

# Synthesis, Properties and Redox Behavior of Tris[1-azulenyltetracyanobutadiene and 1-azulenylbis(tetracyanobutadiene)s] Connected with 1,3,5-Tri(1-azulenyl)benzene Core

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**Abstract:** Tris[1-azulenylacetylene and 1-azulenylethynylarylacetylenes] connected with 1,3,5-tri(1-azulenyl)benzene core have been prepared by Pd-catalyzed alkynylation of 1-ethynylazulene with tris(3-iodo-1-azulenyl)benzene, or iodoarene derivatives substituted by 1-azulenylethynyl group with tris(3-ethynyl-1-azulenyl)benzene under Sonogashira–Hagihara cross-coupling conditions. These compounds reacted with tetracyanoethylene in a formal [2 + 2] cycloaddition–retroelectrocyclization reaction to afford the corresponding tris[1-azulenyltetracyanobutadiene and 1-azulenylbis(tetracyanobutadiene)] chromophores in excellent yields. The redox behavior of the novel 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.

## Introduction

Conjugated organic compounds play an important role in the development of optical and electronic materials for the next

generation. Therefore, a variety of such kinds of compounds have been synthesized to date.<sup>[1]</sup> Since the  $\pi$ -conjugate systems with donor–acceptor units also have a potential for their application to organic electronic and optoelectronic devices, a large number of the donor–acceptor systems bearing a  $\pi$ -electron core have been synthesized and their properties have been extensively studied to date.<sup>[2]</sup> As a strategy to construct the donor–acceptor systems, Diederich et al. have reported the formal [2 + 2] cycloaddition–retroelectrocyclization (CA–RE) reaction of *N,N*-dialkylaniline-substituted (DAA-substituted) ethynylarenes with tetracyanoethylene (TCNE) to produce the DAA-substituted tetracyanobutadiene (TCBD) chromophores in excellent yields.<sup>[3]</sup> They have also reported the preparation of dendritic TCBDs, which have been revealed to exhibit multi-stage reduction properties with high reversibility on cyclic voltammetry (CV).<sup>[4]</sup>

Azulene has attracted the interest of many research groups due to its unusual properties as well as its beautiful blue color.<sup>[5]</sup> The  $\pi$ -electron systems connected by multiple azulenyl groups have attracted much interest due to their characteristic electronic properties.<sup>[6]</sup> As a part of this study, we have reported the synthesis, reactivity and properties of tri(2- and 6-azulenyl)benzene derivatives.<sup>[7]</sup> Beside that, the synthesis of tri(1-azulenyl)benzenes were established by Imafuku et al. utilizing the benzannulation of 1-acetylazulene derivative mediated by both Lewis<sup>[8]</sup> and Brønsted acid<sup>[9]</sup>, but their reactivity and properties have never been examined, so far.

Recently, we have also reported the synthesis and electrochemical properties of tris[1-azulenyltetracyanobutadiene (1-AzTCBD)] chromophores constructed by 1,3,5-benzenetriyl spacer<sup>[10]</sup> and a triphenylamine core,<sup>[11]</sup> which have been obtained by the formal [2 + 2] CA–RE reaction of the corresponding ethynylazulene derivatives with TCNE. Although these tris(1-AzTCBD)s have a  $C_3$  symmetrical structure with the respect to the central 1,3,5-benzenetriyl unit and triphenylamine core, these 1-AzTCBDs displayed a reversible multi-stage reduction wave on CV, due to the electrochemical communication between the TCBD units through the central  $\pi$ -electron cores. Tris(1-AzTCBD)s and their congeners constructed by tri(1-azulenyl)benzene core should become another examples of the redox-active chromophores, because the  $C_3$  symmetrical molecules with multiple 1-AzTCBD units tend to show multi-stage reduction properties on CV under the electrochemical reduction conditions as revealed by our previous works that described in the literatures.<sup>[12]</sup>

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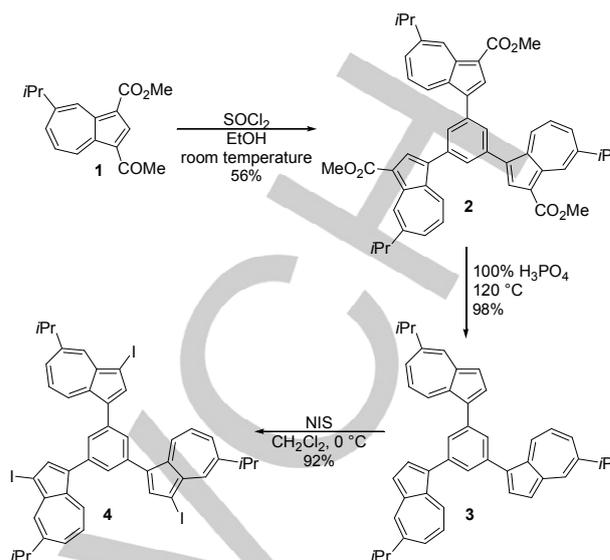
Supporting information for this article is given via a link at the end of the document.

Herein, we describe the synthesis of tris[1-azulenylacetylene and 1-azulenylethynylarylacetylenes] connected with 1,3,5-tri(1-azulenyl)benzene core **10–12** under Sonogashira–Hagihara cross-coupling conditions, as well as the reactivity of the products **10–12** toward the [2 + 2] CA–RE reaction with TCNE to afford the corresponding tris[1-azulenyltetracyanobutadiene (1-AzTCBD) and 1-azulenylbis(tetracyanobutadiene)s (1-AzBisTCBDs)] chromophores **13–15**. The electronic properties of the novel 1-AzTCBD chromophores constructed with 1,3,5-tri(1-azulenyl)benzene core are characterized by electrochemical analysis and absorption spectroscopy.

## Results and Discussion

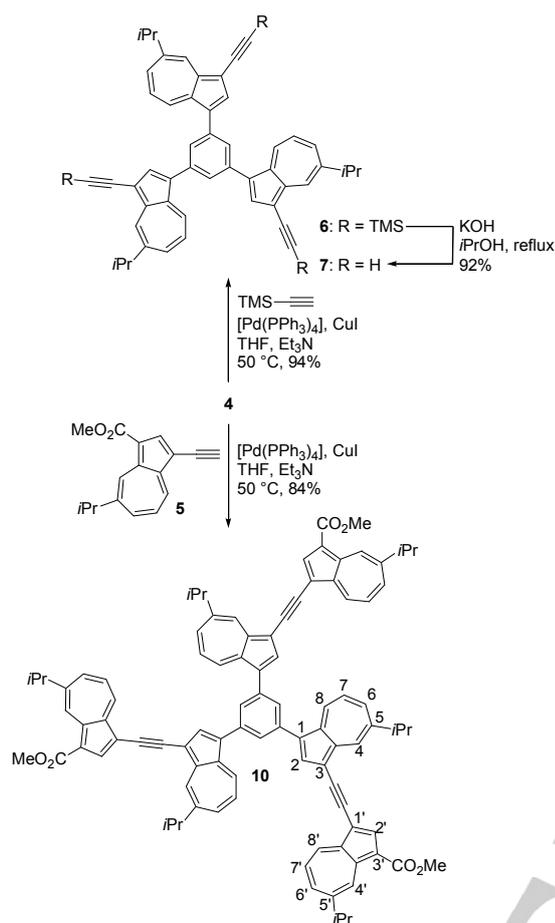
**Synthesis:** Taking the first strategy, the preparation of the core 1,3,5-tri(1-azulenyl)benzene unit was required to construct the novel  $C_3$  symmetrical molecules with multiple 1-AzTCBD units. Thus, preparation of 1,3,5-tris(5-isopropyl-3-iodo-1-azulenyl)benzene (**4**), a precursor for the coupling partner in this research, was examined via three-steps synthetic pathway. An overview of the synthetic path for the compound **4** is illustrated in Scheme 1.

Previously, Hafner and Elwahy demonstrated the cobalt-catalyzed trimerization of 1-ethynylazulene to give 1,3,5-tri(1-azulenyl)benzene derivative, but the reaction afforded 1,2,4-trisubstituted product as a major product.<sup>[13]</sup> We have also reported the synthesis of 1,3,5-tri(6-azulenyl)benzenes from 6-ethynylazulenes by the similar procedure reported by Hafner et al. However, our procedure mainly generated ( $\eta^5$ -cyclopentadienyl)[di(6-azulenyl)cyclobutadiene]cobalt complexes, along with small amount of 1,3,5-tri(6-azulenyl)benzenes.<sup>[7]</sup> Thus, we attempted the acid-mediated aldol-type benzannulation of 1-acetylazulene derivatives, reported by Imafuku et al. previously,<sup>[9]</sup> to construct the 1,3,5-tri(1-azulenyl)benzene core. According to our expectation, the trimerization of methyl 3-acetyl-7-isopropylazulene-1-carboxylate (**1**) using excess thionyl chloride ( $\text{SOCl}_2$ ) in ethanol at room temperature was achieved to afford 1,3,5-tris(5-isopropyl-3-methoxycarbonyl-1-azulenyl)benzene (**2**) in 56% yield (Scheme 1). Thus, the synthesis of **4** was established by the removable of the three ester functions of **2** by heating in 100%  $\text{H}_3\text{PO}_4$ , followed by the iodation of **3** with *N*-iodosuccinimide (NIS) at 0 °C in excellent yield (90% yield by 2 steps). The low temperature reaction is essential for the successful iodation of **3**, since the room temperature reaction of **3** with NIS caused decomposition instead of the formation of **4**.



