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An efficient preparation and spectroscopic and electrochemical properties of quinodimethane derivatives with four 3-(methoxycarbonyl)azulen-1-yl groups

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Abstract

Reaction of methyl 1-azulenecarboxylate (**8**) with terephthalaldehyde (**9**) in acetic acid in the presence of hydrochloric acid at 25 °C for 2 h gives 1,4-bis[bis(3-methoxycarbonyl-1-azulenyl)methyl]benzene (**12**), in 93% yield, which upon oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in dichloromethane in the presence of hexafluorophosphoric acid at 25 °C for 1 h affords the dicarbenium-ion compound **15** in 94% yield. Furthermore, reduction of **15** with zinc powder in a mixed solvent of acetonitrile and chloroform at 25 °C for 1 h yields the target quinodimethane **18** in 90% yield. Similarly, as in the case of **18**, the quinoid compounds **19** and **20** can be derived from the dicarbenium-ion compounds **16** and **17**, quantitatively. A facile preparation as well as spectroscopic and electrochemical properties of **15–20** is reported.

Keywords: Azulenes; Dicarbenium-ions; Electrochemical behavior; Quinodimethanes; Spectroscopic properties; Zinc-reductions

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1. Introduction

Naturally occurring guaiazulene has been widely used clinically as antiinflammatory and antiulcer agents; however, azulenes have not been used as other industrial materials. As a series of our basic studies on creation of novel functional materials with a 3-guaiazulenyl (or another azulenyl) group possessing a large dipole moment and on their potential utility, we have been working on a facile preparation and crystal structures as well as spectroscopic, chemical, and electrochemical properties of the delocalized mono- and dicarbenium-ion compounds stabilized by the expanded π-electron systems with a 3-guaiazulenyl (or an azulen-1-yl) group.[1–16] Along with our basic and systematic investigations, synthesis, stability, spectroscopic and chemical properties, crystal structures, electrochemical behavior, and theoretical studies (e.g., ab initio calculations, DFT, GIAO-NMR, and NICS) of the azulenium-,[17–19] azulenylium- (and azulenylmethylium-)[20–30] ions, and the azulen-1-yl-substituted cations[31–34] have been studied to a considerable extent, and a large number of the results and discussion regarding those delocalized cations have been well documented. During the course of our studies on the 3-guaiazulenyl-substituted carbenium-ion compounds, we recently found that the zinc-reductions of **1** and **3** (see Chart 1) gave several chromatographically inseparable products from **1** and a polar resinous substance from **3**, while the zinc-reduction of **2** (see Chart 1) afforded 2,5-bis[(3-guaiazulenyl)methylidene]-2,5-dihydrothiophene, quantitatively, which was unstable at room temperature under aerobic conditions, gradually converting to a polar resinous substance.[14] In relation to the above studies,[1–34] in 2000 we reported that the oxidation of **12** with DDQ in chloroform gave **18**[35] (45% yield) (see Scheme 1), which served as a strong electron donor and, further, in 2001 Ito et al. reported a highly efficient preparation of **4**[25] (97% yield) and **5**[25] (100% yield) (see Chart 1), which upon reduction with zinc powder afforded **6**[25] (57% yield) and **7**[25] (62% yield) (see Chart 1), along

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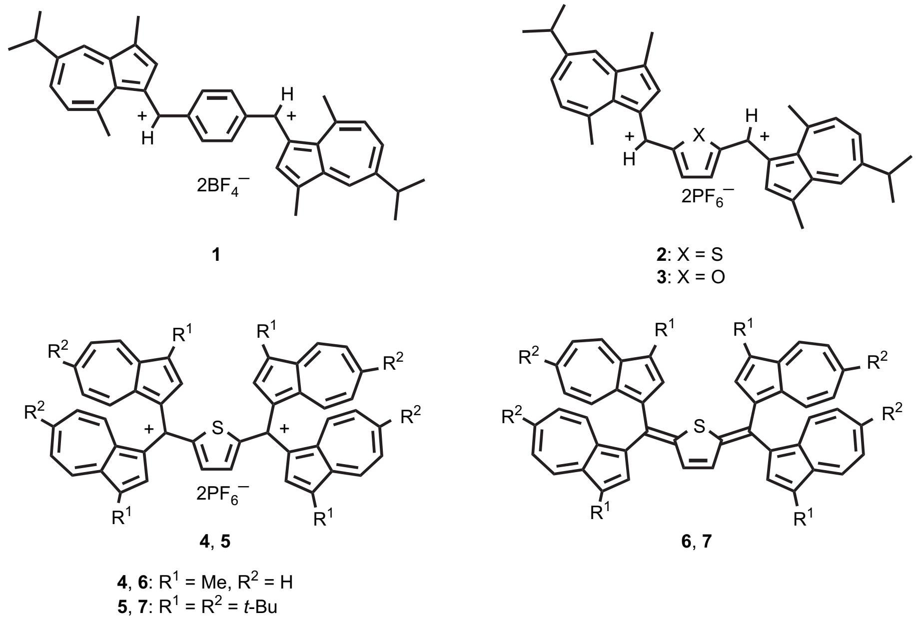


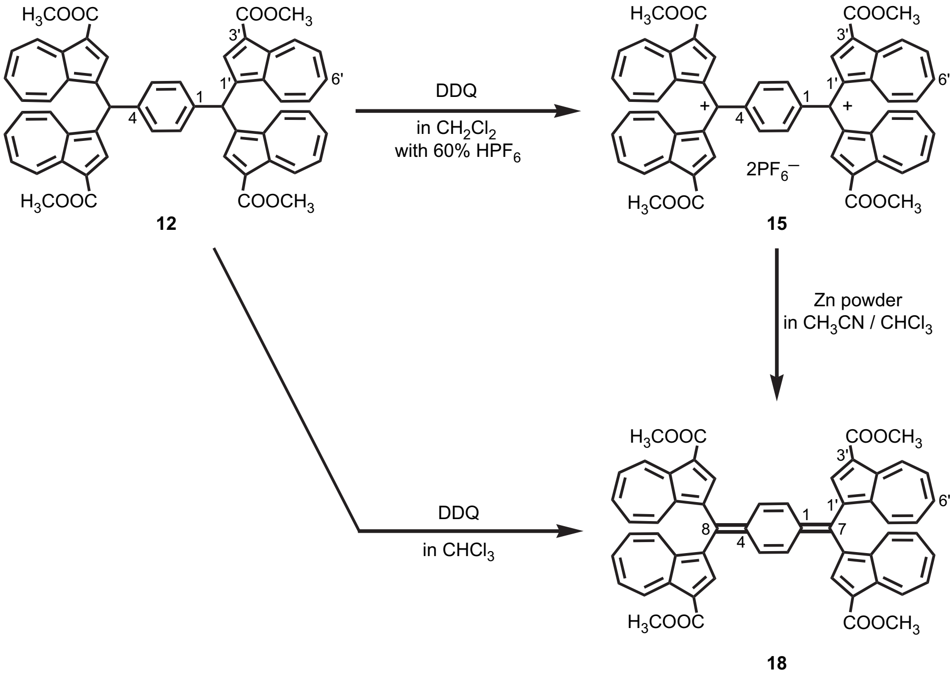
Chart 1.

with properties and redox behavior of **4**–**7**. Thus, our interest has quite recently been focused on the following comparative studies: namely, (i) preparation of the dicarbenium-ion compound **16**, stabilized by the four 3-(methoxycarbonyl)azulen-1-yl groups, compared with those of **4**, **5**, **15**, and **17** (see Schemes 1 and 2); (ii) zinc-reduction of **16**, compared with those of **2**, **4**, **5**, **15**, and **17**, converting to a stable quinoid compound **19** (see Scheme 2) at room temperature under aerobic conditions; and (iii) properties and electrochemical behavior of **16** and **19** compared with those of **5** and **7** along with those of **2**, **15**, **17**, **18**, and **20** (see Scheme 2). We now wish to report the detailed studies on the above three points (i)–(iii).

