Selected Papers

Synthesis and Properties of Mono-, Bis-, Tris-, and Tetrakis[1,1,4,4-tetracyano-2-(1-azulenyl)-1,3-butadien-3-yl] Chromophores Connected to a Benzene Ring by Phenylethynyl- and 2-Thienylethynyl Spacers

Taku Shoji,*[1] Mitsuhisa Maruyama,[1] Shunji Ito,[2] and Noboru Morita[3]

[1]Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto, Nagano 390-8621

[2]Graduate School of Science and Technology, Hirosaki University, Hirosaki, Aomori 036-8561

[3]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, Miyagi 980-8578

Received January 28, 2012; E-mail: tshoji@shinshu-u.ac.jp

Mono-, bis-, tris-, and tetrakis[(1-azulenylethynyl)phenylethynyl- and (1-azulenylethynyl)-2-thienylethynyl]benzenes have been prepared by Pd-catalyzed alkynylation of iodobenzene derivatives or 2-iodothiophene derivatives substituted by 1-azulenylethynyl group with polyethynylbenzenes under Sonogashira–Hagihara cross-coupling conditions. These compounds reacted with tetracyanoethylene (TCNE) in a formal [2 + 2] cycloaddition–cycloreversion reaction to afford the corresponding 1,1,4,4-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1,3-butadien-3-yl chromophores in excellent yields. The redox behavior of the novel azulene-substituted tetracyanobutadiene (TCBD) derivatives was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which revealed their multistep electrochemical reduction properties. Moreover, a significant color change was observed by visible spectroscopy under the electrochemical reduction conditions.

Conjugated organic compounds play an important role in the development of a new generation of optical and electronic materials. Therefore, a variety of conjugated compounds have been synthesized to date.[1]

Particularly, π-electron compounds expanded by polyethynylbenzene derivatives are used as core structures for dendritic materials,[2] and are utilized as functional dyes,[3] supramolecular architectures,[4] and potential nonlinear optical materials.[5] Previously, we have also reported the synthesis of poly(6-azulenylethynyl)benzene derivatives to exhibit multiple functionalities, such as electrochromism and discotic liquid crystalline behavior.[6]

Poly(phenylethynyl)benzenes with donor–acceptor units also have a potential as organic electronics. Diederich et al. have reported that *N*,*N*-dialkylaniline-substituted (DAA-substituted) polyethynylbenzenes react with tetracyanoethylene (TCNE) by a formal [2 + 2] cycloaddition–cycloreversion reaction to give the DAA-substituted tetracyanobutadiene (TCBD) chromophores in excellent yields.[7] They have also reported that the new class of chromophores is characterized by intense intramolecular charge-transfer (ICT) interactions with absorption maxima in the visible region, as well as promising third-order optical nonlinearities.[8] Recently, we have also reported the synthesis and electrochromic properties of TCBD derivatives with 1-azulenyl,[9] 2-oxo-2*H*-cyclohepta[*b*]-3-furyl,[10] and ferrocenyl substituents[11] connected by various π-electron compounds, which have been prepared by the [2 + 2] cycloaddition reaction of the corresponding acetylene derivatives with TCNE. Particularly, azulene-substituted TCBDs represent significant color change with higher reversibility among them under the redox conditions. The expanded π-electron system by polyethynylbenzenes exhibits various functionalities described in the literature.[1–6] However, there are few reports of the synthesis and properties of TCBD derivatives connected with polyethynylbenzenes, except for derivatives reported by Diederich et al.[7] Thus, the spectroscopic and electrochemical properties of the TCBD system binding with polyethynylbenzenes give important insight into the development of donor–acceptor based organic electronic and optoelectronic materials.

We describe herein the synthesis of polyethynylbenzene derivatives connected with (1-azulenylethynyl)phenylethynyl and (1-azulenylethynyl)-2-thienylethynyl groups by Sonogashira–Hagihara cross-coupling reaction, as well as the reactivity of the products toward the [2 + 2] cycloaddition reaction with TCNE to afford the corresponding TCBD chromophores. The electronic properties of the novel π-expanded TCBD derivatives were observed by electrochemical analysis and absorption spectroscopy.

Results and Discussion

Synthesis. Taking the first strategy, the preparation of (1-azulenylethynyl)iodoarene units was required to construct the novel azulene-substituted TCBD derivatives. Thus, the synthesis of methyl 3-[(4-iodophenyl)ethynyl]-7-isopropylazulene-

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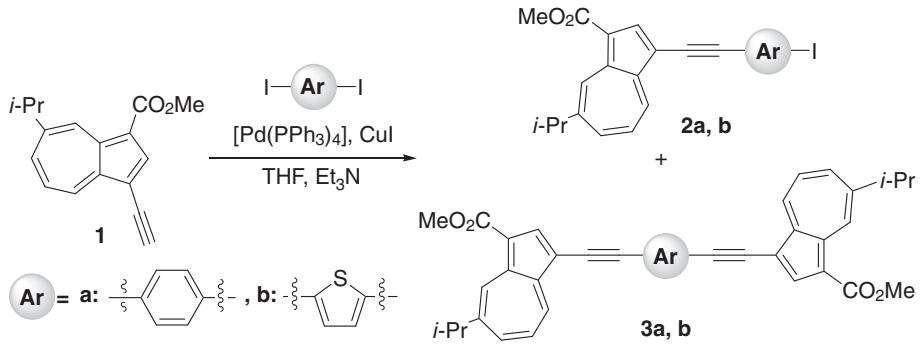
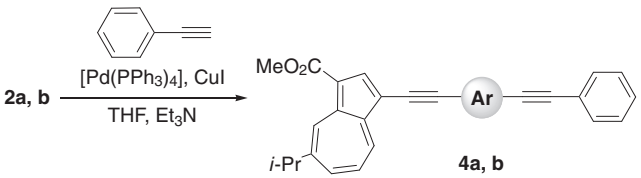


Scheme 1.

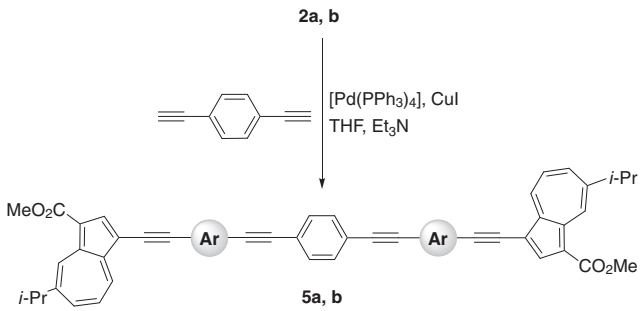


Scheme 2.

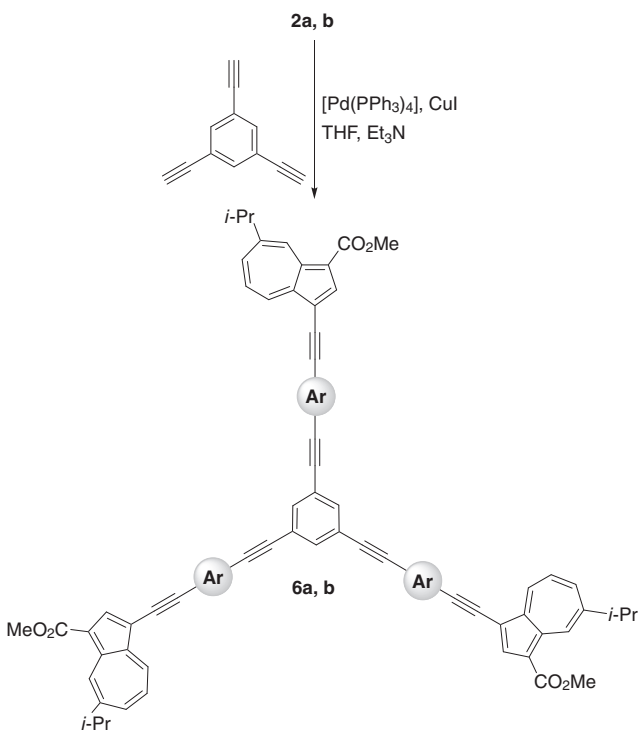
1-carboxylate (**2a**) and methyl 3-[(5-iodo-2-thienyl)ethynyl]-7-isopropylazulene-1-carboxylate (**2b**) were examined via the cross-coupling reaction of methyl 3-ethynyl-7-isopropylazulene-1-carboxylate (**1**) with excess 1,4-diiodobenzene and 2,5-diiodothiophene under Sonogashira–Hagihara conditions.[12] The Sonogashira–Hagihara cross-coupling reaction of 1-ethynylazulene **1**, which was prepared by a procedure reported by us,[9a] with 1,4-diiodobenzene and 2,5-diiodothiophene at room temperature afforded methyl 3-[(4-iodophenyl)ethynyl]-7-isopropylazulene-1-carboxylate (**2a**) and methyl 3-[(5-iodo-2-thienyl)ethynyl]-7-isopropylazulene-1-carboxylate (**2b**) both in 74% yield, along with **3a** and **3b** (**3a**: 12%, **3b**: 10%) (Scheme 1).[9a]

Preparation of polyethynylbenzene derivatives connected with (1-azulenylethynyl)phenylethynyl and (1-azulenylethynyl)-2-thienylethynyl groups **4a**–**7a** and **4b**–**7b** for the precursors of the novel TCBD derivatives was accomplished by a simple one-pot reaction involving repeated Pd-catalyzed alkynylation of the corresponding ethynylbenzenes with **2a** and **2b** under Sonogashira–Hagihara conditions. The cross-coupling reaction of **2a** with ethynylbenzene using $[Pd(PPh_3)_4]$ as a catalyst and subsequent chromatographic purification of the reaction mixture on silica gel afforded the desired **4a** in 97% yield. Likewise, the reaction of **2b** with ethynylbenzene afforded the desired **4b** in 95% yield (Scheme 2). The cross-coupling reaction of 1,4-diethynylbenzene with **2a** and **2b** in the presence of the Pd catalyst afforded bis-adducts **5a** (89%) and **5b** (85%), respectively (Scheme 3).

Tris-adducts **6a** and **6b** were also obtained by similar Pd-catalyzed reaction of 1,3,5-triethynylbenzene[13] with **2a** and **2b** in 85% and 80% yields, respectively (Scheme 4). Tetrakis-adducts **7a** and **7b** were prepared by similar Pd-catalyzed reaction of **2a** and **2b** with 1,2,4,5-tetraethynylbenzene[14] in 77% and 74% yields, respectively (Scheme 5). These new compounds **4a**–**7a** and **4b**–**7b** possess fair solubility in chloroform, dichloromethane, and so on. Moreover, they are stable and show no decomposition even after several weeks at room temperature.