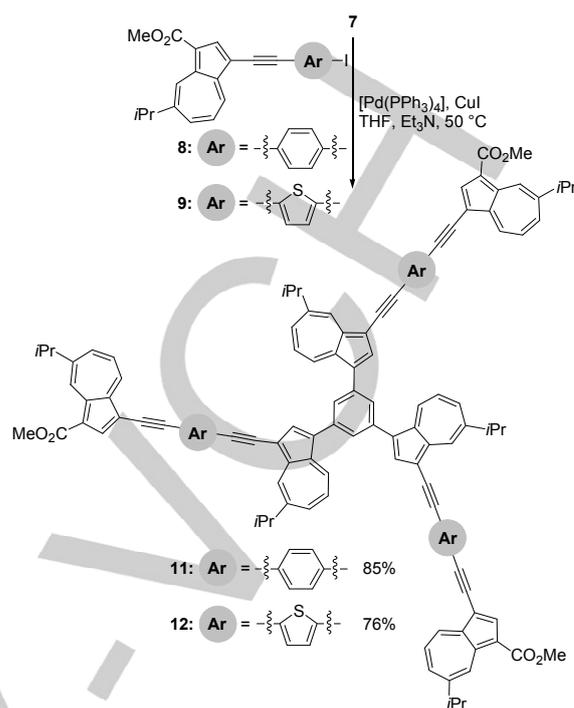
**Scheme 1.** Synthesis of 1,3,5-tri(1-azulenyl)benzene derivatives **2**, **3**, and **4**.

Preparation of tris[1-azulenylacetylene and 1-azulenylethynylarylacetylenes] connected with 1,3,5-tri(1-azulenyl)benzene core **10–12** for the precursors of the novel  $C_3$  symmetrical molecules with multiple 1-AzTCBD units was accomplished by a simple one-pot reaction involving repeated Pd-catalyzed alkylation of the corresponding 1-ethynylazulene derivative **5** with **4**, or **7** with methyl 3-[(4-iodophenyl)ethynyl]-7-isopropylazulene-1-carboxylate (**8**)<sup>[14]</sup> and methyl 3-[(5-iodo-2-thienyl)ethynyl]-7-isopropylazulene-1-carboxylate (**9**)<sup>[14]</sup> under the Sonogashira–Hagihara cross-coupling conditions.<sup>[15]</sup> The cross-coupling reaction of **4** with **5** using  $[\text{Pd}(\text{PPh}_3)_4]$  as a catalyst and subsequent chromatographic purification of the reaction mixture on silica gel afforded the desired product **10** in 84% yield. Reaction of **4** with trimethylsilylacetylene in the presence of  $[\text{Pd}(\text{PPh}_3)_4]$  as a catalyst at 50 °C gave alkyne derivative **6** in 94% yield. Although the compound **5** was easily preparable by desilylation of the corresponding trimethylsilylacetylene derivative using  $\text{K}_2\text{CO}_3$  in methanol, desilylation of trialkyne **6** did not proceed under the similar conditions probably due to the solubility problem in methanol. Thus, the desilylation of compound **6** was established by heating with KOH in *i*PrOH under reflux temperature to afford **7** in 92% yield (Scheme 2).



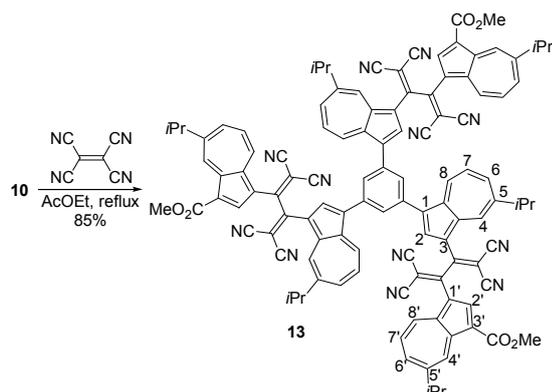
**Scheme 2.** Synthesis of 1,3,5-tris(3-ethynyl-1-azulenyl)benzene derivatives **6**, **7**, and **10**.

Preparation of **11** and **12** was also established by a simple one-pot reaction involving repeated Pd-catalyzed alkylation of alkyne **7** with iodoarenes **8** and **9** under the Sonogashira–Hagihara cross-coupling conditions. The cross-coupling reaction of **7** with **8** using  $[Pd(PPh_3)_4]$  as a catalyst and subsequent chromatographic purification afforded the desired product **11** in 85% yield. Likewise, the cross-coupling reaction of **7** with **9** in the presence of the Pd catalyst afforded the corresponding product **12** in 76% yield (Scheme 3). Compounds **10–12** possess fair solubility in common solvent, e.g., chloroform, dichloromethane, and so on. Moreover, they are stable and show no decomposition even after several weeks at room temperature. Thus, these alkyne derivatives were utilized in further transformations for the synthesis of the novel TCBD chromophores owing to their considerable stability and solubility.

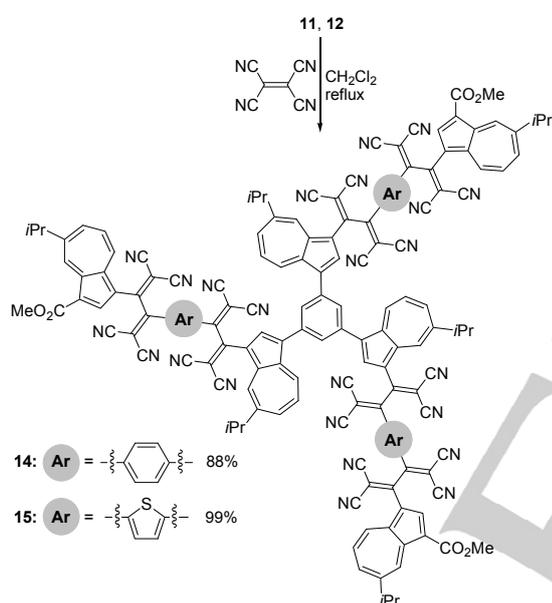


**Scheme 3.** Synthesis of tris(1-azulenylethynyl)arylacetylene)s connected with 1,3,5-tri(1-azulenyl)benzene core **11** and **12**.

The formal [2 + 2] CA–RE reaction of the compounds **10–12** with TCNE was examined according to the procedure described in the literatures<sup>[3, 4, 10, 11]</sup> to obtain the novel tris[(1-AzTCBD) and (1-AzBisTCBD)] chromophores. The reaction of **10** with TCNE yielded the tris(1-AzTCBD) **13** in 85% yield as a sole product (Scheme 4). Similar to the results on **10**, the reaction of **11** with excess TCNE afforded tris(1-AzBisTCBD) **14** in 88% yield (Scheme 5). The [2 + 2] CA–RE of **12** with thiophenediyl spacers with excess TCNE also gave the corresponding tris(1-AzBisTCBD) **15** in 99% yield (Scheme 5). These results imply the reactivity of both inner and outer alkyne moieties in **11** and **12** was not affected by the electron-withdrawing TCBD group introduced by the first addition of TCNE to one of the alkynes in each 1-AzBisTCBD units, since the compounds **11** and **12** were completely converted to tris(1-AzBisTCBD)s **14** and **15**. These novel 1-AzTCBDs **13–15** were obtained as stable reddish crystals and could be stored in the crystalline state under ordinary conditions.