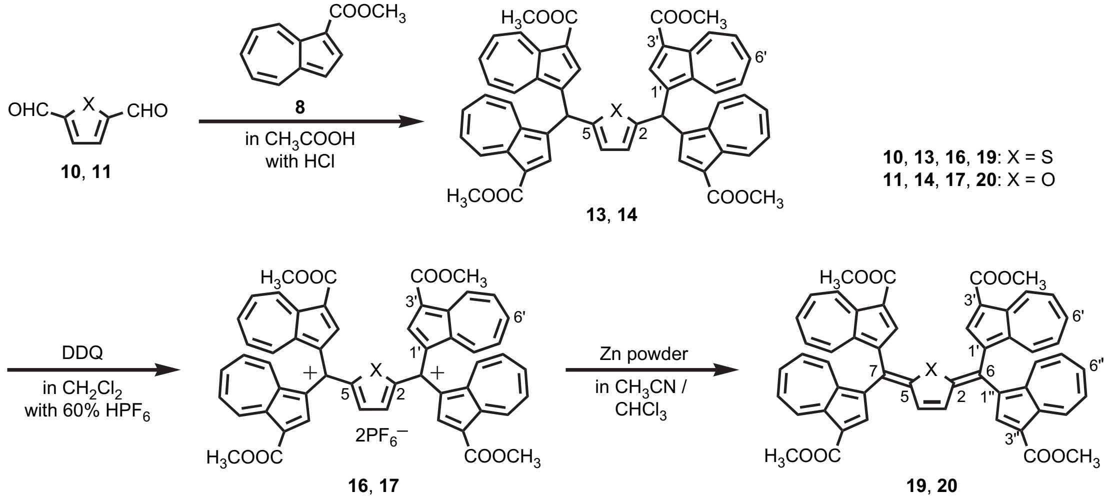
2. Results and discussion

2.1. Preparation of **12**–**14**

In the previous papers, we reported that the reaction of guaiazulene with terephthalaldehyde (**9**) in acetic acid gave 4-[di(3-guaiazulenyl)methyl]benzaldehyde in 92% yield;[36]



Scheme 1.



Scheme 2.

however, the reaction of methyl 1-azulenecarboxylate (**8**) with **9** under the same reaction conditions as for guaiazulene afforded no product[35] and, further, the reaction of guaiazulene with **9** in acetic acid in the presence of hydrochloric acid gave the dicarbenium-ion compound 1,4-phenylenebis(3-guaiazulenylmethylium) dichloride,[1] quantitatively, while the reaction of **8** with **9** under the same reaction conditions as for guaiazulene afforded **12** in 92% yield.[35] Along with the above experimental results, a plausible reaction pathway for the formation of **12** was submitted.[35] For comparative purposes, the reactions of **8** with the two heteroaromatic dicarbaldehydes **10** and **11** in acetic acid in the presence of hydrochloric acid were carried out under the same reaction conditions as for **9**, efficiently yielding new compounds **13** (97% yield) and **14** (90% yield) (see Scheme 2 and Sections 4.1.2 and 4.1.3). Thus, it was found that hydrochloric acid under those reaction conditions served as an important role to provide **12–14**.

2.2. Preparation and spectroscopic properties of 15–17

The oxidations of **12**, **13**, and **14** with DDQ in dichloromethane in the presence of hexafluorophosphoric acid at 25 °C for 1 h gave new dicarbenium-ion compounds **15** (94% yield), **16** (90% yield), and **17** (86% yield), respectively, whose detailed experimental procedures are shown in Sections 4.1.4–4.1.6. Therefore, the yields of **4**[25] (97%) and **5**[25] (100%) were higher than that of **16**. The structures of the products **15–17** were established on the basis of elemental analysis and spectroscopic data (i.e., UV–vis, IR, exact FABMS, ^{1}H NMR including H–H COSY, and ^{13}C NMR including DEPT).

Compound **15** was obtained as a dark-brown powder (decomp. >217 °C). The UV–vis spectrum showed a strong absorption band based on the bis(3-methoxycarbonyl-1-azulenyl)methylium-ion part at λ_{max} 263 nm (log ε=5.01) and the longest absorption wavelength at λ_{max} 635 nm (log ε=4.95) (see Fig. 1). Similarly, as in the cases of **1–3**,[14] the spectrum suggested the formation of a delocalized π-electron system between the two bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts and the 1,4-substituted benzene ring, whose spectral pattern was the same as that of 1,4-phenylenebis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate)[25] (**21**). The IR spectrum showed a specific band based on the C=O group of ester at ν_{max} 1701 cm^{-1}, which was a slightly higher wavenumber shift (Δ 8 cm^{-1}, each) in comparison with those of **12** and **18**, and revealed two specific bands based on the counter anion (PF_6^-) at ν_{max} 876 and 571 cm^{-1}, while the PF_6^- anions of **16** and **17** were observed at ν_{max} 876 and 559 cm^{-1} and ν_{max} 876 and 582 cm^{-1}. The formula $C_{56}H_{40}O_8$ for the dicarbenium-ion part was determined by exact FABMS spectrum. An elemental analysis confirmed the formula $C_{56}H_{40}F_{12}O_8P_2$. Similarly, as in the cases of **2**[14] and **3**,[14] the 600 MHz ^{1}H NMR spectrum, using CD_3CN as a measurement solvent, showed extremely complicated signals,[37] which could not be assigned. The spectrum, measured in CF_3COOD, revealed broad signals for all the protons; however, signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts (i.e., four equivalent 3-methoxycarbonyl-1-azulenic protons: 3′-$COOCH_3$, H-2′, and H-4′–H-8′) and an equivalent signal based on the H-2, 3, 5, and 6 protons of

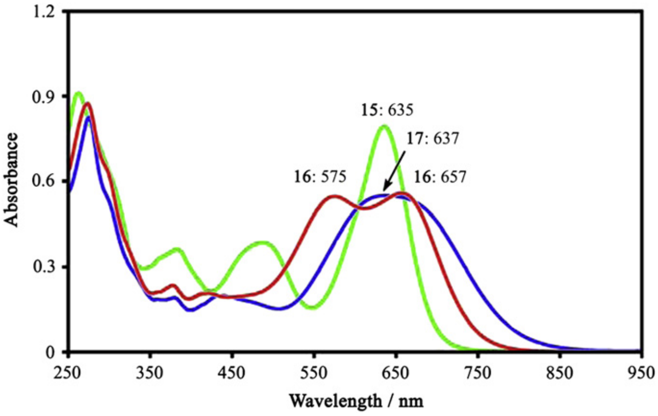


Figure 1. The UV–vis spectra of **15**, **16**, and **17** in CF_3COOH. Concentrations, **15**: 0.10 g/L (88 μmol/L), **16**: 0.10 g/L (88 μmol/L), and **17**: 0.12 g/L (107 μmol/L). Length of the cell, 0.1 cm each. **15**: λ_{max} 635 nm (log ε=4.95). **16**: λ_{max} 575 and 657 nm (log ε=4.79 and 4.80). **17**: λ_{max} 637 nm (log ε=4.71).

the 1,4-substituted benzene ring could be assigned using H—H COSY technique (see Section 4.1.4). The 150 MHz ^{13}C NMR (in CF_3COOD) spectrum exhibited 13 carbon signals, which are shown in Section 4.1.4. Thus, the elemental analysis and the spectroscopic data for **15** led to the structure 1,4-phenylenebis[bis(3-methoxycarbonyl-1-azulenyl)methylium] bis(hexafluorophosphate) (see Scheme 1). In the previous paper,[14] we reported the detailed ^1H and ^{13}C NMR (in CD_3CN and CF_3COOD) spectral data of **1**, whose signals (i.e., δ and J values for all the protons and δ values for all the carbons) could be assigned. The above results suggest an apparent difference between the formation of a delocalized π-electron system of **1** and that of **15**.

Compound **16** was obtained as dark-brown plates (decomp. >221 °C). The UV—vis spectrum showed a strong absorption band based on the bis(3-methoxycarbonyl-1-azulenyl)methylium-ion part at λ_{max} 274 nm (log ε=5.00), which coincided with that of **17** [λ_{max} 275 nm (log ε=4.89)], and revealed two broad absorption bands [λ_{max} 657 and 575 nm (log ε=4.80 and 4.79)] (see Fig. 1), suggesting the formation of a delocalized π-electron system between the two bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts and the 2,5-substituted thiophene ring. The spectral pattern was the same as those of **4** [λ_{max} 724 and 602 nm (log ε=4.66 and 4.62)][25] and **5** [λ_{max} 729 and 594 nm (log ε=4.71 and 4.63)],[25] while its spectral pattern did not resemble that of **15**. The IR spectrum showed a specific band based on the C=O group of ester at ν_{max} 1701 cm^{-1}, which coincided with those of **15** and **17**. The formula $C_{54}H_{38}O_8S$ for the dicarbenium-ion part was determined by exact FABMS spectrum. An elemental analysis confirmed the formula $C_{54}H_{38}F_{12}O_8P_2S$. Similarly, as in the cases of **2**,[14] **3**,[14] and **15**, the 600 MHz ^1H NMR (in CD_3CN) spectrum showed extremely complicated signals,[37] which could not be assigned. The spectrum (in CF_3COOD) revealed broad signals for all the protons; however, signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts (i.e., four equivalent 3-methoxycarbonyl-1-azulenic protons: 3′-$COOCH_3$, H-2′, and H-4′—H-8′) and an equivalent signal based on the H-3 and 4 protons of the 2,5-substituted thiophene ring could be assigned using H—H COSY technique (see Section 4.1.5). The 150 MHz ^{13}C NMR (in CF_3COOD) spectrum exhibited 12 carbon signals, which are shown in Section 4.1.5. Thus, the elemental analysis and the spectroscopic data for **16** led to the structure 2,5-thienylenebis[bis(3-methoxycarbonyl-1-azulenyl)methylium] bis(hexafluorophosphate) (see Scheme 2). Ito et al. reported the detailed ^1H and ^{13}C NMR spectral data of **4** (in CD_3CN) and **5** (in $CDCl_3$), previously, whose signals were carefully assigned.[25] The above results suggest an apparent difference between the formation of a delocalized π-electron system of **4** (or **5**) and that of **16**.