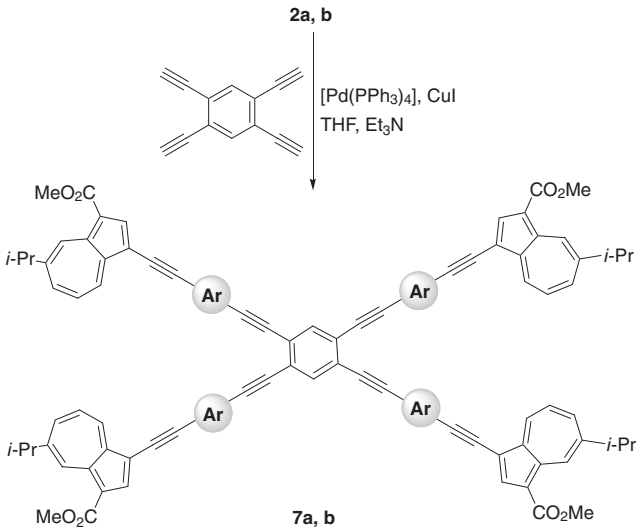


Scheme 3.

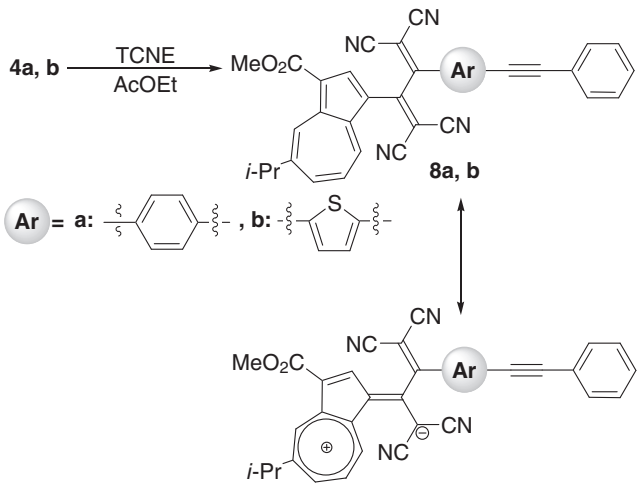


Scheme 4.

The formal [2 + 2] cycloaddition–cycloreversion reaction of the mono-, bis-, tris-, and tetrakis-adducts **4a**–**7a** and **4b**–**7b** with TCNE was examined according to a procedure described in the literature.[7–10] The reaction of **4a** with TCNE in refluxing ethyl acetate yielded **8a** in 97% yield. Likewise, the reaction of **4b** with TCNE afforded **8b** in 96% yield (Scheme 6). The [2 + 2] cycloaddition reaction of **8a** and **8b** in phenylethynyl



Scheme 5.



Scheme 6.

moiety did not proceed in DMF under the refluxing conditions, even though excess TCNE was used. These results indicate the low reactivity of the C≡C triple bond detached from 1-azulenyl moiety, owing to the electron-withdrawing nature of TCBD at the *para*-position.[15]

The TCBD chromophores with multiple TCBD units **9a**–**11a** and **9b**–**11b** were also prepared in the same way starting from the corresponding acetylenes **5a**–**7a** and **5b**–**7b** (Figure 1). The yield of the products **9a**–**11a** and **9b**–**11b** are summarized in Table 1. The double-addition of TCNE with **5a** gave **9a** in 94% yield by stirring with equimolar amounts of the starting materials in refluxing ethyl acetate within 3 h. The TCBD chromophore with 2-thienylethynyl linker **9b** was also prepared by the one-pot formal [2 + 2] cycloaddition–cycloreversion reaction of **5b** with TCNE in 95% yield. The TCBD chromophores with three TCBD units **10a** and **10b** were obtained in 91% and 93% yields, respectively, by the [2 + 2] cycloaddition–cycloreversion sequence between TCNE and the acetylene precursors **6a** and **6b**, respectively. Although long reaction periods were required, compounds **11a** and **11b** were obtained in almost quantitative yields (**11a**: 92%, **11b**: 94%) by

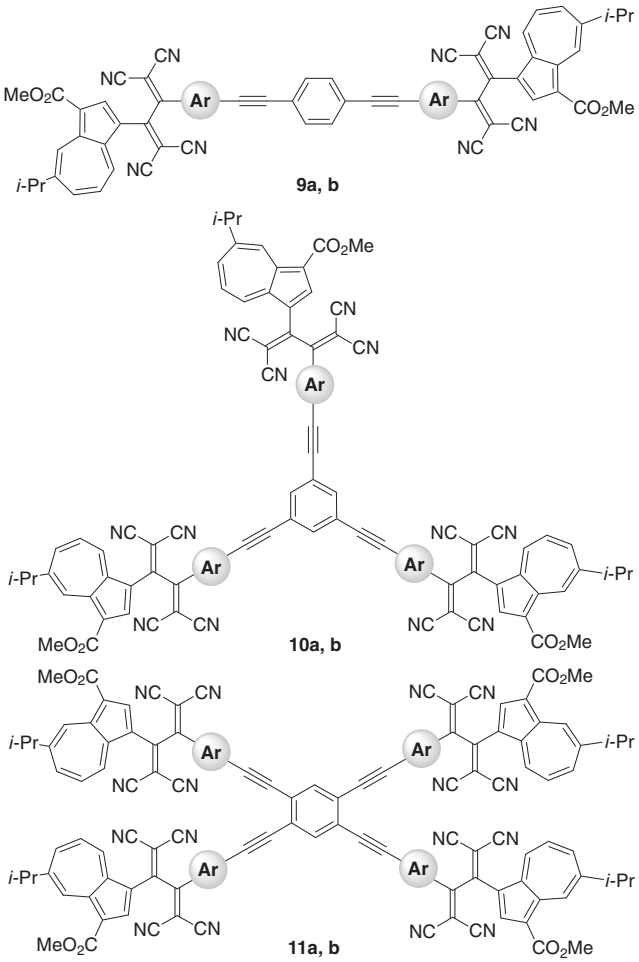


Figure 1. Bis-, tris-, and tetrakis{4-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]arylethynyl}benzenes **9a**–**11a** and **9b**–**11b**.

Table 1. Synthesis of Mono-, Bis-, Tris-, and Tetrakis{4-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]arylethynyl}benzenes **8a**–**11a** and **8b**–**11b**

Substrate	Reaction time/h	Product	Yield/%
4a	3	**8a**	97
4b	3	**8b**	96
5a	5	**9a**	94
5b	5	**9b**	95
6a	5	**10a**	91
6b	5	**10b**	93
7a	12	**11a**	92
7b	12	**11b**	94

the cycloaddition reaction of TCNE with the corresponding alkynes **7a** and **7b**, respectively, followed by the cycloreversion reaction. These novel π-expanded TCBD derivatives **8a**–**11a** and **8b**–**11b** are obtained as stable reddish crystals and can be storable in crystalline state under ambient conditions.

Spectroscopic Properties. The new compounds were fully characterized by spectral data, as shown in the Experimental Section. Mass spectra of **2a**–**11a** and **2b**–**11b** ionized by ESI

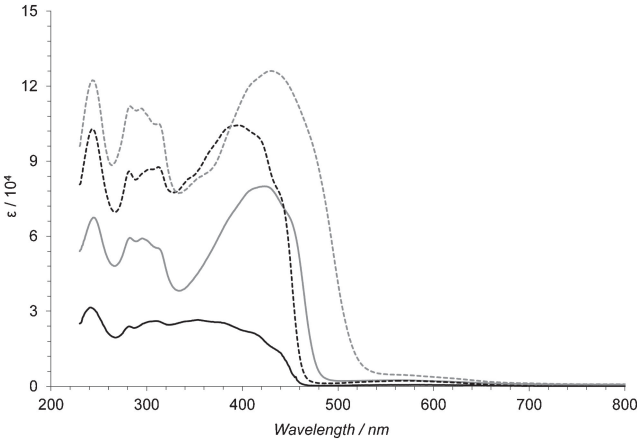


Figure 2. UV–vis spectra of **4b** (black line), **5b** (gray line), **6b** (black broken line), and **7b** (gray broken line) in dichloromethane.

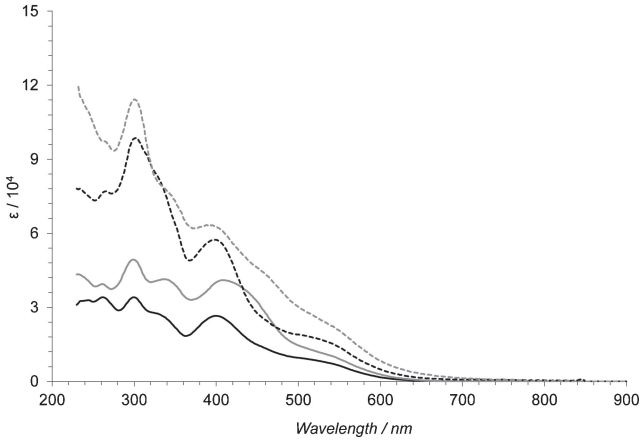


Figure 3. UV–vis spectra of **8a** (black line), **9a** (gray line), **10a** (black broken line), and **11a** (gray broken line) in dichloromethane.

showed the correct molecular ion peaks. The characteristic stretching vibration band of the acetylene moiety of **2a**–**7a** and **2b**–**7b** was observed at $\nu = 2182$–$2204\,\mathrm{cm^{-1}}$ in their IR spectra. The TCBD derivatives **8a**–**11a** and **8b**–**11b** exhibited a characteristic C≡N stretching band at $\nu = 2191$–$2225\,\mathrm{cm^{-1}}$ in their IR spectra. These results are consistent with the structures of these products.

Polyethynylbenzene derivatives have a tendency to form self-aggregates attributable to π–π stacking interaction, which causes significant line broadening and shielding effects in their ^{1}H NMR signals.[16] We have also reported a solution of hexakis(6-azulenylethynyl)benzene derivative exhibits high-field shift of the chemical shifts in the ^{1}H NMR spectrum with increasing concentration, due to self-aggregation caused by their π–π stacking interaction. Furthermore, Diederich et al. have reported the intermolecular CN···C(CN)$_2$ multipolar interaction of TCBDs, recently.[17] Thus, concentration dependence of the ^{1}H NMR chemical shifts for highly conjugated **7a** and **11a** was investigated as a model case. The ^{1}H NMR spectra of **7a** and **11a** for each concentration are shown in the Supporting Information. Despite being described in the literature, compound **7a** did not show concentration dependence in its ^{1}H NMR spectra, even though the concentration of **7a** was increased up to 1.0×10^{-3} M. It means the π–π stacking interaction of **7a** is weak, and the high solubility of **7a** might be ascribed to less effective self-aggregation of the molecules. Similar to **7a**, concentration dependence of the ^{1}H NMR chemical shifts for **11a** was not observed, when the concentration was gradually changed from 1.0×10^{-4} M up to 1.0×10^{-3} M. Thus, these results suggest less effective intermolecular multipolar interaction between the cyano groups of **11a**.

