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Synthesis, Properties, and Redox Behavior of Mono-, Bis-, and Tris[1,1,4,4,-tetracyano-2-(1-azulenyl)-3-butadienyl] Chromophores Binding with Benzene and Thiophene Cores

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Abstract: Mono-, bis-, tris-, and tetrakis(1-azulenylethynyl)benzene and mono- and bis(1-azulenylethynyl)thiophene derivatives **5**–**10** have been prepared by Pd-catalyzed alkynylation of ethynyl arenes with 1-iodoazulene derivative or the 1-ethynylazulene derivative with tetraiodobenzene and iodothiophenes under Sonogashira–Hagihara conditions. Compounds **5**–**10** reacted with tetracyanoethylene in a [2+2] cycloaddition reaction to afford the corresponding 1,1,4,4,-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-3-butadienyl chromophores **12**–**16** in excellent yields, except for the reaction of the tetrakis(1-azulenylethynyl)benzene derivative. 1,1,4,4,-Tetracyano-2,3-bis(1-azulenyl)butadiene (**17**) was also prepared by the similar reaction of bis(1-azulenyl)acetylene (**11**) with tetracyanoethylene (TCNE). The redox behavior of novel azulene derivatives **12**–**17** was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which revealed multistep electrochemical reduction properties. Moreover, a significant color change was observed by visible spectroscopy under electrochemical reduction conditions.

Keywords: azulenes · cycloaddition · electrochemistry · photochromism

Introduction

Tetracyanoethylene (TCNE) is known to be a strong organic electron acceptor. The high reactivity of TCNE toward nucleophiles or electron-rich reagents is frequently used to introduce strong acceptor moieties into organic molecules.[1] In 1981, Bruce et al. reported that the reaction of electron-rich alkynes with TCNE affords [2+2] cycloaddition products, namely cyclobutene derivatives, which exhibit a ring-opening reaction to give the corresponding 1,1,4,4-tetracyano-1,3-butadienes (TCBDs).[2] Recently, Yamashita and coworkers reported that 1,3-dithiol-2-ylidene derivatives react with TCNE to afford the corresponding [2+2] cycloadducts that show amphoteric redox behavior.[3] Diederich et al. reported that a variety of *N*,*N*-dialkylaniline-substituted (DAA-substituted) alkynes react with TCNE to give DAA-donor-substituted TCBDs in excellent yields. They also reported that the new class of chromophores is characterized by intense intramolecular charge-transfer (CT) interactions with absorption maxima in the visible region as well as promising third-order optical nonlinearities.[4]

Azulene ($C_{10}H_8$) has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.[5] In the initial studies of Hafner et al., it is reported that the reaction of azulene with TCNE gives 1-(1,2,2-tricyanoethenyl)azulene via a CT complex between azulene and TCNE.[6] Recently, Hafner et al. also reported the preparation of 1-, 2-, and 5-ethynylazulenes utilizing a Pd-catalyzed cross-coupling reaction under Sonogashira–Hagihara conditions and/or a Cory–Fuchs alkyne synthesis. We have also reported the synthesis of 2- and 6-ethynylazu-

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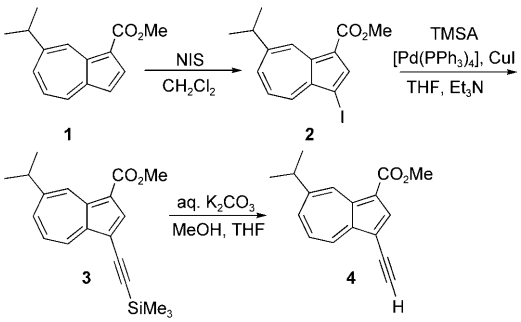
lene derivatives using a similar Pd-catalyzed reaction.[7] However, the reaction between ethynylazulenes and TCNE has not yet been examined. Similar to the DAA-substituent, the 1-position of the azulene ring possesses electron-donating properties with high reactivity toward electrophilic substitution reactions. Thus, 1-ethynylazulene derivatives should be expected to afford [2+2] cycloaddition products with TCNE. Furthermore, azulene-substituted TCBDs may exhibit multistage redox behavior similar to that of DAA-substituted TCBDs as well as polyelectrochromic electrochemical reactions.[4]

We describe herein the synthesis of mono-, bis-, tris-, and tetrakis(1-azulenylethynyl)benzene and mono- and bis (1-azulenylethynyl)thiophene derivatives under Sonogashira–Hagihara reaction conditions as well as the reactivity of the products toward the [2+2] cycloaddition reaction with TCNE to afford the corresponding 1,1,4,4,-tetracyano-2-(1-azulenyl)-3-butadienyl chromophores. The electronic properties of the novel azulene derivatives are characterized by electrochemical analysis and absorption spectroscopy.

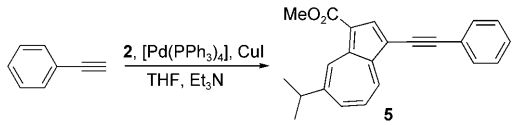
Results and Discussion

Synthesis: Methyl 7-isopropylazulene-1-carboxylate (**1**), which can readily be prepared by Yasunami–Takase's method using the reaction of 5-isopropyl-3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one with acetaldehyde in the presence of diethylamine,[8] reacted with *N*-iodosuccineimide (NIS) in dichloromethane at room temperature to afford methyl 3-iodo-7-isopropylazulene-1-carboxylate (**2**) in 92% yield. The 1-ethynylazulene derivative **4** was synthesized by the Sonogashira–Hagihara reaction.[9] The cross-coupling reaction of **2** with trimethylsilylacetylene and $[Pd(PPh_3)_4]$ as a catalyst at 50°C gave methyl 3-trimethylsilylethynyl-7-isopropylazulene-1-carboxylate (**3**) in 97% yield. Treatment of **3** with K_2CO_3 in a mixed solvent of MeOH/THF/water afforded methyl 3-ethynyl-7-isopropylazulene-1-carboxylate (**4**) in 95% yield (Scheme 1). Although 1-iodoazulene and 1-ethynylazulene derivatives are usually unstable compounds, **2**, **3**, and **4** are stable and showed no decomposition even after several weeks at room temperature. Thus, these azulene derivatives are utilized in further studies on the synthesis of the azulene-substituted TCBDs by considering their stability and the improvement of solubility.



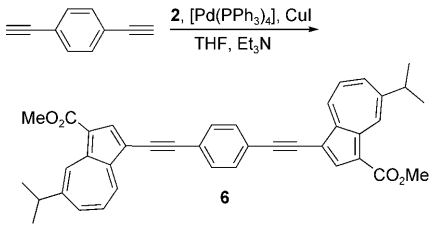
Scheme 1.

Preparation of the corresponding poly(1-azulenylethynyl)benzene derivatives **5**, **6**, **7**, and **8** was accomplished by a simple one-pot reaction involving repeated Pd-catalyzed alkynylation of the corresponding ethynylbenzenes with **2** or the 1-ethynylazulene **4** with 1,2,4,5-tetraiodobenzene under Sonogashira–Hagihara conditions. The cross-coupling reaction of **2** with phenylacetylene using $[Pd(PPh_3)_4]$ as a catalyst and subsequent chromatographic purification on silica gel afforded the desired methyl 7-isopropyl-3-(phenylethynyl)azulene-1-carboxylate (**5**) in 95% yield (Scheme 2).



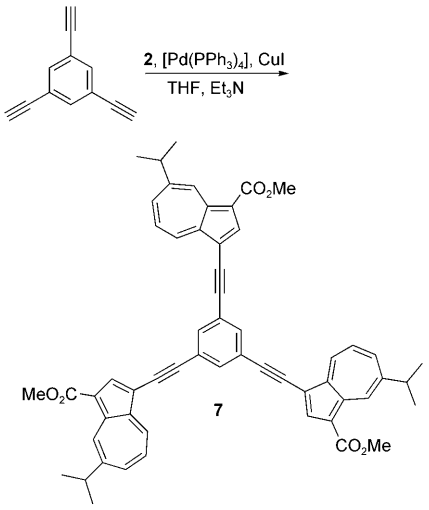
Scheme 2.

Likewise, the reaction of **2** with 1,4-diethynylbenzene afforded 1,4-bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl) ethynyl]benzene (**6**) in 91% yield (Scheme 3). The cross-coupling reaction of **2** with 1,3,5-triethynylbenzene[10] in the presence of the Pd catalyst afforded 1,3,5-tris[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]benzene (**7**) in 84% yield (Scheme 4). 1,2,4,5-Tetrakis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]benzene (**8**) was prepared by a similar Pd-catalyzed reaction of **4** with 1,2,4,5-tetraiodobenzene[11] in 77% yield (Scheme 5).