**Scheme 4.** The formal [2 + 2] CA-RE reaction of **10** with TCNE.

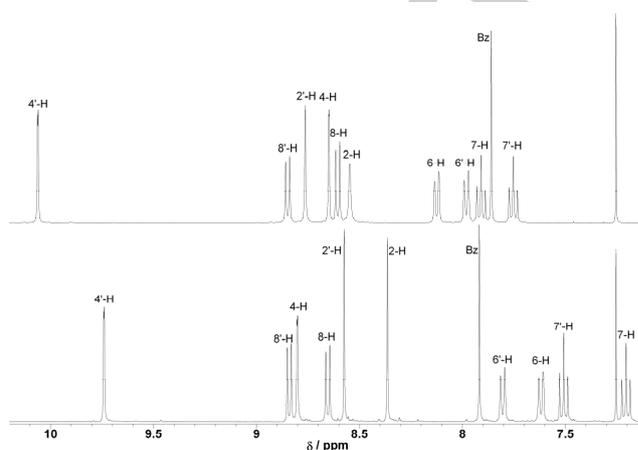


**Scheme 5.** The formal [2 + 2] CA-RE reaction of **11** and **12** with TCNE.

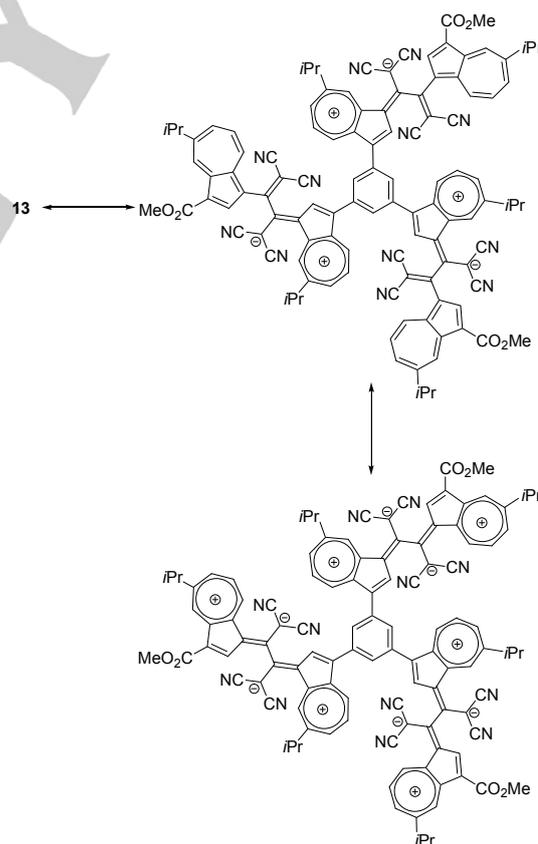
**Spectroscopic properties:** These new compounds were fully characterized on the basis of their spectral data, as summarized in the Experimental Section. The NMR spectroscopic assignment of the reported compounds was confirmed by COSY, HMQC, and HMBC experiments. The HRMS of new compounds ionized by ESI, MALDI, or FAB showed the expected molecular ion peaks. The characteristic stretching vibration band of the C≡N moieties of 1-AzTCBDs **13**–**15** was observed at 2216–2219  $\text{cm}^{-1}$  on each IR spectrum. These results are consistent with the given structure of these products.

$^1\text{H}$  NMR spectra of alkyne **10** and the corresponding tris(1-AzTCBD) **13** are shown in Figure 1. The  $^1\text{H}$  NMR spectra of these compounds was reflected by their  $\text{C}_3$  symmetrical structures. The downfield shift of protons of the both azulene moieties in **13** was observed in  $\text{CDCl}_3$ , relative to those of alkyne **10**, due to the strong electron-withdrawing nature of the TCBD units. A downfield shift of **13** should be ascribed to the tropylium structure caused by resonance effect between the TCBD and two azulenyl groups as illustrated in Scheme 6. Little spectral

shift in 8,8'-H and upfield shift in 4-H and Bz protons of **13** is attributed to the anisotropic effect of the adjacent cyano groups.<sup>[16]</sup>

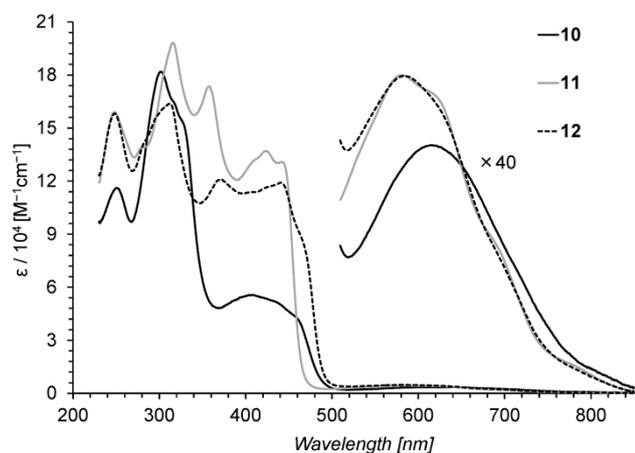


**Figure 1.**  $^1\text{H}$  NMR spectra of **10** (bottom) and **13** (top) with their numbering scheme in  $\text{CDCl}_3$  at 500 MHz; Numbering of protons was shown in Scheme 2 and 4, respectively.



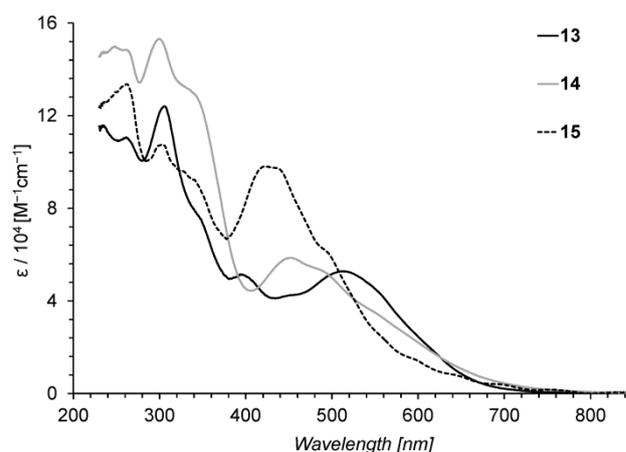
**Scheme 6.** Plausible resonance structure for tris(1-AzTCBD) **13**.

UV/Vis spectra of alkynes **10–12** and 1-AzTCBDs **13–15** are shown in Figures 2 and 3. Alkynes **10–12** showed characteristic weak absorption bands arising from the azulene system on the UV/Vis spectra in the visible region. Extinction coefficients were found to increase with the number of substituted azulene rings, and absorption bands in the visible region of **10** ( $\lambda_{\max} = 615$  nm) showed bathochromic shift compared with those of **11** ( $\lambda_{\max} = 581$  nm) and **12** ( $\lambda_{\max} = 585$  nm), clearly. These results suggest that the alkyne moieties in **10** allow effective  $\pi$ -conjugation between azulene moieties rather than those through phenylethynyl and 2-thienylethynyl groups in **11** and **12**.

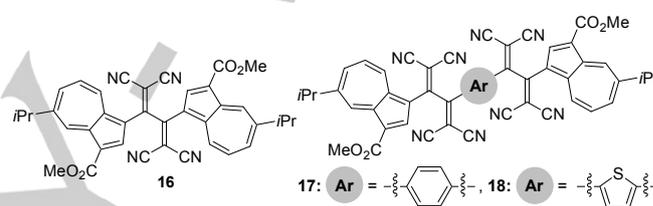


**Figure 2.** UV/Vis spectra of **10** (black line), **11** (gray line), and **12** (broken line) in  $\text{CH}_2\text{Cl}_2$ .

Tris(1-AzTCBD) **13** exhibited a broad absorption band at  $\lambda_{\max} = 512$  nm. Likewise, tris(1-AzBisTCBD) **14** constructed by *p*-phenylene spacers also displayed a broad and strong CT absorption band at  $\lambda_{\max} = 452$  nm. Tris(1-AzBisTCBD) **15** possessed 2,5-thiophenediyl spacers showed a strong and broad absorption band at around  $\lambda_{\max} = 430$  nm, which beyond to 750 nm. Not only the absorption maxima but also the overall shapes for the spectrum of **13–15** were quite similar to those of the much simpler 1-AzTCBD derivatives **16** ( $\lambda_{\max} = 508$  nm), **17** ( $\lambda_{\max} = 444$  nm), and **18** ( $\lambda_{\max} = 434$  nm), although the extinction coefficients show an increasing trend as the number of 1-AzTCBD units substituted (Figure 3). These results suggest that the  $\pi$ -conjugation is less effective by the extension attributable to the 1,3,5-arrangement of the central benzene spacer.



**Figure 3.** UV/Vis spectra of **13** (black line), **14** (gray line), and **15** (broken line) in  $\text{CH}_2\text{Cl}_2$ .



**Figure 4.** Structures of much simpler 1-AzTCBD derivatives previously reported.<sup>[10]</sup>

**Electrochemistry:** To clarify the electrochemical properties, the redox behavior of alkynes **10–12** and 1-AzTCBDs **13–15** was examined by CV and DPV.<sup>[17]</sup> The redox potentials (in volts vs.  $\text{Ag}/\text{AgNO}_3$ ) of these compounds measured under a scan rate of  $100 \text{ mVs}^{-1}$  are summarized in Table 1. The reduction waves of alkynes **10–12** measured by CV and DPV are summarized in the Supporting Information.

**Table 1.** Redox potentials<sup>[a, b]</sup> of alkynes **10–12**, 1-AzTCBDs **13–15**, and **16–18** for the comparison.