The UV–visible spectra of acetylene derivatives **4a**–**7a** and **4b**–**7b** showed characteristic weak absorptions arising from the azulene system in the visible region. Although the extinction coefficients increased with the number of azulene rings substituted, absorption maxima of these compounds were quite different from each other. As shown in Figure 2, the absorption maxima of **5b** ($\lambda_{max} = 423$ nm) and **7b** ($\lambda_{max} = 431$ nm) exhibited bathochromic shifts by 27 and 35 nm, respectively, compared with that of **6b** ($\lambda_{max} = 396$ nm). The absorption

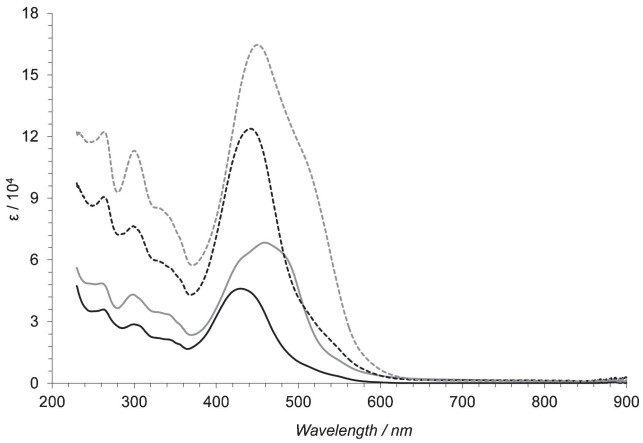


Figure 4. UV–vis spectra of **8b** (black line), **9b** (gray line), **10b** (black broken line), and **11b** (gray broken line) in dichloromethane.

maximum of **6b** rather resembled that of **4b**, although the extinction coefficient of **6b** was apparently larger than that of **4b**. These results indicate the efficient expansion of the π-electron system through the phenylethynyl moiety in 1,4- and 1,2,4,5-arrangement of **5b** and **7b**, rather than that in 1,3,5-arrangement of **6b**.

The UV–visible spectra of TCBD derivatives **8a**–**11a** and **8b**–**11b** in dichloromethane are shown in Figures 3 and 4, respectively. As expected from their resonance structures as illustrated in Scheme 6, TCBD derivatives **8a**–**11a** and **8b**–**11b** showed characteristic ICT absorption in the visible region. Their absorption maxima and coefficients ($\log \varepsilon$) are summarized in Table 2.

The absorption maxima of **9a**–**11a** were nearly equal to that of the simpler TCBD derivative **8a**, although the extinction coefficients show an increasing trend as the number of TCBD units substituted (Figure 3). These effects suggest that the π-conjugation is less effective by the extension attributable to the phenylethynyl spacer connected. The longest absorption maxima of **8b**–**11b** were dependent on the arrangement of the TCBD units on the central benzene ring with the difference from those

Table 2. Absorption Maxima [nm] and Their Coefficients ($\log\varepsilon$) of **8a**–**11a** and **8b**–**11b** in Dichloromethane and in Hexane

Sample	λ_{max} ($\log\varepsilon$) in CH_2Cl_2	λ_{max} ($\log\varepsilon$) in hexane[a)]
8a	400 (4.42), 538 sh (3.87)	—
8b	442 (4.62)	429 (4.62)
9a	410 (4.61), 540 sh (4.02)	—
9b	435 sh (4.85), 481 (4.90)	432 sh (4.85), 462 (4.91)
10a	400 (4.76), 540 sh (4.19)	—
10b	442 (5.13)	435 (5.13)
11a	466 sh (4.61), 546 sh (4.27)	—
11b	451 (5.22), 508 sh (5.04)	445 (5.22), 506 sh (4.98)

a) Dichloromethane (**8b**: 10%, **9b**: 20%, **10b**: 30%, **11b**: 30%) was contained in hexane to maintain solubility of the compounds.

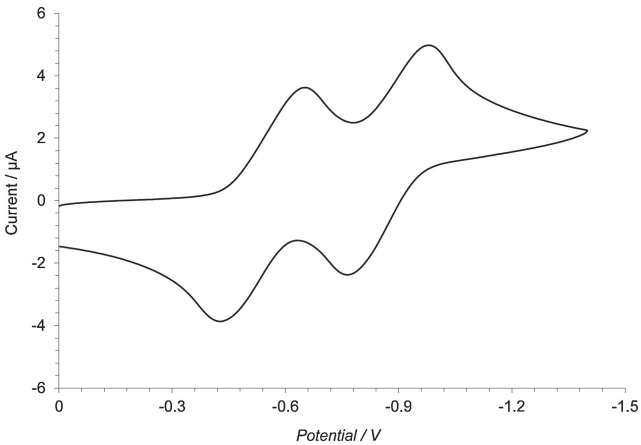
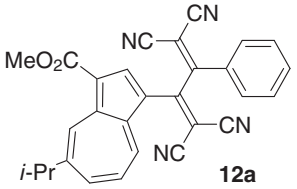


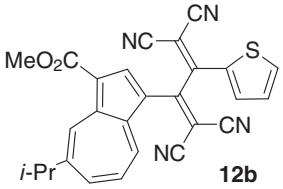
Figure 5. Cyclic voltammogram of the reduction of **9b** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate = 100 mV s^{-1}.

of **8a**–**11a** (Figure 4). The absorption maximum of **10b** (λ_{max} = 442 nm) resembled that of **8b** (λ_{max} = 442 nm), although the extinction coefficient was almost three times larger than that of **8b**. This indicates that the conjugation in **10b** did not effectively expand by the 1,3,5-arrangement on the centered benzene ring, whereas the longest absorption maximum of **9b** (λ_{max} = 481 nm) and **11b** (λ_{max} = 451 nm) exhibited bathochromic shifts compared with that of **10b**. This suggests that the 1,4- and 1,2,4,5-arrangement of TCBDs on the benzene ring efficiently extended the conjugation in **9b** and **11b**, rather than that in the 1,3,5-arrangement of **10b**. As a result, the 2-thienylethynyl spacer between TCBD and the central benzene ring effectively extended the π-electron system, rather than phenylethynyl spacer.

Most of the thiophene-substituted TCBD derivatives **8b**–**10b** showed solvatochromism, when the solvent was changed from CH_2Cl_2 to CH_2Cl_2/hexane. A noticeable spectral feature of **9b** is the presence of a distinct absorption band at 481 nm in CH_2Cl_2, which exhibits blue-shifts by 19 nm (λ_{max} = 462 nm) in less polar 20% CH_2Cl_2/hexane, suggesting the ICT nature of this band (see the Supporting Information). It is assumed that the first excited-state has a larger dipole moment than that in the ground state due to the ICT character from the azulene ring to the TCBD unit substituted.



12a



12b

Figure 6. 1,1,4,4-Tetracyano-2-aryl-3-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1,3-butadienes **12a** and **12b**.

Table 3. Reduction Potentials of Mono-, Bis-, Tris-, and Tetrakis{4-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]arylethynyl}benzenes **8a**–**11a** and **8b**–**11b**[a)] and TCBD Derivatives **12a** and **12b**[b)] for References

Sample	Method	E_1^{red}/V	E_2^{red}/V	E_3^{red}/V
8a	CV	−0.56	−0.97	
	(DPV)	(−0.54)	(−0.95)	(−1.91)
8b	CV	−0.58	−0.90	
	(DPV)	(−0.56)	(−0.88)	(−1.85)
9a	CV	−0.56 (2e$^-$)	−0.97 (2e$^-$)	
	(DPV)	(−0.54)	(−0.95)	(−1.92)
9b	CV	−0.56 (2e$^-$)	−0.89 (2e$^-$)	
	(DPV)	(−0.54)	(−0.87)	(−1.86)
10a	CV	−0.56 (3e$^-$)	−0.97 (3e$^-$)	
	(DPV)	(−0.54)	(−0.95)	(−1.93)
10b	CV	−0.57 (3e$^-$)	−0.89 (3e$^-$)	
	(DPV)	(−0.55)	(−0.87)	(−1.84)
11a	CV	−0.56 (4e$^-$)	−0.97 (4e$^-$)	
	(DPV)	(−0.54)	(−0.95)	(−1.93)
11b	CV	−0.57 (4e$^-$)	−0.88 (4e$^-$)	
	(DPV)	(−0.55)	(−0.86)	(−1.84)
12a	CV	−0.61	−1.03	
12b	CV	−0.64	−1.03	

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]. The peak potentials measured by DPV are shown in parentheses. b) Redox potentials were measured by CV [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].

Electrochemistry. To clarify the electrochemical properties, the redox behavior of **8a**–**11a** and **8b**–**11b** was examined by CV and 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 and disk as auxiliary and working electrodes, respectively. All measurements were carried out under an argon atmosphere, and potentials were related to an $Ag/AgNO_3$ reference electrode and Fc/Fc^+ as an internal reference, which discharges at +0.15 V. A cyclic voltammogram for the reduction of **9b** is shown in Figure 5. The redox potentials (in volts vs. $Ag/AgNO_3$) of TCNE-adducts **8a**–**11a** and **8b**–**11b** and TCBD derivatives **12a** and **12b** (Figure 6) are summarized in Table 3.

