ChemPubSoc
Europe

■ **Donor-acceptor chromophores**

Synthesis of 1,3-Bis(tetracyano-2-azulenyl-3-butadienyl)azulenes by the [2 + 2] Cycloaddition–Retroelectrocyclization of 1,3-Bis(azulenylethynyl)azulenes with Tetracyanoethylene

Taku Shoji,*[a,b] Mitsuhisa Maruyama,[b] Akifumi Maruyama,[b] Shunji Ito,[c] Tetsuo Okujima,[d] Kozo Toyota[e]

Abstract: 1,3-Bis(azulenylethynyl)azulene derivatives **9**–**14** have been prepared by palladium-catalyzed alkynylation of 1-ethynylazulene **8** with 1,3-diiodoazulene **1** or 1,3-diethynylazulene **2** with the corresponding haloazulenes **3**–**7** under Sonogashira–Hagihara conditions. Bis-alkynes **9**–**14** reacted with tetracyanoethylene (TCNE) in a formal [2 + 2] cycloaddition–retroelectrocyclization reaction to afford the corresponding new bis-tetracyanobutadienes (bis-TCBDs) **15**–**20** in excellent yields.

The redox behavior of bis-TCBDs **15**–**20** was examined by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which revealed their reversible multi-stage reduction properties under the electrochemical conditions. Moreover, a significant color change of alkynes **9**–**14** and TCBDs **15**–**20** was observed by visible spectroscopy under the electrochemical reduction conditions.

Introduction

Organic electron donor–acceptor systems, which were featured by intramolecular charge-transfer (ICT) interactions, have

[a]   Dr. T. Shoji
      Department of Chemistry, Faculty School of Science
      Shinshu University
      Matsumoto 390-8621, Nagano, Japan
      Fax: (+)81-263-37-2476
      E-mail: tshoji@shinshu-u.ac.jp

[b]   Dr. T. Shoji, M. Maruyama, A. Maruyama
      Department of Material Science, Graduate School of Science and Technology
      Shinshu University
      Matsumoto 390-8621, Nagano, Japan

[c]   Prof. Dr. S. Ito
      Graduate School of Science and Technology
      Hirosaki University
      Hirosaki 036-8561, Aomori, Japan

[d]   Dr. T. Okujima
      Department of Chemistry and Biology, Graduate School of Science and Engineering
      Ehime University
      Matsuyama 790-8577, Ehime, Japan

[e]   Prof. Dr. K. Toyota
      Department of Chemistry, Graduate School of Science
      Tohoku University
      Sendai 980-8578, Miyagi, Japan

attracted considerable interest as promising candidates for the next generation of organic electronic and optoelectronic devices.[1] As one of the procedures for the construction of donor–acceptor chromophores, there is a click-type formal [2 + 2] cycloaddition–retroelectrocyclization of electron-rich alkynes with tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), which give the corresponding 1,1,4,4-tetracyanobutadienes (TCBDs) and dicyanoquinodimethanes (DCNQs).[2] Especially, Diederich and co-workers have developed the chemistry of TCBDs and DCNQs as a new class of chromophores. They have reported that a variety of electron-rich alkynes react with TCNE and TCNQ to give donor-substituted TCBDs[3] and DCNQs[4] in excellent yields. Furthermore, they have extensively expanded the chemistry by applying the procedure to the other acceptor molecules, such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[5] dicyanovinyl, and tricyanovinyl derivatives.[6] They have also reported that the new class of chromophores was characterized by an intense ICT interaction with a strong absorption band in the visible region and were promising organic electronic and optoelectronic devices.[7]

Azulene has attracted the interest of many research groups due to its unusual properties associated with its remarkable polarizability as well as its beautiful blue color.[8] The azulene system also has a tendency to stabilize both cations and anions, depending on the substitution position, through the contributions of its formal tropylium and cyclopentadienide substructures. Thus, the substitution by azulenyl group via its 1- and 3-positions promotes extreme electron-donating nature, while azulen-4-yl, -6-yl, and -8-yl substituents have a strong electron-withdrawing character. Although the functionalization of other positions (i.e. 2-, 5- and 7-positions) are usually difficult, arylation *via* electrophilic

and cross-coupling reactions has reported by Hawker[9] and our group[10], respectively.

Recently, we have reported the synthesis and electrochemical properties of TCBD and DCNQ derivatives with azulenyl substituents, which have been prepared by the [2 + 2] cycloaddition–retroelectrocyclization reaction of the corresponding ethynylazulene derivatives with TCNE and TCNQ, respectively.[11] Especially, TCBD and DCNQ derivatives substituted by 1-azulenyl group with either 2- or 6-azulenyl functions showed rather high stability in the electrochemical redox cycles and improved electrochromic properties, over TCBDs and DCNQs substituted by two 1-azulenyl groups, since the azulenyl substituent via its 2- or 6-position tend to stabilize an anionic species formed by the electrochemical reduction reasoned by the contribution of their resonance structures.[12] However, azulene derivatives with two TCBD units at their both 1- and 3-positions have not been explored, so far. Azulene derivatives with two TCBD units at their 1- and 3-positions are expected to became new examples of redox-active chromophores by virtue of multiple donor–acceptor units that may be prepared by sequential [2 + 2] cycloaddition–retroelectrocyclization of the corresponding ethynyl derivatives with TCNE, because the molecules with multiple TCBD units tend to show multistage reduction properties on cyclic voltammetry (CV) under the electrochemical reduction conditions.

Herein, we describe the synthesis of 1,3-bis(azulenylethynyl)azulene derivatives 9–14 under Sonogashira–Hagihara reaction conditions, as well as the reactivity of the products toward the [2 + 2] cycloaddition–retroelectrocyclization reaction with TCNE to afford the corresponding azulene-substituted bis-TCBD chromophores 15–20 bearing two azulenyl groups at the periphery. The electronic properties of the novel bis-TCBD derivatives with 1,3-azulendiyl spacer are characterized by electrochemical analysis and absorption spectroscopy.

Results and Discussion

Synthesis of 1,3-bis(1-, 2-, and 6-azulenylethynyl)azulenes: To construct the novel TCBDs, 1,3-bis(azulenylethynyl)azulenes 9–14 as a precursor were prepared by Sonogashira–Hagihara reaction[13] as shown in Schemes 1 and 2. The key precursors, 6-tert-butyl-1,3-diiodo- and 6-tert-butyl-1,3-diethynylazulenes (1 and 2), were prepared by the procedure reported by Hafner et al., previously.[14] Synthesis of 1,3-bis(1-, 2-, and 6-azulenylethynyl)azulenes 9–14 was accomplished by the palladium-catalyzed alkynylation of 1 with 1-ethynylazulene 8[11a] or 2 with the corresponding haloazulenes 3–7 (Figure 1). The reaction of 1 with the 1-ethynylazulene 8 in the presence of Pd(PPh₃)₄ gave 1,3-bis(1-azulenylethynyl)azulene 9 in 95% yield (Scheme 1).
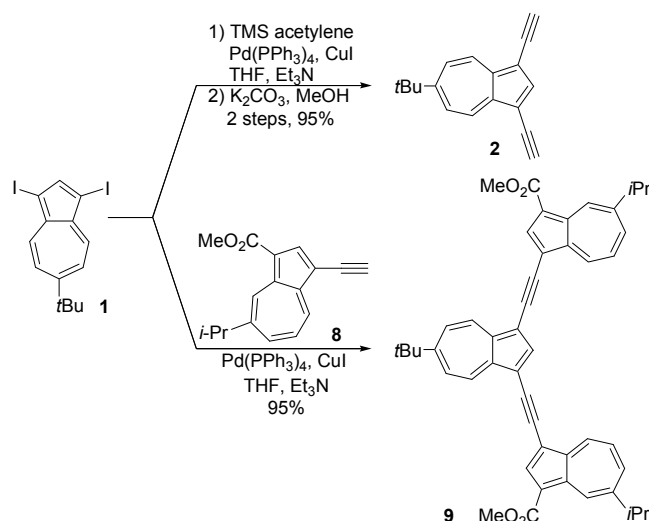
Scheme 1. Synthesis of 1,3-diethynylazulene **2** and 1,3-bis(1-azulenylethynyl)azulene **9**.
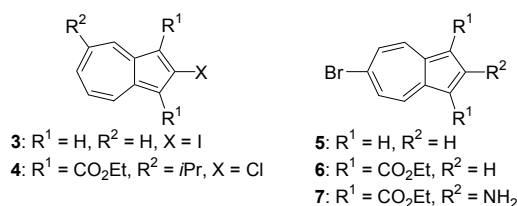

Figure 1. Structure of 2-halo-[15] and 6-bromoazulenes **3–7**.[16]

The reaction of **2** with 2-iodoazulene (**3**) afforded 1,3-(2-azulenylethynyl)azulene (**10**) in 94% yield. Although the aryl chloride usually shows a low reactivity toward the palladium-catalyzed cross-coupling reaction,[17] Sonogashira–Hagihara reaction of **2** with **4** produced the desired coupling product **11** in 83% yield (Scheme 2). The high-yield of the product should be ascribed to the high reactivity of the 2-haloazulenes and also electron-withdrawing nature of the substituted 1,3-bisethoxycarbonyl groups of **4**, likewise results on the reaction of 1-ethynlazulene and ethynylferrocene with **4**.[11e] 6-Bromoazulenes **5–7** were also reacted with **2** under Sonogashira–Hagihara conditions to afford the corresponding 1,3-bis(6-azulenylethynyl)azulenes **12–14** (**12**: 95%, **13**: 96%, and **14**: 87%) as shown in Scheme 2. 1,3-Bis(1-, 2-, and 6-azulenylethynyl)azulene derivatives **9−14** possess fair solubility in general organic solvents, such as chloroform and dichloromethane. Moreover, they are stable and show no decomposition even after several weeks at room temperature. Thus, the 1,3-bis(azulenylethynyl)azulenes could be utilized in further transformations for the synthesis of new TCBDs containing three azulenyl substituents because of their considerable stability and solubility.