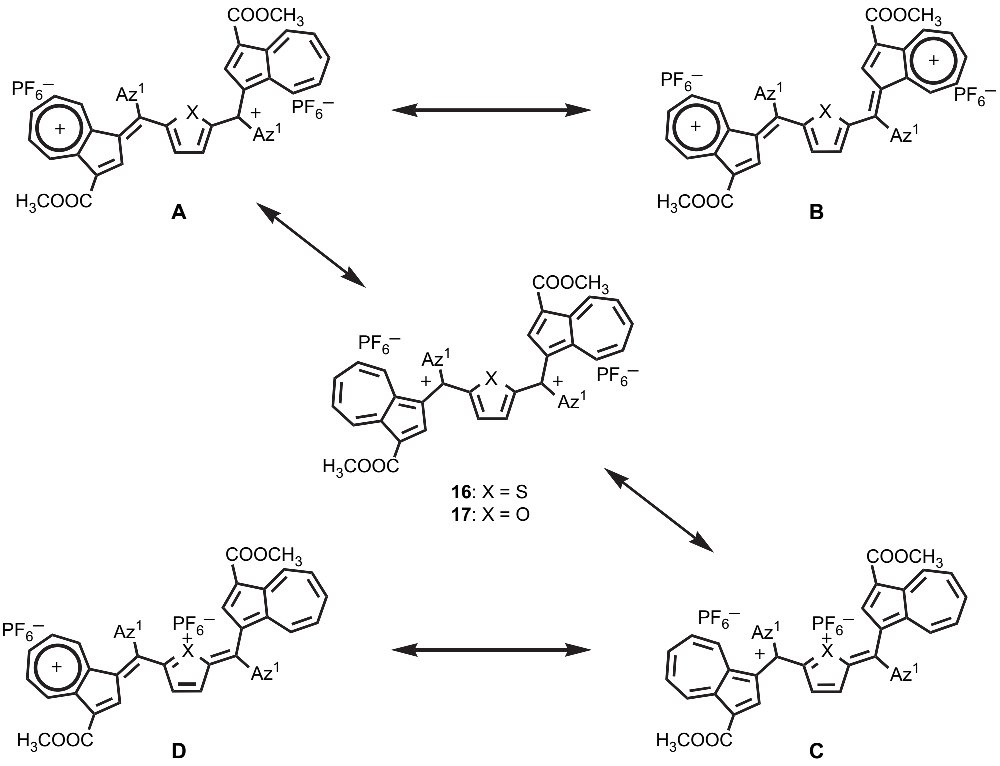
Compound **17** was obtained as dark-brown needles (decomp. >227 °C). From a comparative study on UV—vis spectrum, it was found that, similarly as in the cases of **2**[14] and **3**,[14] two broad absorption bands (λ_{max} 657 and 575 nm) were observed for **16**, while a broad absorption band [λ_{max} 637 nm (log ε=4.71)] was observed for **17** (see Fig. 1), suggesting the formation of a delocalized π-electron system between the two bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts and the 2,5-substituted furan ring. The formula $C_{54}H_{38}O_9$ for the dicarbenium-ion part was determined by exact FABMS spectrum. An elemental analysis confirmed the formula $C_{54}H_{38}F_{12}O_9P_2$. Although the 600 MHz ^1H NMR spectrum in CD_3CN showed broad signals for all the protons, the spectrum in CF_3COOD revealed signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts (i.e., four equivalent 3-methoxycarbonyl-1-azulenic protons: 3′-$COOCH_3$, H-2′, and H-4′—H-8′) and an equivalent signal based on the H-3 and 4 protons of the 2,5-substituted furan ring, whose signals (δ and J values) could be assigned using first-order analysis and H—H COSY technique (see Section 4.1.6). The 150 MHz ^{13}C NMR (in CF_3COOD) spectrum exhibited 14 carbon signals, which are shown in Section 4.1.6. Thus, the elemental analysis and the spectroscopic data for **17** led to the structure 2,5-furylenebis[bis(3-methoxycarbonyl-1-azulenyl)methylium] bis(hexafluorophosphate) (see Scheme 2).

Similarly, as in the cases of **2**[14] and **3**,[14] the UV—vis spectra of **16** and **17**, compared with those of **4**, **5**, and **15**, and their ^1H NMR spectra, compared with those of **4**, **5**, **13**, and **14**, suggested the formation of the dicarbenium-ion structures **16** and **17** with the representative four resonance forms of **A**—**D** (see Scheme 3).

2.3. Preparation and spectroscopic properties of 18—20

Although the oxidation of **12** with DDQ in chloroform at 25 °C for 2 h gave the quinodimethane **18** in 45% yield,[35] the reduction of **15** with zinc powder in a mixed solvent of acetonitrile and chloroform at 25 °C for 1 h afforded **18** in 90% yield (see Scheme 1 and Section 4.1.7). For comparative purposes, the reductions of **16** and **17** with zinc powder under the same reaction conditions as for **15** provided new quinodimethanes **19** (99% yield) and **20** (90% yield), respectively, whose detailed experimental procedures are shown in Sections 4.1.8 and 4.1.9. Preparation of quinodimethane from the reduction of 1,4-phenylenebis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate) (**21**) was not achieved due to instability, ready decomposition, or polymerization of the corresponding reduced species.[25] The yield of **19** was much better than those of **6**[25] (57% yield) and **7**[25] (62% yield). The molecular structures of the products **18**—**20** were established on the basis of spectroscopic data (i.e., UV—vis, IR, exact FABMS, and ^1H and ^{13}C NMR including NOE, H—H COSY, HMQC, and HMBC).

Compound **19** was obtained as dark-red plates (decomp. >332 °C), whose compound was extremely stable at room temperature under aerobic conditions in comparison with the quinoid compound derived from **2**.[14] The UV—vis spectrum showed a strong absorption band based on the 3-(methoxycarbonyl)azulen-1-yl group at λ_{max} 290 nm (log ε=5.12), which coincided with those of **18** [λ_{max} 290 nm (log ε=5.20)] and **20** [λ_{max} 290 nm (log ε=5.11)], and revealed the longest absorption wavelength at λ_{max} 507 nm (log ε=4.54), while those absorption wavelengths of **18** and **20** were observed at λ_{max} 525 nm (log ε=4.67) and λ_{max} 530 nm (log ε=4.40) (see Fig. 2). The UV—vis spectral pattern of **19** resembled those of **18** and **20**. Thus, similarly as in the case of **18**,[35] the spectra of **19** and **20** suggested the formation of a delocalized π-electron system



Scheme 3. Az^1=3-methoxycarbonyl-1-azulenyl group.

between the two bis(3-methoxycarbonyl-1-azulenyl)methylidene parts and the 2,5-dihydrothiophene (or 2,5-dihydrofuran) ring. The IR spectrum showed a specific band based on the C═O group of ester at ν_{max} 1693 cm^{-1}, whose wavenumber coincided with those of **18** and **20**. The molecular formula $C_{54}H_{38}O_8S$ was determined by exact FABMS spectrum. The 600 MHz ^1H NMR (in benzene-d_6) spectrum showed signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylidene parts (i.e., the divided two 3-methoxycarbonyl-1-azulenic protons: 3′,3″-$COOCH_3$, H-2′,2″, and H-4′,4″—H-8′,8″) and an equivalent signal based on the H-3 and 4 protons of the 2,5-dihydrothiophene ring, whose signals were carefully assigned using NOE and H–H COSY techniques and computer-assisted simulation analysis based on first-order analysis (see Section 4.1.8). The 150 MHz ^{13}C NMR (in benzene-d_6) spectrum exhibited 27 carbon signals assigned by HMQC and HMBC techniques (see Section 4.1.8). Thus, these spectroscopic data for **19** led to the molecular structure 2,5-bis[bis(3-methoxycarbonyl-1-azulenyl)methylidene]-2,5-dihydrothiophene (see Scheme 2).