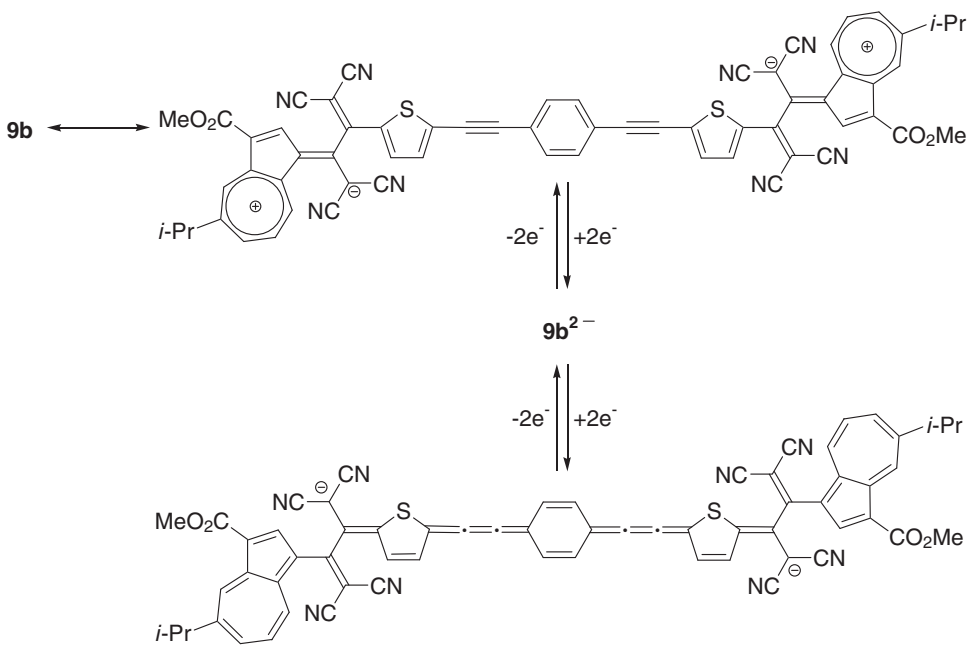
Electrochemical reduction of TCBD derivatives **8a**–**11a** and **8b**–**11b** displayed a reversible two-stage wave containing

multielectron transfer on CV. As shown in Table 3, the difference of the first reduction potentials between **8a–11a** and **8b–11b** was not observed, but the second reduction potentials of **8a–11a** series exhibited a slight negative shift compared with those of **8b–11b**. Recently, we have reported the redox potentials of a series of azulene-substituted TCBD derivatives, such as **12a** and **12b** (Figure 6). The study revealed the first reduction potentials of azulene-substituted TCBD derivatives substituted by benzene and thiophene cores are decreased by increasing the number of substituted TCBD units. On the whole, the reduction potentials of **8a–11a** and **8b–11b** resembled to those of **12a** and **12b**, although the number of TCBD units in the molecule was increased. Therefore, the redox interaction among the azulene-substituted TCBD units are almost negligible in electrochemical reduction of **9a–11a** and **9b–11b**. To investigate the durability of the compound toward electrochemical reduction, repeated reduction of compound **9b** by CV was also examined. The sequential electrochemical reduction of **9b** did not change the shape of the reduction wave after one hundred redox cycles (see the Supporting Information). These results indicate that the compound **9b** possesses high durability toward sequential electrochemical reduction.

We have reported the synthesis of various azulene-substituted redox-active chromophores with the aim of creating stabilized electrochromic materials.[6,18] In these studies, the TCBD units connected with π-electron systems exhibit stabilized electrochromism with strong absorptions in visible and near-infrared regions in their two-electron-reduced state. The polyethynylbenzenes expanded by the TCBD units **8a–11a** and **8b–11b** might exemplify a new class of electrochromic system by their reversible multielectron transfer as observed by CV. Thus, to examine the color changes during the electrochemical reactions, spectral changes of TCBD derivatives **8a–11a** and **8b–11b** were monitored by visible spectroscopy. Constant-current reduction was applied to the solutions of **8a–11a** and **8b–11b**, with a platinum mesh as a working electrode and a wire counter-electrode, and visible spectra were measured in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte at room temperature under the electrochemical reduction conditions (see the Supporting Information).

The longest absorptions of the TCBD derivatives with ethynylbenzene spacer **8a–11a** gradually decreased, and the color of the solution changed from red to yellow during the electrochemical reduction. However, the reversible oxidation of the yellow solution did not regenerate the spectrum of the corresponding starting compounds. The irreversibility of the color changes might be attributed to the instability of the reduced species of **8a–11a** under the conditions for the spectral measurements in contrast with the observation obtained by CV analysis.

Although the TCBD derivatives linked by phenylethynyl spacer **8a–11a** did not show good reversibility of the color changes, reversible color changes were observed in the TCBD derivatives connected by 2-thienylethynyl spacer **8b–11b**. When the spectral changes of **8b** were monitored during the electrochemical reduction, the absorption in the visible region gradually decreased with the development of new absorptions at 550 and 710 nm, which reached the near-infrared region. The color change should be attributable to the formation of radical anionic species formed by the single electron reduction of **8b**. Reverse oxidation of the reduced species decreased the new absorptions and regenerated the original color of **8b**. A reversible color change was also observed in the visible spectral change of **9b** under the electrochemical reduction conditions. Presumed redox behavior is illustrated in Scheme 7. At the beginning, new absorptions in the visible region, which reached the near-infrared region, gradually developed and the red color of the solution changed to blue during the electrochemical reduction (Figure 7, top). As suggested by the results of cyclic voltammetry, the color change of **9b** should be ascribed by the



Scheme 7. Presumed redox behavior of **9b** under the reduction conditions.

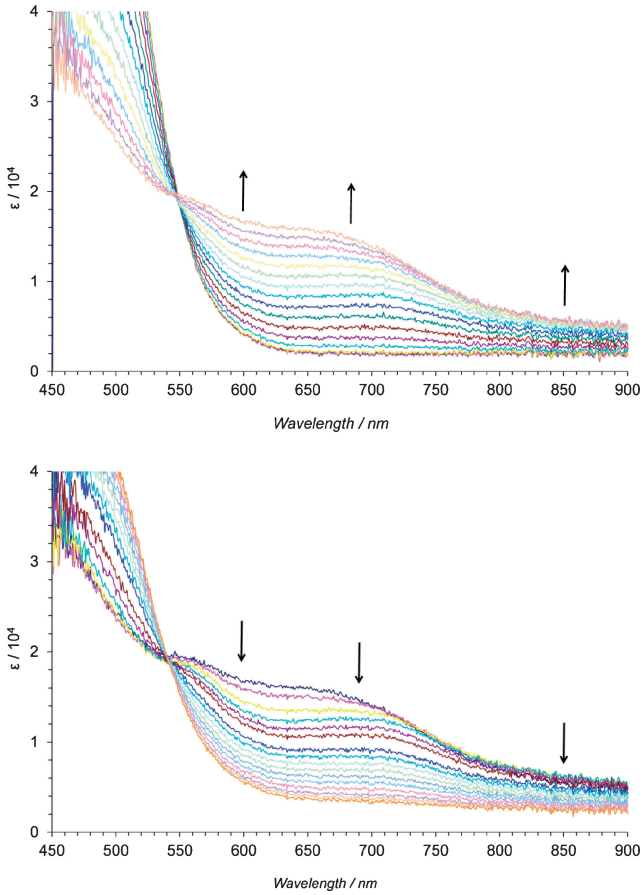


Figure 7. Continuous change in the UV–vis spectrum of **9b**: constant-current electrochemical reduction (100 μA, top) and reverse oxidation of the reduced species (100 μA, bottom) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 s intervals.

two electron reduction of the two TCBD units to form dianionic species, which could be described as closed-shell form as illustrated in Scheme 7. On reverse oxidation of the blue solution, the new absorption in the near-infrared region decreased and the original absorption of **9b** was regenerated in the visible region (Figure 7, bottom).

The longest wavelength absorption band of **10b** and **11b** in the visible region gradually increased, thus, the red solution changed to purple and blue, respectively, during the electrochemical reduction. Reverse oxidation of the purple and blue solutions regenerated the spectrum of **10b** and **11b**, respectively, with good reversibility.

Previously, we reported the synthesis of thienoquinoid compounds **13**–**16** with four 1-azulenyl substituents, which showed broad absorption beyond to the infrared region in UV–vis spectra, by the Zn-mediated reduction of the corresponding dications (Figure 8).[18g,19] Compounds **13**–**16** are relatively stable and can be treated under aerobic conditions. However, the reduction of 1,4-phenylenebis[di(1-azulenyl)methylium] derivatives did not afford satisfactory results by similar reaction, due to the fair instability of *para*-quinoid products. Thus, the reason of the low reversibility for the color change of **8a**–**11a** might be attributable to the instability of *para*-quinoid

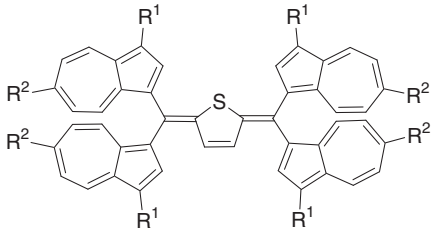


Figure 8. Thienoquinoid compounds **13**–**16** with four 1-azulenyl substituents.

products generated by the electrochemical reduction. Meanwhile, the reversible color change and development of the new absorption bands up to the near-infrared region, along with the isosbestic point in visible region, of the TCBD derivatives connected by 2-thienylethynyl spacer **8b**–**11b** indicate the formation of a stabilized closed-shell dianionic species with a thienoquinoid structure in the two-electron reduction, as suggested by the reversible CV waves under the electrochemical reduction conditions.[20]

A violene–cyanine hybrid was proposed by Hünig et al. for the design of a stabilized organic electrochromic systems.[21] We have also reported a more general structural principle through the combination of violene- and cyanine-type substructures with a large variability.[6,18] We have identified some novel hybrid structures of violenes and cyanines during the study on the synthesis and redox behaviors of azulene-substituted TCBD[9a] and DCNQ derivatives[9b] and 2*H*-cyclohepta[*b*]furan-2-one-substituted TCBD[10a] and DCNQ[10b] derivatives in addition to Hünig's violene–cyanine hybrid structure. The TCBD derivatives connected by 2-thienylethynyl spacer **8b**–**11b**, which exhibit reversible color changes during the electrochemical reaction, should be successful examples of an extension of our novel hybrid structures of violenes and cyanines from the viewpoint of the generation of a closed-shell structure by the two-electron transfer.

Conclusion

Several polyethynylbenzene derivatives connected with (1-azulenylethynyl)phenylethynyl and (1-azulenylethynyl)-2-thienylethynyl groups **4a**–**7a** and **4b**–**7b** were prepared by Sonogashira–Hagihara cross-coupling reaction. A series of TCBD chromophores substituted by 1-azulenyl groups **8a**–**11a** and **8b**–**11b** were synthesized in a one-step procedure consisting of the formal [2 + 2] cycloaddition reaction of **4a**–**7a** and **4b**–**7b** with TCNE, followed by the ring-opening reaction of the initially formed cyclobutene derivatives. Strong intramolecular CT absorption bands were observed in the UV–vis spectra of these azulene-substituted TCBDs **8a**–**11a** and **8b**–**11b**. An analysis by CV and DPV showed that compounds **8a**–**11a** and **8b**–**11b** exhibit a reversible two-stage reduction. Moreover, a significant color change was observed during the electrochemical reduction. In particular, thiophene derivatives **8b**–**11b** exhibited a significant color change, arising from the generation of thienoquinoid substructures during electrochemical reduction. These results showed that the TCBD derivatives with 2-thienylethynyl spacer **8b**–**11b** behave as hybrids of

violene and cyanine in the view of the formation of the stabilized cyanine substructures with thienoquinoid spacers formed by the two-electron reduction.

To evaluate the scope of this class of molecules investigated by this research, the preparation of novel TCBD chromophores connected with various π-electron cores is now in progress in our laboratory.