Scheme 2. Synthesis of 1,3-bis(2- and 6-azulenylethynyl)azulenes **10–14**.

electron-donating properties than ferrocenyl group, from the viewpoint of reactivity with TCNE.

Figure 2. Structure of novel TCBD derivatives **15–20**.

Reaction of 1,3-bis(azulenylethynyl)azulenes with tetracyanoethylene: For the synthesis of novel bis-TCBD derivatives, [2 + 2] cycloaddition–retroelectrocyclization sequence of **9**–**14** with TCNE was conducted according to previously described procedures.[11] Structure of the novel bis-TCBDs **15**–**20** is shown in Figure 2. The reaction of **9**, which has electron-donating 1-azulenyl groups at the periphery, with TCNE in refluxing ethyl acetate gave **15** in 94% yield. Likewise, the [2 + 2] cycloaddition–retroelectrocyclization of **10** and **11** with TCNE afforded **16** and **17** in 95% and 91% yield, respectively. 1,3-Bis(6-azulenylethynyl)azulenes **12**, **13**, and **14** also reacted with TCNE in ethyl acetate by heating at reflux temperature, affording the corresponding [2 + 2] cycloaddition products **18**, **19**, and **20** in 95%, 86%, and 88% yields, respectively.

Although the strong electron-withdrawing TCBD moiety was introduced in the molecule by the first addition of TCNE to one of the acetylene units, the second addition of TCNE molecule smoothly took place to afford bis-adducts **15–20** in excellent yields. Recently, Michinobu reported the reaction of 1,1'-bis(phenylethynyl)ferrocene (**21**) with excess TCNE did not give bis-adduct **23**, but afford mono-adduct **22**, exclusively (Scheme 3). These results were explained by the activation caused by ferrocenyl group that can only one alkyne moiety for the addition of TCNE, due to the less enough electron-donating nature of the ferrocenyl group with a TCBD acceptor unit in **22**.[18] Thus, azulenyl group centered at the molecules possesses higher

Scheme 3. Reaction of 1,1'-bis(phenylethynyl)ferrocene (**21**) with TCNE.[18]

Properties: The new compounds **9–20** were fully characterized on the basis of their spectral data, as summarized in the Experimental Section. The NMR assignment of the reported compounds was confirmed by COSY, HMQC and HMBC experiments. High-resolution mass spectra of **9–20** ionized by ESI, MALDI, or FAB showed the expected molecular ion peaks. The characteristic stretching vibration band of the C≡N moiety of TCBDs **15–20** was observed at 2176−2227 cm^{-1} on each IR spectrum. These results are consistent with the given structure of these products.

^{1}H NMR Spectra of alkyne **10** and bis-TCBD **16** that has 2-azulenyl substituents are shown in Figure 3. The downfield shift of all protons of 2-azulenyl moiety in **16** was observed in CDCl$_3$, compared to those of alkyne **10**, due to the strong electron-

withdrawing nature of TCBD units. Significant downfield shift of 5,7-H protons of **16** was also observed in the ^{1}H NMR spectra, which is ascribed to the resonance effect between the TCBD and 1,3-azulendiyl core as illustrated in Scheme 4. The upfield shift for 2-H protons of **16** is attributed to the anisotropic effect of the adjacent cyano groups.[19]
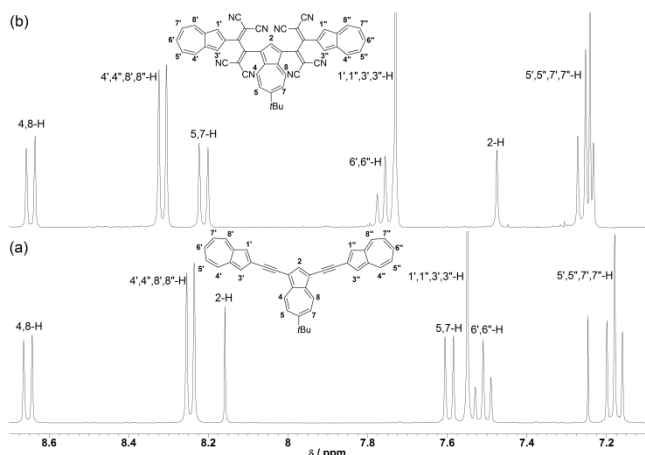

Figure 3. ^{1}H NMR spectra of (a) **10** and (b) **16** in CDCl$_3$ (500 MHz).

The UV−Vis spectra of bis-TCBDs **16**, **17** and **18–20** are shown in Figures 5 and 6, respectively. The UV−Vis spectra of 1,3-bis(azulenylethynyl)azulenes **9–14** showed characteristic weak absorptions arising from the azulene system in the visible region. The longest absorption maxima of **12** (λ_{max} = 602 nm) exhibited bathochromic shift than that of 1,6';3,6"-terazulene **24** (λ_{max} = 579 nm) (Figure 4).[20] This effect reflected to the expansion of π-electron system of **12** by the connected alkyne spacer.
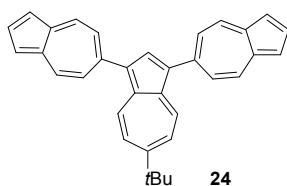
Figure 4. Structure of 6-*tert*-butyl-1,6';3,6"-terazulene (**24**).

The UV−Vis spectrum of the bis-TCBD derivative **15** with 1-azulenyl group showed an absorption in the visible region at λ_{max} = 513 nm. The TCBD derivative with 2-azulenyl substituents **16** exhibited strong absorption band at λ_{max} = 407 nm, which extended beyond 800 nm, in the visible region. The longest wavelength absorption maximum of TCBD **17** (λ_{max} = 552 nm) in CH$_2$Cl$_2$ showed a bathochromic shift relative to that of **16** in the same solvent (Figure 5). Bis-TCBD **18** with 6-azulenyl groups exhibited a broad absorption bands at λ_{max} = 405 nm and 494 nm. Likewise, compound **19** also displayed a broad CT absorption band beyond 800 nm. Bis-TCBD **20** with two 2-aminoazulene moieties, showed a strong absorption band at λ_{max} = 500 nm

(Figure 6). Although the absorption maxima of bis-TCBDs **15–20** were nearly equal to that of the corresponding mono-TCBD derivatives **25–30**,[12] the extinction coefficients show an increasing trend as the number of TCBD units. These effects exhibit an overlap of ICT arising from the resonance effect between the central 1,3-azulendiyl core and two TCBD units as shown in Scheme 4.