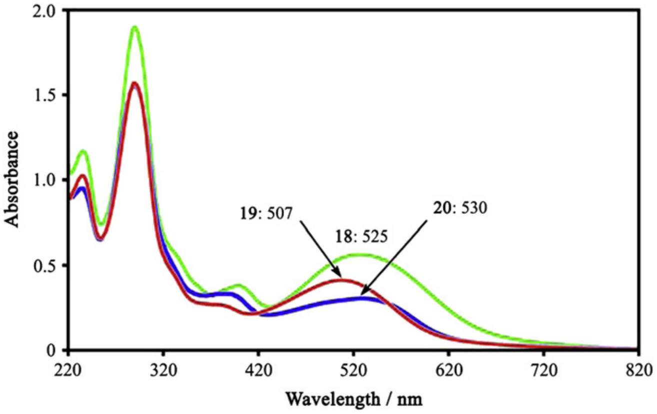


Figure 2. The UV–vis spectra of **18**, **19**, and **20** in CH_2Cl_2. Concentrations, **18**: 0.10 g/L (119 μmol/L), **19**: 0.10 g/L (118 μmol/L), and **20**: 0.10 g/L (120 μmol/L). Length of the cell, 0.1 cm each. **18**: λ_{max} 525 nm (log ε=4.67). **19**: λ_{max} 507 nm (log ε=4.54). **20**: λ_{max} 530 nm (log ε=4.40).

Compound **20** was obtained as dark-red blocks (decomp. >320 °C), whose compound was extremely stable at room temperature under aerobic conditions as well as **19**. The molecular formula $C_{54}H_{38}O_9$ was determined by exact FABMS spectrum. The 600 MHz ^1H NMR (in benzene-d_6) spectrum showed signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylidene parts (i.e., the divided two 3-methoxycarbonyl-1-azulenic protons: 3′,3″-$COOCH_3$, H-2′,2″, and H-4′,4″—H-8′,8″) and an equivalent signal based on the H-3 and 4 protons of the 2,5-dihydrofuran ring, whose signals were carefully assigned using similar techniques to those of **19** (see Section 4.1.9). The 150 MHz ^{13}C NMR (in benzene-d_6) spectrum exhibited 27 carbon signals assigned using similar techniques to those of **19** (see Section 4.1.9). Thus, these spectroscopic data for **20** led to the molecular structure 2,5-bis[bis(3-methoxycarbonyl-1-azulenyl)methylidene]-2,5-dihydrofuran (see Scheme 2).

Similarly, as in the cases of **15**–**17**, the UV–vis and ^1H and ^{13}C NMR spectra of **18**–**20**, with a view to a comparative study, also suggested the formation of a delocalized π-electron system.

2.4. Electrochemical behavior of **18**–**20**

We have been interested in the electrochemical properties of **18**, **19**, and **20** with a view to a comparative study. Those

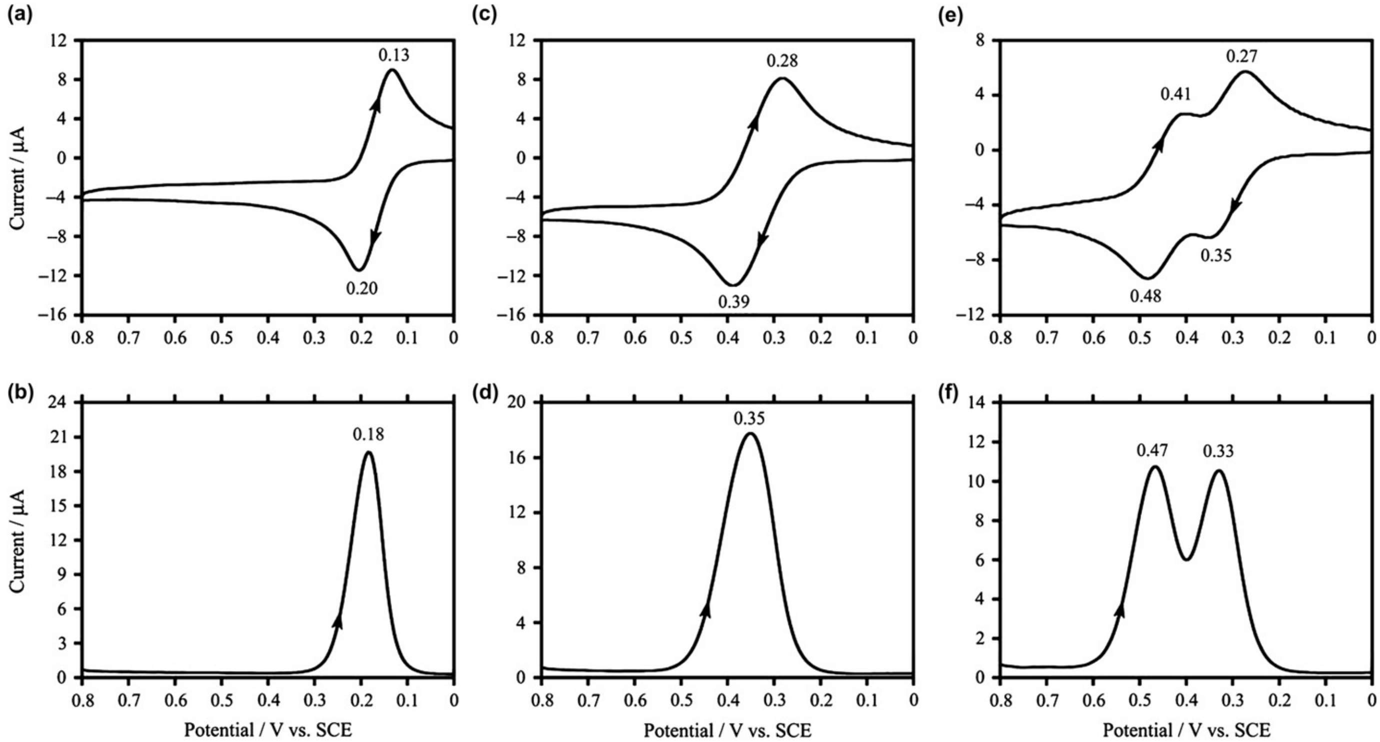
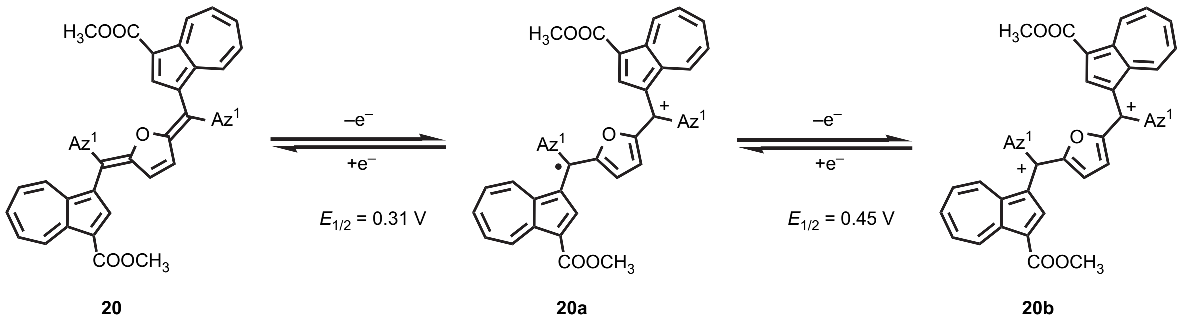


Figure 3. Cyclic and differential pulse voltammograms of **18** (3.0 mg, 3.6 μmol) [see (a), (b)], **19** (3.0 mg, 3.5 μmol) [see (c), (d)], and **20** (3.0 mg, 3.6 μmol) [see (e), (f)] in 0.1 M [n-Bu$_4$N]PF$_6$, CH$_2$Cl$_2$ (10 mL) at a glassy carbon (ID: 3 mm) and a platinum wire served as the working and auxiliary electrodes; scan rates 100 mVs^{-1} at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.42 V (E_p) by DPV and +0.42 V ($E_{1/2}$) by CV under the same electrochemical measurement conditions as the above.

compounds were insoluble in CH$_3$CN, a generally used solvent for CV measurement. The electrochemical behavior of those compounds were, therefore, measured by means of CV and DPV [potential (in volt) vs SCE] in CH$_2$Cl$_2$ containing 0.1 M [n-Bu$_4$N]PF$_6$ as a supporting electrolyte. From the results, it was found that (i) **18** underwent two-electron oxidation, simultaneously, at a potential of +0.17 V ($E_{1/2}$) by CV (+0.18 V by DPV) (see Fig. 3a,b); (ii) **19** also underwent two-electron oxidation, simultaneously, at a potential of +0.34 V ($E_{1/2}$) by CV (+0.35 V by DPV) (see Fig. 3c,d), whose oxidation potential coincided with that of **7** (+0.35 V by CV);[25] however, (iii) **20** stepwise underwent two-electron oxidation at the potentials of +0.31 V ($E_{1/2}$) and +0.45 V ($E_{1/2}$) by CV (+0.33 and +0.47 V by DPV) (see Fig. 3e,f), presumably owing to the difference between the formation of a delocalized π-electron system of **20**, possessing a 2H,5H-furan ring, and that of **18** (or **19**), possessing a 1H,4H-benzene (or a 2H,5H-thiophene) ring.[38] Thus, their CV and DPV data indicated **18**, **19**, and **20** serve as strong two-electron donors and, further, the facility of two-electron oxidation is in the order of **18**>**19**>**20**. A plausible electron transfer mechanism of **20** based on its CV and DPV data can be inferred as illustrated in Scheme 4: namely, **20** undergoes one-electron oxidation at a potential of +0.31 V by CV (+0.33 V by DPV), generating an electrochemically stable cation-radical species of **20a** and, further, the generated cation-radical species undergo one-electron oxidation at a potential of +0.45 V by CV (+0.47 V by DPV), generating an electrochemically stable dication species of **20b**.

