/hexane gave the hexafluorophosphate **5a**·PF_6^- (506 mg, 100%): brown crystals; mp 140.5−144.0 °C dec; MS (FAB) *m*/*z* 359 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 229 (4.60), 247 (4.50), 286 (4.41), 385 (4.12), 495 (4.30), 624 (4.48); ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 9.072 (d, J = 9.6 Hz, 2H), 8.293 (dd, J = 9.9, 9.8 Hz, 2H), 8.163 (dd, J = 9.8, 9.6 Hz, 2H), 8.079 (d, J = 4.5 Hz, 2H), 8.060 (d, J = 9.9 Hz, 2H), 7.956 (d, J = 4.5 Hz, 2H), 7.773 (dd, J = 9.9, 9.9 Hz, 2H), 7.444 (d, J = 8.6 Hz, 2H), 7.173 (d, J = 8.6 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6, 60 °C) δ 164.821 (s), 164.178 (s), 152.336 (s), 146.807 (s), 145.930 (d), 143.180 (d), 141.110 (d), 138.875 (d), 138.484 (d), 134.253 (d), 133.363 (d), 132.251 (s), 131.776 (s), 125.176 (d), 116.532 (d). Anal. Calcd for $C_{27}H_{19}O\cdot PF_6$: C, 64.29; H, 3.80. Found: C, 64.13; H, 4.20.

Bis(3-methyl-1-azulenyl)(4-hydroxyphenyl)methyl Hexafluorophosphate (5b·PF_6^-). The general procedure was followed using DDQ (273 mg, 1.20 mmol) and bis(3-methyl-1-azulenyl)(4-hydroxyphenyl)methane (**7b**) (389 mg, 1.00 mmol). Recrystallization from CH_2Cl_2/hexane gave the hexafluorophosphate **5b**·PF_6^- (533 mg, 100%): dark brown crystals; mp 147.0−150.0 °C dec; MS (FAB) *m*/*z* 387 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 230 (4.74), 291 (4.39), 399 (4.21), 510 (4.17), 657 (4.44); ^{1}H NMR (90 MHz, MeCN-d_3) δ 8.69 (d, J = 11.0 Hz, 2H), 8.04−7.77 (m, 6H), 7.77 (s, 2H), 7.04 (dd, J = 10.3, 10.3 Hz, 2H), 7.26 (s, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 6.84 (br, 1H), 2.63 (s, 6H); ^{13}C NMR (22.5 MHz, MeCN-d_3) δ 163.63 (s), 151.65 (s), 151.10 (s), 149.08 (s), 146.61 (d), 143.60 (d), 139.69 (d), 138.96 (d and d), 135.18 (s), 134.27 (d), 134.14 (s), 134.05 (d), 132.59 (s), 117.04 (d), 12.95 (q). Anal. Calcd for $C_{29}H_{23}O\cdot PF_6$: C, 65.42; H, 4.35. Found: C, 66.18; H, 5.22.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(4-hydroxyphenyl)methyl Hexafluorophosphate (5c·PF_6^-). The general procedure was followed using DDQ (272 mg, 1.20 mmol) and bis(3,6-di-*tert*-butyl-1-azulenyl)(4-hydroxyphenyl)methane (**7c**) (589 mg, 1.01 mmol). Recrystallization from CH_2Cl_2/hexane gave the hexafluorophosphate **5c**·PF_6^- (734 mg, 100%): brown crystals; mp 292.0−293.0 °C dec; MS (FAB) *m*/*z* 583 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 234.3 (4.64), 253 (4.62), 301 (4.53), 397 (4.28), 503 (4.21), 666 (4.64); ^{1}H NMR (90 MHz, $CDCl_3$) δ 9.00 (d, J = 11.0 Hz, 2H), 8.05 (dd, J = 11.0, 1.7 Hz, 2H), 7.87 (d, J = 10.8 Hz, 2H), 7.65 (s, 2H), 7.60 (dd, J = 10.8, 1.7 Hz, 2H), 7.22 (s, 4H), 5.33 (br, 1H), 1.58 (s, 18H), 1.47 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 168.10 (s), 164.51 (s), 162.80 (s), 147.98 (s), 147.83 (s), 146.12 (s), 143.28 (d), 138.62 (d), 138.01 (d), 137.55 (d), 131.82 (s), 130.88 (s), 130.72 (d), 130.45 (d), 117.37 (d), 39.31 (s), 33.31 (s), 31.60 (q), 31.30 (q). Anal. Calcd for $C_{43}H_{51}O\cdot PF_6$: C, 70.86; H, 7.05. Found: C, 71.01; H, 7.09.