Most of the bis-TCBD derivatives showed solvatochromism, when the solvent was changed from CH$_2$Cl$_2$ to a 10% CH$_2$Cl$_2$/*n*-hexane mixture. A noticeable spectral feature of **15** is the presence of a distinct absorption band at λ_{max} = 513 nm in CH$_2$Cl$_2$, which exhibits blue-shift by 30 nm (λ_{max} = 453 nm) in the less polar 10% CH$_2$Cl$_2$/*n*-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.
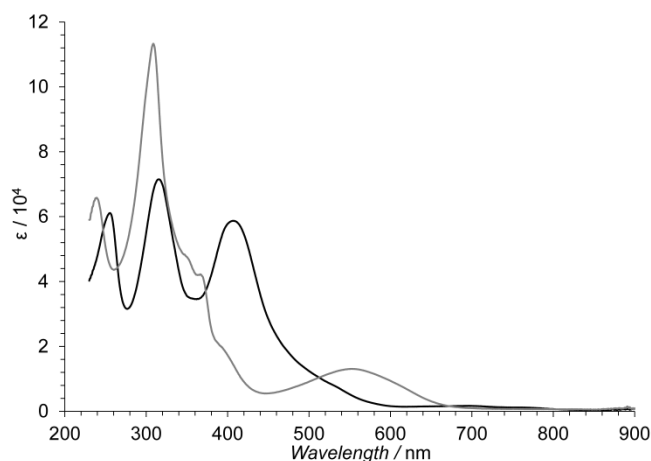

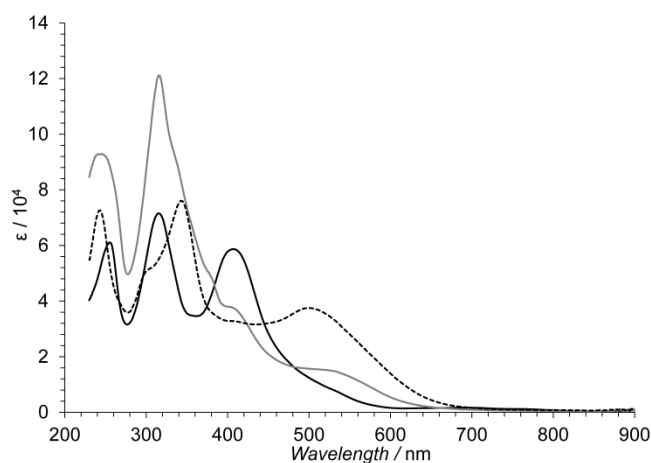**Figure 5.** UV−Vis spectra of **16** (black line) and **17** (gray line) in CH$_2$Cl$_2$.

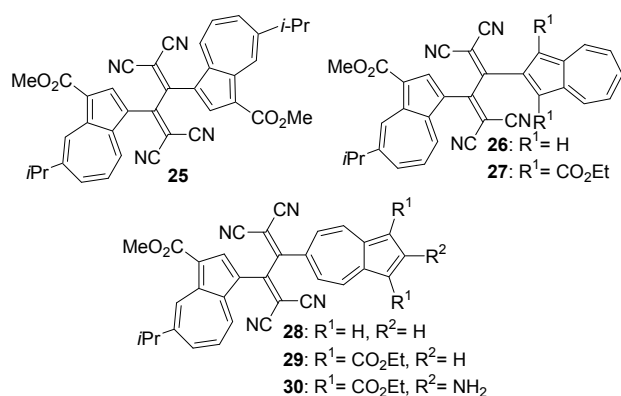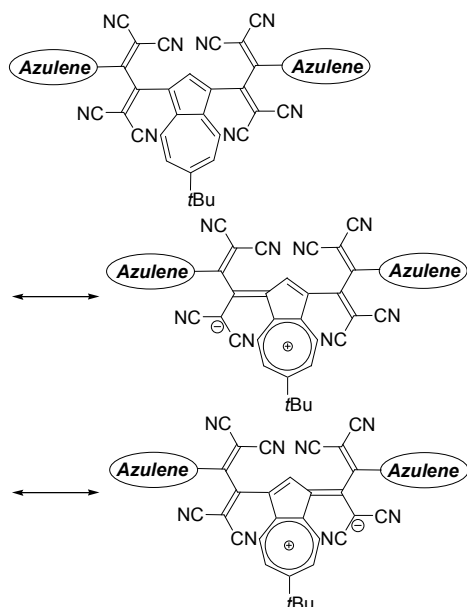**Figure 6.** UV−Vis spectra of **18** (black line), **19** (gray line), and **20** (dashed line) in CH$_2$Cl$_2$.

Figure 7. Structure of mono-TCBDs **25–30** with two azulenyl substituents.[12]

Scheme 4. Plausible resonance structure of bis-TCBDs **15–20**.

Electrochemistry: To clarify the effect of substitution positions on the azulene ring on the electrochemical properties in alkynes **9–14** and bis-TCBDs **15–20** that are composed of three azulenyl groups, the redox behavior of those compounds was examined by CV and DPV.[21] The redox potentials (in volts vs Ag/AgNO₃) of TCBDs **15–20** measured under a scan rate of 100 mVs⁻¹ are summarized in Table 1. The reduction waves of alkynes **9–14** and bis-TCBDs **15–20** measured by CV and DPV are summarized in the Supporting Information.

Table 1. Redox potentials[a,b] of bis-TCBDs **15–20** and mono-TCBDs **25–30** for comparison.

Sample	Method	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]	E_4^{red} [V]
15	CV	−0.53			
	(DPV)	(−0.51)	(−0.70)	(−1.27)	
16	CV	−0.53	−0.66	−1.03	−1.09
	(DPV)	(−0.51)	(−0.64)	(−1.01)	(−1.07)
17	CV	−0.48	−0.68	−1.13	−1.32
	(DPV)	(−0.46)	(−0.66)	(−1.11)	(−1.30)
18	CV	−0.42	−0.59	−0.95	−1.13
	(DPV)	(−0.40)	(−0.57)	(−0.93)	(−1.11)
19	CV	−0.31	−0.50	−0.80	−0.85
	(DPV)	(−0.29)	(−0.48)	(−0.78)	(−0.83)
20	CV	−0.42	−0.60	−0.95	−1.06
	(DPV)	(−0.40)	(−0.58)	(−0.93)	(−1.04)
25[11a]	CV	−0.64	−1.04		
	(DPV)	(−0.62)	(−1.02)	(−1.92)	
26[12]	CV	−0.64	−0.96		
	(DPV)	(−0.62)	(−0.94)	(−1.84)	
27[12]	CV	−0.50	−0.98		
	(DPV)	(−0.48)	(−0.96)	(−1.80)	
28[12]	CV	−0.50	−0.90		
	(DPV)	(−0.48)	(−0.88)	(−1.80)	
29[12]	CV	−0.40	−0.76		
	(DPV)	(−0.38)	(−0.74)	(−1.63)	
30[12]	CV	−0.53	−0.92		
	(DPV)	(−0.51)	(−0.90)	(−1.81)	

[a] V vs. Ag/AgNO₃, 1 mM in benzonitrile containing Et₄NClO₄ (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs⁻¹ and internal reference (Fc/Fc⁺ = +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.

1,3-Diethynylazulenes **9–14** with two azulenyl groups at the periphery exhibited quasi-reversible or irreversible reduction waves on CV (see the Supporting Information). These results suggest the generation of unstable anionic species of **9–14** under the electrochemical reduction conditions. Although the bis-TCBD derivatives **16–20** have a symmetrical structure with the respect to the central 1,3-azulendiyl core, these compounds displayed a reversible four-stage wave on CV (Table 2). Thus, the electrochemical interaction between the two TCBD units through the central 1,3-azulendiyl core by the cross-conjugation should be responsible to the stepwise reduction of the bis-TCBDs **16–20**.

Electrochemical reduction of **15** showed a reversible and irreversible reduction waves on CV. The potentials were identified by DPV at −0.51 V, −0.70 V, and −1.27 V. The irreversibility for reduction wave of **15** might be attributable to the destabilization of highly anionic species due to the electron-donating properties of two 1-azulenyl groups substituted on the TCBD units. A reversible four-stage wave was observed by CV in the bis-TCBD derivatives with 2-azulenyl groups **16** (−0.53 V, −0.66 V, −1.03 V, and −1.09 V) and **17** (−0.48 V, −0.68 V, −1.13 V, and −1.32 V), respectively. These results are reflected on the generation of stabilized tetraanionic species. A positive shift of the first reduction potential of **17** (−0.48 V) compared with that of **16** (−0.53 V) is attributable to the decrement of the LUMO-level arising from the electron-withdrawing nature of the two ethoxycarbonyl groups at the 1,3-positions of 2-azulenyl substituents (Figure 8).

A reversible four-step redox wave was also observed by the electrochemical reduction of bis-TCBDs **18**, **19**, and **20** substituted by two 6-azulenyl groups. The reversibility could be ascribed to the formation of a stabilized tetraanionic species originated by the electron-withdrawing nature of the two 6-

azulenyl groups in addition to the stabilization by the two TCBD units. Reduction potentials of the reversible four-step reduction wave of bis-TCBD derivative **18** with parent 6-azulenyl groups were observed at −0.42 V, −0.59 V, −0.95 V, and −1.13 V. The first reduction potential of **18** (−0.42 V) showed a positive shift by 0.11 V compared with that of **16** (−0.53 V), which was attributable to the effective stabilization of the anionic species by the electron-withdrawing 6-azulenyl groups in comparison with that of the 2-azulenyl groups (Figure 9). The reversible four-step reduction wave of **19** (−0.31 V, −0.50 V, −0.80 V, and −1.13 V) exhibited the increase of electron affinity by the 1,3-diethoxycarbonyl substituents on the 6-azulenyl groups. The combination of the electron-donating 2-amino group with 1,3-diethoxycarbonyl substituents on the 6-azulenyl groups in **20** resulted in a reversible four-step reduction wave (−0.42 V, −0.60 V, −0.95 V, and −1.06 V) that are comparable with those of **18** due to the stepwise formation up to a tetraanionic species by electrochemical reduction. Thus, it is concluded that the electron-donating 2-amino moiety on **20** increased the LUMO-level by its electron-donating nature, but the first reduction potential of **20** still exhibits high electron affinity among bis-TCBDs with two azulenyl groups at the periphery.