Experimental

General. Melting points were determined with a Yanagimoto MPS3 micro melting apparatus. Mass spectra were obtained with a Bruker APEX II instrument. IR and UV–vis spectra were measured with JASCO FT/IR-4100 and Shimadzu UV-2550 spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL GSX 400 (400 and 100 MHz, respectively) or a Bruker AVANCE400 (400 and 100 MHz, respectively). The voltammetry measurements were carried out in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte by utilizing Pt working and auxiliary electrodes and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) in acetonitrile containing *n*-Bu_4NClO_4 (0.1 M) at a scan rate of 100 mV s^{-1}. The internal reference Fc/Fc^+ discharges at +0.15 V under these conditions. Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Methyl 3-[(4-Iodophenyl)ethynyl]-7-isopropylazulene-1-carboxylate (2a). To a degassed solution of **1** (2.52 g, 10.0 mmol), 1,4-diiodobenzene (6.60 g, 20.0 mmol), and CuI (190 mg, 1.00 mmol) in triethylamine (50 mL) and THF (50 mL) was added tetrakis(triphenylphosphine)palladium(0) (580 mg, 0.50 mmol). The resulting mixture was stirred at room temperature for 1 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution 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 CH_2Cl_2 to give **2a** (3.27 g, 74%) as purple crystals and **3a** (694 mg, 12%) as green crystals.[9a]

2a: Mp: 105.0–108.0 °C. HRMS (ESI): calcd for $C_{23}H_{19}IO_2 + Na^+$ $[M + Na]^+$ 477.0327; found 477.0322. IR (KBr disk): ν_{max} 3080 (w), 2966 (w), 2953 (m), 2204 (w), 1686 (s, C=O), 1485 (m), 1448 (s), 1427 (m), 1410 (m), 1390 (m), 1367 (m), 1304 (m), 1244 (s), 1209 (s), 1169 (s), 1136 (m), 1118 (m), 1061 (m), 1047 (w), 1030 (w), 1005 (w), 972 (w), 941 (w), 920 (w), 885 (w), 875 (m), 819 (m), 779 (m), 756 (w), 729 (w), 700 (w), 673 (w), 646 (w), 634 (w), 586 (w), 526 (w), 474 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 249 (4.45), 275 (4.44), 315 (4.66), 330 sh (4.48), 346 (4.50), 398 (4.18), 415 sh (4.11), 568 (2.84), 614 (2.74), 682 (2.18) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (d, $J = 1.2$ Hz, 1H, H_8), 8.63 (d, $J = 10.0$ Hz, 1H, H_4), 8.46 (s, 1H, H_2), 7.81 (dd, $J = 10.0$, 1.2 Hz, 1H, H_6), 7.70 (d, $J = 8.0$ Hz, 2H, $H_{3',5'}$ of Ph), 7.51 (dd, $J = 10.0$, 10.0 Hz, 1H, H_5), 7.31 (d, $J = 8.0$ Hz, 2H, $H_{2',6'}$ of Ph), 3.96 (s, 3H, CO_2Me), 3.24 (sept, $J = 6.8$ Hz, 1H, *i*-Pr), 1.43 (d, $J = 6.8$ Hz, 6H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.39, 150.75, 144.82, 142.79, 141.32, 139.39, 138.42, 137.52, 136.17, 132.81, 127.56, 123.47, 115.20, 108.67, 93.37, 92.77, 86.39, 51.17, 39.24, 24.59. Elemental analysis calcd (%) for $C_{23}H_{19}IO_2$: C, 60.81; H, 4.22%. Found: C, 60.55; H, 4.32%.

Methyl 3-[(5-Iodo-2-thienyl)ethynyl]-7-isopropylazulene-1-carboxylate (2b). The procedure used for the preparation of **2a** was adopted here. The reaction of **1** (2.52 g, 10.0 mmol) with 2,5-diiodothiophene (6.72 g, 20.0 mmol) in triethylamine (50 mL) and THF (50 mL) in the presence of CuI (190 mg, 1.00 mmol) and tetrakis(triphenylphosphine)palladium(0) (580 mg, 0.50 mmol) at room temperature for 1 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **2b** (3.41 g, 74%) as purple crystals and **3b** (584 mg, 10%) as green crystals.[9a]

2b: Mp: 82.0–85.0 °C. HRMS (ESI): calcd for $C_{21}H_{17}IO_2S + Na^+$ $[M + Na]^+$ 482.9892; found 482.9886. IR (KBr disk): ν_{max} 2950 (w), 2198 (w), 1687 (s, C=O), 1499 (w), 1449 (s), 1414 (s), 1373 (w), 1310 (w), 1224 (m), 1213 (s), 1191 (w), 1167 (m), 1126 (w), 1056 (w), 1026 (w), 958 (w), 943 (w), 935 (w), 915 (w), 869 (w), 805 (m), 796 (s), 776 (m), 760 (w), 733 (w), 660 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 243 (4.47), 283 (4.52), 315 (4.57), 362 sh (4.29), 402 (4.20), 426 sh (4.02), 572 (2.86), 627 sh (2.70) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (d, $J = 1.6$ Hz, 1H, H_8), 8.57 (d, $J = 10.0$ Hz, 1H, H_4), 8.43 (s, 1H, H_2), 7.82 (dd, $J = 10.0$, 1.6 Hz, 1H, H_6), 7.52 (dd, $J = 10.0$, 10.0 Hz, 1H, H_5), 7.17 (d, $J = 3.6$ Hz, 1H, $H_{3'}$ of Th), 6.96 (d, $J = 3.6$ Hz, 1H, $H_{4'}$ of Th), 3.95 (s, 3H, CO_2Me), 3.23 (sept, $J = 6.8$ Hz, 1H, *i*-Pr), 1.42 (d, $J = 6.8$ Hz, 6H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.34, 150.92, 144.78, 142.71, 141.38, 139.51, 138.45, 137.09, 136.23, 132.47, 130.16, 127.74, 115.22, 108.09, 90.56, 85.33, 73.87, 51.19, 39.23, 24.58. Elemental analysis calcd (%) for $C_{21}H_{17}IO_2S$: C, 54.79; H, 3.72%. Found: C, 54.77; H, 3.89%.

Methyl 7-Isopropyl-3-[4-(phenylethynyl)phenylethynyl]-azulene-1-carboxylate (4a). The procedure used for the preparation of **2a** was adopted here. The reaction of **2a** (454 mg, 1.00 mmol) with ethynylbenzene (153 mg, 1.50 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.050 mmol) at room temperature for 6 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **4a** (416 mg, 97%) as green crystals. Mp: 107.0–111.0 °C. HRMS (ESI): calcd for $C_{31}H_{24}O_2 + Na^+$ $[M + Na]^+$ 451.1674; found 451.1669. IR (KBr disk): ν_{max} 2957 (w), 2193 (w), 1689 (s, C=O), 1593 (w), 1500 (m), 1444 (s), 1425 (m), 1406 (m), 1373 (m), 1307 (w), 1242 (m), 1211 (s), 1197 (m), 1167 (m), 1132 (m), 1118 (m), 1072 (m), 1047 (m), 960 (w), 920 (w), 871 (w), 802 (w), 775 (w), 754 (w), 721 (w), 688 (w), 648 (w), 542 (w), 524 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 238 (4.84), 316 (5.02), 340 (4.93), 356 sh (4.90), 400 (4.70), 422 sh (4.59), 568 (3.21), 616 sh (3.10) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (d, $J = 1.6$ Hz, 1H, H_8), 8.67 (d, $J = 9.2$ Hz, 1H, H_4), 8.48 (s, 1H, H_2), 7.82 (dd, $J = 10.0$, 1.6 Hz, 1H, H_6), 7.59–7.51 (m, 7H, H_5, Ph), 7.37–7.35 (m, 3H, Ph), 3.96 (s, 3H, CO_2Me), 3.24 (sept, $J = 6.8$ Hz, 1H, *i*-Pr), 1.43 (d, $J = 6.8$ Hz, 6H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.44, 150.75, 144.86, 142.78, 141.35, 139.42, 138.39, 136.23, 131.60, 131.57, 131.20, 128.41, 128.38, 127.59, 123.75, 123.07, 122.51, 115.15, 108.80, 93.51, 91.11, 89.25, 86.86, 51.19, 39.24, 24.60. Elemental analysis calcd (%) for $C_{31}H_{24}O_2$: C, 86.89; H, 5.65%. Found: C, 86.64; H, 5.77%.

Methyl 7-Isopropyl-3-[5-(phenylethynyl)-2-thienylethynyl]azulene-1-carboxylate (4b). The procedure used for

the preparation of **2a** was adopted here. The reaction of **2b** (460 mg, 1.00 mmol) with ethynylbenzene (153 mg, 1.50 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)-palladium(0) (58 mg, 0.050 mmol) at room temperature for 6 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **4b** (413 mg, 95%) as green crystals. Mp: 105.0–108.0 °C. HRMS (ESI): calcd for $C_{29}H_{22}O_2S + Na^+$ $[M + Na]^+$ 457.1238; found 457.1235. IR (KBr disk): ν_{max} 2962 (w), 2187 (w), 1692 (s, C=O), 1589 (w), 1507 (w), 1487 (w), 1460 (m), 1444 (m), 1418 (m), 1270 (w), 1221 (s), 1166 (m), 1132 (m), 1120 (w), 1072 (w), 1049 (m), 915 (w), 869 (w), 800 (s), 775 (m), 752 (s), 721 (w), 689 (m), 668 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 242 (4.50), 282 (4.38), 310 (4.42), 342 sh (4.41), 354 (4.42), 382 sh (4.40), 413 sh (4.32), 440 sh (4.13), 572 (2.80) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (d, $J = 1.6$ Hz, 1H, H_8), 8.61 (d, $J = 10.0$ Hz, 1H, H_4), 8.46 (s, 1H, H_2), 7.83 (dd, $J = 10.0$, 1.6 Hz, 1H, H_6), 7.55–7.50 (m, 3H, H_5, Ph), 7.36–7.34 (m, 3H, Ph), 7.19 (br s, 2H, $H_{3',4'}$ of Th), 3.96 (s, 3H, CO_2Me), 3.24 (sept, $J = 6.8$ Hz, 1H, *i*-Pr), 1.43 (d, $J = 6.8$ Hz, 6H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.37, 150.95, 144.86, 142.80, 141.43, 139.53, 138.49, 136.31, 131.93, 131.46, 131.14, 128.60, 128.40, 127.75, 125.45, 124.03, 122.68, 115.32, 108.24, 93.96, 89.84, 86.31, 82.45, 51.19, 39.25, 24.58. Elemental analysis calcd (%) for $C_{29}H_{22}O_2S$: C, 80.15; H, 5.10%. Found: C, 80.09; H, 5.16%.