Di(1-azulenyl)(3,6-di-*tert*-butyl-4-hydroxyphenyl)methyl Hexafluorophosphate (5d·PF_6^-). The general procedure was followed using DDQ (273 mg, 1.20 mmol) and di(1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane (**7d**) (473 mg, 1.00 mmol). Recrystallization from CH_2Cl_2/hexane gave the hexafluorophosphate **5d**·PF_6^- (617 mg, 100%): brown crystals; mp 154.5−157.0 °C dec; MS (FAB) *m*/*z* 471 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 230 (4.63), 251 (4.50), 289 (4.41), 404 (4.06), 511 (4.40), 622 (4.49); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.79 (d, J = 11.0 Hz, 2H), 8.22−7.81 (m, 8H), 7.72 (d, J = 4.4 Hz, 2H), 7.52 (dd, J = 10.3, 10.3 Hz, 2H), 7.26 (s, 2H), 6.20 (br, 1H), 1.40 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 165.94 (s), 160.66 (s), 152.77 (s), 147.22 (s), 146.12 (d), 143.16 (d), 141.30 (d), 139.05 (d), 137.31 (s), 134.72 (d), 134.32 (d), 133.10 (d), 132.55 (s), 132.28 (s), 125.45 (d), 34.47 (s), 30.08 (q). Anal. Calcd for $C_{35}H_{35}O\cdot PF_6$: C, 68.17; H, 5.72. Found: C, 69.40; H, 5.74.

Bis(3-methyl-1-azulenyl)(3,6-di-*tert*-butyl-4-hydroxyphenyl)methyl Hexafluorophosphate (5e·PF_6^-). The general procedure was followed using DDQ (272 mg, 1.20 mmol) and bis(3-methyl-1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane (**7e**) (501 mg, 1.00 mmol). Recrystallization from CH_2Cl_2/hexane gave the hexafluorophosphate **5e**·PF_6^- (593 mg, 92%): dark brown crystals; mp 208.0−211.0 °C; MS (FAB) *m*/*z* 499 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 234 (4.60), 276 (4.38), 405 (4.09), 525 (4.27), 657 (4.35); ^{1}H NMR (90 MHz, MeCN-d_3) δ 8.74 (d, J = 11.0 Hz, 2H), 8.19−7.75 (m, 6H), 7.83 (s, 2H), 7.45 (dd, J = 10.1, 10.1 Hz, 2H), 7.25 (s, 2H), 3.40 (br, 1H), 2.68 (s, 6H), 1.37 (s, 18H); ^{13}C NMR (22.5 MHz, MeCN-d_3) δ 163.96 (s), 161.07 (s), 151.46 (s), 149.15 (s), 146.65 (d), 143.60 (d), 139.85 (d), 139.02 (d), 138.57 (s), 135.24 (d), 135.03 (s), 134.08 (d), 133.66 (d), 133.44 (s), 132.56 (s), 35.27 (s), 30.30 (q), 12.89 (q). Anal. Calcd for $C_{37}H_{39}O\cdot PF_6$: C, 68.93; H, 6.10. Found: C, 69.32; H, 5.96.