On the whole, bis-TCBDs **15**–**20** exhibited more negative reduction potentials compared with those of the corresponding mono-TCBD chromophores **25**–**30** (Figure 7). These results indicate the higher electron-accepting nature of the bis-TCBDs than that of the corresponding mono-TCBDs **25**–**30**.
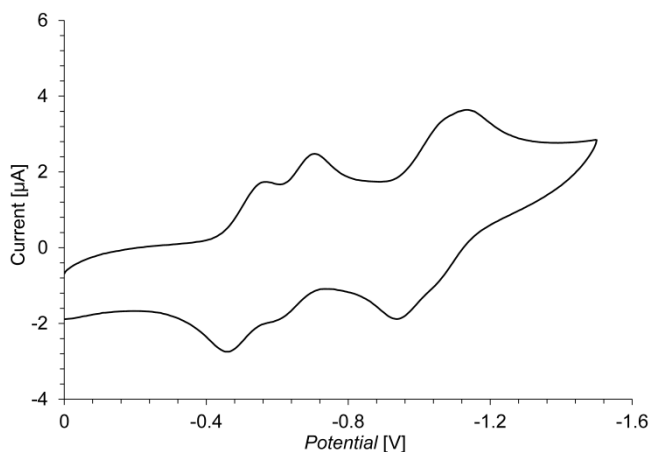

Figure 8. Cyclic voltammogram of **16** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1}.
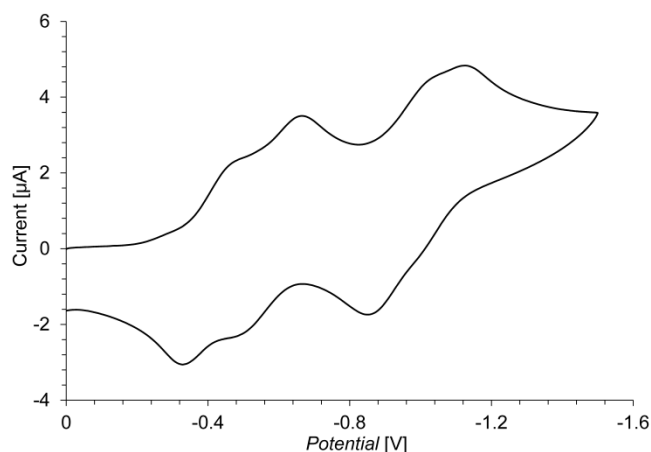

Figure 9. Cyclic voltammogram of **18** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1}.

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. Recently, we have developed various azulene-substituted, redox-active chromophores with the aim of creating stabilized electrochromic materials.[22] As a part of the study, we have reported several TCBD and DCNQ derivatives bearing azulenyl,[11] ferrocenyl,[23] and 2-oxo-2H-cyclohepta[b]-3-furyl[24] substituents, in which we have identified some novel hybrid structures of violene and cyanine with redox activities.[22,25] From our previous study, 2- or 6-azulenyl groups connected by π-electron systems induce electrochromic properties with high reversibility, owing to the generation of stabilized anionic species.[26] Moreover, electrochromic properties of the azulene-substituted TCBD derivatives substituted by 1-azulenyl groups with 2- or 6-azulenyl substituents exhibited color changes with higher reversibility, attributable to the formation of the stabilized anionic species during the electrochemical reduction.[12] Similar to the derivatives, alkynes **9**–**14** and bis-TCBDs **15**–**20** might exemplify a new class of electrochromic materials with multiple-electron transfer. Thus, the visible spectra of alkynes **9**–**14** and bis-TCBDs **15**–**20** were monitored to identify their color changes that occur during the electrochemical reactions. Constant-current reduction and oxidation (100 μA) was applied to the solutions of **9**–**20** with a platinum mesh as the working electrode and a wire counter electrode in an electrolytic cell of 1 mm thickness.[27] Visible spectra were measured in degassed benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as the supporting electrolyte at room temperature under electrochemical reaction conditions.

Alkyne derivatives **9**, **10**, and **12** showed a color change with considerable reversibility under the electrochemical redox conditions, although the CV waves were almost irreversible. However, the color change of compounds **11**, **13**, and **14** with 1,3-bisethoxycarbonyl functions did not recover the original colors, which should be attributable to the instability of anionic species as suggested by CV measurements. The electrochemical reduction of **10** gradually developed an absorption band at around 670 nm

along with a decrement of the absorption band at around 500 nm. The color of the solution gradually changed from yellow to blue during the electrochemical reduction. Reverse oxidation of the blue-colored solution regenerated the spectrum of **10** (Figure 10). When spectral changes of **12** were also monitored during the electrochemical reduction, the absorption band in the visible region gradually increased with the development of a new absorption band at 660 nm, and the color was changed from yellow to blue. Reverse oxidation of the reduced species decreased the new absorption band and regenerated the original color of **12**.
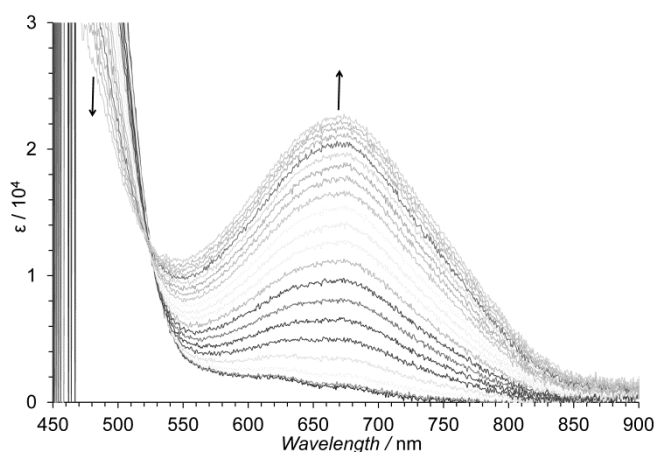
Figure 10. Continuous change in the UV−Vis spectrum of **10**: constant-current electrochemical reduction (100 µA) in benzonitrile containing Et₄NClO₄ (0.1 M) at 30 sec intervals.

The absorption band of **16** in visible region gradually increased and the color of the solution changed from yellow to dark-purple during the electrochemical reduction. Reversible oxidation of the dark-purple solution partially regenerated the original color of the compound. When the spectral changes of bis-TCBD **17** were monitored during the electrochemical reduction, new absorption bands at 570 nm and 750 nm, which spread into the near-infrared region, gradually developed together with a color change from purple to dark green. Reverse oxidation recovered the original spectrum, but incompletely.

The red color of the solution of **18** changed to yellow during the electrochemical reduction, but reverse oxidation of the orange-colored solution did not regenerate the visible spectrum of **18**. Visible spectra of **19** were measured under electrochemical reduction conditions, and the absorption band in the near-infrared region gradually increased along with a color change from red to blue (Figure 11). Reverse oxidation of the reduced species regenerated the original color of **19**, but incompletely. When the visible spectrum of **20** was measured under the electrochemical reduction conditions, the absorption in the visible region at 520 nm gradually decreased and a new absorption band at around 750 nm, which was beyond to near-infrared region, gradually developed. The reverse oxidation decreased the new absorption band, but did not regenerate the absorption band of **20**. The reversible oxidation of the reduced species of **18** and **20** did not regenerate the spectrum of the starting material, although bis-

TCBD **19** showed reversible color changes. The reversibility of the color change of **19** was ascribed to the stability of the generated dianionic species under the measurement conditions, because of the electron-withdrawing property of the ethoxycarbonyl groups on the both 6-azulenyl substituents. While, anionic species generated by electrochemical reduction of bis-TCBD **20** might be destabilized by electron-donating group (i.e., 2-amino group) on each 6-azulenyl group, although two ethoxycarbonyl groups were substituted.
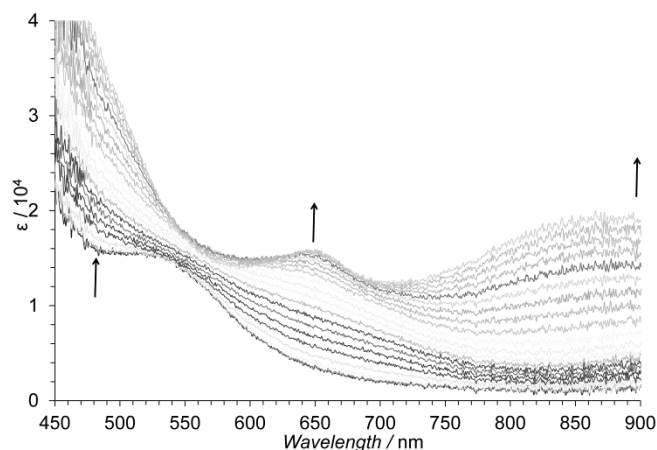

Figure 11. Continuous change in the UV−Vis spectrum of **19**: constant-current electrochemical reduction (100 µA) in benzonitrile containing Et₄NClO₄ (0.1 M) at 30 sec intervals.