Sample	method	$E_1^{\text{red}}$ [V]	$E_2^{\text{red}}$ [V]	$E_3^{\text{red}}$ [V]	$E_4^{\text{red}}$ [V]	$E_1^{\text{ox}}$ [V]
<b>10</b>	(DPV)	(−1.58)	(−1.88)			(+0.30)
<b>11</b>	(DPV)	(−1.55)	(−1.73)			(+0.46)
<b>12</b>	(DPV)	(−1.53)	(−1.73)			(+0.44)
<b>13</b>	CV	−0.77	−1.14			
	(DPV)	(−0.75)	(−1.12)			(+1.00)
<b>14</b>	CV	−0.48	−0.69	−1.05	−1.15	(+1.00)
	(DPV)	(−0.46)	(−0.67)	(−1.03)	(−1.13)	(+1.00)
<b>15</b>	CV	−0.33	−0.58	−1.16	(2e)	(+1.01)

	(DPV)	(-0.31)	(-0.56)	(-1.14, 2e)		
<b>16</b> <sup>[10]</sup>	CV	-0.64	-1.04			
	(DPV)	(-0.62)	(-1.02)		(+1.27)	
<b>17</b> <sup>[10]</sup>	CV	-0.46	-0.64	-1.01	-1.11	
	(DPV)	(-0.45)	(-0.63)	(-1.00)	(-1.09)	(+1.32)
<b>18</b> <sup>[10]</sup>	CV	-0.31	-0.54	-1.10 (2e)		
	(DPV)	(-0.29)	(-0.52)	(-1.09, 2e)	(+1.32)	

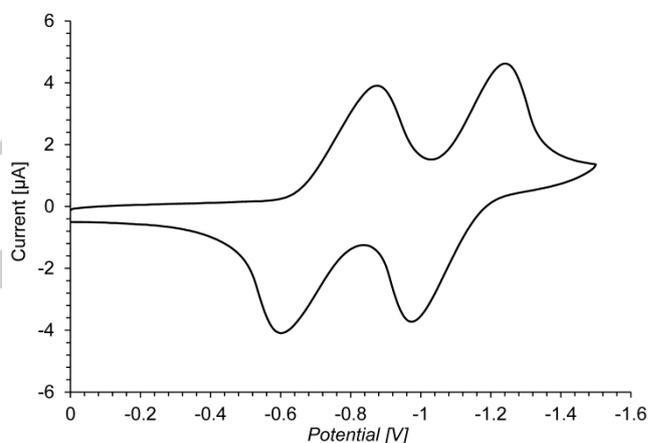
[a] V vs. Ag/AgNO<sub>3</sub>, 1 mM in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs<sup>-1</sup> and internal reference (Fc/Fc<sup>+</sup> = +0.15 V). In the cases of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses. [b] Half-wave potential  $E^{red} = (E_{pc} + E_{pa})/2$  on CV,  $E_{pc}$  and  $E_{pa}$  correspond to the cathodic and anodic peak potentials, respectively.

Reduction waves of all alkynes **10–12** were irreversible on CV (see the Supporting Information). These results suggest the generation of unstable anionic species of **10–12** under the electrochemical reduction conditions. Moreover, the electrochemical oxidation of compounds **10–15** exhibited voltammograms that were characterized by irreversible waves, probably due to the oxidation of the azulene rings (see Supporting Information).

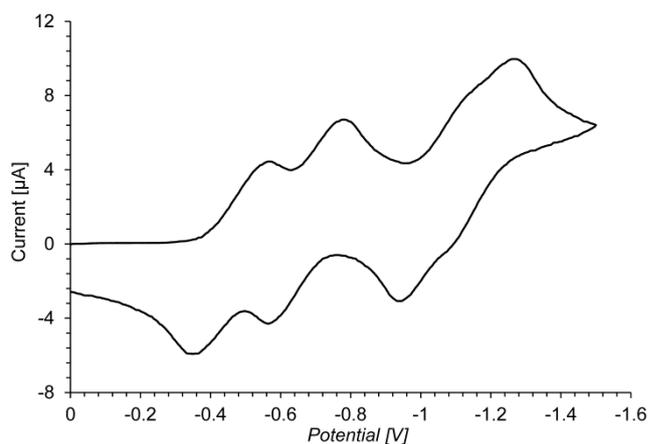
In contrast, electrochemical reduction of tris(1-AzTCBD) **13** showed quasi-reversible reduction waves at -0.77 V and -1.14 V on CV (Figure 5). A quasi-reversible four-stage wave was observed by CV in the tris(1-AzBisTCBD) **14** at -0.48 V, -0.69 V, -1.05 V, and -1.15 V (Figure 6). These results are reflected in the stepwise generation of multi-charged anionic species by the electrochemical reduction. A reversible three-step redox wave was observed on the electrochemical reduction of tris(1-AzBisTCBD) **15** constructed by 2,5-thiophenediyl spacers, in which the third reduction wave should be concluded to be multi-electron transfer in one step to form a hexaanionic species. The reversible three-step reduction wave of tris(1-AzBisTCBD) **15** were observed at -0.33 V, -0.58 V, and -1.16 V on CV (Figure 7).

Recently, we have reported the redox potentials of a series of TCBD derivatives.<sup>[10, 11, 12, 14]</sup> The study revealed the first reduction potentials of the 1-AzTCBDs substituted by  $\pi$ -electron cores are decreased by increasing the number of substituted TCBD units. With respect to the number of stages for the reduction, Diederich et al. reported that the compound with three DAA-substituted TCBD units connected by a 1,3,5-benzenetriyl spacer shows a six-stage reversible reduction wave within a narrow potential range.<sup>[18]</sup> We have also reported the reduction of tris(1-AzTCBD) possessing a 1,3,5-benzenetriyl core exhibited a reversible five-stage reduction wave on CV.<sup>[10]</sup> On the other hand, electrochemical reduction of 1-AzTCBDs **13–15** displayed only reversible two, four, and three waves, respectively, on CV arising from the reduction of the TCBD units,

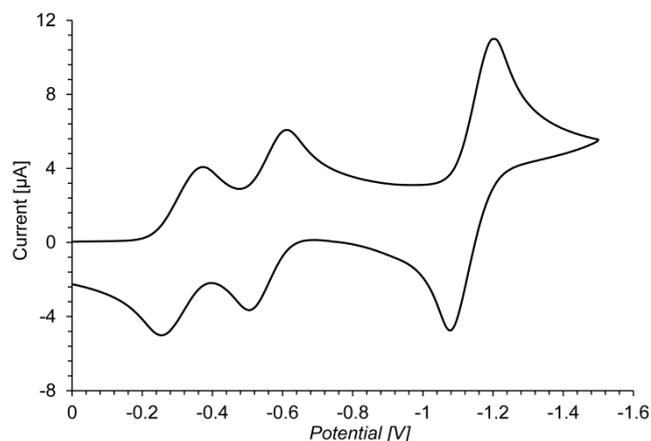
although the multiple TCBD units were existed in the molecules. These results should indicate that the three 1-AzTCBD and 1-AzBisTCBD units in **13–15** reduced independently in each steps under the electrochemical reduction conditions. Moreover, tris(1-AzTCBD) **13** and tris(1-AzBisTCBD)s **14** and **15** exhibited similar reduction potentials compared with those of the corresponding 1-AzTCBD chromophores **16–18** (Table 1). Therefore, the redox interaction among the three 1-AzTCBD and 1-AzBisTCBD units through the central 1,3,5-benzenetriyl spacer could be concluded to be almost negligible in the electrochemical reduction. Thus, the reversible two-stage reduction of tris(1-AzTCBD) **13** should come from the three-electron transfer in each stage to form hexaanionic species and tris(1-AzTCBD)s **14** and **15** show reversible twelve-electron reduction by four- and three-stages to generate stabilized dodecaanionic species by CV.



**Figure 5.** Cyclic voltammogram of **13** (1 mM) in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M) as a supporting electrolyte; scan rate = 100 mVs<sup>-1</sup>.



**Figure 6.** Cyclic voltammogram of **14** (1 mM) in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M) as a supporting electrolyte; scan rate = 100 mVs<sup>-1</sup>.

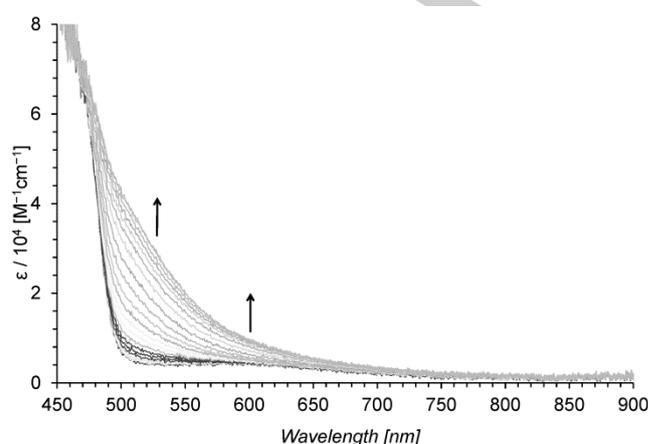


**Figure 7.** Cyclic voltammogram of **15** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate =  $100 \text{ mVs}^{-1}$ .

Electrochromism is observed in reversible redox systems that exhibit significant color changes in different oxidation states. Stabilization of the redox cycle is very important for the construction of electrochromic materials, because the molecules used for this application requires high redox stabilities.<sup>[19]</sup> Recently, we have developed various redox-active chromophores with the aim of creating stabilized electrochromic materials.<sup>[20]</sup> As a part of the study, we have reported several TCBD derivatives bearing azulenyl,<sup>[10, 11, 12, 14]</sup> ferrocenyl,<sup>[21]</sup> and 2-oxo-2H-cyclohepta[b]-3-furyl<sup>[22]</sup> substituents, in which we have identified some novel hybrid structures of violene and cyanine with redox activities.<sup>[23]</sup> Similar with the TCBD derivatives described in the literatures, these new 1-AzTCBDs connected with 1,3,5-tri(1-azulenyl)benzene core should exhibit a reversible color change under the electrochemical reaction conditions, because these compounds showed high reversibility on the redox waves by CV. Thus, the spectral changes of alkynes **10–12** and 1-AzTCBDs **13–15** in the visible region were monitored to identify their color changes that are caused during the electrochemical reactions.