2.5. Electrochemical behavior of 15–17

We have been interested further in the electrochemical properties of the dicarbenium-ion compounds **15**, **16**, and **17** with a view to a comparative study. The electrochemical



Scheme 4. Az^1=3-methoxycarbonyl-1-azulenyl group.

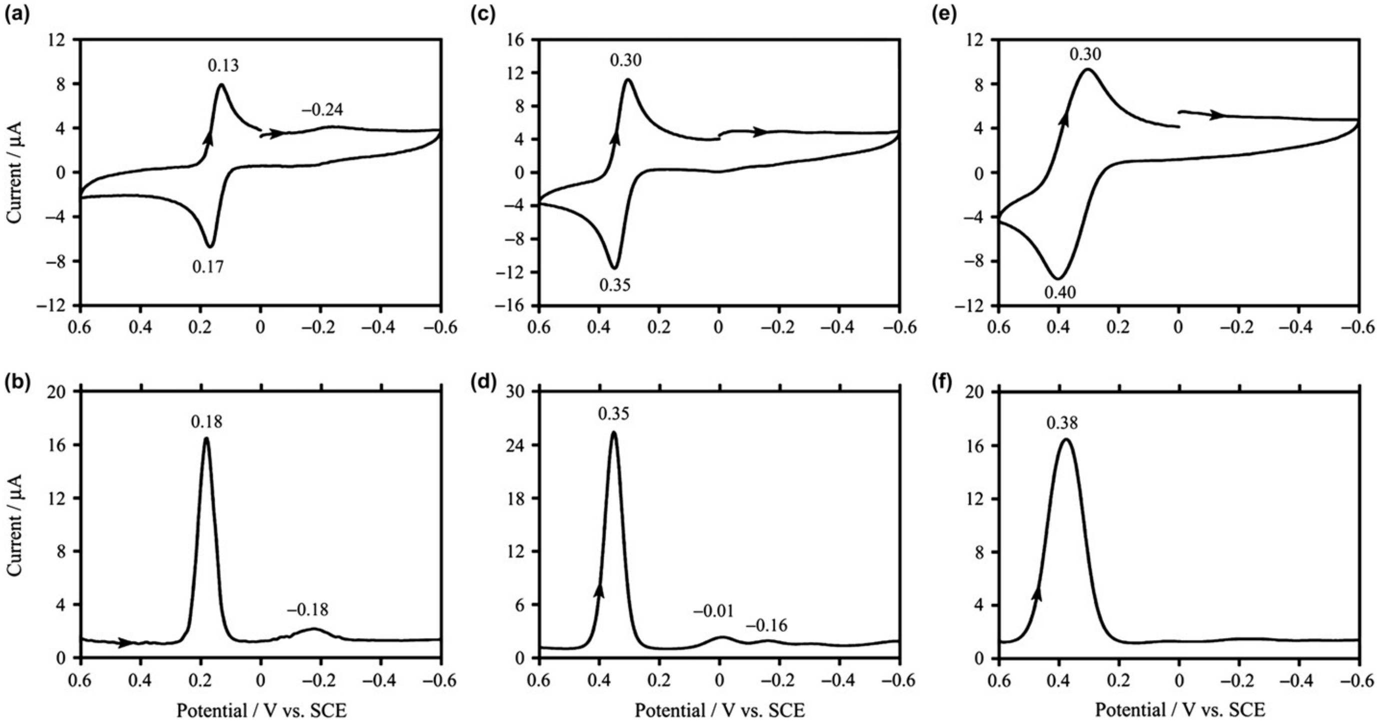


Figure 4. Cyclic and differential pulse voltammograms of **15** (3.0 mg, 2.7 μmol) [see (a), (b)], **16** (3.0 mg, 2.6 μmol) [see (c), (d)], and **17** (3.0 mg, 2.7 μmol) [see (e), (f)] in 0.1 M [n-Bu$_4$N]PF$_6$, CH$_3$CN (10 mL) at a glassy carbon (ID: 3 mm) and a platinum wire served as the working and auxiliary electrodes; scan rates 100 mVs^{-1} at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.42 V (E_p) by DPV and +0.40 V ($E_{1/2}$) by CV under the same electrochemical measurement conditions as the above.

behavior of **15** was, therefore, measured by means of CV and DPV [potential (in volt) vs SCE] in CH$_3$CN containing 0.1 M [n-Bu$_4$N]PF$_6$ as a supporting electrolyte. Two redox potentials observed by DPV were positioned at the E_p values of +0.18 and −0.18 V, and the corresponding oxidation and reduction potentials determined by CV were located at the values of +0.15 V ($E_{1/2}$) and −0.24 V (E_{pc}) (see Fig. 4a,b). Therefore, **15** was susceptible to reduction and oxidation than 1,4-phenylenebis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate) (**21**) [−0.55 V (E_{pc}) and +0.87 V ($E_{1/2}$) by CV].[25] For comparative purposes, the electrochemical behavior of **16** and **17** was measured under the same electrochemical measurement conditions as for **15**. From the results, two redox potentials observed by CV were positioned at the $E_{1/2}$ values of +0.98 and −0.30 V for **5**,[25] while three redox potentials observed by DPV were positioned at the E_p values of +0.35, −0.01, and −0.16 V for **16**, and the corresponding oxidation potential determined by CV was located at a value of +0.33 V ($E_{1/2}$) (see Fig. 4c,d). Therefore, an apparent difference between the redox behavior of **5** and that of **16** was observed. An oxidation potential observed by DPV was positioned at an E_p value of +0.38 V for **17**, and the corresponding oxidation potential determined by CV was located at a value of +0.35 V ($E_{1/2}$) (see Fig. 4e,f). From a comparative study on the redox potentials of **15**–**20**, it could be inferred that (i) although the reduction waves of the CV and DPV for **15**–**17** did not appear, clearly, in comparison with those of **5** and **21**, **15** underwent two-electron reduction at a potential of −0.24 V (E_{pc}, irreversible) by CV (−0.18 V by DPV), generating **18**, which underwent two-electron oxidation, simultaneously, at a potential of +0.15 V ($E_{1/2}$) by CV (+0.18 V by DPV), converting to a starting dication species of **15**; (ii) **16** stepwise underwent two-electron reduction at the potentials of −0.01 and −0.16 V by DPV, generating **19**, which underwent two-electron oxidation, simultaneously, at a potential of +0.33 V ($E_{1/2}$) by CV (+0.35 V by DPV), converting to a starting dication species of **16**; and (iii) the reduction potential of **17** was not observed by CV and DPV; however, **17** was readily converted to **20** under the electrochemical reduction conditions as shown in Figure 4e,f. The generated **20** underwent two-electron oxidation, simultaneously, at a potential of +0.35 V ($E_{1/2}$) by CV (+0.38 V by DPV), converting to a starting dication species of **17**.

3. Conclusion

We have reported the following five points in this paper: (i) the reaction of methyl 1-azulenecarboxylate (**8**) with terephthalaldehyde (**9**) in acetic acid in the presence of hydrochloric acid at 25 °C for 2 h gave 1,4-bis[bis(3-methoxycarbonyl-1-azulenyl)methyl]benzene (**12**) in 93% yield. Similarly, as in the case of **9**, the reactions of **8** with **10** and **11** in acetic acid in the presence of hydrochloric acid were carried out, efficiently yielding new compounds **13** (97% yield) and **14** (90% yield); (ii) the oxidations of **12**, **13**, and **14** with DDQ in dichloromethane in the presence of hexafluorophosphoric acid at 25 °C for 1 h afforded new dicarbenium-ion compounds **15** (94% yield), **16** (90% yield), and **17** (86% yield); (iii) the reduction of **15** with zinc powder in a mixed solvent of acetonitrile and chloroform at 25 °C for 1 h yielded the target quinodimethane **18** in 90% yield. Similarly, as in the case of **18**, new quinoid compounds **19** and **20** could be derived from **16** and **17**, quantitatively; (iv) along with an efficient preparation of **12**–**20**, their spectroscopic properties were reported; and (v) from a comparative study on the redox potentials of **15**–**20**, it could be inferred that **15**–**17** were readily converted to **18**–**20** under the electrochemical reduction conditions as shown in Figure 4 and, further, the CV and DPV data indicated **18**–**20** serve as strong two-electron donors.