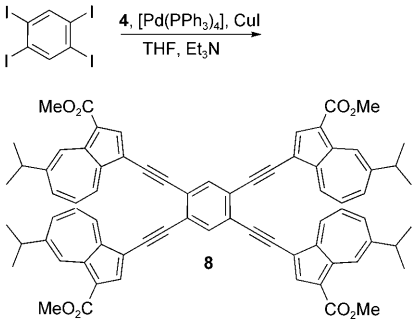


Scheme 3.

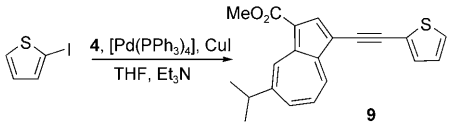
Methyl 7-isopropyl-3-(2-thienylethynyl)azulene-1-carboxylate (**9**) and 2,5-bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]thiophene (**10**) were also synthesized by Pd-catalyzed alkynylation of **4** with the corresponding iodothiophenes. Reaction of **4** with 2-iodothiophene in the presence of $[Pd(PPh_3)_4]$ gave mono-adduct **9** in 93% yield (Scheme 6). Bis-adduct **10** was obtained by the reaction of **4** with 2,5-diiodothiophene in the presence of $[Pd(PPh_3)_4]$ in 72% yield, along with mono-adduct **9** in 9% yield (Scheme 7). A similar Pd-catalyzed reaction of **2** with **4** afforded bis(5-isopropyl-3-methoxycarbonyl-1-azulenyl)acetylene (**11**) in 94% yield (Scheme 8). These compounds (**5**–**11**) possess fair solubility in chloroform, dichloromethane,



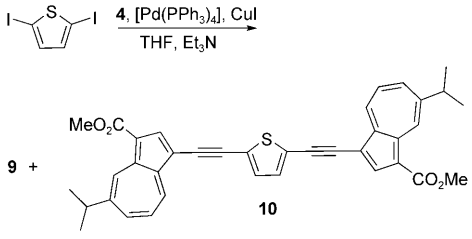
Scheme 4.



Scheme 5.



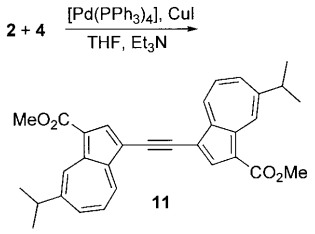
Scheme 6.



Scheme 7.

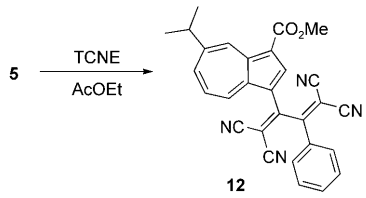
and so on. Moreover, they are stable and show no decomposition even after several weeks at room temperature.

The [2+2] cycloaddition reaction of mono-, bis-, tris-, and tetrakis(1-azulenylethynyl)benzene and mono- and bis(1-azulenylethynyl)thiophene along with bis(1-azulenyl)acetylene derivatives **5**–**11** with TCNE was examined according



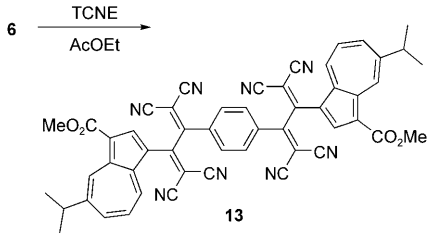
Scheme 8.

to the procedure described in the literature to give the azulene-substituted TCBDs.[4] The reaction of **5** with TCNE in ethyl acetate at room temperature yielded **12** in 96% yield (Scheme 9). Likewise, the reaction of **6** and **7** with TCNE



Scheme 9.

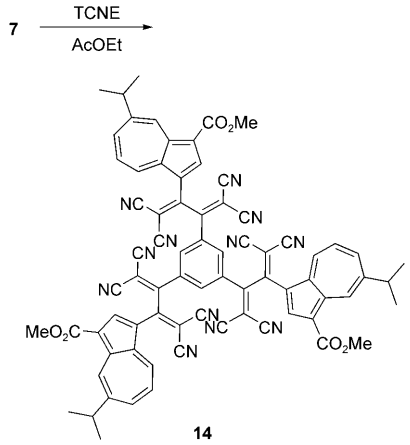
afforded **13** and **14** in 96% and 91% yields, respectively (Schemes 10 and 11). It is noteworthy that these reactions readily proceeded under mild conditions, although the electron-withdrawing group, the methoxycarbonyl group, is substituted on the azulene ring. The high reactivity can be attributed to the highly electron-donating properties of the azulene ring at the 1-position.



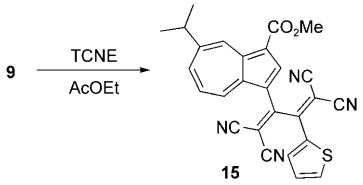
Scheme 10.

In contrast to these results, the reaction of **8** with TCNE formed an insoluble complex mixture. Diederich et al. have reported that the reaction of *o*-phenylene derivatives with TCNE does not produce the expected [2+2] cycloadducts because of the steric effect that prevents the presumed cycloaddition reaction of alkyne with TCNE.[4b] In the cases of the reaction of **8**, therefore, the formation of a complex mixture should be attributable to similar steric reasons.

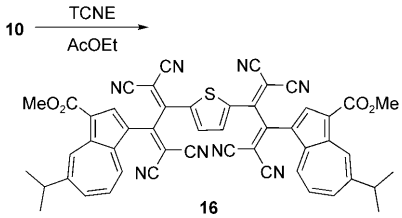
Similar to the results of the benzene derivatives, the reaction of **9** and **10** with TCNE afforded **15** and **16** in 86% and 97% yields, respectively (Schemes 12 and 13). The [2+2] cycloaddition reaction of **11** with TCNE also proceeded under



Scheme 11.

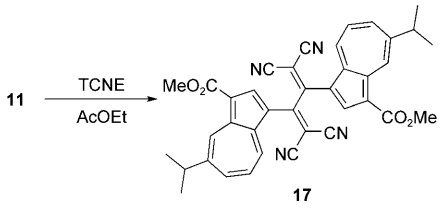


Scheme 12.



Scheme 13.

mild conditions to give **17** in 97% yield (Scheme 14). These new compounds **12**–**17** are stable, deep-colored crystals and can be stored in the crystalline state at room temperature.



Scheme 14.

Spectroscopic properties: Compounds **5**–**17** were fully characterized by the spectral data as shown in the Experimental Section. Mass spectra of **5**–**17** ionized by ESI showed the correct molecular ion peaks. The characteristic stretching-vibration band of the ethynyl group of **5**–**10** was observed at $\tilde{\nu}=2187$–$2201\ cm^{-1}$ in their IR spectra. Compounds **12**–**17** exhibited characteristic C≡N stretching at $\tilde{\nu}=2220$ or $2222\ cm^{-1}$ in their IR spectra. These results are consistent with the structure of these products. The UV-visible spectra of **5**–**11** showed characteristic weak absorptions arising from the azulene system in the visible region. The extinction coefficients increased with the number of azulene rings substituted.

UV-visible spectra of **12**–**14** and **15**, **16** in dichloromethane are shown in Figures 1 and 2, respectively. As expected from their resonance structures (Scheme 15), TCNE adducts **12**–

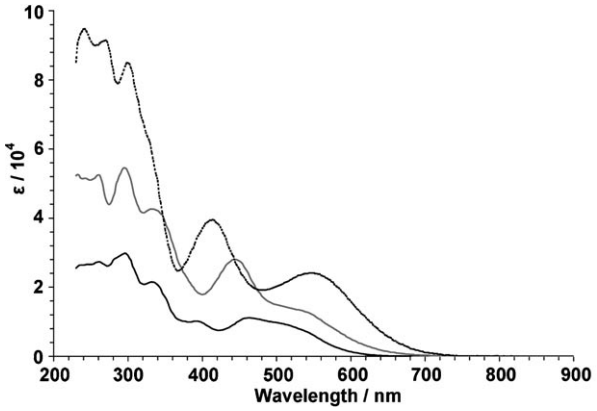


Figure 1. UV/Vis spectra of **12** (——), **13** (——), and **14** (-----) in dichloromethane.