Conclusion

In conclusion, bis(azulenylethynyl)azulenes **9**–**14** were prepared by palladium-catalyzed Sonogashira–Hagihara reactions of 1-ethynylazulene **8** with 1,3-diiodoazulene **1**, or 1,3-diethynylazulene **2** with the corresponding haloazulenes **3**–**7**. The novel bis-TCBDs **15**–**20** with 1,3-azulendiyl spacer were synthesized by a formal [2 + 2] cycloaddition reaction of **9**–**14** with TCNE, respectively, followed by retroelectrocyclization of the initially formed cyclobutene derivatives. Intramolecular CT absorption bands were found in the UV–Vis spectra of the novel chromophores **15**–**20**. An analysis by CV and DPV showed that bis-TCBDs **16**−**20** exhibited a reversible multi-stage reduction wave, due to the stepwise reduction of the two TCBD units. Color changes were also observed during the electrochemical reduction. In particular, bis-TCBD **19** possessing two 6-azulenyl substituents exhibited color changes with rather well reversibility, attributable to the stabilization of anionic species during the electrochemical reaction.

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

Experimental Section

General

7

Melting points were determined with a Yanagimoto MPS3 micro melting apparatus and are uncorrected. High resolution mass spectra 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}H and ^{13}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 Ag/AgNO$_3$ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M). Elemental analyses were measured with Thermo FlashEA1112 or performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

1,3-Bis[1,1,4,4-tetracyano-2-(5-isopropyl-3-methoxycarbonyl-1-azulenyl)-3-butadienyl]azulene (15): To a solution of **9** (342 mg, 0.50 mmol) in EtOAc (10 mL) was added TCNE (192 mg, 1.50 mmol). The resulting mixture was refluxed for 6 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (20:1) to give **15** (442 mg, 94%) as red crystals. M.p. >300 °C (CH$_2$Cl$_2$/n-hexane); IR (KBr disk): v_{max} = 2965 (w), 2221 (m), 1703 (s), 1576 (w), 1539 (w), 1495 (s), 1437 (s), 1419 (s), 1364 (w), 1267 (m), 1213 (s), 1179 (s), 1123 (w), 1087 (w), 1063 (w), 897 (w), 855 (w), 815 (m), 778 (m), 745 (w), 727 (w), 704 (w), 676 (w), 622 (w) cm^{-1}; UV−Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 261 (4.75), 301 (4.76), 337 sh (4.65), 387 sh (4.50), 452 sh (4.43), 513 (4.50) nm; UV−Vis (10% CH$_2$Cl$_2$/n-hexane): λ_{max} (log ε) = 253 (4.78), 301 (4.76), 330 (4.68), 388 sh (4.48), 453 (4.51), 510 sh (4.45) nm; ^{1}H NMR (500 MHz, CDCl$_3$): δ_H = 10.05 (s, 2H, 4',4"-H), 8.68 (d, J = 11.5 Hz, 2H, 4,8-H), 8.66 (s, 2H, 2',2"-H), 8.44 (d, J = 9.8 Hz, 2H, 8',8"-H), 8.23 (s, 1H, 2-H), 8.21 (d, J = 11.5 Hz, 2H, 5,7-H), 8.14 (d, J = 9.8 Hz, 2H, 6',6"-H), 7.91 (dd, J = 9.8, 9.8 Hz, 2H, 7',7"-H), 3.98 (s, 6H, CO$_2$Me), 3.36 (sept, J = 7.0 Hz, 2H, iPr), 1.55 (s, 9H, tBu), 1.47 (d, J = 7.0 Hz, 12H, iPr) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ_C = 171.68 (C-6), 164.42 (CO$_2$Me), 162.32 [C=C(CN)$_2$], 160.99 [C=C(CN)$_2$], 157.39 (C-5',5"), 146.57 (C-3a',3a"), 143.08 (C-2',2"), 142.64 (C-6',6"), 142.58 (C-8a',8a"), 142.28 (C-2), 142.17 (C-3a,8a), 140.96 (C-4',4"), 138.66 (C-4,8), 137.11 (C-8',8"), 132.72 (C-7',7"), 132.67 (C-5,7), 123.80 (C-1,3), 119.85 (C-1',1" or C-3',3"), 119.80 (C-1',1" or C-3',3"), 113.92 (CN), 113.46 (CN), 112.67 (CN), 111.56 (CN), 85.15 [C(CN)$_2$], 80.44 [C(CN)$_2$], 51.76 (CO$_2$Me), 40.16 (tBu), 39.51 (iPr), 31.68 (tBu), 24.45 (iPr) ppm. HRMS (ESI−TOF, positive): calcd for C$_{60}$H$_{44}$N$_8$O$_4$ + Na$^+$ [M + Na]$^+$ 963.3378, found 963.3376. Anal. calcd for C$_{60}$H$_{44}$N$_8$O$_4$ (941.04): C, 76.58; H, 4.71; N, 11.91; found: C, 76.42; H, 4.85; N, 11.87.

1,3-Bis[1,1,4,4-tetracyano-2-(2-azulenyl)-3-butadienyl]azulene (16): To a solution of **10** (242 mg, 0.50 mmol) in EtOAc (10 mL) was added TCNE (192 mg, 1.50 mmol). The resulting mixture was refluxed for 10 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (20:1) to give **16** (352 mg, 95%) as red crystals. M.p. 226.0–228.0 °C (CH$_2$Cl$_2$/n-hexane); IR (KBr disk): v_{max} = 2971 (w), 2227 (m), 1582 (w), 1541 (m), 1517 (w), 1498 (s), 1468 (w), 1435 (s), 1416 (w), 1376 (w), 1340 (m), 1255 (m), 1220 (w), 1183 (m), 1124 (m), 1069 (w), 1031 (w), 894 (w), 853 (w), 807 (s), 761 (m), 735 (s), 691 (w), 667 (w), 635 (w), 611 (w) cm^{-1}; UV−Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 256 (4.79), 316 (4.85), 407 (4.77), 534 sh (3.88), 700 (3.22), 765 sh (3.07) nm; UV−Vis (10% CH$_2$Cl$_2$/n-hexane): λ_{max} (log ε) = 256 (4.79), 316 (4.85), 407 (4.77), 534 sh (3.88), 700 (3.22), 765 sh (3.07) nm; ^{1}H NMR (500 MHz, CDCl$_3$): δ_H = 8.66 (d, J = 11.5 Hz, 2H, 4,8-H), 8.33 (d, J = 9.8 Hz, 4H, 4',8',4",8"-H), 8.23 (d, J = 11.5 Hz, 2H, 5,7-H), 7.77 (t, J = 9.8 Hz, 2H, 6',6"-H), 7.75 (s, 4H, 1',3',1",3"-H), 7.50 (s, 1H, 2-H), 7.27 (d, J = 9.8 Hz, 4H, 5',7',5",7"-H), 1.55 (s, 9H, tBu) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ_C = 171.66 (C-6), 162.38 [C=C(CN)$_2$], 161.25 [C=C(CN)$_2$], 143.64 (C-6',6"), 143.25 (C-4',8',4",8"), 141.53 (C-3a,8a), 140.86 (C-2), 140.57 (C-2',2"), 139.01 (C-4,8), 136.31 (C-3a',8a',3a",8a"), 132.37 (C-5,7), 126.34 (C-5',7',5",7"), 122.32 (C-1,3), 119.23 (C-1',3',1",3"), 112.89 (CN), 112.70 (CN), 112.06 (CN), 111.54 (CN), 84.41 [C(CN)$_2$], 83.80 [C(CN)$_2$], 40.15 (tBu), 31.69 (tBu) ppm. HRMS (FAB−TOF, positive): calcd for C$_{50}$H$_{28}$N$_8$ + H$^+$ [M + H]$^+$ 741.2510, found 741.2578. Anal. calcd for C$_{50}$H$_{28}$N$_8$·1/3H$_2$O (740.81): C, 80.41; H, 3.87; N, 15.00; found C, 80.40; H, 3.88; N, 15.03.