Bis(3,6-di-*tert*-butyl-1-azulenyl)(3,6-di-*tert*-butyl-4-hydroxyphenyl)methyl Hexafluorophosphate (5f·PF_6^-). The general procedure was followed using DDQ (274 mg, 1.21 mmol) and bis(3,6-di-*tert*-butyl-1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane (**7f**) (698 mg, 1.00 mmol). Recrystallization from CH_2Cl_2/hexane gave the hexafluorophosphate **5f**·PF_6^- (827 mg, 98%): dark brown crystals; mp 232.0−233.0 °C; MS (FAB) *m*/*z* 695 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 235 (4.69), 256 (4.60), 299 (4.57), 400 (4.21), 518 (4.36), 666 (4.57); ^{1}H NMR (90 MHz, $CDCl_3$) δ 9.06 (d, J = 11.2 Hz, 2H), 8.10 (dd, J = 11.2, 2.0 Hz, 2H), 7.89 (d, J = 11.0 Hz, 2H), 7.64 (s, 2H), 7.57 (dd, J = 11.0, 2.0 Hz, 2H), 7.23 (s, 2H), 6.11 (br, 1H), 1.61 (s, 18H), 1.45 (s, 18H), 1.41 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 168.29 (s), 161.88 (s), 159.87 (s), 147.95 (s), 147.64 (s), 146.09 (s), 142.83 (d), 139.02 (d), 137.74 (d), 137.03 (s), 134.47 (d), 132.43 (s), 130.94 (d), 130.66 (d and s), 39.31 (s), 34.65 (s), 33.37 (s), 31.57 (q), 31.36 (q), 30.29 (q). Anal. Calcd for $C_{51}H_{67}O\cdot PF_6$: C, 72.83; H, 8.03. Found: C, 72.71; H, 7.85.

General Procedure for the Neutralization of the Hexafluorophosphates 5a−f·PF_6^-. A solution of the appropriate di(1-azulenyl)(4-hydroxyphenyl)methyl hexafluorophosphate **5a**−**f**·PF_6^- (0.92−1.00 mmol) in CH_2Cl_2 (100 mL) was treated with 5% aqueous $NaHCO_3$, washed with water, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on Al_2O_3 to afford the α,α-di(1-azulenyl)-1,4-benzoquinone methides **6a**−**f**. The product was further purified by recrystallization.

α,α-Di(1-azulenyl)-1,4-benzoquinone Methide (6a). The general procedure was followed with di(1-azulenyl)(4-hydroxyphenyl)methyl hexafluorophosphate (**5a**·PF_6^-) (506 mg, 1.00 mmol). The crude material was then purified by column chromatography on Al_2O_3 with MeOH/CH_2Cl_2 to afford the quinone methide **6a** (330 mg, 92%): greenish brown crystals; mp 68.0−74.0 °C dec; MS (70 eV) *m*/*z* (rel inten) 358 (M^+, 29), 267 (30), 265 (44), 231 (40), 128 (48); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 235 (4.61), 276 (4.63), 323 (4.31), 404 (4.07), 522 (4.43); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.482 (d, J = 9.7 Hz, 2H), 7.910 (d, J = 9.8 Hz, 2H), 7.775 (d, J = 4.1 Hz, 2H), 7.715 (dd, J = 9.8, 9.7 Hz, 2H), 7.469 (d, J = 4.1 Hz, 2H), 7.427 (dd, J = 9.7, 9.7 Hz, 2H), 7.287 (d, J = 9.7 Hz, 2H), 7.171 (dd, J = 9.8, 9.8 Hz, 2H), 6.506 (d, J = 9.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.642 (s), 152.571 (s), 145.583 (s), 143.033 (d), 140.812 (s), 140.716 (d), 139.532 (d), 138.394 (d), 136.948 (d), 130.795 (s), 128.246 (s), 126.705 (d), 126.585 (d), 126.545 (d), 119.515 (d).

Anal. Calcd for $C_{27}H_{18}O \cdot 1/2H_2O$: C, 88.26; H, 5.21. Found: C, 88.66; H, 5.40.

α,α-Bis(3-methyl-1-azulenyl)-1,4-benzoquinone Methide (6b). The general procedure was followed with bis(3-methyl-1-azulenyl)(4-hydroxyphenyl)methyl hexafluorophosphate (**5b**·PF_6^-) (533 mg, 1.00 mmol). The crude material was then purified by column chromatography on Al_2O_3 with MeOH/CH_2Cl_2 to afford the quinone methide **6b** (354 mg, 92%): greenish brown crystals; mp 225.0−231.0 °C dec; MS (70 eV) *m*/*z* (rel inten) 386 (M^+, 100); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.62), 283 (4.65), 330 (4.30), 355 (4.31), 534 (4.49); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.365 (d, J = 9.5 Hz, 2H), 7.825 (d, J = 10.0 Hz, 2H), 7.653 (dd, J = 9.8, 9.8 Hz, 2H), 7.607 (s, 2H), 7.362 (dd, J = 9.8, 9.5 Hz, 2H), 7.226 (d, J = 9.7 Hz, 2H), 7.074 (dd, J = 10.0, 9.8 Hz, 2H), 6.497 (d, J = 9.7 Hz, 2H), 2.646 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.36 (s), 152.43 (s), 143.59 (d), 142.72 (s), 141.44 (s), 140.74 (d), 139.37 (d), 136.52 (d), 135.27 (d), 129.34 (s), 128.09 (s), 127.65 (s), 126.16 (d), 126.07 (d), 125.48 (d), 12.62 (q). Anal. Calcd for $C_{29}H_{22}O \cdot 1/2H_2O$: C, 88.07; H, 5.86. Found: C, 88.47; H, 5.85.