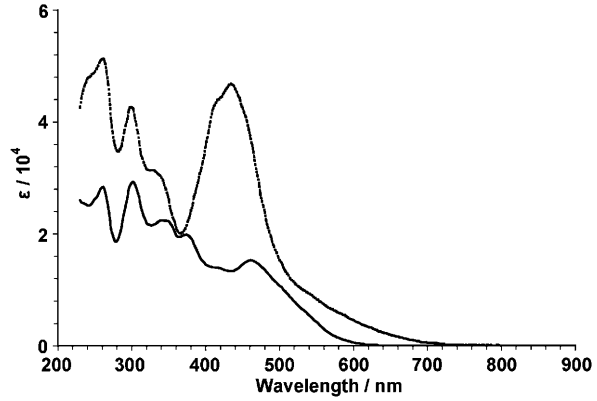
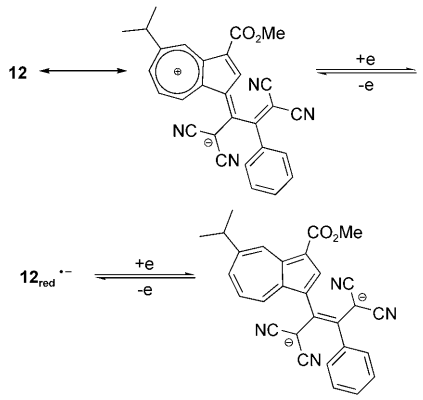


Figure 2. UV/Vis spectra of **15** (——) and **16** (-----) in dichloromethane.

17 showed characteristic CT absorption in the visible region. Their absorption maxima and coefficients ($\log\varepsilon$) are summarized in Table 1. Compound **12** exhibited two relatively weak CT absorptions at $\lambda=462$ and 534 (sh) nm. Compound **13** exhibited strong and weak CT absorptions at $\lambda=444$ and 540 (sh) nm, respectively. The longest CT absorption showed a bathochromic shift of 6 nm compared to that of **12**, probably due to expansion of the π-conjugation. In compound **13**, two strong CT absorptions were observed at $\lambda=414$ and 550 nm. The longest CT absorption also exhibited a further bathochromic shift compared to those of **12** and **13**. Compound **15** showed a relatively weak CT absorption, com-



Scheme 15. Presumed electrochemical behavior of **12**.

Table 1. Absorption maxima [nm] and their coefficients ($\log\varepsilon$) of **5**–**17** in dichloromethane.

Sample	λ_{max} ($\log\varepsilon$)	Sample	λ_{max} ($\log\varepsilon$)
5	412 (4.04), 572 (2.84)	**12**	462 (4.04), 534 sh (3.88)
6	410 (4.64), 570 (3.23)	**13**	444 (4.44), 540 sh (4.10)
7	416 (4.66), 568 (3.37)	**14**	414 (4.60), 550 (4.38)
8	410 (4.79), 568 sh (3.49)	**15**	460 (4.18)
9	400 (4.04), 572 (2.81)	**16**	416 sh (4.64), 434 (4.67)
10	412 (4.60), 570 (3.27)	**17**	508 (4.32)
11	416 (4.33), 588 (3.19)		

pared to those of **16**, centered at $\lambda = 460$ nm, which extended beyond $\lambda = 600$ nm. Broad CT absorptions were observed in **16** centered at $\lambda = 416$ (sh) and 434 nm. The CT absorption band of **16** extended beyond $\lambda = 700$ nm. Cyanovinyl-substituted compounds have been known to exhibit solvatochromic[12] and vapochromic behavior.[13] Solvatochromism was studied with **17**. The solvent dependence of the absorption maxima and coefficients ($\log\varepsilon$) of **17** are summarized in Table 2. The largest solvent effect was observed when the solvent was changed from $CHCl_3$ ($\lambda_{max} = 510$ nm) to ethyl acetate ($\lambda_{max} = 486$ nm).

Table 2. Solvatochromic data for the longest wavelength absorption of **17**.

Solvent	λ_{max} ($\log\varepsilon$)	Solvent	λ_{max} ($\log\varepsilon$)
$CHCl_3$	510 (4.31)	cyclohexane	492 (4.29)
CH_2Cl_2	508 (4.32)	*i*PrOH	491 (4.27)
CH_3CN	504 (4.30)	acetone	491 (4.26)
MeOH	497 (4.28)	THF	490 (4.26)
EtOH	492 (4.25)	AcOEt	486 (4.19)

To obtain the theoretical aspect of the spectroscopic properties of these compounds, B3LYP/6-31G** density functional calculations of the molecular orbitals of **12** and **17** were performed without any substituents on the azulene rings.[14] The resulting HOMO and LUMOs of optimized structures are summarized in the Supporting Information. Geometry optimizations revealed the substantial deviation from planarity in these molecules. The HOMO in **12** is mainly concentrated on the azulene moiety and on the cyanovinyl moiety adjoined to the azulene ring. The LUMO was concentrated on the benzene ring and included the cyanovinyl moiety adjoined to the benzene ring. Examination of the HOMO and the LUMO of **17** also showed a similar CT character in the HOMO–LUMO transition, although the LUMO is mostly localized on an azulene ring. Thus, the longer wavelength absorption in the visible region may include intramolecular CT character from the azulene ring to the other connecting group.

Redox potentials: To clarify the electrochemical properties, the redox behavior of **5**–**17** was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Measurements were carried out with a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as a supporting electrolyte with platinum wire auxiliary and working electrodes. All measurements were carried out under an argon atmosphere, and potentials were related to an Ag/Ag^+ reference electrode and Fc/Fc^+ as an internal reference, which discharges at $+0.15$ V. The redox potentials (in volts vs $Ag/AgNO_3$) of **12**–**17** are summarized in Table 3. The redox potentials of **5**–**11** and oxidation potentials of **5**–**17** are summarized in the Supporting Information.

Table 3. Redox potentials[a] of TCNE adducts **12**–**17**.

Sample	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}	E_5^{red}	E_6^{red}
12	−0.61	−1.03				
	(−0.59)	(−1.01)	(−1.95)	(−2.18)		
13	−0.46	−0.64	−1.01	−1.11		
	(−0.45)	(−0.63)	(−1.00)	(−1.09)	(−1.90)	(−1.97)
14	−0.40	−0.57	−0.73	−1.02	−1.13	
	(−0.39)	(−0.56)	(−0.72)	(−1.03)	(−1.10)	(−1.88)
15	−0.64	−1.03	−1.95			
	(−0.63)	(−1.02)	(−1.93)	(−2.17)		
16	−0.31	−0.54	−1.10			
	(−0.29)	(−0.52)	(−1.09)	(−1.89)	(−2.15)	
17	−0.64	−1.04				
	(−0.62)	(−1.02)	(−1.92)	(−2.17)		

[a] Redox potentials were measured by CV and DPV [V vs $Ag/AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mV s^{-1}, and $Fc/Fc^+ = +0.15$ V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses.

Although (6-azulenylethynyl)benzene derivatives exhibit reversible reduction waves in their cyclovoltammograms,[15] (1-azulenylethynyl)benzenes **5**–**8** and thiophenes **9**, **10** and bis(1-azulenyl)acetylene **11** showed irreversible reduction waves at −1.52 to −2.18 V upon CV, (see the Supporting Information). Electrochemical reduction of **12** showed a reversible two-step reduction wave at half-wave potentials of −0.61 and −1.03 V upon CV, which can probably be attributed to the formation of a radical anionic and a dianionic species, respectively (Figure 3). Thus, the electrochemical behavior of **12** could be explained as shown in Scheme 15. The electrochemical reduction also exhibited irreversible waves at −1.95 and −2.18 V upon DPV, probably due to the

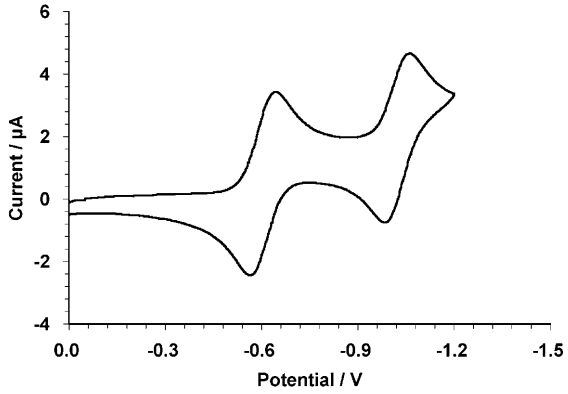


Figure 3. Cyclic voltammograms of the reduction of **12** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

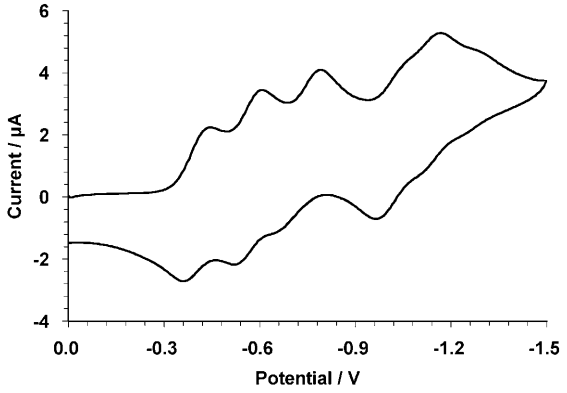


Figure 5. Cyclic voltammograms of the reduction of **14** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

reduction of the substituted azulene ring. Bis-adduct **13** exhibited a reversible four-step reduction wave, whose potentials were identified at −0.45, −0.63, −1.00, and −1.09 V by DPV (Figure 4), which are attributed to the formation of a