Constant-current reduction and oxidation ( $100 \mu\text{A}$ ) was applied to the solutions of **10–15** with a platinum mesh as the working electrode and a wire counter electrode in an electrolytic cell of 1 mm thickness.<sup>[24]</sup> Visible spectra were measured in degassed benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte at room temperature under electrochemical reaction conditions. Alkynes **10–12** showed a color change under the electrochemical redox conditions, although the reverse oxidation of the reduced solution did not recover the original spectra of the compounds. These results should be attributable to the instability of anionic species of **10–12** as suggested by the irreversible CV waves. As an example, electrochemical reduction of **12** gradually developed an absorption band at around 500–600 nm along with a color change of the solution from green to orange during the electrochemical reduction. Although reverse oxidation of the

orange-colored solution regenerated the parent green color, but spectrum of **12** did not recover, completely (Figure 8).



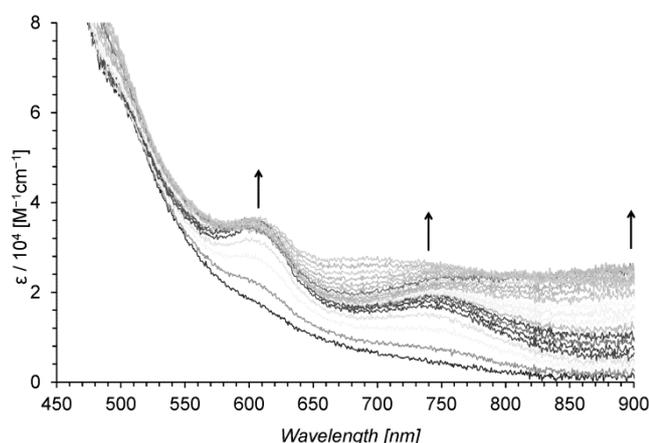
**Figure 8.** Continuous change in the UV/Vis spectrum of **12**: constant-current electrochemical reduction ( $100 \mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 s intervals.

The longest absorption band of tris(1-AzTCBD) **13** at around 520 nm gradually decreased along with a development of the new absorption band at around 650 nm, which beyond to the near infrared region. The color of the solution gradually changed from purple to yellow during the electrochemical reduction. Reverse oxidation of the yellow-colored solution did not regenerate the original spectrum of **13**, although good reversibility was observed in the two-step reduction on CV. The poor reversibility of the color changes might be attributable to the instability of the presumed hexaanionic species, due to the destabilization by the two electron-donating 1-azulenyl groups on the either side of the TCBD moieties. The longest absorption bands of the tris(1-AzBisTCBD) **14** gradually increased and the color of the solution changed from red to yellow during the electrochemical reduction, but reversible oxidation of the yellow-colored solution also did not regenerate the spectrum of the corresponding starting compound.

The reversible color changes were observed in tris(1-AzBisTCBD) with 2,5-thiophenediyl spacers **15** (Figure 9). At the beginning, new absorption bands in the visible region at  $\lambda_{\text{max}} = 600 \text{ nm}$  and  $\lambda_{\text{max}} = 750 \text{ nm}$  gradually developed and the red color of the solution changed to pale blue during the electrochemical reduction. On further reduction, the new bands in the visible region gradually decreased, accompanied by the development of a new absorption band in the near infrared region. On reverse oxidation, the new absorption bands in the near infrared region decreased and the original absorption bands of **15** in the visible region was regenerated. The two-step color change should correspond to the formation of a closed-shell hexaanionic species via a trianionic species in two steps as observed by CV. The absorption up to the near infrared region suggests the formation of the stabilized hexaanionic species

with thienoquinoid structures in the two-stage electron reduction.<sup>[20, 23, 25]</sup>

We examined the color change of **10–15** under electrochemical oxidation conditions owing to the generation of cationic species. However, reversibility was not observed in the electrochromic study of **10–15** under the conditions of the spectral measurements. These results might indicate the instability of cationic species generated by electrochemical oxidation reaction.



**Figure 9.** Continuous change in the UV/Vis spectrum of **15**: constant-current electrochemical reduction (100  $\mu$ A) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 s intervals.

## Conclusions

Tris(1-azulenyl)benzene derivatives bearing 3,3',3''-tris(1-azulenylethynyl), 3,3',3''-tris[(1-azulenylethynyl)phenylethynyl] and (1-azulenylethynyl)thienylethynyl groups **10–12** were prepared by Sonogashira–Hagihara cross-coupling reaction. Tris(1-AzTCBD) and tris(1-AzBisTCBD) chromophores **13–15** were synthesized in a one-step procedure consisting of formal [2 + 2] cycloaddition–retroelectrocyclization reaction of **10–12** with TCNE. Strong intramolecular CT absorption bands were observed in the UV/Vis spectra of these 1-AzTCBDs **13–15**. An analysis by CV and DPV showed that compounds **13–15** exhibit a reversible multi-stage reduction, although the alkynes **10–12** did not display reversibility on the redox wave. Moreover, significant color changes of these compounds were observed during the electrochemical reduction. In particular, tris(1-AzBisTCBD) with 2,5-thiophenediyl spacers **15** exhibited significant two-stage color changes, which might be arising from the generation of thienoquinoid substructures during the electrochemical reduction.

To evaluate the scope of this class of molecules investigated by this research, the preparation of novel donor–acceptor chromophores connected with various  $\pi$ -electron systems is now in progress in our laboratory.

## Experimental Section

### General

Melting points were determined with a Yanagimoto MPS3 micromelting apparatus and are uncorrected. HRMS were obtained with a Bruker Daltonics APEX III instrument. IR and UV/Vis spectra were measured with JASCO FT/IR-4100 and Shimadzu UV-2550 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a JEOL ECA500 at 500 MHz and 125 MHz, respectively. Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from  $\text{Ag}/\text{AgNO}_3$  (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M).

**1,3,5-Tris(5-isopropyl-3-methoxycarbonyl-1-azulenyl)benzene (2):** To a solution of **1** (1.09 g, 4.03 mmol) in EtOH (40 mL) was added thionyl chloride (2 mL). After the resulting mixture was stirred at room temperature for 24 h, the reaction mixture was poured into water and extracted with ethyl acetate. The crude product was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  as an eluent to afford **2** (568 mg, 56%) as green crystals. M.p. 237.0–239.0 °C (MeOH); IR (ATR)  $\nu_{\text{max}}$  = 2959 (w), 1691 (s), 1587 (w), 1508 (w), 1455 (m), 1418 (m), 1380 (w), 1359 (w), 1234 (w), 1208 (s), 1166 (m), 1129 (m), 1044 (m), 921 (w), 876 (w), 863 (w), 825 (w), 804 (w), 772 (m), 725 (w), 704 (w), 688 (w), 676 (w), 659 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 249 (4.85), 299 (5.05), 307 sh (5.04), 387 (4.51), 564 (3.25), 606 sh (3.18), 680 sh (2.60) nm;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 9.83 (d, 3H,  $J$  = 1.5 Hz, 4-H), 8.73 (d, 3H,  $J$  = 9.5 Hz, 8-H), 8.58 (s, 3H, 2-H), 7.82 (s, 3H, 2,4,6-H of Bz), 7.76 (d, 3H,  $J$  = 10.0 Hz, 6-H), 7.40 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7-H), 3.98 (s, 9H,  $\text{CO}_2\text{Me}$ ), 3.25 (sept, 3H,  $J$  = 6.5 Hz, *i*Pr), 1.44 (d, 18H,  $J$  = 6.5 Hz, *i*Pr) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 165.93 ( $\text{CO}_2\text{Me}$ ), 149.17 (C-6), 141.86 (C-8a), 140.16 (C-2), 140.09 (C-3a), 138.80 (C-6), 138.14 (C-4), 137.52 (C-1,3,5 of Bz), 135.37 (C-8), 129.27 (C-1), 129.06 (C-2,4,6 of Bz), 127.07 (C-7), 114.56 (C-3), 51.11 ( $\text{CO}_2\text{Me}$ ), 39.10 (*i*Pr), 24.67 (*i*Pr) ppm; HRMS (FAB, positive): calcd for  $\text{C}_{51}\text{H}_{48}\text{O}_6$   $[\text{M}]^+$  756.3446; found: 756.3445.

**1,3,5-Tris(5-isopropyl-1-azulenyl)benzene (3):** A solution of **2** (460 mg, 0.61 mmol) in 100%  $\text{H}_3\text{PO}_4$  (30 mL) was stirred at 120 °C for 20 min. After the reaction mixture was cooled, the reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The crude product was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  as an eluent to afford **3** (347 mg, 98%) as green crystals. M.p. 162.0–165.0 °C (MeOH/ $\text{H}_2\text{O}$ ); IR (ATR)  $\nu_{\text{max}}$  = 2958 (m), 2925 (w), 2866 (w), 1573 (s), 1507 (w), 1461 (m), 1362 (w), 1313 (w), 1264 (w), 1116 (w), 1065 (w), 1023 (m), 1000 (m), 919 (m), 877 (m), 862 (w), 799 (w), 768 (s), 716 (m), 678 (w), 663 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 253 (4.96), 272 (4.84), 308 (4.94), 383 (4.57), 618 (3.18), 670 sh (3.12), 753 sh (2.69) nm;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 8.68 (d, 3H,  $J$  = 10.0 Hz, 8-H), 8.36 (d, 3H,  $J$  = 1.5 Hz, 4-H), 8.14 (d, 3H,  $J$  = 4.0 Hz, 2-H), 7.87 (s, 3H, 2,4,6-H of Bz), 7.54 (dd, 3H,  $J$  = 10.0, 1.5 Hz, 6-H), 7.41 (d, 3H,  $J$  = 4.0 Hz, 3-H), 7.11 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7-H), 3.10 (sept, 3H,  $J$  = 6.5 Hz, *i*Pr), 1.39 (d, 18H,  $J$  = 6.5 Hz, *i*Pr) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 143.17 (C-5), 141.81 (C-8a), 138.26 (C-3a), 137.23 (C-2), 137.08 (C-4), 137.00 (C-6), 134.71 (C-1,3,5 of Bz), 134.29 (C-8), 130.30 (C-1), 128.59 (C-2,4,6 of Bz), 123.11 (C-7), 116.70 (C-3), 38.41 (*i*Pr), 24.50 (*i*Pr) ppm; HRMS (FAB, positive): calcd for  $\text{C}_{45}\text{H}_{42}$   $[\text{M}]^+$  582.3278; found: 582.3290.