1,3-Bis[1,1,4,4-tetracyano-2-(1,3-bisethoxycarbonyl-5-isopropyl-2-azulenyl)-3-butadienyl]azulene (17): To a solution of **11** (429 mg, 0.50 mmol) in EtOAc (10 mL) was added TCNE (192 mg, 1.50 mmol). The resulting mixture was refluxed for 10 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (20:1) to give **17** (507 mg, 91%) as red crystals. M.p. 172.0–173.0 °C (CH$_2$Cl$_2$/n-hexane); IR (KBr disk): v_{max} = 2968 (w), 2885 (w), 2219 (w), 1692 (s), 1685 (s), 1577 (w), 1485 (m), 1428 (s), 1409 (m), 1283

(w), 1191 (s), 1140 (w), 1059 (w), 1023 (m), 928 (w), 820 (w), 766 (w), 681 (w), 632 (w), 621 (w) cm^{-1}; UV−Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 237 (4.81), 309 (5.05), 350 sh (4.68), 365 (4.62), 401 sh (4.22), 552 (4.12) nm; UV−Vis (10% CH$_2$Cl$_2$/n-hexane): λ_{max} (log ε) = 235 sh (4.91), 309 (5.05), 350 sh (4.68), 368 (4.62), 401 sh (4.22), 547 (4.12) nm; ^{1}H NMR (500 MHz, CDCl$_3$): δ_H = 9.87 (br s, 2H, 4',4"-H), 9.66 (br s, 2H, 8',8"-H), 9.30 (br s, 1H, 2-H), 8.53 (d, J = 9.8 Hz, 2H, 4,8-H), 8.16 (d, J = 9.8 Hz, 2H, 5,7-H), 8.05 (d, J = 10.3 Hz, 2H, 6',6"-H), 7.80 (dd, J = 10.3, 10.3 Hz, 2H, 7',7"-H), 4.51 (br s, 8H, CO$_2$Et), 3.27 (sept, J = 7.0 Hz, 2H, iPr), 1.57 (s, 9H, tBu), 1.46–1.44 (m, 24H, CO$_2$Et, iPr) ppm. Low solubility hampered the measurement of ^{13}C NMR. HRMS (FAB−TOF, positive): calcd for C$_{68}$H$_{56}$N$_8$O$_8$ + H$^+$ [M + H]$^+$ 1113.4294, found 1113.4310. Anal. calcd for C$_{68}$H$_{56}$N$_8$O$_8$ (1113.22): C, 73.37; H, 5.07; N, 10.07; found C, 73.25; H, 5.14; N, 10.05.

1,3-Bis[1,1,4,4-tetracyano-2-(6-azulenyl)-3-butadienyl]azulene (18): To a solution of **12** (242 mg, 0.50 mmol) in EtOAc (10 mL) was added TCNE (192 mg, 1.50 mmol). The resulting mixture was refluxed for 10 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (20:1) to give **18** (352 mg, 95%) as red crystals. M.p. 237.0–239.0 °C (CH$_2$Cl$_2$/n-hexane); IR (KBr disk): v_{max} = 2965 (w), 2176 (w), 1567 (m), 1541 (w), 1504 (s), 1472 (s), 1396 (s), 1362 (m), 1310 (w), 1220 (w), 1179 (w), 1114 (w), 1055 (w), 973 (w), 837 (s), 824 (s), 751 (s), 673 (w), 664 (w), 653 (w), 633 (w) cm^{-1}; UV−Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 266 (4.75), 301 (4.93), 405 (4.46), 494 (4.36) nm; UV−Vis (10% CH$_2$Cl$_2$/n-hexane): λ_{max} (log ε) = 263 (4.75), 299 (4.93), 398 (4.46), 492 (4.31) nm; ^{1}H NMR (500 MHz, CDCl$_3$): δ_H = 8.60 (d, J = 10.6 Hz, 2H, 4,8-H), 8.33 (d, J = 10.6 Hz, 4H, 4',8',4",8"-H), 8.30 (d, J = 10.9 Hz, 2H, 5,7-H), 8.09 (t, J = 3.5 Hz, 2H, 2',2"-H), 7.52 (d, J = 4.0 Hz, 4H, 1',3',1",3"-H), 7.39 (s, 1H, 2-H), 7.18 (d, J = 10.4 Hz, 4H, 5',7',5",7"-H), 1.57 (s, 9H, tBu) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ_C = 172.43 (C-6), 171.20 (C-6',6"), 159.92 [C=C(CN)$_2$], 143.16 (C-2',2"), 141.45 (C-3a,8a), 140.86 (C-3a',8a',3a",8a"), 139.44 (C-2), 138.78 (C-4,8), 137.87 [C=C(CN)$_2$], 135.04 (C-4',8',4",8"), 132.62 (C-5,7), 122.16 (C-5',7',5",7"), 122.03 (C-1',3',1",3"), 121.88 (C-1,3), 112.61 (CN), 111.56 (CN), 111.03 (CN), 110.99 (CN), 90.51 [C(CN)$_2$], 86.14 [C(CN)$_2$], 40.32 (tBu), 31.69 (tBu) ppm. HRMS (FAB−TOF, positive): calcd for C$_{50}$H$_{28}$N$_8$ + H$^+$ [M + H]$^+$ 741.2510, found 741.2515. Anal. calcd for C$_{50}$H$_{28}$N$_8$ (740.81): C, 81.06; H, 3.81; N, 15.13; found C, 80.85; H, 3.92; N, 15.06.

1,3-Bis[1,1,4,4-tetracyano-2-(1,3-bisethoxycarbonyl-6-azulenyl)-3-butadienyl]azulene (19): To a solution of **13** (386 mg, 0.50 mmol) in EtOAc (10 mL) was added TCNE (192 mg, 1.50 mmol). The resulting mixture was refluxed for 10 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (20:1) to give **19** (442 mg, 86%) as red crystals. M.p. 207.0–208.0 °C (CH$_2$Cl$_2$/n-hexane); IR (KBr disk): v_{max} = 2978 (w), 2225 (w), 1698 (m), 1581 (w), 1494 (w), 1460 (w), 1434 (s), 1389 (w), 1352 (w), 1241 (m), 1211 (s), 1107 (w), 1055 (w), 1038 (m), 983 (w), 851 (w), 819 (w), 767 (w), 655 (w), 647 (w), 632 (w), 623 (w), 612 (w) cm^{-1}; UV−Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 244 (4.96), 316 (5.08), 336 sh (4.96), 378 sh (4.69), 403 sh (4.57), 534 (4.12) nm; UV−Vis (CH$_2$Cl$_2$/n-hexane): λ_{max} (log ε) = 244 sh (4.99), 316 (5.08), 333 sh (5.00), 377 sh (4.67), 405 sh (4.55), 447 sh (4.39), 532 sh (4.05) nm; ^{1}H NMR (500 MHz, CDCl$_3$): δ_H = 9.78 (d, J = 10.9 Hz, 4H, 4',8',4",8"-H), 8.97 (s, 2H, 2',2"-H), 8.58 (d, J = 10.9 Hz, 2H, 4,8-H), 8.32 (d, J = 10.9 Hz, 2H, 5,7-H), 7.89 (s, 1H, 2-H), 7.74 (d, J = 10.9 Hz, 4H, 5',7',5",7"-H), 4.45 (q, J = 6.9 Hz, 8H, CO$_2$Et), 1.58 (s, 9H, tBu), 1.46 (t, J = 6.9 Hz, 12H, CO$_2$Et) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ_C = 173.00 (C-6), 169.20 (C-6',6"), 163.96 (CO$_2$Et), 158.85 [C=C(CN)$_2$], 147.87 (C-2',2"), 143.85 (C-3a',8a',3a",8a"), 141.74 (C-3a,8a), 141.09 [C=C(CN)$_2$], 139.67 (C-2), 138.44 (C-4,8), 138.09 (C-4',8',4",8"), 133.11 (C-5,7), 128.92 (C-5',7',5",7"), 121.70 (C-1,3), 119.49 (C-1',3',1",3"), 112.48 (CN), 111.46 (CN), 110.55 (2C, CN), 92.99 [C(CN)$_2$], 86.84 [C(CN)$_2$], 60.76 (CO$_2$Et), 40.46 (tBu), 31.67 (tBu), 14.46 (CO$_2$Et) ppm. HRMS (ESI−TOF, positive): calcd for C$_{62}$H$_{44}$N$_8$O$_8$ + Na$^+$ [M + Na]$^+$ 1051.3175, found 1051.3173. Anal. calcd for C$_{62}$H$_{44}$N$_8$O$_8$·H$_2$O (1029.06): C, 71.12; H, 4.43; N, 10.70; found C, 71.16; H, 4.47; N, 10.70.