1,4-Bis{4-[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-ethynyl]phenylethynyl}benzene (5a). The procedure used for the preparation of **2a** was adopted here. The reaction of **2a** (908 mg, 2.00 mmol) with 1,4-diethynylbenzene (126 mg, 1.00 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.050 mmol) at room temperature for 6 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **5a** (693 mg, 89%) as green crystals. Mp: >300 °C. HRMS (ESI): calcd for $C_{56}H_{42}O_4 + Na^+$ $[M + Na]^+$ 801.2981; found 801.2975. IR (KBr disk): ν_{max} 2959 (w), 2191 (w), 1695 (s, C=O), 1508 (m), 1425 (m), 1408 (m), 1373 (w), 1338 (w), 1309 (w), 1244 (m), 1209 (s), 1197 (m), 1169 (m), 1132 (w), 1118 (w), 1074 (w), 1047 (w), 920 (w), 875 (w), 837 (m), 775 (w), 540 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 240 (4.81), 314 (4.85), 362 (4.97), 376 sh (4.97), 404 (4.90), 426 sh (4.81), 568 (3.26), 616 sh (3.10) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (d, $J = 1.6$ Hz, 2H, H_8), 8.67 (d, $J = 10.0$ Hz, 2H, H_4), 8.48 (s, 2H, H_2), 7.83 (dd, $J = 10.0$, 1.6 Hz, 2H, H_6), 7.60–7.52 (m, 14H, H_5, Ph), 3.96 (s, 6H, CO_2Me), 3.24 (sept, $J = 6.8$ Hz, 2H, *i*-Pr), 1.43 (d, $J = 6.8$ Hz, 12H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.44, 150.80, 144.88, 142.81, 141.38, 139.44, 138.42, 135.56, 131.60, 131.57, 131.24, 127.62, 124.03, 123.06, 122.21, 115.19, 108.75, 93.50, 90.84, 87.10, 80.52, 51.21, 39.26, 24.61. Elemental analysis calcd (%) for $C_{56}H_{42}O_4 \cdot H_2O$: C, 84.40; H, 5.56%. Found: C, 84.64; H, 5.83%.

1,4-Bis{5-[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-ethynyl]-2-thienylethynyl}benzene (5b). The procedure used for the preparation of **2a** was adopted here. The reaction of **2b** (920 mg, 2.00 mmol) with 1,4-diethynylbenzene (126 mg, 1.00 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.050 mmol) at room temperature for 12 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **5b** (672 mg, 85%) as green crystals. Mp: 185.0–188.0 °C. HRMS (ESI): calcd for $C_{52}H_{38}O_4S_2 + Na^+$ $[M + Na]^+$ 813.2109; found 813.2104. IR (KBr disk): ν_{max} 2955 (w), 2183 (m), 1691 (s, C=O), 1585 (w), 1521 (w), 1487 (w), 1447 (m), 1417 (s), 1270 (w), 1218 (s), 1166 (m), 1132 (w), 1072 (w), 1049 (w), 916 (w), 869 (w), 833 (m), 801 (m), 775 (m), 720 (w), 663 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 245 (4.83), 283 (4.77), 296 (4.77), 315 sh (4.73), 423 (4.90), 450 (4.83), 568 (3.26) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (d, $J = 2.0$ Hz, 2H, H_8), 8.62 (d, $J = 10.0$ Hz, 2H, H_4), 8.47 (s, 2H, H_2), 7.84 (dd, $J = 10.0$, 1.6 Hz, 2H, H_6), 7.54 (dd, $J = 10.0$, 10.0 Hz, 2H, H_5), 7.51 (s, 4H, Ph), 7.20 (br s, 4H, $H_{3',4'}$ of Th), 3.96 (s, 6H, CO_2Me), 3.24 (sept, $J = 6.8$ Hz, 2H, *i*-Pr), 1.43 (d, $J = 6.8$ Hz, 12H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.37, 151.02, 144.89, 142.84, 141.48, 139.57, 138.54, 136.32, 132.27, 131.39, 131.20, 127.79, 125.93, 123.64, 122.79, 115.37, 108.18, 93.70, 90.18, 86.29, 84.69, 51.21, 39.27, 24.59. Elemental analysis calcd (%) for $C_{52}H_{38}O_4S_2$: C, 78.96; H, 4.84%. Found: C, 78.80; H, 4.95%.

1,3,5-Tris{4-[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]phenylethynyl}benzene (6a). The procedure used for the preparation of **2a** was adopted here. The reaction of **2a** (681 mg, 1.50 mmol) with 1,3,5-triethynylbenzene (50 mg, 0.50 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.050 mmol) at room temperature for 12 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **6a** (480 mg, 85%) as green crystals. Mp: 175.0–180.0 °C. HRMS (ESI): calcd for $C_{81}H_{60}O_6 + Na^+$ $[M + Na]^+$ 1151.4288; found 1151.4282. IR (KBr disk): ν_{max} 2957 (m), 2189 (m), 1693 (s, C=O), 1578 (m), 1498 (m), 1444 (s), 1425 (m), 1406 (m), 1373 (m), 1333 (w), 1307 (w), 1244 (m), 1209 (s), 1196 (s), 1167 (m), 1132 (m), 1118 (m), 1070 (w), 1047 (w), 1016 (w), 958 (w), 920 (w), 871 (m), 833 (m), 800 (w), 773 (m), 721 (w), 700 (w), 677 (w), 650 (w), 590 (w), 542 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 240 (5.00), 316 (5.16), 358 (5.13), 370 sh (5.09), 402 (4.99), 424 sh (4.88), 568 (3.41), 616 sh (3.29) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (d, $J = 1.6$ Hz, 3H, H_8), 8.66 (d, $J = 10.0$ Hz, 3H, H_4), 8.48 (s, 3H, H_2), 7.82 (dd, $J = 10.0$, 1.6 Hz, 3H, H_6), 7.68 (s, 3H, Ph), 7.61–7.51 (m, 15H, H_5, Ph), 3.97 (s, 9H, CO_2Me), 3.24 (sept, $J = 6.8$ Hz, 3H, *i*-Pr), 1.43 (d, $J = 6.8$ Hz, 18H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.41, 150.79, 144.87, 142.79, 141.36, 139.43, 138.39, 136.21, 134.08, 131.67, 131.25, 127.63, 124.22, 123.96, 121.92, 115.17, 108.72, 93.48, 90.53, 89.46, 87.20, 51.20, 39.24, 24.59. Elemental analysis calcd (%) for $C_{81}H_{60}O_6 \cdot 1/2H_2O$: C, 85.46; H, 5.40%. Found: C, 85.56; H, 5.67%.

1,3,5-Tris{5-[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]-2-thienylethynyl}benzene (6b). The procedure used for the preparation of **2b** was adopted here. The reaction of **2b** (690 mg, 1.50 mmol) with 1,3,5-triethynylbenzene (50 mg, 0.50 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.050 mmol) at room temperature for 24 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **6b** (459 mg, 80%) as green crystals. Mp:

146.0–150.0 °C. HRMS (ESI): calcd for $C_{75}H_{54}O_6S_3 + Na^+$ $[M + Na]^+$ 1169.2980; found 1169.2975. IR (KBr disk): ν_{max} 2957 (w), 2184 (w), 1695 (s, C=O), 1580 (m), 1504 (w), 1464 (m), 1441 (m), 1420 (m), 1372 (w), 1212 (s), 1165 (m), 1130 (w), 1072 (w), 1050 (w), 917 (w), 867 (w), 798 (m), 775 (w), 717 (w), 673 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 243 (5.01), 282 (4.93), 312 (4.94), 341 sh (4.91), 396 (5.02), 415 sh (5.00), 440 sh (4.48), 569 (3.38) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (d, $J = 1.6$ Hz, 3H, H_8), 8.61 (d, $J = 10.0$ Hz, 3H, H_4), 8.46 (s, 3H, H_2), 7.82 (dd, $J = 10.0$, 1.6 Hz, 3H, H_6), 7.63 (s, 3H, Ph), 7.53 (dd, $J = 10.0$, 10.0 Hz, 3H, H_5), 7.21–7.19 (m, 6H, $H_{3',4'}$ of Th), 3.96 (s, 9H, CO_2Me), 3.24 (sept, $J = 6.8$ Hz, 3H, *i*-Pr), 1.43 (d, $J = 6.8$ Hz, 18H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.34, 150.99, 144.88, 142.84, 141.46, 139.54, 138.51, 136.30, 133.65, 132.54, 131.16, 127.79, 126.20, 123.72, 123.24, 115.38, 108.16, 92.18, 90.29, 86.26, 83.98, 51.18, 39.25, 24.58. Elemental analysis calcd (%) for $C_{75}H_{54}O_6S_3$: C, 78.51; H, 4.74%. Found: C, 78.33; H, 4.89%.

1,2,4,5-Tetrakis{4-[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]phenylethynyl}benzene (7a). The procedure used for the preparation of **2a** was adopted here. The reaction of **2a** (908 mg, 2.00 mmol) with 1,2,4,5-tetraethynylbenzene (87 mg, 0.50 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.050 mmol) at room temperature for 12 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **7a** (570 mg, 77%) as green crystals. Mp: 217.0–220.0 °C ($CHCl_3$). HRMS (ESI): calcd for $C_{106}H_{78}O_8 + Na^+$ $[M + Na]^+$ 1501.5584; found 1501.5589. IR (KBr disk): ν_{max} 2959 (w), 2191 (w), 1695 (s, C=O), 1500 (m), 1446 (s), 1425 (w), 1410 (m), 1373 (w), 1244 (m), 1209 (s), 1197 (m), 1169 (m), 1132 (w), 1120 (w), 1072 (w), 1049 (w), 920 (w), 893 (w), 871 (w), 833 (w), 800 (w), 775 (w), 650 (w), 592 (w), 542 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 242 (5.10), 312 (5.20), 364 (5.14), 408 (5.19), 430 sh (5.14), 564 (3.56), 616 sh (3.42) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (d, $J = 1.6$ Hz, 4H, H_8), 8.47 (d, $J = 10.0$ Hz, 4H, H_4), 8.27 (s, 4H, H_2), 8.18 (dd, $J = 10.0$, 1.6 Hz, 4H, H_6), 8.00 (dd, $J = 10.0$, 10.0 Hz, 4H, H_5), 7.85 (d, $J = 8.0$ Hz, 8H, Ph), 7.73 (d, $J = 8.0$ Hz, 8H, Ph), 7.57 (s, 2H, Ph), 3.97 (s, 12H, CO_2Me), 3.37 (sept, $J = 6.8$ Hz, 4H, *i*-Pr), 1.49 (d, $J = 6.8$ Hz, 24H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.15, 164.36, 160.38, 157.23, 146.25, 142.66, 142.42, 142.03, 140.92, 137.63, 132.92, 132.37, 132.01, 131.60, 129.86, 129.70, 122.99, 119.62, 119.43, 113.63, 112.46, 112.03, 111.23, 94.72, 90.39, 87.57, 80.70, 51.74, 39.53, 24.48. Elemental analysis calcd (%) for $C_{106}H_{78}O_8 \cdot 1/4CHCl_3$: C, 84.54; H, 5.22%. Found: C, 84.44; H, 5.21%.