4. Experimental

4.1. General

Melting points were determined using a Yanagimoto MP-S3 instrument. Thermal (TGA/DTA) and elemental analyses were taken on a Shimadzu DTG-50H thermal analyzer and a Yanaco MT-3 CHN corder. FABMS spectra were taken on a JEOL The Tandem Mstation JMS-700 TKM data system. UV–vis and IR spectra were taken on a Beckman DU640 spectrophotometer and a Shimadzu FTIR-4200 Grating spectrometer. NMR spectra were recorded with a JEOL GX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) and JNM-ECA600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) cryospectrometer at 25 °C. The ^{1}H NMR spectra were assigned using the computer-assisted simulation analysis on a Dell Dimension 8300 personal-computer with a Pentium (R) 4 processor (the software: gNMR developed by Adept Scientific plc). Cyclic and differential pulse voltammograms were measured by an ALS Model 600 electrochemical analyzer.

*4.1.1. Preparation of 1,4-bis[bis(3-methoxycarbonyl-1-azulenyl)methyl]benzene (**12**)*

To a solution of methyl 1-azulenecarboxylate (**8**) (77 mg, 0.41 mmol) in acetic acid (1.0 mL) was added a solution of terephthalaldehyde (**9**) (14 mg, 0.11 mmol) in acetic acid (1.0 mL) in the presence of 1.0 M hydrochloric acid (100 μL). The mixture was stirred at 25 °C for 2 h, precipitating a light-purple solid of **12**, and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with acetic acid, water, and methanol, and dried well in a vacuum desiccator. The crude product was recrystallized from chloroform–methanol (1:5, v/v) (several times) to provide pure **12** as stable crystals (80 mg, 95 μmol, 93% yield).

Compound **12**: Bluish-purple prisms, R_f=0.25 on silica-gel TLC (ethyl acetate/hexane=1:1, v/v), mp >295 °C; UV–vis $\lambda_{\max}$ ($CHCl_3$) nm (log ε), 292sh (5.20), 304 (5.24), 368sh (4.55), 384 (4.60), 557 (3.34), 604sh (3.24), and 666sh (2.71); IR $\nu_{\max}$ (KBr) cm^{-1}, 2947 (C–H) and 1693 (C=O); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 842 (M^+); exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 842.2866; calcd for $C_{56}H_{42}O_8$: M^+, 842.2880; 500 MHz ^{1}H NMR ($CDCl_3$), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methyl groups: δ 3.85 (12H, s, 3′,3″-$COOCH_3$), 6.58 (2H, s, >CH-1,4), 7.32 (4H, br dd, *J*=9.5, 9.5 Hz, H-7′,7″), 7.52 (4H, br dd, *J*=9.5, 9.5 Hz, H-5′,5″), 7.76 (4H, br dd, *J*=9.5, 9.5 Hz, H-6′,6″), 7.86 (4H, s, H-2′,2″), 8.36 (4H, br d, *J*=9.5 Hz, H-8′,8″), and 9.64 (4H, br d, *J*=9.5 Hz, H-4′,4″); a signal based on the 1,4-substituted benzene ring: δ 7.10 (4H, s, H-2,3,5,6); 125 MHz ^{13}C NMR ($CDCl_3$), δ 165.7 (3′,3″-*C*$OOCH_3$), 141.7, 140.9, 140.0, 139.1, 137.9, 135.2, 131.8, 130.2, 129.1, 127.7, 126.3, 115.1, 51.0 (3′,3″-COO*C*H_3), and 42.1 (>CH-1,4).

*4.1.2. Preparation of 2,5-bis[bis(3-methoxycarbonyl-1-azulenyl)methyl]thiophene (**13**)*

To a solution of **8** (100 mg, 0.54 mmol) in acetic acid (1.5 mL) was added a solution of thiophene-2,5-dicarbaldehyde (**10**) (20 mg, 0.14 mmol) in acetic acid (1.5 mL) in the presence of 1.0 M hydrochloric acid (150 μL). The mixture was stirred at 25 °C for 2 h, precipitating a dark-blue solid of **13**, and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with acetic acid, water, and methanol, and dried well in a vacuum desiccator. The crude product was recrystallized from benzene–methanol (1:5, v/v) (several times) to provide pure **13** as stable crystals (110 mg, 0.13 mmol, 97% yield).

Compound **13**: Dark-blue plates, R_f=0.25 on silica-gel TLC (ethyl acetate/hexane=1:1, v/v), decomp. >301 °C [determined by thermal analysis (TGA and DTA)]; IR $\nu_{\max}$ (KBr) cm^{-1}, 2943 (C–H) and 1690 (C=O); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 848 (M^+); exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 848.2451; calcd for $C_{54}H_{40}O_8S$: M^+, *m/z* 848.2444; 500 MHz ^{1}H NMR (C_6D_6), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methyl groups: δ 3.51 (12H, s, 3′,3″-$COOCH_3$), 6.69 (2H, s, >CH-2,5), 6.72 (4H, ddd, *J*=10.0, 9.7, 1.0 Hz, H-7′,7″), 6.93 (4H, ddd, *J*=9.8, 9.8, 1.0 Hz, H-5′,5″), 7.06 (4H, dddd, *J*=10.0, 9.8, 1.0, 1.0 Hz, H-6′,6″), 8.22 (4H, dd, *J*=9.7, 1.0 Hz, H-8′,8″), 8.52 (4H, s, H-2′,2″), and 10.02 (4H, dd, *J*=9.8, 1.0 Hz, H-4′,4″); a signal based on the 2,5-substituted thiophene ring: δ 6.44 (2H, s, H-3,4); 125 MHz ^{13}C NMR (C_6D_6), δ 165.3 (3′,3″-*C*$OOCH_3$), 147.5 (C-2,5), 142.2 (C-3a′,3a″), 140.9 (C-2′,2″), 139.9 (C-8a′,8a″), 139.1 (C-6′,6″), 138.6 (C-4′,4″), 135.2 (C-8′,8″), 131.7 (C-1′,1″), 127.8 (C-5′,5″), 126.2 (C-3,4), 126.2 (C-7′,7″), 116.2 (C-3′,3″), 50.6 (3′,3″-COO*C*H_3), and 38.4 (>CH-2,5).

*4.1.3. Preparation of 2,5-bis[bis(3-methoxycarbonyl-1-azulenyl)methyl]furan (**14**)*

To a solution of **8** (50 mg, 270 μmol) in acetic acid (0.5 mL) was added a solution of furan-2,5-dicarbaldehyde (**11**) (9 mg, 73 μmol) in acetic acid (0.5 mL) in the presence of 1.0 M hydrochloric acid (60 μL). The mixture was stirred at 25 °C for 3 h. After the reaction, the reaction solution was carefully neutralized with aq Na_2CO_3, and then the products were extracted with chloroform (3×10 mL). The extract was washed with water, dried ($MgSO_4$), and evaporated in vacuo. The residue thus obtained was carefully separated by silica-gel column chromatography with chloroform–dichloromethane (1:4, v/v) as an eluant. The crude product was recrystallized from chloroform–methanol (1:5, v/v) (several times) to provide pure **14** as stable crystals (50 mg, 60 μmol, 90% yield).

Compound **14**: Dark-blue blocks, R_f=0.30 on silica-gel TLC (ethyl acetate/hexane=1:1, v/v), decomp. >100 °C (determined by TGA and DTA); IR $\nu_{\max}$ (KBr) cm^{-1}, 2947 (C–H) and 1690

(C=O); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 833 $[M+H]^+$; exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 832.2659; calcd for $C_{54}H_{40}O_9$: M^+, *m/z* 832.2672; 600 MHz ^{1}H NMR (C_6D_6), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methyl groups: δ 3.54 (12H, s, 3′,3″-COOCH$_3$), 6.62 (2H, s, $>$CH-2,5), 6.72 (4H, ddd, J=9.6, 9.5, 1.0 Hz, H-7′,7″), 6.93 (4H, ddd, J=9.7, 9.6, 1.0 Hz, H-5′,5″), 7.06 (4H, dddd, J=9.7, 9.6, 1.0, 1.0 Hz, H-6′,6″), 8.20 (4H, dd, J=9.5, 1.0 Hz, H-8′,8″), 8.48 (4H, s, H-2′,2″), and 10.00 (4H, dd, J=9.6, 1.0 Hz, H-4′,4″); a signal based on the 2,5-substituted furan ring: δ 5.75 (2H, s, H-3,4); 150 MHz ^{13}C NMR (C_6D_6), δ 165.3 (3′,3″-*C*OOCH$_3$), 156.4 (C-2,5), 142.2 (C-3a′,3a″), 140.7 (C-2′,2″), 140.1 (C-8a′,8a″), 139.1 (C-6′,6″), 138.5 (C-4′,4″), 135.2 (C-8′,8″), 129.8 (C-1′,1″), 127.8 (C-5′,5″), 126.2 (C-7′,7″), 116.2 (C-3′,3″), 109.1 (C-3,4), 50.6 (3′,3″-COO*C*H$_3$), and 38.4 ($>$CH-2,5).