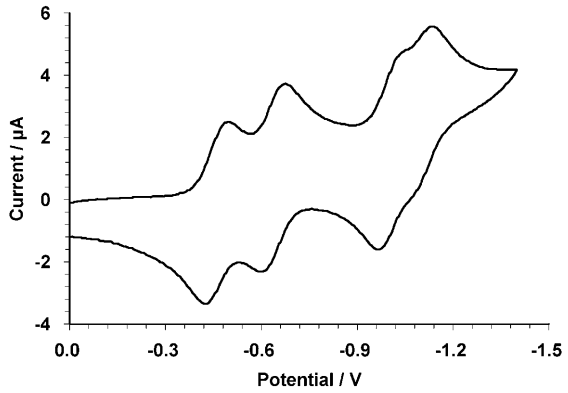


Figure 4. Cyclic voltammograms of the reduction of **13** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

tetraanionic species. The electrochemical reduction of **14** exhibited a reversible five-step reduction wave, whose potentials were identified at −0.39, −0.56, −0.72, −1.03, and −1.10 V by DPV, which are attributed to the formation of up to a pentaanionic species (Figure 5). The first reduction potentials of **12**, **13**, and **14** decreased as the number of azulene-substituted TCBD units increased. This indicates that the TCBD unit reduces the LUMO level and increases the π-acceptance, in spite of the 1,3,5-arrangement in **14**. We have already reported the redox properties of 9-[bis(6-azulenylethynyl)methylene]-9*H*-fluorene and 9-{bis[1,3-bis(hexyloxycarbonyl)-6-azulenylethynyl]methylene}-9*H*-fluorene.[16] These fluorenes exhibit a reversible three-stage reduction within a narrow potential range of 0.54 V (from −1.21 V to −1.75 V) and 0.40 V (from −1.00 V to −1.40 V), respectively. With respect to the TCBD derivatives, Diederich et al. reported that the compound with three DAA-substituted TCBD units connected by a 1,3,5-benzentriyl spacer shows a novel six-stage reversible one-electron reduction within a narrow potential range of 1.00 V (from −0.69 V to −1.69 V vs Fc/Fc^+).[4b] The reduction of **14** exhibited a reversible five-stage reduction within a narrower potential range of 0.71 V (from −0.39 V to −1.10 V), and the lower first reduction potential ($E_1^{red} = -0.54$ V vs Fc/Fc^+) is comparable with the results reported by Diederich et al. The electrochemical reduction of **15** also showed a reversible three-stage reduction wave upon CV (−0.64, −1.03, and −1.95 V), attributed to the formation of up to a trianionic species, including the reduction of either the azulene or the thiophene ring (Figure 6). A reversible three-stage wave was observed in **16** upon CV (−0.31, −0.54, and −1.10 V), in which the third reduction wave should be concluded to be a two-electron transfer in one step to form a tetraanionic species (Figure 7). The electrochemical reduction of **17** showed a reversible two-stage wave upon CV (−0.64 and −1.04 V) attributed to the formation of a dianionic species (Figure 8). The oxidation of these compound exhibited voltammograms that were characterized by irreversible waves, probably due to the oxidation of the azulene rings (see the Supporting Information).

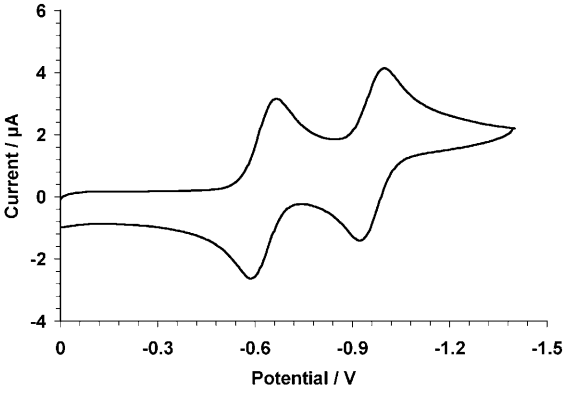


Figure 6. Cyclic voltammograms of the reduction of **15** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

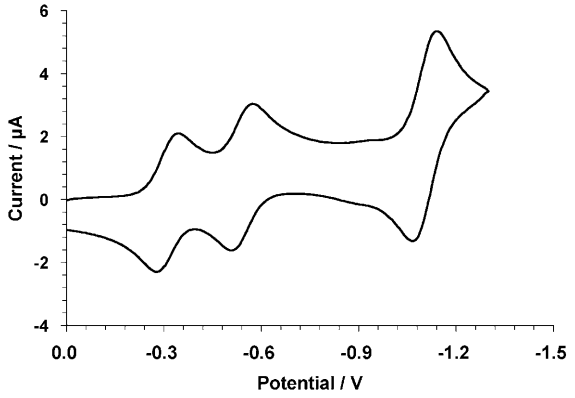


Figure 7. Cyclic voltammograms of the reduction of **16** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

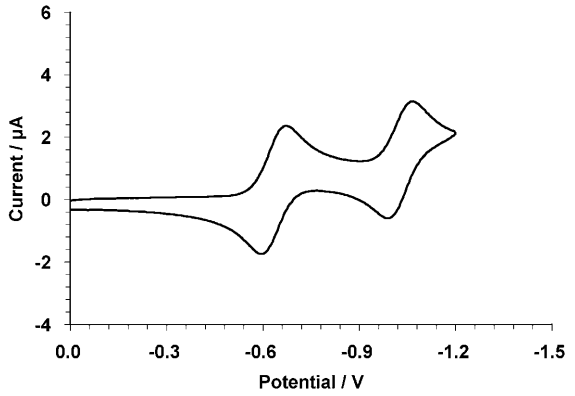


Figure 8. Cyclic voltammograms of the reduction of **17** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

Electrochromic analysis: Visible spectra of **12–17** were monitored to clarify the color changes during the electrochemical reactions. A constant-current reduction was applied to the solutions of **12–17** with a platinum mesh as the working electrode and a wire counterelectrode.

Visible spectra of **12** were measured in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte at room temperature under electrochemical reduction conditions (see the Supporting Information). The longest absorption of **12** at $\lambda = 508$ (sh) nm gradually decreased and thus the color of the solution gradually changed from purple to brown during electrochemical reduction with the development of new absorptions in the visible region at $\lambda = 517$ and 700 nm. On further reduction, the new absorption bands gradually decreased and the color of the solution gradually changed from brown to orange. However, reverse oxidation of the brown-colored solution did not regenerate the spectrum of **12**, although good reversibility was observed in the two-step reduction in the cyclovoltammogram. The poor reversibility of the color changes might be attributable to the instability of the dianionic species produced by two-electron reduction.

The red color of the solution of **13** changed to orange during electrochemical reduction with the development of new absorptions in the visible region at $\lambda = 546$ and 700 nm. Reverse oxidation of the orange-colored solution regenerated the visible spectra of the red-colored **13**. On the basis of a comparison with the results of **12** (see the Supporting Information), the color change of the solution of **13** can thus be attributed to the formation of up to the dianionic species via a radical anion. When the UV-visible spectra of **14** were measured under electrochemical reduction conditions, the absorption of **14** at 550 nm in the visible region gradually decreased and a new absorption in the visible region at 700 nm gradually developed. The reverse oxidation decreased the new absorption band, but did not regenerate the absorption band of **14**. These results indicate the instability of anionic species of **14** under the spectroscopic measurement conditions (see the Supporting Information).

The significant color changes were also observed in thiophene derivatives **15** and **16**. When the visible spectral changes of **15** were measured during the electrochemical reduction, the absorption in the visible region at $\lambda = 460$ nm gradually decreased with the development of new absorptions at $\lambda = 538$ and 696 nm in the visible region. The reverse oxidation decreased the new absorptions and the absorption of **15** was regenerated (see the Supporting Information). A two-stage color change was observed in the visible spectra of **16** under electrochemical reduction conditions (Figure 9). At the beginning, new absorptions in the visible region at $\lambda = 609$ and 740 nm gradually developed and the red color of the solution changed to blue during electrochemical reduction. On further reduction, the new bands in the visible region gradually decreased, accompanied by the development of a new absorption in the near-infrared region. On reverse oxidation, the new absorption in the IR region decreased and the absorptions in the visible region at $\lambda = 609$ and 740 nm were regenerated. Further electrochemical oxidation decreased these absorptions. The two-step color-change should correspond to the formation of a closed-shell dianionic species via a radical anion in two steps. The absorption up to the near-infrared region suggests the formation of the stabilized dianionic species with thienoquinoide structure in the two-electron reduction.

The color of the solution of **17** gradually changed from purple to orange, and electrochemical reduction led to the development of a new absorption band at $\lambda = 700$ nm. However, reverse oxidation of the orange-colored solution did not completely regenerate the spectrum of **17**, although the new absorption did decrease during electrochemical oxidation.