α,α-Bis(3,6-di-*tert*-butyl-1-azulenyl)-1,4-benzoquinone Methide (6c). The general procedure was followed with bis(3,6-di-*tert*-butyl-1-azulenyl)(4-hydroxyphenyl)methyl hexafluorophosphate (**5c**·PF_6^-) (734 mg, 1.01 mmol). The crude material was then purified by column chromatography on Al_2O_3 with MeOH/ethyl acetate/CH_2Cl_2 to afford the quinone methide **6c** (478 mg, 82%): brown crystals; mp 299.0−300.0 °C dec; MS (70 eV) *m*/*z* (rel inten) 582 (M^+, 100); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 240 (4.60), 289 (4.73), 334 (4.36), 359 (4.34), 537 (4.50); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.78 (d, J = 10.8 Hz, 2H), 7.91 (d, J = 10.8 Hz, 2H), 7.56 (dd, J = 10.8, 1.8 Hz, 2H), 7.52 (s, 2H), 7.31 (dd, J = 10.8, 1.8 Hz, 2H), 7.24 (d, J = 9.6 Hz, 2H), 6,51 (d, J = 9.6 Hz, 2H), 1.55 (s, 18H), 1.45 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 186.18 (s), 163.68 (s), 153.38 (s), 141.91 (s), 140.85 (d), 140.72 (d), 140.54 (s), 140.30 (s), 136.30 (d), 135.91 (d), 128.74 (s), 127.37 (s), 125.60 (d), 124.63 (d), 123.31 (d), 38.67 (s), 33.19 (s), 31.94 (q), 31.78 (q). Anal. Calcd for $C_{43}H_{50}O \cdot 1/2H_2O$: C, 87.26; H, 8.68. Found: C, 87.53; H, 9.09.

α,α-Di(1-azulenyl)-3,5-di-*tert*-butyl-1,4-benzoquinone Methide (6d). The general procedure was followed with di(1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl hexafluorophosphate (**5d**·PF_6^-) (617 mg, 1.00 mmol). The crude material was then purified by column chromatography on Al_2O_3 with CH_2Cl_2/CCl_4 to afford the quinone methide **6d** (366 mg, 78%): greenish brown crystals; mp 223.0−224.0 °C; MS (70 eV) *m*/*z* (rel inten) 470 (M^+, 100), 456 (35), 455 (91), 428 (31), 427 (21), 413 (35), 386 (26), 266 (22), 265 (39), 57 (22); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 236 (4.63), 272 (4.72), 323 (4.40), 407 (4.27), 507 (4.42); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.424 (d, J = 9.5 Hz, 2H), 7.906 (d, J = 9.8 Hz, 2H), 7.750 (d, J = 4.0 Hz, 2H), 7.646 (dd, J = 9.8, 9.7 Hz, 2H), 7.439 (d, J = 4.0 Hz, 2H), 7.329 (dd, J = 9.7, 9.5 Hz, 2H), 7.177 (s, 2H), 7.087 (dd, J = 9.8, 9.8 Hz, 2H), 1.203 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.628 (s), 147.001 (s), 145.935 (s), 144.486 (s), 142.397 (d), 139.217 (s), 138.882 (d), 137.825 (d), 136.878 (d), 133.569 (d), 131.335 (s), 128.412 (s), 125.508 (d), 125.036 (d), 118.701 (d), 35.192 (s), 29.733 (q). Anal. Calcd for $C_{35}H_{34}O$: C, 89.32; H, 7.28. Found: C, 89.38; H, 7.53.