**1,3,5-Tris(3-iodo-5-isopropyl-1-azulenyl)benzene (4):** To a solution of **3** (569 mg, 1.01 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) was added *N*-iodosuccinimide (818 mg, 3.63 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 1 h under an Ar atmosphere. After the

solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  to give **4** (944 mg, 97%) as green crystals. M.p. 172.0–174.0 °C (MeOH); IR (ATR)  $\nu_{\text{max}}$  = 2958 (m), 2924 (w), 2865 (w), 1573 (s), 1501 (w), 1460 (m), 1392 (s), 1363 (s), 1325 (w), 1291 (w), 1162 (w), 1116 (w), 1040 (m), 921 (m), 859 (s), 818 (m), 792 (s), 745 (w), 733 (w), 716 (m), 695 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 240 (4.79), 304 (4.93), 375 (4.54), 560 sh (2.97), 606 (3.09), 662 sh (3.01), 740 sh (2.54) nm;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 8.60 (d, 3H,  $J$  = 10.0 Hz, 8-H), 8.36 (d, 3H,  $J$  = 1.5 Hz, 4-H), 8.25 (s, 3H, 2-H), 7.83 (s, 3H, 2,4,6-H of Bz), 7.63 (d, 3H,  $J$  = 10.0 Hz, 6-H), 7.19 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7-H), 3.19 (sept, 3H,  $J$  = 6.5 Hz, *i*Pr), 1.46 (d, 18H,  $J$  = 6.5 Hz, *i*Pr) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 144.46 (C-5), 143.42 (C-2), 140.08 (C-8a), 139.39 (C-4), 138.11 (C-6), 137.25 (C-1,3,5 of Bz), 135.89 (C-3a), 133.83 (C-8), 131.14 (C-1), 128.72 (C-2,4,6 of Bz), 124.38 (C-7), 73.94 (C-3), 38.57 (*i*Pr), 24.64 (*i*Pr) ppm; HRMS (FAB, positive): calcd for  $\text{C}_{45}\text{H}_{39}\text{Si}^+$  [M] $^+$  960.0181; found: 960.0182.

### 1,3,5-Tris(5-isopropyl-3-trimethylsilylethynyl-1-azulenyl)benzene (6):

To a solution of trimethylsilylacetylene (250 mg, 2.55 mmol), **4** (561 mg, 0.58 mmol), and CuI (33 mg, 0.17 mmol) in triethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (50 mg, 0.043 mmol). The resulting mixture was stirred at 50 °C for 3 h under an Ar atmosphere. The reaction mixture was poured into a saturated  $\text{NH}_4\text{Cl}$  solution and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried with  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  to give **6** (479 mg, 94%) as green crystals. M.p. 181.0–183.0 °C ( $\text{CHCl}_3/\text{MeOH}$ ); IR (ATR):  $\nu_{\text{max}}$  = 2959 (m), 2134 (m), 1574 (m), 1541 (w), 1508 (w), 1460 (m), 1394 (m), 1362 (w), 1248 (m), 1161 (w), 1107 (w), 1046 (w), 920 (m), 842 (s), 795 (m), 759 (m), 712 (m), 697 (m), 663 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 256 (4.87), 306 (4.93), 387 (4.46), 463 sh (3.29), 575 sh (2.97), 625 (3.10), 675 sh (3.03), 765 sh (2.49) nm;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 8.61 (d, 3H,  $J$  = 1.7 Hz, 4-H), 8.57 (d, 3H,  $J$  = 10.0 Hz, 8-H), 8.18 (s, 3H, 2-H), 7.76 (s, 3H, 2,4,6-H of Bz), 7.60 (d, 3H,  $J$  = 10.0 Hz, 6-H), 7.18 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7-H), 3.14 (sept, 3H,  $J$  = 6.9 Hz, *i*Pr), 1.42 (d, 18H,  $J$  = 6.9 Hz, *i*Pr), 0.36 (s, 27H, TMS) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 144.92 (C-5), 143.17 (C-8a), 139.25 (C-2), 138.57 (C-6), 137.47 (C-3a), 136.54 (C-4), 136.40 (C-3), 134.76 (C-8), 129.25 (C-1,3,5 of Bz), 128.67 (C-2,4,6 of Bz), 125.15 (C-7), 108.89 (C-1), 101.53 (C $\equiv$ C), 99.08 (C $\equiv$ C), 38.48 (*i*Pr), 24.58 (*i*Pr), 0.41 (TMS) ppm; HRMS (FAB, positive): calcd for  $\text{C}_{60}\text{H}_{66}\text{Si}_3 + \text{H}^+$  [M + H] $^+$  871.4546; found: 871.4539.

### 1,3,5-Tris(5-isopropyl-3-trimethylsilylethynyl-1-azulenyl)benzene (7):

To a solution of **6** (128 mg, 0.147 mmol) in *i*PrOH (10 mL) was added KOH (108 mg, 1.92 mmol). The resulting mixture was refluxed for 1 h. The reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on alumina with  $\text{CH}_2\text{Cl}_2$  to give **7** (88 mg, 92%) as green crystals. M.p. > 300 °C; ( $\text{CH}_2\text{Cl}_2/n$ -hexane); IR (KBr):  $\nu_{\text{max}}$  = 2959 (m), 2927 (w), 2092 (w), 1575 (s), 1508 (w), 1461 (m), 1417 (s), 1388 (w), 1362 (w), 1339 (m), 1305 (w), 1263 (w), 1162 (w), 1119 (w), 1108 (w), 1074 (w), 1048 (w), 1018 (w), 951 (w), 908 (s), 867 (s), 844 (w), 796 (s), 732 (s), 701 (w), 669 (s), 653 (s)  $\text{cm}^{-1}$ ; UV-Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 254 (4.81), 308 (4.83), 394 (4.38), 570 sh (2.93), 617 (3.03), 673 sh (2.94), 760 sh (2.40) nm;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 8.62 (d, 3H,  $J$  = 1.5 Hz, 4-H), 8.60 (d, 3H,  $J$  = 10.0 Hz, 8-H), 8.20 (s, 3H, 2-H), 8.02 (s, 3H, Bz), 7.62 (dd, 3H,  $J$  = 10.0, 1.5 Hz, 6-H), 7.21 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7-H), 3.56 (s, 3H, C=CH), 3.17 (sept, 3H,  $J$  = 6.5 Hz, *i*Pr), 1.41 (d, 18H,  $J$  = 6.5 Hz, *i*Pr) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 145.12 (C-5), 142.96 (C-3a), 139.73 (C-2), 138.33 (C-6), 137.48 (1,3,5-C of Bz), 136.75 (C-4), 136.32 (C-8a), 134.89 (C-8), 129.21 (C-3), 128.82 (2,4,6-C of Bz), 125.21 (C-7), 107.76 (C-1), 81.71 (C $\equiv$ C), 80.15 (C $\equiv$ C), 38.51 (*i*Pr),

24.58 (*i*Pr) ppm; HRMS (FAB, positive): calcd for  $\text{C}_{51}\text{H}_{42} + \text{H}^+$  [M + H] $^+$  655.3360; found: 655.3372.