Conclusion

Several 1-ethynylazulene derivatives **5–11** were prepared by the Sonogashira–Hagihara reaction. These compounds readily reacted with tetracyanoethylene to give the corresponding 1,1,4,4,-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-

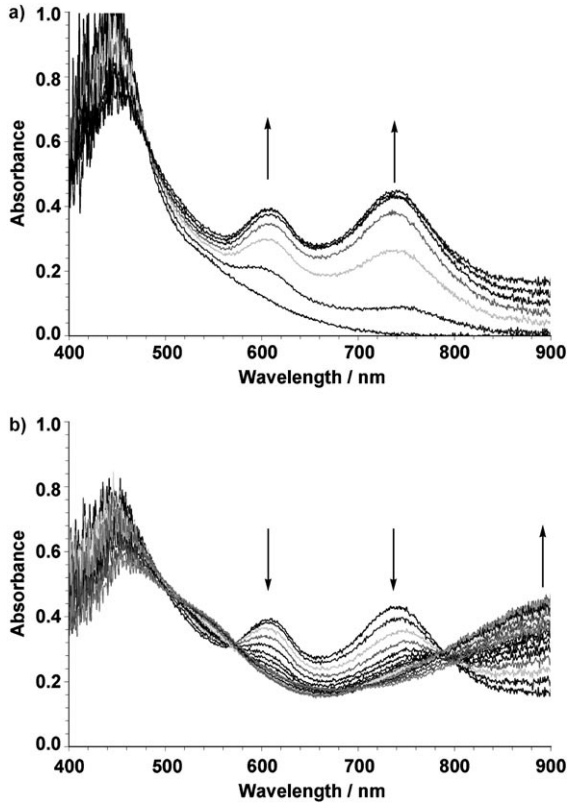


Figure 9. Continuous change in visible spectra of **16** in acetonitrile (2 mL; 2.9×10^{-4} M) containing Et_4NClO_4 (0.1 M) upon constant-current electrochemical reduction (50 uA) at 1 min intervals.

azulenyl)-3-butadienyl chromophores **12–17** in excellent yields. Analysis by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) showed that compounds **12–17** exhibited a multistep reduction wave. Moreover, a significant color change was observed during electrochemical reduction. Preparation of 1,1,4,4,-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-3-butadienyl chromophores with different π-electron cores is now in progress in our laboratory.

Experimental Section

General: For general and electrochemical measurement details, see the Supporting Information. Assignment of peaks in the ^{1}H NMR spectra was accomplished by decoupling, NOE, and/or COSY experiments.

Methyl 3-iodo-7-isopropylazulene-1-carboxylate (2): To a solution of **1** (3.22 g, 14.1 mmol) in CH_2Cl_2 (30 mL) was added *N*-iodosuccinimide (3.81 g, 16.9 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 30 min under an Ar atmosphere. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with CH_2Cl_2 to give **2** (4.60 g, 92%). Purple crystals; m.p. 67.0–69.0 °C (CH_2Cl_2); IR (KBr disk): $\tilde{\nu}_{max}$ = 3246 (s), 2961 (m), 1687 (s), 1452 (s), 1441 (s), 1419 (m), 1217 (s), 1197 (m), 1170 (m), 1124 (m), 1051 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (4.44), 298 sh (4.47), 308 (4.54), 372 sh (3.91), 486 (3.95), 556 (2.81), 594 nm sh (2.77); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.71 (s, 1H, H_8), 8.41 (s, 1H, H_2), 8.27 (d, 1H, J = 10.0 Hz, H_4), 7.78 (d, 1H, J = 10.0 Hz, H_6), 7.50 (dd, 1H, J = 10.0, 10.0 Hz, H_5), 3.94 (s, 3H, CO_2Me), 3.21 (sept, 1H, J = 6.8 Hz, *i*Pr), 1.40 ppm (d, 6H, J = 6.8 Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 150.4, 147.3, 144.0, 141.5, 139.4, 139.1, 137.7, 127.8, 117.3, 73.8, 51.6, 39.6, 25.0 ppm; HRMS (ESI) calcd for $[C_{15}H_{15}IO_2+Na]^+$: 377.0014; found 377.0009; elemental analysis calcd (%) for $C_{15}H_{15}IO_2$: C 50.78, H 4.27; found: C 50.84, H 4.36.

Methyl 7-isopropyl-3-trimethylsilylethynylazulene-1-carboxylate (3): To a degassed solution of **2** (1.77 g, 5.00 mmol), trimethylsilylacetylene (737 mg, 7.50 mmol), and CuI (95 mg, 0.50 mmol) in triethylamine (20 mL) and THF (20 mL) was added tetrakis(triphenylphosphine)palladium(0) (289 mg, 0.25 mmol). The resulting mixture was stirred at 50 °C for 2 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with toluene. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **3** (1.58 g, 97%). Purple crystals; m.p. 71.0–74.0 °C (hexane); IR (KBr disk): $\tilde{\nu}_{max}$ = 2963 (m), 2145 (m), 1703 (s), 1448 (s), 1439 (s), 1421 (m), 1392 (m), 1369 (m), 1224 (m), 1215 (s), 1167 (m), 1128 (m), 1103 (m), 1053 (m), 920 (m), 881 (m), 846 (s), 806 (m), 775 (m), 769 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (4.49), 278 (4.57), 302 (4.49), 314 (4.52), 386 (3.98), 400 (3.96), 564 (2.78), 604 nm sh (2.71); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.71 (s, 1H, H_8), 8.57 (d, 1H, J = 10.0 Hz, H_4), 8.41 (s, 1H, H_2), 7.82 (d, 1H, J = 10.0 Hz, H_6), 7.51 (dd, 1H, J = 10.0, 10.0 Hz, H_5), 3.94 (s, 3H, CO_2Me), 3.23 (sept, 1H, J = 6.8 Hz, *i*Pr), 1.41 (d, 6H, J = 6.8 Hz, *i*Pr), 0.32 ppm (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 149.9, 144.7, 142.5, 140.5, 138.8, 137.6, 135.6, 127.1, 114.3, 108.8, 100.2, 97.9, 50.5, 38.7, 24.1, 0.0 ppm; HRMS (ESI) calcd for $[C_{20}H_{24}O_2Si+Na]^+$: 347.1443; found: 347.1438; elemental analysis calcd (%) for $C_{20}H_{24}O_2Si$: C 74.03, H 7.45; found: C 73.99, H 7.34.

Methyl 3-ethynyl-7-isopropylazulene-1-carboxylate (4): To a solution of **3** (650 mg, 2.00 mmol) in MeOH (10 mL), THF (5 mL), and water (10 mL) was added K_2CO_3 (1.38 g, 10.0 mmol). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was poured into water and extracted with hexane. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **4** (477 mg, 95%). Purple oil; IR (KBr disk): $\tilde{\nu}_{max}$ = 3296 (m), 2961 (m), 2098 (w), 1693 (s), 1446 (s), 1421 (m), 1381 (m), 1213 (s), 1170 (m), 1124 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 242 (4.49), 272 (4.45), 298 (4.49), 310 (4.54), 378 (3.95), 394 (3.95), 560 (2.78), 598 sh (2.72), 666 nm sh (2.18); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (s, 1H, H_8), 8.59 (d, 1H, J = 9.6 Hz, H_4), 8.42 (s, 1H, H_2), 7.79 (d, 1H, J = 10.0 Hz, H_6), 7.48 (dd, 1H, J = 9.6, 10.0 Hz, H_5), 3.94 (s, 3H, CO_2Me), 3.43 (s, 1H, C≡C-H), 3.23 (sept, 1H, J = 6.8 Hz, *i*Pr), 1.41 ppm (d, 6H, J = 6.8 Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 150.9, 145.6, 143.4, 141.2, 139.6, 138.5, 136.3, 127.9, 114.9, 108.2, 81.8, 79.5, 51.4, 39.4, 24.9 ppm; HRMS (ESI) calcd for $[C_{17}H_{16}O_2+Na]^+$: 275.1048; found: 275.1043; elemental analysis calcd (%) for $C_{17}H_{16}O_2$: C 80.93, H 6.39; found: C 80.77, H 6.50.