*4.1.4. Preparation of 1,4-phenylenebis[bis(3-methoxycarbonyl-1-azulenyl)methylium] bis(hexafluorophosphate) (**15**)*

To a solution of **12** (50 mg, 59 μmol) in dichloromethane (6.0 mL) was added a solution of DDQ (27 mg, 119 μmol) in dichloromethane (6.0 mL). The mixture was stirred at 25 °C for 10 min, and then hexafluorophosphoric acid (60% aqueous solution, 1.2 mL) was added and, further, was stirred for 1 h. After the reaction, diethyl ether was added to the mixture, precipitating a black solid of **15**, which was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether and recrystallized from acetone–hexane (1:5, v/v) (several times) to provide pure **15** as a powder (63 mg, 56 μmol, 94% yield).

Compound **15**: Dark-brown powder, decomp. >217 °C (determined by TGA and DTA); Found: C, 61.00; H, 4.25%. Calcd for $C_{56}H_{40}F_{12}O_8P_2+C_6H_{14}$: C, 61.19; H, 4.47%; UV–vis λ_{max} (CF_3COOH) nm (log ε), 263 (5.01), 382 (461), 487 (4.64), and 635 (4.95); IR ν_{max} (KBr) cm^{-1}, 2950 (C–H), 1701 (C=O), and 876, 571 (PF_6^-); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 840 $[M-2PF_6]^{2+}$; exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 840.2738; calcd for $C_{56}H_{40}O_8$: $[M-2PF_6]^{2+}$, 840.2723; 600 MHz ^{1}H NMR (CF_3COOD), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts: δ 4.19 (12H, s, 3′,3″-COOCH$_3$), 7.89 (4H, br s, H-6′,6″), 8.40 (4H, br s, H-2′,2″), 8.40 (4H, br s, H-5′,5″), 8.40 (4H, br s, H-7′,7″), 8.74 (4H, br s, H-8′,8″), and 10.06 (4H, br s, H-4′,4″); a signal based on the 1,4-substituted benzene ring: δ 7.89 (4H, br s, H-2,3,5,6); 150 MHz ^{13}C NMR (CF_3COOD), δ 169.5 (3′,3″-*C*OOCH$_3$), 154.2, 153.1 (C–H), 152.6, 148.5 (C–H), 145.0 (C–H), 143.5 (C–H), 141.5 (C–H), 140.3 (C–H), 138.3 (C–H), 134.6, 127.1, and 55.1 (3′,3″-COO*C*H$_3$).

*4.1.5. Preparation of 2,5-thienylenebis[bis(3-methoxycarbonyl-1-azulenyl)methylium] bis(hexafluorophosphate) (**16**)*

To a solution of **13** (30 mg, 35 μmol) in dichloromethane (2.5 mL) was added a solution of DDQ (16 mg, 70 μmol) in dichloromethane (2.5 mL). The mixture was stirred at 25 °C for 10 min, and then hexafluorophosphoric acid (60% aqueous solution, 0.5 mL) was added and, further, was stirred for 1 h. After the reaction, diethyl ether was added to the mixture, precipitating a dark-blue solid of **16**, which was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether and recrystallized from acetonitrile–diethyl ether (1:5, v/v) (several times) to provide pure **16** as stable crystals (36 mg, 32 μmol, 90% yield).

Compound **16**: Dark-brown plates, decomp. >221 °C (determined by TGA and DTA); Found: C, 56.87; H, 3.67%. Calcd for $C_{54}H_{38}F_{12}O_8P_2S$: C, 57.05; H, 3.37%; UV–vis λ_{max} (CF_3COOH) nm (log ε), 274 (5.00), 377 (4.43), 422 (4.37), 575 (4.79), and 657 (4.80); IR ν_{max} (KBr) cm^{-1}, 2947 (C–H), 1701 (C=O), and 876, 559 (PF_6^-); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 846 $[M-2PF_6]^{2+}$; exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 846.2292; calcd for $C_{54}H_{38}O_8S$: $[M-2PF_6]^{2+}$, *m/z* 846.2287; 600 MHz ^{1}H NMR (CF_3COOD), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts: δ 4.18 (12H, s, 3′,3″-COOCH$_3$), 7.84 (4H, br s, H-7′,7″), 8.35 (4H, br s, H-5′,5″), 8.35 (4H, br s, H-6′,6″), 8.40 (4H, br s, H-8′,8″), 8.98 (4H, br s, H-2′,2″), and 10.03 (4H, br s, H-4′,4″); a signal based on the 2,5-substituted thiophene ring: δ 8.14 (2H, br s, H-3,4); 150 MHz ^{13}C NMR (CF_3COOD), δ 169.5 (3′,3″-*C*OOCH$_3$), 154.0, 152.3 (C–H), 148.6 (C–H), 145.0 (C–H), 143.4 (C–H), 143.1 (C–H), 141.2 (C–H), 140.1 (C–H), 133.6, 126.9, and 55.1 (3′,3″-COO*C*H$_3$).

*4.1.6. Preparation of 2,5-furylenebis[bis(3-methoxycarbonyl-1-azulenyl)methylium] bis(hexafluorophosphate) (**17**)*

To a solution of **14** (30 mg, 36 μmol) in dichloromethane (2.5 mL) was added a solution of DDQ (17 mg, 75 μmol) in dichloromethane (2.5 mL). The mixture was stirred at 25 °C for 10 min, and then hexafluorophosphoric acid (60% aqueous solution, 0.5 mL) was added and, further, was stirred for 1 h. After the reaction, diethyl ether was added to the mixture, precipitating a black solid of **17**, which was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether and recrystallized from acetone–diethyl ether (1:5, v/v) (several times) to provide pure **17** as stable crystals (35 mg, 31 μmol, 86% yield).

Compound **17**: Dark-brown needles, decomp. >227 °C (determined by TGA and DTA); Found: C, 61.62; H, 4.01%. Calcd for $1.5C_{54}H_{38}O_9+2PF_6+CH_3CN$: C, 61.84; H, 3.73%; UV–vis λ_{max} (CF_3COOH) nm (log ε), 275 (4.89), 379 (4.26), 438 (4.27), and 637 (4.71); IR ν_{max} (KBr) cm^{-1}, 2951 (C–H), 1701 (C=O), and 876, 582 (PF_6^-); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 830 $[M-2PF_6]^{2+}$; exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 830.2518; calcd for $C_{54}H_{38}O_9$: $[M-2PF_6]^{2+}$, *m/z* 830.2516; 600 MHz ^{1}H NMR (CF_3COOD), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylium-ion parts: δ 4.13 (12H, s, 3′,3″-COOCH$_3$), 7.79 (4H, dd, J=9.6, 9.6 Hz, H-7′,7″), 8.27 (4H, dd, J=9.8, 9.6 Hz, H-6′,6″), 8.32 (4H, dd, J=9.8, 9.6 Hz, H-5′,5″), 8.35 (4H, d, J=9.6 Hz, H-8′,8″), 8.98 (4H, s, H-2′,2″), and 10.00 (4H, d, J=9.6 Hz, H-4′,4″); a signal based on the 2,5-substituted furan ring: δ 7.93 (2H, s, H-3,4); 150 MHz ^{13}C NMR (CF_3COOD), δ 169.4 (3′,3″-*C*OOCH$_3$), 153.8, 152.8, 151.3 (C–H), 150.7, 148.5 (C–H), 144.8 (C–H), 143.3 (C–H), 141.3 (C–H), 140.1 (C–H), 134.5 (C–H), 131.7, 127.3, and 55.2 (3′,3″-COO*C*H$_3$).

*4.1.7. Preparation of 7,7,8,8-tetrakis(3-methoxycarbonyl-1-azulenyl)-p-quinodimethane (**18**)*

Zinc powder (150 mg, 0.66 mmol) was added to a solution of **15** (30 mg, 27 μmol) in acetonitrile (5.0 mL). The mixture was stirred at 25 °C for 20 min, and then chloroform (10.0 mL) was added, which was stirred further for 40 min. After the reaction, the mixture was filtered and the filtrate was evaporated in vacuo. The residue thus obtained was carefully separated by alumina column chromatography with chloroform as an eluant. The crude product thus obtained was recrystallized from chloroform–hexane (1:5, v/v) (several times) to provide pure **18** as stable crystals (20 mg, 24 μmol, 90% yield).