α,α-Bis(3-methyl-1-azulenyl)-3,5-di-*tert*-butyl-1,4-benzoquinone Methide (6e). The general procedure was followed with bis(3-methyl-1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl hexafluorophosphate (**5e**·PF_6^-) (593 mg, 0.92 mmol). The crude material was then purified by column chromatography on Al_2O_3 with CH_2Cl_2/CCl_4 to afford the quinone methide **6e** (375 mg, 82%): brown needles; mp 286.0−286.5 °C; MS (70 eV) *m*/*z* (rel inten) 498 (M^+, 100), 484 (24), 483 (64), 456 (20), 441 (22), 57 (41); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.62), 277 (4.73), 329 (4.42), 419 (4.21), 523 (4.43); ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.29 (d, J = 9.2 Hz, 2H), 7.86 (d, J = 9.7 Hz, 2H), 7.59 (dd, J = 9.7, 9.5 Hz, 2H), 7.54 (s, 2H), 7.24 (dd, J = 9.7, 9.2 Hz, 2H), 7.11 (s, 2H), 6.99 (dd, J = 9.7, 9.5 Hz, 2H), 2.63 (s, 6H), 1.19 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 185.39 (s), 146.64 (s), 145.54 (s), 142.95 (d), 141.27 (s), 139.53 (s), 138.62 (d), 136.39 (d), 134.60 (d), 133.62 (d), 129.78 (s), 128.25 (s), 126.55 (s), 124.35 (d), 124.05 (d), 35.23 (s), 29.86 (q), 12.67 (q). Anal. Calcd for $C_{37}H_{38}O$: C, 89.11; H, 7.68. Found: C, 89.48; H, 7.87.

α,α-Bis(3,5-di-*tert*-butyl-1-azulenyl)-3,5-di-*tert*-butyl-1,4-benzoquinone Methide (6f). The general procedure was followed with bis(3,5-di-*tert*-butyl-1-azulenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl hexafluorophosphate (**5f**·PF_6^-) (827 mg, 0.98 mmol). The crude material was then purified by column chromatography on Al_2O_3 with CH_2Cl_2/CCl_4 to afford the quinone methide **6f** (627 mg, 92%): dark brown crystals; mp >300 °C; MS (70 eV) *m*/*z* (rel inten) 694 (M^+, 100), 680 (21), 679 (36), 637 (20), 57 (51); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 241 (4.62), 286 (4.78), 336 (4.43), 423 (4.20), 534 (4.46); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.714 (d, J = 10.8 Hz, 2H), 7.791 (d, J = 10.8 Hz, 2H), 7.591 (s, 2H), 7.440 (dd, J = 10.8, 1.8 Hz, 2H), 7.189 (dd, J = 10.8, 1.8 Hz, 2H), 7.147 (s, 2H), 1.560 (s, 18H), 1.420 (s, 18H), 1.223 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.36 (s), 162.55 (s), 147.68 (s), 144.88 (s), 140.55 (d), 139.88 (s), 139.46 (s), 139.24 (s), 135.76 (d), 135.69 (d), 134.19 (d), 128.73 (s), 127.40 (s), 123.13 (d), 121.66 (d), 38.44 (s), 35.20 (s), 33.31 (s), 32.05 (q), 31.69 (q), 29.82 (q). Anal. Calcd for $C_{51}H_{66}O \cdot H_2O$: C, 85.90; H, 9.61. Found: C, 86.09; H, 9.47.

Protonation of α,α-Di(1-azulenyl)-1,4-benzoquinone Methides 6a−f with HPF_6. A solution of the appropriate α,α-di(1-azulenyl)-1,4-benzoquinone methide **6a**−**f** (0.20 mmol) in CH_2Cl_2 (20 mL) was treated with 60% HPF_6 (2 mL) and water (20 mL). The organic layer was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was precipitated from CH_2Cl_2 (3 mL) and hexane (50 mL) to afford the hexafluorophosphates **5a**·PF_6^- (93 mg, 92%), **5b**·PF_6^- (108 mg, 100%), **5c**·PF_6^- (137 mg, 94%), **5d**·PF_6^- (121 mg, 98%), **5e**·PF_6^- (129 mg, 100%), and **5f**·PF_6^- (164 mg, 97%), respectively.

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Supporting Information Available: The IR spectral data for all mentioned compounds (hexafluorophosphates of **5a**−**f**, **6a**−**f**, **7a**−**f**, **9a**−**d**, **10a**,**b**, and **11**) (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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