Methyl 7-isopropyl-3-(phenylethynyl)azulene-1-carboxylate (5): To a degassed solution of **2** (354 mg, 1.00 mmol), phenylacetylene (123 mg, 1.20 mmol), and CuI (19 mg, 0.10 mmol) in triethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol). The resulting mixture was stirred at 50 °C for 2 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with toluene. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **5** (312 mg, 95%). Purple crystals; m.p. 92.0–95.0 °C (CH_2Cl_2); IR (KBr disk): $\tilde{\nu}_{max}$ = 2957 (m), 2201 (w), 1687 (s), 1487 (m), 1468 (m), 1450 (s), 1423 (m), 1406 (m), 1392 (m), 1381 (m), 1371 (m), 1246 (m), 1211 (s), 1196 (m), 1169 (m), 1118 (m), 1072 (m), 871 (m), 804 (m), 777 (m), 756 (m), 688 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.44), 248 (4.45), 306 (4.65), 310 (4.65), 334 (4.43), 396 (4.10), 412 (4.04), 572 (2.84), 616 sh (2.76), 690 nm sh (2.17); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1H, H_8), 8.65 (d, 1H, J = 10.0 Hz, H_4), 8.46 (s, 1H, H_2), 7.78 (d, 1H, J = 10.0 Hz, H_6), 7.60 (m, 2H, *o*-Ph), 7.48 (dd, 1H, J = 10.0, 10.0 Hz, H_5), 7.39–7.32 (m, 3H, *m*-, *p*-Ph), 3.95 (s, 3H, CO_2Me),

3.22 (sept, 1H, $J=6.8$ Hz, *i*Pr), 1.42 ppm (d, 6H, $J=6.8$ Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.8$, 150.9, 145.2, 143.1, 141.6, 139.7, 138.6, 136.6, 131.8, 128.9, 128.3, 127.9, 124.4, 115.5, 109.6, 94.2, 85.4, 51.6, 39.6, 25.0 ppm; HRMS (ESI) calcd for $[C_{23}H_{20}O_2+Na]^+$: 351.1361; found: 351.1356; elemental analysis calcd (%) for $C_{23}H_{20}O_2$: C 84.12, H 6.14; found: C 83.99, H 6.17.

1,4-Bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]benzene (6): The procedure used for the preparation of **5** was adopted here. Reaction of **2** (779 mg, 2.20 mmol) with 1,4-diethynylbenzene (126 mg, 1.00 mmol) in triethylamine (10 mL) and THF (10 mL) in the presence of CuI (38 mg, 0.20 mmol) and tetrakis(triphenylphosphine)palladium(o) (116 mg, 0.10 mmol) at 50 °C for 3 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **6** (527 mg, 91 %). Black crystals; m.p. 238.0–240.0 °C (CH_2Cl_2); IR (KBr disk): $\tilde{\nu}_{max}=2961$ (m), 2199 (m), 1695 (s), 1491 (m), 1444 (s), 1425 (m), 1408 (m), 1371 (m), 1248 (m), 1209 (s), 1197 (s), 1169 (s), 1072 (m), 1049 (m), 873 (m), 839 (m), 775 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$)=244 (4.71), 276 (4.45), 306 (4.62), 312 (4.76), 356 (4.72), 410 (4.64), 432 sh (4.60), 570 (3.23), 614 sh (3.12), 694 nm sh (2.45); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=9.72$ (s, 2H, H_8), 8.67 (d, 2H, $J=9.6$ Hz, H_4), 8.48 (s, 2H, H_2), 7.82 (d, 2H, $J=10.0$ Hz, H_6), 7.60 (s, 4H, Bz-$H_{2,3,5,6}$), 7.53 (dd, 2H, $J=9.6$, 10.0 Hz, H_5), 3.97 (s, 6H, CO_2Me), 3.24 (sept, 2H, $J=7.0$ Hz, *i*Pr), 1.43 ppm (d, 12H, $J=7.0$ Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.4$, 150.7, 144.8, 142.8, 141.4, 139.4, 138.4, 136.2, 131.3, 127.6, 123.2, 115.2, 108.9, 93.7, 86.8, 51.2, 39.3, 24.6 ppm; HRMS (ESI) calcd for $[C_{40}H_{34}O_4+Na]^+$: 601.2355; found: 601.2349; elemental analysis calcd (%) for $C_{40}H_{34}O_4\cdot{}^1/_3\,H_2O$: C 82.17, H 5.98; found: C 82.19, H 5.92.

1,3,5-Tris[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]benzene (7): The procedure used for the preparation of **5** was adopted here. Reaction of **2** (1.27 g, 3.60 mmol) with 1,3,5-triethynylbenzene (150 mg, 1.00 mmol) in triethylamine (10 mL) and THF (10 mL) in the presence of CuI (38 mg, 0.20 mmol) and tetrakis(triphenylphosphine)palladium(o) (116 mg, 0.10 mmol) at 50 °C for 2 h followed by column chromatography on silica gel with toluene afforded **7** (700 mg, 84 %). Green crystals; m.p. 200.0–205.0 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}=2957$ (m), 2197 (m), 1693 (s), 1578 (m), 1508 (m), 1148 (s), 1414 (s), 1371 (m), 1215 (s), 1165 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$)=248 (4.96), 274 sh (4.85), 312 (5.09), 342 (4.92), 400 (4.71), 416 (4.66), 568 (3.37), 608 sh (3.28), 684 nm sh (2.68); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=9.76$ (dd, 3H, H_8), 8.71 (d, 3H, $J=9.5$ Hz, H_4), 8.50 (s, 3H, H_2), 7.84 (d, 3H, $J=10.5$ Hz, H_6), 7.79 (s, 3H, Bz-$H_{2,4,6}$), 7.57 (dd, 3H, $J=9.5$, 10.5 Hz, H_5), 3.98 (s, 9H, CO_2Me), 3.26 (sept, 3H, $J=7.0$ Hz, *i*Pr), 1.44 ppm (d, 18H, $J=7.0$ Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.4$, 150.8, 145.0, 142.8, 141.4, 139.4, 138.4, 136.3, 133.0, 127.7, 124.7, 115.2, 108.6, 92.5, 86.0, 51.2, 39.3, 24.6 ppm; HRMS (ESI) calcd for $[C_{57}H_{48}O_6+Na]^+$: 851.3349; found: 851.3343; elemental analysis calcd (%) for $C_{57}H_{48}O_6$: C 82.58, H 5.84; found: C 82.46, H 6.04.

1,2,4,5-Tetrakis(7-isopropyl-1-methoxycarbonyl-3-azulenylethynyl)benzene (8): The procedure used for the preparation of **5** was adopted here. Reaction of **4** (887 mg, 3.50 mmol) with 1,2,4,5-tetraiodobenzene (407 mg, 0.70 mmol) in triethylamine (15 mL) and THF (15 mL) in the presence of CuI (114 mg, 0.60 mmol) and tetrakis(triphenylphosphine)-palladium(o) (324 mg, 0.30 mmol) at 50 °C for 19 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **8** (582 mg, 77 %). Brown crystals; m.p. >300 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}=2955$ (m), 2187 (m), 1693 (s), 1682 (s), 1481 (m), 1448 (s), 1421 (m), 1373 (m), 1223 (s), 1196 (m), 1169 (m), 1103 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$)= 244 (4.91), 302 (4.95), 354 (4.74), 410 (4.79), 462 (4.49), 568 sh (3.49), 630 sh (3.28), 698 nm sh (2.70); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=9.73$ (s, 4H, H_8), 8.70 (d, 4H, $J=9.5$ Hz, H_4), 8.51 (s, 4H, H_2), 7.97 (s, 2H, Bz-$H_{3,6}$), 7.57 (d, 4H, $J=10.5$ Hz, H_6), 6.93 (dd, 4H, $J=9.5$, 10.5 Hz, H_5), 3.95 (s, 12H, CO_2Me), 3.19 (sept, 4H, $J=7.0$ Hz, *i*Pr), 1.40 ppm (d, 24H, $J=$ 7.0 Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.4$, 150.7, 145.2, 142.9, 141.5, 139.2, 138.2, 136.9, 134.3, 128.0, 124.9, 115.2, 108.7, 92.8, 91.0, 51.2, 39.2, 24.6 ppm; HRMS (ESI) calcd for $[C_{74}H_{62}O_8+Na]^+$: 1101.4342; found: 1101.4337; elemental analysis calcd (%) for $C_{74}H_{62}O_8\cdot{}^1/_3\,H_2O$: C 81.89, H 5.82; found: C 81.94, H 5.82.