1,2,4,5-Tetrakis{5-[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]-2-thienylethynyl}benzene (7b). The procedure used for the preparation of **2a** was adopted here. The reaction of **2b** (920 mg, 2.00 mmol) with 1,2,4,5-tetraethynylbenzene (87 mg, 0.50 mmol) in triethylamine (5 mL) and THF (5 mL) in the presence of CuI (19 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.050 mmol) at room temperature for 24 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **7b** (556 mg, 74%) as green crystals. Mp: 155.0–159.0 °C. HRMS (ESI): calcd for $C_{98}H_{70}O_8S_4 + Na^+$ $[M + Na]^+$ 1525.3851; found 1525.3856. IR (KBr disk): ν_{max} 2958 (w), 2182 (w), 1696 (m, C=O), 1580 (w), 1511 (w), 1464 (m), 1418 (m), 1372 (w), 1213 (s), 1165 (m), 1131 (w), 1073 (w), 1049 (w), 917 (w), 877 (w), 799 (m), 775 (m), 668 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 244 (5.09), 283 (5.05), 294 (5.05), 312 (5.02), 355 sh (4.92), 431 (5.10), 575 sh (3.59) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (br s, 4H, H_8), 8.53 (br s, 4H, H_4), 8.38 (br s, 4H, H_2), 7.66 (br s, 4H, H_6), 7.41 (br s, 4H, H_5), 7.29 (br s, 2H, Ph), 7.22 (m, 8H, $H_{3',4'}$), 3.91 (s, 12H, CO_2Me), 3.15 (br s, 4H, *i*-Pr), 1.38 (br s, 24H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.24, 150.88, 144.81, 142.65, 141.36, 139.44, 138.34, 136.24, 132.88, 132.82, 131.30, 127.82, 126.55, 124.58, 123.33, 115.27, 108.12, 92.19, 90.64, 89.18, 86.54, 51.14, 39.15, 24.51. Elemental analysis calcd (%) for $C_{98}H_{70}O_8S_4$: C, 78.27; H, 4.69%. Found: C, 78.02; H, 4.88%.

Methyl 3-{3,3-Dicyano-1-(dicyanomethylene)-1-[4-(phenylethynyl)phenyl]-2-propenyl}-7-isopropylazulene-1-carboxylate (8a). To a solution of **4a** (214 mg, 0.50 mmol) in ethyl acetate (5 mL) was added TCNE (128 mg, 1.00 mmol). The resulting mixture was refluxed for 3 h 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 **8a** (270 mg, 97%) as reddish brown crystals. Mp: 158.0–160.0 °C. HRMS (ESI): calcd for $C_{37}H_{24}N_4O_2 + Na^+$ $[M + Na]^+$ 579.1797; found 579.1791. IR (KBr disk): ν_{max} 2962 (w), 2217 (m, C≡N), 1698 (m, C=O), 1601 (m), 1499 (s), 1442 (s), 1419 (s), 1366 (m), 1296 (w), 1231 (m), 1217 (s), 1179 (m), 1138 (m), 1053 (w), 900 (w), 846 (w), 815 (w), 779 (w), 758 (w), 728 (w), 690 (m), 672 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 262 (4.53), 300 (4.53), 334 sh (4.42), 400 (4.42), 538 sh (3.87) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (d, $J = 1.6$ Hz, 1H, H_8), 8.47 (d, $J = 10.0$ Hz, 1H, H_4), 8.28 (s, 1H, H_2), 8.17 (dd, $J = 10.0$, 1.6 Hz, 1H, H_6), 7.99 (dd, $J = 10.0$, 10.0 Hz, 1H, H_5), 7.84 (d, $J = 8.8$ Hz, 2H, Ph), 7.71 (d, $J = 8.8$ Hz, 2H, Ph), 7.56 (dd, $J = 8.0$, 2.0 Hz, 2H, Ph), 7.40–7.38 (m, 3H, Ph), 3.96 (s, 3H, CO_2Me), 3.36 (sept, $J = 6.8$ Hz, 1H, *i*-Pr), 1.48 (d, $J = 6.8$ Hz, 6H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.14, 164.37, 160.45, 157.14, 146.23, 142.60, 142.42, 142.01, 140.87, 137.60, 132.86, 132.32, 131.94, 131.21, 130.28, 129.80, 129.37, 128.55, 122.09, 119.57, 119.37, 113.64, 112.46, 112.09, 111.33, 95.60, 88.10, 87.26, 80.76, 51.74, 39.53, 24.49. Elemental analysis calcd (%) for $C_{37}H_{24}N_4O_2$: C, 79.84; H, 4.35; N, 10.07%. Found: C, 79.66; H, 4.44; N, 10.22%.

Methyl 3-{3,3-Dicyano-1-(dicyanomethylene)-1-[5-(phenylethynyl)-2-thienyl]-2-propenyl}-7-isopropylazulene-1-carboxylate (8b). To a solution of **4b** (217 mg, 0.50 mmol) in ethyl acetate (5 mL) was added TCNE (128 mg, 1.00 mmol). The resulting mixture was refluxed for 3 h 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 **8b** (270 mg, 96%) as reddish brown crystals. Mp: 105.0–108.0 °C (CH_2Cl_2/hexane). HRMS (ESI): calcd for $C_{35}H_{22}N_4O_2S + Na^+$ $[M + Na]^+$ 585.1361; found 585.1356. IR (KBr disk): ν_{max} 2962 (w), 2221 (w, C≡N), 2200 (w), 1702 (m, C=O), 1530 (m), 1500 (m), 1440 (m), 1421 (s), 1364 (m), 1309 (w), 1240 (w), 1213 (m), 1179 (m), 1135 (w), 1051 (w), 1021 (w),

898 (w), 809 (w), 779 (w), 756 (m), 733 (w), 688 (w), 673 (w), 666 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 264 (4.54), 298 (4.44), 342 sh (4.28), 442 (4.62) nm. UV–vis (10% CH_2Cl_2/hexane): λ_{max} (log ε) 262 (4.49), 300 (4.41), 340 (4.28), 429 (4.62) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (d, $J = 2.0$ Hz, 1H, H_8), 8.51 (d, $J = 10.0$ Hz, 1H, H_4), 8.24 (s, 1H, H_2), 8.18 (dd, $J = 10.0$, 2.0 Hz, 1H, H_6), 8.02 (dd, $J = 10.0$, 10.0 Hz, 1H, H_5), 7.96 (d, $J = 3.6$ Hz, 1H, $H_{4'}$ of Th), 7.55 (dd, $J = 7.6$, 2.0 Hz, 2H, *o*-Ph), 7.44–7.40 (m, 4H, *m*-Ph, *p*-Ph, $H_{3'}$ of Th), 3.96 (s, 3H, CO_2Me), 3.37 (sept, $J = 6.8$ Hz, 1H, *i*-Pr), 1.48 (d, $J = 6.8$ Hz, 6H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.38, 159.60, 158.13, 157.20, 146.38, 142.58, 142.33, 142.00, 140.77, 137.84, 137.32, 136.86, 135.36, 133.73, 132.42, 131.85, 130.06, 128.67, 121.22, 119.48, 118.59, 113.49, 112.93, 112.40, 111.90, 102.58, 81.40, 80.57, 79.79, 51.69, 39.51, 24.46. Elemental analysis calcd (%) for $C_{35}H_{22}N_4O_2S$: C, 74.71; H, 3.94; N, 9.96%. Found: C, 74.55; H, 4.04; N, 9.90%.

1,4-Bis{4-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]phenylethynyl}benzene (9a). The procedure used for the preparation of **8a** was adopted here. The reaction of **5a** (389 mg, 0.50 mmol) with TCNE (192 mg, 1.50 mmol) in ethyl acetate (10 mL) for 5 h afforded **9a** (487 mg, 94%) as red crystals. Mp: 200.0–203.0 °C. HRMS (ESI): calcd for $C_{68}H_{42}N_8O_4 + Na^+$ $[M + Na]^+$ 1057.3227; found 1057.3232. IR (KBr disk): ν_{max} 2963 (w), 2222 (m, C≡N), 1702 (m, C=O), 1598 (m), 1499 (m), 1440 (m), 1419 (s), 1364 (m), 1295 (w), 1213 (s), 1179 (m), 1139 (w), 1052 (w), 901 (w), 841 (m), 777 (m), 731 (w), 669 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 262 (4.60), 300 (4.69), 338 (4.62), 410 (4.61), 540 sh (4.02) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (d, $J = 1.6$ Hz, 2H, H_8), 8.47 (d, $J = 10.0$ Hz, 2H, H_4), 8.27 (s, 2H, H_2), 8.18 (dd, $J = 10.0$, 1.6 Hz, 2H, H_6), 8.00 (dd, $J = 10.0$, 10.0 Hz, 2H, H_5), 7.85 (d, $J = 8.0$ Hz, 4H, Ph), 7.73 (d, $J = 8.0$ Hz, 4H, Ph), 7.57 (s, 4H, Ph), 3.97 (s, 6H, CO_2Me), 3.37 (sept, $J = 6.8$ Hz, 2H, *i*-Pr), 1.49 (d, $J = 6.8$ Hz, 12H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.15, 164.36, 160.38, 157.23, 146.25, 142.66, 142.42, 142.03, 140.92, 137.63, 132.92, 132.37, 132.01, 131.60, 129.86, 129.70, 122.99, 119.62, 119.43, 113.63, 112.46, 112.03, 111.23, 94.72, 90.39, 87.57, 80.70, 51.74, 39.53, 24.48. Elemental analysis calcd (%) for $C_{68}H_{42}N_8O_4$: C, 78.90; H, 4.09; N, 10.83%. Found: C, 78.77; H, 4.26; N, 10.91%.