Compound **18**: Dark-reddish-purple needles, R_f=0.31 on silica-gel TLC (ethyl acetate/hexane=1:1, v/v), decomp. >340 °C (determined by TGA/DTA); Found: C, 79.79; H, 5.02%. Calcd for $C_{56}H_{40}O_8$: C, 79.98; H, 4.79%; UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 221 (4.95), 235 (499), 290 (5.20), 330sh (4.68), 399 (4.50), and 525 (4.67); IR ν_{max} (KBr) cm^{-1}, 2947 (C–H) and 1693 (C=O); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 841 [M+H]$^+$; exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 841.2816; calcd for $C_{56}H_{41}O_8$: [M+H]$^+$, 841.2802; 600 MHz ^{1}H NMR (C_6D_6), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylidene parts: δ 3.55 (12H, s, 3′,3″-COOCH$_3$), 6.60 (4H, ddd, *J*=9.8, 9.6, 1.0 Hz, H-7′,7″), 6.91 (4H, ddd, *J*=9.6, 9.6, 1.0 Hz, H-5′,5″), 6.97 (4H, dddd, *J*=9.6, 9.6, 1.0, 1.0 Hz, H-6′,6″), 8.23 (4H, dd, *J*=9.8, 1.0 Hz, H-8′,8″), 8.68 (4H, s, H-2′,2″), and 10.02 (4H, dd, *J*=9.6, 1.0 Hz, H-4′,4″); a signal based on the 1*H*,4*H*-benzene ring: δ 6.73 (4H, s, H-2,3,5,6); 150 MHz ^{13}C NMR (C_6D_6), δ 165.3 (3′,3″-*C*OOCH$_3$), 144.1 (C-2′,2″), 143.1 (C-3a′,3a″), 141.3 (C-8a′,8a″), 139.7 (C-6′,6″), 138.5 (C-4′,4″), 137.9 (C-8′,8″), 135.4 (C-1,4), 131.7 (C-1′,1″), 129.4 (C-2,3,5,6), 128.4 (C-5′,5″), 127.2 ($>$C=1,4), 126.8 (C-7′,7″), 117.4 (C-3′,3″), and 50.7 (3′,3″-COO*C*H$_3$).

*4.1.8. Preparation of 2,5-bis[bis(3-methoxycarbonyl-1-azulenyl)methylidene]-2,5-dihydrothiophene (**19**)*

Zinc powder (50 mg, 0.22 mmol) was added to a solution of **16** (20 mg, 18 μmol) in acetonitrile (10.0 mL). The mixture was stirred at 25 °C for 20 min, and then chloroform (10.0 mL) was added, which was stirred further for 40 min. After the reaction, the mixture was filtered and the filtrate was evaporated in vacuo. The residue thus obtained was carefully separated by alumina column chromatography with chloroform as an eluant. The crude product thus obtained was recrystallized from chloroform–hexane (1:5, v/v) (several times) to provide pure **19** as stable crystals (15 mg, 17 μmol, 99% yield).

Compound **19**: Dark-red plates, R_f=0.26 on silica-gel TLC (ethyl acetate/hexane=1:1, v/v), decomp. >332 °C (determined by TGA and DTA); UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 235 (494), 290 (5.12), 382 (4.35), and 507 (4.54); IR ν_{max} (KBr) cm^{-1}, 2947 (C–H) and 1693 (C=O); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 846 (M$^+$); exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 846.2261; calcd for $C_{54}H_{38}O_8S$: M$^+$, *m/z* 846.2287; 600 MHz ^{1}H NMR (C_6D_6), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylidene parts: δ 3.43 (6H, s, 3″-COOCH$_3$), 3.62 (6H, s, 3′-COOCH$_3$), 6.51 (2H, ddd, *J*=9.7, 9.6, 1.0 Hz, H-7′), 6.54 (2H, ddd, *J*=9.7, 9.6, 1.0 Hz, H-7″), 6.76 (2H, ddd, *J*=9.8, 9.8, 1.0 Hz, H-5′), 6.85 (2H, dddd, *J*=9.8, 9.7, 1.0, 1.0 Hz, H-6′), 6.90 (2H, ddd, *J*=9.8, 9.6, 1.0 Hz, H-5″), 6.95 (2H, dddd, *J*=9.8, 9.7, 1.0, 1.0 Hz, H-6″), 8.19 (2H, dd, *J*=9.6, 1.0 Hz, H-8′), 8.25 (2H, dd, *J*=9.6, 1.0 Hz, H-8″), 8.65 (2H, s, H-2″), 8.84 (2H, s, H-2′), 9.79 (2H, dd, *J*=9.8, 1.0 Hz, H-4′), and 10.02 (2H, dd, *J*=9.6, 1.0 Hz, H-4″); a signal based on the 2*H*,5*H*-thiophene ring: δ 6.78 (2H, s, H-3,4); 150 MHz ^{13}C NMR (C_6D_6), δ 165.4 (3′-*C*OOCH$_3$), 165.0 (3″-*C*OOCH$_3$), 145.6 (C-2,5), 142.8 (C-2′), 142.8 (C-2″), 142.8 (C-3a′), 142.5 (C-3a″), 141.1 (C-8a″), 139.7 (C-6″), 139.6 (C-8a′), 139.4 (C-6′), 138.7 (C-4″), 138.6 (C-4′), 137.6 (C-8′), 137.5 (C-8″), 134.2 (C-3,4), 131.2 (C-1′), 131.0 (C-1″), 128.4 (C-5′), 128.3 (C-5″), 126.7 (C-7′), 126.7 (C-7″), 121.1 ($>$C=2,5), 117.2 (C-3′), 116.9 (C-3″), 50.8 (3′-COO*C*H$_3$), and 50.5 (3″-COO*C*H$_3$).

*4.1.9. Preparation of 2,5-bis[bis(3-methoxycarbonyl-1-azulenyl)methylidene]-2,5-dihydrofuran (**20**)*

Zinc powder (100 mg, 0.44 mmol) was added to a solution of **17** (20 mg, 18 μmol) in acetonitrile (10.0 mL). The mixture was stirred at 25 °C for 20 min, and then chloroform (10.0 mL) was added, which was stirred further for 40 min. After the reaction, the mixture was filtered and the filtrate was evaporated in vacuo. The residue thus obtained was carefully separated by alumina column chromatography with chloroform as an eluant. The crude product thus obtained was recrystallized from chloroform–hexane (1:5, v/v) (several times) to provide pure **20** as stable crystals (14 mg, 17 μmol, 90% yield).

Compound **20**: Dark-red blocks, R_f=0.34 on silica-gel TLC (ethyl acetate/hexane=1:1, v/v), decomp. >320 °C (determined by TGA and DTA); UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 235 (490), 290 (5.11), 383 (4.44), and 530 (4.40); IR ν_{max} (KBr) cm^{-1}, 2947 (C–H) and 1693 (C=O); FABMS (3-nitrobenzyl alcohol matrix), *m/z* 830 (M$^+$); exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 830.2535; calcd for $C_{54}H_{38}O_9$: M$^+$, *m/z* 830.2516; 600 MHz ^{1}H NMR (C_6D_6), signals based on two equivalent bis(3-methoxycarbonyl-1-azulenyl)methylidene parts; δ 3.55 (6H, s, 3′-COOCH$_3$), 3.67 (6H, s, 3″-COOCH$_3$), 6.10 (2H, ddd, *J*=9.8, 9.6, 1.0 Hz, H-7′), 6.43 (2H, ddd, *J*=9.8, 9.8, 1.0 Hz, H-7″), 6.79 (2H, dddd, *J*=9.6, 9.6, 1.0, 1.0 Hz, H-6′), 6.87 (2H, ddd, *J*=9.6, 9.6, 1.0 Hz, H-5′), 6.90 (2H, ddd, *J*=9.6, 9.6, 1.0 Hz, H-5″), 6.92 (2H, dddd, *J*=9.8, 9.6, 1.0, 1.0 Hz, H-6″), 7.79 (2H, dd, *J*=9.8, 1.0 Hz, H-8′), 8.17 (2H, dd, *J*=9.8, 1.0 Hz, H-8″), 8.59 (2H, s, H-2′), 8.79 (2H, s, H-2″), 9.88 (2H, dd, *J*=9.6, 1.0 Hz, H-4′), and 10.04 (2H, dd, *J*=9.6, 1.0 Hz, H-4″); a signal based on the 2*H*,5*H*-furan ring: δ 6.59 (2H, s, H-3,4); 150 MHz ^{13}C NMR (C_6D_6), δ 165.4 (3″-*C*OOCH$_3$), 165.3 (3′-*C*OOCH$_3$), 156.3 (C-2,5), 143.3 (C-3a′), 142.7 (C-2″), 142.5 (C-3a″), 142.3 (C-8a″), 142.2 (C-2′), 139.7 (C-6″), 138.8 (C-6′), 138.7 (C-4″), 138.1 (C-8a′), 137.6 (C-8′), 137.6 (C-8″), 137.5 (C-4′), 128.6 (C-1″), 128.1 (C-5′), 128.1 (C-5″), 127.9 (C-1′), 126.6 (C-3,4), 126.6 (C-7″), 125.6 (C-7′), 117.0 (C-3′), 116.7 (C-3″), 105.9 ($>$C=2,5), 50.8 (3″-COO*C*H$_3$), and 50.6 (3′-COO*C*H$_3$).

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37. After the ^{1}H NMR spectral measurement in CD_3CN, the pure sample without decomposition was recovered, quantitatively, by the recrystallization.
38. Details are currently under intensive investigation.