Methyl 7-isopropyl-3-(2-thienylethynyl)azulene-1-carboxylate (9): The procedure used for the preparation of **5** was adopted here. Reaction of **4** (505 mg, 2.00 mmol) with 2-iodothiophene (630 mg, 3.00 mmol) in triethylamine (20 mL) and THF (20 mL) in the presence of CuI (38 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(o) (116 mg, 0.10 mmol) at 50 °C for 3 h followed by column chromatography on silica gel with toluene afforded **9** (623 mg, 93 %). Green crystals; m.p. 63.0–65.0 °C (hexane); IR (KBr disk): $\tilde{\nu}_{max}=3107$ (m), 2959 (m), 2193 (w), 1687 (s), 1500 (m), 1450 (s), 1415 (s), 1381 (m), 1378 (m), 1236 (s), 1213 (s), 1190 (m), 1167 (m), 1130 (m), 1049 (m), 777 (m), 713 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$)=248 (4.38), 278 (4.40), 314 (4.53), 350 sh (4.16), 400 (4.04), 420 sh (3.88), 572 nm (2.81); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=9.72$ (s, 1H, H_8), 8.60 (d, 1H, $J=9.5$ Hz, H_4), 8.44 (s, 1H, H_2), 7.78 (d, 1H, $J=10.5$ Hz, H_6), 7.49 (dd, 1H, $J=9.5$, 10.5 Hz, H_5), 7.31 (dd, 1H, $J=4.0$, 1.0 Hz, Th-H_3), 7.28 (dd, 1H, $J=4.0$, 1.0 Hz, Th-H_5), 7.02 (dd, 1H, $J=4.0$, 1.0 Hz, Th-H_4), 3.95 (s, 3H, CO_2Me), 3.22 (sept, 1H, $J=7.0$ Hz, *i*Pr), 1.42 ppm (d, 6H, $J=7.0$ Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.3$, 150.6, 145.2, 144.7, 142.6, 141.2, 139.4, 138.3, 136.2, 131.3, 127.5, 127.1, 126.7, 124.0, 115.1, 108.6, 88.5, 86.5, 51.1, 39.2, 24.5 ppm; HRMS (ESI) calcd for $[C_{21}H_{18}O_2S+Na]^+$: 357.0925; found: 357.0920; elemental analysis calcd (%) for $C_{21}H_{18}O_2S$: C 75.42, H 5.43; found: C 75.41, H 5.42.

2,5-Bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]thiophene (10): The procedure used for the preparation of **5** was adopted here. Reaction of **4** (757 mg, 3.00 mmol) with 2,5-iodothiophene (504 mg, 1.50 mmol) in triethylamine (20 mL) and THF (20 mL) in the presence of CuI (38 mg, 0.20 mmol) and tetrakis(triphenylphosphine)palladium(o) (116 mg, 0.10 mmol) at 50 °C for 12 h followed by column chromatography on silica gel with toluene afforded **9** (85 mg, 9 %) and **10** (633 mg, 72 %). Green crystals; m.p. 178.0–179.5 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}=2957$ (m), 2189 (m), 1695 (s), 1498 (m), 1444 (s), 1419 (m), 1371 (m), 1240 (m), 1209 (s), 1167 (m), 804 (m), 775 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$)=244 (4.75), 282 sh (4.70), 294 (4.72), 310 sh (4.69), 382 sh (4.59), 412 (4.60), 570 nm (3.27); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=$ 9.75 (s, 2H, H_8), 8.63 (d, 2H, $J=10.5$ Hz, H_4), 8.47 (s, 2H, H_2), 7.84 (d, 2H, $J=10.5$ Hz, H_6), 7.55 (dd, 2H, $J=10.5$, 10.5 Hz, H_5), 7.22 (s, 2H, Th-$H_{3,4}$), 3.97 (s, 6H, CO_2Me), 3.25 (sept, 2H, $J=6.5$ Hz, *i*Pr), 1.44 ppm (d, 12H, $J=6.5$ Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.3$, 150.8, 144.7, 142.6, 141.3, 139.4, 138.3, 136.2, 131.2, 127.7, 124.8, 115.2, 108.3, 89.8, 86.5, 51.1, 39.2, 24.5 ppm; HRMS (ESI) calcd for $[C_{38}H_{32}O_4S+Na]^+$: 607.1919; found: 607.1914; elemental analysis calcd (%) for $C_{38}H_{32}O_4S$: C 78.06, H 5.52; found: C 77.90, H 5.49.

Bis(5-isopropyl-3-methoxycarbonyl-1-azulenyl)acetylene (11): The procedure used for the preparation of **5** was adopted here. The reaction of **2** (390 mg, 1.10 mmol) with **4** (252 mg, 1.00 mmol) in triethylamine (10 mL) and THF (10 mL) in the presence of CuI (38 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(o) (116 mg, 0.10 mmol) at 50 °C for 2 h followed by column chromatography on silica gel with AcOEt/hexane (1:4) afforded **11** (449 mg, 94 %). Green crystals; m.p. 178.0–179.0 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}=2951$ (m), 1693 (s), 1454 (m), 1441 (m), 1412 (m), 1373 (m), 1207 (s), 1201 (s), 1172 (m), 1151 (m), 1116 (m), 1074 (m), 871 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$)=246 (4.68), 288 (4.84), 316 (4.74), 416 (4.33), 452 sh (4.25), 588 nm (3.19); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=9.74$ (s, 2H, H_8), 8.74 (d, 2H, $J=9.5$ Hz, H_4), 8.54 (s, 2H, H_2), 7.81 (d, 2H, $J=10.5$ Hz, H_6), 7.52 (dd, 2H, $J=9.5$, 10.5 Hz, H_5), 3.98 (s, 6H, CO_2Me), 3.24 (sept, 2H, $J=7.0$ Hz, *i*Pr), 1.44 ppm (d, 12H, $J=7.0$ Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.5$, 150.4, 144.5, 142.6, 141.2, 139.2, 138.2, 136.3, 127.3, 115.1, 109.9, 88.7, 51.2, 39.2, 24.6 ppm; HRMS (ESI) calcd for $[C_{32}H_{30}O_4+Na]^+$: 501.2042; found: 501.2036; elemental analysis calcd (%) for $C_{32}H_{30}O_4$: C 80.31, H 6.32; found: C 80.22, H 6.33.

Methyl 5-isopropyl-1-(1,1,4,4,-tetracyano-2-phenyl-3-butadienyl)azulene-1-carboxylate (12): To a solution of **5** (164 mg, 0.50 mmol) in ethyl acetate (10 mL) was added TCNE (96 mg, 0.75 mmol). The resulting mixture was stirred at room temperature for 30 min under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate and Bio-Beads with CH_2Cl_2 to give **12** (220 mg, 96 %). Red crystals; m.p. 175.0–

178.0 °C (CH_2Cl_2); IR (KBr disk): $\tilde{\nu}_{max}$ = 2972 (m), 2222 (s), 1698 (s), 1496 (s), 1464 (m), 1439 (s), 1423 (s), 1371 (s), 1282 (m), 1224 (s), 1213 (s), 1176 (s), 1155 (m), 1132 (m), 1086 (m), 1043 (m), 1028 (m), 1001 (m), 904 (m), 796 (m), 777 (m), 767 (m), 735 (m), 715 (m), 694 cm^{-1} (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 236 (4.43), 262 (4.44), 284 sh (4.45), 296 (4.47), 332 (4.33), 352 sh (4.22), 392 (4.00), 462 (4.04), 534 nm sh (3.88) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.03 (s, 1H, H_8), 8.47 (d, 1H, J = 10.0 Hz, H_4), 8.30 (s, 1H, H_2), 8.17 (d, 1H, J = 10.5 Hz, H_6), 7.99 (dd, 1H, J = 10.0, 10.5 Hz, H_5), 7.83 (d, 2H, J = 8.0 Hz, *o*-Ph), 7.69 (t, 1H, J = 8.0 Hz, *p*-Ph), 7.60 (t, 2H, J = 8.0 Hz, *m*-Ph), 3.96 (s, 3H, CO_2Me), 3.36 (sept, 1H, J = 6.5 Hz, *i*Pr), 1.47 ppm (d, 6H, J = 6.5 Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 164.3, 160.6, 156.9, 146.1, 142.5, 142.4, 141.9, 140.7, 137.5, 134.5, 132.2, 132.1, 130.0, 129.7, 119.4, 119.2, 113.6, 112.4, 112.0, 111.2, 87.7, 80.8, 51.6, 39.4, 24.4 ppm; HRMS (ESI) calcd for $[C_{29}H_{20}N_4O_2+Na]^+$: 479.1484; found: 479.1478; elemental analysis calcd (%) for $C_{29}H_{20}N_4O_2\cdot H_2O$: C 73.40, H 4.67, N 11.81; found: C 73.15, H 4.57, N 11.65.