1,3-Bis[1,1,4,4-tetracyano-2-(2-amino-1,3-biethoxycarbonyl-6-azulenyl)-3-butadienyl]azulene (20): To a solution of **14** (402 mg, 0.50 mmol) in EtOAc (10 mL) was added TCNE (192 mg, 1.50 mmol). The resulting mixture was refluxed for 10 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (10:1) to give **20** (466 mg, 88%) as red crystals. M.p. >300 °C (CH$_2$Cl$_2$/n-hexane); IR (KBr disk): v_{max} = 3327 (w), 2975 (w), 2223 (w), 2144 (w), 1681 (s), 1606 (m), 1576 (w), 1491 (s), 1431 (s), 1386 (w), 1357 (w), 1277 (w), 1238 (w), 1173 (w), 1115 (s), 1076 (m), 1024 (m), 947 (m), 852 (m), 792 (w),

690 (w), 641 (w), 633 (w), 600 (w) cm^{-1}; UV−Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 244 (4.86), 298 sh (4.70), 344 (4.88), 404 sh (4.52), 500 (4.57) nm; UV−Vis (CH$_2$Cl$_2$/n-hexane): λ_{max} (log ε) = 239 (4.87), 296 sh (4.69), 341 (4.86), 411 (4.52), 485 (4.57) nm; ^{1}H NMR (500 MHz, CDCl$_3$): δ$_H$ = 8.85 (d, J = 11.5 Hz, 4H, 4',8',4",8"-H), 8.69 (d, J = 11.5 Hz, 2H, 4,8-H), 8.36 (d, J = 11.5 Hz, 2H, 5,7-H), 8.35 (s, 4H, NH$_2$), 7.55 (d, J = 11.5 Hz, 4H, 5',7',5",7"-H), 7.28 (s, 1H, 2-H), 4.50 (q, J = 6.9 Hz, 8H, CO$_2$Et), 1.60 (s, 9H, tBu), 1.50 (t, J = 6.9 Hz, 12H, CO$_2$Et) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ$_C$ = 172.69 (C-6), 169.67 (C-6',6"), 165.56 [C=C(CN)$_2$], 165.46 (CO$_2$Et), 160.86 [C=C(CN)$_2$], 146.58 (C-3a',8a',3a",8a"), 141.47 (C-3a,8a), 140.41 (C-2), 139.40 (C-4,8), 132.99 (C-5,7), 131.95 (C-2',2"), 131.65 (C-5',7',5",7"), 127.89 (C-4',8',4",8"), 122.77 (C-1,3), 112.79 (CN), 111.75 (CN), 111.69 (CN), 111.58 (CN), 103.26 (C-1',3',1",3"), 86.75 [C(CN)$_2$], 85.32 [C(CN)$_2$], 60.80 (CO$_2$Et), 40.37 (tBu), 31.72 (tBu), 14.60 (CO$_2$Et) ppm. HRMS (FAB−TOF, positive): calcd for C$_{62}$H$_{46}$N$_{10}$O$_8$ + H$^+$ [M + H]$^+$ 1059.3573, found 1059.3579. Anal. calcd for C$_{62}$H$_{46}$N$_{10}$O$_8$ (1059.09): C, 70.31; H, 4.38; N, 13.23; found C, 70.19; H, 4.45; N, 13.20.

Acknowledgements

[1] a) J. L. Brédas, C. Adant, P. Tackx, A. Persoons, B. M. Pierce, *Chem. Rev.* **1994**, *94*, 243−278; b) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891−4945; c) S. Hünig, E. Herberth, *Chem. Rev.* **2004**, *104*, 5535−5563; d) T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681−4727; e) G. Clavier, P. Audebert, *Chem. Rev.* **2010**, *110*, 3299−3314.

[2] a) M. I. Bruce, J. R. Rodgers, M. R. Snow, A. G. Swincer, *J. Chem. Soc. Chem. Commun*. **1981**, 271−272; b) Y. Morioka, N. Yoshizawa, J. Nishida, Y. Yamashita, *Chem. Lett*. **2004**, *33*, 1190−1191; c) W. Zhou, J. Xu, H. Zheng, H. Liu, Y. Li, D. Zhu, *J. Org. Chem*. **2008**, *73*, 7702−7709; d) T. Michinobu, *Chem. Soc. Rev*. **2011**, *40*, 2306−2316; e) T. Yamagata, J. Kuwabara, T. Kanbara, *Eur. J. Org. Chem*. **2012**, 5282−5290; f) T. Michinobu, *Syn. Org. Chem. Jpn*. **2013**, *71*, 149−157; g) R. Misra, P. Gautam, S. M. Mobin, *J. Org. Chem*. **2013**, *78*, 12440−12452.

[3] a) T. Michinobu, I. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J*. **2006**, *12*, 1889−1905; b) A. R. Lacy, A. Vogt, C. Boudon, J.-P. Gisselbrecht, W. B. Schweizer, F. Diederich, *Eur. J. Org. Chem*. **2013**, 869−879; c) B. H. Tchitchanov, M. Chiu, M. Jordan, M. Kivala, W. B. Schweizer, F. Diederich, *Eur. J. Org. Chem*. **2013**, 3729–3740; d) M. Štefko, M. D. Tzirakis, B. Breiten, M.-O. Ebert, O. Dumele, W. B. Schweizer, J.-P. Gisselbrecht, C. Boudon, M. T. Beels, I. Biaggio, F. Diederich, *Chem. Eur. J*. **2013**, *19*, 12693−12704; e) F. Tancini, F. Monti, K. Howes, A. Belbakra, A. Listorti, W. B. Schweizer, P. Reutenauer, J.-L. Alonso-Gómez, C. Chiorboli, L. M. Urner, J.-P. Gisselbrecht, C. Boudon, N Armaroli, F. Diederich, *Chem. Eur. J*. **2014**, *20*, 202−216; f) G. Jayamurugan, A. D. Finke, J.-P. Gisselbrecht, C. Boudon, W. B. Schweizer, F. Diederich, *J. Org. Chem*. **2014**, 79, 426−431.

[4] a) M. Kivala, C. Boudon, J.-P.Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun*. **2007**, 4731−4733; b) M. Kivala, C. Boudon, J.-P. Gisselbrecht, B. Enko, P. Seiler, I. B. Müller, N. Langer, P. D. Jarowski, G. Gescheidt, F. Diederich, *Chem. Eur. J*. **2009**, *15*, 4111−4123.

[5] a) S. Kato, M. T. R. Beels, P. L. Porta, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, I. Biaggio, F. Diederich, *Angew. Chem. Int. Ed*. **2010**, *49*, 6207−6211; b) C. Dengiz, O. Dumele, S. Kato, M. Zalibera, P. Cias, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, G. Gescheidt, F. Diederich, *Chem. Eur. J*. **2014**, *20*, 1279−1286.

[6] a) P. D. Jarowski, Y.-L. Wu, C. Boudon, J.-P. Gisselbrecht, M. Gross, W. B. Schweizer, F. Diederich, *Org. Biomol. Chem*. **2009**, *7*, 1312−1322; b) F. Silvestri, M. Jordan, K. Howes, M. Kivala, P. Rivera-Fuentes, C. Boudon, J.-P. Gisselbrecht, W. B. Schweizer, P. Seiler, M. Chiu, F.

[7] a) B. Esembeson, M. L. Scimeca, T. Michinobu, F. Diederich, I. Biaggio, *Adv. Mater*. **2008**, *20*, 4584−4587; b) C. Koos, P. Vorreau, T. Vallaitis, P. Dumon, W. Bogaerts, R. Baets, B. Esembeson, I. Biaggio, T. Michinobu, F. Diederich, W.Freude, J. Leuthold, *Nat. Photonics* **2009**, *3*, 216−219.

[8] K.-P. Zeller, *Azulene* in *Methoden der Organischen Chemie* (*Houben-Weyl*), 4th ed. (Ed.: H. Kropf), Thieme, Stuttgart, **1985**, Vol. V, Part 2c, pp. 127−418.

[9] a) E. Amir, R. J. Amir, L. M. Campos, C. J. Hawker, *J. Am. Chem. Soc.* **2011**, *133*, 10046–10049; b) M. Murai E. Amir, R. J. Amir, C. J. Hawker, *Chem. Sci.*, **2012**, *3*, 2721–2725.

[10] a) T. Shoji, S. Ito, M. Watanabe, K. Toyota, M. Yasunami, N. Morita, *Tetrahedron Lett*. **2007**, *48*, 3009–3012; b) T. Shoji, S. Ito, K. Toyota, N. Morita, *Eur. J. Org. Chem*. **2010**, 1059–1069; c) T. Shoji, Y. Inoue, S. Ito, T. Okujima, N. Morita, *Heterocycles*, **2012**, *85*, 35-41; d) T. Shoji, A. Maruyama, M. Maruyama, S. Ito, T. Okujima, J. Higashi, K. Toyota, N. Morita, *Bull. Chem. Soc. Jpn*. **2014**, *87*, 141-154.