### 1,3,5-Tris[5-isopropyl-3-(5'-isopropyl-3'-methoxycarbonyl-1'-azulenylethynyl)-1-azulenyl]benzene (10):

To a solution of **5** (455 mg, 1.80 mmol), **4** (385 mg, 0.40 mmol), and CuI (29 mg, 0.15 mmol) in triethylamine (5 mL) and THF (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (70 mg, 0.061 mmol). The resulting mixture was stirred at 50 °C for 19 h under an Ar atmosphere. The reaction mixture was poured into a saturated  $\text{NH}_4\text{Cl}$  solution and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried with  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  to give **10** (451 mg, 84%) as dark green crystals. M.p. 185.0–186.0 °C ( $\text{CH}_2\text{Cl}_2/\text{hexane}$ ); IR (ATR):  $\nu_{\text{max}}$  = 2958 (w), 1694 (m), 1574 (m), 1506 (w), 1443 (m), 1416 (m), 1404 (m), 1377 (m), 1335 (w), 1307 (w), 1263 (w), 1211 (s), 1167 (m), 1126 (w), 1072 (w), 1046 (w), 1017 (w), 985 (w), 956 (w), 921 (w), 905 (w), 881 (w), 863 (m), 799 (m), 774 (m), 733 (w), 722 (w), 699 (w), 666 (m), 653 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 251 (5.06), 302 (5.26), 315 sh (5.22), 327 sh (5.19), 409 (4.74), 433 sh (4.72), 460 (4.63), 615 (3.55) nm;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 9.74 (d, 3H,  $J$  = 1.5 Hz, 4'-H), 8.82 (d, 3H,  $J$  = 10.0 Hz, 8'-H), 8.82 (d, 3H,  $J$  = 1.5 Hz, 4-H), 8.65 (d, 3H,  $J$  = 10.0 Hz, 8-H), 8.57 (s, 3H, 2'-H), 8.36 (s, 3H, 2-H), 7.92 (s, 3H, 2,4,6-H of Bz), 7.80 (dd, 3H,  $J$  = 10.0, 1.5 Hz, 6'-H), 7.62 (dd, 3H,  $J$  = 10.0, 1.5 Hz, 6-H), 7.51 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7'-H), 7.21 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7-H), 3.99 (s, 9H,  $\text{CO}_2\text{Me}$ ), 3.17 (m, 6H, *i*Pr), 1.46 (d, 18H,  $J$  = 7.0 Hz, *i*Pr), 1.44 (d, 18H,  $J$  = 7.0 Hz, *i*Pr) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 165.56 ( $\text{CO}_2\text{Me}$ ), 150.20 (C-5'), 144.56 (C-5 or C-3a'), 144.47 (C-5 or C-3a'), 142.27 (C-8a), 142.04 (C-2'), 141.19 (C-8a'), 139.20 (C-2), 139.02 (C-6'), 138.60 (C-6), 138.17 (C-4'), 137.61 (C-1,3,5 of Bz), 136.71 (C-4 or C-3a), 136.55 (C-4 or C-3a), 136.29 (C-8'), 134.87 (C-8), 129.77 (C-1), 128.84 (C-2,4,6 of Bz), 127.11 (C-7'), 124.97 (C-7), 115.00 (C-3'), 110.41 (C-1'), 109.84 (C-3), 89.93 (C $\equiv$ C), 89.49 (C $\equiv$ C), 51.19 ( $\text{CO}_2\text{Me}$ ), 39.25 (*i*Pr), 38.54 (*i*Pr), 24.65 (*i*Pr), 24.63 (*i*Pr) ppm; HRMS (MALDI-TOF): calcd for  $\text{C}_{96}\text{H}_{84}\text{O}_6 + \text{M}^+$  1332.6263; found: 1332.6262.

**Compound 11:** To a solution of **7** (143 mg, 0.22 mmol), **8** (446 mg, 0.98 mmol), and CuI (12 mg, 0.063 mmol) in triethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (38 mg, 0.032 mmol). The resulting mixture was stirred at 50 °C for 17 h under an Ar atmosphere. The reaction mixture was poured into a saturated  $\text{NH}_4\text{Cl}$  solution and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried with  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  to give **11** (303 mg, 85%) as green crystals. M.p. 195.0–197.0 °C ( $\text{CH}_2\text{Cl}_2/\text{hexane}$ ); IR (ATR):  $\nu_{\text{max}}$  = 2961 (w), 2193 (w), 1695 (m), 1576 (w), 1497 (w), 1445 (s), 1422 (m), 1242 (m), 1211 (s), 1168 (m), 1119 (w), 1048 (m), 920 (w), 869 (m), 830 (s), 796 (m), 774 (m), 720 (s)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 248 (5.20), 277 sh (5.14), 316 (5.30), 358 (5.24), 407 sh (5.11), 424 (5.14), 443 (5.12), 581 (3.65), 618 sh (3.63), 695 sh (3.30), 785 sh (2.56) nm;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 9.74 (d, 3H,  $J$  = 1.5 Hz, 4'-H), 8.71 (d, 3H,  $J$  = 1.5 Hz, 4-H), 8.69 (d, 3H,  $J$  = 10.0 Hz, 8'-H), 8.64 (d, 3H,  $J$  = 10.0 Hz, 8-H), 8.48 (s, 3H, 2'-H), 8.28 (s, 3H, 2-H), 7.86 (s, 3H, 2,4,6-H of Bz), 7.82 (dd, 3H,  $J$  = 10.0, 1.5 Hz, 6'-H), 7.65–7.61 (m, 15H, 6'-H, *o*- and *m*-Ph), 7.53 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7'-H), 7.23 (dd, 3H,  $J$  = 10.0, 10.0 Hz, 7-H), 3.96 (s, 9H,  $\text{CO}_2\text{Me}$ ), 3.27–3.18 (m, 6H, *i*Pr), 1.46 (d, 18H,  $J$  = 6.5 Hz, *i*Pr), 1.43 (d, 18H,  $J$  = 6.5 Hz, *i*Pr) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 165.44 ( $\text{CO}_2\text{Me}$ ), 150.67 (C-5'), 145.08 (C-8a), 144.83 (C-5), 142.76 (C-2'), 142.47 (C-8'), 141.34 (C-8a'), 139.37 (C-6'), 139.22 (C-2), 138.56 (C-6'), 138.36 (C-4'), 137.54 (C-3a or C-3a'), 136.85 (C-4), 136.25 (C-3a or C-3a'), 134.95 (C-8), 131.29 (*o*- or *m*-Ph), 131.14 (*o*- or *m*-Ph), 129.83 (C-1,3,5 of Bz), 128.86 (C-2,4,6 of Bz), 127.53 (C-7'), 125.33 (C-7), 123.69 (*ipso*-Ph),

122.89 (*ipso*-Ph), 115.17 (C-3'), 108.99 (C-3 or C-1'), 108.96 (C-3 or C-1'), 94.61 (C=C), 93.80 (C=C), 87.98 (C=C), 86.61 (C=C), 51.20 (CO<sub>2</sub>Me), 39.27 (*iPr*), 38.56 (*iPr*), 24.63 (*iPr*×2) ppm; HRMS (MALDI-TOF): calcd for C<sub>120</sub>H<sub>96</sub>O<sub>6</sub><sup>+</sup> [M]<sup>+</sup> 1632.7202; found: 1632.7201.

**Compound 12:** To a solution of **7** (82 mg, 0.13 mmol), **9** (259 mg, 0.56 mmol), and CuI (7 mg, 0.04 mmol) in triethylamine (5 mL) and THF (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (22 mg, 0.019 mmol). The resulting mixture was stirred at 50 °C for 16 h under an Ar atmosphere. The reaction mixture was poured into a saturated NH<sub>4</sub>Cl solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give **12** (158 mg, 76%) as green crystals. M.p. 181.0–183.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): ν<sub>max</sub> = 2958 (w), 2185 (w), 1695 (m), 1575 (w), 1501 (w), 1444 (m), 1417 (m), 1376 (w), 1210 (s), 1165 (m), 1130 (w), 1050 (w), 918 (w), 865 (m), 796 (s), 773 (w), 719 (w), 701 (w), 658 (w) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 248 (5.16), 280 sh (5.10), 295 sh (5.15), 312 (5.17), 371 (5.04), 441 (5.03), 468 sh (4.88), 585 (3.61), 628 sh (3.56), 705 sh (3.18) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 9.74 (d, 3H, J = 2.0 Hz, 4'-H), 8.64 (d, 3H, J = 2.0 Hz, 4-H), 8.64–8.61 (m, 6H, 8,8'-H), 8.47 (s, 3H, 2'-H), 8.25 (s, 3H, 2-H), 7.84 (s, 3H, 2,4,6-H of Bz), 7.82 (d, 3H, J = 10.0 Hz, 6'-H), 7.63 (d, 3H, J = 10.0 Hz, 6-H), 7.53 (dd, 3H, J = 10.0 Hz, 7'-H), 7.25–7.22 (m, 9H, 7-H, 3,4-H of Th), 3.96 (s, 9H, CO<sub>2</sub>Me), 3.24 (sept, 3H, J = 6.5 Hz, *iPr*), 3.19 (sept, 3H, J = 6.5 Hz, *iPr*), 1.45 (d, 18H, J = 6.5 Hz, *iPr*), 1.43 (s, 18H, J = 6.5 Hz, *iPr*) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 165.37 (CO<sub>2</sub>Me), 150.85 (C-5'), 145.37 (C-5), 144.81 (C-3a'), 142.75 (C-2'), 142.56 (C-3a), 141.40 (C-8a'), 139.49 (C-6'), 139.05 (C-2), 138.67 (C-6), 138.44 (C-4'), 137.48 (C-8a), 137.00 (C-4), 136.88 (C-8 or C-8'), 136.34 (C-1,3,5 of Bz), 135.01 (C-8 or C-8'), 131.32 (C-3 or C-4 of Th), 130.81 (C-3 or C-4 of Th), 129.89 (C-1), 128.86 (C-2,4,6 of Bz), 127.69 (C-7'), 125.53 (C-2 or C-5 of Th), 125.39 (C-7), 124.46 (C-2 or C-5 of Th), 115.29 (C-3'), 108.45 (C-3 or C-1'), 108.39 (C-3 or C-1'), 90.98 (C=C), 89.60 (C=C), 87.43 (C=C), 86.62 (C=C), 51.21 (CO<sub>2</sub>Me), 39.27 (*iPr*), 38.54 (*iPr*), 24.61 (*iPr*×2) ppm; HRMS (MALDI-TOF): calcd for C<sub>114</sub>H<sub>90</sub>O<sub>6</sub>S<sub>3</sub><sup>+</sup> [M]<sup>+</sup> 1650.5895; found: 1650.5894.