1,4-Bis[1,1,4,4,-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-3-butadienyl]benzene (13): The procedure used for the preparation of **12** was adopted here. The reaction of **6** (289 mg, 0.50 mmol) with TCNE (154 mg, 1.20 mmol) in refluxing ethyl acetate (10 mL) for 1 h afforded **13** (402 mg, 96 %). Reddish purple crystals; m.p. > 300 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}$ = 2222 (m), 1701 (s), 1506 (s), 1419 (s), 1366 (s), 1236 (s), 1219 (s), 1182 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 262 (4.72), 296 (4.74), 334 (4.63), 444 (4.44), 540 nm sh (4.10); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.07 (d, 2H, J = 1.5 Hz, H_8), 8.45 (d, 2H, J = 10.0, 1.5 Hz, H_4), 8.25 (s, 2H, H_2), 8.21 (d, 2H, J = 10.0, 1.5 Hz, H_6), 8.04 (dd, 2H, J = 10.0, 10.0 Hz, H_5), 7.93 (s, 4H, Bz-$H_{2,3,5,6}$), 3.98 (s, 6H, CO_2Me), 3.38 (sept, 2H, J = 7.0 Hz, *i*Pr), 1.49 ppm (d, 12H, J = 7.0 Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 164.2, 159.0, 157.7, 146.5, 143.0, 142.1, 142.0, 141.1, 137.7, 136.4, 132.7, 130.6, 120.0, 118.4, 113.3, 112.5, 111.2, 110.6, 90.8, 80.3, 51.8, 39.5, 24.4 ppm; HRMS (ESI) calcd for $[C_{52}H_{34}N_8O_4+Na]^+$: 857.2601; found: 857.2595; elemental analysis calcd (%) for $C_{52}H_{34}N_8O_4\cdot{}^4/_5\,H_2O$: C 73.54, H 4.23, N 13.19; found: C 73.55, H 4.36, N 13.15.

1,3,5-Tris[1,1,4,4,-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-3-butadienyl]benzene (14): The procedure used for the preparation of **12** was adopted here. The reaction of **7** (166 mg, 0.20 mmol) with TCNE (154 mg, 1.20 mmol) in refluxing ethyl acetate (30 mL) for 1 h afforded **14** (221 mg, 91 %). Brown crystals; m.p. 210.0–214.0 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}$ = 2964 (m), 2222 (m), 1705 (s), 1496 (s), 1442 (s), 1419 (s), 1365 (m), 1221 (s), 1180 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 242 (4.98), 272 (4.96), 302 (4.93), 414 (4.60), 550 nm (4.38); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.10 (s, 3H, H_8), 8.57 (s, 3H, H_2), 8.42 (d, 3H, J = 10.0 Hz, H_4), 8.34 (s, 3H, Bz-$H_{2,4,6}$), 8.20 (d, 3H, J = 10.0 Hz, H_6), 8.01 (dd, 3H, J = 10.0, 10.0 Hz, H_5), 3.98 (s, 9H, CO_2Me), 3.39 (sept, 3H, J = 7.0 Hz, *i*Pr), 1.50 ppm (d, 18H, J = 7.0 Hz, *i*Pr); HRMS (ESI) calcd for $[C_{75}H_{48}N_{12}O_6+Na]^+$: 1235.3717; found: 1235.3712; elemental analysis calcd (%) for $C_{75}H_{48}N_{12}O_6\cdot H_2O$: C 73.45, H 4.38, N 13.44; found: C 73.16, H 4.09, N 13.65. Low solubility hampered the measurement of ^{13}C NMR.

2-[1,1,4,4,-Tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-3-butadienyl]thiophene (15): The procedure used for the preparation of **12** was adopted here. The reaction of **9** (334 mg, 1.00 mmol) with TCNE (128 mg, 1.00 mmol) in ethyl acetate (20 mL) at room temperature for 3 h afforded **15** (396 mg, 86 %). Red crystals; m.p. 101.0–106.0 °C (decomp.) (CH_2Cl_2); IR (KBr disk): $\tilde{\nu}_{max}$ = 2222 (m), 1701 (s), 1529 (s), 1500 (s), 1441 (s), 1419 (s), 1408 (s), 1365 (s), 1348 (m), 1240 (m), 1215 (s), 1178 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 262 (4.45), 302 (4.47), 342 (4.35), 374 (4.30), 418 sh (4.14), 460 nm (4.18); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.01 (d, 1H, J = 1.9 Hz, H_8), 8.51 (dd, 1H, J = 9.9, 1.9 Hz, H_4), 8.25 (s, 1H, H_2), 8.20 (dd, 1H, J = 9.9, 1.9 Hz, H_6), 8.07 (dd, 1H, J = 4.1, 1.0 Hz, Th-H_5), 8.01 (dd, 1H, J = 9.9, 9.9 Hz, H_5), 8.00 (dd, 1H, J = 4.1, 1.0 Hz, Th-H_3), 7.35 (dd, 1H, J = 4.1, 1.0 Hz, Th-H_4), 3.94 (s, 3H, CO_2Me), 3.36 (sept, 1H, J = 7.0 Hz, *i*Pr), 1.47 ppm (d, 6H, J = 7.0 Hz, *i*Pr); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.3, 159.8, 159.4, 157.0, 146.2, 142.5, 142.3, 141.9, 140.7, 138.4, 137.7, 137.2, 135.5, 132.3, 130.1, 119.4, 118.5, 113.5, 112.7, 112.3, 111.7, 80.6, 80.3, 51.6, 39.4, 24.4 ppm; HRMS (ESI) calcd for $[C_{27}H_{18}N_4O_2S+Na]^+$: 485.1048; found: 485.1043; elemental analysis calcd (%) for $C_{27}H_{18}N_4O_2S\cdot{}^1/_3\,H_2O$: C 69.21, H 4.02, N 11.96; found: C 69.26, H 4.01, N 12.01.

2,5-Bis[1,1,4,4,-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-3-butadienyl]thiophene (16): The procedure used for the preparation of **12** was adopted here. The reaction of **10** (292 mg, 0.347 mmol) with TCNE (192 mg, 1.50 mmol) in refluxing ethyl acetate (20 mL) for 1 h afforded **16** (408 mg, 97 %). Reddish brown crystals; m.p. 180.0–186.0 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}$ = 2963 (m), 2222 (s), 1701 (s), 1529 (s), 1441 (s), 1417 (s), 1398 (s), 1368 (s), 1298 (m), 1238 (s), 1213 (s), 1180 (s), 1136 (m), 1089 (m), 1062 (m), 1049 (m), 1024 (m), 900 (m), 812 (m), 779 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 244 sh (4.68), 262 (4.71), 334 (4.49), 416 sh (4.64), 434 nm (4.67); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.04 (s, 2H, H_8), 8.45 (d, 2H, J = 10.0 Hz, H_4), 8.21 (d, 2H, J = 9.5 Hz, H_6), 8.20 (s, 2H, H_2), 8.06 (s, 2H, Th-$H_{3,4}$), 8.04 (dd, 2H, J = 9.5, 10.0 Hz, H_5), 3.97 (s, 6H, CO_2Me), 3.37 (sept, 2H, J = 7.0 Hz, *i*Pr), 1.48 ppm (d, 12H, J = 7.0 Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 157.9, 157.7, 156.9, 146.7, 143.0, 142.8, 142.0, 141.8, 141.1, 137.7, 136.4, 133.0, 120.0, 117.5, 113.0, 112.3, 111.7, 110.8, 85.9, 80.5, 51.7, 39.5, 24.4 ppm; HRMS (ESI) calcd for $[C_{50}H_{32}N_8O_4S+Na]^+$: 863.2165; found: 863.2159; elemental analysis calcd (%) for $C_{50}H_{32}N_8O_4S\cdot{}^3/_2\,H_2O$: C 69.19, H 4.06, N 12.91; found: C 69.34, H 4.20, N 12.77.

1,1,4,4,-Tetracyano-2,3-bis(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-butadiene (17): The procedure used for the preparation of **12** was adopted here. The reaction of **11** (239 mg, 0.50 mmol) with TCNE (77 mg, 0.60 mmol) in ethyl acetate (10 mL) at room temperature for 1 h afforded **17** (293 mg, 97 %). Red crystals; m.p. 164.0–166.0 °C (AcOEt); IR (KBr disk): $\tilde{\nu}_{max}$ = 2220 (m), 1709 (s), 1689 (s), 1496 (s), 1441 (s), 1419 (s), 1367 (m), 1209 (s), 1178 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 234 (4.59), 262 (4.59), 300 (4.63), 340 (4.37), 388 (4.27), 508 nm (4.32); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.07 (d, 2H, J = 1.5 Hz, H_8), 8.60 (s, 2H, H_2), 8.53 (dd, 2H, J = 10.0, 1.5 Hz, H_4), 8.15 (dd, 2H, J = 10.0, 1.5 Hz, H_6), 7.93 (dd, 2H, J = 10.0, 10.0 Hz, H_5), 3.96 (s, 6H, CO_2Me), 3.37 (sept, 2H, J = 7.0 Hz, *i*Pr), 1.49 ppm (d, 12H, J = 7.0 Hz, *i*Pr); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 164.5, 156.9, 146.3, 143.4, 142.4, 142.3, 140.7, 137.3, 132.3, 120.8, 119.5, 114.3, 112.6, 80.9, 51.7, 39.5, 24.5 ppm; HRMS (ESI) calcd for $[C_{38}H_{30}N_4O_4+Na]^+$: 629.2165; found: 629.2159; elemental analysis calcd (%) for $C_{38}H_{30}N_4O_4\cdot{}^1/_3\,H_2O$: C 74.49, H 5.05, N 9.14; found: C 74.55, H 5.16, N 9.09.

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