1,4-Bis{5-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]-2-thienylethynyl}benzene (9b). The procedure used for the preparation of **8a** was adopted here. The reaction of **5b** (396 mg, 0.50 mmol) with TCNE (192 mg, 1.50 mmol) in ethyl acetate (10 mL) for 5 h afforded **9b** (497 mg, 95%) as red crystals. Mp: 170.0–175.0 °C (decomp.). HRMS (ESI): calcd for $C_{64}H_{38}N_8O_4S_2 + Na^+$ $[M + Na]^+$ 1069.2355; found 1069.2350. IR (KBr disk): ν_{max} 2962 (w), 2222 (w, C≡N), 2203 (w), 1711 (m, C=O), 1535 (m), 1512 (m), 1498 (s), 1433 (m), 1416 (s), 1364 (m), 1304 (w), 1274 (w), 1247 (w), 1212 (s), 1179 (m), 1118 (w), 1091 (w), 1031 (w), 899 (w), 835 (w), 813 (w), 775 (w), 730 (w), 670 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 263 (4.78), 300 (4.74), 339 sh (4.60), 435 sh (4.85), 481 (4.90) nm. UV–vis (20% CH_2Cl_2/hexane): λ_{max} (log ε) 260 (4.76), 298 (4.72), 339 sh (4.53), 432 sh (4.85), 462 (4.91) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (d, $J = 2.0$ Hz, 2H, H_8), 8.50 (d, $J = 10.0$ Hz, 2H, H_4), 8.26 (s, 2H, H_2), 8.17 (dd, $J = 10.0$, 1.6 Hz, 2H, H_6), 7.96 (d, $J = 4.4$ Hz, 2H, $H_{4'}$ of Th), 7.60 (dd, $J = 10.0$, 10.0 Hz, 2H, H_5), 7.56 (s, 4H, Ph), 7.43 (d, $J = 4.4$ Hz, 2H, $H_{3'}$ of Th), 3.96 (s, 6H, CO_2Me), 3.36 (sept, $J = 6.8$ Hz, 2H, *i*-Pr), 1.48 (d, $J = 6.8$ Hz, 12H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.37, 159.49, 158.16, 157.31, 146.41, 143.38, 142.65, 142.31, 142.04, 140.83, 137.88, 137.26, 135.84, 134.15, 132.64, 132.49, 131.99, 122.74, 119.57, 118.60, 113.48, 112.85, 112.41, 111.78, 101.29, 84.05, 80.57, 51.74, 39.56, 24.50. Elemental analysis calcd (%) for $C_{64}H_{38}N_8O_4S_2$: C, 73.41; H, 3.66; N, 10.70%. Found: C, 73.29; H, 3.78; N, 10.54%.

1,3,5-Tris{4-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]phenylethynyl}benzene (10a). The procedure used for the preparation of **8a** was adopted here. The reaction of **6a** (282 mg, 0.25 mmol) with TCNE (192 mg, 1.50 mmol) in ethyl acetate (10 mL) for 5 h afforded **10a** (344 mg, 91%) as red crystals. Mp: >300 °C. HRMS (ESI): calcd for $C_{99}H_{60}N_{12}O_6 + Na^+$ $[M + Na]^+$ 1535.4656; found 1535.4651. IR (KBr disk): ν_{max} 2970 (w), 2219 (w, C≡N), 1737 (m, C=O), 1600 (w), 1499 (m), 1440 (m), 1419 (m), 1365 (s), 1215 (s), 1130 (w), 1097 (w), 1051 (w), 878 (w), 834 (w), 777 (w), 727 (w), 678 (w), 669 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 266 (4.89), 302 (4.99), 400 (4.76), 540 sh (4.19) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (d, $J = 1.6$ Hz, 3H, H_8), 8.48 (d, $J = 10.0$ Hz, 3H, H_4), 8.27 (s, 3H, H_2), 8.19 (dd, $J = 10.0$, 1.6 Hz, 3H, H_6), 8.02 (dd, $J = 10.0$, 10.0 Hz, 3H, H_5), 7.87 (d, $J = 8.0$ Hz, 6H, Ph), 7.77 (s, 3H, Ph), 7.74 (d, $J = 8.0$ Hz, 6H, Ph), 3.97 (s, 9H, CO_2Me), 3.38 (sept, $J = 6.8$ Hz, 3H, *i*-Pr), 1.49 (d, $J = 6.8$ Hz, 18H, *i*-Pr). Low solubility hampered the measurement of ^{13}C NMR. Elemental analysis calcd (%) for $C_{99}H_{60}N_{12}O_6$: C, 78.56; H, 4.00; N, 11.10%. Found: C, 78.78; H, 4.09; N, 11.13%.

1,3,5-Tris{5-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]-2-thienylethynyl}benzene (10b). The procedure used for the preparation of **8a** was adopted here. The reaction of **6b** (287 mg, 0.25 mmol) with TCNE (192 mg, 1.50 mmol) in ethyl acetate (10 mL) for 5 h afforded **10b** (356 mg, 93%) as red crystals. Mp: 230.0–235.0 °C. HRMS (ESI): calcd for $C_{93}H_{54}N_{12}O_6S_3 + Na^+$ $[M + Na]^+$ 1553.3349; found 1553.3344. IR (KBr disk): ν_{max} 2969 (w), 2221 (w, C≡N), 1738 (s, C=O), 1521 (m), 1496 (m), 1432 (s), 1419 (s), 1365 (s), 1215 (s), 1179 (m), 1134 (w), 1097 (w), 1061 (w), 1024 (w), 900 (w), 810 (w), 778 (w), 734 (w), 676 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 264 (4.98), 299 (4.90), 344 sh (4.77), 442 (5.13) nm. UV–vis (30% CH_2Cl_2/hexane): λ_{max} (log ε) 263 (4.97), 301 (4.88), 342 sh (4.77), 435 (5.13) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 3H, H_8), 8.51 (d, $J = 10.0$ Hz, 3H, H_4), 8.22 (s, 3H, H_2), 8.20 (dd, $J = 10.0$, 1.6 Hz, 3H, H_6), 8.04 (dd, $J = 10.0$, 10.0 Hz, 3H, H_5), 7.96 (d, $J = 4.4$ Hz, 3H, $H_{4'}$ of Th), 7.75 (s, 3H, Ph), 7.46 (d, $J = 4.4$ Hz, 3H, $H_{3'}$ of Th), 3.96 (s, 9H, CO_2Me), 3.37 (sept, $J = 6.8$ Hz, 3H, *i*-Pr), 1.49 (d, $J = 6.8$ Hz, 18H, *i*-Pr). Low solubility hampered the measurement of ^{13}C NMR. Elemental analysis calcd (%) for $C_{93}H_{54}N_{12}O_6S_3$: C, 72.93; H, 3.55; N, 10.97%. Found: C, 72.70; H, 3.69; N, 10.88%.

1,2,4,5-Tetrakis{4-[3,3-dicyano-1-(dicyanomethylene)-2-

(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]-phenylethynyl}benzene (11a). The procedure used for the preparation of **8a** was adopted here. The reaction of **7a** (370 mg, 0.25 mmol) with TCNE (256 mg, 2.00 mmol) in ethyl acetate (10 mL) for 12 h afforded **11a** (458 mg, 92%) as red crystals. Mp: >300 °C. HRMS (ESI): calcd for $C_{130}H_{78}N_{16}O_8 + Na^+$ $[M + Na]^+$ 2013.6086; found 2013.6081. IR (KBr disk): ν_{max} 2969 (w), 2217 (w, C≡N), 1738 (s, C=O), 1600 (w), 1499 (m), 1440 (m), 1419 (m), 1365 (s), 1215 (s), 1180 (w), 1135 (w), 1052 (w), 905 (w), 814 (w), 777 (w), 731 (w), 669 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 300 (5.06), 346 sh (4.87), 390 (4.80), 466 sh (4.61), 546 sh (4.27) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (d, $J = 1.6$ Hz, 4H, H_8), 8.47 (d, $J = 10.0$ Hz, 4H, H_4), 8.30 (s, 4H, H_2), 8.19 (dd, $J = 10.0$, 1.6 Hz, 4H, H_6), 8.01 (dd, $J = 10.0$, 10.0 Hz, 4H, H_5), 7.86 (d, $J = 8.0$ Hz, 8H, Ph), 7.85 (s, 2H, Ph), 7.73 (d, $J = 8.0$ Hz, 8H, Ph), 3.97 (s, 12H, CO_2Me), 3.37 (sept, $J = 6.8$ Hz, 4H, *i*-Pr), 1.49 (d, $J = 6.8$ Hz, 24H, *i*-Pr). Low solubility hampered the measurement of ^{13}C NMR. Elemental analysis calcd (%) for $C_{130}H_{78}N_{16}O_8 \cdot 3/4H_2O$: C, 77.85; H, 4.00; N, 11.17%. Found: C, 77.86; H, 4.03; N, 11.14%.

1,2,4,5-Tetrakis{5-[3,3-dicyano-1-(dicyanomethylene)-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-1-propenyl]-2-thienylethynyl}benzene (11b). The procedure used for the preparation of **8a** was adopted here. The reaction of **7b** (376 mg, 0.25 mmol) with TCNE (256 mg, 2.00 mmol) in ethyl acetate (10 mL) for 12 h afforded **11b** (474 mg, 94%) as red crystals. Mp: 203.0–207.0 °C (decomp.). HRMS (ESI): calcd for $C_{122}H_{70}N_{16}O_8S_4 + Na^+$ $[M + Na]^+$ 2037.4343; found 2037.4338. IR (KBr disk): ν_{max} 2969 (w), 2221 (w, C≡N), 1738 (s, C=O), 1496 (m), 1439 (m), 1418 (s), 1365 (s), 1215 (s), 1180 (m), 1134 (w), 1090 (w), 1059 (w), 1021 (w), 899 (w), 810 (w), 778 (w), 731 (w), 659 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) 264 (5.07), 301 (5.04), 342 sh (4.90), 451 (5.22), 508 sh (5.04) nm. UV–vis (30% CH_2Cl_2/hexane): λ_{max} (log ε) 263 (4.94), 303 (4.92), 344 sh (4.82), 457 (4.99), 541 sh (4.82) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (d, $J = 1.6$ Hz, 4H, H_8), 8.59 (d, $J = 10.0$ Hz, 4H, H_4), 8.29 (s, 4H, H_2), 8.18 (dd, $J = 10.0$, 1.6 Hz, 4H, H_6), 8.02 (dd, $J = 10.0$, 10.0 Hz, 4H, H_5), 7.86 (s, 2H, Ph), 7.80 (d, $J = 4.4$ Hz, 4H, $H_{4'}$ of Th), 7.53 (d, $J = 4.4$ Hz, 4H, $H_{3'}$ of Th), 3.95 (s, 12H, CO_2Me), 3.36 (sept, $J = 6.8$ Hz, 4H, *i*-Pr), 1.47 (d, $J = 6.8$ Hz, 24H, *i*-Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.38, 159.21, 158.28, 157.41, 146.49, 142.69, 142.51, 142.13, 140.83, 138.30, 137.84, 136.88, 134.06, 132.60, 125.21, 119.72, 118.68, 113.55, 112.80, 112.56, 111.63, 97.80, 97.72, 89.21, 89.13, 81.23, 80.23, 51.75, 39.53, 24.46. Elemental analysis calcd (%) for $C_{122}H_{70}N_{16}O_8S_4 \cdot H_2O$: C, 72.03; H, 3.57; N, 11.02%. Found: C, 72.11; H, 3.60; N, 10.99%.

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Supporting Information

Figure of UV–vis spectra and cyclic voltammograms of reported compounds. This material is available free of charge via the Internet at http://www.csj.jp/journals/bcsj/.

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