**Compound 13:** To a solution of **10** (107 mg, 0.080 mmol) in AcOEt (5 mL) was added TCNE (46 mg, 0.36 mmol). The resulting mixture was refluxed for 15 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (100:1) to give **13** (117 mg, 85%) as red crystals. M.p. 240.0–242.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): ν<sub>max</sub> = 2966 (w), 2216 (w), 1700 (m), 1590 (w), 1576 (w), 1494 (s), 1463 (m), 1440 (s), 1417 (s), 1363 (m), 1312 (w), 1269 (w), 1212 (s), 1177 (m), 1133 (w), 1088 (w), 1057 (w), 1022 (w), 921 (w), 899 (w), 876 (w), 847 (w), 805 (m), 775 (m), 753 (w), 741 (w), 729 (m), 686 (w), 674 (w), 666 (w) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 260 (5.04), 306 (5.09), 346 sh (4.88), 395 (4.71), 512 (4.72) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 10.06 (d, 3H, J = 1.5 Hz, 4'-H), 8.85 (d, 3H, J = 10.0 Hz, 8'-H), 8.76 (s, 3H, 2'-H), 8.65 (d, 3H, J = 1.5 Hz, 4-H), 8.61 (d, 3H, J = 10.0 Hz, 8-H), 8.55 (s, 3H, 2-H), 8.12 (dd, 3H, J = 10.0, 1.5 Hz, 6-H), 7.98 (dd, 3H, J = 10.0, 1.5 Hz, 6'-H), 7.91 (dd, 3H, J = 10.0, 10.0 Hz, 7-H), 7.86 (s, 3H, 2,4,6-H of Bz), 7.75 (dd, 3H, J = 10.0, 10.0 Hz, 7'-H), 3.92 (s, 9H, CO<sub>2</sub>Me), 3.36 (sept, 3H, J = 7.0 Hz, *iPr*), 3.12 (sept, 3H, J = 7.0 Hz, *iPr*), 1.48 (d, 18H, J = 7.0 Hz, *iPr*), 1.20 (d, 18H, J = 7.0 Hz, *iPr*) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 164.54 (CO<sub>2</sub>Me), 163.13 (C=C(CN)<sub>2</sub>), 161.39 (C=C(CN)<sub>2</sub>), 156.97 (C-5'), 153.61 (C-5), 146.33 (C-8a), 144.52 (C-3a), 143.66 (C-2), 142.49 (C-6), 142.41 (C-3a'), 142.12 (C-6'), 141.72 (C-8a'), 140.74 (C-4'), 139.23 (C-2'), 137.48 (C-8), 137.34 (C-4), 137.20 (C-8'), 136.46 (C-1'), 133.82 (C-1,3,5 of Bz), 132.39 (C-7), 131.77 (C-7'), 130.03 (C-2,4,6 of Bz), 121.68 (C-3), 120.48 (C-1), 119.46 (C-3'), 115.26 (CN), 114.51 (CN), 113.32 (CN), 112.74 (CN), 80.17 (C(CN)<sub>2</sub>), 77.81 (C(CN)<sub>2</sub>), 51.64 (CO<sub>2</sub>Me), 39.45 (*iPr*), 39.42 (*iPr*), 24.51 (*iPr*), 24.45 (*iPr*)

ppm; HRMS (MALDI-TOF): calcd for C<sub>114</sub>H<sub>84</sub>N<sub>12</sub>O<sub>6</sub> + H<sup>+</sup> [M + H]<sup>+</sup> 1717.6710; found: 1717.6668.

**Compound 14:** To a solution of **11** (53 mg, 0.032 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added TCNE (37 mg, 0.29 mmol). The resulting mixture was refluxed for 16 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (5:1) to give **14** (69 mg, 88%) as red crystals. M.p. 201.0–203.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): ν<sub>max</sub> = 2961 (w), 2218 (w), 1702 (m), 1493 (s), 1441 (s), 1420 (s), 1363 (s), 1312 (m), 1215 (s), 1180 (m), 1136 (w), 1047 (w), 1032 (w), 903 (w), 811 (m), 776 (m), 728 (w) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 249 (5.18), 260 sh (5.17), 300 (5.18), 340 sh (5.11), 452 (4.77), 487 sh (4.73), 551 sh (4.54) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 10.03 (d, 3H, J = 1.5 Hz, 4'-H), 8.71 (d, 3H, J = 10.0 Hz, 8'-H), 8.54 (d, 3H, J = 1.5 Hz, 4-H), 8.41 (d, 3H, J = 10.0 Hz, 8-H), 8.24 (s, 3H, 2'-H), 8.18 (d, 3H, J = 10.0 Hz, 6'-H), 8.06–8.04 (m, 9H, 6-H and Ph), 7.99 (dd, 3H, J = 10.0, 10.0 Hz, 7'-H), 7.91 (d, 6H, Ph), 7.74 (m, 6H, 2,7-H), 7.65 (s, 3H, Bz), 3.95 (s, 9H, CO<sub>2</sub>Me), 3.39–3.31 (m, 6H, *iPr*), 1.48 (d, 18H, J = 6.5 Hz, *iPr*), 1.47 (d, 18H, J = 6.5 Hz, *iPr*) ppm. Low solubility hampered the measurement of <sup>13</sup>C NMR. HRMS (MALDI-TOF): calcd for C<sub>156</sub>H<sub>96</sub>N<sub>24</sub>O<sub>6</sub><sup>+</sup> [M]<sup>+</sup> 2400.7940; found: 2400.7939.

**Compound 15:** To a solution of **12** (74 mg, 0.045 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added TCNE (52 mg, 0.41 mmol). The resulting mixture was refluxed for 15 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (10:1) to give **15** (109 mg, 99%) as red crystals. M.p. 194.0–196.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (ATR): ν<sub>max</sub> = 2963 (w), 2219 (w), 1703 (m), 1496 (s), 1441 (s), 1418 (s), 1362 (m), 1301 (w), 1238 (m), 1214 (s), 1179 (m), 1136 (w), 1024 (w), 903 (w), 876 (w), 811 (m), 777 (w), 739 (w) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 260 (5.12), 295 sh (5.02), 303 (5.03), 325 sh (4.98), 339 sh (4.97), 423.5 (4.99), 437 sh (4.99), 492 sh (4.79), 567 sh (4.32), 644 sh (3.90), 696 sh (3.59), 755 sh (3.21) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 10.03 (s, 3H, 4'-H), 8.73 (d, 3H, J = 10.0 Hz, 8'-H), 8.49 (s, 3H, 4-H), 8.42 (d, 3H, J = 10.0 Hz, 8-H), 8.22 (s, 3H, 2-H or 2'-H), 8.18–8.16 (m, 6H, 6-H and 3-H or 4-H of Th), 8.09–7.97 (m, 12H, 2-H or 2'-H, 7-H, 6'-H, and 3-H or 4-H of Th), 7.76 (dd, 3H, J = 10.0, 10.0 Hz, 7'-H), 7.72 (s, 3H, 2,4,6-H of Bz), 3.96 (s, 9H, CO<sub>2</sub>Me), 3.36 (sept, 3H, J = 6.5 Hz, *iPr*), 3.28 (sept, 3H, J = 6.5 Hz, *iPr*), 1.48 (d, 18H, J = 6.5 Hz, *iPr*), 1.41 (d, 18H, J = 6.5 Hz, *iPr*) ppm. Low solubility hampered the measurement of <sup>13</sup>C NMR. HRMS (MALDI-TOF): calcd for C<sub>150</sub>H<sub>90</sub>N<sub>24</sub>O<sub>6</sub>S<sub>3</sub><sup>+</sup> [M]<sup>+</sup> 2418.6632; found: 2418.6632.

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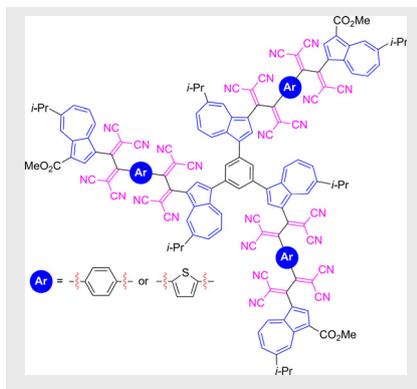
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## Entry for the Table of Contents

## FULL PAPER

Novel tris[1-azulenyltetracyanobutadiene and 1-azulenylbis(tetracyanobutadiene)s] chromophores with a  $C_3$  symmetrical structure were prepared by the formal [2 + 2] cycloaddition–retroelectrocyclization of TCNE with the corresponding alkynes. The redox behavior of the TCBD derivatives was examined by CV, DPV, and spectroelectrogram measurements.



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**Synthesis, Properties and Redox Behavior of Tris[1-azulenyltetracyanobutadiene and 1-azulenylbis(tetracyanobutadiene)s] connected with 1,3,5-Tri(1-azulenyl)benzene core**