[11] a) T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Chem. Eur. J*. **2008**, *14*, 8398−8408; b) T. Shoji, S. Ito, K. Toyota, T. Iwamoto, M. Yasunami, N. Morita, *Eur. J. Org. Chem*. **2009**, 4316−4324; c) T. Shoji, M. Maruyama, S. Ito, N. Morita, *Bull. Chem. Soc. Jpn*. **2012**, *85*, 761−773; d) T. Shoji, S. Ito, T. Okujima, N. Morita, *Org. Biomol. Chem*. **2012**, *10*, 8308−8313; e) T. Shoji, S. Ito, T. Okujima, N. Morita, *Chem. Eur. J*. **2013**, *19*, 5721−5730.

[12] T. Shoji, M. Maruyama, E. Shimomura, A. Maruyama, S. Ito, T Okujima, K Toyota, N. Morita, *J. Org. Chem*. **2013**, *78*, 12513−12524.

[13] a) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett*. **1975**, *16*, 4467−4470; b) S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627−630; c) K. Sonogashira, *Coupling reactions between sp^2 and sp carbon centers* in *Comprehensive Organic Synthesis* vol. 3 (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, UK, **1991**, chapter 2.4, p. 521−549; d) K. Sonogashira, *Cross-coupling reactions to sp carbon atoms* in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, Germany, **1998**, chapter 5, p. 203−229.

[14] a) K. H. H. Fabian, A. H. M. Elwahy, K. Hafner, *Tetrahedron Lett*. **2000**, *41*, 2855−2858; b) A. H. M. Elwahy, K. Hafner, *Tetrahedron Lett*. **2000**, *41*, 2859−2862; c) K. H. H. Fabian, A. H. M. Elwahy, K. Hafner, *Eur. J. Org. Chem*. **2006**, 791−802.

[15] a) S. Ito, A. Nomura, N. Morita, C. Kabuto, H. Kobayashi, S. Maejima, K. Fujimori, M. Yasunami, *J. Org. Chem*. **2002**, *67*, 7295−7302; b) T. Nozoe, S. Seto, S. Matsumura, Y. Murase, *Bull. Chem. Soc. Jpn*. **1962**, *35*, 1990−1998.

[16] R. N. McDonald, J. M. Richmond, J. R. Curtis, H. E. Petty, T. L. Hoskins, *J. Org. Chem*. **1976**, *41*, 1811−1821.

[17] J.-P. Corbet, G. Mignani, *Chem. Rev*. **2006**, *106*, 2651−2710.

[18] T. Michinobu, *Pure Appl. Chem*. **2010**, *82*, 1001−1009.

[19] R. M. Silverstein, F. X. Webster, D. Kiemle, *Spectrometric Identification of Organic Compounds*, 7th ed.; John Wiley and Sons: Weinheim, Germany, **2005**.

[20] T. Shoji, A. Yamamoto, E. Shimomura, M. Maruyama, S. Ito, T. Okujima, K. Toyota, N. Morita, *Chem. Lett*. **2013**, *42*, 638−640.

[21] Measurements were carried out with a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as a supporting electrolyte, with platinum wire auxiliary and disk working electrodes. All measurements were carried out under an argon atmosphere, and the potentials were related to an Ag/AgNO$_3$ reference electrode. The half-wave potential of the ferrocene−ferrocenium ion couple (Fc/Fc$^+$) under these conditions using this reference electrode was observed at +0.15 V on CV. The accuracy of the reference electrode was confirmed by CV measurements of the couple in each sample as an internal ferrocene standard.

[22] a) S. Ito, N. Morita, *Eur. J. Org. Chem.* **2009**, 4567−4579; b) S. Ito, T. Shoji, N. Morita, *Synlett* **2011**, *16*, 2279−2298.

[23] T. Shoji, S. Ito, T. Okujima, N. Morita, *Eur. J. Org. Chem.* **2011**, 5134−5140.

[24] a) T. Shoji, J. Higashi, S. Ito, T. Okujima, M. Yasunami, N. Morita, *Chem. Eur. J.* **2011**, *17*, 5116−5129; b) T. Shoji, J. Higashi, S. Ito, T. Okujima, M. Yasunami, N. Morita, *Org. Biomol. Chem.* **2012**, *10*, 2431−2438.

[25] a) S. Hünig, M. Kemmer, H. Wenner, I. F. Perepichka, P. Bäuerle, A. Emge, G. Gescheidt, *Chem. Eur. J.* **1999**, *5*, 1969−1973; b) S. Hünig, M. Kemmer, H. Wenner, F. Barbosa, G. Gescheidt, I. F. Perepichka, P. Bäuerle, A. Emge, K. Peters, *Chem. Eur. J.* **2000**, *6*, 2618−2632; c) S. Hünig, I. F. Perepichka, M. Kemmer, H. Wenner, P. Bäuerle, A. Emge, *Tetrahedron* **2000**, *56*, 4203−4211; d) S. Hünig, C. A. Briehn, P. Bäuerle, A. Emge, *Chem. Eur. J.* **2001**, *7*, 2745−2757; e) S. Hünig, A. Langels, M. Schmittel, H. Wenner, I. F. Perepichka, K. Peters, *Eur. J. Org. Chem.* **2001**, 1393−1399.

[26] a) S. Ito, H. Inabe, T. Okujima, N. Morita, M. Watanabe, N. Harada, K. Imafuku, *J. Org. Chem.* **2001**, *66*, 7090−7101; b) S. Ito, H. Inabe, N. Morita, K. Ohta, T. Kitamura, K. Imafuku, *J. Am. Chem. Soc.* **2003**, *125*, 1669−1680; c) S. Ito, T. Kubo, N. Morita, T. Ikoma, S. Tero-Kubota, A. Tajiri, *J. Org. Chem.* **2003**, *68*, 9753−9762; d) S. Ito, H. Inabe, N. Morita,

A. Tajiri, *Eur. J. Org. Chem.* **2004**, 1774−1780; e) S. Ito, T. Kubo, N. Morita, T. Ikoma, S. Tero-Kubota, J. Kawakami, A. Tajiri, *J. Org. Chem.* **2005**, *70*, 2285−2293; f) S. Ito, T. Iida, J. Kawakami, T. Okujima, N. Morita, *Eur. J. Org. Chem.* **2009**, 5355−5364; g) T. Shoji, E. Shimomura, M. Maruyama, S. Ito, T. Okujima, N. Morita, *Eur. J. Org. Chem.* **2013**, 957−964.

[27] The spectroelectrogram measurements were carried out by using a two-electrode configuration with a Pt mesh and a wire as the working and counter electrodes, respectively, which were separated by a glass filter. A constant-current reduction and oxidation were applied to the sample solution. The electrical current was monitored by a microampere meter. The potential values are automatically increased by the resistance of the sample solution from 0 V up to ±12 V, but the potential values could not be monitored by our constant current apparatus.
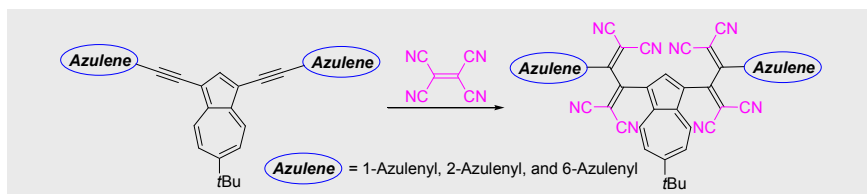
Entry for the Table of Contents (Please choose one layout only)

FULL PAPER

Bis-alkynes, which prepared by Sonogashira–Hagihara reaction, reacted with TCNE in a formal [2 + 2] cycloaddition–retroelectrocyclization to afford the corresponding new bis- TCBDs in excellent yields. The redox behavior of the bis-TCBDs was examined by CV and DPV, which revealed their reversible multi-stage reduction proprties under the electrochemical conditions. Moreover, a significant color change was observed by visible spectroscopy under the electrochemical reduction conditions.

▌ **Donor-acceptor chromophores**

Taku Shoji,* Mitsuhisa Maruyama, Akifumi Maruyama, Shunji Ito, Tetsuo Okujima, Kozo Toyota

■■ – ■■

Synthesis of 1,3-Bis(1,1,4,4-tetracyano-2-azulenyl-3-butadienyl)azulenes by the [2 + 2] Cycloaddition-Retroelectrocyclization Reaction of 1,3-Bis(azulenylethynyl)azulenes with Tetracyanoethylene